Electronic Supplementary Information:

Luminescent metal-organic gels with tetraphenylethylene moieties: porosity and aggregation-induced emission

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Experimental Section

Materials and methods

All chemical reagents were commercially available and used as received unless otherwise stated. Tetrakis(4-carboxyphenyl)ethylene (H_4TCPE) was synthesized according to the reported procedures.[1] Scanning electron micrographs were recorded on a FEI Quanta 400F thermal field emission environmental scanning electron microscope. Samples were prepared by dispersing in ethanol upon sonication and placing on top of aluminum foil. Transmission electron micrographs were conducted on a JEOL JEM-2010HR microscope. Samples for TEM observations were prepared by dispersing the gels in ethanol by sonication and then immersing a carbon-coated copper grid. IR spectra were recorded on a Nicolet/Nexus-670 FT-IR spectrometer with KBr pellets in the range 4000-450 cm^{-1}. X-ray Photoelectron spectra were recorded on a Thermo Fisher Scientific ESCALAB 250 spectrometer with X-ray monochromatised Al Kα radiation. TG analysis was performed on a NETZSCH TG 209 thermal analyzer at a heating rate of $10^{o}C\ min^{-1}$ in nitrogen at a flow rate of 20 $mL\ min^{-1}$. N_2 adsorption-desorption isotherms were measured at 77 K on a Quantachrome Autosorb-iQ analyzer. The aerogels were degassed at $80^{o}C$ for 16 h to remove solvent molecules prior to analysis. UV-vis absorption spectra were recorded using a Shimadzu UV-2400 spectrophotometer. The photoluminescence spectra, life times and quantum yields were measured on EDINBURGH FLSP920 combined fluorescence life time and stead states spectrometer. The quantum yields were determined with quinine sulfate as standard reference, and calculated by using Φ_x =

$\Phi_{std}(F_s/A_s)/(F_{std}/A_{std})$, where A is the absorbancy and F is the area of the emission peak with the subscript x and std representing the gel and the standard, respectively.

Preparation of gels

Typical procedure: A suspension of H_4TCPE (7.6 mg, 0.015 mmol) in EtOH (0.5 mL) was mixed with a solution of $Al(NO_3)_3 \cdot 9H_2O$ (7.5 mg, 0.02 mmol) in EtOH (0.5 mL) to give a clear solution upon sonication. The mixture was allowed to stand in a closed vial at 80°C. A transparent Al-TCPE gel was obtained after 0.5 h.

Microanalysis of Al-TCPE aerogel: Found (calculated) for $C_{100}H_{92}N_2O_{53}Al_4$ ($Al_4(TCPE)_3 \cdot EtOH \cdot 22H_2O \cdot 2HNO_3$) C 50.46(50.46) H 4.35(4.60) N 1.15(1.27)%; Microanalysis of Cr-TCPE aerogel: Found (calculated) for $C_{120}H_{96}N_2O_{59}Cr_4$ ($Cr_4(TCPE)_3 \cdot 3EtOH \cdot 26H_2O \cdot 2HNO_3$) C 46.64(46.99) H 5.01(4.93) N 1.09(1.14)%; Microanalysis of Fe-TCPE aerogel: Found (calculated) for $C_{96}H_{103.5}N_{1.5}O_{49.5}Fe_4$ ($Fe_4(TCPE)_3 \cdot 3EtOH \cdot 18H_2O \cdot 1.5HNO_3$) C 50.14(50.27) H 4.38(4.55) N 0.81(0.92)%.

Detection of PA. The above Al-TCPE gel was dispersed in water in aid of sonication to give a 10 mL gel (1.5 mmol L^{-1} based on TCPE). Fluorescence quenching titrations were carried out by gradually adding aqueous solution of PA (1.0×10^{-2} mol L^{-1}) into 3.00 mL of the gel dispersed medium in an incremental fashion. Their corresponding fluorescence emission spectra were recorded excited at 394 nm.

Fluorescence quenching titrations

The Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE). Various aromatic compounds, benzoic acid, nitrobenzene, 2,4-dinitro-chlorobenzene, chlorobenzene, bromobenzene, 3,5-dinitro-benzoic acid and nitrotoluene, were used as quenchers to check the selectivity of the Al-TCPE gel. All titrations were carried out by gradually adding quenchers (1.0×10^{-2} mol/L in EtOH, 100 μL) into 3.00 mL of the gel dispersed medium in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at RT. Relative fluorescence intensities were

measured for dispersed gel in ethanol and various quenchers in ethanol. The fluorescence efficiency was calculated by $[(I_0-I)/I_0]\times100\%$, where I_0 is the initial fluorescence intensity.

Paper sensor for visual detection of PA

The above Al-TCPE gel was dispersed in EtOH upon sonication to give a 10 mL dispersed medium (1.5 mmol L^{-1} based on TCPE). A piece of filter paper (~1 cm in size) was immersed in the dispersion for 30 min, and then removed from the mixture and dried at 50^{o}C for 10 min. The handwriting with different concentration of PA aqueous solution as ink was put on the filter paper. The paper with handwriting was imaged under 365-nm radiation with a UV lamp.

1) N. B. Shustova, B. D. McCarthy and M. Dincă, *J. Am. Chem. Soc.*, 2011, **133**, 20126–20129.

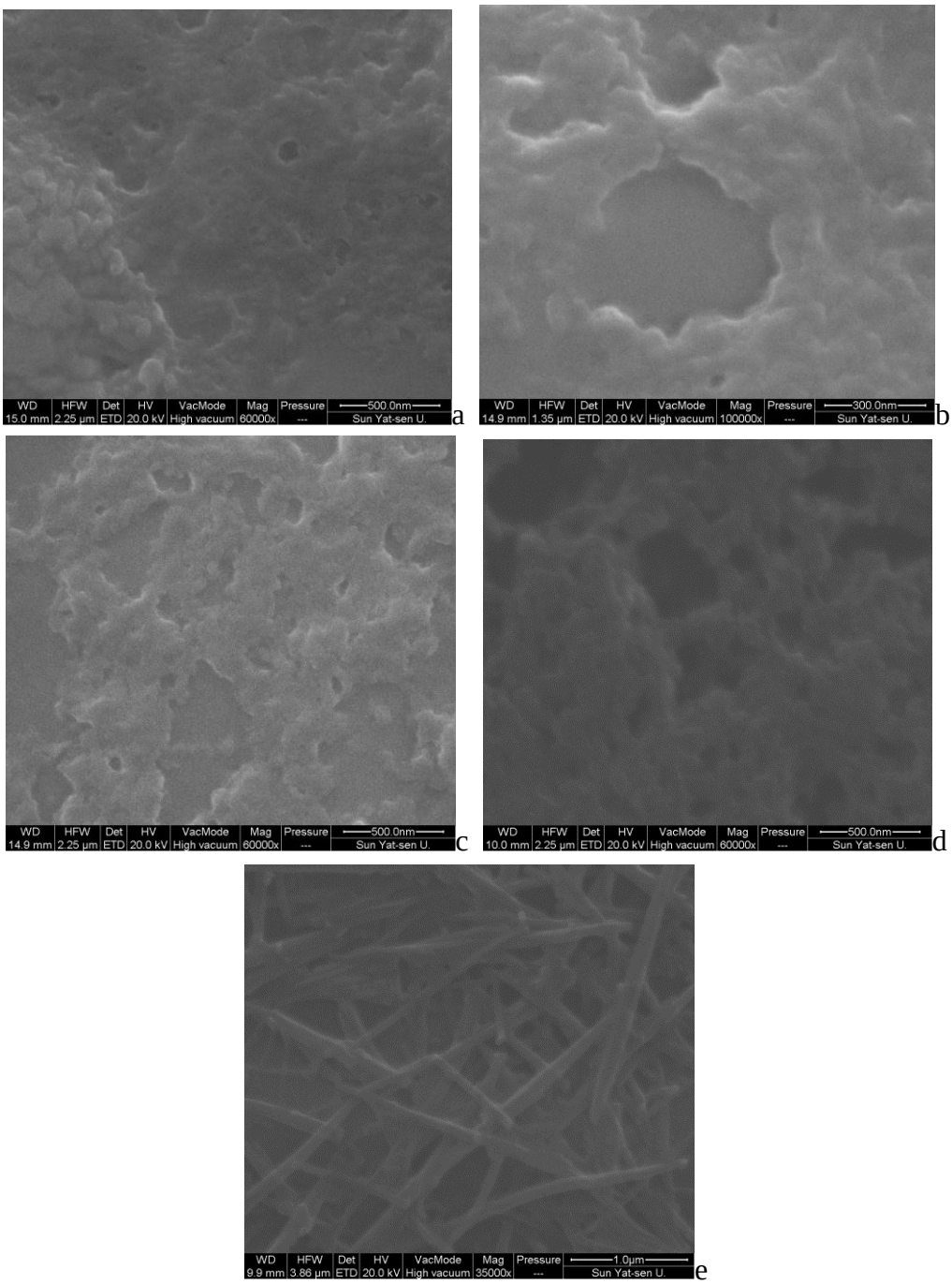

Fig. S1 SEM images of gels a) Al-TCPE, b) Cr-TCPE, c) Fe-TCPE, d) Ga-TCPE and e) In-TCPE.

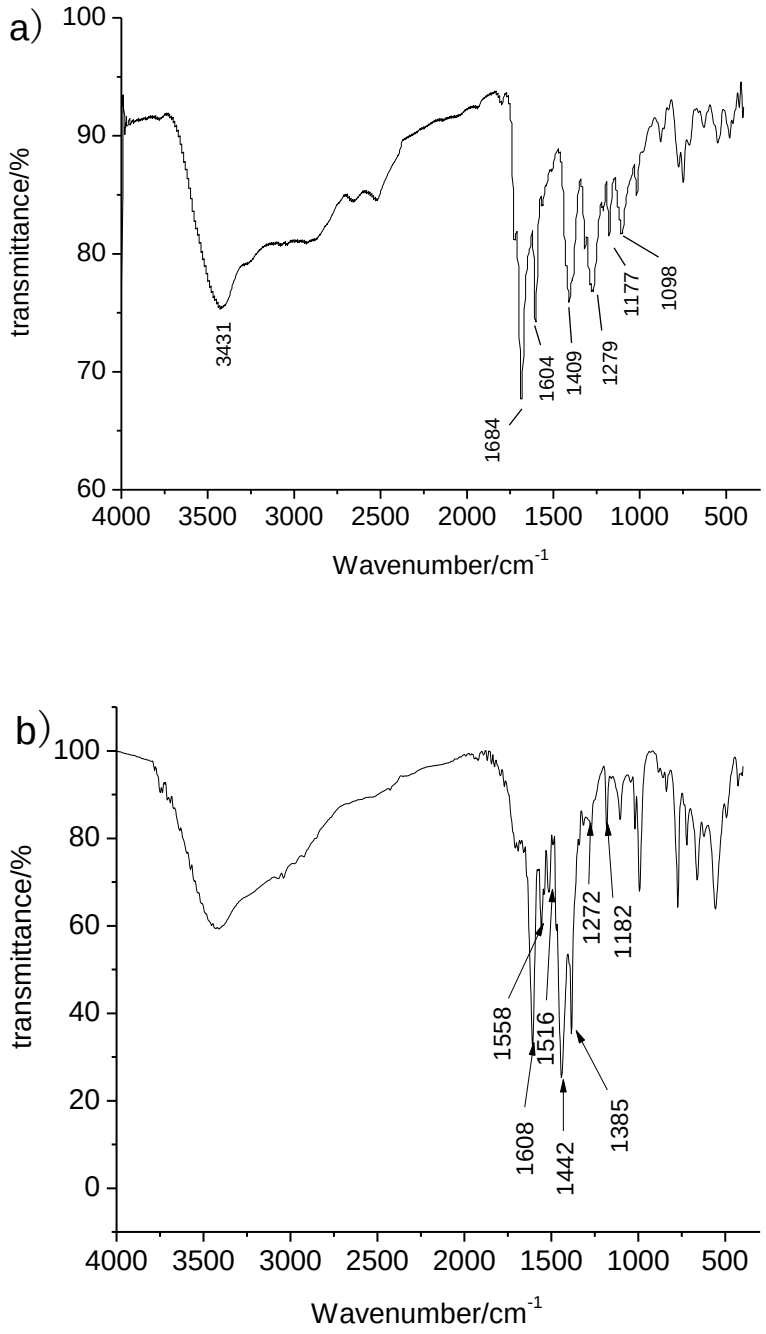

Fig. S2 FT-IR spectra of a) H_4TCPE and b) Al-TCPE aerogel (KBr pellets).

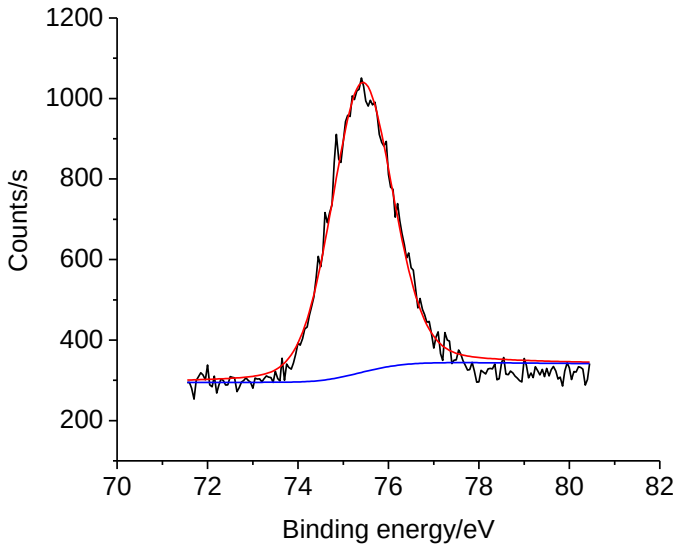

Fig. S3 XPS Al 2p and deconvoluted spectra of Al-TCPE xerogel.

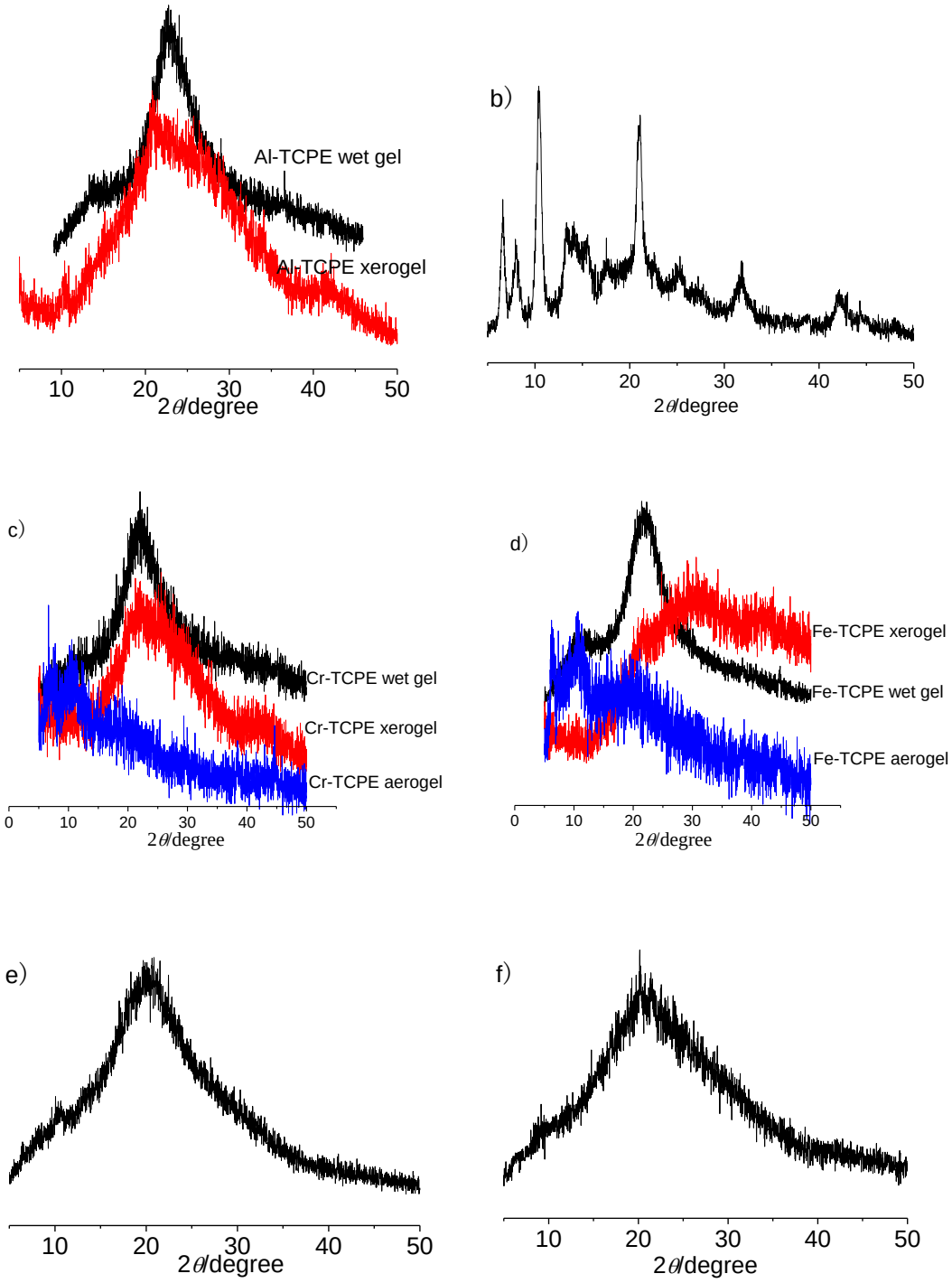

Fig. S4 Powder X-ray diffraction patterns of a) Al-TCPE wet gel, b) Al-TCPE aerogel, c) Cr-TCPE wet gel, xerogel, and aerogel, d) Fe-TCPE wet gel, xerogel, and aerogel, e) Ga-TCPE wet gel, and f) In-TCPE wet gel.

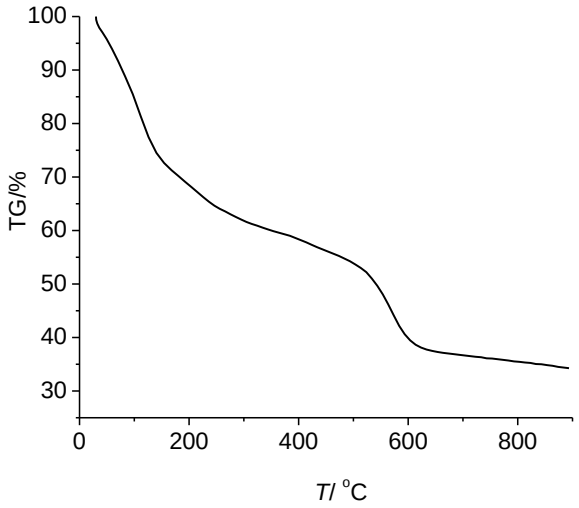

Fig. S5 TGA curve for Al-TCPE xerogel.

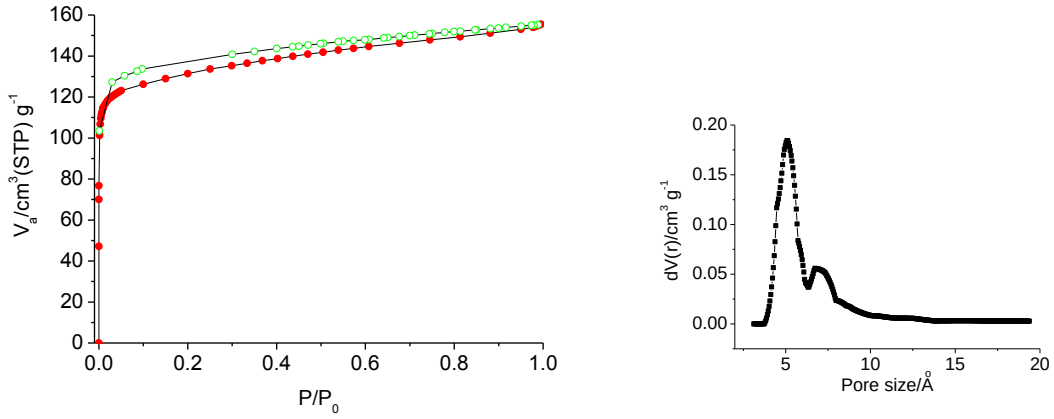

Fig. S6 N_2 adsorption-desorption isotherms at 77 K and HK micropore distribution of the Fe-TCPE aerogel (0.015 mol L^{-1} based on TCPE). BET surface area: 512 m^2 g^{-1}; total pore volume: 0.27 cm^3 g^{-1}.

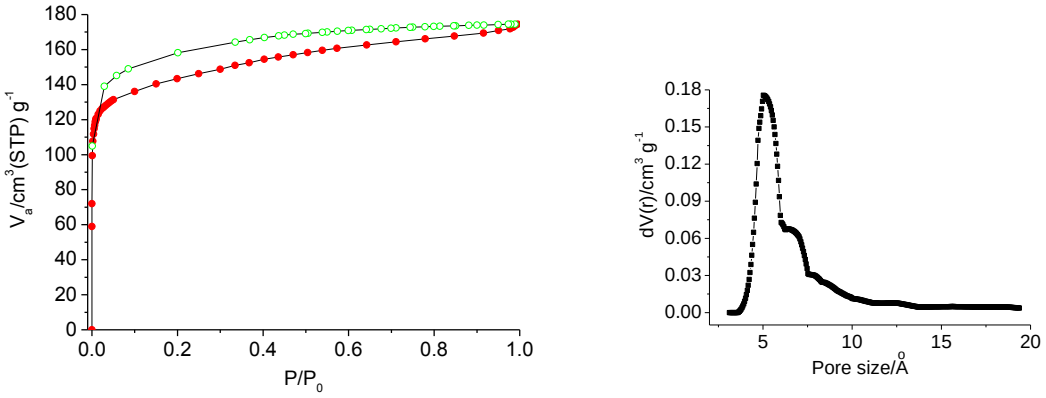

Fig. S7 N_2 adsorption-desorption isotherms at 77 K and HK micropore distribution of the Cr-TCPE aerogel (0.015 mol L^{-1} based on TCPE). BET surface area: 546 m^2 g^{-1}; total pore volume: 0.24 cm^3 g^{-1}.

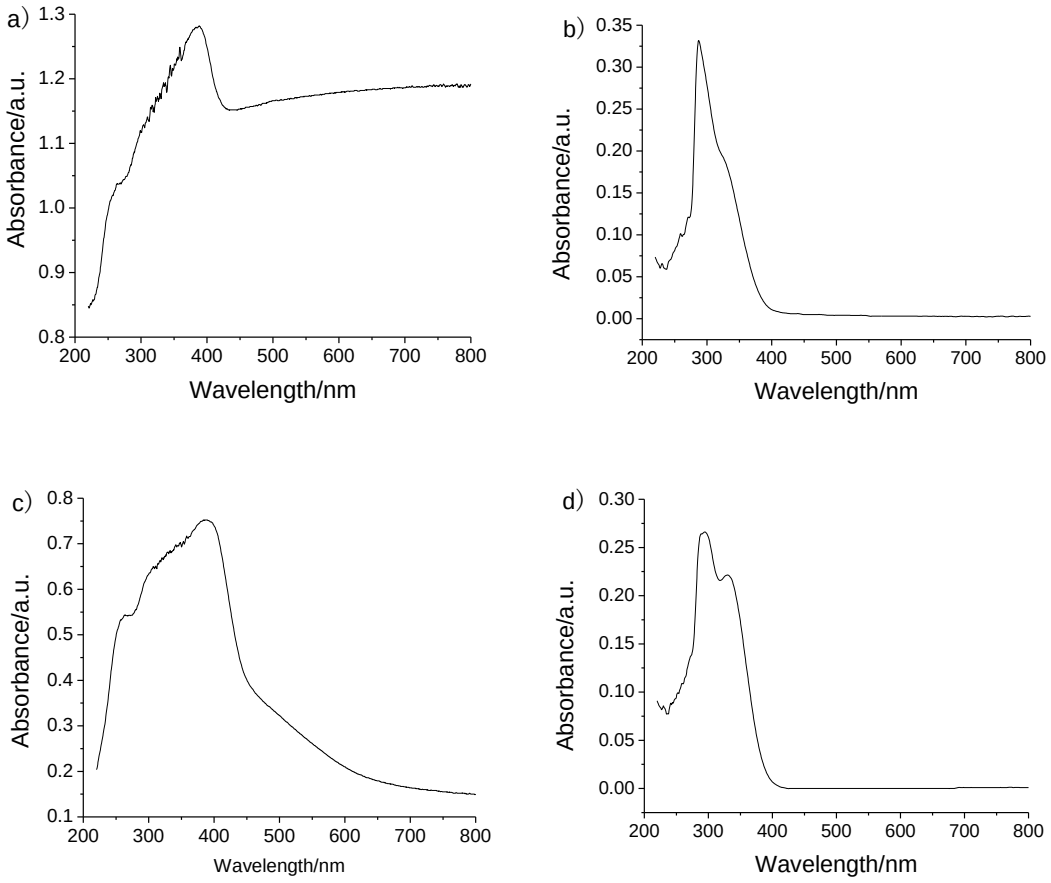

Fig. S8 UV-vis absorption spectra of a) Al-TCPE gel, b) Al-TCPE gel dispersed in EtOH (1.5×10^{-3} mol L^{-1} based on TCPE), c) H_4TCPE in the solid state, and d) H_4TCPE in EtOH (1.5×10^{-3} mol L^{-1}).

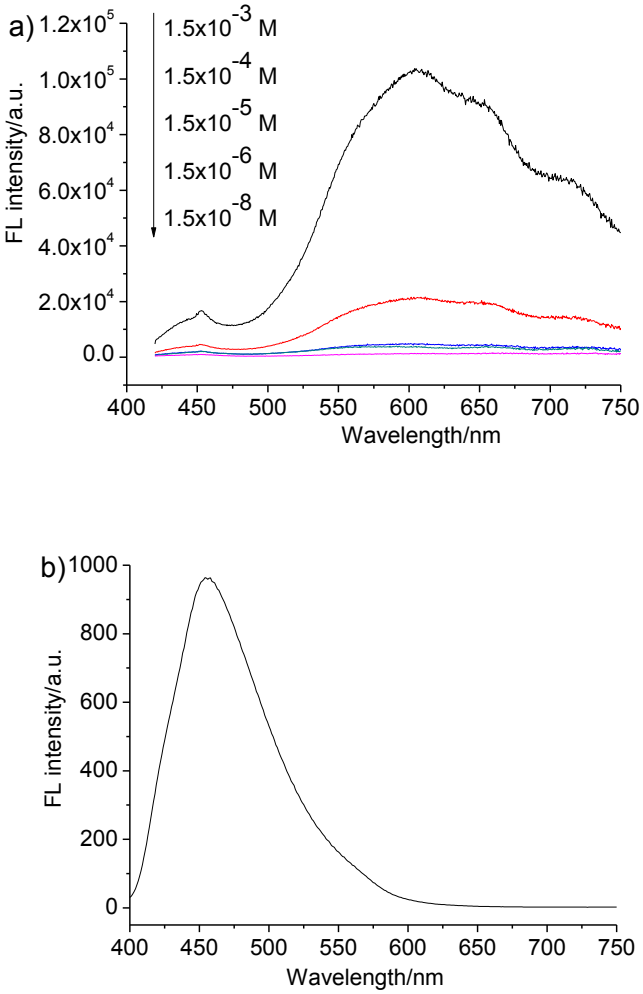

Fig. S9 Fluorescence spectra of H_4TCPE a) in EtOH with different concentration (λ_{ex} = 403 nm) showing AIE feature and b) in the solid state (λ_{ex} = 385 nm).

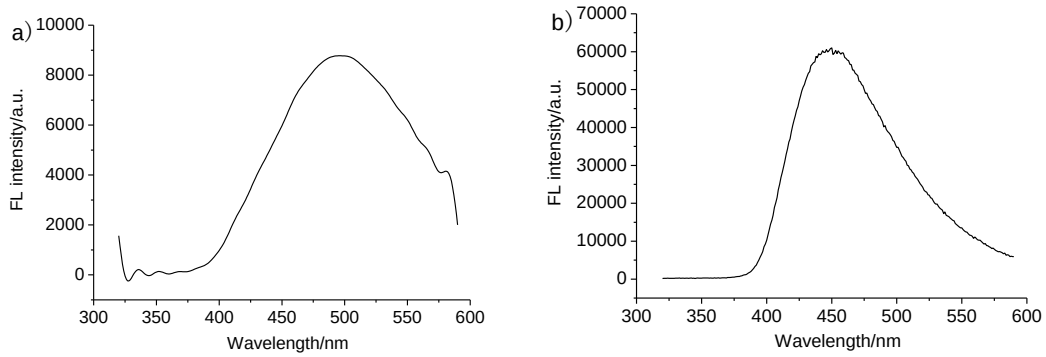

Fig. S10 Fluorescence spectra of Ga-TCPE (λ_{ex} = 300 nm) and In-TCPE gels (λ_{ex} = 298 nm).

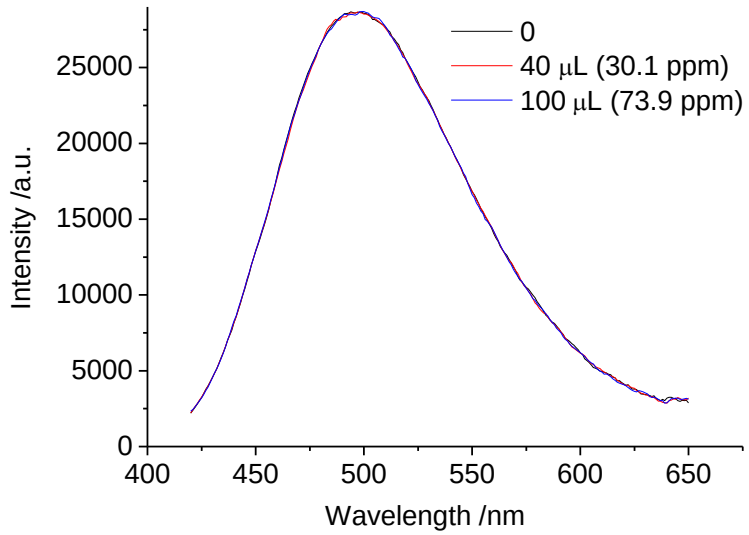

Fig. S11 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of benzoic acid solution in EtOH (1.0×10^{-2} mol/L).

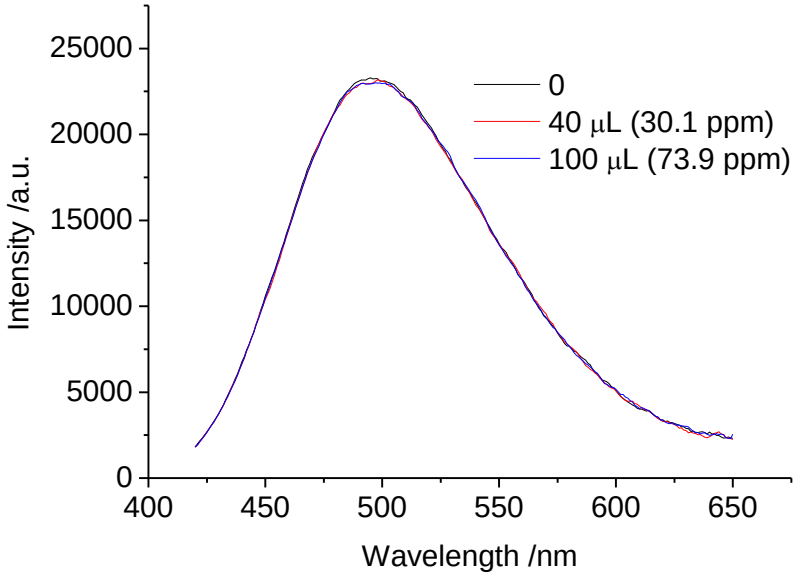

Fig. S12 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of nitrobenzene solution in EtOH (1.0×10^{-2} mol/L).

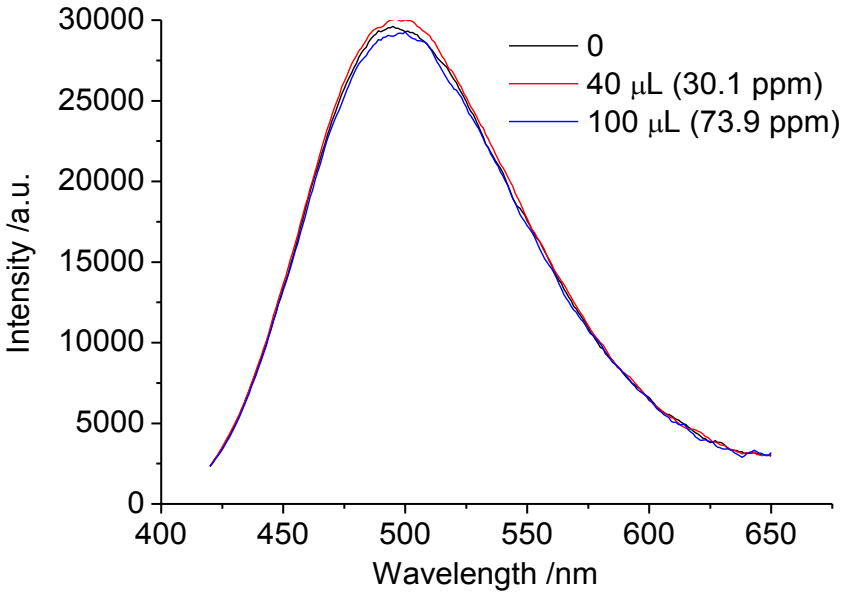

Fig. S13 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of 2,4-dinitro-chlorobenzene solution in EtOH (1.0×10^{-2} mol/L).

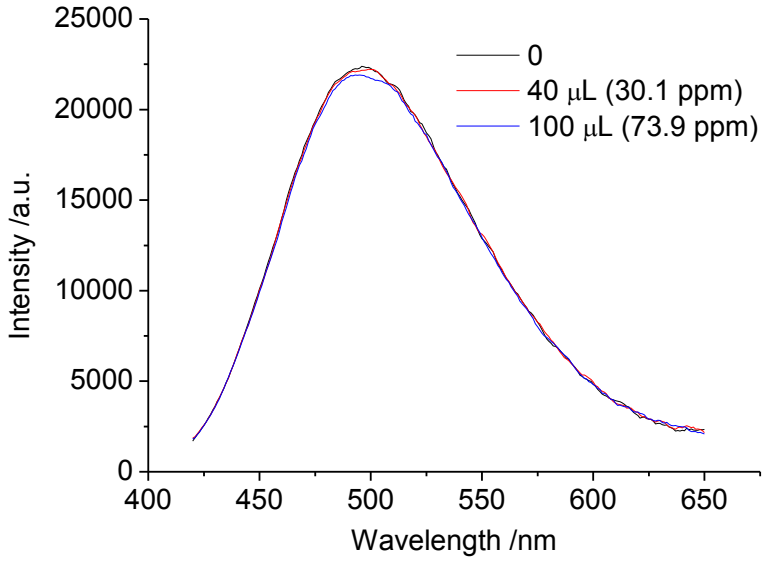

Fig. S14 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of chlorobenzene solution in EtOH (1.0×10^{-2} mol/L).

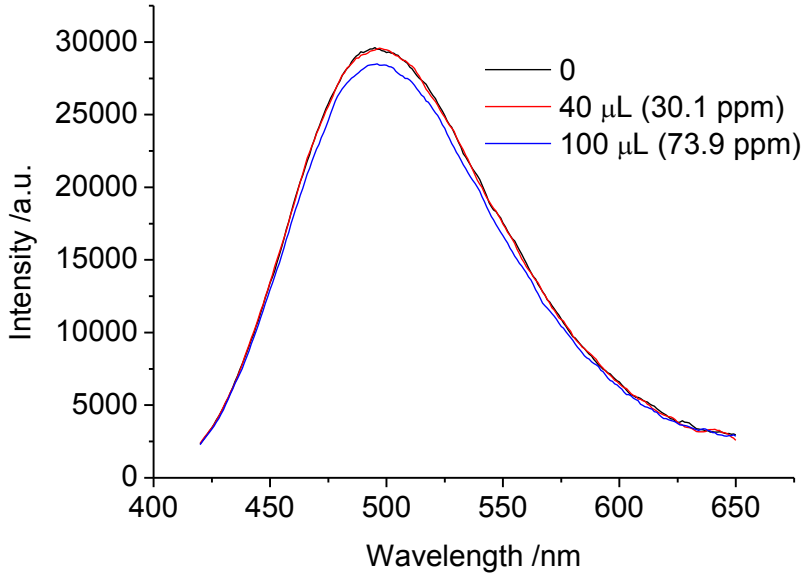

Fig. S15 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of 3,5-dinitrobenzoic acid solution in EtOH (1.0×10^{-2} mol/L).

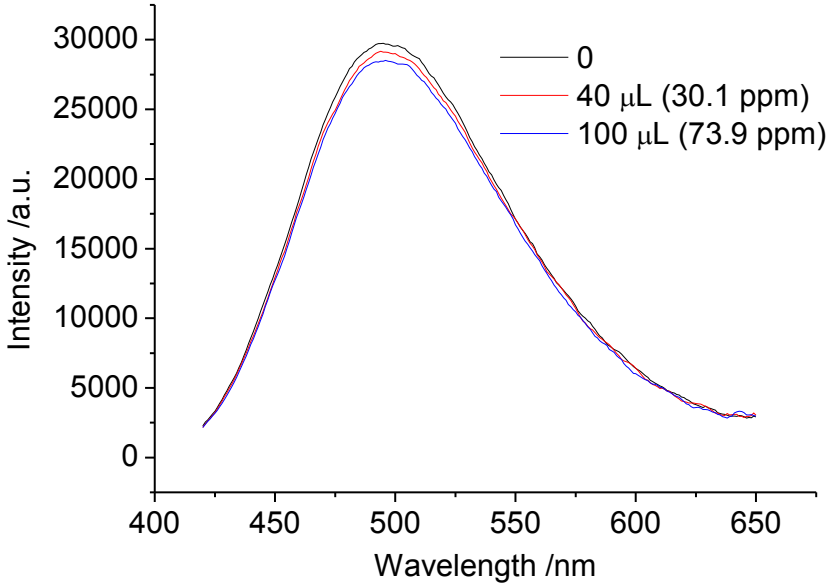

Fig. S16 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of 4-nitrotoluene solution in EtOH (1.0×10^{-2} mol/L).

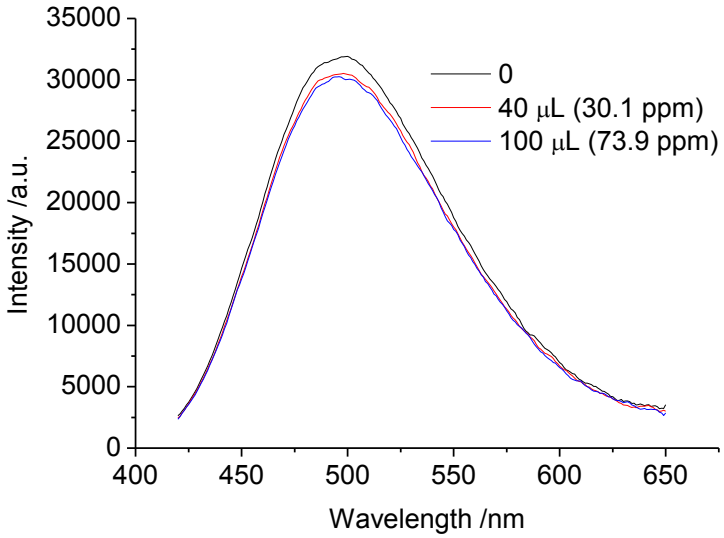

Fig. S17 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of bromobenzene solution in EtOH (1.0×10^{-2} mol/L).

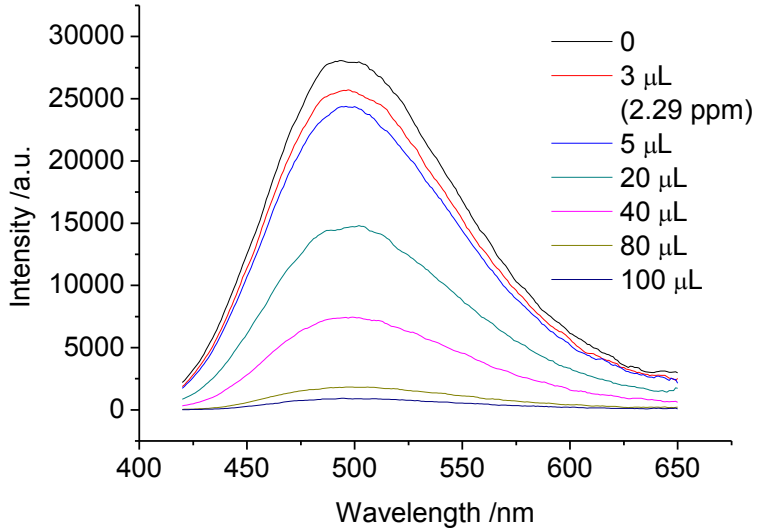

Fig. S18 Fluorescence titration of Al-TCPE gel was dispersed in EtOH (1.5×10^{-3} mol/L based on TCPE) with the addition of different volume of PA solution in EtOH (1.0×10^{-2} mol/L).