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Gelation of a Highly Fluorescent Urea-Functionalized Perylene Bisimide Dye

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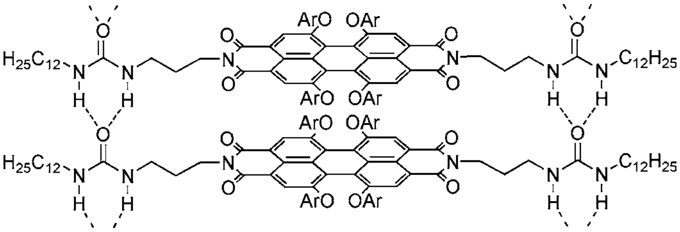
ABSTRACT



A urea-containing tetraphenoxy-substituted perylene bisimide has been synthesized, and its gelation ability has been studied. This functional dye forms fluorescent organogels in toluene and tetrachloromethane through self-assembly by hydrogen-bonding and π–π-stacking interactions. AFM and confocal laser scanning microscopy reveal the formation of fiberlike aggregates.

Organogels are of increasing interest for quite diverse applications, e.g., templates for mineralization[1] and ion-selective membranes,[2] thermo- and mechanoresponsive sensor materials,[3] or nano- and mesoscopic assemblies with interesting optical and electronic properties.[4−7] For these applications, a wide spectrum of low molecular weight compounds has been employed as gelators that form organogels by self-assembly through noncovalent interactions, such as hydrogen bonding, $\pi-\pi$-stacking, donor−acceptor, and van der Waals interactions.[4a,8] In recent years, gelators based on porphyrins,[4d,6b,9] phthalocyanines,[10] and phenylenevinylenes[5] have been reported.

Among functional dyes, perylene bisimides (PBIs) have attracted great interest as a result of their unique optical and photophysical properties. These dyes have been applied in

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(1) (a) Fujita, N.; Asai, M.; Yamashita, T.; Shinkai, S. *J. Mater. Chem.* **2004**, *14*, 2106−2114. (b) Numata, M.; Sugiyasu, K.; Hasegawa, T.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3279−3283.

(2) Beginn, U.; Möller, M. In *Supramolecular Materials and Technologies*; Reinholdt, D. N., Ed.; Wiley & Sons: Chichester, 1999; pp 89−176.

(3) Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 13922−13923.

(4) (a) van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263−2266. (b) Schoonbeek, F. S.; van Esch, J. H.; Wegewijs, B.; Rep, D. B. A.; de Haas, M. P.; Klapwijk, T. M.; Kellogg, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1393−1397. (c) Schoonbeek, F. S.; van Esch, J. H.; Hulst, R.; Kellogg, R. M.; Feringa, B. L. *Chem. Eur. J.* **2000**, *6*, 2633−2643. (d) Shirakawa, M.; Kawano, S.-i.; Fujita, N.; Sada, K.; Shinkai, S. *J. Org. Chem.* **2003**, *68*, 5037−5044. (e) Dulić, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402. (f) de Jong, J. J. D.; Lucas, L. N.; Kellogg, R. M.; van Esch, J. H.; Feringa, B. L. *Science* **2004**, *304*, 278−281.

(5) (a) Ajayaghosh, A.; George, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 5148−5149. (b) Ajayaghosh, A.; George, S. J.; Praveen, V. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 332−335.

(6) (a) Sugiyasu, K. S.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229−1232. (b) Tamaru, S.-i.; Uchino, S.-y.; Takeuchi, M.; Ikeda, M.; Hatano, T.; Shinkai, S. *Tetrahedron Lett.* **2002**, *43*, 3751−3755.

(7) Placin, F.; Desvergne, J.-P.; Lassegues, J.-C. *Chem. Mater.* **2001**, *13*, 117−121.

(8) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133−3159. (b) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237−1247. (c) See the special issue of *Langmuir* on self-assembled fibrillar networks. *Langmuir* **2002**, *12*, 7095−7244.

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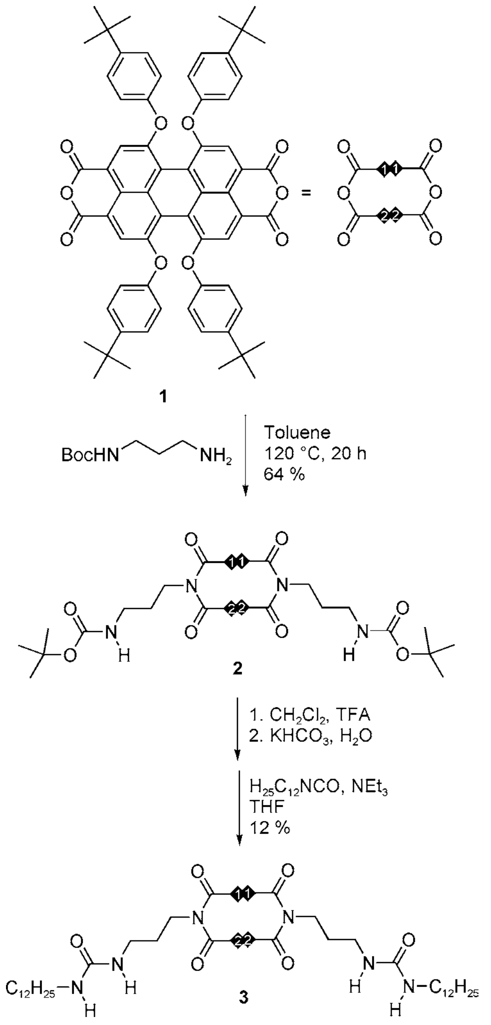
light-harvesting systems, photovoltaic cells, field-effect transistors, and light-emitting diodes.[11] Thus, we have planned to develop gelators derived from PBIs that may provide organogels for applications in optoelectronics. Noteworthy, while our work was under progress,[12] Shinkai and co-workers have published a communication on organogels composed of cholesterol-based PBIs.[6a]

There are numerous urea-based gelators that form organogels through self-complementary and highly directional hydrogen-bonding interactions.[4,6b,13] However, to date no urea-based gelator derived from PBI functional dyes has been reported. Here we present the urea-containing PBI derivative **3**, which forms highly fluorescent organogels through self-assembly mediated by hydrogen-bonding and $\pi-\pi$-stacking interactions.

The urea-containing PBI **3** was synthesized in three steps starting with 1,6,7,12-tetrakis(*tert*-butylphenoxy)-perylene-3,4:9,10-tetracarboxylic acid bisanhydride (**1**)[14] according to Scheme 1. The imidization of **1** with mono BOC-protected 1,3-propanediamine afforded the PBI **2** in good yield. After the deprotection of BOC groups with trifluoroacetic acid and subsequent neutralization with $KHCO_3$ (pH value ca. 7), the free diamine derivative was released, which was reacted with dodecylisocyanate without any further purification to afford the diurea-functionalized PBI **3**. The product **3** was purified by column chromatography on silica gel and characterized by ^{1}H and ^{13}C NMR, MALDI-TOF mass spectroscopy, and elemental analysis.

Scheme 1



The gelation propensity of the urea-containing perylene bisimide dye **3** was assessed in different organic solvents. For this purpose 0.5 mg of **3** was added to 1 mL of a particular solvent and heated until everything was dissolved. After cooling the sample to ambient temperature, the vessel was turned upside down to verify whether nonflowing material was formed, indicating gelation of the employed solvent. If no gelation was observed, the procedure was repeated with an additional 0.5 mg batch of **3**. For toluene a critical gelation concentration of 5.0 mg/mL was determined, whereas for tetrachloromethane this concentration was 1.0 mg/mL. No gels were formed in polar aprotic DMSO and H-bonding methanol, suggesting the crucial role of self-complementary hydrogen bonding in the gelation process of **3**. This compound is insoluble in nonpolar solvents such as methylcyclohexane and *n*-hexane even at elevated temperatures.

The absorption and fluorescent spectra of **3** were measured in gelling solvent tetrachloromethane at dilute concentration (8.71×10^{-7} M) (Figure 1a) and at slightly above critical gelation concentration (5.5×10^{-4} M) (Figure 1b). The spectra in Figure 1 reveal that both the absorption and emission bands are strongly changed upon gelation but the

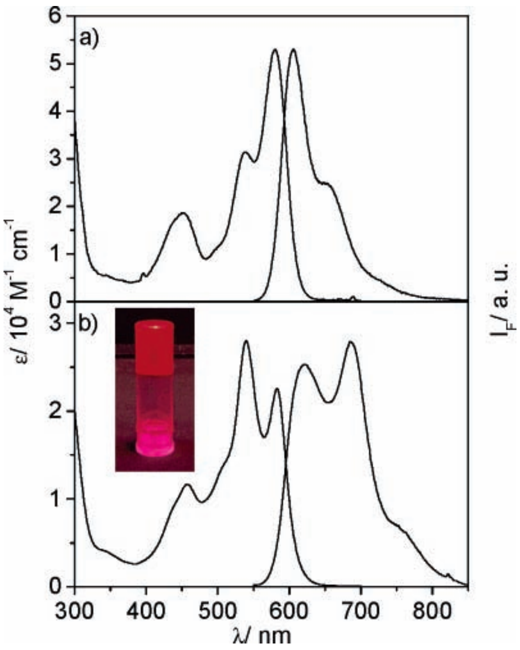


Figure 1. UV−vis absoption and fluorescence spectra of **3** in CCl_4: (a) [**3**] = 8.71×10^{-7} M), (b) [**3**] = 5.5×10^{-4} M, λ_{ex} = 580 nm; inset shows a photograph of the fluorescent gel.

coloristic properties, i.e., the strong red photoluminescence (see inset in Figure 1b), are maintained. On the basis of our earlier work on aggregation of tetraphenoxy-substituted PBIs,[15] these observations are attributed to $\pi-\pi$ stacking of the perylene core in gel.[16] A fluorescence quantum yield of 94% was determined for **3** (8.71×10^{-7} M) in tetrachloromethane by employing *N*,*N*'-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10-tetracarboxylic acid bisimide as reference ($\Phi_{Fl} = 96\%$ in $CHCl_3$).[17]

Absorption spectral changes of gelator **3** in toluene at variable temperature between 5 and 40 °C are shown in Figure 2. Isosbestic points are observed at 550 and 613 nm, revealing transition between two spectroscopically different states. The spectrum at 5 °C resembles that observed for the gel of **3** in CCl_4 (Figure 1b), whereas the spectrum at 40 °C is virtually identical with the solution spectrum in dilute CCl_4 (Figure 1a). Comparison of the spectra at 5 and 40 °C reveals that the absorption band at 584 nm (5 °C) is hypsochromically shifted to 579 nm at 40 °C and its intensity is significantly increased, while the absorbance of the vibronic transition at 539 nm as well as of the shoulder at about 500 nm is decreased. These temperature-dependent spectral changes indicate the existence of $\pi-\pi$ stacked perylene bisimide units in gel and their destacking upon heating. The thermoreversibility of the gelation process was confirmed by several repeated variable-temperature measurements with the same sample. The observed thermoreversibility implies that the gelation of **3** is rendered by self-assembly mediated through noncovalent interactions (in the present case $\pi-\pi$ stacking and hydrogen bonding). From the Boltzmann fit (inset in Figure 2), a melting temperature of about 28 °C is estimated for the toluene gel of **3**.

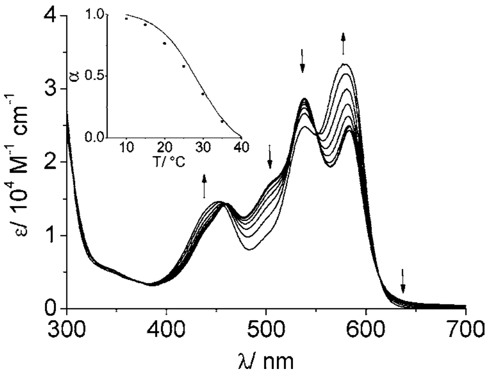


Figure 2. Variable-temperature (5−40 °C) UV−vis absorption spectra of **3** (8.9×10^{-4} M) in gelling solvent toluene. The arrows indicate spectral changes with increasing temperature. Inset shows a plot of α value (α is the fraction of aggregated molecules) against the temperature; the curves were fitted at 579 nm with the Boltzmann equation: $\alpha = 1/(1 + e^{(T-T_m)\Delta T})$.[18]

To confirm the existence of hydrogen bonding in gel aggregate of **3**, IR measurements were carried out. The FT-IR spectrum of tetrachloromethane gel of **3** (3.3×10^{-3} M) exhibits a broad band at 3350 cm^{-1} that can be assigned to the hydrogen-bonded N−H stretching vibration according to literature data.[5a,19] In the dichloromethane solution spectrum of **3** (3.4×10^{-3} M), this stretching frequency is shifted about 100 cm^{-1} toward higher wavenumbers. Similar shifts were reported for the stretching frequencies of hydrogen-bonded N−H groups for other urea-based organogelators.[20] Thus, the IR study provides evidence for the involvement of hydrogen bonding that may act cooperatively with $\pi-\pi$ stacking in gelation of **3** through self-assembly.

The result of a molecular modeling study of four aggregated molecules of **3** is shown in Figure 3. The urea units provide the self-complementary hydrogen bonding to give two hydrogen-bonded tracks separated by a $\pi-\pi$-stacked perylene bisimide core. The twisted perylene core is not visible because of the bulky *tert*-butylphenoxy groups at the periphery.

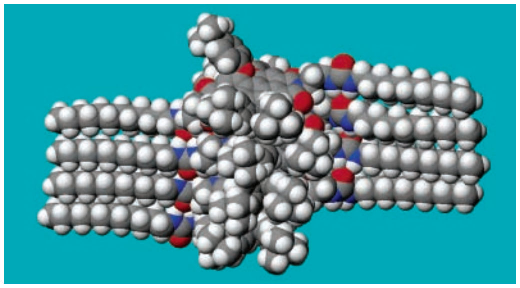


Figure 3. CPK model of four aggregated molecules of **3** (structure calculated with CAChe with MM3 method).

To get some insight into the morphology of the gel aggregate, atomic force microscopy (AFM) analysis was performed. For this purpose, **3** was dissolved in toluene under heating and subsequently spin-coated on graphite at room

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[9] (a) Dammer, C.; Maldivi, P.; Terech, P.; Guenet, J.-M. *Langmuir* **1995**, *11*, 1500−1506. (b) Sagawa, T.; Fukugawa, S.; Yamada, T.; Ihara, H. *Langmuir* **2002**, *18*, 7223−7228.

[10] (a) Van Nostrum, C. F.; Picken, S.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957−9965. (b) Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785−788.

[11] Würthner, F. *Chem. Commun.* **2004**, 1564−1579.

[12] Hanke, B. Diploma Thesis, Universität Würzburg, December, 2003.

[13] (a) Hanabusa, K.; Matsumoto, Y.; Miki, T.; Koyama, T.; Shirai H. *J. Chem. Soc., Chem. Commun.* **1994**, 1401−1402. (b) Hanabusa K.; Shimura, K.; Hirose, K.; Kimura, M.; Shirai, H. *Chem. Lett.* **1996**, 885−886.

[14] Dotcheva, D.; Klapper, M.; Müllen, K. *Macromol. Chem. Phys.* **1994**, *195*, 1905−1911.

[15] (a) Würthner, F.; Thalacker, C.; Sautter, A.; Schärtl, W.; Ibach, W.; Hollricher, O. *Chem. Eur. J.* **2000**, *6*, 3871−3886. (b) Thalacker, C.; Würthner, F. *Adv. Funct. Mater.* **2002**, *12*, 209−217.

[16] Würthner, F.; Thalacker, C.; Sautter, A. *Adv. Mater.* **1999**, *11*, 754−758.

[17] Gvishi, R.; Reisfeld, R.; Burshtein, Z. *Chem. Phys. Lett.* **1993**, *213*, 338−344.

[18] Apperloo, J. J.; Janssen, R. A. J.; Malenfant, P. R. L.; Fréchet, J. M. J. *Macromolecules* **2000**, *33*, 7038−7043.

[19] Syamakumari, A.; Schenning, A. P. H. J.; Mejer, E. W. *Chem. Eur. J.* **2002**, *8*, 3353−3361 and references therein.

[20] Babu, P.; Sangeetha, N. M.; Vijaykumar, P.; Maitra, U.; Rissanen, K.; Raju, A. R. *Chem. Eur. J.* **2003**, *9*, 1922−1932.

temperature. The height AFM image of the xerogel aggregate of **3** (Figure 4) reveals a network of fiberlike structures with little branching. In different samples it was found that the diameter of these fibrous structures varies from 30 to 100 nm. This suggests that the fibers are made up of smaller filaments, which are aligned together.

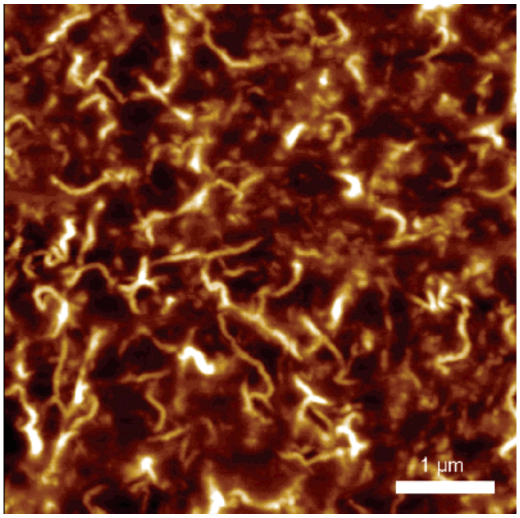

Figure 4. Height AFM image of **3** spin-coated on graphite.

Figure 5 shows the confocal laser scanning microscopy (CSL) image of the fluorescent fibers of the gel, supporting the fact that the fluorescence comes from the gel structure itself and not from amorphous material.

Accordingly, compound **3** forms highly photoluminescent mesoscopic networks similar to our earlier reported perylene bisimide-melamine self-assemblies.[15] However, the present assemblies are much easier to prepare, exhibit stronger luminescence, and can be dissolved at higher concentrations, which is a prerequisite for gel formation. As highly efficient energy- and electron-transfer processes have been already demonstrated for nanosized supramolecular architectures of phenoxy-substituted perylene bisimides,[21] these novel organogels are promising canditates for optoelectronic function on the mesoscopic scale.

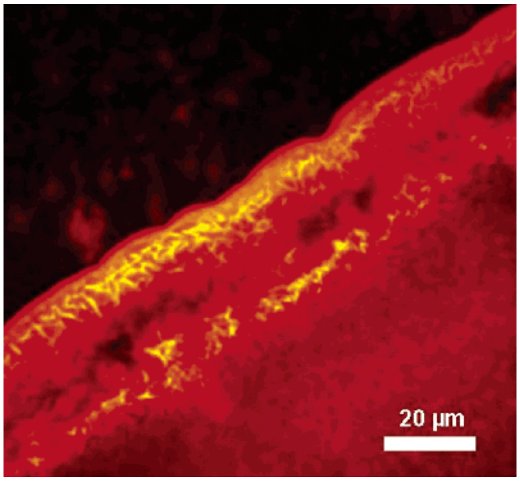

Figure 5. CLS microscopy image of **3** spin-coated on coverglas; $\lambda_{ex} = 543$ nm.

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Supporting Information Available: Procedure for the preparation of **3** and its characterization, general procedures, and a brief description of analytical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] (a) van der Boom, T.; Hayes, R. T.; Zhao, Y.; Burshard, P. J.; Weiss, E. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 9582−9590. (b) Würthner, F.; Sautter, A. *Org. Biomol. Chem.* **2003**, *1*, 240−243. (c) You, C.-C.; Würthner, F. *J. Am. Chem. Soc.* **2003**, *125*, 9716−9725.