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Synthesis and Characterization of a Squarylium Cyanine Dye with Two [60]Fullerene Units

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Abstract: A new [60]fullerene dimer **2** in which two C_{60} units are covalently attached to a squarylium cyanine dye has been synthesized and characterized.

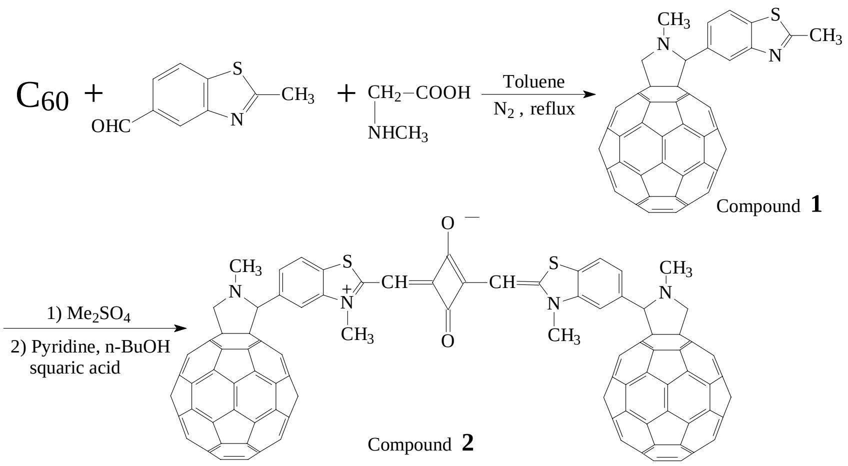
Keywords: [60]Fullerene, dimer, squarylium cyanine dye.

Fullerene derivatives containing two or more [60]fullerene units may exhibit interesting properties[1]. There have been reported a limited number of organofullerenes with two or more cages, and the synthetic procedures are an oxidative coupling reaction of terminal alkynes[2], bifunctional cycloaddition reactions such as diazo compounds[3], dienes[4] or α-amino acids and aldehydes 1, 3-dipolar cycloaddtion[5], cyanogen di-N-oxide as a double 1, 3-dipole[6]. Oxo- and methylene-bridged [60]fullerene dimers containing fullerene-fullerene bonds have also been prepared by heating of $C_{60}O$[7] and $C_{61}Br_2$[8]. Recently, we are interested in synthesis and characterization of dye based on two [60]fullerene units and a squarylium cyanine dye containing two [60]fullerene units is obtained. In this paper, we report the synthesis and characterization of a squarylium cyanine dye convalently linked to two [60]fullerene units (**Scheme 1**).

The compound **1** was prepared by the following method. C_{60} (28.8 mg, 0.04 mmol), sarcosine (7.1 mg, 0.08 mmol), and 5-formyl-2-methyl-benzothiazole (10.6 mg, 0.06 mmol) were added to dry toluene (40 mL). The resulting solution was heated at reflux under nitrogen for 6 h. The brown solution was concentrated and the raw solid product was purified by chromatography on silica-gel using toluene-ethyl ether (8:1, v/v) as eluent to give the compound **1** in a yield of 25%.

The compound **2** was achieved as follows. The mixture of compound **1** (45 mg) and dimethyl sulfate (1 mL) was heated for 2 h at 140°C under nitrogen, and then cooled to room temperature. The resulting mixture was poured into 10 mL of ethyl ether. After filtration, the precipitate was dried 24 h under vacuum. The mixture of the above precipitate, *n*-butyl alcohol (3 mL), pyridine (1 mL) and squaric acid (4 mg) was refluxed for 10 h under nitrogen. After the mixture was evaporated to dryness, the residue was washed with ethanol and benzene, and then was dissolved in chloroform and purified by column chromatography on silica by eluting with 5:1 (v/v) chloroform/methanol to give the compound **2** in a yield of 15%. The compound **2** could dissolve in chloroform and dichloromethane, however the solubility was very low. It did not dissolve in some non-polar such as benzene, toluene and ether or polar solvents: ethanol, methanol, ethyl acetate, acetone *etc*.

Scheme 1



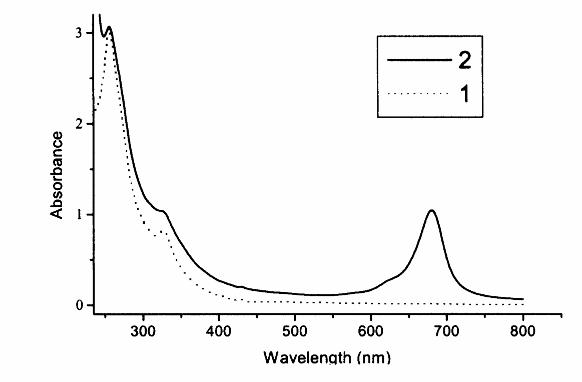
All of the spectroscopic studies including FT-IR, MALDI-TOF mass, ^{1}H NMR, ^{13}C NMR, UV-Vis are consistent with the molecular structure of the compound **1**[9]. However, it is more difficult to characterize the compound **2** because of solubility and structural complexity. At present, we have not found suitable deuterium solvents to do ^{1}H NMR and ^{13}C NMR spectra. Although there are some spatial structural isomers for compound **2**, it is hard to separate these isomers because of low solubility of compound **2**[5a], and chiral configuration in [60]fulleropyrrolidine derivative is seldom mentioned in many literatures[10].

The FD-mass spectrum shows the molecular ion peak at *m/z* 1954 ($C_{148}H_{26}N_4O_2S_2$), and some fragments are found at *m/z* 720 (C_{60}), 908. The FT-IR spectrum (KBr pellet) indicates a band of C_{60} at 526.69 cm^{-1} and the C=O stretching band at 1714.62 cm^{-1}.

The UV-Vis spectrum of compound **2** displays strong absorption bands due to both the squarylium cyanine dye and fullerene moieties. The UV-Vis spectrum of compound **2** (**Figure 1**) exhibits that the absorption peaks are consisted two parts: the visible region λ=683 nm, which is dominated by squarylium cyanine dye, and the UV region, which is dominated by fullerene λ=257, 326 and 430 nm. The maximum absorption of squarylium cyanine dye in compound **2** is red shift 13 nm due to the influence of fullerene (the maximum absorption of squarylium cyanine dye is usually at 670 nm[11]).

The photochemical and photophysical properties of compound **2** will be further investigated.

Figure 1 The UV-Vis spectra of compounds **2** and **1** in dichloromethane at room temperature. solid line: compound **2**; dot line: compound **1**



Acknowledgments

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9. Selected data for compound **1**: ^{1}H NMR (δ (ppm), 300 MHz, CDCl$_3$, 25°C): 2.84 (s, 3H), 2.88 (s, 3H), 4.35 (d, 1H, *J*= 8.4 Hz), 5.22 (dd, 2H, *J*=4.2 Hz, 12.8 Hz), 7.13 (t, 2H, *J*=7.7 Hz, 15.1 Hz), 7.9 (s, 1H). ^{13}C NMR (δ (ppm), 125 MHz, CDCl$_3$): 168.81(C=N), 153.22, 152.39, 147.43, 146.40, 146.33, 146.23, 146.03, 145.85, 145.77, 145.66, 145.50, 145.42, 145.36, 144.91, 144.55, 144.39, 143.15, 142.76, 142.69, 142.35, 142.26, 142.18, 142.05, 141.74, 141.58, 140.26, 135.75, 136.68, 125.88, 123.66, 122.30, 83.53, 68.95, 68.48, 39.99, 20.09. UV/vis (λ_{max} nm, CH$_2$Cl$_2$): 256, 327, 430. MS *m/z* (MALDI-TOF): 923.07 (M$^+$-1). FT-IR (KBr) (cm^{-1}): 2946.40, 2780.18, 1643.94, 1525.00, 1427.99 (C_{60}), 1177.18, 1023.99, 527.05 (C_{60}).

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