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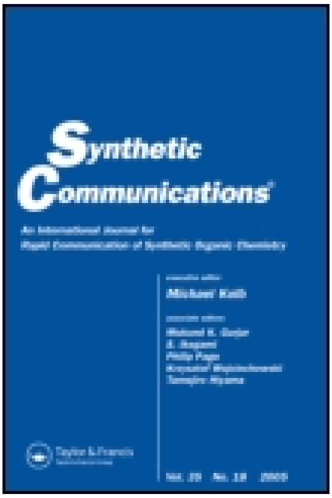

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Synthesis of a Series of Malonic Diester-Introduced Fullerene Derivatives

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SYNTHESIS OF A SERIES OF MALONIC DIESTER–INTRODUCED FULLERENE DERIVATIVES

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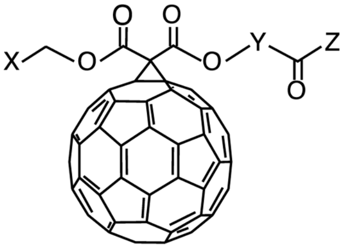
GRAPHICAL ABSTRACT



X: CH_3 or Ph
Y: $(CH_2)_nO$ or $(CH_2CH_2O)_2$, n = 2 or 5 or 8 or 10
Z: phenyl or hexyl or pyrenyl group, etc.

Abstract *A facile preparation method for derivatization of fullerene through the Bingel reaction was introduced. A series of fullerene derivatives, to which malonic diester with different substituents were introduced, were systematically synthesized by Bingel reaction. Malonic diester could be added to fullerene at room temperature in the presence of iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and various substituents such as phenyl, hexyl, thienyl, and pyrenyl were introduced into both sides of the malonic diester. As a result, 17 systematic variations were synthesized. The solubility parameters of the obtained fullerene derivatives calculated by the method reported by Fedors were in the range of 33 to 43* $(J\,cm^{-3})^{1/2}$.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Bingel reaction; fullerene; malonic diester; solubility parameter

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INTRODUCTION

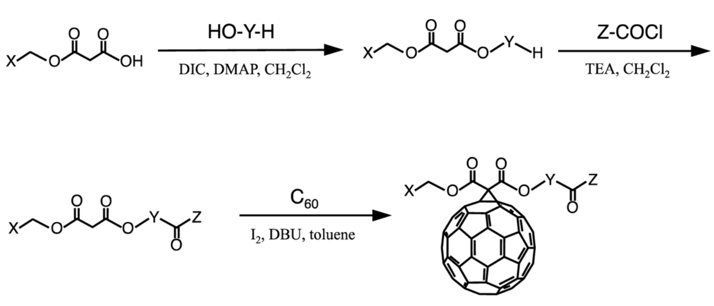
Fullerene has attracted much attention in various fields such as electronic engineering and bioengineering because of its unique chemical and physical properties.[1–3] However, because its solubility or dispersibility in water and organic solvents and compatibility between fullerene and other materials are poor, the use of fullerene is limited. Therefore, the derivatization of fullerene is important to improve its solubility, dispersibility, and compatibility. [6.6]-Phenyl-C61-butyric acid methyl ester (PCBM)[4,5] and bis(dimetylphenylsililmethyl)[60]fullerene (SIMEF)[6] for acceptor materials for organic photovoltaics, tetra(piperazino)[60]fullerene epoxide (TPFE) for gene delivery,[7] (1,2-methanofullerene C60)-61-carboxylic acid,[8] and polyhydroxylated fullerene[9] for antioxidants are well known as fullerene derivatives. Although a large variety of fullerene derivatives has been synthesized for each purpose, there were few studies concerning systematic synthesis of a series of fullerene derivatives. For optimal use of fullerene, the control of compatibility between fullerene derivatives and other materials is important.

Recently, solubility parameters were used to make a prediction of the mixed state of fullerene derivatives and conjugated polymers. The solubility parameters are the square root of the cohesion energy density. The compatibility of fullerene derivatives and conjugated polymers is assumed to be high if solubility parameters of fullerene derivatives and conjugated polymers are close.[10–13] The solubility parameter of fullerene [54 $(\mathrm{J\,cm^{-3}})^{1/2}$] calculated by the method reported by Fedros[14] is much greater than those of the polymer materials [20–30 $(\mathrm{J\,cm^{-3}})^{1/2}$] used for mixing with fullerene.

In this study, we introduce a facile preparation method for derivatization of fullerene through the Bingel reaction,[15–18] and 17 systematic variations [solubility parameter: 33–43 $(\mathrm{J\,cm^{-3}})^{1/2}$] were synthesized.

RESULTS AND DISCUSSION

All the fullerene derivatives were synthesized in the same synthetic route as shown in Scheme 1. A typical reaction procedure is as follows: (1) The esterification



X: CH_3 or Ph
Y: $(CH_2)_nO$ or $(CH_2CH_2O)_2$, n = 2 or 5 or 8 or 10
Z: phenyl or hexyl or pyrenyl group, etc.

Scheme 1. Synthesis of malonic diester–introduced fullerene derivatives.

of 3-(benzyloxy)-3-oxopropanoic acid was carried out by reacting 3-(benzyloxy)-3-oxopropanoic acid with corresponding diol compound, using *N,N′*-diisopropylcarbodiimide as condensation agent and 4-dimethylaminopyridine as catalyst. (2) The esterification of obtained malonic diesters (benzyl 2-hydroxyethyl malonate) was carried out by reacting the malonic diesters [2-(benzoyloxy)ethyl malonate] with corresponding carboxylic acid chlorides, using triethylamine as base. (3) Malonate diester–introduced fullerene derivatives were synthesized by the Bingel reaction, by treatment of [60]fullerene with malonate diester in the presence of iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature. The fullerene derivatives were obtained in yields from 20 to 53%.

The solubility parameters of the obtained fullerene derivatives were calculated by the following formula reported by Fedors:[14]

$$\delta = (\Delta E/V)^{1/2}$$

where ΔE is total of the additive atomic and group contribution for energy of vaporization and V is molar volume. ΔE and V were calculated using the method and the values reported in the literature.[14] The structures, yield, and solubility parameters of obtained fullerene derivatives are summarized in Table 1. The solubility parameters of obtained fullerene derivatives were in the range of 33.5 to 43 $(\mathrm{J\,cm^{-3}})^{1/2}$. These are values between the value of fullerene [54.3 $(\mathrm{J\,cm^{-3}})^{1/2}$] and conjugated polymers that are generally used for organic photovoltaics (for example, poly(3-hexylthiopehe): 22.7 $(\mathrm{J\,cm^{-3}})^{1/2}$, poly[2-methoxy-5-(3′,7′-dimethyl-octyloxy)-1, 4-phenylenevinylene]: 19.6 $[\mathrm{J\,cm^{-3}})^{1/2}]$. Thus, those fullerene derivatives are considered to be useful for the optimization of the bulk heterojunction photoactive layer of organic photovoltaics.

Table 1. Synthesized malonic diester–introduced fullerene derivatives

Product	X	Y	Z	Yield (%)	δ^a $((\mathrm{J\,cm^{-3}})^{1/2})$
1	Phenyl	$(CH_2)_2O$	Phenyl	53	38.5
2		$(CH_2)_5O$	Phenyl	34	36.4
3		$(CH_2)_8O$	Phenyl	27	34.7
4		$(CH_2)_{10}O$	Phenyl	21	34.2
5		$(CH_2CH_2O)_2$	Phenyl	43	37.0
6		$(CH_2)_2O$	Hexyl	36	36.0
7		$(CH_2)_5O$	Hexyl	39	34.4
8		$(CH_2CH_2O)_2$	Hexyl	45	35.0
9		$(CH_2)_2O$	Thienyl	38	39.2
10		$(CH_2CH_2O)_2$	Thienyl	49	37.6
11	Methyl	$(CH_2)_5O$	Pyrenyl	30	33.5
12		$(CH_2CH_2O)_2$	Pyrenyl	34	33.8
13		$(CH_2CH_2O)_2$	Ethyl	33	38.4
14		$(CH_2CH_2O)_2$	Phenyl	36	38.0
15		$(CH_2CH_2O)_2$	Thienyl	36	38.7
16		$(CH_2CH_2O)_2$	Vinyl	30	38.9
17		$(CH_2CH_2O)_2$	Hydroxyl	29	43.0

[a] The solubility parameters.

EXPERIMENTAL

All chemical reagents were obtained from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded with a Jeol JNM-EX400 FT-NMR system using tetramethylsilane (TMS) as an internal standard in $CDCl_3$. Mass spectra were taken with a Voyager RP and Tektronix TDS 540D. Elemental analyses were performed on a Elementar Vario Micro cube.

Synthesis

All fullerene derivatives with phenyl group as terminal group **X** (fullerene derivatives **1**–**12**) were synthesized in the same procedure. A typical reaction procedure is shown in the next section. The synthetic procedure of the fullerene derivatives with methyl group as **X** (fullerene derivative **13**–**17**) was almost the same (see Supplementary Material).

Synthesis of Fullerene Derivative 1

Ethylene glycol (43 g, 700 mmol), 4-dimethylaminopyridine (DMAP, 9.6 g, 78 mmol), and *N,N'*-diisopropylcarbodiimide (8.1 g, 64 mmol) were mixed in tetrahydrofuran (40 ml) at 0 °C. 3-(Benzyloxy)-3-oxopropanoic acid (5.7 g, 28 mmol) was added to the solution from a dropping funnel for 2 h. The mixture was stirred at room temperature for 24 h. The reaction mixture was washed three times with 1 N HCl solution (100 ml) and brine (100 ml). The organic layer was dried over Na_2SO_4. After evaporation, the residue was purified by column chromatography (silica gel, hexane / ethyl acetate = 60/40) to produce benzyl 2-hydroxyethyl malonate as a yellow oil (2.5 g, 10.4 mmol). The structure of the obtained compound was checked by ^1H NMR spectrum (see Supplementary Material). The obtained compound was used for the next reaction without further purification. The obtained benzyl 2-hydroxyethyl malonate (0.92 g, 4.0 mmol) and triethylamine (1.0 g, 6.1 mmol) were mixed in dichloromethane (20 ml) at 0 °C. Benzoyl chloride (0.51 g, 3.6 mmol) was added to the solution from a dropping funnel. The mixture was stirred at 0 °C for 2 h in the dark. The reaction mixture was washed twice with 1 N HCl solution (20 ml) and brine (20 ml). The organic layer was dried over Na_2SO_4. After evaporation, the reaction mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 80/20) to produce benzyl 2-(benzoyloxy)ethyl malonate as a yellow oil (0.61 g, 1.8 mmol). The obtained compound was used for the next reaction without further purification. The structure of the obtained compound was checked by ^1H NMR spectrum (see Supplementary Material). The obtained benzyl 2-(benzoyloxy) ethyl malonate (0.48 g, 1.4 mmol) and C_{60} fullerene (1.0 g, 1.4 mmol) were mixed in toluene (350 ml) at room temperature. 1,8-Diazabicyclo[5. 4. 0]undec-7-ene (DBU, 0.42 ml, 0.43 g, 2.78 mmol) and I_2 (0.35 g, 1.4 mmol) to the solution were added. The mixture was stirred at room temperature for 24 h. After filtration, the reaction mixture was washed twice with distilled water (100 ml) and brine (100 ml). The organic layer was dried over Na_2SO_4. After evaporation, the reaction mixture was purified by column chromatography (silica gel, toluene) to produce a dark brown powder **1** (0.78 g, 0.74 mmol, 53%), mp > 300 °C. ^1H NMR ($CDCl_3$, TMS): δ (ppm) 4.62–4.64 (t, $J = 4.8$ Hz, 2H, CH_2), 4.77–4.80 (t, $J = 4.4$ Hz, 2H, CH_2), 5.47 (s, 2H, CH_2), 7.36–7.41 (m, 5H, Ar-H), 7.45–7.47 (t, $J = 3.4$ Hz, 2H, Ar-H), 7.53–7.56 (dd, 1H, Ar-H), 8.02–8.03 (d, $J = 1.7$ Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, in $CDCl_3$): δ (ppm) 62.29, 64.78, 69.01, 71.61, 128.50, 128.74, 128.96, 128.99, 129.85, 133.30, 134.56, 139.00, 139.06, 140.94, 141.85, 141.87, 142.20, 142.94, 143.00, 143.82, 143.89, 144.58, 144.69, 144.92, 145.02, 145.08, 145.20, 145.26, 163.38, 166.23. MS (MALDI-TOF/MS) m/z: 1059.9 $[M\text{-}H]^-$. Anal. calcd. for $C_{79}H_{16}O_6$: C, 89.43; H, 1.52. Found: C, 88.60; H, 1.53.

SUPPORTING INFORMATION

Characterization of all synthesized fullerene derivatives is described in the Supplementary Material section of this article's Web page.

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