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Head-to-Tail and Back-to-Back Dimerization of an Open-Cage Fullerene Derivative through $\pi-\pi$ Interaction-Based Self-Assembly

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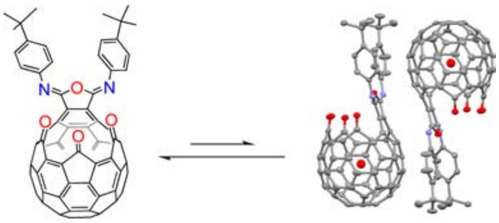
ABSTRACT



Open-cage fullerene derivative 2, $C_{59}(O)_4(NAr)_2$ (Ar = p-tBuC$_6$H$_4$), was prepared from 1, $C_{60}(O)_4(OH)_2(NAr)_2$, through processes involving decarbonylation and elimination of the two hydroxyl groups. The phenyl groups in compound 2 act as chelating ligands for the fullerene cage and induce partial dimerization of 2 in solution. The single crystal X-ray structure of 2 shows strong intradimer $\pi-\pi$ interactions and also weaker interdimer CH$-\pi$ and $\pi-\pi$ interactions.

A supramolecular interaction between fullerenes and various hosts has attracted much attention because of the unique spherical structure of fullerenes. A number of hosts have been developed for fullerenes based on $\pi-\pi$ and CH$-\pi$ interactions.[1] Macrocyclic compounds with an appropriate cavity exhibit very strong binding ability and also selectivity toward fullerenes of different sizes.[2] Molecular clips and tweezers also show excellent binding ability toward fullerenes.[3] These host−guests usually form readily defined 1:1 complexes in solution. Fullerene derivatives with certain aromatic addends can form supramolecular oligomers or polymers through noncovalent intermolecular interaction between the fullerene cage and the aromatic addend. The pentakisfullerene adducts can form well

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(1) (a) Perez, E. M.; Martin, N. *Chem. Soc. Rev.* **2008**, *37*, 1512. (b) Tashiro, K.; Aida, T. *Chem. Soc. Rev.* **2007**, *36*, 189. (c) Bonifazi, D.; Enger, O.; Diederich, F. *Chem. Soc. Rev.* **2007**, *36*, 390. (d) Wu, Y. T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (e) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868. (f) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250. (g) Nielsen, M. B.; Diederich, F. *Chem. Rev.* **2005**, *105*, 1837.

(2) (a) Zhang, C.; Long, H.; Zhang, W. *Chem. Commun.* **2012**, *48*, 6172. (b) Canevet, D.; Gallego, M.; Isla, H.; de Juan, A.; Perez, E. M.; Martin, N. *J. Am. Chem. Soc.* **2011**, *133*, 3184. (c) Zhang, C.; Wang, Q.; Long, H.; Zhang, W. *J. Am. Chem. Soc.* **2011**, *133*, 20995. (d) Wang, L. X.; Zhao, L.; Wang, D. X.; Wang, M. X. *Chem. Commun.* **2011**, *47*, 9690. (e) Wang, L.; Wang, G.-T.; Zhao, X.; Jiang, X.-K.; Li, Z.-T. *J. Org. Chem.* **2011**, *76*, 3531. (f) Gil-Ramırez, G.; Karlen, S. D.; Shundo, A.; Porfyrakis, K.; Ito, Y.; Briggs, G. A. D.; Morton, J. J. L.; Anderson., H. L. *Org. Lett.* **2010**, *12*, 3544. (g) Isla, H.; Gallego, M.; Perez, E. M.; Viruela, R.; Orti, E.; Martin, N. *J. Am. Chem. Soc.* **2010**, *132*, 1772. (h) Pirondini, L.; Bonifazi, D.; Cantadori, B.; Braiuca, P.; Campagnolo, M.; Zorzi, R. D.; Geremia, S.; Diederich, F.; Dalcanale, E. *Tetrahedron* **2006**, *62*, 2008. (i) Kawase, T.; Tanaka, K.; Shiono, N.; Seirai, Y.; Oda, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1722.

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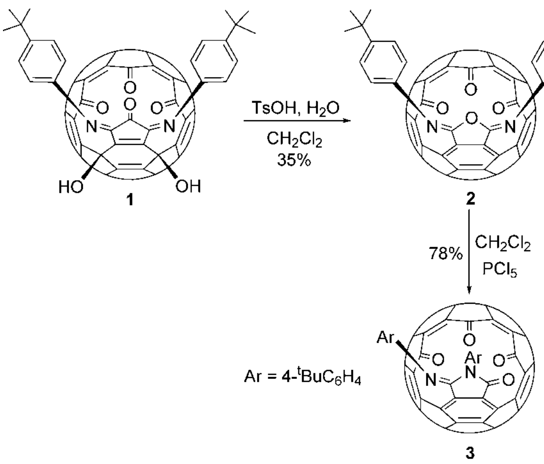
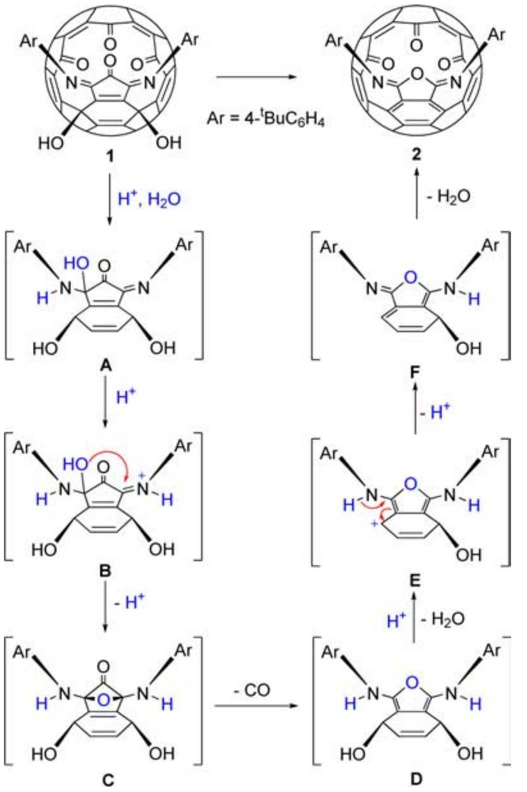
ordered one-dimensional stacks.[4] The head-to-tail donor–acceptor supramolecular polymer reported by Martin et al. is a rare example,[5] in which a tetrathiafulvalene based tweezer is covalently attached to C_{60} and acts as the host for the C_{60} cage from another molecule. The crystal structure of the iridium metal complex $C_{60}Ir(CO)Cl(bobPPh_2)_2$ also shows chelation of the C_{60} by the phenyl groups of the phosphine ligand from another molecule.[6] So far little effort has been devoted to the preparation of noncovalently bonded fullerene dimers.[7] In contrast, a number of covalently bonded dimers have been reported.[8]

We have reported the preparation of open-cage fullerene derivative **1** through a peroxide-mediated pathway.[9] The orifice of **1** is relatively large to encapsulate one water molecule readily at rt.[10] Here we report the conversion of **1** into compound **2**, which forms a dimeric supramolecule through head-to-tail and back-to-back $\pi-\pi$ interactions.

Scheme 1. Synthesis of Compounds **2** and **3**



Scheme 2. Possible Pathway for the Formation of **2**



Compound **1** was prepared as previously reported.[9a] Stirring a CH_2Cl_2 solution of **1** with excess water in the presence of TsOH resulted in complete conversion of **1** into an unknown product with high polarity as indicated by TLC. Chromatography on silica gel eluting with CH_2Cl_2/CH_3OH transformed the unknown product into compound **2** as a green band. It was not possible to characterize the unknown product, i.e. the precursor of **2**. Further treatment of **2** with PCl_5 afforded the isomeric iminoamide **3** (Scheme 1). Compound **3** was also observed as a minor byproduct in the formation of **2** from **1**.

The conversion of **1** to **2** involves replacement of one carbonyl group by an oxygen atom and elimination of two hydroxyl groups. It was an unexpected reaction. The attempted reaction was aimed at hydrolysis of the imino groups. A proposed mechanism for the conversion is

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(3) (a) D'Souza, F.; Amin, A. N.; El-Khouly, M. E.; Subbaiyan, N. K.; Zandler, M. E.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *134*, 654. (b) Hardouin-Lerouge, M.; Hudhomme, P.; Sallé, M. *Chem. Soc. Rev.* **2010**, *40*, 30. (c) Cao, J.; Zhu, X.-Z.; Chen, C.-F. *J. Org. Chem.* **2010**, *75*, 7420. (d) Cheng, Y.-J.; Hsieh, C.-H.; He, Y.; Hsu, C.-S.; Li, Y. F. *J. Am. Chem. Soc.* **2010**, *132*, 17381. (e) Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 3842.

(4) (a) Kennedy, R. D.; Halim, M.; Khan, S. I.; Schwartz, B. J.; Tolbert, S. H.; Rubin, Y. *Chem.—Eur. J.* **2012**, *18*, 7418. (b) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016.

(5) Fernandez, G.; Perez, E. M.; Sanchez, L.; Martin, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 1094.

(6) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5455.

(7) Kumar, K. S.; Patnaik, A. *Chem.—Eur. J.* **2011**, *17*, 5327.

(8) (a) Lu, S.; Jin, T.; Kwon, E.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 802. (b) Sørensen, J. B.; Fock, J.; Pedersen, A. H.; Petersen, A. B.; Jennum, K.; Bechgaard, K.; Kilsa, K.; Geskin, V.; Cornil, J.; Bjørnholm, T.; Nielsen, M. B. *J. Org. Chem.* **2011**, *76*, 25. (c) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086. (d) Yang, W.-W.; Li, Z.-J.; Gao, X. *J. Org. Chem.* **2011**, *76*, 6067. (e) Wang, G. W.; Wang, C. Z.; Zou, J. P. *J. Org. Chem.* **2011**, *76*, 6088. (f) Murata, Y.; Cheng, F.; Kitagawa, T.; Komatsu, K. *J. Am. Chem. Soc.* **2004**, *126*, 8874. (g) Zhang, S.; Gan, L.; Huang, C.; Lu, M.; Pan, J.; He, X. *J. Org. Chem.* **2002**, *67*, 883. (h) Segura, J. L.; Martín, N. *Chem. Soc. Rev.* **2000**, *29*, 13. (i) Bourgeois, J. P.; Diederich, F.; Echegoyen, L.; Nierengarten, J. F. *Helv. Chim. Acta* **1998**, *81*, 1835. (j) Wang, G. W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583. (k) Smith, A. B.; Tokuyama, H.; Strongin, R. M.; Furst, G. T.; Romanow, W. J.; Chait, B. T.; Mirza, U. A.; Haller, I. *J. Am. Chem. Soc.* **1995**, *117*, 9359. (l) Schick, G.; Kampe, K. D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, *19*, 2023. (m) Lebedkin, S.; Ballenweg, S.; Gross, J.; Taylor, R.; Krätschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971.

(9) (a) Liu, S.; Zhang, C.; Xie, X.; Yu, Y.; Dai, Z.; Shao, Y.; Gan, L.; Li, Y. *Chem. Commun.* **2012**, *48*, 2531. (b) Zhang, Q.; Pankewitz, T.; Liu, S.; Klopper, W.; Gan, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 9935. (c) Zhang, Q.; Jia, Z.; Liu, S.; Zhang, G.; Xiao, Z.; Yang, D.; Gan, L.; Wang, Z.; Li, Y. *Org. Lett.* **2009**, *11*, 2772.

(10) (a) Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. *Chem. Soc. Rev.* **2010**, *39*, 817. (b) Gan, L.; Yang, D.; Zhang, Q.; Huang, H. *Adv. Mater.* **2010**, *22*, 1498. (c) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083. (d) Iwamatsu, S.-i.; Murata, S. *Synlett* **2005**, *14*, 2117.

shown in Scheme 2. Addition of one water molecule to **1** afforded intermediate **C** with an oxabicyclo[2.1.1]hexanone moiety. The analogous bicyclo[2.1.1]hexan-5-one C_6H_8O has been prepared by Wiberg et al.[11] The present intermediate **C** is probably unstable due to steric strain. Thus release of steric hindrance and formation of a stable furan ring provide the major driving force for the decarbonylation of **C** to form **D**. The uncharacterizable product observed in the preparation of **2** mentioned above may be due to **C** or **D**. The decarbonylation process is reminiscent of the decarbonylation of indane-1,2,3-trione and other 1,2,3-tricarbonyl compounds. Both photolysis[12] and a Lewis acid[13] have been reported to induce decarbonylation of such tricarbonyl compounds.

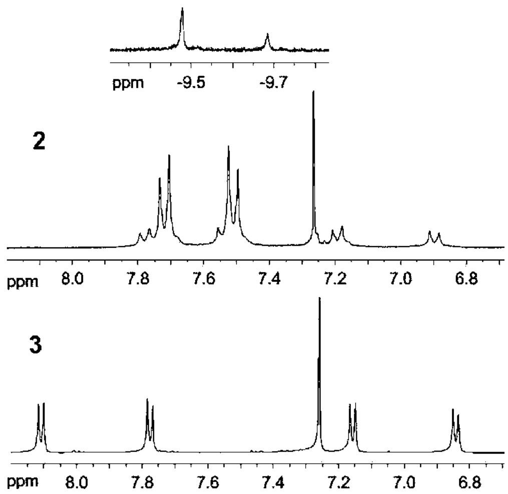

Figure 1. Partial ^{1}H NMR spectra of **2** (top and middle) and **3** (bottom) in $CDCl_3$.

Spectroscopic data of **2** and **3** are in agreement with the structures as depicted in Scheme 1. As expected from its C_1 symmetry, compound **3** showed three signals at 185.2, 184.7, 184.0 ppm on the ^{13}C NMR spectrum for the three carbonyl groups on the rim of the orifice. Compound **2** is C_s symmetric and showed two signals at 185.8, 183.8 ppm in an intensity 2:1 ratio for the same three carbonyl groups. An intriguing feature about the NMR spectra of **2** is that a set of minor signals were always present even after repeated purification procedures. The minor component showed four doublets in the phenyl proton region and two *tert*-butyl signals. There are also two signals due to an encapsulated water molecule at −9.5 and −9.7 ppm, which are comparable to the open-cage fullerene derivative we reported before (around −10 ppm).[9,10] The water encapsulation is around 8% as estimated from the ^{1}H NMR integral. Comparison of the ^{1}H NMR spectra between **2** and **3**, in particular the differences between the four phenyl signals for the minor component in **2** and for **3**, ruled out the possibility that **3** was present in the NMR sample of **2** (Figure 1).

The NMR spectrum of **2** actually reveals the presence of equilibrium between the monomer and dimer. The molar ratio for monomer **2** to dimer **2** is 4:1 as estimated from their ^{1}H NMR integrals. The ESI-HRMS spectrum of **2** also showed a weak dimer signal at 2134.3857 *m*/*z*. The less intensive signal in the mass spectrum is due to $2M + H_2O^+$ (Figure 2). The single crystal X-ray structure of **2** (Figure 3) provides conclusive evidence about the dimer structure.

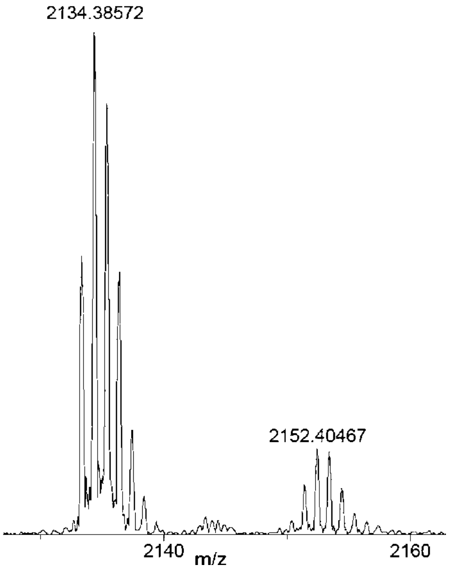

Figure 2. Signals for the dimer of **2** in the ESI-HRMS spectrum of compound **2**.

Single crystals of **2** were obtained from slow evaporation of a mixture in $CHCl_3$/EtOH/PhMe (Figure 3). The encapsulated water molecule was also detected in the X-ray structure. The structure shows a furan moiety with two imino groups located at the 2,5-positions. One of the two phenyl rings is almost coplanar with the furan ring with a dihedral angle of 12°. The other phenyl ring is positioned at 56° from the furan ring. The observed asymmetry is due to interaction with the fullerene cage of another molecule. Simple MM2 modeling indicates that the two phenyl rings cannot be simultaneously coplanar with the furan ring because of steric hindrance between the phenyl C−H groups adjacent to the imino nitrogen. But the two phenyl rings of the monomer **2** must rotate freely in solution at rt as indicated by the two phenyl proton signals of monomer **2** in the ^{1}H NMR spectrum. Rotation of the phenyl groups is effectively stopped in the dimer because of the interaction with the fullerene cage, thus resulting in four unequivalent phenyl proton signals (Figure 1).

Unlike the monomer/dimer equilibrium in solution, compound **2** exists exclusively as a dimer in the crystal.

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(11) Wiberg, K. B.; Lowry, B. R.; Colby, T. *J. Am. Chem. Soc.* **1961**, *83*, 3998.

(12) Adam, W.; Pattersont, W. S. *J. Org. Chem.* **1995**, *60*, 7769.

(13) Mecinović, J.; Hamed, R. B.; Schofield, C. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2796.

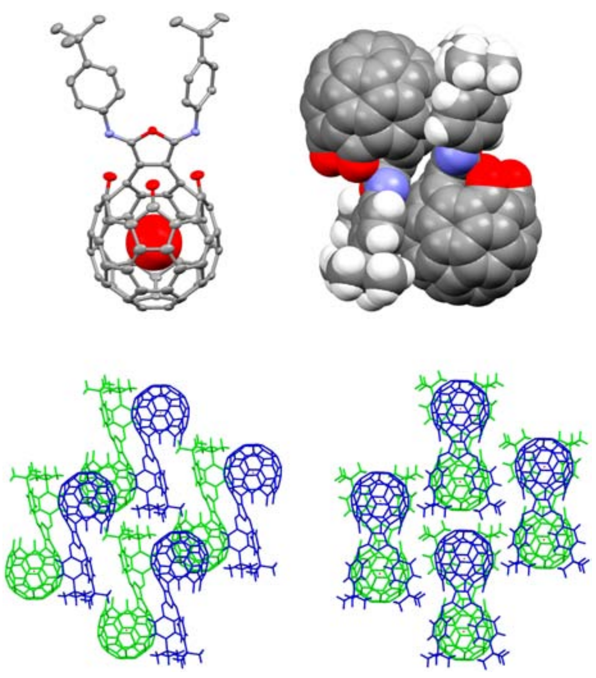
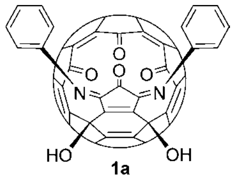


Figure 3. X-ray structure of **2**. For clarity solvent molecules $CHCl_3$ were not drawn in the crystal packing structure. Ellipsoids were at 50%. Color scheme for monomer and dimer structures: gray = C, blue = N, red = O.

There is strong $\pi-\pi$ interaction between the 6,6-junction of the fullerene cage and the phenyl ring coplanar with the furan ring on another molecule, with the distance of this intradimer $\pi-\pi$ interaction ranging from 3.24 to 3.38 Å. Interdimer interactions are also present between the fullerene cage and the phenyl ring at 56° from the furan ring on another molecule; the distance of this interdimer $\pi-\pi$ interaction ranges from 3.35 to 3.40 Å. Other short interdimer contacts include fullerene cage to fullerene cage (3.20 Å), CH$-\pi$ (fullerene) (3.76 Å for CH···C), and C=O to O=C (3.08 Å).

In our previous study, we obtained the single crystal X-ray structure of **1a**,[9c] which is analogous to **1** with aniline instead of *p*-*tert*-butylaniline. The two phenyl groups of **1a** are positioned in a tweezer type orientation and interact with an adjacent fullerene cage in the crystal to form a layer of head-to-tail polymer chains.[14] The closest distance between the phenyl group and the fullerene cage is 3.33 Å in the $\pi-\pi$ polymer. The presence of the hydroxyl groups in **1a** presumably prevented a back-to-back interaction as in the present case for **1**. We failed to obtain single crystals for compound **3**. The small angle between the two phenyl rings in **3** is not suitable for tweezer-like chelation to a fullerene cage. This is in agreement with the NMR spectra of **3**, which showed the presence of just the monomer.



1a

In summary, an unprecedented decarbonylation and dehydroxylation process has been reported for the open-cage fullerene derivative **1** under acidic conditions. The $\pi-\pi$ interaction between the phenyl groups and the fullerene cage in compound **2** results in a head-to-tail and back-to-back supramolecular dimer. It would be interesting to introduce aromatic donor moieties into **2** and explore the photo- and electroproperties of the resulting supramolecular systems.

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Supporting Information Available. NMR, HRMS, and IR spectra for compounds **2** and **3**, X-ray packing structure figure for **1a**, and crystallographic data in CIF format for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) See Supporting Information for figures.

The authors declare no competing financial interest.