Electronic Supplementary Information

Fabrication of efficient and red-emissive salicylaldehyde Schiff base isomers toward multi-scenario information decryption

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Contents

Experimental Section

Materials and instrumentations

All the organic solvents are purchased and used without additional purifications unless specifically emphasized. Midbody A-*o*-TPA and A-*p*-TPA mentioned in Scheme 1 of manuscript are synthesized according to the methods previously reported in the literatures, respectively.[1-2] 4-(Diphenylamino) phenylboronic acid (Aladdin, 98%), 3-bromosalicylaldehyde (Aladdin, 98%), 5-bromosalicylaldehyde (Aladdin, 98%), 2-bromoaniline (Aladdin, 97%), 4-bromoaniline (Energy Chemical, 98%), tetrakis (triphenylphosphine) palladium (Energy Chemical, 99%), chloroform-d_3 ($CDCl_3$) (Energy Chemical, 99.8%), trifluoroacetic acid (TFA) (Energy Chemical, 99%), and triethylamine (TEA) (Sinopharm Chemical Reagent Co., Ltd., 99.0%) are purchased and used directly without further purification. Nuclear magnetic resonance (NMR) spectra are measured using a Bruker AVANCE-III-600 spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz) with $CDCl_3$-d_3 as solvent unless otherwise stated. High-resolution mass spectrometry (HRMS) is recorded using the Q Exactive (Thermo Scientific, Germany) Mass spectrometer and the Xevo G2-XS Q-Tof Mass spectrometer. Ultraviolet-visible (UV–Vis) absorption spectra are performed using a Shimadzu UV-2450 spectrometer. UV–Vis diffuse reflectance (UV-DRS) spectra are collected with a PE Lambda 950 UV Vis-NIR spectrometer. Photoluminescence (PL) spectra are acquired utilizing a Horiba Fluoromax-4 spectrofluorometer. The absolute fluorescence quantum yields (QY) are determined on a Horiba Fluoromax-4 spectrometer by a Quanta-ϕ integrating sphere. Single crystal data of *o*,*p*-2TPA (CCDC = 2343783) was selected and mounted on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Cu Kα radiation (λ = 1.54184 Å). The ground-state geometries and corresponding frontier molecular orbitals were calculated using the density functional theory (DFT) method at the CAM-B3LYP/6-31G(d,p) level. The excited-state geometries and hole-electron analysis were calculated using the time-dependent DFT method at the same level of theory. Analytical frequency calculations were also carried out at the same level of theory to confirm the local minimum point of the optimized structures. The above calculations were performed using the Gaussian 16 program, and the orbitals were visualized using the

IQmol program.

Synthetic procedures

***o*,*p*-2TPA:** 5-Bromosalicylaldehyde (232 mg, 1.16 mmol), 4-(diphenylamino) phenylboronic acid (335 mg, 1.16 mmol), tetrakis (triphenylphosphine) palladium (33 mg, 0.03 mmol), and 1 mL of saturated K_2CO_3 are added rapidly to 2 mL toluene solution under N_2 protection. After 6 h of stirring at 115 °C, the reaction mixture is extracted with CH_2Cl_2/H_2O and then purified by silica gel column chromatography using eluents of petroleum ether/ethyl acetate (volume ratio: 20/1). Then, the yellow intermediate of SA-*p*-TPA is obtained with a yield of 55%. SA-*p*-TPA (110 mg, 0.30 mmol) is slowly added to a vigorously stirred solution of A-*o*-TPA (101 mg, 0.30 mmol) in 25 mL of EtOH. The reaction mixture is refluxed at 80 °C for 3 h and cooled to room temperature afterward. The compound can be obtained by filtration, and the yield is about 73%. Melting point (m. p.): 242.6-243.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$-d_3): δ 12.73 (s, 1H), 8.70 (s, 1H), 7.61-7.56 (m, 2H), 7.50-7.41 (m, 4H), 7.37 (t, J = 7.4 Hz, 1H), 7.31-7.27 (m, 11H), 7.21-7.12 (m, 12H), 7.08-7.01 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$-d_3): δ 162.62, 160.37, 147.85, 147.83, 147.17, 146.97, 146.36, 136.91, 134.42, 131.58, 130.63, 130.53, 130.16, 129.41, 129.34, 128.41, 127.35, 127.18, 124.56, 124.46, 124.29, 123.49, 123.02, 122.93, 119.60, 118.69, 117.80. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{49}H_{38}N_3O$: 684.3009; found: 684.2990.

***p*,*p*-2TPA:** SA-*p*-TPA (110 mg, 0.30 mmol) is slowly added to a vigorously stirred solution of A-*p*-TPA (102 mg, 0.30 mmol) in 25 mL of EtOH. The reaction mixture is refluxed at 80 °C for 3 h and cooled to room temperature afterward. The obtained precipitates were then used for recrystallization in an EtOH/CH_2Cl_2 (1:1, *v*/*v*) solution, producing plenty of red solids, and the yield is around 65%. Melting point (m. p.): 236.3-236.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$-d_3): δ 13.32 (s, 1H), 8.75 (s, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.35-7.26 (m, 8H), 7.19-7.09 (m, 13H), 7.07-7.01 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$-d_3): δ 162.13, 147.86, 147.76, 139.56, 134.39,

132.08, 131.64, 130.19, 129.46, 129.43, 127.73, 127.68, 127.36, 124.69, 124.49, 124.32, 123.93, 123.23, 123.04, 121.79, 119.54, 117.86. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{49}H_{38}N_3O$: 684.3009; found: 684.3015.

***o*,*o*-2TPA:** 4-(Diphenylamino) phenylboronic acid (335 mg, 1.16 mmol), 3-bromosalicylaldehyde (232 mg, 1.16 mmol), tetrakis (triphenylphosphine) palladium (33 mg, 0.03 mmol), and 1 mL of saturated K_2CO_3 are added rapidly to a 2 mL solution of toluene. All feeding and reaction processes are carried out under the N_2 atmosphere. After stirring at 115 °C for 6 h, the reaction mixture is extracted with CH_2Cl_2/H_2O and then purified by silica gel column chromatography using eluents of petroleum ether/Dichloromethane (volume ratio: 10/1). Then, the yellow intermediate of SA-*o*-TPA is obtained with a yield of 55%. SA-*o*-TPA (111 mg, 0.30 mmol) is slowly added to a vigorously stirred solution of A-*o*-TPA (102 mg, 0.30 mmol) in 25 mL of EtOH. The reaction mixture is refluxed at 80 °C for 3 h and cooled to room temperature afterward. The reaction product can be obtained by filtration, and the yield is about 73%. Melting point (m. p.): 249.8-250.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$-d_3): δ 13.32 (s, 1H), 8.67 (s, 1H), 7.54 (d, J = 8.6 Hz, 2H), 7.47-7.45 (m, 2H), 7.41 (t, J = 6.9 Hz, 1H), 7.34 (t, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 6H), 7.16-7.06 (m, 17H), 7.04-6.98 (m, 3H), 6.92 (t, J = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$-d_3): δ 163.17, 147.79, 133.94, 130.66, 130.15, 129.38, 129.35, 128.37, 127.1, 124.75, 124.61, 123.23, 123.15, 123.00, 122.97, 119.05. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{49}H_{38}N_3O$: 684.3009; found: 684.3015.

***p*,*o*-2TPA:** SA-*o*-TPA (111 mg, 0.30 mmol) is slowly added to a vigorously stirred solution of A-*p*-TPA (102 mg, 0.30 mmol) in 25 mL of EtOH. The reaction mixture is refluxed at 80 °C for 3 h and cooled to room temperature afterward. The compound can be directly obtained by filtration, and the yield is around 73%. Melting point (m. p.): 125.6-126.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$-d_3): δ 14.14 (s, 1H), 8.76 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.50 (t, J = 8.4 Hz, 3H), 7.40-7.36 (m, 3H), 7.29 (s, 6H), 7.19-7.14 (m, 13H), 7.08-7.00 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$-d_3): δ 162.16, 158.68, 147.90, 147.73, 147.02, 146.70, 139.64, 134.12, 133.94, 131.72,

131.47, 130.22, 129.73, 129.45, 129.37, 127.71, 127.68, 124.67, 124.60, 123.89, 123.51, 123.21, 122.95, 121.75, 119.56, 119.25. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{49}H_{38}N_3O$: 684.3009; found: 684.2969.

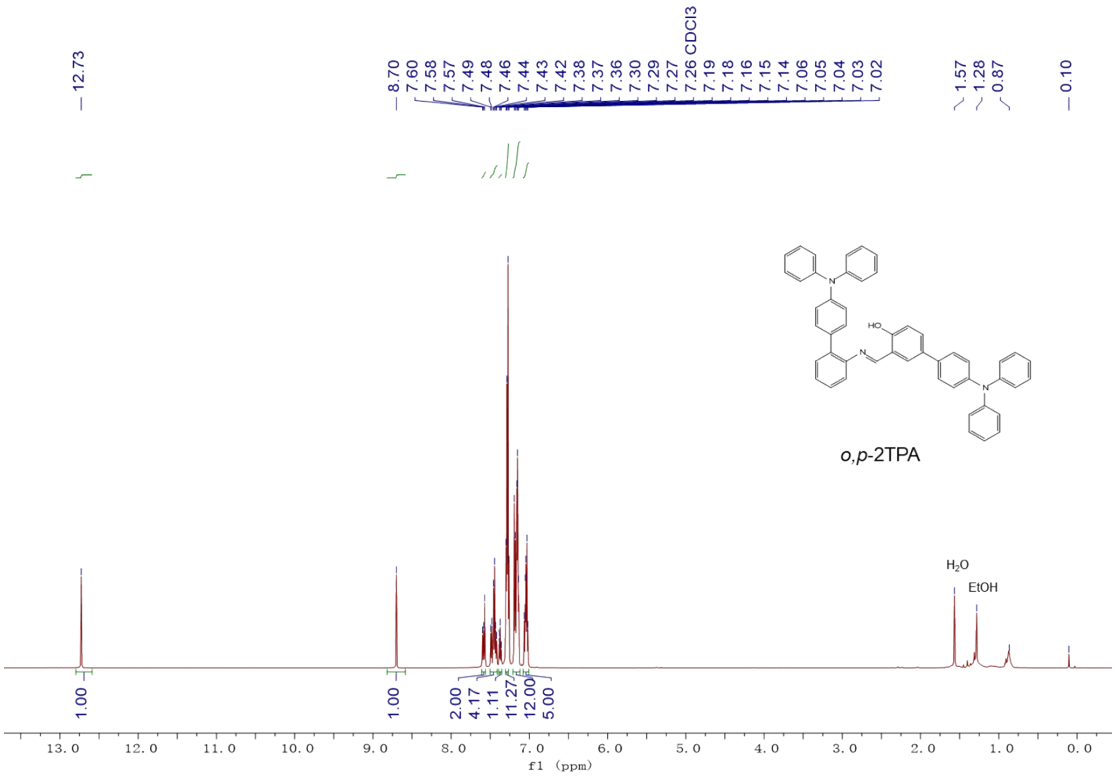

Figure S1. ^{1}H NMR spectrum of *o*,*p*-2TPA in $CDCl_3$.

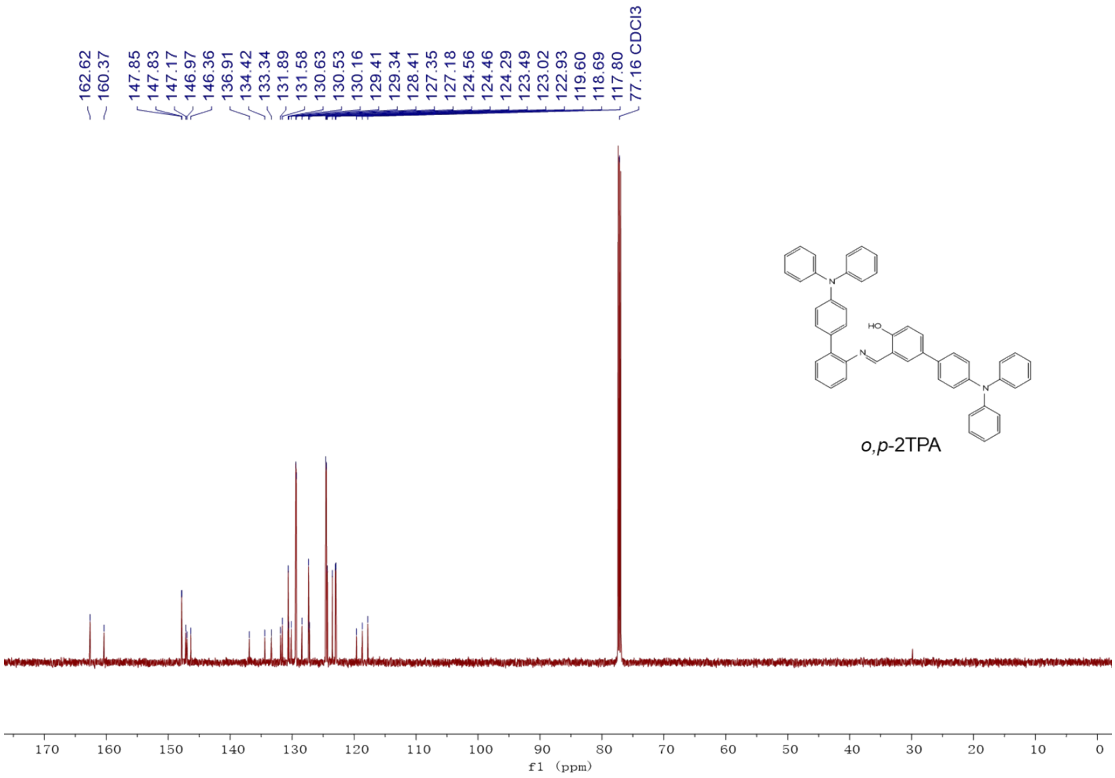

Figure S2. ^{13}C NMR spectrum of *o*,*p*-2TPA in $CDCl_3$.

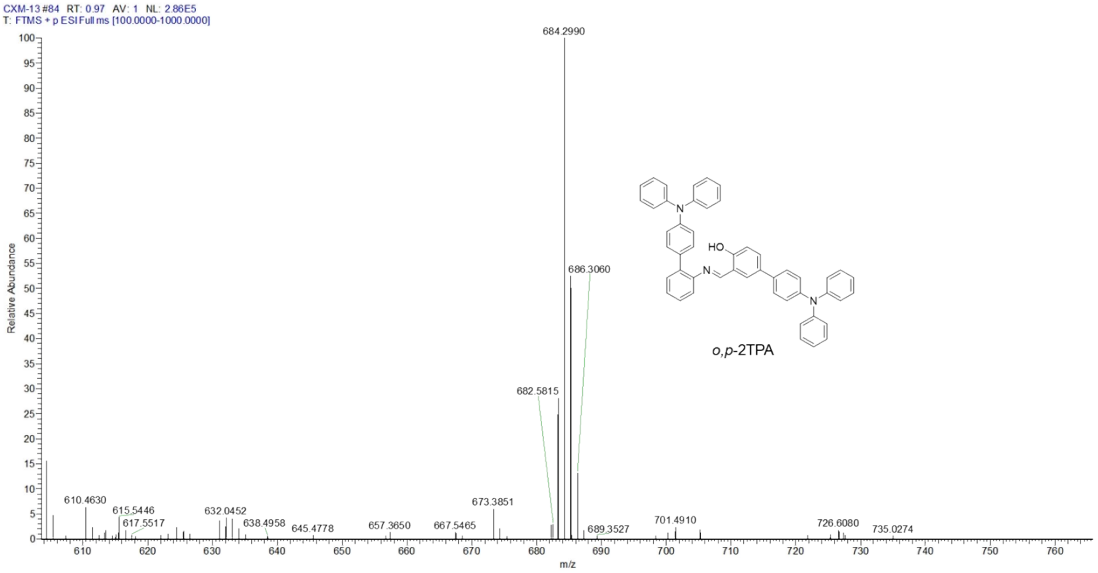

Figure S3. HRMS spectrum of *o*,*p*-2TPA.

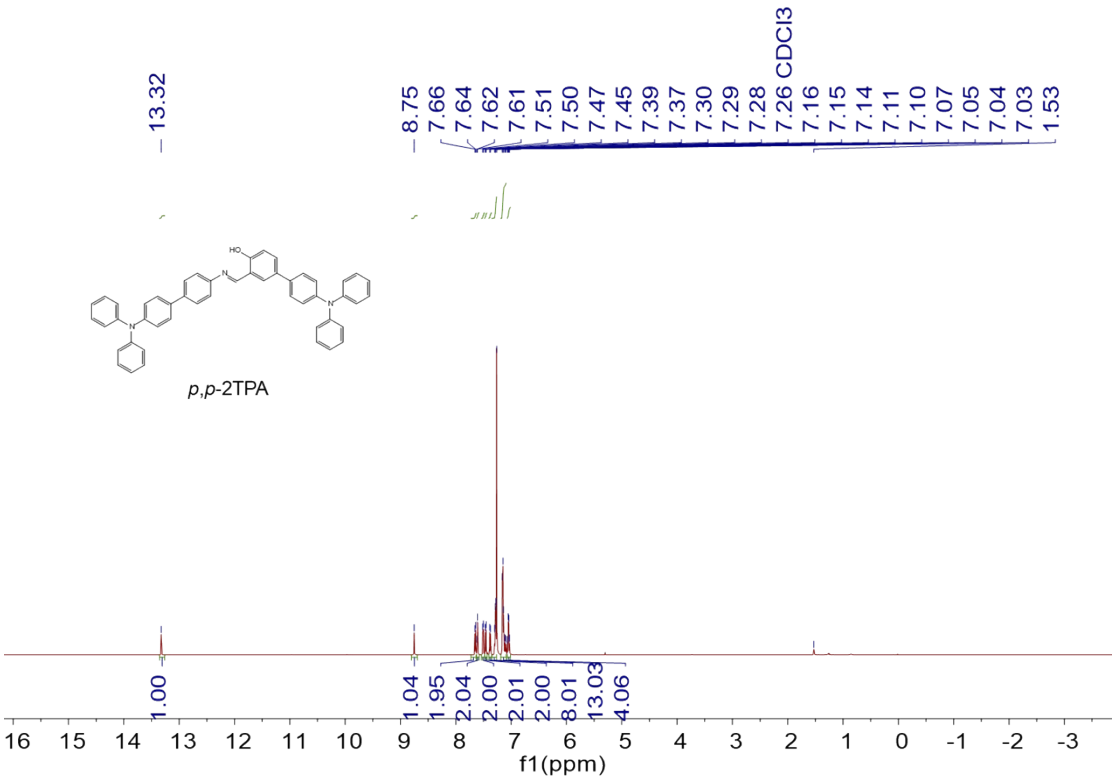

Figure S4. ^{1}H NMR spectrum of *p*,*p*-2TPA in $CDCl_3$.

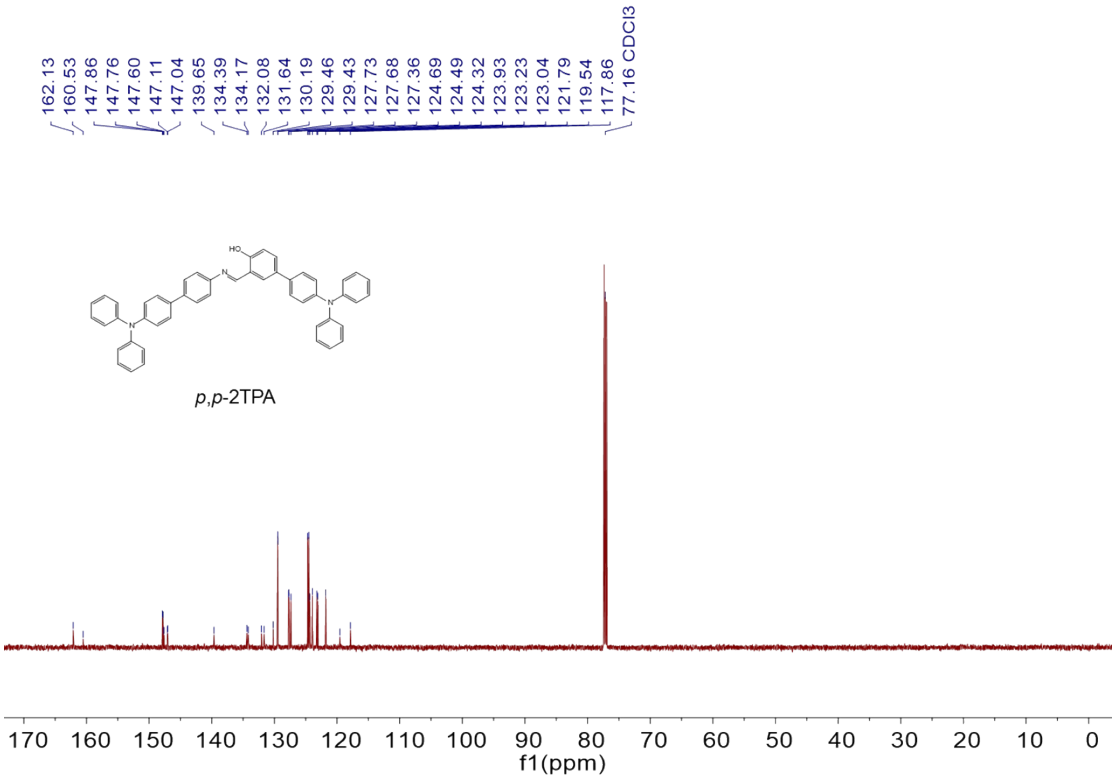

Figure S5. ^{13}C NMR spectrum of *p*,*p*-2TPA in $CDCl_3$.

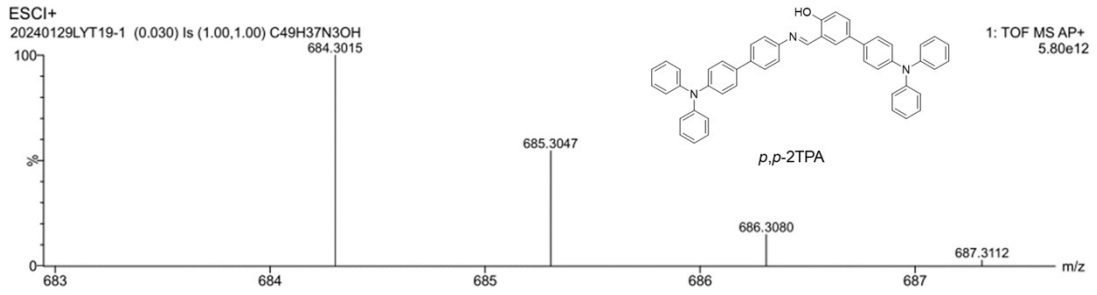

Figure S6. HRMS spectrum of *p*,*p*-2TPA.

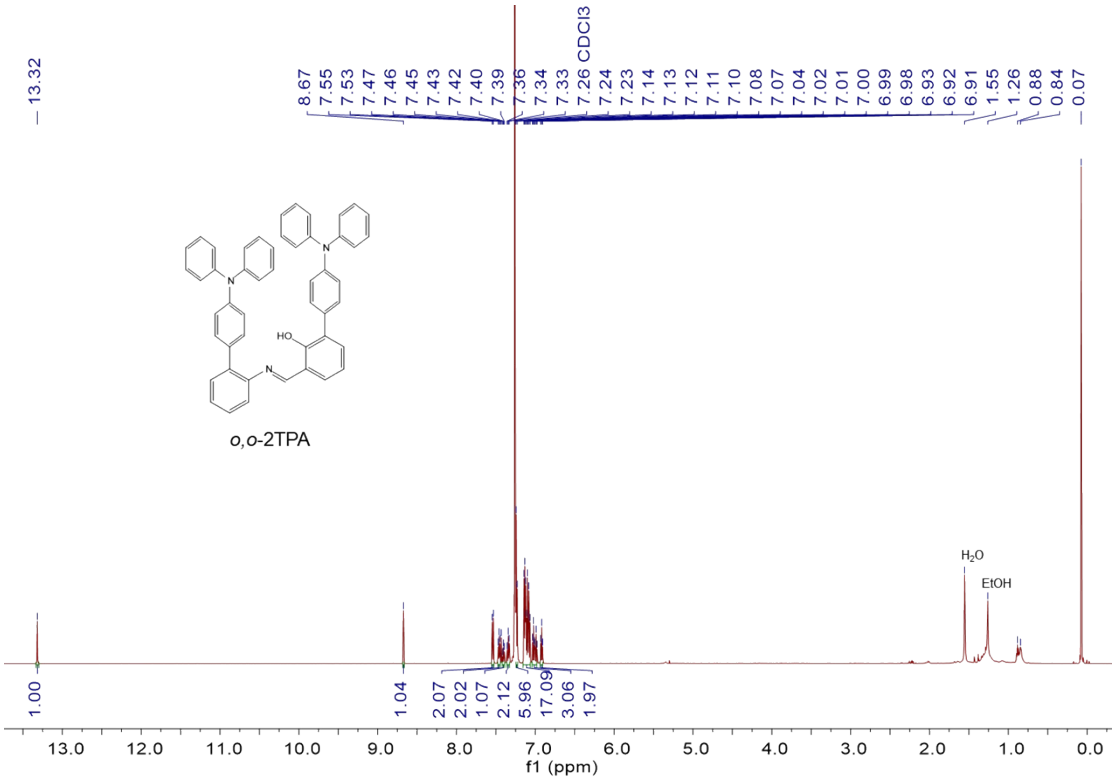

Figure S7. ^{1}H NMR spectrum of *o*,*o*-2TPA in $CDCl_3$.

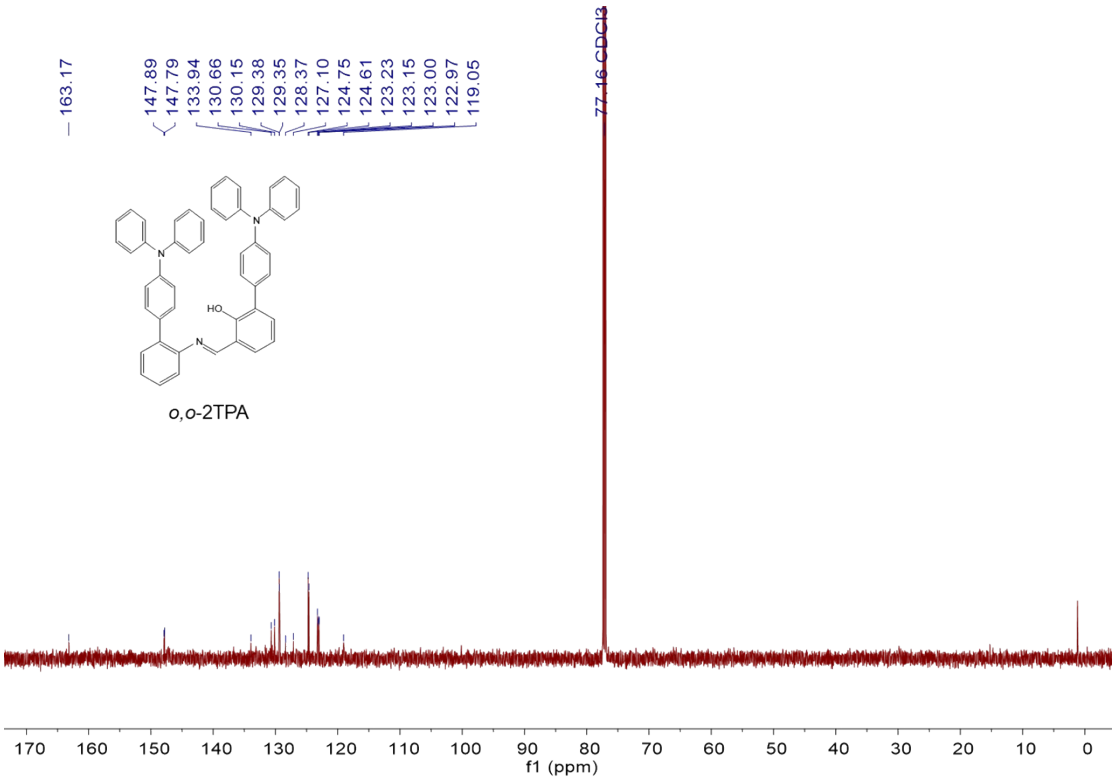

Figure S8. ^{13}C NMR spectrum of *o*,*o*-2TPA in $CDCl_3$.

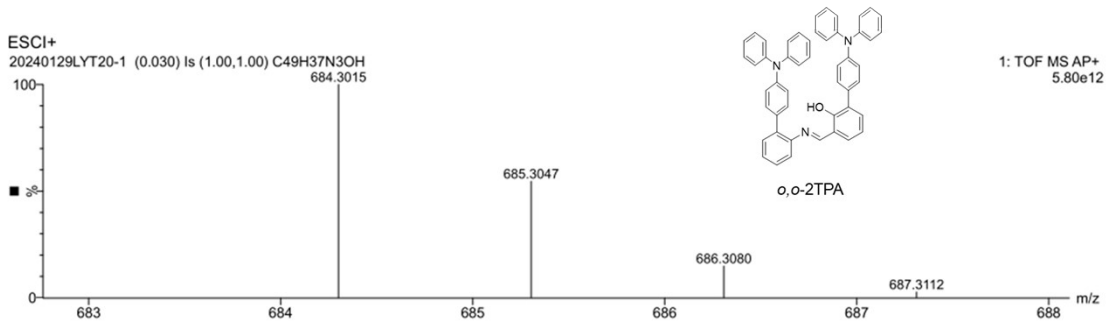

Figure S9. HRMS spectrum of *o*,*o*-2TPA.

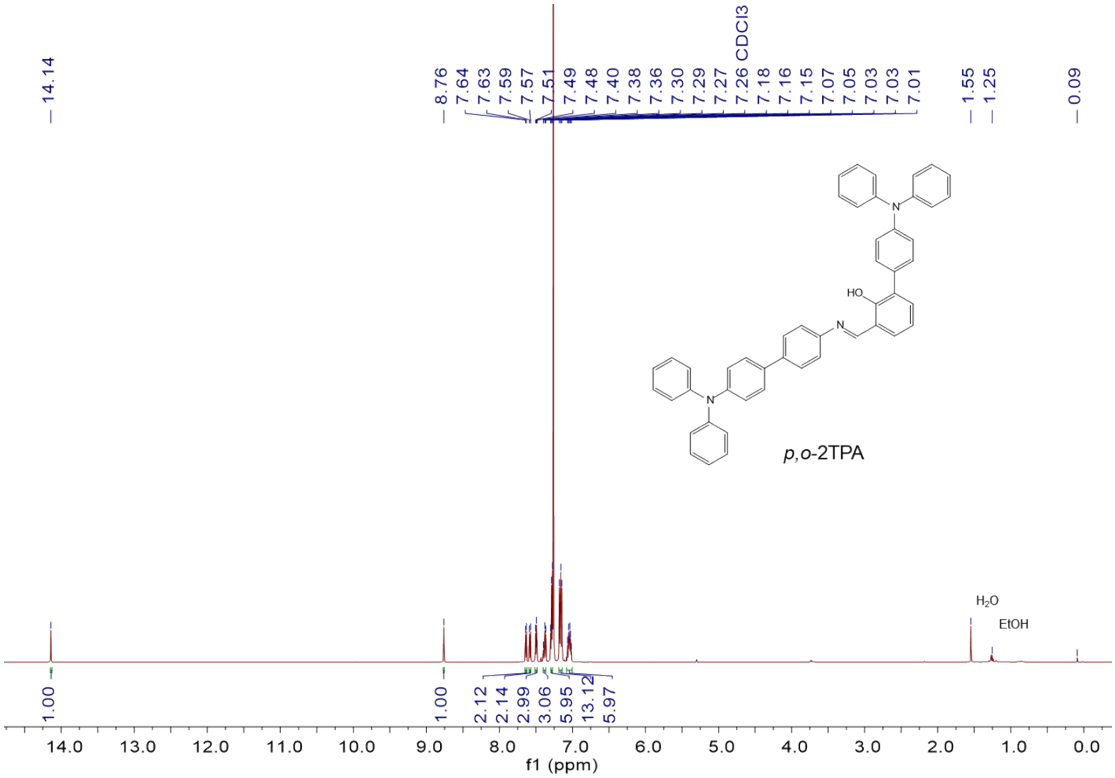

Figure S10. ^{1}H NMR spectrum of *p*,*o*-2TPA in $CDCl_3$.

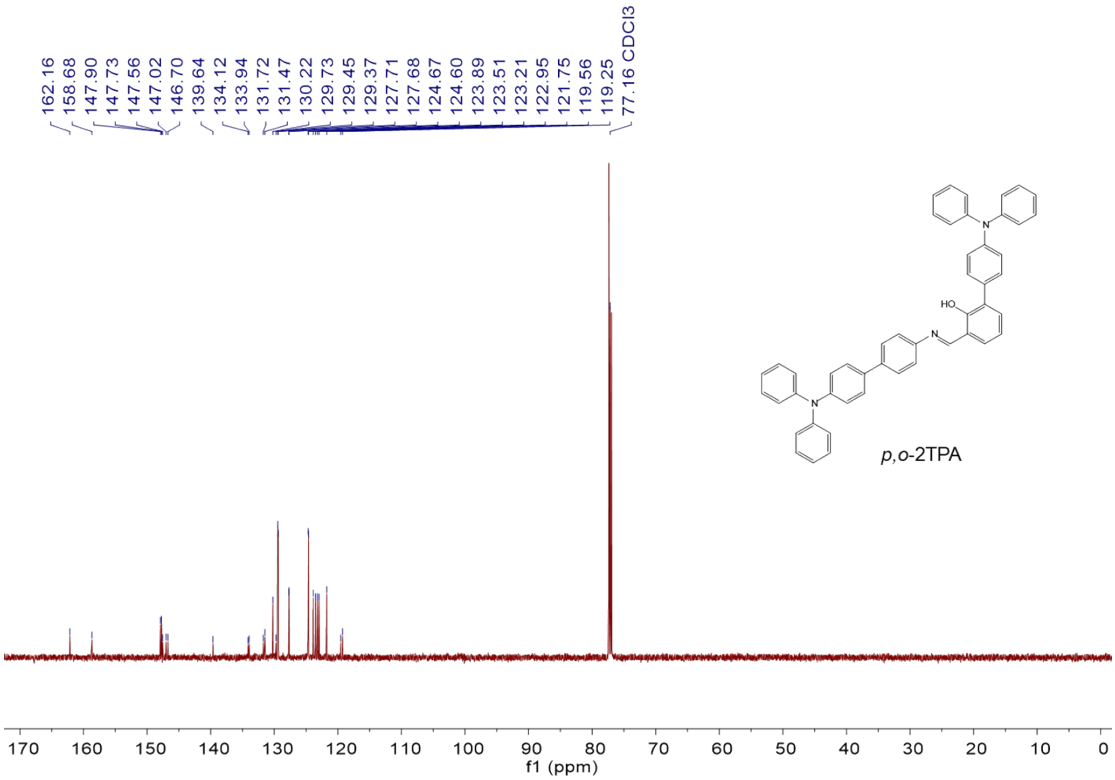

Figure S11. ^{13}C NMR spectrum of *p*,*o*-2TPA in $CDCl_3$.

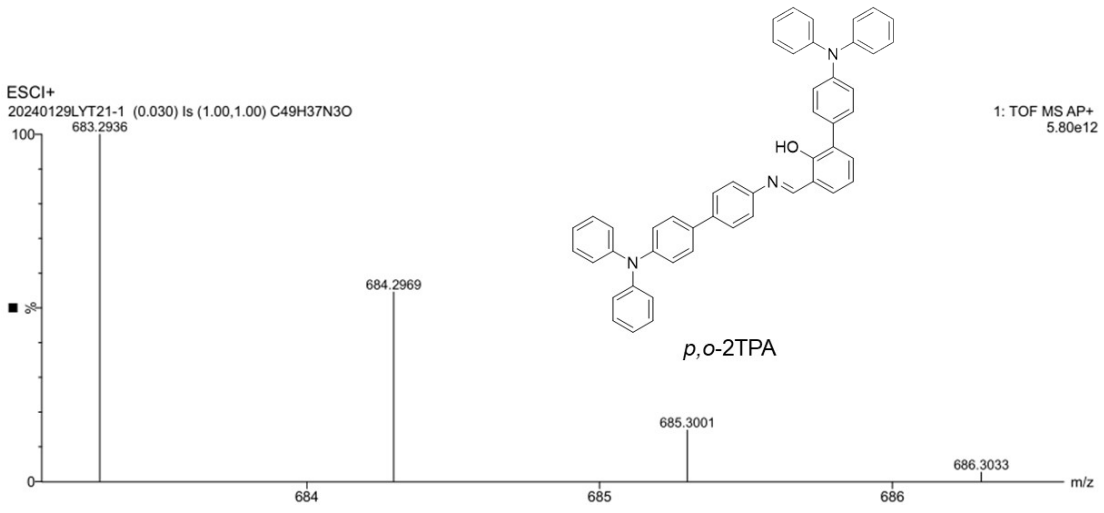

Figure S12. HRMS spectrum of *p*,*o*-2TPA.

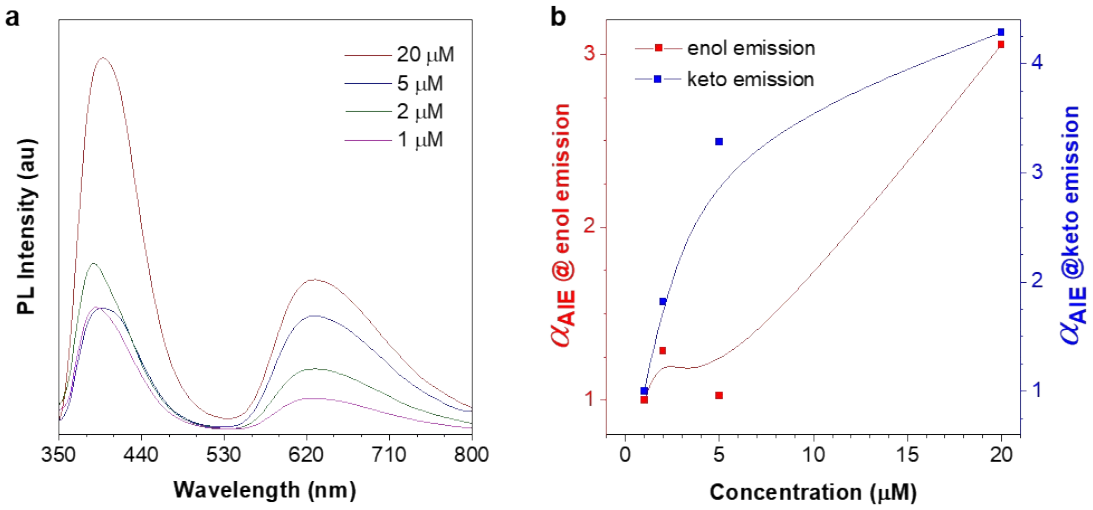

Figure S13. (a) PL spectra of *o*,*p*-2TPA in THF solution with different concentrations. λ_{ex} = 311 nm. (b) The plots of the enol-form and keto-form emission intensity of *o*,*p*-2TPA at the maximum versus the concentrations. $\alpha_{AIE} = I/I_0$, I_0 = PL intensity at a concentration of 1 μM.

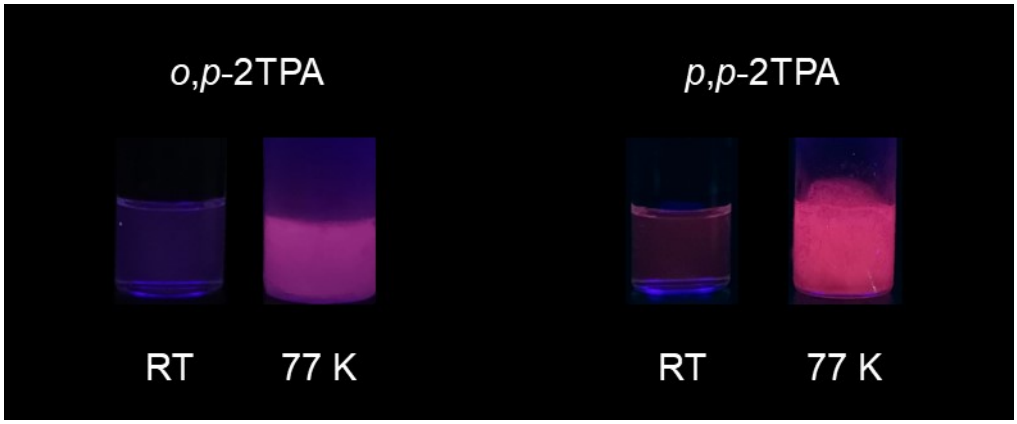

Figure S14. Fluorescence photographs of *o*,*p*-2TPA and *p*,*p*-2TPA in THF at RT and 77 K, respectively. λ_{ex} = 365 nm. Concentration = 20 μM.

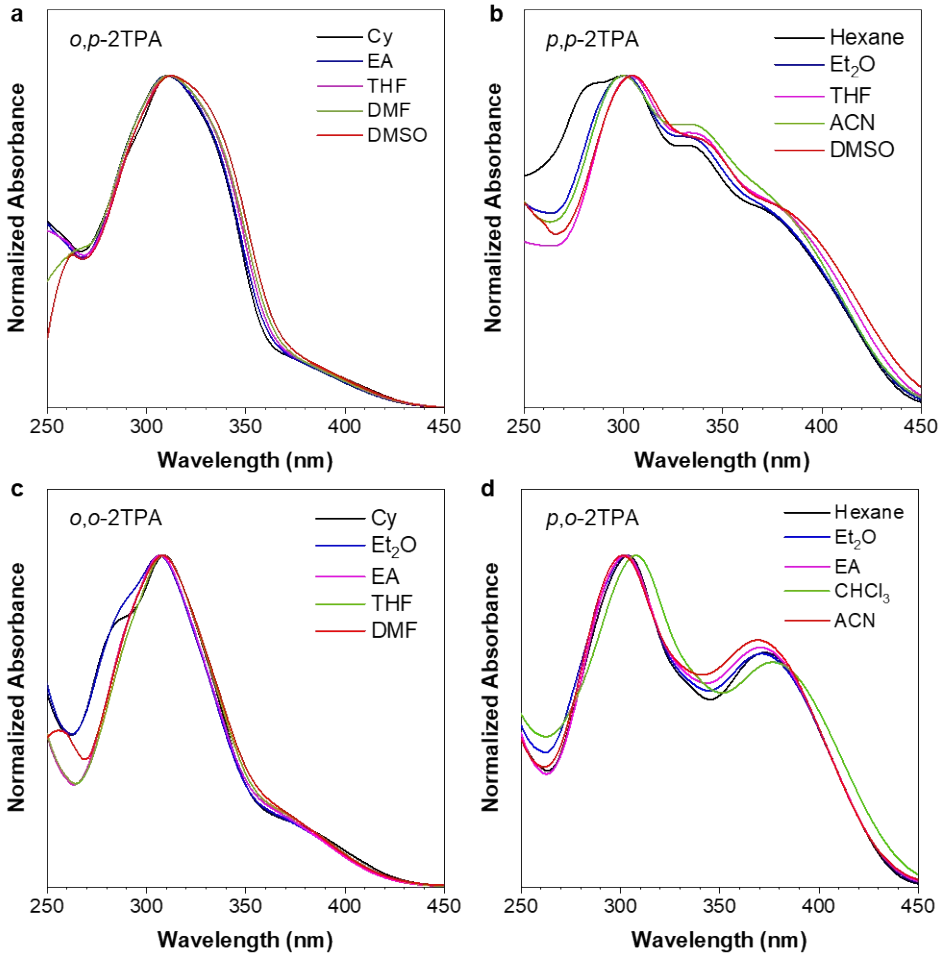

Figure S15. Normalized absorption spectra of (a) *o*,*p*-2TPA, (b) *p*,*p*-2TPA, (c) *o*,*o*-2TPA, and (d) *p*,*o*-2TPA in solvents of varying polarity.

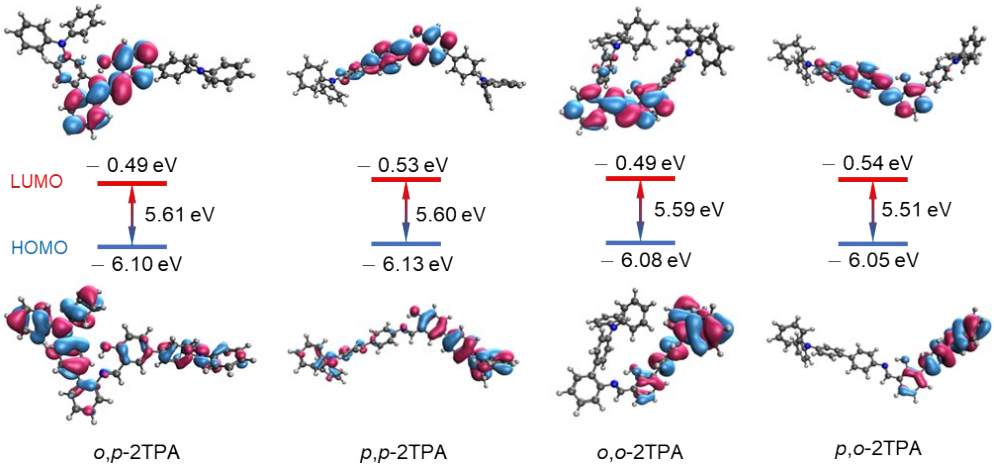

Figure S16. Frontier molecular orbitals of the four isomers based on the optimized ground-state geometries of enol form, calculated at the CAM-B3LYP/6-31G(d,p) level.

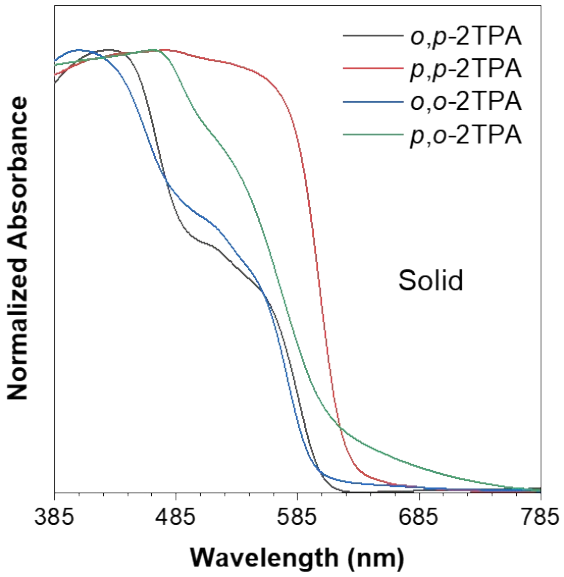

Figure S17. Normalized UV-DRS spectra of *o*,*p*-2TPA, *p*,*p*-2TPA, *o*,*o*-2TPA, and *p*,*o*-2TPA.

Table S1. Crystallographic data for *o*,*p*-2TPA.

	***o*,*p*-2TPA**
empirical formula	$C_{49}H_{37}N_3O$
M_r	683.81
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	17.9212(11)
b (Å)	16.5987(11)
c (Å)	12.3619(6)
α (°)	90
β (°)	101.252(6)
γ (°)	90
V (Å^3)	3606.6(4)
Z	4
ρ_c (g cm^{-3})	1.259
F (000)	1440.0
T (K)	150.00(10)
μ (mm^{-1})	0.583
data / restraints / parameters	7142/0/479
GOF (F^2)	1.014
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0623, 0.1508
R_{int}	0.0620

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

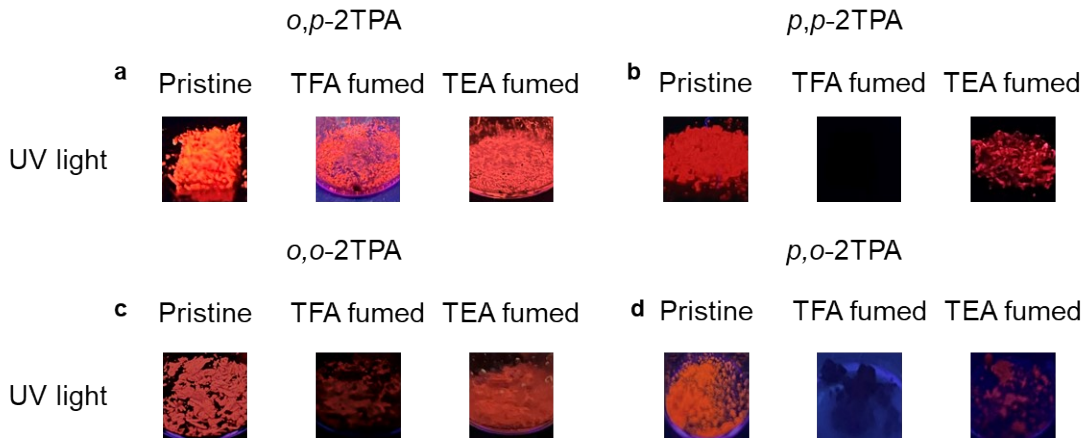

Figure S18. Fluorescence photographs of (a) *o*,*p*-2TPA, (b) *p*,*p*-2TPA, (c) *o*,*o*-2TPA, and (d) *p*,*o*-2TPA as solid (pristine, sample fumed with TFA, sample fumed with TEA).

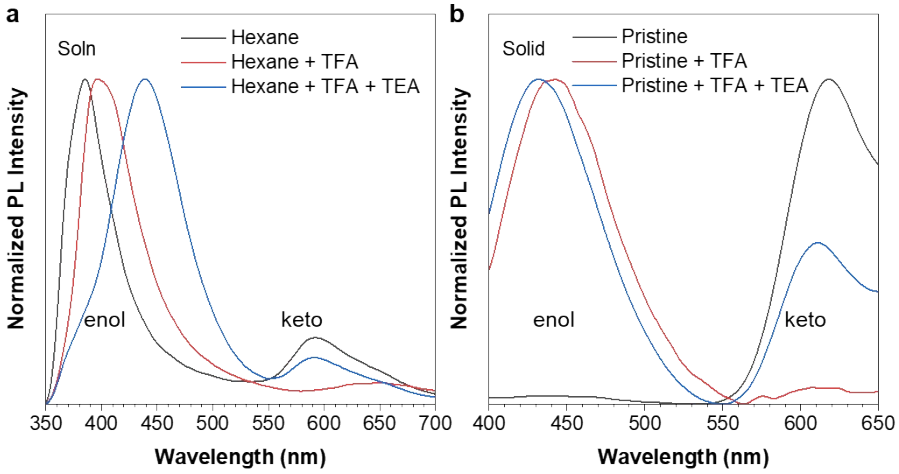

Figure S19. (a and b) Normalized PL spectra of *p*,*p*-2TPA in Hexane and as solid after TFA and TEA treatment.

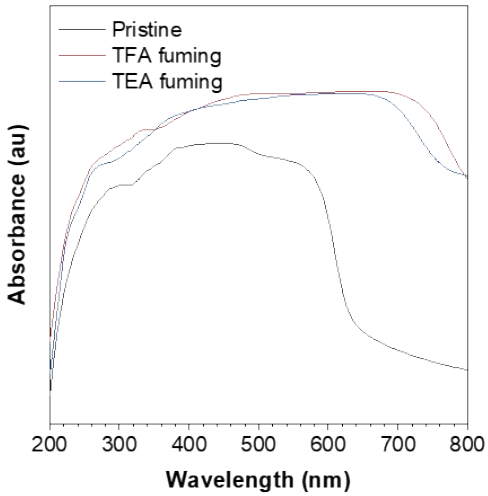

Figure S20. UV-DRS spectra of *p*,*p*-2TPA in its pristine form, fumed with TFA, and fumed with TEA.

References

[1] X.-M. Cai, W. Zhong, Z. Deng, Y. Lin, Z. Tang, X. Zhang, J. Zhang, W. Wang, S. Huang, Z. Zhao and B. Z. Tang, *Chem. Eng. J.*, 2023, **466**, 143353.

[2] W. Zhong, J. Zhang, Y. Lin, S. Li, Y. Yang, W.-J. Wang, C. Si, F. E. Kühn, Z. Zhao, X.-M. Cai and B. Z. Tang, *Chem. Sci.*, 2024. **15**, 3920.