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Fluorescent Litmus Film for Detecting Acid Vapors: Free-Standing and Robust AIE Sensing Film Fabricated by Photopolymerization of Self-Assembled Hierarchical Triphenylamine-Based Gelators

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Materials preparations

Methyl-4-hydroxybenzoate (99%, TCI), 12-Bromo-1-dodecanol (98%, TCI), 2,6-Di-*tert*-butylphenol (99%, Sigma-Aldrich), Triethylamine (TEA, 99%, Sigma-Aldrich), Methacryloyl chloride (97%, Sigma-Aldrich), Tris(4-aminophenyl)amine (98%, TCI), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 98%, TCI), *N*,*N*-Diisopropylethylamine (DIEPA, 99.5%, Sigma-Aldrich), 1-Hydroxybenzotriazole hydrate (HOBt, 97%, Sigma-Aldrich), Potassium carbonate (K_2CO_3, 99.5% Showa), Potassium iodide (KI, 99.5%, Showa), Sodium sulfate (Na_2SO_4, 98%, Showa) were used as received. *N*,*N*-dimethylformamide (DMF), hexane (Hex), ethanol (EtOH), tetrahydrofuran (THF) were purified before use.

Synthesis of Methyl-4-((12-hydroxydodecyl)oxy)benzoate (1): Methyl-4-hydroxybenzoate (7 g, 46 mmol), K_2CO_3 (9.54 g, 69 mmol), and KI (1.15 g, 7 mmol) were dissolved in the 200 ml of acetone. 12-bromo-1-dodecanol (18.3 g, 68.9 mmol) was added to the mixture and stirred for 24 h at 50 °C. After the reaction, the mixture was cooled down to room temperature and the solvent was removed in reduced pressure. The mixture was poured into 300 ml of distilled water and the precipitate was filtered and washed several times with Hex. The resulting product was a beige powder (Yield: 84.1%, 13.02g). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.98-7.96 (m, 2H), 6.91-6.89 (m, 2H), 4.01 (t, 2H), 3.88 (s, 3H), 3.64 (t, 2H), 3.33 (s, 1H), 1.79 (m, 2H), 1.45 (m, 2H), 1.33 (m, 2H), 1.28 (m, 14H) ppm.

Synthesis of 4-((12-hydroxydodecyl)oxy)benzoic acid (2): Compound 1 (2.5 g, 7.43 mmol) and KOH (1.67 g, 29.7 mmol) were dissolved in 80 ml of EtOH. The mixture was stirring for overnight at 75 °C. After the reaction, the mixture was cooled down to room temperature and the solvent was removed in reduced pressure. Then, the resultant was poured into 10 vol% of 300 mL HCl aqueous solution. The white precipitate was filtered and washed several times with distilled water. The residue was recrystallized with EtOH/Hex (1:3) to yield a white powder (Yield: 91.8%, 2.2g). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.04-8.03 (m, 2H), 6.93-6.92 (m, 2H), 4.02 (t, 2H), 3.64 (t, 2H), 1.80 (m, 2H), 1.56 (m, 2H), 1.46 (m, 2H), 1.28 (m, 14H) ppm.

Synthesis of 4-((12-(methacryloyloxy)dodecyl)oxy)benzoic acid (3): Compound 2 (2 g, 6.2 mmol), 2,6-di-*tert*-butylphenol (6 droplets) and TEA (2.51g, 25mmol) were dissolved in the 100 ml of THF. The mixture was stirred for 15 min at 0 °C. After that, a solution of methacryloyl chloride (3.24 g, 31 mmol) in 50 ml of THF was added slowly dropwise and stirred for 48 h at room temperature. After the reaction, the solvent was removed in reduced pressure. Then, the resultant was refluxed in the 50 mL of acetic acid for 1 h at 110 °C and cooled down to room temperature. The 200 mL of distilled water was added, and the precipitate was filtered and washed several times with distilled water. The resulting product was a white powder (Yield: 61.9%, 1.5g). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.05-0.03 (m, 2H), 6.94-6.92 (m, 2H), 6.11 (m, 1H), 5.55 (m, 1H), 4.14 (t, 2H), 4.02 (t, 2H), 1.94 (s, 3H), 1.81 (m, 2H), 1.67 (m, 2H), 1.46 (m, 2H), 1.29 (m, 14H) ppm.

Synthesis of (((((nitrilotris(benzene-4,1-diyl))tris(azanediyl))tris(carbonyl))tris(benzene-4,1-diyl))tris(oxy))tris(dodecane-12,1-diyl) tris(2-methylacrylate) (TPA-3MA): Compound 3 (1.62 g, 4.1 mmol), EDC (1.2 g, 6.2 mmol), HOBt (0.4 g, 3 mmol) and DIPEA (2.93 g, 22.6 mmol) were dissolved in the 20 ml of DMF. The mixture was stirring for 30 min at room temperature under nitrogen atmosphere. After that, a solution of tris(4-aminophenyl)amine (0.3 g, 1 mmol) in 10 ml of DMF was added slowly dropwise and stirred for 48 h at room temperature. After the reaction, the solvent was removed in reduced pressure and the mixture was extracted with MC and washed with distilled water several times. Then, the organic layer was brined with sodium chloride solution in water and dried with Na_2SO_4, and then recrystallization from MC and EtOH to obtain a white solid. (Yield: 76.6%, 1.12g). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.98 (s, 3H), 7.93-7.91 (m, 6H), 7.68-7.66 (m, 6H), 7.02-7.01 (m, 6H), 6.99-6.97 (m, 6H), 5.99 (m, 3H), 5.62 (m, 3H), 4.08 (t, 6H), 4.05 (t, 6H), 1.87 (s, 9H), 1.73 (m, 6H), 1.61 (m, 6H), 1.42 (m, 6H), 1.28 (m, 42H) ppm.

Gelation ability and gel-sol transition temperature

The compound of TPA-3MA (1 wt%) was mixed with various selected organic solvents (0.5 mL) in capped vials. The mixture was heated over by a heat gun until TPA-3MA was clearly dissolved. Then, the solution was slowly cooled down to room temperature to form the gel state. The gel state (G) indicates that the liquid flow was not observed anymore. If the liquid state was a clear solution, it is a soluble sol state (S). If the gelator is not dissolved, it is in an insoluble state (I). To investigate the gel-sol transition temperature (T_{gel}) of TPA-3MA gel, the differential scanning calorimetry (DSC) instrument was used. When the system changed from the gel state to the sol state, an endothermic peak of the DSC curve was observed. The 5 °C/min was applied to monitor the phase transition of TPA-3MA gel.

Fabrication of the Free-standing Film

To fabricate the nanofiber embedded film, the 1.5 wt% of TPA-3MA and 0.1 wt% of 2,2-dimethoxy-2-phenylacetophene (DMPA, photoinitiator) were mixed with hexyl methacrylate (HMA) in the capped vial. The mixture was heated until the TPA-3MA powders were dissolved to become the sol state. The sol state of organogel was injected between two glass substrates by capillary force at around 100 °C. Then, the sol state was cooled down to induced gelation and exposed to UV light for 2 h with an intensity of 30 mW/cm^2 for the photopolymerization. After photopolymerization, the glass substrates were carefully removed and the nanofiber embedded in polymer matrix film was obtained.

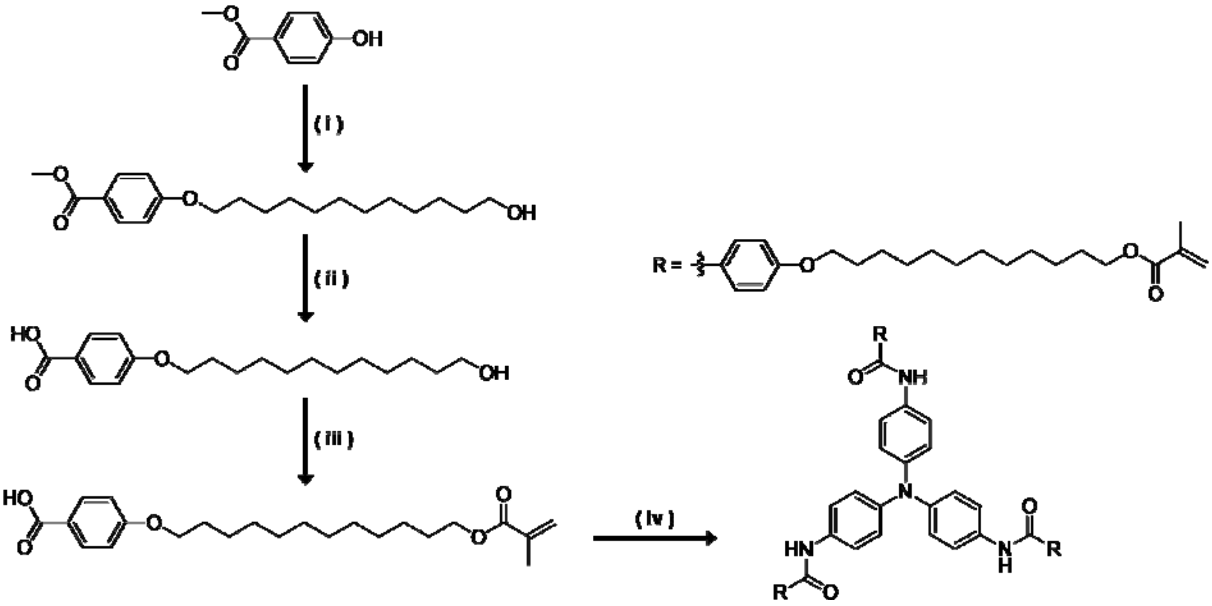

Fig. S1 Schematic illustration of synthetic procedures of TPA-3MA. Reagents and each conditions: (i) 12-bromo-dodecanol, K_2CO_3, KI, acetone, 50 °C for 24 h; (ii) KOH, EtOH, 75 °C for 12 h; (iii) methacryloyl chloride, 2,6-di-tert-butylphenol, TEA, THF, r.t, for 48 h; (iv) tris(4-aminophenyl)amine, EDC, HOBt, DIPEA, r.t. for 48 h under N_2 atmosphere.

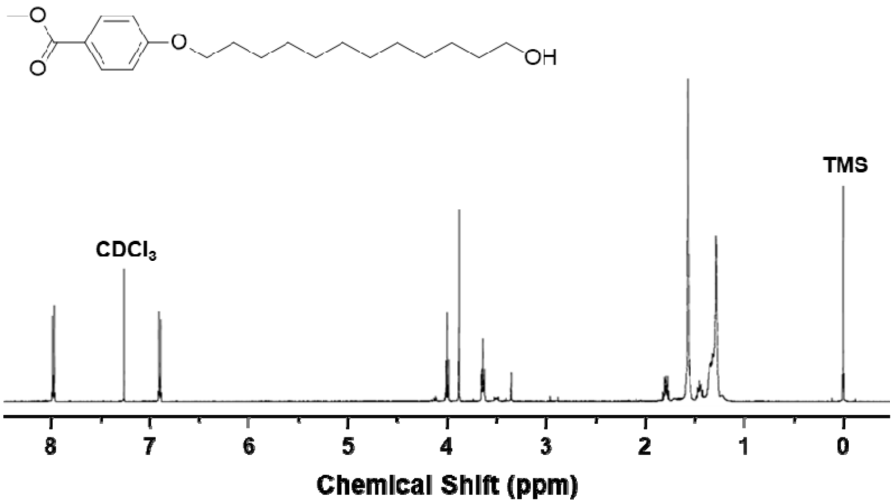

Fig. S2 ^{1}H-NMR spectrum of compound 1

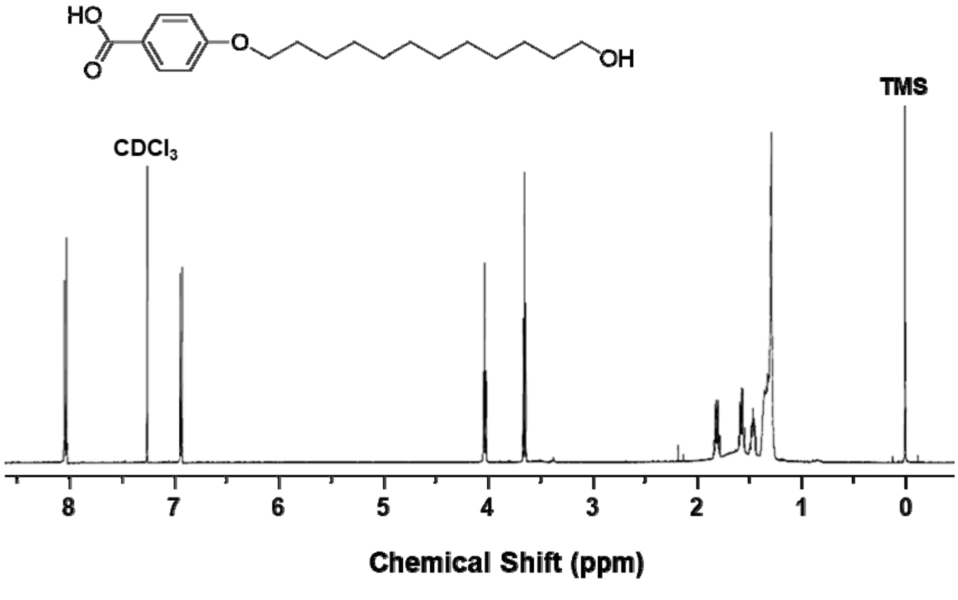

Fig. S3 ^{1}H-NMR spectrum of compound 2.

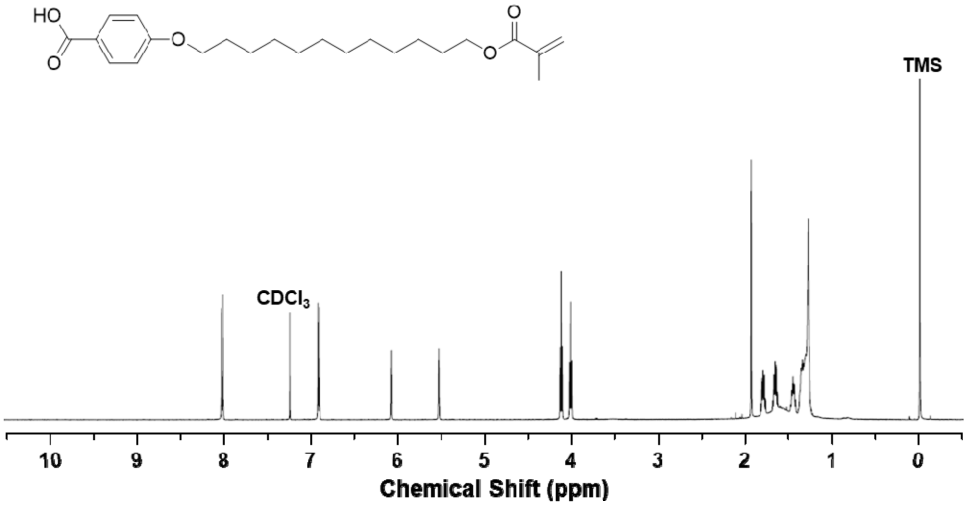

Fig. S4 ^{1}H-NMR spectrum of compound 3.

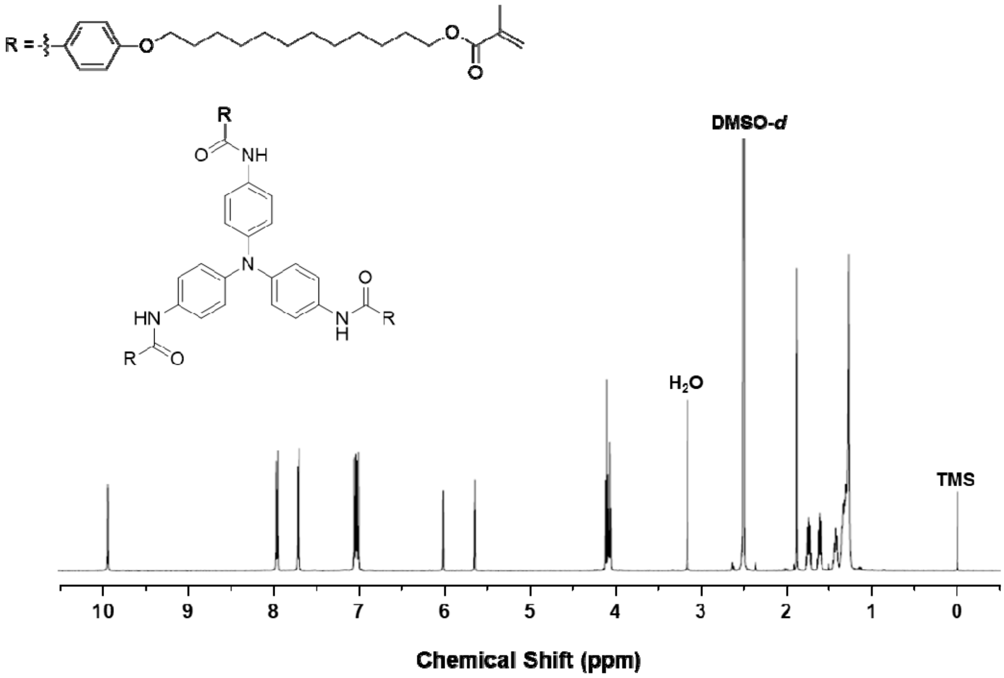

Fig. S5 ^{1}H-NMR spectrum of TPA-3MA.

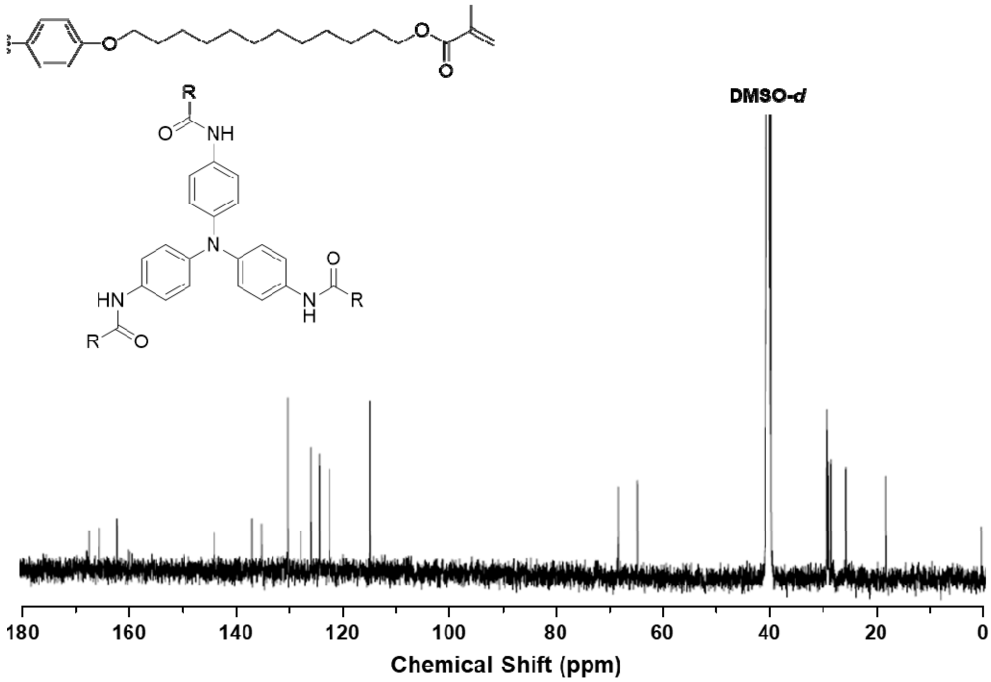

Fig. S6 ^{13}C-NMR spectrum of TPA-3MA.

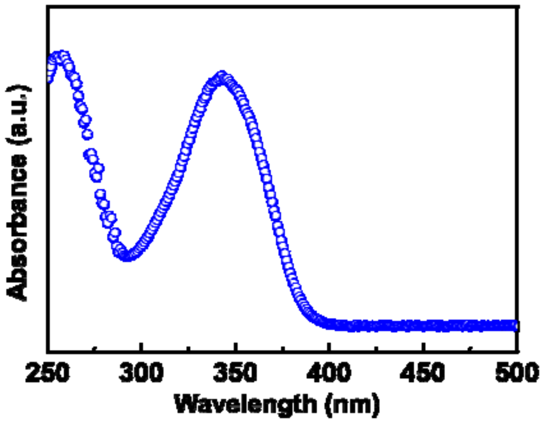

Fig. S7 UV-Vis absorption spectra of TPA-3MA in dilute THF solution (1 x 10^{-5} M).

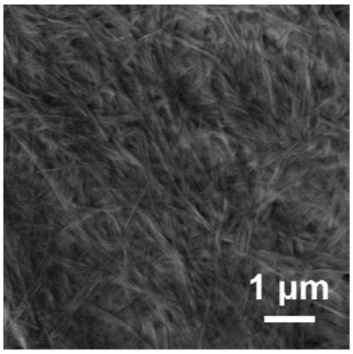

Fig. S8 SEM image of TPA-3MA organogel.

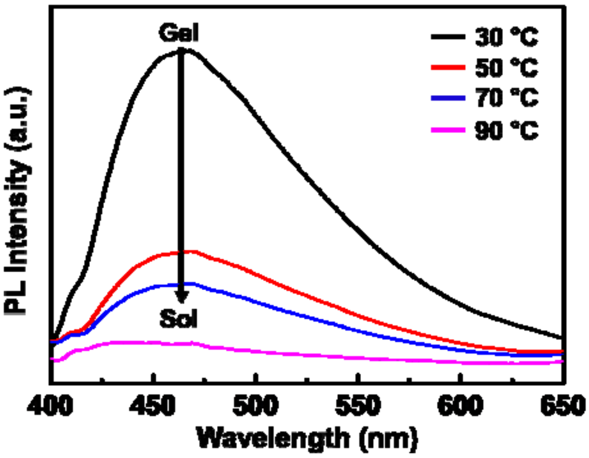

Fig. S9 PL intensity changes upon increasing temperature by gel-sol transition.