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Supporting Information

Manipulating the benzenyl π-bridge of bisanthracene derivatives (BDs) for highly efficient deep-blue OLED emitters with CIE_y =0.06

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1. General methods

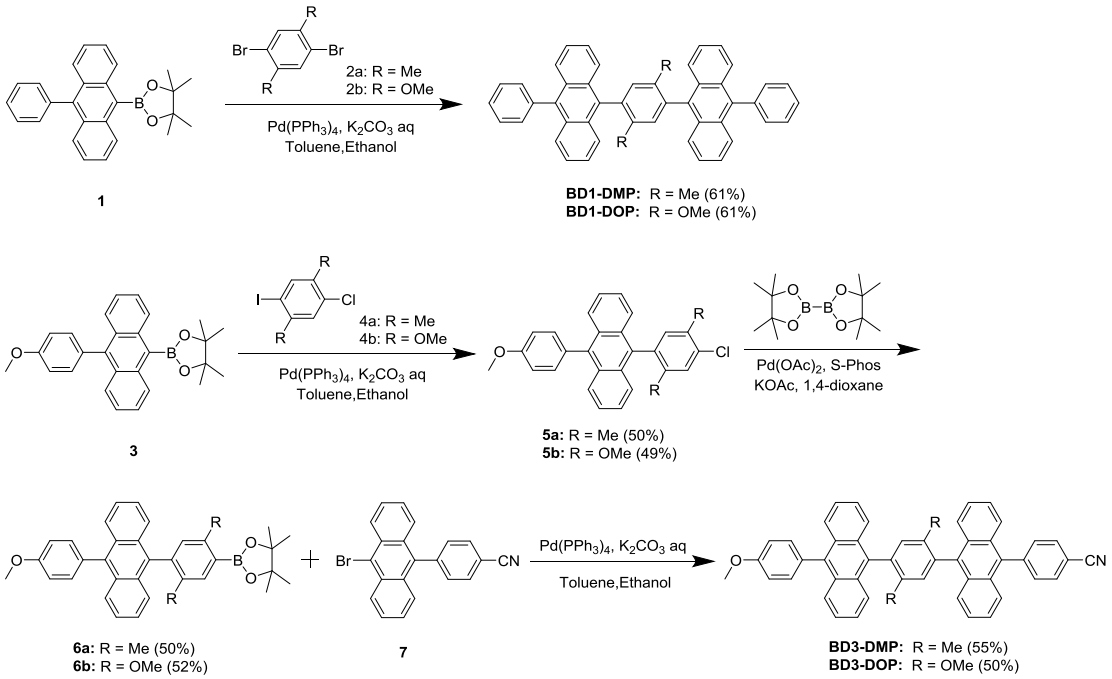
$^{1}H/^{13}C$ NMR spectra (400 MHz) were recorded by a JEOL 400 MHz FT-400 NMR spectrometer referenced to 7.26 and 77.0 ppm for chloroform-D solvent with $SiMe_4$ as an internal reference: *J*-values are given in Hz. Mass spectra were obtained with a Bruker Microflex mass spectrometer in MALDI-TOF mode. Elemental analyses were performed by Vario EL III Elementar Analysensysteme GmbH. Thermogravimetric analysis (TGA) was performed using a USA Waters Q600 under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed using a METTLER TOLEDO DSC instrument under a 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. The frontier orbitals of the molecules based on the ground state geometries were calculated at B3LYP/6-31G* by Gaussian 16 program. Cyclic voltammograms 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 a 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

The multilayer OLEDs were fabricated by the vacuum-deposition method.[S1-2] Electronic grade NPB, TCTA, TAPC, TmPyPB, TPBi, CBP, DSA-Ph, and LiF were obtained from commercial sources. **BD1-DMP**, **BD1-DOP**, **BD3-DMP**, and **BD3-DOP** were purified by vacuum sublimation. Soak the glass coated with ITO in an ultrasonic cleaning agent for 30 minutes, sonicate with deionized water, acetone, and isopropanol solvents for 10 minutes each, and then dry. The cleaned ITO glass is treated with perfluoromethane (CF_4) plasma, and then transferred to the evaporation chamber. In a high vacuum environment (1×10^{-5} Pa), the functional layer materials, luminescent materials, and cathode materials (Al) are sequentially deposited at high temperatures. When evaporating and depositing organic material thin films, the evaporation rate is controlled at 1-2 Å s^{-1}; When evaporating LiF, the evaporation rate is controlled at 0.1 Å s^{-1}; When evaporating Al, the evaporation rate is controlled at 4 Å s^{-1}, and 9 mm^2 of the luminescent area. All the OLEDs were measured without encapsulation at room temperature in the dark. The Current density-Voltage-Luminance (*J-V-L*) characteristics were measured with a Keithley 2400 source meter and a LS110 luminance meter. The electroluminescence (EL) spectra were collected using a spectrascan PR650 spectrophotometer. The EQEs were calculated from the Luminance-Current density characteristics and EL spectra with the hypothesis of Lambertian distribution. The transient EL decay was tested by an Agilent 8114A pulse generator to generate rectangular pulse voltages.

3. Synthesis and characterizations



Scheme S1. Synthetic route for compounds **BD1-DMP**, **BD1-DOP**, **BD3-DMP**, and **BD3-DOP**.

Synthesis of 1,4-bis(10-phenylanthracene-9-yl)-2,5-dimethyl-benzene (BD1-DMP): 4,4,5,5-Tetramethyl-2-(10-phenyl-anthracen-9-yl)-[1,3,2]dioxaborolane (**1**) (5.00 g, 13.15 mmol), 1,4-dibromo-2,5-dimethyl-benzene (2a) (1.14 g, 4.3 mmol), $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol), K_2CO_3 (5.52 g, 40.00 mmol, 2 M, 20 mL), and ethanol (20 mL) were mixed in toluene (40 mL)with a flask containing nitrogen. The reaction mixture was refluxed overnight under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with brine and extracted with toluene (250 mL). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was successfully purified by column chromatography using hexane: dichloromethane (6:1) as the eluent to give **BD1-DMP** as light-green

crystals. Yield: 61% (0.63 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.02 Hz, 4H), 7.75 (d, *J* = 8.00 Hz, 4H), 7.62-7.47 (m, 14H), 7.40 (t, *J* = 16.00 Hz, 6H), 1.98 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.19, 137.26, 135.39, 132.88, 131.50, 130.13, 129.82, 128.50, 127.55, 127.30, 126.88, 125.38, 125.20, 19.61. EI-MS (m/z): calcd for $C_{48}H_{34}$, 610.8; found, 610.7 [M^+].

Synthesis of 1,4-bis(10-phenylanthracene-9-yl)-2,5-dimethoxy-benzene (BD1-DOP): 4,4,5,5-Tetramethyl-2-(10-phenyl-anthracen-9-yl)-[1,3,2]dioxaborolane (**1**) (5.00 g, 13.15 mmol), 1,4-dibromo-2,5-dimethoxy-benzene (2b) (0.5 g, 1.69 mmol), $Pd(PPh_3)_4$ (0.50 g, 0.43 mmol), (5.52 g, 40.00 mmol, 2 M, 20 mL), and ethanol (20 mL) were mixed in toluene (40 mL) with a flask containing nitrogen. The reaction mixture was refluxed overnight under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with brine and extracted with toluene (250 mL). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was successfully purified by column chromatography using hexane: dichloromethane (9:1) as the eluent to give **BD1-DOP** as light-green crystals. Yield: 61% (0.65 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.00 Hz, 4H), 7.77 (d, *J* = 8.04 Hz, 4H), 7.62-7.47 (m, 14H), 7.40-7.37 (m, 4H), 7.16 (s, 2H), 3.58 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =152.47, 131.55, 131.45, 130.21, 128.40, 127.47, 127.25, 126.93, 125.24, 125.05, 116.85, 56.72. EI-MS (m/z): calcd for $C_{48}H_{34}O_2$, 642.8; found, 643.0 [M^+].

Synthesis of 1-(10-(4-methoxyphenyl)anthracen-9-yl)-4-(10-(4-cyanophenyl) anthracen-9-yl)-2,5-dimethylbenzene (BD3-DMP): 2-{4-[10-(4-Methoxy-phenyl) -anthracen-9-yl]-2,5-dimethyl-phenyl}-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (6a)

(0.89 g, 1.75 mmol), 4-(10-bromo- anthracen-9-yl)-benzonitrile (7) (1.25 g, 3.50 mmol), $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol), K_2CO_3 (8.29 g, 60.00 mmol, 2 M, 30 mL), and ethanol (30 mL) were mixed in toluene (60 mL) with a flask containing nitrogen. The reaction mixture was refluxed overnight under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with brine and extracted with dichloromethane (250 mL). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was successfully purified by column chromatography using hexane as the eluent to give **BD3-DMP** as light-green crystals. Yield: 55% (0.64 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.02 Hz, 2H), 7.88 (d, *J* = 8.04 Hz, 2H), 7.83-7.64 (m, 14H), 7.59 (d, *J* = 4.00 Hz, 2H), 7.44-7.41 (m, 4H), 7.17 (d, *J* = 8.00 Hz, 2H), 3.98(s, 3H), 2.30 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.04, 141.24, 133.35, 131.23, 129.87, 126.86, 125.06, 113.94, 113.88, 55.53, 19.76. EI-MS (m/z): calcd for $C_{50}H_{35}NO$, 665.8; found, 665.0 [M^+].

Synthesis of 1-(10-(4-methoxyphenyl)anthracen-9-yl)-4-(10-(4-cyanophenyl) anthracen-9-yl)-2,5-dimethoxy-benzene (BD3-DOP): 2-{2,5-Dimethoxy-4-[10-(4-methoxy-phenyl)-anthracen-9-yl]-phenyl}-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (6b) (0.95 g, 1.75 mmol), 4-(10-bromo-anthracen-9-yl)-benzonitrile (7) (1.25 g, 3.50 mmol), $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol), K_2CO_3 (8.29 g, 60.00mmol, 2 M, 30 mL), and ethanol (30 mL) were mixed in toluene (60 mL) with a flask containing nitrogen. The reaction mixture was refluxed overnight under nitrogen. After it was cooled to room temperature, the reaction mixture was quenched with brine and extracted with dichloromethane (250 mL). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was successfully purified by column chromatography using hexane: dichloromethane (5:1) as the eluent to give **BD3-DOP** as light-green crystals. Yield: 50% (0.60 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ =

7.99-7.91 (m, 6H), 7.82 (d, *J* = 8.06 Hz, 2H), 7.73 (d, *J* = 8.02 Hz, 1H), 7.63 (d, *J* = 8.08 Hz, 1H), 7.58 (d, *J* = 8.10 Hz, 2H) 7.54-7.38 (m, 10H), 7.13 (d, *J* = 8.00 Hz, 4H), 3.98 (s, 3H), 3.57 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.30, 152.75, 132.40, 129.69, 127.44, 127.25, 126.37, 125.88, 125.57, 125.36, 125.07, 56.66, 55.53. EI-MS (m/z): calcd for $C_{50}H_{30}NO_3$, 697.8; found, 696.5 [M^+].

4. Theoretical calculations

4.1. DFT calculations

Table S1 Atom coordinates and absolute energies for **BD1-DMP** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.051623	3.667375	-0.013539
2	6	0	5.742436	2.485098	-0.028456
3	6	0	5.064261	1.222688	-0.018433
4	6	0	3.617773	1.222163	0.005186
5	6	0	2.939268	2.484298	0.018411
6	6	0	3.629344	3.667133	0.010957
7	6	0	5.770052	0.000006	-0.030247
8	6	0	2.910543	0.000042	0.017041
9	6	0	3.617738	-1.222097	0.005022
10	6	0	5.064226	-1.222658	-0.018665
11	6	0	5.742362	-2.485083	-0.029209
12	1	0	6.826593	-2.489983	-0.048701
13	6	0	5.051517	-3.667344	-0.014473
14	6	0	3.629244	-3.667067	0.010327
15	6	0	2.939201	-2.484217	0.018132
16	1	0	5.589871	4.611457	-0.020990
17	1	0	6.826672	2.489973	-0.047669
18	1	0	1.854715	2.486929	0.031763
19	1	0	3.090810	4.611050	0.021716
20	1	0	5.589736	-4.611439	-0.022333
21	1	0	3.090686	-4.610973	0.020988
22	1	0	1.854651	-2.486822	0.031655
23	6	0	7.268402	-0.000018	-0.055037
24	6	0	8.005074	-0.002332	1.139033
25	6	0	7.964695	0.002260	-1.273095
26	6	0	9.400759	-0.002362	1.116217
27	1	0	7.476326	-0.004099	2.088540
28	6	0	9.360363	0.002229	-1.297003
29	1	0	7.404460	0.004046	-2.204363
30	6	0	10.082316	-0.000082	-0.102144
31	1	0	9.955031	-0.004154	2.051230
32	1	0	9.883014	0.003997	-2.250050
33	1	0	11.168942	-0.000107	-0.120327

34	6	0	1.410536	0.000061	0.034515
35	6	0	0.688218	-0.000098	1.244901
36	6	0	0.709461	0.000186	-1.178104
37	6	0	-0.709460	-0.000106	1.178036
38	6	0	-0.688224	0.000194	-1.244968
39	1	0	1.279060	0.000275	-2.104751
40	6	0	-1.410537	0.000053	-0.034590
41	1	0	-1.279066	-0.000250	2.104678
42	6	0	-2.910544	0.000031	-0.017095
43	6	0	-3.617737	-1.222111	-0.005149
44	6	0	-3.617775	1.222150	-0.005167
45	6	0	-5.064225	-1.222674	0.018570
46	6	0	-2.939199	-2.484228	-0.018372
47	6	0	-5.064262	1.222671	0.018487
48	6	0	-2.939273	2.484287	-0.018368
49	6	0	-5.742360	-2.485102	0.029009
50	6	0	-5.770051	-0.000012	0.030261
51	6	0	-3.629240	-3.667081	-0.010653
52	1	0	-1.854649	-2.486831	-0.031913
53	6	0	-5.742440	2.485079	0.028589
54	6	0	-3.629351	3.667119	-0.010843
55	1	0	-1.854720	2.486919	-0.031756
56	6	0	-5.051513	-3.667360	0.014164
57	1	0	-6.826590	-2.490005	0.048506
58	1	0	-3.090681	-4.610984	-0.021398
59	1	0	-6.826675	2.489950	0.047839
60	6	0	-5.051628	3.667358	0.013702
61	1	0	-3.090819	4.611039	-0.021580
62	1	0	-5.589731	-4.611457	0.021945
63	1	0	-5.589878	4.611438	0.021212
64	6	0	-7.268400	-0.000034	0.055114
65	6	0	-8.005152	-0.001967	-1.138898
66	6	0	-7.964612	0.001876	1.273228
67	6	0	-9.400841	-0.001993	-1.115986
68	1	0	-7.476478	-0.003444	-2.088447
69	6	0	-9.360273	0.001849	1.297234
70	1	0	-7.404305	0.003371	2.204453
71	6	0	-10.082311	-0.000086	0.102418
72	1	0	-9.955171	-0.003493	-2.050964
73	1	0	-9.882864	0.003328	2.250313
74	1	0	-11.168936	-0.000107	0.120684
75	6	0	-1.389864	0.000320	-2.583554
76	1	0	-2.033631	-0.879607	-2.699622
77	1	0	-2.033247	0.880526	-2.699658

78	1	0	-0.666041	0.000151	-3.404304
79	6	0	1.389861	-0.000331	2.583485
80	1	0	2.033530	-0.880356	2.699367
81	1	0	2.033341	0.879776	2.699773
82	1	0	0.666039	-0.000598	3.404235

Total Enegy (RB3LYP) = -1775.87712461 Harterr

Table S2 Atom coordinates and absolute energies for **BD1-DOP** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.050367	-3.667330	0.032751
2	6	0	5.741425	-2.485314	0.049590
3	6	0	5.063418	-1.222781	0.034572
4	6	0	3.617389	-1.222302	0.004618
5	6	0	2.938863	-2.483662	-0.013712
6	6	0	3.628142	-3.666619	-0.000481
7	6	0	5.768876	-0.000003	0.049340
8	6	0	2.912617	0.000011	-0.008128
9	6	0	3.617422	1.222315	0.003663
10	6	0	5.063452	1.222782	0.033455
11	6	0	5.741509	2.485307	0.046641
12	1	0	6.825672	2.490444	0.070457
13	6	0	5.050480	3.667326	0.028784
14	6	0	3.628240	3.666623	-0.003782
15	6	0	2.938924	2.483673	-0.015633
16	1	0	5.588305	-4.611617	0.044230
17	1	0	6.825573	-2.490458	0.074065
18	1	0	1.854582	-2.485839	-0.038549
19	1	0	3.089458	-4.610448	-0.016120
20	1	0	5.588455	4.611608	0.038856
21	1	0	3.089577	4.610451	-0.020155
22	1	0	1.854635	2.485855	-0.040143
23	6	0	7.267109	-0.000016	0.080073
24	6	0	7.959445	0.005535	1.300362
25	6	0	8.008011	-0.005592	-1.111396
26	6	0	9.355043	0.005505	1.329192
27	1	0	7.396019	0.009856	2.229713
28	6	0	9.403623	-0.005623	-1.083780
29	1	0	7.482170	-0.009888	-2.062462
30	6	0	10.081120	-0.000079	0.136849

31	1	0	9.874465	0.009812	2.284031
32	1	0	9.961112	-0.009953	-2.016898
33	1	0	11.167700	-0.000105	0.158747
34	6	0	1.414489	0.000025	-0.015101
35	6	0	0.706895	-0.000139	1.192794
36	6	0	0.692674	0.000181	-1.222368
37	6	0	-0.692678	-0.000136	1.222410
38	1	0	1.277565	-0.000265	2.114334
39	6	0	-0.706895	0.000187	-1.192749
40	6	0	-1.414490	0.000028	0.015151
41	1	0	-1.277573	0.000308	-2.114284
42	6	0	-2.912619	0.000016	0.008166
43	6	0	-3.617394	-1.222297	-0.004438
44	6	0	-3.617421	1.222320	-0.003788
45	6	0	-5.063423	-1.222777	-0.034353
46	6	0	-2.938869	-2.483654	0.014047
47	6	0	-5.063450	1.222786	-0.033669
48	6	0	-2.938923	2.483682	0.015374
49	6	0	-5.741439	-2.485310	-0.048902
50	6	0	-5.768877	0.000001	-0.049350
51	6	0	-3.628153	-3.666612	0.001129
52	1	0	-1.854586	-2.485828	0.038771
53	6	0	-5.741498	2.485311	-0.047347
54	6	0	-3.628234	3.666631	0.003190
55	1	0	-1.854638	2.485866	0.040035
56	6	0	-5.050383	-3.667325	-0.031869
57	1	0	-6.825592	-2.490455	-0.073143
58	1	0	-3.089469	-4.610439	0.016889
59	1	0	-6.825656	2.490445	-0.071433
60	6	0	-5.050468	3.667331	-0.029659
61	1	0	-3.089571	4.610461	0.019462
62	1	0	-5.588328	-4.611613	-0.042981
63	1	0	-5.588437	4.611613	-0.040115
64	6	0	-7.267110	-0.000009	-0.080111
65	6	0	-7.959422	0.001516	-1.300427
66	6	0	-8.008036	-0.001542	1.111355
67	6	0	-9.355019	0.001503	-1.329284
68	1	0	-7.395976	0.002708	-2.229775
69	6	0	-9.403648	-0.001557	1.083710
70	1	0	-7.482214	-0.002721	2.062440
71	6	0	-10.081120	-0.000036	-0.136944
72	1	0	-9.874422	0.002687	-2.284143
73	1	0	-9.961155	-0.002751	2.016827
74	1	0	-11.167700	-0.000048	-0.158864

75	6	0	-0.756942	-0.000472	3.613287
76	1	0	-1.535489	-0.000606	4.378414
77	1	0	-0.130998	-0.895077	3.733620
78	1	0	-0.131054	0.894137	3.733892
79	6	0	0.756963	0.000559	-3.613261
80	1	0	1.535515	0.000684	-4.378383
81	1	0	0.131035	-0.894017	-3.733886
82	1	0	0.131061	0.895196	-3.733571
83	8	0	1.437094	0.000330	-2.370036
84	8	0	-1.437089	-0.000304	2.370074

Total Enegy (RB3LYP) = -1775.87712461 Harterr

Table S3 Atom coordinates and absolute energies for **BD3-DMP** standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.913920	3.680515	-0.027167
2	6	0	5.606899	2.500012	0.013054
3	6	0	4.932169	1.236029	0.042902
4	6	0	3.485609	1.232815	0.017552
5	6	0	2.804361	2.493030	-0.020121
6	6	0	3.491687	3.677268	-0.041293
7	6	0	5.642225	0.015102	0.083295
8	6	0	2.780718	0.009482	0.022989
9	6	0	3.489522	-1.211039	0.059139
10	6	0	4.935971	-1.208611	0.094806
11	6	0	5.613609	-2.470073	0.153073
12	1	0	6.696945	-2.472859	0.196102
13	6	0	4.924280	-3.653361	0.158136
14	6	0	3.502834	-3.655709	0.108259
15	6	0	2.812297	-2.474010	0.064080
16	1	0	5.450612	4.625216	-0.050285
17	1	0	6.691060	2.507269	0.020140
18	1	0	1.719734	2.493427	-0.030274
19	1	0	2.951041	4.619617	-0.070451
20	1	0	5.463106	-4.596036	0.203848
21	1	0	2.965173	-4.600211	0.111374
22	1	0	1.727991	-2.478463	0.036553
23	6	0	1.280800	0.006676	-0.001727
24	6	0	0.564303	-0.008299	-1.215605
25	6	0	0.573684	0.019090	1.207264

26	6	0	-0.833656	-0.009821	-1.155881
27	6	0	-0.824337	0.017586	1.267767
28	6	0	-1.539960	0.002777	0.053675
29	6	0	-3.039825	0.000116	0.028415
30	6	0	-3.748537	1.221163	-0.001121
31	6	0	-3.744657	-1.223522	0.026138
32	6	0	-5.194757	1.220508	-0.036011
33	6	0	-3.070251	2.483298	0.000519
34	6	0	-5.191015	-1.228183	-0.002104
35	6	0	-3.062385	-2.483113	0.057998
36	6	0	-5.872195	2.482492	-0.083436
37	6	0	-5.895909	-0.005126	-0.034520
38	6	0	-3.759730	3.665869	-0.034419
39	1	0	-1.986062	2.485509	0.025839
40	6	0	-5.865276	-2.492612	0.017343
41	6	0	-3.748503	-3.668091	0.070024
42	1	0	-1.977989	-2.481444	0.071522
43	6	0	-5.181198	3.664819	-0.080754
44	1	0	-6.955843	2.491498	-0.124631
45	1	0	-3.221722	4.609921	-0.032356
46	1	0	-6.949622	-2.505620	0.008104
47	6	0	-5.170604	-3.672283	0.051662
48	1	0	-3.207515	-4.610107	0.095161
49	1	0	-5.719565	4.608009	-0.117339
50	1	0	-5.706655	-4.617375	0.067003
51	6	0	7.139030	0.018711	0.115721
52	6	0	7.889096	-0.221143	-1.040715
53	6	0	7.838117	0.264053	1.311195
54	6	0	9.287004	-0.219636	-1.023001
55	1	0	7.373766	-0.412016	-1.978391
56	6	0	9.226711	0.268609	1.346619
57	1	0	7.280048	0.451775	2.224590
58	6	0	9.962817	0.026539	0.177343
59	1	0	9.829552	-0.407971	-1.942482
60	1	0	9.766229	0.455734	2.269949
61	6	0	-7.392473	-0.007849	-0.067111
62	6	0	-8.136194	0.209726	1.103857
63	6	0	-8.083525	-0.228032	-1.269444
64	6	0	-9.527537	0.208261	1.080799
65	1	0	-7.613944	0.379883	2.040773
66	6	0	-9.474555	-0.231762	-1.307138
67	1	0	-7.520187	-0.396065	-2.182637
68	6	0	-10.206877	-0.013090	-0.128586
69	1	0	-10.093535	0.375434	1.991669

70	1	0	-9.999610	-0.400921	-2.241851
71	6	0	-11.640532	-0.015750	-0.159904
72	7	0	-12.803717	-0.017905	-0.185317
73	8	0	11.320763	0.052566	0.315438
74	6	0	12.116946	-0.185803	-0.834105
75	1	0	13.153717	-0.119101	-0.499282
76	1	0	11.934891	-1.184888	-1.252041
77	1	0	11.938668	0.567648	-1.612880
78	1	0	1.138853	0.030284	2.136466
79	1	0	-1.398486	-0.021221	-2.085393
80	6	0	1.272778	-0.022391	-2.550406
81	1	0	1.912861	0.859119	-2.673983
82	1	0	1.921138	-0.900758	-2.650997
83	1	0	0.553498	-0.036476	-3.375044
84	6	0	-1.532053	0.031509	2.603202
85	1	0	-2.176769	0.912293	2.707603
86	1	0	-2.174834	-0.848159	2.726974
87	1	0	-0.811714	0.041393	3.426817

Total Enegy (RB3LYP) = -1775.87712461 Harterr

Table S4 Atom coordinates and absolute energies for **BD3-DOP** Standard orientation.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.571836	-0.001371	1.203439
2	6	0	0.827707	0.000921	1.177513
3	6	0	1.538261	0.001579	-0.029089
4	6	0	0.820045	0.000840	-1.238369
5	6	0	-0.579531	-0.003233	-1.211779
6	6	0	-1.290905	-0.004834	-0.006079
7	1	0	1.395671	0.002111	2.100673
8	1	0	-1.148011	-0.004765	-2.134545
9	6	0	3.036001	0.004127	-0.017690
10	6	0	3.743834	-1.214888	-0.088904
11	6	0	3.737712	1.224623	0.083000
12	6	0	5.189497	-1.215450	-0.057561
13	6	0	3.067320	-2.472945	-0.191138
14	6	0	5.183797	1.226768	0.120161
15	6	0	3.056534	2.483536	0.143407
16	6	0	5.869985	-2.474380	-0.135741
17	6	0	5.888705	0.006171	0.048503

18	6	0	3.758125	-3.652789	-0.262060
19	1	0	1.983168	-2.475083	-0.210266
20	6	0	5.858482	2.486456	0.230956
21	6	0	3.742590	3.664047	0.243825
22	1	0	1.972954	2.485578	0.106318
23	6	0	5.180382	-3.653101	-0.235133
24	1	0	6.954251	-2.483067	-0.115546
25	1	0	3.221217	-4.594236	-0.339922
26	1	0	6.942368	2.495797	0.265742
27	6	0	5.164326	3.665064	0.291582
28	1	0	3.202090	4.605709	0.286202
29	1	0	5.719845	-4.594554	-0.293315
30	1	0	5.699717	4.606954	0.374768
31	6	0	-2.788678	-0.009474	-0.019713
32	6	0	-3.490665	-1.230745	0.063069
33	6	0	-3.496046	1.206007	-0.135265
34	6	0	-4.936565	-1.237319	0.031945
35	6	0	-2.808260	-2.484488	0.180740
36	6	0	-4.942141	1.199042	-0.181011
37	6	0	-2.820923	2.467805	-0.207419
38	6	0	-5.610259	-2.497874	0.139549
39	6	0	-5.647165	-0.022291	-0.093604
40	6	0	-3.493576	-3.666113	0.272143
41	1	0	-1.723846	-2.482542	0.196287
42	6	0	-5.620843	2.453308	-0.326170
43	6	0	-3.512030	3.642859	-0.333514
44	1	0	-1.737603	2.477204	-0.159709
45	6	0	-4.915931	-3.672420	0.255146
46	1	0	-6.694270	-2.507119	0.129770
47	1	0	-2.951835	-4.604030	0.361318
48	1	0	-6.703690	2.451555	-0.377936
49	6	0	-4.932998	3.634886	-0.400333
50	1	0	-2.975682	4.586716	-0.384506
51	1	0	-5.451289	-4.614677	0.336036
52	1	0	-5.472197	4.571867	-0.511347
53	6	0	7.385729	0.007171	0.082357
54	6	0	8.128758	0.154095	-1.099793
55	6	0	8.076467	-0.138825	1.295873
56	6	0	9.520286	0.155993	-1.076635
57	1	0	7.605788	0.267518	-2.044710
58	6	0	9.467661	-0.138663	1.333889
59	1	0	7.512985	-0.253191	2.217131
60	6	0	10.199365	0.009240	0.144097
61	1	0	10.086325	0.269845	-1.995578

62	1	0	9.993074	-0.251760	2.276743
63	6	0	-7.143693	-0.029519	-0.134005
64	6	0	-7.837132	-0.349702	-1.315308
65	6	0	-7.899557	0.283122	1.000807
66	6	0	-9.225472	-0.355992	-1.357469
67	1	0	-7.274336	-0.595220	-2.211869
68	6	0	-9.297706	0.281120	0.975837
69	1	0	-7.388855	0.533841	1.926747
70	6	0	-9.967847	-0.040338	-0.209588
71	1	0	-9.761115	-0.601825	-2.269140
72	1	0	-9.844372	0.528642	1.878792
73	6	0	11.632942	0.010350	0.175706
74	7	0	12.796119	0.011243	0.201508
75	8	0	-11.326103	-0.074769	-0.352077
76	6	0	-12.127289	0.244541	0.774539
77	1	0	-13.162913	0.157246	0.440174
78	1	0	-11.955608	-0.453119	1.605024
79	1	0	-11.943442	1.270041	1.123127
80	8	0	1.567446	0.003212	-2.384384
81	8	0	-1.318257	-0.001556	2.349288
82	6	0	-0.641567	0.000179	3.594621
83	1	0	-0.015519	-0.894062	3.718181
84	1	0	-0.016731	0.895536	3.716242
85	1	0	-1.422769	0.000286	4.357172
86	6	0	0.890167	0.002943	-3.630031
87	1	0	0.267579	-0.893539	-3.753606
88	1	0	0.261963	0.895868	-3.750659
89	1	0	1.671200	0.006441	-4.392787

Total Enegy (RB3LYP) = -1775.87712461 Harterr

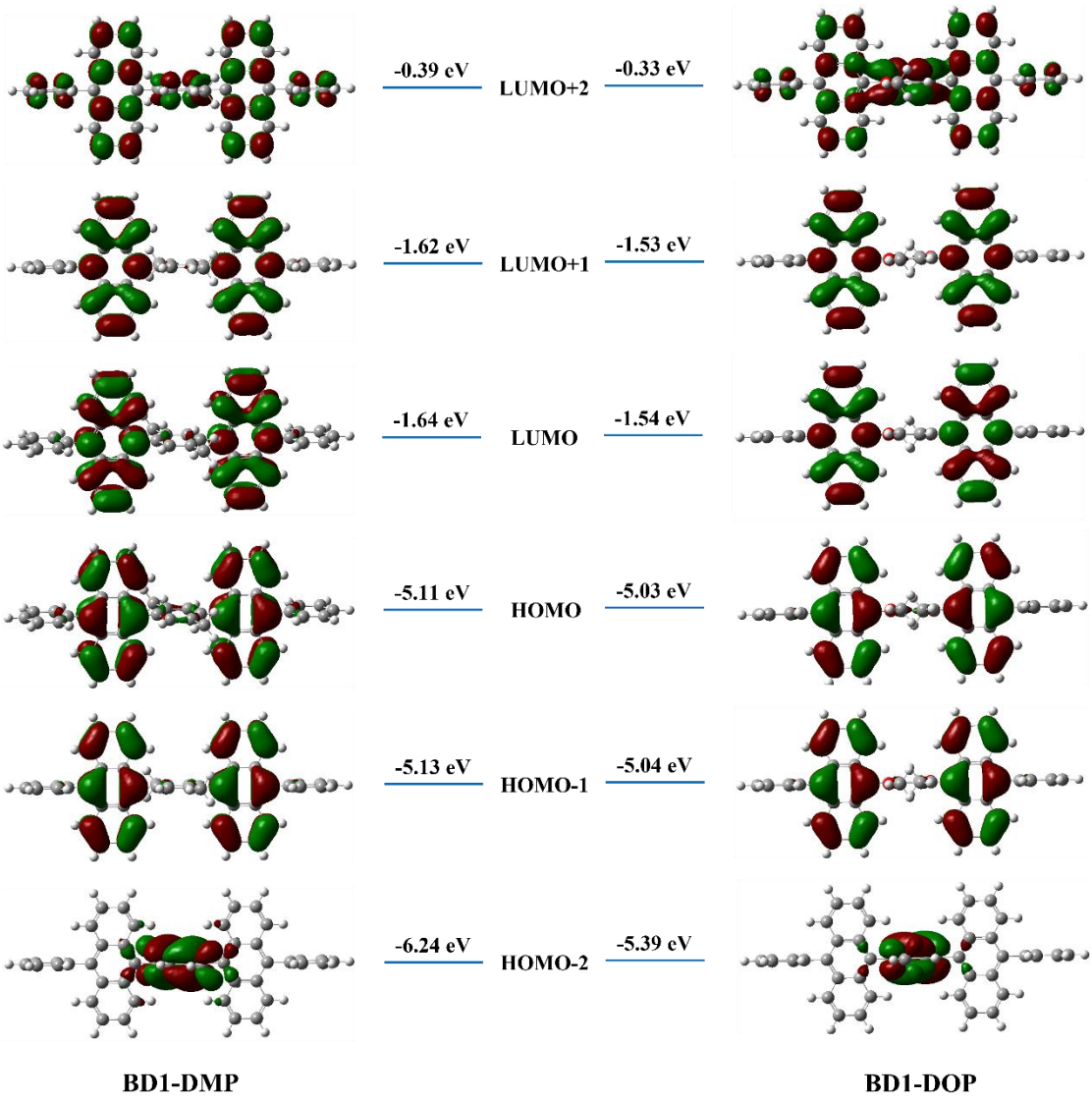


Figure S1 Molecular orbitals and energy levels of molecules **BD1-DMP** and **BD1-DOP** calculated by DFT theory.

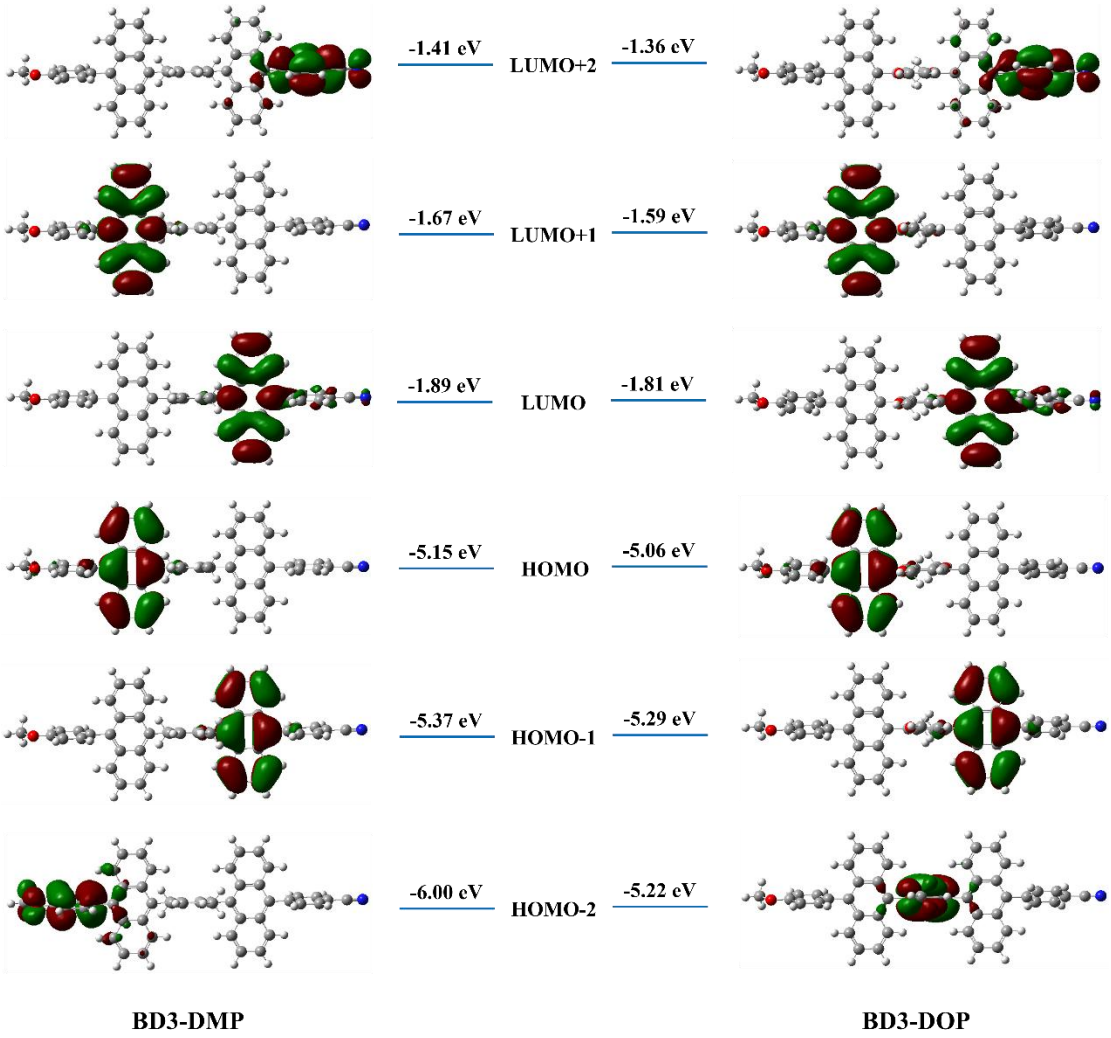


Figure S2 Molecular orbitals and energy levels of molecules **BD3-DMP** and **BD3-DOP** calculated by DFT theory.

4.2. TD-DFT calculations

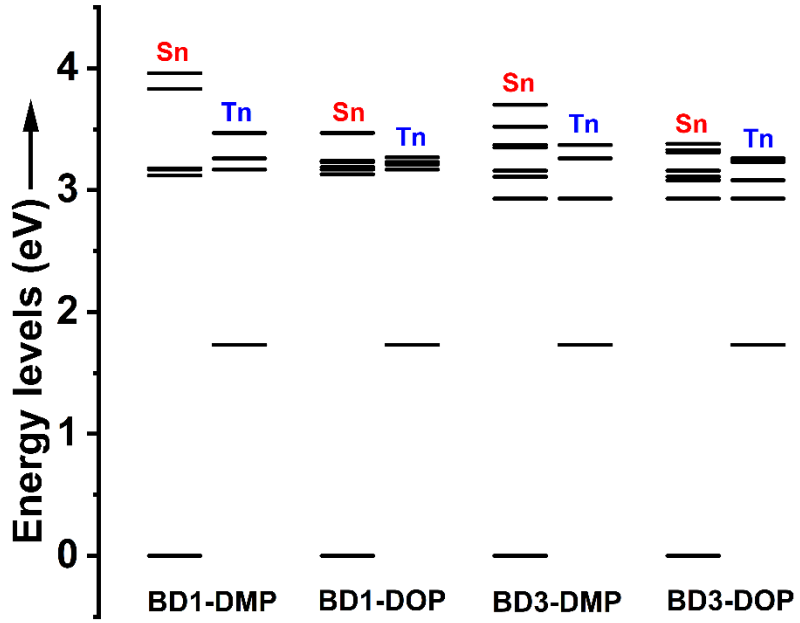


Figure S3. Energy levels of single and triple excited states of molecules are calculated by TD-DFT.

Table S5. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **BD1-DMP**.

Excited state	E_g **[eV]**	E_g **[nm]**	*f*	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	3.1216	397.18	0.3255	HOMO-1	→	LUMO+1	-0.23657
				HOMO	→	LUMO+1	0.66130
S2	3.1662	396.58	0.0000	HOMO-1	→	LUMO	0.57893
				HOMO	→	LUMO+1	0.40546
S3	3.1768	390.28	0.0569	HOMO-1	→	LUMO+1	0.66303
S4	3.1821	389.62	0.0000	HOMO-1	→	LUMO	-0.39993
S5	3.8302	323.70	0.0000	HOMO-4	→	LUMO+1	0.33636

S6	3.8313	323.61	0.0000	HOMO-4	→	LUMO	-0.35107
S7	3.9602	313.08	0.0000	HOMO-4	→	LUMO	0.70033
T1	1.7307	716.40	0.0000	HOMO-1	→	LUMO+1	-0.48686
				HOMO	→	LUMO	0.50321
T2	1.7312	716.19	0.0000	HOMO-1	→	LUMO	0.49542
				HOMO	→	LUMO+1	-0.49477
T3	3.1665	391.55	0.0000	HOMO-1	→	LUMO	0.49969
				HOMO	→	LUMO+1	0.50015
T4	3.1668	391.51	0.0000	HOMO-1	→	LUMO+1	0.50741
T5	3.2647	379.78	0.0000	HOMO-9	→	LUMO+1	0.29828
T6	3.2649	379.75	0.0000	HOMO-9	→	LUMO+1	0.22571
T7	3.4734	356.96	0.0000	HOMO-4	→	LUMO+1	0.37565

Table S6. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **BD1-DOP**.

Excited state	E_g **[eV]**	E_g **[nm]**	f	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	3.1348	395.51	0.3667	HOMO-1	→	LUMO+1	0.35185
				HOMO	→	LUMO	0.60630
S2	3.1733	390.71	0.0000	HOMO-1	→	LUMO	0.56345
				HOMO	→	LUMO+1	-0.42685
S3	3.1762	390.35	0.0214	HOMO-1	→	LUMO+1	0.60942
S4	3.1877	388.95	0.0000	HOMO-1	→	LUMO	0.42142
S5	3.2313	383.70	0.0000	HOMO-2	→	LUMO	0.33636
S6	3.2427	382.35	0.0000	HOMO-2	→	LUMO+1	-0.35107
S7	3.8339	323.39	0.0000	HOMO-4	→	LUMO+1	0.70033
T1	1.7317	715.96	0.0000	HOMO-1	→	LUMO+1	0.49110
				HOMO	→	LUMO	0.50321
T2	1.7318	715.91	0.0000	HOMO-1	→	LUMO	0.49534
				HOMO	→	LUMO+1	0.49480

T3	3.1734	390.70	0.0000	HOMO-1	→	LUMO	-0.49949
				HOMO	→	LUMO+1	0.49949
T4	3.1735	390.68	0.0000	HOMO-1	→	LUMO+1	0.50336
T5	3.2133	385.85	0.0000	HOMO-6	→	LUMO+1	-0.11162
T6	3.2258	384.35	0.0000	HOMO-6	→	LUMO	-0.14234
T7	3.2727	378.85	0.0000	HOMO-5	→	LUMO	0.29450

Table S7. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **BD3-DMP**.

Excited state	E_g **[eV]**	E_g **[nm]**	f	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	2.9323	422.83	0.0059	HOMO	→	LUMO	0.70653
S2	3.1077	398.95	0.4299	HOMO-1	→	LUMO	0.53210
				HOMO	→	LUMO+1	0.45110
S3	3.1592	392.46	0.0027	HOMO-1	→	LUMO	-0.44433
				HOMO	→	LUMO+1	0.53518
S4	3.3543	369.63	0.0012	HOMO-1	→	LUMO	0.10274
				HOMO-1	→	LUMO+2	0.68712
S5	3.3736	367.51	0.0006	HOMO-1	→	LUMO+1	0.70101
S6	3.5245	351.78	0.0000	HOMO	→	LUMO+2	0.70279
S7	3.7041	334.72	0.0004	HOMO-2	→	LUMO+1	0.69770
T1	1.7261	718.31	0.0000	HOMO-1	→	LUMO	0.16920
				HOMO	→	LUMO+1	0.67461
T2	1.7271	717.86	0.0000	HOMO-1	→	LUMO	0.67304
				HOMO	→	LUMO+1	-0.17354
T3	2.9335	422.66	0.0000	HOMO	→	LUMO	0.70403
T4	3.2582	380.53	0.0000	HOMO-1	→	LUMO+2	0.59003
T5	3.2600	380.32	0.0000	HOMO-1	→	LUMO+3	0.11859
T6	3.2645	379.79	0.0000	HOMO-5	→	LUMO+1	-0.12656
T7	3.3723	367.66	0.0000	HOMO-1	→	LUMO+1	0.70549

Table S8. Calculated energy levels, oscillator strengths (*f*), and orbital transition analyses for **BD3-DOP**.

Excited state	E_g **[eV]**	E_g **[nm]**	*f*	**Transition (D: donor unit, A: acceptor unit)**			**Coefficient**
S1	2.9304	423.10	0.0023	HOMO	→	LUMO	0.70407
S2	3.0836	402.07	0.0706	HOMO-2	→	LUMO	0.62715
				HOMO-1	→	LUMO	-0.28189
				HOMO	→	LUMO+1	-0.13375
S3	3.1084	398.87	0.3695	HOMO-2	→	LUMO	0.30352
				HOMO-1	→	LUMO	0.45867
				HOMO	→	LUMO+1	0.42580
S4	3.1570	392.73	0.0043	HOMO-1	→	LUMO	-0.42728
				HOMO-1	→	LUMO+2	0.10795
				HOMO	→	LUMO+1	0.53721
S5	3.3063	375.00	0.0006	HOMO-2	→	LUMO+1	0.68566
				HOMO-1	→	LUMO+1	-0.16174
S6	3.3260	372.77	0.0038	HOMO-1	→	LUMO	0.13505
				HOMO-1	→	LUMO+2	0.68802
S7	3.3768	367.17	0.0001	HOMO-2	→	LUMO+1	0.16067
				HOMO-1	→	LUMO+1	0.68760
T1	1.7265	718.14	0.0000	HOMO	→	LUMO+1	0.69523
				HOMO	→	LUMO+1	0.13812
T2	1.7276	717.65	0.0000	HOMO-1	→	LUMO	0.69066
				HOMO-1	→	LUMO	0.13680
T3	2.9306	423.06	0.0000	HOMO	→	LUMO	0.70296
T4	3.0763	403.03	0.0000	HOMO-2	→	LUMO	0.69607
T5	3.2266	384.26	0.0000	HOMO-11	→	LUMO+3	0.11762
				HOMO-10	→	LUMO+2	0.29189
				HOMO-1	→	LUMO+2	0.61476
T6	3.2527	381.18	0.0000	HOMO-9	→	LUMO+1	-0.11723
				HOMO-8	→	LUMO+1	0.18695

				HOMO-6	→	LUMO+1	0.39432
				HOMO-1	→	LUMO+1	0.33939
				HOMO	→	LUMO+7	0.14807
				HOMO	→	LUMO+10	0.28982
				HOMO	→	LUMO+11	-0.13492
T7	3.2603	380.29	0.0000	HOMO-14	→	LUMO+11	-0.10224
				HOMO-9	→	LUMO	0.36153
				HOMO-8	→	LUMO	0.22858
				HOMO-7	→	LUMO	0.27634
				HOMO-1	→	LUMO+3	0.12777
				HOMO-1	→	LUMO+4	0.10340
				HOMO-1	→	LUMO+8	-0.37126

5. X-Ray Crystallography

Table S9. Summary of crystal data for **BD1-DOP**.

Parameter	BD1-DOP
Empirical formula	$C_{48}H_{34}O_2$
Formula weight [g mol^{-1}]	642.78
Crystal system	Triclinic
Space group	*P*-1
a [Å]	8.4049(5)
b [Å]	14.7394(9)
c [Å]	17.7022(11)
α [°]	108.851(2)
β [°]	101.726(2)
γ [°]	93.378(2)
Volume [Å^3]	2013.6(2)
Z	2
Density, calcd [g cm^{-3}]	1.340
Temperature (K)	153
Reflections collected	59479
Parameters	528
R_{int}	0.0484
R[I>2σ(I)][a]	0.0884
wR[I>2σ(I)][b]	0.2502
GOF on F^2	1.056

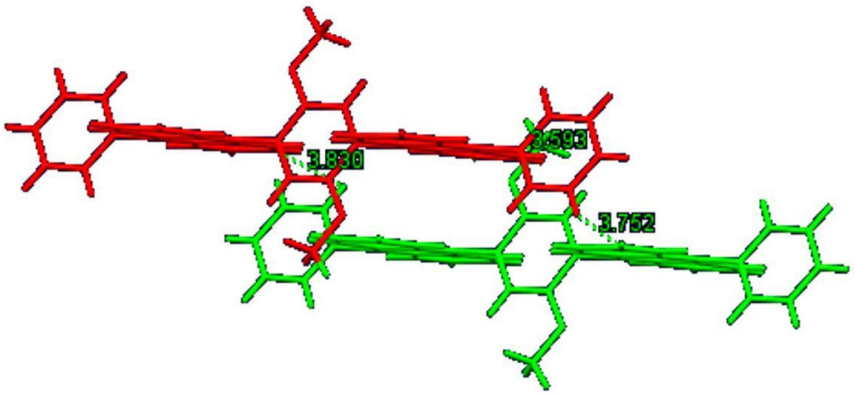


Figure. S4. Packing distances and conformations in **BD1-DOP**: The shortest contact between a substituent on a neighboring molecule and an anthracene ring is 3.7252Å, and the centroid distance is 3.830 Å.

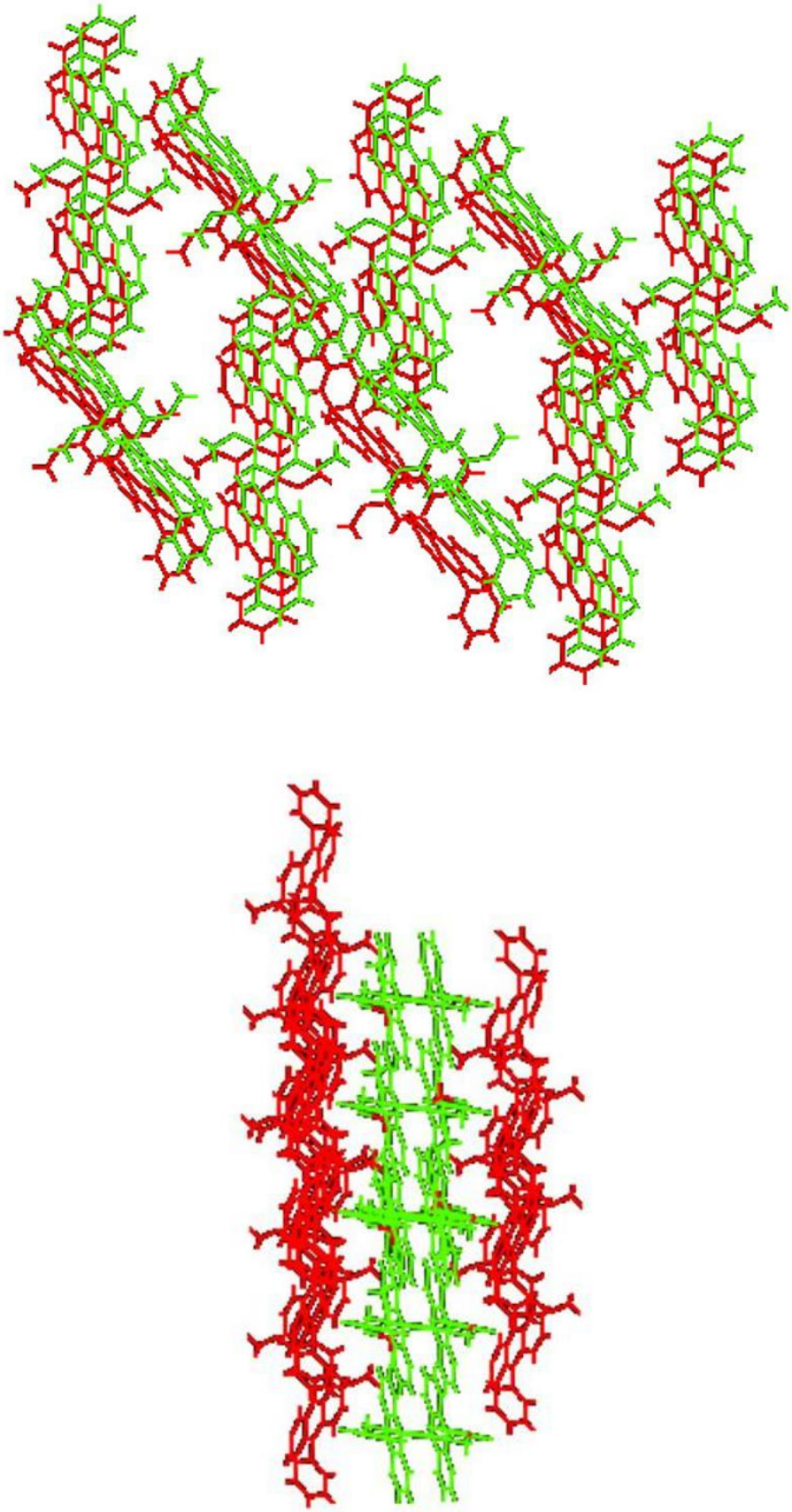


Figure. S5. Packing plots for **BD1-DOP**: Top view (left) and side view (right).

6. Thermal properties

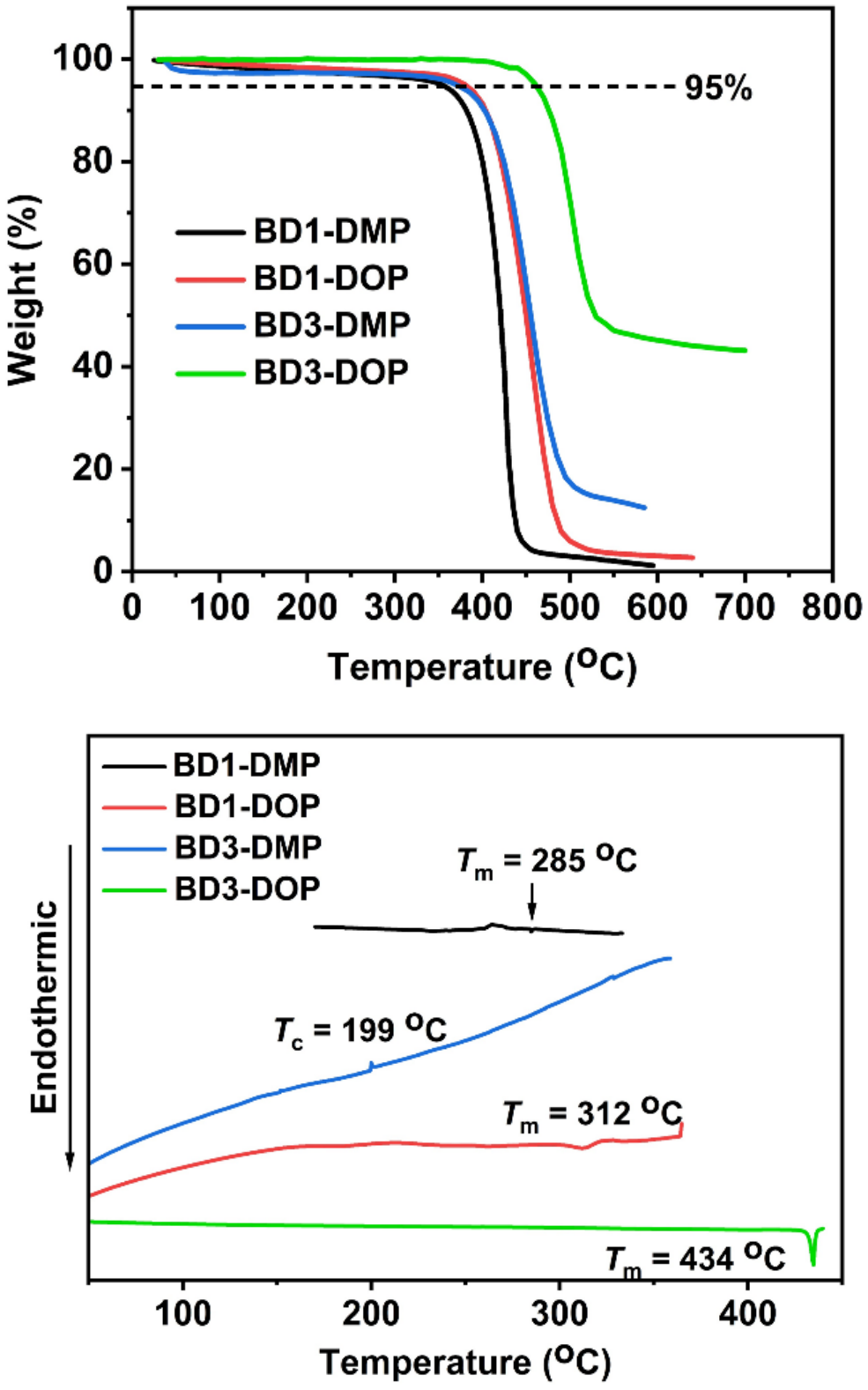


Figure S6. (a) Thermal gravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) of **BD1-DMP**, **BD1-DOP**, **BD3-DMP**, and **BD3-DOP**.

7. Electrochemical properties

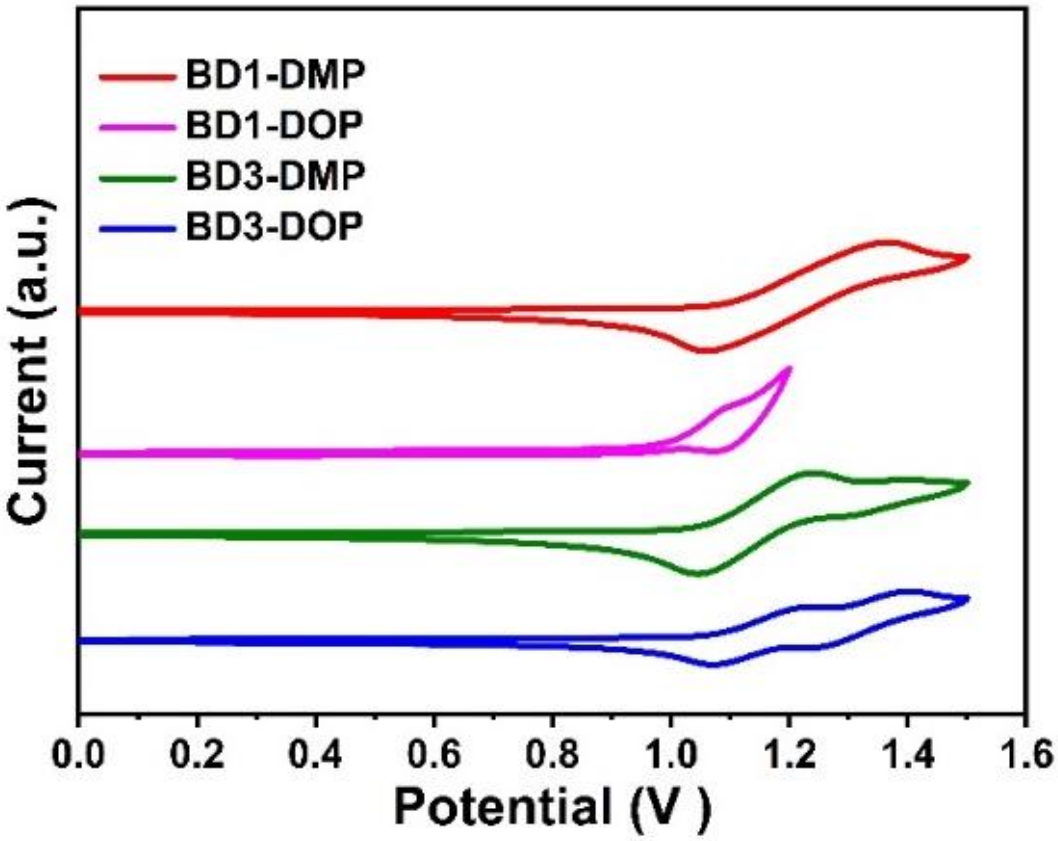


Figure S7. Cyclic voltammetry (CV) measurements of **BD1-DMP**, **BD1-DOP**, **BD3-DMP**, and **BD3-DOP**.

8. Photophysical Properties

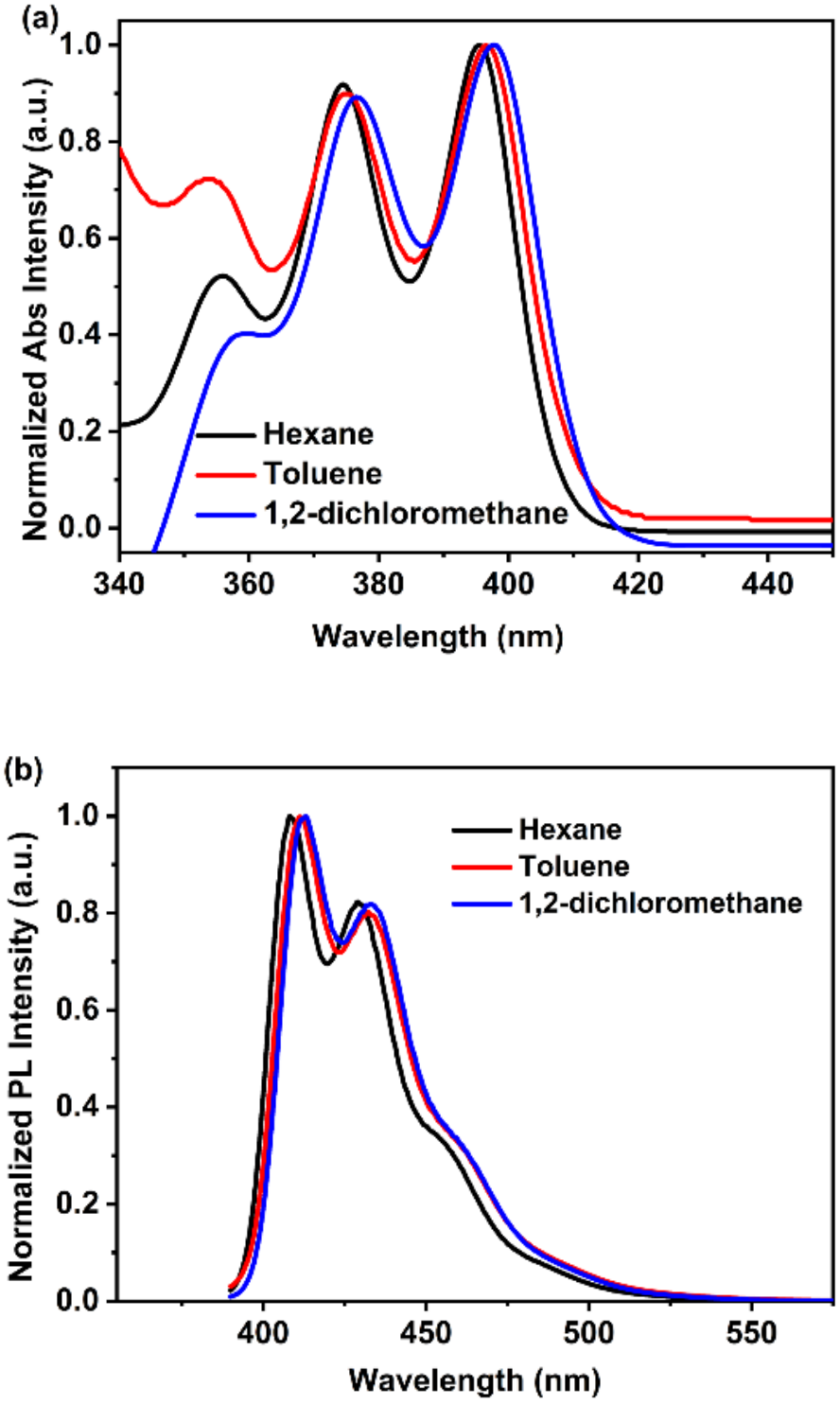


Figure S8. UV-vis absorption (a) and fluorescence spectra (b) of the compound **BD1-DMP** were recorded in seven different solvents at ~10^{-5} M and 25 ºC.

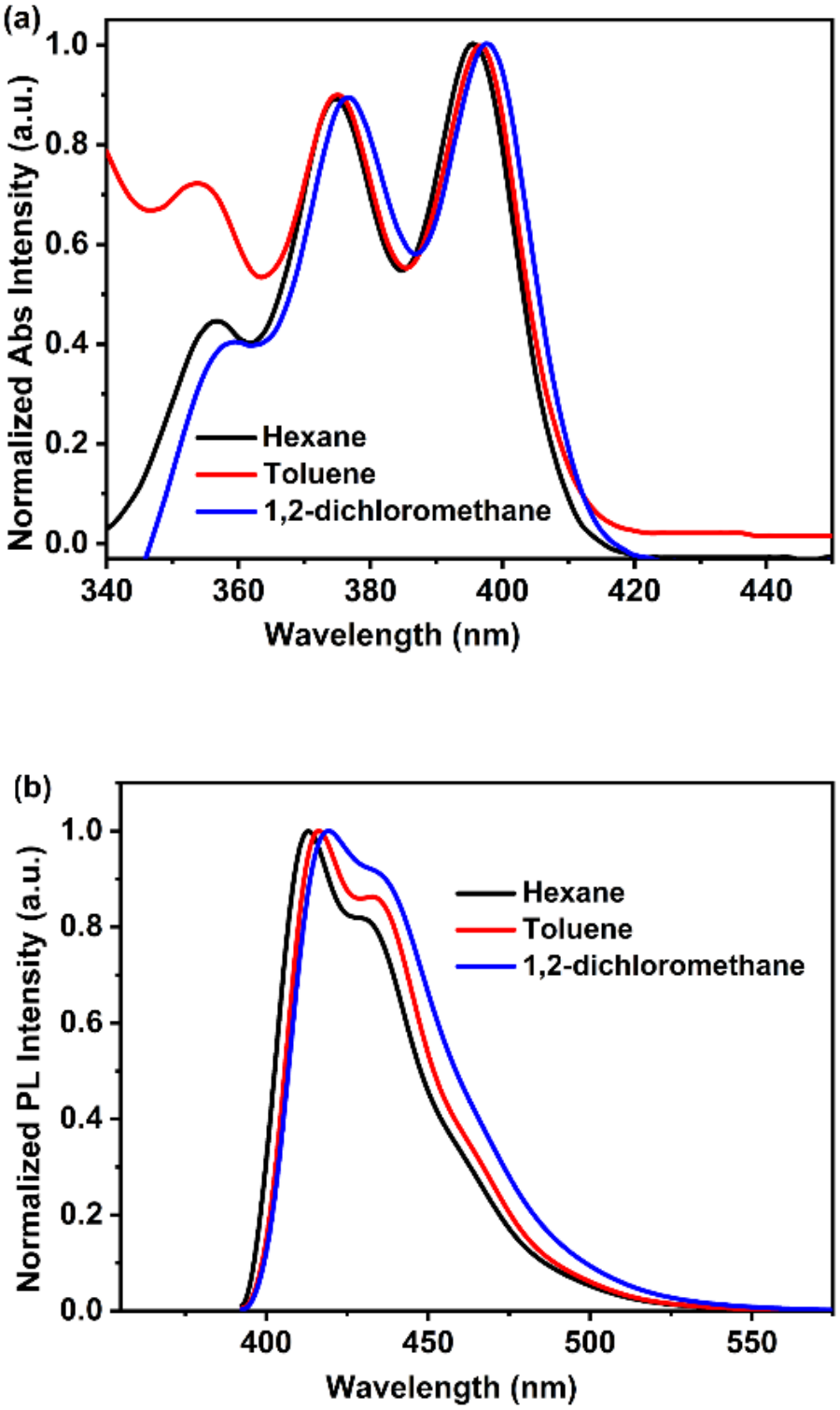


Figure S9. UV-vis absorption (a) and fluorescence spectra (b) of the compound **BD1-DOP** were recorded in seven different solvents at ~10^{-5} M and 25 ºC.

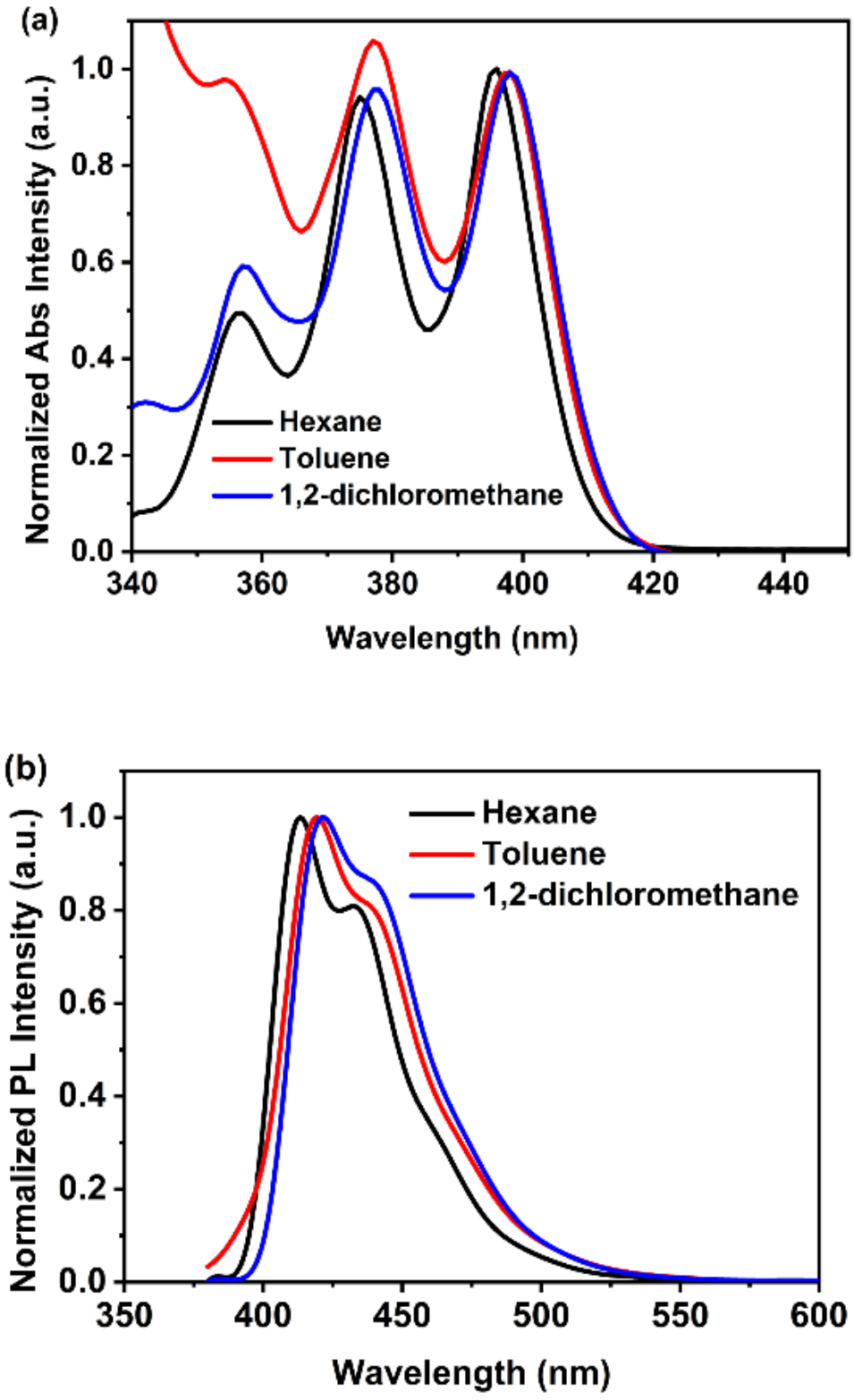


Figure S10. UV-vis absorption (a) and fluorescence spectra (b) of the compound **BD3-DMP** were recorded in seven different solvents at ~10^{-5} M and 25 ºC.

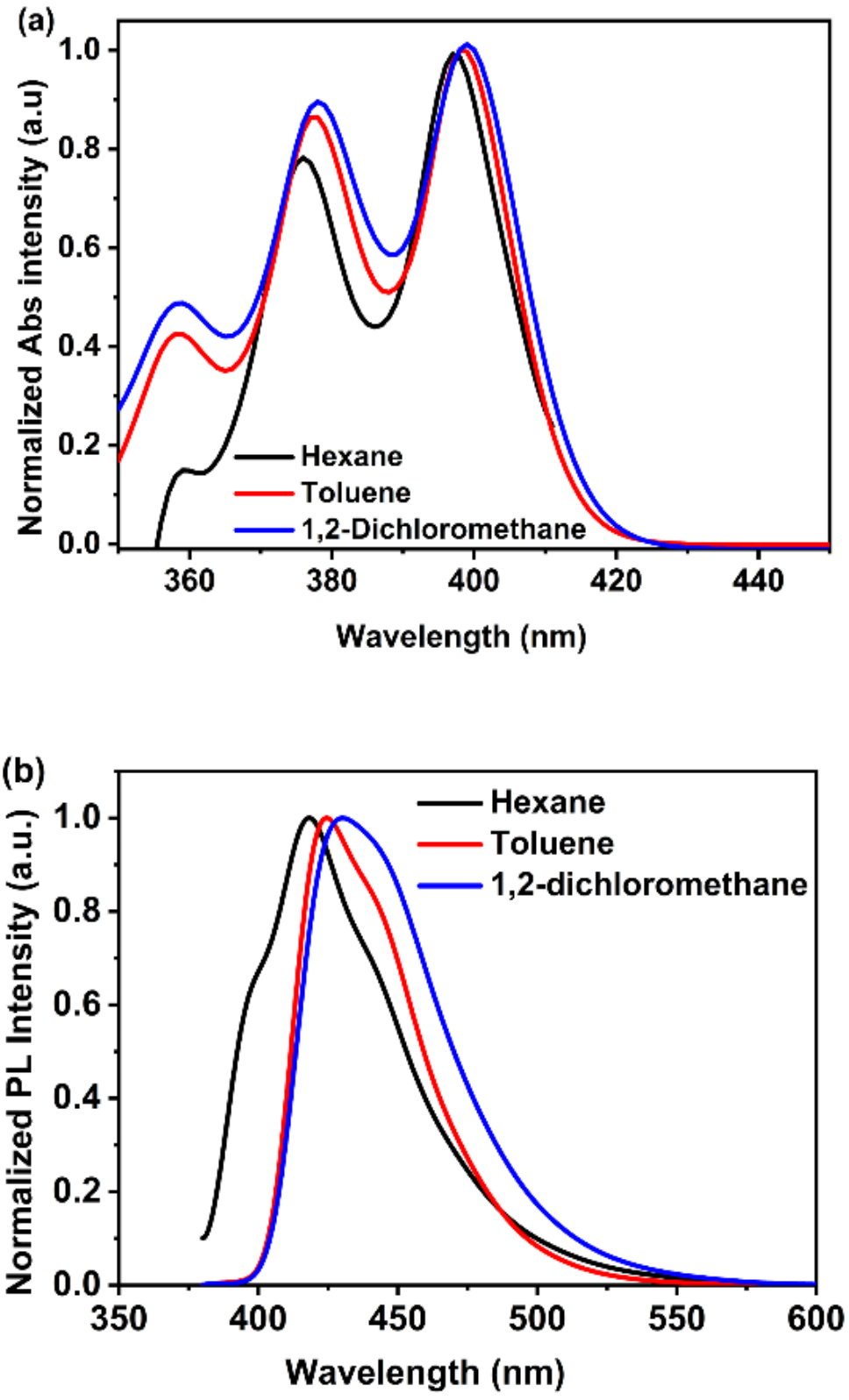
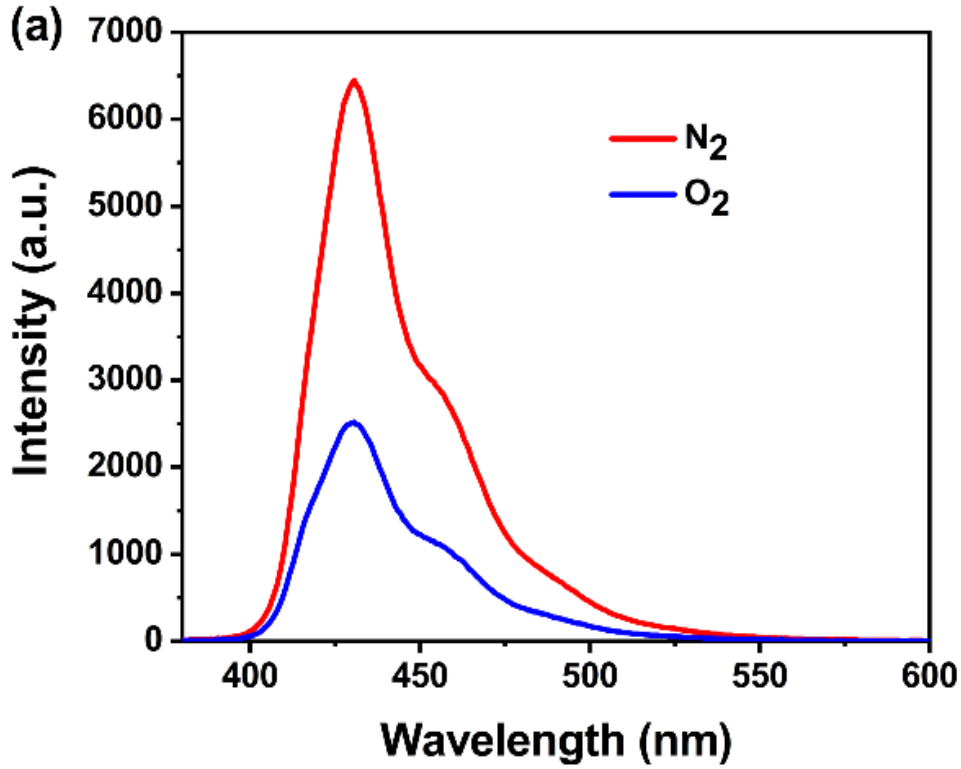
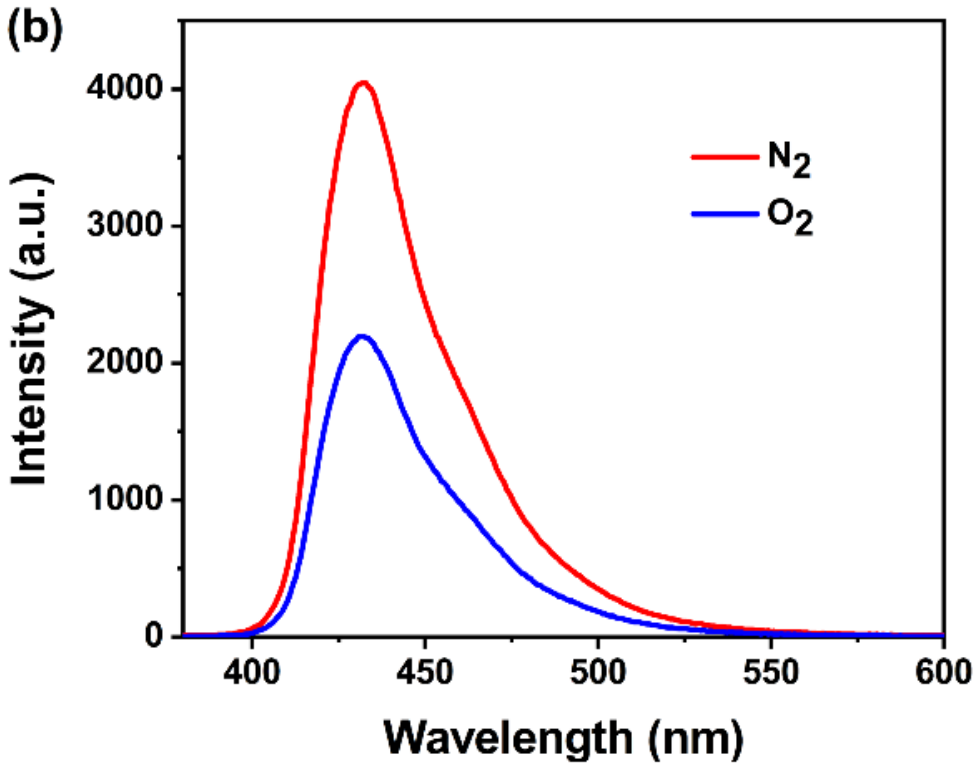


Figure S11. UV-vis absorption (a) and fluorescence spectra (b) of the compound **BD3-DOP** were recorded in seven different solvents at ~10^{-5} M and 25 ºC.


(a)
Intensity (a.u.)
Wavelength (nm)
N2
O2
0
1000
2000
3000
4000
5000
6000
7000
400
450
500
550
600


(b)
Intensity (a.u.)
Wavelength (nm)
N2
O2
0
1000
2000
3000
4000
400
450
500
550
600

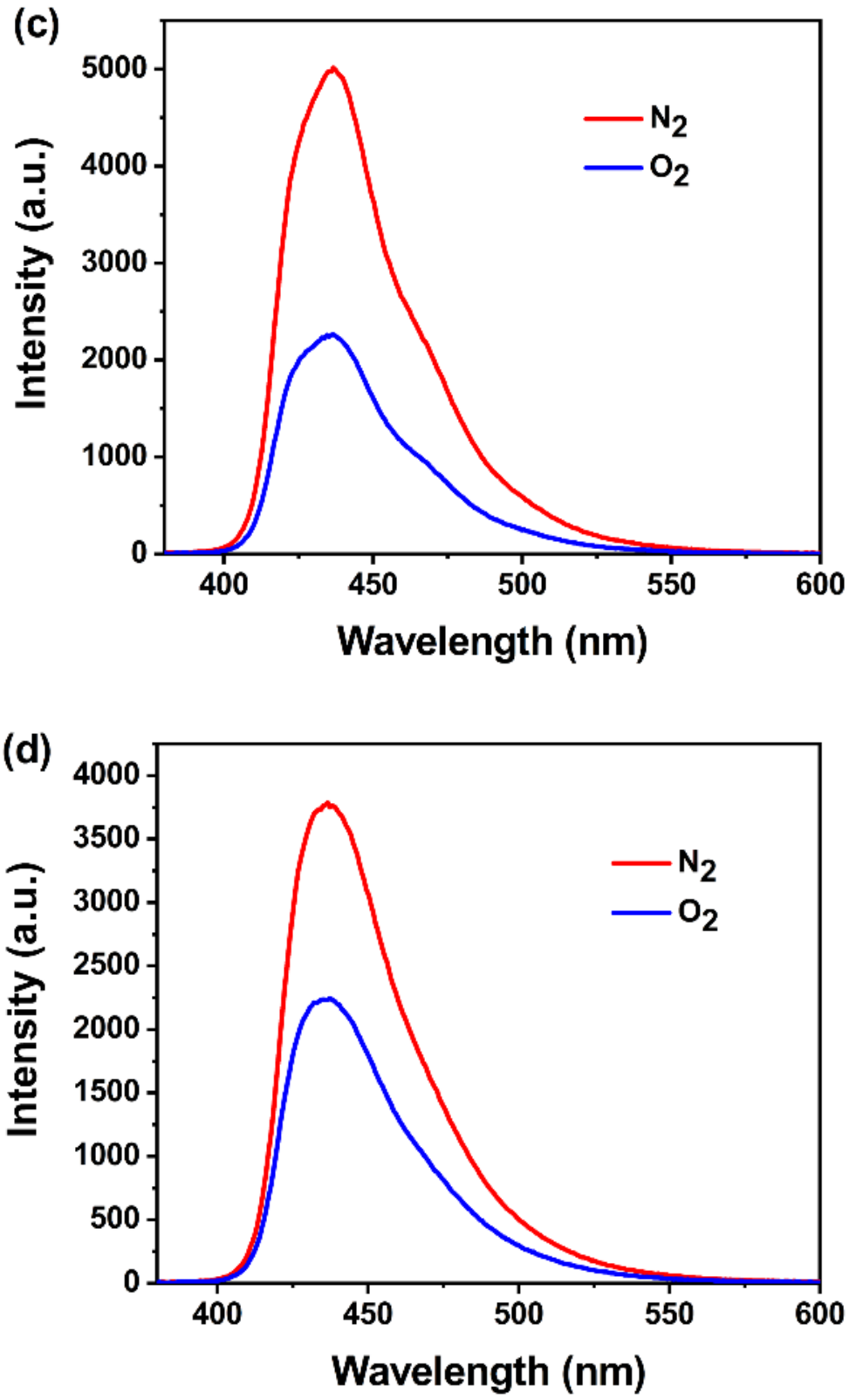


Figure S12. PL spectra in toluene solution after nitrogen bubbling and oxygen bubbling: (a) **BD1-DMP**, (b) **BD1-DOP**, (c) **BD3-DMP** and (d) **BD3-DOP**.

9. Transient EL decay

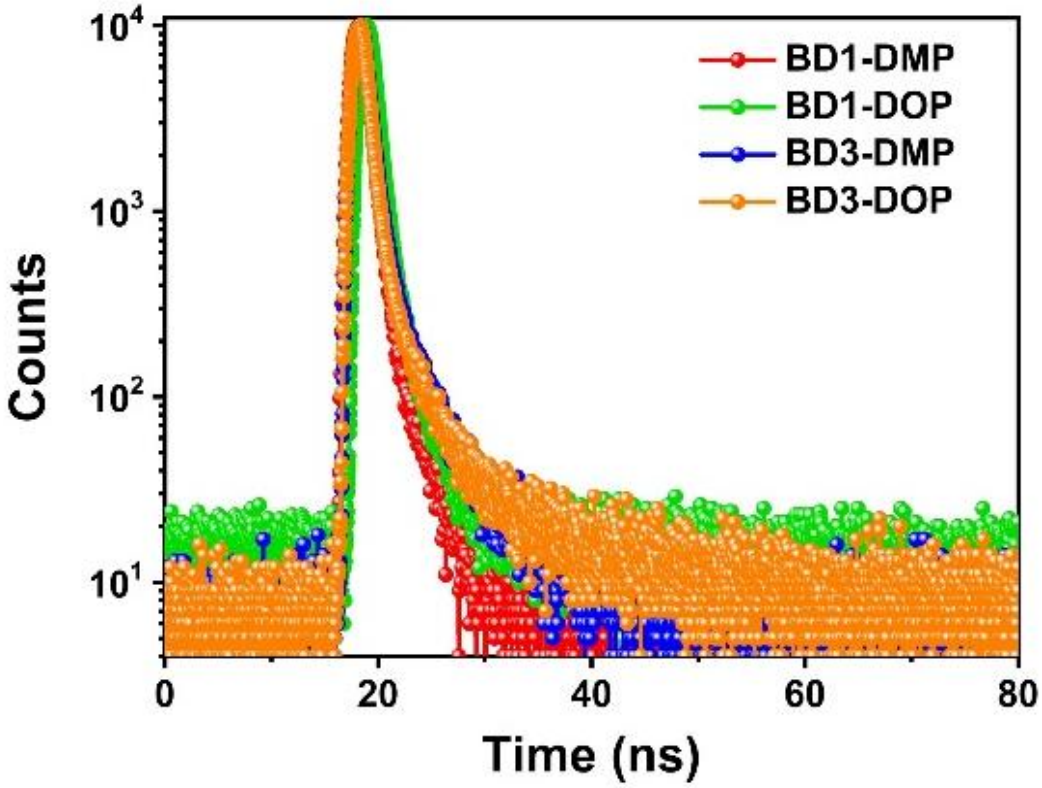


Figure S13. The transient PL decay spectra of **BD1-DMP**, **BD1-DOP**, **BD3-DMP**, and **BD3-DOP** in thin film state.

10. Device performance

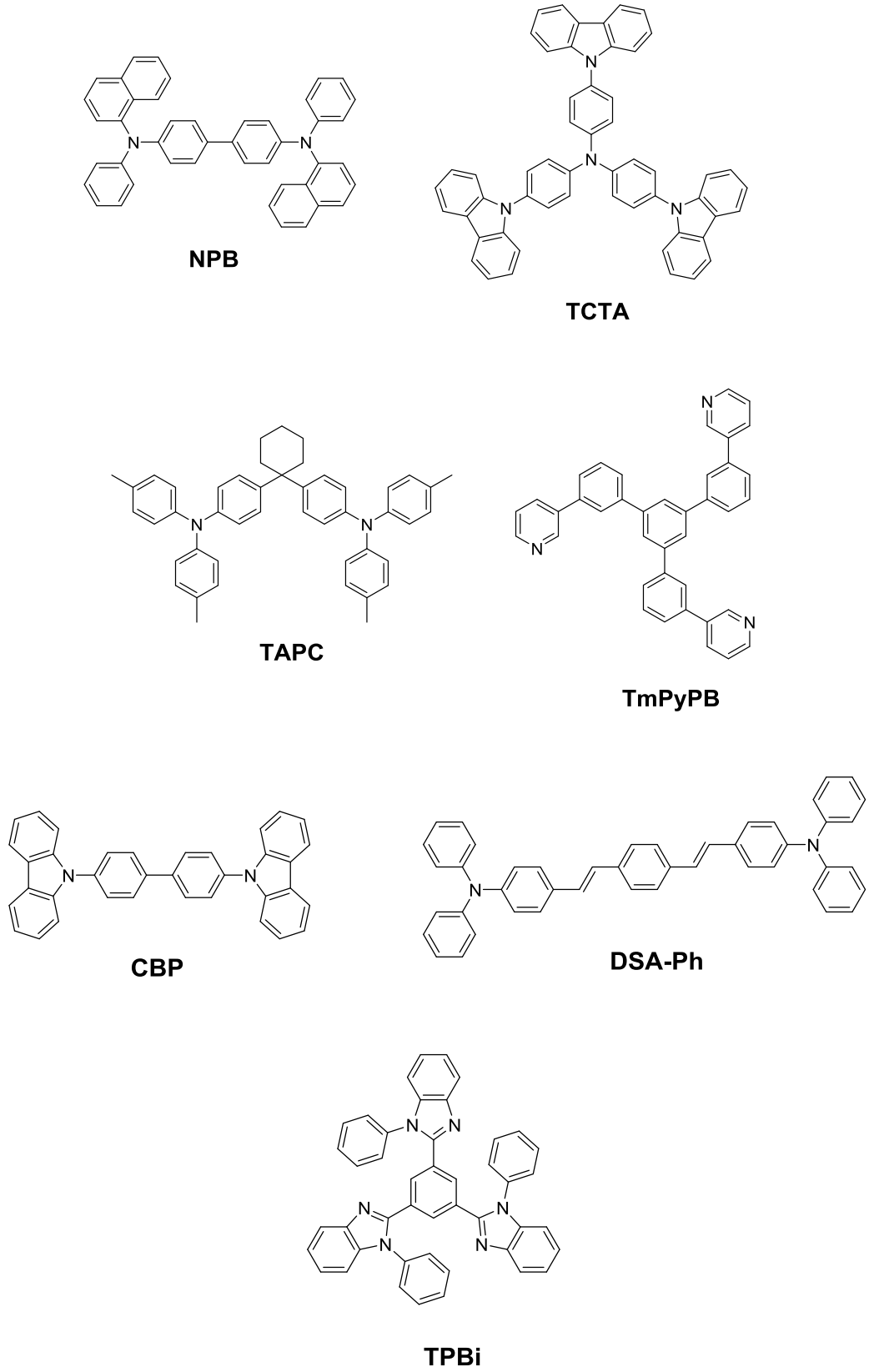


Figure S14. Molecular structures of the materials used in devices.

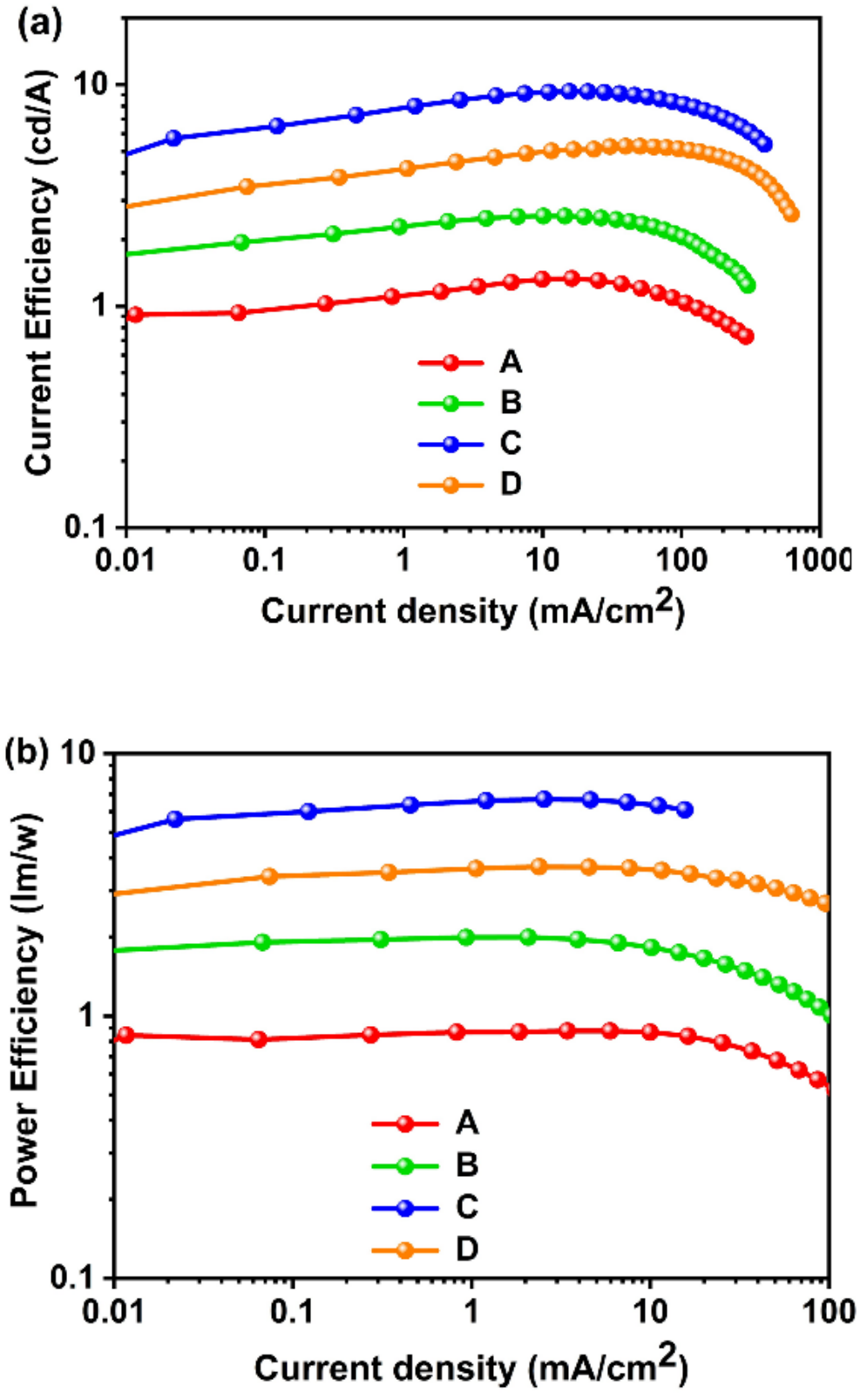


Figure S15. (a) Current Efficiency versus current density curves, (b) Power Efficiencies versus current density curves of Device **A**-**D** based non-doped devices.

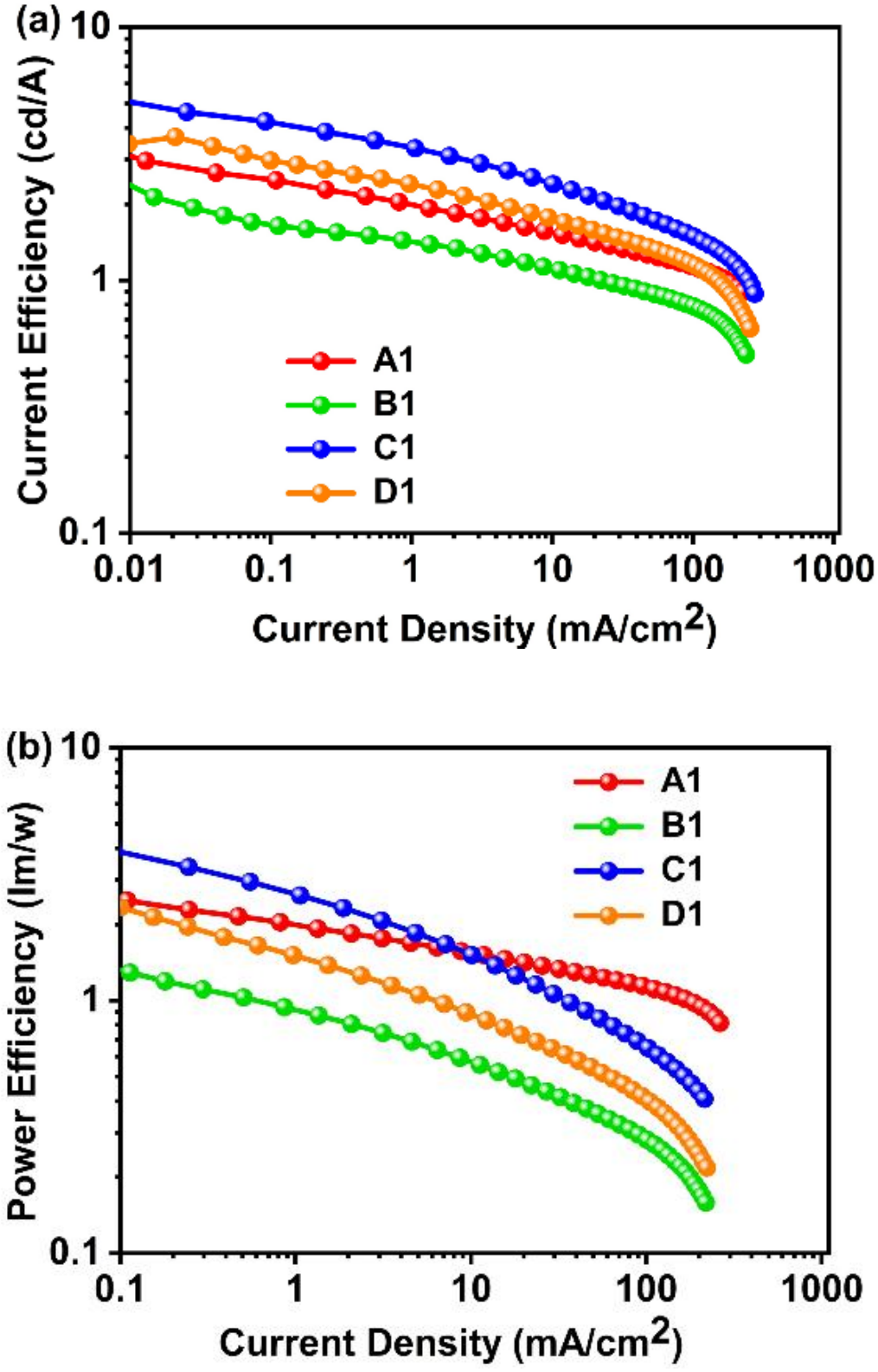


Figure S16. (a) Current Efficiency versus current density curves, (b) Power Efficiencies versus current density curves of Device **A1**-**D1** based CBP doped devices.

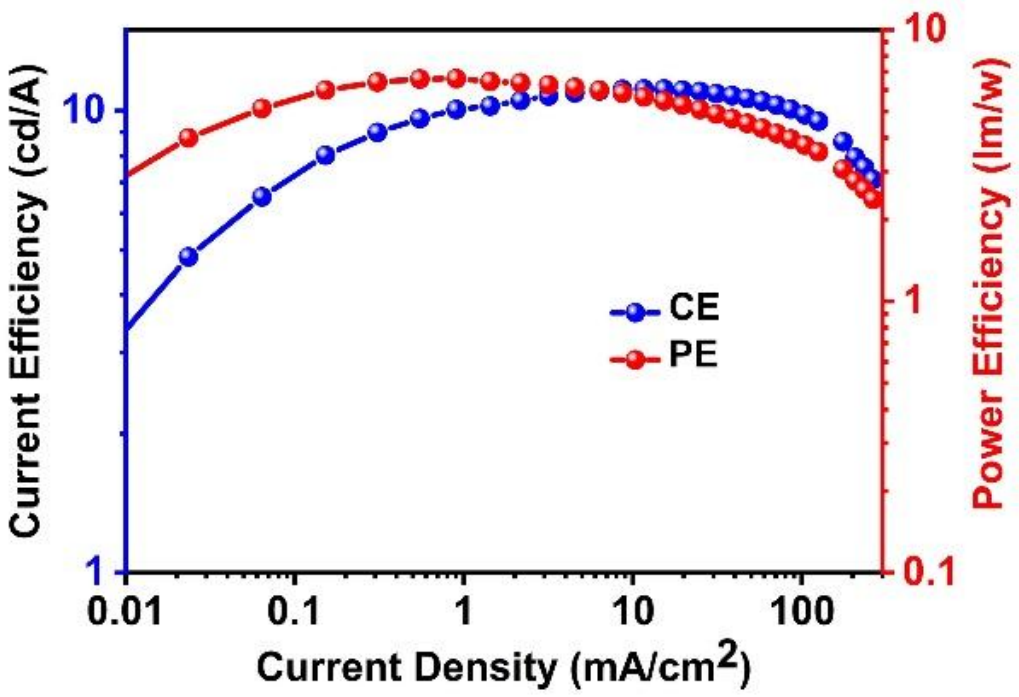
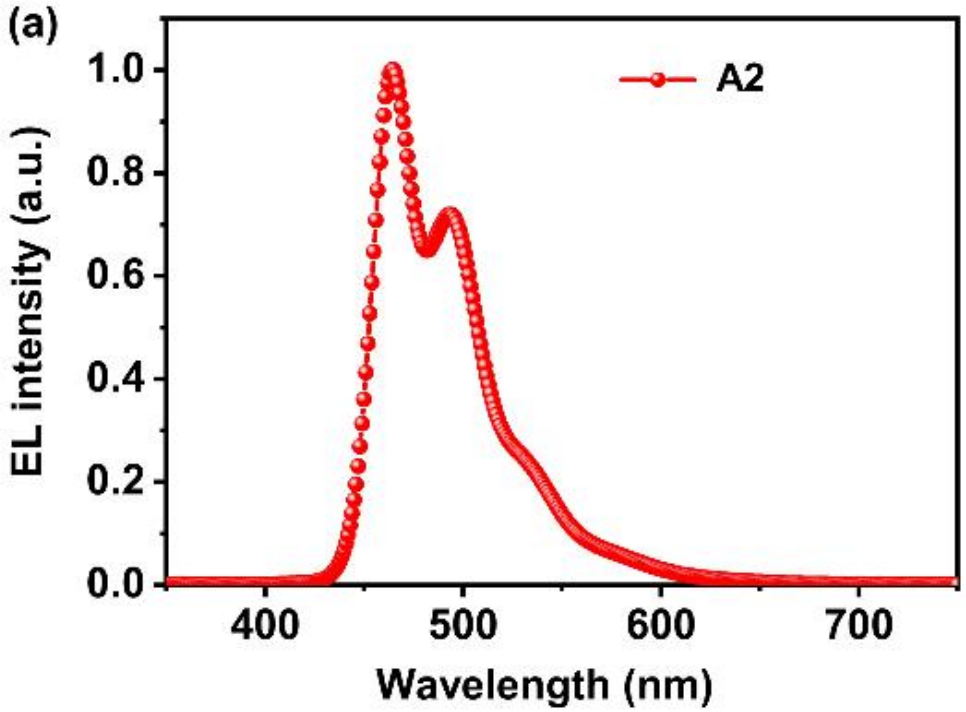


Figure S17. (a) Current Efficiency versus current density curves, (b) Power Efficiencies versus current density curves of Device **A2** based DSA-Ph doped devices.



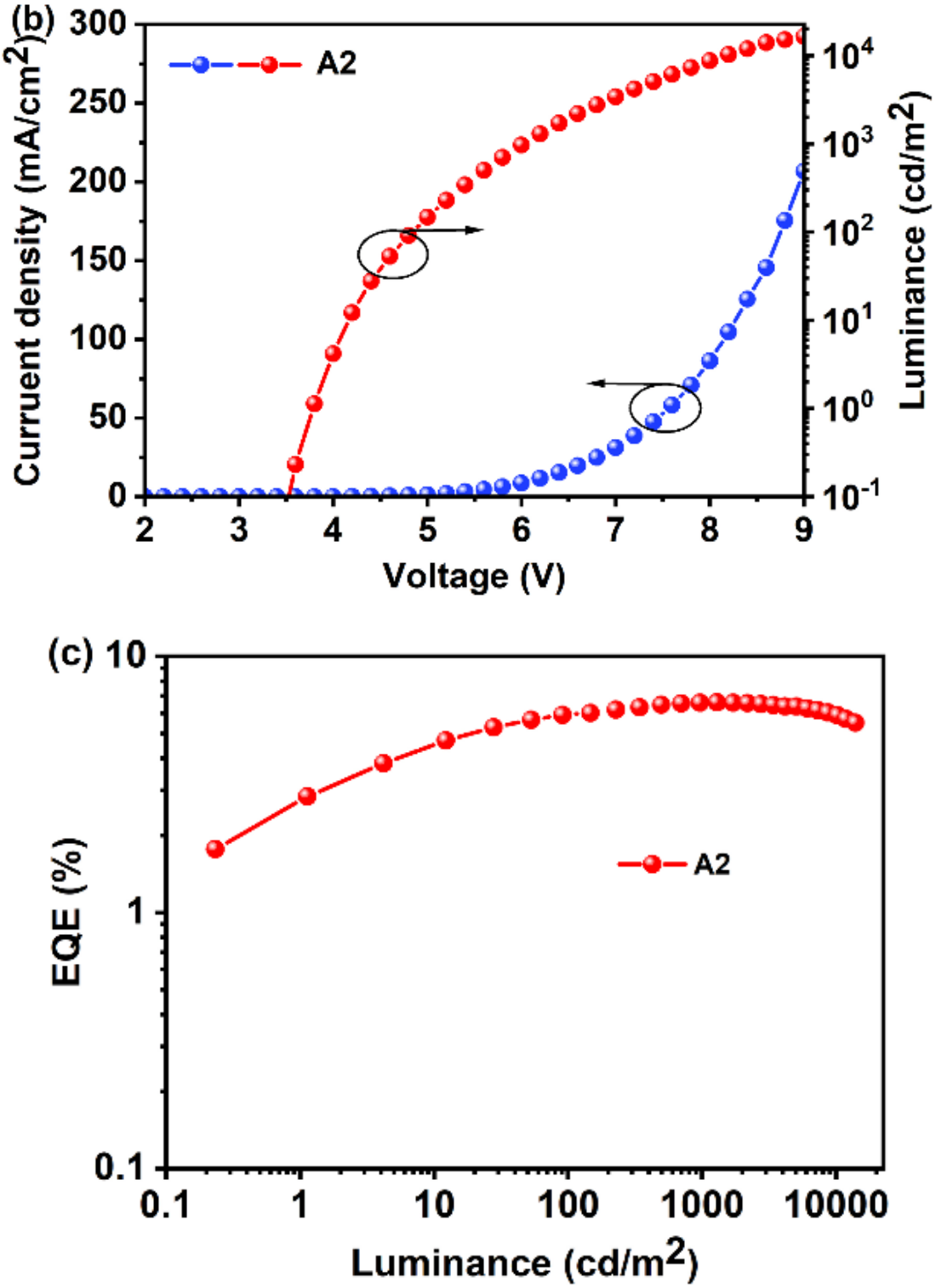
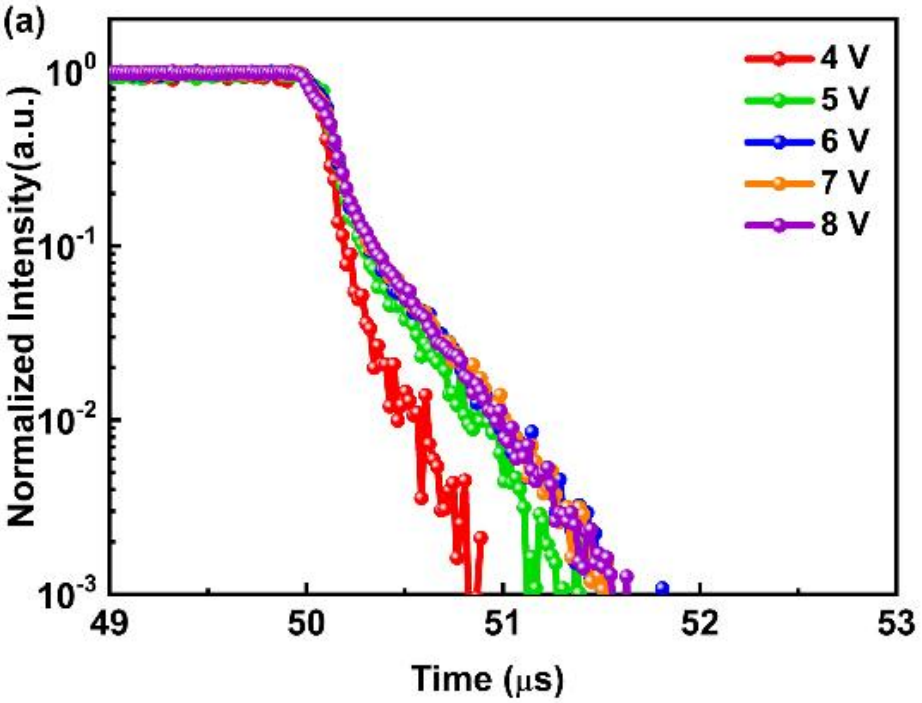
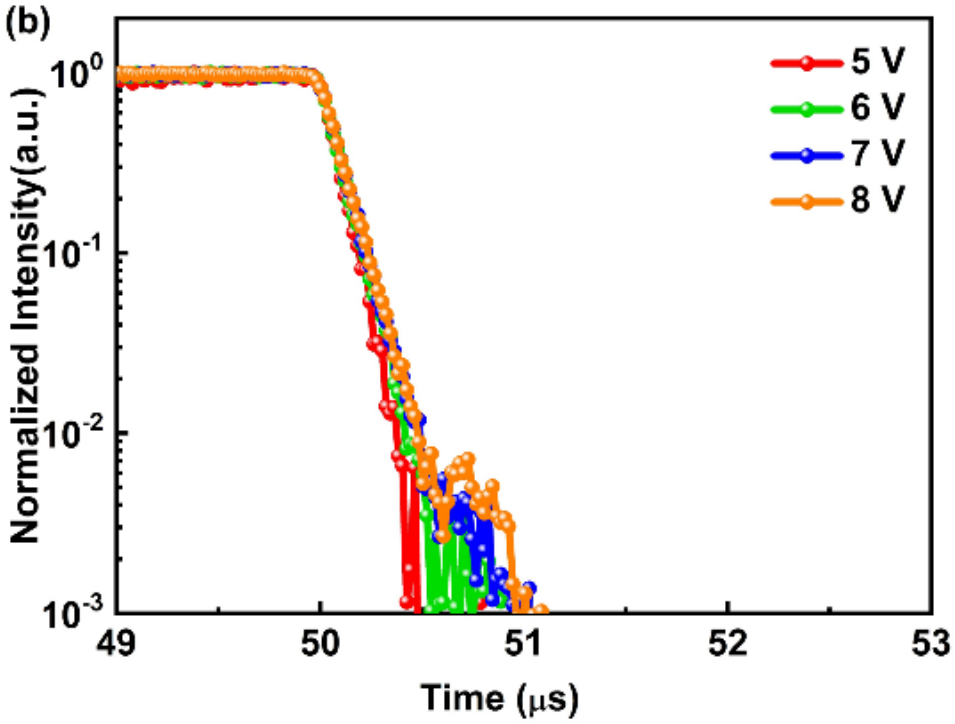


Figure S18. (a) Electroluminescence spectrum of device **A2**, (b) current density and luminescence versus voltage curves, and (c) EQE versus luminance of DSA-Ph based **BD1-DMP** doped devices.


(a)
Normalized Intensity(a.u.)
10^{0}
10^{-1}
10^{-2}
10^{-3}
49
50
51
52
53
Time (μs)
4 V
5 V
6 V
7 V
8 V


(b)
Normalized Intensity(a.u.)
10^{0}
10^{-1}
10^{-2}
10^{-3}
49
50
51
52
53
Time (μs)
5 V
6 V
7 V
8 V

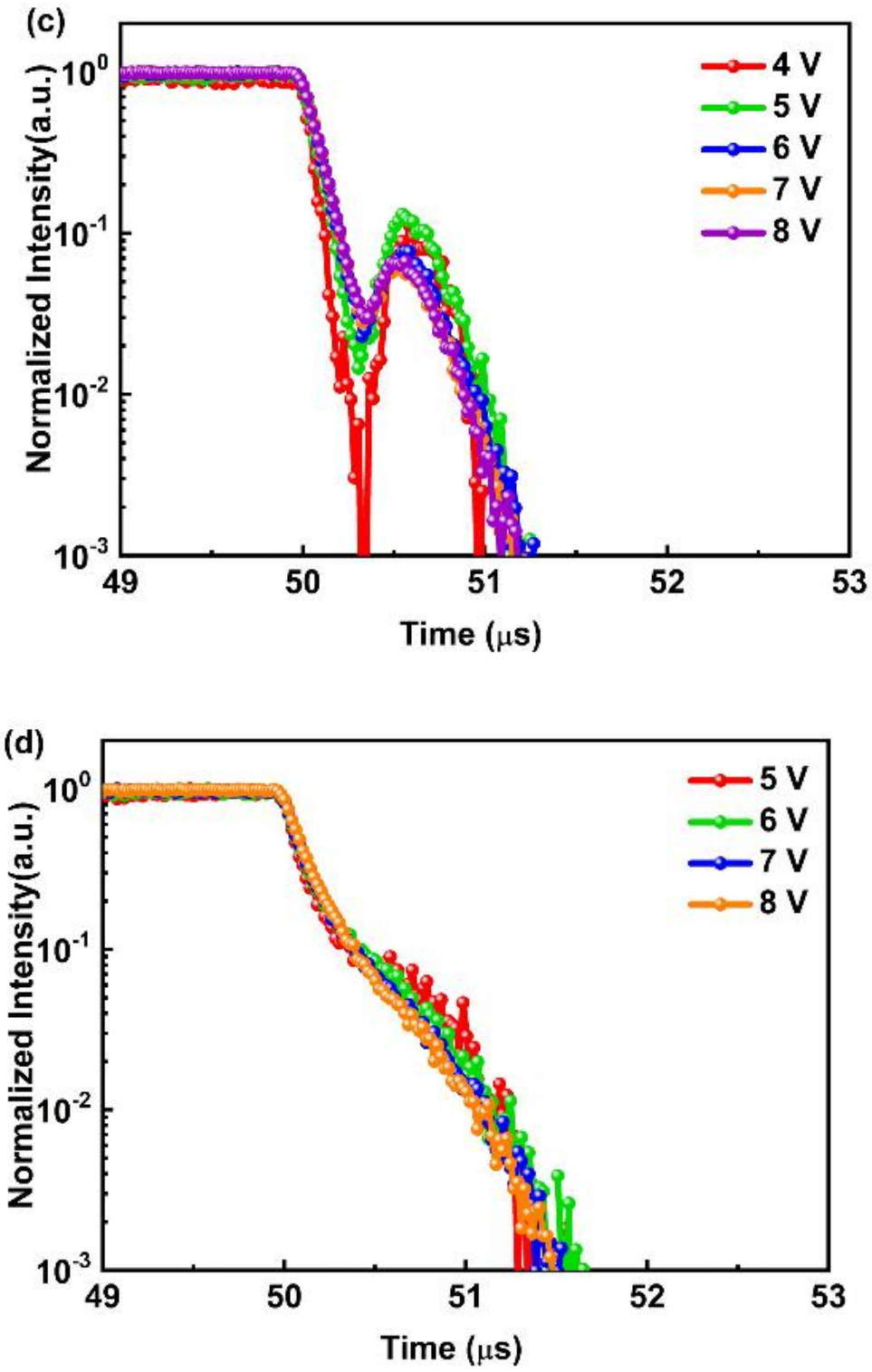


Figure S19. The transient EL decay of the non-doped OLEDs at different driving voltages: (a) **BD1-DMP**, (b) **BD1-DOP**, (c) **BD3-DMP**, and (d) **BD3-DOP**.

11. NMR spectra

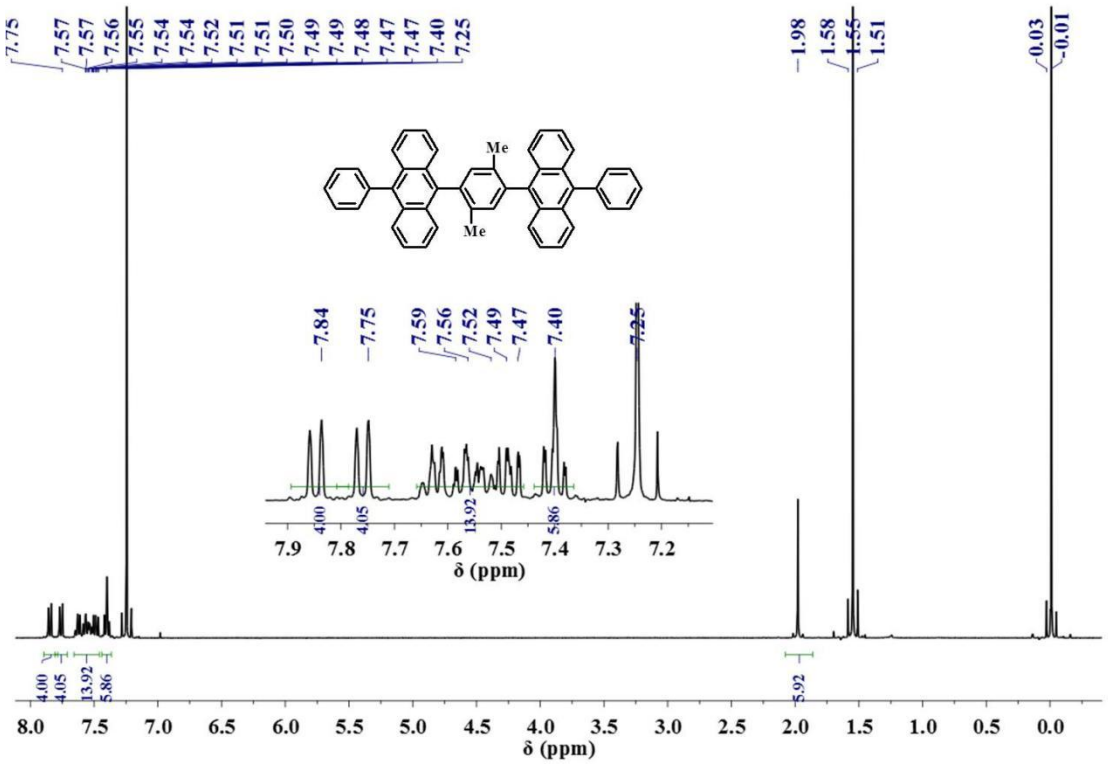


Figure S19. ^{1}H NMR spectrum of **BD1-DMP** (400 MHz, $CDCl_3$, *r.t.*).

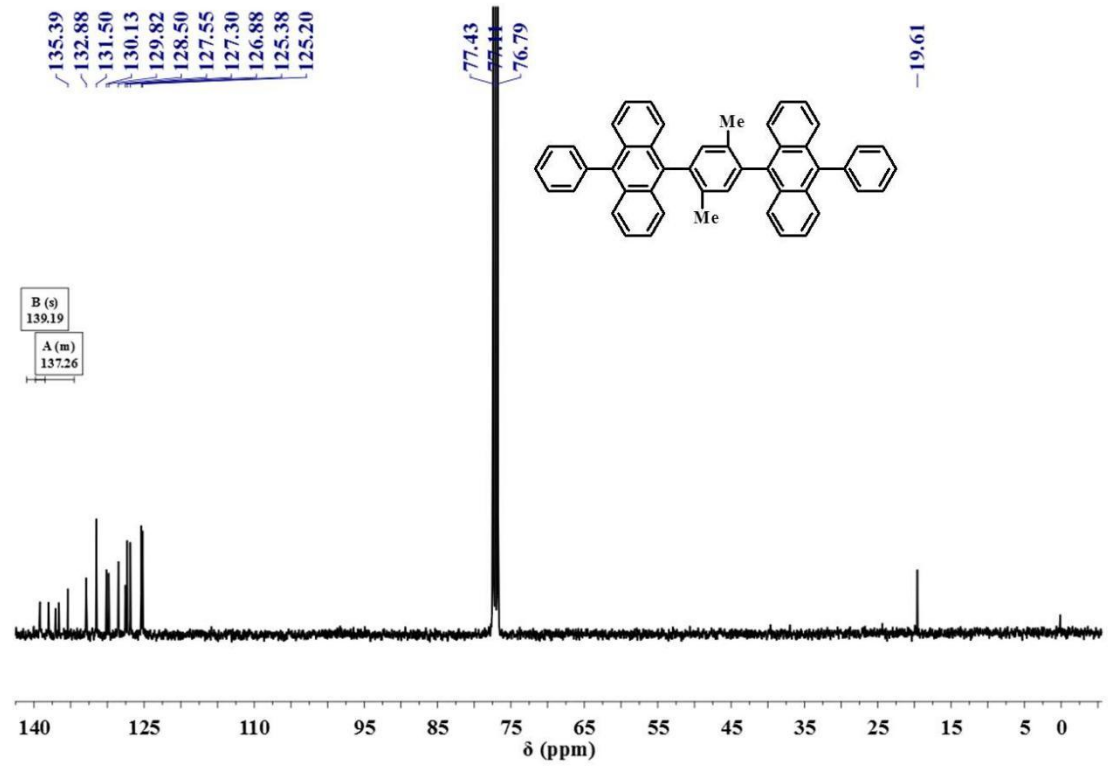


Figure S20. ^{13}C NMR spectrum of **BD1-DMP** (100 MHz, $CDCl_3$, *r.t.*).

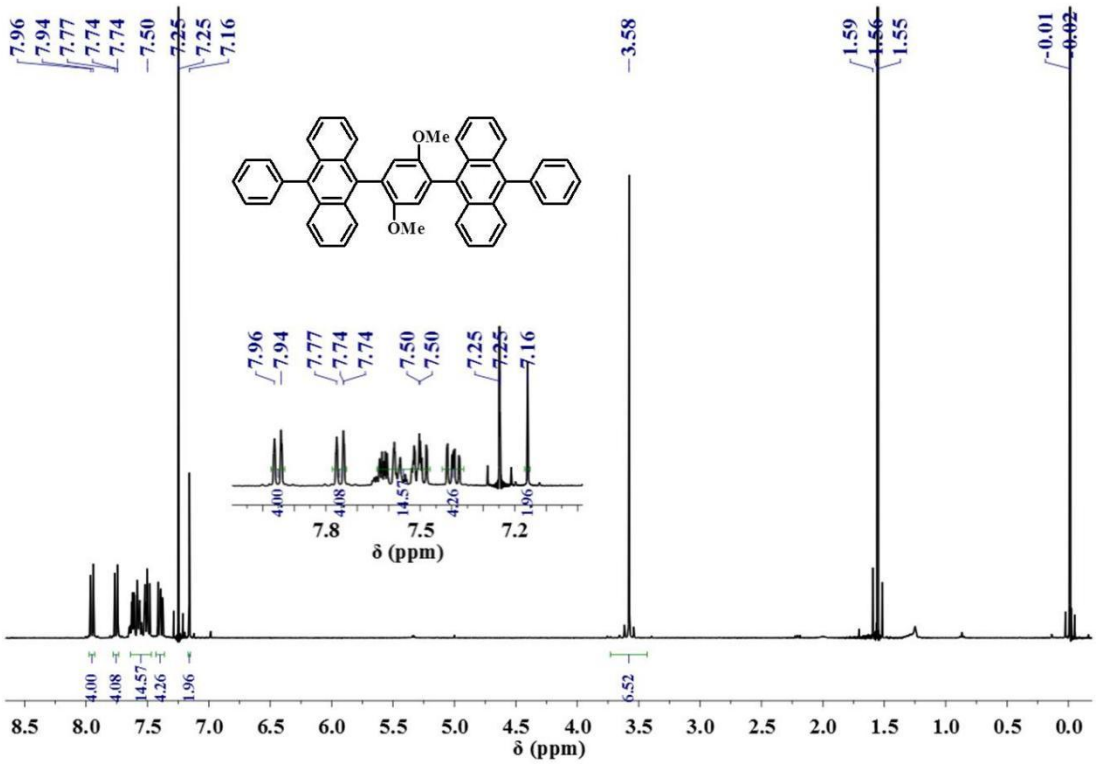


Figure S21. ^{1}H NMR spectrum of **BD1-DOP** (400 MHz, $CDCl_3$, *r.t.*).

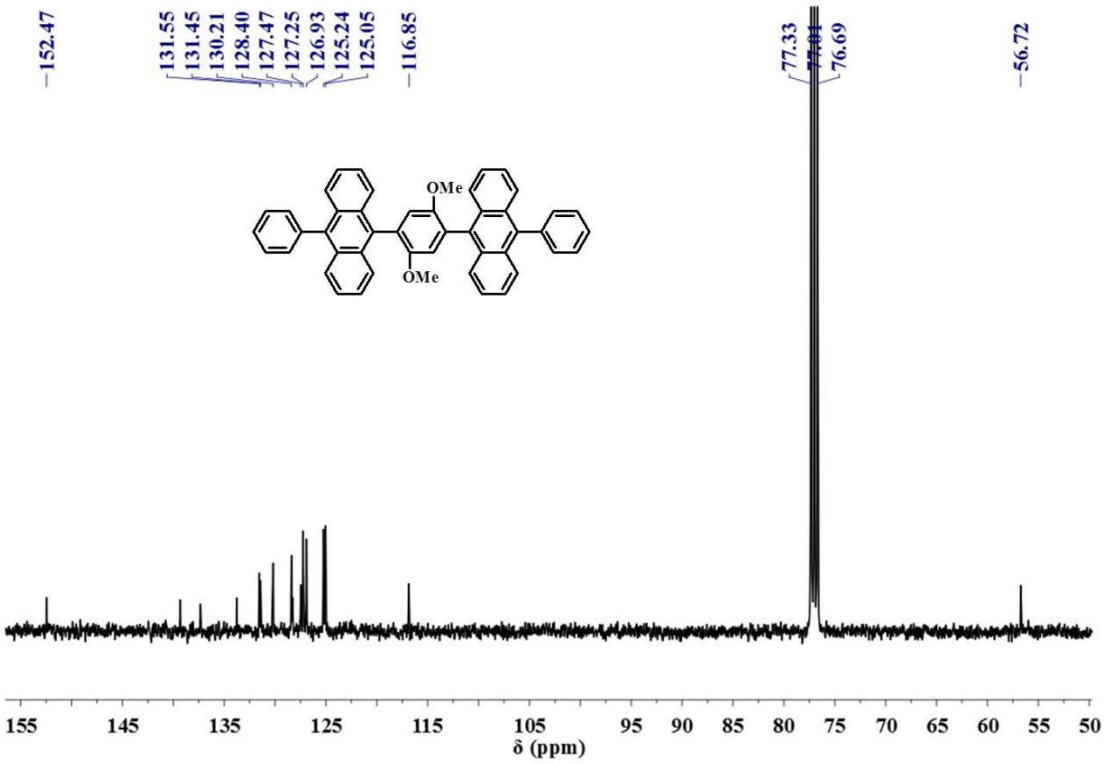


Figure S22. ^{13}C NMR spectrum of **BD1-DOP** (100 MHz, $CDCl_3$, *r.t.*).

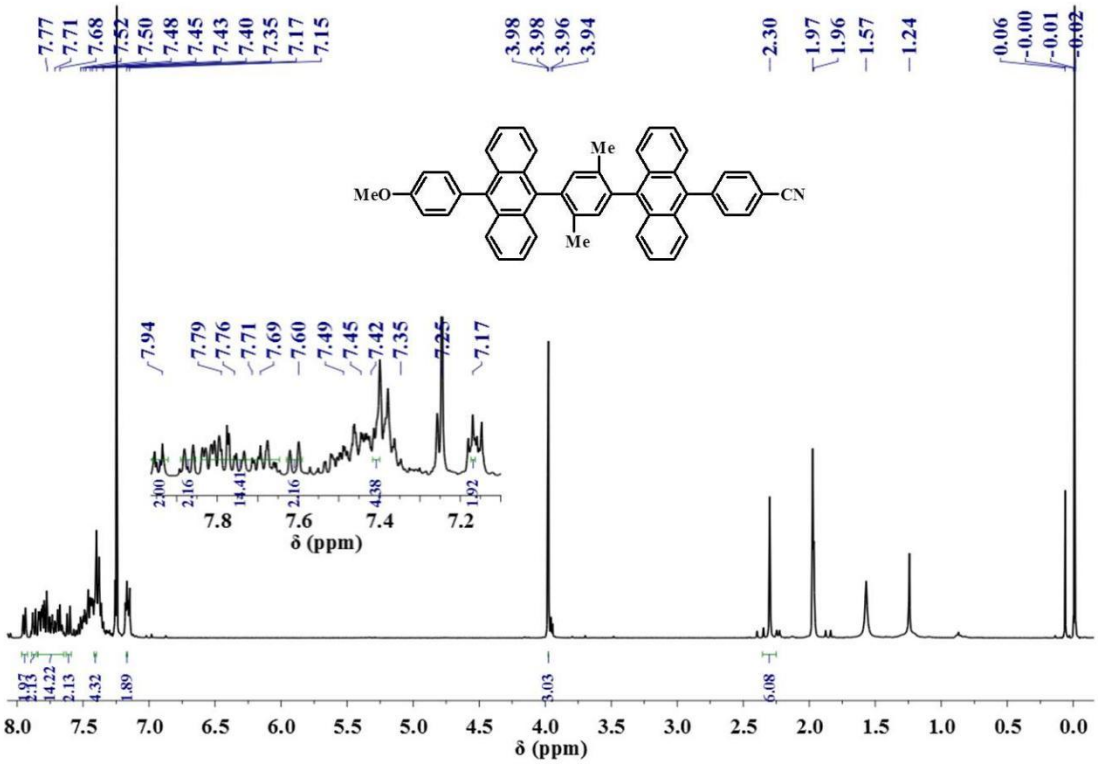


Figure S23. ^{1}H NMR spectrum of **BD3-DMP** (400 MHz, $CDCl_3$, *r.t.*).

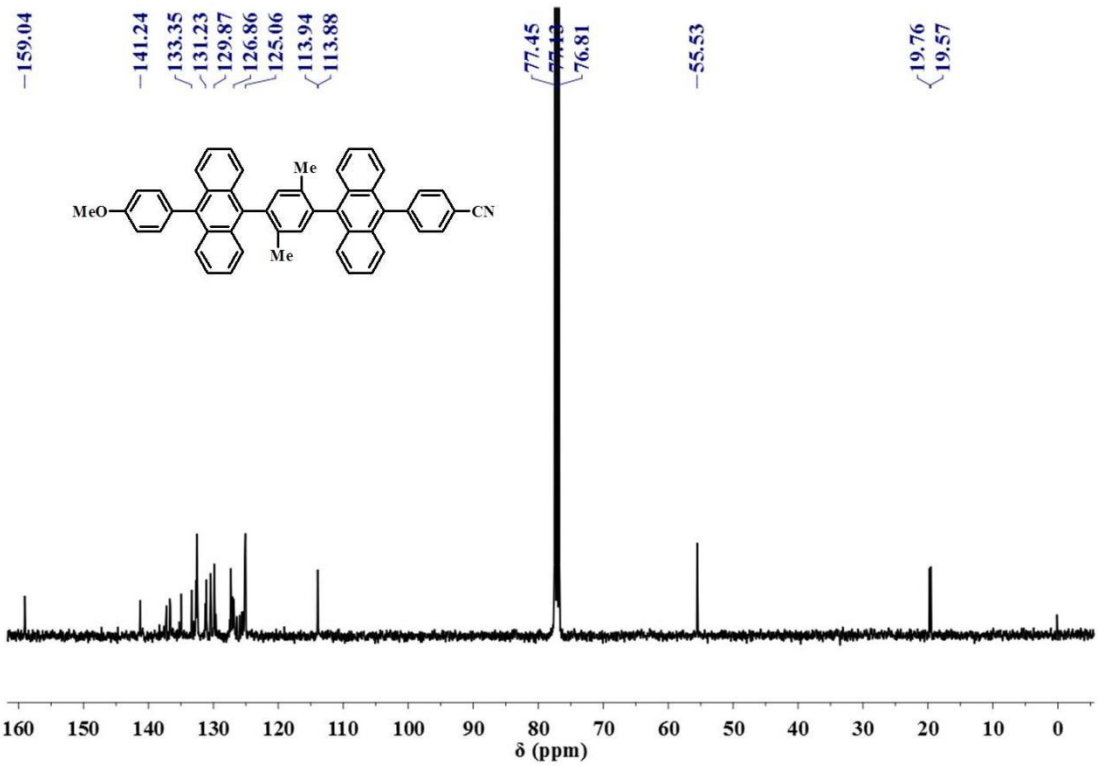


Figure S24. ^{13}C NMR spectrum of **BD3-DMP** (100 MHz, $CDCl_3$, *r.t.*).

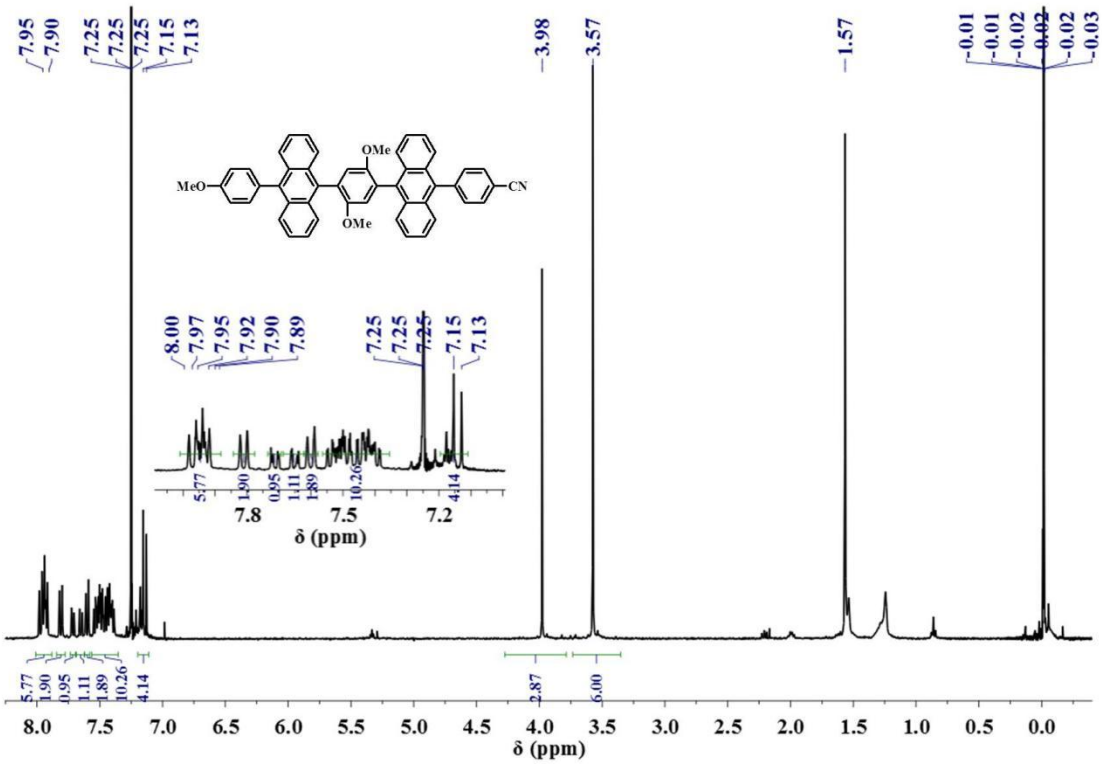


Figure S25. ^{1}H NMR spectrum of **BD3-DOP** (400 MHz, $CDCl_3$, *r.t.*).

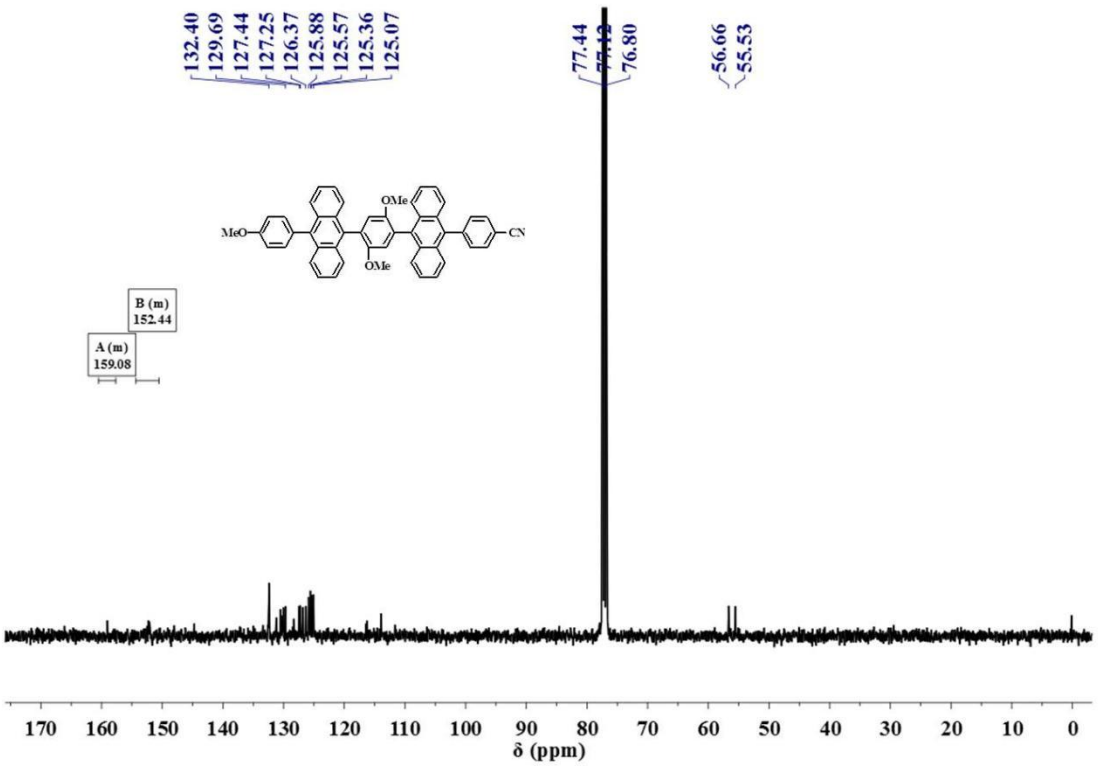


Figure S26. ^{13}C NMR spectrum of **BD3-DOP** (100 MHz, $CDCl_3$, *r.t.*).

12. Mass Spectra

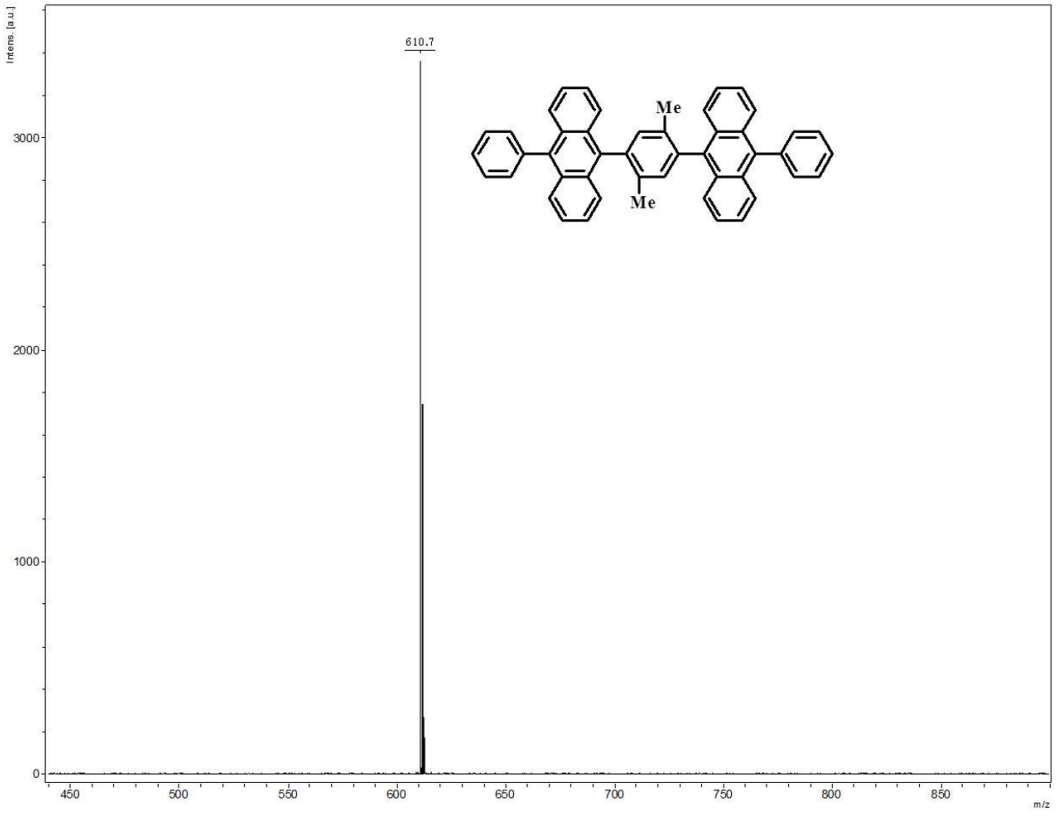


Figure S27. Mass spectra of **BD1-DMP**.

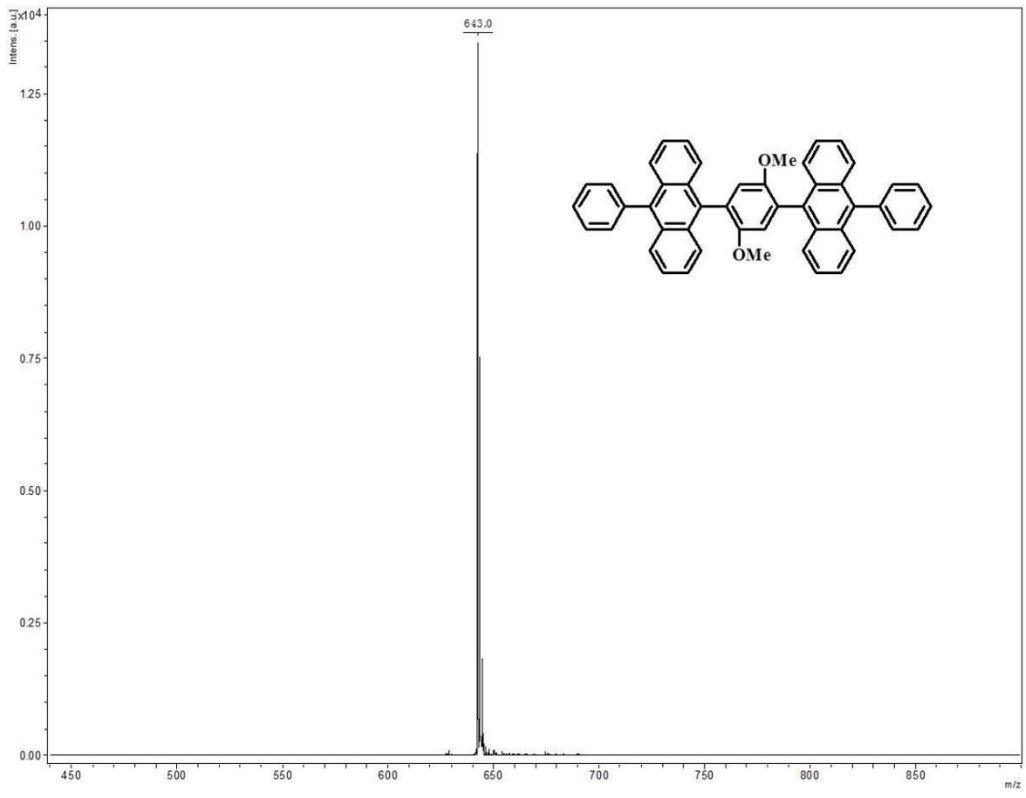


Figure S28. Mass spectra of **BD1-DOP**.

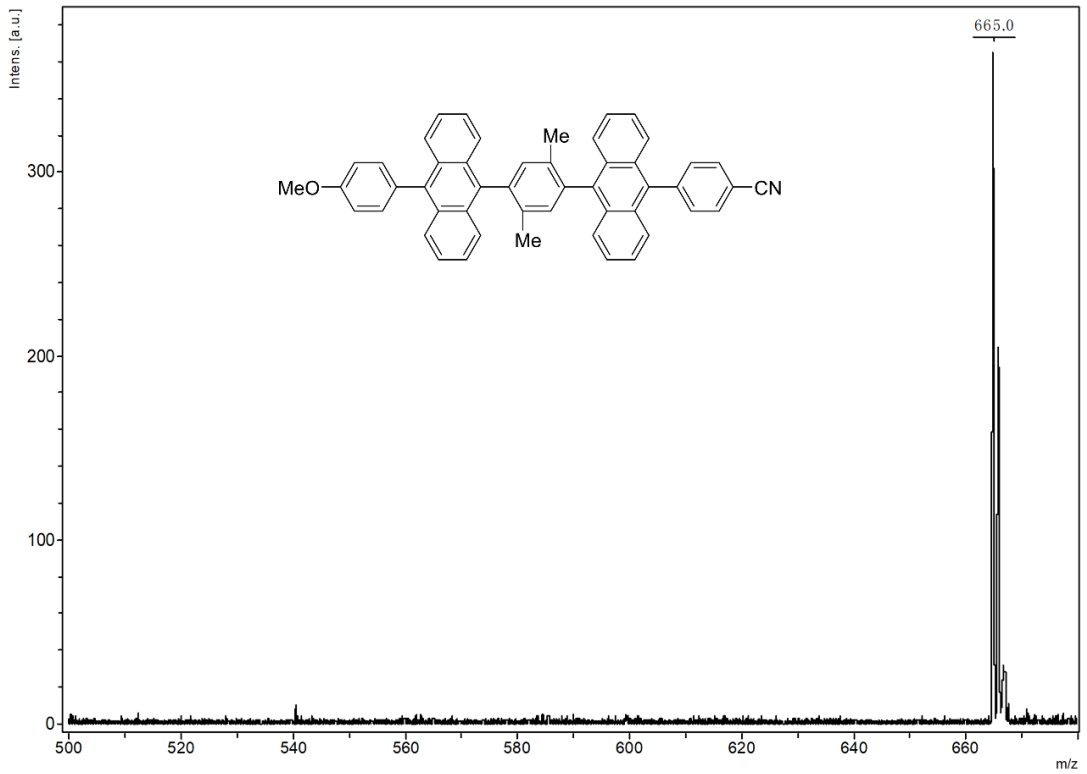


Figure S29. Mass spectra of **BD3-DMP**.

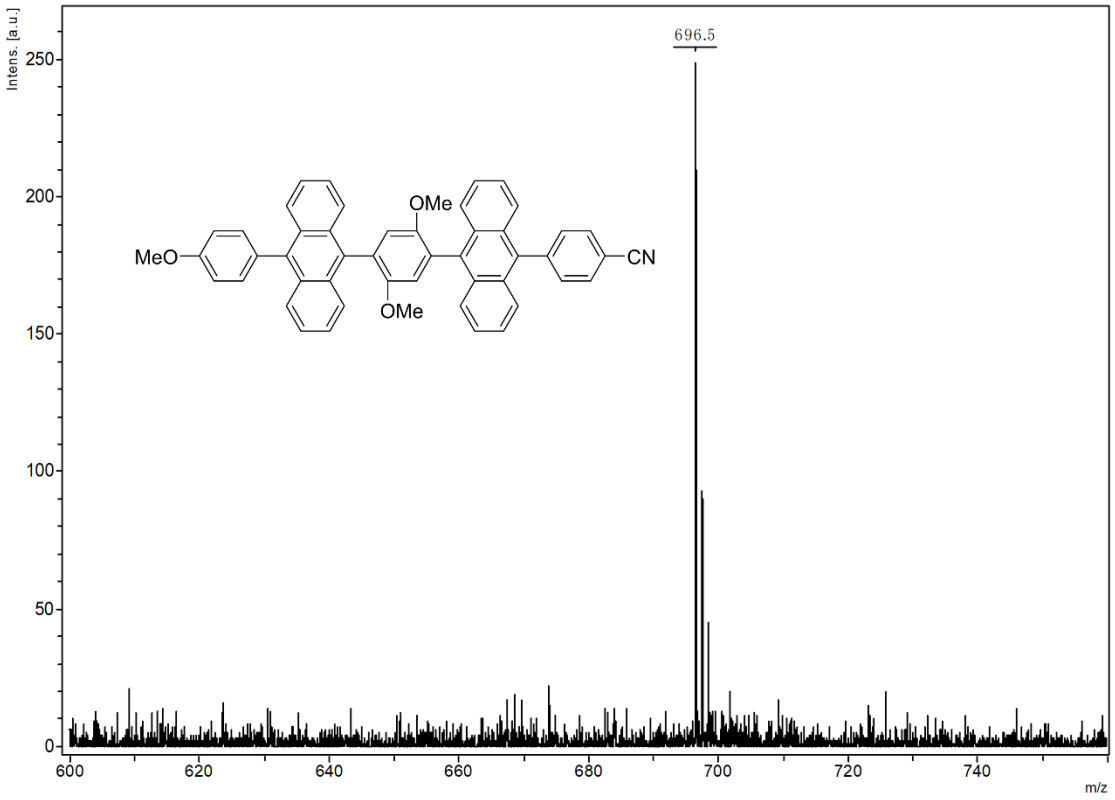


Figure S30. Mass spectra of **BD3-DOP**.

13. References

[S1] L. Chen, Y. Jiang, H. Nie, R. Hu, H. S. Kwok, F. Huang, A. Qin, Z. Zhao, B. Z. Tang, *ACS Appl. Mater. Interfaces*, **2014**, 6, 17215-17225.

[S2] W. Qin, Z. Yang, Y. Jiang, J. W. Y. Lam, G. Liang, H. S. Kwok, B. Z. Tang, *Chem. Mater.*, **2015**, 27, 3892-3901.