

Observation of Structural Change upon Photoinduced Electron Transfer of 9-Mesityl-10-methylacridinium Ion by Pump-Probe X-Ray Crystal Structure Analysis

The molecular structure of 9-mesityl-10-methylacridinium ion (Acr^+-Mes) at the photoinduced electron-transfer (ET) state was determined by pump-probe single crystal X-ray structure analysis. Precise crystallographic analysis of the photoinduced structural change of $[\text{Acr}^+-\text{Mes}]\text{ClO}_4^-$ clearly indicated the bending of the *N*-methyl group by reduction of Acr^+ and the movement of the counter anion, ClO_4^- , by the electrostatic attraction from the oxidized Mes. This allowed the ET state of Acr^+-Mes to be established with its three-dimensional structural features for the first time.

The utilization of sunlight as a renewable and clean energy source by an artificial photosynthetic system is a promising way to solve global energy problems. Many photosynthetic reaction center model compounds have been developed as donor-acceptor linked and supramolecular systems based on the crystal structure of the photosynthetic reaction center. However, crystallographic determination of the photoinduced structural change of these compounds remains a formidable challenge. In this study, we determined the structural change upon photoinduced electron transfer in a simple donor-acceptor-like dyad as a photosynthetic reaction center model compound, Acr^+-Mes , for the first time by pump-probe single crystal X-ray structure analysis [1].

Acr^+-Mes is designed to mimic the charge separation in the natural photosynthesis reaction center [2]. The electron donor (Mes) and acceptor (Acr^+) are directly connected by a covalent bond. There is no π conjugation between them because the dihedral angle between them is approximately perpendicular. The photoinduced ET state of Acr^+-Mes ($\text{Acr}^+-\text{Mes}^{*+}$) is generated via the singlet excited state of the Acr^+ moiety by visible light irradiation [Fig. 1(a)]. The energy of the ET state lies deep within the Marcus-inverted region, so its lifetime is significantly long (e.g., 2 h at 203 K) [1]. Furthermore, $\text{Acr}^+-\text{Mes}^{*+}$ also has very high energy (2.37 eV), which is useful in photocatalyzed reactions [3, 4].

The structural change of Acr^+-Mes by ET was determined by pump-probe single crystal X-ray structure analysis. A femtosecond laser was used as an excitation light source. The laser pulse and the X-ray pulses were synchronized at a frequency of 946 Hz [5]. The single crystal of $[\text{Acr}^+-\text{Mes}]\text{ClO}_4^-$ was cooled at 90 K by a cold nitrogen stream. Photoinduced bending of the *N*-methyl group in Acr^+-Mes and movement of ClO_4^- with its rotation were observed in the Fourier map using the

difference of the observed structural factors in the light-on and -off stages [$F_{\alpha(\text{on})} - F_{\alpha(\text{off})}$] as a coefficient [Fig. 1(b)].

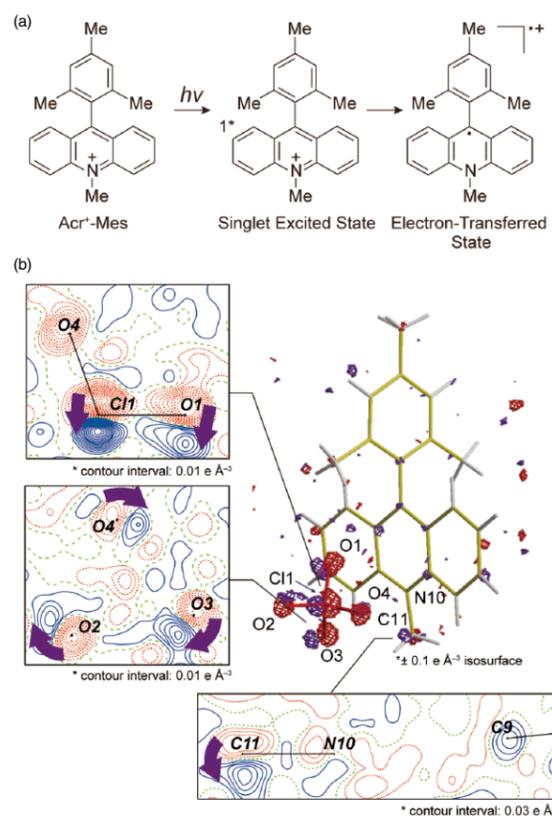


Figure 1 (a) Generation process of photoinduced electron-transfer state of Acr^+-Mes . (b) The $F_{\alpha(\text{on})} - F_{\alpha(\text{off})}$ difference Fourier map of $[\text{Acr}^+-\text{Mes}]\text{ClO}_4^-$. Blue and red contours (isosurfaces) represent negative and positive electron density in the 2D (3D) map. Blue bold arrows indicate the structural change upon photoinduced electron transfer.

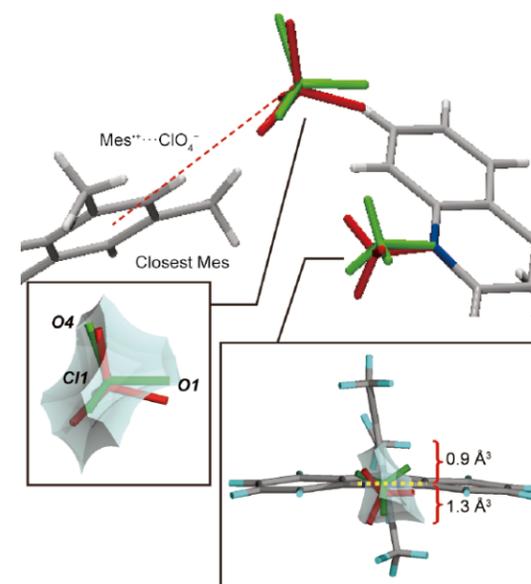


Figure 2 The photoinduced cooperative geometrical rearrangement in $[\text{Acr}^+-\text{Mes}]\text{ClO}_4^-$. Green and red fragments indicate the ground and photoinduced electron-transfer state geometries. The suggested electrostatic interaction between the oxidized Mes and ClO_4^- is indicated by the red dashed line. The reaction cavities around the *N*-methyl group and ClO_4^- are shown as a greenish-blue area in insets. The volumes of the divided cavity formed by the yellow dotted line are added on the side of it.

The photoinduced bending of the *N*-methyl group clearly indicates the reduction of Acr^+ by ET, because the sp^3 hybrid orbital character of the nitrogen atom is enhanced by reduction. Indeed, natural population analysis by theoretical calculation showed that the lone pair orbital of the nitrogen atom is filled by reduction. The reaction cavity drawing, which indicates the free space for an atom and a functional group to move in a crystal [6], shows that the direction of the photoinduced bending of the *N*-methyl group was toward the larger (i.e., sterically favorable) space (Fig. 2).

Oxidation of Mes by ET was reflected by the photoinduced movement of the counter anion, ClO_4^- . ClO_4^- moves toward the closest Mes in the crystal (Fig. 2), showing that ClO_4^- was attracted by the electrostatic interaction between the oxidized Mes and ClO_4^- ($\text{Mes}^{*+}\cdots\text{ClO}_4^-$). The reaction cavity around ClO_4^- indicates that one of the oxygen atoms in ClO_4^- (O1) moved

out of the reaction cavity (Fig. 2). This sterically unfavorable geometrical change is due to the cooperative geometrical rearrangement in the crystal; the bending of the *N*-methyl group enlarged the space for the movement of O1, and ClO_4^- moved and filled that space by the $\text{Mes}^{*+}\cdots\text{ClO}_4^-$ electrostatic interaction. This cooperative geometrical rearrangement suggests the generation of domains of $\text{Acr}^+-\text{Mes}^{*+}$ (ClO_4^-). Domain generation indicates that the intramolecular back-ET is so slow that intermolecular back-ET becomes a dominant deactivation process.

Additionally, there was no intramolecular twisting between Acr^+ and Mes in the generation of the ET state, indicating that intramolecular back-ET by electronic coupling between Acr^+ and Mes^{*+} is restricted in the ET state.

In conclusion, the structural features of $\text{Acr}^+-\text{Mes}^{*+}$ were determined by pump-probe single crystal X-ray structure analysis, definitively proving the formation of a long-lived ET state. This work provides a solid basis for developing efficient artificial photosynthetic systems.

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M. Hoshino^{1,2}, H. Uekusa¹, A. Tomita¹, S. Koshihara^{1,2}, T. Sato³, S. Nozawa³, S. Adachi³, K. Ohkubo^{4,5}, H. Kotani^{4,5}, S. Fukuzumi^{4,5,6} (¹Tokyo Inst. of Tech., ²JST-CREST, ³KEK-PF, ⁴Osaka Univ., ⁵JST-ALCA, ⁶Ewha Womans Univ.)