

## ORIGINAL PAPER

## DFT study on [4+2] and [2+2] cycloadditions to [60] fullerene

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The functionalisation of C<sub>60</sub> fullerene with 2,3-dimethylene-1,4-dioxane (*I*) and 2,5-dioxabicyclo [4.2.0]octa-1(8),6-diene (*II*) was investigated by the use of density functional theory calculations in terms of its energetic, structural, field emission, and electronic properties. The functionalisation of C<sub>60</sub> with *I* was previously reported experimentally. The *I* and *II* molecules are preferentially attached to a C—C bond shared and located between two hexagons of C<sub>60</sub> via [4+2] and [2+2] cycloadditions bearing reaction energies of  $-15.9 \text{ kcal mol}^{-1}$  and  $-72.4 \text{ kcal mol}^{-1}$ , respectively. The HOMO–LUMO energy gap and work function of C<sub>60</sub> are significantly reduced following completion of the reactions. The field electron emission current of the C<sub>60</sub> surface will increase after functionalisation of either the *I* or *II* molecule.

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Fullerene-related materials have attracted considerable attention in the last decade due to their unique physical and chemical properties. In comparison with other carbon structures, fullerenes and carbon nanotubes have exhibited promising applications in a wide variety of important technological processes, such as in the design of electronic devices, superfibres and catalytic materials (Sapurina & Stejskal, 2009; Wang & Zheng, 2010; Robles-Nuñez et al., 2012). As such interesting candidates for constructing units of new materials, an increasing variety of species have been utilised for the functionalisation of fullerenes (Beheshtian et al., 2012a, 2012b; Champeil et al., 2008). These derivatives have also enhanced the stability of fullerenes (Ren et al., 2008), which might be of considerable interest for applications in medicinal chemistry, materials science, and nanotechnology (Prinzbach et al., 2000). However, the fullerenes suffer from poor solubility and are incompatible with solution-based processing. A standard way of improving the solubility is to prepare derivatives by adding some soluble func-

tional groups to the fullerenes. Hendersen and Cahill (1993) reported on the synthesis of C<sub>60</sub>H<sub>2</sub>, the simplest fullerene hydride of C<sub>60</sub>. Many years later, researchers investigated C<sub>50</sub>NCH<sub>3</sub>, C<sub>50</sub>CH<sub>2</sub>, and C<sub>50</sub>NH complexes using semi-empirical AM1 methods and ab initio calculations (Xu et al., 2008). The structure and thermodynamic stability of C<sub>60</sub>(glycine)<sub>*n*</sub> (where *n* = 1–4) were investigated in great detail (Hu & Ruckenstein, 2008; Ben Messaouda et al., 2007).

Exploration of the reactivity in addition to the reactions of the fullerenes aroused special interest in the preparation of specific fullerene derivatives by exohedral functionalisation. The thermal and photochemical cyclo-additions (Skanji et al., 2012) constitute the most useful methods of accessing functionalised fullerene derivatives, as the C<sub>60</sub> exhibits a marked propensity to function as a 2π component. In this context, [2+2], [3+2], [4+2], and higher order cyclo-additions have been performed successfully using this molecule. The Diels–Alder reactions were used extensively under thermal or high pressure conditions (Martin et al., 2010) to functionalise the fullerene surface, thereby obtaining mono- or poly-adducts (Kreher et

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