Part I. SYNTHESIS, SPECTROSCOPIC PROPERTIES AND AGGREGATION BEHAVIOR OF SUBSTITUTED 2,3-NAPHTHALOCYANINES

AND

Part II. SYNTHETIC STUDIES OF SUBSTITUTED DICYANO-ANTHRACENES AND TETRACENS

BY

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To Dad, Mum and Rachel

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ABBREVIATIONS

DBU	1,8-Diazabicyclo[5,4,0]undec-7-ene
DMF	*N,N*-Dimethyl formamide
DMSO	Dimethylsulfoxide
dppp	1,3-Bis(diphenylphosphino)propane
EI	Electron impact
Equiv.	Equivalent
FAB	Fast atom bombardment
FT	Fourier transform
HOMO	Highest occupied molecular orbital
ICR	Ion cyclotron resonance
IR	Infrared
LSI	Liquid secondary-ion
LUMO	Lowest unoccupied molecular orbital
MS	Mass spectrometry
NBS	*N*-Bromosuccinimde
Nc	2,3-Naphthalocyanine
NMR	Nuclear magnetic resonance
OAc	Acetate
Pc	Phthalocyanine
THF	Tetrahydrofuran
UV-vis	Ultraviolet-visible
HPMA	Hexamethyl phosphoramide

ABSTRACT

The first part of this thesis describes the synthesis and spectroscopic properties of several octasubstituted 2,3-naphthalocyaninato zinc(II) complexes. The phthalocyanine analogs with the same substitutents were also synthesized and the aggregation behavior of these macrocycles was investigated by ^{1}H NMR and UV-vis spectroscopy. The dimerization constant and heat of association for these complexes were also determined. One of the naphthalocyanines were found to be lyotropic and its liquid crystalline behavior is also described.

Crown ether side chains can also be incorporated onto the periphery of 2,3-naphthalocyanine by using similar pathways. The resulting macrocycle shows a cation induced aggregation behavior. To our knowledge, this represents the first example of crown ether containing naphthalocyanine. The synthesis and spectroscopic properties of this novel macrocyclic compound is also presented in this part of the thesis.

The second part of this thesis describes our efforts to develop several synthetic routes to anthracocyanines and tetracocyanines, the more extended analogs of phthalocyanines. One substituted 2,3-dicyanoanthracene (compound **118**) was prepared and fully characterized. This compound was found to be photochemically reactive and underwent 4 + 4 dimerization forming a head to tail dimer which was structurally characterized.

摘要

本論文的第一部分，主要詳述數種八取代的二,三-萘菁鋅(II) 絡合物的合成情況及其光譜性質。其次記錄有同類取代基酞菁同系物的合成情況。運用磁核共振及紫外光光譜儀，研究了這種大環共軛體的聚集性質，並測定了二聚體的穩定常數和生成熱。此部分亦會提及其中一種萘菁被發現具有液晶的性質。

以類似的方法，可將冠醚併入二,三-萘菁所得大環體系，表現出陽離子誘導的聚集作用。根據我們所知，這是第一個將冠醚連到萘菁的例子。這種新的環狀合成物的合成法及其光譜性質亦會在本論文中第一部分詳述。

第二部分主要記述我們爲了合成 Anthracocyanines 和 Tetracocyanines,兩類具有更大共軛體系的酞菁同系物所做的努力。其中一種新的二,三-雙氰基蒽（化合物 118）被合成出來，並進行全面的結構鑒定。結果發現，此化合物在光照下呈現化學反應並進行 4+4 "頭－尾" 加成衍生出另一種二聚物。

Part I

SYNTHESIS, SPECTROSCOPIC PROPERTIES

AND AGGREGATION BEHAVIOR OF

SUBSTITUTED 2,3-NAPHTHALOCYANINES

1 Introduction

Phthalocyanine (Pc) **(1)** was synthesized accidentally in 1907.[1] Over the past few decades, this macrocyclic compound and its analogs have been extensively studied.[2] Pcs are among the most stable organic materials showing remarkable optical properties. The conjugated macrocycles which contain 38 π electrons absorb strongly in the far red end of the visible region (*ca.* 670 nm, Q band) and near the ultraviolet region (*ca.* 340 nm, B or Soret band). The intense color, high thermal and chemical stability of these compounds account for their usage as dyes and pigments for long time. Pcs are also of great interest owing to their novel electrical properties.[3] They are well-known as good photoconductors and are, at present, used in electrophotographic systems[4] and photovoltaic cells for energy conversion.[5] They can also form highly conducting materials. The packing of phthalocyanine molecules in columnar stacks leads to an effective overlap between the π molecular orbitals of adjacent macrocycles, which provides an electronic pathway for delocalization of the charge carriers generated upon oxidation. Pcs are thus excellent candidates for molecular electronic materials. Besides, they are widely used as highly sensitive gas sensors,[6] rectifier (molecular diodes),[7] and transistors.[8] The applications of Pcs in many other areas such as optical data storage,[9] nonlinear optics,[10] electrochromic devices,[11] liquid crystals,[12] Langmuir-Blodgett (LB) films,[13] and photosensitizers in photodynamic therapy[14] are also documented.

2,3-Naphthalocyanine (Nc) **(2)** is a Pc's analog which contains linearly annulated benzene rings and consists of 54 π electrons. Both of these

macrocycles belong to an important class of tetrapyrrolic derivatives. Similar to Pcs, this class of extended macrocycles is very thermally and chemically stable, and is only sensitive towards redox reactions. Linear benzoannulation, however, strongly affects the electronic properties of the macrocycles. It produces a destabilization of the HOMO and LOMO energy level resulting in a narrowing of the HOMO-LUMO gap. The intense Q band which is attributed to the lowest energy π - π^* transition is therefore shifted to the near-IR region (*ca.* 800 nm). This bathochromic shift allows Ncs to be the excellent candidates for high-density optical recording (ODR) media since long-wavelength absorbing dyes are required in the writing and reading processes when semiconductor lasers are used. The general physical properties of these two cousins are compared in Table 1.
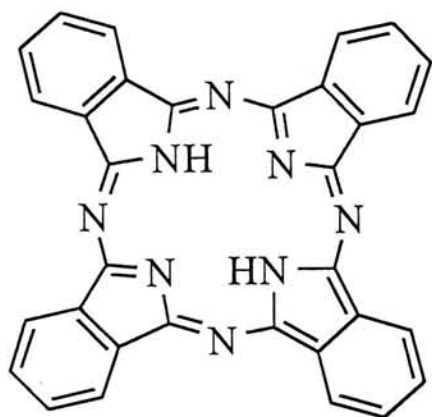
Metal-free Phthalocyanine **1**   Metal-free 2,3-Naphthalocyanine **2**
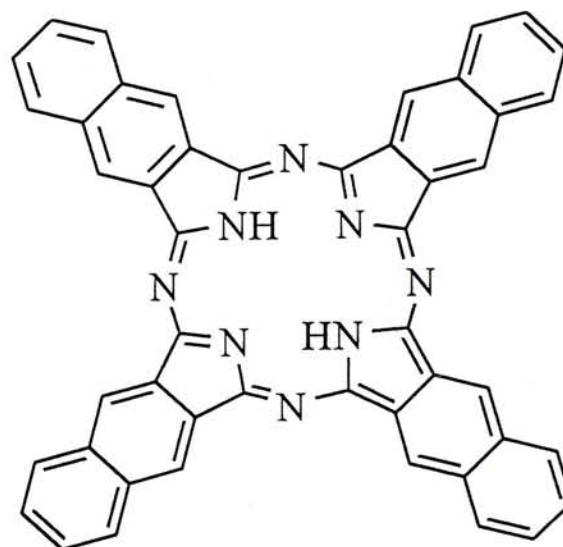
Table 1 : General physical properties of phthalocyanine and 2,3-naphthalocyanine

	Phthalocyanine	2,3-Naphthalocyanine
No. of π electrons	38	54
λ_{max} (Q band)	670-690 nm	750-780 nm
ε (M^{-1}cm^{-1})	ca. 10^5	> 10^5
Color	Blue	Green
HOMO-LUMO gap[15]	1.81 eV	1.65 eV

Although the synthesis, physical properties and applications of Pcs have been studied extensively,[2] the related aspects of Ncs have received relatively little attention. Unsubstituted Nc is almost insoluble in most organic solvents. It can only be dissolved slightly in high boiling solvents such as 1-chloronaphthalene, quinoline, and HMPA, etc. Because of this, spectroscopic data of this compound were mainly obtained in solid states such as single crystals, powder and thin solid films. The poor solubility of Ncs may arise, in large part, from the strong molecular association due to the π-π interactions among the macrocycles. As the π-system of Nc is larger than that of Pc, the aggregation tendency of Nc is expected to be greater and the interactions among Nc rings are more difficult to be disrupted. This aggregation phenomenon hinders both the purification and characterization processes. To overcome this problem, appropriate substituents can be introduced to the macrocycle to increase the distance between two Nc molecules and thereby reduce the degree of aggregation. In general, substituents can be introduced as the axial ligands or to the peripheral of the macrocycle. Substituted 2,3-naphthalocyanines, however, are rare which may be due to the lack of convenient synthetic routes to

the substituted 2,3-dicyanonaphthalenes precursors.   Considerable progress has

only been made in this aspect recently which is summarized below.

1.1 Synthesis of 2,3-Naphthalocyanines

2,3-Naphthalocyanines are usually prepared by base-promoted cyclic tetramerization of the corresponding 2,3-dicyanonaphthalenes. Synthetic pathways to these precursors have recently been developed and are summarized below.

Synthesis of 1,4-disubstituted 2,3-dicyanonaphthalenes

1,4-Dialkoxy-2,3-dicyanonaphthalenes (5) (R = ethyl, propyl, butyl, pentyl or octyl) have been prepared by *o*-alkylation of the diol 4 with the corresponding alkyl iodide (Scheme 1). Diol 4 can be obtained by treating the commercially available 2,3-dichloro-1,4-naphthoquinone (3) with sodium cyanides in ethanol.[16]
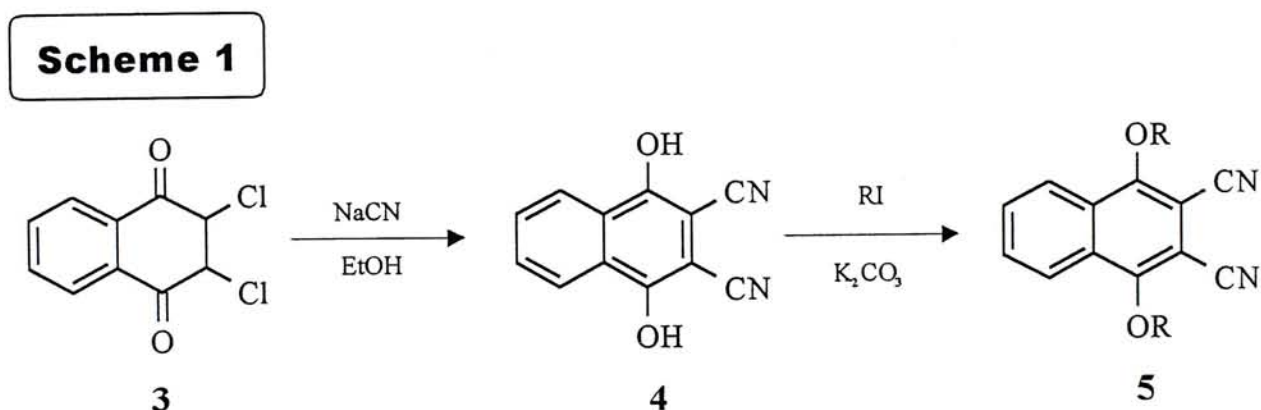
Scheme 1

Very recently, Cook *et al.* have reported the synthesis of a 1,4-dialkyl-2,3-dicyanonaphthalene.[17] The dinitrile 11 can be prepared in five steps as shown in Scheme 2. *o*-Dichlorobenzene (6) reacts with the Grignard reagent $C_7H_{15}MgBr$ in the presence of a nickel catalyst to give the coupled product 7. This diheptyl benzene, upon benzylic bromination, converts into compound 8. Elimination of HBr generates the reactive *o*-quinodimethane derivative 9, which is trapped with fumaronitrile to give 10. Treatment of 10 with NBS followed with ᵗBuOK gives the desired dinitrile.

Scheme 2

Compound **11** and the dimethyl analog **21** have also been prepared by Ng *et al.*[18] using a different synthetic route. As shown in Scheme 3, 1,4-dihexylbenzene **(14)** can be prepared by the nickel-catalyzed coupling reaction of 1,4-dichlorobenzene **(12)** with the Grignard reagent $C_6H_{13}MgBr$. Bromination of **13** and **14** in dichloromethane in the presence of a catalytic amount of iron powder and iodine gives the tetrabromobenzenes **15** and **16** respectively.[19] Treatment of these compounds with *n*-butyllithium generated reactive benzynes which can be trapped with furan leading to the formation of endoxides **17** and **18**.[20,21] Upon reductive deoxygenation with zinc and titanium tetrachloride in THF, these compounds can be converted into **19** and **20** respectively.[20,21] The dinitriles **11** and **21** can be obtained by treating the dibromides with copper(I) cyanide in DMF under the Rosenmund-von Braun reaction conditions.[20,22]

Scheme 3

12 → **13** R = CH₃ / **14** R=C₆H₁₃ → **15** R = CH₃ / **16** R=C₆H₁₃

17 R = CH₃ / **18** R=C₆H₁₃ → **19** R = CH₃ / **20** R=C₆H₁₃

21 R = CH₃ / **11** R=C₆H₁₃

Synthesis of 5,8-disubstituted 2,3-dicyanonaphthalenes

By using the synthetic route shown in Scheme 4, Hanack *et al.* have prepared 2,3-dicyano-5,8-diheptylnaphthalene **(26)**.[23] Treatment of 1,2,4,5-tetrabromobenzene **(23)** with 1 equiv. of *n*-butylithium and 2,5-diheptylfuran **(22)** gives the adduct **24**. Reductive deoxygenation followed by Rosenmund-von Braun reaction leads to the formation of the dinitrile **26**. An identical pathway to 2,3-dicyano-5,8-dihexylnaphthalene has also been reported independently by Ng *et al.*[18]

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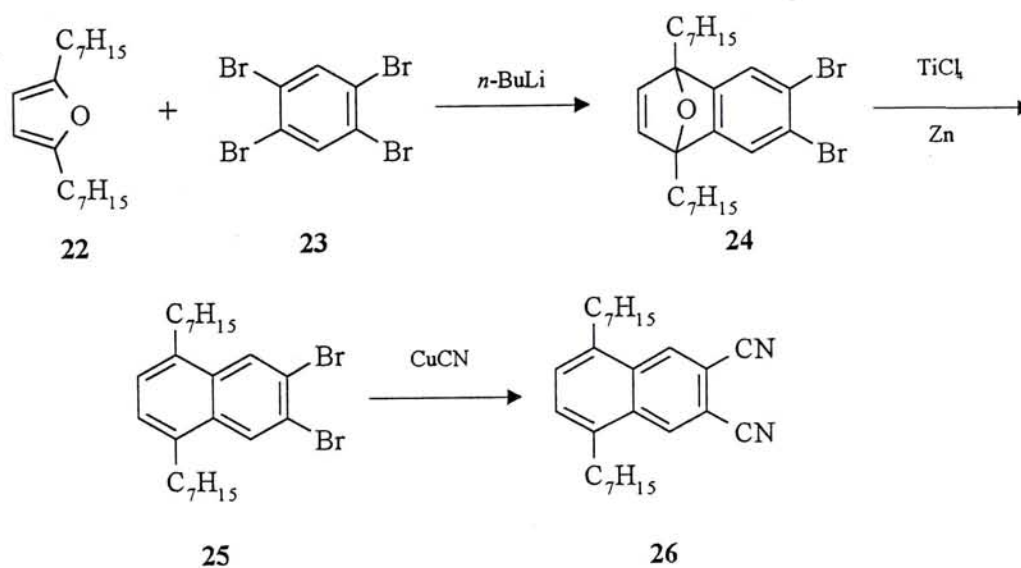
By using 2,5-dimethylfuran instead of 2,5-diheptylfuran and following the same reaction sequence, the endoxide **27** can be produced which undergoes reductive deoxygenation yielding the dibromonaphthalene **28** (Scheme 5). Benzylic bromination followed by alkoxylation or thioalkylation introduces two substitutents to the 5,8-position of the naphthalene ring. The dibromides **30** can be converted into the respective dinitriles **31** under the Rosenmund-von Braun reaction conditions.[24]

$X = OC_6H_{13}$
$OC_2H_4OC_2H_4OC_4H_9$
SC_8H_{17}

9
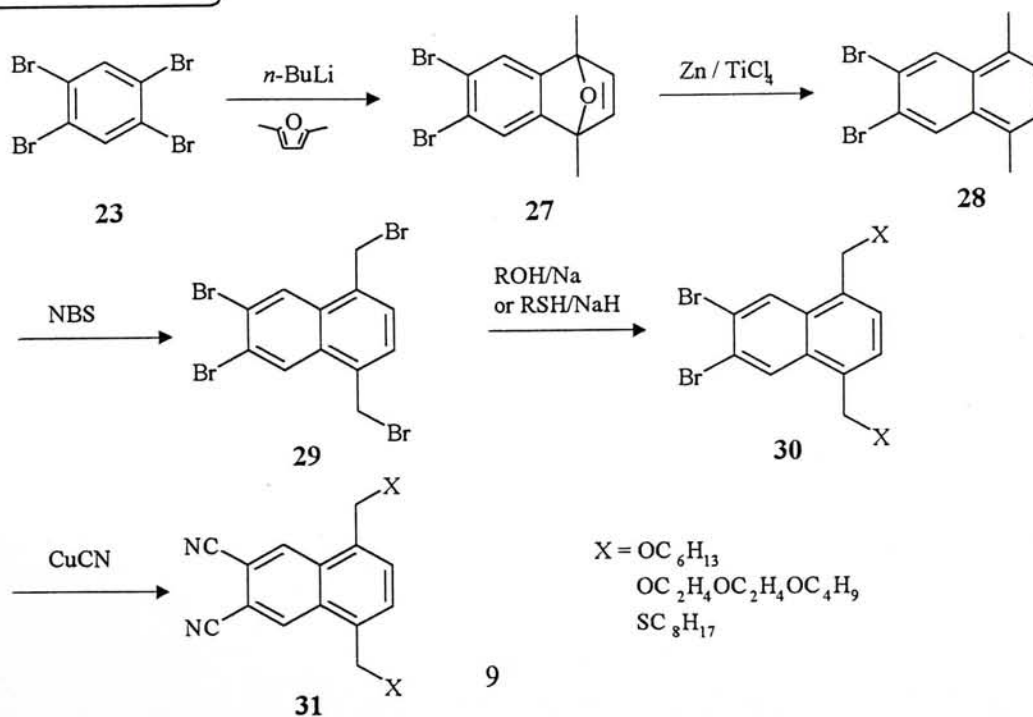
Synthesis of 6,7-disubstituted 2,3-dicyanonaphthalenes

2,3-Dicyano-6,7-dihexyloxynaphthalene **(39)** has been prepared from catechol **(32)** by the route shown in Scheme 6.[25] Standard alkylation of catechol gives ether **33**, which undergoes bromination to yield the dibromide **34**. Treatment of **34** with *n*-butyllithium and furan gives the endoxide **35**. In a second Diels-Alder reaction, **35** reacts with tetraphenylcyclopentadienone affording the adduct **36**. In boiling decaline, **36** decomposes and gives the intermediate dihexyloxyisobenzofuran **(37)**, which reacts with fumaronitrile to give the tetrahydronaphthalene **38**. The dinitrile **39** can be generated from **38** by dehydration using lithium bis(trimethylsily)amide as a base.

Scheme 6

10
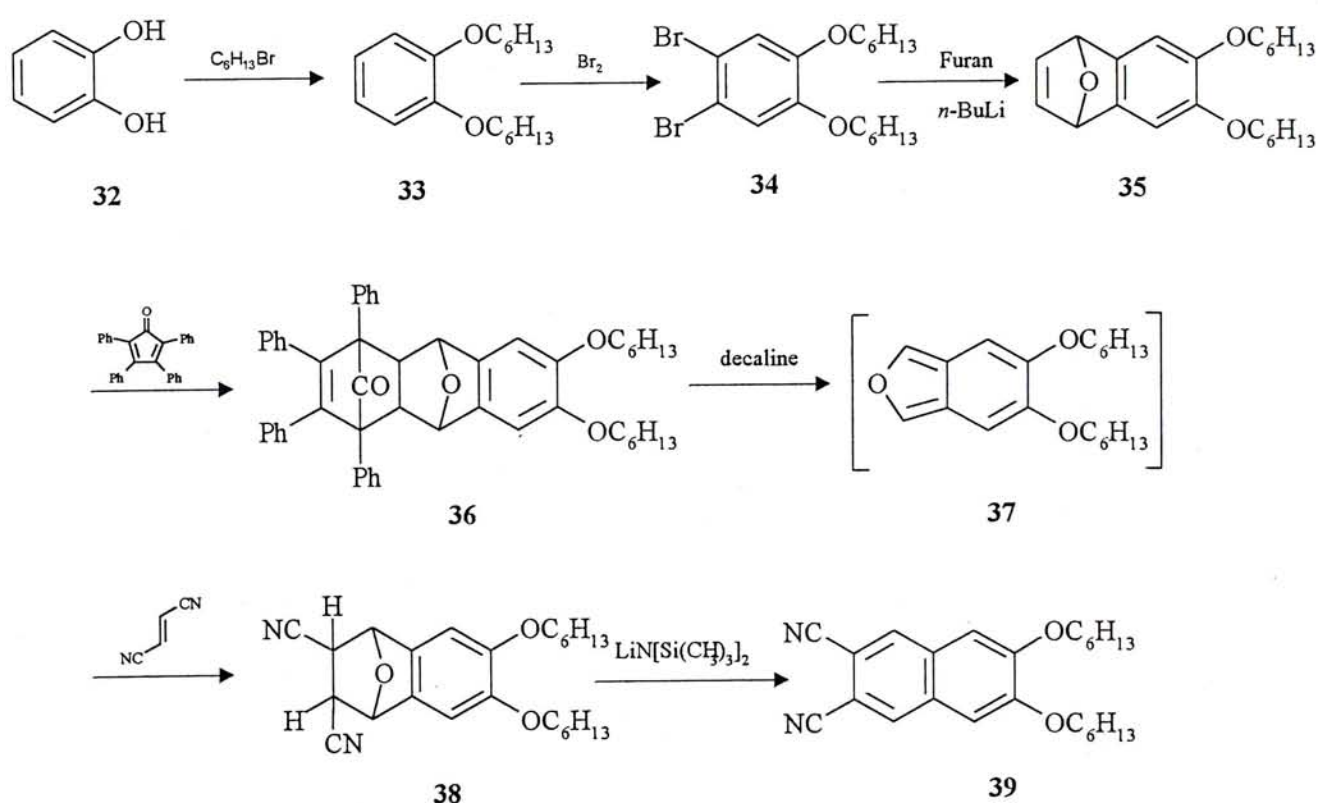
Apart from this method, Cook *et al.* have also developed a synthetic route to 6,7-disubstituted 2,3-dicyanonaphthalenes.[17] As shown in Scheme 7, bromination of 2,3-dihydroxynaphthalene (**40**) in acetic acid yields predominant 1,4,6,7-tetrabromo-2,3-dihydroxynaphthalene (**41**). Selective debromination can be achieved using tin chloride and hydrochloric acid, yielding the dibromo compound **42**. Subsequent alkylation followed by the Rosenmund-von Braun reaction affords the desired dinitriles **44**.
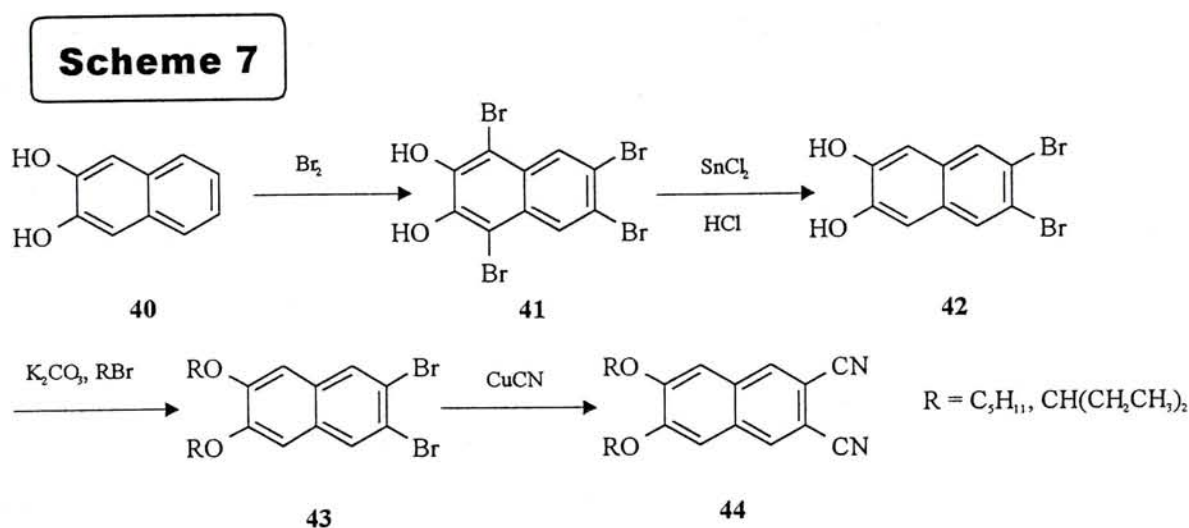
Scheme 7

Scheme 8 shows an alternative route to 6,7-disubstituted 2,3-dicyanonaphthalenes. The bromobenzene **45**, which can be prepared from *o*-xylene in two steps, reacts with fumaronitrile and NaI in DMF to gives 2,3 dibromo-6,7-dicyanonaphthalene (**46**). This compound undergoes nucleophilic aromatic substitution with sodium thiolates giving the respective dinitriles **47**.[18,26]

Scheme 8

R = Ph
R = C_3H_7
R = C_8H_{17}
R = $C_{12}H_{25}$
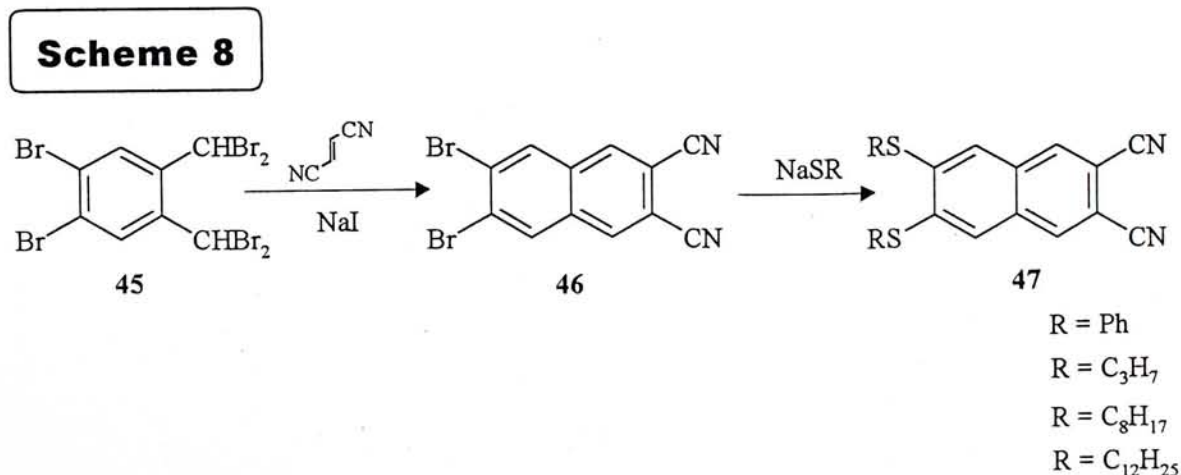
Synthesis of substituted 2,3-naphthalocyanines

A substantial number of metal-free and metallated Ncs have been reported. The former macrocycles can usually be prepared by Li-induced cyclic tetramerization of dicyanonaphthalenes followed by the treatment of acid (Scheme 9, path a[27]). By using DBU as the base and in the presence of $Zn(OAc)_2 \cdot 2H_2O$, the corresponding zinc Ncs can be obtained (Scheme 9, path b[18]). The iron analogs can be synthesized in a similar manner (Scheme 9, path c[25]), but they are unstable and axial ligands are usually added to stabilize the complexes. By treating 2,3-dicyano-5,8-dihexylnaphthalene with $Ti(OEt)_4$ in the presence of urea, the first oxotitanium Nc **48** has recently been synthesized which processes a pyramidal structure (Scheme 9, path d[28]).

As the synthetic methods of substituted Ncs have only been established over the past few years, studies on their physical and spectroscopic properties remain relatively rare. This chapter describes our studies on the synthesis and spectroscopic properties of substituted 2,3-naphthalocyanines. Particular attention has been focused on their aggregation behavior in solutions and macrocycles incorporated with four crown ether moieties. The following sub-sections briefly review the related studies on the Pc systems.

Scheme 9

(a) i) Li, C₅H₁₁OH

ii) AcOH

(b) Zn(OAc)₂·2H₂O

DBU, C₆H₁₃OH

(c) i) Fe(OAc)₂, DBU

ii) ᵗBuCN

(d) Ti(OEt)₄

urea

13
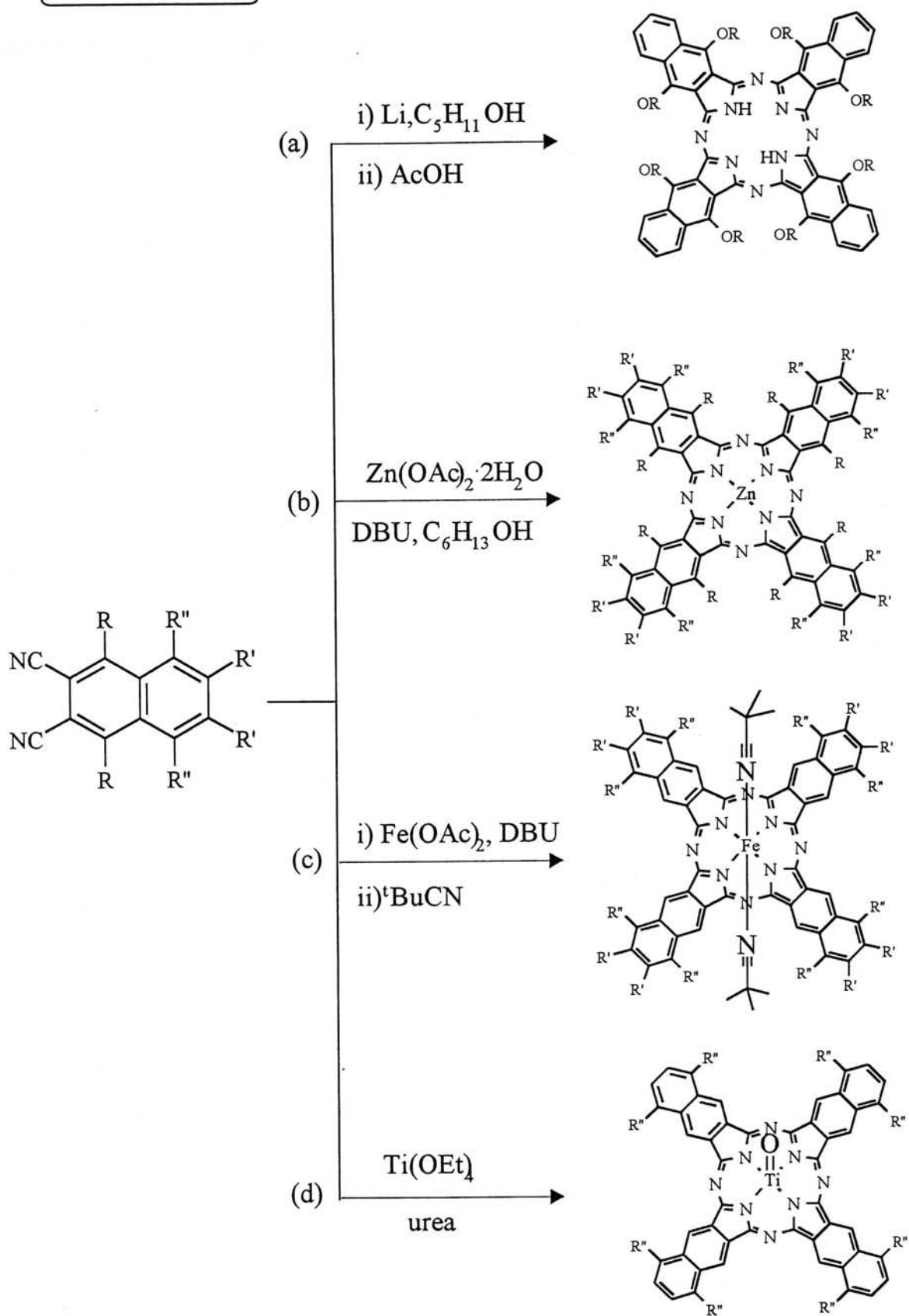
1.2 Aggregation Phenomena of Phthalocyanines

Molecular aggregation is a common phenomenon for dyes like Pcs. These macrocycles tend to form dimers, trimers and oligomers in solutions. The origin, although not very clear, may arise mainly from the π - π interactions.[29,30] There is a substantial evidence showing that dimer is the dominant species and much attention has been focused on the thermodynamic properties of the dimerization process. Since metallophthalocyanines absorb strongly in the visible region, the dimerization constants can usually be determined spectrophotometrically. Some methods require the acquisition of monomer spectrum that is usually achieved by successive dilution of the solution of dye until the spectrum does not change furthermore.[31] The spectrum recorded in this concentration could be assigned to the purely monomeric species.

Assuming that a one-step equilibrium between the phthalocyanine monomer (Pc) and the aggregated species (Pc_n) exists (eq. 1) and by using the method described by Hayashi the values of the aggregation number (n) and the aggregation constant (K) can be determined.[29]

$$nPc \xrightleftharpoons{K} Pc_n \qquad \text{(eq.1)}$$
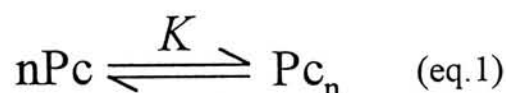
The latter is given by eq. 2, where x represents the ratio of monomer concentration to the total concentration of phthalocyanine, C_t.

$$K = x/[n \cdot C_t^{n-1}(1-x)^n] \qquad \text{(eq.2)}$$

Observed extinction coefficient (ε) at certain wavelength is represented by eq. 3,

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where ε_m and ε_d are extinction coefficients for pure monomer and aggregate at that wavelength respectively. From eq. 2 and 3, eq. 4 is obtained, where $C = n^n/(n-\varepsilon/\varepsilon_m)^{n-1}$.

$$\varepsilon = x\varepsilon_d/n + (1 - X) \varepsilon_m \qquad (eq.3)$$

$$\text{Log}[C_t(1 - \varepsilon/\varepsilon_m)] = \log (CK) + n\log[C_t\{\varepsilon/\varepsilon_m - \varepsilon_n/(n\varepsilon_m)\}] \qquad (eq.4)$$

If the extinction coefficient of n-aggregate, ε_d, is very small relative to ε_m at the absorption maximum of the monomer, eq. 4 is simplified to eq. 5 at the absorption maximum by assuming $\varepsilon/\varepsilon_m >> \varepsilon_d/(n\varepsilon_m)$ and $n >> \varepsilon_d/\varepsilon_m$. A plot of $\text{Log}[C_t(1 - \varepsilon/\varepsilon_m)]$ v.s. $\log[C_t(\varepsilon/\varepsilon_m)]$ can then give the values of n and K.

$$\text{Log}[C_t(1 - \varepsilon/\varepsilon_m)] = \log(nK) + n\log[C_t(\varepsilon/\varepsilon_m)] \qquad (eq.5)$$

The equilibrium between a naphthalocyanine monomer and its aggregated species can be studied similarly. Figure 1(a) shows the electronic spectrum of $CuNc(^tBu)_4$, in a 1.28×10^{-4} M toluene solution, which exhibits absorption maxima at 770 nm and 690 nm, assignable to the monomeric and aggregated forms respectively. When this solution is diluted gradually to 2.56×10^{-7} M, the intensity for the monomeric absorption maximum increases while that for the aggregate diminishes as shown in Fig. 1(d). As further spectral change is not observed at concentrations lower than 2.56×10^{-7} M, the spectrum observed in the 2.56×10^{-7} M solution can be attributed to the purely monomeric $CuNc(^tBu)_4$. By plotting $\log[C_t(1- \varepsilon / \varepsilon_m)]$ vs. $\log [C_t(\varepsilon / \varepsilon_m)]$ (Figure 2), a straight line is obtained from which the values of n and K can be determined. This aggregation number suggests that the Nc prefers to form dimer in solution.
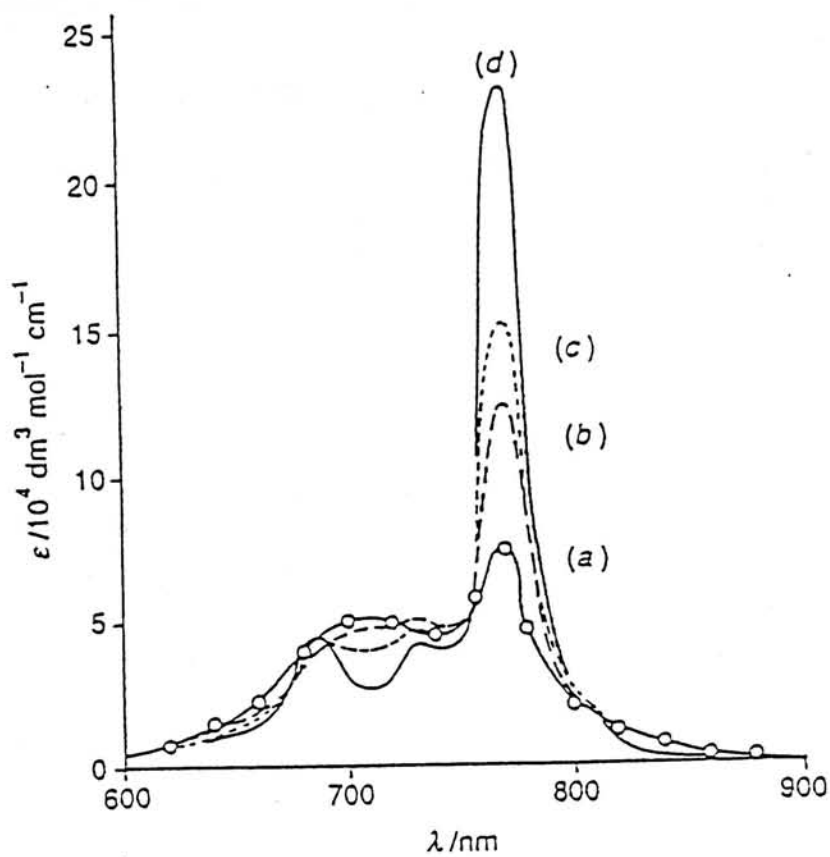
Figure 1 Concentration of electronic absorption spectra of CuNc(^{t}Bu)$_4$ in toluene solution: (a) (-o-o-), 1.28 x 10^{-4} M; (b) (----), 3.20 x 10^{-5} M; (c)(····), 1.28 x 10^{-5} M; (d)(—), 2.56 x 10^{-7} M
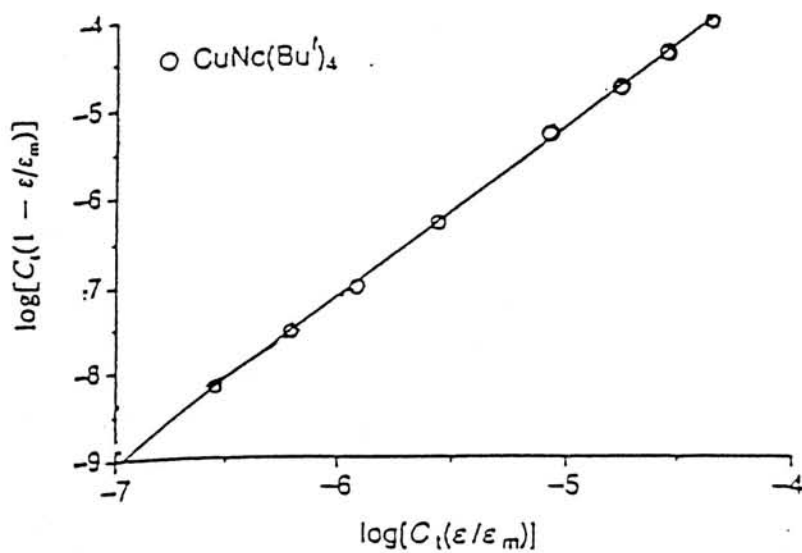
Figure 2 Plot of log[C_t(1- ε / ε_m)] vs. log [C_t(ε / ε_m)] for the spectroscopic changes of naphthalocyanines

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In studies of aggregation behavior of Pcs, particular attention has been focused on the water-soluble tetrasulfonate derivative **48** since Abel *et al.* discovered that the cobalt(II)tetrasulfonated phthalocyanine Co(TSPc) binds to oxygen reversibly.[32] Similar to other water-soluble dyestuffs,[33] transition-metal tetrasulfonated phthalocyaninato complexes aggregate in water and form predominant dimeric species. The spectroscopic and thermodynamic aspects of this dimer formation have been the subject of numerous studies for a variety of transition metals. The molar absorptivity of the Q band for monomer is in general higher than that of dimer by one order of magnitude.

R = SO₃Na (TSPc)

48
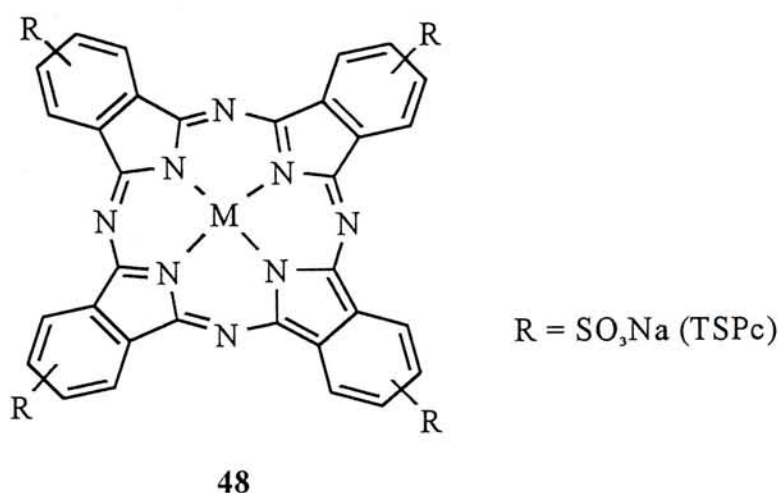
As spectrum due to pure monomeric species cannot be usually obtained, an alternative method can be used. Recently, Zhang and Hui have studied the influence of halogenation and aggregation on the photosensitizing properties of zinc phthalocyanines.[34] By assuming that no higher aggregates than dimers are formed, dimerization equilibrium constants have been calculated using a modified non-linear least-squares fitting method which will be described in detail in the following section. The absorption spectra for pure monomer and dimer have also been calculated which are shown in Figure 3.
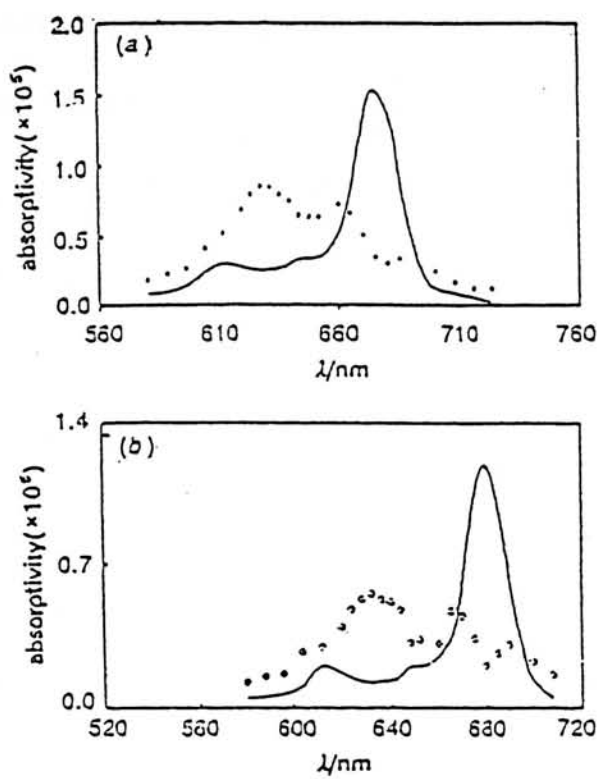
Figure 3 Simulated absorption spectra of pure monomer (———) and dimer (o)
ZnPC(X)$_4$ (a) X = Br, (b) X = I.

Apart from the dimerization constant and the molar absorptivity of the monomer, spectrophotometric methods can also be used to determine thermodynamic quantities of such as the heat of association. Nolte et al.[35] have recently synthesized the metal-free phthalocyanine **50**, which exhibits mesophase behavior at ca. 150°C.   This compound strongly aggregates in chloroform solution to form a gel. Electron micrographs showed that this gel contains a network of fibers, each of which is built up of parallel strands of supermolecules having the thickness of one molecule and a length of several micrometers.   By measuring the absorption spectra at different concentrations and temperatures, the heat of association of **50** in $CHCl_3$ has been estimated to be −125 KJ mol^{-1}, which is by far the highest value reported in literature for the aggregation of Pcs.   For comparison, the heats of association of tetrasulfonato phthalocyanines in water are 2.5-5 times lower.[36]

50
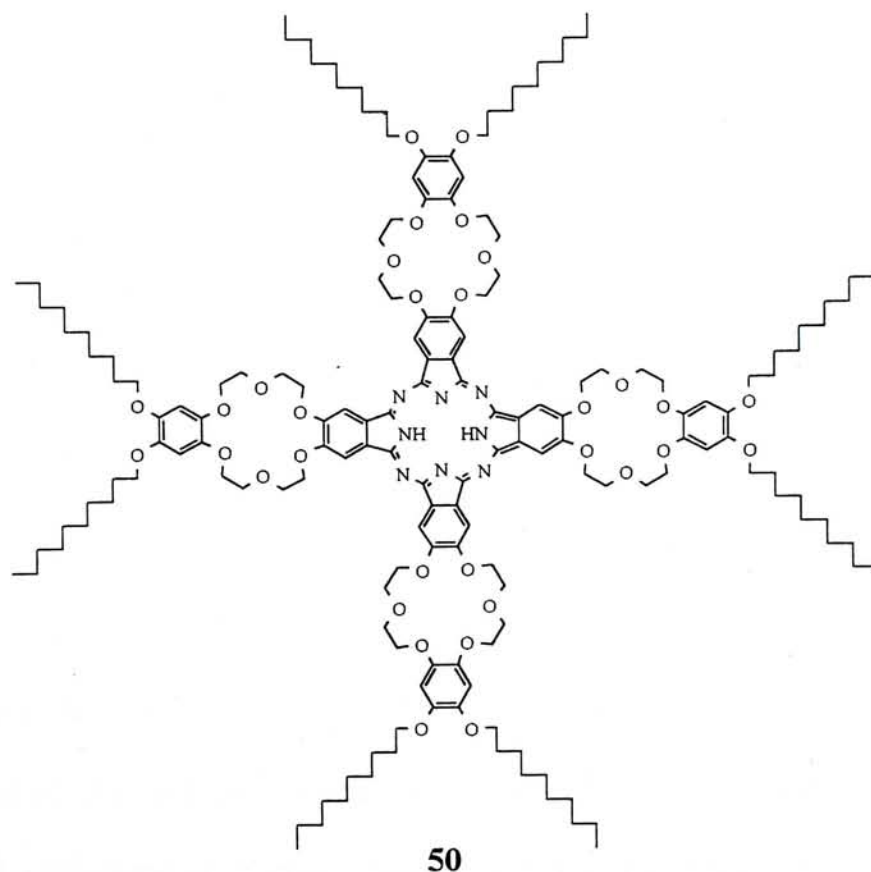
1.3 Phthalocyanines Containing Crown Ether Voids

Molecular ionics is a rapidly growing area in chemistry. It is aimed at the development of molecular systems and devices that can handle and store information using ions as the basic species.[37-39] Crown ethers which are capable of selectively binding alkali metal ions are important building blocks for constructing such devices because metal complexation can lead to a specific response, e.g. a change in absorption spectrum or electrical conductivity. In order to maximize the reliability, the response must be highly nonlinear, which can usually be achieved by introducing a cooperative effect in the binding process.[38,39]

The use of phthalocyanines, porphyrins, and porphyrazines as active components in molecular ionics has received much current attention.[2] Of particular interest are phthalocyanines substituted with four crown ether rings,[38,39] which have been studied extensively by the groups of Bekaroglu, Kobayashi, and Nolte, etc.[40] These compounds display solvent- and metal ion-induced aggregation behavior. Nolte *et. al.*[41] have prepared several crown ether-containing Pcs and studied the variation of electrical properties in the presence of various alkali metal picrates.[42] The ac electrical conductivities of the K^+, Rb^+, and Cs^+ complexes of 18-crown-6 Pcs are shown to be 2-3 orders of magnitude higher than those of the metal free parent Pcs. It has been demonstrated that the higher conductivities are due to the cofacially stacked arrangement of Pcs induced by the alkali metal ions. In the presence of Ba^{2+}, noncofacial aggregates are formed, leading to a lower conductivity. With these properties, the crown ether-containing Pcs are widely used as sensors for various metal ions.[43,44] The synthesis of novel magnesium, copper, and metal-free

porphyrazines, peripherally substituted with dithia-7-crown-2, dithia-15-crown-5, and dithia-18-crown-6 macrocycles have been reported. These "crowned" porphyraines bind silver(I) and mercury(II) perchlorates. UV/vis spectroscopy and electron paramagnetic resonance measurements have revealed that addition of transition-metal ions leads to dimerization of the porphyrazine complexes.

Pcs with azacrown ether and thiacrown ether substituents have also been synthesized and studied. Some of the examples are shown below. All of these macrocycles are capable of binding various transition-metal ions.[45]

M = 2H
Cu
Ni
Co
Zn
Fe

51

52
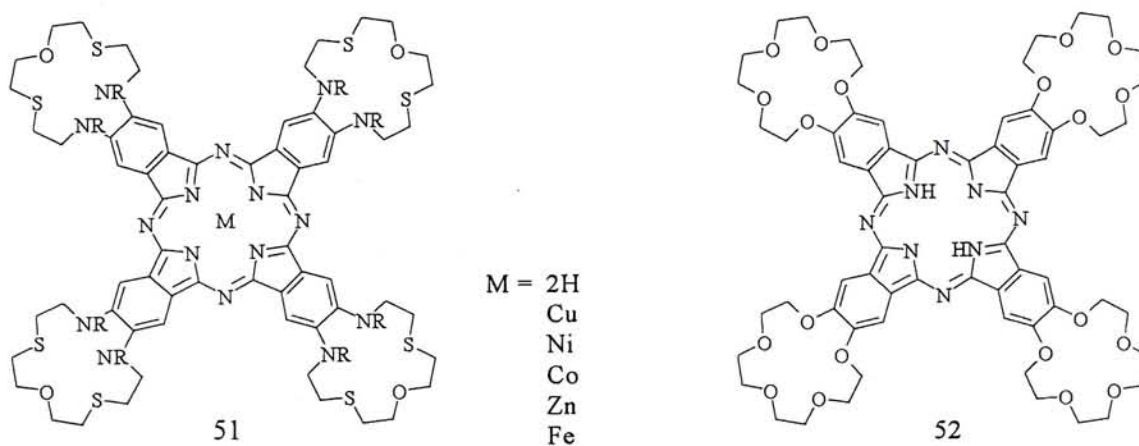
As described in the previous section, the crown ether-containing phthalocyanine **50** forms extremely large linear aggregates in chloroform. This demonstrates that supramolecular wires can be constructed by simple self-assembly of properly designed molecular building blocks. The stacked molecules containing electron-rich central units can form a potentially conducting wire. With polar crown ether units they can generate hollow tubes with lipophilic mantle. The self-assembly is the result of intermolecular *exo*-recognition of the phthalocyanine core and the four peripheral benzene rings.
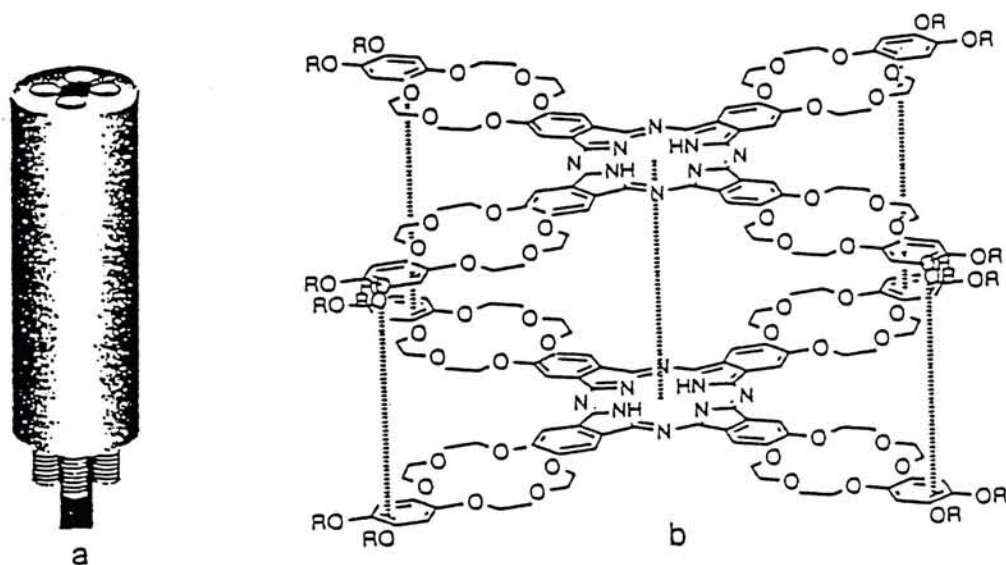
Figure 4. a) Schematic structure of the multiwired supramolecular cable formed by aggregation of molecules **50**. b) Picture showing the five sites of exo-recognition present in the aggregates.

The alkali cation complexation of crown ether-containing phthalocyanines have also been studied by Xu et al.[46] using UV-vis and fluorescence spectroscopy. Cation-induced aggregation of the crown ether-containing phthalocyanines occurs in solutions. When the diameter of the cation slightly exceeds that of the crown ether ring (e.g. K^+, Rb^+), they act cooperatively leading to the formation of a cofacial dimer. Smaller cations such as Li^+ and Na^+, which can be encapsulated into the cavity of the crown ether voids, are unable to cause a complete conversion to a cofacial dimer. Larger Cs^+ ion induces sandwich-like aggregation in solutions more rapidly.

Very recently, crown-ether containing Pc equipped with chiral tails has been shown to form long fibers of molecular diameter and micrometer length by self assembly in chloroform.[47] In the fibers, they have a clockwise, staggered orientation that leads to an overall right-handed helical structure. These structures, in turn, self-assemble to form coiled-coil aggregates with left hand helicity. Addition of potassium ions to the fibers leaves their structure intact but blocks the transfer of the chirality from the tails to the cores, leading to loss of the helicity of the fibers. These tunable chiral materials have potential in optoelectronic applications and as components in sensor devices.

53   54
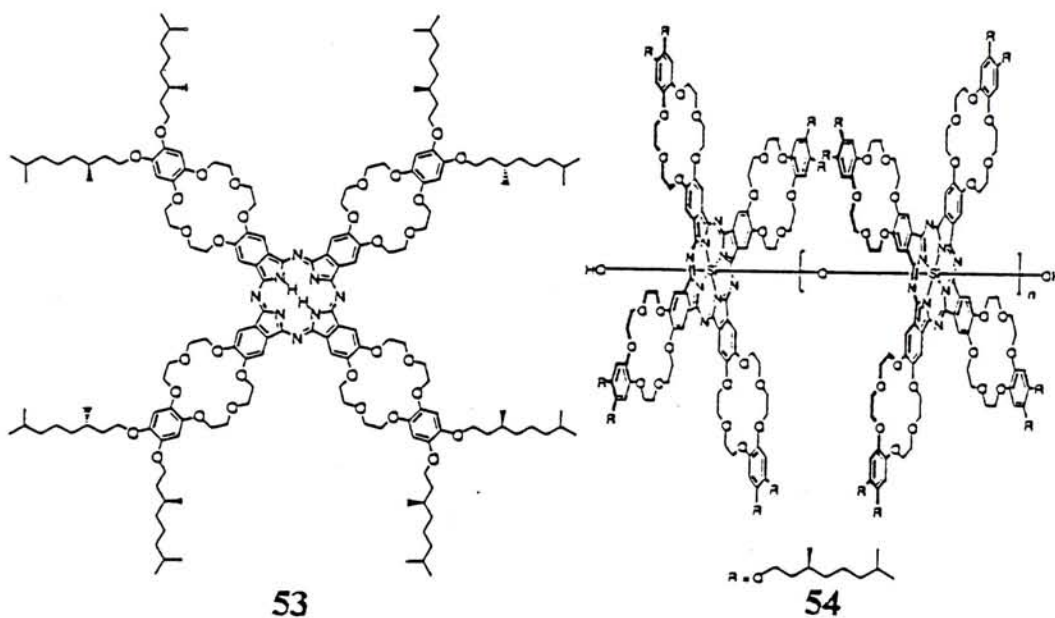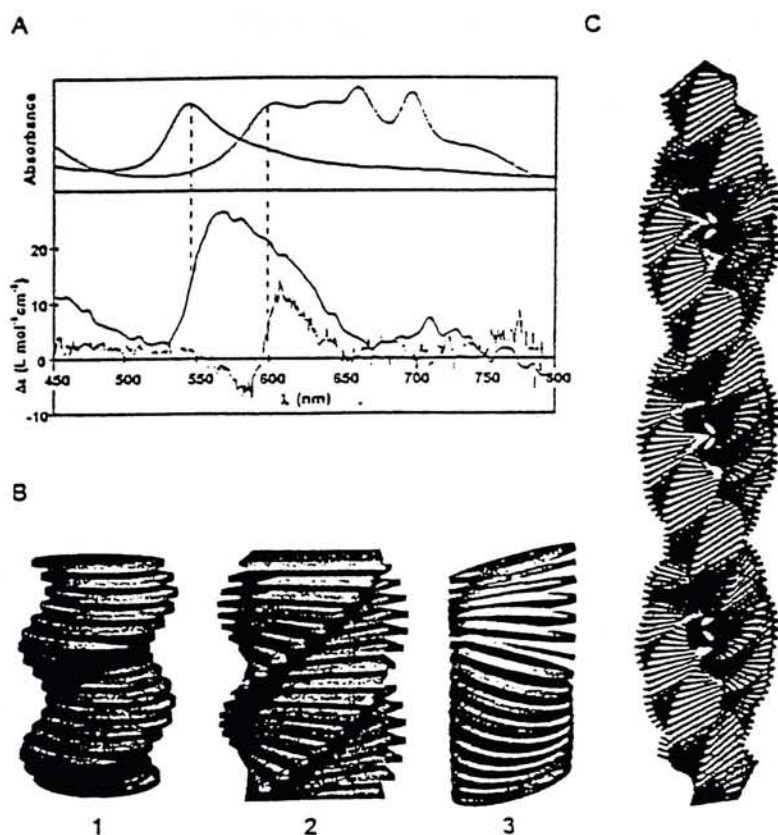
Figure 5. a) Electronic absorption spectra in arbitrary units (top) and CD spectra (bottom) of **53** and polymer **54**. b) Three types of helical aggregates that may be formed by **53**. The molecules are represented as disks in 1 and 3 and as squares in 2 to show more clearly the helical packing arrangement of the building blocks. c) Calculated model of a coiled-coil from **53** reproducing the observed handedness of the single fibers and the super structure.
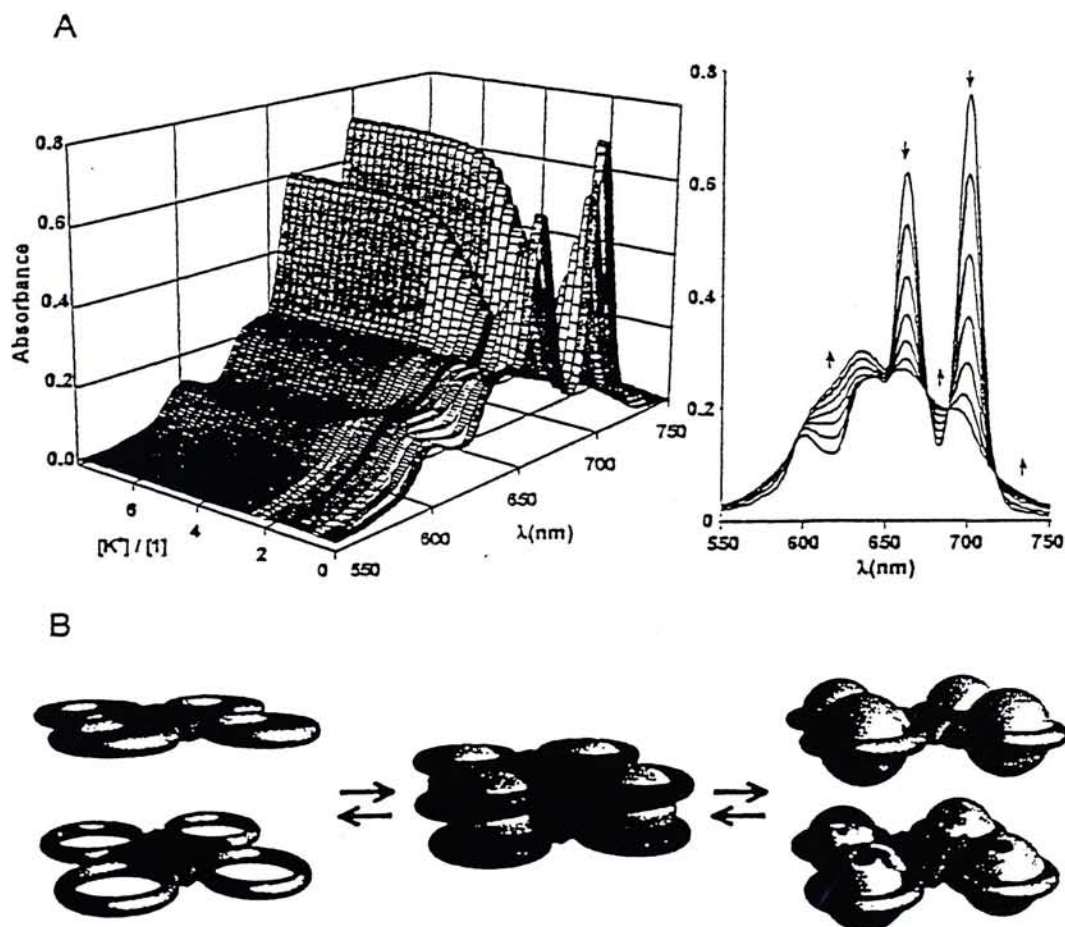
Figure 6. a) (Left) Electronic abosrption spectra of **53** in chloroform (concentration 10 μM) as a function of the ratio of potassium picrate and **53**. (Right) Isosbestic points at 597, 650, 675, 688, and 717 nm that appear when the [K$^+$]/[**53**] ratio is increased from 0 to 2. The arrows indicate increasing potassium picrate concentration. b) Schematic representation of the formation and breakdown of the sandwich-type complexes between K$^+$ ions and **53**.

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This part of the thesis describes the synthesis and spectroscopic properties of two substituted 2,3-naphthalocyanines. The liquid crystalline property of one of these Ncs is also discussed. A direct comparison of the aggregation behavior of these Ncs and their Pc analogs in solutions as probed by UV-vis and ^{1}H NMR spectroscopy is made and the effects of substituents on the aggregation is also discussed. The first example of 2,3-naphthalocyanine incorporated with crown ethers is also described.

2 Results and Discussion

2.1 Synthesis of Substituted 2,3-Naphthalocyanines

Preparation of 2-(2-butoxyethoxy)ethanethiol **(58)**

There are several methods to prepare thiols from halides. The source of sulfur can be alcoholic sodium hydrosulfide, thiourea, elemental sulfur or aqueous sodium trithiocarbonate.[48] Attempts to prepare thiol **58** from 1-chloro-2-(2-butoxyethoxy)ethane **(55)** and thiourea were unsuccessful. However, the thiol was prepared in 71% yield according to the simple one-pot method as shown in Scheme 10. Aqueous sodium trithiocarbonate was prepared by heating a saturated sodium sulfide solution with carbon disulfide.[49] The thiol **58** was obtained by heating the aqueous sodium trithiocarbonate with **55**. It was believed that the sodium salt of the monoalkyl trithiocarbonate **56** was first formed which generated the unstable acid **57** and further decomposed to yield the thiol **58**.[50]

Scheme 10
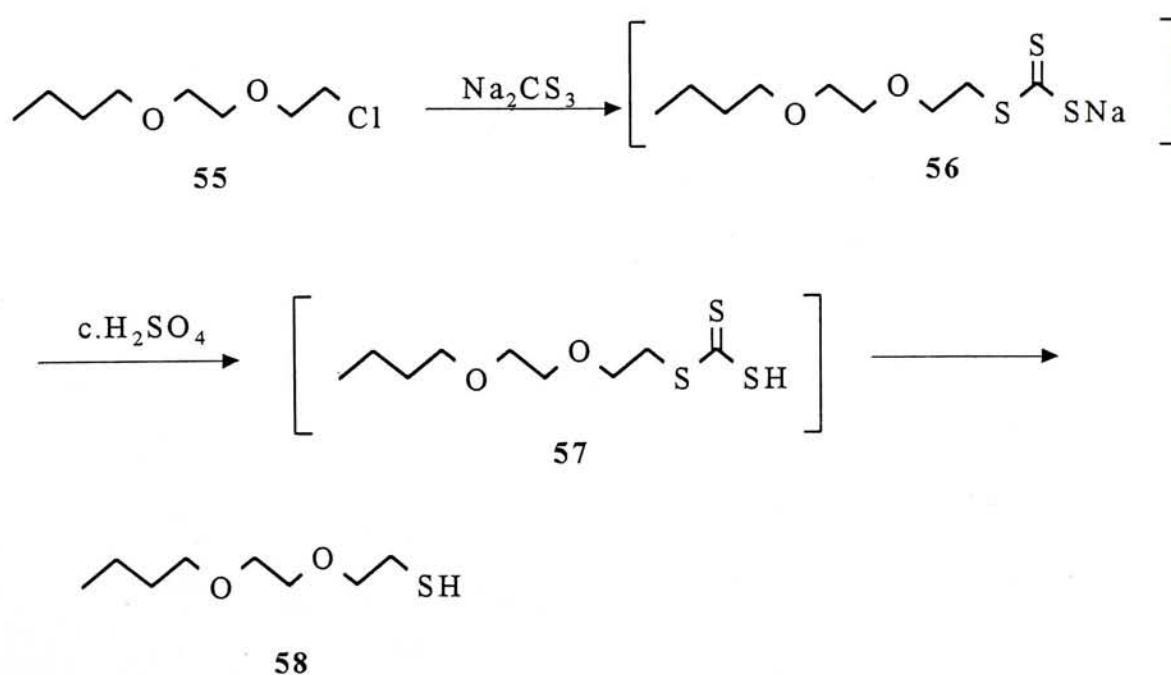
Preparation of 6,7-substituted 2,3-dicyanonaphthalenes

The synthetic route to 6,7-disubstituted 2,3-dicyanonaphthalenes is shown in Scheme 11. The pathway leading to **46** was developed by Luk'yanets *et al.*[51] 1,2-Dibromo-4,5-dimethylbenzene **(60)** was prepared by bromination of *o*-xylene **(59)**. Benzylic bromination with *N*-bromosuccinimide in CCl_4 yielded 1,2-bis(dibromomethyl)-4,5-dibromobenzene **(45)**, which was then treated with fumaronitrile and sodium iodide to give 2,3-dibromo-6,7-dicyanonaphthalene **(46)**, through the proposed intermediates **61** and **62**. Compound **46** then underwent nucleophilic aromatic substitution with sodium thiolates RS^- (R = C_4H_9, $C_4H_9OC_2H_4OC_2H_4$) to give the corresponding substituted dinitriles. In the absence of copper(I) oxide, the products were obtained in about 30% yield. The use of copper(I) oxide therefore promoted the reactions and improved the reaction yields.

Scheme 11

63	R = C_4H_9	65 %
64	R = $C_2H_4OC_2H_4OC_4H_9$	71
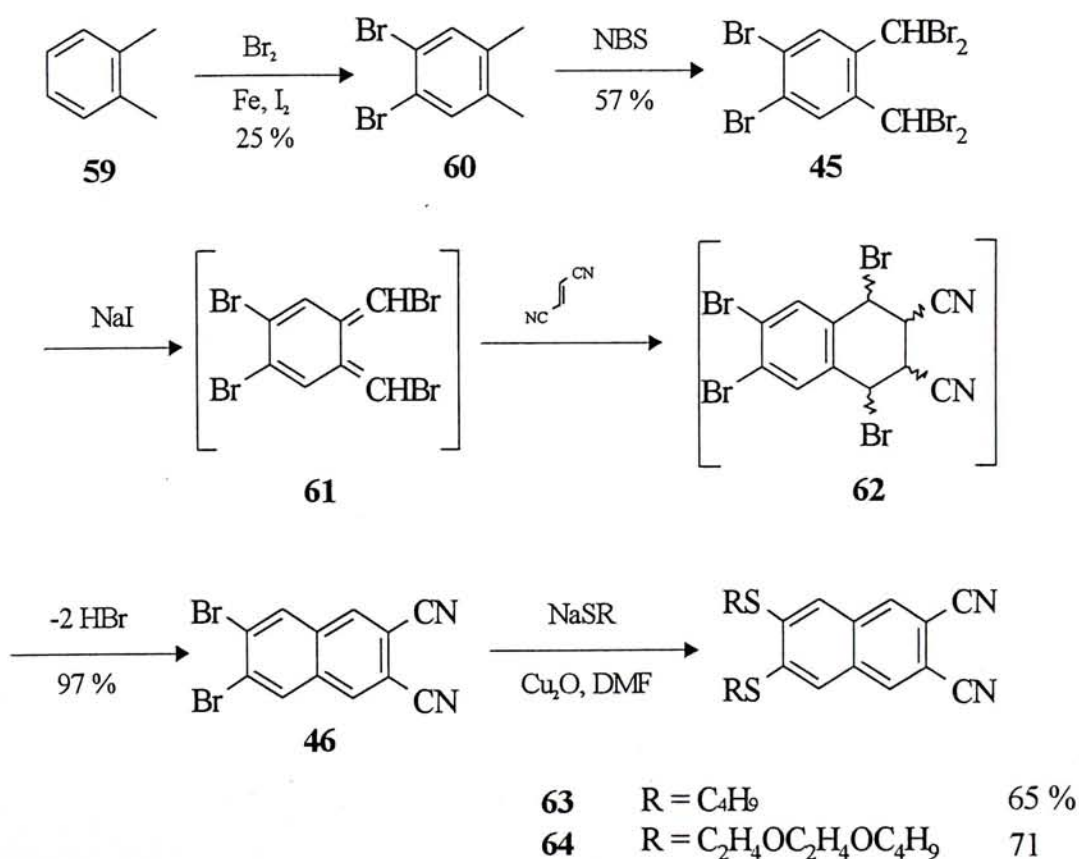
Preparation of octasubstituted naphthalocyaninato zinc(II) complexes

Naphthalocyanines are generally prepared by cyclization of dicyanonaphthalenes under basic conditions.[18,25,27] Typically the dinitrile **63** or **64** was allowed to react with zinc(II) acetate in *n*-hexanol at 150-160°C. The deep green mixture, after being cooled to room temperature, was then added dropwise into a mixture of methanol/acetone (1:1) to give the zinc Nc complex as a precipitate. The crude products were further purified by column chromatography and re-precipitation in $CHCl_3$ solutions by addition of methanol.

Scheme 12

63

64

65   R = SC_4H_9 (64%)

66   R = $SC_2H_4OC_2H_4OC_4H_9$ (45%)
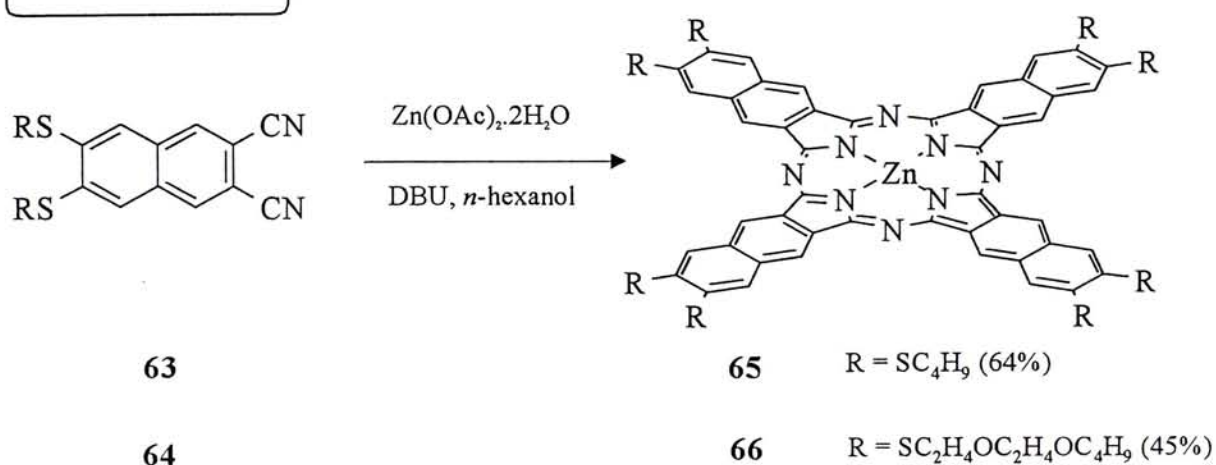
2.2 Synthesis of Substituted Phthalocyanines

In order to directly compare the aggregation behavior of Pcs and Ncs, the Pc analogs of **65** and **66** were prepared as follows.

Preparation of 4,5-disubstituted 1,2-dicyanobenzenes

The synthetic route to 4,5-disubstituted 1,2-dicyanobenzenes is shown in Scheme 13. By following the procedure reported by Wöhrle *et al.*,[52] 1,2-dichloro-4,5-dicyanobenzene (**71**) was prepared from the commercially available 1,2-dichloro-4,5-benzenedicarboxylic acid (**67**) via the anhydride **68**, imide **69** and diamide **70** with an overall yield of 49 %. Compound **71** then underwent nucleophilic aromatic substitution with sodium thiolates RS⁻ (R = C_4H_9, $C_4H_9OC_2H_4OC_2H_4$) to give the corresponding Pc precursors **72** and **73**. These reactions were also performed in the presence of copper(I) oxide, which also increased the reaction yields by about 1.5 folds.

Scheme 13

29
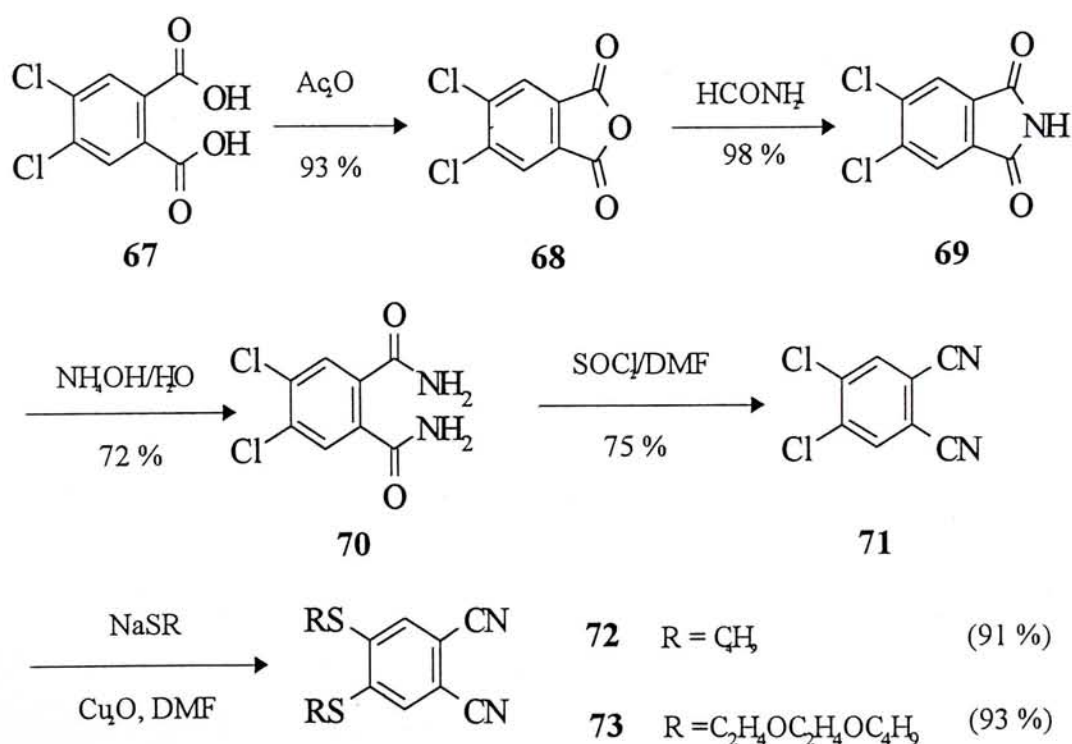
Preparation of octasubstituted phthalocyaninato zinc(II) complexes

Similar to Ncs, Pcs are also prepared from dicyanobenzenes under basic conditions. The substituted dicyanobenzenes **72** and **73** were treated with zinc(II) acetate and a catalytic amount of DBU in *n*-butanol to give the corresponding octasubstituted phthalocyaninato zinc(II) complexes (Scheme 14). Both of these macrocycles are highly soluble in common organic solvents, and can therefore be purified by column chromatography. These deep green compounds are stable in air but decompose readily at high temperature (>300°C).

Scheme 14
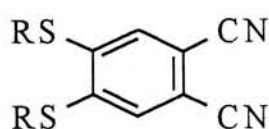
$$72$$

$$73$$
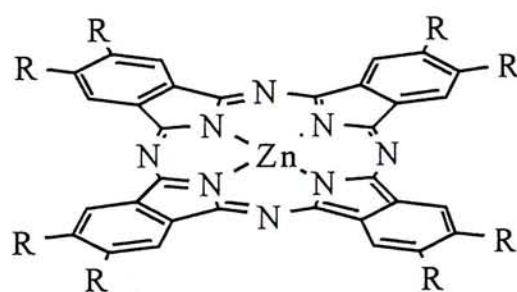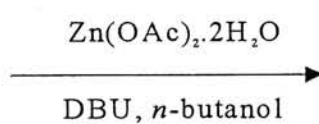
74 R = SC_4H_9 (73%)

75 R = $SC_2H_4OC_2H_4OC_4H_9$ (20%)

2.3 Characterization of the 2,3-Naphthalocyanines and Phthalocyanines

The ^{1}H NMR spectra of Ncs **65** and **66** were first recorded in CDCl$_3$which showed only broad signals due to the side chains, while the signals for the aromatic ring protons could not be observed. This may be due to the strong aggregation tendency of these compounds as observed previously.[28] However, the addition of pyridine-d$_5$(C$_5$D$_5$N) could relief the degree of aggregation and satisfactory spectra could be obtained. Figure 5 shows the ^{1}H NMR spectrum of compound **66** in CDCl$_3$/C$_5$D$_5$N (7 : 3). A broad band at δ 9.00 and a relatively sharp band at δ 8.04 appear which can be attributed to the aromatic ring protons. Such bands, however, could not be observed for **65** under this condition. It appears that this compound has a higher aggregation tendency than **66**.

The ^{1}H NMR spectra of Pcs **74** and **75** were also recorded in CDCl$_3$/C$_5$D$_5$N (7 : 3). The spectrum of **74** is displayed in Figure 6 which shows one downfield aromatic signal at δ 8.61 and well-resolved aliphatic signals at *ca.* δ 1~3 for the side chains. The spectrum of **75**, however, showed poorly resolved signals for both the ring protons and the side chain protons.

From the ^{1}H NMR spectra of Nc **65** and Pc **74**, both of which contain eight butylthio side chains, it appears that Nc **65** has a higher aggregation tendency than Pc **74** as the spectrum for the former shows broad signals under same concentration compared with Pc **74** or even lower concentration while that for the latter shows well-resolved signals. However, by comparing the Nc **66** and Pc **75**, both of which contain 3,6-dioxadecylthio side chains, the latter seems to have higher tendency of aggregation. This result indicated that the 3,6-dioxadecylthio side chains can probably reverse the aggregation tendency of Pc and Nc which may arise from the strong dipole-dipole interactions.

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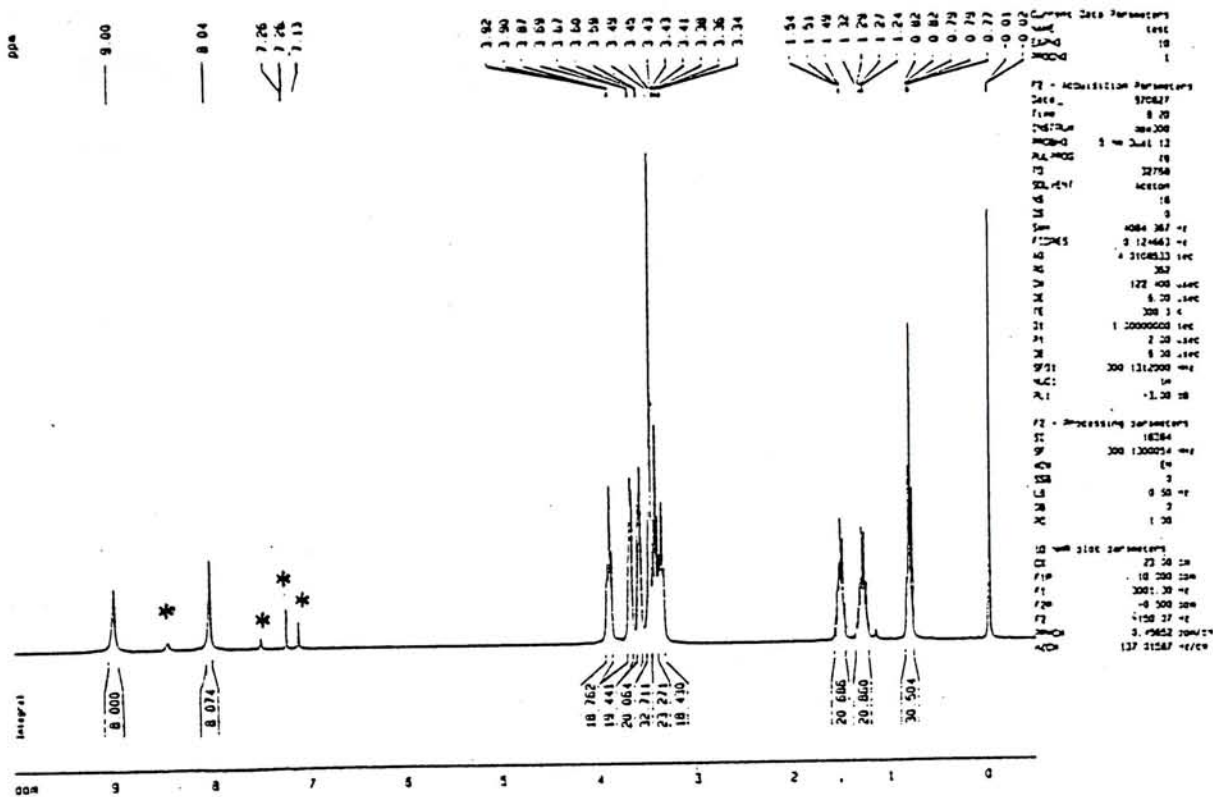
Figure 7 ¹H NMR spectrum of compound **66** in CDCl₃/ C₅D₅N (7:3)

*indicates residual solvent
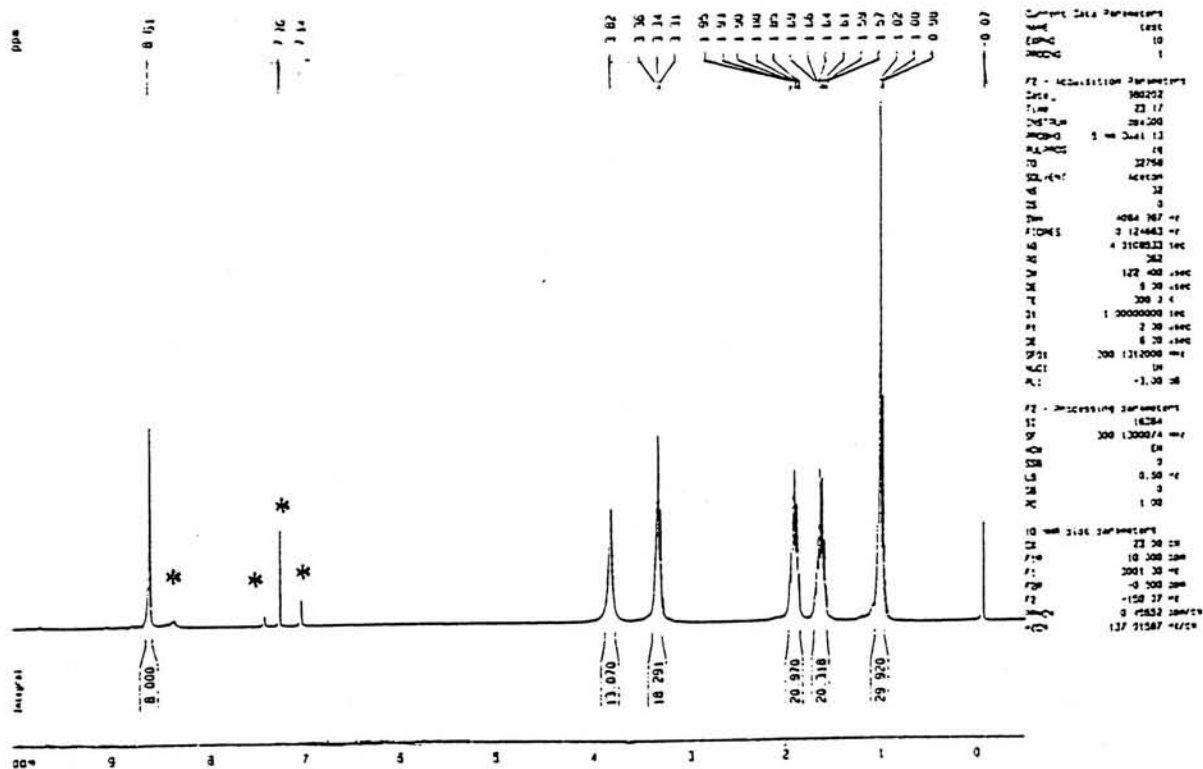
Figure 8 ¹H NMR spectrum of compound **74** in CDCl₃/ C₅D₅N (7:3)

*indicates residual solvent

The liquid secondary ion mass spectra (LSI-MS) of **65**, **66**, **74** and **75** were measured with a FT-ICR mass spectrometer. The protonated molecular ion was detected in all cases with the isotopic distribution in good agreement with the corresponding calculated pattern. The main spectral data along with the analytical data are summarized in Table 2. It can be seen that the experimental carbon content is consistently lower then the calculated value which is rather common in phthalocyanine chemistry and may be ascribed to the difficulty in complete combustion of these compounds.[53]

Table 2 The mass spectral and analytical data for compounds **65**, **66**, **74** and **75**.

Compound	[M+H]$^+$	Analysis^a (%)		
	$(m/z)^{a,b}$	C	H	N
65	1482.33 (1482.42)^b	61.41 (64.77)	5.75 (5.98)	6.76 (7.55)
66	2186.7 (2186.8)^b	60.88 (61.47)	7.35 (7.00)	4.77 (5.12)
74	1282.29 (1282.35)^b	58.92 (59.90)	6.33 (6.28)	8.26 (8.73)
75	1986.7 (1986.8)^b	57.01 (58.00)	7.37 (7.30)	5.33 (5.64)

^{a} By LSI-MS. ^{b} Calculated values given in parentheses.

2.4 Aggregation Behavior of Octasubstituted Naphthalocyanines and Phthalocyanines

The UV-vis absorption spectra of complexes **65**, **66**, **74** and **75** displayed a typical Q band and a Soret band; both are attributed to a π-π^* electronic transition. One to two weaker vibrationally coupled satellite bands were also observed within the Q band region. Representative UV-vis spectra of **66** and the Pc analog **75** recorded in THF are displayed in Figure 9. The Q band absorption for Nc shows a bathochromic shift compared with that of the Pc analog. This is due to the increase of conjugation in the Nc complex. Besides, all the substitutents in these compounds are electron donating, the λ_{max} further shifts to the far-red region in comparison with the unsubstituted analogs (λ_{max} for unsubstituted ZnPc: 600nm; ZnNc: 700nm).[2]
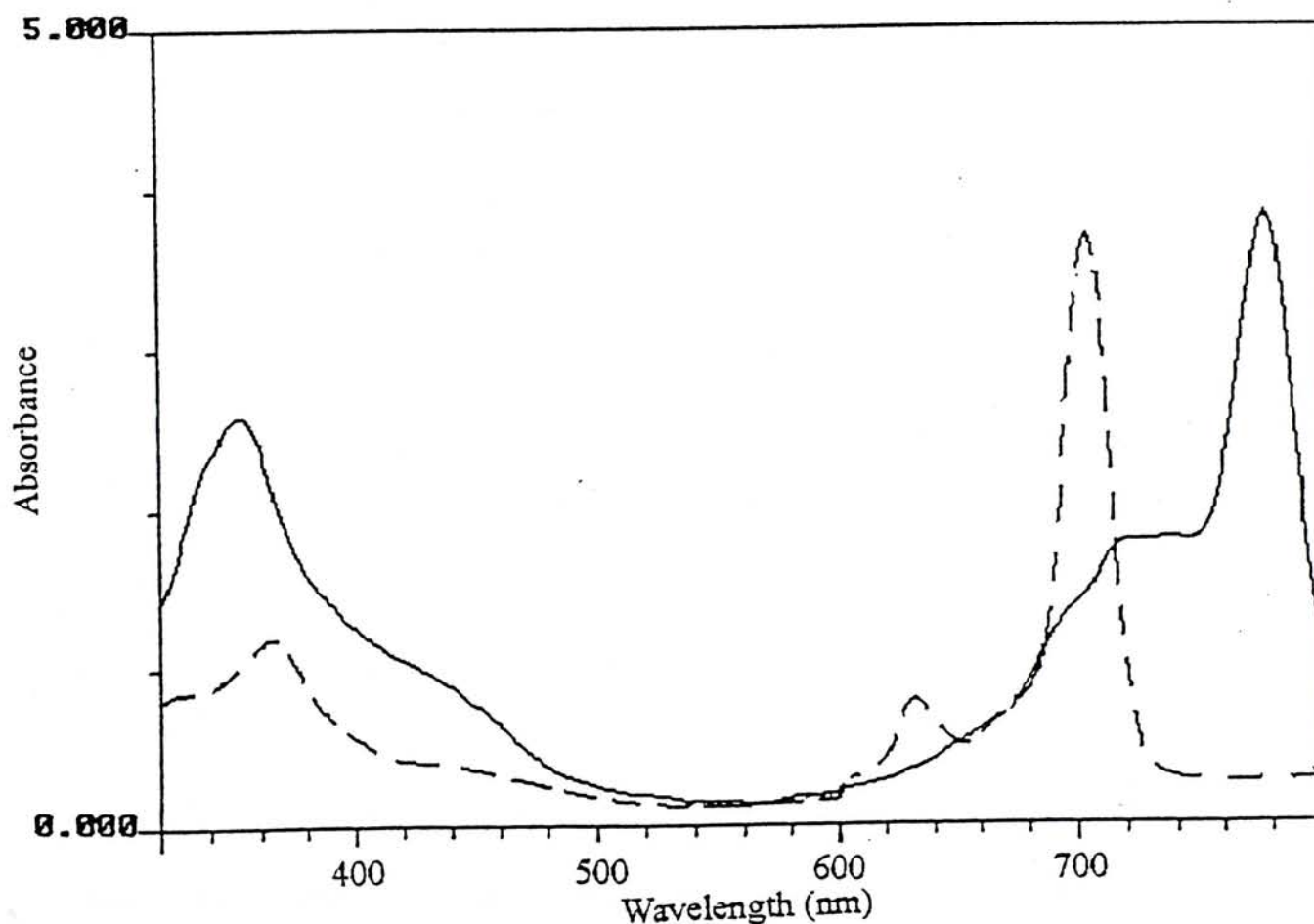
Figure 9 UV-vis spectra of compounds 66 (——) and 75 (---) in THF

It is well known that phthalocyanines, even in dilute solutions, tend to form molecular aggregates such as dimers, trimers, and oligomers.[31,32] Their linear annulated analogs, 2,3-naphthalocyanines, are expected to have a higher aggregation tendency because of the extended π-system. The coupling between the electronic states of two, or more naphthalocyanine units may occur. These aggregated states would have very different characteristics in comparison with the corresponding monomer. The degree of aggregation is largely affected by the nature of the solvent, the temperature, and the concentration of the solution. This aggregation phenomena imparts difficulties in both the chromatographic purification and characterization processes. The mobility of these macrocycles in silica gel columns is greatly reduced, resulting in a lost of material and low efficiency in separation.

For the aggregates of Pcs, a hysochromic shift of the Q band λ_{max} with broadening usually occurs in the UV-vis spectra. The formation of oligomeric or polymeric aggregates also broadens the ^{1}H NMR signals for the ring protons. In this section, the aggregation behavior of substituted 2,3-naphthalocyaninato zinc(II) complexes as studied with UV-vis spectroscopy is discussed and compared with their Pc analogs.

Two methods have been developed to calculate the aggregation number and the equilibrium constant for the aggregating processes. The first method which has been described in the introduction needs to obtain a pure monomer spectrum. Figure 10 shows the visible spectra of **66** in THF in various concentrations, the Q band at 777 nm remains virtually unshifted while the molar absorptivity increases from 9.8×10^5 to 2.2×10^6 M^{-1}cm^{-1} as the concentration decreases from

4.2 x 10^{-6} to 7.3 x 10^{-8} M.   Pure monomer spectrum could not be obtained for this compound even in a very dilute solution up to the detection limit of the spectrometer.   This method therefore could not be applied.
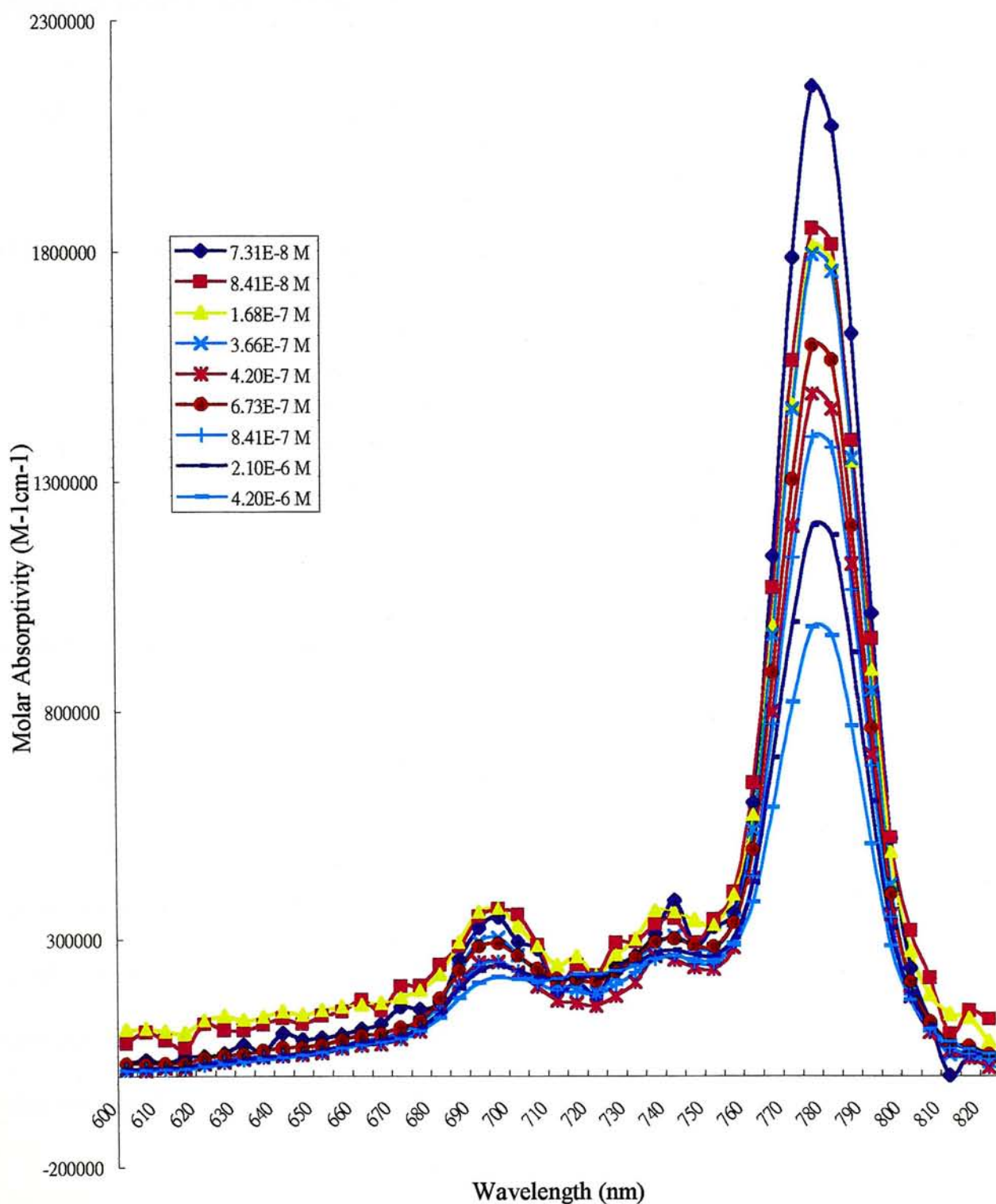
Figure 10 Concentration dependence of electronic absorption spectra of ZnNc **66** in THF

Study of dimerization of naphthalocyanine 66 in THF

An alternative method involves a nonlinear fitting procedure and does not require the spectral feature of a monomeric species.[34] In this method, the following equilibrium is considered:

$$M + M \xrightleftharpoons{K} D \qquad K = C_D/C_M^2 \qquad (6)$$
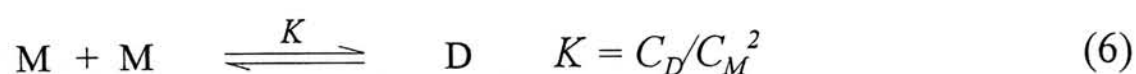
Where M and D represent a monomeric and dimeric Nc, respectively, and K is the equilibrium constant. The total concentration of Nc (C_T) is :

$$C_T = C_M + 2C_D \qquad (7)$$

ε_T may be expressed as the sum of a term due to absorption by the monomer species and a term due to absorption of the dimer species

$$C_T\varepsilon_T = C_M\varepsilon_M + 2C_D\varepsilon_D \qquad (8)$$

In which C_M and C_D are the concentrations and ε_M and ε_D are the extinction coefficients of the monomer and dimer, respectively, per monomer unit. The contribution of higher aggregates is not taken into account. The apparent absorbance A at a given wavelength can be expressed as :

$$A = \frac{(\varepsilon_M - \varepsilon_D)}{4K}[-1 + \sqrt{(1 + 8KC_T)}] + \varepsilon_D C_T \qquad (9)$$

In which A and C_T are measurable quantities, the other three variables could be determined by a nonlinear fitting method using a series of absorbance at a particular wavelength measured in different concentrations. By recording the spectra of **66** in THF solutions of concentration ranging from 10^{-6} to 10^{-7} M, the best fitted values of K, ε_M and ε_D for the Q band were determined to be 2.72 x 10^5 M^{-1}, 1.95 x 10^6 M^{-1} and 1.28 x 10^5 M^{-1}, respectively. Figure 11 shows the discrepancy between A_{obs} and A_{calcd} based on these best-fitted parameters. By repeating the same procedure at different absorption positions while keeping the values of K to be 2.72×10^{-5} M^{-1}, the corresponding values of ε_M and ε_D could be obtained. The simulated monomer and dimer spectra of **66** could then be drawn which are shown in Figure 12.
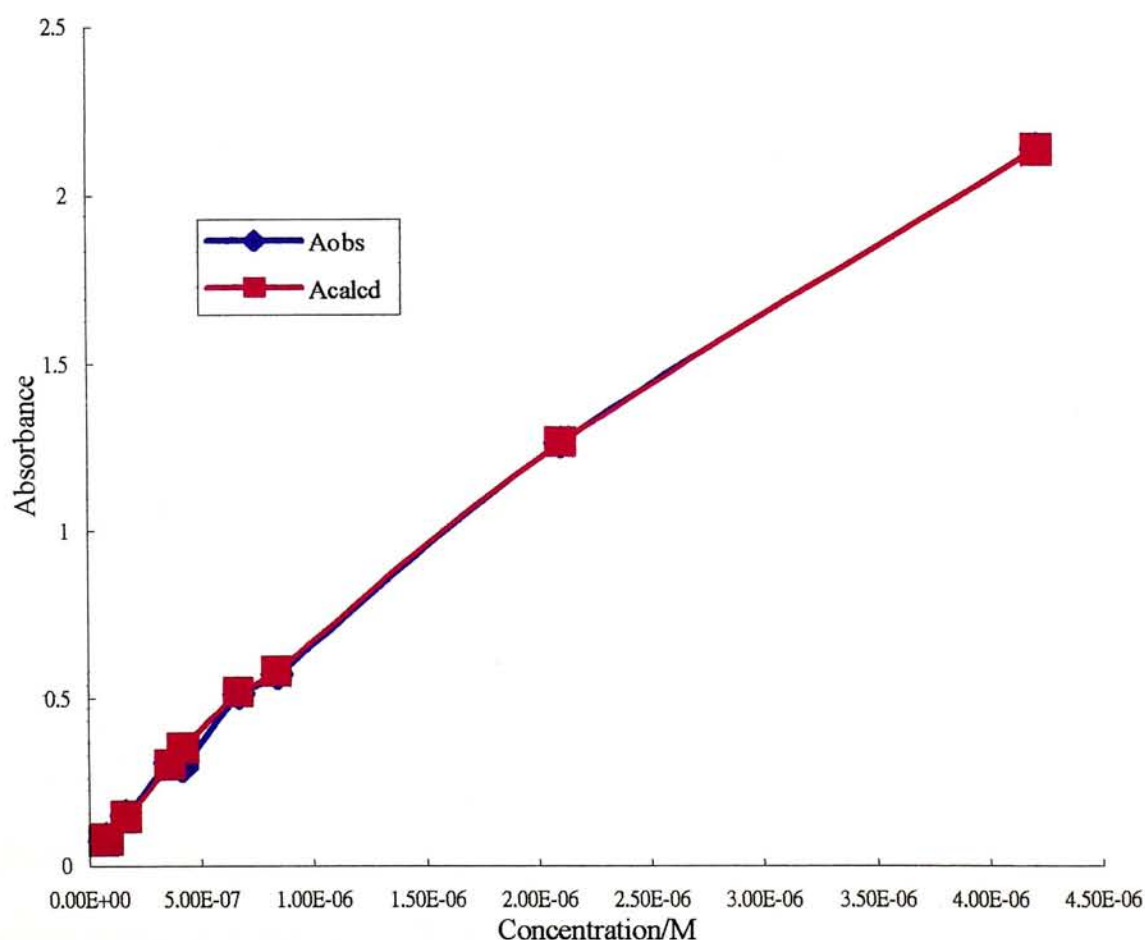
Figure 11 Comparison of the experimental and calculated absorbance of the Q band of **66** in THF
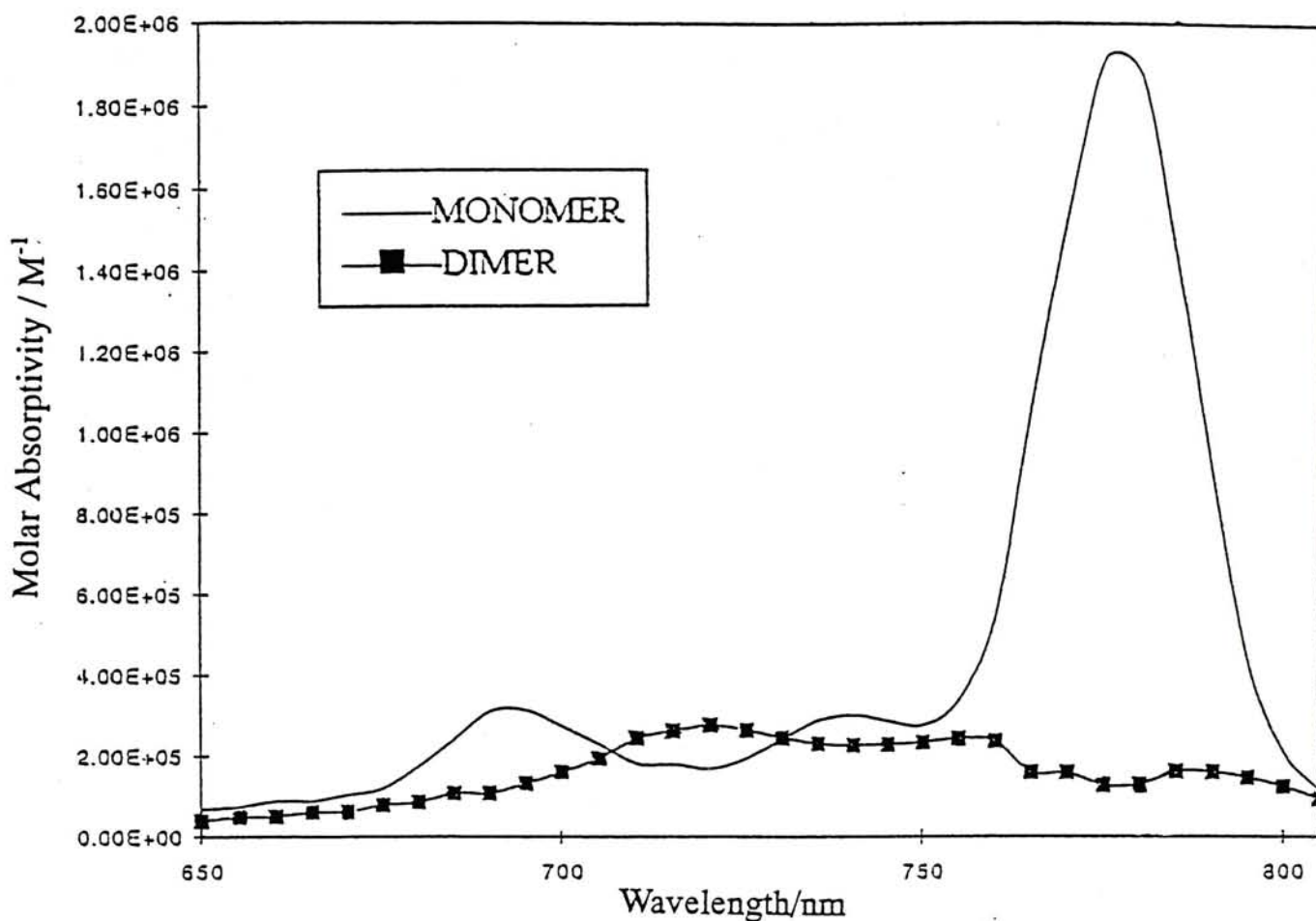
Figure 12 Simulated monomer and dimer spectrum of **66** in THF

According to the spectra, the monomer shows an intense Q band absorption at 777 nm together with two weaker vibrationally coupled satellite bands. This spectrum is typical of spectra of monomeric Pcs. For the simulated dimer spectrum, the absorptions in the Q band region are relatively weak. This may explain why the Q band does not shift to shorter wavelength in higher concentrations as in the case of Pcs.

Study of heat of association of macrocycles 65, 66, 74 and 75 in toluene

The spectra of macrocycles **65**, **66**, **74** and **75** were found to be not only concentration dependent but also temperature dependent. The heat of association can be estimated from the temperature and concentration dependency of the UV/vis spectra according to the method described by Nolte.[35] Since the spectral features were more susceptible to the concentration, range was limited to 2×10^{-6} to 8×10^{-6} M after several trials. The spectral changes in a large concentration range could not be restored by changing the attainable temperature. As shown in Figure 13, the higher the temperature, the higher the molar absorptivity indicating that thermal energy can break the molecular association. Same value of molar absorptivity can be attained by varying the concentration and temperature. Under these conditions, the weight fraction of monomer remains constant and the following equation can be applied:

$$W_1 = R \frac{\Delta \ln c}{\Delta(1/T)} \qquad (10)$$

where W_1 is the heat of association, R is the gas constant, $\Delta \ln c$ is the difference between two macrocycles concentration, and $\Delta(1/T)$ is related to the temperature difference that has to be applied to maintain a constant weight fraction. At an arbitrary value of molar absorptivity, there are several pairs of (C, T) values which can be used to generate the plot of $\ln c$ versus the reciprocal temperature. As shown in Figure 14, a straight line is obtained from which the value of heat of association can be estimated.
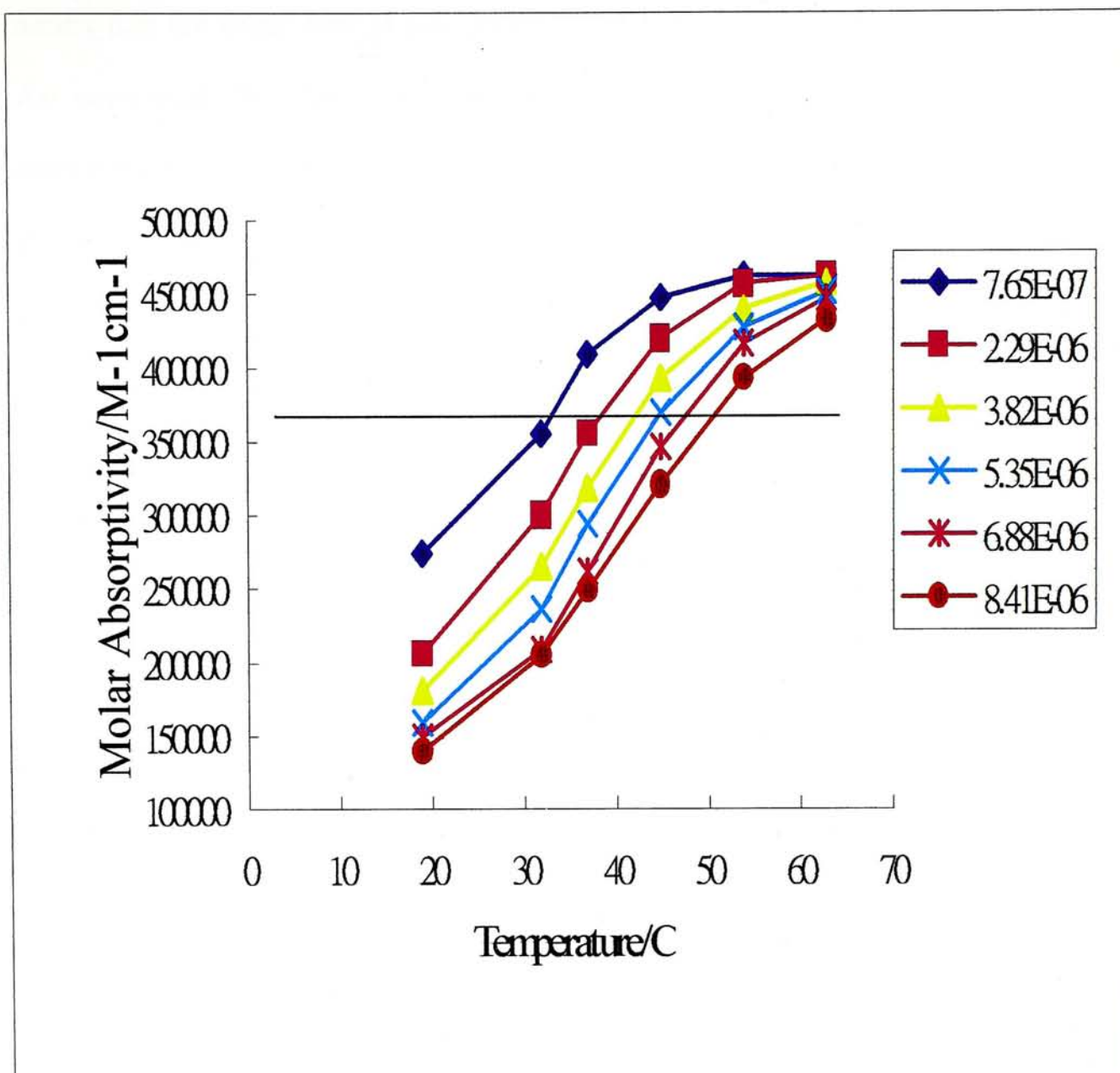
Figure 13 Observed extinction coefficient of the Q band of **75** in toluene at different temperature and concentration

Table 3 summarizes the heat of aggregation for compounds **65**, **66**, **74** and **75**. The results are consistent with the ^{1}H NMR data that the nature of the side chains greatly affects the aggregation tendency. Comparing the Nc **65** and Pc **74**, the Nc system has a larger heat of association. The weak van der Waals force between the butyl side chains is not significant. But for Nc **66** and Pc **75**, a reverse order is observed showing that the dipole-dipole interactions

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associated with the oxyethylene side chains play a significant role. It is worth noting that the larger heat of association of **75** is comparable with that of **50**. As compound **75** does not contain the peripheral benzene rings, the extraordinary high heat of association may not be due to the five pairs attachment as suggested by the authors, but rather arises from the 3,6-dioxadecylthio side chains.
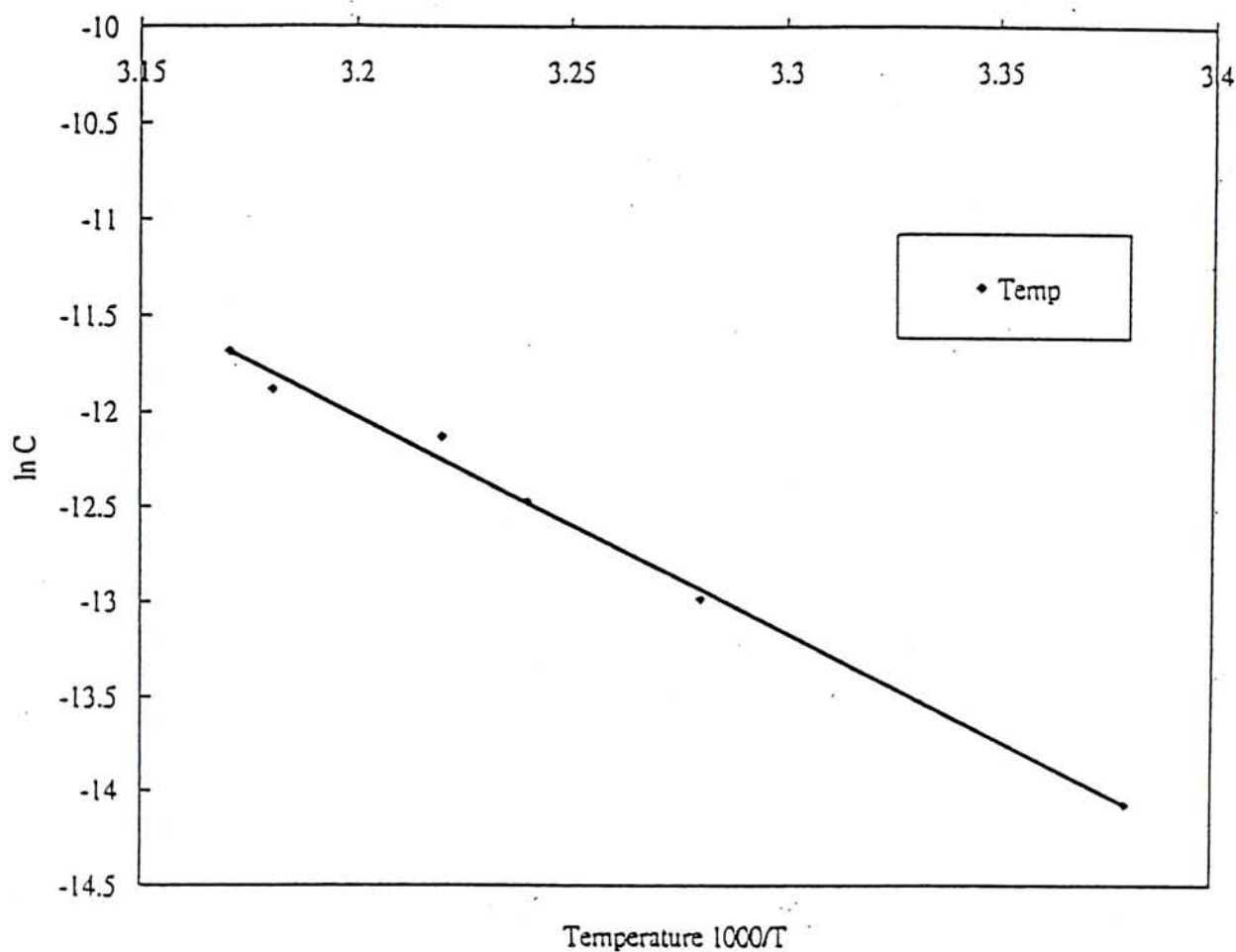
Figure 14 Plot of *ln* C vs 1/T for compound **66** in toluene

Table 3. Heat of association of ZnNc and ZnPc in toluene

Compound	65	66	74	75
Heat of association (kJ/mol)	-26.4	-38.4	-17.1	-105.0

2.5 Liquid Crystalline Properties of 66

It is well-known that phthacyanines substituted with sufficiently long side chains exhibit thermotropic liquid crystalline behavior. The first columnar liquid crystals base on a 2,3-naphthalocyanine core have recently been reported by our group.[24] With eight oxyethylene side chains, compound **66** may also exhibit mesomorphic properties. However, no mesophase was observed through a polarized microscope when the sample was heated to 300°C, where the sample became darken due to decomposition. Therefore, we turned our attention to the lyotropic liquid crystalline behavior. The formation of lyotropic mesophase of **66** was studied by preparing different concentration of Nc solutions in DMF. In order to study the phase transition behavior, the sample solution was sandwiched between two microscope slides and the samples were allowed to stand in a dessicator at room temperature. The lyotropic mesophases formed very slowly (about 5h). The formation of the mesophase began at the critical concentration at which the solution became cloudy and birefringence was observed with an isotropic background. The critical concentration for the formation of mesophase is appoximately 2 to 3 wt %. Figure 15 shows the polarized micrographs of **66** in which a typical fan-shaped texture was observed which is a characteristic texture exhibited by a discotic mesophase. When the solution was heated above the clearing temperature and then cooled down again, the birefrigence reappeared.

a)
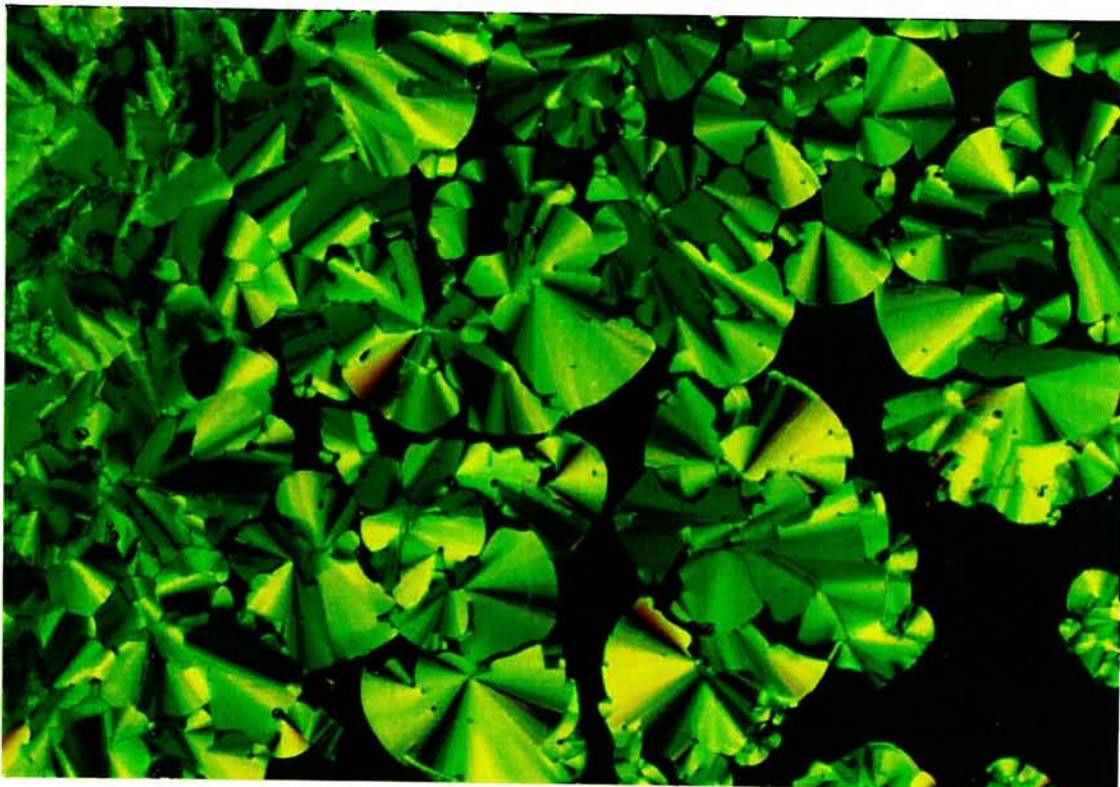
b)
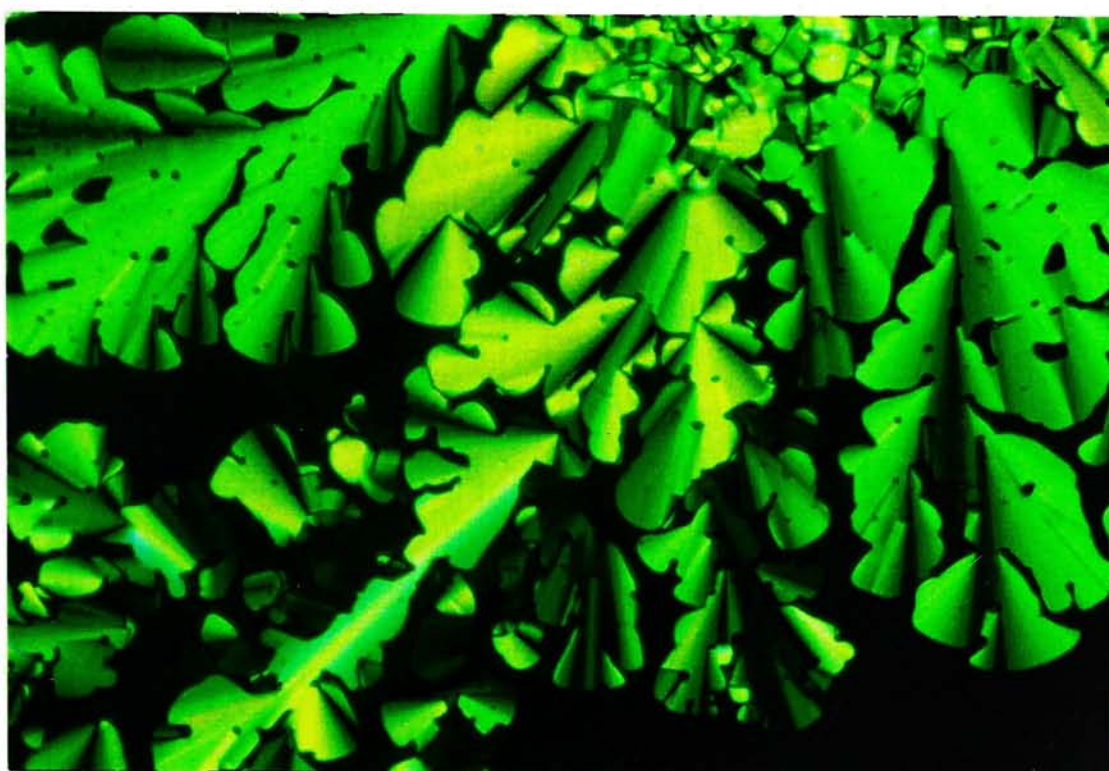
Figure 15 Optical textures of **66** observed through a polarized microscope (a) 2.8 wt % in DMF, 200 X magnification, cooled down from isotropic phase, (b) 7.1 wt % in DMF, 400 X magnification, cooled down from isotropic phase.

2.6 Synthesis of a Crown Ether-Substituted Naphthalocyanine

Owing to the success in the synthesis of octasubstituted naphthalocyaninato zinc(II) complexes, we then extended these synthetic routes to crown ether-substituted Ncs. With extra fused benzene rings, 2,3-naphthalocyanines with crown ether moieties may exhibit enhanced electrical properties compared with the Pc analogs. In this section, the synthesis and spectroscopic studies of a crown-ether containing Nc are described. To our knowledge, crown ether-substituted Ncs have not been reported so far.

The synthetic scheme is similar to that described in previous section and is shown in Scheme 15. Tetraethylene glycol **76** was converted to the corresponding thiol **78** by a typical two-step procedure. Treatment of **78** with **46** in the present of Cu_2O led to the formation of **79**. This reaction was carried out in a highly diluted solution to minimize the formation of side products so that a reasonable yield could be achieved.

Scheme 15

45
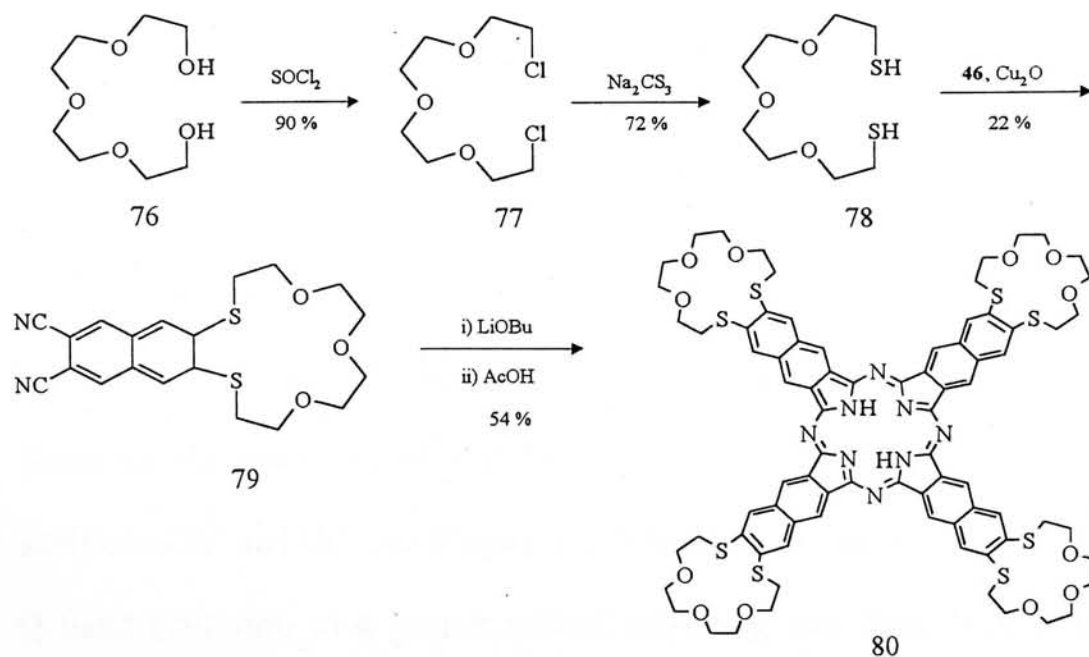
In an attempt to prepare a zinc Nc complex from this precursor, **79** was treated with $Zn(OAc)_2.H_2O$ in the presence of DBU. The reaction mixture turned to deep green after being refluxed for 3 h in *n*-butanol. However, only a very small amount of ZnNc could be isolated which has a poor solubility in common organic solvents. The product was found to be stuck in silica gel columns and could not be eluted out. We therefore tried to prepare a metal-free Nc. Dinitrile **79** was treated with *n*-BuLi in *n*-butanol. The mixture was quenched with acetic acid to yield the metal-free Nc **80**. This Nc showed a higher solubility in chloroform with a mud-green color. As it was also difficult to purify this compound by chromatography, the crude product was washed with methanol by Soxhlet extraction and then extracted out with chloroform. The resulting deep green solid was purified by re-precipitation from methanol.

The UV-vis spectrum of **80** in chloroform showed two broad Q bands at 740 and 781 nm together with a Soret band around 300 nm. In addition, a broad shoulder in the 400-500 nm region was also observed. The broad appearance of the signals suggested that aggregation is significant for this compound. The higher energy Q band might be attributed to an aggregated Nc species.

The addition of Li^+, Na^+, K^+ and Cs^+ salts altered the spectrum appreciably, but not in the same fashion. The addition of Li^+ and Na^+ ions slightly decreased the intensities of both Q bands at 737 and 792 nm. However, the addition of K^+ and Cs^+ ions (Figure 16) reduced the intensity of the lower energy Q band (792 nm) to a greater extend indicating that these ions enhance the aggregation tendency of this compound. As Li^+ and Na^+ ions are relatively

small, they usually coordinate and fit into the center of crown ether. Therefore, this kind of coordination does not significantly affect the aggregation tendency. For the larger metal cations such as K^+ and Cs^+, the 15-crown-5 system is too small to accommodate these ions. The cations therefore induce a dimerization of the Nc macrocycle.
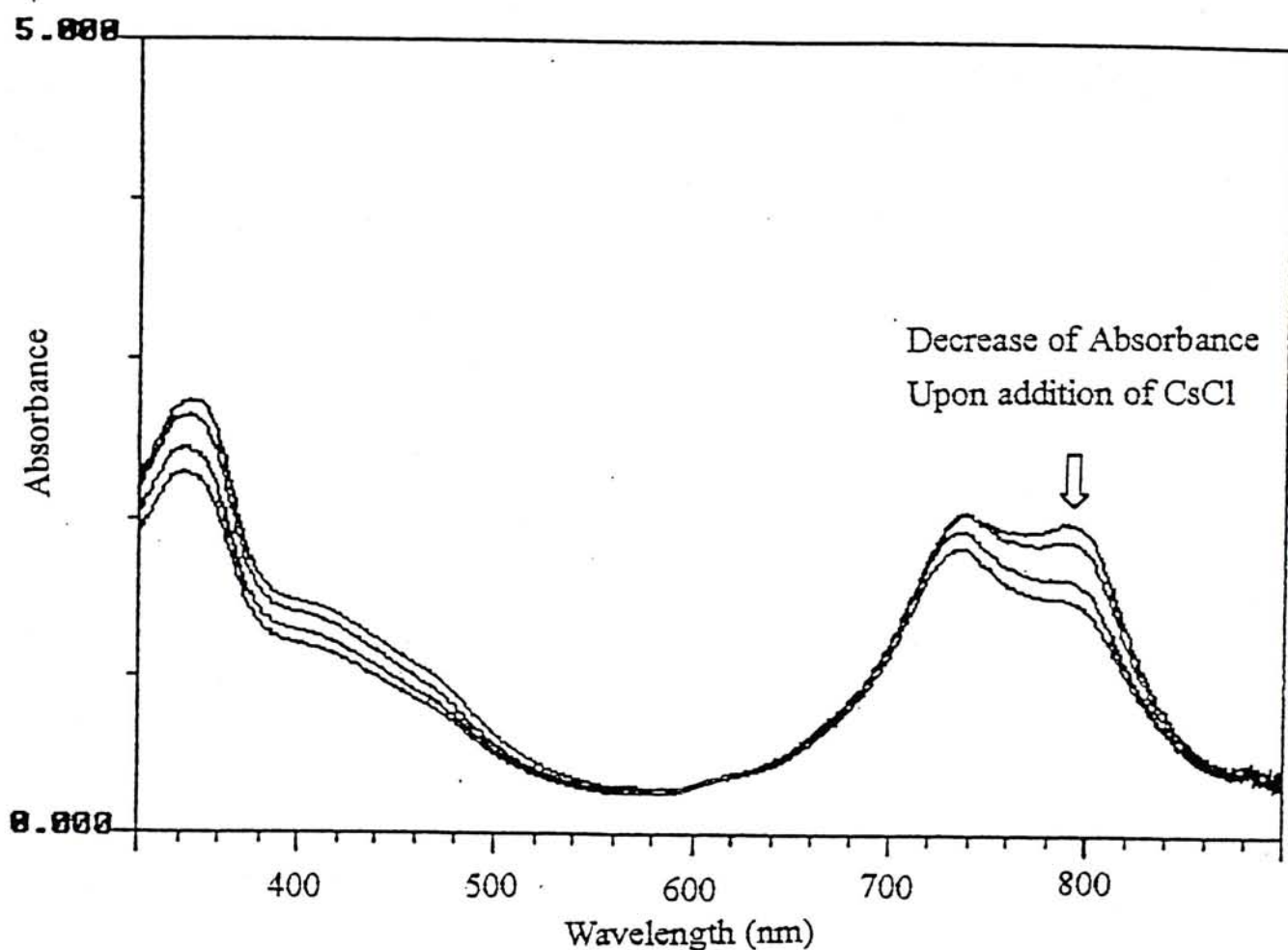
Figure 16 Spectral changes of **80** in $CHCl_3$ (1.25 x 10^{-5} M) upon addition of CsCl (2.7 x 10^{-3} M) in $CHCl_3$-CH_3OH (5:2 v/v)

2.7 Conclusion

A series of Ncs have been synthesized and spectroscopically characterized. These macrocycles having a large π-system tend to form molecular aggregates and this behavior has been studied with ^{1}H NMR and UV-vis spectroscopy and compared with that of the Pc analogs. It has been found that the peripheral substituents play an important role in controlling this aggregation phenomena. The heat of association of these Ncs and Pcs in toluene have also be estimated by variable concentration and temperature UV-vis spectroscopy. The first example of crown ether containing Nc has also been described including its synthesis and cation-dependent UV-vis spectra.

3. Experimental Section

3.1 Materials

Reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. n-butanol and n-hexanol were distilled from sodium prior to use. N,N-Dimethyl foramide (DMF) were pre-dried over barium oxide and distilled under reduced pressure. Chromatographic purifications were performed on silica gel columns (Merck, Kieselgel 60, 70-230 mesh) with the indicated eluents. Hexanes used in chromatography was distilled from anhydrous $CaCl_2$. All other reagents and solvents were of reagent grade and used as received. 2,3-Dibromo-6,7-dicyanonaphthalene (**46**)[26] and 1,2-dichloro-4,5-dicyanobenzene (**72**)[52] were prepared according to literature procedures. 3,6-Dioxa-1-decanethiol (**59**) and bis-2-(2-mercaptoethoxy)ethyl ether (**79**) were prepared using the method described by Gates.[54]

3.2 Physical Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (^{1}H, 300; ^{13}C, 75.4 MHz) or Bruker ARX 500 spectrometer (^{1}H, 500 MHz) with $SiMe_4$ as an internal reference. IR spectra were measured on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. UV-vis absorption spectra were taken on a Hitachi U-3300 spectrophotometer. Electron Impact (EI) and liquid secondary-ion (LSI) mass spectra were recorded on a Hewlett-Packard 5989B mass spectrometer and Brucker APEX 47e. Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, respectively. The latter employed 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The

polarized microscopic observation was performed on a Leica DMR microscope equipped with a Leitz microscope heating stage 350.

General Procedure for the Preparation of Dinitriles

n-Butanethiol, 3,6-dioxa-1-decanethiol (**58**) or bis-2-(2-mercaptoethoxy)ethyl ether (**78**) (2.1 equiv.) was added slowly to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 2.5 equiv.) in DMF. The mixture was stirred for a few min. until the evolution of hydrogen gas was complete. 2,3-Dibromo-6,7-dicyanonaphthalene (**46**) or 1,2-dichloro-4,5-dicyanobenzene (**71**) (1.0 equiv.) and copper(I) oxide (2.0 equiv.) were then added and the mixture was refluxed for 3 h. The cooled mixture was poured into ice then extracted with diethyl ether. The combined organic portions was washed with ammonia solution (35%) and water, then dried over anhydrous CaCl$_2$. The volatiles were rotary evaporated and the residue was purified by column chromatography.

2,3-Dibutylthio-6,7-dicyanonaphthalene (63)

According to the general procedure, compound **63** (0.68 g, 2.0 mmol) was purified by chromatography with CHCl$_3$ as eluent. Yield: 0.46 g (65%), m.p. 148-150°C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.16 (s, 2H, ArH), 7.58 (s, 2H, ArH), 3.09 (t, J = 7.5 Hz, 4H, SCH$_2$), 1.79 (quintet, J = 7.2 Hz, 4H, CH$_2$), 1.55 (sextet, J = 7.5 Hz, 4H, CH$_2$), 0.96 (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 134.1, 123.0, 32.6, 30.1, 22.2, 13.6. MS (EI) : m/z 354 [M]$^+$. Anal. Calcd. for C$_{20}$H$_{22}$N$_2$S$_2$: C, 63.37; H, 7.22; N, 5.28; S, 12.08. Found: C, 63.64; H, 7.24; N, 5.49; S, 12.38.

2,3-Dicyano-6,7-bis(3,6-dioxa-1-decylthio)naphthlene (64)

By using compound **46** (0.34 g, 1.0 mmol) and 3,6-dioxa-1-decanethiol (**58**) (0.37 g, 2.1 mmol) and following the general procedure, compound **64** was obtained as a yellow solid which was purified by chromatography with hexanes / ethyl acetate (3:2) as eluent. Yield 0.38 g, (72 %), m.p. 45-47°C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.18, (s, 2H, ArH), 7.77 (s, 2H, ArH), 3.82 (t, J = 7.5 Hz, 4H, OCH$_2$), 3.65-68 (m, 4H, OCH$_2$), 3.57-3.60 (m, 4H, OCH$_2$), 3.46 (t, J = 7.5 Hz, 4H, OCH$_2$), 3.31 (t, J = 7.5 Hz, 4H, SCH$_2$), 1.56 (quintet, J = 7.5 Hz, 4H, CH$_2$), 1.35 (sextet, J = 7.5 Hz, 4H, CH$_2$), 0.90 (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 142.1, 134.2, 131.1, 124.4, 115.9, 109.5, 71.3, 70.7, 70.0, 69.2, 32.7, 31.6, 19.2, 13.9. MS (EI) : m/z 530 $[M]^+$. Anal. Calcd. for C$_{28}$H$_{38}$N$_2$S$_2$O$_4$: C, 63.37; H, 7.22; N, 5.28; S, 12.08. Found: C, 63.64; H, 7.24; N, 5.49; S, 12.38.

1,2-Dibutylthio-4,5-dicyanobenzene (72)

By using the general procedure, compound **55** (0.79 g, 4.0 mmol) was treated with *n*-butanethiol (0.9 ml, 8.4 mmol) in DMF (50 ml) to give **72** as a white solid which was purified by chromatography with CHCl$_3$ as eluent. Yield: 1.13 g (93%), m.p. 109-111°C (lit.[72] m.p. 110-112°C). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.41 (s, 2H, ArH), 3.02 (t, J = 7.5 Hz, 4H, SCH$_2$), 1.75 (q, J = 7.5 Hz, 4H, CH$_2$), 1.53, (quintet, J = 7.5 Hz, 4H, CH$_2$), 0.96, (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 144.2, 128.1, 115.7, 111.0, 32.4, 30.0, 22.0, 13.6. MS (EI) : m/z 304 $[M]^+$.

1,2-Dicyano-4,5-bis(3,6-dioxa-1-decylthio)benzene (73)

By using compound 71 (0.39 g, 2.0 mmol) and 3,6-dioxa-1-decanethiol (58) (0.75 g, 4.2 mmol) and following the general procedure, compound 73 was obtained as a white solid which was purified by chromatography with hexanes / ethyl acetate (9:1) as eluent. Yield 0.87 g (90 %), m.p. 40-41°C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.63 (s, 2H, ArH), 3.80 (t, J = 7.5 Hz, 4H, OCH$_2$), 3.63-3.66 (m, 4H, OCH$_2$), 3.56-3.59 (m, 4H, OCH$_2$), 3.46 (t, J = 7.5 Hz, 4H, OCH$_2$), 3.24 (t, J = 7.5 Hz, 4H, SCH$_2$), 1.57 (quintet, J = 7.5 Hz, 4H, CH$_2$), 1.35 (sextet, J = 7.5 Hz, 4H, CH$_2$), 0.92 (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 144.0, 129.4, 115.6, 111.5, 71.3, 70.8, 70.0, 69.3, 32.7, 31.7, 19.2, 13.9. MS (EI) : m/z 480 [M]$^{+}$. Anal. Calcd. For C$_{24}$H$_{36}$N$_2$S$_2$O$_4$: C, 59.97; H, 7.55; N, 5.83. Found: C, 59.45; H, 7.88; N, 5.35.

2,3-Dicyano-6,7-(4,7,10-trioxa-1,13-dithiacyclopentadecane)naphthalene (79)

By using compound 46 (0.34 g, 1.0 mmol) and bis-2-(2-mercaptoethoxy)ethyl ether (78) (0.45 g, 2 mmol) and following the general procedure, compound 79 was obtained as a yellow solid which was purified by chromatography with hexanes / ethyl acetate (3:2) as eluent. Yield: 89 mg (22%) ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.18, (s, 2H, ArH), 7.87 (s, 2H, ArH), 3.82 (t, J = 7.5 Hz, 4H, OCH$_2$), 3.57 (m, 4H, OCH$_2$), 3.50 (m, 4H, OCH$_2$), 3.26 (t, J = 7.5 Hz, 4H, OCH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz) δ 143.4, 134.5, 131.4, 128.3, 115.9, 109.8, 70.5, 70.0, 34.6. MS (EI) : m/z 401 [M + H]$^{+}$. Anal. Calcd. for C$_{20}$H$_{20}$N$_2$S$_2$O$_3$: C, 59.98; H, 5.03; N, 6.99; S, 16.01. Found: C, 60.21; H, 4.96; N, 6.84; S, 16.09.

General Procedure for the Cyclization of Dinitriles

A mixture of dinitrile (2.6 equiv.) and $Zn(OAc)_2 \cdot 2H_2O$ (1.0 equiv.) in n-butanol or n-hexanol was heated at 90°C, then DBU (*ca.* 0.5 ml) was added and the mixture was heated at 140°C for 3 h. The mixture was cooled then added in dropwise into a mixture of methanol / water (1:1). The precipitate formed was filtered off and washed with water, acetone and methanol. The green solid was then purified by chromatography.

(3,4,12,13,21,22,30,31-Octabutylthio-2,3-naphthalocyaninato)zinc(II) (65)

According to the general procedure, dinitrile **63** (354 mg, 1.0 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (82 mg, 0.38 mmol) in n-butanol (5 ml) to give **65** which was purified by chromatography with toluene/THF (7:3) as eluent. Yield 236 mg (64%). ^{1}H NMR [CDCl$_3$/pyridine- d^5 (7:3), 300 MHz]: δ 8.87, (br. s, 8H, ArH), 7.85, (br. s, 8H, ArH), 3.04-3.16 (m, 16H, SCH$_2$), 1.70-1.90 (m, 16H, CH$_2$), 1.45-1.65 (m, 16H, CH$_2$), 0.93, (t, J = 7.5 Hz, 24H, CH$_3$). MS (LSI): an isotopic cluster peaking at m/z 1482.33 [Calacd. for $[M]^+$ 1483.42].

(3,4,12,13,21,22,30,31-Octakis(3,6-dioxa-1-decylthio)-2,3-naphthalocyaninato)zinc(II) (66)

By using the general procedure, dinitrile **64** (200 mg, 0.38 mmol) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (30 mg, 0.14 mmol) in n-hexanol (10 ml) to give **66** which was purified by chromatography with toluene / THF (1:1) as eluent. Yield 93 mg (45 %). ^{1}H NMR[CDCl$_3$/pyridine- d^5 (7:3), 300 MHz]: δ 9.00 (br. s, 8H, ArH), 8.04 (br. s, 8H, ArH), 3.90 (t, J = 7.5 Hz, 16H, OCH$_2$), 3.67-3.69 (m, 16H, OCH$_2$), 3.34-3.45 (m, 32H, SCH$_2$ and OCH$_2$), 1.51 (quintet, J = 7.5 Hz, 16H, CH$_2$), 1.28 (sextet, J = 7.5 Hz, 16H, CH$_2$), 0.79 (t, J = 7.5 Hz, 24H, CH$_3$). ^{13}C{^{1}H} NMR [CDCl$_3$/pyridine- d^5 (7:3), 75.4 MHz]: δ 152.0, 131.4, 128.0,

120.0, 71.0, 69.9, 69.4, 32.9, 31.5, 19.0, 13.7.   MS (LSI): an isotopic cluster

peaking at m/z 2186.7 [Calacd. for [M^+] 2186.8].   Anal. Calcd. for

$C_{112}H_{152}N_8S_8O_{16}Zn$: C, 61.47; H, 7.00; N, 5.12; S, 11.72. Found: C, 60.88; H,

7.35; N, 4.77; S, 10.82.

(2,3,9,10,16,17,23,24-Octabutylthiophthalocyaninato)zinc(II) (74)[72]

According to the general procedure, dinitrile **72** (0.61 g, 2.0 mmol) was

treated with $Zn(OAc)_2$·$2H_2O$ (164 mg, 0.75 mmol) in n-butanol (10 ml) to give

74, which was purified by chromatography with toluene/THF (8:2) as eluent.

Yield 471 mg (73%). ^{1}H NMR [CDCl$_3$/pyridine-d^5 (7:3), 300 MHz]: δ 8.61,

(br. s, 8H, ArH), δ 3.34, (t, J = 7.5 Hz, 16H, SCH$_2$), 1.90, (quintet, J = 7.5 Hz,

16H, CH$_2$), 1.63, (sextet, J = 7.5 Hz, 16H, CH$_2$), δ 1.00, (t, J = 7.5 Hz, 24H,

CH$_3$). ^{13}C{^{1}H} NMR [CDCl$_3$/pyridine-d^5 (7:3), 75.4 MHz]: δ 151.4, 138.3,

119.9, 33.1, 30.6, 22.1, 13.5.   MS (LSI): an isotopic cluster peaking at m/z

1282.29 [Calcd. for [M]$^+$ 1283.25].   Anal. Calcd. for $C_{64}H_{80}N_8S_8Zn$: C, 59.90;

H, 6.28; N, 8.73. Found: C, 58.92; H, 6.33; N, 8.26.

(2,3,9,10,16,17,23,24-Octakis(3,6-dioxa-1-decylthio)phthalocyaninato)
zinc(II) (75)

According to the general procedure, dinitrile **73** (0.86 g, 1.8 mmol) and

$Zn(OAc)_2$·$2H_2O$ (140 mg, 0.66 mmol) in n-hexanol (25 ml) to give **75** which

was purified by chromatography with toluene/THF (1:1) as eluent.   Yield 180

mg (20%). ^{1}H NMR [pyridine- d^5, 500 MHz] δ 9.61 (br. s, 8H, ArH), 4.24-

4.25 (m, 16H, OCH$_2$), 3.89-3.93 (m, 16H, OCH$_2$), 3.77-3.82 (m, 32H, OCH$_2$),

3.53 (t, J = 6.3 Hz, 16H, SCH$_2$), 1.61 (quintet, J = 7.0 Hz, 16H, CH$_2$), 1.40

(sextet, J = 7.4 Hz, 16H, CH$_2$), 0.84 (t, J = 7.4 Hz, 24H, CH$_3$).   MS (LSI) : an

isotopic cluster peaking at m/z 1986.7 [Calacd. for $[M]^+$ 1986.8]. Anal. Calcd. for $C_{96}H_{144}N_8S_8O_{16}Zn$: C, 58.00; H, 7.30; N, 5.64. Found: C, 57.01; H, 7.37; N, 5.33.

Metal-free crown ether-containing 2,3-naphthalocyanine 80

A hexane solution of n-BuLi (2.2 ml, 1.6 M) was added under nitrogen to 1-hexanol (5 ml) at r.t.. The solution was heated to 120°C then dicyano naphthalene **79** (170 mg, 0.39 mmol) was added. The mixture was refluxed for a further 2 h, then cooled and poured into glacial acetic acid (20 ml). After 15 min, methanol (100 ml) was added and brown solid was precipitated out and filtered. The crude product was subjected to Soxhlet extraction, washed with boiling methanol (200 ml) in a Soxhlet apparatus for 2 days then extracted with chloroform (250 ml). The solvent was evaporated to a minimum volume, then methanol was added to induce precipitation. Yield 90 mg (54%). Anal. Calcd. for $C_{80}H_{82}N_8S_8O_{12}$: C, 59.90; H, 5.15; N, 6.99. Found: C, 58.96; H, 5.34; N, 6.17.

Part II

SYNTHETIC STUDIES OF SUBSTITUTED

DICYANO-ANTHRACENES AND TETRACENES

1 Introduction

Phthalocyanine (Pc) and its derivatives have been the subject of intensive research for several decades.[2] Owing to their highly delocalized π electron systems, these compounds display a wide range of intriguing physical and chemical properties which render them useful in various disciplines ranging from catalysis, materials science, to medicine. For example, the bis(phthalocyaninato)lutetium(III) [Lu(Pc)$_2$] is the first intrinsic molecular semiconductor with conductivity of 5×10^{-5} Ω^{-1}cm^{-1} in thin films.[55] This sandwich compound is also one of the most promising electrochromic display materials.[2,56,57] It offers not only high contrast, but also virtually a full spectrum of colors by tuning the electric potential applied.

Orti *et al.* have recently performed valence effective Hamiltonian nonempirical calculations on the electronic structures of Pcs and structurally related compounds in a discrete and one-dimensional stacked form.[58] The results show that linear annelation of benzene rings produces a continuous destabilization of the HOMO level and a narrowing of the HOMO-LUMO energy gap. One-dimensional stacks of linearly annelated Pcs have lower ionization potentials and narrower energy gaps separating the valence and conduction bands than angularly annelated systems. This prediction has been confirmed by the studies of 1,2- and 2,3-naphthalocyanines (Ncs) and 9,10-phenanthrocyanine.[59] The analogs 2,3-anthracocyanines (Acs) and 2,3-tetracocyanines (Tcs), being more extended conjugated systems, are expected to have enhanced electrical conductivity. The chemistry of these novel classes of

compounds, however, is relatively unexplored which is partly due to the shortage of convenient synthetic routes to the precursors 2,3-dicyanoanthracenes and 2,3-dicyanotetracenes. Only a few examples of Acs have been documented and most of them have been described by Kobayashi in a monograph.[2] The Tc analogs are virtually unknown.

The first Ac metal complexes were reported in 1971.[60] Heating 2,3-dicyano-9,10-diphenylanthracene (81) with metal salts in urea at 250–300°C gave octaphenyl Ac 82 of which the electronic spectra showed strong bands in the near-infrared region (ca. 900 nm). The dinitrile 81 were prepared by treating 9,10-diphenylanthracene 83 with dicyanoacetylene followed by selective hydrogenation and retrodienic cleavage (Scheme 16).[61] The octa-*tert*-butylphenyl analogs 84 (M = Cu, VO) were also prepared similarly from the corresponding dinitrile, with the exception that a catalytic amount of ammonium molybdate was also added.[62]

Scheme 16

82 R = Ph   M = Cu, VO
84 R = 4-^{t}BuC$_6$H$_4$ M = AlCl
85 R = H   M = Cu, VO
86 R = Br   M = Cu, VO
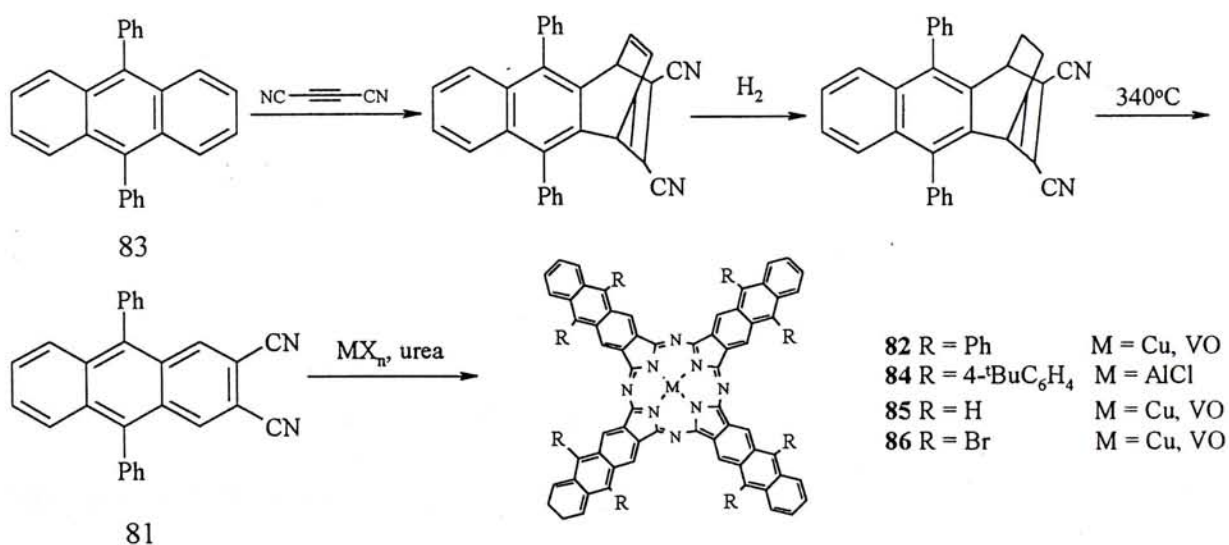
Photophysical properties of the aluminum complex **82** (M = AlCl) was briefly examined which showed that the fluorescence quantum yield ($\Phi<0.10$) is lower and the fluorescence lifetime ($\tau = 1.0$ ns) is shorter than those of the Pc ($\Phi = 0.64$, $\tau = 5.3$ ns) and Nc ($\Phi = 0.18$, $\tau = 2.7$ ns) analogs. This was attributed to an increase in internal conversion or intersystem crossing.[63]

The unsubstituted Ac metal complexes **85** of Al, Cu and V were also prepared in moderate yields with an improved method.[64] The synthesis involved the treatment of anthracene-2,3-dicarboxylic acid or its anhydride with the corresponding metal salt, ammonium molybdate and excess urea, occasionally in α-chloronaphthalene at 230-260°C for several hours. By comparing the Q_{0-0} band in the electronic spectra of vanadyl complexes of tetraazaporphyrin (TAP) (λ_{max} 597 nm), Bu^t_4Pc (λ_{max} 698 nm), Bu^t_4Nc (λ_{max} 807 nm), Ac (λ_{max} 932 nm) and Tc (λ_{max} 1055 nm), it was suggested that this transition had a bathochromic shift of *ca.* 100 nm per annelated benzene ring. The details of VO(Tc) complex were not given. The Al, Cu and V complexes of octabromo Acs **86** were prepared similarly from 9,10-dibromoanthracene-2,3-dicarboxylic anhydride in 43-86 % yield.[64]

It is worth noting that most of these Ac and Tc metal complexes were not well-characterized which is in part due to their poor solubility in common organic solvents. Although analytical data of some of these complexes were reported, spectroscopic data such as NMR, IR, and MS are extremely limited. Their electrochemical and photophysical data are scarce as well.

Recently, Hanack and co-workers have synthesized the iron complexes **87**

and **95** with the synthetic route shown in Scheme 17.[65]   The Diels-Alder reaction of epoxydihydronaphthalene **88** and diene **89** affords the adduct **90**, which undergoes dehydration giving a mixture of dihydroanthracenes **91** and **92**. Aromatization of **91** and **92** by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gives the dibromoanthracene **93**, which reacts with CuCN to give 6-tert-*butyl*-2,3-dicyanoanthracene (**94**).   Treatment of FeSO$_4$·H$_2$O with four equiv. of **94** in *N,N*-dimethylaminoethanol (DMAE) gives the Ac **95** as a mixture of constitutional isomers.   Since **95** is very sensitive towards oxidation and difficult to purify, it has been treated with 2,6-dimethylphenylisocyanide and pyridine to afford the octahedral complexes **87a** and **87b**, which are soluble in organic solvents such as toluene and CH$_2$Cl$_2$ and can be purified by chromatography in the absence of air.

Scheme 17

60
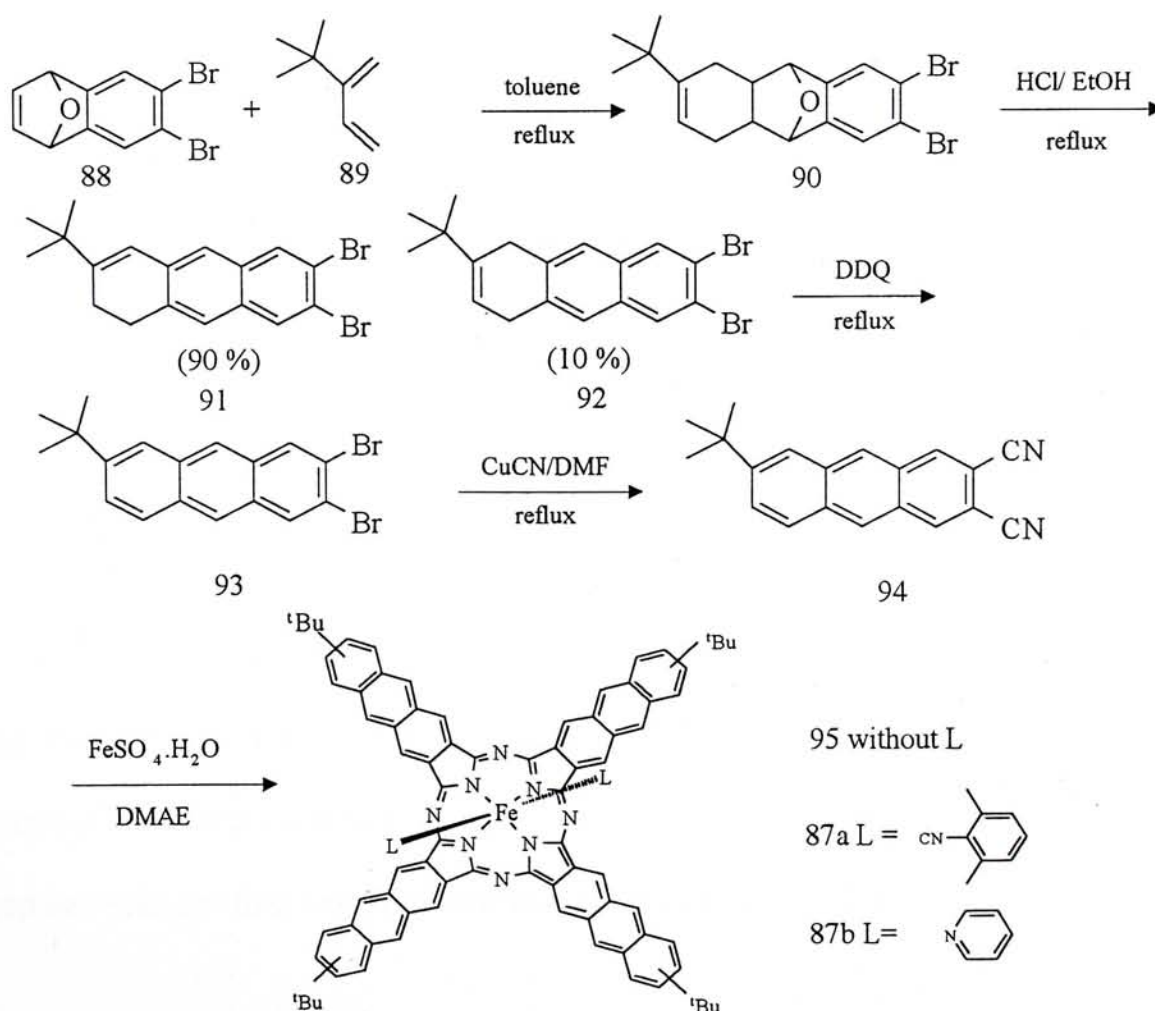
A series of cobalt complexes of tetra-*tert*-butyl substituted TAP, Pc, Nc and Ac have recently be synthesized of which the electronic absorption and magnetic circular dichroism properties have been examined.[66] The studies also show that ring-expansion produces a bathchromic shift of the Q_{0-0} band but the degree of shift decreases with increasing annelation of benzene rings. The absorption coefficient (ε), however, does not have a linear dependence on the molecular size and decreases in the order of CoNc > CoPc > CoAc > CoTAP.

The metal-free H_2Ac **96** has been briefly mentioned.[2] It can be prepared in 12 % yield by treating the dinitrile **94** with ammonia in the presence of NaOMe followed by refluxing the resulting isoindoline **97** in DMAE (Scheme 18). No characterizing data of **96** and **97** have been given.

Scheme 18
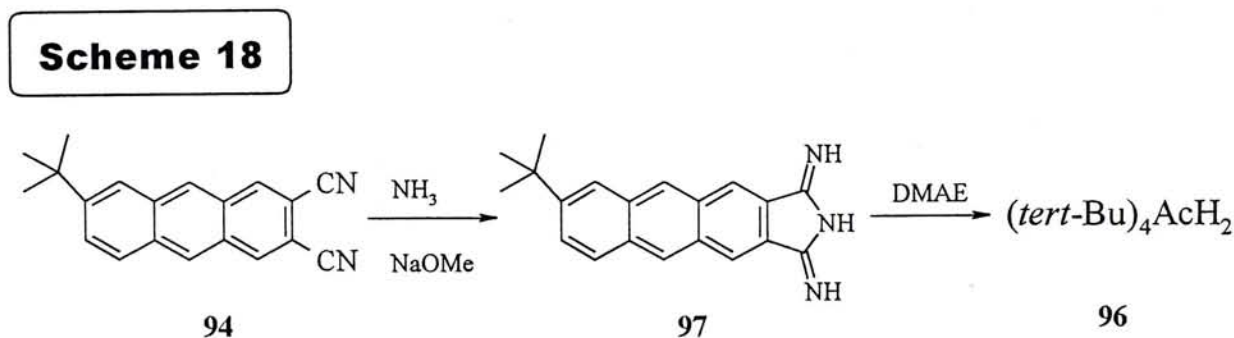
Besides, Marder *et al.* have synthesized a substituted α – octa(isopentoxy)anthracocyanine.[67] Treatment of anthracene-1,4-dione (**98**) with chlorine in acetic acid gives 2,3-dicloroanthracene-1,4-dione (**99**), which reacts with an excess of KCN in hot ethanol to give **100**. *O*-Methylation followed by cyclization using lithium isopentoxide in isopentyl alcohol affords the metal-free Ac **102** in 15 % yield (Scheme 19). Interestingly, this compound displays an unprecedented low-energy Q band absorption at 980 nm and a small gap between the first oxidation and reduction couples (1.07 V)

Scheme 19
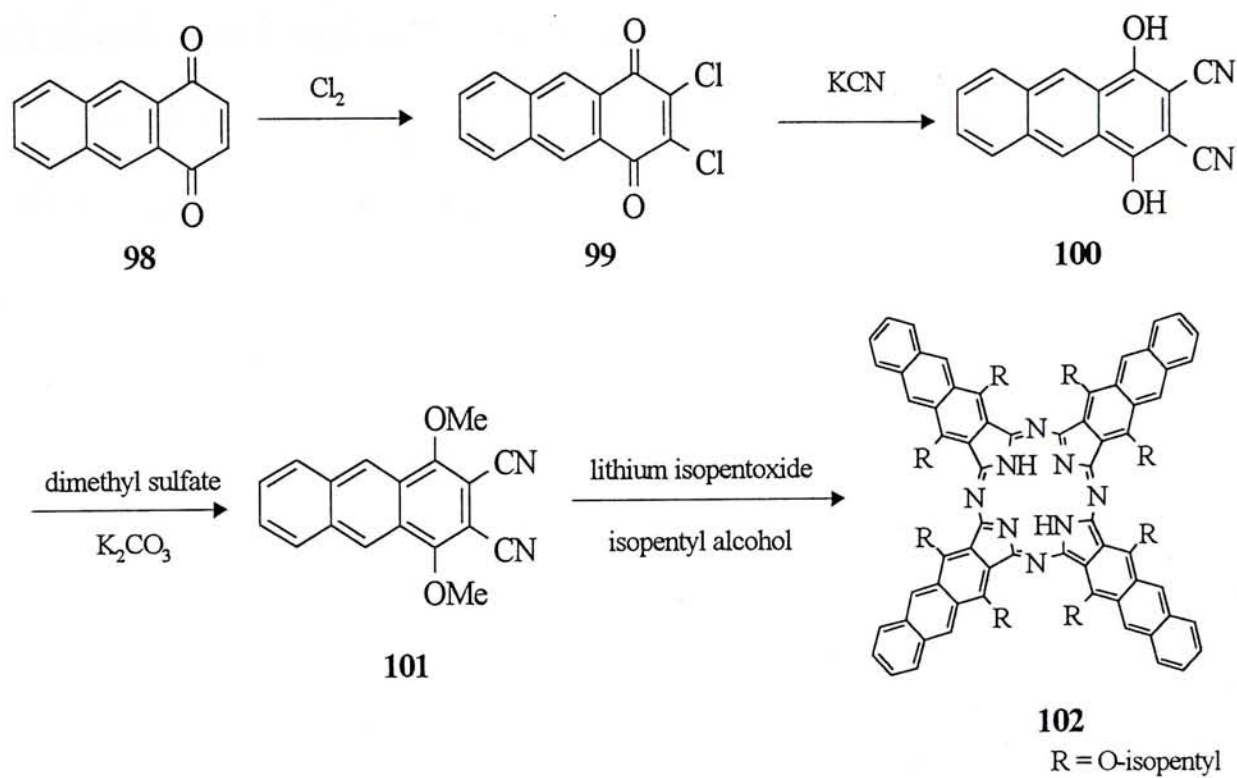
Owing to the rarity and unique properties of Acs and Tcs, we were interested to develop general synthetic pathways to substituted 2,3-dicyanoanthracenes and 2,3-dicyanotetracene which can be subsequently converted to the corresponding Acs and Tcs. The results are reported in this part of thesis.

2 Results and Discussion

2.1 Synthesis of Substituted Anthracenes

In an attempt to prepare the dicyanoanthracene **109**, the reaction sequence shown in Scheme 20 was carried out but failed in the last 2 steps. Bromination of **103** gave **23**, which was then treated with *n*-BuLi and furan to give the endoxide **104**. Diels Alder reaction with 2,3-dimethylbuta-1,3-diene gave **105**, which upon treatment with $HClO_4$ led to the formation of a mixture of **106** and **107** in 1:2 ratio as shown by its ^1H NMR spectrum (Figure 17). Upon oxidation of this mixture with DDQ, the resulting product was found to have poor solubility in most organic solvents which made both the isolation and purification to be difficult.

Scheme 20

63
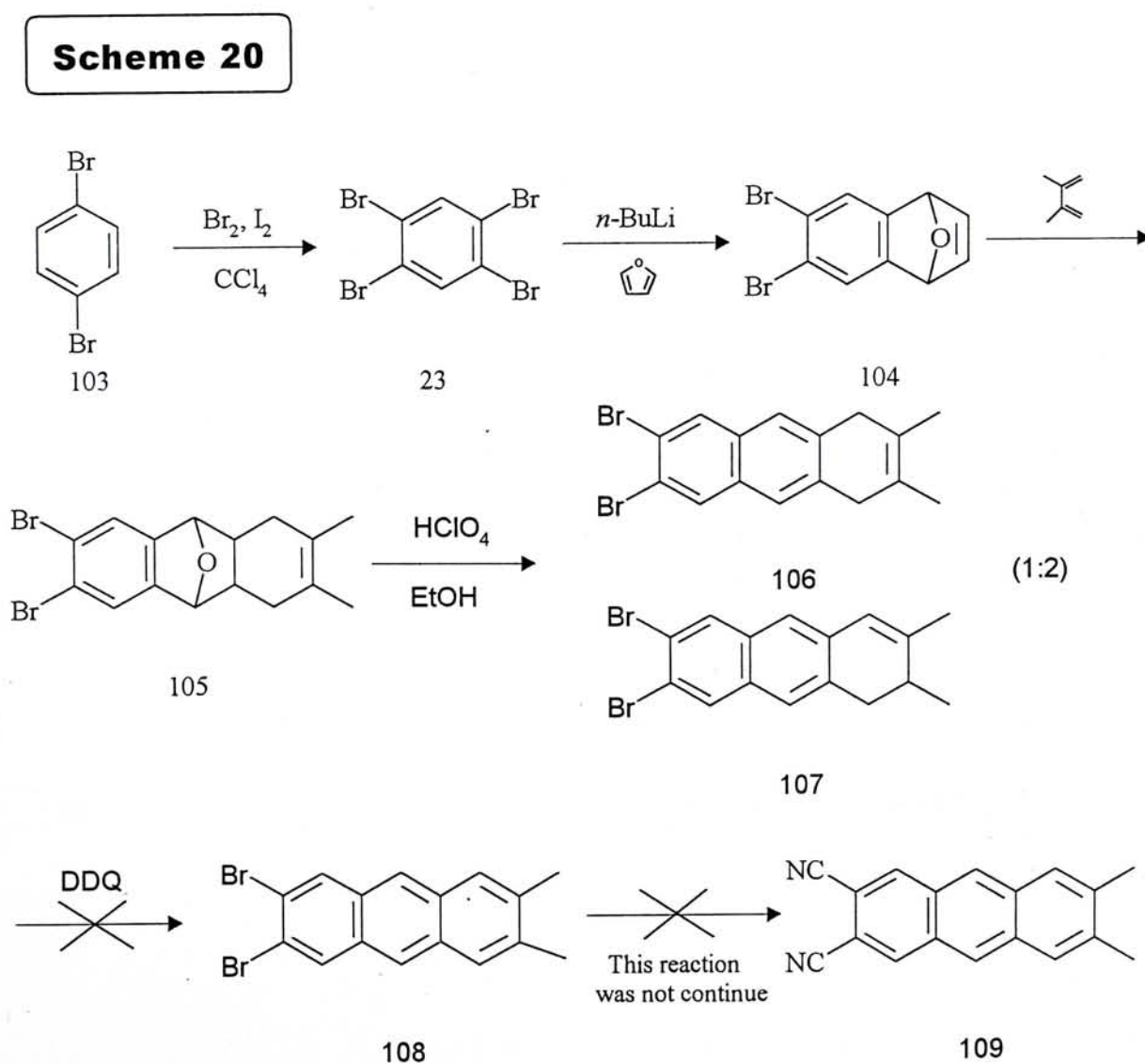
Figure 17 ^{1}H NMR spectrum of mixture **106** and **107** in CDCl$_3$
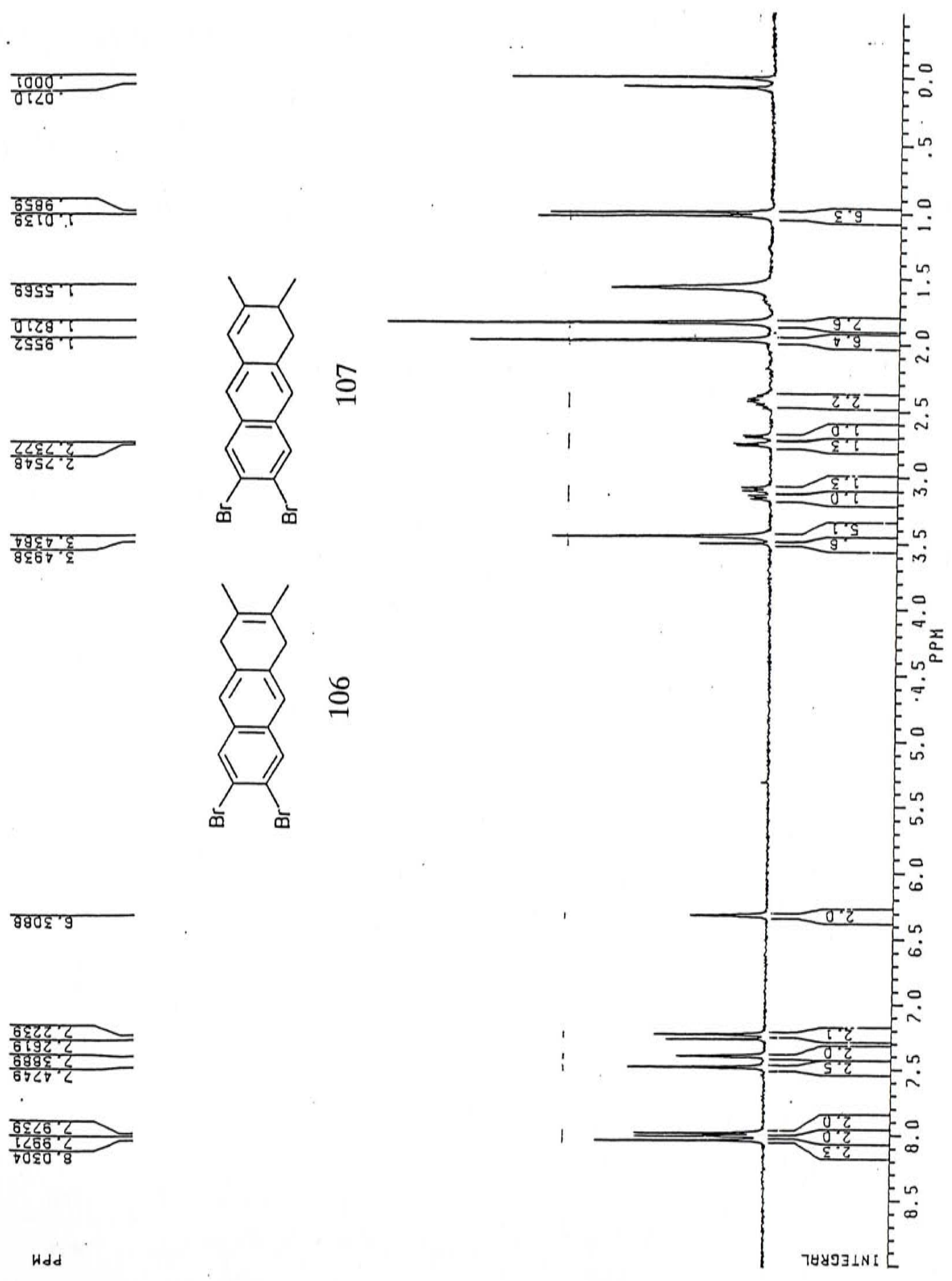
To enhance the solubility of the product, two butoxy side chains were introduced by the route shown in Scheme 21. 1,4-Hydroquinone (110) was treated with K_2CO_3 and butyl bromide to yield 111. Bromination of 111 with a catalytic amount of iodine gave 1,2,4,5-tetrabromo-3,6-dibutoxybenzene (112). Although compound 112 can also be prepared by bromination of 110 followed by butylation, we found that our route was easier to be carried out resulting in a higher yield. Treatment of 112 with n-BuLi and furan led to the formation of the respective Diels-Alder adduct 113. Further Diels-Alder reaction with 2,3-dimethylbuta-1,3-diene gave the endoxide 114. Dehydration of 114 with $HClO_4$ gave the isomers 115 and 116 in a total of 63 % yield. From the ^{1}H NMR spectrum (Figure 18), the ratio of 115 and 116 was found to be 1 : 2. The mixture of 115 and 116 was then refluxed with DDQ to afford the anthracene 117, which was then converted to the respective dinitrile 118 by the action of copper(I) cyanide in DMF.

Scheme 21

65
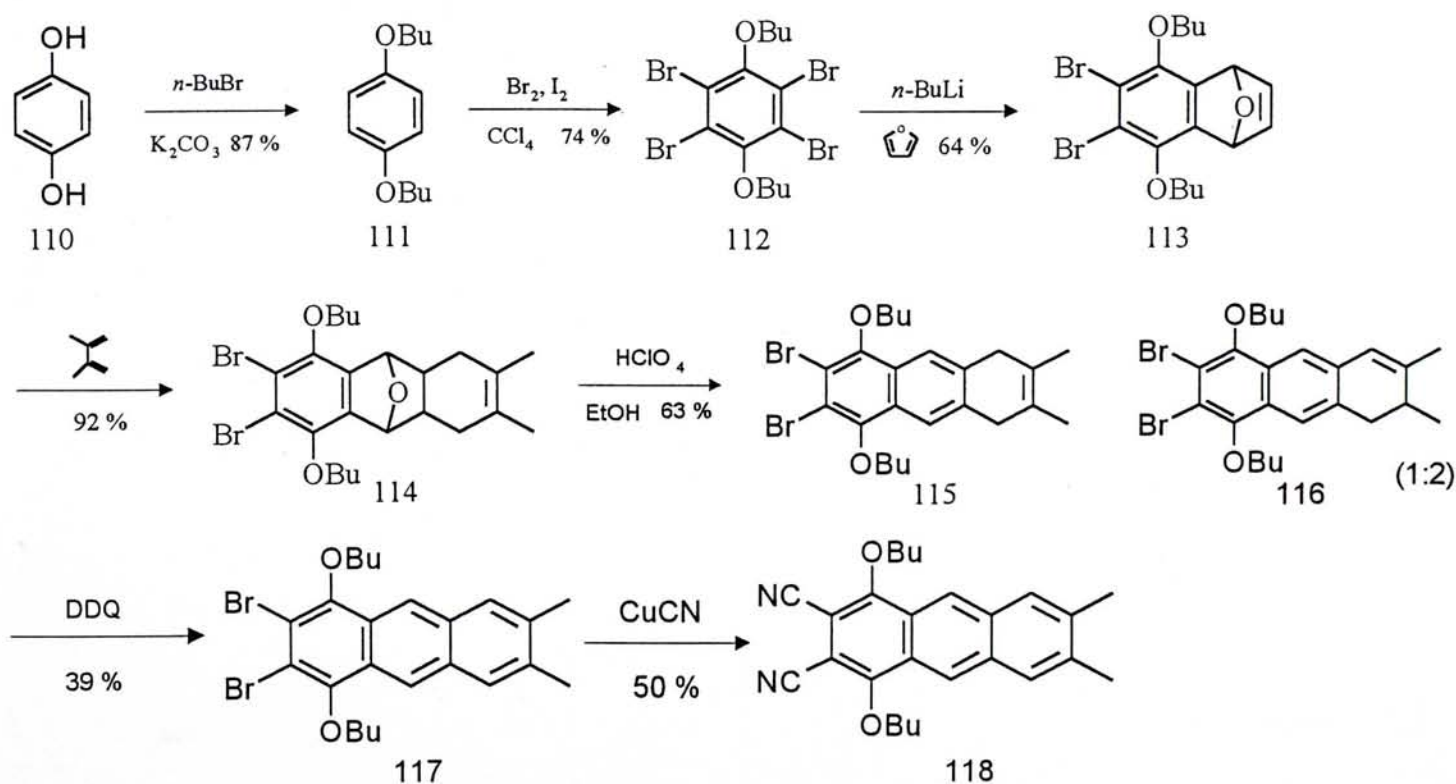
Figure 18 ^{1}H NMR spectrum of mixture 115 and 116 in CDCl$_3$
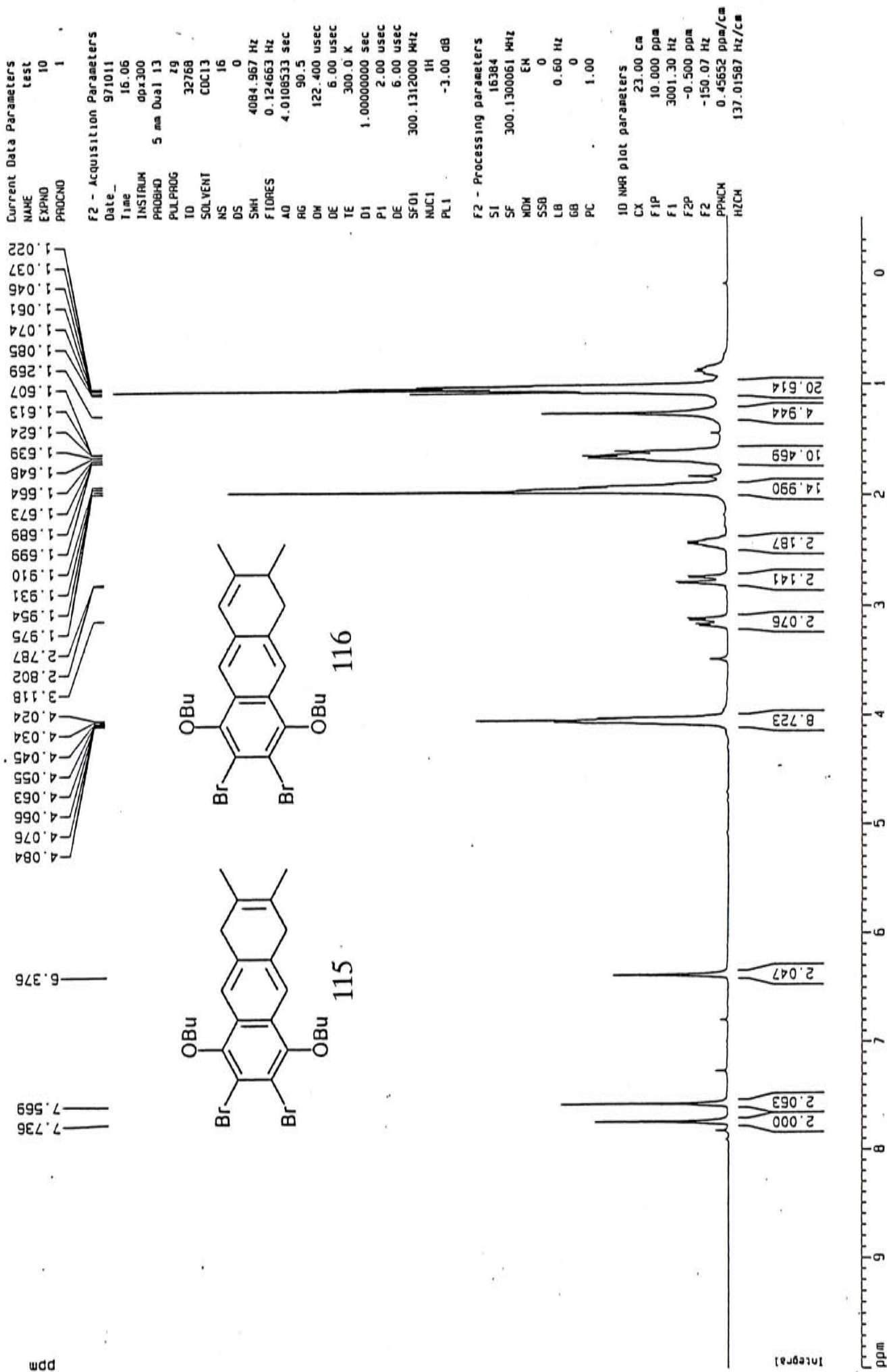
The ^{1}H NMR spectrum of **117** is displayed in Figure 19, which shows downfield aromatic protons signals at δ 8.49 and 7.79, together with signals attributed to the methyl and butoxyl side chains. Compound **118** shows a similar spectra feature (Figure 20) except that the triplet for OCH_2 protons is more downfield shifted. Compound **118** was also characteried by EI mass spectroscopy which give the protonated molecular ion with corrected isotopic distribution pattern. The IR spectrum of **118** shows the CN stretching at 2368 cm^{-1}.
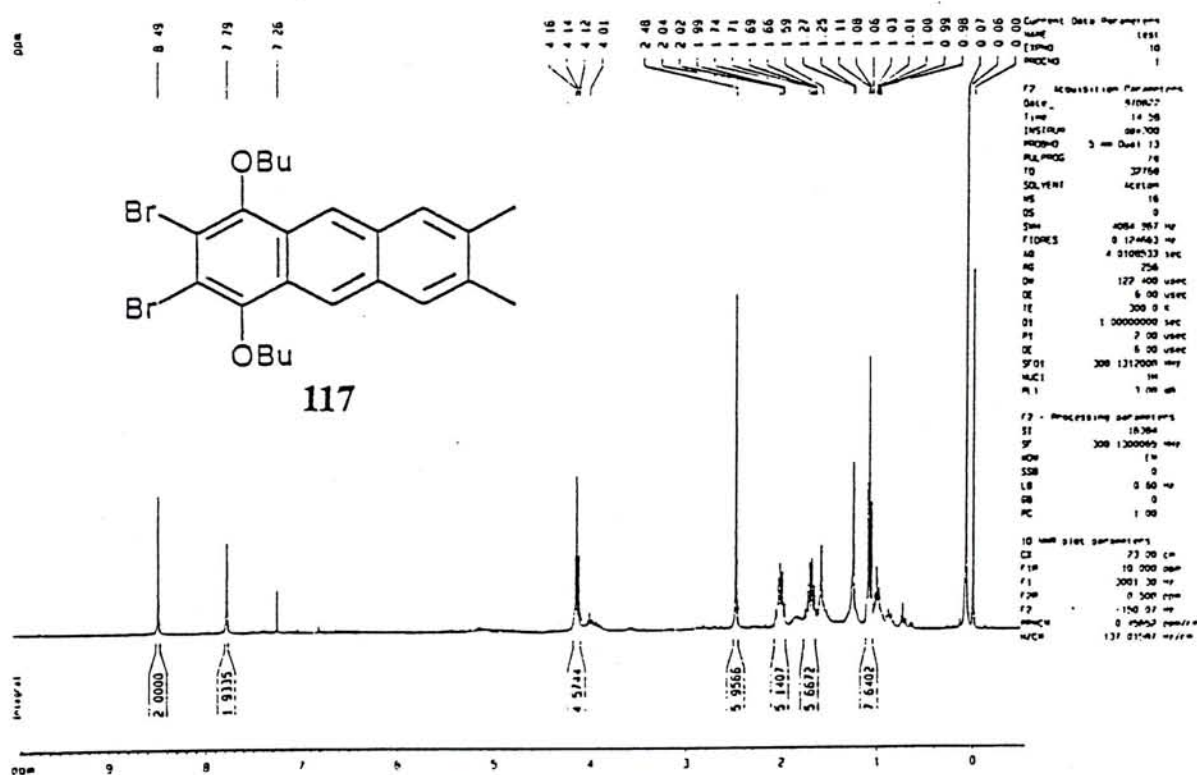
Figure 19 ^{1}H NMR spectrum of compound **117** in CDCl$_3$

Compound **118** was found to be photochemically reactive. During recrystallization from *o*-xylene, yellow needle-shaped crystals were obtained which were suitable for x-ray diffraction analysis. The molecular structure as shown in Figure 21 was found to be a head to tail dimer. It is clear that anthracene **118** undergoes 4 + 4 photodimerization.[68] Selected bond distances and bond angles of this compound are shown in the Appendix which are not unusual. The dimeric structure was also confirmed by ^{1}H NMR spectroscopy. Figure 22 shows the spectrum of the dimeric species in CDCl$_3$. The downfield singlet due to the aromatic protons H9 and H10 (δ 8.62 for **118**) disappears while a singlet at δ 5.08 appears which can be attributed to the protons at the bridging carbon.

Figure 20 ^{1}H NMR spectrum of compound **118** in CDCl$_3$
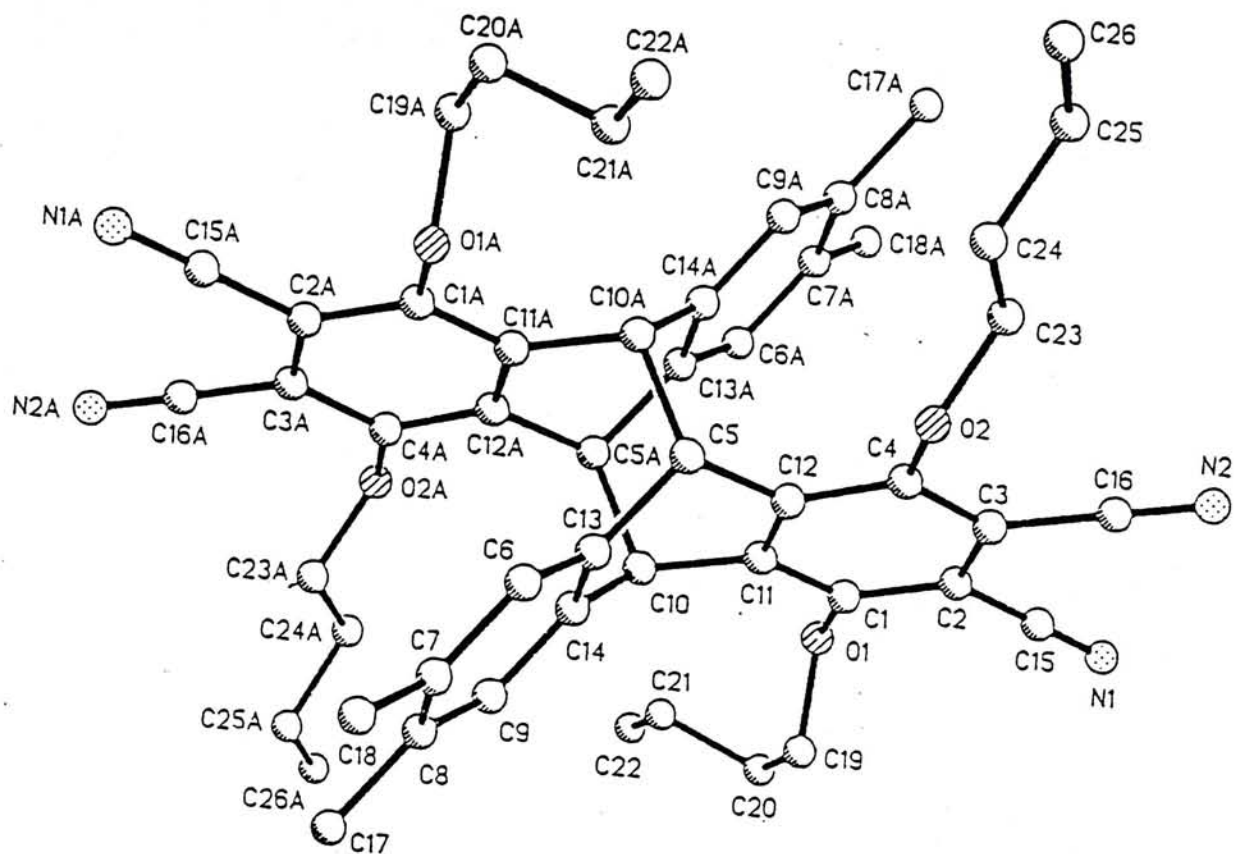
Figure 21 Perspective view of the dimer of **118** with labeling scheme H atoms are omitted for clarity

Figure 22 ^{1}H NMR spectrum of the dimer of **118** in CDCl$_3$

Current Data Parameters
NAME   test
EXPNO   10
PROCNO   1

F2 - Acquisition Parameters
Date_   971208
Time   15.05
INSTRUM   dpx300
PROBHD   5 mm Dual 13
PULPROG   zg
TD   32768
SOLVENT   CDCl3
NS   32
DS   0
SWH   4084.967 Hz
FIDRES   0.124663 Hz
AQ   4.0108533 sec
RG   574.7
DW   122.400 usec
DE   6.00 usec
TE   300.0 K
D1   1.00000000 sec
P1   2.00 usec
DE   6.00 usec
SFO1   300.1312000 MHz
NUC1   1H
PL1   -3.00 dB

F2 - Processing parameters
SI   16384
SF   300.1299473 MHz
WDW   EM
SSB   0
LB   0.60 Hz
GB   0
PC   1.00

1D NMR plot parameters
CX   23.00 cm
F1P   10.000 ppm
F1   3001.30 Hz
F2P   -0.500 ppm
F2   -150.06 Hz
PPMCM   0.45652 ppm/cm
HZCM   137.01584 Hz/cm

1.288
1.299
1.313
1.323
1.337
1.634
1.661
1.685
1.609
2.074
2.077
2.095
2.105
2.117
2.127
2.139
2.143
2.149
2.164
2.319
2.504
4.262
4.273
4.286
4.295
4.316
4.334
4.356
4.365
4.377
4.386
5.080

6.979

7.455

ppm

12.000
7.890
8.072
11.649

8.042

3.799

3.815

1.208

[Integral]

ppm

70

To further functionalize the anthracene **118**, bromination with NBS was attempted. However, bromine gas was generated during reflux and the desired benzyl bromide could not be obtained (Scheme 22). This work was not proceeded further.

Scheme 22

118
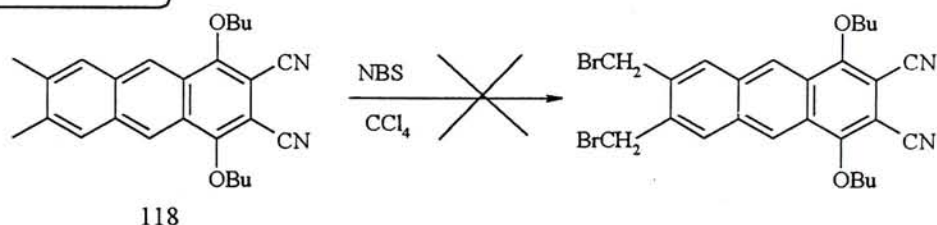
Besides, we also tried to prepare anthracocyanines by cyclization of **118**. The dicyanoanthracene **118** was initially treated with $Zn(OAc)_2 \cdot 2H_2O$ and DBU under the general cyclization conditions which have been described in previous section. However, the crude product did not show a near-infrared absorption but turned into dark brown on heating, indicating that the dicyanoanthracene **118** was decomposed. An alternative approach was therefore employed which involves the treatment of **118** with *n*-butyllithium in *n*-butanol, followed by hydrolysis (Scheme 23). The UV-vis spectra of the crude products showed an intense broad band at near-IR region (950 nm) which could be assigned to the Q band absorption of Ac. However, this product was not stable in a silica gel column. The color turned from reddish-brown to yellow when it was eluted with chloroform. As the desired metal-free Ac **119** is unstable in air and could not be readily purified, this work was not proceeded further.

Scheme 23

118

i) BuLi

ii) AcOH

119
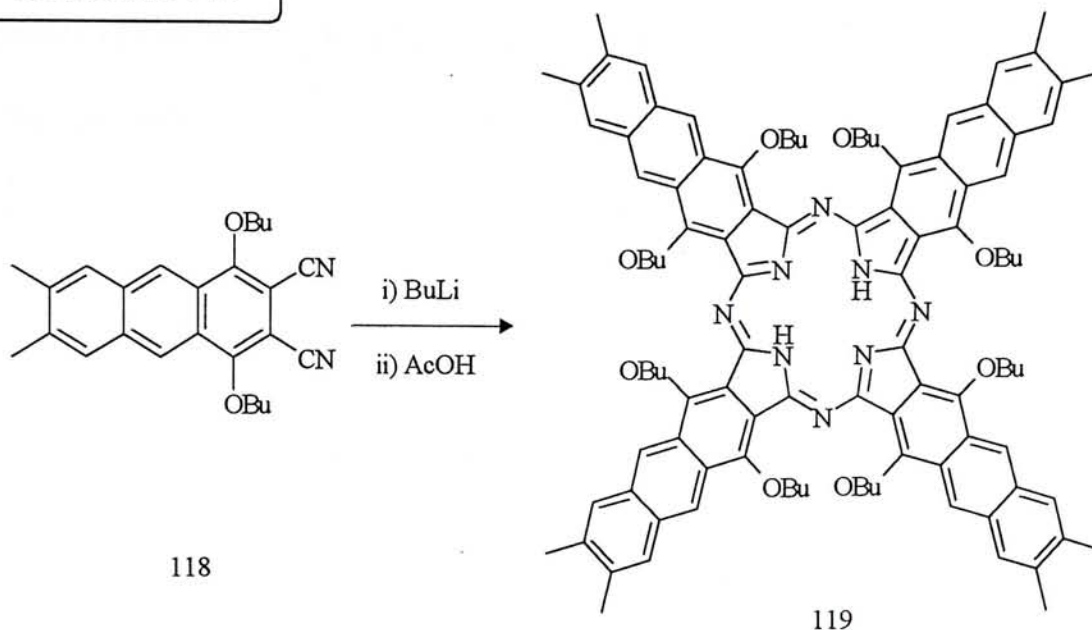
An alternative route to substituted anthracenes has recently been reported by Barranco *et al.*[69] As shown in Scheme 24,

Scheme 24

120

121

R1=R2=H
R1=Me R2=H
R1=R2=Br

122
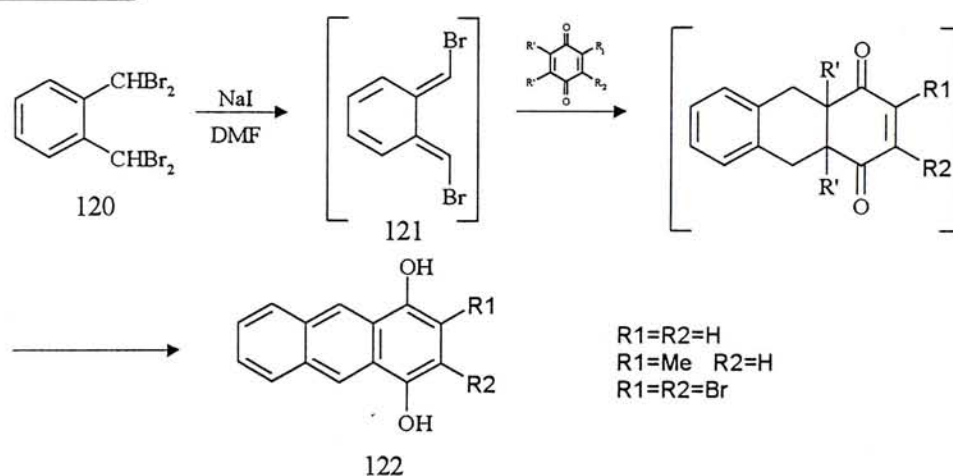
reaction of substituted *p*-benzoquinones with the highly reactive *o*-quinodimethane (**121**), generated favorably from tetrabromo-*o*-xylene **120**, leads to the formation of 1,4-dihydroanthracenes **122** in moderate yields. The intermediate Diels-Alder adducts undergo a facile oxidation to give the corresponding fully aromatized compounds.

2.2 Synthesis of Substituted Tetracenes

This methodology was extended in an attempt to synthesize substituted

72

tetracenes. The proposed synthetic route to 2,3,8,9-tetrabromo-1,4-dibutoxy-

tetracene (124) is shown in Scheme 25.   The endoxide 113 was treated with 45

and NaI in DMF to yield about 50% of endoxide 123 as a yellow solid after

chromatographic purification with toluene.   The ¹H NMR spectrum of 123 is

displayed in Figure 23 which shows two downfield aromatic signals at δ 8.02

and 7.56; one bridge-head proton signal at δ 6.35 and well-resolved aliphatic

signals at *ca.* 4.1 and 1-2 for the butoxy side chains.   Reductive deoxygenation

of 123 by TiCl₄, however, could not lead to the expected product 124 and the

resulting product was difficult to purify.

Scheme 25
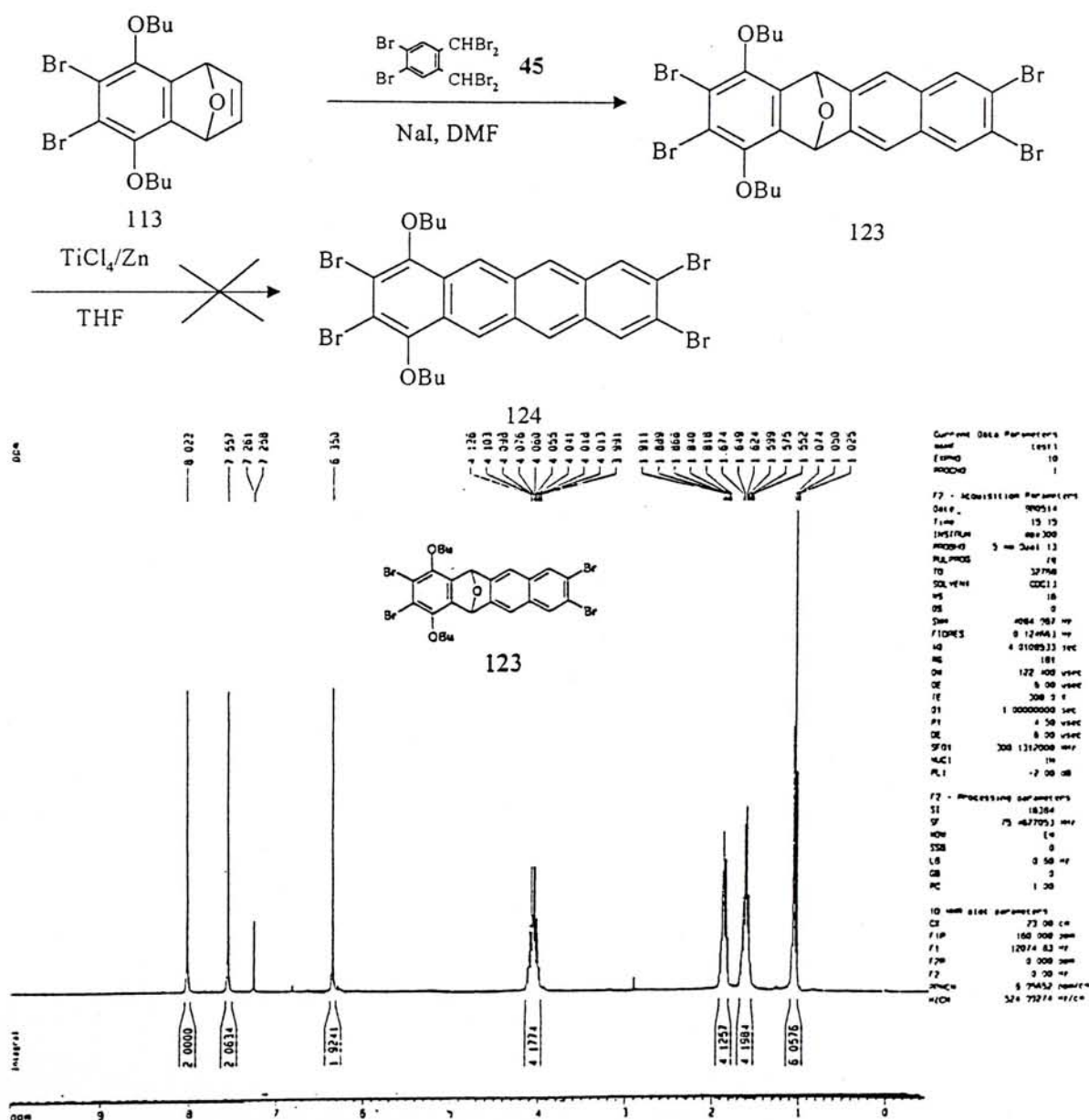
Figure 23 ¹H NMR spectrum of compound 123 in CDCl₃

The above unsuccessful attempt may be due to the fact that ether linkage in butoxyl groups is easy to be broken upon treatment with strong Lewis acid. We therefore replaced the butoxy group with *n*-hexyl group which is more robust toward Lewis acid. 1,4-Dihexylbenzene (**14**) was prepared by nickel-catalyzed coupling reaction of 1,4-dichlorobenzene (**12**) and *n*-hexylmagnesium bromide. Bromination of **14** in dichloromethane with a catalytic amount of iron powder and iodine gave the tetrabromobenzene **16**. Treatment of this compound with *n*-butyllithium generated a reactive benzyne which was trapped with furan leading to the formation of endoxide **18**. Treatment of 4,5-dibromo-1,2-bis(dibromomethyl)benzene (**45**) with sodium iodide gave the reactive intermediate as described previously which further underwent Diels-Alder reaction with endoxide **18** to give the adduct **125**. The ^{1}H NMR spectrum of **125** is displayed in Figure 24 which is similar to that of **123** showing two downfield aromatic signals at δ 7.98 and 7.52, one bridge-head proton signal at δ 6.19 and aliphatic signals for the hexyl side chains. Upon reductive deoxygenation with zinc and TiCl$_4$ in THF, a deep brown oily solid was obtained after chromatography and crystallization (Scheme 26). The 1H NMR spectrum of the crude product (Figure 25) shows downfield aromatic signals up to δ 8.76 while the singlet due to CHO in **125** disappears. These data suggest that the tetracene **126** may be formed but attempts to purified this compound were not successful.

Scheme 26
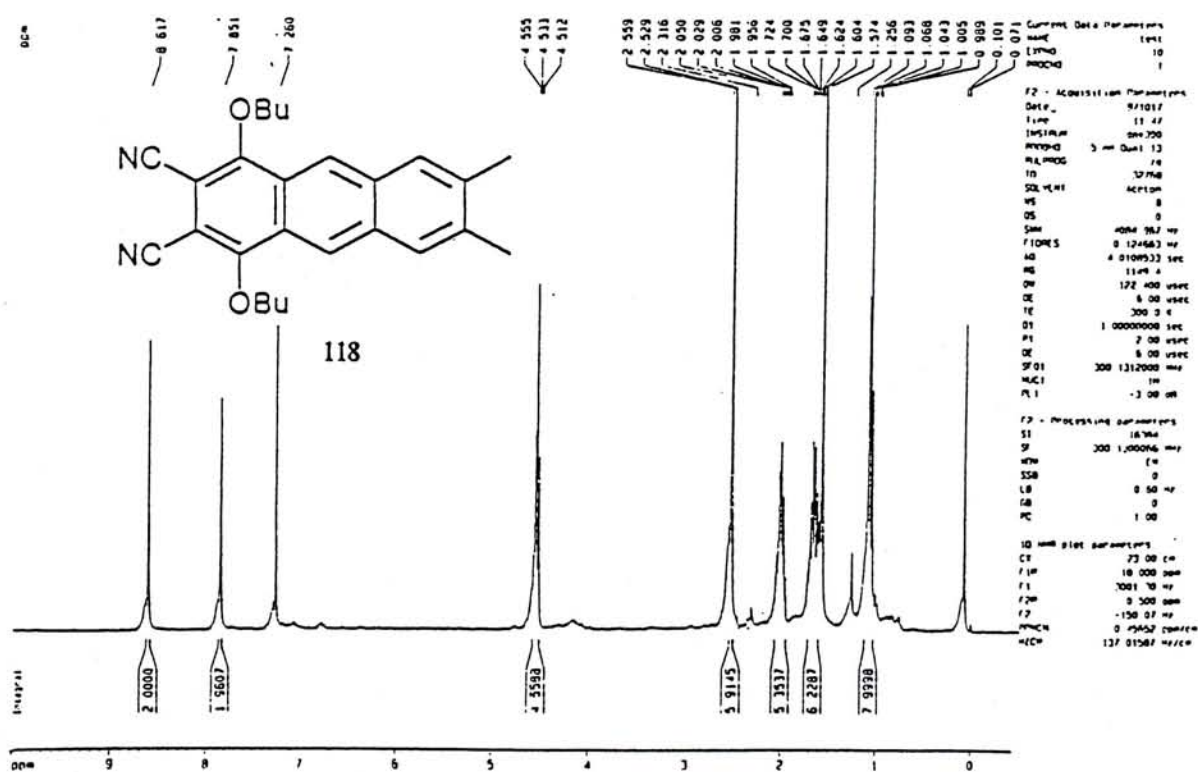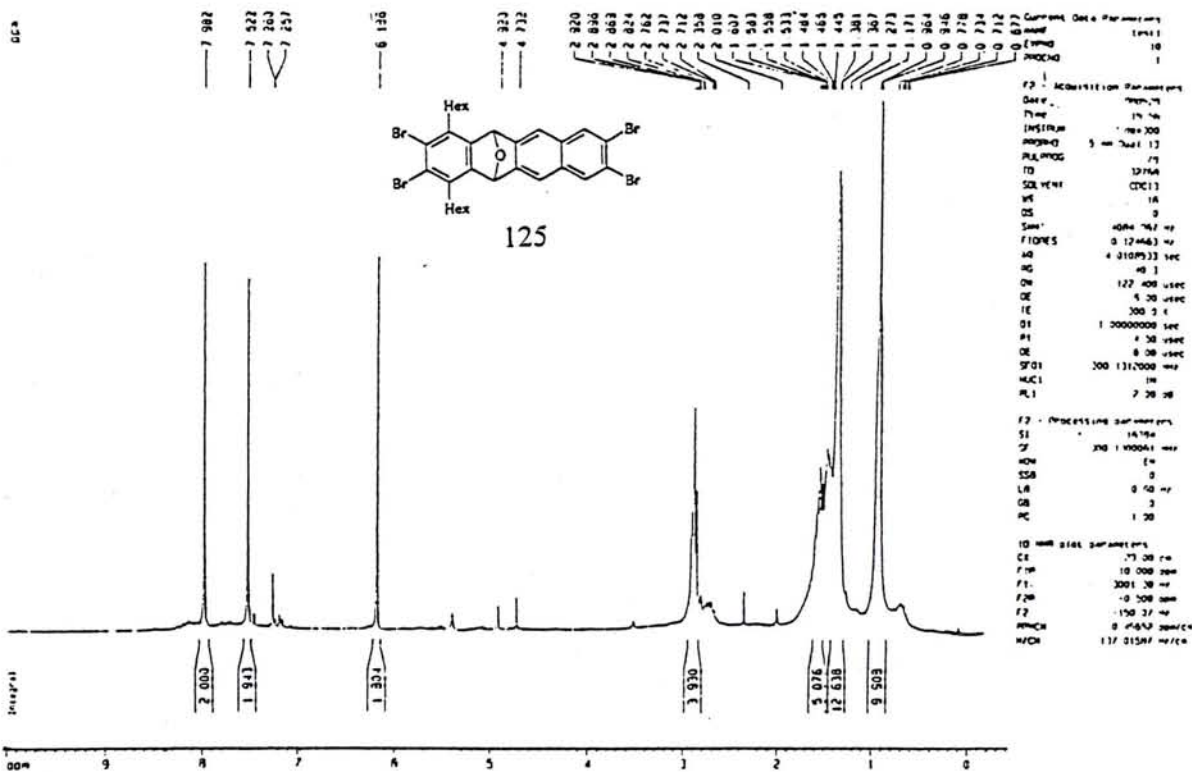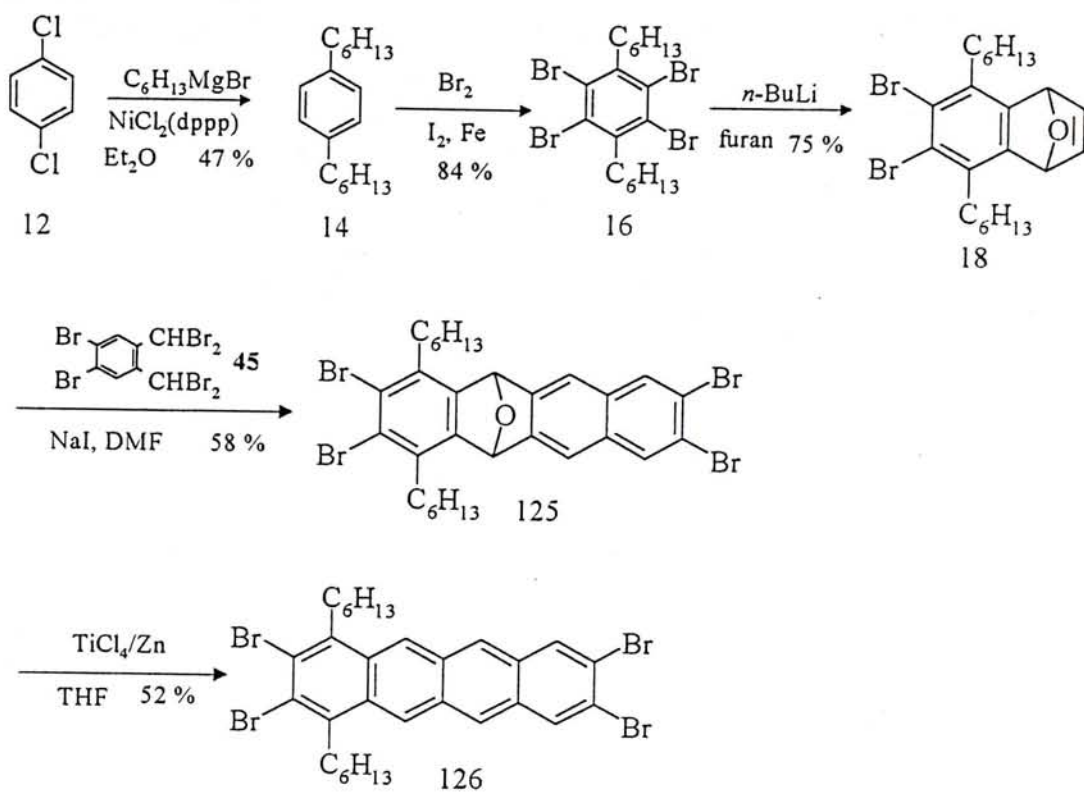

Figure 24 ¹H NMR spectrum of compound **125** in CDCl₃
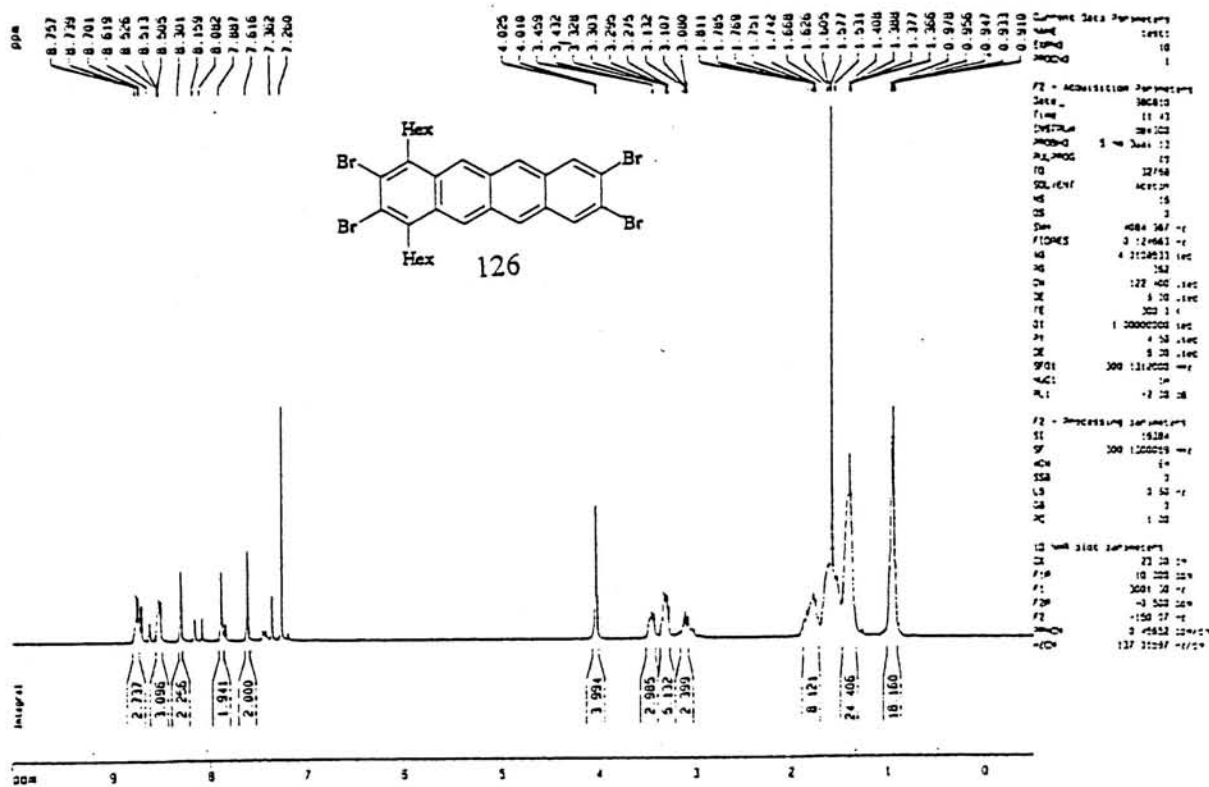
Figure 25 ^{1}H NMR of impure **126** in CDCl$_3$

2.3 Conclusion

Several routes have been used to prepare substituted 2,3-dicyano anthracenes and tetracenes. Although some of these cannot lead to the desired products, one anthracene, namely 1,4-dibutoxy -2,3-dicyano-7,8-dimethylanthracene (**118**), has been synthesized and fully characterized. This compound is photochemically reactive and undergoes dimerization. The structure of the resulting dimer has also been determined.

3. Experimental Section

The general experimental details are described in Part I, 6,7-dibromo-5,8-dibutoxy-1,4-epoxynaphthalene (**113**) was prepared according to literature procedures.[70]

1,4-Dibutoxybenzene (111)

A mixture of 1,4-hydroquinone (**110**) (11 g, 0.1 mol), 1-bromobutane (64 ml, 0.6 mol) and potassium carbonate (53.8 g, 0.109 mol) were mixed in acetone (250 ml). The pale brown mixture was then refluxed for 104 h. The brown solution was filtered and the volatiles were removed. The residue was purified by column chromatography with hexanes as eluent. Yield 19.2 g (87 %), m.p. 44-45°C (lit.[71] m.p. 45-46°C). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.82 (s, 2H, ArH), 3.91 (t, J = 7.5 Hz, 4H, OCH$_2$), 1.74 (quintet, J = 7.5 Hz, 4H, CH$_2$), 1.124 (q, J = 7.5 Hz, 4H, CH$_2$), 0.96 (t, J = 7.5 Hz, 6H, CH$_3$).

1,2,4,5-Tetrabromo-3,6-dibutoxybenzene (112)

To a mixture of 1,4-dibutoxybenzene (**111**) (9 g, 0.04 mol) and iodine (0.25 g, 1 mmol) in tetrachloromethane (104 ml) was added bromine (15 ml, 0.3 mol) in dropwise. After the addition of bromine, the brown mixture was refluxed for 12 h, then cooled slowly to room temperature. The mixture was then washed with 1 N NaOH (3 x 50 ml) and water (3 x 50 ml), then dried over sodium sulfate. The volatiles were removed under reduced pressure. The residue was purified by column chromatography with hexanes as eluent followed by recrystallization from ethanol. Yield 16 g (74 %), m.p. 92-93°C (lit.[70] m.p. 92-93°C). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.97 (t, J = 7.5 Hz, 4H, OCH$_2$), 1.87

(quintet, $J = 7.5$ Hz, 4H, CH_2-), 1.55 (sextet, 4H, -CH_2-), 0.98 (t, $J = 7.5$ Hz, 6H, CH$_3$).

6,7-Dibromo-5,8-dibutyoxy-1,4-epoxynaphthalene (113)

n-BuLi (19.6 ml, 105 mmol) (1.6 M solution in hexane) diluted with dry toluene (200 ml) was added to a solution of 1,2,4,5-tetrabromo-3,6-dibutoxybenzene (**112**) (14 g, 26 mmol) in dry toluene (200 ml) and furan (21 ml) under nitrogen at −78 °C over 2h. The mixture was maintained at this temperature for 1h. The reaction was quenched with methanol (3 ml). The mixture was allowed to reach room temperature, washed with water (3 x 100 ml), dried with MgSO$_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography with hexane / EA (9:1) as eluent. Yield 7.12 g, (64.4 %), m.p. 72-73°C (lit.[70] m.p. 71-72°C). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.04 (s, 2H, HC=CH), 593 (s, 2H, OCH), 3.98 (t, $J = 7.5$ Hz, 4H, OCH$_2$), 1.80 (quintet, $J = 7.5$ Hz, 4H, CH$_2$), 1.53 (sextet, $J = 7.5$ Hz, 4H, CH$_2$), 0.98 (t, $J = 7.5$ Hz, 6H, CH$_3$).

6,7-Dibromo-5,8-dibutoxy-9,10-epoxy-1,4,4a,9,9a,10-hexahydro-2,3-dimethylanthracene (114)

A mixture of 6,7-Dibromo-5,8-dibutyoxy-1,4-epoxynaphthalene (**113**) (10 g, 22 mmol) and 2,3-dimethyl-1,3-butyldiene (15 ml, 0.13 mol) were mixed in dry toluene (300 ml). The mixture was refluxed for 20h. After removal of the volatiles, the residue was purified by column chromatography with hexane / EA (9:1) as eluent. Yield 8.3 g, (92 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.13 (s, 2H, OCH), 3.98 (t, $J = 7.5$ Hz, 4H, OCH$_2$), 2.21 (d, $J = 7.5$ Hz, 2H, CH$_2$), 2.19 (d, $J = 7.5$ Hz, 2H, CH), 1.95 (d, $J = 7.5$ Hz, 2H, CH$_2$), 1.79 (quintet, $J = 7.5$ Hz, 4H,

CH$_2$), 1.69 (s, 6H, CH$_3$), 1.54 (quintet, J = 7.5 Hz, 4H, CH$_2$), 0.99 (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz) δ 145.3, 137.4, 127.2, 118.5, 83.2, 73.7, 42.4, 34.1, 32.0, 19.2, 18.8, 13.8. MS (EI) : m/z 528 [M^+]. Anal. Calcd. for C$_{24}$H$_{32}$O$_3$Br$_2$: C, 54.56; H, 6.10. Found: C, 54.6; H, 6.33.

6,7-Dibromo-5,8-dibutoxy-2,3-dimethyl -1,4-tetrahydroanthracene (115) and 6,7-Dibromo-5,8-dibutoxy-2,3-dimethyl-3,4-dihydroanthracene (116)

To a mixture of endoxide **114** (9.4 g, 17.8 mmol) in 300 ml toluene, hydroperchloric acid (50 ml) in ethanol (70 ml) was added dropwise. The mixture was refluxed for 8h and cooled to room temperature. The brown esolution was extracted with CH$_2$Cl$_2$ (2 x 100 ml) and washed with water (150 ml). The combined organic solution was dried over sodium CaCl$_2$. After removal of volatiles, the residue was purified by column chromatography with hexane / CHCl$_3$ (7:3) as solvent. Yield 5.69 g, (63 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.74 (s, 1H, ArH), 7.57 (s, 1H, ArH), 6.108 (s, 1H, ArH), 4.06 (m, 4H, OCI_2), 2.95 (dd, J = 3 Hz, 1H, CH$_2$), 2.79 (dd, J = 3 Hz, 1H, CH$_2$), 2.120 (m, 1H, CH$_2$), 1.94 (m, 10H, CH$_3$ and CH$_2$), 1.64, (m, 4H, CH$_2$), 1.05, (m, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz) δ 150.0, 149.7, 134.4, 134.2, 128.0, 127.4, 122.2, 120.7, 117.3, 115.4, 115.2, 73.9, 36.6, 33.5, 32.3, 29.7, 22.0, 19.3, 17.6, 14.00. MS (EI) : m/z 510 [M^+]. Anal. Calcd. For C$_{24}$H$_{30}$O$_2$Br$_2$: C, 56.49, H, 5.93. Found: C, 57.02; H, 6.03.

2,3-Dibromo-1,4-dibutoxy-7,8-dimethylanthracene (117)

To a mixture of hydroanthracene **115** & **116** (1 g, 2.0 mmol) and DDQ (0.9 g, 3.78 mmol) in 100 ml dry toluene, The mixture was refluxed under nitrogen for 8 h. The mixture was filtered while still hot. After removal of volatiles, the

residue was purified by column chromatography with chloroform/hexane (4:6) as eluent. Yield 0.39 g (39 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.49 (s, 2H, ArH), 7.79 (s, 2H, ArH), 4.14 (t, J = 7.5 Hz, 4H, OCH$_2$), 2.48 (s, 6H, CH$_3$), 2.02 (m, 4H, CH$_2$), 1.70 (m, 4H, CH$_2$), 1.08 (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz) δ 127.4, 120.4, 73.9, 32.4, 29.7, 20.44 19.4, 14.0, 1.0. MS (EI) : m/z 508 [M^+]. Anal. Calcd. for C$_{24}$H$_{28}$O$_2$Br$_2$: C, 56.71; H, 5.55. Found: C, 57.70; H, 5.45

1,4-Dibutoxy-6,7-dimethyl-2,3-dicyanoanthracene (118)

To a mixture of anthracene 117 (0.5 g, 1.0 mmol) and CuCN (0.27 g, 3.0 mmol) in dry DMF (10 ml) was degassed under reduce pressure and refluxed for 10 h under nitrogen atmosphere. After cooling, the mixture was poured into 110 % NH$_4$OH and strong stream of air was bubbled through the solution for 3 h. The reaction mixture was filtered and the solid residue was extracted with ether (4 x 50 ml). The combined ether layers were washed with water and dried with CaCl$_2$. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography with CHCl$_3$/hexane (7:3) as eluent. Yield 0.2 g (50 %). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.62 (s, 2H, ArH), 7.85 (s, 2H, ArH), 4.53 (t, J = 7.5 Hz, 4H, OCH$_2$), 2.53 (s, 6H, CH$_3$), 2.01 (m, 4H, CH$_2$), 1.68 (m, 4H, CH$_2$), 1.01 (t, J = 7.5 Hz, 6H, CH$_3$). MS (EI) : m/z 400 [M^+]. Anal. Calcd. for C$_{26}$H$_{28}$N$_2$O$_2$: C, 77.97; H, 7.05; C, 6.99. Found: C, 77.56; H, 7.41; N, 6.57.

1,4-Dihexylbenzene (14)

The Grignard reagent prepared from Mg turnings (7.3 g, 0.3 mol) and hexyl bromide (42.2 ml, 0.3 ml) in dry THF (100 ml) was added in dropwise to a

mixture of 1,4-dichlorobenzene (12) (16.8 g, 0.11 mol) and chloro[1,3-bis(diphenylphosphine)propane] nickel(II) (200 mg) in dry THF (70 ml) in a 250 ml 3-necked round bottom flask at r.t.. When the reaction became vigorous, the flask was cooled in an ice-bath and the reaction mixture was refluxed for 12 h. The solutions was then hydrolyzed with HCl (2M). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 ml). The combined organic layers were washed with H_2O (3 x 50 ml), $NaHCO_3$ (5 %, 3 x 50 ml) and H_2O (3 x 50 ml), then dried over anhydrous $CaCl_2$. After removal of volatiles, the residue was dissolved in hexane (100 ml) and passed through a short bed of silica gel. The colorless liquid collected was further distilled to give a colorless liquid. Yield 16 g, (47 %), b.p. 88°C/0.5 mm (lit.[72] b.p. 93°C/1mm). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.92, (t, J = 7.5 Hz, 6H, CH_3), 1.34, (m, 12H, CH_2), 1.61 (m, 4H, CH_2), 2.60 (t, J = 7.5 Hz, 4H, CH_2), 7.12 (s, 4H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz) δ 140.1, 128.2, 35.6, 31.8, 29.1, 22.6, 14.1

2,3,5,6-Tetrabromo-1,4-dihexylbenzene(16)

Iodine (0.12 g, 1 mmol) and iron powder (0.054 g, 1 mmol) were added to the mixture of 1,4-dihexylbenzene (14) (6 g, 24 mmol) and CH_2Cl_2 (10 ml) in a 100 ml 3-necked round-bottom flask. Bromine (5.1 ml, 10 mmol) was added in dropwise into the mixture over 3 h. The whole setup was covered with an aluminium foil. When the addition of bromine was completed, the mixture was heated at 40 °C overnight. The brown mixture was then poured into $NaHSO_3$ (5 %, 500 ml) and the yellow organic layer was separated, washed with H_2O (3 x 50 ml) and dried over Na_2SO_4. After removal of solvent, the crude product was recrystallized from hexane as colorless needle-shaped crystals.

Yield 11.5 g, (84 %), m.p. 89-91°C (lit.[72] m.p. 90-91°C). ^{1}H NMR (CDCl$_3$, 300

MHz): δ 3.17 (t, J = 7.5 Hz, 4H, CH$_2$), 1.60 (m, 4H, CH$_2$), 1.43 (m, 4H, CH$_2$),

1.35, (m, 8H, CH$_2$), 0.91, (t, J = 7.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4

MHz) δ 143.2, 127.5, 41.9, 31.4, 29.3, 27.6, 14.1

6,7-Dibromo-1,4-epoxy-5,8-dihexyl-1,4-dihydronaphthalene (18)

n-BuLi (12 ml, 19.2 mmol) (1.6 M solution in hexane) diluted with dry toluene

(150 ml) was added to a suspension of 1,2,4,5-tetrabromo-3,6-dihexylbenzene

(16) (10 g, 17.8 mmol) in dry toluene (200 ml) and furan (9 ml, 134 mmol)

under nitrogen at −78 °C over 3h. The mixture was maintained at this

temperature for 1h. The reaction was quenched with methanol (3 ml). The

mixture was allowed to reach room temperature, washed with water (3 x 100

ml), dried with MgSO$_4$, and the volatiles was removed under reduced pressure.

The residue was purified by column chromatography with hexane/EA (9:1) as

eluent. Yield 6.3 g, (75 %), m.p. 68-70°C (lit.[18] m.p. 68-70°C). ^{1}H NMR

(CDCl$_3$, 250 MHz): δ 7.02 (s, 2H, HC=CH), 5.75 (s, 2H, OCH), 2.81 (t, J = 7.5

Hz, 4H, CH$_2$), 1.57 (m, 4H, CH$_2$), 1.32 (m, 12H, CH$_2$), 0.90 (s, 6H, CH$_3$).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz) δ 147.5, 142.7, 134.9, 124.5, 81.8, 34.8, 31.6,

29.8, 29.3, 22.6, 14.0.

2,3,8,9-Tetrabromo-6,11-epoxy-7,10-dihexyltetracene (125)

To a mixture of 1,2-bis(dibromomethyl)-4,5-dibromobenzene (45) (12.3 g, 21.2

mmol), endoxide 18 (10 g, 21.2 mmol) and sodium iodide (21.4 g, 0.14 mol)

were mixed in dry DMF (250 ml). The brown mixture was heated at 75 °C for

7 h to give a reddish brown mixture which was cooled and poured slowly into

water (100 ml) with stirring. Sodium bisulfite was added to the mixture until

color changed to pale yellow. The brown sticky solid was dissolved in CH_2Cl_2 (150 ml) and washed with water (3 x 50 ml). The organic layers was dried with anhydrous $CaCl_2$ and then evaporated under reduced pressure. The crude product was purified by column chromatography with hexane/toluene (2:8) as eluent. Yield 9.0 g (58 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.98 (s, 2H, ArH), 7.52 (s, 2H, ArH), 6.19 (s, 2H, OCH), 2.90 (t, J = 7.5 Hz, 4H, CH_2), 1.58 (t, J = 7.5 Hz, 4H, CH_2), 1.37 (m, 12H, CH_2), 0.95 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz) δ 145.1, 144.5, 135.3, 132.1, 131.7, 125.1, 122.3, 117.6, 81.3, 35.1, 31.5, 29.4, 22.6, 14.1.

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APPENDIX   Crystallographic data of dimer of anthracene 118

Table 1. Crystal data and structure refinement for MC1.

Identification code   mc1

Empirical formula $C_{52}H_{56}N_4O_4$

Formula weight   801.00

Temperature   293(2) K

Wavelength   0.71073 Å

Crystal system   Triclinic

Space group $P\bar{1}$

Unit cell dimensions $a = 9.247(2)$ Å   alpha = 77.54(3)$^{\circ}$

                                    $b = 11.385(2)$ Å   beta = 81.10(3)$^{\circ}$

                                    $c = 11.565(2)$ Å   gamma = 74.56(3)$^{\circ}$

Volume, Z   1139.8(4) $Å^3$, 2

Density (calculated)   1.167 Mg/m^3

Absorption coefficient   0.074 mm^{-1}

F(000)   428

Crystal size   0.44 x 0.32 x 0.20 mm

θ range for data collection   1.81 to 24.00°

Limiting indices $-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $0 \leq l \leq 13$

Reflections collected   2614

Independent reflections   2614 ($R_{int} = 0.0000$)

Absorption correction   DIFABS

Refinement method   Full-matrix least-squares on F^2

Data / restraints / parameters   2541 / 0 / 280

Goodness-of-fit on F^2 1.566

Final R indices [I>2σ(I)]   R1 = 0.0838, wR2 = 0.2119

R indices (all data)   R1 = 0.1066, wR2 = 0.2869

Extinction coefficient   0.00(2)

Largest diff. peak and hole   91   0.248 and -0.201 $e Å^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [Å^2 x 10^3] for HCl. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	Y	z	U(eq)
O(1)	189(2)	-3143(2)	2463(2)	57(1)
O(2)	4496(3)	-1073(2)	-524(2)	77(1)
N(1)	3457(3)	-5590(3)	2741(3)	90(1)
N(2)	6489(4)	-4265(3)	586(3)	110(1)
C(1)	1281(3)	-2611(2)	1786(2)	51(1)
C(2)	2751(3)	-3336(2)	1612(2)	56(1)
C(3)	3839(3)	-2851(3)	834(3)	59(1)
C(4)	3465(3)	-1610(3)	209(2)	56(1)
C(5)	1531(3)	447(2)	-197(2)	50(1)
C(6)	710(3)	2372(2)	769(2)	53(1)
C(7)	-191(3)	3027(3)	1618(3)	60(1)
C(8)	-1246(3)	2514(3)	2394(3)	61(1)
C(9)	-1383(3)	1335(2)	2332(2)	58(1)
C(10)	-645(3)	-558(2)	1332(2)	51(1)
C(11)	924(3)	-1378(2)	1192(2)	49(1)
C(12)	2012(3)	-889(2)	421(2)	52(1)
C(13)	578(3)	1188(2)	712(2)	52(1)
C(14)	-487(3)	686(2)	1486(2)	51(1)
C(15)	3131(3)	-4601(3)	2240(3)	62(1)
C(16)	5338(4)	-3624(3)	687(3)	76(1)
C(17)	-2263(4)	3184(3)	3332(3)	85(1)
C(18)	43(4)	4281(3)	1674(3)	75(1)
C(19)	-68(4)	-3042(3)	3703(3)	73(1)
C(20)	-1446(4)	-3505(3)	4210(3)	82(1)
C(21)	-2869(4)	-2785(4)	3639(4)	95(1)
C(22)	-4222(5)	-3308(5)	4098(5)	121(2)
C(23)	5266(4)	-1589(4)	-1528(3)	85(1)
C(24)	5866(5)	-621(4)	-2374(4)	97(1)
C(25)	6793(7)	-1033(6)	-3460(4)	142(2)
C(26)	7502(8)	-120(6)	-4251(5)	166(3)

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Table 3. Bond lengths [Å] and angles [°] for MCl.

O(1)-C(1)	1.369(3)	O(1)-C(19)	1.442(4)
O(2)-C(4)	1.356(3)	O(2)-C(23)	1.420(4)
N(1)-C(15)	1.134(4)	N(2)-C(16)	1.124(4)
C(1)-C(11)	1.399(4)	C(1)-C(2)	1.400(4)
C(2)-C(3)	1.389(4)	C(2)-C(15)	1.443(4)
C(3)-C(4)	1.420(4)	C(3)-C(16)	1.437(5)
C(4)-C(12)	1.392(4)	C(5)-C(12)	1.514(4)
C(5)-C(13)	1.514(4)	C(5)-C(10)#1	1.618(4)
C(6)-C(7)	1.395(4)	C(6)-C(13)	1.402(4)
C(7)-C(8)	1.380(4)	C(7)-C(18)	1.516(4)
C(8)-C(9)	1.399(4)	C(8)-C(17)	1.517(4)
C(9)-C(14)	1.383(4)	C(10)-C(11)	1.508(4)
C(10)-C(14)	1.512(3)	C(10)-C(5)#1	1.618(4)
C(11)-C(12)	1.387(4)	C(13)-C(14)	1.380(4)
C(19)-C(20)	1.497(5)	C(20)-C(21)	1.517(6)
C(21)-C(22)	1.502(6)	C(23)-C(24)	1.474(6)
C(24)-C(25)	1.497(6)	C(25)-C(26)	1.454(7)
C(1)-O(1)-C(19)	116.5(2)	C(4)-O(2)-C(23)	119.9(2)
O(1)-C(1)-C(11)	120.9(2)	O(1)-C(1)-C(2)	119.5(2)
C(11)-C(1)-C(2)	119.4(2)	C(3)-C(2)-C(1)	120.5(2)
C(3)-C(2)-C(15)	119.9(3)	C(1)-C(2)-C(15)	119.6(3)
C(2)-C(3)-C(4)	120.0(2)	C(2)-C(3)-C(16)	118.8(3)
C(4)-C(3)-C(16)	121.3(3)	O(2)-C(4)-C(12)	118.6(3)
O(2)-C(4)-C(3)	122.5(3)	C(12)-C(4)-C(3)	118.8(2)
C(12)-C(5)-C(13)	108.0(2)	C(12)-C(5)-C(10)#1	111.0(2)
C(13)-C(5)-C(10)#1	112.3(2)	C(7)-C(6)-C(13)	120.7(3)
C(8)-C(7)-C(6)	119.6(2)	C(8)-C(7)-C(18)	121.8(2)
C(6)-C(7)-C(18)	118.6(3)	C(7)-C(8)-C(9)	119.6(2)
C(7)-C(8)-C(17)	122.0(2)	C(9)-C(8)-C(17)	118.4(3)
C(14)-C(9)-C(8)	120.7(3)	C(11)-C(10)-C(14)	107.3(2)
C(11)-C(10)-C(5)#1	110.6(2)	C(14)-C(10)-C(5)#1	112.3(2)
C(12)-C(11)-C(1)	120.2(2)	C(12)-C(11)-C(10)	118.0(2)
C(1)-C(11)-C(10)	121.7(2)	C(11)-C(12)-C(4)	121.1(3)
C(11)-C(12)-C(5)	116.9(2)	C(4)-C(12)-C(5)	122.0(2)
C(14)-C(13)-C(6)	119.2(2)	C(14)-C(13)-C(5)	118.3(2)
C(6)-C(13)-C(5)	122.5(2)	C(13)-C(14)-C(9)	120.1(2)
C(13)-C(14)-C(10)	116.9(2)	C(9)-C(14)-C(10)	123.0(2)
N(1)-C(15)-C(2)	178.4(4)	N(2)-C(16)-C(3)	177.5(4)
O(1)-C(19)-C(20)	106.8(3)	C(19)-C(20)-C(21)	114.9(3)
C(22)-C(21)-C(20)	114.4(4)	O(2)-C(23)-C(24)	108.0(3)
C(23)-C(24)-C(25)	115.0(4)	C(26)-C(25)-C(24)	115.6(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Table 4. Anisotropic displacement parameters [$\text{Å}^2 \times 10^3$] for MC1.
The anisotropic displacement factor exponent takes the form:
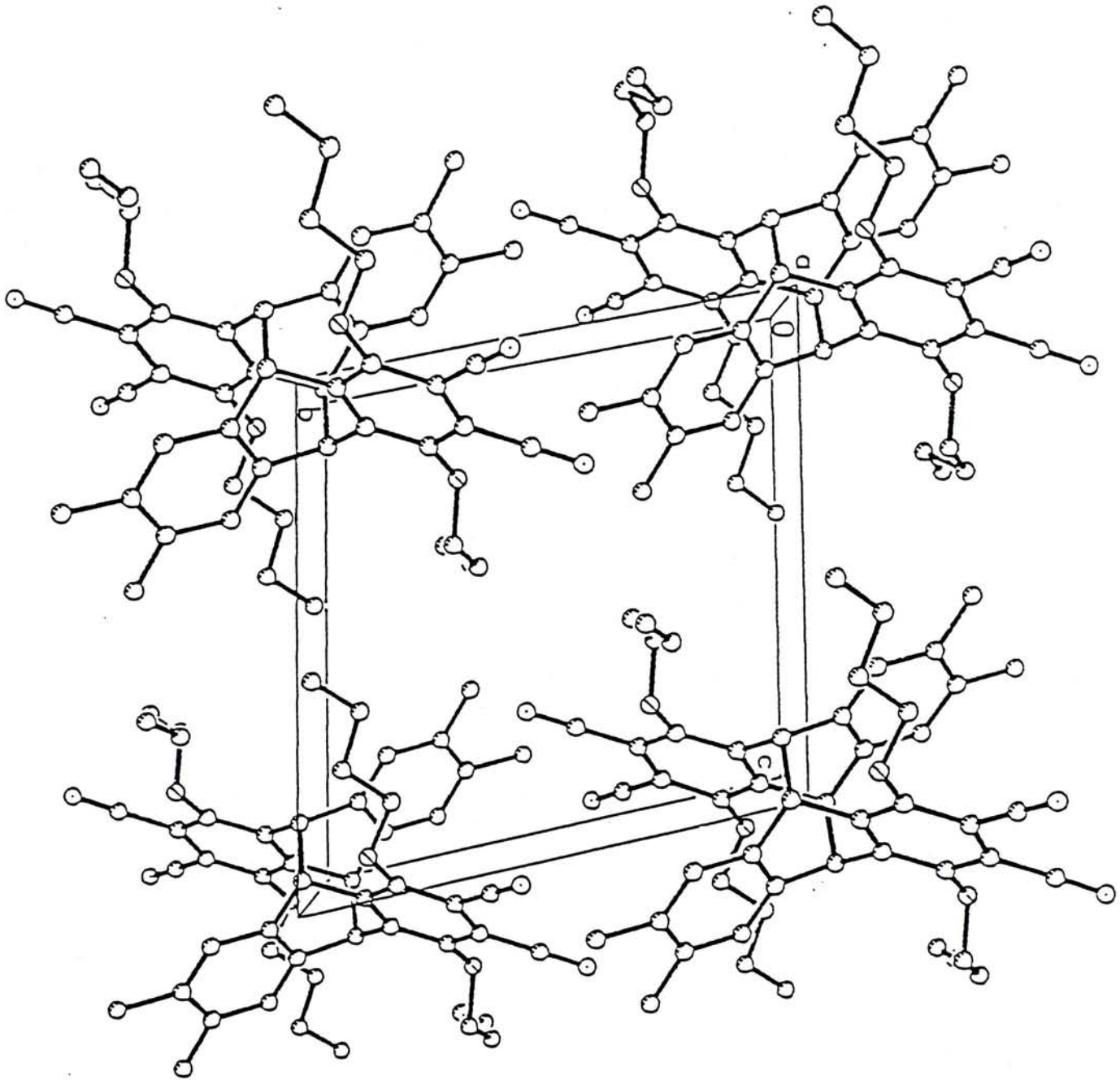$$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2hka^*b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
O(1)	72(1)	51(1)	52(1)	-10(1)	1(1)	-24(1)
O(2)	74(2)	65(1)	94(2)	-24(1)	22(1)	-28(1)
N(1)	93(2)	63(2)	104(2)	-2(2)	-14(2)	-14(2)
N(2)	79(2)	92(2)	119(3)	18(2)	5(2)	7(2)
C(1)	63(2)	48(1)	48(2)	-13(1)	-8(1)	-18(1)
C(2)	68(2)	47(2)	57(2)	-14(1)	-12(1)	-13(1)
C(3)	59(2)	56(2)	65(2)	-12(1)	-10(1)	-12(1)
C(4)	59(2)	57(2)	60(2)	-17(1)	-5(1)	-19(1)
C(5)	57(2)	44(1)	53(2)	-13(1)	-2(1)	-19(1)
C(6)	60(2)	51(2)	56(2)	-13(1)	-9(1)	-22(1)
C(7)	68(2)	51(2)	70(2)	-24(1)	-24(1)	-9(1)
C(8)	70(2)	57(2)	61(2)	-26(2)	-5(1)	-14(1)
C(9)	68(2)	58(2)	51(2)	-16(1)	-6(1)	-15(1)
C(10)	58(2)	42(1)	55(2)	-14(1)	-1(1)	-13(1)
C(11)	59(2)	46(1)	47(2)	-16(1)	-6(1)	-16(1)
C(12)	63(2)	46(2)	53(2)	-16(1)	-6(1)	-16(1)
C(13)	57(2)	47(1)	59(2)	-18(1)	-11(1)	-13(1)
C(14)	57(2)	49(2)	54(2)	-16(1)	-8(1)	-16(1)
C(15)	66(2)	56(2)	63(2)	-10(2)	-9(1)	-14(1)
C(16)	63(2)	66(2)	92(2)	-12(2)	-5(2)	-8(2)
C(17)	105(3)	78(2)	80(2)	-44(2)	5(2)	-18(2)
C(18)	91(2)	52(2)	91(2)	-26(2)	-21(2)	-18(2)
C(19)	86(2)	76(2)	55(2)	-12(2)	-1(2)	-21(2)
C(20)	96(3)	77(2)	61(2)	-4(2)	15(2)	-20(2)
C(21)	80(3)	97(3)	98(3)	-15(2)	9(2)	-18(2)
C(22)	93(3)	135(4)	138(4)	-40(3)	12(3)	-35(3)
C(23)	91(3)	96(2)	69(2)	-20(2)	13(2)	-33(2)
C(24)	89(3)	97(3)	86(3)	-3(2)	0(2)	-8(2)
C(25)	166(5)	173(5)	83(3)	-18(3)	17(3)	-53(4)
C(26)	197(6)	158(5)	110(4)	17(4)	50(4)	-56(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for MC1.

	x	Y	z	U(eq)
H(6)	1406(3)	2726(2)	235(2)	64
H(9)	-2082(3)	983(2)	2863(2)	70
H(17A)	-2913(4)	2678(3)	3781(3)	128
H(17B)	-2862(4)	3955(3)	2951(3)	128
H(17C)	-1657(4)	3343(3)	3856(3)	128
H(18A)	818(4)	4478(3)	1065(3)	113
H(18B)	339(4)	4257(3)	2440(3)	113
H(18C)	-881(4)	4902(3)	1553(3)	113
H(19A)	-222(4)	-2187(3)	3787(3)	87
H(19B)	793(4)	-3538(3)	4116(3)	87
H(20A)	-1621(4)	-3481(3)	5054(3)	98
H(20B)	-1254(4)	-4365(3)	4127(3)	98
H(21A)	-3103(4)	-1938(4)	3770(4)	114
H(21B)	-2675(4)	-2762(4)	2787(4)	114
H(22A)	-5072(5)	-2805(5)	3696(5)	181
H(22B)	-4444(5)	-3313(5)	4938(5)	181
H(22C)	-4014(5)	-4139(5)	3955(5)	181
H(23A)	4579(4)	-1868(4)	-1900(3)	102
H(23B)	6084(4)	-2294(4)	-1284(3)	102
H(24A)	6480(5)	-307(4)	-1962(4)	116
H(24B)	5026(5)	61(4)	-2624(4)	116
H(25A)	7576(7)	-1764(6)	-3207(4)	171
H(25B)	6152(7)	-1277(6)	-3908(4)	171
H(26A)	8070(8)	-469(6)	-4916(5)	249
H(26B)	8165(8)	113(6)	-3827(5)	249
H(26C)	6739(8)	598(6)	-4532(5)	249
H(10)	-1248(31)	-957(26)	2151(26)	55(7)
H(5)	2339(33)	804(24)	-555(24)	55(7)

Molecular packing of dimeric **118** down the b axis