Electronic Supplementary Material (ESI) for Polymer Chemistry.

Facile preparation of pH-responsive AIE-active POSS dendrimers for detection of trivalent metal cations and acid gases

Yunfei Zuo[a,b], Xing Wang*[a], Yanyu Yang[a,b], Da Huang[a,b], Fei Yang[a,b], Hong Shen[a] and Decheng Wu*[a,b]

[a] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics & Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[b] University of Chinese Academy of Sciences, Beijing 100049, P.R. China
E-mail: wangxing@iccas.ac.cn; dcwu@iccas.ac.cn

1. Materials

Octavinyl POSS (98%, Hybrid Plastics), 3-mercaptopropionic acid (99%, J&K), trifluoromethanesulfonic acid (99%, Aldrich), 2-mercaptoethylamine hydrochloride (99%, Energy Chemical), 4-(dimethyl-amino)-pyridine (DMAP, 99%, Aldrich), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (99%, Energy Chemical), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, J&K), succinic anhydride (99%, J&K), triethylamine (TEA, 99%, Beijing Chemical Works), bromotriphenylethylene (98%, Energy Chemical), 4-formylphenylboronic acid (98%, Energy Chemical), tetrabutyl ammonium bromide (TBAB, 99%, Energy Chemical), tetrakis(triphenylphosphine) palladium(0) (99%, Energy Chemical), sodium hydroxide, potassium carbonate, methanol, methylbenzene, hydrochloric acid, hexane and ether (reagent grade, Beijing Chemical Works), tetrahydrofuran (THF), *N*,*N*-dimethyl formamide (DMF), chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) were purified by stirring over calcium hydride for 24 h followed by distillation. All other reagents were purchased from Sigma-Aldrich and used as received without further purification.

2. Characterizations

^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 spectrometer in chloroform-d, dimethylsulfoxide-d_6 and methanol-d_4 using tetramethylsilane (TMS) as internal reference.

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrum was recorded on an Autoflex III MALDI-TOF mass spectrometer equipped with a 337 nm nitrogen laser.

Gel permeation chromatography (GPC) in THF was performed using four Waters Styragel columns (HT 2, HT 3, HT 4, and HT 5), a Waters 1515 isocratic HPLC pump, and a Waters 2414 RI detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Molecular weight (M_n) and polydispersity indexes (PDI) were obtained using the workstation software equipped with the system by the processing method based on a working curve of polystyrene standards.

Transmission electron microscopy (TEM) images were obtained on a JEM-2200FS microscope (JEOL, Japan). A 5 μL droplet of micellar solution was dropped onto a copper grid (300 mesh) coated with a carbon film, followed by drying at room temperature.

UV-vis spectra of the samples were measured over different irradiation time intervals on a Hitachi U-3010 spectrometer, and fluorescence measurements were carried out on a Hitachi F4600 photoluminescence spectrometer with a xenon lamp as a light source.

The volume flow of used gases for gas monitoring is 2.5 L and the volume of the THF/water mixtures is 0.1 L. Besides, the ventilation time is 5 min.

3. Preparations

3.1 Synthesis of TPE-CHO

Bromotriphenylethylene (2.01 g, 6 mmol) and 4-formylphenylboronic acid (1.35 g, 9 mmol) were dissolved in the mixture of toluene (40 mL), TBAB (0.19 g, 0.6 mmol) and 1.2 M potassium carbonate aqueous solution (10 mL). The mixture was stirred at room temperature for 0.5 h under Ar gas followed by adding $Pd(PPh_3)_4$ (60 mg, 5.3×10^{-3} mmol) and then heated to 90 ℃ for 24 h. After that the mixture was poured into water and extracted three times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After moving the solvent under reduced pressure, the residue was chromatographed on a silica gel column with CH_2Cl_2/n-hexane (v/v = 1:2) as an eluent to give faint yellow powder with 90.1% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm = 7.02-7.03 (m, 6H), 7.11 (m, 9H), 7.18 (d, 2H), 7.60-7.63 (d, 2H), 9.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ ppm = 126.9, 127.1, 127.7, 127.9, 129.2, 131.3, 134.3, 139.8, 143.0, 150.6, 191.9.

3.2 Synthesis of (Vinyl)$_7$-POSS-OH

To a solution of octavinyl POSS (3.80 g, 6.00 mmol) in 500 mL of fresh distilled CH_2Cl_2, trifluoromethanesulfonic acid (585 μL, 6.60 mmol) was slowly added dropwise via syringe at room temperature. After 6 hours, the solution was diluted with CH_2Cl_2 and then washed with saturated aqueous Na_2CO_3 three times. The organic layer was then concentrated by evaporating the excess solvent. Then wet acetone was added into the concentrated solution and the hydrolysis process was performed for 6 h. The crude product was yielded after removing the solvent. The final product was separated chromatographically on silica gel with CH_2Cl_2/hexane (v/v = 1/1) to afford a white solid, (Vinyl)$_7$-POSS-OH, (1.22 g, 31.2 %) after obtained in vacuo. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm = 1.62 (s, 1H), 1.22 (t, 2H), 3.82 (t, 2H), 5.85-6.16 (m, 21H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ ppm = 17.3, 58.5, 128.6, 137.2.

3.3 Synthesis of POSS-$(NH_3Cl)_8$

3-aminopropyltriethoxysilane (7.10 g) and 180 mL of methanol were added to a 500 mL round-bottomed flask equipped with a magnetic stirring. The reaction mixture was degassed three times with nitrogen and 15 mL of hydrochloric acid slowly added, via syringe at room temperature. It was heated to 90 ℃ and refluxed for 24 h. After that, allow the mixture to cool to room temperature. Then, 200 mL of tetrahydrofuran was poured into the mixture, and the white precipitate was collected via filtration. Finally, it was washed with tetrahydrofuran to remove the by-product, POSS-$(NH_3Cl)_8$, (3.05 g, 66.1 %) after obtained in vacuo. ^{1}H NMR (DMSO-d_6, 400 MHz): δ ppm = 8.27 (s, 3H), 2.80 (t, 2H), 1.73 (m, 3H), 0.73 (t, 2H). ^{13}C NMR (DMSO-d_6, 400 MHz): δ ppm = 41.0, 20.6, 8.4. ^{29}Si NMR (DMSO-d_6, 300 MHz): δ ppm = -66.9.

3.4 Synthesis of G0 POSS-$(TPE)_8$

POSS-$(NH_3Cl)_8$ (237.2 mg, 0.2 mmol) and TEA (300 μL, 2.0 mmol) were dissolved in 20 mL of methanol. Then 20 mL of methanol containing TPE-CHO (1.08 g, 3.0 mmol) was dropwise added into the solution under a nitrogen atmosphere. The reaction mixture was degassed three times with nitrogen and kept at room temperature for 12 h to produce yellow precipitates. The crude products were obtained after filtration, washing with cold MeOH and drying to afford brilliant yellow powders, G0 POSS-$(TPE)_8$, (550.0 mg , 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm = 8.0-8.2 (s, 1H), 7.5-6.5 (m, 19H), 3.51 (t, 2H), 1.73 (m, 2H), 0.64 (t, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ ppm = 160.9, 146.3, 143.7, 143.6, 141.8, 140.6, 134.5, 132.1, 131.7, 131.5, 131.4, 128.1, 128.0, 127.9, 126.8, 126.7, 64.3, 24.5, 9.9.

3.5 Synthesis of POSS-$(COOH)_8$

To a solution of POSS-$(NH_3Cl)_8$ (1.17 g, 1.0 mmol) and triethylamine (1.40 mL, 10.0 mmol) in MeOH (20 mL), succinic anhydride (1.60 g, 16.0 mmol) was added, and the mixture was stirred at room temperature. After 2 h, chloroform was poured into the solution, and the white precipitate was collected via filtration and washed with chloroform as a white powder, POSS-$(COOH)_8$, (1.28 g, 76%) after obtained in vacuo. ^{1}H NMR (CD_3OD-d_4, 400 MHz): δ ppm = 3.16 (t, 2H), 2.59 (t, 2H), 2.48 (t, 2H), 1.59 (m, 2H), 0.64 (t, 2H). ^{13}C NMR (CD_3OD-d_4, 400 MHz): δ ppm = 176.3, 174.5, 43.0, 31.7, 30.4, 24.0, 10.0.

3.6 Synthesis of $POSS_9$-$(Vinyl)_{56}$

(Vinyl)$_7$-POSS-OH (1.95 g, 3.0 mmol), POSS-$(COOH)_8$ (336.0 mg, 0.20 mmol), EDCI (518.4 mg, 2.70 mmol) and DMAP (50.4 mg, 0.45 mmol) were added to a 100 mL round-bottomed flask equipped with a magnetic stirring bar, followed by the addition of 30 mL of freshly dried DMF to fully dissolve all the solids. The solution was cooled to 0 ℃ for 15 min and allowed to the room temperature, and then further stirred for another 24 h to complete the reaction. After removing DMF, ethyl acetate was added to dissolve the white solids, and then washed with 2M HCl aqueous solution, saturated NaCl aqueous solution and DI water for three times and dried over anhydrous Na_2SO_4. Then the final product was separated chromatographically on silica gel with CH_2Cl_2/methanol (v/v = 20/1) to remove the excess (Vinyl)$_7$-POSS-OH to afford the white powder, $POSS_9$-$(Vinyl)_{56}$, (593.0 mg , 44%) after obtained in vacuo. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm = 6.5-5.3 (m, 14H), 4.19 (t, 2H), 3.4-3.2 (m, 2H), 2.6-2.4 (m, 4H), 1.18 (t, 2H), 0.58 (t, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ ppm = 173.0, 171.6, 137.3, 128.6, 60.9, 42.3, 30.7, 29.6, 28.6, 23.1, 13.1, 9.4.

3.7 Synthesis of G1 $POSS_9$-$(TPE)_{56}$

$POSS_9$-$(Vinyl)_{56}$ (336.8 mg, 0.05 mmol), cysteamine hydrochloride (568.0 mg, 5.0 mmol) and DMPA (50 mg, 0.2 mmol) were dissolved in 20 mL mixture of THF/MeOH (v/v=1/3). After irradiation under a 365 nm UV lamp at room temperature for 6 h to make sure no vinyl groups existed. The product was precipitated into ether for several times and then purified by ultrafiltration (MWCO 500) and collected after freeze-drying to afford the white powder, $POSS_9$-$(NH_3Cl)_{56}$, (472.0 mg , 72%). Then, $POSS_9$-$(NH_3Cl)_{56}$ (262.2 mg, 0.02 mmol) and TEA (240 μL, 1.6 mmol) were dissolved in 30 mL of methanol. 15 mL of methanol containing TPE-CHO (720.0 g, 2.0 mmol) was dropwise added into the solution under a nitrogen atmosphere. The reaction mixture was degassed three times with nitrogen and kept at room temperature for 12 h to produce yellow precipitates. The crude products were obtained after filtration, washing with cold MeOH and drying to afford whity-yellow powders, G1 $POSS_9$-$(TPE)_{56}$ (348.0 mg , 58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ ppm = 8.0-8.2 (s, 1H), 7.5-6.5 (m, 19H), 3.78 (t, 2H), 2.90 (t, 2H), 2.70 (m, 2H), 1.14(t, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ ppm = 160.2, 148.6, 142.7, 142.4, 138.8, 133.3, 131.2, 130.5, 128.2, 127.0, 126.8, 126.1, 126.0, 127.9, 126.8, 126.7, 61.6, 60.1, 32.2, 28.6, 23.0, 13.1.

References

1. X. Wang, Y. Y. Yang, P. Y. Gao, D. Li, F. Yang, H. Shen, H. X. Guo, F. J. Xu and D. C. Wu, *Chem. Commun.*, 2014, **50**, 6126.
2. Y. Y. Yang, X. Wang, Y. Hu, H. Hu, D. C. Wu and F. J. Xu, *ACS Appl. Mater. Interface*, 2014, **6**, 1044.
3. X. Wang, Y. Y. Yang, Y. F. Zuo, F. Yang, H. Shen and D. C. Wu, *Chem. Commun.*, 2016, **52**, 5320.

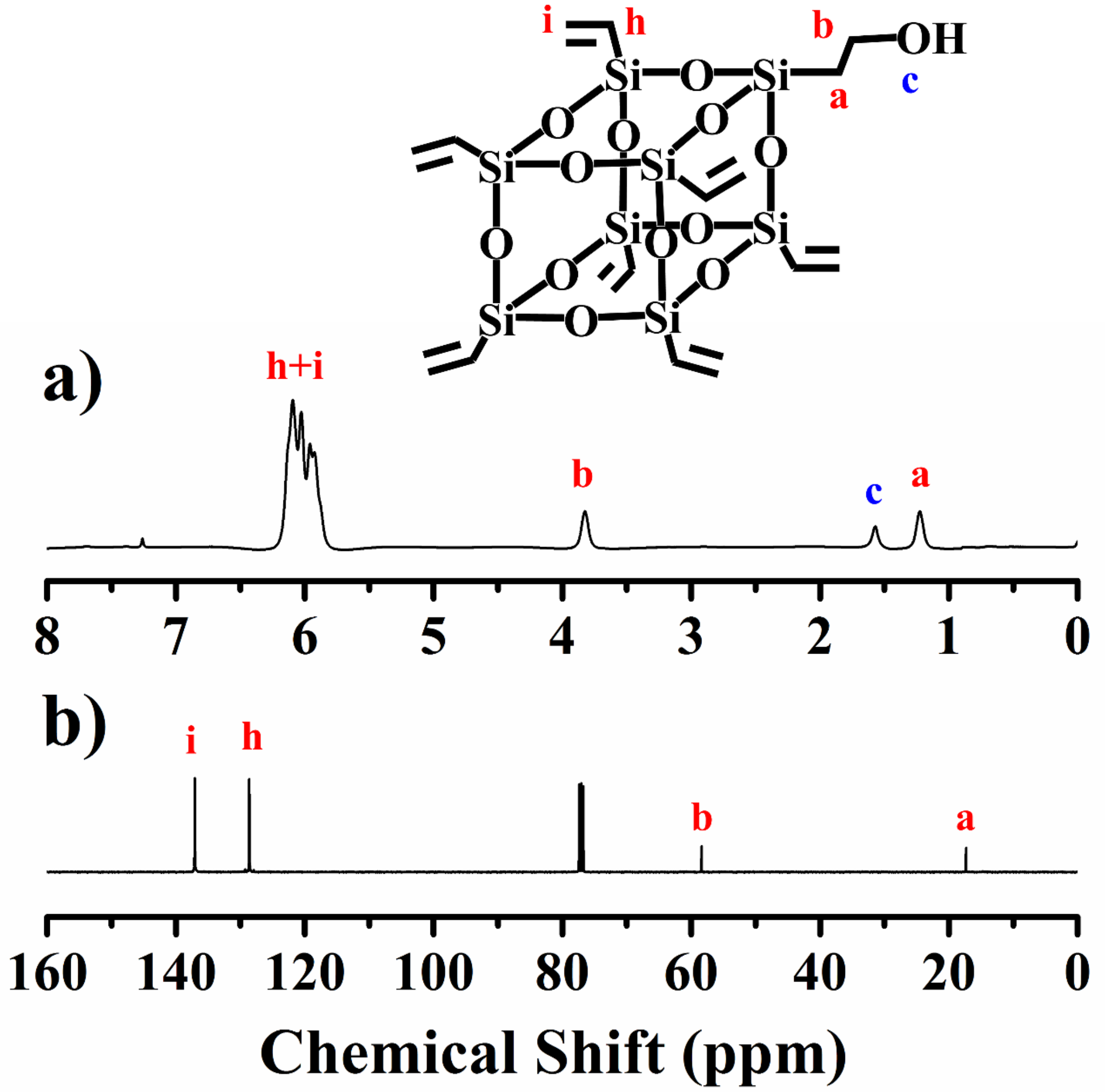


Fig. S1 (a) ^{1}H and (b) ^{13}C NMR spectra of (Vinyl)$_7$-POSS-OH at $CDCl_3$

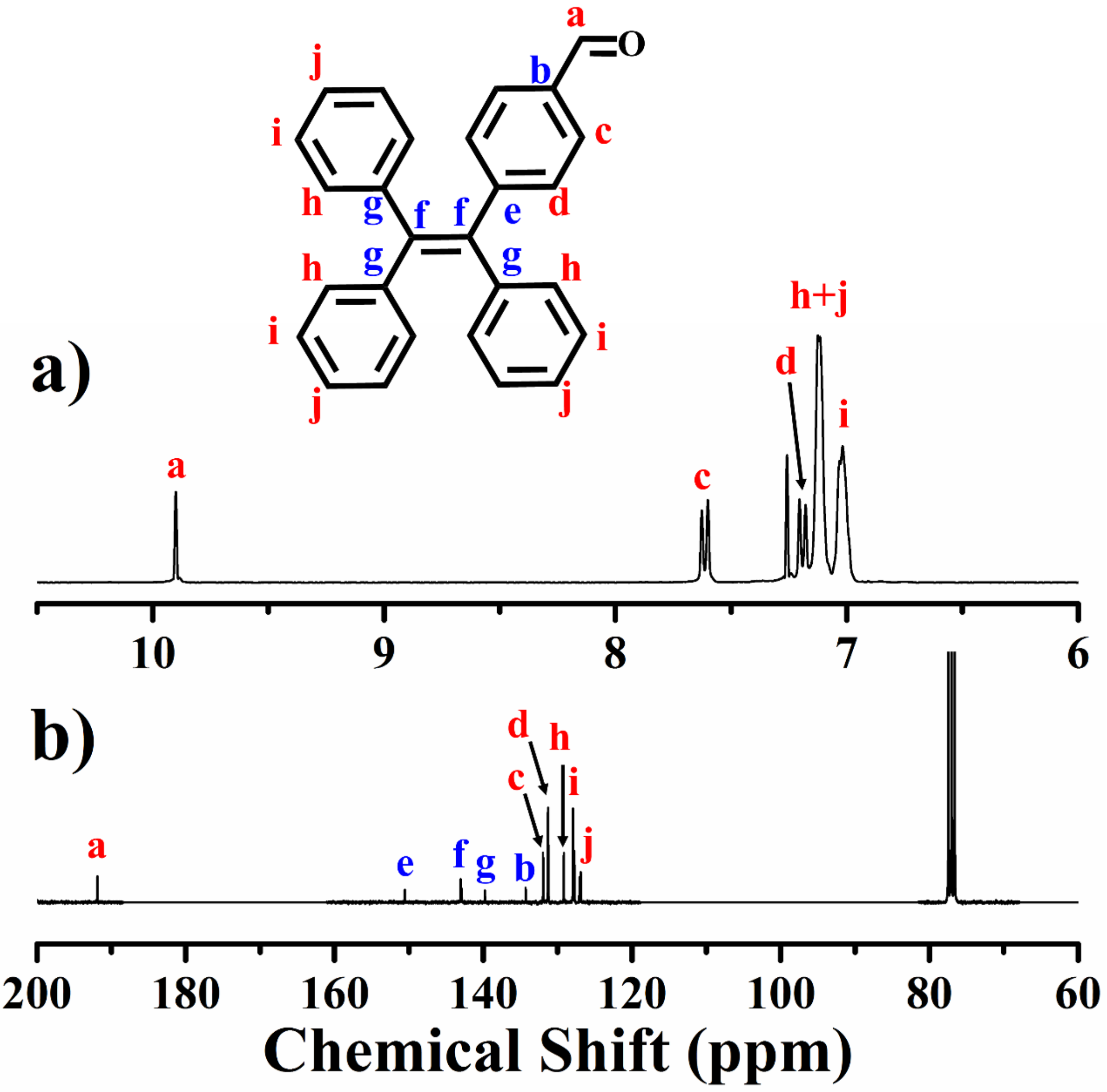


Fig. S2 (a) ^{1}H and (b) ^{13}C NMR spectra of TPE-CHO at $CDCl_3$

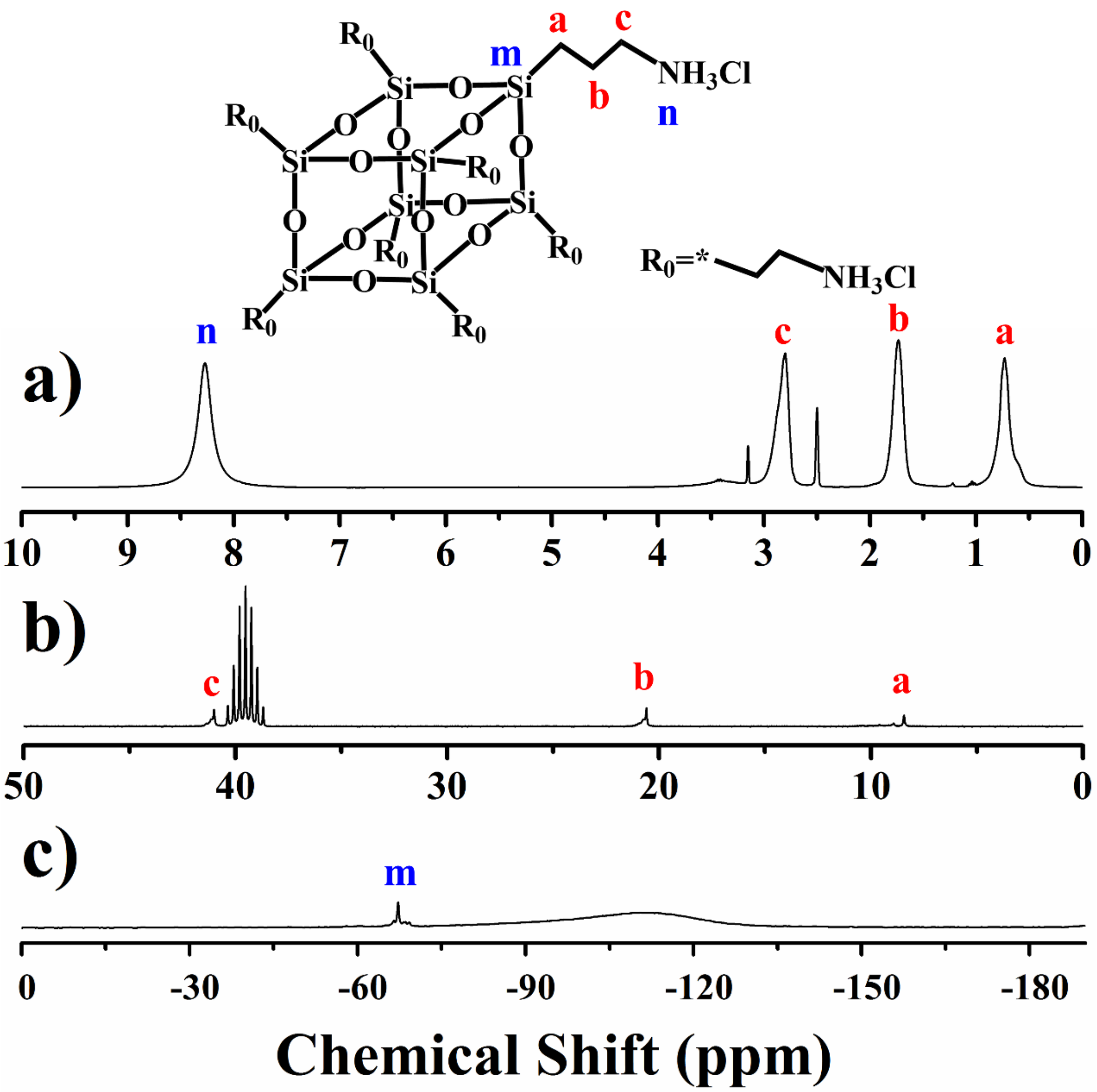


Fig. S3 (a) ^{1}H, (b) ^{13}C and (c) ^{29}Si NMR spectra of POSS-$(NH_3Cl)_8$ at DMSO-d_6

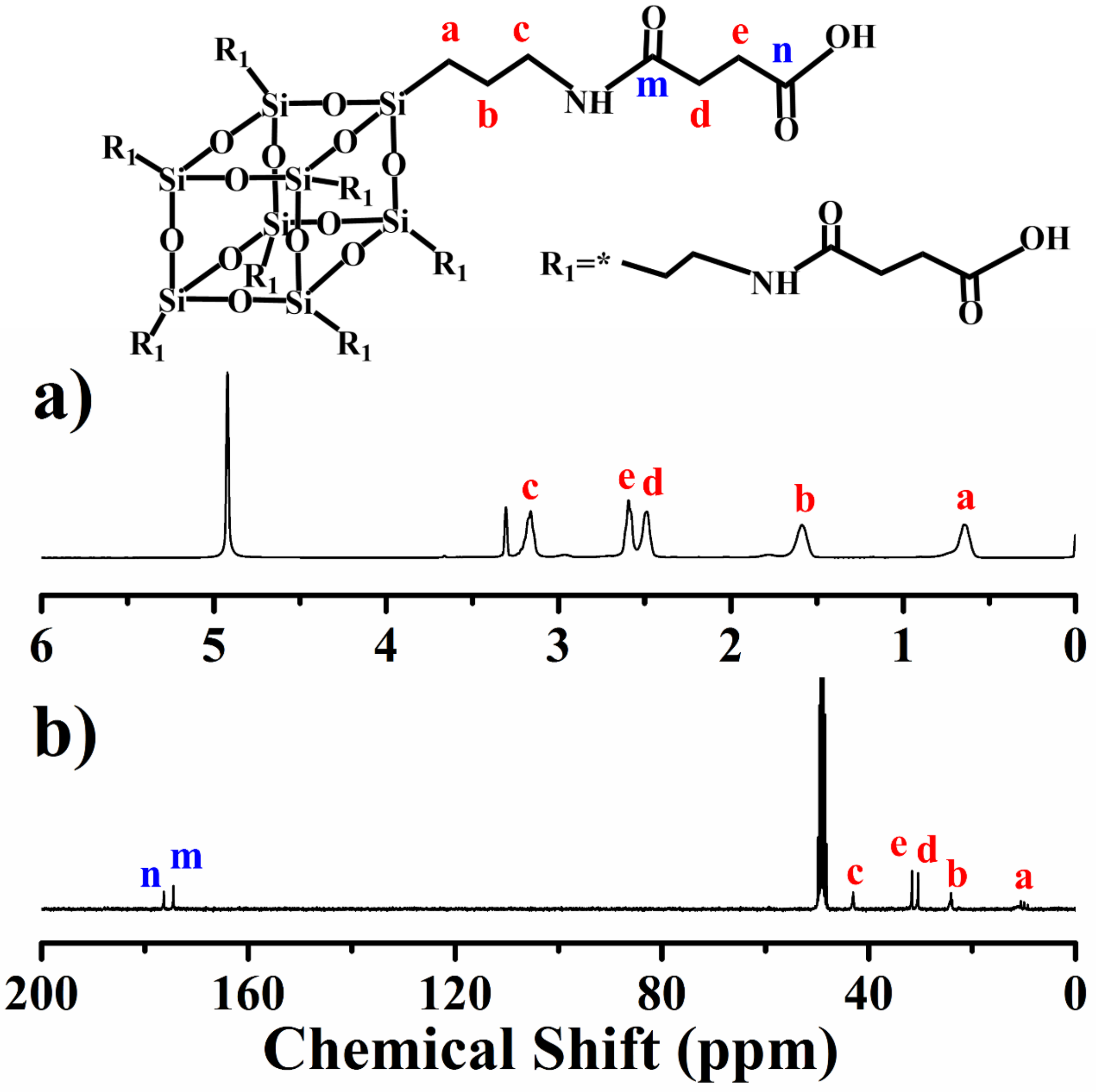


Fig. S4 (a) ^{1}H and (b) ^{13}C NMR spectra of POSS-$(COOH)_8$ at MeOD-d_4

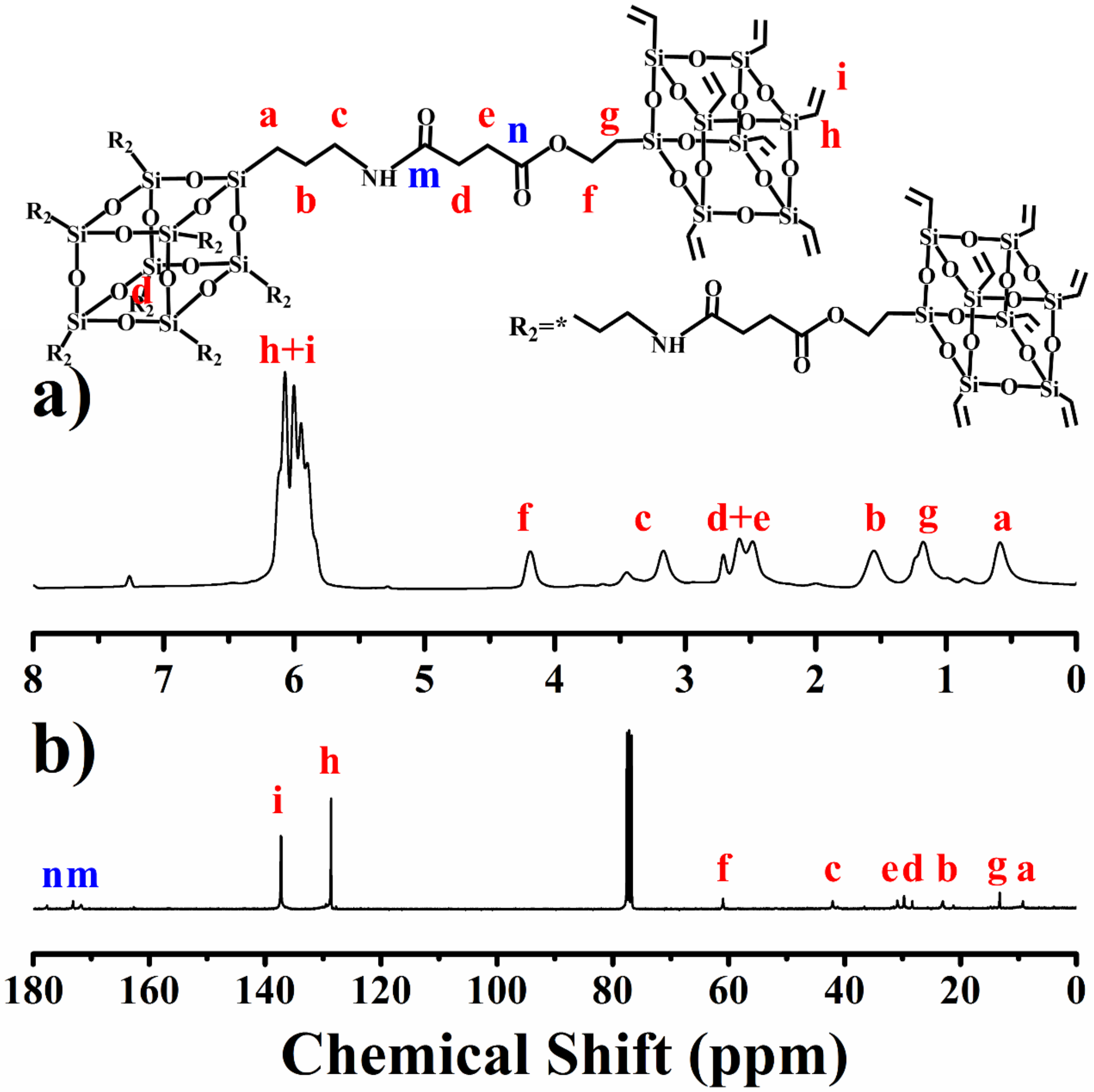


Fig. S5 (a) ^{1}H and (b) ^{13}C NMR spectra of POSS$_9$-(Vinyl)$_{56}$ at CDCl$_3$

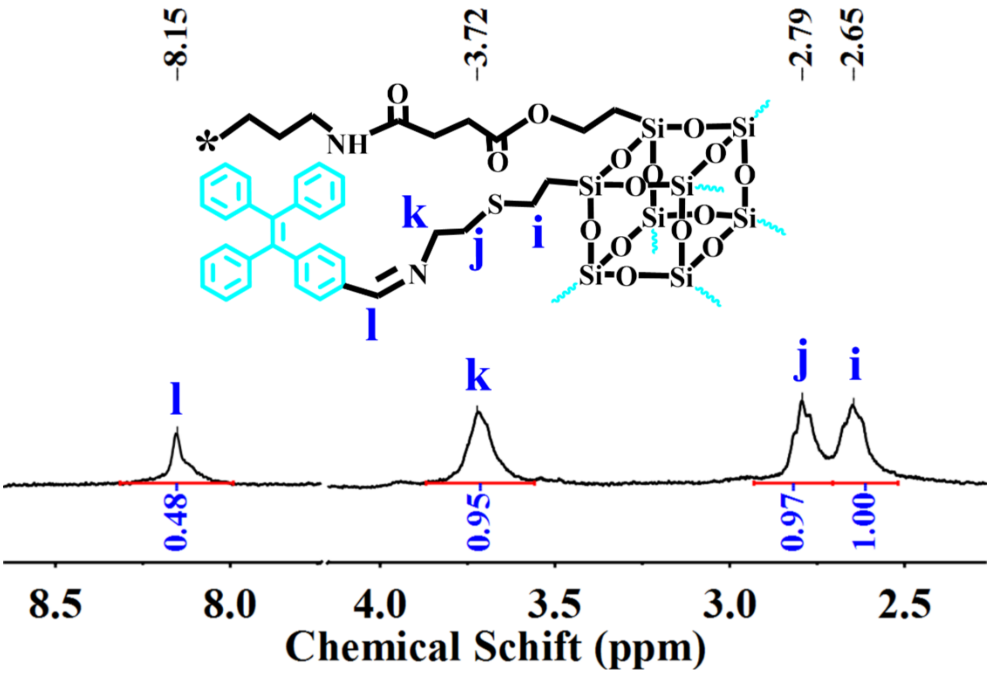


Fig. S6 ^{1}H NMR spectra of $POSS_9$-$(TPE)_{56}$ at $CDCl_3$

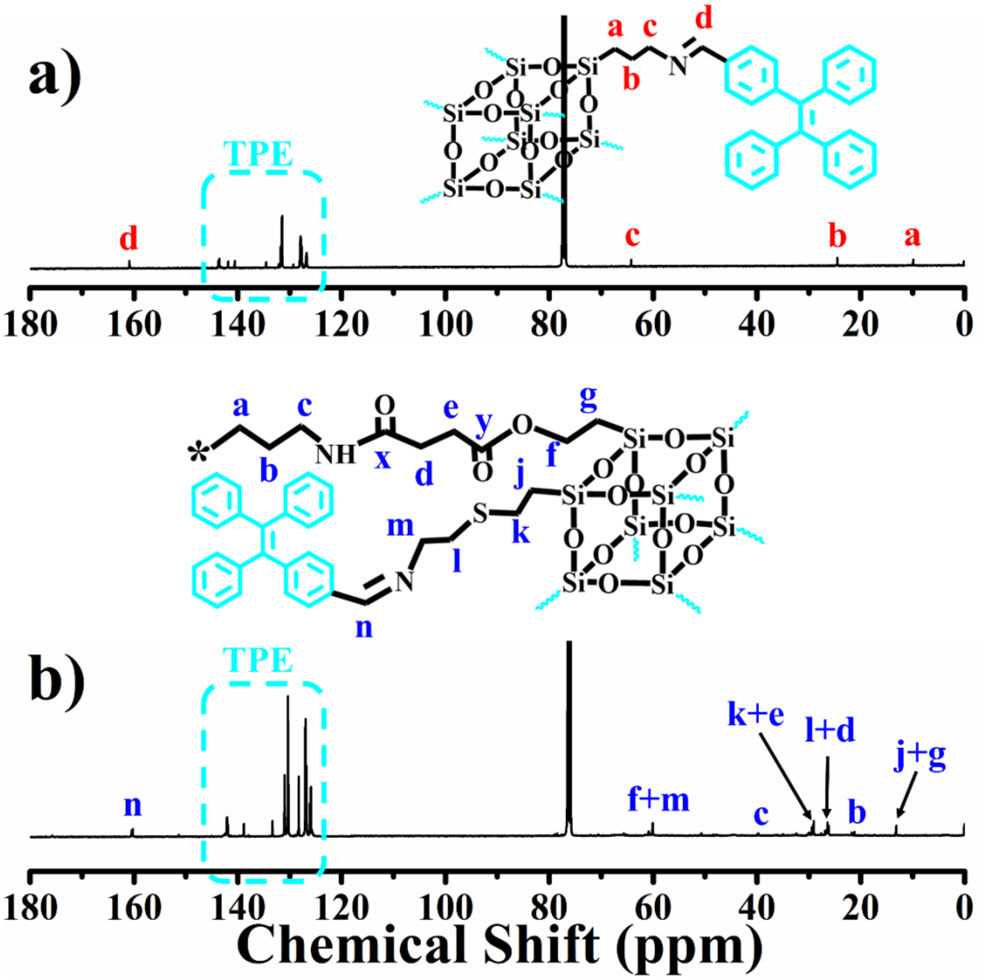


Fig. S7 ^{13}C NMR spectra of (a) POSS-$(TPE)_8$ and (b) $POSS_9$-$(TPE)_{56}$ at $CDCl_3$

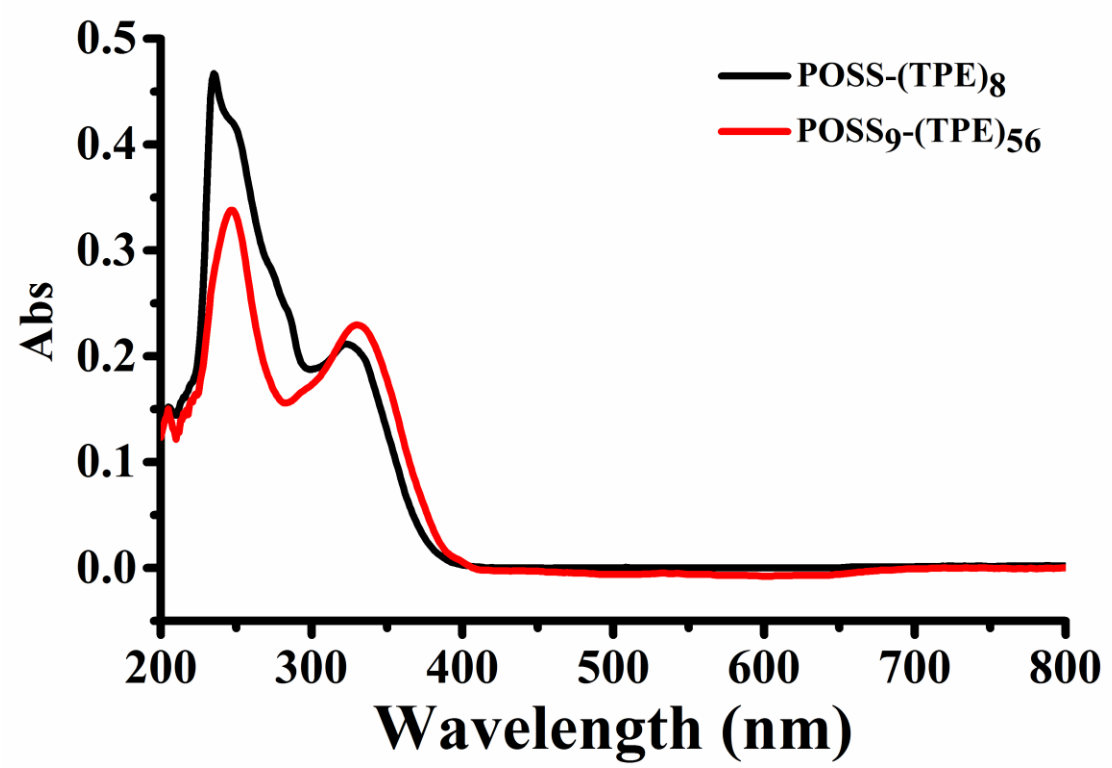


Fig. S8 UV-vis spectra of POSS-$(TPE)_8$ and $POSS_9$-$(TPE)_{56}$ in THF

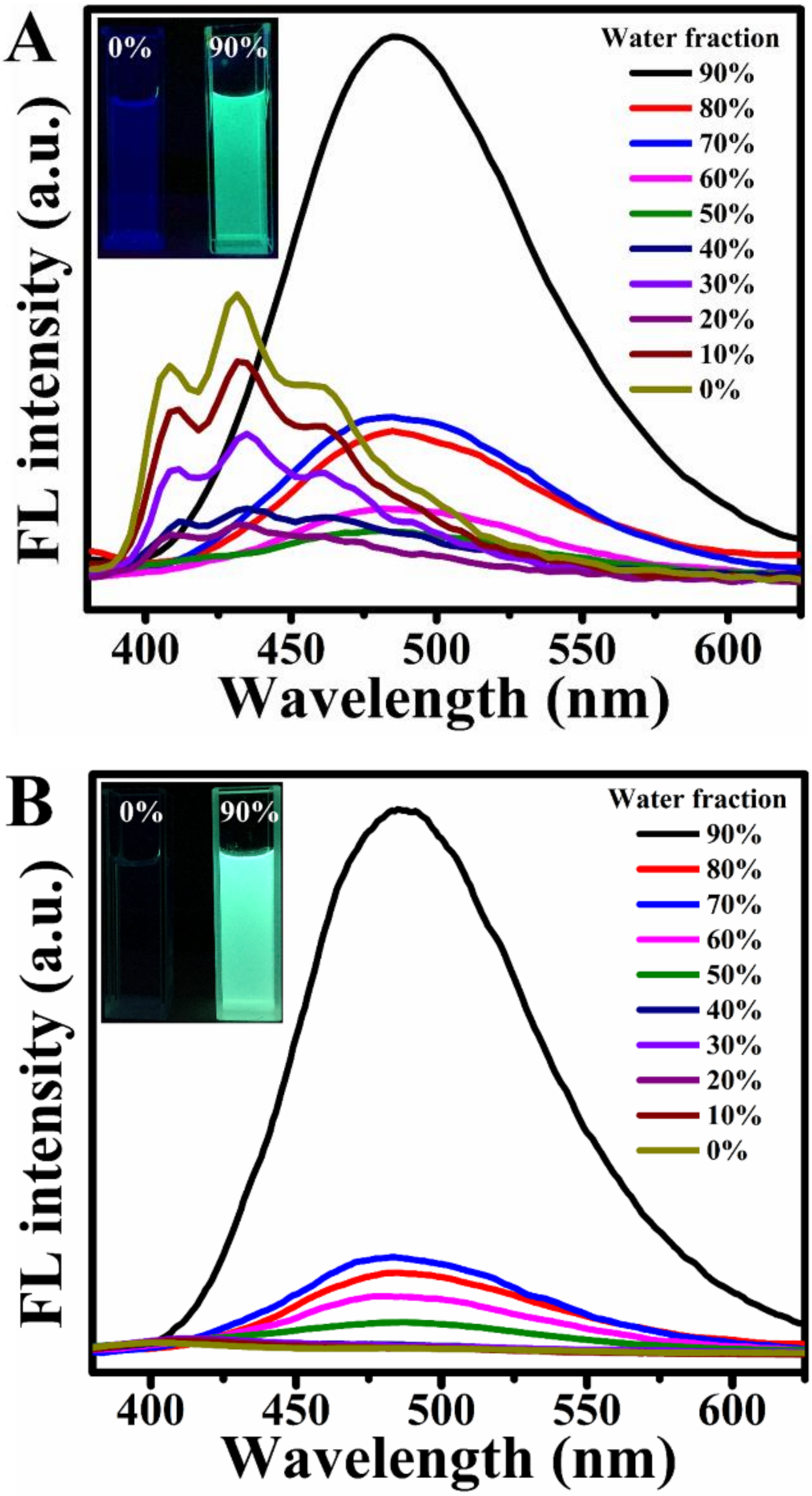


Fig. S9 Fluorescence spectra of (A) POSS-$(TPE)_8$ and (B) $POSS_9$-$(TPE)_{56}$ in THF/water mixtures with different water volume fractions. The inset photographs of POSS-$(TPE)_8$ and $POSS_9$-$(TPE)_{56}$ solutions was taken upon excitation at 365 nm using a UV lamp. Concentration for all samples was 10^{-5} M.

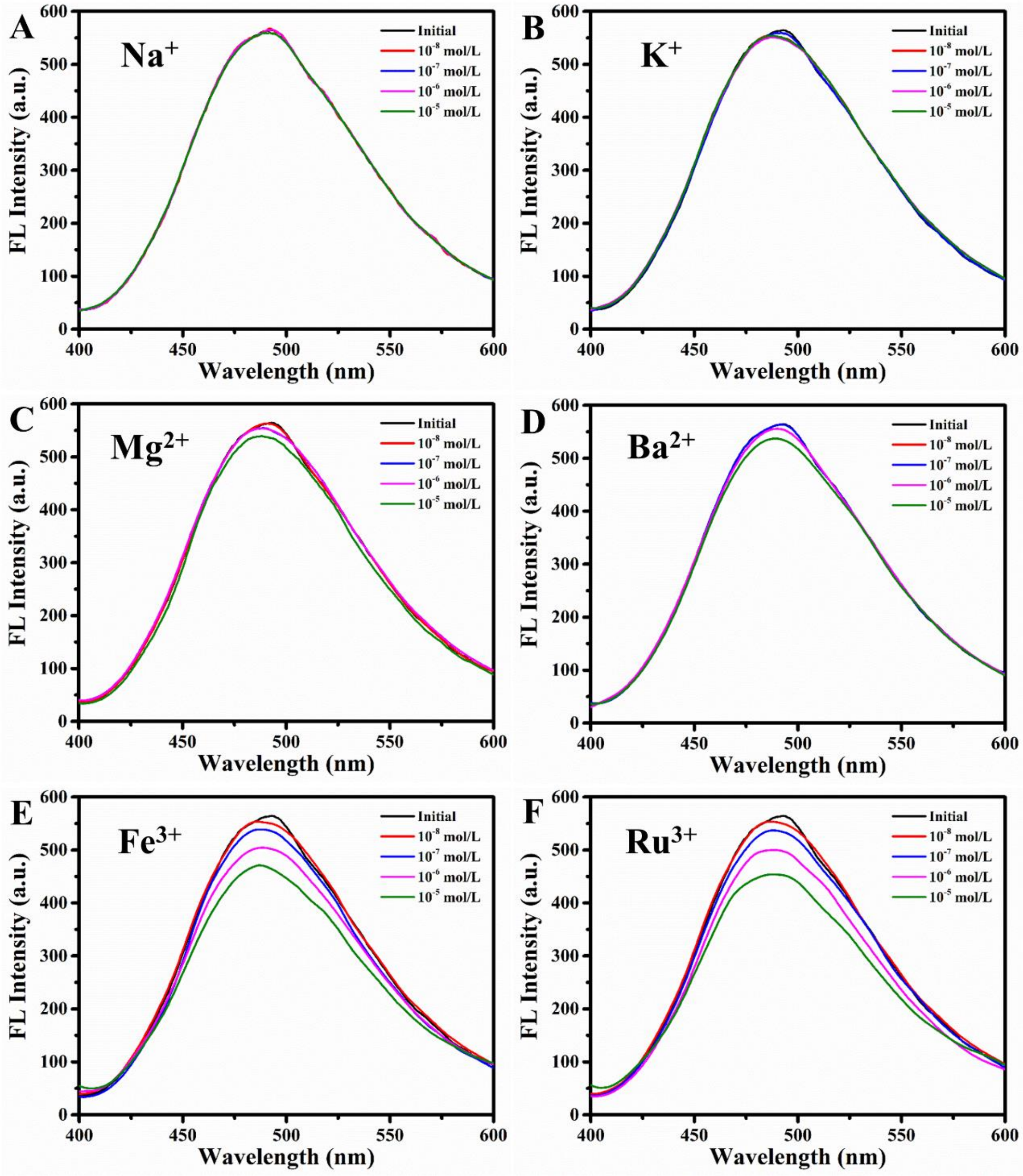


Fig. S10 Fluorescence spectra of POSS$_9$-(TPE)$_{56}$ in THF/water mixtures (10^{-5} M) with different concentrations of (A) Na^+, (B) K^+, (C) Mg^{2+}, (D) Ba^{2+}, (E) Fe^{3+} and (F) Ru^{3+}.

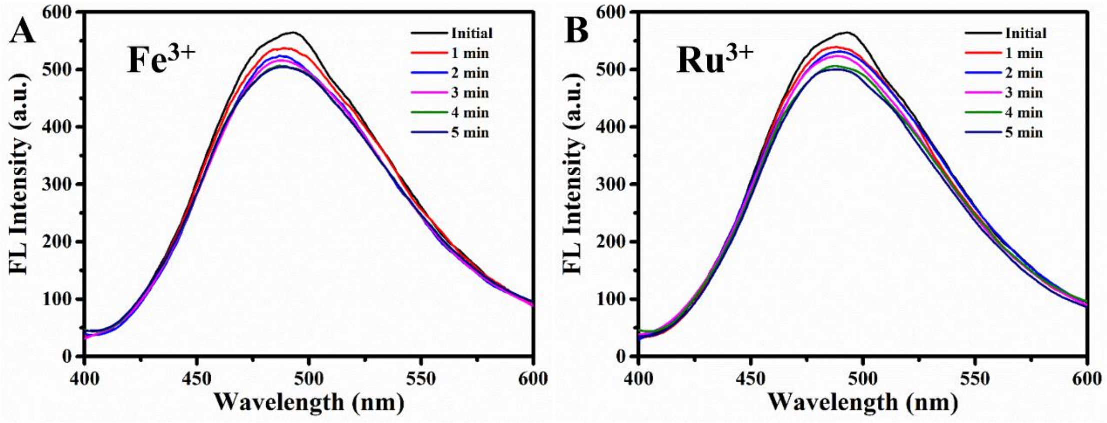


Fig. S11 Time-dependent fluorescence changes of POSS$_9$-(TPE)$_{56}$ in THF/water mixtures (10^{-5} M) in the presence of (A) Fe^{3+} (10^{-6} M) and (B) Ru^{3+} (10^{-6} M).

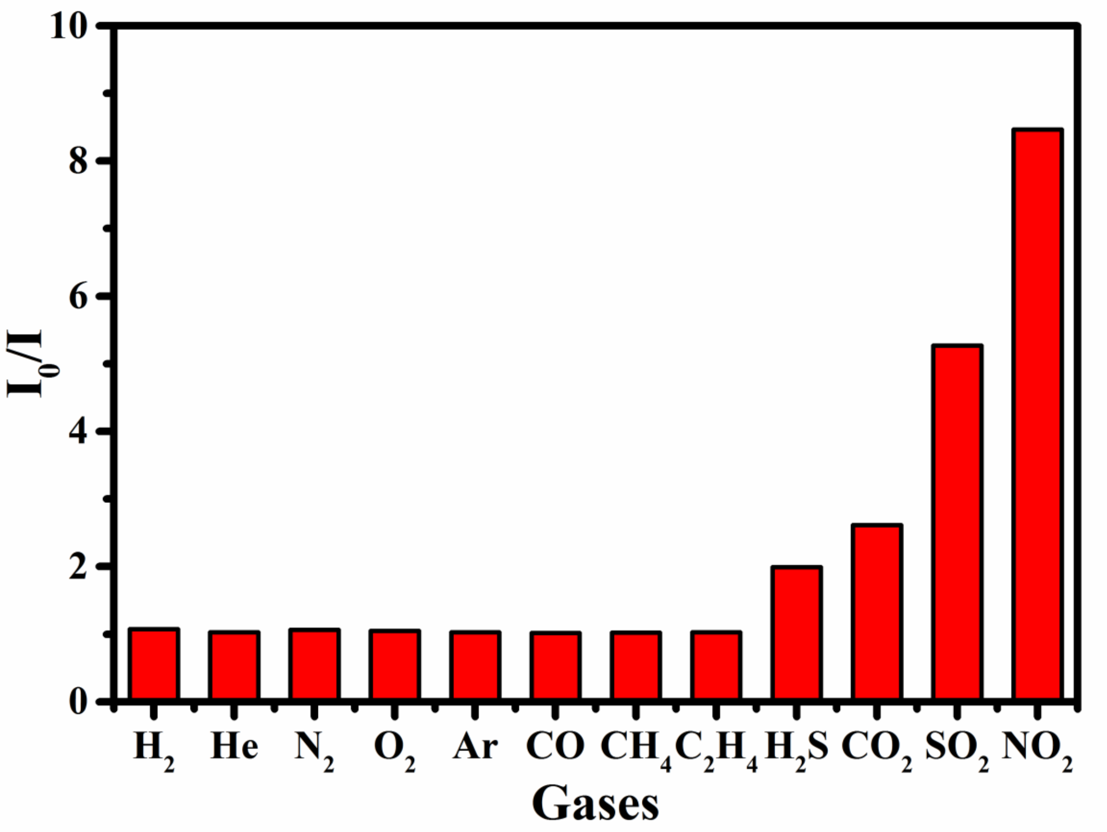
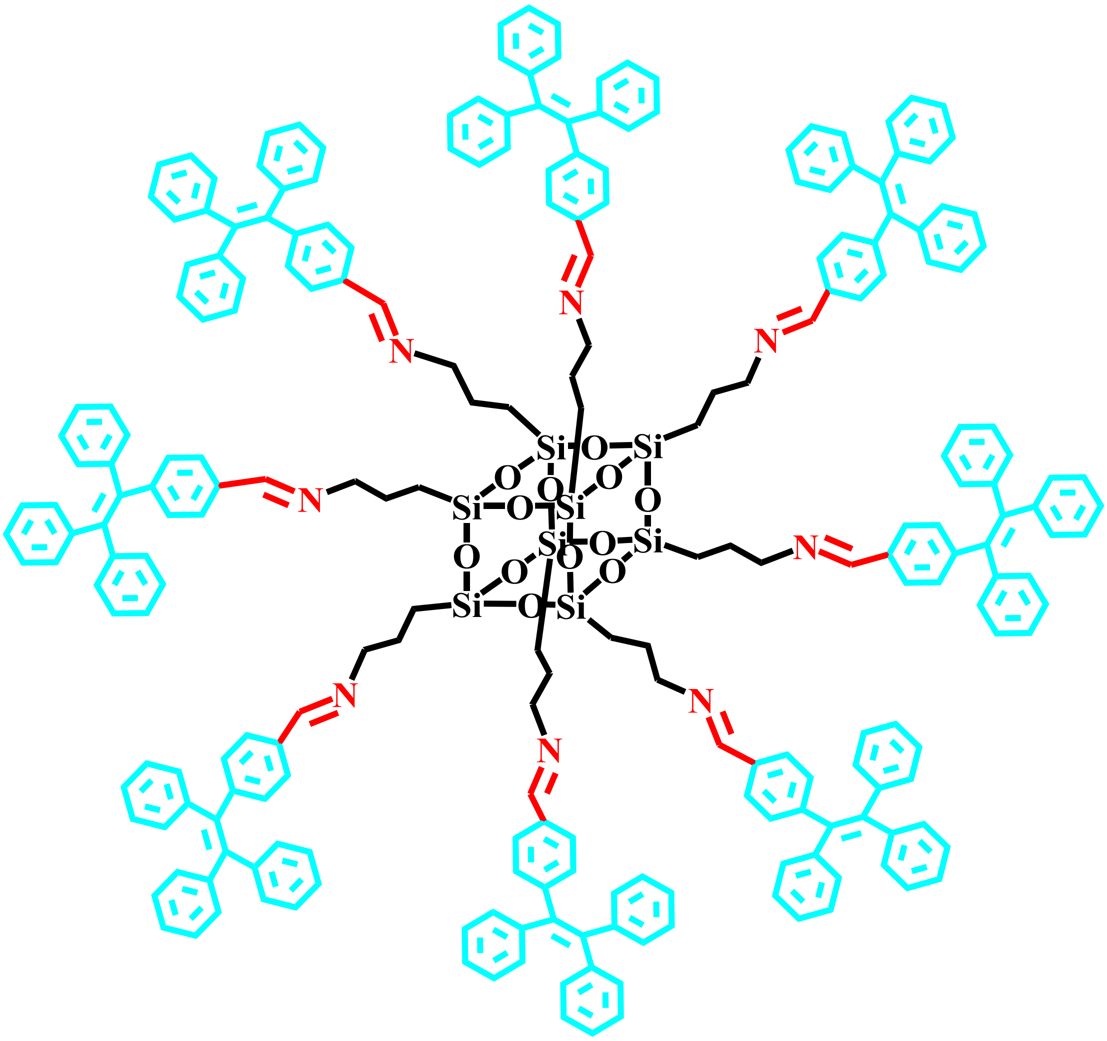


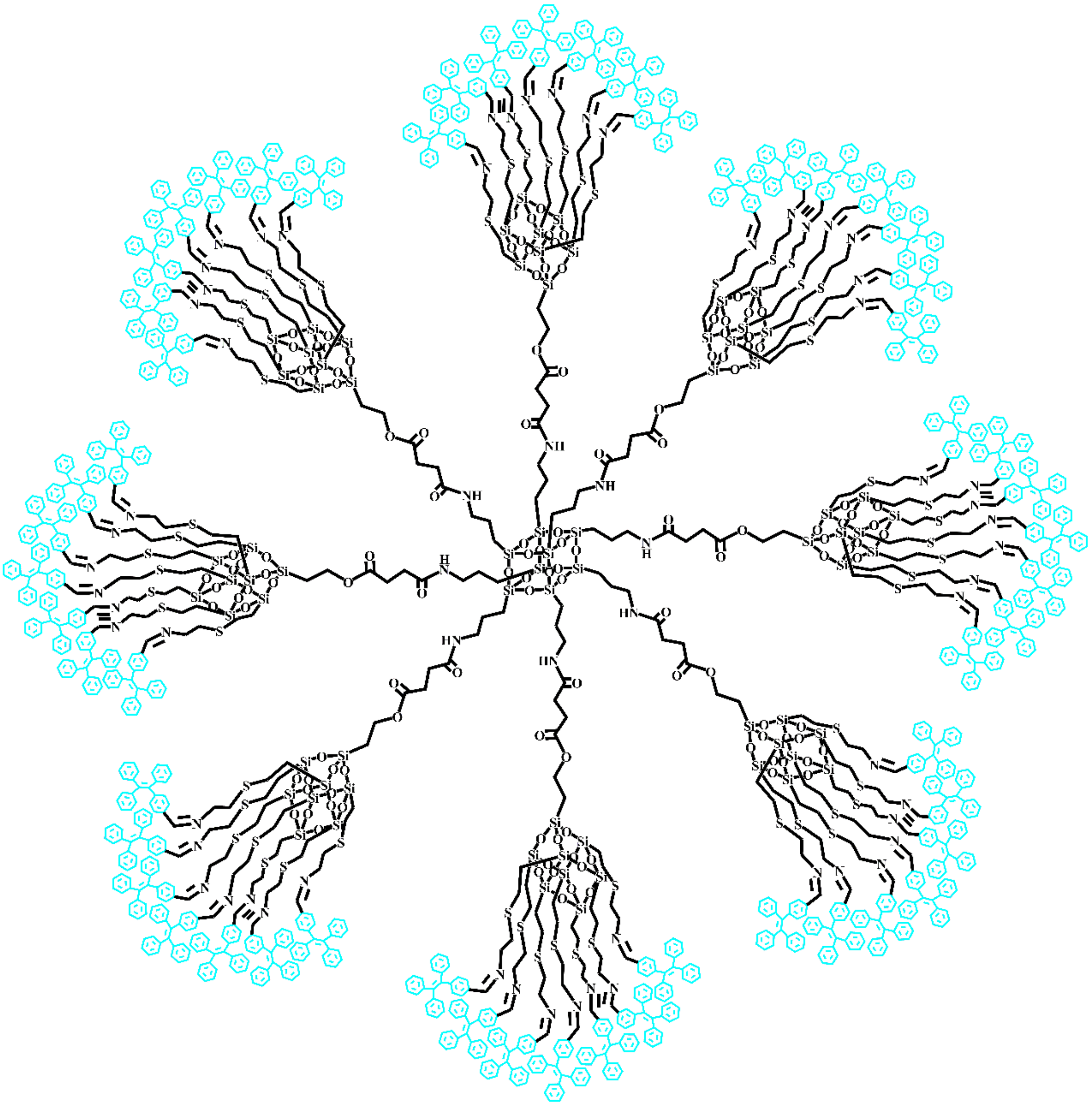
Fig. S12 Changes in relative emission intensities (I_0/I) of POSS$_9$-(TPE)$_{56}$ with injecting various gases. I_0=intensity in the absence of gases. Concentration for POSS$_9$-(TPE)$_{56}$ was 10^{-5} M.

Table S1. GPC data of POSS-(TPE)$_8$, POSS$_9$-(Vinyl)$_{56}$ and POSS$_9$-(TPE)$_{56}$

	M_n (GPC)	M_w/M_n (GPC)
POSS-(TPE)$_8$	2500	1.03
POSS$_9$-(Vinyl)$_{56}$	3800	1.05
POSS$_9$-(TPE)$_{56}$	14300	1.06



Scheme S1 Chemical structure of the POSS-(TPE)$_8$ dendrimer



Scheme S2 Chemical structure of the $POSS_9$-$(TPE)_{56}$ dendrimer