Supporting Information

Targeted Synthesis of A 3D Crystalline Porous Aromatic Framework with Luminescence Quenching Ability for Hazardous and Explosive Molecules

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Experimental Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) was purchased from the TCI Chemical Co. Tetra[4-tetra(4-dihydroxyborylphenyl)germanium was prepared according to the previously reported method. All reactions were performed under a purified nitrogen atmosphere.

Synthesis and Characterization of Monomer.

Tetra[4-(dihydroxyboryl)phenyl]germanium: Tetra(4-bromophenyl)germanium (2.86 g, 4.1 mmol) was dissolved in 35 cm$^3$ of dry ethyl ether and cooled to -70 °C in a dry-ice bath. Under nitrogen 8.2 cm$^3$ of a 2.5 mol dm$^{-3}$, butyllithium-hexane solution (25% excess) was added slowly with stirring. The mixture turned a dark grey-purple but did not become clear. When addition of butyllithium was complete the solution was allowed to warm to room temperature while stirring continued. The dark slurry was then transferred by syringe with a wide bore needle into a stirred solution of trimethyl borate (2.9 g, 50% excess) in 30 cm$^3$ of dry ethyl ether. This solution was stirred at room temperature for 1h. The ether was then removed under vacuum from the solution and the borate ester residue was hydrolysed to the tetraboronic acid with 70cm$^3$ of 2.4mol dm$^{-3}$ HC1 solution. The product was collected by filtration, washed with water and dried in vacuum at room temperature. The acid was purified by dissolving in aqueous alkali, filtration and reprecipitation with dilute acid. Yield, 83%; $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3300-3600 (broad OH), 3060, 1597, 1501, 1009, 822; $^1$H NMR $\delta_H$ of potassium salt in D$_2$O: 'doublets' of equal intensity centred at 7.33 and 7.45.$^{1,2}$

TBPGe (26.1 mg, 0.05 mmol) with HHTP (23.8 mg, 0.07 mmol) in 1.0 mL of a 1:1 v:v solution of mesitylene/dioxane was treated to 85 °C and 150 mTorr for 72 h and afforded purple powder. The product was filtered over a medium glass frit and washed with anhydrous tetrahydrofuran (10 mL) for 4 h, during which the activation solvent was decanted and freshly replenished four times. The solvent was removed under vacuum at room temperature to afford PAF-15 (36.5 mg, 76%).

Physical measurements.

TG analysis was performed using a Netzch Sta 449c thermal analyzer system at the heating rate of 10 °C min⁻¹ in air atmosphere. Fourier Transform Infrared Spectroscopy (FTIR) spectra (film) were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The Ar adsorption isotherm was measured on a Quantachrome Autosorb-iQ. PXRD was performed by a Rigaku D/MAX2550 diffractometer using CuKα radiation, 40 kV, 200 mA with scanning rate of 0.3 °/min (20). SEM and energy-dispersive X-ray spectroscopy (EDS) analyses were performed on a JEOS JSM 6700. The solid-state ¹³C and ¹¹B cross polarization magic angle spinning nuclear magnetic resonance (CP MAS NMR) spectra were recorded on a Bruker AVANCE III 400 WB spectrometer. The absolute quantum yield of fluorescence (Φ₅₉) was recorded on a Edinburgh FLSP920.
**Figure S2** FT-IR spectrum of PAF-15 (blue), HTTP (black) and TBPGe (red).

**Figure S3.** Solid-state $^{13}$C and $^{11}$B NMR spectra for PAF-15 (a and b).

**Figure S4.** SEM image (a) and EDS image (b) of PAF-15.
Figure S5 TGA trace for an as-prepared sample of PAF-15. The solvated sample starts to lose guests at the beginning of heat-up, and there is 7.14 % weight loss attributed to the departure of guests before 200 °C. Furthermore, this sample starts to decompose at about 250 °C, and the decomposition finishes up to 600 °C, and there is 44.65 % weight loss attributed to the loss of organic framework part.

PL Elemental Analysis.
Elemental analysis was performed on a Perkin-Elmer LS55 luminescence spectrometer. PAF-15 (15mg) was added into 100 mL CHCl$_3$ slowly with stirring. Then the suspension was dispersed with ultrasonic oscillation for at least 10 hours. The concentration of the CHCl$_3$ suspension of the PAF-15 which is 150 µg/mL was gained. The suspensions do not undergo degradation during a number of dispersion/deposition cycles in different concentrations CHCl$_3$ solution of analytes.

Figure S6 Solid UV-visible spectra of PAF-15.
**Figure S7** PL decay curves of PAF-15 in CHCl$_3$ solution (excited: 346 nm).

**Figure S8** Simplified model structure of PAF-15 based on ctn

**Figure S9.** PXRD patterns of PAF-15 (as-prepared: black; washed with CHCl$_3$ for 24 hours then activated: red)
References
