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Synthesis of 4-aziridino[C_{60}]fullerene-1,8-naphthalimide (C_{60}-NI dyads) and their photophysical properties

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ABSTRACT

A series of 4-aziridino[C_{60}]fullerene-1,8-naphthalimide (C_{60}-NI) dyads **4** ([6,6]-closed ring) were synthesized as the only addition product from the reaction of C_{60} with the corresponding azide compounds **3** under microwave irradiation in good yield. A quenching of fluorescence was shown in dyads **4**, and this decay was evidenced to be an intramolecular process.

1. Introduction

[C_{60}]Fullerene[1,2] is a redox-active chromophore, which, according to theoretical calculations, exhibits a LUMO (t_{1u}) comparatively low in energy and is triply degenerate. Therefore, C_{60} behaves like an electronegative molecule, which could reversibly accept up to six electrons in solution.[3] And also, the cyclic voltammetry and the electron affinity measured for [C_{60}]fullerene clearly confirm that it is a moderate electron acceptor comparable to other organic molecules such as benzo- and naphthoquinones.[4,5] Consequently, in the design of the new functional materials based on the electron acceptor–donor systems, [C_{60}]fullerene, as the electron-acceptor, has dominated the field compared to any other electron-acceptor.

In recent years, the perylene-3,4:9,10-bis(dicarboximide) (PDI) chromophore has received an increasing interest. It was attached to fullerene C_{60} with the aim of reaching new light-harvesting systems.[6,7] An efficient intramolecular energy transfer from the PDI toward fullerene C_{60} was evidenced in these dyads.[8,9] To our knowledge, the 1,8-naphthalimide (NI) chromophore has never been attached to an acceptor such as [C_{60}]fullerene, especially through the synthesis of fulleroaziridines.[10] As a part of our continuous study on the chemical transformation of C_{60}-fullerene, herein we report an efficient synthetic route to NI-C_{60} dyads (only closed [6,6]-bridged aziridinofullerene) and their spectroscopic properties.

2. Results and discussion

2.1. Synthesis

The strategy for the synthesis of 4-aziridino[C_{60}]fullerene-1,8-naphthalimide **4** (NI-C_{60} dyads) used the starting material 4-bromo-naphthalene anhydride **1** (Scheme 1). 4-Bromo-1,8-naphthalimide **2** was synthesized by treating **1** with aryl or alkyl amines in refluxing ethanol,[11] then the imides were heated with NaN_3 in DMF at 100 °C for 6 h to afford 4-azide-1,8-naphthalimide **3**[12] in moderate yields. Thermal reaction of C_{60} (0.1 mmol) with two equal molar **3b** was first carried out in chlorobenzene (15 mL) at 130 °C. After stirring the reaction mixture for 6 h, the reaction was finished, chromatography on silica gel using toluene as eluent gave unconvered C_{60} (30 mg) and the addition product **4b** (20 mg, 29%). When the molar ratio of **3b** to C_{60} was increased from 2:1 to 3:1 and then to 4:1, the yield of **4b** increased to 40% and 42%, respectively. In order to try higher reaction temperature, *o*-dichlorobenzene (*o*-DCB) was used as solvent. Under 160 °C, C_{60} was stirred with the excess azide **3b** (3:1) for 6 h, and the yield of **4b** was increased up to 56%. Further increasing the reaction temperature (180 °C) leads to the decrease of the yield of **4b** clearly (30%).

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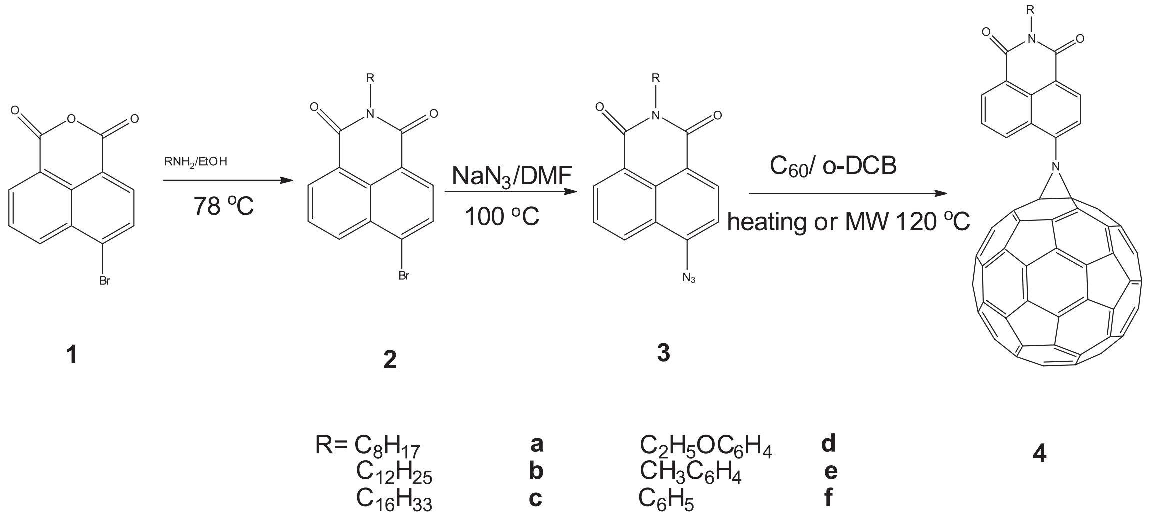

Scheme 1. Preparation of the dyads **4a**–**4f**.

Under microwave irradiation (120 °C, 700 W), the reaction of C_{60} with three equal molar **3b** in *o*-DCB was finished in 3 min and afforded addition product **4b** in high yield (73%). Longer irradiating time decreased the yield of **4b** (Table 1, Entry 10).

Table 1
Reaction results of C_{60} with **3b** under different reaction conditions

Entry	Mole ratio[a]	Method[b]	Solvent	Time	Yield[c] (%)
1	2	130 °C	Chlorobenzene	6 h	29
2	3	130 °C	Chlorobenzene	6 h	40
3	4	130 °C	Chlorobenzene	6 h	42
4	3	160 °C	*o*-DCB	6 h	56
5	3	180 °C	*o*-DCB	6 h	30
6	2	MW	*o*-DCB	3 min	53
7	3	MW	*o*-DCB	3 min	73
8	4	MW	*o*-DCB	3 min	74
10	3	MW	*o*-DCB	5 min	58

[a] Ratio of **3b**/C_{60}.
[b] Heated or irradiated under microwave (120 °C).
[c] Isolated yield based on the reacted C_{60}.

The structure of **4b** was fully identified by standard spectroscopic methods. The TOF mass spectrum of **4b** shows its molecular ion peak at m/z=1098 and the base peak at 720. The ^{13}C NMR shows only 17 peaks for C_{60} skeleton [16 between 141.0 and 146.5 ppm and 1 peak for the sp^3 hybridized carbon at 82.6 ppm]. This indicates for compound **4b** C_{2v}-symmetry with a [6,6] junction on the fullerene core. The two peaks at 163.7, 163.3 ppm are attributed to the two carbonyl carbon atoms for C═O, and 10 peaks at 119.9–134.9 ppm for the naphthalimide or aromatic carbon atoms, furthermore the remaining 12 peaks at 14.5–40.6 belong to the alkyl group ($C_{12}H_{25}$–). The UV spectrum of dyad **4b** exhibits the fullerene bands in the region of around 260 nm, 330 nm, and 420 nm (the typical bands of [6,6]-closed aziridinofullerene derivative) and the bands of the NI moiety around 375 nm (see Fig. 2a).

Generally, the reaction of C_{60} with azide compounds should give both [5 6]-bridged azafulleroid and [6,6]-closed ring aziridinofullerene products. In this case, however, only [6,6]-closed ring product was formed. In our previous study, we also found that the perfluoroalkanesulfonyl azides $R_fSO_2N_3$ reacted with C_{60} giving only [5,6]-open ring products.[13] Therefore, it was believed that the structure of NI gives rise to this unusual consequence.

Under the optimum reaction conditions (Table 1, entry 7), other 4-azide-1,8-naphthalimides (**3a**, **3c**–**3f**) added to C_{60} all affording [6,6]-irradiated azafulleroid products (NI-C_{60}) **4a** and **4c**–**4f** in 70–73% yields (Table 2).

Table 2
Preparation of NI-C_{60} dyads **4** under microwave irradiation condition[a]

Entry	Reactant	Product	Yield[b] (%)
1	**3a**	**4a**	70
2	**3b**	**4b**	73
3	**3c**	**4c**	72
4	**3d**	**4d**	71
5	**3e**	**4e**	71
6	**3f**	**4f**	72

[a] Ratio of **3b**/C_{60}=3:1 irradiated under microwave (120 °C) for 3 min.
[b] Isolated yield based on the reacted C_{60}.

2.2. Theoretical calculations

Quantum chemical calculations on the two dyads **4a**, **4f** have been conducted to get further insights of molecular structure. Geometrical optimization was performed with semiempirical methods using PM3 parametrization with Hyperchem 7.5. The alkyl group is found to be the tail of the planar naphthalimide core, but the phenyl group is nearly perpendicular to the planar naphthalimide core, thus minimizing steric hindrance between phenyl group and the imide functionality (Fig. 1). On the opposite part of the system, the plane of the phenyl spacer is oriented out of the naphthalimide plane.

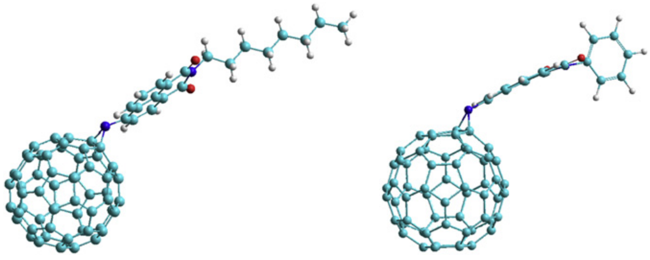

Figure 1. Optimized geometries of C_{60}-NI **4a** (left), **4f** (right).

2.3. UV spectra

Compounds **4** exhibit a typical UV–vis absorption profile of NI–fullerene adducts with four distinct broadband, at 240–430 nm region: a sharp absorption band characteristic of fullerene adducts at 260 nm, as well as the comparably intense band around 330 nm, the typical band of [6,6]-closed aziridinofullerene derivative around 420 nm, and the longest wavelength absorption band at 360–400 nm corresponding to the NI moiety (Fig. 2a). The absorption at 360–400 nm of the dyad **4d** is much stronger than **4b**, which indicates that the substitution (R) on the NI moiety (aromatic or alkyl group) seems to have an obvious influence on the absorption feature corresponding to the NI moiety.

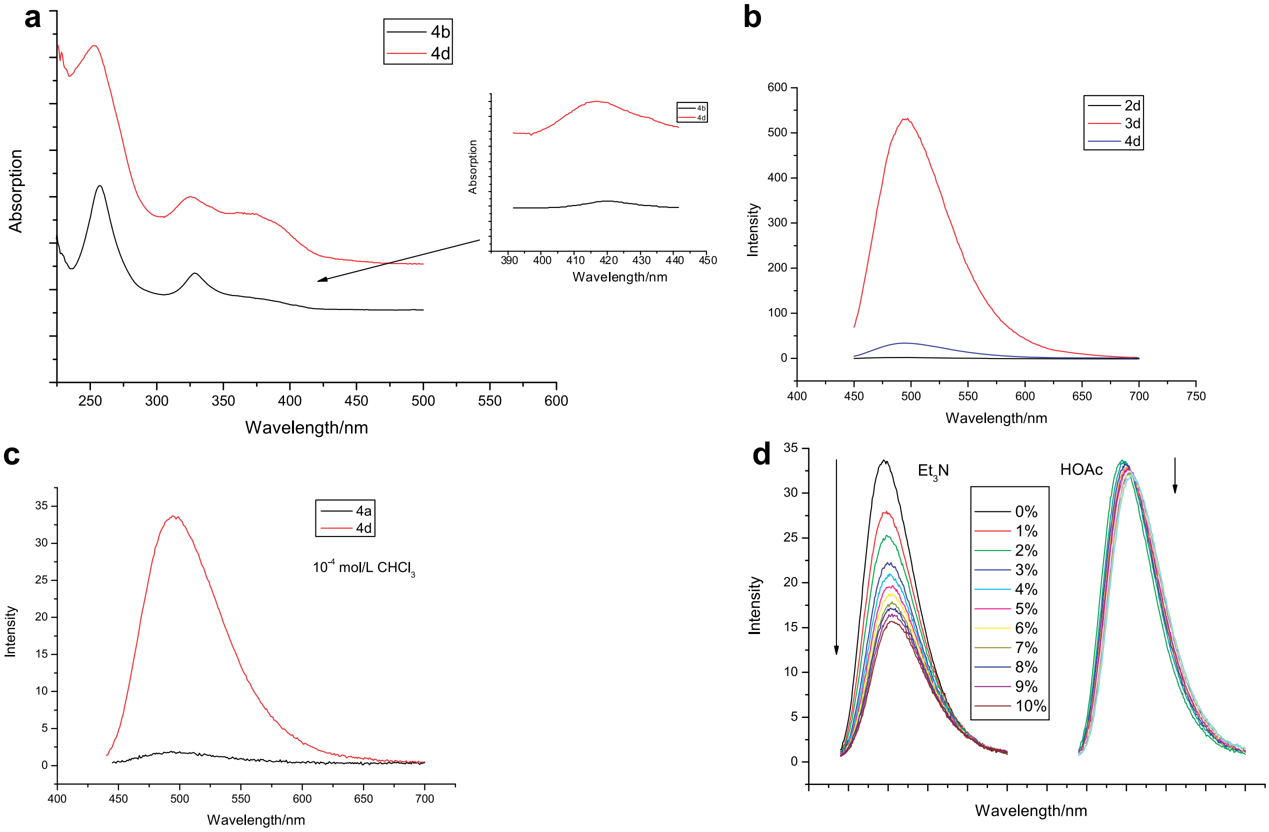

Figure 2. a. UV–vis spectra of **4b** and **4d**, $c<10^{-4}$ mol/L, in CH$_2$Cl$_2$. b. The fluorescence emission spectra of **2d**, **3d**, and **4d**, $c=10^{-4}$ mol/L in CHCl$_3$, excited in 434 nm. c. The fluorescence emissions spectra of **4a** and **4d**, $c=10^{-4}$ mol/L in CHCl$_3$, excited in 434 nm. d. The fluorescence emission spectra of **4d** when Et$_3$N and HOAc were added ($c=10^{-4}$ mol/L in CHCl$_3$).

2.4. Photophysical properties

The dyad's fluorescence is subjected to a strong quenching relative to the corresponding reference 4-azide-1,8-naphthalimide derivative **3d** (Fig. 2b). Figure 2b also shows the emission spectra of **4d** and **2d**, measured with excitation in the region of the NI chromophore in CHCl$_3$. Compared to the strong quenching of **2d**, the dyad **4d**'s quenching is weaker. This quenching suggests that [C$_{60}$] fullerene imido is better than the bromo in restarting fluorescence. The decay process must be intramolecular. This is evidenced by the experiment that the fluorescence of **3d** was not affected using a stoichiometric mixture of **3d** and C$_{60}$ in concentration similar to the case of dyad **4d**. This intramolecular decay of NI-C$_{60}$ has two possibilities. One is between the NI moiety and the fullerene. Such decay was also observed by the experiment that, when **4d** is compared with **3d**, the emission from the NI moiety is markedly depressed (Fig. 2b). The other is between the Ar component and the NI component. This is evidenced by the observation that **4d** also shows a different emission from the NI moiety as compared to **4a** (Fig. 2c).

A closer inspection of the fluorescence quenching, reveals two trends in regarding the magnitude of fluorescence quenching. First, from the *N*-alkyl dyads to *N*-aryl dyads, the quenching decreases, suggesting that as the substitution of NI moiety, the aryl is better than the alkyl in restarting fluorescence (Table 3). Second, the quenching of **4d**–**4f** correlates well with the electron-withdrawing strength of the substituent of NI moiety (Table 3).

When triethylamine (TEA) was added to the solution of **4d** in chloroform, the fluorescence quenching was largely affected. The quenching increased largely as TEA was added from 1% to 10% (Fig. 2d). However, the quenching remained almost unchanged when HOAc was added from 1% to 10% (Fig. 2d). Because of the 'on and off' property when added TEA, the dyad **4d** would be considered as a potential candidate of the fluorescent switch.[14]

Table 3
Selected photophysical data of dyads **4** at 298 K

Dyads	Intensity	Quenching[a]	λ_{max} (nm)	Solvent
4a	1.757	0.951	488	Toluene
4b	0.798	0.978	496	Toluene
4c	0.945	0.974	464	Toluene
4d	35.833	0	476	Toluene
4d	33.600	0	499	CHCl$_3$
4e	22.500	0.330	498	CHCl$_3$
4f	1.878	0.945	502	CHCl$_3$

[a] Quenching=(Intensity$_{\mathbf{4d}}$−Intensity)/Intensity$_{\mathbf{4d}}$.

3. Conclusion

In conclusion, the synthesis and spectroscopic studies of the fulleroaziridines are described. 4-Aziridino[C$_{60}$]fullerene-1,8-naphthalimide(C$_{60}$-NI) dyads **4** ([6,6]-closed ring) were synthesized through the aziridination reaction of C_{60} with the corresponding azide compounds **3** under microwave irradiation in high yield. It was found that this reaction only gave the [6,6]-closed ring compound **4**, without the [5,6]-open ring azafulleroid compound. Maybe, this unusual consequence is caused by the specific structure of NI.[13] It was also clearly demonstrated that the NI moiety can act as a light-harvesting antenna for C_{60}.[15] In the emission spectrum of NI-C_{60} in $CHCl_3$, the intramolecular decay process is shown. When TEA was added, its fluorescence was largely influenced, especially for the quenching magnitude. Consequently, this dyad would be regarded as a potential candidate of fluorescent switch.

4. Experimental section

4.1. General remarks

C_{60} was purchased from Wuhan University and in 99% purity. All reactions for the synthesis of **4** were performed in a microwave oven, under nitrogen atmosphere. *o*-Dichlorobenzene, carbon disulfide, toluene, and ethyl acetate were used in AR quality. ^{1}H, and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively, with chemical shift values being reported in parts per million relative to chloroform for ^{1}H NMR and ^{13}C NMR. Infrared spectra were obtained using an FT-IR spectrometer. Mass spectra were recorded using an ES or EI ion source. Ultraviolet spectra were performed with a UV spectrophotometer. Fluorescent spectra were performed with a spectrofluorometer.

4.2. Synthesis

*4.2.1. Preparation of N-dodecyl-4-azido-1,8-naphthalimide (**3b**).* To a suspension of **2b** (443 mg, 10 mmol) in DMF (10 ml) was added a suspension of sodium azide (65 mg, 10 mmol) in water (0.5 ml). The mixture was heated to 100 °C for 6 h and then poured into ice-water (100 ml). The precipitate formed was filtered, washed with water, and dried under vacuum. Compound **3b** (345 mg, 85%) was obtained as a yellow solid.

*4.2.1.1. N-Octyl-4-azido-1,8-naphthalimide (**3a**).* Yield 86%. IR (KBr, cm^{-1}): ν 3072, 2954, 2924, 2853, 2125, 1699, 1658, 1587, 1387, 1353, 1290, 1234, 782; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.58 (d, J=7.0 Hz, 1H), 8.51 (d, J=7.5 Hz, 1H), 8.37 (d, J=8.5 Hz, 1H), 7.69 (d, J=7.8 Hz, 1H), 7.41 (d, J=8.0 Hz, 1H), 4.12 (t, J=7.8 Hz, 2H), 1.67–1.73 (m, 2H), 1.25–1.42 (m, 10H), 0.85 (t, J=6.8 Hz, 3H); EIMS: (m/z, %): 350 (M^{+}, 7), 322 ($[M-N_2]^+$, 100).

*4.2.1.2. N-Dodecyl-4-azido-1,8-naphthalimide (**3b**).* Yield 85%. IR (KBr, cm^{-1}): ν 2954, 2922, 2851, 2125, 1699, 1659, 1586, 1559, 1386, 1353, 1291, 1235, 781; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.65 (d, J=7.5 Hz, 1H), 8.60 (d, J=8.0 Hz, 1H), 8.45 (d, J=8.5 Hz, 1H), 7.76 (d, J=7.0 Hz, 1H), 7.49 (d, J=8.0 Hz, 1H), 4.18 (t, J=7.5 Hz, 2H), 1.72–1.77 (m, 2H), 1.27–1.45 (m, 18H), 0.90 (t, J=6.5 Hz, 3H); EIMS: (m/z, %): 406 (M^{+}, 2), 378 ($[M-N_2]^+$, 100).

*4.2.1.3. N-Hexadecyl-4-azido-1,8-naphthalimide (**3c**).* Yield 83%. IR (KBr, cm^{-1}): ν 2959, 2920, 2850, 2125, 1699, 1660, 1586, 1353, 781; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.64 (d, J=7.0 Hz, 1H), 8.58 (d, J=8.0 Hz, 1H), 8.43 (d, J=8.0 Hz, 1H), 7.75 (d, J=8.0 Hz, 1H), 7.47 (d, J=8.0 Hz, 1H), 4.17 (t, J=8.0 Hz, 2H), 1.70–1.76 (m, 2H), 1.26–1.43 (m, 26H), 0.89 (t, J=7.0 Hz, 3H); EIMS: (m/z, %): 462 (M^{+}, 11), 434 ($[M-N_2]^+$, 100).

*4.2.1.4. N-(4-Ethoxyphenyl)-4-azido-1,8-naphthalimide (**3d**).* Yield 83%. IR (KBr, cm^{-1}): ν 3067, 2984, 2913, 2873, 2126, 1707, 1665, 1585, 1512, 1361, 783; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.68 (q, J=7.0 Hz, 1H), 8.63 (d, J=8.0 Hz, 1H), 8.50 (q, J=8.5 Hz, 1H), 7.78 (q, J=8.5 Hz, 1H), 7.51 (d, J=8.0 Hz, 1H), 7.21 (d, J=8.5 Hz, 18H), 7.04 (d, J=8.5 Hz, 3H), 4.09 (q, J=7.0 Hz, 2H), 1.45 (t, J=7.0 Hz, 3H); EIMS: (m/z, %): 358 (M^{+}, 63), 330 ($[M-N_2]^+$, 100).

*4.2.1.5. N-(4-Methylphenyl)-4-azido-1,8-naphthalimide (**3e**).* Yield 85%. IR (KBr, cm^{-1}): ν 3067, 3035, 2923, 2116, 1708, 1662, 1589, 1513, 1359, 782; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.68 (q, 1H, J=7.5 Hz), 8.63 (d, J=8 Hz, 1H), 8.50 (q, J=8.5 Hz, 1H), 7.78 (t, J=7.8 Hz, 1H), 7.50 (d, J=8 Hz, 1H), 7.35 (d, J=8 Hz, 2H), 7.19 (t, J=8.5 Hz, 2H); 2.44 (s, 3H); EIMS: (m/z, %): 328 (M^{+}, 30), 300 ($[M-N_2]^+$, 100).

*4.2.1.6. N-Phenyl-4-azido-1,8-naphthalimide (**3f**).* Yield 85%. IR (KBr, cm^{-1}): ν 3064, 2120, 1710, 1662, 1586, 1509, 1360, 782; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.67 (d, 1H, J=7.0 Hz), 8.62 (d, J=8.0 Hz, 1H), 8.50 (d, J=8.5 Hz, 1H), 7.78 (t, J=7.5 Hz, 1H), 7.55 (d, J=7.0 Hz, 2H), 7.50 (d, J=7.5 Hz, 2H), 7.32 (d, J=7.0 Hz, 2H); EIMS: (m/z, %): 314 (M^{+}, 18), 286 ($[M-N_2]^+$, 100).

*4.2.2. Preparation of N-dodecyl-4-aziridinofullerene-1,8-naphthalimide (**4b**) under microwave irradiation condition.* N-Dodecyl-4-azido-1,8-naphthalimide **3b** (122 mg, 0.3 mmol) and C_{60} (72 mg, 0.1 mmol) were mixed in *o*-DCB (5 ml) in a 10 ml flask, then the mixture was exposed to microwave irradiation at 120 °C for 3 min under nitrogen atmosphere. The solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (using toluene as elute) affording 33 mg of unconverted C_{60} (the first fraction) and 44 mg (73%) of the product **4b** (the second fraction). Other dyads **4a** and **4c**–**4f** were prepared similarly.

*4.2.2.1. N-Octyl-4-aziridinofullerene-1,8-naphthalimide (**4a**).* IR (KBr, cm^{-1}): ν 2952, 2921, 2849, 1696, 1661, 1581, 1235, 1098, 1041, 779, 525; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$, 1:3): δ (ppm) 9.31 (d, J=8.5 Hz, 1H), 8.68 (q, J=7.5 Hz, 2H), 7.94 (q, J=7.0 Hz, 2H), 4.16 (t, J=7.5 Hz, 2H), 1.74 (t, J=7.5 Hz, 2H), 1.32–1.35 (m, 10H), 0.91 (t, J=5.8 Hz, 3H); ES-MS: (m/z, %): 1043 ($[M+1]^-$, 8), 323 ($[M-C_{60}+1]^-$, 100).

*4.2.2.2. N-Dodecyl-4-aziridinofullerene-1,8-naphthalimide(**4b**).* IR (KBr, cm^{-1}): ν 2960, 2920, 2849, 1696, 1661, 1582, 1261, 1096, 1022, 802, 526; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$, 1:3): δ (ppm) 9.30 (d, J=8.5 Hz, 1H), 8.69 (d, J=7.5 Hz, 2H), 7.90–7.94 (m, 2H), 4.16 (t, J=7.0 Hz, 2H), 1.71–1.74 (m, 2H), 1.25–1.44 (m, 18H), 0.87 (t, J=6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$, 1:3): δ (ppm) 163.74, 163.33, 146.52, 145.53, 145.42, 145.26, 145.14, 144.75, 144.47, 144.02, 143.81, 143.29, 143.25, 143.15, 143.01, 142.23, 141.29, 141.02, 134.95, 131.77, 131.57, 129.75, 128.48, 127.84, 127.33, 125.22, 124.09, 119.93, 82.56, 40.57, 32.24, 31.20, 30.00, 29.97, 29.92, 29.74, 29.70, 28.39, 27.45, 23.11, 14.46; ES-MS: (m/z, %): 1098 ($[M]^-$, 12), 720 (C_{60}^{-}, 100).

*4.2.2.3. N-Hexadecyl-4-aziridinofullerene-1,8-naphthalimide (**4c**).* IR (KBr, cm^{-1}): ν 2963, 2920, 2850, 1661, 1531, 1261, 801, 701, 520; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$, 1:3): δ (ppm) 9.34 (d, J=8.5 Hz, 1H), 8.74 (d, J=8.0 Hz, 2H), 7.94–7.98 (m, 2H), 4.21 (t, J=7.8 Hz, 2H), 1.75–1.77 (m, 2H), 1.44–1.48 (m, 2H), 1.36–1.38 (m, 2H), 1.25 (s, 22H), 0.88 (t, J=6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$, 1:3): δ (ppm) 164.09, 163.68, 146.62, 145.50, 145.39, 145.21, 145.12, 144.72, 144.44, 143.99, 143.80, 143.25, 143.21, 142.98, 142.20, 142.18, 141.25, 140.96, 131.84, 131.62, 129.70, 128.60, 127.33, 125.20, 124.02, 123.95, 119.94, 118.94, 82.52, 44.11, 40.61, 32.03, 31.47, 30.20, 29.81, 29.80, 29.77, 29.75, 29.70, 29.53, 29.48, 28.28, 27.29, 22.82, 14.24; EIMS: (m/z, %): 1153 ($[M-1]^-$, 20), 720 ($[C_{60}]^-$, 100).

*4.2.2.4. N-(4-Ethoxyphenyl)-4-aziridinofullerene-1,8-naphthalimide (**4d**).* IR (KBr, cm^{-1}): ν 3068, 2963, 2921, 1708, 1666, 1586, 1511, 1361, 783, 531; ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 8.69 (d, J=6.5 Hz, 1H), 8.67 (d, J=7.0 Hz, 1H), 8.62 (t, J=8.0 Hz, 1H), 7.78 (t, J=8.0 Hz, 1H), 7.51 (d, J=8.0 Hz, 1H), 7.19 (d, J=8.5 Hz, 2H), 7.03 (d, J=8.5 Hz, 2H), 4.10 (q, J=7.0 Hz, 2H), 1.46 (t, J=6.8 Hz, 3H); ES-MS: (m/z, %): 1051 ([M+1]$^-$, 20), 330 ([M−C$_{60}$]$^-$, 100).

*4.2.2.5. N-(4-Methylphenyl)-4-aziridinofullerene-1,8-naphthalimide (**4e**).* IR (KBr, cm^{-1}): ν 3067, 3031, 2958, 2922, 1710, 1663, 1586, 1512, 1361, 782, 520; ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$, 1:3): δ (ppm) 8.70 (d, J=6.5 Hz, 1H), 8.64 (d, J=8.0 Hz, 1H), 8.48 (d, J=8.0 Hz, 1H), 8.09 (d, J=7.5 Hz, 1H), 7.90 (t, J=8.0 Hz, 1H), 7.34 (d, J=7.0 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H), 2.46 (s, 3H); ES-MS: (m/z, %): 720 ([C$_{60}$]$^-$, 2), 299 ([M−C$_{60}$−1]$^-$, 100).

*4.2.2.6. N-Phenyl-4-aziridinofullerene-1,8-naphthalimide (**4f**).* IR (KBr, cm^{-1}): ν 3059, 2960, 2921, 1706, 1668, 1583, 1367, 692, 526; ^{1}H NMR (500 MHz, CDCl$_3$/CS$_2$, 1:3): δ (ppm) 8.72–8.74 (m, 2H),7.97–8.00 (m, 2H), 7.54 (t, J=8.0 Hz, 2H), 7.47 (t, J=8.5 Hz, 1H), 7.29 (d, J=8.5 Hz, 2H), 7.20 (t, J=7.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$:CS$_2$, 1:3): δ (ppm) 163.20, 163.17, 145.45, 145.33, 144.66, 144.36, 143.93, 143.93 143.64, 143.20, 143.16, 143.05, 142.93, 142.13, 141.22, 140.93 135.30, 132.03, 131.85, 130.48, 130.04, 129.17, 128.99, 128.71, 128.51, 127.57, 127.31, 125.29, 124.35, 124.35, 123.95, 119.92, 82.47; EIMS: (m/z, %): 1006 (M$^-$, 23), 720 (C$_{60}^-$, 100).

*4.2.3. Preparation of N-dodecyl-4-aziridinofullerene-1,8-naphthalimide (**4b**) under thermal reaction condition.* A solution of C$_{60}$ (101 mg, 0.14 mmol) and **3b** (171 mg, 0.42 mmol) in 30 mL of *o*-DCB was heated at 160 °C for 6 h and the solvent was then evaporated under reduced pressure. Similar work-up as the microwave irradiation reaction gave unconverted C$_{60}$ (51 mg) and **4b** (55 mg, 56%).

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.05.019.

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