

Excitation wavelength effect on the fluorescence of 1,3,5-Trimethoxybenzene (TMB)-Tetracyanoethene (TCNE) CT-complex

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Charge recombination dynamics of excited charge transfer (CT) complexes of electron donor (D) and acceptor (A) has been of interests of ultrafast spectroscopy. Fluorescence from CT complexes has accepted growing attention as techniques in steady-state and time-resolved emission spectroscopies has been remarkably developed by the improvement in the sensitivity and time-resolution.^[1] According to the Mulliken theory, excitation of CT complexes give an electronic state bearing mainly a character of a contact radical ion pair ($[D^{\bullet+}/A^{\bullet-}]$) and small portion of a ground state molecular complex ($[A/D]$).^[2] However, we could expand the theory by increasing the basis wavefunction terms including excited radical ion pairs such as $[D^{\bullet+*}/A^{\bullet-}]$ to describe *the excited CT complex as an electronic wave packet*. This suggests a possibility for observing a fluorescence from excited radical ions, which are commonly recognized as non-fluorescent chemical species. We have reported an observation of radical cation fluorescence from a polar CT complex of hexamethoxybenzene (HMB) and $NO^+BF_4^-$ upon the one-photonic excitation.^[3]

We now report a novel fluorescence behavior of a CT complex of tetracyanoethene (TCNE) and 1,3,5-trimethoxybenzene (TMB) in solution upon selective laser excitation to the S_2 or S_3 state at 308 or 514 nm showing different spectrum similar to that observed for excited TMB radical cation ($TMB^{\bullet+*}$) species of free $TMB^{\bullet+*}$ in solution^[4] or $TMB^{\bullet+*}$ in 77 K matrix,^[5] respectively (Fig. 1). The excitation at the intermediate wavelength of 355 nm gave both of them. This indicates independent pathways of the radiative $S_2 \rightarrow S_0$ and $S_3 \rightarrow S_0$ transitions and the S_3 state does not relax to the S_2 state. Since the spectral difference of $TMB^{\bullet+}$ fluorescence originates from the absence and the presence of the Jahn-Teller distortion due to the degeneracy of the HOMO level two π -orbitals of TMB, the observed spectral features of the radiative $S_2 \rightarrow S_0$ and $S_3 \rightarrow S_0$ transitions can be attributed to different pathways of the $D_2 \rightarrow D_0$ transitions affording a Jahn-Teller distorted and an intact

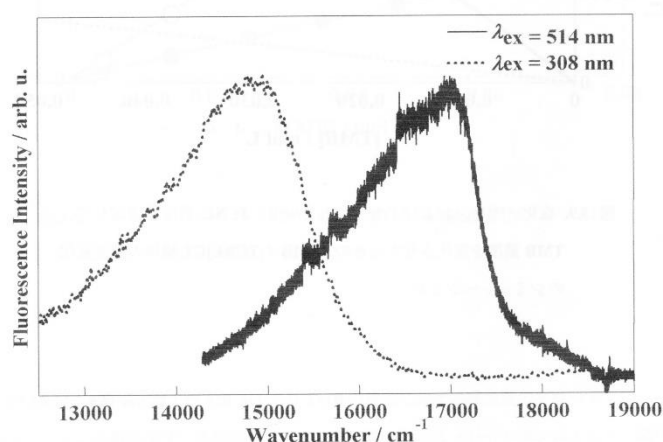


Figure 1. Fluorescence spectra of TMB-TCNE CT-complex in acetonitrile obtained by the excitation at 308 and 514 nm.

TMB \bullet^+ (TMB_{JT} \bullet^+ and TMB_{intact} \bullet^+), respectively.

We have also observed a short-lived transient species and long-lived radical ion species with the lifetime of ≈ 17 and ≈ 400 ps (Figs 2 and 3), respectively, by femtosecond laser flash photolysis of the CT complex in acetonitrile upon excitation at 400 nm corresponding to the $S_2 \leftarrow S_0$ transition. Transient species observed around 700 nm and 600 nm have been assigned to the excited state CT-complex and a radical ion TMB \bullet^+ . The short lifetime (τ) of 17 ps (≈ 700 nm) and the fluorescence quantum yield ($\Phi_f = 1.7 \times 10^{-4}$) gave a radiative rate constant (k_f) for the S_2 state to be $k_f \approx 10^7 \text{ s}^{-1}$ which is in good accordance with that of TMB_{JT} \bullet^+ and not that estimated from the CT absorption. This also supports the one-photon formation of TMB \bullet^{+*} (D_2 state) although the excitation to the S_2 state is corresponding to the first excited state of a contact radical ion pair [TMB \bullet^{+*} (D_1 state)/TCNE \bullet^-]. The electronic wave packet will explain the fluorescence from the S_2 state. Since the fluorescence from the radiative $S_3 \leftarrow S_1$ transition and the electronic character of the S_1 state has mostly a ground state contact radical ion pair [TMB \bullet^+ (D_0 state)/TCNE \bullet^-] (≈ 600 nm), the electronic character of the S_3 state should have an excited contact radical ion pair [TMB \bullet^{+*} (D_2 state)/TCNE \bullet^-]. The absence of the Jahn-Teller distortion in the S_3 state requires a direct promotion of an electron from the non-degenerate π -orbital of TMB to the LUMO of TCNE within the CT complex giving TMB_{intact} \bullet^{+*} which emits the fluorescence without incorporation of the Jahn-Teller active state.

It is concluded that the excited radical cation character in the S_2 and S_3 excited states of the CT complex was extracted by the use of TMB \bullet^+ as a “fluorescent radical cation probe,” even though the excited states have electronic wave-packet characters.

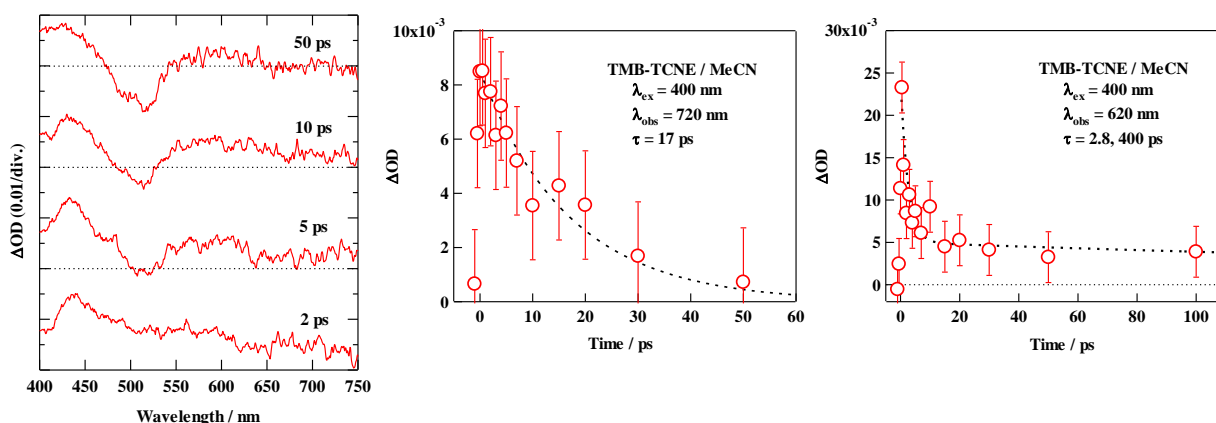


Figure 2. Transient absorption spectra of TMB/TCNE in MeCN observed after the excitation at 400 nm (left).
Figure 3. Decay curves monitored at 720 nm (center) and 620 nm (right).

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