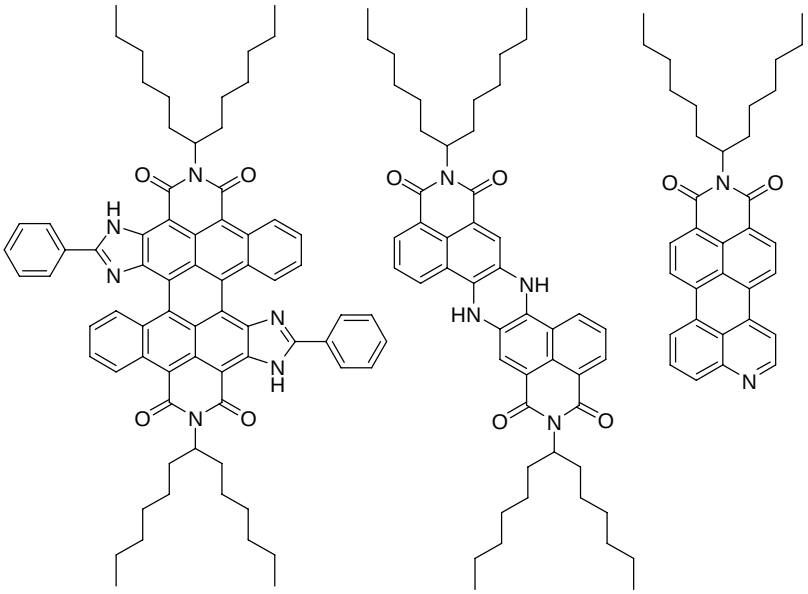
Dissertation zur Erlangung des Doktorgrades
der Fakultät Chemie und Pharmazie
der Ludwig-Maximilians-Universität München

New Routes for the Synthesis of Novel Aceanthrene Green, Phenazine and Azaperylene Dyes and Lateral Ring Extension of Aceanthrene Green Dyes



Sherif Abdel moez Mohamed Ahmed Aly
aus
Kairo, Ägypten

2011

Dissertation zur Erlangung des Doktorgrades
der Fakultät Chemie und Pharmazie
der Ludwig-Maximilians-Universität München

New Routes for the Synthesis of Novel Aceanthrene Green, Phenazine and Azaperylene Dyes and Lateral Ring Extension of Aceanthrene Green Dyes

Sherif Abdel moez Mohamed Ahmed Aly
aus
Kairo, Ägypten

2011

Erklärung

Diese Dissertation wurde im Sinne von § 13 Abs. 3 bzw. 4 der Promotionsordnung der Ludwig-Maximilians-University München vom 29.01.1998 von Herrn Professor Dr. Heinz Langhals betreut.

Ehrenwörtliche Versicherung

Diese Dissertation wurde selbsständig, ohne unerlaubte Hilfe erarbeitet.

München, 07.06.2011

Sherif Aly

Dissertation eingereicht am: 07.06.2011

1. Gutachter: Professor Dr. Heinz Langhals
2. Gutachter: Professor Dr. Paul Knochel

Mündliche Prüfung am: 12.07.2011

Acknowledgement

The presented work was originated in the time between October 2007 until June 2011, under the supervision of Prof. Dr. Heinz Langhals, Department of Chemistry, Ludwig-Maximilians-University, Munich.

I would like to take the opportunity to thank Prof. Langhals for his very interesting topic selection. I really appreciate his time, his advice, especially his patience, and the fact that he is very caring and responding quickly to any issues or problems.

Last, but not least, I would like to thank him for his trust.

A special thanks to Prof. Dr. Paul Knochel for his precious time, reading my thesis, and giving his opinion about my work.

I had very nice time at the laboratory, thanks to my colleagues who were always helpful, caring and make sure that it was never boring.

During the last four years, I had the chance to work with wonderful people, great colleagues and friends. I would like to thank all of them for their support and cheerfulness.

Mrs. Birgit Bischoff, the first person I met in Germany, who helped me a lot for a good start here in Munich, many thanks to her.

Dr. Simon Kinzel, Dr. Andreas Obermeier, Dr. Ana Varja, Dr. Beata Oginski, Dr. Simon Poxleitner, Dr. Armin Pfreitner, Dr. Andreas Esterbauer, Dr. Jan Klitschke, Dr. Ulrike Ritter, Alexander Hofer, Bernd Boeck, Sandra Christian, Andreas Walter, Patricia Braun, Christian Dietl, Matthias Zwiener, Markus Hermann, Tanja Schmidt, Ivone Florido, Nina Behrmann, Sabine Frohnapfel, Carolin Janker (Caro) and Sandra Kostantinou.

I will miss you all, you are the best.

Special thanks to Simon Kinzel and Andreas Obermeier (Obi), your advice was greatly appreciated;

Ana, your music was not only loud, it was also nice;

Alex, for taking care of my never ending computer problems;

Bernd and Caro, for our many lunch breaks we spent together;

Caro, for your fast and accurate measurements.

Also, thank you to all students I met in the laboratory during my work; they show great interest and a good attitude, good luck to all of you.

Many thanks to Mrs. Klaudia Dubler and Dr. David Stephenson (NMR Spectroscopy), Mrs. Sonja Kosak and Dr. Werner Spahl (Mass Spectroscopy), for their support.

I would like to thank Frau Ursula Kopp (Uschi, in Pharmacy Department) for having cup of tea together when I have stress during my work.

Respectful thanks to Prof. Dr. Reda Elshishtawy, who inspired me to start my work in Germany, because of his good advice and guidance.

I want to give special thanks to my Fiancée Elke, for her support, patience, nice time, caring and her love. She is there for me always, we can laugh together.

My thoughts are also with Carol Ann my future step daughter, she always makes me laugh and happy.

My daughter Fatima is always in my mind, 2617 kilometers apart, do not make a difference, I miss her a lot.

My mother is always with me, giving me strength, praying for me and giving me support.

Thanks Aunt Samira for all your support. Thanks to my brothers Amr and Moustafa for being patient with me, that we had spent so little time with each other during my work.

To all my aunts, uncles, cousins, nephews, nieces and grandma, thanks for being there for me when I need you.

My Father who died 1999 is always in my mind, praying for him, and I think he is happy now that I got my doctor degree.

Sherif Abdel Moez Mohamed Ahmed Aly

(Sherif Aly)

1. General Part

1.1. Introduction

Colourants are characterized by their ability to absorb or emit light in the visible range (400-700 nm). Man has used natural colourants since prehistoric times, as reflected by the cave drawings in Europe (Altamira, Spain; Grotto Chauvet, France), in Africa (Zimbabwe), in ancient Egypt, and in China (Terracotta Army, Xian). The sites in Egypt and China are especially remarkable because the oldest known synthetic pigments have been found there, namely Egyptian Blue ($CaCuSiO_{10}$), Han Blue ($BaCuSi_4O_{10}$), and Han Purple ($BaCuSi_2O_4$), colourants that have been studied intensively in recent years with respect both to their structures and productions.[1] This clearly shows that colour had and still has a profound anthropological, psychological, esthetical, functional, and economic impact on society.[2] Colourants may either be inorganic or organic compounds according to chemical structure, and both can be subdivided into natural and synthetic ones, but, today many natural colourants are produced synthetically.[3]

Another classification for colourants are dyes (applied to many substrates like textiles, leather, paper and hair, from a liquid in which they are completely or partly soluble), or pigments (small insoluble particles in the media they are applied, and they need additional compounds like polymers to be attached to their substrate like paints and plastics). [3]

Dyes and pigments are summarized and listed in Colour Index International (*C. I.*) (reference database) for large scale colouration purposes like textile dyeing and pigment colouration of plastics, paints and printing inks.[4]

Each dye and pigment is represented by two numbers in the colour index, referring to the basis of the colourists and the chemical classification [5], the first is called '*C. I. Generic Name*' which refers to field of application and/or method of colouration, and the other '*C. I. Constitution Number* '. [3]

1.2. History of Dyes and Pigments

Man already used natural substances of vegetable and animal origin for dyeing of furs, textiles and other objects in prehistoric times. Ancient Egyptian hieroglyphs described well the way of extraction of natural dyes and their use. Cave drawings demonstrate that pigments were also used. [6]

One of the most important steps towards synthetic colourants was picric acid production by treating Indigo with HNO_3, and that was done by *Woulfe* in 1771.[3]

Under the directions of *August von Hofmann* (who obtained quinoline from coal tar), *William Henry Perkin* in 1856 tried to produce quinine via different method, through oxidation of quinoline and allyltoluidine with potassium dichromate ($K_2Cr_2O_7$), where there were only molecular but not structural formulae known at that time, following the equation:

$$2\ C_{10}H_{13}N + 3\ (\ O\ )\ = C_{20}H_{24}N_2O_2 + H_2O$$

Although *Perkin* was not successful, and 88 years later it was first done by *Woodward* and *Doering,*[7] but Perkin was interested in coal tar bases reactions, and succeeded to dye silk with intense bluish purple solution of a new dye (mauveine) he obtained from oxidation of aniline and toluidine.

In the same year (1856), cyanine dye was isolated by *Williams,* and later fuchsine was discovered by *Verguin* and diazo compounds were prepared with the azo coupling by *Griess*.

The success of *Kekule* about benzene structure opened the door for more preparations of natural and synthetic dyes, like synthesis of alizarin from Turkey Red, indigo structure elucidation, sulphur dyes and indanthrone discovery.

Later, in the 20th century, new dyes and pigments were synthesised like Neolan dyes, phthalocyanine pigments, Irgalan dyes and Reactive dyes.

'The Society of Dyers and Colourists published a two volume book on colourants and auxiliaries, edited by Shore'. [8]

1.3. Fluorescence and Phosphorescence

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation of a different wavelength. In most cases, emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation.

The initial light absorption transforms the molecule to an excited electronic state, and the excited molecule is subjected to collisions with the molecules surrounding, giving up nonradiative energy and stepping down to the lowest vibrational level that exists in the singlet excited state.[9]

However, when the absorbed electromagnetic radiation is very intense, it is possible for one electron to absorb two photons; this two-photon absorption can lead to emission of radiation having a shorter wavelength than the absorbed radiation.

The most striking examples of fluorescence occur when the absorbed radiation is in the ultraviolet region of the spectrum, and thus invisible, and the emitted light is in the visible region. [9]

Phosphorescence is a process in which energy absorbed by a substance is released relatively slowly in the form of light. This is in some cases the mechanism used for "glow-in-the-dark" materials which are "charged" by exposure to light. Unlike the relatively swift reactions in a common fluorescent tube, phosphorescent materials used for these materials absorb the energy and "store" it for a longer time as the processes required to re-emit the light occur less often.

So, we can say that, the first steps in phosphorescence are the same as in fluorescence, but the triplet excited state is the difference here, where, there is a common geometry at a point both singlet and triplet states share in, and their potential energy is the same at that point, and there is possibility for unpairing two electron spins mechanism from singlet (↑↓) to triplet (↑↑). [9]

Fig. 1 (***Jablonski Diagram***) illustrates the electronic states of a molecule and transitions between them. Two of the famous examples for fluorescent organic compounds are fluoresceine **(1)** and rhodamines **(2)**.

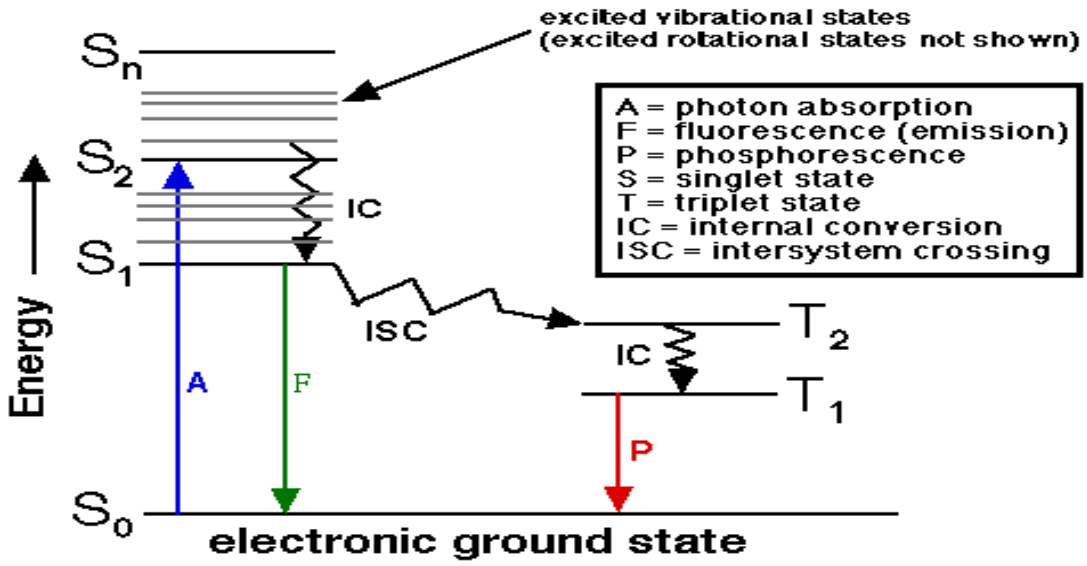
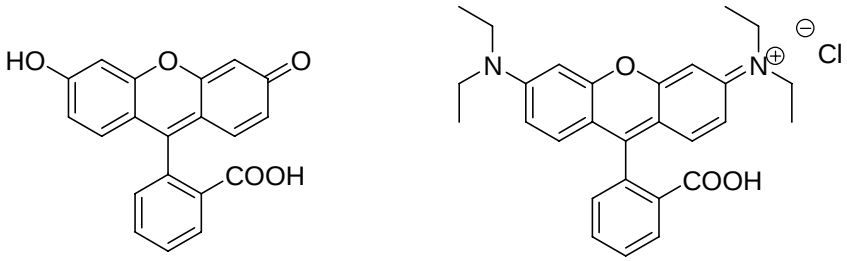


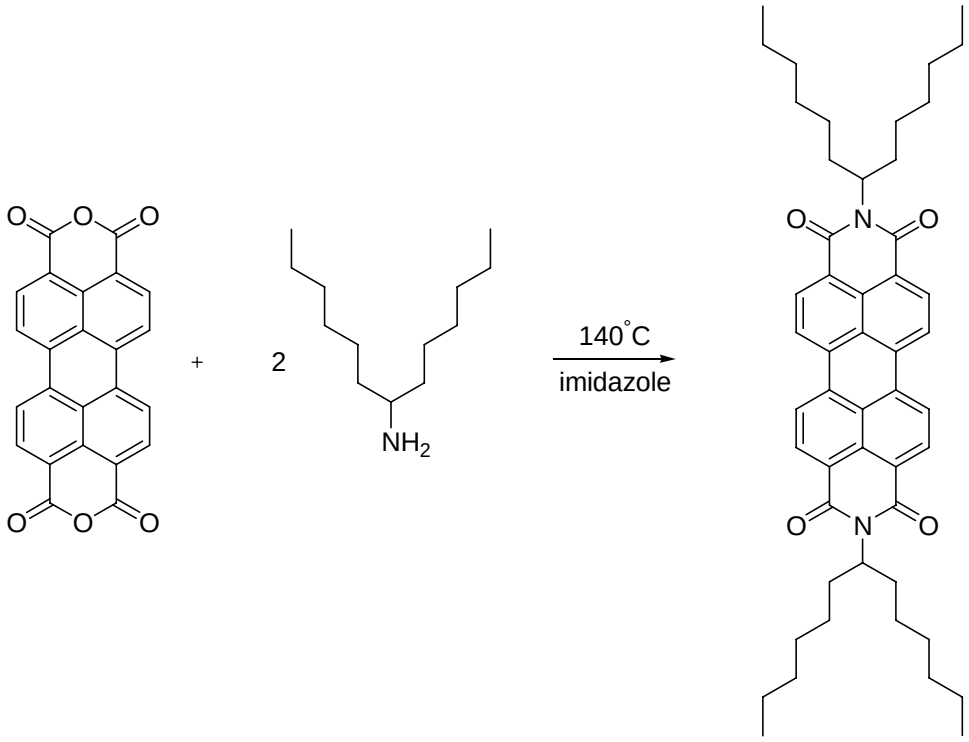
Figure 1. Jablonski Diagram



1 **2**

1.4. Perylenes

Perylene dyes were discovered 1913 by *Kardos,*[10] applied as textile vat dyes, are class of high performance pigments.[11] Scheme 1 shows the synthesis of perylene biscarboximides **(4)** from perylene bis-anhydride **(3)** which is very important nowadays, due to their excellent properties, thermal stability, fluorescence, standing against molten alkali,[12] and their very good light fastness properties.[13,14,15]



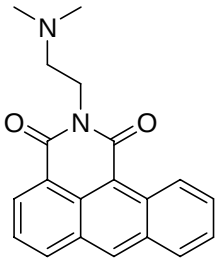
(3) **(4) S-13**

Scheme 1: Synthesis of 2,9-bis-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f]diisoquinoline-1,3,8,10-tetraone (S13).

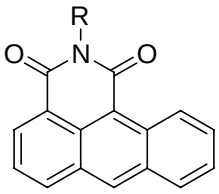
1.5. Anthracenes

Azonafides **(5)** have got an important application as an antitumor agent. [16] Aceanthrene green dyes (**7** and **8**) are used in textile dyeing and can be prepared from anthracene carboxylic acid imides **(6)**. [17]

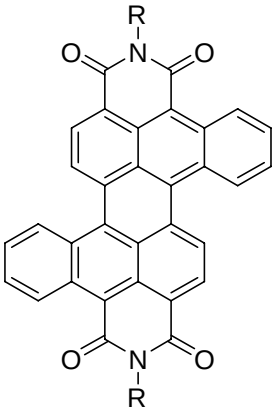
Azonafides and anthracene imides are light sensitive, that photo dimerisation of them could happen from day light. Although these green dyes exhibit no good solubility, they are very important due to their near-infrared absorption, and can be prepared by alkaline fusion of compound **6**. [18]



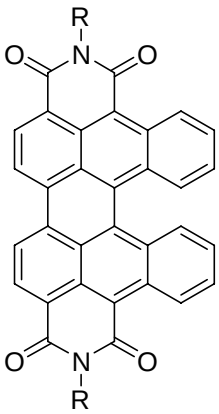
5



6



7



8

1.6. Problems

Alkaline fusion method for the preparation of dyes has got many problems like:

1- The extensive corrosion that can happen to the reaction vessel from molten alkaline salts. [19]

2- It is difficult to isolate the final product from dissolved alkaline salts, because of the primary formation of leuco dyes, and their sometimes difficult oxidation.

3- Big alkaline wastes that can cause pollution to the environment.

4- Compounds **7** (*trans*-Aceanthrene green) and **8** (*cis*-Aceanthrene green) were prepared before via direct alkaline fusion [18] when R = H only, while in other cases (R is aliphatic alkyl group), the *trans* form **(7)** is the only one which is synthesised by the same molten alkaline fusion method. As a consequence a new route is tried in this thesis using new base complex that gave both isomers directly and at lower temperature than the established way (molten alkali fusion).

1.7. Concept

This work will show several steps:

1- Preparation of starting compounds of easily accessable and simple aromatic carboximides (naphthalene dicarboxylic acid imides derivatives and anthracene dicarboxylic acid imides derivatives).

2- Using new route for coupling those carboximides (new base complex) as an alternative to molten alkali salts, avoiding many problems mentioned above in the previous section (**1.6**), preparation and investigation of novel aceanthrene derivatives.

3- Introducing lateral aromatic extension to aceanthrene green derivatives, to reach NIR and IR absorption regions.

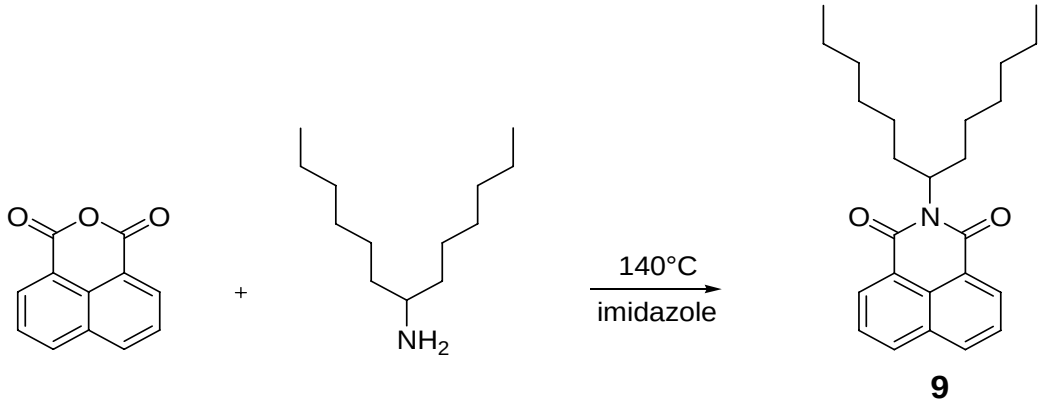
2 Theoretical Part

Perylene dyes (perylene-3,4,9,10-tetracarboxylic bisimide) have different absorption and fluorescence emission spectra compared to aceanthrene green dyes, but the later absorb at appreciably longer wavelength. A lot of work was done on dyes in our working group to let them exhibit bathochromic shift in absorption via the extension of the conjugated π-system of perylene derivatives or by the introduction of a heterocyclic ring axial extension, like formation of obisim dyes by ring extension of perylene nucleus with imidazole attached with benzene ring, [20] or via formation of terrylenetetracarboxdiimides, [21,22,23,24] quaterrylene tetracarboxylic bisimides. [25]
By those above mentioned ways, these dyes become near-infrared absorbing (NIR) for many applications.

2.1. Oxidation, condensation and dehydro halogenation reactions

2.1.1. Synthesis of *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide

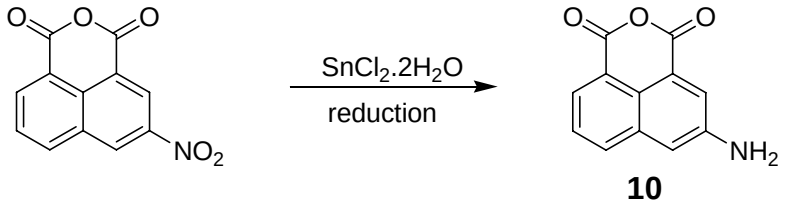
Condensation of aromatic anhydrides with primary amines in molten imidazole [26,27] as a solvent proceed without problems. [12]



Scheme 2: Synthesis of *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide (9).

1,8-naphthalic anhydride reacts with *N*-(1-hexylheptyl)amine in molten imidazole to proceed condensation reaction resulting in *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide **(9)** as shown in scheme 2.

2.1.2. Synthesis of 3-amino-1,8-naphthalic anhydride



10

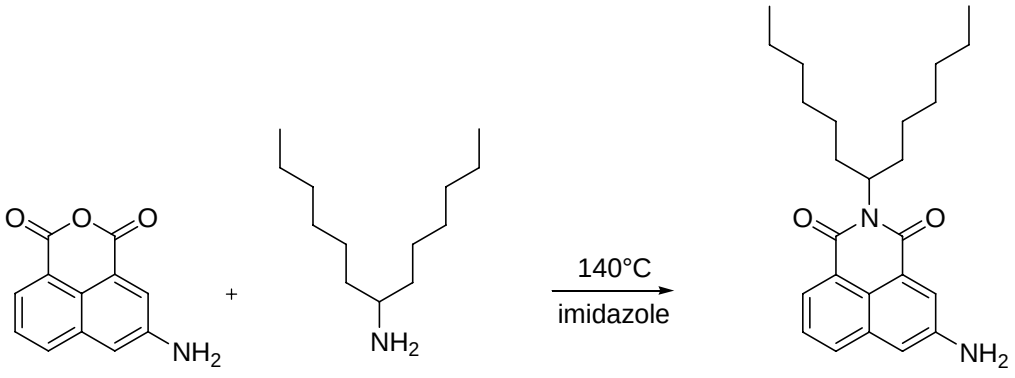
Scheme 3: Preparation of 3-amino-1,8-naphthalic anhydride (10).

Hydrolysis can be carried out with a solution of tin(II)chloride when dissolved in water to form an insoluble basic salt as shown:

$$SnCl_2\ (aq) + H_2O\ (l) \rightleftharpoons Sn(OH)Cl\ (s) + HCl\ (aq)$$

So, it is very important to dissolve stannous chloride in hydrochloric acid of the same or higher molarity to maintain the equilibrium towards the left-hand side (using Le Chatelier's principle), and that was necessary in reduction of 3-nitro-1,8-naphthalimide using tin(II)chloride dissolved in concentrated HCl to obtain 3-amino-1,8-naphthalic anhydride as shown in scheme 3.

2.1.3. Synthesis of *N*-(1-hexylheptyl)-3-amino-1,8-naphthalimide

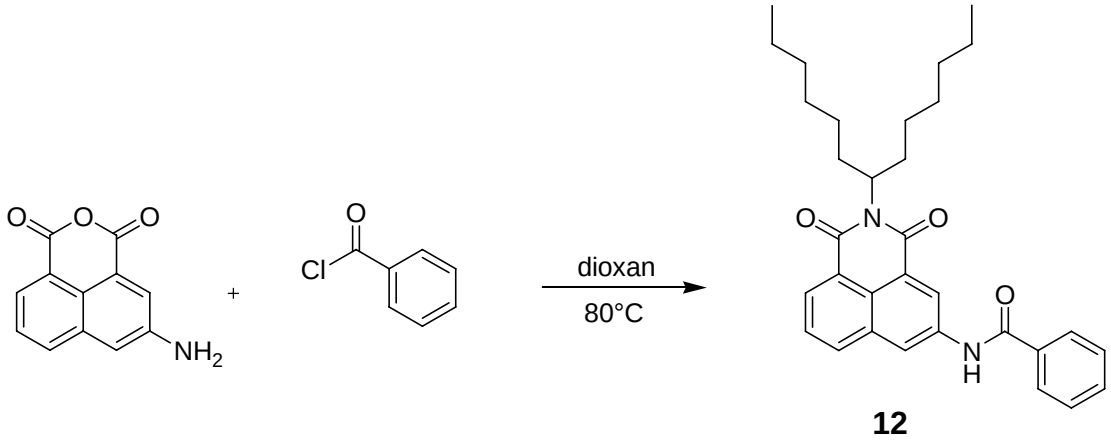


11

Scheme 4: Preparation of *N*-(1-hexylheptyl)-3-amino-1,8-naphthalimide (11).

3-Amino-1,8-naphthalic anhydride **(10)** reacted with *N*-(1-hexylheptyl)amine in molten imidazole to proceed normal condensation reaction obtaining *N*-(1-hexylheptyl)-3-amino-1,8-naphthalimide **(11)**.

2.1.4. Synthesis of *N*-(1-hexylheptyl)-3-(N-benzoylamino)-1,8-naphthalimide

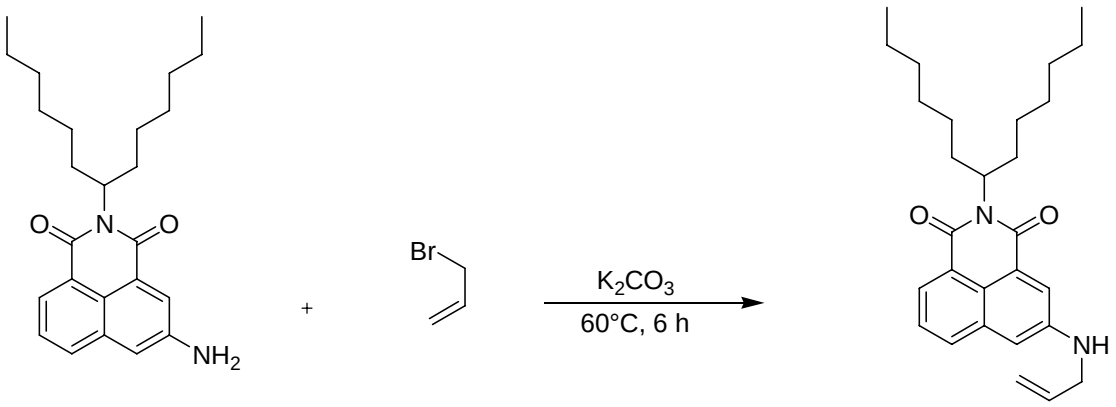


12

Scheme 5: Preparation of *N*-(1-hexylheptyl)-3-(N-benzoylamino)-1,8-naphthalimide (12).

The *Schotten-Baumann* reaction is an important method for the preparation of amides from their correspond acid chlorides and amines, [28] and that was shown in scheme 5, where *N*-(1-hexylheptyl)-3-amino-1,8-naphthalimide reacted with benzoyl chloride to obtain *N*-(1-hexylheptyl)-3-(N-benzoylamino)-1,8-naphthalimide.

2.1.5. Synthesis of *N*-(1-hexylheptyl)-3-(*N*-3-allylamino)-1,8-naphthalimide

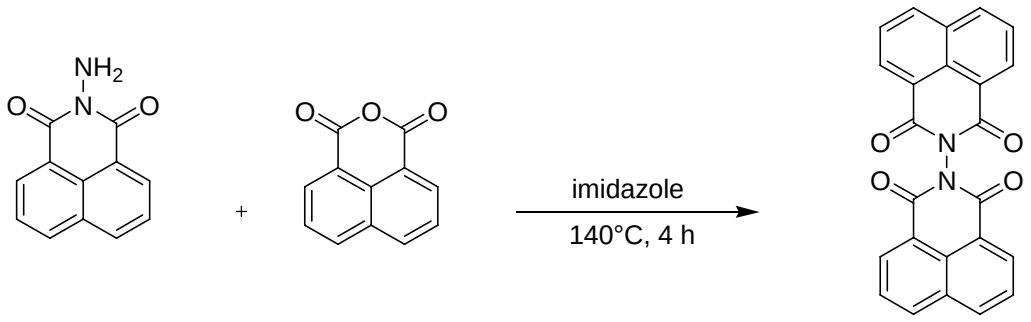


11 **13**

Scheme 6: Preparation of *N*-(1-hexylheptyl)-3-(*N*-3-allylamino)-1,8-naphthalimide (13).

Compound **11** as a primary aliphatic amine undergoes nucleophilic substitution reaction to obtain the secondary amine (**13**), and that reaction could continue to give the tertiary amine if compound **11** was the minor compound, and that is why the ratio between compound **11** to allyl bromide was 1:5.

2.1.6. Synthesis of *N,N*-bisnaphthalimide

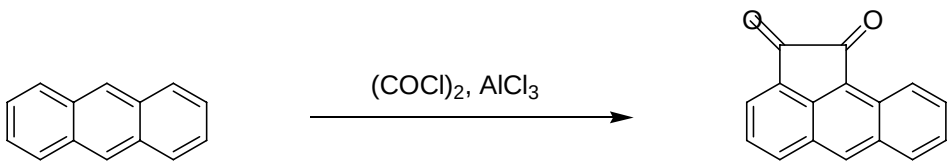


14 **15**

Scheme 7: Preparation of *N,N*-bisnaphthalimide (15).

2-Aminobenzo[*de*]isoquinoline-1,3-dione **(14)** reacts with 1,8-naphthalic anhydride in the presence of molten imidazole to proceed condensation reaction via elimination of one molecule of water from each molecule of the two mentioned reactant compounds.

2.1.7. Synthesis of aceanthrene quinone



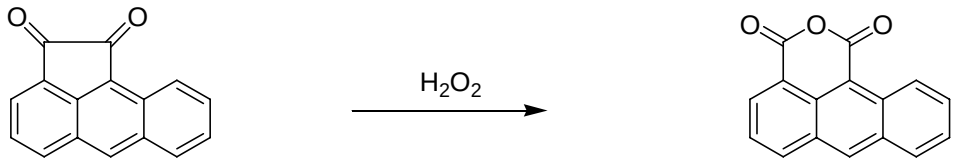
16 **17**

Scheme 8: Preparation of aceanthrene quinone (17) from anthracene.

Anthracene **(16)** reacted with both oxalyl chloride and aluminium chloride by Friedel-Crafts reaction according to Liebermann and Zsuffa [15] procedure to obtain aceanthrene quinone **(17)** as shown in scheme 8, which is better than other procedures. [29,30,31]

Aceanthrene quinone is a bright orange shining solid which exhibits fluorescence, thus, it is considered as a fluorescent pigment. [18]

2.1.8. Synthesis of anthracene-1,9-dicarboxylicacid anhydride [15]

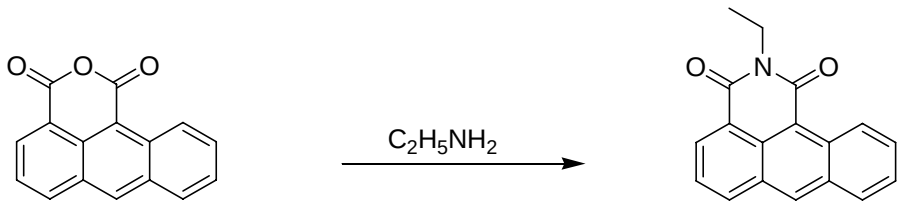


17 **18**

Scheme 9: Preparation of anthracene-1,9-dicarboxylicacid anhydride (18) from aceanthrene quinone.

Anthracene anhydride **(18)** which is considered as a key for preparation of anthracene imides, azonafides and aceanthrene green (will be shown later in this chapter), was prepared **(scheme 9)** by oxidative ring-opening reaction of aceanthrene quinone with H_2O_2 in NaOH solution, followed by ring-closure reaction.

2.1.9. Synthesis of *N*-ethylanthracene-1,9-dicarboxylicacid imide

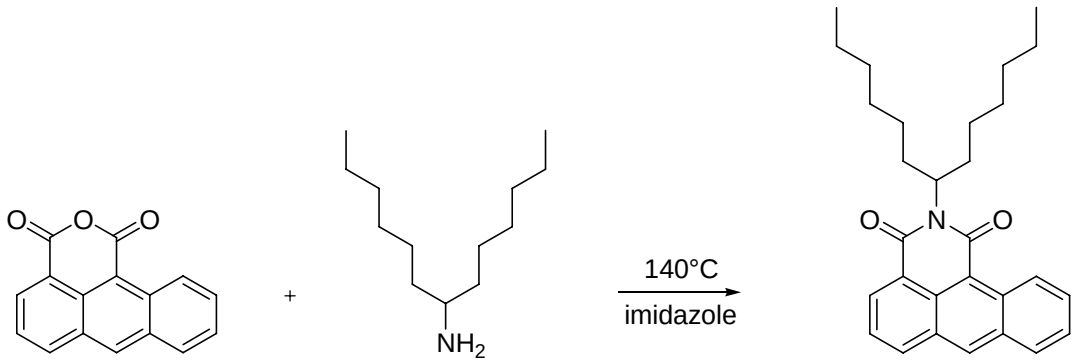


18 **19**

Scheme 10: Preparation of *N*-ethylanthracene-1, 9-dicarboxylicacid imide (19) from anthracene-1,9-dicarboxylicacid anhydride (18).

Anthracene-1,9-dicarboxylicacid anhydride was allowed to react with aqueous ethyl amine solution via modified procedure, [17d] to proceed condensation reaction resulting in *N*-ethyl anthracene-1,9-dicarboxylicacid imide **(19)** as shown in scheme 10.

2.1.10. Synthesis of *N*-(1-hexylheptyl)anthracene-1,9-dicarboxylicacid imide



18 **20**

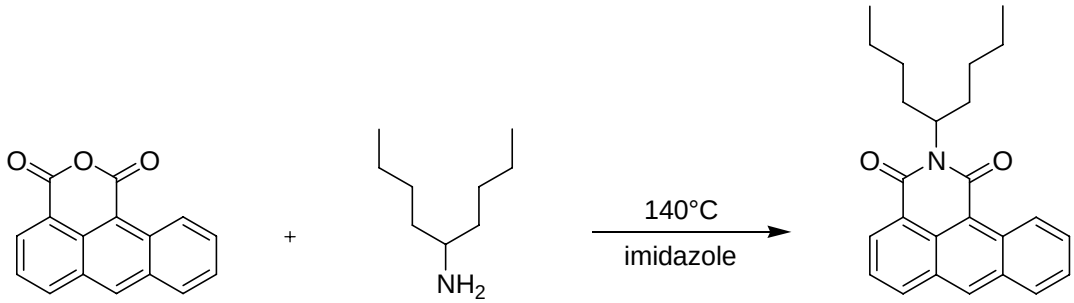
Scheme 11: Preparation of *N*-(1-hexylheptyl)anthracene-1,9-dicarboxylicacid imide (20) from anthracene-1,9-dicarboxylicacid anhydride (18).

N-(1-Hexylheptyl)anthracene-1,9-dicarboxylicacid imide **(20)** was prepared by condensation of anthracene-1,9-dicarboxylicacid anhydride **(18)** with imidazole [26], as shown in Scheme 11. Working with mineral acids by these compounds should be avoided because these acids can affect those anthracene dicarboximides. [12,32]

Preparation of these anthracene dicarboximides with long non-polar alkyl chain '*solubilising swallow-tail substituents*' [33,34], such as *N*-(1-hexylheptyl) in compound

20 [35,36] or *N*-(1-butylpentyl) which will be shown in the next reaction, offers more applications to these compounds due to higher solubility in organic solvents.

2.1.11. Synthesis of *N*-(1-butylpentyl)anthracene-1,9-dicarboxylicacid imide



18 **21**

Scheme 12: Preparation of *N*-(1-butylpentyl)anthracene-1, 9-dicarboxylicacid imide (21) from anthracene-1,9-dicarboxylicacid anhydride (18).

N-(1-Butylpentyl)anthracene-1,9-dicarboxylicacid imide **(21)** was prepared like compound **20**, by the condensation of anthracene-1,9-dicarboxylicacid anhydride **(18)** with imidazole , as shown in Scheme 12.

Mass spectrometry of that compound showed molecular ion peak at 373.2 corresponding to the calculated molecular weight of compound **21**.

The absorption and fluorescence spectra of compound **21** do not show any difference (bathochromic or hypsochromic shift) between that of compound **20**. [25]

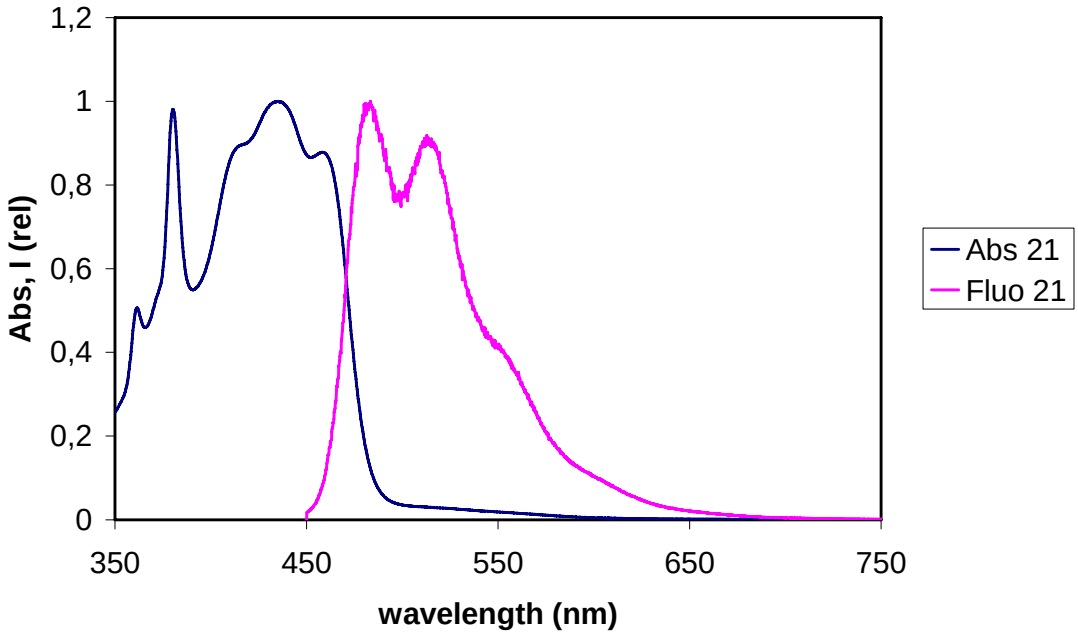
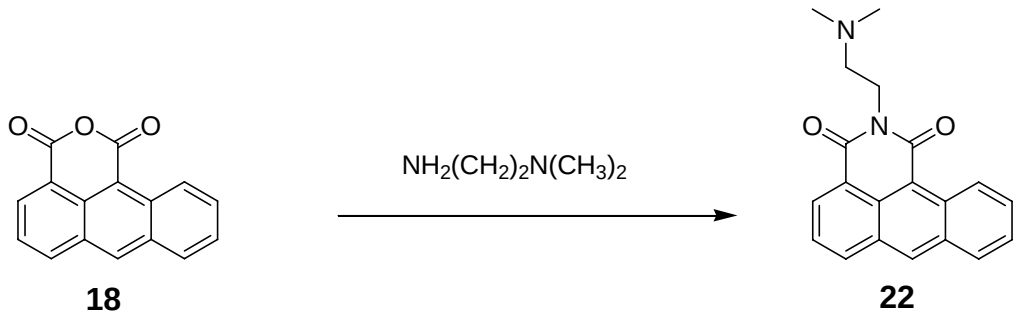


Figure 2: UV/Vis absorption (blue) and fluorescence spectra (pink) of *N*-(1-butylpentyl)anthracene-1, 9-dicarboxylicacid imide (21).

As shown here from figure 2, absorption and fluorescence emission (λ_{exc} = 435 nm) spectra of compound **21** identic with compound **20** which is known and prepared before, where its absorption and fluorescence spectra are well known.

That means there is no influence of 1-butylpentyl and 1-hexylheptyl attached to nitrogen atom on the spectra of both compounds.

2.1.12. Synthesis of 2-[2´-(dimethylamino)ethyl]-1,2-dihydro-3H-dibenz[*de,h*]iso-quinoline-1,3-dione [37]



18 **22**

Scheme 13: Preparation of 2-(2-dimethylaminoethyl)dibenzo[*de,h*]isoquinoline-1,3-dione (azonafide) (22) from anthracene-1,9-dicarboxylicacid anhydride (18).

Anthracene-1,9-dicarboxylicacid anhydride **(18)** reacts with *N,N*-dimethyl ethylene diamine through condensation reaction (scheme 13) to obtain azonafide **(22)** under light precautions to avoid photodimerisation due to its needs as tumour static material. [16,38,39,40,41,42,43,44,45]

Many azonafide analogues with side chain or in the anthracene nucleus structure variation [16,38,39,40,46] were synthesised and their effects on different human solid tumor cells and murine L1210 leukemia cells were studied. [46]

Figure 3 shows absorption and fluorescence spectra for both freshly prepared azonafide (was kept away from light), and spectra of the same compound but after exposing to light for 24 hours dissolved in chloroform.

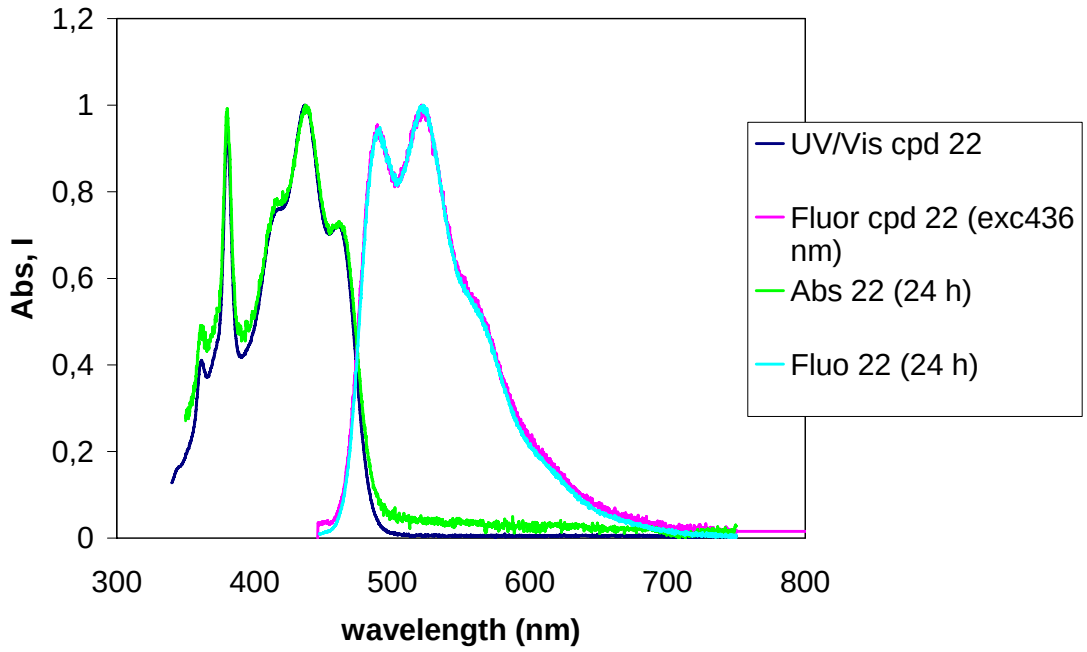
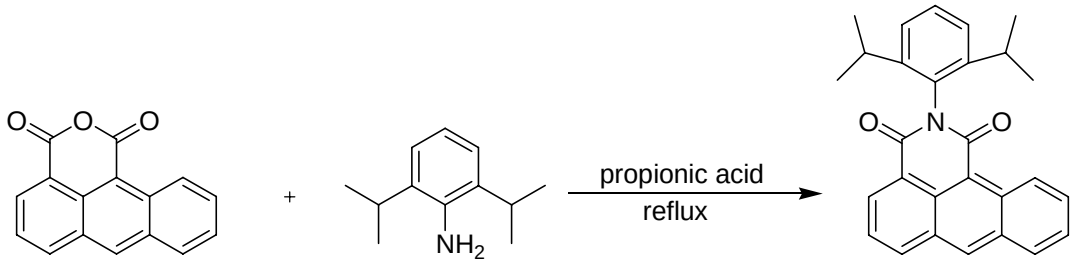


Figure 3: UV/Vis absorption (left) and fluorescence spectra (right) of 2-(2-dimethylaminoethyl)dibenzo[*de,h*]isoquinoline-1,3-dione (22) in chloroform.

From the above curve, azonafide was not affected by light when stayed in chloroform and exposed to normal sun light till the following day. Its mass spectra also showed its calculated molecular weight.

It could be explained that normal daylight has not enough intensity for making photodimerization of azonafides in a short period of time, and it should be allowed to react according to the general procedure for photodimerisation [18] to be photodimerised.

2.1.13. Synthesis of *N*-(2,6-diisopropylphenyl)anthracene-1,9-dicarboxylicacid imide

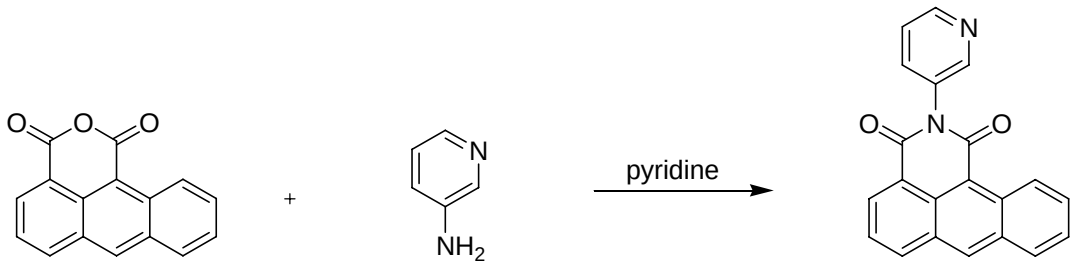


18 **23**

Scheme 14: Preparation of *N*-(2,6-diisopropylphenyl)anthracene-1,9-dicarboxylicacid imide (23) from anthracene-1,9-dicarboxylicacid anhydride (18).

Anthracene-1,9-dicarboxylicacid anhydride **(18)** reacted with 2,6-diisopropylaniline to obtain *N*-(2,6-diisopropylphenyl)anthracene-1,9-dicarboxylicacid imide **(23)** (Scheme 14). [37]

2.1.14. Synthesis of *N*-(3-pyridyl)anthracene-1,9-dicarboxylicacid imide



18 **24**

Scheme 15: Preparation of *N*-(3-pyridyl)anthracene-1,9-dicarboxylicacid imide (24) from anthracene-1,9-dicarboxylicacid anhydride (18).

Condensation of anthracene-1,9-dicarboxylicacid anhydride **(18)** with 3-amino pyridine lead to formation of *N*-(3-pyridyl)anthracene-1,9-dicarboxylicacid imide **(24)**. Compound **24** is considered also poor antitumor active pyridine-containing azonafide analogue with rigidity and low basicity. [38]

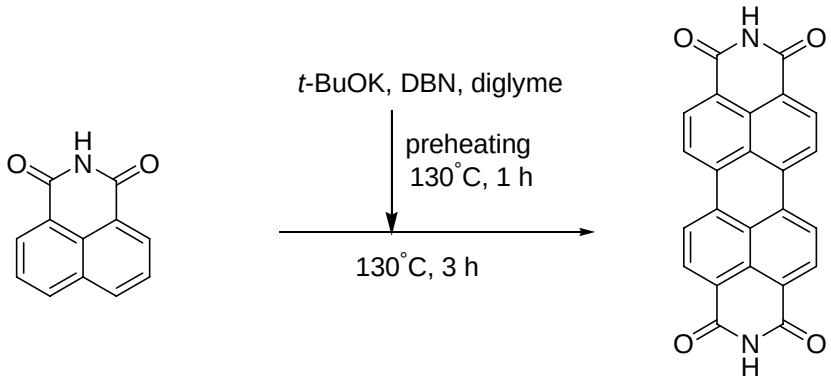
2.2. Coupling reactions using new base complex

Many organic compounds that contain acidic CH, NH or OH precede condensation reactions under mild basic conditions; others with low acidic CH require severe reaction conditions. [19]

Some examples were carried out like perylene and aceanthrene green dyes, where their preparation were carried out under severe basic conditions in molten alkali salts at high temperature, which lead to problems that were mentioned before.

Producing other unknown derivatives of these compounds was carried out using new base complex and lower temperature than the traditional method.

2.2.1. Synthesis of perylene-3,4,9,10-tetracarboxylic bisimide [19]



25

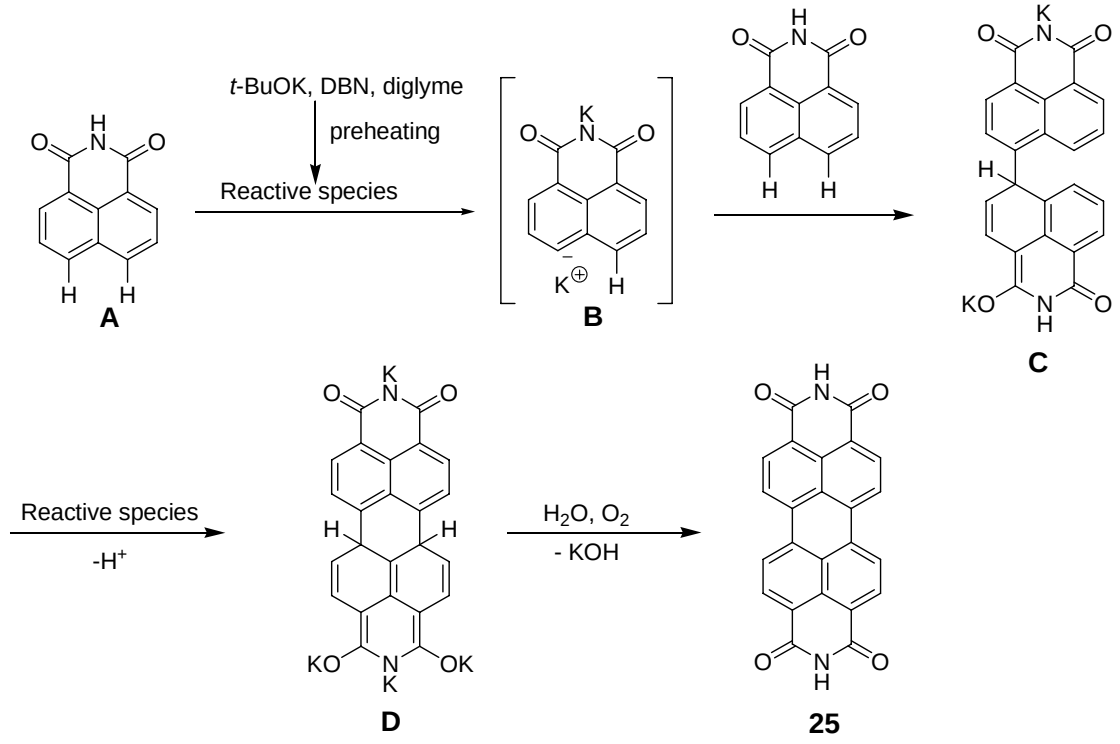
Scheme 16: Preparation of perylene-3,4,9,10-tetracarboxylic bisimide (25) from 1,8-naphthalimide.

Coupling reactions of 1,8-naphthalimides or 1,9-anthracene imides normally occur in molten alkali of inorganic salts at high temperature because of their low basicity. [12,21,47]

Later on, *t*-BuOK/DBN base mixture was found to behave more basic than molten alkaline salts, and reaction temperature could be lower compared with molten alkaline. [19]

In Scheme 17, there is hypothesis for the coupling mechanism using the new base complex (*t*-BuOK/DBN).

Suggested mechanism: [19]



Scheme 17.

After heating that basic complex leading to reactive species which is capable of deprotonation of 1,8-naphthalimide (**A)** from 4-position obtaining the anion B, which proceed further nucleophilic addition to another molecule **A** leads to the formation of **C**.

The reactive species from the base complex played an important role in cyclization of **C** to form **D**, which was also oxidized to the final product compound **25**.

Table 1 shows the effect of changing base, reaction temperature and reaction time on the coupling reaction and the chemical yield.

Condition	Octamethyl ethylene tetramine	DBN	DBU	Reaction temperature	Reaction time	Yield
1	-	12 mmol	-	130°C	3h	36.0 %
2	-	-	12 mmol	130°C	3h	33.0 %
3	-	12 mmol	-	170°C	8h	69.0 %
4	-	-	12 mmol	170°C	8h	60.3 %
5	-	6 mmol	6 mmol	170°C	8h	53.5 %
6	-	12 mmol	-	170°C	1h	36.2 %
7	12 mmol	-	-	130°C	3h	0.0 %
8	12 mmol	-	-	170°C	8h	0.0 %

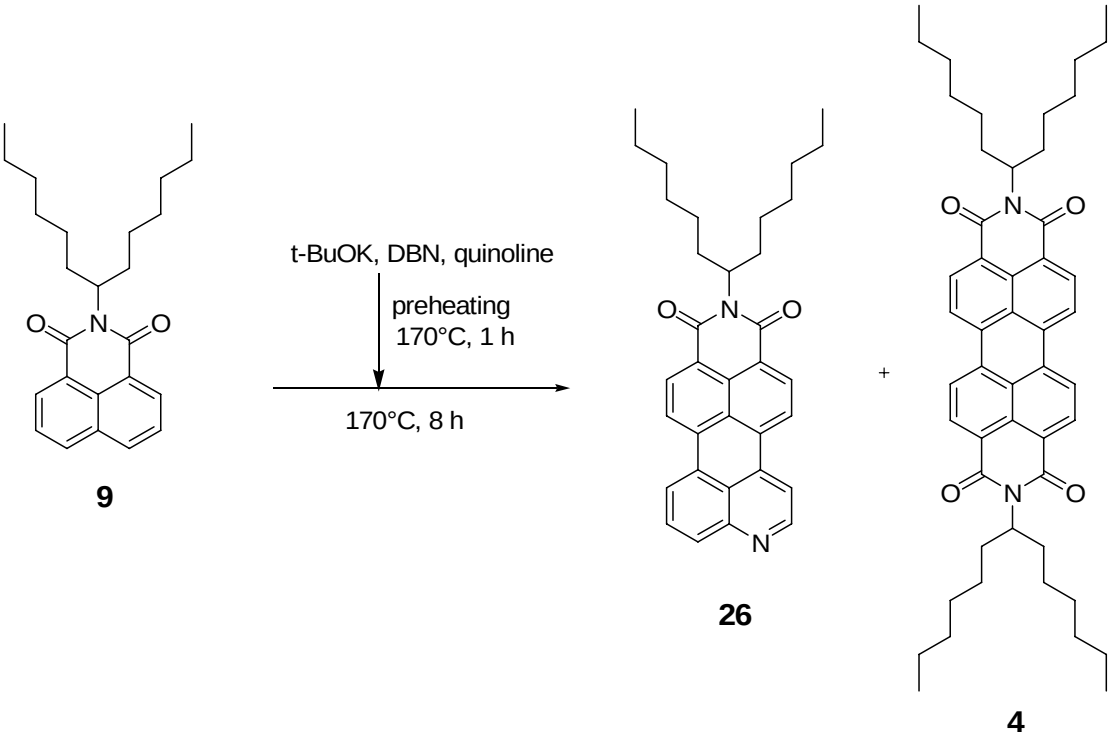
Table 1: Effect of reagent, temperature and time on chemical yield of compound 25.

Different experiments were done by changing the base complex first where DBN is replaced with the same number of moles by DBU (*t*-BuOK/DBU) and preheating with diglyme for 1 hour before addition of naphthalimide, then continuing reaction time after addition of compound **A** to be 3 hours. The same was done also but by using octamethyl ethylene tetramine instead of DBU and preceding the same steps. These experiments were repeated but at different reaction temperature (170°C).

It was found out also that DBU is a good substitute for DBN and probably preced by the same reaction mechanism leading to coupling of 1,8-naphthalimide, with almost the same chemical yield at 130°C and 170°C.

At 170°C and reaction time 8 hours, using DBN/DBU mixture in equal ratio together with *t*-BuOK and diglyme decreased the chemical yield but not remarkable (from 69 % to 54 %). On the other hand, octamethyl ethylene tetramine did show any positive results neither at 130°C nor at 170°C, 3 hours or 8 hours.

2.2.2. Synthesis of N-(1-Hexylheptyl)-3-azaperylene-9,10-dicarboxylic acid imide



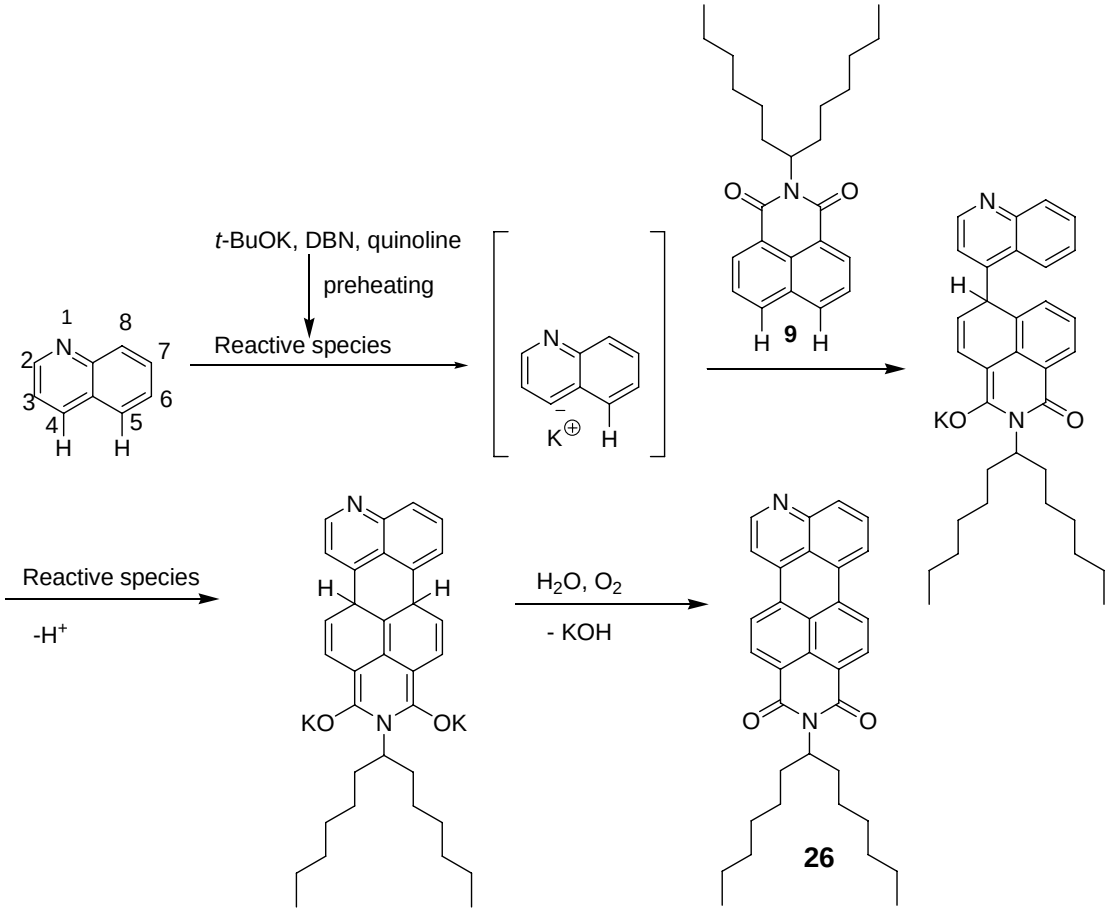
Scheme 18: Preparation of *N*-(1-hexylheptyl)-3-azaperylene-9,10-dicarboxylic acid imide (26) from *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide (9).

Potassium tertiary butoxide, DBN and diglyme mixture were preheated together in absence of air for 1 hour at 130°C, then *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide **(9)** was added to them and heating continued for 3 more hours, where the only product was *N*-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic acid diimide **(S-13) (4)** with 10 % yield. Yield increased to 23 % when the temperature was increased to 170°C and reaction time was 8 hours instead of 3 hours.

When diglyme was substituted with quinoline keeping the same reaction conditions (1 hour preheating of the base mixture at 170°C and 8 more hours after addition of compound **9**), *N*-(1-hexylheptyl)-3-azaperylene-9,10-dicarboxylic acid imide **(26)** appeared as a second product.

The suggested mechanism in Scheme **17** could also be applied here, where deprotonation in position **4** in quinoline (because of the electron withdrawing effect of the nitrogen atom in the ring) could also happen as shown in Scheme 19.

Suggested mechanism:



Scheme 19.

Dye **(26)** (3-azaperylene derivative) is soluble in chloroform and dichloromethane, and its absorption and fluorescence emission spectra compared to those of **S-13** are shown in figure 4.

Another procedure was done for other azaperylene derivative preparation, where 2,6-diisopropyl phenyl group was attached to the nitrogen atom of imide group instead of hexyl heptyl group. [56]

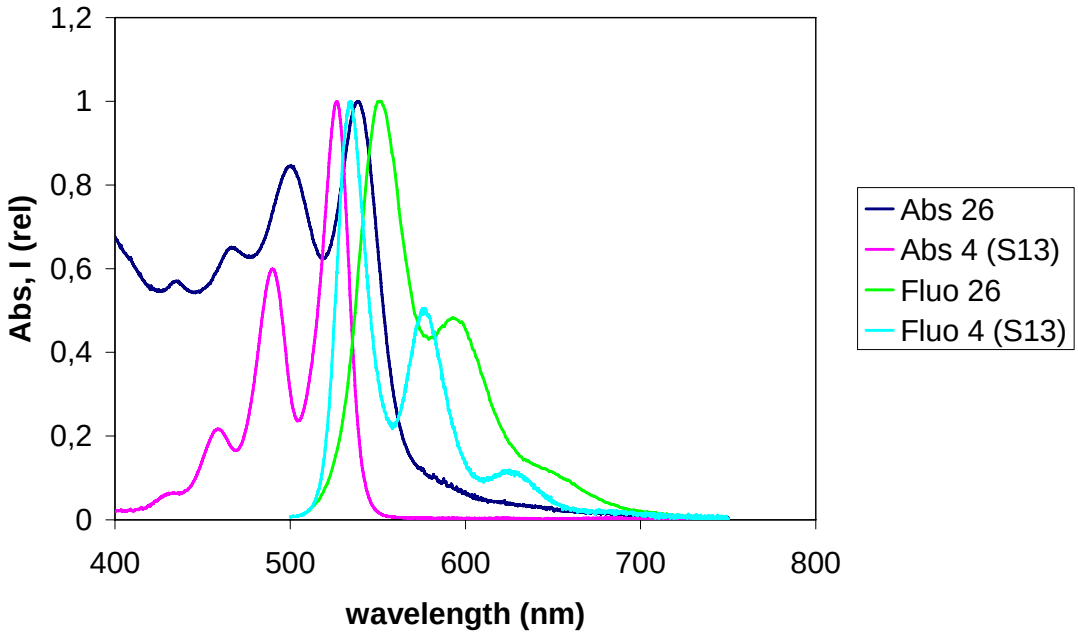
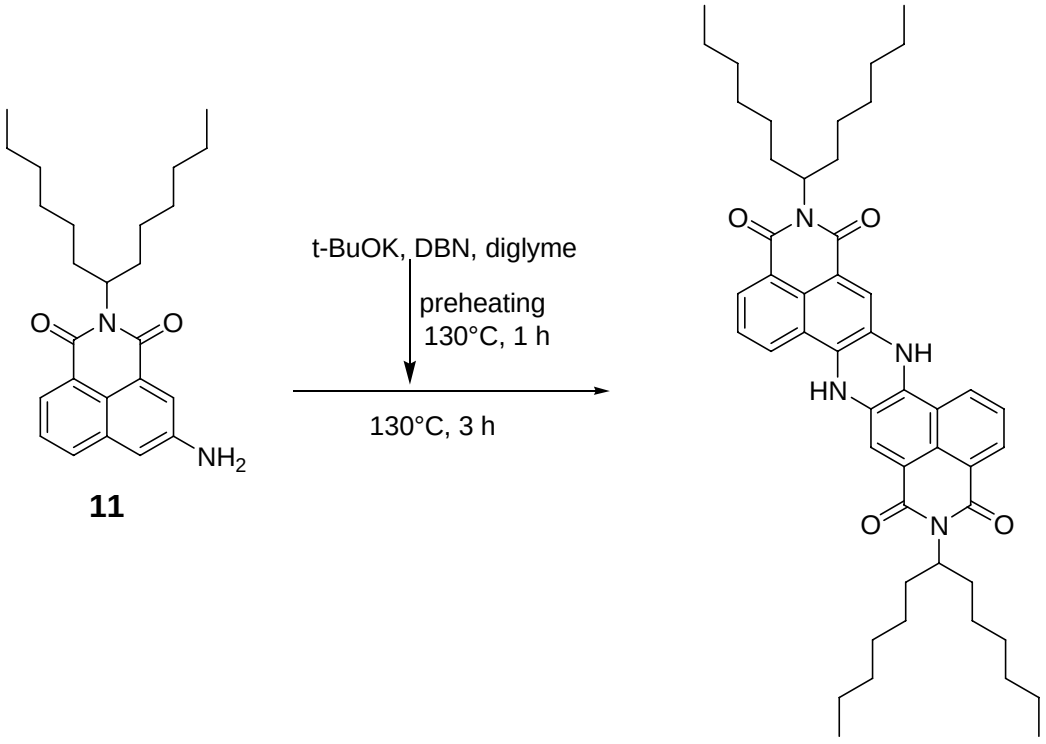


Figure 4: UV/Vis absorption and fluorescence spectra of compounds 26 and 4 in $CHCl_3$.

As shown in figure 4, there is a slight bathochromic shift in the absorption spectrum of compound **26** compared to **S13 (4)** by approximately 14 nm. Consequently, a bathochromic shift of 20 nm in fluorescence emission of compound **26** was found compared with compound **4**.

The existence of a nitrogen atom in the perylene nucleus (*peri* region) instead of one carbon atom could have an effect on that bathochromic shift that appeared in azaperylene derivative, where nitrogen is electron withdrawing atom and with higher electronegativity than that of carbon atom, that could make slight decrease in HOMO-LUMO energy gap as previously calculated. [21,48]

2.2.3. Synthesis of 2,10-bis-(1-hexylheptyl)diisoquinoline[3,2,1-*d,e*:8,7,6- *d'e'*]phenazin-1,3,9,11-(5 H,13 H)-tetraone



Scheme 20: Preparation of 2,10-bis-(1-hexylheptyl)diisoquinoline[3,2,1-*d,e*:8,7,6-*d',e'*]phenazin-1,3,9,11-(5 H,13 H)-tetraone (27) from *N*-(1-hexylheptyl)-3-amino-1,8-naphthalimide (11).

Potassium tertiary butoxide, DBN and diglyme mixture were preheated together in absence of air for 1 hour at 130°C, then *N*-(1-hexylheptyl)-3-amino naphthalene-1,8-dicarboxylicacid imide **(11)** was added to them and heating continued for 3 more hours.

Deprotonation of the primary amino group ($-NH_2$) in compound **11** attached directly to the perylene nucleus that attacked the carbon number **4** in the other molecule with less steric hinderence than carbon **2** in naphthalene nucleus.

The only detected product was 2,10-bis-(1-hexylheptyl)diisoquinoline[3,2,1-*d,e*:8,7,6-*d'e'*]phenazin-1,3,9,11-(5 H,13 H)-tetraone **(27)** with 18 % yield.

That phenazine derivative was prepared before by another procedure [49], but the alkyl group attached to nitrogen atom of the imide was methyl instead of hexyl heptyl group.

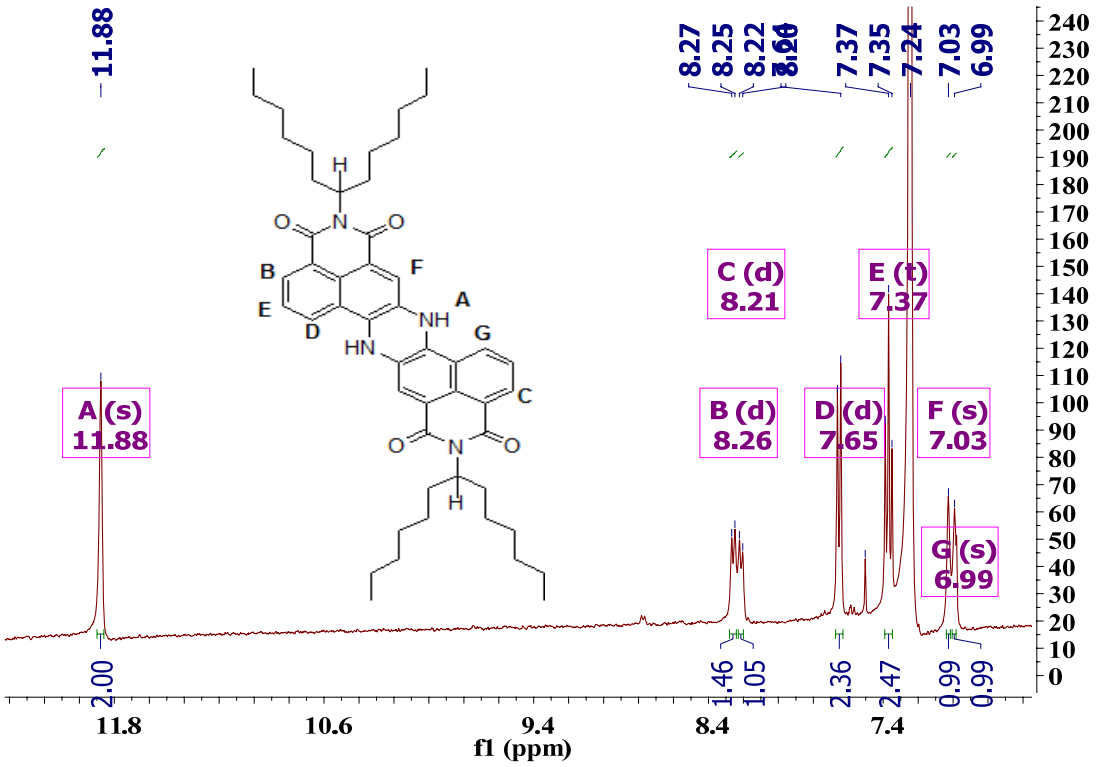


Figure 5: ^{1}H NMR of compound 27 (aromatic part).

Figure 5 shows 2 (H) singlet protons at 11.87 ppm that are down shielded which are attached to nitrogen atom each.

It was found out from ^{1}H NMR also that protons B and C are not symmetrical to each other, both appeared separate doublets at 8.26 and 8.21 ppm.

Also protons F and G appear as two singlets at 7.03 and 6.99 ppm.

An explanation for that could be the position of the two protons that are attached to the two nitrogen atoms in the imide group, these two protons are *trans* to each other, and that could make the slight difference in ppm that happened in protons B, C, F and G. Rotational barriers in *N*-substituted perylene dyes were determined in another work before. [50]

The mass spectrometry of showed peak at 786.9 [M^+ + 2], and that means the two secondary amine nitrogen atoms were protonated by two protons, another peak at 785.9 [M^+ + 1] and the last one at 784.9 which is the molecular ion peak of the product's molecular weight as shown in figure 6.

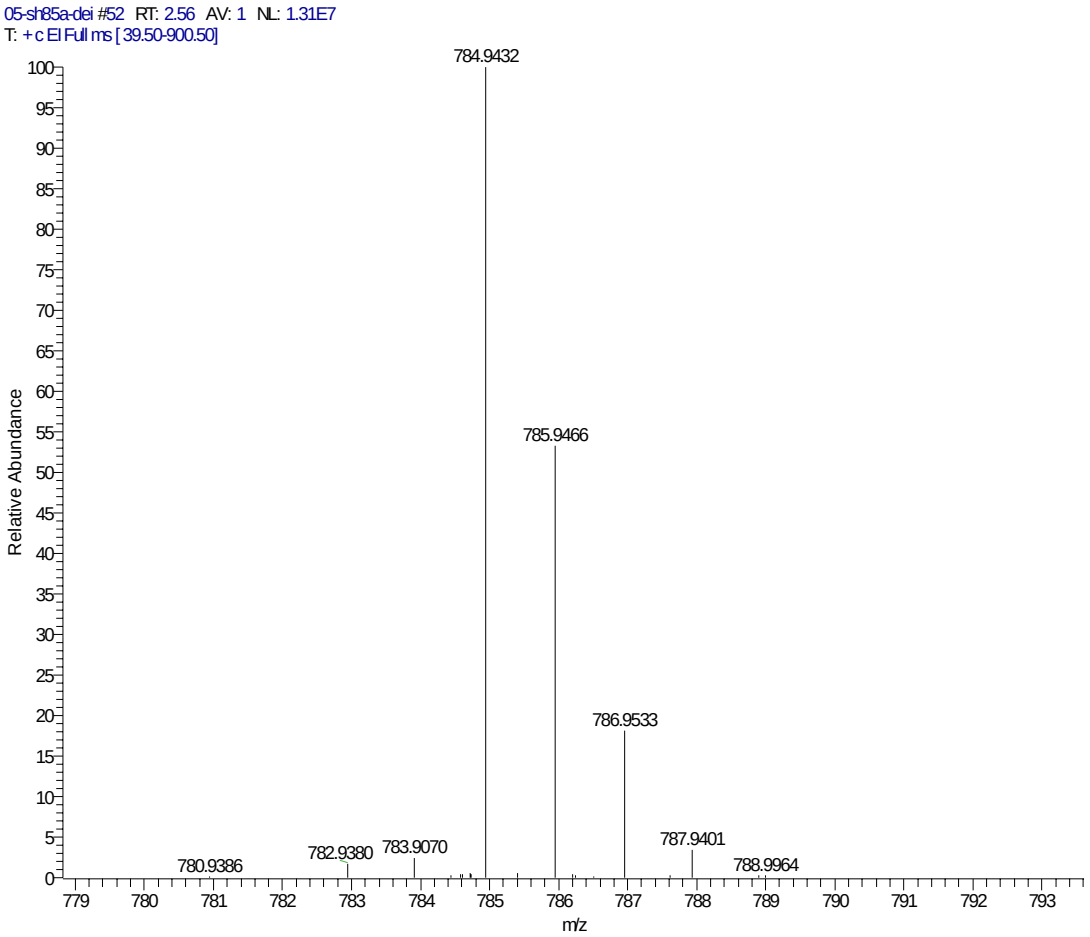


Figure 6: Part of mass spectra of compound 27.

Figure 7 shows the absorption and fluorescence emission spectra of compound **27** compared with **S-13**.

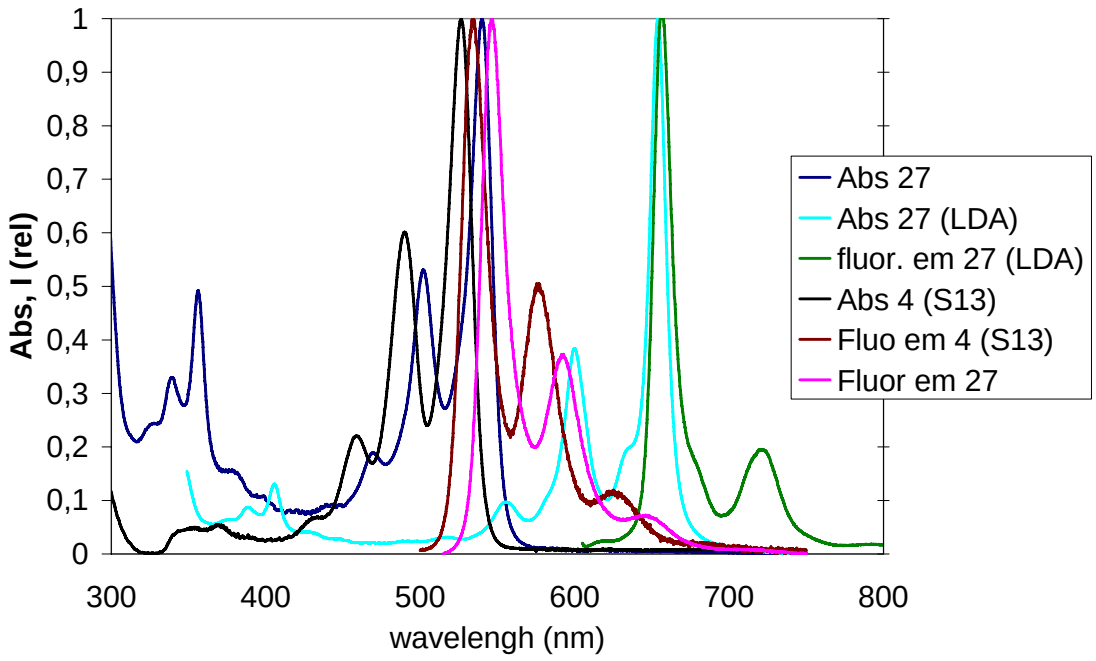


Figure 7: UV/Vis absorption spectra of compounds 27 (dark blue), 27 with Lithium diisopropyl amide (LDA) (turquoise), 4 (S13) (black) and fluorescence emmission spectra of 27 (pink), 27 with LDA (green) and S13 (dark red) in $CHCl_3$.

2,10-Bis-(1-hexylheptyl)diisoquinoline[3,2,1-*d,e*:8,7,6-*d'e'*]phenazin-1,3,9,11-(5H, 13 H)-tetraone **(27)** exhibits 15 nm bathochromic shift than **S-13**, and that is shown in figure 6, where the existence of two nitrogen atoms inside the nucleus which have different shape than that of perylene one, decreased the energy gap between the HOMO and the LUMO that made red shift to the absorption spectrum.

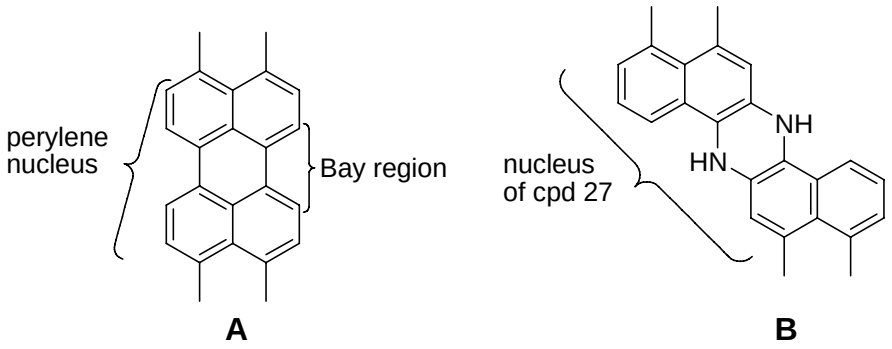
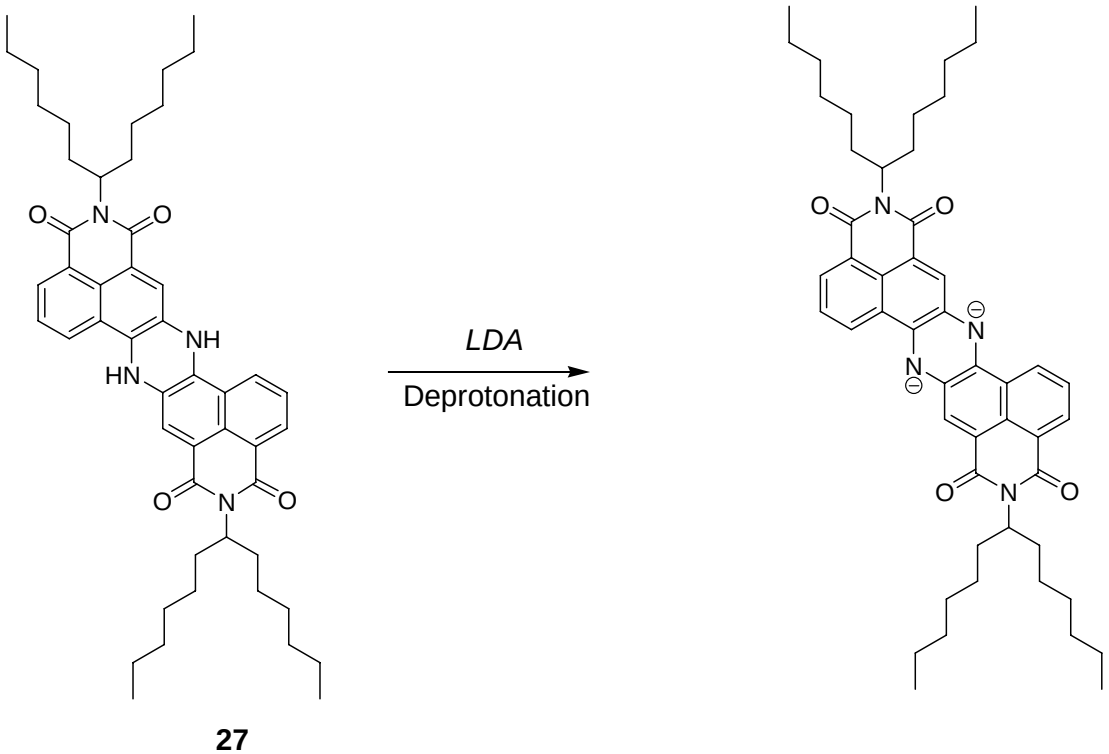


Figure 8: Perylene (A) and Phenazine (B) nucleus.

When compound **27** was dissolved in THF and treated with LDA, the colour changed immediately to blue, and bathochromic shift happened where absorption was shifted to 654 nm, and fluorescence was emitted at maximum wavelength of 656 nm. When excited at 600 nm a fluorescence quantum yield 100 % was found, while when using DBN instead of LDA, it gives 65 % fluorescence quantum yield.

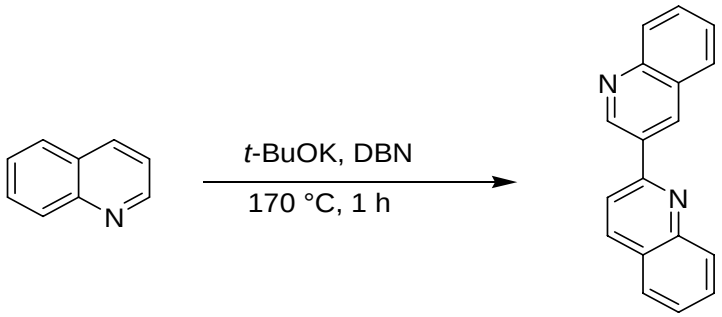
That strong bathochromic shift happened to dye **27** because of deprotonation of both protons on the secondary amine nitrogen atoms by LDA as shown in Scheme 21.



Scheme 21: Deprotonation of dye 27 using LDA.

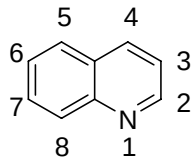
Direct coupling of *N*-(1-hexylheptyl)-1,8-naphthalimide **(9)** instead of compound (**11)** under the same basic conditions mentioned above, gave the known compound **(4)** with 10 % yield, while increasing reaction temperature to 170°C instead of 130°C and reaction time to 8 h instead of 3 h, increased the yield to 23 %. Also using quinoline instead of diglyme gave the same product and the yield was 22.5 %.

2.2.4. Synthesis of 2-(3-quino) quinoline through coupling



28

Scheme 22: Formation of 2-(3-quino)quinoline (28) from quinoline.



It was found out that when quinoline reacts with the base complex (*t*-BuOK/DBN) at high temperature, it undergoes deprotonation, where protons at carbons 2, 3 and 4 are the most active positions for deprotonation, so, the possibilities of attaching two quinoline molecules could be from 2, 3 or 4 positions.

Actually, proton NMR spectra showed 12 different peaks for 12 different protons (figure 8), and ^{1}H-^{1}H Cosy NMR also (Figure 9) showed 2 different systems, and that means the two systems in the two attached quinoline molecules are different.

Another method was developed for the synthesis of 2,3'-biquinolines based on the reaction of *β*-(2-quinolyl)-2-aminostyrenes with acid amides under Vilsmeier reaction conditions. [51]

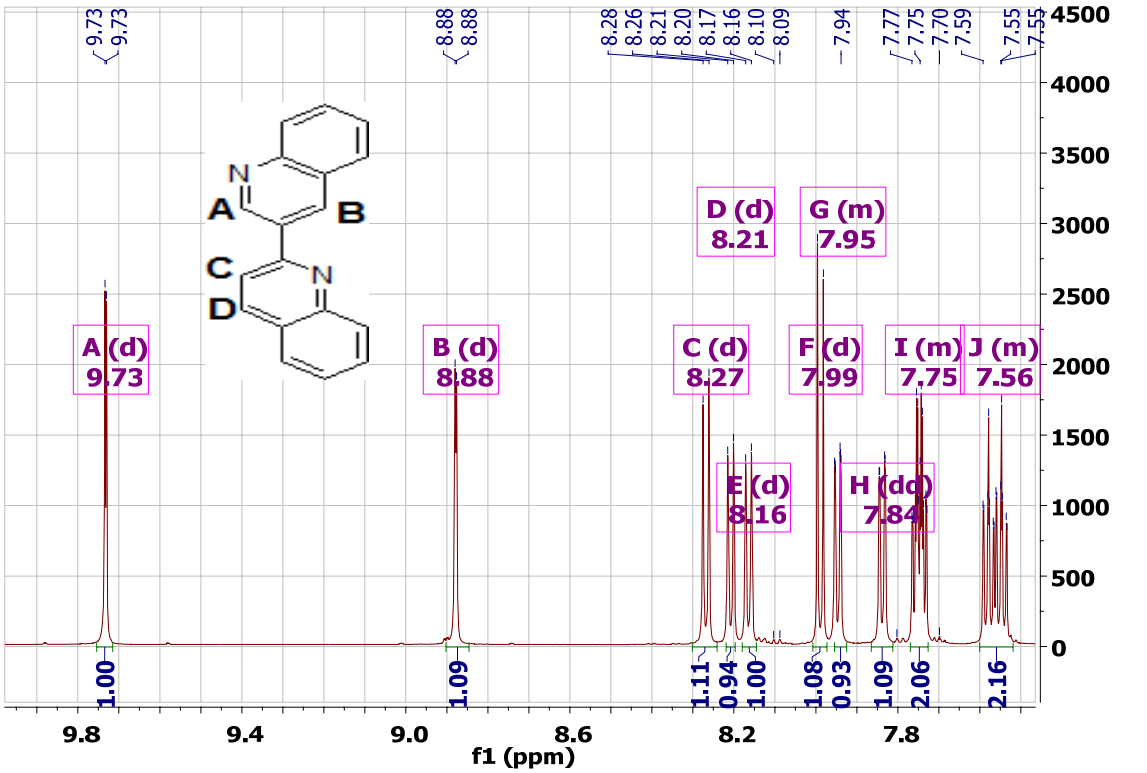


Figure 9: ^{1}H NMR spectra of compound 28.

Figure 9 showed that there are 12 different proton peaks in the aromatic region, and that indicates the different electron cloud around the protons in each quinoline molecule, so, linking should be in different positions and not in the same one in each molecule.

The coupling constant between protons A and B is small in comparison to that of other protons, so, the quinoline molecule that contains these two protons should have a chemical bond at position 3.

Protons C and D are more shielded and appear at lower ppm than A and B, that means there is at least more than two sigma bonds separate them from nitrogen atom in their quinoline molecule, so, they are in positions 3 and 4, which proves the 2-3 attachment and gave compound **28** as a product.

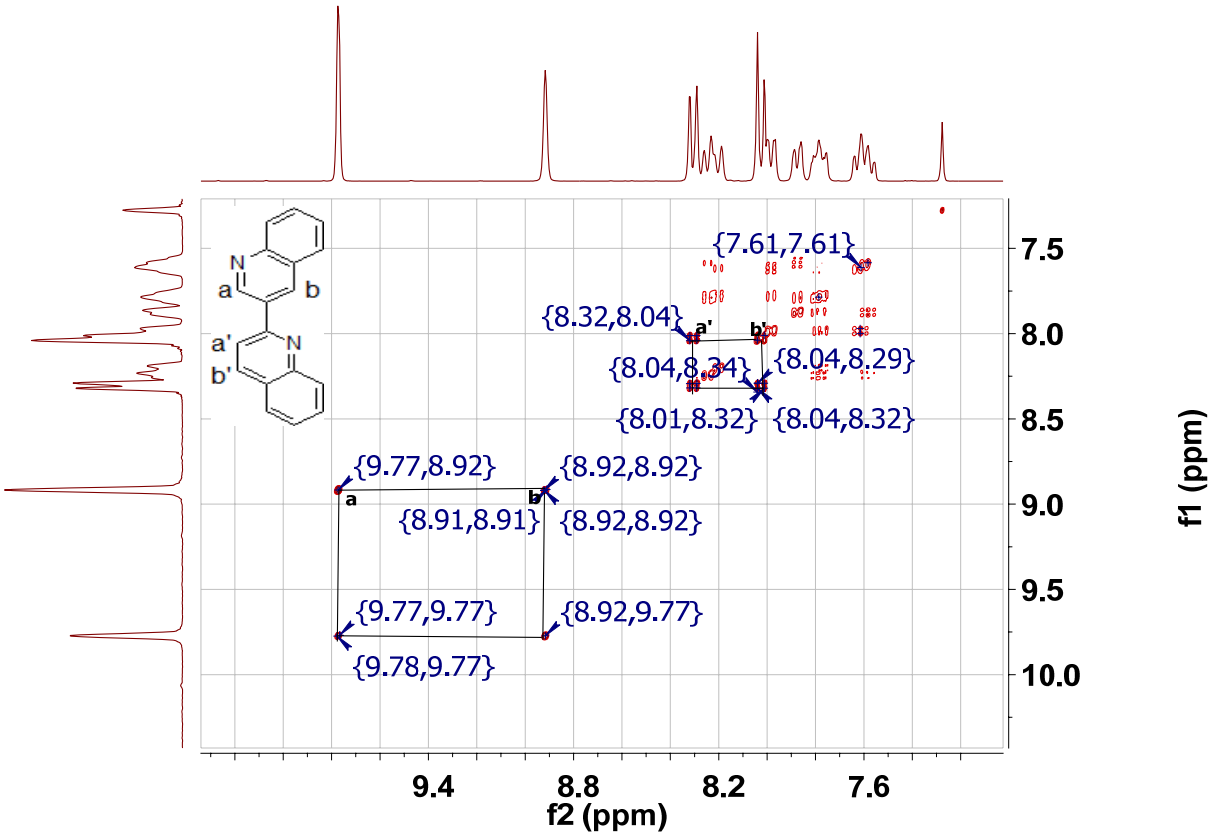


Figure 10: ^{1}H-^{1}H Cosy NMR spectra of compound 28.

As shown in figure 10, there are two different proton-proton coupling systems (a, b) [(8.92, 9.77), (9.77, 8.92) ppm] with coupling constant 2.2 Hz and (a', b') [(8.32, 8.04), (8.04, 8.32)] with coupling constant 8.5 Hz, that means they are in two different rings with different electron clouds surrounding them. The first cross peak was (H_a, H_b) at (9.77, 8.92) and (8.92, 9.77) ppm which are more deshielded than the other pair ($H_{a'}$, $H_{b'}$), which show cross peaks at (8.32, 8.04) and (8.04, 8.32) ppm.

Figure 10 shows also the other part of ^{1}H-^{1}H Cosy NMR of the rest of protons magnified to be more recognised.

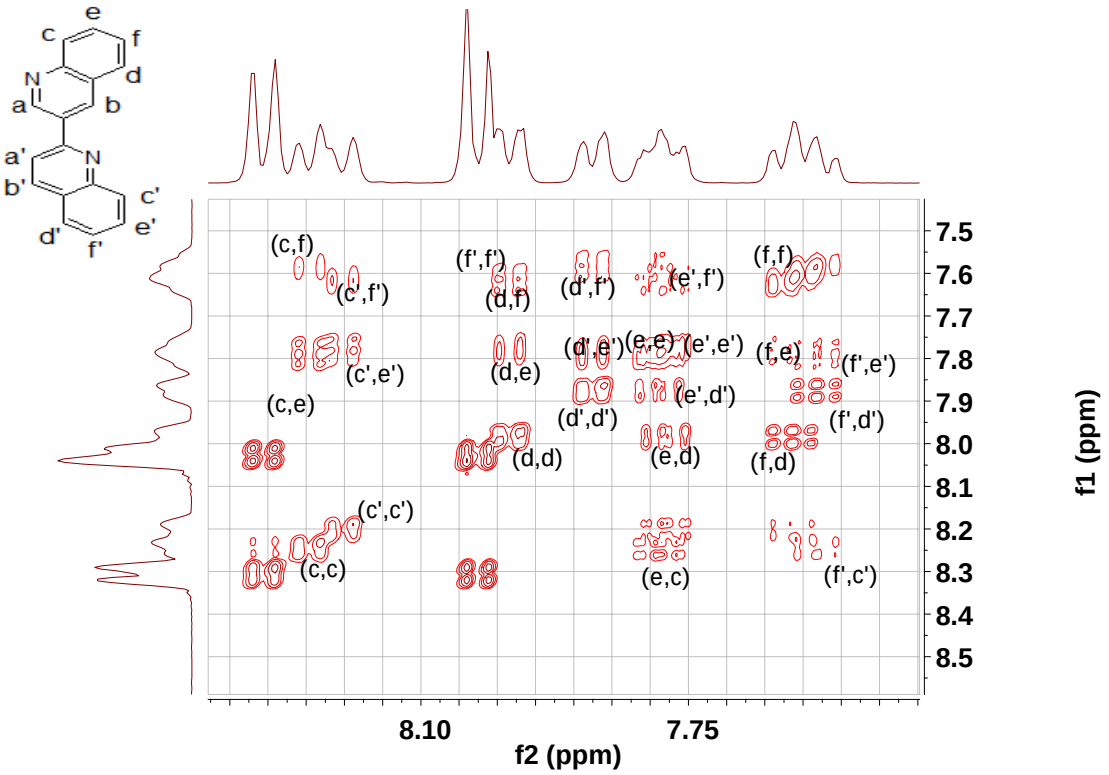


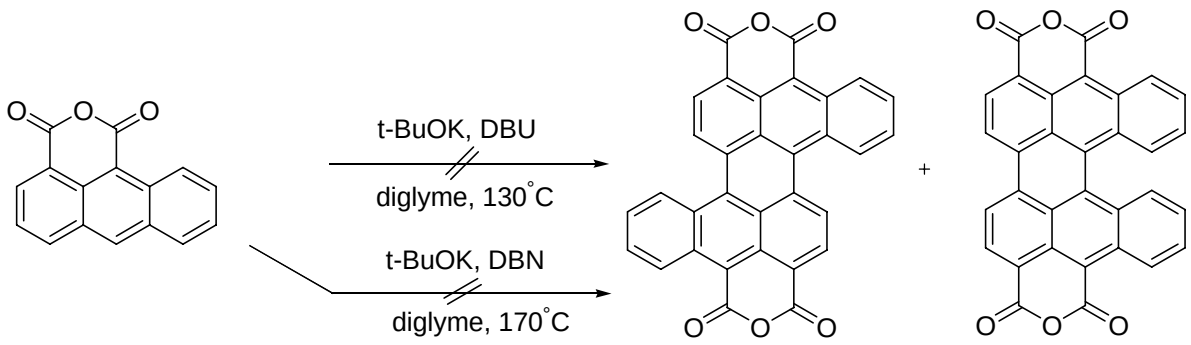
Figure 11: Part of ^{1}H-^{1}H Cosy NMR spectra of compound 28.

As shown in figure 10, it was not clear the coupling between the other protons except (H_a, H_b) and ($H_{a'}$, $H_{b'}$), but figure 11 shows more the cross peaks between other protons in the system.

H_c has cross peaks with H_e and H_f, H_d has cross peaks with H_e and H_f , H_e and H_f are also making cross peak with each other.

On the other quinoline molecule $H_{c'}$ has cross peaks with $H_{e'}$ and $H_{f'}$, and $H_{d'}$ has cross peaks with $H_{f'}$ and $H_{e'}$, $H_{e'}$ and $H_{f'}$ are coupling also with each other.

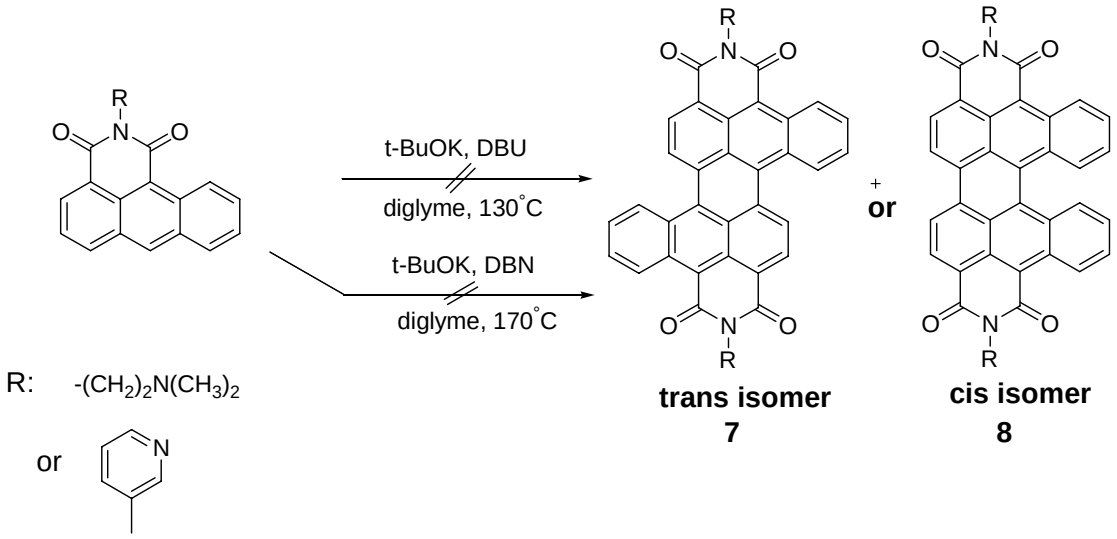
2.2.5. Coupling of anthracene anhydride



(10)

Scheme 23

Reaction of anthracene-1,9-dicarboxylic acid anhydride **(10)** with the strong base complex never proceeds neither in the first (3 hours reaction time) nor in the second one (8 hours reaction time), to obtain one or both *cis* and *trans* isomers.

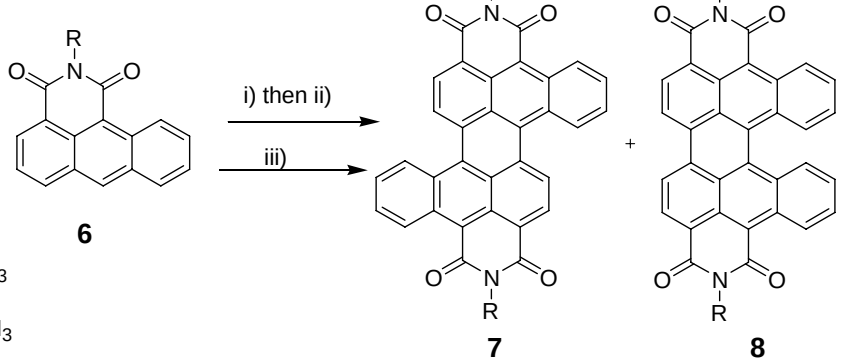


Scheme 24

Scheme 24 shows also that coupling did not happen for azonafides or pyridine containing azonafide molecule.

2.2.6. Synthesis of both N,N'-di-(1-hexylheptyl)-*trans*-aceanthrene tetracarboxylic bisimide and N,N'-di-(1-hexylheptyl)-*cis*-aceanthrene tetracarboxylicbisimide

7,8	R
a	H
b	C_2H_5
c	C_4H_9
d	C_5H_{11}
e	C_9H_{19}
g	$CH(C_6H_{13})_2$
h	2-$(C_2H_5)C_6H_4$
i	2,3-$(CH_3)_2C_6H_3$
j	2,5-$(tC_4H_9)_2C_6H_3$
k	$CH(C_4H_9)_2$
l	2,6-$(sC_3H_7)_2C_6H_3$



i) *t*-BuOK, DBN, diglyme preheated together for 1 h at 130°C without cpd 6

ii) addition of 6 to the base mixtureand heated 3 h at 130°C

iii) Molten KOH

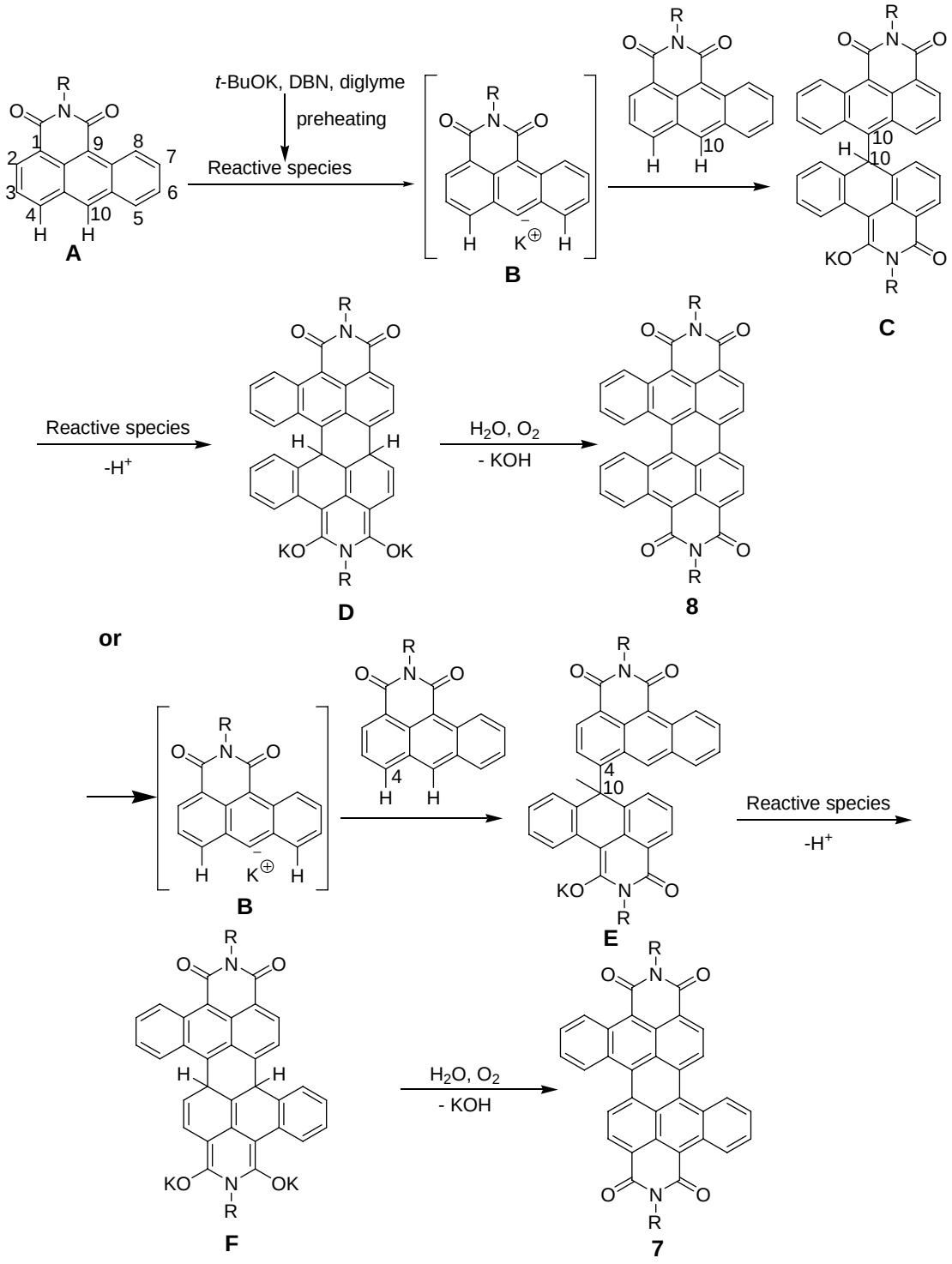
Scheme 25: Synthesis of aceanthrene green derivatives.

Compound **6a** was converted to aceanthrene green **7a** by molten KOH (iii), [17a,b,32,33] with **8a** also as a byproduct with ratio **7a:8a** (8:1), [18] which is higher than for other reported method. [52]

It was also found that compound **7** was the only compound that was obtained from reaction of compound **6** with molten KOH for *N*-alkylated or *N*-arylated starting materials **(6a-j)**. [18,48] A red vat dye was formed as an intermediate where its structure was hard to investigate because of its oxidation to aceanthrene green derivative. [18]

Using the new base complex (i and ii routes) leads to formation of both isomers from **6 g** coupling to obtain both compounds **29 (7g)** and **30 (8g)** that is shown in Scheme 23, but giving only one isomer in **6b** giving **8b (34)**, **6k** giving **8k (35)** and **6l** giving **8l (33)** cases which will be shown in this work later.

Scheme 24 shows a hypothesis how the coupling of anthracene imide derivative forms *cis* or *trans* or both forms of aceanthrene green derivatives (**7** and **8**).

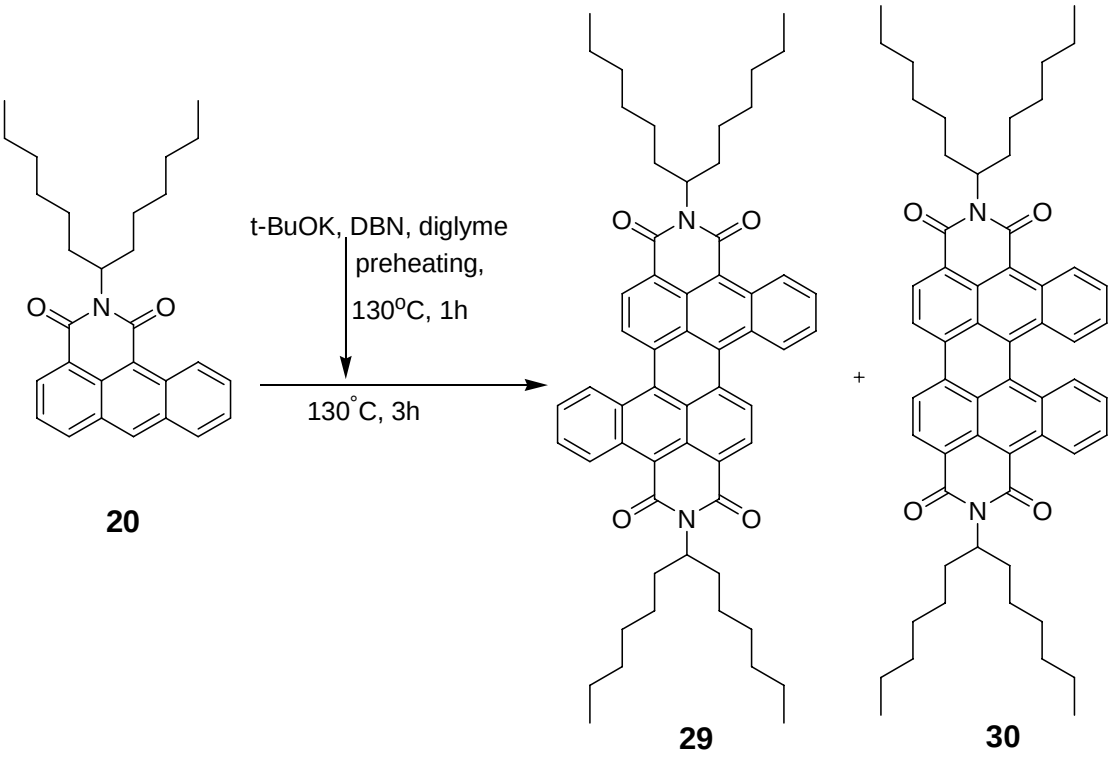


Scheme 26: Suggested mechanism for anthracene imide (6) coupling in the base complex *t*-BuOK/DBN to obtain aceanthrene green derivatives.

As shown in scheme 26, the reactive species from the preheated base complex attack the anthracene imide molecule creating negative charge on the middle aromatic ring (position 10) to give the intermediate **B**. Intermediate **B** has two ways to proceed, either by attacking the same position 10 in another molecule to give compound **8** at the end (cis form), or to attack position 4 in another anthracene imide molecule that gave compound **7** (trans form) at the end.

As shown here the two ways are proceeding through several intermediates which are (C and D) in the first case, (E and F) in the second one, we see that attacking the first molecule at position 10 that already obtained intermediate **B** ended by aromatic distortion of the middle ring and leaving the two edge benzene rings with their aromaticity that gives the compound more stability by decreasing its energy.

Changing the alkyl group (R) attached to nitrogen atom of imide gave only the *cis* form from coupling of compound **6** using the new base complex mentioned in Scheme 26.



Scheme 27: Synthesis of compounds 29 and 30 from *N*-(1-hexylheptyl) anthracene-1, 9-dicarboxylicacid imide (20).

Scheme 27 shows the formation of both aceanthrene green isomers with compound **30** as a byproduct, formed from coupling of *N*-(1-hexylheptyl)anthracene-1,9-dicarbox-ylicacid imide **(20)** preheated base complex *t*-BuOK/DBN.

The applied ratios were 1.0: 5.77: 7.50 (compound **20**: *t*-BuOK: DBN) that obtained directly both isomers in a one step reaction, with the same molar ratio and other reaction conditions whatever using DBN or DBU.

Changing ratios in bases changes completely the products, where, when *t*-BuOK (0.2g, 1.79 mmol), DBN (0.3 g, 2.42 mmol) and diglyme (0.6 mL), which means increasing base complex ratio to be 1.0: 29.8: 40.3 (compound **20**: *t*-BuOK: DBN), it gave red vat dye which requirers air to change slowly to compound **30**.

Figure 12 shows the ^{1}H NMR spectrum of compound **29** that elucidate more its structure.

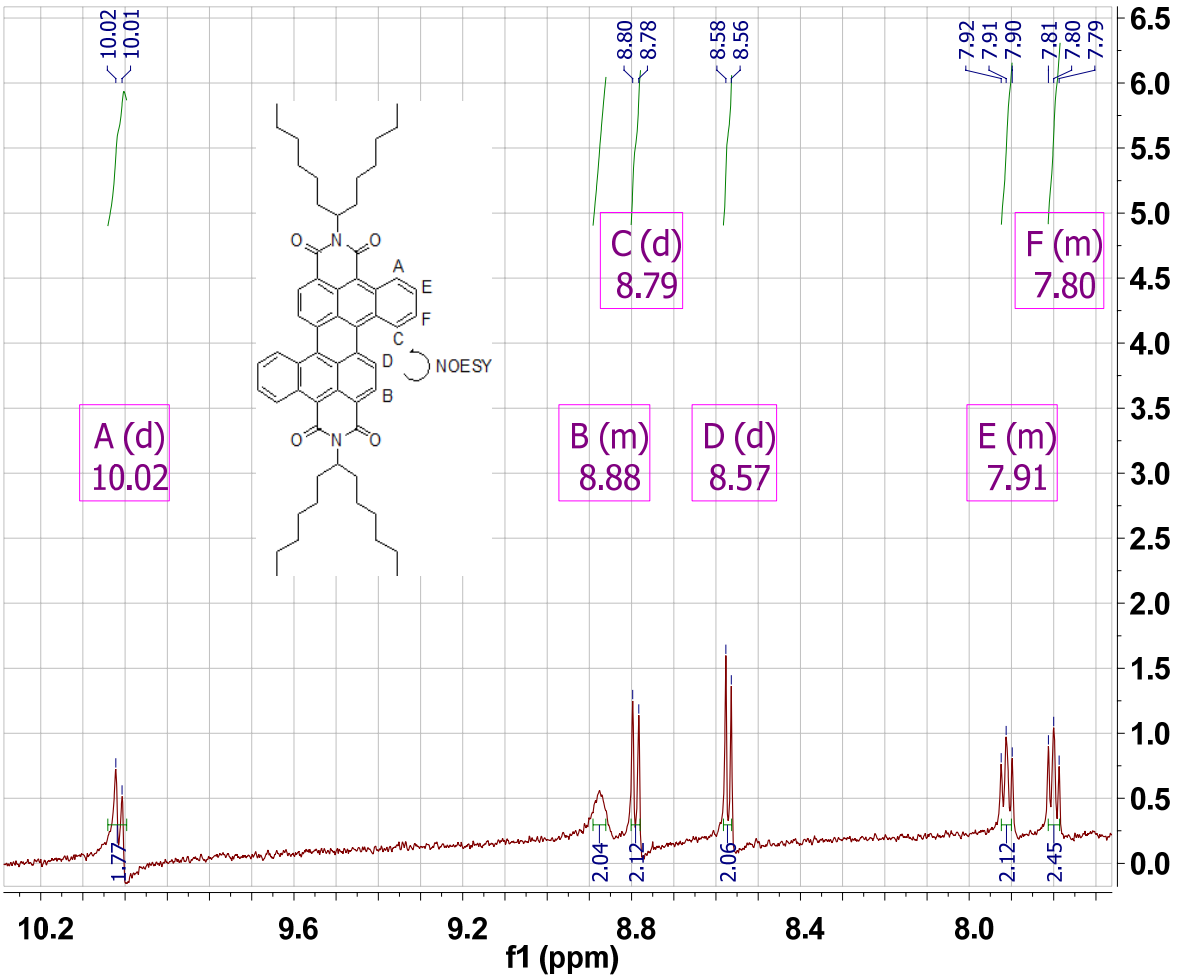


Figure 12: ^{1}H NMR spectrum of compound 29 (aromatic part).

Figure 13 shows NOESY-NMR spectrum of compound **29** which proves its structure through coupling of its aromatic protons.

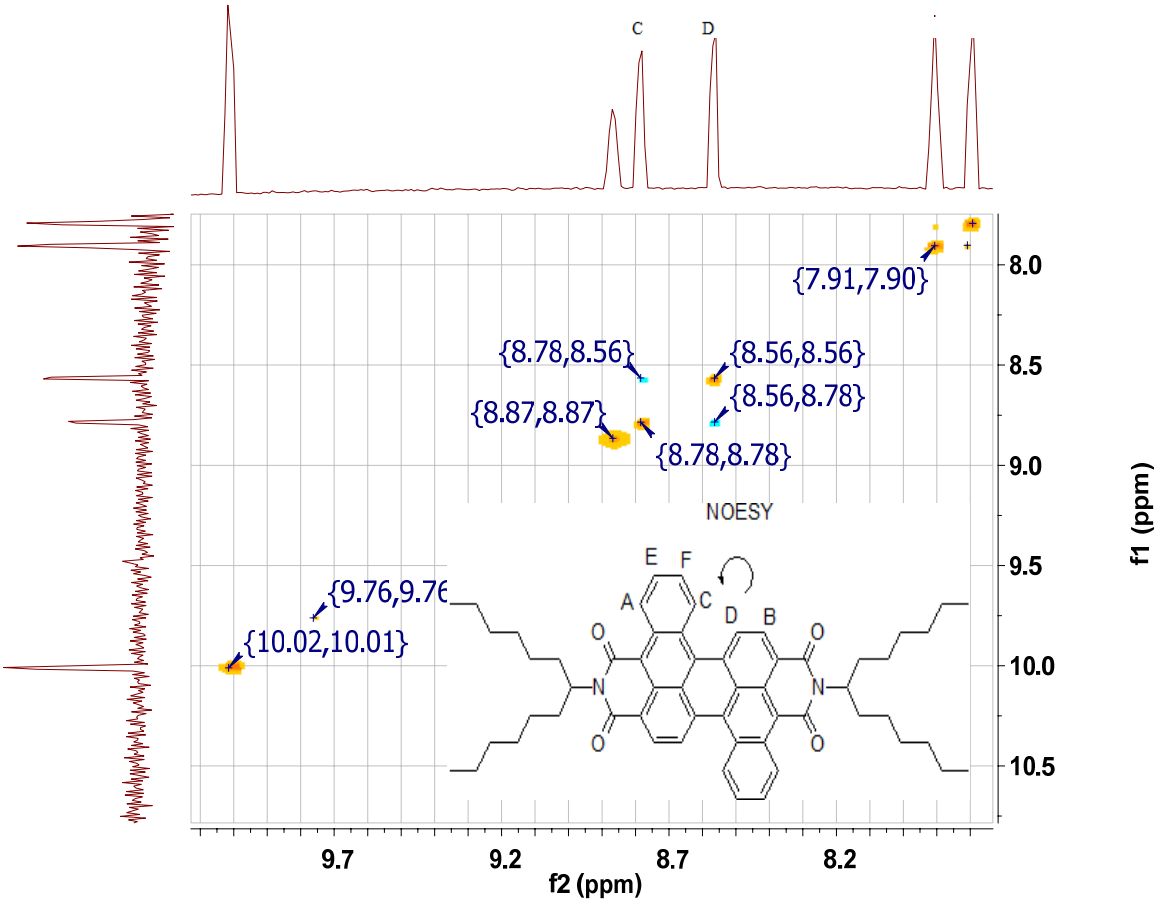


Figure 13: NOESY-NMR spectrum for aromatic part of compound 29.

As shown in figure 13, there is a cross peak between the two protons (H_C and H_D) at ***δ*** (8.78, 8.56) and (8.56, 8.78) ppm.

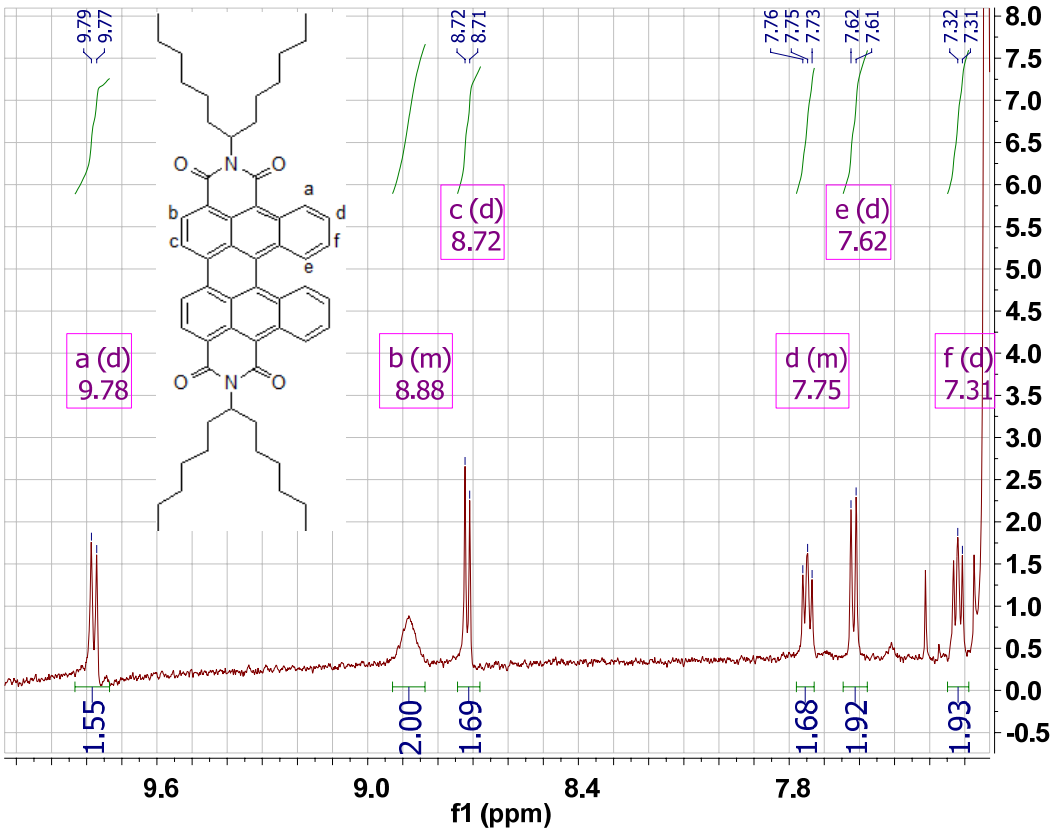


Figure 14: ^{1}H NMR spectrum of compound 30 (aromatic part).

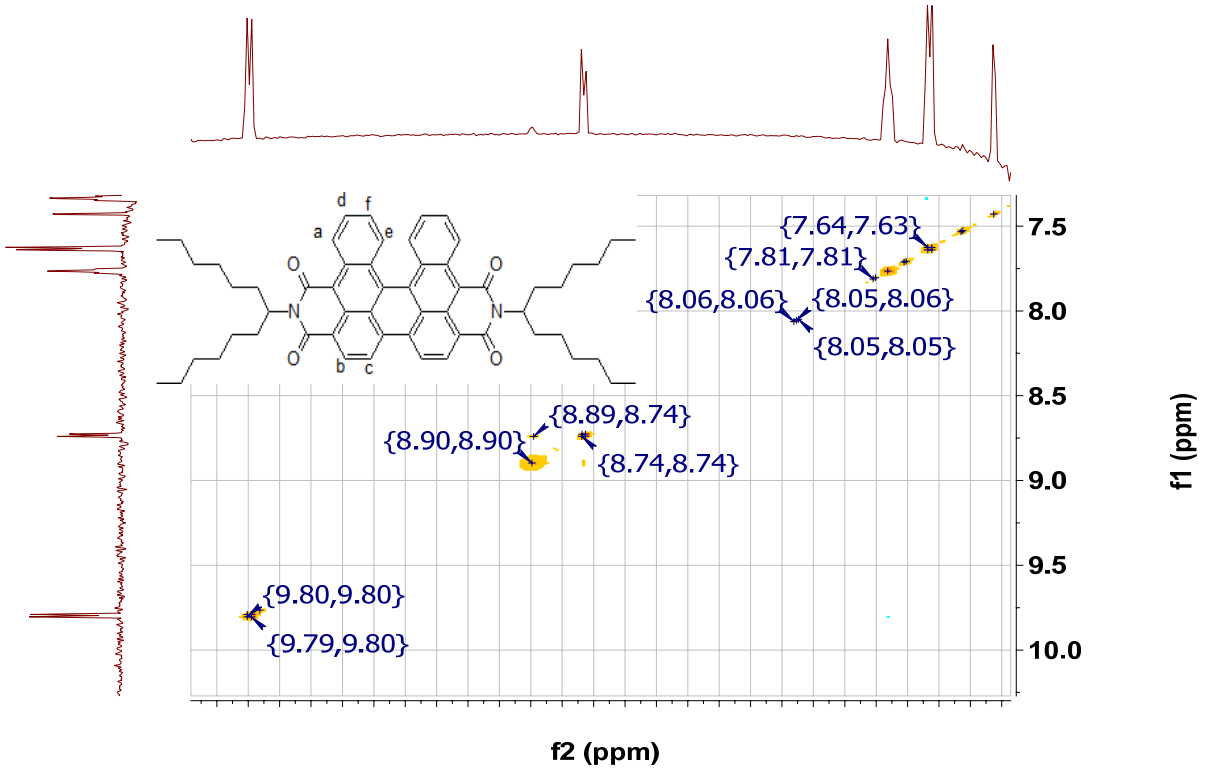


Figure 15: NOESY-NMR spectrum for aromatic part of compound 30.

Noesy NMR in figure 15 showed no coupling in space between protons on carbon c and other protons, but only coupling between b and c that appeared in the cross peaks (8.90, 8.74) and (8.74, 8.90) ppm.

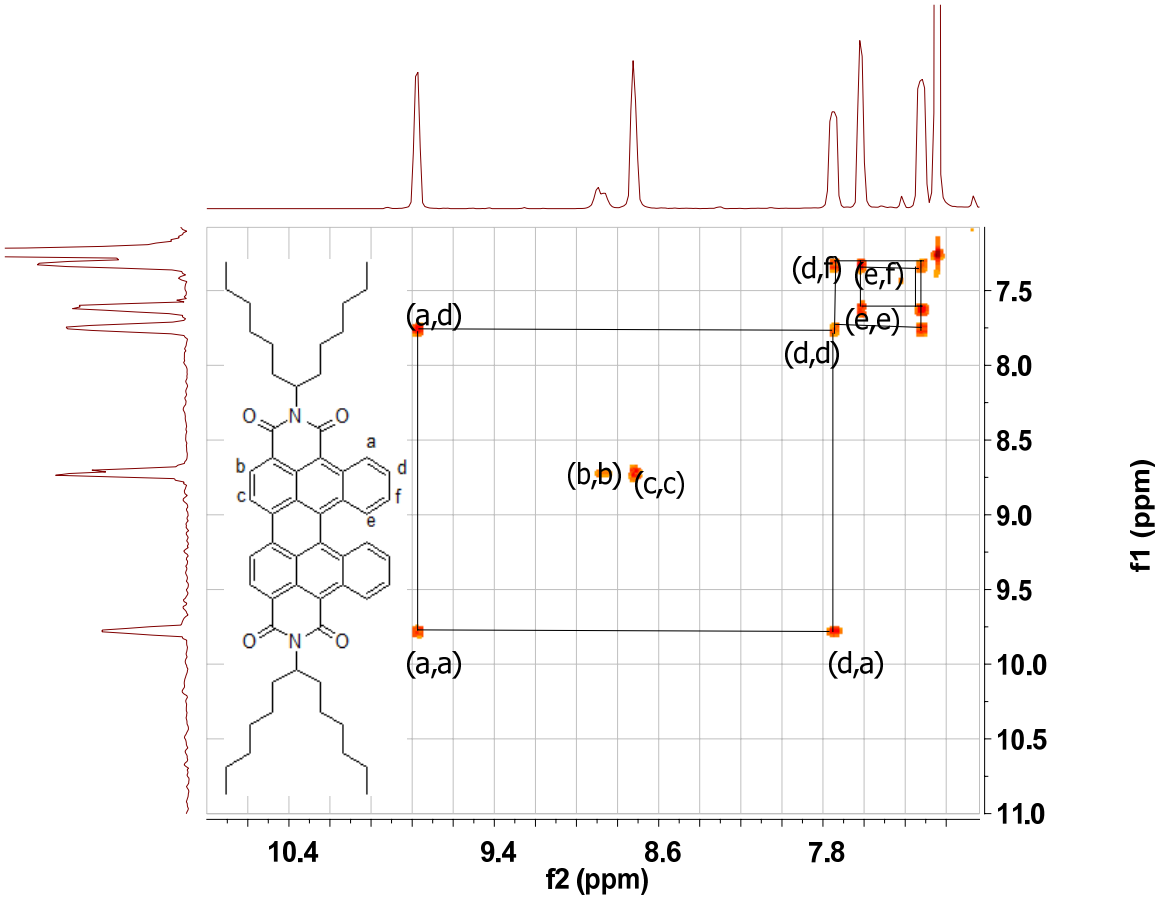
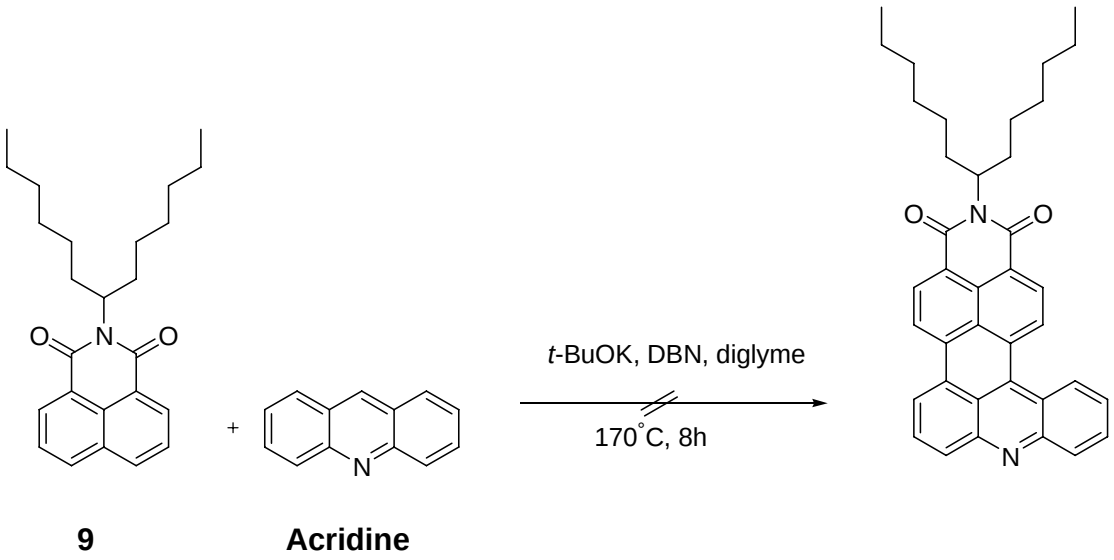


Figure 16: COSY-NMR spectrum for aromatic part of compound 30.

Figure 16 proved also the structure of the *cis* isomer via coupling of protons (H_a- H_d - H_f -H_e system) which is separated from H_b and H_c.

It is clear that H_f makes coupling with both H_e and H_d, H_d also makes with H_a, both H_b and H_c couple only with each other and not with any other proton in the compound, which is also shown in its NOESY-NMR in figure 15, and that proves well the *cis*-aceanthrene structure **(30)**.

2.2.7. Coupling of anthracene imides with naphthalene imides

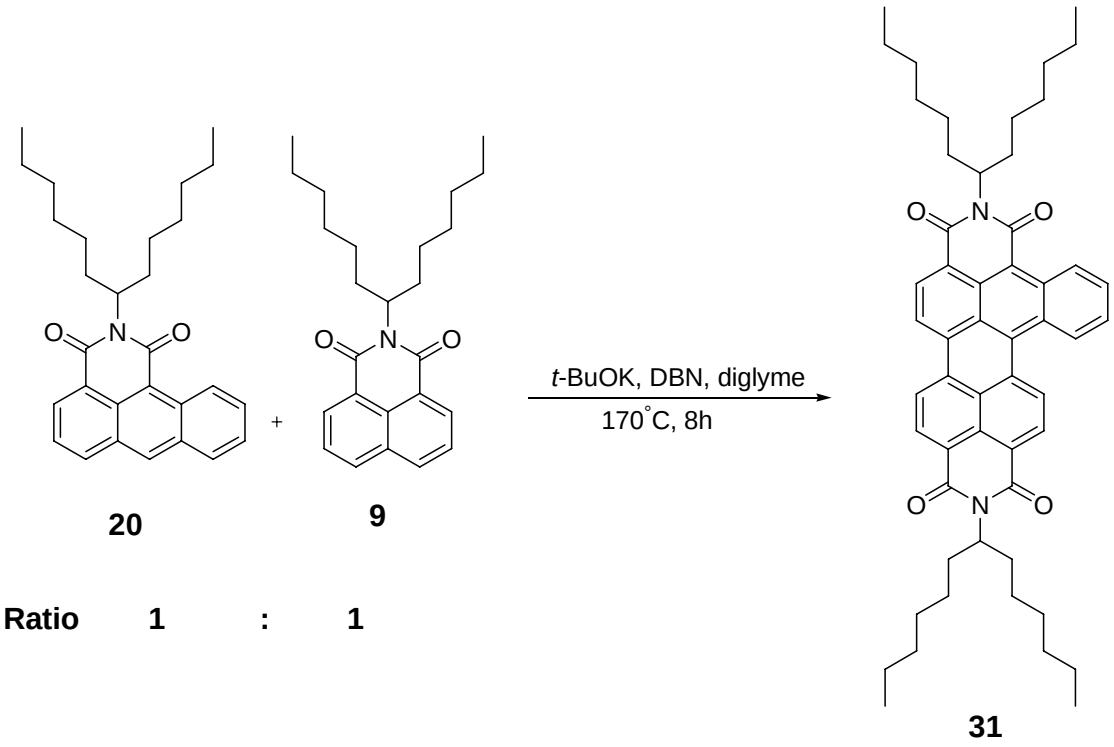


9 **Acridine**

Scheme 28

No success happened during coupling of *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide **(9)** together with acridine using the base complex (*t*-BuOK/DBN) at 130°C and 170°C (3 and 8 hours).

Scheme 29 shows the reaction coupling between compound **9** and **20**.



Scheme 29: Synthesis of 2,9-bis-(1-hexylheptyl)-[4,5]benzoanthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (31).

Scheme 29 shows that coupling finally worked between anthracene and naphthalene derivatives, and that happened when the base complex was preheated for 1 hour at 170°C under nitrogen atmosphere, then added both compounds *N*-(1-hexylheptyl)-naphthalene-1,8-dicarboxylicacid imide **(9)** and *N*-(1-hexylheptyl)anthracene-1,9-dicarboxylicacid imide **(20)** with the same molar ratio 1:1.

Figure 17 shows the absorption spectra of compound **31** compared to the two aceanthrene green isomers and with compound **4** (S-13) also.

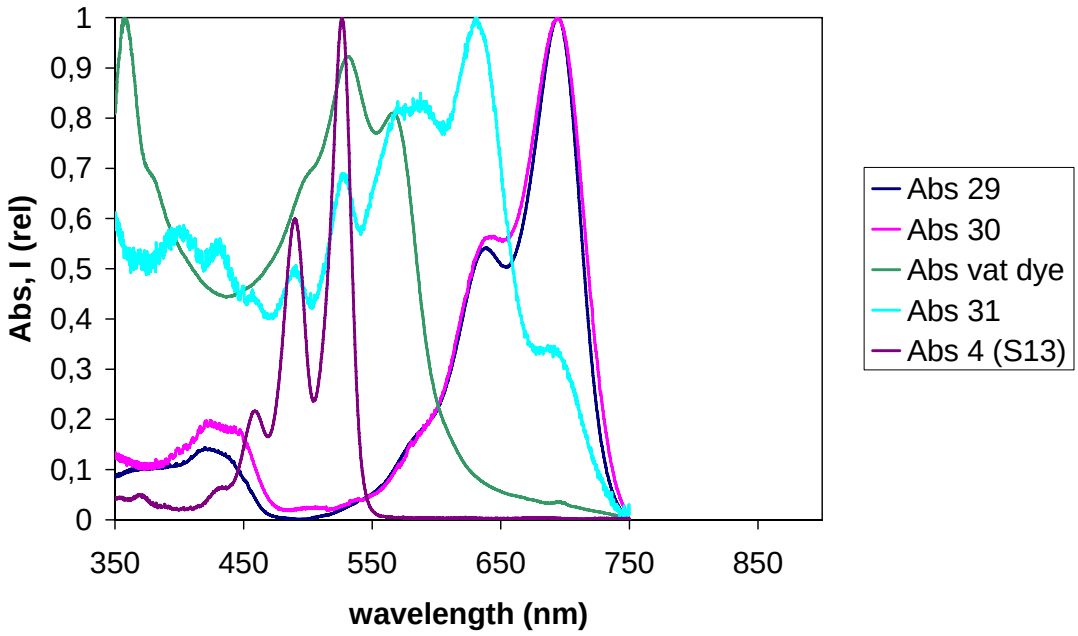


Figure 17: UV/Vis spectra of compounds 4 (S13), 29, 30 and 31 in $CHCl_3$.

As shown from figure 17, there is clear bathochromic shift for aceanthrene green isomers (**29** and **30**) compared with S-13 **(4)** by more than 150 nm.

The absorption spectra of compound **31** lies in an area between aceanthrene green and perylene bisimide (S-13) and also proves the attachement of the two different rings together (anthracene ring and naphthalene ring) in compound **31**.

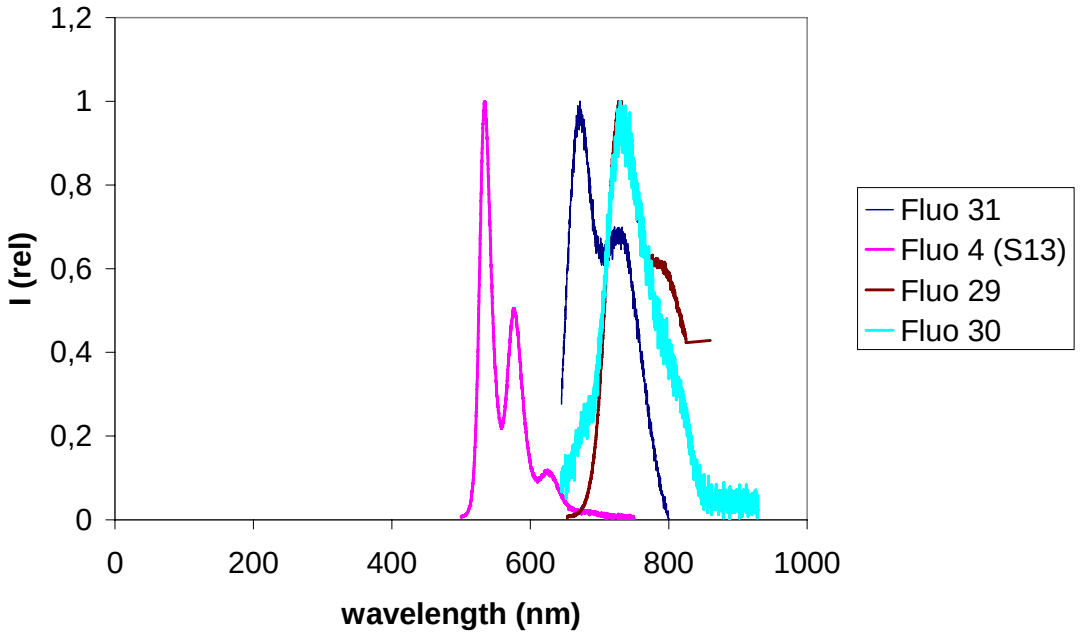
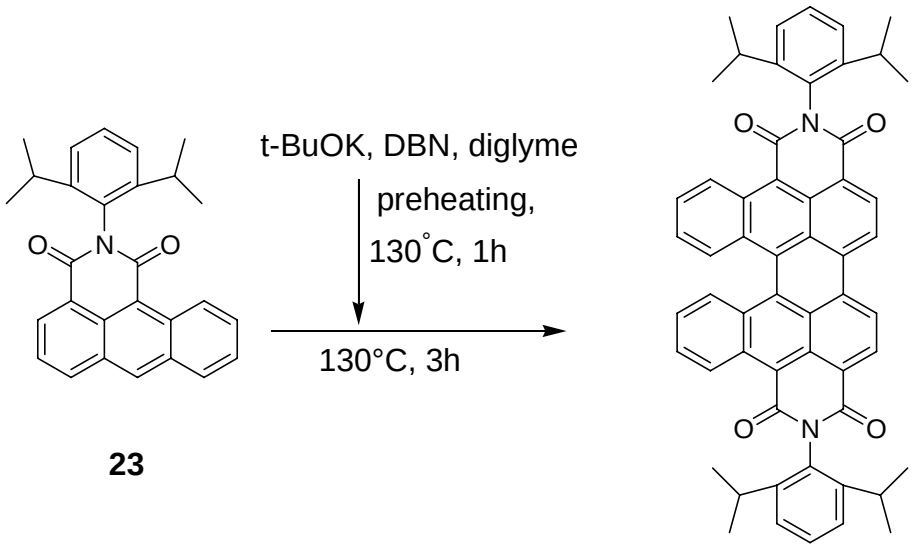


Figure 18: Fluorescence spectra of compounds 4 (S13), 29, 30 and 31 in $CHCl_3$.

Compound **31** exhibits strong fluorescence, with emission at longer wavelength than that of S-13 **(4)** and shorter than aceanthrene green derivatives as shown in figure 18.

2.2.8. Synthesis of *N,N'*-di-(2,6-diisopropylphenyl)-*cis*-aceanthrene tetracarboxylic bisimide



23 **32**

Scheme 30: Synthesis of compound 32 from compound 23.

Scheme 30 shows formation of *N,N'*-di-(2,6-diisopropylphenyl)-*cis*-aceanthrene tetracarboxylic bisimide **(32)** from coupling of *N*-(2,6-diisopropylphenyl)anthracene-1,9-dicarboxylicacid imide **(23)**, via its reaction with the preheated base complex *t*-BuOK/DBN in diglyme.

As mentioned before with compounds **29** and **30**, the used ratios here were 1.0: 5.77: 7.50 (compound **23**: *t*-BuOK: DBN) that obtained directly both isomers in one step reaction, whatever using DBN or DBU with the same molar ratio and other reaction conditions.

Changing ratios in bases changes completely the products, where, when *t*-BuOK (0.2g, 1.79mol), DBN (0.3 g, 2.42 mmol) and diglyme (0.6 mL), which means increasing base complex ratio to be 1.0: 29.8: 40.3 (compound **23**: *t*-BuOK: DBN), it gave red vat dye which changes slowly when exposed to air to compound **30** only. [52]

Figure 19 shows the ^{1}H ^{1}H-COSY-NMR spectrum of compound **32** that elucidate more its structure.

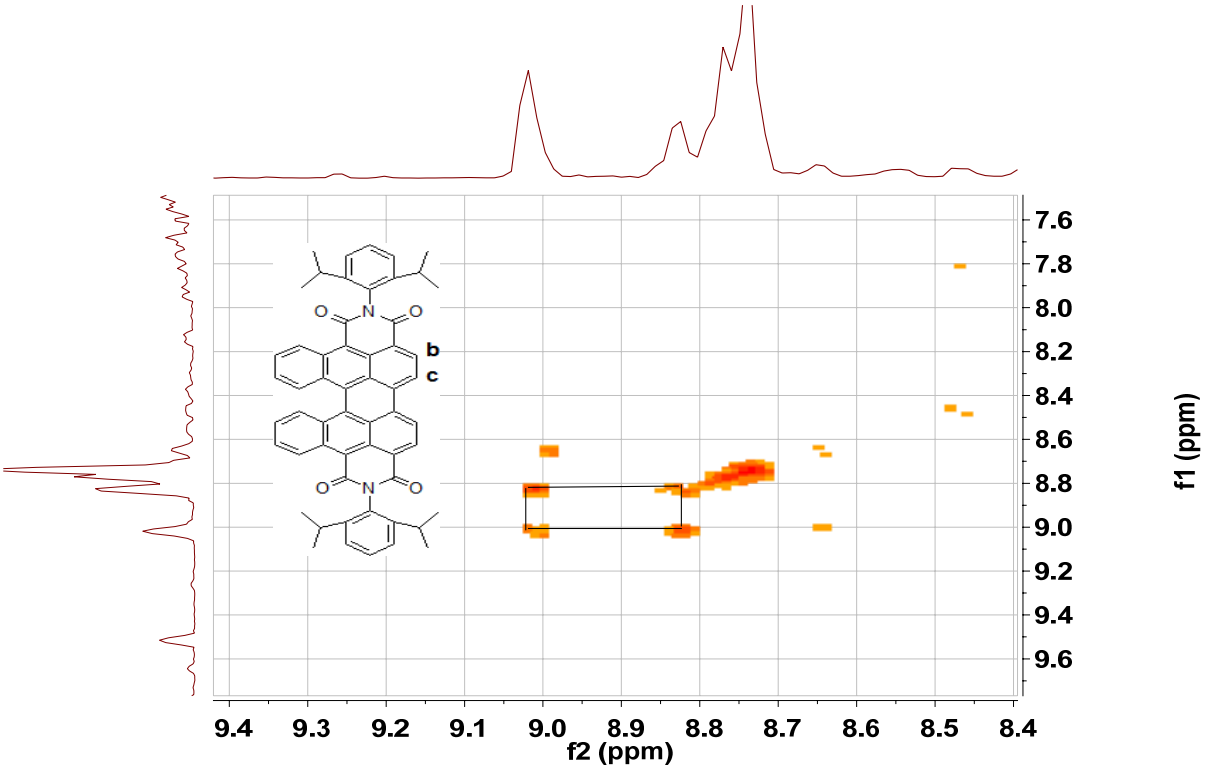


Figure 19: COSY-NMR spectrum for part of compound 32.

Both protons Hb and Hc are making coupling together only and isolated from the whole system.

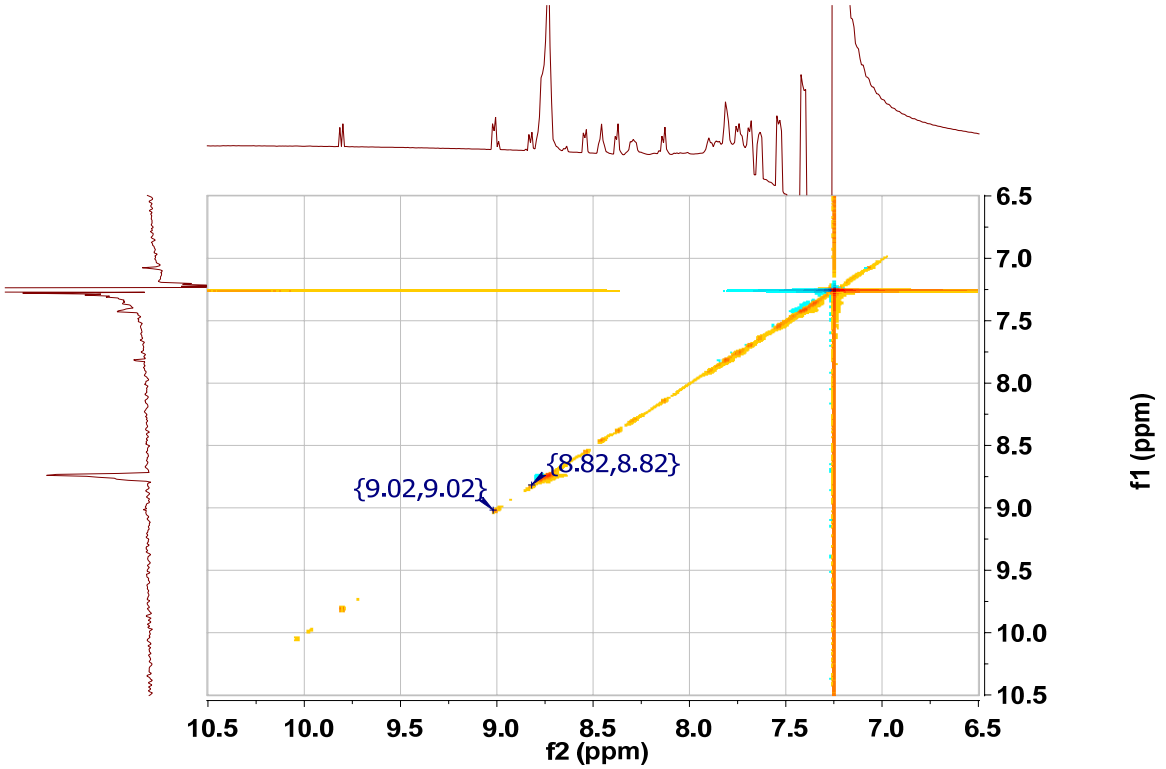
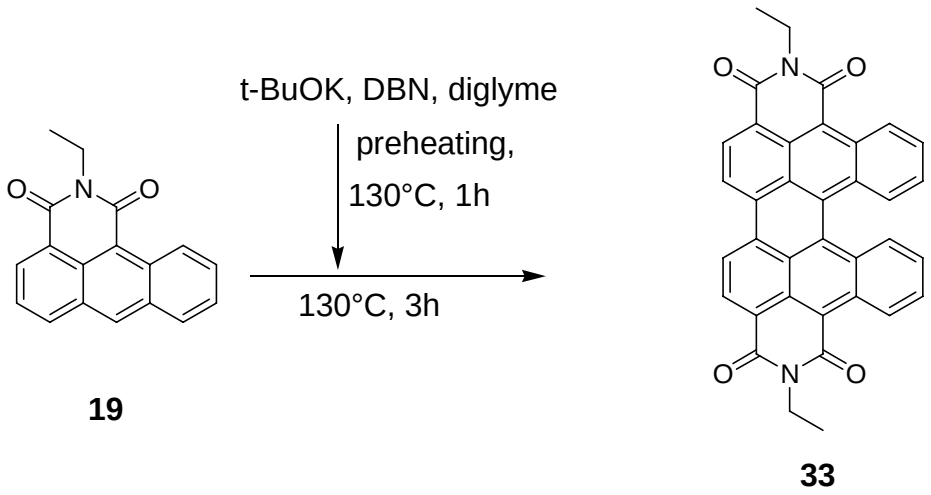


Figure 20: NOESY-NMR spectrum for part of compound 32.

Part of Noesy NMR spectrum of compound **32** proved also that the two protons H_b (9.02, 9.02) and H_c (8.82, 8.82) ppm are not coupling with any other proton in space (figure 20).

2.2.9. Synthesis of *N,N'*-diethyl-*cis*-aceanthrene tetracarboxylic bisimide



19 **33**

Scheme 31: Synthesis of compound 33 from compound 19.

N,N'-diethyl-cis-aceanthrene tetracarboxylic bisimide was obtained also using the same way of coupling in the mentioned base complex, where *N*-ethyl anthracene-1,9-dicarboxylicacid imide **(19)** reacted with the preheated base complex (*t*-BuOK/DBN in diglyme) to give compound **33**.

Figure 20 below shows well the ^{1}H NMR spectrum of **33** of its aromatic part.

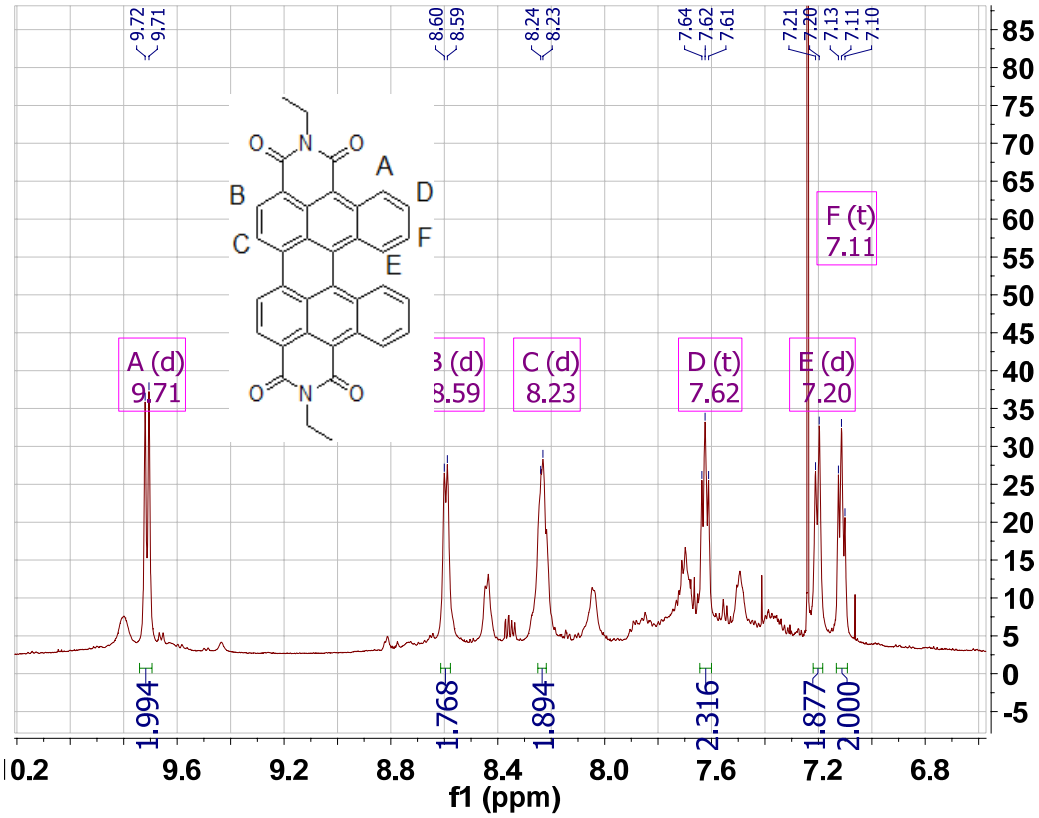


Figure 21: ^{1}H NMR spectrum for aromatic part of compound 33.

Figure 22 shows the proton proton cosy coupling for the aromatic part of compound **33** which will show how the two proton doublets H_B and H_C couple with each other.

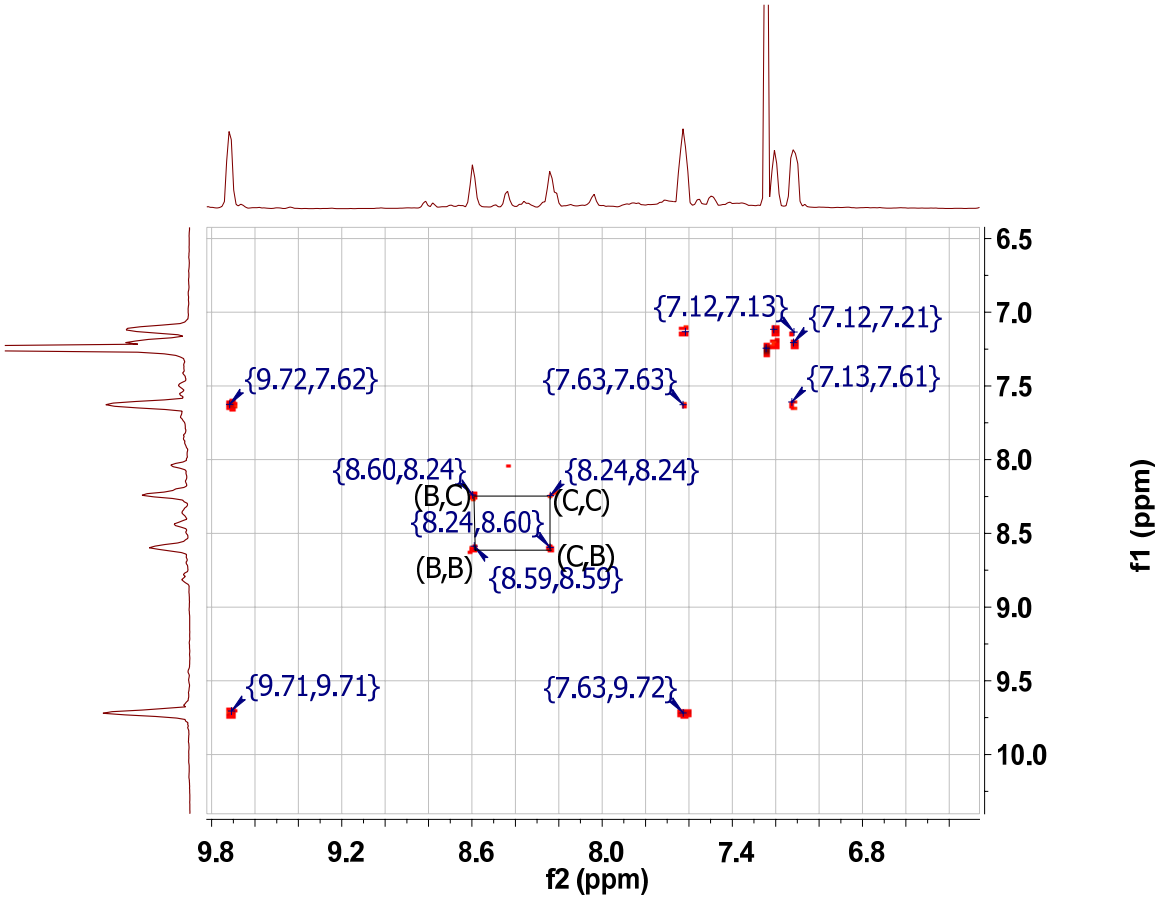


Figure 22: ^{1}H-^{1}H Cosy NMR spectrum for aromatic part of compound 33.

As shown in figure 22, coupling between H_B and H_C in the aromatic system, where they are not coupling with any other proton in the system except with themselves.
The two cross peaks at (8.60, 8.24) and (8.24, 8.60) ppm are showing the cross peak between H_B and H_C.

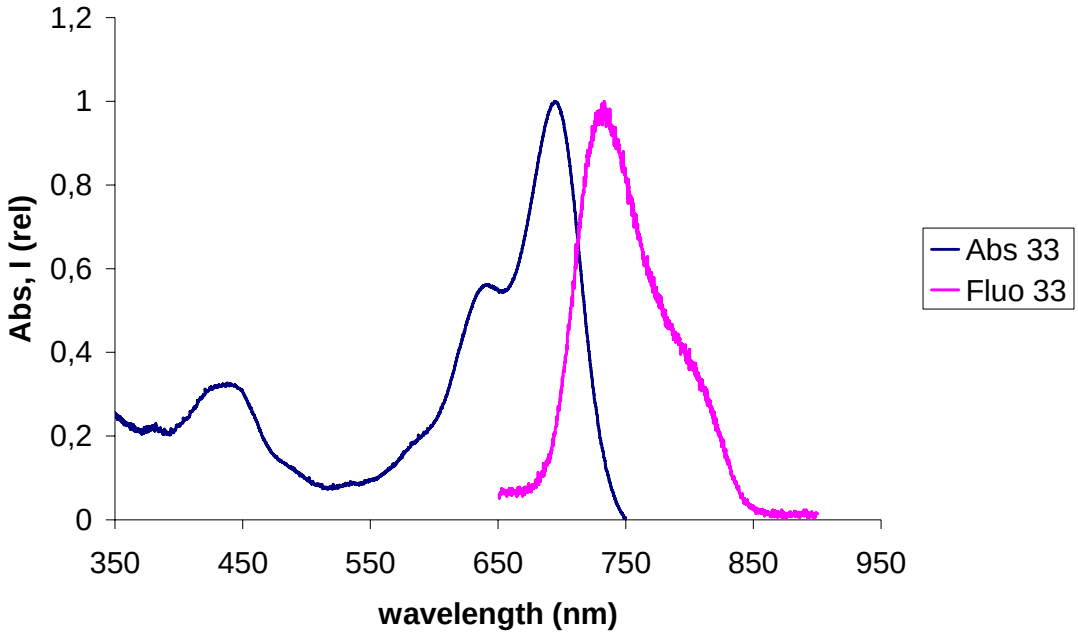
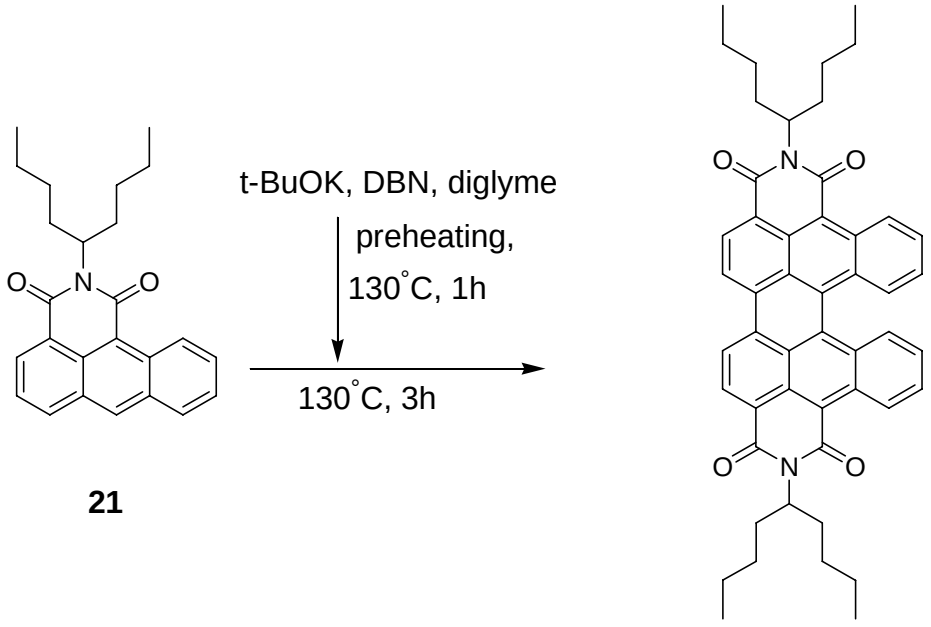


Figure 23: UV/Vis and fluorescence spectra of compound 33.

As shown in figure 23, Aceanthrene green derivative **(33)** shows absorption and intense fluorescence spectra also like other aceanthrene green derivatives (**29**, **30**, **31** and **32**) in the visible and NIR regions.

Compound **33** absorbs at maximum wavelength 694 nm which is in the NIR region, and exhibits fluorescence emission at 733 nm (λ_{max} = 733.1 nm.) when excited at 641 nm (λ_{exc} = 641.0 nm).

2.2.10. Synthesis of N,N'-di-(1-butylpentyl)-*cis*-aceanthrene tetracarboxylic bisimide



21 **34**

Scheme 32: Synthesis of compound 34 from compound 21.

The *cis* isomer **(34)** is the only product that was obtained during coupling of compound **21** with the base mixture (*t*-BuOK/DBN), in contrast to compounds **29** and **30**, even after using the same molar ratios.

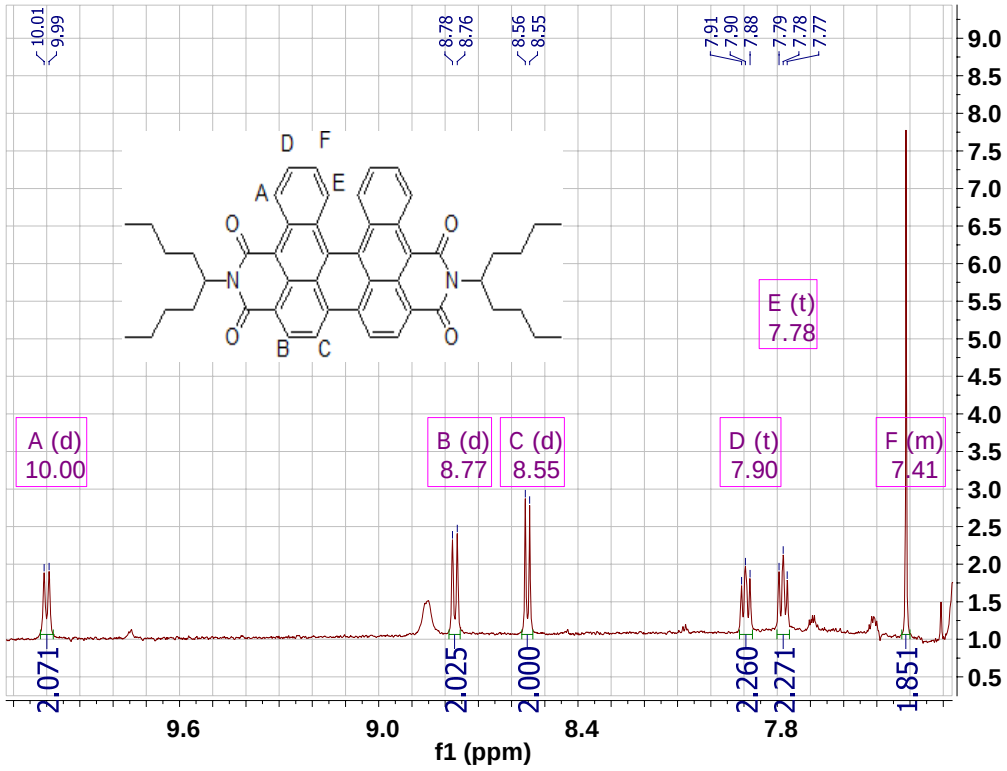


Figure 24: ^{1}H NMR spectrum for aromatic part of compound 34.

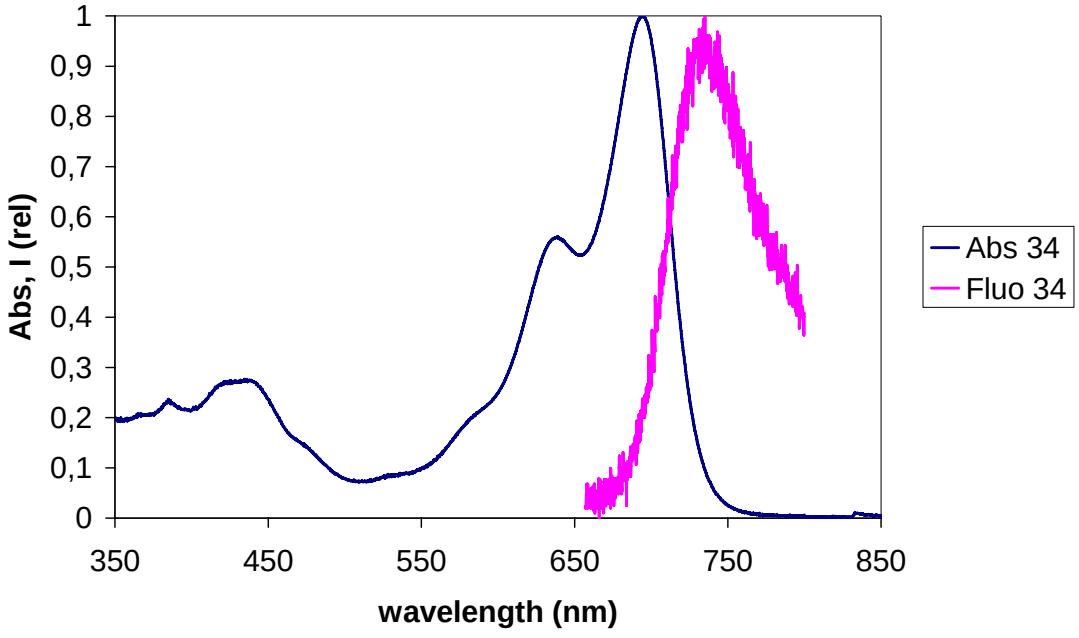


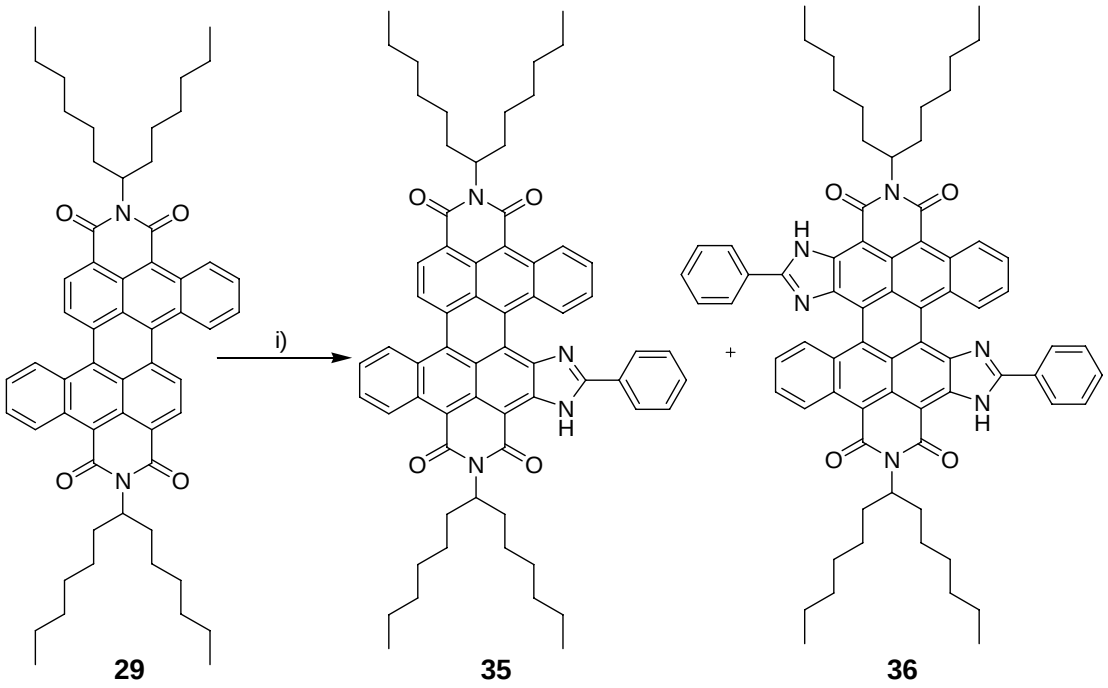
Figure 25: UV/Vis and fluorescence spectra of compound 34.

N,N'-Di-(1-butylpentyl)-*cis*-aceanthrene tetracarboxylic bisimide is not different in NMR (^{1}H, ^{13}C, Noesy or Cosy) from other *N*-alkylated *cis*-aceanthreme green dyes.

Also from figure 21, compound **34** is characterised by absorption and fluorescence emission in the visible and NIR region like other aceanthrene green derivatives.
Figure 27 will show later the absorption spectra of compound **34** compared with **29**, **30** and other compounds.

2.3. Synthesis and final structure elucidation of anthracene with lateral heterocyclic ring expansion

2.3.1. Synthesis of 2,12-bis(1-hexylheptyl)-9-phenylimidazolo [4',5':3,4]benzo-[*h*]anthra[2,1,9-*def*:6,5,10*d'e'f'*]benzo[*h'*]diisoquinoline-1,3,11,13(2 H, 10 H)-tetraone (35) and 2,12-Bis(1-hexylheptyl)-9-phenylimidazolo[4',5':3,4]-15-phenylimidazolo[4'',5'':7,8]benzo[*h*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]benzo[*h'*]diisoquinoline-1,3,11,13(2H,10H)-tetraone (36)

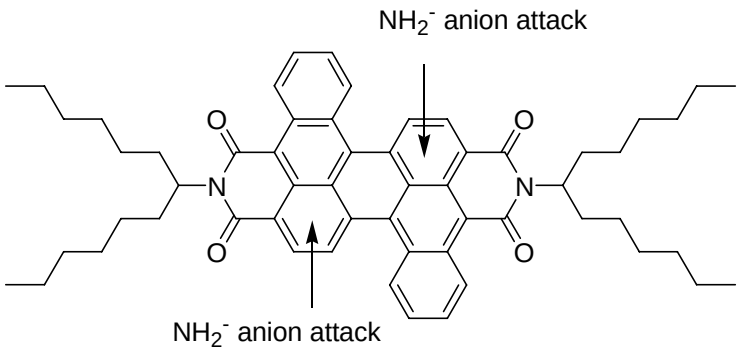


i): $NaNH_2$, benzonitrile (), 165°C.

Scheme 33: Synthesis of compounds 35 and 36 from compound 29.

Compound **29** undergoes nucleophilic substitution reaction (Scheme 33) and reacts with sodium amide and benzonitrile to obtain the two compounds **35** and **36**.

The first nucleophilic attack was done by NH_2^- anion in terms of *Chichibabin reaction* to the anthracene aromatic system, which attacked the benzene ring closer to the imide group as shown in figure 26.



29

Figure 26: NH_2^- attack to *trans*-aceanthrene green derivative (29).

Compound **35** has only one lateral aromatic extension imidazole ring attached to the anthracene nucleus. Mass spectrometry showed molecular ion peak at 970.56 which is the molecular weight of compound **35**.

Compound **36** has two lateral imidazole rings attached to the anthracene aromatic system as shown in its structure in Scheme 31.

Proton NMR also did not show any singlets except the one proton attached to the nitrogen atom in the imidazole ring in case of **35** and 2 singlet protons in case of compound **36**. Mass spectrometry for compound **36** showed also molecular ion peak at 1087.50 which was calculated as its molecular weight.

When imidazole ring was fused with the benzene ring of the anthracene nucleus (compounds **35** and **36**), NH of the imidazole ring was placed in the indicated position mentioned in the structure, where the proton forms an intramolecular hydrogen bond with the carbonyl group of the bisimide which was proved also before but with perylene bisimide **(4)** in the Ph.D. thesis of Dr. Simon Kinzel. [20]

Figure 26 shows the absorption spectra of both compounds **35** and **36** compared to their starting substance **(29)**, and compounds **30**, **34** and the red vat dye that was formed before during compound **30** synthesis.

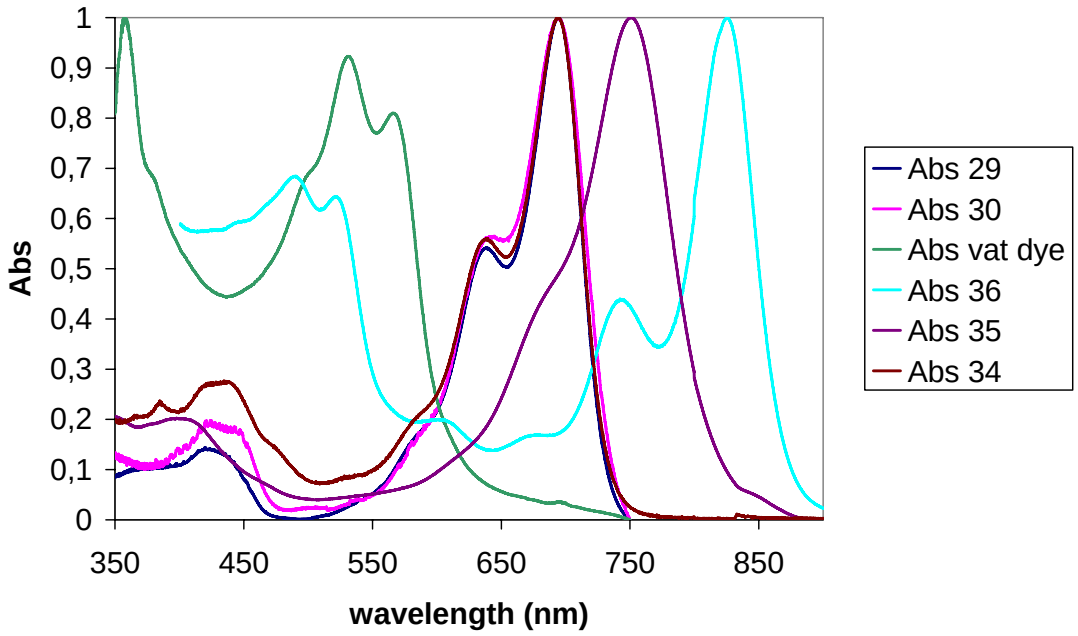


Figure 27: UV/Vis spectra of the red vat dye (sea green), 29 (dark blue), 30 (pink), 34 (dark red), 35 (plum) and 36 (turquoise) in $CHCl_3$.

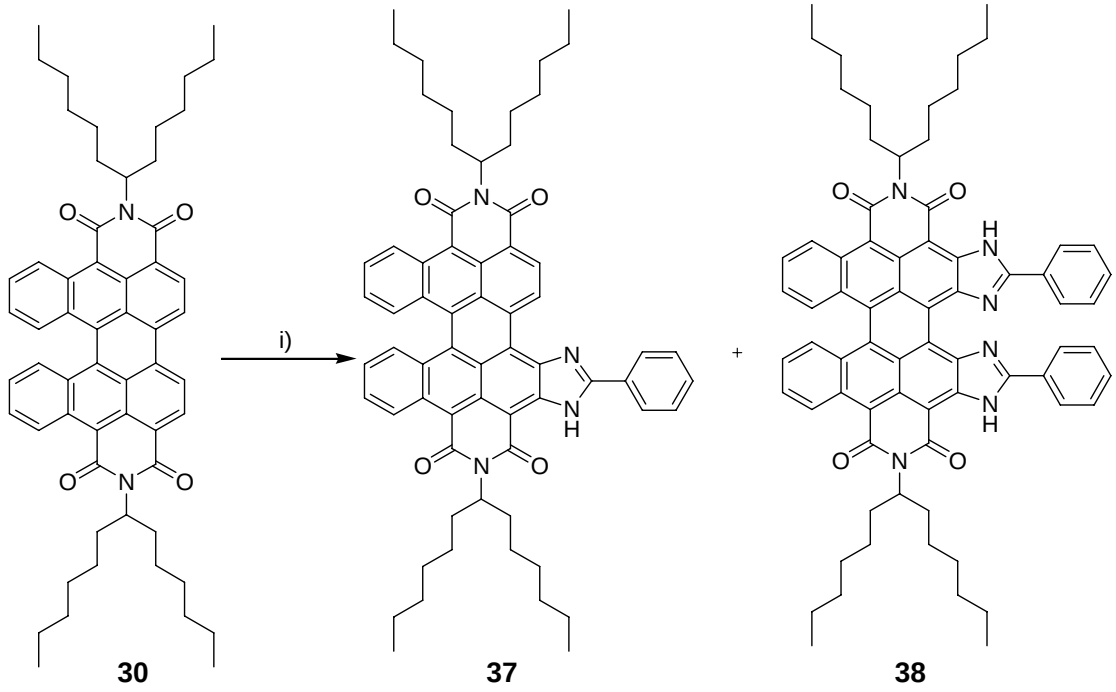
It is clear from the above figure (27) that compound **34** exhibits the same or typical absorption spectra for both compounds **29** and **30**, and that means there is no difference in absorption spectra between *N*(1-butylpentyl) and *N*(1-hexylheptyl) when attached to nitrogen atoms of both imides group in aceanthrene green isomers, in addition to the similarity of these absorption spectra also between *cis* and *trans* isomers.

Compounds **29, 30** and **34** all absorb at 694 nm, while compound **35** absorbs at maximum wavelength 750 nm that exhibits 56 nm bathochromic shift compared with the above mentioned compounds (**29**, **30** and **34**).

Compound **35** showed one phenylimidazolo lateral ring extension in its structure that happened in one side of the *trans*-aceanthrene green **(29)**, which decreases the energy gap between HOMO and LUMO that increased the absorption wavelength of compound **35**.

Another bathochromic shift by 131 nm occurred to compound **36** to absorb at wavelength 825 nm, due to extension of the aromatic system by two imidazole rings each attached to phenyl group in 2-position, and that happened from both sides of anthracene nucleus in trans-aceanthrene green derivative **(29)**.

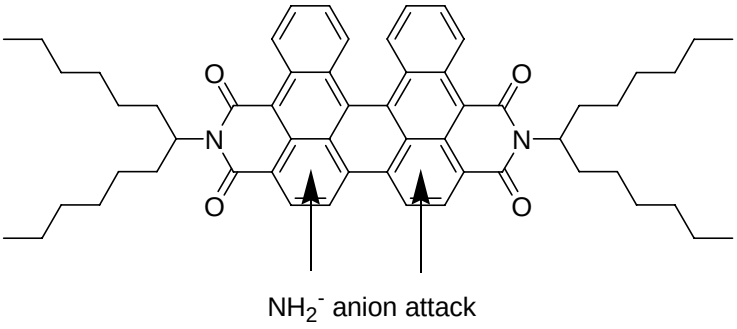
2.3.2. Synthesis of 2,10-bis(1-hexylheptyl)-5–phenylimidazolo[4',5':3,4]benzo[7,8] anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline benzo[*h*]isoquinoline-1,3,9,11(2 H, 10 H)-tetraone **(37)** and 8,19–bis-(1-hexylheptyl)dibenzo[3,4-5,6]phenanthra[2,1,10-*def*:7,8,9-*d'e'f'*]-2,5-diphenyl-1,4,8,19-tetrahydro-imidizo[4,5-*h*:4',5'-*h'*]diisoquinoline-7,9,18,20-tetraone **(38)**



i): $NaNH_2$, benzonitrile, 165°C.

Scheme 34: Synthesis of compounds 37 and 38 from compound 30.

Compound **30** proceeds also the same way like mentioned above in case of compound **29** (**section 2.3.1),** where compound **30** proceeds nucleophilic substitution via NH_2^- anion attack on the benzene ring that is attached directly to the imide group as shown in figure 27.



30

Figure 28: NH_2^- attack to *cis*-aceanthrene green derivative (30).

That nucleophilic attack can happen in one or two rings as shown in figure 28, where there are two available places, leading to nucleophilic substitution in one ring and formation of one imidazole fused with one aromatic ring from the anthracene molecule, to obtain compound **37**, or, for both rings to give compound **38**.

The ^{1}H NMR spectra of compound **37** (figure 29) and compound **38** (figure 31) are shown below:

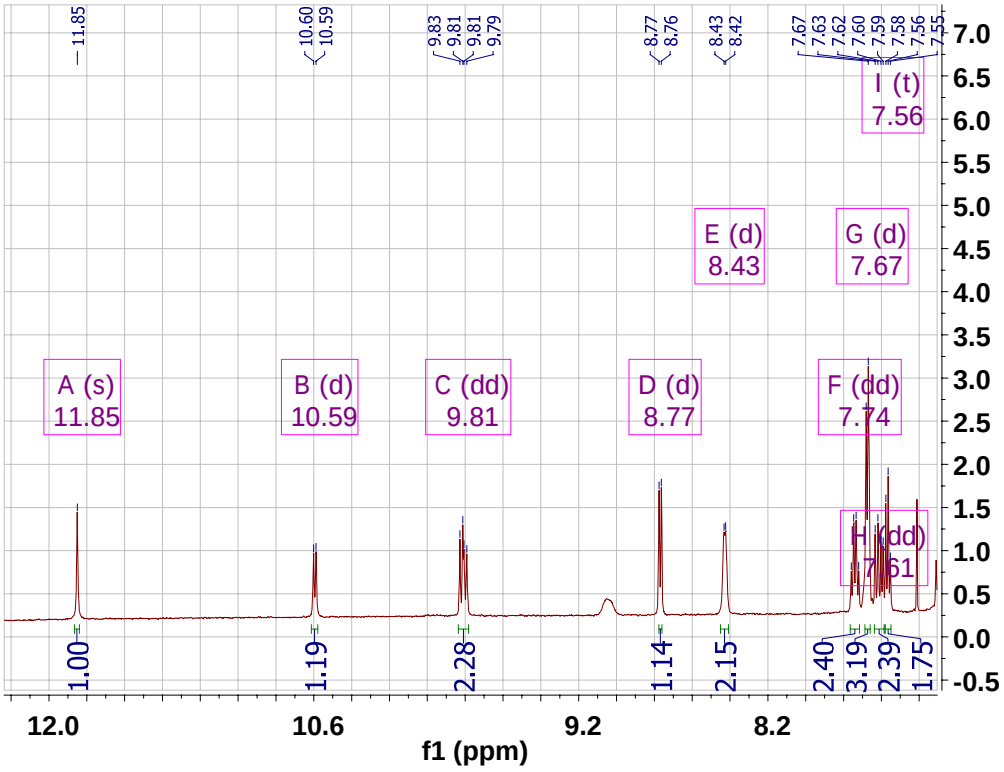


Figure 29: ^{1}H NMR for aromatic part of compound 37.

The singlet proton at 11.85 ppm is clear to be the –NH proton in the imidazole ring, and it is clear also that the signals of the protons of compound **37** which are shown in figure 28 do not exhibit any singlet other than the one at 11.85 ppm. That is evidence that shows also the nucleophilic attack occurred to the benzene rings close to the imide group like mentioned in figure 28 and not to the other benzene rings that are far from the imide group (figure 30).

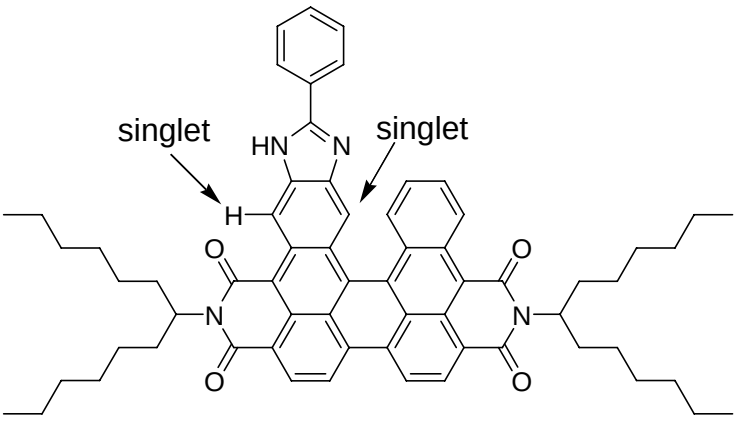


Figure 30: The other possible structure of compound 37 if NH_2^- attack occured in different benzene ring.

As shown above in figure 30, if the structure mentioned in that figure was right, two other singlet protons should appear in the ^1H NMR spectra of the aromatic part of compound **37** (figure 29), and that process also the right suggested structure of compound **37**.

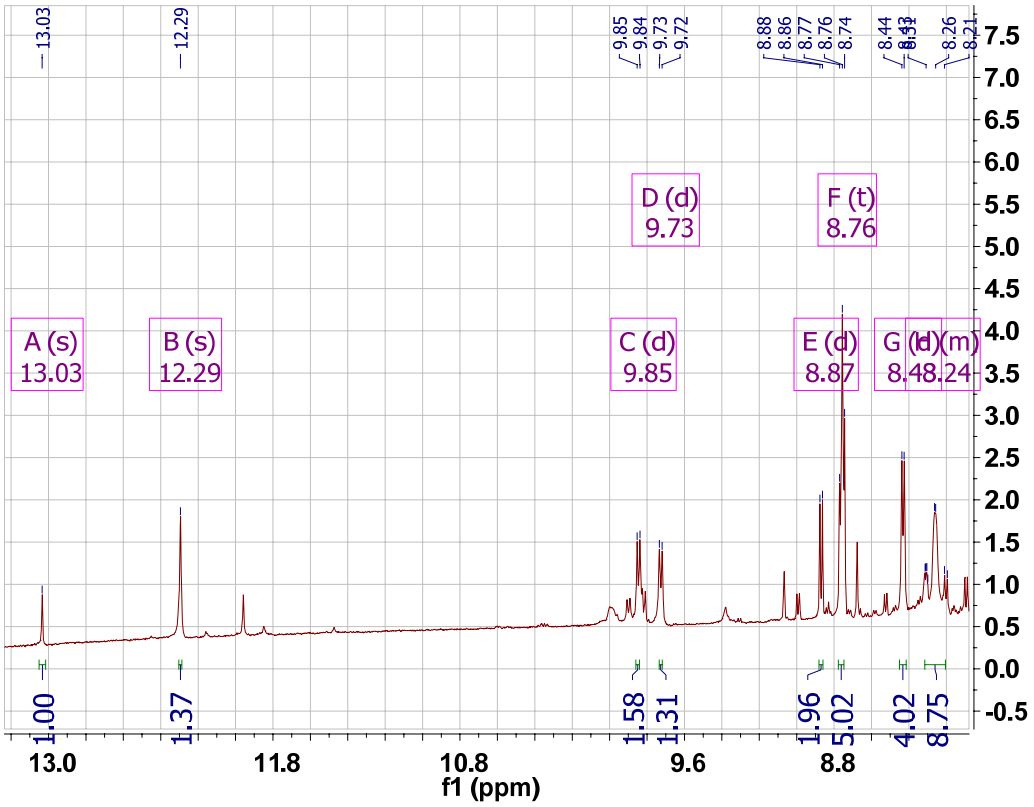


Figure 31: ^{1}H NMR spectra of compound 38 (aromatic part).

From the above mentioned figure (31), two singlet protons are appearing at 13.03 and 12.29 ppm, which are the protons attached to both nitrogen atoms in the two fused imidazole rings in compound **38**, and there are no other singlet peaks in the spectra, that means both imidazole rings are attached to both rings which are close to the imide, which may be a consequence of electron withdrawing effect that enhances the nucleophilic substitution that occurred when cis-aceanthrene green derivative **(30)** reacted with benzonitrile and sodium amide.

Figure 32 also shows the product from the alternative, not verified nucleophilic attack.

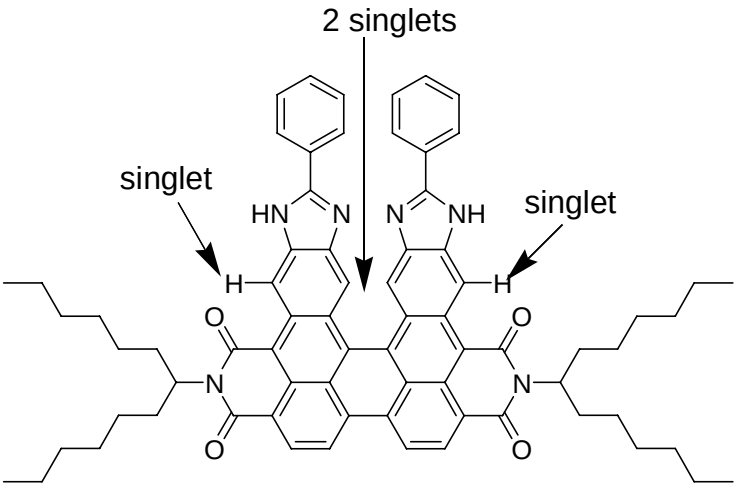


Figure 32: A second possible structure of compound 38 if NH_2^- attack occured in different benzene ring.

As shown above in figure 32, if the structure mentioned in that figure was right, four other singlet protons should appear in the ^1H NMR spectra of the aromatic part of compound **38** (figure 30), and that process also the right suggested structure of compound **38**.

Figure 33 shows the different absorption spectra of compounds **37** and **38** compared with other compounds.

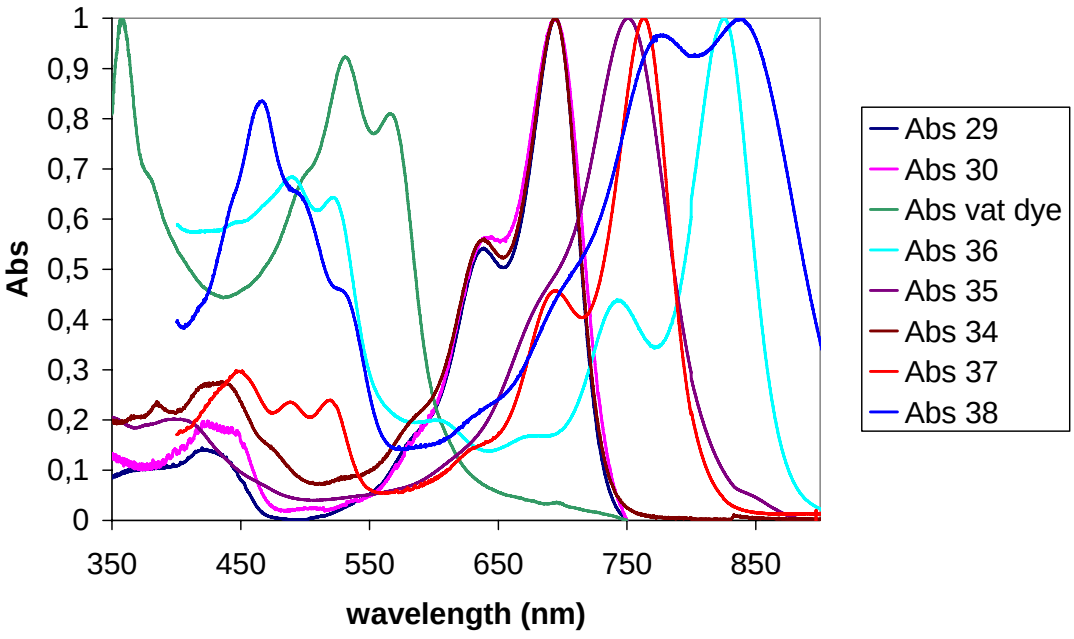


Figure 33: UV/Vis spectra of red vat dye (sea green), 29 (dark blue), 30 (pink), 34 (dark red), 35 (plum), 36 (turquoise), 37 (red) and 38 (blue).

It is clear from the above figure (33) that slight bathochromic shift by 13 nm occurred in case of compound **37** which absorbs at maximum wavelength of 763 nm compared with compounds **35** (750 nm). Both **35** and **37** have one fused phenylimidazole ring as a lateral extension to aceanthrene green nucleus in their structure. That slight bathochromic shift of compound **37** compared with **35** could arise from some kind of stabilisation in the *cis* structure with respect to the *trans* one of aceanthrene green derivatives.

That kind of stability appeared clearly during formation of the *cis* forms (**32**, **33** and **34**) from their starting materials, and not the *trans* derivatives as mentioned above in that part.

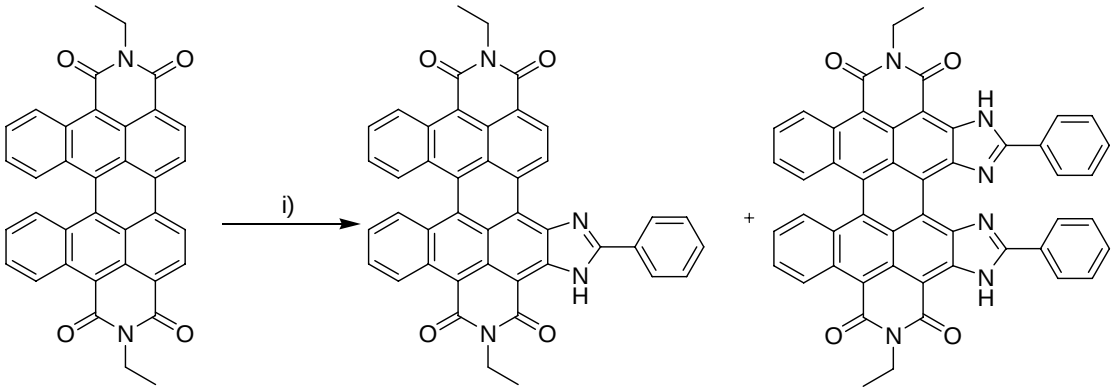
More stability of the *cis* form of aceanthrene green derivative or the extended one with phenyl imidazole ring, decreases the energy gap between HOMO and LUMO , accordingly, increased the absorption wavelength of compound **37** than the trans form of compound **35**.

Another bathochromic shift by 131 nm occurred to compound **36** to absorb at wavelength 825 nm, due to extension of the aromatic system by two imidazole rings each attached to phenyl group in 2-position, and that happened from both sides of anthracene nucleus in trans-aceanthrene green derivative **(29)**.

The same difference was found between compounds **36** and **38**, where the later which is also the *cis* form absorbs at maximum wavelength (839 nm) 14 nm more than that of compound **36** (825 nm).

Fluorescence spectra of these compounds were difficult to obtain because of their absorption in the NIR even more bathochromic emission.

2.3.3. Synthesis of 2,10-bis(ethyl)-5–phenylimidazolo[4',5':3,4]benzo[7,8]anthra-[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinolinebenzo[h]isoquinoline–1,3,9,11(2 H,10 H)-tetra-one **(39)** and 8,19–bis-(ethyl)dibenzo[3,4-5,6] phenanthra-[2,1,10-*def*:7,8,9-*d'e'f'*]-2,5-diphenyl-1,4,8,19-tetrahydro-imidizo[4,5-*h*:4',5'-*h'*]diisoquinoline-7,9,18,20-tetr-aone **(40)**



33 **39** **40**

i): $NaNH_2$, benzonitrile, 165°C.

Scheme 35: Formation of compounds 39 and 40 from reaction of compound 33 with mixture of benzonitrile and sodium amide at 165°C.

Compound **33** undergoes nucleophilic substitution reaction (Scheme 35) and reacts with sodium amide and benzonitrile to obtain the two compounds **39** and **40**.

The first nucleophilic attack as mentioned before was done by NH_2^- anion in terms of *Chichibabin reaction* to the anthracene aromatic system, which attacked the benzene rins closer to the imide group, to give compound **39**, followed by another nucleophilic attack to the other ring to obtain compound **40**.

Mass spectrometry was the first evidence for both compounds' structure determination, where the first compound **(39)** showed molecular ion peak at 662.20 which is its molecular weight, while the second one **(40)** showed peak at 778.23 in its mass spectra, which is its molecular weight also.

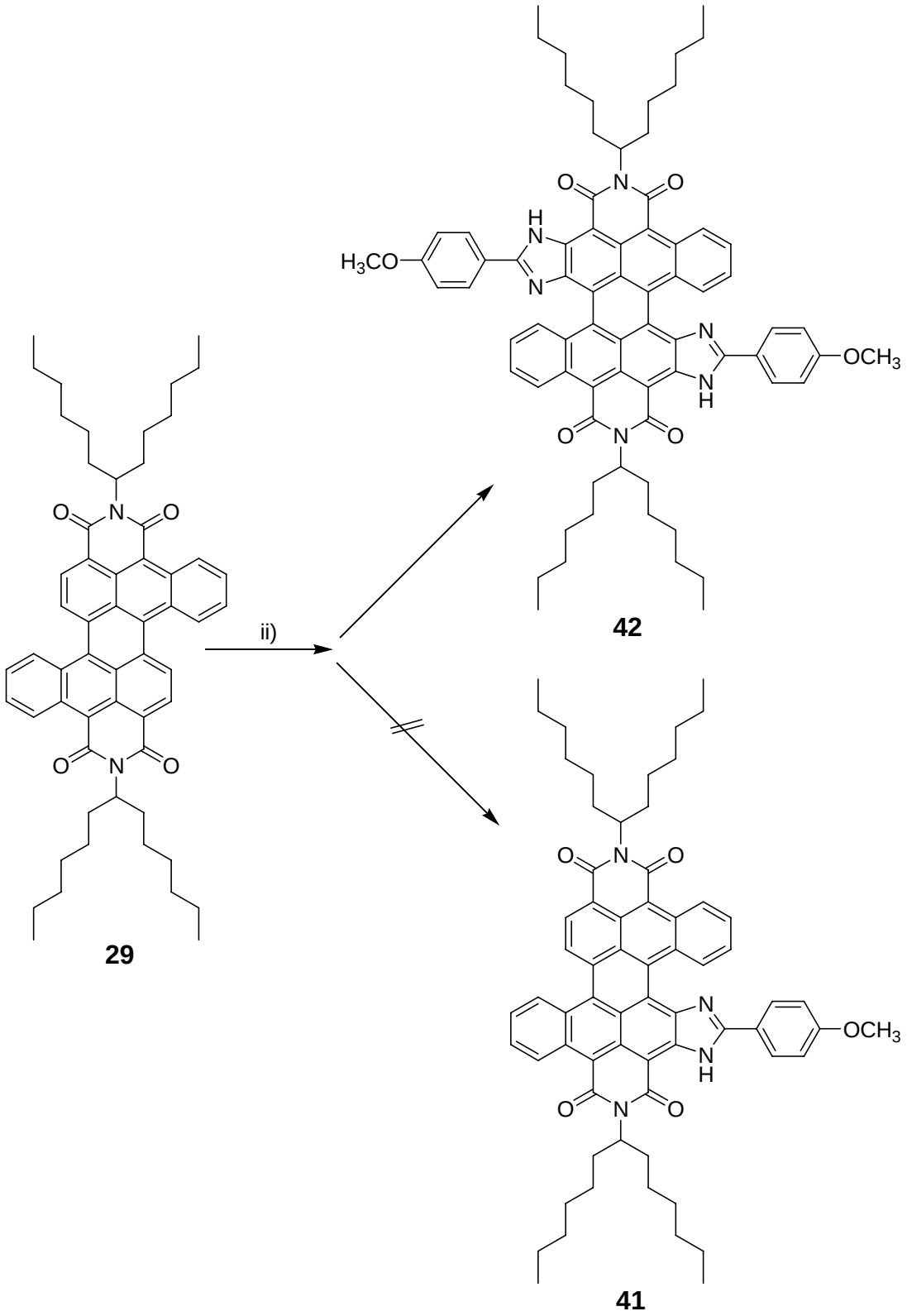
Their ^1H NMR spectra also showed 1 singlet proton deshielded at 11.57 ppm in case of compound **39**, and 2 singlet H at 11.81 ppm in case of compound **40**, and no other singlets were shown in their proton NMR spectra and the same in case of compounds

37 and **38**, that also tells the place of nucleophilic attack to be on the rings closer to the imide group than the far one.

2.3.4. Synthesis of compounds 2,12-bis(1-hexylheptyl)-9,15-di-(4-methoxyphenyl)imidazolo[4',5':3,4]imidazolo[4'',5'':7,8]benzo[*h*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]benzo[*h'*]diisoquinoline-1,3,11,13(2 H,10 H)-tetraone **(42)**, 2,10-bis(1-hexylheptyl)-5–(4-methoxyphenyl)imidazolo[4',5':3,4]benzo[7,8] anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinolinebenzo[h]isoquinoline-1,3,9,11(2 H,10 H)-tetraone **(43)** and 8,19–bis-(1-hexylheptyl)-2,5-di-(4-methoxyphenyl)-dibenzo[3,4-5,6]phenanthra[2,1,10-*def*:7,8,9-*d'e'f'*]-2,5-diphenyl-1,4,8,19-tetrahydroimidazolo [4,5-*h*:4',5'-*h'*]diisoquinoline-7,9,18,20-tetraone **(44)**

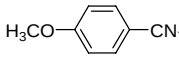
Compound **29** was expected to obtain both products **41** and **42** when reacted with 4-anisonitrile and sodium amide, but actually compound **42** was the only product found as shown in Scheme 36.

On the other hand, compound **30** when reacted with 4-anisonitrile and sodium amide, the products were **43** and **44** as shown in Scheme 37.

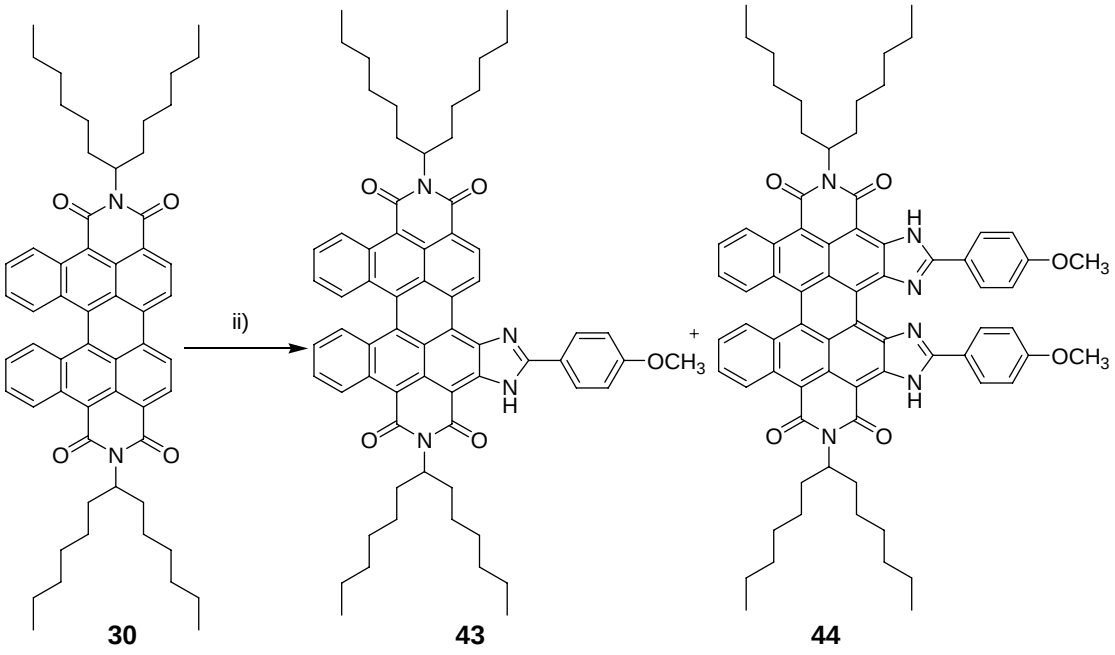


ii): $NaNH_2$, 4-anisonitrile, 165°C.

Scheme 36: Synthesis of compound 42 from 29.

As shown from Scheme 36, the expected products from that reaction of compound **29** with sodium amide and anisonitrile () were compounds **41** and **42**, but the fact was that the only obtained compound was **42**. Nucleophilic attack by NH_2^- anion happened here at both rings together.

The behaviour of the *cis* form **(30)** was different from that of the *trans* one **(29)** in reaction with sodium amide and 4-anisonitrile as shown in Scheme 37.



Scheme 37: Synthesis of compounds 43 and 44 from 30.

As shown in Scheme 37, nucleophilic attack by NH_2^- anion happened at one ring to give compound **43**, and at both rings to give compound **44**.

That diference in behaviour between compounds **29** and **30** appeared only in their reaction with sodium amide and anisonitrile and not in case of sodium amide and benzonitrile.

An explanation could be that beside the stability of *cis* from **(29)** than the *trans* form **(30)**, which lead to more reactivity of *trans* form towards nucleophilic substitution

reactions than the *cis* one, and existence of the electron donating methoxy group in the *para* position of anisonitrile that enhances more its anion formation for nucleophilic attack. All that could be collected together and could not give the chance of only one nucleophilic substitution to occur in case of compound **29**, which continue in a fast step to make the other nucleophilic attack to obtain compound **42**.

Mass spectrometry also did not show any peak at about 1000 which was calculated as the molecular weight of compound **41**, and showed only peak at 1146.60 for compound **42**.

Figure 34 shows also different absorption spectra of compounds **42**, **43** and **44** compared with absorption spectra of some previous compounds.

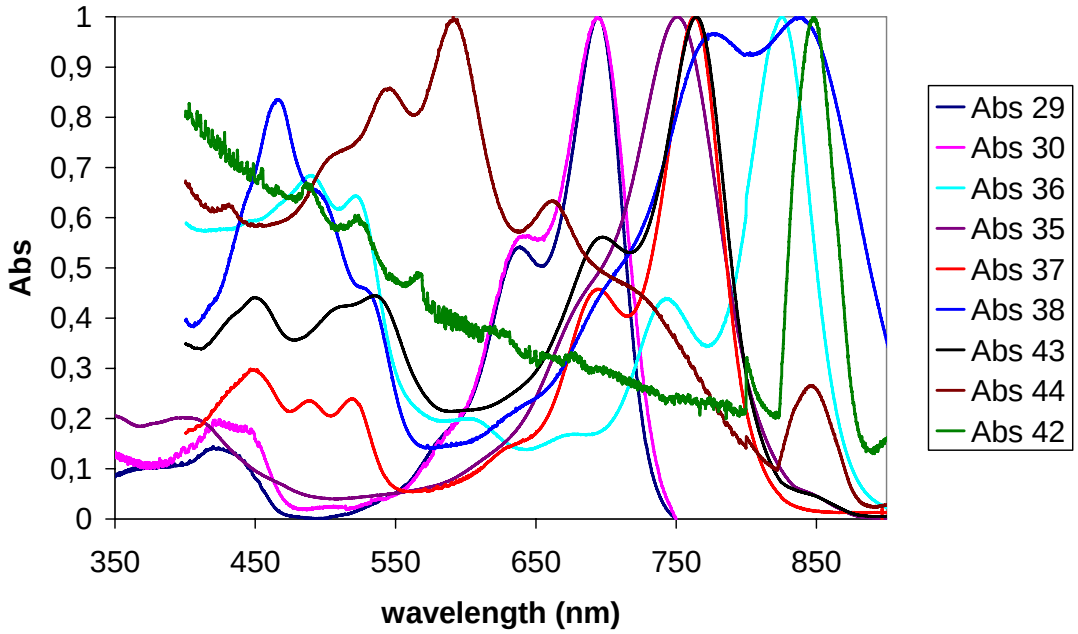


Figure 34: UV/Vis spectra of 29 (dark blue), 30 (pink), 35 (plum), 36 (turquoise), 37 (red), 38 (blue), 42 (green), 43 (black) and 44 (brown).

As shown in figure 34, compound **43** (**black**) exhibits a small bathochromic shift than compound **37** (**red**) by 5 nm, because of one methoxy group existence.

Compound **42** (**green**) absorbs at 848 nm which is longer wavelength than that of compound **36** (**turquoise**) by 23 nm, and that is due to existence of two methoxy groups in compound **42** which are electron donating groups that decrease the electron gap between the HOMO and LUMO, leading to absorption wavelength increase.

3. Summary

It was shown that new route using the new base complex (DBN or DBU/*t*-BuOK) was successful in naphthalene and anthracene carboximides coupling.

1,8-naphthalimide was coupled at 130°C for 3 h reaction time in basic medium (DBN/*t*-BuOK) and diglyme as a solvent, to obtain perylene-3,4,9,10-tetracarboxylic bisimide **(25)** 36 % chemical yield.

Yield increased to 69 % when temperature was increased to 170°C and time to 8 h.

DBU was a good substituent for DBN, where it gave probably the same yield under the same conditions used with DBN.

Under the same basic conditions mentioned above, *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylicacid imide **(9)** was coupled to obtain *N,N'*-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylicacid bisimide (S-13, **4**).

When diglyme was substituted with quinoline, compound **9** couple with quinoline to obtain *N*-(1-hexylheptyl)-3-azaperylene-9,10-dicarboxylicacid imide, and it worked when the temperature was 170°C.

N-(1-Hexylheptyl)-3-amino-1,8-naphthalimide **(11)** was allowed to react with the preheated base complex (DBN/*t*-BuOK, diglyme) for 3 h reaction time to obtain 2,10-bis-(1-hexylheptyl)diisoquinoline[3,2,1-*d,e*:8,7,6-*d',e'*]phenazin-1,3,9,11-(5 H, 13 H)-tetraone **(27)** with 18 % yield.

When quinoline was allowed to react with *t*-BuOK and DBN for 1 h at 170°C, two quinoline molecules lost one proton each and binded together to obtain 4-(2-quino)quinoline **(28)**.

A successful coupling also occurred between *N*-(1-hexylheptyl)naphthalene-1,8-dicarboxylic acid imide **(9)** and *N*-(1-hexylheptyl)anthracene-1,9-dicarboxylic acid imide **(20)** in the presence of the same base complex used before, where the ratios between **9** and **20** was 1:1 and compound **31** was the product.

Compound **20** was coupled by itself and obtained both *cis* and *trans* aceanthrene green isomers.

Coupling reaction of compound **20** was done in the preheated base complex (*t*-BuOK/DBN) or (*t*-BuOK/DBU) in diglyme for 3 h at 130°C, and it was successful to obtain both aceanthrene green isomers **(29)** and **(30)** in both cases.

The same reaction was repeated under the same conditions of compound **20** coupling reaction but using compounds **19**, **21** and **23**, each was alone in a separate reaction, and the product was only the *cis* from of aceanthrene green derivative.

Introducing lateral aromatic extension to aceanthrene green derivatives was also successful, and that was clear when compound **29** reacted with benzonitrile and sodium amide at 165°C, to obtain both compounds **35** (with one lateral phenylimidazole ring) and **36** (with two lateral phenylimidazole rings).

The same reaction was successful also for compound **30** that also obtained compounds **37** and **38**.

The reaction of *cis* aceanthrene green derivative **(33)** was also successful with benzonitrile and sodium amide, where compounds **39** and **40** were obtained.

That lateral ring extension that occurred for aceanthrene green derivatives, made them to absorb at NIR and IR regions.

When benzonitrile was replaced with 4-anisonitrile, compound **29** gave compound **42** (with two lateral *para* methoxy phenylimidazole rings) only, while compound **30** gave the two products **43** (with one lateral *para* methoxy phenylimidazole ring) and **44** (with two lateral *para* methoxy phenylimidazole rings).

Summary

4. Experimental Part

4.1. General Techniques

For reactions under inert gas atmosphere, either nitrogen, with the purity 5.0, from the house line used, or argon, with the purity of 4.8 from pressurized gas bottles. The inert gas passes through three drying tubes (silica gel, KOH, 4 A° molecular sieves) before passing into the reaction apparatus.

Solvents were removed by rotary evaporator (mbar). The weighing of the starting materials was carried out either on a precision balance with an accuracy ± 1 mg, or on an analytical balance with an accuracy ± 0.1 mg.

All chemicals were purchased from Merck/VWR, Fluka, Acros, BASF, Sigma, Riedl-De-Häen or Aldrich.

1-Hexylheptyl amine was synthesised and purified by a standard protocol. [53]

Purification of liquid products were carried out by the cleaning of the fractional distillation under vacuum.

For purification of products for analytical purpose, it was done by thin layer chromatography on silica gel 60 F_{254} or neutral aluminium oxide 60 F_{254} from Merck.

Preparative column separations are also one of the purification methods that were done, and carried out in glass columns of different sizes, depending on the amount of the product to be separated and the number of fractions. The silica gel used in those columns was from Merck and Acros (grain size 0.040-0.063 or 0.063-0.200 mm) or neutral or basic aluminium oxide from Machery and Nagel Company.

4.2. Analytical methods and equipments

For the analytical determinations, the following methods and equipments were used:

4.2.1. Melting point determination:

Stuart SMP 10 (measuring range until 250°C).

Buechi Melting Point B-540 (measuring range until 410°C).

4.2.2. NMR-Spectroscopy:

200 MHz: Varian Mercury 200.

300 MHz: Varian Vnmrs 300.

400 MHz: Varian Inova 400, Varian Vnmrs 400.

600 MHz: Varian Vnmrs 600.

The chemical shifts δ refer to the singlet of tetramethylsilane (TMS) and are given in ppm. Measurements in $CDCl_3$, shifts at 7.26 ppm in ^{1}H NMR and 77.0 ppm in ^{13}C NMR refer to chloroform.
The multiplicities also are indicated as follows:
S (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

4.2.3. IR spectroscopy:

Perkin Elmer spectrum BX FT-IR System, using an ATR-unit sample applied directly to the sample cell.
The vibrational bands are given in wavenumbers ($\tilde{\nu}$ / cm^{-1}).

4.2.4. Mass spectroscopy:

Measurements with the methods of EI (electron impact ionization) and CI (chemical ionization) were performed with a Finnigan MAT 95 with temperature 250°C and 70 eV electron energy.
Fast ion bombardment samples (FIB) are bombarded with 20 kV fast cesium ions, on a 2-nitrobenzyl alcohol (NBA) or glycerol matrix on a copper ionized target.
For high resolution measurements with ESI (electro spray ionization) and APCI (atmospheric pressure chemical ionization) methods, Thermo Finnigan FT LQT is used.
The mass number (m/z) and the relative intensities of the fragments (%) are given.

4.2.5. Optical spectroscopy:

Measurements were done in Hellma quartz cuvettes with thickness of 1 cm, and the solvents were Uvasol solvents from Merck.

UV/Visible spectroscopy:

Varian Cary 5000: Measurements of 200-3200 nm, integration time 0.100 s, data interval 0.200 nm, scan rate 120 nm min^{-1}, spectral band width 0.200 nm, and the sample temperature was via Varian Cary PCB 150 Peltier water system.

Bruins instrument Omega 20: Measurements of 350-750 nm, gap width measurement in UV range 0.350 nm, slit width measurement in the visible region is 0.200 nm and interval data 0.200 nm.

There were both qualitative (relative absorbance E_{rel}) and quantitative (Molar extinction coefficient ε) measurements. The absorption bands were in wavelength (λ / nm) indicated.

Fluorescence spectroscopy:

Perkin Elmer FS 3000: Excitation slit 5 nm, detection slit 5 nm, scan rate 30 nm/min.

Varian Cary Eclipse: Hamamatsu R 3896 detector, excitation slit 5 nm, detection slit 5 m, detection voltage varying, usually 590 nm, scan rate 120 nm/min. Temperature is thermostatically controlled in a cell holder of 4 places for 4 cuvettes.

Fluorescence quantum yield was done by the Perkin Elmer FS 3000 device.

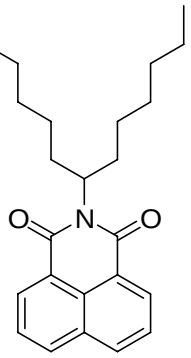
Fluorescence bands are specified by relative intensity (I_{rel}) and wavelength (λ / nm).

4.2.6. Elemental analysis:

Carbon, nitrogen and hydrogen analyses were done by Elemental Vario EL.

4.3. Synthesised Compounds

4.3.1. *N*-(1-Hexylheptyl)-naphthalene-1, 8-dicarboxylicacid imide **(9)**



1,8-naphthalic anhydride (0.408 g, 2.06 mmol), 1-hexyl heptyl amine (2.93 mmol, 0.586 g), imidazole (38.8 mmol, 2.64 g) and zinc acetate dihydrate (0.419 mmol, 0.092 g) were charged in a three necked round flask after suction and nitrogen atmosphere with magnetic Teflon coated bar together.

The temperature was adjusted to be 140°C and left for two hours under magnetic stirring at that temperature, quenched with the addition of conc. HCl (37%, 10 mL) dropwisely with stirring, then cooled and treated with chloroform. The organic phase was washed two times with HCl (2 N), then two times with distilled water, purified by column separation (silica gel, chloroform).

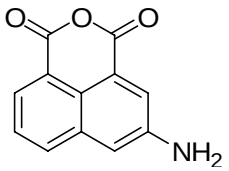
Yield: 0.64 g (81.3 %) greenish yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (m, 2 H), 8.16 (dd, *J* = 1.0, 8.4, 2 H), 7.71 (dd, *J* = 7.3, 8.2, 2 H), 5.16 (m, *J* = 5.8, 9.4, 1 H), 2.42 – 2.10 (m, 2 H), 1.81 (ddd, *J* = 4.9, 10.6, 15.4, 2 H), 1.41 – 0.98 (m, 16 H), 0.78 ppm (t, *J* = 6.9, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 165.7, 162.4, 133.3, 132.5, 132.0, 131.0, 128.1, 126.9, 124.8, 121.6, 120.9, 119.6, 54.2, 32.4, 31.7, 29.5, 26.9, 22.8, 14.0 ppm.

MS (70 eV, DEP^{+}): *m/z* (%) =379 (10) [M^{+}], 199 (13), 198 (100), 180 (13).

4.3.2. 3-Amino-1,8-naphthalic anhydride **(10)**



$SnCl_2.2H_2O$ (13.5 g, 51.0 mmol) were dissolved in conc. HCl (37 %, 18.7 mL) added to 3-nitro-1,8-naphthalic anhydride (3.0 g, 12.3 mmol) and left under stirring for 1.5 h at 85°C, quenched with distilled water (250 mL), and left under stirring in ice bath for 1 h, filtered, treated with hot water (200 mL) and stirred for 1 h, then, treated with Na_2CO_3 to reach pH (6 to 7), then filtered again and left to dry by 110°C to give of 3-amino-1,8-naphthalic anhydride **(10)**.

Yield: 2.16 g (84.3 %) orange solid.

IR (ATR):

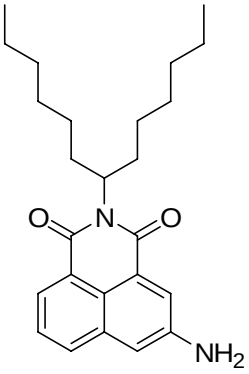
$\tilde{\nu}$ = 3464.9 (s), 3363.4 (s), 3225.3 (w), 3070.8 (w), 1750.6 (s), 1715.5 (s), 1626.6 (m), 1598.8 (m), 1575.3 (s), 1516.5 (m), 1442.7 (m), 1386.3 (m), 1328.8 (m), 1280.4 (s), 1208.8 (w), 1174.6 (w), 1150.1 (m), 1129.9 (m), 1106.8 (m), 1049.0 (s), 1009.8 (s), 981.2 (m), 929.9 (s), 883.8 (m), 780.1 (s), 743.3 (m), 721.0 cm^{-1} (m).

^{1}H NMR (400 MHz, DMSO) δ = 8.11 – 8.07 (m, 1 H), 8.05 (dd, *J* = 1.1, 7.2, 1 H), 7.93 (d, *J* = 2.3, 1 H), 7.62 (dd, *J* = 7.3, 8.3, 1 H), 7.32 (d, *J* = 2.3, 1 H), 6.07 ppm (s, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.0, 160.9, 148.1, 133.6, 132.5, 127.3, 127.1, 123.0, 122.8, 119.2, 118.4, 112.6 ppm.

MS (70 eV, DEP$^+$): *m/z* (%) = 213.0 (100) [M^+], 169.1 (34.4), 141.1 (28.2), 114.0 (10.9).

4.3.3. *N*-(1-Hexylheptyl)-3-amino-1,8-naphthalimide **(11)**



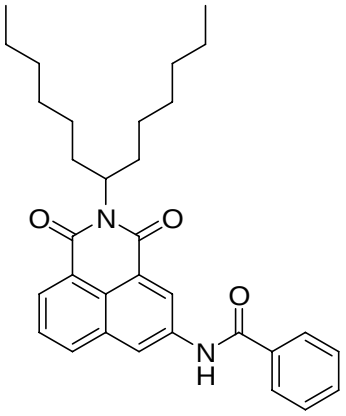
3-Amino-1,8-naphthalic anhydride **(10)** (0.88 g, 4.12 mmol), *N*-(1-hexylheptyl)amine (1.17 g, 5.86 mmol), imidazole (5.28 g, 77.54 mmol) and zinc acetate dehydrate (0.18 g, 0.84 mmol) were mixed together and stirred well for 4 h at 140°C, quenched after that by concentrated HCl (37 %, 200 mL), extracted by diethylether (3 times), dried over magnesium sulphate and separated via column (silica gel, chloroform) to give yellow substance of compound (**11**) as a second fraction (845 mg, 45.7 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 1 H), 8.03 (s, 1 H), 7.91 (dd, *J* = 1.0, 8.4, 1 H), 7.59 (dd, *J* = 7.3, 8.2, 1 H), 7.30 (d, *J* = 2.3, 1 H), 5.27-5.02 (m, 1 H), 4.11 (s, 2H), 2.22 (dd, *J* = 9.4, 13.6, 2 H), 1.79 (dd, *J* = 5.7, 13.6, 2 H), 1.23 (m, 16 H), 0.93-0.72 ppm (t, 6 H).

^{13}C NMR (599 MHz, $CDCl_3$): δ = 165.9, 165.6, 164.8, 145.4, 133.5, 131.5, 128.1, 127.5, 123.0, 122.7, 121.9, 114.0, 77.4, 77.2, 77.0, 54.6, 32.6, 32.0, 29.4, 27.1, 22.8, 14.3 ppm.

MS (70 eV, DEP^+): *m/z* (%) = 394.3 (23) [M^+], 225.2 (11), 213.2 (69), 212.2 (100), 195.2 (11).

4.3.4. *N*-(1-hexylheptyl)-3-(*N*-benzoylamino)-1,8-naphthalimide **(12)**



N-(1-Hexylheptyl)-3-amino-1,8-naphthalimide (**11**) (0.40 g, 1.01 mmol), benzoyl chloride (0.43 g, 3.04 mmol) and dioxane (20 mL) were mixed together at 80°C stirred for 6 h, and allowed to stand at room temperature over night, followed by addition of 0.35 mL benzoyl chloride and heated again at 80°C for another 6h under stirring, quenched by the addition of HCl (2 N), extracted three times by chloroform, dried over magnesium sulphate and purified by column separation (silica gel, chloroform).

Yield 0.441 g, 87.2 % yellow oil.

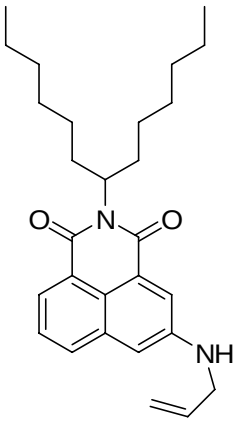
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (s, 1 H), 8.65 – 8.36 (m, 3 H), 8.14 (dd, *J* = 0.9, 8.4, 1 H), 7.94 (d, *J* = 7.0, 2 H), 7.69 (dd, *J* = 7.4, 8.1, 1 H), 7.51 (dt, *J* = 7.2, 28.8, 3 H), 5.08 (d, *J* = 27.0, 1 H), 2.21 – 2.09 (m, 2 H), 1.78 – 1.68 (m, 2 H), 1.32 – 1.09 (m, 16 H), 0.78 ppm (t, *J* = 7.0, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.09, 165.24, 164.20, 136.68, 134.22, 133.45, 132.71, 132.43, 132.27, 132.12, 130.44, 129.66, 129.06, 128.89, 128.36, 127.55, 127.13, 126.76, 125.40, 124.94, 122.53, 54.62, 32.31, 31.70, 29.18, 26.83, 22.52, 13.98 ppm.

MS (70 eV, DEP^{+}): *m/z* (%) = 498.3 (69.7) [M^{+}], 413.2 (15.9), 316.1 (100), 106.0 (20.5), 105.1 (52.4).

HRMS ($C_{32}H_{38}N_2O_3$): calcd. *m/z* 498.2882
found *m/z* 498.2868 Δ= -0.0014 mmu

4.3.5. *N*-(1-Hexylheptyl)-3-(*N*-3-allylamino)-1,8-naphthalimide **(13)**



N-(1-Hexylheptyl)-3-amino-1,8-naphthalimide (**11**) (0.30 g, 0.76 mmol), 3-allyl bromide (0.46 g, 3.8 mmol), potassium carbonate (0.53 g, 3.8 mmol) and DMF (5 mL) were mixed together, stirred at 60°C for 6 h, quenched by the addition of HCl (2 N) and three times by chloroform, dried over magnesium sulphate and purified by column separation (silica gel, chloroform).

Yield 0.220 g, 66.7 % yellow brown oil.

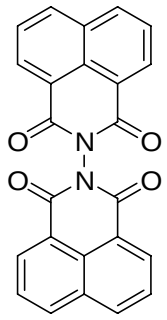
^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** = 8.25 (s, 1 H), 8.00 (s, 1 H), 7.90 (t, *J* = 8.3, 1 H), 7.56 (t, *J* = 7.7, 1 H), 7.09 (d, *J* = 2.3, 1 H), 5.97 (ddt, *J* = 5.2, 10.3, 17.1, 1 H), 5.33 (dd, *J* = 1.4, 17.2, 1 H), 5.21 (dd, *J* = 1.4, 10.4, 1 H), 5.12 (s, 1 H), 4.40 (s, 1 H), 3.93 (d, *J* = 4.8, 2 H), 2.20 (s, 2 H), 1.78 (dd, *J* = 5.4, 13.6, 2 H), 1.41 – 1.01 (m, *16* H), 0.82 ppm (t, *J* = 7.1, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** = 146.5, 134.1, 133.6, 127.2, 122.3, 116.8, 109.9, 46.2, 32.4, 31.7, 29.2, 26.9, 22.6, 14.0 ppm.

MS (70 eV, DEP$^+$): *m/z* (%) = 434.3 (32.2) [M^+], 253.0 (63.1), 252.0 (100), 225.0 (21.1), 180.0 (4.01), 55.0 (14.1).

HRMS ($C_{28}H_{37}N_2O_2$): calcd *m/z* 435.0408
found *m/z* 434.2920 Δ = -0.7488 mmu

4.3.6. *N*,*N*-Bisnaphthalimide **(15)**



1,8-Naphthalic anhydride (0.408 g, 2.06 mmol), 2-Amino-benzo[*de*]isoquinoline-1,3-dione (0.622 g, 2.93 mmol), zinc acetate dihydrate (0.092 g, 0.419 mmol) and imidazole (2.64 g, 38.8 mmol), and a Teflon-coated magnetic bar was added. The mixture was stirred vigorously at 140°C for 4 h under N_2, quenched with the addition of conc. HCl (37 %, 10 mL) dropwisely with stirring, then cooled and treated with chloroform (brown colour appears) and add some distilled water. The organic phase was washed two times with HCl (2 N) then two times with distilled water, evaporated most amount of chloroform (controlled by TLC) and purified by column separation (silica gel, toluene). The second portion was collected and evaporated most amount of the toluene and left in a dark place and under nitrogen for crystallization.

Yield 0.520 g, 64.4 % faint brown solid.

m.p.: > 300°C.

^{1}H NMR (400 MHz, DMSO): δ = 8.69 – 8.64 (m, 6H), 8.02 – 7.98 ppm (m, 6H).

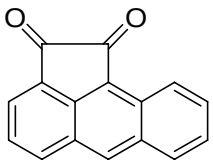
^{13}C NMR (151 MHz, DMSO): δ = 163.6, 160.6, 147.2, 139.3, 137.3, 132.3, 124.2, 123.2, 117.1 ppm.

MS (70 eV, DEP$^+$): *m/z* (%) = 393.1 (22.5), 392.1 (100) [M^+], 347.1 (22.3), 181.0 (10.1), 180.0 (77.5), 154.0 (28.1), 126.0 (43.8).

HRMS ($C_{24}H_{12}N_2O_4$): calcd *m/z* 392.0800
found *m/z* 392.0787 Δ= -0.4502 mmu

$C_{24}H_{12}N_2O_4$ [784.5]: calcd C 73.47, H 3.08, N 7.14
found C 73.14, H 3.07, N 7.24

4.3.7. Aceanthrene quinone **(17)** [15]



Anthracene **(16)** (10.0 g, 56.1 mmole) and anhydrous (sublimied) aluminium chloride (7.93 g, 59.5 mmole) were spread under argon atmosphere in carbon disulfide (75.0 mL) and oxalyl chloride (25.0 mL) with magnetic stirring in an ice bath, allowed to stand for 2 hours, treated with further carbon disulfide (75.0 mL) and anhydrous aluminium chloride (7.32 g) and left for 4 hours at room temperature with stirring, left overnight to cool, (a black solid substance is formed) treated dropwisely and smoothly with HCl (2 N, 200 mL), and then fractionally distillated at 60°C at atmospheric pressure to remove carbon disulfide (b.p. 38°C).
The orange coloured reaction mixture was cooled and filtered with G4 sintered glass and washed with 2 N HCl, treated with 2.5 % potassium carbonate solution (100 mL) heated in an oil bath at 70°C for 20 minutes (foams are formed), filtered by means of a G4 sintered glass, treated another time with K_2CO_3, then washed with distilled water and with methanol, and left it to dry at 115°C overnight.

Yield: 9.60 g (74.0 %) orange solid; (lit. [15]: 9.00 g, 69.0 %).

m.p.: 267°C; (lit. [15] m.p. 263-265°C).

R_f (silicagel, chloroform) = 0.58.

IR (ATR):

$\tilde{\nu}$ = 3051.1 (w), 1735.7 (s), 1707.9 (s), 1626.6 (w), 1576.2 (s), 1529.5 (w), 1454.9 (w), 1436.8 (w), 1339.0 (w), 1282.2 (w), 1226.4 (w), 1152.1 (w), 1086.5 (m), 1016.6 (w), 919.0 (w), 883.3 (w), 752.0 (m), 741.4(m), 700.9 (w), 483.3 (w), 411.2 cm^{-1} (w).

^{1}H NMR (400 MHz, DMSO, 25 °C) :

δ = 8.54 (d, ^3J = 8.6 Hz, 1 H_{arom}), 8.47 (s, 1 H_{arom}), 7.90 (d, ^3J = 8.6 Hz, 1 H_{arom}), 7.75 (d, ^3J = 8.6 Hz, 1 H_{arom}), 7.53 (d, ^3J = 6.7 Hz, 1 H_{arom}), 7.36–7.26 (m, 2 H_{arom}), 7.23 – 7.18 ppm (m, 1 H_{arom}).

^{13}C NMR (151 MHz, DMSO, 25°C):

δ = 121.7, 123.0, 124.2, 127.3, 127.4, 127.5, 127.9, 128.2, 129.8, 130.5, 132.6, 132.8, 134.4, 146.8, 187.7, 188.9 ppm.

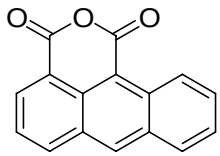
UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 366.0 (1.00), 377.1 (0.83), 404.9 (0.82), 465.0 (0.26), 506.8 nm (0.04).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 412.0 (0.04), 433.2 (0.14), 482.0 (0.95), 512.1 nm (1.00).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 366 nm, $E_{366\ nm\ /\ 1\ cm}$ = 0.2319, ref [2] 12 with Φ = 1): 0.06.

MS (70 eV, DEP$^+$): *m/z* (%) = 233.1 (8), 232.1 (45) *[M^+]*, 205.0 (16), 204.0 (100) [M^+ - CO], 178.0 (2), 177.0 (13), 176.0 (83) [M^+ - 2CO], 175.0 (15), 174.0 (13), 150.0 (16) [M^+ - 2CO - C_2H_2], 149.0 (5), 126 (4).

4.3.8. Anthracene-1,9-dicarboxylicacid anhydride **(18)** [18]



Aceanthrene quinone **16** (2.23 g, 9.60 mmole), 1,4-dioxane (48.2 mL) and 2N NaOH (13.8 mL) were treated with 30 % H_2O_2 (11.2 mL) with stirring, (yellow colour appears in an exothermic reaction; reflux condenser), left for 45 minutes, treated with distilled water (48.2 mL) and 2 N H_2SO_4 (96.4 mL), left over night with stirring (change of its pale yellow colour to apricot orange after 1 hour) allowed to stand for the next day, filtered by means of a G4 sintered glass (the same apricot colour), dissolved in KOH (2 N) solution, separated from the yellow solid by filtration by means of a sintered glass (G4) (brown filtrate) acidified with HCl (37 %) drop wisely where a yellow precipitate is formed, then collected by filtration in a sintered glass (G4), washed several times with distilled water, left in an oven to dry at 115°C.

Yield: 2.31 g (97.0 %) orange solid; (lit.[18] 100 % crude material).

m.p.: 287°C; (lit. [18] m.p. 290°C).

***R_f* (silica gel, chloroform) =** 0.40.

IR (ATR): $\tilde{\nu}$ = 3050.3 w, 1760.1 (s), 1720.4 (s), 1622.0 (w), 1561.1 (s), 1535.8 (m), 1432.2 (w), 1365.7 (w), 1285.0 (w), 1268.8 (w), 1249.0 (w), 1160.0 (w), 1139.4 (m), 1086.8 (m), 1054.5 (w), 1010.1 (m), 940.9 (w), 863.4 (w), 794.0 (m), 745.9 (m), 733.4 (m), 511.1 cm^{-1} (w).

^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ = 9.73 (d, ^3J = 9.1 Hz, 1 H, CH_{arom}), 8.95 (s, 1 H_{arom}), 8.76 (d, ^3J = 7.0 Hz, 1 H_{arom}), 8.46 (d, ^3J = 8.4 Hz, 1 H_{arom}), 8.18 (d, ^3J = 8.4 Hz, 1 H_{arom}), 7.97 – 7.85 (m, 1 H_{arom}), 7.84 – 7.64 ppm (m, 2 H_{arom}).

^{13}C NMR (600 MHz, $CDCl_3$, 25°C): δ = 111.7, 118.9, 125.8, 126.2, 127.2, 128.8, 131.1, 132.3, 134.2, 135.7, 137.9, 160.2, 161.0 ppm.

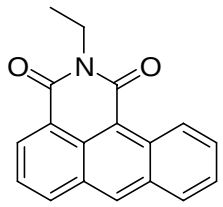
UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 358.8 (0.50), 377.1 (1.0), 414.5 (0.70), 435.7 (0.80), 459.9 nm (0.60).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 481.0 (0.93), 515.0 nm (1.0).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 377 nm, $E_{377\ nm\ /\ 1\ cm}$ = 0.2134, ref 4 with Φ = 1): 0.06.

MS (70 eV, DEP$^+$): *m/z* (%) = 249.1 (5), 248.1 (23) [M^+], 205.1 (6) [M^+ - CO_2], 204.1 (17), 177 (6), 176.0 (22) [M^+ - CO_2 - CO], 175.0 (5), 114.0 (100), 55.0 (17).

4.3.9. *N*-Ethyl anthracene-1,9-dicarboxylicacid imide **(19)** [18]



Anthracene-1,9-dicarbonicacid anhydride **18** (0.97 g, 3.91 mmol) in aqueous ethylamine solution (37.5 mL, 70%) was heated at reflux for 1.5 h (bath 150°C), treated with further ethylamine solution (12.5 mL, 70%), heated at reflux for 3.5 h, and cautiously acidified with concentrated HCl. The product was collected by vacuum filtration (G4 glass filter), thoroughly washed with small amounts of distilled water, dried in air at 115°C, purified by column chromatography (silica gel, chloroform, exclusion of light because otherwise dimers would be formed), rapidly evaporated, dried in an argon gas stream and then in a medium vacuum and stored in the dark. [30]

Yield: 0.41 g (38.1 %) bright yellow powder; (lit.[18] 76.0 %).

m.p. 184–186°C; (lit [18] m.p. 184-186°C).

R_f (silica gel; $CHCl_3$) = 0.30.

^{1}H NMR (600 MHz, $CDCl_3$, 25°C): δ =1.31 (t, J=7.0 Hz, 3 H; CH_3), 4.23 (q, J=6.9 Hz, 2 H; NCH_2CH_3), 7.72 (t, J=7.1 Hz, 1 H_{arom}), 7.88 (m, 2 H_{arom}), 8.31 (d, J=8.0 Hz, 1 H_{arom}), 8.61 (d, J=8.5 Hz, 1 H_{arom}), 8.69 (d, J=7.0 Hz, 1 H_{arom}), 9.22 (s, 1 H_{arom}), 9.95 ppm (d, J=9.1 Hz, 1 H_{arom}).

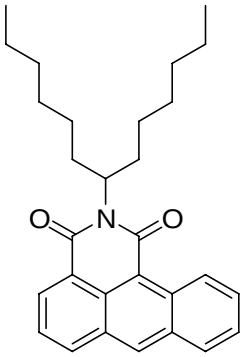
^{13}C NMR (600 MHz, $CDCl_3$, 25°C): δ =13.1 (CH_3), 35.0 (CH_2), 118.0, 122.1, 125.8, 126.0, 126.5, 128.1, 129.0, 130.5, 131.4, 132.3, 132.8, 134.0, 135.1, 136.3, 163.0 (C=O), 164.7 ppm (C=O).

IR (KBr): $\tilde{\nu}$ =3050.1 (w), 2980.9 (w), 2935.5 (w), 1685.4 (s, C=O), 1653.7 (s, C=O), 1640.8 (s, C=O), 1621.2 (w, C=C), 1560.0 (s, C=C), 1533.5 (m, C=C), 1456.6 (m), 1437.3 (m), 1400.7 (m), 1368.8 (m), 1351.1 (m), 1312.2 (s), 1247.7 (m), 1231.3 (m), 1146.9 (w), 1103.0 (m), 900.7 (w), 875.5 (w), 855.0 (w), 795.8 (m), 747.3 (m), 732.3 (s), 539.8 cm^{-1} (m).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 361.3 (0.41), 380.0 (0.89), 416.3 (0.81), 437.2 (1.0), 460.0 nm (0.71).

MS (70 eV, DEP^+): *m/z* (%) = 276.2 (35), 275.2 (89) [M^+], 274.2 (3), 260.1 (13), 248.1 (46), 247.1 (100), 230.1 (7), 205.0 (4), 203.0 (5), 202.0 (5), 177.0 (4), 176.0 (3), 55.0 (3).

4.3.10. *N*-(1-Hexylheptyl)anthracene-1, 9-dicarboxylicacid imide **(20)**



Anthracene-1,9-dicarbonicacid anhydride **18** (0.288 g, 1.16 mmol), 1-Hexylheptyl amine (0.586 g, 2.93 mmol), zinc acetate dihydrate (0.092 g, 0.419 mmol) and imidazole (2.64 g, 38.8 mmol), and a Teflon-coated magnetic bar was added. The mixture was stirred vigorously at 140°C for 4 h under N_2, quenched with the addition of conc. (HCl 37 %, 10 mL) drop wisely with stirring, then cooled and treated with chloroform, then put in a separating funnel (brown colour appears) and treated with some distilled water, separated to extract the organic phase, washed two times with HCl (2 N) then two times with distilled water.

The most amount of chloroform were evaporated (TLC control), and the residue was purified by separation (silica gel, toluene). The second fraction was collected, rapidly evaporated most amount of the toluene then left it in a dark place and under nitrogen for crystallization.

Yield 0.367 g (74 %) bright yellow solid; (lit. [18] 64 %).

m.p.: 245°C; (lit. [18] m.p. 245°C).

***R*$_f$ (silica gel, chloroform)** = 0.76.

***R*$_f$ (silica gel, toluene)** = 0.45.

IR (ATR): $\tilde{\nu}$ = 3050.3 (w), 2955.4 (m), 2925.6 (s), 2855.8 (m), 1689.9 (s), 1653.3 (s), 1617.8 (w), 1563.2 (m), 1533.6 (m), 1457.7 (m), 1430.1 (m), 1399.9 (m), 1309.0

(m), 1280.5 (m), 1243.3 (m), 1212.1 (m), 1191.7 (m), 1150.5 (w), 1114.4 (m), 895.2 (w), 793.3 (w), 750.5 (m), 730.0 (m), 624.4 (w), 610.0 cm^{-1} (w).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.03 – 9.90 (m, 1 H), 8.85 – 8.80 (m, 1 H), 8.72 (s, 1 H), 8.37 – 8.31 (m, 1 H), 8.14 – 8.09 (m, 1 H), 7.85 – 7.79 (m, 1 H), 7.76 – 7.69 (m, 1 H), 7.65 – 7.59 (m, 1 H), 5.27 (m,1 H), 2.27 (m, 2 H), 1.88 (m, 2 H), 1.44 – 1.08 (m, 16 H), 0.79 ppm (t, J = 7.0, 6 H).

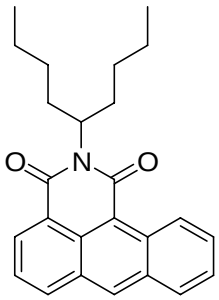
^{13}C NMR (151 MHz, $CDCl_3$): δ = 133.61, 131.60, 130.03, 128.71, 127.81, 127.55, 126.00, 125.36, 124.51, 31.56, 30.87, 30.74, 29.91, 28.26, 25.99, 21.56, 13.01 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 361.7 (0.42), 380.0 (0.93), 415.9 (0.77), 435.7 (1.0), 459.2 nm (0.74).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 483 (0.96), 515 nm (1.0).

MS (70 eV, DEP$^+$): *m/z* (%) = 430.2 (5), 429.2 (16) [M^+], 344.1 (3), 248.1 (46), 247.1 (100), 230.1 (7), 205.0 (4), 203.0 (5), 202.0 (5), 177.0 (4), 176.0 (3), 55.0 (3).

4.3.11. *N*-(1-Butylpentyl)anthracene-1,9-dicarboxylicacid imide **(21)**



Anthracene-1,9-dicarbonicacid anhydride **18** (0.288 g, 1.16 mmol), 1-Butyl pentyl amine (0.420 g, 2.93 mmol), zinc acetate dihydrate (0.092 g, 0.419 mmol) and imidazole (2.64 g, 38.8 mmol), and a Teflon-coated magnetic bar was added. The mixture was stirred vigorously at 140°C for 4 h under N_2, quenched with the addition of conc. HCl (37 %, 10 mL) drop wisely with stirring, then cooled and treated with

chloroform, transferred to separating funnel and treated with some distilled water, separated to extract the organic phase, washed two times with HCl (2 N) then two times with distilled water, dried over magnesium sulphate, then, purified by (silica gel, chloroform) with precaution from light.

Yield 0.151 g (35 %) bright yellow solid.

***R*f (silica gel, chloroform)** = 0.83.

IR (ATR): $\tilde{\nu}$ = 3060.3 (w), 2950.1 (m), 2925.4 (s), 2852.1 (m), 1683.7 (s), 1649.5 (s), 1621.2 (w), 1569.0 (m), 1531.8 (m), 1455.5 (m), 1437.2 (m), 1403.2 (m), 1311.9 (m), 1281.4 (m), 1244.8 (m), 1215.1 (m), 1193.5 (m), 1151.5 (w), 1113.7 (m), 889.0 (w), 784.8 (w), 747.7 (m), 725.5 (m), 633.0 (w), 607.0 cm^{-1} (w).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 9.1, 1 H), 8.87 – 8.67 (m, 2 H), 8.34 (d, *J* = 8.4, 1 H), 8.12 (d, *J* = 8.4, 1 H), 7.88 – 7.54 (m, 3 H), 5.32 – 5.24 (m, 1 H), 2.39 – 2.22 (m, 2 H), 1.99 – 1.79 (m, 2 H), 1.39 – 1.23 (m, 8 H), 0.82 ppm (t, *J* = 7.0, 6 H).

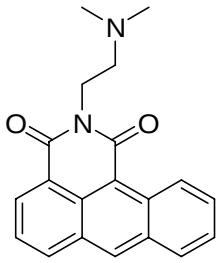
^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.47, 134.64, 132.65, 131.07, 129.74, 128.86, 127.04, 126.41, 125.55, 32.30, 29.25, 22.70, 14.05 ppm.

UV/Vis ($CHCl_3$): λ_{max} **(*E*$_{rel}$)** = 361.6 (0.41), 380.2 (0.92), 415.7 (0.77), 435.2 (1.0), 458.6 nm (0.74).

Fluorescence ($CHCl_3$, λ_{exc} = *435 nm*): λ_{max} (I_{rel}) = 483 (1.0), 513 nm (0.92).

MS (70 eV, DEP^{+}): ***m/z* (%)** = 374.2 (5) [M^+ + 1], 373.2 (20) [M^+], 260.1 (8), 248.1 (42), 247.1 (100), 230.1 (8), 205.1 (5), 203.1 (7), 202.1 (7), 177.0 (5), 176.0 (5), 55.0 (3).

4.3.12. 2-[2´-(Dimethylamino)ethyl]-1,2-dihydro-3H-dibenz[*de,h*]isoquinoline-1,3-dione **(22)**



Anthracene-1,9-dicarbonicacid anhydride **18** (0.862 g, 3.47 mmol) (dissolved in 50 mL toluene), N,N-dimethyl ethylene diamine (0.370 g, 4.19 mmol) (in 15 mL ethanol) and a Teflon-coated magnetic bar were added together. The mixture was stirred vigorously at 115°C for 4 h under N_2 (covered with aluminium foil to prevent from light), quenched with the addition of conc. HCl (37 %, 10 mL) drop wisely with stirring, then cooled and treated with chloroform, transferred to separating funnel (yellow colour), washed with distilled water and HCl (2 N), dried over magnesium sulphate.
The solvent was removed and the residue was crystallized from toluene. [54]

Yield: 0.25 g (23 %) yellow crystals.

***R*$_f$ (silica gel, chloroform/methanol 10:1) =** 0.36.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.97 – 9.91 (m, 1 H), 8.93 – 8.89 (m, 1 H), 8.85 – 8.77 (m, 1 H), 8.13 – 8.08 (m, 1 H), 8.07 (s, 1 H), 7.99 – 7.79 (m, 3 H), 4.49 – 4.41 (t, 2 H), 3.23 – 3.12 (t, 2 H), 1.38 ppm (s, 6 H).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 461.2 (0.72), 436.4 (1.0), 415.7 (0.76), 380.2 (0.93), 361.6 nm (0.41).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 489.1 (0.95), 521.0 nm (1.0).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm\ /\ 1\ cm}$ = 0.2260, ref 4 with Φ = 1): 0.03.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm\ /\ 1\ cm}$ = 0.0490, ref 12 with Φ = 1): 0.06.

When the solid compound was left exposed to sun light one day (24 hours), the UV/Vis, fluorescence and fluorescence quantum yield are:

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 461.4 (0.72), 437.2 (1.0), 415.7 (0.76), 380.2 (0.95), 361.6 nm (0.41).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 489.4 (0.97), 521.9 nm (1.0).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm\ /\ 1\ cm}$ = 0.2250, ref 4 with Φ = 1): 0.28.

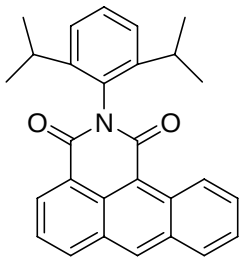
Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm\ /\ 1\ cm}$ = 0.0560, ref 4 with Φ = 1): 0.23.

MS (70 eV, DEP^+): *m/z* (%) = 319.1 [M^+ + 1] (1), 318.1 [M^+] (5), 176.1 (7), 71.1 (29), 58.1 (100).

HRMS ($C_{20}H_{18}N_2O_2$): calcd *m/z* 318.3691
found *m/z* 318.1361 Δ = - 0.2330 mmu

$C_{20}H_{18}N_2O_2$ [318.4]: calcd C 75.45, H 5.70, N 8.80
found C 73.98, H 5.52, N 8.52

4.3.13. *N*-(2,6-diisopropylphenyl)anthracene-1, 9-dicarboxylicacid imide **(23)** [37]



2,6.Diisopropyl aniline (0.71 g, 4.0 mmol) was added to a suspension of anthracene anhydride **18** (0.50 g, 2.0 mmol) in propionic acid (50 mL), and the mixture was refluxed under N_2 atmosphere for 26 hours. After cooling, the mixture was poured into cold water and extracted with dichloromethane (DCM). The organic layer was washed with saturated brine and dried over magnesium sulphate. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM 1:1) to give yellow solid of **33**.

Yield: 0.27 g (33 %) yellow solid (lit. [37] 65 %, yellow solid).

M.p. > 300°C (lit. [37] m.p. > 300°C)

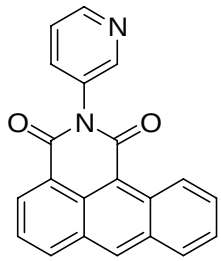
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 9.1 Hz, 1 H), 8.95 (s, 1 H), 8.87 (d, *J* = 7.2 Hz, 1 H), 8.47 (d, *J* = 8.2 Hz, 1 H), 8.20 (d, *J* = 8.6 Hz, 1 H), 7.88 – 7.45 (m, 4 H), 7.35 (d, *J* = 7.5 Hz, 2 H), 2.85 – 2.77 (m, 2 H), 1.29 – 1.15 ppm (m, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.47, 161.64, 145.7, 135.5, 132.65, 131.07, 129.74, 128.86, 127.04, 126.41, 125.55, 124.1, 29.25, 22.70 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 361.6 (0.41), 380.2 (0.92), 415.7 (0.77), 435.2 (1.0), 458.6 nm (0.74).

HRMS ($C_{28}H_{25}NO_2$): calcd *m/z* 407.7080
found *m/z* 407.1890 Δ = - 0.5190 mmu

4.3.14. *N*-(3-Pyridyl)anthracene-1,9-dicarboxylicacid imide **(24)**



1,9-Anthracene dicarboxylic acid anhydride **18** (0.30 mmol), 3-amino pyridine (0.25 mmol), 5 A° molecular sieves, zinc acetate (30 mg) and pyridine (25 mL) were allowed to reflux at 120°C for 8 h, then distilled to remove excess pyridine after reaction and replaced with acetone, concentrated with the use of rotary evaporator, purified by using preparative layer chromatography (silica gel, chloroform).
The first dark yellow fraction is compound **24**.

Yield 0.060 g, 75.0 % dark yellow solid.

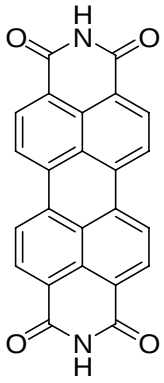
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.94 (d, *J* = 9.1, 1 H), 9.87 (d, *J* = 9.1, 1 H), 8.93 (s, 1 H), 8.86 (d, *J* = 4.5, 34.3, 1 H), 8.80 (d, *J* =6.9, 1 H), 8.45 (d, *J* = 8.3, 1 H), 8.15 (d, *J* = 8.4, 2 H), 7.88 – 7.73 (m, 3 H), 7.66-7.61 ppm (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 176.4, 165.2, 163.8, 149.5, 137.4, 136.0, 134.4, 134.0, 132.5, 131.9, 129.9, 129.1, 126.8, 126.6, 125.6, 122.4, 115.0 ppm.

MS (70 eV, DEP$^+$): *m/z* (%) = 324.1 (100) [M^+], 323.1 (85.1) [M^+ - 1], 279.1 (33.9), 176.1 (16.6), 57.1 (14.5), 43.0 (9.38).

HRMS ($C_{21}H_{12}N_2O_2$):	calcd	*m/z*	324.0899	
	found	*m/z*	324.0877	Δ = - 0.0022 mmu

4.3.15. Perylene-3,4,9,10-tetracarboxylic bisimide **(25)** [19]



A three-necked round-bottom flask was charged with t-BuOK (1.01g, 9 mmol), DBN or DBU or mixture 1:1 (12 mmol total), diglyme (3 mL) and a Teflon coated stirring bar. The mixture was stirred vigorously at 130°C for 1 h under N_2, and then, 1.8-naphthalimide (0.59 g, 3 mmol) was added and stirred at the same temperature for 3 h. The mixture was cooled to room temperature and filtered. The collected solid was washed with diglyme (10 mL x 3), distilled water (10 mL x 3), acetone (10 mL x 3), and then dichloromethane (10 mL x 3) and then dried at 120°C for 6 h under reduced pressure to give dark red pigment as product.

m.p.: > 410°C.

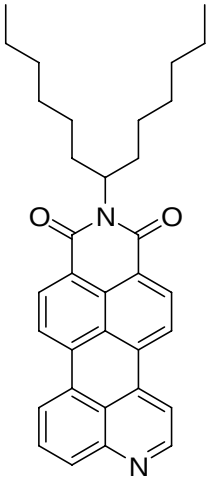
IR (ATR):

$\tilde{\nu}$ = 3834.4 w, 3728.6 (w), 3708.0 (w), 3338.9 (w), 2359.5 (s), 2342.1 (s), 2152.2 (w), 2134.4 (w), 2028.9 (w), 1994.4 (m), 1967.7 (m), 1740.0 (m), 1366.4 cm^{-1} (m).

UV/Vis (quinoline/zinc acetate): λ_{max} **(**E_{rel}**)** = 422.5 (1.0), 459.9 (0.73), 466.5 (0.76), 498.7 (0.90), 536.8 nm (0.89).

MS (70 eV, DEP$^+$): *m/z* (%) = 391 (31), 390 (9) [M^+], 389 (42), 387 (34), 385 (20), 257 (8), 167 (15), 129 (100), 123 (24), 102 (21), 60 (21), 45 (22), 43 (32).

4.3.16. *N*-(1-Hexylheptyl)-3-azaperylene-9,10-dicarboxylic acid imide **(26)**



A three necked round flask was charged with t-BuOK (1.01 g, 9.00 mmol), DBN (1.12g, 9.00 mmol) and quinoline (1.67 mL) after suction and nitrogen in the flask several times with magnetic Teflon coated bar together.

The temperature was adjusted at 170°C, left under vigorous stirring for one hour.

N-(1-Hexylheptyl)-naphthalene-1,8-dicarboxylicacid imide **(9)** (0.380g, 1.00 mmol) was added after the hour and left under stirring for 8 hours at the same temperature.

After 1 hour from adding the imide, 1 mL quinoline was added, then another 1.5 mL after 3 hours because of dryness. The final product was washed with HCl (2 N) and distilled water two times each.

TLC control was done using chloroform as an eluent where two red spots appeared.

The product was purified with silica gel column chromatograph using chloroform and the first red fraction with orange fluorescence **(26)** (40 mg) followed by second red fraction **(4)** (85 mg) were separated.

Yield: 0.040 g (10%) red powder.

***R*$_f$ (silica gel, chloroform)** = 0.89.

IR (ATR): $\tilde{\nu}$ = 2955.9 (m), 2919.2 (s), 2850.5 (s), 2361.2 (w), 2341.6 (w),1698.9 (w), 1660.4 (w), 1597.5 (w), 1462.1 (m), 1376.8 (w), 1345.2 (w),1317.0 (w), 1258.6 (m), 1085.4 (w), 1010.5 (m), 864.2 (w), 788.3 (m),701.5 (w), 668.2 cm^{-1} (w).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (m, 2 H), 8.19 (d, J = 1.0, 1 H), 8.17 (d, J = 1.0, 1 H), 7.74 (d, J = 7.3, 2 H), 7.72 (d, J = 7.3, 2 H), 7.50 (s, 1 H), 5.15 (ddd, J = 5.8, 9.4, 18.4, 1 H), 2.26 – 2.16 (m, 2 H), 1.85 – 1.75 (m, 2 H), 1.38 – 1.16 (m, 16 H), 0.90 – 0.78 ppm (m, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 165.7, 162.4, 133.6, 132.3, 131.6, 131.0, 130.9, 128.8, 128.1, 126.9, 125.8, 124.9, 120.6, 120.1, 119.6, 54.4, 32.4, 31.7, 29.7, 26.9, 22.6, 14.0 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 538.6 (0.3), 499.0 (0.3), 467.8 (0.3), 345.4 (0.97), 334.6 nm (1.0).

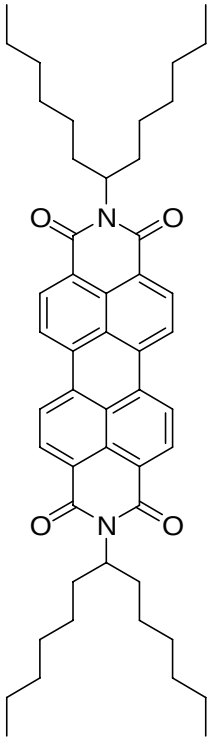
Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 553.1 (1.0), 591.7 nm (0.47).

MS (70 eV, DEP^+): ***m/z*** **(%)** = 504.3, 503.3, 464.2, 379.3, 294.2, 199.1, 198.1, 149.1, 85.2, 57.1.

HRMS ($C_{50}H_{64}N_4O_4$): calcd *m/z* 504.2777
found *m/z* 504.2811 Δ = +3.4 mmu

Fluorescence quantum yield
($CHCl_3$, λ_{exc} = 500 nm, $E_{500\ nm\ /\ 1\ cm}$ = 0.1280, ref [55] 4 with Φ = 1): 0.79.

4.3.17. *N*,*N*'-Bis-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylicacid bisimide by direct coupling **(4)**



Yield: 0.085 g (22.5 %) red solid.

***R*f (silica gel, chloroform)** = 0.8.

IR (ATR):

$\tilde{\nu}$ = 3437.7 (m), 2955.5 (m), 2925.9 (s), 2855.3 (m), 1698.0 (s), 1653.3 (s), 1594.4 (s), 1578.7 (m), 1507.5 (w), 1459.4 (w), 1435.1 (m), 1339.8 (s), 1253.6 (m), 1210.0 (w), 1174.4 (w), 1125.5 (w), 1108.1 (w), 960.3 (w), 852.5 (w), 811.0 (m), 748.8 (m), 726.0 cm^{-1} (w).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.62 (m, 8 H), 5.17 (m, 2 H), 2.23 (m, 4 H), 1.84 (m, 4 H), 1.24 (m, 32 H), 0.8 ppm (t, 12 H, J = 6.95).

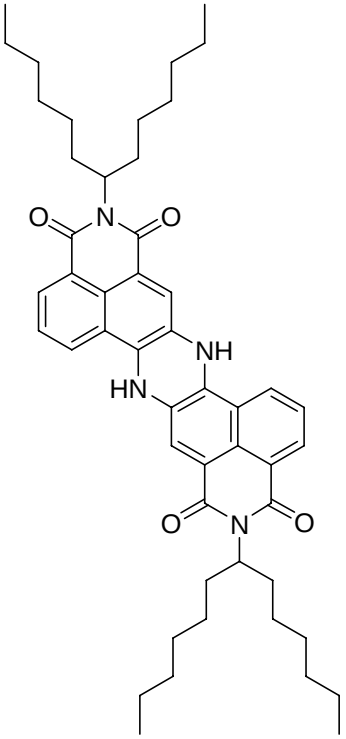
^{13}C NMR (150 MHz, $CDCl_3$, 25°C): δ = 164.65, 163.55, 134.54, 131.92, 131.15, 129.61, 126.48, 123.04, 54.75, 32.36, 31.74, 29.63, 29.20, 26.91, 22.57, 14.02 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 369.5 (0.07), 429.6 (0.08), 457.8 (0.23), 488.9 (0.60), 525.8 nm (1.0).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 533.88 nm

MS (70 eV, DEP^+): ***m/z*** **(%)** = 756 (9), 755 (28), 754 (53) [M^+], 574 (12), 573 (33), 572 (37), 392 (20), 391 (69), 390 (100), 373 (11).

4.3.18. 2,10-Bis-(1-hexylheptyl)diisoquinoline[3,2,1-*d,e*:8,7,6-*d',e'*]phenazin-1,3,9, 11-(5 H, 13 H)-tetraone **(27)**



A three-necked round-bottom flask was charged with t-BuOK (75 mg, 0.67 mmol), DBN (0.35 g, 0.87 mmol), diglyme (0.7 mL) and a Teflon coated stirring bar. The mixture was stirred vigorously at 130°C for 1 h under N_2, then, *N*-(1-hexylheptyl)-3-amino-1,8-naphthalimide **(11)** (46 mg, 0.12 mmol) was added and stirred at the same temperature for 3 h. The mixture was cooled to room temperature and filtered, washed with HCl (2 N) and extracted using chloroform, separated by silica gel in column

using chloroform as an eluent also, where the first red fraction is collected and precipitated by methanol to get compound **27**.

Another procedure also by addition of the reaction mixture all together at the same time instead of preheating the base mixture and leaving them under the same conditions (3 h at 130°C) to get compound (**27**) also but with lower yield (5 %).

Yield 8 mg (18 %) red solid.

m.p.: 260°C.

***R*$_f$ (silica gel, chloroform)** = 0.82.

IR (ATR):

$\tilde{\nu}$ = 3854.4 (w), 3734.3 (w), 3630.0 (w), 2923.9 (s), 2854.5 (s), 2362.2 (s), 2338.8 (s), 2141.3 (w), 1742.0 (w), 1673.5 (m), 1643.6 (w), 1590.0 (m), 1490.9 (m), 1462.4 (m), 1420.1 (w), 1328.8 (w), 1266.7 (m), 668.1 cm^{-1} (m).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 11.88 (s, 2 H), 8.26 (d, *J* = 7.4, 1 H), 8.21 (d, *J* = 7.6, 1 H), 7.65 (d, *J* = 7.3, 2 H), 7.37 (t, *J* = 7.7, 2 H), 7.03 (s, 1 H), 6.99 (s, 1 H), 5.21 – 5.13 (m, 2 H), 2.23 – 2.15 (m, 4 H), 1.86 – 1.78 (m, 4 H), 1.29 – 1.22 (m, 32 H), 0.82 ppm (t, *J* = 6.9, 12 H).

^{13}C NMR (151 MHz, CDCl$_3$): δ = 167.2, 156.9, 133.6, 129.8, 127.5, 124.6, 110.1, 47.2, 31.4, 29.2, 29.1, 26.6, 22.1, 14.3 ppm.

UV/Vis (CHCl$_3$): λ_{max} ***(E$_{rel}$)*** = 265.4 (0.66), 296.2 (0.74), 339.6 (0.34), 356.6 (0.50), 469.4 (0.20), 502.4 (0.54), 540.4 nm (1.0).

Fluorescence (CHCl$_3$): λ_{max} (I_{rel}) = 645.7 (0.08), 592.3 (0.38), 546.5 nm (1.0).

Fluorescence quantum yield

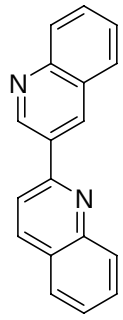
(CHCl$_3$, λ_{exc} = 502 nm, $E_{502\ nm\ /\ 1\ cm}$ = 0.1230, ref [55] 4 with Φ = 1): 0.75.

MS (70 eV, DEP$^+$): *m/z* (%) = 786.5 (16), 785.5 (57) [M^++1], 784.5 (100) [M^+], 421.1 (21.6), 420.1 (61.4), 105.0 (11.2).

HRMS ($C_{50}H_{64}N_4O_4$): calcd *m/z* 784.6679
found *m/z* 784.4924 Δ = + 0.1755 mmu

$C_{50}H_{64}N_4O_4$ [784.5]: calcd C 76.49, H 8.22, N 7.14
found C 77.77, H 8.15, N 7.12

4.3.19. 2-(3-Quino) quinoline **(28)**



A three necked round flask was charged with *t*-BuOK (3.03 g, 27.0 mmol), DBN (3.35g, 27.0 mmol), quinoline (5.00 mL, 41.9 mmol) and a teflon coated magnetic bar after vacuum and nitrogen. Then, the temperature was adjusted at 170°C, and the mixture stirred vigorously for one hour, quenched by the addition of distilled water, washed three times with distilled water, then HCl (2 N), neutralized by KOH, dried over magnesium sulphate , distilled in vacuum to get rid of excess quinoline, and purified by column separation (silica gel, chloroform/methanol 30:1).

Yield 0.19 g (3.5 %) yellow solid.

m.p.: 175°C.

***R*$_f$ (silica gel, chloroform)** = 0.13.

IR (ATR): $\tilde{\nu}$ = 3856 (m), 2919 (w), 2849 (w), 2242 (w), 1957 (w), 1939 (w), 1908 (w), 1881 (w), 1841 (w), 1595 (s), 1574 (s), 1558 (s), 1505 (s), 1494 (s), 1434 (m), 1407 (m), 1371 (w), 1360 (w), 1320 (m), 1305 (s), 1290 (m), 1230 (m), 1253 (w), 1195 (m), 1121 (m), 1046 (m), 956 (m), 929 (m), 836 (s), 786 (s), 744 (s), 650 (m), 623 (m), 606 cm^{-1} (w).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (d, *J* = 2.2, 1 H), 8.88 (d, *J* = 2.1, 1 H), 8.27 (d, *J* = 8.5, 1 H), 8.21 (d, *J* = 8.4, 1 H), 8.16 (d, *J* = 8.4, 1 H), 7.99 (d, *J* = 8.5, 1 H), 7.95 – 7.93 (m, 1 H), 7.84 (dd, *J* = 0.7, 8.1, 1 H), 7.75 (m, 2 H), 7.56 ppm (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.7, 149.8, 148.5, 148.4, 137.2, 134.5, 132.1, 130.1, 130.0, 129.8, 129.4, 128.6, 127.9, 127.6, 127.4, 127.1, 126.8, 118.7 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 385.0 (1.0), 411.1 nm (0.5).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 407.0 (0.71), 428.9 (1.0), 453.5 nm (0.77).

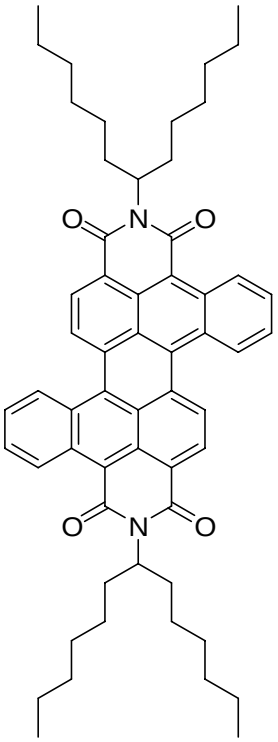
Fluorescence quantum yield
($CHCl_3$, λ_{exc} = 502 nm, $E_{502\ nm\ /\ 1\ cm}$ = 0.22710, ref 12 with Φ = 1): 0.05.

MS (70 eV, DEP^{+}): ***m/z*** **(%)** = 257.1 (21) [M^{+}+1], 256.1 (100) [M^{+}], 255.1 (39), 128.1 (16.6).

HRMS ($C_{18}H_{12}N_2$): calcd *m/z* 256.1695
found *m/z* 256.0996 Δ = -0.0699 mmu

$C_{18}H_{12}N_2$ [256.1]: calcd C 84.35, H 4.72, N 10.93;
found C 83.48, H 4.79, N 10.81

4.3.20. *N*,*N*'-Di-(1-hexylheptyl)-*trans*-aceanthrene tetracarboxylic bisimide **(29)**



A three-necked round-bottom flask was charged with *t*-BuOK (0.75 g, 6.7 mmol), 1.1 mL DBN (1.08 g, 8.7 mmol) or DBU (1.3 g, 8.7 mmol), and diglyme (2.2 mL), and a Teflon coated stirring bar was added. The mixture was stirred vigorously at 130°C for 1 h under N_2 atmosphere.

1 mL of diglyme was added later on because of dryness and to enable well stirring, then, addition of *N*-(1-hexylheptyl)-anthracene dicarboximide **(20)** (0.50 g, 1.16 mmol) and left under stirring with the same conditions for 3 h, treated with chloroform, washed two times with HCl (2 N) and distilled water each and purified by column separation (silica gel, chloroform).

The first yellow fraction was the starting imide **(20)** (yield 25.8%), and then the second green fraction was collected (**29)**, then, the third green fraction (**30)**.

Changing ratios in bases changes completely the products, where, when *t*-BuOK (0.20g, 1.8 mmol), DBN (0.30 g, 2.4 mmol) and diglyme (0.6 mL) are preheated at 130°C for 1 h followed by addition of 0.06 mmol of compound **20** and heated with stirring also for 3 h at 130°C, it gives a red vat dye which changes slowly when exposed to air to compound **30**.

Yield: 0.13 g (26 %) green oil.

***R*$_f$ (silica gel, chloroform) =** 0.86.

IR (ATR): $\tilde{\nu}$ **=** 3854.1 (w), 3734.3 (w), 3676.0 (w), 3649.8 (w), 3629.5 (w), 3360.4 (w), 2955.1 (s), 2923.9 (s), 2854.1 (s), 2362.0 (s), 2339.1 (s), 1734.7 (m), 1685.3 (m), 1651.7 (m), 1566.7 (w), 1540.2 (w), 1457.2 (w), 1421.6 (w), 1377.4 (w), 1323.6 (w), 1260.2 (w), 1227.8 (w), 1020.3 (w), 797.3 (w), 668.0 cm^{-1} (m).

^{1}H NMR (599 MHz, $CDCl_3$): *δ* = 10.02 – 9.95 (d, 2 H), 8.88 – 8.81 (m, 2 H), 8.80 – 8.74 (d, 2 H), 8.58 – 8.52 (d, 2 H), 7.92 – 7.86 (m, 2 H), 7.81 – 7.75 (m, 2 H), 5.35 – 5.31 (m, 2 H), 2.24 – 2.17 (m, 4 H), 2.01 – 1.95 (m, 4 H), 1.26 – 1.23 (m, 32 H), 0.86 ppm (t, *J* = 7.0, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): *δ* = 159.31, 133.63, 132.27, 130.48, 129.79, 128.77, 127.96, 127.55, 126.31, 125.49, 124.75, 121.13, 112.32, 47.21, 34.86, 31.76, 31.75, 29.67, 29.25, 29.24, 26.99, 26.98, 22.57, 22.56, 14.03, 14.00 ppm.

NOESY NMR: cross point between H_c and H_d at ***δ*** = (8.79, 8.57), (8.57, 8.79).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 694.4 (0.74), 638.6 (0.41), 582.6 (0.15), 420.0 (0.13), 301.2 (0.69), 287.6 (0.62), 257.6 nm (1.0).

Fluorescence ($CHCl_3$, λ_{exc}= 638.0 nm): λ_{max} (I_{rel}) = 728.5 nm.

Fluorescence quantum yield (λ_{exc}= 638.0 nm, $E_{638\ nm\ /\ 1\ cm}$ = 0.1280, $CHCl_3$, Reference (4) (S13) with ϕ = 1.00): ϕ1 = 0.20.

ϕ2 = 0.10 (when diluted to half the concentration).

ϕ3 = 0.40 (when the concentration is doubled).

It was found that the fluorescence quantum yield is directly proportional with the concentration by a linear correlation ship.

MS (70 eV, DEP^+): *m/z* (%) = 856.5 (21.8), 855.5 (63.2) [M^++1], 854.5 (100) [M^+], 673.3 (22.8), 492.1 (37.1), 491.1 (70.2), 490.1 (72.2), 420.1 (15.7), 55.0 (21.0).

HRMS ($C_{58}H_{66}N_2O_4$): calcd *m/z* 854.8778

found *m/z* 854.5013 Δ = -0.3765 mmu

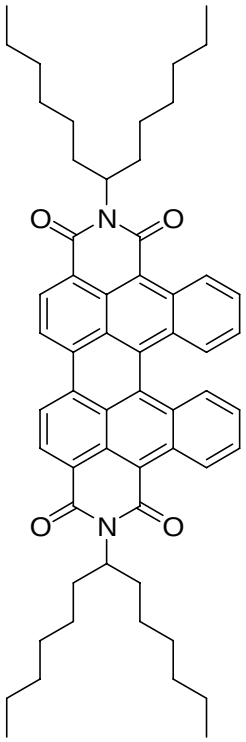
Red Vat dye:

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 530.0 (1.0), 566.4 nm (0.87).

Fluorescence ($CHCI_3$, λ_{exc}= 530.0 nm): λ_{max} (I_{rel}) = 600.0 nm

Fluorescence quantum yield (λ_{exc}= 530.0 nm, $E_{530\ nm\ /\ 1\ cm}$ = 0.1320, $CHCl_3$, Reference 4 (S-13) with ϕ = 1.00): ϕ = 0.15.

4.3.21. *N*,*N*'-Di-(1-hexylheptyl)-*cis*-aceanthrene tetracarboxylic bisimide **(30)**



Yield: 0.10 g (20 %) green oil.

***R*$_f$ (silica gel, chloroform) =** 0.71.

IR (ATR): $\tilde{\nu}$ = 3854.0 (w), 3732.2 (w), 3676.1 (w), 3650.3 (w), 3629.4 (w), 3364.0 (w), 2955.1 (s), 2923.2 (s), 2853.1 (s), 2361.5 (s), 2338.3 (s), 1739.9 (m), 1685.8 (m), 1651.7 (m), 1567.5 (w), 1539.8 (w), 1464.4 (w), 1425.1 (w), 1362.4 (w), 1303.8 (w), 1242.6 (w), 668.0 cm^{-1} (m).

^{1}H NMR (599 MHz, CDCl$_3$): δ = 9.78 (d, *J* = 9.0, 2 H), 8.88 (m, 2 H), 8.72 (d, *J* = 7.8, 2 H), 7.80 – 7.72 (m, 2 H), 7.62 (d, *J* = 8.7, 2 H), 7.35 – 7.30 (d, 2 H), 5.34 (s, 2 H), 2.35 (d, *J* = 9.3, 4 H), 1.94 (s, 4 H), 1.37 (d, *J* = 37.2, 32 H), 0.89 – 0.81 ppm (m, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.56, 133.88, 132.44, 130.61, 128.80, 127.67, 127.14, 126.99, 125.22, 123.03, 50.86, 32.16, 31.90, 31.78, 31.73, 29.26, 29.24, 27.01, 26.96, 22.59, 22.55, 14.02 ppm.

NOESY NMR: cross point between H_b and H_c at δ = (8.88, 8.72), (8.72, 8.88).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 693.8 (0.42), 633.8 (0.24), 443.4 (0.10), 424.2 (0.11), 303.4 (0.33), 281.0 (0.43), 258.6 nm (1.0).

Fluorescence ($CHCl_3$, λ_{exc}= 645.0 nm): λ_{max} (I_{rel}) = 745.8 nm.

Fluorescence lifetime ($CHCl_3$) (τ) = 11 ns (approximately).

Fluorescence quantum yield (λ_{exc} = 645.0 nm, $E_{645\ nm\ /\ 1\ cm}$ = 0.0630, $CHCl_3$, Reference S-13 with ϕ = 1.00): ϕ1 = 0.12.

ϕ2 = 0.07 (when diluted to half the concentration).

ϕ3 = 0.24 (when the concentration is doubled).

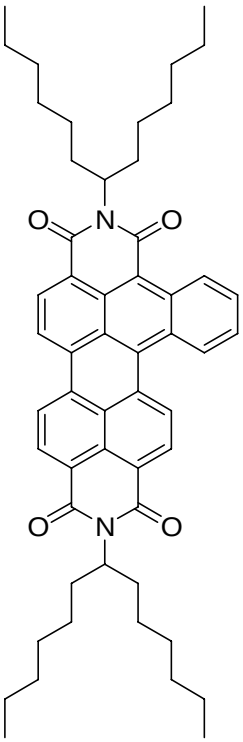
ϕ4 = 1.72 (without any dilution to the sample, that means directly from UV measurement).

It was found also that the fluorescence quantum yield is directly proportional with the concentration by a linear correlation ship.

MS (70 eV, DEP^+): *m/z* (%) = 856.5 (23.4), 855.5 (60.6) [M^++1], 854.5 (100) [M^+], 673.3 (14.8), 492.1 (16.1), 491.1 (24.1), 490.1 (41.8), 419.1 (16.0), 69.1 (5.8), 55.1 (11.3).

HRMS ($C_{58}H_{66}N_2O_4$):	calcd	*m/z*	855.6242	
	found	*m/z*	854.5006	Δ = -1.1236 mmu

4.3.22. 2,9-Bis-(1-hexylheptyl)-[4,5-benzo]anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone **(31)**



A three-necked round-bottom flask was charged with *t*-BuOK (0.54 g, 4.8 mmol), DBN (0.59 g, 4.8 mmol), diglyme (0.53 mL), and Teflon coated stirring bar was added. The mixture was stirred vigorously at 170°C for 1 h under N_2.

N-(1-Hexylheptyl)-anthracen-1,9-dicarboximide **(20)** (0.115 g, 0.265 mmol) and *N*-(1-hexylheptyl)-1,8-naphthalimide **(9)** (0.100 g, 0.265 mmol) were added after one hour [0.8 ml of diglyme were added after two hours, then another 3 mL after 3 h] and stirred at the same temperature for another 3 h to reach total time 8 h, cooled to room temperature, added some distilled water and chloroform.

The organic phase was collected and purified by column separation (silica gel, chloroform).

The first yellow fraction was anthracene imide which is one of the reactants while the second green one is Aceanthrene green (trans isomer) (**29**) (3.52 yield %), third blue one closely to green spot which are attached together and difficult to be separated, which is the blue compound (**31**), and the dark green cis Aceanthrene green isomer (**30**) in a very low yield, ended by the fifth red fraction of perylene bisimide (**4**) (64 %).

These fractions are of very low yield except the last one.

Yield: 16 mg (7.5 %) blue oily dye.

***R*$_f$ (silica gel, chloroform)** = 0.72.

***R*$_f$ (silica gel, CHCl$_3$/isohexane 2:1)** = 0.64.

^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.77 (d, *J* = 8.7, 1 H), 8.72 (t, *J* = 7.6, 1 H), 8.64 (d, *J* = 7.8, 1 H), 8.59 (d, *J* = 7.9, 1 H), 7.87 – 7.82 (m, 1 H),7.79 – 7.71 (m, 2 H), 7.62 (d, *J* = 8.8, 1 H), 7.43 – 7.40 (m, 1 H), 7.35 – 7.30 (m, 1 H), 5.34 – 5.20 (m, 2 H), 2.38 – 2.22 (m, 4 H), 1.97 – 1.83 (m, 4 H), 1.41 – 1.16 (m, 32 H), 0.89 – 0.76 ppm (m, 12 H).

^{13}C NMR (151 MHz, CDCl$_3$): δ = 159.44, 154.14, 154.08, 149.07, 130.61, 129.21, 127.12, 123.10, 54.68, 31.75, 29.69, 29.23, 22.61, 22.57, 14.04 ppm.

UV/Vis (CHCl$_3$): λ_{max} (E_{rel}) = 633.6 (1.0), 569.2 (0.85), 526.6 (0.69), 490.8 (0.45), 431.6 (0.42), 398.4 (0.44), 367.2 nm (0.45).

Fluorescence (CHCl$_3$, λ_{exc} = 492.4 nm): λ_{max} (I_{rel}) = 680.3 (0.56), 625.5 (0.67), 577.1 (1.0), 533.7 nm (0.66).

Fluorescence quantum yield
(CHCl$_3$, λ_{exc} = 491 nm, $E_{491\ nm\ /\ 1\ cm}$ = 0.0200, ref 12 with Φ = 1): 0.58.

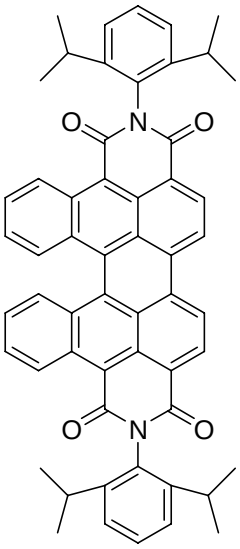
MS (70 eV, DEP$^+$): *m/z* (%) = 806.4 (19.2) [M^++2], 805.4 (65.5) [M^++2], 804.4 (98.7) [M^+], 442.0 (38.3), 441.0 (92.6), 440.0 (100), 357.1 (29.7), 286.0 (17.6), 83.0 (33.3), 57.0 (44.9), 55.0 (68.7).

HRMS (C$_{54}$H$_{64}$N$_4$O$_4$): calcd *m/z* 804.4866
found *m/z* 804.3915 Δ= -0.0951 mmu

$C_{54}H_{64}N_2O_4$ [805.2]: calcd C 80.56, H 8.01, N 3.48
found C 78.38, H 8.66, N 2.67

Note: When the previous reaction was repeated with the same conditions but using 1,8-naphthalimide instead of *N*-(1-hexylheptyl)-1,8-naphthalimide, mass spectra and ^{1}H NMR showed that no coupling happened between both reactants, but, the anthracene imide remained without degradation after the reaction.

4.3.23. *N,N'*-Di-(2,6-diisopropylphenyl)-*cis*-aceanthrene tetracarboxylic bisimide **(32)**



A mixture of potassium *t*-butoxide (0.2 g), DBN (0.3 g) and diglyme (0.6 mL) was heated at 130°C under nitrogen atmosphere for 1 h, then compound **23** (24.5 mg, 0.06 mmol) was added and the mixture was heated at the same temperature for 3 h. After cooling, water was added and the mixture was extracted with DCM (3x50 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexane/DCM 1:1) to give a red vat dye slowly changed to green compound **32**. [37]

Yield: 7 mg (29 %) dark green solid (lit.[37] 8 % dark green product).

***R_f* (silica gel, chloroform)** = 0.38.

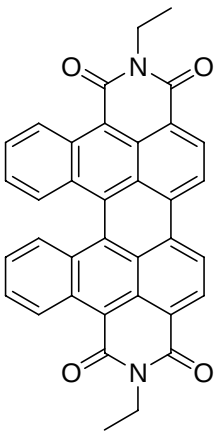
M.p. > 300°C (lit. [37] m.p. > 300°C).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.79 (d, *J* = 9.3, 2 H), 9.00 (d, *J* = 7.7, 2 H), 8.75 – 8.72 (m, 2 H), 8.53 (dd, *J* = 1.4, 7.8, 2 H), 8.45 (dd, *J* = 1.4, 7.6, 2 H), 8.37 (dd, *J* = 1.4, 7.9, 2 H), 7.81 – 7.80 (m, 2 H), 7.54 (t, *J* = 7.0, 2 H), 7.41 (d, *J* = 1.7, 2 H), 2.90 – 2.86 (m, 4 H), 1.28 – 1.26 ppm (m, 24 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.5, 163.2, 151.1, 136.5, 135.5, 134.0, 132.0, 128.7, 127.1, 126.6, 125.9, 123.7, 31.7, 22.5 ppm.

MS (70 eV, DEP^+): *m/z* (%) = 811.2 (30.3) [M^++1], 810.2 (97.4) [M^+], 364.1 (100), 247.1 (67.8), 230.0 (11.0).

4.3.24. *N*,*N*'-Diethyl-*cis*-aceanthrene tetracarboxylic bisimide **(33)**



A three-necked round-bottom flask was charged with *t*-BuOK (0.75 g, 6.7 mmol), 1.1 mL DBN (1.08 g, 8.7 mmol) and diglyme (2.2 mL), and a Teflon coated stirring bar was added. The mixture was stirred vigorously at 130°C for 1 h under N_2 atmosphere. *N*-Ethyl-anthracene dicarboximide **(19)** (0.32g, 1.16 mmol) was added and left under stirring with the same conditions for 3 h, treated with chloroform, washed two times with HCl (2 N) and distilled water each and purified by column separation (silica gel, chloroform).

The first yellow fraction was the starting imide (yield 25.8%), and the second green one was collected by addition of *tert*-butylmethyl ether to chloroform, evaporated and extracted with ethanol to obtain compound **33.**

Yield: 0.11 g (34.7 %) green solid.

***R*$_f$ (silica gel, chloroform)** = 0.17.

IR (ATR): $\tilde{\nu}$ = 3854.1 (w), 3734.3 (w), 3676.0 (w), 3649.8 (w), 3629.5 (w), 3360.4 (w), 2955.1 (s), 2923.9 (s), 2854.1 (s), 2362.0 (s), 2339.1 (s), 1734.7 (m), 1685.3 (m), 1651.7 (m), 1566.7 (w), 1540.2 (w), 1457.2 (w), 1421.6 (w), 1377.4 (w), 1323.6 (w), 1260.2 (w), 1227.8 (w), 1020.3 (w), 797.3 (w), 668.0 cm^{-1} (m).

^{1}H NMR (599 MHz, $CDCl_3$): δ = 9.72 (d, *J* = 8.9, 2 H), 8.6 (d, *J* = 6.9, 2 H), 8.45 (d, *J* = 7.3, 2 H), 8.39 – 8.33 (m, 2 H), 7.76 – 7.59 (m, 2 H), 7.22 – 7.09 (m, 2 H), 4.36 (m, 4 H), 1.46 ppm (t, *J* = 7.0, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.90, 162.75, 133.71, 131.19, 130.70, 128.40, 127.26, 127.02, 126.69, 122.61, 36.01, 29.67, 13.46 ppm.

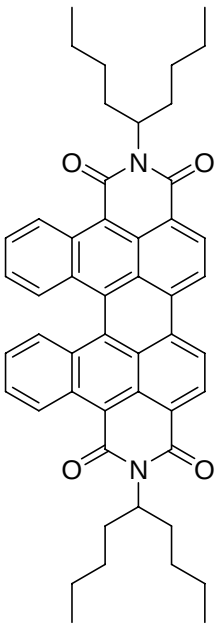
UV/Vis ($CHCl_3$): λ_{max} ***(E*$_{rel}$*)*** = 694.4 (1.0), 641.4 (0.61), 437.8 (0.40), 382.0 (0.31), 345.4 nm (0.36).

Fluorescence ($CHCl_3$, λ_{exc} = 641.0 nm): λ_{max} (I_{rel}) = 733.1 nm.

MS (70 eV, DEP^+): *m/z* (%) = 547.2 (33.3) [M^++1], 546.2 (83.3) [M^+], 447.1 (19.2), 348.1 (7.44), 174.0 (12.0), 173.0 (6.10), 82.95 (100).

HRMS ($C_{36}H_{22}N_2O_4$): calcd *m/z* 546.1580
found *m/z* 546.1577 Δ = - 0.0003 mmu

4.3.25. *N*,*N*'-Di-(1-butylpentyl)-*cis*-aceanthrene tetracarboxylic bisimide **(34)**



A three-necked round-bottom flask was charged with *t*-BuOK (0.06 g, 0.50 mmol), 0.1 mL DBN (0.1 g, 0.6 mmol), and diglyme (0.2 mL), and a Teflon coated stirring bar was added. The mixture was stirred vigorously at 130°C for 1 h under N_2 atmosphere.

N-(1-Butylpentyl)anthracene-1,9-dicarboxylicacid imide **(21)** (0.03 g, 0.09 mmol) was dissolved in toluene (3 mL), and added to the reaction mixture, left under stirring with the same conditions for 3 h, treated with chloroform, washed two times with HCl (2N) and distilled water each and purified by column separation (silica gel, chloroform).

The second green fraction was collected to obtain **34.**

Yield: 0.01 g (31 %) green oil.

***R_f* (silicagel, chloroform)** = 0.75.

IR (ATR): $\tilde{\nu}$ = 3854.1 (w), 3734.3 (w), 3676.0 (w), 3649.8 (w), 3629.5 (w), 3360.4 (w), 2955.1 (s), 2923.9 (s), 2854.1 (s), 2362.0 (s), 2339.1 (s), 1734.7 (m), 1685.3 (m), 1651.7 (m), 1566.7 (w), 1540.2 (w), 1457.2 (w), 1421.6 (w), 1377.4 (w), 1323.6 (w), 1260.2 (w), 1227.8 (w), 1020.3 (w), 797.3 (w), 668.0 cm^{-1} (m).

^{1}H NMR (599 MHz, $CDCl_3$): δ = 10.02 – 9.95 (d, 2 H), 8.88 – 8.81 (m, 2 H), 8.80 – 8.74 (d, 2 H), 8.58 – 8.52 (d, 2 H), 7.92 – 7.86 (m, 2 H), 7.81 – 7.75 (m, 2 H), 5.35 – 5.31 (m, 2 H), 2.24 – 2.17 (m, 4 H), 2.01 – 1.95 (m, 4 H), 1.26 – 1.23 (m, 16 H), 0.86 ppm (t, J = 7.0, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.31, 133.63, 132.27, 130.48, 129.79, 128.77, 127.96, 127.55, 126.31, 125.49, 124.75, 121.13, 112.32, 47.21, 34.86, 31.76, 31.75, 29.67, 29.25, 29.24, 26.99, 26.98, 22.57, 22.56, 14.03, 14.00 ppm.

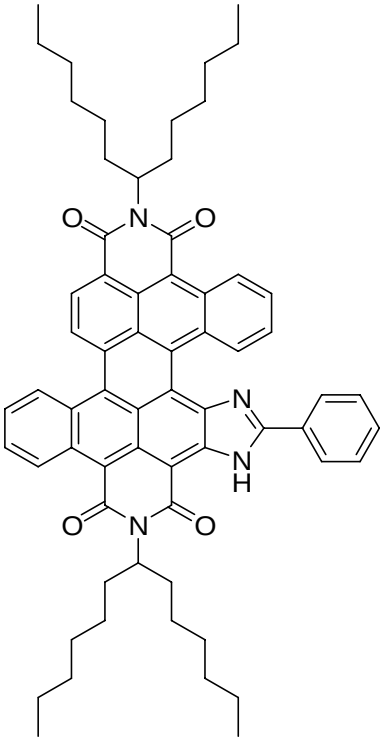
UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 694.2 (1.0), 639.2 (0.56), 434.6 (0.28), 384.4 nm (0.24).

Fluorescence ($CHCl_3$, λ_{exc}= 638.0 nm): λ_{max} (I_{rel}) = 727.0 nm.

MS (70 eV, DEP^+): *m/z* **(%)** = 743.5 (63.2) [M^++1], 742.5 (100) [M^+], 492.1 (37.1), 491.1 (70.2), 490.1 (72.2), 420.1 (15.7), 55.0 (21.0).

HRMS ($C_{50}H_{50}N_2O_4$):	calcd	*m/z*	742.3771	
	found	*m/z*	742.3748	Δ = -0.0023 mmu

4.3.26. 2,12-Bis(1-hexylheptyl)-9-phenylimidazolo[4',5':3,4]benzo[*h*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]benzo[*h'*]diisoquinoline-1,3,11,13(2 H, 10 H)-tetraone **(35)**



Compound **29** (0.02 g, 0.02 mmol) reacted with $NaNH_2$ (0.04 g, 0.95 mmol) and benzonitrile (5 mL) at 165°C for 4 h, then left to cool, treated with a mixture of HCl (2 N) and chloroform (1:1), dried over magnesium sulphate, distilled in vacuum to get rid of excess benzonitrile, separated in column (silica gel, chloroform/isohexane 3:1) to get the two compounds **35** and **36**.

Yield: 11 mg (57 %) reddish brown oily substance.

***R_f* (silica gel, chloroform)** = 0.91.

IR (ATR): $\tilde{\nu}$ = 3849.9 (w), 3829.2 (w), 3804.2 (w), 3735.5 (w), 3701.3 (w), 3677.5 (w), 3638.5 (w), 3629.3 (w), 2951.2 (m), 2921.7 (s), 2850.1 (w), 2365.5 (s), 2337.2 (w), 1944.5 (w), 1708.3 (w), 1667.7 (m), 1571.1 (w), 1542.3 (w), 1455.6 (w), 1411.8 (w), 1283.8 (s), 1072.9 (m), 1021.3 (w), 819.4 (m), 763.9 (s), 720.3 (m), 667.0 cm^{-1} (m).

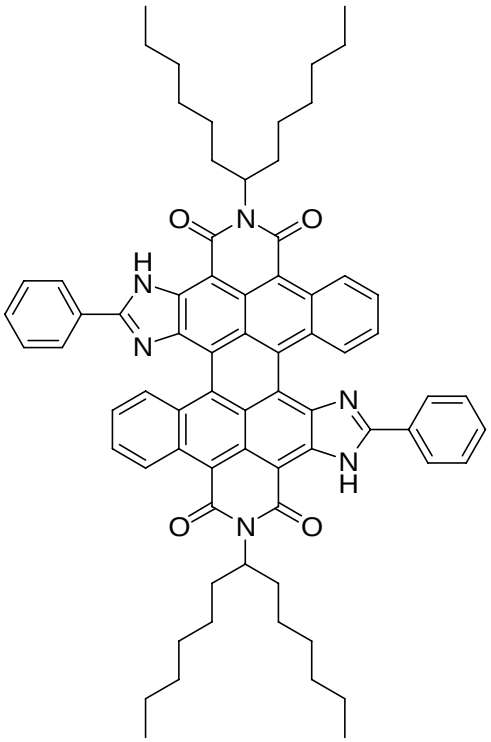
^{1}H NMR (599 MHz, $CDCl_3$): δ = 10.55 (s, 1 H), 9.58 (d, J = 8.0, 1 H), 9.00 – 8.83 (m, 1 H), 8.78 – 8.75 (m, 3 H), 8.43 (d, J = 5.4, 1 H), 7.79 (dd, J = 9.5, 10.8, 2 H), 7.62 – 7.48 (m, 3 H), 7.47 – 7.40 (m, 4 H), 5.44 – 5.35 (m, 2 H), 2.46 – 2.33 (m, 4 H), 2.03 – 1.92 (m, 4 H), 1.29 (d, J = 67.9, 32 H), 0.87 – 0.80 ppm (m, 12 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.65, 169.66, 164.09, 136.23, 133.32, 133.13, 132.50, 132.13, 130.05, 128.95, 128.64, 128.40, 127.93, 127.35, 126.27, 122.00, 121.04, 53.55, 31.80, 29.63, 27.11, 25.37, 22.62, 22.58, 14.05, 14.04 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 750.2 (1.0), 680.7 (0.44), 398.0 nm (0.21).

MS (70 eV, DEP$^+$) : *m/z* (%) = 970.56 [M^+] (99.0), 968.53 (20.1), 788.37 [M^+-($C_{13}H_{26}$)], 607.15 (43.7), 606.15 (57.3), 605.14 (35.2) [M^+-2($C_{13}H_{26}$)], 604.13 (17.0), 535.14 (17.4), 309.14 (30.5), 43.01 (50.7), 44.0 (100), 42.0 (18.4), 41.0 (69.8).

4.3.27. 2,12-Bis(1-hexylheptyl)-9-phenylimidazolo[4',5':3,4]-15-phenylimidazolo [4'',5'':7,8]benzo[*h*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]benzo[*h'*]diisoquinoline-1,3,11,13 (2 H,10 H)-tetraone **(36)**



Yield: 10 mg (42 %) red oily substance.

***R*$_f$ (silica gel, chloroform)** = 0.58.

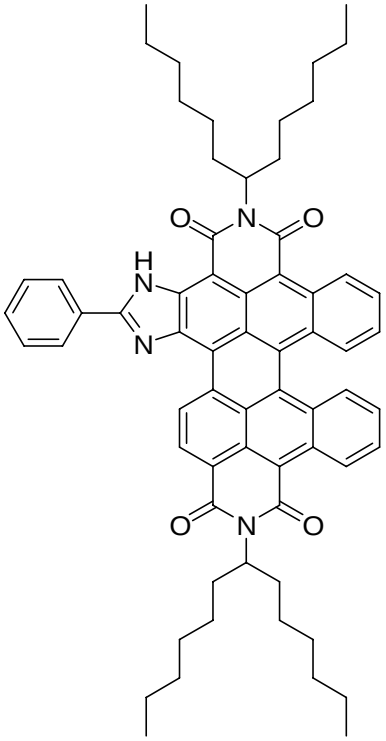
IR (ATR): $\tilde{\nu}$ **=** 3854.1 (w), 3838.9 (w), 3802.2 (w), 3745.9 (w), 3711.9 (w), 3675.9 (w), 3649.7 (w), 3629.8 (w), 2962.5 (s), 2926.7 (s), 2855.0 (s), 2361.5 (s), 2339.2 (s), 1943.5 (w), 1700.0 (w), 1653.6 (w), 1559.4 (w), 1521.3 (w), 1446.9 (w), 1412.2 (w), 1257.9 (s), 1080.8 (s), 1009.1 (s), 864.2 (m), 786.5 (s), 700.9 (m), 661.0 cm^{-1} (m).

^{1}H NMR (599 MHz, $CDCl_3$): δ =11.70 (s, 2 H), 10.06 – 10.04 (m, 2 H), 8.76 – 8.74 (m, 2 H), 8.57 – 8.47 (m, 10 H), 8.11 – 8.09 (m, 2 H), 7.74 – 7.72 (m, 2 H), 5.33 – 5.31 (m, 2 H), 2.20 – 2.19 (m, 2 H), 2.16 – 2.14 (m, 2 H), 2.02 – 2.01 (m, 2 H), 2.00 – 1.99 (m, 2 H), 1.33 – 1.25 (m, 32 H), 0.86 ppm (t, *J* = 6.8, 12 H).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 825.2 (1.0), 742.2 (0.46), 522.0 (0.66), 490.4 nm (0.70).

MS (70 eV, DEP^+): *m/z* (%) = 1087.50 [M^+], 722.50 [M^+-2($C_{13}H_{26}$)], 647.80, 523.60, 489.30, 464.30, 423.50, 369.20, 355.20, 334.20, 281.20, 222.20, 221.20, 207.10, 155.20, 149.10, 114.20, 105.10, 103.10, 69.10.

4.3.28. 2,10-Bis(1-hexylheptyl)-5– phenylimidazolo[4',5':3,4]benzo[7,8]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinolinebenzo[*h*]isoquinolin-1,3,9,11(2 H,10 H)-tetraone **(37)**



Compound **30** (0.04 g, 0.04 mmol) reacted with $NaNH_2$ (0.07 g, 1.90 mmol) and benzonitrile (10 mL) at 165°C for 2 h, stirred for 16 h at room temperature, then 2 h more at 165°C and left to cool. HCl (2 N) and chloroform (1:1) were added, the chloroform phase was separated, dried over magnesium sulphate, distilled in vacuum to get rid of excess benzonitrile, and purified in column (silica gel, chloroform/isohexane 3:1) to obtain compound **37** as the first fraction, and later compound **38**.

Yield: 8 mg (21 %) greenish brown oily substance.

***R_f* (silica gel, chloroform)** = 0.66.

IR (ATR): $\tilde{\nu}$ **=** 3853.2 (w), 3836.9 (w), 3799.2 (w), 3742.5 (w), 3711.3 (w), 3677.0 (w), 3648.5 (w), 3639.7 (w), 2961.5 (m), 2921.9 (s), 2860.1 (w), 2361.5 (s), 2339.2 (w), 1944.5 (w), 1710.3 (w), 1663.7 (m), 1570.1 (w), 1540.3 (w), 1456.5 (w), 1409.8 (w), 1287.4 (s), 1075.7 (m), 1023.3 (w), 824.5 (m), 761.5 (s), 719.9 (m), 667.0 cm^{-1} (m).

^{1}H NMR (599 MHz, $CDCl_3$): ***δ*** = 11.85 (s, 1 H), 10.59 (d, *J* = 7.9, 1 H), 9.81 (dd, *J* = 9.1, 12.8, 2 H), 8.77 (d, *J* = 7.90, 1 H), 8.43 (d, *J* = 5.4, 2 H), 7.74 (dd, *J* = 8.0, 15.4, 2 H), 7.67 (d, *J* = 6.8, 3 H), 7.61 (dd, *J* = 8.0, 17.3, 2 H), 7.56 (t, *J* = 7.2, 2 H), 5.44 – 5.35 (m, 2 H), 2.46 – 2.33 (m, 4 H), 2.03 – 1.92 (m, 4 H), 1.29 (d, *J* = 67.9, 32 H), 0.87 – 0.80 ppm (m, 12 H).

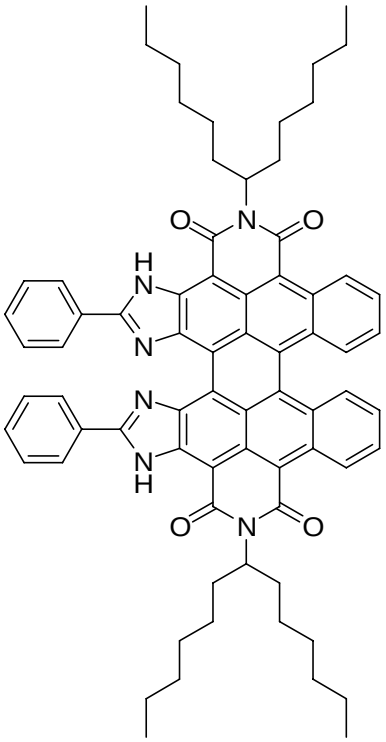
^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** **=** 164.93, 164.09, 161.25, 161.01, 147.97, 146.62, 146.30, 144.09, 138.39, 135.55, 128.61, 128.27, 127.90, 127.22, 127.14, 126.40, 126.27, 122.00, 121.96, 121.04, 116.55, 53.55, 31.80, 29.63, 27.11, 25.37, 22.62, 22.58, 14.05, 14.04 ppm.

UV/Vis ($CHCl_3$): ***λ_{max} (E_{rel})*** = 762.8 (1.0), 695.8 (0.46), 578.08 (0.06), 520.0 (0.23), 489.8 (0.22), 449.0 nm (0.27).

Fluorescence ($CHCl_3$, λ_{exc}= 692.0 nm): ***λ_{max}*** (I_{rel}) = 789.6 nm.

MS (70 eV, DEP^+): ***m/z*** **(%)** = 970.56 [M^+] (99.0), 968.53 (20.1), 788.37 [M^+-($C_{13}H_{26}$)], 607.15 (43.7), 606.15 (57.3), 605.14 (35.2) [M^+-2($C_{13}H_{26}$)], 604.13 (17.0), 535.14 (17.4), 309.14 (30.5), 43.01 (50.7), 44.0 (100), 42.0 (18.4), 41.0 (69.8).

4.3.29. 8,19–Bis-(1-hexylheptyl)dibenzo[3,4-5,6]phenanthra[2,1,10-*def*:7,8,9-*d'e'f'*]-2,5-diphenyl-1,4,8,19-tetrahydro-imidizo[4,5-*h*:4',5'-*h'*]diisoquinoline-7,9,18,20-tetraone **(38)**



Yield: 12 mg (28 %) brown oily substance.

***R*$_f$ (silica gel, chloroform)** = 0.12.

IR (ATR): $\tilde{\nu}$ = 3854.3 (w), 3734.3 (w), 3075.3 (w), 2955.9 (s), 2924.6 (s), 2854.5 (s), 2361.2 (s), 2339.3 (s), 1771.9 (w), 1733.9 (w), 1716.5 (w), 1672.2 (m), 1634.8 (m), 1566.6 (m), 1519.9 (m), 1457.8 (m), 1405.7 (w), 1368.0 (w), 1339.8 (w), 1280.8 (m), 1076.2 (w), 1026.4 (w), 965.1 (w), 813.7 (w), 800.6 (w), 765.1 (w), 690.3 (w), 668.0 cm^{-1} (m).

^{1}H NMR (599 MHz, CDCl$_3$): δ = 13.03 (s, 1 H), 12.29 (s, 1 H), 9.86 – 9.83 (m, 1 H), 9.74 – 9.71 (m, 1 H), 8.87 (d, *J* = 8.3, 1 H), 8.77 – 8.74 (m, 3 H), 8.43 (d, *J* = 7.5, 2 H), 7.87 – 7.84 (m, 2 H), 7.74 – 7.69 (m, 4 H), 7.59 – 7.56 (m, 4 H), 5.36 – 5.31 (m, 2 H), 2.50 – 2.43 (m, 4 H), 2.00 – 1.95 (m, 4 H), 1.44 – 1.32 (m, 32 H), 0.87 – 0.84 ppm (m, 12 H).

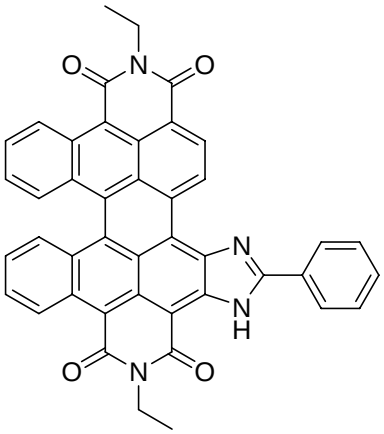
^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.17, 164.90, 146.99, 132.94, 132.48, 131.76, 129.34, 128.94, 128.75, 128.61, 128.07, 128.02, 127.72, 127.18, 54.52, 31.91, 31.72, 29.34, 27.15, 22.68, 14.10 ppm.

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 839.0 (1.0), 778.2 (0.97), 523.8 (0.61), 493.4 (0.68), 466.8 (0.84), 374.2 nm (0.71).

Fluorescence ($CHCl_3$, λ_{exc}= 374.0 nm): λ_{max} (I_{rel}) = 509.4 (0.94), 475.3 nm (1.0).

MS (70 eV, DEP^+) : *m/z* (%) = 1087.66 [M^+] (16.4), 970.58 (17.2), 263.06 (48.0), 111.11 (19.1), 105.03 (40.0), 103.04 (20.0), 83.08 (56.8), 71.08 (30.1), 70.08 (60.0), 69.07 (100), 57.07 (57.6), 56.06 (57.5), 55.05 (96.3), 43.01 (57.1), 42.07 (21.2), 41.07 (77.5).

4.3.30. 22,10-Bis(ethyl)-5–phenylimidazolo[4',5':3,4]benzo[7,8]anthra[2,1,9-*def*: 6,5,10-*d'e'f'*]diisoquinolinebenzo[*h*]isoquinolin-1,3,9,11(2 H,10 H)-tetraone **(39)**



Compound **34** (0.03 g, 0.02 mmol) reacted with $NaNH_2$ (0.08 g, 1.9 mmol) and benzonitrile (5 mL) at 165°C for 4 h, then left to cool, treated with a mixture of HCl (2 N) and chloroform (1:1), dried over magnesium sulphate, distilled in vacuum to get rid of excess benzonitrile, purified by column chromatography (silica gel, chloroform/isohexane 3:1) to obtain compounds **39** and **40**.

Yield: 4 mg (27 %) dark brown solid.

***R_f* (silica gel, $CHCl_3$/isohexane 3:1)** = 0.41.

IR (ATR): $\tilde{\nu}$ = 3847.4 (w), 3829.2 (w), 3804.2 (w), 3735.5 (w), 3701.3 (w), 3677.5 (w), 3638.5 (w), 3629.3 (w), 2951.2 (m), 2921.7 (s), 2850.1 (w), 2365.5 (s), 2337.2 (w), 1944.5 (w), 1708.3 (w), 1667.7 (m), 1571.1 (w), 1539.3 (w), 1451.9 (w), 1411.8 (w), 1283.8 (s), 1072.9 (m), 1021.3 (w), 819.4 (m), 763.9 (s), 719.5 (m), 667.0 cm^{-1} (m).

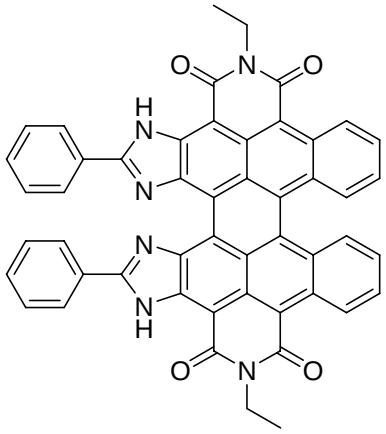
^{1}H NMR (599 MHz, $CDCl_3$): ***δ*** = 11.57 (s, 1 H), 9.58 (d, *J* = 8.0, 1 H), 9.00 – 8.83 (m, 1 H), 8.78 – 8.75 (m, 3 H), 8.43 (d, *J* = 5.4, 1 H), 7.79 (dd, *J* = 9.5, 10.8, 2 H), 7.62 – 7.48 (m, 3 H), 7.47 – 7.40 (m, 4 H), 4.35 (m, 4 H), 1.44 ppm (t, *J* = 7.0, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** = 171.65, 169.66, 164.09, 136.23, 133.32, 133.13, 132.50, 132.13, 130.05, 128.95, 128.64, 128.40, 127.93, 127.35, 126.27, 122.00, 121.04, 31.80, 29.63, 27.11, 14.04 ppm.

UV/Vis ($CHCl_3$): ***λ_{max} (E_{rel})*** = 761.6 (1.0), 693.0 (0.56), 521.2 (0.56), 484.9 (0.60), 442.4 nm (0.72).

MS (70 eV, DEP^+): ***m/z*** **(%)** = 662.20 [M^+], 604.15, 489.30, 423.50, 369.20, 355.20, 281.20, 221.20, 207.10, 149.10, 105.10, 69.10.

4.3.31. 8,19–Bis-(ethyl)dibenzo[3,4-5,6]phenanthra[2,1,10-*def*:7,8,9-*d'e'f'*]-2,5-diphenyl-1,4,8,19-tetrahydroimidizo[4,5-*h*:4',5'-*h'*]diisoquinoline-7,9,18,20-tetraone **(40)**



Yield: 5 mg (32 %) dark brown solid.

***R_f* (silica gel, $CHCl_3$/isohexane 3:1)** = zero.

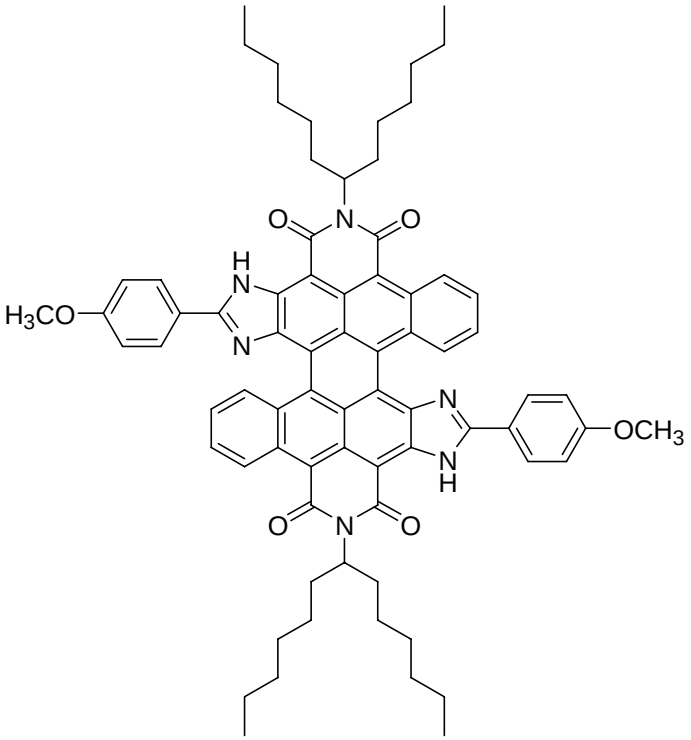
IR (ATR): $\tilde{\nu}$ = 3851.2 (w), 3835.9 (w), 3801.3 (w), 3745.9 (w), 3711.9 (w), 3675.9 (w), 3649.7 (w), 3627.7 (w), 2962.5 (s), 2926.7 (s), 2854.4 (s), 2361.5 (s), 2339.2 (s), 1943.5 (w), 1700.0 (w), 1651.6 (w), 1559.4 (w), 1521.3 (w), 1446.9 (w), 1412.2 (w), 1257.9 (s), 1080.8 (s), 1009.1 (s), 864.2 (m), 776.2 (s), 703.9 (m), 668.0 cm^{-1} (m).

^{1}H NMR (599 MHz, $CDCl_3$): δ = 11.81 (s, 2 H), 10.06 – 10.04 (m, 2 H), 8.76 – 8.74 (m, 2 H), 8.57 – 8.47 (m, 10 H), 8.11 – 8.09 (m, 2 H), 7.74 – 7.72 (m, 2 H), 4.41 (m, 4 H), 1.51 ppm (t, J = 7.0, 6 H).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 848.6 (1.0), 742.2 (0.46), 522.0 (0.66), 490.4 nm (0.70).

MS (70 eV, DEP$^+$): *m/z* (%) = 778.23 [M^+], 720.15, 489.30, 423.50, 369.20, 355.20, 281.20, 221.20, 207.10, 149.10, 105.10, 103.10, 69.10.

4.3.32. 2,12-Bis(1-hexylheptyl)-9,15-di-(4-methoxyphenyl)imidazolo[4',5': 3,4]imidazolo[4'',5'':7,8]benzo[*h*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]benzo[*h'*] diisoquinoline-1,3,11,13(2 H,10 H)-tetraone **(42)**



Compound **29** (0.02 g, 0.02 mmol) reacted with $NaNH_2$ (0.04 g, 0.95 mmol) and anisonitrile (1 g) at 165°C for 4 h, then left to cool, treated with a mixture of HCl (2 N) and chloroform (1:1), dried over magnesium sulphate, distilled in vacuum to get rid of excess anisonitrile, separated in column (silica gel, chloroform/isohexane 3:1) to obtain compound **42**.

Yield: 1 mg (4.4 %) brown oily dye.

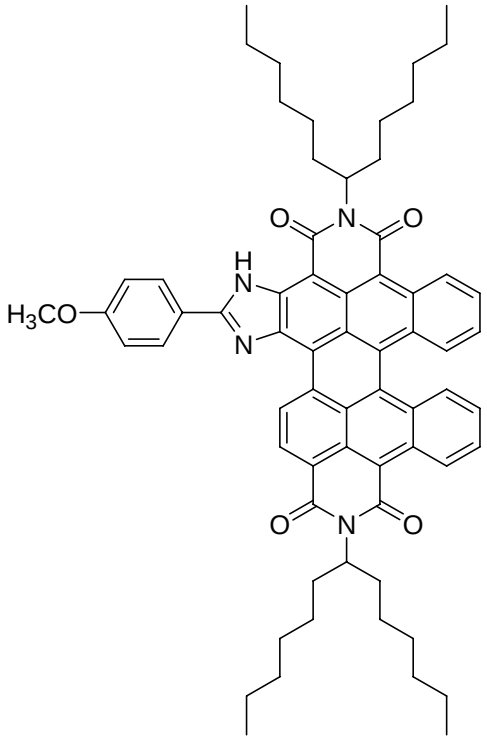
***R_f* (silica gel, chloroform)** = 0.49.

^{1}H NMR (599 MHz, $CDCl_3$): *δ* =11.53 (s, 2 H), 10.06 – 10.04 (m, 2 H), 8.76 – 8.74 (m, 2 H), 8.57 – 8.47 (m, 8 H), 8.11 – 8.09 (m, 2 H), 7.74 – 7.72 (m, 2 H), 5.33 – 5.31 (m, 2 H), 4.09 (s, 6 H), 2.20 – 2.19 (m, 2 H), 2.16 – 2.14 (m, 2 H), 2.02 – 2.01 (m, 2 H), 2.00 – 1.99 (m, 2 H), 1.33 – 1.25 (m, 32 H), 0.86 ppm (t, *J* = 6.8, 12 H).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 848.2 (1.0), 800.4 (0.41), 556.6 (0.82), 523.4 (0.85), 375.0 nm (0.70).

MS (70 eV, DEP^+): *m/z* (%) = 1146.60 [M^+], 781.50 [M^+-2($C_{13}H_{26}$)], 647.80, 523.60, 489.30, 464.30, 423.50, 369.20, 355.20, 334.20, 281.20, 222.20, 221.20, 207.10, 155.20, 149.10, 114.20, 105.10, 103.10, 69.10.

4.3.33. 2,10-Bis(1-hexylheptyl)-5–(4-methoxyphenyl)imidazolo[4',5':3,4]benzo [7,8]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinolinebenzo[*h*]isoquinoline-1,3,9,11(2 H,10 H)-tetraone **(43)**



Compound **30** (0.04 g, 0.04 mmol) reacted with $NaNH_2$ (0.07 g, 1.90 mmol) and anisonitrile (2 g) at 165°C for 2 h, stirred for 16 h at room temperature, then 2 h more at 165°C and left to cool. HCl (2 N) and chloroform (1:1) were added, the chloroform phase was separated, dried over magnesium sulphate, distilled in vacuum to get rid of excess anisonitrile, and purified in column (silica gel, chloroform/isohexane 3:1) to obtain compound **43** as the first fraction, and later compound **44**.

Yield: 2 mg (5 %) dark brown oily dye.

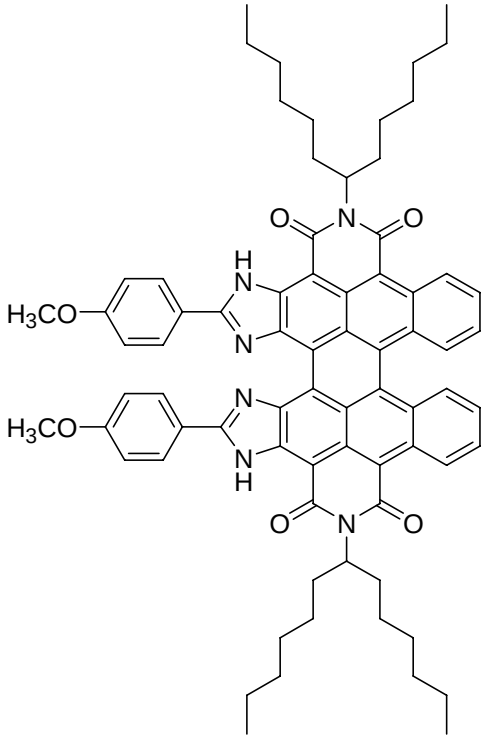
***R_f* (silica gel, chloroform)** = 0.60.

^{1}H NMR (599 MHz, $CDCl_3$): δ = 11.85 (s, 1 H), 10.59 (d, *J* = 7.9, 1 H), 9.81 (dd, *J* = 9.1, 12.8, 2 H), 8.78 – 8.75 (m, 1 H), 8.43 (d, *J* = 5.4, 2 H), 7.74 (dt, *J* = 7.7, 15.3, 2 H), 7.68 (dd, *J* = 5.2, 10.5, 3 H), 7.64 – 7.54 (m, 3 H), 5.44 – 5.35 (m, 2 H), 4.11 (s, 3 H), 2.46 – 2.33 (m, 4 H), 2.03 – 1.92 (m, 4 H), 1.29 (d, *J* = 67.9, 32 H), 0.87 – 0.80 ppm (m, 12 H).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 767.9 (1.0), 699.8 (0.46), 581.30 (0.06), 525.0 (0.23), 492.8 (0.22), 451.0 nm (0.27).

MS (70 eV, DEP^+): *m/z* (%) = 1000.56 [M^+] (99.0), 998.53 (20.1), 818.37 [M^+-($C_{13}H_{26}$)], 607.15 (43.7), 606.15 (57.3), 605.14 (35.2) [M^+-2($C_{13}H_{26}$)], 604.13 (17.0), 535.14 (17.4), 309.14 (30.5), 43.01 (50.7), 44.0 (100), 42.0 (18.4), 41.0 (69.8).

4.3.34. 8,19–Bis-(1-hexylheptyl)-2,5-di-(4-methoxyphenyl)-dibenzo[3,4-5,6]phenanthra[2,1,10-*def*:7,8,9-*d'e'f'*]-2,5-diphenyl-1,4,8,19-tetrahydroimidazolo[4,5-*h*:4',5'-*h'*]diisoquinoline-7,9,18,20-tetraone **(44)**



Yield: 2 mg (2 %) black oily dye.

***R*$_f$ (silica gel, chloroform)** = 0.10.

^{1}H NMR (599 MHz, $CDCl_3$): δ = 13.03 (s, 1 H), 12.29 (s, 1 H), 9.86 – 9.83 (m, 1 H), 9.74 – 9.71 (m, 1 H), 8.87 (d, *J* = 8.3, 1 H), 8.77 – 8.74 (m, 3 H), 8.43 (d, *J* = 7.5, 2 H), 7.87 – 7.84 (m, 2 H), 7.74 – 7.69 (m, 3 H), 7.59 – 7.56 (m, 3 H), 5.36 – 5.31 (m, 2 H), 4.05 (s, 6 H), 2.50 – 2.43 (m, 4 H), 2.00 – 1.95 (m, 4 H), 1.44 – 1.32 (m, 32 H), 0.87 – 0.84 ppm (m, 12 H).

UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 843.0 (1.0), 782.3 (0.97), 525.4 (0.61), 495.6 (0.68), 467.9 (0.84), 374.8 nm (0.71).

MS (70 eV, DEP$^+$): *m/z* (%) = 1146.60 [M^+] (16.4), 981.50 (17.2), 647.80, 523.60, 489.30, 464.30, 423.50, 369.20, 355.20, 334.20, 281.20, 222.20, 221.20, 207.10, 155.20, 149.10, 114.20, 105.10, 103.10, 69.10.

5. Appendix

5.1. Nomenclature of the described compounds

The names of the compounds in this thesis were named according to the rules of IUPAC system.

It is important to take the parent molecule the largest heterocyclic ring in the system, and that is according to the IUPAC system, where in most of the prepared aceanthrene green derivatives, the largest heterocyclic ring was isoquinoline.

Some prepared compounds were named according to the way mentioned in the literature, like azaperylene, and some aceanthrene green derivatives, because of complicated structure.

5.2. Units and abbreviations

Å: Ångstrom, 1 Å = 10^{-10} m = 100 pm

abs.: Absolute

arom.: aromatic

ATR: Attenuated Total reflection

Calcd.: calculated

°C: Temperature scale in Celsius Grade.

CAS: "Chemical abstract service"

cm^{-1}: centimetre to the power minus 1

$\tilde{\nu}$ *:* wavenumber

DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene

DBN: 1,5-Diazabicyclo[4.3.0]non-5-ene

t-BuOK: Potassium tertiary butoxide

diglyme: Diethylene glycol dimethyl ether

LDA: Lithium diisopropyl amide

DMF: Dimethylformamide

DMSO: Dimethylsulfoxide

E: Molar Extinction coefficient

EI: Electron ionisation

eq: Equivalent

h: Hour

HMBC: heteronuclear multiple bond coherence

HRMS: High Resolution Mass Spectroscopy

HOMO: "Highest Occupied Molecular Orbital"

Hz: Hertz

IR: Infrared

IUPAC: "International Union of Pure and Applied Chemistry"

J: Coupling constant in Hz

LUMO: "Lowest Unoccupied Molecular Orbital"

mg: Milligramm = 10^{-3} g

MHz: Megahertz = 10^{6} Hertz

mL: Milliliter = 10^{-3} Liter

mmol: Millimol = 10^{-3} Mol

MS: Mass spectrometry

NMR: Nuclear Magnetic resonance

NOESY: Nuclear Overhauser effect spestroscopy

COSY: Correlation spectroscopy

nm: Nanometer = 10^{-9} Meter

ppm: "Parts per Million"

%: Percentage

R_f : Retention factor

s, d, t, q, m: Singlt, Dublet, Triplet, Quartet, Multiplet (in NMR)

vs, s, m, w, v: "very strong, strong, medium, weak, very weak (in IR-Spectra)

TMS: Tetramethylsilane

UV: Ultraviolet

UV/Vis: Absorption spectroscopy in ultraviolet/visible range

δ: Delta (in NMR)

λ: wavelength

m.p.: melting point

5.3. List of figures and tables

Appendix

5.4. Curriculum Vitae

PERSÖNLICHES:

Name:	Sherif Abdel Moez Mohamed Ahmed Aly
Birthday:	01.07.1975
Place of Birth:	Cairo, Egypt
Nationality:	Egyptian
Veröffentlichungen:	- K. Haggag, H.S. El-sayad, Sh. Abd El-Moez and I. Abd El-Thalouth, *1st. International Conference of TRD, Egypt, March 2-4,* **2004**. - K. Haggag, H.S. El-sayad, Sh. Abd El-Moez and I. Abd El-Thalouth, *Egypt. J. Chem., special issue,* **2004**.

Appendix

References

[1] H. Berke, H. G. Wiedemann, *East Asian Science, Technology, and Medicine* **2000**, *17*, 94; S. Bouherour, H. Berke, H. G. Wiedemann, *Chimia* **2001**, *55*, 942; H. Berke, *Angew. Chem.*, Int. Ed. **2002**, *41*, 2493.

[2] H. Zollinger, Color – A Multidisciplinary Approach, Verlag Helvetica Chimica Acta, Zürich, Wiley/VCH, Weinheim, **1999**; W. G. K. Backhaus, R. Kliegelana, J. S. Werner, Color Vision – Perspectives from Different Disciplines, de Gruyter, Berlin, **1998**.

[3] H. Zollinger, Color Chemistry, 3rd edition, Wiley-VCH Verlag, Weinheim, 2**003**.

[4] Colour Index, 3rd edn., Vols. *1-4* (with supplement and a special volume on pigments and Solvent dyes), Society of dyers and Colourists, Bradford, and American Association of Textile Chemists and Colourists, Research Triangle Park, NC, **1971-1997**; Colour Index International, 4th edn. Online, Society of Dyers and Colourists, Bradford, and American Association of Textile Chemists and Colourists, Research Triangle Park, NC, **2002**.

[5] D. G. Evans, *J. Soc. Dyers Colour.* **1990**, *106*, 192.

[6] W. Dilthey, R. Wizinger, *J. Prakt. Chem.* **1928**, *118*, 321-348.

[7] R. B. Woodward, W. E. von Doering, *J. Am. Chem. Soc.*, **1944**, *66*, 849-850.

[8] J. Shore (Ed.), Colourants and Auxiliaries, 2 Vols., Society of Dyers and Colourists, Bradford, **1990**.

[9] P. W. Atkins, Physical Chemistry, 6th edition, Oxford Melbourne Tokyo, **1998**.

[10] M. Kardos, D. R. P. 276357, june 14, **1913**; Friedlaenders Fortschr Teerfarbenfabr. **1917**, *12*, 492; (*Chem. Abstr.* **1914**, *8*, 3243).

[11] H. M. Smith, High Performance Pigments, Wiley-VCH Verlag, Weinheim, **2002**.

[12] H. Langhals, *Heterocycles*, **1995**, *40*, 477-500.

[13] M. Kardos, *Berichte der Deutschen chemischen Gesellschaft zu Berlin*, **1913**, *46*, 2068- 2091.

[14] C. Liebermann and M. Kardos, *Berichte der Deutschen chemischen Gesellschaft zu Berlin.*, **1914**, *47*, 1203 - 1210.

[15] C. Liebermann and M. Zsuffa, *Berichte der Deutschen chemischen Gesellschaft zu Berlin*, **1911**, *44*, 202- 209.

[16] S. M. Sami, R. T. Dorr, A. M. Solymon, D. S. Alberts, B. S. Iyengar, W. A. Remers, *J. Med. Chem,*. **1996**, *39*, 1609-1618.

[17] [a] M. Kardos, *PhD Thesis*, University of Berlin **1913**, 26. [b] M. Kardos, Ber. *Dtsch. Chem. Ges.* 1913, 46, 2086-2091; *Chem. Abstr.* **1913**, 7, 23197. [c] C. Liebermann, M. Kardos, *Ber. Dtsch. Chem. Ges.* **1914**, 47, 1203-1210. [d] M. Kardos, *Friedländers Fortschritte der Teerfarbenfabrikation* **1914-1916**, *12*, 485-492.

[18] H. Langhals, G. Schönmann, K. Polborn, *Chem. Eur. J.* **2008**, *14*, 5290-5303.

[19] T. Sakamoto, C. Pac., *J. Org. Chem.* **2001**, *66*, 94-98.

[20] S. Kinzel, PhD Thesis, Ludwig-Maximilians-Universität, München, **2010**.

[21] D. Desilets, P. M. Kazmaier, R. A. Burt, *Can. J. Chem.* **1995**, *73*, 319–324.

[22] M. Wehmeier, M. Wagner, K. Mullen, *Chem. Eur. J.* **2001**, *7*, 2197–2205.

[23] M. Adachi, Y. Nagao, *Chem. Mater.* ***2001***, *13*, 662–669.

[24] F. O. Holtrup, R. R. J. Mueller, H. Quante, S. De Feyter, F. C. De Schryver, K. Muellen, *Chem. Eur. J.* **1997**, *3*, 219–225.

[25] H. Langhals, G. Schönmann, L. Feiler, *Tetrahedron Lett.*, **1995**, *36*, 6423-6424.

[26] H. Langhals, *Chem. Ber.*, **1985**, *118*, 4641-4645.

[27] H. Langhals, D. O. S.3703513 (Febr. 5, **1987**) (*Chem. Abstr.*, **1988**, *109*, P212376w).

[28] C. Schotten, *Berichte der Deutschen Chemischen Gesellschaft* **1884**, *17* (2), 2544-2547.

[29] [a] E. D. Bergmann, R. Ikan, *J .Org. Chem.* **1958,** *23*, 907-908. [b] M. M. Sidky, F. H. Osman, *J.Prakt. Chem.* **1973,** *315,* 881- 886.

[30] [a] E. Klingsberg, C. E. Lewis, *J.Org. Chem.* **1975,** *40*, 366-368, [b] T. K. Bandyopadhyay, A. J. Bhattacharya, *Indian J. Chem.* **1982** Sect. B, *21B*, 91-94.

[31] [a] S. Mondal, T. K. Bandyopadhyay, A. J. Bhattacharya, *Curr. Sci.* **1985,** *54*, 455-458, [b] S. J. Chang, B. K. Ravi Shankar, H. Schechter, *J.Org. Chem.* **1982**, *47*, 4226-4234.

[32] H. Langhals, *Helv. Chim. Acta* **2005**, *88*, 1309-1343.

[33] S. Demmig, H. Langhals, *Chem. Ber.* **1988,** *121,* 225-230.

[34] H. Langhals, S. Demmig, T. Potrawa, *J. Prakt. Chem.* **1991,** *333,* 733-748.

[35] H. Langhals, *Nachr. Chem. Tech. Lab.* **1980**, *28*, 716-718; [*Chem. Abstr.*, **1981**, *95*, R9816q].

[36] H. Langhals, Ger. Patent 3016764, **1980;** [*Chem. Abstr.* **1982**, *96,* P70417x].

[37] J. H. Yao, C. Chi., J. Wu, and K-P. Loh, *Chem. Eur. J.* **2009**, *15*, 9299-9302.

[38] D. S. Alberts, R. T. Dorr, W. A. Remers, S. M. Sami (Research Corp. Technologies, Inc., USA) PCT Int. Appl. WO 9200281, **1992;** [*Chem. Abstr.* **1992**, *116*, 214369].

[39] S. M. Sami, R. T. Dorr, D. S. Alberts, W. A. Remers, J. *Med. Chem.* **1993**, *(36)*, 765-770.

[40] S. M. Sami, R. T. Dorr, D. S. Alberts, A. M. Slyom, and W. A. Remers, J. *Med. Chem.* **1995**, *38*, 983-993.

[41] W. A. Remers, R. T. Dorr, S. M. Sami, D. S. Alberts, S. Bear, C.-A. Mayr, A. M. Solyom, Curr. *Topics Med. Chem.* **1997**, *2*, 45-61; [*Chem. Abstr.* **1998**, *130*, 104534].

[42] R. T. Dorr, J. D. Liddil, S. M. Sami, W. Remers, E. M. Hersh, D. S. Alberts, *Anti Cancer Drugs* **2001**, *12*, 213-220; [*Chem. Abstr.* **2001**, *135*, 70842].

[43] R. P. Verma, C. Hansch, *Mol. Pharm.* **2006**, *3*, 441-450; [*Chem. Abstr.* **2006**, *145*, 957948].

[44] N. Habib (Nabil Habib Lab, Lebanon; Vianova Labs, Inc.), PCT Int. Appl. WO 2007064691, **2007**; [*Chem. Abstr.* **2007**, *147*, 46112].

[45] E. Van Quaquebeke, J. Tuti, L. Van Den Hove, R. Kiss, F. Darro (Unibioscreen S. A., Belgium), PCT Int. Appl. WO 2007054292, **2007**; [*Chem. Abstr.* **2007**, *146*, 521689].

[46] Sami, S. M.; Dorr, R. T.; Slyom, A. M.; Alberts, D. S.; Remers, W. A., *J. Med. Chem.* **1996**, *39*, 4978-4987.

[47] Bradely, W; Pexton, F. W.; *J. Chem. Soc.* **1954**, 4432-4434.

[48] Y. Zhao, A.-M. Ren, J.-K. Feng, C.-C. Sun, *J. Chem. Phys.* **2008**, *129*, 014301.

[49] Francis, E. M.; Simonsen, J. L., *Journal of the Chemical Society,* **1935**, 496-499.

[50] H. Langhals, S. Demmig, H. Huber, *Spectrochim. Acta* **1988**, *44A*, 1189-1193.

[51] A. S. Lyakhovnenko1, V. V. Trifonov1, V. I. Goncharov, and A. V. Aksenov *Chemistry of Heterocyclic Compounds, Vol. 42, No. 9,* **2006.**

[52] D. Desilets, P. M. Kazmaier, R. A. Burt, G. K. Hamer, *Can. J. Chem.* **1995**, *73*, 325–335.

[53] H. Langhals, *Instructions of the polymer practical course*, Ludwig-Maximilians-University, Munich, **2009**.

[54] S. M. Sami, R. T. Dorr., D. S. Alberts, A. M. Slyom, and W. A. Remers, J. *Med. Chem.* **2000**, *43 (16)*, 3067-3073.

[55] a) S. M. Bachrach, *Computational Organic Chemistry*, John Wiley & Sons, New York, **2007**, pp. 394–395; ISBN 978-0-471-71342-5; b) R. Villar, M. J. Gil, J. I. Garcia, V. Martinez-Merino, *J. Comput. Chem.* **2005**, *26*, 1347–1358; *Chem. Abstr.* **2005**, *143*, 410902.

[56] Andrew, Trisha L; Van Veller, Brett; Swager, Timothy M, *Synlett* **2010**, *20*, 3045-3048.