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Reaction of [60]fullerene with free radicals generated from active methylene compounds by manganese(III) acetate dihydrate

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The reaction of [60]fullerene with dimethyl malonate and diethyl malonate in the presence of manganese(III) acetate dihydrate ($Mn(OAc)_3{\cdot}2H_2O$) for 20 min afforded singly bonded [60]fullerene dimers **1a** and **1b** in a 1,4-addition pattern. When the reaction time was extended to 1 h, 1,4-bisadducts **2a** and **2b** were obtained. Unsymmetrical 1,4-adduct **5** and C_2 symmetrical 1,16-bisadduct **6** were obtained when diethyl bromomalonate was used as the active methylene compound. Reaction of [60]fullerene with malononitrile and ethyl cyanoacetate with the aid of $Mn(OAc)_3{\cdot}2H_2O$ produced methanofullerenes **7** and **8**. It is proposed that all these products were formed *via* the addition of free radicals from the active methylene compounds generated by $Mn(OAc)_3{\cdot}2H_2O$.

Introduction

Over the past ten years a number of effective methods for fullerene functionalizations have been discovered.[1–5] Fullerene reactions involving free radicals are apparently one of the important methods for fullerene functionalizations.[6–21] Generally, there are three forms of fullerenes that take part in radical reactions, that is, fullerene radical anions (such as $C_{60}^{\bullet -}$) generated by reduction with an electron donor,[6–9] fullerene radical derivatives (such as $RC_{60}^{\bullet}$) produced by nucleophilic addition followed by oxidation,[10–13] and neutral fullerenes (such as C_{60}) which react directly with free radicals.[14–21] Multi-addition is liable to occur when parent fullerenes react with free radicals and tend to give a reaction mixture of many and hardly separable products.[14,15] For example, up to 11 phenyl groups, 15 benzyl groups and 34 methyl groups have been reported to add to [60]fullerene.[14,15] Nevertheless, under appropriate controlled conditions, much fewer products resulting from fullerene radical reaction could be separated and characterized. Yoshida *et al.* reported the preparation of fluoroalkyl-modified fullerene $C_{60}(R_F)H$ and the singly bonded fullerene dimers R_FC_{60}–$C_{60}R_F$ through the radical addition reaction of C_{60} with diacyl peroxide $(CF_3COO)_2$ in the presence of Bu_3SnH upon heating[17] or with perfluoroalkyl iodides R_FI in the presence of $(R_3Sn)_2$ upon photoirradiation.[18] Ando's group described the formation of 1,16-adducts *via* a silyl radical addition process and 1,2-adducts *via* 1,4-silyl migration in the photochemical reactions of substituted phenylpolysilanes with [60]fullerene.[19] Formation of 1,2-, 1,4-, and even 1,16-bisadducts have been achieved by the reaction of [60]fullerene with 2,2′-azo(bisisobutyronitrile) or with 2,2′-azo(bisisobutyrate) under thermal conditions.[20,21] Manganese(III) acetate ($Mn(OAc)_3$) showed a good capability for abstracting a hydrogen radical from active methylene compounds to form carbon radicals which can then add to alkenes and alkynes.[22–25] Through this kind of addition reaction many useful compounds have been synthesized.[26–30] To the best of our knowledge, no radical reaction mediated by $Mn(OAc)_3$ to functionalize fullerenes has been reported. Herein we describe the novel reaction of [60]fullerene with carbon radicals generated from active methylene compounds and $Mn(OAc)_3$.

Results and discussion

Five active methylene compounds which contain at least one activated hydrogen, that is, dimethyl malonate, diethyl malonate, diethyl bromomalonate, malononitrile and ethyl cyanoacetate, were selected in the present study. The reaction of [60]fullerene with dimethyl malonate and manganese(III) acetate dihydrate ($Mn(OAc)_3{\cdot}2H_2O$) was first investigated. It was carried out simply by treating C_{60} with 2 equiv. of dimethyl malonate and 2 equiv. of $Mn(OAc)_3{\cdot}2H_2O$ in refluxing 1-chlorobenzene. After being stirred for only 20 min, the color of the reaction mixture changed from purple to dark brown. After removal of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel to give dimer **1a** in 65% yield based on consumed C_{60} along with 60% of recovered C_{60} (Scheme 1). The assignment of the singly bonded dimer **1a** consisting of two inseparable isomers, that is, meso and racemic isomers, was confirmed by the following spectral data. A typical broad absorption around 445 nm in the UV-vis spectrum was diagnostic of a 1,4-adduct.[18,31] In the ^1H NMR spectrum, six singlets can be classified into two sets of signals with a ratio of 1.5 : 1, which is close to the isomer ratios of other singly bonded fullerene dimers.[18,31] One set displaying one singlet at 5.45 ppm for the methine group and two singlets at 4.00 and 3.77 ppm for the two methoxy groups may be assigned to the meso isomer and another set of signals that was weaker than the former set displaying at 5.48, 3.95 and 3.82 ppm could be assigned to the racemic isomer. This assignment is consistent with theoretical calculation by the B3LYP/3-21G*//PM3 method which showed that the meso isomer was more stable than the racemic isomer by 2.30 kcal mol^{-1}. The ^{13}C NMR peaks included two sp^3-carbon lines of the C_{60} skeleton at 66.83 ppm for the pivot carbon and 56.33 ppm for the sp^3-carbon linked to the methine group.[18,31] As observed in the ^1H NMR spectrum, the carbonyl, methine and methoxy groups also displayed two sets of chemical shifts at 167.06, 166.40, 61.68, 52.96, 52.93 and 167.02, 166.36, 61.45, 53.12, 52.80 ppm, respectively, in the ^{13}C NMR spectrum. In the MALDI-TOF mass spectroscopy of **1a** only the signal at *m*/*z* 851 was detected, which corresponded exactly to half of the molecular weight of dimer **1a** due to the ready cleavage of the weak pivot bond. The easy cleavage of the pivot bond connecting two C_{60} skeletons was also evidenced by the following observation. It was found that a longer reaction time (1 h) gave only a trace of compound **1a** and afforded 1,4-bisadduct **2a** in 45% yield based on consumed C_{60} together with 53% of C_{60} recovered (Scheme 1). In a control experiment, pure **1a** was heated in refluxing 1-chlorobenzene and was found to give **2a** in 23% yield along with 59% of C_{60} (Scheme 2). The structure of **2a** was confirmed by MALDI-TOF MS, which exhibited a molecular ion peak at *m*/*z* 982. A diagnostic broad peak at 445 nm for the 1,4-adduct was

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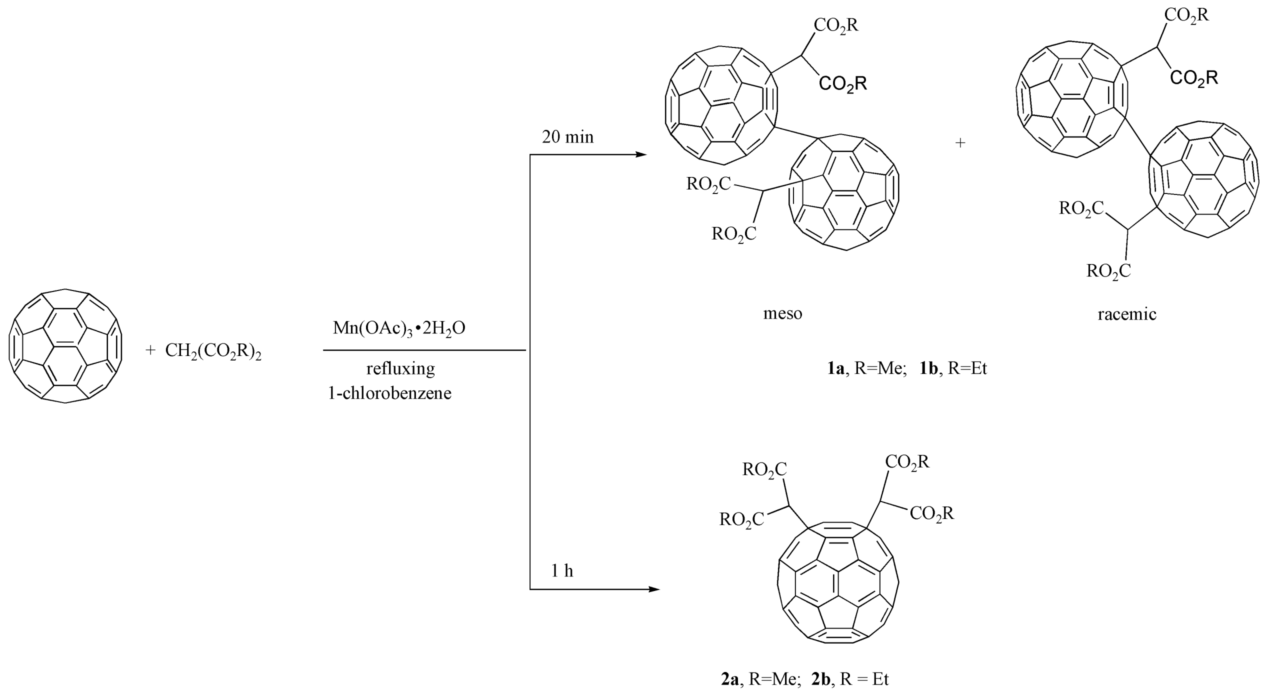
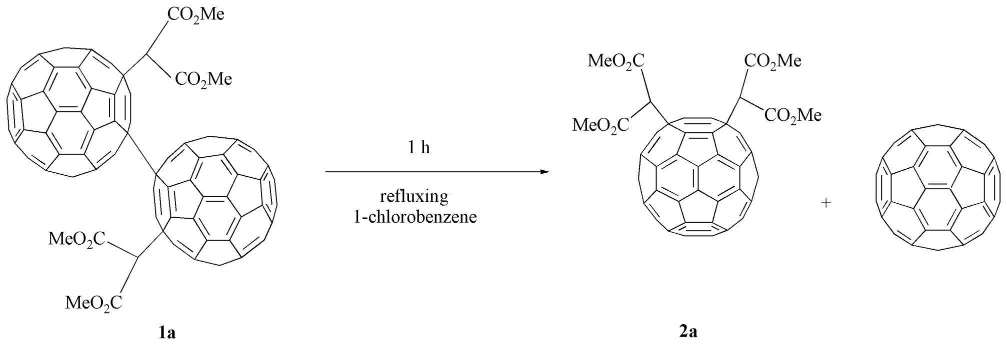


Scheme 1



Scheme 2

seen in the UV-vis spectrum of **2a**. Its ^{13}C NMR spectrum is also in full accordance with the molecular structure of **2a**. The expected 32 resonances (31 lines between 139.13 and 152.63 ppm, four of them with half intensity, and one line at 56.17 ppm) for the fullerene cage as well as non-fullerenic signals at 166.75, 167.23, 61.40, 53.33, and 53.16 ppm were observed for the C_s symmetrical **2a**.

According to previously reported experimental and theoretical studies,[32–39] this singly bonded fullerene dimer $RC_{60}–C_{60}R$ was generally formed by recombination of two $RC_{60}^{\bullet}$ radicals, which were generated *in situ* by addition of free radical $R^{\bullet}$ to C_{60}. The formation of **1a** should follow the same pathway.

The formation pathway of **2a** may involve the equilibrium between dimer **1a** and radical **3a**.[31–33] Dissociation of **3a** affords radical **4a** and C_{60}. Coupling of radical **3a** with radical **4a** gives **2a**. Another possible route for the formation of **2a** is through the direct addition to C_{60} with two **4a** radicals which is produced by hydrogen abstraction from malonate diester in the presence of $Mn(OAc)_3$·$2H_2O$ (Scheme 3).

This efficient $Mn(OAc)_3$·$2H_2O$-based reaction of [60]fullerene can be extended to other β-diesters. As desired we also successfully isolated compounds **1b** and **2b** when dimethyl malonate was replaced by diethyl malonate under the same reaction conditions (Scheme 1). The yields and reaction times for the reaction of C_{60} with malonate diesters in refluxing 1-chlorobenzene along with the meso/racemic ratios are listed in Table 1.

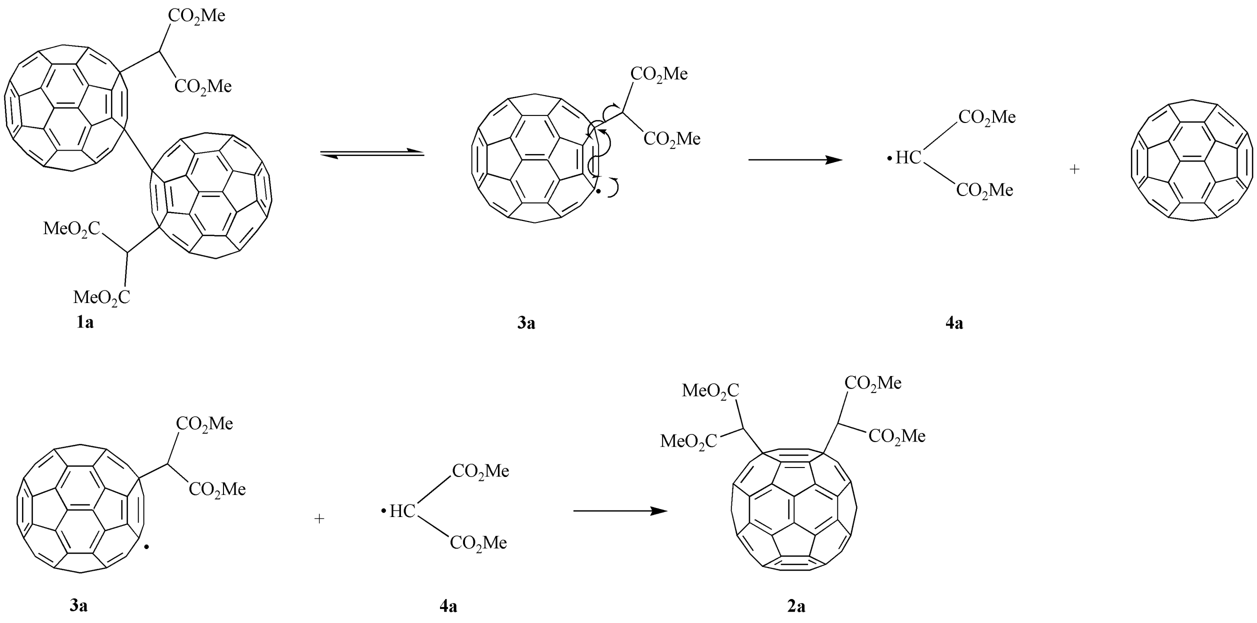
As with compound **1a**, dimer **1b** was also fully determined by ^1H NMR, ^{13}C NMR, MALDI-TOF MS, FT-IR and UV-vis spectra. Compound **2b** is the same as the 1,4-bisadduct produced by the solvent-free reaction of C_{60} with diethyl malonate in the presence of Na_2CO_3 under high-speed vibration milling conditions based on their same spectral data.[40]

Next, diethyl bromomalonate, an extensively used reagent in the Bingel reaction, was utilized in this $Mn(OAc)_3$·$2H_2O$-mediated radical reaction. No dimeric compound with the structure of **1** was formed; instead 1,4-adduct **5** and 1,16-bisadduct **6** were obtained in yields of 30% and 40% based on consumed C_{60}, respectively, together with 60% of recovered C_{60} after refluxing for 40 min in 1-chlorobenzene (Scheme 4). MALDI-TOF MS displayed a strong peak at *m*/*z* 1037 for compound **5** which arose from the loss of a bromine atom. Signals for four ethoxy groups and one methine group were observed in the ^1H NMR spectrum of compound **5**. It should be noted that the chemical shift of the methine proton shifted downfield to 5.93 ppm in the ^1H NMR spectrum compared with that of 1,4-bisadduct **2b**, which showed a singlet at 5.01 ppm for the corresponding proton. The ^{13}C NMR spectrum included two lines at 61.96 and 56.08 ppm due to the two sp^3-carbons and 53 lines with 5 overlapping lines between 152.60 and 138.75 ppm due to sp^2-carbons of the fullerene cage, which were consistent with the C_1 symmetry of compound **5**. There only exist overlapped signals for the ethoxy groups in the ^1H NMR spectrum of adduct **6**. Meanwhile, the 30 peaks with equal intensity in the ^{13}C NMR spectrum for the fullerene core

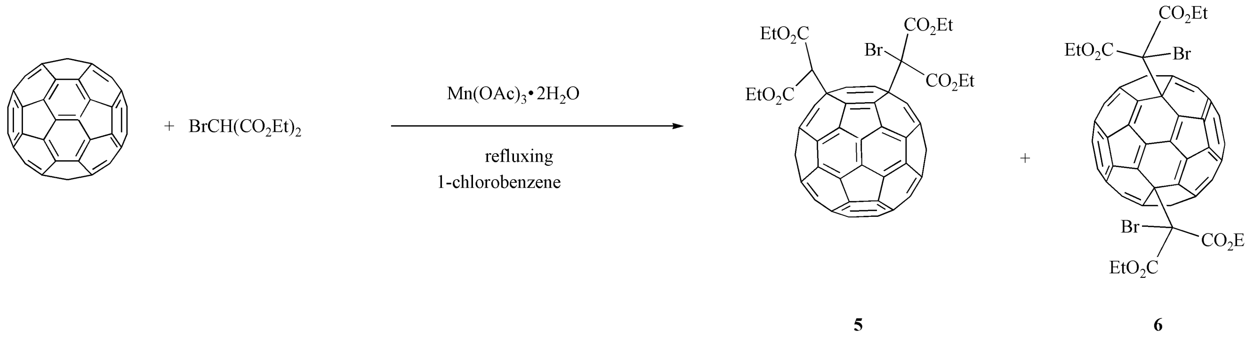
Table 1 Yields and reaction times for the reaction of C_{60} with malonate diesters in the presence of $Mn(OAc)_3{\cdot}2H_2O$

Substrate	Time	Product	Yield[a]	Recovered C_{60}	Meso : racemic[b]
$CH_2(CO_2Me)_2$	20 min	**1a**	65%	60%	1.5 : 1
	1 h	**2a**	45%	53%	
$CH_2(CO_2Et)_2$	20 min	**1b**	71%	59%	1.7 : 1
	1 h	**2b**	36%	50%	

[a] Yield based on consumed C_{60}. [b] Ratio determined from the ^1H NMR spectrum.



Scheme 3



Scheme 4

of compound **6** revealed the C_2 symmetry of its molecular structure. The absorptions at 448, 475, 506, 715, 793, 889 nm displayed in the UV-vis spectrum of compound **6**, resembled those of a known 1,16-bisadduct,[18] suggesting that the addends are at the 1,16 positions. The observed peak at *m*/*z* 1036 in its MS spectrum was caused by the loss of two bromine atoms. The selective formation of **6** with the 1,16-bisaddition pattern instead of the 1,4-bisaddition pattern may be due to the considerable steric interaction between the two bulky bromomalonate groups, and was supported by the B3LYP/3-21G*//PM3 calculation, which showed that the product in the 1,16-addition pattern is more stable than that in the 1,4-addition pattern by 5.5 kcal mol^{-1}. 1,4-Adduct **2b** with two $CH(CO_2Et)_2$ groups was not isolated in this reaction indicating the preferable formation of radical $^{\bullet}CBr(CO_2Et)_2$ over $^{\bullet}CH(CO_2Et)_2$ under our reaction conditions due to the preferred abstraction of hydrogen over halogen atom from diethyl bromomalonate by $Mn(OAc)_3{\cdot}2H_2O$.[41]

Unexpectedly, cyclopropane-fused fullerene derivatives **7** and **8** rather than 1,4-adducts or dimeric compounds were obtained when malononitrile and ethyl cyanoacetate were used in this radical reaction (Scheme 5). The molecular structures of compound **7** with C_{2v} symmetry and methanofullerene **8** with C_s symmetry were assigned based on their spectral data.[42]

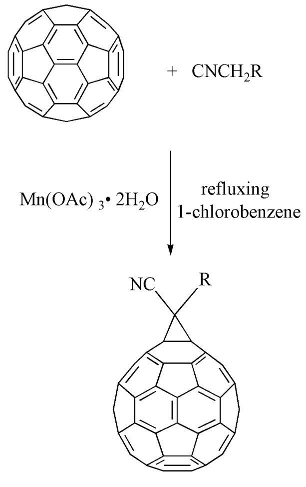
Table 2 The yields and reaction times for the reaction of C_{60} with malononitrile and ethyl cyanoacetate, respectively, in the presence of $Mn(OAc)_3{\cdot}2H_2O$

Substrate	Time	Product	Yield[a]	Recovered C_{60}
$CH_2(CN)_2$	5 h	**7**	36%	56%
$CNCH_2COOEt$	2 h	**8**	51%	53%

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

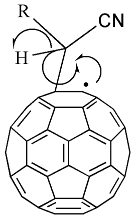
The yields and reaction times for the reaction of C_{60} with malononitrile and ethyl cyanoacetate, respectively, in the presence of $Mn(OAc)_3{\cdot}2H_2O$ in refluxing 1-chlorobenzene are listed in Table 2.

Although the exact mechanism for the formation of compounds **7** and **8** is not very clear at present, a plausible pathway may involve free radical **9** (Fig. 1) which was obtained by the addition of the carbon radical generated from malononitrile or



7, R=CN; **8**, R=CO_2Et

Scheme 5



9 R= CN, COOEt

Fig. 1

ethyl cyanoacetate with the aid of $Mn(OAc)_3{\cdot}2H_2O$, and then intramolecular cyclization through the release of hydrogen radical to give the corresponding methanofullerene.

In conclusion, hydrogen abstraction from β-diesters by the use of $Mn(OAc)_3{\cdot}2H_2O$ provided carbon radicals which add to [60]fullerene to give fullerene dimers and 1,4-bisadducts in fairly good yields through controlled conditions. Meanwhile, bromo-substituted β-diester afforded not only the 1,4-addition product but also the 1,16-bisadduct. In contrast, in the presence of $Mn(OAc)_3{\cdot}2H_2O$, two other active methylene compounds containing one or two cyano groups gave cyclopropane-fused C_{60} derivatives. This method provides a novel protocol for the synthesis of methanofullerene besides the Bingel reaction. It was proposed that all these products were formed *via* the addition of free radicals from the active methylene compounds generated by $Mn(OAc)_3{\cdot}2H_2O$.

Experimental

General methods

^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, in $CDCl_3$ or CS_2–$CDCl_3$. FT-IR spectra were recorded on a Magana 750 FT-IR spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2100PC spectrophotometer. Mass spectra were taken on a BIFLEXIII MALDI-TOF mass spectrometer with 4-hydroxy-α-cyanocinnamic acid as the matrix.

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.

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

A mixture of C_{60} (43.2 mg, 0.06 mmol), dimethyl malonate (14.0 μL, 0.12 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 30 mL of 1-chlorobenzene for 20 min. The solvent was removed by distillation under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give dimer **1a** (13.3 mg, 65% based on consumed C_{60}) along with recovered C_{60} (25.9 mg, 60%). When the reaction was extended to 1 h, 1,4-bisadduct **2a** (12.4 mg, 45% based on consumed C_{60}) and recovered C_{60} (22.9 mg, 53%) were obtained by the same procedure.

Spectral data of **1a**: ^1H NMR (300 MHz, CS_2–$CDCl_3$) meso: δ 3.77 (s, 6H, OCH_3), 4.00 (s, 6H OCH_3), 5.45 (s, 2H, CH), racemic: 3.82 (s, 6H, OCH_3), 3.95 (s, 6H, OCH_3), 5.48 (s, 2H, CH); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$) δ 52.80 (OCH_3, meso), 52.93 (OCH_3, racemic), 52.96 (OCH_3, racemic), 53.12 (OCH_3, meso), 56.33 (sp^3-C of C_{60}, meso and racemic), 61.45 (C*C*H, meso), 61.68 (C*C*H, racemic), 66.83 (sp^3-C of C_{60}, meso and racemic), 139.19–153.03 (sp^2-C peaks of C_{60}), 166.36 (COO, meso), 166.40 (COO, racemic), 167.03 (COO, meso), 167.06 (COO, racemic); UV-vis λ_{max}/nm ($CHCl_3$) 259, 326, 445; MS (MALDI-TOF) *m*/*z* 851; IR ν/cm^{-1} (KBr) 2946, 2922, 2865, 2850, 1758, 1741, 1431, 1317, 1263, 1237, 1221, 1202, 1189, 1162, 1152, 575, 527. Spectral data of **2a**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 6H, CH_3), 4.04 (s, 6H, CH_3), 5.17 (s, 2H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.16 (OCH_3, 2C), 53.33 (OCH_3, 2C), 56.17 (sp^3-C of C_{60}, 2C), 61.41 (CH, 2C), 139.13 (2C), 139.42 (2C), 140.71 (1C), 141.10 (2C), 142.03 (2C), 142.28 (1C), 142.54 (2C), 142.70 (1C), 143.06 (2C), 143.25 (2C), 143.31 (2C), 143.38 (2C), 143.45 (2C), 143.87 (2C), 144.19 (2C), 144.33 (2C), 144.36 (2C), 144.42 (1C), 144.70 (2C), 144.79 (2C), 145.15 (2C), 145.17 (2C), 145.67 (2C), 146.94 (2C), 147.05 (2C), 147.18 (2C), 147.34 (2C), 148.02 (2C), 148.68 (2C), 148.88 (2C), 152.63 (2C), 166.75 (COO, 2C), 167.23 (COO, 2C); UV-vis λ_{max}/nm ($CHCl_3$) 258, 326, 445; MS (MALDI-TOF) *m*/*z* 982; IR ν/cm^{-1} (KBr) 2950, 2846, 1759, 1739, 1432, 1332, 1301, 1264, 1238, 1218, 1213, 1153, 575, 527.

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

A mixture of C_{60} (43.2 mg, 0.06 mmol), diethyl malonate (19.0 μL, 0.12 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 30 mL of 1-chlorobenzene for 20 min. The solvent was removed by distillation under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give dimer **1b** (15.4 mg, 71% based on consumed C_{60}) along with recovered C_{60} (25.5 mg, 59%). When the reaction was extended to 1 h, 1,4-bisadduct **2b** (11.2 mg, 36% based on consumed C_{60}) and recovered C_{60} (21.6 mg, 50%) were obtained by the same procedure.

Spectral data of **1b**: ^1H NMR (300 MHz, $CDCl_3$) meso: δ 1.20 (t, J = 7.1 Hz, 6H, CH_3), 1.38 (t, J = 7.1 Hz, 6H, CH_3), 4.23 (q, J = 7.1 Hz, 4H, OCH_2), 4.45 (q, J = 7.1 Hz, 4H, OCH_2), 5.27 (s, 2H, CH); racemic: 1.23 (t, J = 7.1 Hz, 6H, CH_3), 1.33 (t, J = 7.1 Hz, 6H, CH_3), 4.28 (q, J = 7.1 Hz, 4H, OCH_2), 4.41 (q, J = 7.1 Hz, 4H, OCH_2), 5.36 (s, 2H, CH); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$) δ 13.41 (OCH_2*C*H_3, racemic), 13.64 (OCH_2*C*H_3, meso), 55.72 (sp^3-C of C_{60}, meso and racemic), 60.67, 60.88, 61.16, 61.26, 61.37 (C*C*H, O*C*H_2CH_3, meso and racemic), 66.04 (sp^3-C of C_{60}, meso and racemic), 138.59–153.11 (sp^2-C peaks of C_{60}), 164.75 (COO, racemic), 165.36 (COO, meso); UV-vis λ_{max}/nm ($CHCl_3$) 259, 326, 445; MS (MALDI-TOF) *m*/*z* 879; IR ν/cm^{-1} (KBr) 2977, 2953, 2920, 2849, 1758, 1735, 1470, 1461, 1428, 1367, 1208, 1188, 1135, 1113, 1035, 847, 575, 527.

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

A mixture of C_{60} (43.2 mg, 0.06 mmol), diethyl bromomalonate (21.0 μL, 0.12 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 30 mL of 1-chlorobenzene for 40 min. The solvent was removed by distillation under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give 1,4-adduct **5** (8.0 mg, 30% based on consumed C_{60}) and 1,16-adduct **6** (11.5 mg, 40% based on consumed C_{60}) along with recovered C_{60} (25.9 mg, 60%).

Spectral data of **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H, CH_3), 1.35 (t, J = 7.2 Hz, 3H, CH_3), 1.41 (t, J = 7.2 Hz, 3H, CH_3), 1.44 (t, J = 7.2 Hz, 3H, CH_3), 4.31 (q, J = 7.2, 2H, OCH_2), 4.37–4.63 (m, 6H, OCH_2), 5.93 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.90 ($OCH_2\mathit{C}H_3$, 1C), 13.98 ($OCH_2\mathit{C}H_3$, 1C), 14.14 ($OCH_2\mathit{C}H_3$, 1C), 14.28 (CH_2-$\mathit{C}H_3$, 1C), 56.09 (sp^3-C of C_{60}, 1C), 60.67 (CH, 1C), 61.97 (sp^3-C of C_{60}, 1C), 62.14 ($O\mathit{C}H_2CH_3$, 1C), 62.35 ($O\mathit{C}H_2CH_3$, 1C), 64.07 ($O\mathit{C}H_2CH_3$, 1C), 64.12 ($O\mathit{C}H_2CH_3$, 1C), 68.33 (CBr, 1C), 138.75 (1C), 139.24 (1C), 139.45 (1C), 139.62 (1C), 140.10 (1C), 140.49 (1C), 140.81 (1C), 142.00 (1C), 142.09 (1C), 142.54 (2C), 142.60 (1C), 142.64 (1C), 142.70 (1C), 142.81 (1C), 142.88 (1C), 143.01 (1C), 143.04 (1C), 143.21 (1C), 143.23 (1C), 143.36 (1C), 143.42 (1C), 143.52 (2C), 143.68 (1C), 143.78 (1C), 144.04 (1C), 144.08 (2C), 144.33 (1C), 144.36 (2C), 144.41 (1C), 144.75 (1C), 144.77 (1C), 144.86 (1C), 145.14 (1C), 145.18 (1C), 145.79 (2C), 145.98 (1C), 146.89 (1C), 146.94 (1C), 147.01 (1C), 147.06 (1C), 147.20 (1C), 147.25 (1C), 147.71 (1C), 147.93 (1C), 148.00 (1C), 148.03 (1C), 148.44 (1C), 148.57 (1C), 148.65 (1C), 148.83 (1C), 150.34 (1C), 151.23 (1C), 152.60 (1C), 165.21 (COO, 1C), 165.68 (COO, 1C), 166.62 (COO, 1C), 167.26 (COO, 1C); UV-vis λ_{max}/nm ($CHCl_3$) 256, 320, 445; MS (MALDI-TOF) m/z 1037 (M − Br); IR ν/cm^{-1} (KBr) 2975, 2923, 2851, 1743, 1736, 1440, 1431, 1246, 1207, 1189, 1094, 1029, 575, 527.

Spectral data of **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32–1.41 (m, 12H, CH_3), 4.32–4.52 (m, 8H, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.10 ($OCH_2\mathit{C}H_3$, 4C), 61.49 (sp^3-C of C_{60}, 2C), 63.99 ($O\mathit{C}H_2CH_3$, 2C), 64.06 ($O\mathit{C}H_2CH_3$, 2C), 68.11 ($\mathit{C}Br(COOEt)_2$, 2C), 136.39 (2C), 136.89 (2C), 138.67 (2C), 139.28 (2C), 141.14 (2C), 141.55 (2C), 141.91 (2C), 142.00 (2C), 142.11 (2C), 142.78 (2C), 142.95 (2C), 144.15 (2C), 144.56 (2C), 144.68 (2C), 144.73 (2C), 144.77 (2C), 144.84 (2C), 145.13 (2C), 145.60 (2C), 145.74 (2C), 146.11 (2C), 146.37 (2C), 146.65 (2C), 147.13 (2C), 147.56 (2C), 148.08 (2C), 148.76 (2C), 150.98 (2C), 158.65 (2C), 165.20 (COO, 2C), 165.34 (COO, 2C); UV-vis λ_{max}/nm ($CHCl_3$) 256, 320, 448, 475, 506, 715, 793, 889; MS (MALDI-TOF) m/z 1036 (M − 2Br); IR ν/cm^{-1} (KBr) 2978, 2931, 2867, 1745, 1461, 1441, 1366, 1296, 1248, 1206, 1158, 1094, 1046, 1005, 575, 527.

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

A mixture of C_{60} (43.2 mg, 0.06 mmol), malononitrile (8.0 mg, 0.12 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 30 mL of 1-chlorobenzene for 5 h. The solvent was removed by distillation under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give methanofullerene **7** (7.5 mg, 36% based on consumed C_{60}) along with recovered C_{60} (24.2 mg, 56%).

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 (14.0 µL, 0.12 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (32.0 mg, 0.12 mmol) was refluxed in 30 mL of 1-chlorobenzene for 2 h. The solvent was removed by distillation under reduced pressure and the residue was separated on a silica gel column with toluene as the eluent to give **8** (12.0 mg, 51% based on consumed C_{60}) along with recovered C_{60} (22.9 mg, 53%).

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