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Electronic supplementary information (ESI)

Butterfly-shaped π-extended benzothiadiazoles as promising emitting materials for white OLEDs

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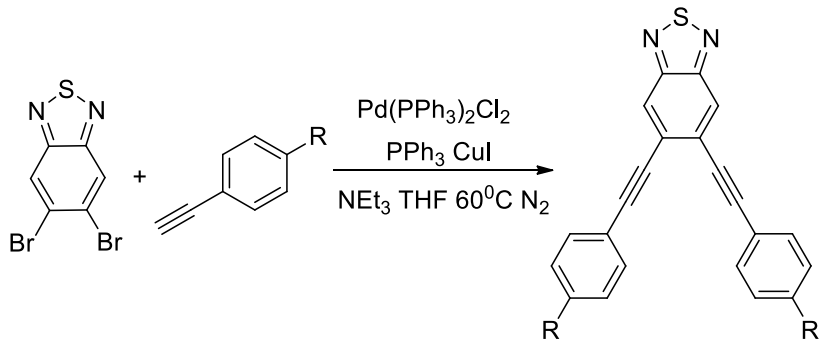
1. General statement

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. For the purpose of the measurement of photophysical properties, THF was distilled from sodium. Melting points were measured with a micro melting point apparatus. Infrared spectra were obtained with an FTIR spectrometer. NMR spectra were operated at 400 or 500 MHz for ^{1}H NMR, 100 or 125 MHz for ^{13}C NMR. All the NMR spectra were recorded at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants *J* were reported in hertz. High-resolution mass spectra (HRMS) data were obtained with electron ionization time-of-flight (EI-TOF) or electron spray ionization time-of-flight (ESI-TOF) mass spectrometer. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254. The absorption spectra were measured using UV-vis spectrometer. FL spectra were recorded on a fluorospectro photometer with a xenon lamp excitation source. Cyclic voltammetry measurements were performed on an electrochemical analyzer in solution at room temperature. Thermogravimetric Analysis (TGA) was obtained with a thermal analyzer at heating and cooling rates of 10 K/min under an N_2 atmosphere.

Device Fabrication: Before device fabrication, the ITO glass substrates were pre-cleaned carefully. Then hole transporting material PEDOT:PSS was made with 4000 r/s for 45 s and annealing 25 min at 150 ^{o}C. Emission Layer was prepared in chlorobenzene with 30 mg/mL. Then it was made with 3000 r/s for 45 s and annealing 25 min at 50 ^{o}C, annealing 25 min at 150 ^{o}C for PVK. After the organic film deposition, 30 or 35 nm of TPBi, 1 nm of LiF and 50 nm of aluminum were thermally evaporated onto the organic surface.

2. Synthesis of the π-extended BTDs in butterfly-shaped D-A-D.



To a 50 mL round bottom flask with magnetic stir bar was added 5,6-dibromobenzo[c][1,2,5]thiadiazole (146 mg, 0.5 mmol), phenylacetylene (143 mg, 1.4 mmol), $Pd(PPh_3)_2Cl_2$ (35mg, 0.05 mmol), PPh_3 (26mg, 0.1 mmol), CuI (9.5mg, 0.05mmol), triethylamine (0.6 mL) and was suspended in tetrahydrofuran (10 mL) at 60 °C under N_2 for 12h. After cooling to room temperature, the solvent was removed via vacuum. Purification of the residue by flash chromatography on silica gel using DCM/HEX as eluent afforded the desired product.

Compound 2Ph-56(1): Green solid, yield 71%, mp 158.2-158.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.21 (s, 2H), 7.60-7.62 (m, 4H), 7.36-7.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.9, 131.9, 129.0, 128.5, 126.7, 124.2, 122.6, 96.1, 87.3. HRMS (EI-TOF): cacld. for $C_{22}H_{12}N_2S$ [M^+], 336.0721; found: 336.0719. IR: 3437, 2916, 2852, 2206, 1735, 1654, 1618, 1560, 1496, 1313, 1069.

Compound 2PMP-56: Green solid, yield 81%, mp 152.3-152.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16 (s, 2H), 7.55 (d, J = 9.2 Hz, 4H), 6.90 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.2, 153.9, 133.4, 127.1, 123.7, 114.8, 114.2, 96.3, 86.4, 55.4; HRMS (EI-TOF): cacld. for $C_{24}H_{16}N_2O_2S$ [M^+], 396.0932; found: 396.0935. IR: 3438, 2925, 2959, 2200, 1654, 1604, 1560, 1513, 1291, 1252, 1175, 1031.

Compound 2DMAP-56: Red solid, yield 64%, mp 215.2-215.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (s, 2H), 7.51 (d, J = 9.2Hz, 4H), 6.68 (d, J = 8.8 Hz, 4H), 3.03 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.9, 150.5, 133.2, 127.6, 122.9, 111.8, 109.4, 98.0, 86.2, 40.2 ; HRMS (EI-TOF): cacld. for $C_{26}H_{22}N_4S$ [M^+], 422.1565; found: 422.1567. IR: 3437, 2923, 2852, 2194, 1605, 1595, 1529, 1438, 1369, 1233, 1188, 1115.

Compound 2TPA-56： Orange solid，yield 68%，mp 200.9-201.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.15 (s, 2H), 7.43 (d, J = 8.8 Hz, 4H), 7.25-7.28 (m, 8H), 7.05-7.13 (m, 12H), 7.00 (d, J =

8.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.9, 148.6, 147.0, 132.8, 129.4, 127.1, 125.2, 123.8, 123.6, 121.8, 115.1, 96.8, 86.9; HRMS (EI-TOF): cacld. for $C_{46}H_{30}N_4S$ [M^+], 670.2191; found: 670.2197. IR: 3452, 2916, 2847, 2198, 1654, 1587, 1561, 1331, 1285, 1178.

Compound 2POZ-56： Orange solid，yield 63%, mp 208.5-209.0 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* (ppm) 8.30 (s, 2H), 7.86 (d, *J* = 8.4Hz, 4H), 7.40 (d, *J* = 8.4Hz, 4H), 6.56-6.69 (m, 12H), 5.97 (dd, *J* = 1.2Hz, 7.6Hz, 8.0Hz, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 154.4, 144.3, 140.2, 134.9, 134.3, 131.6, 126.4, 125.1, 123.7, 123.2, 122.0, 115.8, 113.7, 95.3, 88.7; HRMS (EI-TOF): cacld. for $C_{46}H_{26}N_4O_2S$ [M^+], 698.1776; found: 698.1776. IR: 3451, 2916, 2843, 2206, 1654, 1625, 1512, 1486, 1329, 1293, 1274, 1205, 1043.

3. Figures S1-S10 ^{1}H NMR and ^{13}NMR of compounds in butterfly shaped D-A-D

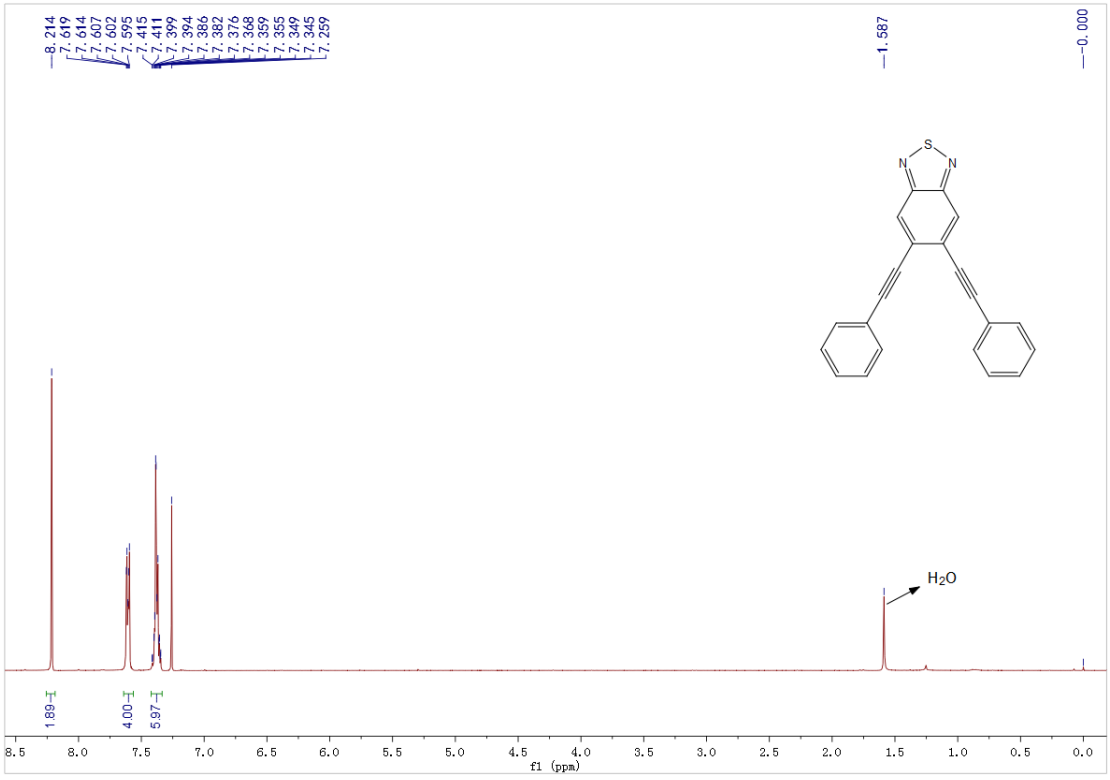


Figure S1 ^{1}H NMR of **2Ph-56** in $CDCl_3$.

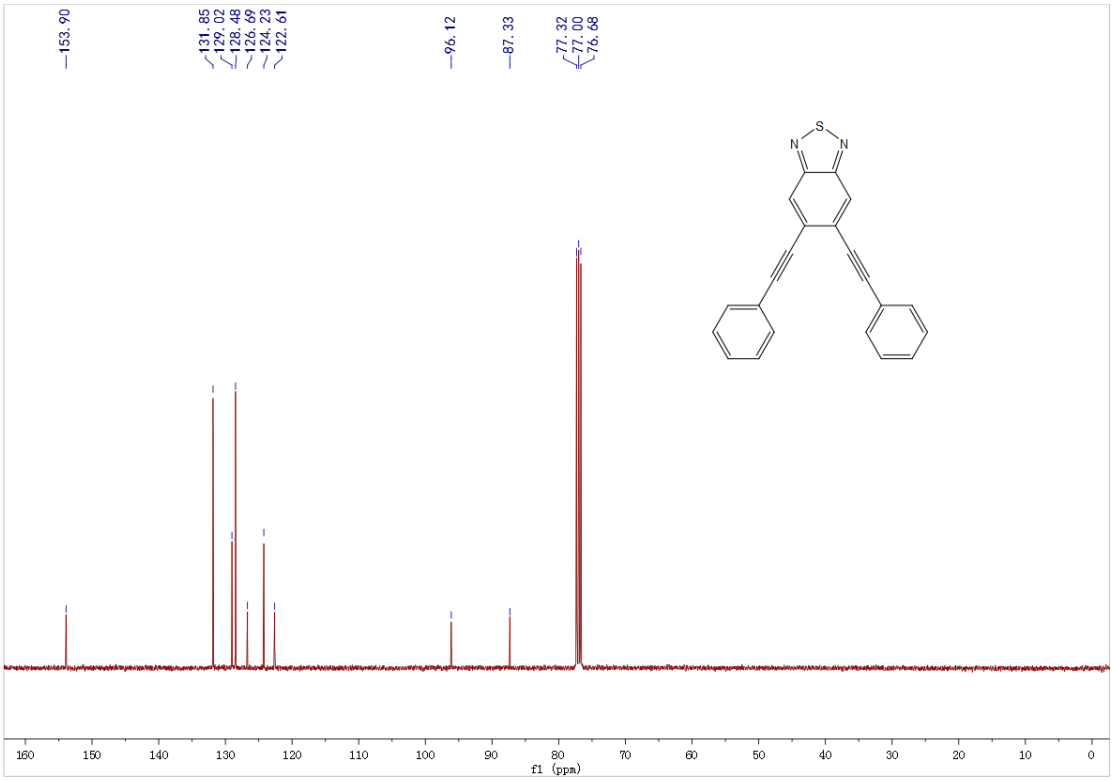


Figure S2 ^{13}C NMR of **2Ph-56** in $CDCl_3$.

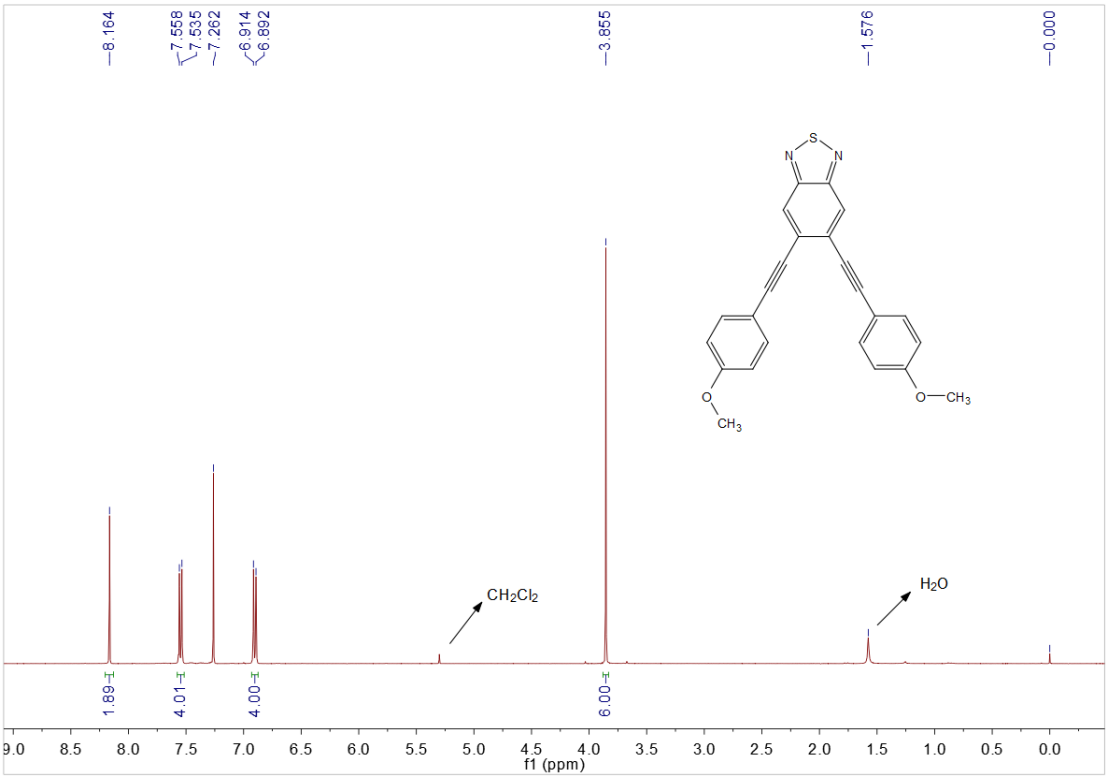


Figure S3 ^{1}H NMR of **2PMP-56** in $CDCl_3$.

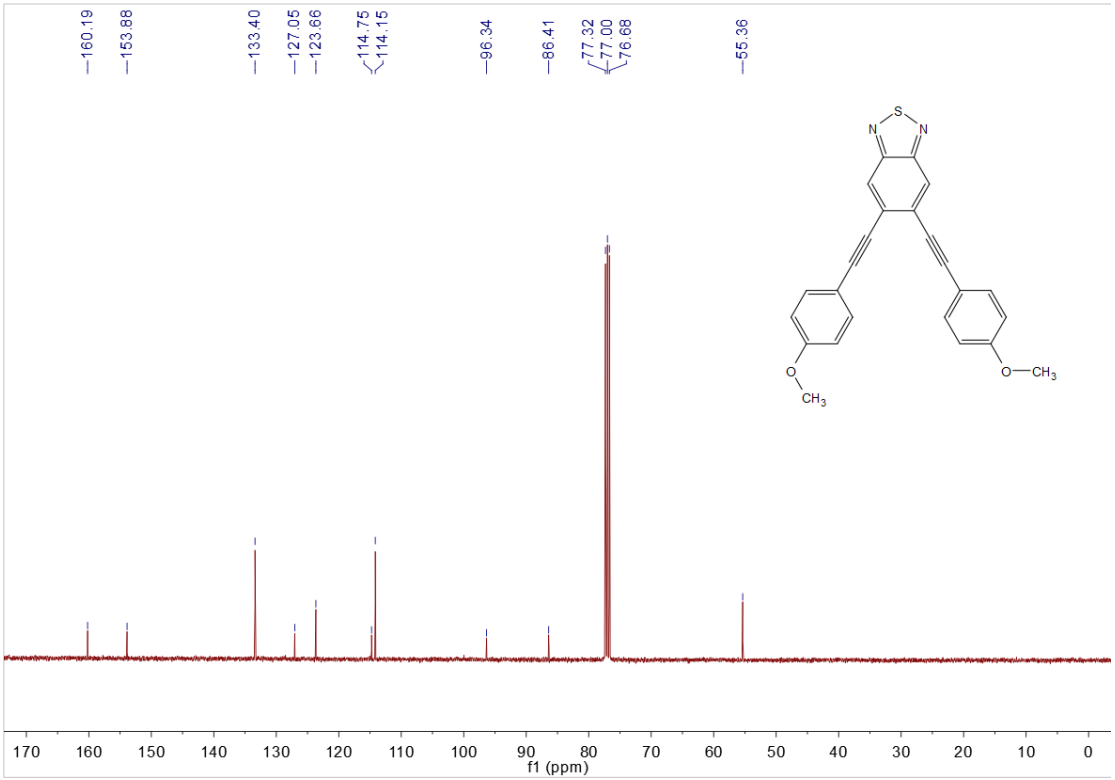


Figure S4 ^{13}C NMR of **2PMP-56** in $CDCl_3$.

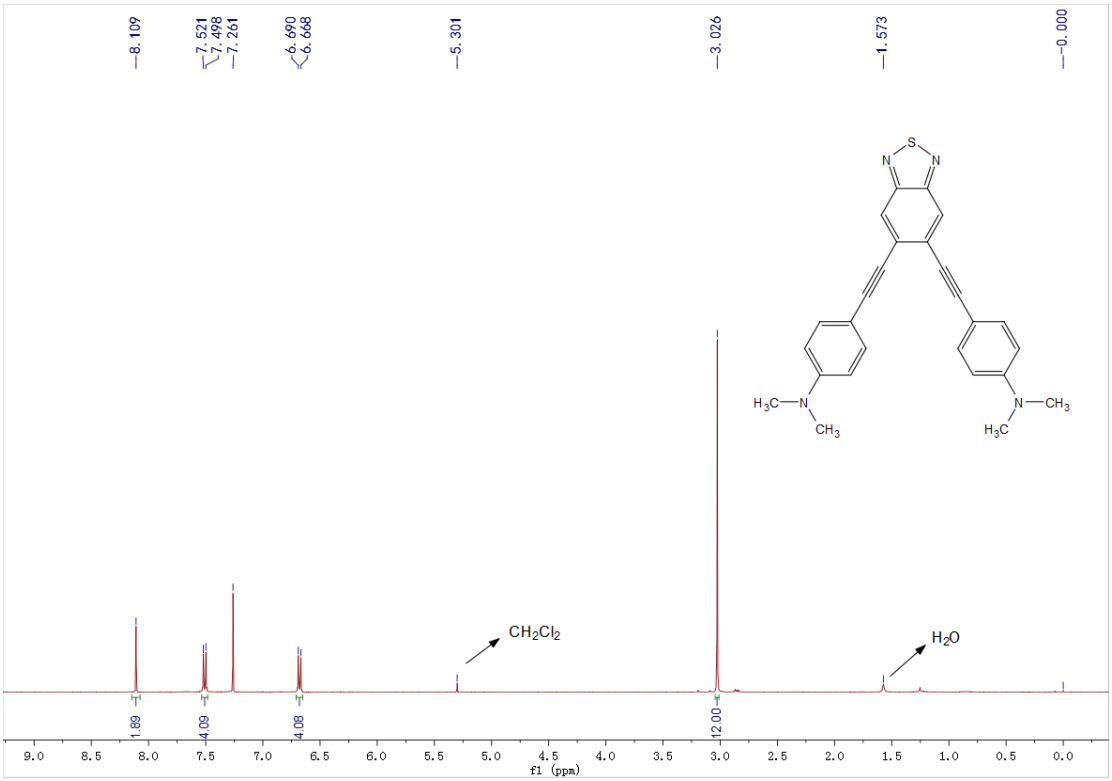


Figure S5 ^{1}H NMR of **2DMAP-56** in $CDCl_3$

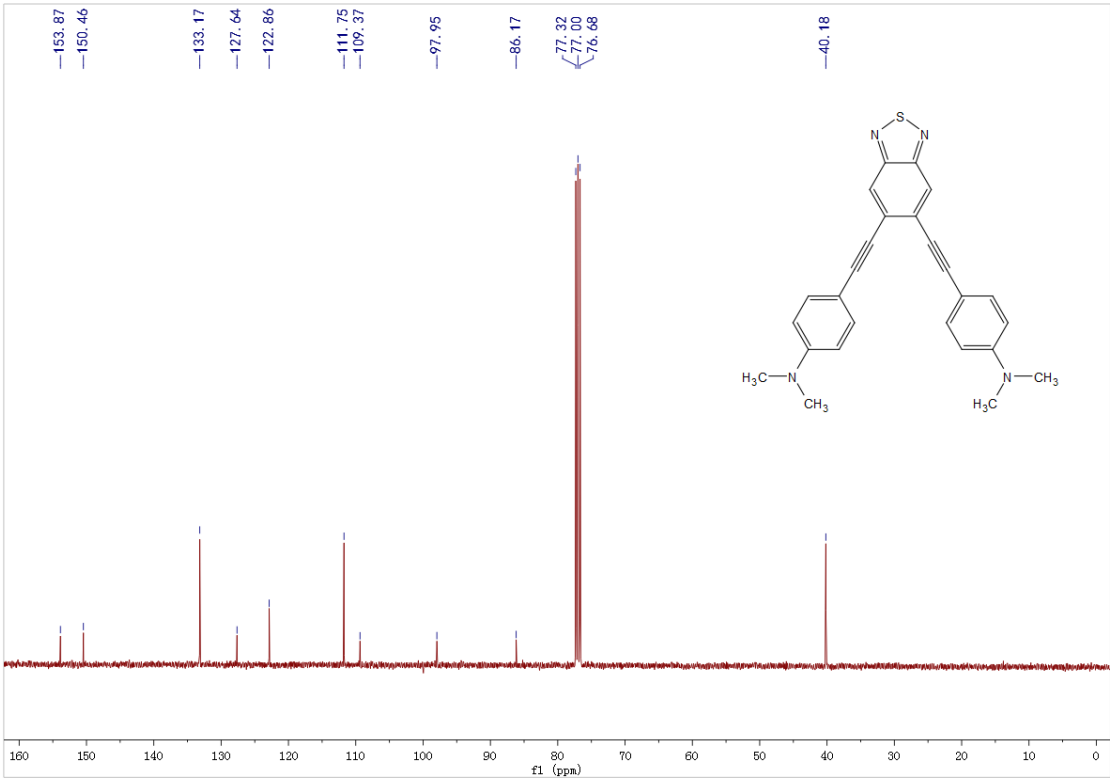


Figure S6 ^{13}C NMR of **2DMAP-56** in $CDCl_3$.

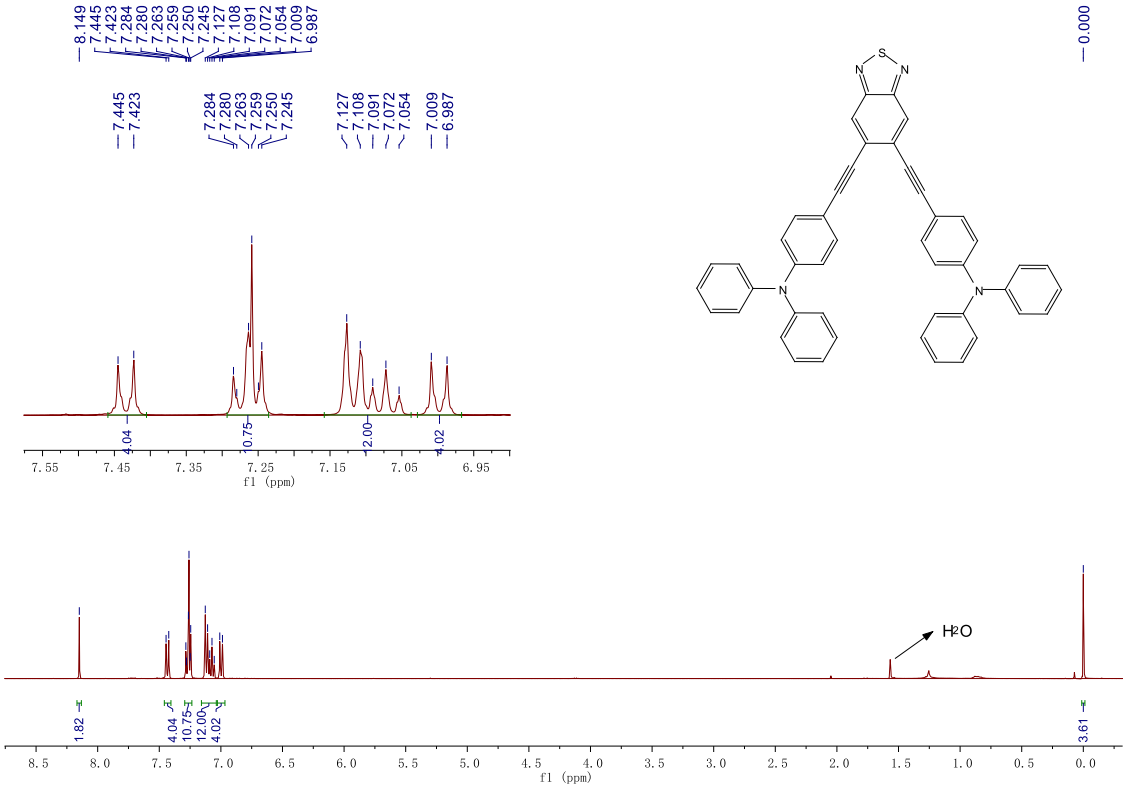


Figure S7 ^{1}H NMR of **2TPA-56** in $CDCl_3$

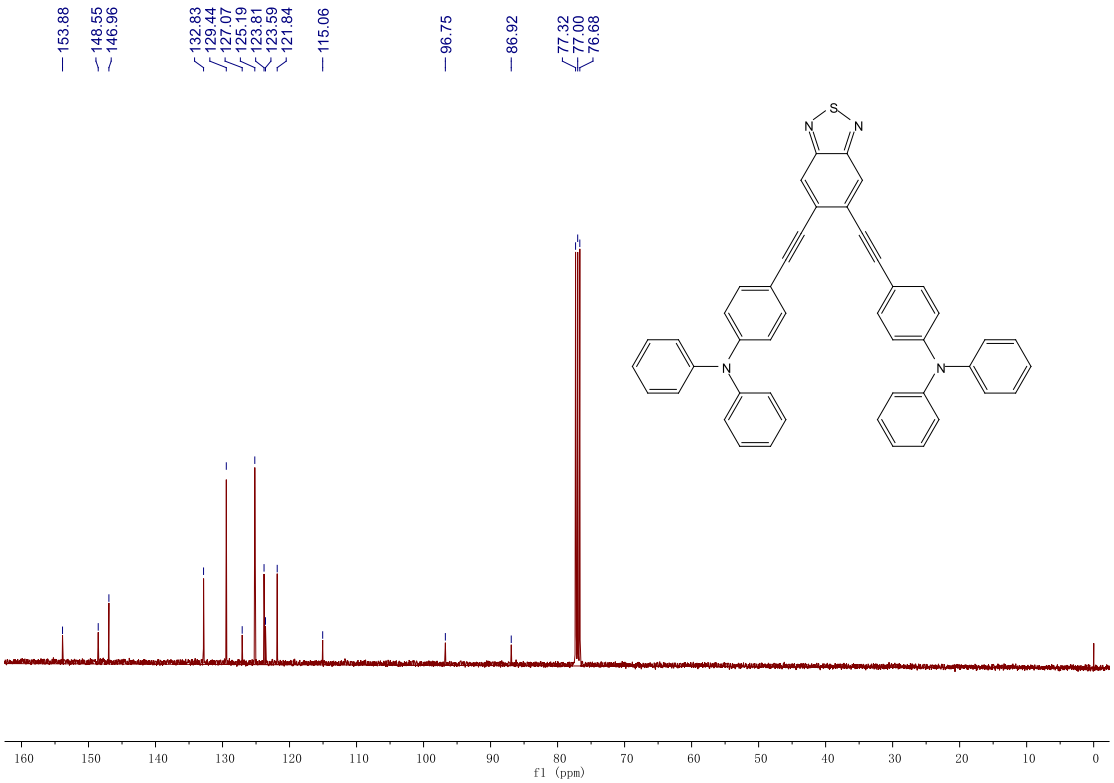


Figure S8 ^{13}C NMR of **2TPA-56** in $CDCl_3$.

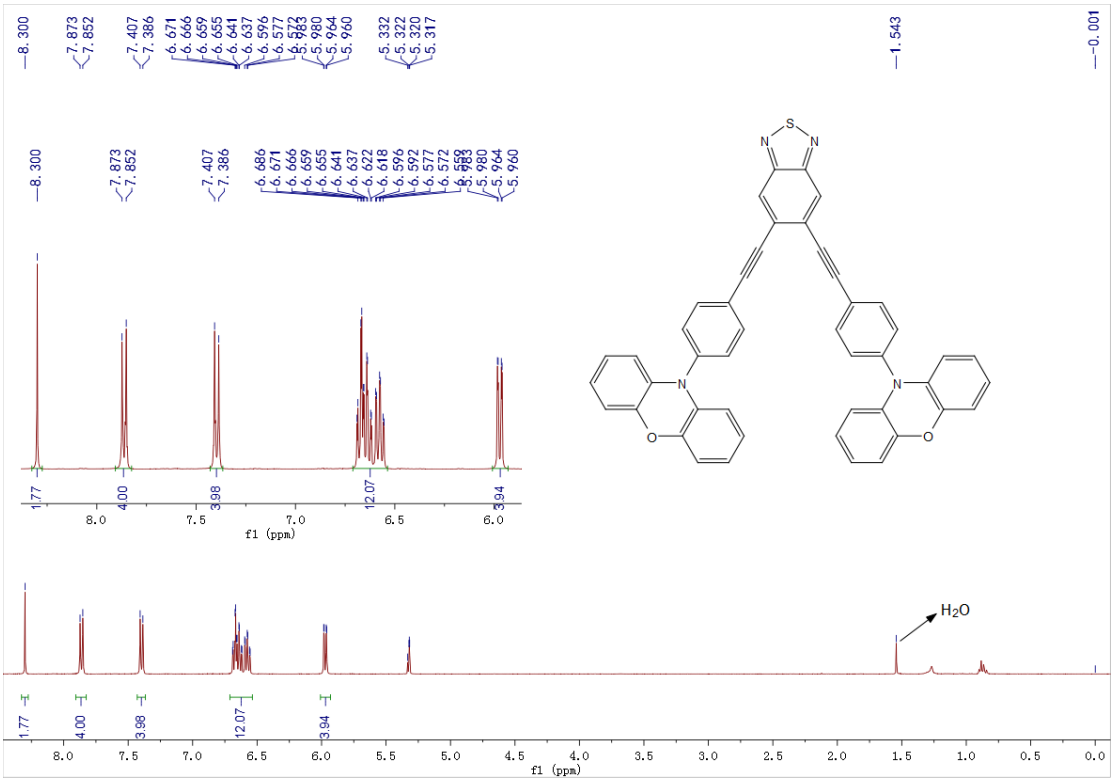


Figure S9 ^{1}H NMR of **2POZ-56** in CD_2Cl_2

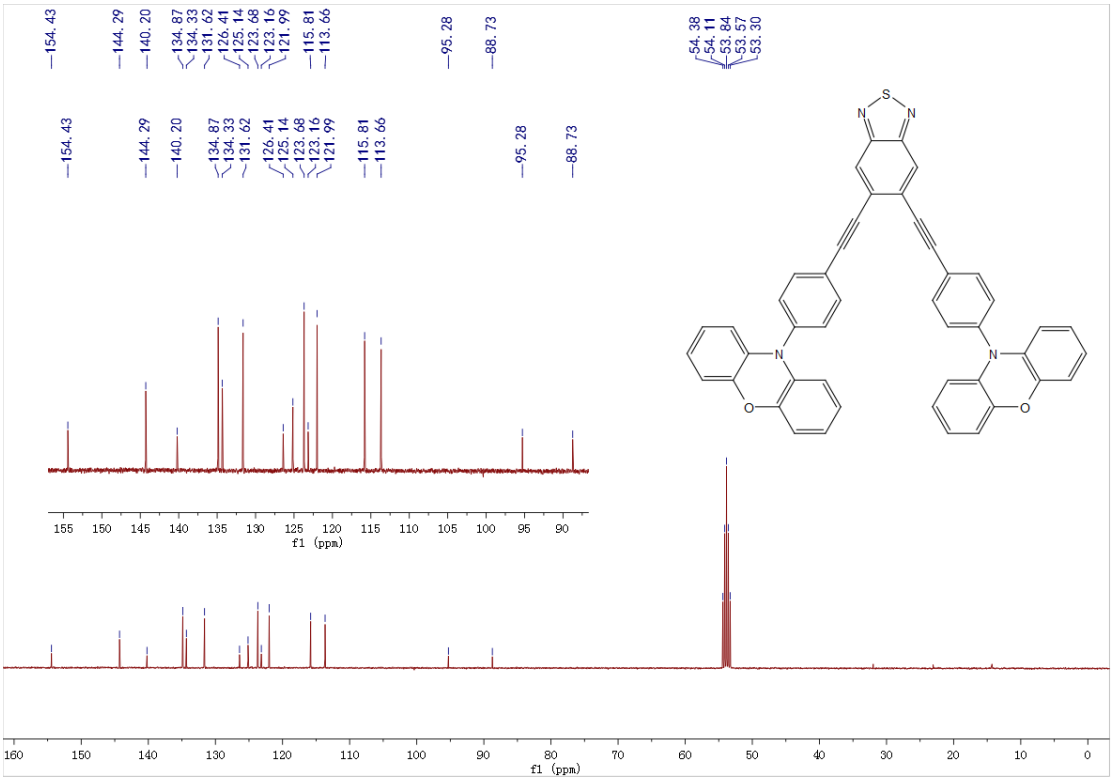
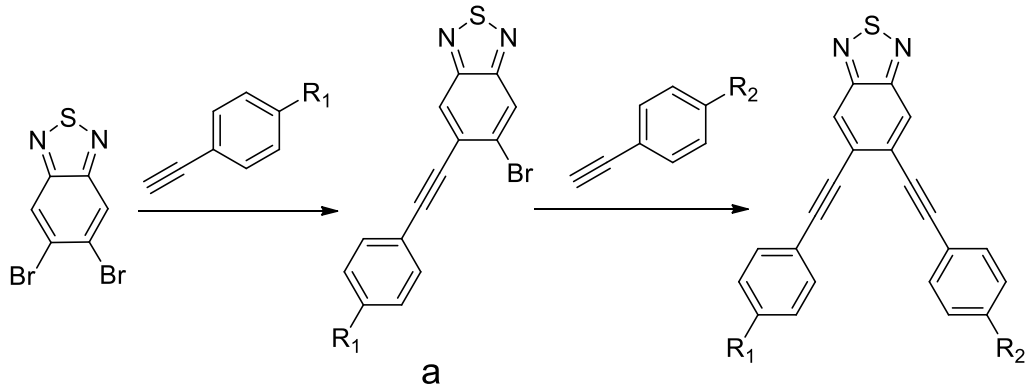


Figure S10 ^{13}C NMR of **2POZ-56** in CD_2Cl_2

4. Synthesis of the π-extended BTDs in butterfly-shaped D-A-A.



a

To a 50 mL round bottom flask with magnetic stir bar was added 5,6-dibromobenzo[c][1,2,5]thiadiazole (146 mg, 0.5 mmol), electron-rich alkyne (0.7 mmol), $Pd(PPh_3)_2Cl_2$ (35mg, 0.05 mmol), PPh_3 (26mg, 0.1 mmol), CuI (9.5 mg, 0.05 mmol), triethylamine (0.6 mL) and was suspended in tetrahydrofuran (10 mL) at 60 °C under N_2 for 12h. After cooling to room temperature, the solvent was removed via vacuum. Purification of the residue by flash chromatography on silica gel using DCM/HEX as eluent afforded the desired intermediate **a** .

To a 50 mL round bottom flask with magnetic stir bar was added

5,6-dibromobenzo[c][1,2,5]thiadiazole (146 mg, 0.5 mmol), electron-deficient alkyne (0.7 mmol), $Pd(PPh_3)_2Cl_2$ (35mg, 0.05 mmol), PPh_3 (26mg, 0.1 mmol), CuI (9.5 mg, 0.05 mmol), triethylamine (0.6 mL) and was suspended in tetrahydrofuran (10 mL) at 60 °C under N_2 for 12h. After cooling to room temperature, the solvent was removed via vacuum. Purification of the residue by flash chromatography on silica gel using DCM/HEX as eluent afforded the desired product .

Compound PMP-5-Br-6: Green solid, yield 82%. mp 168.0-168.4 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 1 H), 8.19 (s, 1H), 7.57(d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.4, 154.2, 153.4, 133.4, 127.3, 127.1, 124.3, 124.1, 114.2, 100.0, 97.3, 86.4, 55.4. HRMS (ESI-TOF): cacld. for $C_{15}H_{10}BrN_2OS$ [M+H$^+$], 344.9697; found: 344.9670. IR: 3437, 2916, 2847, 2200, 1607, 1577, 1534, 1482, 1364, 1179,1168.

Compound PMP-5-BN-6: Green solid, yield 74%, mp 213.1-213.6 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.23 (s, 1 H), 8.19 (s, 1H), 7.67 (s, 4H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.4, 154.2, 153.5, 133.3, 132.3, 132.2, 127.5, 126.8, 125.5, 124.9, 124.0, 118.3, 114.4, 114.2, 112.2, 96.6, 93.7, 91.5, 85.9, 55.4; HRMS (EI-TOF): cacld. for $C_{24}H_{13}N_3OS$ [M$^+$], 391.0779; found: 391.0779. IR: 3450, 2916, 2847, 2215, 1654, 1560, 1512, 1249, 1169, 1021.

Compound DMAP-5-Br-6: Red solid, yield 81%. mp 145.0-145.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.31 (s, 1 H), 8.14 (s, 1H), 7.50(d, *J* = 8.8 Hz, 2H), 6.68(d, *J* = 8.8 Hz, 2H), 3.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 154.0, 153.5, 150.7, 133.1, 127.7, 127.6, 124.2, 123.3, 111.7, 108.6, 99.2, 86.1, 40.1. HRMS (ESI-TOF): cacld. for $C_{16}H_{13}BrN_3S$ [M+H$^+$], 358.0014; found: 357.9991. IR: 3433, 2919, 2843, 2202, 2120, 1611, 1586, 1522, 1366, 1189, 1113, 1064, 994.

Compound DMAP-5-BN-6: Red solid, yield 72%, mp 206.5-207.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.21 (s, 1 H), 8.16 (s, 1H), 7.66-7.71 (m, 4H), 7.43 (d, *J* = 8.8Hz, 2H),6.67 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 153.4, 150.6, 133.0, 132.3, 132.2, 127.4, 125.7, 124.7, 123.3, 118.4, 112.1, 111.7, 108.7, 98.5, 93.6, 91.8, 85.6, 40.1; HRMS (EI-TOF): cacld. for $C_{25}H_{16}N_4S$ [M$^+$], 404.1096; found: 404.1099. IR: 3451, 3095, 2962, 2227, 2197, 1609, 1591, 1526, 1366, 1191, 1116, 1087.

5. **Figures S11-S18 ^{1}H NMR and ^{13}C NMR of compounds in butterfly shaped D-A-A**

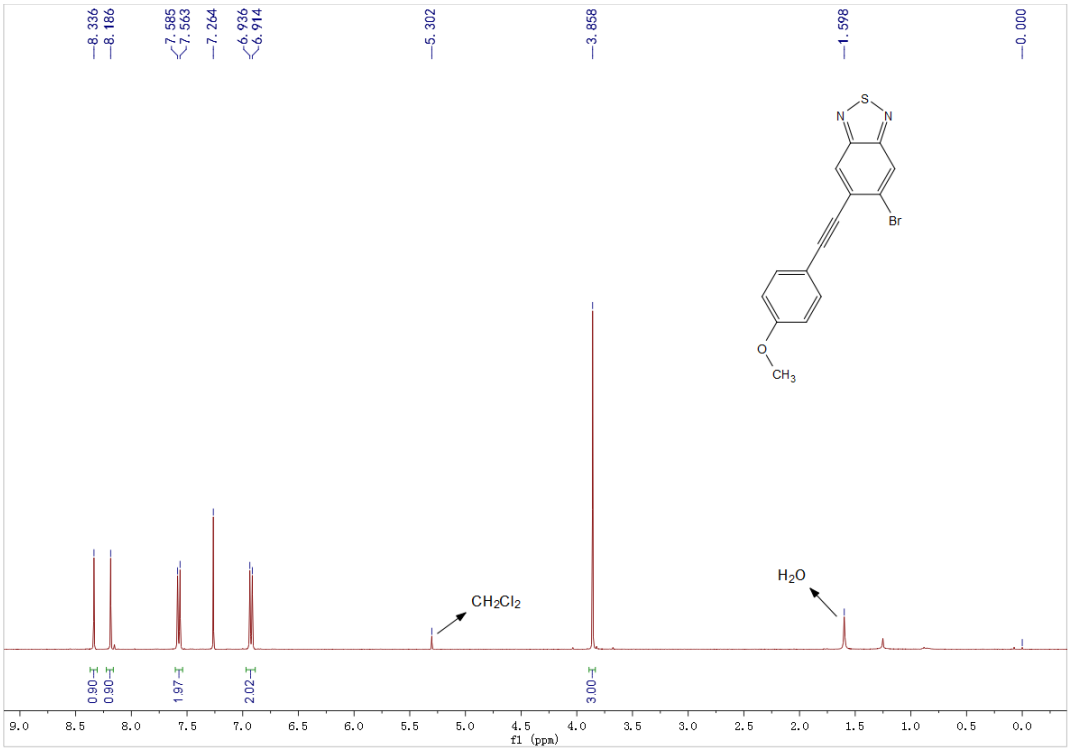


Figure S11 ^{1}H NMR of **PMP-5-Br-6** in $CDCl_3$

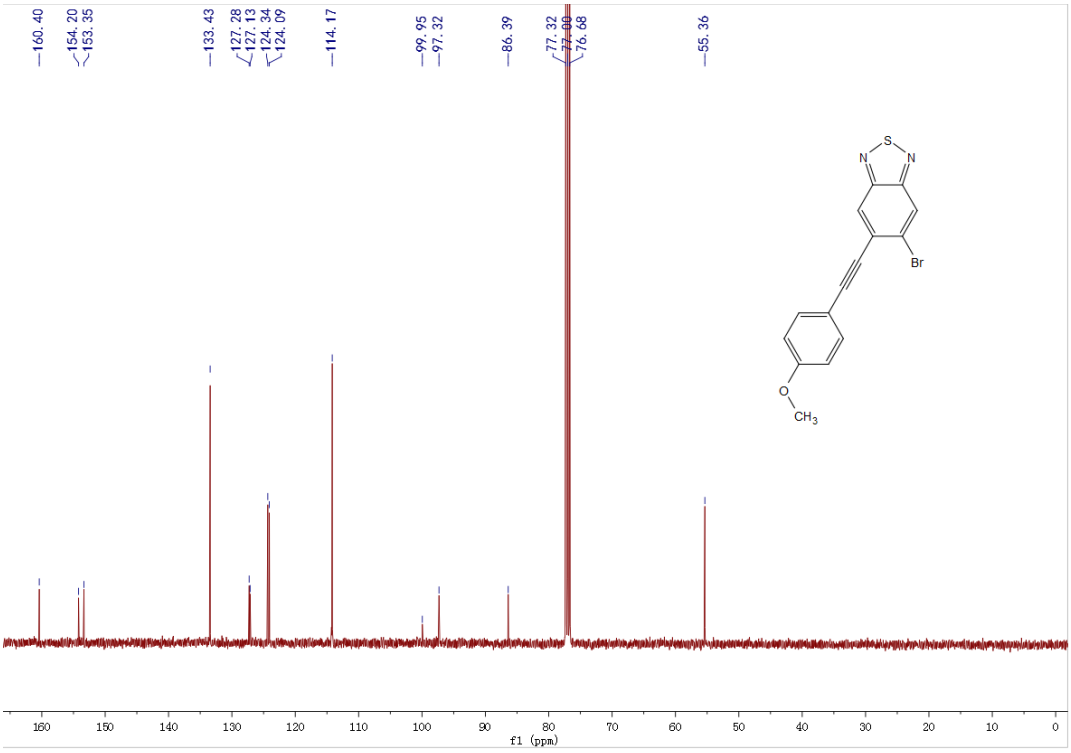


Figure S12 ^{13}C NMR of **PMP-5-Br-6** in $CDCl_3$

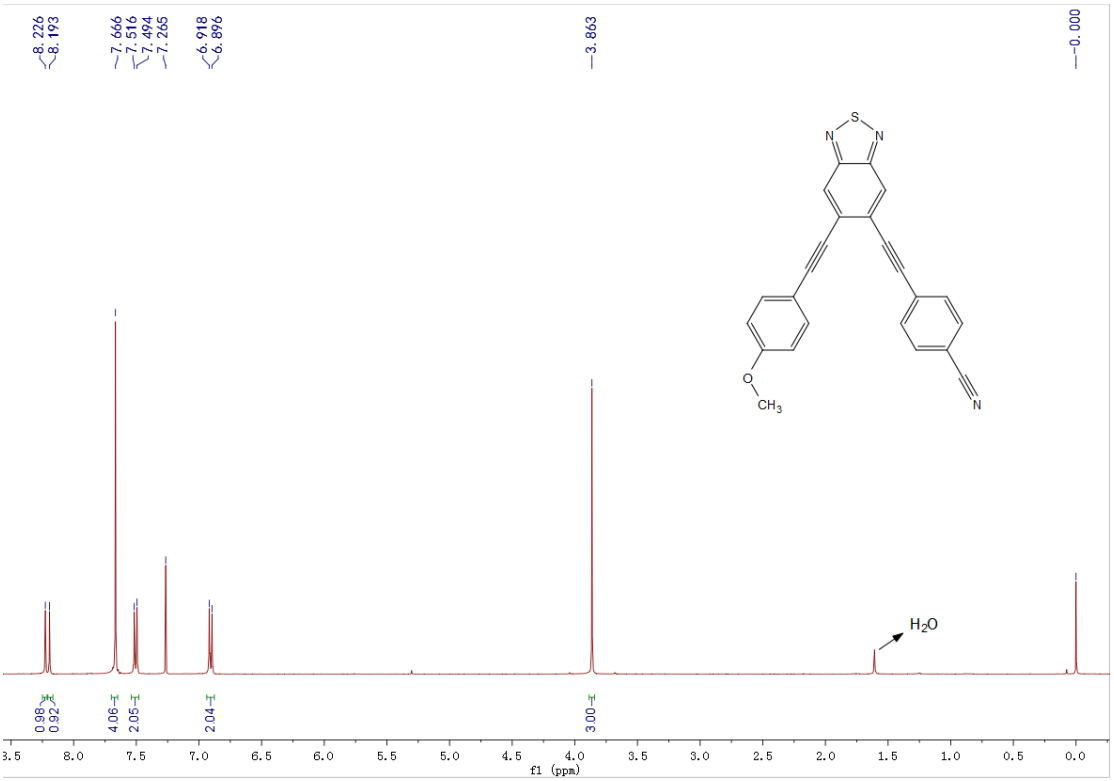


Figure S13 ^{1}H NMR of **PMP-5-BN-6** in $CDCl_3$

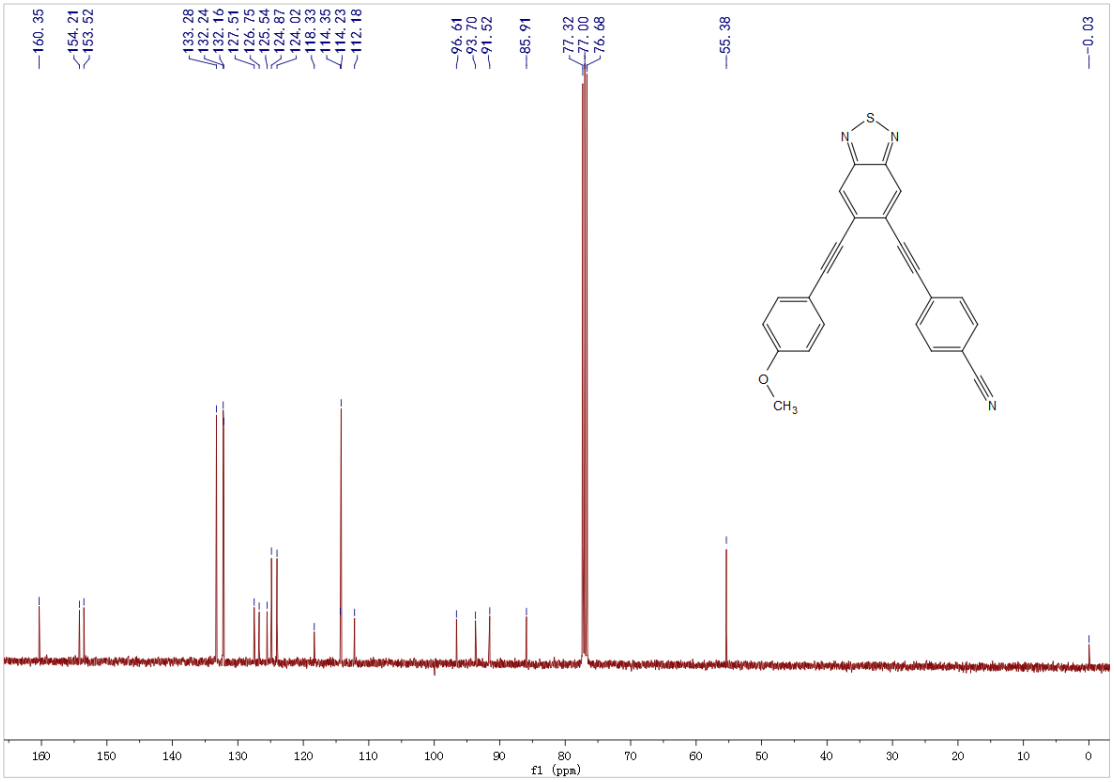


Figure S14 ^{13}C NMR of **PMP-5-BN-6** in $CDCl_3$

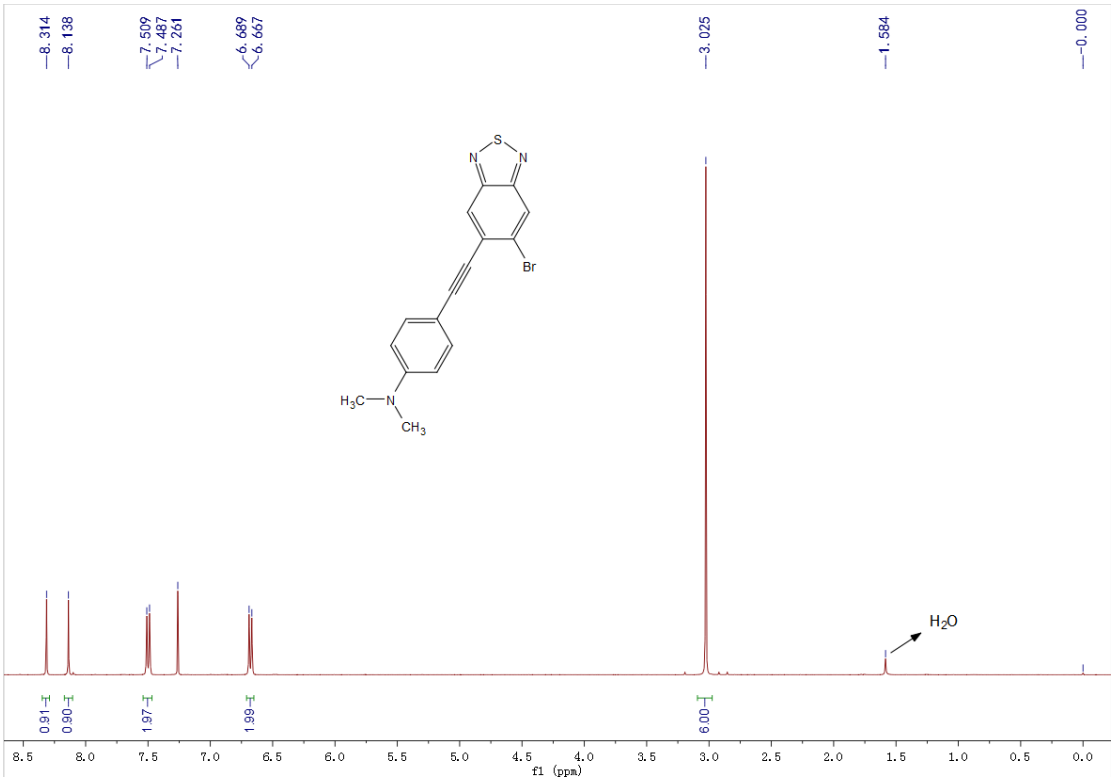


Figure S15 ^{1}H NMR of **DMAP-5-Br-6** in $CDCl_3$

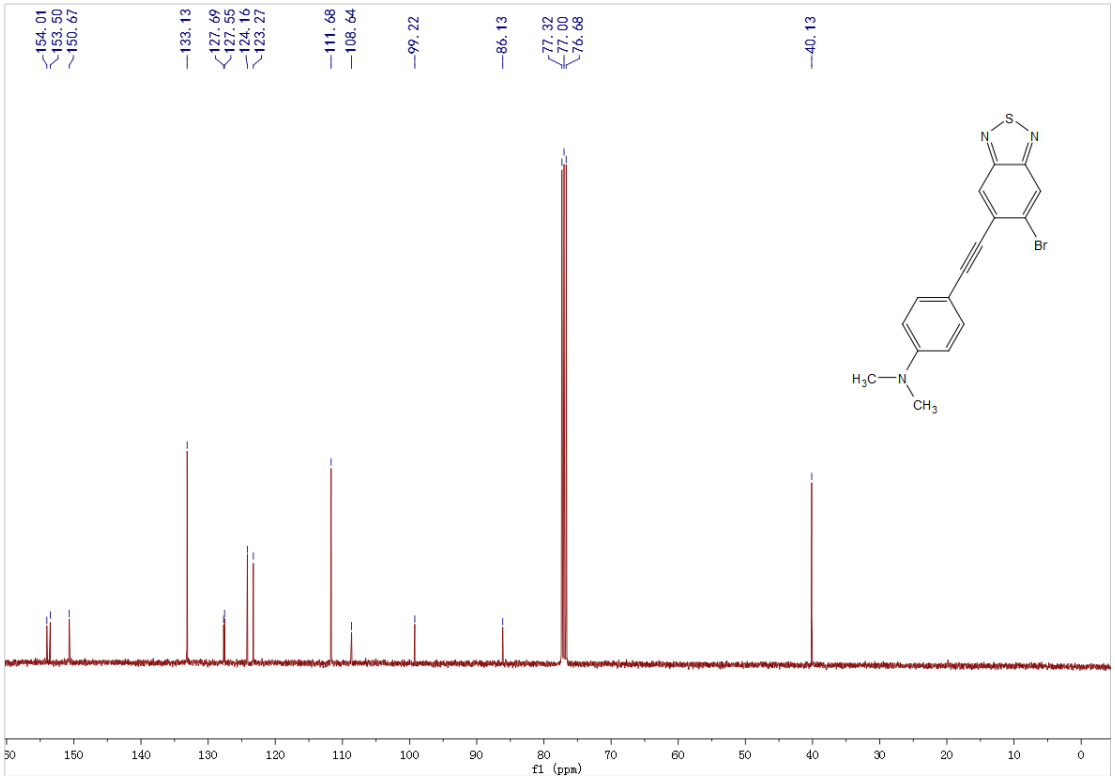


Figure S16 ^{13}C NMR of **DMAP-5-Br-6** in $CDCl_3$

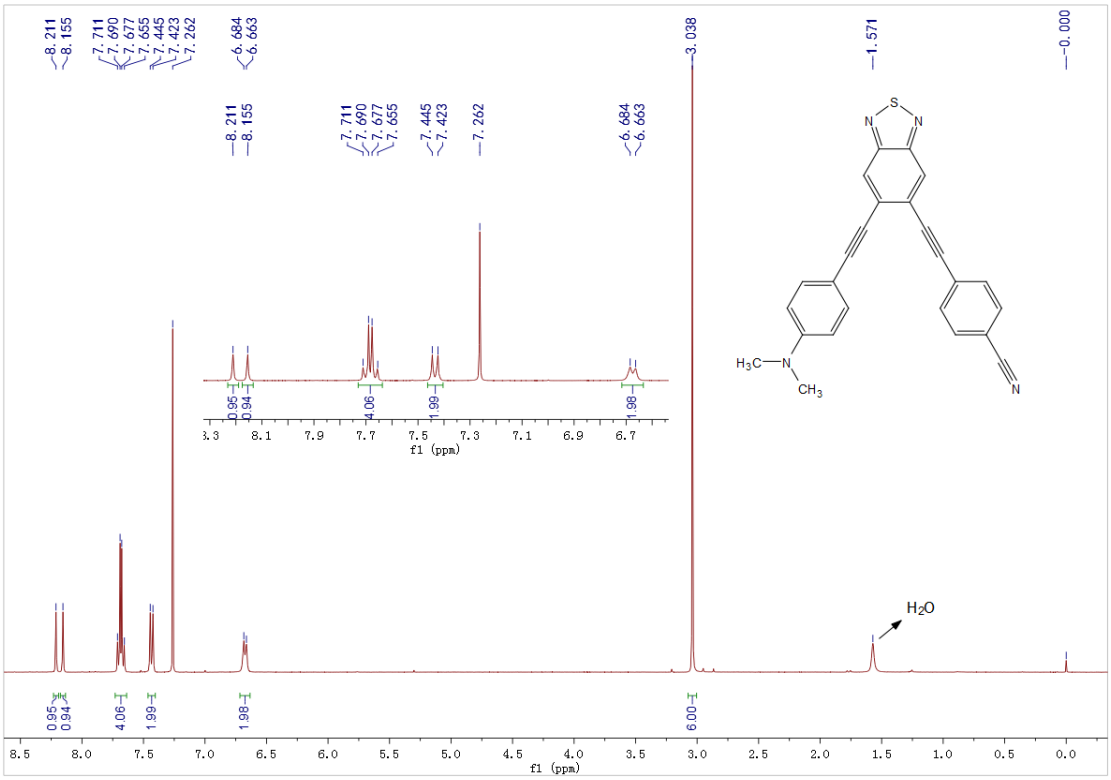


Figure S17 ^{1}H NMR of **DMAP-5-BN-6** in $CDCl_3$

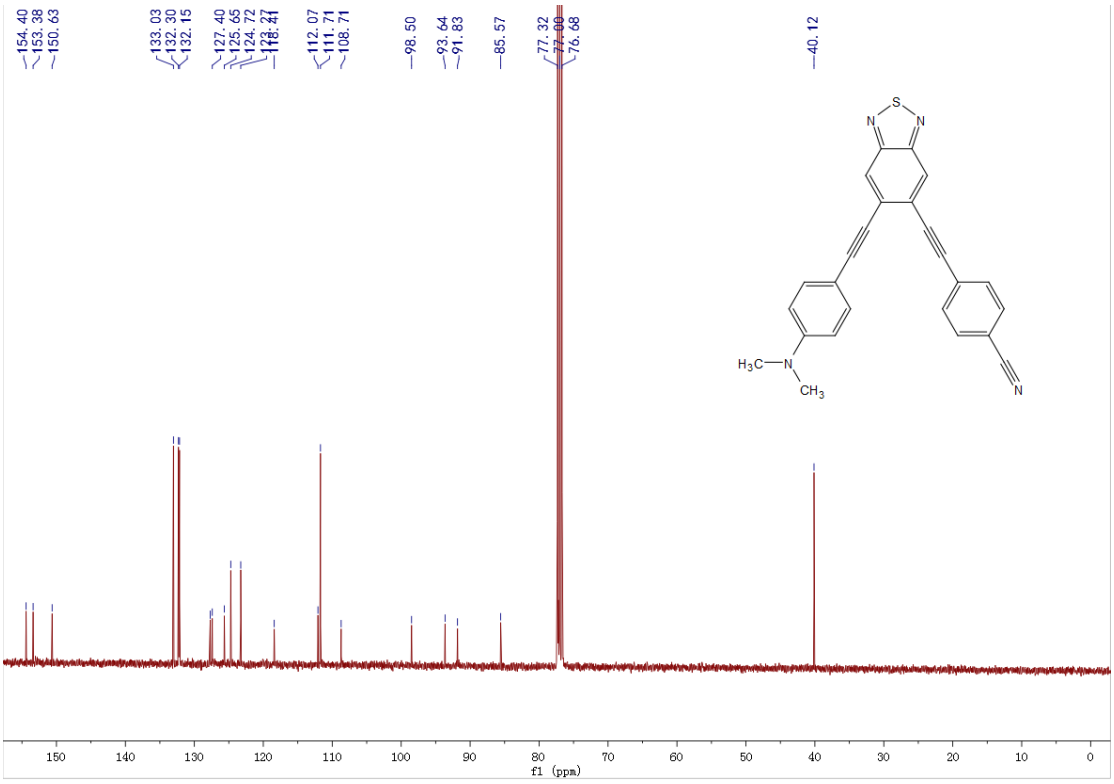


Figure S18 ^{13}C NMR of **DMAP-5-BN-6** in $CDCl_3$

6. Synthesis of the π-extended BTDs in linear-shaped D-A-D

D-A-D Linear-shaped compounds was synthesized according to previous literature[2-3].

Compound 2Ph-47[2]**:** green solid, yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (s, 2H), 7.66-7.69 (m, 4H), 7.39-7.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 132.4, 132.0, 129.1, 128.4, 122.5, 117.2, 97.5, 85.3.

Compound 2PMP-47[2]**:** orange solid, yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (s, 2H), 7.61 (d, J = 8.8 Hz, 4H), 6.92(d, J = 8.8 Hz, 4H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.2, 154.4, 133.5, 132.1, 117.1, 114.6, 114.1, 97.6, 84.3, 55.3.

Compound 2DMAP-47[2]**:** red solid, yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (s, 2H), 7.54 (d, J = 9.2Hz, 4H), 6.69 (d, J = 8.8 Hz, 4H), 3.02 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.5, 150.5, 133.2, 131.7, 117.0, 111.7, 109.2, 99.1, 84.2, 40.2.

Compound 2TPA-47[3]**:** red solid, yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (s, 2H), 7.50 (d, J = 8.4Hz, 4H), 7.28-7.32 (m, 8H), 7.07-7.15 (m, 12H), 7.03 (d, J = 8.8Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 148.6, 147.0, 133.0, 132.0, 129.4, 125.2, 123.8, 121.8, 117.0, 114.9, 98.1,84.9.

7. Synthesis of the π-extended BTDs in linear-shaped D-A-A.

The routes of the synthesis are same with π-extended BTDs in butterfly-shaped D-A-A.

Compound PMP-4-Br-7[4]**:** green solid, yield 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, J = 7.6Hz 1H), 7.59-7.64 (m, 3H), 6.92 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.3, 154.2, 153.1, 133.5, 132.4, 132.0, 117.1, 114.4, 114.1, 114.0, 97.2, 83.5, 55.3.

Compound PMP-4-BN-7: yellow solid, yield 69%. mp 221.9-222.5 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68-7.83 (m, 6H), 7.62 (d, J = 8.4Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.4, 154.3, 154.2, 133.6, 133.2, 132.4, 132.1, 131.8, 127.4, 118.7, 118.4, 115.4, 114.3, 114.1, 112.2, 98.7, 94.9, 89.3, 84.2, 55.4. HRMS (ESI-TOF): cacld. for $C_{24}H_{14}N_3OS$ [M+H$^+$], 392.0858; found: 392.0844. IR: 3452, 2925, 2228, 2210, 1654, 1617, 1605, 1561, 1512, 1296, 1254, 1025, 840.

Compound DMAP-4-Br-7[4]**:** red solid, yield 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, J = 7.6Hz 1H), 7.59 (d, J = 7.6Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.8Hz 2H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ (ppm) 154.2, 153.1, 150.5, 133.2, 132.1, 131.7, 117.7, 113.1, 111.6, 108.8, 99.1, 83.2, 40.1.

Compound DMAP-4-BN-7: red solid, yield 42%. mp 272.8-273.7 °C ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.5(d, J = 7.5Hz 1H), 7.70-7.75 (m, 5H), 7.51 (d, J = 9Hz, 2H), 6.71 (d, J = 8.5Hz 2H) , 3.03(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.8, 151.3, 133.8, 133.6, 132.6, 131.4, 127.8, 119.6, 118.8, 115.0, 112.5, 112.1, 108.7, 100.8, 94.9, 89.9, 84.6, 40.3. HRMS (ESI-TOF): cacld. for $C_{25}H_{17}N_4S$ $[M+H^+]$, 405.1174; found: 405.1167. IR: 3453, 2920, 2804, 2222, 2193, 1604, 1560, 1541, 1523, 1482, 1356, 1182, 1046.

8. Figures S19-S22 ^{1}H NMR and ^{13}NMR of compounds in liner-shaped D-A-A.

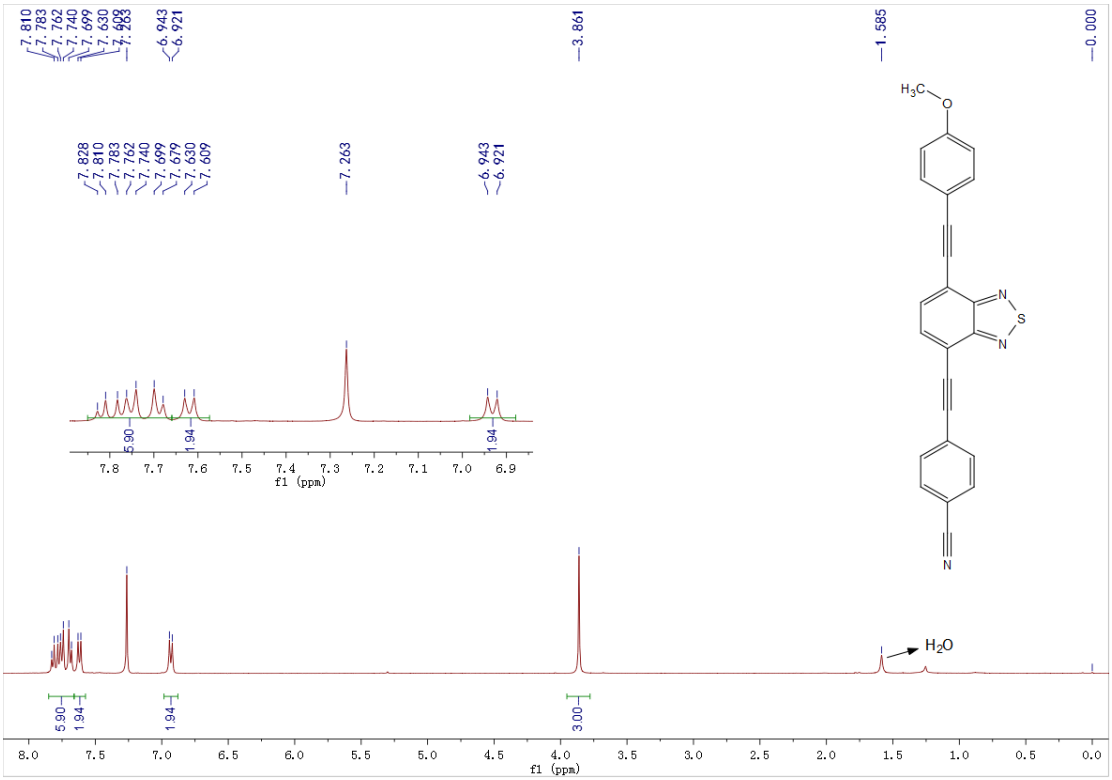


Figure S19 ^{1}H NMR of **PMP-4-BN-7** in $CDCl_3$

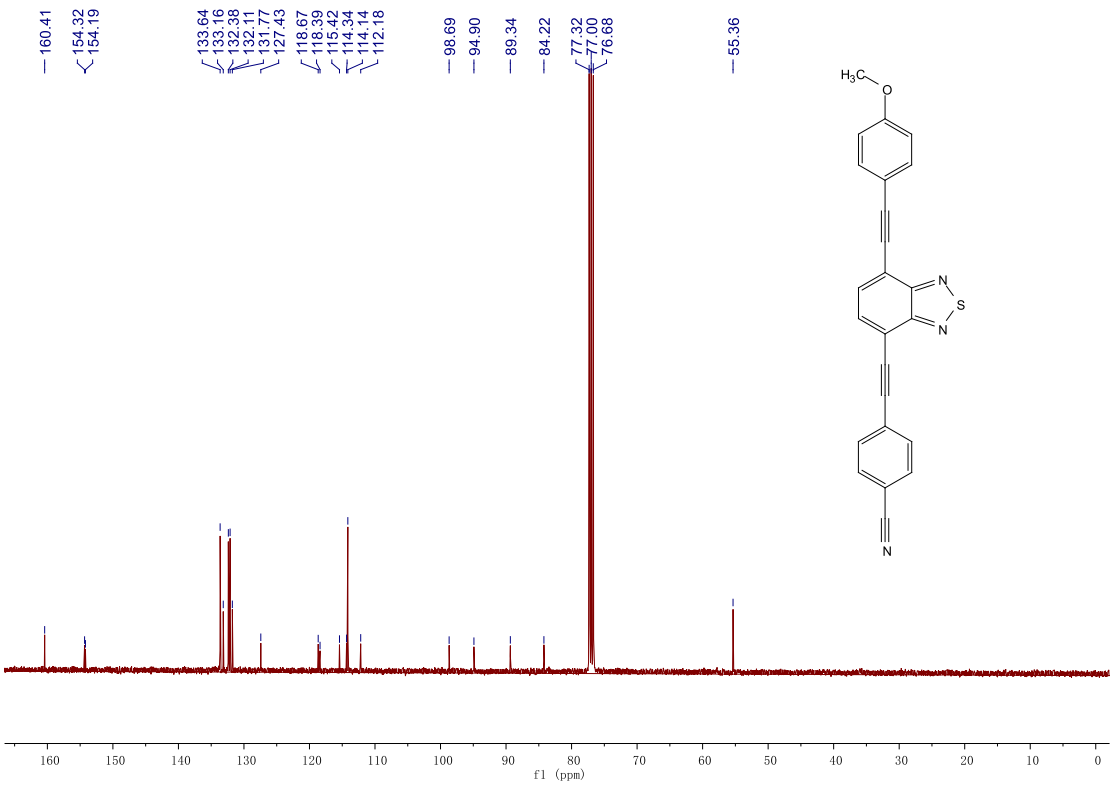


Figure S20 ^{13}C NMR of **PMP-4-BN-7** in $CDCl_3$

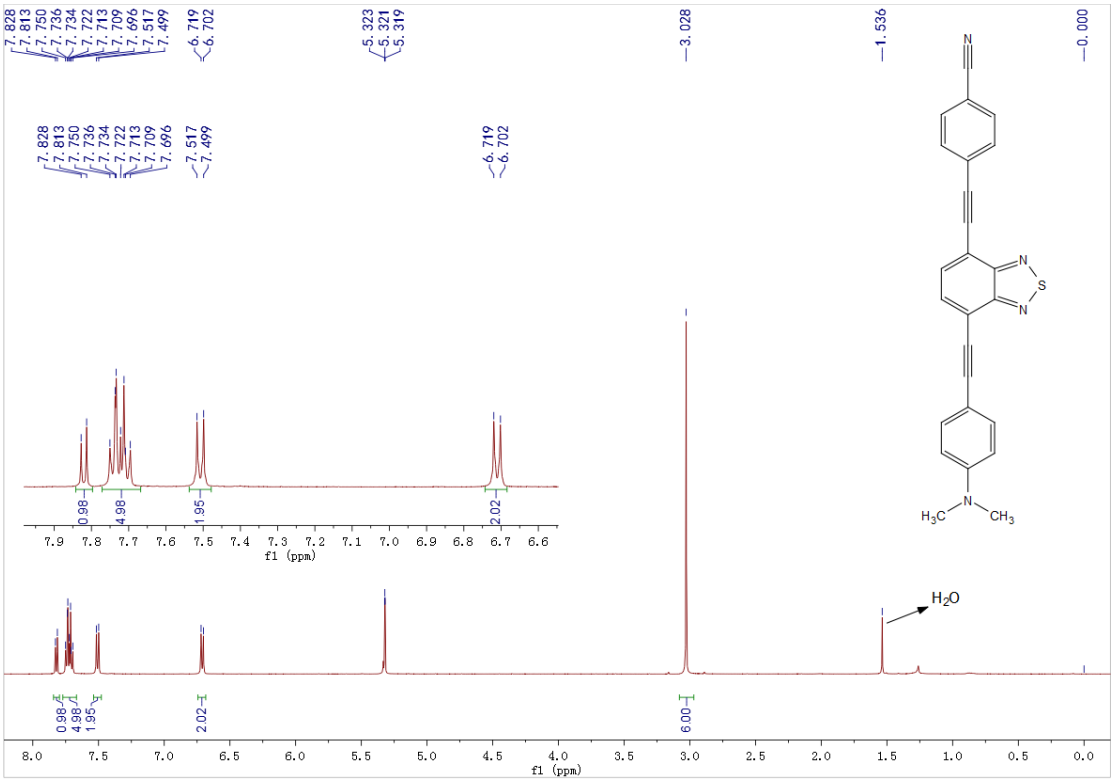


Figure S21 ^{1}H NMR of **DMAP-4-BN-7** in CD_2Cl_2

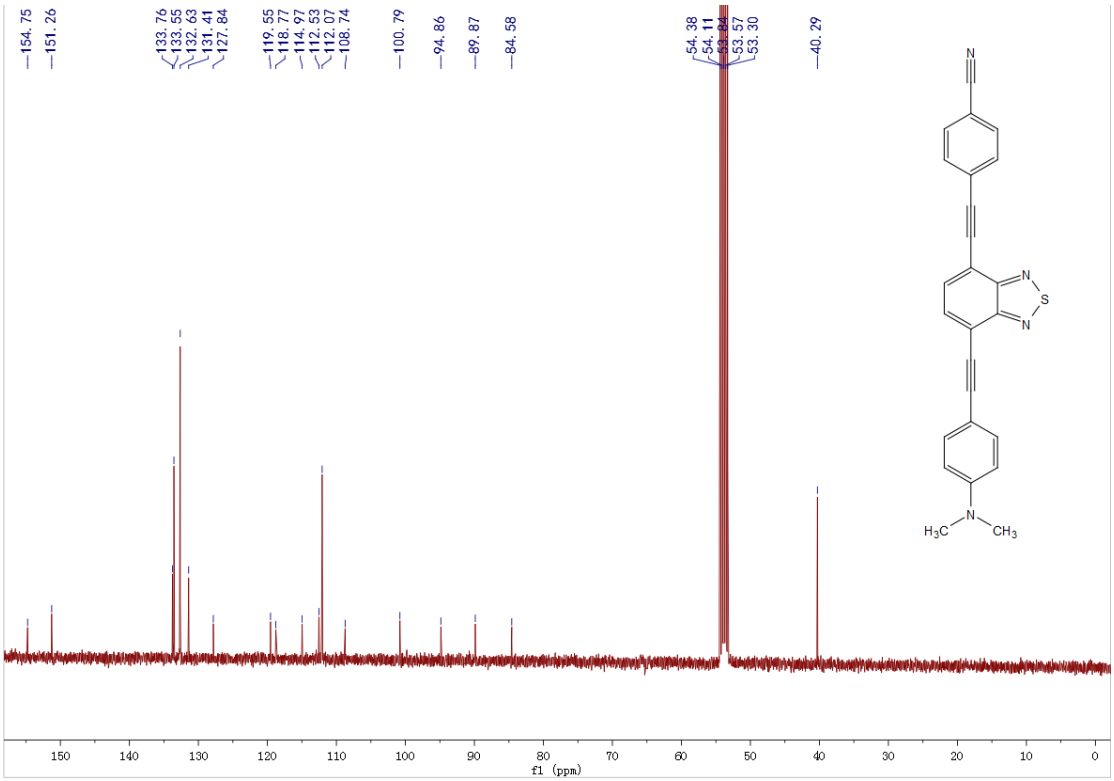


Figure S22 ^{13}C NMR of **DMAP-4-BN-7** in CD_2Cl_2

Table S1 Crystallographic data of compounds in butterfly-shaped

crystals	**2PMP-56**	**2DMAP-56**	**2TPA-56**	**2POZ-56(l)**	**2POZ-56(ll)**	**PMP-5-BN-6**	**DMAP-5-BN-6**
Formula	$C_{24}H_{16}N_2O_2S$	$C_{26}H_{22}N_4S$	$C_{46}H_{30}N_4S$	$C_{46}H_{30}N_4O_2S$	$C_{46}H_{30}N_4O_2S$	$C_{24}H_{13}N_3OS$	$C_{25}H_{16}N_4S$
CCDC	1850546	1850547	1850549	1887113	1887112	1850548	1850544
a [Å]	8.7103	7.6706	11.7169	9.1860	10.1869	8.3327	6.4455
b [Å]	9.1725	13.0303	37.416	13.2712	13.2164	9.9524	11.5324
c [Å]	25.594	21.6554	8.5164	32.6386	16.2017	23.283	13.9706
Alpha [deg]	90	90	90	84.348	104.630	90	96.465
Beta [deg]	97.276	95.183	108.750	88.603	105.673	91.689	93.121
Gamma[deg]	90	90	90	78.751	102.379	90	90.160
Z	4	4	4	2	2	4	2
V [$Å^3$]	2028.4	2155.6	3535.5	3883.5	1936.3	1930.0	1030.29
D [g cm^{-3}]	1.298	1.302	1.260	1.268	1.298	1.347	1.304
Space group	P 1 21/c 1	P 1 21/n 1	P 1 21/c 1	P -1	P -1	P 1 21/c 1	P -1
Mu [mm^{-1}]	0.182	0.171	0.131	0.196	0.133	0.188	0.176
R [b]	0.0531	0.0492	0.0626	0.0733	0.0656	0.0527	0.0529
wR [c]	0.1534	0.1370	0.1582	0.2139	0.2063	0.1659	0.1556

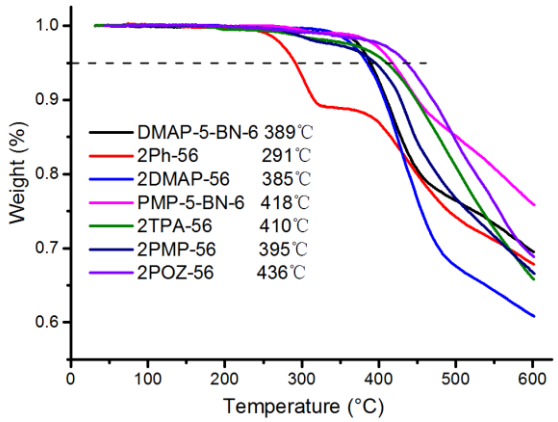


Figure S23 TGA analysis of compounds in butterfly-shaped

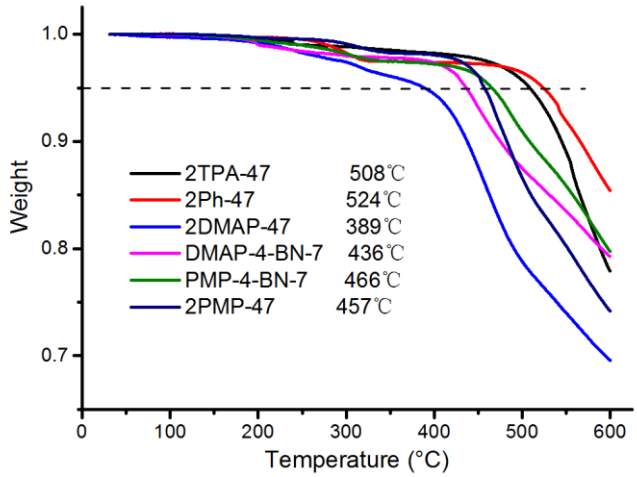
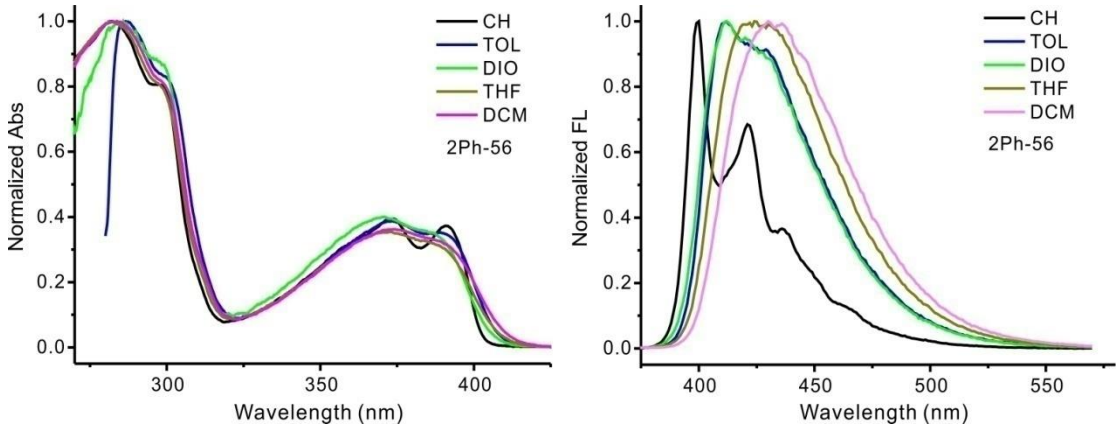
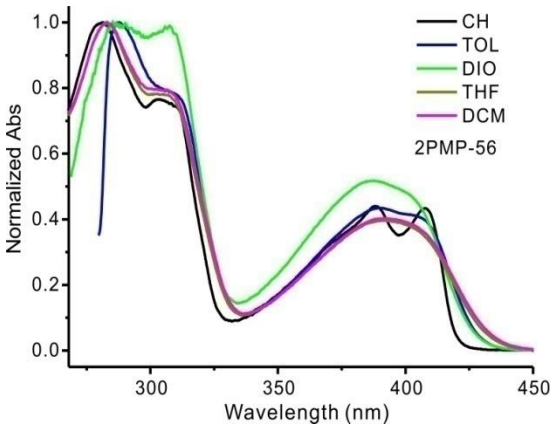
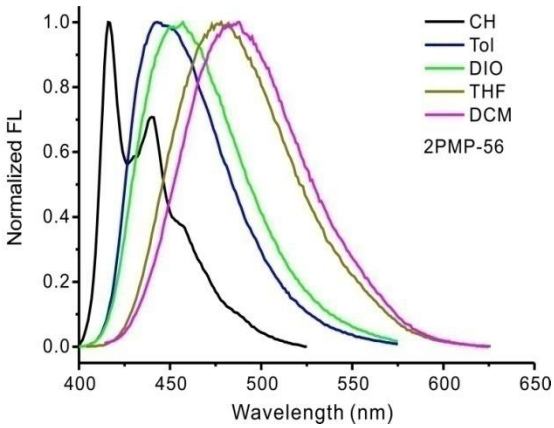
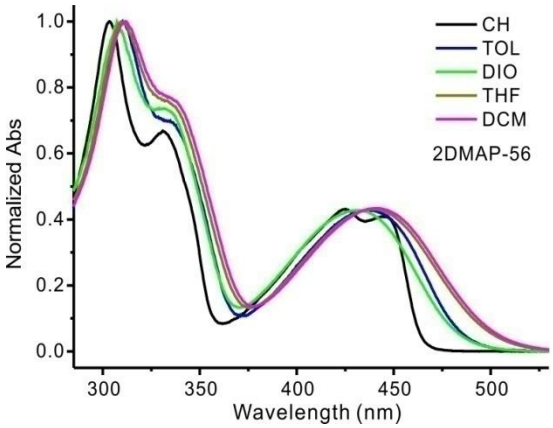


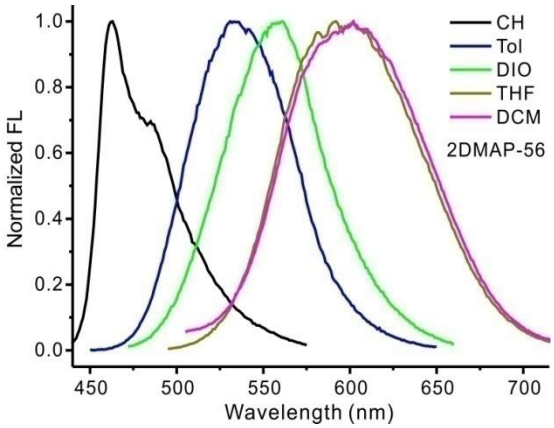
Figure S24 TGA analysis of compounds in linear-shaped

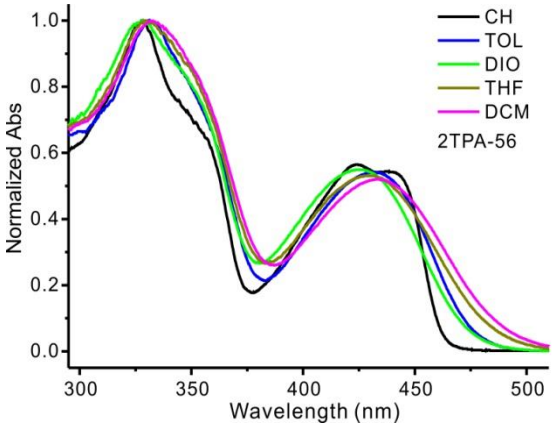


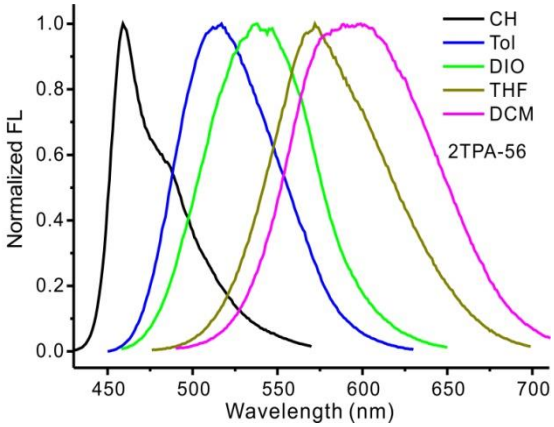

Normalized Abs
Wavelength (nm)
CH
TOL
DIO
THF
DCM
2PMP-56

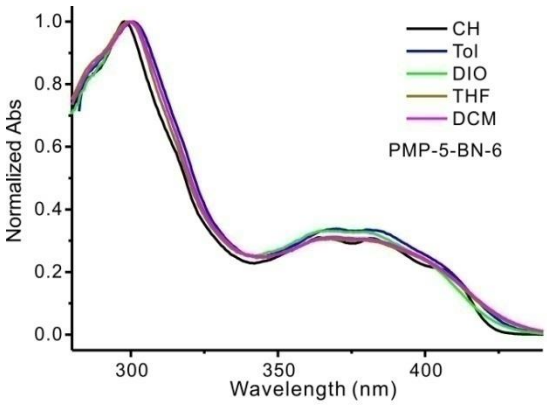

Normalized FL
Wavelength (nm)
CH
Tol
DIO
THF
DCM
2PMP-56

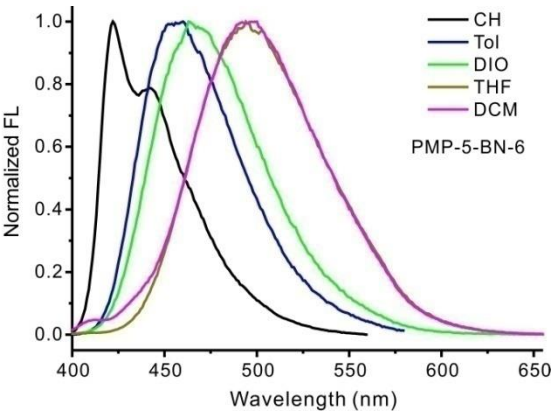

Normalized Abs
Wavelength (nm)
CH
TOL
DIO
THF
DCM
2DMAP-56


Normalized FL
Wavelength (nm)
CH
Tol
DIO
THF
DCM
2DMAP-56


Normalized Abs
Wavelength (nm)
CH
TOL
DIO
THF
DCM
2TPA-56


Normalized FL
Wavelength (nm)
CH
Tol
DIO
THF
DCM
2TPA-56


Normalized Abs
Wavelength (nm)
CH
Tol
DIO
THF
DCM
PMP-5-BN-6


Normalized FL
Wavelength (nm)
CH
Tol
DIO
THF
DCM
PMP-5-BN-6

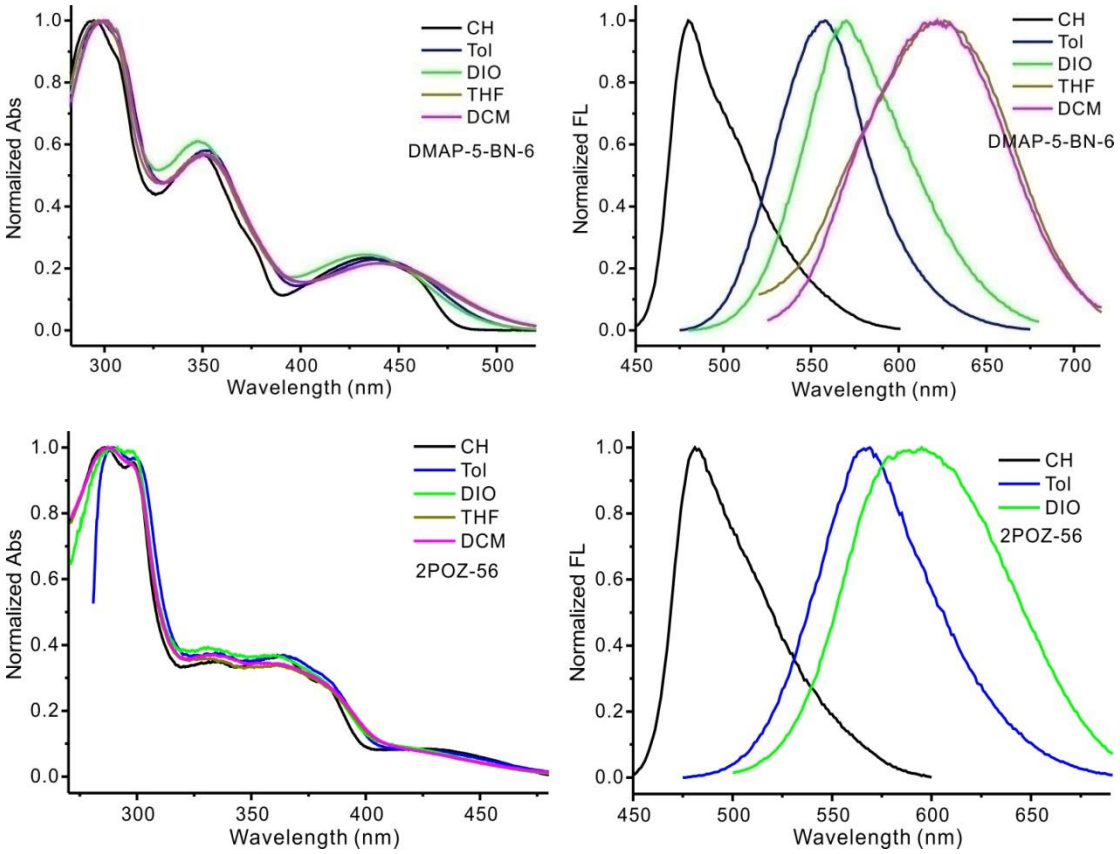
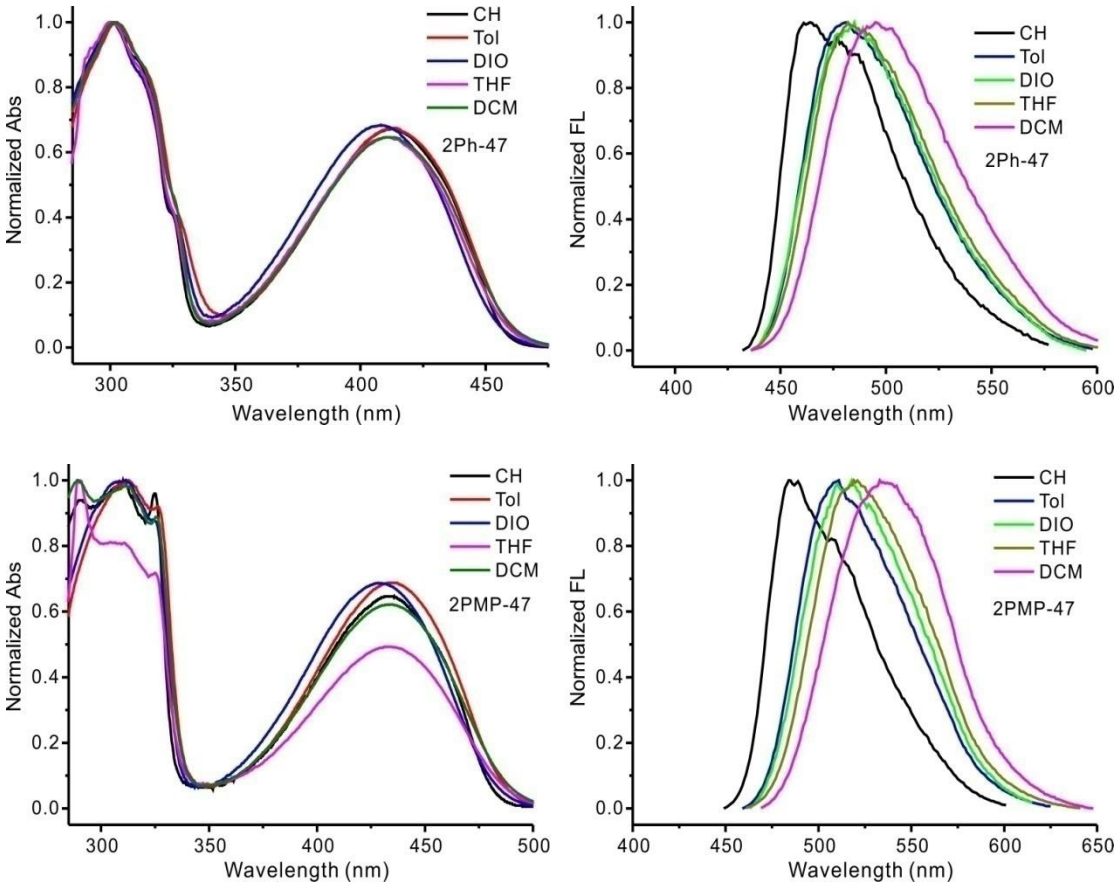


Figure S25 Solvent effect on absorption and emission of butterfly-shaped compounds



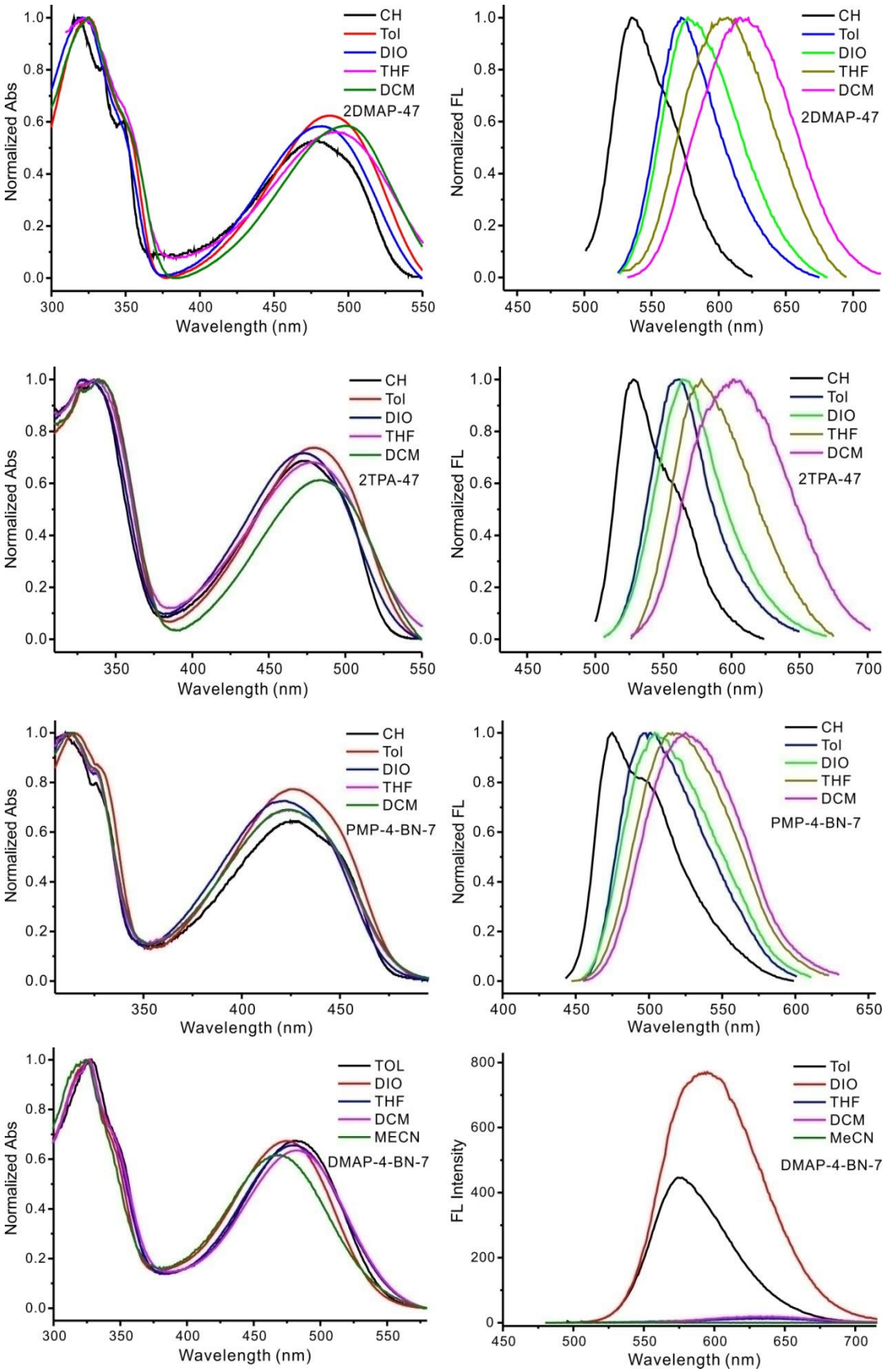


Figure S26 Solvent effect on absorption and emission of linear-shaped compounds

Table S2 Solvent effect on absorption and emission

Compd	CH			Tol			DIO			THF			DCM		
	λ_{max}^{abs}	λ_{SOL}^{em}	Stokes	λ_{max}^{abs}	λ_{SOL}^{em}	Stokes	λ_{max}^{abs}	λ_{SOL}^{em}	Stokes	λ_{max}^{abs}	λ_{SOL}^{em}	Stokes	λ_{max}^{abs}	λ_{SOL}^{em}	Stokes
2Ph-56	282,373 391	400,421，436	9	287,373 389	412	23	284,370	412	42	281,373	424	51	282,374	430	56
2PMP-56	285,388,408	416,440	8	287,390	443	37	284,305, 388	457	69	283,393	478	85	286,392	488	96
2DMAP-56	303,331425,446	463	17	310,436	531	95	307,432	561	129	309,439	600	161	311,441	602	161
2TPA-56	327,423,441	459	18	331,431	517	86	328,424	538	114	329,432	572	140	332,434	599	165
2-POZ-56	286,363,382	481	99	289,364	569	205	287,361	595	234	-------	------	------	------	------	------
2Ph-47	301,413	464,475	51	302,414	481	67	300,408	485	77	300,411	483	72	302,411	495	84
2PMP-47	310,432	484,507	62	313,435	511	76	311,429	518	89	312,433	519	86	310,434	533	99
2DMAP-47	318,478	535	57	325,488	572	84	320,482	577	95	324,492	607	115	323,497	616	119
2TPA-47	336,473	528	55	339,479	561	82	329,474	564	90	339,478	577	99	338,485	601	116
PMP-5-BN-6	298,381	422,442	17	300,380	460	80	300,379	463	84	300,368	494	126	301,379	500	121
DMAP-5-BN-6	349,435	480	45	352,439	558	119	347,433	570	137	298,350,434	626	184	349,443	622	179
PMP-4-BN-7	310,426	475,495	49	315,426	501	75	313,422	504	82	313,423	517	94	314,424	525	101
DMAP-4-BN-7	------	------	------	328,485	574	89	327,475	595	120	325,480	------	------	327,481	------	------

Table S3 Dipole moments of molecules in ground states and in excited states

Compd	μ_g (D)[a]	$\Delta\mu_{eg}$[b]	μ_e(D)[c]
2Ph-56	5.0	10.1	15.1
2PMP-56	5.6	16.5	22.1
2DMAP-56	12.2	18.3	30.5
2TPA-56	8.1	22.4	30.5
PMP-5-BN-6	2.9	16.1	19.0
DMAP-5-BN-6	6.5	16.7	23.2
2Ph-47	2.2	8.3	10.5
2PMP-47	5.4	11.0	16.4
2DMAP-47	2.0	10.4	12.4
2TPA-47	2.2	12.6	14.8
PMP-4-BN-7	9.2	12.2	21.4
DMAP-4-BN-7	12.6	----	---

(a) Dipole moments in ground state (μ_g) are calculated based on Gaussion 09 applying 6-31G-B3LYP as method; (b) dipole moment changes obtained by the modified Lippert-Mataga equation(5); (c) dipole moments in excited states, calculated from the equation of $\mu_e=\Delta\mu_{eg}+\mu_g$.

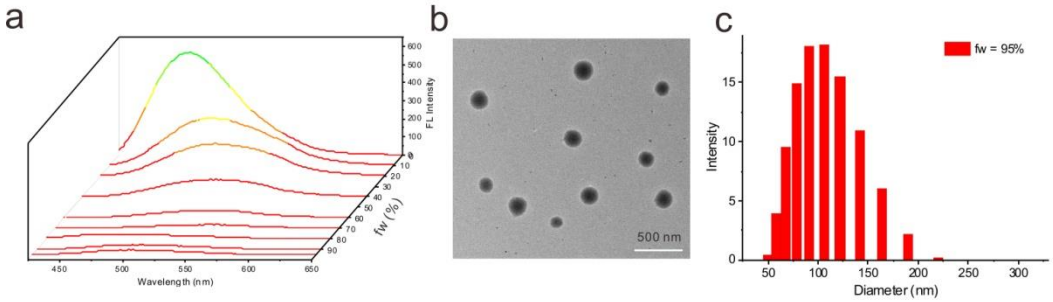


Figure S27 (a) Emission spectra of **2PMP-56** in aqueous THF solutions; (b) TEM image of **2PMP-56** in 95% water faction; (c) DLS analysis of **2PMP-56** in 95% water faction

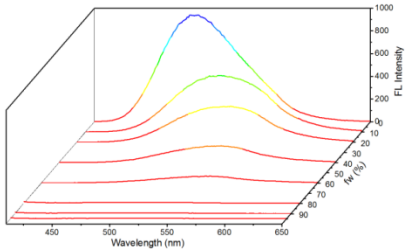


Figure S28 Emission spectra of **PMP-5-BN-6** in aqueous THF solutions

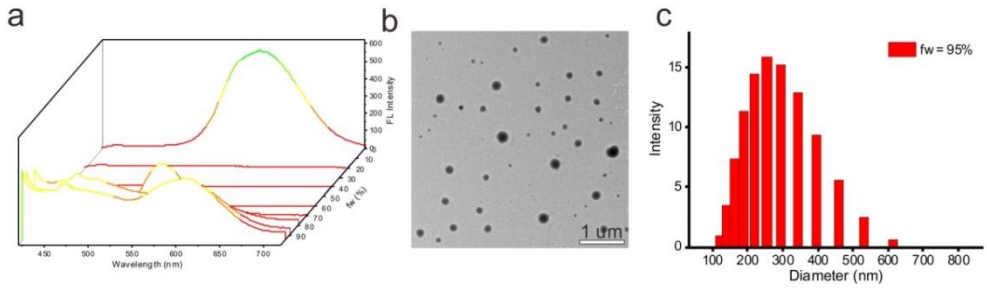


Figure S29 (a) Emission spectra of **2DMAP-56** in aqueous THF solutions; (b) TEM image of **2DMAP-56** in 95% water faction; (c) DLS analysis of of **2DMAP-56** in 95% water faction

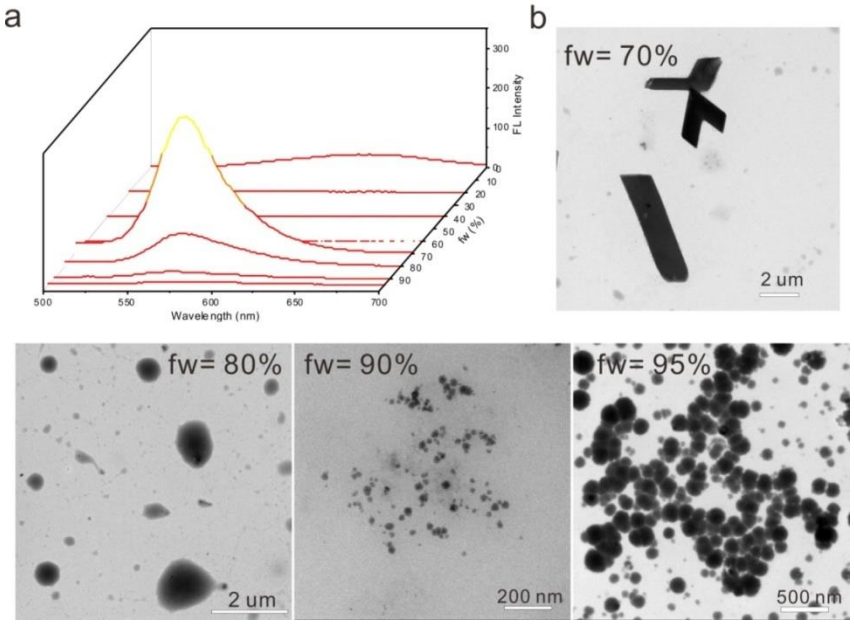


Figure S30 (a) Emission spectra of **DMAP-5-BN-6** in aqueous THF solutions; (b) TEM image of **DMAP-5-BN-6** in70%, 80%, 90%, and 95% water faction, respectively

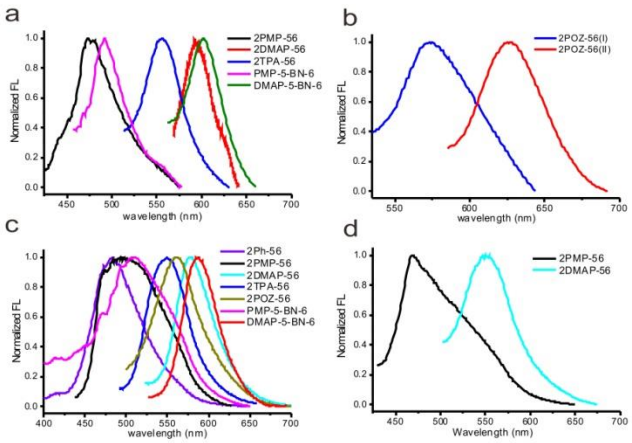


Figure S31 Emission spectra of butterfly-shaped compounds in crystals (a & b), in pristines (c), in films (d)

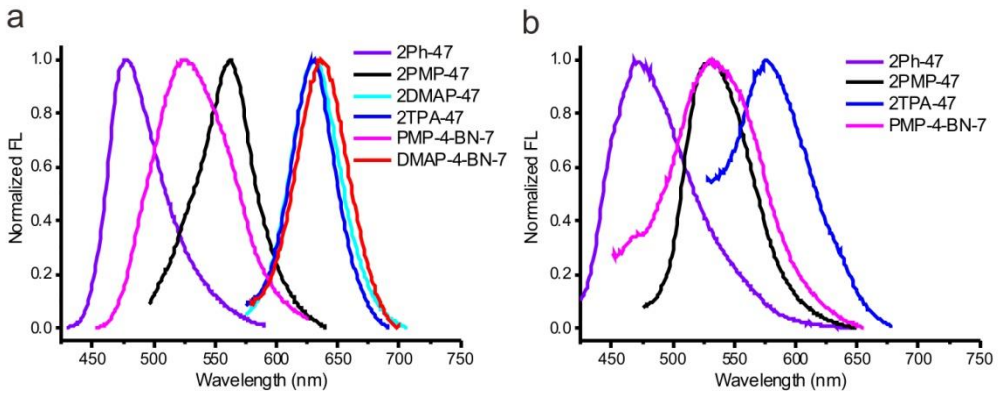


Figure S32 Emission spectra of linear-shaped compounds in pristines (a), in films (b)

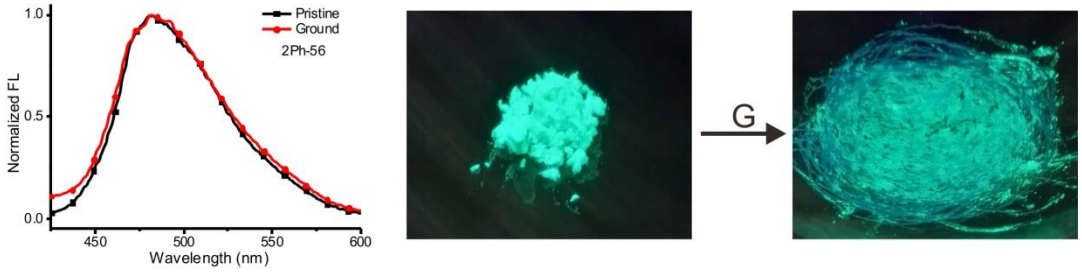


Figure S33 Emission spectra of **2Ph-56** before and after grinding (left), photos of **2Ph-56** before and after grinding (right)

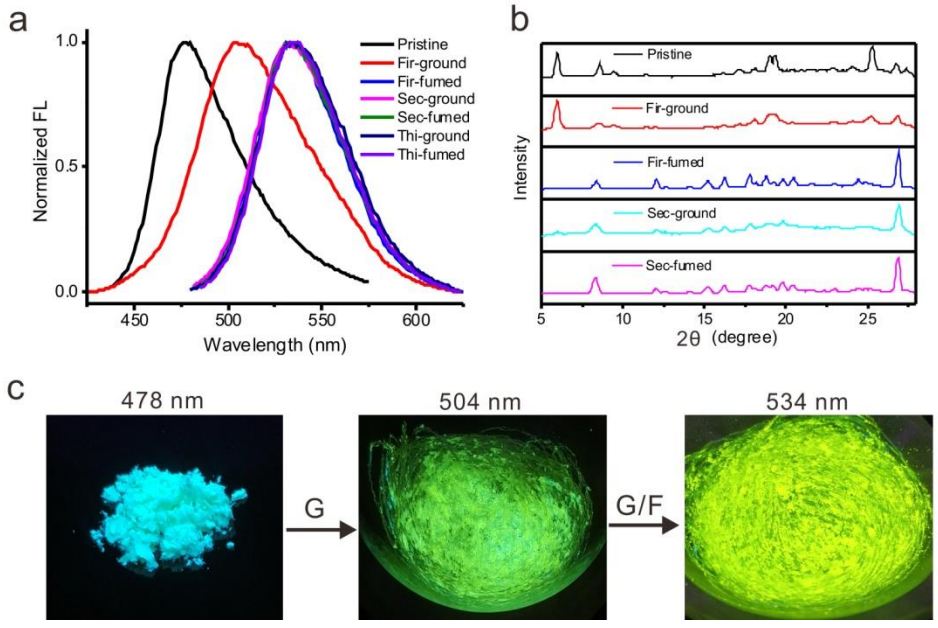


Figure S34 Emission spectra (a) and XRD diffractions (b) of **2Ph-47** before and after grinding; (c) Photos under UV lamp

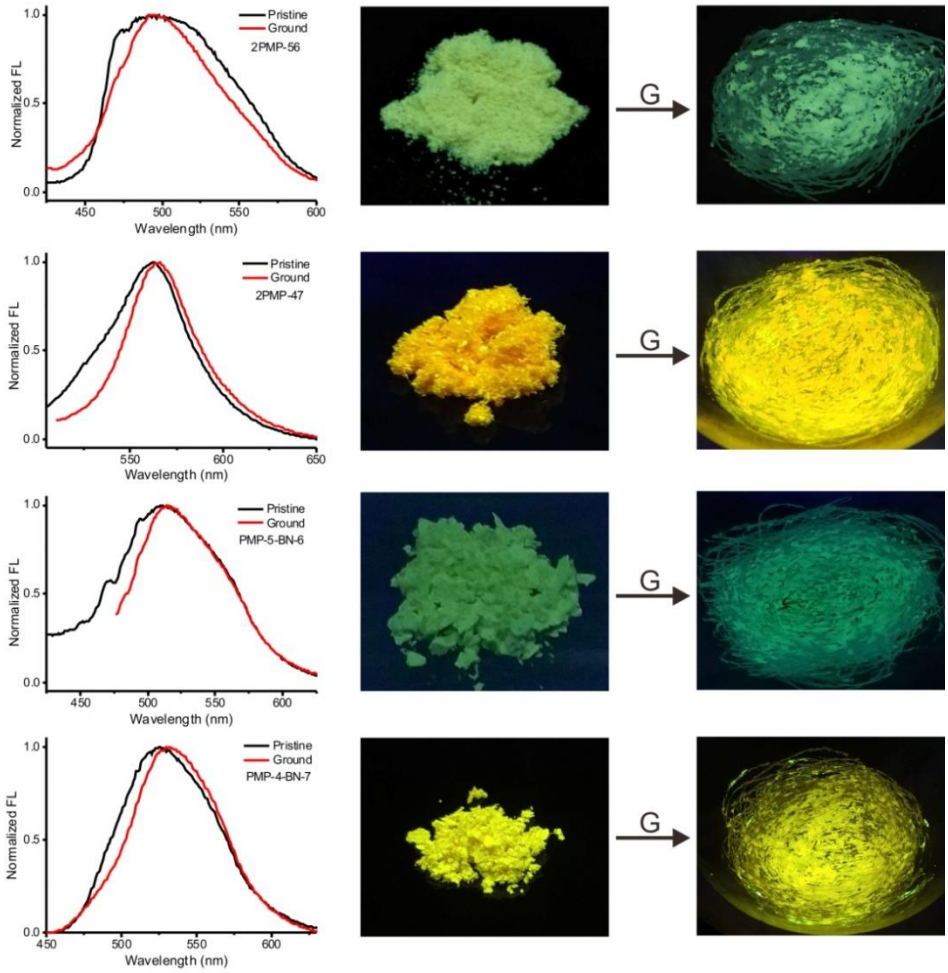


Figure S35 Emission spectra of **2PMP-56**, **2PMP-47**, **PMP-5-BN-6** and **PMP-4-BN-7** before and after grinding (left); photos under UV lamp(right)

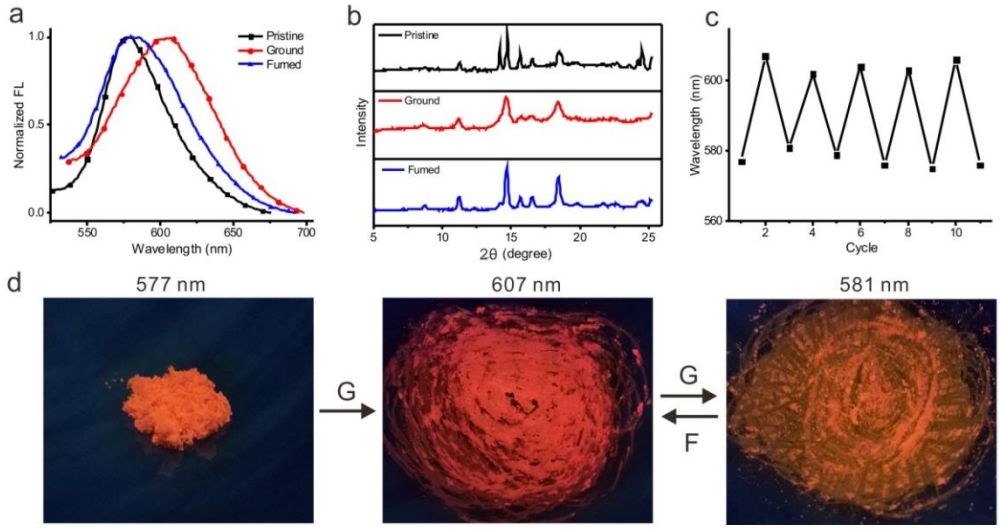


Figure S36 Emission spectra (a) and XRD diffractions (b) of **2DMAP-56** before and after grinding/fuming; (c) Reversible changes of emission intensities of **2DMAP-56** by grinding and fuming; (d) Photos under UV lamp

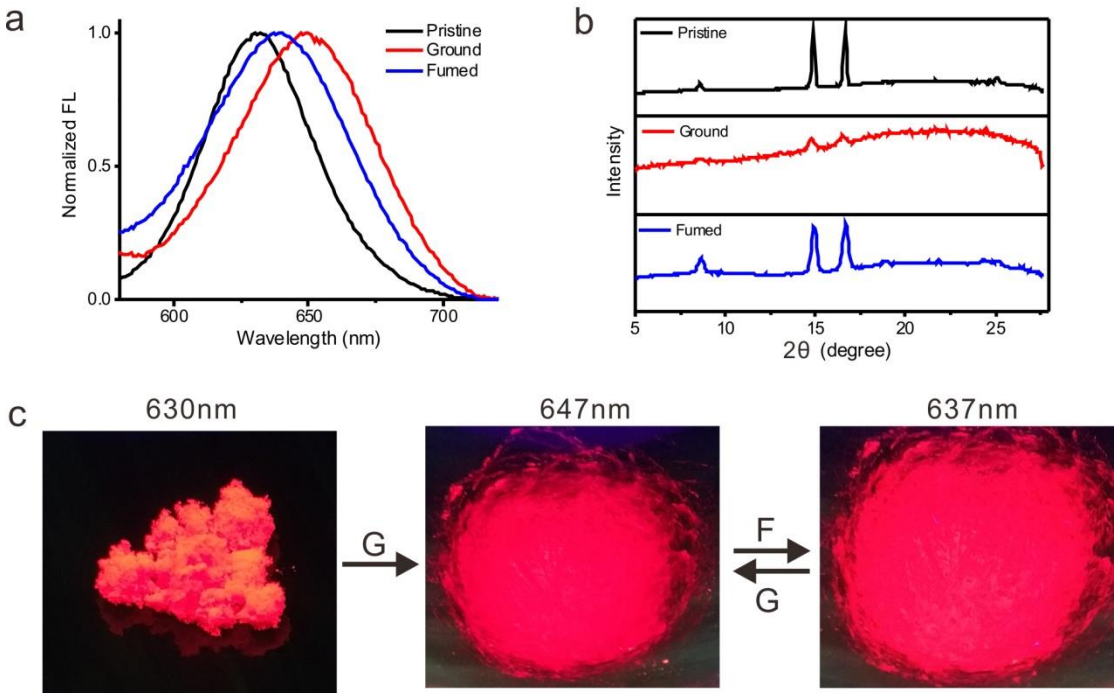


Figure S37 Emission spectra (a) and XRD diffractions (b) of **2DMAP-47** before and after grinding/fuming; (c) Photos under UV lamp

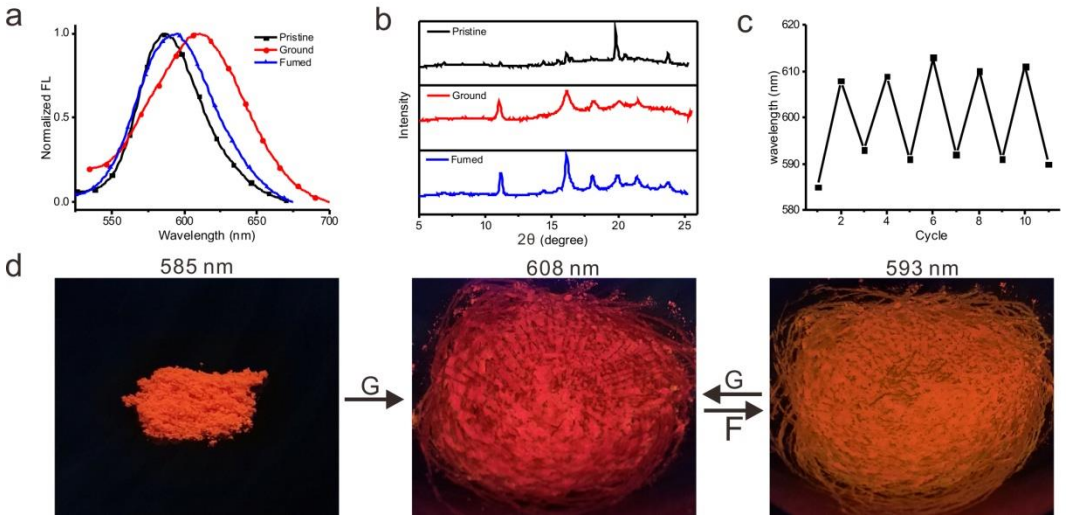


Figure S38 Emission spectra (a) and XRD diffractions (b) of **DMAP-5-BN-6** before and after grinding/fuming; (c) Reversible changes of emission intensities of **DMAP-5-BN-6** by grinding and fuming; (d) Photos under UV lamp

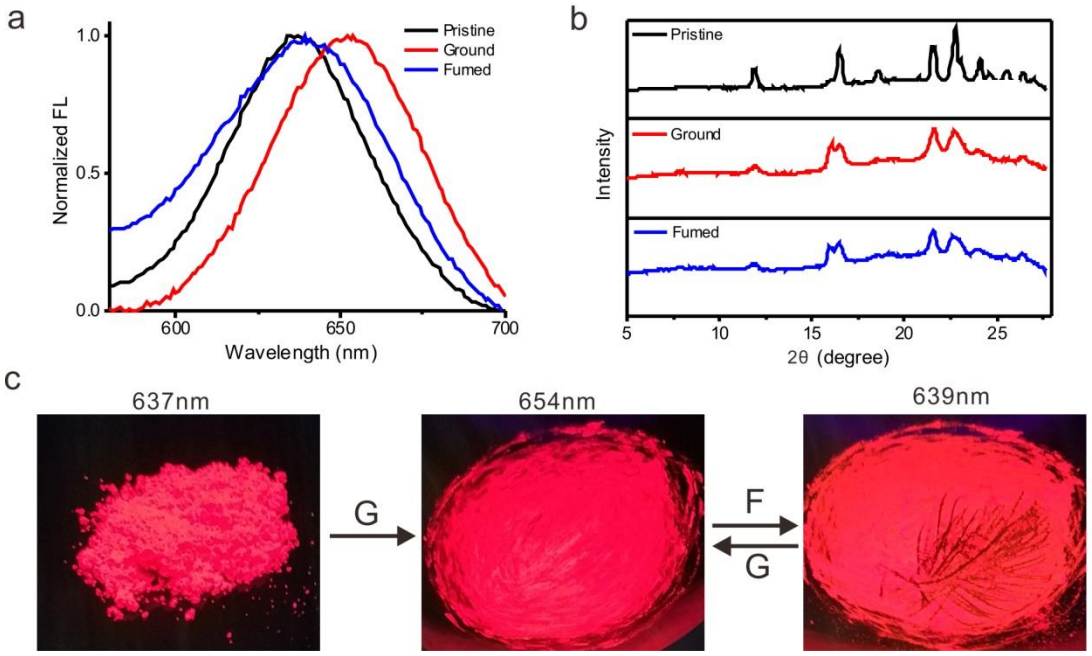


Figure S39 Emission spectra (a) and XRD diffractions (b) of **DMAP-4-BN-7** before and after grinding/fuming; (c) Photos under UV lamp

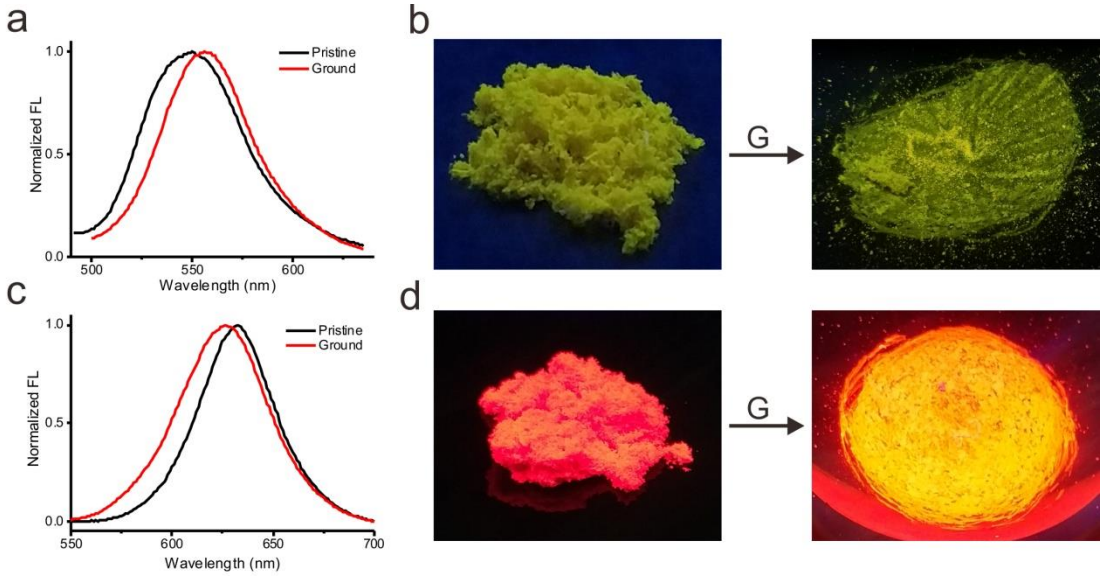


Figure S40 Emission spectra of **2TPA-56** (a) and **2TPA-47** (c) before and after grinding; photos of **2TPA-56** (b) and **2TPA-47** (d) before and after grinding under UV lamp

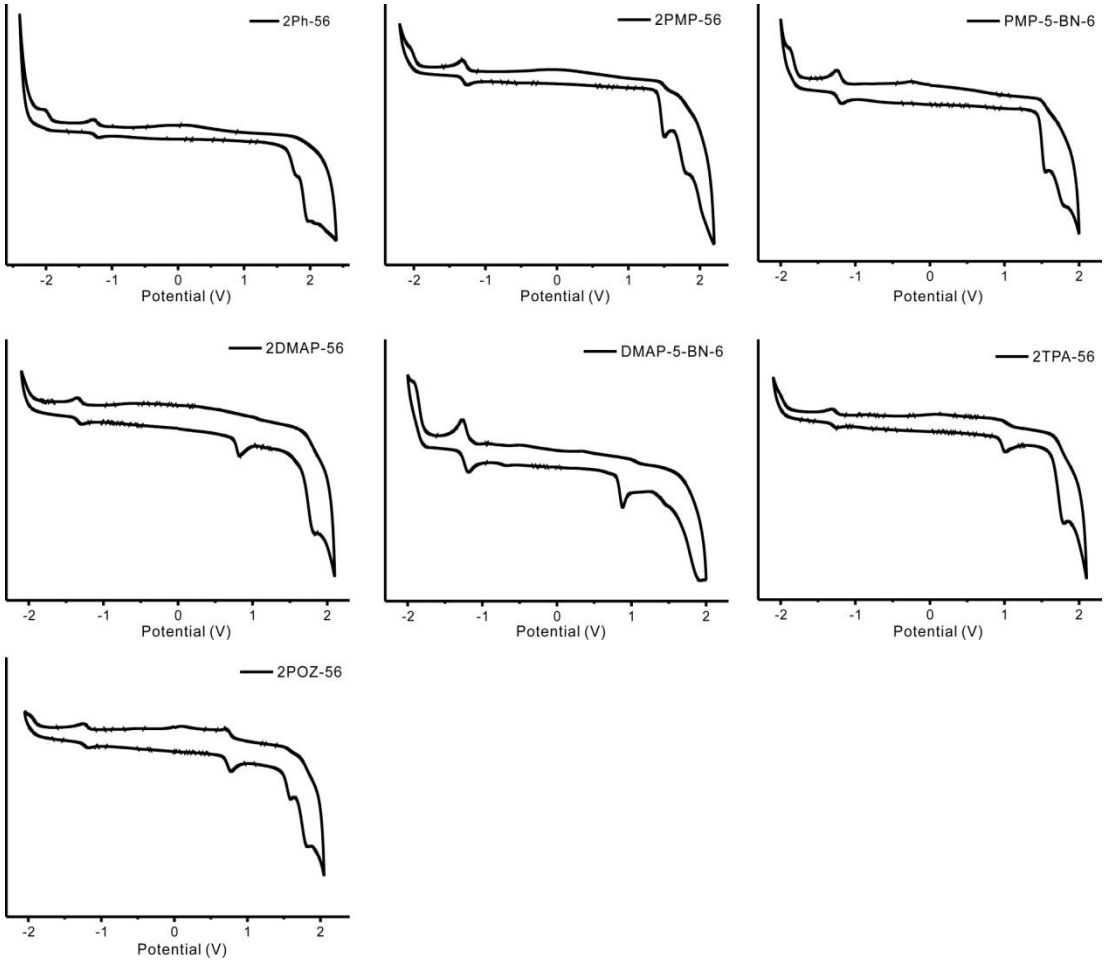


Figure S41. Cyclic voltammograms of butterfly-shaped compounds

Table S4 Electrochemical properties and theoretical calculations

Compounds	HOMO		LUMO		E_g		
	CV[a]	Cald[b]	CV[a]	Cald[b]	CV[a]	Cald[b]	UV[c]
2Ph-56	-6.15	-6.33	-3.16	-3.20	2.99	3.13	3.06
2PMP-56	-5.90	-5.97	-3.11	-3.05	2.79	2.92	2.90
2DMAP-56	-5.23	-5.27	-3.06	-2.75	2.17	2.52	2.52
2TPA-56	-5.41	-5.37	-3.12	-3.00	2.29	2.37	2.59
2POZ-56	-5.15	-5.51	-3.18	-2.94	1.97	2.57	2.87
PMP-5-BN-6	-5.95	-6.21	-3.17	-3.40	2.78	2.81	2.93
DMAP-5-BN-6	-5.28	-5.54	-3.17	-3.23	2.11	2.31	2.48

a. Cyclic voltammograms of compounds measured in MeCN:DCM=3:1 solution using n-Bu_4NPF_6 as the supporting electrolyte and SCE as the reference electrode. HOMO = E_{ref} - $E_{ox\ (peak\ potential)}$, LUMO = E_{ref} – $E_{red\ (peak\ potential)}$, E_g = HOMO – LUMO. b. calculated by the DFT method at the B3LYP/6-31G* basis set, E_g = HOMO – LUMO. c. $E_g = 1241/\lambda_{uv,onset}$ in THF.

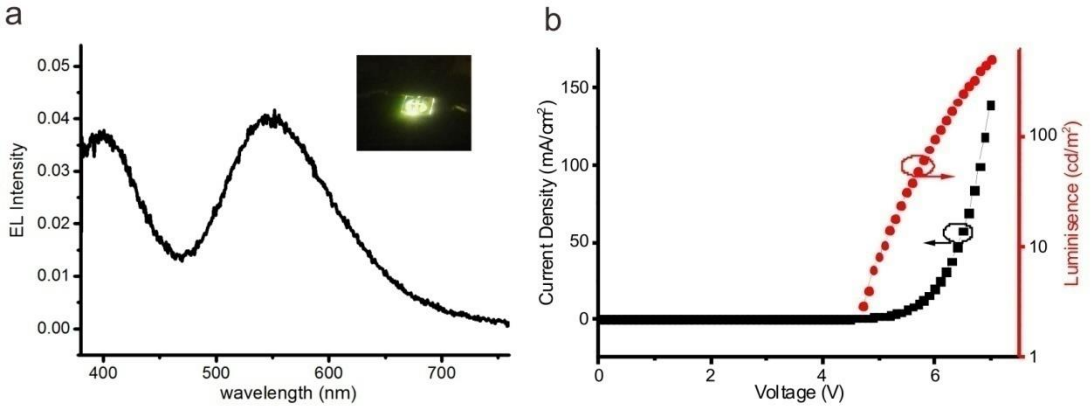


Figure S42 (a) Spectrum of **DMAP-5-BN-6** based device operating at a voltage of 7 v. Inset: Image of device; (b) Current-density-voltage (L-J-V) characteristics

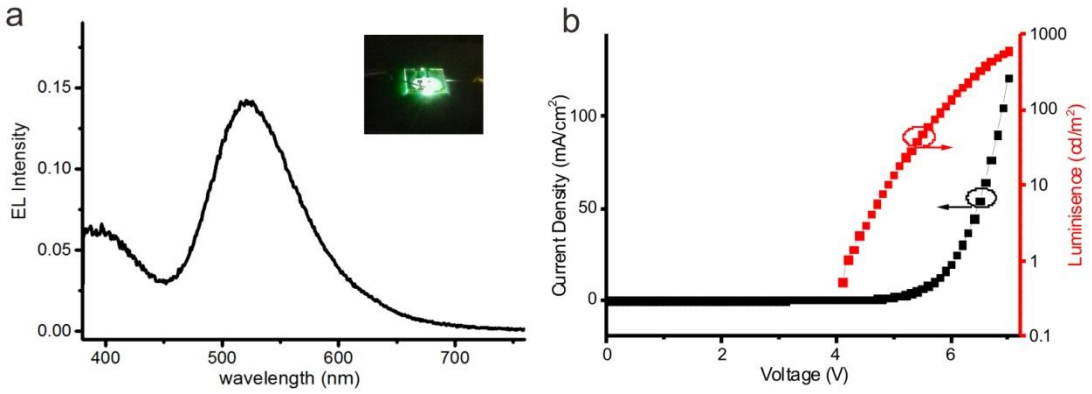


Figure S43 (a) EL Spectrum of **2TPA-56** based device operating at a voltage of 7 v. Inset: Image of device; b) Current-density-voltage (L-J-V) characteristics

Table S5 Performance of OLED devices[a]

Compound	$V^{b}_{turn\text{-}on}$ (v)	CIE^{c}_{1931} (x,y)	EL^{d} (nm)	Device performances at 100cd/m^2		
				EQE (%)	CE (cd/A)	PE (lm/W)
DMAP-5-BN-6	4.5	(0.33,0.41)	400,551	0.19	0.47	0.24
2TPA-56	4.2	(0.27,0.47)	403,521	0.26	0.73	0.40
2POZ-56	4.7	(0.32,0.35)	403,555	0.29	0.53	0.27

[a] Device structure: ITO / PEDOT : PSS (40 nm) / m_{Compd} : m_{PVK} (1 : 16) / TPBI (30nm) / LiF (1 nm) / Al (60 nm), [b] Turn-on voltage at a brightness of 1 cd/m^2, [c,d] at voltage of 7 V.

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