Perylene bisimide J-aggregates with absorption maxima in the NIR†

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NIR absorbing J-aggregates with biomimetic features of chlorophyll dye assemblies are obtained upon hydrogen-bond directed self-assembly of a green 1,7-diamino-substituted perylene bisimide dye.

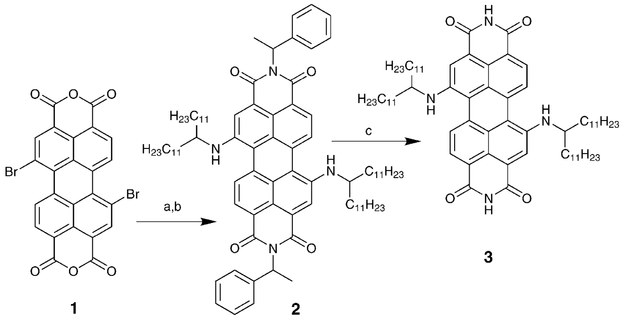
The highly efficient harvesting of sunlight in natural photosynthetic dye assemblies relies on the tunability of the absorption properties of (bacterio)chlorophyll dyes by chemical modification, hydrogen bonding of carbonyl groups as well as J-aggregation.[1] In particular, the latter enables pronounced bathochromic shifts of the absorption maxima into the near infrared (NIR) spectral region as well as efficient excitonic coupling among the dyes.[2,3] For example, in green bacteria a slipped arrangement of closely packed bacteriochlorophyll (BChl) *c* molecules within self-assembled nanorods is given that extends the absorption range for solar light from 660 nm (λ_{max} for monomers) to 750 nm (λ_{max} for J-aggregates) and affords the most efficient non-crystalline exciton transport system known at ambient temperature.[2] Likewise, in purple bacteria, protein-mediated J-aggregation of the already at rather long wavelength absorbing BChl *a* (λ_{max} for monomer at 770 nm) affords intense NIR absorption bands up to 875 nm in the cyclic array of light harvesting complex 1.[3] Taking into consideration that a most efficient system for the utilisation of terrestrial solar energy should collect light of wavelengths up to at least 900 nm,[4] there is a strong interest in developing artificial analogues of natural BChl J-aggregates. Although plenty of dye molecules are available that exhibit absorption bands in the NIR,[5] it is surprising that there are only few examples of non-natural dye aggregates that exhibit bathochromically shifted J-type absorption bands beyond 800 nm.[6,7]

In this paper, we report an aggregate of the "green" perylene bisimides (PBIs), *i.e.*, 1,7-diamino-substituted PBIs. These dyes were introduced by Wasielewski and co-workers as synthetic counterparts of natural chlorophylls owing to their green color that arises from the absorption bands at around 700 and 450 nm.[8] Here we present a "second generation" of such green PBI dyes that exhibits another feature of their natural chlorophyll counterparts: that is a most pronounced bathochromic shift of the absorption band into the NIR (822 nm) upon self-aggregation.

Our work has been initiated by the recent discovery that the typically prevailing formation of aggregates with hypsochromically shifted absorption bands (so-called H-aggregates) for the class of PBI dyes[9] can be switched to give J-aggregates by hydrogen-bond assisted self-assembly.[10] Thus, the green perylene derivative PBI **3** was synthesised (Scheme 1) and its hydrogen-bond directed aggregation behaviour was studied by solvent and temperature-dependent UV-Vis spectroscopy, IR spectroscopy, and atomic force microscopy (AFM) and scanning tunnelling microscopy (STM).

Our synthesis started with the easily accessible mixture of 1,6- and 1,7-dibromoperylene bisanhydride **1**.[11] Imidisation of the latter with racemic α-methylbenzylamine and subsequent nucleophilic displacement of the bromine atoms by tricosan-12-amine, and column chromatographic purification of the crude product afforded the isomerically pure 1,7-disubstituted PBI **2**. Removal of the protecting group by BBr_3 treatment in anhydrous dichloromethane yielded the green PBI dye **3** that was purified successively by column and preparative thin layer chromatography, and characterized using NMR spectroscopy, mass spectrometry, and elemental analysis (ESI†).

In polar solvents such as dichloromethane, PBI **3** exhibits the characteristic UV-Vis absorption spectra of green PBIs, *i.e.*, an absorption maximum at 702 nm with an absorption coefficient of 34 900 M^{-1} cm^{-1}. The emission spectrum is almost the mirror image of the absorption spectrum with a maximum at 760 nm and a quantum yield of 10%. However, in aliphatic solvents like methylcyclohexane (MCH), the absorption band reveals a pronounced bathochromic shift to λ_{max} = 822 nm and, similar to natural BChl *c* rod aggregates,[2] the fluorescence is entirely quenched. Temperature-dependent



Scheme 1 Synthesis of PBI **3**. (a) α-Methylbenzylamine (*rac*), quinoline, $Zn(OAc)_2$, 140 °C, 6 h, 67% of the respective bisimide; (b) tricosan-12-amine, 150 °C, 6 h, argon, 17% of **2**; (c) BBr_3, CH_2Cl_2, 25 °C, 93% of **3**.

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UV-Vis spectra reveal a fully reversible dissociation of these aggregates into monomeric dyes, whose absorption maximum is located at 664 nm in this solvent (Fig. 1). Accordingly, a bathochromic shift of 158 nm (2900 cm^{-1}) is observed for PBI **3** which is one of the most pronounced bathochromic shifts reported for dye aggregates so far.

A closer inspection of the absorption bands of monomeric and aggregated dyes **3** in MCH reveals a significant band narrowing and an increase in the transition dipole moment for the aggregate band. Thus, the absorption band of the monomer exhibits a full-width-at-half-maximum (fwhm) value of 2470 cm^{-1} and a transition dipole moment of 7.5 D. The respective values for the aggregate band are 1230 cm^{-1} and 7.8 D. Both features are characteristic for a coherently delocalised excitonic state.[12]

The structural features of these NIR absorbing dye aggregates were elucidated using spectroscopic and microscopic methods. Solvent-dependent FTIR spectroscopy confirmed the formation of N–H$\cdots$O hydrogen bonds between the imide hydrogen atoms and the carbonyl oxygen atoms in low polarity environments. The free NH stretching vibrations in the FTIR spectra of monomeric **3** in CH_2Cl_2 occur at $\tilde{\nu}$(NH) = 3370 cm^{-1}. Whereas, in MCH and in the solid state this band is split into two bands, one of which is only slightly displaced (~3320 cm^{-1}) and the other one is significantly displaced (~3170 cm^{-1}). Thus, the former band is attributed to the non hydrogen-bonded NH groups in bay positions and the latter to the hydrogen-bonded imide groups (ESI†).

AFM investigations revealed the formation of extended networks of PBI **3** in MCH and solvent mixtures containing a small amount (1–5%) of $CHCl_3$. The images in Fig. 2 show extended networks of thin rod-like fibers with a height value of 1.2 ± 0.1 nm and an average width value of 9 ± 2 nm. The length of the fibrillar and partly interweaved structures ranges from a few nanometres to micrometres.

To gain information on molecular-level resolutions, STM investigations were carried out on highly oriented pyrolytic graphite (HOPG). Fig. 3 shows a typical STM image of PBI **3** at the solution–HOPG interface.[13] The size of the domains are several hundred nm in length and up to one hundred nm in width. Moreover, some defects (dark troughs) can also be observed. These results are indicative of a stronger interaction between the molecules within a row than that between the rows.

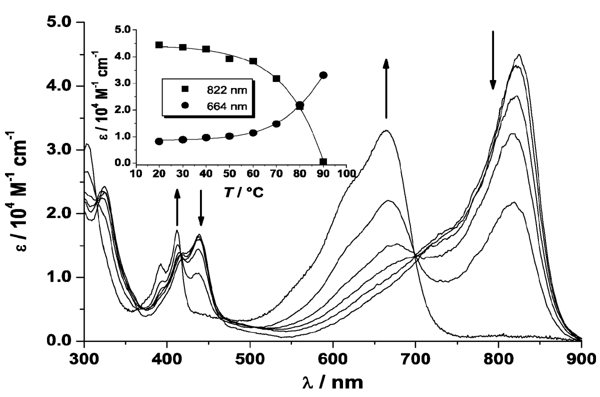


Fig. 1 Temperature-dependent UV-Vis spectra of PBI **3** in MCH (4×10^{-6} M) at 20–90 °C. Arrows indicate the spectral changes with increasing temperature. Inset: change in absorption at 822 (■) and 664 (●) nm with increasing temperature and sigmoidal fit of the collected data points.

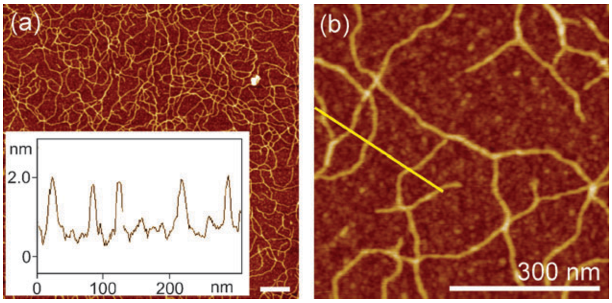


Fig. 2 Tapping-mode AFM images of self-assembled PBI **3** deposited from MCH–$CHCl_3$ (95 : 5) solution ($c = 1 \times 10^{-5}$ M) on silicon wafer. Inset in (a) is a height profile along the yellow line in image (b). The scale bar for both images is 300 nm; the z scale is 5 nm.

The unit cell parameters of the ordered first layer are a = 1.44 ± 0.06 nm, b = 2.34 ± 0.04 nm, and α = 74 ± 4°. Taking into consideration a distance of about 0.2 nm for a hydrogen bond, our STM analysis reveals that the hydrogen-bonded chains are maintained on the HOPG surface and run along the direction of the rows (a direction). The value of a is in good agreement with literature values (1.45 nm) obtained from STM investigation for at bay position unsubstituted perylene bisimides adsorbed on HOPG.[14,15] Thus PBI **3** molecules are self-assembled by hydrogen bonding at the imide groups, and ordered on HOPG as schematically shown in Fig. 3c. The distance between the neighbouring aggregate rows was estimated as 2.34 ± 0.04 nm, which is expected to correlate with the molecular width, but does not agree exactly with the values calculated by the MM+ method (3.9 nm). Taking into account that the alkyl chains of adjacent molecules are interdigitated, a calculated value of approximately 2.6 nm is obtained, and thus correlates well with the experimental data.

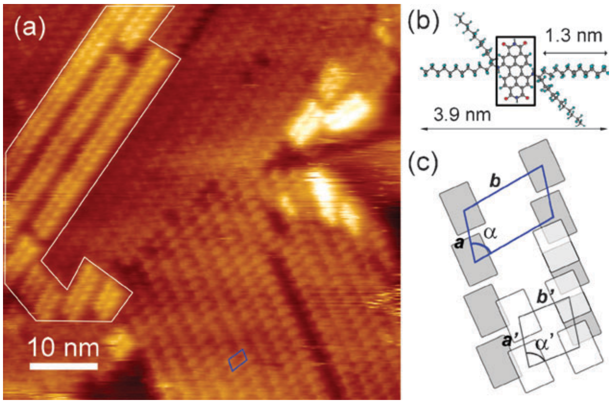
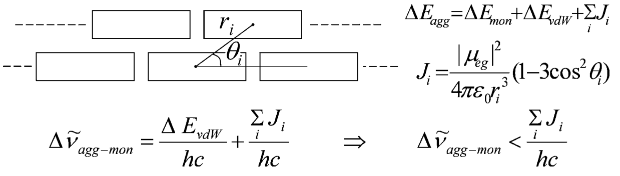


Fig. 3 (a) STM image of assemblies of dye **3** at the octanoic acid–tetradecane (1 : 1) solution–HOPG interface. $V_{\text{bias}} = -1.5$ V, I = 5 pA. The blue rhombus represents the unit cell of the first layer. (b) Molecular dimensions of PBI **3** obtained by MM+ calculations. (c) Schematic representation of the arrangement of PBI units (grey: PBI units in the first layer; white: PBI units in the second layer) and unit cells of each layer.



$$\Delta E_{agg} = \Delta E_{mon} + \Delta E_{vdW} + \sum_i J_i$$

$$J_i = \frac{|\mu_{eg}|^2}{4\pi\varepsilon_0 r_i^3}(1 - 3\cos^2\theta_i)$$

$$\Delta\tilde{\nu}_{agg-mon} = \frac{\Delta E_{vdW}}{hc} + \frac{\sum_i J_i}{hc} \quad \Rightarrow \quad \Delta\tilde{\nu}_{agg-mon} < \frac{\sum_i J_i}{hc}$$

Fig. 4 Arrangement of monomeric PBI units in a double string-type aggregate structure and equations for estimating the spectral shift. ΔE_{agg}, ΔE_{mon}, and ΔE_{vdW} denote the energy differences of ground and excited states of the aggregate, the monomer and the van der Waals energy, respectively. J_i is the excitonic coupling and r_i the distance of adjacent monomeric units with the slip angle θ_i, and μ_{eg} the transition dipole moment of the monomer (for the calculation of μ_{eg}, see ESI†). $\Delta\tilde{\nu}_{\mathrm{agg-mon}}$ denotes the spectral shift of the aggregate band in respect to the monomer band.

A part of the second layer on top of the first layer is visualised as bright rows (Fig. 3a, highlighted with a white frame, and ESI†). The unit cell parameters of the second layer are different from those of the first layer: $a' = 1.4 \pm 0.1$ nm, $b' = 1.4 \pm 0.2$ nm, and $\alpha' = 82 \pm 4°$. The value of a' is similar to that of a of the first layer, indicating hydrogen bonding of PBI molecules at the imide groups in the a' direction. However, the distance between PBI molecules in the direction of the bay position (the value of b') is too narrow to allow the alkyl chains to be sprawled out. Parkinson and co-workers reported that long alkyl chains at the imide positions of PBI are able to protrude from the adsorbate layer into the phenyloctane solution.[16] This might explain the small value of b' that corresponds well with the value of the molecular width without flexible alkyl chains (perpendicular to the *N*,*N*-axis; 1.3 nm). The larger α' value of the second layer compared to the α value of the first layer leads to two different types of arrays that cannot properly adjust on top of each other. This might be the reason why the second layer consists mostly of only two rows.

Moreover, the PBI cores of the second layer are not exactly on top of that of the first layer. They are rather slipped in the a' direction (see ESI†). This phenomenon of a slipped π-stacked arrangement of the PBI units is of significant importance for explaining the pronounced bathochromically shifted J-band in the UV-Vis absorption spectra (Fig. 1). For a double string-type aggregate structure (Fig. 4), a bathochromic shift of $\Delta\tilde{\nu}_{\mathrm{agg-mon}} > 1940\ \mathrm{cm}^{-1}$ is calculated for a π–π distance of 3.5 Å and a slip angle of $\theta = 26°$.[17] This value is in good agreement with the experimental value of 2900 cm^{-1}, if one considers an additional contribution by the van der Waals energy (which is not included in the calculation and only indicated by the "$>$" sign in the calculated value).

To conclude, the first example of perylene bisimide dye aggregates with absorption bands in the NIR region is introduced. The distinct similarities of this dye aggregate to natural light-harvesting bacteriochlorophyll dye aggregates are, on the one hand, the structural features, *i.e.*, slipped π-stacks and hydrogen bonding and, on the other hand, the spectral features, *i.e.*, a J-type absorption band beyond 800 nm and a second higher energy band at around 450 nm. On the basis of these properties, the new PBI dye assemblies are promising materials for NIR light absorption in organic solar cells and NIR photosensitisation where their natural counterparts fail for stability reasons. Such PBI aggregates might enable materials for photonic applications and photodynamic therapy as well.

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