

Supporting Information

Preparation and Optical Properties of Fullerene/Ferrocene Hybrid Hexagonal Nanosheets and Large Scale Production of Fullerene Hexagonal Nanosheets

Takatsugu Wakahara,^{*,†} Marappan Sathish,[†] Kun'ichi Miyazawa,[†] Chunping Hu,[‡] Yoshitaka Tateyama,^{*,‡,\$} Yoshihiro Nemoto,[‡] Toshio Sasaki[#] and Osamu Ito^{\$}

[†]Fullerene Engineering Group, Exploratory Nanotechnology Research Laboratories, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan,

[‡]International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan,

^{\$}PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 333-0012, Japan,

[#]ICYS, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

^{\$}CarbonPhotoScience Institute, Kita-Nakayama2-1-6, Izumi-ku, Sendai, 981-3215, Japan

Table of Contents

Complete ref. 4c and 6b	S2
Calculation details	S3-4
Figure S1. HOMO and LUMO of the C ₆₀ (Fc) ₂ .	S4
Figure S2. The optical microscopic images of the C ₆₀ /Fc nanosheets	S5
Figure S3. IR spectra of the C ₆₀ /Fc nanosheets by KBr method	S5

Complete ref. 4c

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Complete ref. 6b

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Calculation details

We carried out *ab initio* calculations to determine the structural stability and electronic states of the $C_{60}(\text{ferrocene})_2$ crystal on the basis of the local density approximation (LDA) to the density functional theory (DFT). Since the current system was a crystal with extended electronic states, we adopted a plane wave basis set and a norm-conserving pseudopotential scheme, typically used in solid state physics. For Fe, we used a nonlinear core correction to the pseudopotential. The unit cell parameters were taken from the data obtained in the XRD analysis in the present study. PW92-type LDA parameterization of an exchange correlation functional¹ was performed for a reasonable description of intermolecular interactions mainly governed by van der Waals interaction. A cutoff energy of 40 Ry was used for the basis set along with Γ point sampling.

Conventional DFT calculation gives Kohn-Sham orbital energies, and the energy differences between the occupied and unoccupied orbitals are used as a primary approximation of the excitation energies. Generally, intramolecular excitation is reasonably described. However, it is known that the charge-transfer (CT) excitation energy is considerably underestimated due to the spatial separation of the donor and acceptor levels. To remedy this drawback, some calculation techniques have been developed. In this study we use the Slater transition (ST) method and the modified linear response (MLR) scheme of the time-dependent (TD) DFT² for the estimation. All the calculations are performed using the ABINIT code.³

We first carry out the structural optimization of the $C_{60}(\text{ferrocene})_2$ crystal using the unit cell data obtained in this study. Inversion symmetry remains irrespective of no symmetry constraint in the calculation. The resultant structure (Figure 7) is consistent with the structure proposed by Crane *et al.*⁴ The relative position between the ferrocene molecules and C_{60} is slightly different from that in the structure of Crane *et al.*.

The electronic density of states of the relaxed geometry is shown in Figure S1. The sixfold highest occupied molecular orbital (HOMO) consists of $3d$ orbitals ($3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$) of Fe in the two ferrocene molecules, while the triply degenerated lowest unoccupied molecular orbital (LUMO) mainly consists of t_{1u} orbitals of C_{60} and a small part of Fe $3d$ orbitals, which are the cause of the CT excitation. (See Figure S1.)

To this CT excitation, the ST method and TDDFT-MLR scheme are applied. Owing to the degeneracy, excitation energy distribution is obtained.

References

- (1) Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244-13249.
- (2) (a) Hu, C.; Sugino, O.; Miyamoto, Y. Phys. Rev. A 2006, 74, 032508 (1-7). (b) Hu, C.; Sugino, O. J. Chem. Phys. 2007, 126, 074112 (1-10).
- (3) Gonze, X.; Beuken, J.-M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G.-M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent, M.; Roy, A.; Mikami, M.; Ghosez, Ph.; Raty, J.-Y.; Allan, D. C. Comput. Mater. Sci. 2002, 25, 478–492.
- (4) Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. J. Chem. Soc., Chem. Commun. 1992, 1764-1765.

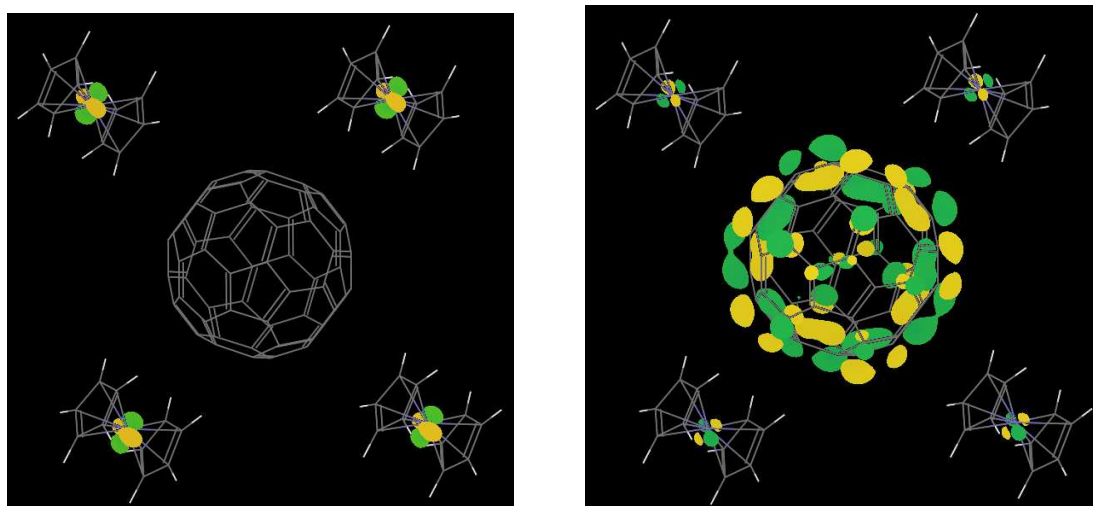


Figure S1. HOMO (left) and LUMO (right) of $C_{60}(Fc)_2$. The HOMO mainly consists of Fe 3d orbitals of Fc, although the density of $C_{60} t_{1u}$ orbitals is too low to be shown owing to the large space of C_{60} . The LUMO involves $C_{60} t_{1u}$ orbitals with small contribution of Fe 3d orbitals, giving rise to CT character. An electronic transition from the HOMO to LUMO corresponds to the CT excitation; the transition is mainly from Fc in the ground state to C_{60} in the excited state.

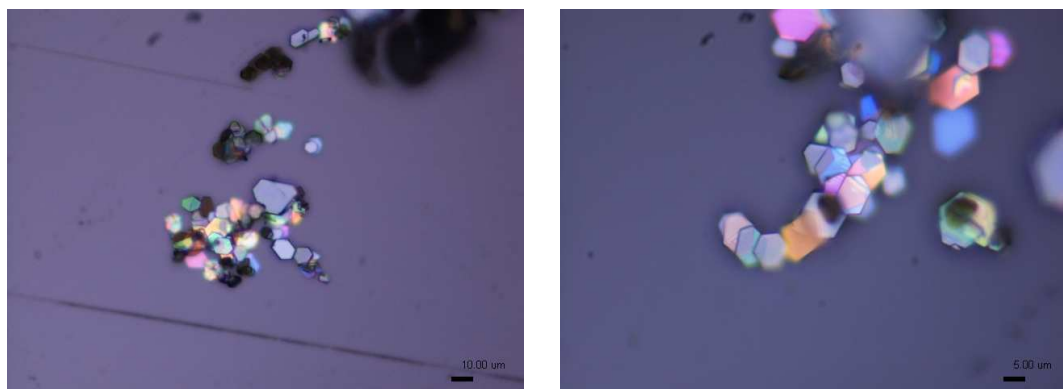


Figure S2. The optical microscopic images of the C₆₀/Fc nanosheets.

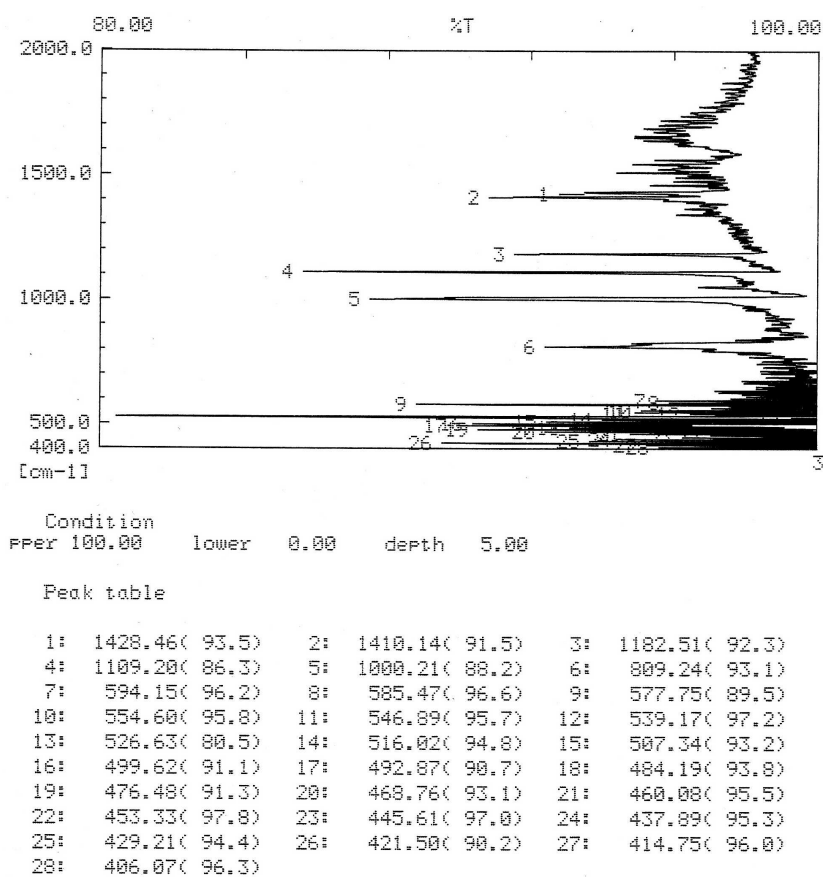


Figure S3. IR spectra of the C₆₀/Fc nanosheets by KBr method