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Self-Assembly Processes

Supramolecular Construction of Fluorescent J-Aggregates Based on Hydrogen-Bonded Perylene Dyes**

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Since their serendipitous discovery in 1936 by Jelley and Scheibe,[1] cyanine-dye-based J-aggregates (also called Scheibe aggregates) have evoked much scientific interest. Such dye aggregates have attracted considerable attention for various technological applications.[2] However, despite enormous effort made during the past few decades, no examples of other dye aggregates[3] have been achieved with optical properties similar to those of cyanine-dye aggregates: strongly bathochromically shifted absorption and fluorescence bands with much narrower bandwidths than those of the respective monomers, combined with a high fluorescence quantum yield. Many synthetic dyes, including the remarkably photostable and highly fluorescent perylene bisimide dyes, form preferentially sandwich-type H-aggregates, which exhibit unfavorable, strongly quenched fluorescence properties.[4,5]

In natural light-harvesting pigments, proteins or metal-ion coordination direct a slipped arrangement of chlorophyll dyes,[6] which leads to the desired J-type aggregation mode with pronounced bathochromic shifts of the absorption bands and high exciton mobility. The latter property is of pivotal importance for efficient light harvesting.[7] Much research has been inspired by such examples from nature and devoted to the self-assembly of structurally related porphyrin dyes. Supramolecular design has indeed resulted in J-type packing arrangements of this class of dyes.[8] However, as a result of the much less favorable optical properties of porphyrin chromophores, in particular an almost-forbidden lowest-energy transition with rather weak photoluminescence, the functional features of porphyrin aggregates compare unfavorably with those of their natural chlorophyll counterparts and cyanine-dye-based synthetic J-aggregates.

Herein, we introduce a highly fluorescent J-aggregate assembled from the outstanding artificial fluorophore perylene bisimide (also called perylene diimide). The unprecedented packing of perylene bisimide dyes in a strongly slipped arrangement could be tailored by supramolecular design through perylene core twisting enforced by bay substituents,[9] the attachment of trialkoxyphenyl wedges,[10] and head-to-tail alignment of the dyes through hydrogen-bonding interactions[11] (Figure 1). Traditional dye aggregates of ionic cyanine dyes are formed only in aqueous systems by van der Waals forces. In contrast, the assembly of J-aggregates of perylene bisimide dyes is driven by hydrogen bonding and can take place in an organic environment. This characteristic further extends the scope of these unique types of aggregates.

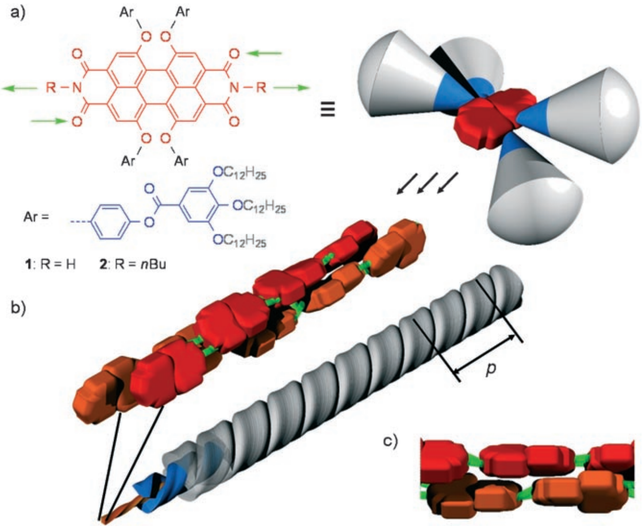

Figure 1. Self-assembly of the perylene bisimide dye **1** into J-type aggregates. a) Molecular structures of **1** and **2** and schematic representation of the monomer **1**. b) Schematic representation of an aggregate of **1**: Red twisted blocks represent the perylene bisimide core, gray cones with a blue apex represent the bay substituents, and green lines represent hydrogen bonds. The dye **1** self-assembles in a helical fashion as shown in the magnification (substituents have been omitted and only the left-handed helical structure is shown for simplicity). c) J-type arrangement of the core perylene bisimide units in a double string cable.

The perylene bisimide dye **1** (Figure 1 a) was synthesized from 1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisanhydride (**3**) as outlined in Scheme 1. The imidization of **3** with racemic α-methylbenzylamine afforded the perylene bisimide **4**, and nucleophilic substitution of the four chlorine atoms in **4** by 4-methoxyphenol gave compound **5**. Cleavage of the methyl ether groups in the bay substituents and the *N*-methylbenzyl groups in the imide positions with BBr_3 in anhydrous dichloromethane provided the deprotected perylene bisimide intermediate. Subsequent esterification of the phenol groups with 3,4,5-tridodecyloxybenzoic acid afforded the target dye **1**[12] in 63 % yield. The reference compound **2** (structure shown in Figure 1 a) was synthesized similarly by using *n*-butylamine for the imidization of **3**.

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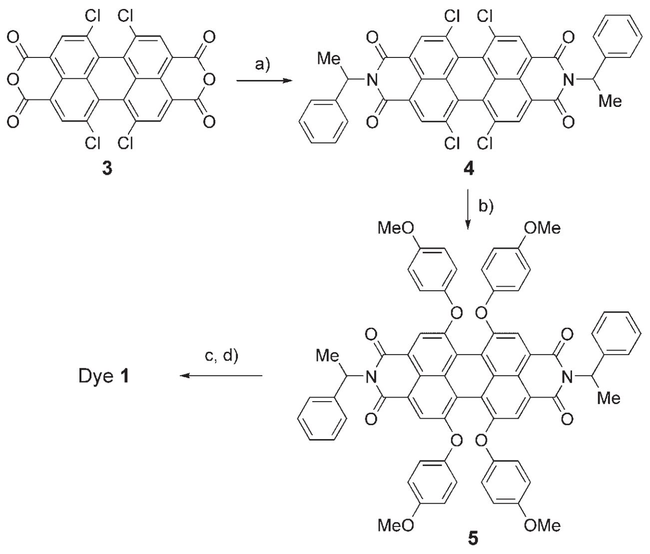
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Reagents and conditions: a) (±)-D,L-α-methylbenzylamine, propionic acid, reflux, 20 h, 45%; b) 4-methoxyphenol, K$_2$CO$_3$, NMP, Ar atmosphere, 120°C, 69 h, 49%; c) BBr$_3$, CH$_2$Cl$_2$, 0°C→RT, 5 h; d) 3,4,5-tridodecyloxybenzoic acid, DCC, DMAP, DPTS, molecular sieves (4 Å), DMF, CH$_2$Cl$_2$, 0→50°C, 91 h, 63%. DCC = *N*,*N'*-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, DMF = *N*,*N*-dimethylformamide, DPTS = 4-(dimethylamino)pyridinium 4-toluenesulfonate, NMP = 1-methyl-2-pyrrolidinone.

The UV/Vis absorption and fluorescence emission spectra of the monomeric dye **1** in CH$_2$Cl$_2$ (Figure 2a) exhibit all the typical spectroscopic features of tetraphenoxy-substituted perylene bisimide chromophores.[9] The absorption maximum of the strongly allowed S$_0$–S$_1$ transition appears at 570 nm (absorption coefficient: $\varepsilon = 41\,600\,\text{M}^{-1}\text{cm}^{-1}$), and the fluorescence emission spectrum with a maximum at $\lambda_{\max} = 602$ nm is a mirror image of the S$_0$–S$_1$ absorption band. Thus, these spectra reveal a Stokes shift of 32 nm. Owing to a pronounced vibronic progression and conformational disorder imparted by the core-twisted chromophore (Figure 1a), the S$_0$–S$_1$ absorption and emission bands are both rather broad with full-width-at-half-maximum (fwhm) values of 2393 cm^{-1} (absorption) and 1660 cm^{-1} (emission).

In striking contrast to those of the monomer, the absorption and emission spectra of aggregated dye **1** in the nonpolar solvent methylcyclohexane (MCH) exhibit strongly bathochromically shifted and unusually narrow bands of greater intensity (Figure 2a). The maximum of the aggregate absorption band is shifted to $\lambda_{\max} = 642$ nm, the fwhm value is reduced to 885 cm^{-1}, and the dipole moment of the S$_0$–S$_1$ transition is increased from 6.7 D (monomer) to 8.3 D (aggregate).[13] The fluorescence spectrum of the aggregate has a mirror-image relationship to the absorption spectrum. It has a maximum at $\lambda_{\max} = 654$ nm with a very small Stokes shift of 12 nm and an equally small fwhm value of 878 cm^{-1}. Temperature-dependent UV/Vis spectroscopy revealed that the formation of aggregates of dye **1** is fully reversible, and a well-defined isosbestic point was observed at 575 nm (Figure 2b). These spectra of the aggregate of dye **1** are distinct from previously observed spectra of aggregates of perylene bisimide dyes,[4,5,14] apparently as a result of the presence of the hydrogen-bonding imide units in **1**. For direct comparison, the *N*-butyl-substituted reference dye **2**, whose imide units can not undergo hydrogen bonding, was investigated by UV/Vis spectroscopy. In contrast to the results with **1**, only a slight bathochromic shift of the absorption band was observed for **2** upon aggregation in MCH at room temperature (see the Supporting Information). This small bathochromic shift can be attributed to the formation of a dimeric aggregate species on the basis of our previous studies.[14]

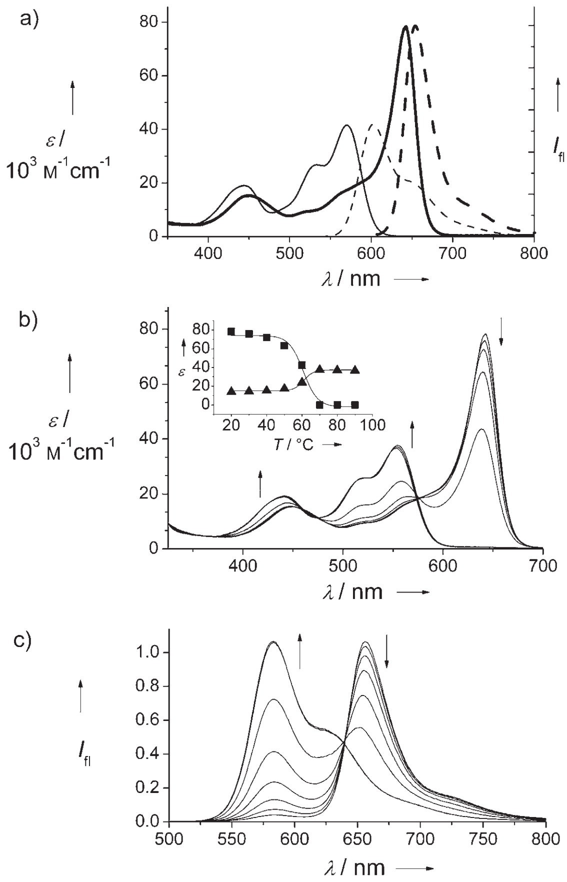


Figure 2. a) UV/Vis (solid lines) and fluorescence spectra (dashed lines) of **1** in CH$_2$Cl$_2$ (10^{-5} M, thin line) and MCH (10^{-5} M, bold line). b) Temperature-dependent UV/Vis spectra of **1** in MCH (1.5×10^{-5} M) at 20–90°C; arrows indicate the spectroscopic changes with increasing temperature. Inset: Changes in absorption at 642 nm (■) and 553 nm (▲) with increasing temperature; lines were calculated according to a sigmoidal fit. c) Temperature-dependent fluorescence spectra of **1** in MCH (6×10^{-7} M, $\lambda_{ex} = 476$ nm) at 15–50°C; arrows indicate the spectroscopic changes with increasing temperature.

The unusual spectroscopic properties of the J-aggregate of **1** are encoded in its molecular structure: a twisted π-conjugated core and two self-complementary arrays of hydrogen-bond donors/acceptors (Figure 1a). Upon self-assembly, these dyes form π–π-stacked dimeric units (consisting of one red and one orange building block in Figure 1c) that interconnect through hydrogen bonds to provide a closely packed one-dimensional supramolecular polymer[15] (Figure 1b) which exhibits all the typical features of a J-aggregate. The most important of these features is a fluorescent excitonic state, which results from the slipped arrangement of the building blocks.

Experimental evidence for the supramolecular model shown in Figure 1 b derives from various spectroscopic and microscopic investigations. The π–π-stacking interaction between the perylene cores in a slipped arrangement is evident from the UV/Vis absorption data, which can be interpreted according to exciton theory.[2c,16] Concentration- and temperature-dependent FTIR and ^{1}H NMR spectroscopy confirmed the formation of N−H···O hydrogen bonds between the imide hydrogen atoms and the carbonyl oxygen atoms. The free-NH stretching vibrations in the FTIR spectra of monomeric **1** in CH_2Cl_2 occur at $\tilde{\nu}(NH) = 3368\ cm^{-1}$. This band shifts upon hydrogen bonding to $3172\ cm^{-1}$ in MCH and $3178\ cm^{-1}$ in the solid state. The concomitant appearance of a new stretching frequency at $\tilde{\nu}(C{=}O) = 1676\ cm^{-1}$ assigned to hydrogen-bonded carbonyl groups was observed along with a decrease in the intensity of the bands at $\tilde{\nu}(C{=}O) = 1734$ and $1700\ cm^{-1}$ as a result of stretching vibrations of non-hydrogen-bonded carbonyl groups (see the Supporting Information). Furthermore, ^{1}H NMR spectroscopy of **1** as solutions in $CDCl_3$ and [D$_8$]toluene revealed pronounced downfield shifts for the imide hydrogen atoms with increasing concentration, whereas the signals in the spectra of **1** in [D$_{14}$]MCH are rather broad even under dilute conditions as a result of the polymeric nature of the aggregates (see the Supporting Information).

Once the existence of local N−H···O hydrogen bonding and π–π-stacking contacts between self-assembled dyes **1** had been confirmed by spectroscopic methods, atomic force microscopy (AFM) was used to elucidate the size and shape of these aggregates. AFM images on silicon wafers (Figure 3; see also the Supporting Information) reveal a network of defined fibers whose size (height: 2.0 ± 0.2 nm; width: 8.4 ± 2.6 nm) is in agreement with the expected dimensions[17] of a double string cable of the type suggested in Figure 1 b. According to this model, we expect quite a rigid inner core (diameter ≈ 3.0 nm) composed of helically twisted perylene bisimides (red) with four appended aromatic substituents (blue) and surrounded by a flexible periphery of twelve $C_{12}H_{25}$ aliphatic chains (gray). The aliphatic chains are wrapped around the helical core as proposed in Figure 1 b. Remarkably, at the highest possible resolution of our AFM imaging (Figure 3 b; see also the Supporting Information), a helical pitch of $p = 13.0 \pm 3.4$ nm becomes apparent for these nanosized fibers. This value is in proper agreement with our model (Figure 1; we carried out AMBER force-field calculations on the molecular model of the aggregate structure (see the Supporting Information)).

We obtained a fluorescence quantum yield of 0.93 ± 0.01 for monomeric **1** in CH_2Cl_2 and a value of 0.96 ± 0.03 for its J-aggregate in MCH by applying the conventional method for the determination of the relative fluorescence quantum yield.[18] The unquenched emission of this aggregate is also evident from the temperature-dependent fluorescence spectra obtained upon excitation at $\lambda_{ex} = 476$ nm, at the isosbestic point (Figure 2 c). These results were further substantiated by the fluorescence quantum yield of 0.85 ± 0.02 measured for a concentrated solution of **1** in MCH with an integrating sphere (by using a system for the measurement of the absolute fluorescence quantum yield).[18]

Several kinds of J-type aggregates, including J-aggregates based on cyanines,[1,2] chlorins, and porphyrins,[6–8] have been reported and investigated extensively in the past. However, most previously reported J-aggregates exhibit only weak fluorescence, which makes them less suitable for many applications, in particular for demanding sensory and photonics applications.[19] To the best of our knowledge, no J-aggregate with fluorescence quantum yield of near unity has been reported previously.[20]

The electronic properties of the J-aggregates of dye **1** were explored by polarization (Figure 4) and time-resolved fluorescence measurements (see the Supporting Information). A strong increase in the fluorescence anisotropy value from 0.032 (monomers at 80 °C in MCH) to 0.158 (aggregates at 20 °C in MCH) was observed for the whole S_0–S_1 band. This result indicates the formation of an extended aggregate and collinearity between the dipole moment of the S_0–S_1 transition and the long axis of the aggregate.

Whereas the observed pronounced bathochromic shift and the band narrowing for the aggregate of dye **1** provide a clear indication of a strong coupling between the aggregated chromophores, the decrease in the fluorescence lifetime from 6.8 ns (monomer in MCH) to 2.6 ns (J-aggregate in MCH) allows the elucidation of exciton delocalization. According to exciton theory, such enhanced radiative decay ("superradiance") is related to the presence of a coherent excited domain of a number, *N*, of monomers.[2c] In the absence of nonradiative quenching processes (as confirmed by the high

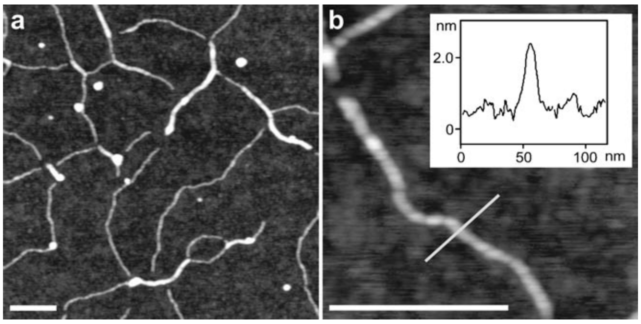


Figure 3. a,b) Tapping-mode AFM images of self-assemblies of **1** on a silicon wafer spin coated (2000 rpm) from a 9×10^{-6} M solution in MCH. Scale bars: 150 nm; *z* scale: 6 nm. Inset in (b): Height profile along the thin line.

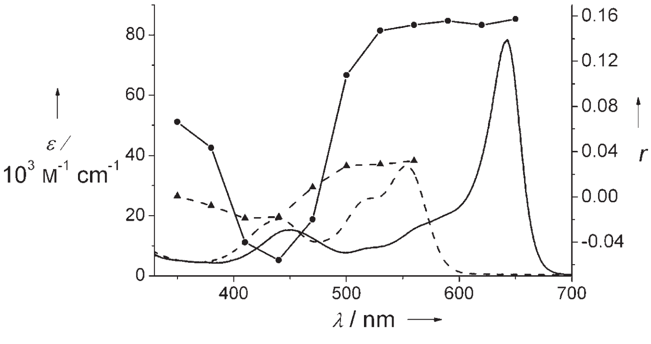


Figure 4. Fluorescence anisotropy, *r*, of the perylene bisimide **1** (10^{-6} M) in MCH at 25 °C (●) and 80 °C (▲). The corresponding nonpolarized absorption spectra of **1** (25 °C: dashed line; 80 °C: solid line) have been added for comparison.

fluorescence quantum yields of the monomer **1** (0.93) and aggregate of **1** (0.96)), the size of the coherent domain could be estimated for **1** at room temperature to be about three dye molecules from Equation (1):

$$N\,\tau_{\mathrm{agg}} = \Phi_{\mathrm{agg}}\,\tau_{\mathrm{mon}} \tag{1}$$

in which Φ_{agg} denotes the fluorescence quantum yield of the aggregate and τ_{agg} and τ_{mon} the fluorescence lifetimes of the aggregate and monomer, respectively.[21] On the basis of previously reported studies on cyanine- and chlorin-dye aggregates,[7,22] we would expect an increase in the size of the coherent domain upon a decrease in temperature.

Previously reported J-aggregates were either discovered by serendipity[1] or developed on the basis of concepts found in nature.[6–8] Herein we have shown that the formation of a J-aggregate can be encoded in the molecular building block according to supramolecular design principles.[11] The outstanding fluorescence properties of the chosen fluorophore provided for the first time J-aggregates that fluoresce with quantum yields of near unity. As the perylene bisimide chromophore also has other favorable properties, such as high photostability and semiconductivity, we anticipate that these perylene bisimide J-aggregates will be integrated into many devices for fluorescence sensing, photonics, and organic photovoltaics.

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