

Supporting Information (SI)

Solvation Controlled Excited-State Dynamics in a Donor-Acceptor Phenazine-Imidazole Derivative

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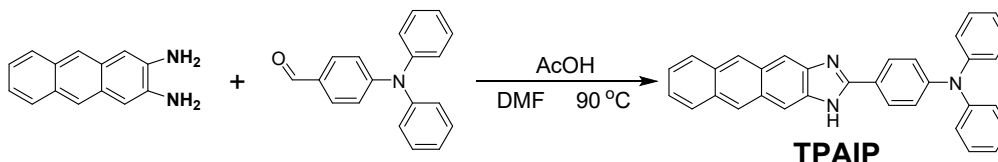
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1. Materials and methods

All solvents were dried according to standard procedures and all of them were degassed under N₂ for 30 minutes before use. ¹H and ¹³C NMR spectra were recorded on Bruker 400MHz Spectrometer (¹H: 400 MHz; ¹³C: 100 MHz) at 298 K. The ¹H and ¹³C NMR chemical shifts are reported relative to the residual solvent signals (δ 0.0). Electrospray ionization (ESI) mass spectra were recorded with a Waters Synapt G2 mass spectrometer. UV-vis spectra were recorded in a quartz cell (light path 10 mm) on a Cary 50Bio UV-Visible spectrophotometer. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Cary Eclipse fluorescence spectrophotometer. DLS measurements were performed under a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U. K.) with a He-Ne laser (633 nm, 4 mW). For the single crystals, the data sets were treated with the SQUEEZE program to remove highly disordered solvent molecules. The crystallographic formulae include the number of solvent molecules was suggested by the SQUEEZE program. All the femtosecond transient absorption spectroscopy was acquired with a typical transmission pump-probe (UV/vis pump-broadband supercontinuum probe) instrument. In this arrangement, a Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra Physics, Inc.) was employed to produce laser pulses (6 mJ, 1 kHz) with a pulse width of 80 fs and center wavelength at 800 nm. The output laser was split into several laser beams, one of which was used to generate wavelength-tunable light serving as the pump laser for TAS via a downstream TOPAS instrument. The pump laser was further chopped with a 500 Hz mechanical chopper. Another laser beam propagated through an optical delay line (0-8 ns) and was then focused into a CaF₂ crystal to produce white light continuum, which serves as the probe light in the fs-TA. For the measurements, both solution and film samples were excited at 500 nm and then probe with a WLC pulse ranging from 350 to 700 nm. The instrument response function (IRF) of this system was determined to be ~120 fs by measuring solvent responses under the same experimental conditions.

2. Synthetic experimental details and characterizations of new compounds

Scheme S1. The synthetic procedure for the **TPAIP**.



Synthesis of TPAIP. A mixture of 2,3-diamino-phenazine (203.2 mg, 1.0 mmol), 4-(N,N-5 Diphenylamino)benzaldehyde (800 mg, 3 mmol), 1.0 mL acetic acid (AcOH) and N,N-dimethylformamide (DMF) were magnetically stirred and heated at 90 °C for 12 h. After cooling to room temperature, the yellow precipitate was filtrated, washed with hot absolute ethanol three times, then recrystallized with DMF-H₂O to get yellow powdery product **TPAIP** (279.6 mg, 0.6 mmol) in 60% yield, ¹H-NMR (DMSO-*d*₆, 400 MHz) δ 13.24 (s 1H, NH), 8.40 (s 1H, ArH), 8.19 (d, $J = 15.8$ Hz, 10 5H), 7.87 (s 2H, ArH), 7.43 (s 4H, ArH), 7.20 (d $J = 7.7$ Hz, 6H, ArH), 7.05 (s 2H, ArH). ¹³C-NMR (DMSO-*d*₆, 100 MHz) δ 130.41, 129.68, 126.30, 125.31, 120.42. ESI-MS m/z : Calcd. for C₃₁H₂₁N₅, 463.54; Found, 464.18.

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2. ACQ effect of TPAIP.

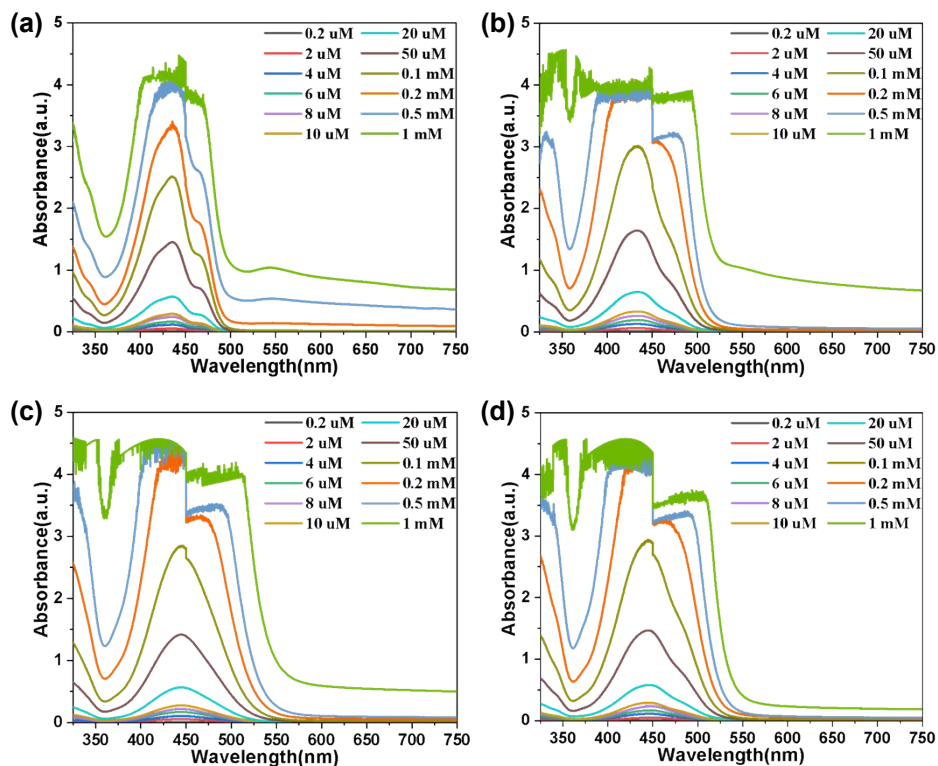


Figure S1. The UV absorption of TPAIP (0.2 μM , 2.0 μM , 4.0 μM , 6.0 μM , 8.0 μM , 10 μM , 0.02 mM, 0.05 mM, 0.1 mM, 0.2 mM, 0.5 mM, 1.0 mM) in toluene (a), acetone (b), methanol (c) and 5 dimethyl sulfoxide solvents.

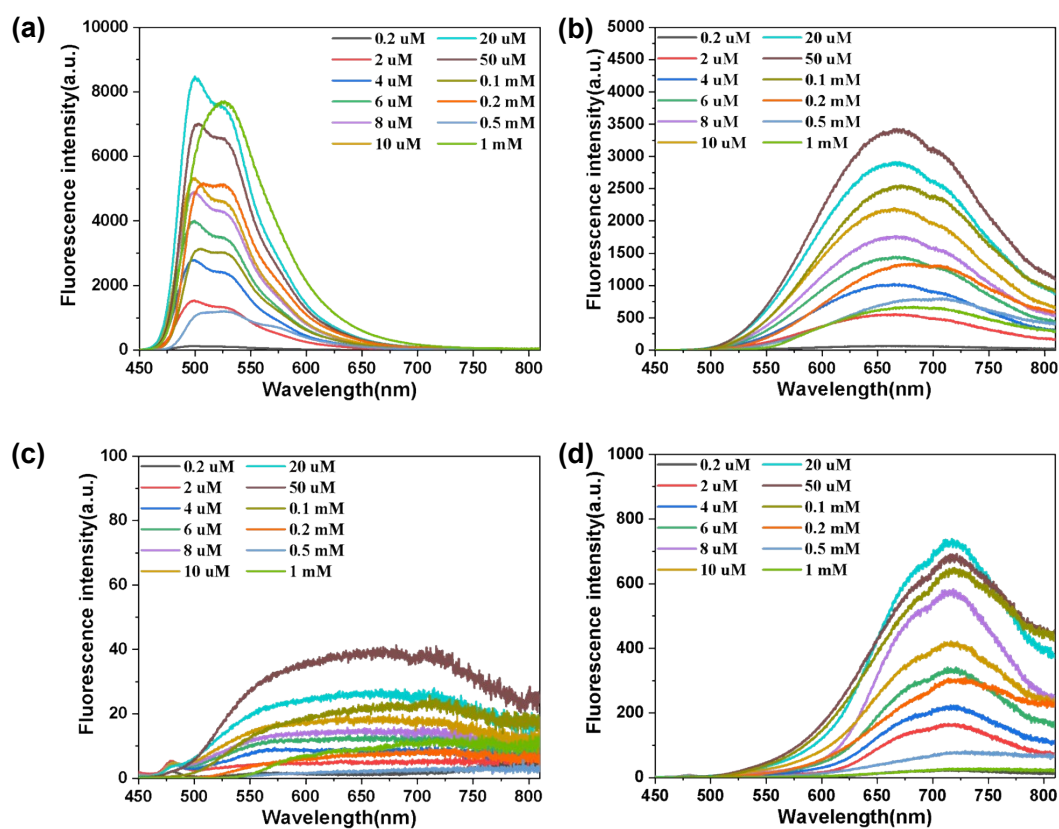


Figure S2. The fluorescence spectra of **TPAIP** (0.2 μM , 2.0 μM , 4.0 μM , 6.0 μM , 8.0 μM , 10 μM , 0.02 mM, 0.05 mM, 0.1 mM, 0.2 mM, 0.5 mM, 1.0 mM) in toluene (a), acetone (b), methanol (c) and dimethyl sulfoxide solvents ($\lambda_{\text{ex}} = 435 \text{ nm}$).

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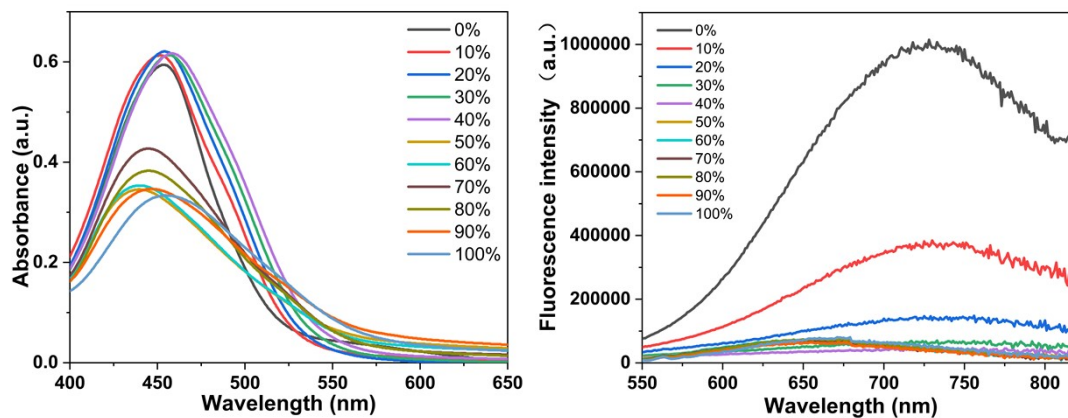


Figure S3. The UV absorption (a) and fluorescence spectra (b) of **TPAIP** ($2 \times 10^{-5} \text{ mol/L}$) in dimethyl sulfoxide/water mixed solvents with 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100% of 10 water content.

3. Dynamic Light Scattering measurement of the TPAIP

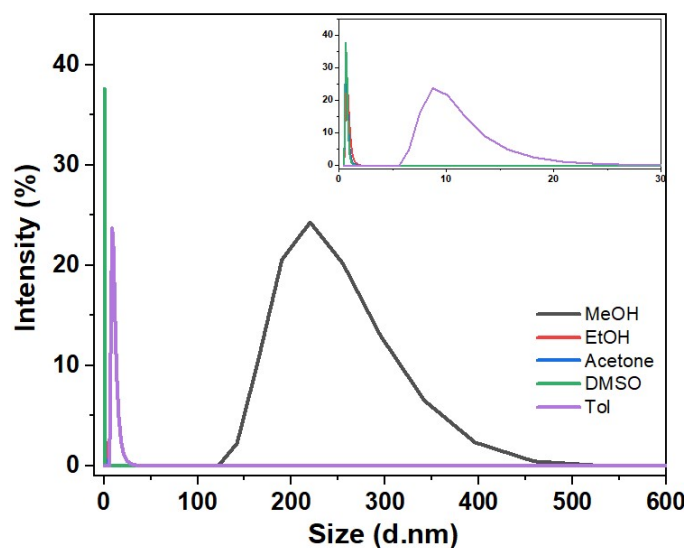


Figure S4. Dynamic Light Scattering: size distributions of TPAIP (0.02 mM) in methanol, ethanol, 5 acetone, dimethyl sulfoxide and toluene.

10 6. Additional experimental and computational results

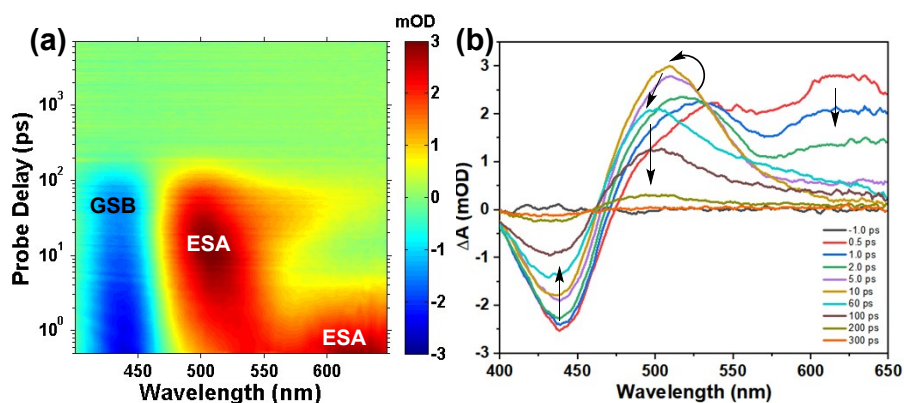


Figure S5. Femtosecond broadband transient absorption spectra of the TAS data (0.02 mM) matrix after 380 nm excitation (a) and time evolution of the TA spectra (b) of TPAIP in ethanol solvent.

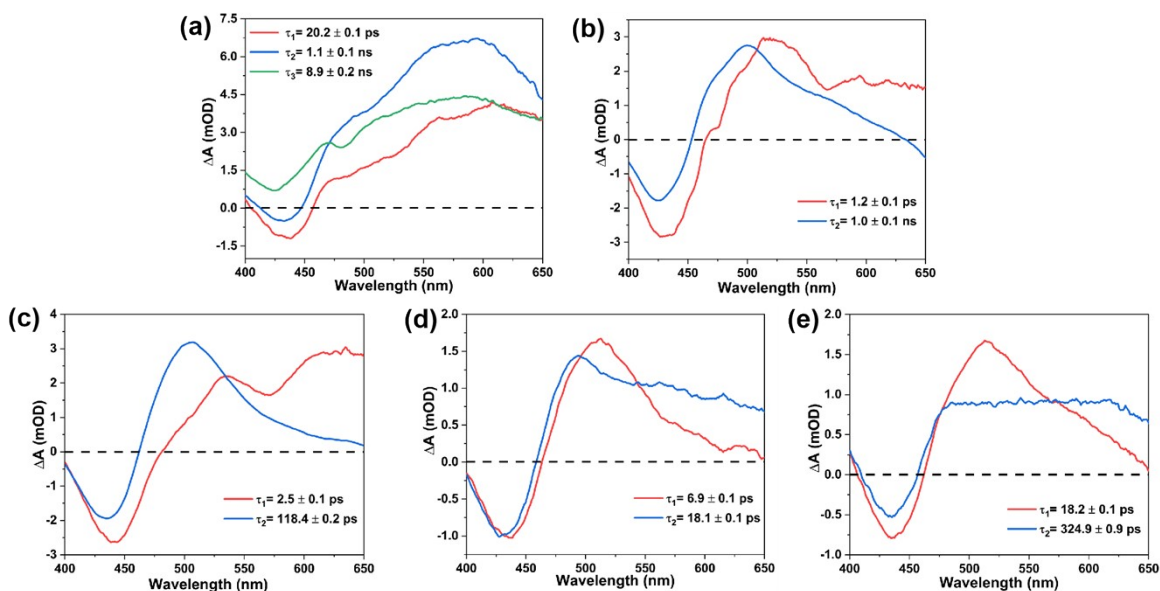
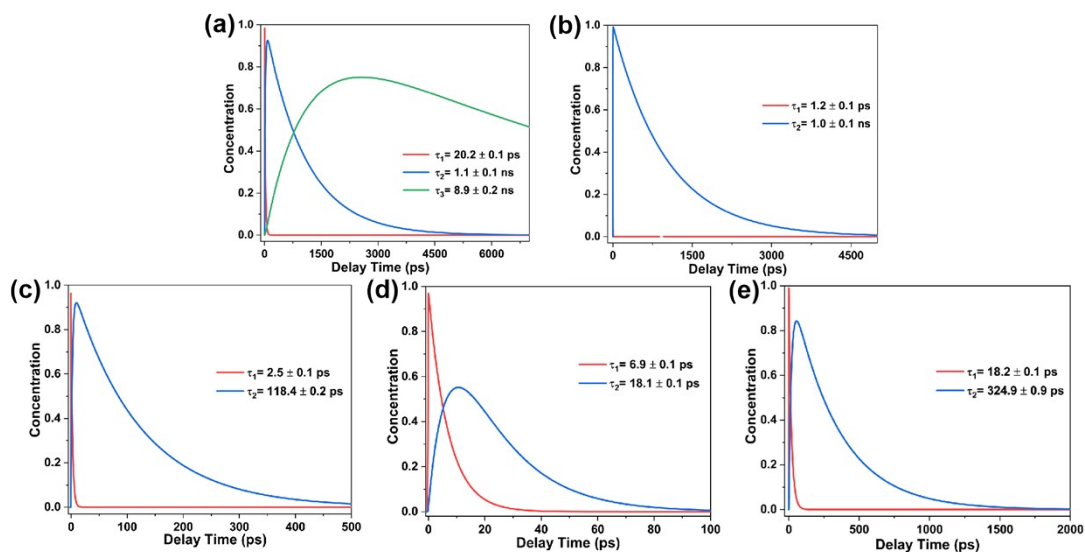


Figure S6. The species-associated difference spectra (SADS) obtained from global fitting in in different viscous solvents (a, toluene; b, acetone; c, ethanol; d, methanol; e, dimethyl sulfoxide).



5 Figure S7. Concentrations of the SADS components as a function of time in different viscous solvents (a, toluene; b, acetone; c, ethanol; d, methanol; e, dimethyl sulfoxide).

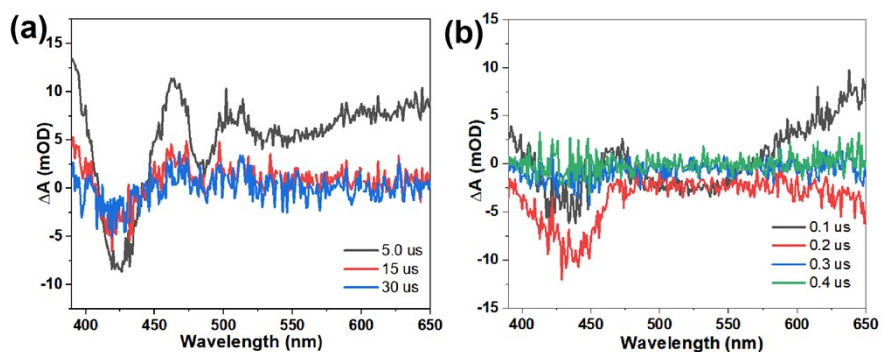


Figure S8. Nano-microsecond broadband TA spectra of **TPAIP** under deaerated (a) and aerobic (b) conditions in toluene.

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6. Molecular strcutres characterization.

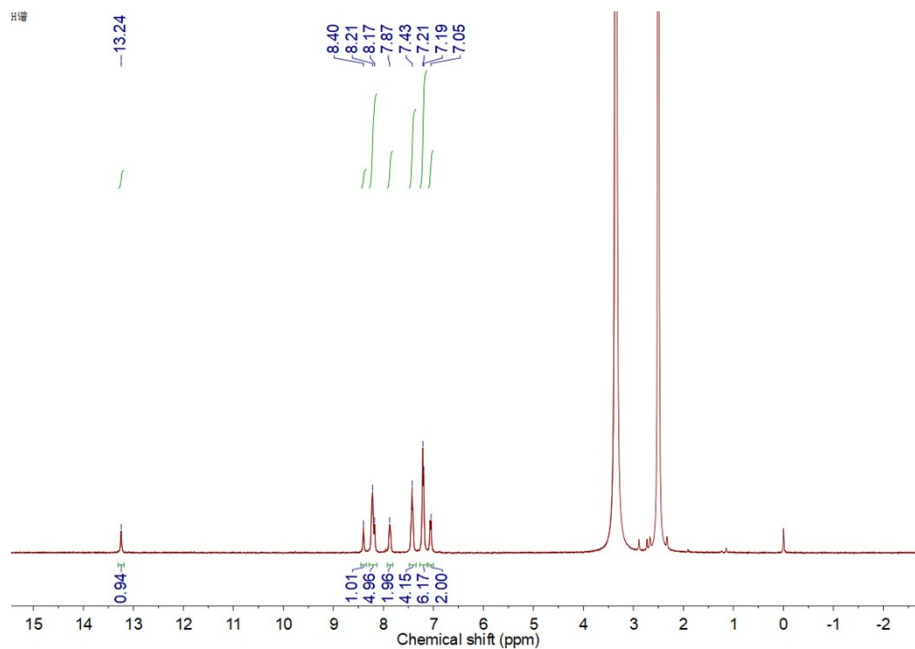


Figure S9. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 298K) of **TPAIP**.

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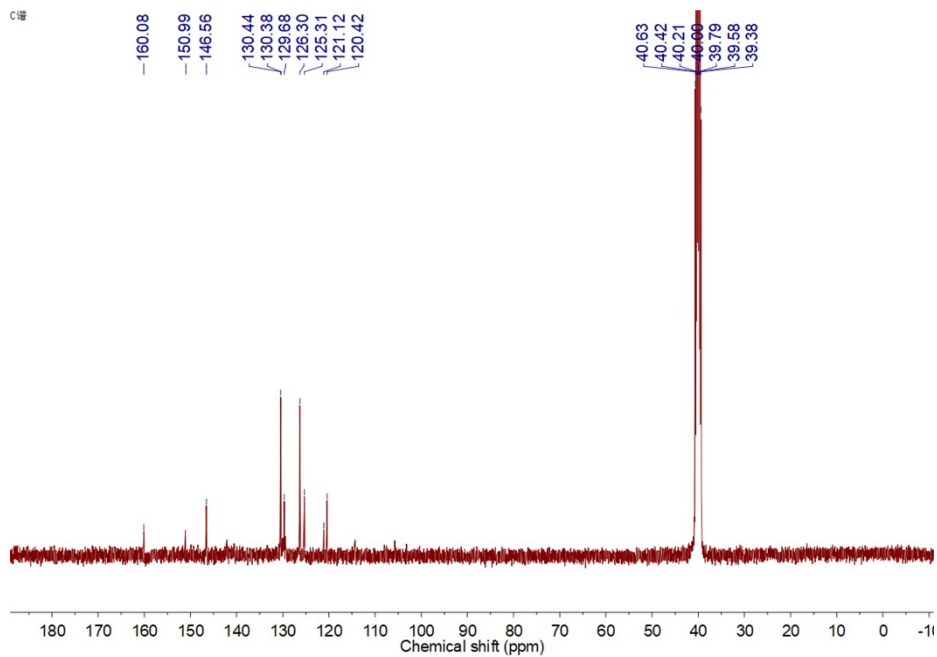


Figure S10. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆, 298K) of TPAIP.

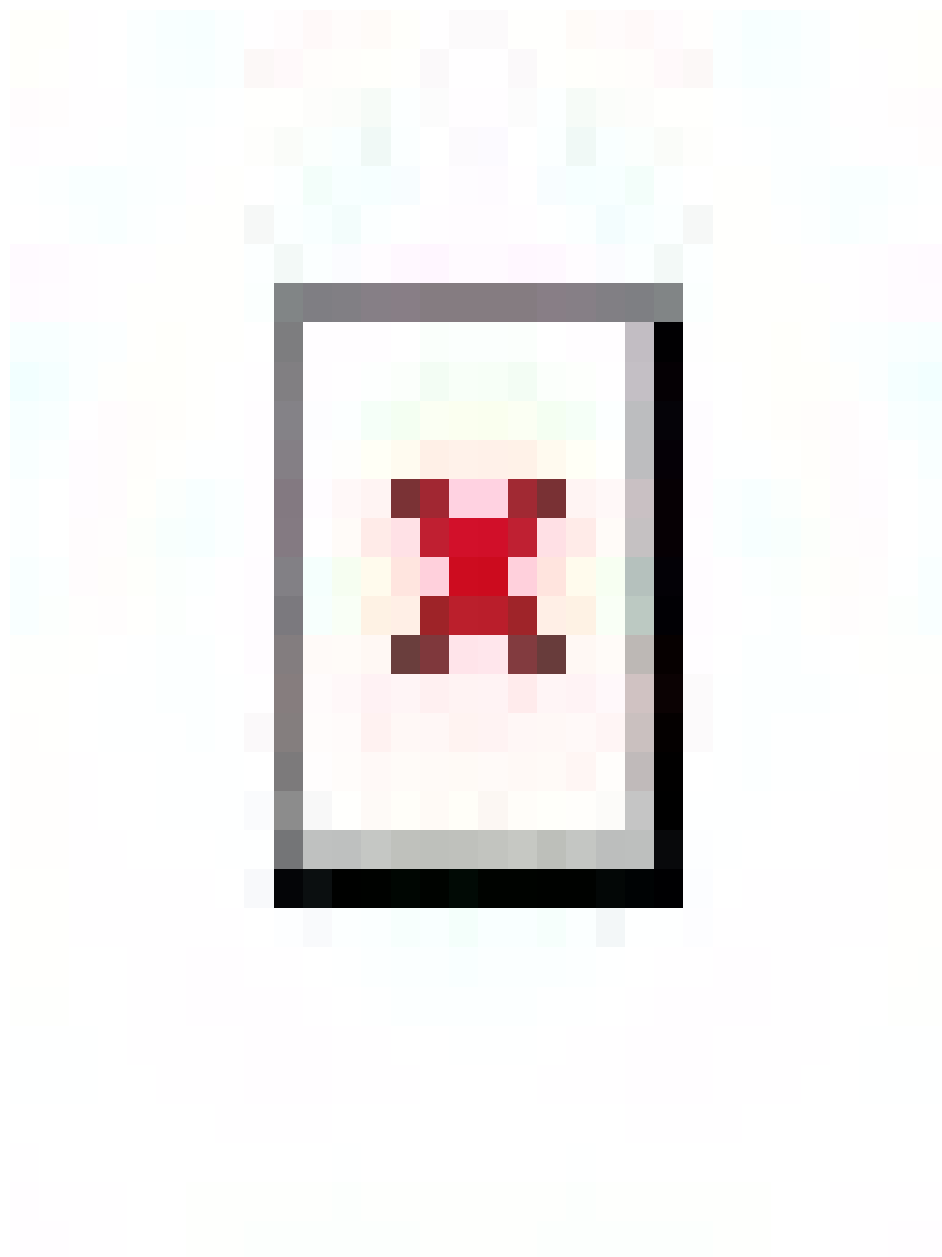


Figure S11. The ESI-MS of TPAIP.