Supplementary Data for

Color-Tunable Emission from Violet-Blue to Pure-Blue Based on 5,9-Disubstituted Pyrene Derivatives by Engineering of Aryl-Side Groups

Fuli Xie,[a] Xilin Yang,[b] Pengcheng Jin,[a] Xiao-Tian Wang,[a] Huijuan Ran,[a] Rong Zheng,[a] Zheng Lei,[a] Hailu Zhang,[a] Shi-Jian Su[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, PR China*

[b]*State Key Laboratory of Luminescent Materials and Devices and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Wushan Road 381, Guangzhou 510640, PR China*

E-mail: hujianyong@snnu.edu.cn; mssjsu@scut.edu.cn

Content

1. **Materials and Instruments**

2. **Synthesis and Characterization**

3. **DFT Calculations**

4. **Photophysical Properties**

5. **Device Performance**

6. **NMR Spectra**

7. **Mass Spectra**

8. **References**

1. Materials and Instruments

All commercially available reagents and chemicals were used as received without further purification. The intermediate of 7-*tert*-butyl-5,9- dibromo-1,3-diphenylpyrene was synthesized in the light of reported literature [S1], and the arylboronic acids were commercialized. The detailed apparatus and methods of the characterization techniques for these compounds were presented in Ref.[S2] ^{1}H NMR spectra were measured on a JEOL 400 MHz FT-400 NMR spectrometer. Mass spectra were obtained with a Bruke microflex mass spectrometer in MALDI-TOF mode. Thermogravimetric analysis (TGA) analysis was performed on a USA Waters Q600 under nitrogen atmosphere at a heating rate of 10 ^{o}C min $^{-1}$ and Differential scanning calorimetry (DSC) analysis was carried out on METTLER TOLEDU DSC at a heating rate of 10 ^{o}C min^{-1}. Cyclic voltammetry (CV) were performed on a BAS 100W Bioanalytical Systems, using a platinum wire as the auxiliary electrode, a glass carbon disk as the working electrode and a silver/Silver chloride (Ag/Ag^{+}) as the reference electrode, standardized for the redox couple ferricinium/ferrocene (Fc/Fc^{+}). Absorption spectrum were measured on a PerkinElmer UV-Lambda 950 spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu F-7000 spectrofluorometer. Absolute PL quantum yields were measured with a Japan Hamamatsu C9920-06G. Fluorescence lifetimes were determined with a Edinburgh FLS1000 Quantaurus-Tau time-

resolved spectrometer. All the OLEDs were charactered by HAMAMATSU PHOTONIC MUlTI-CHANNEL ANALYZER PMA-12, along with a Keithley 2400 Source Meter. The area of the single device was 3 mm × 3 mm and the testing conditions were under ambient conditions. The frontier orbitals of the molecules based on the ground state geometries were calculated at B3LYP/6-31G* by Gaussian 16 program.

2. Synthesis and Characterization

Synthesis of 7-tert-butyl-1,3,5,9-tetraphenylpyrene (Py-BBz): A mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (681 mg, 1.2 mmol),[S1] phenylboronic acid (484 mg, 4.0 mmol) in toluene (50 mL), and ethanol (20 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 16h. After cooling to room temperature, the mixture was quenched with water, extracted with toluene, and washed with water. The organic extracts were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography eluting with petroleum ether (PE) and recrystallized from CH_2Cl_2/hexane (v/v, 1/1) to give **Py-BBz** (465 mg, 69%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 9H), 7.50–7.40 (m, 4H), 7.57–7.50 (m, 8H), 8.17 (s, 2H), 7.65 (dd, J = 8.1, 1.2 Hz, 4H), 7.70 (dd, J = 8.0, 1.0 Hz, 4H), 7.98 (s, 1H), 8.17 (s, 2H), 8.29 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.75, 141.44, 141.21, 139.89, 137.33, 130.73, 130.59, 130.26, 129.81, 128.56, 128.50, 127.52, 127.39, 127.34, 125.68, 124.58, 124.24, 121.49, 35.54, 31.78. MS: m/z calcd. for $C_{44}H_{24}$ 562.2431; Found 562.4787 [M^+].

Synthesis of 7-tert-butyl-5,9-di(naphthalen-2-yl)-1,3-diphenylpyrene (Py-B2Na): adopting the above method with a mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (681 mg, 1.2 mmol) and 2-

naphthaleneboronic acid (687 mg, 4.0 mmol) and obtained **Py-B2Na** (492 mg, 61%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9H), 7.42 (t, J = 7.4 Hz, 2H), 7.58–7.49 (m, 8H), 7.72 (d, J = 8.2 Hz, 4H), 7.79 (dd, J = 8.4, 1.6 Hz, 2H), 7.98–7.91 (m, 3H), 8.00 (d, J = 8.4 Hz, 3H), 8.12 (s, 1H), 8.27 (s, 2H), 8.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.93, 141.15, 139.80, 139.06, 137.46, 133.74, 132.82, 130.71, 128.84, 128.63, 128.55, 128.24, 127.89, 127.71, 127.43, 127.36, 126.39, 126.17, 126.11, 121.65, 35.51, 31.74. MS: m/z calcd. for $C_{52}H_{38}$ 663.1472; Found 662.4326 [M^+].

Synthesis of 7-tert-butyl-5,9-di(phenanthren-9-yl)-1,3-diphenylpyrene (**Py-B9Ph)**: according to the above method, A mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (681 mg, 1.2 mmol), 9-phenanthreneboronic acid (887 mg, 4.0 mmol) and obtained **Py-B9Ph** (439 mg, 49%). MS: m/z calcd. for $C_{60}H_{42}$ 762.3021; Found 762.2671 [M^+].

Synthesis of 7-tert-butyl-5,9-di(phenanthren-2-yl)-1,3-diphenylpyrene (Py-B2Ph): A mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (681 mg, 1.2 mmol), 2-phenanthreneboronic acid (887 mg, 4.0 mmol) and obtained **Py-B2Ph** (467 mg, 51%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9H), 7.43 (t, J = 6.8 Hz, 2H), 7.54 (t, J = 7.6 Hz, 4H), 7.65 (dd, J = 11.4, 4.4 Hz, 2H), 7.78–7.68 (m, 6H), 7.88–7.80 (m, 4H), 8.01–7.92 (m, 4H), 8.04 (s, 1H), 8.18 (d, J = 1.7 Hz, 2H), 8.33 (s, 2H), 8.40 (s, 2H), 8.79 (d, J = 8.2 Hz, 2H), 8.86 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100

MHz, $CDCl_3$): δ = 148.99, 141.16, 139.71, 139.61, 137.51, 132.35, 132.25, 130.75, 130.72, 130.33, 129.77, 129.64, 129.03, 128.78, 128.59, 127.50, 127.44, 127.41, 127.16, 126.88, 126.79, 126.12, 124.77, 124.37, 122.87, 122.71, 121.68, 35.55, 31.76. MS: m/z calcd. for $C_{60}H_{42}$ 762.3458; Found 762.4091 [M^+].

Synthesis of 7-tert-butyl-5,9-di(anthracen-2-yl)-1,3-diphenylpyrene (Py-B2An): A mixture of 7-*tert*-butyl-1,3-diphenyl-5,9-dibromopyrene (681 mg, 1.2 mmol), 4-methylphenylboronic acid (887 mg, 4.0 mmol) and a yellow powder **Py-2An** was obtained (410 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9H), 7.42 (t, J = 7.4 Hz, 2H), 7.57–7.47 (m, 8H), 7.81–7.72 (m, 6H), 8.03 (s, 1H), 8.11–8.04 (m, 4H), 8.16 (d, J = 8.8 Hz, 2H), 8.28 (s, 2H), 8.34 (s, 2H), 8.39 (s, 2H), 8.53 (d, J = 5.6 Hz, 4H). MS: m/z calcd,. for $C_{60}H_{42}$ 762.3356; Found 762.2873 [M^+].

3. DFT Calculations

Table S1-1. Atom coordinates and absolute energies for **Py-BBz** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.442929	-3.323173	-0.035289
2	6	0	0.056822	-3.140973	-0.026664
3	6	0	-0.53236	-1.863258	-0.006999
4	6	0	0.298265	-0.703465	-0.018004
5	6	0	1.716827	-0.880541	-0.020048
6	6	0	2.24996	-2.176681	-0.022194
7	6	0	-1.966022	-1.68969	0.037354
8	6	0	-0.274963	0.607195	-0.017895
9	6	0	-1.697425	0.755796	-0.018419
10	6	0	-2.500566	-0.430246	0.032079
11	6	0	-2.254773	2.062797	-0.008691
12	6	0	-1.390439	3.160655	0.026844
13	6	0	0.001798	3.045967	0.007536
14	6	0	0.581964	1.751711	-0.007142
15	6	0	1.999934	1.53794	0.028662
16	6	0	2.563503	0.293166	0.00881
17	1	0	2.651894	2.404008	0.074544
18	1	0	-0.602207	-4.000009	-0.028613
19	1	0	3.329801	-2.283644	-0.015114
20	1	0	-3.578474	-0.323675	0.096625
21	1	0	-1.824555	4.15797	0.001312
22	6	0	0.805251	4.304251	-0.014907
23	6	0	0.605549	5.283652	0.970492
24	6	0	1.720253	4.576697	-1.046141
25	6	0	1.310107	6.486523	0.93988
26	1	0	-0.098423	5.08717	1.77702
27	6	0	2.42374	5.779383	-1.078741
28	1	0	1.867121	3.842538	-1.835353
29	6	0	2.223618	6.738811	-0.084295
30	1	0	1.145951	7.226471	1.720949
31	1	0	3.123281	5.971275	-1.890082
32	1	0	2.772709	7.677736	-0.110547
33	6	0	-3.719115	2.332877	-0.057828
34	6	0	-4.305997	3.207274	0.872118
35	6	0	-4.540473	1.786362	-1.059871
36	6	0	-5.664669	3.512697	0.814116
37	1	0	-3.688646	3.631672	1.661536
38	6	0	-5.898174	2.093209	-1.120366
39	1	0	-4.101433	1.130605	-1.808439

40	6	0	-6.467717	2.956478	-0.182326
41	1	0	-6.096969	4.184001	1.553702
42	1	0	-6.511376	1.663753	-1.910319
43	1	0	-7.528081	3.195312	-0.229941
44	6	0	-2.881489	-2.873819	0.10863
45	6	0	-2.939395	-3.669806	1.262467
46	6	0	-3.719166	-3.193845	-0.968964
47	6	0	-3.811756	-4.755087	1.336541
48	1	0	-2.295728	-3.429795	2.106802
49	6	0	-4.591793	-4.280206	-0.896681
50	1	0	-3.68016	-2.585025	-1.870409
51	6	0	-4.641472	-5.06392	0.256776
52	1	0	-3.84608	-5.357758	2.242197
53	1	0	-5.233684	-4.51305	-1.744269
54	1	0	-5.321772	-5.91116	0.314276
55	6	0	4.055748	0.162167	0.034765
56	6	0	4.753243	-0.331832	-1.077957
57	6	0	4.787558	0.557257	1.163328
58	6	0	6.144254	-0.428923	-1.061837
59	1	0	4.196393	-0.638558	-1.961642
60	6	0	6.179393	0.46087	1.180614
61	1	0	4.256487	0.940978	2.032357
62	6	0	6.862309	-0.03255	0.06818
63	1	0	6.6679	-0.810753	-1.9363
64	1	0	6.729782	0.772434	2.066376
65	1	0	7.947687	-0.108397	0.081182
66	6	0	2.08544	-4.708078	-0.060183
67	6	0	2.944852	-4.848844	-1.34076
68	6	0	2.988402	-4.89471	1.182416
69	6	0	1.03723	-5.835064	-0.05398
70	1	0	2.330092	-4.732503	-2.242848
71	1	0	3.735944	-4.08999	-1.369654
72	1	0	3.421352	-5.837202	-1.378299
73	1	0	2.405296	-4.811439	2.108978
74	1	0	3.456715	-5.8872	1.161086
75	1	0	3.790038	-4.14672	1.217727
76	1	0	1.540422	-6.810022	-0.069815
77	1	0	0.409714	-5.793996	0.84575
78	1	0	0.381897	-5.789173	-0.933348

Table S1-2. Atom coordinates and absolute energies for **Py-B2Na** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.265985	-3.096021	-0.145391
2	6	0	0.979377	-2.472284	-0.033774
3	6	0	1.111971	-1.074161	0.036503
4	6	0	-0.055249	-0.254681	-0.027721
5	6	0	-1.333884	-0.884834	-0.145552
6	6	0	-1.405053	-2.283096	-0.201848
7	6	0	2.407467	-0.436716	0.158356
8	6	0	0.052237	1.167416	0.012139
9	6	0	1.338341	1.776385	0.120229
10	6	0	2.492097	0.92863	0.192934
11	6	0	1.433691	3.186786	0.157483
12	6	0	0.263365	3.948219	0.084696
13	6	0	-1.008638	3.375988	-0.024672
14	6	0	-1.126732	1.968297	-0.063089
15	6	0	-2.395912	1.308787	-0.17438
16	6	0	-2.519864	-0.052493	-0.211515
17	1	0	-3.290884	1.923042	-0.224251
18	1	0	1.883964	-3.066764	-0.005214
19	1	0	-2.384901	-2.742286	-0.303753
20	1	0	3.468585	1.395492	0.287508
21	1	0	0.345334	5.032602	0.113003
22	6	0	-2.204747	4.272284	-0.10027
23	6	0	-2.656279	4.763185	-1.335002
24	6	0	-2.882864	4.664513	1.064063
25	6	0	-3.752026	5.624007	-1.403796
26	1	0	-2.139532	4.465531	-2.244863
27	6	0	-3.978886	5.525124	0.996547
28	1	0	-2.543341	4.289642	2.027179
29	6	0	-4.41621	6.008482	-0.237782
30	1	0	-4.085704	5.995064	-2.370366
31	1	0	-4.49035	5.818522	1.910627
32	1	0	-5.270068	6.67997	-0.290822
33	6	0	2.75132	3.887131	0.271502
34	6	0	3.282654	4.216362	1.52796
35	6	0	3.470029	4.255348	-0.876197
36	6	0	4.495868	4.896951	1.634171
37	1	0	2.735625	3.935038	2.42519
38	6	0	4.683253	4.936208	-0.771285
39	1	0	3.069041	4.004863	-1.85596
40	6	0	5.199493	5.260009	0.484538
41	1	0	4.890448	5.14424	2.61722

42	1	0	5.224425	5.214574	-1.672904
43	1	0	6.14492	5.7912	0.566879
44	6	0	-3.87957	-0.664529	-0.332366
45	6	0	-4.467766	-1.321551	0.733045
46	6	0	-4.605199	-0.554527	-1.552692
47	6	0	-5.769552	-1.878734	0.639626
48	1	0	-3.926372	-1.411402	1.673377
49	6	0	-5.869005	-1.083306	-1.677022
50	1	0	-4.142623	-0.039955	-2.391613
51	6	0	-6.385077	-2.550801	1.729848
52	6	0	-6.489919	-1.758265	-0.593541
53	1	0	-6.410255	-0.987584	-2.616626
54	6	0	-7.649891	-3.080751	1.608858
55	1	0	-5.837629	-2.640216	2.666355
56	6	0	-7.792808	-2.316122	-0.685392
57	6	0	-8.360915	-2.962629	0.389253
58	1	0	-8.108052	-3.592977	2.451737
59	1	0	-8.337349	-2.223338	-1.623357
60	1	0	-9.359454	-3.38513	0.305018
61	6	0	3.655482	-1.253769	0.255754
62	6	0	4.70254	-1.062345	-0.62579
63	6	0	3.797291	-2.228852	1.285637
64	6	0	5.908049	-1.80559	-0.526052
65	1	0	4.60665	-0.322693	-1.418673
66	6	0	4.952287	-2.964234	1.411617
67	1	0	2.976073	-2.3785	1.98284
68	6	0	6.990188	-1.615865	-1.426533
69	6	0	6.039333	-2.779769	0.516434
70	1	0	5.047483	-3.697984	2.210106
71	6	0	8.147764	-2.351415	-1.304049
72	1	0	6.889054	-0.875654	-2.218097
73	6	0	7.246163	-3.521314	0.615906
74	6	0	8.277393	-3.31344	-0.272723
75	1	0	8.968081	-2.195012	-2.000731
76	1	0	7.343327	-4.25996	1.409576
77	1	0	9.19618	-3.88864	-0.185131
78	6	0	-0.437195	-4.616113	-0.223929
79	6	0	-1.376908	-5.086352	0.913846
80	6	0	-1.076956	-4.979305	-1.583233
81	6	0	0.888966	-5.389109	-0.094846
82	1	0	-0.948957	-4.847505	1.895727
83	1	0	-2.36097	-4.60837	0.848973
84	1	0	-1.525541	-6.172958	0.859739
85	1	0	-0.437499	-4.658235	-2.415416

86	1	0	-1.220293	-6.065312	-1.659666
87	1	0	-2.055598	-4.498165	-1.706772
88	1	0	0.700547	-6.463944	-0.208754
89	1	0	1.609606	-5.095097	-0.86772
90	1	0	1.354864	-5.234924	0.886616

Table S1-3. Atom coordinates and absolute energies for **Py-B9Ph** Standard orientation.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-3.619366	375239 0.	497490
2	6	0	0.683858	-2.882923	0.584999
3	6	0	1.008751	-1.485877	0.536943
4	6	0	-0.109766	-0.567737	0.356116
5	6	0	-1.462845	-1.085312	0.267163
6	6	0	-1.658941	-2.475821	0.352472
7	6	0	2.456712	-0.930151	0.633951
8	6	0	0.099936	0.852099	0.256542
9	6	0	1.411281	1.376135	0.313642
10	6	0	2.50901	0.479565	0.481359
11	6	0	1.613984	2.771167	0.202215
12	6	0	0.529924	3.627975	0.038976
13	6	0	-0.767295	3.133895	-0.018732
14	6	0	-0.998104	1.739348	0.087516
15	6	0	-2.318523	1.189868	0.021753
16	6	0	-2.602719	-0.174549	0.097079
17	1	0	-3.107749	1.904803	-0.121717
18	1	0	1.479771	-3.597418	0.691584
19	1	0	-2.661994	-2.870319	0.296713
20	1	0	3.48018	0.961852	0.519806
21	1	0	0.700402	4.700657	-0.045154
22	6	0	3.01225	3.351308	0.259572
23	6	0	3.571222	3.731334	1.485534
24	6	0	3.757486	3.51389	-0.915023
25	6	0	4.860508	4.267487	1.536118
26	1	0	2.996952	3.607089	2.402433
27	6	0	5.046385	4.050561	-0.863101
28	1	0	3.327515	3.220426	-1.871752
29	6	0	5.598457	4.427828	0.362369
30	1	0	5.289908	4.561002	2.493504
31	1	0	5.621107	4.175082	-1.780469
32	1	0	6.603886	4.845689	0.402369
33	6	0	-1.913233	4.109188	-0.199241
34	6	0	-2.354038	4.454231	-1.482605

35	6	0	-2.53909	4.678271	0.917294
36	6	0	-3.408255	5.356311	-1.64706
37	1	0	-1.871723	4.015831	-2.354956
38	6	0	-3.592636	5.581269	0.751222
39	1	0	-2.199622	4.415338	1.918466
40	6	0	-4.02765	5.920574	-0.530866
41	1	0	-3.746594	5.619959	-2.648559
42	1	0	-4.074643	6.021433	1.623852
43	1	0	-4.849561	6.623957	-0.659846
44	6	0	-7.211314	-3.774271	-2.003699
45	6	0	-5.942547	-3.283563	-1.771811
46	6	0	-5.741227	-2.131278	-0.97157
47	6	0	-6.850152	-1.471447	-0.40257
48	6	0	-8.142653	-1.995154	-0.654901
49	6	0	-8.321154	-3.120828	-1.437547
50	6	0	-4.420735	-1.624926	-0.734592
51	6	0	-6.614719	-0.291992	0.409511
52	6	0	-5.281767	0.199987	0.631508
53	6	0	-4.12951	-0.487283	0.039483
54	6	0	-5.132247	1.357878	1.454082
55	1	0	-4.141936	1.742823	1.650535
56	6	0	-6.21672	2.000208	2.014841
57	6	0	-7.510418	1.518027	1.785126
58	6	0	-7.698834	0.400306	1.003729
59	1	0	-3.6342	-2.173321	-1.218426
60	1	0	-7.359855	-4.660542	-2.619798
61	1	0	-5.07268	-3.779098	-2.204122
62	1	0	-9.017989	-1.510048	-0.230867
63	1	0	-9.323767	-3.506229	-1.619679
64	1	0	-6.071833	2.881572	2.637535
65	1	0	-8.365042	2.027431	2.22929
66	1	0	-8.713025	0.044375	0.845354
67	6	0	-0.988771	-4.899455	0.550305
68	6	0	-1.917378	-5.115923	1.755837
69	6	0	-1.693162	-5.256827	-0.767972
70	6	0	0.269277	-5.763678	0.705709
71	1	0	-1.411385	-4.841084	2.694139
72	1	0	-2.828703	-4.506945	1.670528
73	1	0	-2.221629	-6.17279	1.828268
74	1	0	-1.027912	-5.080797	-1.627106
75	1	0	-1.989403	-6.31837	-0.776414
76	1	0	-2.60057	-4.651869	-0.910428
77	1	0	-0.001204	-6.830942	0.740183
78	1	0	0.95874	-5.617901	-0.138292

79	1	0	0.806979	-5.524737	1.630394
80	6	0	8.877871	-2.723357	1.431175
81	6	0	7.555123	-2.626268	1.816524
82	6	0	6.579714	-2.03867	0.969479
83	6	0	6.976064	-1.547271	-0.274741
84	6	0	8.335008	-1.653296	-0.661228
85	6	0	9.270194	-2.23065	0.17481
86	6	0	5.192591	-1.960157	1.413206
87	6	0	5.962126	-0.955145	-1.084897
88	6	0	4.610449	-0.872649	-0.619964
89	6	0	4.061494	-1.338043	0.647931
90	6	0	3.652272	-0.264031	-1.479165
91	1	0	2.622738	-0.197675	-1.131119
92	6	0	3.98559	0.235383	-2.719687
93	6	0	5.310244	0.15015	-3.165675
94	6	0	6.269651	-0.430145	-2.365013
95	1	0	5.190789	-2.368503	2.367835
96	1	0	9.61693	-3.176971	2.090888
97	1	0	7.239795	-3.003594	2.788603
98	1	0	8.658812	-1.275271	-1.627536
99	1	0	10.312218	-2.30399	-0.134315
100	1	0	3.22836	0.69503	-3.353399
101	1	0	5.578043	0.544435	-4.145309
102	1	0	7.289932	-0.482356	-2.73455

Table S1-4. Atom coordinates and absolute energies for **Py-B2Ph** Standard orientation.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.002799	. -3.027544	-0.009854
2	6	0	-1.182902	-2.325275	-0.004401
3	6	0	-1.25776	-0.936593	-0.004147
4	6	0	0.000563	-0.229527	-0.005242
5	6	0	1.259914	-0.934779	-0.004481
6	6	0	1.187405	-2.323523	-0.00469
7	6	0	-2.543463	-0.1804	-0.003194
8	6	0	-0.000414	1.198714	-0.004188
9	6	0	-1.212421	1.903849	-0.002608
10	6	0	-2.433964	1.166872	-0.002112
11	6	0	-1.208871	3.305368	-0.001209
12	6	0	-0.002284	3.984304	-0.001
13	6	0	1.205241	3.30696	-0.001732
14	6	0	1.210678	1.905491	-0.003107
15	6	0	2.433265	1.170186	-0.002962

16	6	0	2.544593	-0.176947	-0.003842
17	1	0	3.290956	1.790629	-0.002623
18	1	0	-2.062246	-2.90347	0.002269
19	1	0	2.067899	-2.900141	0.001862
20	1	0	-3.292682	1.78601	-0.001261
21	1	0	-0.00298	5.062115	0.000216
22	6	0	2.487247	4.100023	-0.000721
23	6	0	3.08451	4.47312	1.198426
24	6	0	3.084087	4.476519	-1.199258
25	6	0	4.261523	5.207609	1.19953
26	1	0	2.628289	4.18621	2.1323
27	6	0	4.260801	5.211038	-1.198845
28	1	0	2.627169	4.192256	-2.133591
29	6	0	4.851922	5.577316	0.000814
30	1	0	4.716589	5.490981	2.135323
31	1	0	4.715459	5.497275	-2.133955
32	1	0	5.766564	6.148791	0.001279
33	6	0	-2.491965	4.096662	0.000364
34	6	0	-3.090413	4.471744	-1.197569
35	6	0	-3.088646	4.46953	1.200115
36	6	0	-4.268433	5.204614	-1.196297
37	1	0	-2.634325	4.187646	-2.132367
38	6	0	-4.266374	5.202422	1.202078
39	1	0	-2.630807	4.183717	2.133524
40	6	0	-4.858669	5.570696	0.003608
41	1	0	-4.724417	5.489545	-2.131168
42	1	0	-4.720896	5.485849	2.13811
43	1	0	-5.774098	6.140907	0.004991
44	6	0	0.003609	-4.57758	0.021052
45	6	0	0.008849	-5.041503	1.491374
46	1	0	-0.864833	-4.671374	2.01207
47	1	0	0.006581	-6.124166	1.545382
48	1	0	0.888649	-4.675472	2.004656
49	6	0	-1.242864	-5.152705	-0.684085
50	1	0	-1.138413	-6.224559	-0.791319
51	1	0	-2.144181	-4.970728	-0.115475
52	1	0	-1.36452	-4.722261	-1.669647
53	6	0	1.245596	-5.151488	-0.692382
54	1	0	1.348843	-4.735084	-1.686135
55	1	0	2.153161	-4.952264	-0.140047
56	1	0	1.149937	-6.225849	-0.781351
57	6	0	-4.008063	-0.752099	-0.004708
58	6	0	-5.100934	0.108652	0.002942
59	6	0	-4.378998	-2.116683	-0.014255

60	6	0	-6.441118	-0.308242	0.002153
61	1	0	-4.988103	1.167903	0.010402
62	6	0	-5.678397	-2.552119	-0.015323
63	1	0	-3.659133	-2.890081	-0.022844
64	6	0	-6.762497	-1.668954	-0.006985
65	6	0	-7.496702	0.672	0.010424
66	1	0	-5.847293	-3.614832	-0.023479
67	6	0	-8.158495	-2.083258	-0.007987
68	6	0	-8.784459	0.298054	0.008925
69	1	0	-7.225731	1.716427	0.017664
70	6	0	-9.157678	-1.09328	-0.000372
71	6	0	-8.561851	-3.434104	-0.016102
72	1	0	-9.570872	1.036594	0.014892
73	6	0	-10.514562	-1.469639	-0.001917
74	6	0	-9.887324	-3.779737	-0.016794
75	1	0	-7.824569	-4.217927	-0.021845
76	6	0	-10.878283	-2.788586	-0.009789
77	1	0	-11.268148	-0.69743	0.003455
78	1	0	-10.1712	-4.820116	-0.022772
79	1	0	-11.919632	-3.068536	-0.010588
80	6	0	4.009476	-0.748141	-0.005327
81	6	0	5.102846	0.112049	0.001645
82	6	0	4.379733	-2.112892	-0.014
83	6	0	6.442793	-0.305626	0.001005
84	1	0	4.990844	1.171336	0.008639
85	6	0	5.678868	-2.54909	-0.015192
86	1	0	3.659273	-2.885848	-0.021692
87	6	0	6.763444	-1.666519	-0.007564
88	6	0	7.498914	0.674036	0.00958
89	1	0	5.847157	-3.611906	-0.022485
90	6	0	8.159214	-2.081588	-0.008032
91	6	0	8.786464	0.299375	0.009999
92	1	0	7.228515	1.718619	0.015869
93	6	0	9.15893	-1.092164	0.001207
94	6	0	8.561837	-3.432643	-0.017477
95	1	0	9.573276	1.037484	0.016703
96	6	0	10.515606	-1.469275	0.001751
97	6	0	9.887121	-3.779002	-0.017469
98	1	0	7.824131	-4.216053	-0.024987
99	6	0	10.878613	-2.788409	-0.007584
100	1	0	11.269608	-0.697491	0.009446
101	1	0	10.170435	-4.819523	-0.025112
102	1	0	11.919809	-3.068931	-0.007445

Table S1-5. Atom coordinates and absolute energies for **Py-B2An** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.606992	.379619 -0	0.072545
2	6	0	-1.662593	-1.532482	0.007354
3	6	0	-1.535769	-0.150861	0.030619
4	6	0	-0.167305	0.378318	-0.016473
5	6	0	1.031749	-0.50527	-0.081462
6	6	0	0.679966	-1.868254	-0.119463
7	6	0	-2.746263	0.722708	0.099715
8	6	0	-0.016456	1.783369	-0.002937
9	6	0	-1.145987	2.632968	0.062899
10	6	0	-2.434705	2.075164	0.113284
11	6	0	-0.983613	4.037995	0.073708
12	6	0	0.306804	4.558956	0.017652
13	6	0	1.43629	3.743004	-0.048478
14	6	0	1.263236	2.340583	-0.059452
15	6	0	2.382959	1.503427	-0.118674
16	6	0	2.460098	0.101095	-0.126394
17	1	0	3.257319	2.091718	-0.134069
18	1	0	-2.628171	-1.99337	0.047495
19	1	0	1.398775	-2.59906	-0.206732
20	1	0	-3.18622	2.822643	0.15376
21	1	0	0.438404	5.638735	0.025805
22	6	0	2.785091	4.376926	-0.103769
23	6	0	3.483749	4.689008	1.075827
24	6	0	3.372841	4.71792	-1.33431
25	6	0	4.726089	5.320434	1.026733
26	1	0	3.040396	4.432898	2.03563
27	6	0	4.615414	5.349006	-1.383952
28	1	0	2.843523	4.48433	-2.255356
29	6	0	5.296636	5.652745	-0.203626
30	1	0	5.247137	5.554132	1.952331
31	1	0	5.049706	5.604998	-2.347507
32	1	0	6.264827	6.145947	-0.242203
33	6	0	-2.142702	4.974401	0.141275
34	6	0	-2.746304	5.460473	-1.031764
35	6	0	-2.633122	5.42796	1.378038
36	6	0	-3.802621	6.368725	-0.970244
37	1	0	-2.376178	5.119866	-1.996322
38	6	0	-3.689569	6.335957	1.440088
39	1	0	-2.175095	5.061978	2.294239
40	6	0	-4.278235	6.809825	0.26621

41	1	0	-4.252562	6.732895	-1.890973
42	1	0	-4.050919	6.674317	2.408372
43	1	0	-5.10116	7.518757	0.314417
44	6	0	3.965573	-0.438493	-0.158389
45	6	0	5.052329	0.473103	-0.617885
46	6	0	4.587108	-1.664586	0.18275
47	6	0	6.382435	0.195562	-0.711206
48	1	0	4.855981	1.464247	-0.941287
49	6	0	5.976676	-1.998157	0.103277
50	1	0	4.083648	-2.485609	0.573887
51	6	0	6.928718	-1.05151	-0.359964
52	1	0	7.050798	0.974214	-1.074872
53	6	0	6.431476	-3.266904	0.483961
54	6	0	8.279104	-1.380221	-0.435948
55	6	0	7.786225	-3.622395	0.416155
56	1	0	5.713455	-4.003681	0.842594
57	6	0	8.742636	-2.648701	-0.059515
58	1	0	8.990725	-0.637145	-0.793932
59	6	0	8.26043	-4.912875	0.798353
60	6	0	10.118218	-3.016732	-0.12506
61	6	0	9.593576	-5.22929	0.719067
62	1	0	7.541042	-5.64675	1.156628
63	6	0	10.534048	-4.269518	0.251636
64	1	0	10.837358	-2.282374	-0.482755
65	1	0	9.935686	-6.217931	1.015247
66	1	0	11.587501	-4.532339	0.193664
67	6	0	-4.210606	0.227552	0.138393
68	6	0	-5.38948	1.084093	0.377768
69	6	0	-4.608057	-1.09899	-0.05117
70	6	0	-6.683828	0.650346	0.412657
71	1	0	-5.309588	2.134167	0.549286
72	6	0	-5.946991	-1.596454	-0.023522
73	1	0	-3.912335	-1.887724	-0.249404
74	6	0	-7.040715	-0.70676	0.216083
75	1	0	-7.471563	1.377963	0.600224
76	6	0	-6.218851	-2.954895	-0.228567
77	6	0	-8.346203	-1.192163	0.242875
78	6	0	-7.526012	-3.459607	-0.203968
79	1	0	-5.39311	-3.64165	-0.411597
80	6	0	-8.625186	-2.551072	0.039176
81	1	0	-9.168432	-0.501561	0.426232
82	6	0	-7.816645	-4.841761	-0.409258
83	6	0	-9.951353	-3.074355	0.061545
84	6	0	-9.107554	-5.305747	-0.378455

85	1	0	-6.990245	-5.525849	-0.592243
86	6	0	-10.188165	-4.411042	-0.14011
87	1	0	-10.777938	-2.390427	0.244098
88	1	0	-9.308815	-6.362314	-0.537474
89	1	0	-11.206559	-4.791264	-0.118271
90	6	0	-0.846909	-3.861846	-0.112732
91	6	0	-0.268826	-4.465727	-1.423544
92	6	0	-0.151363	-4.552387	1.094642
93	6	0	-2.348021	-4.204497	-0.054583
94	1	0	-0.744804	-4.020588	-2.306973
95	1	0	0.813513	-4.306038	-1.517587
96	1	0	-0.448078	-5.547217	-1.447276
97	1	0	-0.542299	-4.170425	2.046619
98	1	0	-0.331219	-5.633397	1.060097
99	1	0	0.934859	-4.396215	1.100727
100	1	0	-2.464088	-5.292989	-0.087566
101	1	0	-2.817697	-3.850634	0.875234
102	1	0	-2.902401	-3.78797	-0.90811

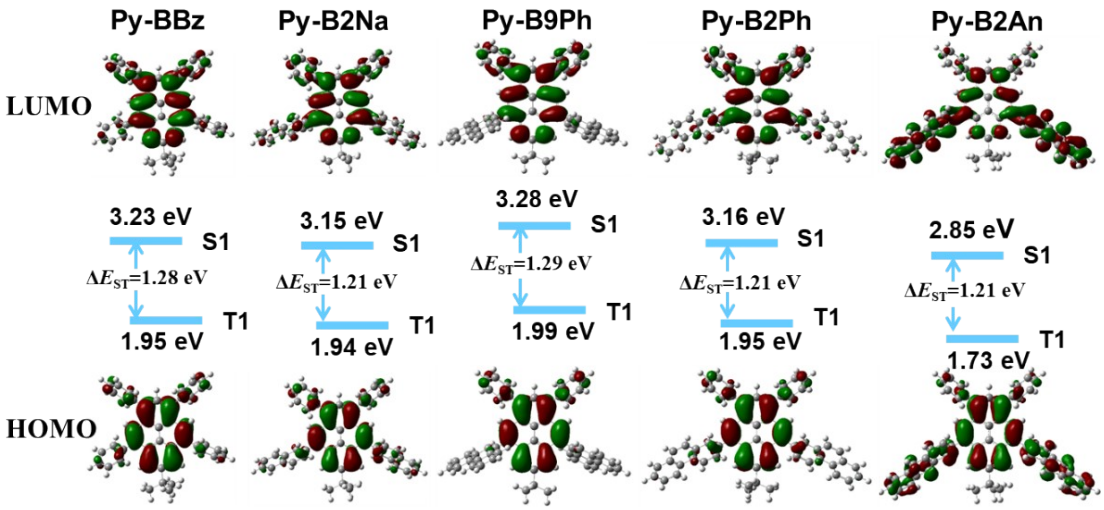


Figure S1. Frontier orbital distributions and energy levels of **Py-BBz, Py-B2Na, Py-B9Ph, Py-B2Ph and Py-B2An** calculated by DFT and TD-DFT/B3LYP/6-31G(d,p)functions.

4. Photophysical Properties

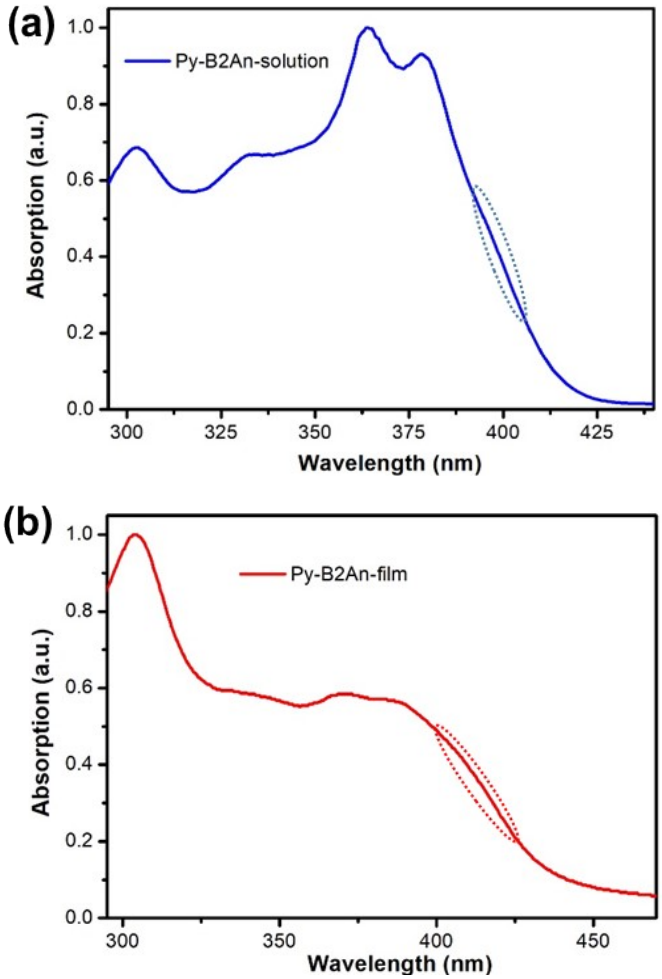


Figure S2. Normalized absorption spectra of Py-B2An: (a) in solution and (b) in film.

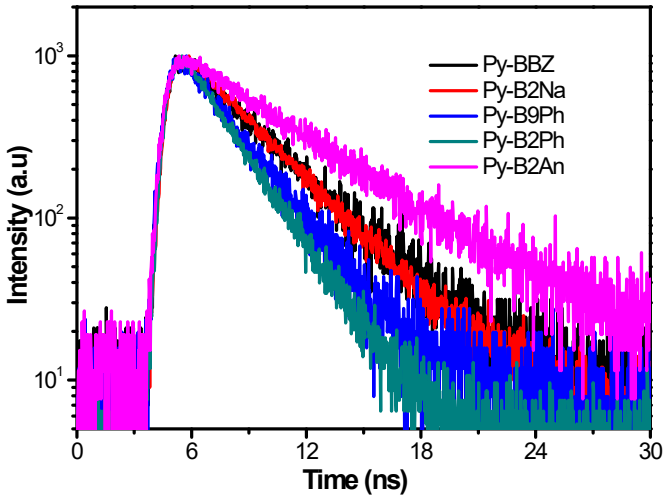


Figure S3. The decay profiles of the fluorescence lifetime of compounds **Py-BBz**, **Py-B2Na**, **Py-B9Ph**, **Py-B2Ph** and **Py-B2An** in toluene solution.

5. Device Performance

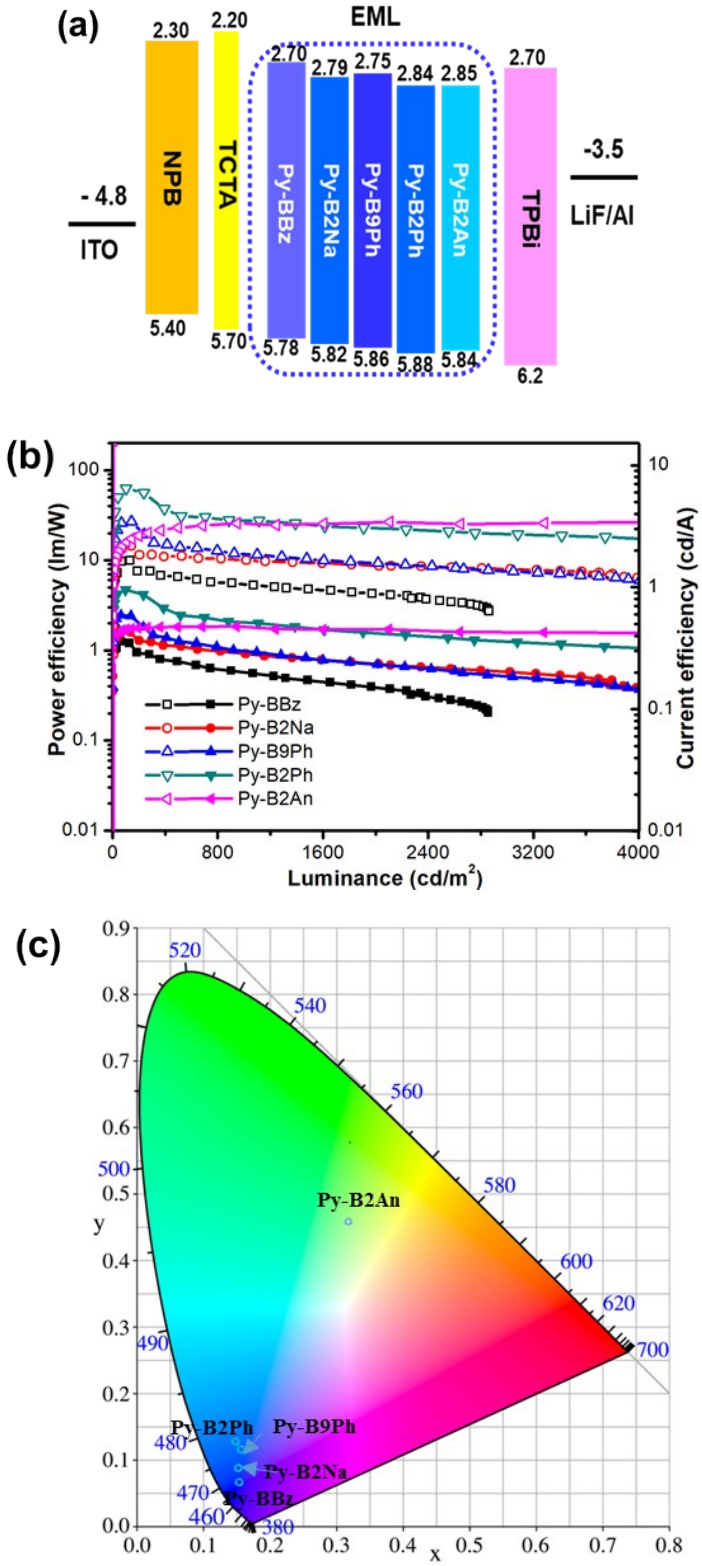
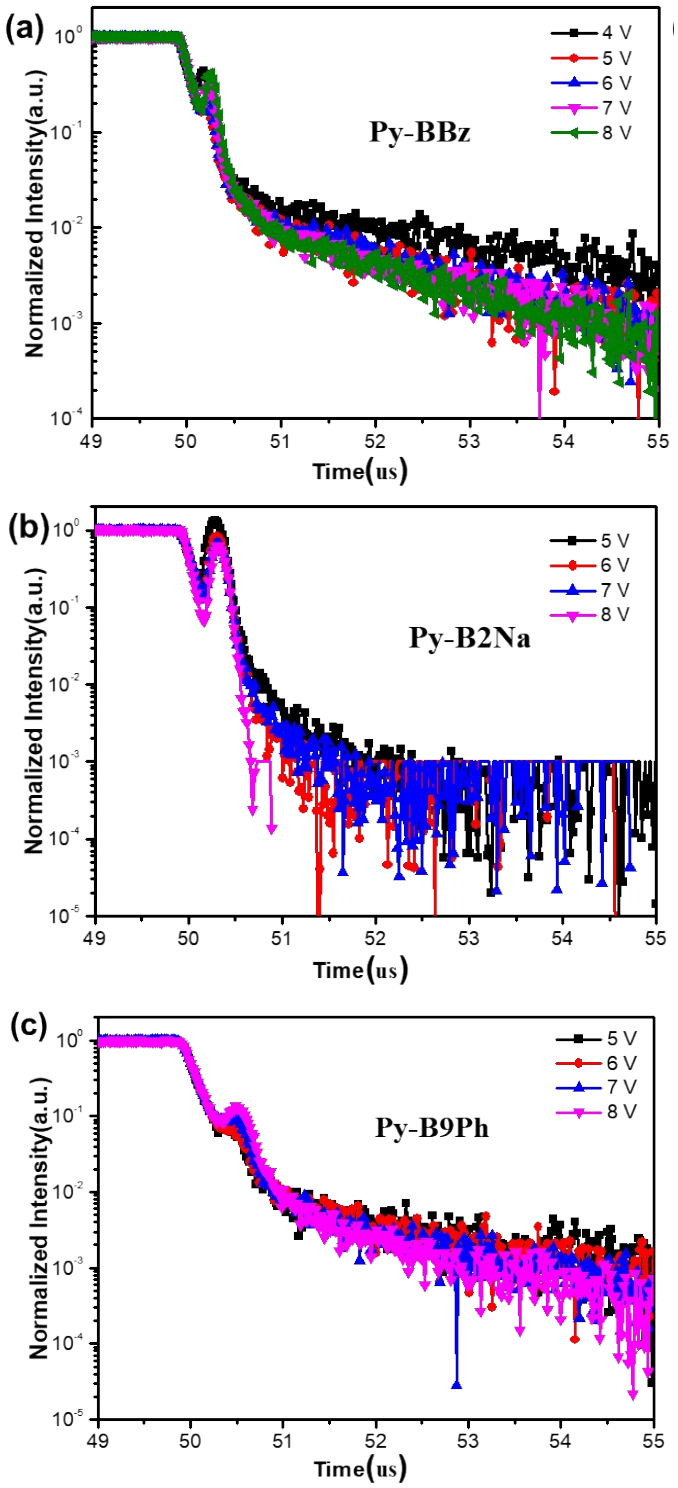


Figure S4. Nondoped devices: (a) energy level diagrams and device configurations, (b)

current efficiency–luminance–power efficiency, (c) Commission Internationale de l'Eclairage (CIE) chromaticity coordinate.



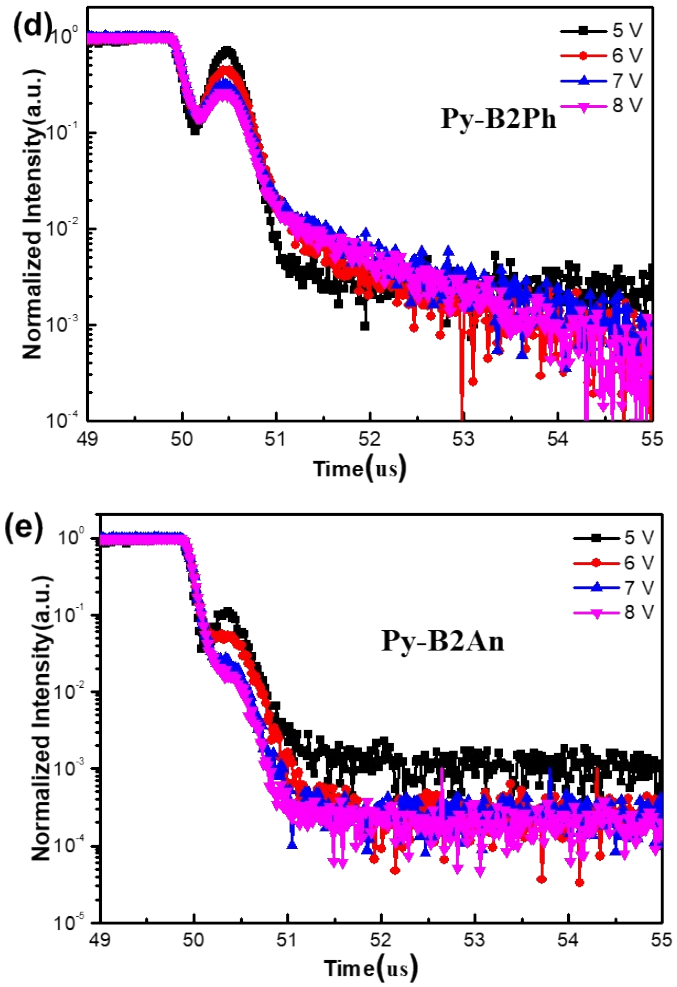


Figure S5. Transient electroluminescent decay of nondoped devices based on **Py-BBz**, **Py-BBz, Py-B9Ph, Py-B2Na**, **Py-B2Ph** and **Py-B2An**.

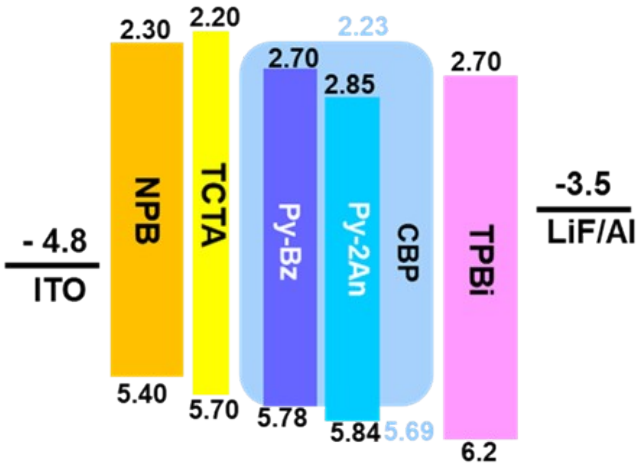


Figure S6. Energy level diagrams and device configurations of doped devices.

6. NMR Spectra

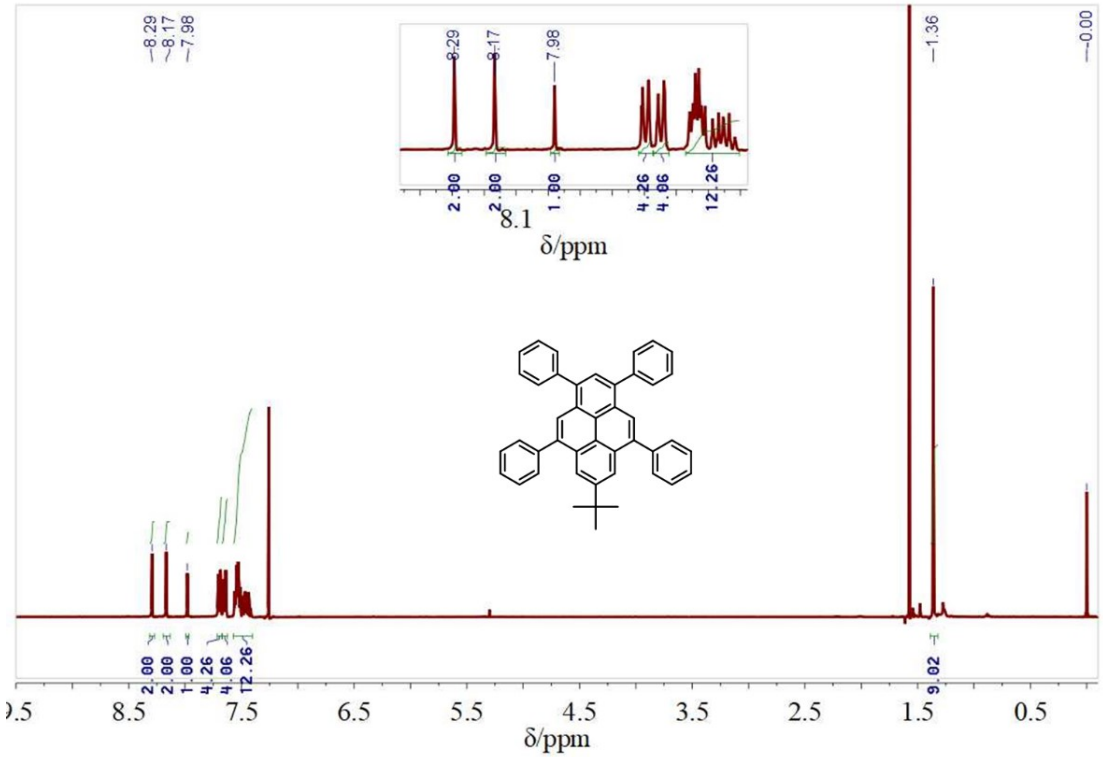


Figure S7. ^{1}H NMR spectrum of compound **Py-BBZ** (400 MHz, $CDCl_3$).

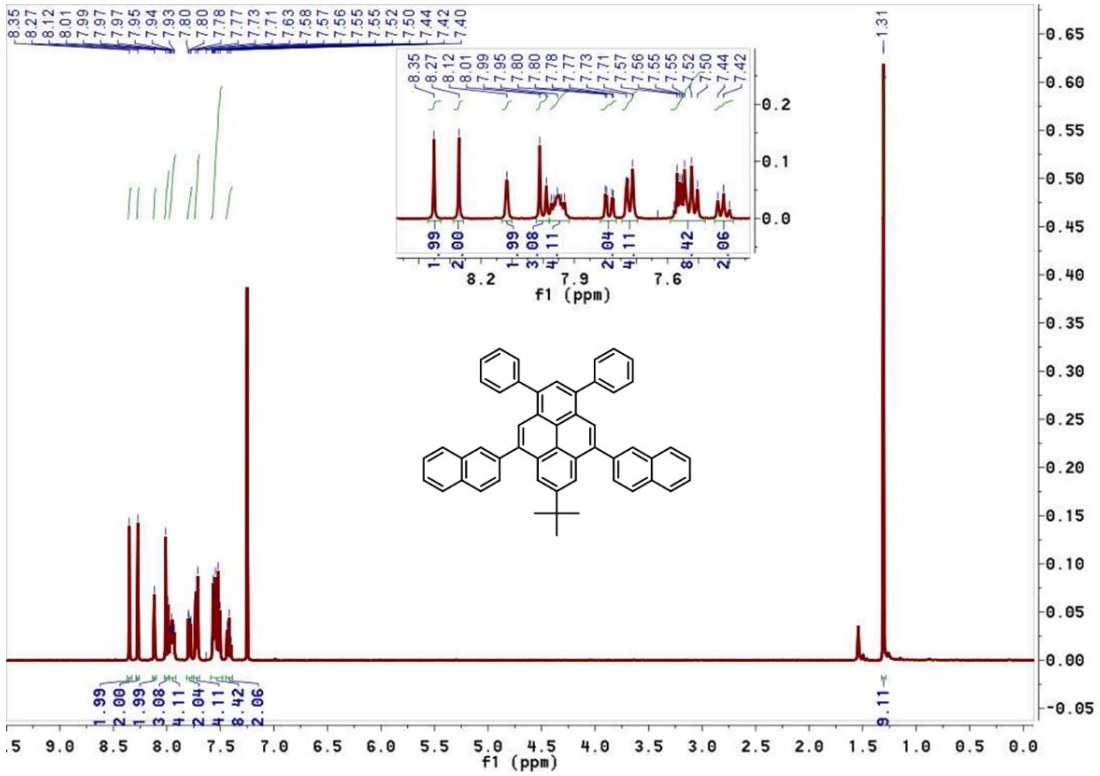


Figure S8. ^{1}H NMR spectrum of compound **Py-B2Na** (400 MHz, $CDCl_3$).

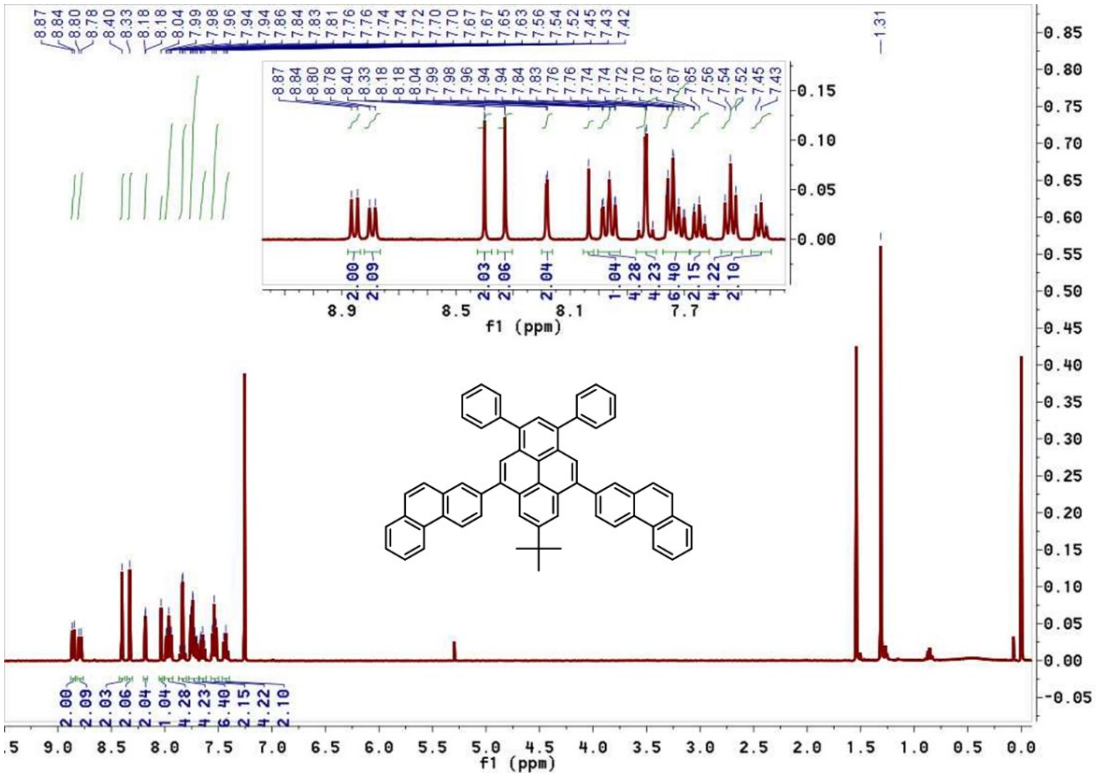


Figure S9. ^{1}H NMR spectrum of compound **Py-B2Ph** (400 MHz, $CDCl_3$).

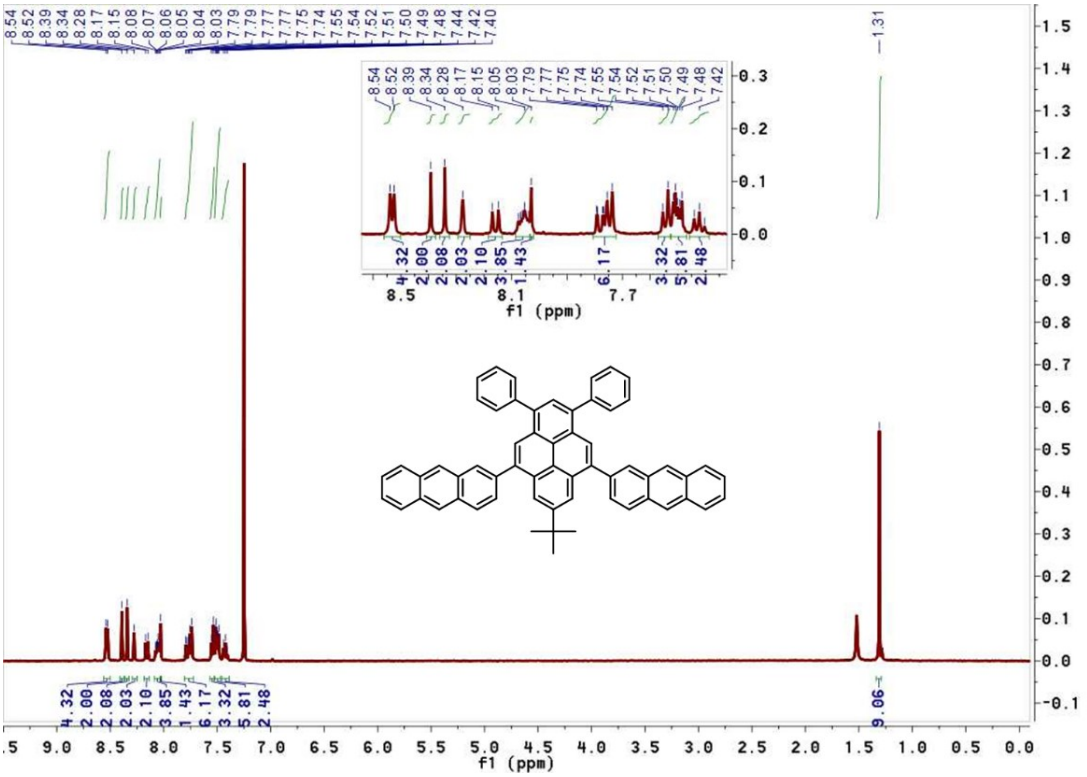


Figure S10. ^{1}H NMR spectrum of compound **Py-B2An** (400 MHz, $CDCl_3$).

7. Mass Spectra

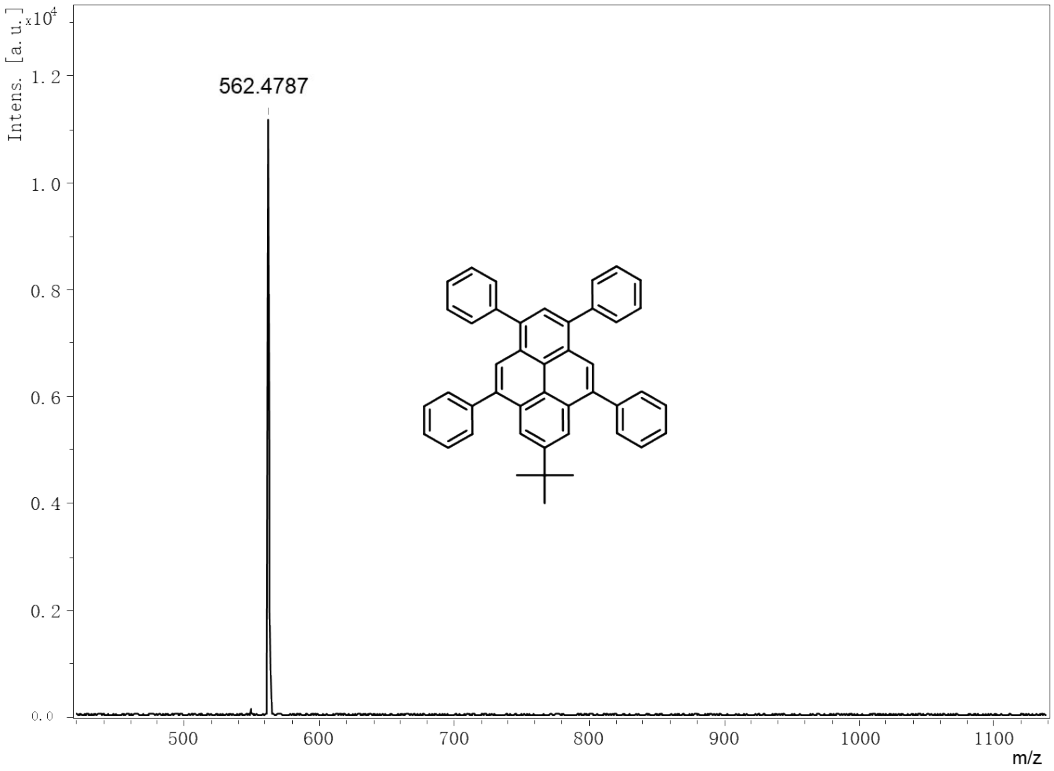


Figure S11. MALDI-TOF Mass spectra of compound **Py-BBZ**.

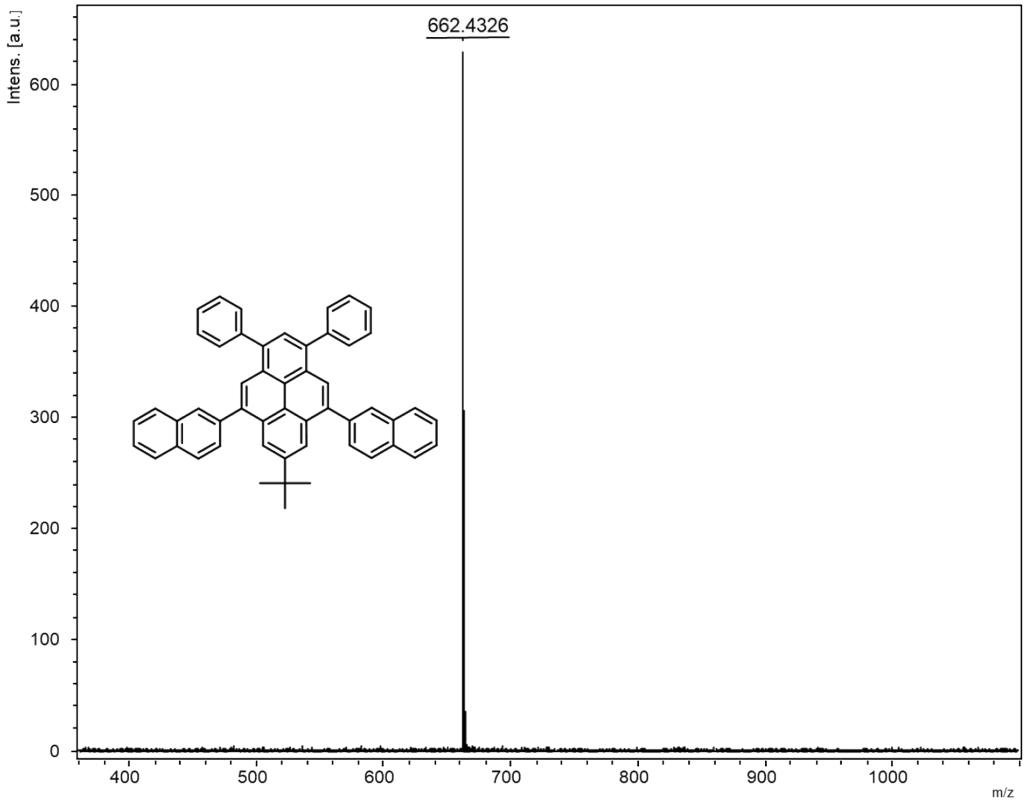


Figure S12. MALDI-TOF Mass spectra of compound **Py-B2Na**.

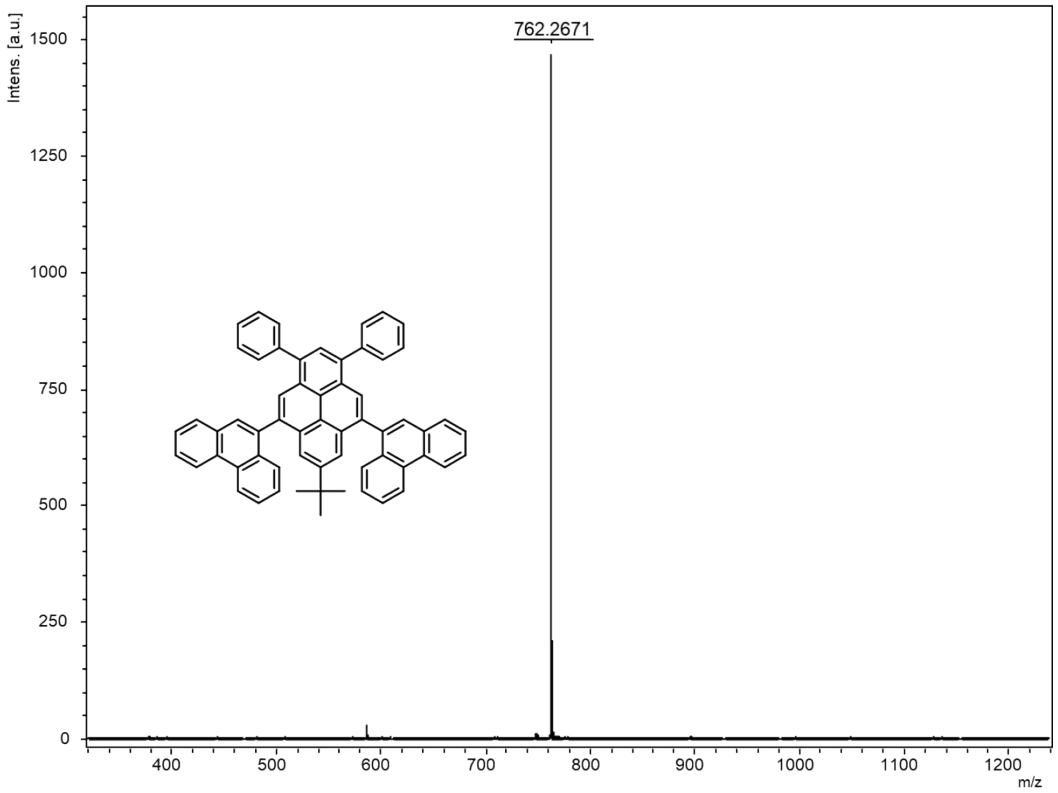


Figure S13. MALDI-TOF Mass spectra of compound **Py-B9Ph**.

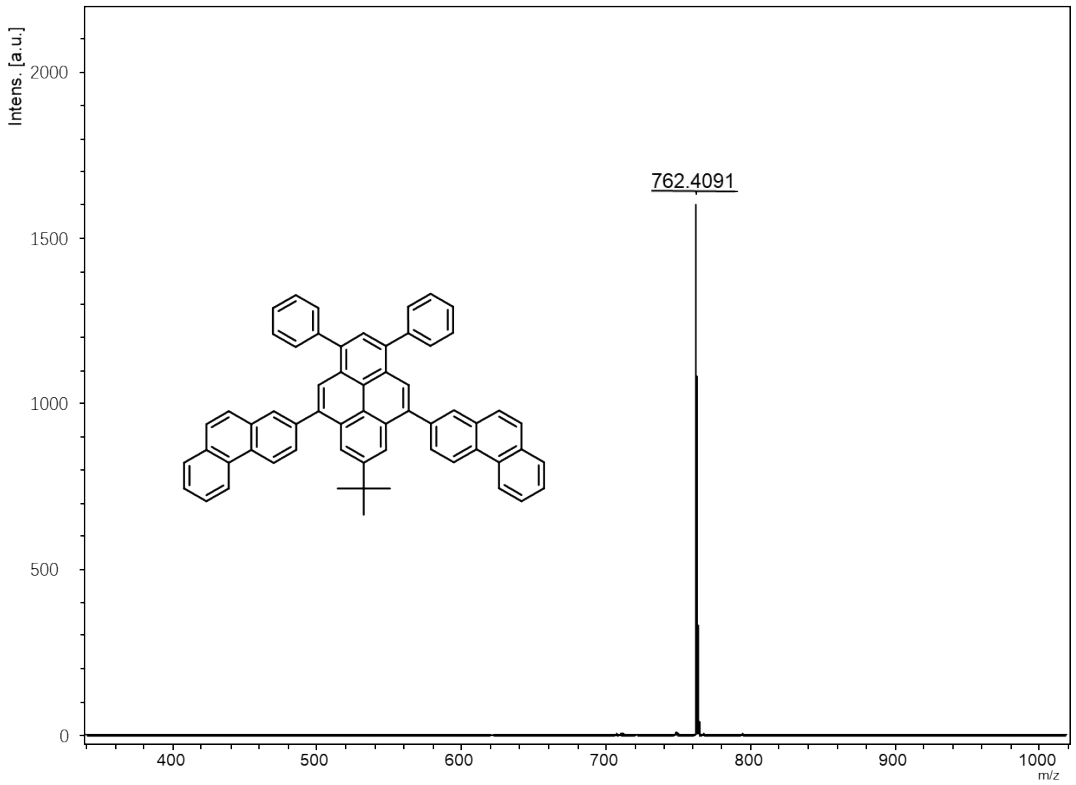


Figure S14. MALDI-TOF Mass spectra of compound **Py-B2Ph**.

Figure S15. MALDI-TOF Mass spectra of compound **Py-B2An**.

8. References

[S1] R. Liu, H. Ran, Z. Zhao, X. Yang, J. Zhang, L. Chen, H. Sun and J.-Y. Hu, *ACS Omega*, 2018, **3**, 5866−5875.

[S2] H. Ran, Z. Zhao, X. Duan, F. Xie, R. Han, H. Sun and J.-Y. Hu, *J. Mater. Chem. C* 2021, **9**, 260−269.