J|A|C|S
COMMUNICATIONS

Published on Web 03/18/2003

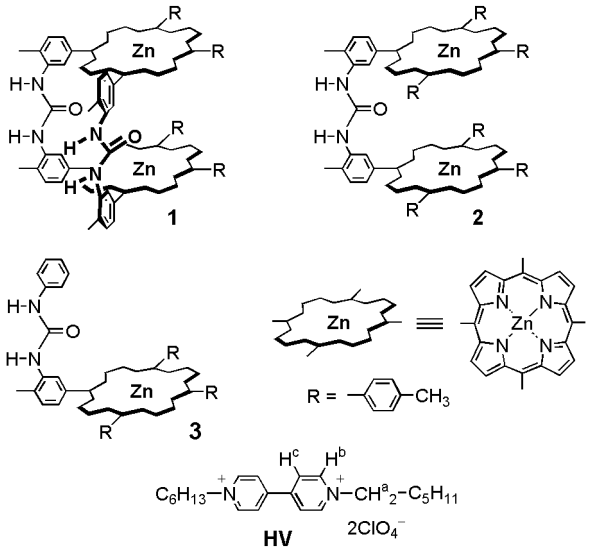
Diarylurea-Linked Zinc Porphyrin Dimer as a Dual-Mode Artificial Receptor: Supramolecular Control of Complexation-Facilitated Photoinduced Electron Transfer

Shigeyuki Yagi,* Masayuki Ezoe, Isamu Yonekura, Toru Takagishi, and Hiroyuki Nakazumi

Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Received November 26, 2002; E-mail: yagi@ams.osakafu-u.ac.jp

Well-defined electron donor−acceptor arrays in the photosynthetic reaction center ensure highly efficient photoinduced electron transfer (PET) and long-lived charge separation.[1] Such natural photochemical functions have been receiving much attention in terms of the development of molecular-scale photonic devices aimed at light-energy conversion,[2] and, thus, the construction of noncovalent assemblies of those components with photochemical and electrochemical properties suitable for PET has been one of the important subjects in supramolecular chemistry.[3] From this viewpoint, porphyrin-based artificial receptors for redox active substrates have been widely studied because of the structural analogy to the photosynthetic pigments, where recognition of the acceptors such as quinone,[3b,c,4] viologen,[5] and fullerene[6] has been intensively investigated. In the next stage, it is a challenging theme to devise molecular photonic systems with on−off controllable triggers, for example, the control of PET by supramolecular regulatory stimuli. Here we report the complexation-facilitated PET system consisting of a novel diarylurea-linked zinc porphyrin dimer **1** and a viologen derivative (hexyl viologen perchlorate, **HV**). We also report the inhibitory control of the PET using an alternative substrate.



We previously reported the construction of cofacial porphyrin arrays using a diarylurea linkage (e.g., the single-linked dimer **2**).[7] The double-linked dimer **1** was synthesized from 5,10-bis(3-amino-4-methylphenyl)-15,20-bis(4-methylphenyl)porphyrin in a manner similar to the preparation of **2**. In Figure 1a are shown electronic absorption spectra of **1**−**3** in the Soret region. The absorption band of **2** exhibits a blue shift by 3 nm as compared with that of **3**, the weak excitonic interaction between the porphyrin chromophores indicating that a cofacial conformer of **2** is predominantly formed.

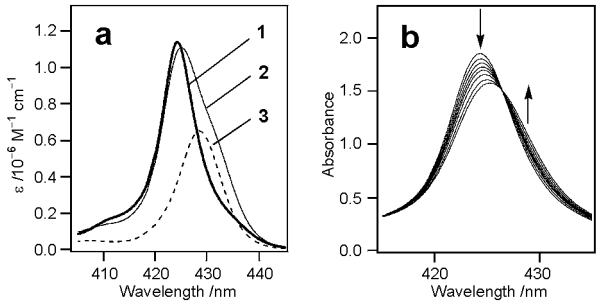


Figure 1. (a) Electronic absorption spectra of **1**−**3**, and (b) absorption spectral changes of **1** upon addition of increasing amounts of **HV** (0, 0.30, 0.70, 0.90, 1.2, 1.5, 2.5, and 5.0 μM; [**1**] = 1.5 μM) in $CHCl_3$/DMSO (10/1, v/v) at 293 K.

Table 1. Binding Constants of **1**−**3** for **HV** As Determined by Electronic Absorption (K_{abs}) and Fluorescence (K_{em}) Spectroscopy

compound	K_{abs}/M^{-1} [a]	K_{em}/M^{-1} [a]
1	546 000[b]	>1 000 000
2	4300[b]	3890[b]
3	1100[b]	2300[b]

[a] In $CHCl_3$/DMSO (10/1, v/v) at 293 K. [b] Errors are within 10%.

The shoulder in the monomer absorption region implies that the excitonic interaction is partially canceled due to the structural flexibility. On the other hand, the dimer **1** shows the narrow blue-shifted band, and, thus, bridging two porphyrin moieties by two diarylurea linkers yielded a tightly fixed cofacial structure.

The compounds **1**−**3** exhibited different binding abilities for **HV**. Adding increasing amounts of **HV** to solutions of **1**−**3** led to red shifts of the Soret absorption accompanying saturation behaviors with an isosbestic point due to the receptor−substrate complexation (Figure 1b). The stoichiometry for each complex was confirmed as 1:1 by either the molar ratio method or Job's analysis.[8] As summarized in Table 1, the binding constant K_{abs} of **1**·**HV** was much larger than those of **2**·**HV** and **3**·**HV**.[9] In the ^{1}H NMR spectra of the **2**·**HV** system, the signals assigned to the **HV**'s protons H^a, H^b, and H^c exhibited large complexation-induced shifts to the upfield due to ring-current anisotropy from the porphyrin π-planes, indicating that **HV** was bound to the cleft consisting of the two porphyrin moieties.[10] Taking it into consideration that **ZnTTolP**[11] did not form a complex with **HV** and that the increase of the diarylurea unit from **2** to **1** led to the increase of affinity to **HV**, charge-dipole interactions between **HV** and the two carbonyl groups in **1** directed into the inner of the cleft play an important role in the formation of the stable complex,[12] in addition to the electrostatic interaction between **HV** and well-organized porphyrin moieties.

The binding of **HV** was accompanied by fluorescence quenching of the porphyrin receptors. The fluorescence emission spectral

10.1021/ja0294717 CCC: $25.00

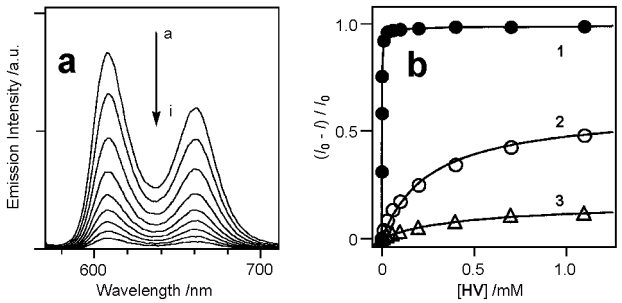


Figure 2. (a) Fluorescence emission spectra of **1** (1.5 μM) in the presence of varying concentrations of **HV** (a−i; 0, 0.30, 0.60, 0.90, 1.2, 1.5, 2.5, 3.0, 6.0 μM). (b) The fluorescence quenching profiles for **1·HV**, **2·HV**, and **3·HV** systems monitored at 608 nm. The emission spectra were obtained in $CHCl_3$/DMSO (10/1, v/v) at 293 K. λ_{ex} = 562 nm.

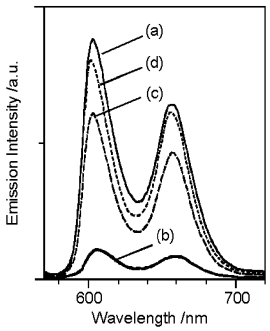
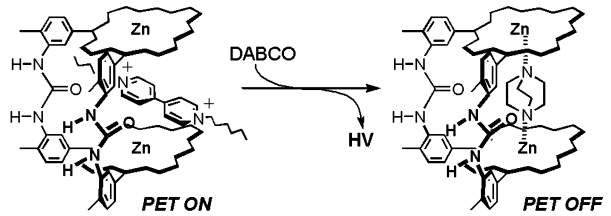


Figure 3. Fluorescence emission spectra of (a) **1**, (b) **1** + **HV** (3.0 μM), (c) **1** + **HV** (3.0 μM) + DABCO (15 μM), and (d) **1** + DABCO (15 μM) in $CHCl_3$/DMSO (10/1, v/v) at 293 K. [**1**] = 1.5 μM. λ_{ex} = 562 nm.

Scheme 1



changes of **1** upon addition of **HV** are shown in Figure 2. As the concentration of **HV** increased, the emission intensity of **1** was reduced due to PET from the porphyrin to **HV** (Figure 2a).[13] The spectral changes finally reached a plateau, indicating that the fluorescence quenching was induced by the complexation (Figure 2b). Although **2** and **3** also exhibited fluorescence quenching upon addition of **HV**, the quenching efficiency varied in the receptors. The binding constant K_{em} for each receptor obtained from the fluorescence spectral changes validly corresponded to K_{abs} (Table 1), and, therefore, the PET was exclusively facilitated by the complexation. It is interesting that the increase in magnitude of the binding constant led to the increase of the fluorescence quenching efficiency. Although the details are not clear at this point, the well-defined structure of **1** affording tight fixation of **HV** should give rise to correct donor−acceptor orientation.

The diarylurea linker also affords enough space between two porphyrin rings to bind 1,4-diazabicyclo[2.2.2]octane (DABCO) through two Zn−N coordination interactions.[7] Thus, the inhibitory control of the PET was examined by addition of DABCO to a solution containing **1** and **HV** (Figure 3). Although the fluorescence emission was suppressed by complexation with **HV**, the addition of DABCO led to recovery of the emission, indicating DABCO competes with **HV** to kick it away from the cleft of **1** (Scheme 1).[14] Indeed, in the ^{1}H NMR spectra, the **HV**'s signals returned to their original positions upon addition of DABCO, whereas DABCO's signal appeared at −4.76 ppm.

In summary, we developed a novel dual-mode porphyrinic receptor **1** that binds **HV** and DABCO in different manners. The PET from **1** to **HV** was facilitated by complexation and suppressed by substrate exchange with DABCO, and, thus, the supramolecular control of the PET was achieved.

Acknowledgment. This work was supported by a grant from the Iketani Science and Technology Foundation.

Supporting Information Available: Synthetic procedure for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Deisenhofer, J.; Michel, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 829. (b) Huber, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 848.
(2) (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: London, 1991. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (c) Osuka, A.; Nakajima, S.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1993**, *115*, 4577. (d) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849. (e) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996. (f) Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S.-C.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature* **1997**, *385*, 239. (g) Uosaki, K.; Kondo, T.; Zhang, X.-Q.; Yanagida, M. *J. Am. Chem. Soc.* **1997**, *119*, 8367. (h) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40. (i) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100.
(3) (a) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 10418. (b) Kuroda, Y.; Ito, M.; Sera, T.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 7003. (c) Hunter, C. A.; Shannon, R. J. *Chem. Commun.* **1996**, 1361. (d) Hayashi, T.; Ogoshi, H. *Chem. Soc. Rev.* **1997**, *26*, 355. (e) Ward, M. D. *Chem. Soc. Rev.* **1997**, *26*, 365. (f) Hu, Y.-Z.; Takashima, H.; Tsukiji, S.; Shinkai, S.; Nagamune, T.; Oishi, S.; Hamachi, I. *Chem.-Eur. J.* **2000**, *6*, 1907. (g) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855.
(4) (a) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, T. *J. Am. Chem. Soc.* **1991**, *113*, 6233. (b) Hayashi, T.; Miyahara, T.; Koide, N.; Kato, Y.; Matsuda, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1997**, *119*, 7281.
(5) (a) Gunter, M. J.; Hockless, D. C. R.; Johnston, M. R.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1994**, *116*, 4810. (b) Gunter, M. J.; Jeynes, T. P.; Johnston, M. R.; Turner, P.; Chen, Z. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1945.
(6) (a) Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477. (b) Kubo, Y.; Sugasaki, A.; Ikeda, M.; Sugiyasu, K.; Sonoda, K.; Ikeda, A.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2002**, *4*, 925. (c) Guldi, D. M.; Ros, T. D.; Braiuca, P.; Prato, M.; Alessio, E. *J. Mater. Chem.* **2002**, *7*, 2001.
(7) Yagi, S.; Yonekura, I.; Awakura, M.; Ezoe, M.; Takagishi, T. *Chem. Commun.* **2001**, 557.
(8) The stoichiometry was determined for **1·HV** by the molar ratio method using fluorescence emission spectroscopy and for **2·HV** and **3·HV** by Job's method using ^{1}H NMR.
(9) The binding constants were determined by the least-squares analyses of the absorbance changes according to a 1:1 complexation model.
(10) The complexation-induced shift of the protons H^a, H^b, and H^c is 0.92, 1.34, and 1.64 ppm upfield, respectively, in the 1:1 mixture of **2** and **HV** ([**2**] = [**HV**] = 1.0 mM in $CDCl_3$/DMSO-d_6 (10/1, v/v) at 293 K). In **1·HV**, the receptor-substrate association and dissociation was slow enough to afford broadening signals of **HV**'s protons, although the upfield shifts of H^a−H^c were observed.
(11) **ZnTTolP**: [5,10,15,20-tetrakis(*p*-tolyl)porphyrinato]zinc(II).
(12) Ong, W.; Gomez-Kaifer, M.; Kaifer, A. E. *Org. Lett.* **2002**, *4*, 1791.
(13) PET from porphyrins to viologens have been well known: (a) Akins, D. L.; Zhu, H.-R.; Guo, C. *J. Phys. Chem.* **1993**, *97*, 8681. (b) Hayashi, T.; Takimura, T.; Ogoshi, H. *J. Am. Chem. Soc.* **1995**, *117*, 11606. (c) Kaganer, E.; Joselevich, E.; Willner, I.; Chen, Z.; Gunter, M. J.; Gayness, T. P.; Johnson, M. R. *J. Phys. Chem. B* **1998**, *102*, 1159.
(14) The K_{abs} for **1**·DABCO was determined as 695 000 M^{-1} (error 8.4%).

JA0294717