Fourth-Generation Carbazole-Phenylazomethine Dendrimer as Size-Selective Host for Fullerenes

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Supporting Information

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1. Experimental section

Chemicals. Chemicals. The double layer-type dendrimers (**ZnPG1-2**, and **ZnPG2-2**),¹ phenylazomethine dendrimer (**ZnpG4-0**),² and **CzG2**³ were synthesized according to a literature method. C_{60} was purchased from TCI Chemicals, C_{70} and **ZnTPP** were purchased from Aldrich, and C_{84} was purchased from Bucky USA and used without further purification. All other solvents were purchased from Kanto Kagaku Co., Ltd., and used without further purification (the solvent for the UV-vis titration was the dehydrated grade).

General. The NMR spectra were obtained using a JEOL JNM-GX400 (400MHz) with TMS as the internal standard. The MALDI TOF-MS data were obtained using an Ultra flex (Bruker) in the negative ion mode. Dithranol was used as the matrix. The UV-vis spectra were recorded using a Shimadzu UV-3150 spectrometer with a quartz cell having a 4mm optical length at 20°C and the spectra (absorption) of the fullerenes were subtracted from the spectra. The fluorescence spectra were recorded by a JASCO FP-6500 spectrofluorometer with a quartz cell having a 1cm optical length. The error bars of the UV-vis and fluorescence titrations were the standard deviation ($\pm 1\sigma$) and all other errors in this article were described with the two-sided 95% confidence intervals ($\pm 1.96\sigma$). The linear regression lines of the Van't Hoff plots were calculated using the free software gnuplot ver.4.6 with the weighted least-squares method including the error of the binding constants.

UV-vis and fluorescence titration, and error analysis. For UV-vis titration, a ca. 1.25 μ M solution (toluene or the mixture of toluene and acetonitrile) of the dendrimer (porphyrin) in a 10ml measurering flask (± 0.025 ml) and ca. 1.25 mM (C60 and C70) in a 1ml measuring flask (± 0.025 ml) or ca. 40 μ M (C84) toluene solution of fullerenes were prepared (the error of the balance was ± 0.001mg). 1 ml of the dendrimer solution was added to the quartz cell with a 1ml volumetric pipette (± 0.01 ml) and the UV-vis absorption was measured each time when the fullerene solution was added with a micro pipette (± 1%) (acetonitrile was also added to maintain the ratio of toluene and acetonitrile). The spectra (absorption) were measured several times to make sure that it is at the equilibrium state. The absorption of the blank fullerene solutions were also measured in each solution ratio and subtracted from the spectra. In all titrations, the final relative concentration error of the complex (multiplication of the relative error of the concentration of the dendrimer and fullerene) was determined to be ±

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⁽²⁾T. Imaoka, R. Tanaka, S. Arimoto, M. Sakai, M. Fujii and K. Yamamoto, *J. Am. Chem. Soc.*, 2005, **127**, 13896.

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3-4% (standard deviation). The subtracted absorption errors of the fullerenes were in maximum 1% of the absorption of the dendrimer at the Soret band region, and the instrument error (maximum 0.1%) was negligible. The fluorescence titration was done with a similar procedure. The solutions were prepared by dilution of higher concentration solutions to have an accurate concentration (1.3 μ M and 1.3 mM). The different point was the cell size and the starting volume of the dendrimer solution (3ml). The larger cell volume and larger volume of the added fullerene solution gave slightly smaller error than the UV-vis titration, but in general, the errors were determined to be similar.

The binding constant K was determined using the titration curve that was obtained from the UV-vis titration. The fitting with the theoretical curve (described later) was performed with weighted least-squares method using the solver program of the Microsoft Office Excel 2007 SP3. The relative error of the binding constant K was determined using the forementioned concentration and subtraction error to be $\pm 14-18\%$ ($\pm 1.96\sigma$). The titration was done multiple times, and the deviation was calculated. In all cases except the titration of C84, the measured deviations were smaller than the theoretical error and the theoretical error was used as the final error. In the case of C84, the measured standard deviation was used as the final error ($\pm 1.96\sigma$).

The complexation model was a simple 1: 1 complexation model and the theoretical curve was calculated from the last equation in the next page.

Where [A] is the concentration of the dendrimer, [B] is the concentration of fullerene, [AB] is the concentration of the complex, and K is the binding constant. If the concentration of [A], [B], and [AB] during the titration is a-x, b-x and x the complexation ratio is described as a/x



to calculate x, the definition of the binding constant K was used

$$K = \frac{[AB]}{[A][B]} = \frac{x}{(a-x)(b-x)}$$
$$Kx^{2} - (Ka + Kb + 1)x + Kab = 0$$
$$x^{2} - (a + b + \frac{1}{K})x + ab = 0$$

using the quadratic formula, x could be calculated as following

$$x = \frac{(a+b+\frac{1}{K}) - \sqrt{(a+b+\frac{1}{K})^2 - 4ab}}{2}$$

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2. Chemical structures



Fig. **S1** Chemical structures of the compounds that are used.

3. MOPAC calculated molecular models

(a) ZnPG2-2



Fig. **S2** MOPAC (optimized by MM/AM1 mozyme) calculated 3D models of (a) **ZnPG2-2** dendrimer (b) **ZnPG2-2** with fullerene in the cavity (red part is the core porphyrin).

4. Solvent dependant association constant



Fig. S3 Association constant of ZnPG2-2 with C_{60} in various mixture of acetonitrile and toluene (at 293K).

5. Fluorescence quenching experiment



Fig. S4 Rate of fluorescence quenching of **ZnPG1-2** (left), and **ZnTPP** (right) with fullerene at several excitation wavelengths (solvent was toluene : acetonitrile = 2 : 1, at RT).

The fluorescence quenching experiment was done with a procedure similar to the UV-vis titration. The excitation wavelength of 444 nm (**ZnPG2-2**) was the isosbestic point of the UV-vis titration. The addition of a 90 eq fullerene solution dilutes the dendrimer solution ca. 15 % and the fluorescence intensity was ca. 10% lower when the dendrimer solution was diluted without the fullerene. For **ZnPG1-2** and **ZnTPP**, the change in the UV-vis spectra by the addition of 90 eq fullerene is negligible (few %) therefore, the Soret band peak (433 and 425nm, respectively) was chosen as the excitation wavelength. For confirmation, the quenching behavior was checked at other excitation wavelengths (Figure S4). The slight difference in the quenching rate can be explained by the difference in the ratio of the absorption of the fullerene and porphyrin. The absorption of the fluorescence intensity of the **ZnPG1-2** and **ZnTPP** can be explained by the dilution, and the absorption of the fullerene, and shows that there is almost no interaction with the fullerene. On the other hand, the behavior of the fluorescence of **ZnPG2-2** clearly shows a difference (Figure 2).

6. Complexation of ZnTPPG2-2 with high order fullerenes



Figure S5. Uv-vis spectra and the titration curve of the titration of ZnPG2-2 with (a) C₇₀, and (b) C₈₄.

7. Thermodynamic parameters



Figure **S6**. Van't Hoff plots of the **ZnPG2-2**-fullerene complexes in Toluene: Acetonitrile = 2: 1.

Table S1. Thermodynamic parameters of the **ZnPG2-2**-fullerene complexes in Toluene: Acetonitrile = 2: 1.

Gest	riangle H (kcal/mol)	imes S (cal/mol)
C60	-18±3	-43±4
C 70	-21±3	-54±5
C84	-28±4	-75±6