Electronic Supplementary information†

Aggregation-enhanced Thermally Activated Delayed Fluorescence in Butterfly-shaped Donors-Acceptor Conjugates

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Table of contents

S1. Experimental details

General information. All the reagents and deuterated solvents were obtained from commercial sources and used without further purification unless otherwise mentioned. Carbazole was prepared by using the literature procedure.[1] Synthesised compounds were purified by column chromatography using silica gel (Acytylis, 60 Å, 230-400 mesh) as stationary phase, and solvent mixtures used during chromatography were reported as volume ratios unless otherwise noted. Deuterated solvents were purchased from Eurisotop (Cambridge Isotope Laboratories, Inc.) and used as received. Spectroscopic grade solvents were used for the spectroscopic measurements.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded in Bruker AVHDN 400 with working frequencies of 400.2 MHz for ^{1}H and 100.6 MHz for ^{13}C nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane (TMS), using the residual solvent peak as the reference standard. High-resolution mass Spectroscopy (HRMS) was carried out using an Agilent 6540 accurate mass Q-TOF LC/MS (Agilent Technologies, U.S.A.). Single crystal X-ray diffraction data were collected using a D8 Venture IµS microfocus dual source Bruker APEX4 diffractometer equipped with a PHOTON 100 CMOS detector and an Oxford cryogenic system. Single crystals were mounted at room temperature on the ends of glass fibers, and data were collected at room temperature. Data collection: APEX4 (Bruker, 2014)[2] cell refinement: SAINT (Bruker, 2014)[2] data reduction: SAINT; program(s) used to solve structure: OLEX 2 (Olexsys)[3] program(s) used to refine structure.

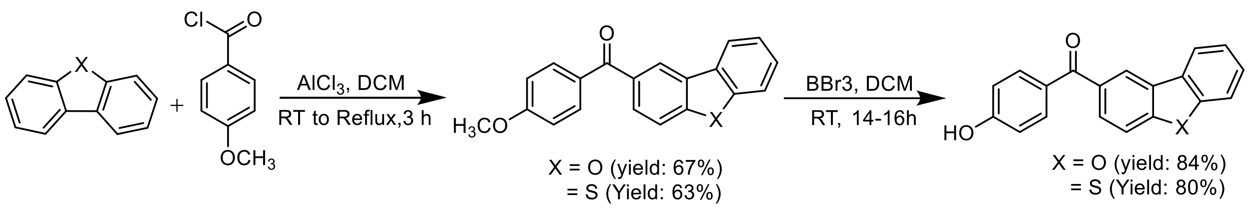
Electrochemical and Thermal analyis. Cyclic voltammetry and differential pulse voltammetry were conducted using a Potentiostat (1204C; CH Instruments Inc.). Thermogravimetric analysis was performed with a Mettler Toledo Analyzer (TGA2 SF/1100), capable of operating from room temperature to 650 ºC, equipped with a gas controller and an XP1U TGA balance. Differential scanning calorimetry (DSC) data were obtained using a Mettler Toledo differential scanning calorimeter (DSC3/500), providing precise thermal analysis.

Theoretical Calculations. Quantum chemistry calculations were performed using density functional theory (DFT) and time-dependent DFT with the Gaussian16 software, employing the M062X functional and the 6-31G(d,p) basis set.[4] Ground and excited states were optimized in the gas phase. Triplet geometries were optimized using the TD (triplet)-M06-2X/6-31G(d,p) method. Hole-electron surfaces were generated from TD calculation, including keyword IOp(9/40=4). Chemcraft and Multifwin software packages were used for visualization and analysis.[5]

Photophysical analysis. The photophysical properties of all compounds were studied in solution and spin-coated doped films. Absorption spectra were recorded using a Cary 8454 spectrometer (Agilent, USA). Fluorescence and phosphorescence spectra and lifetimes were measured with a Fluorolog-3 spectrofluorometer (FL3-2-IHR). Temperature-dependent emission measurements in solution under ambient aerated conditions (i.e., atmospheric gases already dissolved in the solvent) were carried out using a methanol-based chiller assembly, which works in the temperature range of RT to 190K. 77K PL Measurements were performed using a liquid nitrogen-based transparent dewar assembly purchased from Horiba Inc., whereas solid-state temperature-dependent PL studies were conducted with a JANIS-CS204SE-FMX-1AL cryostat. Absolute photoluminescence luminescence quantum yield measurements were performed using an integrating sphere (FS5, Edinburgh, UK). Detailed Photophysical measurement techniques were discussed in earlier reports.[6]

S2. Synthesis and Characterization of compounds

Synthesis of 4-hydroxyphenones.

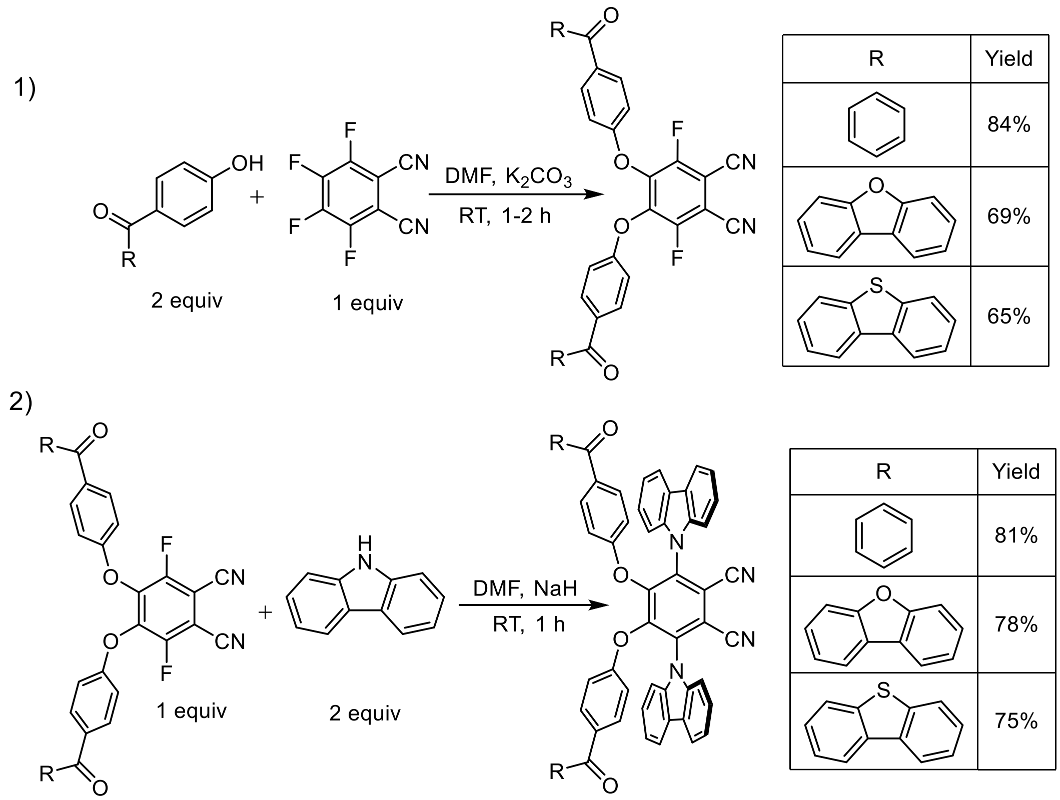


Scheme S1. Representative synthetic scheme of 4-hydroxyphenones (**2a** and **2b**).

(1a and 1b). In a 50 ml round button flask, 4-methoxybenzoyl chloride (1000 mg, 5.86 mmol, 1 equiv.) and dibenzofuran (985 mg, 5.86 mmol, 1 equiv.)/ dibenzothiophene (1079.76 mg, 5.8 mmol,1 equiv.) was dissolved in dry dichloromethane (10 ml), followed by gradual addition of aluminium chloride (1094 mg, 8.20 mmol, 1.4 equiv.) at 0°C. After warming to room temperature and stirring for 10 hours, the reaction was quenched by adding 100 mL of ice-cold water, and the resulting mixture was treated with ethyl acetate (2 × 200 mL). The combined organic layers were washed with saturated $NaHCO_3$ (150 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the products (1a &1b) were purified by column chromatography using a mixture of petroleum ether and ethyl acetate (9:1 v/v).

(2a and 2b). In next step, demethylation reaction of 1a & 1b was performed. 1a (500 mg, 1.65 mmol,) or 1b (525 mg, 1.65 mmol) was dissolved in dry dichloromethane (5 ml) under N_2 atmosphere, followed by slow addition of 1M boron tribromide in dichloromethane (5 ml) at 0°C. Reaction mixture was stirred over night at room temperature, after that it was added dropwise to a stirring mixture of ice water (100 mL). The mixture was stirred for 30 min at room temperature then filtered, dried, and purified via silica gel chromatography using hexane: ethyl acetate (50:50) as eluent to yield the products 2a (yield: 84%) and 2b (yield: 80%).

Synthesis of final compounds:



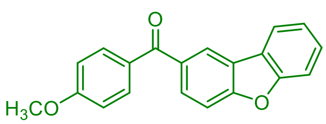
Scheme S2. Representative synthetic scheme of final compounds

(1). In a 25 mL two-neck round bottom flask, anhydrous K_2CO_3 (3.0 equiv.) was added to dry DMF under a nitrogen atmosphere, then respective 4 hydroxy-phenones (2.0 equiv.) were immediately added at room temperature. After 5 minutes, tetrafluorophathonitrile (1.0 equiv.) was added at a time under constant stirring. After an hour, the reaction progress was monitored using TLC. Upon completion, the reaction mixture was quenched by addition to ice-cold water. The resulting precipitate was filtered through G30 sintered funnel and purified via silica gel chromatography using hexane: ethyl acetate (95:5) as eluent to yield the intermediate products in good yield (65 – 84%).

(2). For the final product synthesis, in a separate reaction vessel, sodium hydride (NaH) (2.5 equiv.) was dissolved with dry DMF under nitrogen atmosphere. After 5 minutes, carbazole was added to the reaction mixture. Once the evolution of hydrogen gas had stopped, respective intermediates obtained in the earlier reaction step was added and the reaction continued until consumption of the starting materials. The reaction mixture was then treated with ice-cold water and extracted with dichloromethane. This organic layer was dried with Na_2SO_4 and purified via silica gel column chromatography by using hexane: ethyl acetate (96:4) as eluent to yield the final products. (Yield: 75 – 81 %).

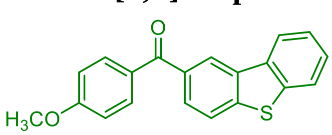
Characteristic Data of Compounds

Dibenzo[b,d]furan-2-yl(4-methoxyphenyl)methanone (1a) ^{1}H NMR (400 MHz, $CDCl_3$) δ



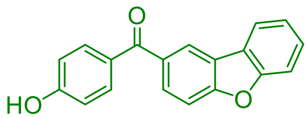
(ppm): 8.40 (d, *J* = 1.5 Hz, 1H), 8.02 – 7.84 (m, 4H), 7.65 – 7.57 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.14, 163.23, 158.43, 156.94, 133.37, 132.70, 132.63, 130.70, 129.62, 127.98, 124.37, 123.88, 123.40, 123.26, 123.19, 121.12, 113.72, 112.02, 111.45, 77.16, 55.62. HRMS(ESI) m/z: calcd. for $C_{20}H_{14}O_3$ $[M+H]^+$ 303.1016, found, 303.0943.

Dibenzo[b,d]thiophen-2-yl(4-methoxyphenyl)methanone (1b) ^{1}H NMR (400 MHz, $CDCl_3$) δ



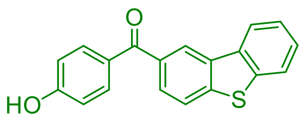
(ppm): 8.57 (d, *J* = 1.2 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 7.96 – 7.84 (m, 5H), 7.53 – 7.45 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.40, 163.33, 143.62, 139.84, 135.48, 135.33, 134.74, 132.69, 130.60, 128.09, 127.46, 124.95, 123.45, 123.05, 122.57, 122.07, 113.77, 77.16, 55.65. HRMS(ESI) m/z: calcd. for $C_{20}H_{14}O_2S$ [M+H]+, 319.0787; found, 319.0584.

Dibenzo[b,d]furan-2-yl(4-hydroxyphenyl)methanone (2a) ^{1}H NMR (400 MHz, DMSO-d_6) δ



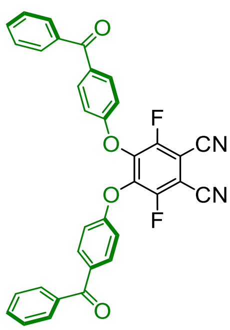
(ppm): 10.43 (s, 1H), 8.52 (d, *J* = 0.9 Hz, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 7.84 (dd, *J* = 8.7, 5.0 Hz, 2H), 7.75 (dd, *J* = 12.2, 8.5 Hz, 3H), 7.61 – 7.54 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.95 – 6.90 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 193.83, 161.88, 157.30, 156.10, 133.44, 132.59, 129.20, 128.33, 128.26, 123.57, 123.54, 123.18, 122.91, 121.85, 115.26, 111.83, 111.55, 39.52.

Dibenzo[b,d]thiophen-2-yl(4-hydroxyphenyl)methanone (2b) ^{1}H NMR (400 MHz, DMSO-d_6)



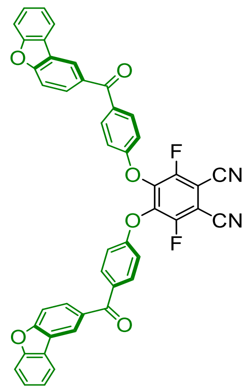
δ (ppm): 10.46 (s, 1H), 8.65 (d, *J* = 1.2 Hz, 1H), 8.48 – 8.44 (m, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.09 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.60 – 7.50 (m, 2H), 6.96 – 6.91 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 194.42, 162.46, 157.88, 156.68, 134.03, 133.18, 129.79, 128.91, 128.85, 124.15, 124.12, 123.76, 123.50, 122.43, 115.85, 112.41, 112.13.

4,5-bis(4-benzoylphenoxy)-3,6-difluorophthalonitrile (3a) ^{1}H NMR (400 MHz, $CDCl_3$)



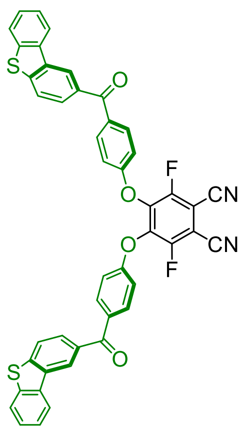
δ(ppm): 7.81 – 7.76 (m, 2H), 7.74 – 7.69 (m, 2H), 7.63 – 7.57 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.95 – 6.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 194.99, 158.65, 137.29, 134.36, 132.84, 132.59, 129.98, 128.59, 115.69, 109.19, 77.16. HRMS (ESI): m/z calcd for C11H8N2O5 [M+H]+ 557.1307, Found 557.1288.

4,5-bis(4-(dibenzo[b,d]furan-2-carbonyl)phenoxy)-3,6-difluorophthalonitrile (3b) ^{1}H NMR



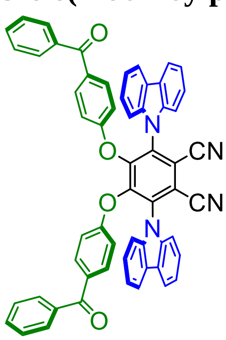
(400 MHz, $CDCl_3$) δ (ppm): 8.39 (d, *J* = 1.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.89 – 7.81 (m, 3H), 7.66 – 7.59 (m, 2H), 7.54 – 7.48 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.29, 158.70, 158.50, 156.90, 134.81, 132.42, 132.21, 129.56, 128.15, 124.60, 123.52, 123.46, 123.20, 121.03, 115.66, 112.00, 111.61, 109.05. HRMS(ESI) m/z: calcd. for $C_{46}H_{22}F_2N_2O_6$ $[M+H]^+$ 737.1519, Found 737.1498.

4,5-bis(4-(dibenzo[b,d]thiophene-2-carbonyl)phenoxy)-3,6-difluorophthalonitrile (3c) ^{1}H



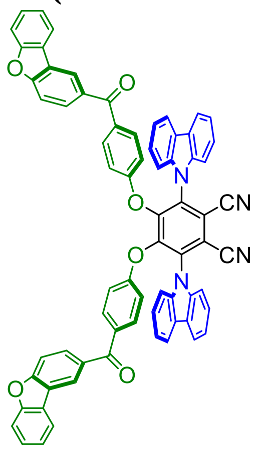
NMR (400 MHz, $CDCl_3$) δ (ppm): 8.56 (d, *J* = 10.1 Hz, 1H), 8.16 (d, *J* = 7.0 Hz, 1H), 7.99 – 7.76 (m, 5H), 7.56 – 7.44 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 194.66, 158.69, 144.46, 139.86, 135.70, 135.10, 134.77, 133.64, 132.78, 132.61, 127.97, 127.71, 125.10, 123.48, 123.10, 122.86, 122.79, 122.06, 115.81, 109.20.HRMS (ESI): m/z calcd for $C_{46}H_{22}F_2N_2O_4S_2$ $[M+H]^+$ 769.1061, Found 769.0918.

4,5-bis(4-benzoylphenoxy)-3,6-di(9H-carbazol-9-yl)phthalonitrile (CBPN) ^{1}H NMR (400



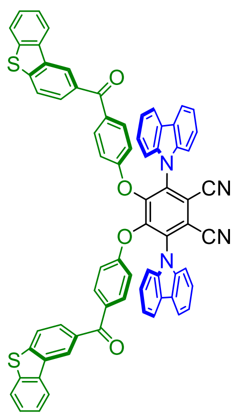
MHz, $CDCl_3$) δ(ppm): 7.99 (d, *J* = 7.7 Hz, 2H), 7.55 (dd, *J* = 16.2, 8.0 Hz, 3H), 7.38 (ddd, *J* = 24.9, 15.8, 8.0 Hz, 8H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.29 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm): 194.82, 158.00, 151.00, 138.94, 137.21, 134.98, 133.54, 132.59, 131.37, 129.94, 128.29, 126.61, 124.37, 122.17, 120.89, 115.53, 115.32, 112.17, 110.17. HRMS (ESI): m/z calcd for $C_{58}H_{34}N_4O_4$ $[M+H]^+$ 851.2653, Found 851.2608.

3,6-di(9H-carbazol-9-yl)-4,5-bis(4-(dibenzo[b,d]furan-2-carbonyl)phenoxy)phthalonitrile



(CDBFPN) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 1.5 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 7.3 Hz, 1H), 7.64 – 7.50 (m, 5H), 7.44 – 7.31 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.18, 158.70, 158.05, 157.01, 151.08, 139.05, 135.17, 133.97, 132.30, 131.47, 129.89, 128.26, 126.67, 124.71, 124.45, 123.70, 123.59, 122.98, 122.22, 121.12, 120.94, 115.64, 115.40, 112.16, 111.23, 110.19, 53.57. HRMS(ESI) m/z: calcd. for $C_{70}H_{38}N4O_6$ $[M+H]^+$ 1031.2864, Found 1031.2815.

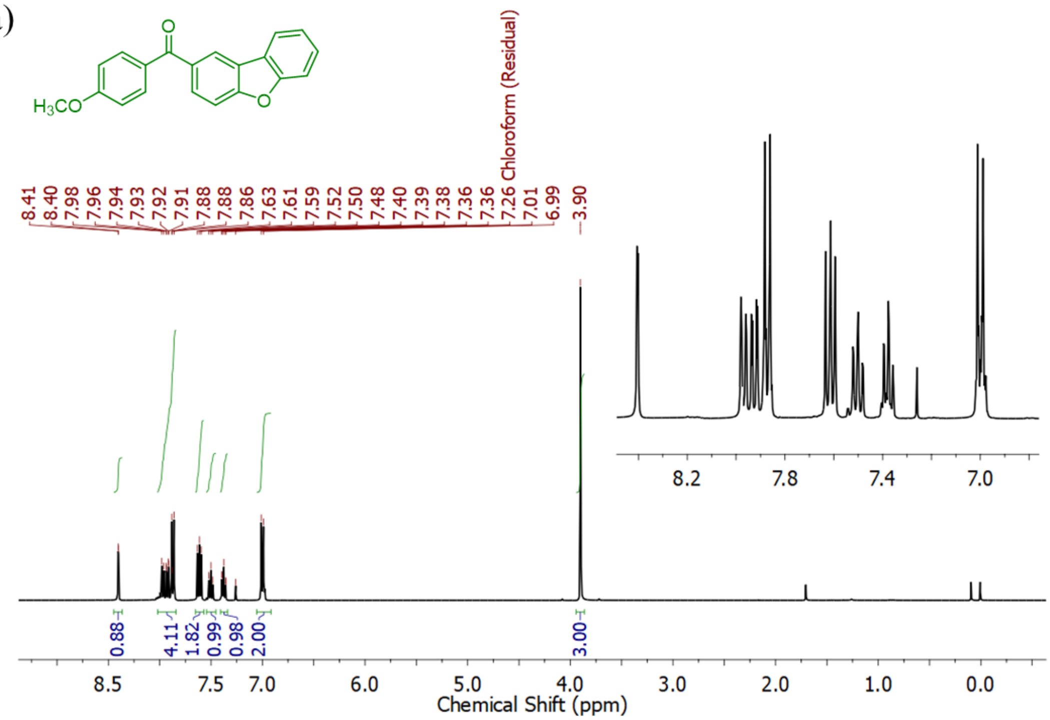
3,6-di(9H-carbazol-9-yl)-4,5-bis(4-(dibenzo[b,d]thiophene-2-carbonyl)phenoxy)



phthalonitrile (CDBTPN) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (d, *J* = 1.2 Hz, 1H), 8.18 – 8.12 (m, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.53 (ddd, *J* = 10.2, 8.8, 4.8 Hz, 4H), 7.42 – 7.32 (m, 4H), 7.26 (ddd, *J* = 10.8, 5.5, 3.4 Hz, 3H), 6.36 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 194.41, 158.11, 151.02, 144.22, 139.82, 139.03, 135.75, 135.19, 135.15, 133.84, 133.58, 131.51, 128.21, 127.69, 126.67, 125.05, 124.43, 123.12, 122.29, 122.21, 122.07, 120.94, 115.66, 115.39, 112.17, 110.18, 77.16. HRMS (ESI): m/z calcd for $C_{70}H_{38}N4O_4S_2$ $[M+H]^+$ 1063.2407, Found 1063.2416.

NMR spectra of compounds

(a)



(b)

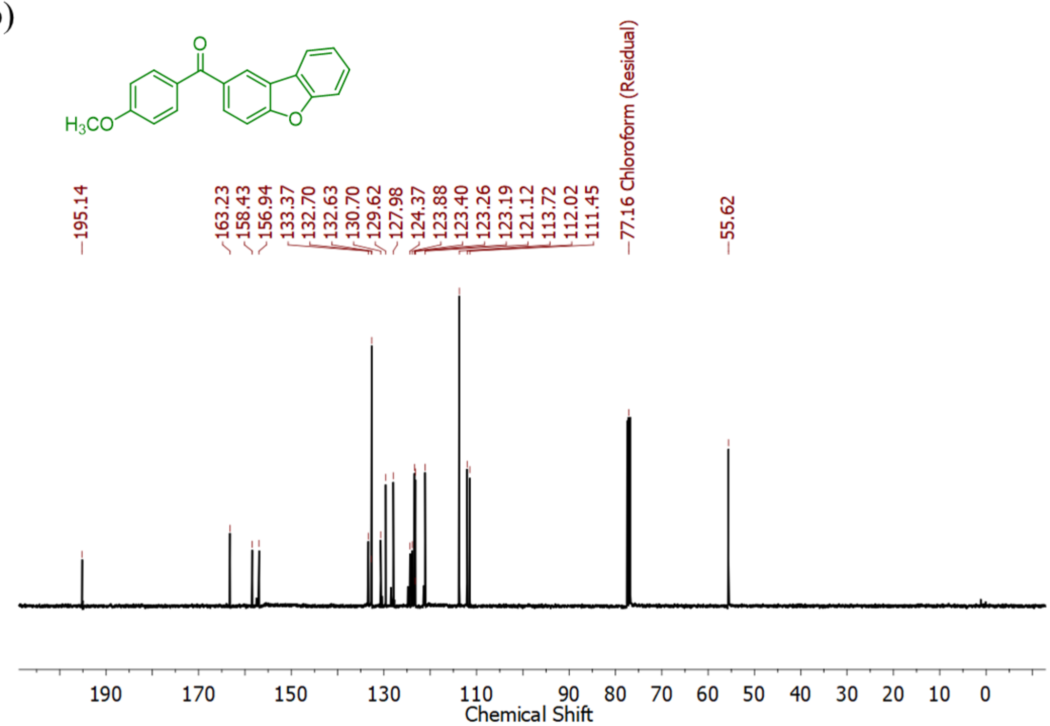
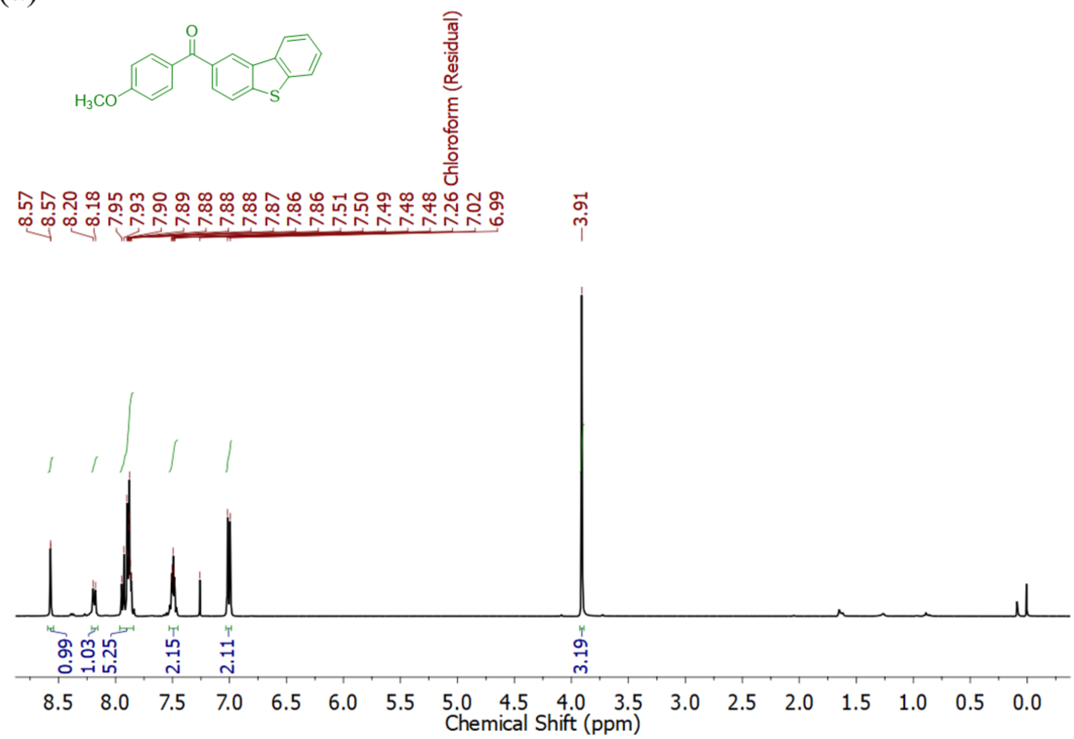


Fig S1. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of Dibenzo[b,d]furan-2-yl(4-methoxyphenyl)methanone (1a).

(a)



(b)

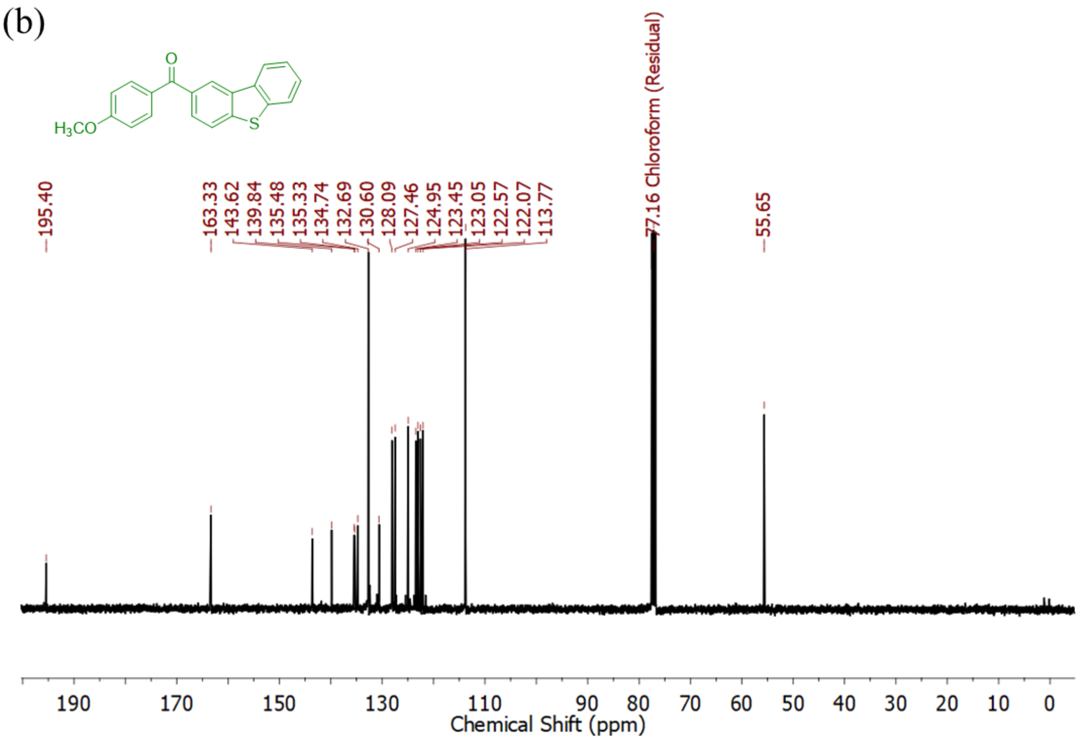
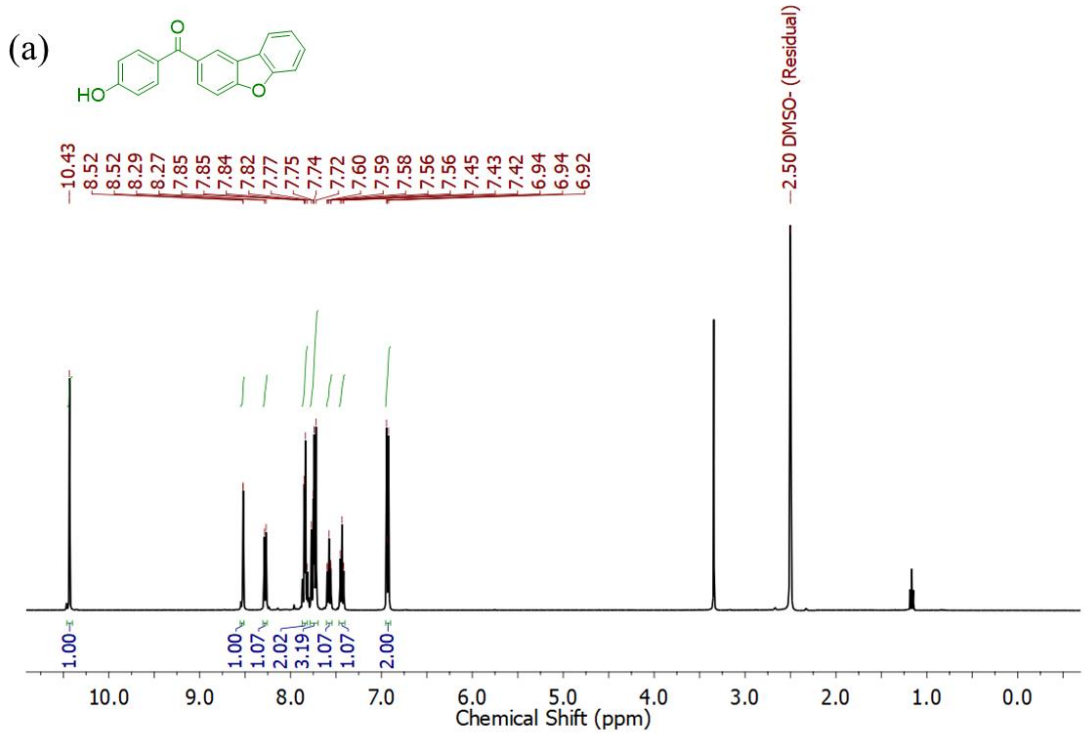


Fig S2. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of Dibenzo[b,d]thiophen-2-yl(4-methoxyphenyl)methanone (1b).



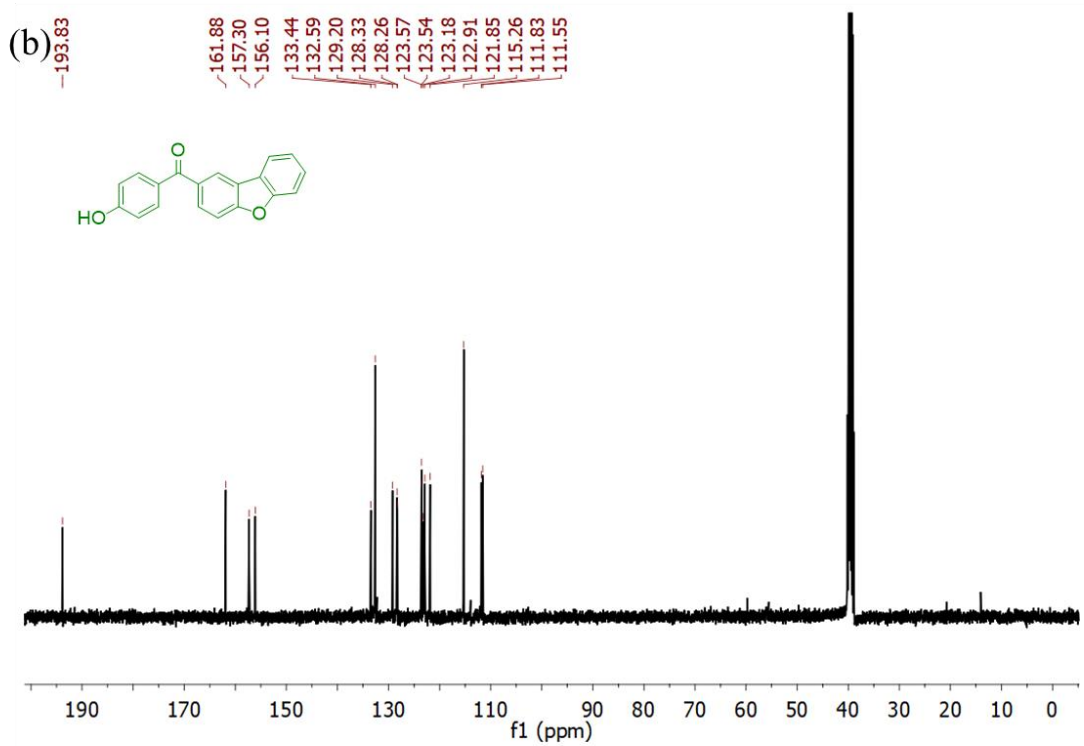


Fig S3. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of Dibenzo[b,d]furan-2-yl(4-hydroxyphenyl)methanone (2a).

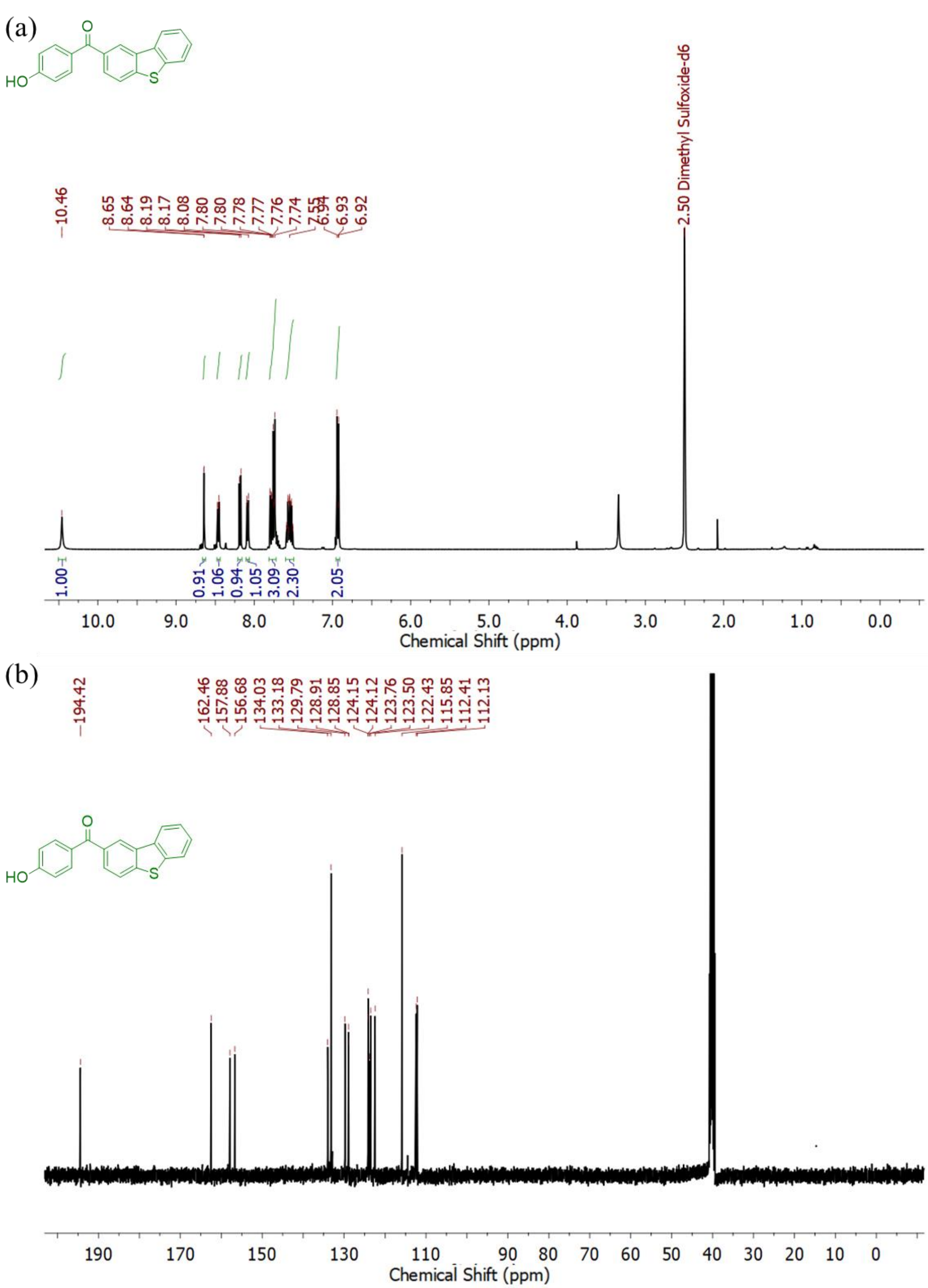


Fig S4. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of Dibenzo[b,d]thiophen-2-yl(4-hydroxyphenyl)methanone (2b).

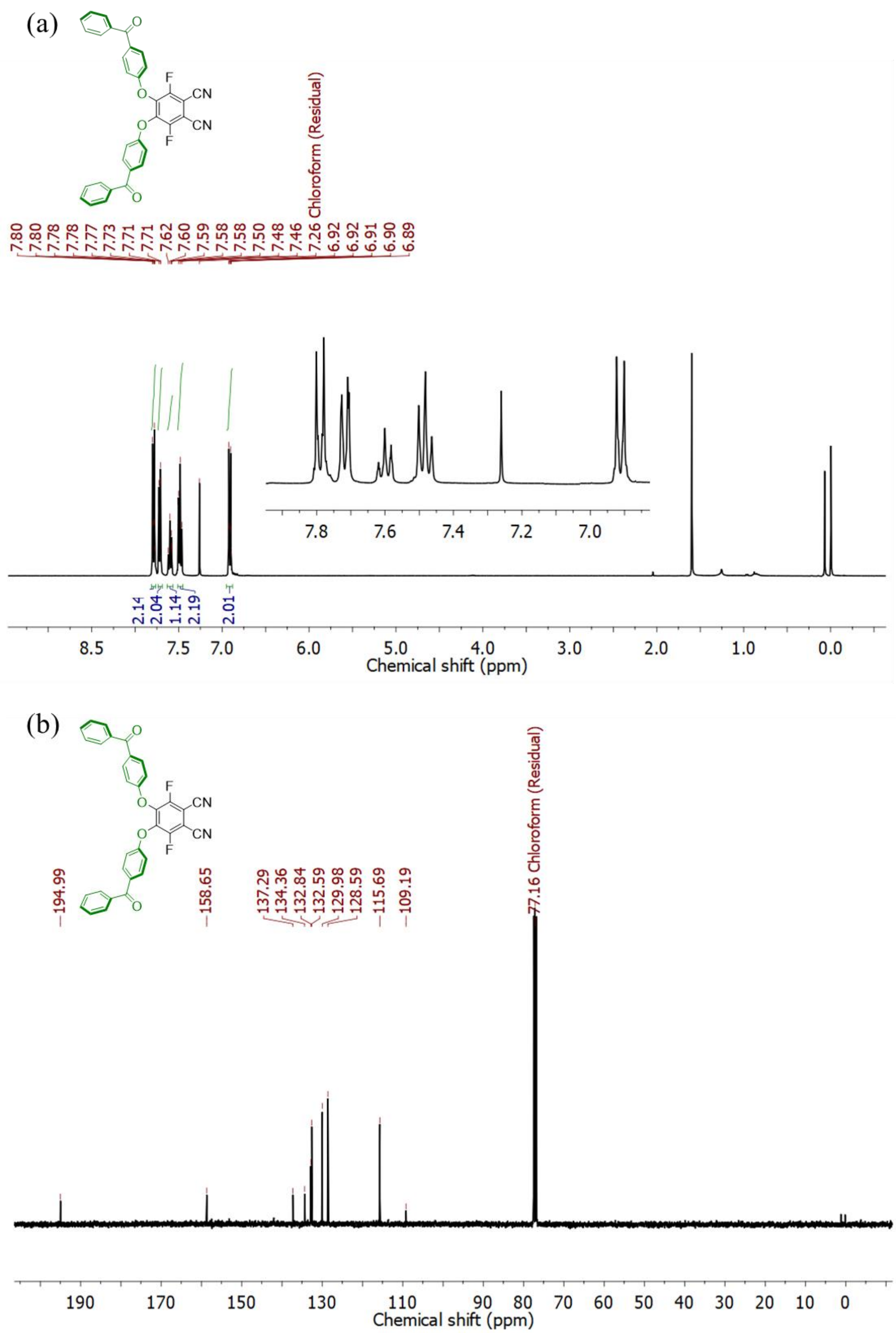


Fig S5. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of 4,5-bis(4-benzoylphenoxy)-3,6-difluorophthalonitrile (3a)

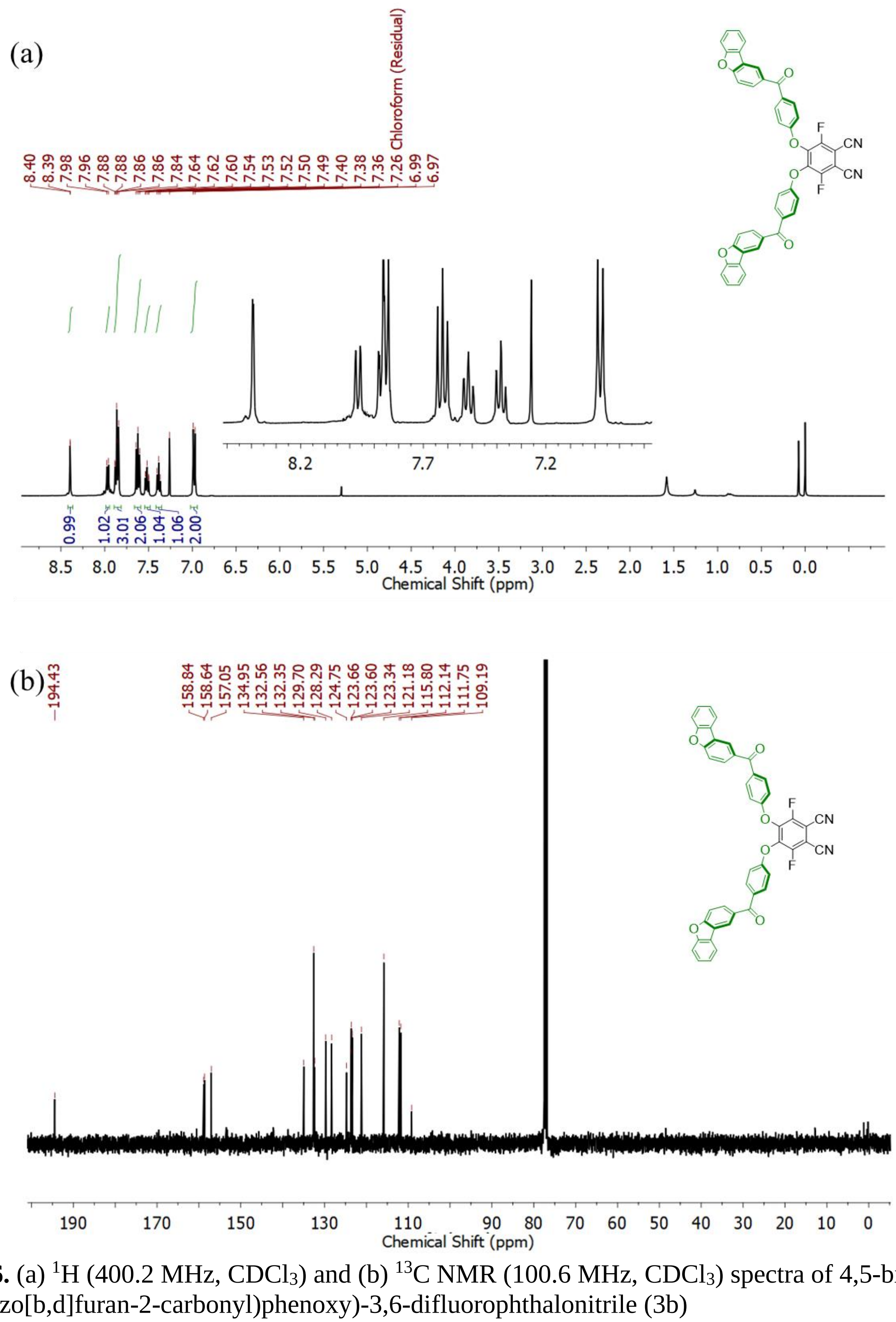
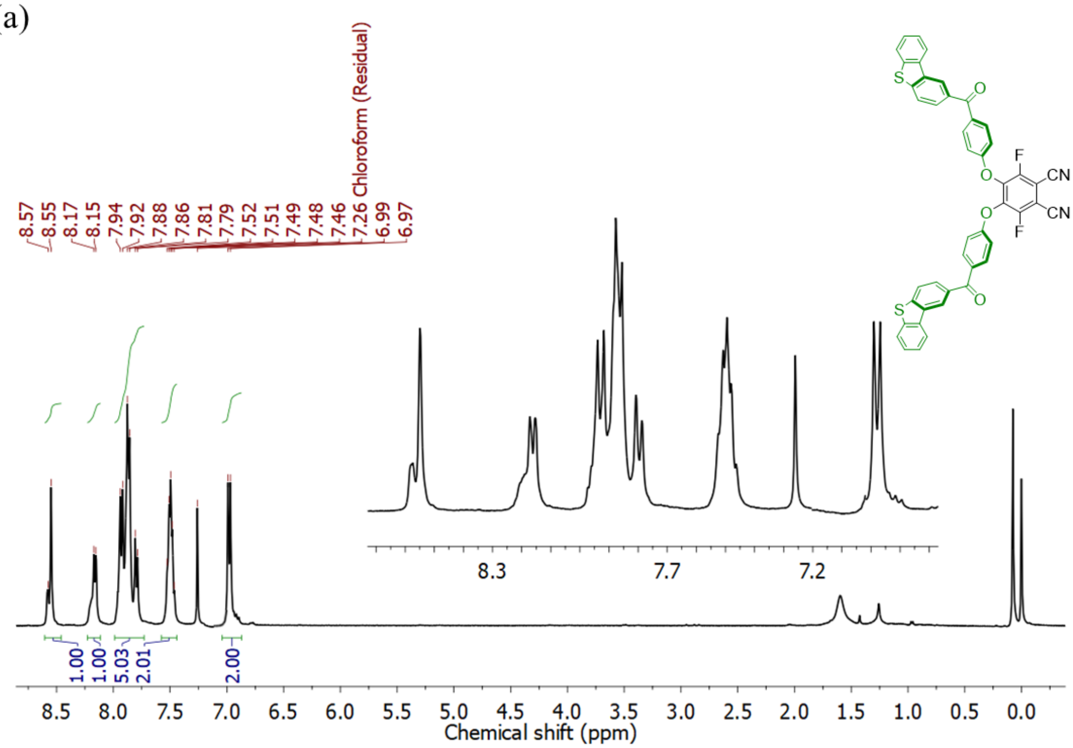


Fig S6. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of 4,5-bis(4-(dibenzo[b,d]furan-2-carbonyl)phenoxy)-3,6-difluorophthalonitrile (3b)

(a)



(b)

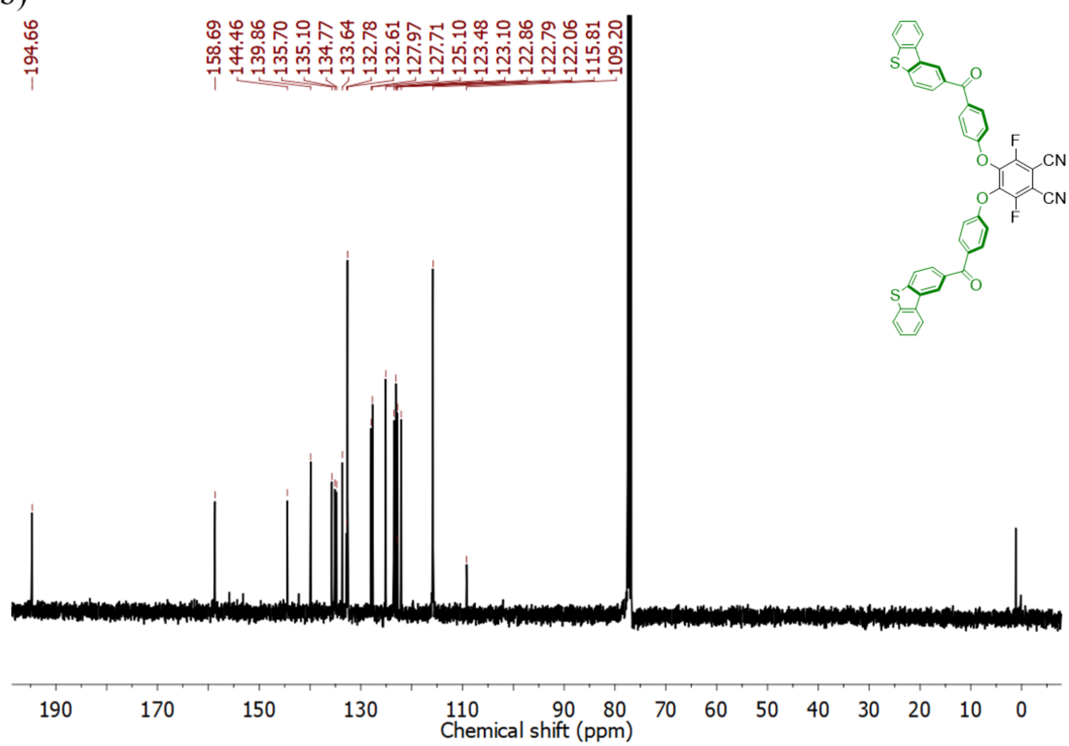
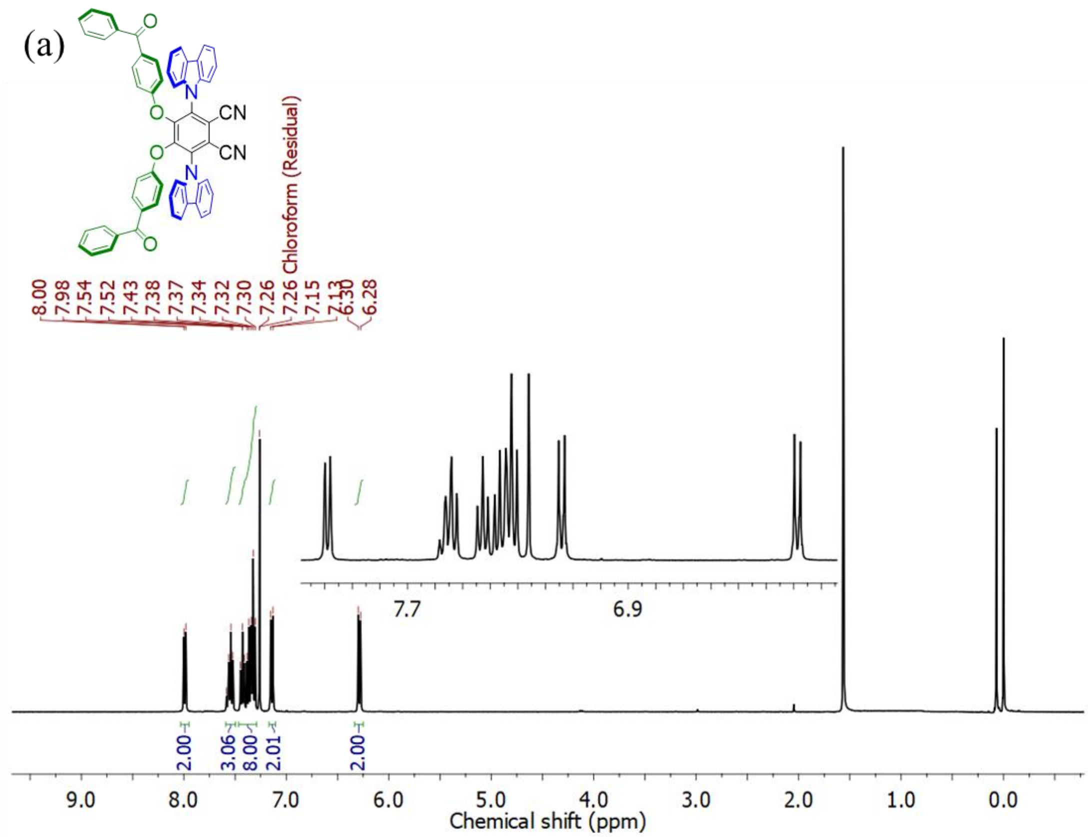


Fig S7. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of 4,5-bis(4-(dibenzo[b,d]thiophene-2-carbonyl)phenoxy)-3,6-difluorophthalonitrile (3c).

(a)



(b)

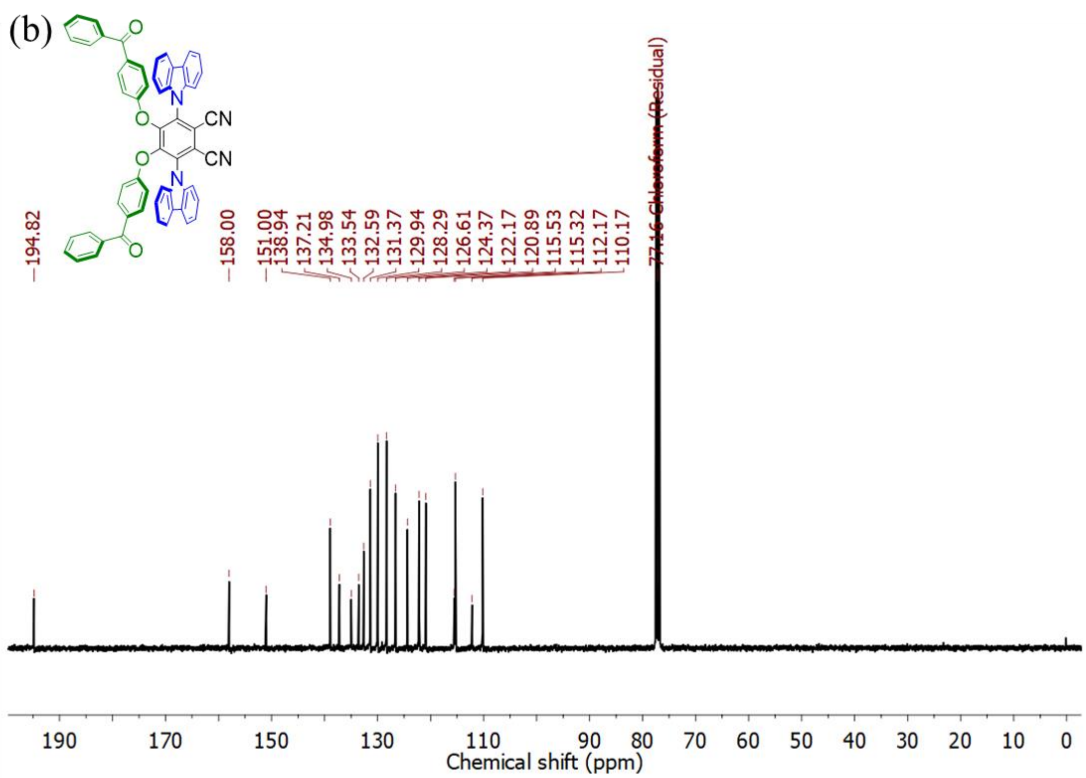


Fig S8. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of 4,5-bis(4-benzoylphenoxy)-3,6-di(9H-carbazol-9-yl)phthalonitrile **(CBPN).**

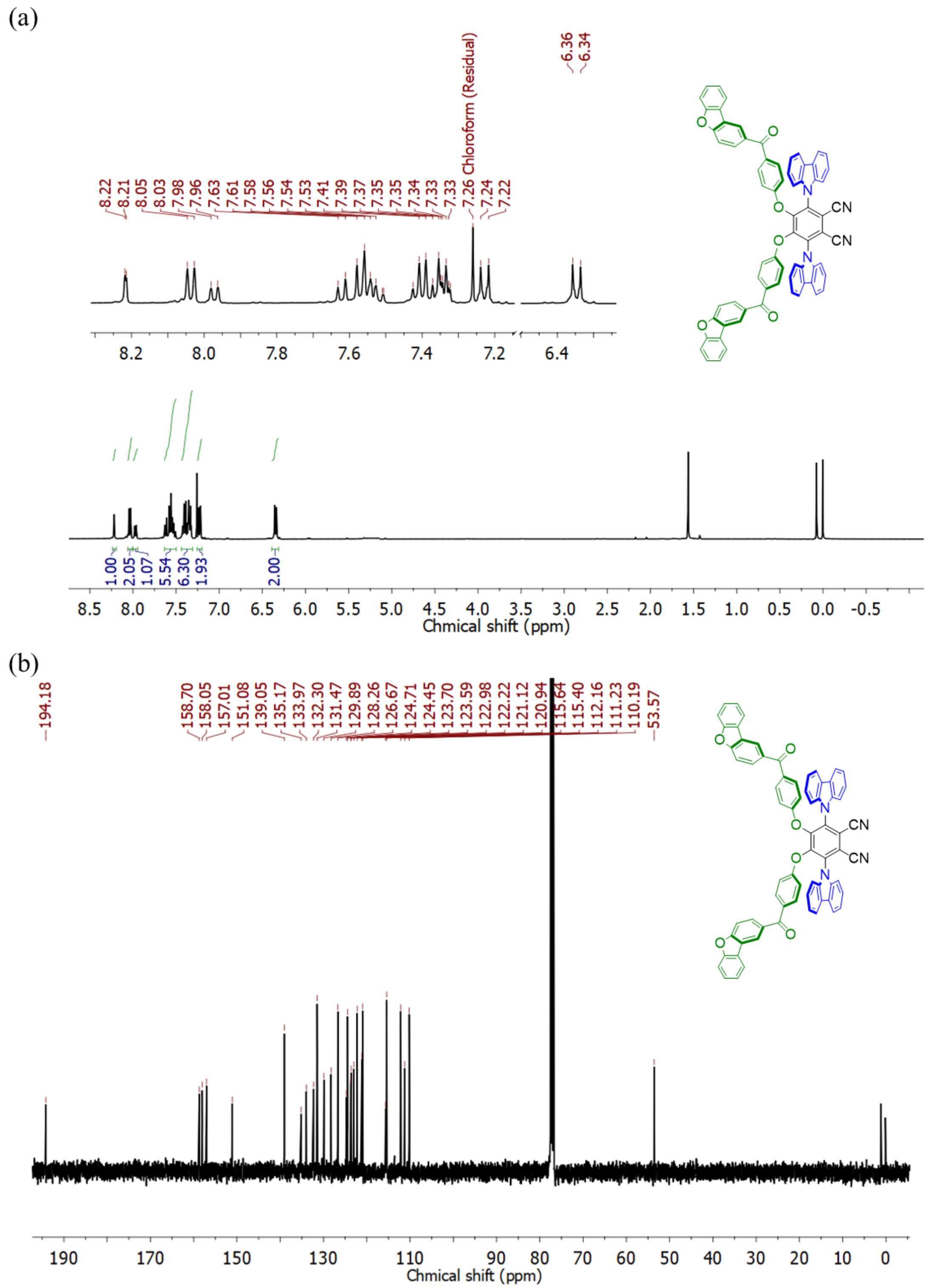


Fig S9. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of 3,6-di(9H-carbazol-9-yl)-4,5-bis(4-(dibenzo[b,d]furan-2-carbonyl)phenoxy)phthalonitrile (**CDBFPN**)

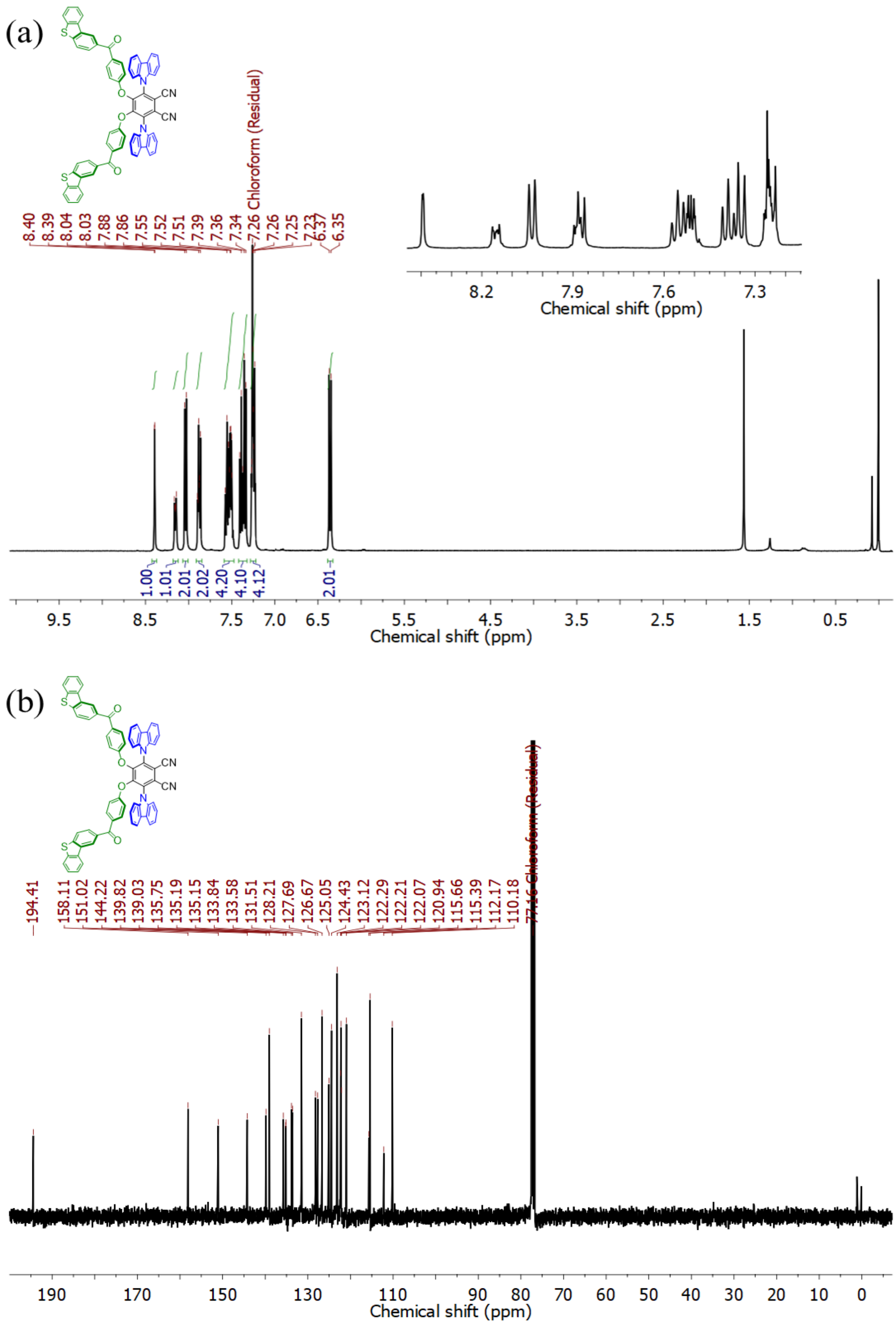
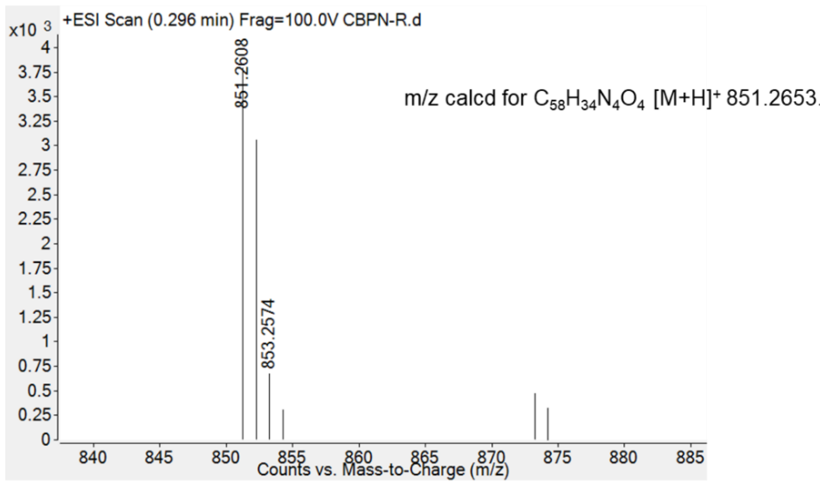


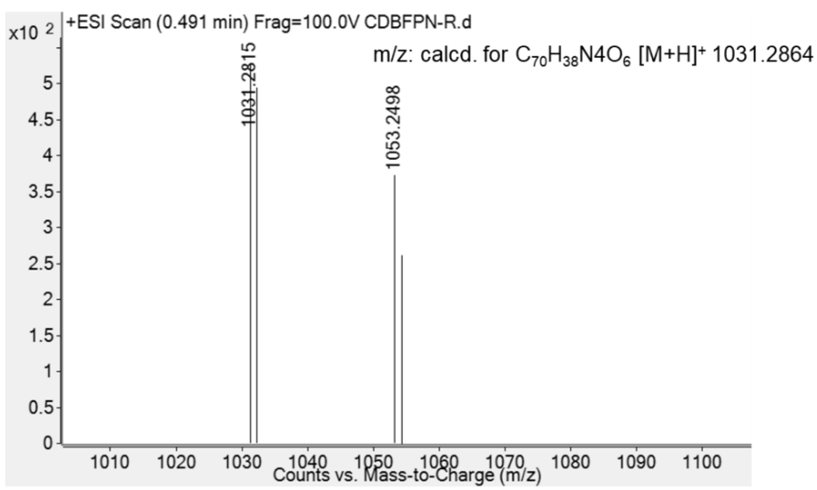
Fig S10. (a) ^{1}H (400.2 MHz, $CDCl_3$) and (b) ^{13}C NMR (100.6 MHz, $CDCl_3$) spectra of 3,6-di(9H-carbazol-9-yl)-4,5-bis(4-(dibenzo[b,d]thiophene-2-carbonyl)phenoxy) phthalonitrile (**CDBTPN**).

Mass Spectrograms of the final compounds

(a)



(b)



(c)

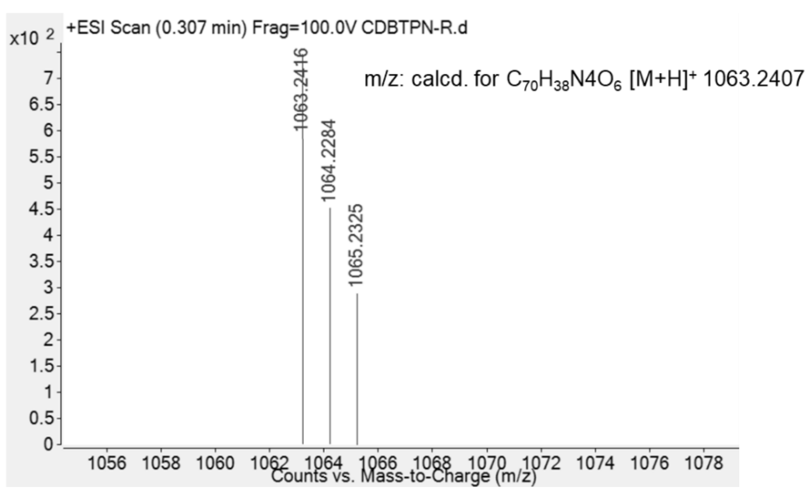
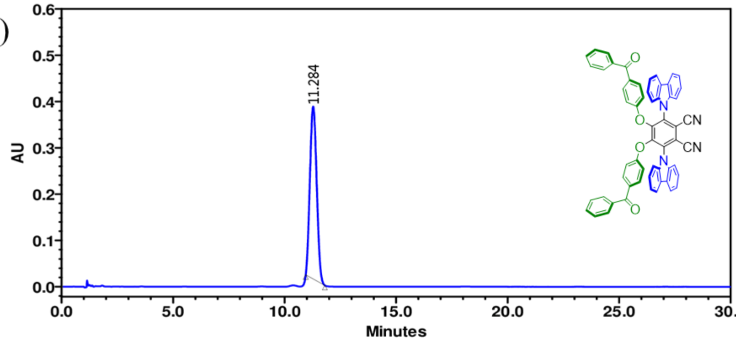


Fig S11. Mass spectrograms of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN.**

HPLC graphs of the final compounds

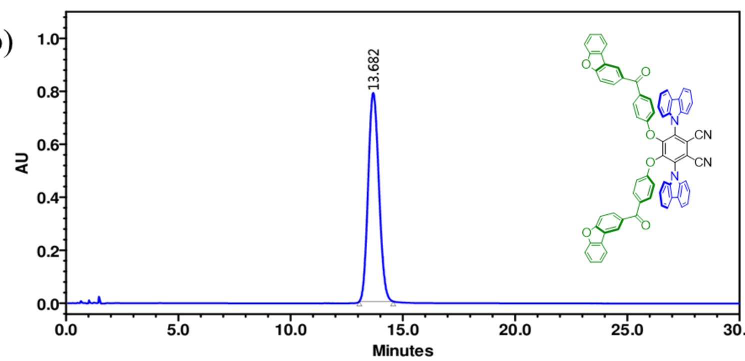
(a)



Processed Channel: 2998 Ch1 254nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 Ch1 254nm@1.2nm	11.284	7832349	100.00	372273

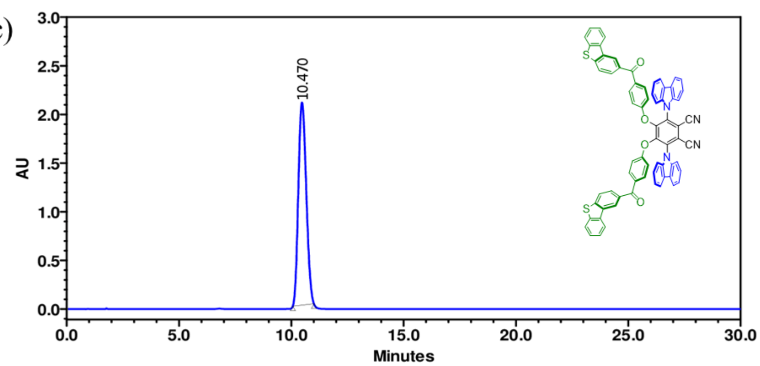
(b)



Processed Channel: 2998 Ch1 254nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 Ch1 254nm@1.2nm	13.682	26197144	100.00	787527

(c)



Processed Channel: 2998 Ch1 254nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 Ch1 254nm@1.2nm	10.470	50920356	100.00	2082459

Fig S12. HPLC chromatograms of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN** obtained using a C18 column as the stationary phase, employing a solvent system consisting of Gradient A (acetonitrile) and B (0.1% formic acid in water).

S3. Single crystal X-ray diffraction analysis

Table S1. Crystal data and structure refinement for **CBPN** and **CDBTPN**.

Identification code	**CBPN**	**CDBTPN**
CCDC deposition number	2413934	2413935
Empirical formula	$C_{58}H_{34}N_4O_4$	$C_{70}H_{38}N_4O_4S_2$
Formula weight	850.89	1063.16
Temperature/K	294	293
Crystal system	monoclinic	monoclinic
Space group	C2/c	Cc
a/Å	19.711(4)	22.499(9)
b/Å	13.865(3)	11.600(5)
c/Å	19.089(5)	21.856(11)
α/°	90	90
β/°	106.378(8)	100.493(16)
γ/°	90	90
Volume/Å^3	5005(2)	5609(4)
Z	4	4
ρ_{calc}g/cm^3	1.129	1.259
μ/mm^{-1}	0.072	0.15
F(000)	1768	2200
Crystal size/mm^3	0.21 × 0.16 × 0.11	0.22 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.938 to 50.844	3.79 to 50.944
Index ranges	-23 ≤ h ≤ 23, -16 ≤ k ≤ 16, -23 ≤ l ≤ 22	-26 ≤ h ≤ 26, -13 ≤ k ≤ 13, -26 ≤ l ≤ 26
Reflections collected	50275	50757
Independent reflections	4605 [R_{int} = 0.0414, R_{sigma} = 0.0198]	10175 [R_{int} = 0.0403, R_{sigma} = 0.0318]
Data/restraints/parameters	4605/0/299	10175/2/722
Goodness-of-fit on F^2	1.111	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0767, wR_2 = 0.2131	R_1 = 0.0826, wR_2 = 0.2280
Final R indexes [all data]	R_1 = 0.1123, wR_2 = 0.2838	R_1 = 0.1364, wR_2 = 0.3141
Largest diff. peak/hole / e Å^{-3}	0.35/-0.20	0.33/-0.25

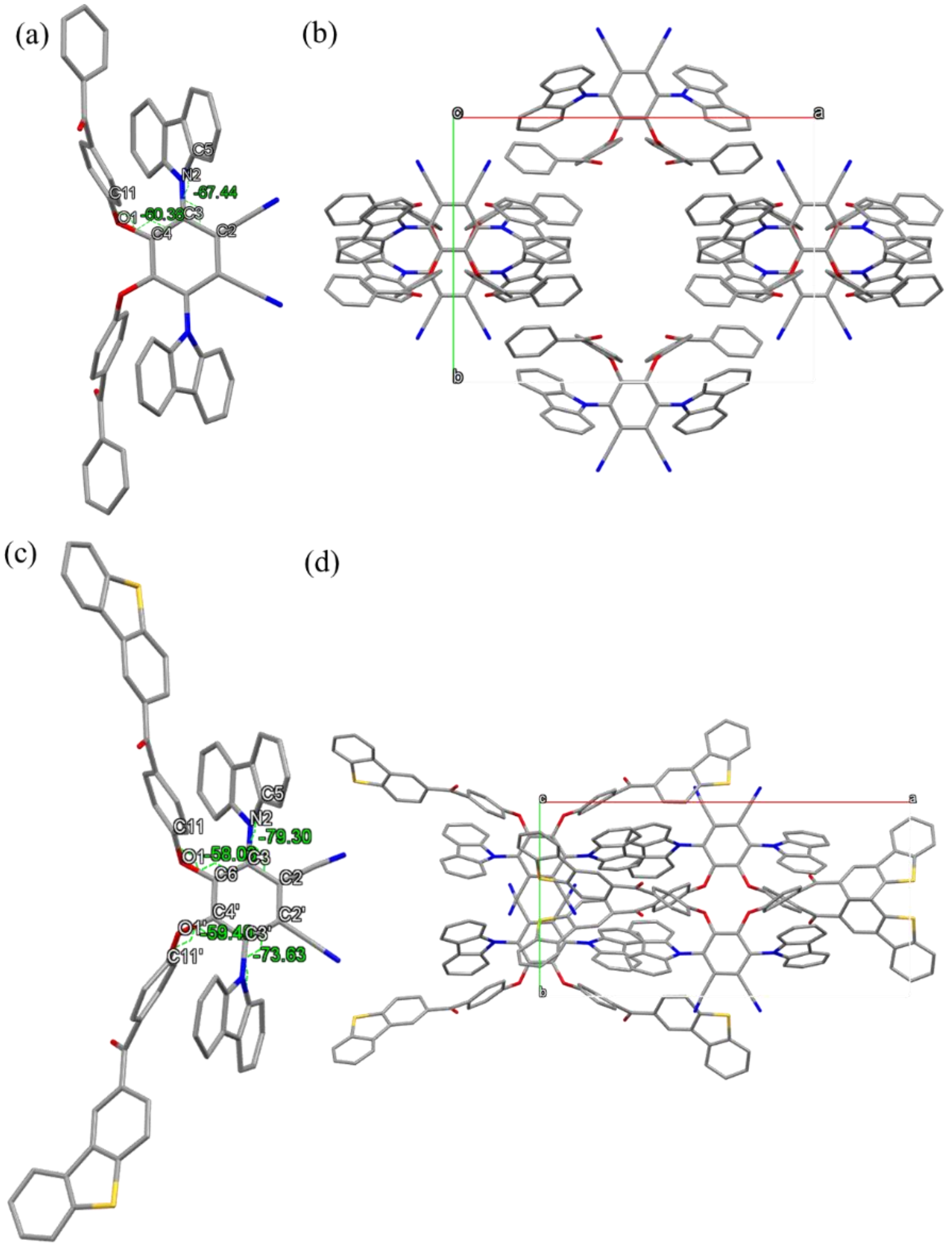


Fig S13. (a) Crytal structure of **CBPN** capped stick structure showing torsion (C2– C3– N3–C) and (C11–O1–C4–C3). (b) Unit cell of **CBPN** viewed along c – axis. (c) Crytal structure of **CDBTPN** Capped stick structure showing Torsion (C2–C3–N3–C5), (C11–O1–C4–C3), (C2′–C3′– N3′–C5′), and (C11′–O1′–C4′–C3′). (d) Unit cell of **CBDPN** viewed along c – axis (C11′–O1′–C4′–C3′).

Table S2. Torsion angles of the X-ray structures

Atoms	Torsions (°)	
	CBPN	**CDBTPN**
C2– C3– N3–C5	-67.44 (5)°	-79.30 (4)°
C11–O1–C4–C3	-60.38 (3)°	58.03 (1)°
C2′– C3′– N3′–C5′	-67.44 (5)°	-73.63 (4)°
C11′–O1′–C4′–C3′);	-60.38 (3)°	59.01 (1)°

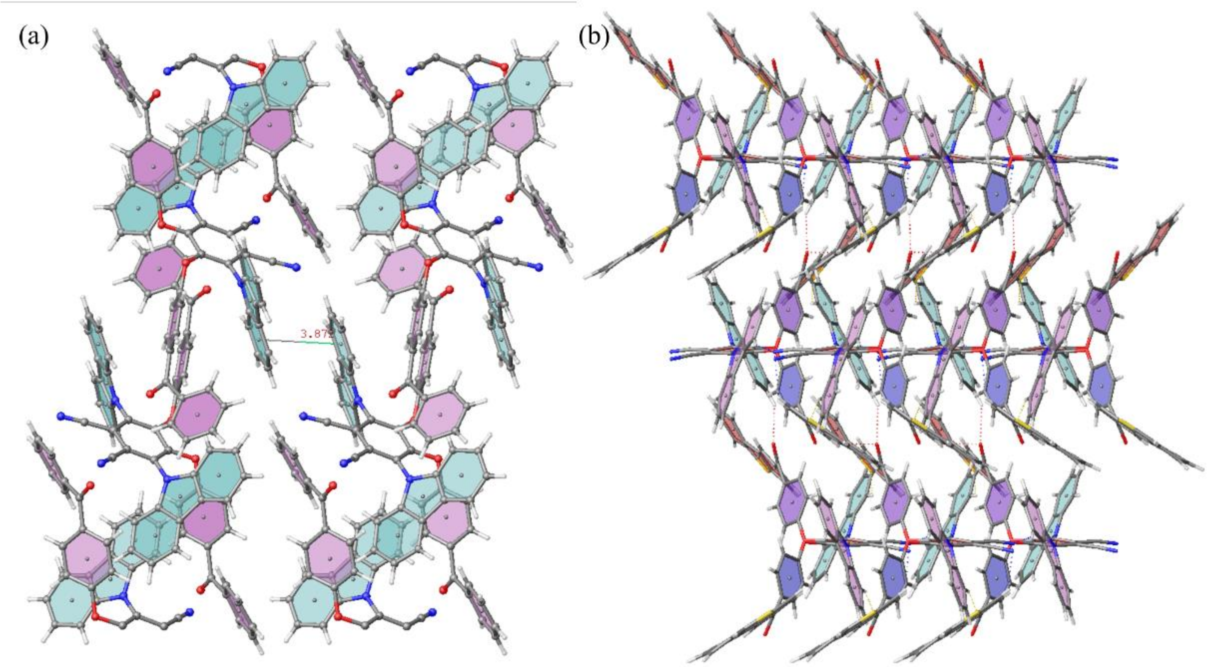


Fig S14. Crystal packing along 100–plane (a) **CBPN**, and (b) **CDBTPN**.

Table S3. Intermolecular interactions and their percentages for **CBPN** and **CDBTPN**

Interaction Type	**CBPN (%)**	**CDBTPN (%)**
C···C	10.5	3.4
C···H	21.5	12
O···H	9.2	8.9
N···H	13.6	12.1
S···H	-	5.1

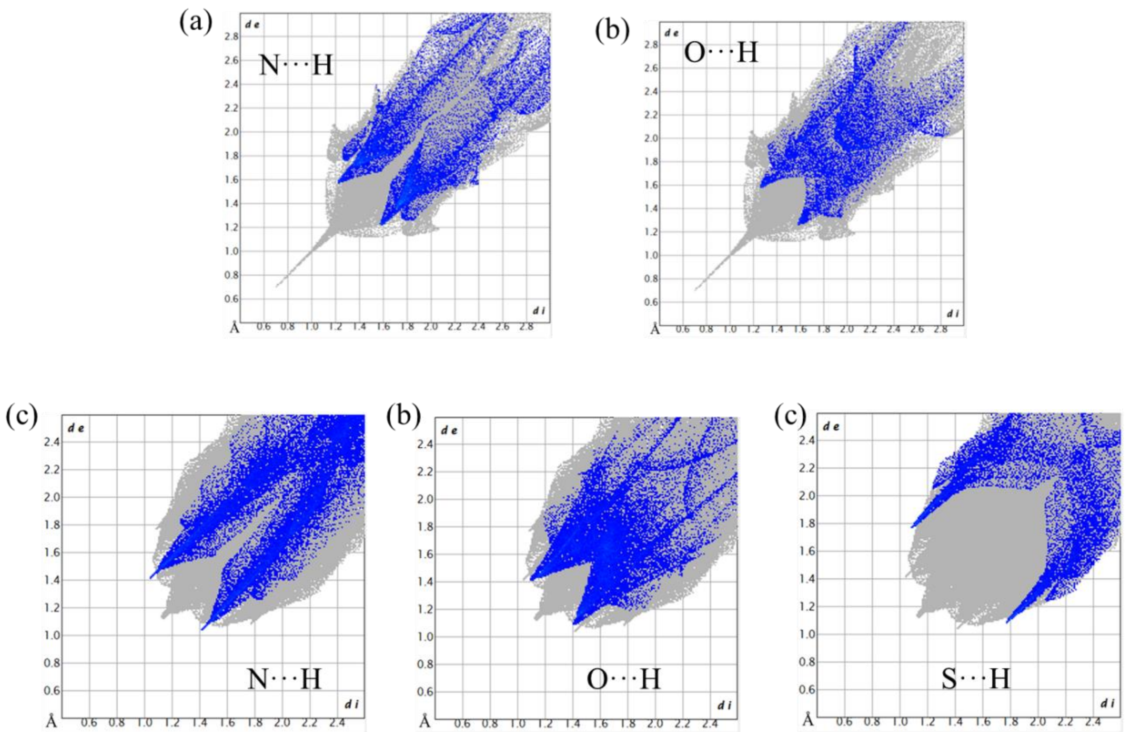


Fig S15. Decomposed fingerprint plots showing the proportion of various intermolecular interactions in (a, b) **CBPN** and (c, d, e) **CDBTPN.**

S4. Electrochemical and thermal analysis

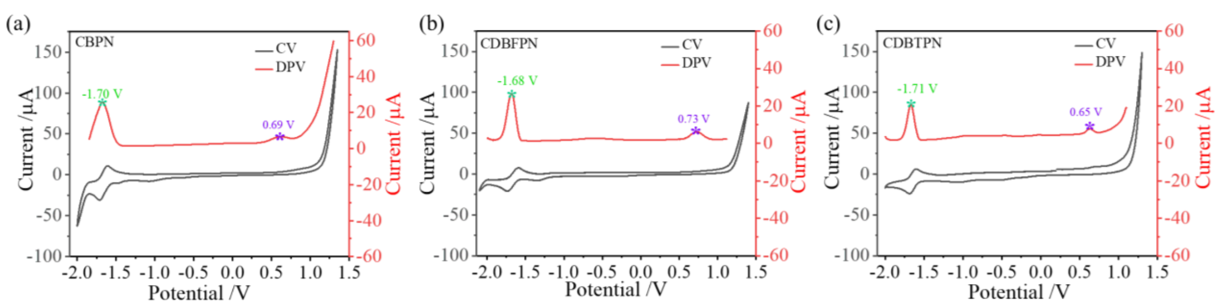


Fig S16. Cyclic voltammograms and differential pulse voltammograms of (a) **CBPN**, **(b) CDBFPN**, and (c) **CDBTPN** versus SCE in 1 mM dichloromethane; electrolyte = 0.1 M $(^{n}Bu)_4N(PF_6)$; working electrode = glassy carbon; reference electrode = Ag/Ag^{+}; counter electrode = Pt -wire; scan rate = 0.05V/s.

Table S4. HOMO, LUMO energies and electrochemical bandgaps based on DPV results

Compound	Oxidation Potential (V)	Reduction Potential (V)	HOMO* (eV)	LUMO* (eV)	Band Gap (eV)
CBPN	0.69	-1.70	-5.49	-3.10	2.39
CDBFPN	0.73	-1.68	-5.53	-3.12	2.41
CDBTPN	0.65	-1.71	-5.45	-3.09	2.36
*E_{HOMO}= −(E_{ox}+4.8); E_{LUMO}= −(E_{red} +4.8)					

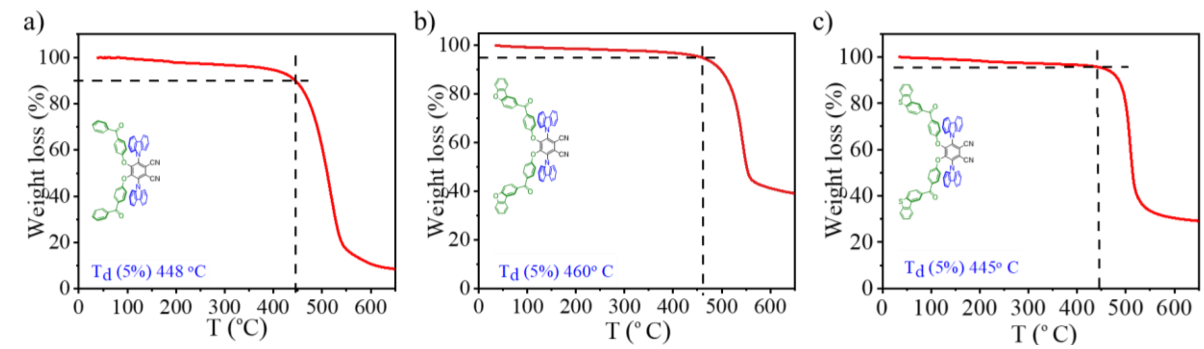


Fig S17. TGA thermograms of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN**. Scan rate of 10 °C/min was used for both cases.

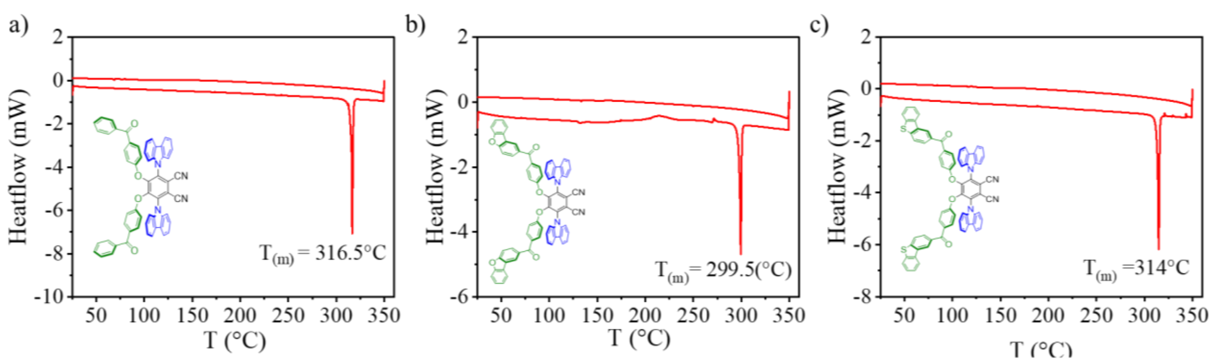


Fig S18. DSC thermograms of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN**. Scan rate of 10 °C/min.

S5. Quantum chemical calculations

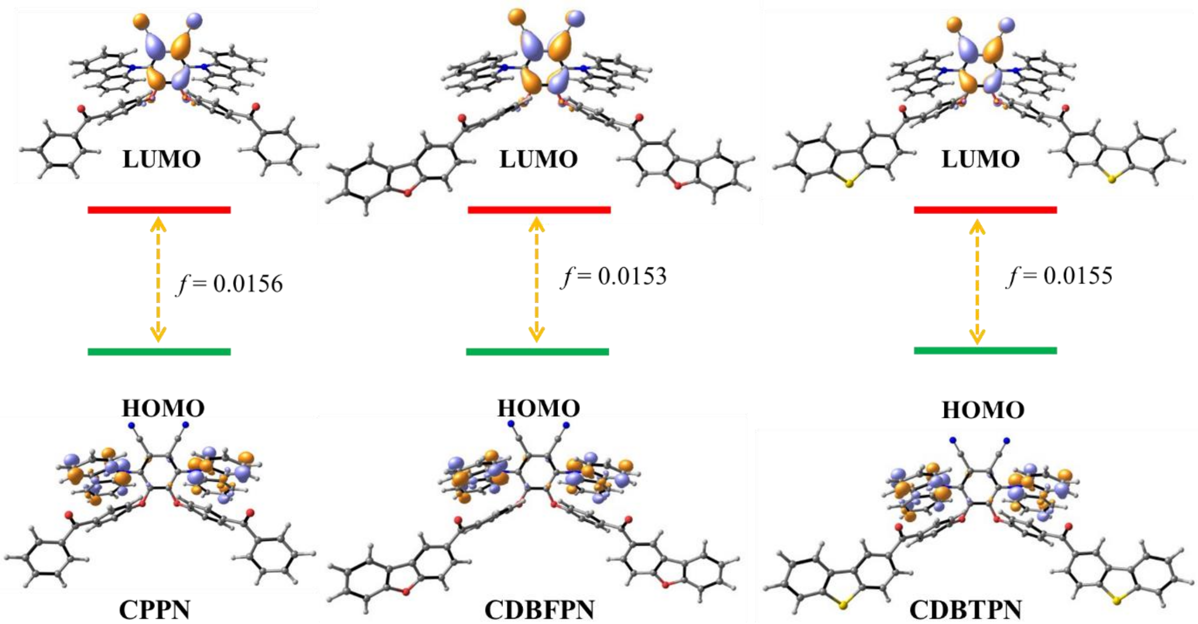


Fig S19. Distribution of frontiers molecular orbitals in **CPPN**, **CDBFPN**, and **CDBTPN**. Calculated at M062X/6-31G(d,p) level of theory.

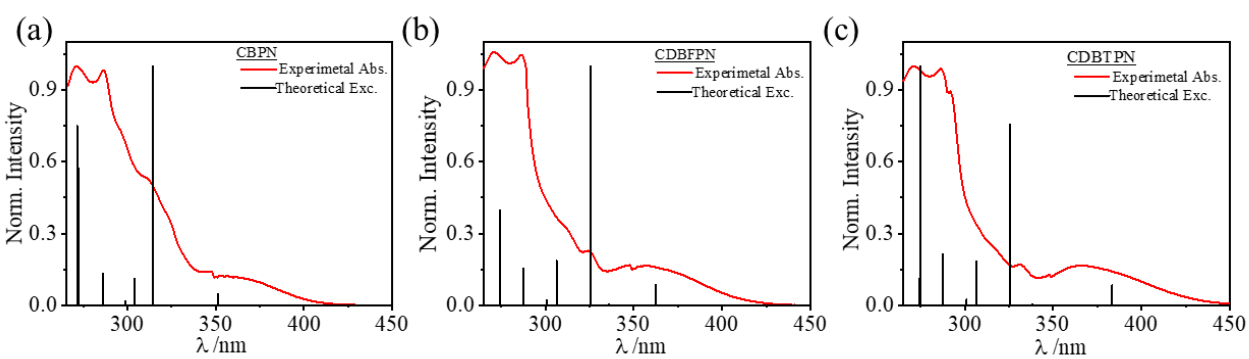


Fig S20. Absorption spectra (Red curve, toluene) and calculated excitation spectra (vertical line, gas phase) of (a) **CBPN**, (b) **CDBFPN**, and (b) **CDBTPN**. Calculated at M062X/6-31G(d,p) level of theory.

Table S5. The calculated (M06-2X/631G(d,p) molecular orbital energy levels and major transition involved in hole-electron (h/e) formulation.

State	CBPN		CDBFPN		CDBTPN	
	Transition	Transition probability	Transition	Transition probability	Transition	Transition probability
S1	H → L	84.5%	H→L	82.2%	H→L	83.3%,
	H-1→L+1	7.3%	H H-1 →L	7.4%	H-1→L+1	6.8%
T1	H→L+1	33.7%	H→L+1	33.9 %	H→L+1	33.3%,
	H-4→L	16.1%	H-8→L	15.9%	H-16→L	16.3%
	H-14→L	12.8%	H-16→L	15.9%	H-8→L	16.0%
T2	H-15→L+3	20.5%	H-17→L+3	16.4 %	H-17→L+3	16.8%
	H-14→L+2	13.5%	H-18→L+2	9.0%	H-18→L+2	9.4%
	H-16→L+2	7.1%	H-13→L+2	7.7%	H-12→L+3	7.8%

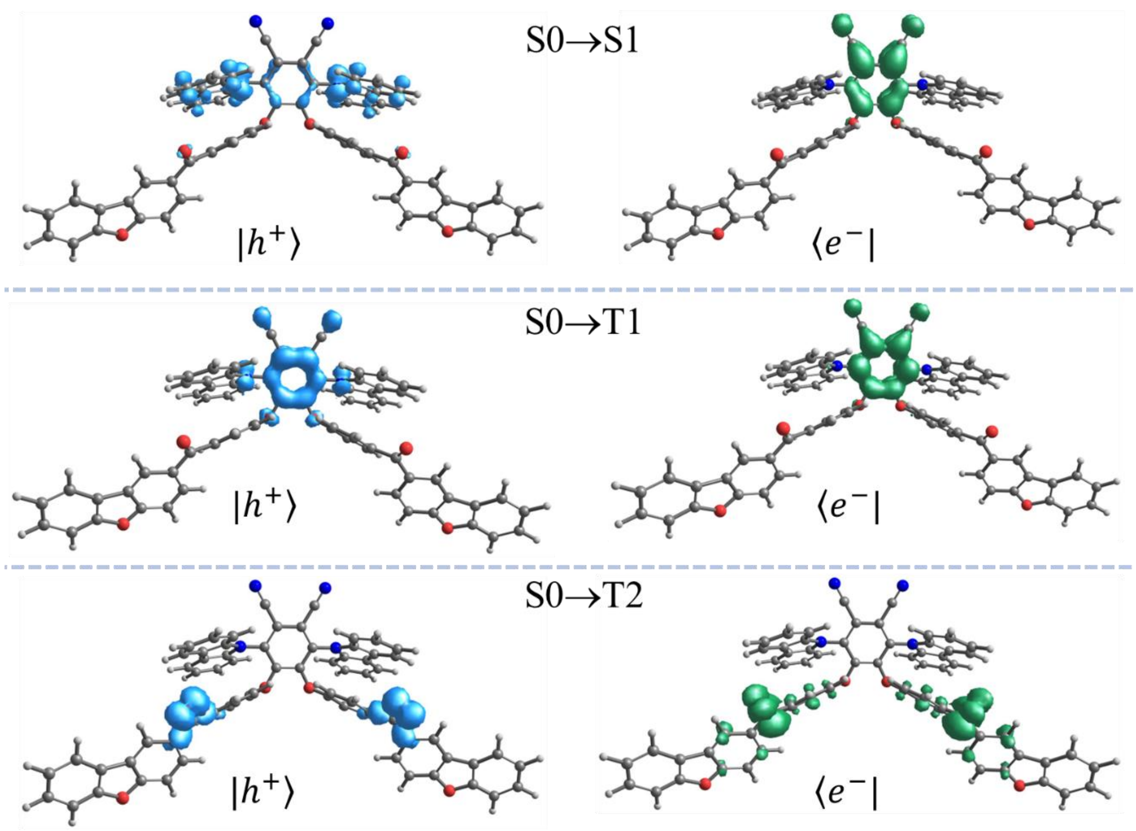


Fig S21. Hole–electron analysis (NTOs: |h+⟩, blue; ⟨e–|, green) for transition corresponding to the S1, T1 and T2 excited states of **CDBFPN** at isosurface values of ±0.002 au [M06-2X/6-31g(d,p)].

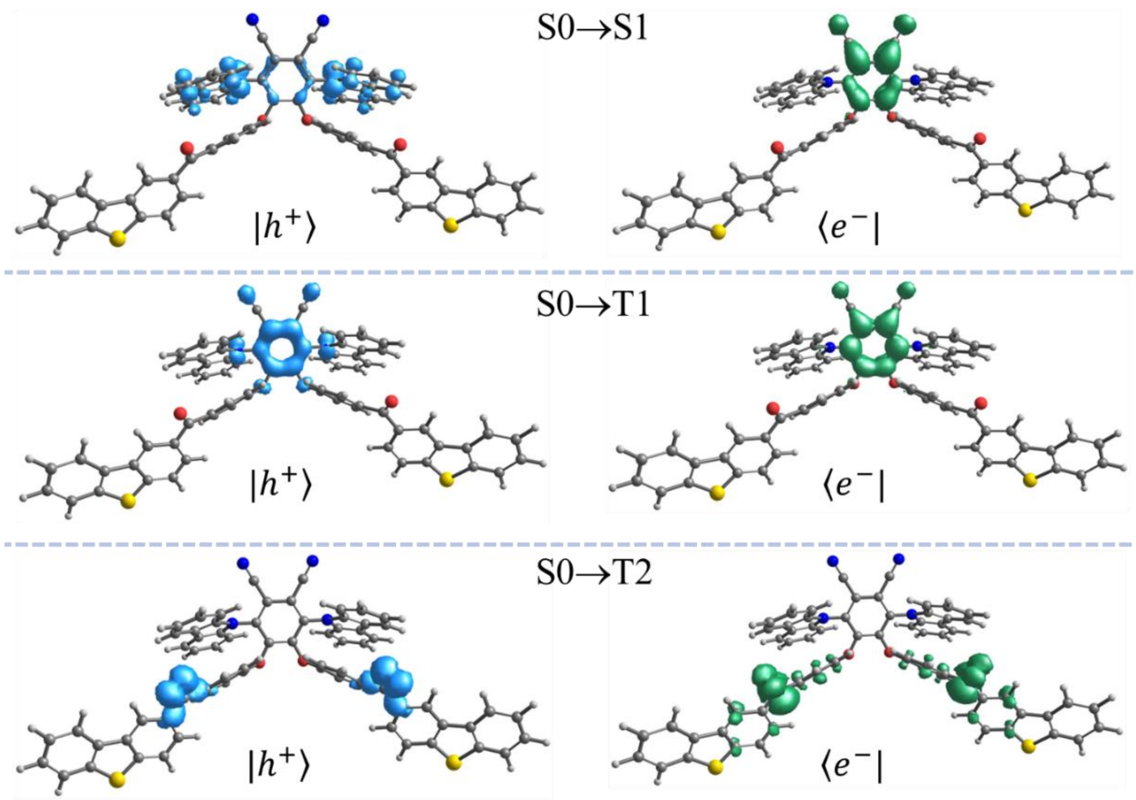


Fig S21. Hole–electron analysis (NTOs: |h+⟩, blue; ⟨e–|, green) for transition corresponding to the S1, T1 and T2 excited states of **CDBTPN** at isosurface values of ±0.002 au [M06-2X/6-31g(d,p)].

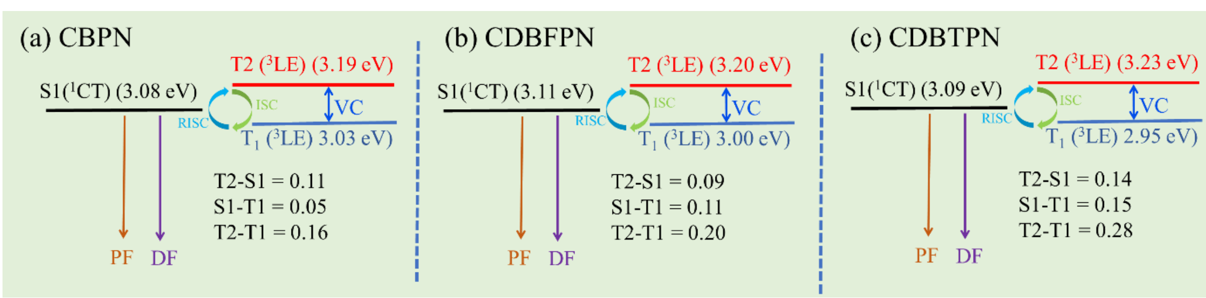


Fig S22. Theoretical energy diagram based on a four-state model of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN**. Calculated at M062X/6-31G(d,p) level of theory.

S6. Photophysical studies in solution

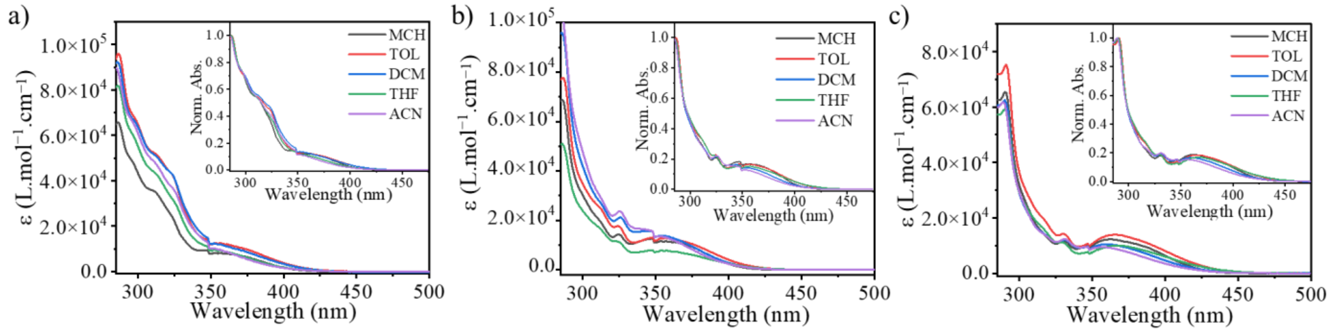


Fig S23. Solvent-dependent absorption spectra of (a) **CBPN**, (b) **CDBFPN** and (c) **CDBTPN** (concentration = 1.0×10^{-5} M). Inset showing normalized absorbance.

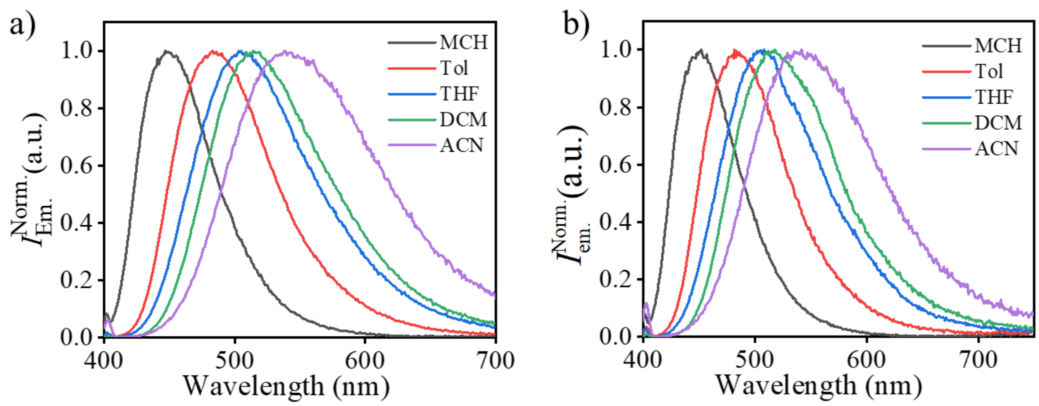


Fig S24. Solvent-dependent emission spectra of (a) **CDBFPN** and (b) **CDBTPN** (concentration = 1.0×10^{-5} M). Inset showing normalized absorbance.

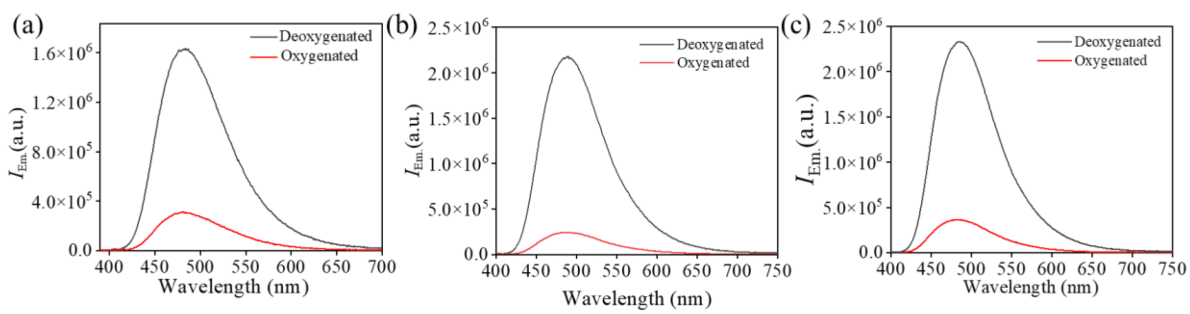


Fig S25. Emission spectra of (a) **CBPN**, (b) **CDBFPN** and (c) **CDBTPN** in toluene under oxygenated and deoxygenated conditions (λ_{ex} = 370 nm).

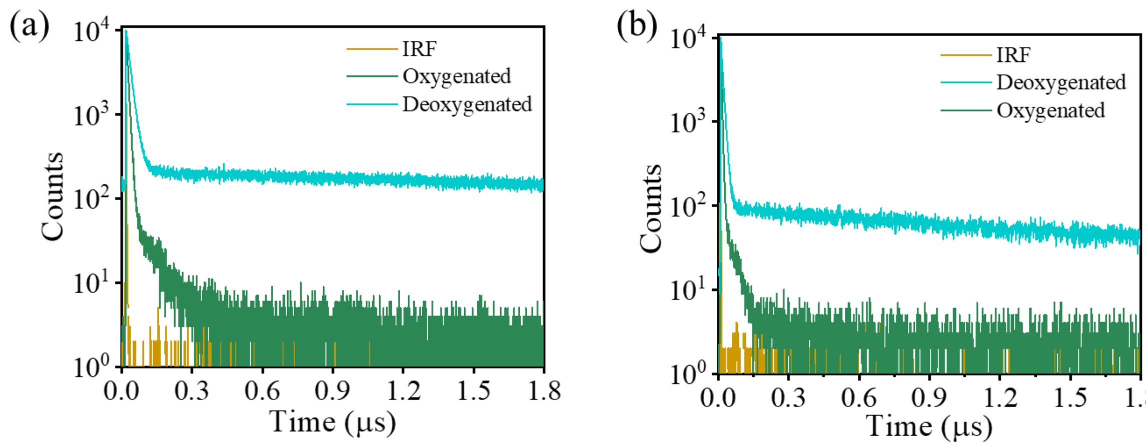


Fig S26. Fluorescence lifetime analysis of (a) **CDBFPN** and (b) **CDBTPN** in toluene under oxygenated and deoxygenated conditions (λ_{ex} = 370 nm).

Table S6. The fluorescence lifetime data under different condition in toluene.

Sample	Condition (λ_{ex} = 370 nm)	τ_1 (ns)	A1 (%)	τ_2 (μs)	A2 (%)
CBPN	Deoxygenated	19.06	39.30	4.6	60.70
	Oxygenated	7.10	93.34	0.077	6.06
CDBFPN	Deoxygenated	18.7	32.43	5.17	67.57
	Oxygenated	7.6	93.33	0.089	6.67
CDBTPN	Deoxygenated	19.1	42.08	3.6	57.92
	Oxygenated	6.26	93.11	0.066	06.89

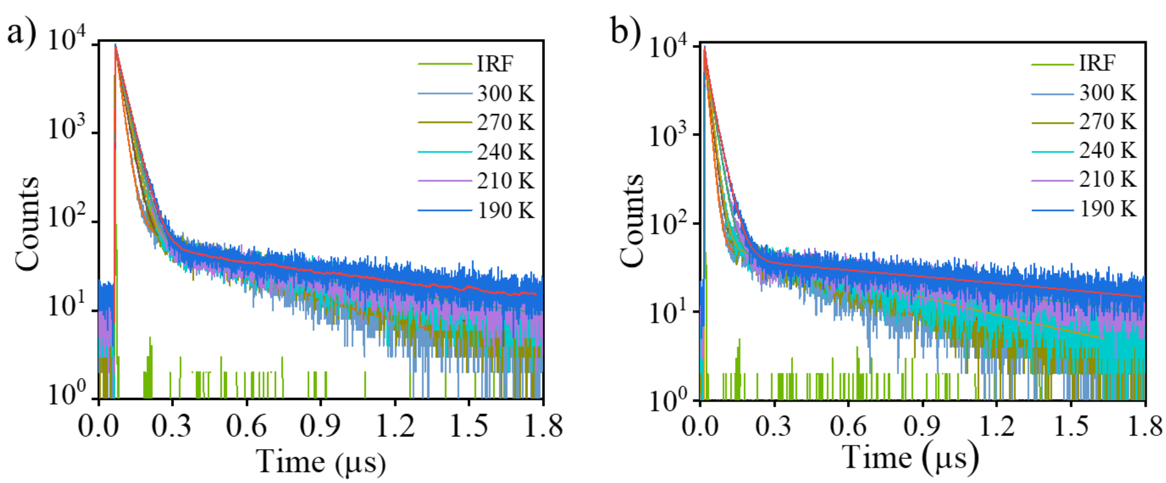


Fig S27. Temperature-dependent fluorescence lifetime decays of (a) **CDBFPN** and (b) **CDBTPN** in toluene at ambient aerated conditions (λ_{ex} = 370 nm).

Table S7. Temperature-dependent fluorescence lifetime data in toluene under ambient aerated conditions*

T (K) (λ_{ex} = 370 nm)	CBPN (λ_{em} = 480 nm)			CDBFPN (λ_{em} = 482 nm)			CDBTPN (λ_{em} = 486 nm)		
	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	χ^2	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	χ^2	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	χ^2
300	14.1 ns (84.45%)	0.37μs (15.55%)	1.196	20.0 ns (84.77%)	0.36 μs (15.23%)	1.164	14.18 ns (83.19%)	0.42 μs (16.81%)	1.394
270	6.2 ns (84.74%)	0.52 μs (15.26%)	1.088	26.6 ns (86.50%)	0.57 μs (13.50%)	1.137	16.3 ns (84.19%)	0.51 μs (15.81%)	1.171
240	17.5 ns (85%)	0.58 μs (15.00%)	1.161	29.9 ns (87.75%)	0.69 μs (12.25%)	1.147	17.9 ns (84.16%)	0.60 μs (15.84%)	1.141
210	21.0 ns (84.85%)	0.80 μs (15.15%)	1.197	33.0 ns (88.00%)	0.72 μs (12.00%)	1.122	18.8 ns (86.63%)	0.56 μs (13.37%)	1.223
190	26.0 ns (85.01%)	1.08 μs (14.99%)	1.196	36.1 ns (90.00%)	0.78 μs (10.00%)	1.442	23.7 ns (86.96%)	0.90 μs (13.04%)	1.285

Lifetimes (τ) are determined from the fitting function of $I(\tau) = A_{PF}e^{-t/\tau PF} + A_{DF}e^{-t/\tau DF}$; A_{PF} and A_{DF} are the pre-exponential factors.

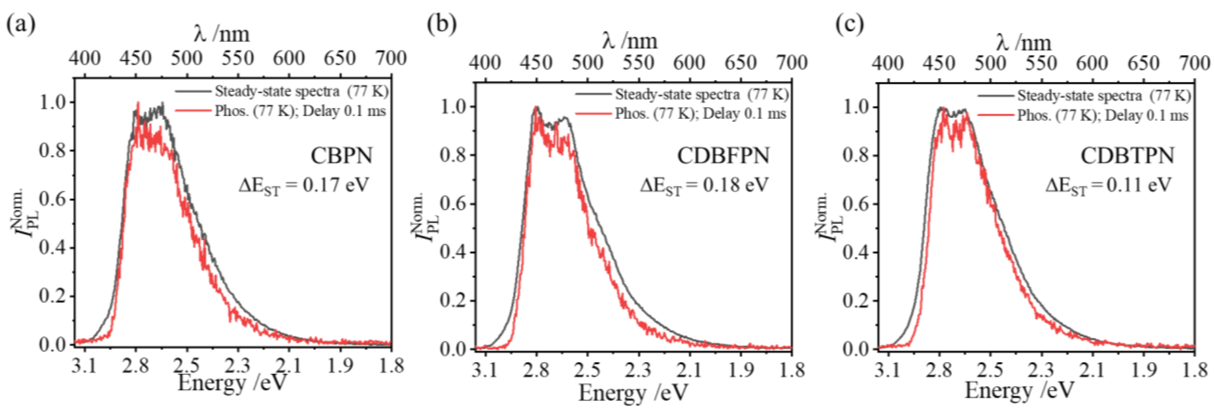


Fig S28. Steady-state emission and phosphorescence spectra of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN** in toluene at 77 K.

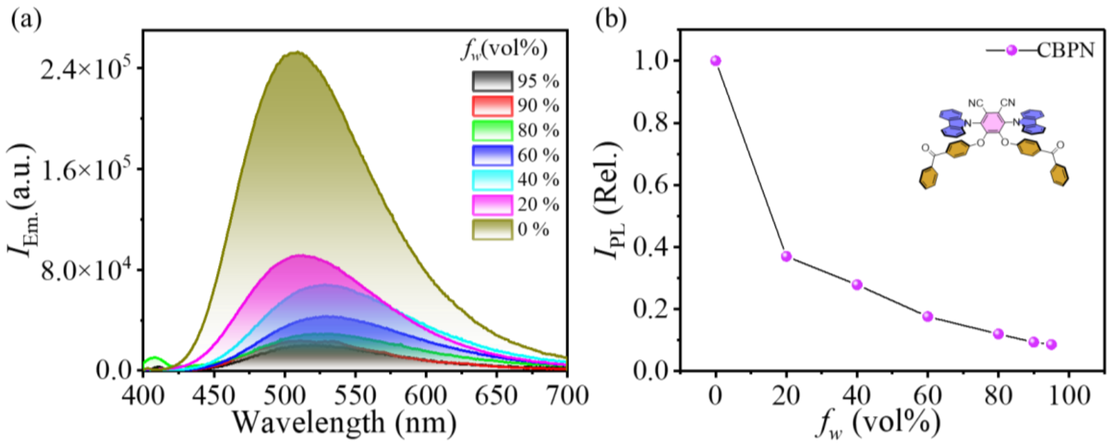


Fig S29. (a) PL spectra of **CBPN** in THF/water mixtures with different water fractions (f_w). (b) Relative PL intensities **CBPN** at different water fractions (f_w). Photos of **CBPN** in THF/water mixtures (f_w = 0% →95%), taken under 365 nm excitation.

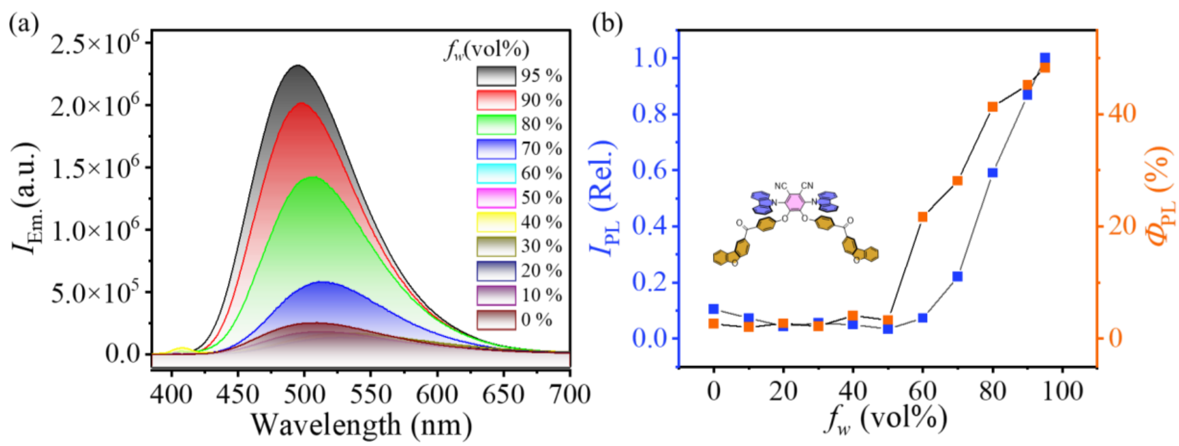


Fig S30. (a) PL spectra of **CDBFPN** in THF/water mixtures with different water fractions (f_w). (b) Relative PL intensities and PLQYs of **CDBFPN** at different water fractions (f_w); Inset: Photos of **CDBFPN** in THF/water mixtures (f_w = 0% →95%), taken under 365 nm excitation.

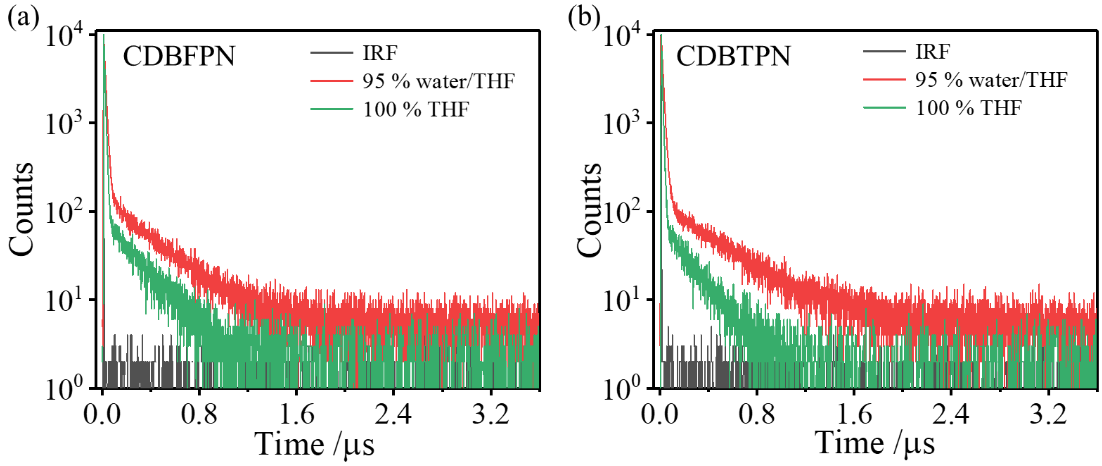


Fig S31. Fluorescence lifetime analysis of (a) **CDBFPN** and (b) **CDBTPN** in THF and aggregated state (95 % water/THF).

Table S8. The fluorescence lifetime data in aggregated state and pure THF.

Sample	Condition (λ_{ex} = 370 nm)	τ_{PF} (ns)	A_{PF} (%)	τ_{DF} (μs)	A_{DF} (%)
CDBFPN	100% THF	16.72	89.72	0.29	10.28
	95% water/ THF	19.5	70.01	0.56	29.99
CDBTPN	100% THF	13.0	87.23	0.36	12.77
	95% water/ THF	23.6	77.55	0.65	28.45

S7. Photophysical studies in films

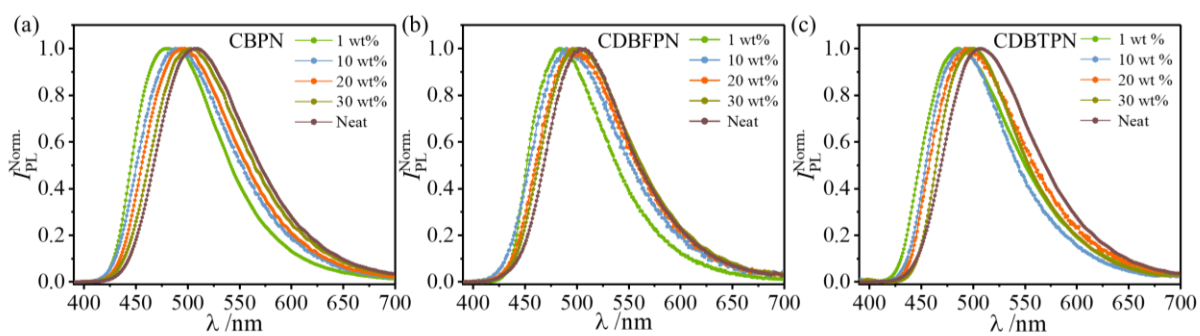


Fig S32. (a) PL spectra of various ratios of (a) **CBPN**, (b) **CDBFPN**, and (c) **CDBTPN** in mCP and in neat film.

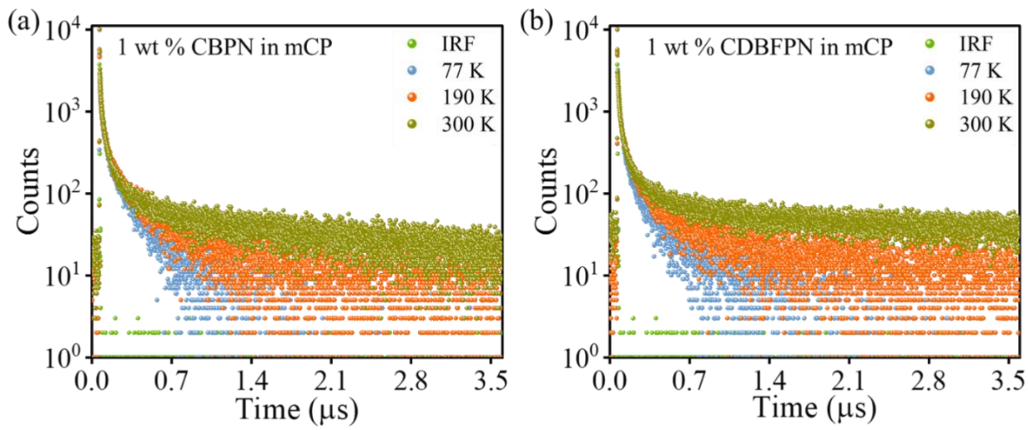


Fig S33. Temperature-dependent PL decays of (a) **CBPN**, and (b) **CDBFPN** (1 wt% in mCP).

Table S9. Temperature-dependent PL lifetime data of 1 wt.% film in mCP.

T (K) (λ_{ex} = 370 nm)	**CBPN** (λ_{em} = 480 nm)		**CDBFPN** (λ_{em} = 489 nm)		**CDBTPN** (λ_{em} = 486 nm)	
	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})
300	15.6 ns (80.08%)	0.36 μs (19.92%)	18.4 ns (78.68%)	0.43 μs (21.32%)	16.3 ns 79.48%)	0.58 μs (20.52%)
190	16.4 ns (81.10%)	0.15 μs (18.90%)	13.4 ns (79.20%)	0.21 μs (19.80%)	15.8 ns (84.13%)	0.19 μs (15.87%)
77	11.4 ns (85.0%)	61.4 ns (15.0%)	12.6 ns (88.32%)	40.2 ns (11.68%)	10.4 ns (83.96%)	59.3 ns (16.04%)
Lifetimes (τ) are determined from the fitting function of $I(\tau) = A_{PF}e^{-t/\tau PF} + A_{DF}e^{-t/\tau DF}$; A_{PF} and A_{DF} are the pre-exponential factors.						

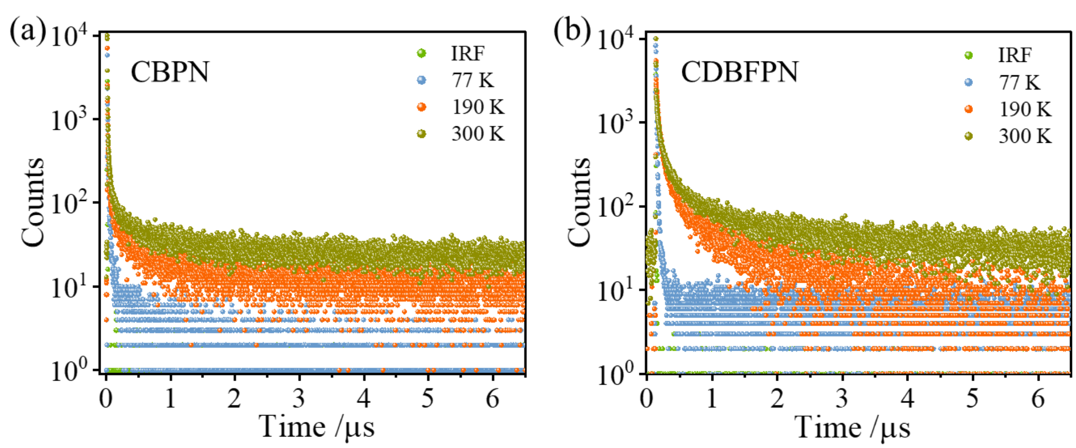


Fig S34. Temperature-dependent PL decay curve of neat film (a) **CBPN**, and (b) **CDBFPN**.

Table S10. Temperature-dependent PL lifetime data of neat film.

T (K) (λ_{ex} = 370 nm)	**CBPN** (λ_{em} = 506 nm)		**CDBFPN** (λ_{em} = 508 nm)		**CDBTPN** (λ_{em} = 509 nm)	
	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})	τ_{PF} (A_{PF})	τ_{DF} (A_{DF})
300	21.2 ns (77.44%)	0.81 μs (22.56%)	34.9 ns (75.38%)	1.03 μs (24.62%)	31.4 ns (73.14%)	0.97 μs (26.86%)
190	23.7 ns (80.46%)	0.27 μs (19.54%)	33.0 ns (77.92%)	0.43 μs (22.08%)	18.8 ns (79.33%)	0.39 μs (20.67%)
77	19.0 ns (85.95%)	31.6 ns (14.05%)	11.2 ns (90.00%)	38.2 ns (10.00%)	14.3 ns (90.22%)	24.5 ns (9.75%)

Lifetimes (τ) are determined from the fitting function of $I(\tau) = A_{PF}e^{-t/\tau PF} + A_{DF}e^{-t/\tau DF}$; A_{PF} and A_{DF} are the pre-exponential factors.

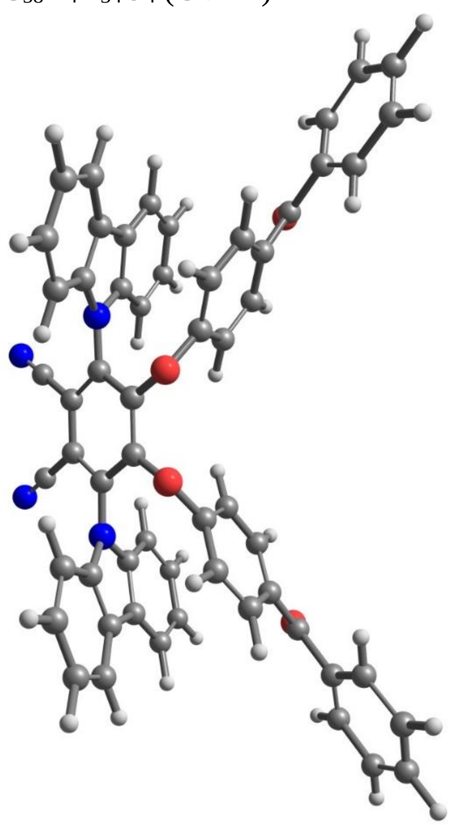
Table S11. Photoluminescence quantum yields (PLQY) and rate parameters at RT.

	CBPN		**CDBFPN**		**CDBTPN**	
Parameters	1 wt%	Neat film	1 wt%	Neat film	1 wt%	Neat film
Φ_{DF}/Φ_{PF}	5.68	11.13	6.33	9.63	9.18	11.34
$^{b}\Phi_{F}$	34.2±0.9	32.10±1.2	37.3±1.1	67.2±2.4	38.5±1.2	70.3±2.3
$^{b}\Phi_{PF}$	5.11±0.2	2.67±0.2	5.08±0.2	6.32±0.3	3.78±0.2	5.69±0.3
$^{b}\Phi_{DF}$	29.09±0.5	29.45±0.5	32.21±0.5	60.86±2.0	34.71±0.5	64.60±2.0
$^{b}\Phi_{ISC}$	85.05±2.4	94.6±2.5	86.35±2.2	90.5±2.4	90.17±2.0	91.8±2.2
k_r^{PF} (× 10^6) (s^{-1})	3.27	1.25	2.76	1.81	2.31	1.79
k_{nr}^{PF} (× 10^7) (s^{-1})	6.07	4.52	5.15	2.83	5.80	2.96
k_{ISC} (× 10^7) (s^{-1})	5.45	4.46	4.69	2.59	5.53	2.92
k_{rISC} (× 10^7) (s^{-1})	1.85	1.48	1.70	1.03	1.75	1.27

λ_{ex} = 370 nm; [b]values are in %.

S8. Optimized Coordinates

$C_{58}N_4H_{34}O_4$ (**CBPN**)



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6	0.702957724	-3.227433224	-0.706783840
6	1.412934900	-2.269371034	0.026894634
7	2.815925765	-2.288916317	0.053202144
7	-2.816076533	-2.288401983	0.053477832
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8	1.322853819	-0.301329627	1.435358468
6	3.640267505	-1.874447677	-1.007081800
6	4.931490553	-1.629639492	-0.505473272
6	4.899792052	-1.926560772	0.914519761
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6	-3.578356746	-2.299203909	1.226481227
6	-4.899829418	-1.925730551	0.914951120
6	-4.931580777	-1.628758661	-0.505028239
6	-3.640422882	-1.873713941	-1.006735390
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6	-5.453977541	-2.127348904	3.239062857
6	-5.846343050	-1.845641998	1.936641297
6	-5.909820242	-1.108882300	-1.355266872
6	-5.580614155	-0.850011928	-2.677747399
6	-4.294035558	-1.126102331	-3.162312111
6	-3.304672454	-1.646071896	-2.337811035
6	5.846387713	-1.846599613	1.936140225
6	5.454063955	-2.128198805	3.238600314
6	4.130614379	-2.492236524	3.527494494
6	3.171739404	-2.586504260	2.525624974
6	3.304444045	-1.646792116	-2.338140020
6	4.293804107	-1.126942643	-3.162719757
6	5.580437251	-0.850950894	-2.678242042
6	5.909713507	-1.109853097	-1.355786826
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6	2.295471273	0.462360604	0.803911170
6	-3.408600733	0.809069494	1.559029832
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6	-3.184641211	1.587408660	-1.112939279
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6	2.157207809	0.869612870	-0.519986313
6	3.185630973	1.586929416	-1.112938110
6	4.322351018	1.937405789	-0.379686836
6	4.419439221	1.551626954	0.961827281

	6	3.409119200	0.808491903	1.559046665
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	6	-5.438473071	2.614320145	-1.112867105
	6	-6.407320412	3.483403827	-0.369133760
	6	7.696615588	3.615981212	-0.893220938
	6	8.624139266	4.440331694	-0.270121905
	6	8.261942840	5.159221474	0.868713268
	6	6.971652388	5.053080456	1.380378328
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	1	-6.319030204	-0.418262532	-3.343421797
	1	-4.062532519	-0.922004344	-4.202258861
	1	-2.306014817	-1.844207357	-2.714070913
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	1	6.177938532	-2.068693352	4.044124982
	1	3.848204948	-2.708088385	4.552524753
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	1	2.305737930	-1.844823007	-2.714324548
	1	4.062255632	-0.922860373	-4.202660390
	1	6.318849755	-0.419257792	-3.343954255
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	1	-3.135115433	1.867200251	-2.159815018
	1	-1.277923098	0.583970955	-1.089923070
	1	1.278791986	0.583705535	-1.090214900
	1	3.136302800	1.866675201	-2.159836259
	1	5.314383440	1.781792498	1.530732385
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	1	7.946290410	3.064292265	-1.793592775

	1	9.627529234	4.530281163	-0.673142968
	1	8.984648199	5.808476767	1.352581483
	1	6.683896277	5.626876047	2.255098451
	1	5.035455668	4.142864488	1.157687841
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	1	-9.628414442	4.526654447	-0.673832718
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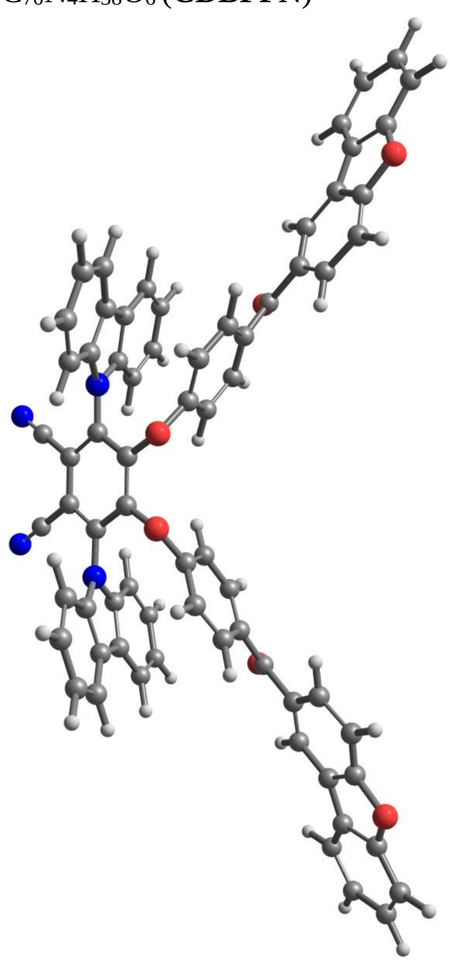	6	-0.699970471	-2.285659729	0.745915333
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	6	4.926509603	-2.635967045	-0.488818725
	6	4.900060308	-2.926986253	0.932563721
	6	3.581268803	-3.305363163	1.249348490
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	6	-4.927464175	-2.633671882	-0.486805866
	6	-3.636430669	-2.887354036	-0.984404629
	6	-3.179481325	-3.586295670	2.552450402
	6	-4.140092769	-3.482620570	3.551747762
	6	-5.461027346	-3.113138151	3.258246263
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	6	5.848957715	-2.837763328	1.951289813
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	6	-4.311069001	0.940732408	-0.355956761
	6	-3.180036427	0.578153297	-1.091832431
	6	-2.155097128	-0.145260312	-0.499754660
	6	2.156795056	-0.146805561	-0.500268728
	6	3.182011612	0.576367699	-1.092169416
	6	4.312878782	0.938903556	-0.356014207
	6	4.409580410	0.555332353	0.986160560
	6	3.403443245	-0.194441697	1.582050746
	6	5.426295961	1.625680558	-1.086063531
	6	6.358321404	2.536387576	-0.348992654
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	6	7.634848326	2.712573723	-0.887062945
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	6	-8.088967920	4.272100558	0.893571476
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	8	-5.574156922	1.434565078	-2.279544625
	8	5.577158362	1.431755824	-2.279079214
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	6	-12.106402642	4.375352591	-1.280015444
	6	-10.879915990	3.735735362	-1.409753423
	6	9.884755786	4.015509643	-0.471535252
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	6	12.106675962	4.377917238	-1.278678224
	6	12.343640052	5.282481900	-0.233773155
	6	11.364765384	5.574222434	0.710560202
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	6	-1.427058693	-5.261886141	-1.386815859
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	1	-2.156039762	-3.867773124	2.778347841

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	1	-6.301551639	-1.426892034	-3.333091384
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	1	6.870657692	-2.547530472	1.726414909
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	1	6.299742329	-1.429718343	-3.335726237
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	1	-1.280388297	-0.438833846	-1.071800924
	1	1.282257769	-0.440395520	-1.072571242
	1	3.133615961	0.852132907	-2.140181775
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	1	3.488434371	-0.560376465	2.600080482
	1	7.904574520	2.172354974	-1.788675406
	1	6.518437898	4.707306744	2.305411190
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	1	-4.948544655	3.134786549	1.171520799
	1	-6.519174777	4.708157375	2.305325352
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	1	-11.532592202	6.268525528	1.522353636
	1	-13.312290963	5.763491197	-0.160677462
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	1	-10.698364695	3.037265437	-2.220062022
	1	10.699761035	3.038752520	-2.218872522
	1	12.894980938	4.177142849	-1.995895650
	1	13.311370459	5.767010808	-0.159238020
	1	11.530949530	6.271037373	1.523332974

$C_{70}N_4H_{38}S_2O_4$ (**CDBTPN**)	6	-0.699968598	-2.388187799	-0.762637128
	6	0.699991532	-2.388364492	-0.762548692
	6	1.412920247	-3.385642368	-0.068885981
	6	0.702828832	-4.344248997	0.664015893
	6	-0.703486642	-4.344074680	0.663919630
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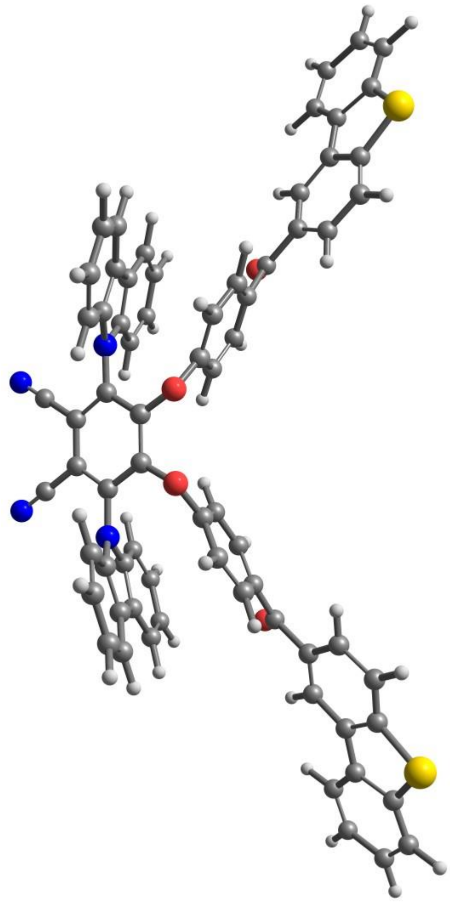
	7	-2.816267513	-3.402595794	-0.092879083



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6	-4.927901567	-2.735005356	0.471045900
6	-4.900480385	-3.030370919	-0.949412952
6	-3.581244927	-3.408728916	-1.264316152
6	3.581120597	-3.409433727	-1.263779614
6	4.900329395	-3.031179507	-0.948650498
6	4.927539313	-2.735853093	0.471822712
6	3.636203932	-2.986623640	0.970181334
6	3.178732804	-3.696132409	-2.564528963
6	4.139518707	-3.596556062	-3.564070903
6	5.460796678	-3.227417534	-3.271670595
6	5.848997297	-2.945976329	-1.967947773
6	5.901572010	-2.213040168	1.324981333
6	5.568118375	-1.957059379	2.646980811
6	4.281581832	-2.238824790	3.128164933
6	3.296238221	-2.761647451	2.300616532
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6	-5.460575164	-3.226614105	-3.272523507
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6	-3.296900348	-2.760855596	2.300106283
6	-4.282346800	-2.237959035	3.127483257
6	-5.568792917	-1.956140399	2.646085930
6	-5.902046152	-2.212125597	1.324037726
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