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Synthesis of a New Crown Ether-Bearing [60]Fulleropyrrolidine Containing a Benzothiazolium Styryl Dye

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Abstract: A novel class of crown ether-bearing [60]fulleropyrrolidines containing a benzothiazolium styryl dye has been synthesized. The compounds have been characterized by FT-IR, NMR and mass spectra. The UV-vis absorption spectra of the compounds have also been studied.

Keyword: fulleropyrrolidine; cycloaddition; supramolecular; dye

Extensive studies have been made on cycloaddition reactions of fullerene derivatives. 1,3-Dipolar cycloaddition reactions have been frequently used to functionalize C_{60}.[1-13] A series of fulleropyrrolidine derivatives have been synthesized by the cycloaddition of C_{60}. These derivatives can be used as intermediates for the preparation of target molecules with unique properties ranging from drug delivery to advanced nano-structural devices. From previous studies, we know that linking a crown ether moiety to a [60]fulleropyrrolidine results in a crown ether-bearing [60]fulleropyrrolidine possessing interesting photo-physical properties.[14] In addition, new styryl dyes containing the benzodithia-18-crown-6 fragment have been synthesized,[15-17] which also show very interesting physicochemical properties. The dyes are intensely colored and show significant hypsochromic shifts upon complexation with alkaline earth cations in acetonitrile. These significant results prompted us to continue our investigation and a novel class of crown ether-bearing [60]fulleropyrrolidines containing a benzothiazolium styryl dye has been synthesized. The molecules are composed of a C_{60} unit, a crown ether moiety and a benzothiazolium styryl moiety.

The supramolecular systems are obtained by 1,3-dipolar cycloaddition of an azomethine ylide, which is generated *in situ* from refluxing a mixture of bis(4′-formylbenzo)-18-crown-6

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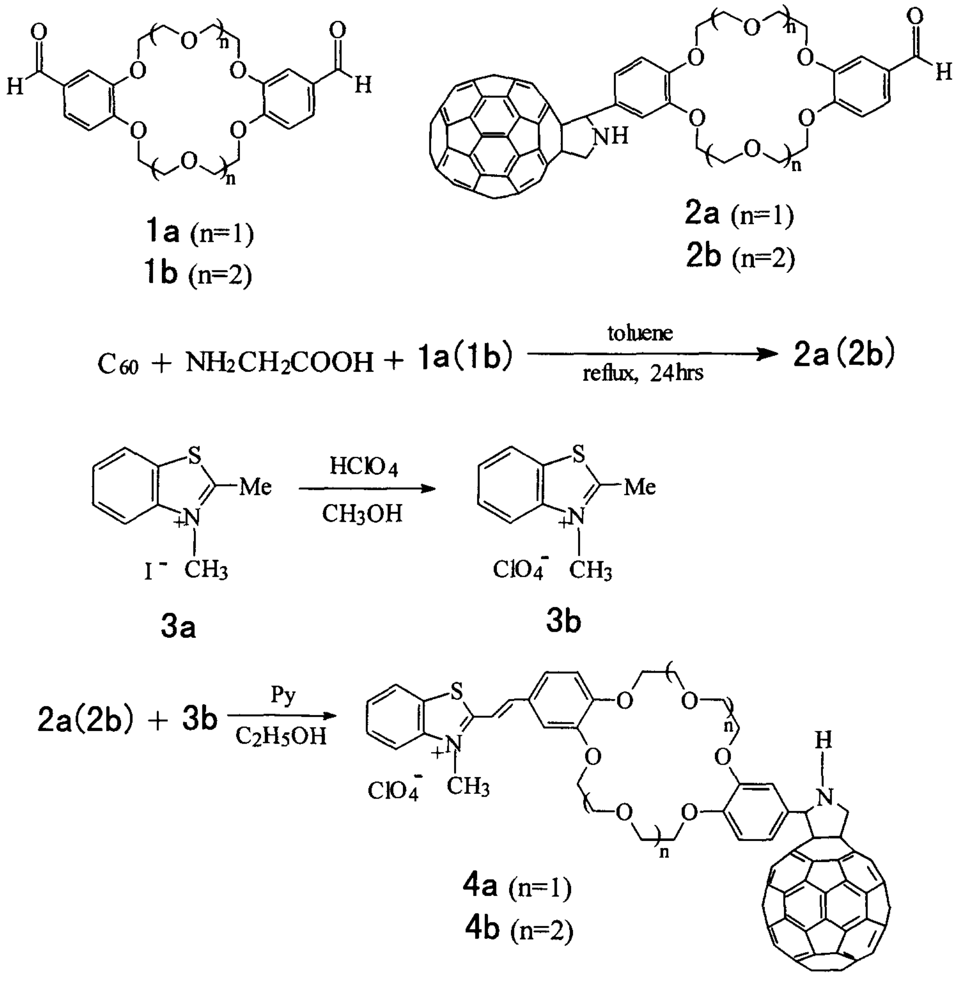
(or bis(4'-formylbenzo)-24-crown-8), C_{60} and glycine. The reactions with C_{60} afforded monoadducts (**2a** and **2b**) after decarboxylation and dehydration perhaps due to steric hindrance. The structures of **2a** and **2b** were confirmed by mass spectra, ^{13}C NMR and ^{1}H NMR spectra. Furthermore, **2a** (or **2b**) can be used in a second reaction using the remaining aldehyde group to give **4a** (or **4b**).



Scheme 1

A general procedure for the preparation and isolation of **2a** and **2b** is as follows. A mixture of C_{60} (0.05 mmol), **1a** (or **1b**)[18] (0.05 mmol) and glycine (0.1 mmol) in toluene was heated at reflux for 24h under nitrogen. The reaction mixture was concentrated under vacuum and separated by chromatography on silica gel (C.P. 200~300) using benzene-methanol (7:2, v/v) to give the product. The purified product was obtained by extraction with hot methyl alcohol in a yield of 25% (based on converted C_{60}). Products **2a** and **2b** were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and mass spectroscopy.[19]

A general procedure for the preparation and isolation of **4a** and **4b** is as follows. A mixture of **3b**[15] (0.02 mmol), **2a** (or **2b**) (0.04 mmol) and pyridine (0.3 cm^3) was suspended in absolute ethanol (6 cm^3) and heated for 8h at 90°C. After cooling, the solids were filtered and dried. The product was purified by extraction with hot ethanol in a yield of 67%. Products **4a** and **4b** were characterized by ^{1}H NMR, FT -IR and mass spectroscopy.[20]

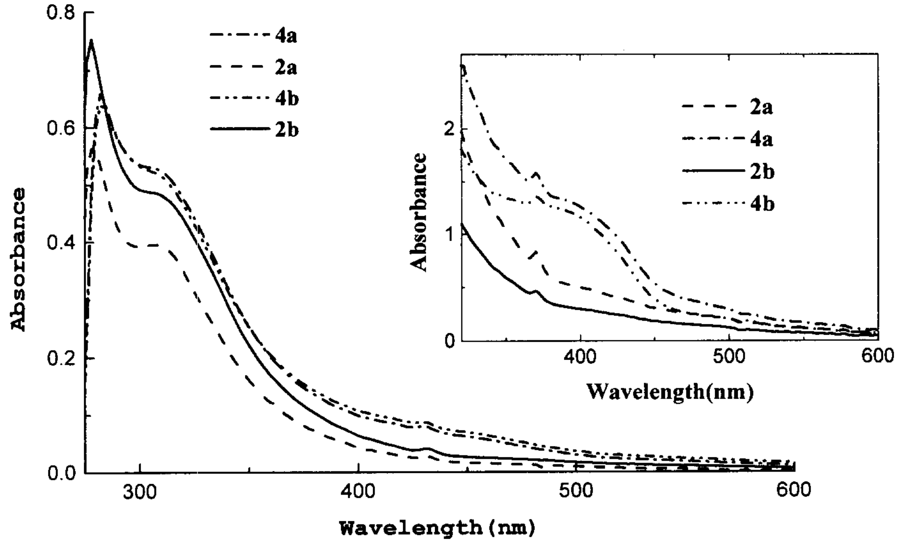


Fig.1 UV-vis absorption spectra of **2a**, **2b**, **4a** and **4b** in chloroform at 1.0×10^{-5} mol dm^{-3}. The insert shows absorption spectra of **2a**, **2b**, **4a** and **4b** at 1.0×10^{-4} mol dm^{-3}.

The UV-vis absorption spectra of **2a**, **2b**, **4a** and **4b** are shown in Fig. 1. Compared with **2a**, the absorption spectrum of **4a** gives a detectable red shift from 278nm to 284nm. As can be seen, the absorption spectra of **2b** and **4b** also give a change similar to those observed for **2a** and **4a**. The absorption maximum of **2b** is also at 278nm, but the absorption maximum of **4b** appears at 286nm. The inserts show the absorption spectra of **4a** and **4b** at 1.0×10^{-4}mol dm^{-3}. When the concentration of **4a** and **4b** is raised to 1.0×10^{-4} mol dm^{-3}, a new peak appears at about 410nm.

The details of this study are on going.

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19. Compound **2a**. ^{1}H NMR (200MHz, $CDCl_3$-CS_2) δ 9.75ppm (s, 1H, CHO), 7.38-7.22 (m, 4H, ArH), 6.86-6.78 (m, 2H, ArH), 5.65(s, 1H, CH), 5.03 (d, 1H, J=10 Hz, CH_2), 4.81 (d, 1H, J=10 Hz, CH_2), 4.13-4.06 (m, 8H, CH_2O), 3.95-3.92 (m, 8H, CH_2O); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 190.80, 152.51, 151.41, 149.21, 149.00, 147.61, 147.09, 146.49, 146.40, 146.21, 145.68, 145.43, 144.60, 144.45, 144.22, 143.18, 142.75, 142.15, 142.09, 141.94, 141.86, 141.68, 140.45, 140.26, 139.83, 136.74, 134.61, 130.31, 126.89, 126.77, 126.68, 121.43, 114.20, 114.00, 113.71, 111.81, 110.85, 74.30, 70.17, 69.66, 69.59, 68.99, 68.91, 68.72, 68.59, 61.79; IR (KBr) 2925, 1636, 1595, 1509, 1453, 1266, 1130, 1023, 746, 527; MS (FAB, m/z) 1149.9.

   Compound **2b**. ^{1}H NMR (200MHz, $CDCl_3$-CS_2) δ 9.75ppm (s, 1H, CHO), 7.38-7.21 (m, 4H, ArH), 6.86-6.62 (m, 2H, ArH), 5.61 (s, 1H, CH), 4.93 (d, 1H, J=10 Hz, CH_2), 4.71 (d, 1H, J=10 Hz, CH_2), 4.13-3.86 (m, 8H, CH_2O), 3.86-3.51 (m, 16H, CH_2O); ^{13}C NMR (125.7MHz, $CDCl_3$) δ 189.49, 154.15, 153.66, 149.23, 149.02, 146.94, 146.81, 145.95, 145.85, 145.69, 145.51, 145.25, 145.20, 145.15, 145.08, 144.45, 144.14, 142.93, 142.47, 142.36, 142.21, 141.80, 141.50, 141.29, 139.97, 135.83, 134.12, 130.92, 126.73, 126.55, 126.07, 121.31, 114.25, 114.02, 113.76, 111.90, 110.88, 72.44, 71.41, 71.33, 69.78, 69.54, 69.49, 69.40, 69.17, 69.07, 60.88; IR (KBr) 2923, 1633, 1593, 1510, 1434,1270, 1130, 1033, 767, 528; MS (FAB, m/z) 1238.
20. Compound **4a**. ^{1}H NMR (500MHz, $CDCl_3$) δ 7.99 (d, 1H, J=7.4 Hz, β -H), 7.47 (d, 1H, J=7.4Hz, α -H), 7.32-7.39 (m, 4H, ArH), 6.99 (d, 1H, J=7.9, ArH), 6.91-6.96 (m, 2H, ArH), 6.88 (d, 1H, J=7.9, ArH), 6.81-6.86 (m, 2H, ArH), 6.46 (s, 1H, CH), 5.99 (d, 1H, J=12.6 Hz, CH_2), 5.76 (d, 1H, J=12.6 Hz, CH_2), 4.20-4.28 (m, 6H, CH_2O), 4.16 (s, 3H, NCH_3), 3.91-4.10 (m, 10H, CH_2O); IR (KBr) 2924, 1668, 1621, 1511, 1452, 1266, 1124, 1060, 941, 898, 861, 810, 734, 695, 623, 527; MS (TOF, m/z) 1295.

    Compound **4b**. ^{1}H NMR (500MHz, $CDCl_3$) δ 8.01 (d, 1H, J=8.1 Hz, β -H), 7.45 (d, 1H, J=8.1Hz, α -H), 7.36-7.42 (m, 4H, ArH), 6.98 (d, 1H, J=8.7, ArH), 6.93-6.96 (m, 2H, ArH), 6.91 (d, 1H, J=8.7, ArH), 6.85-6.89 (m, 2H, ArH), 6.46 (s, 1H, CH), 5.98 (d, 1H, J=12.6 Hz, CH_2), 5.76 (d, 1H, J=12.6 Hz, CH_2), 4.19 (s, 3H, NCH_3), 4.05-3.88 (m, 12H, CH_2O), 3.91-3.68 (m, 12H, CH_2O); IR (KBr) 2925, 1674, 1593, 1511, 1268, 1124, 1058, 945, 901, 858, 808, 734, 695, 526; MS (FD275, m/z) 1382.