Dynamic Control of Dendrimer-Fullerene Association by Axial Coordination to the Core

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Supporting Information

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1. Experimental section

Chemicals. The double layer-type dendrimer **ZnPG2-2**[1] and phenylazomethine dendrons[2] 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). The silica gel for column chromatography was the neutral grade (Kanto Kagaku Co., Ltd.).

General. The NMR spectra were obtained using a Bruker AVANCE Ⅲ 400 (400MHz) with TMS as the internal standard. The MALDI TOF-MS data were obtained using an Ultra flex (Bruker) in the positive ion mode for identification data, and in the negative ion mode to measure the dendrimer-fullerene complex. 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 20ºC. The isothermal titration calorimetry was performed using Microcal VP-ITC isothermal titration calorimeter. The error bars of the UV-vis titrations were the standard deviation ($\pm 1\sigma$) and all other errors in this article were described with the two-sided 95% confidence intervals ($\pm 1.96\sigma$).

UV-vis titration and error analysis. For UV-vis titration, a 1 to 1.5 μM solution (the mixture of toluene and acetonitrile) of the dendrimer (porphyrin) in a 10ml measurering flask (± 0.025 ml) was prepared. Guest solutions were prepared as a ca. 1.25 mM (C60 and C70), ca. 40 μM (C84), or ca. 30mM (pyridines) toluene solution in a 1ml measuring flask (± 0.025 ml) (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). The guest solution and acetonitrile was also added to maintain the ratio of toluene and acetonitrile with a micro pipette (± 1%) (For the allosteric titration, 1000eq of pyridine was added before titrating fullerenes). Then the UV-vis spectra (absorption) were measured several times to make sure that it is at the equilibrium state. The absorption of the blank fullerene or pyridine solutions were also measured 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

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(1) Albrecht, K.; Kasai, Y.; Kimoto, A.; Yamamoto, K. *Macromolecules* **2008**, *41*, 3793.
(2) Takanashi, K.; Chiba, H.; Higuchi, M.; Yamamoto, K. *Org. Lett.* **2004**, *6*, 1709.

dendrimer and fullerene) was determined to be ± 3-4% (standard deviation). The subtracted absorption errors of 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 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 ± 14-20% (± 1.96σ). The actually observed error (deviation) that was obtained by multiple titrations was smaller than the above mentioned error (the theoretical error was used in the main text). However, in the titration of C_{84}, the solubility of C_{84} was low and only 25% saturation of the titration curve could be obtained. The deviation of the K that was obtained by multiple titrations was larger than the above discussed error, but the error was lower than 30% (± 1.96σ) and this value was used.

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

$$[A] + [B] \xrightarrow{K} [AB]$$

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

$$\begin{array}{ccccc} [A] & + & [B] & \xrightarrow{K} & [AB] \\ a & & b & & 0 \\ a-x & & b-x & & x \end{array}$$

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

$$K = \frac{[AB]}{[A][B]} = \frac{x}{(a-x)(b-x)}$$

$$Kx^2 - (Ka + Kb + 1)\,x + Kab = 0$$

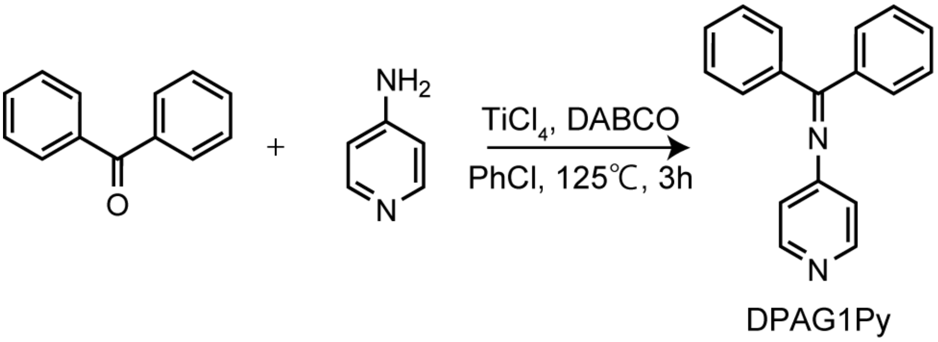
$$x^2 - (a + b + \frac{1}{K})\,x + ab = 0$$

using the quadratic formula, x could be calculated as following and the complexation ration can be calculated from this value.

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

2. Synthesis

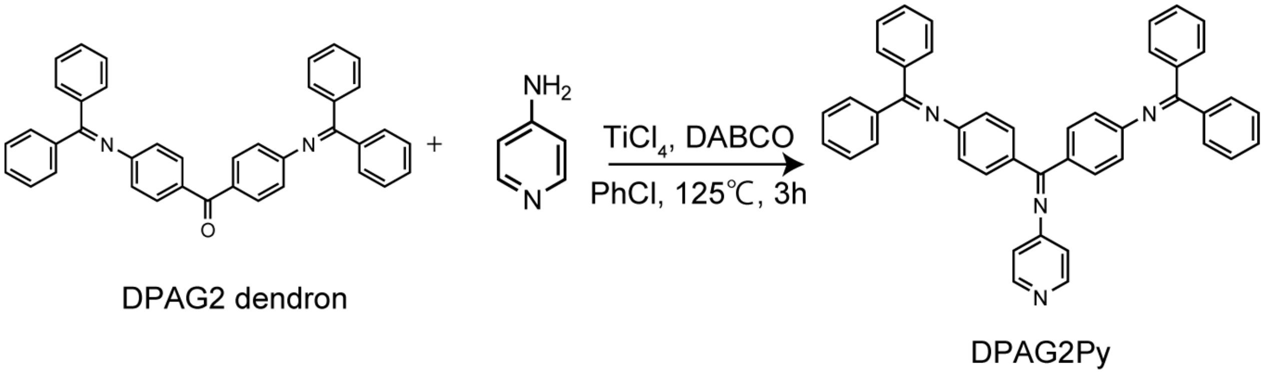
DPAG1Py (general procedure for dehydration reaction with $TiCl_4$)



Scheme S1. Synthesis of **DPAG1Py**.

Benzophenone (182mg, 1.01mmol), **4-aminopyridine** (94.1mg, 1.05mmol), and 4-diazabicyclo[2.2.2]octane(DABCO) (7.22g, 64.1mmol) were dissolved in chlorobenzene (100mL), and heated to 75°C. $TiCl_4$ (1.76ml, 16.0mmol) dissolved in 10ml of chlorobenzene was dropwise added, and the addition funnel was then rinsed with 5ml of chlorobenzene. The mixture was heated to 125 °C and stirred for 3h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and stirred for 2h in air and then filtered through silica gel (Et_3N was added to the reaction mixture and solvent). The filtrate was concentrated and the product was isolated by silica gel column chromatography (THF: Hexane= 1: 1 with 2% Et_3N), and purified by preparative GPC (eluent: Chloroform). Yield: 62% (162mg, 0.63mmol). **DPAG1Py**; ^1H NMR (400 MHz, C_4D_8O, 29.1 °C, ppm): δ 8.20 (2H, dd, J = 4.5, 1.5 Hz), 7.74 (2H, d, J = 6.3 Hz), 7.43-7.31 (6H, m), 7.14 (2H, br s), 6.56 (2H, dd, J = 4.5, 1.6 Hz). ^{13}C NMR (100 MHz, C_4D_8O, 29.4 °C, ppm): δ 169.32, 158.92, 150.77, 139.64, 136.45, 131.91, 130.19, 129.86, 129.65, 128.88, 116.02. MALDI TOF-MS (Matrix: Dithranol): Calcd: 259.1 ($[M+H]^+$), Found: 260.2. Anal. Calcd. for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.60; H, 5.24; N, 10.76.

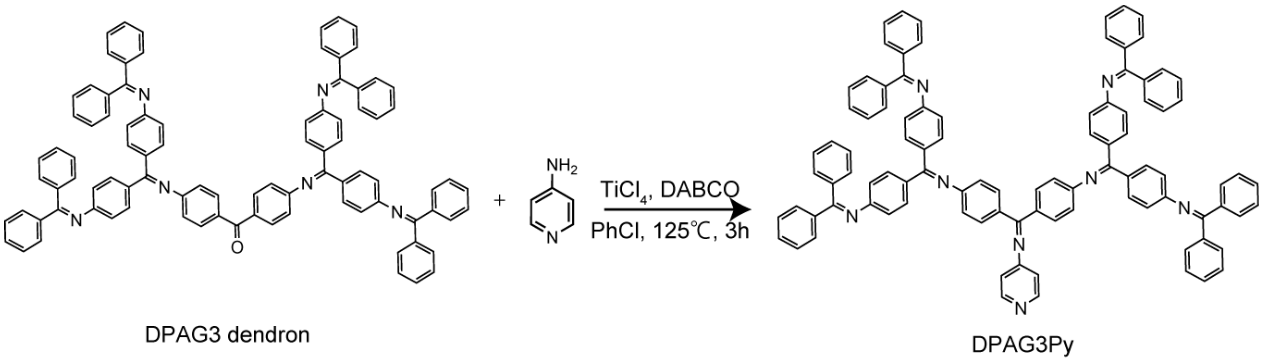
DPAG2Py



Scheme S2. Synthesis of **DPAG2Py**.

As per the general procedure for the dehydration reaction, the **DPAG2 dendron** (703mg, 1.30mmol), **4-aminopyridine** (96.5mg, 1.03mmol) and DABCO (1.80g, 16.0mmol) were dissolved in chlorobenzene (50mL). $TiCl_4$ (761mg, 4.0mmol) was added and the mixture was stirred for 3h at 125ºC. The product was isolated by silica gel column chromatography (THF: Hexane = 1: 1 with 2% Et_3N), and purified by preparative GPC (eluent: Chloroform). Yield: 88% (559mg, 0.91mmol). **DPAG2Py**; ^{1}H NMR (400 MHz, THF, 29.1 ºC, ppm): δ 8.18 (2H, dd, J = 4.6, 1.5 Hz), 7.74 (4H, s), 7.50-7.17 (16H, m), 7.00 (2H, d, J = 5.5 Hz), 6.82 (2H, d, J = 6.4 Hz), 6.69 (2H, d, J = 6.8 Hz), 6.54 (2H, d, J = 6.1 Hz), 6.42 (2H, dd, J = 4.5, 1.6 Hz). ^{13}C NMR (100 MHz, C_4D_8O, 29.1ºC, ppm): δ 169.15, 168.80, 159.27, 155.36, 153.32, 150.70, 140.14, 137.00, 134.35, 131.55, 130.74, 130.08, 129.44, 128.82, 120.98, 116.33. MALDI TOF-MS (Matrix: Dithranol): Calcd: 617.3 ($[M+H]^+$), Found: 616.8. Anal. Calcd. for $C_{44}H_{32}N_4$: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.65; H, 4.97; N, 9.14.

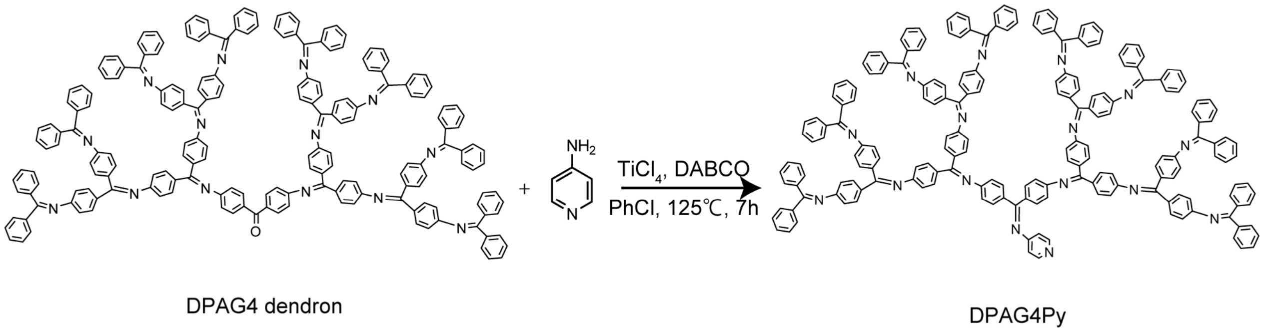
DPAG3Py



Scheme S3. Synthesis of **DPAG3Py**.

As per the general procedure for the dehydration reaction, the **DPAG3 dendron** (1650mg, 1.31mmol), **4-aminopyridine** (95.0mg, 1.01mmol) and DABCO (1.80g, 16.0mmol) were dissolved in chlorobenzene (50mL). $TiCl_4$ (761mg, 4.0mmol) was added and the mixture was stirred for 3h at 125ºC. The product was isolated by silica gel column chromatography (THF: Hexane = 1: 1 with 2% Et_3N), and purified by preparative GPC (eluent: Chloroform). Yield: 59% (781mg, 0.59mmol). **DPAG3Py**; ^1H NMR (400 MHz, THF, 28.1 ºC, ppm): δ,8.23 (2H, dd, J = 4.7, 1.4 Hz), 7.75 (8H, d, J = 7.2 Hz), 7.49-7.36 (18H, m), 7.26-7.20 (16H, m), 7.06 (4H, s), 6.82-6.70 (10H, m), 6.56-6.51 (10H, m). ^{13}C NMR (100 MHz, C_4D_8O, 28.6 ºC, ppm):δ 169.12, 169.02, 168.57, 168.18, 159.33, 155.84, 154.99, 153.66, 153.13, 150.83, 140.23, 137.14, 136.99, 134.93, 133.95, 131.50, 130.68, 130.51, 130.20, 130.12, 129.42, 128.82, 128.73, 121.42, 120.94, 116.55. MALDI TOF-MS (Matrix: Dithranol): Calcd: 1334.6 ($[M+H]^+$), Found: 1333.6. Anal. Calcd. for $C_{96}H_{68}N_8$: C, 86.46; H, 5.14; N, 8.40. Found: C, 86.43; H, 4.95; N, 8.39.

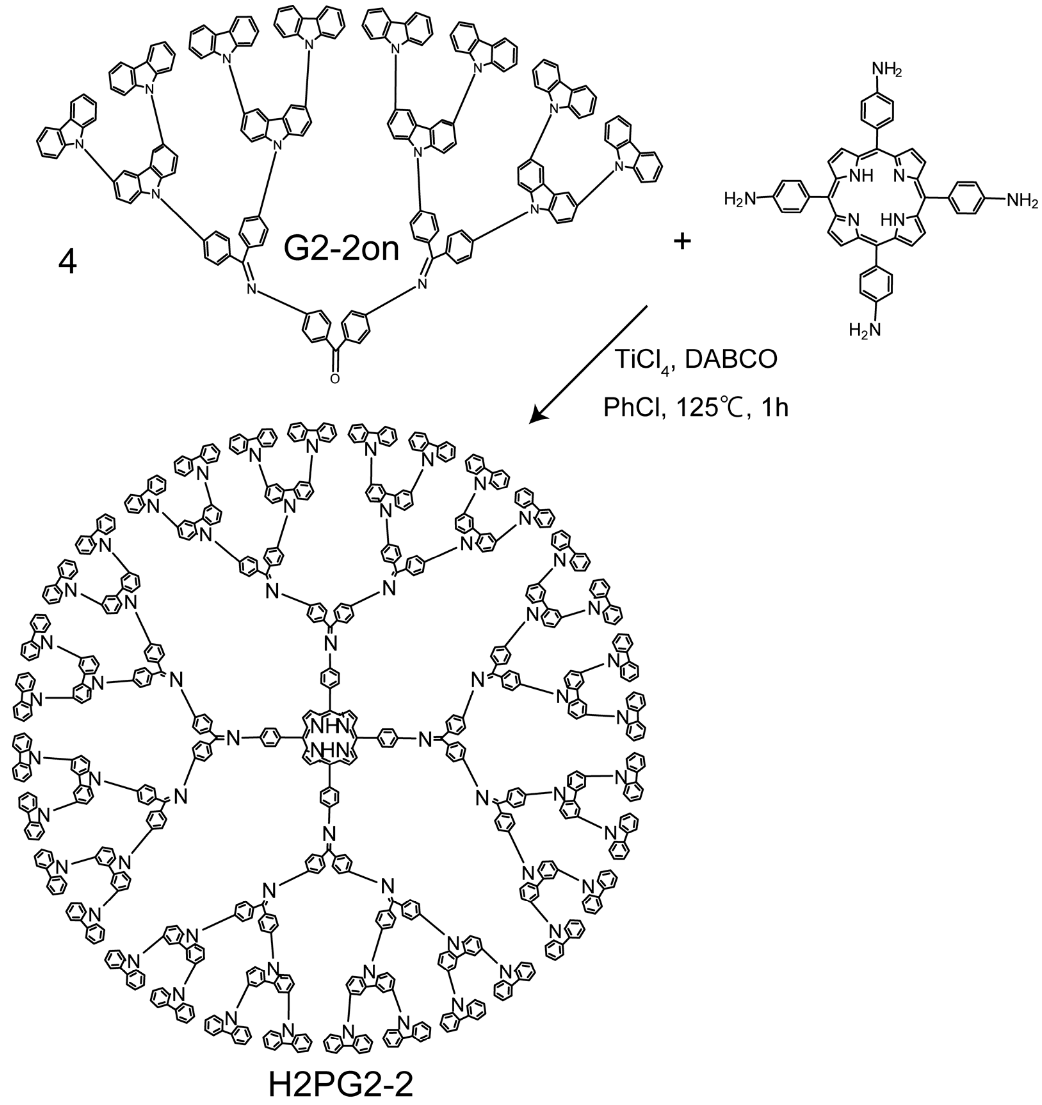
DPAG4Py



Scheme S4. Synthesis of **DPAG4Py**.

As per the general procedure for the dehydration reaction, the **DPAG4 dendron** (251mg, 0.093mmol), **4-aminopyridine** (92.5mg, 0.983mmol) and DABCO (1068mg, 9.52mmol) were dissolved in chlorobenzene (20mL). $TiCl_4$ (100μg, 0.91mmol) was added and the mixture was stirred for 2h at 125°C. $TiCl_4$ (100μg, 0.91mmol) was added again and after stirring for an additional 1.5h, DABCO (538mg, 4.80mmol) and $TiCl_4$ (100μg, 0.91mmol) were added. After stirring for 3.5h, the reaction was quenched. The product was isolated by silica gel column chromatography (Hexane: Chloroform: EtOAc = 3: 3: 1 with 2% Et_3N), and purified by preparative GPC (eluent: Chloroform). Yield: 72% (185mg, 0.067mmol). **DPAG4Py**; ^{1}H NMR (400 MHz, THF, 25.4 °C, ppm): δ 8.10 (2H, d, J = 4.4 Hz), 7.74-7.70 (16H, m), 7.51-7.12 (72H, m), 7.02-6.99 (8H, m), 6.75-6.54 (42H, m). ^{13}C NMR (100 MHz, C_4D_8O, 29.4 °C, ppm): δ 169.08, 168.62, 168.56, 168.51, 168.47, 168.08, 168.03, 155.47, 155.00, 154.88, 153.13, 150.60, 140.26, 140.16, 140.03, 137.12, 137.00, 136.82, 135.17, 134.91, 134.52, 131.57, 130.93, 130.85, 130.71, 130.47, 130.13, 129.47,, 129.35, 128.84, 128.72, 121.66, 121.34, 120.97, 120.80, 116.59. MALDI TOF-MS (Matrix: Dithranol): Calcd: 2768.2 ($[M+H]^+$), Found: 2766.1. Anal. Calcd. for $C_{200}H_{140}N_{16}$: C, 86.80; H, 5.10; N, 8.10. Found: C, 86.96; H, 4.87; N, 8.10.

H2PG2-2



Scheme S5. Synthesis of **H2PG2-2**.

As per the general procedure for the dehydration reaction, **5,10,15,20-tetrakis(4-aminophenyl)porphine** (21.8mg, 0.032mmol), **G2-2on** (496mg, 0.197mmol), and 4-diazabicyclo[2.2.2]octane(DABCO) (316mg, 2.82mmol) were dissolved in chlorobenzene (15mL), and heated to 75°C. $TiCl_4$ (54µl, 0.495mmol) dissolved in 5ml of chlorobenzene was dropwise added, then the addition funnel was then rinsed with 5ml of chlorobenzene. The mixture was heated to 125 °C and stirred for 1h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, stirred 1h in air and then filtered through celite. The filtrate was concentrated and the product was isolated by silica gel column chromatography (Toluene: Hexane= 10: 1 with 2% Et_3N), and purified by preparative GPC (eluent: Chloroform). Yield: 52% (179mg, 0.017mmol). **H2PG2-2**; ^1H NMR (400

MHz, C_4D_8O, TMS standard, 22.8 °C, ppm): δ 8.71 (8H, s), 8.51 (8H, s), 8.44 (8H, s), 8.38 (8H, s), 8.24-8.15 (32H, m), 8.03-7.93 (64H, m), 7.84 (16H, t, J = 7.4 Hz), 7.72-7.20 (224H, m), 7.09-7.02 (88H, m), 6.91 (8H, d, J = 7.9 Hz), 6.59 (8H, d, J = 8.2 Hz), -2.75 (2H, s). ^{13}C NMR (100 MHz, C_4D_8O, 27.9 °C, ppm): δ,168.53, 167.69, 166.88, 154.50, 153.01, 152.96, 142.79, 142.71, 142.67, 142.49, 141.23, 141.04, 140.80, 140.64, 139.13, 138.78, 138.45, 137.76, 136.44, 135.76, 132.61, 132.37, 132.26, 132.11, 131.94, 131.74, 131.36, 130.73, 127.52, 127.16, 126.87, 126.60, 126.51, 125.65, 125.59, 125.41, 125.31, 124.27, 124.21, 124.09, 121.39, 120.93, 120.50, 112.24, 112.02, 111.73, 110.46, 110.34, 110.25. MALDI TOF-MS (Matrix: Dithranol): Calcd: 10691.92 ($[M+H]^+$), Found: 10693.0. Anal. Calcd. for $C_{776}H_{474}N_{64}$: C, 87.15; H, 4.47; N, 8.38. Found: C, 87.14; H, 4.19; N, 8.24.

3. Assotiation of fullerene under excess 4-phenylpyridine

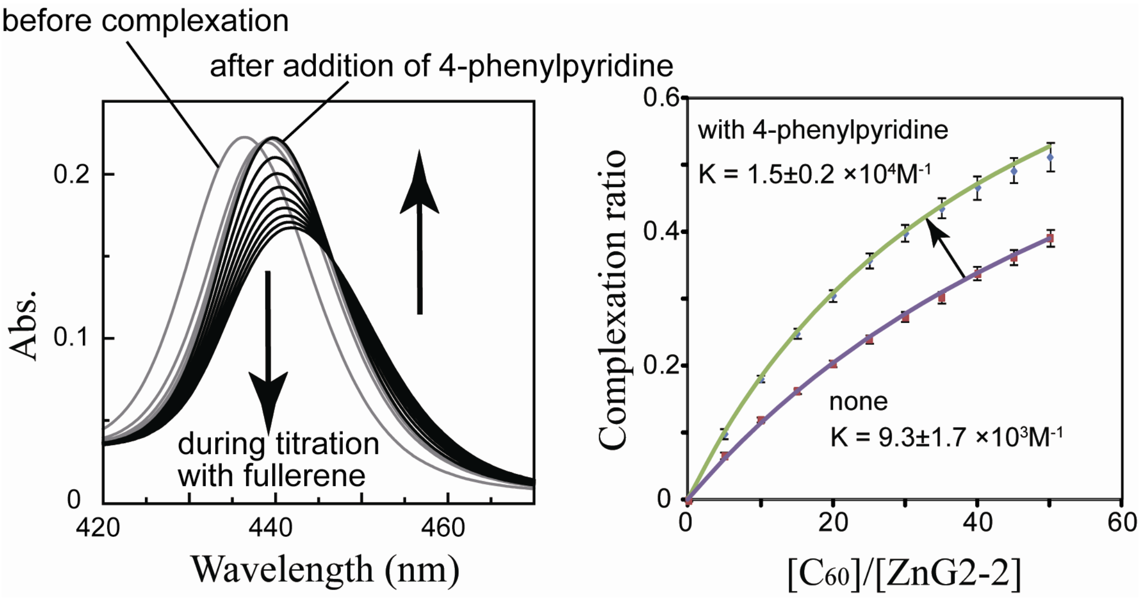


Figure S1. (left) Uv-vis spectra during the titration with C60 after addition of 1000eq. of 4-phenylpyridine. (right) Titration curve of C60 and ZnPG2-2 with and without 1000eq. of 4-phenylpyridine (in toluene: acetonitrile= 2: 1 at 20 ºC).

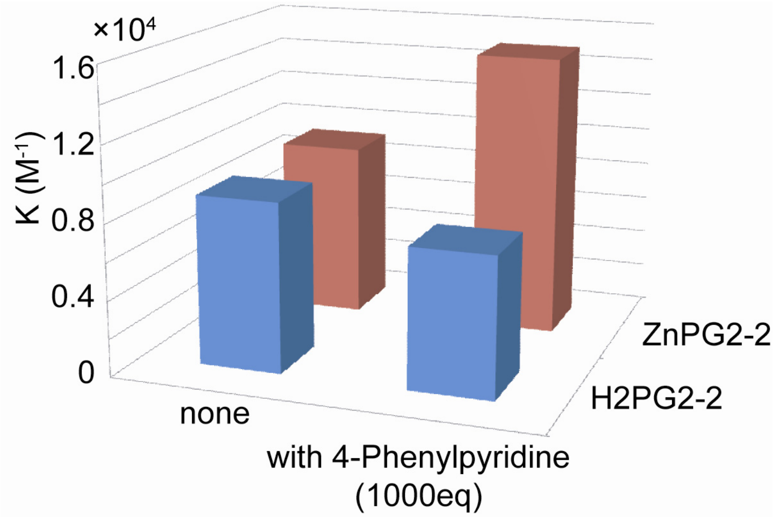


Figure S2. Binding constants of **ZnPG2-2** and **H2PG2-2** with C_{60} with and without 1000eq of 4-phenylpyridine at 20 ºC.

4. Titration of ZnPG2-2 and DPApyridines

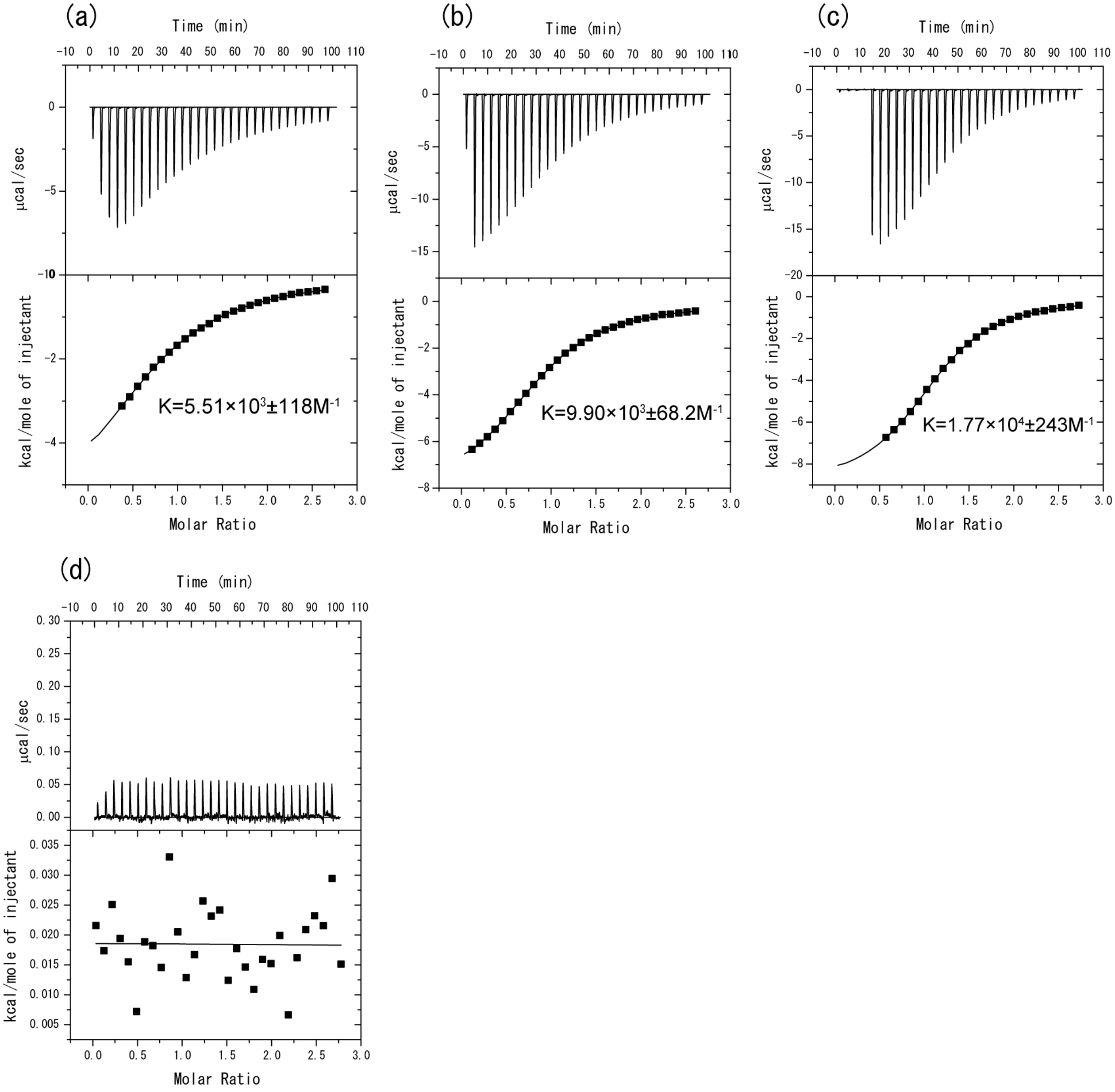


Figure S3. Thermogram of isothermal titration calorimetry of (a) **ZnPG2-2** vs **DPAG1Py**, (b) **ZnPG2-2** vs **DPAG2Py**, (c) **ZnPG2-2** vs **DPAG3Py,** and (d) **ZnPG2-2** vs **DPAG4Py.**

Table S1. Thermodynamic parameters of the **ZnPG2-2-DPAG*n*Py** complexes (293K). The value was determined by isothermal titration calorimetry.

Guest	⊿H⁰	T⊿S⁰	⊿G⁰
DPAG1Py	-6.3±0.12	-1.3	-5.0
DPAG2Py	-8.4±0.02	-3.1	-5.3
DPAG3Py	-9.0±0.04	-3.3	-5.7

(kcal/mol)

5. ΔH-ΔS plot

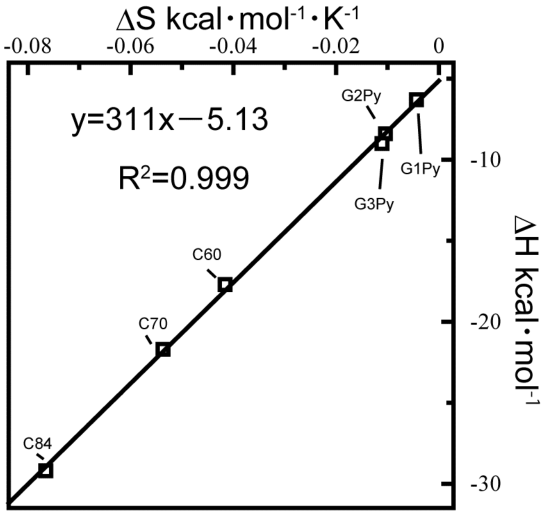


Figure S4. ΔH- ΔS plot of **ZnPG2-2** in toluene: acetonitrile = 2: 1 with several guests.

6. Thermodynamic parameters of fullerene complexation

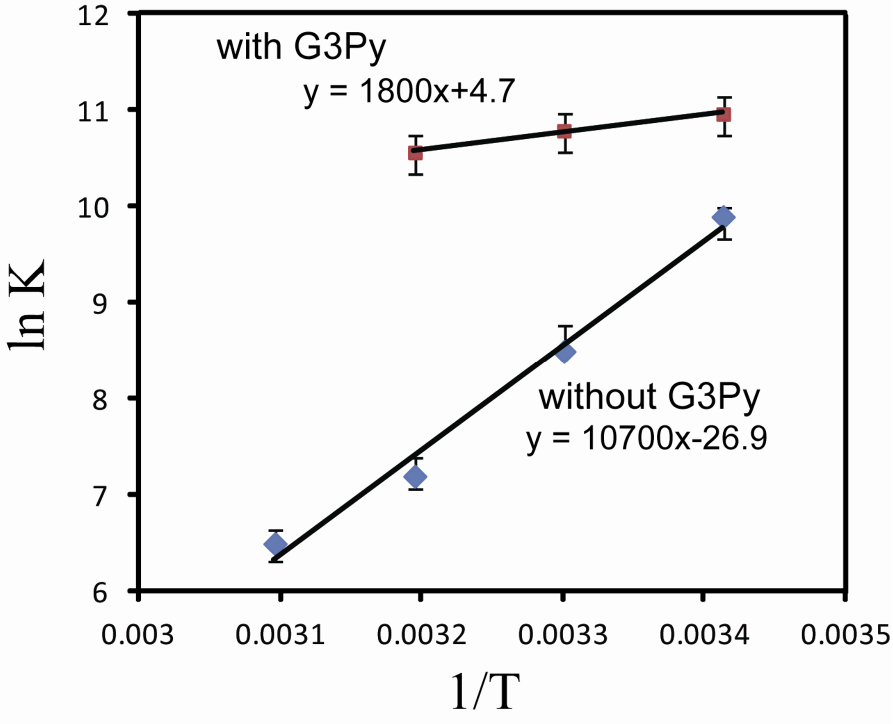


Figure S5. Van’t Hoff plots of the **ZnPG2-2**-C_{70} complexation with and without excess **G3Py** in toluene: acetonitrile = 2: 1.