REVIEW

Control of the Interactions in Multichromophores: Novel Concepts. Perylene Bis-imides as Components for Larger Functional Units

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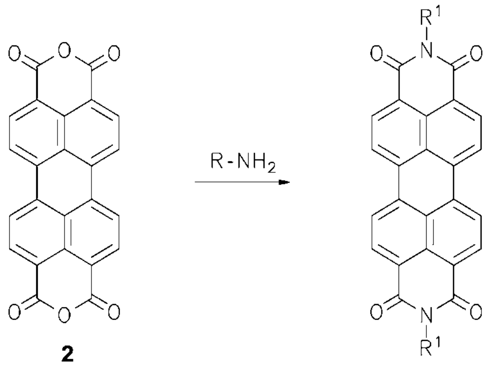
Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

The controlling of the internal interaction in multichromophores leads to functional dyes with novel properties. Such a controlling is demonstrated with perylene dyes and offers a manifold of novel possibilities.

1. Introduction. – Chromophores are responsible for the color of matter and are the basis of well established applications of dyes [1] such as textile dyes, pigments [2], and inks. Whereas the chemistry for such examples is highly developed, chromophores in novel applications are gaining increasing importance; the keywords being 'functional dyes', these novel applications, in contrast to the well established ones, have recently undergone a very rapid development, the end of which cannot yet be seen. Single chromophores are used in the majority of such novel applications, mostly derived from well investigated basic structures the properties of which were adopted to the requirements of the application. However, such a concept does by far not exhaust the possibilities of chromophores because an even larger range becomes accessible by the interactions in multichromophoric systems. Such a range is not just of interest for novel applications. Nature demonstrates, for example with the photosynthesis reaction center [3–5] and the flower pigments [6–8], how special properties can be obtained by such interactions. However, for this, suitable building blocks are required.

2. Soluble Perylene Dyes: Universal Building Blocks for Synthesis. – The perylene bis-imides **1** synthesized from bis-anhydride **2**, are very attractive building blocks for the synthesis of multichromophores because of their unique properties [9] such as their high chemical persistency (*e.g.*, against molten KOH at 220°, concentrated sulfuric acid at 220°, and concentrated bleach [10]; thermal stability up to 550° [11]) and because of their high photostability. Perylene dyes were discovered 1913 by *Kardos* [12] and were firstly applied as vat dyes for textiles, later on as high-performance pigments [13], mainly in the shades red and violet black such as Indanthrene Red GG (**1a**; C. I. 71130 [14]) and Pigment Violet 29 (**1b**, 'Perylimid', C. I. 71129). The pronouncedly low solubility of these dyes was essential for pigment applications but was a handicap for the development of their chemistry. For example, their strong fluorescence was only observed in the fourties by *Geissler* and *Remy* [15]; however, it could not be used for practical applications because of the low solubility of the materials.



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1a R^1 = Me
b R^1 = H
c $R^1 = 2,5\text{-}({}^t\mathrm{Bu})_2\mathrm{C}_6\mathrm{H}_3$
d $R^1 = 2,6\text{-}({}^i\mathrm{Pr})_2\mathrm{C}_6\mathrm{H}_3$
e R^1 = 1-hexylheptyl
f R^1 = 1-heptyloctyl
g R^1 = 1-octylnonyl
h R^1 = 3-butyl-2-(1-butylphenyl)heptyl

Novel possibilities were opened by the introduction of solubility-increasing groups into **1**. For synthetic reasons, the N-atoms are suitable for this (see below).

An appreciable solubility increase could be obtained by the introduction of *tert*-butyl groups [16][17]. These were linked as (*tert*-butyl)phenyl groups to the N-atoms of **1** [18]. A good compromise between preparative accessibility and solubility-increasing effect was the introduction of the 2,5-di(*tert*-butyl)phenyl substituent yielding **1c**. Dyes with isopropyl groups were developed as alternatives [19]. These less bulky groups allowed even the preparation of the 2,6-diisopropylphenyl derivative **1d** with a sufficient solubility in organic solvents (commercial name Lumogen Orange F240). However, preparation of these dyes required comparably rough reaction conditions, and the isopropyl groups are more labile than the *tert*-butyl groups because radical reactions proceed easily at benzylic H-atoms of the isopropylphenyl groups (*cf.* the technical *Hock* process for the synthesis of acetone and phenol from isopropylbenzene).

An increase of solubility could also be achieved with purely aliphatic substituents at the N-atoms of **1** [20][21] and this exceeded that induced by alkylated aromatic substituents appreciably [22]. Unbranched alkyl groups exhibit only a low solubilizing effect which even decreases again when the number of C-atoms in the alkyl chains becomes larger than five (see *Fig. 1* and right inset). Small cycloalkyl groups exhibit no noticeable solubilizing effect, and in the region of common-sized rings, only a small effect is observed for the five-membered ring (see *Fig. 1* and left inset). The solubility then decreases for medium-sized rings, but an appreciable solubility increase is found in going from medium to large rings; the latter form two parallel zig-zag chains. Thus, an even more-efficient increase of solubility is found if these rings are formally cut at the opposite side of the linking to the N-atoms so that long-chain secondary alkyl chains are obtained. The use of two identically long alkyl chains ('swallow-tail' substituents) is to be preferred because thus no additional stereogenic center is introduced. Two or more such chiral groups would result in pairs of diastereoisomers that complicate synthesis, purification, and spectroscopy of the dyes. The solubility of dyes with *sec*-alkyl groups in well solubilizing solvents such as $CHCl_3$ is difficult to determine because highly concentrated viscous solutions are formed where the saturation point is not clear; measurements are possible in the less solubilizing heptane (see *Fig. 1* and left inset). An exponential increase with the chain length is found until 13 C-atoms. A plateau of high solubility is found for longer chains, and an appreciably higher peak solubility is observed for 19 C-atoms. At even higher chain lengths, the solubility decreases again to small values. This complex behavior of solubility as a function of the chain lengths was interpreted as a consequence of the different influences of solvation energy and entropy.

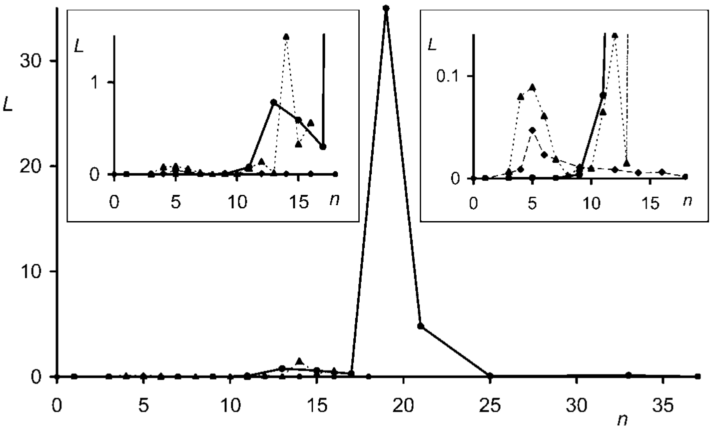


Fig. 1. *Solubility* L [g·l^{-1}] *of* N,N′*-dialkylperylenebis-imides* **1** *as a function of the number* n *of C-atoms in the side chains R^1*. ◆: unbranched *N,N′*-dialkyl derivatives (in $CHCl_3$), ▲: *N,N′*-dicycloalkyl derivatives (in $CHCl_3$); ●: *N,N′*-di(alkyl) derivatives (in heptane).

Dye **1e** with 13 C-atoms in the side chain R^1 is a good compromise between sufficient solubility and not too high ‘dilution’ of the chromophore by the paraffinic side chain. Moreover, the derivative **1e** is obtained in well formed crystals, whereas the higher homologues are more wax-like so that high purification and handling become more complicated. This wax-like consistence finds also its analogy in the melting points of the dyes because these decrease with increasing chain lengths from high values to temperatures below 100° (see *Fig. 2*) so that they can be melted by boiling water [10].

The results of the systematic investigation of the influence of chain lengths on the solubility of **1** can be transferred to other systems, especially to multichromophoric dyes. Thus, the attachment of long-chain *sec*-alkyl groups is a tool for bestowing a high solubility even on multichromophoric systems. This is important for synthesis, purification, and application.

3. Optical Properties of Monochromophoric Perylene Dyes. – The UV/VIS spectra of **1** in solution are strongly structured and are only little influenced by solvent effects [23] and by the substituents R^1; their vibration structure can be constructed from *Gaussian* functions with high precision (see *Fig. 3*) [24].

The low dependence of the UV/VIS spectra of **1** on the substituents R^1 can be explained on the basis of quantum-chemical calculations because nodes or very low atomic coefficients are calculated for the orbital HOMO and LUMO at the N-atoms,

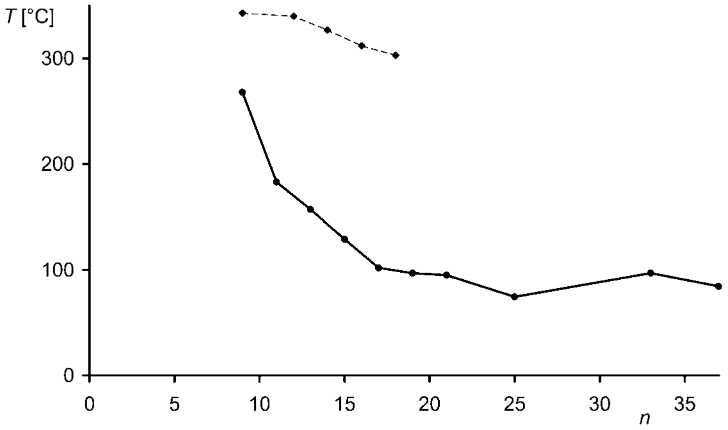


Fig. 2. *Melting points* [°] *of the* N,N′*-dialkylperylenebis-imides* **1** *as a function of the number* n *of the C-atoms in the side chains R*^{1}. ◆: unbranched *N,N*′-alkyl derivatives; ●: *N,N*′-di(*sec*-alkyl) derivatives.

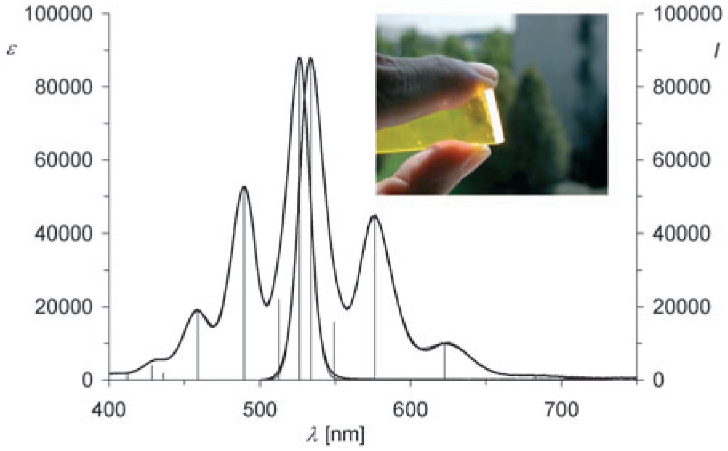


Fig. 3. *UV/VIS Spectrum* (thick line, left) *and fluorescence spectrum* (thick line right; excitation at 490 nm, spectrum normalized to the absorption) *of* **1** (R^1 = 1-hexylheptyl) in $CHCl_3$. Thin lines: simulated spectra on the basis of *Gaussian* analysis. Bars: calculated positions and intensities of bands.

irrespective of the method employed (see, *e.g.*, [25]); nodes or very small coefficients are found even for the orbitals HOMO − 1, and LUMO + 1, and these are important for the configuration interaction. Thus, the N-atoms are decoupled from the chromophore concerning optical excitation which is then quasi that of the 'electron in a box'. The latter is of importance for many theoretical studies. The decoupling of the N-atoms from the chromophore causes the small influence of the substituents R^1 at these atoms. They are, therefore, ideal linking positions for labeling because the spectra are independent from the labeled structure. Moreover the absorption spectrum is suitable for many light sources. The Ar ion laser line at 488.0 nm is suitable for laser excitation because the molar absorptivity of the chromophore is still 52400 at this wavelength. On the other hand, the absorption spectra cannot be tuned by substituents at these atoms. There are principally two possibilities for such a tuning: substitution at the perylene core and an alteration of the dicarboximide group (see below).

The soluble perylene derivatives exhibit a very strong fluorescence in solution and some derivatives also in the solid state. The absorption and fluorescence spectra of dye **1e** (commercial name S-13) are reported in *Fig. 3*, the spectroscopic data in the *Table*. The fluorescence quantum yield [26] in $CHCl_3$ solution is close to 100%, even in the presence of atmospheric O_2. Thus, and because of its high lightfastness, the dye is an easily handled standard for fluorescence spectrometers.

Table. *Spectroscopic Properties of* **1e** ($R^1 = 1$-hexylheptyl)

Absorption:	λ_{max} 526.4 nm	Fluorescence:	λ_{max} 534.5 nm
	$\varepsilon = 88000\ l\ mol^{-1}\ cm^{-1}$	Quantum yield	$\Phi \approx 100\%$
Oscillator strengths[a])	$f = 0.627$	S_1-Life time	$\tau = 3.95$ ns
Transition moment	$\mu = 8.37$ D	T_1 Energy	$27.5\ kcal \cdot mol^{-1}$ (1040 nm, $\tau = 100\ \mu s$)

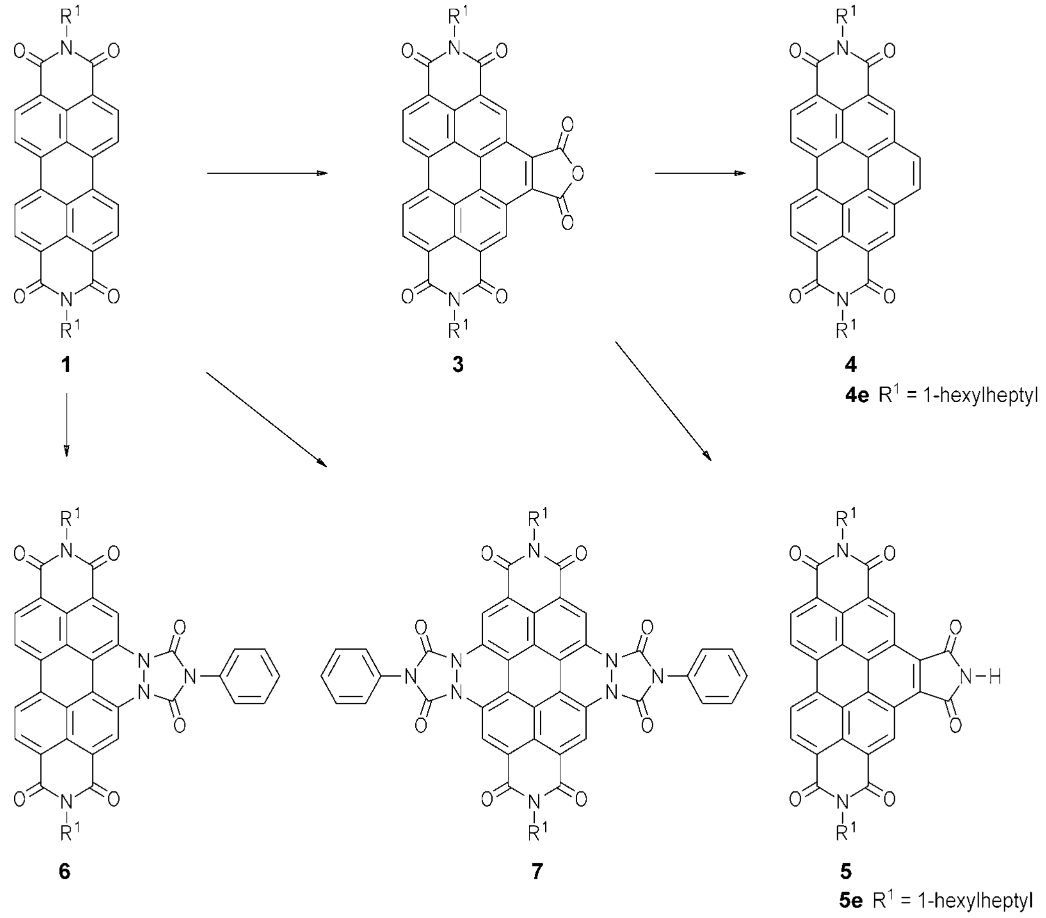
[a]) 400–600 nm.

Measurements of linear dichroism [27] indicate that there is only one electronic transition in the VIS for **1** with a transition moment in the direction of the connection line of the two N-atoms of **1**. The transition moment is parallel to the connection of the two N-atoms both in absorption and fluorescence. This renders the UV/VIS spectra simple and clear and simplifies the interpretation of the spectra of multichromophoric systems.

4. Controlling the Spectral Region of Absorption by Modification of the Perylene Core. – The perylene core of **1** can be replaced by the benzoperylene unit for a hypsochromic shift of the absorption to form **4**. Such a hypsochromic shift is even observed for the basic structures and can be qualitatively interpreted according to the concept of *Clar* [28] by counting the maximal number of complete electron sextets. These are two for the perylene but three for benzoperylene, in accordance with the more hypsochromic absorption of the latter. The benzoperylenebis-imide **3** was prepared from **1** by the *Diels–Alder* reaction with simultaneous aromatization (*Clar* reaction; see *Scheme 1*) [29]. Anhydride **3** is an interesting building block because the anhydride group can function as an electrophile for further synthesis, and the N-atoms can be used to attach solubilizing groups such as the branched *sec*-alkyl groups. Anhydride **3** can be decarboxylized to the benzoperylenebis-imide **4** or be treated with ammonia to give the easily deprotonated benzoperylenetris-imide **5** forming thus a nucleophile (*Scheme 1*). The UV/VIS spectra of **3**–**5** are hypsochromically shifted compared with **1** (see trace of **4** ($R^1 = 1$-hexylheptyl) in *Fig. 4*). Their fluorescence quantum yields are *ca.* 85%.

A concept of bathochromic-shift generation with respect to **1** can be developed on the basis of *König*'s color theory [30]. According to this, the majority of dyes such as Crystal Violet or Malachite Green consist on the donor-π-acceptor-π-donor arrangement (*cf.* also [31]; *Fig. 5,a*). The inverse construction according to *Fig. 5,b* is

Scheme 1. *Synthesis of Core-Extended Perylene Dyes*



equivalent to the first one. This was especially shown for analogues of Crystal Violet or Malachite Green by *Hellwinkel* [32][33]. The perylenebis-imide **1** corresponds to a doubling of the structure in *Fig. 5,b*, where the four carbonyl groups act as acceptors; however, the donor groups are missing so that the maximal attainable bathochromic shift is by far not reached; only the comparably electron-rich central aromatic unit acts here as a donor. Appreciably large bathochromic shifts are expected if additional donor groups are placed at the positions 1, 6, 7, and 12 of **1** (*Fig. 5,c*). This concept explains the bathochromic shifts of the absorption of derivatives with phenoxy [34] or amino substituents [29][35][36] at these positions. Extraordinarily strong donors are generated by application of the α-effect in such a way that two donor groups are connected by a single bond. The α-effect is well established for the reaction of nucleophiles and can also be used for donor groups of dyes [37]. Perylene dyes with such a structure may be principally prepared from **1** by halogenation followed by a

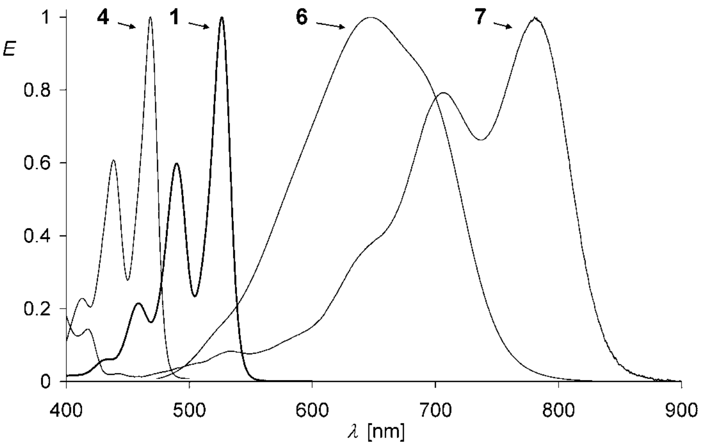


Fig. 4. *Normalized UV/VIS spectra* ($CHCl_3$) *of* **1**, **4**, **6**, *and* **7**. R^1 = 1-hexylheptyl.

reaction with N-nucleophiles and finally by oxydative cyclization. However, incomplete reactions will cause the formation of mixtures difficult to separate. A better synthetic concept is the controlled simultaneous introduction of two N-atoms by the *Clar* variant of the *Diels–Alder* reaction. Thus, in the presence of an aromatization reagent, 4-phenyl-4*H*-1,2,4-triazole-3,5-dione reacts once with **1** to give **6** [29] or with a larger excess twice to give **7** [37] (*Scheme 1*). Dyes **6** and **7** exhibit appreciable bathochromic shifts; the UV/VIS spectrum of **7** with four donor groups and a double α-effect extends far into the NIR (*Fig. 4*). These bathochromic absorbing dyes even exhibit fluorescence.

a) Do-π-A-π-Do

b) A-π-Do-π-A

c)

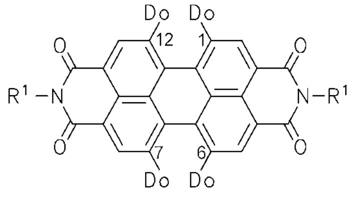
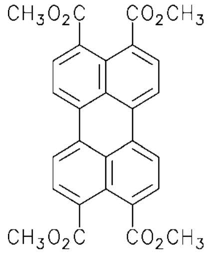


Fig. 5. *Color systems according to* König *with Do as mesomeric donor, π as conjugated π-system, and A as mesomeric acceptor:* a) *common donor-acceptor-system*, b) *inverse system*, c) *perylenebis-imide with donor groups*

5. Further Possibilities for the Modification of Light Absorption. – Besides the substitution at the core, modification of the imide moieties of **1** offers possibilities to influence the absorption of light. The ring-opening of one imide moiety shifts the absorption only slightly but changes the vibronic structure. The opening of both imide rings causes an appreciably strong hypsochromic shift. For example, the tetramethyl perylenetetracarboxylate **8** [38] forms yellow solutions with bluish green fluorescence (*Fig. 6*), and the tetracarboxylate anion absorbs in a similar spectral region. The fluorescence quantum yields of both dyes as well as that of **1e** (R^1 = 1-hexylheptyl) are close to 100% so that both dyes can be used as fluorescence standards [26]; however, the former are not as stable as **1e** (see *Fig. 6*).



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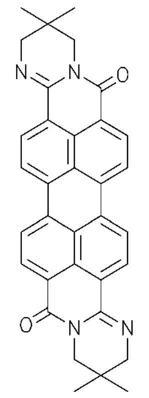

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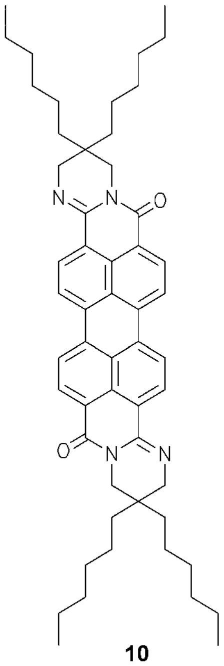

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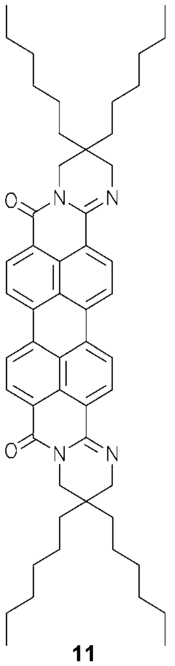

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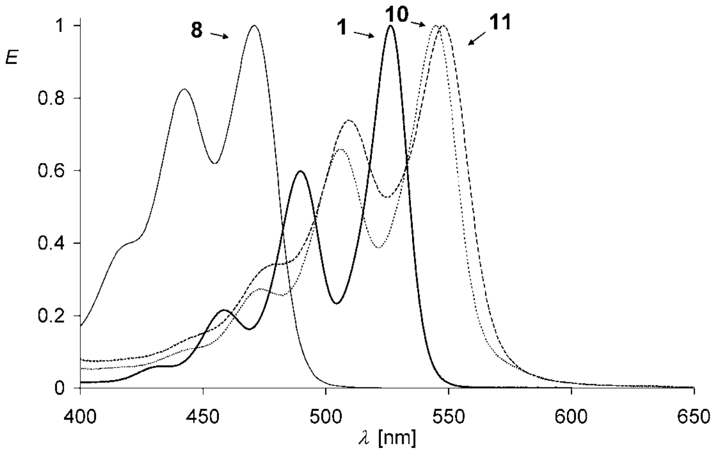
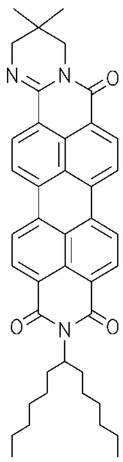


Fig. 6. *Normalized UV/VIS spectra* (CHCl$_3$) *of ester* **8**, **1** (R^1 = 1-hexylheptyl) *tetrazaisoviolanthrone* **10**, *and tetrazaviolanthrone* **11**

A bathochromic shift of the absorption of the perylene dyes can also be achieved by a modification of the carbonyl groups of the imide unit. To this end, the carbonyl groups are replaced by imino groups. As a consequence, the stability of the dyes to hydrolysis is lowered, but this can be compensated by incorporating the imino group into a six-membered ring. A further stabilization may be attained by the presence of geminal Me groups such as in **9** and its '*cis*'-isomer. Another possibility is the incorporation of the imino group into a larger π-system such as in **13**. The solubilities of such dyes are low [39]. However, when the geminal Me groups are replaced by two long-chain alkyl groups, a 'swallow-tail' substituent is again obtained, and the dyes **10** and **11** result with a bathochromic absorption and fluorescence [40] (*Fig. 6*). The solubility of such 'amidines' can be more easily controlled if only one imide moiety of **1** is modified so that the second one can be substituted with the solubility-increasing 'swallow-tail' substituent as realized in dye **12**. Thus, nearly the full bathochromic shift is reached by the incorporation of one 'amidine' unit (see *Fig. 7*). A further extension of the π-system as in dye **13** causes an even stronger bathochromic shift and reaches the NIR region for the naphtho-fused derivative **14**. *Adachi* pointed out on the basis of quantum-mechanical calculations that no further bathochromic shifts may be obtained in this way [41].



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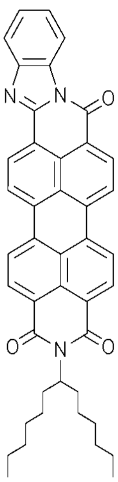

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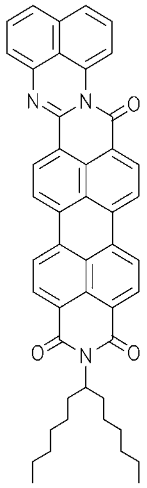

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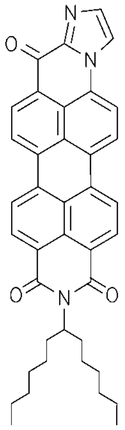

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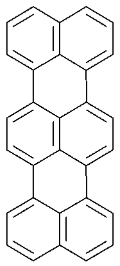

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A remarkable rearrangement was found for the reaction of sterically hindered amines and imidazole with perylene-imide anhydride according to *Regel*'s mechanism [42][43] with the formation of **15** [44]. The UV/VIS spectrum of the latter is nearly congruent with terrylene (=tribenzo[*de*,*kl*,*rst*]pentaphene; **16**) (*Fig. 8*). Dye **15** is appreciably more stable than terrylene (**16**) and exhibits a stronger fluorescence so that it is an ideal replacement of the latter. This is of special interest for physicochemical studies because the absorption of terrylene matches the operating range of the frequently used rhodamine 6G dye laser; however, the use of **16** is limited by the low chemical stability [45].

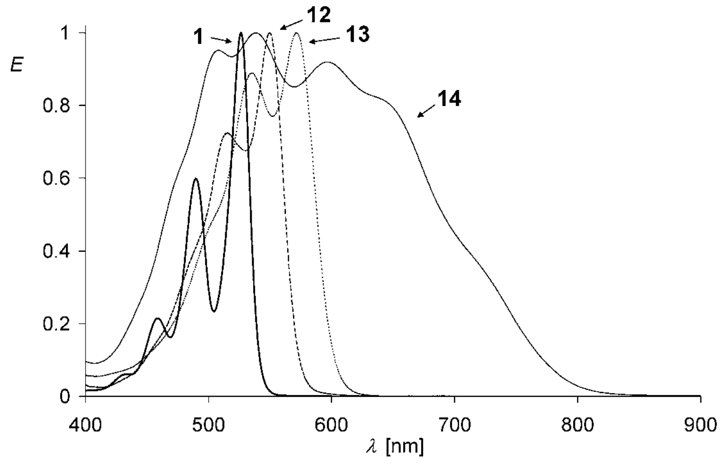


Fig. 7. *Normalized UV/VIS spectra* ($CHCl_3$) *of the 'amidine-imides'* **12**–**14** *and* **1**. R^1 = 1-hexylheptyl.

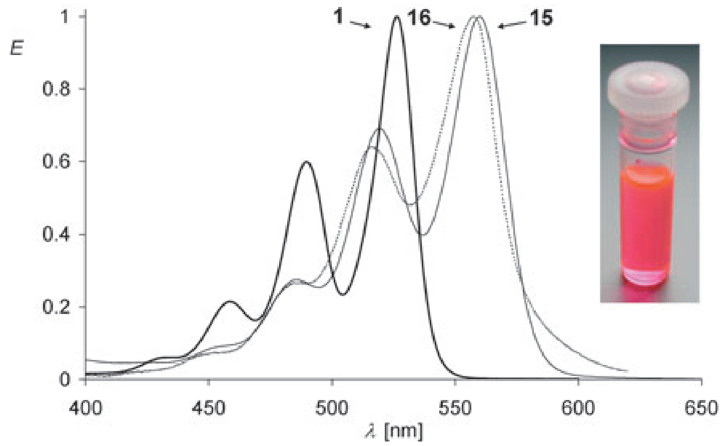
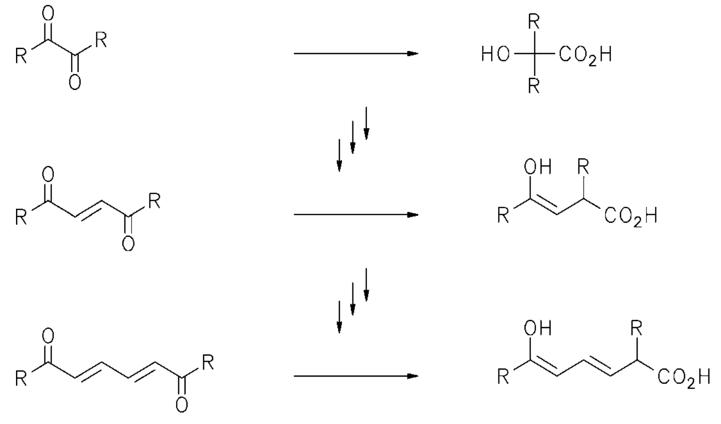


Fig. 8. *Normalized UV/VIS spectra* ($CHCl_3$) *of* **1** (R^1 = 1-hexylheptyl; thick line), *imidazole derivative* **15** (right), *and terrylene* (**16**; left)

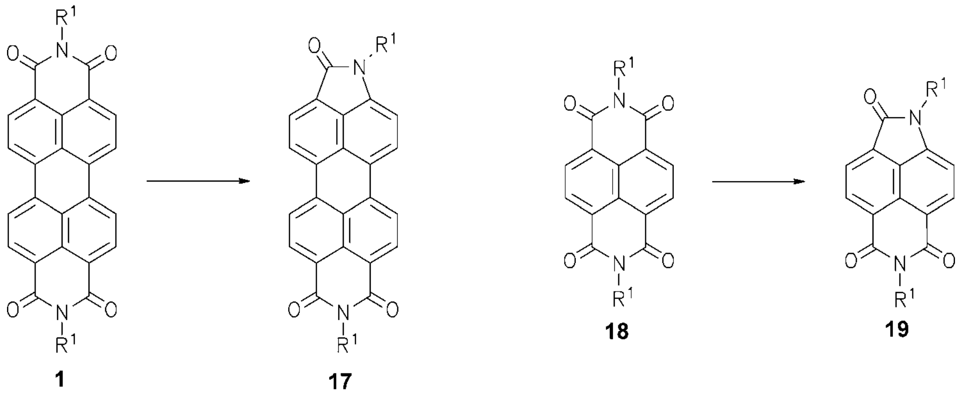
A bathochromic shift of the absorption of **1** can be obtained not only by the replacement of groups at the six-membered imide moieties but also by modification of the ring size. The reaction of **1** with base induced a vinylogous benzilic acid rearrangement (*cf. Scheme 2*) and the formation of the lactame-imides **17** (*Scheme 3*) [46][47]. The latter form purple solutions (see *Fig. 9*). The same reaction proceeds also with the colorless naphthalenebis-imides **18** to give the yellow lactame-imides **19**. These can be used as fluorescence dyes (see *Fig. 9*).

The bis-anhydride **2** is an important starting material for the synthesis of derivatives of perylene-3,4-dicarboxylic acid by the decarboxylation of two neighboring carboxylic groups; the decarboxylation proceeds under common reaction conditions at two different sites of the molecule [48]. However, when the decarboxylation is controlled

Scheme 2. *Normal, Vinylogous, and Doubly Vinylogous Benzilic Acid Rearrangement*



Scheme 3. *Synthesis of Perylenelactam-imides* **17** *and Naphthalenelactam-imides* **19**



by entropy, the formation of the cyclic structure of the *peri*-dicarboxylic acid derivatives is favored, and the derivatives of perylene-3,4-dicarboxylic acid are obtained. The decarboxylation can proceed directly under the conditions of condensation [49] so that the dicarboxylic imides **32** (see below) are obtained. Under controlled reaction conditions, a reaction starting with the perylene-3,4 : 9,10-tetracarboxylic bis-anhydride **2** [50] results in the a dicarboxylic monoanhydride which can generally be condensed with primary amines to give **32**. The perylene-imide anhydrides **22** (*cf.* below, *Scheme 4*) can be decarboxylated with copper in picoline yielding **32** [51]. The UV/VIS absorptions of the dicarboxylic imides **32** appear in a similar spectral region as those of **1**. However, they are differently structured. The fluorescence quantum yield of **32** is *ca.* 85%. The dicarboxylic imides were recently considered as being of appreciable importance because the free *peri* positions can be easily brominated, and the thus obtained derivatives are building blocks for even more-complex structures such as dendrimers [52] or complex structures with porphyrine units [53][54].

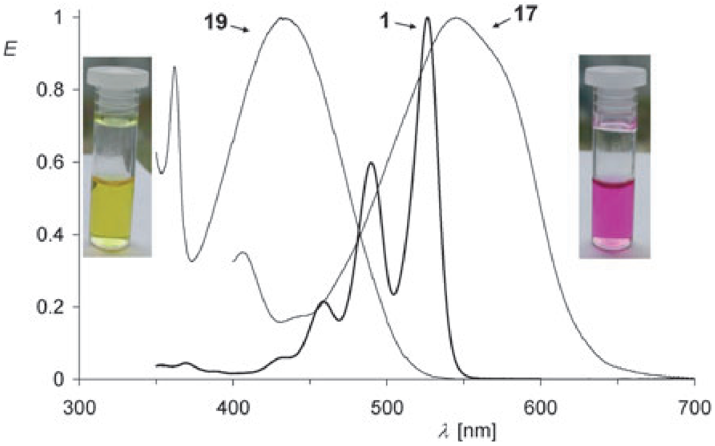


Fig. 9. *Normalized UV/VIS spectra* (CHCl$_3$) *of* **17** (R^1 = 2,5-di(*tert*-butyl)phenyl; right), **19** (R^1 = 2,5-di(*tert*-butyl)phenyl, left) *and* **1** (R^1 = 1-hexylheptyl; thick line)

6. Persistent Fluorescence of Dyes by Steric Inhibition of Aggregation. – Perylene derivatives such as **1e** exhibit pronounced fluorescence in solutions with usual optical densities. However, fluorescence quenching proceeds in concentrated solution. The most important reason for such a concentration quenching is the aggregation of dyes where the chromophores form layered structures. Such an aggregation can be inhibited by bulky groups at the periphery of the dyes, especially at the N-atoms of **1** [55] (see *Fig. 10*).

The presence of highly branched alkyl groups in the dye are therefore suitable. For example, dye **1h** exhibits a strong fluorescence even in concentrated solution and in the solid state. A steric inhibition of aggregation is of special interest for large, multichromophoric systems because their extended π-systems favor aggregation processes.

7. Monofunctionalized Perylene Dyes. – The synthesis of **1** from the easily accessible **2** results in symmetrically substituted dyes, and these are bifunctional when the condensing amine contains a further functional group. However, monofunctionalized dyes are required for the synthesis of complex multichromophoric architectures. It would seem to be straightforward to react an excess of **2** with an amine as the minor compound and to separate the monocondensed and the dicondensed material. However, this synthetic route is barred because there is either no condensation or it proceeds twice to **1**. Even under thoroughly controlled reaction conditions, perylene-imide anhydrides can be only obtained as the minor compounds.

One can prepare nonsymmetrically substituted **1** by the synchronous cocondensation of two different amines. However, significant yields are only obtained when the reactivities of both amines are similar and, moreover, one has to separate two symmetrically substituted imides from one unsymmetrical imide. This may be very difficult because the properties of the materials are mostly dominated by the identical chromophore.

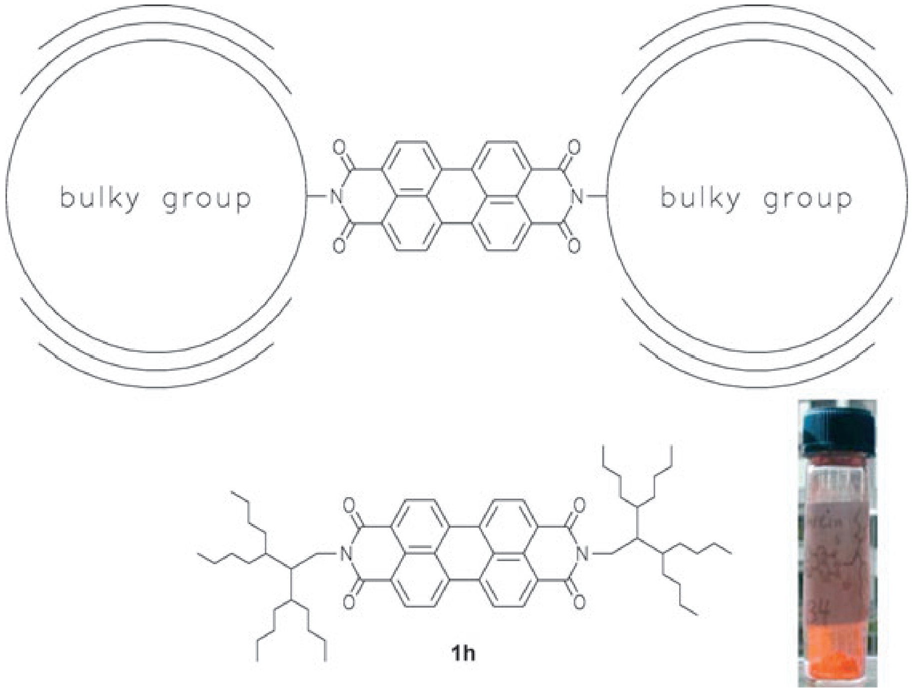
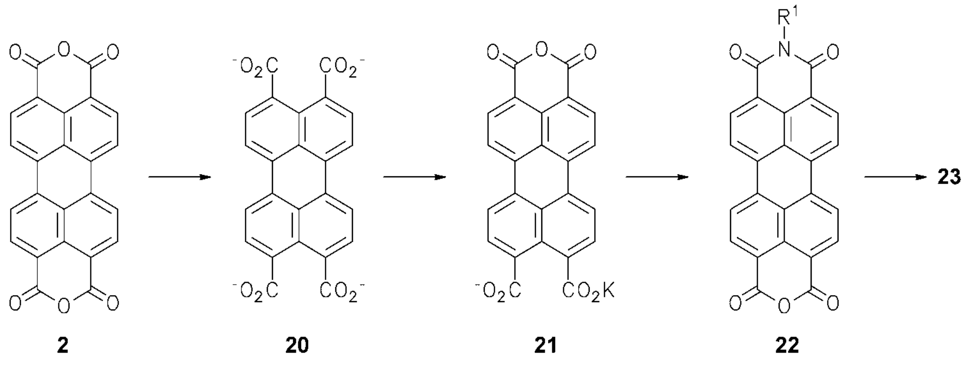


Fig. 10. *Perylene dyes with bulky terminal groups for steric inhibition of aggregation*

Concerning the condensation of water-soluble amines, there is an alternative for the preparation of unsymmetrically substituted dyes: technical-grade **2** is allowed to react with KOH to the readily water-soluble tetrapotassium salt **20** (the solubility of the sodium salt is appreciably lower) (see *Scheme 4*). The monoanhydride monopotassium salt **21** precipitates [56] from this solution on lowering the pH value because of its extremely low solubility so that it escapes the acid–base equilibria. A very pure material **21** is obtained by the application of AcOH for the lowering of the pH [57]. The

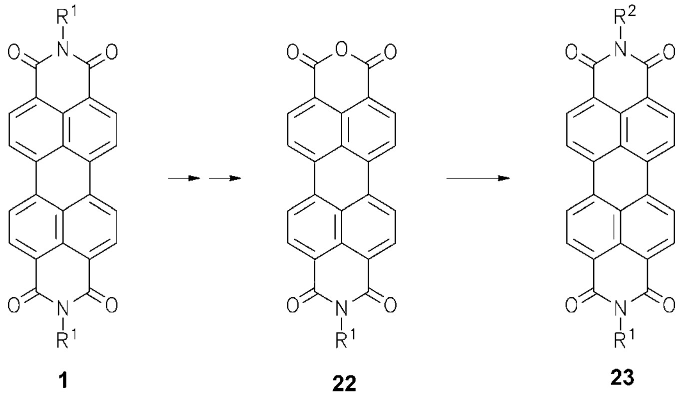
Scheme 4. *Synthesis of Perylene-imide Monoanhydrides* **22** *from Water-Soluble Amines* R^1NH_2



condensation of **21** with primary amines in aqueous phase results in the perylene-imide anhydrides **22**. The latter can be condensed very efficiently with any primary amine to give the unsymmetrically substituted dyes **23**. However, this condensation is limited to water-soluble amines, and, the hydophobic solubilizing long-chain *sec*-alkylamines cannot react in this way.

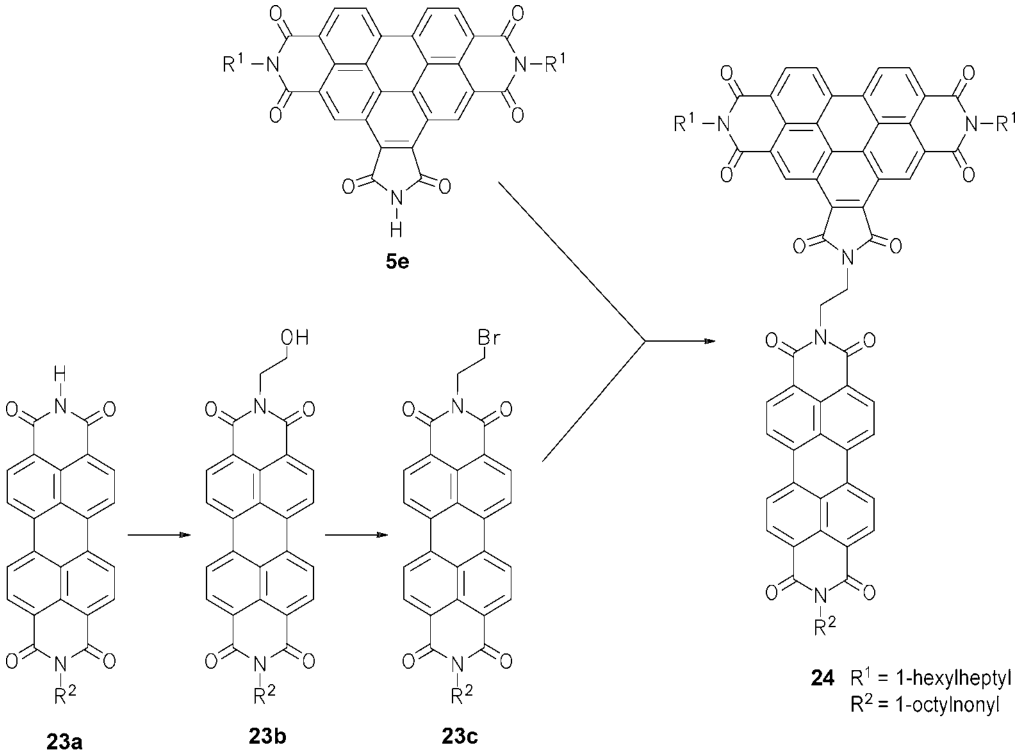
Thus, instead of direct condensation of hydrophobic amines with **2**, the perylenebisimides **1** symmetrically substituted by hydrophobic substituents R^1, were firstly synthesized and then hydrolyzed to **22** (*Scheme 5*). This requires rather rough reaction conditions such as conc. sulfuric acid at 180–200° [58][59] because of the persistency of **1**. This is problematic for many substituents. Dyes **1** are also very stable towards bases (see, *e.g.*, their synthesis with molten KOH). However, alkaline hydrolysis of **1** proceeds under surprisingly mild conditions with KOH in ^{t}BuOH [57], and **22** is thus obtained after acidification and loss of water *cf.* the spontaneous dehydration of perylene-3,4,9,10-tetracarboxylic acid [9], thus giving access to unsymmetrically substituted dyes **23** with hydrophobic groups R^1 (*Scheme 5*). The solubility-increasing effect of the long-chain *sec*-alkyl groups is also observed for the anhydride imides **22** so that they become the ideal starting material for the synthesis of larger assemblies of chromophores.

Scheme 5. *Synthesis of Nonsymmetrically Substituted Perylene Dyes* **23** *with Hydrophobic Substituents* R^1



8. Bichromophoric Perylene Dyes. – The intramolecular interaction of perylene chromophores is demonstrated here firstly with bichromophoric dyes (for further examples, see [60]). Thus bis-imide **23a** (R^2 = 1-octylnonyl) is treated with bromoethanol (→**23b**) and then transformed to the electrophilic bromo derivatives **23c** by means of PBr_3 in a convergent synthesis [61] (*Scheme 6*). Subsequent reaction with the nucleophilic benzoperylenetris-imide **5e** (R^1 = 1-hexylheptyl) results in the bichromophore **24** where three 'swallow-tail' substituents guarantee a good solubility.

Scheme 6. *Synthesis of the Bichromophoric Dye* **24**



The UV/VIS absorption of **24** is exactly the sum of the single absorptions of the chromophores (*Fig. 11*). The individual chromophores of **24** are thus independent from each other. Obviously, the ethylene spacer is long enough for their efficient decoupling. Fluorescence is only observed from the bathochromic absorbing chromophore stemming from **1** (*Fig. 11*). An optical excitation of this chromophore results in a fluorescence quantum yield close to 100%. Surprisingly, such a high fluorescence quantum yield is also observed if the hypsochromically absorbing chromophore stemming from **5** is irradiated. Therefore, also the energy transfer between the two chromophores proceeds with close to 100%. The electrical transition moments in both **1** and **5** are parallel to the connection line between the N-atoms of the two six-membered imide moieties. Therefore, the transition moments of the two chromophores of **24** are nearly orthogonal. This is also indicated by the linear dichroism of the dye that indicates parallel transition moments for absorption and fluorescence in the bathochromic region of the spectrum, whereas they are orthogonal in the hypsochromic region.

The dye **24** indicates that systems with completely novel properties can be obtained by the combination of chromophores. Dye **24** is not only very lightfast but exhibits also close to 100% fluorescence quantum yields, even in the presence of atmospheric O_2.

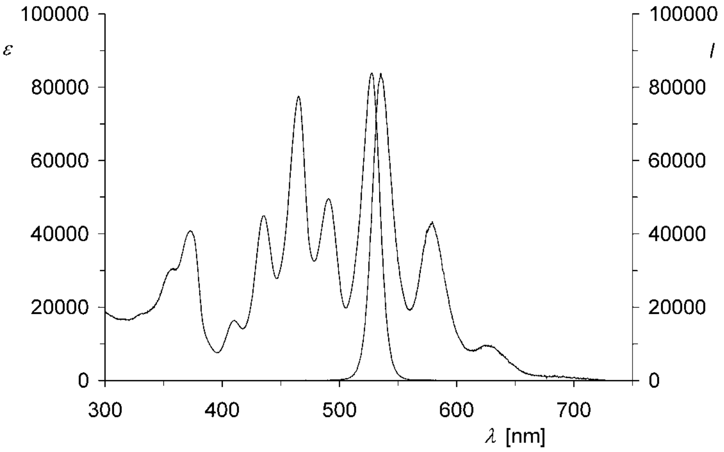


Fig. 11. *UV/VIS* (left) *and normalized fluorescence spectrum* (right) *of* **24** *in* $CHCl_3$ (R^1 = 1-hexylheptyl, R^2 = 1-octylnonyl)

The fluorescence quantum yield is constantly high throughout the whole spectral region and exhibits many absorption bands. The dye is, therefore, a useful standard for the calibration of fluorescence spectrometers.

9. Multichromophoric Antenna Systems from Identical Units. – 9.1 *General Concepts.* The interaction of chromophores offers many novel possibilities as was shown in the preceding chapter [62]. The interaction of several identical chromophores is the subject of this investigation. Exciton interactions proceed if identical chromophores are brought close to each other (see [63–67] for further information). It is of minor importance whether they are interconnected by primary valences, side valences or if they form aggregates. The theoretical background for the description of such exciton effects was established by *Kuhn* [68] and was clearly described by *Förster* [69]. Essentially, the interaction of chromophores results in a splitting (repulsion) of the color-determining occupied and unoccupied orbitals of initially the same energy (*Davydov* splitting [70][71]) and additionally in a synchronization (coupling) of the movement of electrons. The splitting causes the transformation of two identical electronic transitions into two new ones, one of them at shorter wavelength (β) and the other one (α) at longer wavelengths (see *Fig. 12,a*). The intensity of the splitting ($\beta - \alpha$) depends on the strengths of the coupling.

However, only one of these electronic transitions is allowed. The orientation of the transition moments of the chromophores decide which of them is allowed. These moments are directed for perylene dyes parallel to the connection line of the two N-atoms. Two extreme cases may be distinguished. Firstly, if the transition moments lie one above the other, the antisynchronous electron movement is more favorable; this is indicated in *Fig. 12,b* (bottom), as a snapshot concerning the induced partial charges. The β-transition belongs to this situation. Secondly, if the transition moments are shifted as shown in *Fig. 12,b* (top), the synchronous electron movement is more

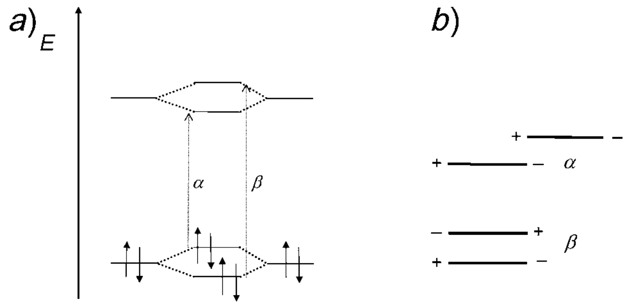


Fig. 12. a) *The interaction of chromophores cause the splitting of originally, energetically identical color-determining orbitals to two new pairs with the electronic transitions α and β;* b) *orientation of the transition moments* (top: synchronous electron movement; bottom: antisynchronous electron movement).

favorable because the electrons are more distant from each other. The α-transition with lower energy belongs to this situation. A continuous alteration of the orientation of the transition moments may result from the combination of two borderline cases. Firstly, the enclosed angle Θ between the two transition moments may be altered. In the region between 0 and 90°, the β-transition is preferred with the hypsochromic absorption; at exactly 90°, the moments are orthogonal so that no exciton effect results, and at angles larger than 90° until 180°, the more bathochromic α-transition becomes more favorable; (see *Fig. 13,a*). Secondly, a continuous change of the exciton effects may be also attained by a shift of the chromophores with respect to each other (see *Fig. 13,b*). The β-transition will be preferred if the transition moments cover each other, *i.e.*, $d=0$. If these are shifted one *vs.* the other, the exciton effect diminishes, becomes zero, and finally, the α-transition becomes important. There are also mixed cases between these extrema where the moments are both shifted and rotated [72]; however, the argumentation can be applied in these cases in the same way. Both transitions may be possible if the dimer is twisted

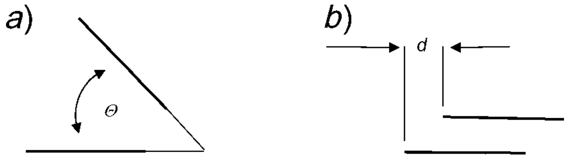


Fig. 13. *Orientation of the transition moments of the bichromophoric dyes in space:* a) *Torsion of the transition moments one* vs. *the other with the angle Θ*; b) *shift of the distance* d

Aggregates of dyes (*Scheibe* aggregates [73]) are an extension of these basic arrangements over many dye molecules. Two basic arrangements are known. The arrangement with shifted chromophores and bathochromic absorption (α) are known as *J*-aggregates (named according to their discoverer *Jelly* [74]) and an arrangement with stacked chromophores (β) named *H*-aggregates (from hypsochromic). Both arrangements have different properties concerning the emission of light. The transition moment of *H*-aggregates vanishes because of the point symmetry of the movement of electrons, and no fluorescence is observed, whereas a net moment results for *J*-aggregates, and thus fluorescence is allowed. However, there are many possibilities for the movement of the chromophores *vs.* each others so that efficient ways are available for the deactivation of the energy of excitation by vibronic relaxation. Therefore, the fluorescence quantum yields of such aggregates are generally low, and a 20% quantum yield would be regarded as a pronouncedly high value.

Exciton interactions have also been observed in dye crystals and are determined by the orientation of the chromophores in the crystal lattice [75]. These are of central importance for the color of organic pigments, such as for the color of the perylenebisimide pigments. Their color extends, *e.g.*, from purely red of **1a** to bluish black of **1b** although the structures of all the chromophores are identical as well as are the spectra of the diverse derivatives of **1** in solution. The distinct colors of the perylene pigments were interpreted with a model employing different covering of the chromophores in the crystals [76–78]. This interpretation was later disputed [79], and, finally, useful empiric color rules were established [80]. One can expect that the exciton model described here is a more useful concept for the description of the color plurality of the perylene dyes, especially by the use of the lateral shift of the chromophores in the crystal lattice. The DPP dyes are a further example illustrating this because their spectra in solution are similar, whereas bright pigments are known in the shades from yellow to deeply red [81]. Moreover, allotropic modifications of one and the same dye with strongly different color are known [82].

Exciton effects are treated here for one electronic transition; however, there are several electronic transitions in the VIS for many dyes, and corresponding overall exciton effects proceed for any of these transitions. Moreover, the orientations of the transition moments are frequently different for different electronic transitions with regard to the molecular geometry. Thus exciton effects can become very complicated. The chromophoric system of **1** is especially advantageous because the absorption in the VIS is based on only one electronic transition. This was established [27] by measurements of linear dichroism and different quantum-mechanical calculations [83]. The $\boldsymbol{E}$ vector of this transition is located on the connection line of the two imide N-atoms. The positions of the energy levels and their splitting are determined in multichromophoric systems as well as in monochromophoric systems by orbitals and their interaction. A novel item in multichromophoric systems is the control of light absorption by the overall geometry. To clarify these items, the chromophores with their delocalized and, therefore, 'electrically conducting' π-systems are compared with antennae for radio frequencies [84], *e.g.*, with VHF and UHF antennae. The wave resistance is a measure for the ability to radiate electromagnetic radiation. This corresponds to the oscillator strengths of dyes and the molar absorptivity derived therefrom.

A direct comparison of both types of antenna makes clear that the dimensions of technical antennae in VHF and UHF are of the order of the wavelengths of the radiation such as $\lambda/2$ or $\lambda/4$ radiators, whereas for dyes the lengths of the radiation much exceed the molecular dimensions. For example, the absorption maximum of **1** at 526 nm is by far much greater than the dimensions of the chromophore with 1.1 nm (distance of the two N-atoms by AM1 calculations). This corresponds to a radio antenna which is too small with the consequence that there are strongly capacitive components at its ends [85]. As a consequence, there are strong electrostatic interactions with the surroundings, and also everything that effectively enlarges the chromophore increases the absorptivity, whereas a shortening diminishes it. The radiation resistance increases with the square of the ratio between effective length and the wavelength (*Rüdberg*'s relation [84]). Therefore, pronounced optical effects are to be expected for multichromophoric dyes by extension of the absorbing structure. A hint of such effects is already given by the comparison of the molar absoptivities of **1** with aliphatic and aromatic substituents R^1. If R^1 is aliphatic such as in **1e**, molar absorptivities of 88000 were observed. With aryl substituents such as in **1c**, the absorptivity increases to 95000 without changing the band shape. This proceeds although the π-systems of the chromophore and the periphery (R^1) are electronically decoupled (see above). The different absorption properties are also reflected in the oscillator strengths of the dyes. These are 0.63 for **1e** ($\lambda > 400$ nm) but 0.68 for **1c**. The latter exists in two atropisomers [86]. These can be used to show that purely electrostatic effects cannot be the reason for the alteration of the absorptivity. Indeed '*E*'-**1c** exhibits exactly the same absorptivity as '*Z*'-**1c** (accuracy better than 0.3%) and congruent UV/VIS spectra [87] although there is point symmetry of '*E*'-**1c** so that there is no dipole moment, whereas there is a C_2 axis in '*Z*'-**1c** with a net dipole. On the other hand, the high polarizability of the terminal aryl substituents can be made responsible for the increase of the absorptivity of **1c**. These enlarge the extent of the π-system for light absorption by a capacitive coupling (*Coulomb* interactions; *cf.* also [88]). This resembles a *Hertz* dipole with top capacity.

A direct consequence of the short antenna is found in the vibration structure of the dyes. There is no perfect symmetry of the vibration bands in absorption and fluorescence, even for **1**: the hypsochromic vibration bands of absorption are relatively more intense than the corresponding bathochromic bands of fluorescence. This increase or decrease is quantitatively described by the *Ross* factor [89] according to *Eqn. 1:* the ratio of the intensities (I_n/I_o) of the different vibration levels (n) is directly related to the wavelengths (λ_o/λ_n). *Eqn. 1* corresponds to the fact that the radiation resistance of a linear dipole is proportional to the square of the ratio of the length of the dipole and the wavelength.

$$I_n/I_o = \lambda_o/\lambda_n \cdot x^{2n}/n! \qquad (1)$$

The usefulness of the concept is further indicated by the fact that *H*-aggregates or dimers with the corresponding geometry exhibit a lowered coefficient of extinction, whereas *J*-aggregates or dimers of this type exhibit an increased coefficient of absorption with respect to each chromophore.

One can take technical antennae as a model for the construction of complex chromophoric systems; the delocalized π-system replaces the electric conductor of the antenna. The perylenebis-imides **1** and the benzoperylenetris-imides **4** are, therefore, of special interest not only because of their high persistency but also because of their single electronic transition in the VIS so that spectra become easy to interpret. The N-atoms are ideal linking positions for the construction of complex structures because there are nodes at these positions in both HOMO and LUMO so that there is an efficient electronic decoupling of the different components of such complex structures.

Finally, a sufficient repertoire of synthetic methods has been developed for the verification of such concepts.

Technically, there are mainly three basic structures of antennae (see *Fig. 14*): *a*) the linear dipole (this may be folded), *b*) the ring antenna, and *c*) the tripod antenna. The latter is mainly applied as a transmittance antenna. It is of interest to test how far these basic structures are found in nature, and which optical effects are to be expected with the molecular simulation of such antennae.

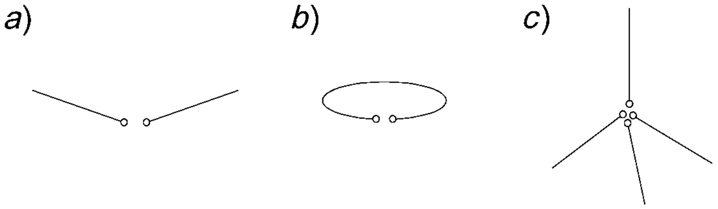
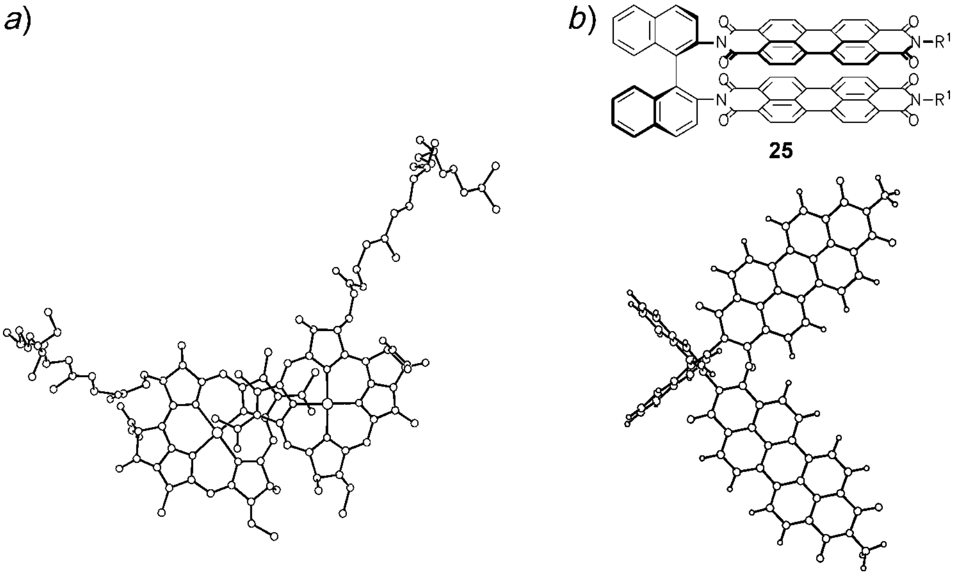


Fig. 14. *Constructions of antennae:* a) *linear dipole*, b) *ring antenna*, *and* c) *tripod antenna*

9.2. *Linear Dipole.* The linear dipole realized by a multichromophoric system (*Fig. 14,a*) is found in nature and forms as the 'special pair' the photosynthesis reaction center [3] of bacteria and higher plants. In this structure, two porphyrine units with an interplanar distance of *ca.* 3 Å are shifted and twisted with respect to each other so that they form an open V (see *Fig. 15,a*).



'special pair'

25 R^1 = Me

Fig. 15. *Examples of a linear dipole:* a) *the 'special pair' of the photosynthesis reaction center*; b) *structure of the bichromophores* **25**

The construction of such a structure was attempted with perylene chromophores. To this end, for each of the enantiomers of **25**, two perylene-imide anhydrides **22** were condensed with 1,1′-[binaphthalene]-2,2′-diamine [90]. 'Swallow-tail' substituents were used as R^1 to obtain a sufficiently high solubility of the whole assembly. The enantiomeric dyes **25** ((*P*) and (*M*)) thus obtained exhibit congruent UV/VIS spectra as one may expect (*Fig. 16*).

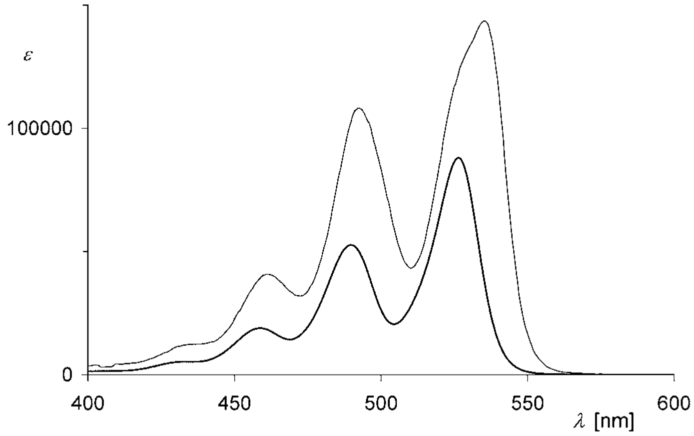


Fig. 16. *UV/VIS Spectra* ($CHCl_3$) *of (*P*)- and (*M*)-***25** (R^1 = 1-hexylheptyl; congruent upper spectra) *and of* **1** (R^1 = 1-hexylheptyl; lower spectrum)

The spectra are essentially identical with the spectra of the monochromophoric dye **1e** (R^1 = 1-hexylheptyl) in the hypsochromic region of the VIS except that the molar absorptivity is two times as high as the value of the latter. At the bathochromic edge of the absorption, there is an additional shoulder for **25** as a consequence of the exciton interaction of the two chromophores. This bathochromic position of the exciton band is unequivocally an indicator that the transition moments of two chromophores form an angle larger than 90° projected to the normal plane between the chromophores; this was verified by quantum-mechanical calculations. The chirality of this assembly causes strong CD effects; $\Delta\varepsilon$ values of $+500$ and -500, respectively, were found for the two enantiomers (see *Fig. 17*).

Dye **25** exhibits a very strong fluorescence in solution. This is of special interest because chiral light is emitted that means that the emitted light is circularly or elliptically polarized. This might be taken as the base for the construction of lasers for circularly polarized light. The strong fluorescence of dye **25** is an additional indicator that the enclosed angle between the two chromophores is larger than 90° because a smaller angle would result in a quenching effect. Strong CD effects were meanwhile found also in the natural photosynthesis reaction center [91] (*cf.* also [92][93]), and these correspond to the effects found for **25**.

The construction of a direct overlapping of the chromophores was also successfully achieved. The ring closure to the cyclophane **26** was possible under dilution conditions

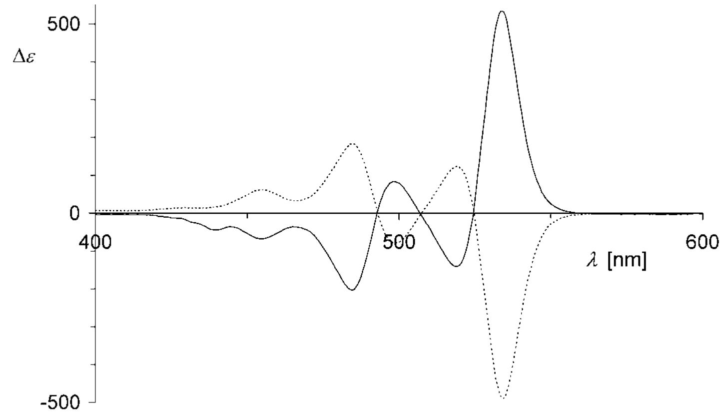


Fig. 17. CD *Spectra* (CHCl$_3$) *of (*P*)-***25** (—) *and (*M*)-***25** (····). R^1 = 1-hexylheptyl.

[94]. This indicates that the dilution method can also be applied with components of low solubility because in the synthesis of **26**, **2** must be added as component of low solubility. The calculated structure of **26** (AM1, see above) is shown in *Fig. 18*. In the UV/VIS spectra, there is a pronounced hypsochromic shift of the absorption of **26** compared with **1** (*Fig. 19*). This is typical for sandwich dimers [95] and *H*-aggregates as an extension of such structure elements. This hypsochromic shift corresponds to an enclosed angle between the transition moments of less than 90°. The absorptivity of **26** decreases remarkably to 66000 and is appreciably lower than twofold the molar absorptivity of **1** ('destructive exciton effect'). This diminishing of the absorptivity can be interpreted as a consequence of the shortening of the antenna because one chromophore is folded over the other.

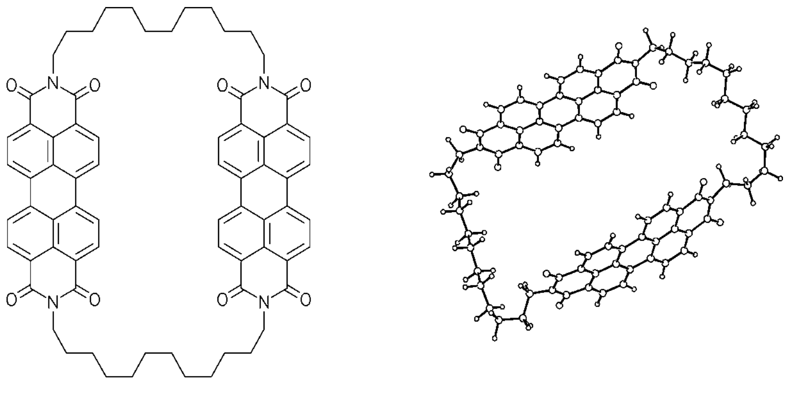


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Fig. 18. *Calculated structure of cyclophane* **26**

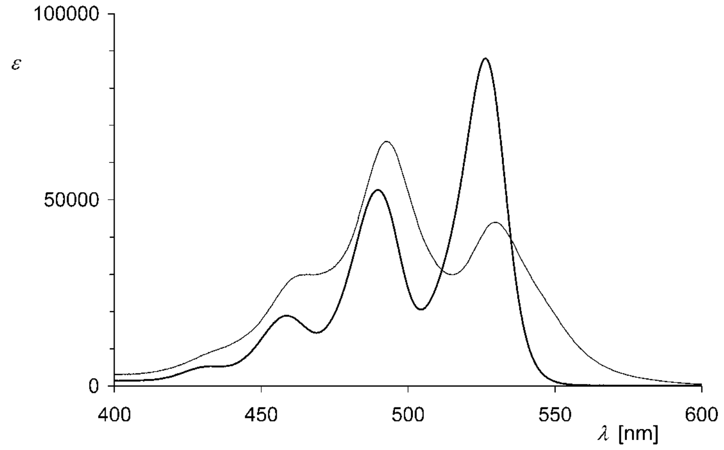


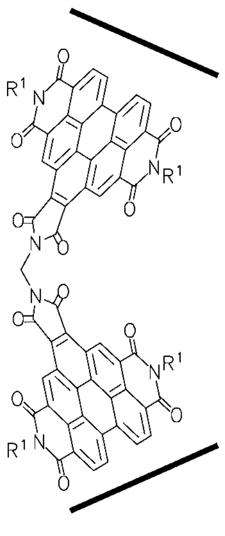
Fig. 19. *UV/VIS Spectrum* ($CHCl_3$) *of* **26** (thin line) *and* **1** (R^1 = 1-hexylheptyl; thick line)

The benzoperylenetris-imide **5** reacts with CH_2Br_2 to the bichromophore **27** [96] that forms an open V and encloses an angle of the transition moment of less than 90° (see the lines in formula **27**). This finds its correspondence in the fact that the molar absorptivity of **27** is less than two times the value of **5**, and this means a destructive exciton effect. On the other hand, one finds a constructive exciton effect for the absorption in the UV. Obviously, the transition moment is differently oriented for this absorption so that there is a constructive exciton effect.

In dye **28**, the perylenebis-imides also form an open V; however, the enclosed angle between the transition moments is larger than 90° (see lines in formula **28**). As a consequence, one finds a slight increase of the molar absorptivity by a constructive exciton effect (for the UV/VIS spectra, see below *Fig. 22*).

In the chiral dye **25**, the transition moments enclose an angle of more than 90°. This causes an additional absorption band at the bathochromic edge of the absorption (see above); it is of interest to bring this band into the region of the inherent absorption of the perylenebis-imide chromophore. This can be achieved by the close, linear alignment of the chromophores. The N-atoms are, therefore, especially suitable because they are in the direct line of the transition moment, there are orbital nodes in HOMO and LUMO, and steric interactions of the carbonyl groups cause an orthogonal arrangement of the chromophores. The synthesis of such dyes requires the *N*-aminoimide **29** as a building block. This component can be prepared by the condensation of hydrazine with the corresponding anhydride **22** under thorough control of the reaction conditions (*Scheme 7*). A condensation of **29** with bis-anhydrides **2** allows the preparation of the bichromophoric and trichromophoric dyes **30** and **31**, respectively [97].

The absorption coefficients of the bi- and trichromophoric dyes are, respectively, twice and three times as high as that of the monochromophoric dye, except for the most bathochromic bands (see *Fig. 20*). The molar absorptivity of **30** is appreciably higher than twice the value of **1** and for **31** appreciably higher than three times; a molar



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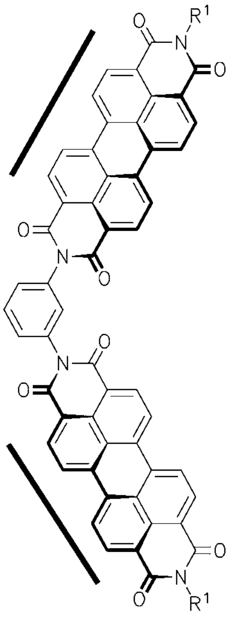

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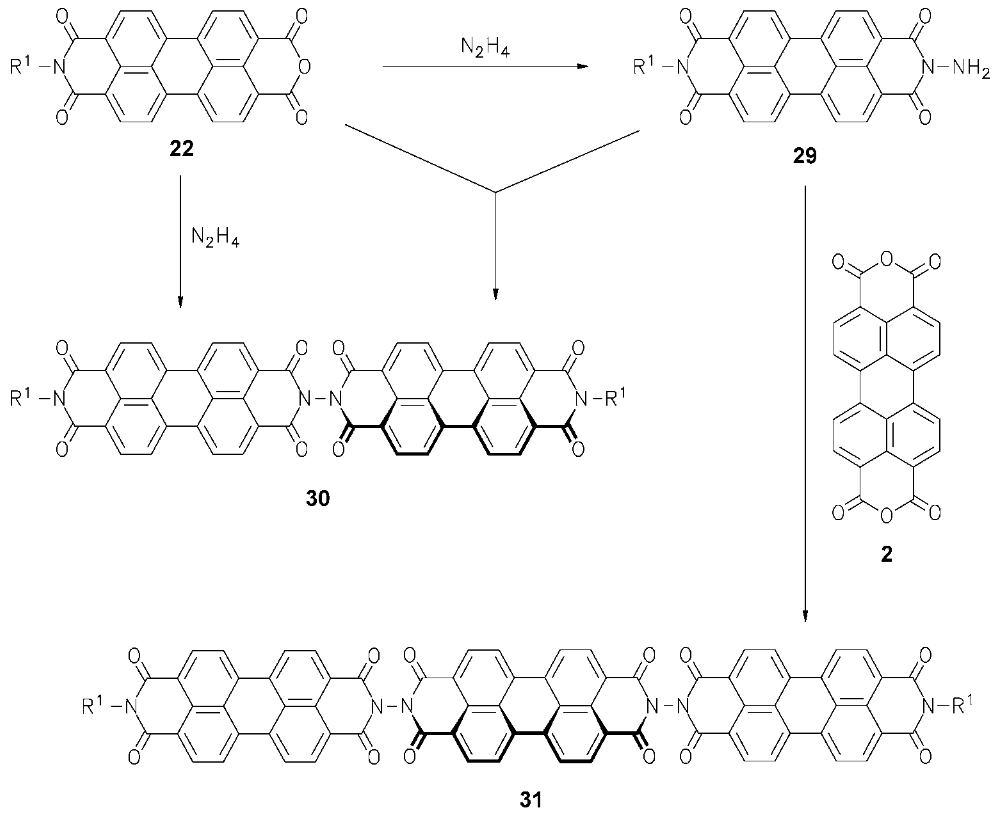
absorptivity of more than 400000 is reached. Thus, the 'constructive exciton effect' can be applied to the construction of highly intense dyes. It is of importance that such exciton effects do not interfere with high fluorescence quantum yields in any way because quantum yields close to 100% were observed for both dyes [97].

Such enhancement of the absorptivity is not limited to perylenebis-imides but can also be observed for other dyes. For example, the perylenemono-imides **32** exhibit absorptivities of *ca.* 30000, whereas the bichromophoric dyes **33** reaches nearly 100000, and the absorptivity is tripled instead of doubled (see *Fig. 21*). Both chromophores are decoupled by being orthogonal [98]. This increase of color strengths is of interest for practical applications, especially because **33** exhibits a bright red fluorescence, whereas the fluorescence of **32** is less shiny yellow and with 84% not so strikingly pronounced as for **1e** (R^1 = 1-hexylheptyl). These differences illustrate the control of the properties of the dyes by their interactions in multichromophores.

9.3. *Ring Antennae.* With molecular ring antennae (see *Fig. 14,b*), the ring-type conductor is replaced by a ring-type arrangement of chromophores. Such arrangements are also found in nature: the light-harvesting system LH2 consists of 9 axially and 18 equatorially arranged chromophores [99–101].

Such a structure can also be reproduced by the use of **1**. Firstly, three chromophores were arranged in a ring-type structure at the 1,3,5-positions of a central benzene moiety [102] (for ring-type arranged (perylene)metal complexes, see [103]). A direct condensation of benzene-1,3,5-triamine with the corresponding anhydride was not successful for the synthesis of such a trichromophore; however, surprisingly, the tris-

Scheme 7. *Synthesis of Linear Bi- and Trichromophoric Perylene Dyes* **30** *and* **31**



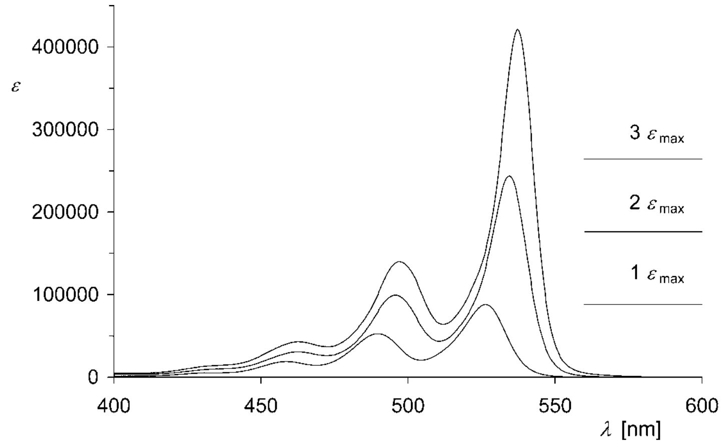
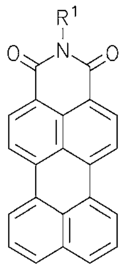


Fig. 20. *UV/VIS Spectra* ($CHCl_3$) *of* **30** (top), **31** (middle), *and* **1** (bottom). R^1 = 1-hexylheptyl.



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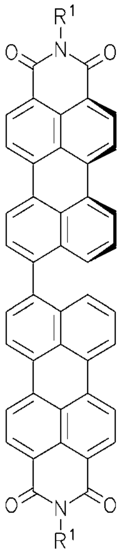

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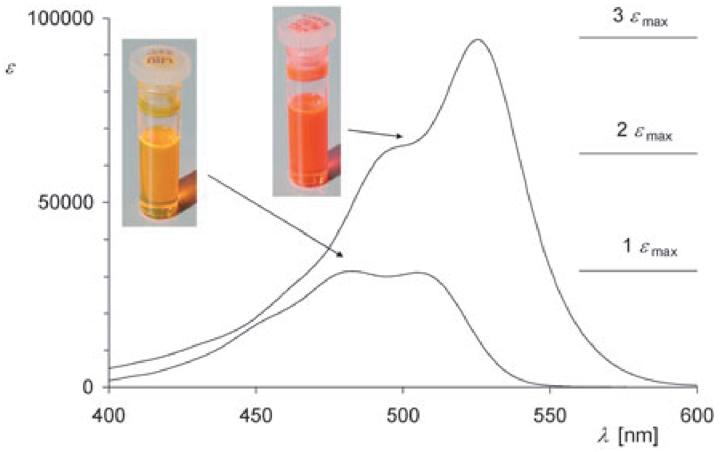
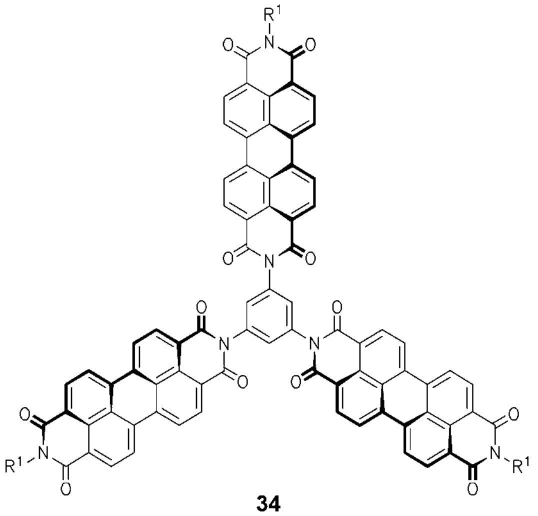


Fig. 21. *UV/VIS Spectrum* (CHCl$_3$) *of* **32** (bottom) *and* **33** (top). R^1 = 1-hexylheptyl.

formamide derivative of benzene-1,3,5-triamine proved to be appreciably more reactive than the triamine [104]. This may be a consequence of the coupling and powering of the condensation reaction with a redox process because no CO but CO$_2$ was evolved during the reaction. Thus, this tris-formamide was condensed without any problem with **22** to give the trichromophore **34** [102]. There are 120° angles between the transition moments in **34**. According to this, a 'constructive exciton effect' is expected. Indeed, an amplification of the absorptivity is observed with the change from the monochromophoric dye **1e** to the bichromophoric dye **28**, and a further amplification to the trichromophoric dye **34** (R^1 = 1-hexylheptyl in all structures; see *Fig. 22*).



34

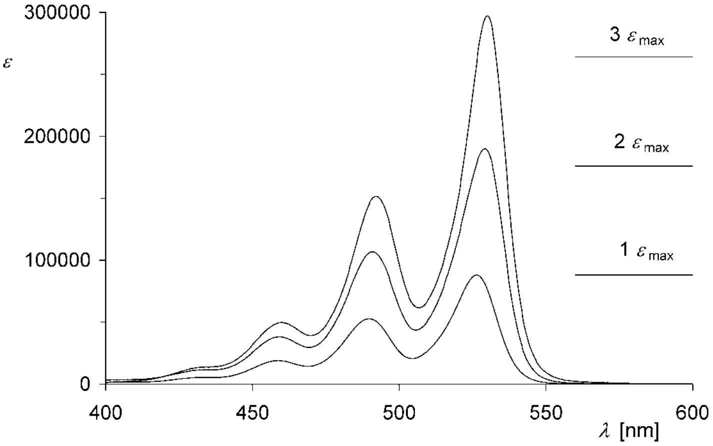
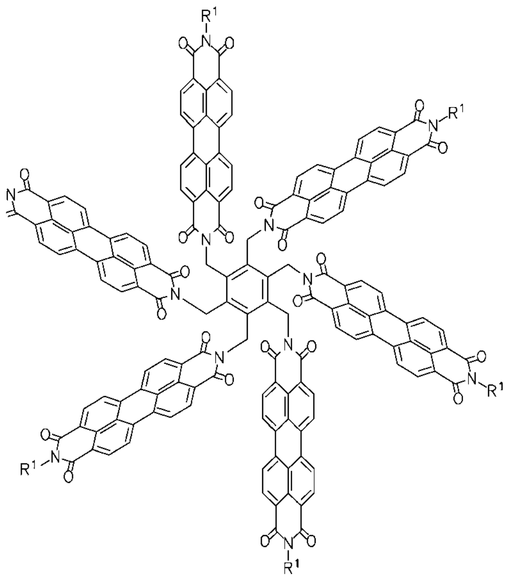
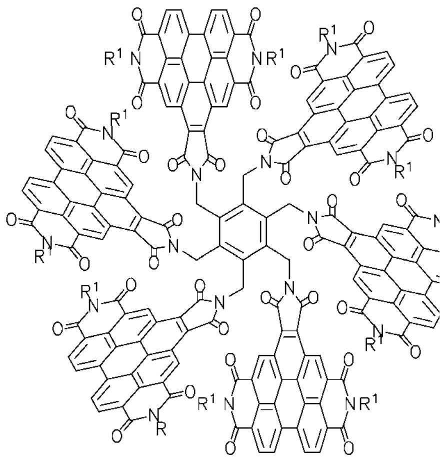


Fig. 22. *UV/VIS Spectrum* ($CHCl_3$) *of* **1** (bottom), **28** (middle), *and* **34** (top). R^1 = 1-hexylheptyl.

The ring-type accumulation of chromophores can be further increased. This is not simple with benzene as the central moiety because of severe steric interactions. However, such a structure is successfully obtained by a nucleophilic displacement reaction by the imide N-atom of **23a** at hexakis(bromomethyl)benzene to give dye **35** (R^1 = 1-hexylheptyl) [96]. The angle between the transition moments of the chromophores is thereby diminished from 120° in **34** to 60° in **35**. The angle of 90° is passed with this structural change, and the exciton effect has switched from 'constructive' to 'destructive'. This has two consequences. Firstly, the molar absorptivity of each chromophore moiety is diminished in **35**. Secondly, the point of gravity of the absorption is shifted to shorter wavelengths; the resulting UV/VIS spectrum (*Fig. 23*) resembles the spectra of the sandwich bichromophore **26** (*Fig. 19*). A further consequence of the strong exciton coupling in **35** is an effective fluorescence quenching (*β*-arrangement).



35



36

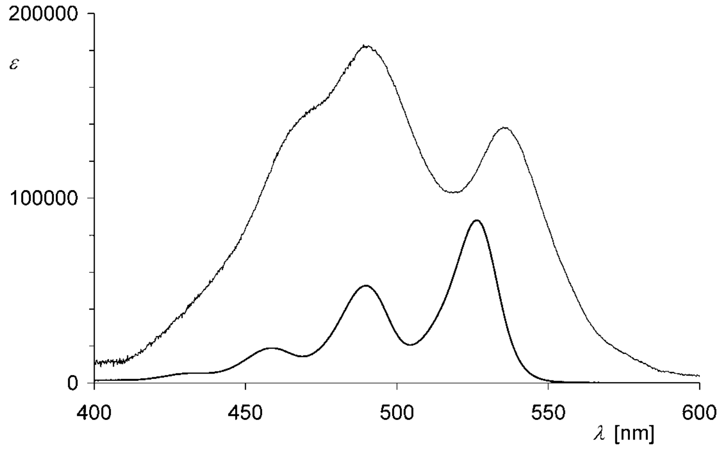


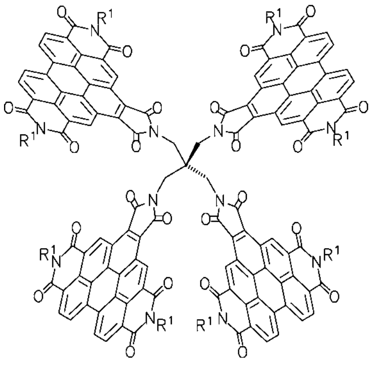
Fig. 23. *UV/VIS Spectrum* ($CHCl_3$) *of* **35** (top) *and* **1** (bottom). R^1 = 1-hexylheptyl.

The perylenebis-imide moieties of **35** were then replaced by the benzoperylenetris-imide moieties. For this, **5g** (R^1 = 1-octylnonyl) is allowed to react under similar conditions with hexabis(bromomethyl)benzene as described for **35** to give **36** [105]. In

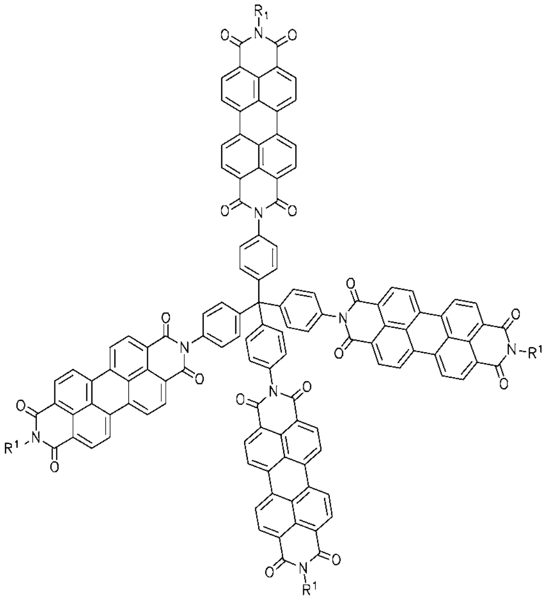
36, the transition moments are turned by 90° to axial orientation. The 'destructive exciton interaction' remains, with reduction of the molar absorptivity; however, the vectors of the transition moments are more distant in **36** than in **35**. As a consequence, the exciton interactions are weaker than in the former case and the spectra of **36** resemble more the monochromophoric compound than in the case of **35**. It is remarkable that the reduction of the molar absorptivity concerns only the most bathochromic absorption, whereas there is amplification for the bands at shorter wavelengths in the UV as was it also observed for **27**.

9.4. *Tripod Antennae.* A tetrahedral arrangement of chromophores (*Fig. 14,c*) has no counterpart in nature. Tetrahedrally arranged π-systems are known; however, no special optical effects were described.

The tetrachromophore **37** can be prepared starting from benzoperylenetris-imides **5** by a nucleophilic displacement reaction [106]. Weak exciton interactions were found that cause a reduction of the molar absorptivity of each chromophore; the transition moments of the individual chromophores are tangentially oriented on the surface of a sphere so that the β-transitions become favored.



37



38

A star-like radial arrangement of chromophores was also successfully achieved by using the tetraphenylmethane moiety as the central unit. Thus 4,4′,4″,4‴-methanetetrayltetrakis[benzenamine] was, activated as its tetrakis-formamide and the latter condensed with the peryleneimide anhydride **22** to give the tetrachromophore **38** [106]. The peripheral N-atoms of the individual chromophores were substituted by 'swallow-tail' substituents to obtain a sufficiently high solubility for spectroscopic investigations. Pronounced exciton effects were observed for **38** with an amplification of the molar absorptivity (see *Fig. 24*). This corresponds to the enclosed angle of the transition

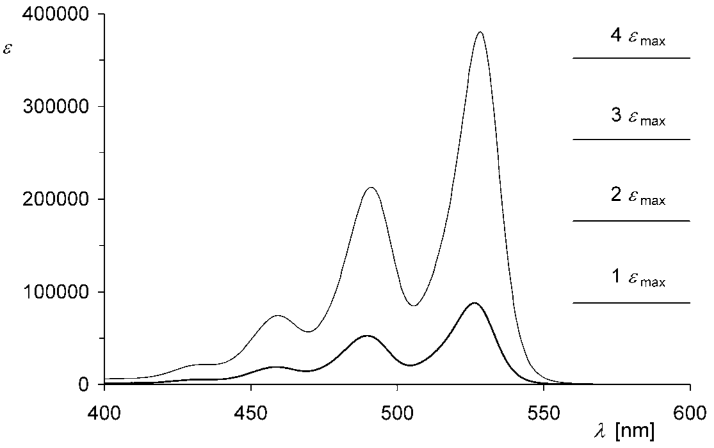


Fig. 24. *UV/VIS Spectrum* ($CHCl_3$) *of* **38** (top) *and* **1** (bottom). R^1 = 1-hexylheptyl.

moments of 120°. One can add three of the transition moments of the chromophores in **38** vectorially to obtain a transition moment with the same strength as the fourth one but pointing in the opposite direction (*Fig. 25*). Therefore, the tetrahedral arrangement of chromophores might be replaced by a simple bichromophore with a linear arrangement which generates the same exciton effect. However, for the tetrahedral arrangement, this holds for all space directions in contrast to the linear arrangement so that even diffuse light can be collected. Therefore, the geometry of **38** is of special interest for solar cells because it does nor requires a tracking of the sun.

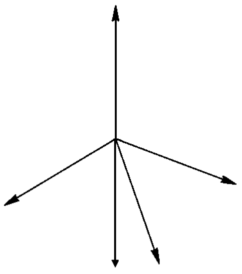


Fig. 25. *Tetrahedrally oriented transition moments and vector addition of three transition moments*

10. Aggregates as Multichromophores. – Dyes exhibit the tendency of aggregation at sufficiently high concentrations. These can be interpreted as multichromophores tied by noncovalent interactions between the dye molecules and also with the medium. Aromatic π-systems of dyes prefer a stacking where the flat aromatic structures overlie each other, however not in an exactly congruent fashion but in shifted and sometimes twisted fashions; this corresponds to the well-known herring-bone structure of the crystals of the aromatic compounds. For the UV/VIS spectra of such an arrangement, it is important to consider how far the individual π-systems are shifted one *vs.* the other.

When they are only slightly shifted, the conditions are similar to those described above for cyclophane **26**; such a type is well-known as *H*-aggregate (β-type), and there are two important consequences: firstly, a hypsochromic shift of the absorption occurs, and secondly, no or very weak fluorescence is observed. The majority of perylene dyes corresponds to this *H*-type [107]. However, if the π-systems are further shifted, the *J*-aggregates are obtained (α-transition). In this case, the absorption is bathochromically shifted, and fluorescence is possible, however seldom remarkable.

The formation of *H*- and *J*-aggregates can be controlled with the solvent for perylene dyes. The *H*-type arrangement is the normal case for concentrated solutions. In some cases, especially in ^{t}BuOH, the formation of *J*-aggregates is observed (*Fig. 26*). A new, sharp absorption maximum is observed in the bathochromic region of the spectrum [108] and an extension to longer wavelengths; for the line-type of aggregates, see [109].

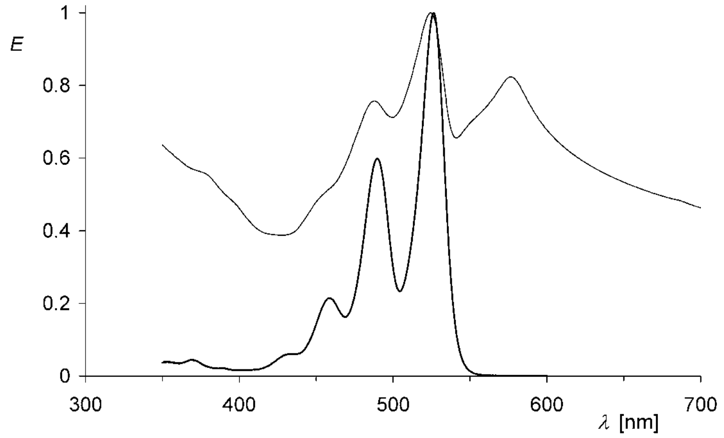


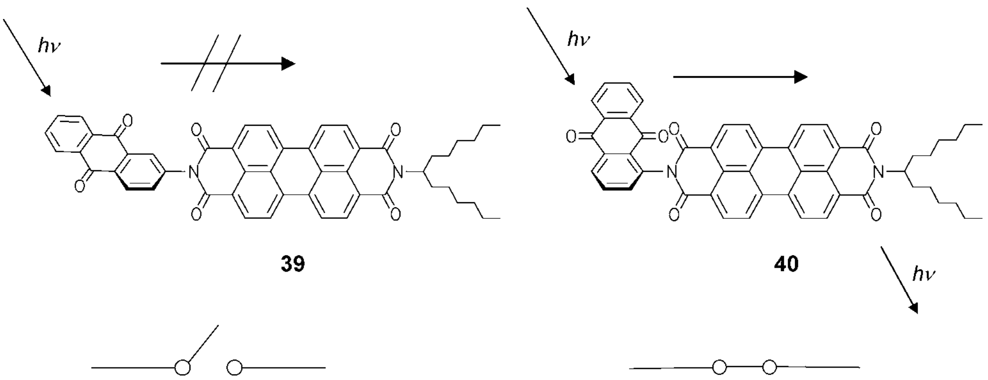
Fig. 26. *Normalized UV/VIS spectrum of a typical* J*-aggregate of perylene dyes induced by* ^{t}*BuOH* (thin line) *and of the molecularly dispersed dye* **1** (R^1 = 1-hexylheptyl) *in* $CHCl_3$ (thick line)

11. Macromolecular Perylene Dyes. – A macromolecular material will be finally obtained if more and more chromophores **1** are linked [88] [110], and completely novel properties such as high DK values are obtained.

12. Bichromophoric Dyes as Components for Computers in Pico-Technology. – The further development of computer technology requires more and more integration of the components and higher and higher rates for signal processing. Optical computers are of special interest here because rates for signal processing in the terahertz range can be expected (10^{12} Hz; 500 nm corresponds to 600 THz). However, an increasing integration is limited by the wavelengths of light of *ca.* 0.5 μm because of diffraction of light. However, if the energy of light is processed instead of the light itself, even smaller dimensions are attained. Devices for the manipulation of light are chromophores so that multichromophoric systems are the target structures for such computers. The preceding work forms a useful basis for the development of such systems.

A gradient of light energy is required for its controlled transport. This can be obtained by a linkage of chromophores with different energies of excitation so that the energy passes from the hypsochromic absorbing chromophore (higher energy) to the bathochromic one such as this is demonstrated for the bichromophoric dye **24**; the driving force for the energy transport is caused by the second law of thermodynamics. Even these energy-transfer systems are limited concerning the density of integration by the *Förster* radius. This is of the order of *ca.* 3 nm for the majority of relevant combinations of chromophores. Below this limit, the energy of excitation is spread indiscriminately over the involved chromophores.

It could be shown recently [111] that a controlled energy transfer is possible, even below the *Förster* radius, if rigid structures are involved. For a demonstration, the perylene chromophore of **1** was linked with one of its N-atoms to the nonfluorescent anthraquinone in position 2 to form **39** (see *Fig. 27*). This N-atom is electronically well decoupled from the anthraquinone unit because of orbital nodes in the HOMO and LUMO (see above). Moreover, both chromophores are orthogonal resulting in a further decoupling. Thus, there is no direct electronic influence between the two chromophores. According to this, the UV/VIS spectra of the bichromophore are purely additive, and the perylenebis-imide chromophore exhibits fluorescence when irradiated and the anthraquinone chromophore not. The deactivation of the latter proceeds so fast that there is no energy transfer to the perylenebis-imide unit. A similar behavior is also observed for other anthraquinone-perylene bichromophores, even if linked with different spacers. A completely different behavior is observed for the bichromophore **40** (see *Fig. 27*) because a complete energy transfer and a strong fluorescence is observed, even if the anthraquinone chromophore is irradiated; the energy transfer in **40** is obviously so fast that it can efficiently compete with quenching processes in the anthraquinone.



39

40

Fig. 27. *Optical switches based on perylene dyes*

Thus, it is possible to switch on energy transfer by the relative orientation of the chromophores, and this is possible with a distance of the units of only 140 pm. The novel concept means an appreciable progress with respect to the already known systems in which the quenching of energy is switched on. This means a loss of the energy of excitation like a short-cut in an electrical circuit. The novel concept enables possibilities for a controlled transport of the energy of excitation. This is the basis for the development of molecular optical components in picometer dimensions, and this means picotechnology. The small dimensions of the switch are not only of interest for obtaining a high density of integration, but also the construction of such components can be carried out with the well-established and far-developed synthetic methods of preparative chemistry.

13. Outlook. – The perylene dyes were a compound class with very special exotic applications, preferably as vat dyes and highly photostable pigments in the past; this has completely changed recently. Especially, the development of soluble derivatives has induced a boom resulting in the present availability of 2000 derivatives described in more than 3000 papers. The potential of these substances has not been completely exhausted by a long way. The work already published about multichromophoric fluorescent dyes has demonstrated how the interaction of the individual chromophores results in substances with completely novel properties. One can expect many important novel developments in this field of functional dyes which find their entrance into very different working areas. This may be not only a revolution in the area of computer technology but also in the construction of completely novel antenna systems for the concentration of diffuse light.

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