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The Strategy for Molecular Design of Aggregation-Induced Emission Units Further Modified by Substitutes

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Contents

S1. Materials and method

All chemicals were purchased from Beijing Chemical Reagent Company and J&K Scientific without further purification. The molecules synthesized in this paper were identified by ^{1}H, ^{13}C NMR spectra and Matrix-Assisted Laser Desorption / Ionization Time of Flight Mass Spectrometry. (^{13}C NMR data of DPP-2CN and DPP-12CN cannot be obtained due to the solubility issue.)

The nuclear magnetic resonance (NMR) spectra was measured on a Bruker AMX-400 (400 MHz) spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) was collected by using α-cyano-4-hydroxy-cinnamic acid (CCA) as the matrix under the reflector mode for data acquisition. The UV-Vis spectra was recorded on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.). Photoluminescence (PL) spectra was collected on a Hitachi F-7000 fluorescence spectrophotometer. Particle size distribution was measured by Malvern ZEN3600 Zetasizer. The crystallographic structures were analyzed with Rigaku CCD Saturn 724+ X-ray single crystal diffractometer.

CCDC 1544597 (DPP-1CN), 1544598 (DPP-2CN), 1544599 (DPP-12CN), 1544600 (DPP-1MF), 1544601 (DPP-12MF), 1544602 (DPP-1MF-2IP), 1544603 (DPP-1IP), 1544604 (DPP-12IP) and 1544605 (DPP-1IP-2MF) contain the supplementary crystallographic data for this paper. These data can be obtained freely from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

S2. Synthesis and characterization of 13 aryl-substituted pyrrolopyrrole-based Derivatives

The 13 aryl-substituted pyrrolopyrrole-based derivatives were synthesized by using the known methods.[1] The concrete steps are listed as follows：A mixture of aryl-benzaldehyde (20.0 mmol), aryl-phenylamine (20.0 mmol), p-methylbenzene sulfonic acid (2.0 mmol) and glacial acetic acid (30 mL) were stirred for 0.5 h at 90 °C. And then butane-2, 3-dione (10.0 mmol) was slowly added and the mixtures were stirred for 3 h at 90 °C. The reaction mixtures were then cooled to room temperature, and the target products can be obtained by filtration, washing and purified by column chromatography.

4,4'-(2,5-diphenylpyrrolo[3,2-b]pyrrole-1,4-diyl)dibenzonitrile (DPP-1CN): Yellow solid, yield 12.1%. ^{1}H NMR (400 MHz, DMSO, ppm): δ 7.91-7.89 (d, J=8.50 Hz, 4H, Ph-H), 7.45-7.43(d, J=8.50 Hz, 4H, Ph-H), 7.35-7.22 (m, 10H, Ph-H), 6.68(s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 143.46, 136.14, 133.25, 132.65, 131.03, 128.65, 128.35, 127.22, 125.01, 118.55, 108.90, 97.0. MADLDI- MS (m/z): calcd. for $C_{32}H_{20}N_4$: 460.17. Found: 460.3 (M^+).

4,4'-(1,4-diphenyl-1,4-dihydropyrrolo[3,2-b]pyrrole-2,5-diyl)dibenzonitrile (DPP-2CN): Yellow solid, yield 12.1%. ^{1}H NMR (400 MHz, DMSO, ppm): δ 7.71-7.69 (m, J=8.50 Hz 4H), 7.52-7.48(d, J=7.70 Hz, 4H, Ph-H), 7.39-7.31 (m, 10H, Ph-H), 6.48 (s, 2H). MADLDI-MS (m/z): calcd. for $C_{32}H_{20}N_4$: 460.17. Found: 460.2 (M^+). (^{13}C NMR is undesirability due to the bad solubility in high concentration.)

4,4',4'',4'''-(pyrrolo[3,2-b]pyrrole-1,2,4,5-tetrayl)tetrabenzonitrile (DPP-12CN): Yellow solid, yield 11.8%. ^{1}H NMR (400 MHz, DMSO, ppm): δ 7.96-7.94 (d, J=8.30 Hz, 4H, Ph-H), 7.78-7.76 (d, J=8.20 Hz, 4H, Ph-H), 7.49-7.47 (d, J=8.40 Hz, 4H, Ph-H), 7.40-7.38 (d, J=8.20 Hz, 4H, Ph-H), 6.93 (s, 2H). MADLDI-MS (m/z): calcd. for $C_{34}H_{18}N_6$: 510.16. Found: 510.2 (M^+). (^{13}C NMR is undesirability due to the bad solubility in high concentration.)

dimethyl 4,4'-(2,5-diphenylpyrrolo[3,2-b]pyrrole-1,4-diyl)dibenzoate (DPP-1MF): Pale yellow solid, yield 15.6%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04-8.02 (d, J=8.60 Hz, 4H, Ph-H), 7.34-7.32 (d, J=8.60 Hz, 4H, Ph-H), 7.28-7.21 (m, 13H, Ph-H), 6.48 (s, 2H), 3.92 (s, 6H). (Extra hydrogens are assigned to D-substituted solvents) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 166.53, 143.8, 136.07, 133.18, 131.29, 130.69, 128.43, 128.33, 127.04, 127.76, 124.41, 96.48, 52.15. MADLDI-MS (m/z): calcd. for $C_{34}H_{26}N_4O_2$: 526.19. Found: 526.30 (M^+).

dimethyl 4,4'-(1,4-diphenyl-1,4-dihydropyrrolo[3,2-b]pyrrole-2,5-diyl)dibenzoate (DPP-2MF): Yellow solid, yield 13.4%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.89-7.87 (d, J=8.40 Hz, 4H, Ph-H), 7.40-7.38 (d, J=7.8 Hz, 4H, Ph-H), 7.30-7.25 (m, 13H, Ph-H), 6.51 (s, 2H), 3.89 (s, 6H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 166.98, 139.68, 137.81, 135.60, 132.94, 129.55, 129.39, 127.52, 127.41, 126.25, 125.34, 95.92, 52.04. MADLDI-MS (m/z): calcd. for $C_{34}H_{26}N_4O_2$: 526.19. Found: 526.10 (M^+).

tetramethyl 4,4',4'',4'''-(pyrrolo[3,2-b]pyrrole-1,2,4,5-tetrayl)tetrabenzoate (DPP-12MF): Yellow solid, yield 12.6%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.07-8.05 (d, J=8.10 Hz, 4H, Ph-H), 7.93-7.91 (d, J=8.00 Hz, 4H, Ph-H), 7.33-7.26 (m, 9H, Ph-H), 6.56 (s, 2H), 3.93-3.90 (d, J=13.9 Hz, 12H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): 166.76, 166.33, 143.37, 137.27, 135.75, 132.25, 130.92, 129.74, 128.06, 127.71, 127.68, 124.61, 97.29, 52.23, 52.08. MADLDI-MS (m/z): calcd. for $C_{38}H_{30}N_2O_8$: 642.2. Found: 643.04 ($[M+H]^+$).

1,4-bis(4-isopropylphenyl)-2,5-diphenyl-1,4-dihydropyrrolo[3,2-b]pyrrole (DPP-1IP): White solid, yield 11.3%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31-7.21 (m, 19H, Ph-H), 6.46(s, 2H), 3.04-2.93 (hept, J=16.80 Hz, 2H), 1.34-1.32 (d, J=7.00 Hz, 12H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 146.17, 137.8, 135.75, 133.9, 131.67, 128.20, 128.08, 126.99, 125.99, 125.04, 94.68, 33.65, 24.01. MADLDI-MS (m/z): calcd. for $C_{36}H_{34}N_2$: 494.27. Found: 494.77 (M^+).

2,5-bis(4-isopropylphenyl)-1,4-diphenyl-1,4-dihydropyrrolo[3,2-b]pyrrole (DPP-2IP): White solid, yield 12.6%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31-7.09 (m, 21H), 6.39 (s, 2H), 2.88-2.83 (m, 2H), 1.22-1.24 (dd, J=0.79 and 6.93 Hz, 12H). (Extra hydrogens are assigned to D-substituted solvents). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): 146.77, 140.18, 135.72, 131.29, 131.17, 128.98, 128.06, 126.19, 125.43, 125.19, 94.54, 33.72, 23.91. MADLDI-MS (m/z): calcd for $C_{36}H_{34}N_2$: 494.27. Found: 494.2 (M^+).

1,2,4,5-tetrakis(4-isopropylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (DPP-12IP): White solid, yield 14.6%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26-7.07 (m, 18H, Ph-H), 6.36 (s, 2H), 2.92-2.86 (d,

J=24.3Hz, 4H), 1.26-1.24 (m, 24H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 146.56, 145.97, 137.95, 135.64, 131.42, 128.03, 126.91, 126.13, 125.01, 94.42, 33.74, 33.61, 24.02, 23.93. MADLDI-MS (m/z): calcd. for $C_{42}H_{46}N_2$: 578.37. Found: 578.87 (M^+).

dimethyl 4,4'-(2,5-bis(4-isopropylphenyl)pyrrolo[3,2-b]pyrrole-1,4-diyl)dibenzoate (DPP-1MF-2IP): Pale yellow solid, yield 13.6%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.88-7.86 (d, J=8.40 Hz, 4H, Ph-H), 7.28-7.18 (m, 13H), 6.48 (s, 2H), 3.88 (s, 6H), 2.98-2.91 (m, 2H), 1.29-1.27 (d, J=6.90 Hz, 12H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 167.03, 146.91, 138.02, 137.38, 135.56, 133.06, 129.47, 127.43, 127.29, 125.17, 95.64, 51.98, 33.69, 23.98. MADLDI-MS (m/z): calcd. for $C_{40}H_{38}N_2O_4$: 610.28. Found: 610.10 (M^+).

dimethyl 4,4'-(2,5-di-p-tolylpyrrolo[3,2-b]pyrrole-1,4-diyl)dibenzoate (DPP-1MF-2Me): Yellow solid, yield 14.2%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03-8.01 (d, J=8.20 Hz, 4H, Ph-H), 7.33-7.05 (m. 14H), 6.43 (s, 2H), 3.92 (s, 6H), 2.33(s, 6H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 166.59, 143.93, 130.64, 129.13, 128.26, 126.88, 124.37, 96.07, 51.13, 31.59. MADLDI-MS (m/z): calcd. for $C_{36}H_{30}N_2O_4$: 554.22. Found: 555.51 ($[M+H]^+$).

dimethyl 4,4'-(1,4-bis(4-isopropylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole-2,5-diyl)dibenzoate (DPP-1IP-2MF): Luminous yellow solid, yield 13.2%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04-8.02 (d, J=8.60 Hz, 4H, Ph-H), 7.34-7.32 (d, J=8.50 Hz, 4H, Ph-H), 7.15-7.10 (m, 8H, Ph-H), 6.44 (s, 2H), 3.93 (s, 6H), 2.90-2.86 (m, 2H), 1.25-1.24 (d, J=6.90 Hz, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 166.63, 147.50, 143.95, 130.63, 128.22, 126.84, 126.48, 124.36, 96.20, 52.14, 33.77, 23.90. MADLDI-MS (m/z): calcd. for $C_{40}H_{38}N_2O_4$: 610.28. Found: 611.44 ($[M+H]^+$).

dimethyl 4,4'-(1,4-bis(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole-2,5-diyl)dibenzoate (DPP-1CN-2MF): Yellow solid, yield 16.5%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.96-7.94 (d, J=8.00 Hz, 4H, Ph-H), 7.69-7.67 (d, J=8.10 Hz, 4H, Ph-H), 7.36-7.34 (m, 4H, Ph-H), 7.26-7.3425 (m, 10H), Ph-H 6.56 (s, 2H), 3.92 (s, 6H). (Extra hydrogens are assigned to D-substituted solvents.) ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 166.64, 143.08, 136.74, 135.80, 133.49, 132.24, 129.94, 128.53, 127.79, 125.23, 118.26, 109.63, 97.85, 52.23. MADLDI-MS (m/z): calcd. For $C_{40}H_{38}N_2O_4$: 576.18. Found: 576.42 (M^+).

S3. Supplementary spectra data

Table S1 Spectroscopic parameters of 13 pyrrolo[3,2-b]pyrrole-based derivatives. (THF, 10^{-5} M)

Compounds	$\lambda_{max\ abs}$ nm	$\lambda_{onset\ abs}$ nm	λ_{em} nm	Stokes shift cm^{-1}	molar abs coeff. ε_{max} $M^{-1}\,cm^{-1}$
DPP-1CN	321	407	500	11100	51000
DPP-2CN	402	440	455	2900	41000
DPP-12CN	390	432	462	4000	27000
DPP-1MF	322	405	504	11200	52000
DPP-2MF	402	443	469	3600	39000
DPP-12MF	397	438	466	3700	45000
DPP-1IP	351	386	419	4600	71000
DPP-2IP	347	388	419	5000	21000
DPP-12IP	352	391	423	4800	40000
DPP-1MF-2IP	323	409	522	11800	85000
DPP-1MF-2Me	322	413	519	11800	85000
DPP-1CN-2MF	396	436	471	4000	29000
DPP-1IP-2MF	402	445	464	3300	60000

Table S2 The △Eg, solid emission, dihedral angles ψ1 and ψ2, AIE/ACQ properties of 13 pyrrolo[3,2-b]pyrrole-based derivatives.

Compounds	△Eg (eV)	λ_{em}, nm (solid)	ψ1	ψ2	AIE/ACQ
DPP-1CN	3.51	472	36.3°	43.4°	AIE
DPP-2CN	3.39	494	56.6°	34.2°	ACQ
DPP-12CN	3.42	498	56.2°	32.8°	ACQ
DPP-1MF	3.45	458	33.6°	56.2°	AIE
DPP-2MF	3.27	497			ACQ (Weak AIE)
DPP-12MF	3.29	492	54.6°(48.9°)	31.3°(34.4°)	ACQ (Weak AIE)
DPP-1IP	3.85	434	55.7°	34.1°	ACQ
DPP-2IP	3.88	423			ACQ
DPP-12IP	3.87	446	47.0°	29.4°	ACQ
DPP-1MF-2IP	3.32	479	51.0°/49.4°	38.9°/27.4°	AIE
DPP-1MF-2Me	3.32	482			AIE
DPP-1CN-2MF	3.37	482			ACQ (Weak AIE)
DPP-1IP-2MF	3.25	497	62.9°	23.7°	ACQ

(△Eg obtained from calculated results between HOMO and LUMO energy, ψ1: the dihedral angles between 1,4-position phenyl and pyrrolo[3,2-b]pyrrole core; ψ2: the dihedral angles between 2,5- position phenyl and pyrrolo[3,2-b]pyrrole core.)

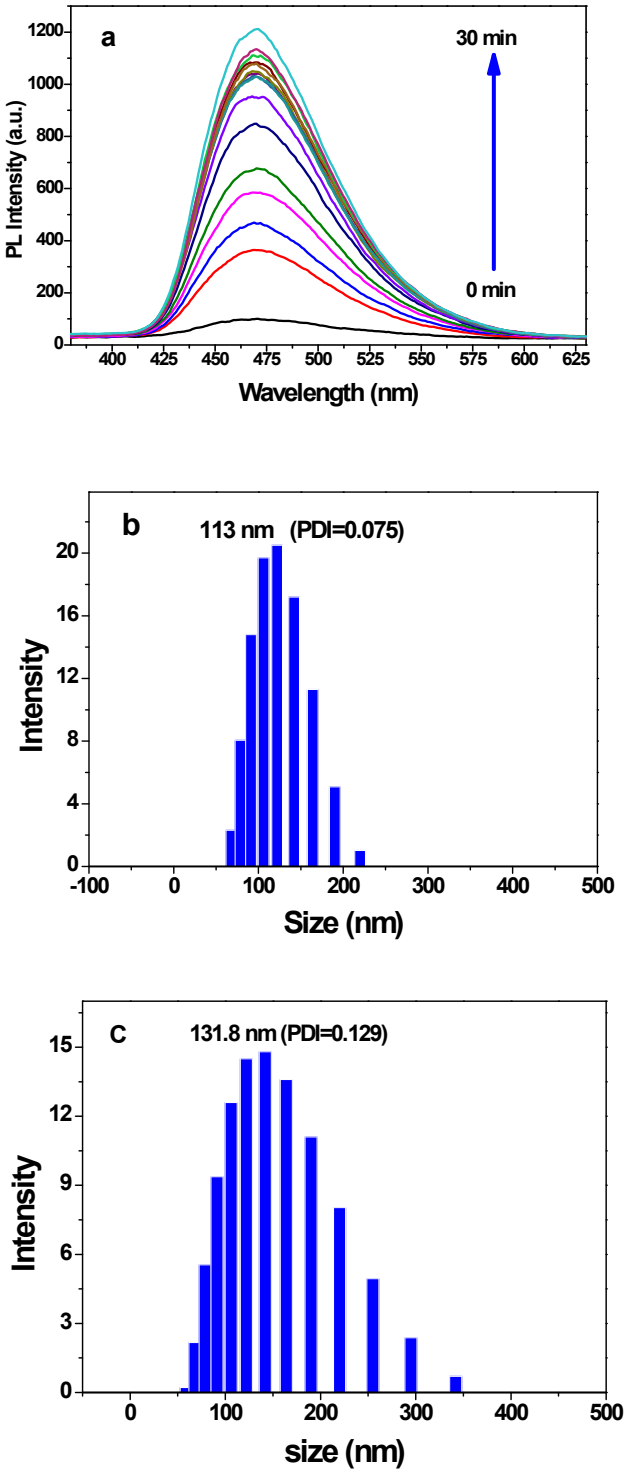

Fig.S1 Emission intensity (a) with the increase of time and aggregated particle sizes for 2min (b) and 30 min (c) of DPP-1CN monitored in THF/water mixture with f_w = 70%.

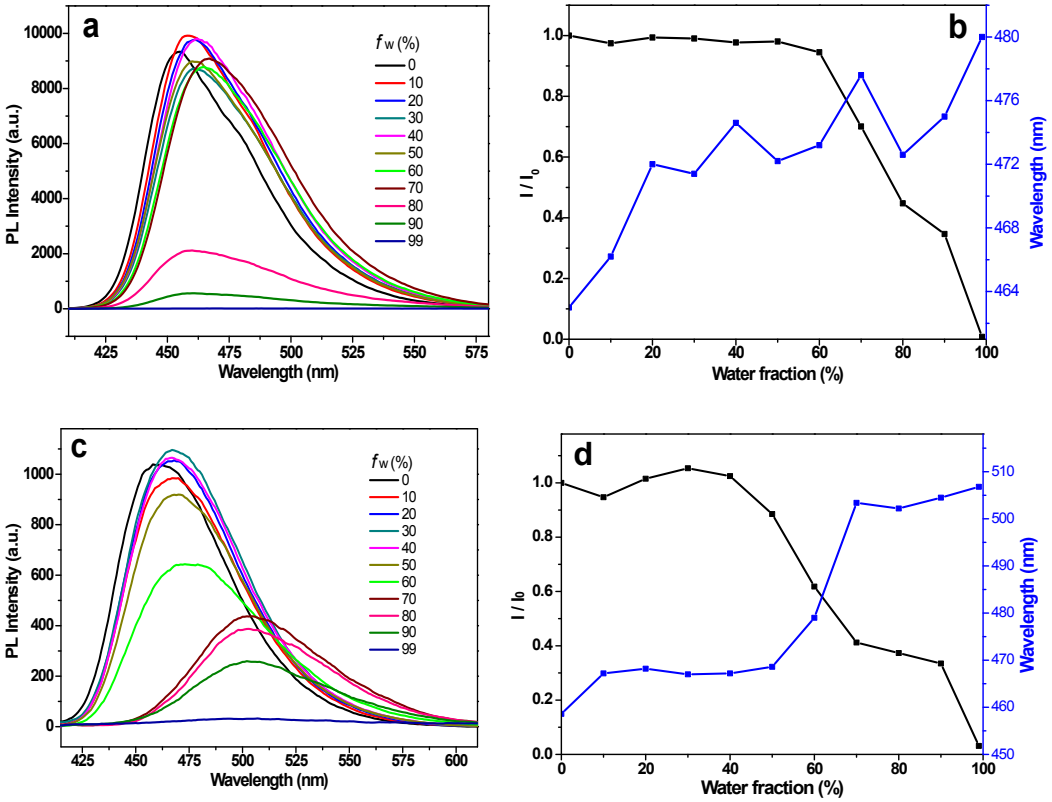

Fig. S2 Fluorescence spectra of DPP-2CN (a) and DPP-12CN (c) in THF/water mixtures with different water fractions. Plots of ratio between maximum PL intensity and the initial PL intensity of DPP-2CN (b) and DPP-12CN (d) and emission wavelength vs. water fraction. (10^{-5} M, λex = 400 nm)

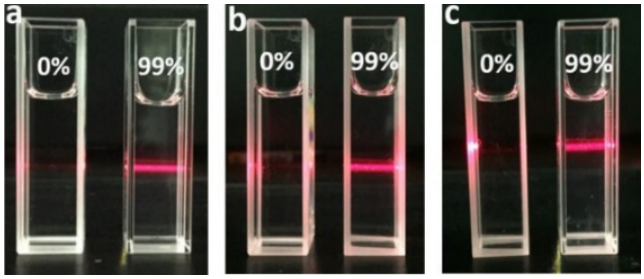

Fig. S3 The Tyndall effect of DPP-1MF (a), DPP-1MF-2Me (b) and DPP-1MF-2IP (c) in THF solution with f_w = 0 (left) and 99% (right).

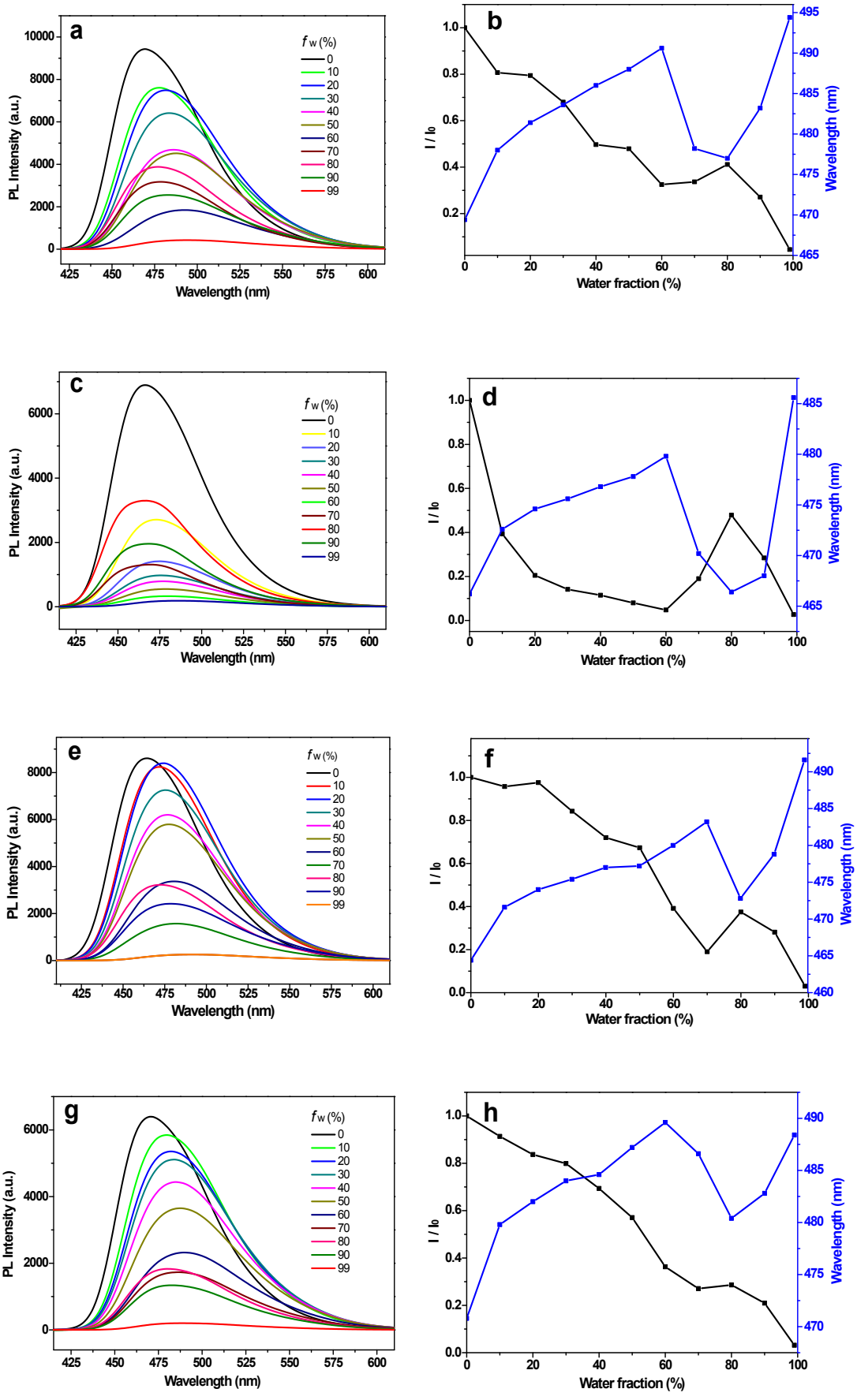
a
PL Intensity (a.u.)
Wavelength (nm)
fw (%)
0
10
20
30
40
50
60
70
80
90
99
b
I / I0
Wavelength (nm)
Water fraction (%)
c
PL Intensity (a.u.)
Wavelength (nm)
fw (%)
d
I / I0
Wavelength (nm)
Water fraction (%)
e
PL Intensity (a.u.)
Wavelength (nm)
fw (%)
f
I / I0
Wavelength (nm)
Water fraction (%)
g
PL Intensity (a.u.)
Wavelength (nm)
fw (%)
h
I / I0
Wavelength (nm)
Water fraction (%)

Fig. S4 Fluorescence spectra of DPP-2MF (a), DPP-12MF (c), DPP-1CN-2MF (e) and DPP-1IP-2MF (g)(10^{-5} M, λex = 400 nm) in THF/water mixtures with different water fractions. Plots of ratio between maximum PL intensity and the initial PL intensity of DPP-2MF (b), DPP-12MF (d), DPP-1CN-2MF (f) and DPP-1IP-2MF (h) and emission wavelength vs. water fraction. (10^{-5} M, λex = 400 nm)

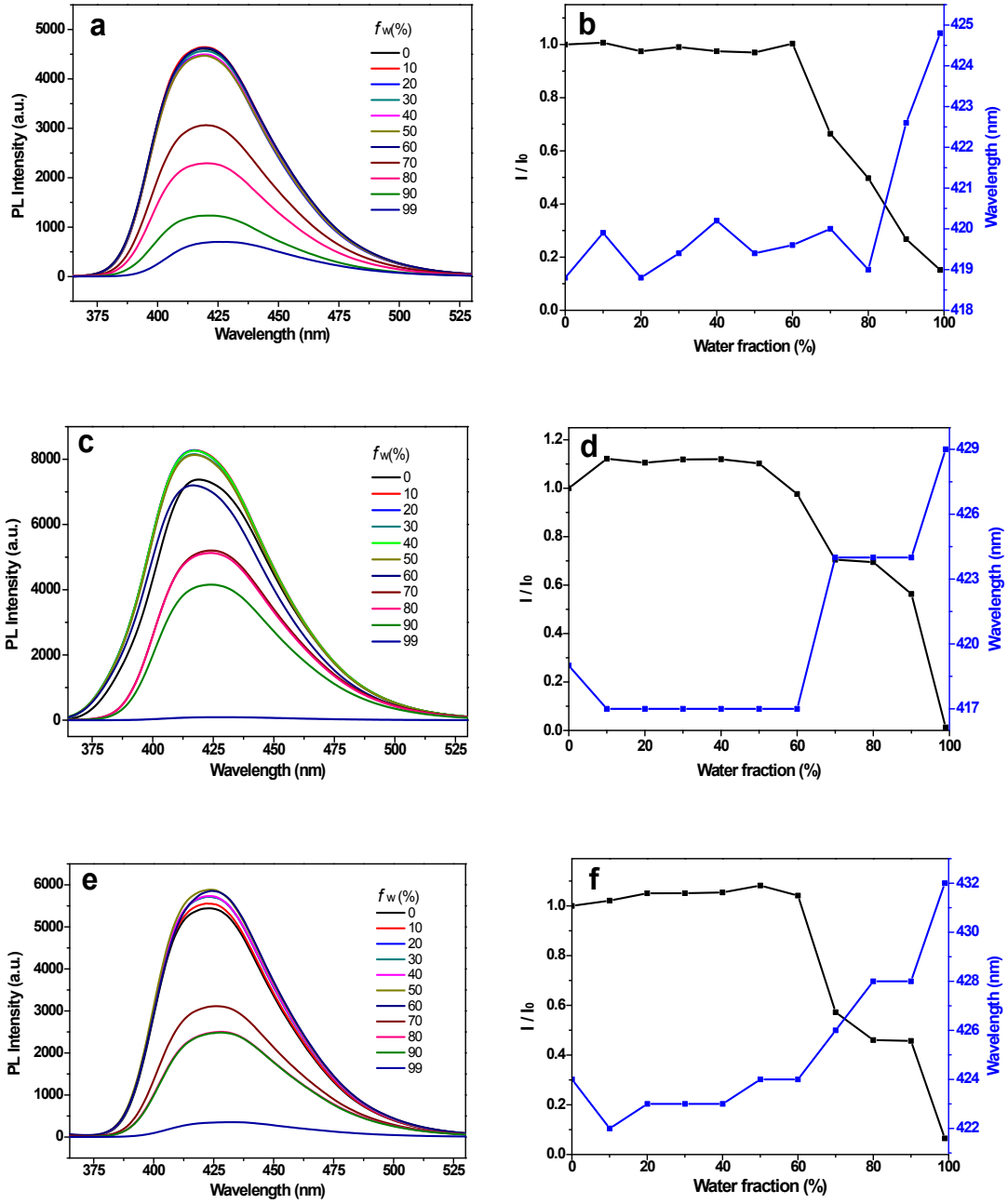

Fig. S5 Fluorescence spectra of DPP-1IP (a), DPP-2IP (c) and DPP-12IP (e) in THF/water mixtures with different water fractions. Plots of ratio between maximum PL intensity and the initial PL intensity of DPP-1IP (b), DPP-2IP (d) and DPP-12IP (f) and emission wavelength vs. water fraction. (10^{-5} M, λex = 350 nm)

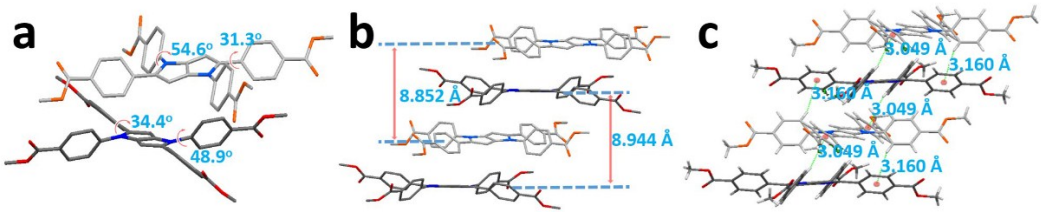

Fig. S6 The crystal structure (a), packing patterns (b) and intermolecular interactions (c) of DPP-12MF.

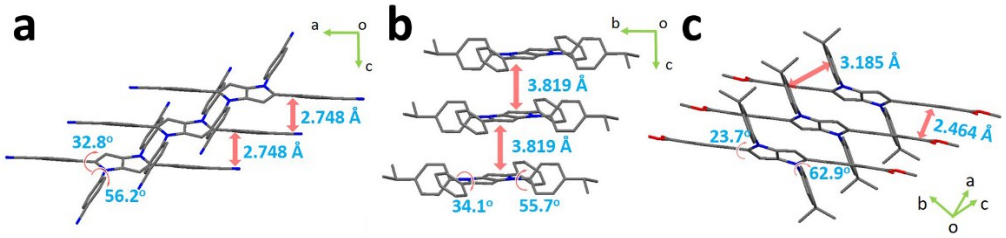

Fig. S7 The crystal structure, packing patterns and intermolecular interactions of DPP-12CN (a), DPP-1IP (b) and DPP-1IP-2MF (c).

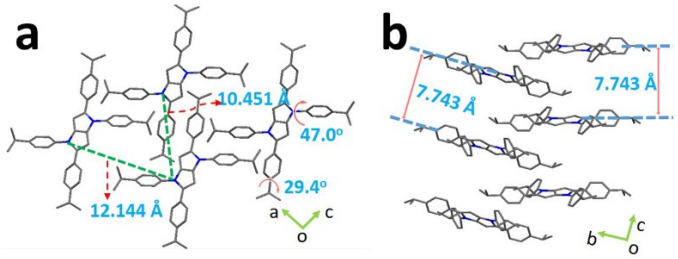

Fig. S8 The crystal structure (a) and packing patterns (b) of DPP-12IP.

S4. Reference

1. M. Krzeszewski, B. Thorsted, J. Brewer and D. T. Gryko, *J. Org. Chem.*, 2014, **79**, 3119-3128.