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Emissive Triplex Formation in a Methylene-Bridged A-D-D' System. Intramolecular Long-Range Electron Transfer[1]

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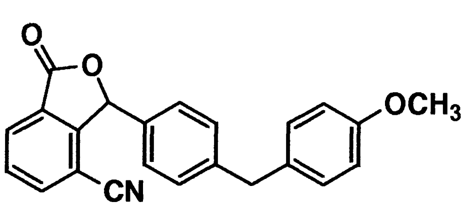
Methylene-bridged trichromophoric **A-D-D'** reveals only triplex emission at longer wavelength than bichromophoric **A-D'** and **A-D**, providing a model for long-range emissive and nonemissive electron transfer between **A** and **D'** through π spacer **D**.

Excited termolecular complexes (triplexes)[2] are supposed to play key roles in photochemistry involving excited-state termolecular interactions.[3-5] Either formation or decay of charge-separated triplexes is a typical electron transfer process under termolecular interactions,[6] which can be considered to be a useful prototype for electron transfer in multi-chromophoric synthetic and biological molecular assemblies. In particular, emissive triplex systems consisting of three different chromophores (*e.g.* **A**, **D**, and **D'** or **A**, **A'**, and **D**) are interesting, since the triplex emissions can be effectively used as mechanistic and kinetic probe for long-range electron transfer through a π spacer. However, there has appeared only a few precedents of such emissive triplexes,[7] while interesting works have been performed on some σ-bridged **A-D-D**[8] and nonemissive **A-D-D'**[9] systems. We wish to report here a preliminary result on photophysical behavior of the emissive charge-separated triplex state of methylene-bridged trichromophoric **A-D-D'** molecule **1.**[10]



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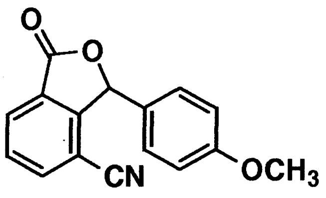

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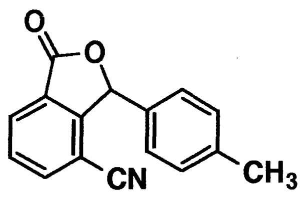

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The absorption spectrum of **1** is essentially identical with the sum of each spectrum of cyanobenzo-γ-butyro-lactone, *p*-xylene, or 4-methylanisole, revealing no new absorption at longer wavelength. This is again true for bichromophoric **A-D'** **2** and **A-D** **3**. Selective photoexcitation of these compounds at the absorption edge of the lactone chromophore (300 nm) commonly gave structureless broad emissions with large Stokes shifts (Fig. 1), which are highly dependent on solvent polarity (Table 1). The emission of **1** appeared at considerably longer wavelength than that of either **2** or **3**, demonstrating that the emitting species of **1** should be a *triplex* of high charge-transfer character. The solvent-dependent emission maxima (ν/cm^{-1}) of **1**, **2**, and **3** showed linear correlations with solvent polarity parameter f(ε,n) following Eq. 1. Table 1 summarizes the emission characteristics, the slopes ($-2\mu_{ex}^2/hc\rho^3$) of the linear correlations, and the calculated excited-state dipole moment (μ_{ex}).[11]

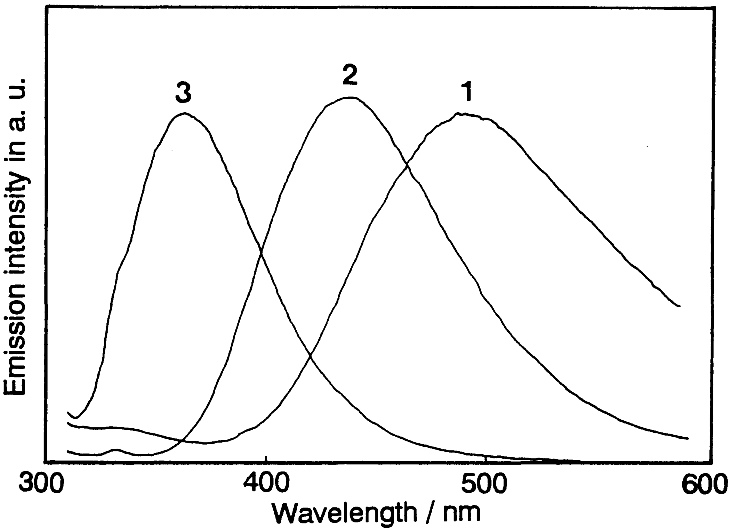


Fig. 1. Emission spectra of **1**, **2** and **3** in CH_2Cl_2; [**1**], [**2**],and [**3**] = 4.0 x 10^{-4} mol dm^{-3}. The spectra were recorded by excitation at 300 nm after correction for the spectral responce of the instrument.

$$\nu = \nu_0 - (2\mu_{ex}^2/hc\rho^3)\cdot f(\varepsilon,n) \qquad (1)$$
$$f(\varepsilon,n) = (\varepsilon - 1)/(2\varepsilon - 1)-(n^2 - 1)/(4n^2 + 2)$$

In all the cases, the slopes of Eq. 1 are commonly very large, indicating that charge separation of the emitting species should be virtually complete, *i.e.* $[\mathbf{A}^-\text{-}\mathbf{D}\text{-}\mathbf{D}'^+]^*$, $[\mathbf{A}^-\text{-}\mathbf{D}'^+]^*$, and $[\mathbf{A}^-\text{-}\mathbf{D}^+]^*$. Since **1** shows the emission at longer wavelength than **2**, the triplex state of **1** might be stabilized by larger solvation of the spacer-separated charges and/or by a contribution of charge resonance between **D** and **D'**, *i.e.* $\mathbf{D}^{\delta+}\text{-}\mathbf{D}'^{(1-\delta)+}$.

Notably, fluorescence measurements at 180 K - 373 K failed to detect a new emission attributable to $[\mathbf{A}^-\text{-}\mathbf{D}^+]^*\text{-}\mathbf{D}'$, but only the $[\mathbf{A}^-\text{-}\mathbf{D}\text{-}\mathbf{D}'^+]^*$ emission appeared in quantum yields comparable with those of **2** and **3**. This can be attributed to very rapid electron exchange between $\mathbf{D}^+$ and **D'** following electron transfer from **D** to $^1\mathbf{A}^*$ or to direct electron transfer between $^1\mathbf{A}^*$ and **D'** through **D** by a superexchange mechanism[12] or through

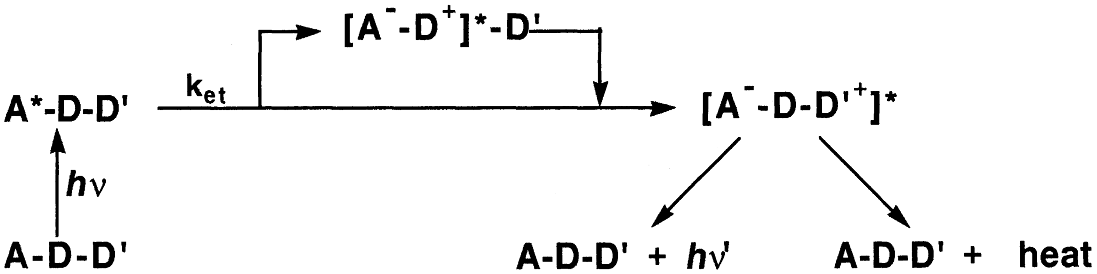
Table 1. Properties of Intramolecular Triplex and Exiplex Emissions

Solvents	(f(ε, n))	λ_{max} a) / nm (ϕ_f b)) (τ c) / ns) 1	 2	 3
n-Butyl ether	(0.192)	410 (0.010) (5.8)	388 (0.014) (1.3)	d)
Isopropyl ether	(0.237)	423 (0.018) (14)	393 (0.010) (1.5)	d)
Ethyl ether	(0.256)	436 (0.024) (22)	407 (0.012) (1.9)	342 (0.029) (0.58)
Ethyl acetate	(0.293)	487 (0.009) (111)	448 (0.024) (12)	372 (0.014) (1.1)
Tetrahydrofuran	(0.309)	495 (0.025) (203)	448 (0.034) (14 e))	379 (0.011) (1.1)
Dichloromethane	(0.320)	490 (0.021) (161)	438 (0.026) (7.3 e))	364 (0.016) (0.93)
tert-Butyl alcohol	(0.339)	524 (0.002) (14)	472 (0.003) (19)	381 (0.007) (0.98)
$-2\mu_{ex}^2 / hc\rho^3 / 10^3$ cm^{-1}		37.8	28.2	26.3
μ_{ex} (calcd) / D		57	17	16

a) Emission maxima; ± 3 nm . b) Emission quantum yields. c) Emission lifetimes; ± 0.5 ns .
d) No emission was observed. e) Another lifetime component was observed.

space. Through-space electron transfer is unlikely to occur, since **1** can not take folded conformations that would allow close contact between **A** and **D'**. At any rate, spacer **D** seems to mediate rapid electron transfer between ^{1}**A*** and **D'**. In contrast, the emission lifetimes of **1** are longer by an order of magnitude than those of **2**, probably due to larger spatial separation between **A**$^-$ and **D'**$^+$. Therefore, it is suggested that π spacer **D** might not act as a "passage" for the long-range back electron transfer *via* either the radiative or nonradiative pathway.[13]

Further discussions require comparisons with electron transfer through a σ spacer of size similar to that of **D** and variation of **D** and **D'** and, more generally, effects of energy gap, distance, and geometry on photodynamic behavior of triplexes. Works in this line are in progress.



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10) Lactones **1** - **3** were prepared by reaction of 2-lithio-di(N-tert-butyl)-isophtalamide with the corresponding aryl aldehydes followed by dehydration with $POCl_3$ or $SOCl_2$ and were purified by repeated re-crystallization. The structures were fully confirmed by spectroscopic and elemental analysis.

11) The values of μ_{ex} were calculated from the slopes in Eq. 1 by assuming the effective radius of solvent cavity (ρ) as 9.5 Å for **1** and 4.7 Å for **2** and **3**. The parameters in Eq. 1 are as follows: ν_0, the emission maxima in vacuum; *h*, Plank's constant; c, the velocity of light; ε, dielectric constant of solvent; n, refractive index of solvent.

12) J. L. Sessler, M. R. Johnson, and T. Y. Lin, *Tetrahedron*, **45**, 4767 (1989); D. Gust and T. A. Moore, *Science*, **244**, 35 (1989).

13) A drastic decrease in the radiative electron-transfer rate constant (ϕ_f/τ) of **1** occurs upon changing solvent from ethyl ether to ethyl acetate, suggesting solvent-induced changes in the electronic structure and/or stable conformations of the triplex state. Detailed will be discussed in a full paper together with other triplex formation systems.

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