Supporting Information

Cyclic Boron Esterification: Screening Organic Room Temperature Phosphorescence and Mechanoluminescence Materials

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excited @ 310 nm) and DME (Luminescent peaks 363 nm, excited @ 320 nm) solution in THF at 298K.

Figure S11. The photofluorescence time-resolved emission decay curves of crystalline EE (Luminescent peaks 366 nm, excited @ 320 nm), IPE (Luminescent peaks 367 nm, excited @ 320 nm), TME (Luminescent peaks 366 nm, excited @ 320 nm), PE (Luminescent peaks 368 nm, excited @ 320 nm) and DME (Luminescent peaks 370 nm, excited @ 320 nm) powder at 298K.

3. Tables

Table S1a The singlet and triplet excited state transition configurations of the **EE** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

Table S1b The singlet and triplet excited state transition configurations of the **IPE** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

Table S1c The singlet and triplet excited state transition configurations of the **TME** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

Table S1d The singlet and triplet excited state transition configurations of the **PE** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

Table S1e The singlet and triplet excited state transition configurations of the **DME** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

Table S1f The singlet and triplet excited state transition configurations of the **NPC-BA** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

Table S2 Structure data of single crystals of **EE**, **IPE, TME**, **PE** and **DME.**

1. Experimental section

Materials

(4-(9H-carbazol-9-yl)phenyl)boronic acid, ethylene glycol, 1,2-propanediol, 1,3-propylenediol, neopentyl glycol, 2,3-dimethyl-2,3-butanediol and magnesium sulfate anhydrous ($MgSO_4$) were obtained from Energy Chemical Ltd. Shanghai, China, and used without further purification. The other solvents were of analytical grade and are obtained commercially from available resources.

Measurements

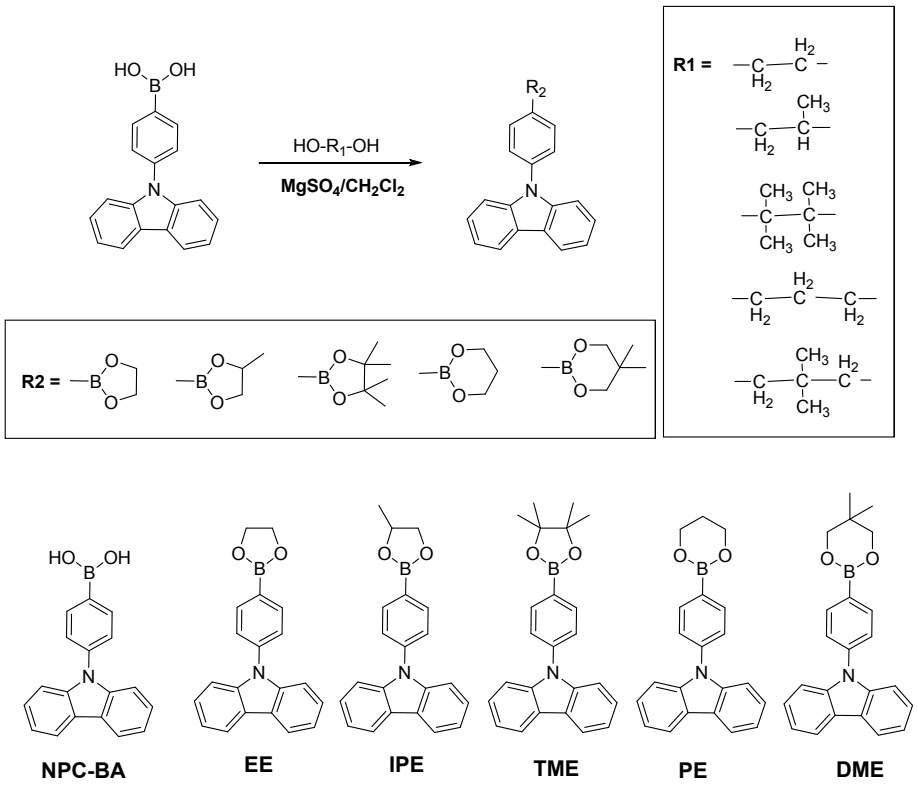
^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded by a Bruker-AC500 spectrometer in $CDCl_3$ at 298 K and tetramethylsilane (TMS) as the internal standard. UV-visible absorption and photofluorescence/phosphorescence emission spectra were recorded on Hitachi U-4100 and Hitachi F-4600 spectrophotometers, respectively. The ML spectrum was collected from a spectrometer of Acton SP2750 with a liquid-nitrogen-cooled CCD (SPEC-10, Princeton) as a power detector. Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC (204F1) instrument at a heating (or cooling) rate of 10 ^oC min^{-1}. The gas chromatograpy and mass spectroscopy were recorded by Agilent Technologic 5975C and Agilent Technologic 7890A, respectively. Time-resolved spectra were recorded by Hamamatsu compact fluorescence lifetime spectrometer. Solution fluorescence quantum yields (Φ_F) and fluorescence efficiencies of solid states were carried out with FLS980 Spectrometer.

The Gaussian 09 program was utilized to perform the TD-DFT calculations. The ground state (S_0) geometry was obtained from the single crystal structure and no further geometry optimization was conducted in order to maintain the specific molecular configuration and corresponding intermolecular locations. The exciton energies of the n-th singlet (S_n) and n-th triplet states (T_n) were obtained on the corresponding ground state structure using the TD-B3LYP/6-31G*. Kohn-Sham frontier orbital analysis and spin density distributions were obtained in order to elucidate the mechanisms of possible singlet-triplet intersystem crossings (ISC). The possible S_1 to T_n ISC channels are believed to share part of the same transition orbital compositions, and the energy levels of T_n are considered to lie within the range of ES_1 ± 0.3 eV. Especially, the major ISC channels are mainly determined based on two elements. First, the ratio of the same transition configuration in S_1 and T_n should be large in all the transition orbital compositions. Secondly, the energy gap between S_1

and the specific T_n state should be small. The red arrows refer to the ISC channels.

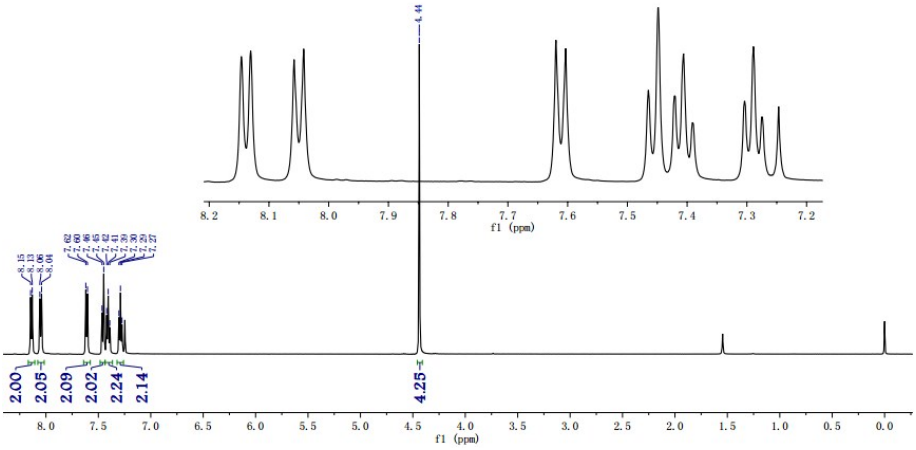
Synthesis

The cyclic boron esters could be readily synthesized by the simple reaction of commercially available NPC-BA with various cheap dihydric alcohols based on previous literature.[1]

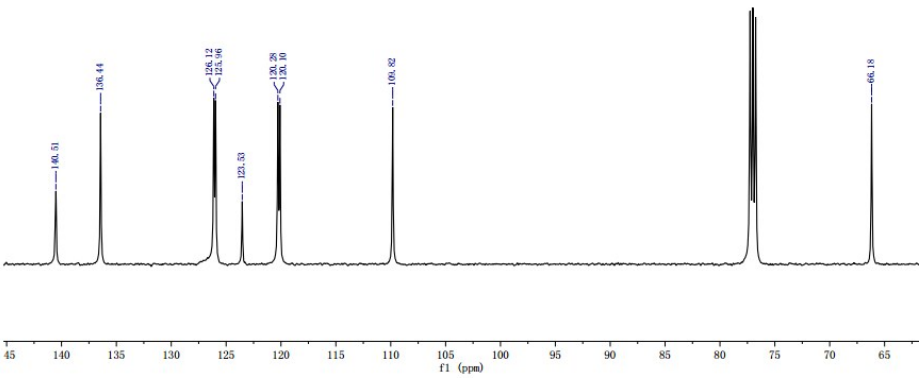


Synthesis of 9-(4-(1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (EE).

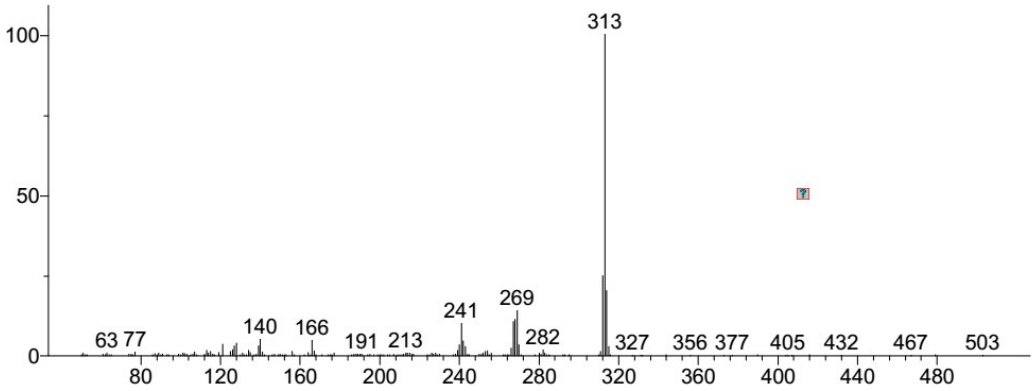
A mixture of 1 g of (4-(9H-carbazol-9-yl)phenyl)boronic acid (3.48 mmol), 0.26 g of anhydrous ethylene glycol (4.18 mmol), 0.42 g of magnesium sulfate (3.48 mmol) and 20 mL of dichloromethane was stirred for 20 h at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$.The desired compound (white solid, 0.95 g, yield: 86%) was isolated by flash chromatography on a silica gel column using dichloromethane as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 7.7 Hz, 2H), 8.10 – 8.05 (m, 2H), 7.65 – 7.60 (m, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.43 (ddd, J = 8.2, 6.9, 1.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 4.46 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.51, 136.44, 126.12, 125.96, 123.53, 120.28, 120.10, 109.82, 66.18. MS: m/z Calcd. for $C_{18}H_{13}N$: 313.1274; found 313 [M^+]. Anal. Calcd. for $C_{18}H_{13}N$: C, 76.71; H, 5.15; B, 3.45; N, 5.76. Found: C, 76.66; H, 5.18; B, 3.51; N, 5.72.



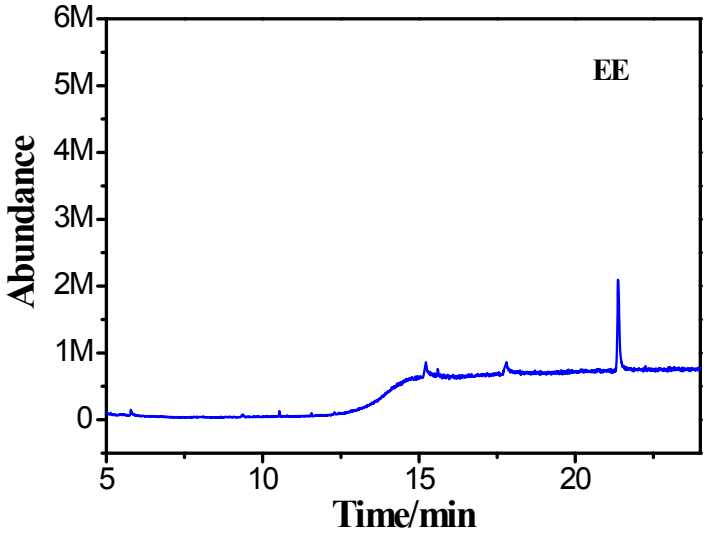
^{1}H NMR spectra of **EE**.



^{13}C NMR spectra of **EE**.

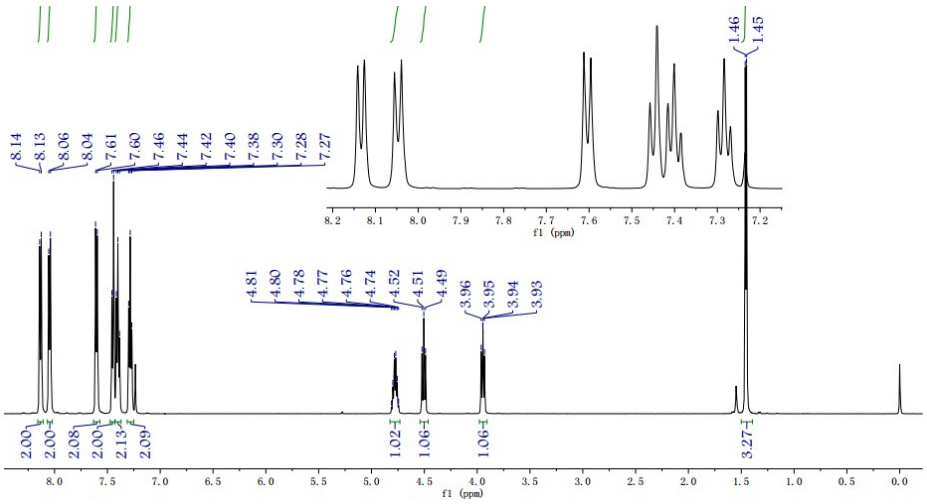


The mass spectra of **EE**.

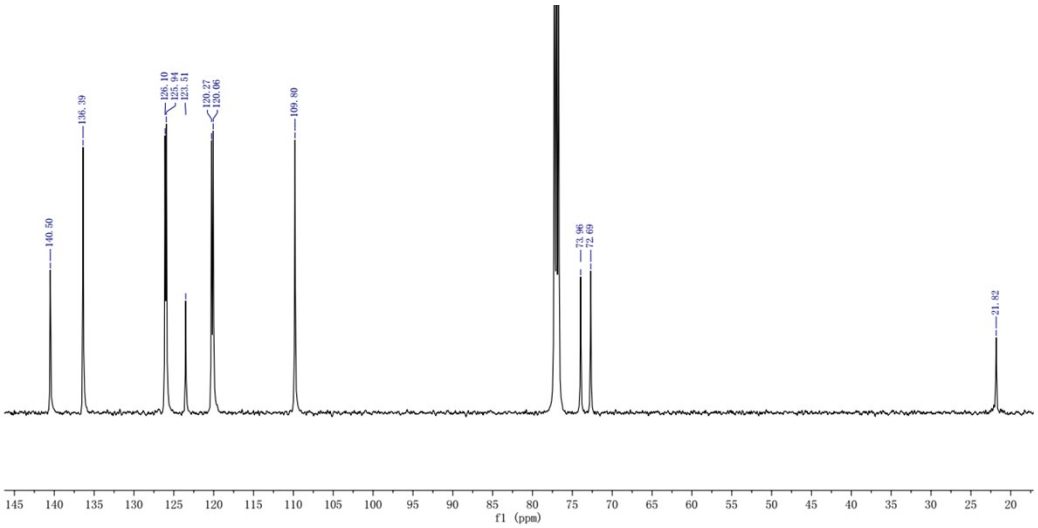


The gas chromatogram of **EE**.

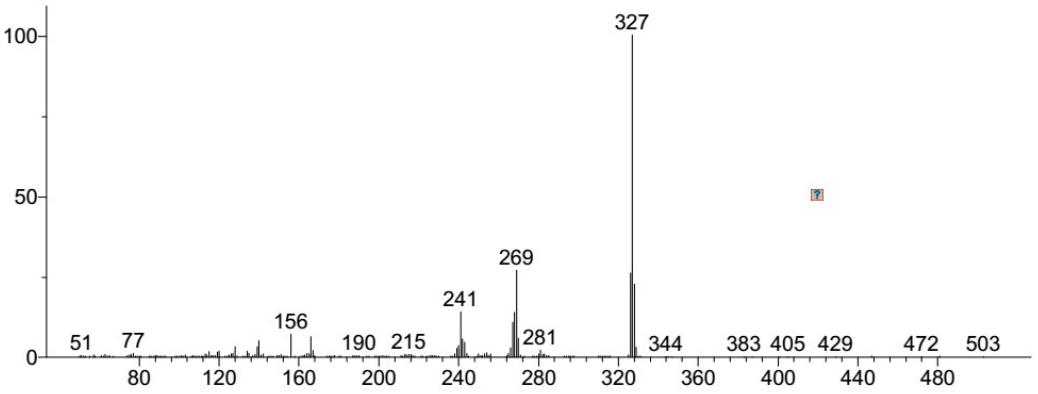
Synthesis of 9-(4-(4-methyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (IPE). The compound was synthesized as described for M1. The target compound was obtained (white solid, 0.97 g, yield: 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 7.8 Hz, 2H), 8.10 – 8.03 (m, 2H), 7.65 – 7.59 (m, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 4.80 (h, J = 6.6 Hz, 1H), 4.56 – 4.49 (m, 1H), 3.97 (dd, J = 8.9, 7.1 Hz, 1H), 1.48 (d, J = 6.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.50, 136.39, 126.10, 125.94, 123.51, 120.27, 120.06, 109.80, 73.96, 72.69, 21.82. MS: m/z Calcd. for $C_{18}H_{13}N$: 327.1841; found 327 [M^+]. Anal. Calcd. for $C_{18}H_{13}N$: C, 77.09; H, 5.55; B, 3.30; N, 4.28. Found: C, 77.05; H, 5.57; B, 3.29; N, 4.31.



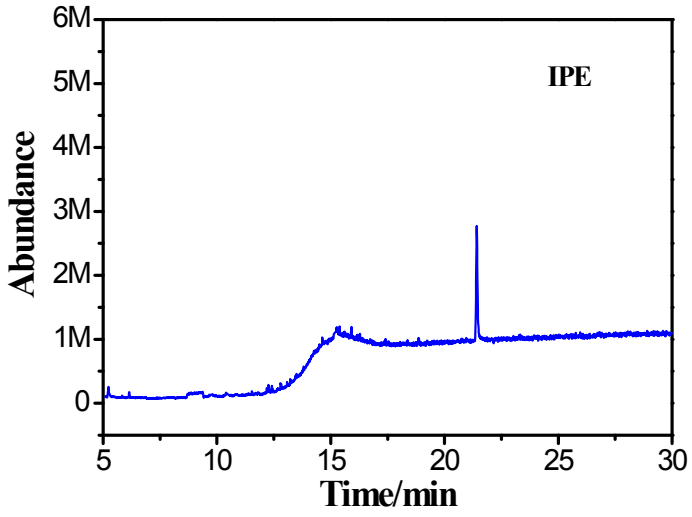
^{1}H NMR spectra of **IPE**.



^{13}C NMR spectra of **IPE**.



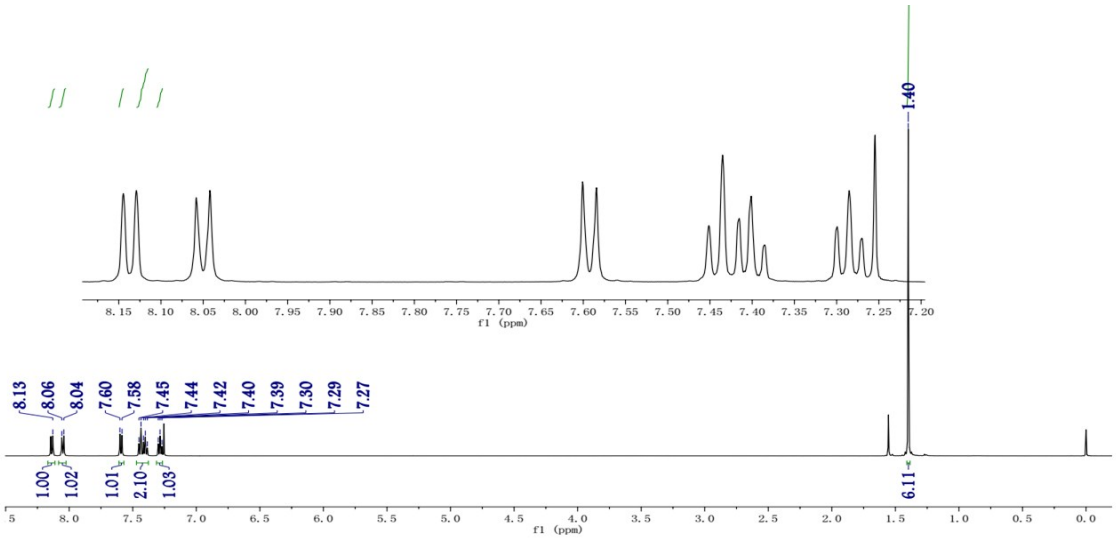
The mass spectra of **IPE**.



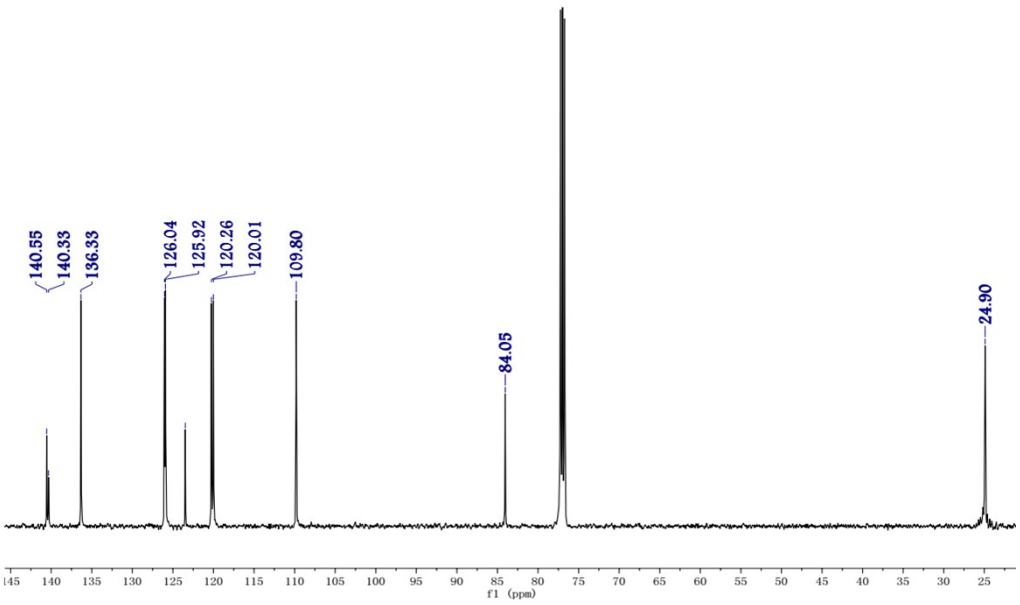
The gas chromatogram of **IPE**.

Synthesis of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (TME)

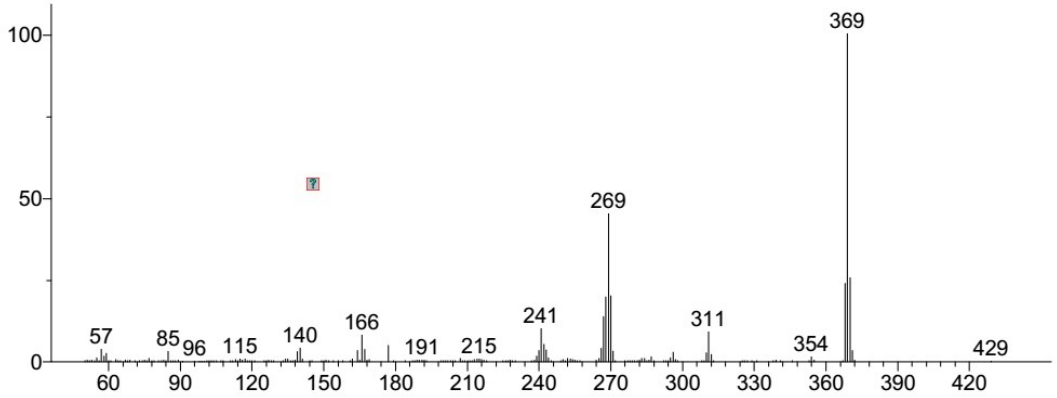
The compound was synthesized as described for M1. The target compound was obtained (white solid, 1.00 g, yield: 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 2H), 8.08 – 8.02 (m, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.31 – 7.26 (m, 2H), 1.40 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.55, 140.33, 136.33, 126.04, 125.92, 123.48, 120.26, 120.01, 109.80, 84.05, 24.90. MS: m/z Calcd. for $C_{18}H_{13}N$: 327.1841; found 327 [M^+]. Anal. Calcd. for $C_{18}H_{13}N$: C, 78.06; H, 6.55; B, 2.93; N, 3.79. Found: C, 78.01; H, 6.57; B, 2.95; N, 3.80.



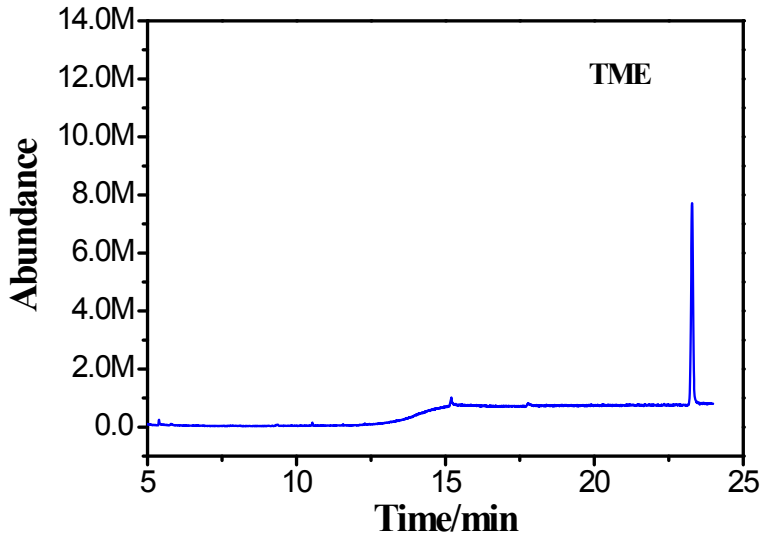
^{1}H NMR spectra of **TME**.



^{13}C NMR spectra of **TME**.



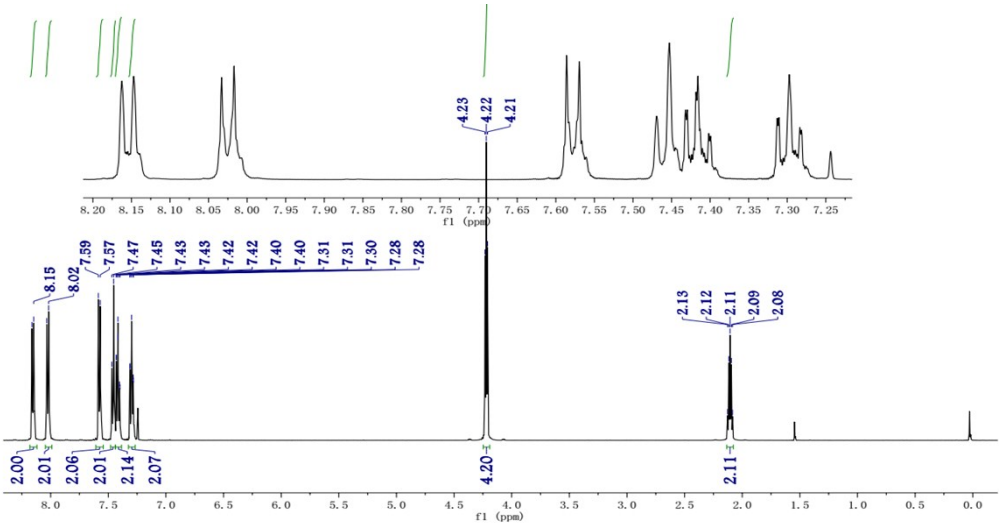
The mass spectra of **TME**.



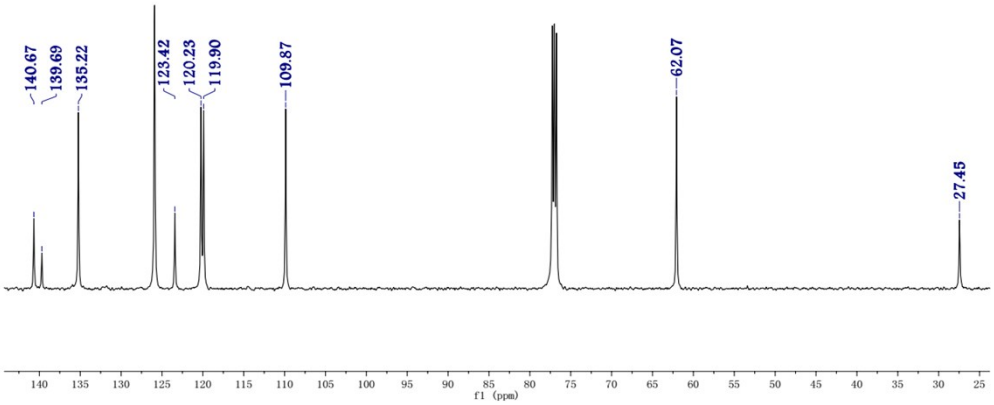
The gas chromatogram of **TME**.

Synthesis of 9-(4-(1,3,2-dioxaborinan-2-yl)phenyl)-9H-carbazole (PE).

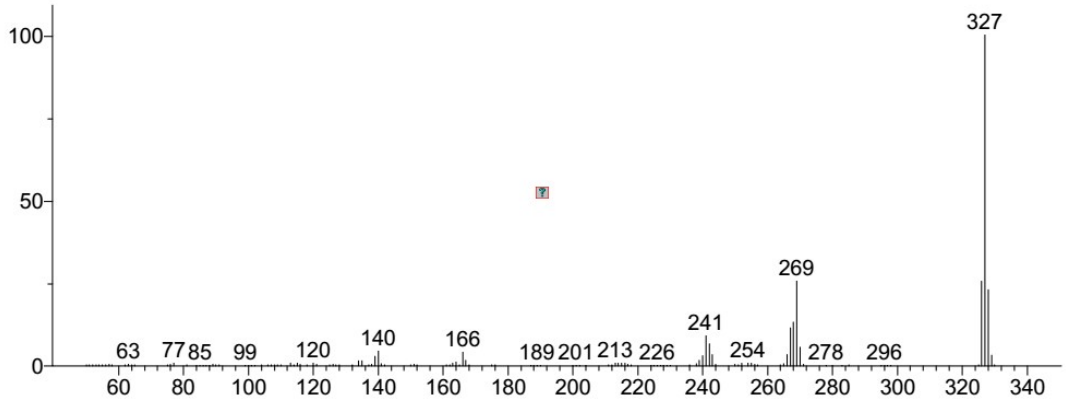
The compound was synthesized as described for M1. The target compound was obtained (white solid, 0.95 g, yield: 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.7, 1.1 Hz, 2H), 8.05 – 7.99 (m, 2H), 7.60 – 7.55 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.41 (ddt, *J* = 8.3, 7.1, 2.2 Hz, 2H), 7.32 – 7.27 (m, 2H), 4.22 (t, *J* = 5.5 Hz, 4H), 2.11 (p, *J* = 5.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.67, 139.69, 135.22, 123.42, 120.23, 119.90, 109.87, 62.07, 27.45. MS: m/z Calcd. for $C_{18}H_{13}N$: 327.1841; found 327 [M^+]. Anal. Calcd. for $C_{18}H_{13}N$: C, 77.09; H, 5.55; B, 3.30; N, 4.28. Found: C, 77.06; H, 5.56; B, 3.28; N, 4.32.



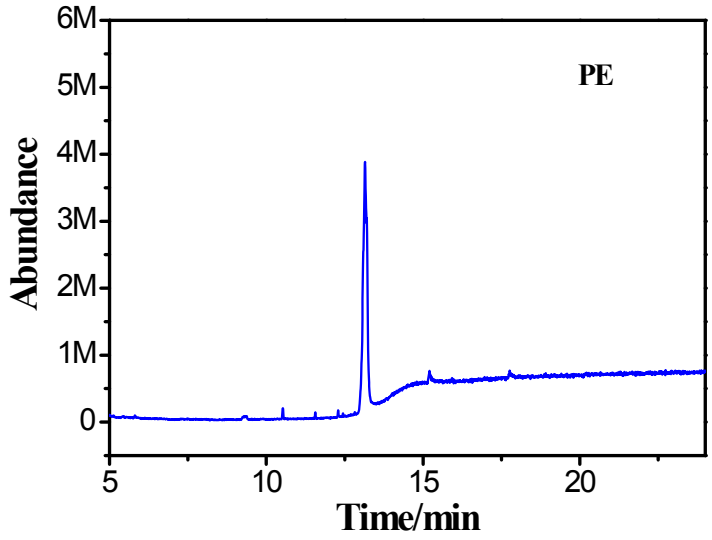
^{1}H NMR spectra of **PE**.



^{13}C NMR spectra of **PE**.



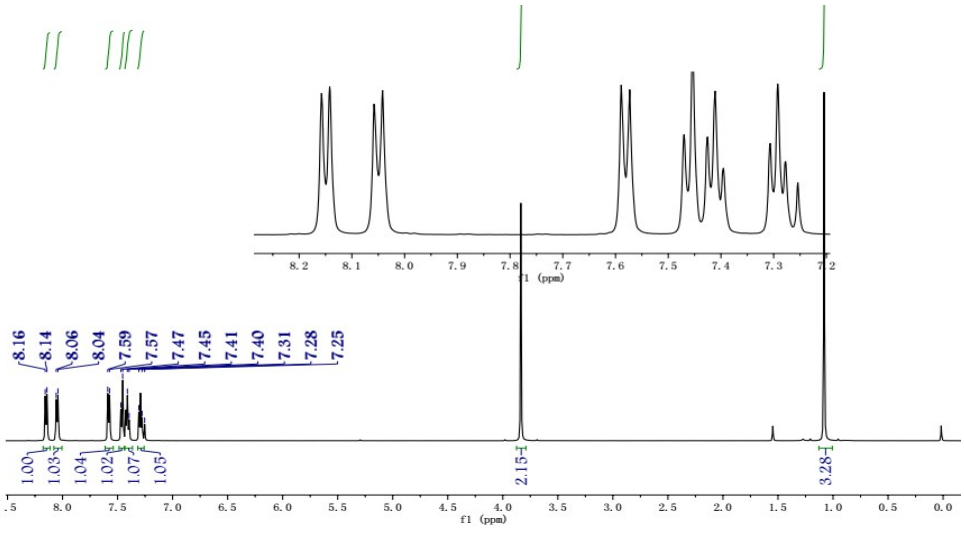
The mass spectra of **PE**.



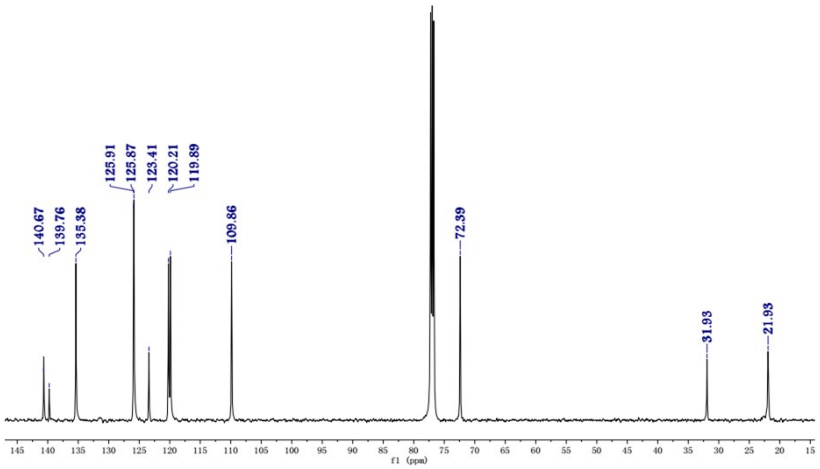
The gas chromatogram of **PE.**

Synthesis of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (DME).

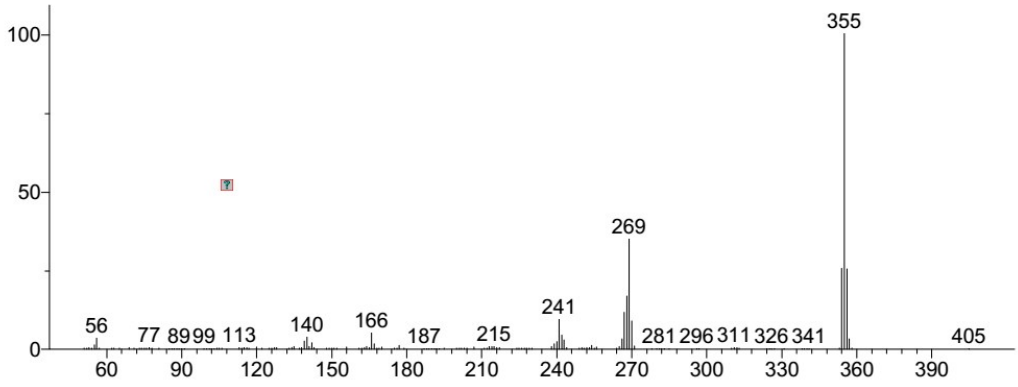
The compound was synthesized as described for M1. The target compound was obtained (white solid, 1.00 g, yield: 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 2H), 8.08 – 8.01 (m, 2H), 7.61 – 7.54 (m, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.32 – 7.26 (m, 2H), 3.84 (s, 4H), 1.08 (d, J = 2.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.67, 139.76, 135.38, 125.91, 125.87, 123.41, 120.21, 119.89, 109.86, 72.39, 31.93, 21.93. MS: m/z Calcd. for $C_{18}H_{13}N$: 355.2373; found 355 [M^+]. Anal. Calcd. for $C_{18}H_{13}N$: C, 77.76; H, 6.24; B, 3.04; N, 3.94. Found: C, 77.74; H, 6.25; B, 3.01; N, 3.98.



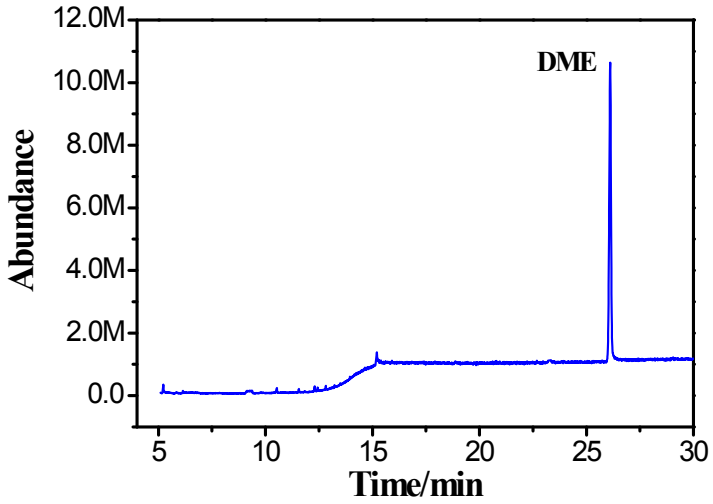
^{1}H NMR spectra of **DME**.



^{13}C NMR spectra of **DME**.



The mass spectra of **DME**.



The gas chromatogram of **DME**.

2. Figures

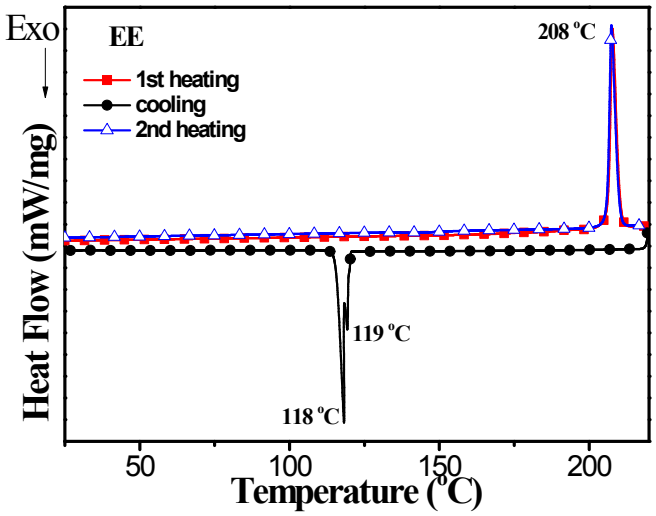


Figure S1. Differential scanning calorimetric (DSC) curves of EE crystalline powder.

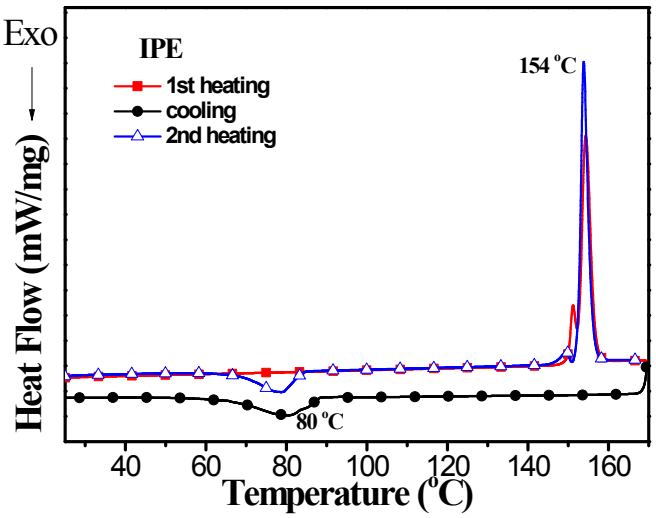


Figure S2. Differential scanning calorimetric (DSC) curves of IPE crystalline powder.

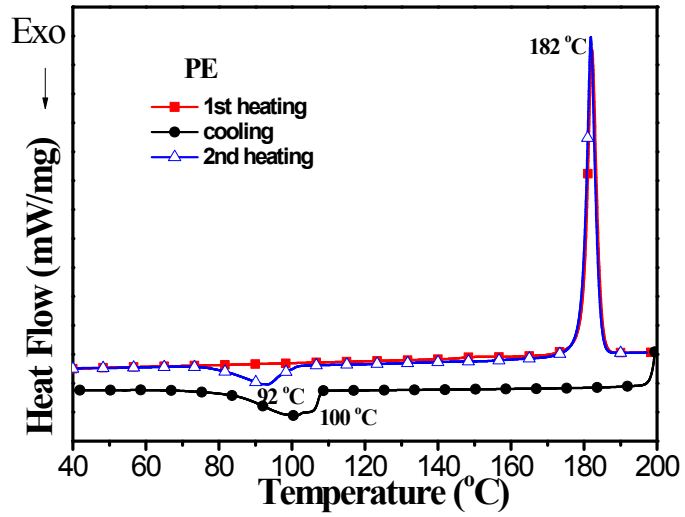


Figure S3. Differential scanning calorimetric (DSC) curves of PE crystalline powder.

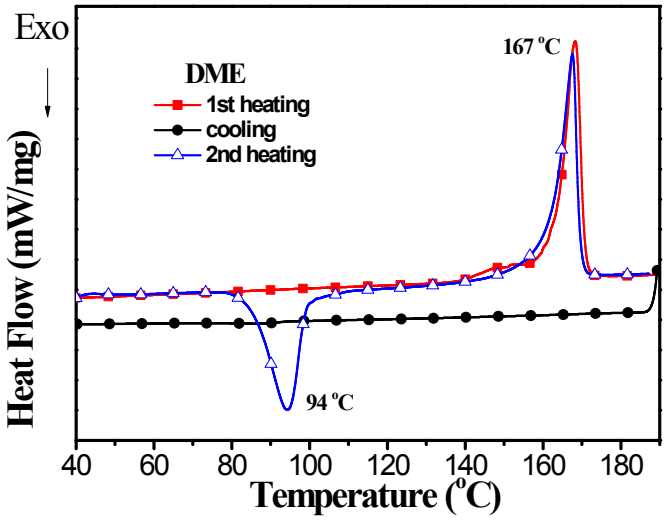


Figure S4. Differential scanning calorimetric (DSC) curves of DME crystalline powder.

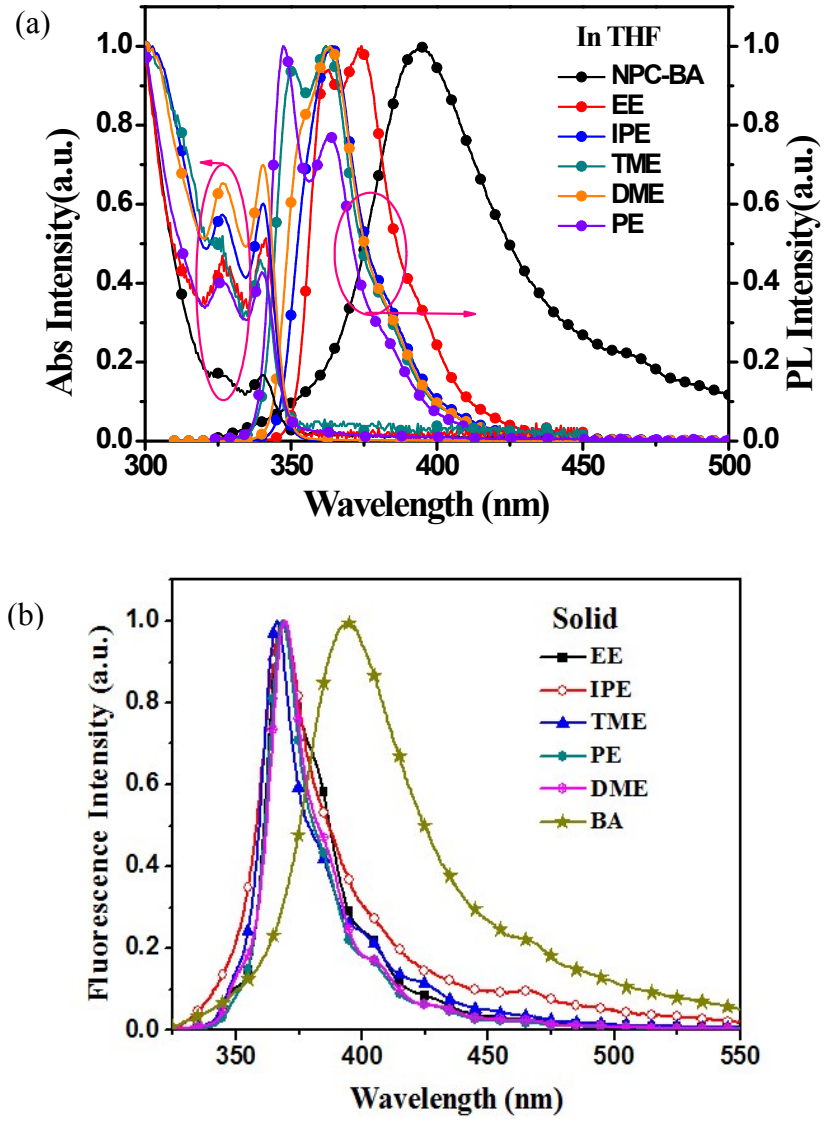


Figure S5. The absorption and emission spectra of NPC-BA, EE, IPE, TME, DME and PE solutions in THF (a) and crystalline states (b). The solution concentration was 1.0×10^{-5} M.

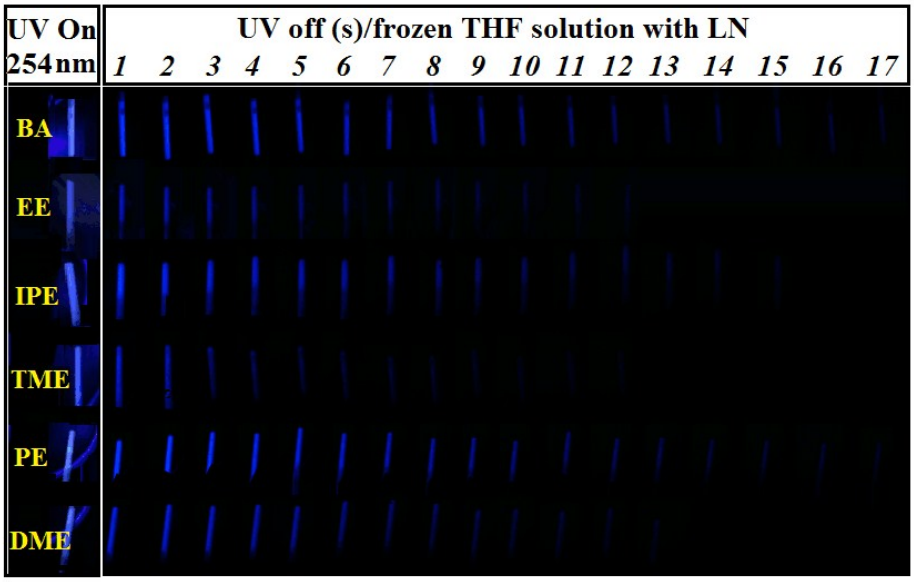


Figure S6. Photographs of NPC-BA, EE, IPE, TME, DME and PE in THF solution at 77 K upon UV on and after UV off in the dark.

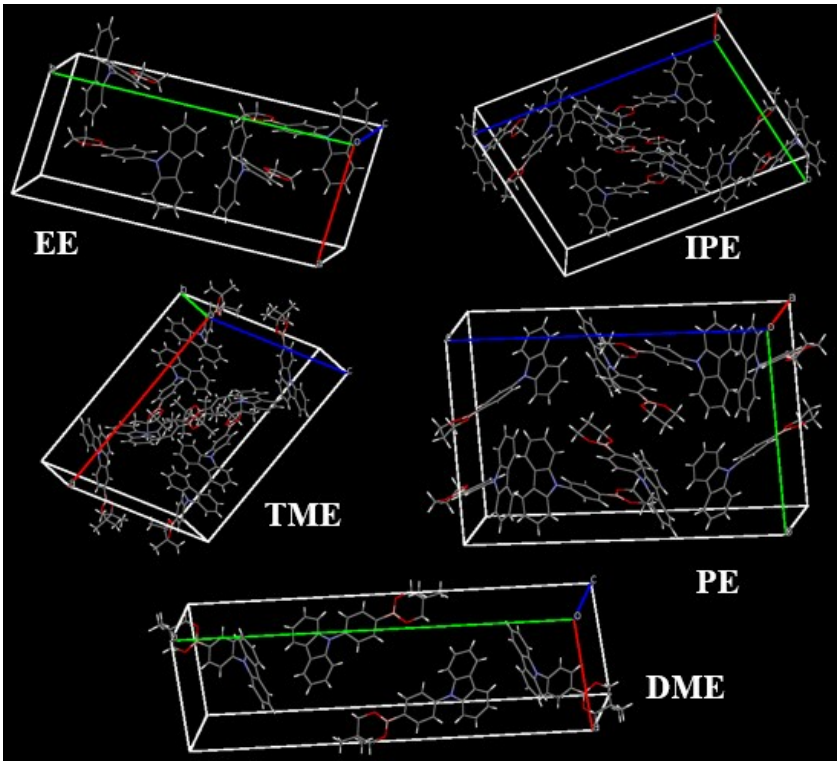


Figure S7. The unit cells of EE, IPE, TME, DME and PE single crystals.

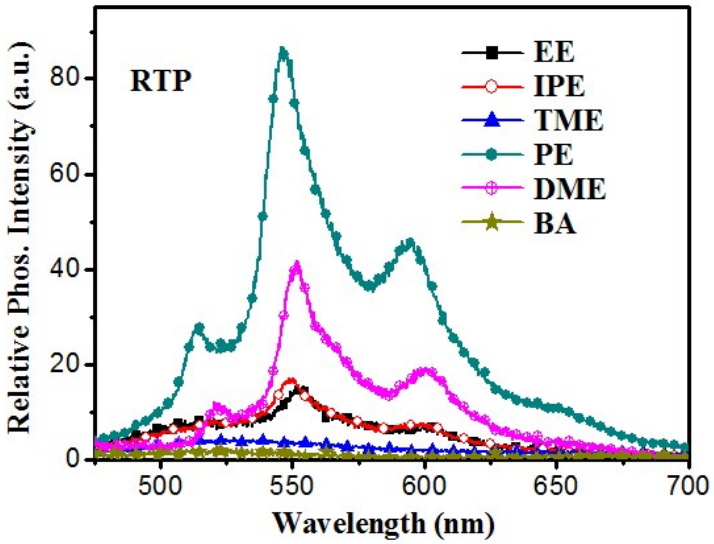


Figure S8. Phosphorescence spectra of NPC-BA, EE, IPE, TME, DME and PE in crystal powder. The excitation light was 365 nm.

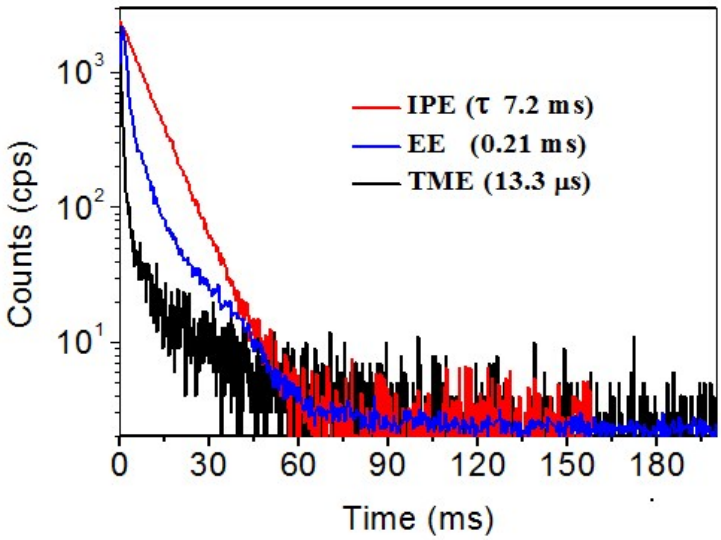


Figure S9. The photofluorescence time-resolved emission decay curves of crystalline IPE (Luminescent peaks 550 nm, excited @ 365 nm), EE (Luminescent peaks 553nm, excited @ 365 nm), and TME (Luminescent peaks 525 nm, excited @ 365 nm) powder at 298 K.

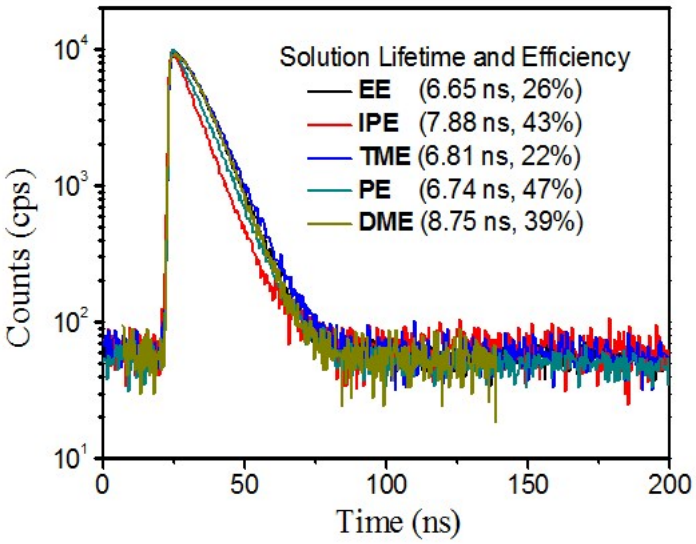


Figure S10. Time-resolved emission decay curves of EE (Luminescent peaks 374 nm, excited @ 320 nm), IPE (Luminescent peaks 364 nm, excited @ 320 nm), TME (Luminescent peaks 363 nm, excited @ 320 nm), PE (Luminescent peaks 348 nm, excited @ 310 nm) and DME (Luminescent peaks 363 nm, excited @ 320 nm) solution in THF at 298K.

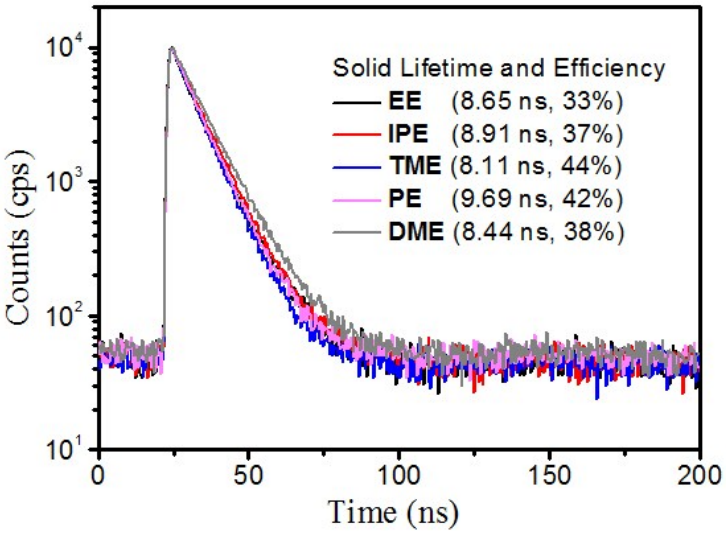


Figure S11. The photofluorescence time-resolved emission decay curves of crystalline EE (Luminescent peaks 366 nm, excited @ 320 nm), IPE (Luminescent peaks 367 nm, excited @ 320 nm), TME (Luminescent peaks 366 nm, excited @ 320 nm), PE (Luminescent peaks 368 nm, excited @ 320 nm) and DME (Luminescent peaks 370 nm, excited @ 320 nm) powder at 298K.

3. Tables

Table S1a The singlet and triplet excited state transition configurations of the **EE** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1-T_n| < 0.3$ eV were highlighted in red.

	n	Energy	Orbitals	Transition
S_n	S_1	3.6127 eV	HOMO -> LUMO	0.89664797
			HOMO -> LUMO+2	0.090363507
T_n	T_1	3.2324 eV	HOMO-16 -> LUMO+16	0.031290013
			HOMO-7 -> LUMO+4	0.0389205
			HOMO-4 -> LUMO+4	0.675865885
			HOMO-1 -> LUMO+4	0.115593936
			HOMO-1 -> LUMO+10	0.091831837
	T_2	3.2350 eV	HOMO-15 -> LUMO+17	0.027448245
			HOMO-6 -> LUMO+5	0.035960256
			HOMO-5 -> LUMO+3	0.021049416
			HOMO-3 -> LUMO+5	0.615251059
			HOMO-2 -> LUMO+5	0.059188642
			HOMO -> LUMO+5	0.08195581
			HOMO -> LUMO+11	0.085515937
	T_3	3.2375 eV	HOMO-17 -> LUMO+15	0.029393426
			HOMO-8 -> LUMO+3	0.033654557
			HOMO-5 -> LUMO+3	0.63955788
			HOMO-2 -> LUMO+3	0.10941842
			HOMO-2 -> LUMO+9	0.080593095
	T_4	3.3800 eV	HOMO-12 -> LUMO	0.034050061
			HOMO-3 -> LUMO+5	0.042422019
			HOMO -> LUMO	0.493362178
			HOMO -> LUMO+2	0.115468957
			HOMO -> LUMO+5	0.18629408
	T_5	3.3903 eV	HOMO-8 -> LUMO+9	0.027448245
			HOMO-5 -> LUMO+3	0.119443169
			HOMO-3 -> LUMO+3	0.036818125
			HOMO-2 -> LUMO+1	0.041259154
			HOMO-2 -> LUMO+3	0.687565738
			HOMO -> LUMO+3	0.022024807
	T_6	3.4061 eV	HOMO-7 -> LUMO+10	0.032696359
			HOMO-4 -> LUMO+4	0.107406855

			HOMO-1 -> LUMO	0.024438183
			HOMO-1 -> LUMO+2	0.049279162
			HOMO-1 -> LUMO+4	0.725964301
	T_7	3.4537 eV	HOMO-12 -> LUMO	0.020503125
			HOMO-3 -> LUMO+5	0.047026311
			HOMO -> LUMO	0.172495885
			HOMO -> LUMO+2	0.022353437
			HOMO -> LUMO+5	0.641708547
	T_8	3.5450 eV	HOMO-14 -> LUMO	0.033857224
			HOMO-14 -> LUMO+2	0.056804722
			HOMO-10 -> LUMO+6	0.029011587
			HOMO-10 -> LUMO+8	0.043536103
			HOMO-9 -> LUMO	0.042079005
			HOMO-9 -> LUMO+2	0.065826433
			HOMO-1 -> LUMO	0.304777474
			HOMO-1 -> LUMO+2	0.28065032
			HOMO-1 -> LUMO+4	0.08016008
	T_9	3.5786 eV	HOMO-13 -> LUMO+1	0.215706256
			HOMO-12 -> LUMO+1	0.026408616
			HOMO-11 -> LUMO+7	0.103585313
			HOMO-3 -> LUMO+1	0.029301363
			HOMO-2 -> LUMO+1	0.500620192
			HOMO-2 -> LUMO+3	0.044503378
	T_{10}	3.9065 eV	HOMO-15 -> LUMO	0.022650433
			HOMO-14 -> LUMO+6	0.054595297
			HOMO-14 -> LUMO+8	0.030420578
			HOMO-12 -> LUMO	0.105322141
			HOMO-12 -> LUMO+2	0.04572288
			HOMO-10 -> LUMO	0.024495698
			HOMO-9 -> LUMO+6	0.058331617
			HOMO-9 -> LUMO+8	0.033628618
			HOMO-3 -> LUMO	0.05986492
			HOMO -> LUMO	0.284770951
			HOMO -> LUMO+2	0.171159303
	T_{11}	3.9554 eV	HOMO -> LUMO+1	0.953746227
	T_{12}	3.9701 eV	HOMO-3 -> LUMO	0.575728882
			HOMO-3 -> LUMO+2	0.043831683
			HOMO-2 -> LUMO	0.073084291
			HOMO -> LUMO	0.021403805
			HOMO -> LUMO+2	0.233053299

	T_{13}	4.0037 eV	HOMO-14 -> LUMO	0.042567784
			HOMO-14 -> LUMO+2	0.043677857
			HOMO-12 -> LUMO+2	0.020349514
			HOMO-10 -> LUMO+6	0.046830241
			HOMO-10 -> LUMO+8	0.112727016
			HOMO-9 -> LUMO	0.047592295
			HOMO-9 -> LUMO+2	0.068568451
			HOMO-9 -> LUMO+6	0.027701872
			HOMO-3 -> LUMO	0.056899138
			HOMO-1 -> LUMO	0.251879629
			HOMO -> LUMO+2	0.074258872
	T_{14}	4.0039 eV	HOMO-14 -> LUMO+2	0.027664224
			HOMO-14 -> LUMO+6	0.030623175
			HOMO-14 -> LUMO+8	0.020775373
			HOMO-12 -> LUMO	0.072458631
			HOMO-10 -> LUMO+6	0.042783975
			HOMO-9 -> LUMO+2	0.022399978
			HOMO-9 -> LUMO+6	0.028331521
			HOMO-9 -> LUMO+8	0.037133575
			HOMO-3 -> LUMO	0.0968088
			HOMO-1 -> LUMO	0.083845125
			HOMO -> LUMO+2	0.341865267
	T_{15}	4.0221 eV	HOMO-2 -> LUMO+3	0.024976125
			HOMO -> LUMO+3	0.945697539
	T_{16}	4.0573 eV	HOMO-13 -> LUMO+1	0.199661443
			HOMO-12 -> LUMO+1	0.023362573
			HOMO-11 -> LUMO+7	0.229516675
			HOMO-8 -> LUMO+7	0.04817408
			HOMO-2 -> LUMO+1	0.333826205
			HOMO-2 -> LUMO+3	0.020922397
			HOMO-2 -> LUMO+12	0.028298205

Table S1b The singlet and triplet excited state transition configurations of the **IPE** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1\text{-}T_n| < 0.3$ eV were highlighted in red.

	n	Energy	Orbitals	Transition
S_n	S_1	3.3409 eV	HOMO -> LUMO	0.720648146
			HOMO -> LUMO+1	0.04363058

			HOMO -> LUMO+2	0.218024458
T_n	T_1	3.0639 eV	HOMO-18 -> LUMO+16	0.028924935
			HOMO-6 -> LUMO+3	0.484561057
			HOMO-6 -> LUMO+4	0.024371904
			HOMO-2 -> LUMO+3	0.3080968
			HOMO-2 -> LUMO+4	0.020144259
			HOMO-2 -> LUMO+11	0.043873144
	T_2	3.0889 eV	HOMO-17 -> 276	0.031045336
			HOMO-5 -> LUMO+5	0.632115192
			HOMO-4 -> LUMO+5	0.049084711
			HOMO-3 -> LUMO+5	0.041899335
			HOMO-1 -> LUMO+5	0.082263792
			HOMO-1 -> LUMO+10	0.056092402
	T_3	3.1387 eV	HOMO -> LUMO	0.365991457
			HOMO -> LUMO+1	0.023518467
			HOMO -> LUMO+2	0.165105565
			HOMO -> LUMO+4	0.348128368
	T_4	3.2173 eV	HOMO-19 -> LUMO+15	0.025941864
			HOMO-7 -> LUMO	0.163626322
			HOMO-7 -> LUMO+1	0.026708227
			HOMO-7 -> LUMO+2	0.305589984
			HOMO-3 -> LUMO	0.085053377
			HOMO-3 -> LUMO+2	0.189001816
			HOMO-3 -> LUMO+9	0.059209287
	T_5	3.3593 eV	HOMO-5 -> LUMO+5	0.068909569
			HOMO-4 -> LUMO+5	0.028402978
			HOMO-1 -> LUMO	0.033499073
			HOMO-1 -> LUMO+1	0.111307056
			HOMO-1 -> LUMO+5	0.604890005
	T_6	3.3805 eV	HOMO-6 -> LUMO+3	0.289530061
			HOMO-6 -> LUMO+4	0.022697282
			HOMO-2 -> LUMO+3	0.474221127
			HOMO-2 -> LUMO+4	0.082612995
			HOMO -> LUMO+3	0.027032775
	T_7	3.3936 eV	HOMO-7 -> LUMO	0.07105696
			HOMO-7 -> LUMO+2	0.16233602
			HOMO-3 -> LUMO	0.052656615
			HOMO-3 -> LUMO+2	0.428960269
			HOMO-3 -> LUMO+9	0.025596794
			HOMO-1 -> LUMO+2	0.024548848

			HOMO -> LUMO+2	0.038016274
	T_8	3.4019 eV	HOMO -> LUMO	0.327693697
			HOMO -> LUMO+2	0.055337991
			HOMO -> LUMO+3	0.070222529
			HOMO -> LUMO+4	0.461337757
	T9	3.4342 eV	HOMO-15 -> LUMO+1	0.104296579
			HOMO-13 -> LUMO+7	0.05126402
			HOMO-5 -> LUMO+5	0.046354035
			HOMO-1 -> LUMO	0.029354645
			HOMO-1 -> LUMO+1	0.49602792
			HOMO-1 -> LUMO+5	0.140895553
	T_{10}	3.4585 eV	HOMO -> LUMO	0.197141763
			HOMO -> LUMO+1	0.041385645
			HOMO -> LUMO+2	0.719448106
	T_{11}	3.4945 eV	HOMO-16 -> LUMO	0.021832141
			HOMO-16 -> LUMO+4	0.02575996
			HOMO-16 -> LUMO+6	0.02037373
			HOMO-14 -> LUMO+6	0.03266568
			HOMO-8 -> LUMO+6	0.070748173
			HOMO-3 -> LUMO	0.293853112
			HOMO-3 -> LUMO+2	0.026638936
			HOMO-3 -> LUMO+3	0.020426247
			HOMO-3 -> LUMO+4	0.110412403
	T_{12}	3.5443 eV	HOMO-14 -> LUMO+8	0.020232673
			HOMO-11 -> LUMO+4	0.037051864
			HOMO-8 -> LUMO+8	0.035346087
			HOMO-2 -> LUMO	0.199181473
			HOMO-2 -> LUMO+2	0.09400448
			HOMO-2 -> LUMO+3	0.035393962
			HOMO-2 -> LUMO+4	0.236094433
			HOMO -> LUMO+4	0.04488008
	T_{13}	3.6112 eV	HOMO -> LUMO	0.077020275
			HOMO -> LUMO+1	0.914357645
	T_{14}	3.6413 eV	HOMO -> LUMO+5	0.979328115
	T_{15}	3.7271 eV	HOMO-2 -> LUMO+3	0.028886465
			HOMO -> LUMO+3	0.876858759
			HOMO -> LUMO+4	0.075334093
	T_{16}	3.8872 eV	HOMO -> LUMO+6	0.964271619

Table S1c The singlet and triplet excited state transition configurations of the **TME** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1-T_n| < 0.3$ eV were highlighted in red.

	n	Energy	Orbitals	Transition
S_n	S_1	3.7885 eV	HOMO -> LUMO	0.851930151
			HOMO -> LUMO+3	0.059202405
			HOMO -> LUMO+4	0.077373912
T_n	T_1	3.2911 eV	HOMO-20 -> LUMO+15	0.027000232
			HOMO-9 -> LUMO+2	0.028450666
			HOMO-5 -> LUMO+1	0.3469445
			HOMO-5 -> LUMO+2	0.411941491
			HOMO-2 -> LUMO+2	0.02594642
			HOMO-2 -> LUMO+9	0.086162307
	T_2	3.3525 eV	HOMO-15 -> LUMO+17	0.028622674
			HOMO-6 -> LUMO+5	0.036390624
			HOMO-3 -> LUMO+5	0.667867474
			HOMO-2 -> LUMO+5	0.021607047
			HOMO -> LUMO+5	0.053281537
			HOMO -> LUMO+11	0.103867704
	T_3	3.3536 eV	HOMO-19 -> LUMO+16	0.030905952
			HOMO-7 -> LUMO+3	0.023030872
			HOMO-4 -> LUMO+3	0.421527256
			HOMO-4 -> LUMO+4	0.2850276
			HOMO-1 -> LUMO+3	0.047315032
			HOMO-1 -> LUMO+4	0.028790401
			HOMO-1 -> LUMO+10	0.103039841
	T_4	3.3963 eV	HOMO-9 -> LUMO+9	0.022298496
			HOMO-2 -> LUMO+1	0.207393761
			HOMO-2 -> LUMO+2	0.6440898
	T_5	3.4461 eV	HOMO-7 -> LUMO+10	0.020212562
			HOMO-4 -> LUMO+3	0.036910445
			HOMO-4 -> LUMO+4	0.023397171
			HOMO-1 -> LUMO	0.024913584
			HOMO-1 -> LUMO+3	0.587636405
			HOMO-1 -> LUMO+4	0.243937155
	T_6	3.4511 eV	HOMO-6 -> LUMO+11	0.02832676
			HOMO-3 -> LUMO+5	0.041731605
			HOMO -> LUMO	0.045402898

			HOMO -> LUMO+2	0.03099552
			HOMO -> LUMO+4	0.022561128
			HOMO -> LUMO+5	0.734156914
	T_7	3.5539 eV	HOMO-12 -> LUMO+1	0.028345805
			HOMO-12 -> LUMO+2	0.020092106
			HOMO-12 -> LUMO+8	0.042264874
			HOMO-11 -> LUMO+1	0.063538995
			HOMO-11 -> LUMO+2	0.03953672
			HOMO-10 -> LUMO+1	0.025664717
			HOMO-2 -> LUMO+1	0.535923045
			HOMO-2 -> LUMO+2	0.137865005
	T_8	3.5874 eV	HOMO-14 -> LUMO+7	0.020414122
			HOMO-10 -> LUMO	0.036563488
			HOMO-8 -> LUMO+7	0.026796125
			HOMO -> LUMO	0.498900605
			HOMO -> LUMO+3	0.081874858
			HOMO -> LUMO+4	0.108233434
			HOMO -> LUMO+5	0.079880045
	T_9	3.6523 eV	HOMO-14 -> LUMO+6	0.03808248
			HOMO-13 -> LUMO	0.07113992
			HOMO-13 -> LUMO+4	0.026519045
			HOMO-8 -> LUMO+6	0.022731384
			HOMO-7 -> LUMO+6	0.027181793
			HOMO-1 -> LUMO	0.50843528
			HOMO-1 -> LUMO+4	0.168223201
	T_{10}	4.0010 eV	HOMO -> LUMO+1	0.44732557
			HOMO -> LUMO+2	0.476932378
			HOMO -> LUMO+5	0.052061191
	T_{11}	4.0192 eV	HOMO-14 -> LUMO+7	0.07444397
			HOMO-11 -> LUMO	0.025452192
			HOMO-10 -> LUMO	0.053792
			HOMO-10 -> LUMO+3	0.025596794
			HOMO-10 -> LUMO+4	0.03785101
			HOMO-8 -> LUMO+7	0.109680545
			HOMO-7 -> LUMO+7	0.029407975
			HOMO-6 -> LUMO+7	0.02594642
			HOMO -> LUMO	0.375463117
			HOMO -> LUMO+3	0.034705586
			HOMO -> LUMO+4	0.05471432
	T_{12}	4.0414 eV	HOMO -> LUMO+1	0.52005721

			HOMO -> LUMO+2	0.457216594
	T_{13}	4.0827 eV	HOMO-14 -> LUMO+6	0.122532301
			HOMO-13 -> LUMO	0.0861042
			HOMO-13 -> LUMO+3	0.022222536
			HOMO-13 -> LUMO+4	0.046189762
			HOMO-13 -> LUMO+6	0.036753027
			HOMO-10 -> LUMO	0.028312481
			HOMO-8 -> LUMO+6	0.079744205
			HOMO-7 -> LUMO+6	0.103366951
			HOMO-1 -> LUMO	0.29521928
	T_{14}	4.1339 eV	HOMO-14 -> LUMO+7	0.036358258
			HOMO-8 -> LUMO+7	0.054760642
			HOMO -> LUMO	0.055864874
			HOMO -> LUMO+3	0.21151008
			HOMO -> LUMO+4	0.302439754
			HOMO -> LUMO+11	0.074791649
	T_{15}	4.1683 eV	HOMO-8 -> LUMO+3	0.020901946
			HOMO-7 -> LUMO+3	0.049877453
			HOMO-4 -> LUMO+3	0.123385249
			HOMO-4 -> LUMO+4	0.043112225
			HOMO-1 -> LUMO+10	0.53766376
			HOMO -> LUMO+11	0.04470648
	T_{16}	4.1691 eV	HOMO-6 -> LUMO+5	0.06294152
			HOMO-3 -> LUMO	0.090465565
			HOMO-3 -> LUMO+5	0.100065485
			HOMO-1 -> LUMO+10	0.061327024
			HOMO -> LUMO+3	0.025465731
			HOMO -> LUMO+4	0.038580864
			HOMO -> LUMO+11	0.38283

Table S1d The singlet and triplet excited state transition configurations of the **PE** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1-T_n| < 0.3$ eV were highlighted in red.

	n	Energy	Orbitals	Transition
Sn	S_1	4.0012 eV	HOMO-2 -> LUMO	0.052235584
			HOMO-2 -> LUMO+2	0.020305155
			HOMO -> LUMO	0.052760513
			HOMO -> LUMO+2	0.827824179

T_n	T_1	3.2966 eV	HOMO-15 -> LUMO+17	0.033447325
			HOMO-7 -> LUMO+5	0.027014177
			HOMO-3 -> LUMO+5	0.774663939
			HOMO-2 -> LUMO+5	0.020260845
			HOMO -> LUMO+11	0.081083645
	T_2	3.2985 eV	HOMO-16 -> LUMO+16	0.03432724
			HOMO-9 -> LUMO+3	0.032436045
			HOMO-4 -> LUMO+3	0.784954381
			HOMO-1 -> LUMO+10	0.079904029
	T_3	3.3465 eV	HOMO-17 -> LUMO+15	0.022209889
			HOMO-5 -> LUMO	0.059051098
			HOMO-5 -> LUMO+1	0.471653569
			HOMO-2 -> LUMO	0.06918456
			HOMO-2 -> LUMO+1	0.13371689
			HOMO-2 -> LUMO+9	0.077783568
	T_4	3.3761 eV	HOMO-5 -> LUMO	0.02358792
			HOMO-5 -> LUMO+1	0.158777395
			HOMO-2 -> LUMO	0.303202419
			HOMO-2 -> LUMO+1	0.230411873
			HOMO-2 -> LUMO+9	0.031580871
			HOMO-1 -> LUMO	0.02648221
			HOMO -> LUMO	0.031170051
			HOMO -> LUMO+1	0.025461218
	T_5	3.4231 eV	HOMO-9 -> LUMO+10	0.022880883
			HOMO-2 -> LUMO+3	0.053883879
			HOMO-1 -> LUMO+3	0.862877571
	T_6	3.4509 eV	HOMO-7 -> LUMO+11	0.022722856
			HOMO-2 -> LUMO+5	0.026261736
			HOMO -> LUMO+2	0.043707418
			HOMO -> LUMO+5	0.831250392
	T_7	3.4598 eV	HOMO-14 -> LUMO+8	0.032085511
			HOMO-13 -> LUMO	0.040453057
			HOMO-8 -> LUMO	0.116750784
			HOMO-6 -> LUMO+8	0.032906386
			HOMO-2 -> LUMO	0.175160967
			HOMO-2 -> LUMO+1	0.342278832
			HOMO-2 -> LUMO+4	0.039385018
			HOMO-1 -> LUMO	0.026321357
			HOMO-1 -> LUMO+1	0.03280385
			HOMO -> LUMO+1	0.033235576

	T_8	3.5525 eV	HOMO-12 -> LUMO+2	0.099529373
			HOMO-11 -> LUMO+2	0.054833473
			HOMO-11 -> LUMO+6	0.031842785
			HOMO-10 -> LUMO+6	0.050016519
			HOMO-2 -> LUMO+2	0.025155245
			HOMO -> LUMO+2	0.603219312
			HOMO -> LUMO+5	0.059016737
	T_9	3.5881 eV	HOMO-14 -> LUMO+7	0.045825754
			HOMO-13 -> LUMO+4	0.079736218
			HOMO-8 -> LUMO+4	0.072131616
			HOMO-6 -> LUMO+7	0.081656487
			HOMO-1 -> LUMO	0.095615645
			HOMO-1 -> LUMO+1	0.02335825
			HOMO-1 -> LUMO+4	0.449029738
	T_{10}	4.0605 eV	HOMO-2 -> LUMO+1	0.071881153
			HOMO -> LUMO	0.243448464
			HOMO -> LUMO+1	0.6105346
	T_{11}	4.1022 eV	HOMO-5 -> LUMO	0.059678215
			HOMO-5 -> LUMO+1	0.142962739
			HOMO-2 -> LUMO+5	0.022041601
			HOMO-2 -> LUMO+9	0.378136865
			HOMO-1 -> LUMO+9	0.026014805
			HOMO -> LUMO+1	0.075334093
			HOMO -> LUMO+9	0.040549824
	T_{12}	4.1205 eV	HOMO-2 -> LUMO+9	0.053151041
			HOMO-1 -> LUMO	0.109250077
			HOMO -> LUMO	0.369146689
			HOMO -> LUMO+1	0.143991245
	T_{13}	4.1333 eV	HOMO-14 -> LUMO+7	0.052585245
			HOMO-13 -> LUMO+4	0.029325576
			HOMO-8 -> LUMO+4	0.026459201
			HOMO-6 -> LUMO+7	0.104982784
			HOMO-2 -> LUMO	0.060447645
			HOMO-1 -> LUMO	0.281835304
			HOMO-1 -> LUMO+1	0.05081672
			HOMO-1 -> LUMO+7	0.02020452
			HOMO-1 -> LUMO+13	0.02207941
			HOMO -> LUMO	0.129937824
			HOMO -> LUMO+1	0.044276928
	T_{14}	4.1453 eV	HOMO-12 -> LUMO+2	0.0946125

			HOMO-12 -> LUMO+6	0.048590914
			HOMO-11 -> LUMO+2	0.077295256
			HOMO-11 -> LUMO+6	0.125821345
			HOMO-10 -> LUMO+6	0.185513587
			HOMO-7 -> LUMO+6	0.020495026
			HOMO-7 -> LUMO+11	0.020012002
			HOMO -> LUMO	0.020624805
			HOMO -> LUMO+2	0.206146205
			HOMO -> LUMO+14	0.039048946
	T_{15}	4.1744 eV	HOMO-14 -> LUMO+8	0.036595946
			HOMO-9 -> LUMO+3	0.028852824
			HOMO-8 -> LUMO	0.065608909
			HOMO-6 -> LUMO+7	0.054952755
			HOMO-6 -> LUMO+8	0.021441063
			HOMO-4 -> LUMO+3	0.035617805
			HOMO-2 -> LUMO	0.099048103
			HOMO-2 -> LUMO+1	0.051001792
			HOMO-2 -> LUMO+12	0.034563463
			HOMO-1 -> LUMO+4	0.077815125
			HOMO-1 -> LUMO+10	0.133758264
			HOMO -> LUMO	0.057501187
			HOMO -> LUMO+11	0.020088097
	T_{16}	4.1797 eV	HOMO-9 -> LUMO+3	0.074683395
			HOMO-9 -> LUMO+13	0.02244233
			HOMO-8 -> LUMO	0.029267482
			HOMO-4 -> LUMO+3	0.115430515
			HOMO-2 -> LUMO	0.040203137
			HOMO-2 -> LUMO+1	0.023177045
			HOMO-2 -> LUMO+10	0.026569735
			HOMO-1 -> LUMO+10	0.40768644
	T_{17}	4.2002 eV	HOMO-7 -> LUMO+5	0.06924409
			HOMO-3 -> LUMO+2	0.030371266
			HOMO-3 -> LUMO+5	0.103721906
			HOMO-1 -> LUMO	0.029466209
			HOMO-1 -> LUMO+4	0.061313016
			HOMO -> LUMO	0.04084082
			HOMO -> LUMO+6	0.07144956
			HOMO -> LUMO+11	0.37792818
	T_{18}	4.2047 eV	HOMO-14 -> LUMO+7	0.029616912
			HOMO-13 -> LUMO	0.02509248

			HOMO-8 -> LUMO+4	0.02186977
			HOMO-6 -> LUMO+7	0.039925728
			HOMO-6 -> LUMO+8	0.0295245
			HOMO-2 -> LUMO+4	0.033225264
			HOMO-1 -> LUMO	0.182552989
			HOMO-1 -> LUMO+1	0.032629906
			HOMO-1 -> LUMO+4	0.2047872
			HOMO-1 -> LUMO+7	0.025969205
			HOMO-1 -> LUMO+10	0.025191146
			HOMO -> LUMO	0.021719448
			HOMO -> LUMO+11	0.067366522
	T_{19}	4.2418 eV	HOMO-12 -> LUMO+6	0.054258768
			HOMO-2 -> LUMO+6	0.027298498
			HOMO -> LUMO+6	0.749455245
			HOMO -> LUMO+11	0.060461554
	T_{20}	4.2670 eV	HOMO-8 -> LUMO+8	0.020276952
			HOMO-2 -> LUMO+4	0.445870131
			HOMO-2 -> LUMO+8	0.134794704
			HOMO -> LUMO+4	0.176097386
	T_{21}	4.2980 eV	HOMO-2 -> LUMO+1	0.045493345
			HOMO-1 -> LUMO	0.19456322
			HOMO-1 -> LUMO+1	0.545887107
			HOMO-1 -> LUMO+7	0.145605665
	T_{22}	4.3217 eV	HOMO-13 -> LUMO+7	0.031360097
			HOMO-8 -> LUMO+7	0.025859928
			HOMO-6 -> LUMO+4	0.021250973
			HOMO-1 -> LUMO+1	0.240304714
			HOMO-1 -> LUMO+7	0.538078632
	T_{23}	4.3221 eV	HOMO-7 -> LUMO+5	0.035250435
			HOMO-3 -> LUMO+2	0.799480125
			HOMO-3 -> LUMO+14	0.022510176
			HOMO-2 -> LUMO+2	0.059491802
			HOMO -> LUMO+11	0.031320039
	T_{24}	4.3703 eV	HOMO-3 -> LUMO	0.209602226
			HOMO-3 -> LUMO+1	0.71928018
			HOMO-2 -> LUMO+5	0.022872327
	T_{25}	4.3762 eV	HOMO-3 -> LUMO+1	0.021532275
			HOMO-2 -> LUMO+4	0.030910925
			HOMO-2 -> LUMO+5	0.050842227
			HOMO-2 -> LUMO+8	0.093113386

			HOMO -> LUMO+4	0.657873322

Table S1e The singlet and triplet excited state transition configurations of the **DME** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1-T_n| < 0.3$ eV were highlighted in red.

	n	Energy	Orbitals	Transition
S_n	S_1	3.8629	HOMO-1 -> LUMO	0.028828807
			HOMO -> LUMO	0.942070285
T_n	T_1	3.201	HOMO-15 -> LUMO+18	0.02535752
			HOMO-3 -> LUMO	0.020543645
			HOMO-3 -> LUMO+3	0.079616461
			HOMO-3 -> LUMO+4	0.105947251
			HOMO-3 -> LUMO+5	0.590284586
			HOMO -> LUMO+11	0.060266976
	T_2	3.2079	HOMO-16 -> LUMO+17	0.024633121
			HOMO-4 -> LUMO+1	0.085152391
			HOMO-4 -> LUMO+3	0.300126529
			HOMO-4 -> LUMO+4	0.285420346
			HOMO-4 -> LUMO+5	0.117564005
			HOMO-1 -> LUMO+10	0.051219202
	T_3	3.2151	HOMO-17 -> LUMO+15	0.031385146
			HOMO-5 -> LUMO+1	0.71808128
			HOMO-5 -> LUMO+2	0.040027522
			HOMO-5 -> LUMO+5	0.021441063
			HOMO-2 -> LUMO+9	0.053484122
	T_4	3.3986	HOMO-2 -> LUMO+1	0.67050516
			HOMO-2 -> LUMO+2	0.036861555
			HOMO-2 -> LUMO+4	0.038353421
			HOMO-1 -> LUMO+1	0.133241544
	T_5	3.4338	HOMO-13 -> LUMO	0.108829786
			HOMO-10 -> LUMO	0.035863776
			HOMO-10 -> LUMO+6	0.021470064
			HOMO-1 -> LUMO	0.024055018
			HOMO -> LUMO	0.610247329
			HOMO -> LUMO+5	0.027481057
	T_6	3.4475	HOMO-2 -> LUMO+3	0.028136664
			HOMO-2 -> LUMO+4	0.022697282
			HOMO-1 -> LUMO+1	0.05971968

			HOMO-1 -> LUMO+3	0.302113191
			HOMO-1 -> LUMO+4	0.287327482
			HOMO-1 -> LUMO+5	0.109568167
			HOMO -> LUMO+3	0.037068199
			HOMO -> LUMO+4	0.03474248
	T_7	3.4727	HOMO -> LUMO	0.035863776
			HOMO -> LUMO+3	0.083624141
			HOMO -> LUMO+4	0.11366912
			HOMO -> LUMO+5	0.622237057
	T_8	3.5017	HOMO-12 -> LUMO+7	0.073774087
			HOMO-11 -> LUMO+2	0.165634657
			HOMO-2 -> LUMO+2	0.053372979
			HOMO-1 -> LUMO+1	0.035729991
			HOMO-1 -> LUMO+2	0.494913005
			HOMO -> LUMO+2	0.042079005
	T_9	3.5612	HOMO-9 -> LUMO+3	0.096018384
			HOMO-9 -> LUMO+4	0.08249922
			HOMO-8 -> LUMO+8	0.043920552
			HOMO-7 -> LUMO+3	0.024182403
			HOMO-7 -> LUMO+8	0.050447585
			HOMO-2 -> LUMO+3	0.254826605
			HOMO-2 -> LUMO+4	0.1978205
			HOMO-1 -> LUMO+3	0.038931661
			HOMO-1 -> LUMO+4	0.031195024
	T_{10}	4.0549	HOMO-14 -> LUMO	0.031943809
			HOMO-14 -> LUMO+6	0.062813857
			HOMO-13 -> LUMO	0.145325187
			HOMO-13 -> LUMO+6	0.056535394
			HOMO-12 -> LUMO+6	0.029509922
			HOMO-10 -> LUMO	0.060565921
			HOMO-10 -> LUMO+6	0.092665125
			HOMO -> LUMO	0.207741688
			HOMO -> LUMO+14	0.026782237
	T_{11}	4.076	HOMO -> LUMO+1	0.805891297
			HOMO -> LUMO+2	0.020353549
			HOMO -> LUMO+3	0.039728167
			HOMO -> LUMO+4	0.071994946
	T_{12}	4.0998	HOMO-3 -> LUMO	0.097823491
			HOMO-1 -> LUMO+3	0.025155245
			HOMO -> LUMO+1	0.06749138

			HOMO -> LUMO+3	0.373196162
			HOMO -> LUMO+4	0.22271138
	T_{13}	4.1013	HOMO-12 -> LUMO+2	0.022071005
			HOMO-12 -> LUMO+7	0.16750472
			HOMO-11 -> LUMO+2	0.150909192
			HOMO-10 -> LUMO+7	0.026436202
			HOMO-1 -> LUMO+2	0.138422173
			HOMO-1 -> LUMO+10	0.054853344
			HOMO-1 -> LUMO+13	0.029272321
			HOMO -> LUMO+2	0.044467584
			HOMO -> LUMO+3	0.030628125
	T_{14}	4.1123	HOMO-3 -> LUMO	0.70140168
			HOMO-3 -> LUMO+5	0.026042184
			HOMO -> LUMO+1	0.033354279
			HOMO -> LUMO+3	0.060656445
			HOMO -> LUMO+4	0.034489885
			HOMO -> LUMO+11	0.02416921
	T_{15}	4.1295	HOMO-17 -> LUMO+1	0.020955139
			HOMO-9 -> LUMO+3	0.028651392
			HOMO-9 -> LUMO+4	0.025254034
			HOMO-8 -> LUMO+8	0.037966657
			HOMO-7 -> LUMO+8	0.044910045
			HOMO-5 -> LUMO+1	0.041569978
			HOMO-5 -> LUMO+9	0.02585538
			HOMO-2 -> LUMO+3	0.054694474
			HOMO-2 -> LUMO+4	0.042824938
			HOMO-2 -> LUMO+9	0.211289002
			HOMO-2 -> LUMO+12	0.036660904
			HOMO-1 -> LUMO+9	0.03402397
			HOMO -> LUMO+3	0.029846131
	T_{16}	4.1537	HOMO-2 -> LUMO+1	0.131123205
			HOMO-1 -> LUMO+1	0.69007752
			HOMO-1 -> LUMO+2	0.04187618
			HOMO-1 -> LUMO+4	0.039824064
			HOMO -> LUMO+3	0.024633121
	T_{17}	4.1998	HOMO-4 -> LUMO+2	0.12507001
			HOMO-4 -> LUMO+3	0.024762026
			HOMO-4 -> LUMO+4	0.022480481
			HOMO-1 -> LUMO+10	0.094412506
			HOMO -> LUMO+2	0.343653661

			HOMO -> LUMO+3	0.039795847
			HOMO -> LUMO+4	0.022795395
			HOMO -> LUMO+5	0.027495125
			HOMO -> LUMO+6	0.094082544
	T_{18}	4.2043	HOMO-13 -> LUMO+6	0.028838413
			HOMO-4 -> LUMO+2	0.086303506
			HOMO-2 -> LUMO+9	0.040829389
			HOMO-1 -> LUMO+10	0.076651786
			HOMO -> LUMO+3	0.046293159
			HOMO -> LUMO+6	0.449883037
			HOMO -> LUMO+8	0.021899059
	T_{19}	4.2111	HOMO-4 -> LUMO+2	0.083599605
			HOMO-1 -> LUMO+2	0.075435048
			HOMO-1 -> LUMO+10	0.066138845
			HOMO -> LUMO+2	0.209731738
			HOMO -> LUMO+3	0.040470125
			HOMO -> LUMO+4	0.134940125
			HOMO -> LUMO+5	0.076503073
			HOMO -> LUMO+6	0.078384242
	T_{20}	4.2251	HOMO-8 -> LUMO+8	0.029079073
			HOMO-7 -> LUMO+8	0.033452498
			HOMO-5 -> LUMO+1	0.048416496
			HOMO-2 -> LUMO+3	0.114902592
			HOMO-2 -> LUMO+9	0.20467202
			HOMO-2 -> LUMO+12	0.03648781
			HOMO-1 -> LUMO+3	0.032344418
			HOMO-1 -> LUMO+9	0.036812698
			HOMO -> LUMO+6	0.072916167
	T_{21}	4.2366	HOMO-1 -> LUMO+2	0.040191795
			HOMO-1 -> LUMO+3	0.020076072
			HOMO-1 -> LUMO+4	0.031260001
			HOMO -> LUMO+2	0.304839936
			HOMO -> LUMO+3	0.143926855
			HOMO -> LUMO+4	0.218024458
			HOMO -> LUMO+5	0.135501768
	T_{22}	4.2422	HOMO-2 -> LUMO	0.11596928
			HOMO-1 -> LUMO	0.664358645
			HOMO -> LUMO	0.02464644
			HOMO -> LUMO+11	0.073237299
	T_{23}	4.2541	HOMO-6 -> LUMO+5	0.059140483

			HOMO-6 -> LUMO+14	0.02125922
			HOMO-3 -> LUMO	0.075520525
			HOMO-3 -> LUMO+5	0.033457671
			HOMO-2 -> LUMO	0.023228746
			HOMO-1 -> LUMO	0.092932227
			HOMO -> LUMO+6	0.026898082
			HOMO -> LUMO+11	0.395978803
	T_{24}	4.2726	HOMO-4 -> LUMO+1	0.051417831
			HOMO-4 -> LUMO+2	0.46214498
			HOMO-1 -> LUMO+7	0.049059649
			HOMO-1 -> LUMO+10	0.147142275
	T_{25}	4.2889	HOMO-2 -> LUMO	0.65345312
			HOMO-2 -> LUMO+3	0.042003613
			HOMO-2 -> LUMO+4	0.036223553
			HOMO-1 -> LUMO	0.157517619
			HOMO -> LUMO	0.029412826

Table S1f The singlet and triplet excited state transition configurations of the **NPC-BA** from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S_1 and $|S_1-T_n|$ < 0.3 eV were highlighted in red.

	n	Energy	Orbitals	Transition
S_n	S_1	3.8598 eV	HOMO -> LUMO	0.985186845
T_n	T_1	3.1788 eV	HOMO-5 -> LUMO+6	0.03944117
			HOMO-2 -> LUMO+1	0.047672544
			HOMO-2 -> LUMO+4	0.026033056
			HOMO-1 -> LUMO+1	0.710789645
			HOMO -> LUMO+3	0.133448112
	T_2	3.2665 eV	HOMO-4 -> LUMO+2	0.070770744
			HOMO-3 -> LUMO	0.184601032
			HOMO -> LUMO	0.59638489
			HOMO -> LUMO+1	0.09730225
	T_3	3.3559 eV	HOMO-3 -> LUMO	0.033789601
			HOMO-2 -> LUMO+3	0.024208801
			HOMO -> LUMO	0.070485106
			HOMO -> LUMO+1	0.817792605
	T_4	3.9795 eV	HOMO-5 -> LUMO+1	0.024766477
			HOMO-4 -> LUMO+2	0.236218138
			HOMO-3 -> LUMO	0.2738

			HOMO-2 -> LUMO+3	0.055145205
			HOMO-1 -> LUMO+6	0.025937309
			HOMO -> LUMO	0.193093837
			HOMO -> LUMO+4	0.107008632
	T_5	4.0088 eV	HOMO-2 -> LUMO+1	0.080280245
			HOMO-2 -> LUMO+4	0.034726666
			HOMO-1 -> LUMO+1	0.244552205
			HOMO -> LUMO+3	0.569159143
	T_6	4.1860 eV	HOMO-2 -> LUMO+1	0.037461319
			HOMO-1 -> LUMO	0.870197089
			HOMO-1 -> LUMO+4	0.03825378
	T_7	4.2086 eV	HOMO-4 -> LUMO	0.12859549
			HOMO-3 -> LUMO+2	0.098284045
			HOMO -> LUMO+2	0.730163617
	T_8	4.3016 eV	HOMO-5 -> LUMO+1	0.100459549
			HOMO-4 -> LUMO+2	0.176263594
			HOMO-2 -> LUMO+2	0.02205
			HOMO-2 -> LUMO+3	0.113716805
			HOMO-1 -> LUMO+3	0.04422338
			HOMO-1 -> LUMO+6	0.099761511
			HOMO -> LUMO	0.101358029
			HOMO -> LUMO+1	0.025088
			HOMO -> LUMO+4	0.256055992
	T_9	4.4818 eV	HOMO-4 -> LUMO	0.71983201
			HOMO-2 -> LUMO	0.09165193
			HOMO -> LUMO+2	0.165600125
	T_{10}	4.5172 eV	HOMO-5 -> LUMO+1	0.102577322
			HOMO-1 -> LUMO+3	0.816488647
			HOMO-1 -> LUMO+6	0.02711189
	T_{11}	4.6396 eV	HOMO-4 -> LUMO+1	0.027181793
			HOMO-2 -> LUMO+1	0.556111672
			HOMO-1 -> LUMO	0.047075393
			HOMO-1 -> LUMO+4	0.04646981
			HOMO -> LUMO+3	0.103376045
			HOMO -> LUMO+6	0.161630237
	T_{12}	4.6947 eV	HOMO-5 -> LUMO+1	0.03406572
			HOMO-4 -> LUMO+2	0.390975559
			HOMO-3 -> LUMO	0.424894493
			HOMO-2 -> LUMO+2	0.03875328
			HOMO-1 -> LUMO+3	0.02032128

			HOMO-1 -> LUMO+6	0.034805773
			HOMO -> LUMO	0.026976999
	T_{13}	4.8764 eV	HOMO-5 -> LUMO+1	0.195662657
			HOMO-3 -> LUMO	0.028331521
			HOMO-2 -> LUMO+3	0.031230003
			HOMO-1 -> LUMO+2	0.059740418
			HOMO-1 -> LUMO+3	0.056166113
			HOMO-1 -> LUMO+6	0.19418912
			HOMO -> LUMO+4	0.355526849
	T_{14}	5.0262 eV	HOMO-5 -> LUMO+1	0.034149298
			HOMO-1 -> LUMO+2	0.919151053
	T_{15}	5.2534 eV	HOMO-4 -> LUMO	0.050995405
			HOMO-2 -> LUMO	0.493580737
			HOMO-2 -> LUMO+1	0.03485328
			HOMO-1 -> LUMO	0.020992005
			HOMO-1 -> LUMO+4	0.257360077
			HOMO -> LUMO+3	0.090593218
	T_{16}	5.2672 eV	HOMO-5 -> LUMO+3	0.040248519
			HOMO-4 -> LUMO	0.037204464
			HOMO-2 -> LUMO	0.313394445
			HOMO-1 -> LUMO+4	0.546409672

Table S2 Structure data of single crystals of **EE**, **IPE, TME**, **PE** and **DME.**

Name	EE	IPE	TME	PE	DME
Formula	$C_{20}H_{16}BNO_2$	$C_{21}H_{17}BNO_2$	$C_{24}H_{24}BNO_2$	$C_{21}H_{18}BNO_2$	$C_{23}H_{22}BNO_2$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space Group	Cc	P-1	P2/c	P21/c	P21/c
Cell Lengths (Å)	a=10.1937(12) b=24.9479(16) c=7.566(2)	a=8.0038(19) b=17.3205(12) c=26.7265(10)	a=24.979(2) b=8.940(1) c=19.1000(5)	a=8.113(3) b=16.548(6) c=25.312(10)	a=9.833(4) b=35.533(2) c=5.6192(19)
Cell Angles (°)	α=90 β=119.872(17) γ=90	α=101.028(11) β=91.667(10) γ=100.889(2)	α=90 β=104.664(12) γ=90	α=90 β=91.568(9) γ=90	α=90 β=102.816(6) γ=90
Cell Volume ($Å^3$)	1668.5(5)	3563.0(9)	4126.3(6)	3397(2)	1914.4(10)
Z	4	8	8	8	4
Density (g/cm^3)	1.247	1.216	1.189	1.279	1.232
F(000)	656.0	1368.0	1568.0	1376.0	752.0

h_{max}, k_{max}, l_{max}	12,29,8	9,20,31	29,10,22	9,19,30	12,46,7
CCDC Number	1848439	184840	1848441	1848442	1848443

References

[1] Z. Li, C. Gelbaum, W. L. Heaner IV, J. Fisk, A. Jaganathan, B. Holden, P. Pollet, and C. L. Liotta, *Org. Process Res. Dev.*, 2016, **20**, 1489.