Macromolecules and Chromophores. Novel Possibilities by the Architecture of Complex Molecular Structures

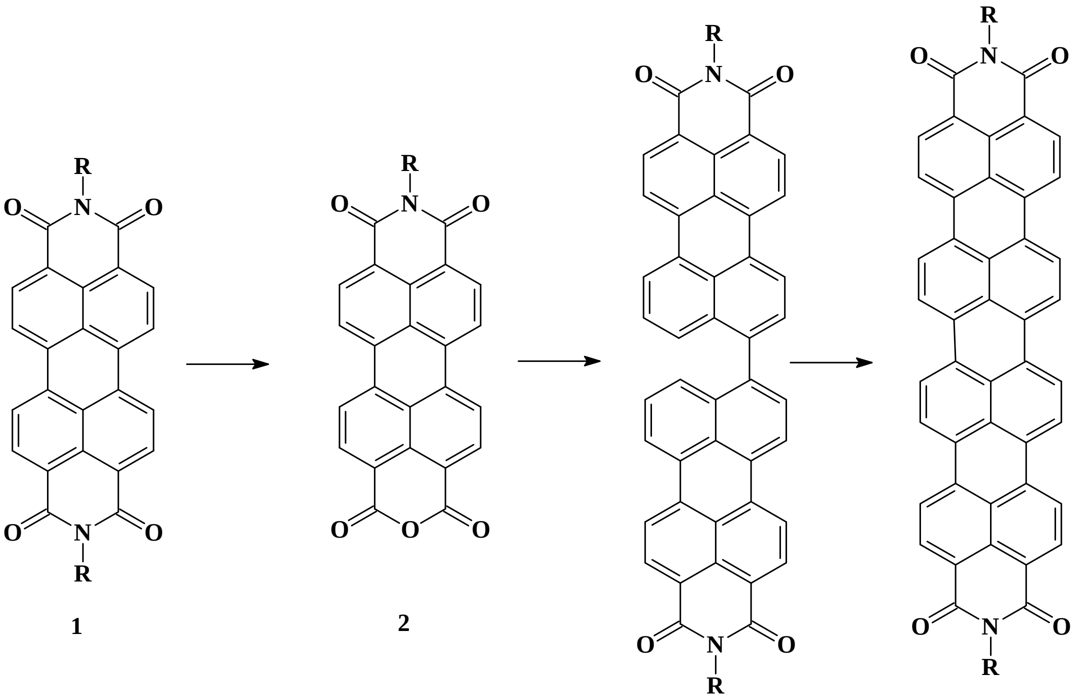
H. Langhals
LMU Munich, Department of Chemistry and Biochemistry
Butenandtstr. 5-13, D-81377 Munich, Germany

Introduction

Colour generating structures – chromophores – are commonly realized with monochromophoric compounds such as, for example, traditional applications in textile dyes and pigments. The molecular periphery of well-established chromophores is often altered for the novel applications of dyes. These are adapted to the individual requirements. However, the possibilities of chromophores are not exhausted by far in this way. An appreciably larger range is formed by multichromophoric systems where the interactions of chromophores allow to expect special optical effects. Such effects may be of interest for modern high technology- applications. The necessity of increasing integration and complexity of electronic devices exceeds even nano technology and requires pico meter dimensions. Therefore, molecular structures of devices are targeted. On the other hand, the increasing complexity requires increasing operating frequencies so that the spectral region of visible light with about 500 THz becomes targeted. Thus, chromophores are operating units which far exceed the electronic devices of today. Many chromophores have to be exactly oriented in space for such devices so that macromolecular dimensions are obtained. Therefore, suitable molecular building blocks and synthetic methods have to be developed.

Building Blocks

Very stable molecular building blocks are required for the synthesis of complex molecular architectures because they must be tolerant concerning various synthetic methods. The perylene dyes **1** are of special interest as basic structures because they possess not only extraordinarily high chemical and photochemical stability, but also high fluorescence quantum yields so that the energy of optical excitation will be preserved for processing on the molecular scale. An alteration of the basic structure of **1** makes the whole visible region accessible until the near infrared; see, for example, dyes **1-4.**

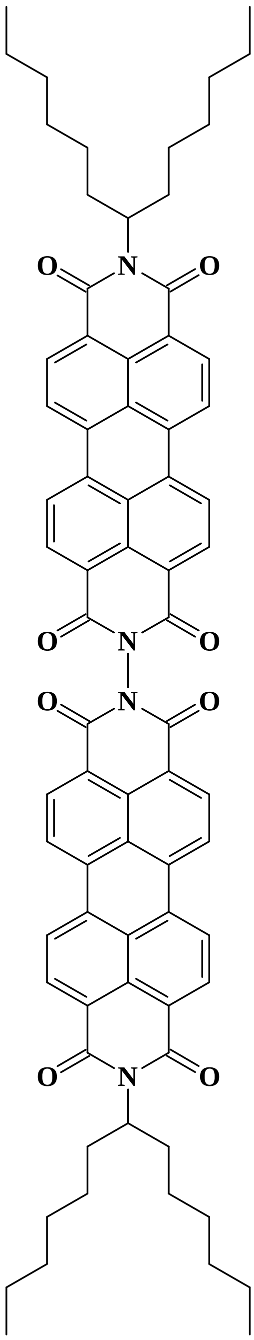


1 2 3 4

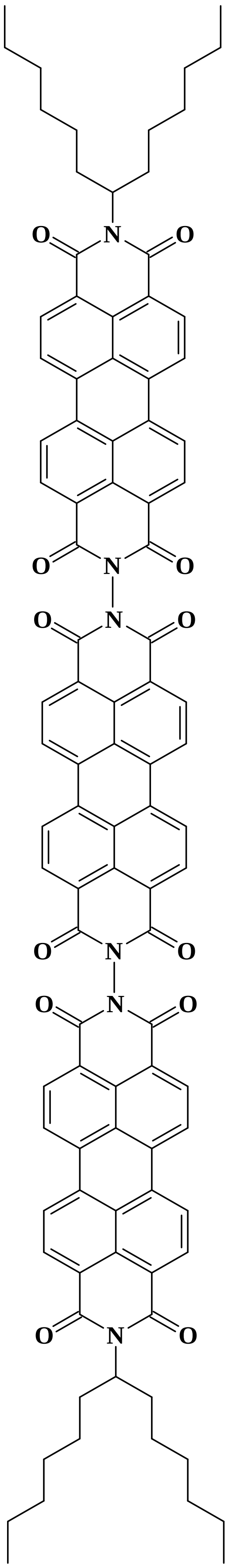
The nitrogen atoms in **1-4** are ideal positions for bonding to larger functional units because they are easily accessible by chemical synthesis and because of orbital nodes at these positions in HOMO and LUMO so that the optical properties of the chromophore remain unaltered by the further molecular construction.

Multichromophoric Dyes

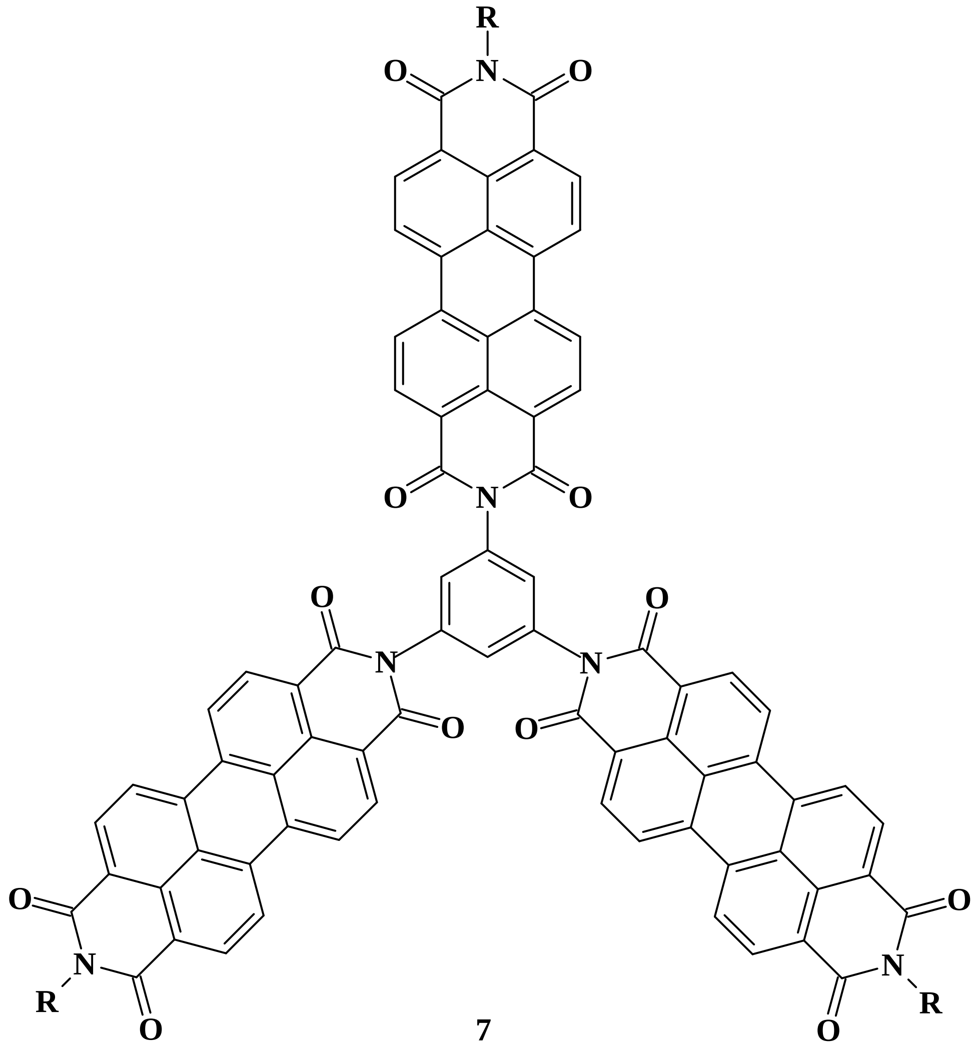
The interaction of chromophores causes exciton effects and results in functional dyes with special properties **5, 6, 8.** The linear alignment of chromophores such as in **5** and **6** results in an amplification of the molar absorptivity so that highly intense dyes will be obtained, where the molar absorptivity of **6** exceeds 420 000 L·mol-1·cm-1. Special effects are also observed for ring-type arrangement of chromophores such as in **7** and **9**. These simulate the natural light harvesting systems.



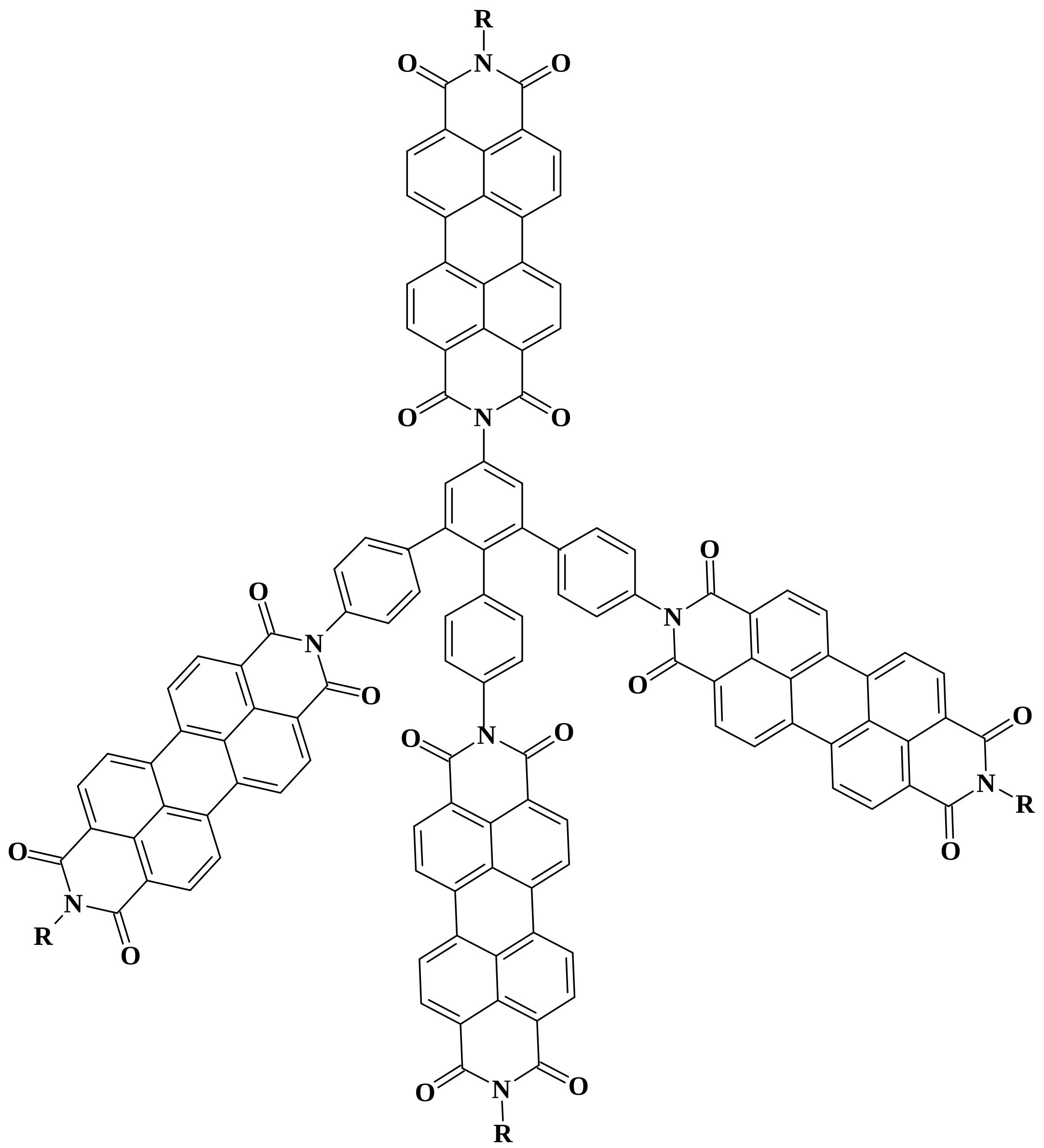
5



6



7



8

A tetrahedral arrangement of chromophores such as in **8** is not realized in nature, The special optical properties of this arrangement makes it of interest for the collection of diffuse radiation of light and makes it of interest for solar energy systems.

Picotechnology

Possibilities for the controlling of energy transport on the molecular scale were investigated with bichromophoric dyes. To this end, a non fluorescent anthraquinone unit with an absorption at short wavelengths was linked to a highly fluorescent perylene unit with light emission at lower energies. The arrangement in OETa exhibits the expected spectroscopic behaviour where an optical excitation of the anthraquinone unit does not cause fluorescence because an energy transfer cannot compete with the loss of energy of excitation. However, if the anthraquinone chromophore is turned by chemical synthesis to the arrangement of **OETb**, energy transfer proceeds so fast that the perylene unit becomes highly fluorescent even if the anthraquinone unit is optically excited. This demonstrates that **o**riented **e**nergy **t**ransfer is possible even on a molecular scale. This is the experimental basis of a novel type of optical switching devices because the energy of excitation is preserved whereas in other known molecular arrangements the energy of excitation was lost by quenching so that no further processing will be possible. The dimensions of the novel device are picometer scale so that pico technology was established beyond nano technology.

Macromolecular Dyes

The covalent linkage of chromophores with the main chain of polymers as a backbone is a good prerequisite for the construction of complex molecular architectures. Perylene dyes have been incorporated into the main chain of such polymers. However, the properties of such chains are appreciably altered by the dye units. As an alternative, the main chain is left unchanged and the dyes are linked to the side chains. Thus, highly fluorescent materials with a controlled incorporation of the dye are obtained. These are not only materials with special properties, but such arrangements are basic structures for molecular signal processing devices.