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AIE luminogen-functionalised mesoporous nanomaterials for efficient detection of volatile gases

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Experimental section

Materials. Cetyltrimethylammonium bromide (CTAB, Shanghai Huishi Chemical Co., Ltd.), 2,4-dinitrotoluene (DNT, Tianjin Guangfu Chemical Co., Ltd.), tetraethoxysilane (TEOS, Beijing Beihua Chemical Co., Ltd.), hydrochloric acid (HCl, Beijing Beihua Chemical Co., Ltd.), 1,3,5-trimethylbenzene (TMB, Shanghai Kefeng Chemical Co., Ltd.), 3-aminopropyltriethoxysilane (APTS, Sigma-Aldrich). All the initial chemicals in this work were used without further purification. The HCl gas was generated by an aqueous 36% HCl solution, and the ammonia vapour was generated by an aqueous 25% NH_3 solution.

Preparation of 4',4''-(1,2-diphenylethene-1,2-diyl)dibiphenyl-4-carbaldehyde (BTPEC)

The compound BTPEC was synthesized from 1,2-bis(4-bromophenyl)-1,2-diphenylethene (compound **1**, 0.99 g, 2 mmol), 4-formylphenylboronic acid (0.75 g, 5 mmol), K_2CO_3 (1.38 g, 10 mmol), $Pd(PhCN)_2Cl_2$ (10 mg), and DMF (25 mL). The reaction mixture was stirred and heated to 80 °C for 48 h. The product was purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (2:1 by volume) as the mobile phase. A light yellow solid was obtained (yield: 0.84 g, 78%); ^1H NMR (300 MHz, $CDCl_3$): δ 10.03 (s, 2H), 7.93-7.89 (m, 4H), 7.73-7.70 (m, 4H), 7.46-7.40 (m, 4H), 7.21-7.06 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): 191.8, 144.0, 143.3, 140.9, 137.5, 132.0, 131.3, 130.1, 127.9, 127.8, 127.3, 126.8, 126.7, 126.5; HRMS (micrOTOF): m/z calcd for $C_{40}H_{28}O_2$: 540.65 [M]; found: 540.80.

Synthesis of aminated large-pore mesoporous silica nanoparticles (MSN)

Molar ratio of CTAB/ TEOS/ NH_3/ H_2O/ APTS/ TMB/ Ethyl acetate in the reaction mixture was 1.0: 3.7: 150.7: 28759.1: 4.3: 18.7: 32.8. In a typical procedure, the aqueous solution of CTAB, NH_3, TMB, and ethyl acetate were stirred in the water bath at 40 °C for 30 min, and then the mixture of silane precursors (TEOS and APTS) was added into the mixture rapidly under stirring for 5 minutes. Additional water was then added into the reaction. After 24 hours, the sample was cleaned by centrifugation and re-dispersed in ethanol to remove CTAB. The final product was marked as MSN. Elemental analysis confirmed the amine content of 2.09 mmol g^{-1} for MSN.

Synthesis of AIE luminogen-modified mesoporous SiO_2 nanopaticles (MSNF)

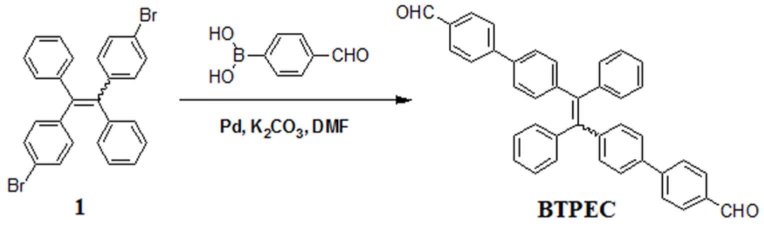
BTPEC (5 mg) and MSN (200 mg) were added into 20 mL of DMSO solution. The mixture was stirred at 80 ^{o}C for 24 h, and then the white solid was filtered off, and transferred into the Soxhlet extractor, washed with THF for 48 h. The as-prepared material was named as MSNF.

Preparation of films and the response measurements to vapours

3 mg of MSNF was dispersed well into 3 mL of water, and then the films were prepared by using dip-coating method. The sensing properties of films to the vapours were measured by sticking the film to the cover of the quartz cell making sure that the same point was measured before and after exposure to vapours. Finally the detected material was put into the cell. After it reached its constant vapour pressure at room temperature, then the film was put back in to the cell and its fluorescence intensity was recorded at different time with excitation at 365 nm.

Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2500/PC X-ray diffractometer with CuKα radiation (λ = 0.15405 nm). N_2 adsorption-desorption isotherms were measured on a Micromeritics ASAP 2010 M apparatus at 77 K. Transmission-electron-microscopy (TEM) images were recorded with a Tecnai F20 electron microscope. CHN elemental analyses were carried out on a varioMICRO elemental analyzer. The UV/Vis excitation and emission spectra were obtained on a Shimadzu RF-5301PC spectrofluorometer.



Scheme S1. The synthetic route of BTPEC.

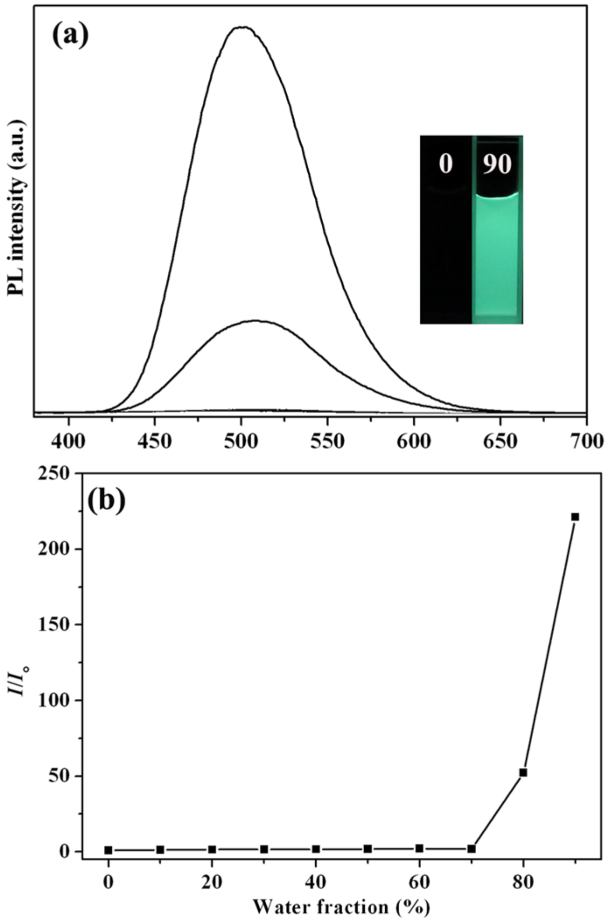


Figure S1. (a) PL spectral changes of BTPEC depending on the water fractions in DMSO. (b) Plot of I/I_0 values versus the compositions of aqueous mixtures, I_0 = emission intensity in pure DMSO solution. Excitation wavelength: 365 nm. Concentration: 10 µM. Inset shows the fluorescence emission of BTPEC taken under the UV light (365 nm).

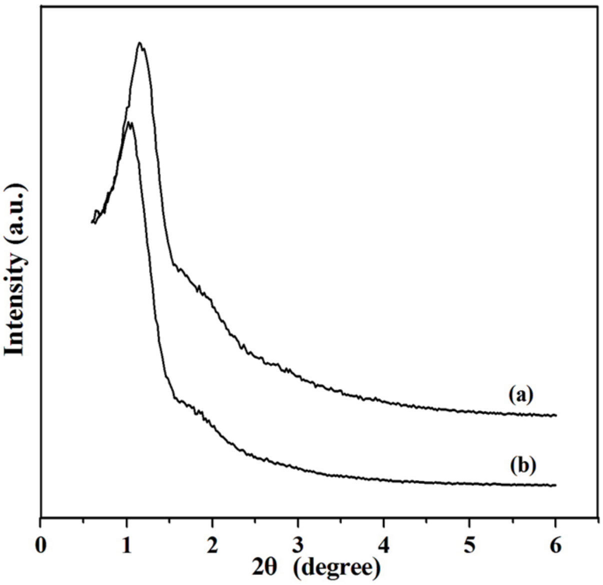


Figure S2. XRD patterns of the prepared materials (a) MSNF, (b) MSN.

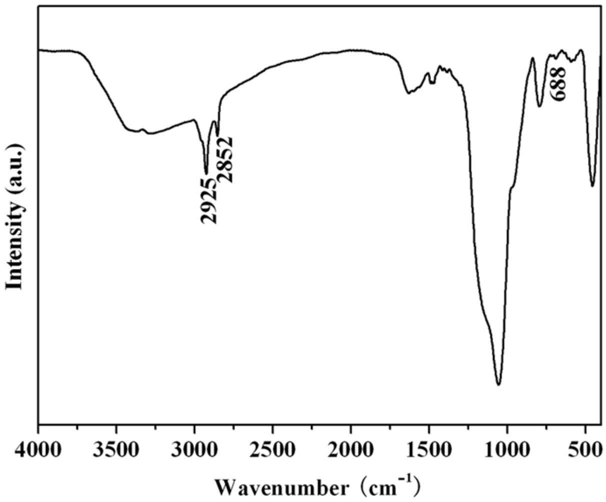


Figure S3. FT-IR spectrum of amino group functionalised mesoporous silica nanoparticles.

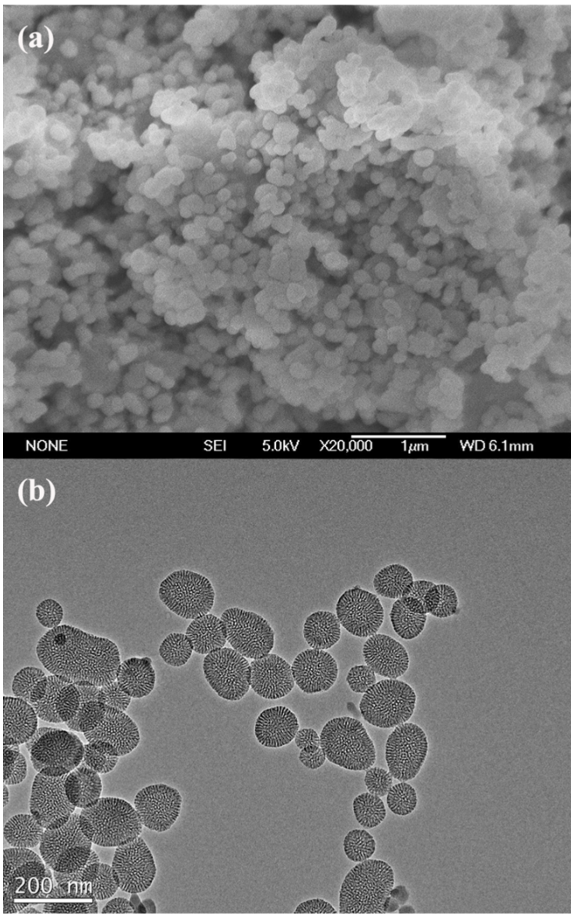


Figure S4. (a) SEM and (b) TEM images of MSNF.

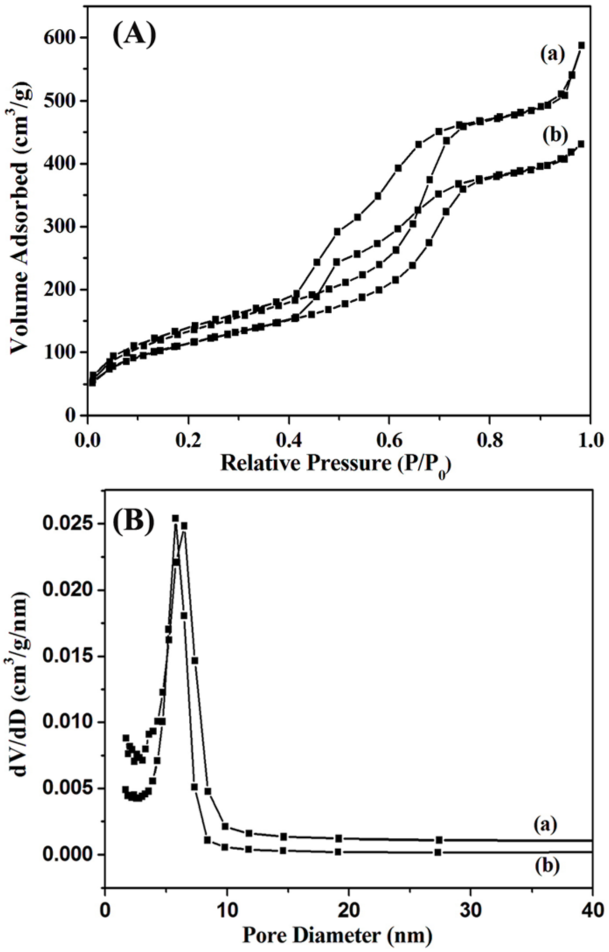


Figure S5. (A) N_2 adsorption/desorption isotherms of (a) MSN, (b) MSNF and (B) their corresponding pore size distributions.

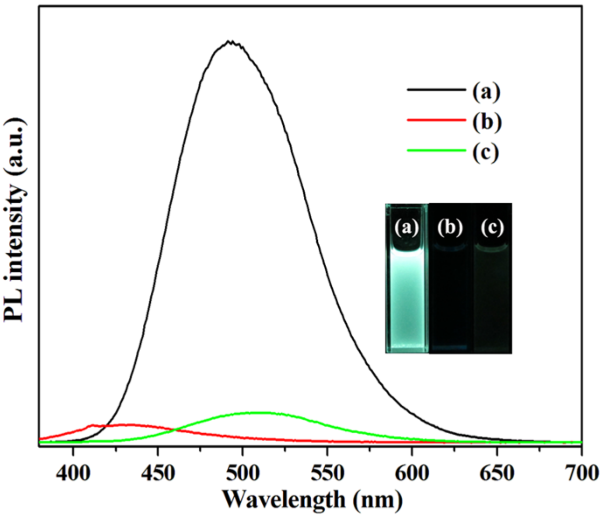


Figure S6. Fluorescence spectra of samples in DMSO solvent. (a) MSNF; (b) MSN (c) BTPEC. Excitation wavelength: 365 nm.

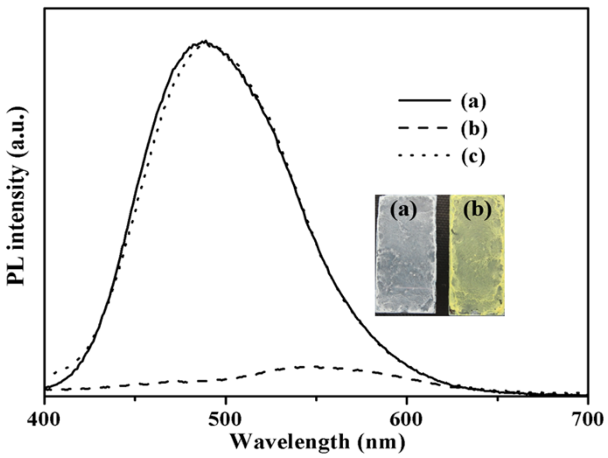


Figure S7. Fluorescence spectra of MSNF film (a) before HCl gas exposure, (b) after HCl gas exposure for 2 s, (c) the same film after NH_3 vapour exposure for 2 s (excitation wavelength: 365 nm). Insert show the photograph of the MSNF film (a) before and after HCl gas exposure under day light.

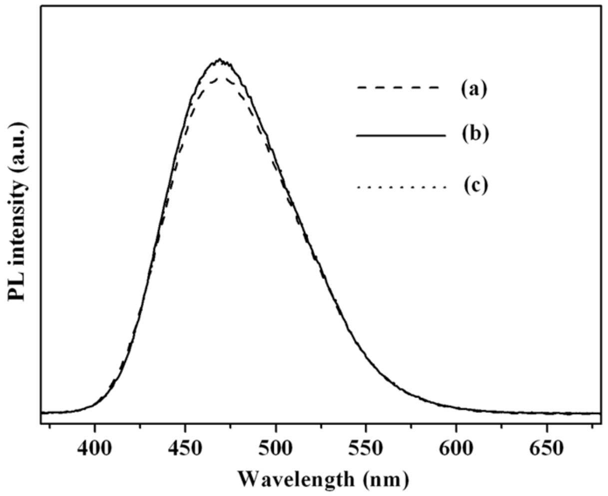


Figure S8. Fluorescence spectra of TPE film (a) before HCl gas exposure, (b) after HCl gas exposure for 2 s, (c) the same film after NH_3 vapour exposure for 2 s.

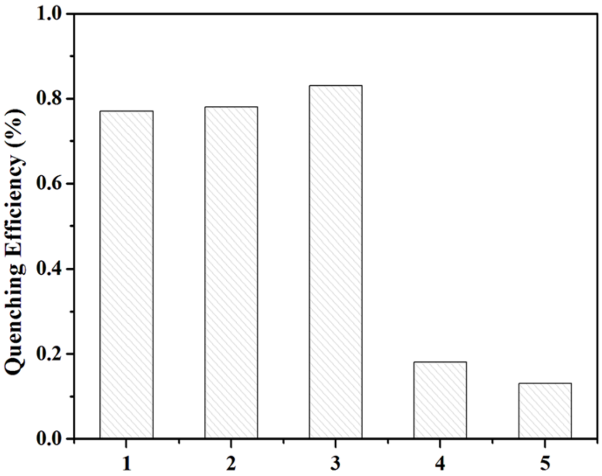


Figure S9. Quenching efficiencies of various acids in the vapour state to the fluorescence emission of the films for 2 s. The samples are ordered as HCl (1), CH_3COOH (2), HNO_3 (3), H_2SO_4 (4), H_3PO_4 (5).

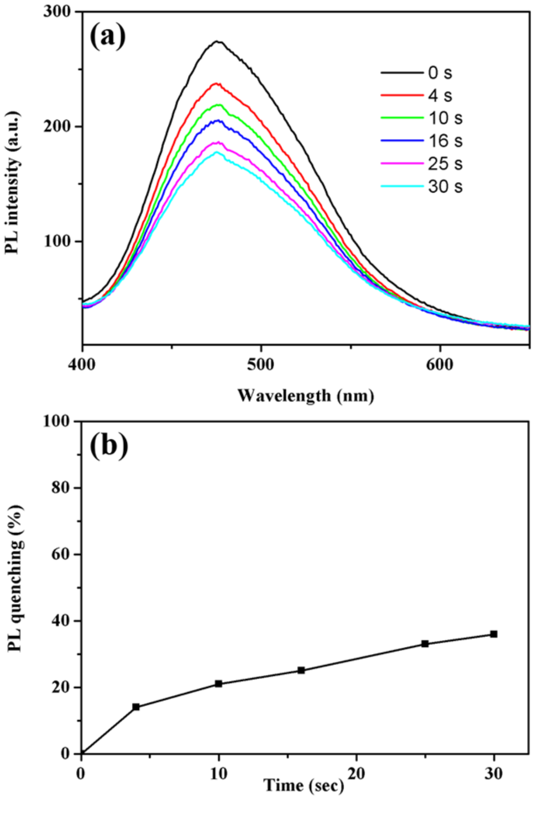


Figure S10. (a) Time-dependent fluorescence spectra and of MSNF film in DNT vapour (ca. 60 ppb). (b) Time-course of fluorescence quenching efficiency of MSNF film exposed to DNT vapour; the intensity was monitored at 485 nm.