Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Enhancement of Entrapping Ability by Cubic Silsesquioxane Core in Dendrimers

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Experimental Section.

Materials. G2 PAMAM dendrimer in methanol solution was obtained from Aldrich. The PAMAM dendrimer / water blank solution was prepared by diluting it with water at 1 mM. The POSS-core dendrimer / water blank solution was made by dissolving it in water at 1 mM. They were then stored in darkness. To prepare the solute / dendrimer / water samples, appropriate volumes of the solute stock solutions and dendrimer stock solutions were transferred into 500 μL microtube. Samples were then diluted with buffer solution, sonicated for 30 min, and allowed to equilibrate in darkness overnight.

Octaammonium POSS (1). The G2 POSS-core dendrimer was prepared according to the reference, *Chem. Commun.* **1997**, 1185. The synthesis of **1** was according to the reference 5 in the main text. (3-Aminopropyl)triethoxysilane (100 mL, 0.427 mol) and 35–37% HCl (135 mL) in MeOH (800 mL) produced **1** as a white precipitate after 2 days at room temperature. The crude product obtained after filtration, washing with cold MeOH, and drying. The product was spectroscopically pure in 30% yield (18.8 g). Recrystallization from hot MeOH afforded **1** (4.29 g, 3.66 mmol, 7%) as a white solid. ^{1}H NMR ($(CD_3)_2SO$, 25 °C): δ 8.23 (s, 24H), 2.76 (t, 16H), 1.71 (m, 16H), 0.72 (t, 16H). ^{13}C NMR ($(CD_3)_2SO$, 25 °C): δ 40.53, 20.13, and 7.96. ^{29}Si NMR($(CD_3)_2SO$, 25 °C): δ –66.4 (s): MALDI–TOF [$(M+H)^+$] calcd. 880.41, found 879.42.

Methyl ester-terminated POSS-core dendrimer (2). Amberlite IRA-400 ion-exchange resin (100 g) was prepared by successive washing with water (4 × 150 mL), 1 M NaOH (3 × 150 mL), water (6 × 150 mL), and MeOH (6 × 150 mL), which was the elution solvent; the resin was suspended in eluent and chilled (–10 °C, 2 h) before use. Half of the resin beads were loaded onto a column (3.5 cm outside diameter), and the other half were used to dissolve a suspension of neutralized POSS-NH_3^+ (5.0 g, 4.27 mmol) in the minimum amount of eluent below 0 °C. Elution across the column produced a MeOH solution of neutralized **1**. Immediately, methyl acrylate (100 mL, 1.11 mol) was added via syringe to a solution of neutralized **1**, and the resulting mixture was heated for 48 h at 80 °C. The reaction solution was concentrated *in vacuo*, and extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$. The product **2** (6.10 g, 2.60 mmol, 63%) as a colorless oil was obtained after evaporation: ^{1}H NMR (CD_3OD, 25 °C) δ 3.62 (s, 24 H), 2.18 (s, 16 H), 1.40 (m, 16 H), 0.96 (s, 48 H), 0.57 (m, 16 H): ^{13}C NMR(CD_3OD, 25 °C) δ 174.48, 57.24, 52.17, 50.39, 33.13, 21.39, 10.19: ^{29}Si NMR (D_2O, 25 °C) δ –66.2: MALDI–TOF [$(M+H)^+$] calcd. 1811.08, found 1812.01.

The G2 POSS-core dendrimer (3). The solution containing **2** (6.1 g, 2.60 mmol) with an excess of

ethylenediamine (100 mL, 1.48 mol) was stirred for 4 days at 4 °C. After removing ethylenediamine, washing with diethylether, and dialyzing in water, the G2 POSS-core dendrimer **3** was obtained in 92% yield (6.3 g, 2.39 mmol) as a colorless oil: ^{1}H NMR ($CDCl_3$, 25 °C) δ3.23 (t, 32 H), 2.72 (t, 32 H), 2.66 (t, 32 H), 2.43 (t, 16 H), 2.39 (t, 32 H), 1.46 (m, 16 H), 0.54 (t, 16 H): ^{13}C NMR ($CDCl_3$, 25 °C) δ171.97, 80.03, 49.19, 33.67, 28.18, 28.06, 21.12, 10.57: ^{29}Si NMR (D_2O, 25 °C) δ–66.2 (s). MALDI–TOF [$(M+H)^+$] calcd. 2722.86, found 2722.18.

Complexation with the dendrimers. General procedure for the entrapping by the dendrimers is described here. Samples containing the guest molecules and each dendrimer were sonicated for 30 sec, and allowed to equilibrate in darkness overnight.

Determinations of the enhancement solubilization factor (ESF). The absorption spectra were measured by using Shimadzu UV-3600 at 25 °C. In the studies with pyrene the solute concentration was varied from 10 μM to 100 μM. In phenanthrene the solute concentration was varied from 10 μM to 80 μM. In the studies with anthracene the solute concentration was varied from 10 μM to 60 μM. In the studies with naphthacene the solute concentration was varied from 1 μM to 7 μM. In the studies with the solute / dendrimer / water samples, the molar ratio of dendrimers and ligand molecules were increased from 0.2 to 2.4. All samples were measured in 50 mM sodium phosphate buffer (pH = 7.0). The ESF values were determined according to the reference, *Proc. Natl. Acad. Sci. USA* **1998**, 95, 15351. To quantify the effectiveness of a particular dendrimer in solubilizing the studied aromatic compounds, the enhancement solubilization factor (ESF) defined as the number of moles of compound solubilized per number of moles of dendrimers was calculated, using Equation (1).

$$ESF = \frac{[H]_d}{[D]_W} = \frac{[H]_0 - S_W}{[D]_W} \qquad (1)$$

Where $[H]_d$ is the guest concentration in aqueous solutions, $[H]_0$ is the analytical concentration of the guest and S_W is the water solubility of the guest.

Fluorescence measurements of the DAN complexes. The fluorescence emission of DAN solution (1 μM) in the presence and absence of the dendrimers (10 μM) under excitation at 300 nm was monitored using a Perkin Elmer LS50B at 25 °C using 1 cm path length cell. The excitation bandwidth was 3 nm. The emission bandwidth was 3 nm.

The measurement of dissociation temperature (T_d). All T_ds of the complexes (10 μM) were taken

in 50 mM sodium phosphate buffers (pH = 7.0). Absorbance vs temperature profiles were measured using a Shimadzu UV-3600 spectrophotometer equipped with a Peltier temperature controller using 1 cm path length cell. The absorbance of the samples was monitored at 290 nm with pyrene, 250 nm with phenanthrene, 400 nm with anthracene, and 264 nm with naphthacene from 20 °C to 90 °C with a heating rate of 1 °C/min. From these profiles, first derivatives were calculated to determine T_d values.

Photobleaching of Rh6G. The photolysis of Rh6G solutions (1 μM) with or without G2 POSS-core dendrimer (10 μM) was carried out at 25 °C by using the low pressure mercury lamp. The fluorescence emission of Rh6G under excitation at 500 nm was monitored.

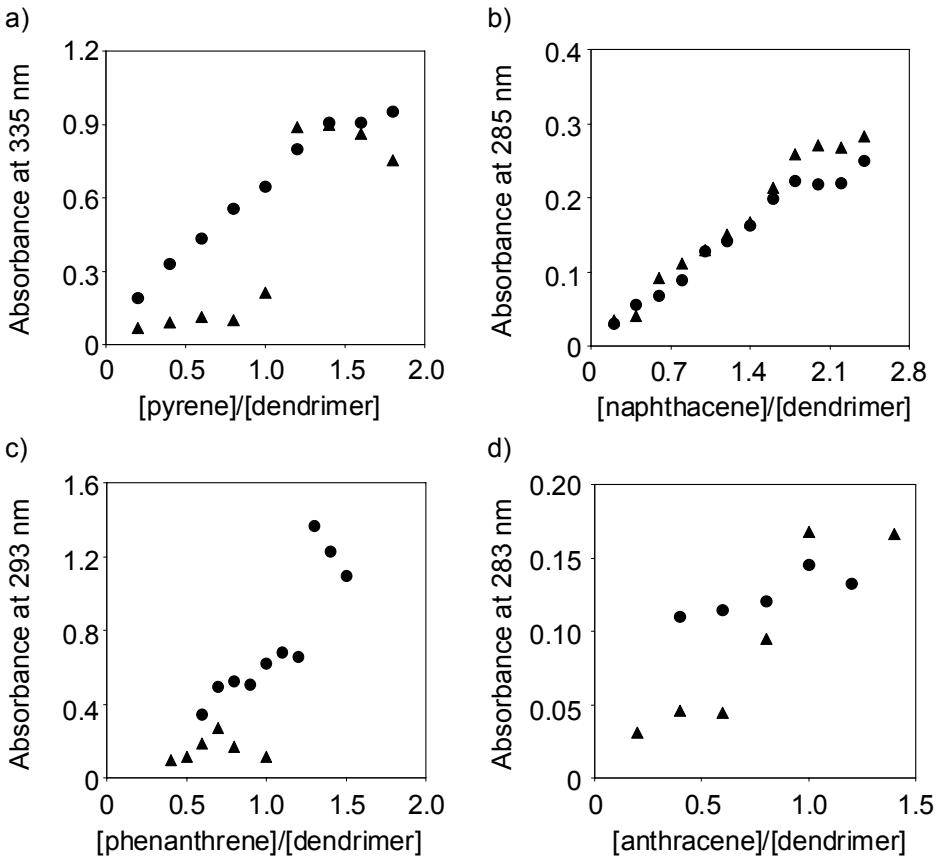

Figure S1. Comparisons of absorbance for various ratios of the guest molecules to the G2 POSS-core dendrimer (circular dots) and the G2 PAMAM dendrimer (triangular dots). The maximum number of the guest molecules entrapped within the dendrimers was evaluated, and the ESF values were calculated.

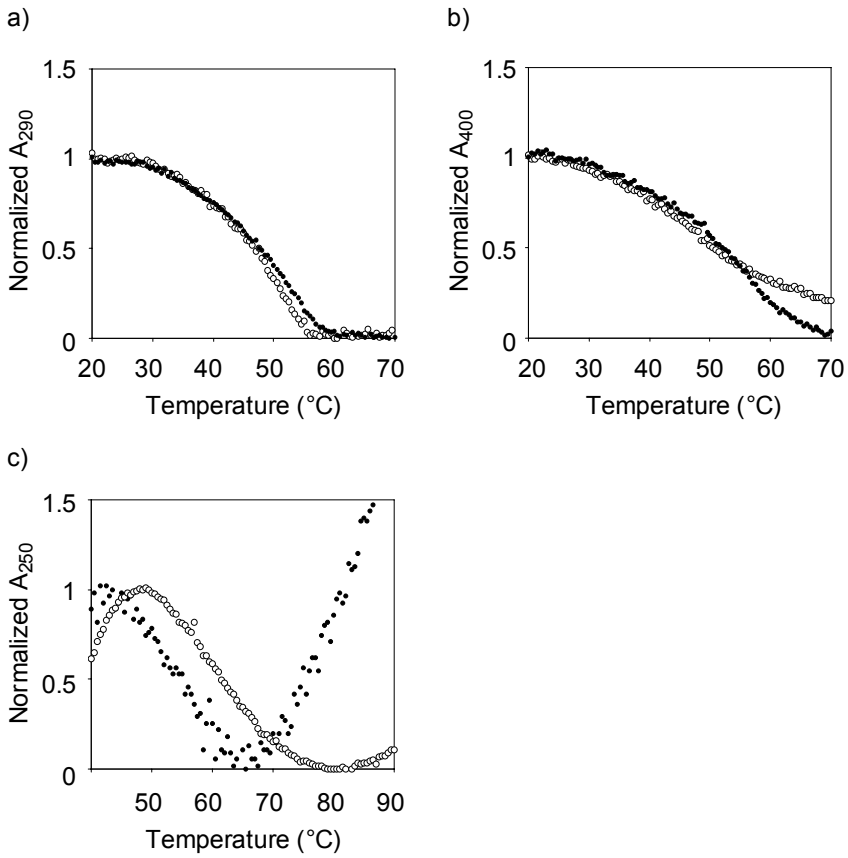

Figure S2. Normalized dissociation profile of the complex of (a) pyrene, (b) anthracene, and (c) phenanthrene with G2 POSS-core dendrimer (center dots) or G2 PAMAM dendrimer (black dots).

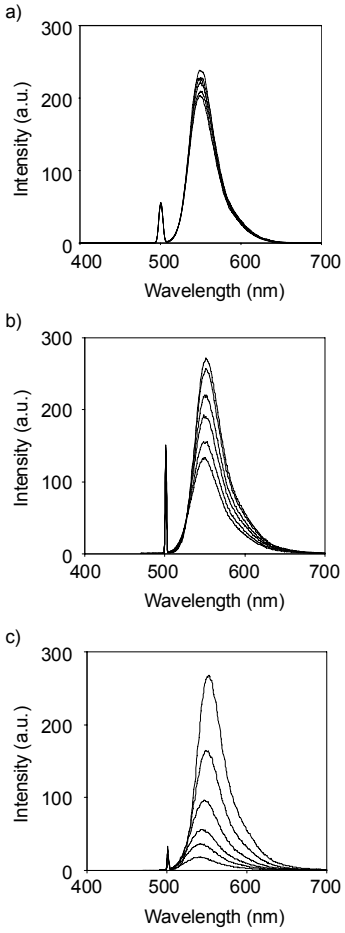

Figure S3. Fluorescence photobleaching of Rh6G (1 μM) in aerated water in the presence of (a) 10 μM G2 POSS-core dendrimer and (b) G2 PAMAM dendrimer and (c) absence of dendrimers followed through the decrease of the fluorescence emission with increasing time of UV irradiation with a low pressure mercury lamp at 25 °C. Excitation wavelength was at 500 nm.

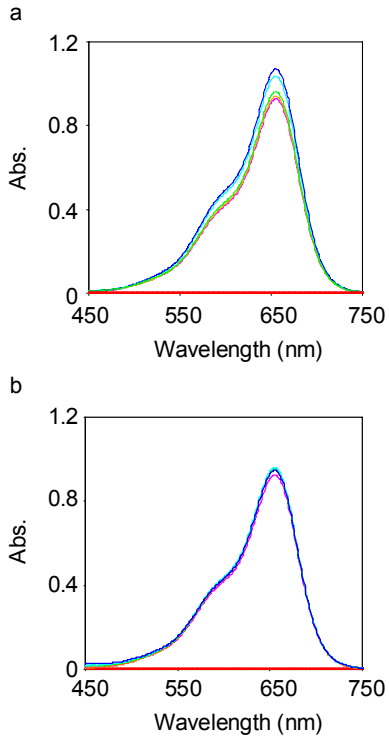

Figure S4. UV–vis absorption spectra of Rh6G (10 μM) with 0 μM (magenta line), 10 μM (orange line), 100 μM (green line), 200 μM (light blue line), and 400 μM (blue line) of (a) G2 POSS-core dendrimer and (b) G2 PAMAM dendrimer at 25 °C. Absorption spectra of each dendrimer represent red lines.