Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Pyrene-based Aggregation-induced Emission Luminogens (AIEgen): Structure Correlated with Particle Size Distribution and Mechanochromism

Xing Feng,[*ab]‡ Jun Zhang,[b]‡ Zhen Hu,[a] Qingsong Wang,[a] Md. Monarul Islam,[a] Jen-Shyang Ni,[c] Mark R. J. Elsegood,[d] Jacky W. Y. Lam,[b] Erjun Zhou,[*e] Ben Zhong Tang[*bc]

[a.] *Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, School of Material and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China. *E-mail: hyxhn@sina.com.*

[b.] *Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. *E-mail: tangbenz@ust.hk.*

[c.] *HKUST-Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Shenzhen 518057, China*

[d.] *Chemistry Department, Loughborough University, Loughborough LE11 3TU, UK.*

[e.] *CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China. *E-mail: zhouej@nanoctr.cn*

1. NMR spectrum

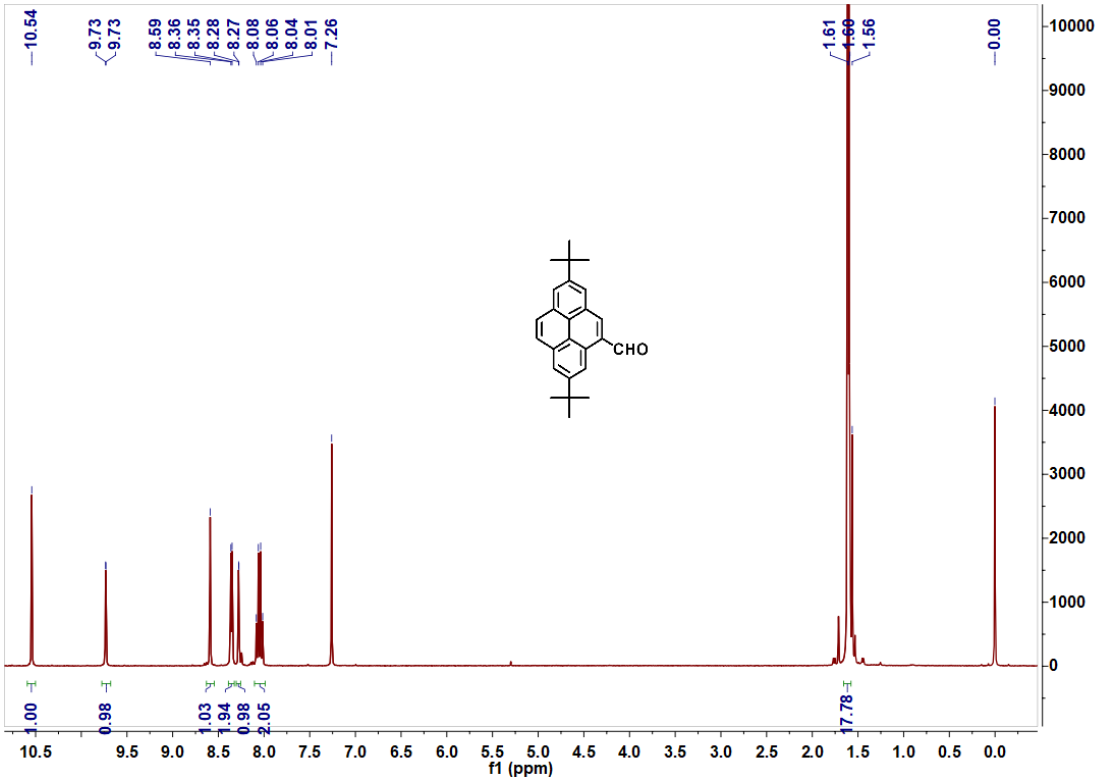


Figure S1. ^{1}H NMR spectrum of **2,7-di-tert-butylpyrene-4-carbaldehyde** (400 MHz, $CDCl_3$, 293 K).

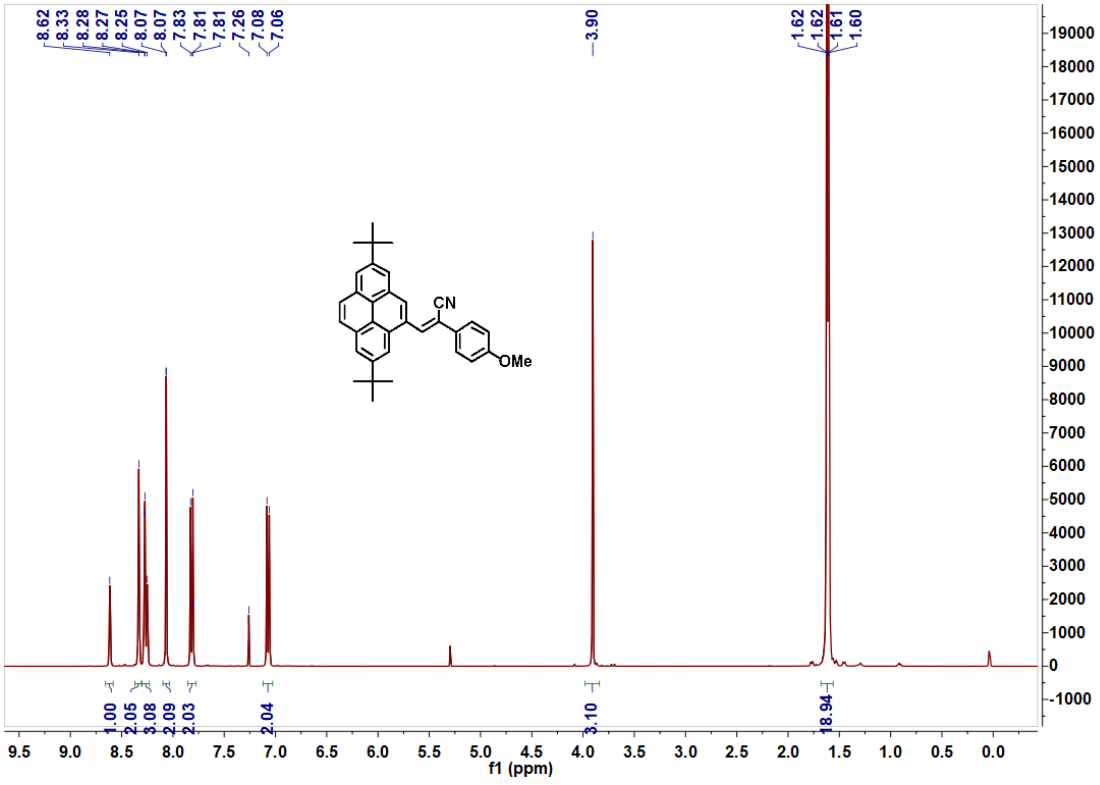


Figure S2. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$, 293 K).

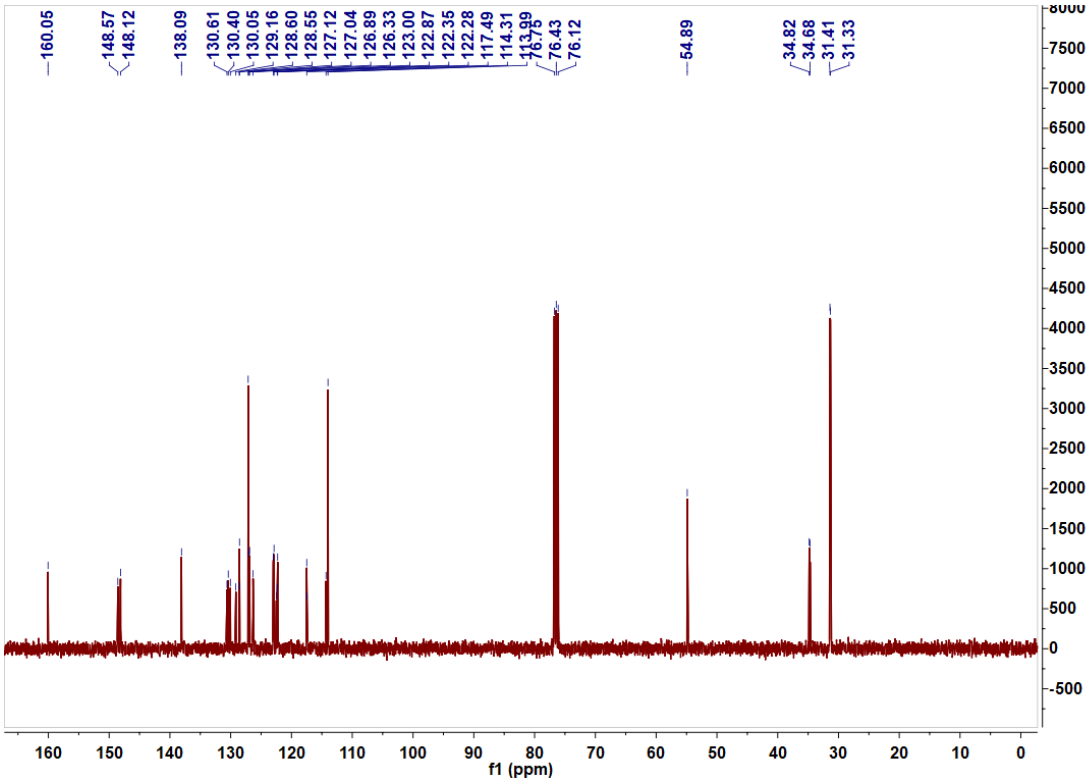


Figure S3. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$, 293 K).

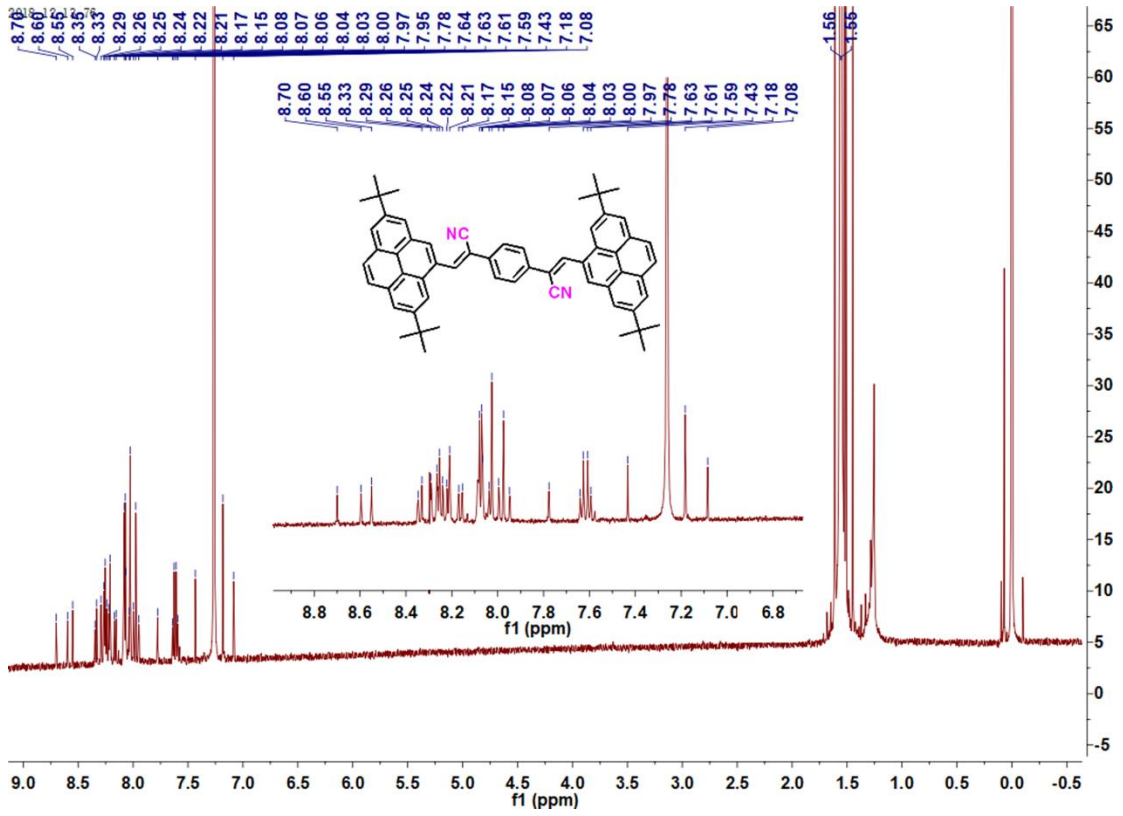


Figure S4. ^{1}H NMR spectrum of **3** (600 MHz, $CDCl_3$, 293 K).

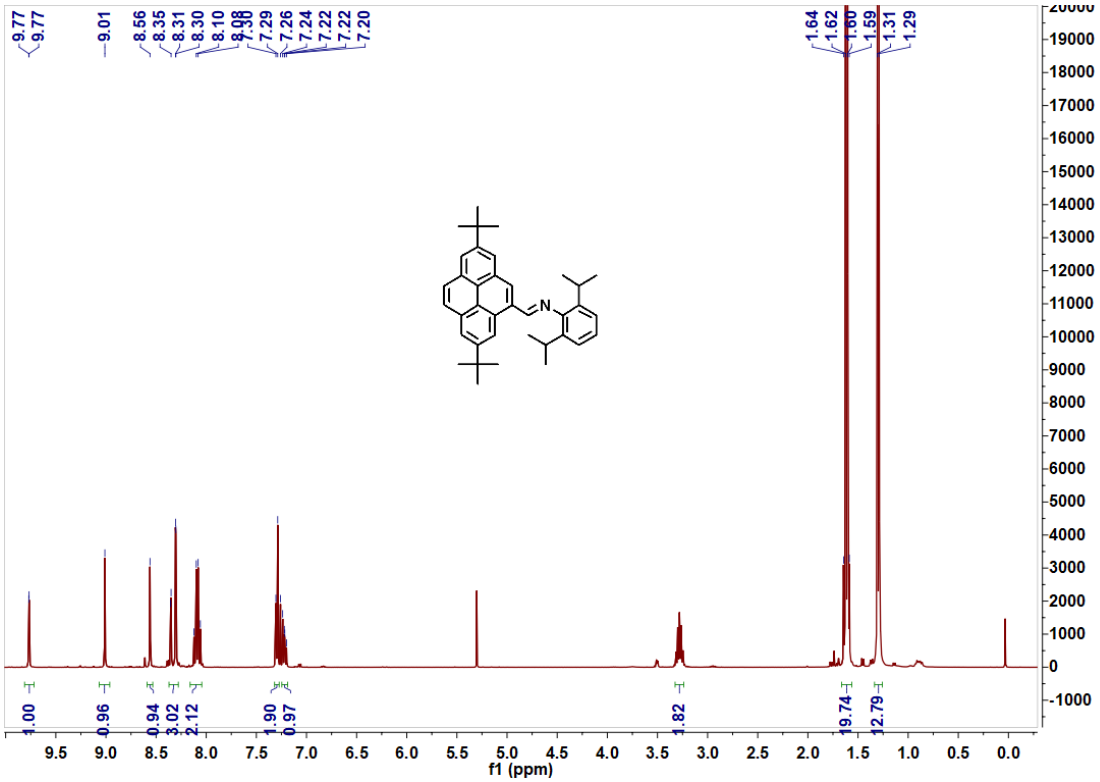


Figure S5. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$, 293 K).

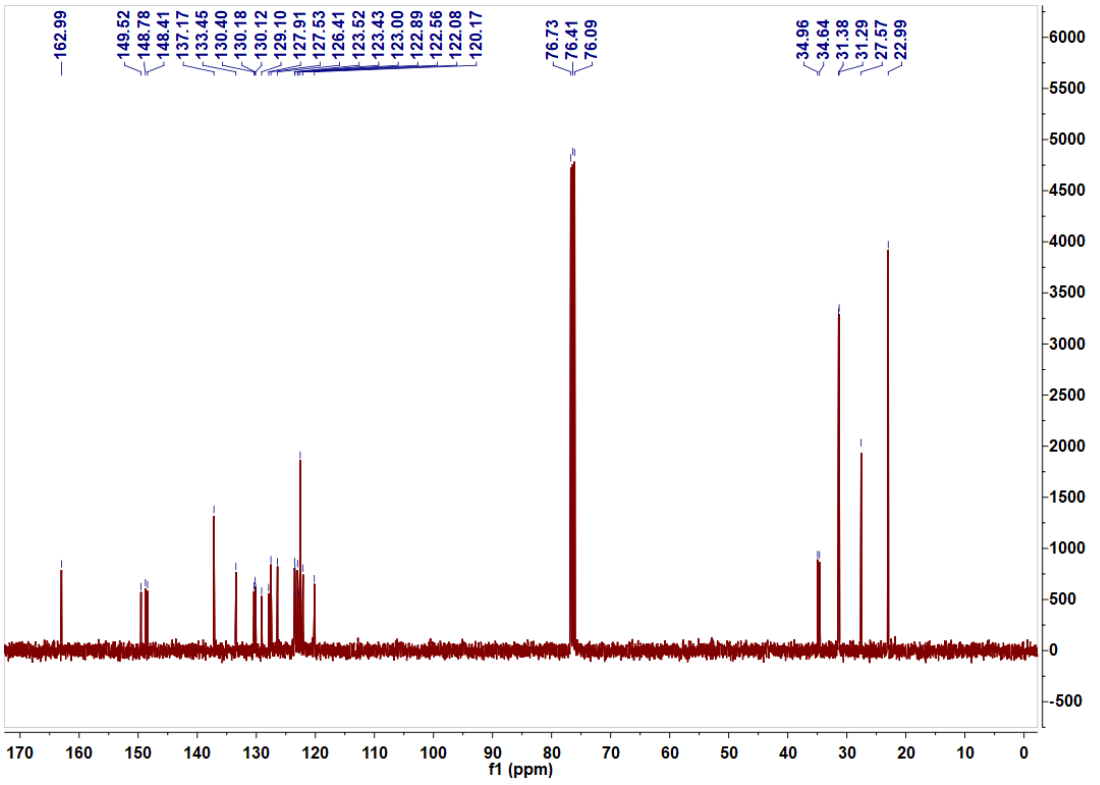


Figure S6. ^{13}C NMR spectrum of **4** (125 MHz, $CDCl_3$, 293 K).

2. Mass spectrum

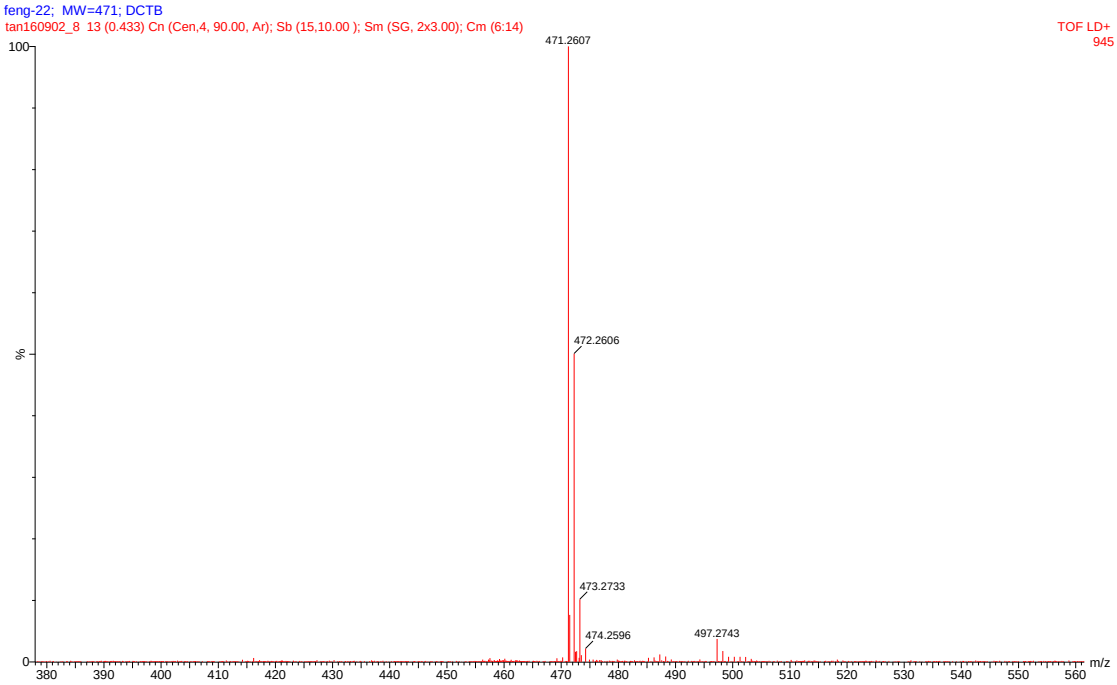


Figure S7. Mass spectrum of **2**.

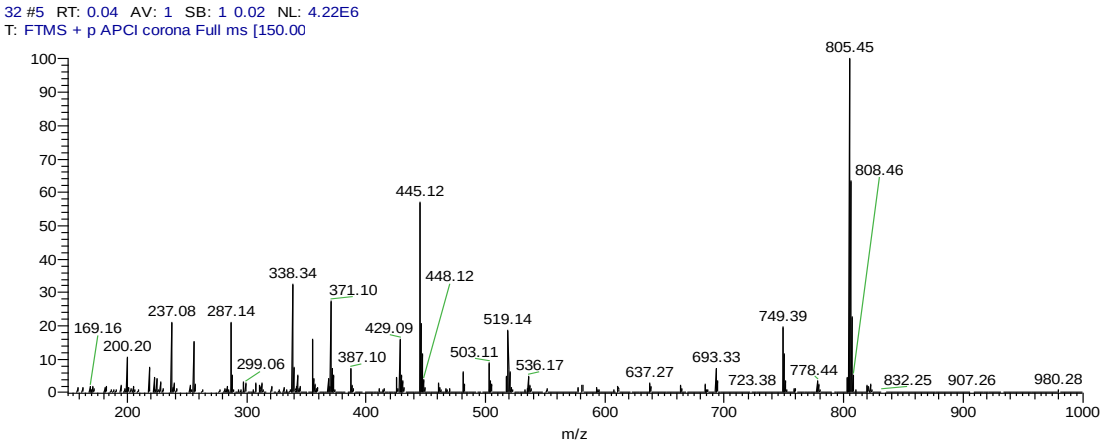


Figure S8. Mass spectrum of **3**.

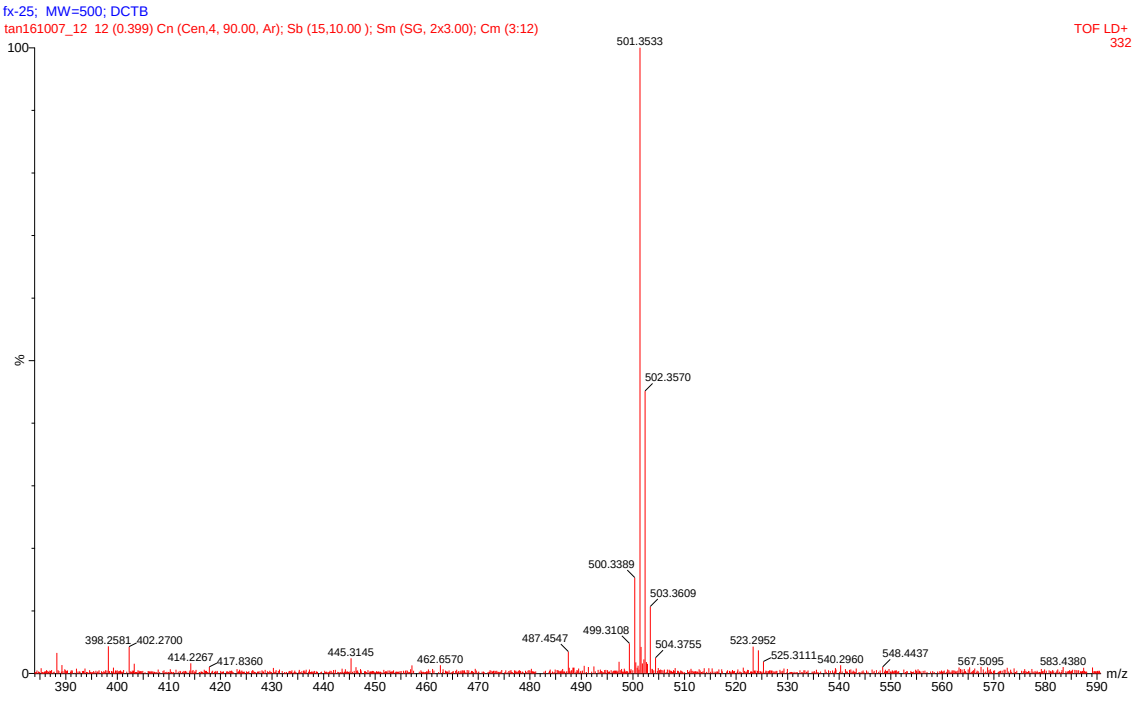


Figure S9. Mass spectrum of **4**.

3. Thermal stability

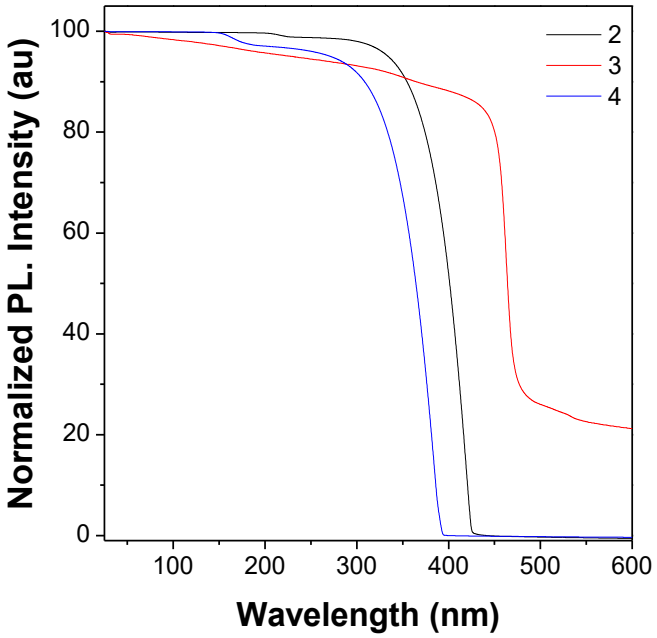


Figure S10. TGA thermograms of **2-4** under nitrogenat a heating rate of 10 ºC/min.

4. Photophysical properties

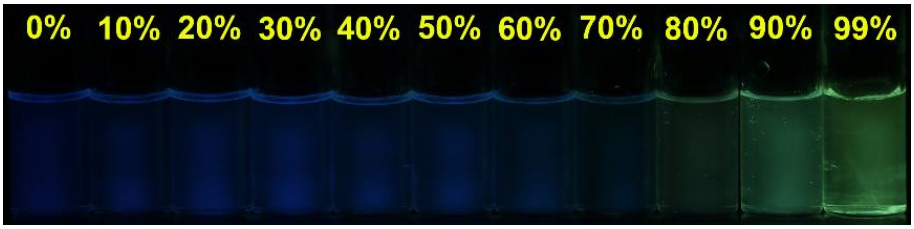
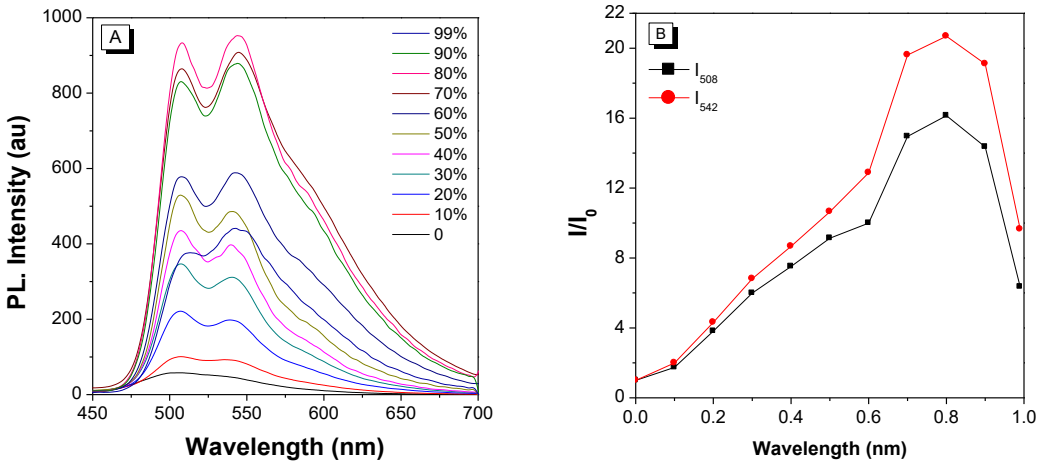


Figure S11. Fluorescent photographs of **2** in THF/ water mixtures from f_w = 0 to 99% taken under UV illumination (λ_{ex} =365nm).



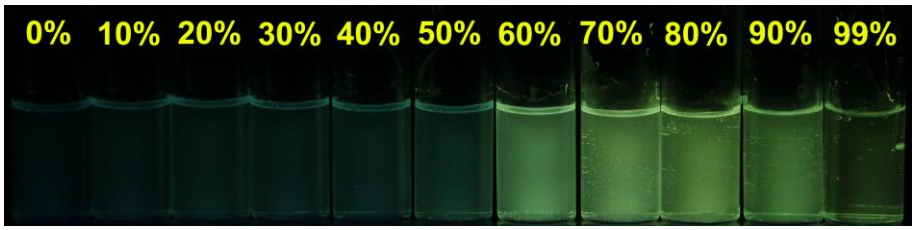


Figure S12. (A) PL spectra of **3** in THF/water mixture with different water fractions (f_w). (B) Plot of I/I_0 versus the composition of THF/water mixture of **3**, where I_0 is the PL intensity in pure THF solution at 508 and 542 nm. Down) fluorescent photographs of **Py-TriPE** in THF/ water mixtures (f_w = 0 and 99%) taken under UV illumination (λ_{ex} = 365 nm).

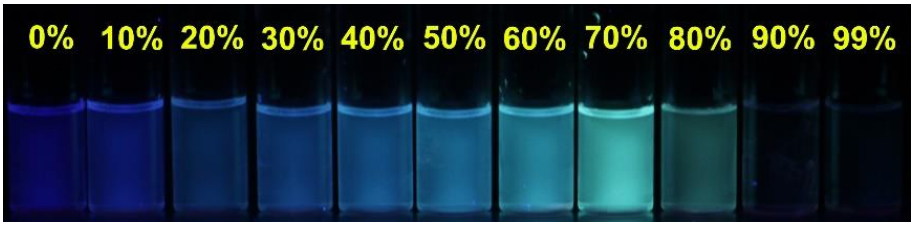


Figure S13. Fluorescent photographs of **4** in THF/ water mixtures from f_w = 0, to 99% taken under UV illumination (λ_{ex} =365nm).

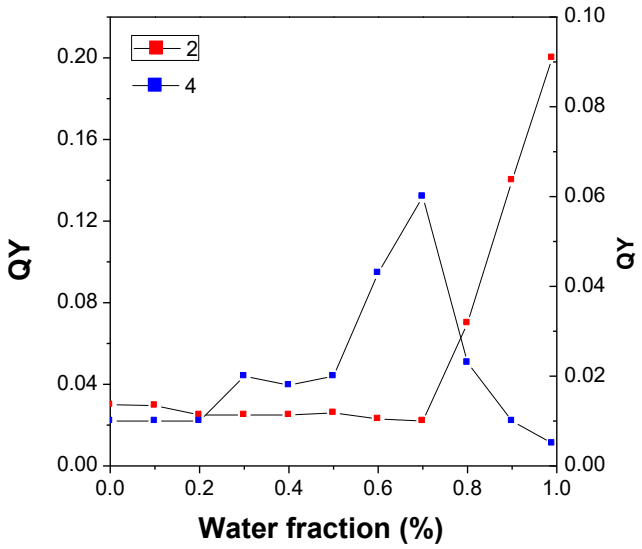


Figure S14. Fluorescent quantum yield of **2** and **4** in THF/ water mixtures from f_w = 0, to 99%.

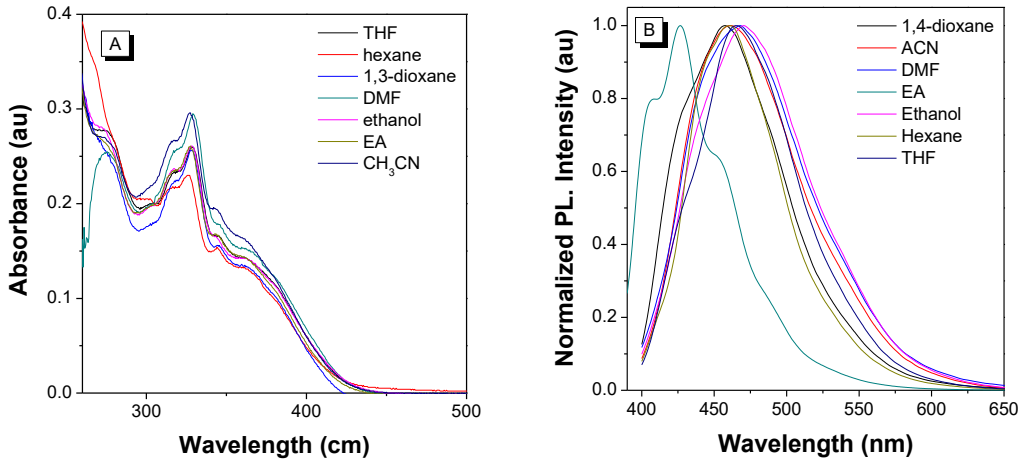


Figure S15. UV absorption and Fluorescence spectra of the compound **2**recorded in seven solvents at ~10^{-5} M and 25 °C.

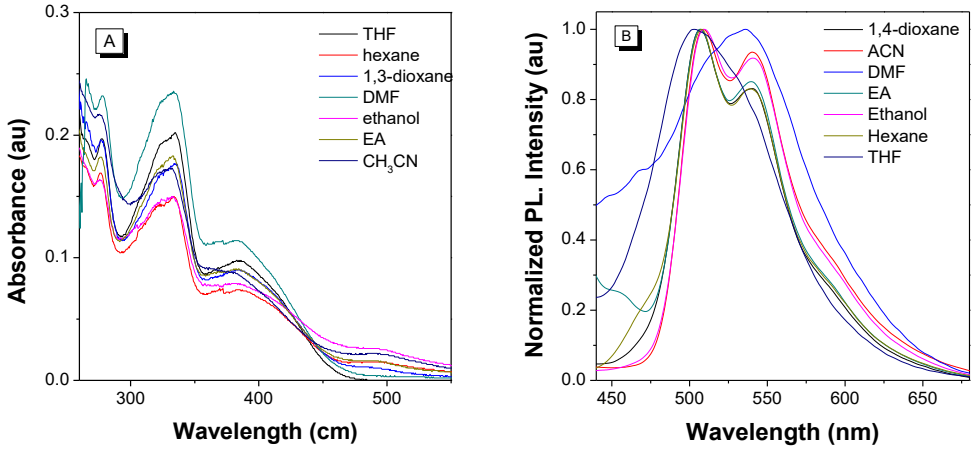


Figure S16. UV absorption and Fluorescence spectra of the compound **3**recorded in seven solvents at ~10^{-5} M and 25 °C.

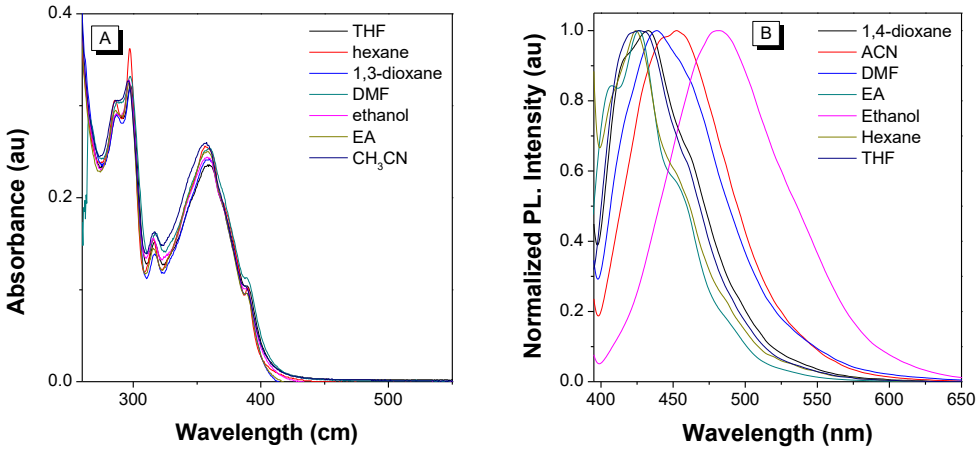


Figure S17. UV absorption and Fluorescence spectra of the compound **4**recorded in seven solvents at ~10^{-5} M and 25 °C.

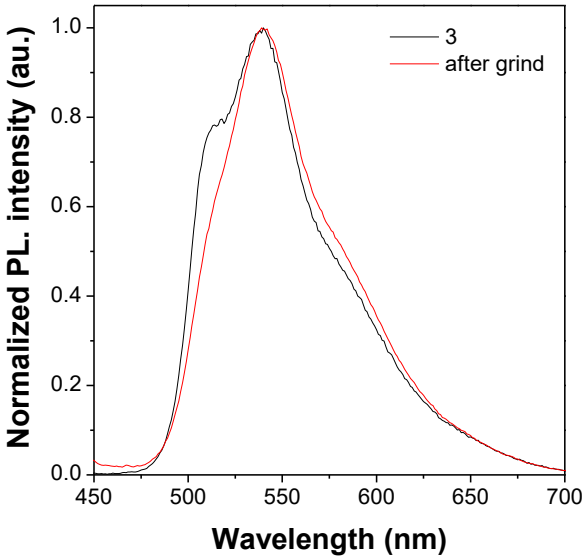


Figure S18. PL spectra of **3** in solid state.

DLS analysis

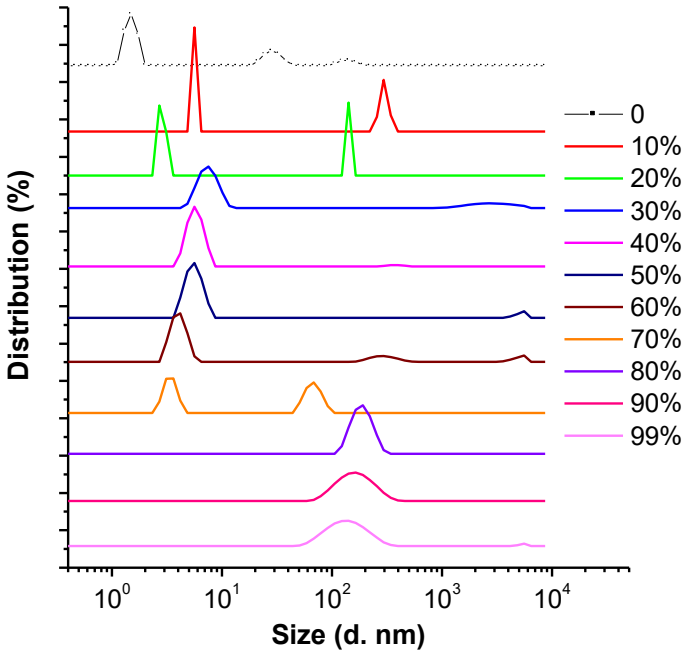


Figure S19. DLS study on nanoparticle size distribution of **2** in THF/water mixture with different water fractions (f_w).

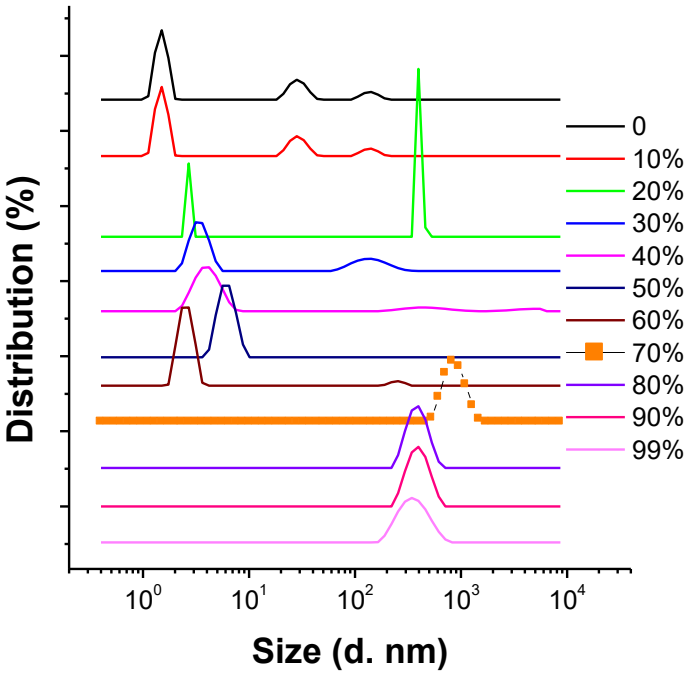


Figure S20. DLS study on nanoparticle size distribution of **4** in THF/water mixture with different water fractions (f_w).

Morphology analysis

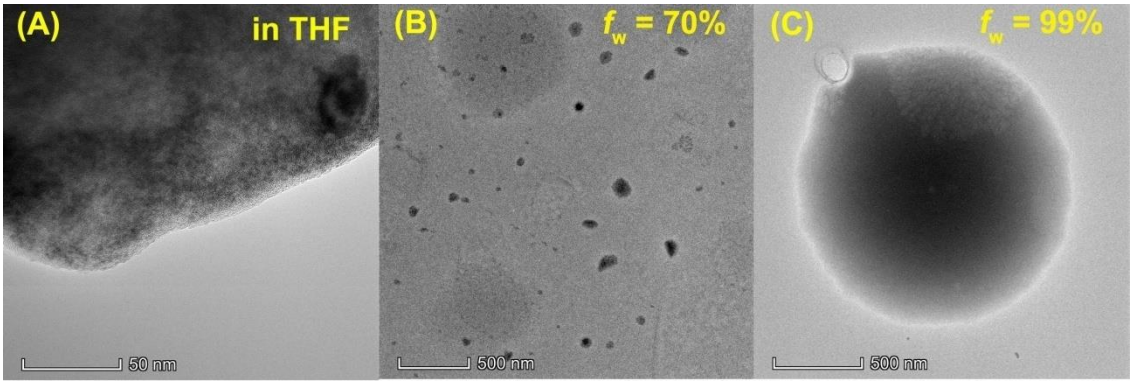


Figure S21. TEM image of **2** (A) in THF, (B) in 70 % water and (C) in water fraction f_w = 99%.

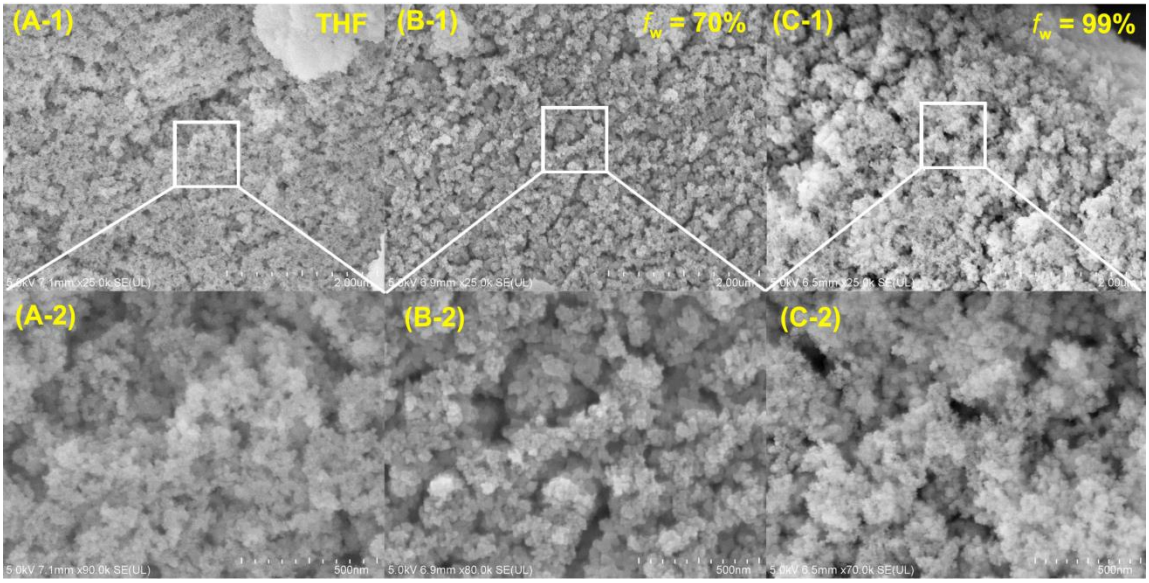


Figure S22. FE-SEM image of self-assembled morphology of **3** (A) in THF; (B) in water fraction f_w = 70%; (C) in water fraction f_w = 99%, (A-2, B-2 and C-2) SEM image of the extending regions.

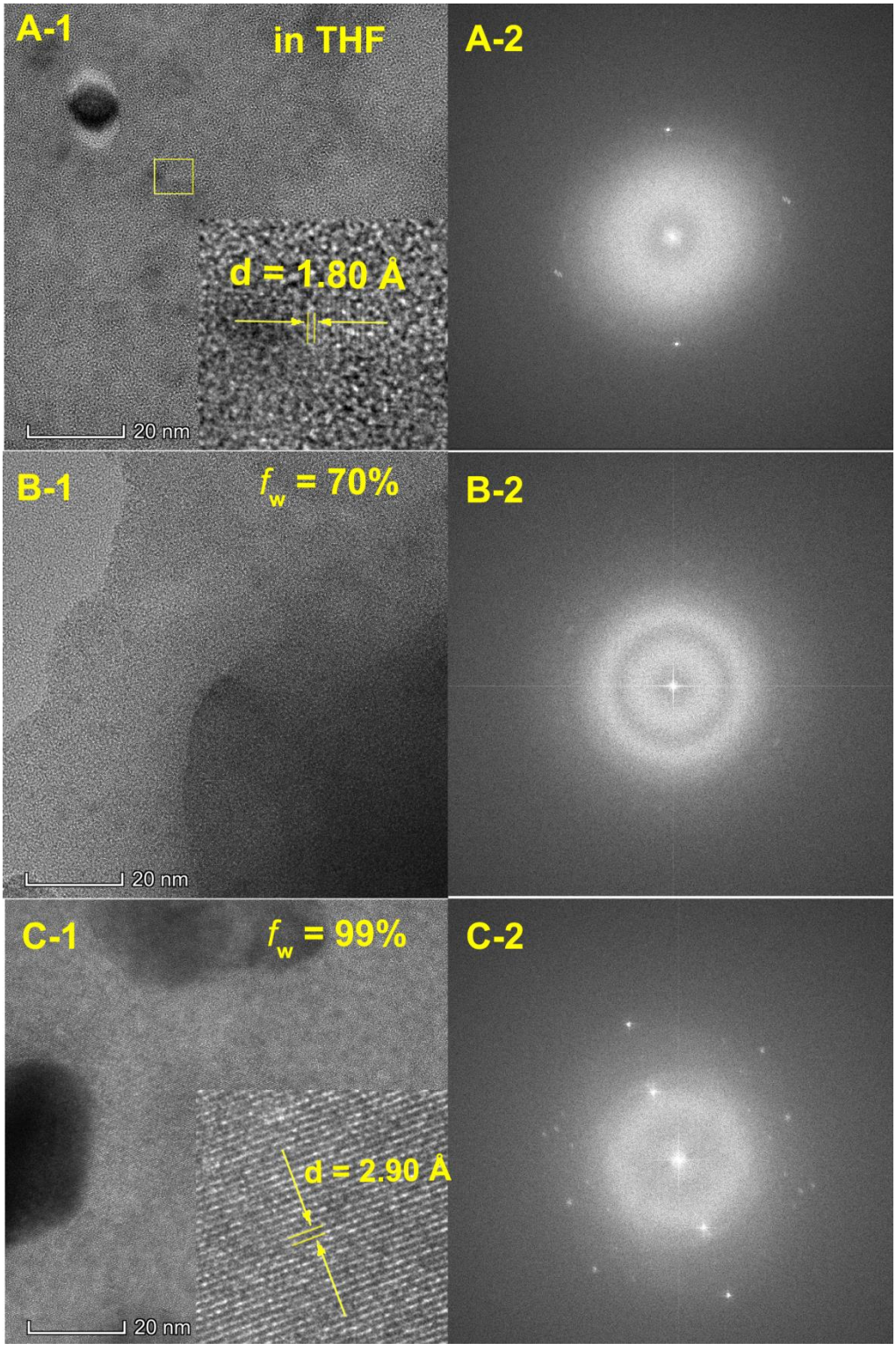


Figure S23. high-resolution TEM images of self-assembled morphology of **3** (A) in THF; (B) in water fraction f_w = 70%; (C) in water fraction f_w = 99%, Insert: HR-TEM image taken from the yellow square and the corresponding (A-2, B-2 and C-2) selected-area electron diffraction (SAED) pattern.

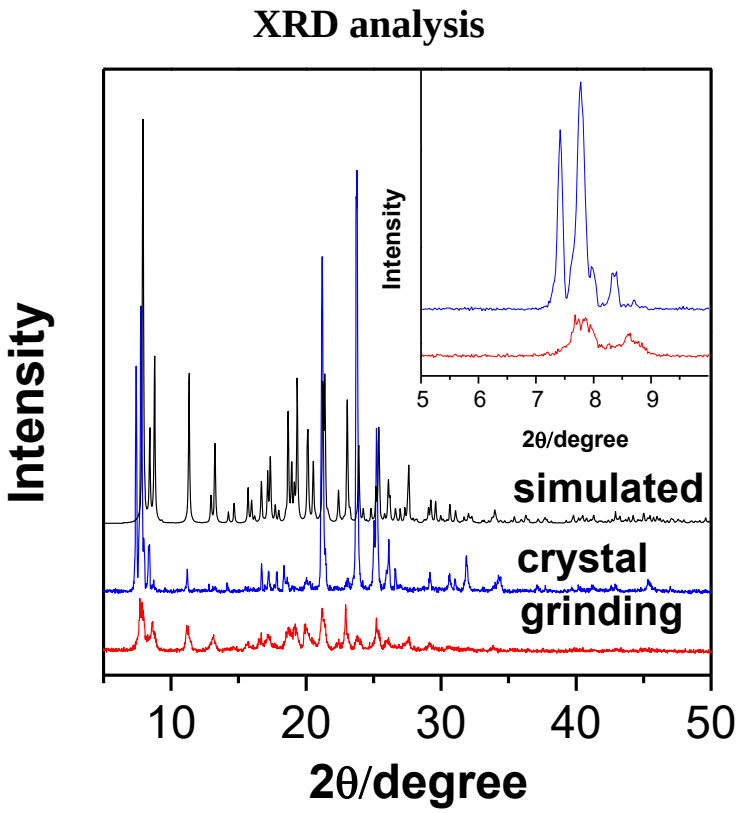


Figure 24. Wide angle XRD diffractograms of **2** in different state

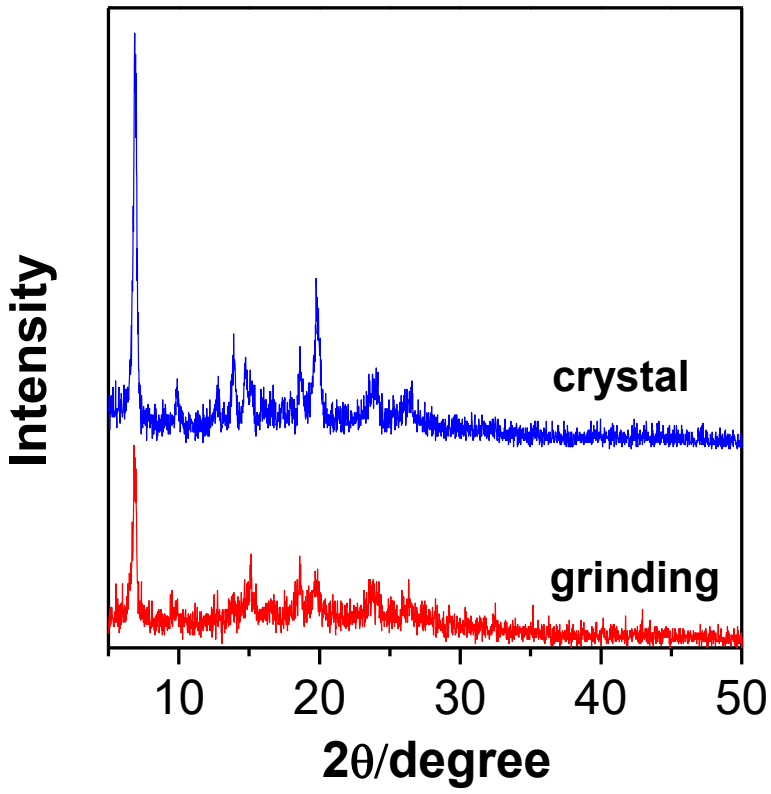


Figure 25. Wide angle XRD diffractograms of **3** in different state

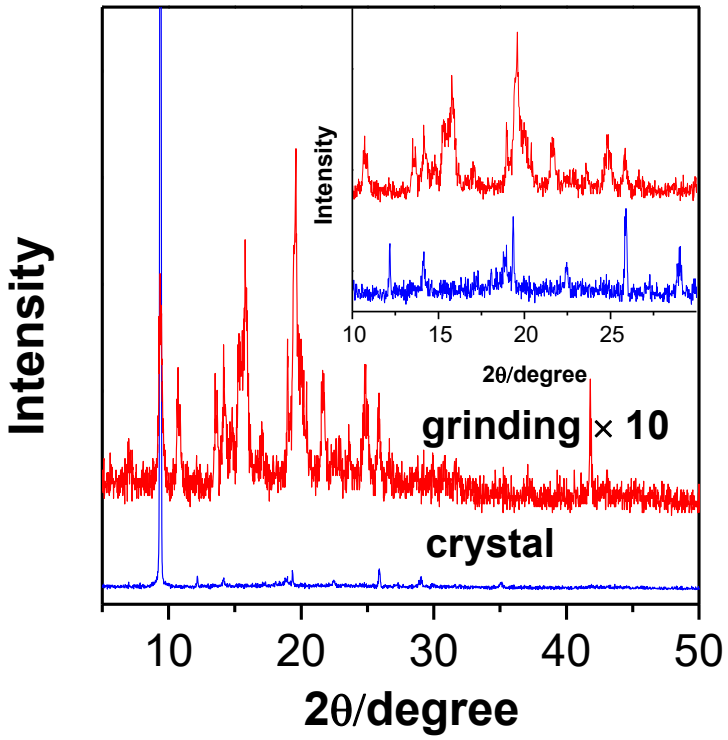


Figure 26. Wide angle XRD diffractograms of **4** in different state

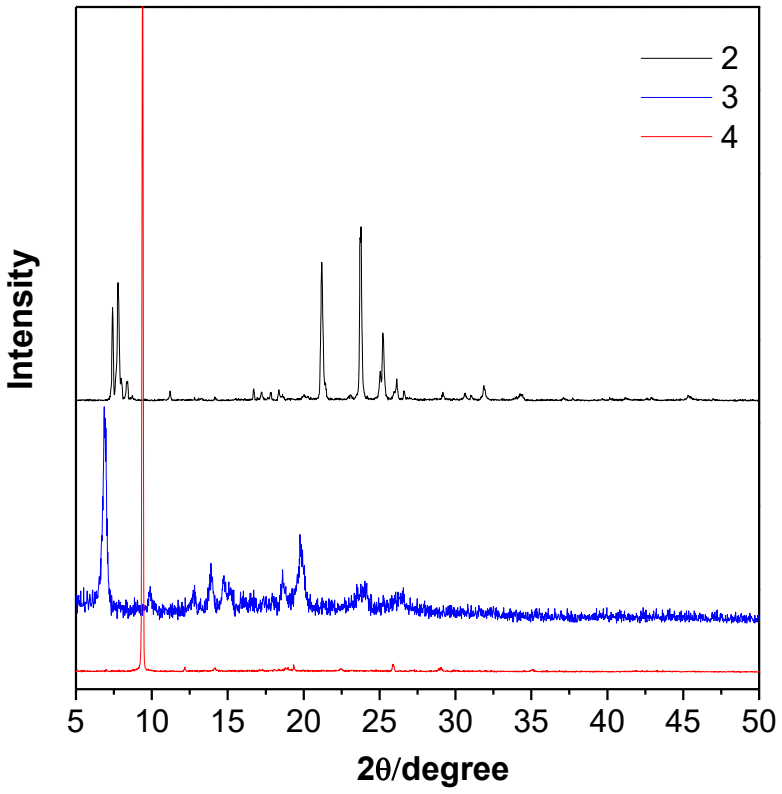


Figure 27. Wide angle XRD diffractograms of **2-4.**

Table S1 Summarized of XRD parameter **2**

simulated[a]		**crystal**		**Grind**		**Heavy grind**	
2θ (°)	FWHM (°)	**2θ**(°)	FWHM (°)	**2θ**(°)	FWHM (°)	**2θ**(°)	FWHM (°)
7.906	0.173	7.773	0.152	7.805	0.419	7.806	0.371
8.772	0.165	8.700	0.061	8.605	0.449	8.578	0.499
11.322	0.179	11.183	0.072	11.235	0.335	11.221	0.340
12.947	0.121	12.803	0.034	13.091	0.394	13.092	0.368
15.685	0.124	15.701	0.034	15.667	0.303	15.707	0.454
17.132	0.114	17.215	0.096	17.197	0.462	17.138	0.825
18.646	0.256	18.578	0.187	18.702	0.444	18.608	0.449
20.097	0.230	20.033	0.347	20.054	0.445	20.092	0.744
20.521	0.181	21.184	0.150	21.219	0.330	21.203	0.390

[a] fitted based on crystal

Table S2 Summarized of XRD parameter **2**

d-spacings (Å) / h k l	simulated[a]	crystal	Grind	Heavy grind
0 2 0	11.165	11.157	11.177	11.113
1 0 0	10.497	10.512	10.544	10.516
0 1 1	10.070	10.129	10.069	10.107
1 1 0	9.499	9.509	9.536	9.506
0 2 1	7.936	7.962	7.939	7.940
1 -1 -1	7.801	7.847	7.802	7.820
1 2 0	7.648	7.651	7.669	7.638
1 1 1	6.828	6.843	6.853	6.850
1 -2 -1	6.674	6.701	6.677	6.678
0 3 1	6.213	6.224	6.217	6.203
1 3 0	6.072	6.071	6.085	6.056
1 2 1	6.034	6.043	6.053	6.043
0 0 2	5.641	5.683	5.639	5.674
0 4 0	5.582	5.578	5.588	5.556
1 -3 -1	5.549	5.563	5.552	5.543
0 1 2	5.469	5.507	5.467	5.497

[a] fitted based on crystal

Table S3. Summarized of crystal parameter **4.**

Compound	**simulated[a]**	**crystal[a]**	**Grind[a]**
Crystal system	orthorhombic	orthorhombic	orthorhombic
A [Å]	12.9755	9.6250	13.0454
B [Å]	36.6305	37.7916	36.9103
C [Å]	12.4367	13.0498	12.6440
Crystallinity (%)	98.86	78.38	96.95
2θ (°)	9.6435	9.3767	9.3907
FWHM (°)	0.0838	0.0725	0.2691

[a] fitted based on crystal

Table S4 Summarized of XRD parameter **4**

simulated[a]		**crystal**		**Grind**	
2θ (°)	FWHM (°)	**2θ** (°)	FWHM (°)	**2θ** (°)	FWHM (°)
7.216	0.092	4.668	0.048	4.621	1.206
9.644	0.084	9.377	0.073	7.046	2.792
10.958	0.083	12.170	0.051	9.391	0.269
12.217	0.088	14.130	0.158	10.747	0.304
13.225	0.001	18.842	0.834	13.562	0.223
13.822	0.119	19.340	0.061	14.197	0.293
14.452	0.088	22.428	0.135	15.351	0.345
15.023	0.079	25.875	0.119	15.798	0.301
15.580	0.078	28.989	0.238	16.991	0.419
15.973	0.086			18.961	0.066
16.129	0.058			19.563	0.378
17.013	0.078			21.633	0.255
17.379	0.108			22.147	20.000
18.225	0.126			24.831	0.322

19.356	0.080	25.827	0.190
19.748	0.079	41.784	0.088
19.936	0.086		
20.356	0.058		
20.649	0.079		
21.189	0.050		
21.856	0.072		
22.262	0.067		
22.614	0.080		
22.908	0.083		
23.252	0.050		
23.964	0.087		
24.560	0.084		
25.072	0.096		
25.173	0.063		
25.561	0.113		
26.102	0.077		
26.900	0.125		
27.622	0.092		
27.861	0.143		
28.250	0.088		
28.685	0.101		
28.816	0.064		
29.183	0.558		
29.598	0.070		
30.218	0.050		
30.413	0.050		
31.131	0.116		
31.933	0.120		
33.300	0.226		
35.192	0.165		
35.600	0.137		
35.860	0.081		
36.887	0.283		
37.591	0.259		
38.884	0.050		
40.143	0.087		
40.833	0.158		
41.068	0.092		
41.714	0.097		
42.108	0.119		
42.597	0.050		
42.888	0.050		
43.122	0.070		

43.538	0.089
43.556	0.005
44.207	0.099
44.908	0.136
45.857	0.649
47.454	0.118
47.643	0.093

[a] fitted based on crystal

Cyclic Voltammetry

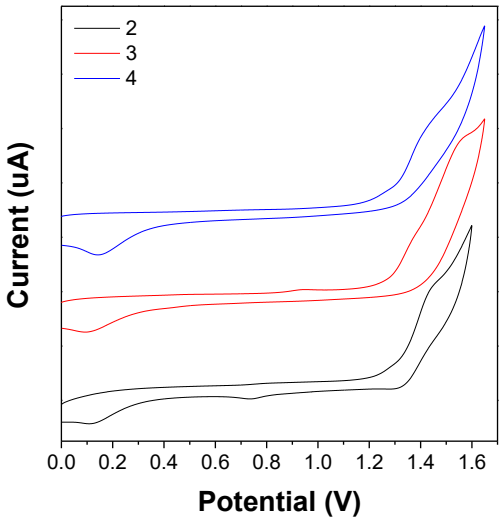


Figure S28. Cyclic voltammograms recorded for the compounds 2-4.

DFT calculation

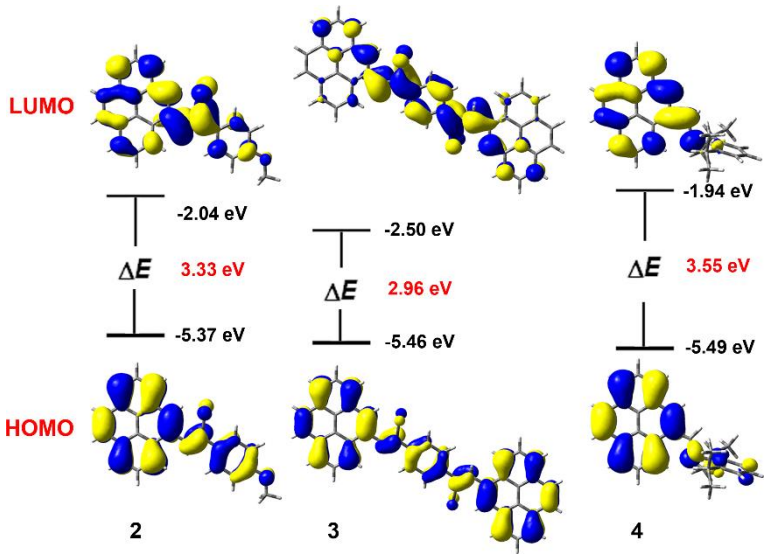


Figure S29. Computed molecular orbital plots (B3LYP/6–31G*) of compounds of **2-4**. The up plotsrepresent the HOMOs, and the down plots represent the LUMOs.