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Enhancing solution-phase supramolecular interactions between monomeric porphyrins and [60]fullerene by simple chemical modification

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Introduction

The porphyrin/fullerene combination has been studied extensively in the past decades as an attractive host-guest motif in the area of supramolecular chemistry^{1,2} due to its possible application in the selective extraction³ and non-covalent modification⁴ of fullerenes and related nanocarbons, such as carbon nanotubes. carbon nanohorns, and graphenes. Numerous crystallographic studies on porphyrin/fullerene assemblies have identified their close contact in the crystal form, indicating the presence of attractive π - π interactions.⁵ For instance, the close approach (~2.75 Å) of a fullerene carbon atom to the center of a porphyrin plane, which is shorter than the separation of common π - π interactions (i.e., 3.0-3.5 Å), was observed in the crystal structure of a covalently-linked porphyrin–fullerene dyad.⁶ However, it is apparent that non-covalent interactions between monomeric porphyrins and fullerenes are generally too weak to be observed spectroscopically in solution.^{5b} Therefore, supramolecular porphyrin/fullerene complexation generally requires additional stabilization by incorporating two or more porphyrin units via a covalent linkage, as seen in Aida's cyclic dimers,⁷ Boyd's acyclic 'Jaws' porphyrins,⁸ Anderson's⁹ and Zhang's¹⁰ cyclic trimers, and Osuka's cyclic

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ABSTRACT

The supramolecular interactions of *N*-methylporphyrin and iridium porphyrin with C_{60} in toluene solution were investigated using NMR spectroscopy and absorption spectroscopy. Our results demonstrate that both the *N*-methylation and iridium metalation of porphyrin are effective means to enhance the binding affinity to C_{60} , resulting in 1:1 complexation for *N*-methylporphyrin/ C_{60} and 2:1 complexation for iridium porphyrin/ C_{60} .

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tetramer.¹¹ In contrast to such oligomeric porphyrin/fullerene systems, only a few limited examples of the host-guest complexation of monomeric porphyrins with fullerenes in solution have been reported to date. Boyd et al. stated that no clear stoichiometry could be distinguished in his Job plot analysis of C₆₀ using tetraphenylporphyrin monomer.^{5b} In 2002, Kimura et al. found that a rigid phenylene-based dendritic porphyrin formed a stable complex with [60] fullerene (C_{60}) to give an estimated association constant of $2.57 \times 10^4 \,\mathrm{M^{-1}}$ in toluene.¹² They suggested that the dendritic substituents formed a regulated nanospace to accommodate the C₆₀ sphere. In addition, Kojima et al. recently reported that a zinc complex of a quadruply fused porphyrin derivative bearing an extended concave surface binds with C₆₀ to form both 1:1 and 2:1 complexes with association constants of $K_1 = 1.0 \times 10^4 \,\mathrm{M}^{-1}$ and $K_2 = 1.2 \times 10^3 \text{ M}^{-1}$ in 1,2-dichlorobenzene (1,2-DCB), possibly due to the presence of complementary concave and convex surfaces.^{7c,e,13} However, the syntheses of such porphyrin receptors tend to be low yielding and time-consuming. As such, the molecular design of monomeric porphyrins with high association constants towards nanocarbon species remains a challenge in the context of balancing the high affinity with facile synthesis. Particularly, for using porphyrins in supramolecular solubilization and nanocarbon functionalization, the use of monomeric porphyrins is a better choice than cyclic porphyrins because the molecular structures of the latter could never fit well with such nanocarbons (they have tubular or sheet-like







structures). 3a,4a,4i,14 In this study, C_{60} is considered to be a model molecule of such nanocarbon materials. Thus, we herein describe a simple modification of monomeric porphyrins to enhance their binding ability towards C_{60} , with the aim of producing 1:1 or 2:1 porphyrin/C₆₀ complexes in toluene. Notably, toluene is an excellent solvent for both C₆₀ and porphyrin. Therefore, any supramolecular interaction between porphyrin and fullerene must compete with potentially superior solvation.^{5b} Therefore, the supramolecular interaction in toluene is considered a suitable condition to evaluate spontaneous attraction, as Boyd had previously.^{5b} pointed out То enhance solution-phase supramolecular interaction between porphyrin and C₆₀, inner *N*-methylation of porphyrin was first chosen, which increases the planarity distortion and the basicity of the inner nitrogen. The second strategy involves iridium metalation of porphyrin. Aida et al. reported that metalloporphyrin monomers like rhodium porphyrin hardly interact with fullerenes in solution.^{7d} the only exception being iridium porphyrin. Aida et al. also reported that iridium octaethylporphyrin binds with C_{60} to form a 1:1 complex.^{7d} Herein we found that iridium porphyrin, bearing peripheral alkyl chains, possesses the binding ability with C_{60} to form not only a 1:1 complex but also a 2:1 complex in toluene.

Results and discussion

We herein employed tetraarylporphyrin **1** (see Scheme 1) as the scaffold for simple chemical modification by *N*-methylation and iridium metalation. More specifically, *N*-methylporphyrin **2** was obtained in 34% yield by the reaction of **1** with an excess amount of iodomethane (MeI) in the presence of acetic acid (AcOH),^{7c} while iridium porphyrin **3** was obtained in 33% yield by the reaction of **1** with $[Ir(cod)CI]_2$ (cod = cyclooctadiene) followed by treatment with iodine and subsequent transmetalation with trimethylaluminium.^{7d} Interestingly, the



Scheme 1. Synthesis of *N*-methylporphyrin **2** and iridium porphyrin **3** from the freebase porphyrin **1**. (a) MeI, AcOH, CHCl₃, 55 °C, 7 d, 34%, (b) (i) [Ir(cod)Cl]₂, xylene, reflux, 2 d, (ii) I₂, CH₂Cl₂, 1 h, (iii) Me₃Al/*n*-hexane, CH₂Cl₂, r.t., 2 h, 33%.

use of *N*-methylporphyrin as a binding motif for molecular recognition remains rare.¹⁵

The association of **2** with C_{60} in toluene solution was then investigated using the continuous variation plot (Job plot) method based on ¹H NMR spectroscopic observations. As shown in Fig. 1a, the signals corresponding to the *N*-methyl protons (designated as H_{2a}), phenyl protons (designated as H_{2b} , H_{2c} , and H_{2d}), and β -pyrrole protons (designated as H_{2e} , H_{2f} , and H_{2g}) shifted upon varying the molar fractions of **2** and C_{60} in a linear fashion. In particular, the *ortho*-phenyl protons H_{2c} and H_{2d} exhibited a clear downfield shift upon increasing the molar fraction of C_{60} , thereby indicating the presence of non-covalent interactions in solution (see Fig. 1b). The stoichiometry of the binding was confirmed to be 1:1 by Job plot analysis, which showed a maximum centered at a molar fraction of 0.50 (see Fig. 1c). The obtained results also suggest that the *ortho*-phenyl protons are in close contact with the fullerene surface in the 1:1 complex (i.e., **2**· C_{60}).

The binding affinity of **2** with C_{60} was then examined by combining the standard titration technique with absorption spectroscopy, as shown in Fig. 2. Upon the successive addition of C_{60} to a toluene solution of **2**, gradual but continuous changes were observed in the absorption spectra, thereby suggesting the formation of a complex between **2** and C_{60} . The association constant $K_a(\mathbf{2})$ for the $\mathbf{2}/C_{60}$ complexation was then calculated to be $(3.5 \pm 0.9) \times 10^3 \text{ M}^{-1}$ through a non-linear curve fitting of the absorbance at 436 nm based on a 1:1 stoichiometry. Measurement errors were reflected as relative standard deviation (RSD) values, as determined from experiments carried out in triplicate. It was therefore expected that the non-planarity of the porphyrin's π -electronic surface caused by the introduction of a methyl group to a single



Fig. 1. (a) Partial ¹H NMR spectra (400 MHz, 293 K, toluene d_8) of **2** in the presence of C_{60} and variation in the shown signals upon changing the molar fractions of **2** and C_{60} . [**2**] + [C_{60}] = 0.50 mM. (b) Plots representing the changes in ¹H NMR chemical shift with the molar fraction of **2**. (c) Job plots for the variations in ¹H NMR chemical shift with the molar fraction of **2**. H_{2a} = red, H_{2b} = green, H_{2c} = blue, H_{2d} = black, H_{2e} = pink, H_{2f} = purple, and H_{2e} = orange.

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