Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Controllable construction of red thermally activated delayed fluorescence molecules based on spiro-acridine donor

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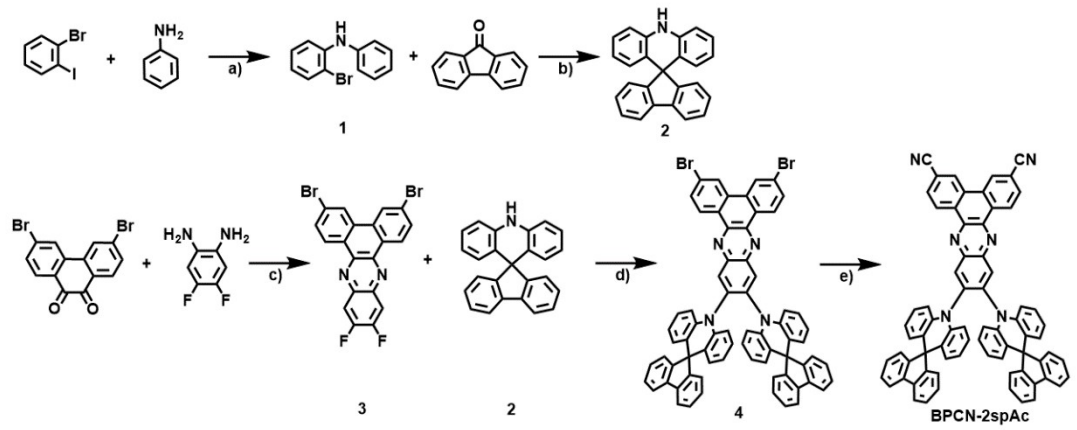

Schme S1. Synthetic procedures of **BPCN-2spAc**: a) $Pd_2(dba)_3$, DPPF, t-BuONa, Tol, 100 ^oC, 12 h; b) n-BuLi, -78 ^oC, 4h; RT, 12 h; $MeSO_3H$, $CHCl_3$, 12 h; c)/i) AcOH, 120 ^oC, 12 h; d) NaH, 80 ^oC, 12 h; e)/j) CuCN, NMP, 180 ^oC, 6 h; f) Na_2CO_3, 2-nitropropane, H_2O : CH_3CN = 1 : 1, 80 ^oC, 4 h; g) $Pd_2(dba)_3$, $P(t\text{-}Bu)_3H\ BF_4$, t-BuONa, Tol, 120 ^oC, 12 h; h) TsOH, Tol, 100 ^oC, 4h.

2-bromo-N-phenylaniline (1)

A mixture of aniline (4 g, 42.95 mmol), 1-bromo-2-iodobenzene (13.37 g, 47.2 mmol), t-BuONa (8.25 g, 85.90 mmol), $Pd_2(dba)_3$ (0.39g, 0.43 mmol) and DPPF (0.95g, 1.72 mmol) was dissolved in 80 mL dry toluene under nitrogen atmosphere. The reaction mixture was stirred at 100 ^oC for 12 h. After cooling to room temperature, the resulting solution was filtered through a Celite pad and removed the toluene, then extracted three with CH_2Cl_2. The oil liquid product (10.22 g) was obtained by column chromatography silica gel eluted with PE. Yield: 96.3 %. ^1H NMR (300 MHz, DMSO-d_6) δ 7.59 (d, J = 7.9 Hz, 1H), 7.51 (s, 1H), 7.27 – 7.19 (m, 4H), 7.04 (d, J = 7.9 Hz, 2H), 6.91 – 6.82 (m, 2H).

10H-spiro[acridine-9,9'-fluorene] (2)

Compound 1 (4 g, 16.20 mmol) was added to 160 mL dry THF in flask and cooled to -78 ^oC under nitrogen atmosphere. A stirred solution was slowly added a solution of n-BuLi (22.3 mL, 35.63 mmol, 1.6 M in hexane) via syringe, and then reacted 4 hours

at this temperature. 9H-fluoren-9-one (3.5 g, 19.44 mmol) was quickly added to the solution for 30 minutes, then reacted 12 hours at room temperature. The reaction mixture was quenched by adding of 100 ml ice water. The THF was removed from the mixture, extracted three with CH_2Cl_2, and dried by Na_2SO_4. The dark oil was got and dissolved in 100 mL $CHCl_3$, and methanesulfonic acid (1.2 mL, 17.82 mmol) was added at 65 ^oC for overnight. The resulting solution was cooled to room temperature and poured into $NaHCO_3$ aqueous solution to neutralize the acid, then extracted three with CH_2Cl_2. The crude product was purified by column chromatography silica gel eluted with PE/DCM (6/1, v/v) as a white solid (2.33 g). Yield: 43.47 %. ^1H NMR (300 MHz, DMSO-d_6) δ 9.24 (s, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 7.26 – 7.14 (m, 4H), 6.99 (dd, J = 21.0, 7.6 Hz, 4H), 6.48 (t, J = 7.4 Hz, 2H), 6.10 (d, J = 7.8 Hz, 2H).

3,6-dibromo-11,12-difluorodibenzo[a,c]phenazine (3)

3,6-dibromophenanthrene-9,10-dione (0.89 g, 2.43mmol) and 4,5-difluorobenzene- -1,2-diamine (0.35 g, 2.43mmol) were suspended in AcOH (30 mL) and heated at 120 ^oC overnight under nitrogen. The crude product was washed with water, then extracted three with CH_2Cl_2 and recrystallized from ethanol as a orange solid (0.85 g). Purple solid (Yield: 73.86 %). ^1H NMR (400 MHz, $C_6D_4Cl_2$) δ 9.28 (d, *J* = 8.5 Hz, 2H), 8.52 (s, 2H), 8.06 (t, *J* = 10.5 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H).

10,10''-(3,6-dibromodibenzo[a,c]phenazine-11,12-diyl)bis(10H-spiro[acridine-9,9'-fluorene]) (4)

Compound 3 (0.5 g, 1.06 mmol), Compound 2 (0.86 g 2.33 mmol) and NaH (112 mg, 4.66 mmol) were added to dry DMF (30 mL) under nitrogen, and then stirred at 80 ^oC for 12h. After reaction completed, the solvent was removed from the mixture, and then extracted three with CH_2Cl_2. The crude product was purified by column chromatography silica gel eluted with PE/DCM (4/1, v/v) as a red solid (84 mg). Yield: 7.24 %. MALDI-TOF-MS: m/z calcd for $C_{70}H_{40}Br_2N_4$: 1096.16, found: 1097.233.

BPCN-2spAc

Compound 4 (84 mg, 0.08mmol) and CuCN (18mg, 0.2 mmol) were suspended in 1-methyl-2-pyrrolidinone (20 mL). This reaction was carried out at 180 ^{o}C under microwave for 2 h. Removing the solvent by decompress distillation. The crude product was washed with aqueous solution of ferric chloride hexahydrate and then purified by column chromatography silica gel with PE/CH_2Cl_2 (3/2, v/v) to obtain red solid (431 mg). Yield: 50.61 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, J = 8.3 Hz, 2H), 9.07 (s, 2H), 8.95 (d, J = 1.5 Hz, 2H), 8.15 (dd, J = 8.4, 1.4 Hz, 2H), 7.82 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.51 – 7.33 (m, 6H), 6.97 – 6.89 (m, 4H), 6.88 – 6.73 (m, 6H), 6.59 (td, J = 7.5, 7.1, 1.1 Hz, 4H), 6.38 (dd, J = 7.8, 1.6 Hz, 4H), 5.91 (td, J = 7.5, 1.1 Hz, 2H). MALDI-TOF-MS: m/z calcd for $C_{72}H_{40}N_6$: 988.33, found: 987.358.

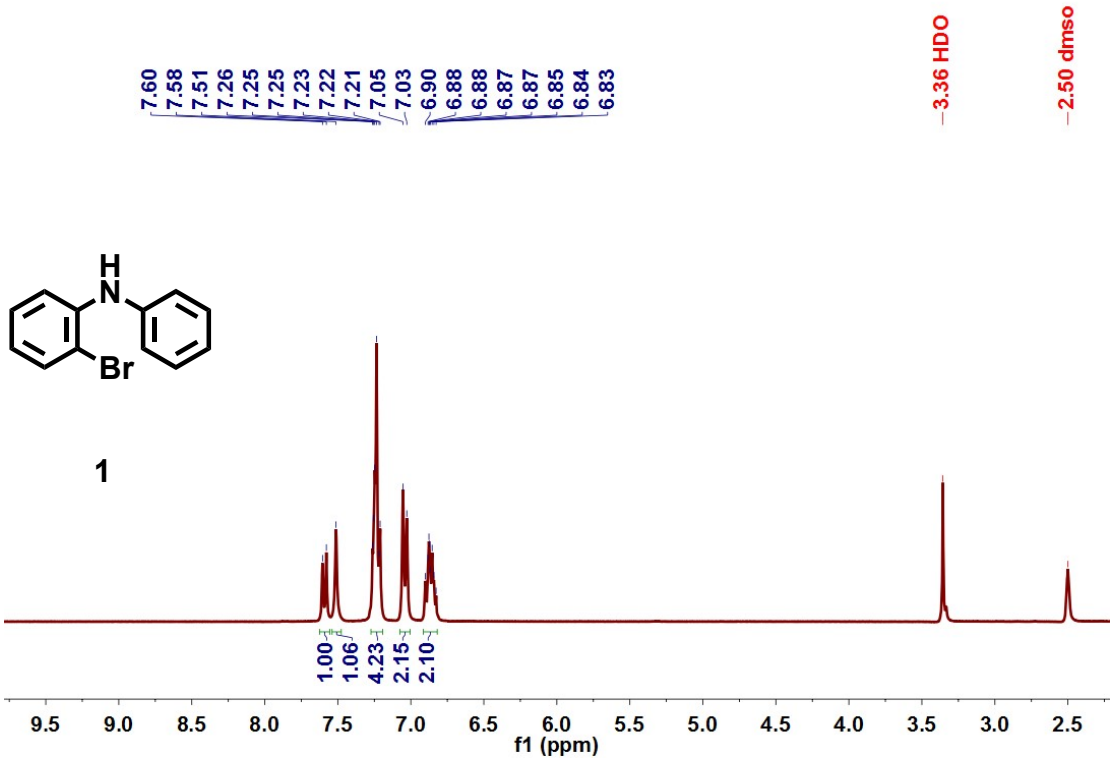

Figure S1 ^{1}H NMR spectrum (DMSO-d_6, 300 MHz) of compound 1.

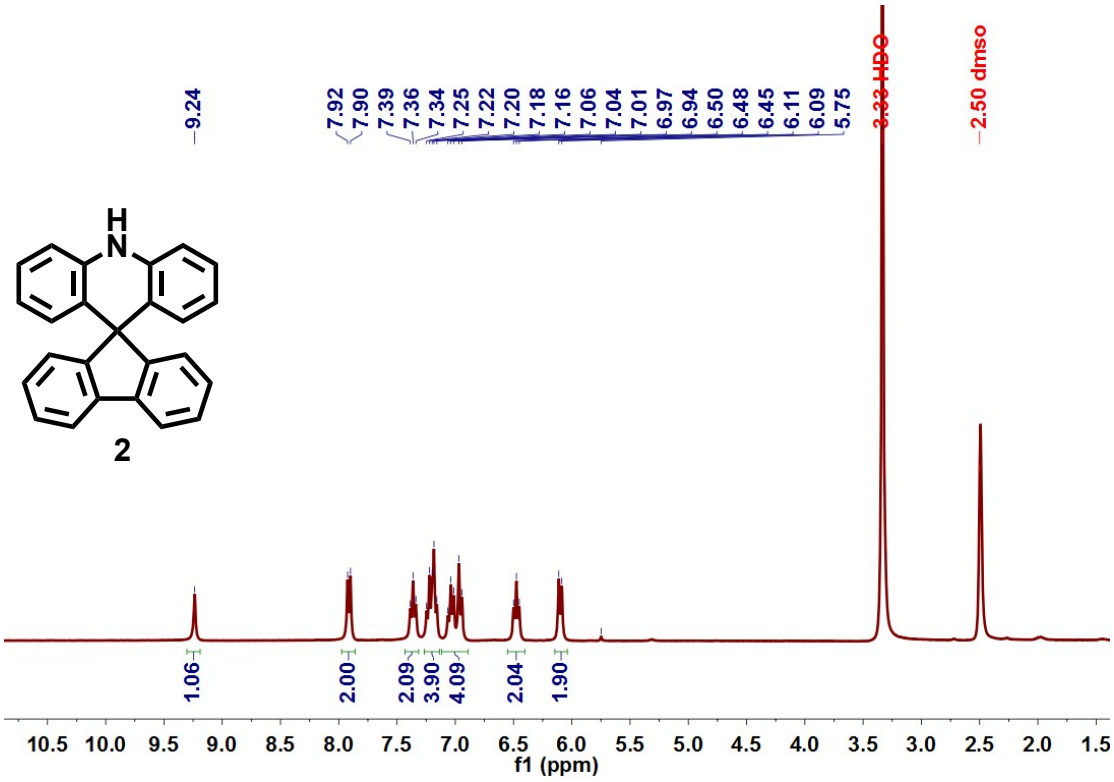

Figure S2 ^{1}H NMR spectrum (DMSO-d_6, 300 MHz) of compound 2.

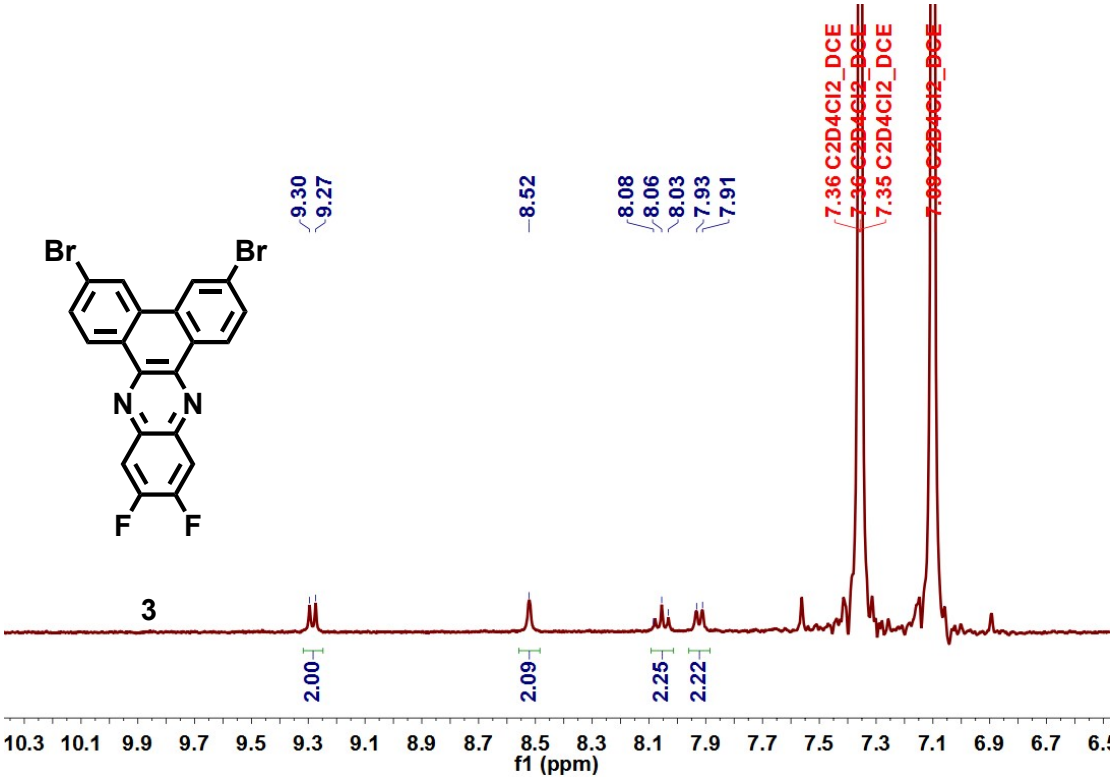

Figure S3 ^{1}H NMR spectrum ($C_2D_4Cl_2$, 400 MHz) of compound 3.

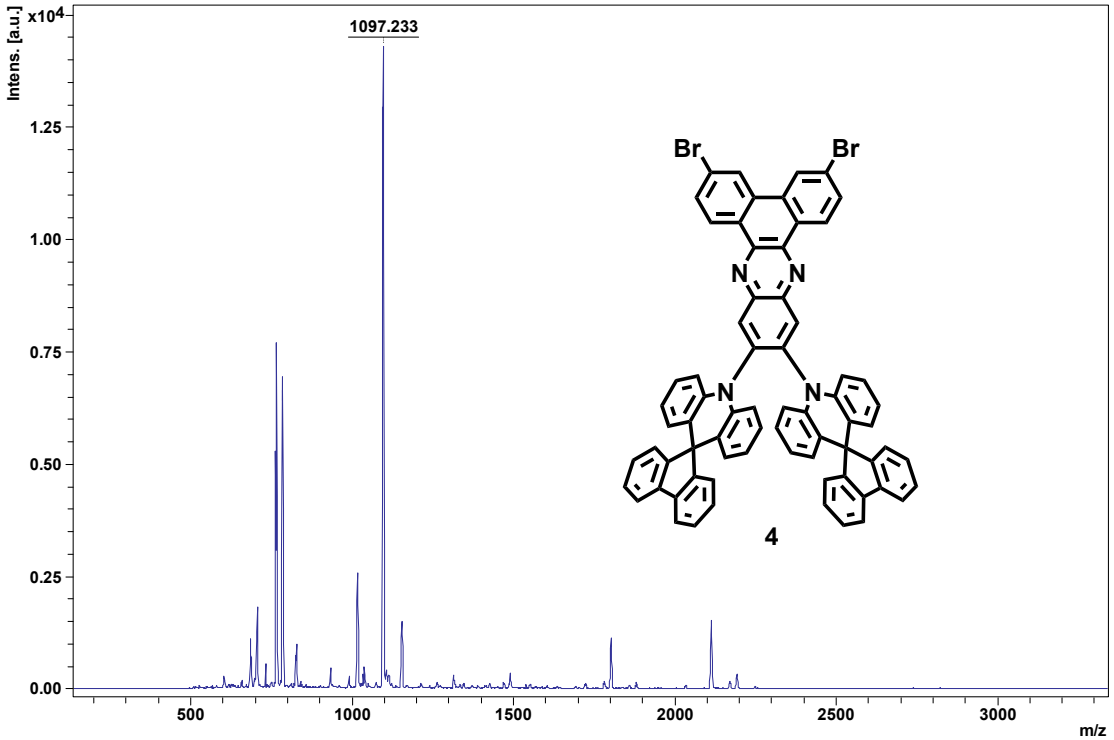

Figure S4 MALDI-TOF mass spectrum of BPCN-2spAc

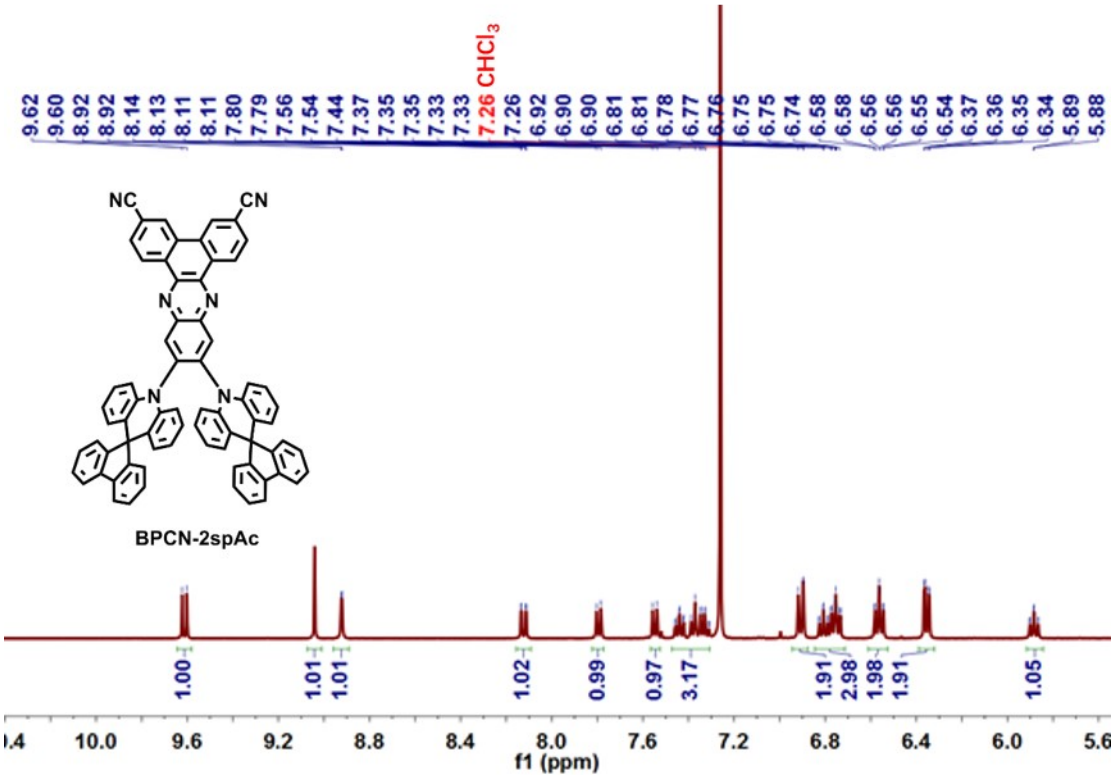

Figure S5 ^{1}H NMR spectrum ($CHCl_3$, 400 MHz) of BPCN-2spAc.

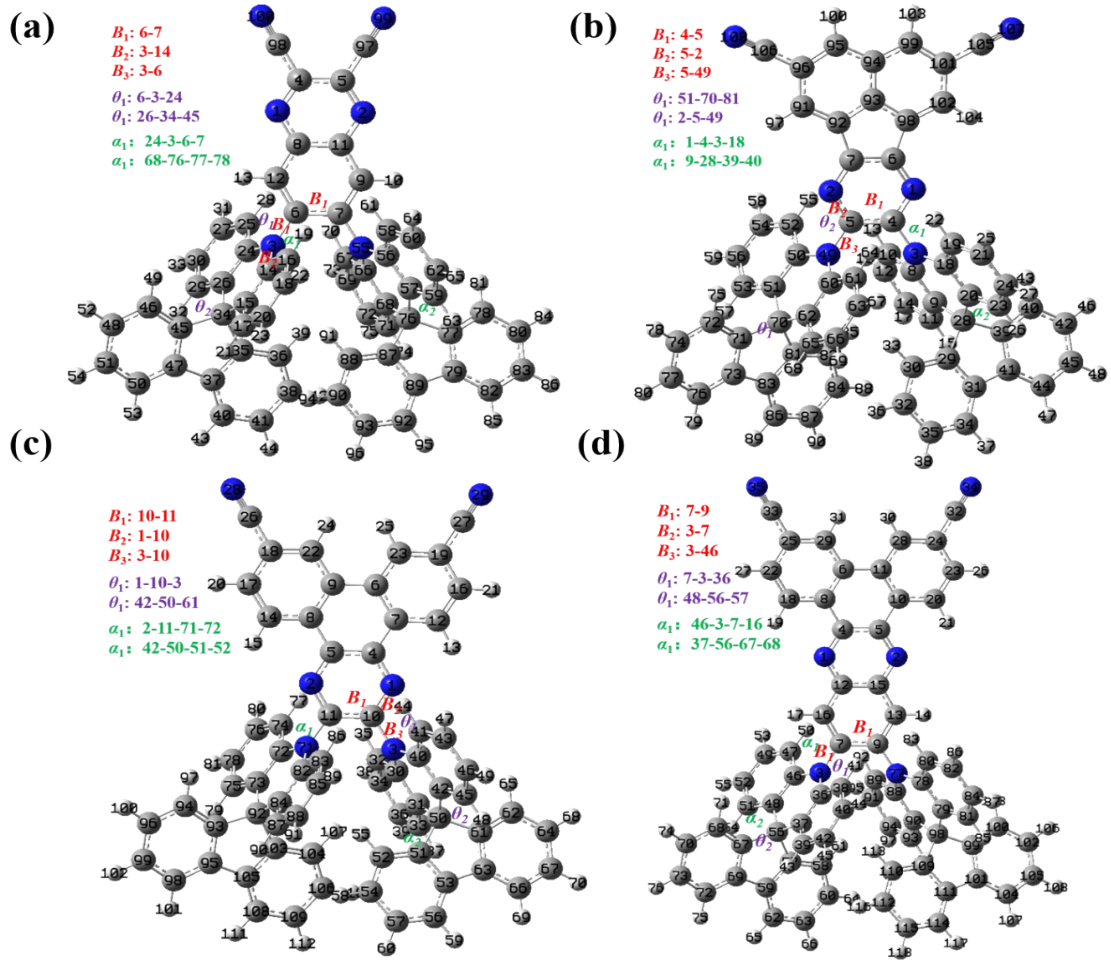

Figure S6. The atomic labels and the interesting bond lengths (B_1, B_2 and B_3), bond angles (θ_1 and θ_2) and the dihedral angles (α_1 and α_2) of (a) DQCN-2spAs, (b) TPCN-2spAs, (c) DPCN-2spAs and (d) BPCN-2spAs.

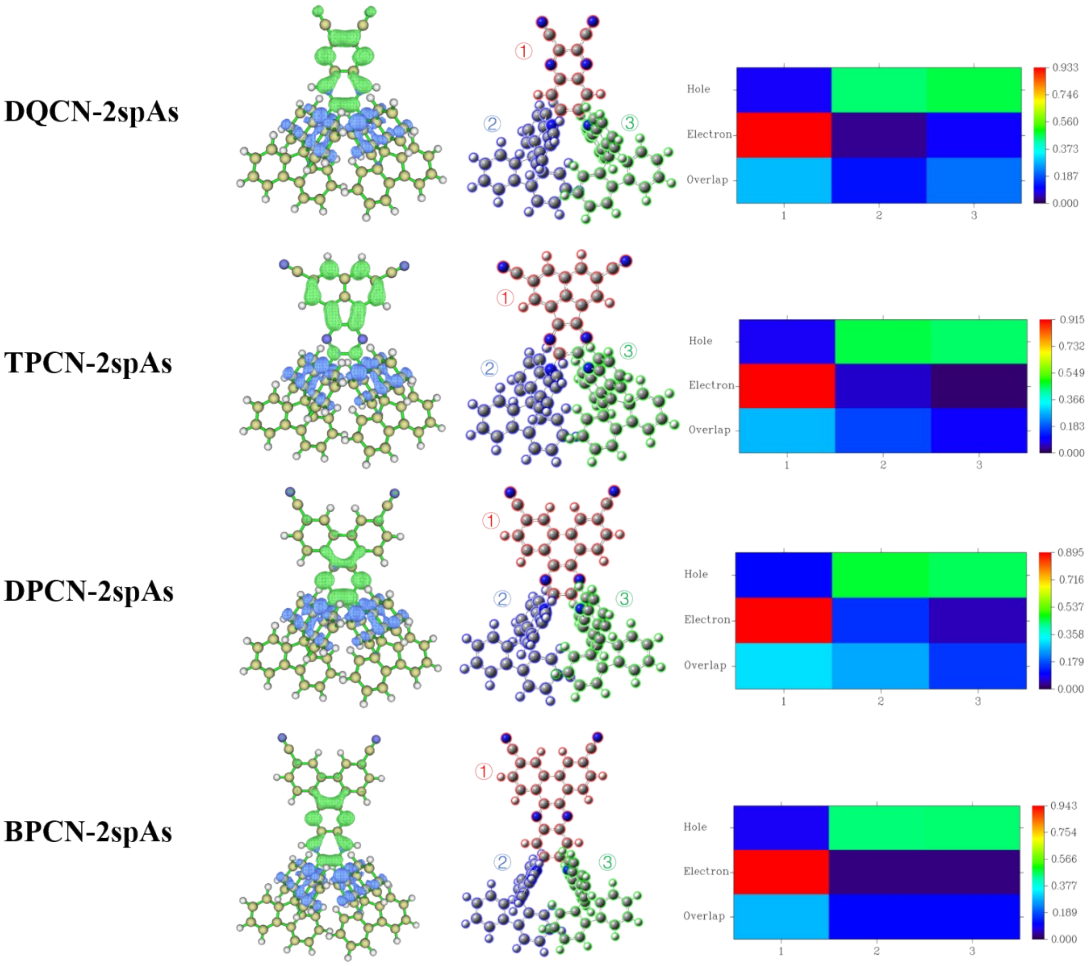

Figure S7. Isosurface distributions of holes and electrons and heat map of the S_1 state for DQCN-2spAs, TPCN-2spAs, DPCN-2spAs and BPCN-2spAs in toluene.

Table S1 Geometry parameters of S_0, S_1 and T_1 states for TPCN-2spA and their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta\|S_0 - S_1\|$	$\Delta\|S_1 - T_1\|$
Bond length	B_1	4-5	1.415	1.404	1.425	0.011	0.021
	B_2	5-2	1.330	1.320	1.319	0.010	0.001
	B_3	5-49	1.409	1.433	1.420	0.024	0.013
Bond angle	θ_1	51-70-81	110.597	110.928	110.926	0.331	0.002
	θ_2	2-5-49	116.583	116.546	116.455	0.037	0.091
Dihedral angle	α_1	1-4-3-18	59.829	71.814	62.056	11.985	9.758
	α_2	9-28-39-40	62.630	62.241	62.288	0.389	0.047

Table S2 Geometry parameters of S_0, S_1 and T_1 states for DPCN-2spA and their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta\|S_0 - S_1\|$	$\Delta\|S_1 - T_1\|$
Bond length	B_1	10-11	1.425	1.369	1.373	0.056	0.004
	B_2	1-10	1.310	1.339	1.340	0.029	0.001
	B_3	3-10	1.407	1.437	1.389	0.030	0.048
Bond angle	θ_1	1-10-3	117.493	115.803	115.591	1.690	0.212
	θ_2	42-50-61	111.359	110.823	110.853	0.536	0.030
Dihedral angle	α_1	2-11-71-72	58.880	73.929	68.701	15.049	5.228
	α_2	42-50-51-52	60.823	59.215	60.103	1.608	0.888

Table S3 Geometry parameters of S_0, S_1 and T_1 states for BPCN-2spA and their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta\|S_0 - S_1\|$	$\Delta\|S_1 - T_1\|$
Bond length	B_1	7-9	1.437	1.399	1.405	0.038	0.006
	B_2	3-7	1.417	1.445	1.417	0.028	0.028
	B_3	3-46	1.407	1.378	1.393	0.029	0.015
Bond angle	θ_1	7-3-36	119.193	120.404	120.125	1.211	0.279
	θ_2	48-56-57	110.428	110.087	109.942	0.341	0.145
Dihedral angle	α_1	46-3-7-16	62.398	74.532	60.983	12.134	13.549
	α_2	37-56-67-68	62.412	62.483	62.955	0.071	0.472