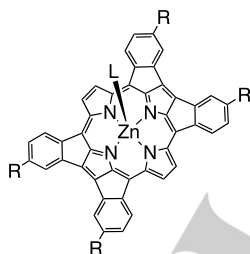


Supramolecular Interaction of Fullerenes with a Curved π -Surface of a Monomeric Quadruply Ring-Fused Porphyrin

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Abstract: Molecular binding of fullerenes, C₆₀ and C₇₀, with the Zn^{II} complex of a monomeric ring-fused porphyrin derivative (**2-py**) as a host molecule, which has a concave π -conjugated surface, has been confirmed spectroscopically. The structures of associated complexes composed of fullerenes and **2-py** have been explicitly established by X-ray diffraction analysis. The fullerenes in the 2:1 complexes, which consist of two **2-py** molecules and one fullerene molecule, are fully covered by the concave surfaces of the two **2-py** molecules in the crystal structure. In contrast, in the crystal structure of the 1:1 complex consisting of one **2-py** molecule and one C₆₀ molecule, the C₆₀ molecule formed a π - π stacked pair with a C₆₀ molecule in the neighboring complex using a partial surface, which was uncovered by the **2-py** molecule. Additionally, the molecular size of fullerene adopted significantly affects the ¹H NMR spectral changes and the redox properties of **2-py** upon the molecular binding.

Formation of supramolecular assemblies consisting of fullerenes and porphyrins have attracted great interest from a wide range of chemists,^[1-4] because it can conduct efficient photoinduced electron transfer reactions.^[5,6] The planar structure of porphyrin and the curved surfaces of fullerenes are not well matched to



1 (R = H, L = none), **1-py** (R = H, L = pyridine)
2 (R = Mesityl, L = none), **2-py** (R = Mesityl, L = pyridine)

Figure 1. Molecular Structures of ZnQFP Derivatives.

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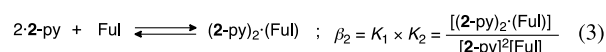
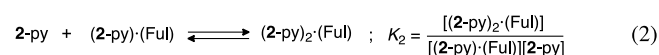
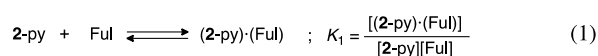
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form strong π - π interaction, and thus, the interaction between fullerenes and monomeric porphyrins is too weak to be observed in solution.^[7] Consequently, for efficient binding of fullerenes in solution, porphyrin hosts need to be dimers or higher oligomers.^[2,3,8] A concave-structured molecule with a curved surface, however, can be expected to form more stable molecular complexes with convex-shaped fullerenes on the basis of a suitable fit to gain stronger intermolecular π - π interaction.^[9]

Recently, we have reported the synthesis of a Zn^{II} complex of a quadruply fused porphyrin (ZnQFP, **1**) and elucidated that the planar structure of **1**, which is most stable as suggested by DFT calculations, changes to a concave structure by axial coordination of pyridine at the zinc center.^[10] Herein, we utilize the extensively π -conjugated concave surface of a pyridine-coordinated ZnQFP derivative to recognize the convex surfaces of fullerenes.

We used a ZnQFP derivative (**2**) having mesityl groups at the fused benzene rings (Figure 1)^[11] to improve the solubility for molecular binding with fullerenes, C₆₀ and C₇₀. At first, we determined the association constant between **2** and pyridine (K_{py}). UV-Vis titration experiments of **2** with pyridine in 1,2-dichlorobenzene (DCB) at 298 K indicated the binding constant for the 1:1 complex as $K_{py} = (2.0 \pm 0.6) \times 10^6 \text{ M}^{-1}$ (See Figure S1 in the Supporting Information (SI)). The structure of the pyridine complex of **2** (**2-py**) was revealed by single-crystal X-ray diffraction analysis (Figure S2 in the SI). The asymmetric unit included a half molecule of **2-py**. In the crystal, the porphyrin core consisting of four pyrrole rings, four *meso*-carbons and four fused *meso*-benzene rings is bowl-shaped and the mean deviation of the core 48 atoms is 0.389 Å, which is larger than that of **1-py** (0.212 Å).^[10] The Zn^{II} center is positioned at 1.278 Å above from the mean plane to the direction of the coordinated pyridine.

To confirm the interaction between **2-py** and fullerenes in solution, the solution of **2-py** in DCB ($7.5 \times 10^{-5} \text{ M}$)^[12] was titrated with the solution of fullerenes in DCB ($1.9 \times 10^{-3} \text{ M}$) at 298 K (Figure S3 in the SI). In all cases using C₆₀ and C₇₀, the Q bands of **2-py** showed hypsochromic shifts. The binding constants were obtained from the titration curves based on the absorbance at 778 nm for C₆₀ and that at 668 nm for C₇₀, using a nonlinear least-squares regression program.^[13] Based on eqs



Ful = fullerene

a)

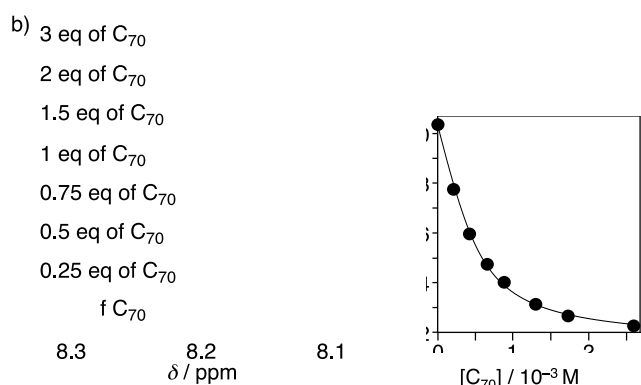


Figure 2. Left: ^1H NMR spectral change of **2-py** in $\text{DCB-}d_4$ with addition of C_{60} (a) and C_{70} (b) in the presence of pyridine (1.2×10^{-2} M) at 298 K. Right: the fitting curves of the signal of pyrrole- β -protons.

1 and 2, the stepwise constants, K_1 and K_2 , were estimated to be $(1.1 \pm 0.1) \times 10^4 \text{ M}^{-1}$ and $(1.2 \pm 0.2) \times 10^3 \text{ M}^{-1}$ for C_{60} , and $(1.3 \pm 0.1) \times 10^4 \text{ M}^{-1}$ and $(2.2 \pm 0.3) \times 10^3 \text{ M}^{-1}$ for C_{70} , respectively (Table 1). Therefore, the total binding constants (β_2) for the complexes of QFP : fullerene = 2 : 1 were calculated to be $(1.3 \pm 0.3) \times 10^7 \text{ M}^{-2}$ for C_{60} and $(2.9 \pm 0.2) \times 10^7 \text{ M}^{-2}$ for C_{70} , respectively (Table 1). As far as we know, this is the first example that the molecular binding between monomeric porphyrins and fullerenes has been demonstrated in solution.^[7,9c] Additionally, the constants are not significantly different between the cases of C_{60} and C_{70} . Although the K_1 values are larger than the K_2 values for both C_{60} and C_{70} , the differences are not large enough to clearly observe the stepwise binding from the 2:1 to 1:1 fashions. In fact, the Job's plots for the association between **2-py** and fullerenes, obtained under the relatively concentrated conditions at 298 K (total concentration of **2-py** and fullerenes: 1.7×10^{-4} M), indicated the formation of the 2:1 complex (Figure S4 in the SI). We also conducted the titration experiments of **2** with fullerenes in the absence of pyridine in DCB (Figure S5 in the SI). As results, the addition of fullerenes brought drastic absorption changes, in comparison to the cases in the presence of pyridine. These changes probably derive from the association with fullerenes, causing structural changes of **2** from the planar form to the bowl-shaped structure to strengthen the π - π interaction with fullerenes. Compound **2**, however, exhibits self-aggregation in DCB in the concentration for the titration experiments (7.5×10^{-5} M). Increasing the concentration of **2** in

Table 1. Binding constants of **2-py** with fullerenes, C_{60} and C_{70} , in DCB at 298 K, obtained from a nonlinear least-squares regression analysis of the absorbance changes at 778 nm for C_{60} and 668 nm for C_{70} and ^1H NMR chemical shift changes of the β -pyrrole proton of **2-py**.

| fullerene | method | $K_1 / 10^3 \text{ M}^{-1}$ | $K_2 / 10^3 \text{ M}^{-1}$ | $\beta_2 / 10^7 \text{ M}^{-2}$ |
|-----------------|------------------|-----------------------------|-----------------------------|---------------------------------|
| C_{60} | UV-Vis | 11 ± 1 | 1.2 ± 0.2 | 1.3 ± 0.3 |
| | ^1H NMR | 10 ± 1 | 1.2 ± 0.1 | 1.2 ± 0.2 |
| C_{70} | UV-Vis | 13 ± 1 | 2.2 ± 0.3 | 2.9 ± 0.2 |
| | ^1H NMR | 12 ± 1 | 2.3 ± 0.5 | 2.8 ± 0.6 |

DCB caused a blue shift of the Soret band; for instance, 619 nm at 1.4×10^{-6} M and 597 nm for 1.4×10^{-4} M (Figure S6 in the SI). In contrast, the Soret band of **2-py** did not show any dependence on the concentration in DCB in the presence of pyridine. These results indicate that compound **2** exhibits H-type π - π stacking under concentrated conditions and the pyridine coordination to give rise to deformation of the porphyrin core prevents the π - π stacking. Therefore, the self-aggregation of **2** by the π - π stacking disturbs the analysis of the titration experiments with fullerenes in the absence of pyridine in the solution.

For further confirmation of the association between **2-py** and fullerenes in solution, ^1H NMR titration experiments were also performed in $\text{DCB-}d_4$ at 298 K (Figures 2, S7 and S8 in the SI). Addition of C_{60} caused upfield shifts of the p - CH_3 groups of the peripheral mesityl groups in **2-py** (8.8×10^{-4} M) from δ 2.159 ppm in the absence of C_{60} to 2.147 ppm in the presence of 3 equiv of C_{60} . Slight downfield shifts of the o - CH_3 groups of the mesityl groups and the pyrrole- β -protons were also observed with increasing amount of C_{60} (Figure 2a). The shift widths of the NMR signals of **2-py** were relatively small in the titration with C_{60} . In sharp contrast, addition of C_{70} to the solution of **2-py** in $\text{DCB-}d_4$ induced clear shifts of the ^1H NMR signals (Figures 2b and S8 in the SI). The chemical shift changes of the ^1H NMR signals for the o - and p - CH_3 groups of the mesityl groups and the β -pyrrole protons of **2-py** were used to estimate the association constants, K_1 , K_2 , and β_2 , using the nonlinear least-squares regression program (Tables 1 and S1 in the SI).^[13] All of the association constants obtained from the analyses of the chemical shift changes are comparable to those obtained with UV-Vis titration experiments (see Table 1). The downfield shift of the o - CH_3 groups can be explained by a result of CH/π interaction with C_{70} and the upfield shift of the β -pyrrole protons can be ascribed to the ring current effect of aromatic C_{70} surfaces in the associated complexes. This explanation is well matched with the crystal structure of the 2:1 complex between **2-py** and C_{70} (see below). In addition, the downfield shifts of the p - CH_3 groups indicate the decrease of the electron densities of the mesityl groups upon formation of the associated complexes between **2-py** and C_{70} , probably caused by charge-transfer (CT) interaction from **2-py** to C_{70} (see the electrochemical studies described below). On the other hand, the shift widths of the ^1H NMR signals for the o - CH_3 groups and the β -pyrrole protons for the C_{60} complexes are modest, which can be elucidated by considering the small volume of C_{60} relative to the cavity composed of the o - CH_3

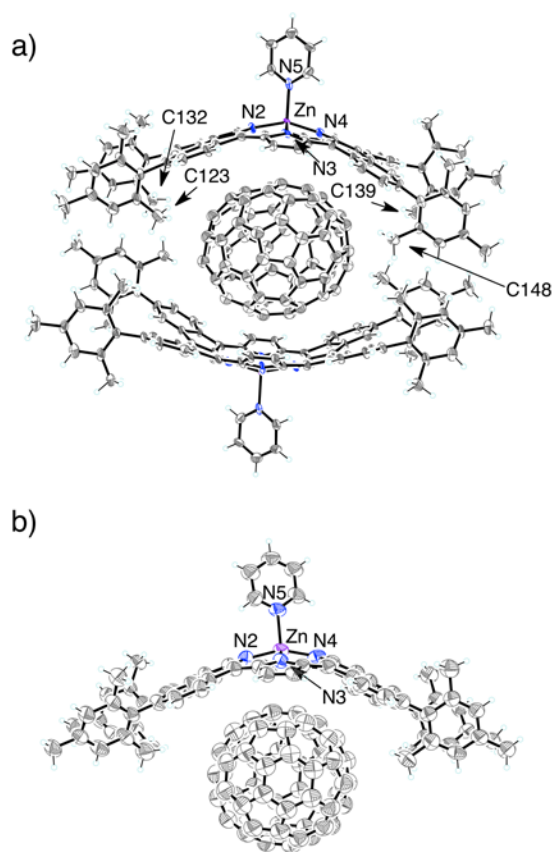


Figure 3. ORTEP drawings of crystal structures of $(2\text{-py})_2\cdot\text{C}_{70}$ (a) and $2\text{-py}\cdot\text{C}_{60}$ (b). The thermal ellipsoids are drawn with 50% probability. One of the disordered pair of the fullerenes is shown for clarity.

groups of **2-py**. The small shift of the pyrrole- β -Hs is probably ascribed to that the C_{60} molecule is not located on the top of the β -Hs in the solution due to the smaller size than that of C_{70} .

The structures of supramolecular assemblies of **2-py** with fullerenes have been explicitly revealed by single-crystal X-ray diffraction analysis (Figure 3). The single crystal of the 2:1 complex between **2-py** and C_{70} was obtained with slow evaporation of the solvent from the toluene solution (Figure 3a).

The C_{70} molecule, which exhibited crystallographic disorder in the crystal, was covered with two molecules of **2-py** and the longer axis of C_{70} was tilted to **2-py** by 29.4° . The concave surface of **2-py** and the convex surface of C_{70} are well matched each other to form strong π - π interaction. On the other hand, the single crystal obtained from the solution of **2-py** and C_{60} in DCB in the presence of methanol vapor as a poor solvent gave a preliminary crystal structure of the 2:1 complex (Figure S9 in the SI). Interestingly, alteration of the poor solvent to the acetonitrile vapor gave a single crystal of the 1:1 complex with C_{60} (Figure 3b), where the half sphere of C_{60} was covered with a molecule of **2-py**. The uncovered surface of C_{60} was used to form a π - π stacked pair of the two C_{60} molecules, in which the C-C bonds between a six- and five-membered rings came closer and the closest C...C distance in the paired C_{60} molecules was 2.89(4) Å. The porphyrin cores in all associated structures determined are more distorted relative to that of free **2-py**: The mean deviations of the core 48 atoms of **2-py** are 0.584, 0.571, and 0.502 Å for the 1:1 and 2:1 complexes with C_{60} and the 2:1 complex with C_{70} , respectively. This increase in the degree of the curved distortion for the porphyrin structures in the associated complexes should be induced to strengthen the π - π interaction with the fullerenes.^[14] As results, the distances between the planes of **2-py** and fullerenes are 3.30, 3.23, and 3.23 Å, for the 1:1 and 2:1 complexes with C_{60} and the 2:1 complex with C_{70} , respectively. Additionally, the molecular size of C_{70} is matched to the cavity provided by four *o*- CH_3 groups of **2-py** and three among the four CH_3 groups are close enough in the distances to form CH/π interaction with C_{70} ; the distances from C_{70} to the four *o*- CH_3 groups, which are represented by C123, C132, C139, and C148 in Figure 3a, are 3.33(3), 3.81(4), 4.95(3), and 3.64(4) Å, respectively. On the other hand, the size of C_{60} is small for the cavity and thus the C_{60} molecule both in the 1:1 and 2:1 complexes is located on a side of the two fused rings of **2-py**, and in consequence, the distances from C_{60} to two *o*- CH_3 groups are in the range of the C-H... π distances (ca. 3.8 Å), whereas the other two show longer distances from the C_{60} molecule (ca. 4.2 Å) (See the SI).

The association between **2-py** and fullerenes affect the redox potentials of **2-py** and fullerenes in DCB (Table 2 and Figures S10 and S11 in the SI). The cyclic and differential pulse voltammograms (CV and DPV) of **2-py** in DCB (1.3×10^{-3} M) exhibited two oxidation waves at +0.11 and +0.52 V vs Fc/Fc⁺

Table 2. Redox potentials of **2-py** and fullerenes, C_{60} and C_{70} , in DCB in the presence of 0.2 M TBAP and 0.012 M pyridine at 298 K.

| | $E_{1/2} / \text{V vs Fc/Fc}^+$ | | | | | | |
|-------------------------------|-------------------------------------|-----------------------|----------------------|-------------------------------------|--------------------------------------|-------------------------------------|-----------------------|
| | Por ²⁺ /Por ⁺ | Por ⁺ /Por | Por/Por ⁺ | Por ⁺ /Por ²⁺ | Ful ³⁺ /Ful ²⁺ | Ful ²⁺ /Ful ⁺ | Ful ⁺ /Ful |
| 2-py | -1.58 ^a | -1.28 ^a | +0.11 ^[a] | +0.52 ^[a] | — | — | — |
| C_{60} | — | — | — | — | -1.97 | -1.48 | -1.07 |
| 2-py + C_{60} | -1.60 ^a | -1.20 | +0.16 | +0.53 ^[a] | -2.01 | -1.50 | -1.06 |
| ΔE , V | +0.02 | +0.08 | +0.05 | +0.01 | -0.04 | -0.02 | +0.01 |
| C_{70} | — | — | — | — | -1.79 | -1.37 | -1.00 |
| 2-py + C_{70} | -1.57 | -1.26 | +0.13 | +0.52 | -1.89 | -1.44 | -1.06 |
| ΔE , V | +0.01 | +0.02 | +0.02 | +0.00 | -0.06 | -0.07 | -0.06 |

[a] The values were obtained from DPV.

and two reduction waves at -1.28 and -1.58 V vs Fc/Fc⁺ in the presence of pyridine (1.2×10^{-2} M) and tetrabutyl-ammonium perchlorate (TBAP, 0.2 M) as an electrolyte at 298 K. The CVs and DPVs of C₆₀ and C₇₀ measured under the same conditions displayed three reduction waves at -1.06 , -1.50 and -2.01 V vs Fc/Fc⁺ for C₆₀, and -1.00 , -1.37 and -1.79 V vs Fc/Fc⁺ for C₇₀, respectively. The 2:1 mixture of **2**-py (1.3×10^{-3} M) and the C₇₀ (6.4×10^{-4} M)^[15] showed the redox waves with significant shifts (Table 2). The redox potentials of **2**-py were positively shifted in the association with C₇₀, whereas those of C₇₀ exhibited negative shifts. The tendencies of the potential shifts can be accounted for the charge-transfer (CT) interaction from **2**-py to the fullerenes.^[16] As results of the CT interaction, the electron density of **2**-py decreased, whereas that of fullerenes increased; this makes reduction of fullerenes and oxidation of **2**-py harder in the associated complexes. The degree of potential shifts of C₇₀ was larger than that of **2**-py, because of difference between degree of associated C₇₀ and that of **2**-py;^[15] totally, 72% of **2**-py formed complexes with C₇₀, whereas 97% of C₇₀ participated in complexation with **2**-py. The 2:1 mixture of **2**-py (1.3×10^{-3} M) and C₆₀ (6.4×10^{-4} M) showed the redox waves with modest shifts. This can be explained on the basis of the fact that the first redox potential of C₆₀ is lower than that of C₇₀, therefore the CT interaction from **2**-py to the C₆₀ is weaker in comparison with the case of C₇₀.

In conclusion, the association equilibria between the mononuclear Zn^{II} complex of a QFP derivative, **2**-py, and fullerenes, C₆₀ and C₇₀, have been fully investigated spectroscopically and electrochemically. The concave surface of **2**-py is well matched to the convex surface of fullerenes for strong π - π interaction, especially for C₇₀. In addition, the CH/ π interaction of the *o*-CH₃ groups of the mesityl groups and the CT interaction assisted the association between **2**-py and fullerenes. The molecular sizes of the fullerenes significantly affected the ¹H NMR spectral changes and redox potential shifts of **2**-py. The structures of the associated complexes have been explicitly elucidated by the X-ray diffraction analysis. The fullerenes are fully covered by the concave surfaces of two **2**-py molecules in the 2:1 complexes. In contrast, in the crystal structure of the 1:1 complex of C₆₀, the C₆₀ molecules formed a π - π stacked pair using the partial surface, uncovered by one **2**-py molecule.

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Keywords: porphyrin • fullerene • molecular binding • crystal structure • electrochemistry

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COMMUNICATION



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Supramolecular Interaction of Fullerenes with a Curved π -Surface of a Monomeric Quadruply Ring-Fused Porphyrin

Molecular binding of fullerenes, C₆₀ and C₇₀, with a monomeric Zn^{II} complex of ring-fused porphyrin derivative (2-py), having a concave π -conjugated surface induced by the axial coordination, has been confirmed by spectroscopies and X-ray diffraction analysis. The molecular sizes of the fullerenes significantly affect the ¹H NMR spectral changes and the redox properties of 2-py upon molecular binding.

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