

# Molecular Devices. Chiral, Bichromophoric Silicones: Ordering Principles in Complex Molecules

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**Abstract** The interaction of chromophores is proposed as a basis for the construction of devices with high complexity. Silicones are promising elements of structure to control the function of such devices.

## 1 Introduction

There is a demand in modern technology for IT devices with high speeds of operation and high integration. Moore's law [1] predicts a doubling of complexity for storage every two years and is one popular expression for the tendencies to increase the performance of devices concerning size and speed. One can ask if there is a natural limit for the speed of operation, what factors are limiting this speed and what type of devices are expected for such a technology.

## 2 Optical Technology

The speed of operation is interlinked with the properties of electromagnetic radiation at the corresponding frequencies. The frequencies of operation in modern IT devices have reached some GHz in the region of microwave radiation. A further increase would step to infrared radiation, visible light and so on; see Fig. 1.

Ionization is coming about as a novel problem with such an increase of operating frequencies; see Fig. 1. Only very special structures allow ionization in

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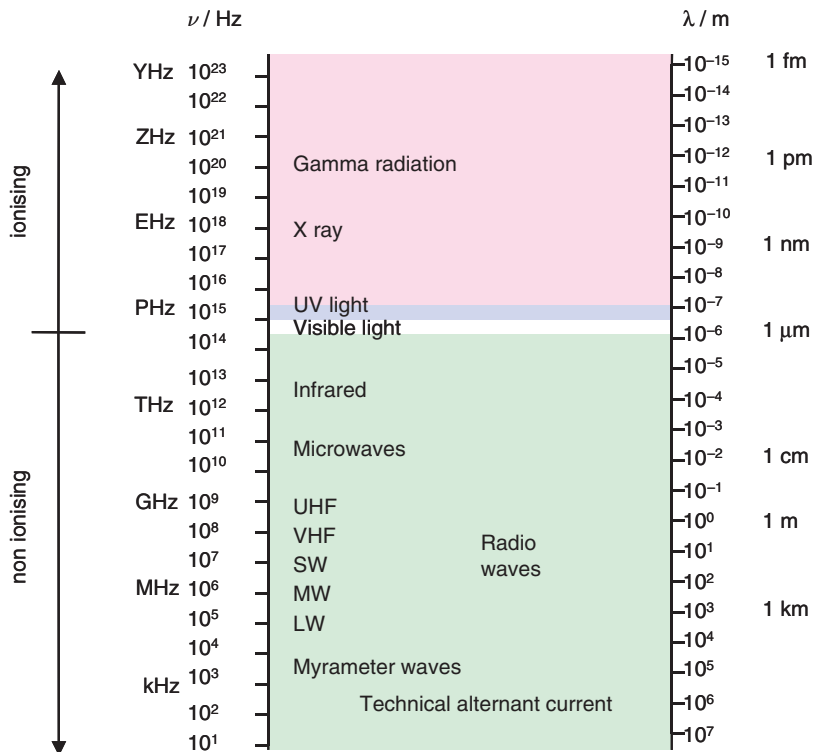


Fig. 1 Electromagnetic radiation (See also Plate 3 in the Colour Plate Section)



the near infrared and the visible so that this problem can be efficiently controlled. More and more chemical structures are becoming suitable for ionization with further increasing frequencies so that this process will finally become ubiquitary. Ionization will cause damage of materials. Such defects are becoming more and more important if increasing integration forces a diminishing of the size of operating structures. Thus, even small defects may cause a complete breakdown of the entire function. As a consequence, PHz operating devices (Petahertz,  $10^{15}$  Hz) are supposed to be a good compromise for high frequency of operation where problems concerning damage by ionization can be still controlled by suitable chemical structures and thus, may be the limiting technology for IT devices and should be targeted for future developments. Petahertz technology means the application of light; see Fig. 1.

The entire devices should be appreciably smaller than the wavelengths of radiation in order to concentrate the operation to one single device. The wavelength of light is in the order of half a micron and this corresponds to 500 nm and 5000 Å, respectively. Dimensions some magnitudes smaller can hardly be reached with conventional concepts in electronics. Thus, molecular devices are required for the construction of complex functional structures.

### 3 Molecular Devices for Optical Technology

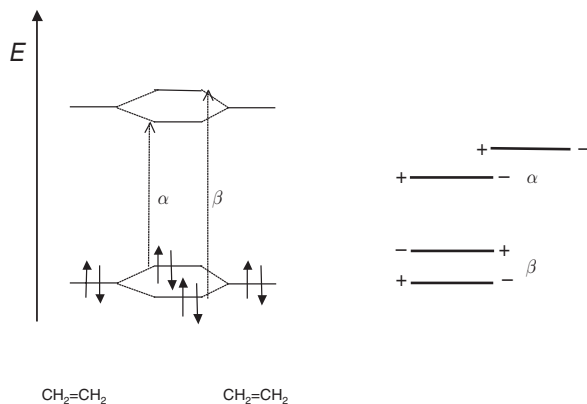
The components of electrical IT devices find their equivalents with elements of molecular structures for molecular devices; see Table 1. Macroscopic metallic conductors may be replaced by conjugated  $\pi$ -systems where electrons can be shifted because of delocalization. Many of the macroscopic concepts can still be retained because the wavelengths of light of the order of  $0.5\ \mu\text{m}$  correspond to macroscopic dimensions. However, the rules of quantum mechanics have to be applied to chromophores as molecular resonators; this will be the central item of this chapter. Molecular resonators, chromophores, are of special importance for molecular devices because of their ability to store energy and transfer it to other devices. A non fluorescent chromophore corresponds to a strongly damped resonator and a fluorescent chromophore to a slightly damped one being able to conserve the energy of excitation during the fluorescence lifetime and transfer it to other structures. Transistors are to be replaced by molecular switches for the transfer of energy [2,3]. It is important to avoid quenching of the energy transfer because this would terminate further processing of the energy of excitation. A coupling of chromophores will be of special importance for such processes and may be a promising concept for molecular processing and is the center of further treatment.

**Table 1** Macroscopic and molecular IT devices compared

IT Devices	Macroscopic devices	Molecular devices
		
<b>Conductors</b>	Metallic wires	$\pi$ -systems
<b>Resonators</b>	Resonating circuits	Chromophores
<b>Switching devices</b>	Transistors	Molecular switches

### 4 Coupled Chromophores: Bichromophores

The general interaction of two or more chromophores was theoretically treated by Kuhn [4] and Davydov [5,6], experimentally investigated by Scheibe [7] and Jelley [8] and clearly expressed by Förster [9]. A simplest example of two interacting  $\pi$ -systems is given for two molecules of ethylene in Fig. 2. Starting for each molecule with two  $\pi$ -orbitals, the HOMO electronically occupied and the LUMO not, leads to remaining four orbitals when interacting. However, the energetic levels are split so that two electronic transitions will result, one with lower energy ( $\alpha$ ) and the other with higher ( $\beta$ ) than the initial transitions. The energy of transition ( $E$ ) is interrelated with the wavelengths of absorption ( $\lambda$ ) by Einstein's equation (1).

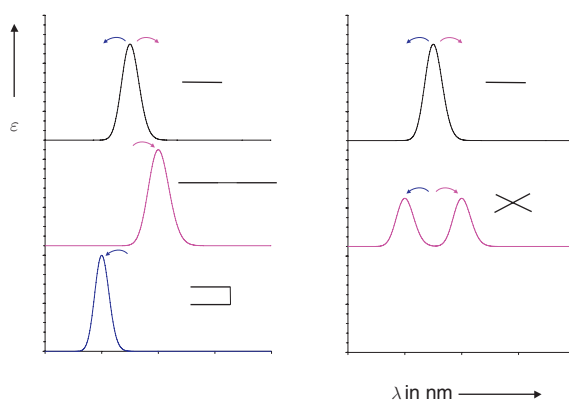


**Fig. 2** FMO of two interacting ethylene molecules (*left*) and orientation of transition moments (*right*) for two arrangements

$$E = h \cdot \nu = h \cdot c / \lambda \quad (1)$$

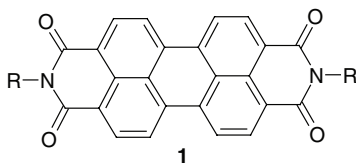
The orientation of the transition moments discriminates which of the transition is allowed and which one not. Only one transition is preferred for parallel arrangements of the moments according to Fig. 2, right, because of electrostatic interaction. The more hypsochromic  $\beta$  transition is allowed if the two moments are opposed, whereas the staggered arrangement will prefer the more bathochromic  $\alpha$  transition; see Fig. 3.

The characteristic splittings of the absorption by the exciton interaction shown in Fig. 3 are of interest both to control UV/Vis-spectra by the orientation of interacting chromophores and to monitor the orientation of molecular segments.



**Fig. 3** Splitting of UV/Vis absorption (*black line*) caused by various orientation of the transition moments in bichromophores. *Left side*:  $\alpha$  orientation (*light gray line*) and  $\beta$  orientation (*dark gray line*). *Magenta line on the right side*: Skew arrangement (See also Plate 4 in the Colour Plate Section)

A suitable building block is required for the construction of such complex structures of multichromophores.



## 5 Perylene Tetracarboxylic Bisimides as Building Blocks for Molecular Electronics

The perylene tetracarboxylic bisimides **1** [10, 11] exhibit unique properties such as high chemical and photochemical persistency as a prerequisite for complicated chemical synthesis and sufficiently long-term operating of functional structures. Moreover, there is only one electronic transition in the visible along the *N-N* connection line [12] that facilitates planning molecular functions. There are orbital nodes at the nitrogen atoms of **1** in HOMO and LUMO [13] making these positions suitable for linkage without interfering with operating functions. On the other hand, the energy of the electronic transition can be controlled with substituents at the aromatic core. This makes **1** an ideal component of complex functional structures.

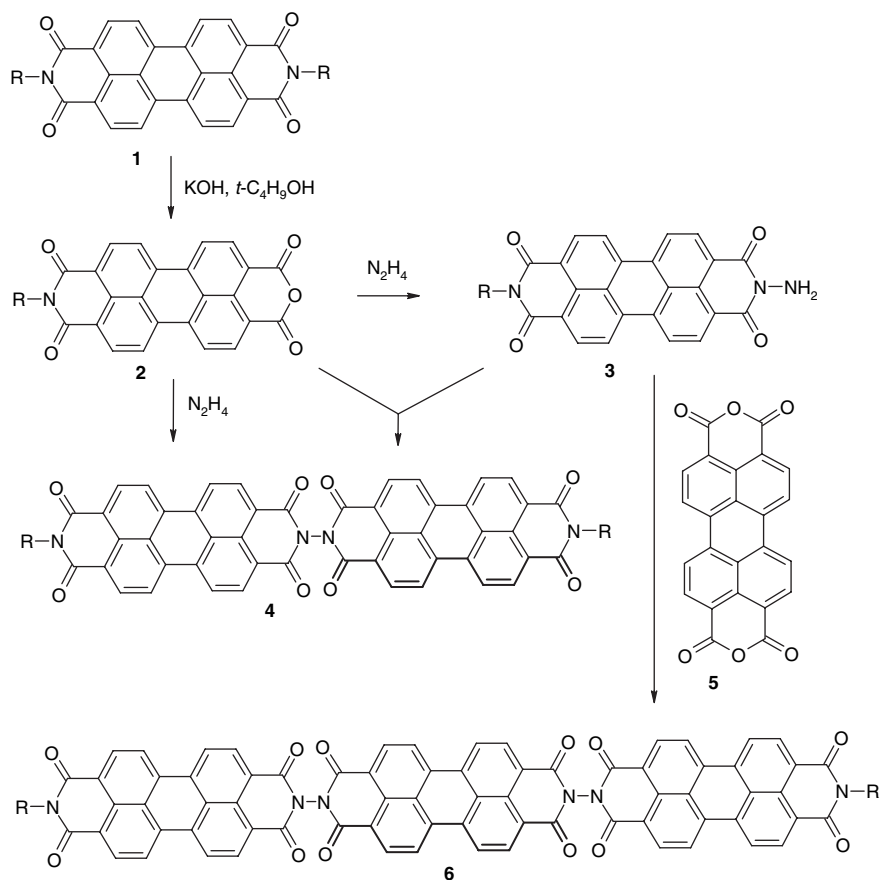
## 6 Linearly Arranged Multichromophores

Linearly arranged perylene bisimides [14] can be synthesized according to the reaction sequence of Scheme 1 where the starting material **1** was prepared from the technical perylene bisanhydride **5** and primary amines.

The low solubility of perylene carboxylic bisimides is a general obstacle for their application in homogeneous solution. This can be solved by the introduction of long-chain secondary alkyl groups (“swallow-tail-substituents”) [15, 16,17] to the nitrogen atoms such as R = 1-hexylheptyl.

The carboxylic bisimide **1** is partially hydrolyzed [18] to form the anhydride carboxylic imide **2** according to Scheme 1. The bichromophore **4** is directly formed from **2** and stoichiometric amounts of hydrazine, whereas an excess of hydrazine allows the preparation of the amino derivative **3**. A condensation of **2** with **3** is an alternative to prepare **4**. The trichromophore **6** is obtained from **3** and the bisanhydride **5**.

The UV/Vis absorption spectra of **1**, **4** and **6** are reported in Fig. 4 and show clearly the effect of coupling chromophores. A bathochromic shift is observed because of the preference of the  $\alpha$  transition according to Fig. 2. Moreover, there is an amplification of the absorption because the absorptivity of **6** exceeds the expected threefold absorptivity of **1** by far; see Fig. 4. The linear alignment of chromophores

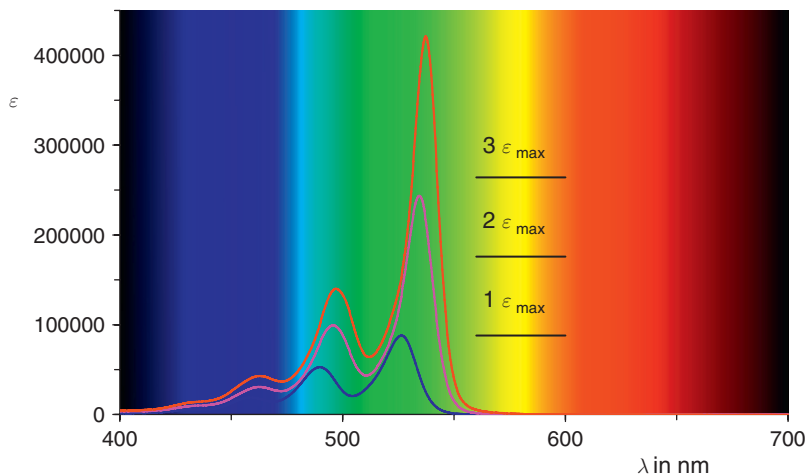


**Scheme 1** Syntheses of the bi- and trichromophoric perylene dyes **4** and **6**, respectively

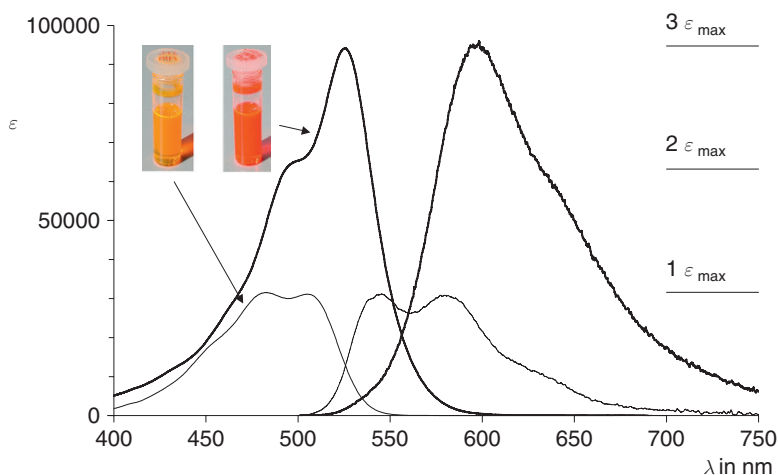
does not interfere with high fluorescence quantum yields because close to 100% is found for **6**. This experimental result is important for the construction of complex arrangement of chromophores where the preservation of the energy of excitation is a prerequisite for the processing of information.

## 7 Molecular Dynamics

Novel properties can be obtained with the combination of exciton effects with dynamic molecular processes such as for the coupling of the perylene derivative **7** to form the bichromophore **8**. **7** forms yellow fluorescent solutions [19] as is shown in Fig. 5. The coupling of two chromophores such as in **8** induces an appreciable increase of the absorptivity by exciton interaction; both

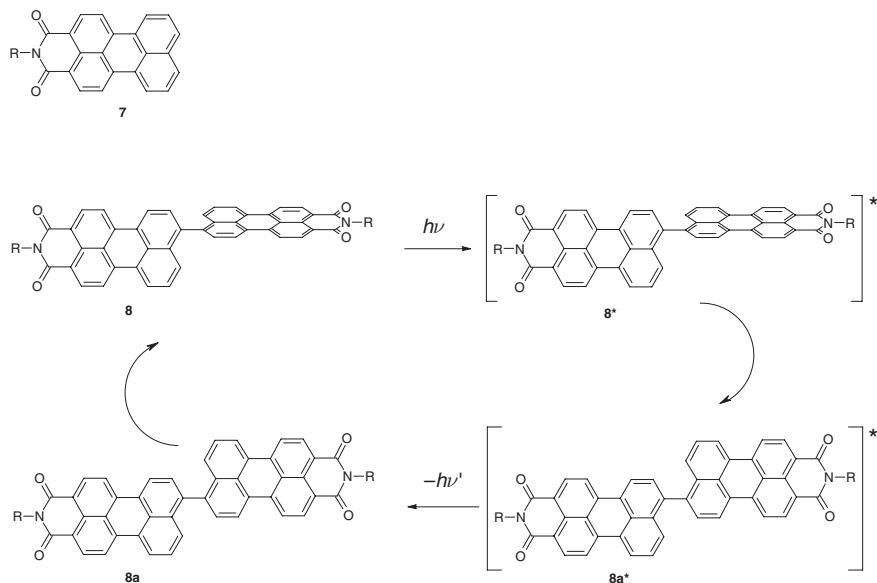


**Fig. 4** UV/Vis absorption spectra of **1** (blue), **4** (magenta), and **6** (red) in chloroform (See also Plate 5 in the Colour Plate Section)



**Fig. 5** UV/Vis absorption and fluorescence spectra of **7** (thin lines) and **8** (thick lines) in chloroform (See also Plate 6 in the Colour Plate Section)

chromophores arrange with orthogonal  $\pi$ -systems because of steric interactions; see Scheme 2. The absorption of light is a vertical transition so that the geometry remains unchanged in **8\*** that relaxes subsequently to the more stable arrangement of **8a\***. This causes a bathochromic shift concerning the fluorescence to the unfavorable ground state **8a** that relaxes to the initial structure **8**. This cyclic process causes an increase of the Stokes' shift and a brilliant, intensely red fluorescence; see Fig. 5.



**Scheme 2** Perylene-3,4-dicarboxylic imides **7** and molecular dynamics of the bichromophore **8**

## 8 Chirality

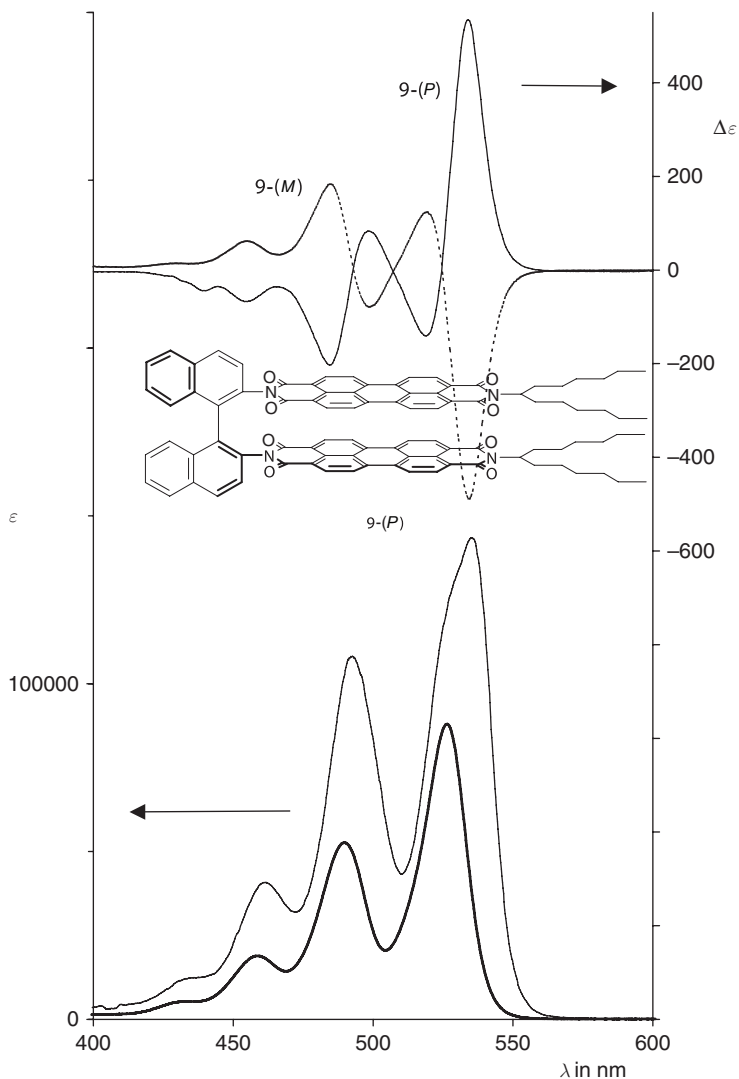
Even more complex functionalities can be established with chiral functional units. There is a very pure  $\pi\text{-}\pi^*$  transition of **1** in the visible. As a consequence, no CD effects are observed in the visible for chiral aliphatic substituents R. This allows the construction of complex chiral structures without interference with the optical properties of **1**.

However, very strong CD effects are introduced by exciton interactions for interacting chromophores in chiral arrangements such as for the axial chiral [20] dyes [21] **9-(P)** and **9-(M)**; see Fig. 6. Both enantiomers of **9** exhibit high fluorescence quantum yield and ellipticity of even circularly polarized light is expected in such arrangements of chromophores. Their orientation in space can be generally controlled by attached molecular segments such as the axially chiral binaphthyl unit in **9**. Silicones are therefore of special interest because of their unique type of interactions with other structures.

## 9 Silicones as Element of Structure for Controlling Intramolecular Interactions

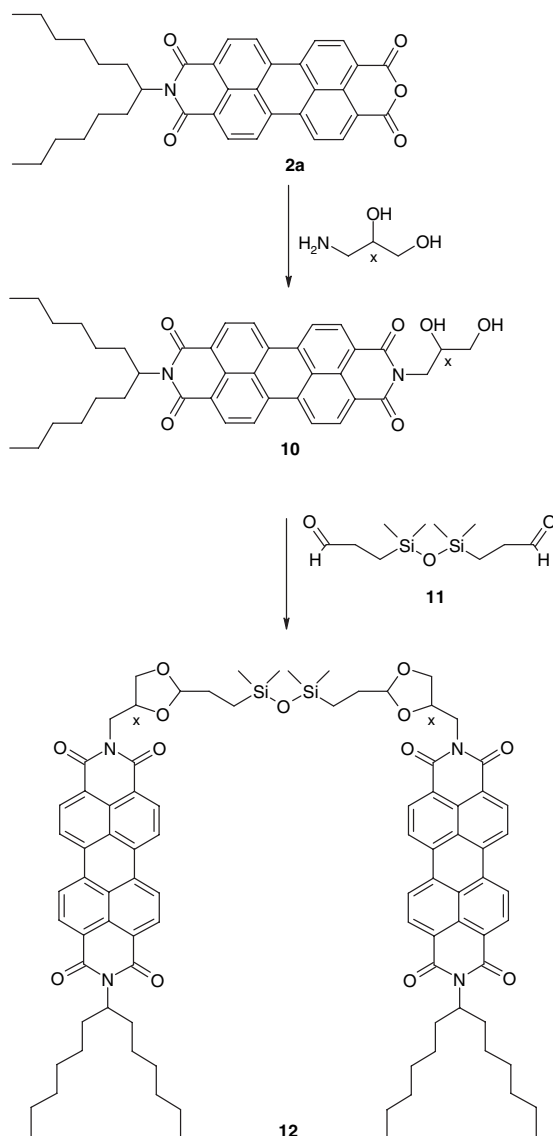
The linkage of two chromophores with a silicone spacer is an attractive concept for establishing a complex arrangement because the shape of such a linker will determine the orientation of the terminal chromophores in space and thus,





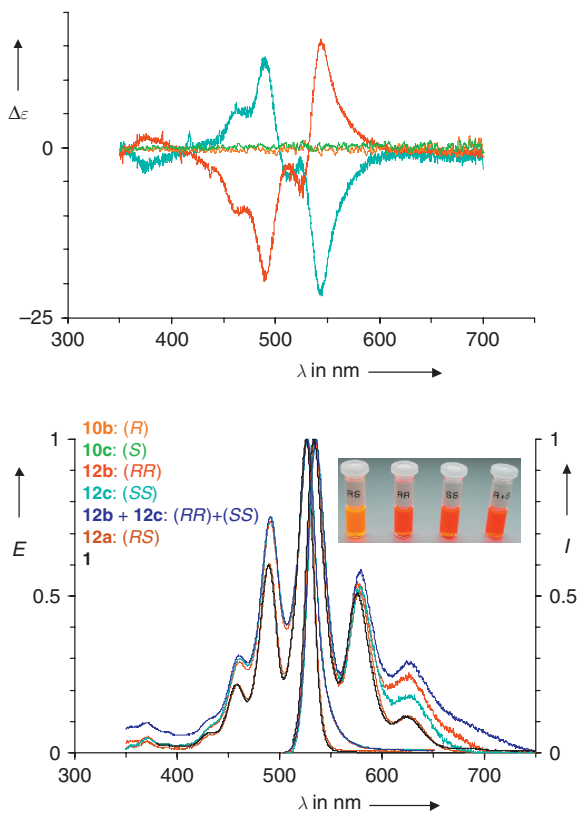
**Fig. 6** UV/Vis absorption spectrum of **9** (*thin, lower line*) compared with **1** (*thick line*) in chloroform. Upper lines: CD spectra of the enantiomers of **9**

control exciton interactions. Therefore, the perylene anhydride carboximide **2a** was condensed with the chiral 2,3-dihydroxy propyl amine to form the chiral dye **10** with a terminal diol group; see Scheme 3. This can be further condensed with the silicone dialdehyde **11** to form the bichromophoric dye **12** [22, 23]. The control of the stereochemistry of **12** proceeds very efficiently because the *meso* diastereomer **12a** is formed exclusively from the racemic diol (less than 0.4% racem form). Identical UV/Vis absorption and fluorescence spectra of **12a**



**Scheme 3** Synthesis of the chiral silicone perylene bichromophores **12**

and **1** exclude exciton interaction; see Fig. 7. A completely different behavior is exhibited by the pure enantiomers **12b** (*RR*) and **12c** (*SS*), respectively, where exciton interactions not only alter the vibronic structure of the absorption spectra but also the fluorescence spectra from yellow to red so that even a visual discrimination becomes possible to decide if the starting material **10** was a pure enantiomer or a racemate. Moreover, even an artificial racemate formed from equimolar amounts of **12b** and **12c** exhibit the absorption spectra of the

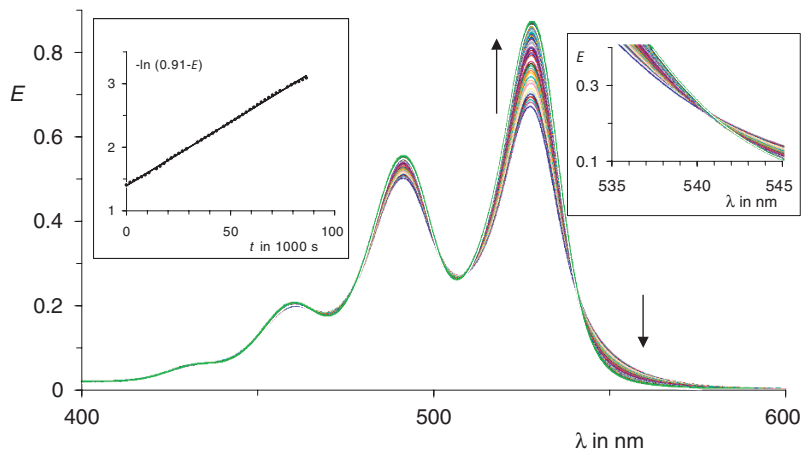


**Fig. 7** Bottom: UV/Vis absorption (*left*) and fluorescence spectra (*right*) in chloroform. Blue: 1:1-Mixture of **12b** and **12c**, red: **12b**, turquoise: **12c**, brown: **12a**, black: reference of standard perylene dyes (**1**). Top: CD spectra of **12b** (red) and **12c** (turquoise) in chloroform and negligible CD effect of the enantiomers **10b** (orange) and **10c** (green) (See also Plate 7 in the Colour Plate Section)

pure enantiomers (**12b** + **12c**). However, a complete transformation proceeds to the *meso* form **12a** if a catalytic amount of acid is added to this racemate (**12b** + **12c**); see Fig. 8. This reaction proceeds precisely with first order and the isosbestic point at 541 nm indicates the exact stoichiometry of this reaction. Thus, the molecular shape seems to be dominated by the silicone backbone, whereas the interactions of chromophores seem to be of minor importance.

## 10 Conclusion and Outlook

The spectral properties of **12** indicate a controlling of the shape of silicones across a rather large molecular distance. Remarkably, there are no rigid rings in this type of backbone such as commonly applied in carbon chemistry. This makes silicones



**Fig. 8** Change of the UV/Vis spectra by the acid-catalysed transformation of a 1:1 mixture of **12b** and **12c** into **12a**. Right insert: amplification of the region of the isosbestic point at 541 nm. Left insert: kinetic analysis of the transformation according to pseudo first order at 527.2 nm (See also Plate 8 in the Colour Plate Section)

interesting structures for the construction of the backbone for complex functional materials. On the other hand, silicones can be efficiently prepared by the condensation of silanol units. Furthermore, a broad variation is possible to construct complex structures by the combination of such sub units. This is expected to be a good prerequisite for future developments.

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