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Charge transfer from donor to photoexcited Ru(bpy)$_3^{2+}$ in solution and polymer matrix

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Abstract

Electron transfer quenching of photoexcited Ru(bpy)$_3^{2+}$ (bpy, bipyridine) by three kinds of hole transport material, phenothiazine (PTZ) and 10-methylphenothiazine (MPTZ) was studied in acetonitrile solution and a polymer film. The quenching rate constants (k_q) with respect to ΔG in acetonitrile solution are discussed in terms of Marcus theory. In poly(ethyleneoxide) (PEO) films, quenching of photoexcited Ru(bpy)$_3^{2+}$ was observed and analysed by a static quenching model. The electron transfer distance in the polymer film was found to be 1.1–1.9 nm using a modified Perrin equation considering the excluded volume effect. The dependence of the electron transfer rate on ΔG in the PEO film was larger than that in acetonitrile solution.

Keywords: Charge transfer; Photoexcited Ru(bpy)$_3^2$; Polymer matrix

1. Introduction

In the past 15 years, Ru(bpy)$_3^{2+}$ (bpy, bipyridine) has attracted considerable interest as a photocatalyst for water decomposition by visible light [1–9]. In particular, many hydrogen evolving systems containing Ru(bpy)$_3^{2+}$ have been investigated using sacrificial donors such as ethylenediaminetetraacetic acid (EDTA) or triethanolamine (TEA) [2–9]. These donors are not reversible and cannot act as hole transport molecules. A large number of hole transport materials behave as reversible redox molecules in organic photoconductors used in photocopiers, laser beam printers, etc. Such hole transport materials can also be used for hole transport in photochemical processes, but few reports have investigated the use of such hole transport materials as hole mediators or electron donors for photoexcited Ru(bpy)$_3^{2+}$.

The use of a polymer membrane is a promising approach for the establishment of photoenergy conversion systems [10]. Polymeric materials have many merits for practical applications in the fabrication of devices. Indeed, many organic photoconductor systems consist of photoconducting molecules dispersed in a polymer film.

In this paper, the photoinduced reaction between hole transport materials and Ru(bpy)$_3^{2+}$ was investigated in solution and polymer films. Ru(bpy)$_3^{2+}$ is a photoluminescent probe, providing information on the electron transfer rate [2,8,9,11,12], distance for charge hopping [13–15], acceptor concentration [16–18], etc. The electron transfer quenching of photoexcited Ru(bpy)$_3^{2+}$ by various hole transport materials, including phenothiazines, was studied in solution; the photoinduced electron transfer in a poly(ethyleneoxide) (PEO) film was also investigated to obtain the electron transfer distance and rate associated with the redox potentials of the hole transport materials and Ru(bpy)$_3^{2+}$.

2. Experimental details

2.1. Materials and film preparation

The complex [Ru(bpy)$_3$]Cl$_2\cdot$6H$_2$O [19] and hole transport materials, 2-methyl-4-(*N,N*-dibenzylamino)-benzaldehyde-*N*-2-benzothiazolyl-*N*-*n*-butylhydrazone (**1**), 1-(3-methylphenyl)-1,2,3,4-tetrahydroquinoline-6-carboxyaldehyde- 1′,1′-diphenylhydrazone (**2**) and 1,1-bis(*p*-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene (**3**) [20] (see Scheme 1), were prepared by the methods reported

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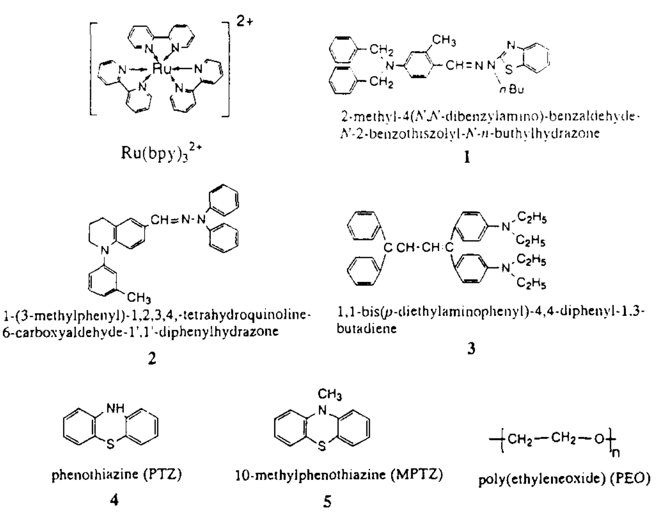


Scheme 1. Structures of hole transport materials (**1–3**) and phenothiazines (**4**, **5**).

earlier. $[Ru(bpy)_3](PF_6)_2$ was obtained from a mixture of $[Ru(bpy)_3]Cl_2$ and NH_4PF_6 aqueous solution, and was recrystallized from acetonitrile solution. Commercially available phenothiazine (**4**) (Tokyo Kasei Kogyo Co., Ltd.) and 10-methylphenothiazine (**5**) (Eastmann Kodak Co., Ltd.) were recrystallized from ethanol solutions. PEO ($M_W = 8.5 \times 10^3$) was purchased from Tokyo Kasei Kogyo Co., Ltd, and purified three times by reprecipitation with an *n*-hexane–methanol system. Acetonitrile was distilled over CaH_2. The PEO films containing 5×10^{-3} mol dm^{-3} of $[Ru(bpy)_3](PF_6)_2$ and 0–0.3 mol dm^{-3} of **1–5** were obtained from acetonitrile solution by a cast method using a Baker-type applicator (Tester Industry Co., Ltd.). After the solution had been cast on a glass plate, the films were allowed to dry under vacuum at 30 °C. The estimated thickness of the films was 1 μm calculated from the density of PEO (1.19 g cm^{-3}) [21].

2.2. Measurements

The visible absorption spectra were measured with a Hitachi spectrophotometer U-2000, and the emission spectra with a Hitachi fluorospectrophotometer F-2000. Emission decay was measured by a time-correlated single photon counting apparatus (Hitachi-Horiba NAES-1100) equipped with a 10 atm hydrogen lamp. In an acetonitrile solution system, the concentrations of $[Ru(bpy)_3](PF_6)_2$ and **1–5** were 5 μmol dm^{-3} and 0–1.2 mmol dm^{-3} respectively. For all measurements of the films, samples were placed at a diagonal position in the quartz cell and were irradiated by 500 nm monochromatic light at the front surface of the film. Emission was monitored through a cut-off filter (Toshiba O-58) from the back side of the glass plate at right angles to the excitation light beam to minimize the scattering effect. All photochemical measurements were carried out under argon at 25 °C.

Cyclic voltammograms of 1×10^{-3} mol dm^{-3} acetonitrile solutions containing compounds **1–5** and $[Ru(bpy)_3](PF_6)_2$ were obtained by a voltammetry controller (BAS Company CV-27) operated at a scan rate of 100 mV s^{-1}. All the electrochemical measurements were carried out under argon at ambient temperature with a supporting electrolyte of 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate. A glassy working carbon electrode, a Pt counterelectrode and a saturated calomel electrode (SCE) were used.

3. Results and discussion

Quenching of the emission from photoexcited $Ru(bpy)_3^{2+}$ ($Ru(bpy)_3^{2+*}$) by the hole transport materials and phenothiazines was studied in acetonitrile solution. The quenching rate constants (k_q) of $Ru(bpy)_3^{2+*}$ by **1–5** were estimated by measuring the emission intensities at various concentrations of **1–5** as well as the emission lifetimes of $Ru(bpy)_3^{2+*}$. The k_{SV} values were determined by conventional Stern–Volmer plots

$$I_0/I = 1 + k_{SV}[Q] \quad (k_{SV} = k_q\tau_0) \tag{1}$$

where I_0 and I are the emission intensities of $Ru(bpy)_3^{2+*}$ in the absence and presence of quencher respectively. The lifetime of $Ru(bpy)_3^{2+*}$ in acetonitrile solution in the absence of quencher (τ_0) was 8.0×10^{-7} s.

The electron transfer quenching process can be analysed on the basis of Scheme 2, which consists of the association of donor and acceptor, electron transfer and cage escape. From Scheme 2, the quenching rate constant (k_q) is expressed by

$$1/k_q = 1/k_q' + 1/k_a \tag{2}$$

where k'_q is the quenching rate constant corrected for diffusional effects [12]. Therefore

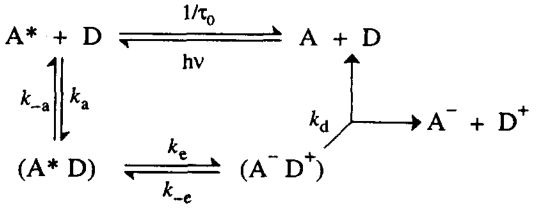
$$k_q' = k_e[k_a k_d / k_{-a}(k_d + k_{-e})] \tag{3}$$

In the present analysis, $k_a = 2.1 \times 10^{10}$ mol^{-1} dm^3 s^{-1} was used [12]. Table 1 summarizes the k_q and k'_q values.

Bock et al. [12] investigated the relation between the quenching rate constant and the free energy gap (ΔG) for electron transfer from aromatic amines to $Ru(bpy)_3^{2+*}$, and reported that it follows

$$RT \ln k_q' = RT \ln k_q'(0) - \Delta G/2(1 + \Delta G/2\lambda) \tag{4}$$

where $k'_q(0)$ and λ are the k'_q value for $\Delta G = 0$ and the reorganization energy respectively. Eq. (4) was derived from



Scheme 2. Electron transfer process from donor to excited acceptor: k_a, k_{-a}, k_e, k_{-e} and k_d are the rate constants for association between acceptor and donor, dissociation, electron transfer from donor to acceptor, recombination and cage escape respectively.

Table 1
Rate constants of electron transfer quenching of $Ru(bpy)_3^{2+}$ by donors in acetonitrile solution

Donor	k_q ($dm^3 mol^{-1} s^{-1}$)	k_q' ($dm^3 mol^{-1} s^{-1}$)	E_{ox} [a] (V)	ΔG (eV)
1	5.4×10^9	7.3×10^9	0.64	−0.17
2	7.0×10^9	1.1×10^{10}	0.54	−0.27
3	6.8×10^9	1.0×10^{10}	0.46	−0.35
4	4.2×10^9	5.3×10^9	0.60	−0.21
5	1.7×10^9	1.9×10^9	0.72	−0.09

[a] Vs. SCE.

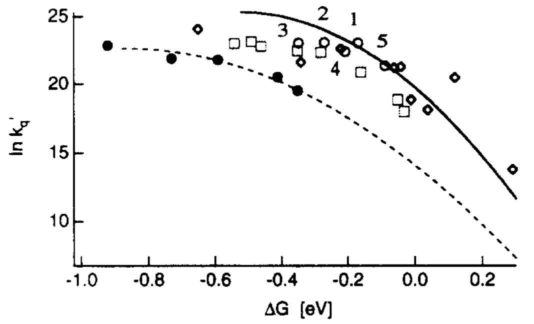


Fig. 1. ln k_q' vs. ΔG for the electron transfer quenching of $Ru(bpy)_3^{2+}$ by donors **1–5** in acetonitrile (full line) and dioxan (broken line) solution: ○, present experiment; □, ◇, ●, data in Refs. [11], [12] and [13].

Marcus theory when back electron transfer does not give the excited state, i.e. $k_{-e}=0$. ΔG was estimated from

$$\Delta G = -E[Ru(bpy)_3^{2+/+}] + E(Q^{+/0}) - E^* - e^2/\epsilon d \qquad (5)$$

where $E[Ru(bpy)_3^{2+/+}]$ and $E(Q^{+/0})$ are the redox potentials of $Ru(bpy)_3^{2+/+}$ and quencher respectively. In the electrochemical measurements in acetonitrile solution, all the donors showed reversible redox peaks, from which the $E(Q^{+/0})$ values were calculated as the halfwave potentials ($E_{1/2}$, see Table 1). E^* is the excited state energy of $Ru(bpy)_3^{2+}$, which was estimated from the emission wavelength at the emission maximum (600 nm) to be 2.1 eV. The term $-e^2/\epsilon d$ is the work term where ϵ and d are the dielectric constant of the solvent and the distance between the nuclei of the electron donor and acceptor respectively. ϵ is 38.8 [13] for acetonitrile and 5 [22] for PEO. The d value was estimated to be 1 nm [12]. The work terms were obtained to be −0.04 eV and −0.29 eV for the acetonitrile solution and PEO film respectively.

Fig. 1 shows the relation between lnk'_q and ΔG, where the open circles represent the present data and the other symbols are reported values [11–13]. The full line is based on Eq. (4), where $k'_q(0) = 8.8\times10^8$ $mol^{-1} dm^3 s^{-1}$ and $\lambda = 11$ kcal mol^{-1} (0.48 eV), reported for the aromatic amine–$Ru(bpy)_3^{2+*}$ systems [12]. The plots for the hole transport materials and phenothiazines (**1–5**) agree well with the curve reported for amines, so that we can assume that the present hole transport materials and phenothiazines behave like aromatic amines, i.e. as reductive quenchers for $Ru(bpy)_3^{2+*}$.

Table 2
Quenching radius and rate constants for electron transfer quenching of $Ru(bpy)_3^{2+}$ by donors in PEO film

Donor	a (nm)	b (nm)	c (nm)	s (nm)	R_0 (nm)	ΔG (eV)	$k(s)$ (s^{-1})
1	1.88	0.96	0.84	1.1	1.3	−0.42	3.6×10^6
2	1.67	1.00	1.00	1.1	1.5	−0.52	4.2×10^6
3	1.80	1.40	0.44	1.0	1.9	−0.60	6.5×10^7
4	1.02	0.66	0.45	0.83	1.3	−0.46	1.0×10^7
5	1.04	0.70	0.54	0.86	1.1	−0.34	3.4×10^6

The emission from $Ru(bpy)_3^{2+*}$ is also quenched in PEO film. Generally, quenching of doped molecules in solid systems, such as a polymer film, is caused by quencher molecules in the nearest neighbour position. In a film system containing dispersed molecules, the quenching behaviour can be analysed by the so-called Perrin model (Eq. (6)), which is derived from the statistical analysis of the distribution of dispersed quencher molecules [13–15,18,23]

$$I/I_0 = \exp(-k[Q]) \qquad (6)$$

When the excluded volume effect is taken into account, Eq. (6) is rewritten as follows [13,18]

$$\ln(I_0/I) = (V_0 - V_s)N_A[Q] \times 10^{-24} \qquad (7)$$

where V_0, V_s and N_A are the quenching sphere $V_0 = 4\pi R_0^3/3$ (nm^3), the excluded volume $V_s = 4\pi s^3/3$ (nm^3) of the Ru complex and the quencher and Avogadro's number respectively. The factor of 10^{-24} transforms the unit of length decimetres to nanometres. R_0 and s are the quenching sphere radius and the excluded sphere radius respectively.

In the present system, the excluded volume radius is the sum of the radii of $Ru(bpy)_3^{2+}$ and quencher. The radius of $Ru(bpy)_3^{2+}$ was obtained from crystallographic data as 0.41 nm [24]. The volume of the donor was estimated using a cuboid model whose length, width and thickness are a (nm), b (nm) and c (nm) respectively (Table 2). In order to estimate the contact distance with $Ru(bpy)_3^{2+}$, the shape of the donor was assumed to be a sphere whose volume is the same as the cuboid form (abc nm^3); the apparent sphere radius of the quencher was obtained by assuming that the sphere has

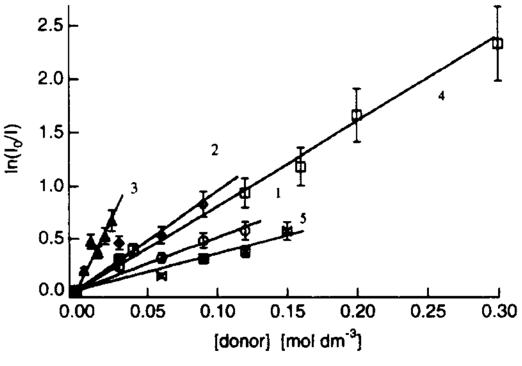


Fig. 2. Perrin plots for the quenching of photoexcited $Ru(bpy)_3^{2+}$ by donors **1–5** in PEO film.

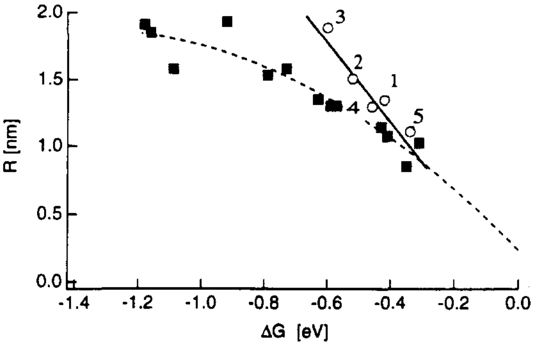


Fig. 3. Quenching radius R_0 vs. ΔG for the electron transfer quenching of $Ru(bpy)_3{}^{2+}$ by donors **1–5** in PEO film: full line, PEO film (present experiment); broken line, polycarbonate film [13].

the same volume as the quencher. The s values are shown in Table 2.

Fig. 2 shows the relation between the quencher concentration and the logarithm of the relative emission intensity according to Eq. (7). The plots show linear relationships, indicating that the present system can be analysed by Eq. (7). From the slope of Fig. 2 and Eq. (7), the R_0 values were obtained as 1.1–1.9 nm (Table 2). These R_0 values are the electron transfer distances between $Ru(bpy)_3{}^{2+*}$ and the quenchers. The electron transfer distances in Table 2 are close to those given for polycarbonate (0.65–1.88 nm) [13] and for electron transfer in proteins (e.g. 1.1–1.5 nm for photosystem 1 (PS 1)) [25]. The following order of R_0 was similar to that of k_q in acetonitrile solution: $\mathbf{5} < \mathbf{4} \approx \mathbf{1} < \mathbf{2} < \mathbf{3}$.

The R_0 vs. ΔG plots show a relation (Fig. 3) similar to that in acetonitrile solution (Fig. 1). Generally, the electron transfer rate constant $k(r)$ is represented by Eq. (8) as a function of the distance (r) between the donor and the photoexcitation centre

$$k(r) = 1/\tau_0 \exp[-\alpha(r - R_0)] \qquad (8)$$

where α is a damping factor [13]. The following relation between R_0 and ΔG is obtained when $k_q{}'$ in Eq. (4) is substituted for $k(r)$ in Eq. (8)

$$R_0 = \ln(\tau_0)/\alpha + A - \Delta G/2\alpha(1 + \Delta G/2\lambda) \qquad (9)$$

where A is a constant equal to $[RT/\alpha \ln(k(r)_0) + r\ ]$ and $k(r)_0$ is $k(r)$ for $\Delta G = 0$. The present electron transfer reactions are those in the normal region of Marcus theory, and therefore the high ΔG induces a long R_0 value. It was difficult to obtain the α and λ values from the fitting of Eq. (9) for the present R_0 vs. ΔG curves. The broken curve in Fig. 3 is the reported relation for electron transfer from aromatic amines to a $Ru(bpy)_3{}^{2+}$ derivative in polycarbonate. The line for the PEO system shows a slight shift from the curve for the polycarbonate system. This shift is caused by the higher dielectric constant of the matrix microenvironment of PEO (5) than that of polycarbonate (2.6). Generally, the charge separation process is favourable in a polar matrix. However, the reported electron transfer rates from aromatic amines to a photoexcited $Ru(bpy)_3{}^{2+}$ derivative are larger in acetonitrile solution ($\epsilon = 38.8$) than in dioxan solution ($\epsilon = 2.0$) as shown in Fig. 1.

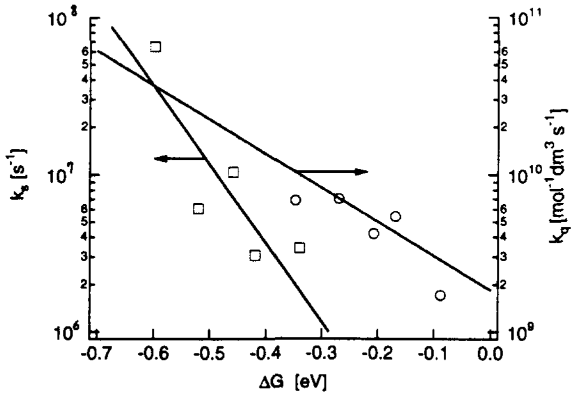


Fig. 4. k_q and $k(s)$ vs. ΔG for the electron transfer quenching of $Ru(bpy)_3{}^{2+}$ by donors **1–5**; ○, acetonitrile solution; □, PEO film.

When the donor is in contact with $Ru(bpy)_3{}^{2+*}$, r is equal to s. The $k(s)$ value, quenching rate in contact, is then calculated from

$$k(s) = 1/\tau_0 \exp[-\alpha(s - R_0)] \qquad (10)$$

The $k(s)$ values were calculated from Eq. (10) assuming α to be 5 nm^{-1} [13], and are shown in Table 2. These $k(s)$ values (3.4×10^6–6.5×10^7 s^{-1}) in the solid system are much larger than the $1/\tau_0$ value (1.0×10^6 s^{-1}), and therefore photoexcited $Ru(bpy)_3{}^{2+}$ is almost quenched when in contact with hole transport materials. Fig. 4 shows the dependence of $k(s)$ and k_q on ΔG. The dependence of $k(s)$ on ΔG is larger than that of k_q on ΔG. This means that the selection of the reaction couple is more important for solid systems than for solution in order to design the optimal conditions for the photochemical reaction.

4. Conclusions

Photoexcited $Ru(bpy)_3{}^{2+}$ is efficiently quenched by hole transport materials containing hydrazone or butadiene groups in polymer films and solution. The relationships between the rate and ΔG and between the distance and ΔG for the quenching by hole transport materials and aromatic amines can be explained in terms of Marcus theory. The change in rate with ΔG in the polymer film was larger than that in acetonitrile solution. This large dependence of the rate on ΔG is important when designing a photoenergy conversion system consisting of hole transport materials.

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