Supporting Information

A benzoindole-cored building block for deep blue fluorescent material: synthesis, photophysical properties, and applications in organic light-emitting diodes

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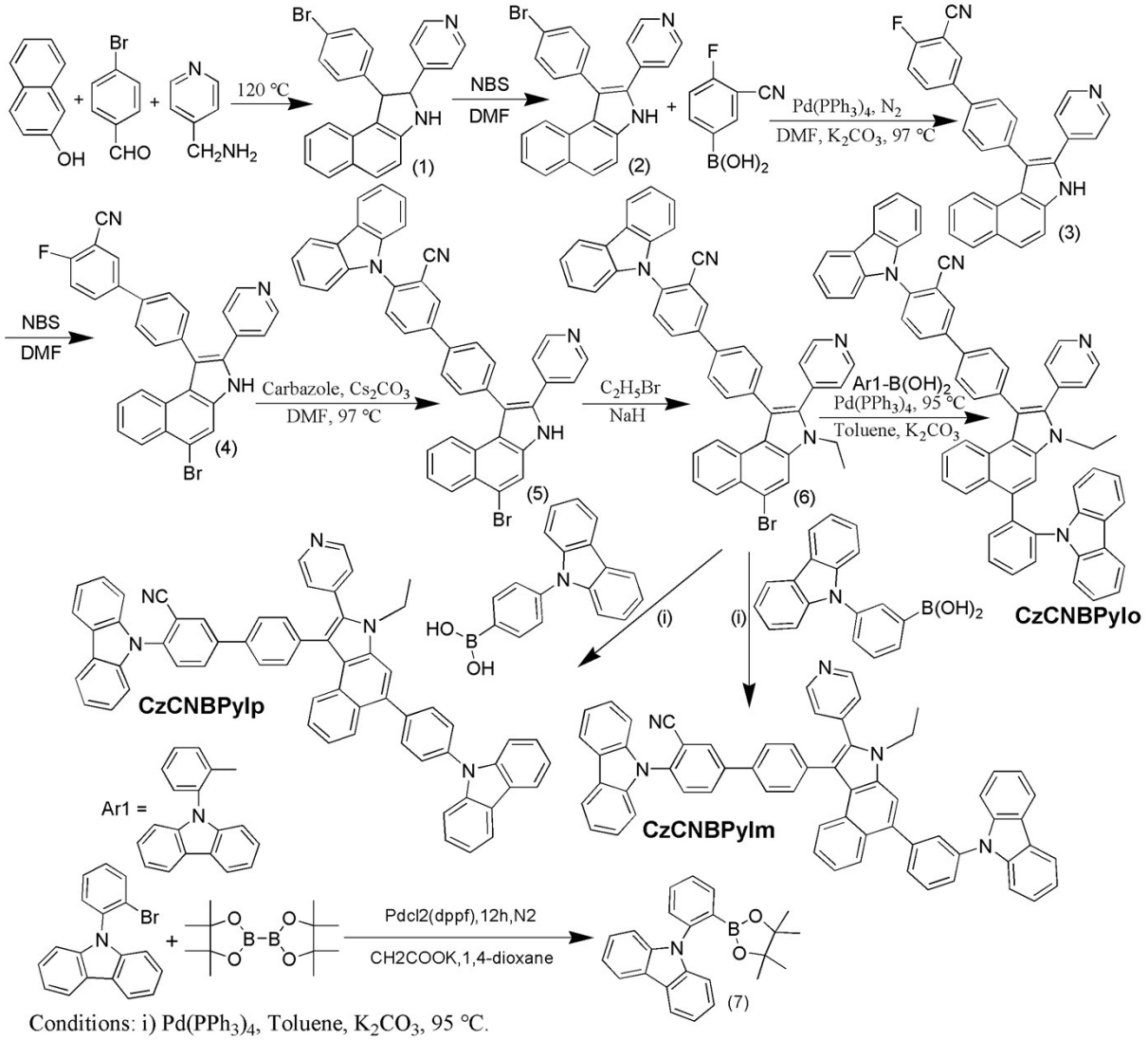
1. Materials and general methods

CzCNBPyIo, CzCNBPyIm and CzCNBPyIo were first synthesized through Suzuki reaction. The chemical structure was systematically characterized and confirmed via magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). All the target products were purified by column chromatography before the characterization. NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR (1H: 400 MHz, 13C:100 MHz). The matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS) measurements were carried out with a Shimadzu AXIMA-CFR mass spectrometer. UV-visible absorption spectra were recorded on a Shimadzu UV-3600. Transient lifetime decay curves and absolute PLQY measurement were conducted on Edinburgh Instruments Fluorescence spectrometer (EPL-375). Photoluminescence (PL) spectra were measured on Shimadzu spectrofluorophotometer (RF-5301PC). Electrochemical behaviors were investigated on Electrochemical working station by cyclic voltammetry (CV) method with a standard three-electrode electrochemical cell in a 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile solution at room temperature under nitrogen atmosphere with a scanning rate of 50 mV/s. A platinum working electrode, a glassy carbon electrode, and an $Ag/AgNO_3$ (0.1 M) reference electrode were configured. The CV curves were calibrated using ferrocene/ferrocenium (Fc/Fc+) redox couple (4.8 eV below the vacuum level) as the internal standard. Differential scanning calorimetry (DSC) were conducted on Shimadzu DSC-60A equipment.



Scheme S1. Synthetic route of CzCNBPyIo, CzCNBPyIm, and CzCNBPyIp.

1-(4-bromophenyl)-2-(pyridin-4-yl)-2,3-dihydro-1H-benzo[e]indole (1). A mixture of 2-Hydroxynaphthalene (14.711 g, 100 mmol), 4-picolylamine (10.814 g,100 mmol) and 4-Bromobenzaldehyde (18.5 g, 100 mmol) were heated to 120 ℃ under nitrogen and stirred overnight, then the reaction mixture was cooled to room temperature, extracted with ethanol and dried over anhydrous Na_2SO_4. The solvent was evaporated to afford the crude product, which was purified by column chromatography using ethyl acetate/petroleum ether (5:1) to get the target product. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.52 (m, 2H), 7.77 (dd, J = 6.8, 3.6 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.24 – 7.21 (m, 2H), 7.20 – 7.14 (m, 3H), 7.06 (dd, J = 9.6, 6.4 Hz, 3H), 4.80 (dd, J = 7.6, 3.2 Hz, 1H), 4.59 (d, J = 7.2 Hz, 1H), 4.42 (d, J = 3.2 Hz, 1H). GC-MS, m/z cacld for $C_{23}H_{17}BrN_2$, 401.31; found, 402.

1-(4-bromophenyl)-2-(pyridin-4-yl)-3H-benzo[e]indole (2). DMF (6 mL) was added to a mixture of 1-(4-bromophenyl)-2-(pyridin-4-yl)-2,3-dihydro-1H-benzo[e]indole (1) (1.1603 g, 2.89 mmol) and NBS (0.5293 g, 3.03 mmol) under the condition of dark and nitrogen flux. The reaction mixture was stirred for 12 h. Then cooling to room temperature, the mixture was extracted with ethyl acetate and water and dried over Na_2SO_4. The crude product was purified by column chromatography using ethyl acetate/petroleum ether (3:1). Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.23 (s, 1H), 8.59 – 8.52 (m, 2H), 7.77 (dd, *J* = 6.8, 3.6 Hz, 2H), 7.72 – 7.62 (m, 2H), 7.48 – 7.40 (m, 2H), 7.20 – 7.14 (m, 3H), 7.10 – 7.06 (m, 3H). GC-MS, m/z cacld for $C_{23}H_{15}BrN_2$, 400.06; found, 401.

4-fluoro-4'-(2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-[1,1'-biphenyl]-3-carbonitrile (3). (2) (0.8099 g, 2.03 mmol), (3-cyano-4-fluorophenyl)boronic acid (0.4029 g, 2.442 mmol), K_2CO_3 (2 mol/L) 3.01 mL, tetrakis(triphenylphosphine)palladium (0.149 g, 0.129 mmol) were dissolved in DMF under nitrogen atmosphere. This reaction mixture was stirred at 97 °C for 12 h. The mixture was diluted with ethyl acetate and washed with water three times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in reduce pressure to give the crude product, which was purified on column chromatography using ethyl acetate/petroleum ether (3:1) as eluent, yield: 70.5%. ^{1}H NMR (400 MHz, DMSO) δ 12.37 (s, 1H), 8.44 (s, 1H), 8.39 – 8.31 (m, 2H), 8.13 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.88 – 7.81 (m, 2H), 7.63 – 7.46 (m, 2H), 7.41 – 7.34 (m, 2H), 7.20 – 7.14 (m, 2H), 7.11 – 7.07 (m, 3H), GC-MS, m/z cacld for $C_{30}H_{18}FN_3$, 439.15; found, 440.37.

4'-(5-bromo-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-4-fluoro-[1,1'-biphenyl]-3-carbonitrile (4). (3) (0.6283 g, 1.432 mmol), NBS (0.3125 g, 1.791 mmol), DMF 6 mL were stirred for 12 h at 50 °C under a dark and nitrogen atmosphere. The crude product was purified by column chromatography using ethyl acetate/petroleum ether (3:1) as eluent; yield: 69.98%. ^{1}H NMR (400 MHz, DMSO) δ 12.46 (s, 1H), 8.43 (s, 1H), 8.33 – 8.27 (m, 2H), 8.03

– 7.98 (m, 2H), 7.94 (d, *J* = 6.4 Hz, 2H), 7.91 – 7.85(m, 2H), 7.81 – 7.73 (m, 2H), 7.61 – 7.55 (d, *J* = 6.4 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.45 – 7.2 (s, 1H), GC-MS, m/z cacld for $C_{30}H_{17}BrFN_3$, 517.06; found, 518.28.

4'-(5-bromo-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-4-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (5). (4) (0.5182 g, 1.002 mmol), carbazole (0.640 g, 3.789 mmol), Cs_2CO_3 (0.986 g, 2.96 mmol) were dissolved in DMF 5 mL under nitrogen atmosphere. This reaction mixture was stirred for 12 h at 97 °C. The crude product was purified by column chromatography using ethyl acetate/petroleum ether (2:1) as eluent, yield: 60%. ^{1}H NMR (400 MHz, DMSO) δ 12.50 (s, 1H), 8.73 (s, 1H), 8.53 – 8.47 (m, 4H), 8.45 – 8.38 (m, 2H), 8.30 – 8.28 (m, 2H), 8.22 – 8.06 (m, 2H), 7.96 – 7.88 (m, 3H), 7.70 (s, 1H), 7.68 – 7.62 (m, 1H), 7.56 – 7.52 (m, 1H), 7.41–7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.26 – 7.21 (m, 2 H), GC-MS, m/z cacld for $C_{42}H_{25}BrN_4$, 664.13; found, 665.32.

4'-(5-bromo-3-ethyl-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-4-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (6). (5) (0.1423 g, 0.214 mmol), bromoethane (0.041 g, 0.369 mmol), NaH (0.021 g, 0.525 mmol) were dissolved in 10 mL of anhydrous DMF at room temperature for 10 minutes, then a solution of bromine ethane was added, dropwise. The mixture was then stirred 10 h at room temperature. The white powdery product was obtained to be 0.104 g (69.8%). ^{1}H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 8.55 – 8.35 (m, 6H), 8.29 – 8.24 (m, 2H), 8.18 – 8.01 (m, 2H), 7.95 – 7.83 (m, 3H), 7.72 (s, 1H), 7.61 – 7.56(m, 1H), 7.51 – 7.43 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 4H), 7.29 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 4.36 (q, *J* = 6.4Hz, 2H), 1.46 (t, *J* = 6.4Hz, 3H) MALDI-TOF, m/z cacld for $C_{44}H_{29}BrN_4$, 692.16; found, 693.22.

4'-(5-(2-(9H-carbazol-9-yl)phenyl)-3-ethyl-2-(pyridin-4-yl)-2,3-dihydro-1H-benzo[e]indol-1-yl)-4-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (CzCNBPyIo). The title compound was synthesized according to method (conditions: (1)) as a yellowish powder in 24.1% yield (0.024 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.57 – 8.43 (m,

4H), 8.41 – 8.35 (m, 2H), 8.31 – 8.27 (m, 6H), 8.21 – 8.11 (m, 6H), 7.93 – 7.81 (m, 3H), 7.77 – 7.69 (m, 4H), 7.62 – 7.57(m, 1H), 7.50 – 7.41 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 4H), 7.26 – 7.20 (s, 1H), 7.19 – 7.11 (m, 2H), 3.65 (q, *J* = 7.2Hz, 2H), 1.35 (t, *J* = 7.2Hz, 3H). MALDI-TOF, m/z cacld for $C_{62}H_{41}N_5$, 855.34; found, 855.31.

4'-(5-(3-(9H-carbazol-9-yl)phenyl)-3-ethyl-2-(pyridin-4-yl)-2,3-dihydro-1H-benzo[e]indol-1-yl)-4-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (CzCNBPyIm).

The title compound was synthesized according to method (conditions (1)) as a yellowish powder in 29.8% yield (0.042 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.17 – 8.11 (m, 6H), 8.0 – 7.98(s, 1H), 7.84 (m, 8H), 7.79 – 7.77 (s, 1H), 7.73 – 7.71 (m, 3H), 7.68 – 7.41 (m, 6H), 7.37 – 7.20 (m, 10H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). MALDI-TOF, m/z cacld for $C_{62}H_{41}N_5$, 855.34; found, 855.62.

4'-(5-(4-(9H-carbazol-9-yl)phenyl)-3-ethyl-2-(pyridin-4-yl)-2,3-dihydro-1H-benzo[e]indol-1-yl)-4-(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (CzCNBPyIp).

The title compound was synthesized according to method (conditions: (1)) as a yellowish powder in 49.3% yield (0.120 g). ^{1}H NMR (400 MHz, DMSO) δ 8.73 (s, 1H), 8.60 (dd, *J* = 14.4, 3.6 Hz, 2H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.28 –8.15 (m, 3H), 8.10 – 7.92 (m, 4H), 7.92 – 7.75 (m, 6H), 7.59 (s, 1H), 7.59 – 7.22 (m, 18H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* =7.2Hz, 3H). MALDI-TOF, m/z cacld for $C_{62}H_{41}N_5$, 855.34; found, 855.57.

2-fluoro-5-(2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)benzonitrile (2a).

The title compound was synthesized according to method (i). Yield: 65%. ^{1}H NMR (400 MHz, DMSO-d6) δ 12.42 (s, 1H), 8.54 – 8.48 (m, 2H), 8.11 (s, 1H), 7.95 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.89 (ddd, *J* = 8.4, 5.2, 2.4 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.73 – 7.67 (m, 2H), 7.40 – 7.33 (m, 2H), 7.30 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.27 – 7.24 (m, 2H). GC-MS, m/z Cacld for $C_{24}H_{14}FN_3$, 363.40; found, 364.

5-(5-bromo-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-2-fluorobenzonitrile (2b).

The title compound was synthesized according to method (ii). ^{1}H NMR (400 MHz, DMSO-d6) δ 12.54 (s, 1H), 8.54 – 8.48 (m, 2H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 8.03 (d, *J* = 1.2 Hz, 1H), 7.87 (ddd, *J* = 7.6, 5.2, 2.4 Hz, 1H), 7.72 (t, *J* = 9.2 Hz, 1H), 7.50 (t, *J* = 7.6, 1.3 Hz, 1H), 7.44 (s, 1H), 7.39 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.24 – 7.21 (m, 2H). GC-MS, m/z cacld for $C_{24}H_{13}BrFN_3$, 442.29; found, 442.497.

5-(5-bromo-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-2-(9H-carbazol-9-yl)benzonitrile (2c). The title compound was synthesized according to method (iii). Yield: 46%. ^{1}H NMR (400 MHz, d-DMSO) δ ^{1}H NMR (400 MHz, DMSO-d6) δ 12.63 (s, 1H), 8.63 – 8.58 (m, 2H), 8.35 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 2H), 8.26 (dd, *J* = 7.6, 2.0 Hz, 1H), 8.08 (d, *J* = 2.0 Hz, 1H), 8.05 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 – 7.50 (m, 4H), 7.46 (s, 1H), 7.41 – 7.33 (m, 5H). MA LDI-TOF, m/z cacld for $C_{36}H_{21}BrN_4$, 589.50; found, 588.716.

5-(5-(4-(9H-carbazol-9-yl)phenyl)-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-2-(9H-carbazol-9-yl)benzonitrile (2d). The title compound was synthesized according to method (iv). Yield: 60%. ^{1}H NMR (400 MHz, d-DMSO) δ 12.62 (s, 1H), 8.64 – 8.59 (m, 2H), 8.39 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 2H), 8.31 – 8.27 (m, 2H), 8.10 (d, *J* = 2.0 Hz, 1H), 8.04 – 7.98 (m, 2H), 7.88 – 7.83 (m, 3H), 7.81 – 7.74 (m, 2H), 7.63 – 7.54 (m, 5H), 7.54 – 7.49 (m, 4H), 7.45 (s, 1H), 7.42 – 7.37 (m, 5H), 7.36 – 7.30 (m, 2H). MALDI-TOF, m/z cacld for $C_{54}H_{33}N_5$, 751.89; found, 752.067.

5-(5-(3-(9H-carbazol-9-yl)phenyl)-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-2-(9H-carbazol-9-yl)benzonitrile (2e). The title compound was synthesized according to method(v). Yield: 71%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.56 (s, 1H), 8.65 – 8.48 (m, 2H), 8.37 (s, 1H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.29 – 8.26 (m, 2H), 8.12 (d, *J* = 2.0 Hz, 1H), 8.05 – 7.93 (m, 2H), 7.86 - 7.81 (m, 3H), 7.76 – 7.69 (m, 2H), 7.64 (s, 1H), 7.59 – 7.52 (m, 4H), 7.48

– 7.40 (m, 4H), 7.38 (s, 1H) 7.36 – 7.31 (m, 5H), 7.28 – 7.21 (m, 2H). MALDI-TOF, m/z cacld for $C_{54}H_{33}N_5$, 751.89; found, 751.137.

5-(5-(4-(9H-carbazol-9-yl)phenyl)-3-ethyl-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-2-(9H-carbazol-9-yl)benzonitrile (CzCNPyIp).

The title compound was synthesized according to method (vi). Yield: 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.26 – 8.10 (m, 6H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 6.4, 3.4 Hz, 1H), 7.89 – 7.84 (m, 3H), 7.81 – 7.72 (m, 3H), 7.70 – 7.60 (m, 3H), 7.56 – 7.51 (m, 6H), 7.46(s, 1H), 7.42 – 7.37 (m, 3H), 7.30 (d, *J* = 5.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H). MALDI-TOF, m/z cacld for $C_{56}H_{37}N_5$, 779.50; found, 778.628.

5-(5-(3-(9H-carbazol-9-yl)phenyl)-3-ethyl-2-(pyridin-4-yl)-3H-benzo[e]indol-1-yl)-2-(9H-carbazol-9-yl)benzonitrile (CzCNPyIm).

The title compound was synthesized according to method (vi). Yield: 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.17 – 8.11 (m, 5H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.92 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.89 – 7.77 (m, 4H), 7.78 – 7.68 (m, 3H), 7.67 – 7.62 (m, 5H), 7.59 (s, 1H), 7.57 – 7.46 (m, 3H), 7.41 (s, 1H), 7.30 – 7.23 (m, 3H), 7.16 – 7.11 (m, 4H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2Hz,3H). MALDI-TOF, m/z cacld for $C_{56}H_{37}N_5$, 779.95; found, 779.076.

2. MALDI-TOF, NMR spectra and photophysical data

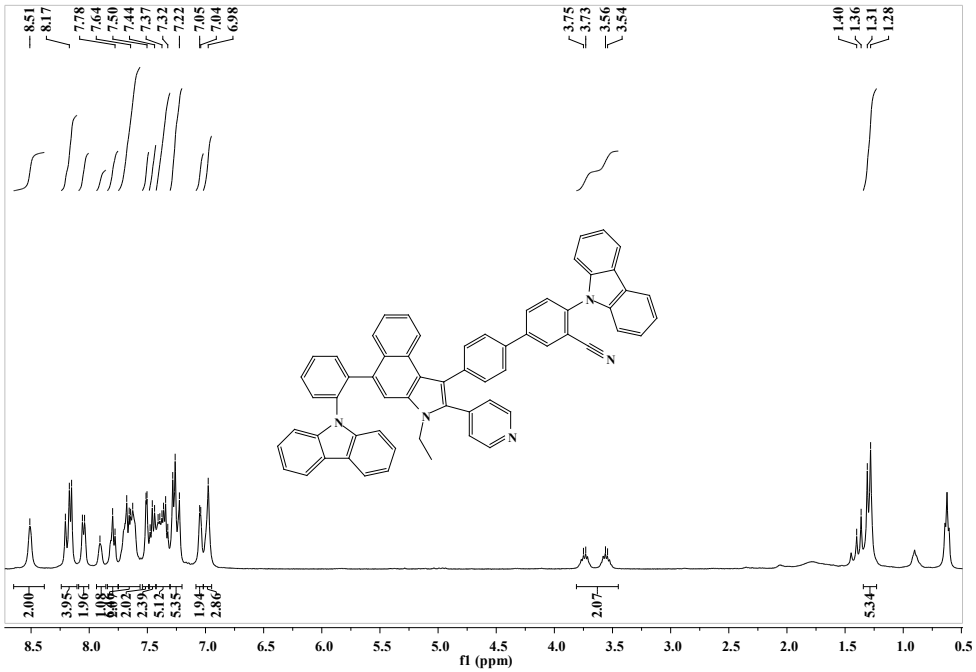


Figure S1. ^{1}H NMR spectra of **CzCNBPyIo.**

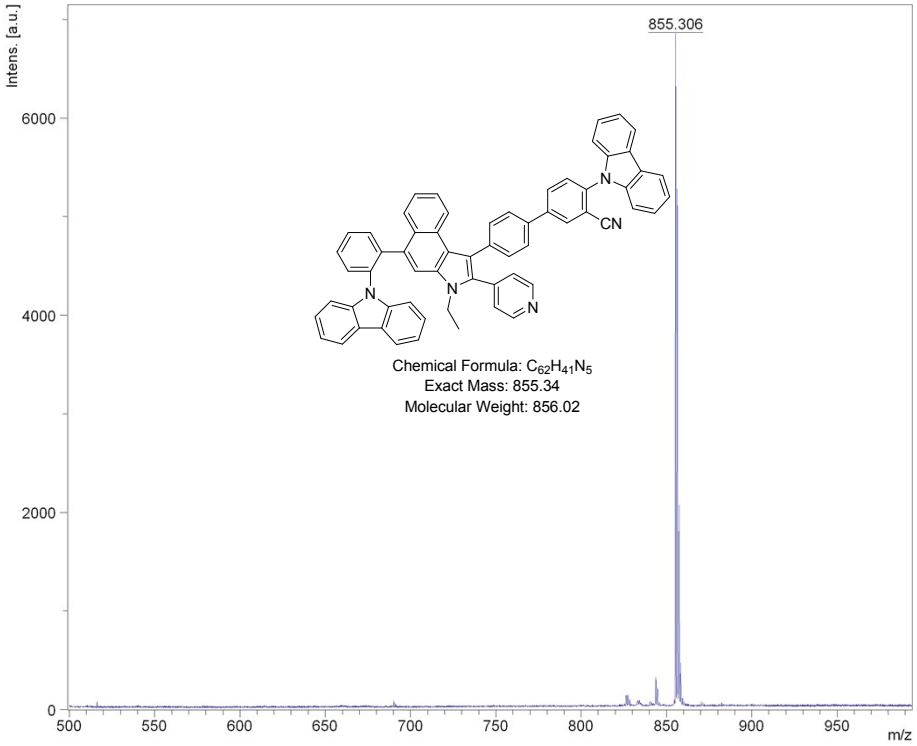


Figure S2. MALDI-TOF MS of **CzCNBPyIo.**

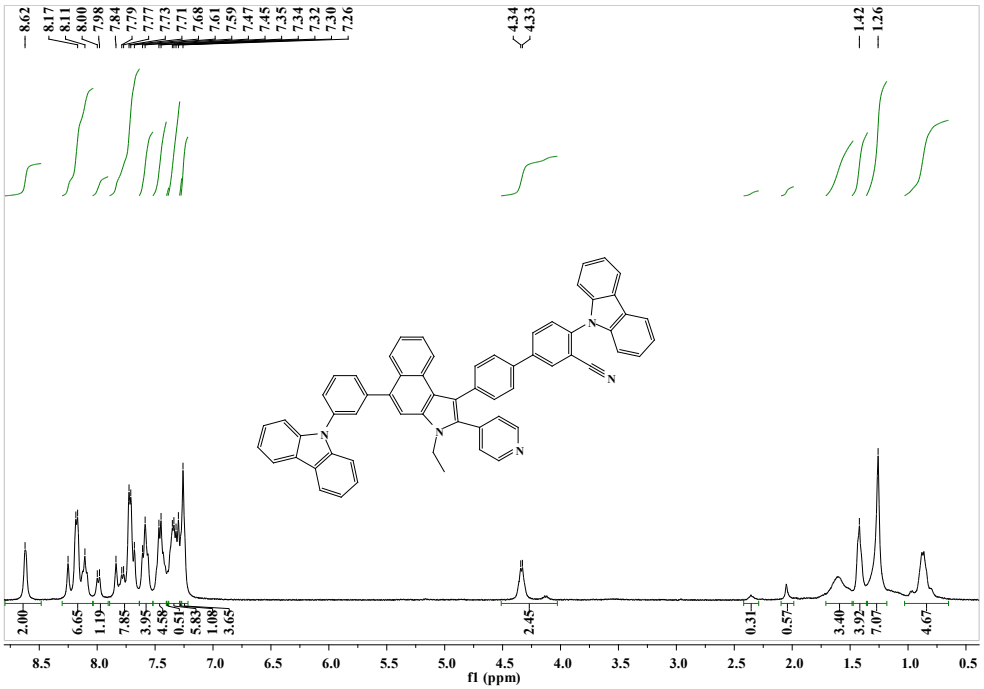


Figure S3. ^{1}H NMR spectra of **CzCNBPyIm.**

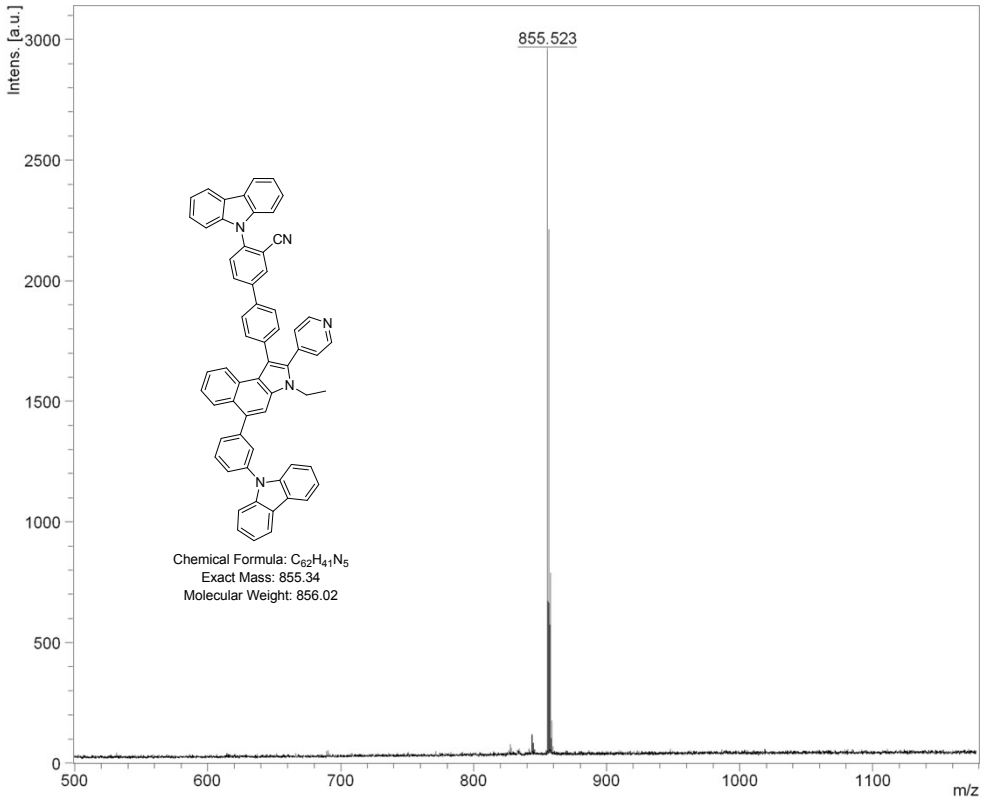


Figure S4. MALDI-TOF MS of **CzCNBPyIm.**

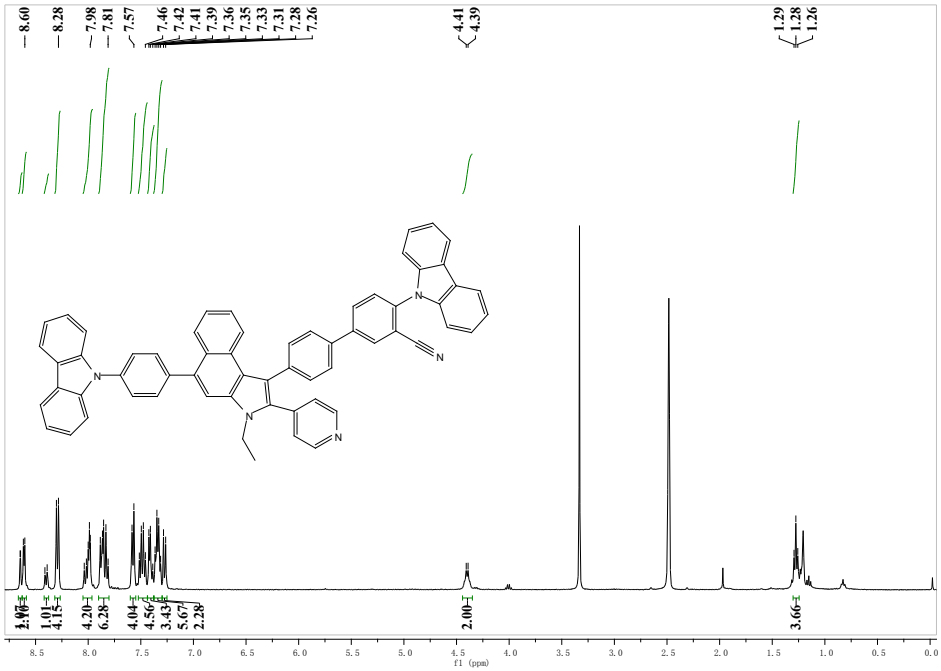


Figure S5. ^{1}H NMR spectra of **CzCNBPyIp.**

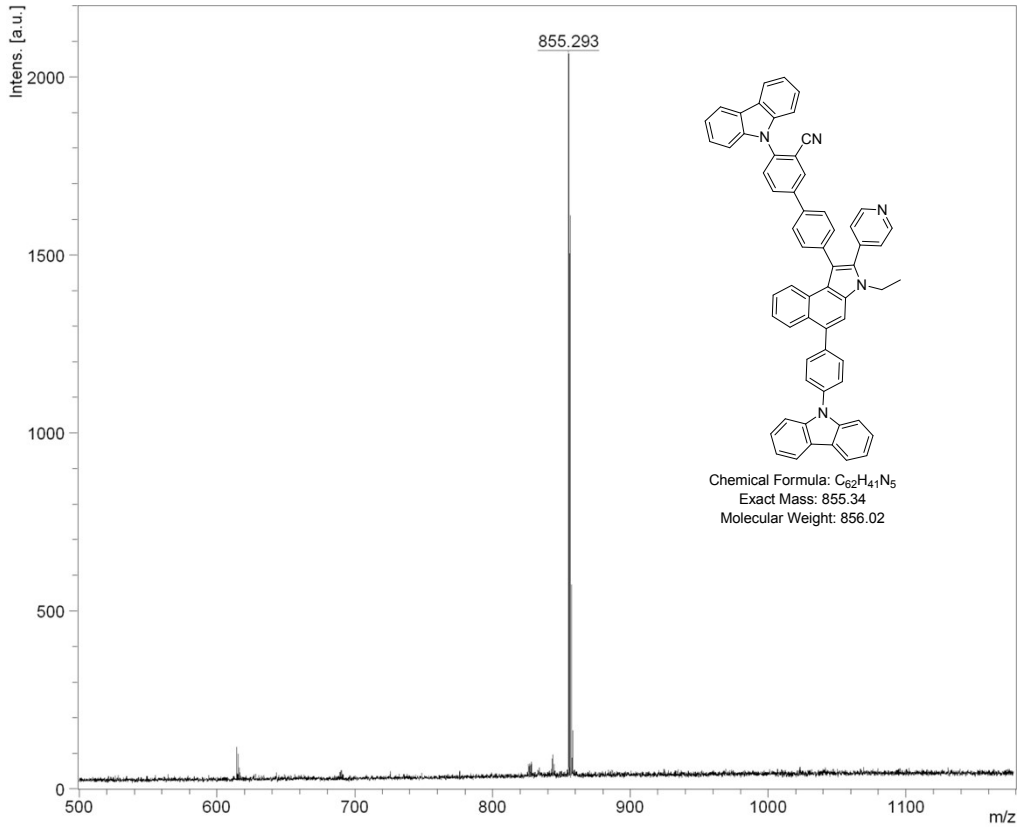


Figure S6. MALDI-TOF MS of **CzCNBPyIp.**

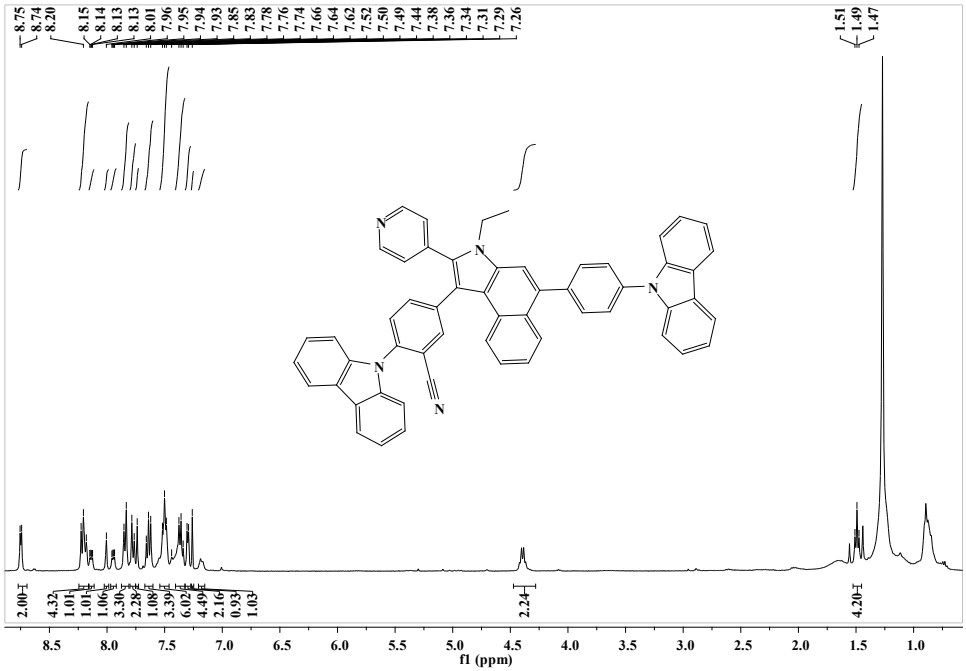


Figure S7. ^{1}H NMR spectra of **CzCNPyIp.**

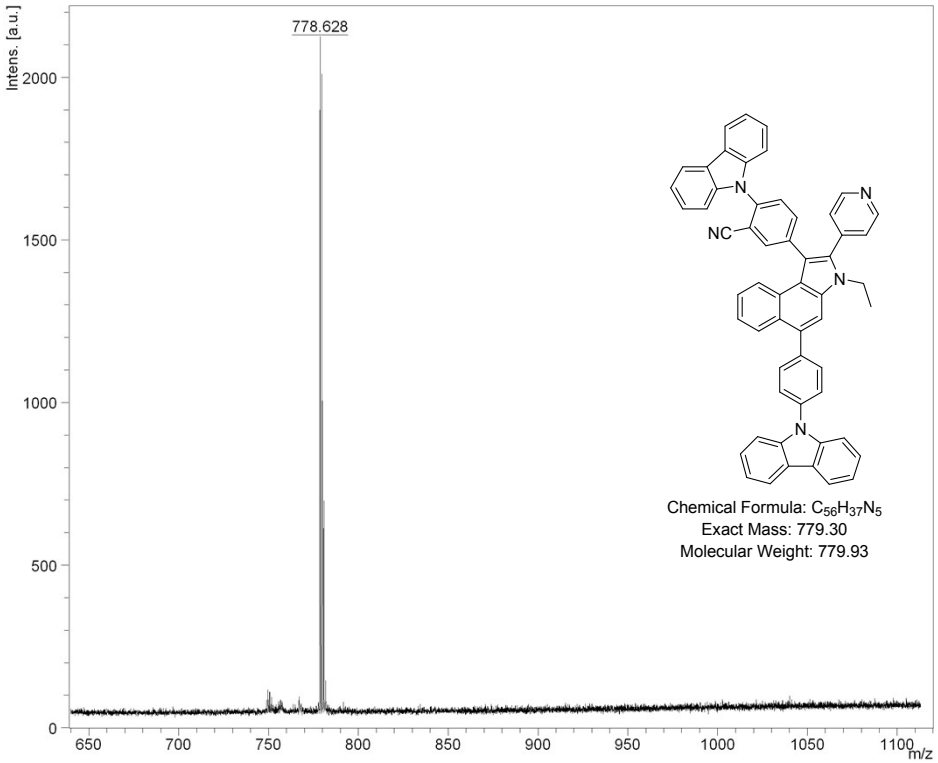


Figure S8. MALDI-TOF MS of **CzCNPyIp.**

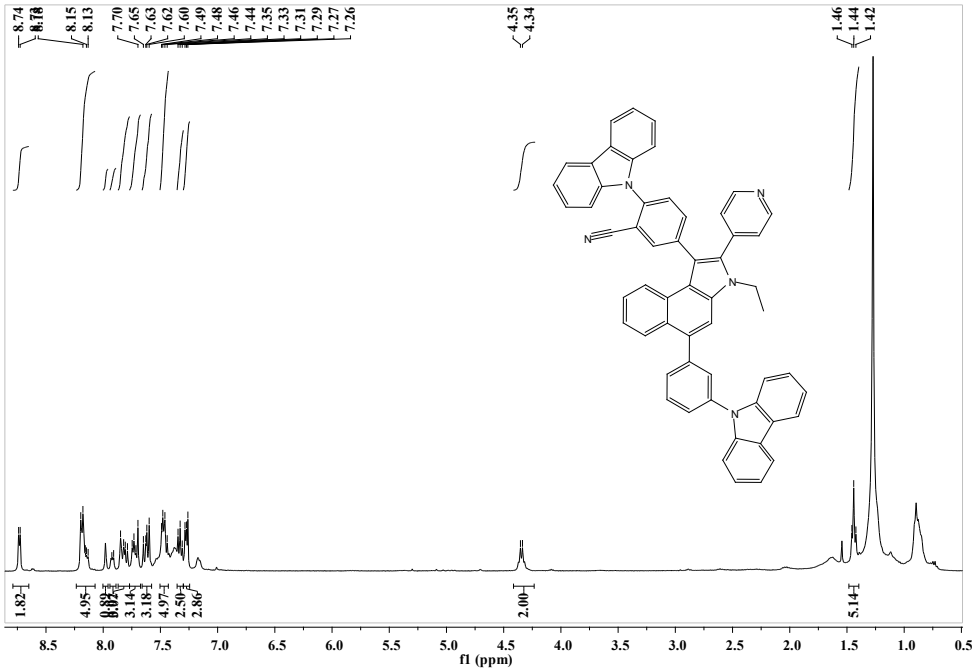


Figure S9. ^{1}H NMR spectra of **CzCNPyIm.**

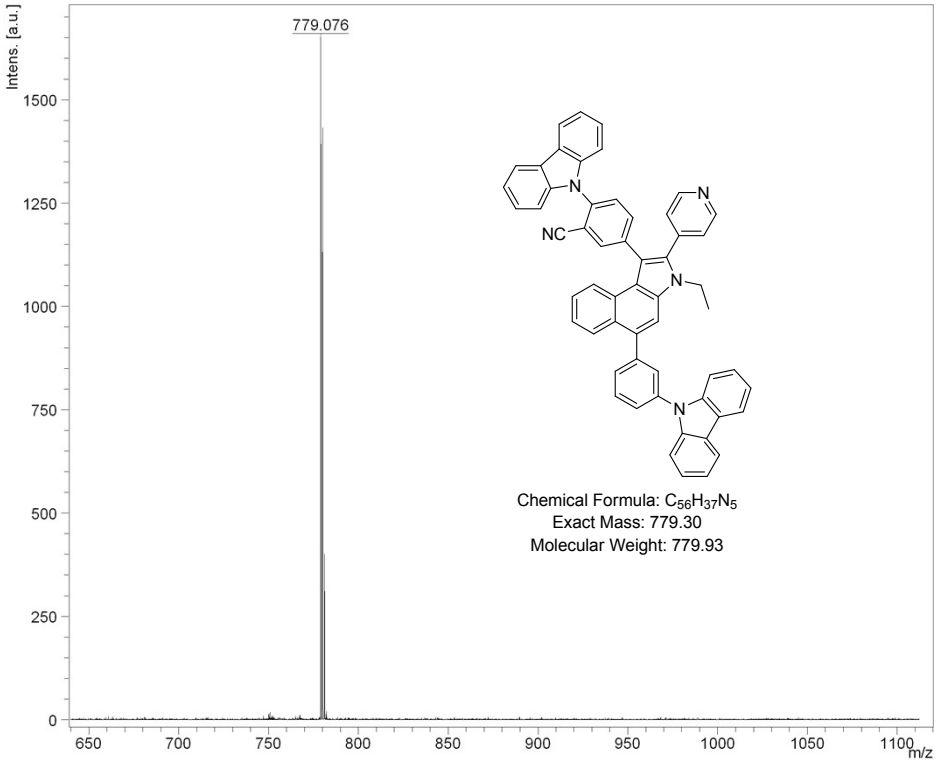


Figure S10. MALDI-TOF MS of **CzCNPyIm.**

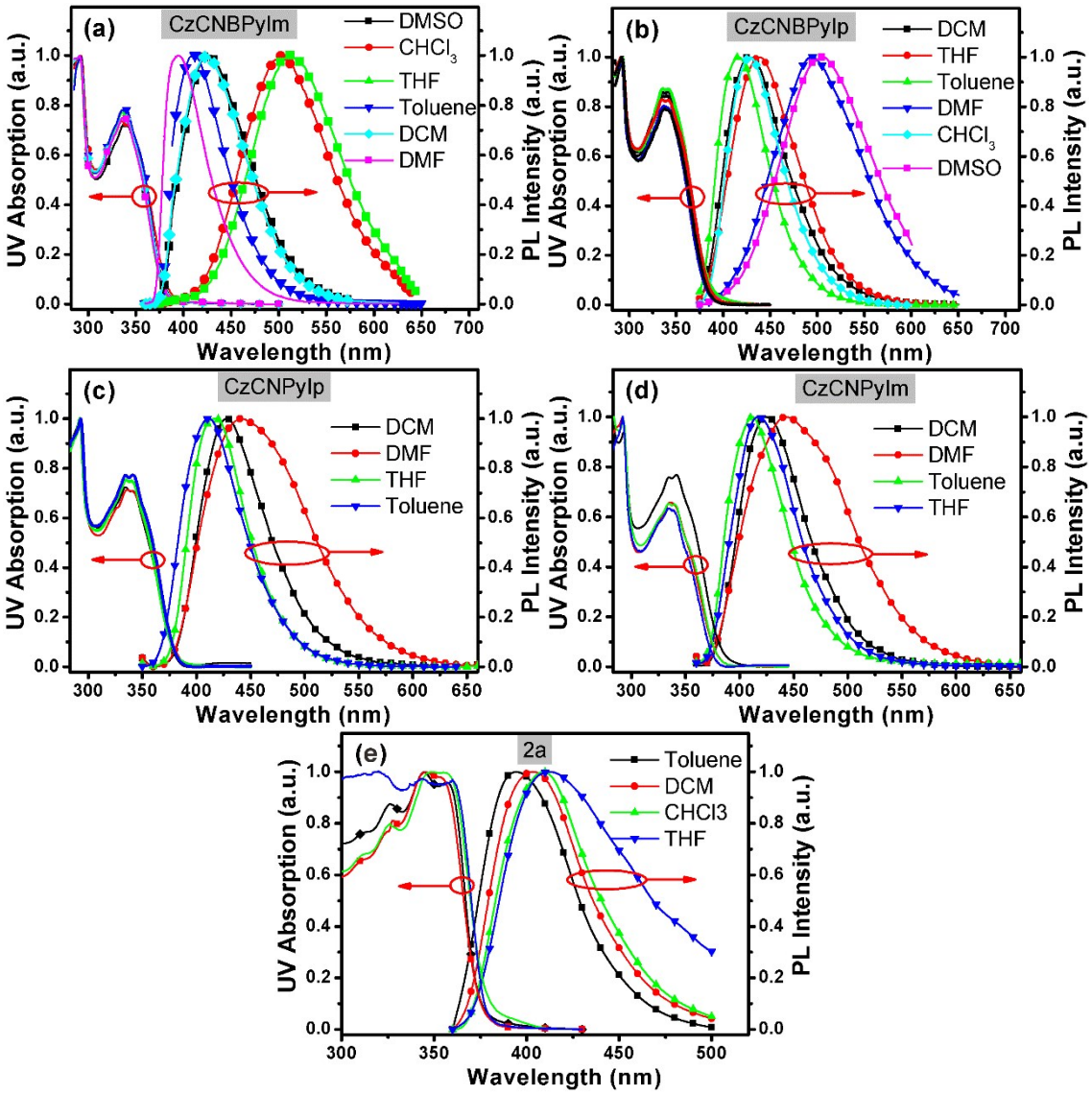


Figure S11. UV-vis absorption and PL spectra of CzCNBPyIm (a), CzCNBPyIp (b), CzCNPyIp (c), CzCNPyIm (d) and **2a** (e) at room-temperature in dilute solution (1×10^{-5} M).

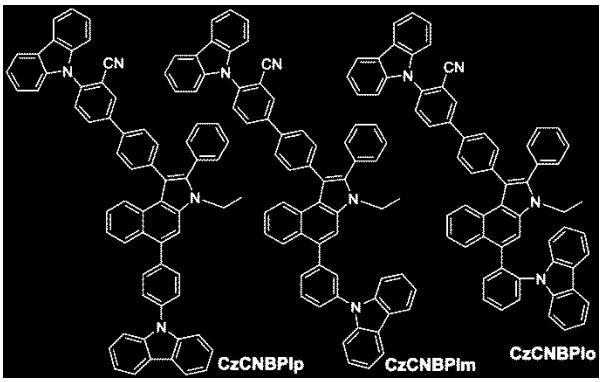


Figure S12. Molecular structure of CzCNBPIp, CzCNBPIm, and CzCNBPIo.

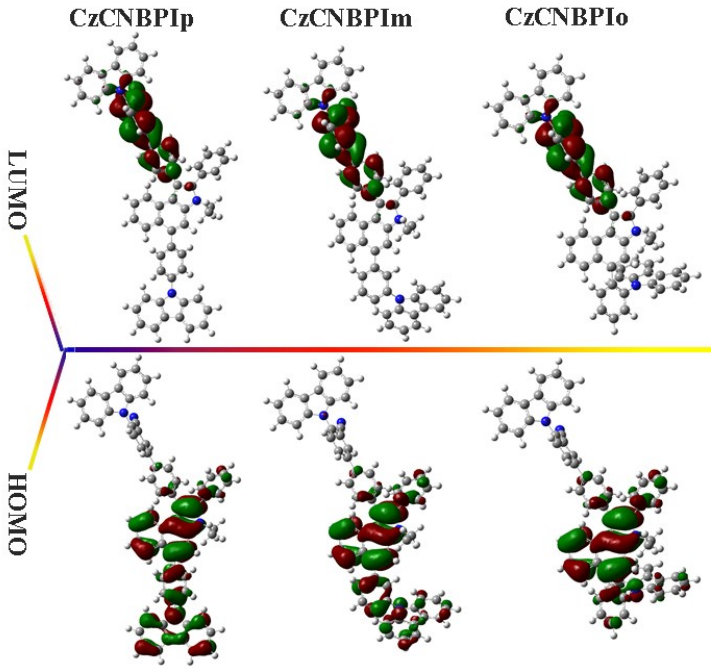


Figure S13. HOMO and LUMO distribution on CzCNBPIp, CzCNBPIm, and CzCNBPIo molecules.

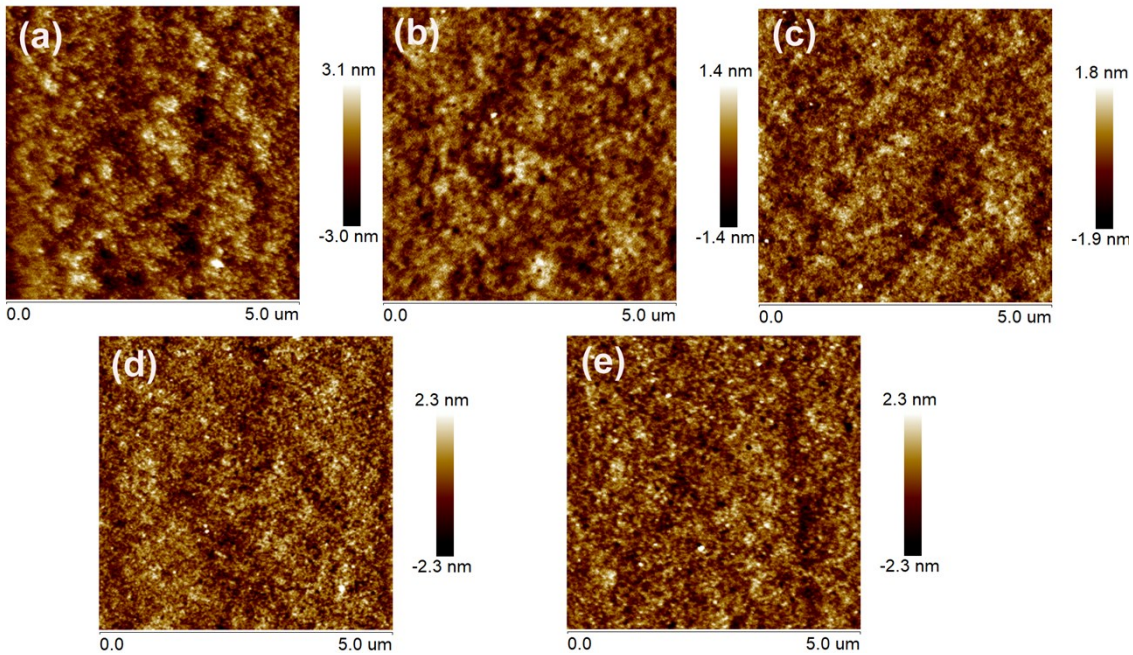


Figure S14. AFM images of CzCNPylm (a), CzCNPylp (b), CzCNBPylm (c), CzCNBPylp (d), and CzCNBPylo (e) thin films from chloroform solution on ITO/PEDOT:PSS substrate.

Table S1. DFT calculation results of **CzCNBPyIo, CzCNBPyIm, CzCNBPyIp, CzCNBPIo, CzCNBPIm** and **CzCNBPIp.**

Samples	CzCNBPyIo	CzCNBPyIm	CzCNBPyIp	CzCNBPIo	CzCNBPIm	CzCNBPIp
HOMO (eV)	-5.32	-5.41	-5.32	-5.15	-5.22	-5.18
LUMO (eV)	-1.70	-1.73	-1.74	-1.63	-1.67	-1.67
Eg (eV)	3.63	3.68	3.57	3.52	3.56	3.51

[a] Measured in film. [b] Measured in dilute toluene solution. [c] Estimated from the onset of oxide/reduction potentials. [d] Measured in film at 77 K.