

Directional photochemical processes with an amphiphilic anthraceno–ruthenium complex in dihexadecyl phosphate vesicles

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Excitation of an amphiphilic anthraceno–ruthenium complex, which serves as an antenna-sensitizer complex, leads to two kinds of anthracene triplet states, one of which is bleached by a hydrophilic acceptor and the other by a hydrophobic acceptor in dihexadecyl phosphate vesicles; the latter process is directional from the surface to the interior of the bilayer membrane.

Numerous model studies have appeared on photo-induced electron-transfer systems across vesicle membranes, since vesicles have been considered to be useful in providing desirable microheterogeneous environments for the charge separation processes required in photosynthesis.¹ However, nearly all studies involve diffusional processes of redox-active components and the organization of components is thus limited. O'Brien and coworkers recently addressed this problem and reported some systems in which components are partitioned selectively in various parts of the membrane.² Another approach would be to connect the components covalently and incorporate them into vesicles with a defined direction by rational design of the hydrophobic–hydrophilic balance. There are only a few reports on covalently linked chromophores in vesicles³ in spite of the fact that the covalent approach has been met with great success in elucidating factors determining the rate of electron transfer in homogeneous solutions.^{4,5} Here we report on vectorial processes effected by a covalently linked anthraceno–ruthenium complex **1** in dihexadecyl phosphate (DHP) vesicles.

The [Ru(bpy)₃]²⁺–anthracene system was chosen as the covalently linked photoactive centre because the intramolecular triplet energy transfer process of a related compound from the ruthenium centre to the anthracene unit is well documented and its excited-state lifetime is longer than that of [Ru(bpy)₃]²⁺ itself.⁶ The antenna-sensitizer complex **1**, which has two anthracenes on one of the bipyridine ligands, is designed so that half of the molecule (Ru centre) is hydrophilic, whereas the other half including anthracene is hydrophobic.

The bis-anthracene ligand was prepared from 9-anthracenemethanol and 4,4'-bis(bromomethyl)-2,2'-bipyridine⁷ with KOH in Me₂SO (64%, mp 184–185 °C). The complexation of this ligand with *cis*-[Ru(bpy)₂Cl₂]·2H₂O⁸ followed by the addition of NaClO₄ provided **1** (80%, mp 175–179 °C). *N,N'*-

Didodecylpyromellitimide **2** was prepared from pyromellitic anhydride and 1-aminododecane in refluxing dmf (82%, mp 156.5–158.5 °C).[†]

The absorption spectrum of **1** is nearly the superposition of [Ru(bpy)₃]²⁺ and 9-anthracenemethanol, thus the intramolecular electronic interaction in the ground state is negligible. On the other hand, emission properties of **1** are totally different from the model compounds as shown in Table 1.[‡] Upon excitation of **1** at 455 or 470 nm, the emission intensity from the metal-to-ligand charge transfer (MLCT) state is diminished by a factor of 20 from that of [Ru(bpy)₃]²⁺. It was established by Meyer and coworkers⁸ that the quenching is caused by the intramolecular triplet energy transfer to anthracene (An). Although anthracenemethanol also quenches the emission from [Ru(bpy)₃]²⁺ in DHP vesicles, the intramolecular quenching in **1** is more efficient. The fluorescence from ¹An is diminished by a factor of 100 in the vesicular solution. The loss of emission may be caused by an enhanced rate for ¹An to ³An intersystem crossing facilitated by the spin–orbit coupling due to the heavy-atom effect of ruthenium.⁸ Indeed, the transient absorption spectrum§ after excitation at 337 nm coincides with that of ³An (data not shown). According to these observations, it is concluded that excitation, either to MLCT or to ¹An, leads to ³An.

The triplet anthracene in **1** in vesicular solution decays by two exponential processes of comparative amplitudes with lifetimes of 3 and 13 μs [Fig. 1(a)], whereas the decay in MeCN is single exponential (τ = 150 μs). In the presence of 0.2 mM of methyl viologen (MV²⁺), which is known to adsorb on the surface of DHP vesicles,¹⁰ only the longer lifetime component is bleached, while the shorter one is unaffected, as shown in Fig. 1(b).

An acceptor with alkyl chains, **2**, was prepared aiming at being incorporated in bilayer membranes, which was indeed confirmed by gel permeation chromatography. Electron-transfer quenching of the MLCT state by the imide should be possible on the basis of redox potentials {–0.84 V for [*Ru(bpy)₃]^{2+/3+}¹¹ and –0.71 V for the diimide^{1–/0}¹² vs. SCE}. However, the emission intensity of [Ru(bpy)₃]²⁺ adsorbed on the vesicle surface is unaltered by up to ca. 50 μm of **2**. Hence, **2** must be separated from the ruthenium complex on the membrane surface and so located in the hydrophobic part of the bilayer membrane. In sharp contrast to the case with MV²⁺,

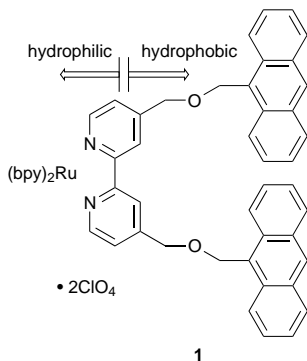


Table 1 Relative emission intensities^a

$\lambda_{\text{ex}}/\text{nm}$ $\lambda_{\text{em}}/\text{nm}$	MeCN		DHP vesicles	
	455	364	470	366
1	0.05	0.09	0.06	0.01
[Ru(bpy) ₃] ²⁺ , AnMeOH	1.07	0.96	0.16	0.32
[Ru(bpy) ₃] ²⁺	1	—	1	—
AnMeOH	—	1	—	1

^a The concentrations of Ru units were 3 and 30 μM, while those of An units were 6 and 60 μM in MeCN and in vesicle dispersions, respectively. AnMeOH = 9-anthracenemethanol.

transient absorption of **1** with **2** (10 μM) in DHP vesicles shows that the shorter-lifetime component is completely bleached [Fig. 1(c)], suggesting electron transfer from ^3An to **2**,[¶] whereas the longer-lifetime component is not affected at all.

To summarize, there are two types of ^3An in DHP vesicles with different lifetimes, the longer-lifetime component being located near the surface of the membrane and bleached by

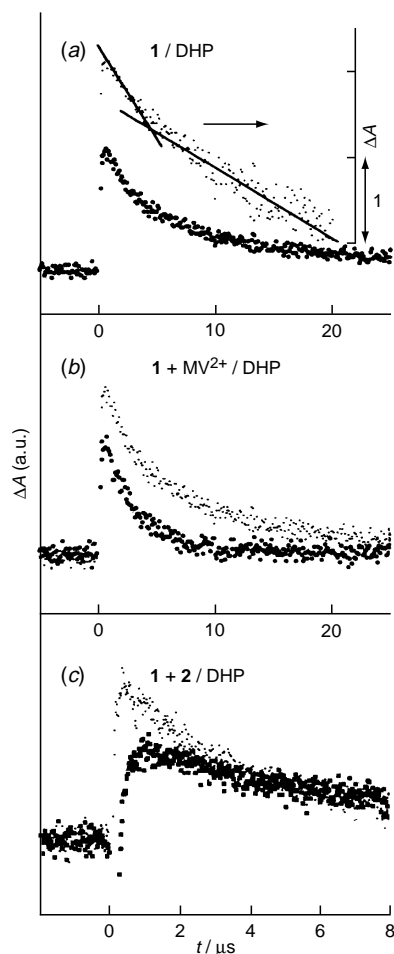


Fig. 1 (a) Transient absorption decay of **1** incorporated in DHP vesicles at 418 nm following excitation at 337 nm. The logarithm plot is also shown. (b) The transient absorption in the presence of MV^{2+} . (c) The transient absorption in the presence of **2**. In (b) and (c), the decay curve without an acceptor is also shown for comparison by small dots. The experimental conditions are the same as in Table 1.

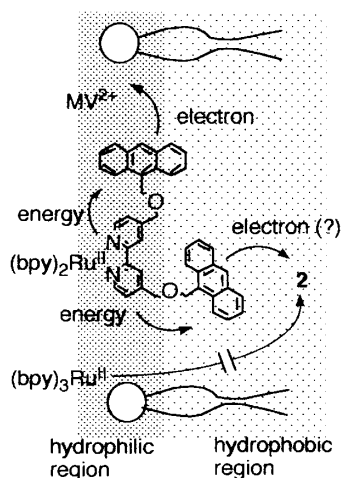


Fig. 2 Schematic representation of the processes taking place in DHP vesicles involving **1** and acceptors

MV^{2+} , while the shorter-lifetime component is located deeper in the membrane and bleached by the diimide (Fig. 2).[¶] In the latter process, the photochemical events proceed directionally from the initial excitation of the ruthenium centre on the membrane surface to the final bleaching by the imide in the hydrophobic region in the membrane. Thus it is demonstrated that the covalent approach is useful to effect directional processes across the interface.

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Footnotes

Selected data for 1: $^1\text{H NMR}$ [$(\text{CD}_3)_2\text{SO}$] δ 4.90 (s, 4 H), 5.68 (s, 4 H), 7.36 (d, 2 H, J 6 Hz), 7.48–7.57 (16 H), 7.64 (d, 2 H, J 6 Hz), 7.67 (d, 2 H, J 6 Hz), 8.07 (d, 4 H, J 8 Hz), 8.13 (t, 2 H, J 8 Hz), 8.15 (t, 2 H, J 8 Hz), 8.44 (d, 4 H, J 8 Hz), 8.58 (s, 2 H), 8.75 (d, 2 H, J 8 Hz), 8.76 (d, 2 H, J 8 Hz); IR (KBr, cm^{-1}) 1622, 1464, 1446, 1121, 1094, 765, 624; Anal. Calc. for $\text{C}_{62}\text{H}_{48}\text{Cl}_2\text{N}_6\text{O}_{10}\text{Ru}\cdot 2.5\text{H}_2\text{O}$: C, 59.38; H, 4.26; N, 6.70. Found: C, 58.96; H, 3.61; N, 7.40%. For **2**: $^1\text{H NMR}$ (CDCl_3) δ 0.87 (t, 6 H), 1.2–1.4 (36 H), 1.69 (m, 4 H), 3.73 (t, 4 H), 8.26 (s, 2 H); IR (KBr, cm^{-1}) 2917, 2848, 1720, 1694, 1408, 1061, 723; HRMS Calc. for $\text{C}_{34}\text{H}_{52}\text{N}_2\text{O}_4$: m/z 552.4106; found m/z 552.3907; Anal. Calc. C, 73.87; H, 9.48; N, 5.08. Found C, 73.84; H, 9.33; N, 5.26%.

[‡] DHP vesicles were prepared according to a reported procedure.⁹ Incorporation of the respective components was confirmed by passing the vesicle solution through Sephadex G50 and observing the coelution of vesicles and the components. Samples were substituted by Ar prior to measurements.

[§] Laser flash photolysis experiments were conducted using a home-made system including an N_2 laser as the excitation source and a Xe lamp as the monitor light.

[¶] We were unable to detect any direct evidence of 2^- probably due to its small concentration and fast ($< 0.2 \mu\text{s}$ with our instrumentation) back electron transfer. Bleaching by energy transfer is unlikely, since the triplet energy of the diimide (2.54 eV for N,N' -dimethylpyromellitimide¹³) is much larger than that of anthracene (1.85 eV).⁸

^{||} It is not clear whether the two ^3An species belong to the same molecule (as implied in Fig. 2) or to different molecules.

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