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Assessment of Fullerene Derivatives as Rolling Journals in a Finite Carbon Nanotube Bearing

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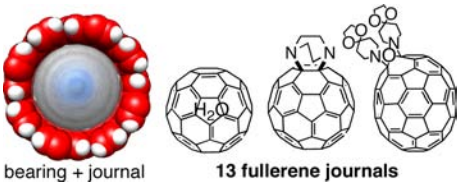
ABSTRACT



Conformance assessment of rolling journals in a molecular bearing has been carried out with a combination of fullerenes and finite single-wall carbon nanotube molecules through quantitative analysis of the binding affinities. Endohedral fullerenes were applicable to three-body molecular bearings with slightly weaker binding affinities. Exohedral shaft moieties on C_{60} journals affected the binding affinities to reduce the binding constants to a considerable extent, and oval-spherical C_{70} journals were superior in tolerating bulky shaft attachments.

Nanomechanical systems of nanocarbons have attracted much attention after the discovery of ultralow friction at the carbonaceous interface of a linear molecular bearing of multiwall carbon nanotubes.[1,2] Recently, the nanocarbon bearings have been further miniaturized in a combination of a finite single-wall carbon nanotube (SWNT) bearing and a fullerene journal in quantity, and the anisotropic rolling motion of the shaft has been spectroscopically demonstrated.[3,4] The anisotropic rolling motion has been enabled by the tight binding of the bearing, (*P*)-(12,8)-[4]cyclo-2,8-chrysenylene [(*P*)-(12,8)-[4]CC; Figure 1],[5] with the fullerene journal blocking the run-out motion. For this unique molecular bearing to be developed further in future, a conformance assessment of the fullerene journals is necessary. We herein report the assessment of binding with 13 fullerene compounds (four unsubstituted fullerenes and nine functionalized fullerenes **1**–**9**) in the [4]CC bearing to clarify the fundamental structure–binding relationships for the rolling journals. The effects of endohedral entities and exohedral shafts have been disclosed, and the highest fullerene binding constant of log K_a = 9.7 has been recorded.

One of the most intriguing possibilities of the fullerene journals is in the inner nanospace of the carbon cage, because the bearing properties can potentially be manipulated by endohedral entities. We therefore examined two endohedral fullerenes for the binding with (*P*)-(12,8)-[4]CC in *ortho*-dichlorobenzene (*o*DCB) at 25 °C. As shown in Figure 2, the binding constants of log K_a = 9.2 and 9.1 were recorded for $Li^+@C_{60}•PF_6^-$ and $H_2O@C_{60}$, respectively.[6–8] The endohedral entities affected the binding constants, and

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(1) Cummings, J.; Zettl, A. *Science* **2000**, *289*, 602–604.

(2) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.

(3) Isobe, H.; Hitosugi, S.; Yamasaki, T.; Iizuka, R. *Chem. Sci.* **2013**, *4*, 1293–1297.

(4) We adopted the terminology of engineers for the description of bearings. See: Harnoy, A. *Bearing Design in Machinery: Engineering Tribology and Lubrication*; Dekker: New York, 2003; Chapter 1.

(5) Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H. *Nat. Commun.* **2011**, *2*, doi: 10.1038/ncomms1505 (5 pages); Hitosugi, S.; Nakanishi, W.; Isobe, H. *Chem.—Asian J.* **2012**, *7*, 1550–1552.

(6) Aoyagi, S.; Nishibori, E.; Sawa, H.; Sugimoto, K.; Takata, M.; Miyata, Y.; Kitaura, R.; Shinohara, H.; Okada, H.; Sakai, T.; Ono, Y.; Kawachi, K.; Yokoo, K.; Ono, S.; Omote, K.; Kasama, Y.; Ishikawa, S.; Komuro, T.; Tobita, H. *Nat. Chem.* **2010**, *2*, 678–683.

(7) Kurotobi, K.; Murata, Y. *Science* **2011**, *333*, 613–616.

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the values were slightly smaller than that of empty C_{60} (log K_a = 9.6). Because we did not observe much difference between cationic Li^+ and electroneutral H_2O, the weakened binding from the empty congener most likely originates from the steric characters of the endohedral congeners that have slightly larger diameters. Nonetheless, the endohedral entities do not alter the binding constants dramatically, which suggests potential exploration of electronic or thermal tunings for the journal motions in these three-body molecular bearings.

The shaft moieties, i.e., exohedral functional groups, attached on the C_{60} journal exerted a much higher influence on the binding affinity. For five derivatives with two appendages on the C_{60} journal (**2**–**6**),[9] the binding constants became 1 to 2 orders of magnitude less than that of naked C_{60} (Figure 2). The steric bulkiness, derived either from the positions of appendages or from the substituents at the atom directly attached to C_{60}, affected the binding, which resulted in the variation of binding constants ranging from log K_a = 8.6 to 7.8. Introduction of larger numbers of appendages further reduced the binding constants by 4 orders of magnitude, and the log K_a values were lowered to the level of 5 for compounds **7**–**9**. As can be seen in the comparison of **8** and **9**, the substituents located remotely from the C_{60} core did not affect the binding.

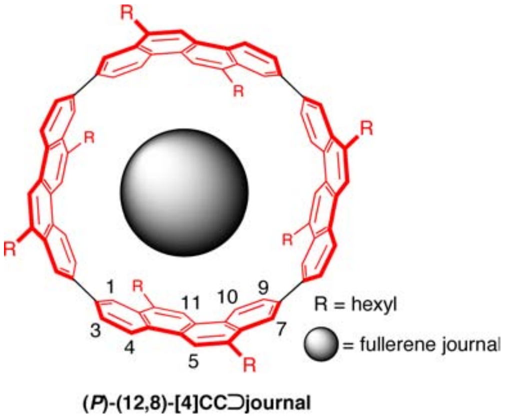

Figure 1. Molecular bearing of (*P*)-(12,8)-[4]CC with fullerene journal.

Despite the weakened binding, the journal **9** with the smallest log K_a rolled anisotropically in the [4]CC bearing. Thus, seven ^1H resonances were observed in the aromatic region of (*P*)-(12,8)-[4]CC⊃**9** in CD_2Cl_2 at 25 °C (Figure 3). The resonances were assignable to the eight inequivalent protons at the 1-, 3-, 4-, 5-, 7-, 9-, 10-, and 11-positions of one chrysenylene panel (See also Figure 1),[3] which, more importantly, suggested the equivalent relationship of four chrysenylene panels in the bearing.[10] Thus, the anisotropic rolling motion of **9** around the central C_4 axis of the bearing was confirmed.[3] We further confirmed the absence of run-out motion by diffusion ordered spectroscopy (DOSY) (Figures S14–S16). The DOSY spectrum of (*P*)-(12,8)-[4]CC⊃**9** showed that the two components, the journal and the bearing, possessed an identical diffusion constant, confirming that the complex did not fall apart at the NMR time scale.

Finally, we found C_{70} to be superior as the journal compared to C_{60}. The binding constant of C_{70} in *o*DCB was log K_a = 9.7 which is the highest value for host–guest complexes of fullerene derivatives in this medium (Figure 1).[3,11] An additional advantage of C_{70} was the oval-spherical shape of the molecule, which tolerated the introduction of bulky shaft moieties without any adverse effect on the binding. Diaminated C_{70} **1** was thus accommodated in the bearing with the same binding constant as naked C_{70}.[12,13] The result encourages the future development of C_{70} journals for functional molecular bearings.[14]

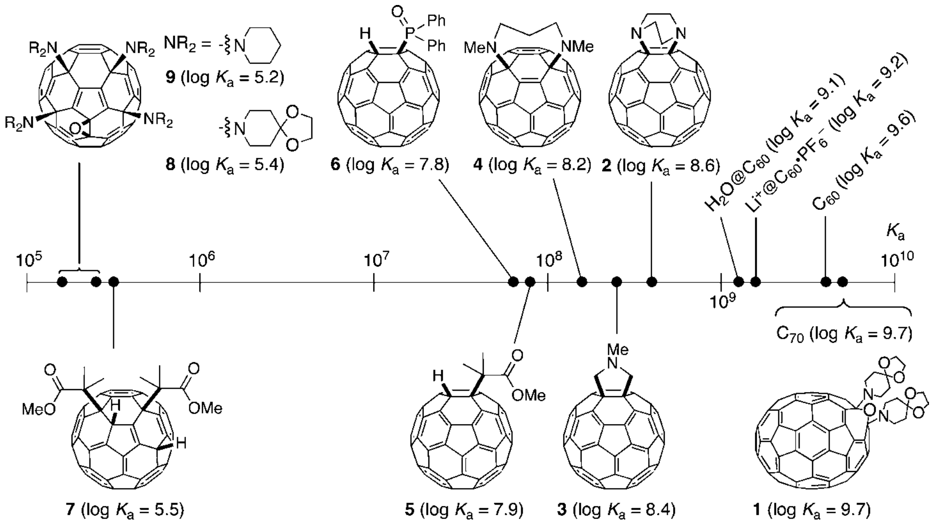

Figure 2. Binding constants of fullerene journals with (*P*)-(12,8)-[4]CC in *o*DCB at 25 °C.

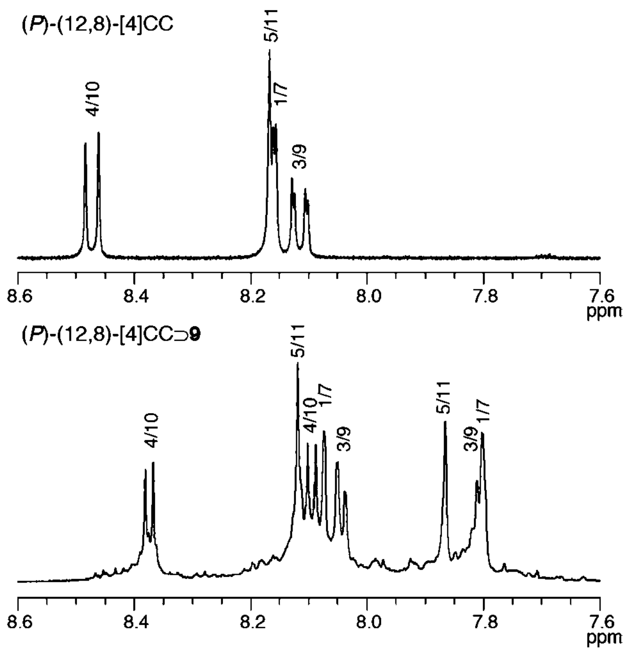

Figure 3. Aromatic region of ^{1}H NMR spectrum for (*P*)-(12,8)-[4]CC$\supset$**9**. A reference spectra of empty (*P*)-(12,8)-[4]CC is shown as the reference (ref 5). The numbers above the resonances show the position of protons on chrysenylene. See Figure 1 for the numbering.

In summary, we report the first conformance assessment of journals in a finite SWNT bearing. The three-body bearing system comprising endohedral fullerenes and a finite SWNT bearing is unique among other molecular machines,[2] and along with the encapsulated Li$^+$ for the electronic tuning,[15] the encapsulated water is of particular interest for the microwave-assisted motorization of the molecular bearing.[16,17] The first screening results of exohedral appendages may be informative for the future design of bearings with a van der Waals assembly,[18] and the C$_{70}$ derivatives should be promising journals due to the high tolerance for bulky functional groups.

Acknowledgment. This paper is dedicated to Professor Teruaki Mukaiyama in celebration of the 40th anniversary of the monumental Mukaiyama aldol reaction. This study is partially supported by KAKENHI (24241036, 25810018), the Asahi Glass Foundation, and NEDO.

Supporting Information Available. Raw data for titration analysis, experimental details, and DOSY spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) See Supporting Information for raw data of the titration experiments.

(9) The C$_{60}$ derivatives were synthesized by methods reported in the literature. Compounds **2**, **8**, and **9**: Isobe, H.; Tanaka, T.; Nakanishi, W.; Lemiègre, L.; Nakamura, E. *J. Org. Chem.* **2005**, *70*, 4826–4832. Isobe, H.; Tomita, N.; Nakamura, E. *Org. Lett.* **2000**, *2*, 3663–3665. Compound **3**: Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799. Compound **4**: Isobe, H.; Ohbayashi, A.; Sawamura, M.; Nakamura, H. *J. Am. Chem. Soc.* **2000**, *122*, 2669–2670. Compound **5** and **7**: Nakamura, E.; Mouri, S.; Nakamura, Y.; Harano, K.; Isobe, H. *Org. Lett.* **2008**, *10*, 4923–4926. Compound **6**: Isobe, H.; Chen, A.; Solin, N.; Nakamura, E. *Org. Lett.* **2005**, *7*, 5633–5635.

(10) Upon mixing the analytically pure components for (*P*)-(12,8)-[4]CC$\supset$**9**, there appeared minor resonances in the ^{1}H NMR spectrum immediately (Figure 3). As the minor resonances did not change further for two weeks, we concluded that the structural fluctuation of cyclic amine moieties affected the spectrum to show the presence of minor conformers. The details of the minor resonances will be investigated in due course.

(11) Canevet, D.; Pérez, E. M.; Martín, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 9248–9259. Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 8342–8344.

(12) We synthesized **1** by the method reported in the literature: Lemiègre, L.; Tanaka, T.; Nanao, T.; Isobe, H.; Nakamura, H. *Chem. Lett.* **2007**, *36*, 20–21.

(13) We found that the original structure of **1** reported in ref 12 was incorrect and correctly assigned as reported in another paper: Troshina, O. A.; Troshin, P. A.; Peregudov, A. S.; Kozlovski, V. I.; Lyubovskaya, R. N. *Eur. J. Org. Chem.* **2006**, 5243–5248.

(14) Hirsh, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley: Weinheim, 2005.

(15) Kamimura, T.; Ohkubo, K.; Kawashima, Y.; Nobukuni, H.; Naruta, Y.; Tani, F.; Fukuzumi, S. *Chem. Sci.* **2013**, *4*, 1451–1461.

(16) Kappe, C. O.; Pieber, B.; Dallinger, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 1088–1094. de la Hoz, A.; Díaz-Ortiz, A.; Moreno, A. *J. Org. Chem.* **2000**, *65*, 2499–2507.

(17) Matsuo, Y.; Isobe, H.; Tanaka, T.; Murata, Y.; Murata, M.; Komatsu, K.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 17148–17149.

(18) Matsuno, T.; Kamata, S.; Hitosugi, S.; Isobe, H. *Chem. Sci.* **2013**, published online (doi: 10.1039/c3sc50645b).

The authors declare no competing financial interest.