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Selective addition to [60]fullerene of two different radicals generated from Mn(III)-based radical reaction

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Received 5th January 2004, Accepted 27th February 2004
First published as an Advance Article on the web 18th March 2004

Reaction of [60]fullerene in toluene with diethyl methylmalonate (**3a**), diethyl ethylmalonate (**3b**), diethyl bromomalonate (**3c**), triethyl methanetricarboxylate (**3d**) and ethyl cyanoacetate (**3e**) in the presence of manganese(III) acetate dihydrate afforded benzyl-substituted unsymmetrical 1,4-adducts **4a**–**4e**. Dibenzylated 1,4-adduct **5** and methanofullerene **6** were also obtained in the case of **3d** and **3e**, respectively. A possible reaction mechanism for the formation of the 1,4-adducts **4a**–**4e** is proposed.

Introduction

Fullerene radical reactions were one of the first fullerene reactions to be investigated and are still of interest for adding functional groups to fullerenes.[1–5] Fullerene radicals can be formed by single electron transfer,[6–12] oxidation of fullerene anions[13–17] and direct addition of radicals to fullerenes.[18–28] When free radicals react with fullerenes, many, barely separable, multiaddition products are usually obtained.[18,19] For example, it was reported that up to eleven phenyl groups, fifteen benzyl groups and thirty four methyl groups were added to [60]fullerene (C_{60}).[18,19] However, for certain fullerene radical reactions a limited number of products were generated and could be separated out. Fukuda and co-workers reported the synthesis of the 1,4-bisadduct $C_{60}(CHPhCH_2O_2CPh)_2$ by using BS-TEMPO as a radical source.[21] Formation of 1,2-, 1,4-, and even 1,16-bisadduct $C_{60}(C(CH_3)_2R)_2$ has been achieved by the reaction of C_{60} with 2,2′-azobisisobutyronitrile or with 2,2′-azobisisobutyrate under thermal conditions.[24,25] Gan *et al.* reported that fullerenes can be used as a *tert*-butylperoxy radical trap to form fullerene mixed peroxides $C_{60}(O)(OO^tBu)_4$ and $C_{70}(OO^tBu)_{10}$.[26] Recently Aksaka *et al.* described the formation of bisadducts $C_{60}(SiRR'_2)_2$ and tetrakisadduct $C_{60}(SiPh_2{}^tBu)_4$, with a 1,16-addition pattern, by photochemical reaction of C_{60} with disilanes.[27,28] As shown from the above radical addition reactions, the addends of fullerene derivatives were commonly the same. Here, we describe the novel selective radical addition reaction of C_{60} and two different radicals, *i.e.*, $PhCH_2\cdot$ and $\cdot CR_1R_2COOEt$.

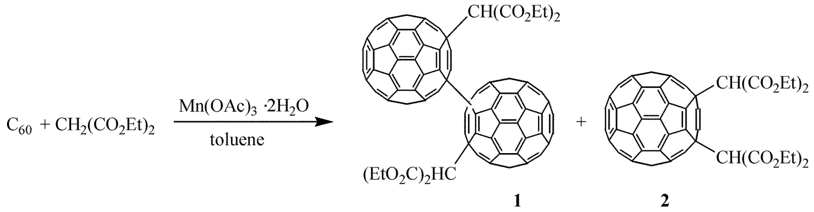
Results and discussion

We have recently reported that manganese(III) acetate dihydrate successfully abstracts a hydrogen radical from active methylene compounds to form methine radicals which then react with C_{60}.[29] The facile C_{60}–C_{60} bond cleavage of dimer **1** was found to occur in refluxing chlorobenzene and lead to the formation of compound **2** and C_{60}.[29] In order to determine if the transformation of dimer **1** to compound **2** can be avoided at a lower temperature, toluene was chosen as the solvent to investigate this reaction again. As expected, the reaction of C_{60} (43.2 mg), diethyl malonate and manganese(III) acetate dihydrate in 1 : 2 : 2 molar ratio afforded dimer **1** in 16% yield (55% based on consumed C_{60}) after 1 h reflux in toluene, along with a trace of 1,4-adduct **2** (Scheme 1).

Krusic *et al* reported that a number of adducts R_nC_{60} ($R = C_6H_5CH_2$, n = 1–15) were produced when they irradiated a toluene solution of C_{60} and di-*tert*-butyl peroxide.[18] The benzyl radical was generated through hydrogen atom abstraction, from the bulk solvent toluene, by the photochemically-formed *tert*-butoxy radical. Here the benzyl radical was not involved in the manganese(III) acetate dihydrate-mediated radical reaction of C_{60} with diethyl malonate (Scheme 1), just as no solvent participated in the photochemical reaction of 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-1,2-disilane with a toluene solution of C_{60}.[28] However, several benzyl-substituted unsymmetrical 1,4-adducts were obtained in moderate yields when substituted malonates and ethyl cyanoacetate were used. As shown in Scheme 2, a mixture of 43.2 mg of C_{60}, 2 equivalents of compound **3** and 2 equivalents of manganese(III) acetate dihydrate was refluxed in toluene for 2 h to provide products **4a**, **4b**, **4c**, **4d** and **4e** in moderate yields (Scheme 2).

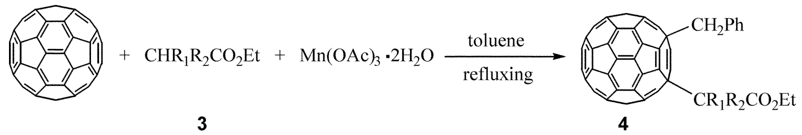
The product yields along with the amount of recovered C_{60} for the reaction of C_{60} with substituted malonates **3a**–**3d** and ethyl cyanoacetate **3e** in refluxing toluene for 2 h are listed in Table 1.

The structure of **4a**, having a C_1 symmetry with a benzyl and a malonyl group attached to the 1,4-position of a six-membered-ring of C_{60}, was determined based on its APCI MS, UV-vis, FT-IR, ^{1}H NMR and ^{13}C NMR spectral data. APCI-MS of **4a** gave a weak molecular ion peak at *m*/*z* 984 but a relative strong peak at *m*/*z* 811 that arose from the fragment of a benzyl group attached to C_{60}. The facile C_{60}-malonyl bond cleavage of **4a** occurred in the MS measurement. The UV-vis spectrum of **4a** exhibited a characteristic absorption pattern for the 1,4-adduct of C_{60}, *i.e.*, a rather broad absorption at 447 nm. In the ^{13}C NMR spectrum of **4a** the signals at 47.79 ppm for CH_2 in the benzyl group and at 59.72 ppm for the *sp*^{3} carbon



Scheme 1

DOI: 10.1039/b317084e



	R_1	R_2
3a, **4a**:	CO_2Et	Me
3b, **4b**:	CO_2Et	Et
3c, **4c**:	CO_2Et	Br
3d, **4d**:	CO_2Et	CO_2Et
3e, **4e**:	CN	H

Scheme 2

Table 1 Yields of **4a**–**4e** for the reaction of C_{60} with substituted malonates **3a**–**3d** and ethyl cyanoacetate **3e**

Substrate	Product	Yield[a]	Recovered C_{60}
$CH_3CH(COOEt)_2$	**4a**	62%	53%
$CH_3CH_2CH(COOEt)_2$	**4b**	62%	58%
$BrCH(COOEt)_2$	**4c**	56%	48%
$CH(CO_2Et)_3$	**4d**	31%	42%
$CNCH_2CO_2Et$	**4e**	19%	52%

[a] Yield based on consumed C_{60}.

of C_{60} that is linked directly with benzyl group are very close to other benzyl-substituted [60]fullerene derivatives.[30,31] The phenyl carbons were located at 126.97, 127.83, 130.49 and 135.13 ppm. Forty nine signals between 136 ppm and 157 ppm, of which 7 peaks corresponded to two carbon atoms and 1 peak corresponded to three carbon atoms, and two sp^3 carbons of C_{60} at 59.72 and 61.65 ppm were assigned to 60 carbons of the C_{60} skeleton, fully consistent with its molecular structure with C_1 symmetry.

The identities of 1,4-adducts **4b**–**4e** were confirmed similarly by the APCI MS, UV-vis, FT-IR, ^{1}H NMR and ^{13}C NMR spectral data. It should be noted that the ^{1}H NMR and ^{13}C NMR spectra of compound **4e** showed the existence of two isomers due to the different space orientations of the cyano and ester groups. This observation was consistent with theoretical calculations by the B3LYP/3-21G*//PM3 method, which showed that isomer **A** is more stable than isomer **B** by 3.8 kcal mol^{-1}. In addition, the ^{1}H NMR signal arising from the methine group bonded to C_{60} in **4e** appeared at an unexpectedly high field (2.70 and 2.41 ppm for isomers **A** and **B,** respectively), which may be attributed to the magnetic anisotropy effect on the methine proton caused by the phenyl group.[32] The conformations of **4e** calculated by the PM3 method revealed that the methine proton is very close to the phenyl group and lies in the shielding region of the phenyl ring (Fig. 1).

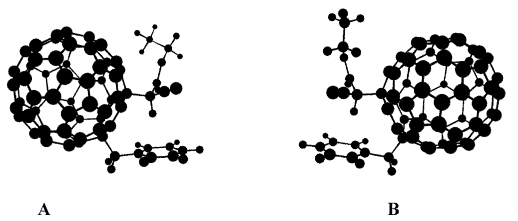


Fig. 1 The optimized structures of isomers **A** and **B** of **4e** obtained by PM3 calculations.

It is noteworthy that in the reaction of C_{60} with diethyl bromomalonate and manganese(III) acetate dihydrate, bromomalonyl radical was formed preferentially, which was consistent with the results in the literature[29,33] In addition, an obvious difference between **3d** and **3a-3c** for the Mn(III)-based radical reactions was observed. Under the same reaction conditions, compound **3d** afforded an additional product: a dibenzylated 1,4-adduct **5** in low yield (8%, 14% based on consumed C_{60}), which resulted from the addition of two benzyl radicals. Comparison of the ^{1}H NMR and ^{13}C NMR spectra of compound **5** with those reported in the literature[30] proved its identity (Fig. 2). When our protocol was extended to the manganese(III) acetate dihydrate-mediated radical reaction of C_{60} with ethyl cyanoacetate in toluene, methanofullerene **6**[34] (Fig. 2) was obtained in 16% yield (33% based on consumed C_{60}) in addition to the expected 1,4-adduct **4e**.

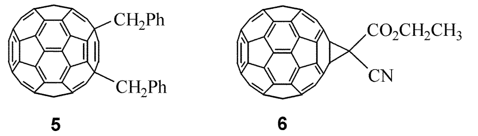


Fig. 2

Although at present the detailed mechanism of the selective addition of benzyl radical and substituted malonyl radical/cyanoacetate radical is not very clear, a possible pathway is proposed in Scheme 3.

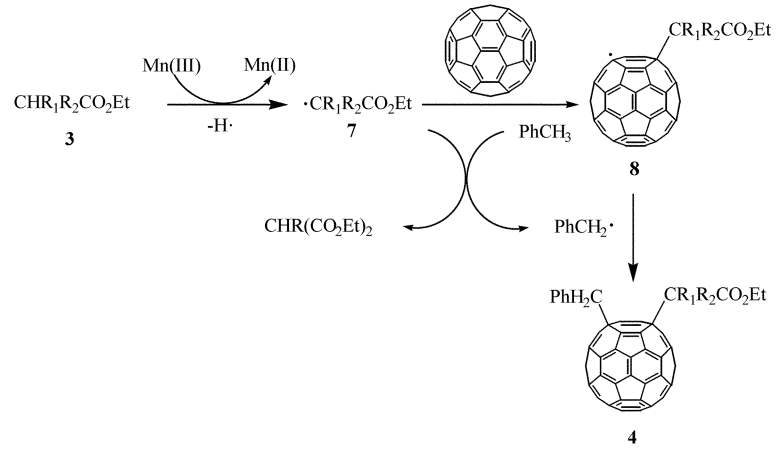
Radical **7** is formed *in situ via* the oxidation of substituted malonates and ethyl cyanoacetate by manganese(III) acetate dihydrate. As a good electron acceptor, C_{60} can be easily attacked by radical **7** to provide fullerene radical **8**. Radical coupling of **8** with benzyl radical, which is generated from the hydrogen atom abstraction from the bulk toluene by radical **9**, affords unsymmetrical 1,4-adduct **4**. The lack of the formation of 1,2-adduct is due to strong steric interaction between the bulky substituted malonate/ethyl cyanoacetate and benzyl groups. The symmetrical 1,4-dibenzyl fullerene C_{60} derivative **5** is produced by the addition of two benzyl radicals to C_{60}. The formation mechanism of methanofullerene derivative **6** should be the same as we proposed previously.[29]

In conclusion, addition of two different free radicals to C_{60} to afford benzyl-substituted unsymmetrical 1,4-adducts **4a**–**4e** has been achieved for the reactions of diethyl methylmalonate, diethyl ethylmalonate, diethyl bromomalonate, triethyl methanetricarboxylate and ethyl cyanoacetate with toluene solutions of C_{60} in the presence of maganese(III) acetate dihydrate. This result is different from previous work on the free radical reactions of the toluene solution of C_{60}, in which toluene was either not involved or where numerous products by the multiple addition of benzyl groups were obtained. The possible formation mechanism of the 1,4-adduct **4a**–**4e** is proposed.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, in $CDCl_3$ or CS_2-$CDCl_3$. All intensities in the ^{13}C NMR spectral data are 1C unless otherwise noted. FT-IR spectra were recorded on a VECTOR22 FT-IR spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2100PC spectrophotometer. Mass spectra were taken on a Finigan-MAT TSQ 700 Spectrometer. C_{60} (>99.9%) was purchased from 3D Carbon Cluster Material Co. of Wuhan University in China. All other reagents were commercially obtained and of R. A. grade.



Scheme 3

Reaction of C_{60} with diethyl methylmalonate and $Mn(OAc)_3·2H_2O$

A mixture of C_{60} (43.2 mg, 0.06 mmol), diethyl methylmalonate (21.0 μL, 0.12 mmol) and $Mn(OAc)_3·2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 40 mL of toluene for 2 h. The solvent was removed under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give product **4a** (17.1 mg, 62% based on consumed C_{60}) along with recovered C_{60} (23.0 mg, 53%).

Spectral data of **4a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 3H, CH_3), 1.43 (t, J = 7.2 Hz, 3H, CH_3), 2.62 (s, 3H, CH_3), 4.31–4.57 (m, 6H, OCH_2 and $PhCH_2$), 7.30–7.42 (m, 3H, Ph), 7.61 (d, J = 7.0 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.64 ($OCH_2\mathit{C}H_3$), 13.71 ($OCH_2\mathit{C}H_3$), 21.64 ($\mathit{C}H_3$), 47.80 ($\mathit{C}H_2Ph$), 59.72 (*sp*^{3}-*C* of C_{60}), 61.16 ($\mathit{C}CH_3$), 61.65 (*sp*^{3}-*C* of C_{60}), 61.78 ($O\mathit{C}H_2CH_3$), 61.86 ($O\mathit{C}H_2CH_3$), 126.97 (aryl *C*), 127.83 (aryl *C*, 2C), 130.49 (aryl *C*, 2C), 135.13 (aryl *C*), 136.68, 138.39, 138.52, 138.92, 139.73, 139.76, 141.25, 141.58, 141.82 (2C), 141.99, 142.10, 142.17 (2C), 142.27, 142.32, 142.42, 142.46, 142.67 (2C), 142.75, 142.80, 143.20 (2C), 143.35, 143.45, 143.54, 143.64 (2C), 143.67, 143.76, 143.80, 143.94, 143.97, 143.02, 144.28, 144.40, 144.49, 145.07 (2C), 145.91, 146.17, 146.27, 146.43 (2C), 146.46, 146.58, 146.68, 147.34, 147.82, 147.94, 148.24, 148.71 (3C), 151.60, 153.59, 156.68, 169.27 (COO), 169.64 (COO); MS (APCI) *m*/*z* 984 (M^-); IR υ/cm^{-1} (KBr) 2921, 2851, 1732, 1637, 1493, 1453, 1378, 1257, 1109, 1020, 753, 670, 575, 528; UV-vis λ_{max}/nm ($CHCl_3$) 256, 330, 447, 534, 618, 688.

Reaction of C_{60} with diethyl ethylmalonate and $Mn(OAc)_3·2H_2O$

A mixture of C_{60} (43.2 mg, 0.06 mmol), diethyl ethylmalonate (22.6 μL, 0.12 mmol) and $Mn(OAc)_3·2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 40 mL of toluene for 2 h. The solvent was removed under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give product **4b** (15.6 mg, 62% based on consumed C_{60}) along with recovered C_{60} (25.1 mg, 58%).

Spectral data of **4b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36–1.49 (m, 9H, CH_2CH_3 and OCH_2CH_3), 3.08–3.22 (m, 2H, CH_2CH_3), 4.27–4.55 (m, 4H, OCH_2), 4.39 (d, J_{ab} = 12.9 Hz, 1H, $PhCH_2$), 4.56 (d, J_{ab} = 12.9 Hz, 1H, $PhCH_2$), 7.29–7.38 (m, 3H, Ph), 7.58 (d, J = 7.0 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.92 ($CCH_2\mathit{C}H_3$), 14.28 ($OCH_2\mathit{C}H_3$), 14.39 ($OCH_2\mathit{C}H_3$), 28.92 ($\mathit{C}H_2CH_3$), 48.18 ($Ph\mathit{C}H_2$), 60.17 (*sp*^{3}-*C* of C_{60}), 61.81 ($O\mathit{C}H_2CH_3$), 61.98 ($O\mathit{C}H_2CH_3$), 62.06 (*sp*^{3}-*C* of C_{60}), 66.55 ($\mathit{C}CH_2CH_3$), 127.34 (aryl *C*), 128.27 (aryl *C*, 2C), 130.90 (aryl *C*, 2C), 135.48 (aryl *C*), 137.18, 138.37, 138.92, 138.98, 140.23, 140.27, 141.79, 142.07, 142.29 (2C), 142.46, 142.51, 142.60 (2C), 142.77 (2C), 142.83, 142.90, 143.08, 143.13, 143.17, 143.24, 143.58, 143.69, 143.78 (2C), 143.93, 144.06, 144.09, 144.13, 144.16, 144.19, 144.22, 144.37, 144.44, 144.81 (2C), 144.99, 145.50, 145.53, 146.01, 146.69, 146.71, 146.83 (2C), 146.90, 147.01, 147.14, 147.64, 148.24, 148.37, 148.66, 149.00, 144.08, 149.31, 152.03, 153.86, 157.02, 168.51 (COO), 168.94 (COO); MS (APCI) *m*/*z* 998 (M^-); IR υ/cm^{-1} (KBr) 2974, 1727, 1493, 1453, 1429, 1365, 1234, 1189, 1127, 1023, 750, 698, 575, 527; UV-vis λ_{max}/nm ($CHCl_3$) 258, 328, 448, 537, 617, 688.

Reaction of C_{60} with diethyl bromomalonate and $Mn(OAc)_3·2H_2O$

A mixture of C_{60} (43.2 mg, 0.06 mmol), diethyl bromomalonate (21.0 μL, 0.12 mmol) and $Mn(OAc)_3·2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 40 mL of toluene for 2 h. The solvent was removed under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give product **4c** (18.3 mg, 56% based on consumed C_{60}) along with recovered C_{60} (20.7 mg, 48%).

Spectral data of **4c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.50 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 4.39–4.68 (m, 4H, OCH_2), 4.58 (d, J_{ab} = 13.0 Hz, 1H, $PhCH_2$), 4.79 (d, J_{ab} = 13.0 Hz, 1H, $PhCH_2$), 7.32–7.42 (m, 3H, Ph), 7.65 (d, J = 7.2 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.38 ($OCH_2\mathit{C}H_3$), 13.45 ($OCH_2\mathit{C}H_3$), 47.80 ($Ph\mathit{C}H_2$), 59.85 (*sp*^{3}-*C* of C_{60}), 61.50 (*sp*^{3}-*C* of C_{60}), 63.43 ($O\mathit{C}H_2$, 2C), 68.33 ($\mathit{C}Br$), 126.81 (aryl *C*), 127.70 (aryl *C*, 2C), 130.45 (aryl *C*, 2C), 135.41 (aryl *C*), 136.28, 137.74, 138.74, 139.15, 139.35, 139.69, 140.78, 141.22, 141.45, 141.65, 141.78, 141.85 (2C), 141.98, 142.03 (2C), 142.10, 142.33, 142.59, 142.66, 142.68, 142.78, 143.16, 143.27 (3C), 143.35 (2C), 143.40, 143.53 (2C), 143.59, 143.74, 143.84, 143.87, 144.11, 144.25, 144.56, 145.01 (2C), 145.74, 145.94, 146.13, 146.27, 146.35 (2C), 146.46, 146.60, 147.27, 147.45, 147.77 (2C), 148.23, 148.53, 149.99, 151.15, 151.96, 156.62, 164.65 (COO), 165.10 (COO); MS (APCI) 969 (M − Br); IR υ/cm^{-1} (KBr) 2921, 1743, 1493, 1453, 1429, 1365, 1245, 1181, 1042, 758, 699, 575, 527; UV-vis λ_{max}/nm ($CHCl_3$) 257, 328, 448, 536, 617, 688.

Reaction of C_{60} with triethyl methanetricarboxylate and $Mn(OAc)_3·2H_2O$

A mixture of C_{60} (43.2 mg, 0.06 mmol), triethyl methanetricarboxylate (25.0 μL, 0.12 mmol) and $Mn(OAc)_3·2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 40 mL of toluene for 2 h. The solvent was removed under reduced pressure and the residue was separated on silica gel column with toluene as the eluent to give product **4d** (11.3 mg, 31% based on consumed C_{60}) and product **5**[30] (4.3 mg, 14% based on consumed C_{60}) along with recovered C_{60} (18.0 mg, 42%).

Spectral data of **4d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (t, J = 7.2 Hz, 9H, CH_3), 4.48 (d, J_{ab} = 12.9 Hz, 1H, $PhCH_2$), 4.53 (q, J = 7.2 Hz, 6H, OCH_2), 4.66 (d, J_{ab} = 12.9 Hz, 1H, $PhCH_2$), 7.26–7.40 (m, 3H, Ph), 7.65 (d, $J = 7.0$ Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.70 ($OCH_2\mathit{C}H_3$, 3C), 47.26 ($Ph\mathit{C}H_2$), 59.21 (sp^3-*C* of C_{60}), 60.48 (sp^3-*C* of C_{60}), 62.70 ($O\mathit{C}H_2$, 3C), 72.30 ($\mathit{C}(CO_2Et)_3$), 126.84 (aryl *C*), 127.81 (aryl *C*, 2C), 130.85 (aryl *C*, 2C), 135.92 (aryl *C*), 136.24, 138.09, 138.97, 139.14, 139.45, 139.79, 141.15, 141.40, 141.78, 141.95, 141.98, 142.12 (2C), 142.28, 142.30 (2C), 142.35, 142.58, 142.83, 142.90, 142.92, 143.03, 143.45 (2C), 143.55, 143.58, 143.61, 143.72, 143.80 (3C), 143.95 (2C), 144.14 (2C), 144.37, 144.61, 144.74, 145.25 (2C), 146.20, 146.24, 146.38, 146.54, 146.61, 146.69 (2C), 146.89, 147.56, 147.95, 147.99, 148.34, 148.46, 149.27, 150.34, 152.07, 153.06, 157.32, 164.47 (COO), 164.68 (COO); MS (APCI) m/z 811 ($M - C(CO_2Et)_3$); IR υ/cm^{-1} (KBr) 2976, 2923, 1750, 1493, 1453, 1440, 1429, 1365, 1255, 1180, 1082, 1047, 1011, 670, 575, 527; UV-vis λ_{max}/nm ($CHCl_3$) 257, 329, 448, 537, 617, 688.

Reaction of C_{60} with ethyl cyanoacetate and $Mn(OAc)_3 \cdot 2H_2O$

A mixture of C_{60} (43.2 mg, 0.06 mmol), ethyl cyanoacetate (25.6 µL, 0.24 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 40 mL of toluene for 3 h. The solvent was removed under reduced pressure and the residue was separated on silica gel column with toluene as the eluent to give product **6**[34] (8.0 mg, 33% based on consumed C_{60}) and compound **4e** (5.0 mg, 19% based on consumed C_{60}) along with recovered C_{60} (22.4 mg, 52%).

Spectral data of **4e**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, $J = 6.9$ Hz, 3H, for isomer **B**), 1.42 (t, $J = 6.9$ Hz, 3H, for isomer **A**), 2.41 (s, 1H, for isomer **A**), 2.70 (s, 1H, for isomer **B**), 4.27 (q, $J = 6.9$ Hz, 2H, for isomer **A**), 4.31 (d, $J_{ab} = 12.9$ Hz, 1H, for isomer **A**), 4.35 (d, $J_{ab} = 12.9$ Hz, 1H, for isomer **B**), 4.36 (q, $J = 6.9$ Hz, 2H, for isomer **B**), 4.45 (d, $J_{ab} = 12.9$ Hz, 1H, for isomer **A**), 4.48 (d, $J_{ab} = 12.9$ Hz, 1H, for isomer **B**), 7.48–7.72 (m, 4H, for isomer **A** and **B**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.10 ($OCH_2\mathit{C}H_3$, isomer **B**), 14.18 ($OCH_2\mathit{C}H_3$, isomer **A**), 46.84 ($Ph\mathit{C}H_2$, isomer **B**), 47.05 ($Ph\mathit{C}H_2$, isomer **A**), 48.62 (*C*H, isomer **A**), 48.77 (*C*H, isomer **B**), 55.39 (sp^3-*C* of C_{60}, isomer **A**), 55.60 (sp^3-*C* of C_{60}, isomer **B**), 60.48 (sp^3-*C* of C_{60}, isomer **A**), 60.55 (sp^3-*C* of C_{60}, isomer **B**), 62.88 ($O\mathit{C}H_2$, isomer **B**), 62.97 ($O\mathit{C}H_2$, isomer **A**), 114.08 (CN, isomer **A**), 114.79 (CN, isomer **B**), 127.80 (aryl *C*, isomer **B**), 127.98 (aryl *C*, isomer **A**), 128.82 (aryl *C*, 2C, isomer **B**), 128.94 (aryl *C*, 2C, isomer **A**), 131.03 (aryl *C*, 4C, isomers **A** and **B**), 136.10 (aryl *C*, 2C, isomer **B**), 136.32 (aryl *C*, 2C, isomer **A**), 137.55–157.19 (sp^2 carbons of C_{60}, isomers **A** and **B**), 162.24 (*C*OO, isomer **B**), 162.84 (*C*OO, isomer **A**); MS (APCI) *m*/*z* 922 ($M - H$); IR υ/cm^{-1} (KBr) 2916, 1747, 1510, 1456, 1429, 1242, 1188, 1028, 701, 575, 528, 418; UV-vis λ_{max}/nm ($CHCl_3$) 257, 329, 448, 538, 617, 688.

Acknowledgements

We thank financial support from the National Science Fund for Distinguished Young Scholars (21025205), Fund for Innovative Research Group of the National Science Foundation of China (20321101) Anhui Provincial Bureau of Personnel Affairs (2001Z019) and Anhui Provincial Natural Science Foundation (00045306). We appreciate Professor Koichi Komatsu at Kyoto University for his encouragement and helpful discussions and Dr Yasujiro Murata at Kyoto University for recording the MS spectra of **4** and NMR spectra of **4e**.

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