

INTERNATIONAL Convention on Colorants - 2009

The Club, Andheri (West), Mumbai - 5th and 6th February 2009



Novel Functional Dyestuffs Constructed by Interacting Chromophores

Heinz Langhals
University of Munich

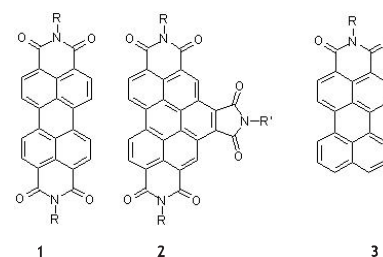
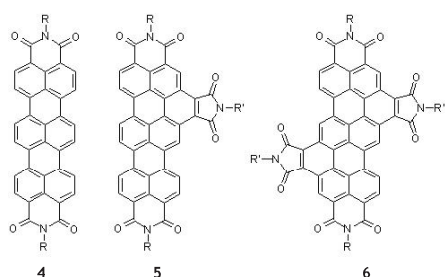
Heinz Langhals studies chemistry at the University of Munich, Germany. He is a Bachelor in Chemistry at the University of Münster; A Diploma in organic chemistry at the University of Münster; A PhD in organic chemistry at the University of Freiburg; A Post doctorate at Ecole Normale Supérieure in Paris and a Post doctorate at the University of Zürich/Switzerland. He is a recipient of the Liebig scholarship.

A Professor of organic and macromolecular chemistry at the University of Munich, Germany, he did a stint in Research at Bingmayong-Museum in Lintong, China on the "Conservation of the polychromy of the first Chinese emperor's terracotta army." His research interests include Organic chemistry; dye chemistry; preparation and investigation of highly stable fluorescent dyes; reaction mechanisms; rearrangements, solvent effects, polar properties of solvent mixture; analytics: water determination, fluorescent market, fluorescent immunoassays; polymer chemistry and polymeric natural products



ABSTRACT

Chromophores are the working units for the interaction of light with matter both for traditional applications such as textile dyes and modern functional applications. One single chromophore is conventionally applied for both types of applications. However, an even larger manifold would be obtained with two or more interacting chromophores. The properties of such assemblies are expected to be additive for simple cases. However the interaction of the components may enable completely novel properties in terms of optical molecular machines. The transfer of energy between the components may a key process for their novel functionalities. Thus, fluorescent chromophores are of special interest for the construction of such interacting functional units because they are able to preserve the energy of excitation for processing.



Chromophores are commonly built by an accumulation of aromatic or hetero aromatic structures where the solubility will be decreased with growing size of such structures. This problem becomes even worse for multichromophoric arrangements. The low solubility is an obstacle for synthesis, investigation and many applications and can be overcome by the attachment of solubilising groups. We found that tert-butyl groups cause an appreciable increase in solubility and an even stronger effect of increasing the solubility is given by the application of long-chain sec-alkyl groups ("swallow-tail" substituents) such as R = 1-hexylheptyl. The application of the similar isopropyl group is an alternative, however, may be more easily degraded by radical reactions; compare the technical Hock process.

INTERNATIONAL Convention on Colorants - 2009

The Club, Andheri (West), Mumbai - 5th and 6th February 2009

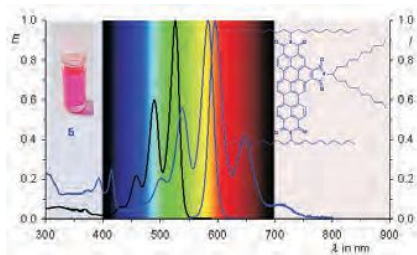


Fig. 1: UV/Vis absorption and fluorescence spectra of 5 in chloroform compared with 1.

hypsochromically shifted with respect to 1.

An extension of 1 in the peri position leads to the terrylene tetracarboxylic bisimides 4, however, the fluorescence quantum yield drops to 60%. A lateral extension of 4 to 5 and 6, respectively, re-establishes fluorescence quantum yields of close to 100%; see Figure 1. The building blocks 2, 3, and 5 are of special interest for the construction of complex chromophoric

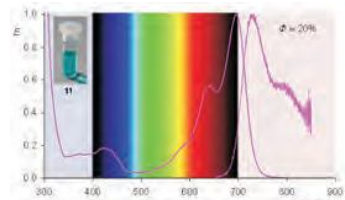


Fig. 2: UV/Vis absorption and fluorescence spectrum of 11 in chloroform

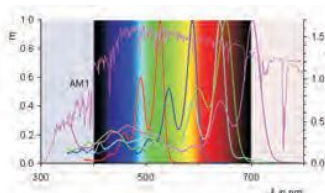
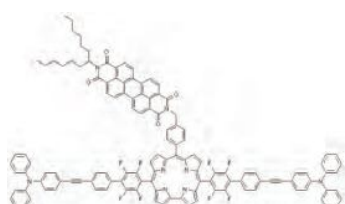
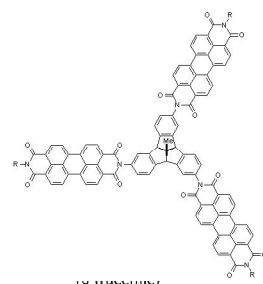


Fig. 3: UV/vis spectra of novel perylene dyes and Am1 solar radiation



15



10 (micelles)

structures because they can be easily mono functionalised. The lateral extension of 1 is a further possibility for a bathochromic shift in the absorption. We started synthesis with the anthracene derivative 7 where firstly the preparation procedure was improved and secondly the novel photo dimerization of 7 to form 8 and 9 was found. This reaction is not only important for the use of the 7 as highly fluorescent yellow dye (100%), but also for therapy of cancer because derivatives of 7 are used as anti tumour agents with the medical name Azonafides. The treatment with these agents without further precautions make the therapy insecure because of arbitrary dose as a consequence of efficient photo dimerization even by ambient illumination.

The coupling of 7 under strongly alkaline conditions forms the aceanthrene derivatives 10 and 11 with strongly bathochromically shifted absorption forming green solutions; see Figure 2. The dimethyl derivative 12 could be prepared by the alkylation of 11.

A further development of the extension of the structure of 1 leads to a whole series of novel strongly fluorescent dyes covering the whole range of the visible; see Figure 3.

Anchor groups were attached to the previously reported chromophores such as diols, aldehydes and agents for the 1,3 dipolar cyclo addition. This type of derivatives may be applied for fluorescence labelling, for example for natural products such as 13 and 14 and for the construction of complex multichromophoric systems.

The interaction of identical chromophores can cause strong exciton effects and very intensely absorbing dyes can be constructed. Multichromophores with different components are systems where Foerster-type energy transfer and

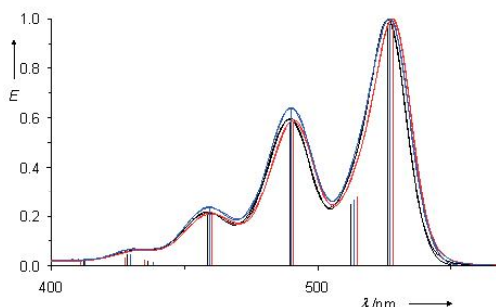
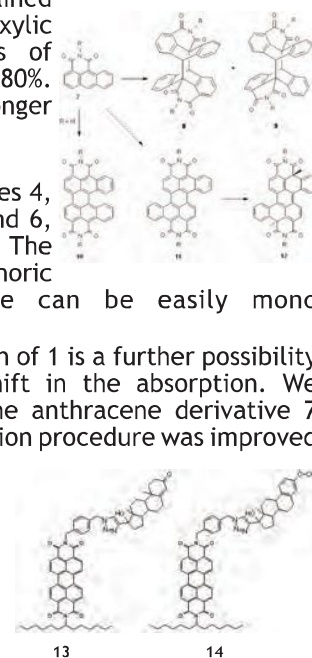


Fig. 4: UV/Vis spectrum of 16 (red line) compared with an isomer (blue line) and 1 (black line); bars: Gaussian analyse of the spectra.



13

14

INTERNATIONAL Convention on Colorants - 2009

The Club, Andheri (West), Mumbai - 5th and 6th February 2009

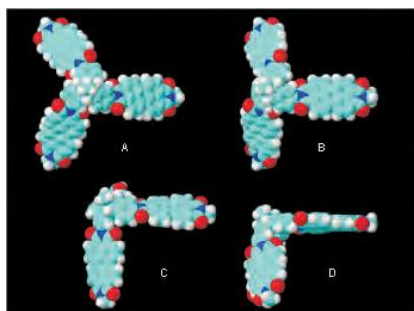


Fig. 5: Arrangement of chromophores in 16 calculated by the AM1 method.

electron transfer can proceed such as in the dyes 15. Both energy and electron transfer are of interest for light collection and charge separation and this is of interest for the collection of solar energy.

Exciton interaction between chromophores is well investigated both experimentally and theoretically and is going to become a key tool in Biochemistry. However, the orientation of the components did not obtain attention. On the other hand, both exciton interaction and energy transfer should be switched off for orthogonally arranged transition moments in dyes. The transition moment is parallel to the N-N-connection line in 1 and the connection line for the six-membered rings in 2. We applied tribenzotriquinacene as a Cartesian framework and arranged three chromophores of 1 orthogonally to form 16. This arrangement could extinguish exciton interactions because the UV/Vis spectrum 16 is congruent with the spectrum of 1; see Figure 4, red line. The calculated geometry of 16 is shown in Figure 5.

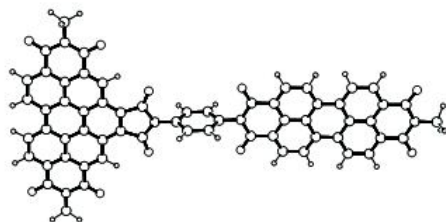


Fig. 6: Geometry of 17 calculated by the AM1 method.

Orthogonal identical chromophores are of interest for the investigation of exciton interactions. Foerster-type energy transfer (FRET) can be more efficiently studied if different chromophores are arranged orthogonally. Thus we combined 1 with 2 to form 17 where the transition moment of the two chromophores are orthogonally fixed because of the stiff tetra methyl phenylene spacer.

One might expect an extinguishing of a FRET in 17 by the orthogonality. Surprisingly fluorescence with close to 100% quantum yield was observed of the sub unit 1 if the sub unit 2 in 17 was irradiated; see Figure 6. This was interpreted in terms that the FRET energy transfer was interrelated with a bending vibration. Novel possibilities are expected on the basis of the knowledge of this mechanism.

Multichromophoric dyes are expected to open a manifold of possibilities were some basic concepts and results are overviewed in this review. The knowledge about the effects caused by the interaction of chromophores allows the construction of highly intense dyes, light-driven molecular machines or systems for the collection and conversion of solar energy.

Perylene dyes (1) are interesting building blocks for more complex structures because of their high chemical and photochemical stability, high fluorescence quantum yield, and low toxicity. We have altered this basic structure for obtaining components for other spectral regions.

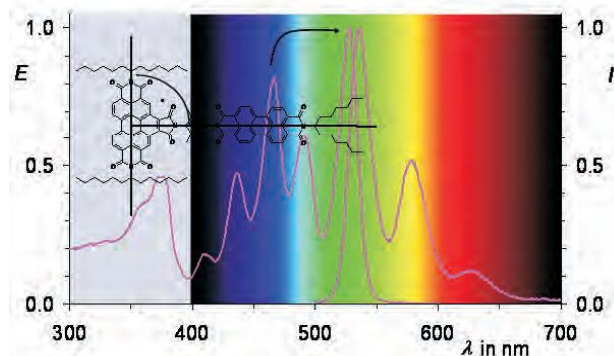
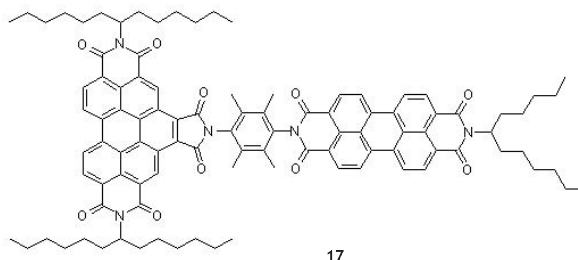


Fig. 6: FRET in the orthogonally arranged bichromophore 17.