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Supporting Information

The solvatochromism and aggregation-induced enhanced emission based on triphenylamine-propenone

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Experimental

Chemicals and instruments

All reagents and materials used for the synthesis were commercial available. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ^{o}C using a Bruker Avance 400 MHz spectrometer. Mass spectra were determined with a Microflex mass spectrograph. UV-vis absorption spectra were recorded on Varian Cary 50 spectrophotometer. Fluorescence measurements and quantum yields were carried out with an Edinburgh FLS920 fluorescence spectrometer. Single-crystal X-ray diffraction measurements were conducted on an Oxford Diffraction Gemini E diffractometer. The structures were solved by direct methods and refined by a full-matrix least-squares technique on F^2 using SHELX-97 programs.

Synthesis

4-(1-phenylprop-2-en-1-one-3-yl)triphenylamine (PhO-TPA)

At room temperature, a sodium hydroxide solution (0.5 M, 22 mL) was added with dropwise to the 50 mL methanol solution containing 4-(diphenylamino)benzaldehyde (2.73 g, 10 mmol) and acetophenone (1.20 g, 10 mmol). After complete addition, stirring was continued for 24 h. The precipitate was filtered and was chromatographed on the silica gel using petroleum/chloroform (1:15, v/v) as eluent, to give a light yellow solid 2.26 g. Yield: 60.2%.

^{1}H NMR (DMSO, 400 MHz, ppm) δ: 8.01 (d, 2H, J = 7.2 Hz), 7.60-7.67 (m, 4H), 7.57 (t, 1H, J = 7.2 Hz), 7.47 (t, 2H, J = 7.6 Hz), 7.29 (t, 4H, J = 8.0 Hz), 7.02-7.09 (m, 6H), 6.82 (d, 2H, J = 8.8 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 119.49, 121.59, 124.14, 125.49, 127.87, 128.40, 128.54, 129.52, 129.73, 132.45, 138.68, 144.70, 146.85, 150.21, 190.58.

MS (EI) m/z (%): 375.1 (M^+, 100).

Anal. Calcd for $C_{27}H_{21}NO$: C, 86.37; H, 5.64; N, 3.73. Found: C, 86.63; H, 5.47; N, 4.03.

4-(1-(Pyridin-2-yl)prop-2-en-1-one-3-yl)triphenylamine (PyO-TPA)

The compound PyO-TPA was prepared in a similar procedure as that used for PhO-TPA from 4-(diphenylamino)benzaldehyde and 2-acetylpyridine. Column chromatography (silica gel, chloroform) gave an orange solid in 66.4% yield.

^{1}H NMR (DMSO, 400 MHz, ppm) δ: 8.78 (d, J = 4.4 Hz, 1H), 8.04-8.13 (m, 3H), 7.79 (d , J= 16.0 Hz, 1H), 7.67-7.71 (m, 3H), 7.36-7.40 (m, 4H), 7.12-7.18 (m, 6H), 6.92 (d, J = 8.8 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 118.25, 121.51, 122.84, 124.09, 125.49, 126.61, 128.28, 129.49, 130.15, 136.93, 144.68, 146.88, 148.78, 150.21, 154.66, 189.33.

MS (EI) m/z (%): 376.2 (M^+, 100).

Anal. Calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44. Found: C, 82.68; H, 5.44; N, 7.12.

4,4′,4″-(Tri(1-(pyridin-2-yl)prop-2-en-1-one-3-yl))triphenylamine (TPyO-

TPA)

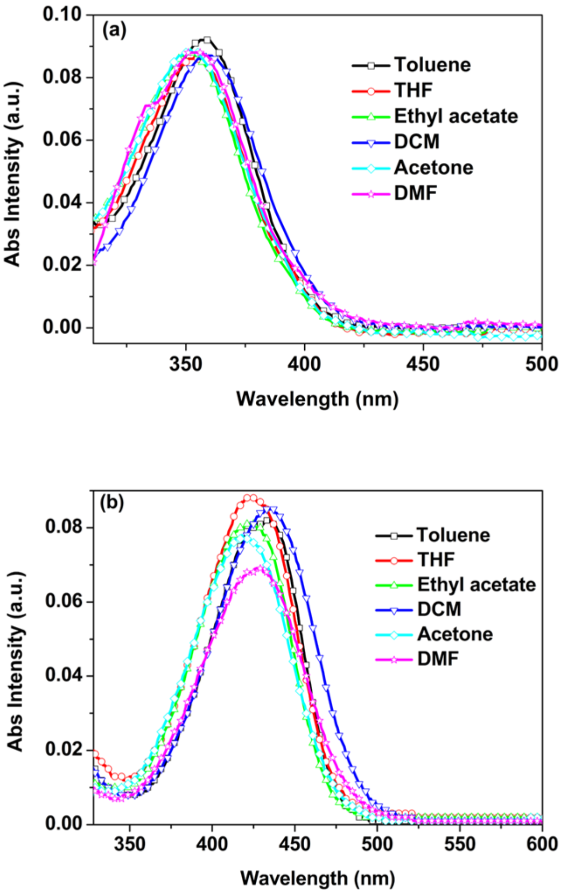
The compound TPyO-TPA was prepared in a similar procedure as that used for PhO-TPA from tri(4-formylphenyl)phenylamine and 2-acetylpyridine. Column chromatography (silica gel, chloroform) gave TPyO-TPA as a red solid in 52.3% yield.

^{1}H NMR (DMSO, 400 MHz, ppm) δ: 8.80 (d, J = 4.4 Hz, 3H), 8.31 (s, 1H), 8.24 (s, 1H), 8.19 (s, 1H), 8.04-8.13 (m, 6H), 7.83-7.87 (m, 9H), 7.68-7.71 (m, 3H), 7.18 (d, J = 8.8 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 119.76, 122.92, 124.41, 126.81, 130.31, 130.80, 137.01, 143.96, 148.49, 148.84, 154.40, 189.33.

MS (EI) m/z (%): 638.4 (M^+, 100).

Anal. Calcd for $C_{42}H_{30}N_4O_3$: C, 78.98; H, 4.73; N, 8.77. Found: C, 79.30; H, 4.70; N, 7.91.



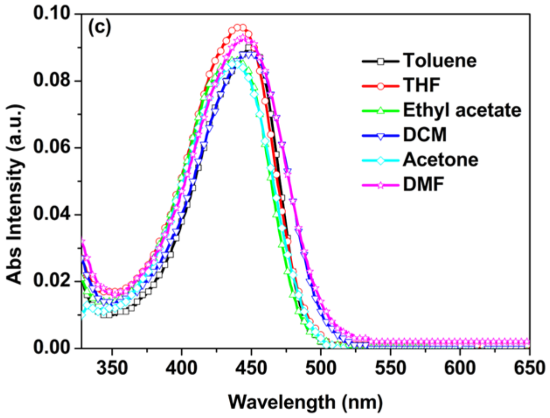
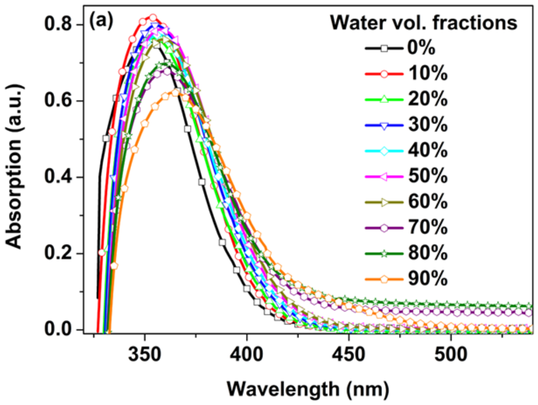
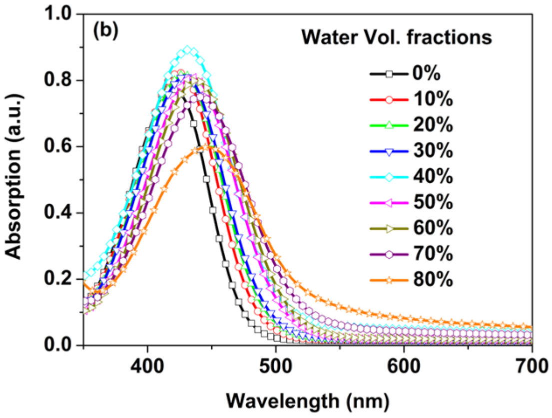


Figure S1 UV-visible absorption spectra of PhO-TPA (a), PyO-TPA (b), and TPyO-TPA in different polar solvents (2.5 × 10^{-6} M).





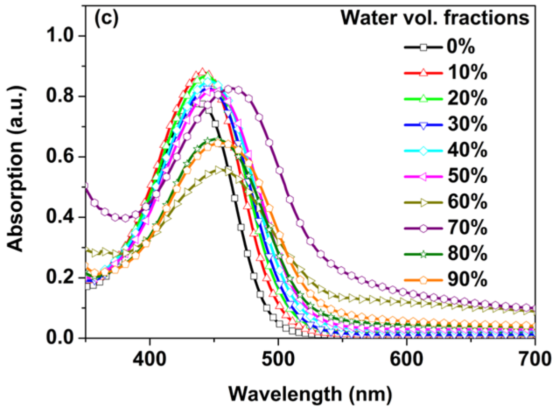


Figure S2 UV–visible absorption spectra of PhO-TPA (a), PyO-TPA (b), and TPyO-TPA (c) (2.0 × 10^{-5} mol L^{-1}) in acetone/water mixtures with different volume fractions of water.

Table S1. Crystal data and structure refinement of PhO-TPA and PyO-TPA.

Compound	PhO-TPA	PyO-TPA
Formula	$C_{27}H_{21}NO$	$C_{26}H_{20}N_2O$
Formula weight	375.45	376.44
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 12.1179(7)	a = 12.0342(3)
	b = 17.3412(10)	b= 17.4069(4)
	c = 9.5281(6)	c = 9.4392(2)
	α = 90.00	α = 90.00
	β = 91.210(4)	β = 91.757(2)
	γ = 90.00	γ = 90.00
Volume (Å^3), Z	2001.78(19), 4	1976.38(8), 4
Calculated density (Mgm^{-3})	1.246	1.265
Absorption coefficient (mm^{-1})	0.075	0.078
F(000)	792	792
θ range for data collection (°)	2.89 to 26.37	1.69 to 25.00
Limiting indices	$-15 \leq h \leq 13$	$-14 \leq h \leq 14$

	$-21 \le k \le 21$	$-17 \le k \le 20$
	$-10 \le l \le 11$	$-11 \le l \le 11$
Reflections collected / unique	10334 / 4060	15074 / 3488
	[R(int) = 0.0322]	[R(int) = 0.0458]
Absorption correction	multi-scan	multi-scan
Data / restraints / parameters	4060 / 0 / 263	3488 / 0 / 263
Goodness-of-fit on F^2	0.981	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0461$, $wR_2 = 0.0944$	$R_1 = 0.0567$, $wR_2 = 0.1507$
R indices (all data)	$R_1 = 0.0905$, $wR_2 = 0.1142$	$R_1 = 0.0960$, $wR_2 = 0.1864$
Largest diff. peak and hole (e·Å^3)	0.131 and -0.122	0.189 and -0.175
CCDC reference number	933078	933077

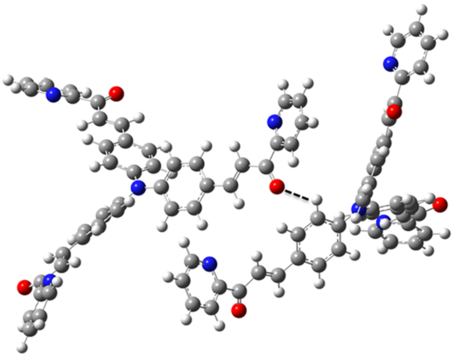


Fig. S3 The calculated packing structure and the interaction of TPyO-TPA for dimer (b).

The calculated packing structure and the interaction of TPyO-TPA for dimer (b) are shown in Fig. S3. In the packing structure of dimer (b), the stacking forces are the intermolecular C-H···O interaction, without intermolecular π-π interactions. The interaction distance of three hydrogen bonds is 2.44(4) Å. In order to further analyze the intermolecular interactions, the geometry of dimer (b) obtained from B3LYP/6-311+G**was used to perform NBO analysis. In this packing structure, the origin of the interaction between two TPyO-TPA is the electron donation from the oxygen lone pair into the anti-bonding orbital of the C-H bond. The charge transfer energy $E^{(2)}$ are 1.18 kcal/mol. There are no significant interactions between other groups.