Bistable Charge-Transfer Complex Formation in the TCNE-Biphenylene System Based on the Intermolecular HOMO-LUMO Interaction in the Neutral and Dianionic Redox States of TCNE

Bunji Uno* and Noriko Okumura
Gifu Pharmaceutical University, Mitahora-higashi, Gifu 502-8585

(Received May 17, 1999; CL-990386)

It has been demonstrated that the tetracyanoethylene dianion ($TCNE^{2-}$) forms the charge-transfer complex with biphenylene (BP), caused by the favorable intermolecular HOMO–LUMO interaction. The TCNE–BP system involving the bistable charge-transfer (CT) complex formation modulated by redox reactions of TCNE is characterized by the geometrical properties and the trichromic change.

Molecular recognition is well recognized to play crucial roles in molecular redox switch systems involving bistable molecular or supramolecular species presenting two forms whose interconversion can be modulated by redox reactions, as well as in various molecular switch systems.[1-3] The conformational and physical properties in the switch systems result in the difference in metal coordinate,[4] hydrophobic,[3,5] hydrogen bonding and aromatic stacking interactions[2,6] in the redox states of the components. Considerable interest is devoted to the organic π–dianions as well as dications[3] contributive to such molecular-level switching systems as a part of the redox species, exhibiting specific interaction and strong electron-donation arising from their peculiar electronic states. However, very few investigations on the π–dianions have appeared in the literature, being regarded to the dianion–metal coordinate and hydrogen-bonding interactions.[7,8] We report here the π–π type CT complex formation of $TCNE^{2-}$ governed by the MO symmetry active to the CT interaction, and the redox-mediated bistable complex formation with the geometrical alteration and the chromatic change in the TCNE–BP system (see Figure 1).

It is well known that TCNE forms the π–π CT complex with hydrocarbons, functioning as an electron acceptor.[9] The CT bands of the TCNE–BP and TCNE–hexamethylbenzene (HMB) systems were observed at 620 nm and 520 nm, respectively. Sequential electroreduction of TCNE in CH_2Cl_2 generated the corresponding anion radical and π–dianion, giving the two reversible waves on the cyclic voltammogram.[10] Spectroelectrochemistry for TCNE gave the spectra of $TCNE^-$ and $TCNE^{2-}$ at 430 nm and 300 nm, respectively.[10] Electrolysis of the TCNE solution containing BP allowed a new band resulting from the CT interaction between $TCNE^{2-}$ and BP to appear at 550 nm with the electrogeneration of $TCNE^{2-}$, whereas in the absence of BP and in the presence of HMB the spectral change in a wavelength region longer than 500 nm resulted in only decrease of the absorbance of $TCNE^-$ (Figure 2). Thus, the trichromic change has been attained by the chromatic bistable complex formations in the TCNE–BP system upon redox state change, as shown in Figure 1; green-blue for the TCNE–BP complex, yellow for $TCNE^-$, and purple for the $TCNE^{2-}$–BP complex.

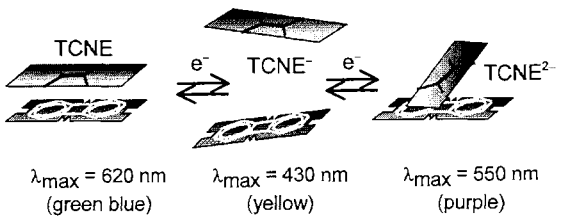

Figure 1. Redox-mediated bistable complex formation with the geometrical alteration and the trichromic change in the TCNE–BP system.

To quantify the binding of $TCNE^{2-}$ we investigated the change in half-wave reduction potentials of TCNE upon addition of BP and HMB. The addition of BP allowed the second half-wave reduction potential to be significantly shifted to the positive direction keeping the wave reversible, being indicative of substantial stabilization of $TCNE^{2-}$.[11] Dependence of the potential shift upon concentrations of BP allowed the complex formation constant ($K^=$) of the $TCNE^{2-}$–BP system to be estimated as 20.3 $dm^3\ mol^{-1}$ at 25 °C.[7] Temperature dependence of the $K^=$ values yielded the formation energy as 39.8 $kJ\ mol^{-1}$. These values are explained by the strong CT complex formation.[9] Addition of HMB, in contrast, resulted in a shift of the first potential to less negative value without apparent affection to the second wave. The positive shift of the second wave could not be observed for addition of anthracene whose electron negativity is larger than BP.[11] These behaviors indicate that the $TCNE^{2-}$–BP complex formation is governed by a determining factor rather than electron negativity of acceptors.

Next the discussion has been extended to the geometrical configuration of the $TCNE^{2-}$–BP complex, giving clear-cut theoretical evidence for the intermolecular interaction. HF/6-31G* energy gradient calculation results show that the geometry of the CT complex alters with the dianion generation (Figure 3).[12] The formation of the most stable $TCNE^{2-}$–BP complex was observed at the stacking angle (θ) of 90°, causing charge transfer

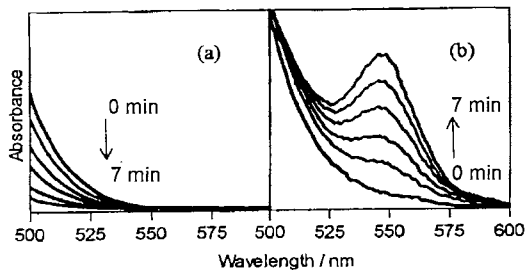

Figure 2. Spectral change of 4.76×10^{-4} mol dm^{-3} TCNE in CH_2Cl_2 containing 0.5 mol dm^{-3} tetrabutylammonium perchlorate with the controlled-potential electrolysis, corresponding to the $TCNE^{2-}$ generation from $TCNE^-$ in the absence of BP (a) and in the presence of 7.50×10^{-3} mol dm^{-3} BP (b). The electrode potential was −1.4 V vs. $Ag/AgNO_3$ (in CH_3CN).

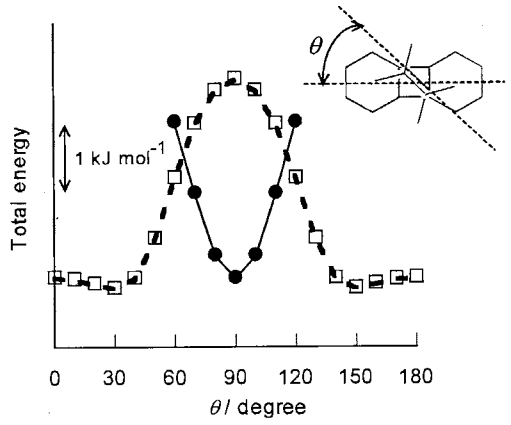

Figure 3. Dependence of the relative HF/6-31G* total energies of the TCNE–BP (□ and dashed line) and $TCNE^{2-}$–BP (● and solid line) systems upon the stacking angle (θ) shown here. The conformational energies were optimized in rotations at every 10° angle of θ.

from $TCNE^{2-}$ to BP. The optimized stacking distance (D) of 3.89 Å is suitable for the favorable π–π intermolecular interaction.[9] On the other hand, TCNE forms the stable CT complex with BP at θ = ca. 0 and D = 3.90 Å, functioning as an electron acceptor with the charge transfer from BP to TCNE. These imply that the intermolecular CT interaction of TCNE/$TCNE^{2-}$ plays a crucial role in the geometrical alteration. The favorable interaction between the b_{2g}-HOMO of $TCNE^{2-}$ as an electron donor and the b_{3g}-LUMO of BP as an electron acceptor makes the intermolecular HOMO–LUMO interaction possible around θ = 90° in terms of bonding character in the MO phases active to the CT complex formation (Figure 4).[13] These orbital characteristics may appear in the 4nπ electronic system. The θ = 0° configuration of the TCNE–BP and TCNE–HMB complex is reasonably interpreted as the favorable HOMO–LUMO interaction, whereas the interaction between $TCNE^{2-}$ and HMB is unfavorable at any values of θ. These results reasonably indicate that the complex formation of $TCNE^{2-}$ is governed by conversion of the MOs active to the CT interaction upon reduction of TCNE to $TCNE^{2-}$.

It has been demonstrated that *tetracyanoethylene* forms the bistable CT complexes with BP characterized by the distinguishable optical and geometrical properties through redox control of the active MOs, as is shown in Figure 1. The present conclusion is important to the extended discussion on the redox-mediated recognition and the redox switch system involving the electrogenerated π–dianions.

We thank the Computer Center of the Institute for Molecular Science for the use of the NEC HSP computer and the Library Program Gaussian 94. This work was supported in part by a Grant-in-Aid for Scientific Research No. 11672148 from the Ministry of Education, Science, Sports and Culture of Japan.

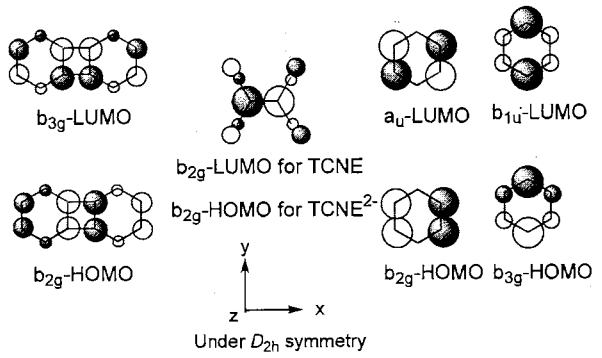

Figure 4. Illustration of the HOMOs and LUMOs active to the complex formation for TCNE, $TCNE^{2-}$, BP, and HMB with point groups under D_{2h} symmetry and the coordinate given here.

References and Notes

1 a) J. M. Lehn, "Supramolecular Chemistry. Concepts and Perspectives," VCH, Weiheim (1995). b) P. D. Beer, *Acc. Chem. Res.*, **31**, 71(1998).
2 A. Niemz and V. M. Rotello, *Acc. Chem. Res.*, **32**, 44 (1999).
3 E. A. Kaifer, *Acc. Chem. Res.*, **32**, 62 (1999).
4 a) S. Zahn and J. W. Canary, *Angew. Chem., Int. Ed. Engl.*, **37**, 305 (1998). b) P. D. Beer, F. Szemes, V. Balzani, C. M. Sala, M. G. B. Drew, S. W. Dent, and M. Maestri, *J. Am. Chem. Soc.*, **119**, 11864 (1997). c) L. Zelikovich, J. Libman and A. Shanzer, *Nature*, **374**, 790 (1995). d) J. A. Wytko, C. Boudon, J. Weiss, and M. Gross, *Inorg. Chem.*, **35**, 4469 (1996). e) A. Livoreil, C. O. Dietrich-Buchecker, and J. –P. Sauvage, *J. Am. Chem. Soc.*, **116**, 9399 (1994). f) S. H. Kawai, S. L. Gilet, R. Ponsiner, and J. M. Lehn, *Chem. Eur. J.*, **1**, 285 (1995).
5 a) Z. Chen, A. J. Pilgrim, and P. D. Beer, *J. Electroanal. Chem.*, **444**, 209 (1998). b) R. M. Nielson, L. A. Lyon, and J. T. Hupp, *Inorg. Chem.*, **35**, 970 (1996).
6 a) D. S. Francis, *J. Am. Chem. Soc.*, **118**, 923 (1996). b) T. Hayashi, T. Miyahara, N. Hashizume, and H. Ogoshi, *J. Am. Chem. Soc.*, **115**, 2049 (1993).
7 a) N. Okumura and B. Uno, *Bull. Chem. Soc. Jpn.*,**72**, 1213 (1999). b) B. Uno, A. Kawabata, and K. Kano, *Chem. Lett.*, **1992**, 1017.
8 M. Oyama, A. Takei, and S. Okazaki, *J. Chem. Soc., Chem. Commun.*, **1995**, 1909.
9 R. S. Mulliken and W. B. Person, "Molecular complexes," Wiley Interscience, New York (1969).
10 The experimental conditions are the same as those in our previous work.[7]
11 Hydrocarbons used here are not reduced in the potential range. The half-wave reduction potential of BP in CH_2Cl_2 is less than –2.2 V vs. SCE.
12 The planar D_{2h} structure of $TCNE^{2-}$ in CH_2Cl_2 was confirmed by spectroelectrochemistry of $TCNE^{2-}$ and CNDO/S-CI calculations.
13 The b_{2g} symmetry is same as b_{3g} under the point group D_{2h} on rotation of 90° with regard to the central C_2 axis (z) in Figure 4. This is thus explained by the favorable HOMO–LUMO interaction belong the b_{3g} symmetry species.