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Metal-induced conformational changes in calix[*n*]arenes can control the electron-transfer efficiency between porphyrin and [60]fullerene in an on–off manner

Masaru Kawaguchi, Atsushi Ikeda, Itaru Hamachi and Seiji Shinkai *

Department of Chemistry & Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

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Abstract

Calix[*n*]aryl esters ($\mathbf{1}_n$:n=4 and 6) bearing a Zn(II)·porphyrin group as a fluorophore and a [60]fullerene group as a quencher on the lower rim were synthesized. In $\mathbf{1}_6$ a metal-induced 1,2,3-alternate-to-cone conformational change shortened the distance between these two groups and the electron-transfer efficiency was sharply increased. In $\mathbf{1}_4$ the electron-transfer efficiency was slightly increased in spite of a metal-induced rotation of the carbonyl groups which enlarges the distance between these two groups. These are novel responsive systems to control the electron-transfer efficiency between porphyrin and [60]fullerene. © 1999 Elsevier Science Ltd. All rights reserved.

Photoinduced electron-transfer followed by charge separation is an essential unit process in a photosynthetic system. To mimic this process a number of fluorophore-quencher couples have so far been investigated.[1,2] Recently, the combination of a porphyrin–[60]fullerene couple has been of much concern because in this couple the photoinduced electron-transfer occurs efficiently and the charge separation state is preserved more stably than those in other couples.[3–7] It is known that the electron-transfer efficiency is basically sensitive to the distance between the fluorophore and the quencher. Thus, it occurred to us that the electron-transfer efficiency in this potential couple would be finely tuned by the control of the distance. In particular, if the distance can be changed by some stimulus from the outside, it should act as an on–off-switched electron-transfer system. We noticed that calix[*n*]arenes would satisfy this requirement as a scaffold to design such a switch-functionalized electron-transfer system because calix[*n*]aryl esters ($\mathbf{1}_n$) can readily change their conformations in response to added alkali metal cations.[8–10] In calix[4]aryl esters, carbonyl groups are directed outwards to reduce electrostatic repulsion among the C=O groups whereas the *exo*-annulus carbonyls are changed to the *endo*-annulus carbonyls to coordinate to bound Na^+ (Fig. 1).[8–10] In calix[6]aryl esters, the most stable conformation is 1,2,3-alternate but it is isomerized to cone in the presence of K^+, Cs^+ so that all carbonyl groups can coordinate to bound K^+, Cs^+ (Fig. 1).[10–13] These findings suggest that if a porphyrinyl group and a [60]fullerenyl group are introduced

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* Corresponding author. Fax: +81 92 642 361; e-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

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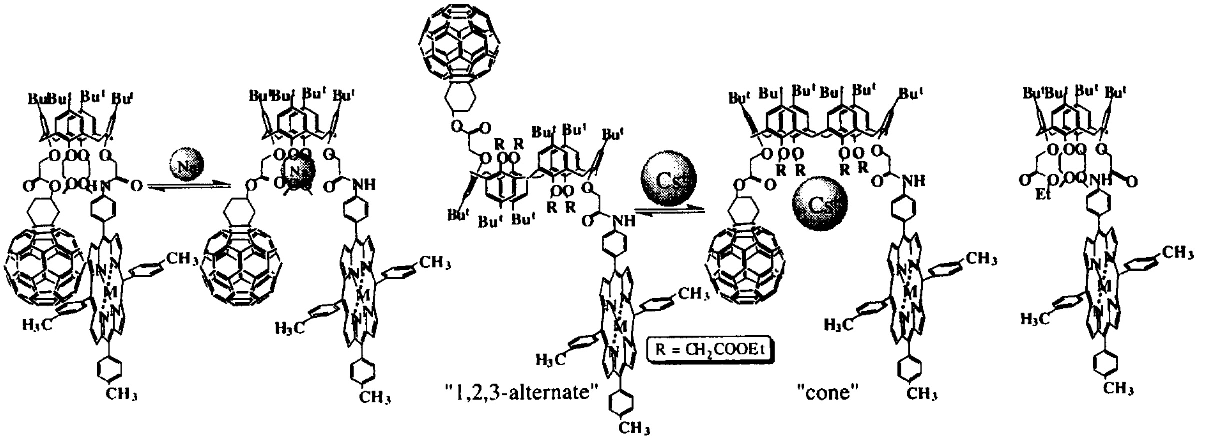


1_4a: M = H$_2$
1_4b: M = Zn

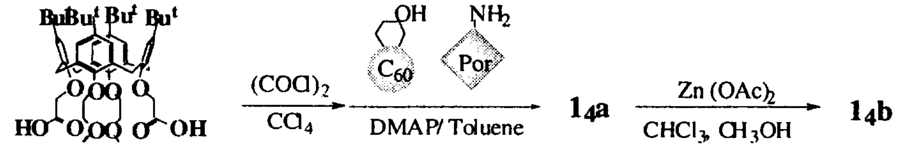
1_6a: M = H$_2$
1_6b: M = Zn

2_4a: M = H$_2$
2_4b: M = Zn

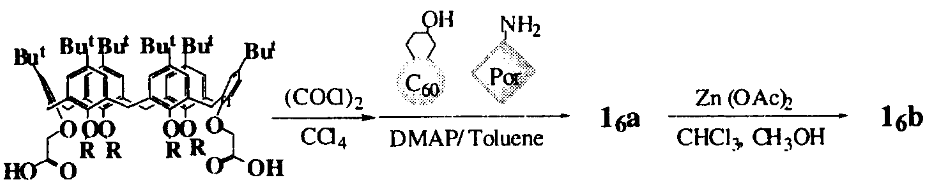
Figure 1. Structures of **1** and **2** and conformational changes of calixarene moieties by addition of alkali metal cations

into the ester moieties as terminal groups, the porphyrin–[60]fullerene distance can be changed and the electron-transfer efficiency can be controlled by added metal cations. To realize this intriguing idea we synthesized compounds 1_4 and 1_6. Compound 1_4 is conformationally immobilized to cone but the distance can be changed in response to the C=O rotation. Compound 1_6 is still conformationally mobile but two functionalized groups always occupy an *anti* position as long as it adopts in a 1,2,3-alternate conformation. On the other hand, when they adopt a *syn* position in the presence of alkali metal cations, the distance becomes much shorter.

Compounds **1_4a** and **1_6a** were synthesized according to Schemes 1 and 2, respectively. The products were identified by IR, NMR, and mass (TOF) spectral evidence and elemental analyses. These compounds were treated with Zn(OAc)$_2$ in chloroform:methanol (1:1 v/v) mixed solvent to give **1_4b** and **1_6b**. The products were also identified by the similar analytical methods. Compound **2_4b** was synthesized from a monocarboxylic acid derivative and used as a reference.



Scheme 1.



Scheme 2.

The metal-induced rotation of the carbonyl groups in **1_4b** can be confirmed by upfield shift of the OCH$_2$CO methylene protons in ^{1}H NMR spectroscopy.[14] This shift is induced by the shielding effect of the phenyl rings on these *exo*-annulus protons.[14] In THF-d_8 at 25°C, a singlet peak in the

Zn(II)·porphyrin-carrying amide group and a pair of doublets in the [60]fullerene-carrying ester group[15] shifted from 5.22 ppm and 5.16 and 5.12 ppm in the absence of metal cation to 4.71 ppm and 4.59 and 4.52 ppm in the presence of $NaBPh_4$ (5 equivalents to $\mathbf{1_4b}$). Furthermore, most chemical shifts for the Zn(II)·porphyrin protons moved to higher magnetic field, indicating that they leave from the shielding area of the [60]fullerene moiety.

The 1,2,3-alternate conformation, the most stable one in calix[6]aryl ester derivatives is characterized by a symmetrical splitting pattern in ^1H NMR spectroscopy.[10–13] In the ^1H NMR spectrum of $\mathbf{1_6b}$ (THF-d_8, −80~25°C, 600 MHz) the peaks were significantly broadened and clear evidence supporting the 1,2,3-alternate conformation was not obtained. Presumably, this broadening is due to several conformational equilibria related to the porphyrin–fullerene interaction. When $KBPh_4$ (5 equivalents to $\mathbf{1_6b}$) was added, both the $ArCH_2Ar$ methylene protons (six pairs of doublets) and the *tert*-Bu protons (six singlets)[14] gave the splitting patterns commensurate with the cone conformation. The similar change in the ^1H NMR spectrum was also induced by the addition of $CsBPh_4$.

When $NaBPh_4$ [$(1-100)\times10^{-5}$ mol dm^{-3}] was added to a THF solution of $\mathbf{1_4a}$ (5.00×10^{-6} mol dm^{-3}) at 25°C, the Soret band[16] (λ_{max} 428 nm) shifted to 427 nm with a tight isosbestic point (429 nm). This implies that the porphyrin–[60]fullerene interaction already exists at the ground state.[3–7,16] In fluorescence spectroscopy [λ_{ex} 557 nm (a Q-band where the absorbance scarcely changes), λ_{em} 654 nm], the $NaBPh_4$ addition induced a slight decrease in the fluorescence intensity.[17] The finding implies that in $\mathbf{1_4a}$ the distance change is not sufficiently induced by the $NaBPh_4$ addition because of the significant porphyrin–[60]fullerene interaction.

Compound $\mathbf{1_4b}$ possesses a more electron-deficient Zn(II)·porphyrin than the free-base porphyrin (as in $\mathbf{1_4a}$). When $NaBPh_4$ was added, the Soret band[16] (λ_{max} 434 nm) showed a blue-shift (λ_{max} 432 nm) but the spectral change was much smaller (Fig. 2A). This indicates that the interaction at the ground state in this couple is much weaker. This spectral change supports the view, together with the above ^1H NMR data, that the distance between [60]fullerene and Zn(II)·porphyrin is elongated. From plots of A_{432} versus [$NaBPh_4$], the association constant (K_{ass}) was estimated to be 1.7×10^4 dm^3 mol^{-1}. However, contrary to our expectation, the fluorescence emission from the Zn(II)·porphyrin moiety showed only a slight decrease with increasing $NaBPh_4$ concentration (Fig. 2B).[17] On the other hand, neither the absorption nor the fluorescence spectra of $\mathbf{2_4b}$ were changed by the $NaBPh_4$ addition, indicating that BPh_4^- anion has no effect on the fluorescence of Zn(II)·porphyrin.[17] It is known that the addition of certain metal salts facilitates the electron-transfer efficiency (particularly, when the cationic charge exists in the neighbor of the quencher).[18] Conceivably, in $\mathbf{1_4b}$ the distance elongation which should suppress the electron-transfer efficiency is offset by the cationic charge effect arising from bound Na^+ which should enhance the electron-transfer efficiency. The K_{ass} value was estimated from the plots in Fig. 2B to be 1.4×10^4 dm^3 mol^{-1} for $NaBPh_4$. This value was in good agreement with the K_{ass} estimated by the absorption spectral method, indicating that this change is also induced by the Na^+ binding.

The absorption spectra of $\mathbf{1_6a}$ also changed by the addition of $KBPh_4$ or $CsBPh_4$.[16] Hence, we confined the measurements to a $\mathbf{1_6b}$ system. Although the metal-induced spectral change was very minute, we could estimate the K_{ass} values to be 1.5×10^6 dm^3 mol^{-1} for $KBPh_4$ and 1.6×10^5 dm^3 mol^{-1} for $CsBPh_4$. In fluorescence spectroscopy, the addition of $KBPh_4$ or $CsBPh_4$ sharply decreased the fluorescence intensity[17] (Fig. 3), contrary to the effect of $NaBPh_4$ on $\mathbf{1_4b}$. The result supports the view that the distance is shortened by a conformational change from 1,2,3-alternate to cone to facilitate the electron-transfer from Zn(II)·porphyrin to [60]fullerene. The K_{ass} values were estimated from the plots in Fig. 3B to be 1.7×10^6 dm^3 mol^{-1} for $KBPh_4$ and 1.3×10^5 dm^3 mol^{-1} for $CsBPh_4$. These values show an excellent agreement with those obtained from the absorption spectral method (see above).

In conclusion, the present study demonstrated for the first time that the electron-transfer efficiency

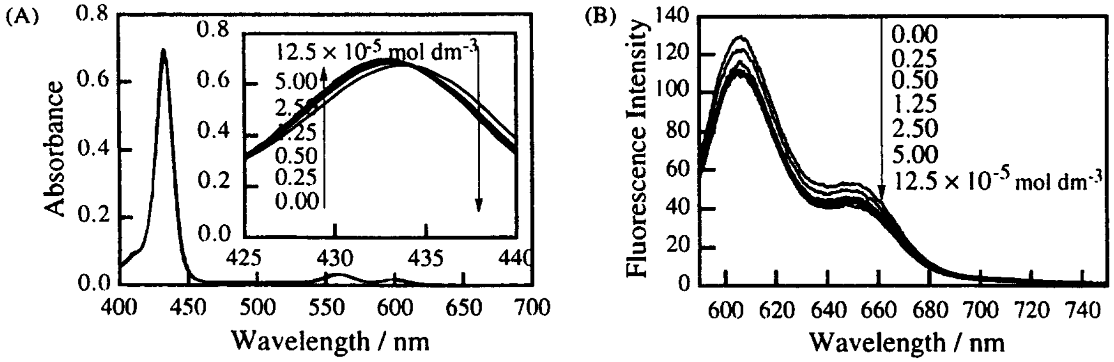


Figure 2. Absorption (A) and fluorescence spectra (B) of 1_4**b** (2.50×10^{-6} mol dm^{-3}) in the absence and the presence of NaBPh$_4$ [$(0\text{–}12.5)\times10^{-5}$ mol dm^{-3}]: 25°C, THF, λ_{ex} 560 nm

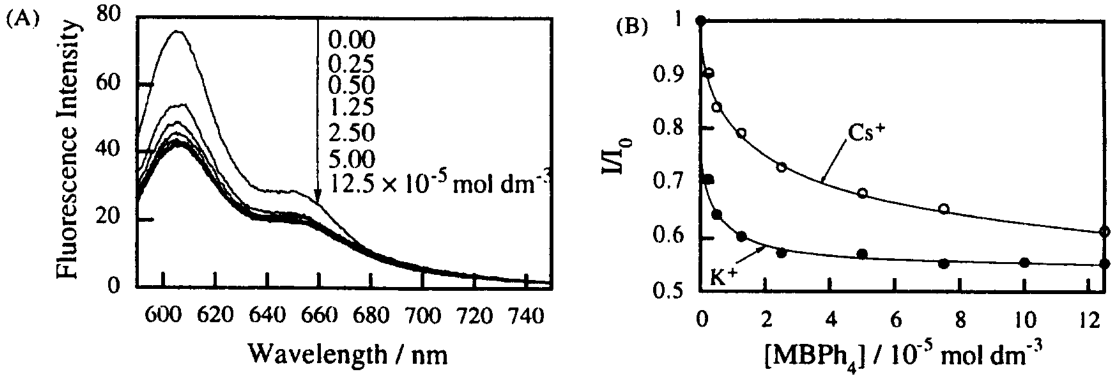


Figure 3. Fluorescence spectra of 1_6**b** (2.50×10^{-6} mol dm^{-3}) in the absence and the presence of KBPh$_4$ [$(0\text{–}12.5)\times10^{-5}$ mol dm^{-3}] (A) and plots of I/I_0 at 605 nm against [MBPh$_4$] (B): 25°C, THF, λ_{ex} 560 nm, λ_{em} 605 nm

between Zn(II)·porphyrin and [60]fullerene, a potential redox couple to mimic the photosynthetic system, can be controlled by a switch function. This implies that the reverse reaction which eventually leads to the creation of a long-lived charge-separated species can also be controlled. In addition, it was shown that calix[*n*]aryl esters are very useful as a scaffold to design such switch-functionalized systems. Further extensions to time-resolved fluorescence measurements, 1_4**b**- or 1_6**b**-mediated redox reactions, membrane transport etc. are now continued.

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15. The splitting into a pair of doublets is due to a racemic carbon in the neighboring cyclohexane ring.
16. Comparing with **2**$_4$, the Soret bands of **1** showed red-shifts (9–10 nm) and the fluorescence intensities of **1** from the Zn(II)·porphyrin moiety were decreased by one-tenth due to the intermolecular quenching by fullerene.
17. Although BPh_4^- is weakly fluorescent, we set up the measurement conditions where this contribution is negligible. This was also confirmed by the fact that $NaClO_4$ used instead of $NaBPh_4$ gives the same results.
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