Supporting Information for

Water Soluble Octa–Functionalized POSS: All Click Chemistry Synthesis and Efficient Host-Guest Encapsulation

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1. Experimental procedures

Materials

Octavinyl POSS (**1**) was purchased from Hybrid Plastics. Benzyl bromide and allyl bromide were obtained from Sinopharm Chemical Reagent Co., Ltd. Propargyl bromide, propargyl chloride, 1-bromododecane, 1,3-propanesultone, and 1-bromooctadecane were supplied by Aladdin Chemical Co.. 9-(Chloromethyl)anthracene was purchased from Sigma Aldrich. 3-(Dimethylamino)-1-propanethiol was acquired from Atomax Chem Co. Ltd. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA), chloromethylstyrene, 1-(chloromethyl)naphthalene, and 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) were purchased from TCI Chemical Co.. 2-Azidoethyl-2-bromoacetate was prepared from bromoacetyl bromide and 2-azidoethanol in the presence of a bulk amine, *N,N*-diisopropylethylamine, following the procedure described before.[1] Cuprous bromide was purchased from Alfa Aesar Co. All the solvents were purchased from Shanghai No.3 Chemical Reagent Factory. Before use, DMF was dried over $MgSO_4$. THF was refluxed in the presence of sodium foil and distilled prior to use. Rose bengal (RB) and methylene violet 3RAX (MV) were purchased from Shanghai No.3 Chemical Reagent Factory and Shanghai Yuanhang Chemical Reagent Co., respectively. Methyl orange (MO) and eosin Y (EY) were purchased from Sinopharm Chemical Reagent Co. Ltd. Styrene-*b*-butadiene-*b*-styrene block copolymer (SBS) and poly (methyl methacrylate) (PMMA) were the products from Qi Mei Corp. (Taiwan).

Synthesis of Octa(*N,N*-dimethylaminopropylthioethyl) POSS (2).

Octavinyl POSS (**1**) (0.63 g, 1 mmol) and 3-(dimethylamino)-1-propanethiol (DPT) (1.19 g, 10 mmol) were successively added into dried THF (5 mL) in a 25 mL Schlenk flask. The flask was wrapped up with aluminium foil, and then the photoinitiator, DMPA (41 mg, 0.16 mmol), was added into it. After being sealed, the mixture was purged with high-purity N_2 to eliminate oxygen. Then, aluminium foil was removed and the reaction was triggered by UV-irradiation at 365 nm under stirring at room temperature. As the reaction proceeded, **1** gradually dissolved in the solution. After 1 h, the UV-light was turned off and the flask was connected to a distillation system. THF and excess 3-(dimethylamino)-1-propanethiol were removed by vacuum evaporation at 30 ^{o}C. The resulted viscous liquid was the targeted product, **2** in quantitative yield. *(Caution: It is better to immediately use the freshly prepared **2** in the subsequent reactions, because moisture can induce the Si-O-Si bonds quickly turn into Si-OH bonds under the existence of dimethylamino groups.)* ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.00 (t, 2H, Si-CH_2-CH_2-S), 1.65-1.84 (m, 2H, S-CH_2-CH_2-CH_2-N), 2.16-2.26 (m, 6H, N(CH_3)$_2$), 2.30-2.36 (t, 3H, S-CH_2-CH_2-CH_2-N), 2.47-2.70 (m, 4H, Si-CH_2-CH_2-S, S-CH_2-CH_2-CH_2-N). ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 58.4, 45.6, 29.4, 27.2, 25.9, 12.8. ^{29}Si NMR (500 MHz, $CDCl_3$), δ (ppm): -69.55. MALDI-TOF MS: 1587.4 g mol^{-1}, calculated 1586.9 g mol^{-1}.

Synthesis of Quaternary Ammonium POSS (3).

The achieved **2** was subsequently diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of active bromide or chloride compounds (10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. After that,

the mixture was further stirred for 10 min and then poured into diethyl ether at 0 ^{o}C to afford white precipitates. In order to fully removing the residuals, the white solid product was precipitated twice in cold diethyl ether again. The final precipitates were dried in vacuum at room temperature to give the quaternary ammonium POSS (**3**). ^{1}H NMR (400 MHz, D_2O), δ (ppm): 1.06 (2H, Si-C*H*$_2$-CH$_2$-S), 1.98-2.13 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.60-2.76 (4H, Si-CH$_2$-C*H*$_2$-S, S-C*H*$_2$-CH$_2$-CH$_2$-N), 3.07-3.31 (7H, C≡C*H*, N^+(C*H*$_3$)$_2$), 3.44-3.63 (2H, S-CH$_2$-CH$_2$-C*H*$_2$-N^+), 4.15-4.34 (2H, -C*H*$_2$-C≡CH).^{13}C NMR (400 MHz, D_2O), δ (ppm): 82.2, 71.4, 63.1, 54.8, 51.2, 28.1, 25.9, 22.8, 12.8. ^{29}Si NMR (500 MHz, $CDCl_3$), δ (ppm): -67.65.

Synthesis of octa-anthracene POSS (4)

The obtained **2** was immediately diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of 9-(chloromethyl) anthracene (2.36 g, 10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. Then, the mixture was further stirred for 3 h and then poured into diethyl ether at 0 ^{o}C to afford white precipitates. It was further purified by dissolvation in DMF and precipitation in diethyl ether again. The obtained solids were dried in vacuum at room temperature to give the quaternary ammonium POSS (**4**). ^{1}H NMR (400 MHz, *d6*-DMSO), δ (ppm): 1.08 (2H, Si-C*H*$_2$-CH$_2$-S), 2.05 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.60-2.76 (4H, Si-CH$_2$-C*H*$_2$-S-C*H*$_2$-CH$_2$-CH$_2$-N), 2.95 (6H, N^+(C*H*$_3$)$_2$), 3.84 (2H, S-CH$_2$-CH$_2$-C*H*$_2$-N^+), 5.80 (2H, -C*H*$_2$-anthracenyl), 7.50, 8.10, 8.80 (9H, anthracenyl). ^{13}C NMR (400 MHz, *d6*-DMSO), δ (ppm): 133.6~120.1, 64.5, 59.8, 50.1, 28.4, 25.8, 23.2, 13.1.

Synthesis of octa-naphthalene POSS (5)

Once **2** was prepared, it was diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of 1-(chloromethyl) naphthalene (1.83 g, 10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. Then, the mixture was further stirred for 1 h and then poured into diethyl ether at 0 ^{o}C to afford white precipitates. It was further purified by dissolvation in DMF and precipitation in diethyl ether again. The obtained solids were dried in vacuum at room temperature to give the quaternary ammonium POSS (**5**). ^{1}H NMR (400 MHz, *d6*-DMSO), δ (ppm): 1.03 (2H, Si-C*H*$_2$-CH$_2$-S), 2.05 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.50-2.75 (4H, Si-CH$_2$-C*H*$_2$-S-C*H*$_2$-CH$_2$-CH$_2$-N), 3.04 (6H, N^{+}(C*H*$_3$)$_2$), 3.64 (2H, S-CH$_2$-CH$_2$-C*H*$_2$-N^{+}), 5.21 (2H, -C*H*$_2$-naphthalenyl). 7.4~8.6 (7H, naphthalenyl). ^{13}C NMR (400 MHz, *d6*-DMSO), δ (ppm): 134.0~125.2, 63.8, 63.7, 49.9, 28.1, 25.7, 22.6, 12.9.

Synthesis of octa-zwitterionic POSS (6)

The obtained **2** was immediately diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of 1,3-propanesultone (1.27 g, 10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. In about 1 h, white precipitates appeared. The mixture was further stirred for 24 h. The precipitates were collected, washed with dried DMF, and finally with diethyl ether. The obtained solids were dried in vacuum at room temperature to give the zwitterionic POSS (**6**). ^{1}H NMR (400 MHz, D$_2$O), δ (ppm): 1.05 (2H, Si-C*H*$_2$-CH$_2$-S), 1.96 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.13 (2H, C*H*$_2$-CH$_2$-SO$_3^{-}$), 2.57 (2H, Si-CH$_2$-C*H*$_2$-S), 2.66 (2H, S-C*H*$_2$-CH$_2$-CH$_2$-N^{+}), 2.87 (2H, C*H*$_2$-SO$_3^{-}$), 3.03 (6H, N^{+}(C*H*$_3$)$_2$), 3.36 (4H, C*H*$_2$-N^{+} -C*H*$_2$).

Synthesis of octa-allyl POSS (7)

Once **2** was prepared, it was diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of allyl bromide (1.25 g, 10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. Then, the mixture was further stirred for 1 h and then poured into diethyl ether at 0 ^{o}C to afford white precipitates. After reprecipitation in diethyl ether, the obtained solids were dried in vacuum at room temperature to give the quaternary ammonium POSS (**7**). ^{1}H NMR (400 MHz, D_2O), δ (ppm): 1.03 (2H, Si-C*H*$_2$-CH$_2$-S), 1.98 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.56, 2.65 (4H, Si-CH$_2$-C*H*$_2$-S-C*H*$_2$-CH$_2$-CH$_2$-N), 2.96 (6H, N^{+}(C*H*$_3$)$_2$), 3.24 (2H, S-CH$_2$-CH$_2$-C*H*$_2$-N^{+}), 3.83 (2H, -C*H*$_2$-CH=CH$_2$), 5.63 (2H, CH=C*H*$_2$), 5.90 (1H, C*H*=CH$_2$). ^{13}C NMR (400 MHz, D_2O), δ (ppm): 129.5~124.8, 66.2, 62.5, 50.8, 28.0, 26.0, 22.6, 12.6. ^{29}Si NMR (500 MHz, D_2O), δ (ppm): -67.88.

Synthesis of octa-methyl styrene POSS (8)

Once **2** was prepared, it was diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of 4-chloromethylstyrene (1.58 g, 10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. Then, the mixture was further stirred for 2 h and then poured into diethyl ether at 0 ^{o}C to afford white precipitates. After reprecipitation in diethyl ether, the obtained solids were dried in vacuum at room temperature to give the quaternary ammonium POSS (**8**). ^{1}H NMR (400 MHz, D_2O), δ (ppm): 0.90 (2H, Si-C*H*$_2$-CH$_2$-S), 1.82 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.31, 2.50 (4H, Si-CH$_2$-C*H*$_2$-S-C*H*$_2$-CH$_2$-CH$_2$-N), 2.83 (6H, N^{+}(C*H*$_3$)$_2$), 2.90 (2H, S-CH$_2$-CH$_2$-C*H*$_2$-N^{+}), 4.22 (2H, -C*H*$_2$-styrenyl), 5.19, 5.68 (2H, CH=C*H*$_2$), 6.51 (1H, C*H*=CH$_2$), 7.26 (4H, styrenyl). ^{13}C NMR (400 MHz, D_2O), δ (ppm): 139.3, 135.7,

133.2, 126.8, 126.7, 116.4, 66.7, 61.3, 50.8, 27.9, 25.7, 22.2, 12.5. ^{29}Si NMR (500 MHz, D_2O), δ (ppm): -68.14.

Synthesis of octa-azidoethyl POSS (9)

2 was immediately diluted with 8 mL of dried DMF and cooled to 0 ^{o}C. A DMF (2 mL) solution of 2-azidoethyl-2-bromoacetate (2.15 g, 10.4 mmol) was added dropwise slowly into DMF solution of **2** under vigorous stirring. Then, the mixture was further stirred for 2 h and then poured into diethyl ether at 0 ^{o}C to afford white precipitates. After reprecipitation in diethyl ether, the obtained solids were dried in vacuum at room temperature to give the quaternary ammonium POSS (**9**). ^{1}H NMR (400 MHz, D_2O), δ (ppm): 1.02 (2H, Si-C*H*$_2$-CH$_2$-S), 1.98 (2H, S-CH$_2$-C*H*$_2$-CH$_2$-N), 2.50~2.75 (4H, Si-CH$_2$-C*H*$_2$-S-C*H*$_2$-CH$_2$-CH$_2$-N), 3.23 (6H, N^+(C*H*$_3$)$_2$), 3.53~3.75 (2H, S-CH$_2$-CH$_2$-C*H*$_2$-N^+ and C*H*$_2$-N$_3$), 4.20~4.40 (2H, -C*H*$_2$-COO-C*H*$_2$). ^{13}C NMR (400 MHz, D_2O), δ (ppm): 165.0, 65.3, 64.0, 61.8, 53.5, 49.8, 28.1, 26.0, 23.1, 13.0. ^{29}Si NMR (500 MHz, D_2O), δ (ppm): -68.26.

Synthesis of 1-Azidododecane and 1-Azidooctadecane

1-Bromododecane (2.48 g, 10 mmol) and sodium azide (NaN_3) (0.85 g, 13 mmol) were dissolved in 12 mL of dried DMF. The mixture was heated at 70 ^{o}C for 24 h and then diluted with 100 mL of petroleum ether (60-90 ^{o}C). The organic phase was washed with distilled water (50 mL×2), and then dried over $MgSO_4$. After removing organic solvents by rotary evaporation, it afforded 2.1 g of 1-azidododecane ($N_3C_{12}H_{25}$). 1-azidooctadecane ($N_3C_{18}H_{37}$) was prepared from 1-bromooctadecane in the same way.

Synthesis of the Amphiphilic POSS-C12

3 (0.50 g, 0.20 mmol), 1-azidododecane (0.44 g, 2.08 mmol), and sodium ascorbate (5.9 mg, 0.03 mmol) were mixed in 4 mL of dried CH_3OH in a 25 mL Schlenk flask. After purging with N_2 for 15 min, $CuSO_4 \cdot 5H_2O$ (7.2 mg, 0.03 mmol) was added into the mixture to start the reaction. When the click reaction carried out for 2 h at room temperature, the mixture was poured into cold diethyl ether (0 ^oC). The collected precipitates were redissolved in methanol and precipitated out from cold diethyl ether. After being dried at 30 °C for 12 h, the product, POSS-C12, (0.80 g) was obtained with the yield of 95.4%. ^1H NMR (400 MHz, D_2O), δ (ppm): 0.86 (3H, C*H*$_3$-$(CH_2)_{10}$), 1.03-1.34 (14H, CH_3-(C*H*$_2$)$_7$, Si-C*H*$_2$-CH_2-S), 1.83-1.96 (N-CH_2-C*H*$_2$-$(CH_2)_9$-CH_3), 2.26-2.41 (2H, S-CH_2-C*H*$_2$-CH_2-N^+), 2.60-2.93 (4H, S-C*H*$_2$-CH_2-CH_2-N^+, Si-CH_2-C*H*$_2$-S), 3.14-3.41 (6H, N^+(C*H*$_3$)$_2$), 3.69-3.91 (2H, S-CH_2-CH_2-C*H*$_2$-N^+), 4.27-4.46 (2H, N-C*H*$_2$-CH_2-$(CH_2)_9$-CH_3), 4.88-5.16 (2H, $^+$N-C*H*$_2$-triazole ring), 8.56 (1H, triazole ring).^{13}C NMR (400 MHz, D_2O), δ (ppm): 135.4, 128.8, 63.9, 58.2, 50.9, 32.0, 29.8, 26.9, 22.8, 14.5, 14.1. ^{29}Si NMR (500 MHz, $CDCl_3$), δ (ppm): -68.60.

Dyes Encapsulation

0.250 g of POSS-C12 was dissolved into $CHCl_3$ to make a 250 mL solution. All the dye powders were dissolved in distilled water with the concentrations of 1.0×10^{-3} M, respectively. Then, 2 mL aqueous solution of the dye was mixed with 2 mL of a chloroform solution of the POSS-C12 in a 20mL glass bottle. The mixture was vigorously stirred by a magnetic stirrer for 15 min to make it fully mixed. After the upper aqueous phase and bottom organic phase were thoroughly separated, 2mL of

the bottom layer, the $CHCl_3$ solution of POSS-C12-dye complexes, was diluted 50 times with $CHCl_3$ and carried out on UV-Vis spectrophotometer to calculate the transforming capacity of dye (C_{dye}) from aqueous phase into organic phase.

Fluorescence character of octa-anthracene POSS (4)

The fluorescence microscope was captured by the Nikon Eclipse TE200. The fluorescence spectra of **4** and 9-(chloromethyl) anthracene excited at 344 nm. As shown in Figure S11a, the maximum absorption peak at 374 nm slightly increased from 1.12 to 1.19. The intensity of emitting light showed no significant differences between **4** and 9-(chloromethyl) anthracene excited at 344 nm (**Fig.** S12b).

Cytotoxicity Assay

The cytotoxicity of quaternary ammonium POSS was evaluated by MTT assay using COS7, HEK-293 and NIH-3T3 cells (**Fig.** S13). Generally, the cells were seeded in a 96-well tissue culture plate at a density of 1×10^4 cells/well in 200 mL 10 % serum medium for 18 h. The medium was then replaced with 200 mL serum-free one containing serial dilutions of quaternary ammonium POSS solutions for 24 h. Then, the solutions were replaced with 100 mL serum-free media containing 0.5 mg/mL MTT and incubated for another 4 h. Finally, each well was replaced with 100 mL DMSO and measured spectrophotometrically in an ELISA plate reader (Model 550, Bio-Rad) at a wavelength of 570 nm. The relative cell growth (%) related to control cells cultured in media without the material was calculated by $[A]_{test}/[A]_{control}\times100$.

Cellular Uptake Test

For microscopic observation, 10^5/well MCF-7 and MCF-7/ADR cells were seeded

onto 12-well plates and grown for 18 h. The cells were incubated for 4 h with the media containing 0.05mM quaternary ammonium POSS-Rhodamine B. The cells were then washed 3 times with PBS, fixed with fresh 4% paraformaldehyde and treated with DAPI for 10 min. The microscopic images were captured by inverted fluorescence microscope (**Fig.** S14). The uptake of quaternary ammonium POSS-Rhodamine B by MCF-7 and MCF-7/ADR cells was studied quantitatively with a flow cytometer. MCF-7 cells were firstly seeded onto 6-well plates at a seeding density of 3×10^5 cells/well and grown overnight in RPMI1640 growth medium supplemented with 10% FBS, and 1% penicillin–streptomycin. On the following day, the cells were treated with free Rhodamine B and quaternary ammonium POSS-Rhodamine B at the concentration of 0.05 mM. After 4 h of incubation, the cells were washed three times with PBS, followed by trypsinization and centrifugation at 1000 rpm for 5 min to harvest the cells. The cells were re-suspended in PBS, and measured for its fluorescent intensity per cells in FL2-H channel with a BD FACSCalibur flow cytometer (BD Biosciences, San Diego, CA) (**Fig.** S15).

Agarose gel electrophoresis assay

The plasmid DNA was amplified in E. Coli and purified by using a commercialized kit according to the supplier's protocol (Qiagene, Hilden, Germany). The quantity and quality of the purified pDNA were assessed by optical density at 260 and 280 nm. The purified pDNA was suspended again in TE buffer (10 mM Tris-Cl, pH 7.5, 1 mM EDTA), and kept in aliquots of 0.5 mg/mL in concentration. Plasmid DNA stock solution was diluted to a chosen concentration (0.1 mg/mL) before use.

The amount of quaternary ammonium POSS added was calculated based on a designed N/P ratio (5:1, 15:1, 25:1, 35:1, 50:1) of quaternary ammonium POSS/DNA. Polyplexes were prepared by adding 10 μL of polymer solution dropwise to equal volume of plasmid solution, followed by vortexing for 6 s and incubated for 30 min at room temperature. The formed quaternary ammonium POSS/DNA complexes were mixed with 5 μL of 5 × loading buffer and loaded onto 0.9% agarose gel containing 0.5 μg/mL ethidium bromide. Gel electrophoresis was conducted in 1 × Tris-acetate-EDTA (TAE) buffer (40 mM Tris-acetate, 1 mM EDTA) at 80 V for 40 min in a Sub-Cell system (Biorad Laboratories, CA) and the result was shown in **Fig.** S16.

Dye-coloring Polymer Films

SBS or PMMA (5.0 g) was dissolved in 50.0 mL chloroform, and then mixed with 2.0 mL chloroform solution of POSS-C12-dye complexes, offering colorfully transparent polymer solutions. The SBS or PMMA solution was poured into a culture dish, keeping the solvent of chloroform naturally volatilized at room temperature for 24 h and drying in an oven at 60 ^{o}C for 48 h. Finally, the dried samples were peeled off to give colorful free-standing films. As a comparison, the control samples were prepared by mixing the polymer solutions directly with dye powders, followed by the same treating process as mentioned above. At last, the dye-coloring polymer films were cut up into strips with the similar size. The strips were immersed in distilled water at room temperature to evaluate the coloring stability of the colorful films (Fig. S17-S18).

Measurement and Techniques

Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^{1}H and ^{13}C NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 20 ^{o}C. The samples were dissolved with $CDCl_3$ or D_2O and the solutions were measured with tetramethylsilane (TMS) as an internal reference. ^{29}Si NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer at 20 ^{o}C.

Matrix-assisted Laser Desorption and Ionization Time of Flight (MALDI-TOF) Mass Spectroscopy

The matrix-assisted laser desorption and ionization time of flight (MALDI-TOF) mass spectra were obtained on an ABI Super Voyager-DE-STR spectrometer. 2,5-Dihydroxybenzoic acid was used as matrix and dissolved in methanol. **2** was dissolved in dried THF.

Ultraviolet-Visible (UV-Vis) Spectroscopy

Ultraviolet-Visible (UV-Vis) spectra were recorded on a Varian Cary 300 Bio UV-Vis spectrometer at room temperature.

Fluorescence Spectroscopy (FS)

The fluorescence spectra (FS) were recorded by the Nikon Eclipse TE200.

Cytotoxicity Assay

The cytotoxicity of quaternary ammonium POSS was evaluated by MTT assay using COS7, HEK-293 and NIH-3T3 cells.

Agarose gel electrophoresis assay

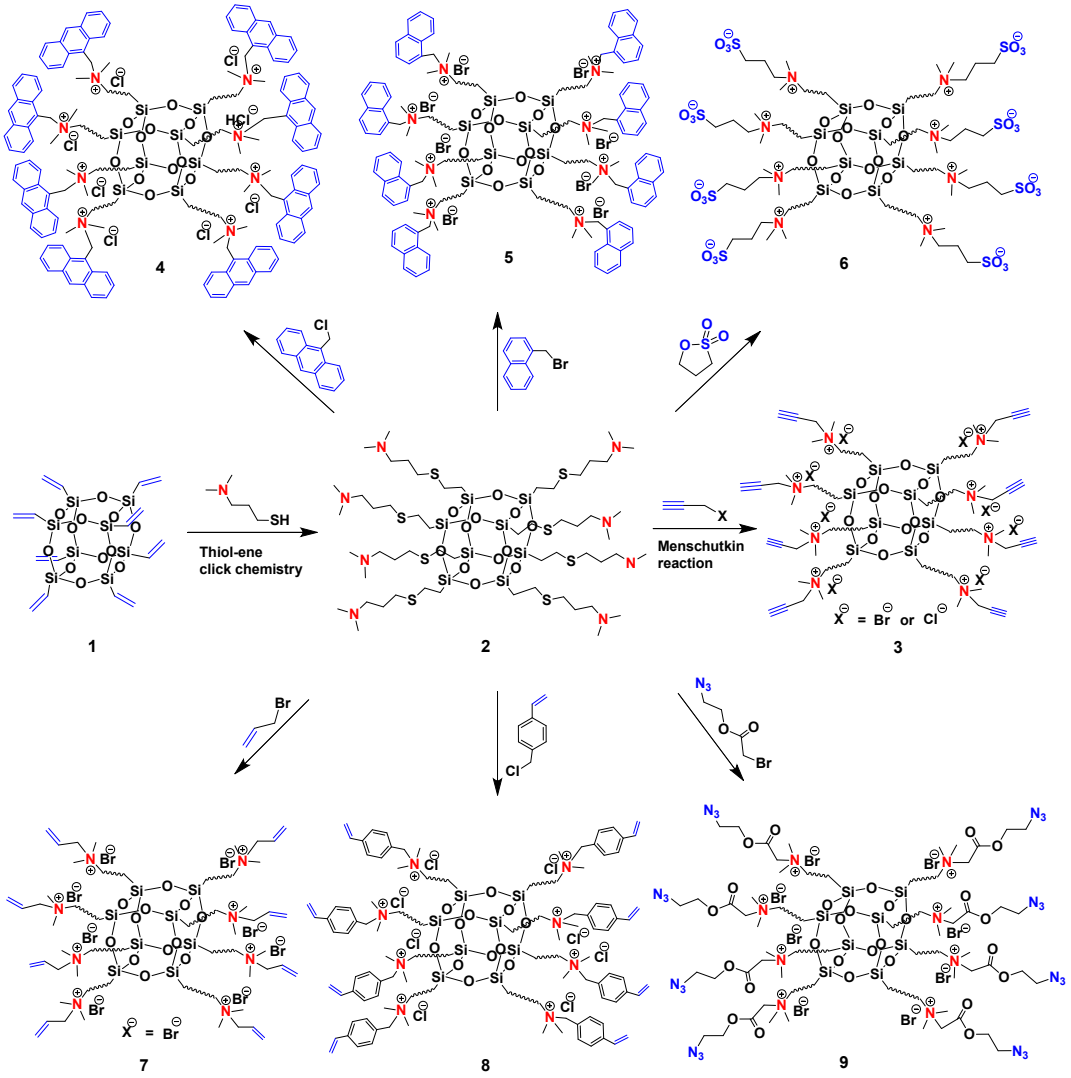
The plasmid DNA was amplified in E. Coli and purified by using a

commercialized kit according to the supplier's protocol (Qiagene, Hilden, Germany). DNA bands were visualized by a UV lamp using a GelDoc system (Synoptics Ltd., UK).

Dynamic laser scattering

Particle size of the POSS-C18 and POSS-C18-dye complex in chloroform solution was measured by dynamic laser scattering (DLS) experiments. The measurement was performed at 25 ^{o}C. The concentration of POSS-C18 and POSS-C18-MO complex in chloroform was 0.5 mg mL^{-1}.

2. **Supplementary figures and tables**



Scheme S1. Variously octa-functional POSSs synthesized *via* sequential thiol-ene and Menschutkin click chemistries.

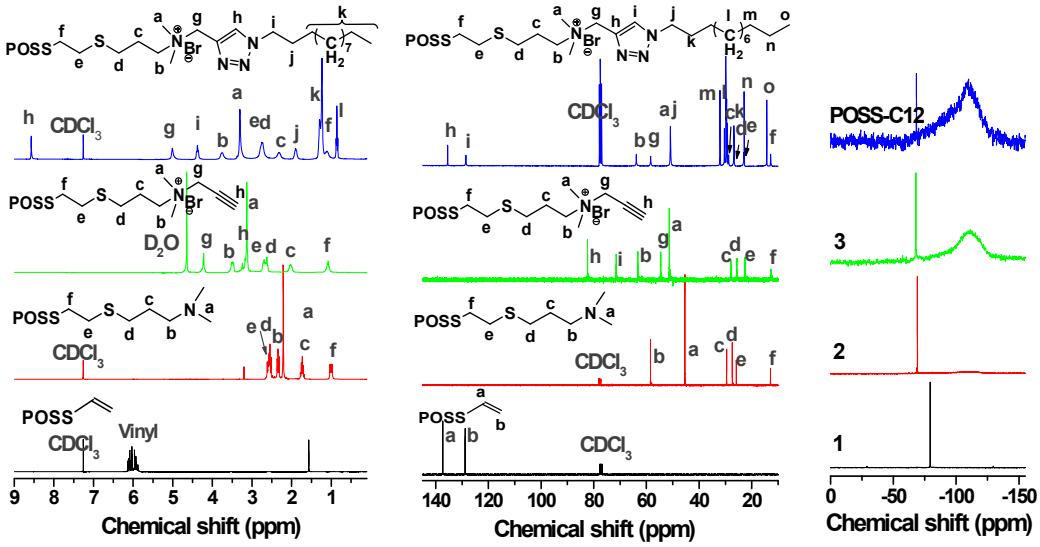


Fig. S1. ^{1}H, ^{13}C and ^{29}Si NMR spectra of **1**, **2**, **3** and POSS-C12, respectively.

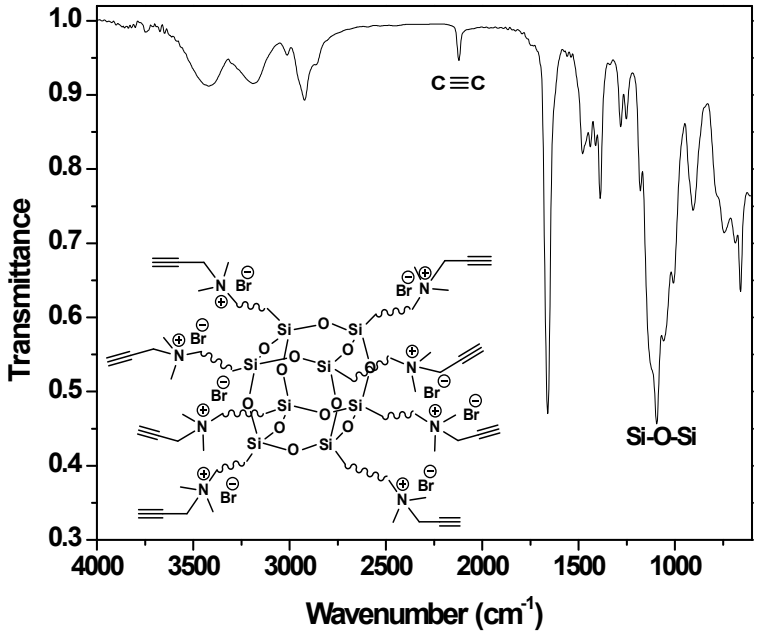


Fig. S2. FTIR spectrum of **3**.

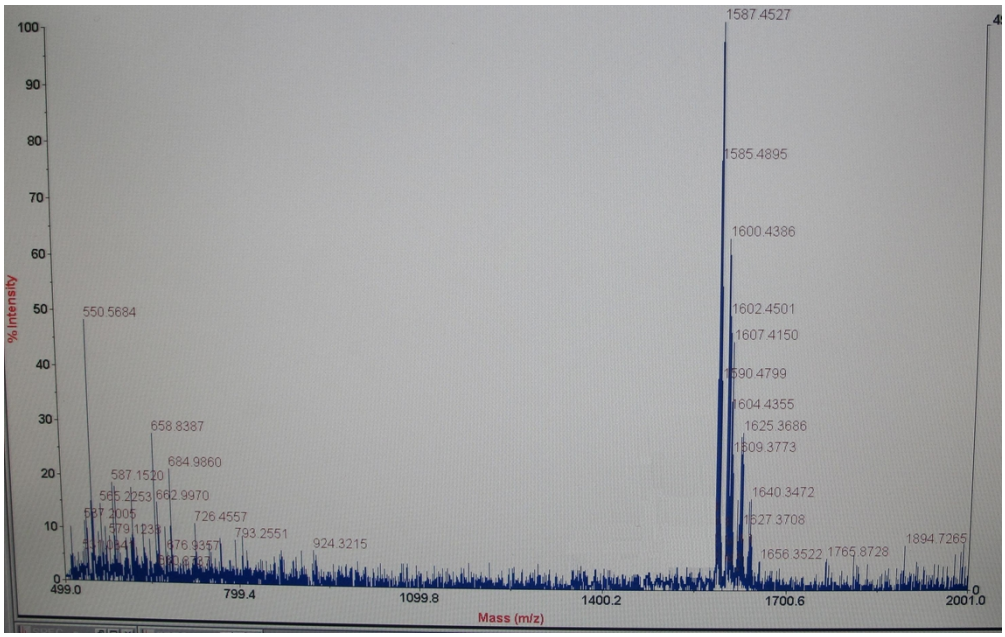
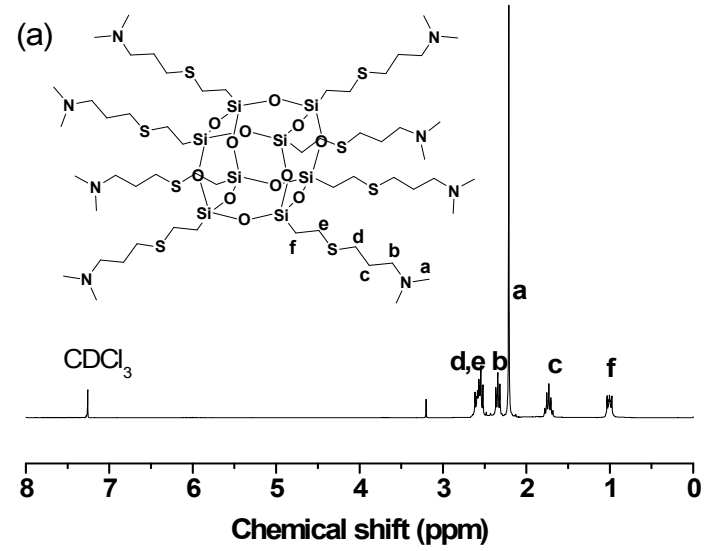
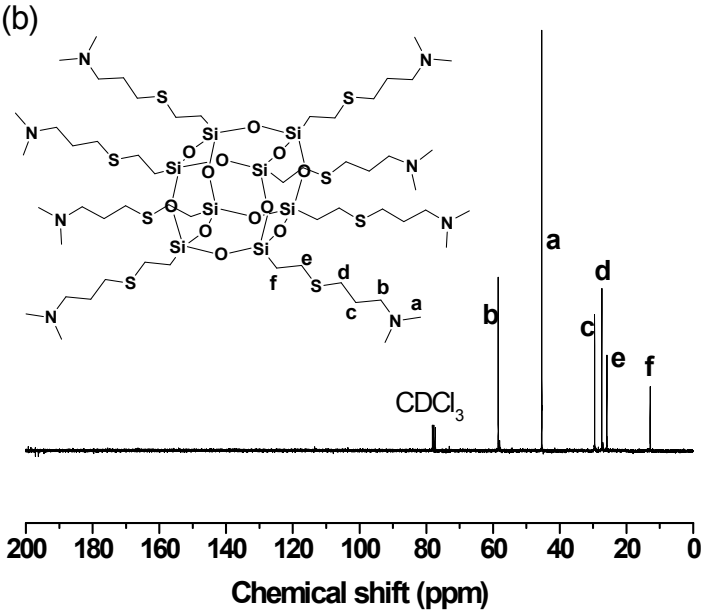


Fig. S3. MALDI-TOF MS spectrum of **2**.


(a)
CDCl3
d,e
b
a
c
f
8
7
6
5
4
3
2
1
0
Chemical shift (ppm)


(b)
CDCl3
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d
c
e
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Chemical shift (ppm)

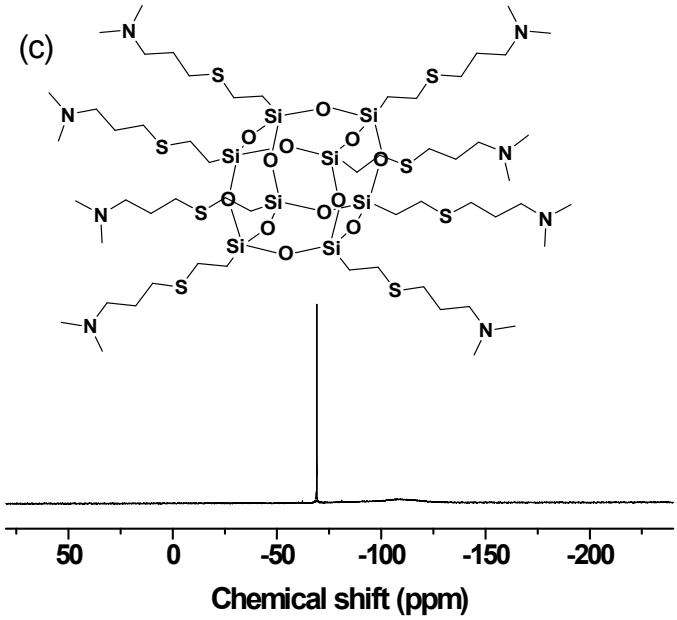


Fig. S4. ^{1}H, ^{13}C and ^{29}Si NMR spectra of **2**.

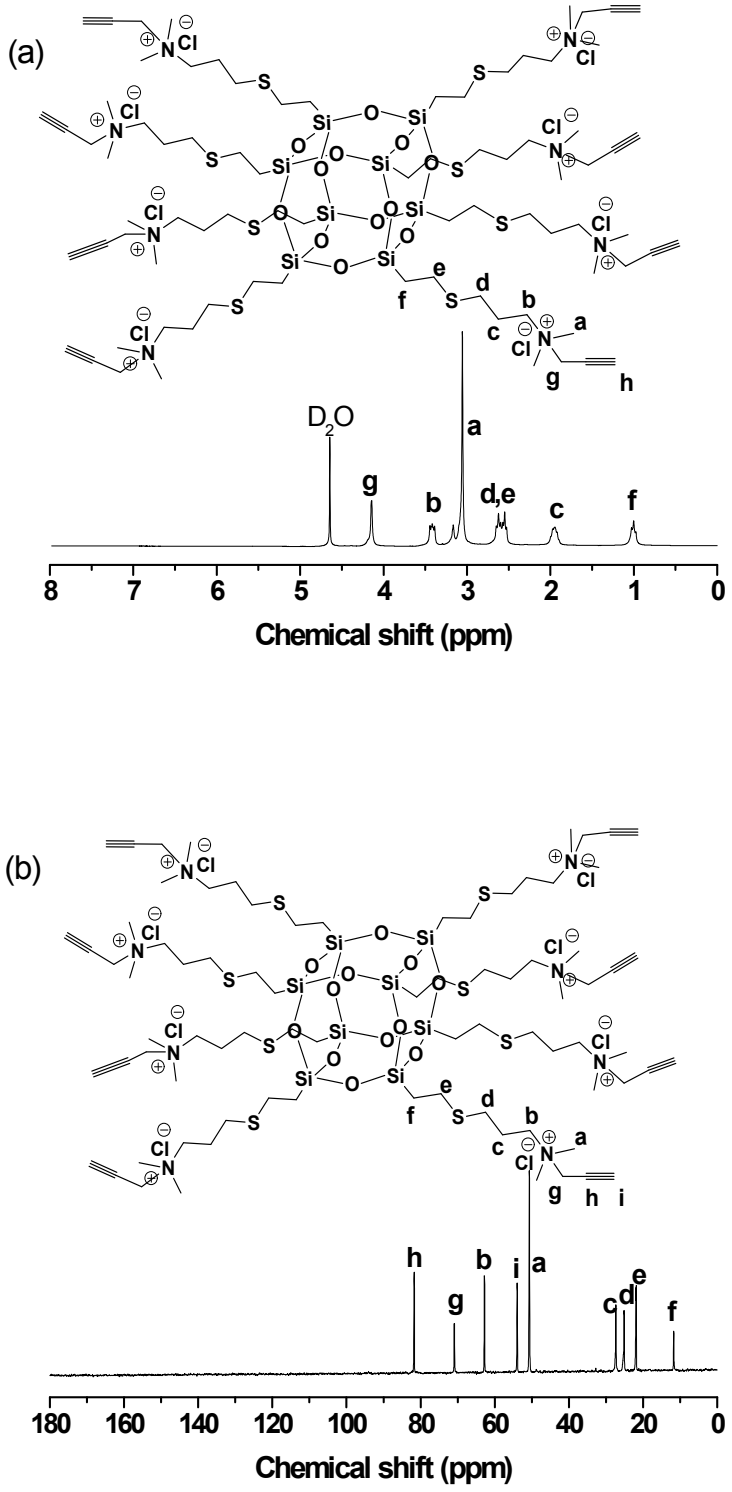


Fig. S5. ^{1}H and ^{13}C NMR spectra of **3**.

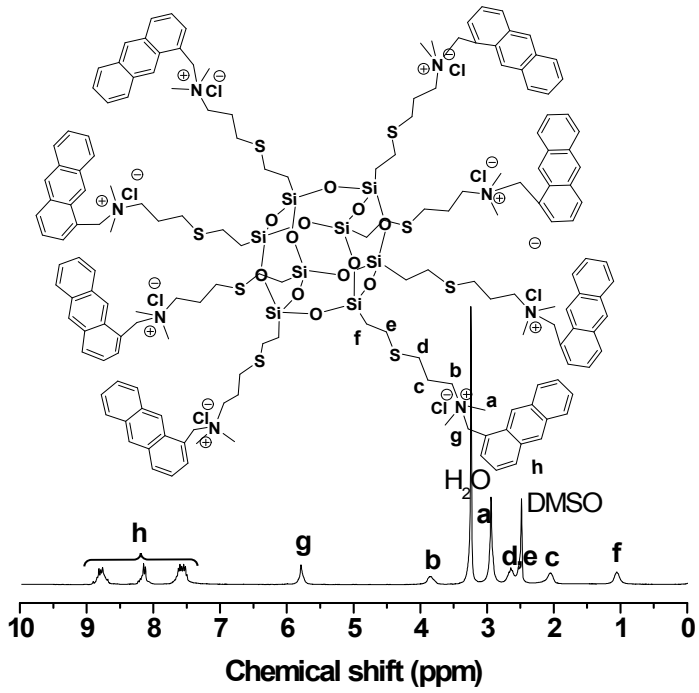


Fig. S6. ^{1}H NMR spectrum of **4**.

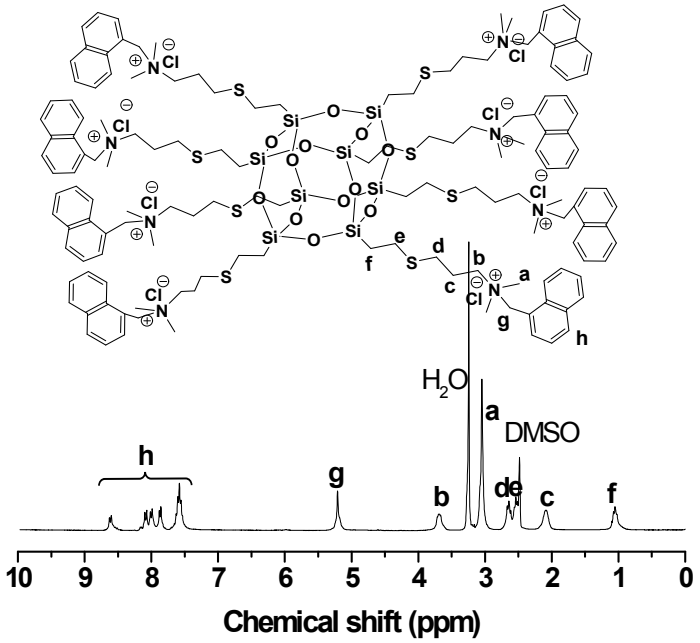


Fig. S7. ^{1}H NMR spectrum of **5**.

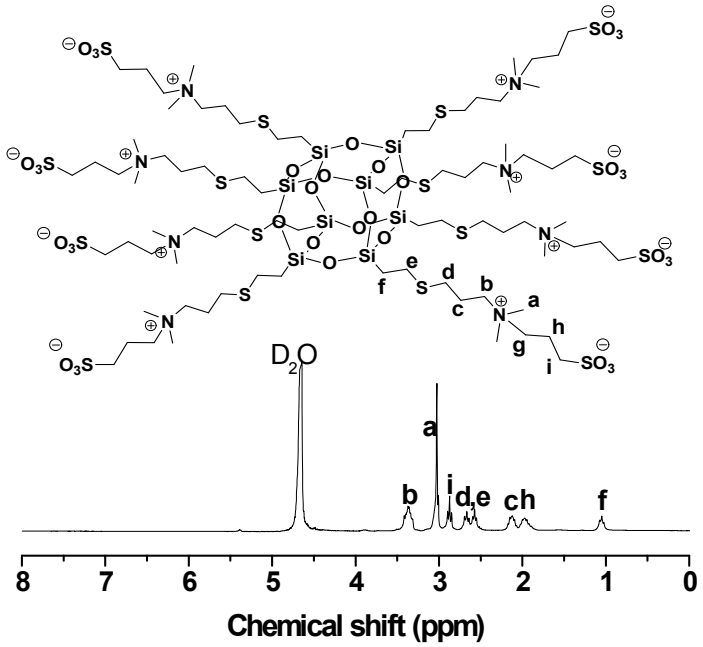
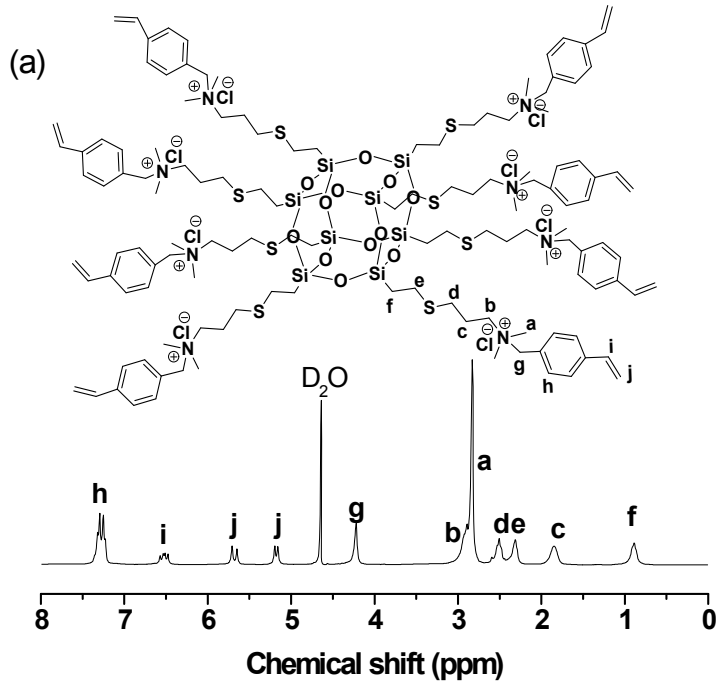
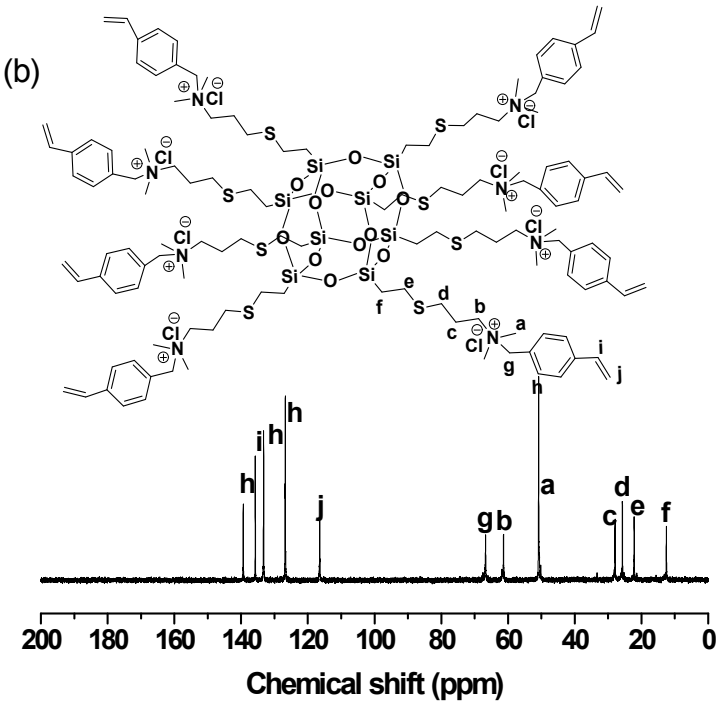


Fig. S8. ^{1}H spectrum of **6**.


(a)
D2O
h
i
j
j
g
b
a
de
c
f
8
7
6
5
4
3
2
1
0
Chemical shift (ppm)


(b)
h
j
i
h
h
j
g
b
a
c
d
e
f
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

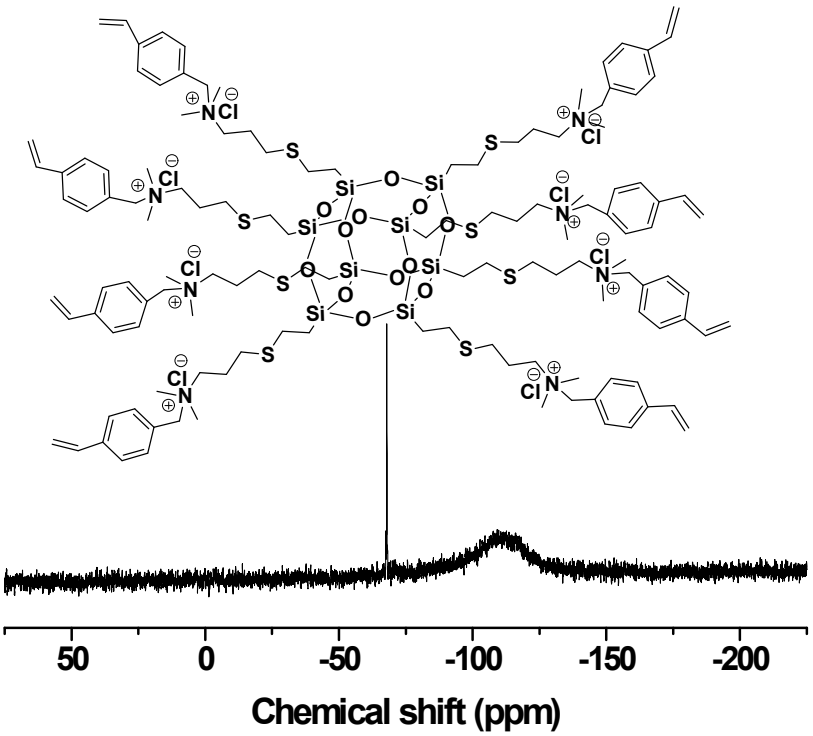
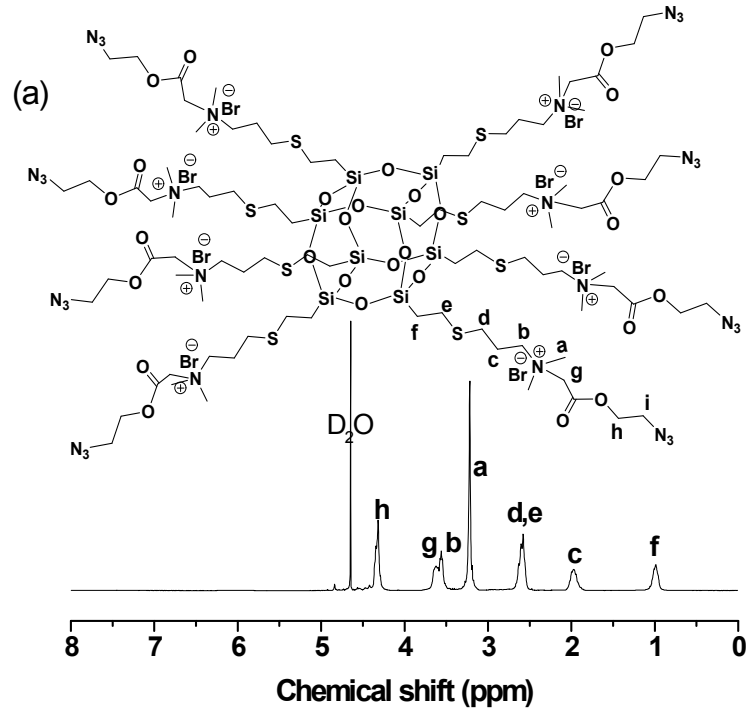
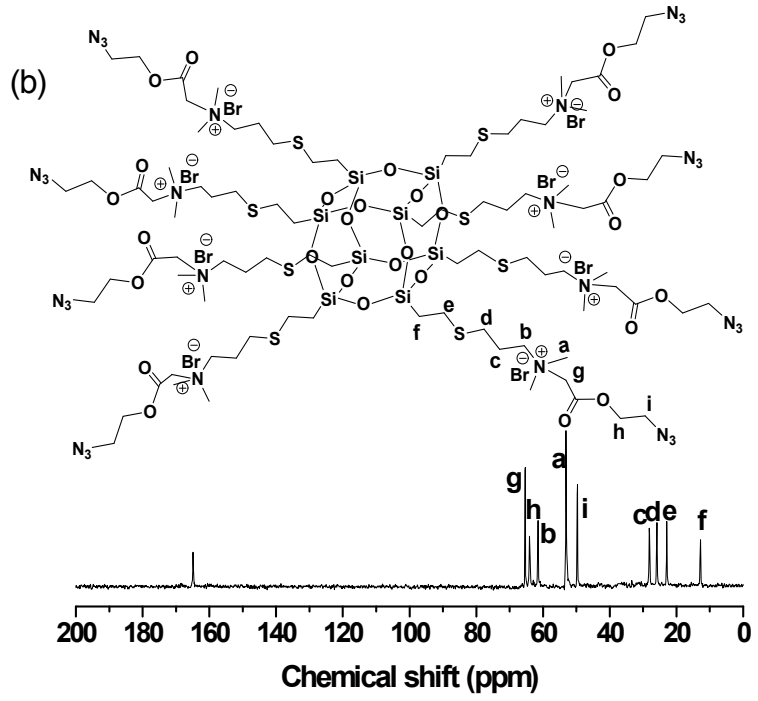


Fig. S9. ^{1}H, ^{13}C and ^{29}Si NMR spectra of **8**.


(a)
D2O
h
g
b
a
d,e
c
f
8
7
6
5
4
3
2
1
0
Chemical shift (ppm)


(b)
g
h
b
a
i
c
d
e
f
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

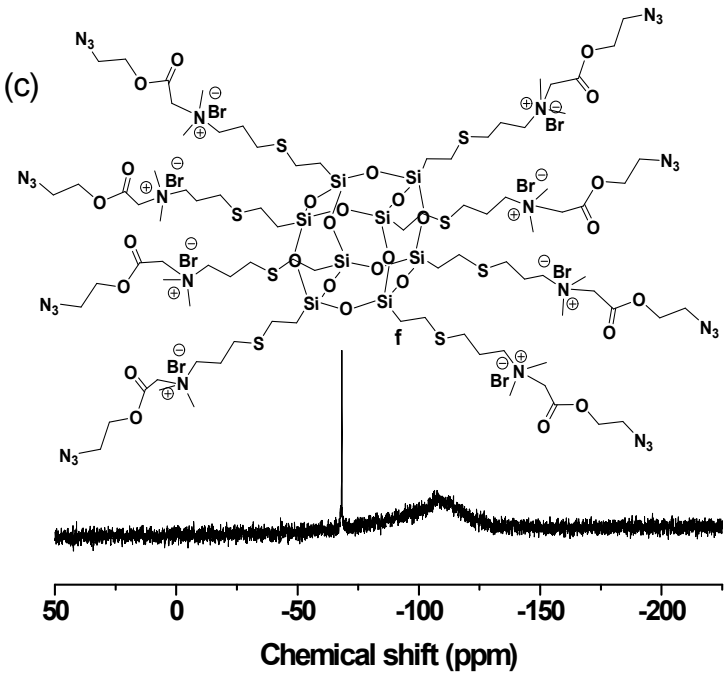
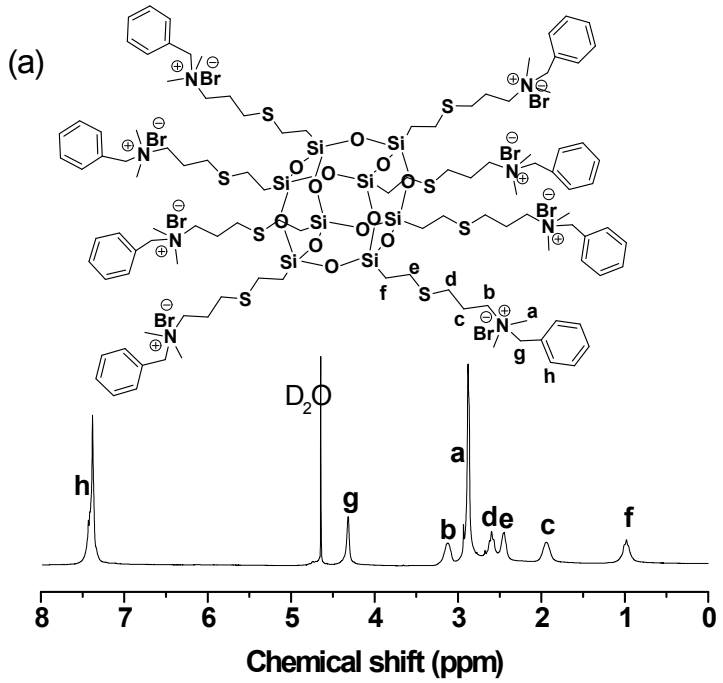


Fig. S10. ^{1}H, ^{13}C and ^{29}Si NMR spectra of **9**.


(a)
D2O
h
g
a
b
de
c
f
8
7
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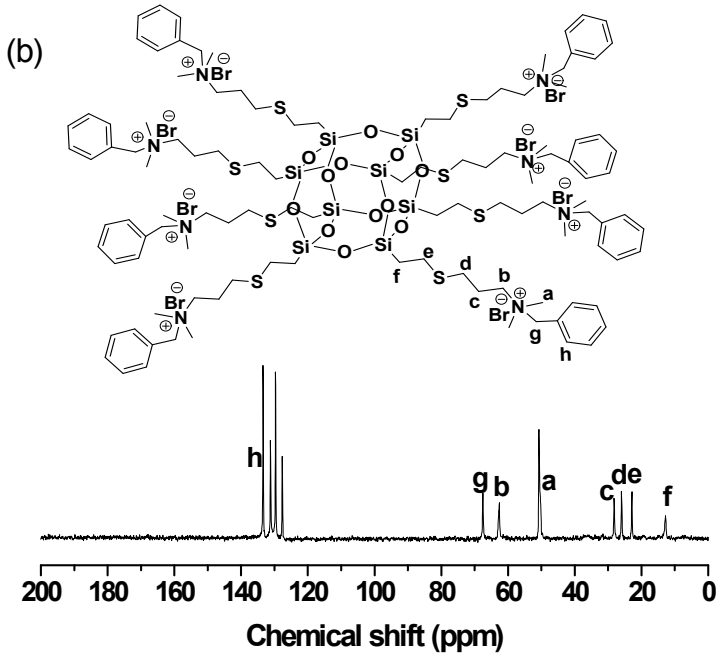
5
4
3
2
1
0
Chemical shift (ppm)


(b)
h
g
b
a
c
de
f
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

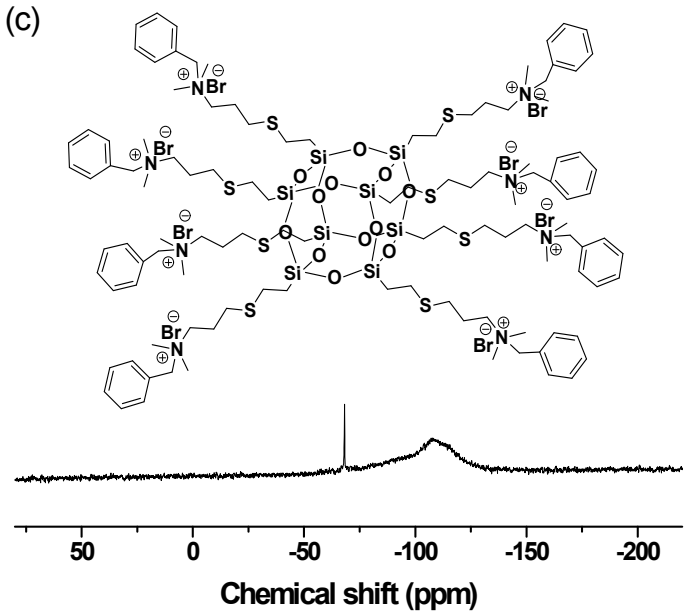


Fig. S11. ^{1}H, ^{13}C and ^{29}Si NMR spectra of octa-benzyl POSS.

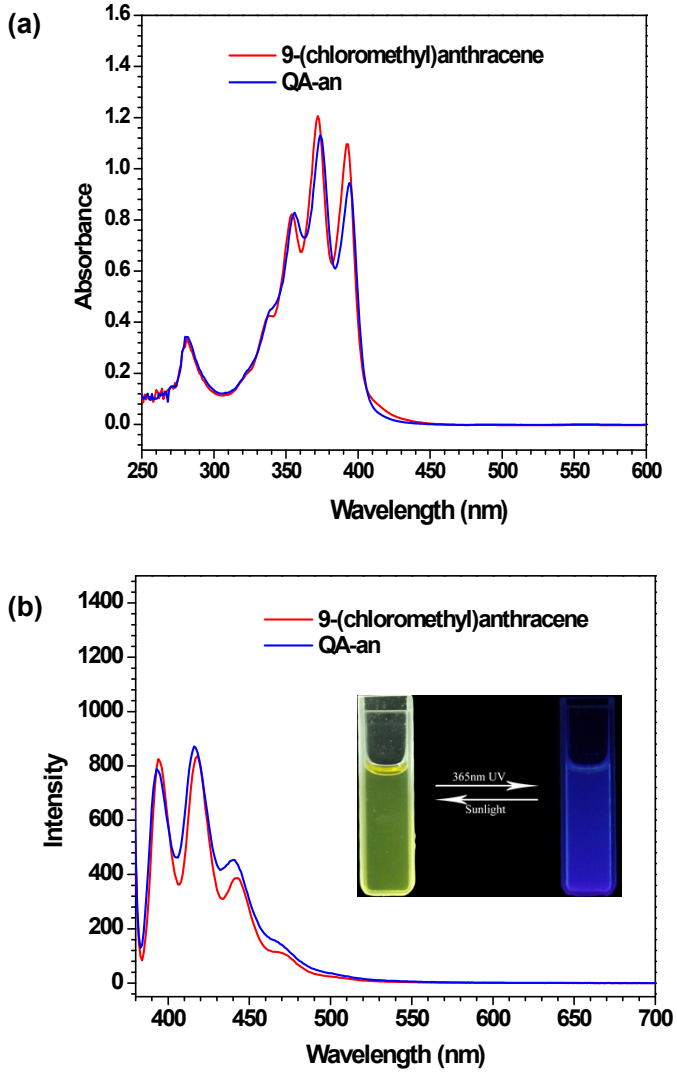


Fig. S12. The fluorescence spectra of **4** and 9-(chloromethyl) anthracene (a); the fluorescence spectra of **4** and 9-(chloromethyl) anthracene excited at 344 nm (b); the photograph of the **4** solution in sunlight (left) and exposed to 365 nm UV light (right), respectively.

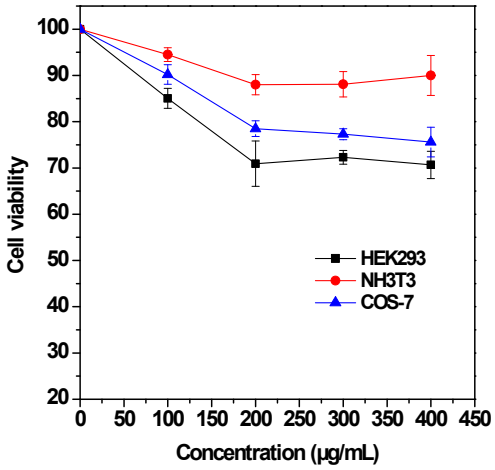


Fig. S13. The cytotxicity of quaternary ammonium POSS on three mammalian cell lines.

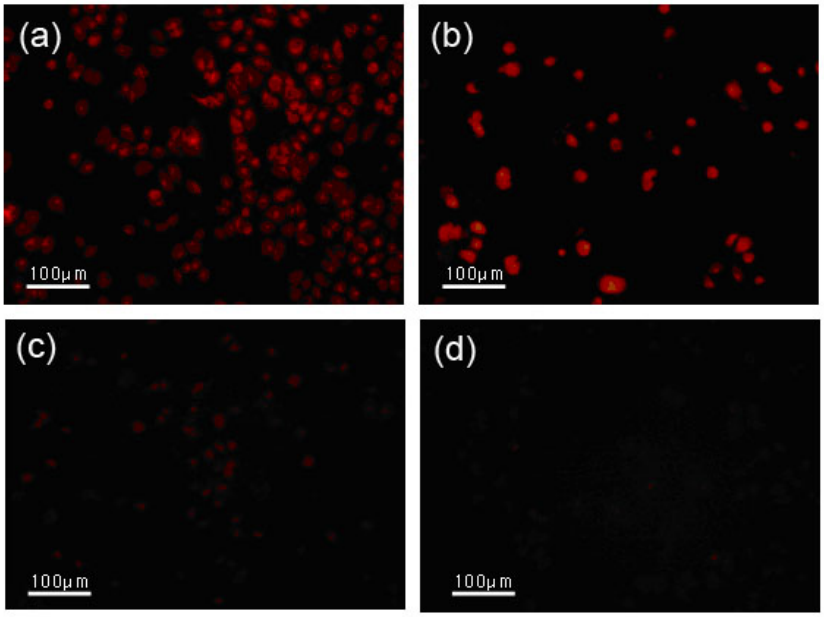


Fig. S14. The distributions of POSS-Rhodamine B in MCF-7 cell and MCF-7/ADR at 0.05 mM: (a) POSS-Rhodamine B in MCF-7; (b) POSS-Rhodamine B in MCF-7/ADR; (c) free Rhodamine B in MCF-7; (d) free Rhodamine B in MCF-7/ADR.

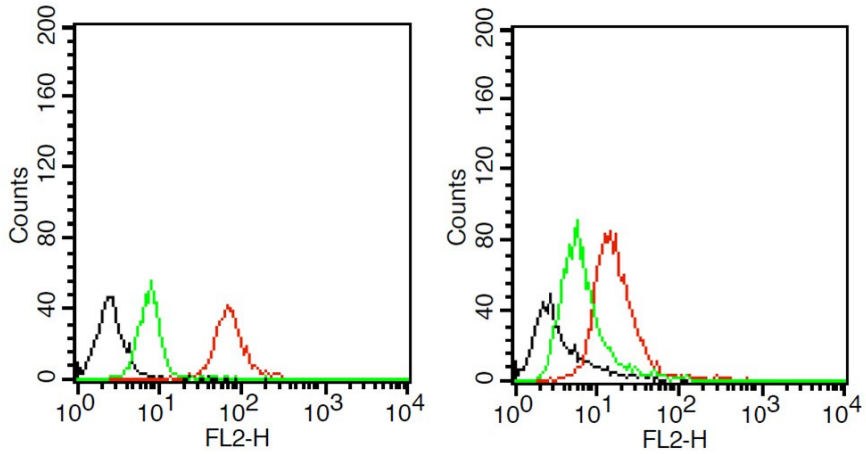


Fig. S15. Cell fluorescence by flow cytometry.

Red: POSS- Rhodamine B; Green: Rhodamine B; Black: blank.

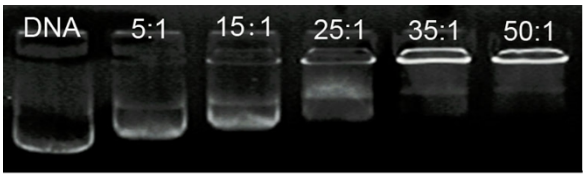


Fig. S16. Agarose gel electrophoresis assay. Lane 1, EGFP plasmid DNA.

Lanes 2-6 represent POSS/DNA with N/P ratios of 5:1, 15:1, 25:1, 35:1, and 50:1, respectively.

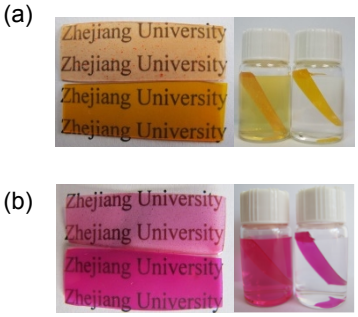


Fig. S17. Photographs of MO (a) and RB (b) colored SBS films of the control samples (upper) and of the samples with POSS-C18-dye complex (bottom) placed on paper; photographs of MO and RB-colored SBS of the control films (left) and SBS films with POSS-C18-dye complex (right) immersed in water.

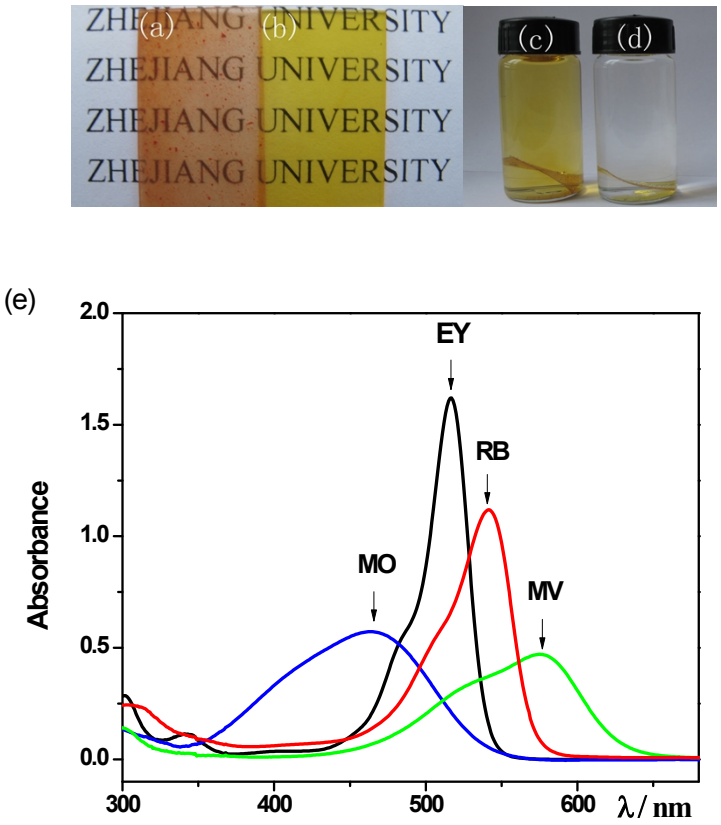


Fig. S18. Photographs of MO-colored PMMA films of the control sample (a) and of the sample with amphiphilic POSS-dye complex (b) placed on paper; photographs of MO-colored PMMA of the control films (c) and PMMA films with amphiphilic POSS-dye complex (d) immersed in water; UV-vis spectra of the remained MO in aqueous solution after extraction by the chloroform solution of POSS-C12 (e).

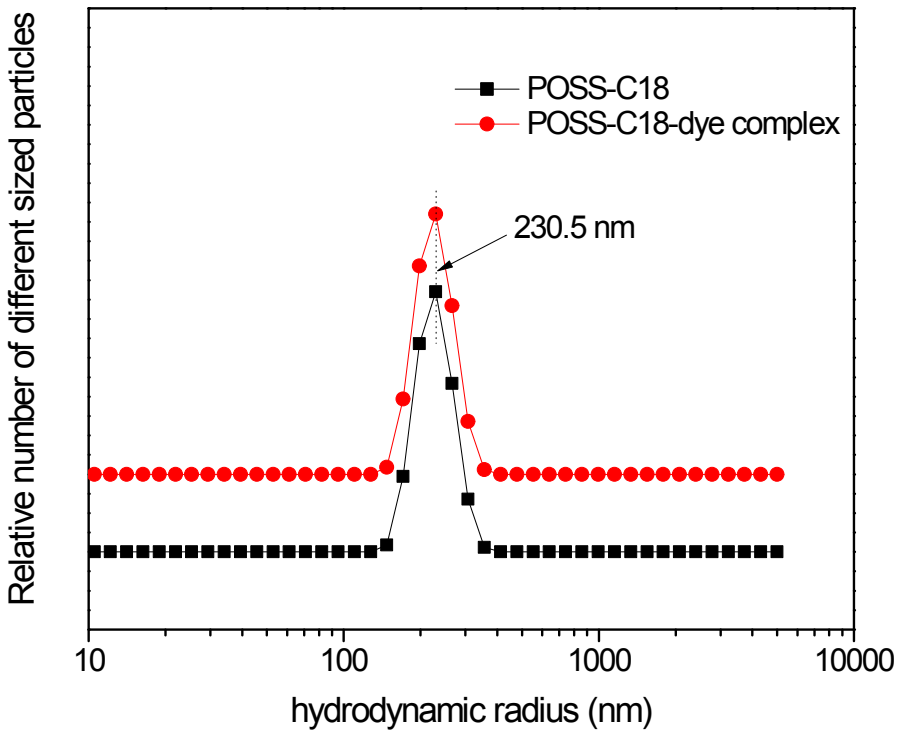


Fig. S19. Dynamic light scattering (DLS) diagram of POSS-C18 and POSS-C18-MO complex in chloroform at a concentration of 0.5 mg mL^{-1}.

Table S1. Solubility of various octa-functional POSSs in different solvents and the mass fraction of inorganic POSS core in the POSS **1-9** (f_{POSS}).

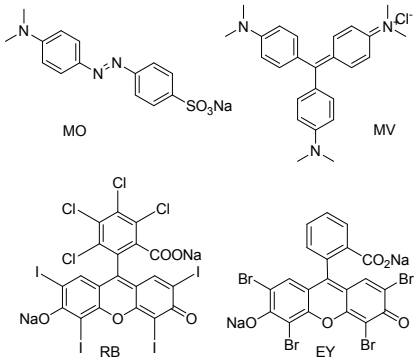
Code	H_2O	DMF	DMSO	CH_3OH	$CHCl_3$	f_{POSS} (%)
1	×	×	×	×	√	97.4
2	- [a]	√	√	- [a]	√	38.9
3[b]	√	√	√	√	×	24.3
4	×	√	√	√	×	22.0
5	×	√	√	√	×	22.6
6	√	√	√	√	×	31.3
7	√	√	√	√	×	31.4
8	√	√	√	√	×	27.8
9	√	√	√	√	×	23.2
POSS-$(C_6H_5)_8$	√	√	√	√	×	33.6
POSS-$(OH)_8$	√	√	√	√	×	45.5
POSS-C12	×	√	×	√	√	13.5
POSS-C18	×	√	×	√	√	11.8

[a] In H_2O or CH_3OH, destruction of Si-O-Si bonds by NMe_2 groups.

[b] The **3** obtained from propargyl bromide and chloride exhibited the same solubility.

1 and **2** are water-insoluble in nature. After the quaternary ammonium reaction, the resulted **3** become water-soluble. The amphiphilic POSS-C18 (or POSS-C12) was $CHCl_3$-soluble and water-insoluble after CuAAc click chemistry, implying the strategy is successful.

Table S2. C_{dye}s of QA-C_{12} and QA-C_{18} for hydrophilic dyes



Hosts	MO	RB	EY	MV
POSS-C18 (mmol g^{-1})	1.82	1.68	1.05	1.00
POSS-C18 (g g^{-1})	0.596	1.706	0.722	0.407
POSS-C12 (mmol g^{-1})	1.78	0.73	0.41	0.60
POSS-C12 (g g^{-1})	0.583	0.741	0.282	0.244
QHPEI [9] (mmol g^{-1})	1.71	-	0.87	-
QHPEI [9] (g g^{-1})	0.560	-	0.598	-
HPSA[10] (mmol g^{-1})	1.53	-	-	-
HPSA[10] (g g^{-1})	0.501	-	-	-
PHEMA[9] (mmol g^{-1})	1.48	-	-	-
PHEMA[9] (g g^{-1})	0.485	-	-	-
PAMAM[11] (mmol g^{-1})	0.84	0.30	0.17	-
PAMAM[11] (g g^{-1})	0.275	0.305	0.117	-

Reference

(1) Han, J.; Li, S. P.; Tang, A. J.; Gao, C. *Macromolecules* **2012**, *45*, 4966-4977.