

## Electronic Supplementary Material (ESI)

### Predictable Luminescence Performance of Polyphenylpyrazine Derivatives based on Theoretical Model via Electron Cloud Overlap

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### General information and materials

All solvents and reagents from commercial sources are used directly without further purification. Spectral grade reagents are used for optical properties. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 500 spectrometer in deuterated CDCl<sub>3</sub>. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. A Shimadzu UV-2600 spectrophotometer is used for measurements of UV-vis absorption spectrum. Photoluminescence spectrum were tested on Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields in solutions and solid states depended on a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaaurus\_QY. Fluorescence lifetimes were recorded on a Hamamatsu C11367-11 Quantaaurus-Tau time-resolved spectrometer.

### Calculation methods

#### 1) Calculation detail.

The optimized S<sub>0</sub> and S<sub>1</sub> geometries were calculated on density functional theory (DFT) and time dependent density functional theory (TDDFT) respectively at the M062X/6-31G (d, p) level in toluene. The toluene phase was considered by the linear-response polarizable continuum model (PCM) as implemented via *Gaussian 16* package. Hole-electron analysis, including NTO, the hole-electron distribution ratios on each unit, and transition density matrix, were performed on *Multiwfn version 3.6* (a multifunctional wavefunction analyzer) based on the optimized S<sub>1</sub> geometries.

#### 2) The equations and definitions detail of hole-electron overlap

These parameters are obtained by the following equation defined by *Multiwfn* program.

To investigate which MOs (Molecule orbital) have significant contributions to hole and electron, the contribution of occupied MO to hole and contribution of virtual MO to electron were defined as follows. The data can reflect which molecular orbitals play an important role in the transition. Therefore, it is convenient for quantitative analysis and discussion.

$$\Theta_i^{\text{hole}} = \sum_a [(w_i^a)^2 - (w_i'^a)^2] \quad \Theta_i^{\text{ele}} = \sum_a [(w_i^a)^2 - (w_i'^a)^2]$$

where  $i$ ,  $a$ ,  $w$  and  $w'$  respectively represent occupied MOs, virtual MOs, configuration coefficient of excitation and configuration coefficient of de-excitation.

below normalization conditions are held evidently

$$\sum_i \Theta_i^{\text{hole}} = 1 \quad \sum_a \Theta_a^{\text{ele}} = 1$$

Contribution to hole/electron by an atom can be derived as follows. Considering the normalization condition of the hole (de-excitation part is temporarily ignored for simplicity).

$$\begin{aligned} \int \left( \sum_{i,j \rightarrow a} w_i^a w_j^a \varphi_i \varphi_j \right) d\mathbf{r} &= 1 \\ \int \left( \sum_{i,j \rightarrow a} w_i^a w_j^a \sum_{\mu} \sum_{\nu} C_{\mu,i} C_{\nu,j} \chi_{\mu} \chi_{\nu} \right) d\mathbf{r} &= 1 \\ \sum_{i,j \rightarrow a} w_i^a w_j^a \sum_{\mu} \sum_{\nu} C_{\mu,i} C_{\nu,j} \int \chi_{\mu} \chi_{\nu} d\mathbf{r} &= 1 \\ \sum_{i,j \rightarrow a} w_i^a w_j^a \sum_{\mu} \sum_{\nu} C_{\mu,i} C_{\nu,j} S_{\mu,\nu} &= 1 \end{aligned}$$

where  $\chi$  denotes basis function,  $S$  and  $C$  are overlap matrix and coefficient matrix, and  $\mu$  and  $\nu$  represent basis function respectively. Mulliken-like method are employed to partition the term  $\sum_{\mu} \sum_{\nu} C_{\mu,i} C_{\nu,j} S_{\mu,\nu}$  as atomic contributions, then the contribution of atom A to hole are defined in below form.

$$\Theta_A^{\text{hole}} = \sum_{i,j \rightarrow a} w_i^a w_j^a \frac{1}{2} \left( \sum_{\mu \in A} \sum_{\nu} C_{\mu,i} C_{\nu,j} S_{\mu,\nu} + \sum_{\mu} \sum_{\nu \in A} C_{\mu,i} C_{\nu,j} S_{\mu,\nu} \right)$$

Apply above treatment on de-excitation part of hole as well as electron. The actual equations used to evaluate atomic contribution to hole and electron are

$$\begin{aligned} \Theta_A^{\text{hole}} &= \sum_{i,j \rightarrow a} w_i^a w_j^a \frac{1}{2} \left( \sum_{\mu \in A} \sum_{\nu} T_{\mu,\nu}^{ij} + \sum_{\mu} \sum_{\nu \in A} T_{\mu,\nu}^{ij} \right) - \sum_{i,j \rightarrow a} w_i'^a w_j'^a \frac{1}{2} \left( \sum_{\mu \in A} \sum_{\nu} T_{\mu,\nu}^{ij} + \sum_{\mu} \sum_{\nu \in A} T_{\mu,\nu}^{ij} \right) \\ \Theta_A^{\text{ele}} &= \sum_{i \rightarrow a,b} w_i^a w_i^b \frac{1}{2} \left( \sum_{\mu \in A} \sum_{\nu} T_{\mu,\nu}^{ab} + \sum_{\mu} \sum_{\nu \in A} T_{\mu,\nu}^{ab} \right) - \sum_{i \rightarrow a,b} w_i'^a w_i'^b \frac{1}{2} \left( \sum_{\mu \in A} \sum_{\nu} T_{\mu,\nu}^{ab} + \sum_{\mu} \sum_{\nu \in A} T_{\mu,\nu}^{ab} \right) \\ T_{\mu,\nu}^{ij} &= C_{\mu,i} C_{\nu,j} S_{\mu,\nu} \end{aligned}$$

Fragment contribution to hole and electron can be simply evaluated by summing up atomic contributions

$$\Theta_{\text{frag}}^{\text{hole}} = \sum_{A \in \text{frag}} \Theta_A^{\text{hole}} \quad \Theta_{\text{frag}}^{\text{ele}} = \sum_{A \in \text{frag}} \Theta_A^{\text{ele}}$$

Overlap between hole and electron in atom and fragment spaces are defined as geometry average of their contributions:

$$\Theta_A^{ovlp} = \sqrt{\Theta_A^{ele} \Theta_A^{hole}} \quad \Theta_{frag}^{ovlp} = \sqrt{\Theta_{frag}^{ele} \Theta_{frag}^{hole}}$$

Therefore, the percentages of hole-electron overlap on TPP are obtained by follow equation.

$$\Theta_{TPP}^{ovlp} = \sqrt{\Theta_{TPP}^{ele} \Theta_{TPP}^{hole}}$$

3) The equations and definitions detail of TDM.

$$P_{\mu\nu}^{tran} = \sum_i^{occ} \sum_a^{vir} w_i^a C_{\mu i} C_{\nu a}$$

$$T(\mathbf{r}; \mathbf{r}') = \sum_{\mu} \sum_{\nu} P_{\mu\nu}^{tran} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}')$$

$C_{\mu i}$  denotes the expansion coefficient of basis function  $\mu$  in MO  $i$ .  $\chi$  denotes basis function.

The off-diagonal elements of TDM essentially represent the coupling between various basis functions during electron excitation. Assume there are only two basic functions and meantime the excitation can be perfectly represented as  $i \rightarrow a$  MO transition, then the TDM could be explicitly written as below form.

$$\mathbf{p}^{tran} = \begin{bmatrix} 1,2 & 2,2 \\ 1,1 & 2,1 \end{bmatrix} = \begin{bmatrix} C_{1i}C_{2a} & C_{2i}C_{2a} \\ C_{1i}C_{1a} & C_{2i}C_{1a} \end{bmatrix}$$

The TDM can be contracted to atoms based on form according to correspondence between basis functions and atoms, it will be symbolized as  $\mathbf{p}$ .

$$p_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} (P_{\mu\nu}^{tran})^2$$

$\mu$  and  $\nu$  represent the basic functions centered at atom A and on B. the general structure of the resulting  $\mathbf{p}$  could be expressed in below form

$$\mathbf{p} = \begin{bmatrix} 1, N & \cdots & N, N \\ \vdots & \ddots & \vdots \\ 1, 1 & \cdots & N, 1 \end{bmatrix}$$

Diagonal terms: If (A, A) is large, it implies that atom A has large contribution to both hole and electron. Therefore, the electron excitation should result in evident charge reorganization within atom A.

Off-diagonal terms: If (A, B) is large, then atom A should have large contribution to hole and meantime atom B should have large contribution to electron, implying that electron excitation leads to CT from A to B.

If fragments are defined, the  $\mathbf{p}$  (or other kinds of atom transition matrix) can further be contracted to fragment based on form:

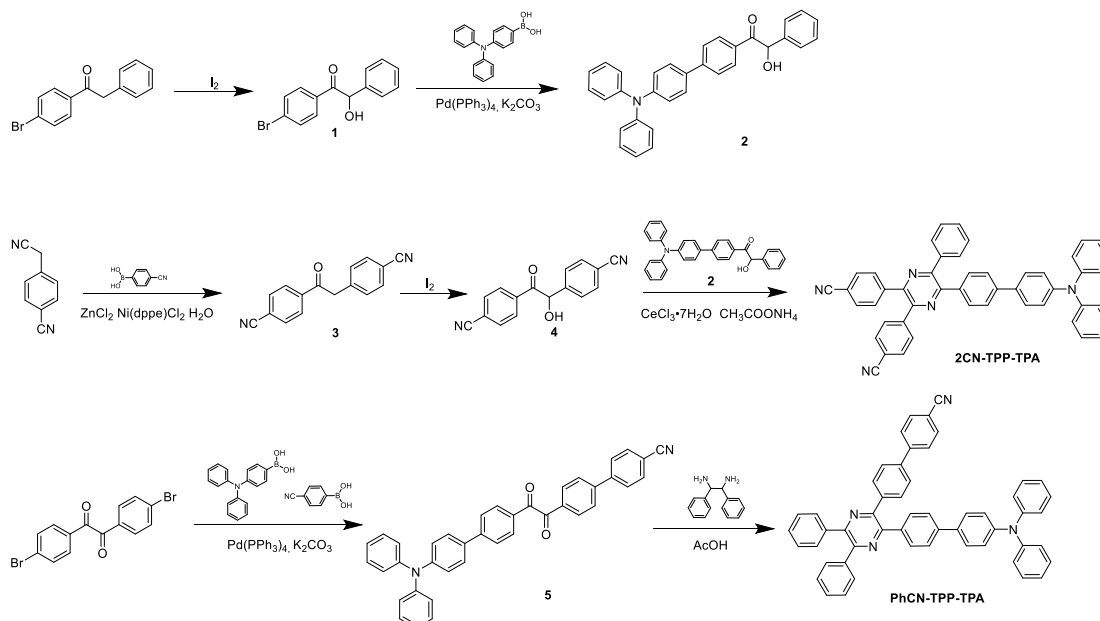
$$p_{RS} = \sum_{A \in frag R} \sum_{B \in frag S} p_{AB}$$

Therefore, the transition density matrix (TDM) of {TPP, TPP} are computed by the equation.

$$p_{TPP\ TPP} = \sum_{A \in frag\ TPP} \sum_{B \in frag\ TPP} p_{AB}$$

The Atom of A and B all belong to TPP.

## Additional data



**Scheme S1.** The synthetic route of **2CN-TPP-TPA** and **PhCN-TPP-TPA**.

**Synthesis of compound 1:** compound 1 (18.70 g, 68 mmol), Iodine (3.45 g, 13.6 mmol) were added into 250 mL single neck, round-bottomed flask. Then 80 mL dimethyl sulfoxide (DMSO) were added into the flask. The mixtures were stirred for 24 h at 60°C. After it was cooled to room temperature, added dichloromethane and water for extraction. The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. White solid was obtained in 67.6 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.40–7.27 (m, 5H), 5.89 (s, 1H), 4.46 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.04, 138.66, 132.19, 132.10, 130.57, 129.29, 128.82, 127.77, 76.33.

**Synthesis of compound 2:** compound 2 (4.3 g, 15 mmol), 4-(diphenylamino) phenylboronic acid (5.2 g, 18 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.86 g, 0.75 mmol), K<sub>2</sub>CO<sub>3</sub> (6.2 g, 45 mmol) were added into 250 mL two-necked, round-bottomed flask under nitrogen. Then 40 mL tetrahydrofuran (THF) and 10 mL distilled water were injected into the flask. The mixtures were refluxed for 24 h at 80°C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow solid was obtained in 54.3 % yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.83–7.00 (m, 21H), 6.10 (s, 1H), 4.75 (s, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 198.49, 148.55, 147.45, 145.90, 139.74, 138.41, 132.53, 131.74, 129.92,

129.75, 129.59, 129.49, 129.22, 128.60, 128.21, 128.05, 127.95, 126.64, 126.53, 126.10, 125.31, 125.04, 123.68, 123.07, 76.23.

**Synthesis of compound 3:** 4-cyanophenylacetonitrile (8.52 g, 60 mmol), 4-cyanophenylboronic acid (17.64 g, 120 mmol), Ni(dppe)Cl<sub>2</sub> (3.16 g, 6 mmol), ZnCl<sub>2</sub> (12.24 g, 90 mmol) were added into 250 mL two-necked, round-bottomed flask under nitrogen. Then 80 mL 1,4 dioxane and 1.08 mL H<sub>2</sub>O were injected into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and was concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. White solid was obtained in 53.2 % yield. <sup>1</sup>H NMR (500 MHz, DMSO) δ 8.20 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 4.64 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO) δ 196.77, 141.16, 139.95, 133.33, 132.53, 131.66, 129.33, 119.40, 118.61, 115.84, 110.01, 45.35.

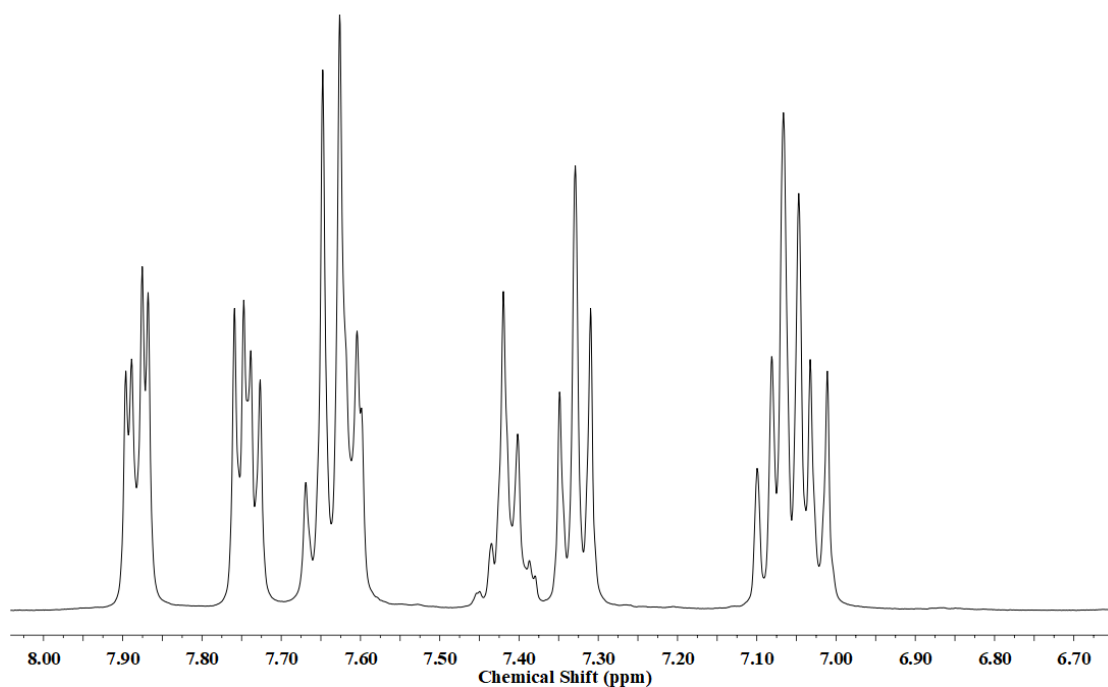
**Synthesis of compound 4:** compound 3 (6.15 g, 25 mmol), Iodine (1.26 g, 5 mmol) were added into 250 mL single neck, round-bottomed flask. Then 120 mL dimethyl sulfoxide (DMSO) were added into the flask. The mixtures were stirred for 24 h at 60 °C. After it was cooled to room temperature, added dichloromethane and water for extraction. The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow solid was obtained in 67.6 % yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.77–7.38 (m, 8H), 6.09 (d, *J* = 8.6 Hz, 1H), 4.44 (s, 1H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 198.78, 144.18, 137.71, 136.61, 134.33, 134.23, 134.02, 131.61, 130.63, 129.67, 119.59, 119.41, 118.78, 118.68, 114.10, 77.38.

**Synthesis of 2CN-TPP-TPA:** compound 3 (2.3 g, 5 mmol), compound 5 (1.31 g, 5 mmol), ammonium acetate (0.7 g, 10 mmol), Cerium (III) chloride heptahydrate (0.09 g, 0.25 mmol) were added into 250 mL single-necked, round-bottomed flask. Then 20 mL ethanol were added into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:1 by volume) as eluent. Yellow solid was obtained in 35.6 % yield. <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.88 (dd, *J* = 8.3, 3.0 Hz, 4H), 7.74 (dd, *J* = 8.2, 4.7 Hz, 4H), 7.69–7.57 (m, 8H), 7.45–7.37 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 4H), 7.12–6.99 (m, 8H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 149.62, 149.23, 147.63, 147.48, 147.38, 147.31, 142.55, 140.55, 138.05, 136.23, 133.12, 132.88, 131.13, 130.69, 130.11, 130.07, 129.69, 128.97, 128.11, 126.38, 124.80, 123.90, 123.42, 119.01, 112.07. HRMS (MALDI-TOF): *m/z* [M<sup>+</sup>] calcd. For C<sub>48</sub>H<sub>31</sub>N<sub>5</sub>; 677.2579. found, [M+1] 678.2652.

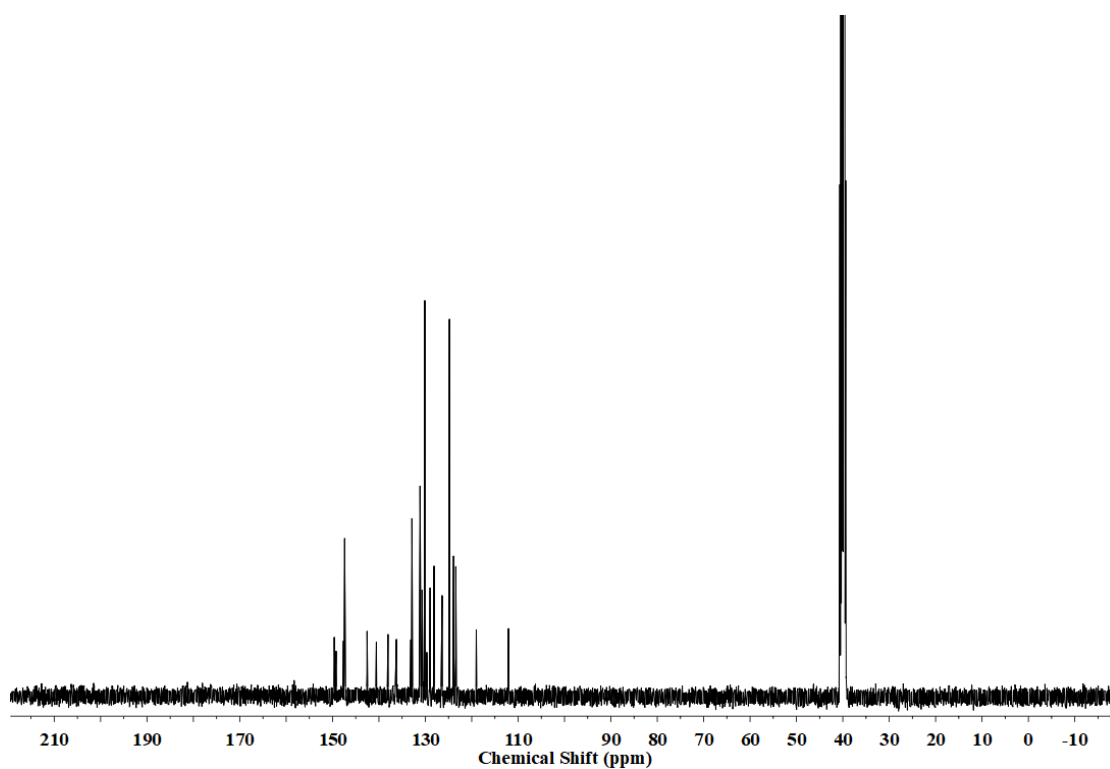
**Synthesis of compound 5:** 1,2-bis(4-bromophenyl)ethane-1,2-dione (3.7 g, 10 mmol), 4-(diphenylamino)phenylboronic acid (2.9 g, 10 mmol), 4-cyanophenylboronic acid (1.7 g, 10 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.86 g, 0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (6.2 g, 30 mmol) were added into 250 mL two-necked, round-bottomed flask under nitrogen. Then 40 mL tetrahydrofuran (THF) and 10 mL distilled water were injected into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-

gel column with DCM/hexane (1:2 by volume) as eluent. White solid was obtained in 50.6 % yield.  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.10–7.81 (m, 13H), 7.69 (d,  $J = 8.1$  Hz, 2H), 7.34 (t,  $J = 7.4$  Hz, 4H), 7.16–6.93 (m, 7H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  194.73, 194.34, 148.66, 147.09, 146.71, 145.10, 143.35, 133.50, 133.10, 132.51, 132.03, 131.69, 131.01, 130.90, 130.87, 130.76, 130.19, 128.67, 128.65, 128.62, 127.21, 125.26, 124.34, 122.59, 119.09, 111.84.

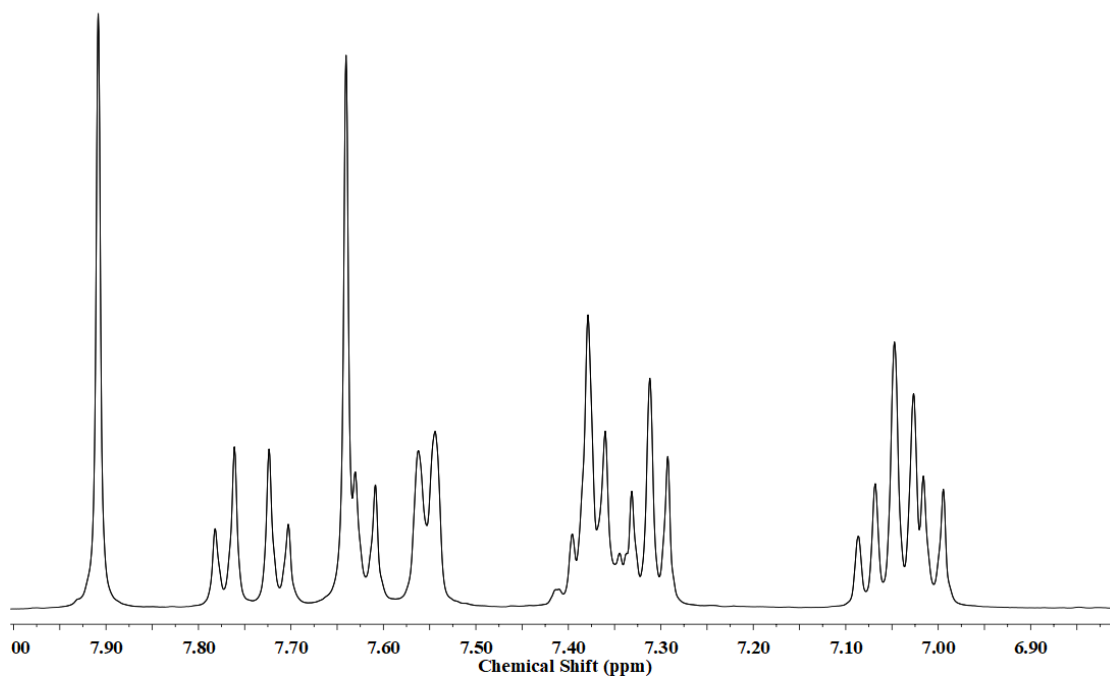
**Synthesis of compound PhCN-TPP-TPA:** A mixture of **5** (1.1 g, 2 mmol), 1,2 diphenylethane 1,2-diamine (0.64 g, 3 mmol), and glacial acetic acid (20 mL) were added in 100 mL two-neck bottle and then refluxed under air for 3 h. After cooling down, the solid product was filtrated and washed with ethanol. The crude product was purified by a silica-gel column with DCM/hexane (1:2 by volume) as eluent, Yellow solid was obtained in 50.6 % yield.  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.91 (s, 4H), 7.77 (d,  $J = 8.4$  Hz, 2H), 7.71 (d,  $J = 8.3$  Hz, 2H), 7.68–7.59 (m, 6H), 7.55 (d,  $J = 7.2$  Hz, 4H), 7.35 (m, 10H), 7.13–6.95 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  148.81, 148.61, 148.31, 147.76, 147.55, 147.39, 144.10, 140.28, 138.88, 138.73, 138.40, 136.72, 133.34, 133.24, 130.83, 130.67, 130.08, 129.29, 128.78, 128.06, 127.96, 127.44, 126.39, 124.74, 123.84, 123.47, 119.28, 110.77. HRMS (MALDI-TOF):  $m/z$  [ $\text{M}^+$ ] calcd. For  $\text{C}_{53}\text{H}_{36}\text{N}_4$ ; 728.294. found, [ $\text{M}+1$ ] 729.3013.



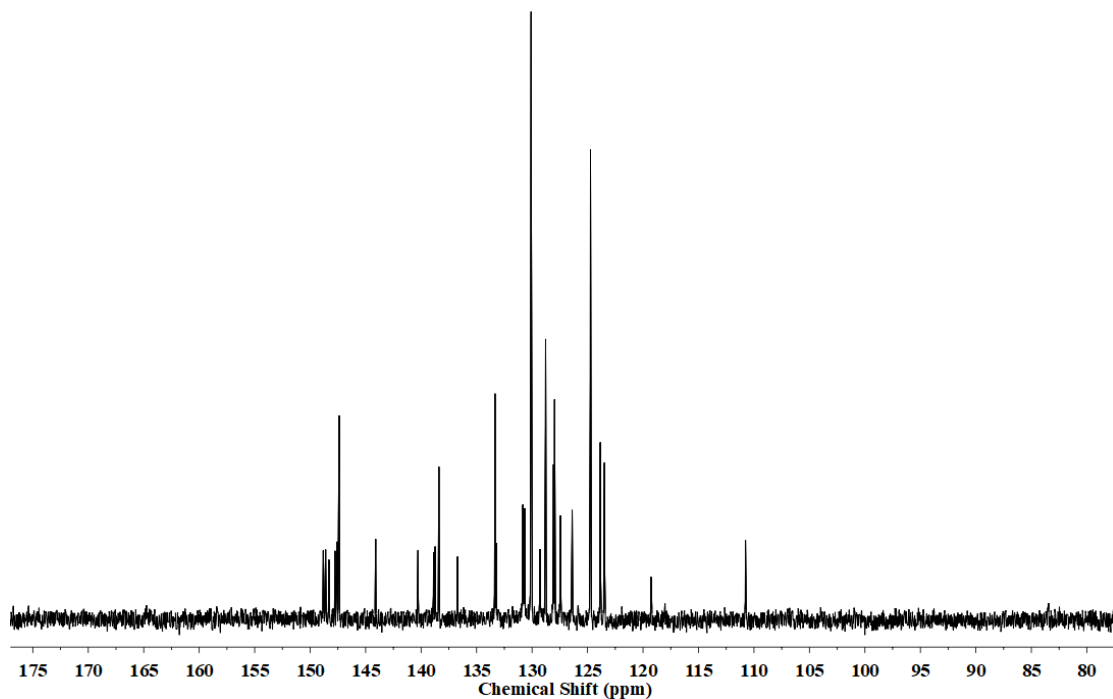
**Figure S1.**  $^1\text{H}$  NMR spectrum of **2CN-TPP-TPA** in DMSO.



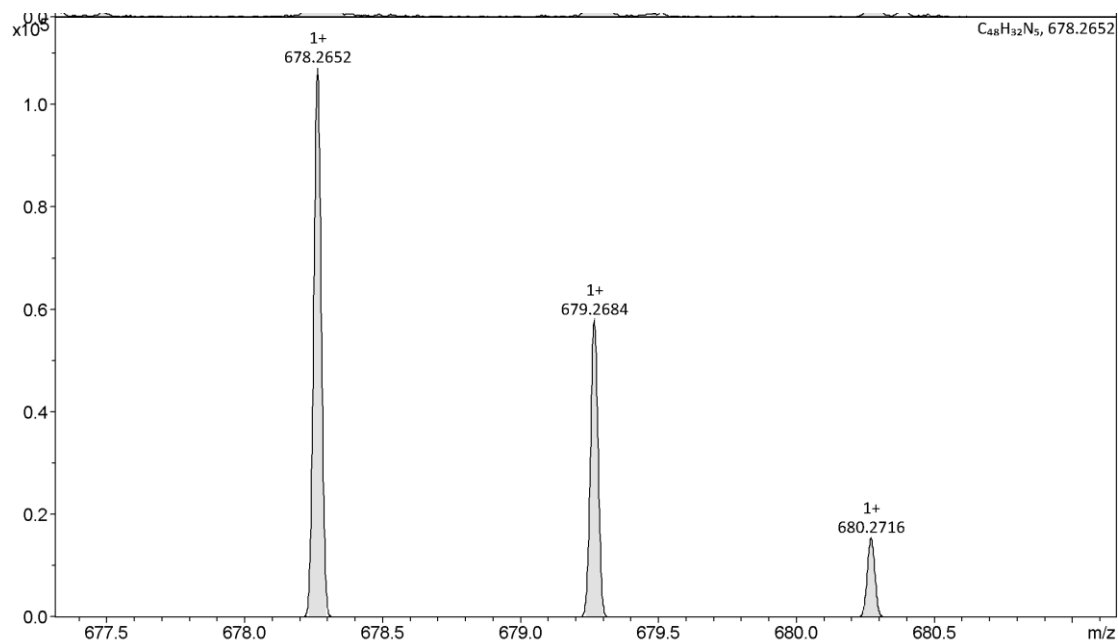
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **2CN-TPP-TPA** in DMSO.



**Figure S3.**  $^1\text{H}$  NMR spectrum of **PhCN-TPP-TPA** in DMSO.

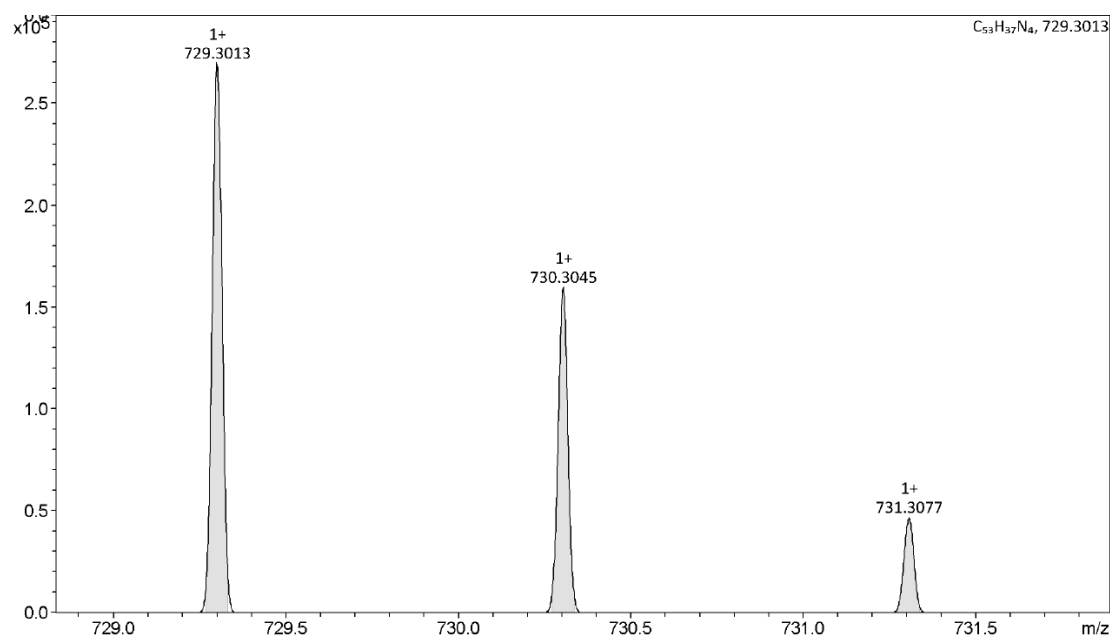


**Figure S4.**  $^{13}\text{C}$  NMR spectrum of **PhCN-TPP-TPA** in DMSO.

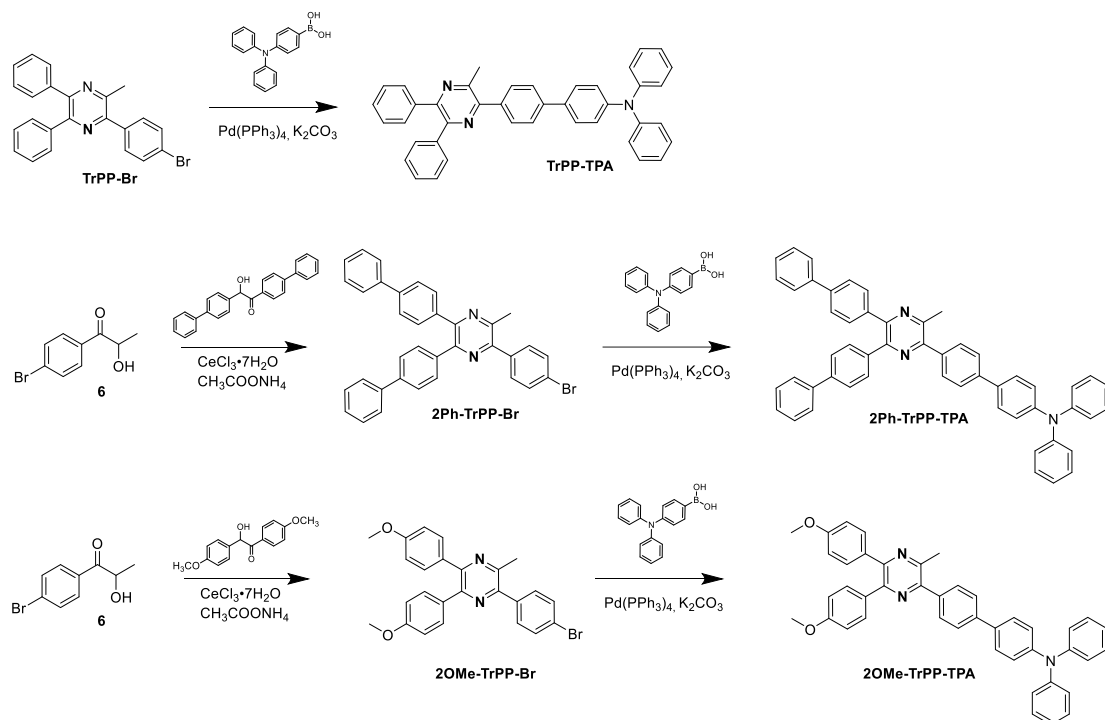


**Figure S5.** HRMS spectrum of **2CN-TPP-TPA**.





**Figure S6.** HRMS spectrum of **PhCN-TPP-TPA**.



**Scheme S2.** The synthetic route of **TrPP-TPA**, **2Ph-TrPP-TPA**, **2OMe-TrPP-TPA**. The intermediate **6** and **TrPP-Br** are prepared according to the previous literature.<sup>1,2</sup>

**Synthesis of TrPP-TPA:** 4-(diphenylamino) phenylboronic acid (0.86 g, 3 mmol), TrPP-Br (0.8 g, 2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.1 mmol), K<sub>2</sub>CO<sub>3</sub> (0.8 g, 6 mmol) were added into 250 mL two-necked, round-bottomed flask under nitrogen. Then 40 mL tetrahydrofuran (THF) and 10 mL distilled water were injected into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The

organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow solid was obtained in 70.5 % yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 4H), 7.29 (dd, *J* = 18.5, 7.7 Hz, 10H), 7.13 (t, *J* = 7.0 Hz, 6H), 7.05 (t, *J* = 7.2 Hz, 2H), 2.75 (s, 3H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 150.58, 149.54, 149.21, 148.66, 148.01, 141.21, 139.37, 139.23, 137.43, 134.50, 130.17, 130.13, 130.11, 129.70, 128.74, 128.63, 128.49, 128.45, 128.11, 126.76, 124.94, 124.06, 123.51, 23.11. HRMS (MALDI-TOF): *m/z* [M<sup>+</sup>] calcd. For C<sub>41</sub>H<sub>31</sub>N<sub>3</sub>; 565.2518. found, [M+1] 566.2591.

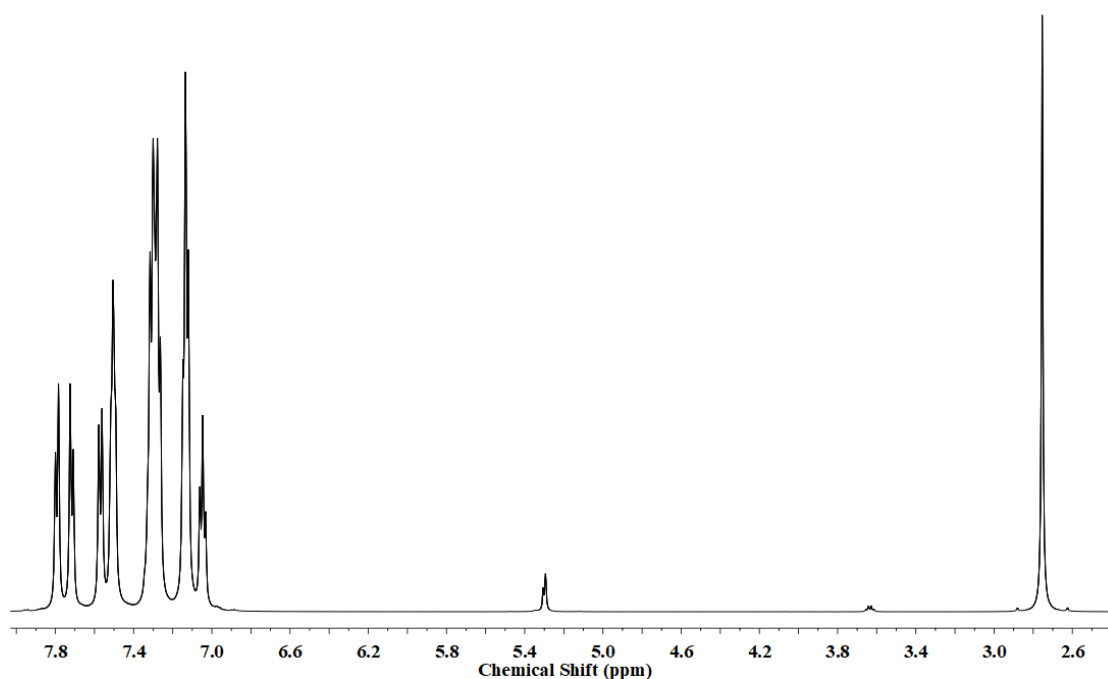
**Synthesis of 2Ph-TrPP-Br:** compound 6 (2.2 g, 10 mmol), 2-hydroxy-1,2-bis(4-phenylphenyl)ethan-1-one (3.6 g, 10 mmol), ammonium acetate (1.4 g, 20 mmol), Cerium(III) chloride heptahydrate (0.18 g, 0.5 mmol) were added into 250 ml single-necked, round-bottomed flask. Then 30ml ethanol were added into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:1 by volume) as eluent. Yellow solid was obtained in 32.3 % yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69–7.53 (m, 16H), 7.38–7.31 (td, *J* = 7.5, 4.0 Hz, 4H), 7.34 (td, *J* = 7.3, 4.4 Hz, 2H), 2.76 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.85, 149.17, 149.01, 148.80, 148.19, 141.64, 141.52, 141.47, 140.90, 140.89, 138.48, 138.22, 137.55, 134.67, 130.84, 130.82, 130.32, 129.89, 129.40, 129.39, 128.30, 128.15, 128.12, 127.52, 127.37, 127.34, 126.97, 125.14, 124.23, 123.70, 23.26. HRMS (MALDI-TOF): *m/z* [M<sup>+</sup>] calcd. For C<sub>35</sub>H<sub>25</sub>BrN<sub>2</sub>; 552.1201. found, [M+1] 553.1274.

**Synthesis of 2Ph-TrPP-TPA:** 4-(diphenylamino) phenylboronic acid (0.86 g, 3 mmol), 2Ph-TrPP-Br (1.1 g, 2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.1 mmol), K<sub>2</sub>CO<sub>3</sub> (0.8 g, 6 mmol) were added into 250 mL two-necked, round-bottomed flask under nitrogen. Then 40 mL tetrahydrofuran (THF) and 10 mL distilled water were injected into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow solid was obtained in 70.5 % yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.84–7.75 (m, 4H), 7.68–7.58 (m, 14H), 7.45 (dd, *J* = 13.1, 7.4 Hz, 4H), 7.39–7.26 (m, 6H), 7.15 (t, *J* = 7.7 Hz, 6H), 7.07 (t, *J* = 6.9 Hz, 2H), 2.80 (s, 3H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 151.59, 149.91, 149.75, 149.54, 148.93, 142.38, 142.26, 142.21, 141.64, 141.63, 139.22, 138.96, 138.29, 135.41, 131.57, 131.56, 131.06, 130.63, 130.14, 130.12, 129.04, 128.89, 128.85, 128.26, 128.10, 128.08, 127.71, 125.88, 124.97, 124.44, 24.00. HRMS (MALDI-TOF): *m/z* [M<sup>+</sup>] calcd. For C<sub>53</sub>H<sub>39</sub>N<sub>3</sub>; 717.3144. found, [M+1] 718.3217.

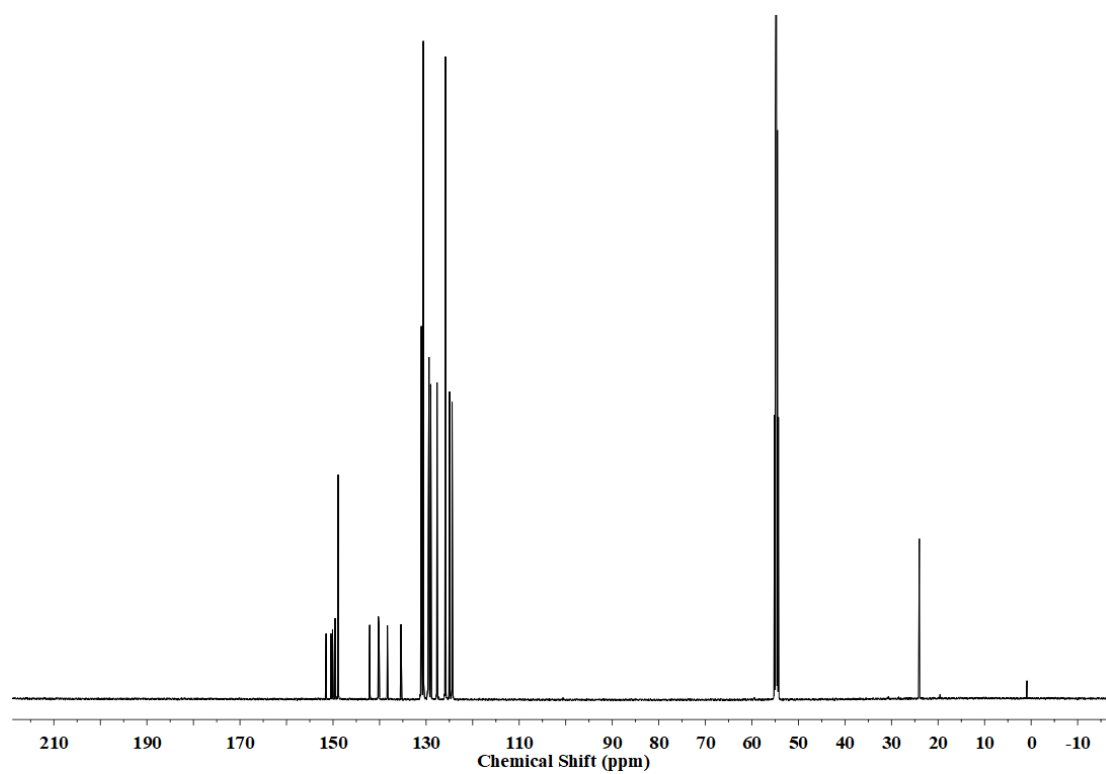
**Synthesis of 2OMe-TrPP-Br:** compound 6 (2.2 g, 10 mmol), anisoin (2.8 g, 10 mmol), ammonium acetate (1.4 g, 20 mmol), Cerium(III) chloride heptahydrate (0.18 g, 0.5 mmol) were added into 250 ml single-necked, round-bottomed flask. Then 20 ml ethanol were added into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over MgSO<sub>4</sub> and concentrated. Finally the crude product was purified by a silica-gel column with

DCM/hexane (1:1 by volume) as eluent. Yellow solid was obtained in 31.2 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54–7.33 (m, 8H), 6.73 (dd,  $J = 11.7, 8.7$  Hz, 4H), 3.70 (d,  $J = 5.7$  Hz, 6H), 2.59 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.87, 158.73, 147.98, 147.62, 147.26, 146.21, 136.62, 130.44, 130.11, 130.09, 129.96, 129.91, 129.87, 121.87, 112.75, 112.60, 54.21, 54.18, 21.74. HRMS (MALDI-TOF):  $m/z$  [ $\text{M}^+$ ] calcd. For  $\text{C}_{25}\text{H}_{21}\text{BrN}_2\text{O}_2$ ; 460.0786. found, [ $\text{M}+1$ ] 461.0859.

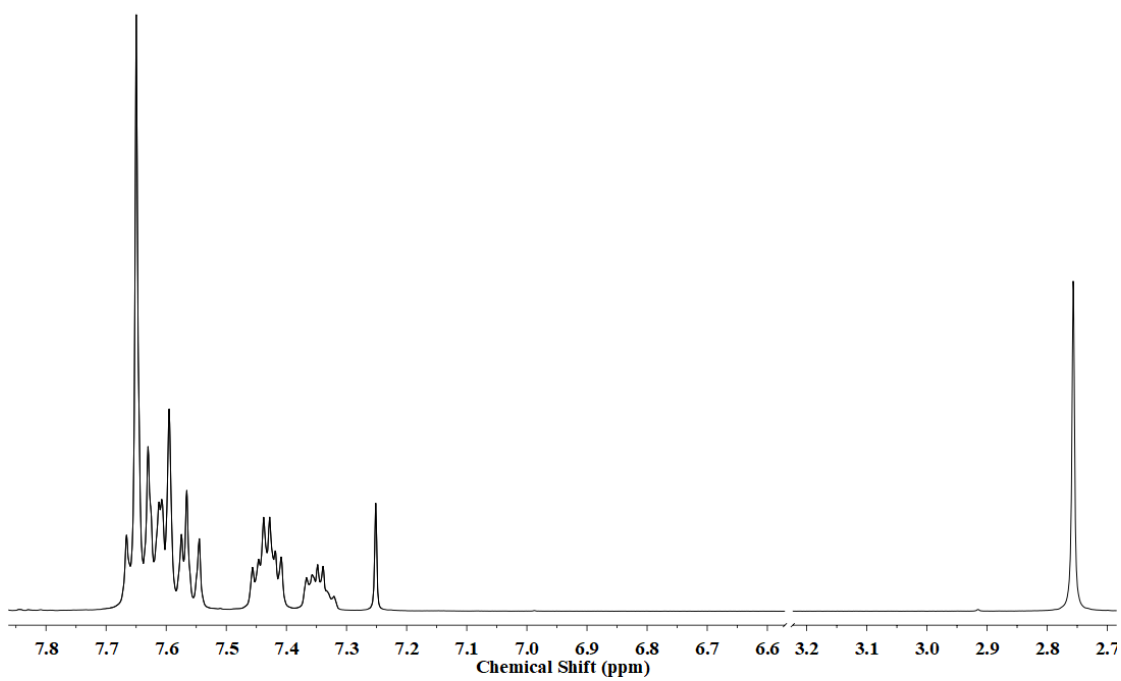
**Synthesis of 2OMe-TrPP-TPA:** 4-(diphenylamino) phenylboronic acid (0.86 g, 3 mmol), 2OMe-TrPP-Br (0.92 g, 2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.12 g, 0.1 mmol),  $\text{K}_2\text{CO}_3$  (0.8 g, 6 mmol) were added into 250 mL two-necked, round-bottomed flask under nitrogen. Then 40 mL tetrahydrofuran (THF) and 10 mL distilled water were injected into the flask. The mixtures were refluxed for 24 h at 80 °C. After it was cooled to room temperature, concentrated and added dichloromethane (DCM). The mixture was washed with water three times. The organic phase was dried over  $\text{MgSO}_4$  and concentrated. Finally, the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow solid was obtained in 69.5 % yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.79–7.69 (m, 4H), 7.59–7.54 (m, 2H), 7.49–7.42 (m, 4H), 7.31–7.25 (m, 4H), 7.17–7.09 (m, 6H), 7.07–7.03 (m, 2H), 6.88–6.79 (m, 4H), 3.80 (d,  $J = 6.2$  Hz, 6H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  160.31, 160.21, 149.88, 148.87, 148.53, 148.03, 147.98, 147.84, 141.06, 137.66, 134.58, 131.91, 131.69, 131.39, 130.08, 129.71, 128.10, 126.73, 124.94, 124.09, 123.51, 113.94, 113.91, 55.64, 55.63, 23.01. HRMS (MALDI-TOF):  $m/z$  [ $\text{M}^+$ ] calcd. For  $\text{C}_{43}\text{H}_{35}\text{N}_3\text{O}_2$ ; 625.2729. found, [ $\text{M}+1$ ] 625.2678.



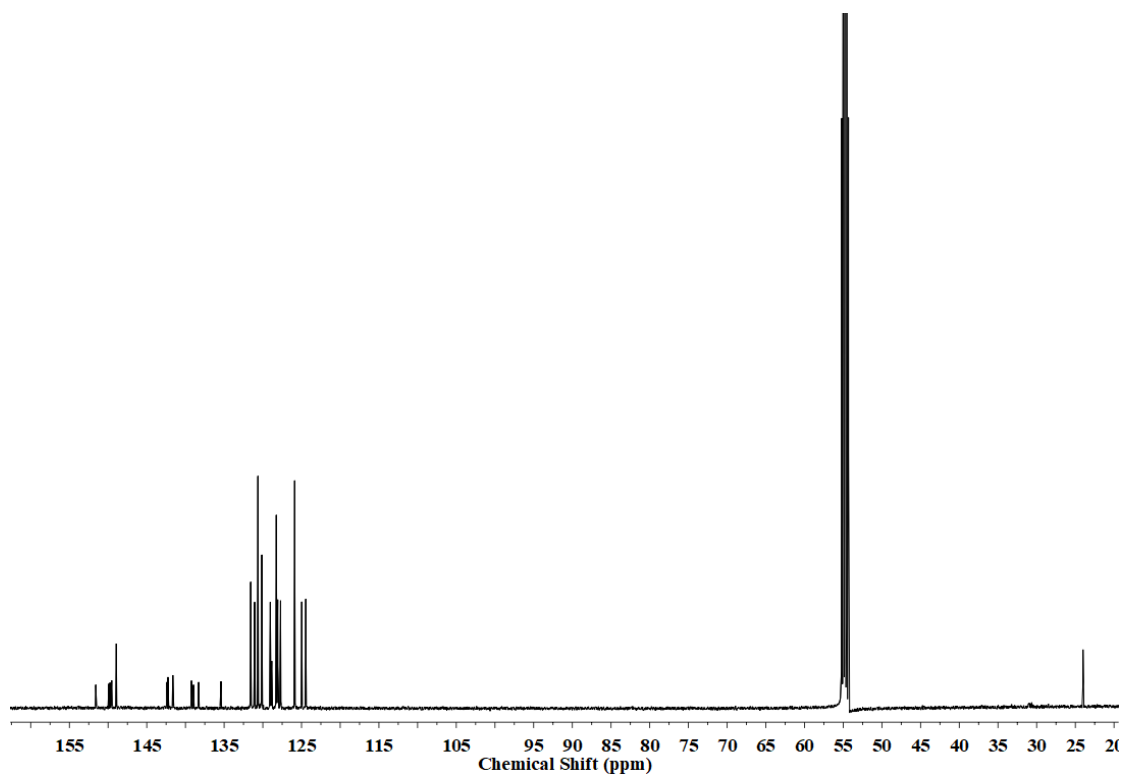
**Figure S7.**  $^1\text{H}$  NMR spectrum of TrPP-TPA.



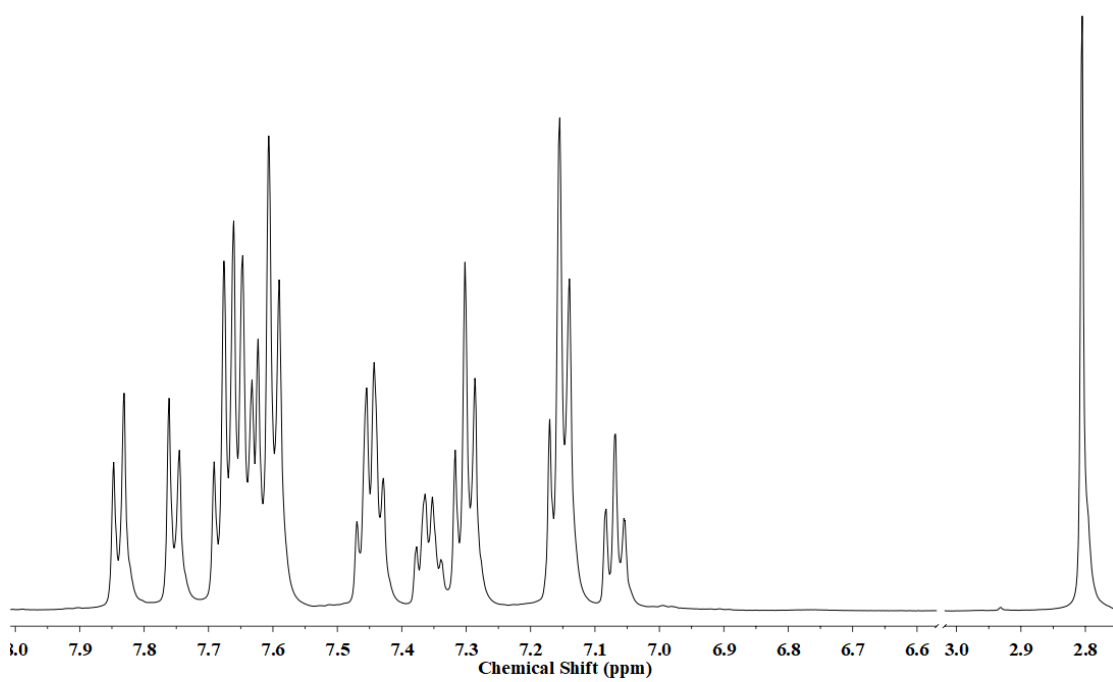
**Figure S8.**  $^{13}\text{C}$  NMR spectrum of TrPP-TPA.



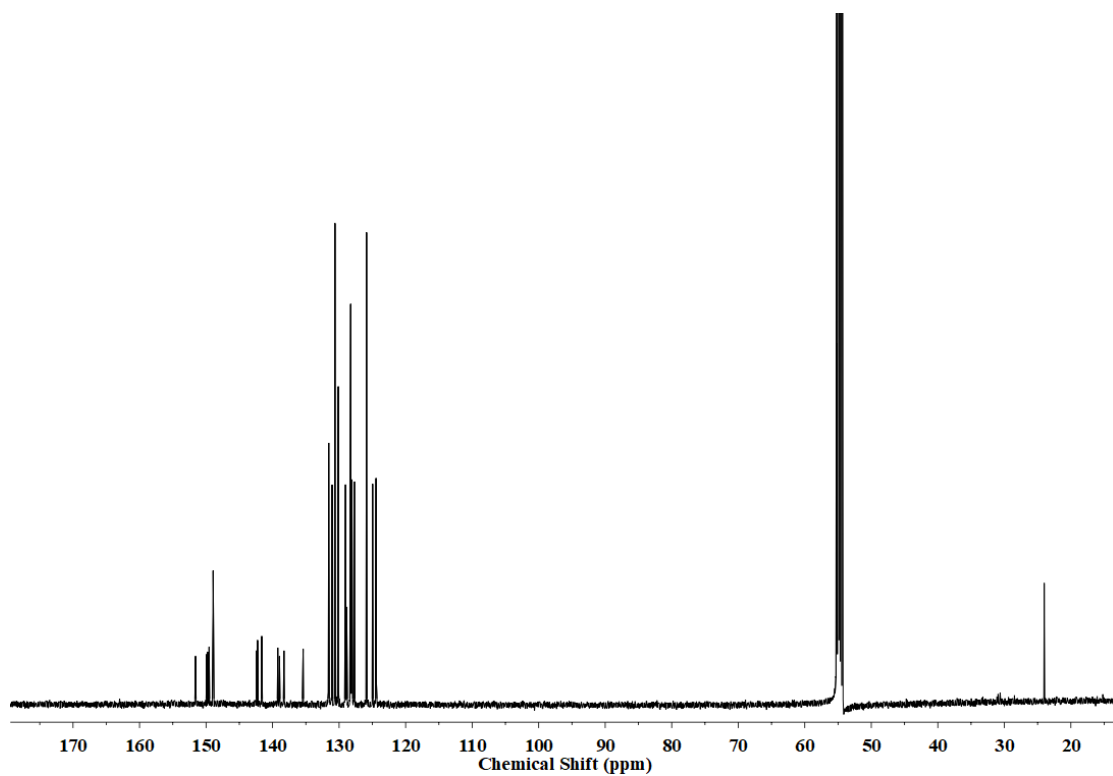
**Figure S9.**  $^1\text{H}$  NMR spectrum of 2Ph-TrPP-Br.



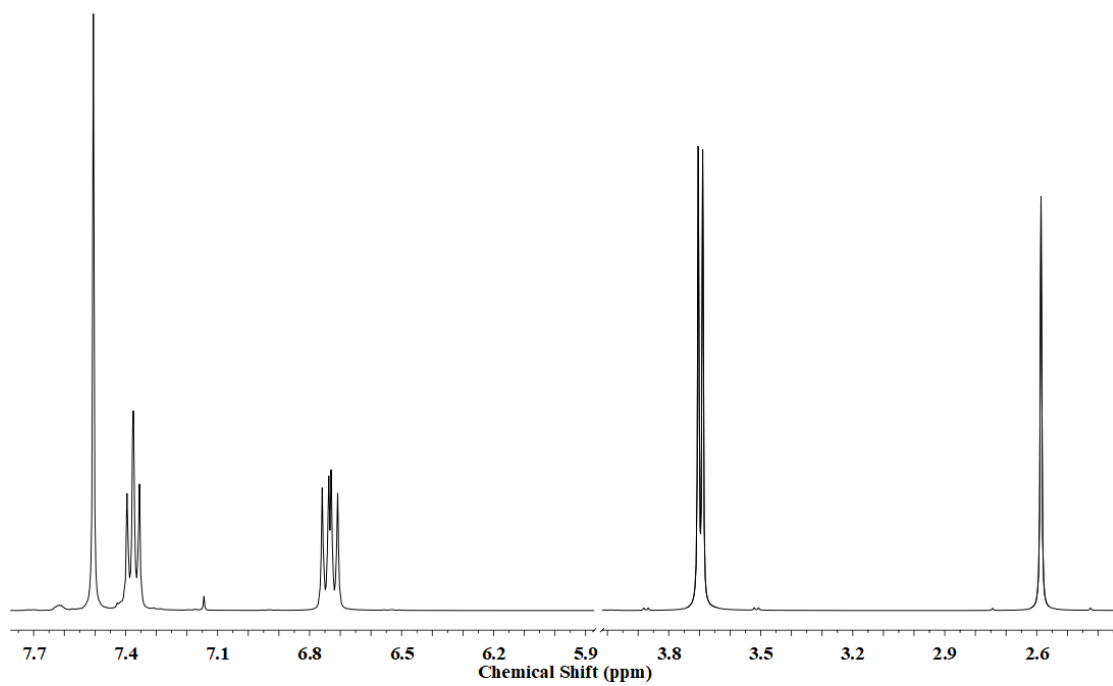
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of 2Ph-TrPP-Br.



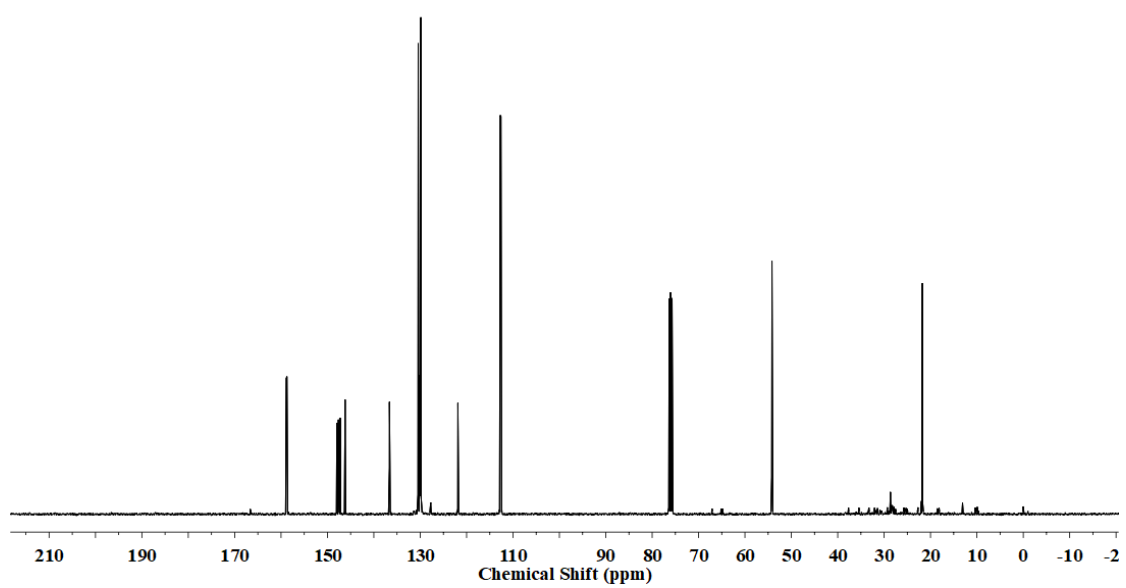
**Figure S11.**  $^1\text{H}$  NMR spectrum of 2Ph-TrPP-TPA.



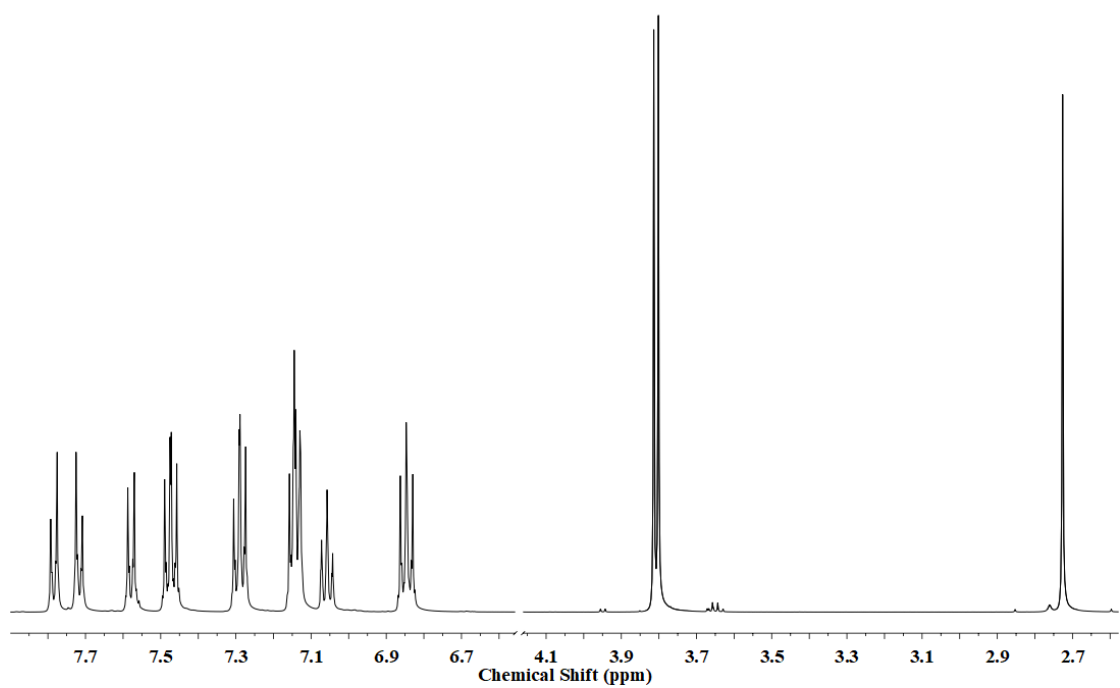
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of 2Ph-TrPP-TPA.



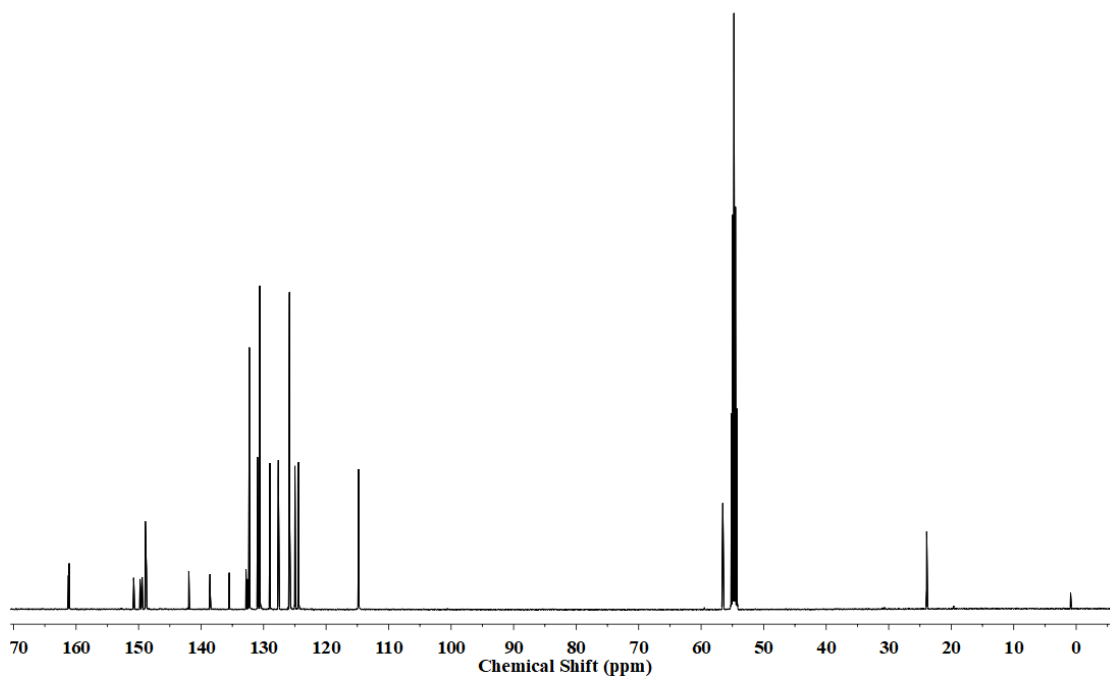
**Figure S13.**  $^1\text{H}$  NMR spectrum of 2OMe-TrPP-Br.



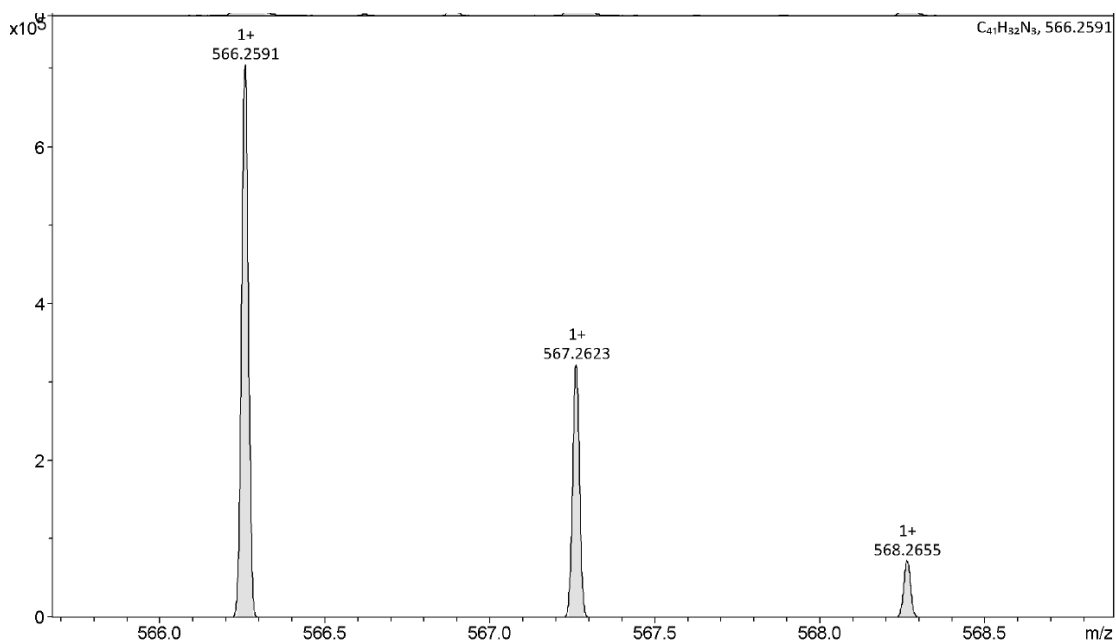
**Figure S14.**  $^{13}\text{C}$  NMR spectrum of 2OMe-TrPP-Br.



**Figure S15.**  $^1\text{H}$  NMR spectrum of 2OMe-TrPP-TPA.

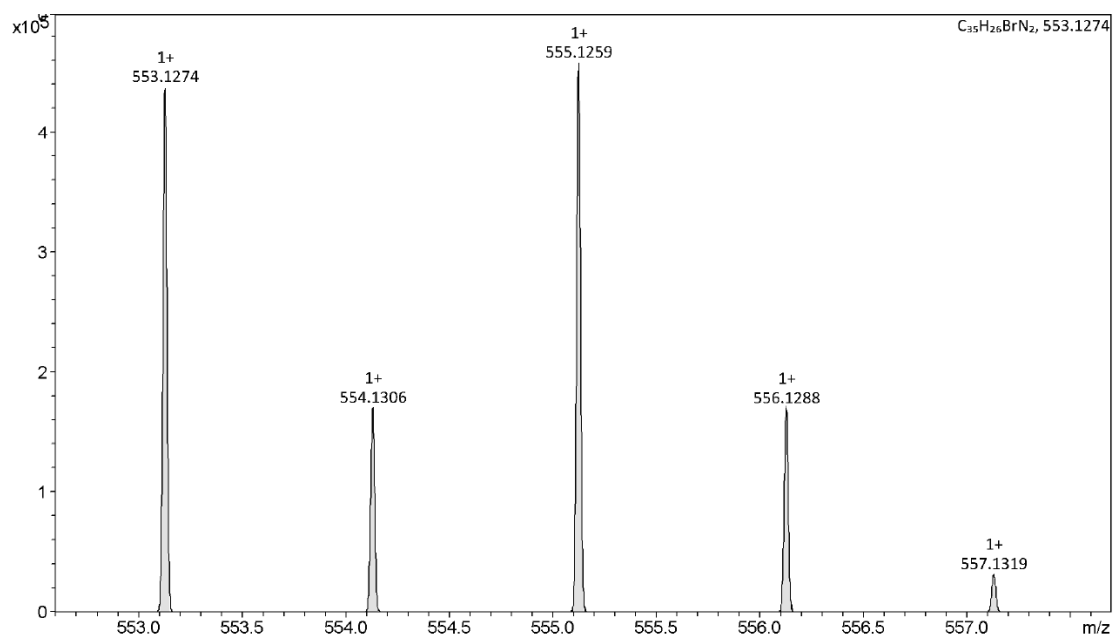


**Figure S16.**  $^{13}\text{C}$  NMR spectrum of 2OMe-TrPP-TPA.

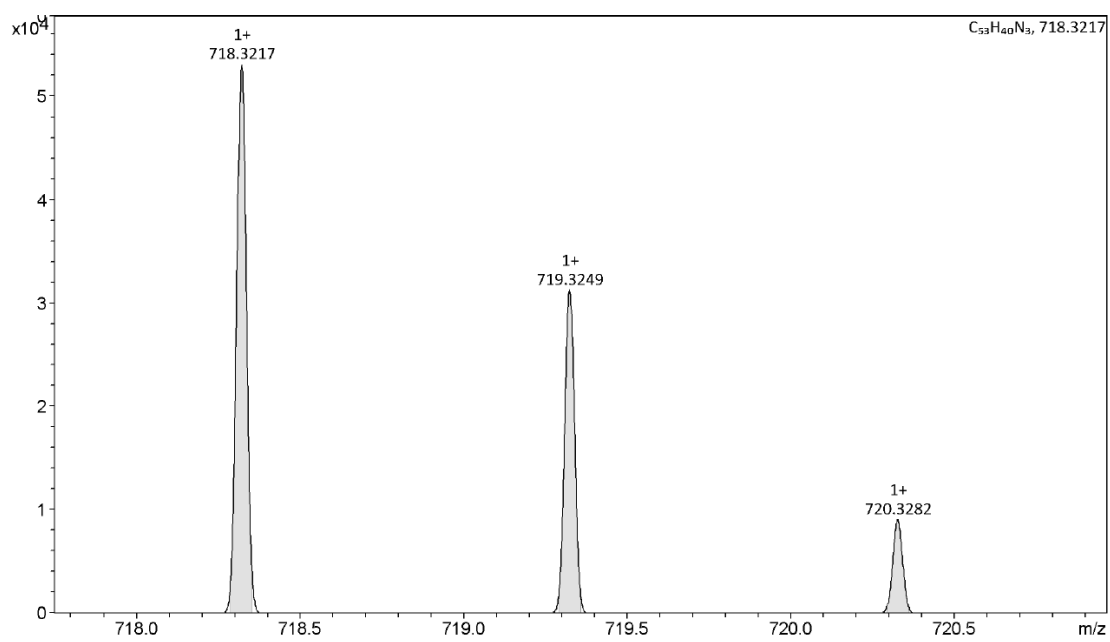


**Figure S17.** HRMS spectrum of TrPP-TPA.

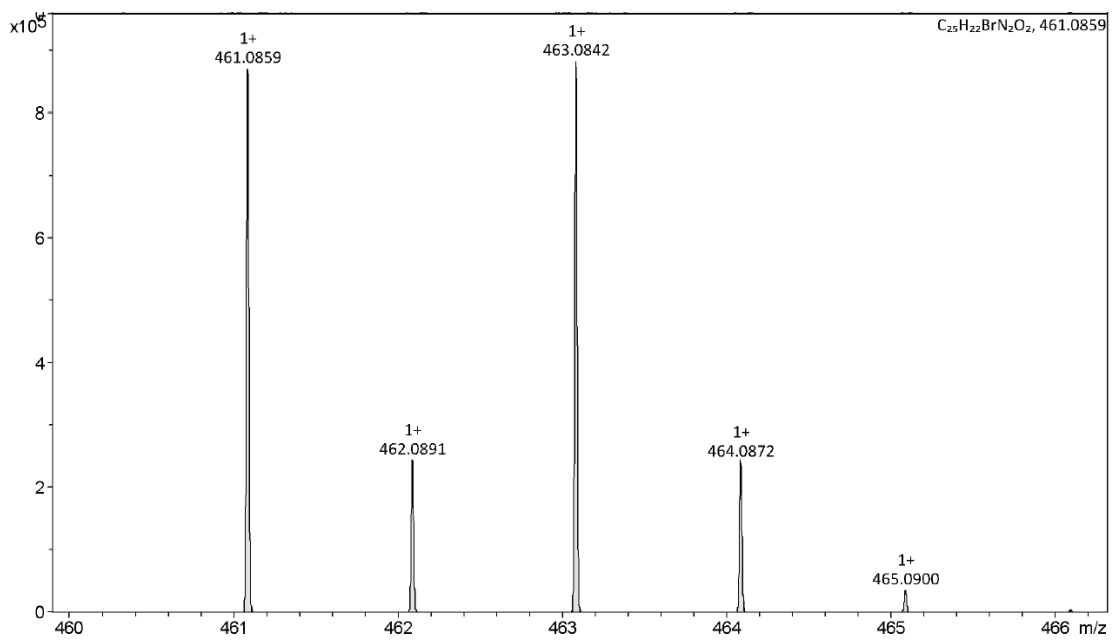




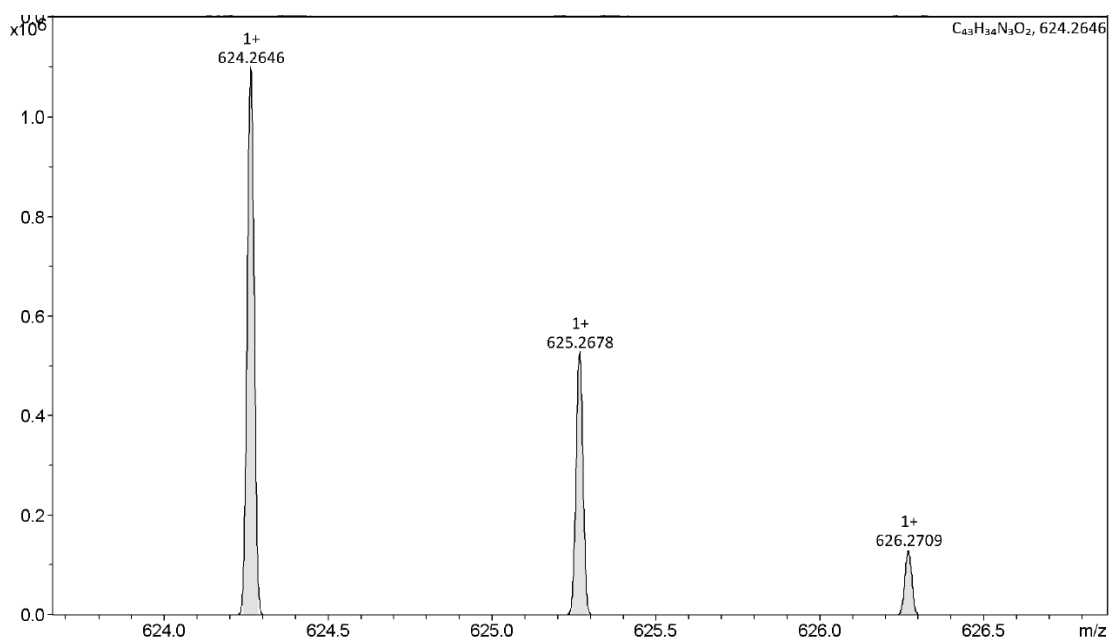
**Figure S18.** HRMS spectrum of 2Ph-TrPP-Br.



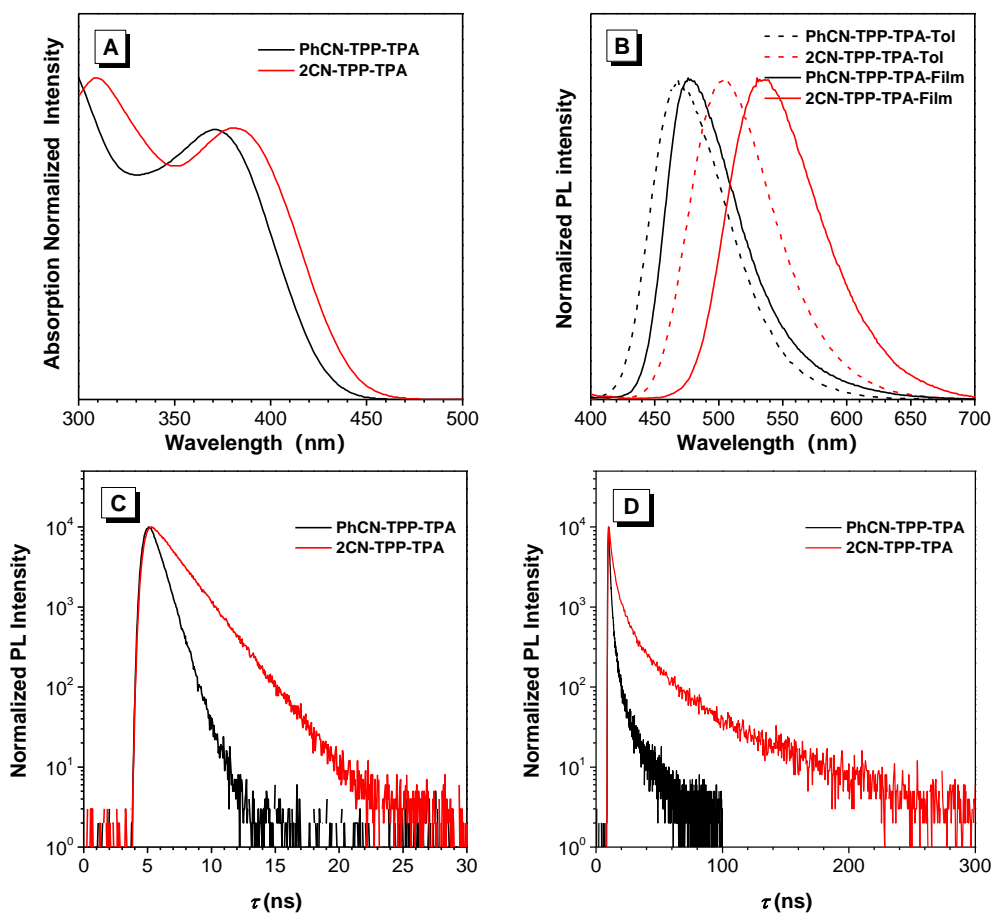
**Figure S19.** HRMS spectrum of 2Ph-TrPP-TPA.



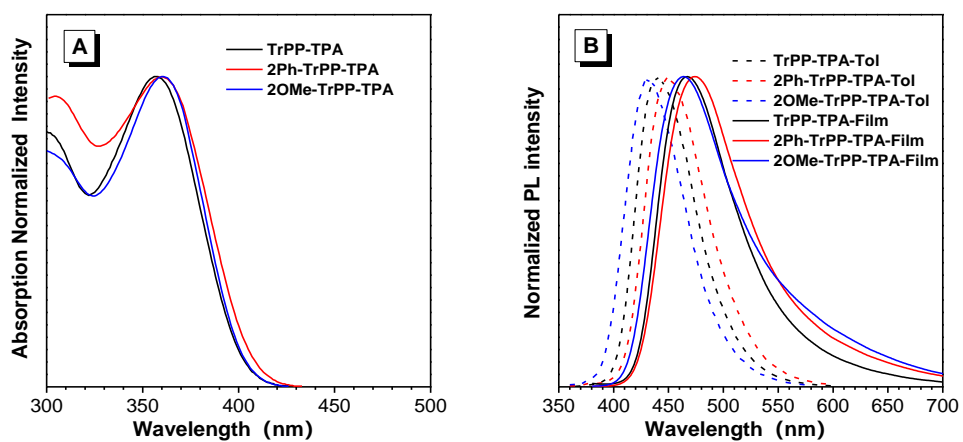
**Figure S20.** HRMS spectrum of 2OMe-TrPP-Br.

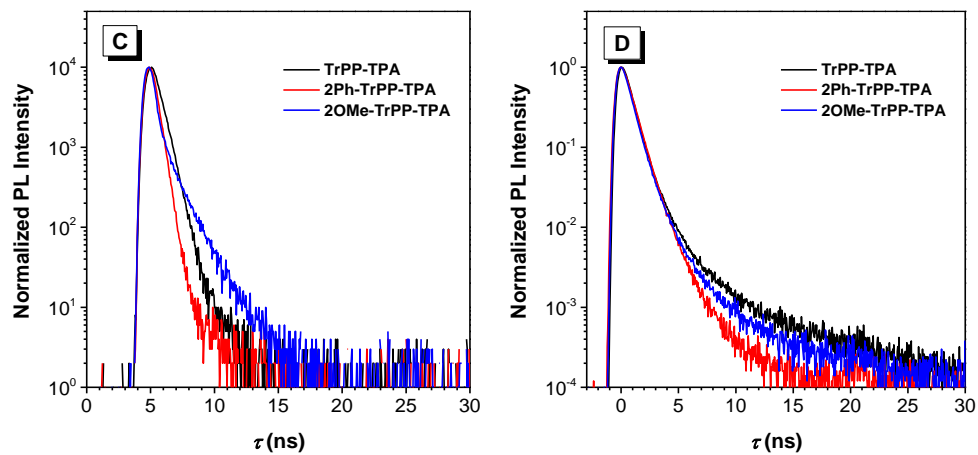


**Figure S21.** HRMS spectrum of 2OMe-TrPP-TPA.

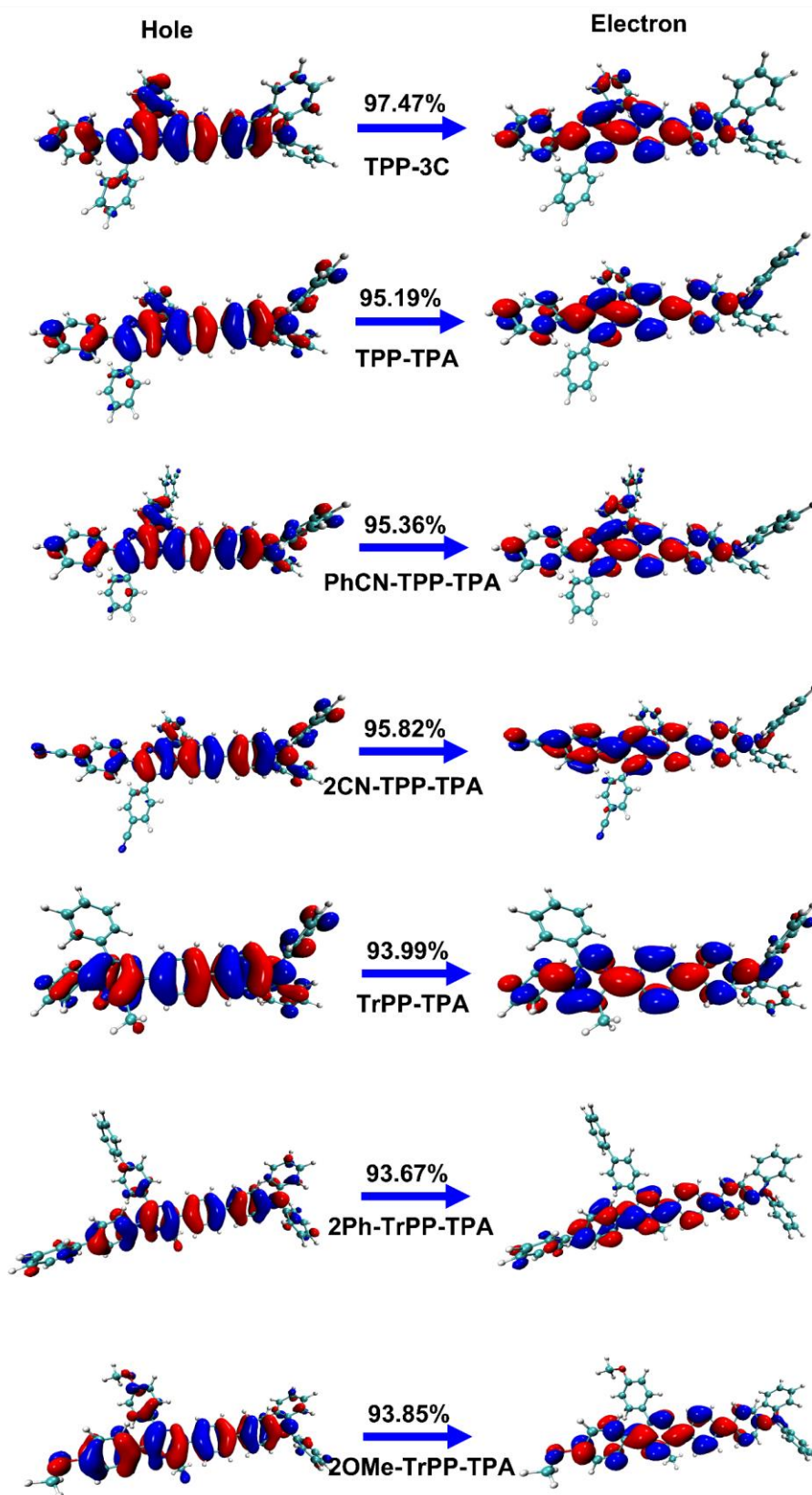


**Figure S22.** Absorption spectra (A), and PL spectra (B) of PhCN-TPP-TPA and 2CN-TPP-TPA; Time-resolved fluorescence spectra of PhCN-TPP-TPA and 2CN-TPP-TPA (C) in toluene solution (D) in film.





**Figure S23.** Absorption spectra (A), and PL spectra (B) of TrPP derivatives; Time-resolved fluorescence spectra of TrPP derivatives (C) in toluene solution (D) in film.



**Figure S24.** Natural transition orbitals of TPP-3C, TPP-TPA, PhCN-TPP-TPA, 2CN-TPP-TPA, TrPP-TPA, 2Ph-TrPP-TPA, 2OMe-TrPP-TPA in the S<sub>1</sub> states.

**Table S1.** The energy of the frontier orbitals of TPP, 3C, TPA, **TPP-3C**, **TPP-TPA** in  $S_1$  by M062X/6-31G (d,p).

Molecule	HOMO (eV)	LUMO (eV)	HOMO→LUMO <sup>a</sup>
TPP	-6.29	-1.50	97.4 %
3C	-6.58	-0.17	91.1 %
TPA	-5.98	0.14	96.6 %
TPP-3C	-6.19	-1.69	91.4 %
TPP-TPA	-5.94	-1.46	83.2 %

<sup>a</sup>The ratio of main electron configurations.

**Table. S2.** Hole-electron distribution ratios of **TPP-3C** and **TPP-TPA** on different fragments.

Molecule	Fragment	Hole (%)	Electron (%)	Overlap (%)
TPP-3C	TPP	83.76	88.30	86.00
	3C	16.24	11.70	13.79
TPP-TPA	TPP	64.23	82.20	72.66
	TPA	35.77	17.80	25.23

**Table. S3.** The energy of the frontier orbitals of PhCN-TPP, **2CN-TPP**, **2CN-TPP-TPA**, and **PhCN-TPP-TPA** in  $S_1$  by M062X/6-31G (d,p).

Molecule	HOMO (eV)	LUMO (eV)	HOMO→LUMO <sup>a</sup>
PhCN-TPP	-6.41	-1.82	95.2 %
2CN-TPP	-6.77	-2.16	95.2 %
PhCN-TPP-TPA	-5.99	-1.61	78.6 %
2CN-TPP-TPA	-6.09	-1.94	74.4 %

<sup>a</sup> the ratio of main electron configurations.

**Table. S4.** Hole-electron distribution ratios of **TPP-TPA**, and **PhCN-TPP-TPA** and **2CN-TPP-TPA** on different fragments.

Molecule	Fragment	Hole (%)	Electron (%)	Overlap (%)
TPP-TPA	TPP	64.23	82.20	72.66
	TPA	35.77	17.80	25.23
PhCN-TPP-TPA	PhCN	1.25	2.70	1.84
	TPP	64.84	82.19	73.00
	TPA	33.91	15.10	22.64
2CN-TPP-TPA	2CN	0.61	2.04	1.11
	TPP	57.91	84.23	69.84
	TPA	41.49	13.73	23.86

**Table S5.** The energy of the frontier orbitals of TrPP, 2Ph-TrPP, 2OMe-TrPP, TrPP-TPA, 2Ph-TrPP-TPA, and 2OMe-TrPP-TPA in S<sub>1</sub> by M062X/6-31G (d,p).

Molecule	HOMO (eV)	LUMO (eV)	HOMO→LUMO <sup>a</sup>
TrPP	-6.35	-1.50	95.2
2Ph-TrPP	-6.26	-1.58	96.3
2OMe-TrPP	-6.04	-1.23	96.6
TrPP-TPA	-5.97	-1.32	81.9
2Ph-TrPP-TPA	-5.99	-1.49	72.0
2OMe-TrPP-TPA	-5.92	-1.27	81.6

<sup>a</sup> the ratio of main electron configurations.

**Table. S6.** Hole-electron distribution ratio of TrPP derivatives on different fragments.

Molecule	Fragment	Hole (%)	Electron (%)	Overlap (%)
TrPP-TPA	TrPP	48.74	71.79	59.15
	TPA	51.26	28.21	38.03
2Ph-TrPP-TPA	2Ph	3.36	3.27	3.31
	TrPP	69.07	83.80	76.08
	TPA	27.57	12.93	18.88
2OMe-TrPP-TPA	2OMe	2.45	0.94	1.52
	TrPP	71.91	84.36	77.89
	TPA	25.64	14.70	19.41

## References

- 1 Y. F. Liang, K. Wu, S. Song, X. Li, X. Huang and N. Jiao, *Org. Lett.*, 2015, **17**, 876–879.
- 2 H. Wu, J. Zeng, Z. Xu, B. Zhang, H. Zhang, Y. Pan, Z. Wang, D. Ma, A. Qin and B. Z. Tang, *J. Mater. Chem. C*, 2019, **7**, 13047–13051.