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

Supporting Information for

Blue-Emitting Butterfly-Shaped Donor–Acceptor-Type 1,3,5,9-Tetraarylpyrenes: Easily Available, Low-Cost Conventional Fluorophores for High-Performance Near Ultraviolet Electroluminescence with $CIE_y < 0.05$

Huijuan Ran,[a] Zhen Zhao,[a] Xuewei Duan,[a] Fuli Xie,[a] Ruijun Han,[a] Huaming Sun,[b] and Jian-Yong Hu[,a]*

[a]*Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xian 710119, China.*

[b]*National Demonstration Center for Experimental Chemistry Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xian 710119, China.*

1. Materials and Methods

All materials were obtained from commercial suppliers and used without purification unless otherwise noted. 7-*tert*-Butyl-5,9-bis(4-methoxy-phenyl)-1,3-diphenylpyrene (**3c**) was synthesized according to the reported procedure.[1]

$^{1}H/^{13}C$ NMR spectra (300 MHz) were recorded on a JEOL 300 MHz FT-300 NMR spectrometer referenced to 7.26 and 77.0 ppm for chloroform-D solvent with $SiMe_4$ as an internal reference: *J*-values are given in Hz. Mass spectra were obtained with a Bruke microflex mass spectrometer in MALDI-TOF mode. Elemental analyses were performed by Vario EL III Elementar Analysensysteme GmbH. Thermogravimetric analysis (TGA) was performed using a USA Waters Q600 under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed using a METTLER TOLEDU DSC instrument under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. UV-vis absorption spectra were measured on a PerkinElmer UV-Lambda 950 spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu F-7000 spectrofluorometer. Fluorescence quantum yields were measured using absolute methods with a Japan Hamamatsu C9920-06G. Fluorescence lifetimes were determined with a Edinburgh FLS1000 Quantaurus-Tau time-resolved spectrometer. The frontier orbitals of the molecules based on the ground state geometries were calculated at

B3LYP/6-31G* by Gaussian 16 program. Cyclic voltamogramms were measured on a CHI 610E A14297 in a solution of *tetra-n*-butylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/Silver chloride (Ag/Ag^+) reference electrode in dichloromethane at a scan rate of 100 mV s^{-1} at room temperature under N_2 atmosphere. X-ray diffraction patterns were collected using an X-ray diffractometer from Rigaku Japan. The data collection from single crystal was conducted using a Bruker D8 venture diffractometer, equipped with graphite-monochromated Cu K α radiation (λ = 1.54178 Å).

2. Device fabrication and characterization

Multilayer OLEDs were fabricated by the vacuum-deposition method. Electronic grade HAT-CN, TAPC, CBP, DSA-Ph, B3PyPB and LiF were obtained from commercial sources. **3a-c** were purified by vacuum sublimation. Commercial ITO-coated glass was used as the starting substrate. Before device fabrication, the ITO glass was pre-cleaned carefully and treated with UV/O_3 for 2 min. Organic layers were deposited by high-vacuum (1×10^{-5} Pa) thermal evaporation onto a glass substrate pre-coated with an ITO layer. All organic layers were deposited sequentially. HAT-CN was used as the hole-injecting layer. TAPC was used as the hole-transporting layer. CBP and **3c** was used as the hosts. **3a-**

c and DSA-Ph were used as the dopants. B3PyPB was used as the electron-transporting layer and LiF/Al was used as the cathode. The thermal deposition rates for the organic materials, LiF and Al were 1.0, 0.1 and 3.0 Å s^{-1}, respectively. The active area of each device was 9 mm^2. The thicknesses of the organic materials and the cathode layers were controlled using a quartz-crystal thickness monitor. The electroluminescence spectra, the current density-voltage characteristics and the current density-voltage-luminance curves characterizations of the OLEDs were carried out with a Photo Research SpectraScan PR-650 Spectroradiometer and a Keithley 2400 Source Meter and they are recorded simultaneously. All measurements were carried out on the devices without encapsulations in ambient atmosphere in the dark.

3. Synthesis

Synthesis of 7-tert-Butyl-5,9-bis(4-methylphenyl)-1,3-diphenylpyrene (**3a**): A mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (500 mg, 0.88 mmol), 4-methylphenylboronic acid (359 mg, 2.64 mmol) in toluene (50 mL), and ethanol (30 mL) at room temperature was stirred under N_2 atmosphere, and a 2.0 M aqueous solution of K_2CO_3 (20 mL) and $[Pd(PPh_3)_4]$ (170 mg) were added. The mixture was heated to 110 °C under stirring for 16 h. After cooling to room temperature, the mixture was quenched with water, extracted with toluene, and washed with water and brine. The organic extracts were dried with $MgSO_4$, and the solvent

was evaporated. The residue was purified by column chromatography eluting with CH_2Cl_2/n-hexane (v/v, 1/6) and recrystallized from CH_2Cl_2/hexane (v/v, 1/1) to give **3a** (380 mg, 73%) as a light-yellow powder. Mp 316 °C. ν_{max} (KBr)/cm^{-1} 3026.40, 2963.70, 2864.90, 2363.30, 2342.60, 1590.77, 1444.07, 1365.99, 1251.24, 1172.56, 1109.86, 1046.16, 901.05, 822.97, 765.59, 702.89, 614.16, 592.86. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (s, 9H, *t*Bu), 2.48 (s, 6H, Me), 7.33 (m, 4H, Ar-H), 7.42 (d, J = 7.2 Hz, 2H, Ar-H), 7.52 (m, 8H, Ar-H), 7.68 (d, J = 6.9 Hz, 4H, Ar-H), 7.96 (s, 1H, pyrene-H), 8.14 (s, 2H, pyrene-H), 8.32 (s, 2H, pyrene-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.60, 141.26, 139.80, 138.52, 137.12, 130.68, 130.10, 129.16, 128.50, 127.43, 127.24, 125.58, 124.42, 124.23, 121.47, 35.53, 31.80, 21.39. MS: m/z calcd. for $C_{46}H_{38}$ 590.79; Found 590.30 [M^+]. Anal. calcd for $C_{46}H_{38}$: C,93.56; H, 6.44; found: C, 93.58; H, 6.42.

Synthesis of 7-tert-Butyl-5,9-bis(4-tert-butylphenyl)-1,3-diphenylpyrene (**3b**): A mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (430 mg, 0.76 mmol), 4-*tert*-butylphenylboronic acid (406 mg, 2.28 mmol) in toluene (50 mL), and ethanol (30 mL) at room temperature was stirred under N_2 atmosphere, and a 2.0 M aqueous solution of K_2CO_3 (20 mL) and [$Pd(PPh_3)_4$] (170 mg) were added. The mixture was heated to 110 °C under stirring for 16 h. After cooling to room temperature, the mixture was quenched with water, extracted with toluene, and washed with water

and brine. The organic extracts were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography eluting with CH_2Cl_2/n-hexane (v/v, 1/6) and recrystallized from CH_2Cl_2/hexane (v/v, 1/1) to give **3b** (320 mg, 68%) as a white powder. Mp. 363 ^oC. ν_{max} (KBr)/cm^{-1} 3024.31, 2964.83, 2897.83, 2864.70, 2352.76, 1788.12, 1595.40, 1502.80, 1462.90, 1395.89, 1362.77, 1270.17, 1183.59, 1117.34, 1010.43, 897.50, 831.25, 758.23, 704.78, 605.39, 558.72. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.39 (s, 9H, *t*Bu), 1.43 (s, 18H, *t*Bu), 7.56 (m, 14H, Ar-H), 7.70 (d, J = 6.9 Hz, 4H, Ar-H), 7.95 (s, 1H, pyrene-H), 8.16 (s, 2H, pyrene-H), 8.37 (s, 2H, pyrene-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.24, 148.48, 141.22, 139.63, 138.34, 136.97, 130.63, 129.80, 128.42, 128.21, 127.36, 127.13, 125.57, 125.36, 123.23, 121.40, 35.45, 34.66, 33.01, 31.54, 31.46. MS: m/z calcd. for $C_{52}H_{50}$ 674.95; Found 674.40 [M^+]. Anal. calcd for $C_{52}H_{50}$: C, 92.58; H, 7.42; found: C, 92.55; H, 7.45.

4. Thermal properties

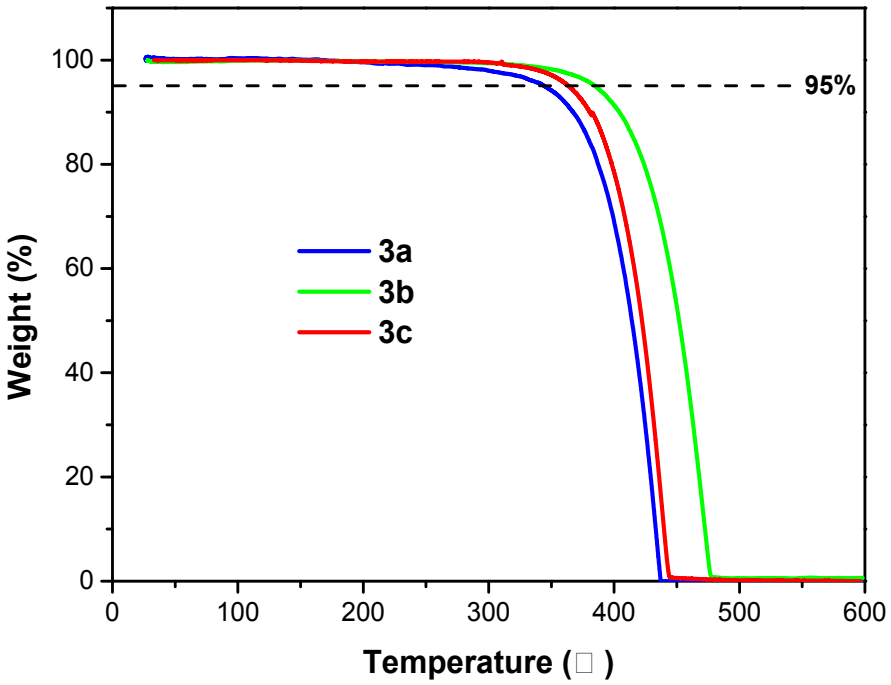


Figure S1. TGA thermograms of the compounds **3a-c** in N_2 atomosphere.

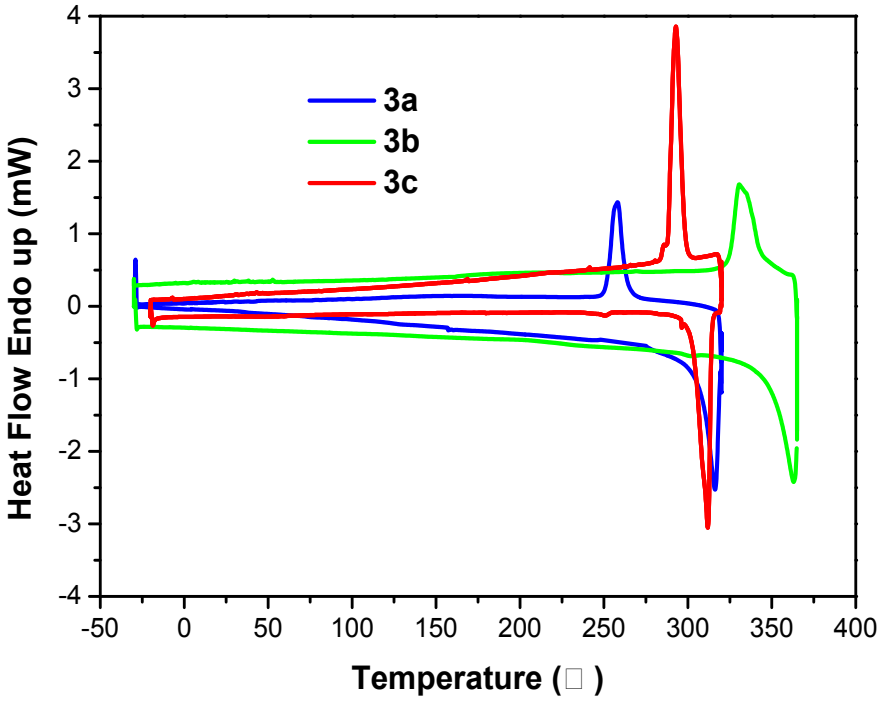


Figure S2. DSC thermograms of the compounds **3a-c** in N_2 atomosphere.

5. DFT calculations

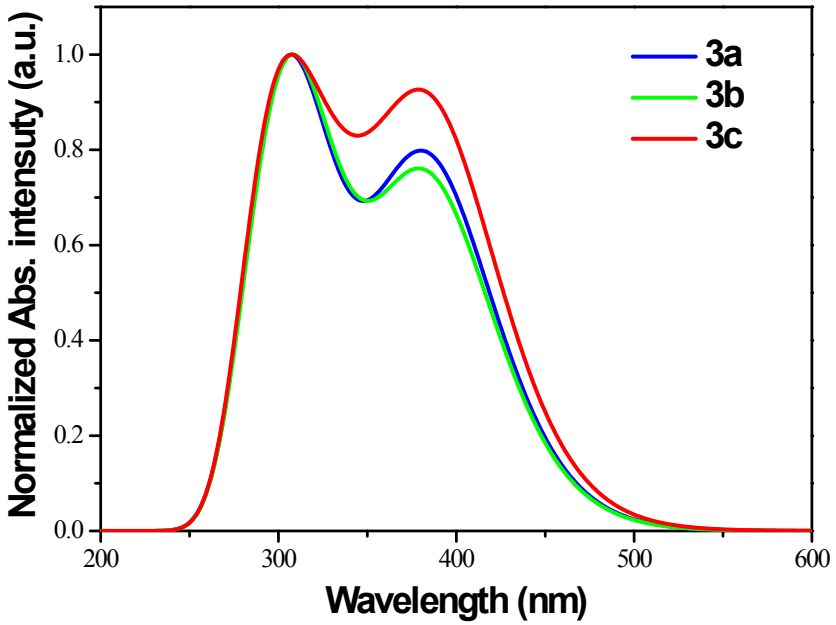


Figure S3. The computed UV-Vis absorption spectra of compounds **3a-c**.

Table S1-1 Atom coordinates and absolute energies for **3a** standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.035898	-3.461995	-0.072191
2	6	0	-1.168933	-2.757479	-0.089146
3	6	0	-1.220634	-1.352676	-0.036605
4	6	0	-0.000242	-0.607546	-0.029241
5	6	0	1.242197	-1.320594	-0.022066
6	6	0	1.223893	-2.722431	-0.019285
7	6	0	-2.48023	-0.63278	-0.001596
8	6	0	-0.019616	0.823185	-0.024036
9	6	0	-1.271306	1.512889	-0.054843
10	6	0	-2.474957	0.736173	-0.024866
11	6	0	-1.278588	2.931844	-0.047495
12	6	0	-0.058791	3.611875	0.013641
13	6	0	1.181034	2.964375	0.030645
14	6	0	1.212632	1.546894	0.018405
15	6	0	2.436497	0.80179	0.067289

16	6	0	2.481853	-0.564855	0.023821
17	1	0	3.370046	1.350213	0.116391
18	1	0	-2.105805	-3.295118	-0.141017
19	1	0	2.172531	-3.243726	0.025765
20	1	0	-3.422365	1.259902	0.03213
21	1	0	-0.072104	4.697796	-0.009642
22	6	0	2.411365	3.805838	0.040282
23	6	0	2.588872	4.781918	1.034809
24	6	0	3.389569	3.694469	-0.962758
25	6	0	3.710111	5.611657	1.034369
26	1	0	1.844163	4.87757	1.820551
27	6	0	4.510453	4.524375	-0.964275
28	1	0	3.258028	2.963556	-1.755595
29	6	0	4.676434	5.485087	0.035179
30	1	0	3.829924	6.355214	1.818153
31	1	0	5.251489	4.424679	-1.753159
32	1	0	5.55038	6.130981	0.033615
33	6	0	-2.530027	3.736921	-0.120852
34	6	0	-2.788594	4.729842	0.838705
35	6	0	-3.45017	3.57288	-1.170543
36	6	0	-3.931502	5.525255	0.758583
37	1	0	-2.090765	4.865166	1.660738
38	6	0	-4.592437	4.368736	-1.252103
39	1	0	-3.254605	2.828101	-1.936914
40	6	0	-4.838899	5.347065	-0.286933
41	1	0	-4.114718	6.282297	1.516746
42	1	0	-5.287026	4.22933	-2.076501
43	1	0	-5.729581	5.966398	-0.35051
44	6	0	-3.790282	-1.3399	0.083224
45	6	0	-4.08705	-2.222675	1.136158
46	6	0	-4.793724	-1.095313	-0.86518
47	6	0	-5.33546	-2.8322	1.23026
48	1	0	-3.334901	-2.419107	1.895259
49	6	0	-6.042081	-1.710451	-0.767904
50	1	0	-4.58584	-0.425282	-1.695098
51	6	0	-6.338103	-2.588049	0.280777
52	1	0	-5.53811	-3.505753	2.060552
53	1	0	-6.797231	-1.507015	-1.524173
54	6	0	3.813804	-1.235851	0.033327
55	6	0	4.222739	-2.080078	-1.013219
56	6	0	4.725273	-0.994021	1.071323
57	6	0	5.490347	-2.657414	-1.01488

58	1	0	3.544244	-2.272278	-1.840003
59	6	0	5.99294	-1.57614	1.0657
60	1	0	4.429327	-0.352967	1.89735
61	6	0	6.400815	-2.416532	0.02369
62	1	0	5.780823	-3.302489	-1.841683
63	1	0	6.674782	-1.376222	1.889536
64	6	0	0.098817	-5.001106	-0.098028
65	6	0	0.925491	-5.464691	-1.321059
66	6	0	0.776228	-5.506815	1.198081
67	6	0	-1.297251	-5.645317	-0.193514
68	1	0	0.465456	-5.124836	-2.256111
69	1	0	1.949829	-5.078955	-1.29193
70	1	0	0.982714	-6.559834	-1.349092
71	1	0	0.205077	-5.202242	2.082602
72	1	0	0.838044	-6.602135	1.193758
73	1	0	1.793106	-5.115505	1.306318
74	1	0	-1.198251	-6.736603	-0.213511
75	1	0	-1.927459	-5.386876	0.664846
76	1	0	-1.82441	-5.344084	-1.105832
77	6	0	-7.697556	-3.235944	0.40314
78	1	0	-7.616328	-4.289296	0.695026
79	1	0	-8.310034	-2.737073	1.166119
80	1	0	-8.249711	-3.189388	-0.541117
81	6	0	7.7834	-3.025672	0.002482
82	1	0	8.462257	-2.45209	-0.642929
83	1	0	8.226669	-3.047797	1.003431
84	1	0	7.764983	-4.051798	-0.381697

Total Enegy (RB3LYP) = -1775.87712461 Harterr

Table S1-2 Atom coordinates and absolute energies for **3b** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.016528	-3.003743	0.182278
2	6	0	-1.184065	-2.294801	0.120088
3	6	0	-1.22694	-0.891984	0.02226
4	6	0	-0.001727	-0.154509	0.000897
5	6	0	1.236291	-0.874635	0.032857
6	6	0	1.209806	-2.272802	0.131456
7	6	0	-2.482232	-0.163678	0.000128

8	6	0	-0.011433	1.276392	-0.017997
9	6	0	-1.258901	1.974496	-0.020051
10	6	0	-2.466991	1.205337	0.001252
11	6	0	-1.256947	3.393546	-0.015793
12	6	0	-0.031721	4.065756	0.009482
13	6	0	1.203894	3.410188	-0.006302
14	6	0	1.226121	1.992487	-0.010424
15	6	0	2.446231	1.24046	0.019644
16	6	0	2.481851	-0.127184	0.019355
17	1	0	3.384166	1.783413	0.0273
18	1	0	-2.124624	-2.825799	0.170674
19	1	0	2.156277	-2.796393	0.192833
20	1	0	-3.412975	1.734224	0.003018
21	1	0	-0.03897	5.151723	-0.014895
22	6	0	2.439509	4.243439	-0.033434
23	6	0	2.651215	5.222062	0.951826
24	6	0	3.388725	4.121363	-1.06274
25	6	0	3.777646	6.044013	0.916868
26	1	0	1.929283	5.325944	1.757521
27	6	0	4.514788	4.943434	-1.098761
28	1	0	3.230093	3.388279	-1.848612
29	6	0	4.714961	5.906877	-0.108223
30	1	0	3.924244	6.789809	1.693946
31	1	0	5.23292	4.835587	-1.907508
32	1	0	5.592854	6.546768	-0.136705
33	6	0	-2.504353	4.208553	-0.052262
34	6	0	-2.737161	5.184826	0.930571
35	6	0	-3.444656	4.071604	-1.087889
36	6	0	-3.875162	5.990268	0.886989
37	1	0	-2.022441	5.299842	1.741159
38	6	0	-4.582274	4.877153	-1.132506
39	1	0	-3.270057	3.340116	-1.871854
40	6	0	-4.803275	5.83854	-0.144388
41	1	0	-4.037969	6.734554	1.662288
42	1	0	-5.293207	4.758047	-1.946017
43	1	0	-5.69021	6.465498	-0.17956
44	6	0	-3.800138	-0.860627	-0.011331
45	6	0	-4.767199	-0.576643	0.965919
46	6	0	-4.150477	-1.769451	-1.01947
47	6	0	-6.021476	-1.179465	0.933805
48	1	0	-4.524537	0.118383	1.765362
49	6	0	-5.410496	-2.369488	-1.04771

50	1	0	-3.435026	-1.998341	-1.804816
51	6	0	-6.378433	-2.09278	-0.072365
52	1	0	-6.733715	-0.93156	1.716291
53	1	0	-5.631248	-3.058421	-1.855784
54	6	0	3.808071	-0.807642	0.016247
55	6	0	4.173527	-1.714303	-0.993725
56	6	0	4.764724	-0.515759	0.996145
57	6	0	5.436869	-2.296919	-1.012188
58	1	0	3.4645	-1.949307	-1.783059
59	6	0	6.030654	-1.10521	0.973623
60	1	0	4.510869	0.175674	1.795256
61	6	0	6.400353	-2.010914	-0.02871
62	1	0	5.676285	-2.984498	-1.819052
63	1	0	6.729851	-0.846599	1.761301
64	6	0	0.069986	-4.5376	0.316045
65	6	0	0.841935	-5.132131	-0.886042
66	6	0	0.79874	-4.91419	1.628119
67	6	0	-1.332184	-5.174744	0.34702
68	1	0	0.343239	-4.888186	-1.831248
69	1	0	1.867513	-4.752409	-0.940795
70	1	0	0.895135	-6.22463	-0.802164
71	1	0	0.26852	-4.512436	2.499109
72	1	0	0.8515	-6.004749	1.735187
73	1	0	1.822463	-4.52669	1.652309
74	1	0	-1.239822	-6.263208	0.435466
75	1	0	-1.92228	-4.823079	1.200712
76	1	0	-1.897545	-4.963983	-0.567839
77	6	0	-7.776168	-2.737474	-0.069077
78	6	0	7.784979	-2.680515	-0.087678
79	6	0	8.483985	-2.301903	-1.415258
80	1	0	8.623561	-1.217359	-1.488921
81	1	0	9.470839	-2.777094	-1.476223
82	1	0	7.905138	-2.623791	-2.287286
83	6	0	8.696363	-2.244409	1.075134
84	1	0	9.667208	-2.745754	0.991097
85	1	0	8.880959	-1.164176	1.06601
86	1	0	8.270585	-2.510719	2.049254
87	6	0	7.618152	-4.217261	-0.018043
88	1	0	7.133236	-4.516698	0.918146
89	1	0	7.011265	-4.599544	-0.84552
90	1	0	8.596913	-4.710225	-0.066973
91	6	0	-7.972668	-3.533979	1.24291

92	1	0	-7.882577	-2.89311	2.126211
93	1	0	-8.968179	-3.994316	1.264792
94	1	0	-7.226929	-4.332197	1.332082
95	6	0	-7.978539	-3.704112	-1.251264
96	1	0	-8.984215	-4.137127	-1.205968
97	1	0	-7.88209	-3.194204	-2.216592
98	1	0	-7.261333	-4.532523	-1.22849
99	6	0	-8.854267	-1.631428	-0.161905
100	1	0	-9.857702	-2.07467	-0.153033
101	1	0	-8.792618	-0.930243	0.676897
102	1	0	-8.745258	-1.054885	-1.087591

Total Enegy (RB3LYP) = -2011.75125435 Harterr

6. X-Ray Crystallography

Table S2 Summary of crystal data for **3b**.

Parameter	3b
Empirical formula	$C_{52}H_{50}$
Formula weight [g mol^{-1}]	674.92
Crystal system	Triclinic
Space group	*P*-1
***a* [Å]**	9.2562(4)
***b* [Å]**	13.5966(5)
***c* [Å]**	17.0228(7)
***α* [°]**	106.122(2)
***β* [°]**	91.734(2)
***γ* [°]**	106.113(2)
Volume [Å^3]	1963.85(14)
Z	2
Density, calcd [g cm^{-3}]	1.141
Temperature (K)	152.93
Reflections collected	28307
Parameters	546
R_{int}	0.0395
R[I>2σ(I)]^a	0.0843
wR[I>2σ(I)]^b	0.2503
GOF on F^2	1.051

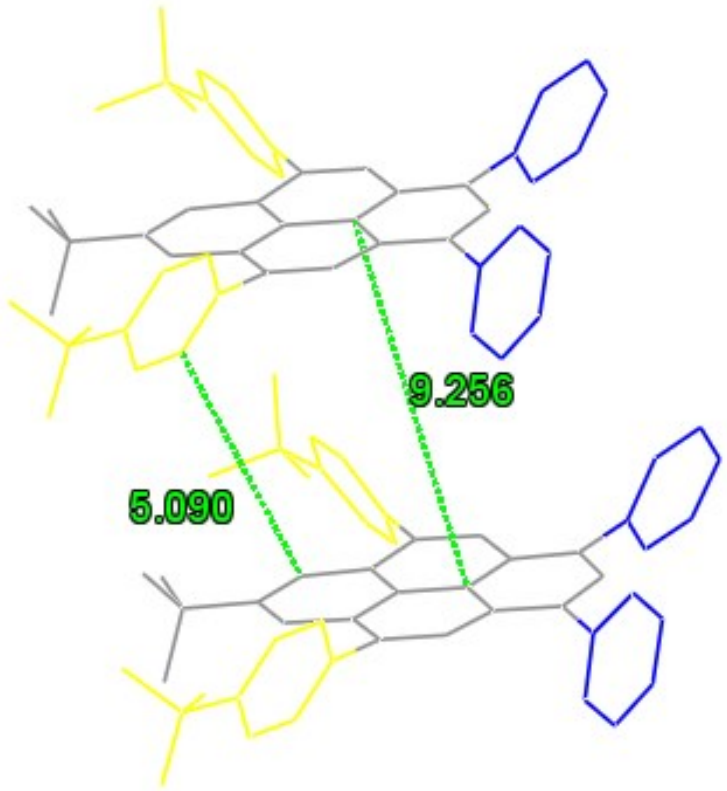


Figure S4. Packing distances and conformations in **3b**: The shortest contact between pyrene ring and a substituent on a neiboring molecule is 5.090Å, and the centroid • • • centroid distance is 9.256 Å

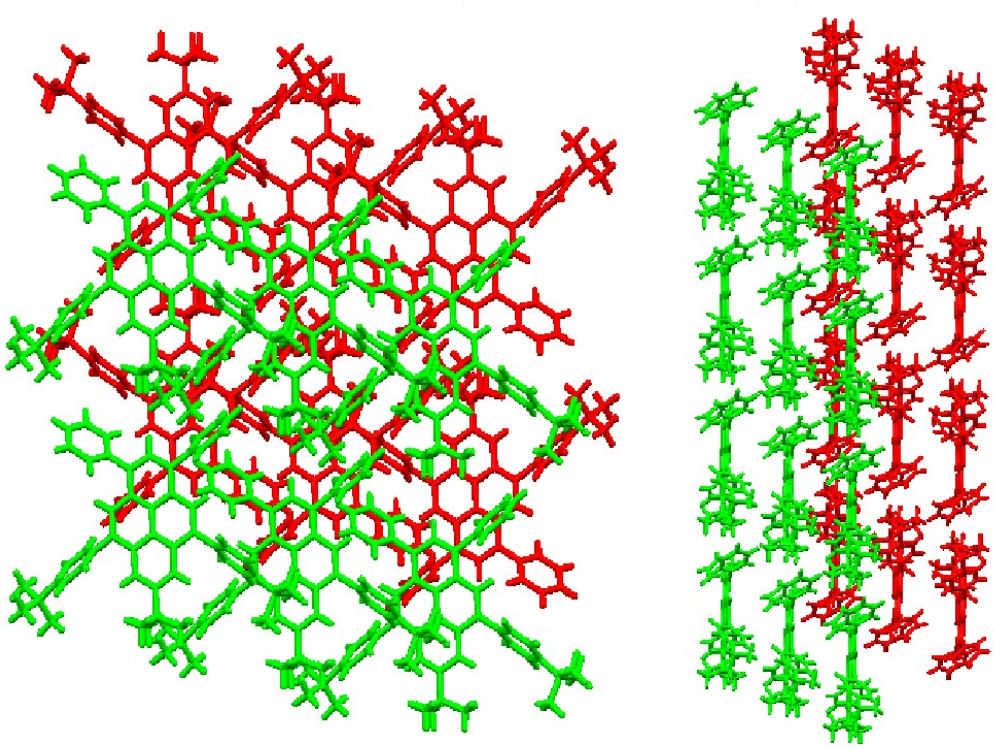
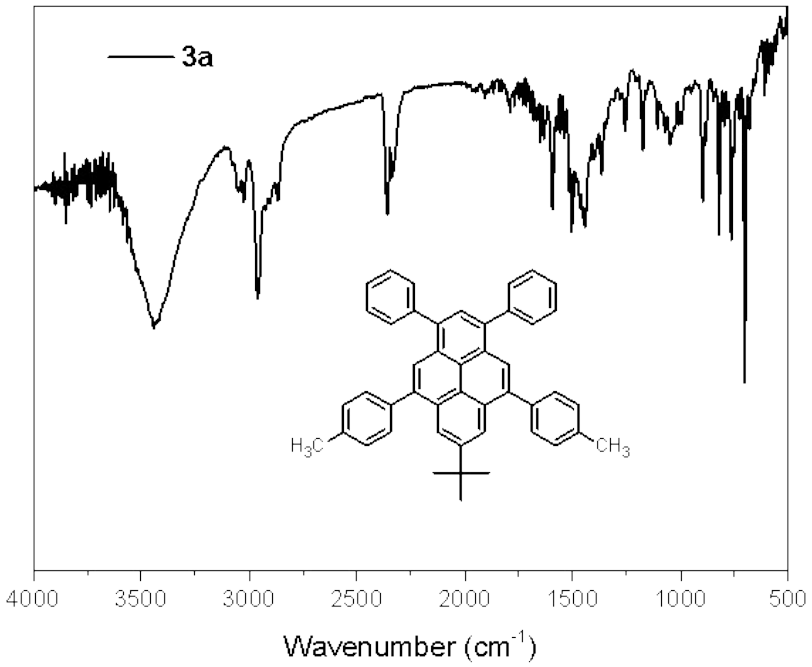


Figure S5. Packing plots for **3b**: Top view (left) and side view (right).

7. FT-IR spectrum



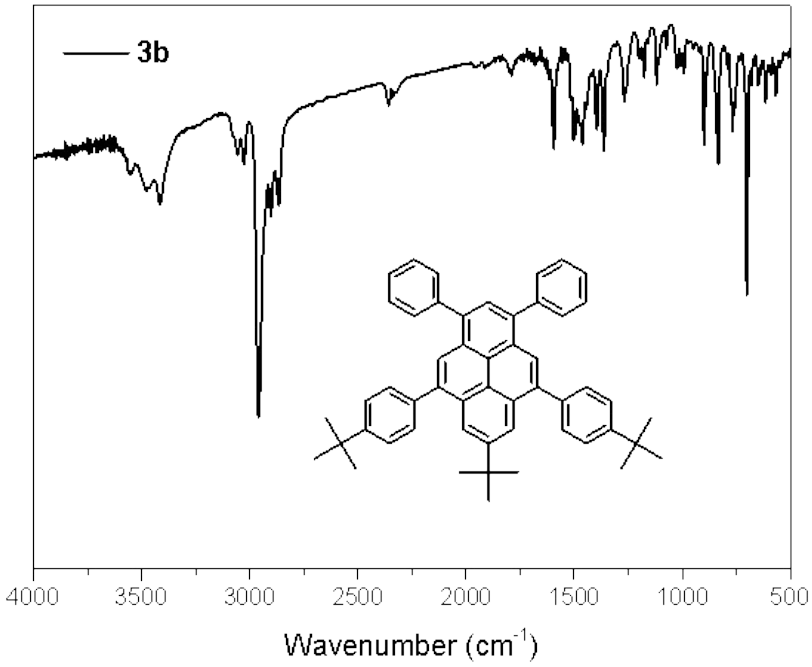


Figure S6. FT-IR spectra of the DA pyrenes **3a** and **3b**.

8. Photophysical Properties

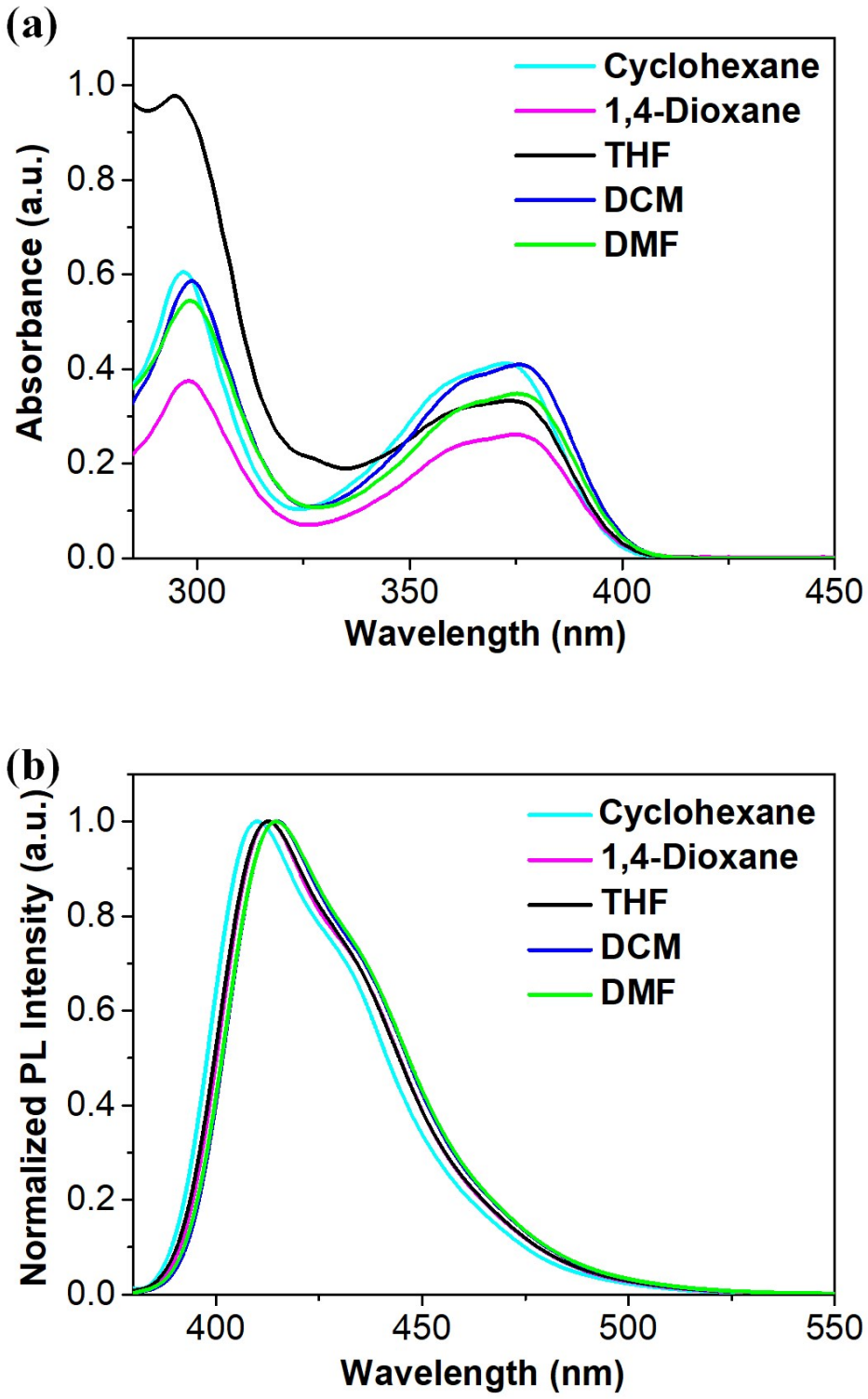


Figure S7. UV/Vis absorption (a) and fluorescence spectra (b) of the compound **3a** recorded in five different solvents.

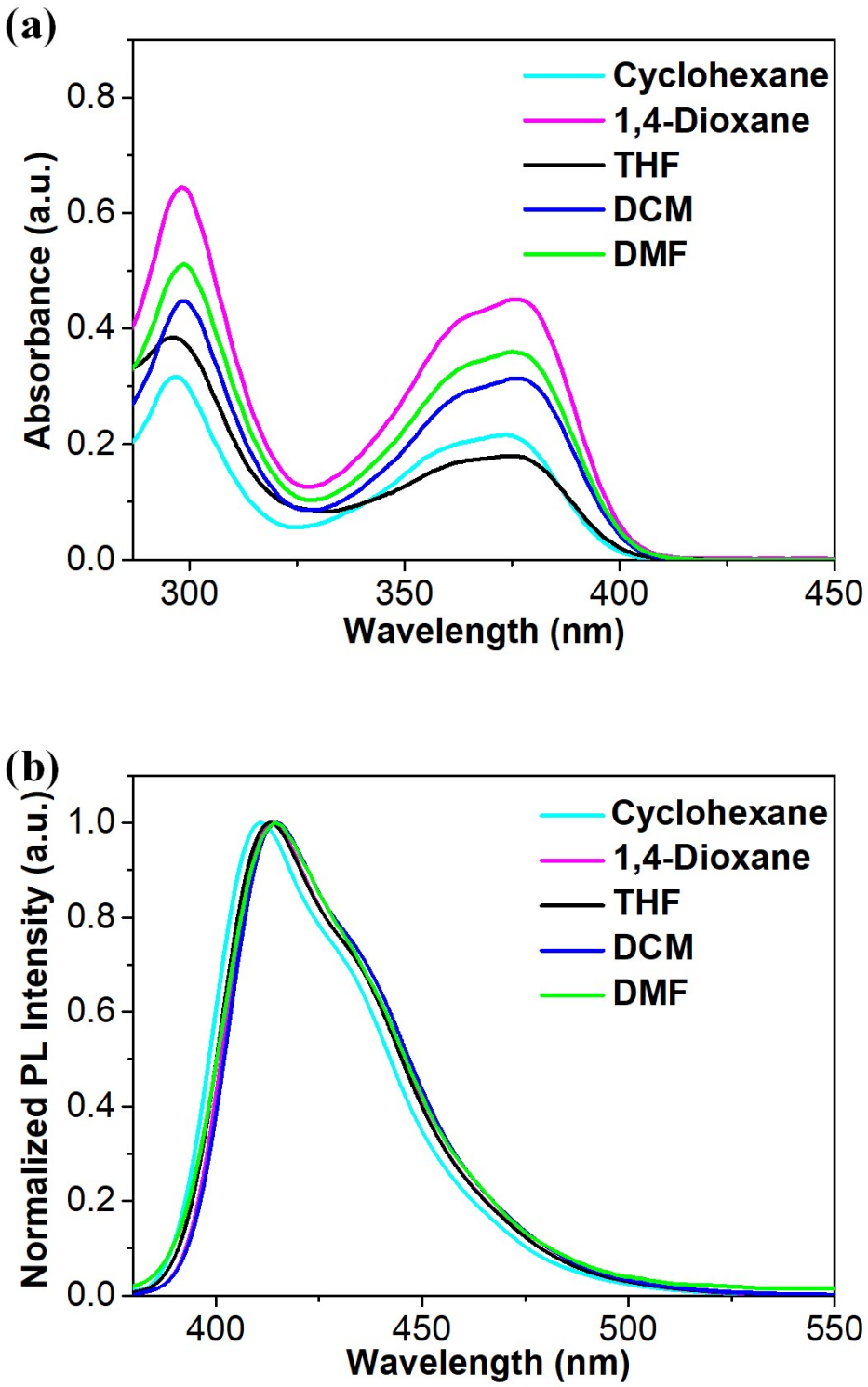


Figure S8. UV/Vis absorption (a) and fluorescence spectra (b) of the compound **3b** recorded in five different solvents.

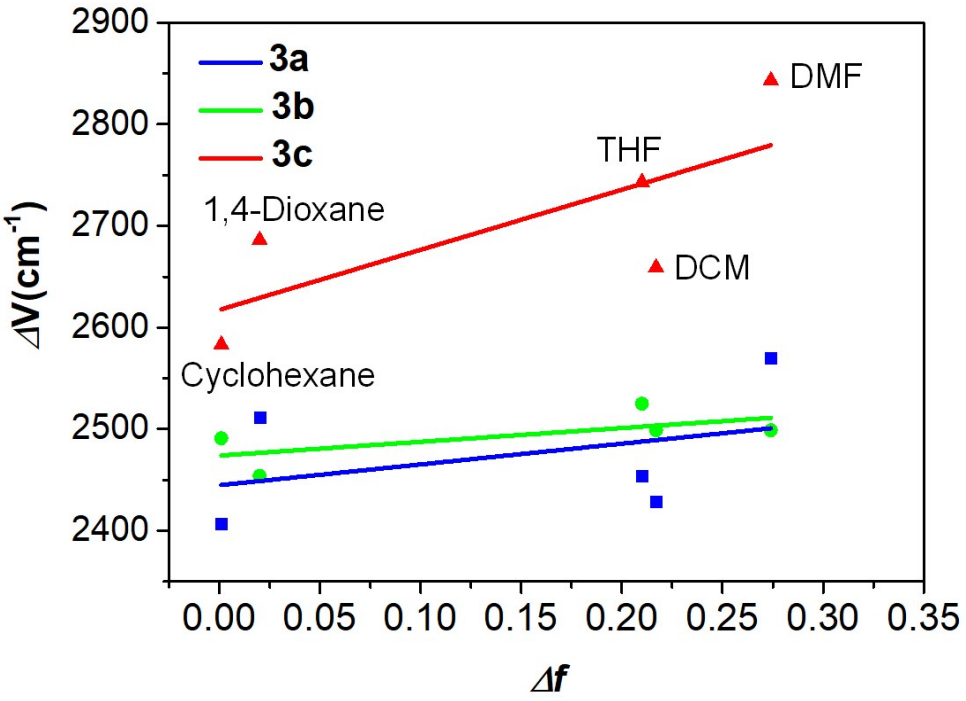


Figure S9. Liner correlation of orientation polarization (f) of solvent media with the stokes-shifts for the compounds **3a-c**.

Table S3 Spectroscopic parameter of **3a**, **3b** and **3c** in different organic solvents.

solvent	Δf	stokes shift [cm^{-1}]			$\lambda_{abs,\,max}$ [nm]			$\lambda_{em,\,max}$ [nm]			Φ_f [%]		
		3a	**3b**	**3c**[1]	**3a**	**3b**	**3c**[1]	**3a**	**3b**	**3c**[1]	**3a**	**3b**	**3c**[1]
Cyclohexane	0	2407	2491	2583	374	372	374	411	410	414	69	66	63
1,4-Dioxane	0.020	2512	2454	2686	375	375	375	414	413	417	76	76	71
THF	0.210	2454	2525	2743	375	374	375	413	413	418	66	62	60
CH_2Cl_2	0.217	2429	2499	2659	377	376	377	415	415	419	68	67	74
DMF	0.274	2570	2499	2843	375	376	376	415	415	421	67	78	74

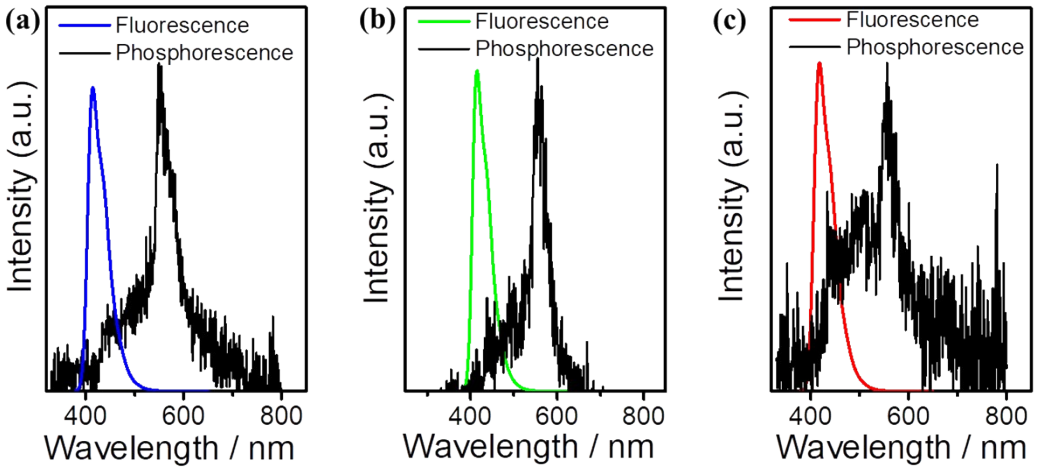


Figure S10. The fluorescence (at room temperature) and phosphorescence (at 77K) spectra of **3a-c i**n toluene.

9. OLED Performance

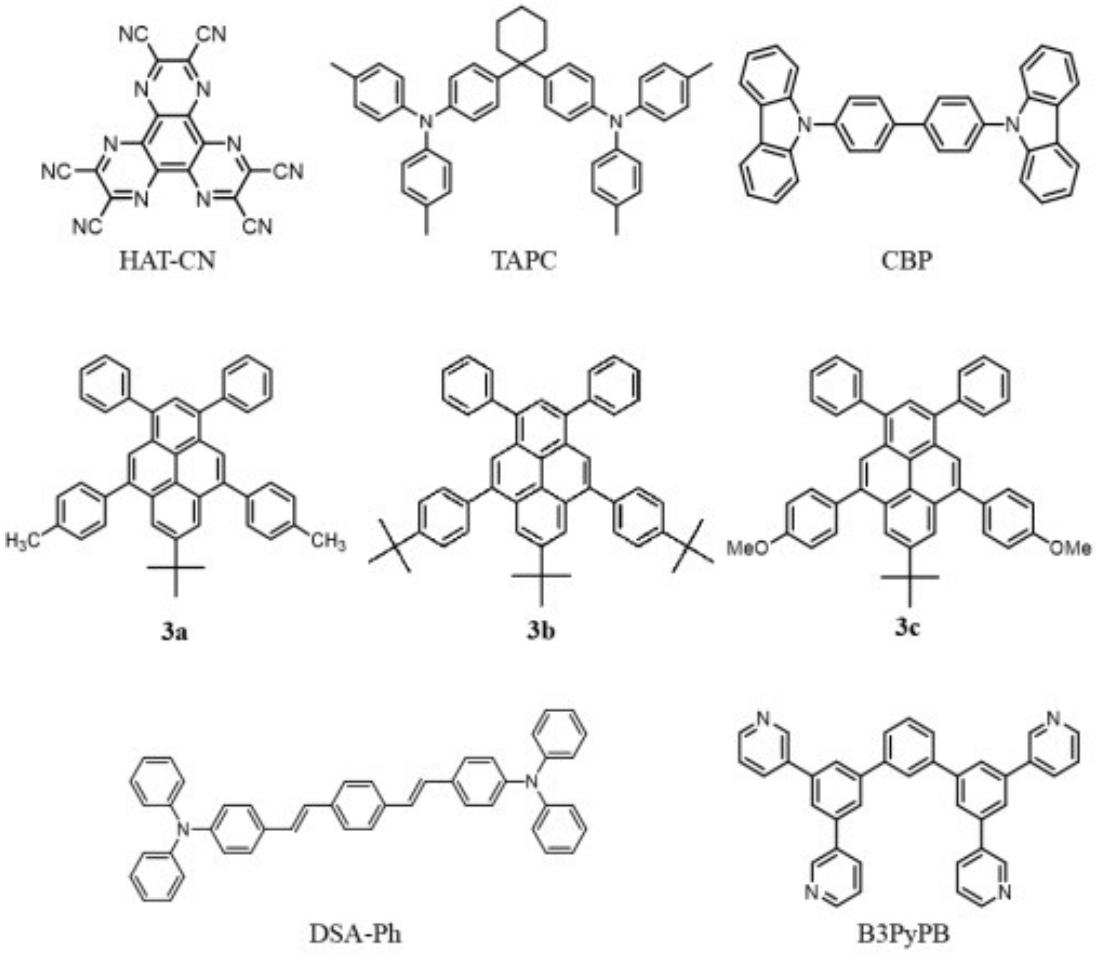


Figure S11. Molecular structures of the materials used in devices A-D.

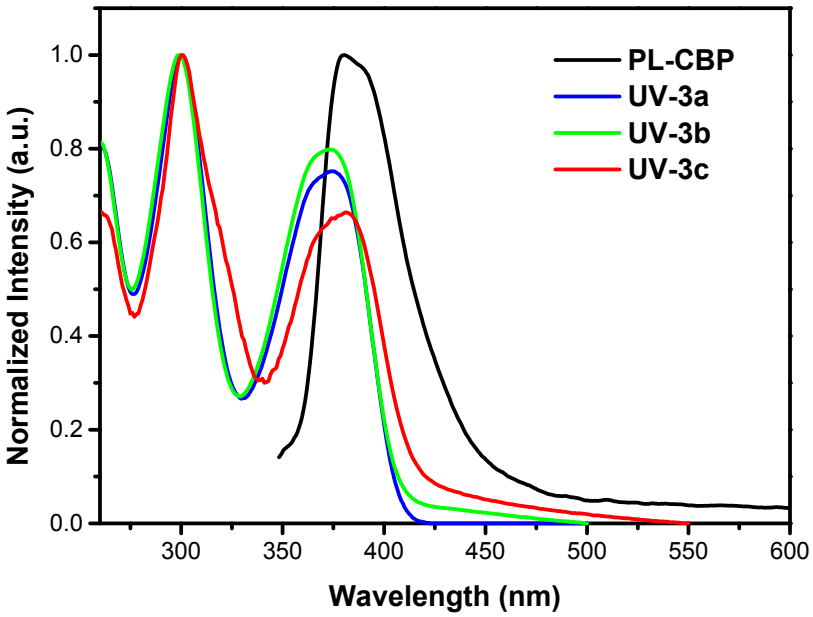


Figure S12. UV-vis absorption spectra of **3a-c** in a neat film and PL of CBP in a film.

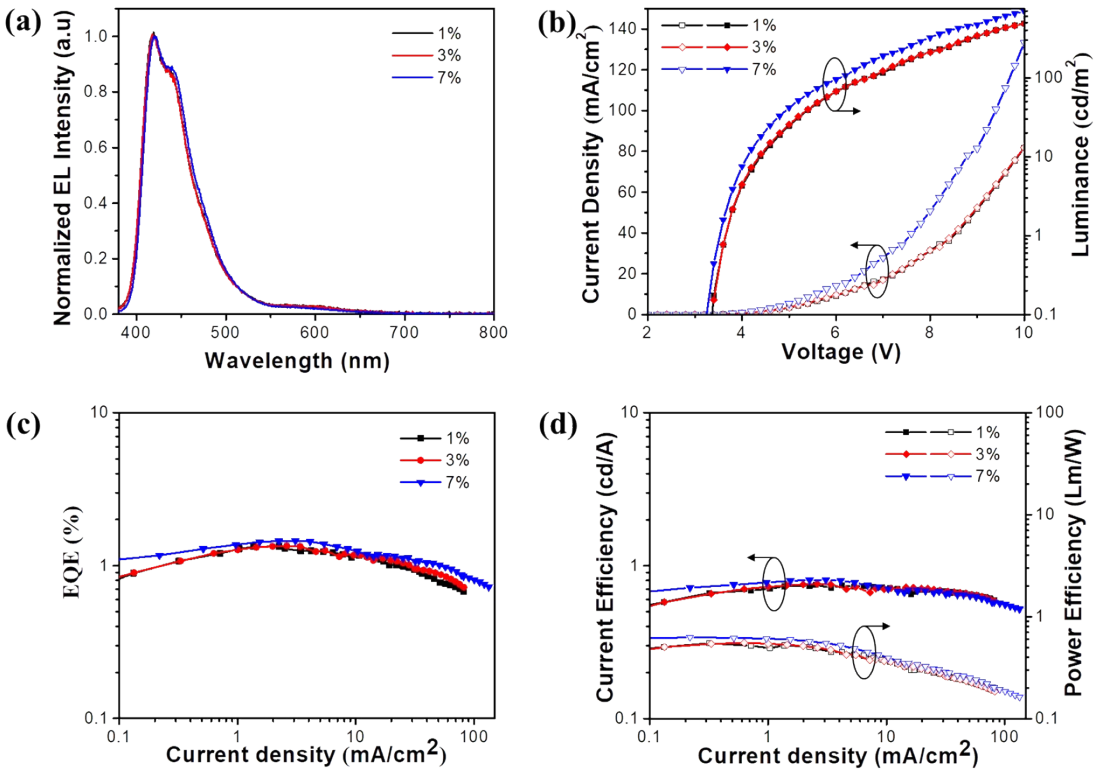


Figure S13. Doping concentration dependent EL performance of device based-**3a**: (a) EL spectra; (b) J-V-L curve; (c) CE-L-PE curve; (d) EQE-L curve.

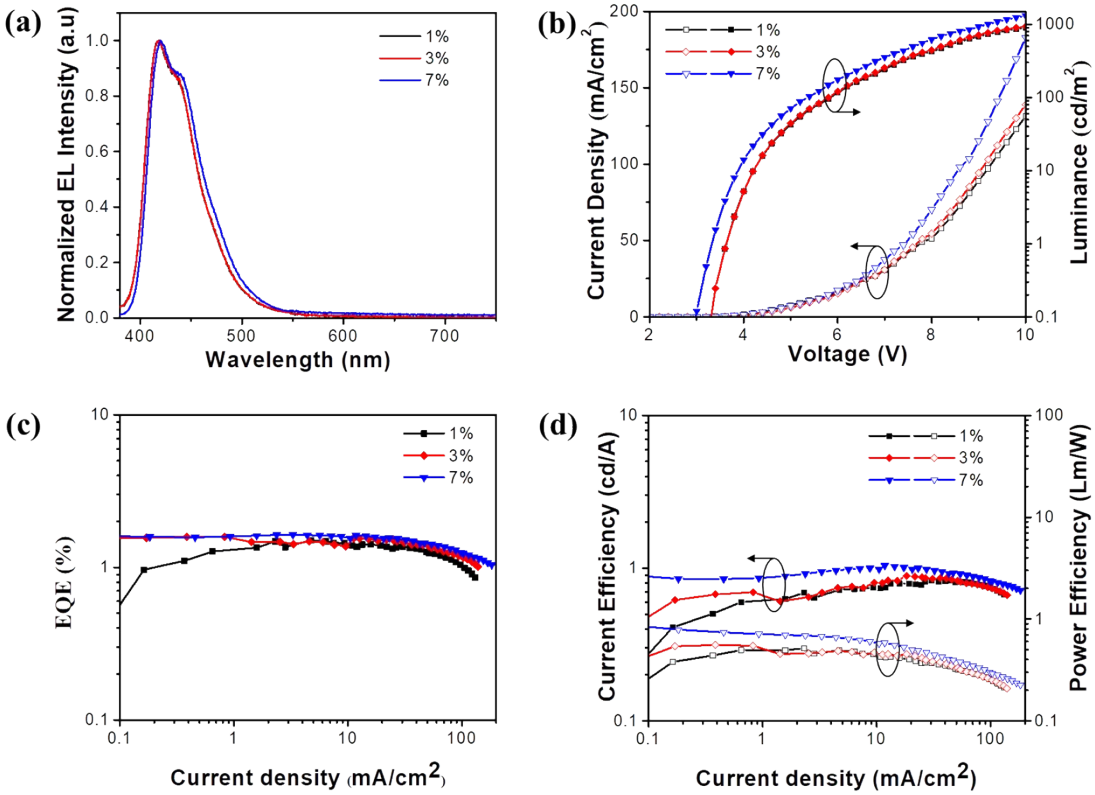


Figure S14. Doping concentration dependent EL performance of device based-**3b**: (a) EL spectra; (b) J-V-L curve; (c) CE-L-PE curve; (d) EQE-L curve.

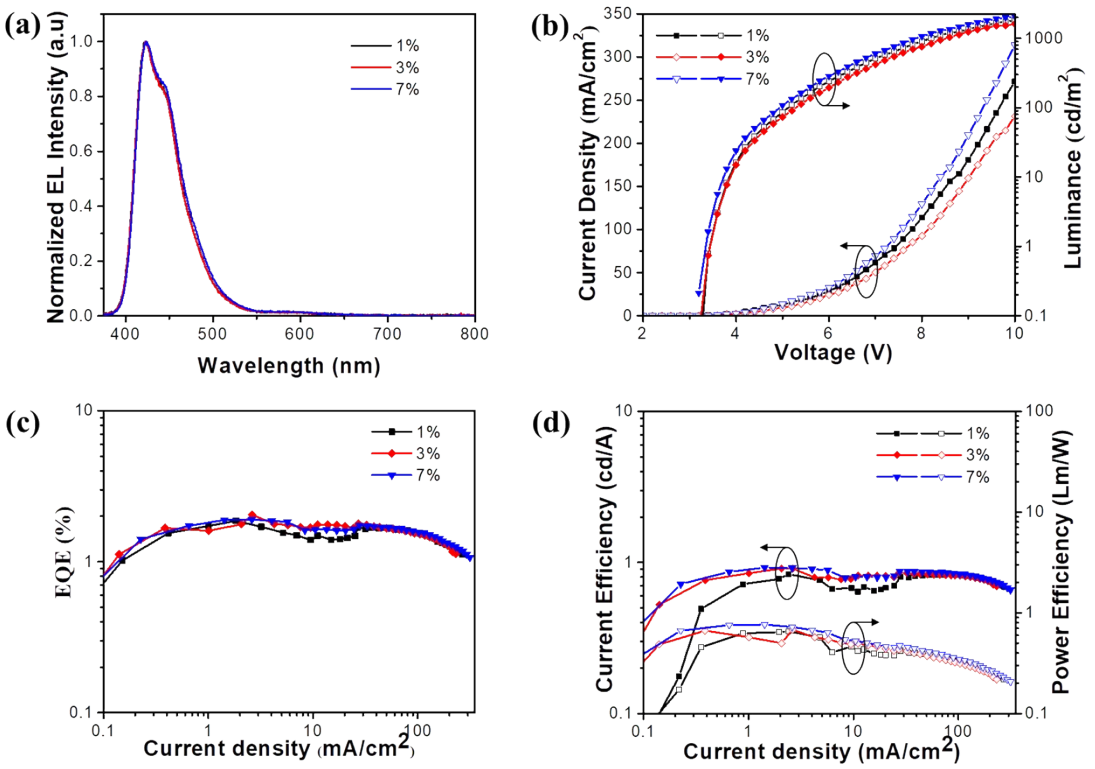


Figure S15. Doping concentration dependent EL performance of device based-**3c**: (a) EL spectra; (b) J-V-L curve; (c) CE-L-PE curve; (d) EQE-L curve.

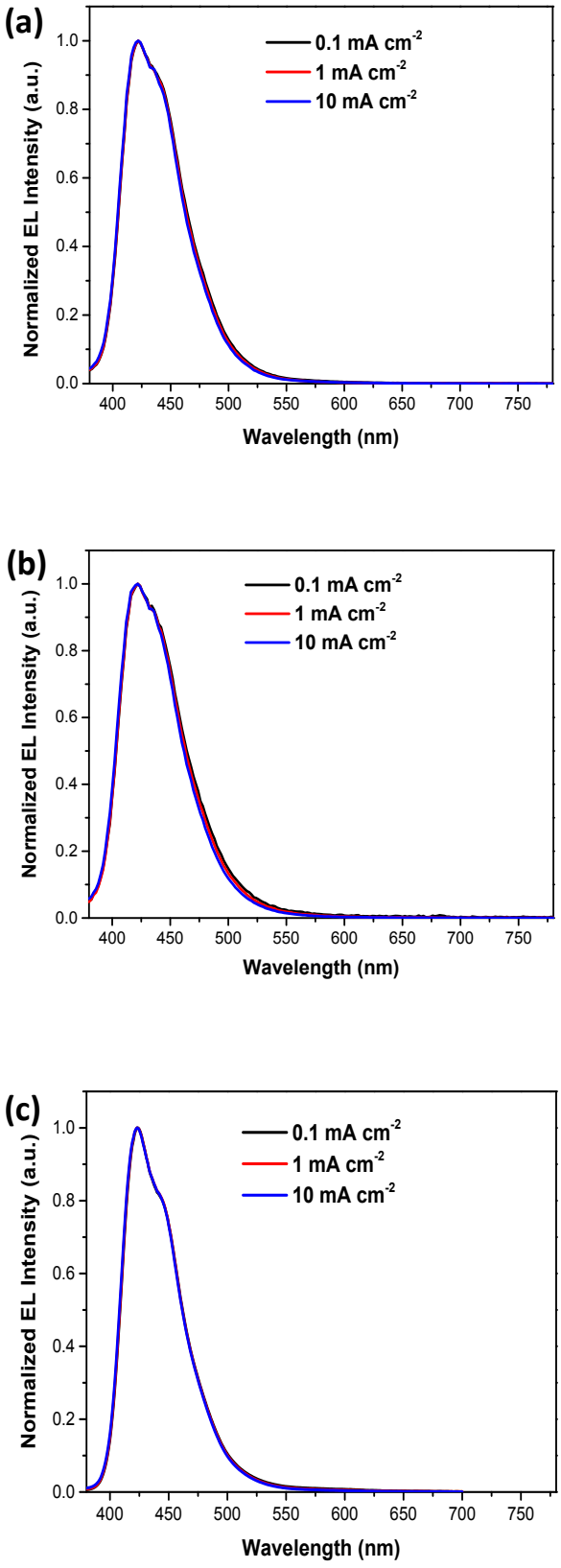


Figure S16. EL spectra stability of device A (a), device B (b) and device C (c) under different current densities.

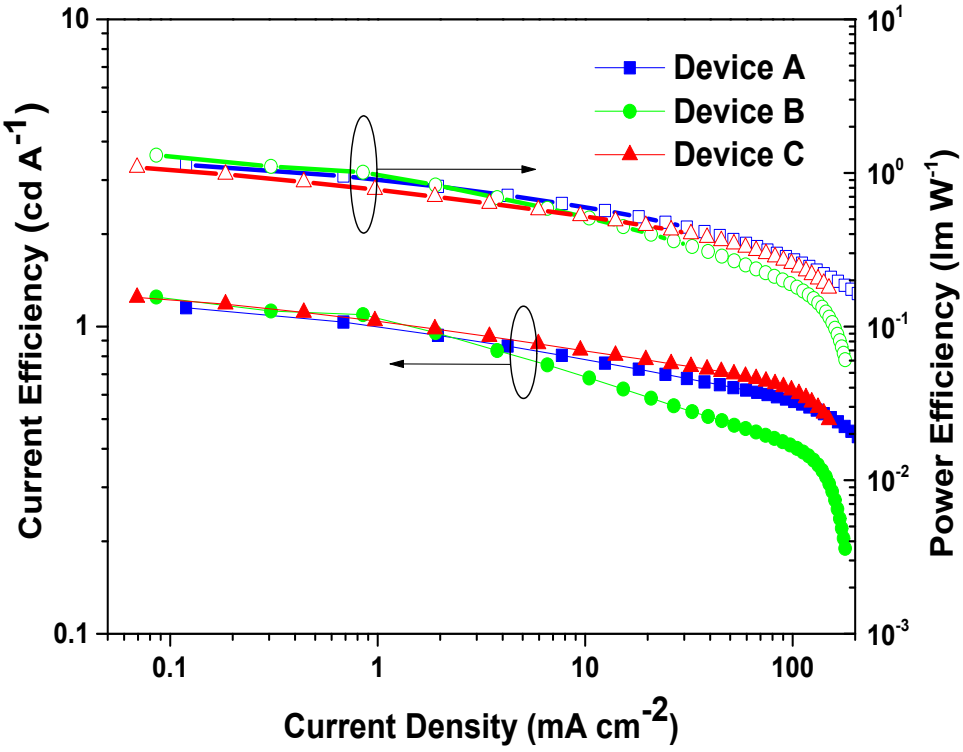


Figure S17. Performance of representative devices current efficiency (CE) and power efficiency (PE) versus current density characteristics of device A-C.

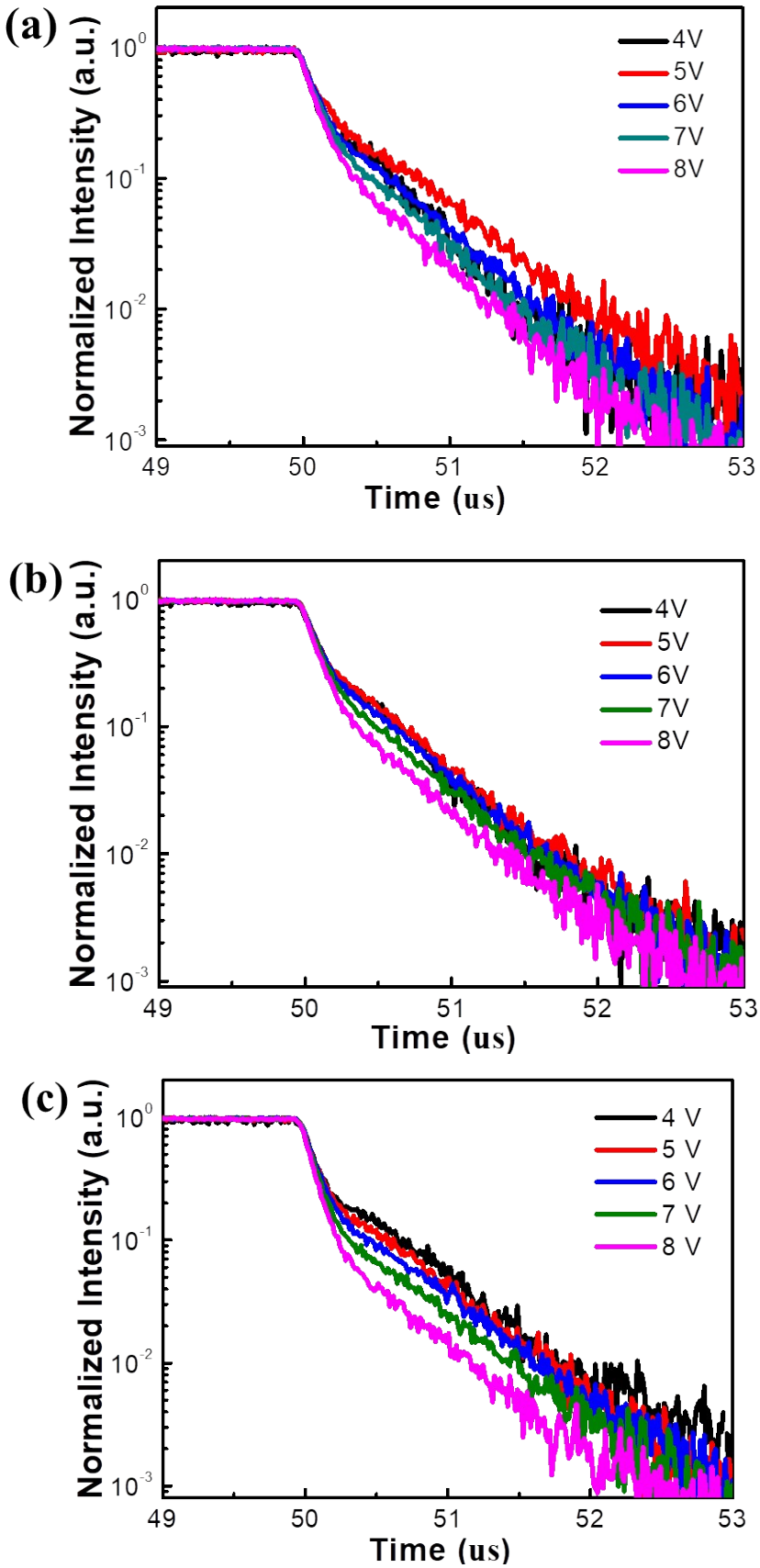


Figure S18. Transient EL decay of device A (a), device B (b) and device C (c) at different voltages.

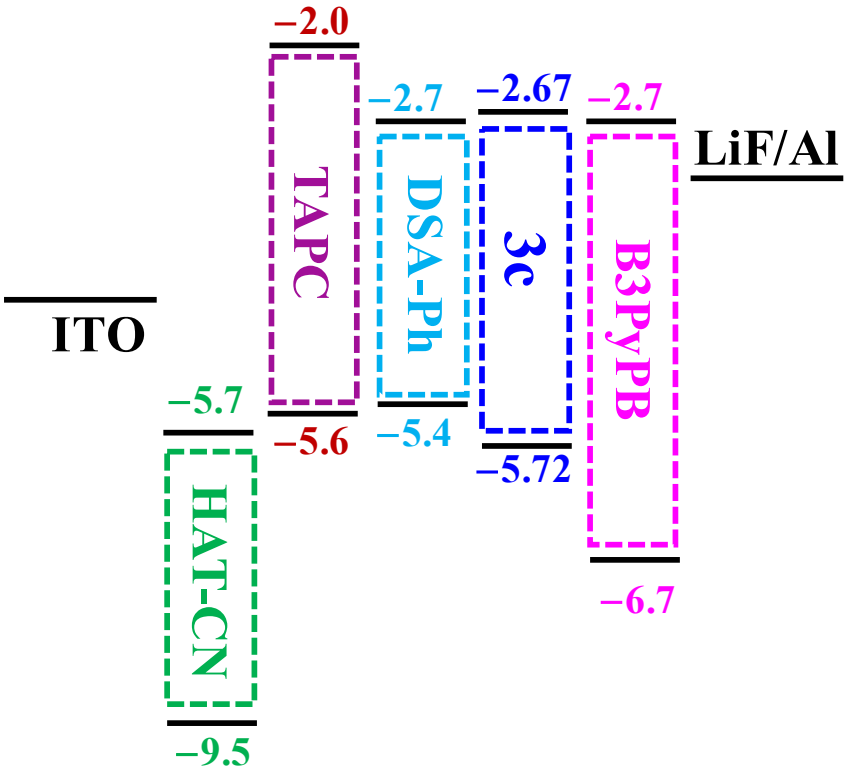


Figure S19. Energy level diagrams of device D.

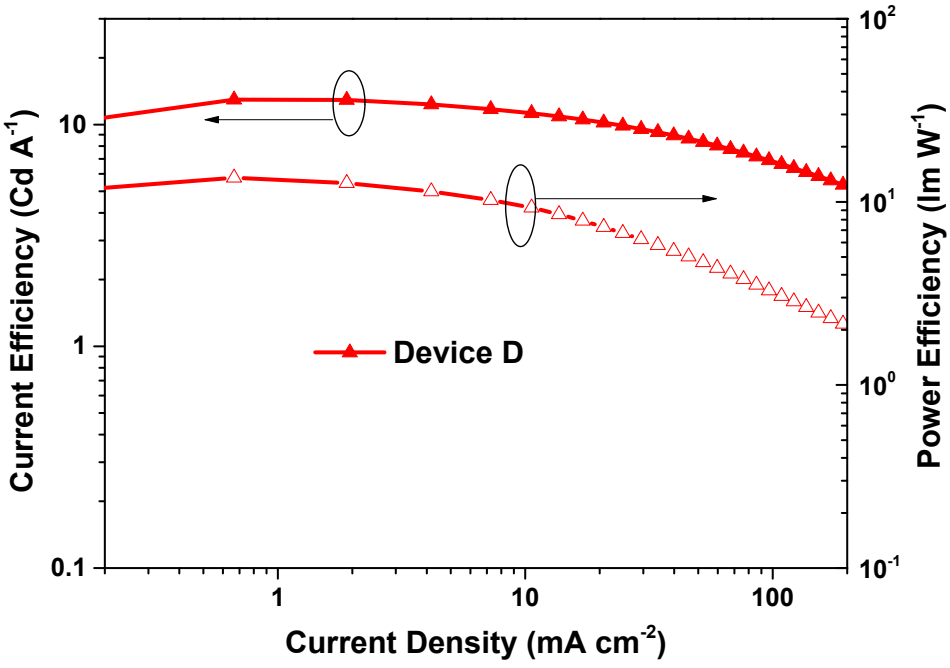


Figure S20. Current efficiency (CE) and power efficiency (PE) versus current density characteristics of device D.

10. NMR Spectra

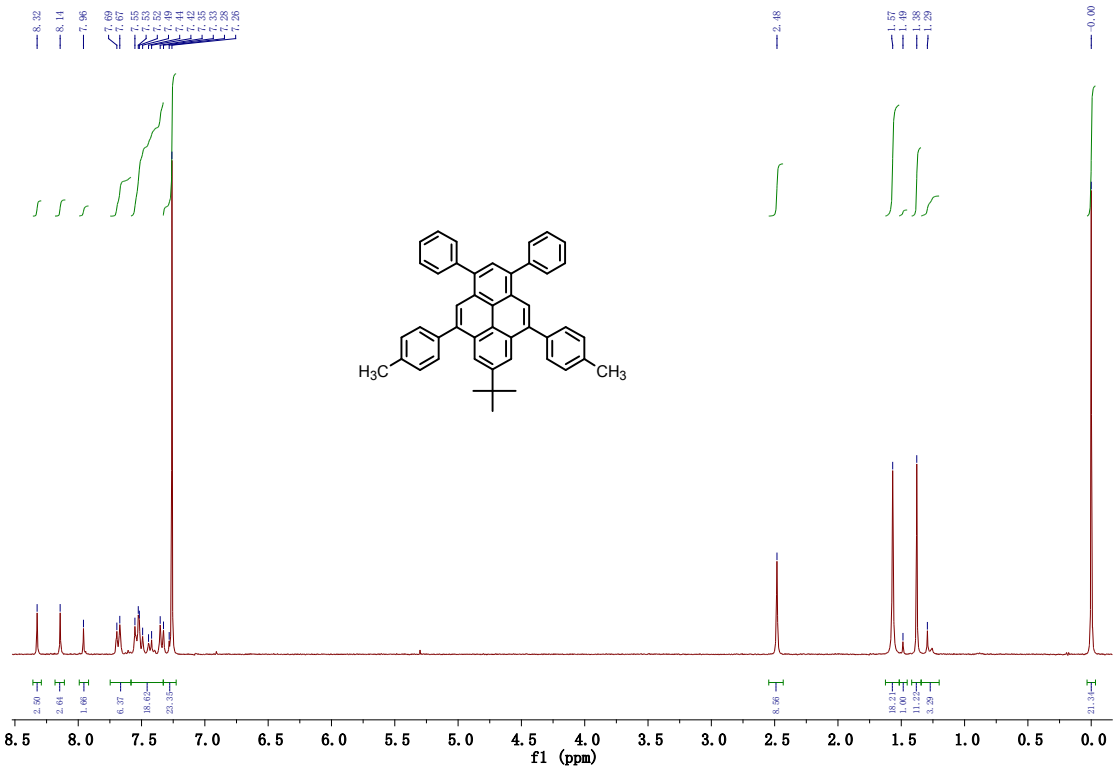


Figure S21. ^{1}H NMR spectrum of **3a** (300 MHz, $CDCl_3$, *r.t.*).

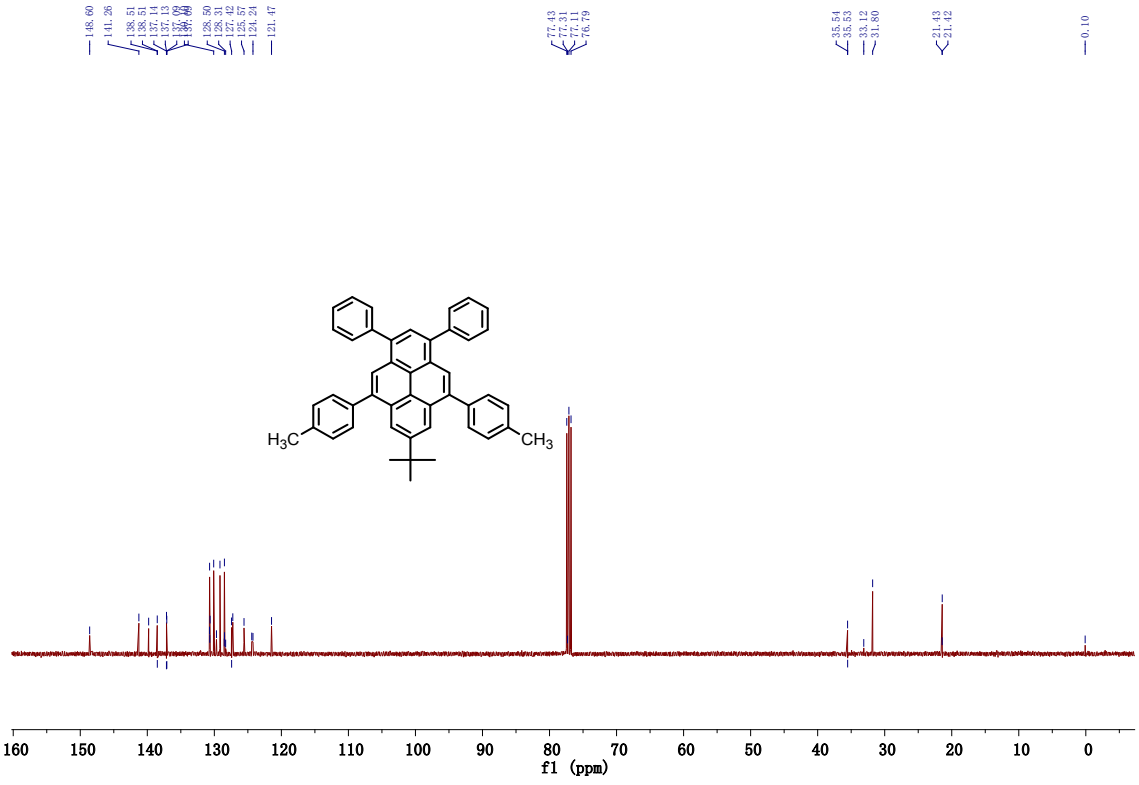


Figure S22. ^{13}C NMR spectra of **3a** (100MHz, $CDCl_3$, *r.t.*)

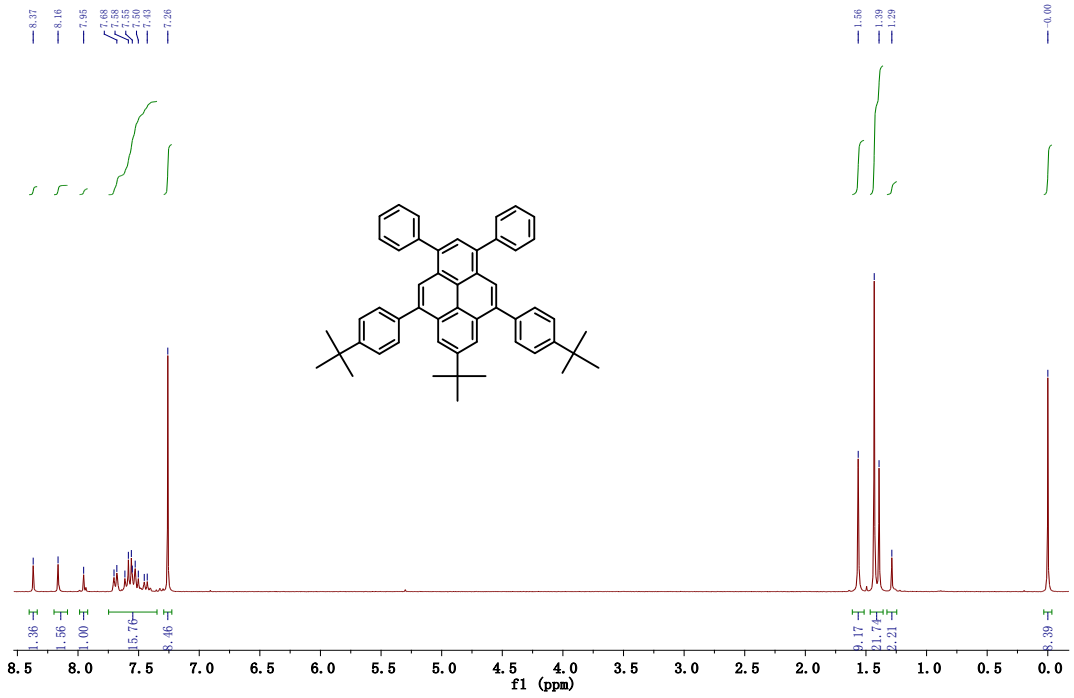


Figure S23. ^{1}H NMR spectrum of **3b** (300 MHz, $CDCl_3$, *r.t.*).

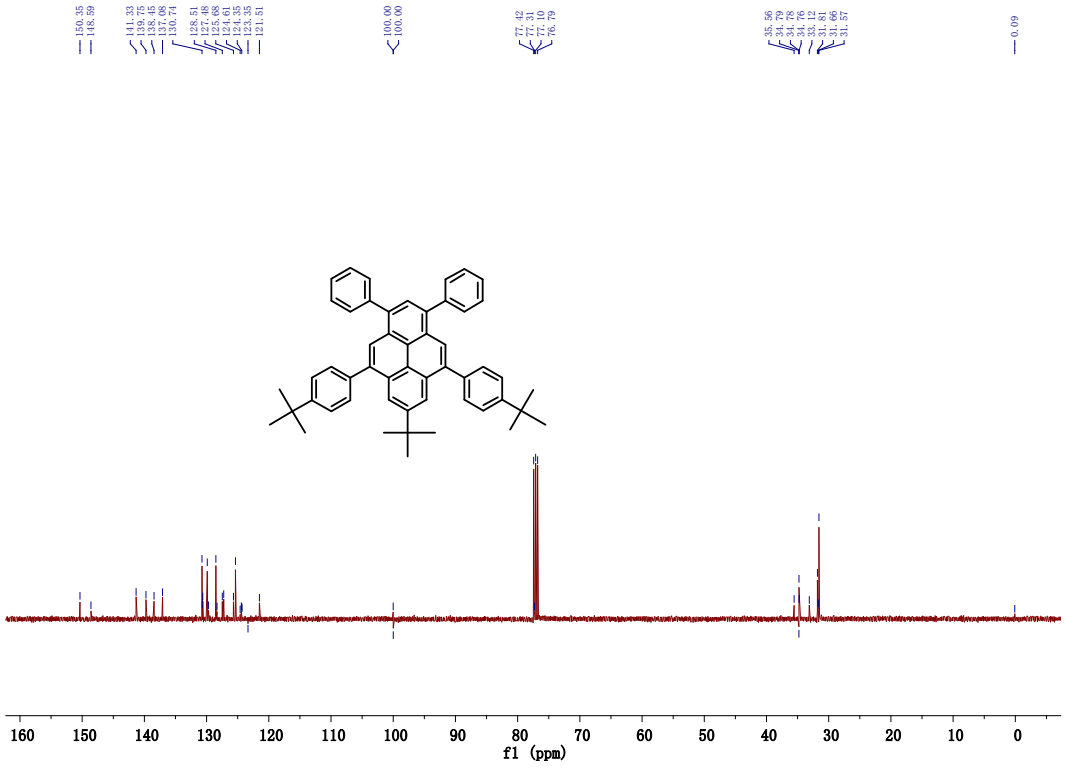


Figure S24. ^{13}C NMR spectra of **3b** (100MHz, $CDCl_3$, *r.t.*)

11. Mass Spectra

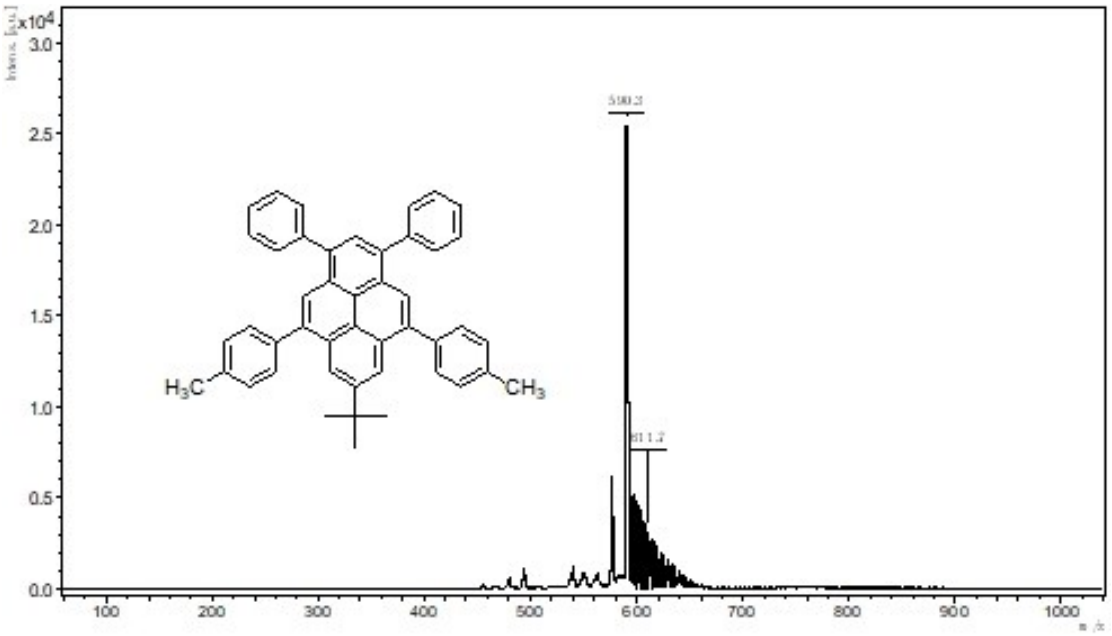


Figure S25. Mass spectra of **3a**.

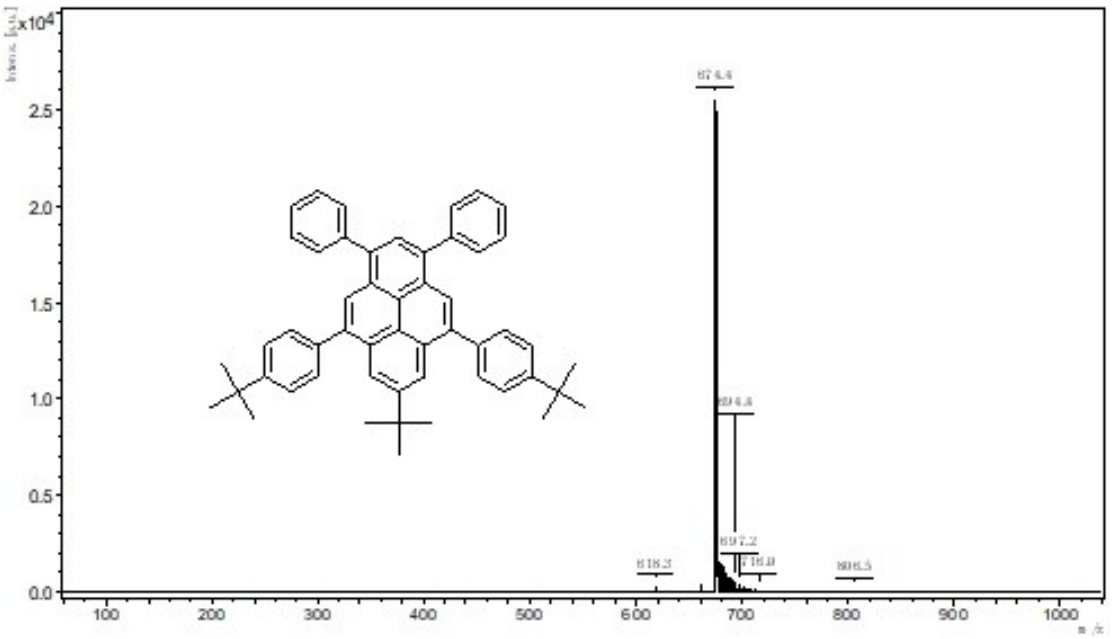


Figure S26. Mass spectra of **3b**.

12. References

1. R. Liu, H. Ran, Z. Zhao, X. Yang, J. Zhang, L. Chen, H. Sun and J.-Y. Hu, *ACS Omega*, **2018**, *3*, 5866.