

Efficient S₁-S₁ Radiationless Energy Transfer in Solid Cyclohexane and 1,4-Dioxane Solutions at Unusually Low Concentration

Toshiki Mutai and Koji Araki*

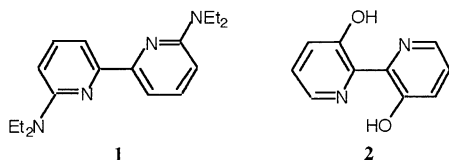
Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106

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Singlet-singlet radiationless energy transfer between 6,6'-bis(diethylamino)-2,2'-bipyridine (**1**) and 3,3'-dihydroxy-2,2'-bipyridine (**2**) was observed at unusually low concentration (3×10^{-5} mol dm⁻³ of **1** with 10 mol% of **2**) only in solid solutions of cyclohexane and 1,4-dioxane but not of methylcyclohexane, cyclohexanol, hexane, 3-methylpentane, cyclopentane, and tetrahydrofuran.

Singlet-singlet (S₁-S₁) radiationless intermolecular energy transfer (ET) is one of the important processes from photoexcited state, and its mechanism has been studied for decades from physicochemical interest and also because of importance of this process in biological, photochemical, and opto-electronics fields. Critical distance (R₀) that this process operates is the essential parameter for characterizing the process, and has been reported for various systems such as organic single crystals,¹ polymers,² liquid crystals,³ self-assembled layers,⁴ flavin photoenzyme,⁵ and light harvesting system.⁶ The R₀ values are within 5 nm. In frozen solution, ET had been observed only in highly concentrated ($\sim 10^{-2}$ mol dm⁻³) solution.

We report here ET from 6,6'-bis(diethylamino)-2,2'-bipyridine (**1**) to 3,3'-dihydroxy-2,2'-bipyridine (**2**) at very low concentration ($\sim 10^{-5}$ mol dm⁻³). It was only observed in frozen cyclohexane and 1,4-dioxane solutions.



The compounds **1**⁷ and **2**⁸ exhibited a typical fluorescence at 394 nm (blue) and 498 nm (green), respectively, from the lowest singlet excited state (S₁) in fluid hexane or cyclohexane at 20 °C (Figure 1a, Table 1). Absorbance and fluorescence intensity of **1** and **2** were linearly dependent on their concentration up to 1.0×10^{-4} mol dm⁻³, showing that there was no self-association in fluid state. Dissolved oxygen in the solvents only slightly affected the fluorescence intensity. In frozen state⁹ at -196 °C in hexane (mp -95 °C), and -15, -78 and -196 °C in cyclohexane (mp 6 °C), fluorescence spectra of **1** or

2 alone were not largely different from those at room temperature (Table 1).

For the solution of the mixture of **1** (3.0×10^{-5} mol dm⁻³) + **2** (10 mol%), absorption spectrum was the summation of that of **1** and **2**, indicating absence of the intermolecular interaction between **1** and **2** at ground state in fluid solutions. When the solution was excited at 285 nm, at which contribution of **2** to the total absorbance was only 0.04, fluorescence of the **1** (3.0×10^{-5} mol dm⁻³) + **2** (10 mol%) mixture was predominantly from **1** in fluid cyclohexane and hexane. In frozen hexane, fluorescence from **1** was also dominant (Figure 1b), and excitation spectrum monitored at 550 nm was identical to that of **2**, showing no ET from **1** to **2**.

In frozen cyclohexane at -15 °C, however, intensity of the fluorescence from **1** (397 nm, blue) decreased and that from **2** (484 nm, green) became apparent (Figure 1b). The green fluorescence further increased as the sample was cooled down to -78 and -196 °C (Figure 1c). At -196 °C, fluorescence at 484 nm was five times larger compared to that from **2** alone. Higher concentration of **2** caused larger quenching of the blue fluorescence (Figure 1d). The edge of the fluorescence of **1** and the absorption tail of **2** is overlapping in between 370-410 nm,

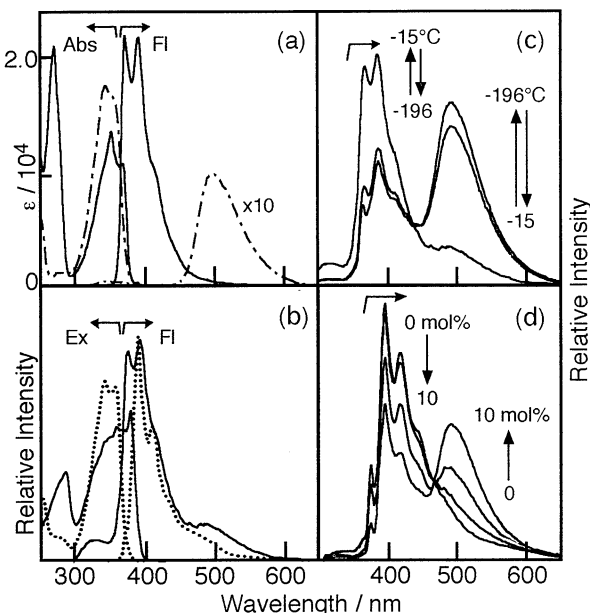


Figure 1. Electronic spectra of **1** and **2** in cyclohexane. Concentration of **1** was 3.0×10^{-5} mol dm⁻³. Excitation wavelength was 285 nm. (a) Absorption (at 20 °C) and fluorescence spectra (at room temperature) of **1** (—), and **2** (3.0×10^{-6} mol dm⁻³; - - -). (b) Fluorescence and excitation spectra ($\lambda_{\text{em}}=550$ nm) of **1+2** (10 mol%) in cyclohexane (—) at -15 °C, and in hexane (•••••) at -196 °C. (c) Fluorescence spectra of **1+2** (10 mol%) in solid cyclohexane at -15, -78, and -196 °C. (d) Fluorescence spectra of **1+2** (0–10 mol%) in solid cyclohexane at -196 °C.

Table 1. Absorption and fluorescence maxima of **1** and **2**

Compound	Solvent	Absorption		Fluorescence			
		20 °C		R.T. ^a	-195 °C		
		λ /nm	λ /nm (Φ^b)	τ /ns	λ /nm	τ /ns	
1	Cyclohexane	352	394 (0.50)	1.4	398	4.3	
	Hexane	351	393 (0.56)	1.3	399	2.7	
2	Cyclohexane	345	498 (0.19)	1.0	484	2.4	
	Hexane	345	498 (0.21)	1.7	484	2.2	

^a Measured at room temperature. ^b Relative fluorescence quantum yield was obtained by using 2-aminopyridine as a standard (in ethanol, excitation at 285 nm, $\Phi=0.37$).

and excitation spectrum monitored at 550 nm corresponds to the absorption of **1** and **2** (Figure 1b). Therefore, increase of the green fluorescence and quenching of the blue fluorescence is ascribed to the ET from excited **1** to **2**.

Repeated temperature cycles between -15 and -196 °C confirmed temperature dependence of the ratio of the blue and green fluorescence, which was reproducible within an error of 10%. Therefore, the ET efficiency from **1** to **2** was temperature dependent and lower temperature enhances the ET from **1** to **2**. The green fluorescence of the **1**+**2** (10 mol%) mixture in frozen cyclohexane was slightly reduced by addition of 0.1 vol% of hexane but was dramatically suppressed by the presence of 1 vol% of hexane. Temperature dependence and such distinctive solvent dependence of the ET process can hardly be expected for the radiative ET process. Thus, it is concluded that the S₁-S₁ radiationless rather than "trivial" or radiative ET process is responsible for the green fluorescence. Though the S₁-S₁ radiationless ET generally requires much higher concentration, the results showed that the efficient ET from excited **1** to **2** does take place at unusually low concentration in solid cyclohexane.

Similar ET-induced green fluorescence of the **1**+**2** (10 mol%) mixture was also observed in 1,4-dioxane (mp 12 °C) in solid state but not in fluid state. No green fluorescence was observed in solid solutions of other solvents tested at -196 °C; i.e., methylcyclohexane (mp -126 °C), cyclohexanol (mp 20-22 °C), hexane, 3-methylpentane (mp -118 °C), cyclopentane (mp -94 °C), and tetrahydrofuran (mp -108 °C).

Obviously, polarity of the solvent is not the determining factor of the ET process. Though melting points of cyclohexane and 1,4-dioxane are relatively high, cyclohexanol was ineffective as a solid matrix for the ET process. Only in the solid solutions of cyclohexane and 1,4-dioxane that have purely hexagonal structure, the ET at unusually low concentration was observed.¹⁰

To understand the efficient S₁-S₁ radiationless ET in solid state at unusually low concentration, we estimated the radius of the quenching sphere (R_s) of **1** according to the Perrin model.^{11,12} Assuming homogeneous distribution of the substrates in the solid solutions, R_s of **1** at -196 °C for each concentration of **2** (0-10 mol%) were calculated to be 42.5±4.1 (SD) nm (n=9)¹³ in cyclohexane, which is an order of magnitude larger than the reported values.¹⁴

Heterogeneous distribution may be responsible for the apparent large R_s value. Association of **1** and **2** can be the reason for the heterogeneous distribution. However, no sign of association was observed in fluid hexane and cyclohexane. It is unlikely that **1** and **2** form the complex or exciplex *only* in frozen cyclohexane but not in frozen hexane. Indeed, no absorption spectral change was observed for the **1**+**2** mixture in fluid and frozen cyclohexane.

Another possible cause is a condensation effect due to exclusion of the substrates from microcrystalline region of cyclohexane. Condensation of **1** and **2** in amorphous or inter-crystalline region of cyclohexane might decrease distance between **1** and **2** short enough for energy transfer. However, this condensation effect should be equally applicable to the frozen cyclohexane at -15 and -196 °C in the absence of diffusion, and observed marked temperature dependence of the ET process cannot be explained by this effect. Moreover, quenching of the blue fluorescence was observed in frozen cyclohexane containing 0.1 vol% of hexane, in which the concentration of **1** (3.0×10⁻⁵ mol dm⁻³) could become 10³ times

higher by assuming that the solutes were totally excluded from the frozen cyclohexane region. However, higher concentration (10³ times) of **1** (3.0×10⁻² mol dm⁻³) with **2** (5 mol%) in frozen hexane showed no quenching of the blue fluorescence at all.

Thus, the observed green fluorescence in solid solution at low concentration cannot be interpreted simply from the association of **1** and **2** or condensation effect by exclusion from crystalline cyclohexane.

Since effective distance of electron exchange process (Dexter type) or dipole-dipole interaction (Förster type) is up to 0.5 nm and 10 nm, respectively, these ET models cannot apply to this anomalous ET process. There were reports on the energy migration process¹⁴ that ET distance of 50 nm through chromophores aggregated on surface of layer¹⁵ and up to 40 nm in organic single crystals¹⁶ were observed. In our system, however, the energy migration process is not operative because cyclohexane or 1,4-dioxane has no favorable energy levels to mediate the S₁-S₁ excitation energy transfer from **1** to **2**. To our best knowledge, this is the first to report the anomalous ET process at unusually low concentration of the substrates. Because relatively few has been known as to the properties and role of frozen matrices, more has to be studied in order to understand the anomalous ET process. Since it was observed only in purely hexagonal solvents, crystal field of the frozen solvent may play some role on this energy transfer.

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References and Notes

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- 8 H. Bulska, *Chem. Phys. Lett.*, **98**, 398 (1983); J. Sepiol, H. Bulska, and A. Grabowska, *Chem. Phys. Lett.*, **140**, 607 (1987).
- 9 Fluorescence spectra of **1**, **2**, and **1**+**2** (10 mol%) were measured using a quartz tube (5 mm diameter) at room temperature, -15, -78, or -196 °C.
- 10 Similar quenching of the blue fluorescence was observed at -196 °C in benzene but not in toluene. However, increase of the green fluorescence was not so apparent.
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- 12 Quenching sphere around excited donor (D*) was calculated from the equation, $\ln(\Phi_0/\Phi_d) = VN[A]$, where Φ_0 and Φ_d are the quantum yields of donor fluorescence in the absence and presence of the acceptor, respectively, V is the effective quenching sphere volume of donor, N is Avogadro's number, and [A] is the concentration of the acceptor. Radius of the quenching sphere (R_s) is then obtained as $R_s = (3/4\pi N)^{1/3}$. Because Φ could not be determined in frozen state, the relative intensity of the fluorescence was used instead.
- 13 The values of R_s at -196 °C were determined for **1**+**2** (0, 1, 3, 5, 10 mol%), **1**+**2** (10 mol%) after temperature cycle, and **1** (3.0×10⁻⁵, 10⁻⁶, 10⁻⁷ mol dm⁻³) + **2** (10 mol%).
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