

Antenna functions of 5,15-bis(imidazol-4-yl)-10,20-bis(4-dodecyloxyphenyl)-porphyrin supramolecular assembly through imidazole–imidazole hydrogen bonding†

Naoto Nagata, Shin-ichi Kugimiya and Yoshiaki Kobuke*

Graduate School of Materials Science, Nara Institute of Science and Technology, CREST, Japan Science and Technology Corporation (JST), 8916-5 Takayama, Ikoma City, 630-0101, Japan. E-mail: kobuke@ms.aist-nara.ac.jp

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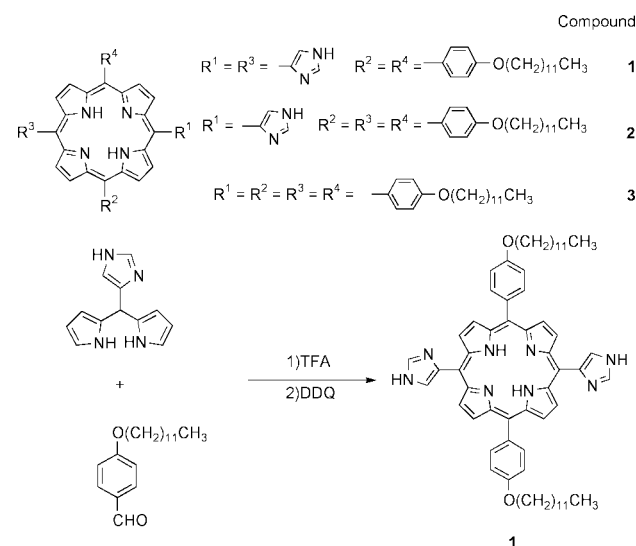
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The title bis(imidazol-4-yl)porphyrin **1** gave supramolecular assemblies through hydrogen bonding; efficient excited energy transfer followed by electron transfer to quenchers has been observed in toluene.

Chromophore assemblies play important roles in light-harvesting antenna functions of photosynthesis. In bacterial antenna complexes, 18^{1a} or 16^{1b} bacteriochlorophylls are arranged in a macro-ring with slipped cofacial structures by coordination of imidazolyl side chains from transmembrane α -helices in B850,^{1a,b} and 9^{1a} or 8^{1b} bacteriochlorophylls are arranged in a macro-ring of coplanar orientation in B800.^{1a,b} In contrast to these well-organized structures in bacterial antennae, antenna complexes from plant sources are more or less disordered.^{1c} In both cases the arrangements are provided by non-covalent interactions, and supramolecular assembly formation by hydrogen bonding and metal-to-ligand coordination is thought to be a promising way to achieve the construction of artificial antenna models.^{2,3}

In this communication, we introduce the use of bis(imidazol-4-yl)porphyrin **1** to mimic light-harvesting antenna function by supramolecular assembly formation through hydrogen bonds between imidazol-4(5)-yls substituted at two facing *meso* positions of the porphyrin ring.⁴ 5,15-Bis(imidazolyl)porphyrin **1** was prepared conventionally⁵ from imidazol-4(5)-yl-2,2'-dipyrrylmethane and 4-dodecyloxybenzaldehyde as shown in Scheme 1.

The ¹H NMR spectrum of **1** in CDCl₃ gave broad peaks, which were sharpened gradually by the addition of CD₃OD.



Scheme 1 Preparation of bis(4-imidazolyl)porphyrins.

† Electronic supplementary information (ESI) is available: experimental details and ¹H NMR of **1** in CDCl₃. See <http://www.rsc.org/suppdata/cc/b0/b003267k/>

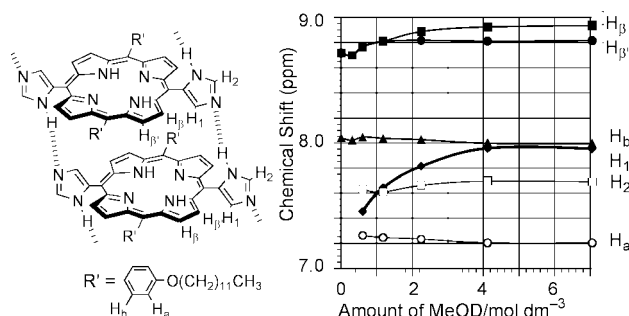


Fig. 1 NMR Titration of **1** (4 mmol dm⁻³) in CDCl₃ with CD₃OD at 20 °C.

Fig. 1 shows the titration behaviour of the imidazolyl, pyrrolic and aromatic protons. The characteristic up-field shift with decreasing CD₃OD concentration was observed most specifically at the *meso*-imidazol-4-yl proton (H₁),⁶ and less significantly at one of the β -pyrrolic protons (H _{β}). Other peaks were insensitive to CD₃OD addition. The shift behaviour is accounted for by the breaking of hydrogen bonds between imidazolyl substituents by the addition of CD₃OD. The selective shielding of the H₁ proton compared to H₂ in the aggregate suggests that H₁ is brought above the facing porphyrin plane by hydrogen bond formation between imidazolyl substituents of different porphyrins. Therefore, the slipped cofacial arrangement **1** is proposed as the structural unit of hydrogen bonded porphyrin rather than the head-to-tail one. The former orientation can be stabilized by cooperative interaction of maximal hydrogen bonds of imidazolyls and π -stacking of porphyrins and is thought to be the more stable. In accord with this orientation, the H _{β} proton received the second largest up-field shift with decreasing CD₃OD concentration. In contrast, monoimidazolyl-substituted porphyrin **2**, gave quite a normal NMR spectrum without any specific shielding or peak broadening.

This porphyrin–porphyrin interaction is sensitively reflected in their UV spectra. Characteristics of the Soret band of **1** are compared with those of mono- and non-imidazolyl substituted porphyrins **2** and **3**, respectively, in Table 1. The half bandwidth of **1** (29 nm) in a CHCl₃ solution (free from EtOH) is significantly broadened compared with that of **2** (16 nm) at the same concentration in the same solvent. A further broadening is

Table 1 Comparison of absorption spectral characteristics of **1** and porphyrin analogs in various solvents

Compound	λ_{\max} (Half band width)/nm			
	MeOH	CHCl ₃ ^a	Toluene	Cyclohexane
1	418(24)	424(29)	426(34)	426(84)
2	419(16)	424(16)	424(16)	422(18)
3	421(13)	420(13)	420(13)	420(13)

[porphyrin] = 1.6 μ mol dm⁻³; ^a EtOH free, CHCl₃ was used.

Table 2 Comparison of fluorescence intensities of **1** in various solvents

Compound	Relative intensity at peak maximum (λ_{\max}/nm)			
	MeOH	CHCl ₃ ^a	Toluene	cyclohexane
1	507 (662)	442 (668)	428 (669)	36 (664)

[**1**] = 1.6 $\mu\text{mol dm}^{-3}$; ^a EtOH free, CHCl₃ was used.

observed in toluene for **1**, but there is observed solvent dependence in the halfwidth of the Soret band observed for **2**. This behaviour is explained by exciton coupling theory for two porphyrin chromophores in a slipped cofacial orientation,⁷ where two transition moments interact in face-to-face and parallel orientations to give rise to blue and red shifts, respectively. The peak splitting could not be observed in the present case and the overall spectral maxima shifted to longer wavelengths. The increased broadening of Soret bands of **1** in increasingly less polar solvents was incompatible with the idea that they contained split absorptions as components. In the case of **3**, having no hydrogen bonding group, no solvent dependence was observed for MeOH, CHCl₃ and toluene either for absorption maxima or half bandwidths. Monoimidazolyl-substituted porphyrin **2** seemed to be too weak to interact significantly in this fashion and showed behaviour similar to unsubstituted porphyrin **3** in the range 2×10^{-3} – 4 mmol dm^{-3} . This may suggest the cooperation of hydrogen bonds and π -stacking interaction in the present supramolecular structure formation.⁸ Interestingly, the fluorescence intensity of bis(imidazolyl)porphyrin **1** remained almost constant for the change of solvent from MeOH to toluene as shown in Table 2. This result indicates that bis(imidazolyl)porphyrin **1** in the supramolecular assembly showed no significant self-quenching by supramolecular complex formation.

In order to obtain direct evidence of assembly formation, the toluene solution of **1** was analyzed by static light scattering at 26 °C. From a Zimm plot⁹ of the data obtained at 3.3, 6.6, 9.9 and 13 $\mu\text{mol dm}^{-3}$, the radius of gyration was estimated as 23 nm. Although the molecular weight could not be obtained because the refractive indices of the solution and pure solvent were too close, we could observe particles from **1** in similarly dilute concentrations (3.3–13 $\mu\text{mol dm}^{-3}$) in toluene.

The efficiency of energy–electron transfer from the assembly to external acceptors was estimated by fluorescence quenching experiments. Stern–Volmer plots for two acceptor molecules, chloranil and tetraphenylporphyrinatoMn(III) chloride (CIMntpp) in toluene, are illustrated in Figs. 2a and b, respectively, together with the plot obtained by using non-imidazolyl substituted porphyrin **3** as the reference.

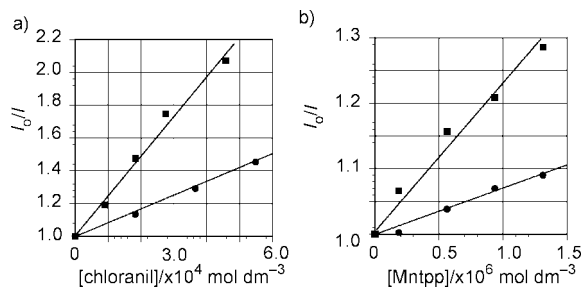
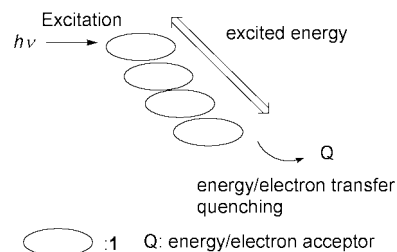


Fig. 2 Stern–Volmer plots for **1** (1.6 $\mu\text{mol dm}^{-3}$, ■) and **3** (1.6 $\mu\text{mol dm}^{-3}$, ●) with (a) chloranil and (b) CIMntpp in toluene.

Chloranil quenched the fluorescence of **1** 2.9 times faster than that of **3**. This result suggests that the supramolecule **1** is a more efficient energy–electron donor than the monomeric species. There is a possibility, however, that chloranil becomes a better acceptor through the formation of a hydrogen bonded complex with the imidazolyl part of **1**, but not with **3**. This possibility was excluded by experiment: CIMntpp, having no hydrogen bond site, quenched the fluorescence of **1** more efficiently than that of **3** by the same factor of 2.9. The possibility that **1** specifically interacts with CIMntpp through coordination of an imidazolyl



Scheme 2 Excitation energy storage in supramolecular bis(imidazolyl)porphyrin assembly.

group to Mn was safely excluded by there being no shift of the Soret band of CIMntpp, in accord with the small coordination equilibrium constant reported for imidazole and CIMntpp.⁸ A possible explanation for efficient energy transfer and/or electron transfer from the supramolecule may be based on the idea that the excitation energy is delocalized over the whole supramolecule and transferred to acceptors from any components of the supramolecule as in the oxinylporphyrin.¹⁰ These results establish the usefulness of the supramolecular porphyrin assembly as a mimic of the energy storage function of light harvesting antenna complexes (see Scheme 2).

In conclusion, imidazolyl porphyrin is a useful component for obtaining porphyrin assemblies, not only through hydrogen bonding but also by metal coordination.³ Further applications for bis(imidazolyl)porphyrin **1** and its derivatives are now under active investigation.

Notes and references

- (a) G. McDermott, S. M. Prince, A. A. Free, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell and N. W. Isaacs, *Nature*, 1995, **374**, 517; (b) J. Koepke, X. Hu, C. Muenke, K. Schulten and H. Michel, *Structure*, 1996, **4**, 581; (c) W.-D. Schubert, O. Klukas, N. Krauss, W. Saenger, P. Fromme and H. T. Witt, *J. Mol. Biol.*, 1997, **272**, 741.
- J. L. Sessler, B. Wang, S. L. Spring and C. T. Brown, in *Comprehensive Supramolecular Chemistry*, ed. Y. Murakami, Pergamon, UK, 1996, vol. 4, ch. 9, pp 311 and references therein; J. L. Sessler, C. T. Brown, D. O'Connor, S. L. Springs and R. Wang, *J. Org. Chem.*, 1998, **63**, 7370 and references therein; A. Osuka, R. Yoneshima, H. Shiratori, T. Okada, S. Taniguchi and N. Mataga, *Chem. Commun.*, 1998, 1567; C. Ikeda, N. Nagahara, E. Motegi, N. Yoshioka and H. Inoue, *Chem. Commun.*, 1999, 1759; Y. Aoyama, T. Kamohara, A. Yamagishi, H. Toi and H. Ogoshi, *Tetrahedron Lett.*, 1987, **28**, 2143; X. Chi, A. J. Guerin, R. A. Haycock, C. A. Hunter and L. Sarson, *Chem. Commun.*, 1995, 2567; R. T. Stibrany, J. Vasudevan, S. Knapp, J. A. Potenza, T. Emge and H. J. Schugar, *J. Am. Chem. Soc.*, 1996, **118**, 3980; R. K. Kumar, S. Balasubramanian and I. Goldberg, *Chem. Commun.*, 1998, 1435; T. Miyatake, H. Tamiaki, A. R. Holzwarth and K. Schaffner, *Photochem. Photobiol.*, 1999, **69**, 448; S. Knapp, B. Huang, T. J. Emge, S. Sheng, K. Krgh-Jespersen, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, 1999, **121**, 7977.
- Supramolecular assemblies of imidazolylporphyrin: Y. Kobuke and H. Miyaji, *J. Am. Chem. Soc.*, 1994, **116**, 4111; Y. Kobuke and H. Miyaji, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3563.
- Strong hydrogen bondings and π stacking of imidazol-2-yl substituted Pd porphyrins and their proton conductivity have been reported in the solid state: L. R. Milgrom, S. Bone, D. W. Bruce and M. P. Macdonald, *J. Mol. Electronics*, 1991, **7**, 95.
- C.-H. Lee and J. S. Lindsey, *Tetrahedron*, 1984, **39**, 11427.
- The imidazolyl H₁ and H₂ protons were assigned unequivocally by observing the ¹H ¹³C COSY spectrum, where N–CH=C and N–CH=N carbons appeared at 135 and 120 ppm, respectively.
- M. Kasha, H. R. Rawls and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371.
- The coordination equilibrium constant K_{eq} between imidazole and CIMntpp is reported in S. Banfi, F. Montaniri and S. Quici, *J. Org. Chem.*, 1989, **54**, 1850 as $182 \pm 15 \text{ mol}^{-1} \text{ dm}^3$ in CH₂Cl₂ at 25 °C. Contribution of possible coordination species is calculated as less than 0.1% of free [CIMntpp].
- B. H. Zimm, *J. Chem. Phys.*, 1948, **16**, 1099.
- I. V. Rubtsov, Y. Kobuke, H. Miyaji and K. Yoshihara, *Chem. Phys. Lett.*, 1999, **308**, 323. Another possibility was suggested by a referee, who pointed out that lowering of S₁ or even S₀ could affect either the pre-exponential or Marcus like terms and mediate the rate favourably. Photophysical studies may address the mechanism and will be reported elsewhere.