Communication

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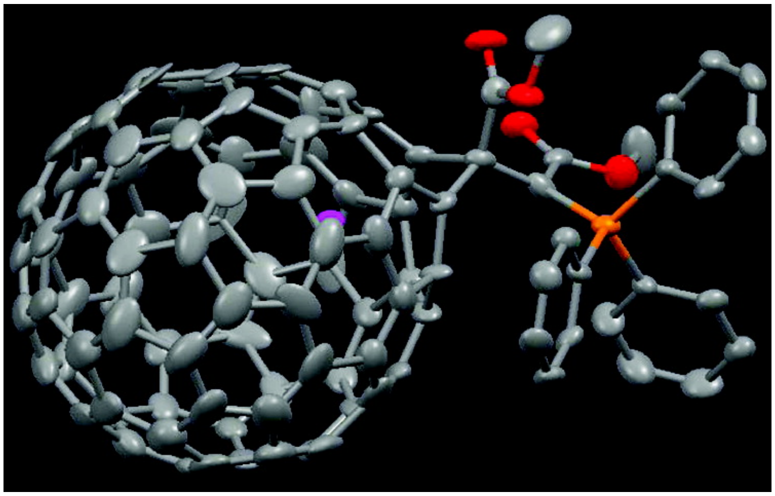

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Synthesis of a Dy@C_{82} Derivative Bearing a Single Phosphorus Substituent via a Zwitterion Approach

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Endohedral metallofullerenes (EMFs), with one or more metal atoms encapsulated inside a hollow fullerene cage, possess unique electronic structures and properties that are not expected for empty fullerenes.[1,2] Exohedral functionalization of EMFs is a key step to open their potential applications in many more fields. However, methods developed for the exohedral functionalization of EMFs are so far limited to Bingel−Hirsch reaction,[3] fluoroalkylation reaction,[4] and addition of carbenes,[5] azomethine ylides,[6] diene,[7] and disilirane.[8]

Recently, the derivatization of EMFs with polar substituents has attracted considerable attention due to their potential biomedical relevance.[9] The introduction of new polar functional groups onto a EMF moiety is not only helpful for understanding the intriguing chemistry of EMFs but also of practical significance in developing biomedical agents. One of the most difficult problems in the functionalization of metallofullerenes is to identify suitable, clean, and high yield reactions, which will facilitate the studies and applications of the EMF derivatives because purified EMFs are still not readily available. In this context, we report the regioselective synthesis of a Dy@C_{82} derivative bearing a single phosphorus substituent via a zwitterion intermediate, generated by the addition of a nucleophile to an activated electrophile.[10] This new metallofullerene reaction shows a high chemoselectivity markedly different from that of C_{60}.[11]

Scheme 1 illustrates the overall functionalization reaction. The synthesis is clean and simple, yet with a yield as high as 90%. Treatment of a toluene solution of Dy@C_{82} (C_{2v})[12] with dimethyl acetylenedicarboxylate (DMAD) and triphenylphosphine for 10 h at ambient temperature under nitrogen gave a metallofullerene monoadduct **1**.

As shown in Figure 1a, the HPLC chromatogram of the reaction mixture on a 5YPE column shows only one strong and sharp peak at ~7 min, which is attributed to monoadduct **1**. Notice that the Dy@C_{82} reagent was completely consumed and no bisadduct was formed under this reaction condition.

The monoadduct identity of the reaction product was verified by the matrix-assisted laser desorption ionization time-of-flight mass spectrum (MALDI-TOF MS) in Figure 1b. Aside from a distinct peak at m/z 1148, which is assigned to the fragment Dy@C_{82} arising from the laser desorption ionization, the mass spectrum also shows a weak but clear peak at m/z 1553, which can be precisely ascribed to the monoadduct **1**.

The UV−visible−NIR absorption spectrum of **1** (see Supporting Information) is similar to that of the reactant Dy@C_{82}, but the peaks are shifted from 640, 937, and ~1400 nm, respectively, to 653, 923, and ~1539 nm.[12] Similar observations have been reported on other EMF derivatives. This suggests that the localized covalent linkage of the substituents does not modify significantly the global electronic structure of the EMF.

Finally, the structure of **1**, which is shown in Figure 2, was unambiguously determined by the single-crystal X-ray diffraction measurement.[13] The dihedral angle for planes P1−C91−C90 and C93−O3−O4 is 18.6°, indicating the $\pi-\pi$ interaction between C91 and C93. The bond length of C91−C93 is 1.421 Å, consistent with a partial double bond between these two atoms. These data are in accord with those of the correspondent C_{60} derivative,[11a] showing that they both have the same adduct structure. Most remarkable is the large C1−C2 distance (2.153 Å), revealing the bond breakage due to the reaction as in the open structure of the carbene derivative of La@C_{82} (2.097 Å).[5]

Further insight into the electronic structure of **1**, modified from the intriguing electronic structure of Dy@C_{82}, can be gained by electrochemical measurements. Cyclic voltammograms of **1** and Dy@C_{82} (see Supporting Information) show similar features of reversible redox waves, which is reminiscent of their similar UV−vis−NIR spectra. However, the redox potentials of **1** experience a uniform negative shift of about 0.2 V relative to that of Dy@C_{82} (Table 1). Presumably, the covalent functionalization opens the C═C double bonds with an unpaired electron left behind on each carbon and thus modifies the local electronic structure and results in the negative shifts of the redox potentials. Nevertheless, the global electronic structure of the EMF is still largely preserved.

Our result shows that the addition of the zwitterion intermediate, which is generated by the attack of PPh_3 at an acetylene carbon,[11a] onto Dy@C_{82} occurs regioselectively on a [6,6] double bond, which also happens to be the position for addition of carbene to La@C_{82}.[5] On the other hand, the addition mode on Dy@C_{82} is in marked contrast with that on C_{60}. Whereas the [6,6]-fused fullerene structure was formed in the reaction of C_{60} with dimethyl acetylenedicarboxylate and triphenylphosphine,[11a] we obtained the [6,6]-bridged product rather than the [6,6]-fused product with Dy@C_{82} under the same reaction conditions. To understand this chemoselectivity, we have computed the [6,6]-bridged adduct at the BLYP/DNP level using DMol3.[14] The exothermicity for the [2 + 1] addition of the zwitterion intermediate to the Dy@C_{82} is about 16 kcal/mol. Upon the addition, the EMF C═C bond is cleaved with the C, C distance increasing from 1.44 to 2.16 Å, in agreement with the X-ray diffraction structure. We have tried to optimize the corresponding [6,6]-fused structure at the same theoretical level, but the geometry optimization leads eventually to the [6,6]-bridge structure. These computational results support that the [2 + 1] addition onto the

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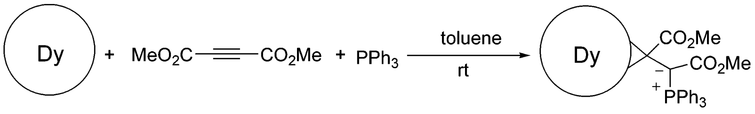
Scheme 1



Dy@C$_{82}$

1

Table 1. $E_{1/2}$ Potential (V vs Ag/AgCl) of the Dy@C$_{82}$ Derivative **1** and Dy@C$_{82}$ in Toluene/MeCN (4:1 v/v) Solution Containing 0.1 mol·L^{-1} TBAPF$_6$ (Scan Rate = 50 mV·s^{-1})

	reduction steps				
compound	1st	2nd	3rd	4th	oxidation step
1	−0.181	−1.155	−1.567		0.279
Dy@C$_{82}$	0.034	−0.686	−1.269	−1.643	0.461

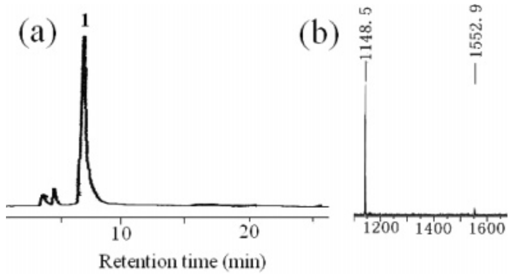


Figure 1. (a) HPLC chromatogram of the reaction mixture on a 5YPE column. Note that the two small peaks at ∼3.5 and 4.2 min are due to PPh$_3$ and its reaction product with DMAD, respectively (see Supporting Information). (b) MALDI-TOF mass spectrum of purified **1**.

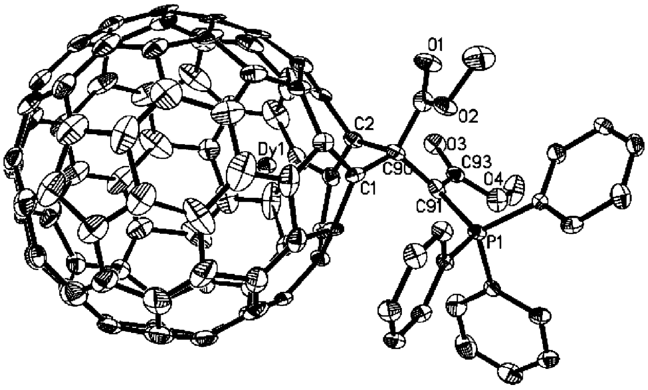


Figure 2. Thermal ellipsoid plot (30% probability) for compound **1**.

Dy@C$_{82}$ preferentially gives rise to a [6,6]-bridged adduct, not a [6,6]-fused adduct. The energetically favorable C=C bond breakage upon [2 + 1] cycloaddition can be ascribed to the high electron density in the bond-breaking region, to the strain energy release of the otherwise available three-membered ring, and to the aromatic stabilization of homoconjugation in the open structure.[15]

In conclusion, a Dy@C$_{82}$ derivative bearing a single phosphorus substituent has been obtained in a 90% yield by the regio- and chemoselective reaction of Dy@C$_{82}$ with dimethyl acetylenedicarboxylate and triphenylphosphine. The structure of the derivative has been determined by single-crystal X-ray diffraction measurement. Contrary to the product with a [6,6]-fused structure in the reaction of C$_{60}$, the reaction of the EMF leads to exclusively the product with a [6,6]-bridged structure. This chemoselectivity is supported by theoretical calculations. This EMF functionalization scheme is clean, simple, efficient, and amenable to additional chemical manipulations. Further derivatizations of **1** and the extension of the reaction to other endohedral metallofullerenes such as Sc$_3$N@C$_{80}$ are underway in our laboratory and will be reported in due course.

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Supporting Information Available: Detailed experimental procedures, UV−visible−NIR spectrum, cyclic voltammograms of **1**, selected X-ray crystallographic data of **1** in CIF format at 173 K, and complete lists of authors for references 3a,b, 5, 6a,b, 7a,d, and 8a−d. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data of **1**: C$_{106}$H$_{21}$DyO$_4$P, FW = 1551.7, 0.40 mm × 0.12 mm × 0.03 mm, monoclinic, space group $P2(1)/c$, a = 16.7121(6) Å, b = 18.3146(6) Å, c = 22.2350(7) Å, $\alpha = 90°$, $\beta = 110.742(2)°$, $\gamma = 90°$, $V = 6364.5(4)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.619$ g cm^{-3}, μ (Mo Kα) = 1.116 mm^{-1}, Bruker SMART, $\theta = 1.73-25.00°$, $T = 173$ K, $R_1 = 0.0754$ ($I > 2.0\sigma(I)$), $wR_2 = 0.2022$ (all data). The full list of coordinates of the other atomic sites and the X-ray data at 173 K are available in the Supporting Information.
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