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Behavior of Ruthenium Trisbipyridine–Anthraquinone Conjugates Connected with Alkyl Spacers in Homogeneous and Microheterogeneous Media

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A series of mononuclear Ru trisbypiridine complexes connected to an anthraquinone unit by a flexible alkyl chain of varying lengths and a bolaamphiphilic dinuclear ruthenium complex bearing an anthraquinone unit in the middle of alkyl chain spacers were synthesized. Their conformational preference in CH_3CN and in dihexadecyl phosphate vesicles was probed by utilizing the intramolecular electron-transfer quenching of the metal-to-ligand charge-transfer excited state of the Ru center by the appended quinone moiety. The length of the alkyl chain spacer had little effect on the quenching efficiency in either medium. A marked difference in the quenching behavior was observed only in the case of the dinuclear Ru complex in vesicles. These results indicate that the bolaamphiphilic structure is necessary and effective for the set of immobilized molecules to take a stretched conformation spanning a bilayer membrane.

In the initial stage of photosynthesis, an electron is transferred across a lipid bilayer membrane through the array of highly organized chromophores in the reaction center.[1] To better understand photosynthesis, and, ultimately, to make artificial photosynthetic molecular devices, numerous model studies have appeared on photoinduced electron-transfer (PET) reactions across bilayer membranes.[2] However, most studies have involved diffusional processes of redox-active components; systems with a fixed arrangement of chromophores are rare.[3—8] Thus, the organization of active components is limited. Another persistent and inherent problem associated with systems involving transmembrane diffusion is that a possibility of leakage of active components cannot be precluded.[9] To realize vectorial PET through a defined and fixed supramolecular architecture, as is the case in natural photosynthesis, it is essential to invent a strategy to control the arrangement of photo- and redox-active components in bilayer membranes.

A basic structure required for molecules to be immobilized in bilayer membranes may be divided into three parts: a polar head group, a spacer, and an active component to be fixed. The polar head group, which is fixed at the hydrophilic surface of a bilayer membrane, immobilizes the active component through the spacer. An obvious way to fix the component at a defined depth is to use a rigid spacer, such as peptides[10] and steroids.[11] However, this puts some limits on generality in designing molecules. If alkyl spacers can be used as the spacer and effectively separate components, it should open a wide opportunity for the organization of molecules in bilayer membranes. While it may be obvious that alkyl chains do not serve as effective spacers in homogeneous solutions because of their flexibility, it might be anticipated that they do in bilayer membranes in which surrounding alkyl chains of membrane-forming amphiphiles take a stretched and extended conformation.

A way to evaluate the effectiveness of alkyl spacers is to measure a quantity associated with the distance between the active component and the head group or the membrane surface. If the alkyl spacer takes a stretched conformation, and thus works effectively in separating the component from the head group, a certain distance dependence should be observed for alkyl spacers of varied lengths (Fig. 1a). Indeed, such a distance dependence of the alkyl chain length was reported for a limited family of molecules in relation to PET. Matsuo and co-workers found that the quenching efficiency decreases as the alkyl spacer length increases for a

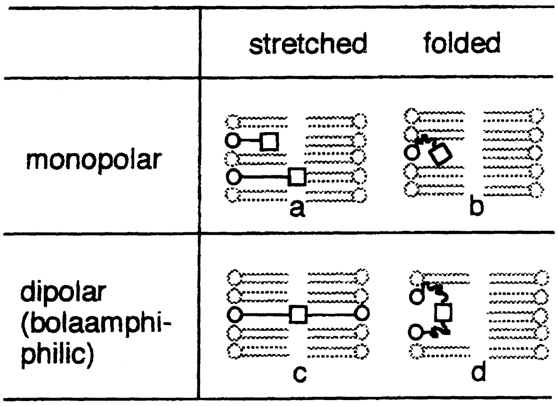


Fig. 1. Possible conformations of molecules in which an active component (square) is tethered to one (monopolar) or two (dipolar) hydrophilic groups (circle) through a flexible alkyl spacer in a bilayer membrane.

system in which porphyrin-viologen linked molecules are immobilized in vesicles.[5] Tsuchida and co-workers observed that liposome-embedded alkanephosphocholine-substituted porphyrins with different alkyl chain lengths reduce methylviologen added in the bulk solution at different rates.[6] It may also be possible, however, for this kind of molecule to take folded conformations. In such cases, the distance dependence would be lost (Fig. 1b).

Another strategy which might control the arrangement of components is to use a dipolar (bolaamphiphilic) structure. If both polar head groups are at opposite surfaces, and the length of the alkyl chain is just enough to span the bilayer membrane, the active component must be fixed in the center of a bilayer membrane (Fig. 1c). Some reports indicate the advantage of dipolar structures over monopolar ones for immobilizing redox and photoactive components.[7,12] However, it is also possible for dipolar molecules to take a U-shaped folded structure (Fig. 1d). In this case, the advantage of the dipolar structure would be lost and the situation would become similar to the case of monopolar structures.

To clarify these points for the important species in PET, viz. Ru polypyridine complexes and quinones, we synthesized a series of Ru trisbipyridine–anthraquinone conjugates connected with an alkyl chain of different lengths, $\mathbf{1}_n$ ($n=4$, 6, 8, and 10) (Chart 1). If the alkyl chain takes a stretched conformation, it should be observed that the quenching efficiency of the emission from the Ru center decreases as the chain length increases. A dipolar bis(ruthenium trisbipyridine)–anthraquinone conjugate, **2**, in which two Ru complexes are connected with a central anthraquinone moiety through alkyl spacers was also synthesized to see the effect of the dipolar structure. Separations of the photoredox active components were probed and the conformation of these molecules was estimated by comparing the quenching behavior of these molecules with that of a model compound, **3**, in homogeneous CH_3CN solutions and in dihexadecyl phosphate (DHP) vesicle dispersions.

Results and Discussion

Design and Synthesis. The combination of a Ru complex and a quinone was chosen as sensitizer–acceptor conjugates to be studied in a vesicle system according to the following considerations. The Ru polypyridyl complex is one of the best utilized sensitizer components, thanks to its preferable photochemical and redox properties.[13] It is positively charged, hydrophilic, and know to adsorb on the surface of anionic DHP bilayer membranes.[14] On the other hand, quinones are used as an electron and proton mediator in hydrophobic bilayer membranes.[8,15] It is well documented that quinones quench the metal-to-ligand charge-transfer (MLCT) excited state of Ru complexes through the mechanism of electron transfer.[16,17] Thus, it was anticipated that while the Ru center would be fixed on the surface, the quinone moiety might be buried in the hydrophobic region of bilayer membranes, and the chain-length dependence of the intrammolecular quenching could be observed for the series of $\mathbf{1}_n$ (which turned out not to be the case as described in the following sections).

Although the synthetic route (Scheme 1) is straightforward, reactions between difunctional compounds could be problematic in that they could result in a polymeric material. Fortunately, α,ω-alkanedioic acids are cheap reagents, and can thus be used in large excess to ensure that only one acid function is amidated.

4-Amino-2,2′-bipyridine[18] was prepared by reducing 4-nitro-2,2′-bipyridine 1-oxide with $NaBH_4$ and Pd/C. Solid $NaBH_4$ was added to a suspension of the oxide and Pd/C in $MeOH/H_2O$ cooled in an ice bath. The reaction mixture turned through a dark-red solution to a nearly colorless solution as the reaction proceeded. Care should be taken to maintain the reaction temperature below 10 °C by adding $NaBH_4$ slowly. If the reaction mixture is heated to reflux at the time it is dark red, a reductive coupling reaction occurs to yield 4,4′-azo-(2,2′-bipyridine).[19]

An attempt was made to make a compound with a shorter

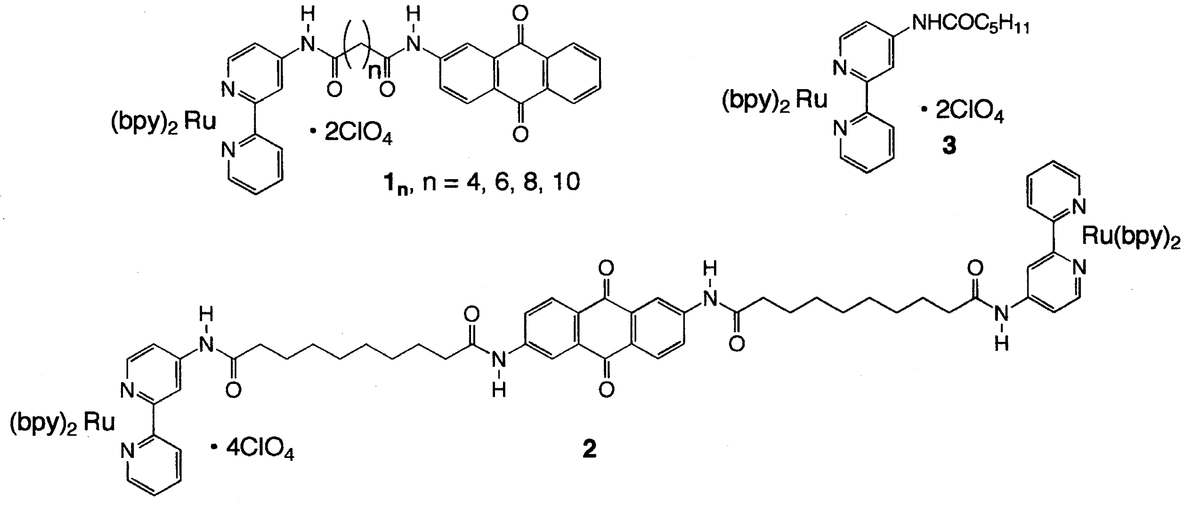
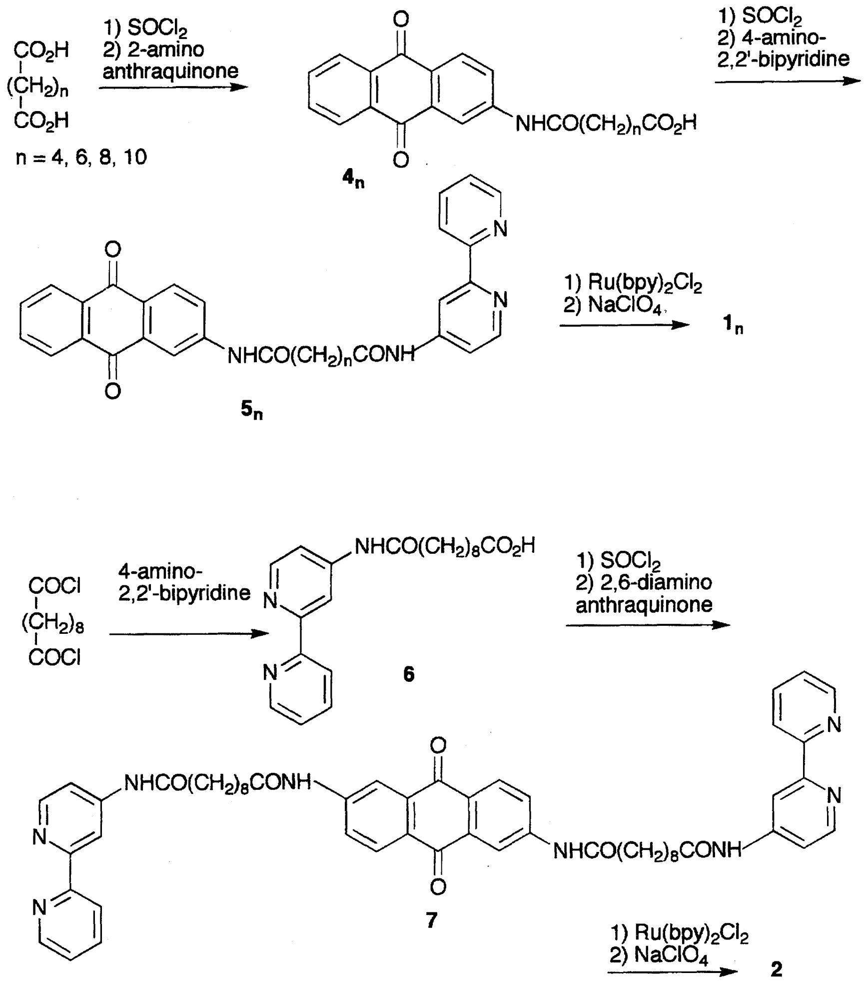


Chart 1.



Scheme 1.

alkyl chain ($n = 2$). However, $\mathbf{4}_2$ could not be prepared, probably due to cyclic succinimide formation based on an inspection of the mass spectrum.

In the preparation of **2**, two possibilities were considered for connecting the quinone and the bipyridine, depending on whether decanedioic acid dichloride was first attached to the anthraquinone as was the case for the mononuclear family ($\mathbf{4}_n$) or to the bipyridine to give **6**. A reaction between 2, 6-diaminoanthraquinone and decanedioic acid dichloride led to an untractable insoluble material, although the mass spectrum showed the presence of the desired diamide. Hence, the reaction scheme through **6** was the route of choice.

All Ru complexes were purified and used in measurements as ClO_4^- salts. Satisfactory results for elementary analyses were obtained as di- and tetrahydrate for $\mathbf{1}_n$ and **2**, respectively.

Quenching in Acetonitrile Solutions. Table 1 summarizes the results obtained in this study. In the course of the following discussion, although representative examples are given in figures to aid understanding, the values in Table 1 are always referred.

Figure 2 shows the absorption spectra for one of the mononuclear complexes $\mathbf{1}_8$, the dinuclear complex **2**, and the Ru center model **3** in CH_3CN solutions. The MLCT absorption bands[13] of all complexes are at similar wavelengths and with similar molar-absorption coefficients, which indicates that there is little electronic interaction between the Ru center and the anthraquinone moiety in the ground state.

Although all complexes exhibit emission with the same $\lambda_{\max}$ at 602—603 nm, the intensities for **1** and **2** relative to **3** are in the range of 0.1—0.15 (Fig. 3). The decrease in the intensity is ascribed to electron transfer from the MLCT state of the Ru center to the pendant anthraquinone.[16,17] That only small fluctuations are observed for $\mathbf{1}_4$ through $\mathbf{1}_{10}$ indicates that the spacer length has a negligible effect on the quenching efficiency. Having two head groups with a positive charge (**2**) does not affect the quenching efficiency, either. Figure 4 shows traces of emission after excitation at 337 nm with a 5-ns pulse from a N_2 laser. The emission lifetimes can be fitted assuming two components, except for **3**; the results are presented in the Table 1. However, a more realistic picture may be that the rate is a superposition of many lifetime components corresponding to various conformations and their dynamics.

It is not surprising that, in homogeneous solutions, the length of a flexible spacer hardly affects the intramolecular quenching efficiency, since it is likely to be easy for the spacer to fold back and the quinone moiety to reach in proximity

Table 1. Absorption and Emission Properties of **1**—**3** in CH_3CN and in DHP Vesicles

	CH_3CN[a]						DHP vesicles[b]				
	λ_{abs}	$\varepsilon \times 10^{-4}$	λ_{em}[c]	rel. int.	τ_1[d]	τ_2	λ_{abs}	$\varepsilon \times 10^{-4}$	λ_{em}[c]	rel. int.[e]	τ_1[f]
	nm	$cm^{-1}M^{-1}$	nm		μs	μs	nm	$cm^{-1}M^{-1}$	nm		μs
$\mathbf{1}_4$	454	1.54	602	0.13	0.1(0.92)	1.1	456	1.17	619	0.17	0.43
$\mathbf{1}_6$	455	1.40	603	0.10	0.1(0.98)	1.3	457	1.25	625	0.20	0.47
$\mathbf{1}_8$	456	1.58	602	0.13	0.1(0.80)	1.0	455	1.25	623	0.16	0.48
$\mathbf{1}_{10}$	456	1.41	602	0.10	0.1(0.83)	1.0	455	1.04	622	0.21	0.49
2	457	2.92	603	0.15	0.1(0.79)	0.6	457	2.41	621	0.49	0.61
3	455	1.62	602	1	1.4(1.00)		456	1.35	625	1	0.95

a) $[\mathbf{1}_n]=[\mathbf{3}]=3$ μM, $[\mathbf{2}]=1.5$ μM. b) [DHP] = 1.5 mM, $[\mathbf{1}_n]=[\mathbf{3}]=30$ μM, $[\mathbf{2}]=15$ μM. c) Excited at 450 nm. d) In parentheses are relative amplitudes of τ_1. e) Repeated runs agreed within ±0.05 for $\mathbf{1}_n$ and **2**, and ±0.15 for **3**. f) Repeated runs agreed within ±0.05 μs.

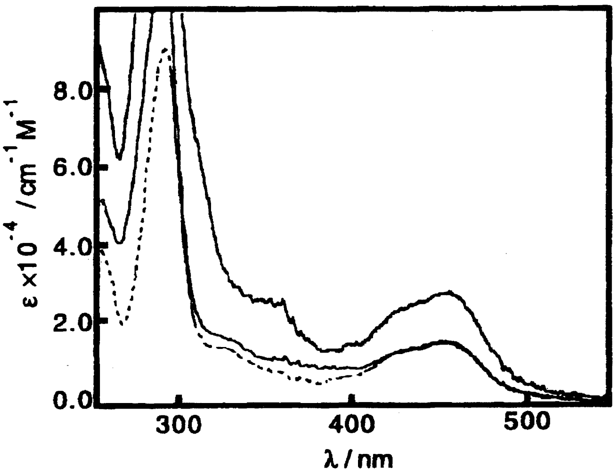


Fig. 2. Absorption spectra for $\mathbf{1}_8$ (lower solid line), **2** (upper solid line), and **3** (dashed line) in CH_3CN.

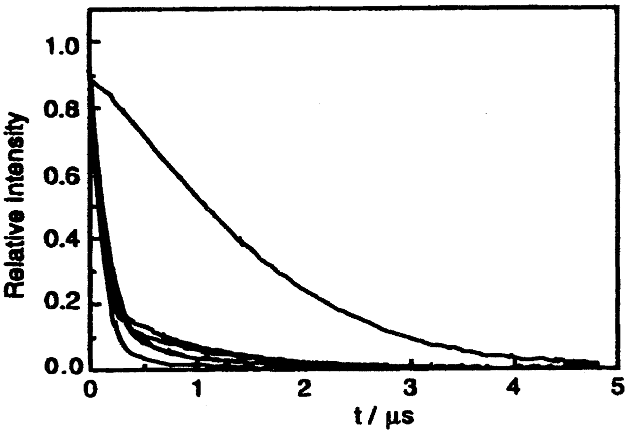


Fig. 4. Time traces of emission at 610 nm after excitation at 337 nm for $\mathbf{1}_n$, **2**, and **3** (top) in CH_3CN. The lower 5 traces (some of which overlapping) are of $\mathbf{1}_n$ and **2**. The concentration of $\mathbf{1}_n$ and **3** is 3 μM, while that of **2** is 1.5 μM.

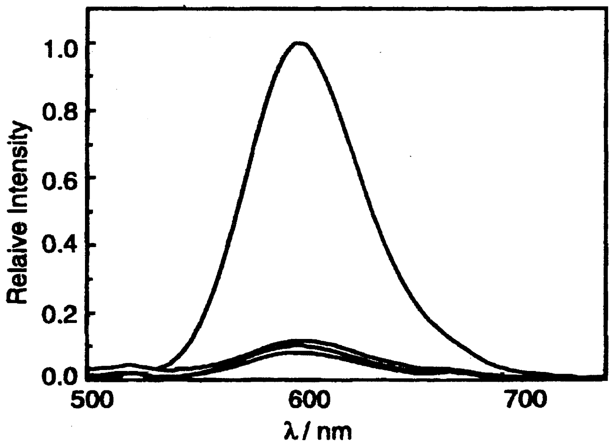


Fig. 3. Normalized emission spectra for $\mathbf{1}_n$, **2**, and **3** (top) in CH_3CN excited at 450 nm. The lower 5 curves (some of which overlapping) are of $\mathbf{1}_n$ and **2**. The concentration of $\mathbf{1}_n$ and **3** is 3 μM, while that of **2** is 1.5 μM.

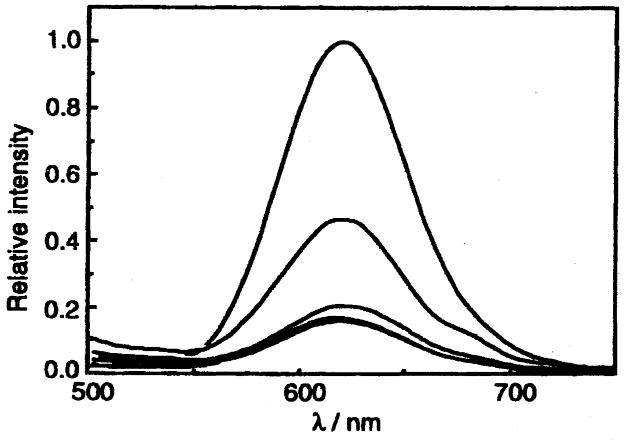


Fig. 5. Normalized emission spectra for $\mathbf{1}_n$ (the lowest 4 curves, one of which overlapping), **2** (middle), and **3** (top) in DHP vesicle dispersions excited at 450 nm. The concentration of $\mathbf{1}_n$ and **3** is 30 μM, while that of **2** is 15 μM.

with the Ru center within its excited-state lifetime.

Quenching in DHP Vesicle Dispersions. Figures 5 and 6 show the emission spectra and the time-course of the emission intensity, respectively, of $\mathbf{1}_n$, **2**, and **3** in DHP vesicles. In the vesicle dispersions, the λ_{abs} and λ_{em} of these complexes are red-shifted by several nm and ca. 20 nm, respectively, from those in CH_3CN due to adsorption of the Ru complex onto the anionic DHP vesicle surface.[14e] The relative emission intensities are again nearly constant irrespective of the spacer length in the series $\mathbf{1}_4$—$\mathbf{1}_{10}$, as in homogeneous CH_3CN solutions. Furthermore, the variance in the emission lifetime is within the experimental error for

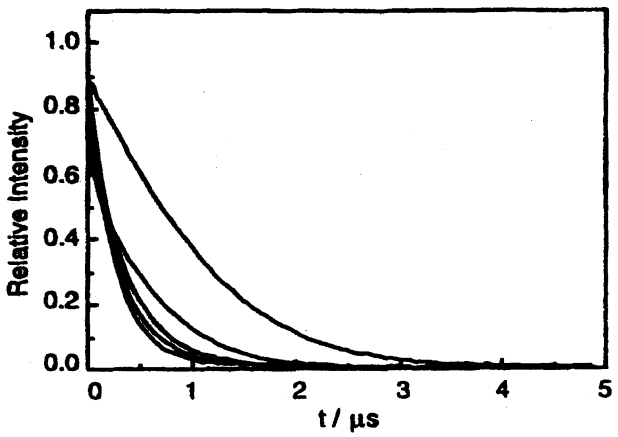


Fig. 6. Time traces of emission at 610 nm after excitation at 337 nm for $\mathbf{1}_n$ (the lowest 4 curves, one of which overlapping), **2** (middle), and **3** (top) in DHP vesicle dispersions. The concentration of $\mathbf{1}_n$ and **3** is 30 μM, while that of **2** is 15 μM.

the series of mononuclear complexes. These observations indicate that $\mathbf{1}_n$ does not take a stretched conformation in DHP vesicles, in spite of the fact that the alkyl chains of surrounding DHP molecules are in the solid state at ambient temperature[20] and take an extended structure. The anthraquinone amide unit in $\mathbf{1}_n$ might be too hydrophilic to be incorporated deep within the hydrophobic interior of the bilayer membrane. This insensitivity towards the alkyl chain spacer length is in contrast to a previously reported behavior of a porphyrin-viologen linked system.[5]

However, a significant increase in the relative emission intensity from that in CH_3CN is observed for the dinuclear **2** in DHP vesicles. The emission intensity of **2** is more than twice that for the mononuclear $\mathbf{1}_8$, which has a spacer of the same length. In other words, the quenching efficiency in **2** is about half that for $\mathbf{1}_8$. In addition, the emission lifetime of **2** is clearly longer than those of $\mathbf{1}_n$. This is most rationally explained by assuming that (at least about half of) the dinuclear **2** exists in a stretched conformation in DHP vesicles, spanning the bilayer membrane. A schematic illustration of the conformation of **2**, together with that of $\mathbf{1}_n$, is given in Fig. 7, and a chemical structural illustration to an approximate scale is given in Fig. 8. This conformation necessarily restricts the anthraquinone moiety in the center of the bilayer membrane far from the Ru centers on the inside and outside surfaces, which accounts for the less-effective quenching in **2** than that in $\mathbf{1}_n$.

To obtain further insight into the state of Ru complexes in bilayer membranes, methylviologen (MV) was added externally to a vesicle dispersion containing $\mathbf{1}_8$, **2**, or **3** (Fig. 9).[21] Upon the addition of MV, the emission intensity decreased and approached to a certain value with 0.67 mM of MV. Further addition of MV resulted in the aggregation and precipitation of vesicles. In a short-term experiment, MV dose not penetrate through the bilayer membrane. Hence, the decrease in the emission intensity is due to quenching of the excited state of Ru complexes which are adsorbed on the external surface of the vesicles. Thus, the ratios of the emission intensity without MV to that with 0.67 mM of MV is

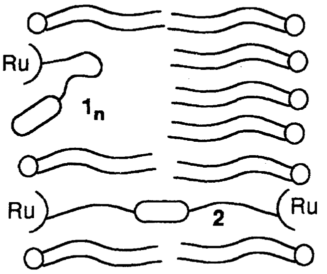


Fig. 7. Schematic illustration of conformations of $\mathbf{1}_n$ and **2** in DHP vesicles that account for the quenching behavior by intramolecular electron transfer.

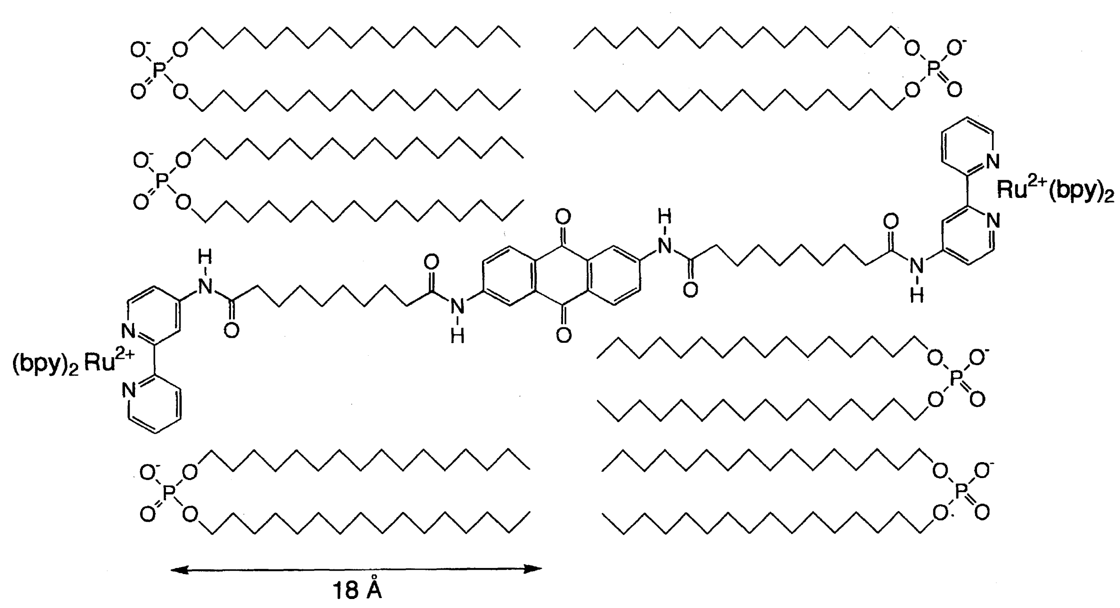


Fig. 8. Structural illustration of **2** embedded in a DHP vesicle membrane to an approximate scale.

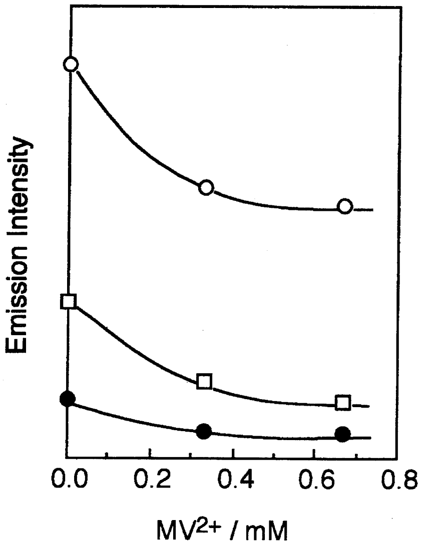


Fig. 9. Decrease in emission intensity upon addition of MV for **1**$_8$ (dot), **2** (square), and **3** (circle) in DHP vesicles. The concentration of **1**$_8$ and **3** is 30 μM, while that of **2** is 15 μM.

assumed to be equal to the ratios of the total number of Ru complex units to the number of entrapped Ru units inside vesicles, which are ca. 0.6 for **3** and ca. 0.4 for **1**$_8$ and **2**. These results may allow the following assertions. First, that more or less half of the emission is quenched supports the idea that the vesicles are single-layered. Second, **1**$_8$ and **2** prefer the outer surface than dose **3**, probably because they are more bulky. Bulky compounds may prefer the outer surface with less spatial restriction due to differences in the packing of DHP molecules.[14e] It is noted that more than half of **3** is trapped inside vesicles, in spite of the fact that the inner surface area is smaller than the outer one. However, this is not too surprising, since it is known that entrapped percentages vary greatly depending on the preparation conditions of vesicles in the case of Ru(bpy)$_3$$^{2+}$.[14e] Finally, if all molecules of **2** take the stretched conformation, the ratio must be 0.5. The actual value of 0.4 sets the upper limit on the percentage of molecules of **2** in the stretched conformation to be 80%. Therefore, combining the results in the intramolecular quenching described above, it is estimated that 50—80% of molecules of **2** take the stretched conformation.

Some other examples are known that indicate that dipolar structures are effective for molecules to be embedded in bilayer membranes in stretched conformations spanning a bilayer membrane, which include a bolaamphiphilic anthraquinone of a structure analogous to that of **2**,[7] which was probed by *inter*molecular redox reactions, and a dipolar benzophenone derivative[12] which was studied by site-selective photo-labeling experiments.

For the moment, it is not clear whether, and at what rate, electron transfer takes place in **2** in the extended form in bilayer membranes. The emission intensity of **2** in vesicles is still less than that of **3**, although it is much larger compared with those of **1**$_n$. This decrease in emission may be accounted for by assuming either that electron transfer occurs in the extended form or that not all molecules of **2** take the extended conformation. Further study will be required to clarify these points and to realize photoinduced redox systems using such organized molecules in bilayer membranes.

In conclusion, for the series of monopolar Ru complexes tethered with an anthraquinone unit through an alkyl spacer of varying length, no distance dependence of the intramolecular PET quenching efficiency is observed when they are immobilized in DHP vesicles, which indicates that these molecules take folded conformations. On the other hand, a marked decrease in the quenching efficiency is observed for a dipolar complex with two head groups, **2**, which indicates that it takes a stretched conformation. Thus, the central quinone component is fixed at the center of the bilayer membrane. To use a dipolar structure may be a strategy to be considered when one wishes to fix a component in a bilayer membrane.

Experimental

All photophysical studies were made in a N$_2$-saturated solution at room temperature. Absorption and emission spectra were taken on a Shimadzu UV-2200 spectrophotometer and Hitachi F-2000 spectrofluorimeter, respectively. The emission lifetimes were measured on a home-made system including a Usyo YKN900 N$_2$ laser (5 mJ/pulse), a Shimadzu SPG-100S monochromator, a Hamamatsu R374 photomultiplier, a Yokokawa Hewlett Packard 54510A digitizing oscilloscope (1 G Sa/s), and an Apple Macintosh SE computer connected through GPIB interfaces.

DHP vesicles were prepared according to a reported procedure.[14d] A specified amount of additives were co-sonicated with DHP. The final DHP concentration was 1.5 mM (1 M = 1 mol dm^{-3}).

The melting points were measured on a Yanaco MP-500D. ^{1}H NMR spectra were recorded on a JEOL JNM-GX400 (400 MHz) spectrometer with Me$_4$Si as an internal standard. IR spectra were recorded on a Simadzu DR-8000 infrared spectrophotometer. 4-Amino-2,2′-bipyridine[18] and Ru(bpy)$_2$Cl$_2$[22] were prepared according to literature procedures.

4$_4$. A solution of hexanoic acid (14.6 g, 100 mmol) in SOCl$_2$ (100 ml) was refluxed for 1 h. After evaporation of SOCl$_2$, 2-aminoanthraquinone (2.23 g, 10 mmol) and dry benzene were added to the residue, and the mixture was refluxed for 3 h. The precipitate was collected by filtration, washed with H$_2$O, and crystallized from acetone to give a yellow powder (1.40 g, 44%), mp 244—247 °C. ^{1}H NMR ((CD$_3$)$_2$SO) $\delta_H = 12.03$ (s, 1H), 10.59 (s, 1H), 8.47 (d, 1H, $J = 2.2$ Hz), 8.15—8.2 (3H), 8.09 (dd, 1H, $J = 8.3$, 2.2 Hz), 7.9—8.1 (2H), 2.42 (t, 2H, $J = 7.2$ Hz), 2.26 (t, 2H, $J = 7.2$ Hz), 1.55—1.65 (4H). IR (KBr) 3351, 1700, 1663, 1590, 1532, 1456, 1424, 1337, 1296, 1240, 1213, 1173, 1146, 994, 932, 872, 716 cm^{-1}. HRMS Found: m/z 351.1111. Calcd for C$_{20}$H$_{17}$NO$_5$: M, 351.1106.

4$_6$. (0.76 g, 20%), mp 234—235 °C. ^{1}H NMR ((CD$_3$)$_2$SO) $\delta_H = 11.97$ (s, 1H), 10.55 (s, 1H), 8.47 (d, 1H, $J = 1.1$ Hz), 8.17—8.22 (3H), 8.10 (dd, 1H, $J = 8.3$, 1.1 Hz), 7.9—7.95 (2H), 2.4 (t, 2H, $J = 7.2$ Hz), 2.21 (t, 2H, $J = 7.2$ Hz), 1.62 (t, 2H, $J = 7.2$ Hz), 1.51 (t, 2H, $J = 7.2$ Hz), 1.32 (t, 4H, $J = 3.3$ Hz). IR (KBr) 3348, 1701, 1667, 1590, 1530, 1495, 1428, 1337, 1295, 1240, 1213, 1165, 1150, 994, 934, 858, 714 cm^{-1}. HRMS Found: m/z 379.1433. Calcd for C$_{22}$H$_{21}$NO$_5$: M, 379.1419.

4$_8$. (0.26 g, 13%), mp 225—226 °C. ^{1}H NMR ((CD$_3$)$_2$SO) $\delta_H = 10.56$ (s, 1H), 8.46 (d, 1H, $J = 2.2$ Hz), 8.15—8.2 (3H), 8.05

(dd, 1H, $J = 8.3$, 2.2 Hz), 7.91—7.93 (2H), 2.39 (t, 2H, $J = 7.2$ Hz), 2.19 (t, 2H, $J = 7.2$ Hz), 1.62 (t, 2H, $J = 7.2$ Hz), 1.49 (t, 2H, $J = 7.2$ Hz), 1.27 (s, 8H). IR (KBr) 3347, 1710, 1671, 1586, 1530, 1495, 1470, 1330, 1300, 1231, 1100, 994, 934, 855, 714 cm^{-1}. HRMS Found: *m/z* 407.1746. Calcd for $C_{24}H_{25}NO_5$: M, 407.1732.

4$_{10}$. (0.24 g, 11%), mp 212—213 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.55$ (s, 1H), 8.47 (d, 1H, $J = 2.2$ Hz), 8.16—8.22 (3H), 8.09 (dd, 1H, $J = 8.3$, 2.2 Hz), 7.89—7.94 (2H), 2.39 (t, 2H, $J = 7.2$ Hz), 2.17 (t, 2H, $J = 7.2$ Hz), 1.62 (t, 2H, $J = 6.6$ Hz), 1.47 (t, 2H, $J = 6.6$ Hz), 1.25 (s, 12H). IR (KBr) 3347, 1709, 1668, 1582, 1530, 1472, 1339, 1300, 1238, 1105, 994, 934, 855, 712 cm^{-1}. HRMS Found: *m/z* 435.2025. Calcd for $C_{26}H_{29}NO_5$: M, 435.2045.

5$_4$. A mixture of **4**$_4$ (0.51 g, 1.46 mmol), $SOCl_2$ (100 ml), and dry benzene (100 ml) was refluxed for 2 h. To the residue obtained by evaporating the solvents, dry dioxane (100 ml) and 4-amino-2,2′-bipyridine (0.75 g, 4.38 mmol) were added, and the mixture was refluxed for 6 h. After removing the precipitate by filtration, the solvent was evaporated. The resulting residue was treated with MeOH, and insoluble material was collected by filtration and washed with MeOH (0.18 g, 24%), mp 224—227 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.59$ (s, 1H), 10.43 (s, 1H), 8.66 (d, 1H, $J = 3.9$ Hz), 8.61 (d, 1H, $J = 3.9$ Hz), 8.51 (d, 1H, $J = 5.5$ Hz), 8.48 (d, 1H, $J = 2.2$ Hz), 8.53 (d, 1H, $J = 7.7$ Hz), 8.15—8.2 (3H), 8.09 (dd, 1H, $J = 8.5$, 2.2 Hz), 7.9—7.95 (3H), 7.69 (dd, 1H, $J = 5.5$, 1.7 Hz), 7.43 (dd, 1H, $J = 8.5$, 2.2 Hz), 2.45 (d, 4H, $J = 7.2$ Hz), 1.70 (s, 4H). IR (KBr) 1673, 1590, 1458, 1329, 1296, 1142, 994, 932, 853, 795, 714 cm^{-1}. HRMS Found: *m/z* 504.1813. Calcd for $C_{30}H_{24}N_4O_4$: M, 504.1797.

5$_6$. (0.30 g, 57%), mp 175—177 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.55$ (s, 1H), 10.43 (s, 1H), 8.67 (d, 1H, $J = 3.9$ Hz), 8.60 (d, 1H, $J = 3.9$ Hz), 8.50 (d, 1H, $J = 5.5$ Hz), 8.43 (d, 1H, $J = 2.2$ Hz). 8.33 (d, 1H, $J = 7.7$ Hz), 8.11—8.18 (3H), 8.04 (dd, 1H, $J = 8.8$, 2.2 Hz), 7.88—7.94 (3H), 7.68 (dd, 1H, $J = 5.5$, 1.7 Hz), 7.44 (ddd, 1H, $J = 8.2$, 4.9, 1.1 Hz), 2.35—2.45 (4H), 1.65 (s, 4H), 1.38 (s, 4H). IR (KBr) 1670, 1590, 1462, 1330, 1296, 992, 932, 857, 795, 714 cm^{-1}. HRMS Found: *m/z* 532.2118. Calcd for $C_{32}H_{28}N_4O_4$: M, 532.2110.

5$_8$. (0.20 g, 35%), mp 169—170 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.54$ (s, 1H), 10.38 (s, 1H), 8.67 (d, 1H, $J = 5.0$ Hz), 8.61 (d, 1H, $J = 2.2$ Hz), 8.5 (d, 1H, $J = 5.0$ Hz), 8.48 (d, 1H, $J = 2.2$ Hz). 8.36 (d, 1H, $J = 7.2$ Hz), 8.15—8.2 (3H), 8.09 (dd, 1H, $J = 8.8$, 2.2 Hz), 7.9—7.95 (3H), 7.68 (dd, 1H, $J = 5.5$, 2.2 Hz), 7.44 (dd, 1H, $J = 7.1$, 5.0 Hz), 2.35—2.45 (4H), 1.63 (d, 4H, $J = 7.1$ Hz), 1.31 (s, 8H). IR (KBr) 1670, 1590, 1458, 1329, 1294, 1215, 992, 932, 857, 795, 714 cm^{-1}. HRMS Found: *m/z* 560.2433. Calcd for $C_{34}H_{32}N_4O_4$: M, 560.2423.

5$_{10}$. (0.13 g, 22%), mp 146—148 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.51$ (s, 1H), 10.36 (s, 1H), 8.67 (d, 1H, $J = 4.4$ Hz), 8.6 (s, 1H), 8.5 (d, 1H, $J = 5.1$ Hz), 8.46 (d, 1H, $J = 1.1$ Hz). 8.36 (d, 1H, $J = 8.1$ Hz), 8.15—8.2 (3H), 8.08 (dd, 1H, $J = 8.4$, 2.2 Hz), 7.9—7.95 (3H), 7.68 (d, 1H, $J = 5.5$ Hz), 7.44 (t, 1H, $J = 5.9$ Hz), 2.35—2.4 (4H), 1.6—1.65 (4H), 1.26 (s, 12H). IR (KBr) 1673, 1590, 1460, 1329, 1294, 1213, 992, 932, 857, 795, 714 cm^{-1}. HRMS Found: *m/z* 588.2736. Calcd for $C_{36}H_{36}N_4O_4$: M, 588.2736.

1$_4$. A solution of **5**$_4$ (0.51 g, 1 mmol) and $Ru(bpy)_2Cl_2$ (0.52 g, 1 mmol) in EtOH (150 ml) was refluxed for 3 h. After removing insoluble material, the solvent was evaporated. The residue was dissolved in H_2O and washed with $CHCl_3$. To the aqueous solution was added a solution of $NaClO_4$ (1.4 g) in H_2O (50 ml). The resulting precipitate was purified by reprecipitation from CH_3CN–Et_2O (0.52 g, 45%), mp 197—200 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.95$ (s, 1H), 10.60 (s, 1H), 8.94 (s, 1H), 8.83 (d, 4H, $J = 7.7$ Hz), 8.49 (d, 1H, $J = 2.2$ Hz), 8.45 (d, 1H, $J = 8.3$ Hz), 8.1—8.2 (8H), 8.08 (dd, 1H, $J = 8.8$, 2.2 Hz), 7.9—7.95 (2H), 7.83 (d, 1H, $J = 5.5$ Hz), 7.7—7.75 (4H), 7.5—7.55 (7H), 1.68 (s, 4H). IR (KBr) 1698, 1671, 1590, 1516, 1445, 1424, 1329, 1296, 1240, 1094, 930, 766 cm^{-1}. SIMS 918 ($M - 2ClO_4$). Found: C, 51.61; H, 3.31; N, 9.64%. Calcd for $C_{50}H_{40}Cl_2N_8O_{12}Ru \cdot 2H_2O$: C, 52.09; H, 3.85; N, 9.72%.

1$_6$. (0.12 g, 51%), mp 189—192 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.89$ (s, 1H), 10.57 (s, 1H), 8.94 (s, 1H), 8.84 (d, 4H, $J = 8.3$ Hz), 8.48 (d, 1H, $J = 2.2$ Hz), 8.48 (d, 1H, $J = 8.3$ Hz), 8.15—8.2 (8H), 8.08 (dd, 1H, $J = 8.8$, 2.2 Hz), 7.9—7.95 (2H), 7.84 (d, 1H, $J = 5.5$ Hz), 7.7—7.75 (4H), 7.5—7.55 (7H), 2.4—2.45 (4H), 1.64 (s, 4H), 1.37 (s, 4H). IR (KBr) 1701, 1673, 1590, 1518, 1445, 1422, 1329, 1296, 1235, 1094, 930, 762, 623 cm^{-1}. SIMS *m/z* 946 ($M - 2ClO_4$). Found: C, 52.79; H, 3.70; N, 9.44%. Calcd for $C_{52}H_{44}Cl_2N_8O_{12}Ru \cdot 2H_2O$: C, 52.89; H, 4.10; N, 9.49%.

1$_8$. (0.12 g, 53%), mp 181—183 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.85$ (s, 1H), 10.55 (s, 1H), 8.92 (s, 1H), 8.83 (d, 4H, $J = 8.3$ Hz), 8.48 (d, 1H, $J = 2.2$ Hz), 8.45 (d, 1H, $J = 8.3$ Hz), 8.15—8.2 (8H), 8.08 (dd, 1H, $J = 8.3$, 2.2 Hz), 7.9—7.95 (2H), 7.83 (d, 1H, $J = 5.5$ Hz), 7.7—7.75 (4H), 7.5—7.75 (7H), 2.4—2.45 (4H), 1.62 (d, 4H, $J = 7.2$ Hz), 1.31 (s, 8H). IR (KBr) 1700, 1671, 1590, 1518, 1445, 1424, 1329, 1296, 1240, 1098, 930, 766, 714 cm^{-1}. SIMS *m/z* 1072 ($M - ClO_4$). Found: C, 53.22; H, 3.90; N, 9.22%. Calcd for $C_{54}H_{48}Cl_2N_8O_{12}Ru \cdot 2H_2O$: C, 53.65; H, 4.34; N, 9.27%.

1$_{10}$. (0.13 g, 48%), mp 171—174 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.83$ (s, 1H), 10.55 (s, 1H), 8.91 (s, 1H), 8.82 (d, 4H, $J = 8.3$ Hz), 8.48 (d, 1H, $J = 2.2$ Hz), 8.45 (d, 1H, $J = 8.3$ Hz), 8.15—8.2 (8H), 8.08 (dd, 1H, $J = 8.8$, 2.2 Hz), 7.9—7.95 (2H), 7.82 (d, 1H, $J = 5.5$ Hz), 7.7—7.75 (4H), 7.5—7.55 (7H), 2.39 (t, 4H, $J = 7.2$ Hz), 1.6—1.65 (4H), 1.28 (12H). IR (KBr) 1700, 1671, 1590, 1520, 1445, 1424, 1329, 1294, 1095, 930, 766, 714 cm^{-1}. SIMS *m/z* 1101 ($M - 2ClO_4$). Found: 54.07; H, 4.45; N, 8.79%. Calcd for $C_{56}H_{52}Cl_2N_8O_{12}Ru \cdot 2H_2O$: C, 54.37; H, 4.56; N, 9.06%.

6. Decanedionic acid dichloride (2.4 g, 10 mmol) was added to a solution of 4-amino-2,2′-bipyridine (0.5 g, 2 mmol) in dry dioxane (50 ml), and the mixture stirred for 1 h at room temperature. After the precipitate was removed by filtration, the solvent was evaporated. The residue was sonicated in ethyl acetate, collected by filtration, and washed with H_2O (0.23 g, 32%), mp 129—131 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 11.18$ (s, 1H), 10.39 (s, 1H), 8.68 (d, 1H, $J = 4.4$ Hz), 8.62 (d, 1H, $J = 4.4$ Hz), 8.52 (d, 1H, $J = 5.5$ Hz), 8.37 (d, 1H, $J = 7.7$ Hz), 7.93 (t, 1H, $J = 7.7$ Hz), 7.69 (dd, 1H, $J = 5.5$, 2.2 Hz), 7.45 (m, 1H), 2.37 (t, 2H, $J = 7.7$ Hz), 2.19 (t, 2H, $J = 7.7$ Hz), 1.51 (t, 2H, $J = 7.1$ Hz), 1.49 (t, 2H, $J = 7.2$ Hz), 1.27 (d, 8H, $J = 5.5$ Hz). IR (KBr) 1717, 1690, 1593, 1526, 1462, 1395, 1358, 1321, 1229, 1163, 1009, 874, 845, 791, 745, 716, 631 cm^{-1}. HRMS Found: *m/z* 355.1869. Calcd for $C_{20}H_{25}N_3O_3$: 355.1896.

7. A solution of **6** (1.42 g, 4 mmol) in $SOCl_2$ (50 ml) was refluxed for 1 h. After evaporating excess $SOCl_2$, dry dioxane (100 ml), pyridine (0.2 ml), and 2,6-diaminoanthraquinone (0.48 g, 2 mmol) were added to the residue, and the mixture refluxed for 24 h under N_2. The precipitate was collected by filtration, washed with H_2O, and crystallized from dioxane (0.21 g, 23%), mp 231—234 °C. ^{1}H NMR (($(CD_3)_2SO$)) $\delta_H = 10.54$ (s, 2H), 10.41 (s, 2H), 8.67 (d, 2H, $J = 3.6$ Hz), 8.61 (s, 2H), 8.51 (d, 2H, $J = 4.5$ Hz), 8.43 (s, 2H), 8.36 (d, 2H, $J = 8.0$ Hz), 8.14 (dd, 2H, $J = 8.6$, 2.4 Hz), 8.05 (m, 2H), 7.93 (t, 2H, $J = 7.6$ Hz), 7.68 (dd, 2H, $J = 5.5$, 2.1 Hz), 7.45 (m, 2H), 2.35—2.4 (8H), 1.61 (s, 8H), 1.32 (s, 16H). IR (KBr) 3345, 2924, 1713, 1659, 1578, 1524, 1329, 1302, 1140, 853, 791, 745, 716, 559, 407 cm^{-1}. FDMS *m/z* 913 (M+1). This compound did not give the correct analysis.

2. A solution of **7** (0.18 g, 0.2 mmol) and $Ru(bpy)_2Cl_2$

(0.18 g, 0.35 mmol) in EtOH was refluxed for 48 h. After removing the precipitate, the solvent was evaporated. The residue was chromatographed through alumina with CH_3CN and then EtOH. The obtained materials was dissolved in H_2O and precipitated by adding a solution of $NaClO_4$ (1.4 g) in H_2O (20 ml). The precipitate was purified by reprecipitation from CH_3CN–Et_2O (0.01 g, 23%). This compound gradually decomposed at above 220 °C. ^1H NMR $((CD_3)_2SO)$ $\delta_H = 10.87$ (s, 2H), 10.56 (s, 2H), 8.91 (s, 2H), 8.82 (d, 8H, $J = 8.0$ Hz), 8.47 (s, 2H), 8.45 (s, 2H), 8.15—8.2 (12H), 8.08 (m, 2H), 7.83 (d, 2H, $J = 5.7$ Hz), 7.7—7.75 (8 H), 7.5—7.55 (14H), 2.4—2.45 (8H), 2.00 (m, 4H), 1.62 (s, 8H), 0.85—0.9 (12H). IR (KBr) 1700, 1667, 1586, 1518, 1464, 1445, 1424, 1308, 1146, 1086, 770, 626 cm^{-1}. Found: C, 51.00; H, 4.18; N, 9.88%, Calcd for $C_{94}H_{88}Cl_4N_{16}O_{22}Ru_2 \cdot 4H_2O$: C, 51.09; H, 4.38; N, 10.14%.

4-Hexanoylamino-2,2′-bipyridine. Hexanoyl chloride (0.62 g, 5 mmol) was added dropwise to a solution of 4-amino-2,2′-bipyridine (0.86 g, 5.1 mmol) in dry benzene (50 ml) and the mixture was stirred for 2 h at room temperature. The precipitate was collected by filtration and a $CHCl_3$-soluble portion was purified by preparative TLC (SiO_2, $CHCl_3$) (0.50 g, 47%), mp 117—118 °C. ^1H NMR $((CD_3)_2SO)$ $\delta_H = 8.65$ (d, 1H, $J = 3.9$ Hz), 8.56 (d, 1H, $J = 5.5$ Hz), 8.37 (d, 1H, $J = 7.7$ Hz), 8.02 (dd, 1H, $J = 5.5$, 2.2 Hz), 7.89 (s, 1H), 7.83 (td, 1H, $J = 7.7$, 1.7 Hz), 7.33 (ddd, 1H, $J = 7.7$, 5.0, 1.1 Hz), 2.43 (t, 2H, $J = 7.7$ Hz), 1.7—1.75 (2H), 1.35—1.4 (4H), 0.91 (s, 3H). IR (KBr) 2957, 1709, 1686, 1590, 1566, 1530, 1464, 1393, 1225, 1096, 795, 747 cm^{-1}. HRMS Found: m/z 269.1498. Calcd for $C_{16}H_{19}N_5O$: M, 269.1528.

3. A solution of 4-hexanoylamino-2,2′-bipyridine (0.13 g, 0.5 mmol) and $Ru(bpy)_2Cl_2$ (0.26 g, 0.5 mmol) in EtOH (150 ml) was refluxed for 3 h. After removing insoluble material, the solvent was evaporated. The residue was dissolved in H_2O and washed with $CHCl_3$. To the aqueous solution was added a solution of $NaClO_4$ (1.4 g) in H_2O (50 ml). The resulting precipitate was purified by reprecipitation from CH_3CN–Et_2O (0.22 g, 47%), mp 183—186 °C. ^1H NMR $((CD_3)_2SO)$ $\delta_H = 10.86$ (s, 1H), 8.93 (s, 1H), 8.83 (d, 4H, $J = 8.3$ Hz), 8.47 (d, 1H, $J = 8.3$ Hz), 8.15—8.2 (5H), 7.84 (d, 1H, $J = 5.5$ Hz), 7.7—7.75 (4H), 7.5—7.55 (7H), 2.42 (t, 2H, $J = 7.2$ Hz), 1.62 (t, 2H, $J = 7.2$ Hz), 1.25—1.35 (4H), 0.88 (t, 3H, $J = 7.2$ Hz). IR (KBr) 1702, 1588, 1516, 1466, 1445, 1426, 1330, 1271, 1242, 1171, 930, 766, 623 cm^{-1}. SIMS m/z 782 $(M - 2ClO_4)$. Found: C, 47.20; H, 3.82 N, 10.31%. Calcd for $C_{36}H_{35}Cl_2N_7O_9Ru \cdot 2H_2O$: C, 47.12; H, 4.28; N, 10.68%.

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20) Temperature variation experiments have been done for $\mathbf{1_8}$, **2**, and **3** in the range 25—70 °C. Increasing temperature results in a gradual decrease in the emission intensity for $\mathbf{1_8}$ and **2** in a similar manner. The quenching by the anthraquinone unit is not involved in the observed decrease in the emission, since **3**, without the appended quinone, also exhibits a similar trend. Any particular change is not observed at around 66 °C, which is the phase transition temperature of DHP (Y. Okahata, R. Ando, and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, **85**, 789 (1981)).

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