CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

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

Xue-Qing Li, Xin Zhang, Suhrit Ghosh and Frank Würthner*

Universität Würzburg
Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems
Am Hubland, D-97074 Würzburg, Germany
E-mail: wuerthner@chemie.uni-wuerzburg.de

General methods

All solvents and reagents were purchased from commercial sources and used as received without further purification. The solvents for spectroscopic studies were of spectroscopic grade and used as received. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer and all the spectra were calibrated against TMS. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Daltronik GmbH (autoflex II) mass spectrometer. Typically, samples were dissolved in dichloromethane (1.0 mg/mL), and 2-[(2*E*)-3- (4-*tert*-butylphenyl) -2-methylprop-2-enylidene] malononitrile (DCTB) was used as matrix, which was also dissolved in dichloromethane and mixed with the sample solution in a 1:10 (v/v) ratio. UV/Vis spectra were measured on a Perkin-Elmer Lambda 40P spectrometer equipped with a Peltier system as temperature controller. FT-IR spectra were measured on a Jasco FT/IR-410 instrument. Optical textures at crossed polarizers were obtained with an Olympus BX-41 polarization microscope equipped with a Linkam THMS 600 hot stage and a temperature controller unit.

Transmission electron microscope (TEM)

TEM measurements were performed on a Siemens Elmiskop 101 Electron Microscope, operating at an acceleration voltage of 80-100 kV. For the observation of aggregates or gel morphologies, a drop of sample solution or a suspension of diluted gel was placed on 400-mesh formvar copper grids coated with carbon. About 2 min after the deposition, the grid was tapped with filter paper to remove surface water. This step was performed without any staining. The samples are stable on the copper grids and the morphologies can remain at least for 1 week.

Fluorescence measurements

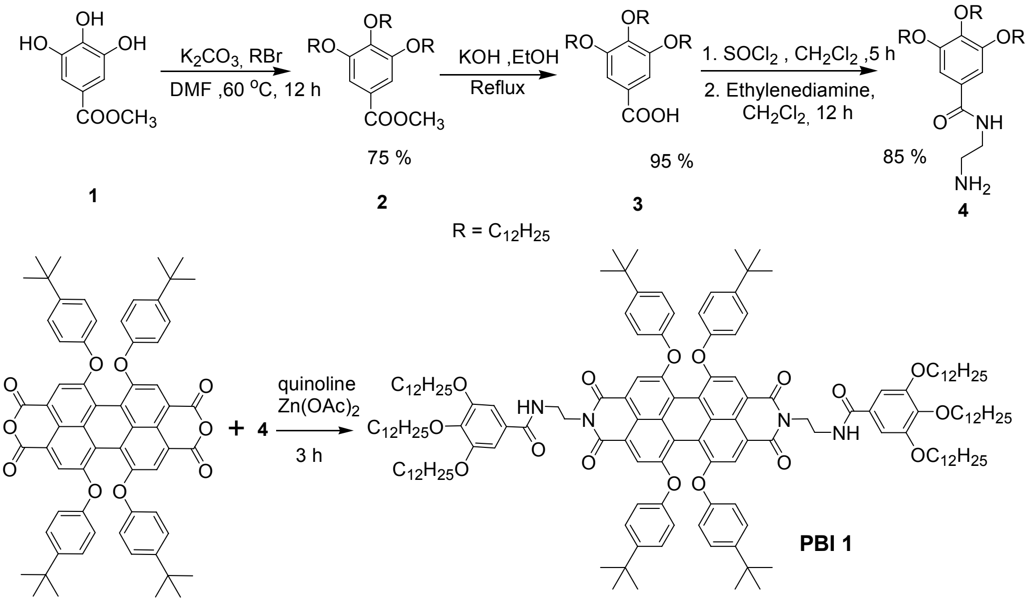
The steady state fluorescence spectra were recorded on a PTI QM4/2003 spectrofluorometer. For all the measurements on the aggregated state (e.g., **PBI 1** in MCH at c = 1.0 × 10^{-4} M), two Glan-Thomson polarizers under magic angle and front face setup were adopt due to the high optical densities of the samples. All the data were corrected against photomultiplier and lamp intensity. The fluorescence quantum yields were determined by optical dilute method.[S1] Fluorescein (Φ_{fl} = 0.92 in 1N aqueous NaOH, for **PBI 2**) and *N,N'*-di(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide (Φ_{fl} = 0.96 in $CHCl_3$, for **PBI 1** in solutions) were used as references. The given quantum yields are averaged from values measured at three different excitation wavelengths.

Absolute fluorescence quantum yield determination

The quantum yields for the gel phases were determined using a Hamamatsu Absolute PL Quantum Yield Measurement System CC9920-02. The system is composed of an excitation source that uses a 150 W CW Xenon light source, a monochromator (250-700 nm, FWHM 10 nm), an integrating sphere, and a multi-channel spectrometer capable of simultaneously measuring multiple wavelengths between 300 and 950 nm and counting the number of absorbed and emitted photons. With this system the absolute fluorescence quantum yield of gels from **PBI 1** in acetone (c = 2.0 × 10^{-3} M) and in dioxane (c = 5.0 × 10^{-3} M) were determined by excitation at λ = 540 nm under ambient conditions.

For comparison, a dilute solution (c = 1.0 × 10^{-6} M in $CHCl_3$) of the fluorescence standard *N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-(tetraphenoxy) perylene-3,4:9,10-tetracarboxylic acid bisimide was determined under identical conditions and a fluorescence quantum yield of 0.92 ± 0.02 was obtained upon excitation at λ = 540 nm (literature value:[S2] 0.96 - 1.01).

Synthesis and characterization of PBI 1



***N,N'*-Di[*N*-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide]-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene -3,4:9,10-tetracarboxylic acid bisimide (PBI 1):**

1, 6, 7, 12-Tetra (4-*tert*-butyl phenoxy) perylene- 3,4:9,10-tetracarboxylic acid bisanhydride (150 mg, 0.15 mmol), compound **4** (220 mg, 0.31 mmol) and zinc acetate (33 mg, 0.18 mmol) were mixed in 5 mL dry quinoline. The reaction mixture was stirred at 180 °C for 3 h. After cooling to room temperature, the mixture was poured into 150 mL MeOH. The precipitate was collected by filtration and washed thoroughly with methanol. The solid was dried in vacuum. After that, the crude product was further purified by silica gel column chromatography (50/1 CH_2Cl_2/MeOH) to give a purple solid. Yield: 51%; m.p.: 177 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 300 K): δ = 8.23 (s, 4H, H_{pery}), 7.22 (m, 8H, Ar-H), 6.89 (s, 4H, Ar-H), 6.78 (m, 8H, Ar-H), 6.75 (t, J = 4.8, 2H, NH), 4.45 (t, 4H, J = 5.2, CH_2), 3.91 (m, 12H, Ar-OCH_2), 3.78 (br, 4H, CH_2), 1.8-1.2 (m, 156H, CH_2), 0.87 (m, 18H, CH_3). UV-vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 583 (47600), 544 (29500), 457 (18200), 421 (21300 $M^{-1}\,cm^{-1}$). MS (MALDI-TOF, matrix: DCTB): m/z, calculated for $C_{154}H_{220}N_4O_{16}$: 2383.66, found 2383.58

$[M]^+$; Elemental analysis (%) calculated for $C_{154}H_{220}N_4O_{16}$: C 77.61, H 9.30, N 2.35; found: C 77.50, H 9.00, N 2.35.

Gelation test of PBI 1 in various organic solvents

The gelation property of perylene bisimide **PBI 1** was assessed in 17 different organic solvents. For this purpose, the gelator and the solvent were put together in a screw-capped sample vial and it was heated until everything was dissolved. After leaving the sample over night at ambient temperature, the formation of gel was defined by the "stable-to-inversion of a vial" method. In most of solvent such as methylcyclohexane, cyclohexane, *n*-hexane, *n*-pentane, benzene, thiophene, toluene, THF, chloroform, dichloromethane, 1-octanol, **PBI 1** can be well dissolved (in all the cases, concentration > 5 mM). For the solvents DMF, DMSO, ethanol and methanol precipitates could be observed. The opaque gels were formed only in acetone and dioxane. The critical gelation concentration (CGC) was determined as 0.9 mM (0.27 wt%) in acetone and 4.6 mM (1.05 wt%) in dioxane at room temperature.

Figure S1. Optimized molecular structures of twisted **PBI 1** and planar **PBI 2** (HyperChem, MM+; the alkyl chains were replaced by methyl groups).

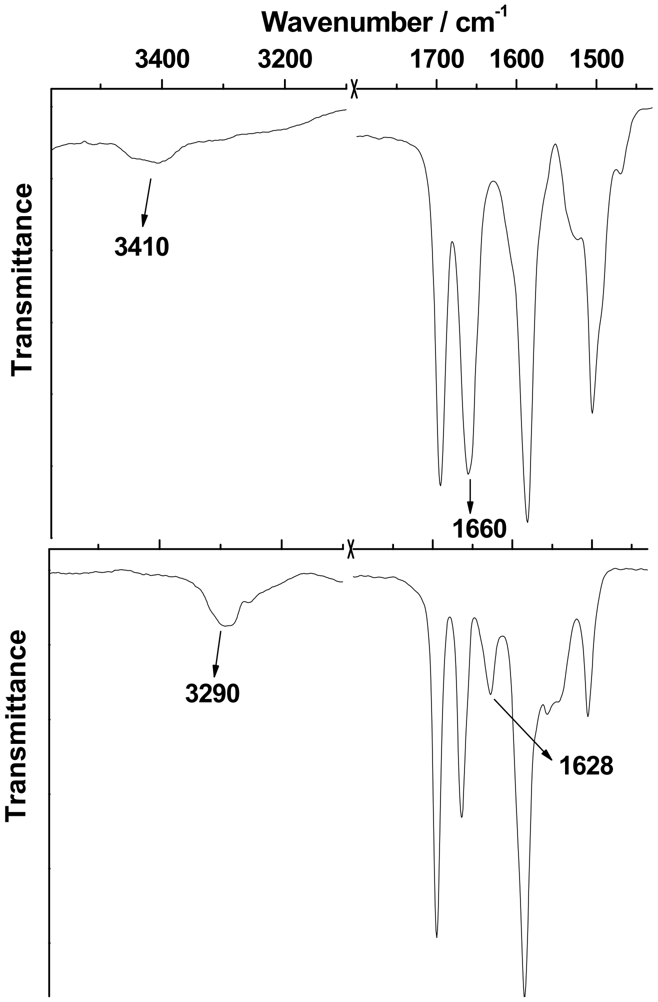


Figure S2. FT-IR spectra of **PBI 1**: (top) In CH_2Cl_2 solution (1.0×10^{-3} M) and (bottom) in MCH solution (1.0×10^{-3} M).

The IR spectrum of **PBI 1** in CH_2Cl_2 shows a broad N-H stretching band at 3410 cm^{-1} which indicates the absence of hydrogen bonding. The benzamide carbonyl group vibration band overlap with the carbonyl group vibration of the perylene imide groups at 1660 cm^{-1}.

In concentrated MCH solution **PBI 1** shows N-H stretching band at 3290 cm^{-1} and a benzamide carbonyl group vibration at 1628 cm^{-1}. Both displacements to lower frequency are indicative for the hydrogen-bonding interactions among the amide moieties.

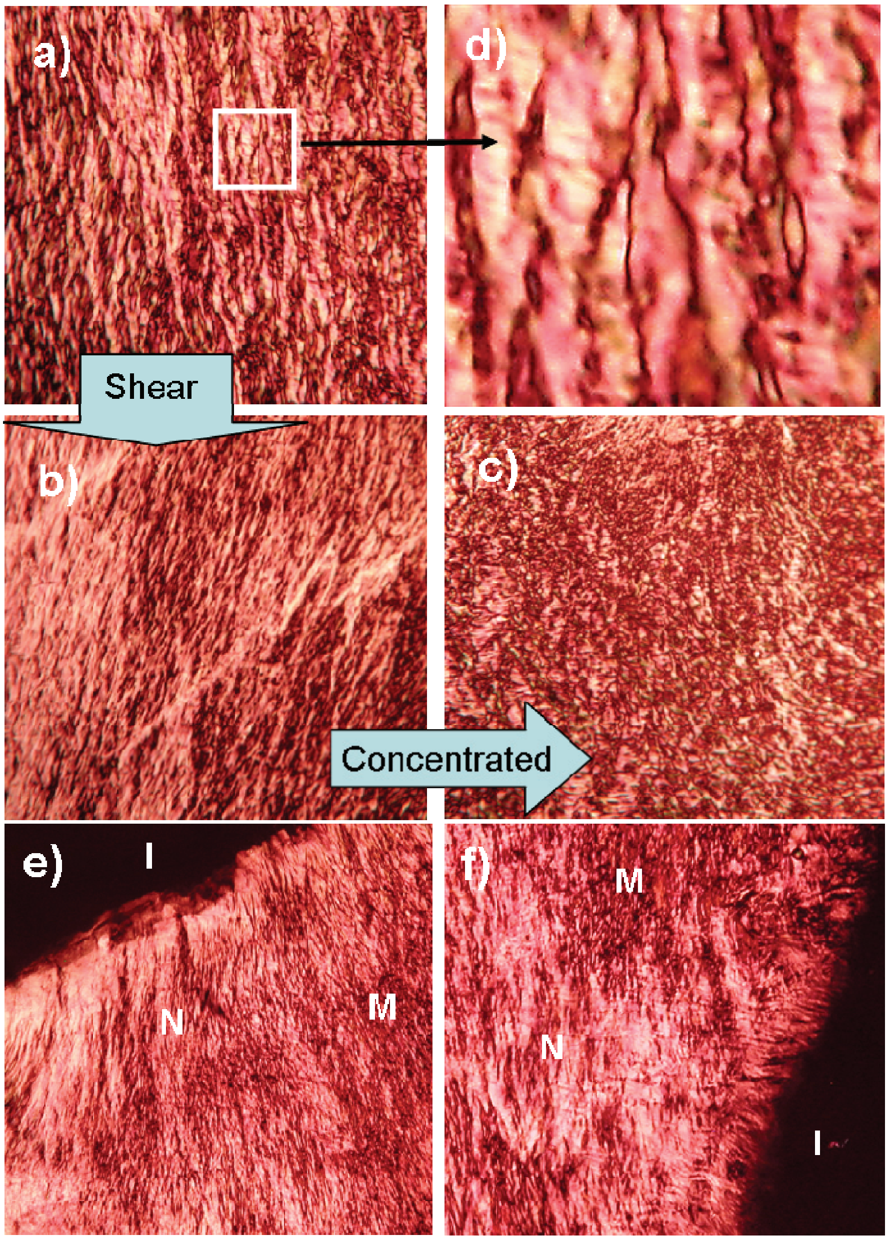


Figure S3. Polarized optical microscopy images (crossed polarizers) of (a) schlieren textures from a viscous solution of **PBI 1** in MCH (8 mM; 2.3 wt%); (b) after shearing, the texture can recover; (c) grainy textures after the film was edge evaporated for 2 hours; (d) is zoomed region from image from (a); (e) and (f) indicate the co-existence of the mesophases (N and M) and isotropic phase (I) of **PBI 1** in cyclohexane (15 mM, 4.3 wt%) and *n*-hexane (15 mM, 5.4 wt%), respectively.

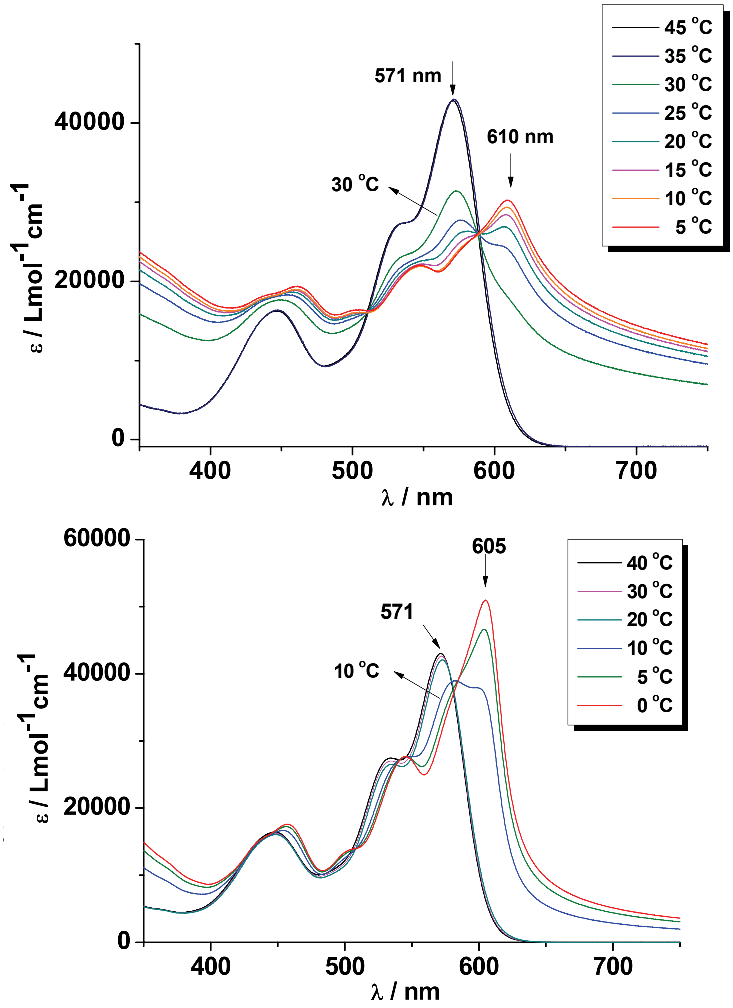


Figure S4. Variable-temperature UV/Vis absorption spectra of **PBI 1** in acetone (top, 1.0 × 10^{-3} M) and in dioxane (bottom, 2.5 × 10^{-3} M).

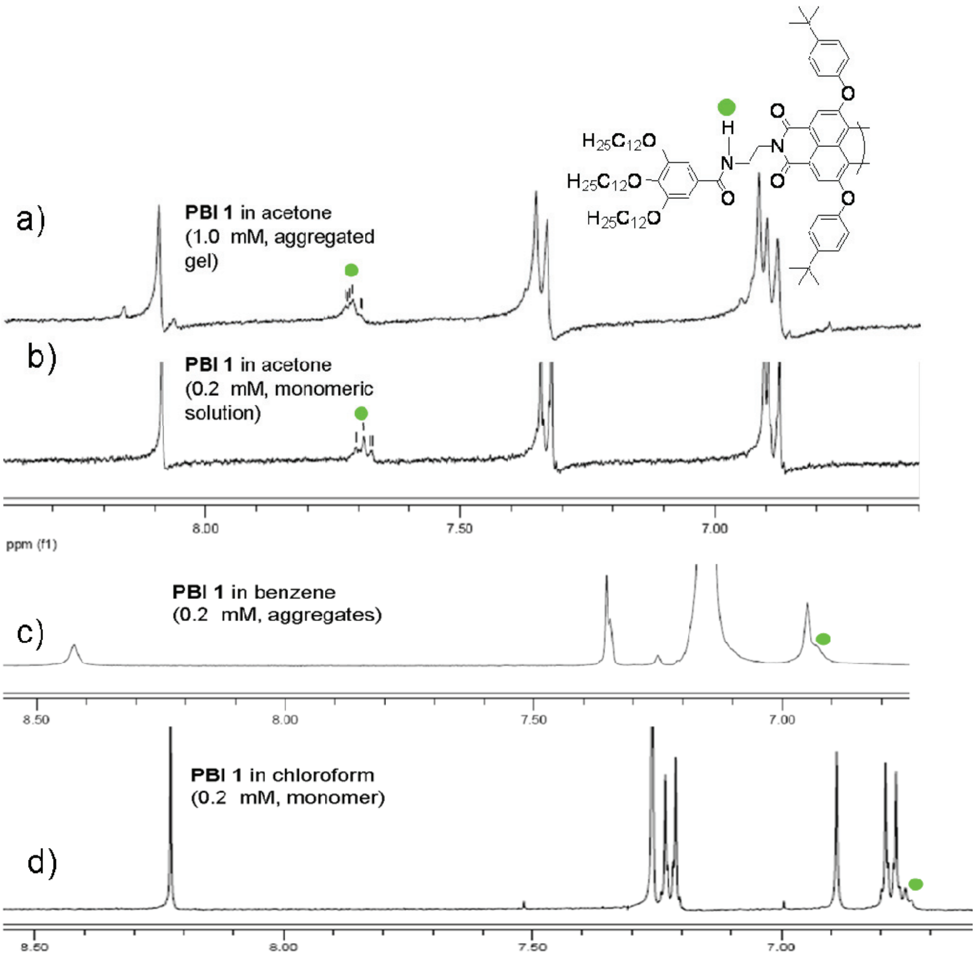


Figure S5. ^{1}H NMR spectra of **PBI 1**:

(a) in acetone, c = 1.0 mM, aggregated dyes in gel phase

(b) in acetone, c = 0.2 mM, primarily monomeric dyes

(c) in benzene, c = 0.2 mM, aggregated dyes

(d) in chloroform, c = 0.2 mM, monomeric dyes.

The amide proton of **PBI 1** (labeled with green dots) was found to be significantly downfield shifted in acetone (either for aggregates gel or for monomers) compared to that in chloroform (monomers) or in benzene (aggregates). This suggests the proposed hydrogen-bonding interaction with the solvent molecule. On the other hand, no obvious change of amide protons could be observed from spectra (a) and (b), which indicates the absence of amide-amide hydrogen bonding between the self-assembled dye building blocks.

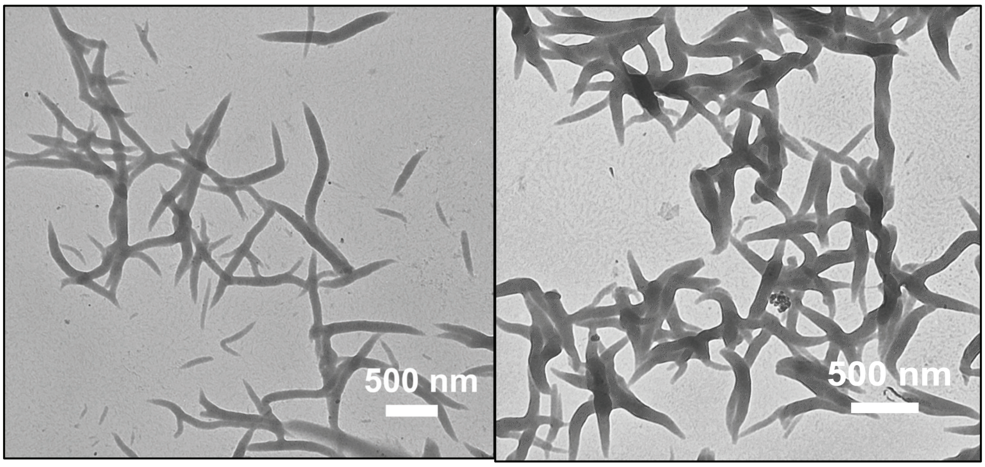
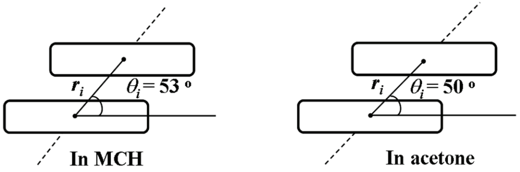


Figure S6. TEM images of a suspension of **PBI 1** gel in dioxane ($c = 2.5 \times 10^{-3}$ M).

Calculation of excitonic coupling:



$$\left|\mu_{eg}\right|^2 = \frac{3hc\varepsilon_0 \ln 10}{2\pi^2 N_A}\int_{\tilde{\nu}_1}^{\tilde{\nu}_2}\frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}}d\tilde{\nu} \tag{1}$$

$$\Delta E_{agg} = \Delta E_{mon} + \Delta E_{vdW} + \sum_i J_i \tag{2}$$

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

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

Figure S7. Arrangement of monomeric **PBI 1** units in a J-type aggregate structure and equations for estimating the spectral shift. μ_{eg} is the transition dipole moment of the monomer, J_i is the excitonic coupling and r_i the distance of adjacent monomeric units with the slip angle θ_i. 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. $\Delta\tilde{\nu}_{agg-mon}$ denotes the spectral shift of the aggregate band with respect to the monomer band.

The transition dipole moment of **PBI 1** was calculated as 6.9 D for monomer and 7.8 D for aggregate according to equation 1. For a H-bond-fixed aggregate structure, a bathochromic shift of $\Delta\tilde{\nu}_{\text{agg-mon}} < -\ 470\ \text{cm}^{-1}$ is calculated for a inter core distance of 4.8 Å and a slip angle of $\theta = 53°$, which is close to the magic angle 54.7°. This value is in good agreement with the experimental value of - 560 cm^{-1}, if one considers an additional contribution by the van-der-Waals energy.

In acetone, the chromophores of **PBI 1** are slightly more displaced in longitudinal direction because of the incorporation of solvent molecules. The transition dipole moment was calculated as 7.0 D for monomer and 8.6 D for aggregate. The molecular modeling study in this case suggests a larger distance between the dyes' centers of 5.2 Å and a slip angle of 50°. The calculated bathochromic shift is determined as $\Delta\tilde{\nu}_{\text{agg-mon}} < -\ 900$, which is in good accordance with the experimental value of - 1080 cm^{-1}.[S3]

Additional Reference.

[S1] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991-1024.

[S2] a) G. Seybold, G. Wagenblast, *Dyes Pigments* **1989**, *11*, 303-317; b) R. Gvishi, R. Reisfeld, Z. Burshtein, *Chem. Phys. Lett.* **1993**, *213*, 338-344.

[S3] a) M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.,* **1965,** *11*, 371-392; b) F. Würthner, S. Yao, T. Debaerdemaeker, R. Wortmann, *J. Am. Chem. Soc.,* **2002**, *124*, 9431-9447; c) H. Wang, T. E. Kaiser, S. Uemura, F. Würthner, *Chem. Commun.,* **2008**, 1181-1183.