Supporting information for:

Organogels Based on *J* and *H*-type Aggregates of Amphiphilic Perylene Tetracarboxylic Diimides

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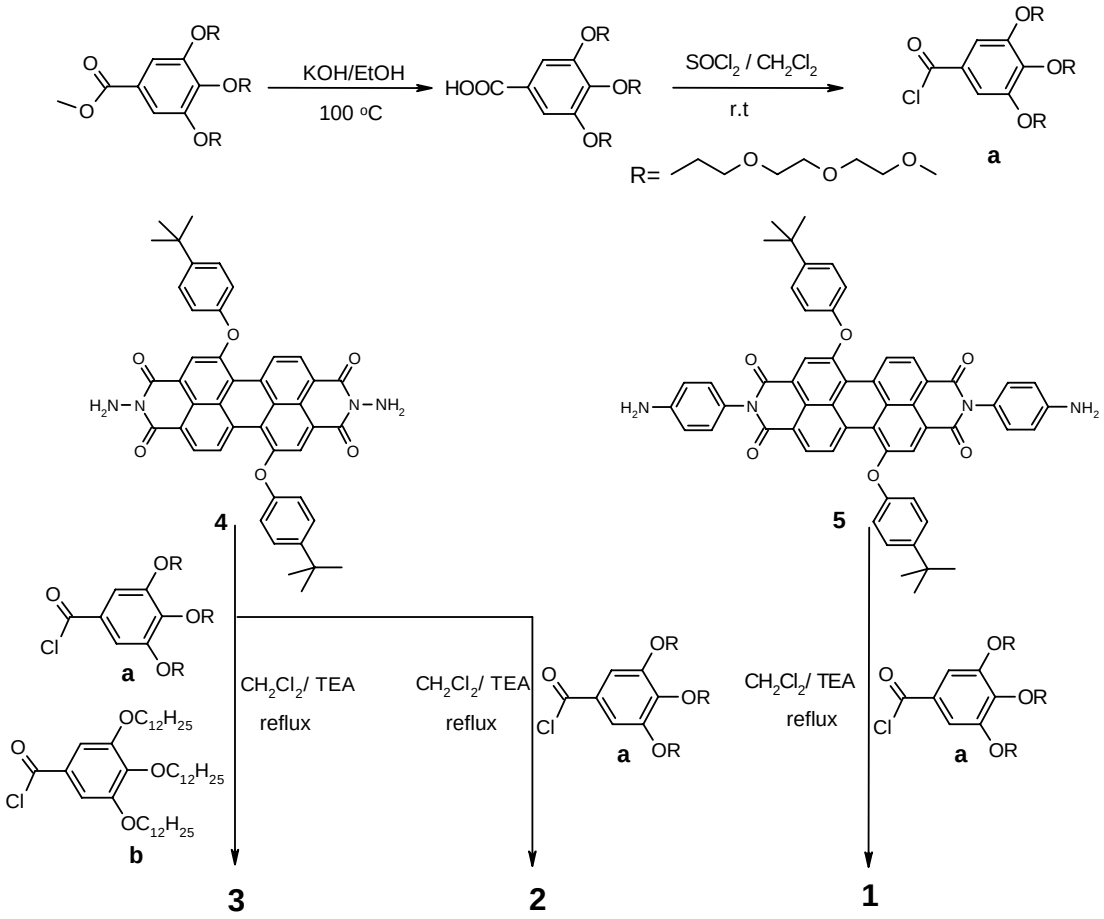
Scheme S1: Synthetic procedures of PDIs.



Methyl 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate,[1] 3,4,5-tris (dodecyloxy)benzoyl chloride,[2] *N*,*N'*-di[4-aminophenyl]-1, 7-di(4-*tert*-butylphenoxy) perylene-3,4;9,10-tetracarboxylate diimide (**5**) and *N*,*N'*-diamido-1,7-di(4-*tert*-butylphenoxy)perylene-3,4;9,10-tetracarboxylate diimide (**4**)[3] were prepared according to the literature.

3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid

KOH (1.67 g, 29.82 mmol) dissolved in 20 mL water was added to a solution of Methyl 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (1.86 g, 2.98 mmol) in ethanol (20 mL), and the emulsion was stirred at 100 ℃ for 5 h. The reaction mixture was cooled to room temperature and poured into a solution of concentrated

HCl (15 mL) in water (350 mL). After extraction with chloroform (3 × 350 mL), the organic phase was dried and concentrated. The crude product was obtained as light yellow oil, which was taken to the next step without further purification.

3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoyl chloride (a)

3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (4.17 g) was dissolver in dry CH_2Cl_2 (36 mL). $SOCl_2$ (18 mL) was added slowly along with 4 drops dry DMF. The reaction mixture was stirred at room temperature for 12 h. The solvent and residual $SOCl_2$ were removed under vacuum at room temperature. The product was obtained as yellow oil, which was used immediately in the next step without further purification.

N,N'-di[N-(4-aminophenyl)-3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzamide]-1,7-di(p-tert-butylphenoxy)perylene-3,4;9,10-tetracarboxylic diimide (1)

Compound **5** (100 mg, 0.12 mmol) and benzoyl chloride **a** (288 mg) were mixed in 10 mL dry CH_2Cl_2 along with 4 drops dry TEA. The reaction mixture was stirred at room temperature for 3 days. The solvent was removed on a rotary evaporator and the residual reaction mixture was washed several times with water. The crude product was purified by silica gel column chromatography using 3 % MeOH in $CHCl_3$ as eluent. Compound **1** (yield 36 %) was collected as bright red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (d, 2H, H_{pery}), 8.73 (d, 2H, H_{pery}), 8.46 (s, 2H, NH),8.39 (s, 2H, H_{pery}), 7.91 (m, 4H, Ar-H), 7.48 (m, 4H, Ar-H), 7.36 (m, 8H, Ar-H), 7.13 (m, 4H,

Ar-H), 4.28 (m, 12H, Ar-OCH_2), 3.88 (m, 12H, Ar-OCH_2CH_2), 3.74 (m, 36H, OCH_2), 3.57 (m, 12H, CH_2OCH_3), 3.34 (s, 18H, OCH_3), 1.37 (s, 18H, CH_3); MS (MALDI-TOF): Calcd. for $C_{112}H_{136}N_4O_{32}$: 2050.3; Found: 2050.9.

N,N'-di[N-amido-3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzamide]-1,7-di(p-tert-butylphenoxy)perylene-3,4;9,10-tetracarboxylic diimide (2)

Compound **2** was synthesized by the same procedure of **1**. The crude product was chromatographed (eluenting with 3:97 v/v MeOH/$CHCl_3$) to yield a red solid (yield 33 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.67 (d, 2H, H_{pery}), 9.27 (s, 2H, NH), 8.65 (d, 2H, H_{pery}), 8.39 (d, 2H, H_{pery}), 7.49 (m, 4H, Ar-H), 7.39 (m, 4H, Ar-H), 7.13 (m, 4H, Ar-H), 4.25 (m, 12H, Ar-OCH_2), 3.82 (m, 12H, Ar-OCH_2CH_2), 3.72 (m, 36H, OCH_2), 3.57 (m, 12H, CH_2OCH_3), 3.38 (s, 18H, OCH_3), 1.37 (s, 18H, CH_3); MS (MALDI-TOF): Calcd. for $C_{100}H_{128}N_4O_{32}$: 1898.1; Found: 1899.2.

N-amido-3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzamide-N'-amido-3,4,5-tris(dodecyloxy)benzamide-1,7-di(p-tert-butylphenoxy)perylene-3,4;9,10-tetracarboxylate diimide (3)

Compound **3** was synthesized by the same procedure described for the preparation of **1**. The crude product was chromatographed (eluenting with 2:98 v/v MeOH/$CHCl_3$) to yield a red solid (yield 18 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.66 (d, 2H, H_{pery}), 9.19 (s, 2H, NH), 8.63 (d, 2H, H_{pery}), 8.39 (s, 2H, H_{pery}), 7.47 (m, 4H, Ar-H), 7.39 (m, 4H, Ar-H), 7.13 (m, 4H, Ar-H), 4.53 (m, 6H, Ar-OCH_2), 4.24 (m, 6H, Ar-OCH_2), 4.04

(m, 6H, Ar-OCH_2CH_2), 3.72 (m, 18H, OCH_2), 3.56 (m, 6H, CH_2OCH_3), 3.38 (s, 9H, OCH_3), 1.37-1.26 (m, 87H, CH_3); MS (MALDI-TOF): Calcd. for $C_{115}H_{158}N_4O_{23}$: 1964.6; Found: 1965.4.

Reference

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2. (a) Mukhopadhyay, P.; Iwashita, Y.; Shirakawa, M.; Kawano, S.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1592-1595. (b) Percec, V.; Ahn, C.-H.; Bera, T. K.; Ungar, G.; Yeardley, D. J. P. *Chem. Eur. J.*, **1999**, *5*, 1070-1083.

3. Würthner, F.; Thalacker, C.; Sautter, A. *Adv. Mater*. **1999**, *11*, 754-758.

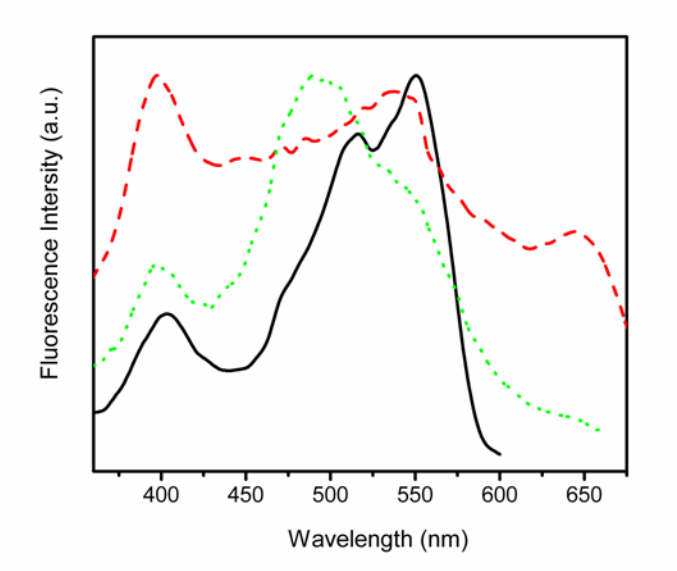

Figure S1. The normalized excitation spectra of compound **3** in $CHCl_3$ (solid), hexane (dot) and gel **III** in gelling solvent hexane (dash).

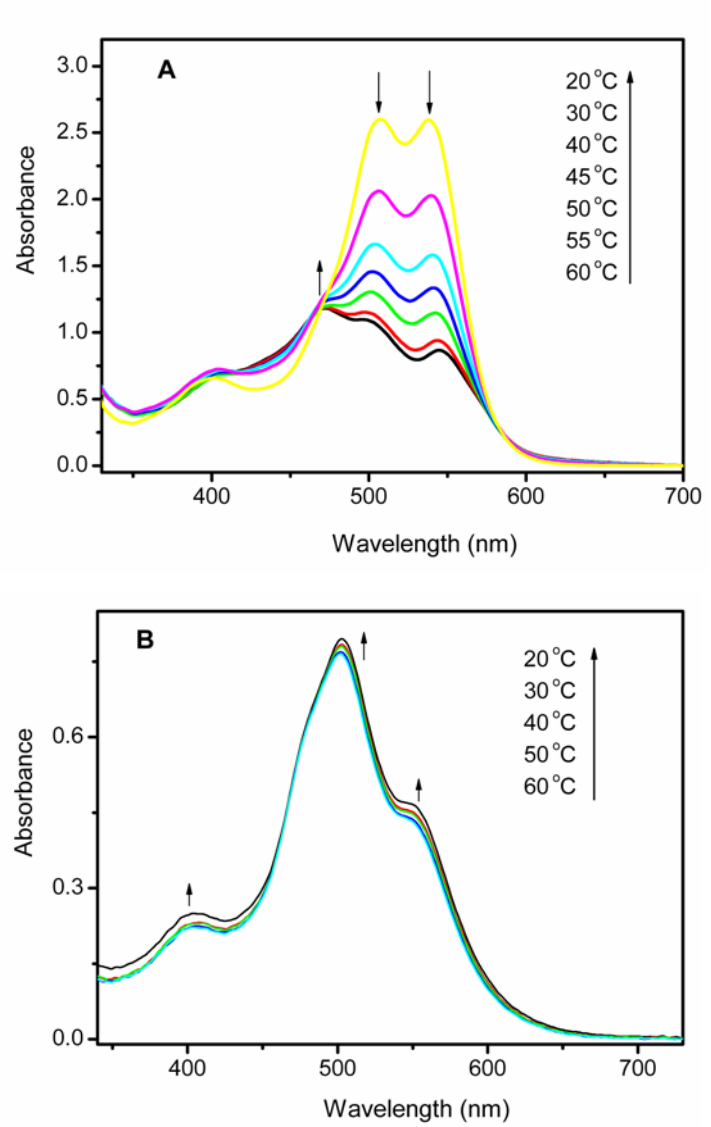

Figure S2. Temperature-dependent absorption spectra of dilute gels **I** (A) and gel **III** (B). The arrows indicate spectral changes with decreasing temperature.

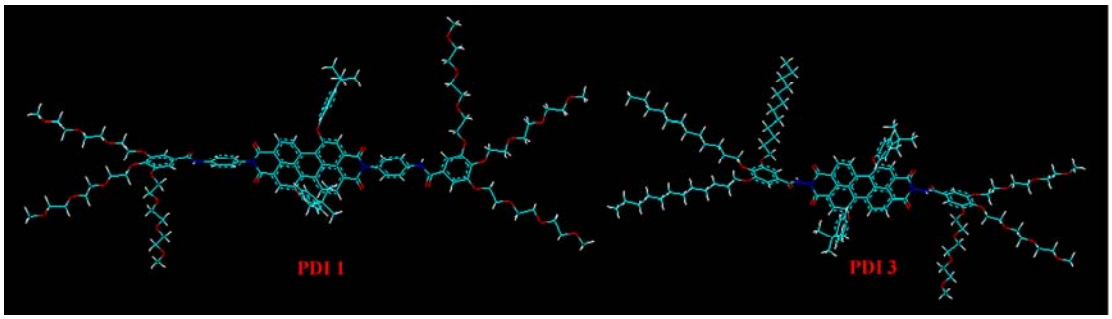

Figure S3. Optimized molecular structures of PDIs **1** and **3** calculated with MM^{+} molecular mechanical modeling.

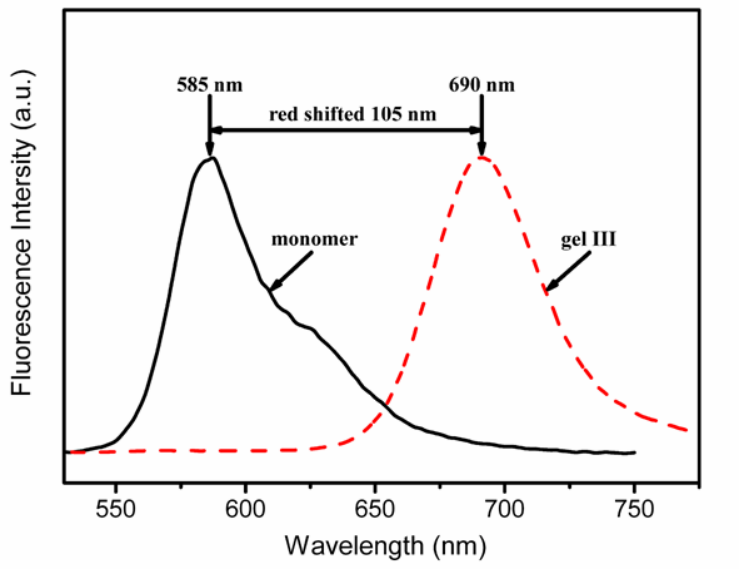

Figure S4. The comparison of the fluorescence spectra of gel **III** with that of compound **3** in monomer.