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Enhanced room-temperature phosphorescence of triphenylphosphine derivatives without metal and heavy atom in crystal phase

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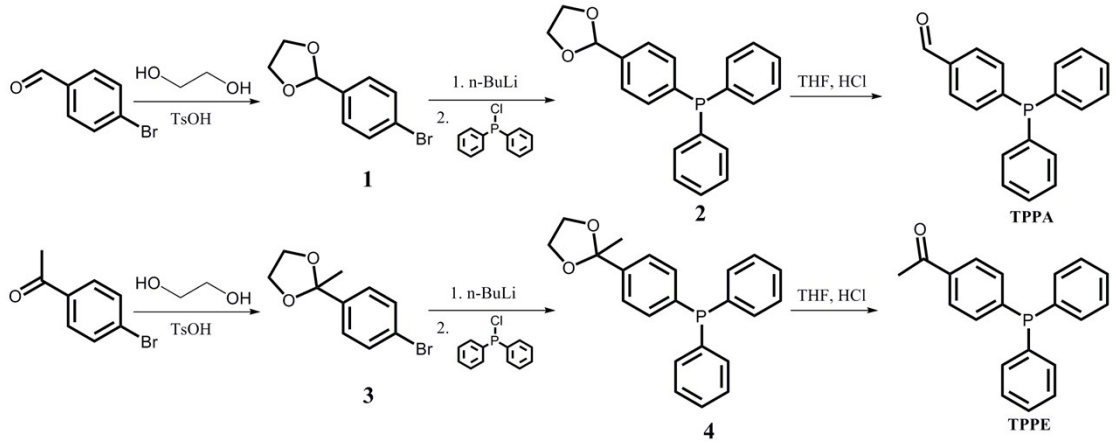
EXPERIMENTAL SECTION

Instruments and experimental methods: The UV-vis spectra were determined on a Mapada UV-1800pc spectrophotometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Photoluminescence measurements were taken on a Shimadzu RF-5301 Luminescence Spectrometer. The absolute fluorescence quantum yields were measured on an Edinburgh FLS920 steady state spectrometer using an integrating sphere. Luminescent decay experiments were measured on an Edinburgh FLS920 spectrometer. EPLED-360 picosecond flash lamp with 898ps pulse duration and μF920 microsecond flash lamp (pulse width < 2 μs) were used to measure time-resolved fluorescent and phosphorescent spectra, respectively. ^{1}H and ^{13}C NMR spectra were recorded on Mercury plus 400 MHz. The fluorescence quantum yields in methylcyclohexane were measured by comparing to standards (9,10-diphenylantrancene in cyclohexane, Φ_F = 0.9). Geometrical optimization was performed by density functional theory (DFT) calculations at B3LYP/6-311G (d, p) level with the Gaussian 09W program package. Electronic transition data obtained by the TD/DFT-B3LYP/6-311G(d,p) calculation based on the configuration at ground state.

Single crystals of **TPPA** and **TPPE** were obtained by slowing solvent evaporation in *n*-hexane and selected for X-ray diffraction analysis on in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program. The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically.

Synthesis of **TPPA** and **TPPE**

The compounds **1** and **3** were synthesized based on the reported method.



Scheme S1. Synthesized route of **TPPA** and **TPPE**.

2-(4-bromophenyl)-1,3-dioxolane (1)

4-bromobenzaldehyde (5.0 g, 27 mmol), ethylene glycol (3.35 g, 54 mmol) and p-toluenesulfonic acid (10 mg) were dissolved in toluene (100 mL) and the mixture was refluxed with a Dean-Stark trap to azeotropically remove water. After 10 h, the solution was cooled to room temperature and washed with saturated $NaHCO_3$ solution and then with saturated NaCl solution. The solution was dried over $MgSO_4$ and the solvent was evaporated to yield **1**. Yield = 92 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 5.77 (s, 1H), 4.15-4.00 (m, 4H).

2-(4-Bromophenyl)-2-methyl-1,3-dioxolane (3)

A solution of 4'-bromoacetophenone (5.0 g, 25 mmol), ethylene glycol (3.5 g, 56 mol), *p*-toluenesulfonic acid (10 mg) were dissolved in toluene (100 mL) and the mixture was refluxed with a Dean-Stark trap to azeotropically remove water. After 10 h, the solution was cooled to room temperature and washed with saturated $NaHCO_3$ solution and then with saturated NaCl solution. The solution was dried over $MgSO_4$ and the solvent was evaporated to yield **3**. Yield = 93 %. 7.46 (d, J = 8.4 Hz, 2 H); 7.36 (d, J = 8.5 Hz, 2 H); 4.08-3.69 (m, 4 H) 1.62 (s, 3 H).

4-(diphenylphosphino)benzaldehyde (TPPA)

3 (3.8 g, 16.6 mmol) was dissolved in dry THF (50 mL) and stirred at -78 ºC for 30

min. n-BuLi (8.0 mL, 2.5 M in hexane) was slowly dropped the above solution within 20 min, and the mixture was stirred for another 30 min. After chlorodiphenylphosphine (4.0 g, 18.0 mmol) was added slowly, the mixture was stirred overnight at room temperature. NH_4NO_3 aqueous solution and ethyl acetate (50 mL) were added, and organic layer was washed by water and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was dissolved in THF/water (50 ml/10 mL), and then concentrated HCl (1 mL) was added and the mixture was stirred for 1h. CH_2Cl_2 (50 mL) was added and water phase was extracted by CH_2Cl_2 (50 mL). Organic phase was dried over anhydrous Na_2SO_4 and the crude product was obtained after solvent was removed. The product was obtained by column chromatography (silica, CH_2Cl_2/PE = 1:2). Yield = 12 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.46 – 7.29 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.93 (s), 146.52 (d, J = 15.3 Hz), 136.02 (s), 135.81 (d, J = 10.3 Hz), 134.17 (s), 133.97 (s), 133.63 (s), 133.45 (s), 129.32 (s), 129.31 (d, J = 5.5 Hz), 128.79 (d, J = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ = -4.32. Element analysis (%): calculated for $C_{19}H_{15}OP$: C, 78.61; H, 5.21; found: C, 78.65; H, 5.27.

1-(4-(diphenylphosphino)phenyl)ethanone (TPPE)

TPPE was synthesized based on the similar procedure to **TPPA**. Yield = 23 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 7.9 Hz, 2H), 7.34 (m, 12H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.93 (s), 144.47 (d, J = 14.0 Hz), 136.96 (s), 136.14 (d, J = 10.3 Hz), 134.20 (s), 134.01 (s), 133.56 (s), 133.38 (s), 129.34 (s), 128.85 (d, J = 7.2 Hz), 128.16 (d, J = 6.4 Hz), 26.78 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ = -5.05. Element analysis (%): calculated for $C_{20}H_{17}OP$: C, 78.93; H, 5.63; found: C, 78.91; H, 5.66.

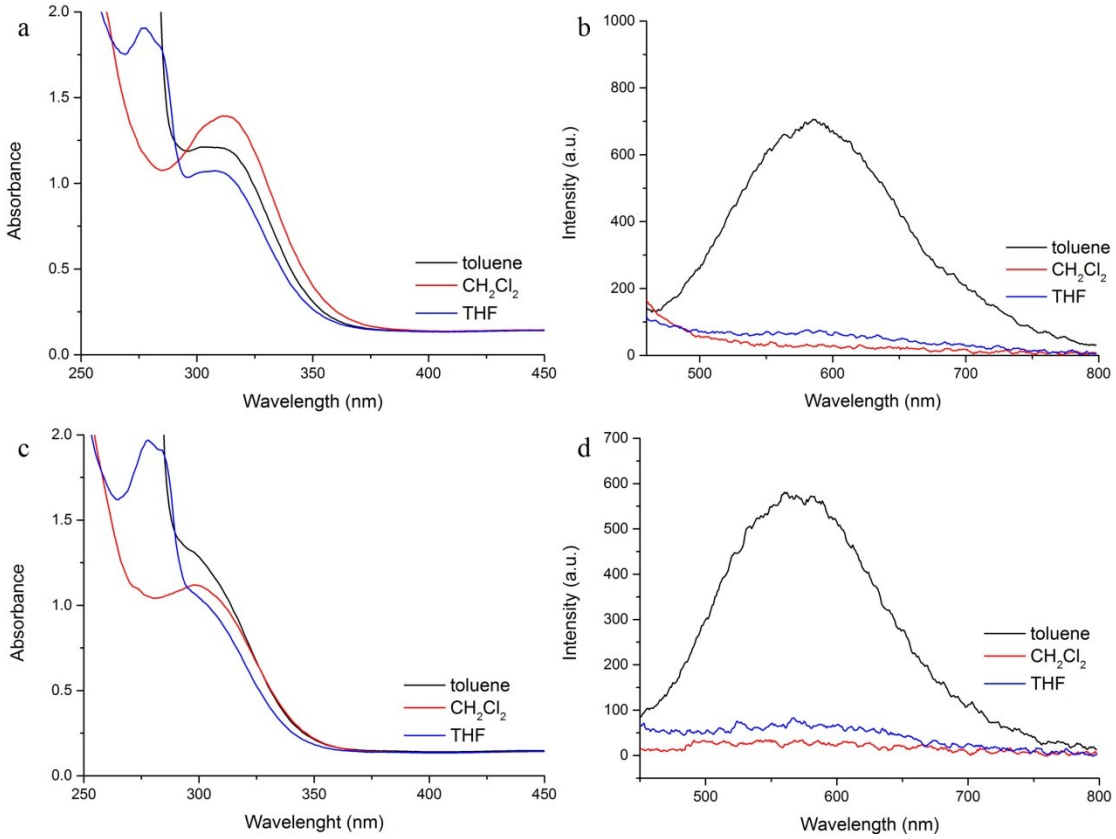


Fig. S1 Absorption and emission spectra of **TPPA** (a and b) and **TPPE** (c and d) in different solvents in N_2 atmosphere. λex = 300 nm.

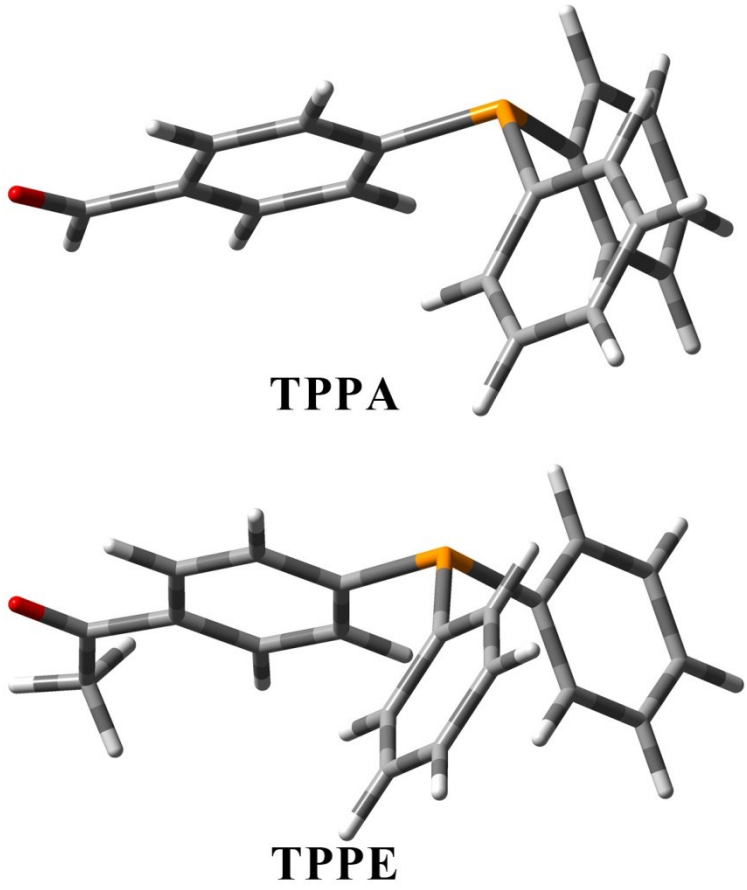


Fig. S2 Optimal molecular structures of **TPPA** and **TPPE**.

Table S1. Computed vertical excitation spectra of **TPPA** in vacuum based on the optimal structure at ground state.

Excited State	Transition	Bandgap (eV)	Absorption (nm)	Oscillator strength
Triplet (T_1)	HOMO-7–LUMO (9.8%); HOMO-5–LUMO (2.6%); HOMO-4–LUMO (7.7%); HOMO-2–LUMO (5.7%); HOMO–LUMO (74.2%)	2.9665	417.95	0.0000
Triplet (T_2)	HOMO-1–LUMO (93.7%); HOMO-2–LUMO+6 (6.3%)	3.0891	401.36	0.0000
Triplet (T_3)	HOMO-6–LUMO+1 (3.82%); HOMO-6–LUMO+3 (3.25%); HOMO-5–LUMO+3 (10.4%); HOMO-4–LUMO+1 (6.8%); HOMO-4–LUMO+4 (3.6%); HOMO-3–LUMO+2 (11.1%); HOMO-2–LUMO+3 (7.2%); HOMO-2–LUMO+5 (6.9%); HOMO–LUMO (46.9%)	3.5861	345.73	0.0000
Single (S_1)	HOMO-1–LUMO (96.7%); HOMO-1–LUMO+6 (3.4%);	3.6314	341.43	0.0003
Triplet (T_4)	HOMO-5–LUMO+1 (4.2%); HOMO-5–LUMO+2 (7.6%); HOMO-4–LUMO+2 (5.0%); HOMO-4–LUMO (2.4%); HOMO-4–LUMO+1 (9.6%); HOMO-4–LUMO+3 (3.0%); HOMO-3–LUMO+1 (7.1%); HOMO-3–LUMO+2 (5.4%); HOMO-3–LUMO+5 (4.6%); HOMO-2–LUMO+1 (7.2%); HOMO-2–LUMO+1 (3.2%); HOMO-2–LUMO+1 (8.7%); HOMO-2–LUMO+4 (8.9%); HOMO–LUMO+3 (23.1%)	3.6478	339.89	0.0000
Singlet (S_2)	HOMO–LUMO (100%)	3.7702	328.85	0.2170

Table S2. Computed vertical excitation spectra of **TPPE** in vacuum based on the optimal structure at ground state.

Excited State	Transition	Bandgap (eV)	Absorption (nm)	Oscillator strength
Triplet (T_1)	HOMO-7–LUMO (8.6%); HOMO-6–LUMO (4.4%); HOMO-4–LUMO (9.0%); HOMO-2–LUMO (6.5%); HOMO–LUMO (71.5%)	3.0591	405.29	0.0000
Triplet (T_2)	HOMO-1–LUMO (93.3%); HOMO-1–LUMO+6 (6.7%)	3.1632	391.95	0.0000
Triplet (T_3)	HOMO-6–LUMO+1 (5.3%);HOMO-3–LUMO+3 (6.0%); HOMO-5–LUMO+3 (7.1%);HOMO-5–LUMO+4 (2.8%); HOMO-4–LUMO+1 (5.5%);HOMO-4–LUMO+2 (2.6%); HOMO-3–LUMO+4 (9.8%);HOMO-2–LUMO+52 (7.1%); HOMO-2–LUMO+5 (5.4%);HOMO–LUMO+1 (48.4%)	3.5826	346.07	0.0000
Triplet (T_4)	HOMO-6–LUMO+1 (7.7%); HOMO-6–LUMO+3 (2.6%); HOMO-5–LUMO+1 (5.4%); HOMO-5–LUMO+2 (6.5%); HOMO-5–LUMO+5 (2.6%); HOMO-4–LUMO+1 (7.9%); HOMO-4–LUMO+4 (6.9%); HOMO-3–LUMO+1 (6.9%); HOMO-3–LUMO+2 (3.2%); HOMO-3–LUMO+5 (5.1%); HOMO-2–LUMO (2.9%); HOMO-2–LUMO+3 (7.5%); HOMO-2–LUMO+4 (9.6%); HOMO–LUMO+2 (3.1 %); HOMO–LUMO+3 (22.1%)	3.6464	340.02	0.0000
Single (S_1)	HOMO-1–LUMO (96.5%); HOMO-1–LUMO+6 (3.5%)	3.6828	336.66	0.0003
Singlet (S_2)	HOMO–LUMO (100%)	3.8460	322.37	0.2073

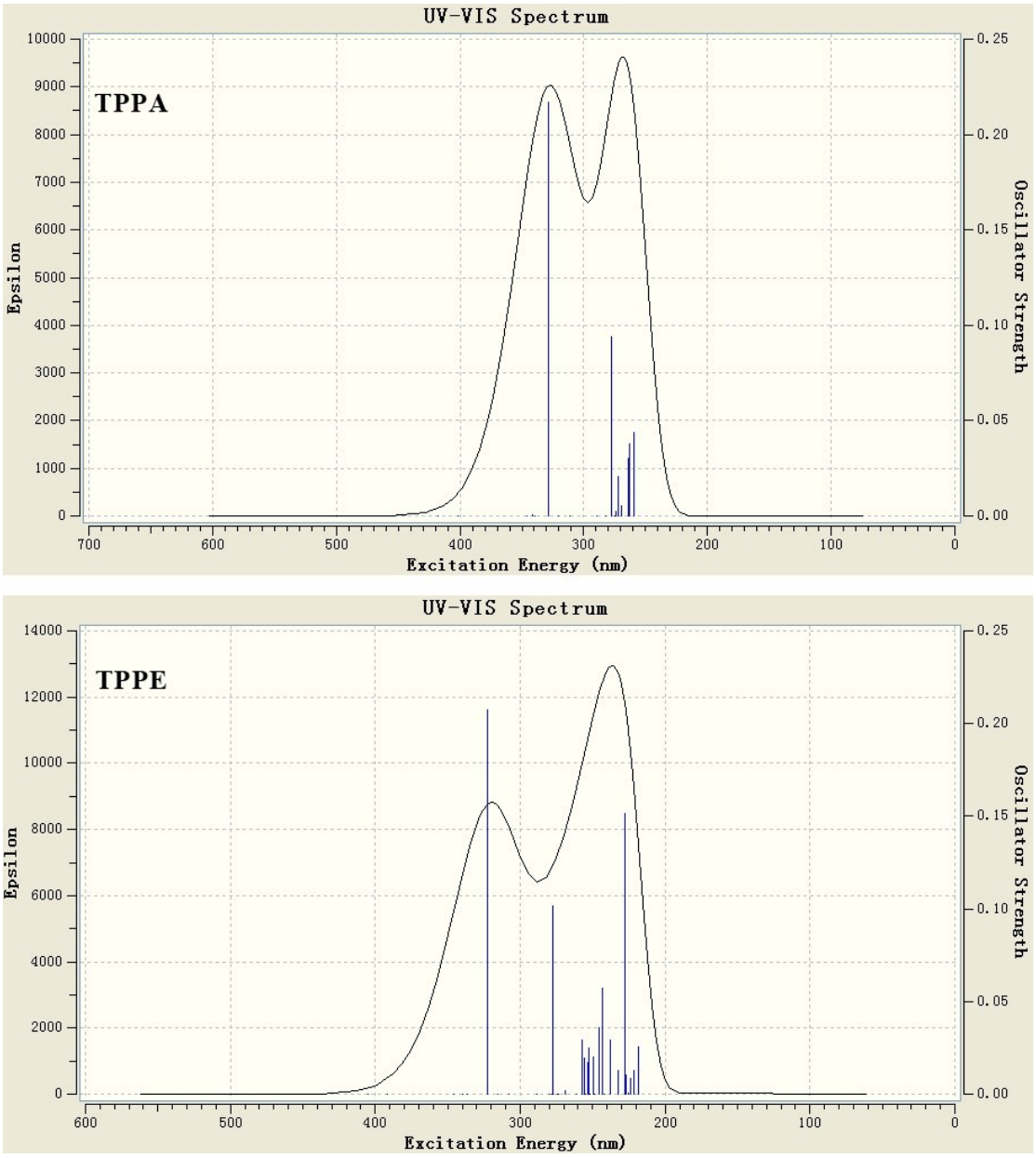


Fig. S3 UV-Vis absorption spectra of **TPPA** and **TPPE** based on the optimal structure at ground state.

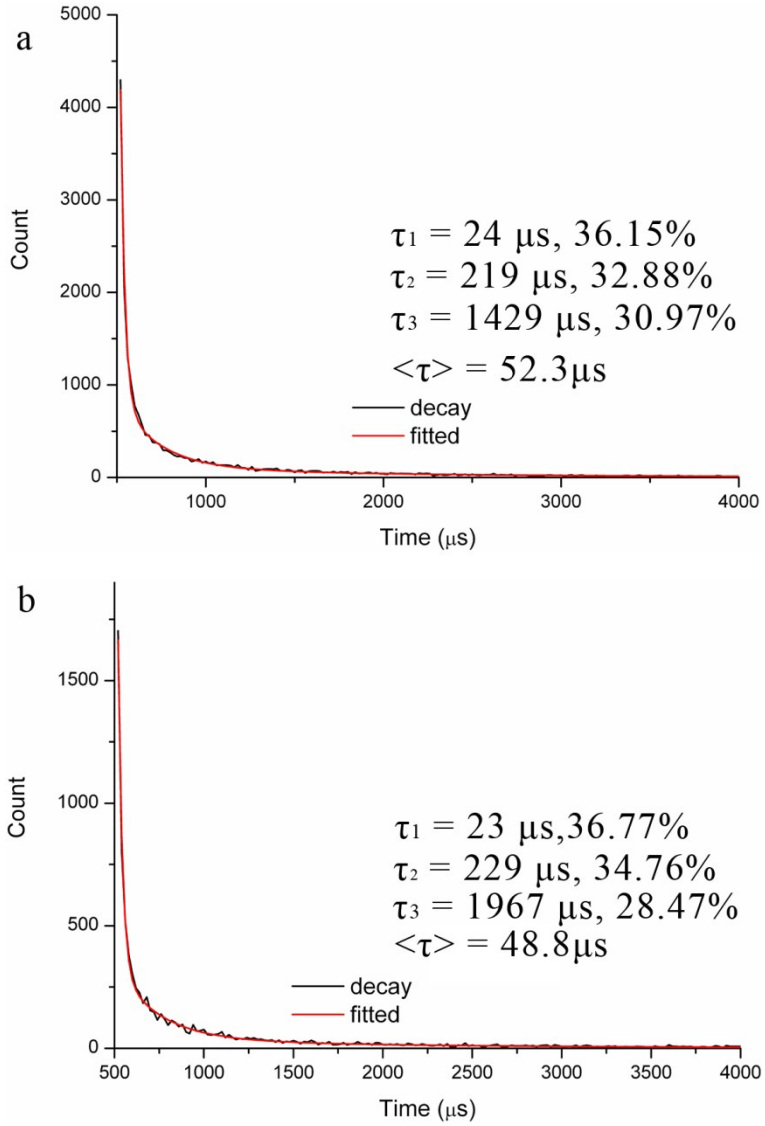


Fig. S4 Decay curves of **TPPA** (a) and **TPPE** in methylcyclohexane in N_2 atmosphere. λ_{ex} =300 nm, λ_{em} = 547, and 530 nm for **TPPA** and **TPPE**, respectively.

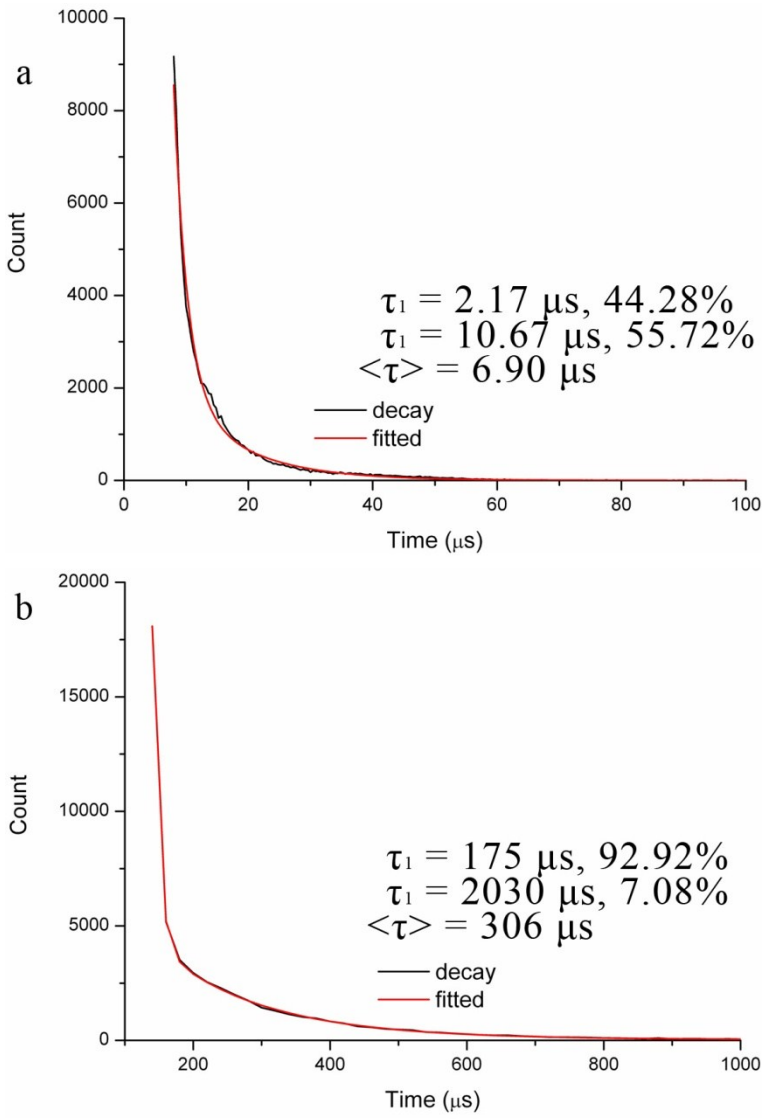


Fig. S5 Decay curves of **TPPA** and **TPPE** crystals. λ_{ex} =300 nm, λ_{em} = 550nm and 515 nm for **TPPA** and **TPPE**, respectively.

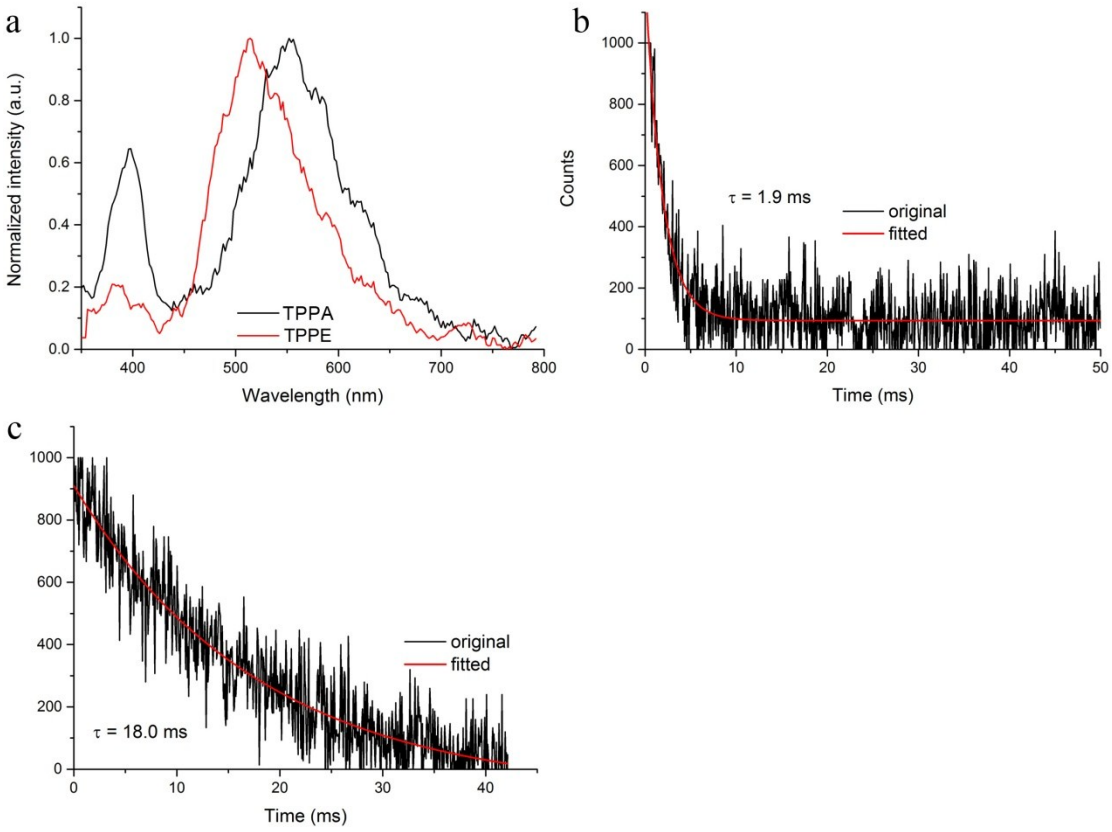


Fig. S6 (a) Luminescence spectra of TPPA and TPPE crystals at 77k. Decay curves of (b) **TPPA** and (c) **TPPE** crystals at 77k. λ_{ex} =300 nm, λ_{em} = 550nm and 515 nm for **TPPA** and **TPPE**, respectively.

Table S3. Crystallographic data and details of measurements for **TPPA** and **TPPE**.

	TPPA	**TPPE**
Formula	$C_{19}H_{15}OP$	$C_{20}H_{17}OP$
Fw	290.28	304.31
cryst system	orthorhombic	triclinic
space group	Pbca	p-1
Z	8	2
a (Å)	10.1947(6)	8.5525(14)
b (Å)	8.7300(5)	10.3525(17)
c (Å)	34.4274(16)	10.5874(17)
α (deg)	90.000	114.517(16)
β (deg)	90.000	99.585(14)
γ (deg)	90.000	90.156(13)
V (Å^3)	3064.0(3)	838.3(3)
D_{calc} (g/cm^3)	1.259	1.206
μ (mm$^{-1)}$	0.175	0.163
Measd reflns	3475	3389
wR_2	0.1291	0.1460
R	0.0548	0.0516
CCDC number	1446727	1446729

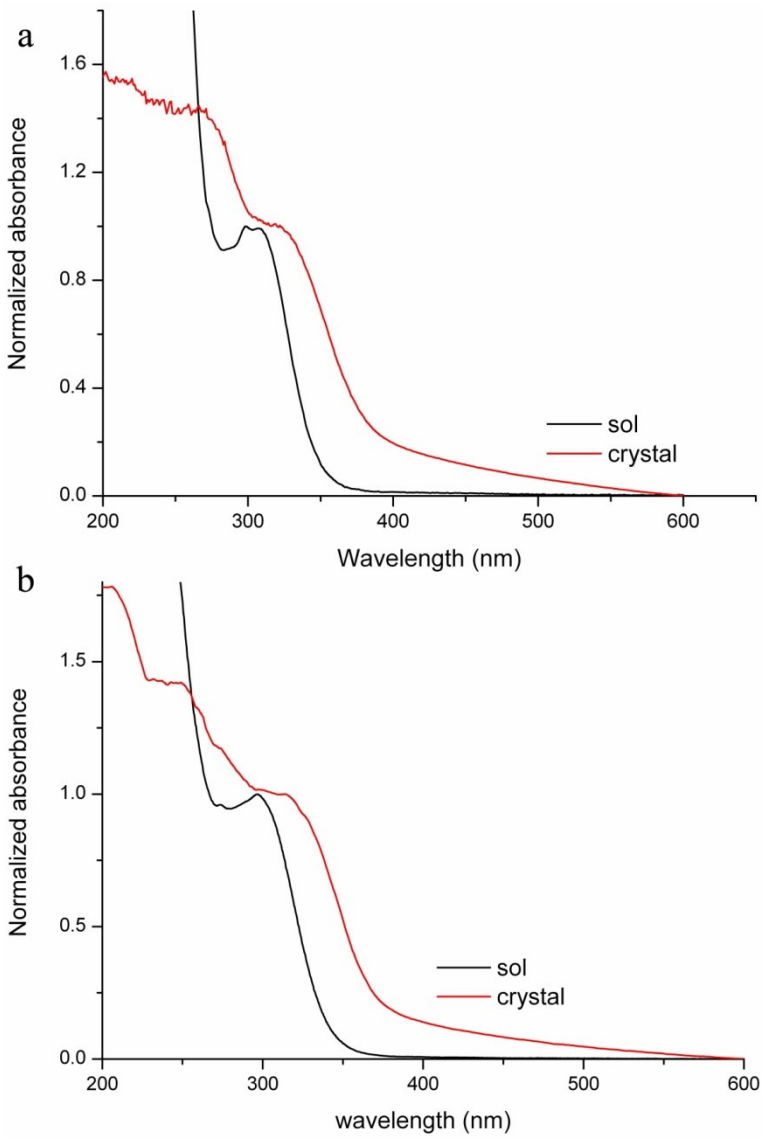


Fig. S7 UV-Vis absorption spectra of **TPPA** (a) and **TPPE** (b) in methylcyclohexane solution and crystal phase.

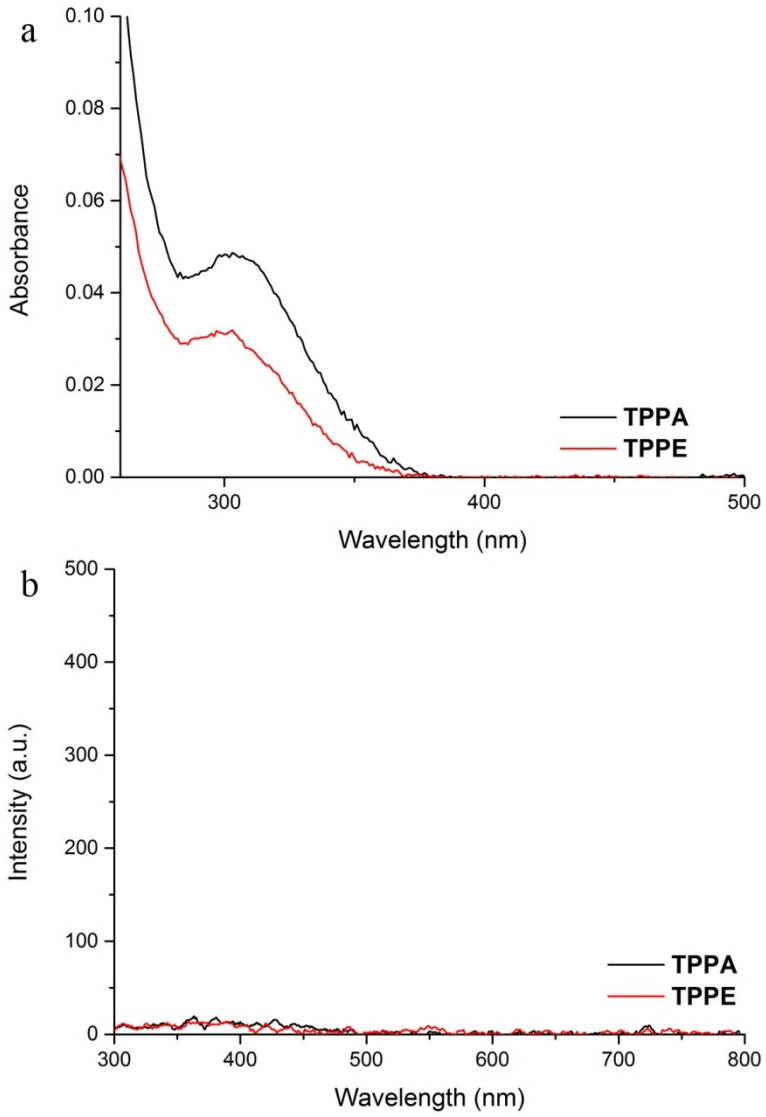


Fig. S8 (a) Absorption and (b) emission spectra of **TPPA** and **TPPE** in the mixtures of DMSO/H_2O (V/V = 1/9).

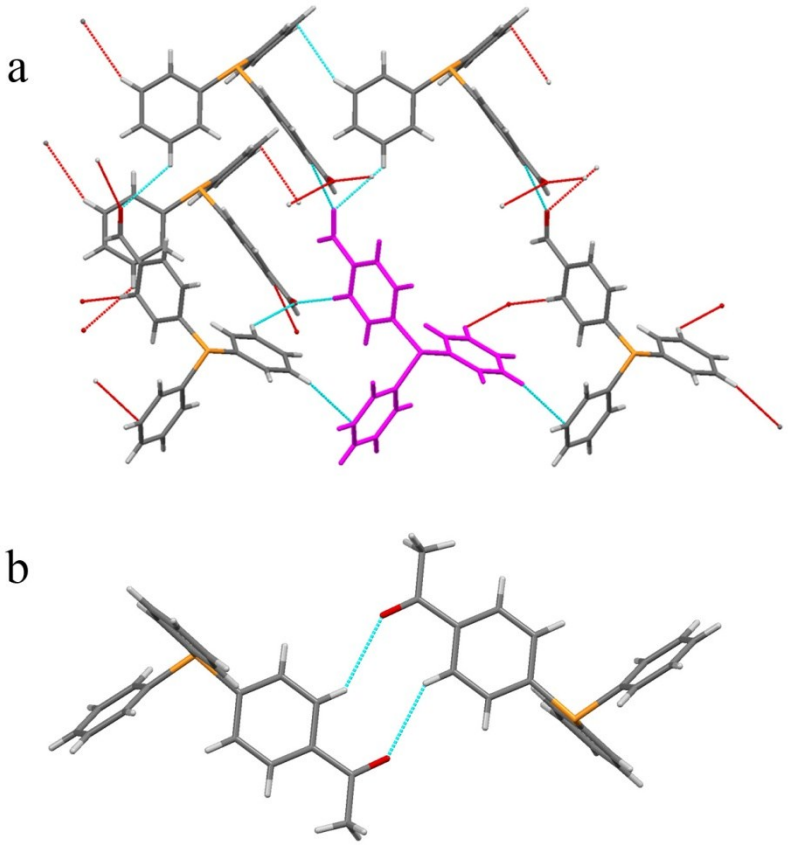


Fig. S9 Intermolecular interactions in **TPPA** (a) and **TPPE** (b).