Supporting Information

Efficient Small Molecule Photovoltaic Donor Based on 2,3-Diphenyl-Substituted Quinoxaline Core for Solution-Processed Organic Solar Cells

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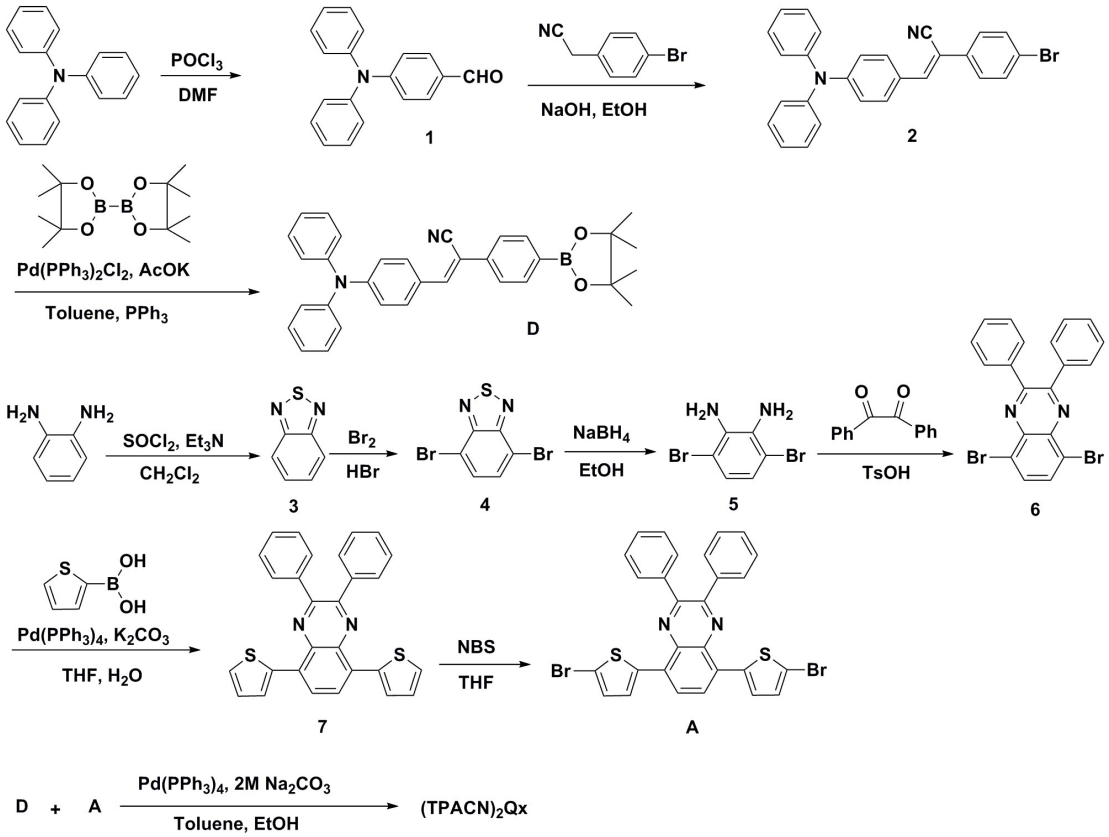
1. Synthesis

1.1 Reagents and Materials

Tetrahydrofuran (THF) and toluene were dried by distillation from metallic sodium/benzophenone under N_2 atmosphere. Other chemicals were commercially purchased and used without further purification. All column chromatographic separations were carried out on 200-300 mesh silica gel.

1.2 Synthetic procedures



Scheme S1 Synthetic route of **$(TPACN)_2Qx$**

4-(diphenylamino)benzaldehyde (1) [1] $POCl_3$ (1.5 mL) was added dropwise to anhydrous DMF (15 mL) at 0 ℃ and stirred for 1 h in a 100 mL flask. Then triphenylamine (3.68 g, 15 mmol) was added to the solution and the mixture was stirred at 70 °C for 2 h. After being cooled to room temperature, the reaction solution was poured into 150 mL ice water and then neutralized with 2M aqueous NaOH. The crude product was collected by filtration and purified by silica column chromatography，eluting with petroleum ether/ethyl acetate (v:v, 20:1) to afford a white solid **1** in a yield of 94% (3.84 g). M.p.: 128-130 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 9.81 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 8.0 Hz, 4H), 7.18-7.15 (m, 6H), 7.01 (d, J = 8.8 Hz, 2H).

2-(4-bromophenyl)-3-[4-(diphenylamino)phenyl]-acrylonitrile (2) [2] Compound

1 (0.81 g, 3.0 mmol) and 4-bromophenyl acetonitrile (0.69 g, 3.5 mmol) was added to ethanol (50 mL) in a 100 mL three neck flask. Then a solution of NaOH (0.14 g, 3.5 mmol) in 5 mL EtOH was added dropwise and the mixture was stirred at room temperature for 40 h. The crude residue was filtered and washed with ethanol for 3 times. A yellow powder compound **2** was obtained in a yield of 91% (1.23 g). M.p.: 163-164 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.77 (d, J = 8.8 Hz, 2H), 7.56-7.53 (m, 4H), 7.40 (s, 1H), 7.34-7.30 (m, 4H), 7.17-7.11 (m, 6H), 7.04 (d, J = 8.8 Hz, 2H).

2-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)phenyl]-3-[4-(diphenylamino)phenyl]-acrylonitrile (D) [2] A mixture of compound **2** (0.90 g, 2.0 mmol), bis(pinacolato)diborane (0.56 g, 2.2 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), PPh_3 (53 mg, 0.2 mmol) and KOAc (0.78 g, 8.0 mmol) in distilled toluene (20 mL) was refluxed at 110 °C under nitrogen atmosphere for 24 h. After being cooled to room temperature, the mixture was poured into water (100 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography，eluting with petroleum ether/ethyl acetate (v:v, 5:1) to obtain a yellow powder solid **D** in a yield of 81% (0.81g). M.p.: 173-176 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.48(s, 1H), 7.34-7.30 (m, 4H), 7.17-7.10 (m, 6H), 7.05 (d, J = 8.9 Hz, 2H), 1.36 (s, 12H).

2,1,3-Benzothiadiazole (3) [2] Thionyl chloride (8.25g, 70 mmol) was added dropwise slowly to the solution of 1,2-benzenediamine (5.0 g, 46.3 mmol) and triethylamine (18.7 g, 185.0 mmol) in dichloromethane (200 mL) at room temperature and the mixture was refluxed for 4 h. After being cooled to room temperature, the solvent was evaporated and water (350 mL) was added. Concentrated HCl was added to the mixture till pH = 2. The crude product was purified by steam distillation following addition of water to the mixture. The steam distilled mixture was extracted with dichloromethane (3 × 100 ml) and dried over Na_2SO_4. The solvent was removed to afford a pale yellow solid compound **3** in a yield of 82% (5.17 g). M.p.: 42-44 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 2H), 7.60 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 2H).

4,7-Dibromo-2,1,3-benzothiadiazole (4) [2] To a stirred solution of compound **3** (10.0 g, 73.43 mmol) in 48% hydrobromic acid (150 mL, 1.32 mol) at room temperature under argon, a solution of Br_2 (7.49 mL, 220.29 mmol) in 48% hydrobromic acid (100 mL, 0.88 mol) was added dropwise very slowly. After being stirred at 100 °C for 6 h, the reaction mixture was cooled to room temperature and neutralized using saturated aqueous sodium bisulfate. The solid was collected by filtration, washed with distilled water followed by cold ether, and dried in vacuum oven. An ivory crystal compound **4** in a yield of 92% (20.05 g) was afforded. M.p.: 190-191 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.73 (s, 2H).

3,6-Dibromo-1,2-benzenediamine (5) [3] To a stirred solution of compound **4** (3.5 g, 11.91 mmol) in ethyl alcohol (150 mL) at 0 °C under nitrogen, sodium borohydride (8.11 g, 214.31 mmol) was added portion-wise. After being stirred at 0 °C for 10 min,

the reaction mixture was stirred at room temperature for 3 h. After removing the solvent under reduced pressure, the residue was treated with distilled water (100 mL). The mixture was extracted with ethyl acetate (3 × 30 mL), the combined organic layers were dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 5:1) to give an ivory solid compound **5** in a yield of 96% (3.05 g). M.p.: 103-107°C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 6.85 (s, 2H), 3.89 (s, 4H).

5,8-Dibromo-2,3-diphenylquinoxaline (6) [4] A 50 mL flask was charged with benzil (420 mg, 2 mmol), compoud **5** (585 mg, 2.2 mmol) and *p*-toluenesulfonic acid (34 mg, 0.20 mmol) in $CHCl_3$ (20 mL). The reaction mixture was stirred under reflux for 12 h. After being cooled to room temperature, the mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL), and then the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (v:v, 30:1) to give an offwhite solid **6** in a yield of 96% (845 mg). M.p.: 215-216 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.91 (s, 2H), 7.67-7.64 (m, 4H), 7.43-7.34 (m, 6H).

2,3-Diphenyl-5,8-di(thiophen-2-yl)quinoxaline (7) [4] A 50 mL three-necked round-bottomed flask was charged with compound **6** (440 mg, 1.0 mmol), thiophen-2-ylboronic acid (310 mg, 2.4 mmol), K_2CO_3 (690 mg, 5 mmol) and $Pd(PPh_3)_4$ (120 mg, 0.1 mmol) in THF (10 ml), H_2O (2.5 mL) under nitrogen atmosphere. The mixture was refluxed at 70 °C for 12 h. After being cooled to room temperature, the solvent was evaporated and water (150 mL) was added, the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 5:1) to obtain a yellow powder solid **7** in a yield of 64% (285 mg). M.p.: 175-180°C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.14 (s, 2H), 7.87 (d, J = 3.6 Hz, 2H), 7.75-7.73 (m, 4H), 7.51 (d, J = 5.2 Hz, 2H), 7.39-7.36 (m, 6H), 7.19-7.17 (dd, J_1 = 4.8 Hz, J_2 = 4.0 Hz , 2H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) 151.72, 138.76, 138.70, 137.23, 131.29, 130.50, 129.01, 128.89, 128.24, 127.06, 126.63, 126.44. MALDI-TOF HRMS: 446.0894 [M^+] (calcd for $C_{28}H_{18}N_2S_2$: 446.0911).

5,8-Bis(5-bromothiophen-2-yl)-2,3-diphenylquinoxaline(A) [4] NBS (0.39 g, 2.2 mmol) was added slowly in the dark to a solution of compound **7** (0.67 g, 1.0 mmol) in THF (12 mL). The mixture was stirred for 3 h. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 5:1), then washed with hot methanol to yield a deep purple solid **A** in a yield of 80% (660 mg). M.p.: 203-207°C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.01 (s, 2H), 7.69-7.66 (m, 4H), 7.52 (d, J = 4.0 Hz 2H), 7.45-7.37 (m, 6H), 7.10 (d, J = 4.0 Hz 2H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) 152.20, 139.58, 138.19, 136.67, 130.63, 130.50, 129.23, 129.15, 128.32, 125.75, 125.63, 117.18. MALDI-TOF HRMS: 601.9139 [M^+] (calcd for $C_{28}H_{16}N_2S_2Br_2$: 601.9122).

2. ^{1}H-NMR and ^{13}C-NMR spectra

2.1 ^{1}H-NMR

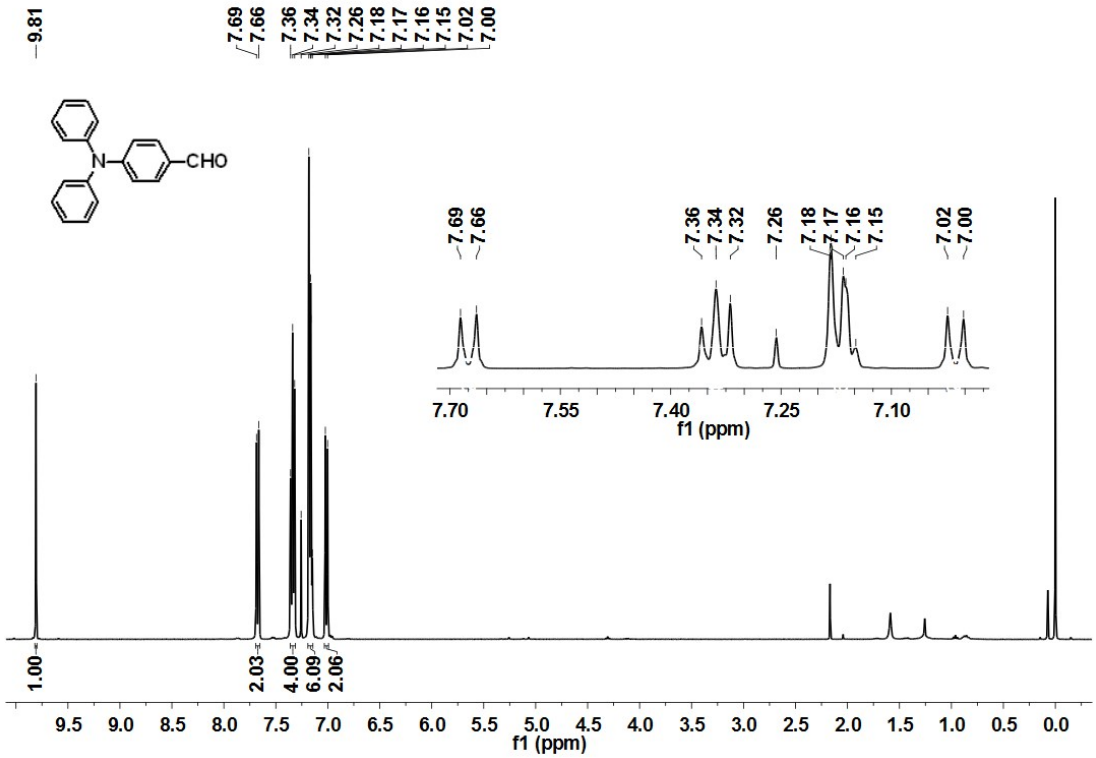


Fig. S1 ^{1}H-NMR spectrum of compound 1

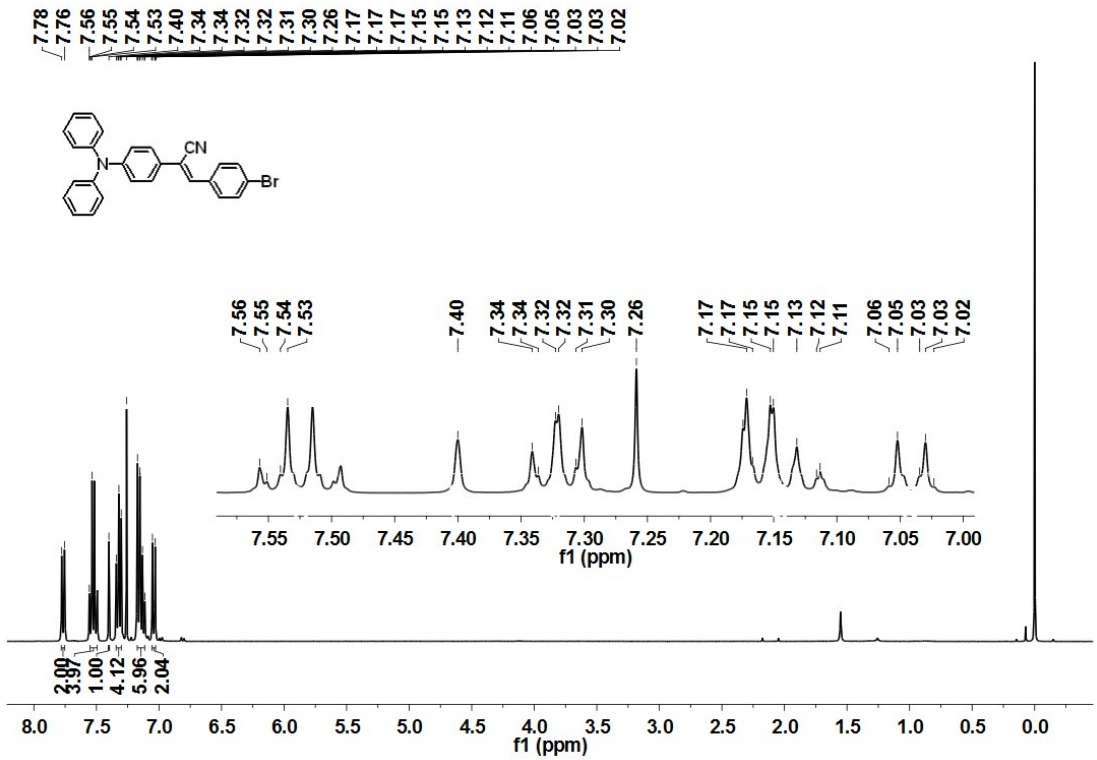


Fig. S2 ^{1}H-NMR spectrum of compound 2

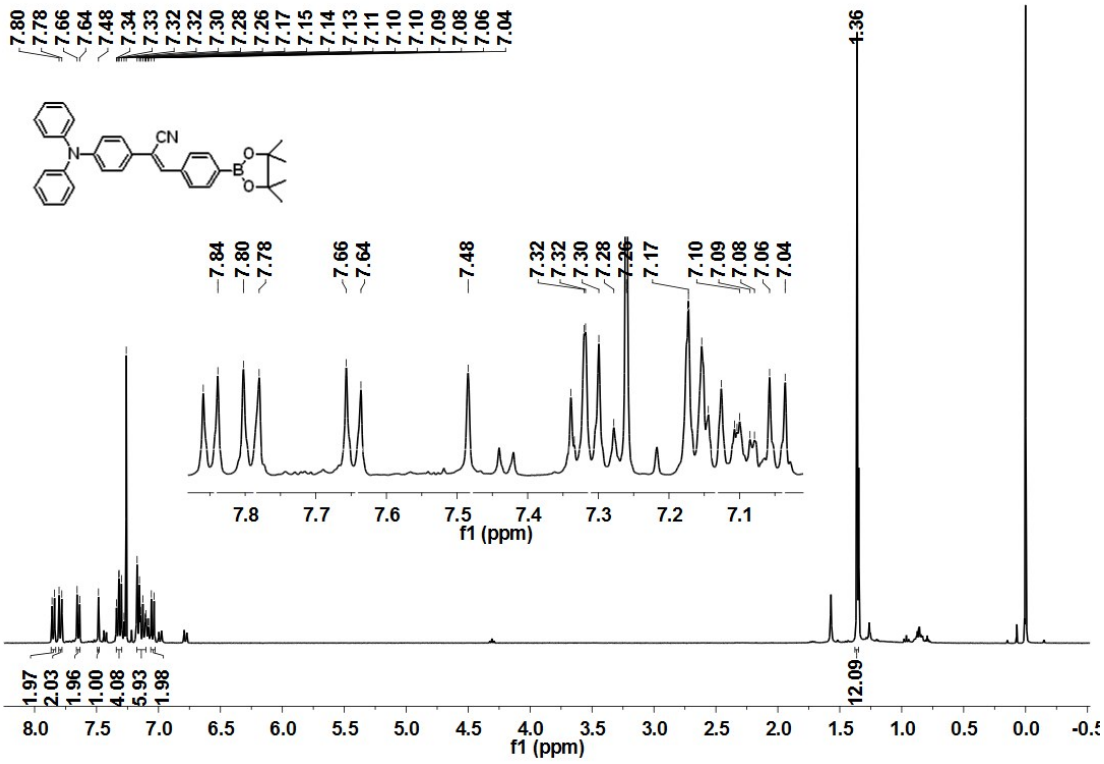


Fig. S3 ^{1}H-NMR spectrum of compound D

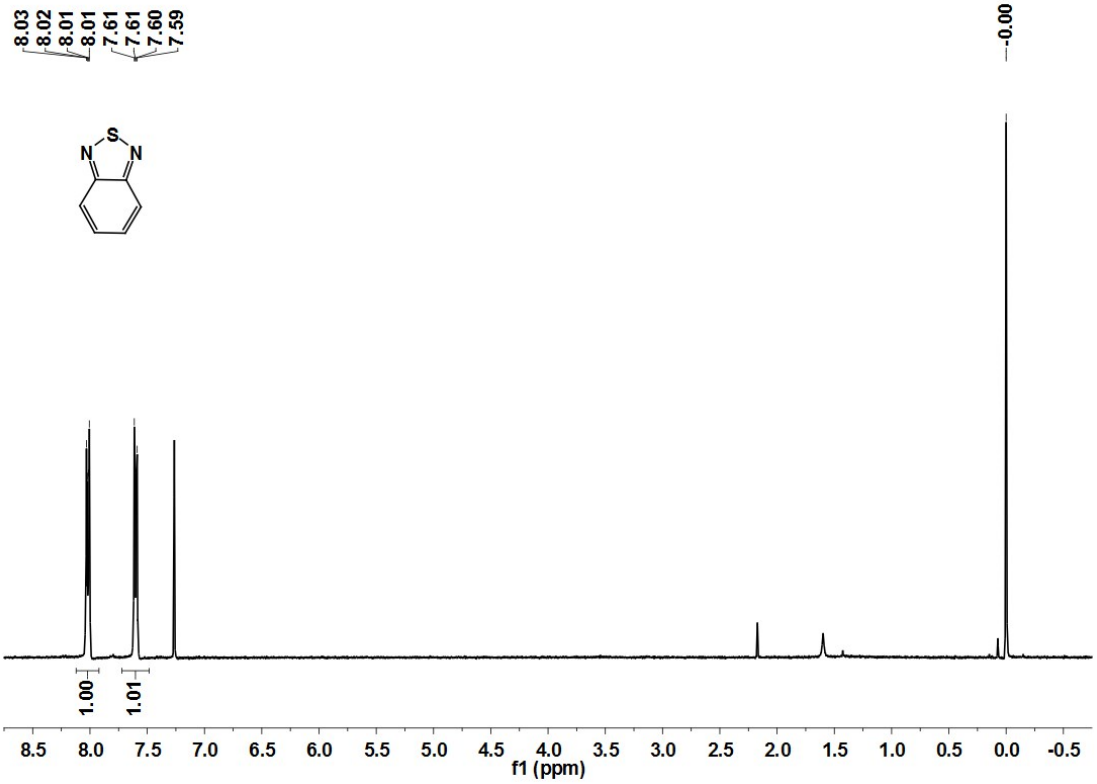


Fig. S4 ^{1}H-NMR spectrum of compound 3

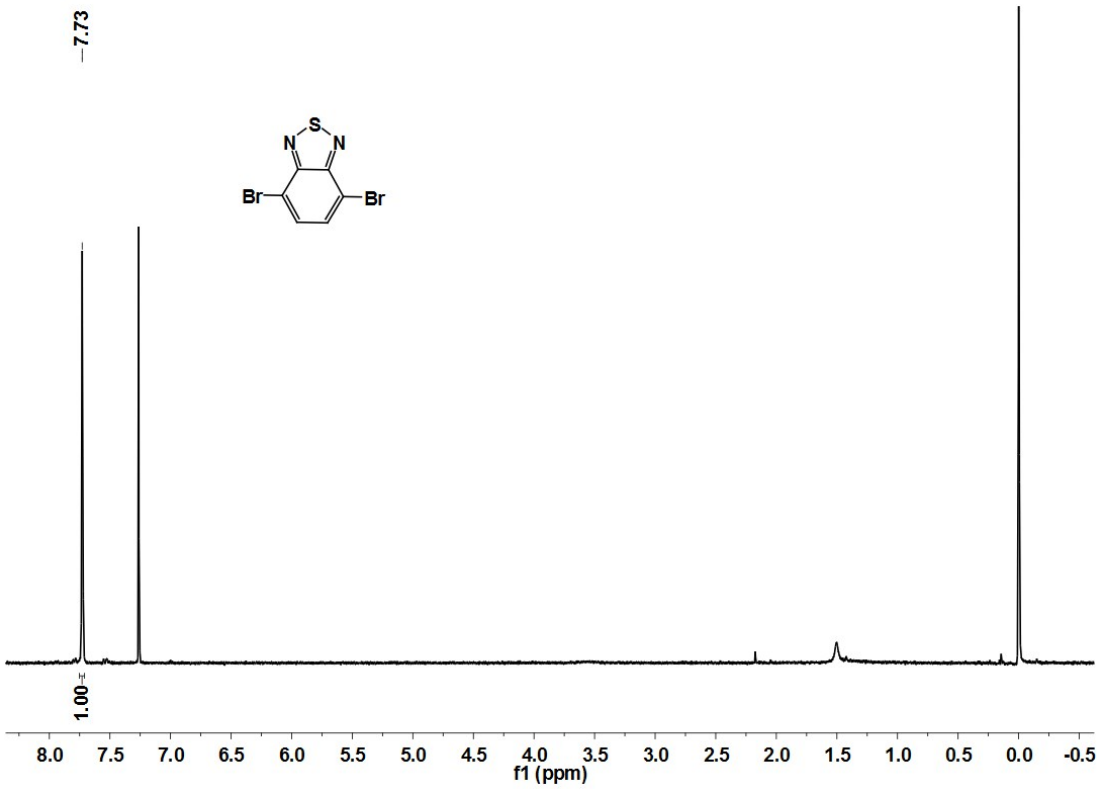


Fig. S5 ^{1}H-NMR spectrum of compound 4

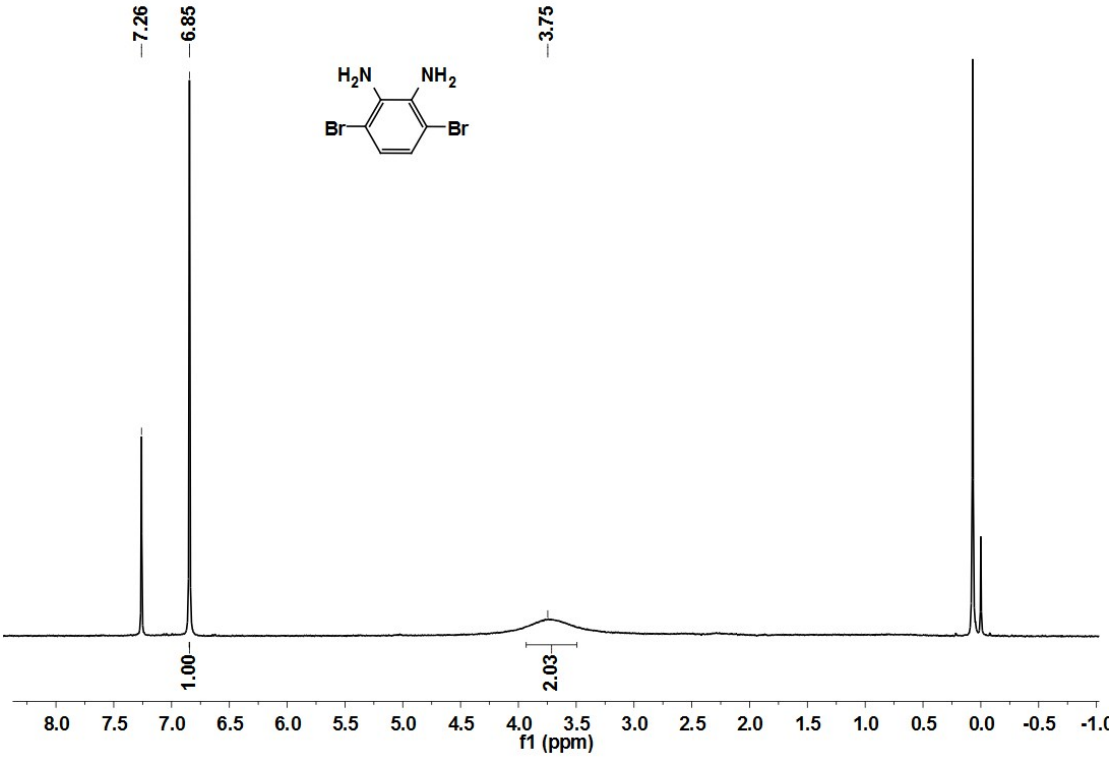


Fig. S6 ^{1}H-NMR spectrum of compound 5

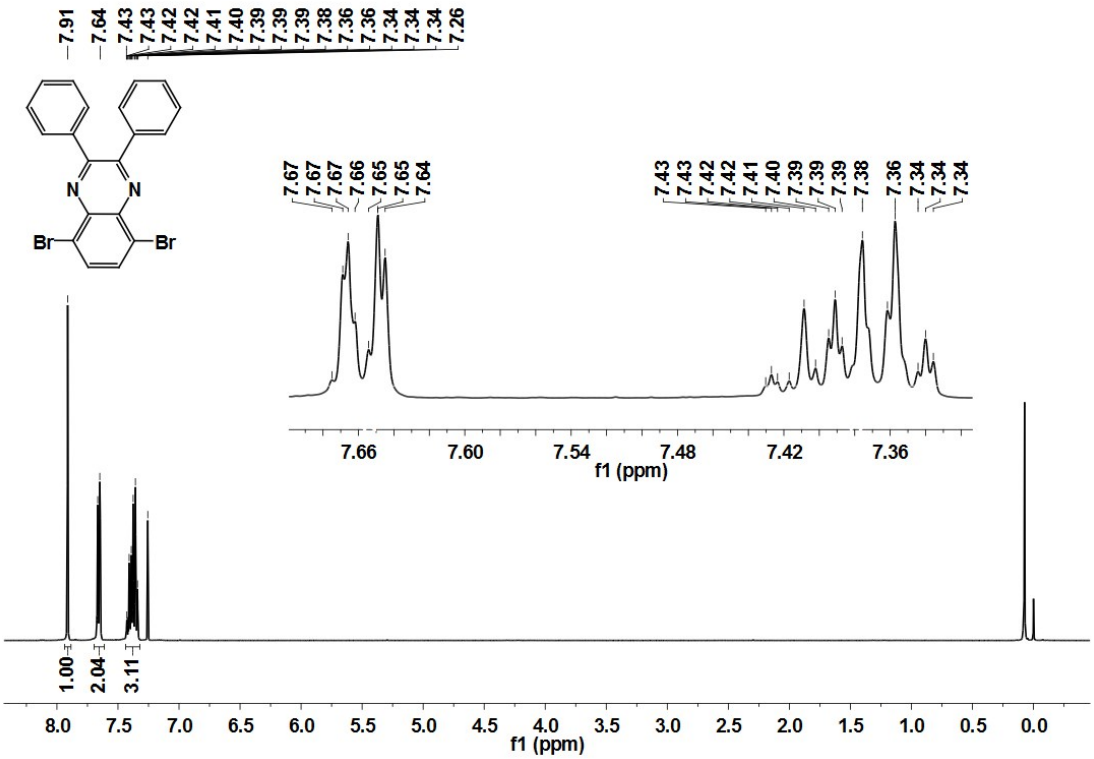


Fig. S7 ^{1}H-NMR spectrum of compound 6

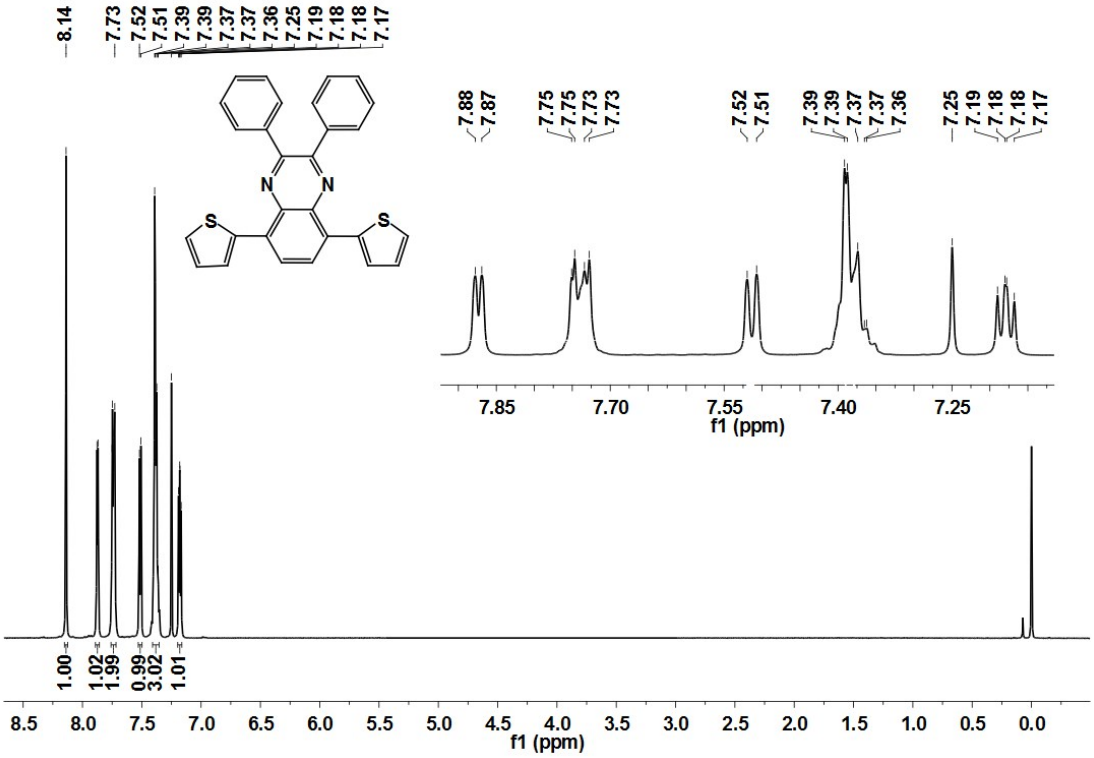


Fig. S8 ^{1}H-NMR spectrum of compound 7

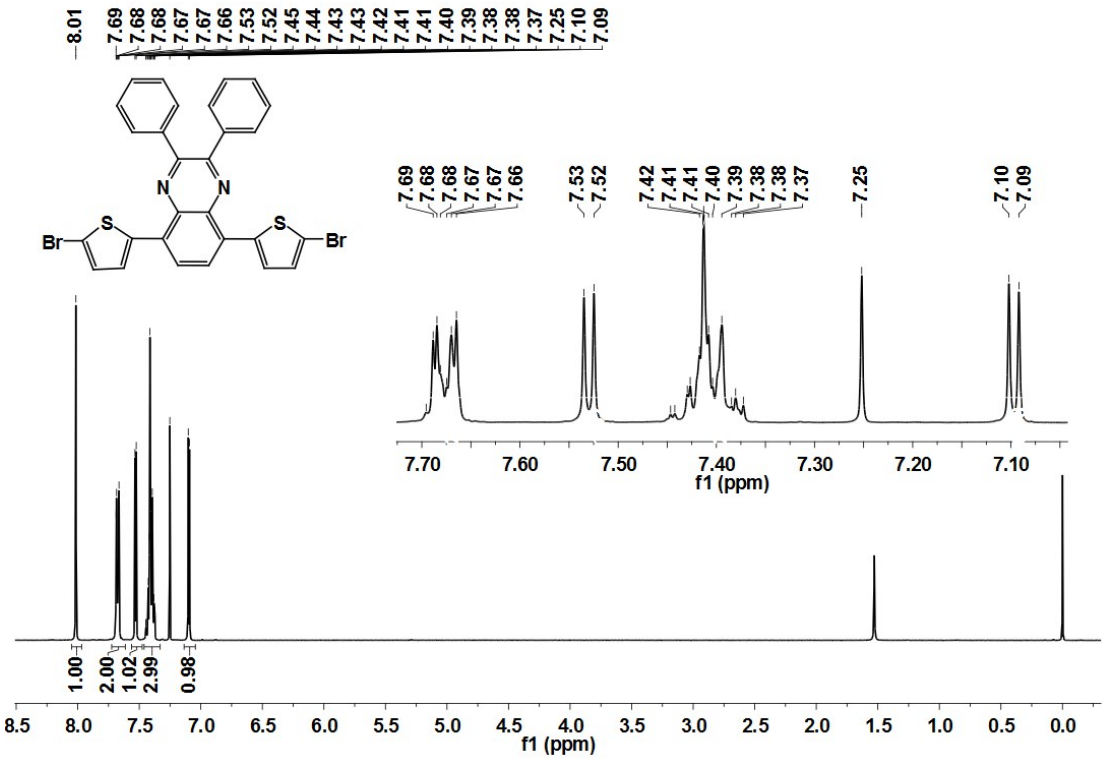


Fig. S9 [1]H-NMR spectrum of compound A

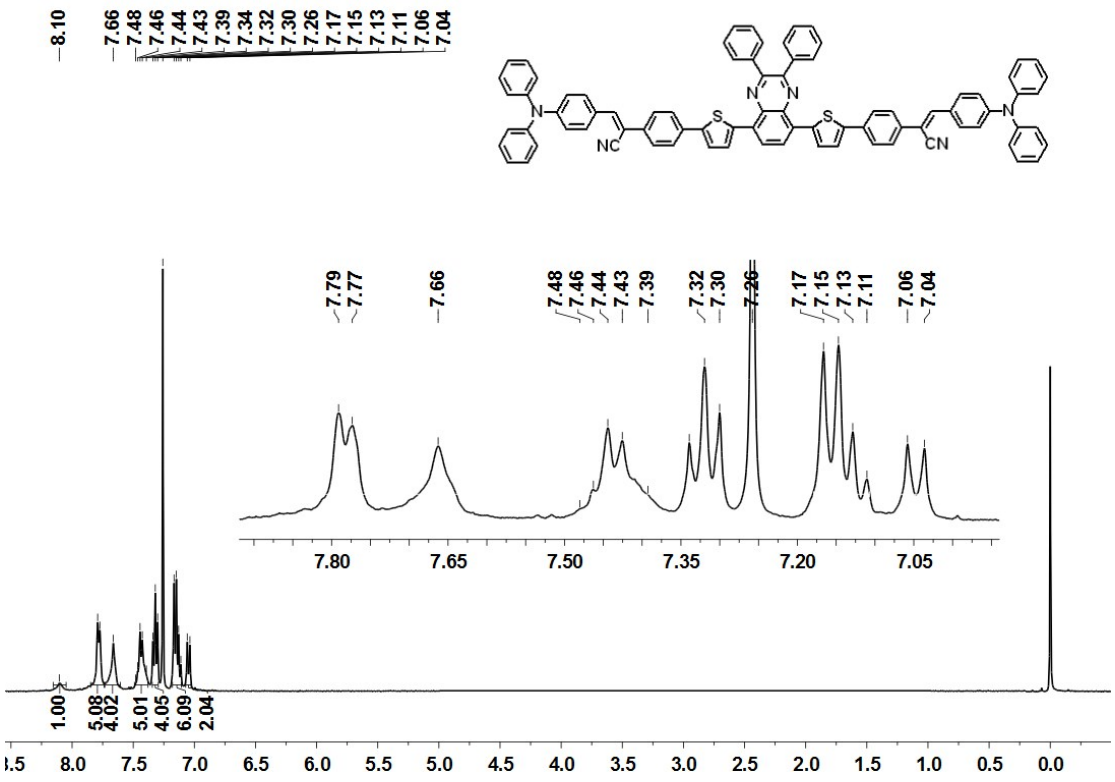


Fig. S10 [1]H-NMR spectrum of **$(TPACN)_2Qx$**

2.2 ^{13}C-NMR

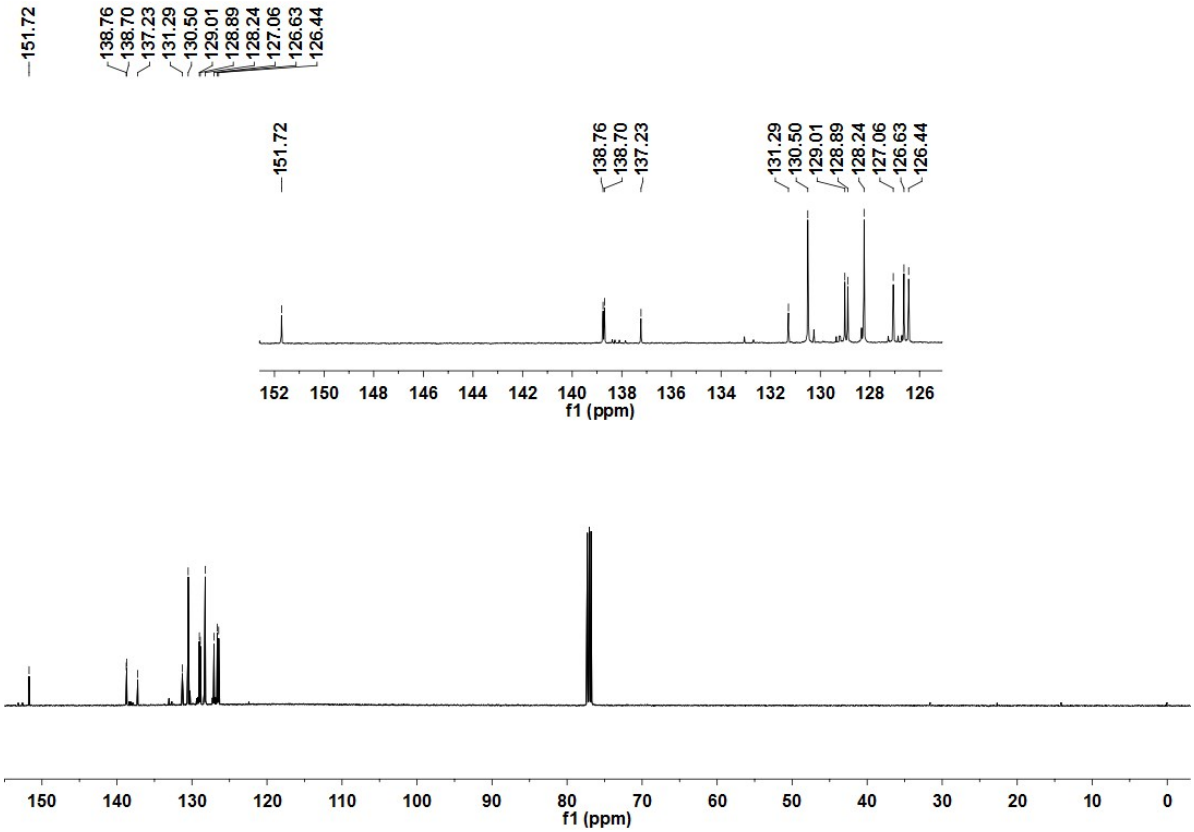


Fig. S11 ^{13}C-NMR spectrum of compound 7

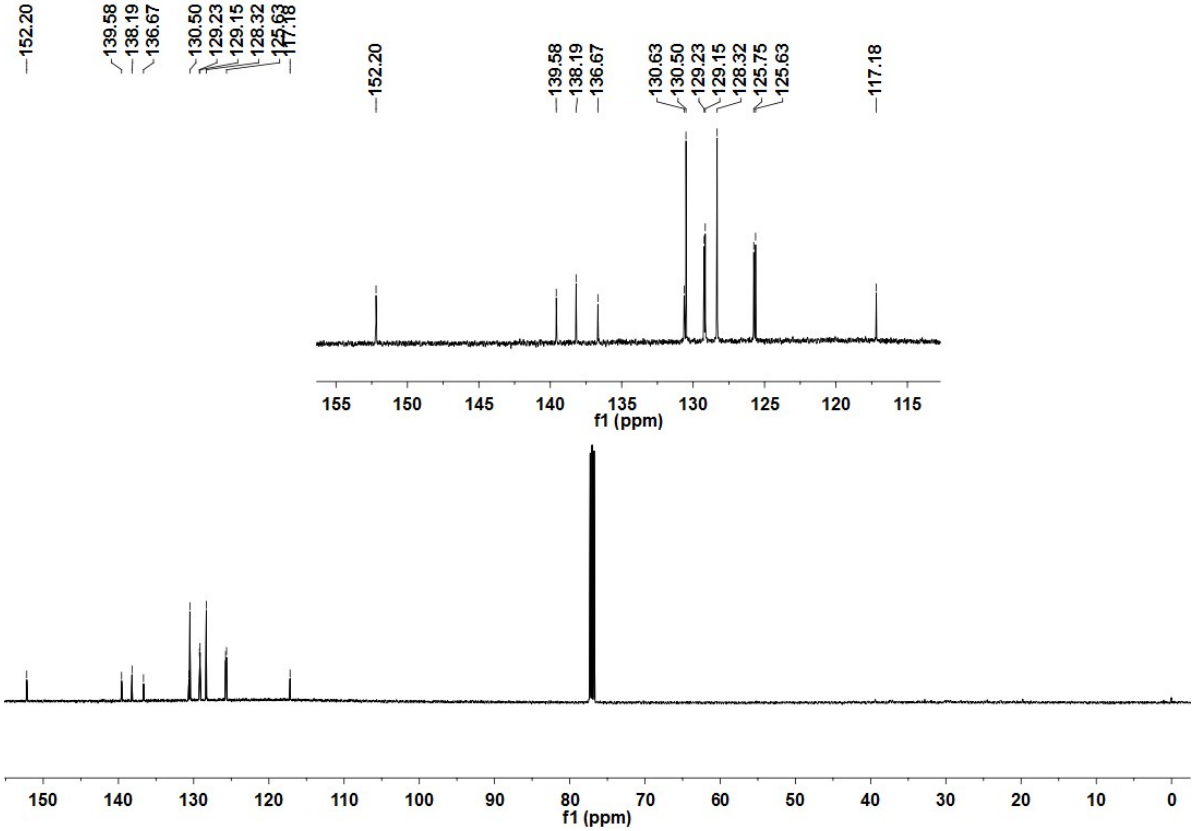


Fig. S12 ^{13}C-NMR spectrum of compound A

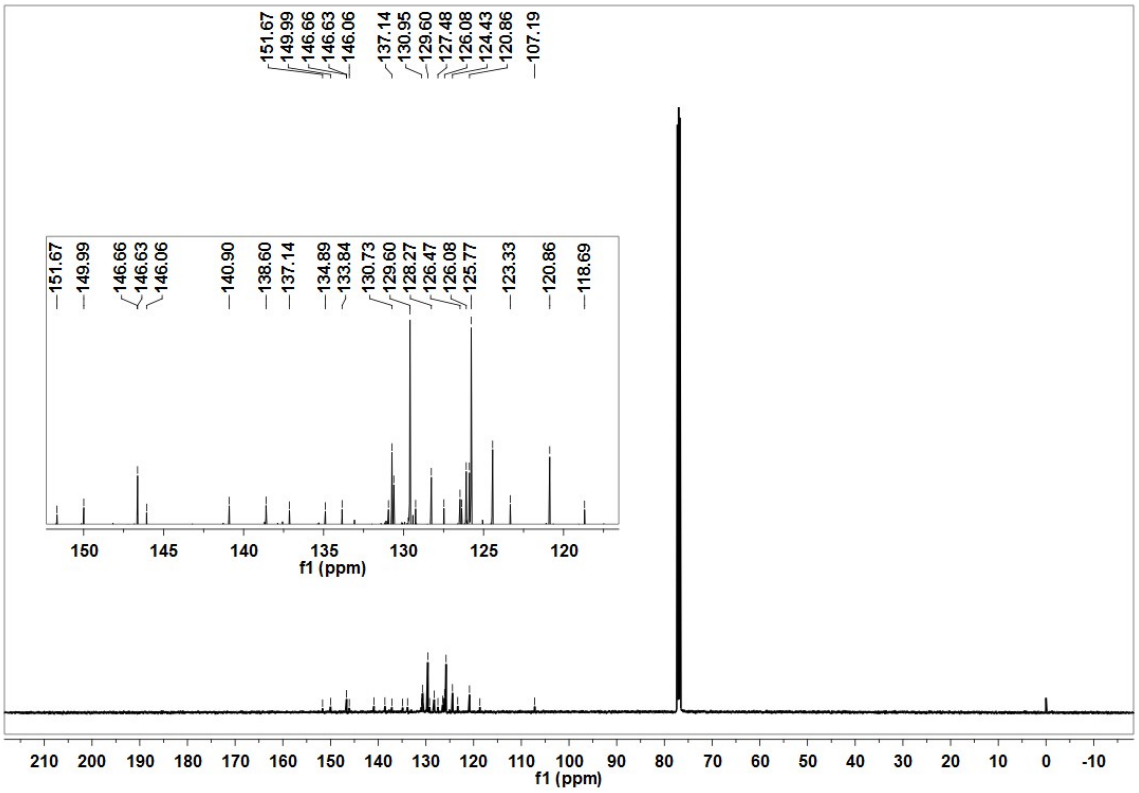


Fig. S13 ^{13}C-NMR spectrum of **(TPACN)$_2$Qx**

3. Computational data of electronic transitions

Table S1. Calculated electronic transitions of **(TPACN)$_2$Qx** using TD-DFT methods.

Compound	State	E^{opt} (eV)	λ (nm)	f	Composition
(TPACN)$_2$Qx	S1	2.10	590	2.0558	HOMO → LUMO (69%)
	S3	2.64	470	0.6594	HOMO → LUMO+2 (48%)
	S5	2.66	466	0.5745	HOMO → LUMO+2 (66%)
	S6	2.91	426	0.7556	HOMO → LUMO+2 (58%)
	S13	3.37	368	0.1583	HOMO-4 → LUMO (58%)
	S14	3.39	365	0.2390	HOMO → LUMO+4 (67%)

4. AFM images

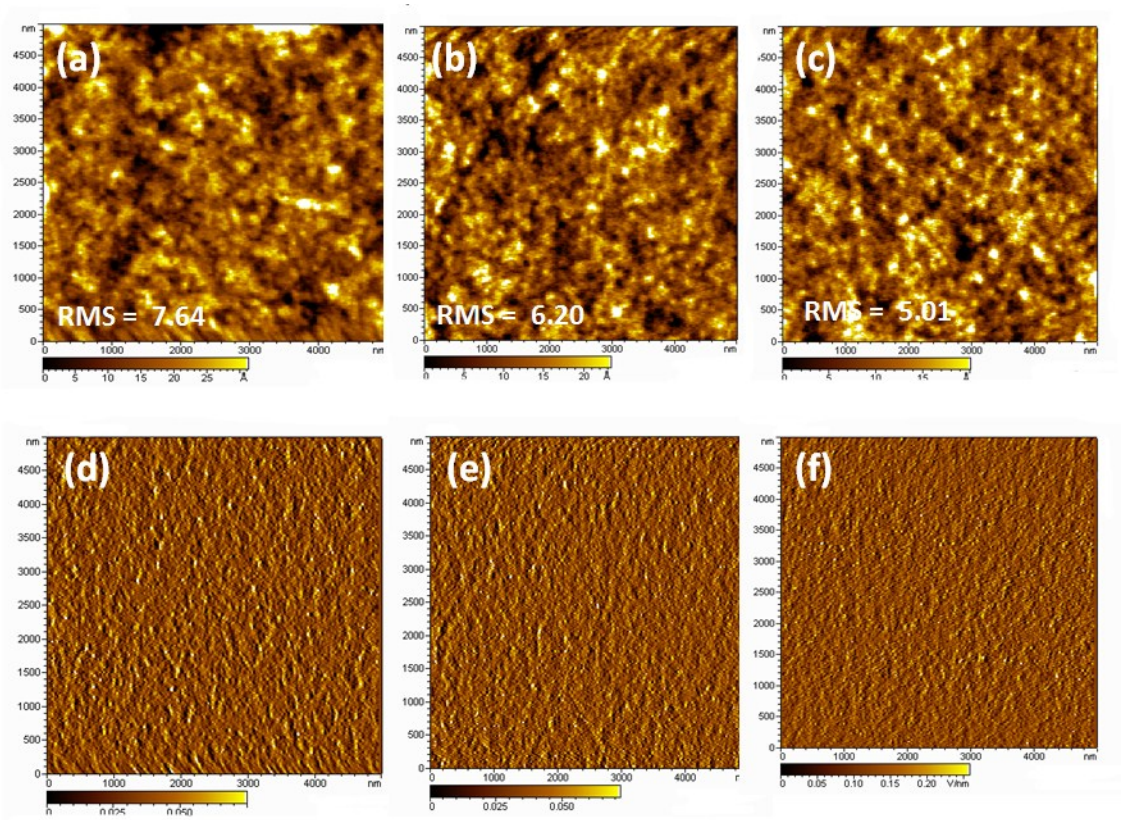


Fig. S14 AFM images of different D/A blend films: (a, d) $(TPACN)_2Qx:PC_{61}BM$ (1:1, w/w); (b, e) $(TPACN)_2Qx:PC_{61}BM$ (1:3, w/w); (c, f) $(TPACN)_2Qx:PC_{61}BM$ (1:2, w/w).

5. References

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