

# High yield selective synthesis of C<sub>60</sub> dimers

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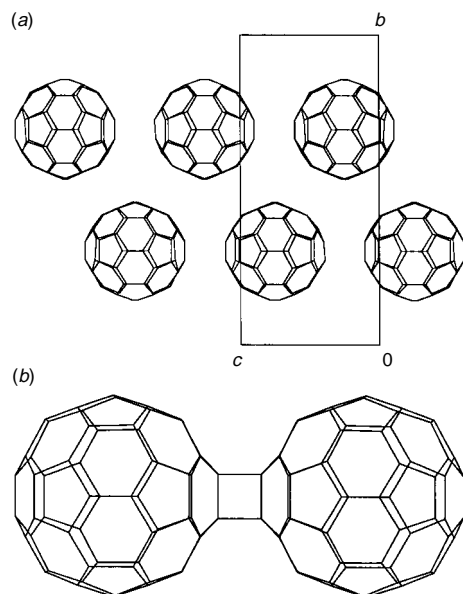
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**Squeezing the organic molecular crystal (ET)<sub>2</sub>C<sub>60</sub> at 5 GPa and 200 °C followed by removing unreacted ET molecules produces C<sub>60</sub> dimers, with a yield of ca. 80%.**

Polymeric fullerenes have attracted considerable interest because of their various structures and properties.<sup>1</sup> Both neutral and doped polymers have been synthesized by various techniques. While doped polymers are found to be formed spontaneously by slow cooling to room temperature,<sup>2</sup> polymerization in the neutral state requires activation of C<sub>60</sub> via light irradiation<sup>3</sup> or application of external pressure at high temperature.<sup>4,5</sup> An advantage of high pressure synthesis is that by tuning the temperature and pressure, one can selectively synthesize one- and two-dimensional polymers in bulk. Recently, a new technique, called the mechanochemical method, produced a bulk amount of C<sub>60</sub> dimers in 25–30% yield.<sup>6</sup> X-Ray crystallographic analysis of the dimer revealed that the dimer is formed via a 2 + 2 cycloaddition [Fig. 1 (b)].

To control the dimensionality and the degree of polymerization, here we report a novel method of squeezing the crystals of a molecular compound of C<sub>60</sub> and ET [ET = bis(ethylenedithio)tetrathiafulvalene].<sup>7</sup> In the (ET)<sub>2</sub>C<sub>60</sub> crystal, a novel arrangement of C<sub>60</sub> is achieved by covering a part of the C<sub>60</sub> molecules with ET molecules. Fig. 1(a) shows the arrangement of C<sub>60</sub> in a crystal of (ET)<sub>2</sub>C<sub>60</sub>, where C<sub>60</sub> molecules form a one-dimensional closest packing arrangement with a regular triangle lattice framework along the *c*-axis.<sup>7</sup> Interfullerene distances parallel and diagonal to the *c*-axis are 9.923(2) and 9.919(3) Å, respectively. Since they are very close to that of the face-centred cubic lattice of neat C<sub>60</sub> (10.02 Å), pressure-induced cross-linking of C<sub>60</sub> molecules in the (ET)<sub>2</sub>C<sub>60</sub> crystals is highly promising. Incidentally, the charge transfer interaction between



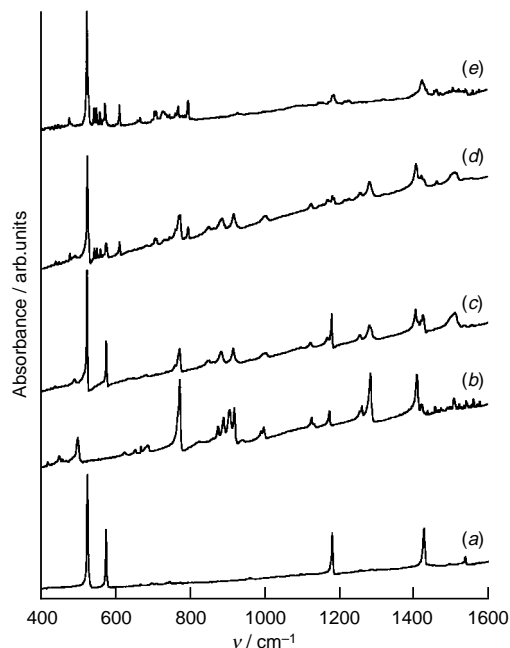
**Fig. 1** (a) Arrangement of C<sub>60</sub> in (ET)<sub>2</sub>C<sub>60</sub> crystal; (b) C<sub>60</sub> dimer

ET and C<sub>60</sub> in this crystal is estimated to be small, as judged by the difference between redox potentials of each element.

The starting (ET)<sub>2</sub>C<sub>60</sub> crystals were obtained by slow evaporation of a CS<sub>2</sub> solution of a stoichiometric amount of C<sub>60</sub> and ET. High pressure treatment was performed following previously described procedures.<sup>4</sup> Polycrystalline (ET)<sub>2</sub>C<sub>60</sub> (50–100 mg) loaded in a gold capsule was reacted at 5 GPa and 200 °C using a wedge-type cubic anvil high pressure apparatus. After squeezing, the sample was recovered from the reaction capsule, and subjected to characterization under ambient conditions.

Raman spectra of the pentagonal pinch mode A<sub>g</sub>(2) for the I<sub>h</sub> of C<sub>60</sub>, which is a sensitive probe for the occurrence of interfullerene bonds, were obtained.<sup>3</sup> Reflecting the almost neutral nature of the (ET)<sub>2</sub>C<sub>60</sub> complex, the A<sub>g</sub>(2) mode was observed at 1469.3 cm<sup>-1</sup>, which is identical to the position for pure C<sub>60</sub>. In the as-pressurized (ET)<sub>2</sub>C<sub>60</sub>, the corresponding mode appeared at 1462.9 cm<sup>-1</sup>, displaying a 6.4 cm<sup>-1</sup> red-shift. This result indicates that interfullerene bonds are formed in the pressurized sample.

Earlier work has proved that infrared spectroscopy is a useful tool to identify the C<sub>60</sub> polymer phases.<sup>8,9</sup> Fig. 2 shows the infrared absorption spectra of several samples dispersed in KBr pellets. The spectrum of starting (ET)<sub>2</sub>C<sub>60</sub> is shown in Fig. 2(c). This spectrum is approximately explained as the sum of those for the constituent molecules, C<sub>60</sub> [Fig. 2(a)] and ET [Fig. 2(b)], this being consistent with the absence of charge transfer suggested by the structural analysis. The spectrum of the as-



**Fig. 2** Infrared absorption spectra for (a) C<sub>60</sub>, (b) ET, (c) pristine (ET)<sub>2</sub>C<sub>60</sub>, (d) as-pressurized (ET)<sub>2</sub>C<sub>60</sub>, and (e) (ET)<sub>2</sub>C<sub>60</sub> washed by CH<sub>2</sub>Cl<sub>2</sub>. ET molecules were removed in the final product.

pressurized sample is displayed in Fig. 2(d), which is remarkably different from the spectrum of the starting (ET)<sub>2</sub>C<sub>60</sub>. By a careful comparison between the two spectra, we found that the peaks attributable to ET were not changed by pressurization, while those from C<sub>60</sub> exhibited notable changes. In order to confirm the change more precisely, the unreacted ET molecules were removed by sonication in CH<sub>2</sub>Cl<sub>2</sub>. The infrared spectrum [Fig. 2(e)] of the washed sample shows no trace of ET and can be ascribed to reacted C<sub>60</sub>. Since this substance was soluble to *o*-dichlorobenzene, the degree of polymerization is expected to be substantially smaller than those for the one- and two-dimensional polymers, which are insoluble to *o*-dichlorobenzene.

The infrared spectrum [Fig. 2 (e)] of the obtained sample differs significantly from those for the polymers reported in previous papers, but is very similar to that for photodimerized C<sub>60</sub>.<sup>10</sup> Furthermore, the spectrum of the mechanochemically synthesized dimer<sup>6</sup> turned out to be almost identical to Fig. 2(e), including the peak positions and intensity distributions. These spectral results strongly indicate that the dominant product of high pressure treatment of (ET)<sub>2</sub>C<sub>60</sub> is the C<sub>60</sub> dimer [Fig. 1(b)].

High performance liquid chromatographic analysis of the obtained sample was performed on a Cosmosil Buckyprep column with toluene as the eluent. The retention volume (14.5 ml) of the main peak was exactly the same as that for the mechanochemically obtained dimer.<sup>6</sup> Although several weak peaks are observed in the chromatogram, no signal derived from unreacted monomer C<sub>60</sub> was found. The purity of C<sub>60</sub> dimer was estimated to be about 79% based on the peak area of the chromatogram, detected by monitoring UV light at 326 nm. Since the weight-loss during the pressure treatment and purification is negligible, we can conclude that roughly 80% of the C<sub>60</sub> monomer is converted to the dimer. This yield is considerably higher than that of the mechanochemical method.

Although most of the product of the above method is soluble in *o*-dichlorobenzene, there remains a small amount of insoluble material. Thus a substantial amount of one-dimensional oligomers or ladder polymers might be synthesized according to the

current method by optimizing the reaction conditions. The reaction mechanism in the restricted spaces in such types of molecular compounds could be an interesting issue to be explored in the future.

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## Notes and References

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- 1 For example, *Appl. Phys. A*, 1997, **64** (Special issue, *Polymeric Fullerenes*), *Fullerene Polymers and Fullerene-Polymer Composites*, ed. P. C. Eklund and A. M. Rao, Springer, 1997.
- 2 O. Chauvet, G. Oszlanyi, L. Forro, P. W. Stephens, M. Tegze, G. Faigel and A. Janossy, *Phys. Rev. Lett.*, 1994, **72**, 2721.
- 3 A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan and I. J. Amster, *Science*, 1993, **259**, 955.
- 4 Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter Jr., A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas and T. Yagi, *Science*, 1994, **264**, 1570.
- 5 M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Bethoux and M. Perroux, *Phys. Rev. Lett.*, 1995, **74**, 278.
- 6 G.-W. Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, 1997, **387**, 583.
- 7 A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.
- 8 A. M. Rao, P. C. Eklund, J.-L. Hodeau, L. Marques and M. Nunez-Regueiro, *Phys. Rev. B*, 1997, **55**, 4766.
- 9 K. Kamaras, Y. Iwasa and L. Forro, *Phys. Rev. B*, 1997, **55**, 10 999.
- 10 J. Onoe and K. Takeuchi, *Phys. Rev. B*, 1996, **54**, 6167.

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