## ChemComm

This article is part of the

## Carbon Nanostructures web themed issue

This issue showcases high quality research in the field of nanotechnology, specifically research that deals with carbon nanostructures

Guest Editors: Professors Nazario Martín, Dirk Guldi and Luis Echegoyen

Please visit the website to access the other articles in this issue:http://www.rsc.org/chemcomm/carbonnanostructures



## Face-to-face $C_6F_5$ -[60]fullerene interaction for ordering fullerene molecules and application to thin-film organic photovoltaics<sup>†‡</sup>

Chang-Zhi Li,<sup>a</sup> Yutaka Matsuo,<sup>\*ab</sup> Takaaki Niinomi,<sup>ac</sup> Yoshiharu Sato<sup>ac</sup> and Eiichi Nakamura<sup>\*ab</sup>

Received 4th August 2010, Accepted 4th October 2010 DOI: 10.1039/c0cc03028g

Treatment of [60]fullerene with potassium methylnaphthalenide and excess  $C_6F_5CH_2Br$  afforded 1,4-bis(pentafluorobenzyl)[60]fullerene, the study of which showed that there is a face-to-face interaction between [60]fullerene and a perfluoro aromatic ring, allowing the molecule to be utilized for high-performance organic photovoltaic devices.

Weak molecular interactions play a key role in the ordering of molecules in molecular science. Among a number of such weak interactions, the interactions that control molecular ordering of fullerene are rather rare, despite the fact that the designing of fullerene-based photovoltaic devices<sup>1</sup> and field effect transistors<sup>2</sup> requires rational methods for ordering fullerene molecules in the solid state—a crucial element to achieve high carrier mobility.<sup>3</sup> We previously exploited the isotropic shape and large molecular size of fullerene for one-dimensional ordering,<sup>4</sup> and the fullerene-fullerene facial interaction for vesicle,<sup>5</sup> lamellar ordering.<sup>6</sup> We report herein that a face-toface interaction between a C<sub>6</sub>F<sub>5</sub> group and [60]fullerene causes molecular ordering, as illustrated in the organization of 1,4-bis(pentafluorobenzyl)[60]fullerene,  $C_{60}(CH_2C_6F_5)_2$  (1), in the solid state. We also noted that perfluorobenzene  $(C_6F_6)$  caused deaggregation of 1 in solution, suggesting that this interaction is effective even in solution. The face-to-face interaction between a  $C_6F_5$  group and [60]fullerene is formally related to the well-established face-to-face  $\pi$ - $\pi$  stacking in a  $C_6H_6/C_6F_6$  pair,<sup>7</sup> where a quadrupole interaction results in a stabilization energy gain of 4 to 5 kcal mol<sup>-1.8</sup> We utilized compound 1 as an electron acceptor in a solution-processable, small-molecule-based thin-film photovoltaic device that showed a power conversion efficiency of 1.5%.

We synthesized 1 in one pot from [60]fullerene (Scheme 1).<sup>9</sup> Reduction of  $C_{60}$  with potassium as mediated by 1-methylnaphthalene at room temperature in THF afforded  $C_{60}^{2-}$  as a



Scheme 1

dark red solution in 3 h. The reaction of the dianion with 10 equiv. of  $C_6F_5CH_2Br$  afforded a 1,4-bis(pentafluorobenzyl) adduct 1 (Scheme 1) in 55% yield from fullerene. Compound 1 was characterized by high resolution APCI–TOF MS, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, as well as elemental analysis. This compound has a high thermal stability, as determined by TG–DTA measurement under a nitrogen atmosphere ( $T_{95} = 308$  °C, 5% weight loss).

During the characterization study, we made an interesting observation that molecule **1** in chloroform forms aggregates, which are converted to a monomer upon addition of 10 equiv. of  $C_6F_6$  to the solution. Thus, a dynamic light scattering (DLS) analysis of the chloroform solution (0.2 M) showed two peaks with average radii of 190.0 nm and 1.3 nm (Fig. 1a, top). Addition of 5 equiv. of  $C_6F_6$  shifted both peaks to the smaller side, and addition of 10 equiv. caused complete deaggregation, converting the two broad peaks into one sharp peak at 0.6 nm (Fig. 1a, middle and bottom, and Fig. 1b). We surmised that  $C_6F_6$  has a strong interaction with the fullerene molecule. We then studied the crystal structure to discover if such a  $C_6F_6$ -fullerene interaction manifests itself in the crystal of **1**.

Crystallographic analysis of a single crystal (containing no solvent molecules) showed that there is a face-to-face interaction between the C<sub>6</sub>F<sub>5</sub> group and the fullerene core, and that the two fluorinated benzyl groups catch another fullerene molecule and form an interlocked one-dimensional zigzag array along the *c*-axis, as shown in Fig. 2a. Thus, a red fullerene core is caught by two C<sub>6</sub>F<sub>5</sub> groups of the neighboring fullerene (space-filling representation). Along the *c*-axis, the fullerene's centroid-to-centroid distance was 10.36 Å, which is comparable to the reported value of  $[C_{60}]PCBM\cdotPhCl$  co-crystal (less than 10.13 Å)<sup>10</sup> and the crystals of C<sub>60</sub> (fcc, 10.0 Å).<sup>11</sup> The one-dimensional zigzag columns further aggregate in a rectangular fashion to form a densely packed crystal structure, as shown in Fig. 2b.

Details of the crystal structure showed that the  $C_6F_5$ -fullerene interaction occurs on a fullerene's C=C double bond that connects two hexagons. The  $C_6F_5$  group precisely faces toward

<sup>&</sup>lt;sup>a</sup> Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: matsuo@chem.s.u-tokyo.ac.jp, nakamura@chem.s.u-tokyo.ac.jp; Fax: +81 3-5800-6889;

пакатига@спет.s.u-tokyo.ac.jp; гах: + 81 5-3800-0889; Tel: + 81 3-5800-6889

<sup>1</sup>ei: +81 3-3800-688

<sup>&</sup>lt;sup>c</sup> Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

<sup>†</sup> This article is part of the 'Carbon Nanostructures' web-theme issue for ChemComm.

<sup>‡</sup> Electronic supplementary information (ESI) available: Experimental procedures and compound characterisation data, XRD, DSC, and TG-DTA data. CCDC 785439. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03028g



**Fig. 1**  $C_6F_5$ -[60]fullerene interaction of **1** in solution. (a) Aggregation/ deaggregation of **1** in chloroform in the presence of  $C_6F_6$ . Apparent hydrodynamic radius ( $R_h$ ) from the DLS study of **1** (0.2 mM) in chloroform with varying amounts of  $C_6F_6$ . (b) Schematic illustration of deaggregation process of aggregates.

the center of this nonplanar double bond, as illustrated in Fig. 2c.

The solid-state morphology, in particular, its temperature dependence, is important for small organic molecules to be utilized for organic photovoltaic applications. For instance, bis(dimethylphenylsilylmethyl)[60]fullerene (SIMEF)<sup>12</sup> shows a transition from amorphous glass to crystal ( $T_c$ ) at 149 °C, and it forms a morphologically stable n-layer by annealing after device fabrication. We found a  $T_c$  value of 185 °C for **1** upon a first heating process in the differential scanning calorimetric (DSC) measurement (ESI‡). The crystalline phase at 190 °C exhibited a characteristic powder X-ray diffraction (XRD) pattern, which matches the simulation based on single-crystallographic data (ESI‡), indicating that the crystals obtained by heating an amorphous solid have the same structure as those obtained for a single-crystal growth.

As shown in Fig. 3, compound  $\mathbf{1}$  (and the protio compound, 1,4-bisbenzyl[60]fullerene  $\mathbf{2}$ )<sup>13</sup> was found to be electrochemically



Fig. 2 Single-crystal analysis of compound 1. (a) A columnar zigzag array of the fullerene molecule along the *c*-axis. The red fullerene molecules interact face-to-face with two  $C_6F_5$  groups shown as a space-filling model. (b) Rectangular packing of the zigzag columns in a crystal. Fluorine atoms are shown in yellow. (c) A close-up view of the face-to-face interaction between the  $C_6F_5$  group and a fullerene C=C bond (red) after removal of disordered atoms. Black prism crystals of 1 suitable for single-crystal X-ray diffraction were obtained by slow diffusion of methanol gas into a chloroform solution. The fullerene core shows disorder. The tetragonal unit cell (Fig. 1a) with space group  $P4_32_12$  (a = 13.897 Å, b = 13.897 Å, c = 20.108 Å,  $\alpha = \beta = \gamma = 90^{\circ}$ ) and the cell volume (3883.39 Å<sup>3</sup>) were determined.



Fig. 3 Electrochemical properties of  $1 [C_{60}(CH_2C_6F_5)_2]$  (upper) and  $2 [C_{60}(CH_2C_6H_5)_2]$  (lower).

stable, and showed three reversible reduction waves at  $E_{1/2}^{\text{red}} = -0.93$ , -1.57, and -2.17 V (Fig. 3, black line) as measured in THF containing tetrabutylammonium perchlorate as a supporting electrolyte (*vs.* Fc/Fc<sup>+</sup>). The LUMO levels of **1** and **2** were deduced by the established equation LUMO =  $-(4.80 + E_{1/2}^{\text{red}1})$ .<sup>14</sup> Thus, the LUMO level of **1** (-3.87 eV) was found to be 0.1 eV lower than that of **2** (-3.76 eV) and SIMEF (-3.74 eV).

We examined the OPV performance of **1** in our own p-i-n device configuration that showed 5.2% efficiency using SIMEF as an electron acceptor.<sup>12b</sup> We fabricated a device (ITO/PEDOT:PSS/BP/BP:SIMEF/1/BCP/AI) by spin coating **1** (0.8 wt%) in a solvent mixture (C<sub>6</sub>F<sub>6</sub>/toluene = 2/3) as an n-layer. The device exhibited a power conversion efficiency of 1.51% (open circuit voltage,  $V_{OC} = 0.48$  V; short circuit current density,  $J_{SC} = 7.0$  mA cm<sup>-2</sup>; fill factor, FF = 0.45;

Downloaded by Universite de Sherbrooke on 27 November 2012 Published on 21 October 2010 on http://pubs.rsc.org | doi:10.1039/C0CC03028G series resistance,  $R_{\rm s} = 5.5 \,\Omega \,{\rm cm}^2$ ). Although we cannot draw a solid conclusion from this unoptimized experiment, the  $V_{\rm OC}$  value is expectedly low. This observation is consistent with a recent proposal that the open circuit voltage ( $V_{\rm OC}$ ) of OPV is proportional to the energy difference between the LUMO of the acceptor and the HOMO of the donor.<sup>15</sup> We speculate that the fluoroaromatic–C<sub>60</sub> moieties mediated structure ordering of 1 discussed above may have contributed to the lowering of the series resistance.

In conclusion, we have found that there is a favorable interaction between a perfluoroaromatic ring and the  $\pi$  surface of fullerene, and that this interaction contributes to the self-organization of compound **1** in the solid phase and perhaps in solution. The attachment of a pentafluorobenzyl group to fullerene resulted in a thermo- and electrochemically stable acceptor. Detailed physical studies on the device performance are the subject of future studies.

Financial supports from MEXT, Japan (KAKENHI, #22000008 and Global COE Program for Chemistry Innovation) and Japan Science and Technology Agency, JST (Strategic Promotion of Innovative Research and Development) are gratefully acknowledged.

## Notes and references

- (a) N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky and F. Wudl, *Appl. Phys. Lett.*, 1993, 62, 585; (b) G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, 270, 1789.
- 2 (a) C. Waldauf, P. Schilinsky, M. Perisutti, J. Hauch and C. J. Brabec, *Adv. Mater.*, 2003, **15**, 2084; (b) T. D. Anthopoulos, C. Tanase, S. Setayesh, E. J. Meijer, J. C. Hummelen, P. W. M. Blom and D. M. de Leeuw, *Adv. Mater.*, 2004, **16**, 2174.
- (a) M. Chikamatsu, S. Nagamatsu, Y. Yoshida, K. Saito, K. Yase and K. Kikuchi, *Appl. Phys. Lett.*, 2005, **87**, 203504; (b) H. Kusai, T. Nagano, K. Imai, Y. Kubozono, Y. Sako, Y. Takaguchi, A. Fujiwara, N. Akima, Y. Iwasa and S. Hino, *Appl. Phys. Lett.*, 2006, **88**, 173509; (c) R. D. Kennedy, A. L. Ayzner, D. D. Wanger, C. T. Day, M. Halim, S. I. Khan, S. Tolbert, B. Schwarz and Y. Rubin, J. Am. Chem. Soc., 2008, **130**, 17290.
- 4 (a) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato and E. Nakamura, *Nature*, 2002, 419, 702; (b) Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato and E. Nakamura, J. Am. Chem. Soc., 2004, 126, 432; (c) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato and E. Nakamura, J. Am. Chem. Soc., 2006, 128, 9586.
- 5 (a) T. Homma, K. Harano, H. Isobe and E. Nakamura, Angew. Chem., Int. Ed., 2010, 49, 1665; (b) H. Isobe, T. Homma and

E. Nakamura, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 14895;
(c) M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler,
H. Isobe, E. Nakamura, S. Zhou and B. Chu, *Chem. Lett.*, 2000,
1098; (d) S. Zhou, C. Burger, B. Chu, M. Sawamura,
N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe and
E. Nakamura, *Science*, 2001, **291**, 1944.

- 6 (a) Y.-W. Zhong, Y. Matsuo and E. Nakamura, J. Am. Chem. Soc., 2007, 129, 3052; (b) C.-Z. Li, Y. Matsuo and E. Nakamura, J. Am. Chem. Soc., 2009, 131, 17058.
- 7 C. R. Patrick and G. S. Prosser, Nature, 1960, 187, 1021.
- 8 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem.*, *Int. Ed.*, 2003, **42**, 1210.
- 9 Experimental procedure: potassium metal (124 mg, 3.19 mmol) was added in one portion to a freeze-thaw degassed mixture of  $C_{60}$  (1000 mg, 1.39 mmol) and 1-methylnaphthalene (5.93 mL, 41.7 mmol, 30 equiv.) in 150 mL THF. A dark red solution was produced after stirring under argon at room temperature for 3 h. Pentafluorobenzyl bromide (3628 mg, 13.9 mmol) was then added. After stirring for an additional 8 h, the reaction mixture was quenched with aq. NH<sub>4</sub>Cl (0.5 mL). After concentration to a volume of *ca.* 10 mL, the desired product was precipitatedby methanol. Purification on a silica gel column (eluent: first CS<sub>2</sub>/hexane = 1/1, then CS<sub>2</sub>) afforded 1,4-bis(pentafluorobenzyl)[60]-fullerene 1 in 55% yield (830 mg). Further purification of the sample for measurements and OPV evaluation was achieved with preparative HPLC and GPC. The compound was stable under air as a solid or in solution.
- 10 M. T. Rispens, A. Meetsma, R. Rittberger, C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Chem. Commun.*, 2003, 2116.
- 11 P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley Jr., A. B. Smith III and D. E. Cox, *Phys. Rev. Lett.*, 1991, **66**, 2911.
- 12 (a) Y. Matsuo, A. Iwashita, Y. Abe, C.-Z. Li, K. Matsuo, M. Hashiguchi and E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 15429; (b) Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka and E. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 16048.
- 13 S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa and K. M. Kadish, J. Am. Chem. Soc., 1998, **120**, 9220.
- 14 W.-Y. Wong, X.-Z. Wang, Z. He, A. B. Djurii, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S. K. Mak and W.-K. Chan, *Nat. Mater.*, 2007, 6, 521.
- (a) Organic Photovoltaics: Mechanism, Materials and Devices, ed. S.-S. Sun and N. S. Sariciftci, Taylor & Francis, London, 2005; (b) B. P. Rand, D. P. Burk and S. R. Forrest, Phys. Rev. B: Condens. Matter Mater. Phys., 2007, 75, 115327; (c) C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, Adv. Funct. Mater., 2001, 11, 374; (d) F. B. Kooistra, J. Knol, F. Kastenberg, L. M. Popescu, W. J. H. Verhees, J. M. Kroon and J. C. Hummelen, Org. Lett., 2007, 9, 551; (e) T. Niinomi, Y. Matsuo, Y. Sato and E. Nakamura, J. Mater. Chem., 2009, 19, 5804; (f) M. D. Perez, C. Borek, S. R. Forrest and M. E. Thompson, J. Am. Chem. Soc., 2009, 131, 9281.