

## Photoisomerization of a Fullerene Dimer

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A photo-switchable fullerene dimer and its analogous nitrogen endohedral species have been synthesized and characterized. Irradiation by ultraviolet and visible light has been used to switch between the trans and cis isomers of both the C<sub>60</sub>- and N@C<sub>60</sub>- based dimers. Environmental perturbations experienced by the encapsulated nitrogen atom upon switching between the two isomers in degassed carbon disulfide has been determined by pulse electron paramagnetic resonance. Both T<sub>1</sub> and T<sub>2</sub> electron spin relaxation times of the two isomers of the endohedral fullerene containing dimer revealed a biexponential decay. Although the zero field splitting parameter D<sub>eff</sub> for both isomers in solution was similar, around 13.0 MHz, the molecular rotation correlation time τ<sub>c</sub> of the trans and cis isomers was calculated to be 37.2 ± 1.6 and 34.8 ± 2.7 ps, respectively.

## Introduction

Endohedral fullerenes, such as N@C<sub>60</sub>, in which unpaired electrons are isolated on the encapsulated species or the fullerene cage, have been proposed as potential qubits for solid-state quantum computing.<sup>1</sup> Linear arrays and two-dimensional lattices have been investigated experimentally as nanoscale structures for controlling the spatial separation, and thus spin–spin coupling interactions, between spins centered on the encapsulated species.<sup>2</sup> Several different fullerene dimers have already been produced and investigated, but the spatial separation, and hence interaction, between the two fullerenes is fixed.<sup>3</sup> A photo-switchable fullerene dimer enables the possibility of controllably switching a qubit–qubit interaction between two known states. The azobenzene moiety has been widely exploited as a photoactive component in a large number of supramolecular systems. The trans isomer can be switched to the cis isomer upon UV irradiation, and the cis isomer back to the trans by either thermal treatment or visible light irradiation.<sup>4</sup> Its cis–trans isomerization is one of the cleanest photoreactions known.

In this letter, we describe the synthesis of two optically switchable fullerene dimers, one of which is comprised of two empty fullerene cages and the other dimer of one endohedral, N@C<sub>60</sub>, and one empty fullerene cage, linked by an azobenzene bridge. The magnetic behavior of the two photoisomers of the endohedral fullerene containing dimer is investigated by electron paramagnetic resonance (EPR).

## Experimental Section

**C<sub>60</sub>-azo-C<sub>60</sub> (1).** A mixture of 4,4'-azobenzaldehyde (**4**) (2.84 mg), C<sub>60</sub> (27 mg, three molar equiv), and *N*-methylglycine (sarcosine) (6.53 mg, 4 molar equiv) in toluene (50 mL) was heated to reflux for 2 days under a nitrogen atmosphere to produce the symmetric azo-bridged fullerene dimer C<sub>60</sub>-azo-C<sub>60</sub> (**5**) (Yield: 95%). MALDI *m/z* 1733.2 (M<sup>-</sup>, C<sub>138</sub>H<sub>20</sub>N<sub>4</sub> requires 1733.2). UV–vis (toluene) λ<sub>max</sub>(nm)(ε = m<sup>2</sup> mol<sup>-1</sup>): 330 (3114.3), 433 (389.4). FTIR (KBr disk) (cm<sup>-1</sup>): 527 (S), 801 (S), 1021–1090 (S, B), 1260.5 (S), 1458 (M), 1617–1709.5 (W, B), 2774 (W), 2848 (W), 2917.5 (S), 2940.5 (M), 3416.5 (S, B). <sup>1</sup>H NMR (600 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> = 3:1): δ (ppm) = 2.89 (S, 6H, H-3); 4.33 (D, *J* = 9.4 Hz, 2H, H-2a); 5.03 (D, *J* = 9.4 Hz, 2H, H-2b); 5.05 (S, 2H, H-1); 7.53 (D, *J* = 7.4 Hz, 2H, H-9 or H-5); 7.84 (D, *J* = 7.4 Hz, 2H, H-5 or H-9); 7.95 (D, *J* = 7.4 Hz, 4H, H-6 and H-8). <sup>13</sup>C NMR (125.8 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> = 3:1): δ(ppm) = 40.13 (2C, C-3); 70.15 (2C, C-2); 71.82 (2C, C-11); 76.96 (2C, C-10); 83.22 (2C, C-1); 123.55 (4C, C-6,8); 127.95, 129.05 (4C, C-5 and C-9); 129.75 (2C, C-4); 130.39; 131.09; 132.60; 133.38; 134.14; 135.82; 136.57; 138.45; 139.65; 140.32; 141.55 (2C, C-7); 141.61; 141.75; 141.89; 141.92; 142.09; 142.20; 142.61; 142.65; 142.75; 143.08; 143.15 (>10); 144.40; 144.66; 144.74; 145.22; 145.26; 145.29; 145.36; 145.38; 145.44; 145.51; 145.64; 145.67; 145.76; 145.95; 145.98; 146.14; 146.18; 146.23; 146.26; 146.30; 146.36; 146.38; 146.58; 147.32; 152.53; 152.75; 153.02; 153.75; 155.96. <sup>13</sup>C DEPT-135 NMR: CH, CH<sub>3</sub>: 40.13, 83.22, 123.55, 129.05. CH<sub>2</sub>: 70.15. Tetra-C: 71.82, 127.95, 129.75, 130.39, 131.09, 132.60, 133.38, 134.18, 135.82, 136.57, 138.45, 139.65, 140.32, 141.55, 141.61, 141.75, 141.89, 141.92, 142.09, 142.20, 142.61, 142.65, 142.75, 143.08, 143.15, 144.40, 144.66, 144.74, 145.22, 145.26, 145.29, 145.36, 145.38, 145.44, 145.51, 145.64, 145.67, 145.76, 145.95, 145.98, 146.14, 146.18, 146.23, 146.26, 146.30,

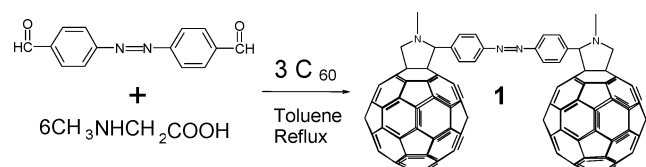
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**SCHEME 1: Chemical Reactions of Photo-switchable Fullerene Dimer C<sub>60</sub>-azo-C<sub>60</sub>**


146.36, 146.38, 146.58, 147.32, 152.53, 152.75, 153.02, 153.75, 155.96. HSQC NMR (H (ppm)-C (ppm) direct correlation): 2.89 (H-3)-40.13 (C-3); 4.33 (H-2a)-70.15 (C-2); 5.03 (H-2b)-70.15 (C-2); 5.05 (H-1)-83.22 (C-1); 7.53 (H-5 or H-9)-129.05 (C-5,9); 7.84 (H-9 or H-5)-129.05 (C-5,9); 7.95 (H-6,8)-123.55 (C-6,8). 2D COSY proton proton correlation NMR (H-H coupling): 7.84 (H-5 or H-9)-7.95 (H-6,8); 7.53 (H-9 or H-5)-7.95 (H-6,8); 4.35 (H-2a)-5.04 (H-2b). HMBC NMR (long distance H-C correlation): 2.89 (H-3)-70.15 (C-2), 83.22 (C-1); 4.33 (H-2a)-71.82 (C-11), 127.95, 140.32; 5.03 (H-2b)-76.96 (C-10), 83.22 (C-1), 155.96; 5.05 (H-1)-40.13 (C-3), 76.96 (C-10), 129.75 (C-4), 153.26; 7.53 (H-5 or H-9)-129.75 (C-4); 7.84 (H-5 or H-9)-129.75 (C-4), 7.95 (H-6,8)-141.55 (C-7).

Fullerene dimers were purified by HPLC (Buckyprep M, 20 mm × 250 mm, toluene eluent, 12 mL/min).

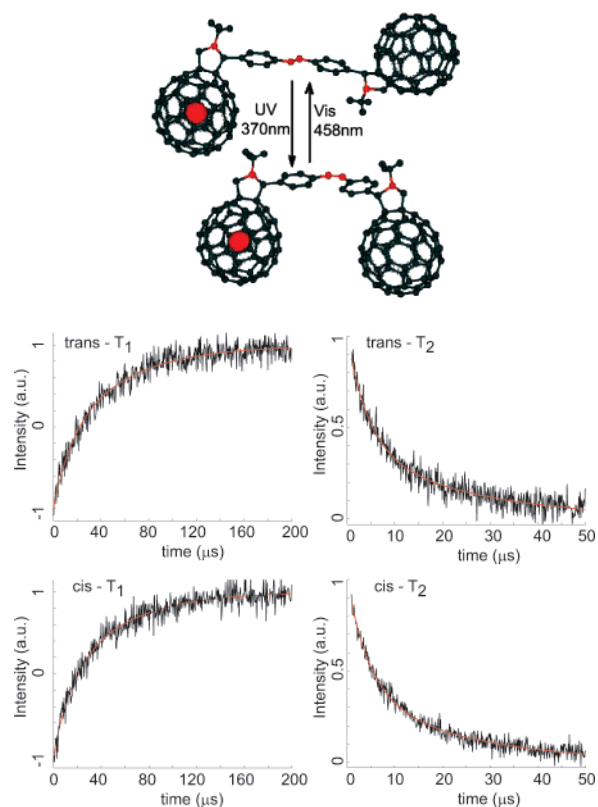
CW EPR sample preparation: About 5 mg N@C<sub>60</sub>-azo-C<sub>60</sub>/C<sub>60</sub>-azo-C<sub>60</sub> (around 1/1000) sample was dissolved in CS<sub>2</sub> and dried using vacuum line sealed in quartz EPR tubes (3 mm diameter).

CW EPR measurements were performed on a Magnetech Miniscope MS200 using a 2G modulation, 270 s scan time, and 99 scans at room temperature. Spectral simulation was performed using the EASYSPIN software package.<sup>S1</sup>

Pulse EPR measurements were performed using an X-band Bruker Elexsys580e spectrometer. Spin lattice relaxation time  $T_1$  and spin dephasing time  $T_2$  were measured by an inversion recovery sequence and Hahn echo sequence, respectively. The  $\pi/2$  and  $\pi$  pulse durations were 56 and 112 ns, respectively. Phase cycling was used to eliminate the contribution of unwanted free induction decay (FID) signals.

**Results and Discussion**

The azobenzene bridged fullerene dimer, **1**, was synthesized according to the pyrrolidine functionalization method<sup>5</sup> by reaction of pristine C<sub>60</sub> with 4,4'-azobenzaldehyde (Scheme 1); the latter prepared according to literature methods.<sup>6</sup> HPLC (Buckyprep-M, 20 mm × 250 mm, toluene eluent, 12 mL/min) of the product mixture revealed that the C<sub>60</sub> dimer product (**1**) elutes more slowly (21.7 min) than C<sub>60</sub> (10.4 min), as would be expected from its structure. MALDI mass spectrometry revealed the expected molecular ion peak at  $m/z = 1733.2$  and an isotopic distribution pattern in agreement with that calculated. An absorption peak in the UV-vis spectrum was observed at 430 nm, strongly indicative of pyrrolidine functionalization of C<sub>60</sub>.<sup>5,7-10</sup> FTIR revealed a series of strong transitions at 801, 1021-1090 (band), and 1260.5 cm<sup>-1</sup>, consistent with the FTIR spectra of other fullerene dimers such as C<sub>120</sub>, C<sub>120</sub>O, and C<sub>120</sub>O<sub>2</sub>.<sup>11</sup> Finally, <sup>1</sup>H, <sup>13</sup>C, and 2D NMR provides confirmation of the proposed structure. Seven different proton environments were observed in the fullerene dimer **1**, with H-2a and H-2b, H-5 and H-9 found to be inequivalent and consistent with fulleropyrrolidine compounds reported previously.<sup>8-10</sup> Four different aromatic carbon environments arising from the azobenzene bridge, three different carbon environments from the pyrrolidine ring, two different sp<sup>3</sup> and fifty-one different sp<sup>2</sup> carbon environments from the fullerene cage itself were detected.

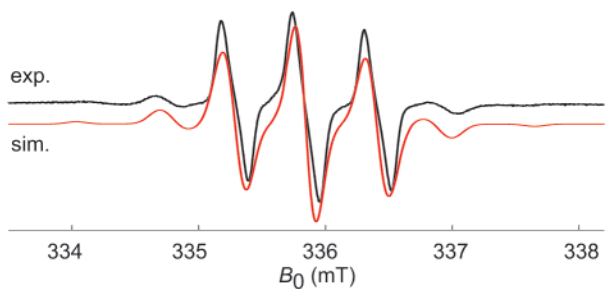
**SCHEME 2: Azo-bridged Fullerene Dimer Photoisomerization**


**Figure 1.** Electron spin  $T_1$  and  $T_2$  decay curves measured with an inversion recovery and a Hahn echo pulse sequence, respectively. The fit (red line) assumes relaxation by a fluctuating ZFS.

The endohedral fullerene species, N@C<sub>60</sub>-azo-C<sub>60</sub>, was prepared and purified in an analogous fashion using N@C<sub>60</sub>/C<sub>60</sub> (1/100) as starting material. The purification of N@C<sub>60</sub> is a very time-consuming process. Indeed it is not possible to produce the multimilligram quantities of high-purity N@C<sub>60</sub> (that would be required for the synthesis of N@C<sub>60</sub>-azo-N@C<sub>60</sub>) in a reasonable time scale. Nevertheless, the synthesis of N@C<sub>60</sub>-azo-C<sub>60</sub> is a useful “proof of principle” experiment.

The unpaired electron spin concentration of the endohedral containing fullerene dimer as determined from its CW EPR spectrum was found to be approximately 70% of that of the starting material. Photoisomerization of the N@C<sub>60</sub>-azo-C<sub>60</sub> dimer was implemented by the use of UV and visible light irradiation (Scheme 2). However, although the trans and cis isomers of azo dyes typically have distinct absorption spectra, in this case they could not be distinguished because of the comparatively much stronger absorption of the fullerene cage at 360 and 430 nm. We have shown previously that measurements of the electron spin lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times of a pyrrolidine-functionalized N@C<sub>60</sub> cage, N@C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>, show a biexponential decay in degassed CS<sub>2</sub> at room temperature. The zero field splitting (ZFS) parameter  $D_{\text{eff}}$  and the molecular rotational correlation time  $\tau_c$  can be deduced from  $T_1$  and  $T_2$  decay curves.<sup>10</sup> Similar pulse EPR measurements were adopted here to probe the switching between the two isomers of the fullerene dimer N@C<sub>60</sub>-azo-C<sub>60</sub>.

Electron spin  $T_1$  and  $T_2$  relaxation decays of the two isomers of N@C<sub>60</sub>-azo-C<sub>60</sub> in degassed CS<sub>2</sub> solution at room temperature, taken using the central nitrogen hyperfine line ( $M_1 = 0$ ), are shown in Figure 1. Data were obtained by illuminating using a light-emitting diode (LED) at the appropriate wavelength for



**Figure 2.** X-band CW EPR spectra of N@C<sub>60</sub>-azo-C<sub>60</sub> (powder, 2 G modulation, 270 s scan time, 99 scans, room temperature) and the fitted simulation.

20 min before each acquisition. As expected, both  $T_1$  and  $T_2$  decay curves show a biexponential decay as in the fulleropyrrolidine N@C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>.<sup>10</sup> Both  $T_1$  and  $T_2$  curves were fitted using ZFS fluctuation relaxation terms as described in work on fulleropyrrolidine N@C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>,<sup>10,12,13</sup> yielding a molecular rotation correlation time of  $\tau_c = 37.2 \pm 1.6$  ps (trans),  $\tau_c = 34.8 \pm 2.7$  ps (cis) and a ZFS term  $D_{\text{eff}} = 12.8 \pm 0.2$  MHz (trans),  $D_{\text{eff}} = 13.0 \pm 0.4$  MHz (cis). These values and errors were obtained from a nonlinear least-squares fit of the relaxation equations to the data (see the Supporting Information). These results suggest that the correlation time  $\tau_c$  of the trans isomer is slightly longer than that of the cis isomer, as might be expected from the change in molecular shape of the two isomers (trans being the bulkier of the two). Molecular tumbling of the fullerene dimer is slower than that of the fulleropyrrolidine N@C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> ( $\tau_c = 31.4$  ps),<sup>10</sup> resulting in longer electron spin relaxation times (Table S1 in the Supporting Information). The ZFS parameter  $D_{\text{eff}}$  is much bigger than that for N@C<sub>60</sub> but slightly smaller than that of the fulleropyrrolidine N@C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>10</sup> because of the cage deformation.

The powder CW EPR spectrum of the dimer is shown in Figure 2 and suggests a ZFS and hyperfine coupling similar to that measured in the fulleropyrrolidine N@C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>10</sup>:  $D = 16.1$  MHz,  $E = 0.7$  MHz,  $A_{xx} = A_{yy} = 14.6$  MHz, and  $A_{zz} = 18.6$  MHz. This  $D_{\text{eff}}$  is about 3 MHz larger than that deduced from pulse EPR relaxation measurements on a liquid solution. The ZFS depends on the electron density distribution of the encaged nitrogen, which reflects a distortion of the surrounded fullerene cage. This discrepancy could be explained by an additional strain present in the dimer in the solid state caused by a preference for the two fullerene moieties to occupy adjacent lattice sites.

## Conclusions

In summary, we have synthesized a photo-switchable fullerene dimer, one half of which comprised the endohedral N@C<sub>60</sub>. Evidence for the switching was obtained through molecular dynamics studies using pulse EPR. The same synthetic procedure could be used to produce a doubly filled dimer, amenable to investigation using electron–electron double resonance techniques.

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**Supporting Information Available:** Complete experimental details, molecular structure model, full HPLC chromatogram, mass spectra, UV–vis spectra, FTIR spectra, <sup>1</sup>H NMR spectra, <sup>13</sup>C NMR, 2D NMR spectra of the synthesis compounds, and EPR computation details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Benjamin, S. C.; Ardavan, A.; Briggs, G. A. D.; Britz, D. A.; Gunlycke, D.; Jefferson, J.; Jones, M. A. G.; Leigh, D. F.; Lovett, B. W.; Khlodystov, A. N.; Lyon, S.; Morton, J. J. L.; Porfyrakis, K.; Sambrook, M. R.; Tyryshkin, A. M. *J. Phys. Condens. Matter* **2006**, *18*, S867. (b) Meyer, C.; Harneit, W.; Weidinger, A.; Lips, K. *Phys. Status Solidi B* **2002**, *3*, 462.
- (2) Watt, A. A. R.; Sambrook, M. R.; Porfyrakis, K.; Lovett, B. W.; Mkami, H. E.; Smith, G. M.; Briggs, G. A. D. *Chem. Commun.* **2006**, *18*, 1944.
- (3) (a) Wang, G.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583. (b) Lebedkin, S.; Ballenweg, S.; Gross, J.; Taylor, R.; Kratschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971. (c) Balch, A.; Costa, D.; Noll, B.; Olmstead, M. *J. Am. Chem. Soc.* **1993**, *117*, 8926. (d) Drago, N.; Shimotani, H.; Wang, J.; Iwaya, M.; Bettencourt-Dias, A. de; Balch, A. L.; Kitazawa, K. *J. Am. Chem. Soc.* **2001**, *123*, 1294. (f) Paquette, L. A.; Graham, R. J. *J. Org. Chem.* **1996**, *60*, 2958. (g) Olmstead, M. M.; Costa, D. A.; Maitra, K.; Noll, B. C.; Phillips, S. L.; Calcar, P. M. Van; Balch, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 7090.
- (4) Hugel, T.; Holland, N. B.; Cattani, A.; Moroder, L.; Seitz, M.; Gaub, H. E. *Science* **2002**, *296*, 1103.
- (5) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
- (6) Masciello, L.; Potvin, P. G. *Can. J. Chem.* **2003**, *81*, 209.
- (7) Rodriguez, D. G.; Torres, T.; Guldi, D. M.; Rivera, J.; Herranz, M. A.; Echegoyen, L. *J. Am. Chem. Soc.* **2004**, *126*, 6301.
- (8) Maggini, M.; Dono, A.; Scorrano, G.; Prato, M. *Chem. Commun.* **1995**, 845.
- (9) Ros, T. D.; Prato, M.; Novello, F.; Maggini, M.; Banfi, E. *J. Org. Chem.* **1996**, *61*, 9070.
- (10) Zhang, J.; Morton, J. J. L.; Sambrook, M. R.; Porfyrakis, K.; Ardavan, A.; Briggs, G. A. D. *Chem. Phys. Lett.* **2006**, *432*, 523.
- (11) Zhang, J.; Porfyrakis, K.; Sambrook, M. R.; Ardavan, A.; Briggs, G. A. D. *J. Phys. Chem. B* **2006**, *110*, 16979.
- (12) Morton, J. J. L.; Tyryshkin, A. M.; Ardavan, A.; Porfyrakis, K.; Lyon, S. A.; Briggs, G. A. D. *J. Chem. Phys.* **2006**, *124*, 014508.
- (13) Carrington, A.; Luckhurst, G. R. *Mol. Phys.* **1964**, *8*, 125.