Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Synthesis and Fluorescence Properties of a Novel Supramolecular Complex Containing [60]Fullerene Moiety

Zhongxin Ge[a]; Yuliang Li[a]; Na Sun[a]; Shu Wang[a]; Daoben Zhu[a]
[a] Center of Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P. R. China

To cite this Article Ge, Zhongxin , Li, Yuliang , Sun, Na , Wang, Shu and Zhu, Daoben(2001) 'Synthesis and Fluorescence Properties of a Novel Supramolecular Complex Containing [60]Fullerene Moiety', Supramolecular Chemistry, 12: 4, 451 — 455

To link to this Article: DOI: 10.1080/10610270108027477

URL: http://dx.doi.org/10.1080/10610270108027477

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 451-455
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Fluorescence Properties of a Novel Supramolecular Complex Containing [60]Fullerene Moiety

ZHONGXIN GE, YULIANG LI*, NA SUN, SHU WANG and DAOBEN ZHU

Center of Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

(Received April 17, 2000)

A new crown ether styryl dye containing [60]Fullerene moiety has been synthesized, and characterized by FT-IR, NMR and Mass spectra. Fluorescence spectra of the compound have also been studied. The results indicate a strong hypsochromic shift from 548 nm to 526 nm is observed on cation complexation, and the intensity of peaks at 504 nm, 548 nm and 590 nm decrease as the metal cation concentration is increased at 77K.

Keywords: fulleropyrrolidine, cycloaddition, supramolecular, dye

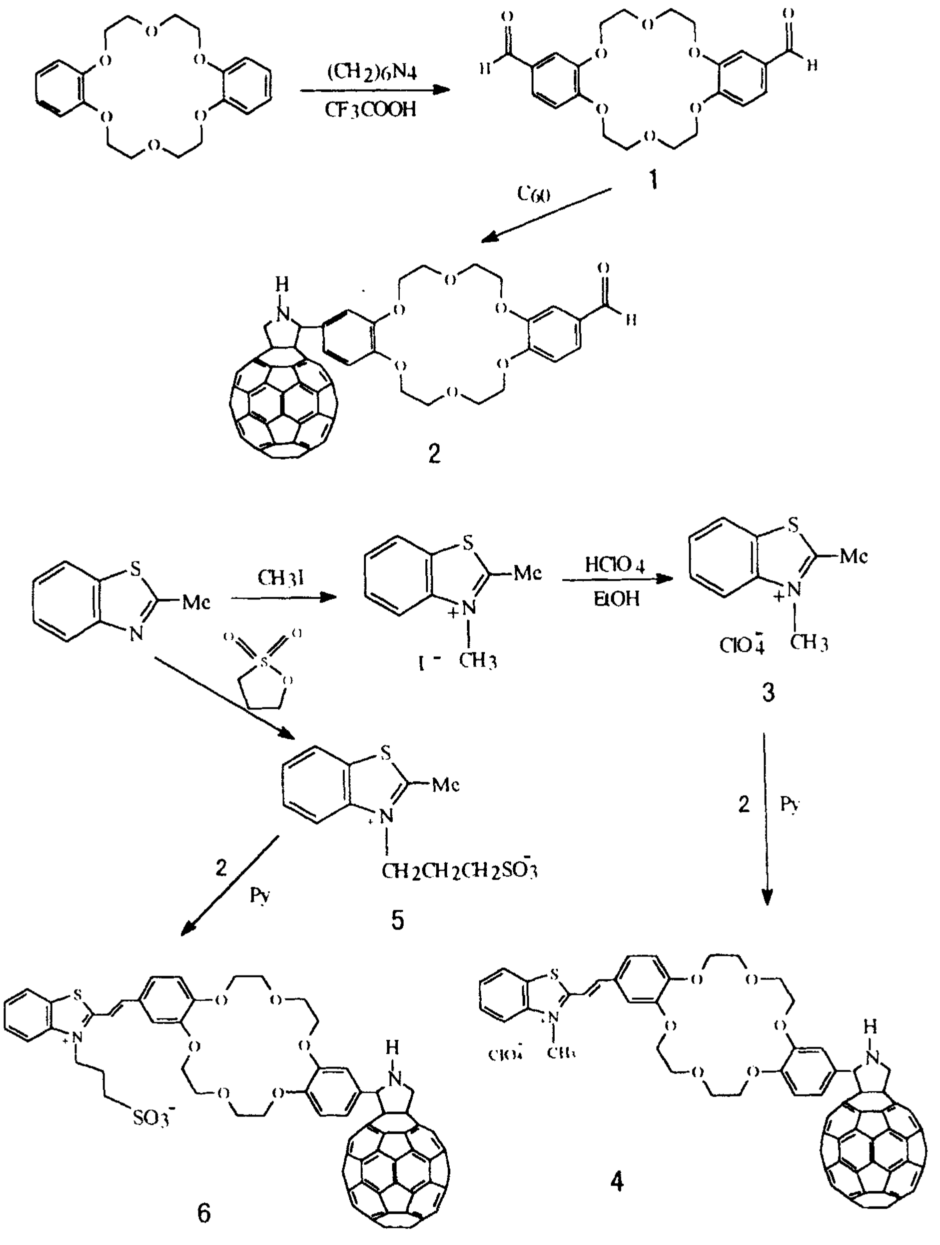
Fullerenes possess a wide range of physical and chemical properties, which make them interesting buliding blocks for supramolecular systems and new materials. Modification of fullerene through a wide variety of addition reactions is of considerable interest to chemist. Among them, 1,3-dipolar cycloaddition of azomethine ylides has been frequently used to functionalize C_{60}. A munber of fulleropyrrolidine derivatives have been synthesized.[1–7] The electronic absorption and fluorescence properties of these derivatives draw much attention to chemists and spectroscopists. 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.[8] In addition, a benzothiazolium styryl azacrown ether dye have been synthesized by Moore and Alfimov et al, which shows significant hypsochromic shifts upon complexation with alkaline earth cations in acetonitrile.[9–11] These significant results prompt us to continue our investigation on new supramolecular systems, which are composed of a C_{60} unit, a crown ether moiety and a benzothiazolium styryl moiety. The supramolecular systems are first obtained by 1,3-dipolar cycloaddition of an azomethine ylide and show a strong optical response upon complexation with alkaline earth cations due to interaction between the metal cation with a crown ether moiety.

Compounds **2** and **4** were prepared according to Scheme 1. A general procedure for the preparation and isolation of compound **2** is shown as follows. A mixture of C_{60} (36 mg, 0.05 mmol), compound **1**[12] (21 mg, 0.05 mmol) and glycine (7.5 mg, 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.

---

* Corresponding Author.

200~300) using benzene-methanol (7:2, v/v) to give product. The purified product was obtained by extraction with hot methyl alcohol in a yield of 25.4% (based on converted C_{60}). Product **2** was characterized by ^1H NMR, ^{13}C NMR, FT-IR and mass spectroscopy[13].



SCHEME 1

A general procedure for the preparation and isolation of compound **4** is shown as follows. A mixture of compound **3**[9] (10.6 mg, 0.04 mmol), compound **2** (23.0 mg, 0.02 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 solid was filtered and dried. The product was further purified by extraction with hot ethanol in the yield of 67%. Compound **4** was characterized by ^1H NMR, FT-1R and mass spectroscopy[14].

Compound **5** was obtained as described previously[15]. Compound **6** was prepared according to Scheme 1. A mixture of **5** 23.0 mg (0.02 mmol), **2** 10.8 mg (0.04 mmol) and pyridine (0.3 cm^3) was suspended in absolute ethanol (6 cm^3) and refluxed for 8h. After cooling, the solids were filtered and dried. The product was purified by chromatography on silica gel (C.P. 200~300) using chloroform-methanol (20:1, v/v) to give the product (R_f=0.35) in a yield of 53%. Compound **6** was characterized by ^1H NMR, FT -IR and mass spectroscopy.[16]

The fluorescence emission spectra of **4** at room temperature in the absence and presence of $Ba(ClO_4)_2$ are shown in Figure 1. A Peak at 540 nm is observed in the absence of $Ba(ClO_4)_2$. The peak is blue-shifted to 510 nm and the fluorescence intensity of **4**is found a large decrease on the complexation with the barium ions. This large shift and intensity decrease is ascribed to interaction between the metal cation with the crown moieties. This interaction distorts the conjugation of the Π-system of the dye moieties and results in a strong hypsochromic shift and a large decrease of fluorescence intensity. Similarly, the fluorescence peak at 532 nm of **6** is blue-shifted to 522 nm and the fluorescence intensity is decreased with complexation of the barium ions.

Figure 1 also shows the blue shift of **6** is beyond that of **4** on the same condition, which suggests that cation association with the sulfonate plays an important role and the cis-isomer of **6** is stabilized by the presence of Ba^{2+}. The *cis*-isomer form is likely that a "tail-biting" intramolecular Barium cation bridge connects the alkysulfonate and crown ether moieties of **6** (scheme 2), which draws close between benzothiazolium styryl dye and C_{60}. The short distance lead to interaction between benzothiazolium styryl dye moieties and C_{60} moieties. This interaction causes the fluorescence of benzothiazolium styryl dye of **6** to red shift, which is opposite to results in the reduced interaction between benzothiazolium styryl dye moieties and crown ether moieties in presence of Ba^{2+}. So the reduced blue shift of **6** is observed in compared with **4**.

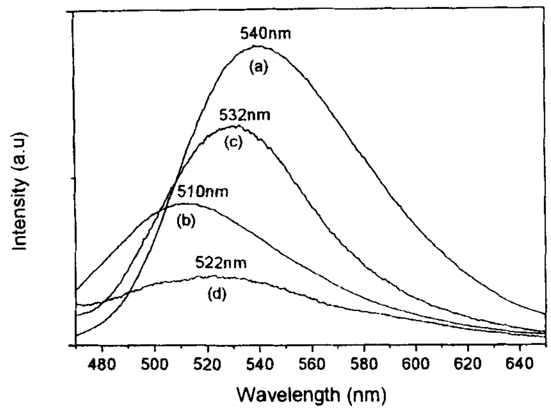
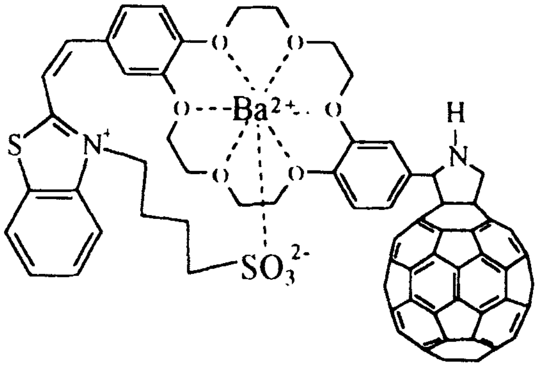


FIGURE 1 Luminescence spectrum of **4** and **6** dissolved in chloroform/acetonitrile (v/v, 1:1) at room temperature on 450nm excitation. **4**: (a) absence of barium salt, (b) $Ba(ClO_4)_2$(ca. 0.01 M). **6**: (c) absence of barium salt, (d) $Ba(ClO_4)_2$ (ca. 0.01 M)

Figure 2 show the fluorescence emission spectra of **6** at 77K at different concentration of the barium salt. At the low temperature, there are four peaks at 504 nm, 548 nm, 590 nm and 725 nm respectively in the absence of $Ba(ClO_4)_2$. A strong hypsochromic shift from 548 nm to 526 nm was observed at low cation concentrations, and intensity of peaks at 504 nm, 548 nm and 590 nm was decreased as the metal cation concentration was increased. When the cation concentration is beyond 10^{-3}M, the peak at 548 nm disappears. The insert shows changes of fluorescence intensity of 725 nm at different cation concentrations. Similarly it can be seen, the fluorescence intensity decrease with the cation concentration increasing. These large changes in the spectrum on cation complexation indicate that intramolecular coordination of the metal cation to the crown cavity alters the electronic structure of 6 and results in charge redistribution with the extended chromophore.

The authors thank NSFC and The Major State Basic Research Development Program for the financial support of the research.



SCHEME 2

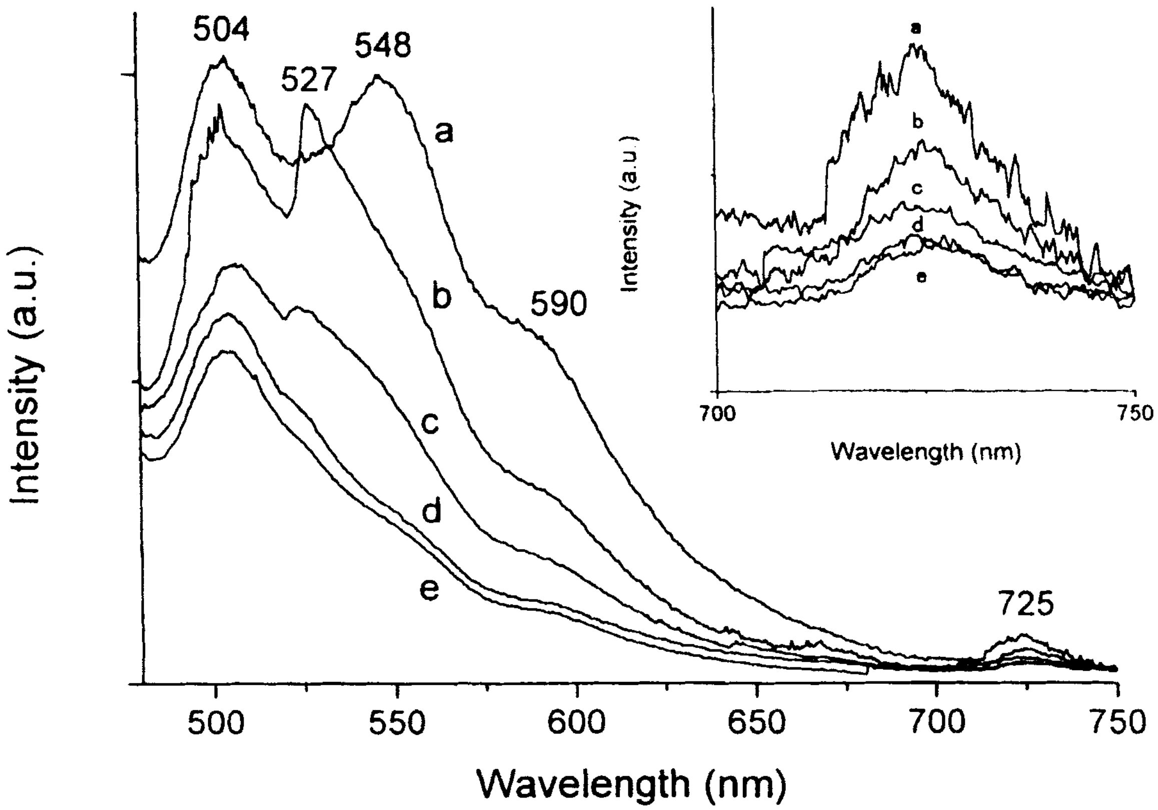


FIGURE 2 Luminescence spectrum of 6 dissolved in chloroform/acetonitrile (v/v, 1:1) at 77K on 450nm excitation, in the presence of $Ba(ClO_4)_2$ at (a) 0, (b) 2×10^{-5}, (c) 2×10^{-4}, (d) 2×10^{-3}, and (e) 2×10^{-2} M

References

1. Maggini, M.; Scorrano, G.; Prato, M.; *J. Am. Chem. Soc.*, 1993, 115, 9798.
2. Iyoda, M.; Sultana, F.; Komatsu, M.; *Chem. Lett.*, 1995, 1133.
3. Lucas, S. I.; Martin, N.; Sanchez, L.; Seoane, C.; *Tetrahedron Lett.*, 1996, 37, 9391.
4. Ros, T.D.; Prato, M.; *J. Org. Chem.*, 1996, 61, 9070.
5. Liddle, P.; Kuciauskas, D.; Sumida, J. P.; Nash, B.; Nguyen Moore, T. A.; Gust, D.; *J. Am. Chem. Soc.*, 1997, 119, 1400.
6. Xu, J. H.; Li, Y. L.; Zheng, D. G.; Yang, J. K.; Mao, Z.; Zhu, D. B.; *Tetrahedron Lett.*, 1997, 38, 6613.
7. Yamada, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *Chem. Lett.*, 1999, 895.
8. Guo, Z.X.; Li, Y.L.; Xu, J.H.; Mao, Z.; Wu, Y.; Zhu, D.B.; *Synth. Commun.*, 1998, 28, 1957.
9. Alfimov, M. V.; Fedorov, Y. V.; Fedorova, O. A.; Gromov, S. S.; Hester, R. E.; Lednev, I. K.; Moore, J. N.; Oleshko, V. P.; Vedernikov, A. I.; J. *Chem. Soc., Perkin Trans.* 2, 1996, 1441.
10. Alfimov, M. V.; Churakov, A. V.; Fedorov, Y. V.; Fedorova, O. A.; Gromov, S. P.; Hester, R. E.; Howard, J. A. K.; Kuz mina, L. G.; Lednev, I. K.; Moore, J. N.; *J.* Chem. Soc., Perkin Trans. 2, 1997, 2249.
11. Lednev, K.; Hester, R. E.; Moore, J. N.; *J. Am.* Chem. Soc., 1997, 119, 3456.
12. Wada, F.; Hirayama, H.; Namiki, H.; Kikukawa, K.; Matsuda, T. *Bull. Chem. Soc. Jpn.* 1980, 53, 1473.
13. **2**: ^{1}H NMR (200MHz, $CDCl_3$-CS_2) δ 9.75 (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=10.01 Hz, CH_2), 4.81 (d, 1H, J=10.01 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.
14. **4**: ^{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.
15. Gromov, S. P.; Fedorova, O. A.; Ushakov, E. N.; Stanislavsky, O. B.; Lednev, I. K.; Alfimov, M. V.; *Dokl. Akad. Nauk SSSR*, 1991, 317, 1134.
16. **6**: ^{1}H NMR (500MHz, $CDCl_3$) δ 7.85 (d, 1H, J=15.1 Hz, β -H), 7.75 (d, 1H, J=15,1Hz, α-H), 7.69 (m, 2H, ArH), 7.51 (m, 2H, ArH), 7.41 (d, 1H, J=7.9 Hz, ArH), 7.28 (m, 2H, ArH), 6.98 (d, 1H, J=7.9 Hz, ArH), 6.91 (m, 2H, ArH), 6.45 (s, 1H, CH), 5.99 (d, 1H, J=12.6 Hz, CH_2), 5.75 (d, 1H, J=12.6 Hz, CH_2), 5.09 (m, 2H, NCH_2), 4.18–4.28 (m, 8H, CH_2O), 4.02–3.84 (m, 8H, CH_2O), 2.61 (m, 2H, $CH_2SO_3^-$), 2.26 (m, 2H, CH_2); IR (KBr) 2956, 2922, 2852, 1716, 1586, 1513, 1463, 1435, 1263, 1169, 1137, 1063, 958, 869, 804, 740, 576, 553, 527, 466; MS (TOF, m/z) 1402.