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A Thermally Stable and Reversible Microporous Hydrogen-Bonded Organic Framework: Aggregation Induced Emission and Metal Ion-sensing Properties†

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A microporous hydrogen-bonded organic framework (HOF) derived from a polyhedral oligomeric silsesquioxane (POSS) intermediate and an aggregation-induced emission (AIE) luminogen tetraphenylethene (TPE) derivative has been synthesized and structurally characterized by various methods. This unique HOF exhibits a permanent porosity with the Brunauer-Emmett-Teller (BET) surface area of 101.9 m²/g. This HOF could be well dispersed in organic solvents in a form of nanoparticles with a size of a few hundred nanometers. These nanoparticles are highly fluorescent in organic solution, and exhibit a high fluorescence quenching selectivity towards copper ion. Furthermore, the fluorescence of this HOF could be recovered by removal of copper ion upon addition of cyanide and, more interestingly, this process could be repeated several times without considerably sacrificing the sensing activity towards copper ion.

Introduction

Recently, porous hydrogen bonded organic frameworks (HOFs) have attracted increasing interest as stimuli sensitive materials, but HOFs have lagged significantly behind metal-organic frameworks in terms of framework design, topological rationalization and functionalization. This is because hydrogen bonds are weaker and more flexible in conformation when compared to coordination interactions in other frameworks, such as zeolites and metal-organic frameworks (MOFs), leading to lower stabilities. Thousands of HOFs have been prepared during the last decades, but HOFs with permanent porosity are rarely offered, as HOFs easily collapse once the guest molecules are removed from the super-molecular network system. To the best of our knowledge, only very limited HOFs display high thermal stability and exhibit permanent porosity after removal of guest molecules, in which the host molecules can form strong hydrogen bonds and π-π stacking each other. Therefore, it is still challenging to obtain porous HOFs, which are stable enough for their potential applications as storage and separation, heterogeneous catalysis, sensing and so on.

Aggregation-caused quenching (ACQ) of fluorescence is commonly observed in fluorescent materials in solid state, which has undermined its potential for solid-state sensors or probes. Recently, AIE materials have attracted increasing interest in the areas of optoelectronics and sensory systems due to the absence of ACQ effect. However, the stimuli sensitive HOFs materials with AIE properties have been rarely reported, and their sensing application was not found mainly due to the lack of suitable processable HOFs materials with AIE activity, which is tolerant to solvents, moisture, temperature, etc.

Herein, we report on a feasible method without using any guest molecules to prepare AIE active HOF, which responds to the external stimuli. This HOF (POSS-T₈A) was prepared by the condensation of AIE precursor 4-(1,2,2-triphenylvinyl)benzoic acid and octa(aminoo)-substituted POSS derivative (Scheme 1). For comparison, another analogue POSS-T₈B with ester linkages was prepared as well. POSS have been demonstrated as effective building blocks to generate porous materials through thermolysis, hydrosilation, coupling reactions, as well as free radical copolymerization with other monomers. Several porous materials derived from octa(vinyl)-POSS exhibit BET surface area as high as 700 m²/g and maximum tunable mesopore volume of 2.0 cm³/g. In this paper, POSS-T₈A molecules show enhanced AIE properties,
and display high sensitivity (Stern-Volmer co-efficient $K_{sv} = 30305$ M$^{-1}$) and fluorescence quenching selectivity for Cu$^{2+}$ ion due to the presence of amide linkages, which is effectively able to bind with Cu$^{2+}$ ion, leading to the conformation change of TPE units in the POSS-T$_A$ molecules and eventually resulting in fluorescence turn-off (Scheme 1). This is the first demonstration for the fluorescence signaling via conformational changes of pendant luminogen moieties in HOFs materials.

![Scheme 1](image)

Scheme 1 Synthetic route leading to POSS-T$_A$, POSS-T$_B$, and structural illustration of POSS-T$_A$ for Cu$^{2+}$ sensing.

**Results and Discussion**

POSS-T$_A$ and POSS-T$_B$ were prepared using a similar method as shown in Scheme 1. POSS-T$_B$ was easily purified by column chromatography. In contrast, POSS-T$_A$ was first purified by precipitating diluted POSS-T$_A$ CHCl$_3$ solution in methanol. Then resulting material was isolated by centrifugation, and then collected solid residue was washed with hexane and methanol followed by Soxhlet extraction with Et$_2$O. Both POSS-T$_A$ and POSS-T$_B$ were well characterized by $^1$H, $^{13}$C and $^{29}$Si nuclear magnetic resonance (NMR), matrix-assisted laser desorption ionization time of flight (MALDI TOF) mass spectrometer and elemental analysis. POSS-T$_B$ shows very good solubility in most organic solvents such as chloroform, tetrahydrofuran (THF), ethyl acetate (EA); however, POSS-T$_A$ is only fully soluble in pyridine but well-dispersed in other common organic solvents such as THF, chloroform, EA, etc., in a form of nanoparticles. This indicates that POSS-T$_A$ molecules form hydrogen-bonded aggregates, which limits the solubility in organic solvents. Good solubility in pyridine is due to the fact that pyridine can act as electron acceptors to form hydrogen bonds with amide linkages and hence dissociate the self-aggregation of the POSS-T$_A$ molecules. This is confirmed by the $^1$H NMR study of POSS-T$_A$ in pyridine-$d_5$ and DMSO-$d_6$. The proton signals of POSS-T$_A$ in pyridine-$d_5$ are readily identified, while its protons in DMSO-$d_6$ were not observed under the same condition (Fig. S10). In contrast, the ester linkages do not facilitate to form any strong hydrogen-bonded networks and no hydrogen-bonded self-aggregation was observed for POSS-T$_B$ molecules. Therefore, POSS-T$_B$ shows very good solubility in many organic solvents. The nanoparticle structure of POSS-T$_A$ was characterized by dynamic light scattering and it forms nanoparticles with an average size of 291.4 nm in DMSO, which was supported by transmission electron microscope (TEM) analysis (Fig. 1a and 1b). Both POSS-T$_A$ and POSS-T$_B$ (Fig. 1c and S1) exhibited good thermal stability in air with a decomposition temperature of more than 370 °C.

![Fig. 1](image)

Fig. 1 (a) Particle size distribution of POSS-T$_A$ in DMSO. (b) TEM image of POSS-T$_A$ particles prepared in the DMSO; scale bar is 0.5 µm. (c) TGA thermogram of POSS-T$_A$ recorded at a heating rate of 20 °C/min in air. (d) Gas absorption isotherms for POSS-T$_A$, POSS-T$_A$·Cu$^{2+}$ and Octa(NH$_3$)-POSS (CO$_2$) at 0 °C, N$_2$ at -196 °C.

Physical gas adsorption is widely used to study the pore characteristics of solid materials. The porosity of POSS-T$_A$ was studied by CO$_2$ gas adsorption and desorption at 273 K (Fig. 1d). POSS-T$_A$ shows type II isotherms with a significant amount of CO$_2$ adsorbed at low pressure ($P/P_0 < 0.03$), followed by a much increased adsorption at higher pressure ($P/P_0 > 0.9$) attributable to gas condensation into voids among particles. The CO$_2$ adsorption capacity was measured by CO$_2$ isothermal adsorption at 273 K. The micropore BET surface area is calculated to be 101.9 m$^2$/g in terms of Dubinin–Astakhov method. The pore size distribution was evaluated by applying a non-local density functional theory (NLDFT) model. The NLDFT model was applied under the assumption that the slit-shaped pores have uniformly dense carbon walls and that
Cu(NO$_3$)$_2$ solvents, such as THF, chloroform and DMSO, to form macroscopically homogeneous but visually transparent solutions without observing any precipitates. Taking the mixture of POSS-T$_8$A upon addition of Cu$^{2+}$ ion (Fig. 2c). It was known that Cu$^{2+}$ ion can quench the fluorescence in different organic solvents and it shows the highest quenching efficiency in DMSO (Fig. 2d). The fluorescence microscopy also clearly showed that the fluorescent nanoparticles appeared non-fluorescent upon addition of enough Cu$^{2+}$ ion (Fig. 3b and 3d).

POSS-T$_8$A shows strong blue-white emission both in solid state and organic solvents (Fig. 2). POSS-T$_8$A could be dispersed in organic solvents, such as THF, chloroform and DMSO, to form macroscopically homogeneous but visually transparent solutions without observing any precipitates. Taking the mixture of POSS-T$_8$A in THF as an example, no tendency towards agglomeration was observed when the dispersion was stored at 4 °C for 6 months. Typically, most of TPE-containing materials are non-emissive in good solvents, such as THF. However, as shown in Fig. 2a, dispersion of POSS-T$_8$A displays strong fluorescent emission with an emission maximum at 458 nm and a wide of spectrum ranging from 375 nm to 600 nm, which can be seen even by naked eyes under the bright light when UV illuminated when the concentration is as low as 1.0 × 10$^{-6}$ M. On the contrary, POSS-T$_8$A is not fluorescent in pyridine as it is completely soluble in it without forming any nanoparticles like in other organic solvents (Fig. S3). Similarly, POSS-T$_8$B displays normal AIE properties, as shown in Fig. S4, and its fluorescence would be turned on in the mixture of THF/H$_2$O$_2$, when the water volume fraction is increased up to 60%. Considering enhanced AIE property and morphology of POSS-T$_8$A particles, together with the amides’ nature to form hydrogen bonds, it is therefore confirmed that the amide groups of POSS-T$_8$A form the hydrogen-bonded networks (Scheme 1). Within this HOFs structure, the restricted intra- and inter-molecular rotation blocks the non-radiative channel and further enhances the light emission. The time-resolved fluorescence spectrum of POSS-T$_8$A was examined and it exhibited dual exponential decay with a life-time of 2.09 and 5.00 ns (Fig. 2b).

Fig. 2 (a) UV-Vis and fluorescence spectra of POSS-T$_8$A and POSS-T$_8$B in THF. Insert is the photographs of samples under UV in THF taken under UV illumination ($\lambda_{ex}$ = 365 nm), [C] = 1.0 × 10$^{-5}$ M. (b) The time-resolved fluorescence lifetimes of POSS-T$_8$A in THF under excitation of a femtosecond pulsed laser at 375 nm. (c) Fluorescence titration spectra of POSS-T$_8$A upon addition of Cu(NO$_3$)$_2$ in DMSO. $\lambda_{ex}$ = 314 nm, [POSS-T$_8$A] = 1.0 × 10$^{-6}$ M. (d) Fluorescence quenching efficiency of POSS-T$_8$A with Cu$^{2+}$ ion in various solvents, [POSS-T$_8$A] = 1.0 × 10$^{-6}$ M, [Cu$^{2+}$] = 1.0 × 10$^{-5}$ M.

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Fig. 4 (a) PXRD pattern of POSS-T\(_2\)A, POSS-T\(_2\)A•Cu\(^{2+}\) and POSS-T\(_2\)A recovered by CN. (b) TEM image of POSS-T\(_2\)A particles recovered by CN. Electron diffraction (ED) patterns of POSS-T\(_2\)A (c), POSS-T\(_2\)A•Cu\(^{2+}\) (d), and POSS-T\(_2\)A recovered by CN (e).

Wide angle X-ray diffractograms of POSS-T\(_2\)A and POSS-T\(_2\)A•Cu\(^{2+}\) are illustrated in Fig. 4a. A very weak broad scattering at 9.48° corresponding to d-spacing of 9.33 Å is observed for POSS-T\(_2\)A, which is due to the Si-O clusters in the POSS core.\(^{12}\) The POSS-T\(_2\)A is crystalline as evidenced by a group of the sharp reflection peaks from 2\(\theta\) = 19.04° (4.66 Å, 2\(^{nd}\) order diffraction, 200), to 38.66° (2.33 Å). Upon addition of Cu\(^{2+}\) ion, the diffraction profile of POSS-T\(_2\)A•Cu\(^{2+}\) completely differs from the POSS-T\(_2\)A; however recovered POSS-T\(_2\)A goes back to the same diffraction pattern as the pristine POSS-T\(_2\)A after Cu\(^{2+}\) ion is removed by CN\(^{-}\), which is also supported by the similar TEM image (Fig. 4b), revealing the excellent reversibility of this HOF structure.

Fig. 5 (a) Fluorescence quenching efficiency of POSS-T\(_2\)A upon addition of various metal ions. \(\lambda_{ex} = 314 \) nm. (b) Fluorescence intensity changes during sensing and recovering by CN. (c) Concentration-dependent fluorescence quenching of POSS-T\(_2\)A by Cu\(^{2+}\). (d) The fluorescence recovery of POSS-T\(_2\)A on addition of CN. (e) Photographs of samples with and without addition of metal ions under UV illumination (365 nm). [POSS-T\(_2\)A] = 1.0 \times 10^{-6} \text{ M}, [ion] = 1.0 \times 10^{-3} \text{ M}, (f) Photographs of POSS-T\(_2\)A, POSS-T\(_2\)A•Cu\(^{2+}\) and POSS-T\(_2\)A•Cu\(^{2+}\) with tetrabutylammonium cyanide under UV illumination (365 nm). [POSS-T\(_2\)A] = 1.0 \times 10^{-6} \text{ M}, [Cu\(^{2+}\)] = 1.0 \times 10^{-3} \text{ M}, [CN\(^{-}\)] = 1.0 \times 10^{-3} \text{ M}.

The fluorescence response of POSS-T\(_2\)A to other metal ions was also studied. As shown in Fig. 5a, transition metal ions, such as Mn\(^{2+}\), Co\(^{3+}\), Ni\(^{2+}\), and Fe\(^{3+}\) exhibited limited fluorescence quenching with 10 - 26% efficiency. In contrast, almost no fluorescence quenching was observed for alkaline-earth metal ions, such as Mg\(^{2+}\) and Ca\(^{2+}\) ions. In contrast, the Cu\(^{2+}\) ion shows the highest quenching efficiency (97%). Specifically, the quenching effect of metal ions was quantified by the Stern-Volmer equation (Table 1).\(^{16}\) The largest quenching coefficient (\(K_{sv}\)) value was obtained for Cu\(^{2+}\) ion to be 30305 M\(^{-1}\) (Fig. 5c), which is much higher than 7847 M\(^{-1}\) of MOFs material CPP-16.\(^{18}\) The selective response to metal ions was visualized in Fig. 5e. The influence of interrupting Cu\(^{2+}\) ion sensing by other metal ions was studied by conducting Cu\(^{2+}\) sensing in the presence of many other metal ions. Emission spectra (Fig. 5f) described no disturbance on selective Cu\(^{2+}\) sensing by any of the other metal ions. It is worthy to note that the quenched fluorescence could be recovered by addition of tetrabutylammonium cyanide (Fig. 5b and 5f), and the recovered HOFs material still displayed sensing ability to Cu\(^{2+}\) ion. After 4 off-on cycles (Fig. 5d), the fluorescence quenching towards to Cu\(^{2+}\) ion still remained around 80%, suggesting high reversibility and responsiveness of POSS-T\(_2\)A based HOFs structure.
Table 1 Fluorescence Quenching Coefficients ($K_v$) of POSS-T$_8$A on Different metal ions

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Conclusions

In conclusion, we reported on two AIE-active POSS-based molecules. POSS-T$_8$B with ester linkages did not form HOF and only showed a normal AIE property. Being different from usual HOF materials, POSS-T$_8$A with amide linkages enables to form very stable super-molecular HOF structure without the assistance of any guest molecules. This HOF showed enhanced AIE activity in solutions. Specific response of POSS-T$_8$A to Cu$^{2+}$ ion led to the dissociation of HOFs structure and subsequent release of the restricted intramolecular rotation of TPE moieties so as to activate their non-radiative channel and as a result turn off the emission. The fluorescence of POSS-T$_8$A and HOF structure could be recovered by removal of Cu$^{2+}$ ion by addition of CN ion to form more stable Cu(CN)$_2$ species. This type of AIE-active POSS-based HOF materials could be used as a promising chemosensor for potential applications in the detection of Cu$^{2+}$ ion as well as for gas storage and separation provided POSS structures are appropriately tailored with desired substituents.

Experimental

General.

All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. 1-Bromotriphenylethylene was purchased from Tokyo Chemical Industry Co., Ltd. All solvents were degassed and purified before use according to standard literature methods. Diethyl ether, hexanes, tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl before use. Other commercially available reagents and solvents were used as received.

Instrumentation.

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400-MHz NMR spectrometer in CDCl$_3$ at room temperature using tetramethylsilane (TMS) as an internal standard. Operating frequencies of the NMR spectrometer were 400.13 MHz ($^1$H), 100.61 MHz ($^{13}$C) and 79.49 MHz ($^{29}$Si). Electron impact mass spectra (EIMS) and high resolution MS (HRMS) were recorded using a Micromass 7034E mass spectrometer. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer for C, H, and N determination. UV-vis and fluorescence spectra were obtained using a Shimadzu UV3101PC UV-vis-NIR spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer with a Xenon lamp as light source, respectively. Thermal analysis was performed on a Perkin-Elmer thermogravimetric analyzer (TGA 7) in nitrogen or in air at a heating rate of 20 °C/min and on a TA Instruments Differential Scanning Calorimetry (DSC) 2920 at a heating rate and a cooling rate of 5 °C min$^{-1}$ in nitrogen. Dynamic light scattering experiments were performed on a Brookhaven 90 plus spectrometer with a temperature controller. An argon ion laser operating at 633 nm was used as light source. ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To have a guest-free framework, the sample was purified by successive Soxhlet extraction with methanol, ethyl acetate, 1,4-dioxane and chloroform. The result product was vacuumed at room temperature for 24 hours followed by 100 °C until the outgas rate was 5 mmHg/min prior to measurements. A sample of 187.9 mg was used for the sorption measurement and was maintained at 77 K with liquid nitrogen, at 273 K with an ice–water bath. The CO$_2$ adsorption capacity was measured by CO$_2$ isothermal adsorption at 273 K. Furthermore, the parameters of the Dubinin–Astakhov equation:

$$\log(V) = \log(V_0) - \frac{RT}{BE_0} \left[ \log \left( \frac{P_0}{P} \right) \right]^n$$

were obtained from CO$_2$ adsorption. $P$, $P_0$, $V$, $V_0$, $n$, $R$, $E_0$, and $\beta$ are the equilibrium pressure, the saturation vapor pressure of the gas at the analysis temperature ($T$), the volume adsorbed at equilibrium pressure, the monolayer capacity, the Astakhov exponent, the gas constant, characteristic energy, and the affinity coefficient of the analysis gas, respectively.

Synthesis of compounds.

Generally procedures. As shown in Scheme 1, POSS-T$_8$A was synthesized from a 4-(1,2,2-triphenylvinyl)benzoic acid (2), which was synthesized by two steps with 91% yield staring from 1-bromotriphenylethylene. After that, compound 2 reacts with octaammonium POSS in the present of 1-hydroxybenzotriazole and N,N’-dicyclohexylcarbodiimide to generate POSS-T$_8$A with reasonable yield of 70%. POSS-T$_8$A was structurally characterized by various spectroscopic methods and elemental analysis. The $^1$H NMR spectrum of POSS-T$_8$A is illustrated in Fig. S6. The presence of signals at $\delta$ 7.54 and 7.09-6.90 with an integration ratio of 2 : 17, which were assigned to protons of tetraphenylethene (TPE). Furthermore, the integration ratio for signals at $\delta$ 7.54, 3.11, 1.51 and 0.58 is 1 : 1 : 1 : 1. Those $^1$H NMR data together with results of MALDI-TOF indicate that eight TPE moieties are introduced into octa-ammonium POSS successfully. Similarly, POSS-T$_8$B can be prepared through the same route by 3 steps with overall yield as 53%. All of those POSS materials are structurally characterized by various spectroscopic methods and elemental analysis.

Ethyl 4-(1,2,2-triphenylvinyl)benzoate (1). Bromotriphenylethylene (670.5 mg, 2.00 mmol), 4-(ethoxy carbonyl)phenylboronic acid (456.2 mg, 2.40 mmol), Na$_2$CO$_3$ (2.76 g, 20.00 mol) and Pd(PPh$_3$)$_4$ (115.6 mg, 0.10 mmol) were placed in a Schlenk flask and the flask was evacuated and charged with Ar gas. Toluene (40.0 mL), ethanol (10.0 mL) and water (10.0 mL) was added, then the resulting mixture was degassed for 30 min and the mixture was stirred for 12 h at 110 °C under Ar gas. After cooling to room temperature, the mixture was poured into saturated aqueous NaHCO$_3$, extracted with dichloromethane (3 x 40.0 mL), dried over Na$_2$SO$_4$, filtered, and evaporated. The resulting residue was purified by chromatography over silica gel eluting with
hexane-dichloromethane (1 : 4), affording compound as an off white solid 862.2 mg (92.0%). 1H NMR (DMSO-d6): δ 7.77 (d, 2H, J = 8.6 Hz), 7.10 (m, 1H), 7.01 (m, 6H), 4.32 (q, 2H, J = 7.1 Hz), 1.35 (t, 3H, J = 7.3 Hz). 13C NMR (DMSO-d6): δ 166.7, 148.9, 143.4, 143.3, 142.6, 142.5, 140.1, 131.5, 131.4, 129.1, 128.0, 127.8, 127.0, 126.9, 126.8, 60.9, 14.4. IR (thin film): v = 3432, 3304, 2930, 2968, 1639, 1607, 1538, 1493, 1444, 1303, 1195, 1111, 1030, 861, 760, 749, 628 cm⁻¹. HRMS (ESI): [M + H⁺] calc'd for C29H30O2, m/z 405.1855; found, m/z 405.1855.

4-(1,2,2-triphenylyvinyl)benzoic acid (2). To the solution of methyl 4-(1,2,2-triphenylyvinyl)benzoate (1) (808.4 mg, 2.00 mmol) in mixture of THF (10 mL) and H2O (10 mL) was added NaOH (240 mg, 6 mmol). The resulting solution was stirred for 12 h at 90 °C under Ar gas. After cooling to room temperature, pH value of the mixture was adjusted to 4.0 by 1 M HCl solution, then extracted with dichloromethane (3 × 40.0 mL), dried over Na2SO4, filtered, and evaporated. The resulting residue was purified by chromatography over silica gel eluting with Ethyl acetate-dichloromethane (1 : 10), affording compound as a yellow semi solid (126.0 mg, 58%). 1H NMR (400.13 MHz, DMSO-d6): δ 7.77 (d, 2H, J = 8.3 Hz), 7.10 (m, 1H), 7.00 (m, 6H), 4.21 (t, 2H, J = 6.9 Hz), 1.73 (m, 2H), 0.58 (m, 2H), 0.07 (s, 6H). 13C NMR (100.61 MHz, CDCl3): δ 166.7, 148.8, 143.4, 143.2, 142.5, 140.2, 131.4, 131.3, 129.1, 128.4, 128.0, 127.9, 127.1, 126.9. IR (thin film): v = 3421, 3075, 3052, 2924, 2852, 1717, 1666, 1492, 1444, 1405, 1383, 1273, 1177, 1102, 1051, 841, 761, 749, 699, 627 cm⁻¹. MALDI-TOF: [M] calc'd for C25H20O2Na, m/z 435.05; found, m/z 435.06. Anal. Calc'd for C25H20O2Na (1H) : C, 60.9; H, 5.75; S, 10.33. Found: C, 70.59; H, 5.81; S, 10.31.

Acknowledgement

The authors would like to acknowledge the financial support (Grant No.: 1321760011) from the Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR).

Notes and References


A hydrogen-bonded organic framework derived from a polyhedral oligomeric silsesquioxane and an aggregation-induced emission luminogen tetraphenylethene derivative was reported.