

Highly Fluorescent Lyotropic Mesophases and Organogels Based on J-Aggregates of Core-Twisted Perylene Bisimide Dyes

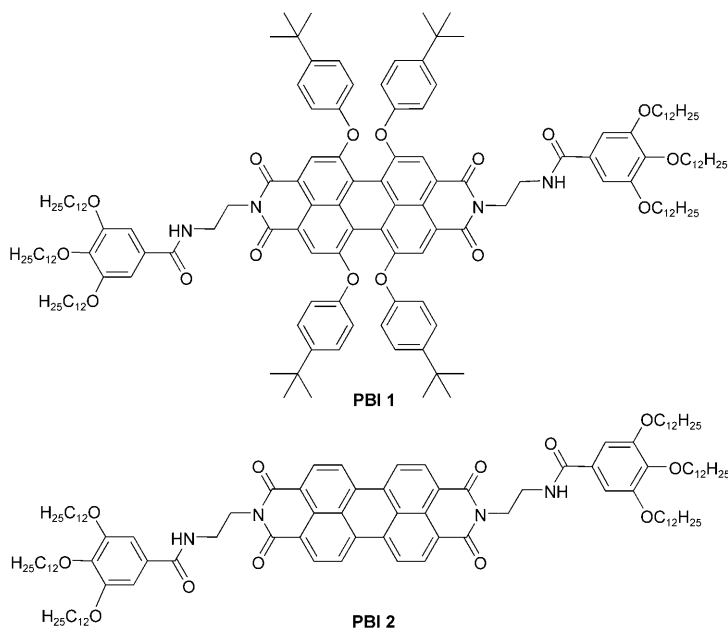
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Over the past decade, low molecular weight organic gelators have attracted considerable interest because of their diverse applications as supramolecular soft materials.^[1] The formation of organogels^[2] is facilitated by highly directional self-assembly through non-covalent interactions such as π - π stacking, hydrogen bonding, metal-ion coordination, dipole-dipole interactions. In the last few years, several functional dye based building blocks have been reported to form organogels and the unique features of the 3D network superstructures have been applied for example, for sensors, optoelectronic devices, light harvesting, nucleation of inorganic materials.^[3–8]

Organogelators based on numerous electron-rich aromatic building blocks such as porphyrins, phthalocyanines, oligo(phenylenevinyls), oligothiophenes and tetrathiafulvalenes have been investigated in the recent past.^[7] However, such examples for electron-poor aromatic systems are still rare.^[8] Perylene bisimides (PBIs) have been extensively studied as n-type semiconductors in various applications such as optical recording media, organic photo- and semiconductors, and solar cells.^[9] Recently, the groups of Shinkai and Yagai as well as our group have reported the first PBI based organogelators.^[10–12] In these examples, well-defined fibrous aggregates were observed by atomic force microscopy (AFM) and their formation has been attributed to π - π stacking and intermolecular hydrogen bonding between the constituent PBI molecules. However, for these gels broadened UV/Vis absorption bands and inferior emission properties were observed compared to solutions of the monomeric dyes. In this work, we introduce a new perylene bisimide based organogelator (**PBI1**) with an unprecedented sharp J-type absorption band and favorable emission properties.

These features can be attributed to strong excitonic coupling as demanded for exciton transport in photonic and photovoltaic applications.

The structures of **PBI1** and **PBI2**^[11b] are shown in Scheme 1. **PBI1** was synthesized by imidization of *tert*-butyl-phenoxy perylene tetracarboxylic acid bisanhydride with aminoethyltris(dodecyloxy)benzamide in quinoline using $\text{Zn}(\text{OAc})_2$ as catalyst and isolated as a purple powder in 51% yield (details for synthesis and characterization of **PBI1** are given in Supporting Information). The calculated



Scheme 1. Molecular structures of **PBI1** and **PBI2**.

molecular models as well as several crystal structures for related compounds indicate that **PBI2** possesses a planar perylene core, whereas **PBI1** exhibits a distorted perylene core with a twist angle of about 25–30° due to the presence of four bulky *tert*-butylphenoxy substituents at the bay posi-

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tions^[13] (see Figure S1 in Supporting Information). We previously found that **PBI2** is an efficient gelator, which can gel various types of organic solvents at low critical gelation concentrations (CGC) by virtue of π - π stacking and hydrogen-bonding interactions.^[11b] In order to examine whether similar hydrogen-bonding interaction exists among the bay-substituted **PBI1** chromophores, we performed FT-IR spectroscopy of **PBI1** in apolar solvent methylcyclohexane (MCH) which revealed the formation of intermolecular hydrogen bonds between the benzamide functional groups (Figure S2 in Supporting Information). Next, gelation tests were performed for **PBI1** in 17 different organic solvents (Supporting Information). To our surprise, no gelation was observed in aromatic solvents such as toluene, benzene and aliphatic solvents such as methylcyclohexane and cyclohexane, but opaque gels were observed in acetone and dioxane, which are known as hydrogen-bond breaking solvents (Figure 1a and b). Despite their failure to gel apolar organic sol-

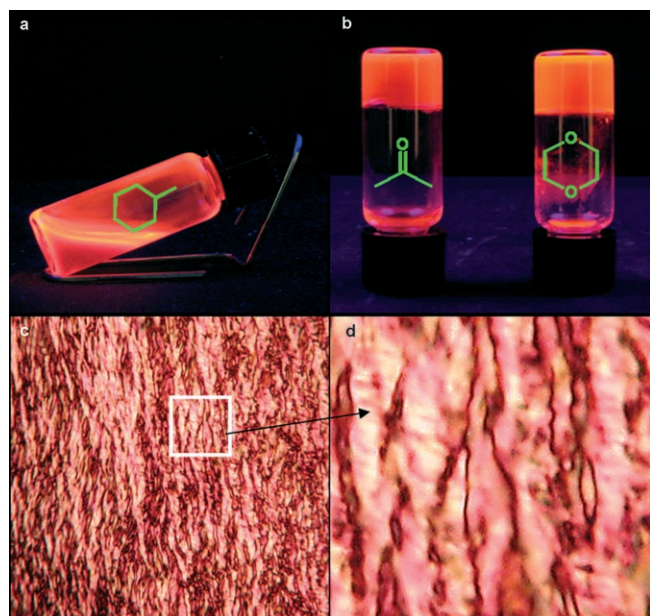


Figure 1. Photographs of **PBI1** in different solvents under a UV lamp (366 nm): a) in MCH at $c=10$ mM (2.9 wt %); b) in acetone at $c=1.5$ mM (0.4 wt %) and in dioxane at $c=4$ mM (1.1 wt %); c) OPM image of a viscous solution of **PBI1** in MCH (8 mM, 2.3 wt %); d) a zoomed region from c).

vents, the signature of aggregate formation was evident in these aliphatic solvents (e.g., methylcyclohexane, cyclohexane, and *n*-hexane) from the increased viscosity of the solutions at higher concentrations ($c > 10$ mM). Notably, no precipitation took place at these rather high concentrations but textures that resemble those found for chromonic liquid crystals^[14] were observed under the optical polarizing microscope (OPM). The formation of a nematic (N) phase in a concentrated MCH solution was indicated by a schlieren texture (Figure 1c and d). In this phase, the mesogens typically stack to form columns, but there is no positional order

among the columns. As the sample was concentrated (edge evaporated for 2 h), a grainy optical texture can be observed, which is characteristic of the columns arranged in a hexagonal order in the hexagonal (M) phase.^[14b] Similar textures can also be observed in cyclohexane and *n*-hexane that show both N and M phases in concentrated solutions (see details in Figure S3, Supporting Information).

To investigate the aggregation properties of **PBI1** in more detail, we carried out photophysical studies in solution. Firstly, optical properties of **PBI1** in the monomeric and aggregated states were investigated by temperature-dependent UV/Vis and fluorescent spectroscopy in different solvents (Figure 2). The UV/Vis spectra of **PBI1** in CH_2Cl_2 (or in MCH at higher temperature) exhibit typical spectroscopic features that are expected for monomeric tetraaryloxy-substituted PBI chromophores.^[15] The absorption maximum at 583 nm indicates a strongly allowed $S_0 \rightarrow S_1$ transition. The fluorescent emission spectrum with a peak maximum at 621 nm is mirror image of the absorption band. The absorption and emission bands are rather broad with full-width-at-half-maximum (fwhm) values of 2311 and 1780 cm^{-1} , respectively. The broadness of these bands results from the distortion of the chromophore and various conformational states of the four aryloxy groups.

Unlike those in CH_2Cl_2 , the absorption spectra of **PBI1** in MCH exhibit a sharp intense band that is bathochromically shifted by ca. 13 nm from the monomer band (Figure 2a). The fluorescent spectrum has a mirror image relationship to

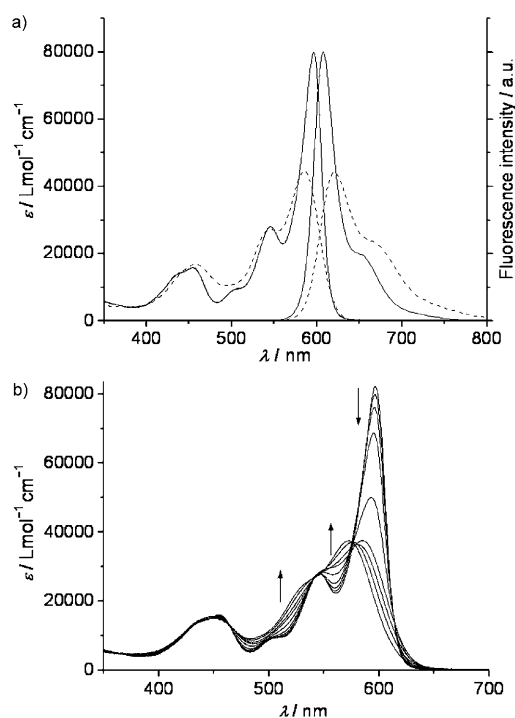


Figure 2. a) UV/Vis (left) and fluorescence (right) spectra of **PBI1** in CH_2Cl_2 (dashed lines, 1.1×10^{-5} M) and MCH (solid lines, 1.1×10^{-4} M) at 20 °C; b) temperature-dependent absorption spectra of **PBI1** (1.1×10^{-4} M, in MCH) from 10 °C to 90 °C. The arrows indicate spectral changes with increasing temperature.

the absorption spectrum with a Stokes shift of only 11 nm. The fwhm values of absorption and emission spectra are significantly reduced to 850 and 786 cm^{-1} , respectively. Temperature-dependent UV/Vis experiments in MCH testify the reversibility of the self-assembly process. When the temperature is raised from 10 to 90 °C, the sharp band at 598 nm gradually disappears and the monomeric species is recovered as evidenced by re-appearance of the broad spectrum (Figure 2b). These spectral features clearly indicate the reversible formation of J-aggregates of **PBI1** in apolar solvent which is in contrast to the H-aggregating **PBI2** and other PBI-based organogelators.^[10,11] The very intense J-band of **PBI1** with relatively small bathochromic shift suggests the presence of tightly aggregated chromophores at a slip angle close to the magic angle of 54.7° that is unprecedented for this class of chromophores.^[16,17] These unusual spectral and packing features are encoded in the unique molecular structure of **PBI1**: a twisted π -conjugated core and additional amide groups that can assist intermolecular H-bonds.

Similar optical properties of **PBI1** can also be found in acetone and dioxane, in which organogels were formed. Temperature-dependent UV/Vis spectra of **PBI1** in these hydrogen-bond breaking solvents (Figure S4) clearly show J-type aggregating behavior, that is, upon aggregation the absorption maximum shifts bathochromically. However, in these solvents aggregation took place only at considerably higher concentrations and lower temperatures (in acetone: $c > 1.0 \text{ mM}$, $T < 30^\circ\text{C}$ and in dioxane: $c > 2.5 \text{ mM}$, $T < 20^\circ\text{C}$; see Supporting Information) when compared with that in apolar solvent such as MCH. The relatively lower propensity to aggregate formation of **PBI1** in acetone and dioxane is conceivable since the solvent molecules in these cases are capable of interacting with the amide functionality of the dye molecules through hydrogen bonding,^[18] and thus can weaken the inter-chromophoric interactions. However, at significantly higher concentration and lower temperature, dye aggregation was evidenced from distinct spectral changes (bathochromic shift of ca. 39 nm in acetone) that are indicative of a packing motif with more displaced dye molecules according to exciton coupling theory^[17] (see calculations in the Supporting Information). Further evidence of solvent participation in hydrogen bonding with the amide functionality of **PBI1** was gathered from ^1H NMR studies (Figure S5). The amide protons of **PBI1** were found to be significantly downfield shifted in acetone compared to that in chloroform or benzene as expected for hydrogen-bonding interactions with the solvent molecules.

Whilst the solution spectroscopic studies revealed the aggregate formation in various solvents, transmission electron microscopy (TEM) studies provided direct evidences for the formation of extended networks. Figure 3 shows typical TEM images of aggregated structures of **PBI1** and **PBI2** in different solvents. As reported previously, **PBI2** can form long well-defined fibers and further entangle to network structures in many apolar solvents.^[11b] In contrast, for **PBI1** less regular structures are observed. In MCH loosely connected bundles of aggregate structures are visualized by

TEM (Figure 3a,b) as expected for lyotropic mesophases.^[14] These aggregates appear much more fluid-like as compared to the entangled fibers observed for gels of **PBI2**^[11b] (Figure 3e,f). They are able to cause an increase in viscosity of the medium (Figure 1a) but are unable to gel the solvent.^[19] Interestingly, TEM images from a suspension of **PBI1** gel in acetone revealed distinctly different aggregate morphologies as shown in Figure 3c and d. The willow-leaf-like aggregated units appear to be more flexible and they can gradually entangle to each other at the ends to give star-shaped structures. Those “stars” further intercross to form the 3D network structures, which are essential for gelation. Similar spectroscopic and microscopic features of **PBI1** could also be observed in dioxane (Figures S4 and S6).

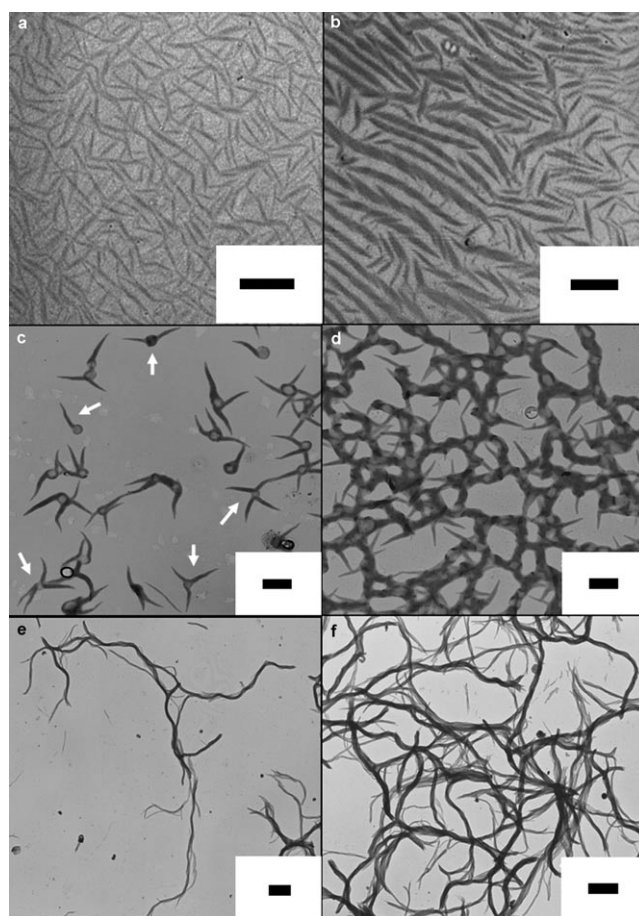


Figure 3. TEM images of **PBI1** in MCH ($1.0 \times 10^{-4} \text{ M}$, a and b) and a suspension of a gel in acetone (ca. $1.0 \times 10^{-3} \text{ M}$, c and d); e) and f) show the long aggregated fibers of **PBI2** from a suspension of a gel in dioxane (ca. $1.0 \times 10^{-3} \text{ M}$). The scale bar in a)–d) corresponds to 500 nm and in e) and f) corresponds to 1000 nm.

In contrast to the morphology of core-twisted **PBI1**, the core-planar **PBI2** gives very long (several microns) 1D fiber in dioxane. This observation strongly indicates that the differences in gelation behavior of these dyes are originated from the structural change of the perylene cores. Possibly, strong π – π interaction among planar **PBI2** chromophores

rules out the possibility of solvent insertion irrespective of the nature of the solvent, while the core-twisted **PBI1** allows solvent participation in H-bonding because of the relatively weaker inter-chromophoric interactions.

It is noteworthy that the fluorescence of **PBI2** is rather weak due to a photoinduced electron transfer process from the electron-rich trialkoxyphenyl group to the electron poor PBI core.^[20] Thus, the fluorescence quantum yield is 0.03 for the monomers in dichloromethane and less than 0.01 for the aggregates in toluene. In contrast, very exciting fluorescence properties for **PBI1** are given under various conditions that are attributed to a more electron-rich PBI core and a more favorable dye packing. The fluorescence quantum yields for monomeric **PBI1** were found to be 0.78 ± 0.02 , 0.76 ± 0.01 , and 1.00 ± 0.01 in dichloromethane, acetone, and dioxane, respectively. For the J-aggregate in MCH, the quantum yield was found to be 0.82 ± 0.01 . Such unquenched emission upon dye aggregation in solution is indeed a rare phenomenon.^[16] Even in the gel phases, remarkable fluorescence quantum yields were determined: 0.20 ± 0.01 in acetone and 0.39 ± 0.01 in dioxane where the concentrations were 2.0 mM and 5.0 mM, respectively (see details in Supporting Information).

In summary, we have introduced highly fluorescent PBI J-aggregate based lyotropic mesophases and gels of organic solvents. UV/Vis studies revealed more pronounced aggregation in apolar solvents like MCH due to intermolecular π - π stacking and hydrogen bonding interactions. On the other hand, in polar solvents like acetone and dioxane, participation of the solvent molecules in hydrogen bonding significantly reduced the aggregation propensity but enforced the gel formation at higher concentrations (Figure 4). The

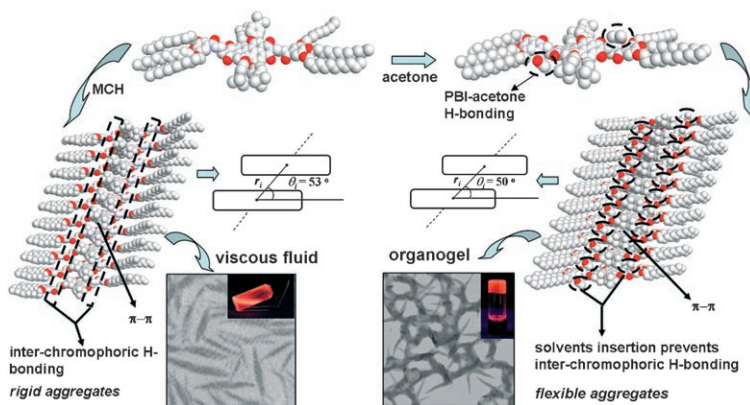


Figure 4. Schematic illustration for the formation of viscous lyotropic fluids and gels from **PBI1** in MCH and acetone.

outstanding fluorescent properties of the dye in both J-aggregated viscous lyotropic mesophases and bulk gel phases suggest very promising applications in photonics, photovoltaics, security printing, or as fluorescent sensors.

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