Supporting Information

Bright NUV mechanofluorescence from a terpyridine-based pure organic crystal

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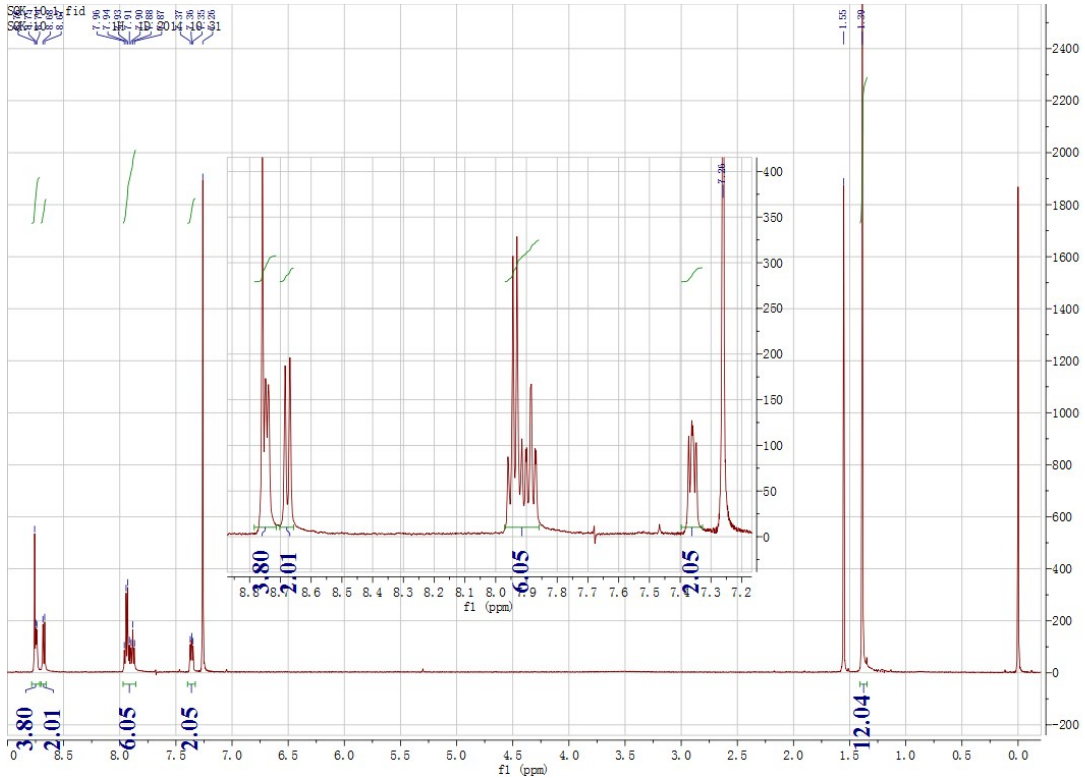
Experimental Section

4'-(4-bromophenyl)-2,2':6',2''-terpyridine(Br-TPY) In a 250mL round bottom flask, 2-acetylpyridine (1.22 g, 10.0 mmol), NH_3 (aqueous)(15 mL, 12.6 mmol), KOH (0.78 g, 12.0 mmol) was respectively added to a solution of 4-bromobenzal-dehyde(0.93 g, 5.0 mmol) in EtOH (25 mL). The solution was refluxed for 24 h. After cooling down to the room temperature, the solution was evaporated to dryness under reduced pressure to give the crude product. The crude product was washed by cool methanol twice then recrystallized by acetone. A pure white solid with a yield of (58%, 1.10 g) was obtained. ^{1}H-NMR (500 HMz, $CDCl_3$): δ 8.73 (d, 2H), 8.70 (s, 2H), 8.68 (d, J = 8.0 Hz, 2 H), 7.87 – 7.90(m, 2 H), 7.79(d, J=4.0 Hz, 2 H), 7.65 (d, J=3.5 Hz, 2H), 7.35 – 7.38 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.97, 154.93, 148.04, 136.32, 135.96, 131.07, 127.85, 122.93, 122.46, 120.39, 117.56.

4'-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2':6',2''-terpyridine(BP-TPY) In a 250 mL round bottom flask, 4′-(4-bromophenyl)-2,2′:6′,2″- terpyridine (1.0 g, 25.8 mmol) and KOAc (0.764 g, 7.8 mmol) were dissolved in DMSO (200 mL) on an ultrasonic bath. Bis-(pinacolato)diboron (0.672 g, 2.64 mmol) and Pd(dppf)Cl_2 (0.06 g, 0.078 mmol) were added and the reaction mixture was stirred at 80 ^{o}C under N_2 for 6h. After cooling down to the room temperature, extracted with toluene. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (petroleum ether/acetone, 1/1, v/v). A white solid was obtained (0.72 g, 64.3%). ^{1}H NMR(500HMz, $CDCl_3$) δ 8.78 – 8.72 (m, 4H), 8.68 (d, J = 7.9 Hz, 2H), 7.91 (d, J = 22.9, 7.9 Hz, 6H), 7.40 – 7.33 (m, 2H), 1.39 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.10, 154.82, 149.12, 148.01, 139.88, 135.97, 134.33, 125.54, 122.84, 120.43, 117.96, 82.94, 23.89. MALDI-TOF MS: m/z Calcd. for $C_{27}H_{26}BN_3O_2$: 435.3340; found 458.1257 $[M+Na]^+$.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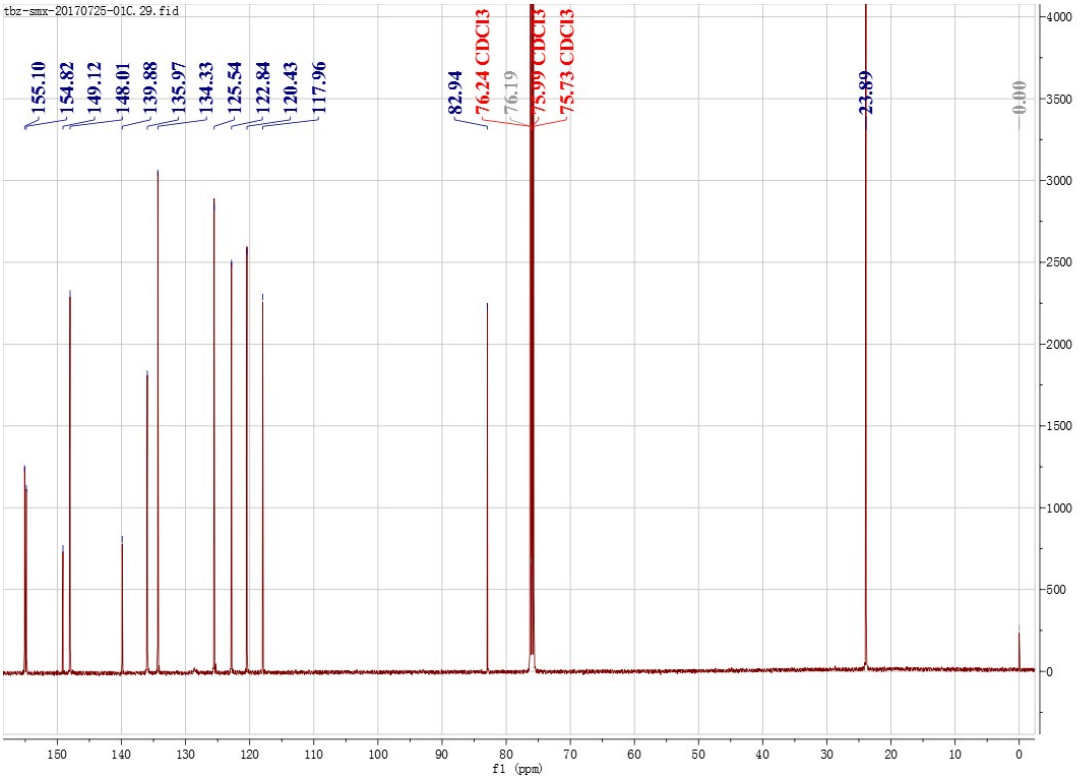
2.01
6.05
2.05
12.04
f1 (ppm)


155.10
154.82
149.12
148.01
139.88
135.97
134.33
125.54
122.84
120.43
117.96
82.94
76.24 CDCl3
76.19
75.99 CDCl3
75.73 CDCl3
23.89
0.00
f1 (ppm)

Measurement

NMR spectra were recorded in $CDCl_3$ on a Bruker-AC500 spectrometer (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR) with tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFR^{TM} plus instrument. UV-vis absorption and diffuse reflectance absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were carried out with Hitachi F-4600 spectrophotometer. The fluorescence quantum yield (Φ) was determined by the dilution method using fluorescein in water (pH = 11) as the reference in which the absolute absorption maxima are less than 0.1. Fluorescence decay was measured on Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER320) as the excitation source. The ML spectrum was collected from a spectrometer of Acton SP2750 with a liquid-nitrogen-cooled CCD (SPEC-10, Princeton) as a power detector.

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 E_{S1} ± 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.

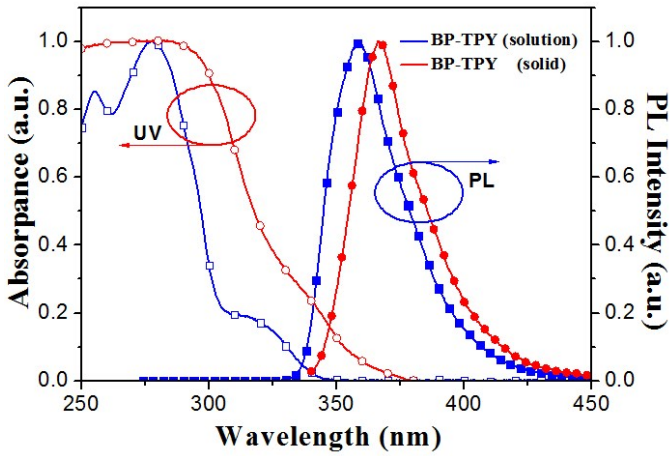


Fig. S1 The absorption and PL spectra of BP-TPY in THF solution and solid states.

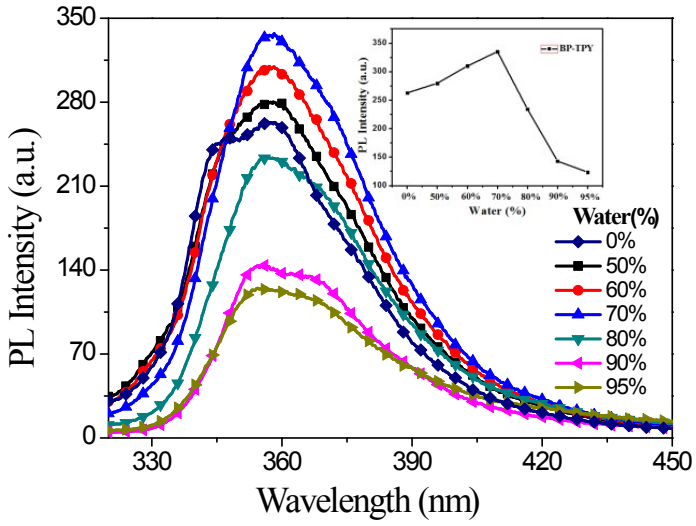


Fig. S2 The PL spectra of BP-TPY in the THF/water mixture.(Inset: Trend graph of PL intensity with the increase of water fraction.)

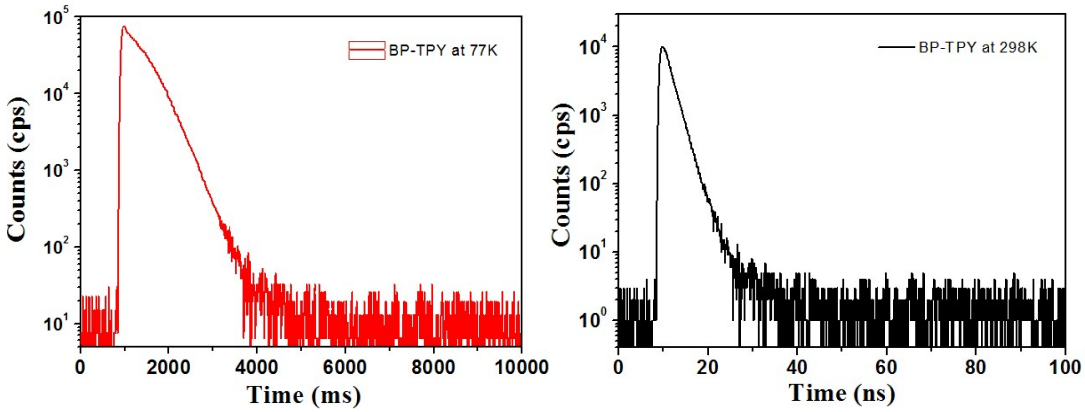


Fig. S3 The fluorescence decay of BP-TPY crystal at 77 K and 298K respectively.

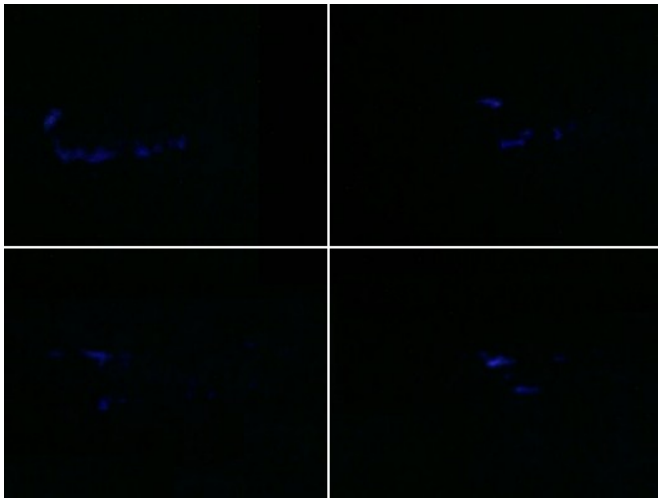


Fig. S4 The ML photographs of BP-TPY upon grinding in a glass bottle by metal or plastic spade in dark room.

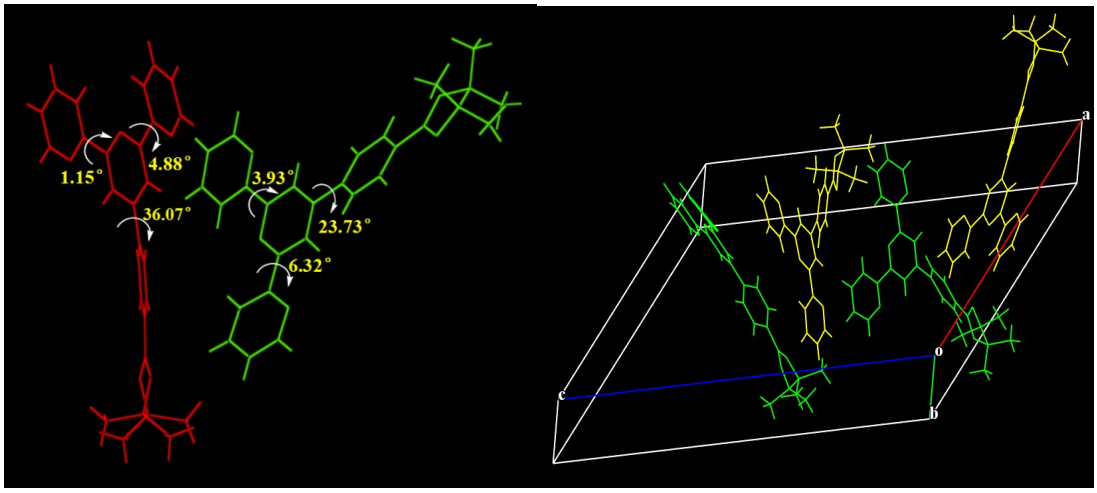


Fig. S5 Crystal structure diagram of compound BP-TPY with the neighboring molecule.

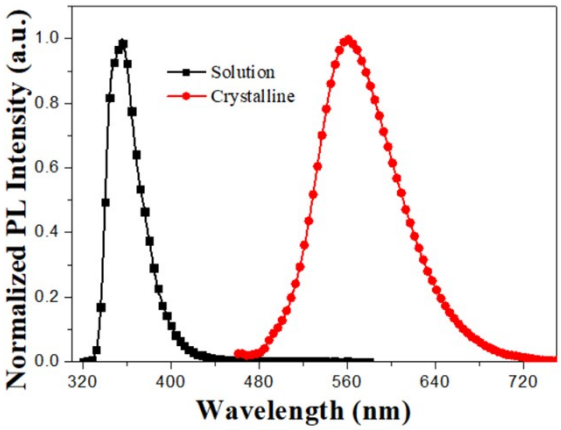


Fig. S6 The photoluminescence spectra of the intermediate Br-TPY in both solution and crystalline states.

Table S1 Single crystal structural parameters of BP-TPY.

Compound reference	colorless BP-TPY crystal
Chemical formula	C27 H26 B N3 O2
Formula weight	435.32
Crystal system	Monoclinic
a/Å	18.7210(10)
b/ Å	6.5310(10)
c/ Å	23.8400(10)
α/°	90.00
β/°	128.652(16)
γ/°	90.00
Unit cell volume/ Å3	2276.4(4)
Temperature/K	100(2)
Space group	Pc
Z	4
Density (calculated) /g cm^{-3}	1.270
F(000)	920
Theta range for data collection	1.39 to 25.00 deg.
Index ranges	-21<=h<=22, -7<=k<=6, -28<=l<=22
Reflections measured	10867
Independent reflections	5921
Rint	0.0701
Completeness to theta = 72.13°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9857 and 0.9794
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5921 / 2 / 596
Goodness-of-fit on F^2	0.983
Final R_1 values ($I > 2\sigma(I)$)	0.0651
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1334
Final R_1values (all data)	0.0981
Final $wR(F^2)$ values (all data)	0.1470
CCDC number	1580060

Table S2 The singlet and triplet excited state transition configurations of the two closely coupled BP-TPY molecules 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	Obitals	Transition
S_n	S_1	4.0288 eV	HOMO-1 -> LUMO	0.04
			HOMO -> LUMO	0.73
			HOMO -> LUMO+1	0.11
			HOMO -> LUMO+2	0.04
T_n	T_1	3.0428 eV	HOMO-8 ->LUMO+2	0.02
			HOMO-1 ->LUMO+2	0.22
			HOMO ->LUMO+2	0.02
			HOMO ->LUMO+3	0.49
			HOMO ->LUMO+9	0.02
	T_2	3.0476 eV	HOMO-12 ->LUMO	0.04
			HOMO-4 ->LUMO	0.10
			HOMO-4 ->LUMO+1	0.05
			HOMO-2 ->LUMO	0.24
			HOMO-2 ->LUMO+1	0.30
			HOMO-1 ->LUMO	0.03
			HOMO-1 ->LUMO+1	0.02
	T_3	3.4650 eV	HOMO-8 ->LUMO+2	0.02
			HOMO-7 ->LUMO+13	0.06
			HOMO-2 ->LUMO+2	0.02
			HOMO-1 ->LUMO+2	0.40
			HOMO-1 ->LUMO+6	0.04
			HOMO-1 ->LUMO+8	0.03
			HOMO ->LUMO+1	0.02
			HOMO ->LUMO+2	0.10
			HOMO ->LUMO+3	0.12
	T_4	3.4704 eV	HOMO-10 ->LUMO+11	0.03
			HOMO-4 ->LUMO	0.22
			HOMO-4 ->LUMO+1	0.11
			HOMO-4 ->LUMO+4	0.03
			HOMO-4 ->LUMO+5	0.06
			HOMO-2 ->LUMO	0.07
			HOMO-2 ->LUMO+1	0.02
			HOMO ->LUMO+2	0.16

			HOMO ->LUMO+3	0.02
	T_5	3.4727 eV	HOMO-8 ->LUMO+3	0.03
			HOMO-4 ->LUMO	0.09
			HOMO-4 ->LUMO+1	0.05
			HOMO-4 ->LUMO+5	0.02
			HOMO-2 ->LUMO	0.04
			HOMO-1 ->LUMO+2	0.02
			HOMO ->LUMO+2	0.38
			HOMO ->LUMO+3	0.07
			HOMO ->LUMO+6	0.02
	T_6	3.5036 eV	HOMO-12 ->LUMO+1	0.03
			HOMO-12 ->LUMO+7	0.03
			HOMO-4 ->LUMO	0.02
			HOMO-2 ->LUMO	0.31
			HOMO-2 ->LUMO+1	0.27
			HOMO-2 ->LUMO+4	0.03
			HOMO-2 ->LUMO+5	0.02
			HOMO-1 ->LUMO	0.03
			HOMO-1 ->LUMO+1	0.02
	T_7	3.6761 eV	HOMO-11 ->LUMO+2	0.10
			HOMO-6 ->LUMO+3	0.07
			HOMO-3 ->LUMO+1	0.03
			HOMO-3 ->LUMO+2	0.57
			HOMO-3 ->LUMO+6	0.06
	T_8	3.6895 eV	HOMO-13 ->LUMO	0.03
			HOMO-9 ->LUMO	0.13
			HOMO-5 ->LUMO	0.07
			HOMO-5 ->LUMO+1	0.37
			HOMO-5 ->LUMO+4	0.18
			HOMO-5 ->LUMO+7	0.06
	T_9	3.7484 eV	HOMO-13 ->LUMO+1	0.07
			HOMO-10 ->LUMO	0.04
			HOMO-9 ->LUMO	0.21
			HOMO-9 ->LUMO+4	0.10
			HOMO-5 ->LUMO	0.26
			HOMO-5 ->LUMO+1	0.11
			HOMO-5 ->LUMO+4	0.04
			HOMO-5 ->LUMO+7	0.06

	T_{10}	3.8115 eV	HOMO-11 ->LUMO+3	0.06
			HOMO-6 ->LUMO+2	0.08
			HOMO-6 ->LUMO+5	0.03
			HOMO-6 ->LUMO+6	0.16
			HOMO-6 ->LUMO+8	0.03
			HOMO-3 ->LUMO	0.02
			HOMO-3 ->LUMO+3	0.43
			HOMO-3 ->LUMO+9	0.02
	T_{11}	3.8772 eV	HOMO-13 ->LUMO	0.23
			HOMO-13 ->LUMO+4	0.09
			HOMO-10 ->LUMO+1	0.04
			HOMO-9 ->LUMO	0.03
			HOMO-9 ->LUMO+1	0.25
			HOMO-9 ->LUMO+4	0.03
			HOMO-9 ->LUMO+5	0.02
			HOMO-5 ->LUMO	0.09
			HOMO-5 ->LUMO+1	0.02
			HOMO-5 ->LUMO+4	0.02
	T_{12}	3.8908 eV	HOMO-11 ->LUMO+2	0.12
			HOMO-11 ->LUMO+6	0.07
			HOMO-6 ->LUMO	0.02
			HOMO-6 ->LUMO+3	0.39
			HOMO-6 ->LUMO+9	0.06
			HOMO-3 ->LUMO+2	0.04
			HOMO-3 ->LUMO+6	0.07
			HOMO-3 ->LUMO+8	0.04
	T_{13}	4.0466 eV	HOMO-18 ->LUMO+7	0.05
			HOMO-12 ->LUMO	0.10
			HOMO-12 ->LUMO+1	0.05
			HOMO-12 ->LUMO+7	0.03
			HOMO-4 ->LUMO	0.10
			HOMO-4 ->LUMO+5	0.04
			HOMO-2 ->LUMO	0.03
			HOMO-2 ->LUMO+1	0.07
			HOMO-2 ->LUMO+7	0.05
			HOMO ->LUMO	0.17
			HOMO ->LUMO+1	0.03
	T_{14}	4.0698 eV	HOMO-15 ->LUMO+9	0.06

			HOMO-8 ->LUMO+1	0.03
			HOMO-8 ->LUMO+2	0.16
			HOMO-8 ->LUMO+8	0.05
			HOMO-7 ->LUMO+2	0.03
			HOMO-7 ->LUMO+13	0.02
			HOMO-1 ->LUMO+2	0.04
			HOMO-1 ->LUMO+3	0.03
			HOMO-1 ->LUMO+8	0.04
			HOMO ->LUMO+2	0.03
			HOMO ->LUMO+3	0.10
			HOMO ->LUMO+6	0.03
			HOMO ->LUMO+9	0.04
	T_{15}	4.0849 eV	HOMO-16 ->LUMO+3	0.03
			HOMO-12 ->LUMO	0.05
			HOMO-8 ->LUMO+3	0.05
			HOMO-2 ->LUMO+7	0.02
			HOMO-1 ->LUMO+3	0.03
			HOMO ->LUMO	0.24
			HOMO ->LUMO+1	0.02
			HOMO ->LUMO+2	0.05
			HOMO ->LUMO+6	0.08
	T_{16}	4.1098 eV	HOMO-23 ->LUMO	0.02
			HOMO-19 ->LUMO+4	0.04
			HOMO-12 ->LUMO	0.04
			HOMO-12 ->LUMO+5	0.03
			HOMO-8 ->LUMO+2	0.04
			HOMO-4 ->LUMO	0.03
			HOMO-4 ->LUMO+1	0.10
			HOMO-1 ->LUMO+3	0.06
			HOMO ->LUMO	0.10
			HOMO ->LUMO+3	0.04
	T_{17}	4.1316 eV	HOMO-4 ->LUMO	0.09
			HOMO-4 ->LUMO+1	0.19
			HOMO-2 ->LUMO	0.04
			HOMO-1 ->LUMO+3	0.05
			HOMO ->LUMO	0.28
			HOMO ->LUMO+1	0.04
			HOMO ->LUMO+3	0.02

	T_{18}	4.1660 eV	HOMO-8 ->LUMO+3	0.05
			HOMO-2 ->LUMO	0.04
			HOMO-1 ->LUMO	0.02
			HOMO-1 ->LUMO+3	0.30
			HOMO ->LUMO+1	0.28
			HOMO ->LUMO+6	0.02
	T_{19}	4.1810 eV	HOMO-12 ->LUMO	0.02
			HOMO-12 ->LUMO+1	0.04
			HOMO-8 ->LUMO+3	0.02
			HOMO-4 ->LUMO	0.05
			HOMO-4 ->LUMO+1	0.04
			HOMO-2 ->LUMO	0.06
			HOMO-2 ->LUMO+4	0.04
			HOMO-1 ->LUMO	0.04
			HOMO-1 ->LUMO+1	0.02
			HOMO-1 ->LUMO+3	0.19
			HOMO ->LUMO	0.03
			HOMO ->LUMO+1	0.09
			HOMO ->LUMO+2	0.08
	T_{20}	4.2019 eV	HOMO-7 ->LUMO+1	0.03
			HOMO-7 ->LUMO+2	0.59
			HOMO-7 ->LUMO+6	0.07
			HOMO-7 ->LUMO+8	0.05
			HOMO-1 ->LUMO+13	0.02
	T_{21}	4.2099 eV	HOMO-18 ->LUMO+7	0.04
			HOMO-12 ->LUMO+7	0.04
			HOMO-4 ->LUMO	0.07
			HOMO-4 ->LUMO+1	0.03
			HOMO-2 ->LUMO	0.02
			HOMO-2 ->LUMO+1	0.06
			HOMO-2 ->LUMO+7	0.03
			HOMO-1 ->LUMO+3	0.03
			HOMO ->LUMO	0.05
			HOMO ->LUMO+1	0.23
			HOMO ->LUMO+2	0.05
	T_{22}	4.2591 eV	HOMO-20 ->LUMO+2	0.07
			HOMO-16 ->LUMO+6	0.03
			HOMO-16 ->LUMO+8	0.02

			HOMO-15 ->LUMO+9	0.05
			HOMO-10 ->LUMO	0.02
			HOMO-8 ->LUMO+8	0.06
			HOMO-7 ->LUMO+2	0.04
			HOMO-7 ->LUMO+13	0.11
			HOMO-4 ->LUMO+1	0.04
			HOMO-1 ->LUMO+2	0.04
			HOMO-1 ->LUMO+6	0.04
			HOMO ->LUMO+9	0.03
	T_{23}	4.2790 eV	HOMO-20 ->LUMO+2	0.02
			HOMO-12 ->LUMO+1	0.03
			HOMO-10 ->LUMO	0.07
			HOMO-10 ->LUMO+1	0.04
			HOMO-10 ->LUMO+5	0.02
			HOMO-10 ->LUMO+11	0.02
			HOMO-7 ->LUMO+13	0.04
			HOMO-4 ->LUMO+1	0.08
			HOMO-4 ->LUMO+4	0.03
			HOMO-4 ->LUMO+5	0.02
			HOMO-2 ->LUMO+1	0.03
			HOMO-2 ->LUMO+4	0.02
			HOMO ->LUMO+1	0.14
	T_{24}	4.3156 eV	HOMO-12 ->LUMO+1	0.03
			HOMO-12 ->LUMO+7	0.02
			HOMO-10 ->LUMO	0.24
			HOMO-10 ->LUMO+1	0.09
			HOMO-10 ->LUMO+4	0.03
			HOMO-10 ->LUMO+5	0.05
			HOMO-9 ->LUMO	0.04
			HOMO-9 ->LUMO+1	0.03
			HOMO-8 ->LUMO	0.03
			HOMO-4 ->LUMO+4	0.02
			HOMO-4 ->LUMO+11	0.02
			HOMO-2 ->LUMO+4	0.03
	T_{25}	4.3511 eV	HOMO-19 ->LUMO+4	0.02
			HOMO-18 ->LUMO+5	0.02
			HOMO-13 ->LUMO	0.02
			HOMO-13 ->LUMO+1	0.02

			HOMO-12 ->LUMO	**0.03**
			HOMO-12 ->LUMO+1	**0.02**
			HOMO-12 ->LUMO+5	**0.04**
			HOMO-12 ->LUMO+7	**0.04**
			HOMO-9 ->LUMO	**0.02**
			HOMO-5 ->LUMO+1	**0.07**
			HOMO-5 ->LUMO+7	**0.07**
			HOMO-4 ->LUMO+1	**0.05**
			HOMO-2 ->LUMO+4	**0.21**
			HOMO-2 ->LUMO+5	**0.05**