

Spin-Site Exchange System Constructed from Endohedral Metallofullerenes and Organic Donors

Takahiro Tsuchiya,[†] Kumiko Sato,[†] Hiroki Kurihara,[†] Takatsugu Wakahara,[†] Yutaka Maeda,[‡] Takeshi Akasaka,^{*†} Kei Ohkubo,[§] Shunichi Fukuzumi,[§] Tatsuhisa Kato,^{||} and Shigeru Nagase[⊥]

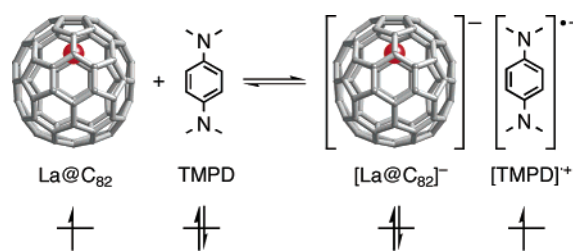
Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan, Department of Material and Life Science, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan, Department of Chemistry, Josai University, Sakado, Saitama 350-0295, Japan, and Department of Theoretical Molecular Science, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

Received April 15, 2006; E-mail: akasaka@tara.tsukuba.ac.jp

Endofullerenes have attracted special interests with unique electronic properties and reactivities, which are not seen in empty fullerenes.¹ The fact that endohedral metallofullerenes are more easily reduced than empty fullerenes is one of the most important factors in controlling their reactivities.² Since the first report about the complex of C₆₀ with tetrakis(dimethylamino)ethylene by Wudl and co-workers,³ charge-transfer (CT) interaction between C₆₀ and organic donors in solid state has been widely examined.⁴ The photoinduced electron transfer from *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) to the triplet C₆₀ in nitrobenzene has been also reported by Foote et al.;⁵ in this report no electron transfers occur thermally. Recently, we have found the complexation behavior of the paramagnetic endohedral metallofullerene La@C₈₂ (C_{2v}) with aza- and thiocrown ethers in solution.⁶ La@C₈₂ forms a 1:1 complex with the host molecules in nitrobenzene by the electron transfer between them. The facile electron transfer is characteristic of endohedral metallofullerenes having low reduction potentials. In these systems, however, oxidized species of crown ethers are still unidentified because of their instability, whereas the formation of reduced species of La@C₈₂ ([La@C₈₂]⁻) was confirmed. In this context, we examined the complexation and electron transfer behavior between La@C₈₂ and organic donor molecules such as TMPD, which forms a stable radical cation (Scheme 1).

The complexation behavior of La@C₈₂ with TMPD in nitrobenzene was followed by the standard titration technique using vis-NIR spectroscopy, as shown in Figure 1a. As the characteristic absorption maxima of La@C₈₂ at 635 and 998 nm disappear, new absorption maxima appear at 572, 621, and 937 nm with increasing amounts of TMPD. This indicates that the electron-transfer from TMPD to La@C₈₂ occurs, which leads to the [TMPD]^{•+} radical cation (λ_{max}: 572 and 621 nm, Figure 1b)⁷ and the [La@C₈₂]⁻ anion (λ_{max}: 937 nm, Figure 1b).⁸ The titration plot in the inset of Figure 1a shows an inflection point at [TMPD]/[La@C₈₂] = 1, indicating the formation of a 1:1 complex. The equilibrium constant for the La@C₈₂-TMPD system is evaluated to be log K_{obs} = 5.4 by nonlinear least-square curve fitting into the titration plots. This value depends on the measurement solvent; the equilibrium constants in benzonitrile and *o*-dichlorobenzene are log K_{obs} = 5.0 and 3.1, respectively.⁹ In contrast, the equilibrium constant in toluene is too small to be detected. These results show good correspondence with the permittivity ε_r of the measurement solvents. The vis-NIR

Scheme 1



absorptions of the La@C₈₂/TMPD pair and the [La@C₈₂]⁻/[TMPD]^{•+} pair are apparently different, which reveals a solvatochromism.⁹ The spin-site exchange process between La@C₈₂ and TMPD in nitrobenzene is also confirmed by EPR measurement, as shown in Figure 2a; as the intensity of EPR signals of La@C₈₂ is weakened in the presence of TMPD, the signals of [TMPD]^{•+} appear. The line width of the resulted spectrum is as narrow as that of [TMPD]^{•+} PF₆⁻ salt in solution,⁹ indicating that the stable spin is located on the time scale of the EPR experiment. Variable-temperature EPR measurements from 320 to 240 K in *o*-dichlorobenzene/benzonitrile (= 4:1) showed that the equilibrium shifts to the formation of the ion pair at low temperatures (Figure 2b). The repeated temperature change afforded the same spectra, denoting that La@C₈₂ and TMPD are in equilibrium with [La@C₈₂]⁻/[TMPD]^{•+} in solution. The equilibrium shift accompanied by temperature change can be observed by applying the process in the solvent having the appropriate permittivity like *o*-dichloroben-

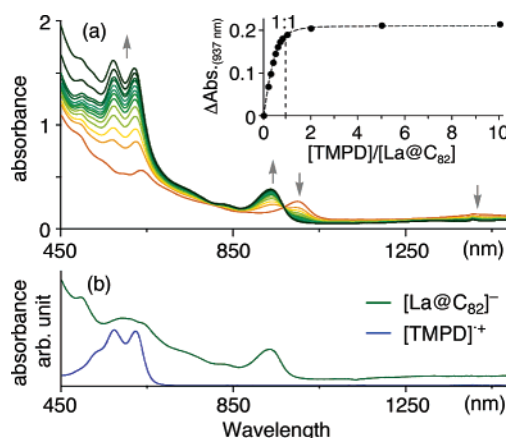


Figure 1. Visible-NIR spectra of (a) La@C₈₂ (1.0 × 10⁻⁴ M) in the presence of TMPD (0–10 equiv) and (b) *n*-Bu₄N⁺ [La@C₈₂]⁻ and [TMPD]^{•+} PF₆⁻ at 296 K.

[†] University of Tsukuba.

[‡] Tokyo Gakugei University.

[§] Osaka University.

^{||} Josai University.

[⊥] Institute for Molecular Science.

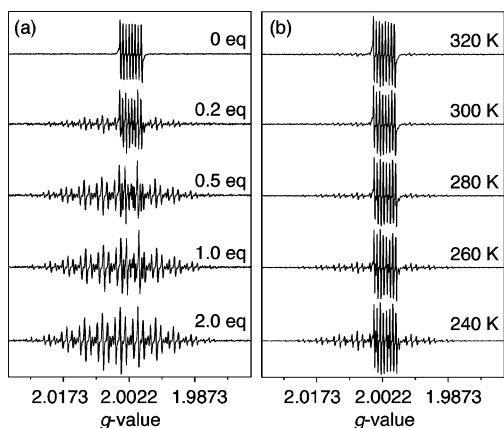


Figure 2. EPR spectra of (a) La@C₈₂ in the presence of 0–2 equiv of TMPD in nitrobenzene at 296 K and (b) La@C₈₂ with 1 equiv of TMPD in *o*-dichlorobenzene/benzonitrile (= 4:1) at 320–240 K.

Table 1. Reduction (^{red}E₁) and Oxidation (^{ox}E₁) Potentials^a and Thermodynamic Parameters for the System of La@C₈₂ and Organic Donors

compd	^{red} E ₁ (V ^b)	^{ox} E ₁ (V ^b)	ΔG _{et} (kcal/mol)	log K _{obs}	ΔG _{obs} (kcal/mol)	log K _{assoc}
La@C ₈₂	-0.25					
FeCp* ₂		-0.52	-7.4	6.7	-9.1	1.2
TMPD		-0.30	-2.3	5.4	-7.3	3.7
DHDMP		-0.26	-1.4	4.7	-6.4	3.7

^a Obtained by CV. Conditions: 0.1 M *n*-Bu₄NPF₆ in nitrobenzene; working electrode, Pt wire; counter electrode, Pt wire; scan rate, 20 mV s⁻¹. ^b Versus Fc/Fc⁺.

zene/benzonitrile, whereas the nitrobenzene solution shows the too strong affinity between La@C₈₂ and TMPD at the practical temperature range for the EPR measurement. The dissociation and association states can be controlled reversibly by changing the temperature, which results in the appearance of a thermochromism phenomenon.⁹

The interaction of La@C₈₂ with decamethylferrocene (FeCp*₂) and 5,10-dihydro-5,10-dimethylphenazine (DHDMP) in nitrobenzene was also examined (See Table 1). Both cases show electron-transfer from organic donors to La@C₈₂, and the reversible electron-transfer phenomenon is observed in the equilibrium state.⁹ The equilibrium constants for La@C₈₂ with FeCp*₂ and DHDMP in nitrobenzene at 296 K are log K_{obs} = 6.7 and 4.7, respectively. The equilibrium constants for FeCp*₂, TMPD, and DHDMP exhibit a good correlation with their first oxidation potentials. The oxidation potentials (^{ox}E₁ vs Fc/Fc⁺) of FeCp*₂, TMPD, and DHDMP determined by cyclic voltammetry (CV) technique are -0.52, -0.30, and -0.26 V, respectively. By using the reduction potential (^{red}E₁ = -0.25 V) of La@C₈₂, the free energy changes (ΔG_{et}) for the electron transfer from FeCp*₂, TMPD, and DHDMP to La@C₈₂ are evaluated to be -7.38, -2.31, and -1.38 kcal/mol, respectively, from the Rehm–Weller equation.¹⁰ These negative ΔG_{et} values mean that the electron transfer is thermodynamically favorable. On the other hand, the free energy changes (ΔG_{obs}) for the whole reaction between La@C₈₂ and the donor molecules are -9.07 (FeCp*₂), -7.31 (TMPD), and -6.36 (DHDMP) kcal/mol from the aforementioned equilibrium constants. The ΔG_{et} values calculated by using the difference of redox potentials is not well

consistent with the ΔG_{obs} values for the whole reaction. This is because the complexation of La@C₈₂ and donor molecules facilitates the sequential electron transfer. The difference values of ΔG_{obs} and ΔG_{et} for FeCp*₂, TMPD, and DHDMP are -1.69, -5.00, and -4.98 kcal/mol, respectively. From these values, the association constants of La@C₈₂ with FeCp*₂, TMPD, and DHDMP are estimated to be log K_{assoc} = 1.2, 3.7, and 3.7, respectively. The K_{assoc} value for FeCp*₂ is smaller than those for TMPD and DHDMP. This reflects the larger steric hindrance of the bulkier FeCp*₂ for the complexation.

In conclusion, reversible intermolecular spin-site exchange systems at complete equilibrium in solution are first accomplished by utilizing paramagnetic La@C₈₂ and organic donor molecules, which form stable diamagnetic anion and radical cations, respectively. It is interesting to note that the systems are found to show the thermo- and solvatochromism. This is an important stepping-stone on the way to developing the materials useful for optical and magnetic applications.

Acknowledgment. This work was supported in part by a Grant-in-Aid, the 21st Century COE Program, Nanotechnology Support Project, NAREGI Nanoscience Project from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and a grant from the Kurata Memorial Hitachi Science and Technology Foundation and Mitsubishi Chemical Corporation Fund.

Supporting Information Available: Complete references 6a and 8; titration experiments of La@C₈₂ with TMPD, FeCp*₂, and DMDHP; solvent- and temperature-dependent color changes of the solution of La@C₈₂ with TMPD; EPR spectra of TMPD in the presence of La@C₈₂ and NOPF₆. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer: Dordrecht, The Netherlands, 2002. (b) Nagase, S.; Kobayashi, K.; Akasaka, T.; Wakahara, T.; In *Fullerenes: Chemistry, Physics and Technology*; Kadish, K., Ruoff, R. S., Eds.; John Wiley & Sons: New York, 2000; pp 231–251. (c) Naydenov, B.; Spudat, C.; Harnett, W.; Süß, H. I.; Hulliger, J.; Nuss, J.; Jansen, M. *Chem. Phys. Lett.* **2006**, *424*, 327–332.
- (2) (a) Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature* **1995**, *374*, 600–601. (b) Koltover, V. K.; Logan, J. W.; Heise, H.; Bubnov, V. P.; Estrin, Y. I.; Kareev, I. I.; Lodygina, V. P.; Pines, A. *J. Phys. Chem. B* **2004**, *108*, 12450–12455. (c) Koltover, V. K.; Bubnov, V. P.; Estrin, Y. I.; Lodygina, V. P.; Davydov, R. M.; Subramoni, M.; Manoharan, P. T. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2774–2777.
- (3) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Dcnovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301–303.
- (4) (a) Konarev, D. V.; Neretin, I. S.; Saito, G.; Slovokhotov, Y. L.; Otsuka, A.; Lyubovskaya, R. N. *J. Chem. Soc., Dalton Trans.* **2003**, 3886–3891. (b) Saito, G.; Hirate, S.; Nishimura, K.; Yamochi, H. *J. Mater. Chem.* **2001**, *11*, 723–735. (c) Izuoka, A.; Tachikawa, T.; Sugawara, T.; Suzuki, Y.; Konno, M.; Saito, Y.; Shinohara, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1472–1473.
- (5) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277–2279.
- (6) (a) Tsuchiya, T.; et al. *J. Am. Chem. Soc.* **2006**, *128*, 6699–6703. (b) Tsuchiya, T.; Kurihara, H.; Sato, K.; Wakahara, T.; Akasaka, T.; Shimizu, T.; Kamigata, N.; Mizorogi, N.; Nagase, S. *Chem. Commun.* **2006**, 3585–3587.
- (7) Rawashdeh, M. A. M.; Sotiriou-Leventis, C.; Gao, X.; Leventis, N. *Chem. Commun.* **2001**, 1742–1743.
- (8) Akasaka, T.; et al. *J. Am. Chem. Soc.* **2000**, *122*, 9316–9317.
- (9) See Supporting Information.
- (10) The ΔG value was calculated according to the Rehm–Weller equation¹¹ (ΔG = 23.06[E(D/D⁺) - E(A/A⁻) + e₀²/aε]). The coulombic interaction energy (e₀²/aε) in nitrobenzene is -0.05 eV.
- (11) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

JA062634X