Supporting information for:

Understanding the molecular orientation growth at nanometer scale and adjustable electron transition performance of a terpyridyl derivative under different external environments

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Contents

S1 Characterization instruments

The X-ray diffraction measurement of single crystal was performed on a Bruker SMART CCD area detector using graphite monochromated Mo Ka radiation (k = 0.71073 Å) at 296(2) K. Intensity data were collected in the variable π- and ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed using the SHELXTL-97 program package. The morphologies were obtained on field-emission scanning electron microscope (FESEM, Hitachi S-4800) and high-resolution transmission electron microscope (JEOL JEM 2100, 300 kV). UV-vis absorption spectra were obtained on a UV-3100 spectrophotometer in the wavelength range 300-800 nm. Fluorescence spectra were recorded at room temperature using a Hitachi F-7000 spectrophotometer.

S2. Preparation and characterization

To prepare intermediate **1**: p-Tolualdehyde (3 mL), 2-acetyl pyridine (3 mL) and NaOH aqueous solution (2%, 100 mL) were mixed in a round-bottom flask (250 mL). the mixture was stirred violently for about 8 hours. Then, additional 2-acetyl pyridine (3 mL) was added into the mixture and some other NaOH was added to let the concentration of NaOH rise to 20%. The mixture was heated to 80 °C and stirred violently for another 8 hours to get brownish red dope. The reaction mixture was then cooled to room temperature. The aqueous phase was wiped off and the organic phase was washed with water for two times. 250 mL ethanol was added under ultrasonic to dissolve the dope, then filtrated to remove insoluble impurities and get some brown transparent solution. The as-got solution was heated to 80 °C, added with ammonium acetate (18.0 g), refluxed for 4 hours to get dark green solution, which was heated to remove part of ethanol and cooled to room temperature and let undisturbed to crystal into bright yellow needles. The needle crystals were filtrated and re-recrystallized to get intermediate 1 as white needles. Yiled: 50%. ^{1}H- NMR (400 MHz, $CDCl_3$) δ(ppm): 8.74~8.69 (m, 4H), 8.67 (d, *J* = 8.0 Hz, 2H), 7.88 (td, *J* = 7.6, 1.6 Hz, 2H), 7.83 (d, *J*

= 8.0 Hz, 2H), 7.37~7.33(m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H).

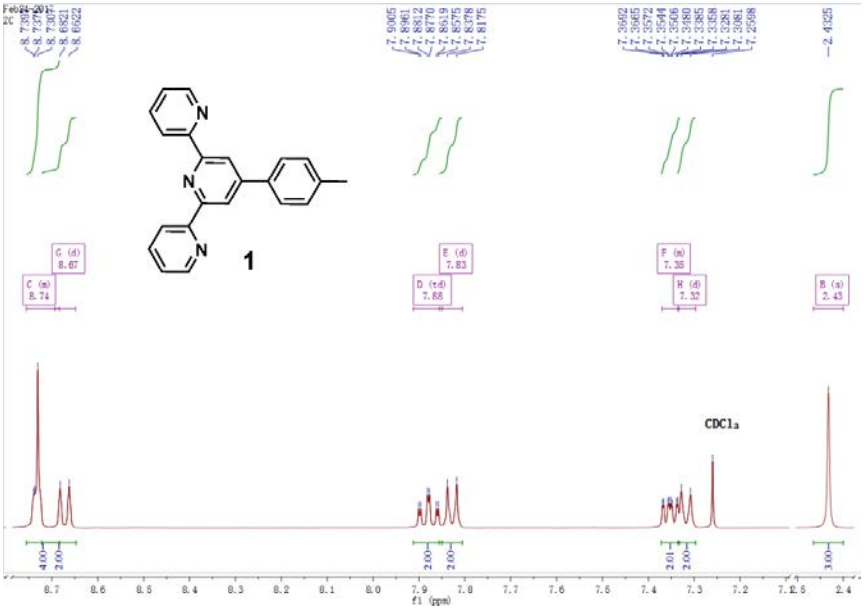

Figure S1 ^{1}H-NMR of the intermediate **1**

Preparation of intermediate **2**:

Intermediate **1** (5.0 g) was dissolved in benzene (150 mL), a small amount of peroxidation benzoin formyl (BPO) was added under reflux and used as the initiator. After stirred for some minutes, N-Bromosuccinimide (NBS, 2.9 g) was added and the mixture was refluxed for 8 hours to get dark brown solution. Then, triphenylphosphine (3.6 g) was added into the above solution followed for reflux for another 3 hours to get white yellow solid. The intermediate **2** was obtained after suction filtration and recrystallization in ethanol. Yield: 40%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ(ppm): 8.75~8.66 (m, 4H), 8.57 (s, 2H), 7.92 (t, *J* = 7.6 Hz, 2H), 7.83~7.77 (m, 9H), 7.68~7.61 (m, 8H), 7.40~7.36 (m, 2H), 7.24 (dd, *J* = 8.2, 2.2 Hz, 2H), 5.58 (d, *J* = 14.8 Hz, 2H).

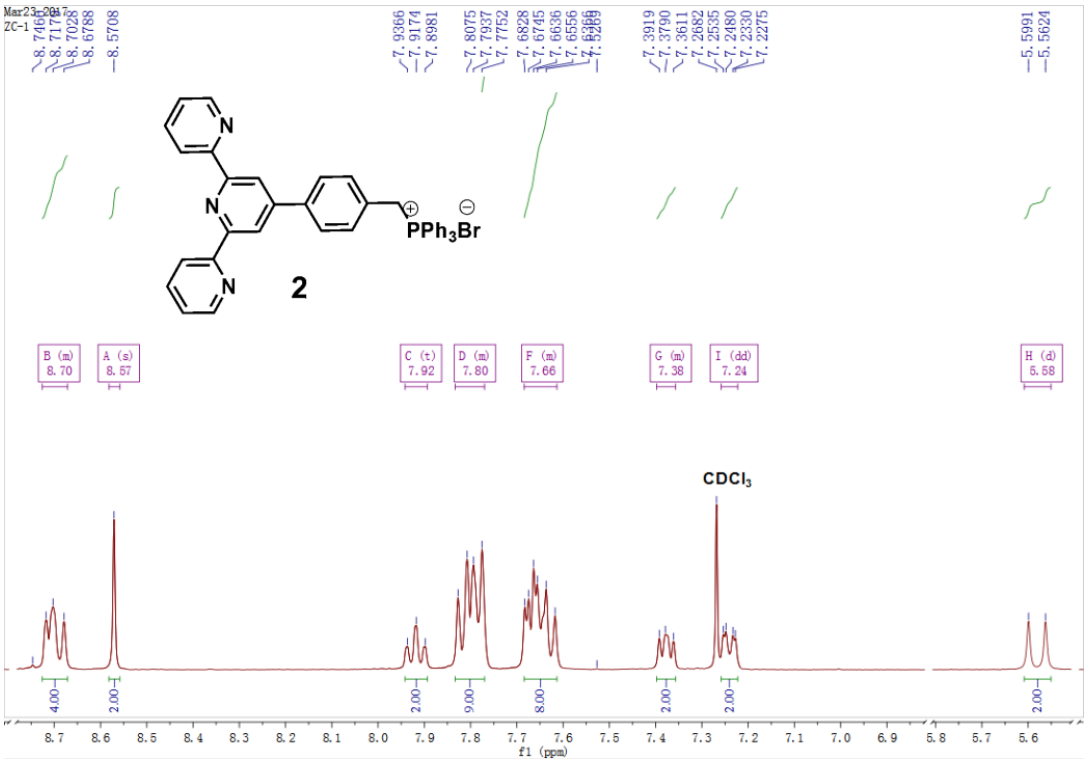

Figure S2 ^{1}H-NMR of the intermediate **2**

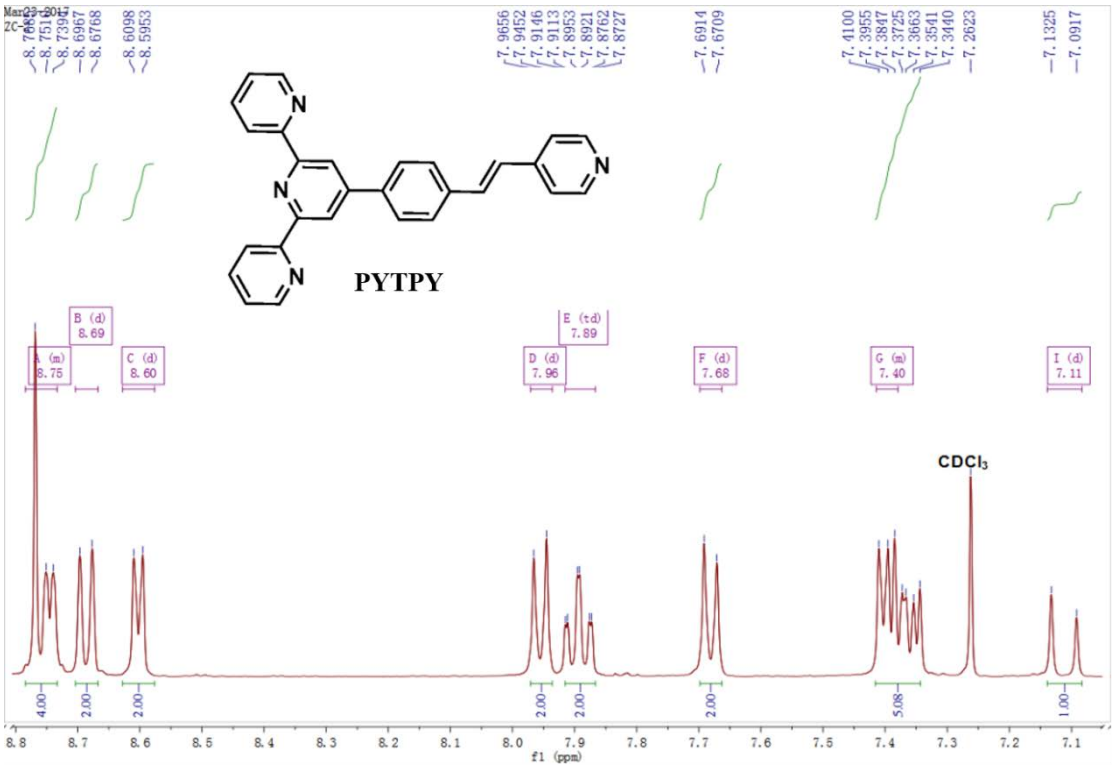

Figure S3 ^{1}H-NMR of the target compound PYTPY

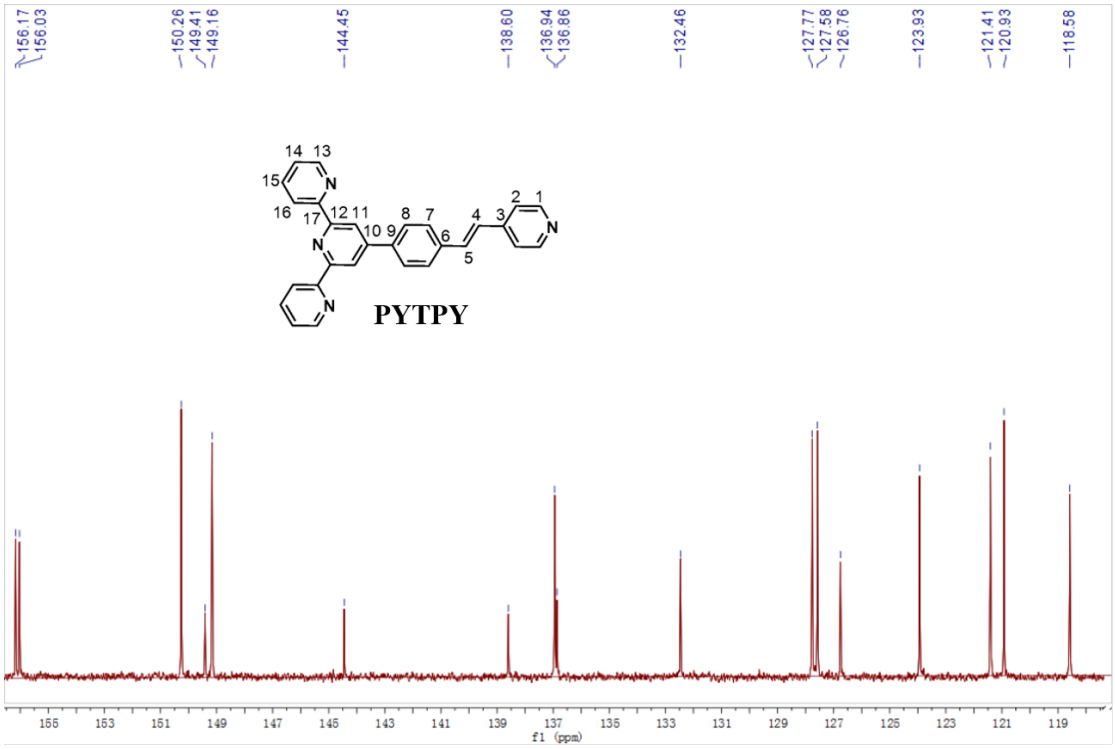

Figure S4 ^{13}C-NMR of the target compound PYTPY

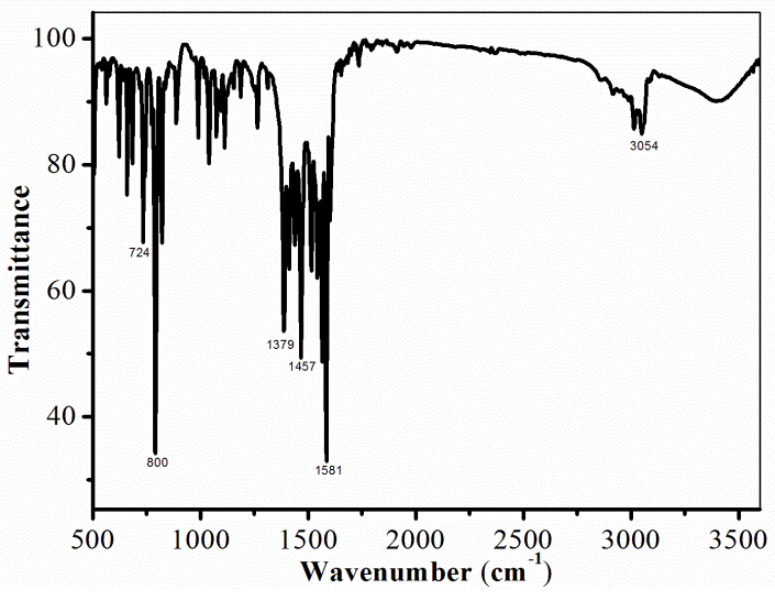

Figure S5 FT-IR spectrum of PYTPY

S3. Single crystal of PYTPY

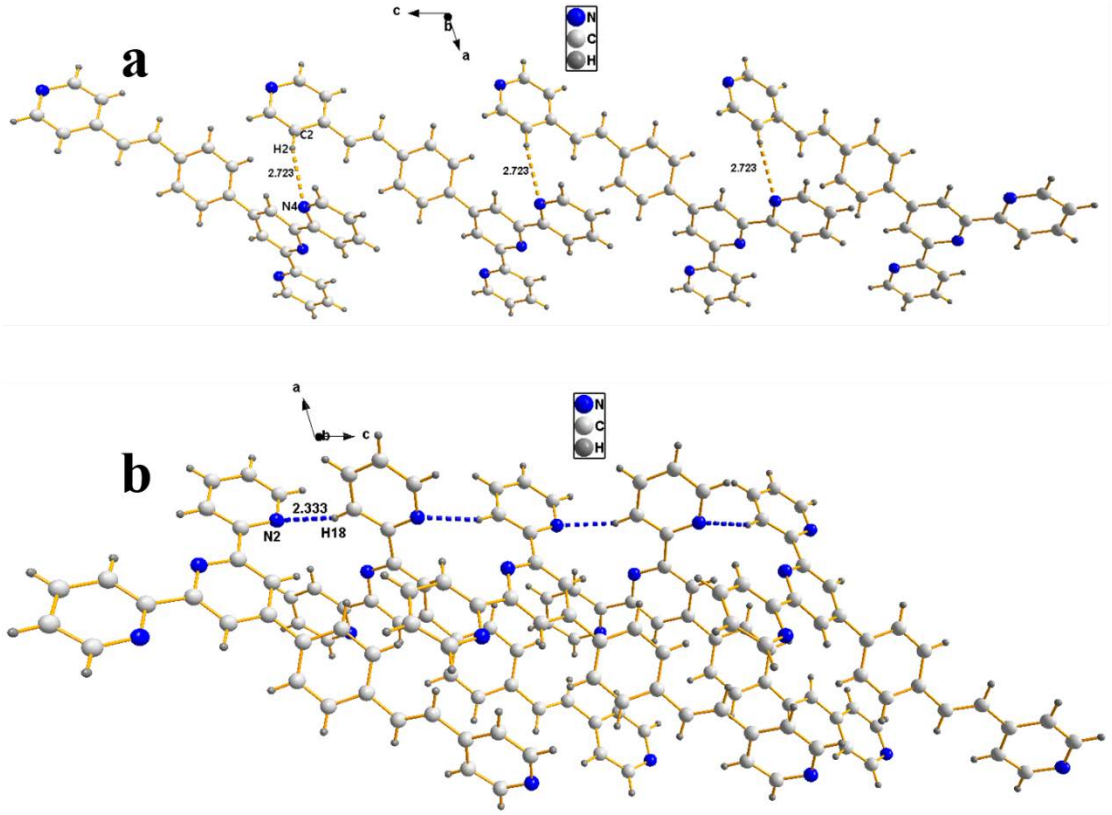

Figure S6 (a) One dimensional chain along *a* axis through C2-H2···N4 weak interactions with N···H distance being 2.723 Å and ∠C-H···N being 156.95(22)º. (b) One dimensional assembly of PYTPY along *c* axis through C18-H18···N2 weak interactions with N···H distance being 2.333 Å and ∠C-H···N being 159.143(192)º

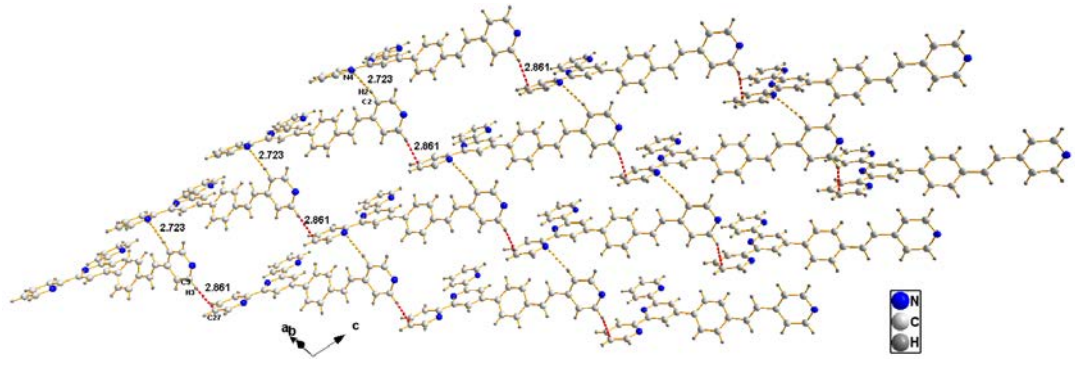

Figure S7 The 2D architecture of PYTPY along *bc* plane

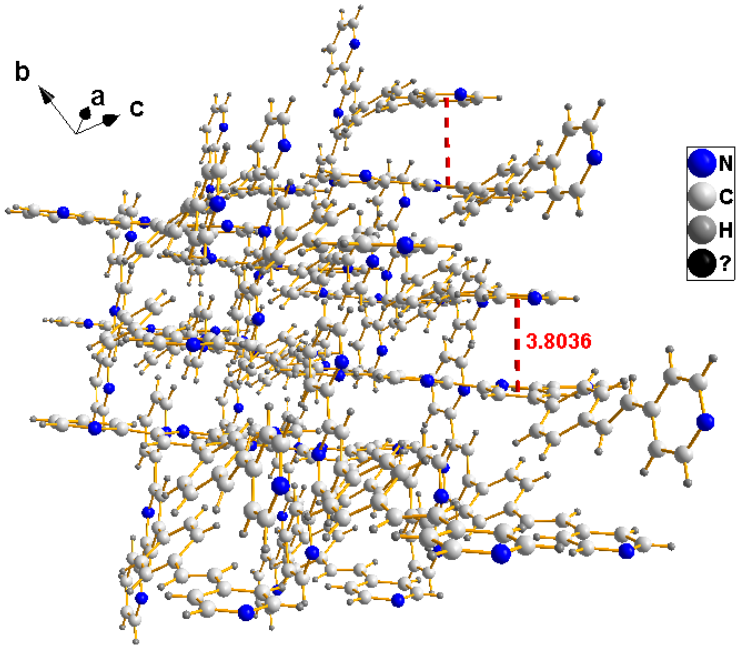

Figure S8 The packing diagram of PYTPY shows the very weak π–π (red) interactions between C4-C5-C2-C1-N1-C3 ring and C23-N1-C16-C15-C14-C22 ring at a distance of 3.8036 Å.

Table S1 Selected bond lengths (Å) and angles (°) of PYTPY single crystal

N(1)-C(3)	1.330(4)	N(3)-C(23)	1.343(4)
N(1)-C(1)	1.330(4)	N(3)-C(16)	1.349(4)
N(2)-C(21)	1.329(4)	N(4)-C(28)	1.332(4)
N(2)-C(17)	1.345(4)	N(4)-C(24)	1.349(4)
C(6)-C(7)	1.339(4)	C(14)-C(13)	1.492(4)
C(17)-C(16)	1.488(4)	C(24)-C(23)	1.484(4)
C(1)-C(2)	1.389(4)	C(3)-N(1)-C(1)	1115.3(3)
C(23)-N(3)-C(16)	117.7(2)	C(21)-N(2)-C(17)	118.3(3)
C(28)-N(4)-C(24)	118.3(3)	N(3)-C(23)-C(22)	122.3(3)
N(3)-C(23)-C(24)	117.3(2)	N(2)-C(17)-C(16)	116.6(2)
N(2)-C(17)-C(18)	121.5(2)	C(18)-C(17)-C(16)	121.8(2)

S4. Optical properties of PYTPY

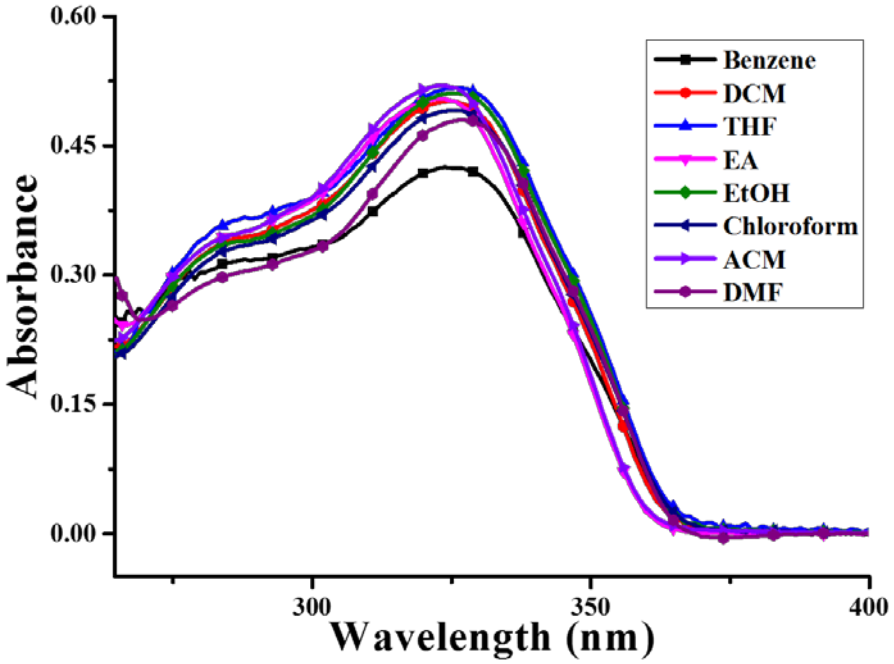

Figure S9 UV-vis spectra of PYTPY in different solvents

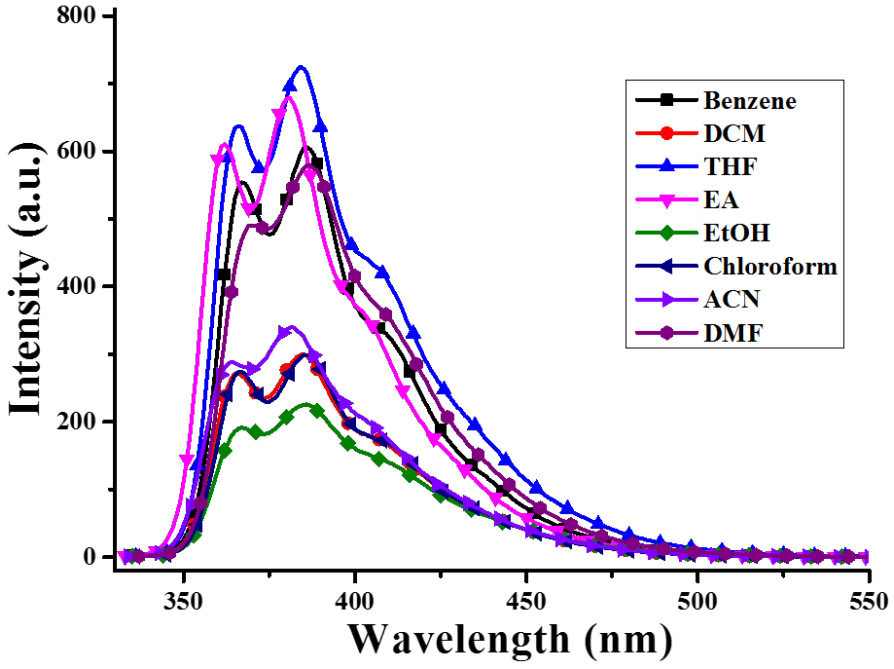

Figure S10 Fluorescence emission spectra of PYTPY in different solvents

S5. Calculation results under different conditions

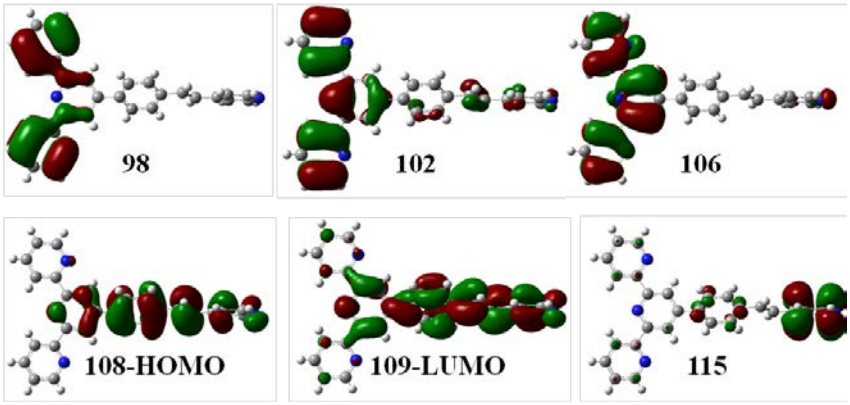

Figure S11 Molecular orbital diagrams of PYTPY monomer molecule (the geometry was optimized using the bp86 functional and the cc-pvtz basis set).

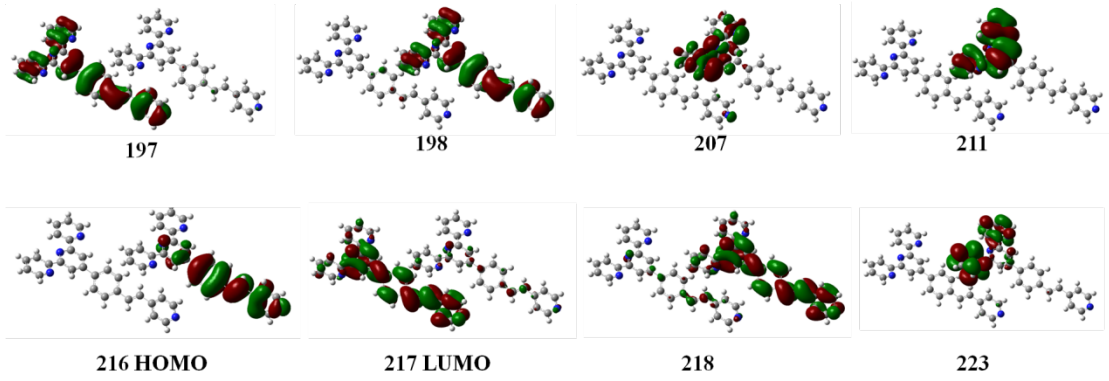

Figure S12 Molecular orbital diagrams of PYTPY dimer according to TD-DFT calculation at bp86/cc-pvtz basis set.

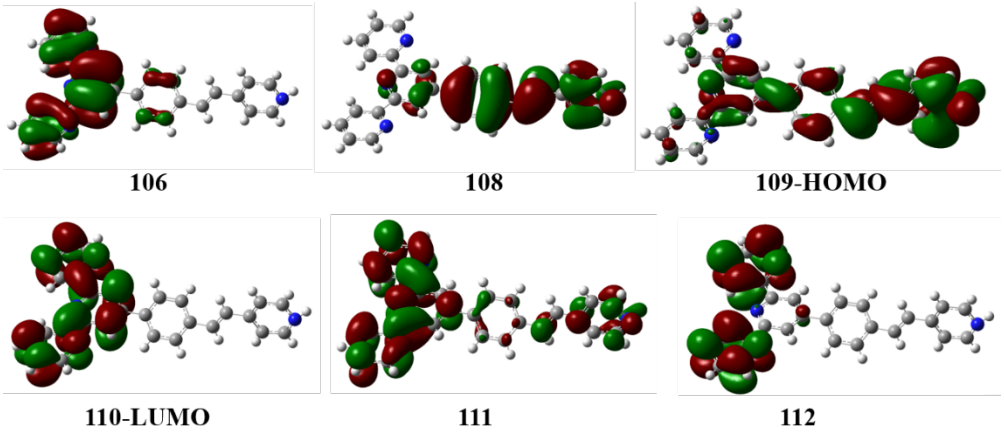

Figure S13 Molecular orbital diagrams of PYTPY monomer with the addition of 1 equivalent H^+ under b3lyp/cc-pvtz level basis.

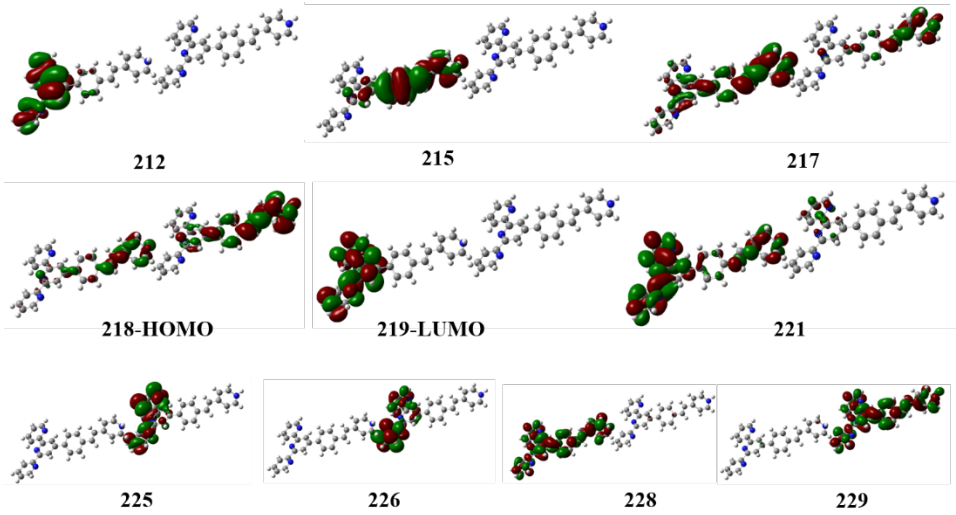

Figure S14 Molecular orbital diagrams of PYTPY dimer with the addition of 1 equivalent H^+ according to b3lyp/cc-pvtz level basis.

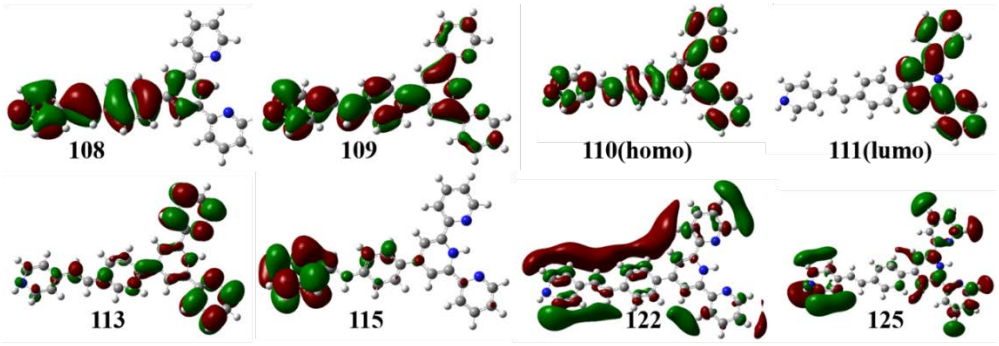

Figure S15 Molecular orbital diagrams of PYTPY with the addition of 2 equivalent H^+ according to b3lyp/cc-pvtz basis set.

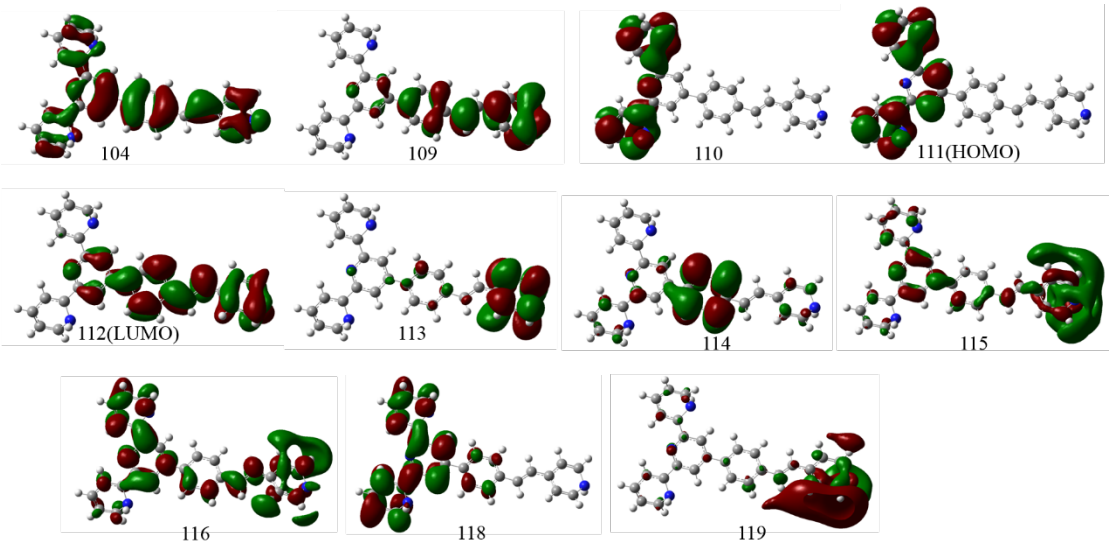

Figure S16 Molecular orbital diagrams of PYTPY with the addition of 3 equivalents H^+ according to b3lyp/cc-pvtz basis set.

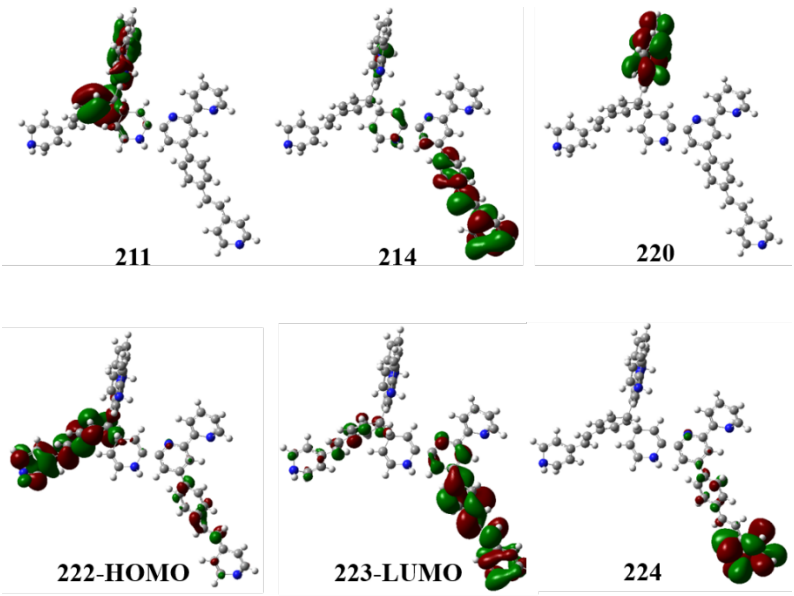

Figure S17 Molecular orbital diagrams of PYTPY aggregated dimer with the addition of 3 equivalent H^+ according to TD-DFT calculation under b3lyp/cc-pvtz basis set.

Table S2 Some of calculated excitation energies (E), oscillator strengths (f), corresponding wavelengths (λ_{abs}) and major contributors for PYTPY in dilute THF solution when 1 or 3 equivalent H^+ ion was added

	E (eV)	λ (nm)	f	composition (C)
absorbance for PYTPY-1H^+ monomer	4.4670*	277.55	0.1694	106(H_3-3)→112(L_3+2) (0.59663)
	3.3718*	367.71	0.1823	108(H_3-1)→111(L_3+1) (0.59067)
absorbance for PYTPY-1H^+ dimer	2.1428	578.61	0.2512	217(H_4-1)→ 229(L_4+10) (0.33016) 218(H_4)→228(L_4+9) (0.16823)
	3.0750	403.20	0.0029	215(H_4-3)→ 219(L_4) (0.69974)
	3.3679	368.14	0.1571	215(H_4-3)→ 221(L_4+2) (0.55978)
	3.7366	331.81	0.0013	217(H_4-1)→246(L_4+27) (0.23948)
	3.8202	324.55	0.0008	/
	4.0301	307.65	0.0068	215(H_4-3)→ 225(L_4+6) (0.15580) 215(H_4-3)→226(L_4+7) (0.67149)
	4.1361	299.76	0.1524	212(H_4-6)→220(L_4+1) (0.12720) 212(H_4-6)→221(L_4+2) (0.49774)
absorbance for PYTPY-2H^+ monomer	2.1692*	571.57	0.0669	110(H_{S1})→115(L_{S1}+4) (0.63108)

absorbance for PYTPY-3H$^+$ monomer	3.4897	355.28	0.0199	109(H_5-2)→117(L_5+5)	(0.69930)
	3.5685	347.44	0.0012	110(H_5-1)→122(L_5+10)	(0.43756)
	3.7757	328.37	0.0320	111(H_5)→126(L_5+14)	(0.46322)
	4.3312	286.26	0.0198	110(H_5-1)→129(L_5+17)	(0.38130)
absorbance for PYTPY-3H$^+$ dimer	3.0150*	411.22	0.0483	221(H_6-1)→238(L_6+15)	(0.46197)
	3.1539*	393.12	0.0867	214(H_6-8)→224(L_6+1)	(0.56106)
	3.3954*	365.15	0.1445	211(H_6-11)→223(L_6)	(0.15646)

* main transition

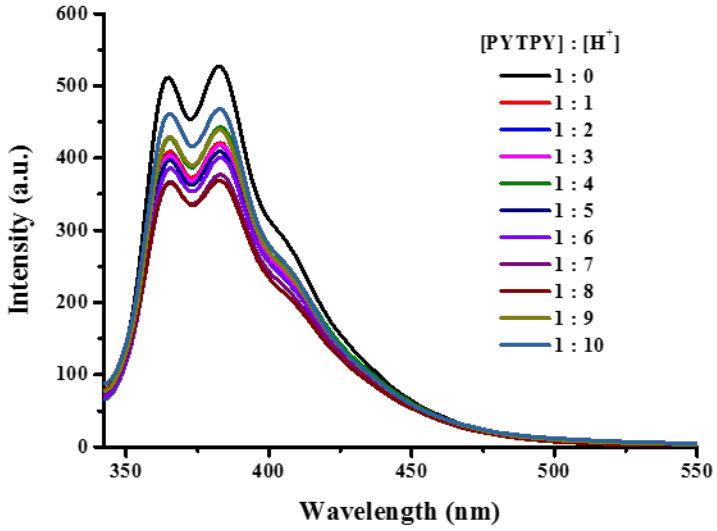

Figure 18 Fluorescence spectra of PYTPY in THF solution with different equivalents of H^+

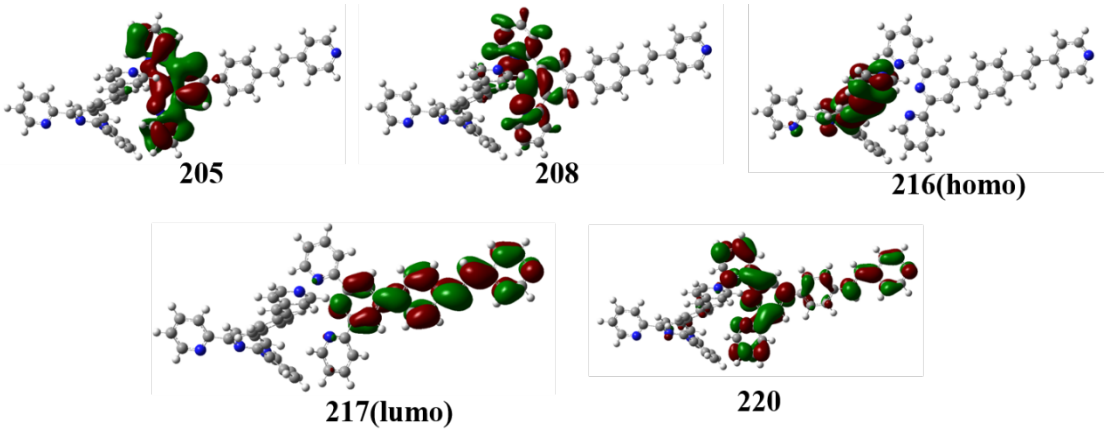

Figure S19 Molecular orbital diagrams of PYTPY dimers with Ag^+ ion existence under bp86/6-311g* basis set.

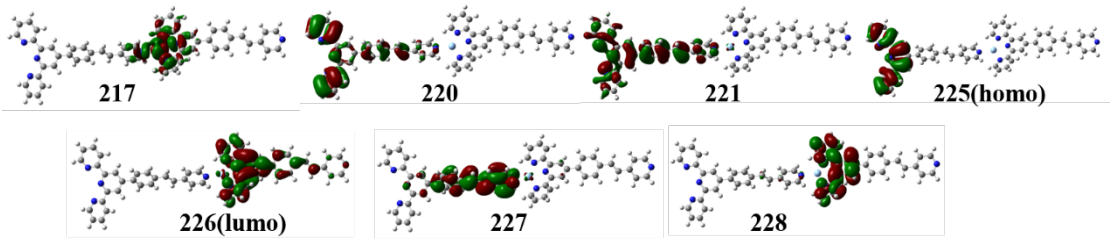

Figure S20 Molecular orbital diagrams of possible PYTPY-Ag complex under b3lyp method, cc-pvtz basis set was used for the non-metal atoms while lanl2dz was used for silver atom. The structure was constructed from the calculated results of Figure 6 in the main text.

S6. Experimental results with Ag^{+} coordination

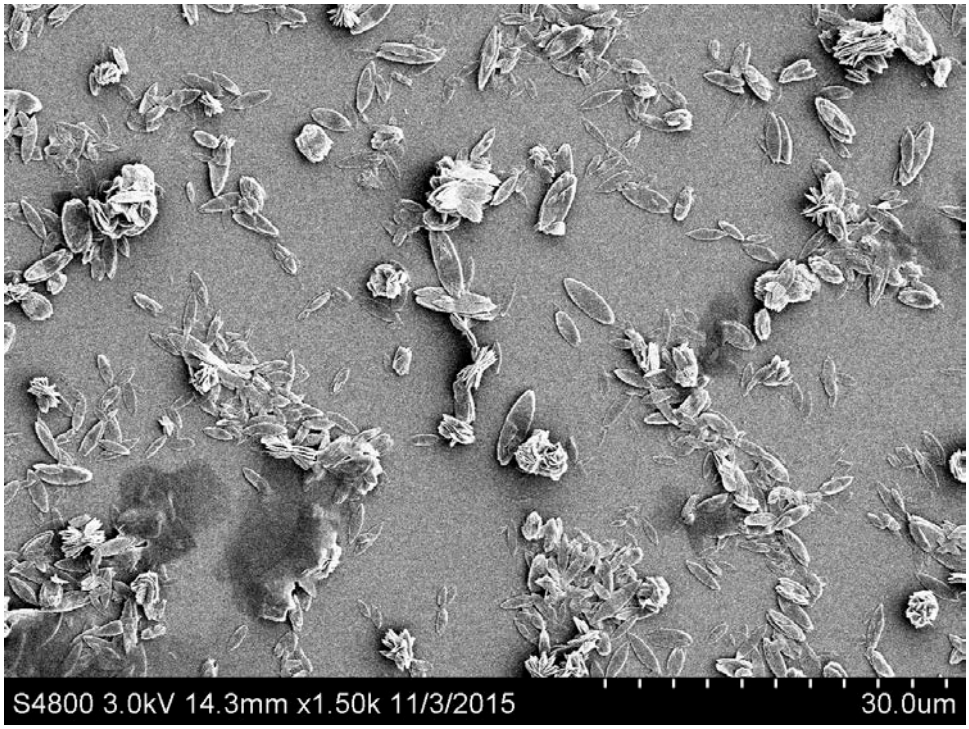

Figure 21 SEM image of precipitation samples when 3 equivalents of $AgNO_3$ were added into PYTPY-DMF solution, refluxed under violently stirring overnight.

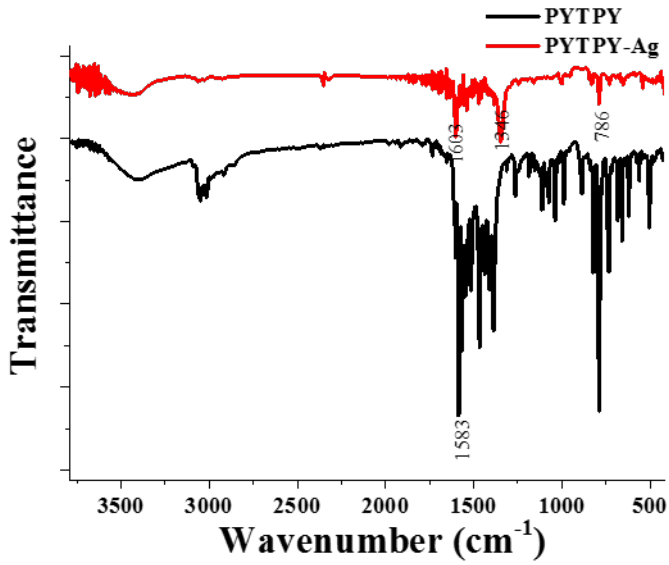

Figure S22 FT-IR spectra of PYTPY and the related Ag-complex

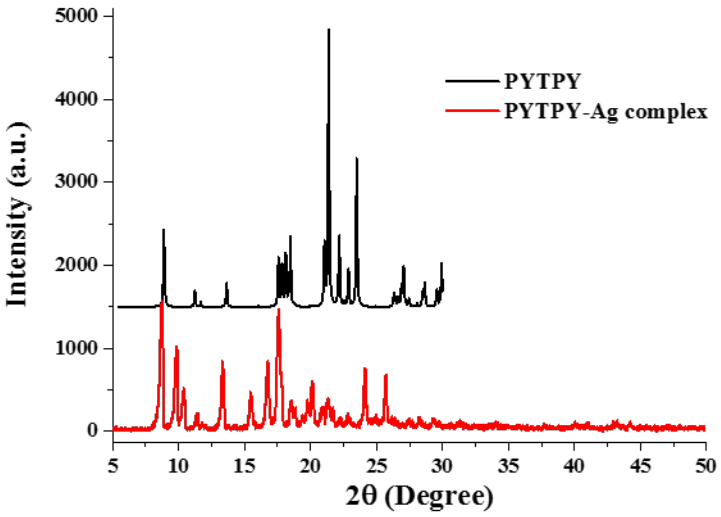

Figure S23 XRD pattern of PYTPY and PYTPY-Ag complex