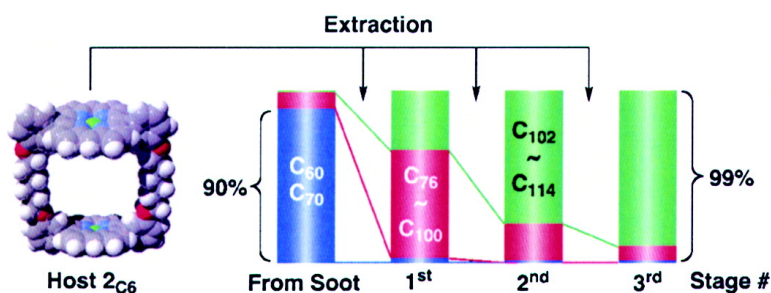


Selective Extraction of Higher Fullerenes Using Cyclic Dimers of Zinc Porphyrins

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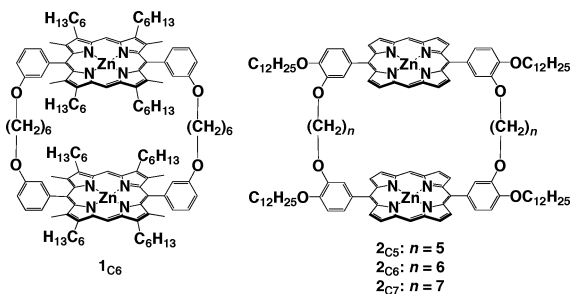
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Since the discovery of C_{60} in 1985,¹ spherical carbon nanoclusters of different sizes have caught special attention, as they are expected to possess high potentials in broad scientific areas and industrial applications. In particular, higher fullerenes² are interesting, which allow studies on structure–property relationships of discrete π -conjugated materials. However, a practical difficulty in isolating such low-yield products has prevented exploration of their physical properties as well as their applications in materials sciences. Examples of obtaining fullerenes enriched in higher homologues ($\geq C_{76}$) include (1) utilization of a HfC-doped graphite electrode for the arc-discharge production,³ (2) multistep chromatographic separation from carbon soot,⁴ and (3) electrochemical reduction to enhance their solubilities for separation, followed by reoxidation.⁵ However, unlike the case of C_{60} ,⁶ host molecules that can selectively extract higher fullerenes have never been reported to date.⁷ Recently, we have reported that cyclic dimers of metalloporphyrins 1_{C6} (zinc complex; Chart 1) serve as excellent host molecules for C_{60} and C_{70} .^{8,9} On the basis of this finding, we expected that a synthetic flexibility of 1_{C6} could allow us to design metalloporphyrin hosts that are capable of selectively binding higher fullerenes. Here we report the first host–guest approach using a series of cyclic dimers of zinc porphyrins 2_{C5} – 2_{C7} (Chart 1) as designer host molecules for selective extraction of higher fullerenes from a combustion-based industrial production source.

Chart 1



Cyclic hosts 2_{C5} – 2_{C7} with C5–C7 alkylene spacers were synthesized by alkaline-mediated coupling of the corresponding bromoalkylated zinc porphyrins with a zinc porphyrin bearing phenol functionalities, and unambiguously characterized by MALDI-TOF-MS and 1H NMR analyses.¹⁰ A typical example of the extraction of fullerenes with 2_{C5} – 2_{C7} is described below. A host molecule (0.2 mg) was added to a toluene solution (60 mL) of a fullerene mixture obtained from carbon soot (as-received fullerene mixture; 20 mg), and the resulting solution, after being stirred for 30 min at room temperature, was concentrated to a volume of 20 mL. To this solution was added THF (20 mL), and the resulting suspension was allowed to stand for 5 min and then filtered. The filtrate was evaporated to dryness, and the residue was chromatographed on alumina, where a fraction containing the zinc porphyrin host was isolated and treated with 4,4'-bipyridine (1 mg) to allow dissociation of included fullerenes from the host cavity.^{8a} The reaction mixture was subjected to size exclusion chromatography (SEC) to isolate a fraction containing fullerenes, which was washed with aqueous AcOH (0.1 M) to remove 4,4'-bipyridine and was then subjected to analytical HPLC on 5-PBB with chlorobenzene as eluent. As shown in Figure 1a, C_{60} and C_{70} are the most abundant fullerenes in the as-received fullerene mixture, while the total content of higher fullerenes ($\geq C_{76}$) is only 10 abs %.¹¹ On the other hand, single extraction of the fullerene mixture with 2_{C5} – 2_{C7} resulted in considerable enrichment in higher fullerenes (Figure 1, HPLC profiles b–d). For example, when 2_{C5} was used as the host, the total content of higher fullerenes ($\geq C_{76}$) was increased to 74 abs %. Use of 2_{C6} and 2_{C7} bearing longer spacers for the extraction resulted in further enrichment in higher fullerenes up to 93 and 97 abs %, respectively, while only negligible contents of C_{60} and C_{70} were detected. The HPLC profiles (Figure 1) also showed that the extracts with 2_{C5} – 2_{C7} are highly enriched in C_{96} (0.4 abs % in the as-received fullerene mixture), where 2_{C6} achieved a much greater enrichment in C_{96} (36 abs % in total fullerenes) than the other two host molecules (2_{C5} , 10 abs %; 2_{C7} , 25 abs %). It is interesting to note that such a subtle difference in spacer length of the host significantly affects the affinity toward fullerenes. We also found that the structure of the porphyrin moieties affects the selectivity. For example, cyclic host 1_{C6} , a β -substituted analogue of 2_{C6} , showed a lower efficiency than 2_{C6} for the extraction of higher fullerenes ($\geq C_{76}$, 68 abs %; C_{96} , 6 abs % in total fullerenes extracted).¹⁰

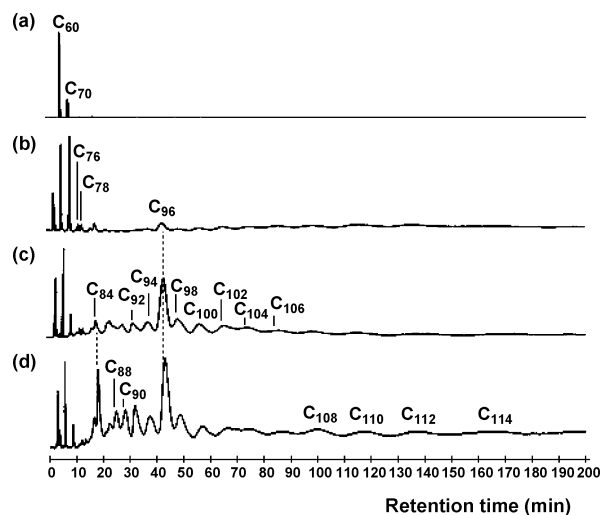


Figure 1. HPLC profiles on 5-PBB of (a) an as-received fullerene mixture and extracts with (b) 2_{C5} , (c) 2_{C6} , and (d) 2_{C7} , monitored at 356 nm with chlorobenzene as eluent (1 mL min⁻¹). The peak assignment was made on the basis of MALDI-TOF-MS measurements.

graphed on alumina, where a fraction containing the zinc porphyrin host was isolated and treated with 4,4'-bipyridine (1 mg) to allow dissociation of included fullerenes from the host cavity.^{8a} The reaction mixture was subjected to size exclusion chromatography (SEC) to isolate a fraction containing fullerenes, which was washed with aqueous AcOH (0.1 M) to remove 4,4'-bipyridine and was then subjected to analytical HPLC on 5-PBB with chlorobenzene as eluent. As shown in Figure 1a, C_{60} and C_{70} are the most abundant fullerenes in the as-received fullerene mixture, while the total content of higher fullerenes ($\geq C_{76}$) is only 10 abs %.¹¹ On the other hand, single extraction of the fullerene mixture with 2_{C5} – 2_{C7} resulted in considerable enrichment in higher fullerenes (Figure 1, HPLC profiles b–d). For example, when 2_{C5} was used as the host, the total content of higher fullerenes ($\geq C_{76}$) was increased to 74 abs %. Use of 2_{C6} and 2_{C7} bearing longer spacers for the extraction resulted in further enrichment in higher fullerenes up to 93 and 97 abs %, respectively, while only negligible contents of C_{60} and C_{70} were detected. The HPLC profiles (Figure 1) also showed that the extracts with 2_{C5} – 2_{C7} are highly enriched in C_{96} (0.4 abs % in the as-received fullerene mixture), where 2_{C6} achieved a much greater enrichment in C_{96} (36 abs % in total fullerenes) than the other two host molecules (2_{C5} , 10 abs %; 2_{C7} , 25 abs %). It is interesting to note that such a subtle difference in spacer length of the host significantly affects the affinity toward fullerenes. We also found that the structure of the porphyrin moieties affects the selectivity. For example, cyclic host 1_{C6} , a β -substituted analogue of 2_{C6} , showed a lower efficiency than 2_{C6} for the extraction of higher fullerenes ($\geq C_{76}$, 68 abs %; C_{96} , 6 abs % in total fullerenes extracted).¹⁰

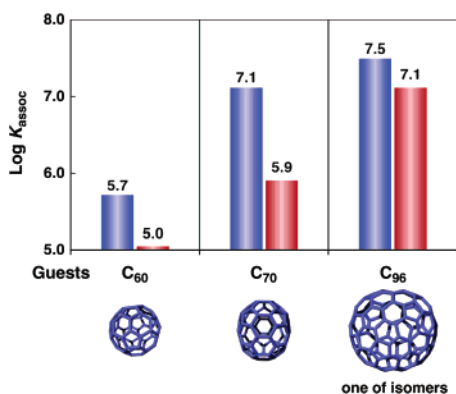


Figure 2. Association constants (K_{assoc}) of 1C_6 (blue bars) and 2C_6 (red bars) with C_{60} , C_{70} , and C_{96} in toluene/THF (1/1) at 25 °C.

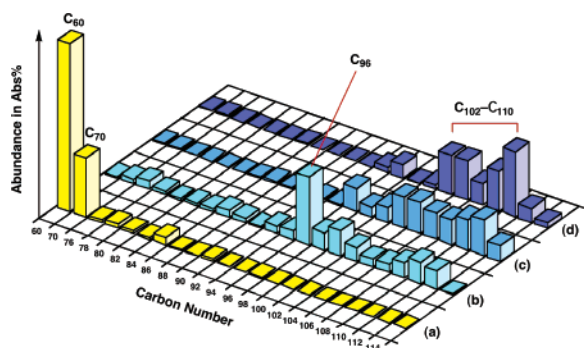


Figure 3. Abundances (abs %) of C_{60} – C_{114} in (a) an as-received fullerene mixture and extracts with 2C_6 after (b) the first-, (c) second-, and (d) third-stage extractions, as estimated by HPLC monitored at 356 nm.

Analogous to C_{60} and C_{70} , higher fullerenes form inclusion complexes with the cyclic hosts. For example, upon mixing with C_{96} ¹² in toluene/THF (1/1), 2C_6 displayed a bathochromic shift in the Soret absorption band from 413 to 420 nm. ¹H NMR spectroscopy of a mixture of 2C_6 and C_{96} (1:2) in chlorobenzene-*d*₅ at 60 °C showed a singlet signal due to meso-H at δ 10.3 ppm. In contrast, 2C_6 without guest C_{96} showed a rather complicated spectral profile with two singlet meso-H signals at δ 10.1 and 10.4 ppm, due to the existence of conformational isomers.⁸ The above spectral changes upon mixing of 2C_6 with C_{96} are characteristic of the inclusion of C_{60} with cyclodimeric zinc porphyrins.^{8a} A spectroscopic titration of 2C_6 with C_{96} in toluene/THF (1/1) at 25 °C gave an association constant (K_{assoc}) of $1.3 \times 10^7 \text{ M}^{-1}$, which is 118 and 16 times larger than those with C_{60} ($1.1 \times 10^5 \text{ M}^{-1}$) and C_{70} ($7.9 \times 10^5 \text{ M}^{-1}$), respectively (red bars, Figure 2). In contrast, when β -substituted 1C_6 with a lower preference toward C_{96} in the extraction was titrated with these three fullerenes (blue bars, Figure 2), the K_{assoc} value with C_{96} ($3.0 \times 10^7 \text{ M}^{-1}$), compared to that with C_{60} ($5.1 \times 10^5 \text{ M}^{-1}$), was still rather high, whereas it was only 2.3 times as large as that with C_{70} ($1.3 \times 10^7 \text{ M}^{-1}$).

Since populations of individual fullerenes in the single-step extracts are greatly affected by those in the as-received fullerene mixture, we conducted a sequential three-stage extraction with the best-behaved 2C_6 to estimate its inherent preference. Thus, in the first stage, 500 mg of the as-received fullerene mixture (Figure 3a) was extracted with 10 mg of 2C_6 , and a mixture of the inclusion complexes was isolated and then treated with 4,4'-bipyridine. A fullerene mixture thus released from the cavity of 2C_6 (Figure 3b; 3.2 mg) was collected and then subjected to the second-stage

extraction with 1 mg of 2C_6 . In the third-stage extraction, 0.1 mg of 2C_6 was submitted to a fullerene mixture extracted in the second stage (Figure 3c). Interestingly, the extract finally obtained (Figure 3d) was considerably enriched in C_{102} – C_{110} (C_{102} , 15 abs %; C_{104} , 16 abs %; C_{106} , 9 abs %; C_{108} , 16 abs %; C_{110} , 26 abs % in total fullerenes), while C_{96} was less abundant (5 abs %). Furthermore, C_{60} and C_{70} were hardly detected even in the second-stage extract (Figure 3c).

In conclusion, we have demonstrated the first example of selective extraction of higher fullerenes ($\geq \text{C}_{76}$) from a fullerene mixture, obtained from a combustion-based industrial production source, by using cyclodimeric zinc porphyrins 2C_5 – 2C_7 with C_5 – C_7 alkylene spacers as the hosts. The selectivities toward higher fullerenes are much dependent on the size of the host cavity and the structure of the porphyrin moieties. Three cycles of the extraction with 2C_6 allow enrichment in very rare fullerenes C_{102} – C_{110} (<0.1 abs %) up to 82 abs % of total fullerenes. Use of such cyclic host molecules immobilized on solid supports for chromatographic separation¹³ is one of the interesting subjects worthy of further investigation.

Acknowledgment. We thank Frontier Carbon Corporation for a generous supply of a fullerene mixture obtained from a combustion-based industrial production source.

Supporting Information Available: Synthesis of 2C_5 – 2C_7 , spectral data of inclusion complexes of 1C_6 and 2C_5 – 2C_7 with fullerenes, and isolation and characterization of C_{96} for titration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Peak integral ratio (%) in HPLC monitored at 356 nm.
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