



ABSTRACT

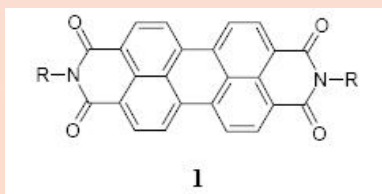
NOVEL PERYLENE AND NAPHTHALENE FLUORESCENT DYESTUFFS BY CONTROL WITH PERIPHERAL SUBSTITUENTS

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Session 4: Paper 3

Introduction

Chromophores are the chemical key structures for the interaction matter with light. This is important both for application in aesthetics such as for textile dyes and for functional applications, even for high technology applications. It will be shown how the properties of one and the same chromophore can be controlled and varied in wide limits by peripheral groups. A second interacting chromophore will further multiply the possible variations of such materials. Suitable chromophores are required for such novel developments.



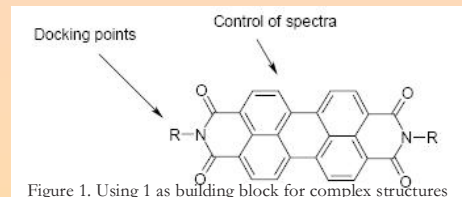
Perylene Dyes

Perylene dyes [1] are well established as high performance pigments. Industrial applications were concentrated in this field. However, the extraordinarily high photo stability, chemical and thermal persistency and low toxicity of the bisimides

[1] are good prerequisites for an even wider field of applications. Such developments were delayed by the low solubility of the derivatives of [1] being a severe handicap for investigations. Thus, the strong fluorescence of [1] remained unrecognised for more than forty years after the first synthesis. This situation completely changed with the development of solubility increasing groups and a manifold of novel applications was opened for [1] such as solar energy applications.

Solubility Increasing Groups

The solubility of [1] could be increased with the attachment of tert-butyl aryl groups to the positions of R. The similar iso-propyl group was developed later on as an alternative. An even more pronounced solubilising effect by long-chain sec-alkyl groups ("swallow-tail" substituents) such as R = 1-hexylheptyl (1a) was found seven years later. This allowed not only the synthesis of readily soluble perylene dyes, but also the construction of more complex structures with one or more perylene bisimide unit as the building blocks.



The Control of Properties by Attached Groups

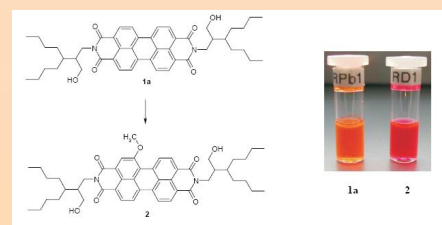
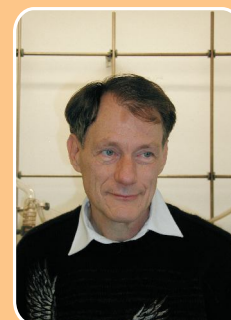
The perylene bisimides 1 exhibit nodes in the orbitals HOMO and LUMO at the nitrogen atoms.

Thus, these are ideal docking positions for the construction of complex structures or the control of physical properties such as solubility without influencing light absorption. On the other hand, the UV/Vis spectra can be controlled by the attachment of substituents at the perylene core; see Figure 1. The perylene dyes

with long-chain sec-alkyl groups such as [1a] are very resistant against acid conditions such as concentrated sulphuric acid and even appreciably strong bases. However, a severe attack of concentrated, strong bases causes a slow hydrolyses. Alternatively, a similar reaction with powerful nucleophiles results in a novel-type ring contraction reaction of the carboxylic imide.

Surprisingly, alkyl substituents R with hydroxy groups in γ -position protect the carboxylic imide groups completely against bases or nucleophiles. Thus, novel reaction pathways become accessible for [1] such as a nucleophilic substitution reaction of the aromatic core with methoxide analogously to the Tschitschibabin reaction. The methoxy derivative [2] can be prepared from [1b] and exhibits a brilliant red fluorescence.

Heinz Langhals studied chemistry at the University of Münster; Germany. He is a Bachelor in chemistry at the University of Münster. He is a Diploma in organic chemistry at the University of Münster. He is a PhD in organic chemistry at the University of Freiburg. He is 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. He is 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 mixtures; analytics: water determination, fluorescent marker, fluorescent immunoassays; polymer chemistry and polymeric natural products.



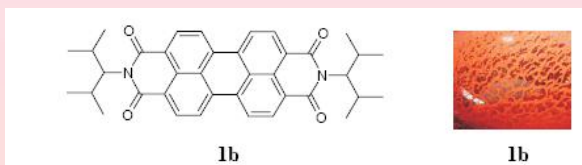


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Highly Fluorescent Pigments

The interaction of chromophores induces special optical effects and is a consequence of the molecular arrangement in the crystalline pigments. This is organized by the substituents R in [1]. The N-substituents in [1b] cause special packing in the crystal with the consequence of a very intense solid-state fluorescence. The crystal structure of [1b] could be solved with X-rays and demonstrates the special arrangement of chromophores. The small Stokes' shift of [1b] in the solid-state is a prerequisite for the development of devices for cooling with light.

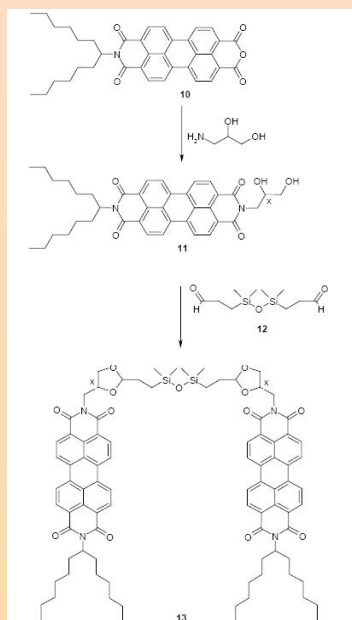


Dyes by Naphthalene Bisimides

The naphthalene bisimides [6] are the smaller homologous of [1] and can be prepared by the condensation of primary amines with [3]. The carboxylic bisimides [6] with aliphatic substituents R are colorless materials in contrast to [1]. Thus, the carboxylic bisimides [6] cannot be applied as dyes; however, they are useful and efficient UVA protecting materials. This is of special interest because of the low toxicity of the material. The absorption of naphthalene carboxylic imides [6] can be shifted into the visible by the exchange of carbonyl oxygen atoms by imino groups such as in [4] and [5] or in the unsymmetrically substituted dye [7]. A novel exchange reaction was developed for the synthesis of the latter. The donor groups induce an even more pronounced bathochromic shift in [8]. Such naphthalene derivatives are interesting building blocks for the synthesis of multichromophoric dyes.

Bichromophoric Silicones

Novel optical effects are expected as a consequence of the interaction of two or more chromophores. We applied a silicone backbone for novel bichromophoric perylene dyes. Thus, the anhydride-carboxylic imide [10] was condensed to form the diol [11] and further allowed to react with the dialdehyde [12] to form the bis-acetale [13]. The properties of this bichromophore are remarkable because racemic [11] forms exclusively the meso form of [13] where no exciton interaction can be detected. Thus, the well-known purple light absorption and yellow fluorescence of [1] is also observed for [13]; see Figure 2, [13] RS. A completely different behaviour is found for the pure enantiomers (13 RR and SS, respectively) where pronounced exciton interactions turn the colour into red.



The exciton interaction indicates a P-chiral arrangement of chromophores for the RR enantiomer. The interaction of chromophores must proceed intramolecularly because an artificial racemate prepared by a 1:1 mixture of the enantiomers exhibits the spectra of the pure enantiomers; [13] R+S. However, such an arrangement suitable for exciton interaction is energetically disfavoured because the addition of acid as a catalyst converts the racemate [13] R+S into the meso form [13] RS. The unusual behaviour of [13] and [1b], respectively, indicates how the properties of dyes can be tuned by the interacting of chromophores. This may be applied both to homo and hetero bichromophoric dyes and is expected to be of importance for future developments.

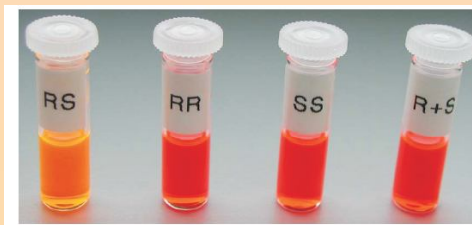
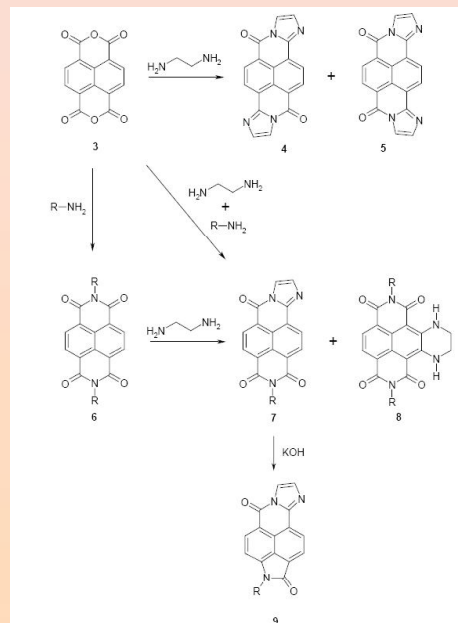


Figure 2. Bichromophoric dyes [13] in chloroform. From left to right: The meso form (RS) the racemate of [11], the pure enantiomers (RR and SS) and an artificial racem form (R+S).