ELECTRONIC SUPPORTING INFORMATION (ESI) *for*

Influence of imide-substituents on the H-type aggregates of perylene diimides bearing cetyloxy side-chains at bay positions†

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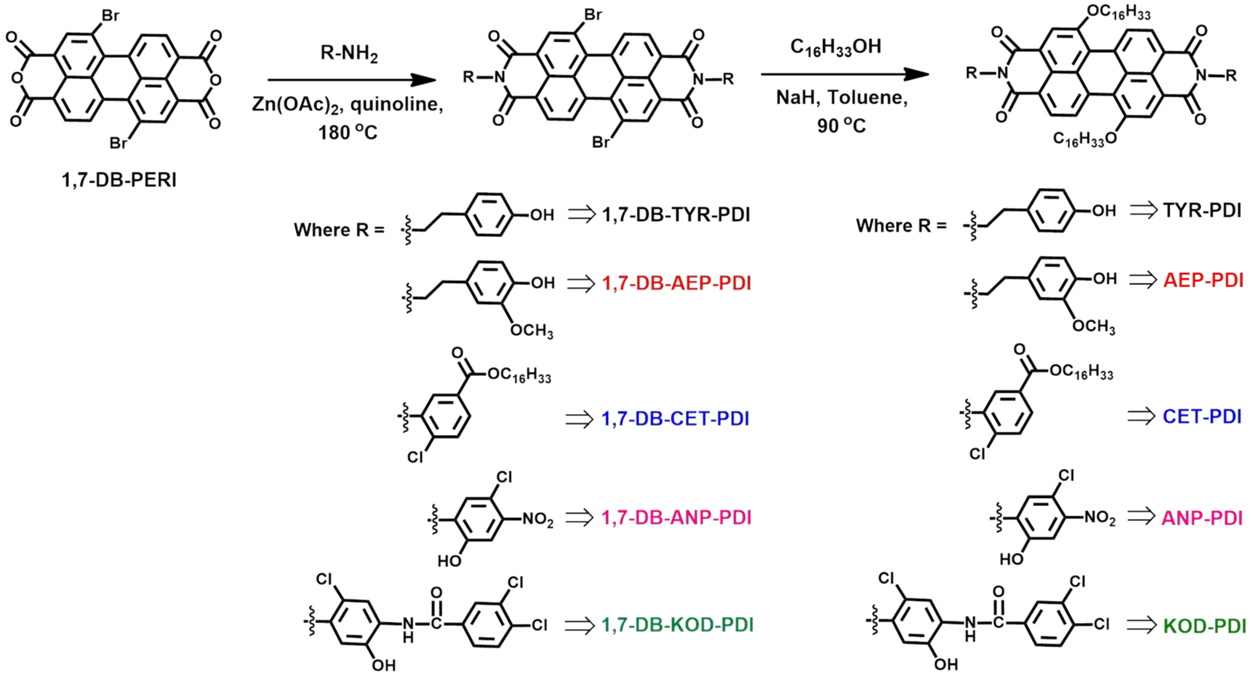
1. Synthetic methods for the synthesis of intermediate compounds and perylene diimides (**TYR-PDI**, **AEP-PDI**, **CET-PDI**, **ANP-PDI** and **KOD-PDI**).

The compound of 1,7-dibromo-3,4:9,10-perylenetetracarboxylic dianhydride (**1,7-DB-PERI**) was synthesized according to previously reported procedures.[1–4] The substituted alkyl/aromatic amine compounds were previously reported by our groups.[5] The imidization reaction of 1,7-dibromo-3,4:9,10-perylenetetracarboxylic dianhydride with substituted alkyl/aromatic amine compounds were carried out according to following procedures.



Scheme S1. Synthetic routes for the synthesis of intermediate compounds of PDIs and imide-substituents substituted perylene diimides bearing long linear cetyloxy side-chains functionalized at the 1,7-bay positions (**TYR-PDI**, **AEP-PDI**, **CET-PDI**, **ANP-PDI** and **KOD-PDI**).

2. Synthetic methods for the preparation of intermediates compounds.

*2.1. Synthesis of 5,12-Dibromo-2,9-bis(4-hydroxyphenethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**1,7-DB-TYR-PDI**).*

A mixture of 1,7-Dibromo-3,4:9,10-perylenetetracarboxylic dianhydride (**1,7-DIBROMO-PERI**) (1 g, 1.8181 mmol), 4-(2-aminoethyl)phenol (Tyramine, **1**) (0.55 g, 4.00 mmol), and $Zn(OAc)_2.2H_2O$ (0.399 g, 1.8181 mmol) in quinoline (10 mL) was heated at 180 °C for overnight under nitrogen atmosphere. After being cooled to room temperature, the reaction mixture was poured into HCl (2 N aq., 25 mL) and stirred for 15 min. The resulting precipitate was filtered off, washed with water (25 mL) and methanol (25 mL), and dried under vacuum to obtain a crude product. The crude product was column chromatographed on silica gel using initially started with 100% DCM to finally a mixture of CH_2Cl_2/methanol (98:2 v/v) as eluent. The collected pure fractions were concentrated under vacuum to afford pure product. The resulting product was dissolved in a minimum volume of CH_2Cl_2 and precipitated by the addition of methanol to afford regio isomerically pure **1,7-DB-TYR-PDI** upon three successive recrystallizations as reddish brown powder; yield: 77% (1.1 g). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.69 (d, 2H, *J*=9.02 Hz, H-perylene), 8.12 (d, 2H, *J*=9.02 Hz, H-perylene), 7.56 (d, 2H, *J*=7.24 Hz, H-perylene), 7.05 (d, 4H, *J*=7.76 Hz, C–H aromatic), 6.60 (d, 2H, *J*=7.04 Hz, C–H aromatic), 5.37 (brs, 2H, O–H aromatic), 3.68 (t, 4H, C–H aliphatic), 2.33 (t, 4H, C–H aliphatic). HR-MASS: calcd for $C_{40}H_{24}Br_2N_2O_6$ (m/z): 788.44 [M^+]; found: 789.20 [M+1]. Anal. Calcd. for $C_{40}H_{24}Br_2N_2O_6$: C, 60.93; H, 3.07; N, 3.55. Found: C, 60.58; H, 3.22; N, 3.81.

2.2. *Synthesis of 5,12-Dibromo-2,9-bis(4-hydroxy-3-methoxyphenethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**1,7-DB-AEP-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**1,7-DB-TYR-PDI**). But starting from the compound of 4-(2-aminoethyl)-2-methoxyphenol (**2**) (0.67 g, 4.00 mmol). The isolated product yield is 65 % (1.0 g) as reddish brown powder. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (d, 2H, *J*=3.6 Hz, H-perylene), 7.72 (d, 2H, *J*=10.4 Hz, H-perylene), 7.54 (d, 2H, *J*=8.4 Hz, H-perylene), 6.88 (q, 4H, C–H aromatic), 6.72 (d, 2H, *J*=1.6 Hz, C–H aromatic), 5.84 (brs, 2H, O–H aromatic), 3.78 (s, 6H, C-H aromatic). HR-MASS: calcd for $C_{42}H_{28}Br_2N_2O_8$ (m/z): 848.49 [M^+]; found: 844 [M–4]. Anal. Calcd. for $C_{42}H_{28}Br_2N_2O_8$: C, 59.45; H, 3.33; N, 3.30. Found: C, 58.96; H, 3.74; N, 3.81.

2.3. *Synthesis of Dihexadecyl 3,3'-(5,12-dibromo-1,3,8,10-tetraoxoanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-2,9(1H,3H,8H,10H)-diyl)bis(4-chlorobenzoate) (**1,7-DB-CET-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**1,7-DB-TYR-PDI**). But starting from the compound of hexadecyl 3-amino-4-chlorobenzoate (**3**) (1.58 g, 4.00 mmol). The isolated product yield is 77 % (1.83 g) as bright orange powder. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, *J*=1.76 Hz, H-perylene), 7.39 (d, 2H, *J*=1.80 Hz, H-perylene), 7.37 (d, 2H, *J*=1.8 Hz, H-perylene), 7.32 (s, 2H, H-aromatic), 7.30 (d, 2H, *J*=1.72 Hz, C–H aromatic), 7.28 (s, 2H, C–H aromatic), 4.30 (t, 4H, C–H aliphatic), 1.79–1.72 (m, 4H, C–H aliphatic), 1.43–1.27 (m, 60H, C–H aliphatic), 0.90 (m, 6H, C–H aliphatic). HR-MASS: calcd for $C_{70}H_{78}Br_2Cl_2N_2O_8$ (m/z): 1306.09 [M^+]; found: 1310.5 [M+4]. Anal. Calcd. for $C_{70}H_{78}Br_2Cl_2N_2O_8$: C, 64.37; H, 6.02; N, 2.14. Found: C, 63.90; H, 6.41; N, 2.49.

2.4. *Synthesis of 5,12-dibromo-2,9-bis(5-chloro-2-hydroxy-4-nitrophenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**1,7-DB-ANP-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**1,7-DB-TYR-PDI**). But starting from the compound of 2-amino-4-chloro-5-nitrophenol (**4**) (0.75 g, 4.00 mmol). The isolated product yield is 74 % (1.2 g) as reddish-brown powder. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.50 (d, 2H, *J*=1.72 Hz, H-perylene), 7.99 (d, 2H, *J*=1.8 Hz, H-perylene), 7.73 (d, 2H, *J*=2.44 Hz), 7.62 (q, 4H, *J*=1.82 Hz, C–H-aromatic), 7.16 (d, 2H, *J*= 6.2Hz, C–H aromatic), 5.36 (brs, 2H, O–H aromatic). HR-MASS: calcd for $C_{36}H_{12}Br_2Cl_2N_4O_{10}$ (m/z): 891.22 [M^+]; found: 887 [M–4]. Anal. Calcd. for $C_{36}H_{12}Br_2Cl_2N_4O_{10}$: C, 48.52; H, 1.36; N, 6.29. Found: C, 48.02; H, 1.78; N, 6.44.

2.5. *Synthesis of N,N'-((5,12-dibromo-1,3,8,10-tetraoxoanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-2,9(1H,3H,8H,10H)-diyl)bis(5-chloro-2-hydroxy-4,1-phenylene))bis(3,4-dichlorobenzamide) (**1,7-DB-KOD-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**1,7-DB-TYR-PDI**). But starting from the compound of N-(4-amino-5-chloro-2-hydroxyphenyl)-3,4-dichlorobenzamide (**5**) (1.33 g, 4.00 mmol). The isolated product yield is 81 % (1.74 g) as reddish-orange solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.38 (br, 2H, N-H aromatic), 8.55 (s, 2H, J=10.4 Hz, H-perylene), 8.23 (d, 2H, *J*=8.12 Hz H-perylene), 7.80 (d, 2H, *J*=8 Hz, C–H aromatic), 7.65 (d, 2H, *J*=1.64 Hz, C-H aromatic), 7.10 (d, 2H, *J*=1.54 Hz, C-H aromatic), 6.8 (d, 2H, *J*=1.72 Hz, C-H aromatic), 5.77 (brs, 2H, O–H aromatic). HR-MASS: calcd for $C_{50}H_{20}Br_2Cl_6N_4O_8$ (m/z): 1177.24 [M^+]; found: 1178.05 [M+1]. Anal. Calcd. for $C_{50}H_{20}Br_2Cl_6N_4O_8$: C, 51.01; H, 1.71; N, 4.76. Found: C, 50.67; H, 2.03; N, 4.90.

3. Synthetic methods for the final perylene diimide derivatives:

3.1. *Synthesis of 5,12-bis(hexadecyloxy)-2,9-bis(4-hydroxyphenethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**TYR-PDI**).*

A mixture of **1** (0.5 g, 0.6341 mmol), Cetyl alcohol (0.54 g, 2.22 mmol), and sodium hydride (NaH, 60 % dispersion in mineral oil) (58 mg, 2.41 mmol) in 30 ml anhydrous toluene were heated to 85–90 °C for 12 h under argon atmosphere. The progress of the reaction was monitored by Thin Layer Chromatography for every 2 hr using DCM/hexane (4:1) as an eluent. The reddish brown reaction mass was cooled to room temperature and then poured into ice water (100 mL) containing 2N HCl solution. The yielded precipitate was filtered on a G4 funnel, washed with hot water (~50 mL), and finally rinsed with methanol and dried under vacuum. The crude product was chromatographed on silica gel 230–400 mesh using $CHCl_3$/acetone (30 : 1 ratio) as eluent to afford the product: **reddish brown powder; yield: 88% (0.62 g)**. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.41 (s, 2H, H-perylene), 7.30 (d, 2H, *J*=9.02 Hz, H-perylene), 7.08 (d, 2H, *J*=7.24 Hz, H-perylene), 6.69 (d, 4H, *J*=7.76 Hz, C–H aromatic), 6.60 (d, 2H, *J*=7.04 Hz, C–H aromatic), 5.66 (brs, 2H, O–H aromatic), 4.22–4.19 (t, 4H, C–H aliphatic), 3.88 (q, 4H, C-H aromatic), 3.69

(t, 6H, C–H aliphatic), 2.87 (brs, 4H, C–H aliphatic), 1.67 (t, 4H, C–H aliphatic), 1.36–1.22 (m, 60H, C–H aliphatic), 0.85 (t, 6H, C–H aliphatic). ESI-MASS: calcd for $C_{72}H_{90}N_2O_8$ (m/z): 1110.67 [M^+]; found: 1128.10 [$M+NH_4$]. Anal. Calcd. for $C_{72}H_{90}N_2O_8$: C, 77.80; H, 8.16; N, 2.52. Found: C, 77.38; H, 8.02; N, 2.70.

3.2. *Synthesis of 5,12-Bis(hexadecyloxy)-2,9-bis(4-hydroxy-3-methoxyphenethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**AEP-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**TYR-PDI**). But starting from the compound (**1,7-DB-AEP-PDI**) (0.5 g, 0.59 mmol), Cetyl alcohol (0.50 g, 2.06 mmol), and NaH (54 mg, 2.24 mmol) in 30 mL anhydrous toluene. The product was obtained after column purification using $CHCl_3$/acetone (30:1 ratio) as eluent. The isolated product yield is 87 % (0.6 g) as **reddish brown solid**. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.53 (s, 1H, H-perylene), 7.45 (s, 1H, H-perylene), 7.34 (d, 2H, *J*=9 Hz, H-perylene), 7.18 (d, 2H, *J*=7.3 Hz, C–H aromatic), 6.69 (d, 4H, *J*=7.76 Hz, C–H aromatic), 6.60 (d, 2H, *J*=7.04 Hz, C–H aromatic), 5.66 (brs, 2H, O–H aromatic), 4.20 (t, 4H, C–H aliphatic), 3.88 (brs, 4H, C-H aromatic), 3.69 (d, 6H, C–H aliphatic), 2.69 (brs, 4H, C–H aliphatic), 1.68–1.64 (q, 4H, C–H aliphatic), 1.36–1.33 (m, 60H, C–H aliphatic), 0.84 (t, 6H, C–H aliphatic). ESI-MASS: calcd for $C_{74}H_{94}N_2O_{10}$ (m/z): 1170.69 [M^+]; found: 1139.09 [$M–2NH_4$]. Anal. Calcd. for $C_{74}H_{94}N_2O_{10}$: C, 75.86; H, 8.09; N, 2.39; Found: C, 75.32; H, 8.15; N, 2.50.

3.3. *Synthesis of Dihexadecyl 3,3'-(5,12-bis(hexadecyloxy)-1,3,8,10-tetraoxoanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-2,9(1H,3H,8H,10H)-diyl)bis(4-chlorobenzoate) (**CET-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**TYR-PDI**). But starting from the compound (**1,7-DB-CET-PDI**) (0.5 g, 0.38 mmol), Cetyl alcohol (0.32 g, 1.32 mmol), and NaH (35 mg, 1.45 mmol) in 30 ml anhydrous toluene. The product was obtained after column purification using $CHCl_3$/acetone (30:1 ratio) as eluent. The isolated product yield is 95 % (0.59 g) as **bright orange solid**. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.47 (d, 2H, *J*=1.76 Hz, H-perylene), 7.39 (d, 2H, *J*=1.8 Hz H-perylene), 7.37 (q, 2H, *J*=1.8 Hz and *J*=1.8 Hz, H-perylene), 7.32 (d, 2H, *J*=1.2 Hz, C–H-aromatic), 7.30 (m, 2H, C–H aromatic), 7.28 (d, 2H, C–H aromatic), 4.29 (t, 8H, C–H aliphatic), 1.79–1.72 (m, 8H, C–H aliphatic), 1.43–1.27 (m, 120H, C–H aliphatic), 0.90 (m, 12H, C–H aliphatic). ESI-MASS: calcd for $C_{102}H_{144}Cl_2N_2O_{10}$ (m/z): 1627.02 [M^+]; found: 1645 [$M+NH_4$]. Anal. Calcd. for $C_{102}H_{144}Cl_2N_2O_{10}$: C, 75.20; H, 8.91; N, 1.72; Found: C, 74.88; H, 9.01; N, 1.90.

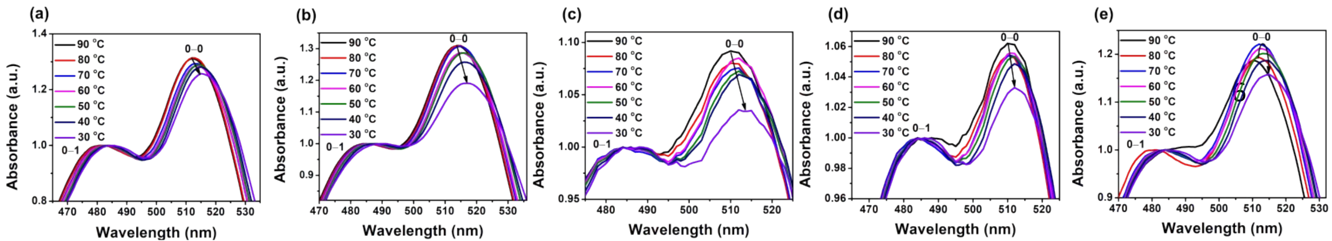
3.4. *Synthesis of 2,9-bis(5-chloro-2-hydroxy-4-nitrophenyl)-5,12-bis(hexadecyloxy)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**ANP-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**TYR-PDI**). But starting from the compound (**1,7-DB-ANP-PDI**) (0.5 g, 0.56 mmol), Cetyl alcohol (0.47 g, 1.96 mmol), and NaH (51 mg, 2.12 mmol) in 30 ml anhydrous toluene. The product was obtained after column purification using $CHCl_3$/acetone (30:1 ratio) as eluent. The isolated product yield is 80 % (0.55 g) as reddish-brown solid. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.45 (d, 2H, J=1.74 Hz, H-perylene), 7.39 (d, 2H, J=1.8 Hz H-perylene), 7.25 (q, 2H, J=1.82 Hz and J=1.82 Hz, H-perylene), 6.73 (d, 2H, J=1.82 Hz, C–H-aromatic), 6.50 (d, 2H, J= 9.0Hz, C–H aromatic), 5.66 (brs, 2H, O–H aromatic), 4.18 (t, 4H, C–H aliphatic), 2.00–1.68 (m, 4H, C–H aliphatic), 1.70–1.63 (q, 4H, C–H aliphatic), 1.50–1.20 (m, 60H, C–H aliphatic), 0.88 (t, 6H, C–H aliphatic). ESI-MASS: calcd for $C_{68}H_{78}Cl_2N_4O_{12}$ (m/z): 1212.50 [M^+]; found: 1194.80 [$M–NH_4$]. Anal. Calcd. for $C_{68}H_{78}Cl_2N_4O_{12}$: C, 67.26; H, 6.47; N, 4.61; Found: C, 67.04; H, 6.85; N, 4.95.

3.5. *Synthesis of N,N'-((5,12-bis(hexadecyloxy)-1,3,8,10-tetraoxoanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-2,9(1H,3H,8H,10H)-diyl)bis(5-chloro-2-hydroxy-4,1-phenylene))bis(3,4-dichlorobenzamide) (**KOD-PDI**).*

The above compound was synthesized similar to the synthetic procedure for the synthesis of compound (**TYR-PDI**). But starting from the compound (**1,7-DB-KOD-PDI**) (0.5 g, 0.425 mmol), Cetyl alcohol (0.36 g, 1.48 mmol), and NaH (39 mg, 1.61 mmol) in 30 ml anhydrous toluene. The product was obtained after column purification using $CHCl_3$/acetone (30:1 ratio) as eluent. The isolated product yield is 92 % (0.58 g) as reddish-orange solid. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.58 (brs, 2H, N-H aromatic), 8.18 (s, 2H, H-perylene), 7.91 (d, 2H, J=8.12 Hz H-perylene), 7.78 (d, 2H, J=8 Hz, C–H aromatic), 7.41 (d, 2H, J=1.64 Hz, C-H aromatic), 7.29 (t, 4H, C-H aromatic), 5.66 (brs, 2H, O–H aromatic), 4.23–4.09 (t, 4H, C–H aliphatic), 1.70–1.63 (q, 4H, C–H aliphatic), 1.37–1.22 (m, 60H, C–H aliphatic), 0.85 (t, 6H, C–H aliphatic). ESI-MASS: calcd for $C_{82}H_{86}Cl_6N_4O_{10}$ (m/z): 1496.45 [M^+]; found: 1514.02 [$M+NH_4$]. Anal. Calcd. for $C_{82}H_{86}Cl_6N_4O_{10}$: C, 65.65; H, 5.78; N, 3.73; Found: 65.27; H, 5.91; N, 3.94.

Figure S1. The extended temperature-dependent absorption spectrum of 0–0 and 0–1 vibrational peaks in the region of 470–530 nm for the corresponding PDIs: (a) **TYR-PDI**; (b) **AEP-PDI**; (c)



CET-PDI; (d) **ANP-PDI**; (e) **KOD-PDI** in chloroform/methylcyclohexane ($CHCl_3$/MCH ratio of 1:5) mixed solvent (condition: $C_T = 2\text{x}10^{-5}$ M) during cooling process from 90 to 30 °C.

Figure S2. (a) The photoluminescence spectra of PDIs in thin-film prepared by spin-coating at 1000 rpm and at room temperature. (b) The extended emission spectrum of PDI thin-films.

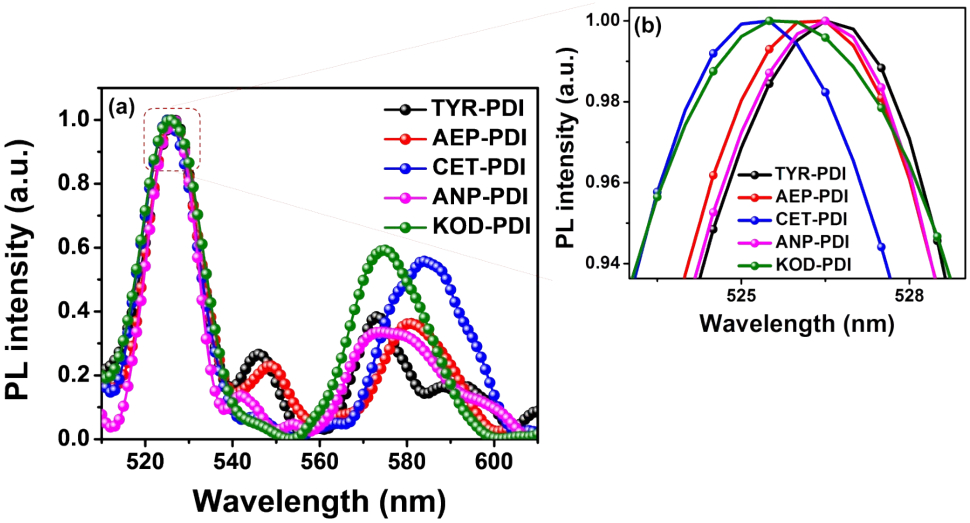


Figure S3. Cyclic voltammetry curves of PDI compounds, (a) in solution and (b) in thin films, in ACN solution containing 0.1 M n-Bu_4NPF_6 as electrolyte. The measurements were recorded from chloroform solution (concentration of 5 mM) as well as thin films of PDIs drop-casted from chloroform solutions onto a glassy carbon disk as the working electrode (3.0 mm in diameter) against Ag/Ag^+ as a reference. Each measurement was calibrated with ferrocene at a scan rate of 50 mV s^{-1}.

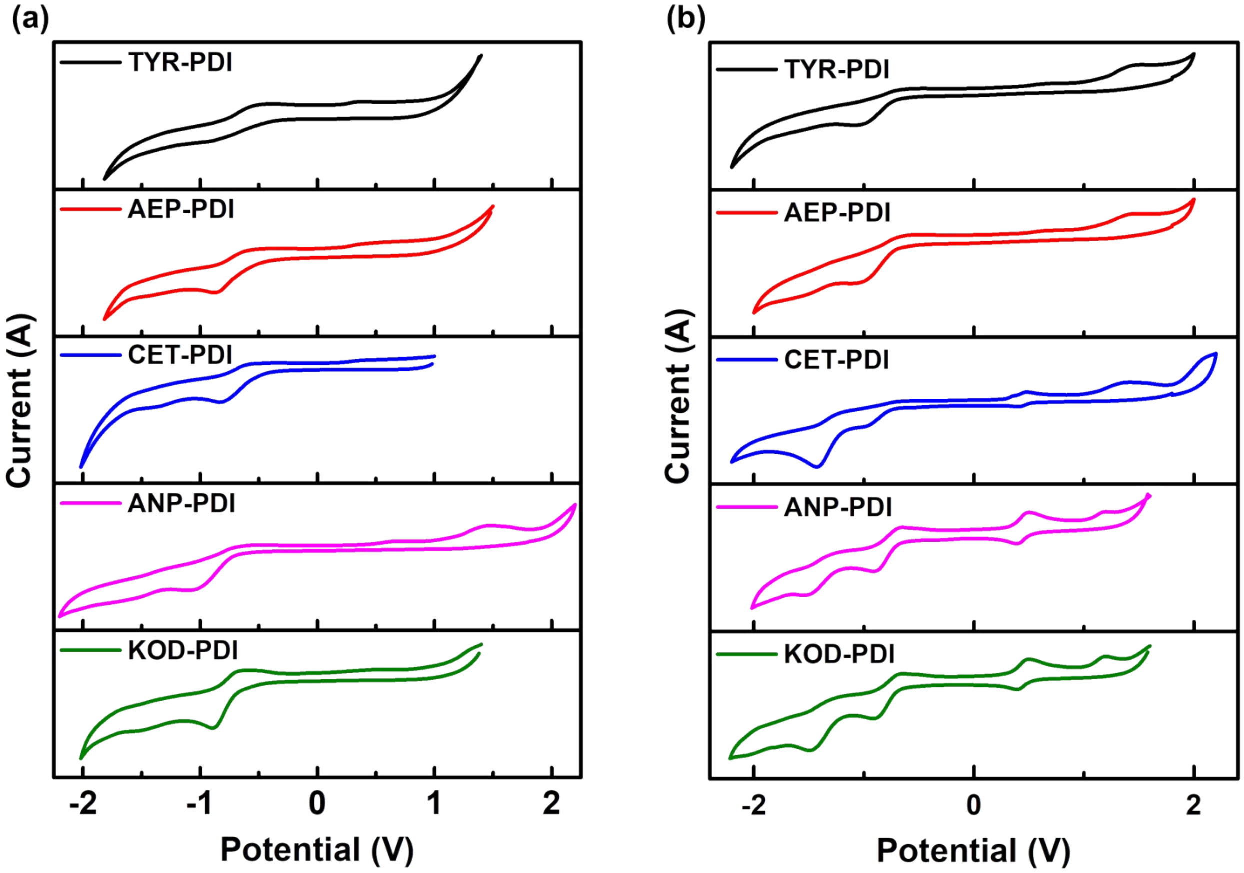


Figure S4. The top view of optimized geometry structure of PDIs: (a) **TYR-PDI**, (b) **AEP-PDI**, (c) **CET-PDI**, (d) **ANP-PDI** and (e) **KOD-PDI** by using AM1 Hamiltonian semi-empirical methods.

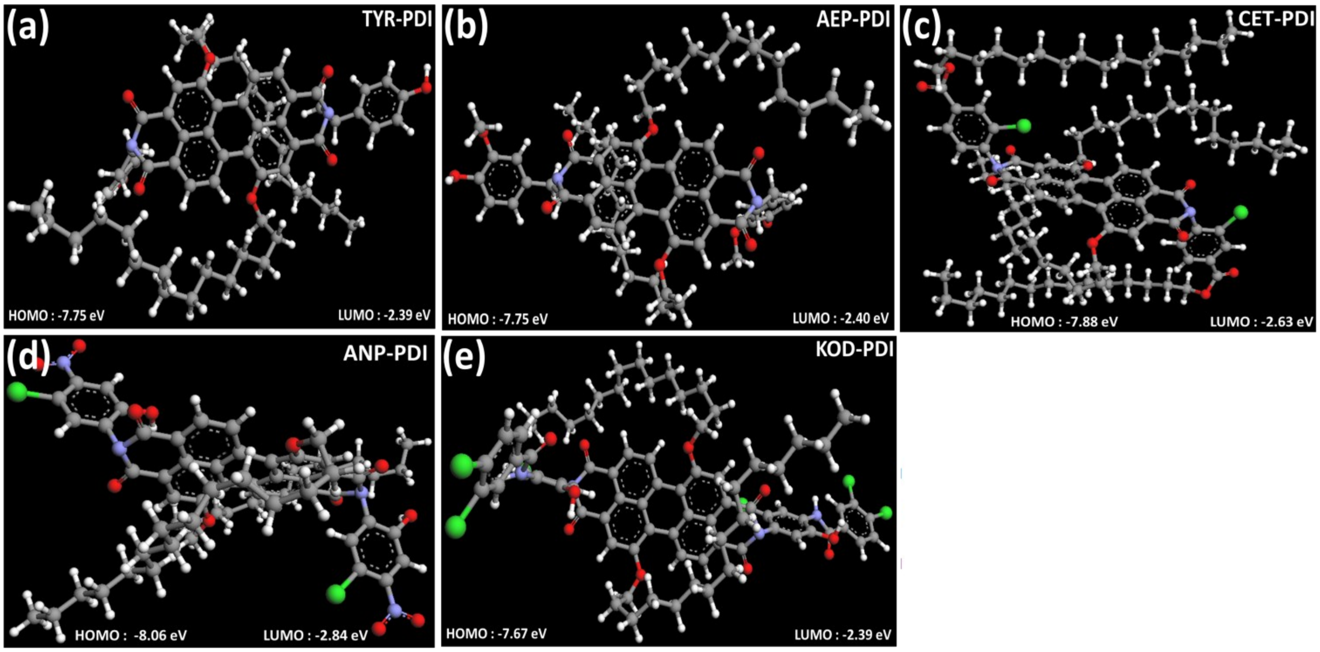


Figure S5. Typical SEM images of the rod-like microstructures formed by formed by (a) **TYR-PDI**; (b) **AEP-PDI**; (c) **CET-PDI**; (d) **ANP-PDI**; (e) **KOD-PDI** in methanol-DCM mixed solvents. The SEM image of (c) is obtained at different places indicates the different size of rod-like microstructure with relatively smooth surface and regular edges governed by **CET-PDI**. SEM images of columnar rectangular ordered H-type PDI aggregates formed in methanol-DCM mixed solvents with volume ratios of 50/50. The scale bar of all images is 10 μm.

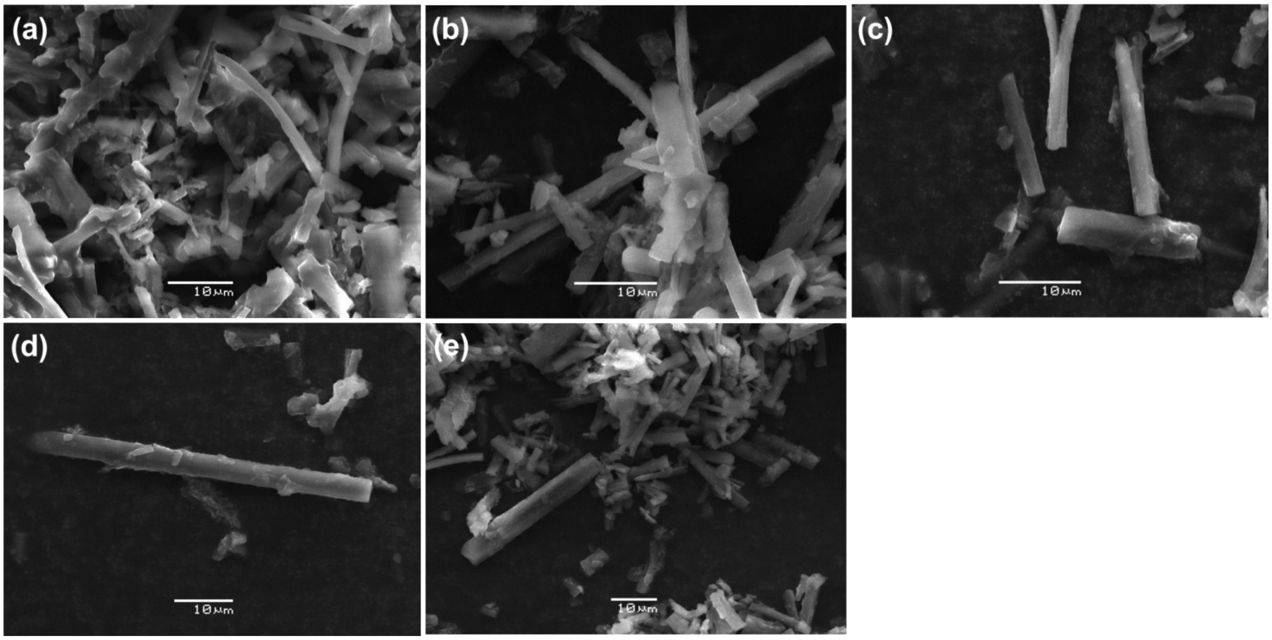


Figure S6. Photographs of Water (top) and Glycerol droplets (bottom) on the surface of PDI thin films with their respective contact angles.

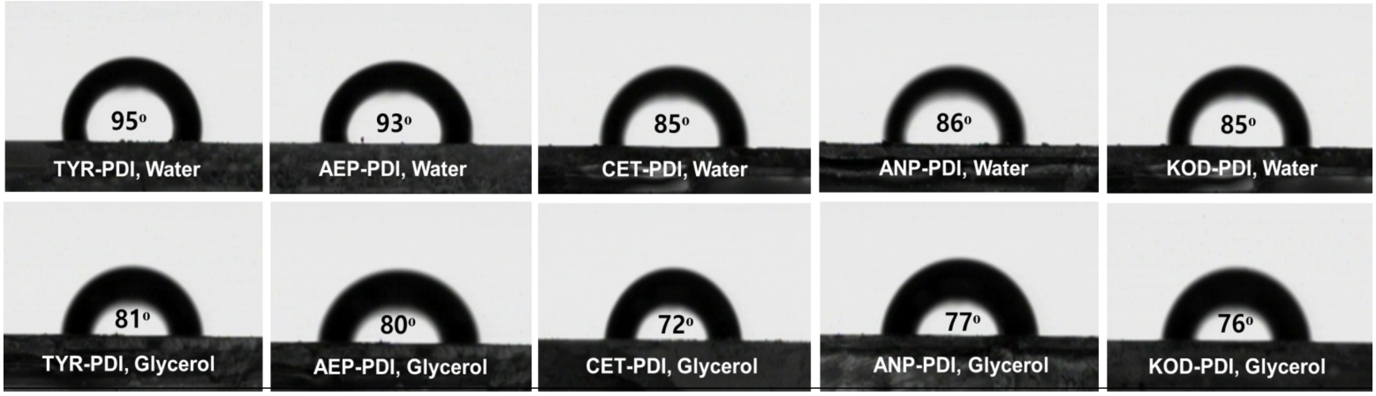


Table S1. The optical properties of aggregate state of PDIs formed at high and low temperature.

Perylene Diimides	**condition**	$\lambda_{max}^{0-0}soln$ **(nm)**[a]	$\lambda_{max}^{0-1}soln$ **(nm)**[a]	$\lambda_{max}^{Sh.p}soln$ **(nm)**[b]	**A_{0-0}/A_{0-1}**
TYR-PDI	90 °C	512	482	--	1.34

	30 °C	515	484	561	1.29
AEP-PDI	90 °C	514	485	--	1.33
	30 °C	515	488	561	1.03
ANP-PDI	90 °C	510	488	--	1.06
	30 °C	512	486	561	1.03
KOD-PDI	90 °C	510	484	--	1.17
	30 °C	515	484	561	1.15

[a] The spectral data are obtained from the concentration of $2x10^{-5}$M in chloroform/methylcyclohexane mixed solvent ($CHCl_3$/MCH ratio of 1:5); [b] Sh.p: Shoulder peaks are appeared at longer wavelength; A_{0-0}/A_{0-1} is obtained from 0–0/0–1 absorption peak ratio.

Perylene Diimides	**Emission (wavelength in nm)**	**t_f (ns) (τ_1, τ_2 & τ_3)**
TRY-PDI	410	0.80 & 1.31
	440	0.96 & 3.91
	565	1.35 & 3.90
AEP-PDI	410	0.90 & 1.42
	440	0.90 & 1.54
	540	0.79 & 1.60
CET-PDI	395	0.85 & n.d.
	490	0.81 & 2.65
	565	0.93 & 4.52
ANP-PDI	395	0.82 & n.d.
	495	0.56 & 4.84
	565	1.43 & 3.98
KOD-PDI	490	0.81, 1.56 & 5.70
	570	0.78, 2.22 & 5.96
	635	0.57, 1.81 & 5.71

Table S2. The fluorescence lifetime results of PDIs.

n.d.: not detected

Table S3. The electrochemical properties and computational results of PDIs.

Perylene Diimides	E_{Oxd}^{CV} **(V)**[a]	E_{Red}^{CV} **(V)**[a]	E_{HOMO}^{CV} **(eV)**[a]	E_{LUMO}^{CV} **(eV)**[a]	E_{Oxd}^{CV} **(V)**[b]	E_{Red}^{CV} **(V)**[b]	E_{HOMO}^{CV} **(eV)**[b]	E_{LUMO}^{CV} **(eV)**[b]	E_{HOMO}^{AM1} **(eV)**[c]	E_{LUMO}^{AM1} **(eV)**[c]

TYR-PDI	1.059	-0.395	-5.37	-3.92	1.102	-0.735	-5.41	-3.57	-7.75	-2.39
AEP-PDI	1.056	-0.482	-5.36	-3.82	1.065	-0.701	-5.37	-3.61	-7.75	-2.40
CET-PDI	0.994	-0.479	-5.30	-3.83	1.040	-0.757	-5.35	-3.55	-7.88	-2.63
ANP-PDI	1.092	-0.674	-5.40	-3.63	1.028	-0.693	-5.34	-3.62	-8.06	-2.84
KOD-PDI	1.040	-0.653	-5.35	-3.66	1.045	-0.696	-5.35	-3.61	-7.67	-2.39

E_{ox} is onset oxidation potential and E_{red} is onset reduction potential are estimated by using Cyclic voltammetric (CV) analysis, [a]Cyclic voltammetry determined in chloroform solution (Conc., of 5 mM) of PDIs vs. Fc/Fc$^+$ (E_{HOMO} = –4.80 eV); [b]Cyclic voltammetry determined in thin-film of PDIs vs. Fc/Fc$^+$ (E_{HOMO} = –4.80 eV) as an internal standard; [c]Computational analysis was performed by using Austin Model 1 (AM1) Hamiltonian semi-empirical method.

Table S4. Packing parameters derived from XRD measurements.

Perylene diimides	Crystallographic parameters			
	2θ (degree)	*d*-spacing (Å)	Miller index (*hkl*)	Phase (lattice constants)
TYR-PDI	3.20	27.58	(100)	
	6.45	13.69	(200)	Col_{rd} (a = 27.38 Å)
	6.95	12.75	(110)	(b = 14.40 Å)
	9.46	9.34	(300)	
	12.25	7.22		
	13.03	6.79	(400)	
	16.50	5.37	(500)	
	18.00	4.93	(600)	
	19.63	4.52	(700)	
	22.66	3.92	(002)	
	25.92	3.44	(102)	
AEP-PDI	3.27	27.0	(100)	
	6.53	13.53	(200)	Col_{rp} (a = 27.06 Å)
	6.95	12.75	(110)	(b = 14.40 Å)
	9.40	9.40	(300)	
	13.11	6.75	(400)	
	13.65	6.48		
	16.42	5.39	(500)	
	18.14	4.89	(600)	
	19.73	4.50	(700)	
	22.75	3.90	(002)	
	26.02	3.42	(102)	
CET-PDI	3.27	27.00	(100)	
	6.54	13.50	(200)	Col_{rp} (a = 27.00 Å)
	6.97	12.78	(110)	(b = 14.43 Å)
	9.40	9.34	(300)	
	12.31	7.18	(400)	
	13.11	6.75		
	16.44	5.39	(500)	
	18.10	4.90	(600)	
	19.71	4.50	(700)	
	22.73	3.91	(002)	
	26.00	3.42	(102)	
ANP-PDI	3.25	27.20	(100)	
	6.53	13.53	(200)	Col_{rp} (a = 27.06 Å)
	6.95	12.75	(110)	(b = 14.40 Å)
	9.44	9.36	(300)	
	12.31	7.18	(400)	
	13.10	6.76		
	16.42	5.39	(500)	
	18.08	4.90	(600)	
	19.71	4.50	(700)	
	22.73	3.91	(002)	
	26.00	3.42	(102)	
KOD-PDI	3.25	27.20	(100)	
	6.53	13.53	(200)	Col_{rp} (a = 27.06 Å)
	6.95	12.75	(110)	(b = 14.40 Å)
	9.38	9.42	(300)	
	12.31	7.18	(400)	
	13.11	6.75		
	16.46	5.38	(500)	
	18.08	4.90	(600)	
	19.69	4.50	(700)	
	22.73	3.91	(002)	
	25.60	3.47	(102)	

Col_{rp}: Columnar rectangular ordered phase; **Col_{rd}**: Columnar rectangular disordered phase.

Table S5. Contact angles and calculated interfacial energy of PDI derivative films using water and glycerol as hydrophilic liquids.

PDIs	**θ_{water} (deg)**	**$\theta_{glycerol}$ (deg)**	**Interfacial energy (mN m^{-1})**
TYR-PDI	95	81	24.9
AEP-PDI	93	80	24.5
CET-PDI	85	72	29.0
ANP-PDI	86	77	24.0
KOD-PDI	85	76	24.7

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