Supporting Information

Touch-sensitive mechanoluminescence crystals consisted of a simple purely organic molecule regardless of crystallization methods

Kai Zhang,[†a] Qikun Sun,[†a] Zhenzhen Zhang,[a] Linagliang Tang,[a] Zongliang Xie,[b] Zhenguo Chi,[b] Shanfeng Xue,[a] Haichang Zhang,*[a] Wenjun Yang*[a]

[a]Key Laboratory of Rubber-plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science &Technology, 53-Zhengzhou Road, Qingdao, 266042, P. R. China. E-mail: haichangzhang@hotmail.com; ywjph2004@qust.edu.cn.

[b]State Key Laboratory of Optoelectronic Material and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University Guangzhou, 510275， P. R. China.

Contents

Table S4 The singlet and triplet excited state transition configurations of the two closely coupled NPC molecules with IP3 coupled mode 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 S5 The singlet and triplet excited state transition configurations of the two closely coupled NPC molecules with IP4 coupled mode 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.

4. Video

Video 1 The shaking mechanoluminescence of NPC sample.

Video 2 The grinding mechanoluminescence of naturally evaporated NPC sample in the dark.

Video 3 The grinding mechanoluminescence of naturally evaporated NPC sample in the soft light.

1. Experimental Procedures

Materials

9-*H*-carbazole (CZ), iodobenzene, CuI, K_2CO_3, L-Proline, Dimethyl sulfoxide (DMSO) was 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.

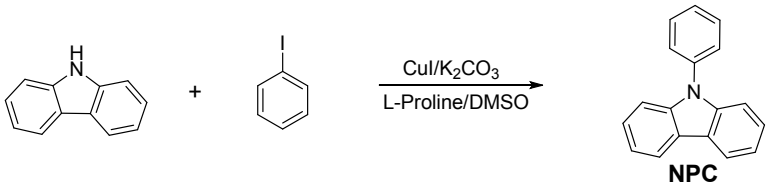
Methods and Instruments.

^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 $^oC\ min^{-1}$. Time-resolved spectra was recorded by Hamamatsu compact fluorescence lifetime spectrometer. The gas chromatograpy and mass spectroscopy were recorded by Agilent Technologic 5975C and Agilent Technologic 7890A, respectively. The crystalline and solution fluorescence efficiencies were all carried out on a FLS980 Spectrometer with a fluorescence integrating sphere.

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 Tn are considered to lie within the range of $ES_1 \pm 0.3$ 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



Scheme 1. Structure and synthetic route of NPC.

***N*-phenylcarbazole (NPC)**: Under nitrogen atmosphere, 9-*H*-carbazole (4.00 g, 23.9 mol), iodobenzene (5.86 g, 28.7mmol) , CuI (0.45 g, 2.39 mmol), K_2CO_3 (6.60 g, 47.8 mol) , *L*-Proline (0.276 g, 2.39 mol) and DMSO (50 mL) were added to a 100 ml one-neck flask. The mixture was stirred for 36 h at 110 ^oC. And then cooled and extracted with CH_2Cl_2 (3×50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed via rotary evaporation. The crude product was purified by silica column chromatography using petroleum ether as the eluent to afford the pure white target compound (5.82 g, yield 90%). NPC was purified twice by vacuum sublimation. ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 7.8 Hz, 2H), 7.65 – 7.56 (m, 4H), 7.49 (t, J = 7.2 Hz, 1H), 7.44 (d, J = 4.0 Hz, 4H), 7.32 (dt, J = 7.7, 3.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.91, 137.72, 129.86, 127.44, 125.92, 123.36, 120.30, 119.90, 109.77. GC-MS: m/z Calcd. for $C_{18}H_{13}N$: 243.3090; found 243 [M^+]. Anal. Calcd. for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.84; H, 5.43; N, 5.72.

2. Figure

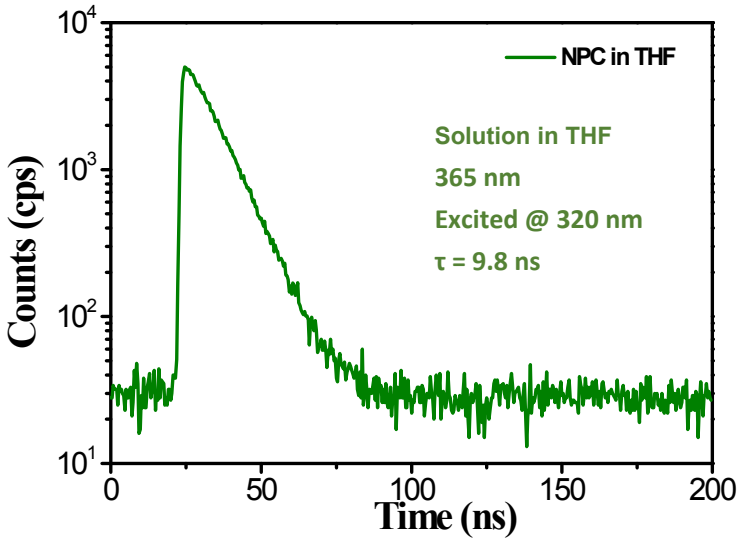


Fig. S1 Time-resolved emission decay curve NPC solution in THF at 298K. Luminescent peaks and lifetimes (τ) are indicated.

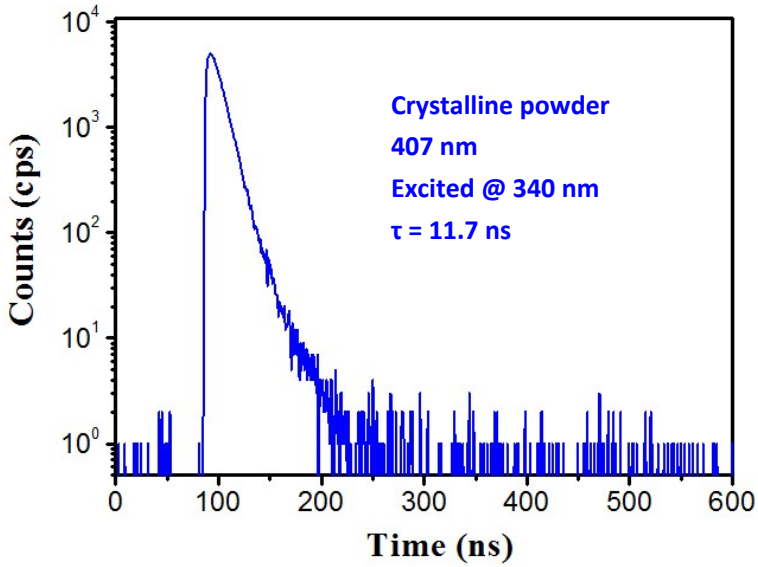


Fig. S2 The photofluorescence time-resolved emission decay curve of crystalline NPC powder at 298K. Luminescent peaks and lifetimes (τ) are indicated.

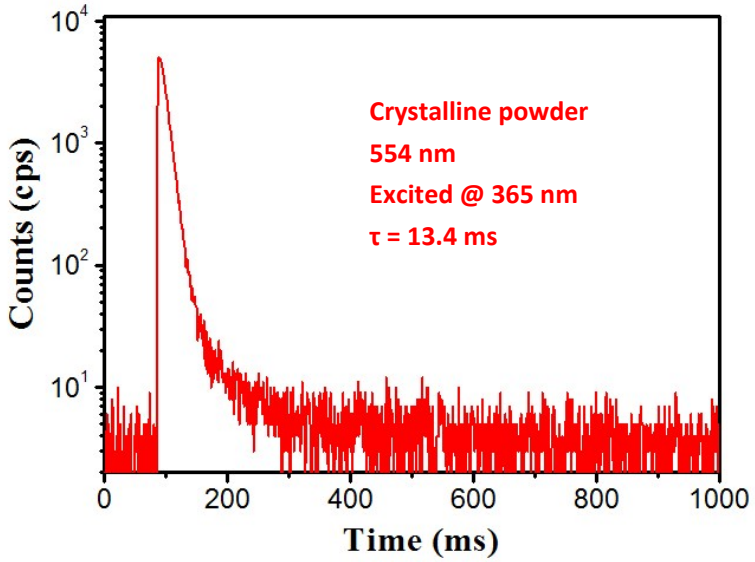


Fig. S3 The photofluorescence time-resolved emission decay curve of crystalline NPC powder at 298K. Luminescent peaks and lifetimes (τ) are indicated.

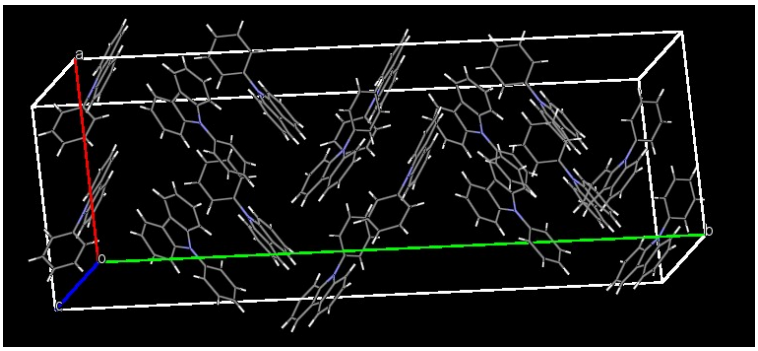


Fig. S4 The unit cell of NPC single crystal.

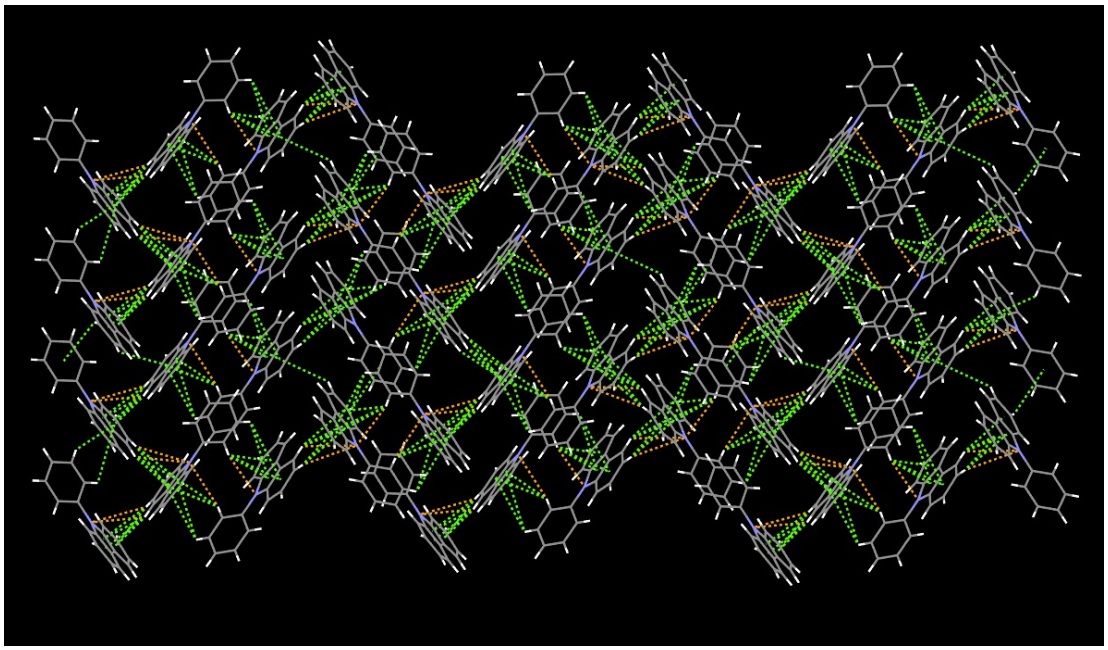


Fig. S5 The 3D supramolecular H-bonding network of NPC single crystal. Green and yellow dotted lines represent intermolecular CH···π and CH···N interactions, respectively.

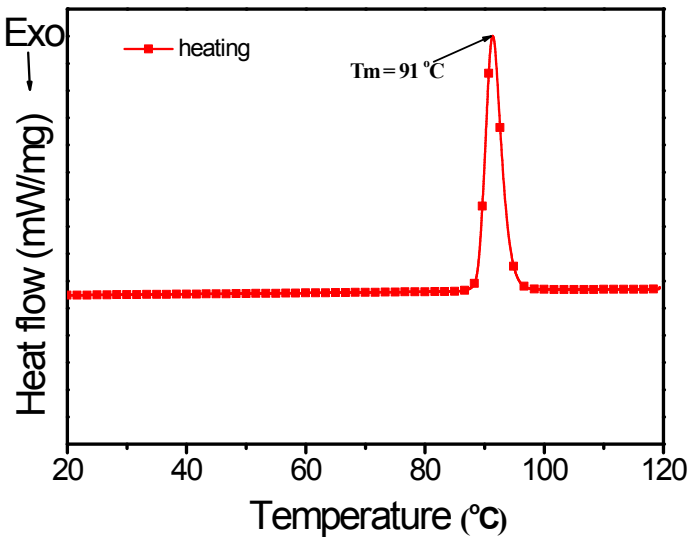


Fig. S6 Differential scanning calorimetric (DSC) curve of NPC.

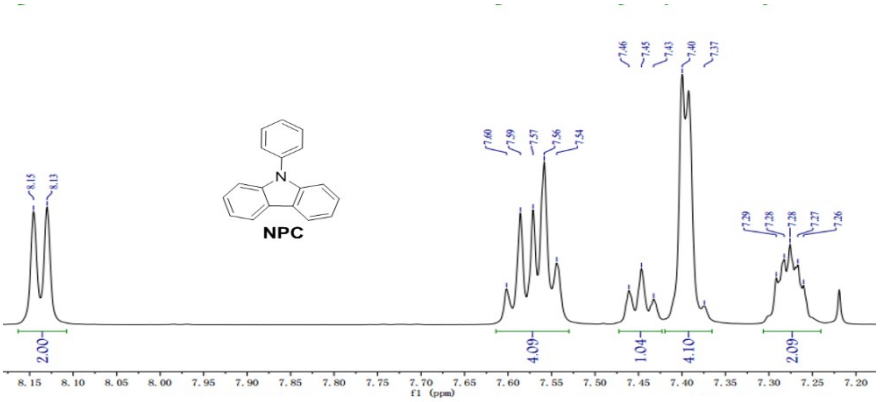


Fig. S7 ^{1}H NMR spectra of NPC in $CDCl_3$.

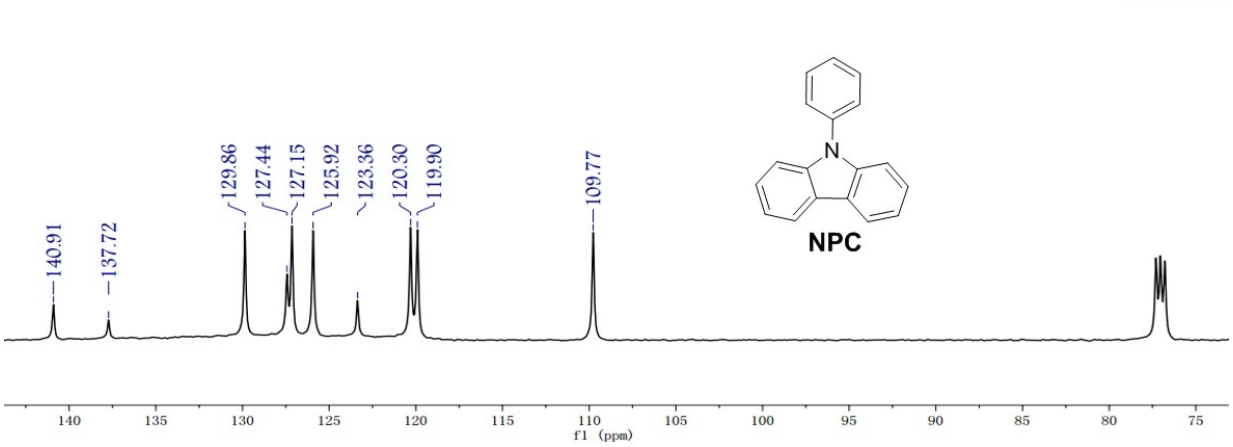


Fig. S8 ^{13}C NMR spectra of NPC in $CDCl_3$.

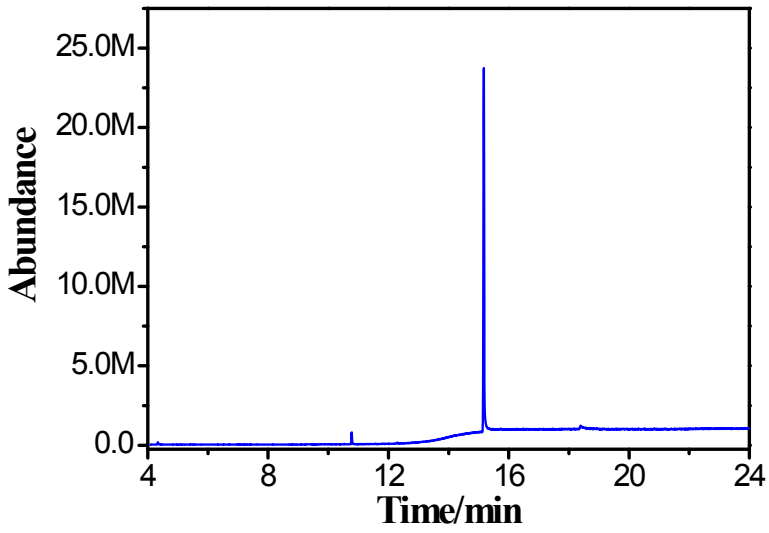
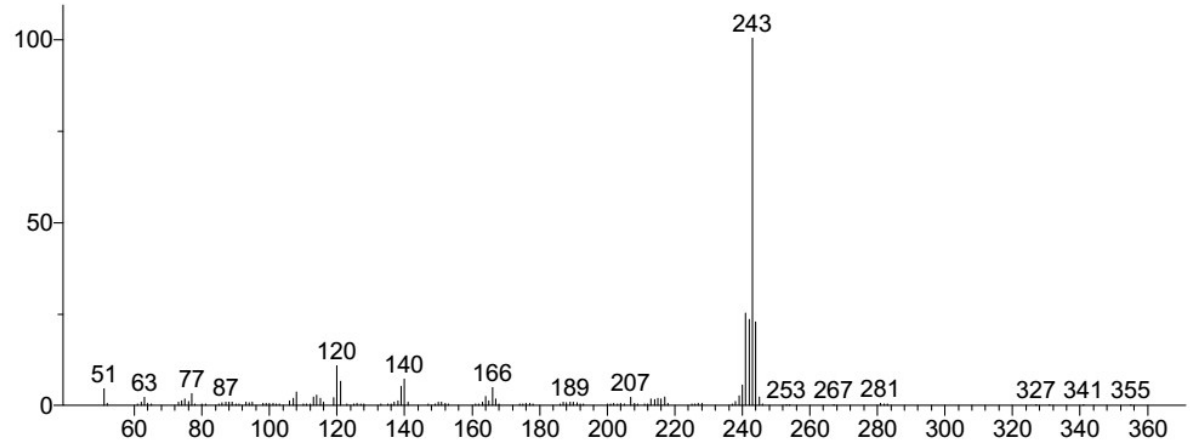


Fig. S9 The gas chromatogram of NPC.



Hit 1 : 9H-Carbazole, 9-phenyl-
C18H13N; MF: 904; RMF: 933; Prob 81.4%; CAS: 1150-62-5; Lib: replib; ID: 28481.

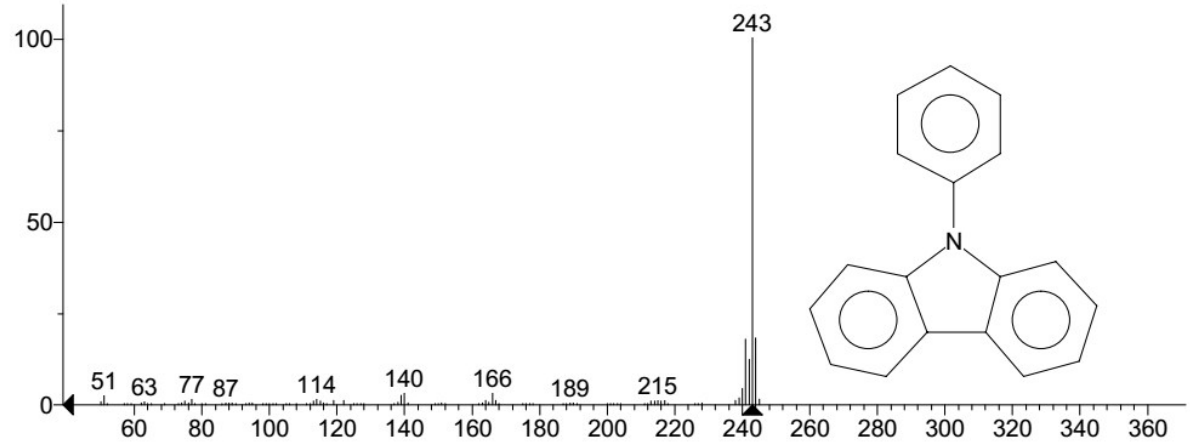


Fig. S10 The mass spectra of NPC. Experimental value (top) and the reference value in the instrument database (down).

3. Table

Table S1 Single crystal structural parameters of NPC.

Compound reference	colorless NPC crystal
Chemical formula	C_{18} H_{13} N
Formula weight	243.29
Crystal system	orthorhombic
a/Å	12.7887(15)
b/ Å	38.1950(19)
c/ Å	10.8230(15)
α/°	90.00
β/°	90.00
γ/°	90.00
Unit cell volume/ Å3	5286.6(10)
Temperature/K	296
Space group	Fdd2
Z	16
Density (calculated) /g cm^{-3}	1.223
F(000)	2048.0
Theta range for data collection	2.52 to 24.99 deg.
Index ranges	-15<=h<=15, -43<=k<=45, -12<=l<=7
Reflections measured	6523
Independent reflections	1834
Rint	0.0936
Completeness to theta = 72.13°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9852 and 0.9769
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1834 / 1 / 173
Goodness-of-fit on F^2	0.982
Final R_1 values ($I> 2\sigma(I)$)	0.0427
Final $wR(F^2)$ values ($I> 2\sigma(I)$)	0.0544
Final R_1values (all data)	0.1072
Final $wR(F^2)$ values (all data)	0.0633
CCDC number	1584272

Table S2 The singlet and triplet excited state transition configurations of the two closely coupled NPC molecules with the IP1 coupled mode 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	4.0347 eV	HOMO-3 ->LUMO+6	0.03
			HOMO-1 ->LUMO	0.57
			HOMO ->LUMO	0.36
			HOMO ->LUMO+1	0.03
T_n	T_1	3.2207 eV	HOMO-10 ->LUMO+11	0.03
			HOMO-4 ->LUMO+1	0.04
			HOMO-2 ->LUMO+1	0.61
			HOMO ->LUMO+1	0.20
			HOMO ->LUMO+7	0.07
	T_2	3.2221 eV	HOMO-11 ->LUMO+10	0.02
			HOMO-5 ->LUMO	0.04
			HOMO-3 ->LUMO	0.57
			HOMO-1 ->LUMO	0.25
			HOMO-1 ->LUMO+6	0.07
	T_3	3.3949 eV	HOMO-5 ->LUMO+6	0.02
			HOMO-3 ->LUMO	0.23
			HOMO-1 ->LUMO	0.68
	T_4	3.4184 eV	HOMO-4 ->LUMO+7	0.02
			HOMO-2 ->LUMO+1	0.19
			HOMO ->LUMO+1	0.73
	T_5	3.7832 eV	HOMO-9 ->LUMO+5	0.02
			HOMO-8 ->LUMO+3	0.03
			HOMO-8 ->LUMO+5	0.08
			HOMO-6 ->LUMO+3	0.11
			HOMO-6 ->LUMO+4	0.07
			HOMO ->LUMO+3	0.41
			HOMO ->LUMO+4	0.18
	T_6	3.8332 eV	HOMO-9 ->LUMO+3	0.02
			HOMO-9 ->LUMO+4	0.07
			HOMO-9 ->LUMO+5	0.05
			HOMO-7 ->LUMO+2	0.21
			HOMO-1 ->LUMO+2	0.51
	T_7	4.0416 eV	HOMO ->LUMO	0.99
	T_8	4.1156 eV	HOMO-7 ->LUMO+2	0.02
			HOMO-5 ->LUMO	0.13
			HOMO-5 ->LUMO+8	0.03
			HOMO-3 ->LUMO	0.14
			HOMO-1 ->LUMO+6	0.53

T_9	4.1230 eV	HOMO-4 ->LUMO+1	0.12
		HOMO-4 ->LUMO+9	0.02
		HOMO-2 ->LUMO+1	0.11
		HOMO ->LUMO+3	0.03
		HOMO ->LUMO+4	0.02
		HOMO ->LUMO+5	0.10
		HOMO ->LUMO+7	0.42
T_{10}	4.1533 eV	HOMO-6 ->LUMO+5	0.03
		HOMO-2 ->LUMO+1	0.02
		HOMO ->LUMO+3	0.10
		HOMO ->LUMO+4	0.17
		HOMO ->LUMO+5	0.49
		HOMO ->LUMO+7	0.09
T_{11}	4.2705 eV	HOMO-10 ->LUMO+1	0.05
		HOMO-9 ->LUMO+5	0.03
		HOMO-8 ->LUMO+3	0.04
		HOMO-8 ->LUMO+4	0.03
		HOMO-8 ->LUMO+5	0.12
		HOMO-6 ->LUMO+3	0.06
		HOMO-6 ->LUMO+4	0.04
		HOMO-4 ->LUMO+7	0.07
		HOMO-2 ->LUMO+1	0.02
		HOMO-2 ->LUMO+11	0.05
		HOMO ->LUMO+3	0.09
		HOMO ->LUMO+4	0.03
		HOMO ->LUMO+7	0.07
		HOMO ->LUMO+9	0.17
T_{12}	4.2804 eV	HOMO-11 ->LUMO	0.06
		HOMO-9 ->LUMO+3	0.02
		HOMO-9 ->LUMO+4	0.06
		HOMO-9 ->LUMO+5	0.04
		HOMO-7 ->LUMO+2	0.09
		HOMO-5 ->LUMO+6	0.08
		HOMO-3 ->LUMO	0.02
		HOMO-3 ->LUMO+10	0.05
		HOMO-1 ->LUMO+1	0.04
		HOMO-1 ->LUMO+2	0.10
		HOMO-1 ->LUMO+6	0.07
		HOMO-1 ->LUMO+8	0.21
T_{13}	4.2876 eV	HOMO-7 ->LUMO+4	0.03
		HOMO-7 ->LUMO+5	0.02
		HOMO-1 ->LUMO+1	0.03
		HOMO-1 ->LUMO+3	0.16
		HOMO-1 ->LUMO+4	0.40

			HOMO-1 ->LUMO+5	0.27
	T_{14}	4.3678 eV	HOMO-2 ->LUMO	0.98
	T_{15}	4.4030 eV	HOMO-1 ->LUMO+1	0.91

Table S3 The singlet and triplet excited state transition configurations of the two closely coupled NPC molecules with IP2 coupled mode 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	3.9554 eV	HOMO-1 ->LUMO+1	0.22
			HOMO ->LUMO	0.65
T_n	T_1	3.2116 eV	HOMO-3 ->LUMO+1	0.26
			HOMO-2 ->LUMO	0.28
			HOMO-1 ->LUMO+1	0.09
			HOMO-1 ->LUMO+7	0.03
			HOMO ->LUMO	0.18
			HOMO ->LUMO+6	0.04
	T_2	3.2194 eV	HOMO-5 ->LUMO	0.02
			HOMO-3 ->LUMO	0.29
			HOMO-2 ->LUMO+1	0.28
			HOMO-1 ->LUMO	0.12
			HOMO-1 ->LUMO+6	0.03
			HOMO ->LUMO+1	0.11
			HOMO ->LUMO+7	0.04
	T_3	3.3592 eV	HOMO-3 ->LUMO+1	0.12
			HOMO-2 ->LUMO	0.13
			HOMO-1 ->LUMO+1	0.25
			HOMO ->LUMO	0.41
	T_4	3.3673 eV	HOMO-3 ->LUMO	0.11
			HOMO-2 ->LUMO+1	0.10
			HOMO-1 ->LUMO	0.35
			HOMO ->LUMO+1	0.35
	T_5	3.8284 eV	HOMO-9 ->LUMO+3	0.02
			HOMO-9 ->LUMO+4	0.07
			HOMO-8 ->LUMO+5	0.08
			HOMO-7 ->LUMO+3	0.07
			HOMO-6 ->LUMO+2	0.10
			HOMO-5 ->LUMO+5	0.03
			HOMO-1 ->LUMO+1	0.08
			HOMO-1 ->LUMO+2	0.14
			HOMO-1 ->LUMO+5	0.04
			HOMO ->LUMO+3	0.17
			HOMO ->LUMO+4	0.10
	T_6	3.8325 eV	HOMO-9 ->LUMO+2	0.07
			HOMO-8 ->LUMO+3	0.08

		HOMO-7 ->LUMO+5	0.07
		HOMO-6 ->LUMO+4	0.10
		HOMO-5 ->LUMO+3	0.03
		HOMO-1 ->LUMO	0.03
		HOMO-1 ->LUMO+3	0.09
		HOMO-1 ->LUMO+4	0.09
		HOMO ->LUMO+1	0.07
		HOMO ->LUMO+2	0.17
		HOMO ->LUMO+5	0.07
T_7	4.0858 eV	HOMO-5 ->LUMO+1	0.03
		HOMO-4 ->LUMO	0.07
		HOMO-3 ->LUMO+1	0.05
		HOMO-2 ->LUMO	0.09
		HOMO-1 ->LUMO+1	0.06
		HOMO-1 ->LUMO+7	0.19
		HOMO ->LUMO+6	0.29
T_8	4.0912 eV	HOMO-5 ->LUMO	0.06
		HOMO-4 ->LUMO+1	0.05
		HOMO-3 ->LUMO	0.09
		HOMO-2 ->LUMO+1	0.05
		HOMO-1 ->LUMO+6	0.25
		HOMO ->LUMO+2	0.02
		HOMO ->LUMO+5	0.02
		HOMO ->LUMO+7	0.24
T_9	4.1768 eV	HOMO-6 ->LUMO+4	0.02
		HOMO-1 ->LUMO	0.45
		HOMO ->LUMO+1	0.42
		HOMO ->LUMO+2	0.03
T_{10}	4.1971 eV	HOMO-1 ->LUMO+1	0.48
		HOMO-1 ->LUMO+2	0.03
		HOMO-1 ->LUMO+7	0.02
		HOMO ->LUMO	0.34
		HOMO ->LUMO+6	0.03
T_{11}	4.2559 eV	HOMO-11 ->LUMO	0.03
		HOMO-10 ->LUMO+1	0.03
		HOMO-9 ->LUMO+2	0.02
		HOMO-8 ->LUMO+3	0.04
		HOMO-7 ->LUMO+5	0.05
		HOMO-6 ->LUMO+4	0.03
		HOMO-5 ->LUMO+3	0.02
		HOMO-5 ->LUMO+6	0.02
		HOMO-4 ->LUMO+7	0.05
		HOMO-3 ->LUMO+10	0.03
		HOMO-2 ->LUMO+11	0.03
		HOMO-1 ->LUMO+3	0.03
		HOMO-1 ->LUMO+4	0.02
		HOMO-1 ->LUMO+6	0.04
		HOMO-1 ->LUMO+8	0.10

			HOMO ->LUMO+2	0.14
			HOMO ->LUMO+7	0.06
			HOMO ->LUMO+9	0.09
	T_{12}	4.2662 eV	HOMO-11 ->LUMO+1	0.03
			HOMO-10 ->LUMO	0.04
			HOMO-9 ->LUMO+4	0.02
			HOMO-8 ->LUMO+5	0.04
			HOMO-7 ->LUMO+3	0.04
			HOMO-6 ->LUMO+2	0.05
			HOMO-5 ->LUMO+7	0.04
			HOMO-4 ->LUMO+6	0.04
			HOMO-3 ->LUMO+11	0.03
			HOMO-2 ->LUMO+10	0.03
			HOMO-1 ->LUMO+2	0.05
			HOMO-1 ->LUMO+7	0.04
			HOMO-1 ->LUMO+9	0.10
			HOMO ->LUMO+3	0.06
			HOMO ->LUMO+6	0.02
			HOMO ->LUMO+8	0.13

Table S4 The singlet and triplet excited state transition configurations of the two closely coupled NPC molecules with IP3 coupled mode 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	4.0581 eV	HOMO-3 ->LUMO+6	0.02
			HOMO-3 ->LUMO+7	0.02
			HOMO-1 ->LUMO	0.24
			HOMO-1 ->LUMO+1	0.11
			HOMO ->LUMO	0.46
			HOMO ->LUMO+1	0.12
T_n	T_1	3.2213 eV	HOMO-3 ->LUMO	0.34
			HOMO-3 ->LUMO+1	0.19
			HOMO-2 ->LUMO	0.08
			HOMO-1 ->LUMO	0.10
			HOMO-1 ->LUMO+7	0.03
			HOMO ->LUMO	0.03
			HOMO ->LUMO+1	0.05
			HOMO ->LUMO+6	0.04
	T_2	3.2216 eV	HOMO-3 ->LUMO	0.10
			HOMO-2 ->LUMO	0.11
			HOMO-2 ->LUMO+1	0.43
			HOMO-1 ->LUMO+1	0.08
			HOMO-1 ->LUMO+6	0.03

		HOMO ->LUMO	0.06
		HOMO ->LUMO+1	0.04
		HOMO ->LUMO+7	0.03
T_3	3.4055 eV	HOMO-3 ->LUMO	0.12
		HOMO-3 ->LUMO+1	0.04
		HOMO-1 ->LUMO	0.22
		HOMO-1 ->LUMO+1	0.09
		HOMO ->LUMO	0.32
		HOMO ->LUMO+1	0.11
T_4	3.4116 eV	HOMO-2 ->LUMO	0.05
		HOMO-2 ->LUMO+1	0.12
		HOMO-1 ->LUMO	0.11
		HOMO-1 ->LUMO+1	0.26
		HOMO ->LUMO	0.10
		HOMO ->LUMO+1	0.28
T_5	3.7983 eV	HOMO-9 ->LUMO+5	0.08
		HOMO-8 ->LUMO+4	0.03
		HOMO-7 ->LUMO+2	0.12
		HOMO-6 ->LUMO+3	0.04
		HOMO-1 ->LUMO+2	0.17
		HOMO-1 ->LUMO+3	0.06
		HOMO-1 ->LUMO+5	0.04
		HOMO ->LUMO+2	0.22
		HOMO ->LUMO+3	0.07
T_6	3.7986 eV	HOMO-9 ->LUMO+5	0.03
		HOMO-8 ->LUMO+3	0.03
		HOMO-8 ->LUMO+4	0.09
		HOMO-7 ->LUMO+2	0.04
		HOMO-6 ->LUMO+3	0.11
		HOMO-6 ->LUMO+4	0.02
		HOMO-1 ->LUMO+2	0.10
		HOMO-1 ->LUMO+3	0.14
		HOMO ->LUMO+2	0.05
		HOMO ->LUMO+3	0.21
		HOMO ->LUMO+5	0.05
T_7	4.1210 eV	HOMO-5 ->LUMO+1	0.05
		HOMO-4 ->LUMO	0.07
		HOMO-3 ->LUMO	0.05
		HOMO-3 ->LUMO+1	0.04
		HOMO-2 ->LUMO	0.03
		HOMO-1 ->LUMO+7	0.22
		HOMO ->LUMO+6	0.28
T_8	4.1220 eV	HOMO-5 ->LUMO	0.06

		HOMO-4 ->LUMO+1	0.07
		HOMO-3 ->LUMO	0.05
		HOMO-2 ->LUMO+1	0.07
		HOMO-1 ->LUMO+1	0.02
		HOMO-1 ->LUMO+6	0.25
		HOMO ->LUMO+7	0.25
T_9	4.1819 eV	HOMO-6 ->LUMO+4	0.04
		HOMO-1 ->LUMO+3	0.05
		HOMO-1 ->LUMO+4	0.26
		HOMO-1 ->LUMO+5	0.03
		HOMO ->LUMO+3	0.07
		HOMO ->LUMO+4	0.42
		HOMO ->LUMO+5	0.03
T_{10}	4.2690 eV	HOMO-7 ->LUMO+5	0.04
		HOMO-1 ->LUMO+2	0.03
		HOMO-1 ->LUMO+4	0.07
		HOMO-1 ->LUMO+5	0.32
		HOMO ->LUMO+2	0.03
		HOMO ->LUMO+3	0.02
		HOMO ->LUMO+4	0.05
		HOMO ->LUMO+5	0.35
T_{11}	4.2690 eV	HOMO-10 ->LUMO	0.02
		HOMO-8 ->LUMO+3	0.04
		HOMO-8 ->LUMO+4	0.13
		HOMO-6 ->LUMO+3	0.06
		HOMO-5 ->LUMO+7	0.03
		HOMO-4 ->LUMO+6	0.03
		HOMO-3 ->LUMO+10	0.03
		HOMO-1 ->LUMO	0.02
		HOMO-1 ->LUMO+3	0.04
		HOMO-1 ->LUMO+9	0.08
		HOMO ->LUMO+3	0.04
		HOMO ->LUMO+7	0.02
		HOMO ->LUMO+8	0.08
		HOMO ->LUMO+9	0.02
T_{12}	4.2718 eV	HOMO-10 ->LUMO+1	0.03
		HOMO-9 ->LUMO+2	0.02
		HOMO-9 ->LUMO+4	0.03
		HOMO-9 ->LUMO+5	0.13
		HOMO-7 ->LUMO+2	0.08
		HOMO-5 ->LUMO+6	0.03
		HOMO-4 ->LUMO+7	0.03
		HOMO-2 ->LUMO+10	0.03
		HOMO-1 ->LUMO+2	0.04

		HOMO-1 ->LUMO+7	0.03
		HOMO-1 ->LUMO+8	0.08
		HOMO ->LUMO+2	0.05
		HOMO ->LUMO+6	0.02
		HOMO ->LUMO+9	0.07
T_{13}	4.3209 eV	HOMO-1 ->LUMO	0.13
		HOMO-1 ->LUMO+1	0.34
		HOMO ->LUMO	0.11
		HOMO ->LUMO+1	0.36
T_{14}	4.3615 eV	HOMO-1 ->LUMO	0.38
		HOMO-1 ->LUMO+1	0.15
		HOMO ->LUMO	0.33
		HOMO ->LUMO+1	0.10
T_{15}	4.5463 eV	HOMO-11 ->LUMO+1	0.03
		HOMO-10 ->LUMO	0.02
		HOMO-10 ->LUMO+1	0.04
		HOMO-9 ->LUMO+5	0.11
		HOMO-5 ->LUMO+1	0.02
		HOMO-4 ->LUMO+1	0.03
		HOMO-2 ->LUMO+2	0.22
		HOMO-2 ->LUMO+6	0.03
		HOMO-2 ->LUMO+7	0.03
		HOMO-2 ->LUMO+9	0.02
		HOMO-2 ->LUMO+10	0.02
		HOMO-1 ->LUMO+2	0.04
		HOMO-1 ->LUMO+9	0.02
		HOMO ->LUMO+2	0.06
		HOMO ->LUMO+8	0.02
T_{16}	4.5483 eV	HOMO-11 ->LUMO	0.06
		HOMO-10 ->LUMO	0.02
		HOMO-8 ->LUMO+3	0.03
		HOMO-8 ->LUMO+4	0.15
		HOMO-4 ->LUMO	0.03
		HOMO-3 ->LUMO+3	0.12
		HOMO-3 ->LUMO+9	0.02
		HOMO-3 ->LUMO+10	0.03
		HOMO-3 ->LUMO+11	0.02
		HOMO ->LUMO+3	0.13
		HOMO ->LUMO+9	0.03

Table S5 The singlet and triplet excited state transition configurations of the two closely coupled NPC molecules with IP4 coupled mode 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	4.0593 eV	HOMO-3 ->LUMO+6	0.04
			HOMO-1 ->LUMO	0.92
T_n	T_1	3.2220 eV	HOMO-4 ->LUMO+1	0.03
			HOMO-3 ->LUMO	0.12
			HOMO-3 ->LUMO+1	0.03
			HOMO-2 ->LUMO+1	0.48
			HOMO-1 ->LUMO	0.03
			HOMO ->LUMO+1	0.13
			HOMO ->LUMO+7	0.06
	T_2	3.2236 eV	HOMO-5 ->LUMO	0.03
			HOMO-3 ->LUMO	0.44
			HOMO-3 ->LUMO+1	0.03
			HOMO-2 ->LUMO	0.06
			HOMO-2 ->LUMO+1	0.10
			HOMO-1 ->LUMO	0.14
			HOMO-1 ->LUMO+6	0.06
			HOMO ->LUMO+1	0.04
	T_3	3.4029 eV	HOMO-5 ->LUMO+6	0.02
			HOMO-3 ->LUMO	0.14
			HOMO-1 ->LUMO	0.75
	T_4	3.4029 eV	HOMO-4 ->LUMO+7	0.02
			HOMO-3 ->LUMO+1	0.02
			HOMO-2 ->LUMO+1	0.14
			HOMO ->LUMO+1	0.74
	T_5	3.8031 eV	HOMO-8 ->LUMO+3	0.02
			HOMO-8 ->LUMO+5	0.14
			HOMO-6 ->LUMO+3	0.17
			HOMO-6 ->LUMO+5	0.03
			HOMO ->LUMO+3	0.52
			HOMO ->LUMO+5	0.04
	T_6	3.8097 eV	HOMO-9 ->LUMO+2	0.02
			HOMO-9 ->LUMO+4	0.15
			HOMO-7 ->LUMO+2	0.18
			HOMO-7 ->LUMO+4	0.02
			HOMO-1 ->LUMO+2	0.52
			HOMO-1 ->LUMO+4	0.03
	T_7	4.1193 eV	HOMO-5 ->LUMO	0.08
			HOMO-4 ->LUMO+1	0.05
			HOMO-3 ->LUMO	0.07
			HOMO-2 ->LUMO+1	0.04

		HOMO-1 ->LUMO+6	0.33
		HOMO ->LUMO+7	0.19
T_8	4.1224 eV	HOMO-5 ->LUMO	0.05
		HOMO-4 ->LUMO+1	0.08
		HOMO-3 ->LUMO	0.05
		HOMO-2 ->LUMO+1	0.08
		HOMO-1 ->LUMO+6	0.21
		HOMO ->LUMO+7	0.33
T_9	4.2008 eV	HOMO-6 ->LUMO+5	0.06
		HOMO ->LUMO+3	0.06
		HOMO ->LUMO+5	0.82
T_{10}	4.2179 eV	HOMO-7 ->LUMO+4	0.06
		HOMO-1 ->LUMO+2	0.05
		HOMO-1 ->LUMO+4	0.84
T_{11}	4.2724 eV	HOMO-10 ->LUMO+1	0.06
		HOMO-8 ->LUMO+3	0.02
		HOMO-8 ->LUMO+5	0.18
		HOMO-6 ->LUMO+3	0.09
		HOMO-4 ->LUMO+7	0.08
		HOMO-2 ->LUMO+1	0.02
		HOMO-2 ->LUMO+10	0.02
		HOMO-2 ->LUMO+11	0.03
		HOMO ->LUMO+3	0.10
		HOMO ->LUMO+7	0.06
		HOMO ->LUMO+8	0.03
		HOMO ->LUMO+9	0.16
T_{12}	4.2749 eV	HOMO-11 ->LUMO	0.06
		HOMO-9 ->LUMO+2	0.02
		HOMO-9 ->LUMO+4	0.18
		HOMO-7 ->LUMO+2	0.09
		HOMO-5 ->LUMO+6	0.09
		HOMO-3 ->LUMO+10	0.03
		HOMO-1 ->LUMO+2	0.10
		HOMO-1 ->LUMO+6	0.06
		HOMO-1 ->LUMO+8	0.17
		HOMO-1 ->LUMO+9	0.02
T_{13}	4.3511 eV	HOMO ->LUMO	0.93
T14	4.4027 eV	HOMO-1 ->LUMO+1	0.98
T^{15}	4.5532 eV	HOMO-10 ->LUMO+1	0.09
		HOMO-8 ->LUMO+5	0.15
		HOMO-4 ->LUMO+1	0.08
		HOMO-4 ->LUMO+7	0.02
		HOMO-2 ->LUMO+3	0.17
		HOMO-2 ->LUMO+7	0.05

			HOMO-2 ->LUMO+9	0.04
			HOMO-2 ->LUMO+10	0.02
			HOMO-2 ->LUMO+11	0.02
			HOMO ->LUMO+3	0.11
			HOMO ->LUMO+9	0.06
			HOMO-11 ->LUMO	0.10
			HOMO-9 ->LUMO+4	0.18
			HOMO-5 ->LUMO	0.07
			HOMO-5 ->LUMO+6	0.03
			HOMO-3 ->LUMO+2	0.11
T_{16}	4.5612 eV		HOMO-3 ->LUMO+6	0.03
			HOMO-3 ->LUMO+8	0.03
			HOMO-3 ->LUMO+10	0.03
			HOMO-3 ->LUMO+11	0.02
			HOMO-1 ->LUMO+2	0.14
			HOMO-1 ->LUMO+8	0.07