

Photoinduced electron transfer and multiple states mechanisms

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Abstract – Results of our ps–fs laser photolysis studies on interactions between unlinked D(donor)–A(acceptor) systems in luminescence quenching reactions and reaction dynamics of produced transient CT (charge transfer) or IP (ion pair) states and also on some D–A systems linked by flexible chains or directly can be interpreted satisfactorily by considering the formation of multiple CT and/or IP states with different structures depending on solvation, strength of D–A interaction and energy gap for ET (electron transfer) and change of the distribution of those states in the course of reaction. Also, the most fundamental factors regulating the photoinduced ET have been examined by using fixed distance dyads and some new critical aspects concerning the energy gap dependences of ET reactions have been demonstrated.

INTRODUCTION

Dynamics and mechanisms of photoinduced electron transfer (ET) or charge transfer (CT) between electron donor (D) and acceptor (A) and related phenomena, leading to the formation of transient ion pair (IP), and subsequent behaviors of those IP states are the most important and fundamental problems in photophysical and photochemical processes in condensed phase. In this article, we will discuss mainly results of our ps–fs laser photolysis studies on various ET reaction processes, especially mutual relations among them and fundamental mechanisms underlying those reactions.

I. PHOTOINDUCED CS AND CR OF PRODUCED IP'S IN UN-LINKED D···A SYSTEMS

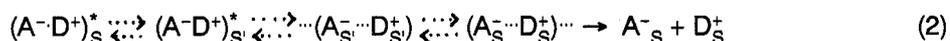
Our early investigations concerning the effects of solvent polarity upon the exciplex fluorescence yield and lifetime showed that both of them decreased with increase of the solvent polarity but the extent of the decrease of the yield was much larger (1). From this result, it was suggested that the radiative transition probability of the exciplex fluorescence decreased and corresponding radiationless transition probability increased with increase of solvent polarity (1). The former may be caused by the change of the exciplex electronic and geometrical structures to more polar ones due to the interaction with polar solvent and the latter seems to be the consequence of the decrease of the relevant energy gap owing to the lowering of the CT state energy by solvations (1).

The above mechanism of the change of exciplex electronic and geometrical structures depending upon the interaction with polar solvents suggests that, in polar solvent, existence of an ensemble of exciplexes distributed over multiple states with slightly different electronic and geometrical structures may be possible. In strongly polar solvents like acetonitrile, photoinduced CS (charge separation) reaction results dominantly in the formation of the geminate IP's which may constitute also an ensemble of IP's with slightly different structures (different degree of solvation and different inter-ionic distance).

In relation to such possibilities of the multiple states mechanism of photoinduced ET and exciplex phenomena, we made previously detailed picosecond laser photolysis studies on the exciplex fluorescence decay times and rise times of photoconductivity due to the ionic dissociation of LIP's (loose IP's) of pyrene-DMA (N,N-dimethylaniline) system in various solvents of different polarities such as acetonitrile, acetone, pyridine, etc. (2). It was demonstrated that the exciplex fluorescence decay time (τ_f^{ex}) and photoconductivity rise time τ_f^{ion} in the same solvent were rather close to each other. Nevertheless, τ_f^{ex} was a little larger than τ_f^{ion} in all cases (2). This result cannot be interpreted by "two-state" model,



where $(A^-D^+)^*$ is the fluorescent exciplex and $(A_s^- \cdots D_s^+)$ is the LIP. In this scheme, the fluorescence decay curve must exactly correspond to the photocurrent rise curve contrary to the observation. Therefore, we need "multiple states" model of various kinds of exciplexes and LIP's which undergo partial interconversions between each other but the LIP's which undergo dissociation may not be directly combined with the fluorescing exciplexes (2).



We confirmed that very similar conclusion can be derived also in the case of the pyrene-DCNB(p-dicyanobenzene) exciplex systems (2).

We have recently demonstrated by experimental and theoretical studies on ET mechanisms in fluorescence quenching reaction that the concept of "multiple states" mechanism of the exciplex and photoinduced ET phenomena proposed by us (2) many years ago is very closely related with the long standing problem of the energy gap ($-\Delta G$) dependences of the photoinduced CS rate constant (k_{CS}) and CR (charge recombination) rate constant (k_{CR}) of the produced IP's. Namely, contrary to the theoretical prediction (3), observation of the inverted region in the $k_{\text{CS}} \sim -\Delta G_{\text{CS}}$ relation studied in the case of the fluorescence quenching reaction by ET has not been possible until now (4), while we have confirmed rather recently the bell-shaped $k_{\text{CR}} \sim -\Delta G_{\text{CR}}$ relation of geminate IP's produced by fluorescence quenching reaction in acetonitrile for the first time by means of direct observation of the CR process with picosecond laser photolysis method (5).

In the usual fluorescence quenching experiment, the true k_{CS} value in the favorable $-\Delta G_{\text{CS}}$ region is masked by the diffusion-limit of the reaction. Nevertheless, we have estimated recently approximate k_{CS} values for the diffusion-limited region by measurements of fluorescence decay curves and by analyzing the transient effect in fluorescence quenching process for a series of fluorescer-quencher pairs covering a wide $-\Delta G$ range (4b). The obtained k_{CS} values in acetonitrile solutions, however, do not show any such typical bell-shaped $-\Delta G$ dependence as observed in the case of the CR reaction of geminate IP's (5) but the observed $-\Delta G$ dependence of "true" k_{CS} in the diffusion-limited region is much broader and flat shape. Therefore, the quite remarkable difference between the energy gap dependence of k_{CS} and k_{CR} of the produced IP in the fluorescence quenching reaction (5) and the very broad and rather flat $k_{\text{CS}} \sim -\Delta G_{\text{CS}}$ relation (4b) are due to the intrinsic natures of these reactions. The above results seem to be difficult to interpret by applying simply the usual ET theories (3,6). Various possibilities have been examined theoretically and experimentally in order to give a satisfactory interpretation of these results; e.g., the participation of excited electronic states of transient IP which causes apparent lack of the inverted effect in CS even at very large $-\Delta G_{\text{CS}}$ (4a,7), distance distribution between fluorescer and quencher at encounter which makes the $k_{\text{CS}} \sim -\Delta G_{\text{CS}}$ relation rather broad and flat (8), and nonlinear polarization of polar solvent around transient IP which affects the free energy potential curvature and produces the different $-\Delta G$ dependence between CS and CR (9). Our detailed theoretical analyses of these mechanisms have led to the following conclusion with respect to the $k_{\text{CS}} \sim -\Delta G_{\text{CS}}$ relation (10). Namely, for a quantitative treatment of this problem, it is necessary to take into account the distance distribution between the fluorescer and the electron donating or accepting quencher at CS and a moderate nonlinear polarization of the polar solvent around the charged solute. This distance distribution is related to the $-\Delta G_{\text{CS}}$ dependence of k_{CS} through the dependence of the solvent reorganization energy λ_s and electron tunneling matrix element. For the CS corresponding to

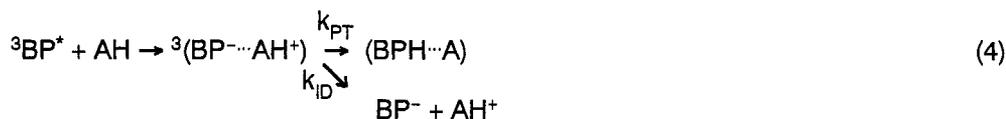
the larger $-\Delta G_{CS}$, a little larger distance for ET (which gives larger λ_s) is favorable as suggested by the simple Eq. 3.

$$k_{CS} \propto \exp\{-(\lambda_s + \Delta G)^2 / 4\lambda_s k_B T\} \quad (3)$$

By taking into account the $-\Delta G_{CS}$ dependence of the inter-ionic distance distribution in the geminate IP and a little change of the distance distribution before the CR of the IP and also by considering a moderate nonlinear polarization of polar solvent around charged solutes, we have given recently a satisfactory interpretation on this large difference between the $-\Delta G$ dependences of photoinduced CS and CR of the produced IP (10).

It should be noted here that the observed rise of k_{CS} with increase of $-\Delta G_{CS}$ around zero energy gap is very steep (7a), which means very short inter-ionic distances of produced IP and very sharp bell-shaped $k_{CS} \sim -\Delta G_{CS}$ relation with small λ_s values in this energy gap region. Probably the IP formed by ET around zero energy gap region will include a kind of exciplex of a compact structure with face to face or plane parallel configuration as a main component in addition to CIP (compact IP) and LIP, although it is rather difficult to take into consideration the effect of such configuration in the theoretical calculation of $k_{CS} \sim -\Delta G_{CS}$ relation.

The above results of the "multiple states" model invoked to interpret the apparent lack of the inverted region in the $k_{CS} \sim -\Delta G_{CS}$ relation and quite different energy gap dependence of photoinduced CS and CR of the produced IP are in agreement with the conclusions derived from our previous investigations on the exciplex fluorescence decay time and picosecond laser induced photocurrent rise time as represented by Eq. 2 (2). Namely, even in the case of one kind of A-D pair, pyrene-DMA (with relatively small $-\Delta G_{CS} \sim 0.5$ eV), there is a distribution of IP's with different structures including a small amount of fluorescent exciplex even in acetonitrile solution. Moreover, the above results of theoretical calculations demonstrate clearly that the inter-ionic distance averaged over the distribution increases with increase of $-\Delta G_{CS}$ (10). Although the experimental confirmation of this $-\Delta G_{CS}$ dependence of the inter-ionic distance in the geminate IP is a difficult problem, we have found direct experimental evidence which supports the above conclusions, in the case of the hydrogen abstraction of triplet benzophenone ($^3BP^*$) from various tertiary aromatic amines (AH) via LIP state in acetonitrile solution (11).

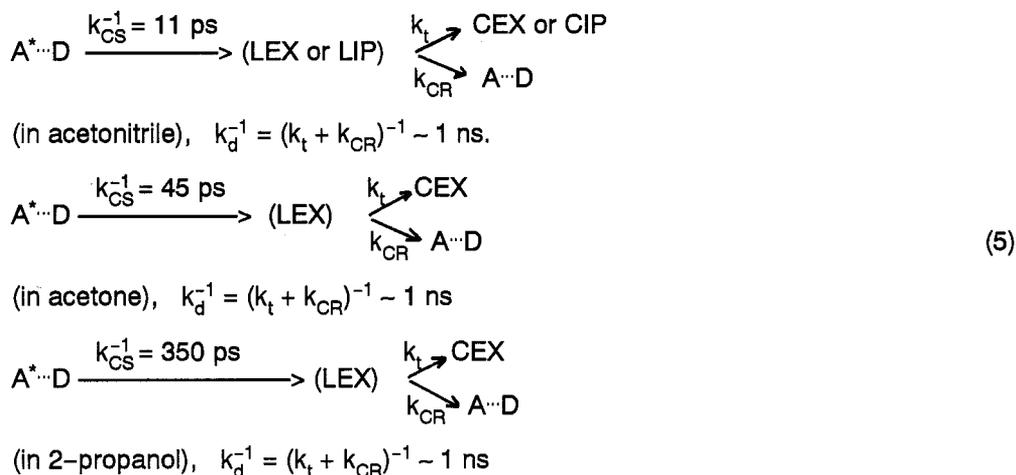


Namely, k_{PT} decreases with decrease of the oxidation potential of AH as follows: $k_{PT} = 8.2 \times 10^9 s^{-1}$, $5.4 \times 10^9 s^{-1}$ and $7.3 \times 10^8 s^{-1}$ for N-methyldiphenylamine, DMA and N,N-diethylaniline with oxidation potentials 0.86, 0.76 and 0.72 V vs. SCE, respectively. Moreover, k_{ID} increases a little corresponding to the increase of the inter-ionic distance in 3LIP in this order.

II. INTRAMOLECULAR PHOTOINDUCED ET PHENOMENA IN LINKED D...A SYSTEMS

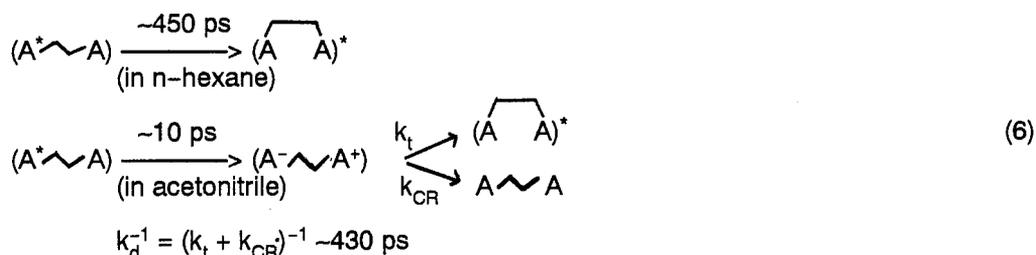
As discussed in I., the intermolecular photoinduced ET, and exciplex as well as IP state formation processes are profoundly affected by solvent polarity and $-\Delta G$ for ET, etc and, especially in polar solvents, the "multiple states" mechanism seems to play a very important role in the photoinduced ET phenomena. In relation to this problem, we have demonstrated previously that loose intramolecular exciplex (LEX) or intramolecular LIP state is formed in the case of P_3 ($p-(CH_3)_2N-Ph-(CH_2)_n-(1-pyrenyl)$, Pn) in polar solvent and those LEX or LIP undergo transformation to compact intramolecular exciplex (CEX) or intramolecular CIP as well as CR decay. In those intramolecular exciplex systems with rather large configurational freedom, configuration distribution may be present and intramolecular exciplex or IP states with different configurations may be realized depending upon the solvent polarity and the $-\Delta G$ for ET, etc.

The reaction processes of P_3 in polar solvents are as follows (12).



In *n*-hexane, where the interaction of the CT state with the polar solvent is absent, only the CEX formation is possible and it takes longer time than LEX formation due to larger extent of configuration change.

In the above systems, the photoinduced ET is prescribed to occur from D to A groups. However, photoinduced CS takes place also in some systems with identical halves linked by spacer. A typical example is the 1,2-di(1-anthryl)ethane (D(1-A)E) which shows an enhancement of the intramolecular excimer formation with an increase of solvent polarity (13). This result suggests the solvation-induced intramolecular photoinduced CS in a loose configuration, which accelerates a configuration change to a more compact one leading to the intramolecular excimer formation (13). This is very similar to the case of P_3 in polar solvent as indicated in Eq. 5, except that the CEX turns to excimer in D(1-A)E. Actually, our detailed ps laser photolysis investigation on this system has elucidated such mechanism (13b,c). Namely, relatively slow process of direct excimer formation by intramolecular configuration rearrangement with time constant of several hundreds ps takes place in *n*-hexane, while the formation of LIP followed by excimer formation is observed in addition to direct excimer formation with increase of solvent polarity. In acetonitrile, very rapid formation of LIP (~10 ps) observed. The value of k_{CS}^{-1} ~ 10 ps is reasonable in view of $-\Delta G_{CS}$ ~ 0.33 eV. It should be noted here that the transient absorption spectra of the reaction intermediate in acetonitrile solution can be reproduced almost exactly by the superposition of the spectra of anion radical and cation radical of 1-methylantracene (13c).



Another well-known example of the system with identical halves which shows the photoinduced intramolecular CS in polar solvents is 9,9'-bianthryl (BA). The minimum position of the configuration distribution in the ground state of BA is the perpendicular configuration but that of the excited equilibrium state is at a considerably inclined position in the torsional potential. Immediately after excitation, relaxation of configuration distribution to the one with minimum at inclined position where the electronic interaction between the halves is stronger takes place. We have directly observed this relaxation process in several nonpolar solvents by time-resolved absorption spectral measurements with fs laser spectroscopy, from which the relaxation time has been obtained to be ca. 5–10 ps (14b). The relaxation time does not show much

dependence upon the solvent viscosity. In view of the above results of the configuration change in torsional potential, whether the solvation-induced broken symmetry takes place from the locally excited state immediately after excitation or from the relaxed state is an important problem. Our detailed ps-fs studies show that, in 1-pentanol with rather long τ_L value, the intramolecular CT takes place from the relaxed S_1 state and rise time τ_r (= 170 ps) of the CT state is approximately in agreement with τ_L (14a). In alkanenitriles such as acetonitrile (ACN), butyronitrile (BuCN) and hexanenitrile (HeCN), the photoinduced CT can compete with or faster than the configurational relaxation (14c) because of the much shorter solvent orientation relaxation times τ_L or τ_S . The rise curves of the CT states obtained by transient absorption measurements contain in addition to the rapid component, slow component with τ_r much longer than τ_L or τ_S as follows: $\tau_r = 1.8$ ps in ACN, $\tau_r = 3.4$ ps in BuCN and $\tau_r = 7.5$ ps in HexCN, compared with $\tau_L = 0.19$ ps and $\tau_S = 0.4-0.9$ ps in ACN, $\tau_L = 0.53$ ps and $\tau_S = 1.5-2.1$ ps in BuCN and $\tau_L = 1.0$ ps and $\tau_S = 3.5-4.5$ ps in HexCN (15). This result indicates that the photoinduced CT in this system involves rapid process induced by solvent orientation but for the equilibrium CT state formation the relaxation of the configuration distribution to the more or less inclined one with longer rise time τ_r is necessary. This circumstance seems to be somewhat similar to the LEX formation followed by transformation to CEX or excimer in the case of P_3 or D(1-A)E in polar solutions. Corresponding to this results, it should be noted here that the absorption spectrum of the equilibrium excited state of BA is much broader and shifted compared with the superposition of the spectra of anion and cation radicals of anthracene even in acetonitrile, which indicates rather strong electronic interaction between the halves in the inclined configuration.

The above described results concerning the photoinduced CT phenomena in D-A linked systems also demonstrate the important roles of "multiple states" mechanisms.

III. EXAMINATION OF FACTORS REGULATING PHOTOINDUCED ET PHENOMENA WITH WEAKLY INTERACTING FIXED DISTANCE DYADS

The results in I and II demonstrate the crucial importance of the "multiple states" mechanisms in the studies of the photoinduced ET phenomena of various systems in solutions. Nevertheless, there are still many problems to be elucidated concerning the most fundamental aspects of ET theories such as the energy gap dependence of photoinduced CS and CR of transient IP's, the solvent polarity and the temperature effects on those reactions and energy gap dependences, etc. Especially, for an unambiguous experimental examination of such problems, investigations by using D-A systems with various $-\Delta G$ values for ET and linked by spacer at a fixed distance in order to avoid the distribution of the system over multiple states will be of crucial importance. We have made recently such investigations by employing a series of fixed distance dyads of etioporphyrin (P) and quinone derivatives (Q): $H_3C-Ph-MP-Ph-CH_2-Q$, $M=Zn, H_2$, and $Q=naphthoquinone, benzoquinone (BQ), methyl-, dimethyl-, monochloro-, trichloro-BQ$, and $Ph = 1,4\text{-phenylene}$, results of which are summarized briefly in the following (16).

In the case of the ET reaction by weak electronic interaction, the simplified equation (Eq. 7) assuming that the high frequency vibrations can be replaced by one mode with an averaged angular frequency $\langle\omega\rangle$ is frequently used in the analysis of the experimental results.

$$k_{ET} = (\pi/\hbar^2 \lambda_S k_B T)^{1/2} V^2 \sum_n (e^{-S} S^n / n!) \exp\{ -(\Delta G + \lambda_S + n \hbar \langle\omega\rangle)^2 / 4 \lambda_S k_B T \} \quad (7)$$

where V is the electronic interaction, $S = \lambda_V / \hbar \langle\omega\rangle$ the coupling constant, λ_V the reorganization energy associated with $\langle\omega\rangle$, λ_S the solvent reorganization energy, $-\Delta G$ the energy gap for ET reaction. Results of fs-ps laser photolysis measurements of k_{CS} and k_{CR} of the intramolecular IP state in nonpolar or slightly polar benzene and toluene solutions have indicated that k_{CS} is in the normal region up to near the top region and k_{CR} in the inverted region, and their $-\Delta G$ dependences at room temperature can be approximately reproduced by Eq. 7, although the observed k_{CS} near top region does not show indication of the shift to the inverted region contrary to the calculation. Temperature effect studies have revealed that the activation barrier for CS increases with decrease of $-\Delta G_{CS}$ while CR is activationless at all $-\Delta G_{CR}$ examined indicat-

ing the dominant effect of high frequency quantum mode. However, it was difficult to find optimum parameter values in Eq. 7 which could reproduce both the temperature dependences of k_{CS} and k_{CR} at the same time, indicating a serious limitation of such a theoretical equation. Furthermore, we have examined the solvent polarity effects on k_{CS} and k_{CR} by using the same series of dyads. The dependence of k_{CS} on $-\Delta G_{CS}$ showed a systematic change corresponding to the increase of λ_S with increase of solvent polarity while the dependence of k_{CR} on $-\Delta G_{CR}$ showed a very little solvent polarity dependence, leading to the crossing between the $k_{CS} \sim -\Delta G_{CS}$ curve in the normal to near the top region and $k_{CR} \sim -\Delta G_{CR}$ curve in the inverted to near the top region. This result is difficult to interpret by Eq. 7, which seems to require new theoretical considerations. One possibility which causes this result is the nonlinear interactions between the IP state and surrounding polar solvent (9,17), and another is the predominant effect of the quantum mechanical tunneling in the inverted region even in polar solution.

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REFERENCES

1. N. Mataga, T. Okada and N. Yamamoto, *Chem. Phys. Lett.* **1**, 119 (1967).
2. Y. Hirata, Y. Kanda and N. Mataga, *J. Phys. Chem.* **87**, 1659 (1983).
3. (a) R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956). (b) R. A. Marcus, *Annu. Rev. Phys. Chem.* **15**, 155 (1964).
4. (a) N. Mataga, Y. Kanda, T. Asahi, H. Miyasaka, T. Okada and T. Kakitani, *Chem. Phys.* **127**, 239 (1988). (b) S. Nishikawa, T. Asahi, T. Okada, N. Mataga and T. Kakitani, *Chem. Phys. Lett.* **185**, 237 (1991).
5. N. Mataga, T. Asahi, Y. Kanda, T. Okada and T. Kakitani, *Chem. Phys.* **127**, 249 (1988).
6. J. Jortner, *J. Chem. Phys.* **64**, 4860 (1976).
7. (a) D. Rehm and A. Weller, *Isr. J. Chem.* **8**, 259 (1970). (b) N. Mataga, *Bull. Chem. Soc. Jpn.* **43**, 3623 (1970).
8. R. A. Marcus and P. Siders, *J. Phys. Chem.* **88**, 622 (1982).
9. (a) T. Kakitani and N. Mataga, *J. Phys. Chem.* **89**, 8 (1985). (b) A. Yoshimori, T. Kakitani, Y. Enomoto and N. Mataga, *J. Phys. Chem.* **93**, 8316 (1989).
10. T. Kakitani and N. Yoshimori and N. Mataga, *J. Phys. Chem.* **96**, 5385 (1992).
11. (a) H. Miyasaka, K. Kamada, K. Morita, T. Nagata, M. Kiri and N. Mataga, *Bull. Chem. Soc. Jpn.* **64**, 3229 (1991). (b) H. Miyasaka, T. Nagata, M. Kiri and N. Mataga, *J. Phys. Chem.* **96**, (1992), in press.
12. (a) N. Mataga, S. Nishikawa, T. Asahi and N. Mataga, *J. Phys. Chem.* **94**, 1443 (1990). (b) N. Mataga, *Pure & Appl. Chem.* **56**, 1255 (1984).
13. (a) T. Hayashi, T. Suzuki, N. Mataga, Y. Sakata and S. Misumi, *J. Phys. Chem.* **81**, 420 (1977). (b) N. Mataga, H. Yao and T. Okada, *Tetrahedron*, **45**, 4683 (1989). (c) H. Yao, T. Okada and N. Mataga, *J. Phys. Chem.* **93**, 7388 (1989).
14. (a) N. Mataga, H. Yao, T. Okada and W. Rettig, *J. Phys. Chem.* **93**, 3383 (1989). (b) T. Okada, S. Nishikawa, K. Kanaji and N. Mataga, *Ultrafast Phenomena VII*, C.B. Harris et al. (Eds.), Springer, Berlin, 1990, p.397. (c) N. Mataga, S. Nishikawa, T. Okada and W. Rettig, to be published.
15. (a) M. A. Kahlou, T.J. Kang and P.F. Barbara, *J. Phys. Chem.* **91**, 6452 (1987). (b) I. Rips, J. Klafter and J. Jortner, *J. Phys. Chem.* **94**, 9557 (1990).
16. (a) T. Asahi, M. Ohkohchi, N. Mataga, R. P. Zhang, A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, submitted. (b) T. Asahi, M. Ohkohchi, R. Matsusaka, N. Mataga, R. P. Zhang, A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, submitted.
17. Y. Enomoto, T. Kakitani, A. Yoshimori and Y. Hatano, *Chem. Phys. Lett.* **178**, 235 (1991).