Star-like oriented chromophores

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The tetrahedral arrangement of perylene bisimide chromophores gives a novel molecular system of antennae for the conversion of diffuse solar radiation. A detailed analysis of their UV/Vis spectra gives an impression of the consolidation of the single chromophores.

The spacial orientation of chromophores has gained an increasing interest since analyses of the structures of the photosynthetic assemblies of the higher plants[1] and bacteria[2] were performed. The photosynthetic assembly of the higher plants essentially corresponds to a tracked dipole antenna [Fig. 1(a)] to the solar radiation where the conducting wire in Fig. 1(a) is replaced by an arrangement of π-systems, and the electrical connector by a redox system. The assembly in bacteria[2] corresponds to a ring antenna [Fig. 1(b), compare ref. 3–5]. Another technically important principle for the construction of antennae has not been realized in nature: star-like constructed antennae[6] [Fig. 1(c)]; see, for example, the triple-leg antenna. The tetrahedrally arranged segments of such antennae are expected to be of particular importance for the collection of diffuse light radiation so that technically simpler assemblies for the conversion of solar radiation become possible.

Results and discussion

We have used chemically inert tetraphenylmethane as the central unit for such an assembly and the highly fluorescent and photostable perylene-3,4:9,10-tetracarboxylic bisimides[7] as chromophores. The transition moment of the latter is along the main molecular axis[8] so that the nitrogen atoms of the bisimides are ideal linking positions for the construction of tetrahedral antennae.

We have used the easily obtainable triphenylmethylaniline as the starting material for the construction of such antennae (compare also ref. 9 and 10 for other tetrahedral chromophores), have reduced it *via* its diazonium salt to tetraphenylmethane and nitrated the four *p*-positions.[11] The reduction of the tetra(*p*-nitrophenyl)methane proved to be difficult (no significant reduction by hydrogen at 200 bar/catalyst, $TiCl_3$/hydrochloric acid, Fe/acetic acid, $SnCl_2$/hydrochloric acid, Pd/C/ hydrazine hydrate/ethanol), but could be achieved with Raney nickel/hydrazine hydrate/tetrahydrofuran. The tetramine thus obtained was activated[12] by conversion to the tetra formamide **1**, and condensed with the perylene anhydride imide **2**[13] to the tetrachromophoric dye **3** (Scheme 1). The long-chain secondary 1-hexylheptyl substituent ("swallow-tail substituent"[14]) provides sufficiently high solubility for the dyes.

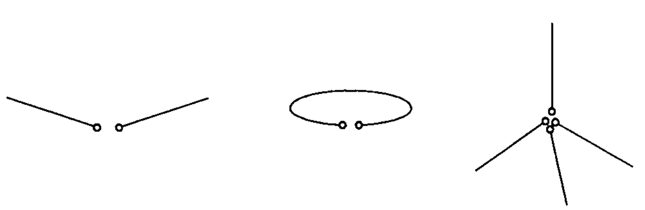
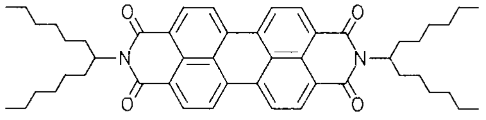


Fig. 1 Building principles of antennae with electrical conductors and connectors: (a) dipole antenna, (b) ring antenna, (c) star antenna. The conductors may be replaced by π-systems.



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The UV/Vis absorption spectrum of **3** is as well structured as that of the monochromophoric dye **4** and the fluorescence spectrum, with a fluorescence quantum yield of about 100%, is of the mirror-type with respect to the absorption spectrum; see Fig. 2. The tetrahedral arrangement of chromophores should result in an amplification of the absorption due to an exciton interaction[15,16] because the angle between the transition moment of the single chromophores is larger than 90° and all chromophores are within the Förster radius of about 30 Å. If three tetrahedral components of the transition moment are added together, the component obtained will be equally large, but opposite, to the fourth. As a consequence, the exciton effect corresponds to two linearly connected chromophores. However, this is true for all four corners of the tetrahedron. Therefore, one is not limited to a certain orientation of the chromophores relative to the light to be absorbed. A molar absorptivity of more than 380 000 was found for **3** and this is significantly more than the fourfold value of **4** (88 000[17]). The comparatively large distance between the single chromophores must be taken into account with this calculation because it allows only small exciton effects. A more detailed investigation into the interaction of chromophores in **3** was done by a Gaussian analysis of the UV/Vis spectra according to eqn. (1) by analogy with ref. 18:

$$\varepsilon(\lambda) = \sum \varepsilon_0 \cdot \exp\left[-\frac{(1/\lambda - 1/\lambda_0)^2}{2\sigma^2}\right] \qquad (1)$$

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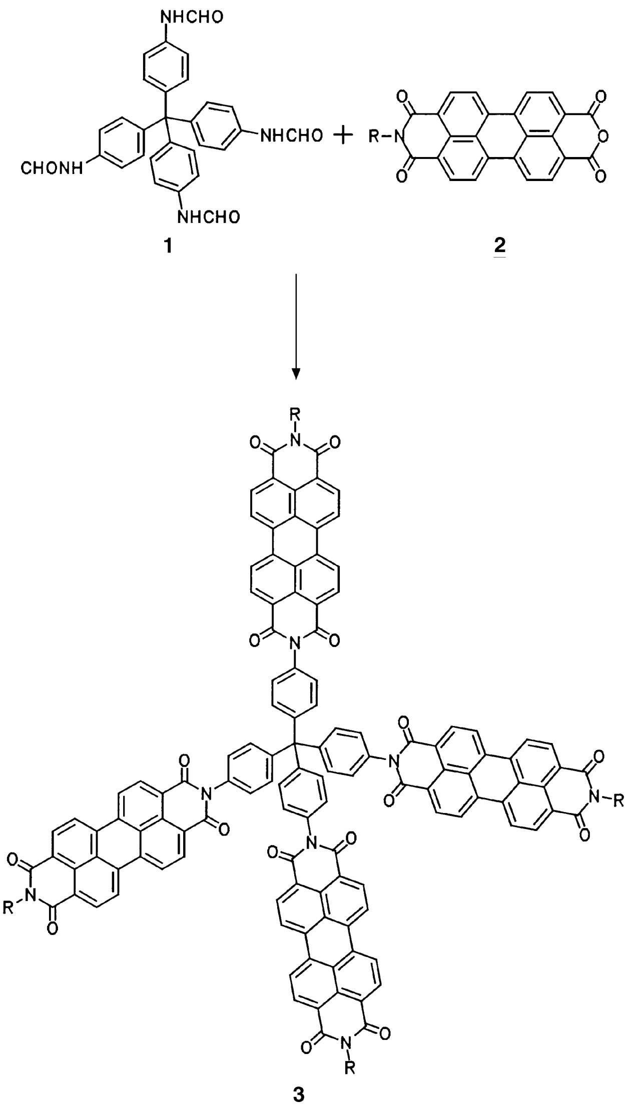

Scheme 1 Synthesis of 3.

This was successful, with an R value of 2.1%; see Fig. 2. A similar cascade of vibronic bands was found as for **4**; see Table 1. The wavelengths of the first three vibronic bands are identical within 3 nm with the bands of **4** and are slightly bathochromically shifted. The σ widths of the vibronic bands of the two dyes are similar, however the first vibronic band is slightly narrower than that of the monochromophoric dye **4**; this effect has already been qualitatively described for linear oligo chromophores.[19] However, the molar absorptivities of the vibronic bands of **3** are greater when compared with **4** (this is also true for the integrals); the exciton interaction is constructive because of the tetrahedral arrangement of the chromophores (Fig. 3).

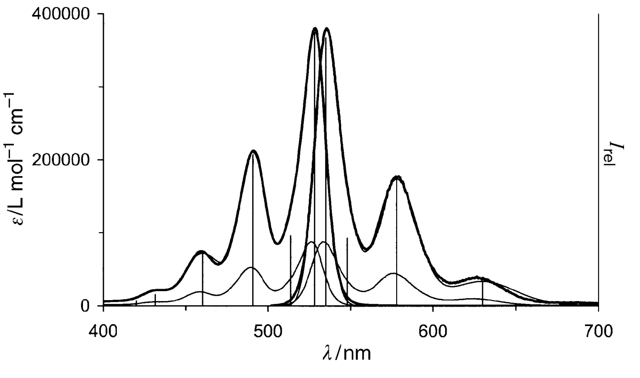

Fig. 2 UV/Vis spectra of **3** and **4** in chloroform. Upper thick line: absorption and fluorescence spectra of the tetrachromophore **3** (the fluorescence spectra are normalized to the absorption spectra). Upper thin line: simulated spectra from Gaussian analysis. Lower thin line: UV/Vis absorption and fluorescence spectra of the monochromophore **4**. Bars: calculated line positions and absorptivities of **3**.

Table 1 Gaussian analysis of UV/Vis spectra in chloroform (330–757 nm)

	3 (abs.)	**3** (fluo.)	**4** (abs.)	**4** (fluo.)
$n_{\mathrm{chrom.}}$ [a]	4	4	1	1
$\lambda_{\max}(1)$ [b]	528.1	535.0	526.3	533.7
$2\sigma^2(1)$ [c]	0.118	0.119	0.123	0.147
$\varepsilon_{\max}(1)$ [d]	374 400	367 300	86 700	87 100
$\lambda_{\max}(2)$	513.7	548.0	512.5	549.4
$2\sigma^2(2)$	0.091	0.098	0.085	0.082
$\varepsilon_{\max}(2)$	95 800	92 700	22 100	15 900
$\lambda_{\max}(3)$	490.8	578.0	489.4	576.1
$2\sigma^2(3)$	0.249	0.268	0.268	0.250
$\varepsilon_{\max}(3)$	207 300	173 400	51 600	43 800
$\lambda_{\max}(4)$	460.3	630.0	458.7	622.2
$2\sigma^2(4)$	0.633	0.467	0.526	0.420
$\varepsilon_{\max}(4)$	71 900	33 500	18 700	9800
$\lambda_{\max}(5)$	431.5	680.0	436.0	682.7
$2\sigma^2(5)$	0.226	0.215	0.127	0.233
$\varepsilon_{\max}(5)$	15 300	1000	1900	1100
$\lambda_{\max}(6)$	420.0		428.4	750.2
$2\sigma^2(6)$	0.556		0.252	1.246
$\varepsilon_{\max}(6)$	6500		3900	500
$\lambda_{\max}(7)$	379.9		412.2	
$2\sigma^2(7)$	4.209		0.777	
$\varepsilon_{\max}(7)$	8500		1700	
R [e]	0.021	0.037	0.017	0.016

[a] Number of chromophores. [b] Calculated wavelength in nm. [c] Linewidth in 10^6 cm^{-2} (kK^2). [d] Calculated absorptivity in L mol^{-1} cm^{-1}. [e] Residual: $R = \sqrt{\int[\varepsilon(\lambda)_{\mathrm{calc.}} - \varepsilon(\lambda)_{\mathrm{exp.}}]^2\,\mathrm{d}\lambda / \int[\varepsilon(\lambda)_{\mathrm{exp.}}]^2\,\mathrm{d}\lambda}$

The interaction of the single chromophores is further characterized by the Ross parameter x,[19] which is a measure of the movement of the nuclei caused by optical excitation and can be taken from vibronic spectra. x is zero if there is the same geometry in the electronic ground and excited state and increases if exitation elongates any of the bonds. A Ross analysis was successful for the vibronic bands (1), (3), (4) and (5) with an R value of 3.2%[20] (compare with ref. 18). The x value of **3** is 0.729 and is significantly smaller than for the monochromophoric dye **4** ($x = 0.745$). It may be concluded that the excitation of the dye is spread over several chromophores because of the exciton effect and therefore the disturbance of each π system becomes smaller. Further photophysical properties of **3** will be reported elsewhere.

Experimental

General methods

All starting materials were supplied by Aldrich. The IR and UV/Vis spectra were acquired on IFS 45 (Bruker) and OMEGA 20 (Bruins Instruments) spectrometers, respectively.

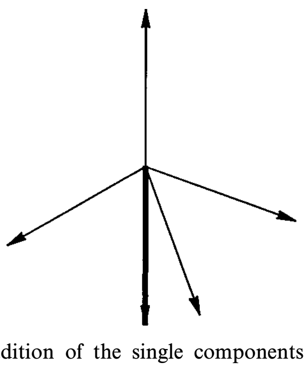

Fig. 3 Vector addition of the single components of the transition moments in **3**.

The fluorescence spectra were obtained using an FS 3000 from Perkin-Elmer with total spectral correction, as described previously.[21] A VXR 400S (Varian) instrument operating at 400 and 100.6 MHz was used to acquire the ^1H and ^{13}C NMR spectra, respectively. Mass spectra were recorded on an SN 1B instrument (Varian MAT).

Syntheses

Tetra(4-aminophenyl)methane. Tetra(4-nitrophenyl)methane (1.5 g, 3.0 mmol), hydrazine hydrate (1.88 g, 37.5 mmol), Raney nickel (10 g) and tetrahydrofuran (200 ml) were refluxed together for 3 h. Then, the mixture was hot filtered, washed twice with hot ethanol, the products precipitated from solution and re-crystallized twice from ethanol. Yield 520 mg (46%) of light beige crystals, m.p. 318 °C (dec., ref. 11 319–320 °C). IR (KBr): $\tilde{\nu}$/cm^{-1} 3421 s, 3396 s, 3351 s, 3214 m, 3025 m, 1621 s, 1581 m, 1508 s, 1428 w, 1273 s, 1183 s, 1131 w, 1015 m, 942 w, 828 s, 814 s, 578 s, 514 m. ^1H NMR ([D]$_6$-acetone): δ 4.43 (s, 8 H, NH_2), 6.53 ($^3J = 8.5$, d, 8 H, aromatic H), 6.86 ($^3J = 8.5$ Hz, d, 8 H, aromatic H). MS (70 eV, EI): *m/z* (%) 381 (12) $[M + 1]^+$, 380 (43) $[M]^+$, 289 (23), 288 (100) $[M^- - C_6H_4NH_2]^+$, 196 (10), 195 (14) $[M^- - 2\,C_6H_4NH_2]^+$, 190 (5).

Tetra(4-formylaminophenyl)methane (1). Tetra(4-aminophenyl)methane (400 mg, 1.05 mmol) and anhydrous formic acid (10 ml) were refluxed for 4 h. After cooling, the product was precipitated from solution with diethyl ether (20 ml), collected by vacuum filtration and re-crystallized from DMF. Yield 170 mg (33%) of light brown crystals of **1**. IR (KBr): $\tilde{\nu}$/cm^{-1} 3436 s, 3267 s, 3190 m, 3105 m, 3053 m, 2888 w, 1677 s, 1604 s, 1533 s, 1513 s, 1405 m, 1319 m, 1296 m, 1256 w, 1192 m, 1018 w, 822 m, 768 m. MS (70 eV, EI): *m/z* (%) 492 (8) $[M]^+$, 465 (8), 464 (28) $[M^- - CO]^+$, 462 (8), 436 (12) $[M^- - 2CO]^+$, 408 (2) $[M^- - 3CO]^+$, 373 (14), 372 (56) $[M^- - C_6H_5NHCHO]^+$, 370 (10), 345 (26), 344 (100), 343 (6), 342 (20), 317 (10), 316 (35), 314 (5), 252 (3) $[M^- - 2C_6H_5NHCHO]^+$, 224 (5), 196 (6), 195 (18), 180 (6), 44 (17). Anal. for $C_{29}H_{24}N_4O_4 \cdot H_2O$ (510.6): calc. C 68.21, H 5.14, N 10.98; found C 68.83, H 5.27, N 10.83%.

Tetra-4-[*N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylicbisimid-*N'*-yl]phenylmethane (3). *N*-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10carboximide[13] (**2**, 200 mg, 0.35 mmol) tetra(4-formylaminophenyl) methane (**1**, 90 mg, 0.2 mmol) and imidazole (4 g) were heated under argon (180 °C, 4 h) and then suspended in ethanol (50 ml), acidified with 2 N HCl and stirred at room temperature (2 h). The product was collected by vacuum filtration, thoroughly washed with distilled water, dried in air (100 °C) and purified by two column separations ($Al_2O_3 + 2\%\ H_2O$, chloroform–ethanol 10 : 1 and silica gel, chloroform–acetone 15 : 1). Yield 320 mg of **3** (35%) as a red solid, m.p. > 350 °C. R_f (silica gel, chloroform–acetone 20 : 1) = 0.20. IR (KBr): $\tilde{\nu}$/cm^{-1} 3436 m, 2952 m, 2926 m, 2855 m, 1712 s, 1699 s, 1659 s, 1594 s, 1579 m, 1505 m, 1457 w, 1427 m, 1406 m, 1341 s, 1252 m, 1154 m, 1137 w, 1123 w, 1107 w, 1020 w, 965 w, 853 w, 811 m, 794 w, 747 m, 500 w. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 528 (380 900), 491 (213 000), 460 (75 000), 434 (22 100). Fluorescence ($CHCl_3$): λ_{max}/nm 624, 576, 534. Fluorescence quantum yield (chloroform): $\Phi = 100\%$, reference *N,N'*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**4**).[21] ^1H NMR ($CDCl_3$): δ 0.85 (t, 24 H, 8 CH_3), 1.27 (m_c, 64 H, 32 CH_2), 1.94 (m_c, 8 H, 4 α-CH_2), 2.27 (m_c, 8 H, 4 α-CH_2), 5.16 (p, 4 H, 4 CH), 7.52 (d, 8 H, aromatic H), 7.67 (d, 8 H, aromatic H), 8.30 (m_c, 16 H, perylene aryl H), 8.55 (m_c, 16 H, perylene aryl H). ^{13}C NMR ($CDCl_3$): δ 14.1 (8 C, CH_3), 22.6 (8 C, CH_2), 27.1 (8 C, CH_2), 29.3 (8 C, CH_2), 31.8 (8 C, CH_2), 32.4 (8 C, CH_2), 55.0 (4 C, CH), 122.9 (perylene C), 123.3 (perylene C), 125.9, 128.1, 129.2, 131.3, 132.5, 133.4, 133.8, 134.4, 146.6, 163.2 (16 C, C=O). MS (70 eV, ESI): *m/z* (%) 2629 (8), 2628 (19), 2627 (33), 2626 (49) $[M + Na]^+$, 2070 (100) $[M + Na - 1\ \text{chromophore}]^+$. Anal. for $C_{173}H_{156}N_8O_{16}$ (2603.2): calc. C 79.81, H 6.05, N 4.31; found C 79.05, H 5.95, N 4.23%.

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