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Synthesis of fulleropyrrolidine–imidazolium salt hybrids and their solubility in various organic solvents

Toshiyuki Itoh [a,*], Makoto Mishiro [a], Kei Matsumoto [a], Shuichi Hayase [a], Motoi Kawatsura [a], Minoru Morimoto [b]

[a] *Department of Material Sciences, Faculty of Engineering, Tottori University, Tottori 680-8552, Japan*
[b] *Research Center for Bioscience and Technology, Tottori University, Tottori 680-8552, Japan*

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Abstract

Eight types of fulleropyrrolidine–imidazolium hybrids have been synthesized and their solubility determined in various types of organic solvents. The solvent solubility of fullerene derivatives depends on the alky side chain on the imidazolium ring; modification of solvent solubility of the fulleropyrrolidine–imidazolium hybrids has thus been accomplished by introduction of an appropriate alkyl group using imidazoyl moiety as the 'functional group connector'. The imidazolium group seems to act not only as the connector but also as an important functional group that controls the solubility.

1. Introduction

Fullerene is an attractive target material for nano-sciences; various types of fullerene derivatives have been developed and extensive studies have been made on their applications in the fields of both material[1] and biomedical sciences.[2] Generally, fullerene derivatives have poor solubility in conventional organic solvents.[3,4] Synthesis of 'water soluble fullerene derivatives' has also attracted growing interest from the standpoint of creating biologically active fullerene derivatives and several strategies have been demonstrated.[5] A rational design for fullerene derivatives that have good solubility in organic solvents or water using simple protocols is therefore needed.

Prato and co-workers established the method of synthesizing fulleropyrrolidine derivatives and it has now been acknowledged as the most widely used means to prepare fullerene analogs.[6] For example, fulleropyrrolidine salts, which have oligoethyleneoxide side chains are moderately soluble in tetrahydrofuran (THF), dichloromethane, dimethylsulfoxide, and dimethylsulfoxide/water.[6a]

Recently imidazolium salt has been recognized not only as a new class of solvent but also as source of material sciences; in particular, it showed unique solubility in many organic and inorganic materials.[7,8] Aida et al. reported the high affinity of single-walled carbon nanotubes with imidazolium based ionic liquids.[9] Aso and co-workers recently reported the synthesis of a unique imidazolium salt hybrid of fulleropyrrolidine; the authors prepared zinc–porphyrin–oligothiophene–fullerene derivative that has diethylthieno[3,4-*d*]imidazolium moiety and discovered that photoinduced intramolecular electron transfer was controlled by the electronic perturbation of the imidazolium group.[10] We hypothesize that an imidazole hybrid of fulleropyrrolidine might become a versatile intermediate for fullerene analogs that have unique solubility toward various types of solvent systems. We would be able to prepare various types of alkyl substituted fulleropyrrolidine–imidazolium hybrids very simply because it is easy to modify both pyrrolidine and imidazole moieties by introduction of an alkyl side chain (Fig. 1). Aiming to obtain basic information on the relationship between solubility and alkyl functionality of the fulleropyrrolidine–imidazolium hybrids, we investigated their solubility in several typical organic solvents. In this paper, we report the synthesis of eight types of novel fulleropyrrolidine–imidazolium

* Corresponding author. Tel./fax: +81 857 31 5259.
E-mail address: titoh@chem.tottori-u.ac.jp (T. Itoh).

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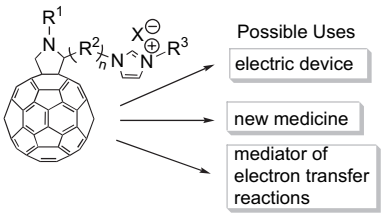
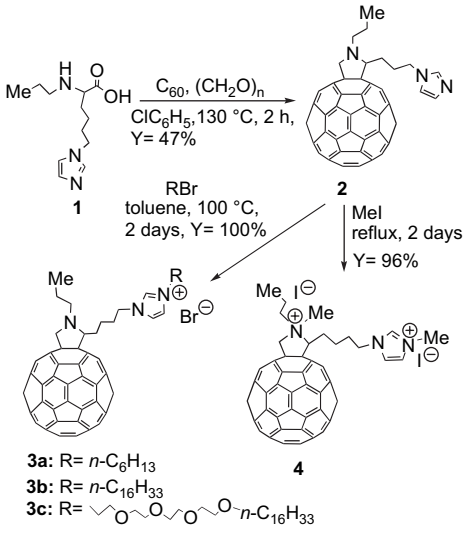


Figure 1. Design of fulleropyrrolidine–imidazolium hybrids as candidates of novel functional molecules.

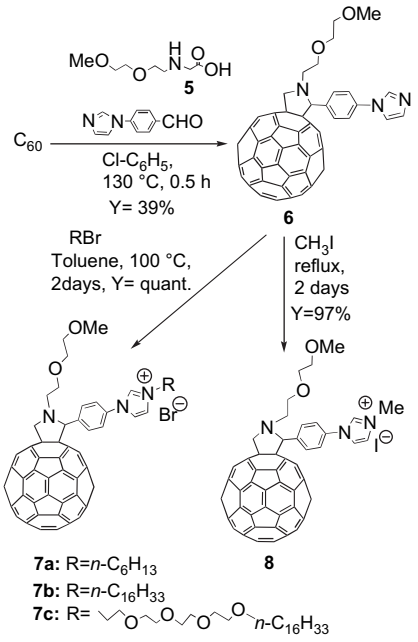
hybrids and the results of investigations of their solubility in various types of organic solvents or water.

2. Synthesis of fulleropyrrolidine–imidazolium salt hybrids

To accomplish the synthesis of fulleropyrrolidine derivatives, we used the conventional protocol of 1,3-dipolar cycloaddition of azomethine ylide to C_{60} fullerene developed by Prato and co-workers.[6] Fulleropyrrolidine–imidazole hybrid **2** was first synthesized (Scheme 1). 2-(*N*-Propyl)amino-6-(*N*-imidazolyl)hexanoic acid (**1**) was treated with C_{60} fullerene in the presence of paraformaldehyde in chlorobenzene and the mixture was heated at 130 °C for 2 h.[5g] Although three types of fulleropyrrolidine derivatives were produced, we succeeded in separating them by silica gel flash column chromatography; use of a mixed solvent of carbon disulfide (CS_2) and ethyl acetate as a developing solvent was essential to separate these derivatives and the desired mono-adduct **2** was obtained in 47% yield. The structure of **2** was determined by NMR spectra and MALDI-TOF MS experiment. Next, fullerene derivative **2** was reacted with alkyl bromide and it was found that N-alkylation took place only at the nitrogen atom of the imidazole ring; salts **3a–c** were obtained in excellent yield as black to brown powder. On the other hand, methylation took place at both nitrogen atoms of compound **2**, and diiodonium salt **4** was obtained when **2** was treated with excess amount of methyl iodide under reflux conditions for 2 days. It was thus



Scheme 1. Preparation of *N*-propyl fulleropyrrolidine–imidazolium hybrids.



Scheme 2. Preparation of fulleropyrrolidine–imidazolium hybrids.

established that various types of alkyl substituted fullerene derivatives could be prepared very simply using the imidazolium moiety as a useful connector to introduce various types of alkyl functional groups to the fullerene.

The synthesis of 4-(imidazol-1-yl)benzaldehyde has recently been reported,[11] so we prepared another four types of fullerene–imidazolium hybrids using 4-(imidazol-1-yl)benzaldehyde as starting material following Scheme 2. *N*-Methoxyethoxyethylglycine (**5**)[5g] was treated with 4-(imidazol-1-yl)benzaldehyde[11] in the presence of C_{60} in chlorobenzene at 130 °C for 0.5 h to give the desired adduct **6** in 35% isolated yield, though multiadducts were also produced as by-products. Compound **6** was successfully converted to the corresponding salts **7a–c** and **8** as brown powder through the same route as in Scheme 1. Interestingly methylation took place only on the imidazolium nitrogen to give mono-methylated salt **8** even when **6** was treated with excess amount of methyl iodide under reflux conditions for 2 days. Compounds **3**, **4**, **7**, and **8** were fully characterized by NMR, FTIR, and MALDI-TOF-MS spectroscopies.

3. Solubility of fulleropyrrolidine–imidazolium salt hybrids in various solvents

Since we have in hand eight types of novel fullerene derivatives, their solubility to six types of organic solvents was evaluated (Table 1). Solubility of the fullerene derivatives was determined by the following experiment and reported in mg solute/mL of the solvent at 25 °C:[3] a fullerene derivative saturated solution in an organic solvent was prepared and filtered through a paper filter. Then, the weight of the filtrate solution was measured, and the solvent was removed under vacuum. The solubility was calculated based on the result of the amount of fullerene derivative remaining in a flask after

Table 1
Solubility[a] of fulleropyrrolidine–imidazolium hybrids in various types of organic solvents

Compound		Toluene	THF	$CHCl_3$	Acetone	DMF	MeOH
	E_T^{N}[b]	0.099	0.207	0.259	0.355	0.386	0.762
	ε[c]	2.43	7.47	4.89	21.36	37.06	32.35
	μ[d]	1.0	5.8	3.8	9.0	10.8	5.7
	DN[e]	2.38[f]	20.0	—	17.0	26.6	19.0
	AN[e]	—	—	23.1[g]	12.5[g]	16.0[g]	41.3[g]
3a		0	0	12.3	0	166	0
3b		0	4.15	16.5	0	13.7	0
3c		178	77.0	71.0	0	68.6	2.92
7a		0	0	9.85	0	145	0
7b		0	1.41	10.2	0	14.0	0
7c		83.9	28.1	111	1.12	281	9.67
4		0	0	Trace[h]	Trace[h]	318	Trace[h]
8		0	0	Trace[h]	Trace[h]	218	Trace[h]

[a] Solubility=mg of solute/mL of the solvent at 25 °C.
[b] Polarity parameter based on the solvatochromism reported by Reichardt.[12]
[c] Dielectric constant at 20 °C.
[d] Dipole moment (10^{-30} cm); 1 debye=3.336×10^{-30} cm.
[e] DN=donor number (Kcal/mol), AN=acceptor number (Kcal/mol).[13]
[f] Reported value by Kothandaraman.[14]
[g] Estimated values using calculation reported by Abe et al.[15]
[h] No detectable fullerene derivative was obtained from the filtrate, though the filtrate was colored light brown.

removing the solvent compared to the weight of the starting solution. As can be seen in Table 1, it was confirmed that introduction of alkyl side chain on the imidazole moiety determined the solubility of the fullerene derivatives. Although compound **2** did not dissolve in THF or chloroform ($CHCl_3$) at all, alkylated products **3b**, **3c**, **7b**, and **7c** dissolved in both THF and $CHCl_3$. Introduction of a long alkyl group (hexadecyl group) to compound **2** caused significantly increased solubility in various types of organic solvents as expected. *n*-Hexyl substituted imidazolium salts **3a** and **7a** showed good solubility in DMF, while these did not dissolve in acetone or methanol (MeOH).

An interesting solubility of **3a** was found: the compound was not soluble in toluene, though fullerene itself was soluble in toluene; the imidazolium group might contribute this unique solubility but it is difficult to get a clear answer to this question at present. The best solubility in toluene and $CHCl_3$ was obtained for compound **3c**. Compound **7c** showed the greatest solubility in $CHCl_3$, *N*,*N*-dimethylformamide (DMF), acetone, and MeOH. Presence of the polyoxyethylene group for compounds **3c** and **7c** obviously contributed to increased solubility of these compounds for organic solvents, though we recognized that it was difficult to know the origin behind the modified solubility of the compounds after looking at the relationship of solubility among three typical parameters of the solvents:[12,13] polarity parameter (E_T^{N} value),[12] dielectric constant (ε value),[12] dipole moment of the solvent (μ value),[12] donor number (DN),[13] and acceptor number (AN)[13] as shown in Table 1. It should be noted that all fullerene derivatives dissolved in DMF and connection of the alkylpolyoxyethylene group was effective in increasing solubility of the fullerene–imidazolium hybrids. Fullerene–imidazolium hybrids dissolved well in DMF that has the largest DN among tested

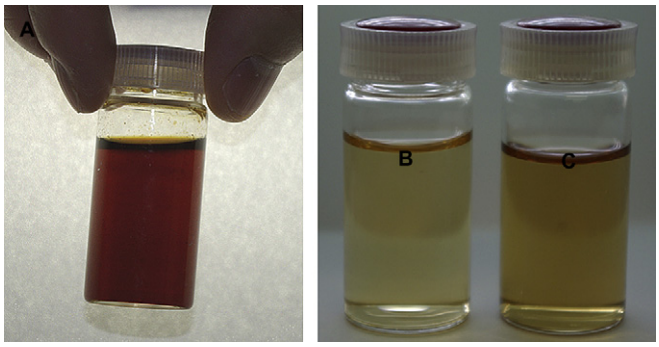


Figure 2. A water solution of fullerene derivative **4** or **8**. (A) 5.0 mg of **8** (4.0 μmol)+DMF (40 μL)+Water (8 mL): no precipitate was formed while standing at rt for several weeks. (B) 1.0 mg of **4** (1.0 μmol)+DMF (40 μL)+Water (8 mL). (C) 1.0 mg of **8** (0.98 μmol)+DMF (40 μL)+Water (8 mL).

solvents, while no relationship between solubility and AN of the solvents was observed (Table 1). Nakamura et al. reported that there was a certain relationship between donor number of solvents and reactivity of amino-substituted fullerene derivatives in the electron transfer reaction; an increased reactivity was obtained in large DN solvent.[16] This seems to suggest that the present fullerene–imidazolium hybrids may form complexes with solvent molecules and ease of complexation reflects on their solubility.

It was further found that compounds **4** and **8** have a unique solubility to water; we found that a DMF mixture of compound **4** or **8** easily dissolved in water, while these compounds individually did not. A mixture of 40 μL of DMF and 5.0 mg of **8** (4.89×10^{-6} mol) dissolved in 8.0 mL of water to give a clear brownish aqueous solution, and no precipitate was formed after allowing the solution to stand at rt for several weeks (see Fig. 2A and B). We discovered that DMF played a very important role in dissolving fullerene derivatives in water; it was essential to mix the DMF mixture with compound **4** or **8** to make it soluble in water, while neither compound **4** nor **8** dissolved in DMF aqueous solution. Since a typical Tyndall phenomenon was observed when an aqueous solution of DMF mixture with compound **4** was irradiated by laser light, it was confirmed that fullerene derivative **4** made a colloid particle with DMF molecules. It has been reported that C_{60} and C_{70} formed colloidal particles with THF and dissolved in water.[17] Therefore, we assume that both imidazolium and pyrrolidinium salt moieties cooperatively contribute to form good DMF complexes and form colloid particles, because such a phenomenon was not significant for other fullerene derivatives.[18]

4. Conclusion

In summary, we demonstrated that an imidazolium group worked very effectively to modify a fullerene derivative, which made it possible to prepare various types of these derivatives that have different solubility in various types of organic solvents. The imidazolium group seems to act not only as the connector but also as an important functional group that controls the solubility. Since a DMF mixture of fulleropyrrolidine

derivatives **4** or **8** is highly soluble in water, we anticipate that unique biological activities might be found for these compounds. Further investigation on the scope and limitation of the present strategy for controlling physical properties of fullerene derivatives using this 'imidazolium connector' will make it even more valuable.

5. Experimental section

5.1. Synthesis of N-propyl-2-(4-1H-imidazol-1-yl)butyl-fulleropyrrolidine *2*

A solution of C_{60} (500 mg, 0.694 mmol), 6-(1*H*-imidazol-1-yl)-2-(propylamino) hexanoic acid (329 mg), and paraformaldehyde (104 mg, 3.47 mmol) in chlorobenzene (200 mL) was stirred at 130 °C for 30 min under argon. The solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (CS_2/AcOEt=1/0, 20/1, 2/1) affording product **2** (300 mg, 0.323 mmol) as dark brownish solid in 47% yield: R_f 0.61 (toluene/methanol=2/1); ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*=Hz) δ 1.19 (t, 3H, *J*=6.9 Hz), 1.91–1.96 (m, 6H), 2.40–2.52 (m, 2H), 2.84 (quin, 1H, *J*=6.1 Hz), 3.42 (quin, 1H, *J*=8.6 Hz), 4.00 (t, 2H, *J*=6.4 Hz), 4.13–4.16 (m, 2H), 4.89 (d, 1H, *J*=10.1 Hz), 6.87 (s, 1H), 7.00 (s, 1H), 7.43 (s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 13.19, 23.20, 25.35, 31.78, 32.69, 47.72, 55.48, 67.57, 71.66, 77.00, 77.73, 119.23, 130.47, 136.16, 136.46, 136.88, 137.61, 137.90, 140.46, 140.75, 141.02, 141.08, 142.53, 142.56, 142.83, 142.89, 142.92, 142.99, 143.43, 143.86, 143.99, 145.12, 145.20, 145.27, 145.48, 145.95, 145.99, 146.05, 146.13, 146.17, 146.27, 146.36, 146.43, 146.72, 146.77, 146.80, 146.91, 146.95, 146.99, 147.04, 147.08, 147.89, 147.94, 153.97, 155.42, 155.67, 157.14; IR (KBr, cm^{-1}) 2950, 2866, 2789, 1460, 1425, 1226, 1184, 1074, 729, 527; HRMS (MALDI-TOF MS, matrix: sinapinic acid (SA)) found 927.1737 ($C_{72}H_{21}N_3$, calcd=927.1735).

5.2. Synthesis of *3a*

A solution of **2** (166 mg, 0.179 mmol) and 1-bromohexane (1.0 mL) was stirred for 2 days at 100 °C under argon. After being cooled to rt, the reaction mixture was washed with toluene (three times) and hexane (two times). The solvent was removed in a rotary evaporator to give **3a** (196 mg, 0.179 mmol) as a brown solid in 100% yield: ^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*=Hz) δ 0.87 (t, 3H, *J*=6.4 Hz), 1.22 (t, 3H, *J*=7.3 Hz), 1.25–1.38 (m, 8H), 1.87–1.93 (m, 2H), 2.10–2.19 (m, 2H), 2.58 (br s, 2H), 3.60–3.69 (m, 1H), 4.44–4.56 (m, 3H), 4.98 (d, 1H, *J*=10.5 Hz), 7.25 (s, 1H), 7.50 (s, 1H), 10.60 (s, 1H): ^{13}C NMR (125 MHz, ppm, $CDCl_3$+DMSO-d_6) δ 11.80, 13.75, 13.64, 22.25, 22.55, 23.75, 25.66, 29.88, 30.86, 31.40, 48.44, 49.71, 72.19, 45.12, 46.00, 121.61, 121.92, 135.18, 135.57, 135.86, 136.18, 139.14, 139.27, 139.93, 140.00, 141.37, 141.43, 141.51, 141.67, 141.75, 141.81, 141.87, 142.34, 142.39, 142.77, 142.87, 143.94, 144.06, 144.10, 144.36, 144.40, 144.83, 144.88, 144.97, 145.02, 145.06, 145.12, 145.24, 145.65, 145.70, 145.81, 145.88, 145.97, 146.80, 146.90; IR (KBr, cm^{-1}) 3433, 2922, 2860, 1184, 1159, 900, 727, 527: HRMS (MALDI-TOF MS, matrix: SA) found 1012.2753 ($C_{78}H_{34}N_3^+$, calcd: 1012.2750).

5.3. Salt *3b*

^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*=Hz) δ 0.88 (t, 3H, *J*=6.8 Hz), 1.21–1.33 (m, 29H), 1.84 (quin, 2H, *J*=7.3 Hz), 2.06–2.16 (m, 2H), 2.19–2.34 (m, 2H), 2.72 (br s, 2H), 3.38 (t, 2H, *J*=6.9 Hz), 4.25–4.34 (m, 2H), 4.49–4.61 (m, 2H), 5.09 (d, 1H, *J*=7.4 Hz), 7.24 (s, 1H), 7.67 (s, 1H), 10.48 (s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 11.88, 13.98, 21.72, 22.64, 23.72, 26.10, 28.88, 29.24, 29.28, 29.43, 29.58, 29.96, 30.14, 30.40, 31.78, 49.54, 49.77, 54.05, 65.92, 70.25, 75.54, 76.31, 121.58, 121.75, 124.96, 127.87, 128.65, 135.07, 135.46, 135.73, 136.13, 136.84, 139.20, 139.46, 139.91, 139.96, 141.32, 141.35, 141.47, 141.57, 141.61, 141.71, 141.78, 141.83, 142.29, 142.35, 142.74, 142.84, 143.92, 144.04, 144.09, 144.36, 144.79, 144.85, 144.92, 145.03, 145.14, 145.23, 145.59, 145.65, 145.76, 145.83, 145.88, 145.91, 146.74, 146.84, 152.50, 153.92, 154.19, 155.70; IR (KBr, cm^{-1}) 3402, 2916, 2839, 1458, 1184, 1157, 750, 527; HRMS (MALDI-TOF MS, matrix: SA) found 1152.4311 ($C_{88}H_{54}N_3^+$, calcd: 1152.4318).

5.4. Salt *3c*

^{1}H NMR (500 MHz, ppm, $CDCl_3$, *J*=Hz) δ 0.88 (t, 3H, *J*=7.1 Hz), 1.21 (t, 3H, *J*=7.3 Hz), 1.25 (br s, 26H), 1.54 (quin, 2H, *J*=6.8 Hz), 1.91–2.03 (m, 4H), 2.13 (quin, 2H, *J*=7.8 Hz), 2.49–2.54 (m, 2H), 2.87 (quin, 1H, *J*=6.4 Hz), 3.41 (t, 2H, *J*=7.1 Hz), 3.45–3.49 (m, 1H), 3.55–3.57 (m, 2H), 3.60–3.66 (m, 8H), 3.90 (t, 2H, *J*=4.6 Hz), 4.15–4.21 (m, 2H), 4.36 (dt, 2H, *J*=3.3 Hz, 7.4 Hz), 4.62 (t, 2H, *J*=4.6 Hz), 4.92 (d, 1H, *J*=10.1 Hz), 7.20 (s, 1H), 7.68 (s, 1H), 10.63 (s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 13.07, 14.92, 22.86, 23.40, 24.88, 26.86, 30.13, 30.30, 30.43, 30.48, 31.46, 31.67, 32.68, 50.49, 55.37, 67.46, 69.76, 70.74, 70.94, 71.00, 71.12, 71.26, 71.70, 72.27, 77.00, 77.48, 121.95, 124.61, 136.15, 136.57, 136.81, 137.94, 138.00, 140.35, 140.60, 140.99, 141.05, 142.46, 142.56, 142.76, 142.78, 142.80, 142.83, 142.96, 143.01, 143.39, 143.44, 143.85, 143.97, 145.08, 145.20, 145.23, 145.50, 145.92, 145.97, 146.05, 146.08, 146.32, 146.41, 146.43, 146.72, 146.77, 146.86, 146.95, 147.02, 147.14, 147.88, 147.97, 154.05, 155.46, 155.79, 157.31: IR (KBr, cm^{-1}) 3412, 2922, 2849, 1655, 1458, 1109, 1938, 527; HRMS (MALDI-TOF MS, matrix: SA) found 1328.5368 ($C_{96}H_{70}N_3O_4^+$, calcd: 1328.5366).

5.5. Synthesis of *4*

A solution of fullerene derivative (80 mg, 0.0826 mmol) and iodomethane (1.0 mL) was refluxed with stirring for 2 days under argon. After being cooled to rt, excess

iodomethane was removed under reduced pressure. Then, the residue was washed with toluene (three times) and hexane (twice). The solvent was removed under vacuum to give **4** (100 mg, 0.0826 mmol) as brownish solid in 96% yield: IR (KBr, cm^{-1}) 3414, 3082, 2964, 2860, 1560, 1458, 1431, 1165, 768, 527; HRMS (MALDI-TOF MS, matrix: SA) found 957.2200 ($C_{74}H_{27}N_3^+$, calcd: 957.2205). Due to poor solubility in $CDCl_3$, CD_3OD, and DMSO-d_6, no NMR spectra with good resolution could be obtained.

5.6. Synthesis of N-methoxyethoxyethyl-2-(4-(1H-imidazol-1-yl)phenylfulleropyrrolidine (6)

A solution of C_{60} (500 mg, 0.694 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid[5g] (185 mg, 1.04 mmol), and 4-(imidazol-1-yl)benzaldehyde[11] (358 mg, 2.08 mmol) in chlorobenzene (200 mL) was stirred for 0.5 h at 130 °C under argon. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (CS_2/AcOEt=1/0, 20/1, 2/1) affording the product **6** (272 mg, 0.270 mmol) as a dark brown solid in 39% yield: R_f 0.61 (toluene/methanol=2/1): ^{1}H NMR (500 MHz, ppm, $CDCl_3$, J=Hz) δ 2.93 (quin, 1H, J=6.2 Hz), 3.42–3.48 (m, 1H), 3.45 (s, 3H), 3.68 (sep, 2H, J=1.9 Hz), 3.78–3.85 (m, 2H), 4.05 (dquin, 2H, J=5.4 Hz, 34.8 Hz), 4.34 (d, 1H, J=9.6 Hz), 5.23 (d, 1H, J=9.6 Hz), 5.24 (s, 2H), 7.20 (s, 1H), 7.31 (s, 1H), 7.46 (d, 2H, J=8.7 Hz), 7.89 (s, 1H), 7.96 (br s, 2H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 52.08, 58.80, 67.37, 68.83, 70.21, 70.51, 71.93, 75.77, 81.39, 117.48, 121.05, 130.43, 130.72, 134.95, 135.33, 135.74, 136.13, 136.81, 137.04, 139.28, 139.73, 139.96, 141.29, 141.43, 141.53, 141.56, 141.65, 141.76, 141.86, 141.89, 141.96, 141.98, 142.29, 142.33, 142.35, 142.44, 142.76, 142.89, 144.04, 144.15, 144.26, 144.45, 144.87, 144.91, 145.00, 145.06, 145.11, 145.18, 145.30, 145.40, 145.63, 145.66, 145.82, 145.92, 146.01, 146.07, 146.16, 147.01, 152.44, 152.70, 153.63, 155.92; IR (KBr, cm^{-1}) 3412, 2883, 1522, 1300, 1182, 1107, 656, 527: HRMS (MALDI-TOF MS, matrix: SA) found 1007.1621 ($C_{76}H_{21}N_3O_2$, calcd: 1007.1634).

5.7. Salt 7a

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J=Hz) δ 0.88 (t, 3H, J=7.1 Hz), 1.29–1.36 (m, 4H), 1.39–1.43 (m, 2H), 1.99 (quin, 2H, J=7.6 Hz), 2.91–2.95 (m, 1H), 3.36–3.39 (m, 1H), 3.46 (s, 3H), 3.68 (t, 2H, J=4.8 Hz), 3.80–3.84 (m, 2H), 4.00 (quin, 1H, J=5.1 Hz), 4.07 (br s, 1H), 4.36 (d, 1H, J=8.7 Hz), 4.59 (dt, 2H, J=2.8 Hz, 4.9 Hz), 5.24 (d, 1H, J=9.6 Hz), 5.28 (s, 1H), 7.45 (t, 1H, J=1.8 Hz), 7.62 (s, 1H), 7.93 (d, 2H, J=8.2 Hz), 8.10 (br s, 2H), 10.70 (s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 13.92, 22.38, 25.88, 30.36, 31.15, 50.54, 52.06, 59.16, 69.05, 70.17, 70.65, 71.93, 75.76, 81.21, 120.22, 121.63, 122.75, 131.62, 134.16, 135.53, 136.00, 136.08, 136.28, 136.43, 137.18, 139.41, 139.96, 140.06, 140.12, 140.59, 140.98, 141.53, 141.66, 141.79, 141.83, 142.00, 142.07, 142.14, 142.18, 142.47, 142.54, 142.66, 142.70, 142.97, 143.11, 144.27, 144.38, 144.69, 145.12, 145.24, 145.26, 145.30, 145.33, 145.44, 145.50, 145.61, 145.90, 146.05, 146.16, 146.24, 146.31, 147.17, 147.24, 147.29, 152.26, 152.61, 152.77, 153.80; IR (KBr, cm^{-1}) 2930, 2853, 1541, 1508, 1460, 1182, 1111, 833, 527; HRMS (MALDI-TOF MS, matrix: SA) found 1092.2657 ($C_{82}H_{34}N_3O_2^+$, calcd: 1092.2651).

5.8. Salt 7b

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J=Hz) δ 0.88 (t, 3H, J=7.1 Hz), 1.23 (br s, 26H), 1.98 (quin, 2H, J=7.5 Hz), 2.92 (quin, 1H, J=5.8 Hz), 3.37 (quin, 1H, J=6.0 Hz), 3.45 (s, 3H), 3.68 (dt, 2H, J=1.6 Hz, 4.8 Hz), 3.75–3.85 (m, 2H), 3.99 (quin, 1H, J=5.2 Hz), 4.05–4.10 (m, 1H), 4.36 (d, 1H, J=9.6 Hz), 4.56–4.66 (m, 2H), 5.24 (d, 1H, J=9.6 Hz), 5.27 (s, 1H), 7.40 (s, 1H), 7.62 (s, 1H), 7.93 (d, 2H, J=9.2 Hz), 8.09 (br, 2H), 11.24 (s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 13.91, 22.54, 25.85, 28.97, 29.22, 29.29, 29.43, 29.53, 29.56, 30.28, 31.78, 50.47, 51.94, 59.06, 67.28, 69.02, 70.03, 70.42, 71.86, 75.72, 81.09, 120.42, 121.64, 122.96, 131.45, 134.13, 135.49, 136.01, 136.19, 137.10, 139.34, 139.73, 139.89, 140.08, 141.44, 141.56, 141.60, 141.73, 141.89, 141.97, 142.09, 142.12, 142.37, 142.42, 142.54, 142.89, 142.99, 144.18, 144.29, 144.60, 145.01, 145.12, 145.15, 145.21, 145.29, 145.35, 145.40, 145.50, 145.54, 145.80, 145.95, 146.05, 146.14, 146.21, 147.13, 147.18, 152.20, 152.52, 153.69, 156.04; IR (KBr, cm^{-1}) 3402, 2922, 2849, 1541, 1508, 1458, 1182, 746, 527; HRMS (MALDI-TOF MS, matrix: SA) found 1232.4151 ($C_{92}H_{54}N_3O_2^+$, calcd: 1232.4216).

5.9. Compound 7c

^{1}H NMR (500 MHz, ppm, $CDCl_3$, J=Hz) δ 0.86 (t, 3H, J=6.9 Hz), 1.23 (br s, 26H), 1.50 (quin, 2H, J=6.9 Hz), 2.94 (quin, 1H, J=6.1 Hz), 3.35–3.41 (m, 3H), 3.45 (s, 3H), 3.53–3.55 (m, 2H), 3.59–3.63 (m, 8H), 3.66–3.69 (m, 4H), 3.78–3.85 (m, 2H), 3.97–4.02 (m, 3H), 4.06–4.09 (m, 1H), 4.36 (d, 1H, J=9.7 Hz), 4.85 (t, 2H, J=4.4 Hz), 5.25 (d, 1H, J=9.7 Hz), 5.27 (s, 1H), 7.64 (s, 1H), 7.85 (t, 2H, J=8.7 Hz), 7.96 (s, 1H), 8.08 (br s, 2H), 10.98 (s, 1H); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 14.06, 22.59, 25.98, 29.30, 29.46, 29.53, 29.61, 29.66, 31.88, 50.04, 52.00, 59.12, 67.52, 68.93, 69.15, 69.87, 70.00, 70.09, 70.22, 70.27, 70.45, 70.54, 71.38, 71.98, 75.84, 81.27, 119.65, 121.80, 124.89, 131.54, 134.31, 135.52, 135.89, 136.07, 136.25, 137.19, 139.39, 139.97, 140.19, 141.54, 141.67, 141.78, 141.83, 141.99, 142.08, 142.14, 142.19, 142.22, 142.47, 142.54, 142.66, 142.98, 143.11, 144.27, 144.40, 144.71, 145.11, 145.21, 145.24, 145.29, 145.34, 145.37, 145.46, 145.49, 145.52, 145.59, 145.62, 145.91, 146.06, 146.14, 146.16, 146.22, 146.25, 146.30, 147.24, 147.30, 152.29, 152.62, 153.83, 156.16; IR (KBr, cm^{-1}) 3439, 2916, 2849, 1541, 1508, 1458, 1107, 527; HRMS (MALDI-TOF MS, matrix: SA) found 1408.5262 ($C_{100}H_{64}N_3O_6^+$, calcd: 1408.5265).

5.10. Salt **8**

IR (KBr, cm^{-1}) 3435, 3063, 2922, 2814, 1508, 1429, 1107, 527; HRMS (MALDI-TOF MS, matrix: SA) found 1022.1867 ($C_{77}H_{24}N_3O_2$, calcd: 1022.1869). Due to poor solubility in $CDCl_3$, CD_3OD, DMSO-d_6, NMR spectra with sufficient resolution could not be obtained.

5.11. Solubility of a fullerene derivative

A saturated solution of a fullerene derivative in an organic solvent was prepared at 25 °C and filtered through a paper filter (Whatman No. 2). Then, the weight of the filtrate solution was measured, and the solvent was removed under vacuum. The solubility was calculated and reported in mg of solute/mL of the solvent at 25 °C based on the result of the amount of fullerene derivative remaining in a flask after removing the solvent.

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Supplementary data

Experimental procedure, ^1H, ^{13}C NMR, IR and HRMS spectra of **3a–c** and **7a–c**. HRMS and IR spectra of **4** and **8**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.11.097.

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