Metallofullerenes

DOI: 10.1002/ange.201311268

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

Yusuke Nakanishi, Haruka Omachi, Sanae Matsuura, Yasumitsu Miyata, Ryo Kitaura, Yasutomo Segawa, Kenichiro Itami, and Hisanori Shinohara**

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

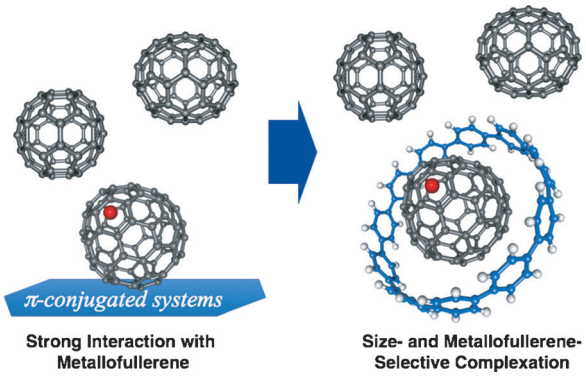

Figure 1. Strategy for the size- and metallofullerene-selective complexation and extraction with CPP.

[*] Y. Nakanishi, Dr. H. Omachi, S. Matsuura, Prof. Dr. Y. Miyata, Prof. Dr. R. Kitaura, Prof. Dr. Y. Segawa, Prof. Dr. K. Itami, Prof. Dr. H. Shinohara
Department of Chemistry, Graduate School of Science
Nagoya University, Chikusa
Nagoya 464-8602 (Japan)
E-mail: itami@chem.nagoya-u.ac.jp
noris@cc.nagoya-u.ac.jp
Prof. Dr. K. Itami
Institute of Transformative Bio-Molecules (WPI-ITbM)
Nagoya University
Chikusa, Nagoya 464-8602 (Japan)
Prof. Dr. Y. Segawa, Prof. Dr. K. Itami
JST, ERATO, Itami Molecular Nanocarbon Project
Nagoya University
Chikusa, Nagoya 464-8602 (Japan)

[**] This work was supported by a Grant-in-Aid for Scientific Research S (22225001 to H.S.) of MEXT (Japan) and the Funding Program for Next Generation World-Leading Researchers from JSPS (220GR049 to K.I.). H.O. thanks JSPS for a fellowship. Prof. Cathleen M. Crudden (Queen's University, Canada) is acknowledged for comments and discussion. Computer resources for theoretical calculations were provided by the Research Center for Computational Science in the National Institute of Natural Sciences (Japan). ITbM is supported by the World Premier International Research Center (WPI) Initiative (Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201311268.

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 C_{60} and C_{70} 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 C_{82}-based metallofullerenes by [11]CPP was confirmed by ^{1}H NMR analysis of a $CDCl_3$ solution of [11]CPP to which $Lu_2@C_{82}$(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

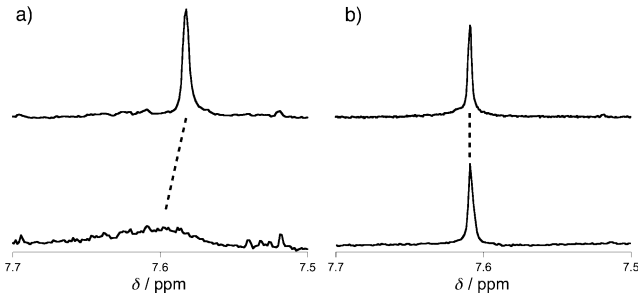

Figure 2. a, b) ^{1}H NMR spectra of [11]CPP (a) and [12]CPP (b) in $CDCl_3$ before and after the addition of $Lu_2@C_{82}$.

(Figure 2b). These experiments indicate that the diameter of the C_{82} 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 $CHCl_3$. The absorption spectrum of $Gd@C_{82}$(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 $Gd@C_{82}$ 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

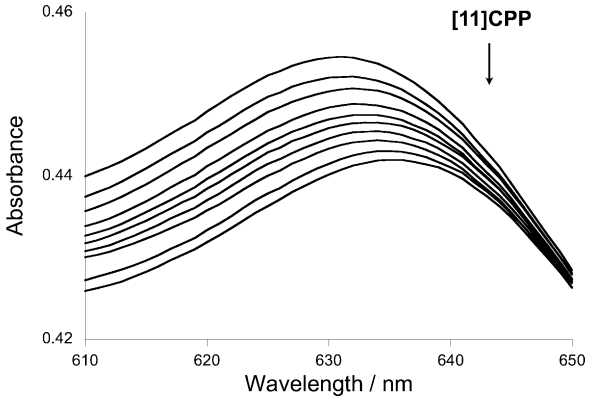

Figure 3. Absorption spectra of $Gd@C_{82}$ (5.0×10^{-5} M) in $CHCl_3$ on successive additions of solutions of [11]CPP (5.0×10^{-3} M) in $CHCl_3$ at 25 °C.

charge–transfer interactions between [11]CPP and $Gd@C_{82}$ (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 $Gd@C_{82}$ and [11]CPP (Figure S3).

The binding abilities of [11]CPP to C_{82}-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 $Gd@C_{82}$, $Tm@C_{82}$, and $Lu_2@C_{82}$ (the C_{2v} isomer in each case) were determined to be (1.8 ± 0.1), (1.8 ± 0.2), and $(1.8\pm0.2)\times10^6$ M^{-1}, respectively (Table 1). These titration results suggest that [11]CPP strongly captures $M_x@C_{82}$, irrespective of the kind and the number of encapsulated metal atoms. These binding constants are very similar to that of $C_{60}@$[10]CPP, which was reported previously.[10c] To the best

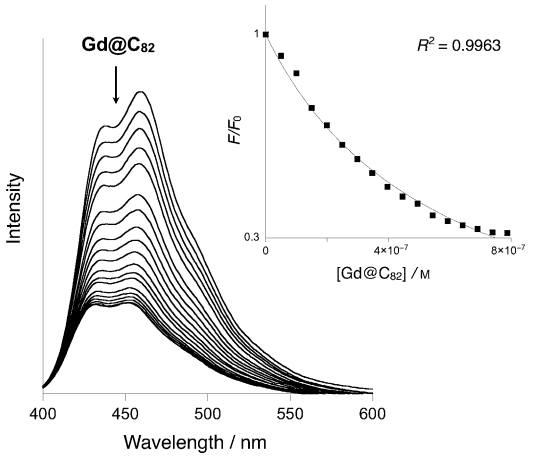

Figure 4. Fluorescence spectra of [11]CPP (5.0×10^{-7} M, $\lambda_{exc}=370$ nm) in toluene in the presence of various amounts of $Gd@C_{82}$ (0–5.0×10^{-7} M) at 25 °C.

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

Fullerene	K_a [$\times 10^6$ M^{-1}]
C_{60}	Not reliable
C_{70}	0.53 ± 0.08
C_{3v}-C_{76}	1.82 ± 0.06
C_{2v}-C_{78}	1.41 ± 0.04
$Sc_3N@I_h$-C_{80}	0.72 ± 0.05
$Gd@C_{2v}$-C_{82}	1.8 ± 0.1
$Tm@C_{2v}$-C_{82}	1.8 ± 0.2
$Lu_2@C_{2v}$-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 $(1.41 \pm 0.04) \times 10^6$ 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 C_{82}@[11]CPP was calculated to be 41.4 kcal mol^{-1}, which is significantly higher than that of C_{60}@[11]CPP (23.6 kcal mol^{-1}). A space-filling model of C_{82}@[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).

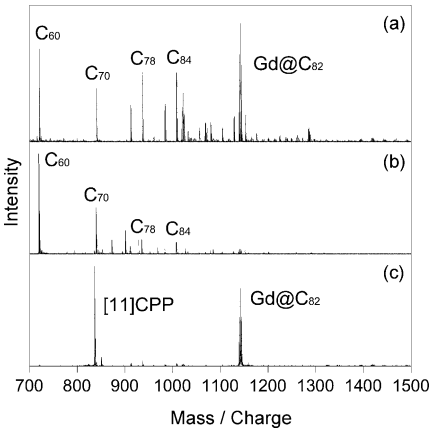

Figure 5. a–c) Positive-ion LD mass spectra of the crude extract (a), the filtrate (b), and the precipitate (c) after addition of [11]CPP.

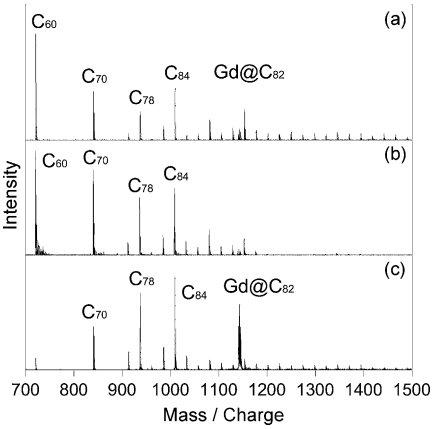

Figure 6. a–c) Negative-ion LD mass spectra of the crude extract (a), the filtrate (b), and the precipitate (c) after addition of [11]CPP.

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

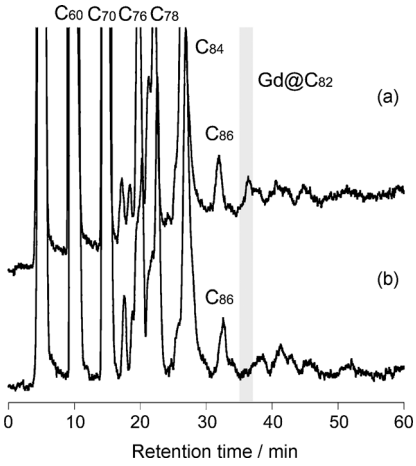

Figure 7. a, b) HPLC chromatogram of the crude mixture (a) and the filtrate (b) after addition of [11]CPP.

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 $M@C_{60}$.

Received: December 29, 2013
Published online: February 24, 2014

Keywords: conjugation · cycloparaphenylenes · host–guest systems · macrocycles · metallofullerenes

[1] a) H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843; b) S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maita, A. J. Fisher, A. L. Balch, H. C. Dorn, *Nature* **1999**, *401*, 55; c) C.-R. Wang, T. Kai, T, Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Nature* **2001**, *408*, 426; d) S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H. C. Dorn, *Nature* **2001**, *408*, 428.

[2] a) M. Mikawa, H. Kato, M. Okumura, M. Narazaki, Y. Kanazawa, N. Miwa, H. Shinohara, *Bioconjugate Chem.* **2001**, *12*, 510; b) Y. Horiguchi, S. Kudo, Y. Nagasaki, *Sci. Technol. Adv. Mater.* **2011**, *12*, 044607; c) S. W. Cagle, S. J. Kennel, S. Mirzaden, J. M. Alford, L. J. Wilson, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 5182; d) Y. Yasutake, Z. Shi, T. Okazaki, H. Shinohara, Y. Majima, *Nano Lett.* **2005**, *5*, 1057; e) R. B. Ross, C. M. Cardona, D. M. Guldi, S. G. Sankaranarayanan, M. O. Reese, N. Kopidakis, J. Peet, B. Walker, G. C. Bazan, E. V. Keuren, B. C. Holloway, M. Drees, *Nat. Mater.* **2009**, *8*, 208.

[3] For recent progress in the non-chromatographic separation of metallofullerenes, see: a) K. Akiyama, T. Hamano, Y. Nakanishi, E. Takeuchi, S. Noda, Z. Wang, S. Kubuki, H. Shinohara, *J. Am. Chem. Soc.* **2012**, *134*, 9762; b) Z. Wang, Y. Nakanishi, S. Noda, K. Akiyama, H. Shinohara, *J. Phys. Chem. C* **2012**, *116*, 25563; c) T. Tsuchiya, T. Wakahara, Y. Lian, Y. Maeda, T. Akasaka, T. Kato, N. Mizorogi, S. Nagase, *J. Phys. Chem. B* **2006**, *110*, 22517; d) J. W. Raebiger, R. D. Bolskar, *J. Phys. Chem. C* **2008**, *112*, 6605; e) S. Stevenson, M. A. Mackey, J. E. Pickens, M. A. Stuart, B. S. Confait, J. P. Phillips, *Inorg. Chem.* **2009**, *48*, 11685.

[4] For reviews on CPP chemistry, see: a) H. Omachi, Y. Segawa, K. Itami, *Acc. Chem. Res.* **2012**, *45*, 1378; b) E. S. Hirst, R. Jasti, *J. Org. Chem.* **2012**, *77*, 10473; c) U. H. F. Bunz, S. Menning, N. Martín, *Angew. Chem.* **2012**, *124*, 7202; *Angew. Chem. Int. Ed.* **2012**, *51*, 7094.

[5] a) H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, Y. Saito, *J. Phys. Chem.* **1993**, *97*, 4259; b) H. Shinohara, M. Inakuma, N. Hayashi, H. Sato, Y. Saito, T. Kato, S. Bandow, *J. Phys. Chem.* **1994**, *98*, 8597; c) K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, Y. Achiba, *Chem. Phys. Lett.* **1993**, *216*, 67.

[6] For representative papers that describe the enrichment of empty fullerenes by host–guest chemistry using macrocycles, see: a) J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, *368*, 229; b) T. Suzuki, K. Nakashima, S. Shinkai, *Chem. Lett.* **1994**, 699; c) D. Canevet, E. M. Pérez, N. Martín, *Angew. Chem.* **2011**, *123*, 9416; *Angew. Chem. Int. Ed.* **2011**, *50*, 9248.

[7] R. Jasti, J. Bhattacharjee, J. B. Neaton, C. R. Bertozzi, *J. Am. Chem. Soc.* **2008**, *130*, 17646.

[8] a) H. Takaba, H. Omachi, Y. Yamamoto, J. Bouffard, K. Itami, *Angew. Chem.* **2009**, *121*, 6228; *Angew. Chem. Int. Ed.* **2009**, *48*, 6112; b) Y. Segawa, H. Omachi, K. Itami, *Org. Lett.* **2010**, *12*, 2262; c) H. Omachi, S. Matsuura, Y. Segawa, K. Itami, *Angew. Chem.* **2010**, *122*, 10400; *Angew. Chem. Int. Ed.* **2010**, *49*, 10202; d) Y. Segawa, S. Miyamoto, H. Omachi, S. Matsuura, P. Šenel, T. Sasamori, N. Tokitoh, K. Itami, *Angew. Chem.* **2011**, *123*, 3302; *Angew. Chem. Int. Ed.* **2011**, *50*, 3244; e) Y. Segawa, P. Šenel, S. Matsuura, H. Omachi, K. Itami, *Chem. Lett.* **2011**, *40*, 423; f) Y. Segawa, A. Fukazawa, S. Matsuura, H. Omachi, S. Yamaguchi, S. Irle, K. Itami, *Org. Biomol. Chem.* **2012**, *10*, 5979; g) Y. Ishii, Y. Nakanishi, H. Omachi, S. Matsuura, K. Matsui, H. Shinohara, Y. Segawa, K. Itami, *Chem. Sci.* **2012**, *3*, 2340; h) T. Nishihara, Y. Segawa, K. Itami, Y. Kanemitsu, *J. Phys. Chem. Lett.* **2012**, *3*, 3125; i) C. Camacho, T. A. Niehaus, K. Itami, S. Irle, *Chem. Sci.* **2013**, *4*, 187; j) H. Omachi, T. Nakayama, E. Takahashi, Y. Segawa, K. Itami, *Nat. Chem.* **2013**, *5*, 572; k) F. Sibbel, K. Matsui, Y. Segawa, A. Studer, K. Itami, *Chem. Commun.* **2014**, *50*, 954.

[9] For other related carbon nanorings and carbon nanocages, see: a) H. Omachi, Y. Segawa, K. Itami, *Org. Lett.* **2011**, *13*, 2480; b) A. Yagi, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2012**, *134*, 2962; c) K. Matsui, Y. Segawa, K. Itami, *Org. Lett.* **2012**, *14*, 1888; d) K. Matsui, Y. Segawa, T. Namikawa, K. Kamada, K. Itami, *Chem. Sci.* **2013**, *4*, 84; e) A. Yagi, G. Venkataramana, Y. Segawa, K. Itami, *Chem. Commun.* **2014**, *50*, 957.

[10] a) T. J. Sisto, M. R. Golder, E. S. Hirst, R. Jasti, *J. Am. Chem. Soc.* **2011**, *133*, 15800; b) J. Xia, R. Jasti, *Angew. Chem.* **2012**, *124*, 2524; *Angew. Chem. Int. Ed.* **2012**, *51*, 2474; c) T. J. Sisto, X. Tian, R. Jasti, *J. Org. Chem.* **2012**, *77*, 5857; d) J. Xia, J. W. Bacon, R. Jasti, *Chem. Sci.* **2012**, *3*, 3018; e) E. R. Darzi, T. J. Sisto, R. Jasti, *J. Org. Chem.* **2012**, *77*, 6624; f) J. Xia, M. R. Golder, M. E. Foster, B. M. Wong, R. Jasti, *J. Am. Chem. Soc.* **2012**, *134*, 19709.

[11] a) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem.* **2010**, *122*, 769; *Angew. Chem. Int. Ed.* **2010**, *49*, 757; b) T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki, S. Yamago, *J. Am. Chem. Soc.* **2011**, *133*, 8354; c) T. Iwamoto, Y. Watanabe, T. Sadahiro, T. Haino, S. Yamago, *Angew. Chem.* **2011**, *123*, 8492; *Angew. Chem. Int. Ed.* **2011**, *50*, 8342; d) E. Kayahara, Y. Sakamoto, T. Suzuki, S. Yamago, *Org. Lett.* **2012**, *14*, 3284; e) T. Iwamoto, Y. Watanabe, H. Takaya, T. Haino, N. Yasuda, S. Yamago, *Chem. Eur. J.* **2013**, *19*, 14061.

[12] a) S. Hitosugi, W. Nakanishi, T. Yamasaki, H. Isobe, *Nat. Commun.* **2011**, *2*, 492; b) S. Hitosugi, T. Yamasaki, H. Isobe, *J. Am. Chem. Soc.* **2012**, *134*, 12442; c) T. Nishiuchi, X. Feng, V. Enkelmann, M. Wagner, K. Müllen, *Chem. Eur. J.* **2012**, *18*, 16621; d) H. Isobe, S. Hitosugi, T. Yamasaki, R. Iizuka, *Chem. Sci.* **2013**, *4*, 1293.

[13] T. Tsuchiya, K. Sato, H. Kurihara, T. Wakahara, T. Nakahodo, Y. Maeda, T. Akasaka, K. Ohkubo, S. Fukuzumi, T. Kato, N.

Mizorogi, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.* **2006**, *128*, 6699.
[14] J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, *Supramolecular Chemistry*, *Vol. 8*, Pergamon, Oxford, **1996**.
[15] C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez, J. L. Sessler, *J. Am. Chem. Soc.* **1999**, *121*, 10438.
[16] a) S. Yang, S. Yang, *Langmuir* **2002**, *18*, 8488; b) G. Pagona, S. P. Economopoulos, T. Aono, Y. Miyata, H. Shinohara, N. Tagmatarchis, *Tetrahedron* **2010**, *51*, 5896.
[17] a) T. Kawase, K. Tanaka, N. Fujiwara, H. R. Darabi, M. Oda, *Angew. Chem.* **2003**, *115*, 1662; *Angew. Chem. Int. Ed.* **2003**, *42*, 1624; b) T. Kawase, K. Tanaka, N. Shiono, Y. Seirai, M. Oda, *Angew. Chem.* **2004**, *116*, 1754; *Angew. Chem. Int. Ed.* **2004**, *43*, 1722; c) T. Kawase, N. Fujiwara, M. Tsutumi, M. Oda, Y. Maeda, T. Wakahara, T. Akasaka, *Angew. Chem.* **2004**, *116*, 5170; *Angew. Chem. Int. Ed.* **2004**, *43*, 5060.
[18] K. Akiyama, K. Sueki, T. Kodama, K. Kikuchi, I. Ikemoto, M. Katada, H. Nakahara, *J. Phys. Chem. A* **2000**, *104*, 7224.
[19] S. Okada, M. Otami, A. Oshiyama, *Phys. Rev. B* **2003**, *67*, 205411.
[20] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157. In a report by Yamago and co-workers (Ref [11c]), the M062X functional provided a reliable description of the interaction between C_{60} and CPPs.
[21] P. Delhaes, *Graphite and Precursors*, Gordon and Breach Science Publishers, Amsterdam, **2001**.

