

Supramolecular complexes of La@C₈₂ with unsaturated thiocrown ethers

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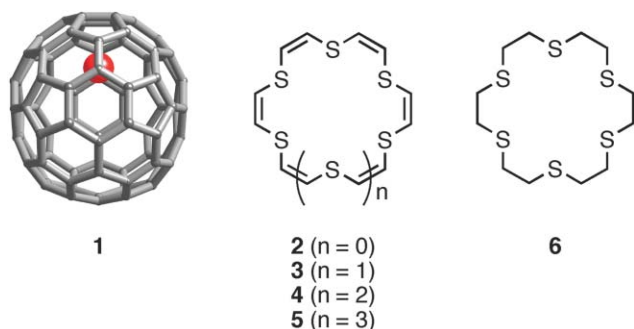
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The paramagnetic La@C₈₂-A(C_{2v}) with unsaturated thiocrown ethers forms 1 : 1 host-guest complexes of [La@C₈₂-A(C_{2v})] [D]⁺ in solution as a result of electron transfer.

Endohedral metallofullerenes have attracted special interest as new spherical molecules with unique properties that are not found in empty fullerenes.¹ The redox potentials of endohedral metallofullerenes are well known to be lower than those of empty fullerenes.¹ The electrical conductivity of a sulfur-doped C₆₀ film² and the atomic charge distribution for eutectic crystals consisting of C₆₀ and S₈³ have been reported, in which the weak charge-transfer from sulfur to C₆₀ takes place. Several host-guest complexes of empty fullerenes with macrocyclic compounds have also been reported.⁴ In this context, supramolecular systems constructed from endohedral metallofullerenes and donor molecules might be valuable as new hybrid materials. Recently, we have reported the complexation behavior of the paramagnetic lanthanum metallofullerene La@C₈₂-A(C_{2v}) (**1**) with the 18-membered azacrown compound, 1,4,7,10,13,16-hexaazacyclooctadecane, as a donor in an electron-transfer process.⁵ Meanwhile, unsaturated thiocrown ethers (**D**) are known to have sulfur atoms forced to orient toward the inside of the ring and include metal atom(s) inside the ring selectively.⁶ In this context, we have investigated the inclusion behavior of 15-, 18-, 21- and 24-membered unsaturated thiocrown ethers (**2–5**) with **1** in solution and the ring-size effect toward the inclusion of **1**.



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The inclusion behavior of **1** with 18-membered unsaturated thiocrown ether **3** was firstly examined in nitrobenzene using visible–near infrared (vis–NIR) spectroscopy, as shown in Fig. 1(a). Upon addition of a stock solution of **3** to a solution of **1** (2.0×10^{-4} M), a new absorption maximum appeared at 940 nm with the disappearance of the characteristic absorption maximum of **1** at 1010 nm. The resulting spectrum was identical with that of the anion [1][−].⁷ Fig. 2 shows that the EPR signal of **1** in nitrobenzene decreases upon the addition of **3**. These results reveal that **1** forms a complex with **3**, in which **1** is reduced to its anion form. The stoichiometry of the complexation of **1** with **3** in solution was determined by means of a Job plot based on the absorption change, as shown in Fig. 1(b). A continuous variation plot of absorption vs. [1]/([1] + [3]) in nitrobenzene gave a maximum value at 0.5, indicating the formation of a 1 : 1 complex. The formation constant of the complex of **1** with **3** was estimated by the standard titration technique using vis–NIR spectroscopy, as shown in the inset of Fig. 1(a). The formation constant *K* was obtained as 112 M^{-1} by nonlinear least-square curve fitting of the titration plots. Titration experiments for C₆₀ with **3** using the vis–NIR spectroscopic data showed an increase of the absorption intensity in the 430–500 nm region with the addition of **3** to C₆₀ (Fig. 3), which is a characteristic absorption of a host–guest complex

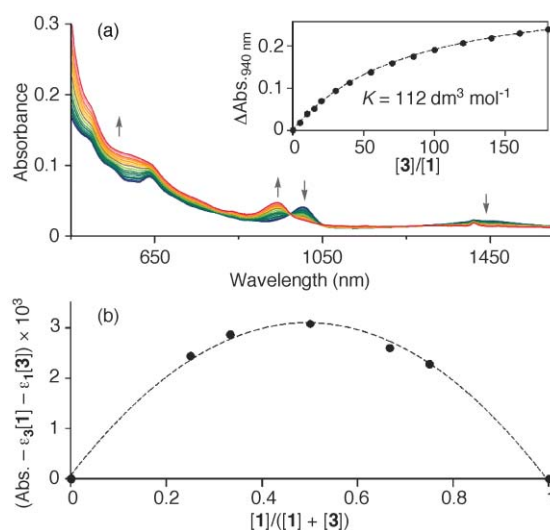


Fig. 1 (a) Vis–NIR spectra in the titration experiment of **1** with **3** (0–180 equiv.) in nitrobenzene. Initial concentration of **1** is 2×10^{-4} M. Inset: titration plots at 940 nm. (b) A continuous variation plot in nitrobenzene. The total concentration of **1** + **3** was maintained constant at 1.0×10^{-4} M.

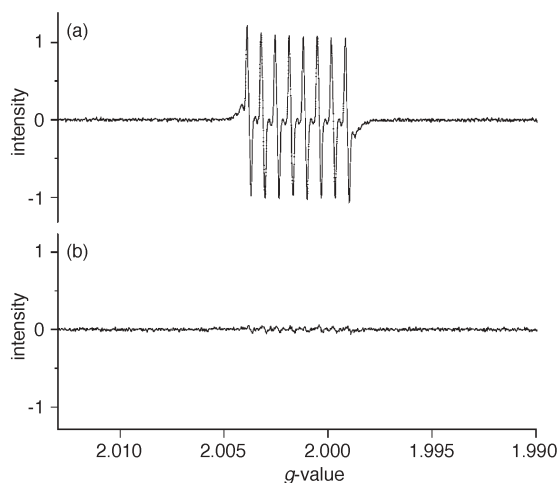


Fig. 2 EPR spectra of **1** (a) before and (b) after addition of **3**: $[1] = 2.0 \times 10^{-4}$ M, $[3] = 8.6 \times 10^{-2}$ M.

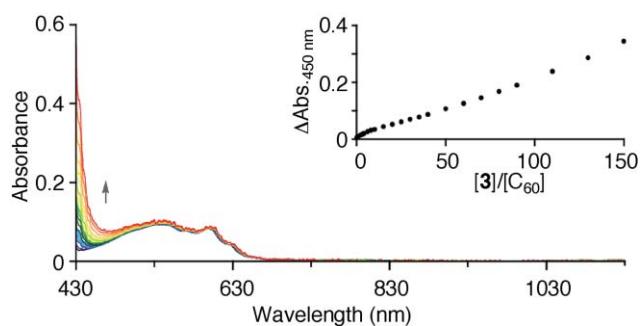


Fig. 3 Vis-NIR spectra in the titration experiment of C_{60} with **3** (0–150 equiv.) in nitrobenzene. Initial concentration of C_{60} is 2×10^{-4} M. Inset: titration plots at 450 nm.

reported for a weak donor–acceptor interaction of C_{60} and a host molecule.⁸ The complexation constant of C_{60} with **3** was too small to be determined by a linear least-square curve fitting with the titration plots. The host–guest complexation of **1** should be compared with that of a similar empty fullerene to highlight the modified behaviour of **1**. Since the amount of C_{82} ⁹ existing in the extracts from soot, however, is appreciably less than that of **1**, it is very difficult to compare the complexation behavior between **1** and C_{82} toward **3**.¹⁰ Meanwhile, the complexation behavior of **1** with an 18-membered saturated thiocrown ether (**6**) was also investigated to compare with the complexation abilities of unsaturated thiocrown ethers (**2–5**) (Fig. 4). Fig. 4 shows that the vis-NIR spectrum of **1** is hardly changed with the addition of **6**. This result may suggest that the olefinic moiety of the unsaturated thiocrown ethers plays an important role for the complexation with **1**. The ring-size effect of unsaturated thiocrown ethers toward the complexation of **1** may also correlate with the binding strength with **1**. Fig. 5(a)–(c) show the disappearance of the absorption maximum at 1010 nm and the appearance of the characteristic absorption maximum of the anion of **1** around 940 nm (**2**: 938 nm, **4**: 942 nm, and **5**: 946 nm) in a solution of **1** with 15-, 21- and 24-membered unsaturated thiocrown ethers (**2**, **4** and **5**). By utilizing the titration plots, the complexation constants K of **1** with **2**, **4** and **5** were estimated to be 48, 123 and 96 M^{-1} , respectively.

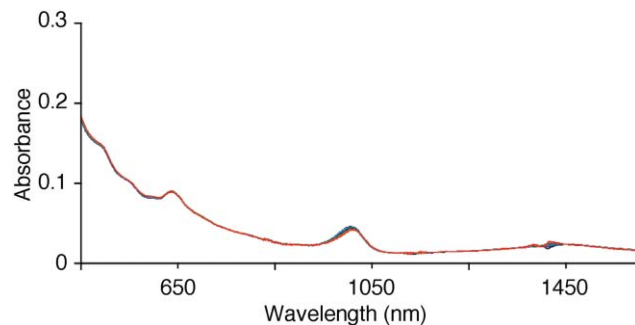


Fig. 4 (a) Vis-NIR spectra in the titration experiment of **1** with **6** (0–180 equiv.) in nitrobenzene. Initial concentration of **1** is 2×10^{-4} M.

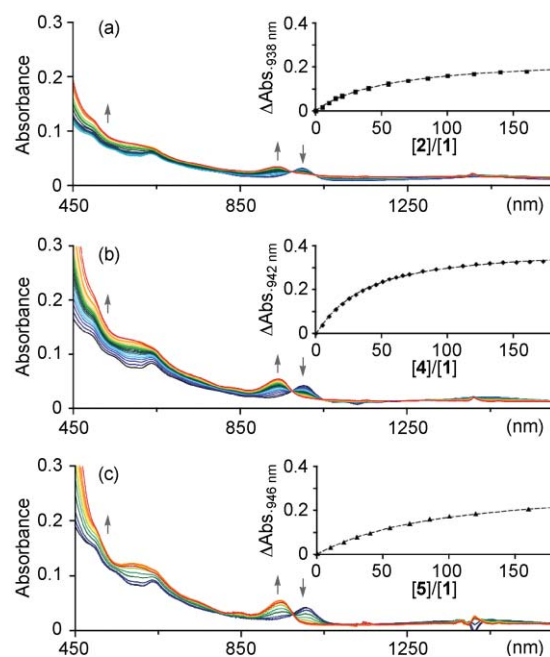


Fig. 5 Vis-NIR spectra in the titration experiment of **1** with (a) **2**, (b) **4** and (c) **5** (0–180 equiv.) in nitrobenzene. Initial concentration of **1** is 2×10^{-4} M. Inset: titration plots.

The reduction potentials of **1** and C_{60} and the oxidation potentials of **2–6** vs. Fc/Fc^+ by cyclic voltammetry measurements are shown in Table 1. The free energies (ΔG_{et}) for the electron

Table 1 Reduction potentials $^{\text{red}}E_1^a$ of C_{60} and **1**, oxidation potentials $^{\text{ox}}E_1^a$ of thiocrown ethers (**2–6**) and free energies for the electron transfer ΔG_{et} to **1** and C_{60}

Compound	$^{\text{red}}E_1^b/\text{V}$	$^{\text{ox}}E_1^b/\text{V}$	$\Delta G_{\text{et}}/\text{kcal mol}^{-1}$	
			C_{60}	1
C_{60}	−0.96			
1	−0.25			
2		0.82	40	24
3		0.79	40	23
4		0.73	38	21
5		0.69	37	20
6		1.09	40	30

^a Obtained by CV. *Conditions*: 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in nitrobenzene; working electrode, Pt wire; counter electrode, Pt wire; scan rate, 20 mV s^{-1} . ^b Potentials vs. Fc/Fc^+ .

transfer from **2–6** to **1** were calculated by the Rehm–Weller equation (Table 1).¹¹ The ΔG_{et} values of **2–6** with C_{60} are much higher than that with **1**. The positive ΔG_{et} values may reveal that the host–guest complexation between **1** and **2–5** facilitates the sequential electron transfer to afford the 1 : 1 complexes $[I]^- [D]^+$.

The ΔG_{et} values between **1** and **2–5** decrease with increase in the ring size. Meanwhile, **4** has the largest K value as estimated from the titration experiment. The highest affinity of **4** toward **1** among **2–5** would therefore seem to be caused by a size matching in **4** and **1**. The optimized structure of **1** is known to have an elliptic shape of $\sim 8.5 \text{ \AA}$ ^{7,12} whilst the sizes of **2–5** were reported as 6.1, 7.6, 8.9 and 10.1 \AA , respectively.^{6c,13}

In conclusion, 15-, 18-, 21- and 24-membered unsaturated thiacyclopentadiene derivatives (**2–5**) form 1 : 1 complexes with $\text{La}@C_{82}\text{-A}(C_{2v})$ (**1**) in solution by an electron transfer process. Among the above unsaturated thiacyclopentadiene derivatives, the 21-membered one (**4**) has the best ring-size for the complexation with **1**. The conformationally restricted unsaturated thiacyclopentadiene derivatives having sulfur atoms forced to orient toward the inside of the ring are known to include metal atom(s) inside the ring selectively.⁶ By utilizing the thiacyclopentadiene derivatives as the host molecule, it is demonstrated for the first time that the complexation strength toward **1** depends on the size of the host molecules, suggesting the formation of inclusion complexes.

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Notes and references

- (a) *Endofullerenes: A New Family of Carbon Clusters*, ed. T. Akasaka and S. Nagase, Kluwer, Dordrecht, 2002; (b) S. Nagase, K. Kobayashi, T. Akasaka and T. Wakahara, in *Fullerenes: Chemistry, Physics and Technology*, ed. K. Kadish and R. S. Ruoff, John Wiley & Sons, New York, 2000, pp. 231–251.
- (a) J. Dai, G. Xu, Y. Ding and Q. Wang, *Microelectron. Eng.*, 2003, **66**, 186–191; (b) J. Yao, Y. Zou, D. He and G. Chen, *Mater. Lett.*, 1997, **33**, 27–30; (c) J. Gong, Y. Li, S. Lin, G. Ma, Y. Yang and G. Chen, *Thin Solid Films*, 1997, **302**, 256–259.
- (a) H. Takahashi, E. Matsubara, R. V. Belosludov, S. Matsubara, N. Sato, A. Muramatsu, Y. Kawazoe and K. Toji, *Mater. Trans.*, 2002, **43**, 1530–1532; (b) N. D. Kushch, I. Majchrzak, W. Ciesielski and A. Graja, *Chem. Phys. Lett.*, 1993, **215**, 137–140.
- Selected examples: (a) Y. Shoji, K. Tashiro and T. Aida, *J. Am. Chem. Soc.*, 2004, **126**, 6570–6571; (b) A. Saha, S. K. Nayak, S. Chottopadhyay and A. K. Mukherjee, *J. Phys. Chem. B*, 2003, **107**, 11889–11892; (c) T. Haino, Y. Yamanaka, H. Araki and Y. Fukazawa, *Chem. Commun.*, 2002, 402–403; (d) S. Takekuma, H. Takekuma, T. Matsumoto and Z. Yoshida, *Tetrahedron Lett.*, 2000, **41**, 1043–1046; (e) A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai, *Tetrahedron*, 1998, **54**, 2497–2508; (f) J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229–231.
- T. Tsuchiya, K. Sato, H. Kurihara, T. Wakahara, T. Nakahodo, Y. Maeda, T. Akasaka, K. Ohkubo, S. Fukuzumi, T. Kato, N. Mizorogi, K. Kobayashi and S. Nagase, *J. Am. Chem. Soc.*, 2006, **128**, 6699–6703.
- (a) T. Tsuchiya, T. Shimizu, K. Hirabayashi and N. Kamigata, *J. Org. Chem.*, 2003, **68**, 3480–3485; (b) T. Tsuchiya, T. Shimizu, K. Hirabayashi and N. Kamigata, *J. Org. Chem.*, 2002, **67**, 6632–6637; (c) T. Tsuchiya, T. Shimizu and N. Kamigata, *J. Am. Chem. Soc.*, 2001, **123**, 11534–11538.
- T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, R. Nagahata, X. Gao, E. Van Caemelbecke and K. M. Kadish, *J. Am. Chem. Soc.*, 2000, **122**, 9316–9317.
- (a) B. Poór, L. Biczók and M. Kubinyi, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2047–2052; (b) H. Matsubara, S. Oguri, K. Asano and K. Yamamoto, *Chem. Lett.*, 1999, 431–432; (c) A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai, *Tetrahedron*, 1998, **54**, 2497–2508; (d) T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259–260; (e) K. Araki, K. Akao, A. Ikeda, T. Suzuki and S. Shinkai, *Tetrahedron Lett.*, 1996, **37**, 73–76; (f) R. Seshadri, F. D'souza, V. Krishnan and C. N. R. Rao, *Chem. Lett.*, 1993, 217–220.
- The isolation of $C_{82}(C_2)$ has been reported so far among nine isomers of C_{82} which satisfy the isolated pentagon rule (IPR):¹⁴ K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, H. Matsumiya, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto and Y. Achiba, *Chem. Phys. Lett.*, 1992, **188**, 177–180.
- The constructive comments from the reviewers are highly appreciated.
- The ΔG_{et} value was calculated according to the Rehm–Weller equation ($\Delta G_{\text{et}} = 23.06[E(D/D^+) - E(A/A^-) + e_0^2/a\epsilon]$).¹⁵ As the coulombic interaction energy ($e_0^2/a\epsilon$) in nitrobenzene, the value of -0.03 eV was employed.
- The distance along the long axis of the spheroid between end-to-end carbon atoms of **1**.
- The sizes were obtained as twice the value of the average distances between the center of the molecule and carbon atoms in the crystalline structures of **2–5**.
- P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, 1995.
- D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.