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Supporting Information

Study of Configuration Differentia and Highly Efficient Deep-Red Thermally Activated Delayed Fluorescence Organic Light-Emitting Diode Based on Phenanthro[4,5-fgh]quinoxaline Derivatives

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1. General Information

All the reactants and solvents in the study were used as received from commercial sources unless otherwise stated. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer at 500 MHz and 125 MHz at 298K respectively, using$CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were measured using an AXIMA-CFRTM plus instrument. Thermogravimetric analysis (TGA) was undertaken with a PerkinElmer thermal analysis system. The thermal stability of the samples was determined by measuring their weight loss while heating at a rate of 10 ℃ min $^{-1}$ from 30 to 900 ℃ under a nitrogen atmosphere. UV-vis and PL spectra were respectively recorded on a UV-3100 spectrophotometer and a FLS980 Spectrometer. The PL efficiency of doped film was measured on quartz plate by integrating sphere. Cyclic voltammetry (CV) was performed with a BAS 100W Bioanalytical Systems. The conventional three-electrode configuration was performed with using silver chloride electrode and Pt disk as reference electrode and working electrode. All solutions were purged with a nitrogen stream for 10 min before measurement, simultaneously using ferrocene/ferrocenium (Fc/Fc^+) served as internal reference with a scan rate of 0.1 V/s under nitrogen atmosphere. During positive scanning, the material is dissolved in the newly steamed dichloromethane. The material was dissolved in ultra-dry N, N-dimethylformamide during negative scanning. The concentration of the solution is 0.1 M.

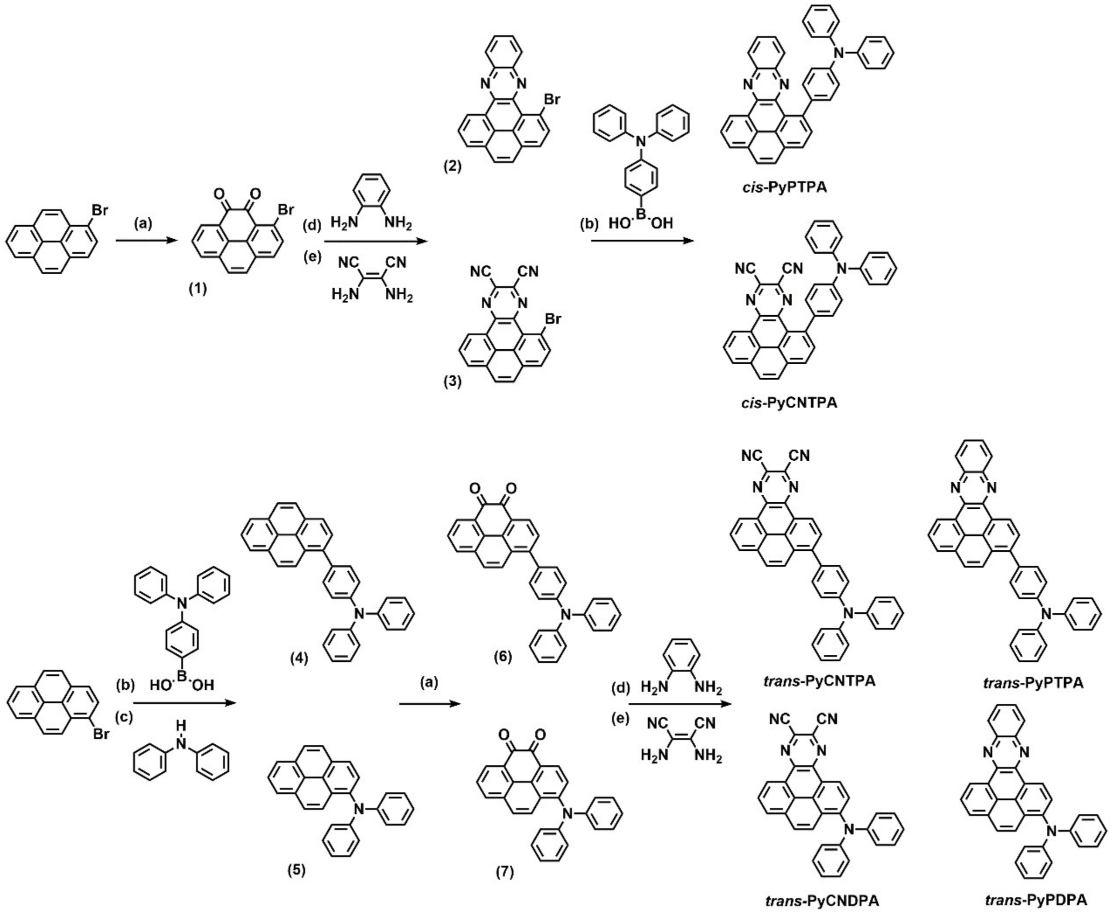
2. Theoretical Calculations

All the calculations were performed using Gaussian 09 program package. The ground state structure was optimized by B3LYP density functional method with basis set 6-31G(d). Time-dependent DFT (TDDFT) with a nonempirically tuned rangeseparated functional TD-M062X with basis set 6-31G(d,p) were than performed to further analysis the lowest-lying singlet (S_1) and triplet states (T_1).

3. Device Fabrication

OLEDs were fabricated on the ITO-coated glass substrates with multiple organic layers sandwiched between the transparent bottom indium-tin-oxide (ITO) anode and the top metal cathode. ITO substrates were pretreated according to conventional procedures then treated with UV-zone for 20 min finally transferred to a vacuum deposition system with a base pressure lower than 5×10^{-6} mbar for organic and metal deposition. The organic layers are deposited on the ITO substrates with an evaporation rate around 1.0 Å s^{-1}. While, the cathode layers of LiF and Al are completed by thermal deposition at rates of 0.1 Å s^{-1} and 4 Å s^{-1}, respectively. Electroluminescence spectra and the corresponding luminance were recorded by a PR650 spectra scan spectrometer. The current density-voltage-luminance characteristics were measured by computer-controlled Keithley 2400 power source under ambient atmosphere.

4. Synthesis Procedure



Scheme S1. Synthetic routes and molecular structures of*cis*-PyPTPA, *cis*-PyCNTPA, *trans*-PyCNTPA, *trans*-PyPTPA, *trans*-PyCNDPA and *trans*-PyPDPA. (a) CH_2Cl_2, ACN, H_2O, $NaIO_4$, $RuCl_3$. (b) Tol/H_2O, K_2CO_3, $Pd(PPh_3)_4$, 90 °C. (c) Tol, $Pd_2(dba)_3$, t-BuOK, $(t\text{-}Bu)_3PhBF_4$, 110 °C. (d) AcOH, 125°C. (e) AcOH, 125 °C.

Synthesis of (1)

The mixture of 1-bromopyrene (2.8 g, 10.00 mmol) and $NaIO_4$ (8.75 g, 40.89 mmol) were dissolved in CH_2Cl_2 (40 mL) and acetonitrile (40 mL). $RuCl_3\cdot 3H_2O$ (0.25 g, 0.98 mmol) and H_2O (50 mL) were added in small portions over 30 min. The resulting slurry was stirred at room temperature over night. The mixture was extracted with large of dichloromethane, and further purified by column chromatography of silica gel using dichloromethane as the eluent to give an orange powder of (1) (1.24 g, yield: 40%). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.43 (s, 1H), 8.32 (s, 1H), 8.15 (d, J = 7.9 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.85-7.84 (m, 1H). MALDI-TOF (m/z): [M^+]

calcd for $C_{16}H_7BrO_2$, 309.96; found: 310.07.

Synthesis of (2)

The mixture of (1) (1.55 g, 5.00 mmol) and o-phenylenediamine(0.81 g, 7.5 mmol) were dissolved in acetic acid (30 mL). The solution was heated at 125 ℃ for 4 hours under argon atmosphere. After cooling to room temperature, the resulting mixture was poured into water and filtered. The solid was washed several times with water and further purified by column chromatography of silica gel using dichloromethane/ petroleum (v/v = 2/1) as the eluent to give an orange powder of (2) (1.82 g, yield: 95%).^{1}H NMR (500 MHz, DMSO) δ (ppm): 8.57 (s, 2H), 8.46 (s, 1H), 8.31 (d, *J* = 2.8 Hz, 2H), 8.29 (d, *J* = 2.8 Hz, 2H), 8.22 (s, 1H), 8.17 (s, 1H), 8.12 (s, 1H), 8.04 (s, 1H). MALDI-TOF (m/z): [M^+] calcd for $C_{22}H_{11}BrN_2$, 382.01; found: 382.23.

Synthesis of (3)

Follow similar steps to (2) but with diaminomaleonitrile (0.81 g, 7.5 mmol) instead of o-phenylenediamine, yielding an orange solid of (3) (1.72 g, yield: 90%).^{1}H NMR (500 MHz, DMSO) δ (ppm): 8.35 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 2H), 8.00 (s, 1H), 7.99-7.98 (m, 1H), 7.86 (s, 1H), 7.85 (s, 1H). MALDI-TOF (m/z): [M^+] calcd for $C_{20}H_7BrN_4$, 381.99; found: 382.03.

Synthesis of (4)

The mixture of 1-bromopyrene (0.42 g, 1.50 mmol), 4-(diphenylamino)phenylboronic acid (0.52 g, 1.80 mmol), $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) and K_2CO_3 (0.66 g, 4.78 mmol) were dissolved in toluene (9 mL), THF (6 mL) and distilled water (6 mL). The solution was heated at 90 ℃ for 24 hours under argon atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane, and further purified by column chromatography of silica gel using dichloromethane/petroleum (v/v = 2/1) as the eluent to give a blue powder of (4) (0.64

g, yield: 95%). ^{1}H NMR (500 MHz, DMSO) δ (ppm): 8.38-8.28 (m, 3H), 8.15-8.17 (m, 4H), 8.09 (t, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 4H), 7.18 (t, *J* = 8.1 Hz, 6H), 7.11 (t, *J* = 7.3 Hz, 2H). MALDI-TOF (m/z): [M$^+$] calcd for $C_{34}H_{23}N$, 445.18; found: 445.07.

Synthesis of (5)

The mixture of 1-bromopyrene (0.42 g, 1.50 mmol), N-phenylaniline (0.31 g, 1.80 mmol), $Pd_2(dba)_3$ (0.05 g, 0.05 mmol), $(t\text{-}Bu)_3PhBF_4$ (0.03g, 0.09 mmol) and t-BuOK (0.28 g, 2.50 mmol) were dissolved in toluene (20 mL). The solution was heated at 110 ℃ for 24 hours under argon atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane, and further purified by column chromatography of silica gel using dichloromethane/petroleum (v/v = 2/1) as the eluent to give a light blue powder of (5) (0.51 g, yield: 90%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.39-8.30 (m, 2H), 8.25 (dd, *J* = 7.7, 1.1 Hz, 1H), 8.21 (s, 2H), 8.13-8.05 (m, 3H), 7.87 (d, J = 8.1 Hz,1H), 7.29-7.21 (m, 4H), 7.02-6.93 (m, 6H). MALDI-TOF (m/z): [M$^+$] calcd for $C_{28}H_{19}N$, 369.15; found: 369.47.

Synthesis of (6)

The mixture of (4) (4.45 g, 10.00 mmol) and $NaIO_4$ (8.75 g, 40.89 mmol) were dissolved in CH_2Cl_2 (40 mL) and acetonitrile (40 mL). $RuCl_3{\cdot}3H_2O$ (0.25 g, 0.98 mmol) and H_2O (50 mL) were added in small portions over 30 min. The resulting slurry was strongly stirred at room temperature overnight. The mixture was extracted with large of dichloromethane, and further purified by column chromatography of silica gel using dichloromethane as the eluent to give a deep-red powder of (6) (1.67 g, yield: 35%). ^{1}H NMR (500 MHz, DMSO) δ (ppm): 8.54 (s, 1H), 8.51 (d, *J* = 1.3 Hz, 1H), 8.27 (s, 1H), 8.15 (s, 1H), 7.85 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 7.65 (s, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 7.36 (s, 2H), 7.27 (d, *J* = 5.2 Hz, 2H), 7.25 (s, 2H), 7.16 (d, J = 7.4 Hz, 4H), 7.01 (s, 1H), 6.99 (s, 1H). MALDI-TOF (m/z): [M^+] calcd for $C_{34}H_{21}NO_2$, 475.16; found: 475.06.

Synthesis of (7)

The mixture of (5) (3.70 g, 10.00 mmol) and $NaIO_4$ (8.75 g, 40.89 mmol) were dissolved in CH_2 Cl_2 (40 mL) and acetonitrile (40 mL). $RuCl_3·3H_2O$ (0.25 g, 0.98 mmol) and H_2O (50 mL) were added in small portions over 30 min. The resulting slurry was strongly stirred at room temperature overnight. The mixture was extracted with large of dichloromethane, and further purified by column chromatography of silica gel using dichloromethane as the eluent to give a deep-red powder of (7) (1.60 g, yield: 40%). ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.41 (t, J = 2.5 Hz, 1H), 8.40 (d, J = 1.1 Hz, 1H), 8.25 (s, 1H), 7.92-7.91 (m, 1H), 7.81 (s, 1H), 7.79-7.78 (m, 1H), 7.69 (s, 1H), 7.28 (s, 4H), 7.10 (s, 4H), 7.05-6.98 (m, 4H). MALDI-TOF (m/z): [M^+] calcd for $C_{28}H_{17}NO_2$, 399.13; found: 399.02.

Synthesis of *cis*-PyPTPA

The mixture of (2) (0.57 g, 1.50 mmol), 4-(diphenylamino)phenylboronic (0.52 g, 1.80 mmol), $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) and K_2 CO_3 (0.66 g, 4.78 mmol) were dissolved in toluene (9 mL), THF (6 mL) and distilled water (6 mL). The solution was heated at 90 ℃ for 24 hours under argon atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane, and further purified by column chromatography of silica gel using dichloromethane/petroleum (v/v = 2/1) as the eluent to give a yellow powder of *cis*-PyPTPA (0.57 g, yield: 70%). ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm) 9.40 (dd, J = 7.9, 3.8 Hz, 2H), 8.48 (d, J = 7.8 Hz, 1H), 8.39-8.35 (m, 1H), 8.20 (dt, J = 8.0, 5.1 Hz, 3H), 8.11 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.41-7.37 (m, 4H), 7.34-7.24 (m, 7H), 7.16 (dd, J = 15.7, 8.3 Hz, 2H), 7.03 (d, J = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm) 148.15, 147.71, 145.92, 141.29, 141.16, 131.43, 131.19, 130.06, 129.99, 129.48, 129.38, 129.21, 128.82, 128.34, 127.18, 127.12, 126.81, 124.68, 124.25, 123.86, 123.75, 123.21, 123.15, 122.46. MALDI-TOF (m/z): [M^+] calcd for $C_{40}H_{25}N_3$, 547.18; found: 547.22. Elem. anal. calcd (%) for $C_{40}H_{25}N_3$: C, 87.73; H, 4.60; N, 7.67; found: C, 87.82; H,4.55; N, 7.59.

Synthesis of *cis*-PyCNTPA

The mixture of (3) (0.57 g, 1.50 mmol), 4-(diphenylamino)phenylboronic (0.52 g, 1.80 mmol), $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) and K_2 CO_3 (0.66 g, 4.78 mmol) were dissolved in toluene (9 mL), THF (6 mL) and distilled water (6 mL). The solution was heated at 90 °C for 24 hours under argon atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane, and further purified by column chromatography of silica gel using dichloromethane/ petroleum (v/v = 2/1) as the eluent to give a deep-red powder of *cis*-PyCNTPA (0.53 g, yield: 65%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 9.41 (dd, *J* = 6.2, 0.8 Hz, 2H), 8.52 (d, *J* = 6.2 Hz, 2H), 8.48 (d, *J* = 6.4 Hz, 2H), 8.22 (t, *J* = 6.2 Hz, 3H), 8.09 (d, *J* = 6.4 Hz, 2H), 7.35 (s, 2H), 7.23 (d, *J* = 6.8 Hz, 4H), 7.10 (t, *J* = 5.8 Hz, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm) 145.92, 143.64, 136.41, 134.31, 131.74, 131.43, 131.19, 130.75, 128.34, 127.13, 126.81, 126.81, 125.11, 124.68, 123.75, 123.50, 123.21, 123.14, 122.46, 121.54, 120.04. MALDI-TOF (m/z): [M^+] calcd for $C_{38}H_{21}N_5$, 547.20; found: 547.35. Elem. anal. calcd (%) for $C_{38}H_{21}N_5$: C, 83.35; H, 3.87; N, 12.79; found: C, 83.42; H,3.83; N, 12.69.

Synthesis of *trans*-PyCNTPA

The mixture of (6) (2.38 g, 5.00 mmol) and diaminomaleonitrile (0.81 g, 7.5 mmol) were dissolved in acetic acid (30 mL). The solution was heated at 125 °C for 4 hours under argon atmosphere. After cooling to room temperature, the resulting mixture was poured into water and filtered. The solid was washed several times with water and further purified by column chromatography of silica gel using dichloromethane/ petroleum (v/v = 2/1) as the eluent to give a deep-red powder of *trans*-PyCNTPA (2.46 g, yield: 90%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 9.64 (d, J = 8.4 Hz, 2H), 8.43 (dd, J = 6.3, 3.5 Hz, 2H), 8.30 (d, J = 7.7 Hz, 1H), 8.20-8.13 (m, 2H), 7.95 (dd, J = 11.6, 5.9 Hz, 4H), 7.32-7.27 (m, 4H), 7.17-7.14 (m, 4H), 7.05 (t, J = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm) 145.92, 143.64, 141.61, 140.58, 134.31, 131.19, 129.10, 128.51, 128.27, 126.96, 126.81, 126.44, 126.28, 126.13, 125.11, 123.86, 123.75, 123.50, 123.14, 122.46, 121.52, 121.32. MALDI-TOF (m/z): [M^+] calcd for $C_{38}H_{21}N_5$, 547.18; found: 547.23. Elem. anal. calcd (%) for $C_{38}H_{21}N_5$: C, 83.35; H, 3.87; N, 12.79; found: C, 83.47; H,3.79; N, 12.69.

Synthesis of *trans*-PyPTPA

Follow similar steps to *trans*-PyCNTPA but with o-phenylenediamine (0.81 g, 7.5 mmol) instead of diaminomaleonitrile, yielding an orange solid of *trans*-PyPTPA (2.45 g, yield: 89%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 9.57 (dd, J = 7.3, 5.5 Hz, 2H), 8.38 (dd, J = 6.5, 3.3 Hz, 2H), 8.27 (dd, J = 13.8, 8.4 Hz, 2H), 8.09 (dd, J = 16.8, 7.8 Hz, 2H), 8.00 (d, J = 9.2 Hz, 1H), 7.93 (dd, J = 6.4, 3.4 Hz, 2H), 7.59 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.9 Hz, 4H), 7.29 (dd, J = 15.1, 8.1 Hz, 6H), 7.18-7.10 (m, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm) 147.71, 147.54, 142.45, 142.38, 141.61, 134.32, 131.19, 129.96, 129.88, 129.62, 129.55, 129.37, 129.06, 129.00, 128.37, 126.97, 126.90, 126.49, 126.17, 125.12, 124.68, 123.83, 123.47, 123.20, 123.15. MALDI-TOF (m/z): [M^+] calcd for $C_{40}H_{25}N_3$, 547.20; found: 547.27. Elem. anal. calcd (%) for $C_{40}H_{25}N_3$: C, 87.73; H, 4.60; N, 7.67; found: C, 87.85; H,4.57; N, 7.54.

Synthesis of *trans*-PyCNDPA

The mixture of (7) (2.00 g, 5.00 mmol) and diaminomaleonitrile (0.81 g, 7.5

mmol) were dissolved in acetic acid (30 mL). The solution was heated at 125 °C for 4 hours under argon atmosphere. After cooling to room temperature, the resulting mixture was poured into water and filtered. The solid was washed several times with water and further purified by column chromatography of silica gel using dichloromethane/petroleum (v/v = 2/1) as the eluent to give a deep-red powder of *trans*-PyCNDPA (2.12 g, yield: 90%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 9.41 (d, *J* = 7.0 Hz, 1H), 9.36 (d, *J* = 8.4 Hz, 1H), 8.44-8.41 (m, 1H), 8.22-8.16 (m, 2H), 7.95 (t, *J* = 8.5 Hz, 2H), 7.32 (dd, *J* = 8.5, 7.5 Hz, 4H), 7.15-7.10 (m, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm) 148.47, 148.07, 131.39, 129.71, 129.48, 129.12, 127.97, 127.84, 127.48, 127.23, 126.12, 125.10, 123.89, 123.53, 123.33, 123.20, 122.79, 114.18. MALDI-TOF (m/z): [M^+] calcd for $C_{32}H_{17}N_5$, 471.15; found: 471.32. Elem. anal. calcd (%) for $C_{32}H_{17}N_5$: C, 81.51; H, 3.63; N, 14.85; found: C, 81.60; H,3.58; N, 14.77.

Synthesis of *trans*-PyPDPA

Follow similar steps to *trans*-PyCNDPA but with o-phenylenediamine (0.81 g, 7.5 mmol) instead of diaminomaleonitrile, yielding an orange solid of *trans*-PyPDPA (2.24 g, yield: 95%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm) 9.68-9.61 (m, 2H), 8.49-8.40 (m, 2H), 8.29 (d, *J* = 7.0 Hz, 1H), 8.20-8.11 (m, 2H), 7.98-7.90 (m, 4H), 7.34-7.26 (m, 4H), 7.16 (dd, *J* = 8.6, 0.9 Hz, 4H), 7.06 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm) 148.58, 145.57, 143.06, 142.84, 142.22, 131.36, 130.24, 130.01, 129.53, 129.32, 129.28, 128.35, 128.14, 128.02, 127.34, 127.20, 126.91, 126.28, 125.13, 124.10, 123.27, 122.65, 122.36, 122.35. MALDI-TOF (m/z): [M^+] calcd for $C_{34}H_{21}N_3$, 471.17; found: 471.22. Elem. anal. calcd (%) for $C_{34}H_{21}N_3$:C, 86.60; H, 4.49; N, 8.91; N, 14.85; found: C, 86.77; H,4.41; N, 8.78.

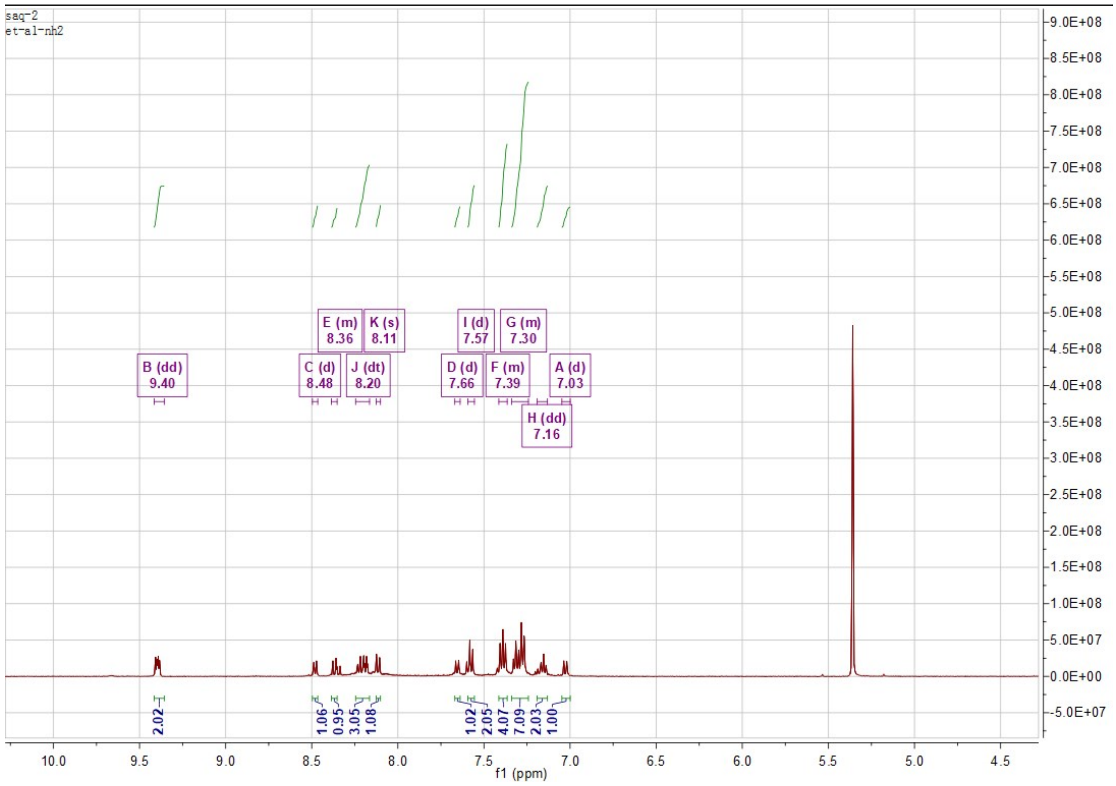


Fig. S1. ^{1}H NMR spectra of *cis*-PyPTPA in deuterated CD_2Cl_2.

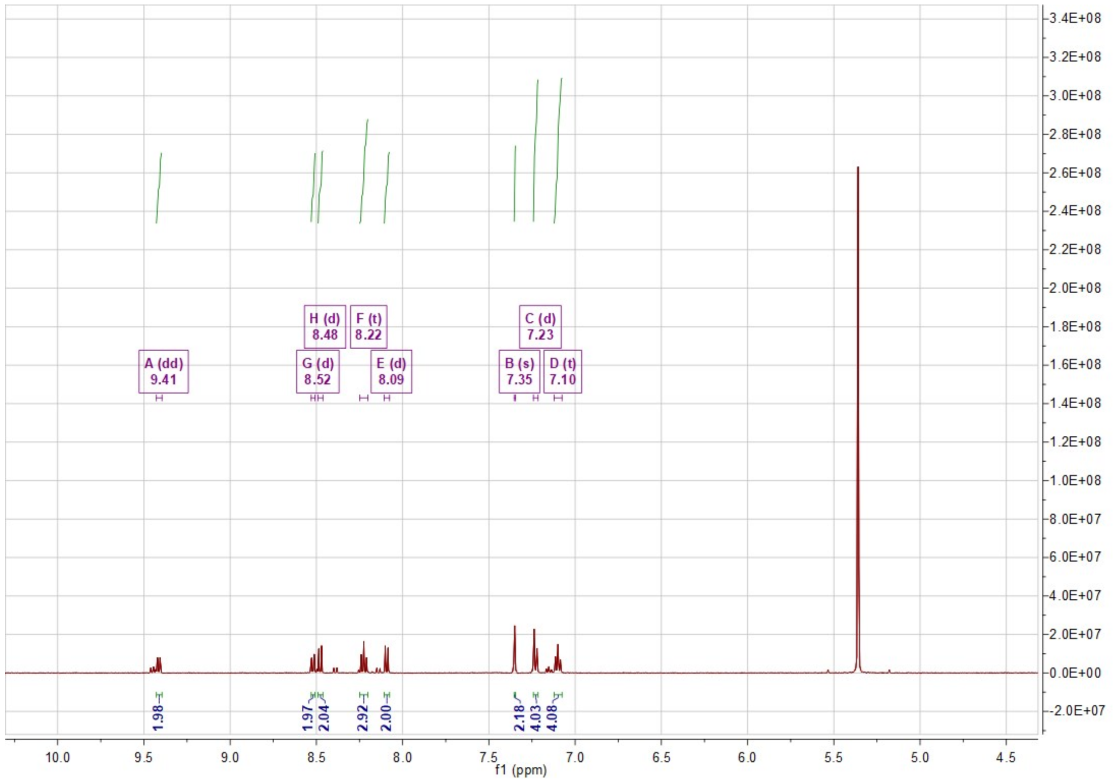


Fig. S2. ^{1}H NMR spectra of *cis*-PyCNTPA in deuterated CD_2Cl_2.

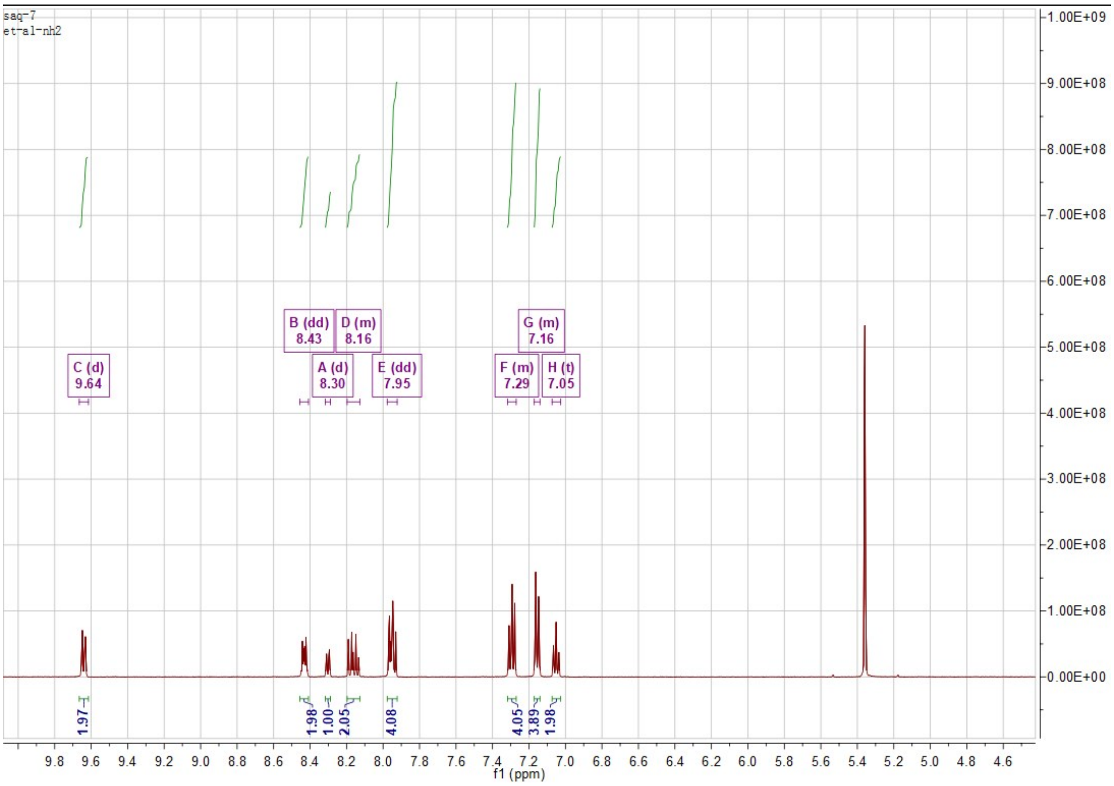


Fig. S3. ^{1}H NMR spectra of *trans*-PyCNTPA in deuterated CD_2Cl_2.

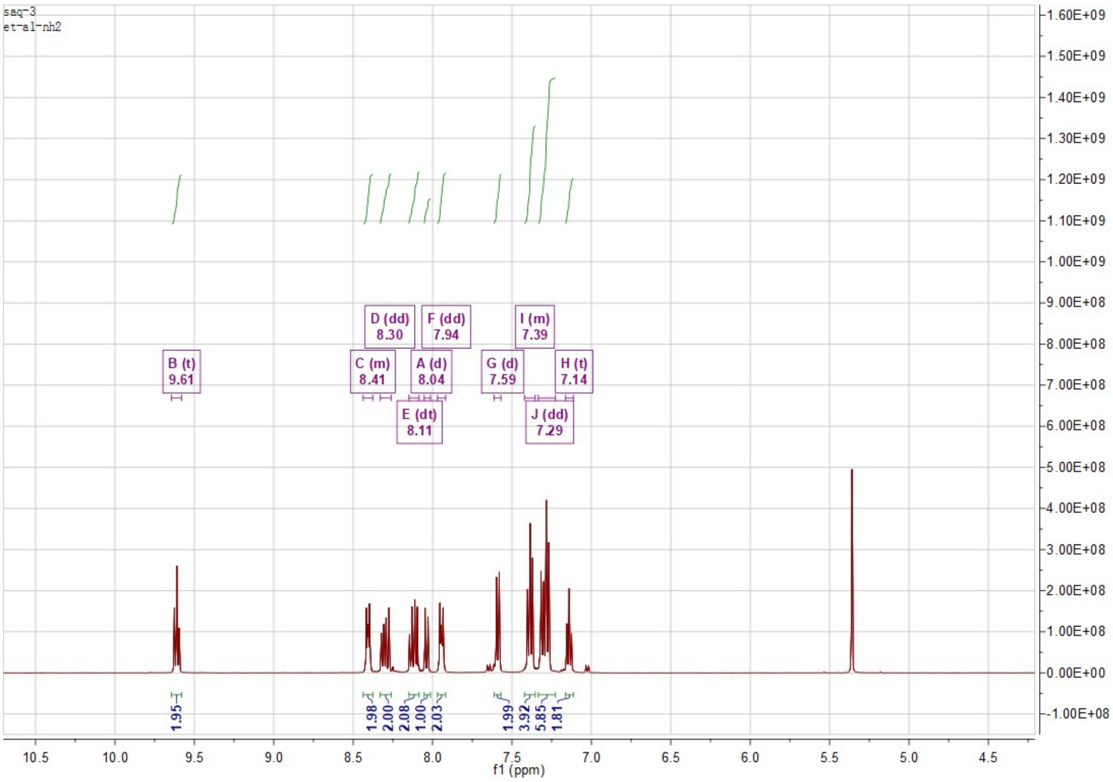


Fig. S4. ^{1}H NMR spectra of *trans*-PyPTPA in deuterated CD_2Cl_2.

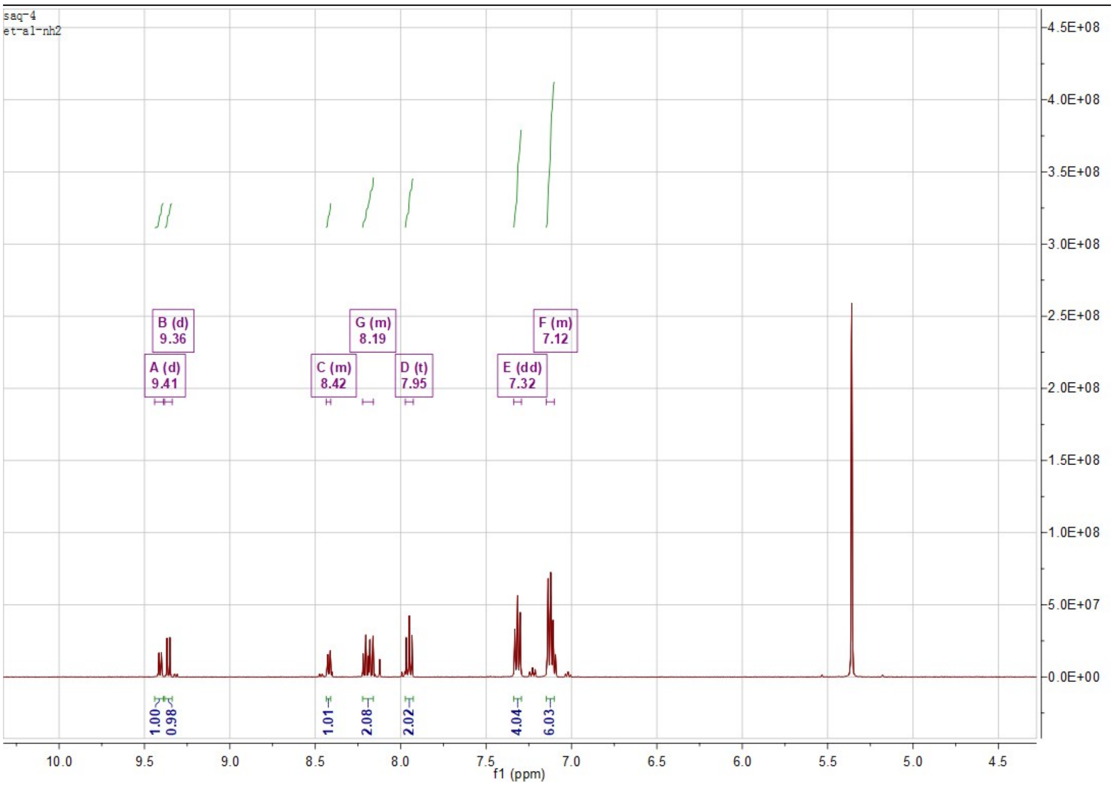


Fig. S5. ^{1}H NMR spectra of *trans*-PyCNDPA in deuterated CD_2Cl_2.

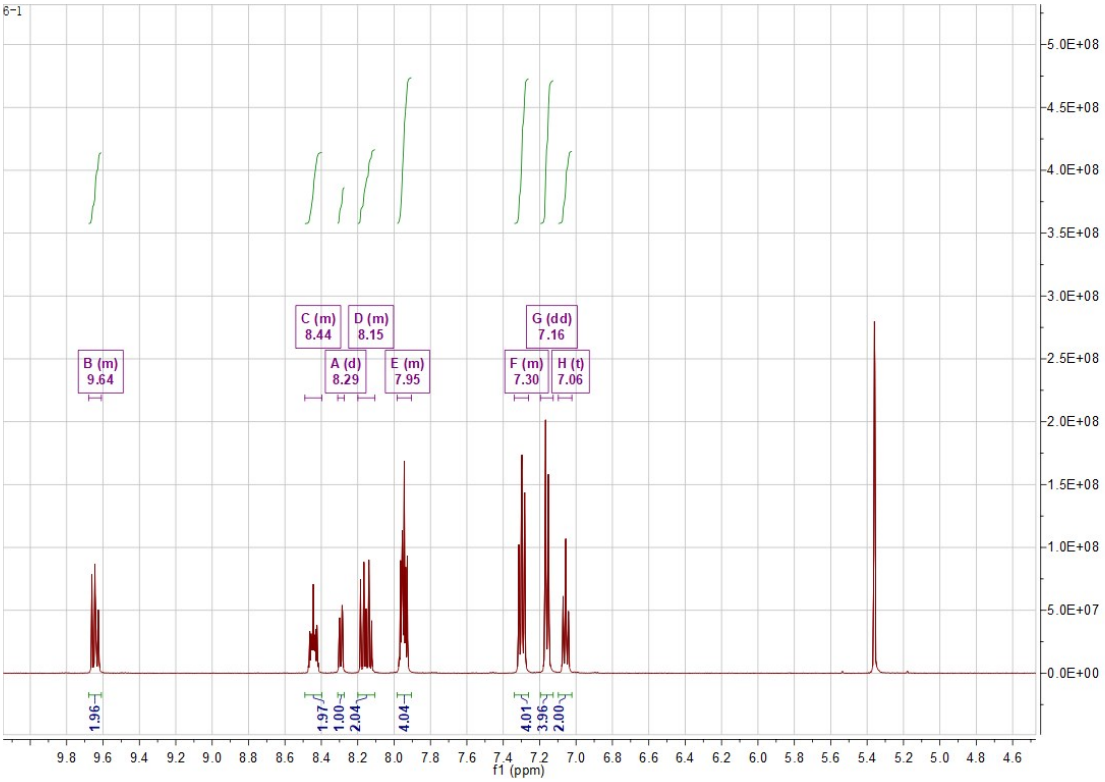


Fig. S6. ^{1}H NMR spectra of *trans*-PyPDPA in deuterated CD_2Cl_2.

5. Supplementary Figures and Tables

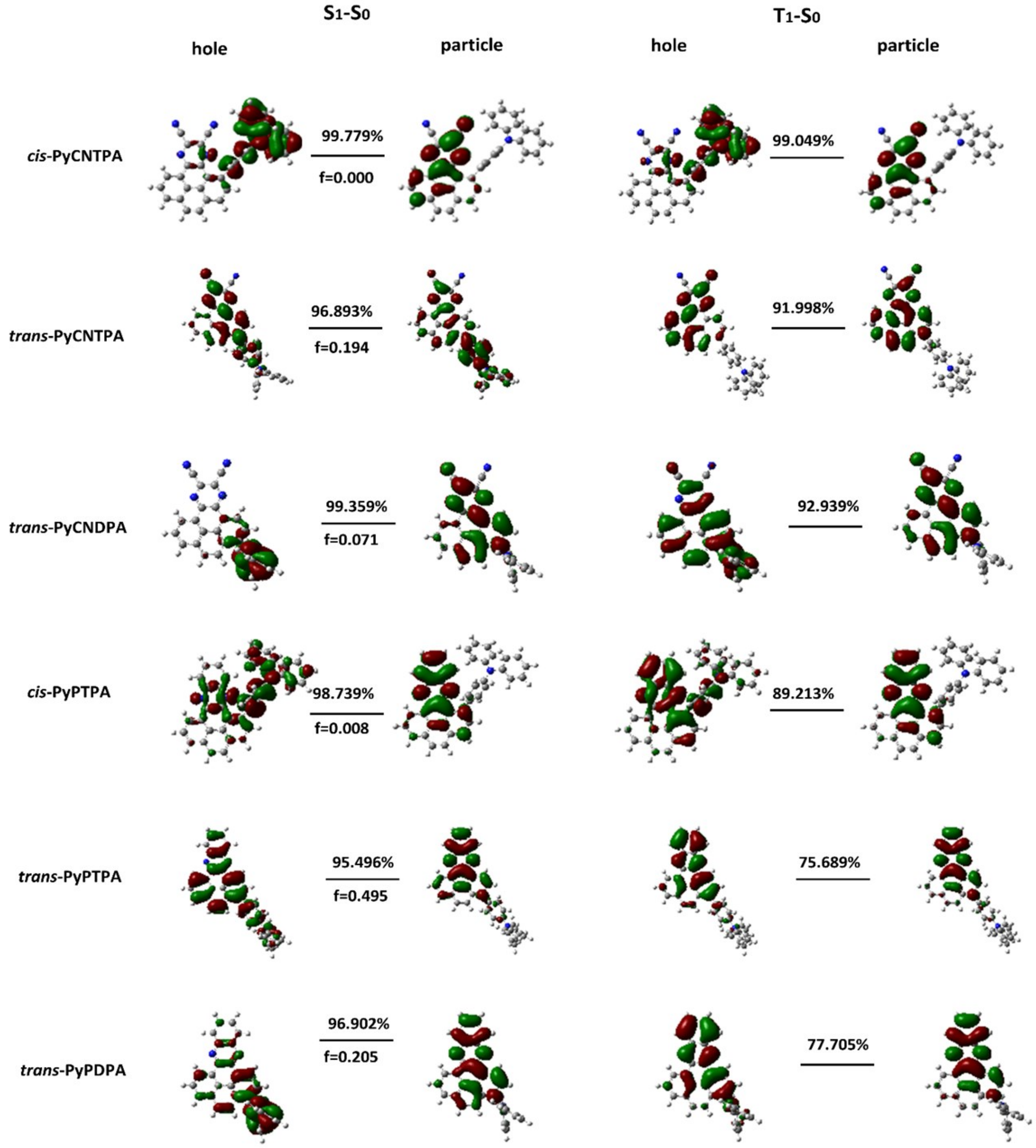


Fig. S7. Calculated natural transition orbitals (NTO) distribution and relevant orbital components with the optimized structures of excited states of *cis*-PyCNTPA, *cis*-PyPTPA, *trans*-PyCNTPA, *trans*-PyCNDPA, *trans*-PyPTPA and *trans*-PyPDPA.

Table S1.

The singlet/triplet excited states and ΔE_{ST} calculated by DFT/TDDFT (eV).

	cis-PyCNTPA	*cis*-PyPTPA	*trans*-PyCNTPA	*trans*-PyPTPA	*trans*-PyCNDPA	*trans*-PyPDPA
S_1	2.41	2.69	3.12	3.19	2.76	3.09
T_1	2.36	2.34	2.56	2.39	2.49	2.41
$\triangle E_{st}$	0.05	0.35	0.56	0.80	0.27	0.68

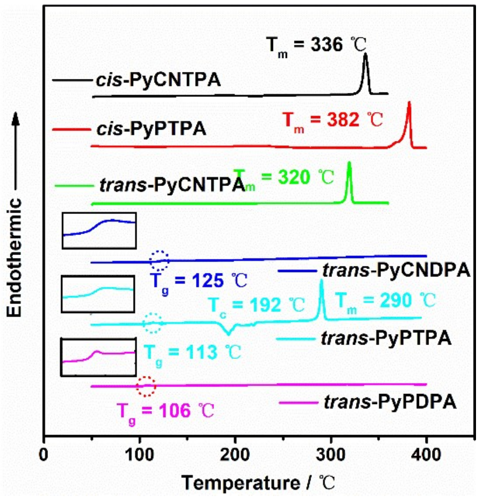
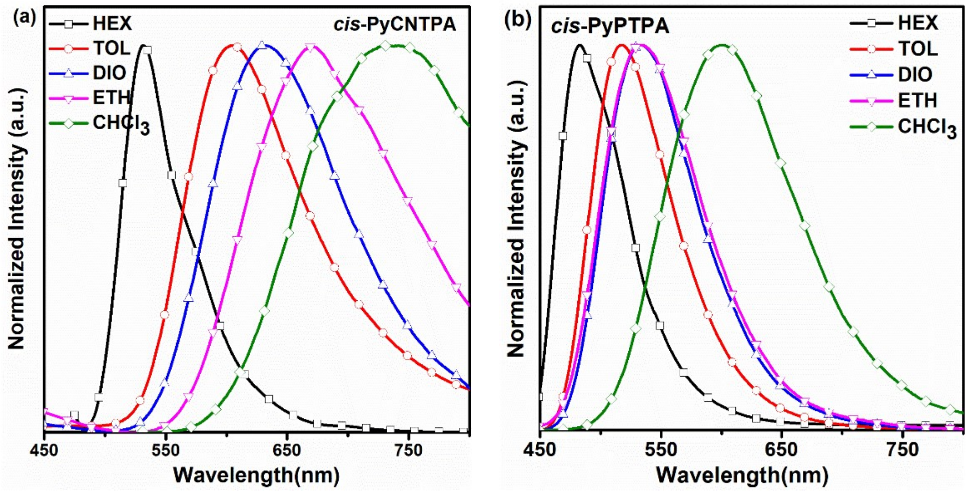


Fig. S8. DSC traces of the samples recorded at a heating rate of 10 ℃ min $^{-1}$.



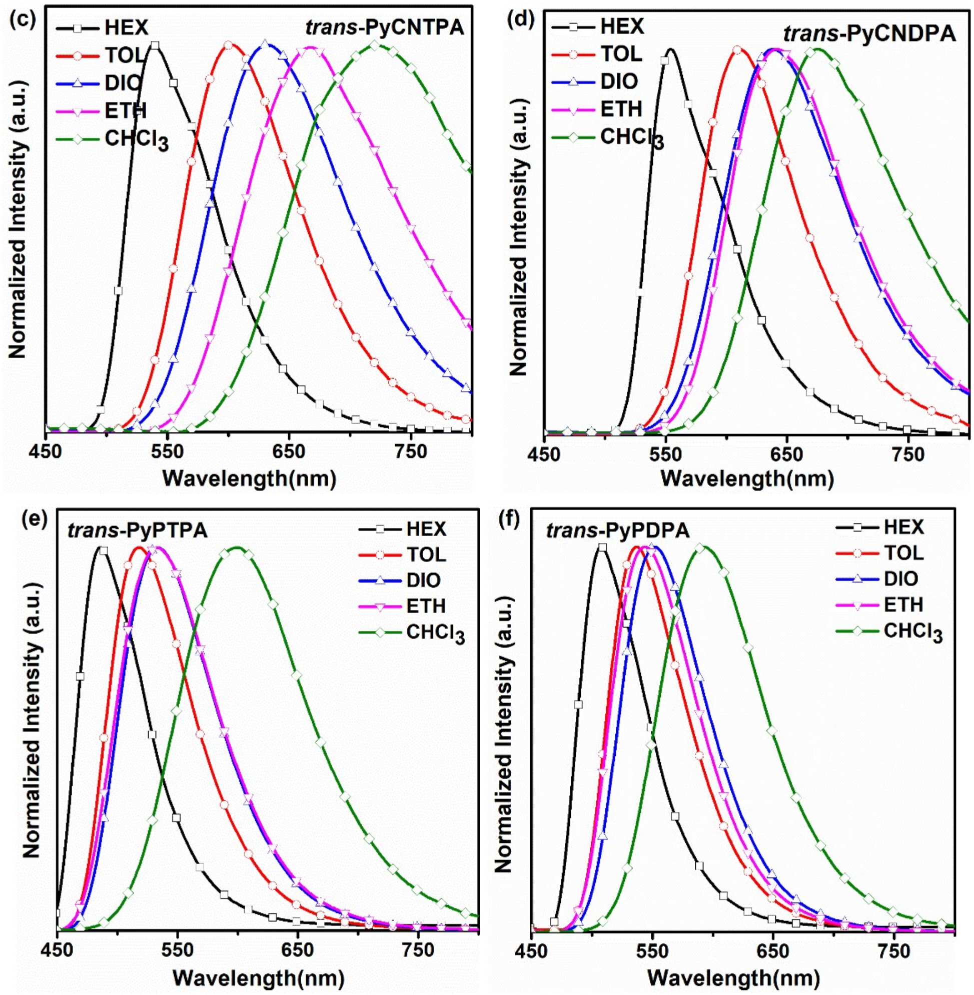
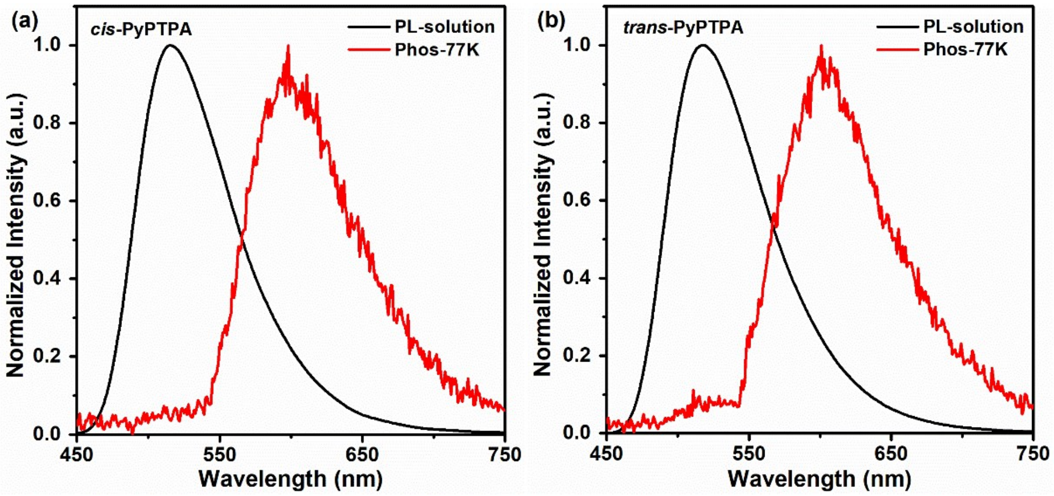


Fig. S9. PL spectra of the (a) *cis*-PyCNTPA, (b) *cis*-PyPTPA, (c) *trans*-PyCNTPA, (d) *trans*-PyCNDPA, (e) *trans*-PyPTPA and (f) *trans*-PyPDPA (10^{-5} M) measured in different solvents at 298 K.

Table S2.

The fluorescence spectra of *cis*-PyCNTPA, *cis*-PyPTPA, *trans*-PyCNTPA, *trans*-PyCNDPA, *trans*-PyPTPA and *trans*-PyPDPA in hexane (HEX), toluene (TOL), dioxane (DIO), diethyl ether (ETH) and chloroform ($CHCl_3$).

	HEX (nm)	TOL (nm)	DIO (nm)	ETH (nm)	$CHCl_3$ (nm)
cis-PyCNTPA	532	605	633	670	740
cis-PyPTPA	484	518	533	534	601
trans-PyCNTPA	540	602	632	668	722
trans-PyCNDPA	554	611	638	642	676
trans-PyPTPA	486	518	533	534	599
trans-PyPDPA	508	537	551	543	592



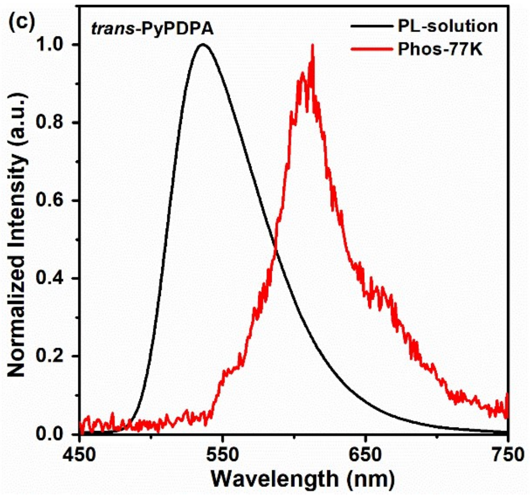


Figure S10. Normalized fluorescence (300 K) and phosphorescence (77 K) spectra of *cis*-PyPTPA, *trans*-PyPTPA and *trans*-PyPDPA in diluted toluene solutions (10^{-5} M).

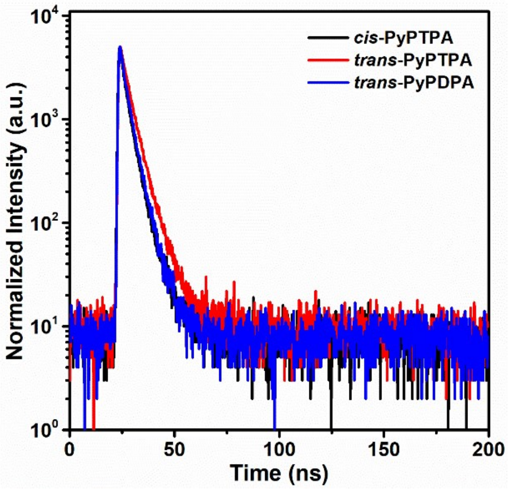


Fig. S11. Transient PL curves of *cis*-PyPTPA, *trans*-PyPTPA and *trans*-PyPDPA doped into PMMA hosts (1.0wt%).

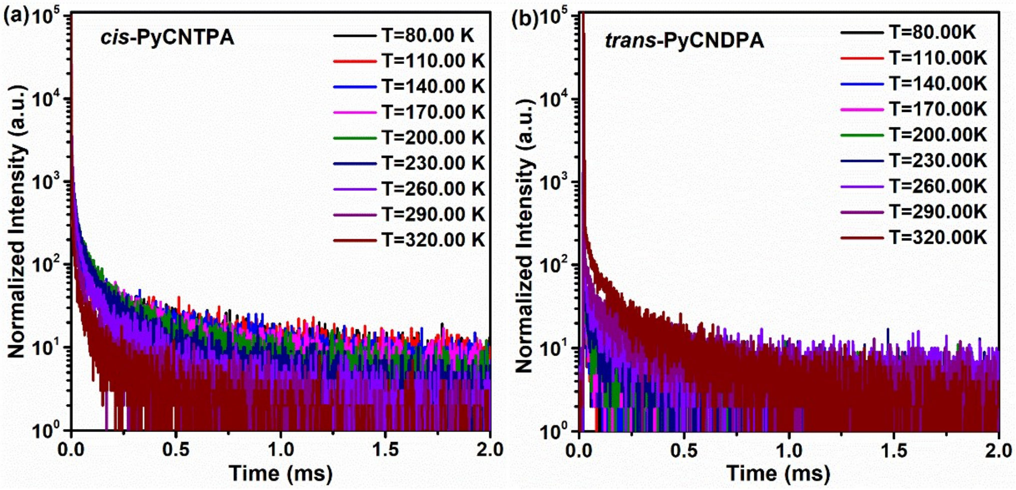


Fig. S12. Transient PL decay curves of 1.0wt% *cis*-PyCNTPA (a) and *trans*-

PyCNDPA (b) doped in PMMA film at different temperatures.

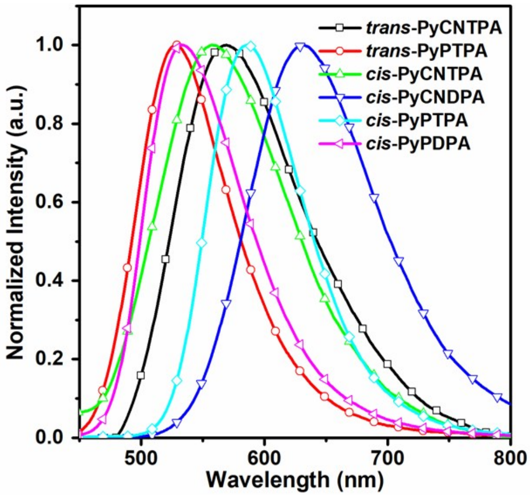
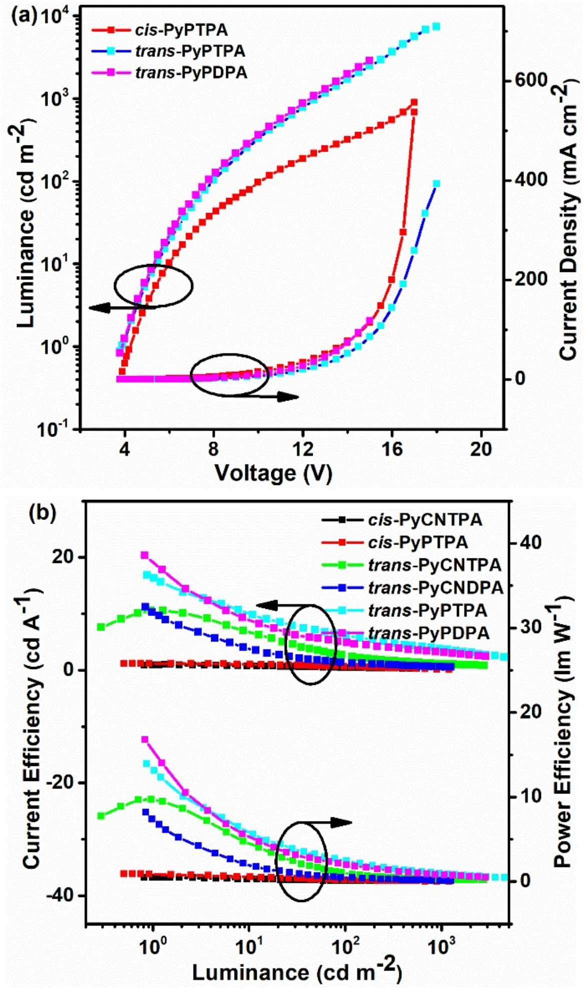


Fig. S13. Normalized fluorescence spectra of target compounds doped into PMMA hosts (1.0wt%).



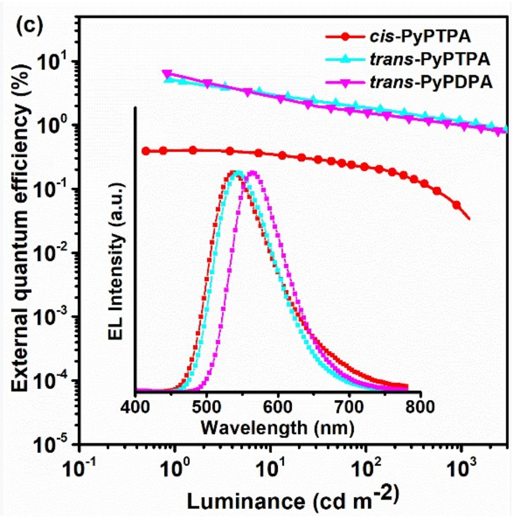
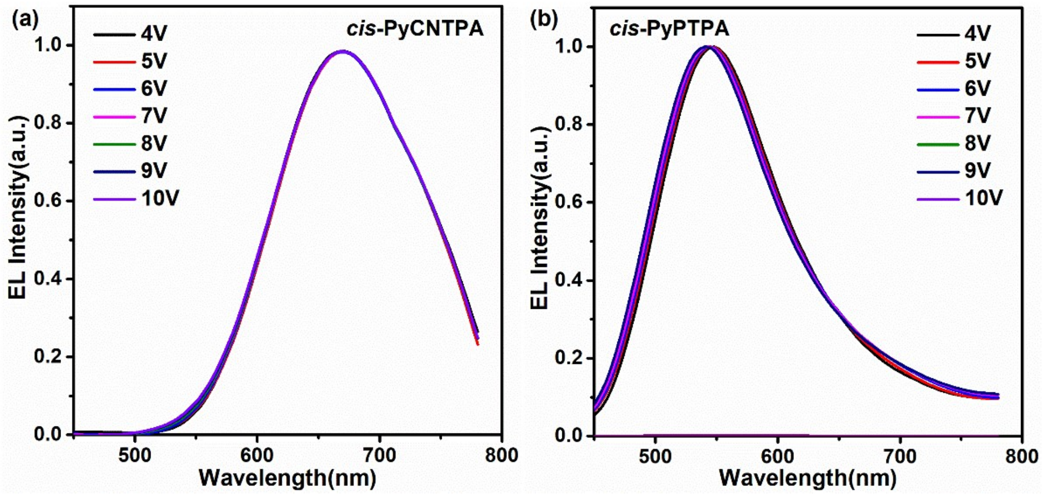


Fig. S14. (a) Luminance curves-voltage-current density curves of devices based on *cis*-PyPTPA, *trans*-PyPTPA and *trans*-PyPDPA; (b) Current efficiency-luminance-power efficiency curves of devices based on *cis*-PyCNTPA, *cis*-PyPTPA, *trans*-PyCNTPA, *trans*-PyCNDPA, *trans*-PyPTPA and *trans*-PyPDPA; (c) EQE–luminance and the normalized EL spectra of devices based on *cis*-PyPTPA, *trans*-PyPTPA and *trans*-PyPDPA.



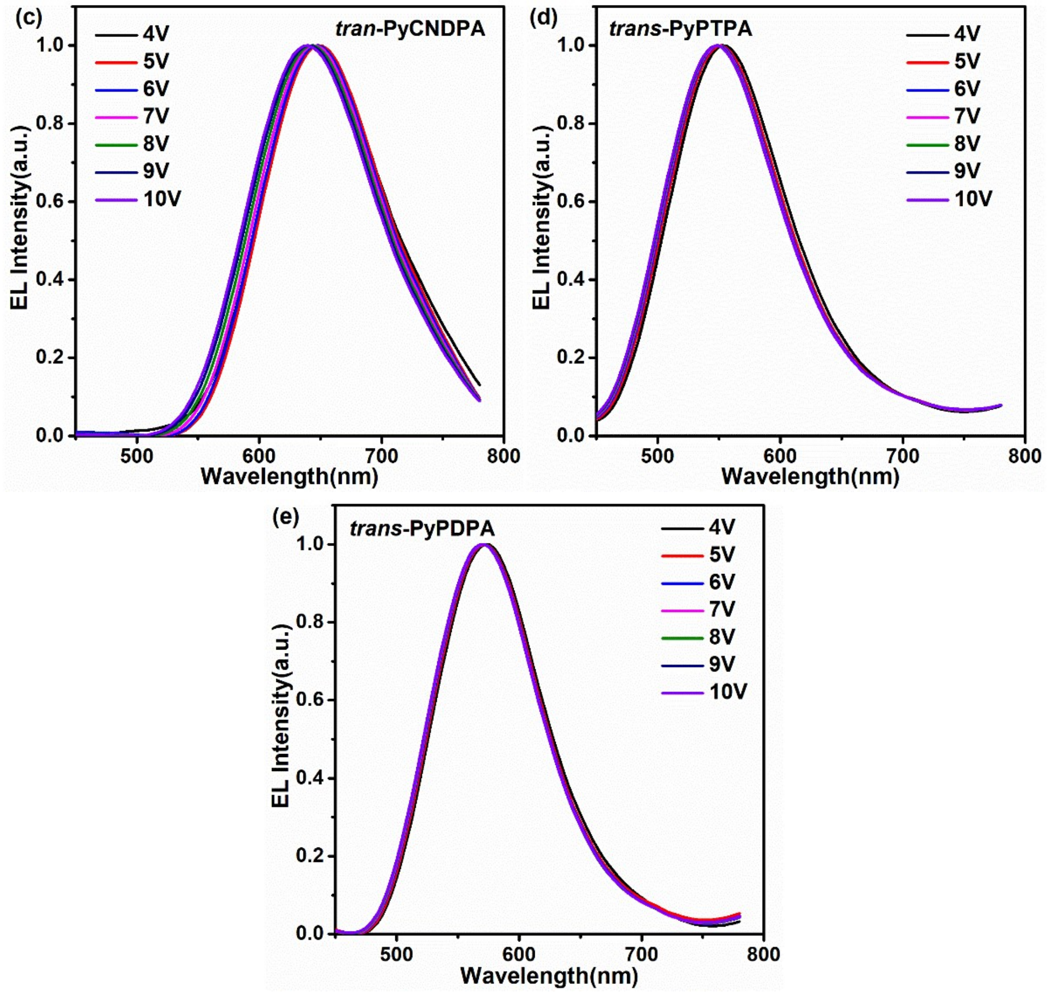


Fig. S15. The EL spectra of *cis*-PyCNTPA, *cis*-PyPTPA, *trans*-PyCNDPA, *trans*-PyPTPA and *trans*-PyPDPA measured at 4-10 V.

Table S3.

The EL performances of non-doped devices based on *cis*-PyCNTPA, *cis*-PyPTPA, *trans*-PyCNTPA, *trans*-PyCNDPA, *trans*-PyPTPA and *trans*-PyPDPA.

Device	V_{on}[a]	L_{max}[b]	CE_{max}[c]	PE_{max}[d]	EQE[e] (%)	EL λ_{max}[f]	CIE[g]
	(V)	(cd m^{-2})	(cd A^{-1})	(lm W^{-1})	max	(nm)	(x, y)
cis-PyCNTPA	7.1	21.55	0.02	0.01	0.13	732	(0.65, 0.31)
cis-PyPTPA	4.4	51.77	0.05	0.03	0.02	592	(0.51, 0.47)
trans-PyCNTPA	5.4	273.57	0.07	0.04	0.62	716	(0.67, 0.31)
trans-PyCNDPA	3.8	126.35	0.13	0.12	1.24	712	(0.67, 0.30)
trans-PyPTPA	2.8	5453.81	5.17	5.15	1.53	552	(0.42, 0.55)
trans-PyPDPA	3.1	3595.59	3.01	2.38	0.93	560	(0.45, 0.54)

[a] V_{on}: turn-on voltage at the luminescence of 1 cd m^{-2}; [b] L_{max}: maximum luminance; [c] CE_{max}: maximum current efficiency; [d] PE_{max}: maximum power efficiency; [e] EQE: external quantum

efficiency of maximum; f) EL λ_{max}: EL emission peak of EL spectrum at 7V; g) CIE: Commission International de l'Éclairage (CIE) coordinates at 7V.