Synthesis and Properties of a Novel Redox System containing Fullerene and *p*-Benzoquinone

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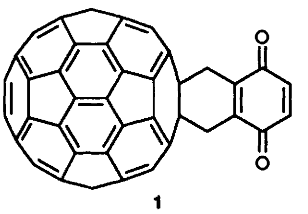
Synthesis of a fullerene derivative of *p*-benzoquinone was carried out using the [4 + 2]cycloaddition of C_{60} to 3,6-dihydroxybenzocyclobutene, followed by DDQ oxidation.

Buckminsterfullerene, C_{60}, is known to possess considerably high electron affinity and low ionization potential on the basis of both experimental measurements and theoretical calculations.[1] Thus, C_{60} can play the role as a π-acceptor and π-donor. Especially, the abilities of C_{60} as the π-acceptor are very important properties,[2] and the chemical and electrochemical reductions of C_{60} and its derivatives have been extensively studied.[3,4]

We are interested in the title compound **1**, because of a potential donor–acceptor interaction between fullerene and *p*-benzoquinone parts in **1**, and because of the opposite acceptor-donor interaction between C_{60} part and semiquinone radical or hydroquinone dianion in **2** and **3**. We report here the first synthesis of the fullerene derivative of quinones.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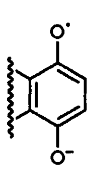
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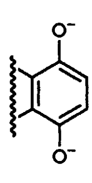
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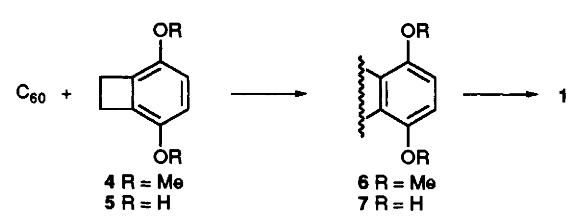

Scheme 1

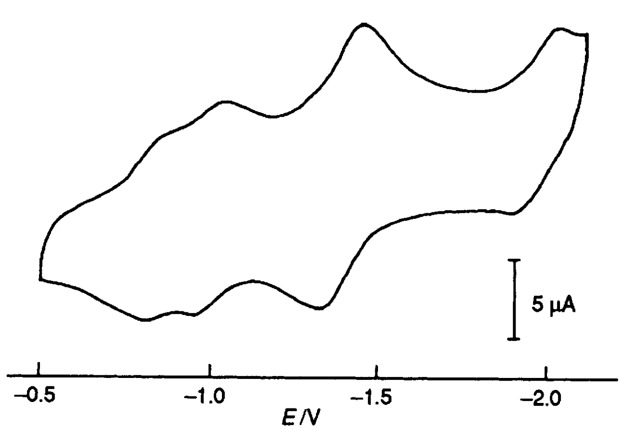

Fig. 1 Cyclic voltammogram of **1** in benzonitrile: sample, 2.5×10^{-4} mol dm^{-3}; supporting electrolyte (Bu_4NClO_6) 0.1 mol dm^{-3}; scan rate 0.1 V s^{-1}, *vs.* ferrocene/ferrocinium

Table 1 Redox potentials of C_{60}, **6**, and **1**[a]

Compound	$E_{red}^{quinone}$	E_{red}^{1}	E_{red}^{2}	E_{red}^{3}
C_{60}		−0.95	−1.35	−1.83
6		−1.07	−1.48	−2.00
1	−0.92	−1.10	−1.50	−2.07

[a] All potentials in V *vs.* ferrocene/ferrocinium; benzonitrile; 0.1 mol dm^{-3} Bu_4NPF_6; 0.1 Vs^{-1}.

To construct the novel redox system composed of fullerene and 1,4-hydroquinone or *p*-benzoquinone, C_{60} was allowed to react with 3,6-dimethoxybenzocyclobutene **4**[5] in *o*-dichlorobenzene at 220 °C for 24 h to give the mono-adduct **6**† in 44% yield, together with a mixture of isomers of the bis-adduct (34%) and the tris-adduct (11%). The removal of methyl groups in **6** was satisfactorily carried out using BBr_3. Thus, the reaction of **6** with an excess of BBr_3 in benzene at 5 °C–room temp. for 24 h to give the hydroquinone derivative **7**† in 80% yield. Furthermore, the reaction of C_{60} with 3,6-dihydroxybenzocyclobutene **5**[6] in *o*-dichlorobenzene at 230–235 °C for 24 h produced the mono-adduct **7** in one step in 32% yield. Oxidation of **7** with an excess of DDQ in benzene at room temp. for 15 min afforded the desired *p*-benzoquinone derivative **1**† in 98% yield. The compound **1** is stable and can be stored under air at room temp.

It is known that the adducts of C_{60} to *o*-quinodimethane usually show the inversion of six-membered ring, and the activation energy for the ring inversion is estimated to be $\Delta G\ddagger = 13.2–14.6$ kcal mol^{-1} (1 cal = 4.184 J).[7] Thus, **6** and **7** show similar activation energies for the ring inversion (**6**: $\Delta G\ddagger = 13.7$ kcal mol^{-1} at 25 °C; **7**: $\Delta G\ddagger = 14.2$ kcal mol^{-1} at 40 °C). Interestingly, **1** shows the much lower activation energy ($\Delta G\ddagger$ 11.0 kcal mol^{-1} at −30 °C), although the quinone part of **1** may reduce the torsional and angular constraints. We now expect that the low barrier of inversion in **1** might be attributable to an electronic repulsion between the fullerene π-electron and the quinone part (acceptor-acceptor interaction).

In order to estimate the π–π interaction between the fullerene and quinone parts in **1**, redox potentials of **1**,**6** and C_{60} were measured by cyclic voltammetry. As shown in Table 1 and Fig. 1, **1** shows interesting redox properties. Thus, **6** shows typical three reduction waves which are cathodically shifted by 0.12 to 0.17 V as compared with those of C_{60}.[8] In contrast, four reduction waves were observed in the case of **1** (Fig. 1). The first reduction is assigned to the reduction of *p*-benzoquinone part to the corresponding semiquinone radical **2**. The second reduction (E_{red}^{1}) corresponds to the reduction of the fullerene part to the fullerene anion radical. The third reduction (E_{red}^{2}) seems to be two electron reduction to form the tetraanion, *i.e.* C_{60}^{2-}–$(CH_2)_2$–$C_6H_2O_2^{2-}$. Therefore, some interactions between the fullerene and *p*-benzoquinone parts can be expected in the anionic species.

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Footnote

† Selected data for new fullerene derivatives. **6**: mp 350–360 °C (decomp.); FAB-MS *m/z* 885 (M + 1); ^1H NMR ($CDCl_3$, −50 °C) δ 3.96 (s, 6H, OCH_3), 4.33 (d, 2H, *J* 13.9 Hz, CH_2), 4.93 (d, 2H, *J* 13.9 Hz, CH_2) and 7.05 (s, 2H, =CH). **7**: mp 280–300 °C (decomp.);

FAB–MS *m/z* 857 (M + 1); ^{1}H NMR ([^{2}H$_8$]toluene, −15 °C) δ 4.00 (d, 2H, *J* 14.2 Hz, CH$_2$), 4.86 (d, 2H, *J* 14.2 Hz, CH$_2$), 4.14 (s, 2H, OH) and 6.25 (s, 2H, =CH). **1**: mp 330–340 °C (decomp.); FAB–MS *m/z* 856 (M + 2); ^{1}H NMR (CD$_2$Cl$_2$, −70 °C) δ 4.11 (d, 2H, *J* 15.1 Hz, CH$_2$), 4.80 (d, 2H, *J* 15.1 Hz, CH$_2$), 7.09 (s, 2H, =CH); ^{13}C NMR (CS$_2$/[^{2}H$_6$]acetone, room temp.) δ 38.5 (CH$_2$), 65.8 (C$_{60}$), 136.3 (CH=CH), 137.3 (C=C), 184.0 (C=O), 141.0, 142.5, 142.9, 143.4, 143.9, 144.6, 145.4, 146.0, 146.3, 146.4, 146.6, 147.1, 147.3, 148.5 and 159.7 (15 signals of C$_{60}$).

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