Intramolecular "Through-Bond" and "Through-Space" Electron Transfer Pathways in Covalently Linked Porphyrin-Quinone Molecules[1)]

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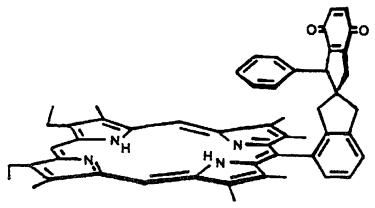
In order to understand electron transfer (ET) pathways through bonds and through space, a porphyrin-spacer-benzoquinone molecule, where the spacer is spiro[4.4]nonane and a phenyl group is inserted between the space of the redox pair, was prepared. On the basis of MM2 calculation, the edge-to-edge distances between the phenyl and the porphyrin or quinone rings are in the range of 2.5—4.2 Å. Therefore, it was expected that there are two possible intramolecular ET pathways in the compound, i.e., through bond and through space. The ET rates for charge separation process (k_{cs}) were obtained on the basis of fluorescence lifetime. The k_{cs} value of the above compound is almost identical with that of a reference compound in which no inserted phenyl ring is present. Therefore, it was concluded that the inserted π-system between the redox pair is not used as a stepping stone in ET pathways; in other words, ET in the present molecules takes place in a through-bond mechanism. To compete with fast ET with through-bond pathways in covalently linked donor–acceptor systems where the two ET pathways are possible, through-space ET may function under quite limited conditions.

In the early events of photosynthesis efficient electron transfer (ET) and stable charge separation are the key steps to convert solar energy into useful chemical energy. The results of X-ray analysis[2—4)] on a bacterial photosynthetic reaction center have given us a deep understanding of how the well-arranged chromophores play an important role in the achievement of charge separation by efficient forward and inefficient back ET. The pictures drawn by X-ray analysis are, however, the final results of evolution of organisms for several billion years. If we could see intermediate pictures in the course of evolution, we could have more deep insight into the mechanism of ET and could apply the principles to build up artificial photosynthesis or molecular devices. One of the best ways to get information on the mechanism of photosynthetic ET without seeing such intermediates is to prepare model compounds from which particular factors controlling ET can be extracted. A number of synthetic models[5—7)] have so far appeared to understand various factors on the ET process, such as separation distance,[8—13)] free energy change associated with the reaction,[14—16)] relative orientation between a redox pair,[17—21)] and environmental factors[22—26)] such as protein matrix. Most of the model compounds are composed of a porphyrin and a quinone ring which are connected by a flexible or a rigid spacer. To avoid complex factors which arise from facile rotation around the single bond of linking chains, rigid spacers are superior to flexible ones. By using rigid spacers the factors controlling ET have been well-analyzed. However, model systems have several limitations. The most serious one is the effect of spacer bonds, i.e., ET with through-bond mechanism. It was pointed out that ET in donor–acceptor linked systems takes place much faster than in protein.[27—29)] The effect has been explained by superexchange mechanism.[30,31)] On the other hand, for ET in protein it is a matter of controversy whether ET pathways are mainly through chemical bonds[32)] of surrounding molecules or entirely through space[33)] with the shortest route along a line connecting a redox pair. It is likely that ET in protein takes place with different pathways as compared with that in covalently linked models, because in a protein a donor and an acceptor are not connected by chemical bonds. This situation makes it difficult to compare directly ET rates in the two systems. Therefore, much information is needed for the differentiation between through-bond and through-space ET for the better understandings of ET in protein.

Here we report the synthesis and ET rates of the compound **1**, where a phenyl group is spatially inserted between the electron donor (porphyrin) and acceptor (benzoquinone) of **3**, in which the porphyrin and the quinone rings are fixed by a rigid spacer of spiro[4.4]nonane and by hindered rotation around a single bond between the porphyrin and phenyl rings (Chart 1). In the compound **1** two ET routes are formally possible, i.e. through bonds of the spacer and through space via the inserted phenyl ring. By comparing ET rates of **1** and **3**, we expect to gain useful information on the two pathways.



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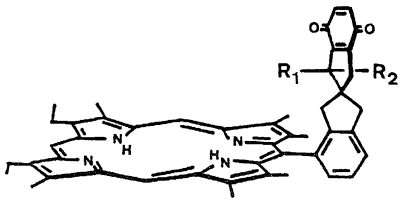
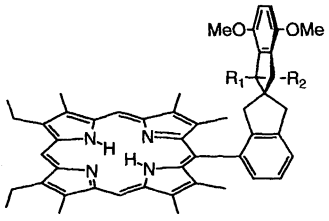


2: R_1=H, R_2=Ph
3: R_1=R_2=H

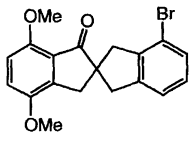
Chart 1.

Results

Synthesis and Structure. The introduction of a phenyl group into the spacer unit was carried out by treatment of **7** with phenylmagnesium bromide in THF to give quantitatively diastereoisomeric alcohol, which was reduced with a combination of triethyl- or triphenylsilane and trifluoroacetic acid to give **8s** and **8a** (Suffixes s and a mean that the Br and Ph groups are *syn* and *anti* with respect to one another.) (Chart 2). The ratio of the products varied with reducing agent: **8s**/**8a** = 1/1.42 (triethylsilane); 1/2.26 (triphenylsilane). The stereochemistry was assigned on the basis of ^{1}H NMR. Thus, all the protons of **8s** and **8a** were assigned by decoupling technique and the compound whose H_c proton resonates at higher field by 0.1 ppm due to the ring current effect of the facing phenyl ring was assigned to **8a**, while the other isomer was assigned to **8s**. Treatment of **8s** and **8a** with BuLi and DMF in THF gave **9s** and **9a**. The stereochemistry of these compounds was reconfirmed carefully by using nuclear Overhauser effect (NOE). Thus, for the compound **9a** NOE signals were observed for H_e, (H_f, H_g, and H_m (aldehyde proton)), and (H_e and H_j) by irradiation of H_m, H_e, and H_f, respectively. These results clearly support the assignment of *anti* configuration for **9a**. Similar NOE experiments were somewhat difficult for **9s**, because of the overlapping of signals. However, the irradiation of aldehyde proton gave an NOE signal for methylene protons which appeared at higher field by 0.1 ppm than the other methylene protons due to the ring current effect of the inserted phenyl ring and hence, could be assigned to H_e. When H_e protons were irradiated, weak NOE signals were observed for H_j protons, but not for H_f. The result also supports the stereochemistry of **9s**. An acid-catalyzed coupling reaction of aldehydes **9** and tetrapyrrole **10** in methanol gave porphyrins **4** and **5**. The compounds **1** and **2** were obtained by demethylation of **4** and **5** with BBr_3 in CH_2Cl_2, followed by oxidation with PbO_2 in a manner similar to the synthesis of **3**[21b] and analogous compounds. NMR chemical shift differences between **1** and **3** were well-explained by the assigned structures. The energy minimized structure of **1** was calculated by MM2[34] and the following results were obtained. (i) The shortest distances (edge-to-edge) between the porphyrin and the phenyl chromophores and between the phenyl and the quinone chromophores are 4.2 and 2.5 Å, respectively. (ii) Dihedral angles between the phenyl and porphyrin rings and between the phenyl and quinone rings are 38.7° and 94.9°, respectively. (iii) The relative orientation and separation distance of the D–A pair in **1** remain unchanged compared with those in **3**.



4: R_1=Ph, R_2=H
5: R_1=H, R_2=Ph
6: R_1=R_2=H



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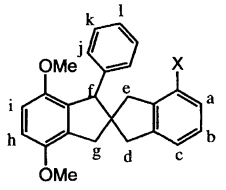

8: X=Br
9: X=CHO

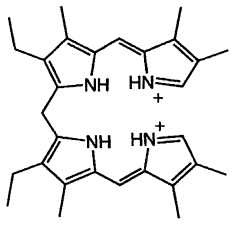

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Chart 2.

Photophysical and Redox Measurements. Electronic absorption spectra of **1**—**3** in THF are superimposable, indicating no special interaction between the inserted phenyl and the other chromophores in the ground state of **1**. Fluorescence lifetimes of **1**—**3** and the corresponding references were measured at 697 nm in benzene, THF, and DMF by a time-correlated single photon counting apparatus excited at 403 nm. Typical decay profiles of **1** and **3** in benzene are shown in Figs. 1 and 2. The decay curves in all the solvents used here can be analyzed by the sum of two exponential functions. The lifetimes of longer component with small contribution always agree quite well with those of the reference compounds **4**—**6** lacking quinone group. Some decomposed products of quinone chromophores in **1**—**3** may be responsible for the minor component. The other major component with shorter lifetimes (τ) was taken for the value of **1**—**3** and used for the calculation of ET rates for charge separation (k_{cs}) using the following equation:

$$k_{cs} = 1/\tau - 1/\tau_0,$$

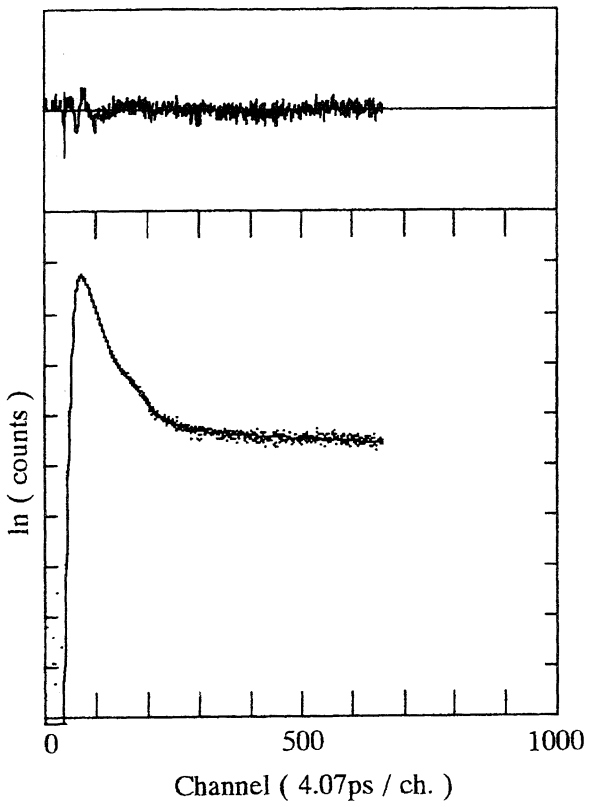

Fig. 1. Fluorescence decay profile of **1** in benzene.

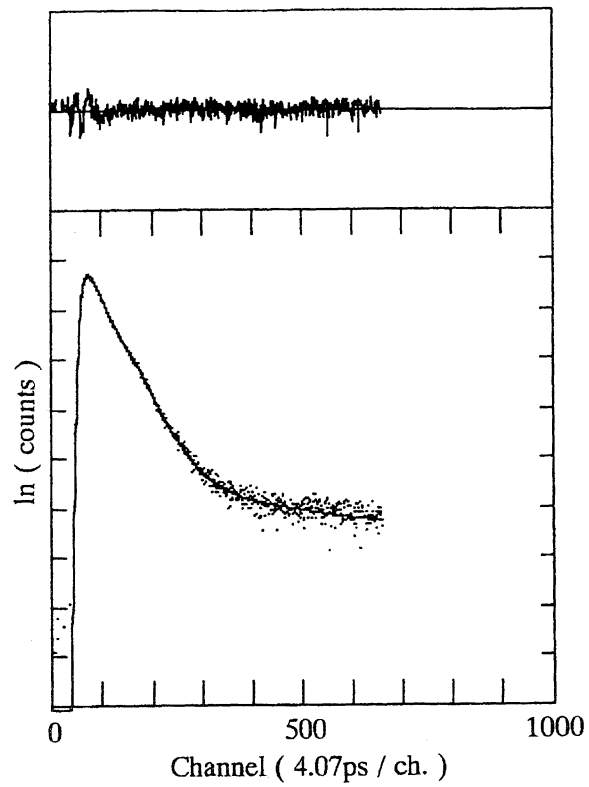

Fig. 2. Fluorescence decay profile of **2** in benzene.

where τ_0 is the fluorescence lifetime of the corresponding references **4**—**6**. The time resolved absorption spectra of **1**—**2** in benzene, THF, and DMF were measured with a picosecond dye laser photolysis system excited at 590 nm. The spectra of **1** in benzene and the time dependence of the transient absorbance at 445 and 700 nm are indicated in Figs. 3a and 3b, respectively. The spectrum at the delay time of 30 ps in Fig. 3a is mainly assigned to $S_n \leftarrow S_1$ absorption of porphyrin and that obtained at delay time longer than 150 ps is mainly due to the porphyrin cation. The lifetimes of S_1 state and charge-separated state were obtained by analyzing these spectra to give k_{cs} and ET rates for charge-recombination process (k_{cr}). The k_{cs} values estimated from transient

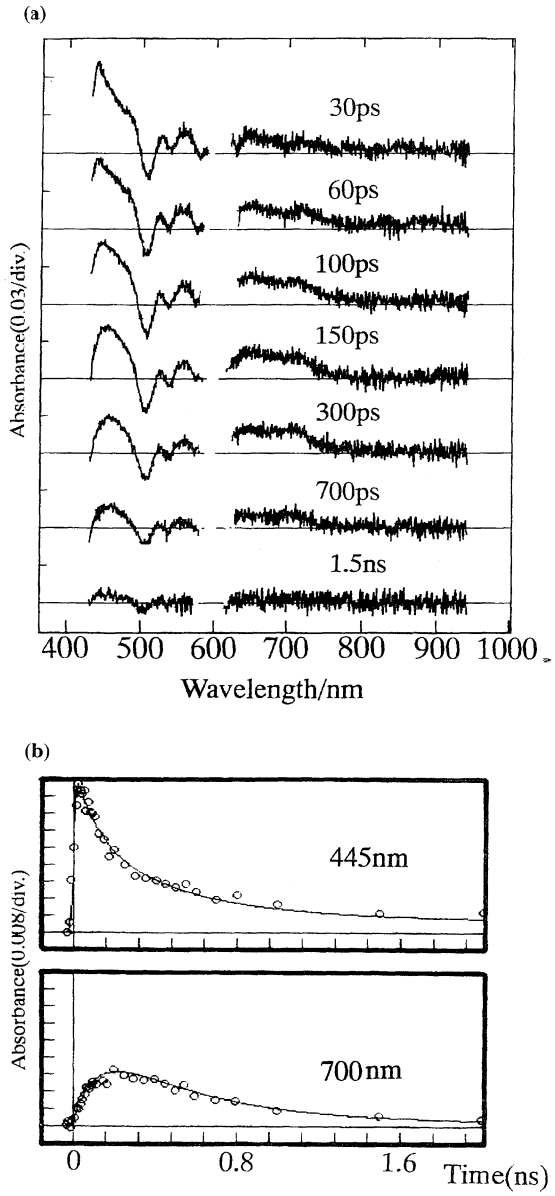

Fig. 3. Picosecond time resolved absorption spectra of **1** in benzene at room temperature (a) and time dependence of the absorbance at 445 and 700 nm (b). Solid lines are simulated curves using $k_{cs}=8.3\times10^9 s^{-1}$, $k_{cr}=2.0\times10^9 s^{-1}$.

absorption measurements agree within the experimental error with the values obtained by the fluorescence measurements. The τ, τ_0, k_{cs}, and k_{cr} values are summarized in Table 1.

Redox properties of **1**—**3** have been examined by cyclic voltammetry (CV) and by differential pulse voltammetry (DPV). One reversible one-electron oxidation and reduction wave and several irreversible ones were observed between +1.5 V and −1.5 V. The values of the DPV peak potentials (vs. Ag/AgCl) in CH_2Cl_2 are shown in Table 2.

Discussion

As described before ET rates are governed by several factors such as separation distance, orientation, driving force, and environmental factors. Among these factors, edge-to-edge distance and mutual orientation between the redox pair are almost the same in **1**—**3** based on MM2 calculation described previously. From the results of redox potential measurements in Table 2, one can see that the exothermicity of **1** and **2** remains unchanged as compared with that of **3**. Therefore, we can roughly conclude that the ET governing factors in **1**—**3** are the same except for the inserted phenyl ring in **1** and **2**. This indicates that we can distinguish clearly between the two possible ET pathways, that is through bond and through space. If the through-space mechanism is operating, the ET rate of **1** should be larger than that of the reference compound **3**, because the inserted phenyl ring would accelerate ET by superexchange mechanism. Aromatic π-systems inserted between redox pair sometimes play an important role in efficient ET pathways. Such examples are reported in co-polymers of poly(4-vinylbiphenyl-*co*-1-vinylpyrene),[35] DNA helices,[36] stacked porphyrins[37] in solid state, and inserted benzene participation between U shaped redox pairs.[38] In these cases where through-space ET is predominant, interplanar distances between the adjacent π-systems are assumed to be 3—4 Å. As seen in the result of MM2 calculation for **1**, the edge-to-edge distances (r) between the inserted phenyl ring and the redox pair are in the range of 2.5 Å$<r<$4.2 Å and are close to the above value. Therefore, through-space ET in **1** seems to be able to compete with through-bond ET. To examine this possibility in more detail, we roughly estimated relative ET rates of possible pathways by using decay parameters of through-bond (ε^B) and through-space (ε^S), formulated by Beratan et al.[32] as follows.

$$\varepsilon^B = 0.6,$$
$$\varepsilon^S = 0.6 \times \exp[-1.7(R - 1.4)],$$

where R is distance between chromophores in Ångstroms. There are five possible ET pathways from porphyrin to quinone in **1**. Namely, (a) through intervening six bonds, (b) through six intervening bonds to phenyl ring and from there through space to quinone, (c) through space from porphyrin to phenyl ring and then, through two bonds, (d) stepwise two through space via phenyl ring, and (e) direct through space from porphyrin to quinone. Using the data of edge-to-edge distances between the chromophores, the decay parameters for the five ET pathways were calculated.

$$\text{path a} = (0.6)^6 = 0.047$$
$$\text{path b} = (0.6)^6 \times 0.6 \times \exp[-1.7(2.5 - 1.4)] = 0.0043$$
$$\text{path c} = 0.6 \times \exp[-1.7(4.2 - 1.4)] \times (0.6)^2 = 0.0019$$
$$\text{path d} = 0.6 \times \exp[-1.7(4.2 - 1.4)] \times 0.6 \times \exp[-1.7(2.5 - 1.4)] = 0.0048$$
$$\text{path e} = 0.6 \times \exp[-1.7(6.2 - 1.4)] = 0.00017$$

Relative values of paths b—d against path a are

$$\text{path b/path a} = 0.09$$
$$\text{path c/path a} = 0.04$$
$$\text{path d/path a} = 0.01$$
$$\text{path e/path a} = 0.004$$

Paths b—d include the participation of the inserted phenyl ring in ET. If we assume that other factors such as energetics and orientation between chromophores are the same, parallel ET paths increase by about 10% in **1** compared with in **3** and such an increase should be reflected in the ET rate.[39] As one can see from Table 1, k_{et} values of **1** are almost the same as those of **3** lacking the inserted phenyl ring. The rates did not change in the three solvents with large differences in dielectric constant. The above result clearly indicates that intramolecular ET in **1** and **3** takes place with through-bond mechanism.

One possible reason why the phenyl ring is not used as a "stepping stone" in intramolecular ET is that the LUMO level of the phenyl ring is not low enough. Energy lev-

Table 1. Observed Flurescence Lifetimes and Charge Separation and Charge Recombination Rate Constants of **1**—**3**

			Benzene	THF	DMF
1	τ	/ps	110	280	280
	τ_0	/ns	13.4[a]	14.9	16.7
	k_{cs}	/s^{-1}	9.0×10^9	3.5×10^9	3.5×10^9
	k_{cr}	/s^{-1}	2.5×10^9	1.3×10^{10}	$>1\times10^{11}$ [b]
2	τ	/ps	47	110	110
	τ_0	/ns	13.4[a]	16.6	16.2
	k_{cs}	/s^{-1}	2.1×10^{10}	9.0×10^9	9.0×10^9
	k_{cr}	/s^{-1}	7.7×10^9	2.5×10^{10}	$>1\times10^{11}$ [b]
3	τ	/ps	135	300	260
	τ_0	/ns	13.4[a]	17.5	17.5
	k_{cs}	/s^{-1}	7.3×10^9	7.3×10^9	3.8×10^9
	k_{cr}	/s^{-1}	2.5×10^9	2.5×10^9	$>1\times10^{11}$ [b]

a) Fluorescence lifetime of the phenylporphyrin. b) The value of k_{cr} in DMF solution is faster than the time response of the system.

Table 2. Redox Potentials of **1**—**3** Determined by DPV vs. Ag/AgCl

Compound	Ox/mV	Red/mV
1	896	−434
2	880	−430
3	896	−456

els which are involved in ET from excited porphyrin (P^*) to quinone (Q) through phenyl ring (Ph) or through saturated spacer bonds (S) are estimated roughly, as shown in Fig. 4, using reduction potentials of benzene (−3.4 V vs. SCE)[40] and of benzoquinone (−0.4 V vs. SCE) in **1**—**3**, oxidation potentials of benzene (2.4V vs. SCE)[41] and of the porphyrins (0.9 V vs. SCE) in **1**—**3**, and the excited singlet state energy of the porphyrins (2.0 eV). The contribution of virtual state P^+–Ph^-–Q to the charge separation process is determined by the energy difference between this state and P^*–Q state. The difference (2.3 eV) may be too large to compete with facile through-bond ET although the energy of P^+–S^-–Q state is far above P^+–Ph^-–Q. Another possible reason for the non-participation of the inserted π-system to ET may be that the relative orientation of the phenyl ring is not adequate. In solid-state porphyrins or DNA helices where efficient through-space ET was observed, π-systems are stacked in parallel in face-to-face fashion. The geometry is quite different in **1**, where the dihedral angle between the phenyl and the benzoquinone rings is almost perpendicular. Although the partial overlap of p-orbitals in the two chromophores is possible for the present geometry, the overlap may not enough for the strong participation of the phenyl ring for the through-space ET pathways.

It is quite surprising that the compound **2**, in which a phenyl group locates outside of the space between the redox pair, has somewhat larger k_{cs} and k_{cr} values than those of **1** and **3** (Table 1). Calculated geometry of the porphyrin and quinone rings in **2** is not so different from those of **1** and **3**. Therefore, the reason for the rate acceleration in **2** is hard to explain at this moment. One of the possible explanations is that the reorganization energy of the solvent in the course of the reaction is different in **2** and in **1** or **3**. Further experimental and theoretical studies must be awaited for a convincing interpretation of the observed phenomena.

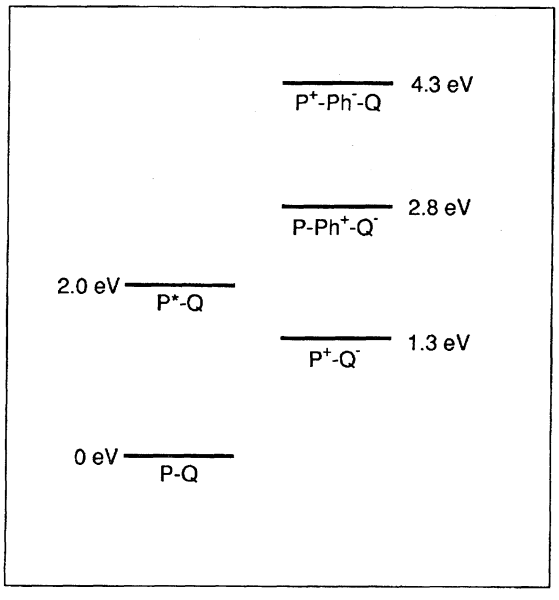

Fig. 4. Energy level diagram for **1**—**3**.

Table 2 shows that k_{cr} of **2** are faster than those of **1** and **3** by a factor of about three in benzene and about two in THF. These ratios are not very much changed in the two solvents with different polarity and are quite similar to that for the charge separation process (Table 1), indicating that the rate-determining factors for k_{cs} and k_{cr} in **1** and **2** are not changed.

In summary, we may conclude that through-space ET functions under the quite limited conditions to compete with overwhelmingly fast ET with through-bond pathways, when the two routes exist in covalently linked donor–acceptor systems.

Experimental

General Procedures. Melting points were not corrected. NMR spectra were obtained on a Bruker WM-360 (360 MHz) and/or JEOL JNM-EX270 (270 MHz) in $CDCl_3$ solutions using Me_4Si as an internal standard. Electronic spectra were recorded on Hitachi 330 in THF solution. Mass and IR spectra were taken on a JEOL DX300 and/or ESCO EMD-05S and on a Hitachi 270-30, respectively. Silica gel of Wako C-200 was used for column chromatography. Electrochemical measurements were performed on a BAS CV-50W in CH_2Cl_2 using 0.1 M tetrabuthylammonium perchlorate (1 M=1 mol dm^{-3}) as a supporting electrolyte and glassy carbon as an electrode with 20 mV s^{-1} (DPV) or 100 mV s^{-1} (CV) scan rate vs. Ag/AgCl. Time-resolved absorption spectra were measured by using a dye laser (Rh-6G) pumped by a second harmonic of a mode-locked Nd^{3+} : YAG laser (Quantel, Pico-chrome YG-503C/PTL-10). The repetition rate of the laser pulse was 10 Hz and the signal was accumulated for 30 shots.[42] The solutions with the concentration of about 10^{-4} M were used and excited at 590 nm. The time resolution of the system was about 10 ps. Fluorescence lifetimes of ca. 10^{-7} M solution were taken by a picosecond time correlated single-photon counting system exciting at 403 nm (a second harmonic of a mode-locked Ti : sapphire laser (Spectra-Physics, Tsunami)) with repetition rate of 16 MHz. The measurements were made under the conditions with a polarizer set at a magic angle. All the solutions used were deaerated by a nitrogen stream.

Reaction of 7 with Phenylmagnesium Bromide. A solution of C_6H_5MgBr in THF was prepared from magnesium (0.486 g, 20 mmol), a small amount of iodine, bromobenzene (2.1 ml, 20 mmol), and dry THF (20 ml) under nitrogen atmosphere. A portion (11 ml, ca. 10 mmol of C_6H_5MgBr) of the supernatant was added to a stirred solution of **7** (747 mg, 20 mmol) over a period of 20 min through a syringe at 0 °C. Stirring was continued for 1 h at room temperature. To the cooled mixture, water and dil HCl were added and it was extracted with chloroform. The organic layer was washed with an aq solution of $NaHCO_3$. After evaporation of the solvent, the crude product was separated by column chromatography on silica gel with benzene–ethyl acetate (9 : 1). *Anti* alcohol (530 mg, 58%) eluted at first and later *syn* alcohol (360 mg, 40%) was obtained.

***Anti* Alcohol:** Colorless needles from benzene–hexane (1 : 1), mp 155.0—156.0 °C. ^{1}H NMR (360 MHz, δ ppm) δ=7.19—7.30 (m, 6H, H_a+H_j+H_k+H_e), 6.91—6.96 (m, 2H, H_b and H_c), 6.77 (d, J=8.7 Hz, 1H), 6.72 (d, J=8.7 Hz, 1H), 3.82 (s, 3H, OMe), 3.81 (d, J=16.4 Hz, 1H, H_e), 3.67 (s, 3H, OMe), 3.02 (d, J=15.8 Hz, 1H, H_d), 2.97 (d, J=16.0 Hz, 1H, H_g), 2.64 (d, J=16.0 Hz, 1H, H_g), 2.63 (d, J=16.4 Hz, 1H, H_e), 2.14 (d, J=15.8 Hz, 1H, H_d); IR (Nujol) 3353 cm^{-1} (OH). MS (EI) 450, 452 (M^+).

***Syn* Alcohol:** Colorless needles from benzene–hexane (1 : 1), mp 187.0—188.0 °C. ^{1}H NMR ($CDCl_3$) δ=7.18—7.33 (m, 6H, H_a+H_h+H_i+H_j+H_k+H_l), 7.07 (d, J=7.7 Hz, 1H, H_c), 6.96 (t, J=7.7

Hz, 1H, H_b), 6.76 (d, J=8.7 Hz, 1H), 6.72 (d, J=8.7 Hz, 1H), 3.88 (d, J=16.0 Hz, 1H, H_d), 3.81 (s, 3H, OMe), 3.65 (s, 3H, OMe), 2.96 (d, J=15.9 Hz, 1H, H_g), 2.91 (d, J=16.6 Hz, 1H, H_e), 2.66 (d, J=15.9 Hz, 1H, H_g), 2.64 (d, J=16.0 Hz, 1H, H_d), 2.18 (d, J=16.6 Hz, 1H, H_e); IR (Nujol) 3523 cm^{-1} (OH). Anal. Calcd for $C_{25}H_{23}O_3Br$: C, 66.53; H, 5.14; Br, 17.70%. Found: C, 66.46; H, 5.19; Br, 17.89%.

Synthesis of 9. To a mixture of *syn*- and *anti*-alcohol (460 mg, 1.0 mmol) in CH_2Cl_2 (4 ml) was added under nitrogen atmosphere triethylsilane (0.16 ml, 1.0 mmol) and then trifluoroacetic acid (0.20 ml, 2.6 mmol). After stirring for 3 h at room temperature, the solvent was evaporated. The residue was dissolved in $CHCl_3$ and it was washed with water and dried over Na_2SO_4. Solvent was evaporated and the residue was passed through a short column of silica gel with benzene–hexane to give a mixture of crude **8a** and **8s** (485 mg, 86.0% yield). Without further purification, the mixture was dissolved in dry THF (20 ml). To the cooled solution with dry ice-acetone, *n*-BuLi (1.6 M, 1.7 ml, 2.7 mmol) was added dropwise in 3 min. After stirring for 5 min, DMF (3.5 ml, 51 mmol) was added to the mixture. Stirring was continued at that temperature for 1 h and then at room temperature for 1 h. Aqueous solution of ammonium chloride was added to the mixture and it was extracted with chloroform. The extract was washed with water and dried over Na_2SO_4. The solvent was evaporated and yielded oily mixture was separated by PLC (Merk 5717) with benzene–hexane. This process was repeated six times to give pure **9a** (107 mg, 32% yield) and **9s** (63 mg, 18% yield).

9s: Colorless powder from benzene–hexane (1 : 1), mp 174.0—175.0 °C. ^{1}H NMR ($CDCl_3$) δ=9.96 (s, 1H, CHO), 7.64 (d, J=7.2 Hz, 1H), 7.42 (d, J=7.2 Hz, 1H), 7.31 (t, J=7.2 Hz, 1H), 7.16—7.20 (m, 3H), 6.75—6.88 (m, 2H), 6.74 (d, J=8.4 Hz, 1H), 6.66 (d, J=8.4 Hz, 1H), 4.19 (s, 1H), 3.84 (s, 3H, OMe), 3.57 (s, 3H, OMe), 2.9—3.1 (m, 6H). MS (EI) 384 (M^+).

9a: Colorless powder from benzene–hexane, mp 130.0—132.0 °C. ^{1}H NMR ($CDCl_3$) δ=10.09 (s, 1H, CHO), 7.6—7.7 (m, 1H), 7.29—7.32 (m, 2H), 7.18—7.26 (m, 3H), 6.86 (dd, J=8.0 Hz, J'=1.8 Hz), 6.73 (d, J=8.7 Hz, 1H), 6.65 (d, J=8.7 Hz, 1H), 4.22 (s, 1H), 3.82 (s, 3H, OMe), 3.58 (s, 3H, OMe), 3.39 (d, J=16.5 Hz, 1H), 3.32 (d, J=16.5 Hz, 1H), 3.01 (d, J=15.9 Hz, 1H), 2.96 (d, J=15.9 Hz, 1H), 2.63 (d, J=15.9 Hz, 1H), 2.53 (d, J=15.9 Hz, 1H). MS(EI) 384 (M^+).

Synthesis of 4 and 5. To a solution of 8,12-diethyl-2,3,7,17,18-hexamethylbiladiene-ac dihydrobromide **10** (33.1 mg, 0.055 mmol) and **9s** (19.2 mg, 0.05 mmol) in methanol (20 ml) was added a saturated solution of HBr in AcOH (0.2 ml). The mixture was refluxed for 24 h. An aqueous solution of sodium hydrogencarbonate was added to the mixture and then, it was extracted with chloroform. The extract was washed with water and the solvent was evaporated. After passing through a short column of silica gel, the crude product was purified by PLC (Merk 5745, Whatman PLK-5) with chloroform containing a small amount of triethylamine to give pure **4** (18.9 mg, 47.0% yield).

4: Reddish violet powder, decomp>300 °C. ^{1}H NMR ($CDCl_3$) δ=10.13 (s, 1H), 10.12 (s, 1H), 9.91 (s, 1H), 7.5—7.8 (m, 3H), 7.20—7.25 (m, 2H), 6.4—6.7 (m, 5H), 4.30 (s, 1H), 4.1 (m, 4H), 2.8—3.8 (m, 18H), 3.30 (s, 3H, OMe), 3.15 (s, 3H, OMe), 1.8—1.9 (m, 6H). MS (FAB) 805 (M^+).

Synthesis of 5. The synthesis of **5** was carried out in a manner similar to that of **4**.

5: Reddish violet powder, decomp>300 °C. ^{1}H NMR ($CDCl_3$) δ=10.13 (s, 1H), 10.11 (s, 1H), 9.90 (s, 1H), 7.85 (d, J=7.1 Hz, 1H), 7.56 (t, J=7.1 Hz, 1H), 7.51 (d, J=7.1 Hz, 1H), 7.2—7.3 (m, 3H), 6.90—6.95 (m, 2H), 6.22 (d, J=8.8 Hz, 1H), 6.13 (d, J=8.8 Hz, 1H), 4.09 (s, 1H), 4.05 (q, J=7.8 Hz, 4H), 3.62 (s, 3H), 3.61 (s, 3H), 3.55 (s, 3H), 3.52 (s, 3H), 3.50 (s, 3H, OMe), 3.22 (s, 3H, OMe), 3.03 (d, J=16.6 Hz, 1H), 2.93 (d, J=16.6 Hz, 1H), 2.87 (d, J=15.8 Hz, 1H), 2.84 (d, J=15.8 Hz, 1H), 2.59 (s, 3H), 2.50 (s, 3H), 2.49 (d, J=16.2 Hz, 1H), 2.39 (d, J=16.2 Hz, 1H), 1.85 (t, J=7.8 Hz, 6H). MS (FAB) 805 (M^+).

Synthesis of 1. To a stirred solution of **4** (4.2 mg, 0.0052 mmol) in CH_2Cl_2 (10 ml) at −78 °C was added under nitrogen atmosphere BBr_3 (0.15 ml, 1.6 mmol) in CH_2Cl_2 (2 ml). Stirring was continued at the same temperature for 1 h and then at room temperature for 3 h. Water was added to the mixture and it was extracted with CH_2Cl_2. The extract was washed with water and dried over Na_2SO_4. After evaporation of the solvent, the solid was dissolved in CH_2Cl_2 (5 ml). To the solution PbO_2 (0.1 g) was added and the mixture was stirred for 2 h at room temperature. The crude product was purified by PLC (Whatman PLK-5) with chloroform containing a small amount of triethylamine to give pure **1** (4.0 mg, 100% yield).

1: Reddish violet powder from chloroform–hexane, decomp >300 °C. ^{1}H NMR ($CDCl_3$) δ=10.13 (s, 1H, meso), 10.11 (s, 1H, meso), 9.92 (s, 1H, meso), 7.79 (d, J=7.3 Hz, 1H), 7.61 (d, J=7.3 Hz, 1H), 7.56 (t, J=7.3 Hz, 1H), 6.67 (d, J=10.1 Hz, 1H, quinone), 6.56 (d, J=10.1 Hz, quinone), 6.7—6.4 (m, 5H), 4.23 (s, 1H), 4.06 (m, 4H), 3.63 (s, 3H), 3.62 (s, 3H), 3.54 (s, 3H), 3.52 (s, 3H), 3.41 (d, J=15.7 Hz, 1H), 3.29 (d, J=15.7 Hz), 3.10 (d, J=18.2 Hz, 1H), 2.76 (d, J=18.2 Hz, 1H), 2.47 (s, 3H), 2.38 (s, 3H), 2.29 (d, J=17.0 Hz, 1H), 2.00 (d, J=17.0 Hz, 1H), 1.85 (t, J=7.6 Hz, 6H), −3.30 (br. s, 2H). MS (FAB) 777 (M^++2).

Synthesis of 2. Synthesis of **2** was carried out in a manner similar to that for **1**.

2: Reddish violet powder from chloroform–hexane, decomp >300 °C. ^{1}H NMR ($CDCl_3$) δ=10.15 (s, 1H, meso), 10.14 (s, 1H, meso), 9.92 (s, 1H, meso), 7.9—8.0 (m, 1H), 7.58 (t, J=7.5 Hz, 1H), 7.47 (d, J=7.5 Hz, 1H), 7.3—7.4 (m, 3H), 6.9—7.0 (m, 2H), 6.30 (d, J=10.0 Hz, quinone), 6.19 (d, J=10.0 Hz, quinone), 4.05 (q, J=8.0 Hz, 4H), 3.93 (s, 1H), 3.63 (s, 3H), 3.62 (s, 3H), 3.57 (s, 3H), 3.54 (s, 3H), 2.7—3.0 (m, 4H), 2.56 (s, 3H), 2.47 (s, 3H), 2.3—2.5 (m, 2H), 1.86 (t, J=8.0 Hz, 6H). MS (FAB) 777 (M^++2).

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