Electronic supplementary information (ESI)

Turning on the solid emission from non-emissive 2-aryl-3-cyanobenzofurans by tethering tetraphenylethene for green electroluminescence

Zhixing Peng, Kai Huang, Yuhan Tao, Xihui Li, Lianpeng Zhang, Ping Lu*, Yanguang Wang*

Department of Chemistry, Zhejiang University, Hangzhou, P. R. China

Content

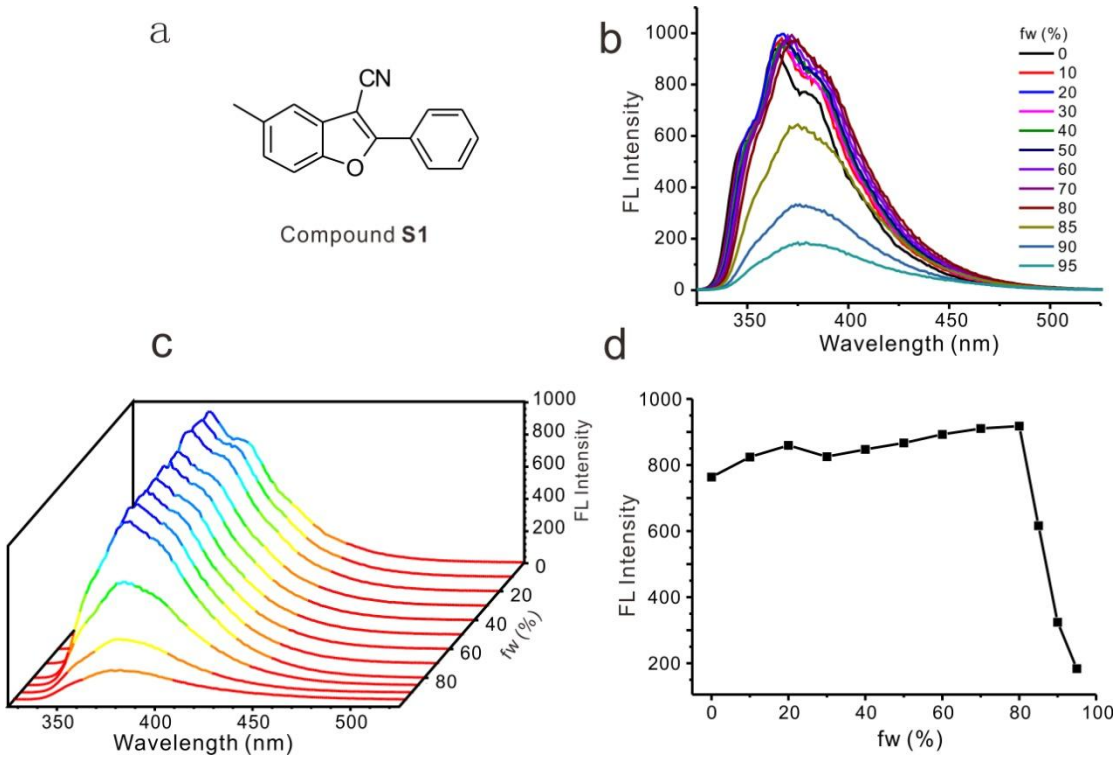
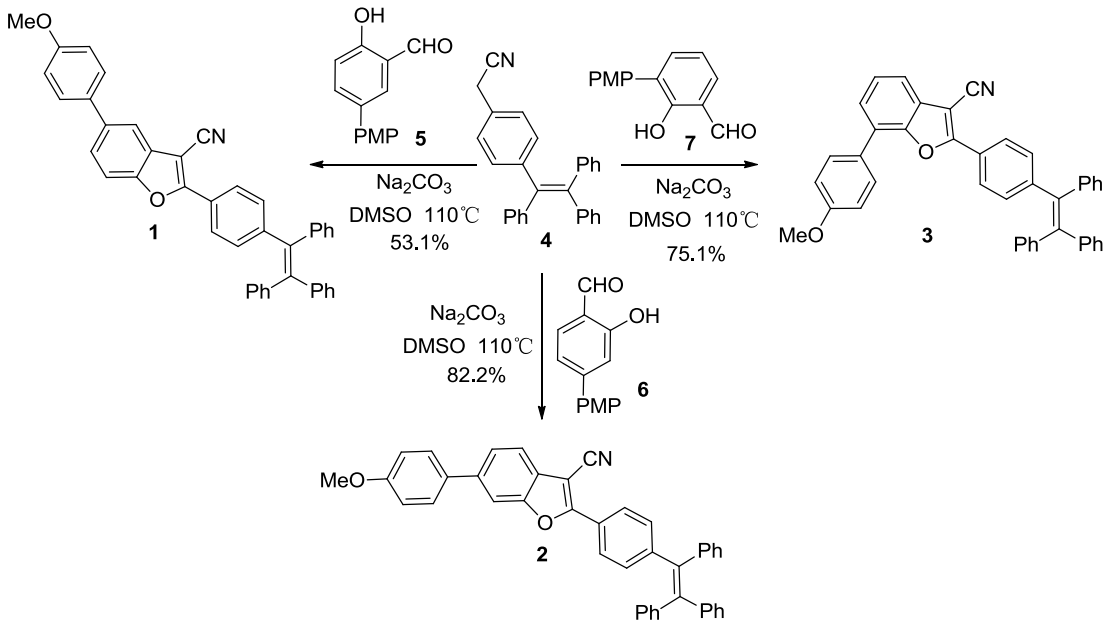


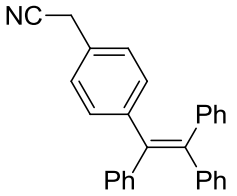
Figure S1 Emission of compound **S1** in different water / THF (f_w). (a) The structure of **S1**, (b) 2D diagram of emission of compound **S1** at varying f_w, (c) 3D diagram of emission of compound **S1** at varying f_w, (d) FL Intensity of compound **S1** at varying f_w.



Scheme S1. Synthetic route of compound **1**, **2**, **3**.

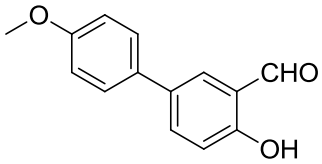
Compound **4** was prepared according to the reported procedure.[1] Compound **5**, **6**, and **7** were prepared according to the reported procedure.[2]

2-(4-(1,2,2-Triphenylvinyl)phenyl)acetonitrile (4)



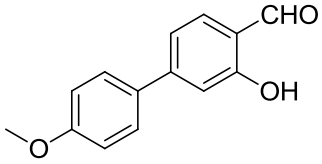
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.06 (m, 9H), 7.04-6.99 (m, 10H), 3.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 143.4, 143.4, 143.3, 131.2, 131.2, 131.2, 127.8, 127.7, 127.6, 117.8, 23.3.

4-Hydroxy-4'-methoxy-[1,1'-biphenyl]-3-carbaldehyde (5)



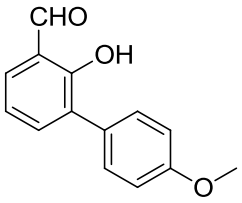
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.96 (s, 1H), 9.93 (s, 1H), 7.72-7.67 (m, 2H), 7.48-7.44 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.98-6.95 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 160.4, 159.1, 135.4, 133.0, 131.8, 131.3, 127.6, 120.6, 118.0, 114.3, 55.3.

3-Hydroxy-4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (6)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.14 (s, 1H), 9.89 (s, 1H), 7.61-7.57 (m, 3H), 7.24-7.18 (m, 2H), 7.02-6.98 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 162.0, 160.4, 149.4, 134.1, 131.6, 128.5, 119.1, 118.3, 115.0, 114.4, 55.4.

2-Hydroxy-4'-methoxy-[1,1'-biphenyl]-3-carbaldehyde (7)



Light green solid, mp 73.8-74.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.53 (s, 1H), 9.94 (s, 1H), 7.59 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.56-7.52 (m, 3H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.01-6.97 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 159.2, 158.8, 137.5, 132.7, 130.4, 130.1, 128.6, 120.8, 119.9, 113.8, 55.3. HRMS (EI-TOF): cacld. for $C_{14}H_{12}O_3$ [M^+], 228.0786; found: 228.0789. IR: 3039, 2837, 1658, 1610, 1515, 1441, 1388, 1285, 1246, 1217, 1182, 1032, 915, 831, 788, 752, 678 cm^{-1}.

Copies of all compounds NMR Spectra

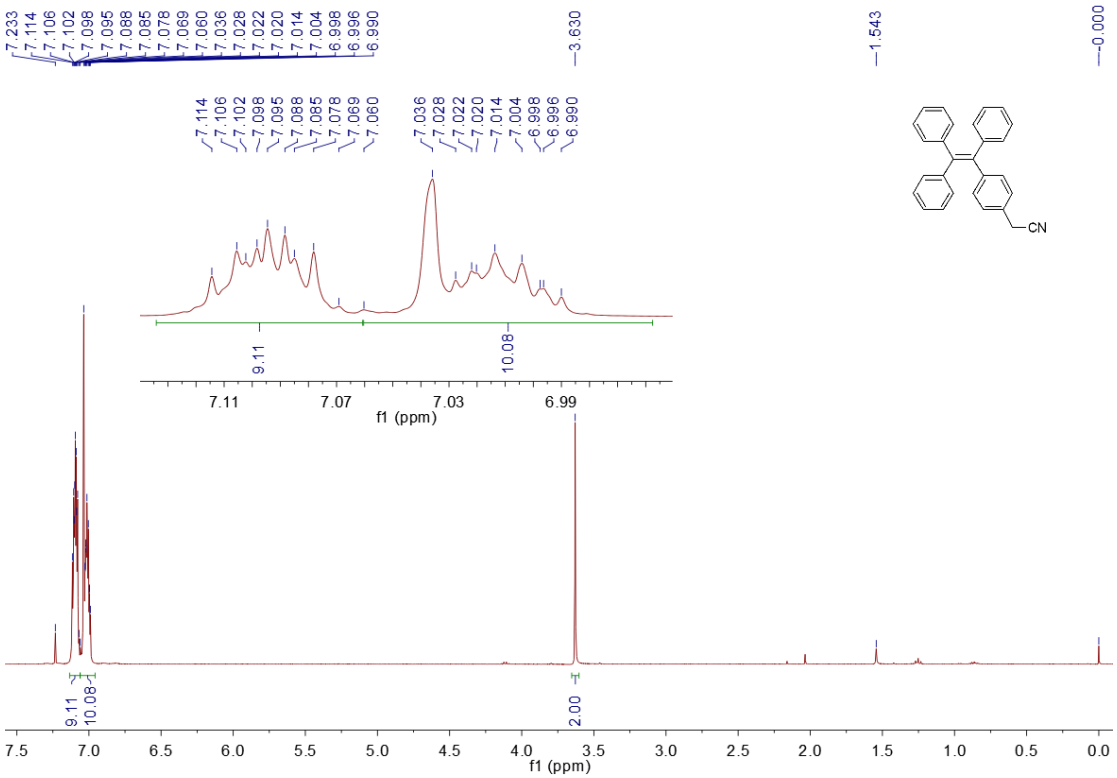


Figure S2 ^{1}H NMR spectrum of compound **4**

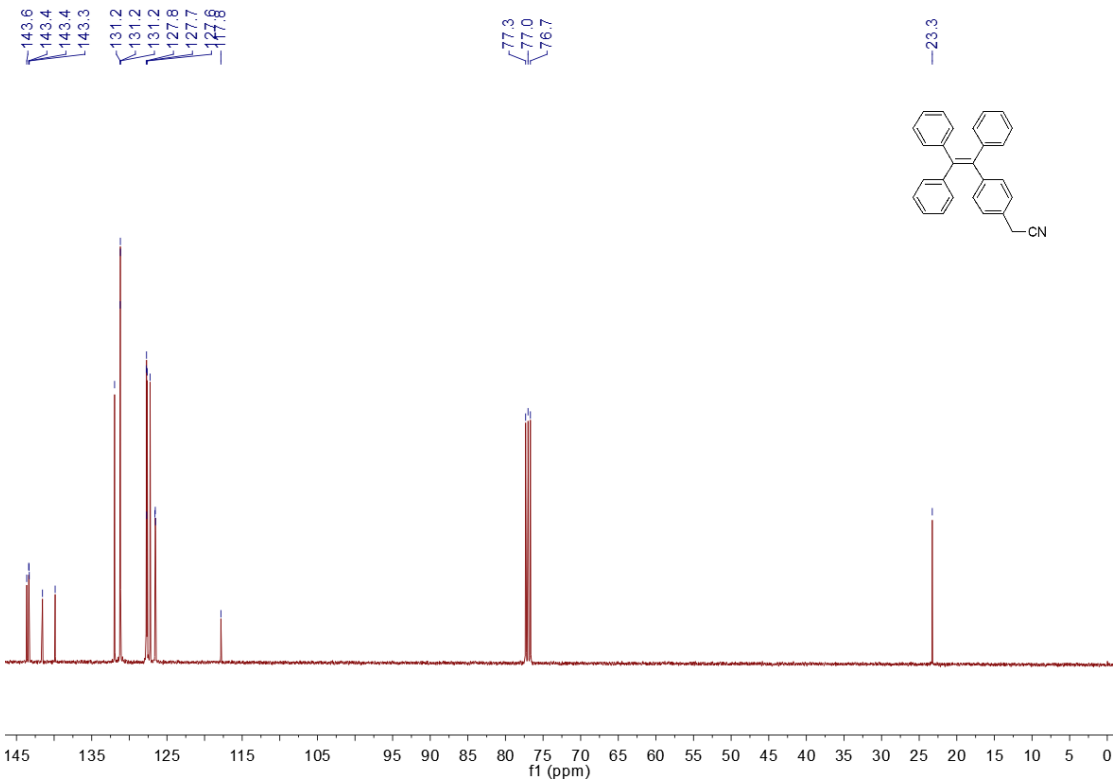


Figure S3 ^{13}C NMR spectrum of compound **4**

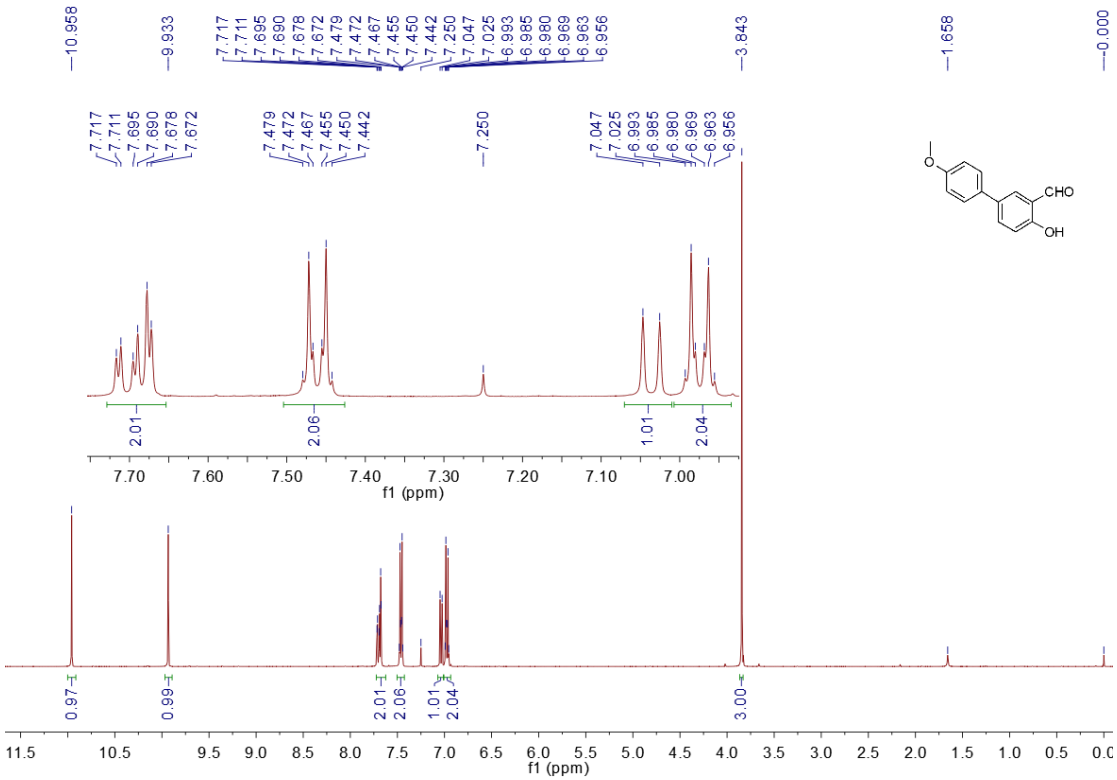


Figure S4 ^{1}H NMR spectrum of compound **5**

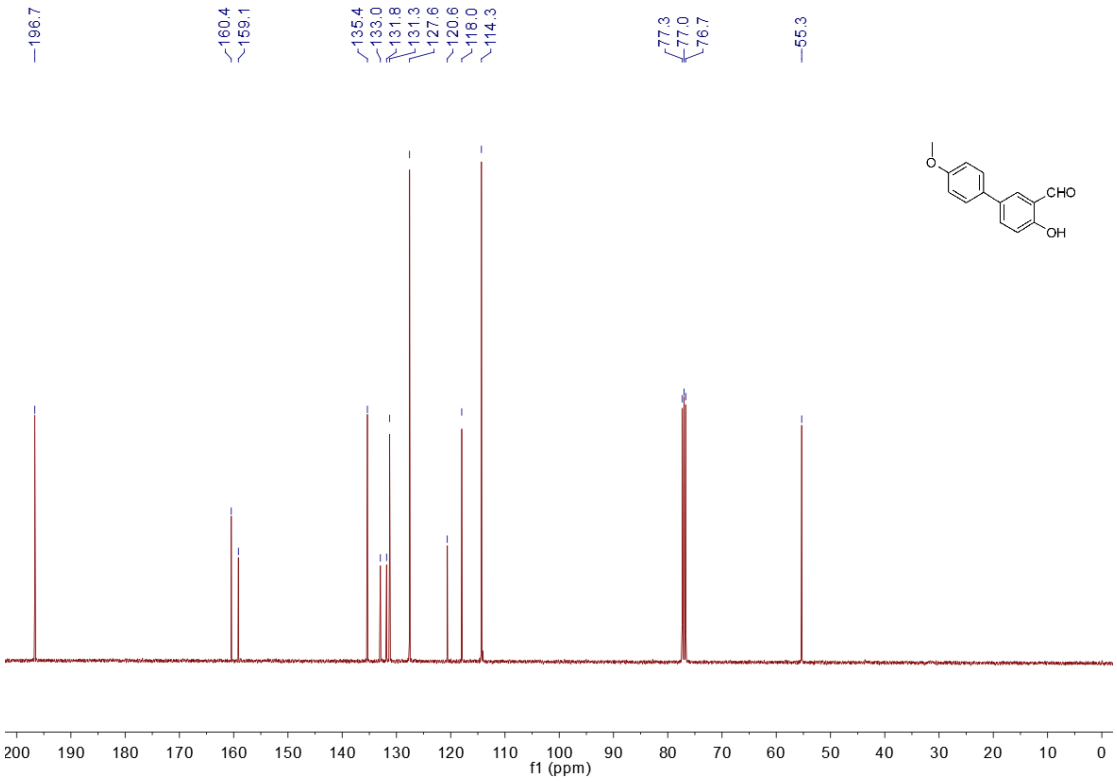


Figure S5 ^{13}C NMR spectrum of compound **5**

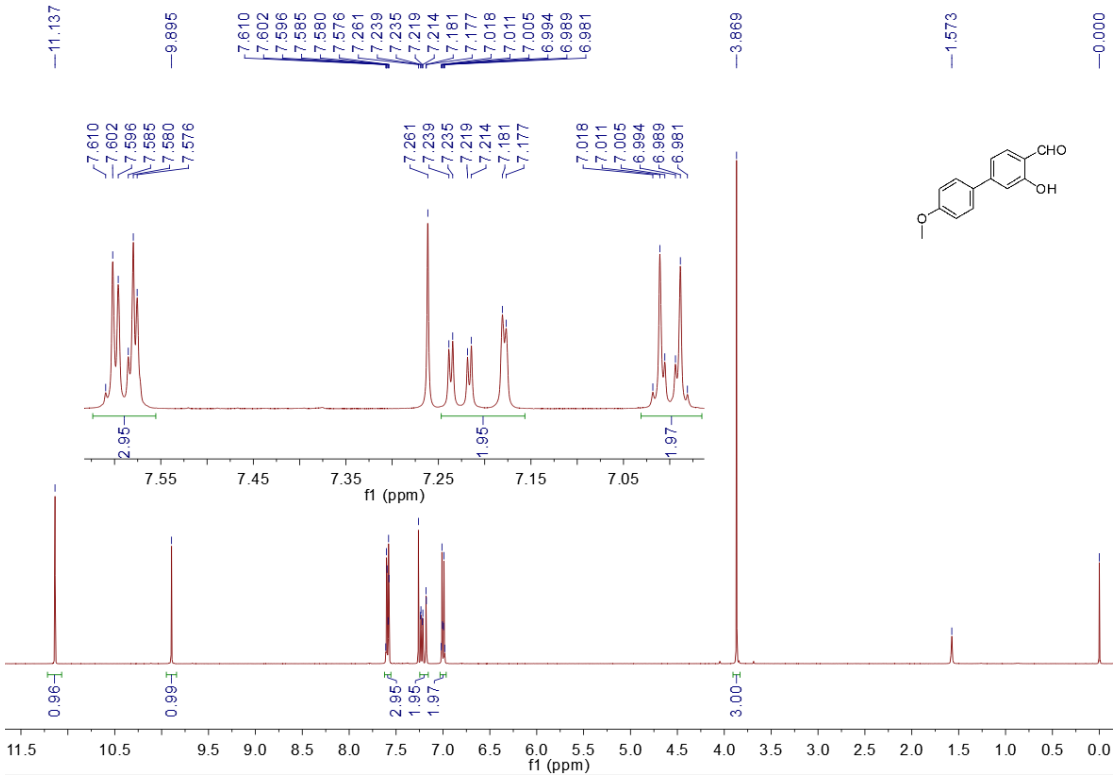


Figure S6 ^{1}H NMR spectrum of compound **6**

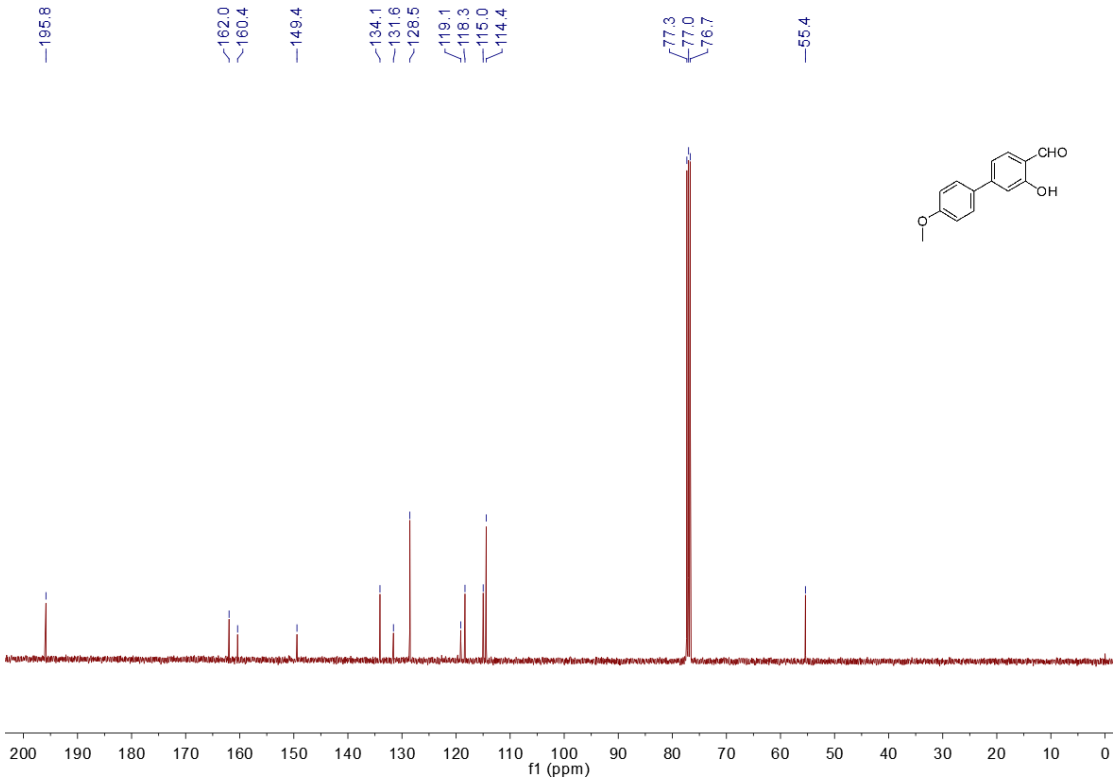


Figure S7 ^{13}C NMR spectrum of compound **6**

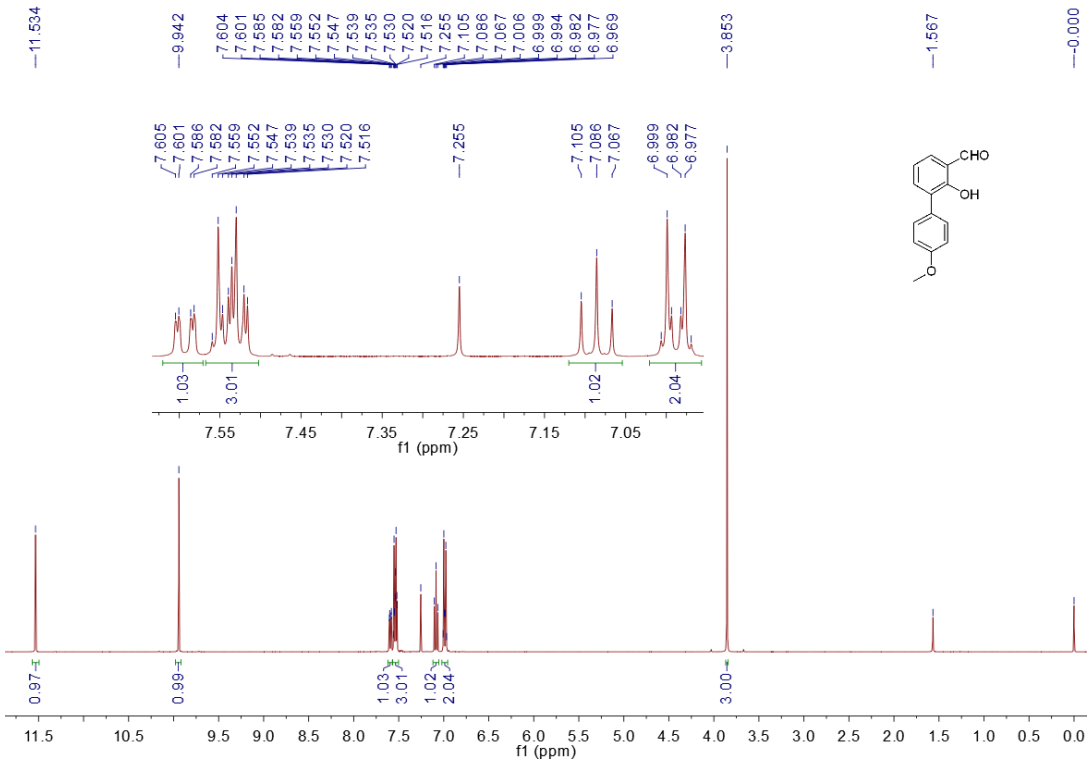


Figure S8 ^{1}H NMR spectrum of compound **7**

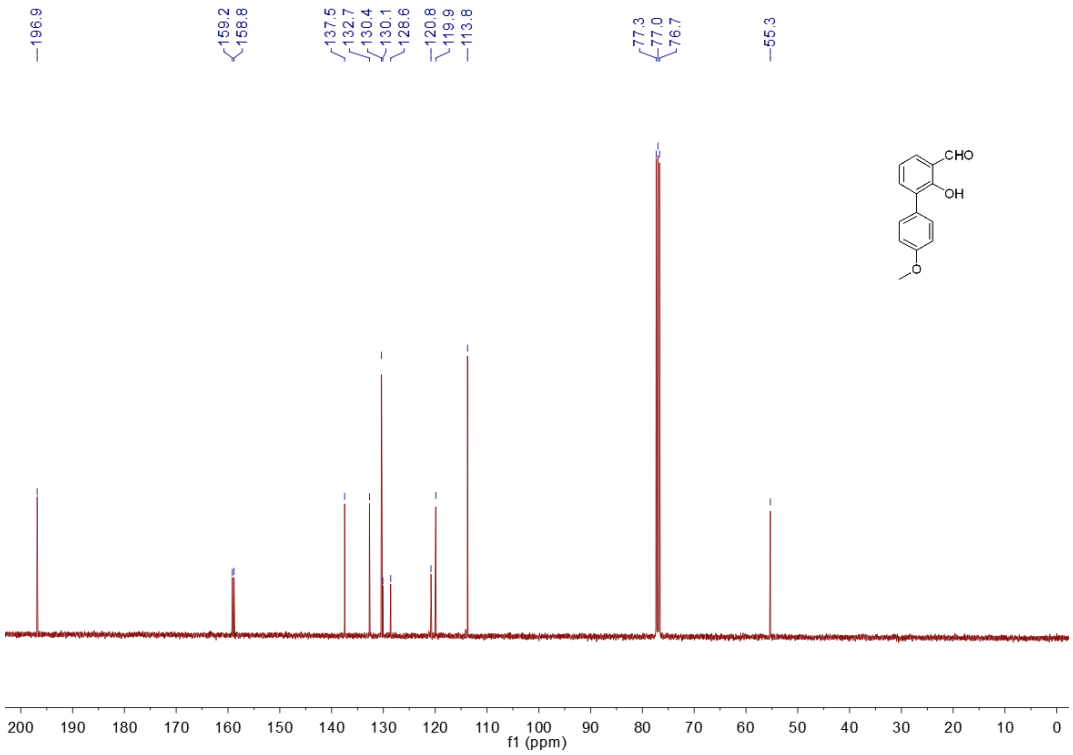


Figure S9 ^{13}C NMR spectrum of compound **7**

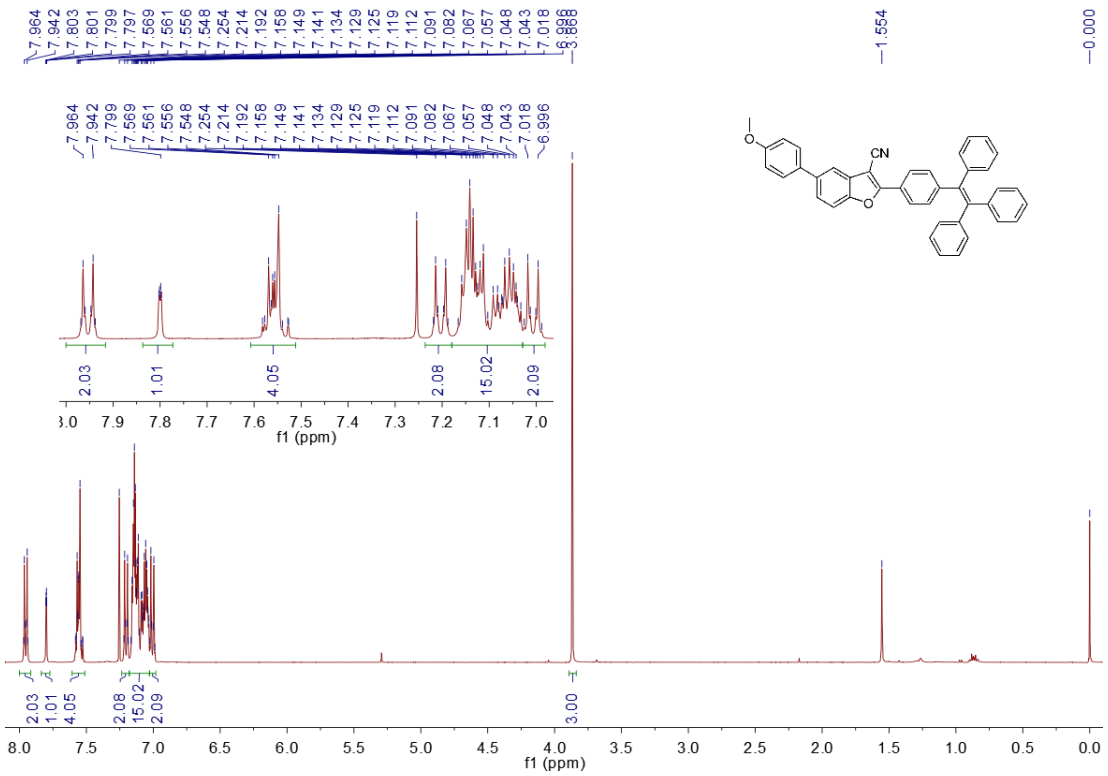


Figure S10 ^{1}H NMR spectrum of compound **1**

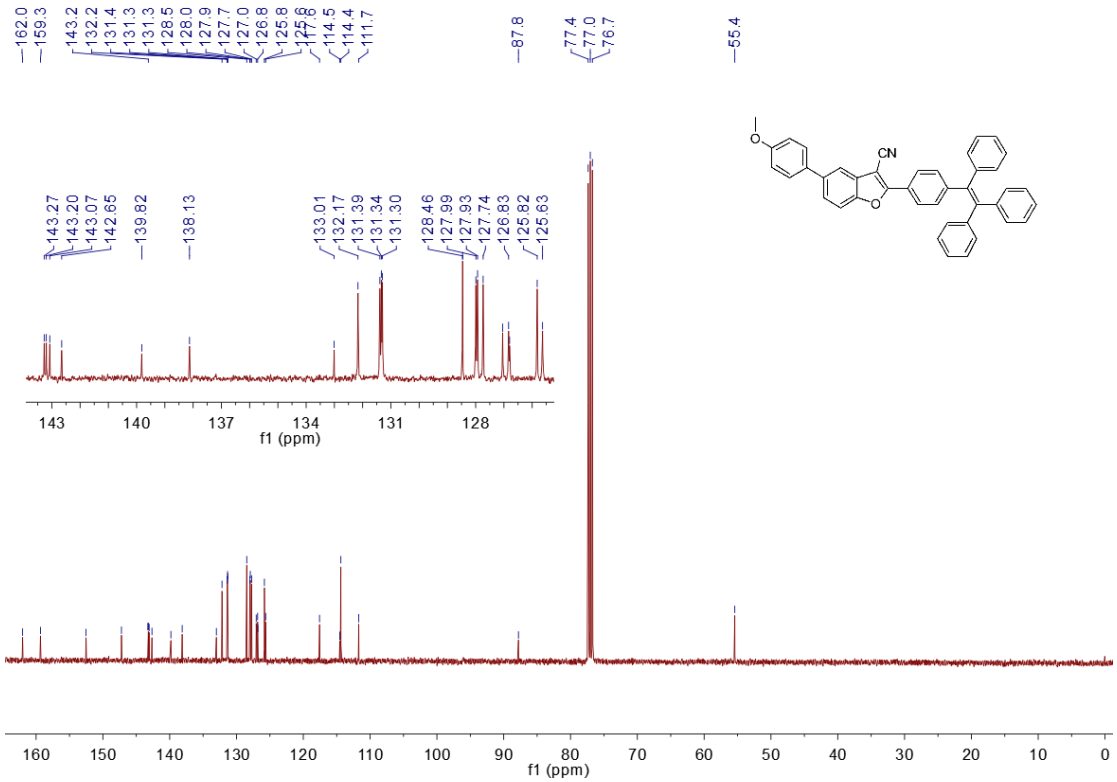


Figure S11 ^{13}C NMR spectrum of compound **1**

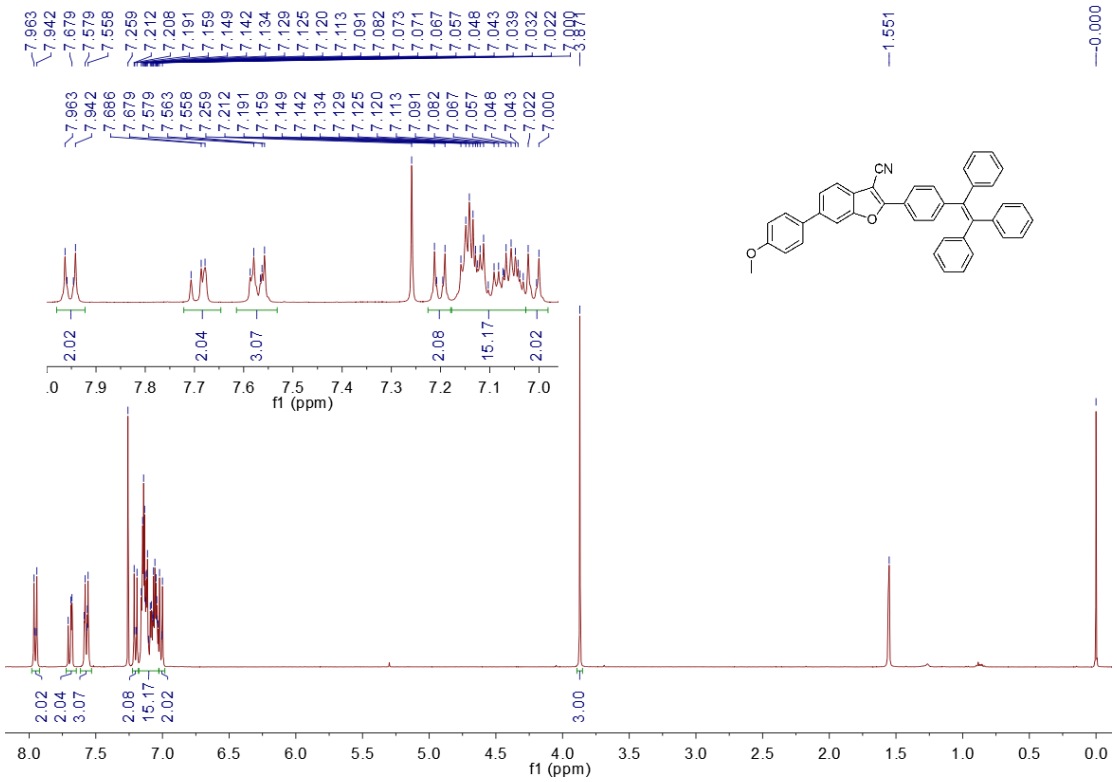


Figure S12 ^{1}H NMR spectrum of compound **2**

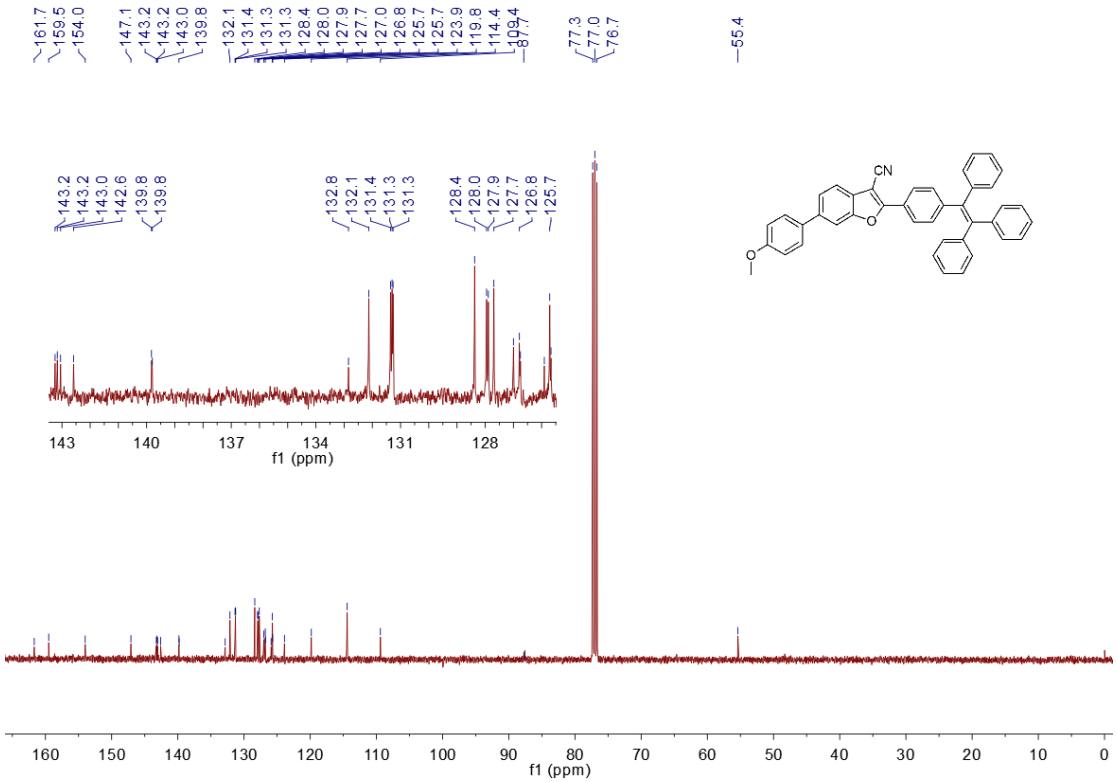


Figure S13 ^{13}C NMR spectrum of compound **2**

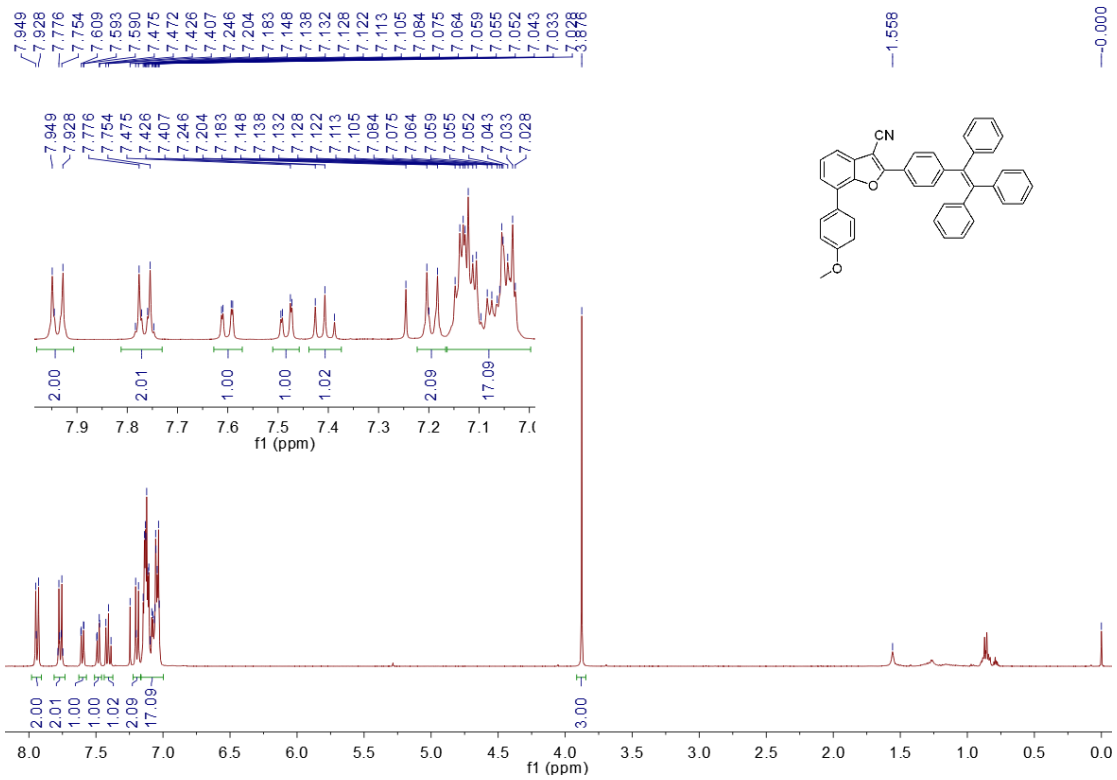


Figure S14 ^{1}H NMR spectrum of compound **3**

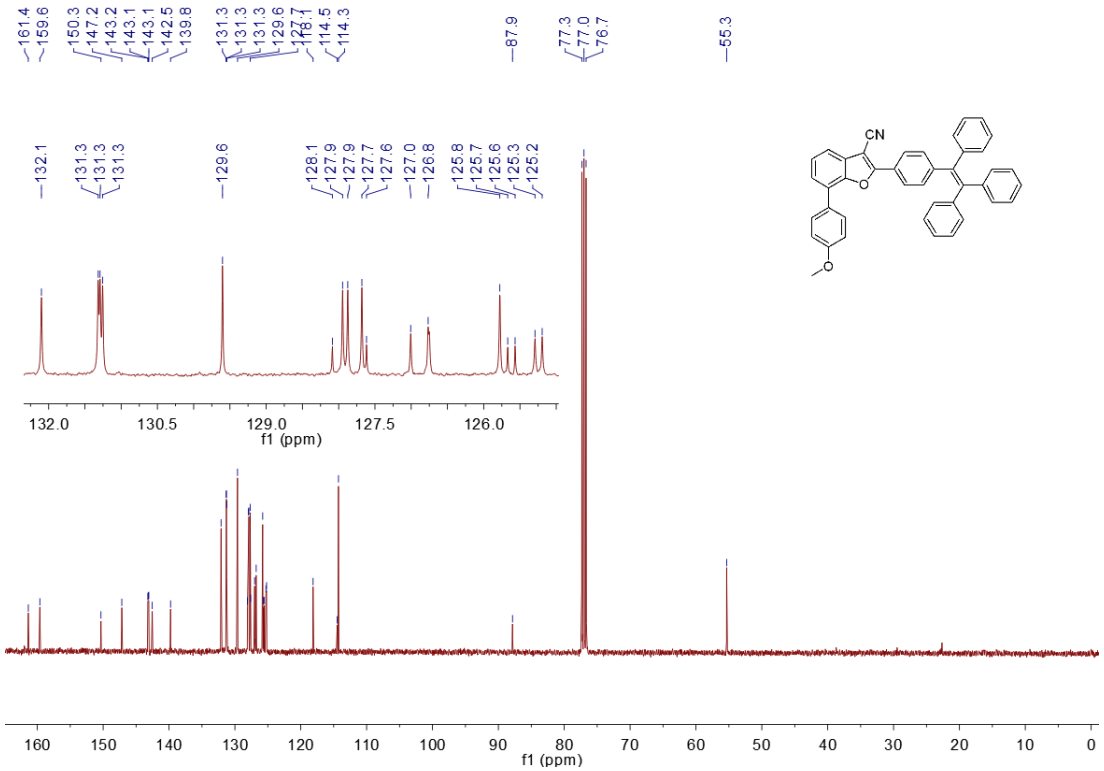


Figure S15 ^{13}C NMR spectrum of compound **3**

Compounds	**1**	**2**	**3**
Formula	$C_{42}H_{29}NO_2$	$C_{42}H_{29}NO_2$	$C_{42}H_{29}NO_2$
a [Å]	18.2932	9.4456	9.4088
b [Å]	19.3313	9.9577	11.4520
c [Å]	9.1613	16.2906	15.1598
[deg]	90	102.183	90.309
[deg]	103.67	93.914	105.929
[deg]	90	93.086	93.468
Z	4	2	2
V [$Å^3$]	3148.0	1490.57	1567.45
D [g cm^{-3}]	1.223	1.292	1.228
Space group	P 1 21/c 1	P -1	P -1
[mm^{-1}]	0.074	0.079	0.075
R [b]	0.0593	0.0844	0.0502
wR [c]	0.1674	0.1896	0.1273

Table S1 Crystal parameters of compound **1**, **2**, **3**.

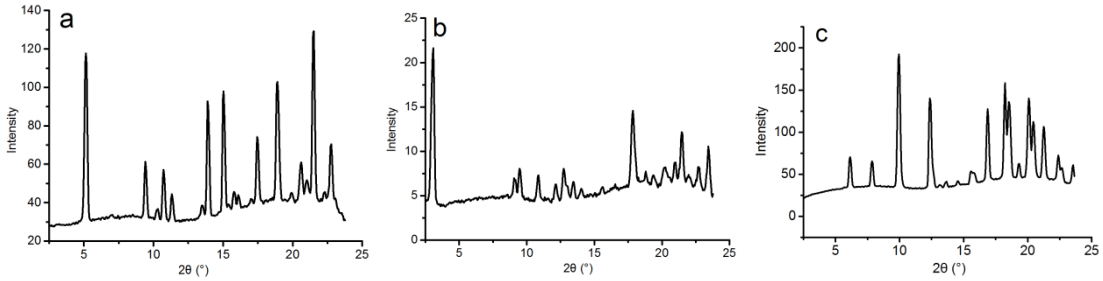


Figure S16 Powder XRD of compounds **1** (a), **2** (b), **3** (c).

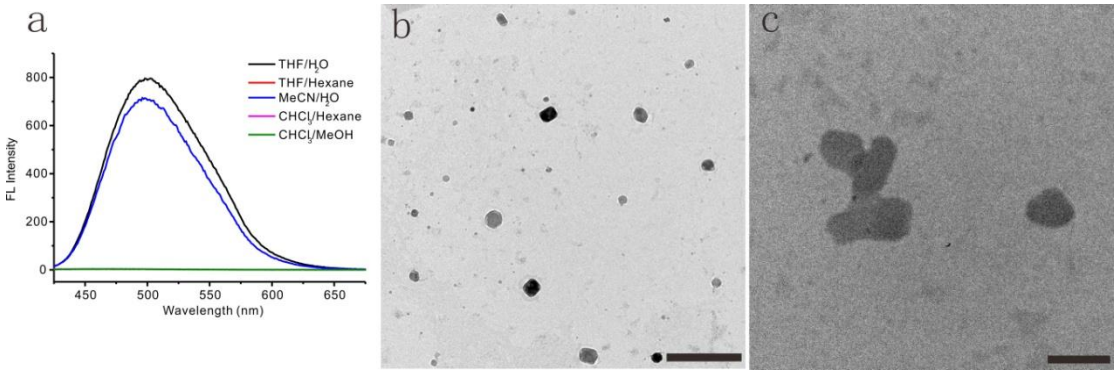


Figure S17 Fluorescence spectra and TEM images of compound **2** in different kinds of complex, the concentration is 2×10^{-5} mol/L. (a) Emission of compound **2** in different complex (fp = 95%, p = Poor solvent), (b) 2 in Water / THF (fw = 95%, scale bar = 500 nm), (c) 2 in Water / Acetonitrile, (fw = 95%, scale bar = 200 nm).

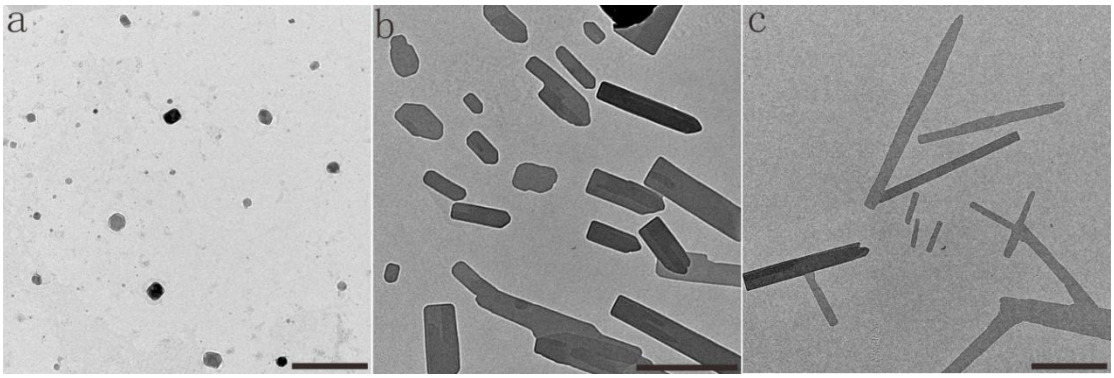


Figure S18 TEM images of compound **2** in Water / THF (fw = 95%), the concentration is different. (a) C = 2 × 10^{-5} mol/L, scale bar = 500 nm; (b) C = 1 × 10^{-4} mol/L, scale bar = 1 μm; (c) C = 1 × 10^{-3} mol/L, scale bar = 2 μm.

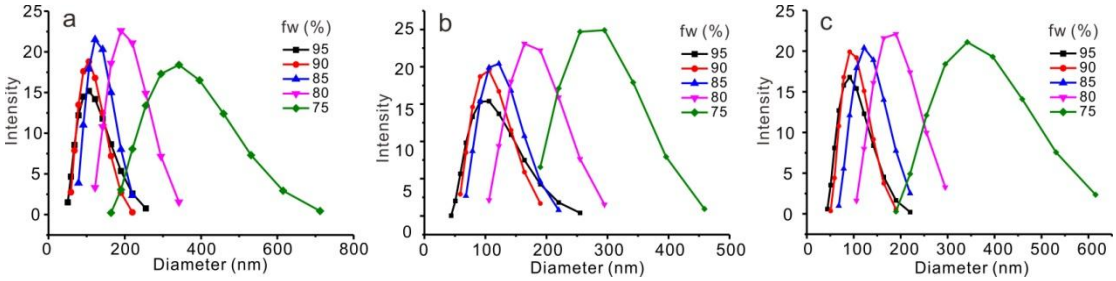


Figure S19 The size distribution of nanoparticles in different water / THF (fw) by DLS. (a) nano-particles size distribution of compounds **1**, (b) nano-particles size distribution of compounds **2**, (c) nano-particles size distribution of compounds **3**.

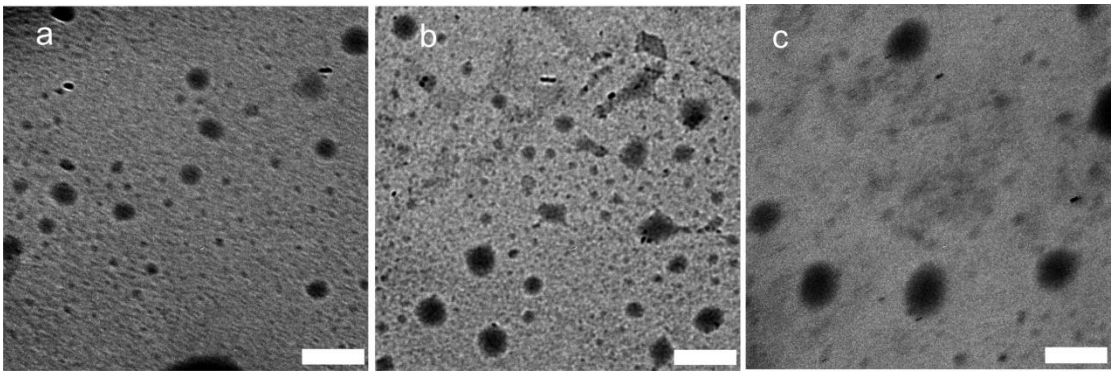


Figure S20 TEM images of nanoparticles for compounds **1** in different water / THF (fw) and the concentration is 2 × 10^{-5} mol/L. (a) fw = 95%, (b) fw = 85%, (c) fw = 80%. Scale bar = 200nm.

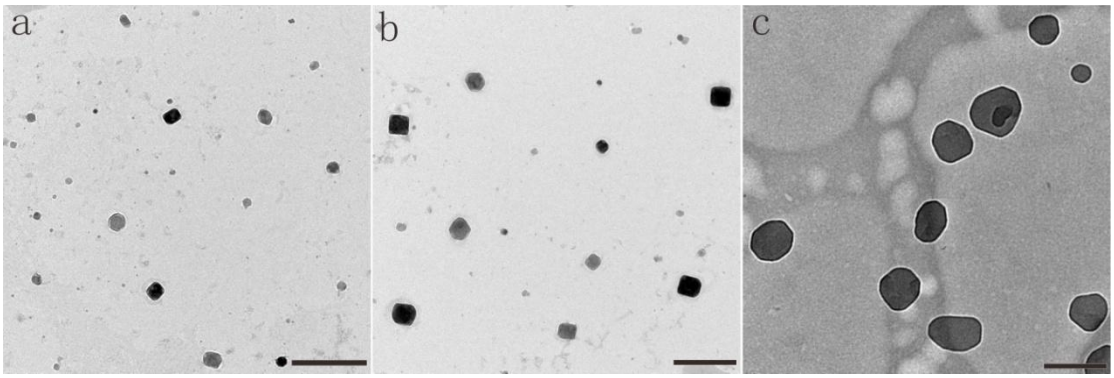


Figure S21 TEM images of nanoparticles for compounds **2** in different water / THF (fw) and the concentration is 2×10^{-5} mol/L. (a) fw = 95%, (b) fw = 85%, (c) fw = 80%. Scale bar = 500 nm.

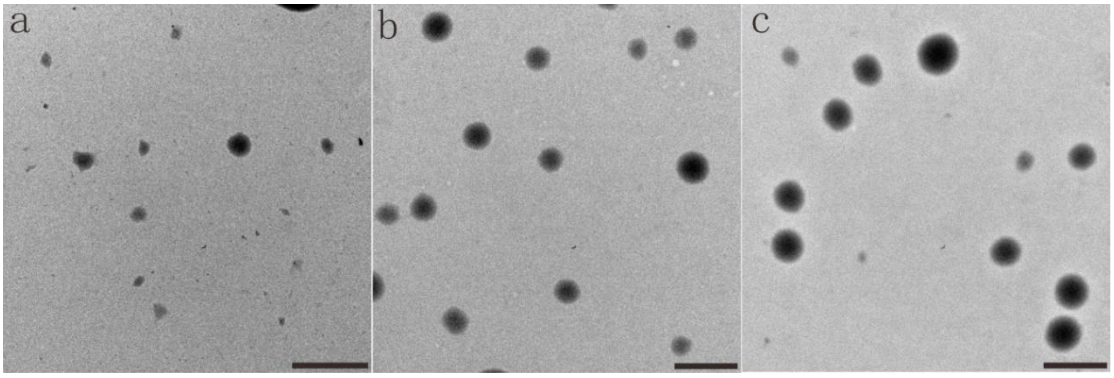


Figure S22 TEM images of nanoparticles for compounds **3** in different water / THF (fw) and the concentration is 2×10^{-5} mol/L. (a) fw = 95%, (b) fw = 85%, (c) fw = 80%. Scale bar = 1 μm.

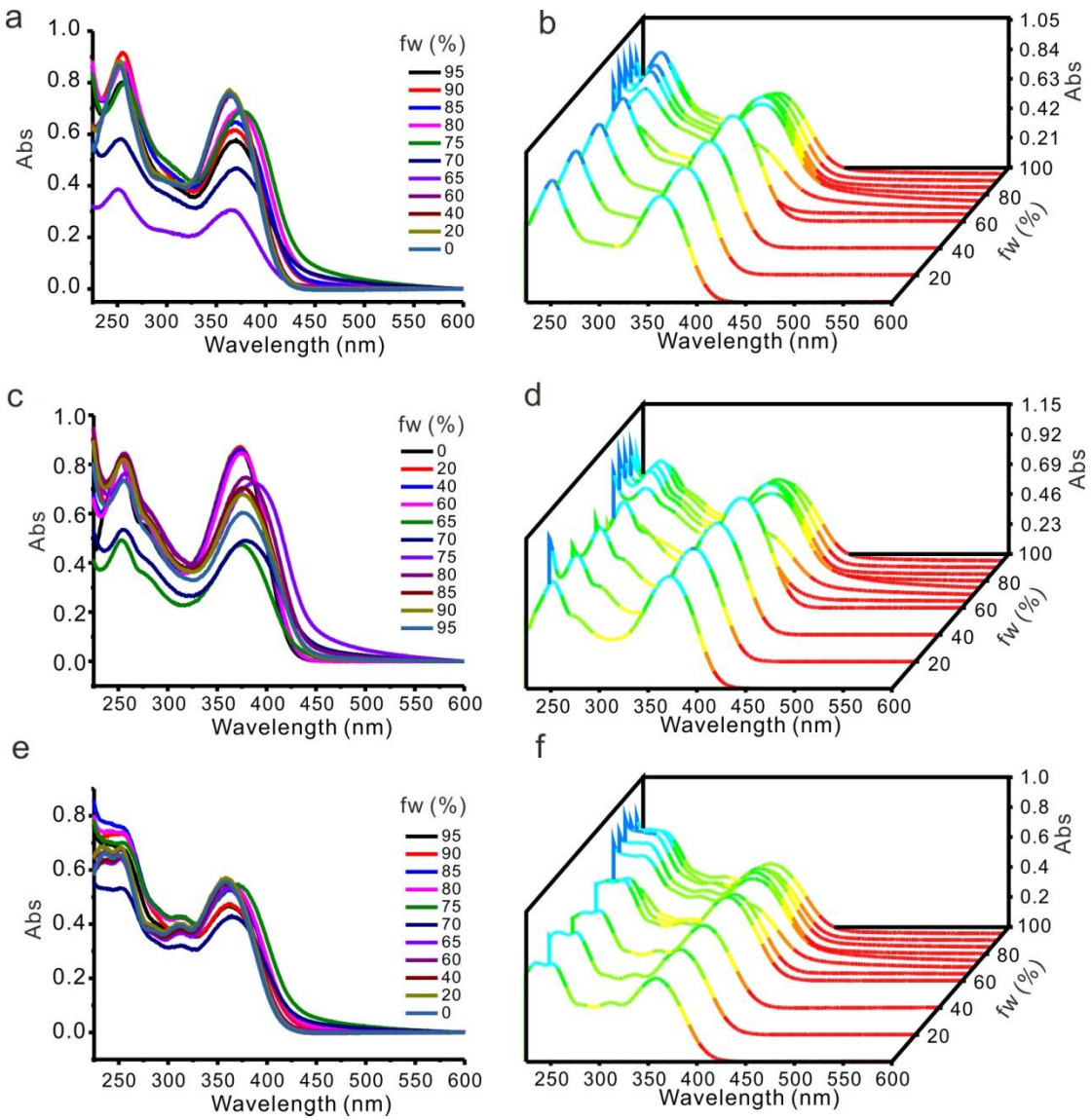


Figure S23 Absorption of compound **1**, **2**, **3** in different water / THF (fw). (a), (c), (e) 2D diagram of absorption of compound **1**, **2**, **3** at varying f_w, respectively; (b), (d), (f) 3D diagram of absorption of compound **1**, **2**, **3** at varying f_w, respectively.

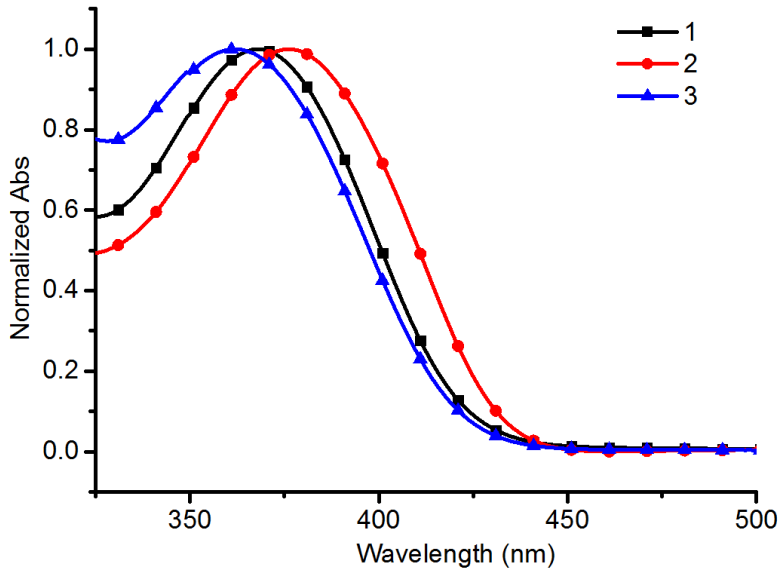


Figure S24 Normalized absorption spectra of compound **1**, **2**, **3** in film.

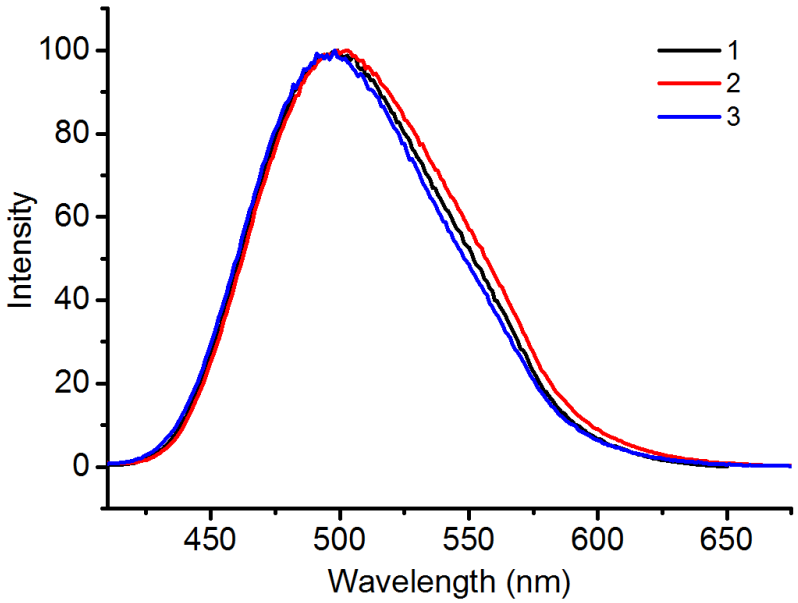


Figure S25 Normalized emission spectra of compound **1**, **2**, **3** at fw=95%.

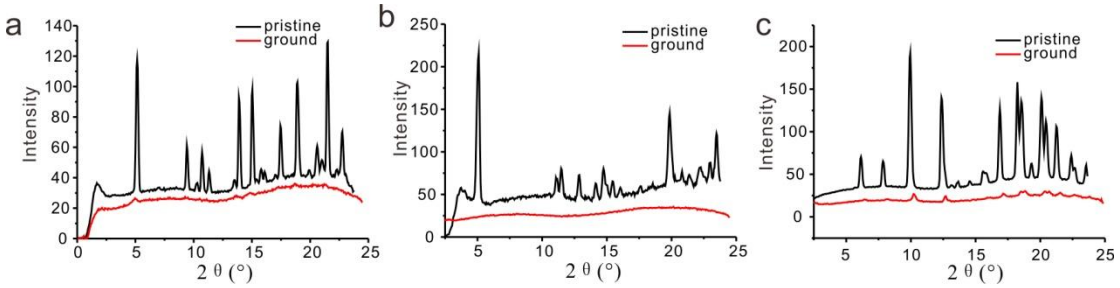


Figure S26 XRD before and after grinding of compound **1**, **2**, **3**. (a) compound **1**, (b) compound **2**, (c) compound **3**.

compound	fw	τ1/ns	Rel/%	τ2/ns	Rel/%
	75	0.5582	84.96	2.3842	15.04
	80	0.7373	76.95	2.4656	23.05
1	85	0.9780	68.06	2.8505	31.94
	90	1.3840	67.82	3.8191	32.18
	95	1.4166	63.36	3.3480	36.54
	75	0.5220	91.37	2.4847	8.63
	80	0.7436	75.98	2.1520	24.02
2	85	1.1715	64.72	2.5484	35.28
	90	1.2575	40.43	2.7097	59.57
	95	1.5457	47.85	3.0927	52.15
	75	0.7144	31.91	3.0758	68.09
	80	0.7643	67.16	2.9860	32.84
3	85	0.9984	58.69	3.1650	41.43
	90	1.3936	57.98	3.6015	42.02
	95	1.5320	55.13	3.5503	44.87

Table S2 Fluorecent lifetime and relativity of compound **1**, **2**, **3**.

Compound	HOMO				LUMO				E_g				
	CV[a] (eV)	CV[b] (eV)	Calcd[c] (eV)	Calcd[d] (eV)	CV[e] (eV)	CV[f] (eV)	Calcd[g] (eV)	Calcd[h] (eV)	CV[i] (eV)	CV[j] (eV)	Calcd[k] (eV)	Calcd[l] (eV)	UV[m] (eV)
1	-5.907	-5.837	-5.691	-5.873	-2.711	-2.743	-2.328	-1.980	3.196	3.094	3.363	3.893	3.419
2	--5.887	-5.798	-5.635	-5.671	-2.705	-2.762	-2.325	-2.035	3.182	3.036	3.310	3.636	3.346
3	-5.921	-5.711	-5.683	-5.728	-2.677	-2.746	-2.310	-2.048	3.244	2.965	3.373	3.680	3.487

[a] Potentials vs reference electrode SCE, working electrode glassy carbon, auxiliary electrode Pt, c = 2×10^{-3} mol/L, 0.1 M $Bu_4N^+PF_6^-$-MeCN, scan rate 100 mV/s, HOMO = E_{ref} - $E_{ox\,(peak\ potential)}$. [b] The onset being defined as the potential at which 20% of the current value at the peak potential was reached,[3] HOMO = E_{ref} - $E_{ox\cdot(onset\ potential)}$. [C] Obtained from DFT using the B_3LYP functional and the 6-31G* basis set. [d] Theoretical calculations were done with their crystal structures without any structure optimization using the B_3LYP functional and the 6-31G* basis set. [e] LUMO= E_{ref} - $E_{red\,(peak\ potential)}$. [f] LUMO= E_{ref} - $E_{red\ (onset\ potential)}$. [g] Obtained from DFT using the B_3LYP functional and the 6-31G* basis set. [h] Theoretical calculations were done with their crystal structures without any structure optimization using the B_3LYP functional and the 6-31G* basis set. [i] E_g = HOMO (CV[a]) - LUMO (CV[e]). [j] E_g = HOMO (CV[b]) - LUMO (CV[f]). [k] E_g = HOMO (Calcd[c]) - LUMO (Calcd[g]). [l] E_g = HOMO (Calcd[d]) - LUMO (Calcd[h]). [m] E_g= 1241 / $\lambda_{(UV\ peak)}$.

Table S3 The detailed HOMO, LUMO, and energy gap of compounds **1**, **2**, and **3.**

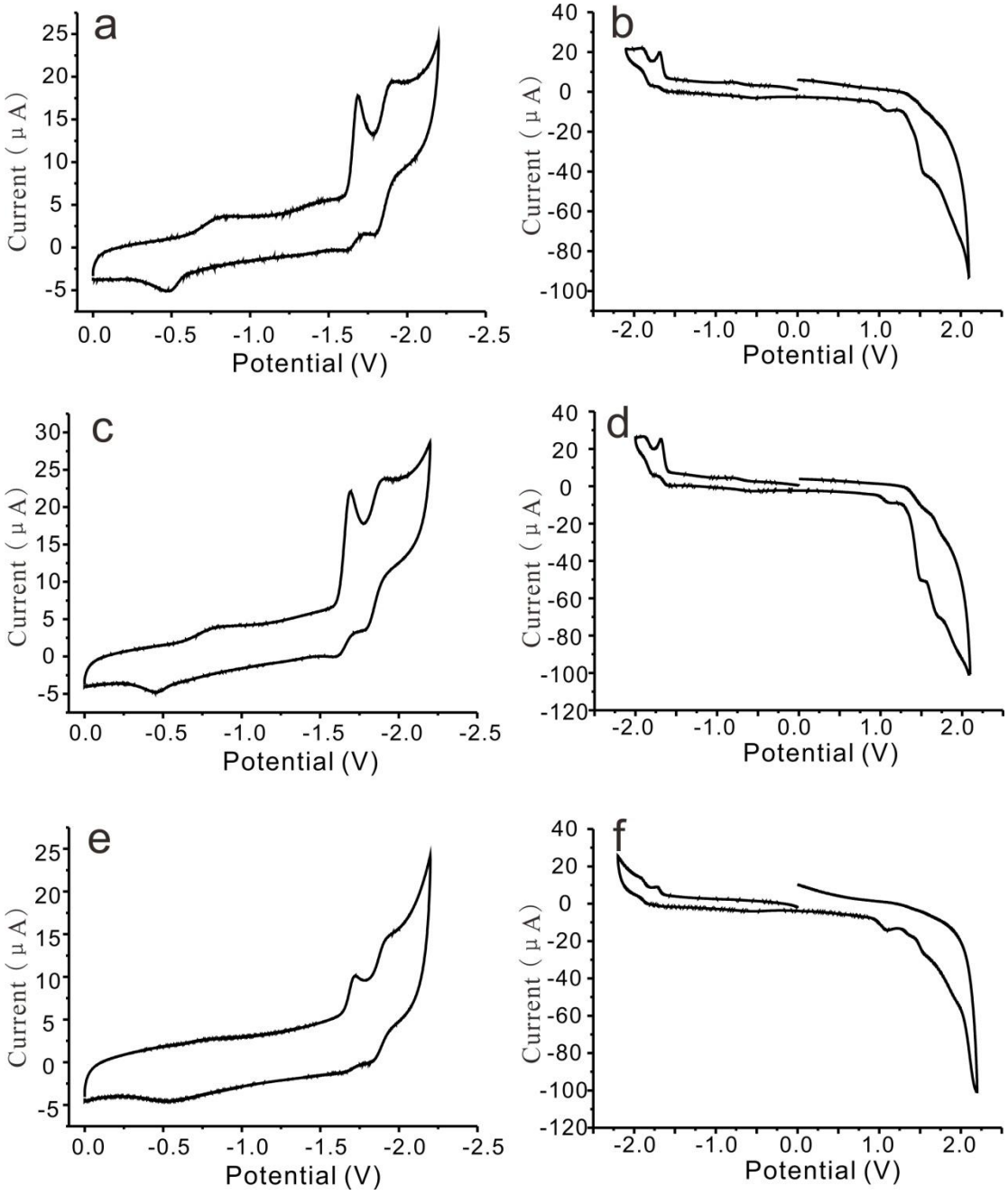


Figure S27 Cyclic voltammograms of compounds **1**, **2**, and **3**. (a), (c), (e) only negative voltage part of compound **1**, **2**, **3** respectively, (b), (d), (f) whole CV curve of compound **1**, **2**, **3** respectively.

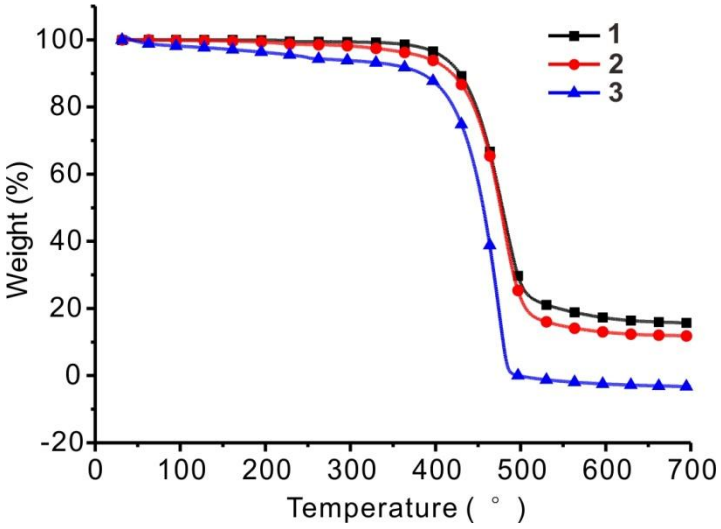


Figure S28 Thermogravimetric Analysis (TGA) of compounds **1**, **2**, and **3**. Black, blue, red line represents compound **1**, **2**, **3**, respectively.

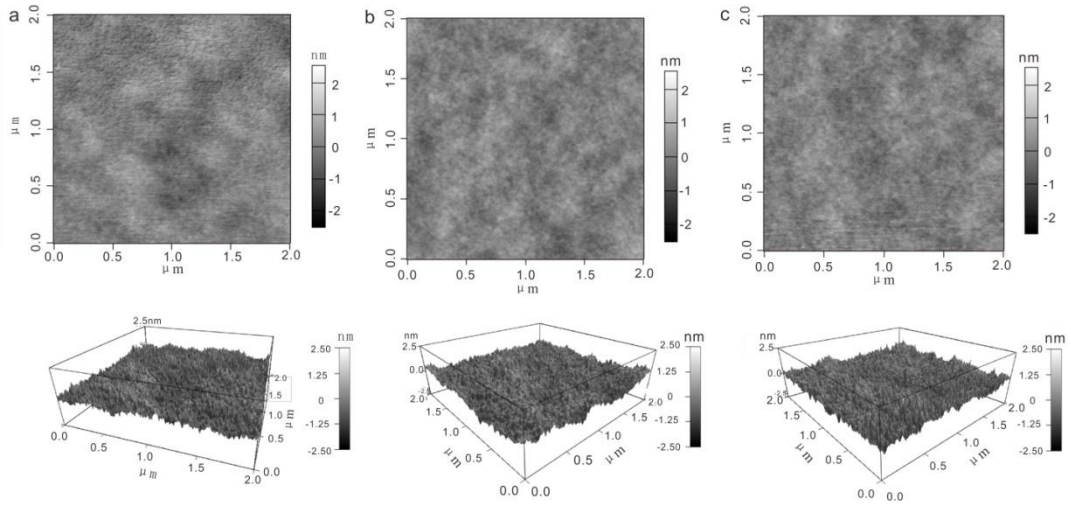


Figure S29 AFM images compounds **1** (a), **2** (b), **3** (c)

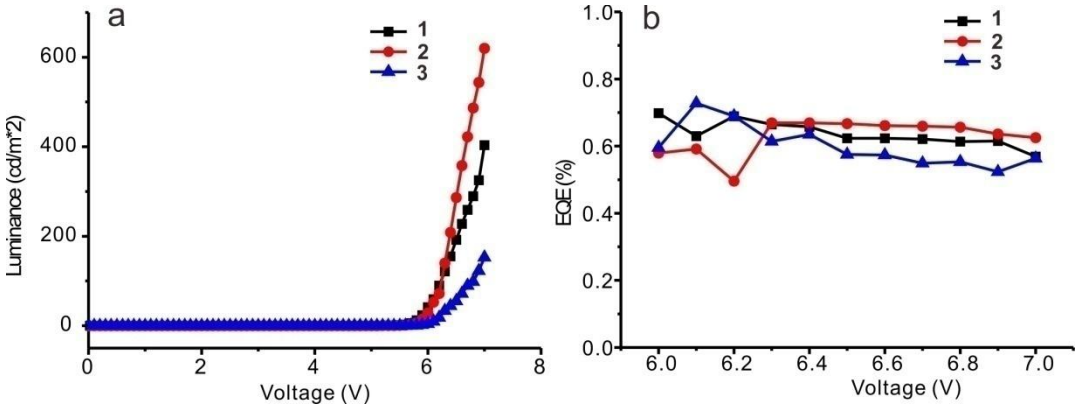


Figure S30 Voltage–luminance and EQE. (a) Voltage – Luminance curve, (b) Voltage – EQE curve. **1** , **2**, **3** represents compound **1**, **2**, **3**, respectively.

References

1. Q. Y. Lu, X. F. Li, J. Li, Z. Y. Yang, B. J. Xu, Z. G. Chi, J. R. Xu and Y. Zhang, *J. Mater. Chem. C*, 2015, **3**, 1225–1234.

2. F. Minutolo, R. Bellini, S. Bertini, I. Carboni, A. Lapucci, L. Pistolesi, G. Prota, S. Rapposelli, F. Solati, T. Tuccinardi, A. Martinelli, F. Stossi, K. E. Carlson, B. S. Katzenellenbogen, J. A. Katzenellenbogen and M. Macchia, *Journal of Medicinal Chemistry*, 2008, **51**, 1344-1351.

3. F. Maillar, A. Bonnefont, M. Chatenet, L. Guetaz, B. Doisneau-Cottignies, H. Roussel, U. Stimming, *Electrochimica Acta* ,2007, **53**, 811–822.