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Base-promoted reaction of $C_{60}Cl_6$ with thioamides: an access to [60] fullereno[1,9-*d*] thiazoles

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ABSTRACT

Regioselective reaction of $C_{60}Cl_6$ with thioamides via a radical annulation to form fullereno thiazole derivatives is reported. The reaction is promoted by K_2CO_3, which might deprotonate thioamide to initiate a single electron transfer from thioamide anion to $C_{60}Cl_6$. The experiments with various thioamides establish the proposed base-promoted reaction as a facile route for synthesis of fullereno fused thiazole derivatives starting from $C_{60}Cl_6$, a prevalent synthon in fullerene chemistry. In addition, the tunable electrochemical properties of the fullereno thiazole products have been investigated for their potential photovoltaic application.

1. Introduction

Fullerene derivatives have attracted considerable attention due to their potential applications in the fields such as photovoltaic and biological materials.[1] Various derivatization methods have been developed to modify the fullerene cage over the years. Among them, hexachlorofullerene $C_{60}Cl_6$ is a prevalent synthon for preparation of novel fullerene derivatives by substitution of chlorine atoms with appropriate organic groups.[2] For example, Troshin et al.[3] reported a highly water-soluble fullerene derivative through Arbuzov-type reaction of $C_{60}Cl_6$ with trialkyl phosphites. Darwish and co-workers[4] treated $C_{60}Cl_6$ with phenol to give corresponding benzo[*b*]furano fullerenes. Stable pentacyanofullerene anion $[C_{60}(CN)_5]^-$ was obtained by reaction of $C_{60}Cl_6$ with organic cyanide.[5] Recently, our group succeeded in converting $C_{60}Cl_6$ into fullerocyclobutene derivatives through a copper(I)-mediated radical annulation reaction.[6] Herein we report another unexpected regioselective reaction involving $C_{60}Cl_6$ and thioamide in the presence of K_2CO_3. Promoted by K_2CO_3 base, two out of six chlorine atoms on fullerene skeleton are replaced by thiazole regioselectively, and the other four chlorine atoms leave from the fullerene cage to result in fullerene-fused thiazole compound. The mechanism responsible for the reaction is different from those previously reported by Itami and co-workers[7] for synthesis of fullerene-fused thiazole derivatives using aziridinofullerene as precursor. The present regioselective reactions starting from the prevalent $C_{60}Cl_6$ (with quantitative yield) is efficient over Itami's method using aziridinofullerene (with ~43% yield) as reactant, and is different from the fullerene-fused oxazole derivatization with the heteroatom involved.[8]

2. Results and discussion

4-*tert*-Butylthiobenzamide (**1a**) was used as a model substrate for optimizing the reaction conditions, including bases, phase transfer catalysts (PTCs), and solvent systems. Only a trace amount of product **2a** was obtained without base added (Table 1, entry 1). The reaction was improved in the presence of K_2CO_3, but the isolated yield of **2a** (<10%) was unsatisfactory (Table 1, entry 2). The effect of solvent was also critical to the catalytic reaction. With a mixture of *o*-DCB (5 mL) and toluene (50 mL) as solvent media, product **2a** was obtained in 15% yield (Table 1, entry 3), which was significantly improved by applying tetrabutylammonium hydrogen sulfate (TBAHS) as phase transfer catalyst (Table 1, entry 4). Using Na_2CO_3 as the base in replacement of K_2CO_3 reduced the yield to 9% (Table 1, entry 5). Stronger base such as Cs_2CO_3 resulted in dechlorination of reactant $C_{60}Cl_6$ leading to lower yield under otherwise the same reaction conditions. Replacing TBAHS with

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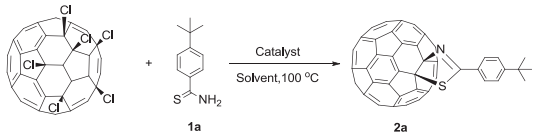
0040-4020/

Table 1
Reaction of $C_{60}Cl_6$ with **1a** under selected conditions[a]



Entry	Base	PTC[b]	Solvent (mL)[c]	Yield (%)[d]
1	None	None	$PhCH_3$	Trace
2	K_2CO_3	None	$PhCH_3$	<10%
3	K_2CO_3	None	*o*-DCB/$PhCH_3$(5:50)	15
4	**K_2CO_3**	**TBAHS**	***o*-DCB/$PhCH_3$(5:50)**	**32**
5	K_2CO_3	TBAHS	*o*-DCB/PhCl(5:50)	20
6	Na_2CO_3	TBAHS	*o*-DCB/$PhCH_3$(5:50)	9
7	K_2CO_3	PEG600	*o*-DCB/$PhCH_3$(5:50)	16
8	K_2CO_3	TOMAB	*o*-DCB/$PhCH_3$(5:50)	13
9[e]	K_2CO_3	TBAHS	*o*-DCB/$PhCH_3$(5:50)	28
10[f]	K_2CO_3	TBAHS	*o*-DCB/$PhCH_3$(5:50)	20
11[f]	K_2CO_3	TBAHS	*o*-DCB/$PhCH_3$(5:50)	25
12[g]	K_2CO_3	TBAHS	*o*-DCB/$PhCH_3$(5:50)	23
13[h]	K_2CO_3	TBAHS	*o*-DCB/$PhCH_3$(5:50)	0

The bold values represent the optimal reaction conditions.
[a] All reactions were performed with 0.05 mmol of $C_{60}Cl_6$, 0.10 mmol of **1a**, 0.50 mmol of base and 0.005 mmol of PTC in the indicated solvent at 100 °C for 12 h unless otherwise noted.
[b] PTC=phase transfer catalyst, TBAHS=tetrabutylammonium hydrogen sulfate, PEG600=polyethylene glycol 600, TOMAB=trioctyl methyl ammonium bromide.
[c] *o*-DCB=*o*-dichlorobenzene.
[d] Isolated yield.
[e] 20 equiv of K_2CO_3.
[f] The experiments were carried out at a temperature of 80 or 120 °C.
[g] The reaction time was 24 h.
[h] The experiment was carried out starting from C_{60} and **1a**.

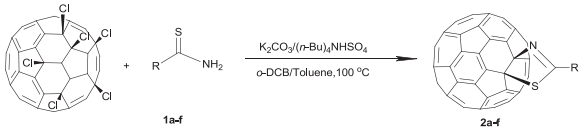
polyethylene glycol 600 or trioctyl methyl ammonium bromide under otherwise the same conditions resulted in a decrease in the yield too (Table 1, entries 7–8). It is noteworthy that increasing the loading of K_2CO_3 from 10 to 20 equiv leads a negative result (Table 1, entry 4 vs entry 9). Neither the reaction temperature nor the reaction time showed serious influence on the reaction (Table 1, entries 10–12). Accordingly, the optimal reaction conditions were selected with 2 equiv **1a**, 10 equiv K_2CO_3, and 0.1 equiv TBAHS (Table 1, entry 4). It should be noted that reaction of **1a** with C_{60} failed to give the expected product under the same reaction condition (Table 1, entry 13). Both ^1H and ^{13}C NMR spectra of **2a** match well with the identified structures [see Supplementary data (SD)].

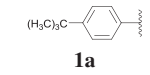
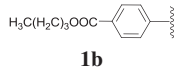
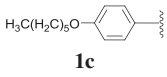
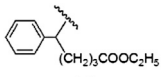
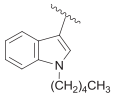
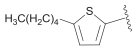
Reactions of $C_{60}Cl_6$ with other thioamides under the optimized reaction conditions (as described above) were carried out. As shown in Table 2, substrates **1a**–**f** bridged with aromatic or nonaromatic groups afforded the desired products **2a**–**f** in 23–42% yields. In principle, the aromatic thioamides linked with electron-donating groups are of higher reactivity. The reactions involving the aromatic thioamides having electron-donating groups thus afford higher yields than those containing electron-withdrawing groups (Table 2, entries 1–3). The reaction of nonaromatic thioamide **1d** gives a relatively high yield of 42% (Table 2, entry 4). While heterocyclic thioamides **1e** and **1f** participated in the reaction to afford **2e** and **2f** in 28 and 23% yield, respectively (Table 2, entries 5–6).

New compounds **2b**–**f** were characterized by ^1H NMR, ^{13}C NMR, IR, and UV–Vis spectral data. All of the mass spectra of these fullerothiazole products gave matchable molecular ion peaks. In addition, geometrical structure of product **2f** was further identified by X-ray diffraction analysis (see the SD).[9] In agreement with NMR spectra data, as shown in Fig. 1, the thiazole was regioselectively fused onto the [6,6] bond of the fullerene cage.

A possible mechanism for the reaction is shown in Scheme 1, which is proposed according to the present experimental evidence and literature.[6,10] Considering electron absence in both C_{60} cage and chlorine atom, single electron transfer (SET) from thioamide anion

Table 2
Reaction of $C_{60}Cl_6$ with **1a**–**f** under optimized conditions[a]



Entry	R	2	Yield (%)[b]	Recovered C_{60} (%)
1	 **1a**	**2a**	32	52
2	 **1b**	**2b**	25	65
3	 **1c**	**2c**	35	48
4	 **1d**	**2d**	42	45
5	 **1e**	**2e**	28	62
6	 **1f**	**2f**	23	58

[a] All reactions were performed with 0.05 mmol of $C_{60}Cl_6$, 0.10 mmol of **1**, 0.5 mmol of K_2CO_3 and 0.005 mmol of TBAHS in *o*-DCB (5 mL)/$PhCH_3$ (50 mL) at 100 °C for 24 h.
[b] Isolated yield.

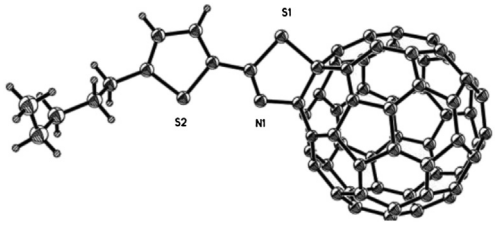
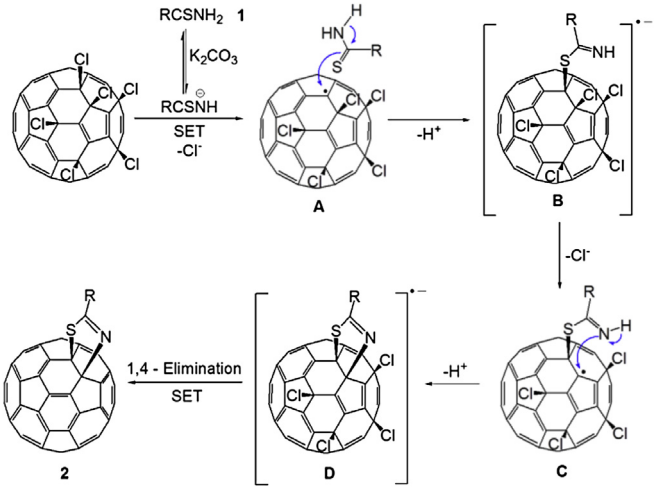


Fig. 1. Crystallographic structure of **2f**.



Scheme 1. Proposed mechanism for the formation of [60]fullereno[1,9-*d*] thiazole derivatives **2** (SET = single electron transfer).

(i.e., promoted by K_2CO_3) to $C_{60}Cl_6$ is reasonably supposed. Then the so-formed radical anion loses the chloride-anion at one of the hexagon–hexagon (6–6) fusion sites. Considering the loss of chlorine atom attached to the centre cyclopentadienyl ring and the subsequently nucleophilic attack process seems to be an end road due to the steric hindrance, the chloride-anion next to the centre cyclopentadienyl ring (as shown in Scheme 1) is most likely lost from the cage to form radical **A**, which is attacked by thioamide **1**, followed by deprotonation to produce radical anion **B** in the presence of base. In the similar way, loss of the second chloride-anion gives radical **C**, followed by a ring closure and deprotonation to form radical anion **D**. In the final stage, the intermediate **D**, similar to the products reported in our previous reaction involving $C_{60}Cl_6$ with aryl acetylenes,[6] undergoes the well-known chlorine 1,4-elimination[11] to form the final product **2**.

The electrochemical properties of the thiazole fullerene derivatives are exemplified with **2d** and **2f** and compared with their analogue PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester), the most widely useful electronic acceptor in organic/polymer solar cells. In the cyclic voltammogram of **2d** (Fig. 2), an oxidation wave and six pairs of reduction peaks were observed. Among them the first three pairs of redox peaks are reversible with 450±50 mV potential difference, which is a typical interval between two successive redox peaks in fullerene derivatives.[12] However, the other redox waves are irreversible, with implication of a possible reaction between **2d** and the working solution to result in the potential interval less than 450±50 mV. Taking the first three redox waves as examples, the electron transfer involving in each corresponding reversible redox reaction can be evaluated as a one-electron process based on the ~56 mV peak separation ($\Delta E=E_a-E_c$) between the anodic and cathodic peaks recorded at a low scan rate [ΔE is an indication of the number (n) of electron transfer according to the equation of $\Delta E=56.5/n$].[13] Similar one-electron transfer is observed in PCBM as well. The first reduction potential of **2d**, however, was shifted to an anodic potential by ca. 50 mV relative to that of PCBM,[14] reflecting the electron-withdrawing effect of the substituted thiazole unit. Interestingly, the electrochemical properties can be tuned depending on the functional groups that could be replaced by base-promoted reaction described in this paper. The reduction of **2f**, for example, showed four well-defined reversible waves, with implication of potential usefulness as electronic acceptor comparable with PCBM (Table 3).

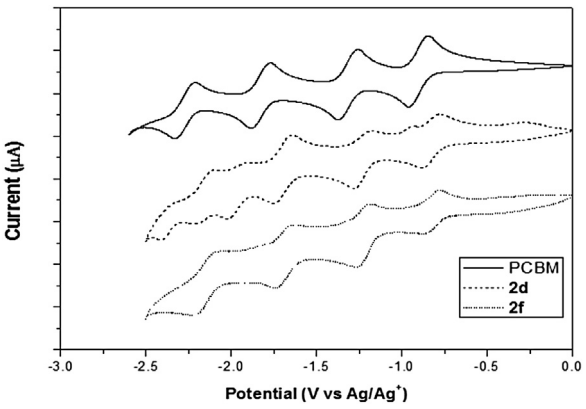


Fig. 2. Cyclic voltammograms of PCBM, **2d** and **2f**, the measurements were performed in a mixed solution of *o*-dichlorobenzene/acetonitrile (5:1) containing 0.1 M (n-Bu)$_4$NPF$_6$ in the potential range of 0 to −2.6 V versus Ag/Ag$^+$.

3. Conclusion

In summary, a versatile base-promoted reaction involving $C_{60}Cl_6$ and thioamide to form [60]fullereno[1,9-*d*] thiazole has been developed. Six chloride groups on fullerene skeleton are replaced and one fused thiazole effectively forms during one-step featuring a high regioselectivity for the present reaction. A radical mechanism possibly responsible for the formation of fullerene-fused thiazole is proposed, in which the base might serves as a deprotonated reagent initiating the SET process. This work provides a facile route to synthesize fullereno fused thiazole derivatives, and a complement to the existing reactions involving $C_{60}Cl_6$. Encouraged by valuable electrochemical properties of the fullerene-fused thiazole derivatives, further studies on potential application of the novel reaction on making functional fullerene-based materials (e.g., the electron acceptors for organic/polymer solar cells) are underway.

Table 3
Electrochemical onset reduction potentials and half-wave potentials of the fullerene derivatives

Compound	E_{red}^{on} (V)	$E1$ (V)	$E2$ (V)	$E3$ (V)	$E4$ (V)
PCBM	−0.80	−0.90	−1.31	−1.82	−2.27
2d	−0.75	−0.82	−1.23	−1.69	—
2f	−0.74	−0.82	−1.22	−1.69	−2.16

4. Experimental section

4.1. General

All starting materials were purchased commercially and used without further purification. All solvents are ACS grade unless otherwise noted. High performance liquid chromatography (HPLC) was performed on a LC-20AT Shimadzu instrument equipped with a 5PBB column (10×250 mm). Toluene was used as elution at a flow rate of 2 ml/min. The elution components were detected at 330 nm and concentrated by rotary evaporator at room temperature. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-600 (or AV-500, AV-400) spectrometer. Chemical shifts were reported in parts per million. ^{1}H and ^{13}C NMR spectra were referenced to $CHCl_3/CDCl_3$ (7.26 ppm for ^{1}H NMR and 77.26 ppm for ^{13}C NMR). All ^{13}C NMR spectra were measured with complete proton decoupling. IR spectra were detected on a Nicolet AVATER FTIR 330 spectrometer for thin film samples. Absorptions were given in wave numbers (cm^{-1}). UV–vis spectra were measured on a Cary5000 UV–vis spectrometer. Absorptions were given in wavelengths (nm). MS data were obtained via a Bruker-Esquire HCT instrument with atmospheric pressure chemical ionization (APCI) source. FT-MS data were measured on a Bruker APEX 7.0 instrument with APCI source. The diffraction data were collected on a Bruker Smart Apex-2000 CCD diffractometer using a graphite-monochromated Mo Kα (λ=0.71073 Å) radiation with a ω scan mode at 173 K. The structure was solved by direct methods with SHELXS-97 program and refined by full-matrix least-squares calculations based on F^2 with SHELXL-97 program.[15,16] All non-hydrogen atoms were refined anisotropically. Cyclic voltammetry (CV) measurements were performed with a three-electrode cell in a 0.1 M tetra-*n*-butylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) solution in *o*-dichlorobenzene/acetonitrile (5:1) solutions at a scan rate of 100 mV/s at room temperature. An Ag/Ag$^+$ electrode, a platinum wire, and a platinum disk were used as the reference electrode, the counter electrode, and the working electrode, respectively.

4.2. General procedures for the synthesis of fullereno[1,9-*d*] thiazoles 2a–f

To a 50 mL flask containing a magnetic stirring bar was added a solution of $C_{60}Cl_6$ (46 mg, 0.05 mmol, 1.0 equiv) in dry *o*-dichlorobenzene (5.0 mL). The mixture was stirred at 100 °C when K_2CO_3 (9×10^{-3} mol/L) and phase transfer catalyst TBAHS

(9×10^{-5} mol/L) were added. To the resulting solution was added a solution of thioamides (0.1 mmol, 2.0 equiv) in dry toluene (50 mL). The reaction mixture was stirred for 12 h at 100 °C and afterwards cooled down to room temperature. All insoluble products were filtered off, while the filtrate was concentrated in vacuum to give brown solid and dried in vacuum. Purification by HPLC (elution with toluene at 2 ml/min flow rate) afforded **2a**–**f** (23–42%).

*4.2.1. 2′-(4-tert-Butylphenyl)[60]fullereno[1,9-d] thiazole (**2a**).* Yield 32%; ^{1}H NMR (600 MHz, CS_2/$CDCl_3$=1:1) δ 1.45 (s, 9H), 7.64 (d, J=8.4 Hz, 2H), 8.15 (d, J=8.4 Hz, 2H); ^{13}C NMR (150 MHz, CS_2/$CDCl_3$=1:1) δ 31.43, 35.36, 74.77, 104.91, 126.18, 129.10, 129.68, 135.20, 135.73, 139.96, 140.59, 141.95, 142.04, 142.13, 142.36, 142.60, 142.86, 142.94, 142.97, 143.25, 143.29, 143.94, 144.57, 144.68, 145.51, 145.54, 145.65, 145.89, 146.00, 146.24, 146.33, 146.37, 146.41, 146.65, 146.82, 148.08, 148.13, 149.83, 156.31, 168.51; FTIR ν/cm^{-1} (KBr) 526, 797, 1018, 1090, 1260, 1602, 2961; UV–vis λ_{max}/nm (toluene) 320, 433; FT-MS (APCI negative mode) m/z calcd for $C_{71}H_{13}NS$ 911.0769, found 911.0763.

*4.2.2. Butyl-4-([60]fullereno[1,9-d] thiazole)benzoate (**2b**).* Yield 25%; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$=1:1) δ 1.07 (t, J=7.2 Hz, 3H), 1.54–1.62 (m, 2H), 1.82–1.89 (m, 2H), 4.29 (t, J=6.8 Hz, 2H), 8.29(d, J=1.2 Hz, 4H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$=1:1) δ 13.84, 19.36, 30.81, 65.44, 74.91, 104.76, 128.99, 130.15, 133.88, 135.04, 135.65, 135.92, 139.83, 140.48, 141.78, 141.87, 142.19, 142.42, 142.70, 142.72, 142.83, 143.09, 143.67, 144.38, 144.48, 145.37, 145.40, 145.54, 145.72, 145.77, 146.01, 146.04, 146.19, 146.23, 146.27, 146.52, 147.94, 147.98, 149.08, 165.84, 168.06; FTIR ν/cm^{-1} (KBr) 526, 1018, 1104, 1273, 1721, 2922; UV–vis λ_{max}/nm (toluene) 320, 432; FT-MS (APCI negative mode) m/z calcd for $C_{72}H_{13}O_2NS$ 955.0668, found 955.0662.

*4.2.3. 2′-(4-Hexyloxyphenyl)[60]fullereno[1,9-d] thiazole (**2c**).* Yield 35%; ^{1}H NMR (600 MHz, CS_2/$CDCl_3$=1:1) δ 0.97 (t, J=6.0 Hz, 3H), 1.40–1.43 (m, 4H), 1.53–1.58 (m, 2H), 1.86–1.91 (m, 2H), 4.12 (t, J=6.0 Hz, 2H), 7.09 (d, J=12.0 Hz, 2H), 8.14 (d, J=1.2 Hz, 2H); ^{13}C NMR (150 MHz, CS_2/$CDCl_3$=1:1) δ 14.39, 23.04, 26.08, 29.49, 31.94, 68.51, 74.81, 104.73, 114.88, 124.75, 130.22, 130.96, 135.15, 135.60, 139.87, 140.50, 141.88, 141.97, 142.08, 142.28, 142.52, 142.78, 142.86, 142.89, 143.17, 143.87, 144.50, 144.62, 145.42, 145.44, 145.58, 145.79, 145.91, 146.16, 146.24, 146.28, 146.33, 146.55, 146.98, 147.98, 148.04, 149.88, 162.68, 167.55; FTIR ν/cm^{-1} (KBr) 525, 605, 728, 831, 1022, 1169, 1249, 1505, 1560, 2922; UV–vis λ_{max}/nm (toluene) 319, 432; FT-MS (APCI negative mode) m/z calcd for $C_{73}H_{17}ONS$ 955.1031, found 955.1027.

*4.2.4. 2′-(4-(Methylperoxy)-1-phenylpent-4-en-1-yl)[60]fullereno [1,9-d] thiazole (**2d**).* Yield 42%; ^{1}H NMR (500 MHz, CS_2/$CDCl_3$=1:1) δ 1.28 (t, J=8.5 Hz, 3H), 1.84–2.00 (m, 2H), 2.32–2.42 (m, 1H), 2.45–2.52 (m, 2H), 2.61–2.69 (m, 1H), 4.14–4.19 (m, 2H), 4.32–4.35 (m, 1H), 7.41–7.68 (m, 5H); ^{13}C NMR (125 MHz, CS_2/$CDCl_3$=1:1) δ 14.56, 23.45, 34.37, 34.45, 51.21, 60.65, 74.70, 104.83, 128.31, 128.65, 129.44, 135.08, 135.22, 135.66, 135.82, 139.93, 140.00, 140.64, 141.97, 142.09, 142.14, 142.17, 142.41, 142.64, 142.92, 142.94,143.04, 143.32, 143.91, 143.95, 144.63, 144.72, 145.58, 145.62, 145.65, 145.95, 145.99, 146.30, 146.40, 146.45, 146.52, 146.59, 146.73, 148.14, 148.21, 149.67, 149.75, 173.53, 175.36; FTIR ν/cm^{-1} (KBr) 526, 698, 1028, 1146, 1181, 1732, 2923; UV–vis λ_{max}/nm (toluene) 321, 432; FT-MS (APCI negative mode) m/z calcd for $C_{74}H_{17}O_2NS$ 983.0980, found 983.0975.

*4.2.5. 2′-(1-Pentyl-1H-indol-3-yl)[60]fullereno[1,9-d] thiazole (**2e**).* Yield 28%; ^{1}H NMR (500 MHz, CS_2/$CDCl_3$=1:1) δ 1.01(t, J=6.0 Hz, 3H), 1.27–1.34 (m, 2H), 1.42–1.50 (m, 2H), 2.03–2.07 (m, 2H), 4.32(t, J=8.5 Hz, 2H), 7.26–7.46 (m, 3H), 7.87(s, 1H), 8.59(d, J=9.0 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/$CDCl_3$=1:1) δ14.48, 23.05, 29.61, 30.31, 47.37, 74.42, 104.27, 109.69, 109.79, 122.26, 123.08, 123.61, 126.34, 132.06, 135.05, 135.23, 136.89, 139.64, 140.34, 141.72, 141.86, 142.10, 142.12, 142.39, 142.60, 142.72, 142.78, 143.01, 143.83, 144.36, 144.54, 145.24, 145.39, 145.59, 145.92, 146.00, 146.05, 146.10, 146.15, 146.34, 147.81, 147.85, 147.97, 150.40, 160.44; FTIR ν/cm^{-1} (KBr) 525, 801, 1020, 1097, 1262, 2963; UV–vis λ_{max}/nm (toluene) 323, 432; FT-MS (APCI negative mode) m/z calcd for $C_{74}H_{16}N_2S$ 964.1034, found 964.1028.

*4.2.6. 2′-(5-Pentylthiophen-2-yl)[60]fullereno[1,9-d] thiazole (**2f**).* Yield 23%; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$=1:1) δ 1.02 (t, J=5.6 Hz, 3H), 1.42–1.50 (m, 4H), 1.84–1.90 (m, 2H), 3.02 (t, J=6.0 Hz, 2H), 6.99 (d, J=2.8 Hz, 1H), 7.62 (d, J=3.2 Hz, 1H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$=1:1) because of the low solubility of the sample, not all carbon signals were adequately acquired. δ 14.42, 22.99, 30.90, 31.55, 31.70, 125.34, 126.27, 128.61, 129.62, 132.34, 135.02, 135.29, 139.70, 140.34, 141.83, 141.96, 142.12, 142.68, 143.01, 143.63, 144.32, 144.49, 145.26, 145.46, 145.63, 145.74, 145.94, 146.11, 146.37, 146.87, 147.83, 149.58, 153.20; FTIR ν/cm^{-1} (KBr) 526, 800, k1035, 1461, 1595, 2926; UV–vis λ_{max}/nm (toluene) 321, 432; FT-MS (APCI negative mode) m/z calcd for $C_{70}H_{13}NS_2$ 931.0489, found 931.0484.

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Supplementary data

Supplementary data containing characterization spectra and X-ray crystallographic data. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.07.067.

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