Mass spectrometric studies of competitive binding of C_{60} and C_{70} to meso-substituted porphyrins

Sunghan Jung and Seung Koo Shin*

FT-ICR Laboratory, Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea
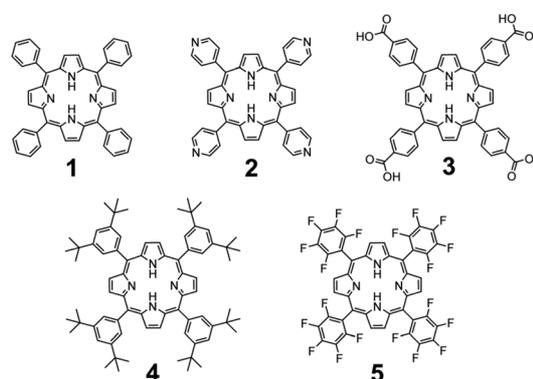
Abstract: Competitive binding of C_{60} and C_{70} to meso-substituted porphyrins was studied by mass spectrometry (MS). Electrospray ionization MS was employed to acquire the mass spectra of 1 : 1 porphyrin–fullerene complexes formed in a mixture of meso-substituted porphyrin and fullerite to determine the ratio of complexes between C_{60} and C_{70}. Matrix-free laser desorption ionization MS was used to obtain the mass spectra of fullerite to measure the mole fraction of C_{60} and C_{70}. The binding constant ratio (K_{70}/K_{60}) was determined from the mass spectral data. The difference in standard Gibbs free energy change, $\Delta(\Delta G^{o})_{70-60}$, for the competitive binding of C_{60} and C_{70} was calculated from K_{70}/K_{60}. Of the five porphyrins, tetraphenyl, tetra(4-pyridyl), tetra(4-carboxyphenyl), tetra(3,5-di-*tert*-butylphenyl), and tetra(pentafluorophenyl) porphyrins, the first three non-bulky porphyrins yield negative values of $\Delta(\Delta G^{o})_{70-60}$, whereas the other two bulky porphyrins result in positive values of $\Delta(\Delta G^{o})_{70-60}$. This result indicates that C_{70} binding to porphyrin is thermodynamically favored over C_{60} binding in non-bulky porphyrins, but disfavored in bulky ones. It also suggests that the binding mode of C_{70} is different between non-bulky and bulky porphyrins, which is in line with previous experimental findings of the "side-on" binding to non-bulky porphyrins and the C_{60}-like "end-on" binding to bulky porphyrins.

Key words: Protonated porphyrin, Fullerene, Porphyrin–fullerene complex, Binding constant

Noncovalent binding of curved fullerene to flat porphyrin has attracted much interest because of their unique structures[1] and potential applications to photovoltaic solar cells.[2] Selective binding of fullerenes to porphyrin receptors has been used to separate fullerenes using chromatography.[3,4] Although several binding constant measurements have been reported to date, most of them deal with fullerene binding to bisporphyrins,[5–9] because bisporphyrin–fullerene complexes show characteristic spectral changes, such as charge-transfer bands in the near-infrared region[5,6] and redshift in the Soret band.[5,7–9] However, the fullerene binding to monomeric porphyrins has rarely been studied because of the absence of characteristic spectral changes.[8,10,11] In such a case, mass spectrometry (MS) is a powerful alternative tool to measure the binding constant of host–guest complexes in solution.[12]

Most recently, we utilized collision-induced dissociation MS to study the relative stabilities of protonated porphyrin–fullerene complexes in the gas phase.[13] In the present study, we employed MS to examine the competitive binding of C_{60} and C_{70} to five different meso-substituted porphyrins; tetraphenyl porphyrin (**1**), tetra(4-pyridyl) porphyrin (**2**), tetra(4-carboxyphenyl) porphyrin (**3**), tetra(3,5-di-*tert*-butylphenyl) porphyrin (**4**), and tetra(pentafluorophenyl) porphyrin (**5**). Fullerite (a mixture of C_{60} and C_{70}) was used as guest molecules.

Electrospray ionization (ESI) MS was used to take the

mass spectra of 1 : 1 porphyrin–fullerene complexes formed in a mixture of porphyrin and fullerite in order to determine the relative abundances of 1 : 1 porphyrin–C_{60} and porphyrin–C_{70} complexes. Matrix-free laser desorption ionization (LDI) MS was used to acquire the mass spectra of fullerite to determine the mole fraction of C_{60} and C_{70}. The binding constant ratio (K_{70}/K_{60}) was calculated from the complex and C_{60}/C_{70} ratios, and then converted to the Gibbs free energy change. Thermodynamic data for the competitive binding of C_{60} and C_{70} to porphyrins show the effects of meso-substituents on the binding mode.

Experimental

Porphyrins **1** (97%), **2** (97%), **3** (75%), and **5**, as well as

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*Reprint requests to Dr. Seung Koo Shin
E-mail:skshin@postech.ac.kr

fullerite and pure C_{60} (99.5%) were purchased from Sigma-Aldrich (St. Louis, MO). Pure C_{70} (99.5%) was obtained from Materials Technologies Research (Cleveland, OH). Porphyrin **4** was provided by Dr. P. D. W. Boyd (University of Auckland, New Zealand). HPLC-grade methanol and dichloromethane were purchased from J. T. Baker (Phillipsburg, NJ).

Both porphyrin and fullerite were mixed in a 3 : 1 (v/v) dichloromethane/methanol solution by 10-min sonication. The solute concentration was 50 μM for porphyrin and 168 μM for fullerite. For ESI, 0.5% formic acid was added to the sample solution. The ESI mass spectra of a porphyrin–fullerene mixture were taken with a triple quadrupole-time-of-flight (TOF) mass spectrometer (QSTAR Pulsar-*i*, AB Sciex, Foster City, CA), as previously described in detail.[13] The LDI mass spectra of fullerite as well as pure C_{60} and C_{70} were obtained using a TOF mass spectrometer (4700 Proteomics Analyzer, AB Sciex) equipped with a Nd : YAG laser (355 nm). The known molar ratio of $[C_{60}]/[C_{70}] = 0.2$, 0.33, 1.0, 3.0, and 5.0 was prepared by dissolving 0.017/0.101, 0.029/0.101, 0.072/0.084, 0.086/0.034, and 0.086/0.020 mg of pure C_{60}/C_{70} in 1 mL of toluene. A fullerite solution was prepared by dissolving 0.075 mg of fullerite in 1 mL of toluene.

Results and Discussion

The mass spectra of fullerite are shown in Figure 1(a). The molar ratio of $[C_{60}]/[C_{70}]$ in fullerite was determined from a plot of the intensity ratio of $I(C_{60}{}^+)/I(C_{70}{}^+)$ as a function of

the known molar ratio of pure $[C_{60}]/[C_{70}]$ (Figure 1(b)), as previously described by Cristadoro *et al.*[14] Since ionization energies of C_{60} (7.6 eV[15]) and C_{70} (7.47 eV[16]) are different, their response factors for LDI are not identical. A least-squares fit to the data yields the slope of 0.535 as the response factor for C_{60} relative to C_{70}. Thus, the measured intensity ratio of $I(C_{60}{}^+)/I(C_{70}{}^+) = 1.54 \pm 0.01$ divided by 0.535 results in the molar ratio of $[C_{60}]_0/[C_{70}]_0 = 2.88 \pm 0.03$, suggesting the mole fraction of 0.742 for C_{60} and 0.258 for C_{70} in fullerite, which corresponds to 125 μM of C_{60} and 43 μM of C_{70} in 168 μM of fullerite.

The ESI mass spectra of protonated porphyrin–fullerene complexes are displayed in Figure 2(a)–(e). Porphyrin (P) forms 1 : 1 $[P + H]^+ \cdot C_m$ ($m = 60$, 70) complexes. Their intensity ratio, $I([P + H]^+ \cdot C_{60})/I([P + H]^+ \cdot C_{70})$, significantly varies with meso-substituent, indicating that meso-substituents affect the binding equilibrium between porphyrin and fullerene. In the ESI solution containing 0.5% formic acid, all of the porphyrins
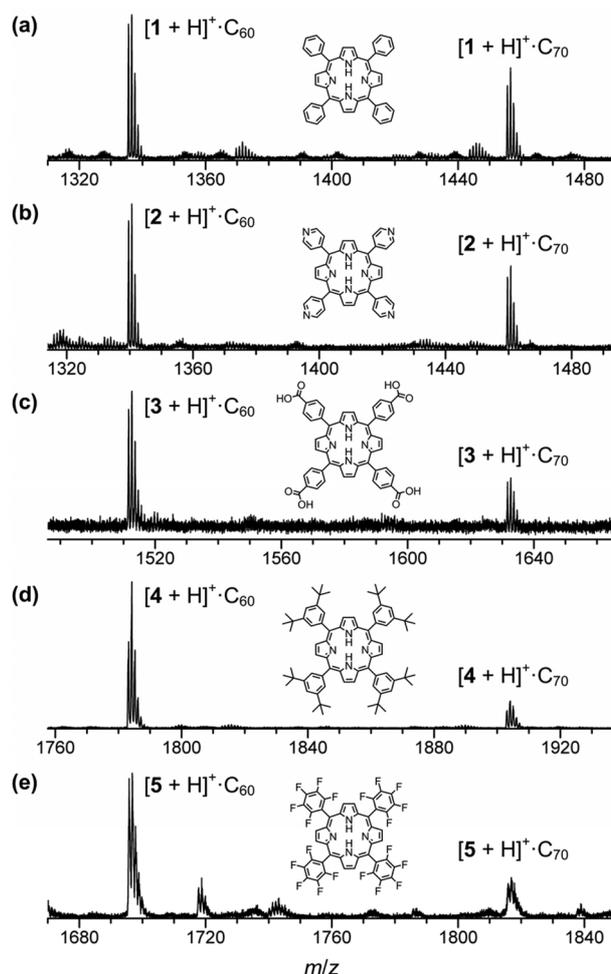

Figure 1. (a) LDI mass spectra of fullerite (a mixture of C_{60} and C_{70}). (b) Plot of the measured intensity ratio of $I(C_{60}{}^+)/I(C_{70}{}^+)$ as a function of the premixed molar ratio of pure C_{60} and C_{70}, $[C_{60}]/[C_{70}]$. The slope is the response factor for LDI. Error bars are from standard deviations of five measurements.
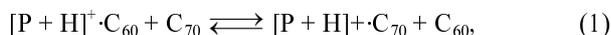

Figure 2. ESI mass spectra of 1:1 porphyrin–fullerene complexes in a porphyrin–fullerite mixture: (a) tetraphenyl porphyrin (**1**); (b) tetra(4–pyridyl) porphyrin (**2**); (c) tetra(4-carboxyphenyl) porphyrin (**3**); (d) tetra(3,5-di-*tert*-butylphenyl) porphyrin (**4**); (e) tetra(pentafluorophenyl) porphyrin (**5**).

are considered to be protonated, as the proton affinity of porphyrin is $233-263$ kcal mol^{-1}.[13] Thus, the protonated porphyrin $[P + H]^+$ competitively forms 1:1 $[P + H]^+ \cdot C_m$ ($m = 60, 70$) complexes, as expressed in eq 1.

$$[P + H]^+ \cdot C_{60} + C_{70} \rightleftharpoons [P + H]+\cdot C_{70} + C_{60}, \qquad (1)$$

$$\frac{[[P+H]^+ \cdot C_{70}]}{[[P+H]^+ \cdot C_{60}]} \cdot \frac{[C_{60}]}{[C_{70}]} = \frac{K_{70}}{K_{60}} \approx \frac{I([P+H]^+ \cdot C_{70})}{I([P+H]^+ \cdot C_{60})} \cdot \frac{[C_{60}]_0}{[C_{70}]_0}, \qquad (2)$$

where $[[P + H]^+ \cdot C_m]$ and $[C_m]$ are the equilibrium concentrations of complex and uncomplexed fullerene present in solution, respectively, and K_m is the 1 : 1 binding constant. By assuming identical ESI response factors for the two complex ions, we can replace the concentration ratio $[[P + H]^+ \cdot C_{70}]/[[P + H]^+ \cdot C_{60}]$ with the intensity ratio $I([P + H]^+ \cdot C_{70})/I([P + H]^+ \cdot C_{60})$. Moreover, the ratio of $[C_{60}]/[C_{70}]$ is set to be equal to the initial concentration ratio of $[C_{60}]_0/[C_{70}]_0 = 2.88 \pm 0.03$ in fullerite, because the concentrations of complexed fullerenes are negligible as compared to the initial concentrations of C_{60} (125 μM) and C_{70} (43 μM). The complexed fullerene concentrations ($0.5-3.3$ μM for C_{60} and $0.3-0.9$ μM for C_{70}) are estimated by multiplying the initial concentration of porphyrin and the intensity ratio of the complexed porphyrin ions to the sum of all porphyrin-containing ions.

Values of $I([P + H]^+ \cdot C_{70})/I([P + H]^+ \cdot C_{60})$ for porphyrins **1−5** are obtained from the ESI mass spectra (Figure 2(a)−(e)). Calculated K_{70}/K_{60} values are listed in Table 1. K_{70}/K_{60} values are greater than one; 1.58 ± 0.02, 1.62 ± 0.02, and 1.26 ± 0.03 for **1**, **2**, and **3**, respectively, indicating that equilibrium is shifted toward the binding of C_{70} for the three non-bulky porphyrins. On the other hand, K_{70}/K_{60} values are less than one; 0.54 ± 0.01 and 0.81 ± 0.01 for **4** and **5**, respectively, suggesting that the binding of C_{60} is favored over the C_{70} binding for the two bulky porphyrins.

In comparison, fluorescence studies yielded $K_{70}/K_{60} = 8.7$

Table 1. The ratio of binding constants, K_{70}/K_{60}, the change in Gibbs free energy, $\Delta(\Delta G^\circ)_{70-60}$, and the difference in binding energy, $\Delta(\Delta E)_{70-60}$, for competitive binding of C_{60} and C_{70} to protonated porphyrins.

porphyrin	K_{70}/K_{60}[a]	$\Delta(\Delta G^\circ)_{70-60}$[b] (kcal mol^{-1})	$\Delta(\Delta E)_{70-60}$[c] (kcal mol^{-1})	
			side-on	end-on
$[\mathbf{1} + H]^+$	1.58 ± 0.02	-0.27 ± 0.01	-2.1	-0.4
$[\mathbf{2} + H]^+$	1.62 ± 0.02	-0.29 ± 0.01	-2.3	-0.4
$[\mathbf{3} + H]^+$	1.26 ± 0.03	-0.14 ± 0.02	-2.6	-0.8
$[\mathbf{4} + H]^+$	0.54 ± 0.01	0.36 ± 0.01	2.2	-0.5
$[\mathbf{5} + H]^+$	0.81 ± 0.01	0.13 ± 0.01	-0.9	-0.3

[a]Errors are from the standard deviation of the signal-to-noise ratio and curve fitting.
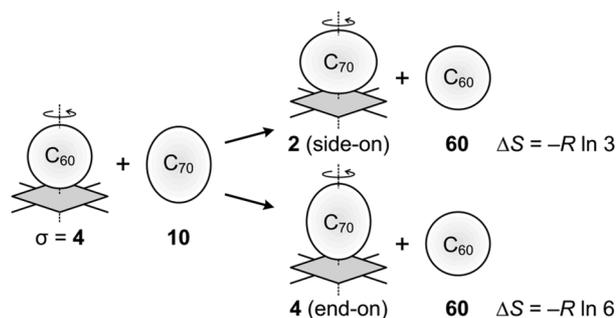[b]$\Delta(\Delta G^\circ)_{70-60} = -RT \ln(K_{70}/K_{60})$
[c]$\Delta(\Delta E)_{70-60}$ is the difference in binding energy.[13]

in toluene for tetra(octadecyloxyphenyl) porphyrin,[11] and UV/visible and fluorescence studies resulted in $K_{70}/K_{60} = 1.9$ and 9.0 in toluene for calix[4]arene-linked bisporphyrins with pentafluorophenyl and 3,5-di-*tert*-butylphenyl meso-substituents, respectively.[6] Although other studies show that porphyrins favor the binding of C_{70} over C_{60} in toluene, we find that non-bulky porphyrins prefer the binding of C_{70}, whereas bulky ones favor the binding of C_{60}.

The change in Gibbs free energy for the reaction 1, $\Delta(\Delta G^\circ)_{70-60} = -RT \ln(K_{70}/K_{60})$, is calculated from K_{70}/K_{60}. R is the gas constant and T is the temperature (298 K). Values of $\Delta(\Delta G^\circ)_{70-60}$ are listed in Table 1 along with the change in binding energy at 0 K, $\Delta(\Delta E^\circ)_{70-60} = \Delta E^\circ_{70} - \Delta E^\circ_{60}$, obtained from density functional theory (DFT) calculations.[13] DFT predicted the two different modes of C_{70} binding to porphyrins, "side-on" and C_{60}-like "end-on" binding. The equatorial belt of C_{70} is used for the side-on binding, whereas the pole of C_{70} is used for the end-on binding. The side-on binding offers more contact area to porphyrin than the C_{60}-like end-on binding. Porphyrins **1−3** showing negative values of $\Delta(\Delta G^\circ)_{70-60}$ have $\Delta(\Delta E^\circ)_{70-60}$ values of -2.6 to -2.1 kcal mol^{-1} for the side-on binding and of -0.8 to -0.4 kcal mol^{-1} for the end-on binding. On the other hand, porphyrins **4** and **5** presenting positive values of $\Delta(\Delta G^\circ)_{70-60}$ have $\Delta(\Delta E^\circ)_{70-60}$ values of -0.9 to 2.2 kcal mol^{-1} for the side-on binding and of -0.3 to -0.5 kcal mol^{-1} for the end-on binding. The binding energy also suggests a preference for the side-on binding of C_{70} to non-bulky porphyrins, but no preference toward either side-on or end-on binding of C_{70} to bulky porphyrins.

Meanwhile, the entropy change involved in the competitive binding of C_{60} and C_{70} to porphyrin can be estimated by considering molecular symmetry.[17] The symmetry number (σ) is 60 for spherical C_{60} (I_h),[18] 10 for ovoid C_{70} (D_{5h}),[18] and 4 for square planar porphyrin. Porphyrin−fullerene complexes have the symmetry number of 4 for the C_{60} binding or the end-on binding of C_{70}, and 2 for the side-on binding of C_{70}. The change in symmetry number results in the entropy change by $-R \ln(3)$ for the side-on and by $-R \ln(6)$ for the end-on binding of C_{70} relative to the C_{60} binding, respectively.

Thus, the contribution of entropy, $-T\Delta(\Delta S)_{70-60}$, to the change in Gibbs free energy is 0.65 and 1.06 kcal mol^{-1} for the side-on and end-on binding of C_{70}, respectively. The entropy factor based on molecular symmetry favors the side-on

binding over the end-on binding and the C_{60} binding over the C_{70} binding.

Conclusion

Meso-substituents in porphyrin affect porphyrin–fullerene interactions. Porphyrins with non-bulky substituents thermodynamically favor the binding of C_{70} that offers more contact area than the binding of C_{60}, whereas those with bulky substituents show thermodynamic preference for the C_{60} binding that exerts less steric hindrance to meso-subsituents. The molecular symmetry yields the negative entropy change for the binding of C_{70} over C_{60}, but less negative entropy change for the side-on binding of C_{70} than the end-on binding.

Acknowledgments

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