

Metallofullerenes

Size-Selective Complexation and Extraction of Endohedral Metallofullerenes with Cycloparaphenylene**

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Abstract: A new strategy for the non-chromatographic extraction of metallofullerenes from solutions of arc-processed raw soot is based on the size-selective complexation with cycloparaphenylene (CPP). [11]CPP has a high affinity for $M_x@C_{82}$ ($x=1, 2$); for example, $Gd@C_{82}$ can be selectively extracted from a fullerene mixture by the addition of [11]CPP. This approach should open new opportunities in metallofullerene chemistry, including for the bulk extraction of metallofullerenes.

Endohedral metallofullerenes, which are fullerenes with encapsulated metallic species, have attracted much interest during the past two decades.^[1] Their intriguing structures and electronic properties, which are very different from those of empty fullerenes, have been used for a variety of new applications.^[2b] For example, Gd-based metallofullerenes have great potential for biomedical applications and may be used as magnetic resonance imaging (MRI) contrast agents^[2a] or in neutron-capture therapy for the treatment of cancer.^[2b] In spite of these promising applications that could make metallofullerenes the next-generation nanomaterials, real applications of metallofullerenes have been limited by the

known difficulties that hamper their efficient separation and purification.^[1] Generally, metallofullerenes, which are produced together with various empty fullerenes, need to be purified by multistage high-performance liquid chromatography (HPLC).^[1] However, this conventional purification process may not be used for the effective separation and purification of milligram quantity of metallofullerenes. HPLC methods also require large amounts of solvent. To overcome these difficulties, several non-chromatographic techniques have been developed.^[3] Very recently, we have reported an efficient separation of metallofullerenes from empty cages with $TiCl_4$.^[3a,b] However, the selective extraction of a single metallofullerene from a mixture of various metallofullerenes in a specific solvent has not been reported. Herein, we report a new strategy for the non-chromatographic extraction of metallofullerenes directly from solutions of arc-processed raw soot. The present method relies on size-selective complexation with commercially available cycloparaphenylene (CPP), a carbon nanoring that consists of paraphenylene units.^[4]

To achieve the selective extraction of a given endohedral metallofullerene from a mixture of various metallofullerenes in solution, two critical hurdles have to be overcome: A single metallofullerene must be separated from 1) empty fullerenes with the same carbon cage (metallofullerene-selective), and 2) other metallofullerenes with different carbon cages (size-selective). To fulfil the first requirement, we decided to rely on the use of extended π -conjugated systems. We hypothesized that metallofullerenes, which comprise negatively charged fullerene cages with positively charged metal atom(s), interact with π -conjugated molecules more strongly than their empty counterparts (Figure 1).^[1,5] For instance, column chromatography with stationary phases that are based

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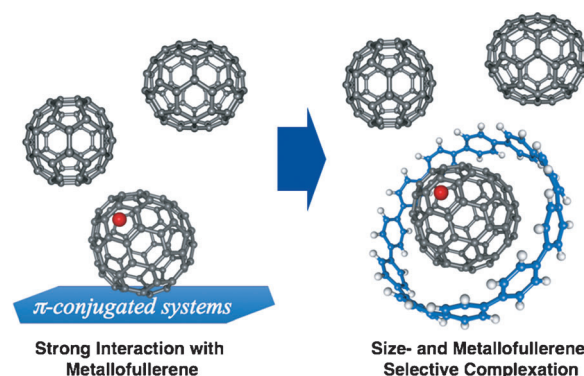


Figure 1. Strategy for the size- and metallofullerene-selective complexation and extraction with CPP.

on aromatic compounds can be used to separate metallofullerenes from the empty fullerene analogues.^[5]

To attain size selectivity, we decided to make use of a host–guest system with a hoop-shaped π -conjugated macrocycle.^[6] In this regard, CPP^[4] was chosen as a suitable host molecule for metallofullerenes (Figure 1). Recent extensive investigations by the groups of Bertozzi,^[7] Itami,^[8,9] Jasti,^[10] Yamago,^[11] and others^[12] have elaborated the chemistry of CPPs and related carbon nanorings. For example, the modular and size-selective synthesis of [7]–[16]CPP (diameters: 1.0–2.2 nm) has become possible using the procedures that we have previously developed. A series of [n]CPPs, which have size-tunable cavities, should form complexes with a variety of fullerenes. Indeed, the complexation of [n]CPP or related analogues with C₆₀ and C₇₀ was reported by the groups of Yamago,^[11c,e] Jasti,^[10d] and Isobe.^[12d] However, the complexation of [n]CPPs with metallofullerenes has not yet been reported. To verify our strategy, we began by studying the complexation of [11]CPP with representative metallofullerenes and empty fullerenes.

Initially, the size-selective encapsulation of C₈₂-based metallofullerenes by [11]CPP was confirmed by ¹H NMR analysis of a CDCl₃ solution of [11]CPP to which Lu₂@C₈₂(II) (C_{2v} isomer) was added (Figure 2a). The signal for [11]CPP shifted downfield by 0.02 ppm and broadened. In contrast, the signal position and width for [12]CPP did not change at all

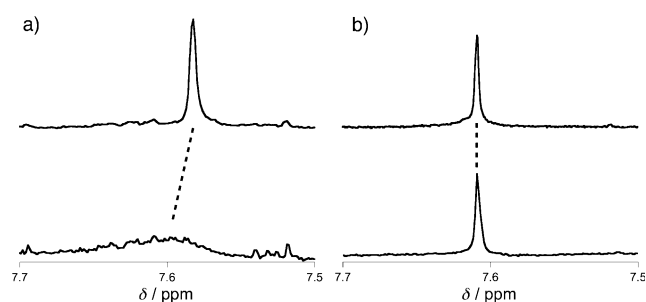


Figure 2. a, b) ¹H NMR spectra of [11]CPP (a) and [12]CPP (b) in CDCl₃ before and after the addition of Lu₂@C₈₂.

(Figure 2b). These experiments indicate that the diameter of the C₈₂ cage is compatible with the inner diameter of [11]CPP. It should be noted that the use of this type of metallofullerene, which has no unpaired electrons, can avoid an accidental downfield shift by a general paramagnetic effect.

A UV/Vis/NIR spectroscopic titration was carried out in CHCl₃. The absorption spectrum of Gd@C₈₂(I) (C_{2v} isomer) changed on addition of [11]CPP (Figure 3). The intensity of the absorption maximum at 631 nm gradually decreased with an isosbestic point of 450 nm (Supporting Information, Figure S1b), and a red shift of the peak was observed with an increase in the amount of [11]CPP (Figure 3). This is attributed to a host–guest interaction between the fullerene cage and [11]CPP. Such a peak shift was not observed upon addition of [12]CPP (Figure S2). On the other hand, the characteristic absorption peak of Gd@C₈₂ at 966 nm, which is due to electron transfer from Gd to the fullerene cage, was observed throughout the titration, which suggests a lack of

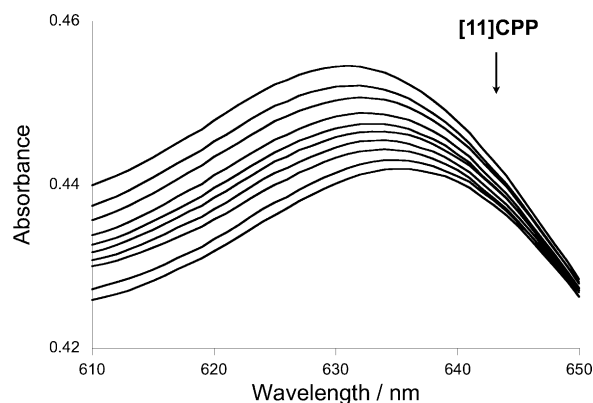


Figure 3. Absorption spectra of Gd@C₈₂ (5.0×10^{-5} M) in CHCl₃ on successive additions of solutions of [11]CPP (5.0×10^{-3} M) in CHCl₃ at 25 °C.

charge–transfer interactions between [11]CPP and Gd@C₈₂ (Figure S1c).^[13]

The complexation stoichiometry was determined by a Job's plot based on the absorption change at 340 nm (absorption peak due to [11]CPP).^[14] The continuous variation plot with a maximum value of 0.5, together with the titration results and an isosbestic point at 450 nm, provided evidence for the formation of a 1:1 complex of Gd@C₈₂ and [11]CPP (Figure S3).

The binding abilities of [11]CPP to C₈₂-based metallofullerenes in toluene were characterized by fluorescence quenching experiments.^[15] In the presence of metallofullerenes, the fluorescence intensity of [11]CPP decreased (Figure 4 and Figure S4). By monitoring this decrease in fluorescence at 460 nm, the binding constants (K_a) of [11]CPP with Gd@C₈₂, Tm@C₈₂, and Lu₂@C₈₂ (the C_{2v} isomer in each case) were determined to be (1.8 ± 0.1) , (1.8 ± 0.2) , and $(1.8 \pm 0.2) \times 10^6$ M^{−1}, respectively (Table 1). These titration results suggest that [11]CPP strongly captures M_x@C₈₂, irrespective of the kind and the number of encapsulated metal atoms. These binding constants are very similar to that of C₆₀@[10]CPP, which was reported previously.^[10c] To the best

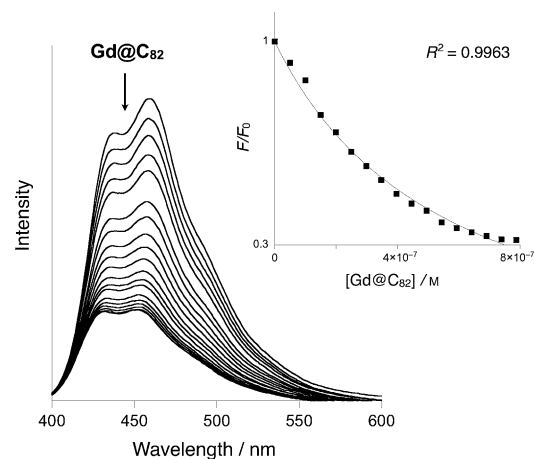


Figure 4. Fluorescence spectra of [11]CPP (5.0×10^{-7} M, $\lambda_{\text{exc}} = 370$ nm) in toluene in the presence of various amounts of Gd@C₈₂ (0– 5.0×10^{-7} M) at 25 °C.

Table 1: Binding constants of [11]CPP with fullerenes in toluene at 25 °C.

Fullerene	K_a [$\times 10^6 \text{ M}^{-1}$]
C_{60}	Not reliable
C_{70}	0.53 ± 0.08
$\text{C}_{3v}\text{-C}_{76}$	1.82 ± 0.06
$\text{C}_{2v}\text{-C}_{78}$	1.41 ± 0.04
$\text{Sc}_3\text{N@I}_h\text{-C}_{80}$	0.72 ± 0.05
$\text{Gd@C}_{2v}\text{-C}_{82}$	1.8 ± 0.1
$\text{Tm@C}_{2v}\text{-C}_{82}$	1.8 ± 0.2
$\text{Lu}_2\text{@C}_{2v}\text{-C}_{82}$	1.8 ± 0.2

of our knowledge, these values are the highest that have been reported for complexes of higher metallofullerenes with simple hydrocarbons thus far.^[1b,16,17]

The same experiments were also independently performed for empty fullerenes (Figure S4). The binding constants of [11]CPP with C_{76} (C_{3v} isomer) and C_{78} (C_{2v} isomer) were determined to be (1.82 ± 0.06) and $(1.41 \pm 0.04) \times 10^6 \text{ M}^{-1}$, respectively (Table 1). It is expected that the longer axis of these ellipsoidal fullerenes is arranged perpendicularly to the axis of [11]CPP, similar to fullerene nano-peapods.^[19] The interactions are stronger than those for the smaller fullerene C_{70} (ca. 10^5 M^{-1}). In the presence of C_{60} , on the other hand, the fluorescence spectrum of [11]CPP hardly changed. The binding ability of [11]CPP to C_{60} is clearly inadequate in comparison with higher fullerenes. The complexation of [11]CPP with fullerenes is based primarily on the size and shape of the fullerene cages, regardless of their charge state.

The size-selective fullerene encapsulation by [11]CPP was also studied by DFT calculations at the M062X/6-31G* level of theory.^[20] These simulations were performed for [11]CPP with empty fullerenes (see the Supporting Information for details). These calculations permit us to discuss the correlation between the stability of the complexes and the size of the fullerene cages. The stabilization energy for $\text{C}_{82}\text{@[11]CPP}$ was calculated to be $41.4 \text{ kcal mol}^{-1}$, which is significantly higher than that of $\text{C}_{60}\text{@[11]CPP}$ ($23.6 \text{ kcal mol}^{-1}$). A space-filling model of $\text{C}_{82}\text{@[11]CPP}$ reveals that the cavity of [11]CPP (1.51 nm) is filled by C_{82} (ca. 0.85 nm). The optimized distance between C_{82} and [11]CPP is approximately 0.33 nm, which is close to the interlayer space of graphite^[21] and to the preferable inter-wall distance of fullerene nano-peapods.^[19]

Despite being sparingly soluble in CHCl_3 , Gd@C_{82} is more soluble in the presence of [11]CPP. In toluene, on the other hand, the mixture gave a dark brown complex of Gd@C_{82} with [11]CPP, which precipitated out at high concentration. Such a change in solubility that is controlled by complexation and the solvent is exceptionally useful for the non-chromatographic extraction of metallofullerenes.

A toluene solution of the fullerene mixture from raw soot that included Gd@C_{82} was prepared. A laser desorption mass spectrum (LD-MS) of this mixture shows that Gd@C_{82} is a minor component of this mixture (Figure 5a and 6a). After the addition of [11]CPP to the solution and an increase in the concentration of the solution, a solid precipitated out. A positive-ion LD-MS of the separated precipitate entails a strong and enhanced peak of Gd@C_{82} (Figure 5c).

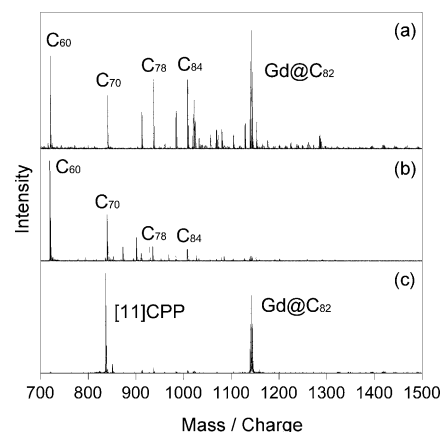


Figure 5. a–c) Positive-ion LD mass spectra of the crude extract (a), the filtrate (b), and the precipitate (c) after addition of [11]CPP.

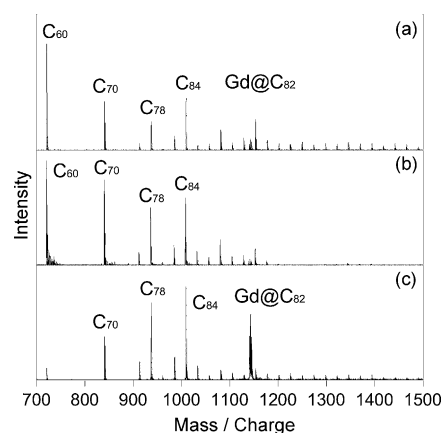


Figure 6. a–c) Negative-ion LD mass spectra of the crude extract (a), the filtrate (b), and the precipitate (c) after addition of [11]CPP.

Meanwhile, negative ion LD mass spectra of the precipitate indicate the presence of Gd@C_{82} together with several empty fullerenes, such as C_{70} , C_{78} , and C_{84} (Figure 6c). Positive and negative ion LD mass spectra are biased towards the preferential detection of metallofullerenes and empty fullerenes, respectively.^[1] Given that the peaks that are due to empty fullerenes are enhanced in negative-ion LD mass spectra, these LD mass spectra demonstrate that Gd@C_{82} was highly enriched through the complexation with [11]CPP. Also, the LD mass spectrum and the HPLC chromatogram of the filtrate solution suggest that most of the Gd@C_{82} has been separated from the filtrate (Figure 5b, 6b, and 7). It should be mentioned that the purity of the extracted Gd@C_{82} depends on the amount of Gd@C_{82} in the synthesized soot. The percentage of Gd@C_{82} that is extracted from a Gd@C_{82} -rich soot is large (Figure S5).

In summary, the selective complexation of C_{82} -based metallofullerenes with [11]CPP has been demonstrated. [11]CPP has a high affinity for C_{82} -based metallofullerenes, regardless of the kind and the number of metal atoms encapsulated. Furthermore, the complexation can be applied to the facile extraction and enrichment of Gd@C_{82} from crude

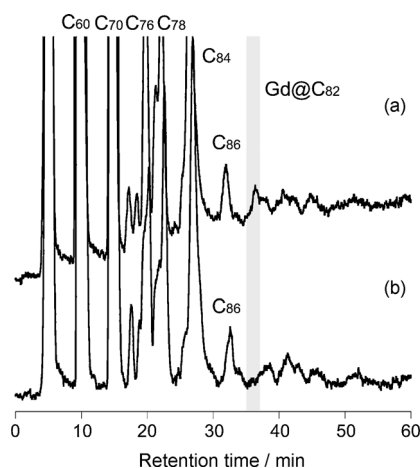


Figure 7. a, b) HPLC chromatogram of the crude mixture (a) and the filtrate (b) after addition of [11]CPP.

mixtures. This approach not only provides a basis for the non-chromatographic extraction of metallofullerenes, but also opens further opportunities for the discovery of new types of fullerenes, such as metallofullerenes with small HOMO–LUMO gaps, including $M@C_{60}$.

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