

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

# Control of the Conformational Dynamics of *meso-meso* Vinylene-bridged Zn(II) Porphyrin Dimers through Diamine Coordination

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

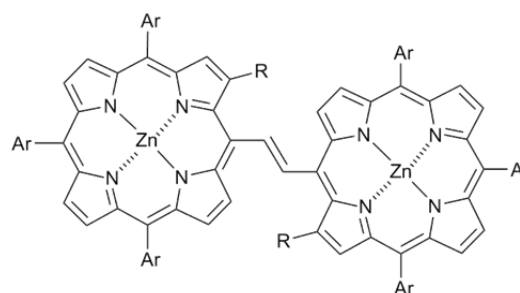
www.rsc.org/

Minjung Son,<sup>a</sup> Young Mo Sung,<sup>a</sup> Sumito Tokuji,<sup>b</sup> Norihito Fukui,<sup>b</sup> Hideki Yorimitsu,<sup>b</sup> Atsuhiko Osuka,<sup>\*b</sup> and Dongho Kim<sup>\*,a</sup>

Two *meso-meso* vinylene-bridged Zn(II) porphyrin dimers **1** and **2** were analyzed in terms of the control of their conformational dynamics induced by the rotation around the double bond bridge. The dihedral angles between the two porphyrin rings were modulated through coordination with  $\alpha,\omega$ -diaminoalkanes of varying chain lengths.

There have been strenuous efforts to unravel the mechanism and dynamics of conformational alteration in double-bond linked  $\pi$ -conjugated systems over decades, stemming from the spectroscopic studies on the *cis-trans* photoisomerization of stilbene, one of the simplest  $\pi$ -conjugated molecules known with rotating double bond linkage in the excited state.<sup>1</sup> Especially, a careful control of these conformational dynamics has recently become a subject of considerable attention, which bears significance in that this controllability, or even photo-switchability, can serve as a milestone for molecular robots or molecular switches.<sup>2</sup> As porphyrins have been extensively investigated as one of the most outstanding building blocks of conjugated molecular arrays due to their potential application in artificial photosynthesis and nonlinear optical materials,<sup>3</sup> an attempt to link two porphyrin molecules with a vinylene bridge has also been made.<sup>4</sup>

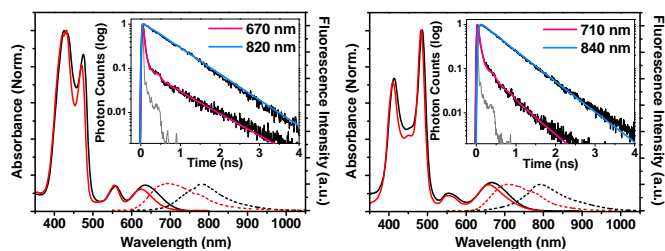
Although it is already known from the UV/Vis absorption and X-ray crystallographic studies that there exists a distribution in the dihedral angles between the porphyrin moieties, *meso-meso* porphyrin dimers linked through a vinylene bridge have remained largely unexplored so far,<sup>4,5</sup> in contrast to its *meso-meso* directly-linked<sup>6a-c</sup> and butadiyne-linked<sup>6d</sup> counterparts. In this context, we have prepared two *meso-meso* vinylene-bridged Zn(II) porphyrin dimers **1** and **2** (Chart 1)<sup>5b</sup> and focused on the control of their rotational dynamics around the double bond bridge by steady-state and time-resolved spectroscopic techniques.



**Chart 1** Molecular structures of Zn(II) porphyrin dimers **1** and **2**. R = H for **1** and 3,5-dimethylphenyl for **2**. The aryl substituents, Ar, are 3,5-di-*tert*-butylphenyl.

In particular, the possibility of a systematic modulation of the dihedral angles has been sought by introducing simple bidentate ligands of varying carbon chain lengths,  $\alpha,\omega$ -diaminoalkanes (*nDA*,  $n = 3, 4, \dots, 10, 12$ ).<sup>7</sup>

The UV/Vis absorption and fluorescence spectra of **1** and **2** measured at room temperature are shown in Fig. 1. In the absorption spectra, a splitting of Soret bands is observed due to the excitonic dipole-dipole coupling<sup>8</sup> between the porphyrin moieties. Red-shifted Q bands and fluorescence emission spanning the near-infrared region as compared to those of a *meso-meso* directly-linked dimer<sup>6a-c</sup> imply an effective  $\pi$ -conjugation of the systems through the mediation of the vinylene bridge, **2** being even more red-shifted owing to the more effective conjugation by the introduction of  $\beta$ -aryl groups.<sup>5b</sup> Interestingly, unlike previously reported porphyrin arrays,<sup>6</sup> both **1** and **2** showed extremely broad and structureless fluorescence emission with very large Stokes shift values of 2711 and 2312  $\text{cm}^{-1}$ , respectively. This implies the high flexibility of the vinylene bridge, which can rotate to give rise to numerous conformations with a range of dihedral angles between the two porphyrin rings.<sup>5a,9</sup> The relatively small Stokes shift of **2** compared to **1**



**Fig. 1** Steady-state absorption (solid line) and fluorescence (dashed line) spectra of **1** (left) and **2** (right) in toluene (black) and paraffin oil (red). Insets show the fluorescence decay profiles ( $\lambda_{\text{exc}} = 470$  nm) measured at indicated wavelengths, and the instrumental response functions are represented by the gray traces.

can be regarded as a result of the  $\beta$ -aryl substitution, which restrains the free rotation of the porphyrin cores to some extent.<sup>4,5b</sup>

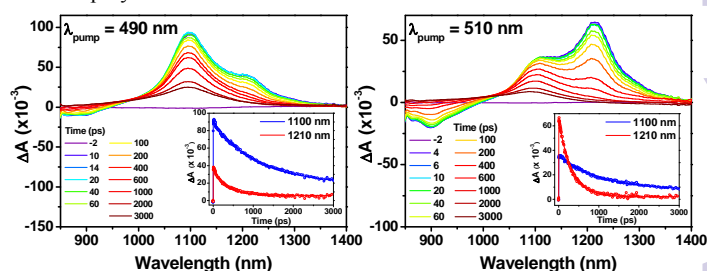
Viscosity-controlled steady-state fluorescence spectra and fluorescence decay profiles further corroborate the existence of a fast rotational dynamics. While there was almost no difference between the absorption spectra measured in toluene and in a viscous medium (paraffin oil), a remarkable blue-shift was observed in the fluorescence spectra with increasing viscosity and accordingly the Stokes shifts of **1** and **2** were greatly reduced to 1533 and 768  $\text{cm}^{-1}$ , respectively. The fluorescence decay profiles (insets in Fig. 1) of both compounds measured in toluene exhibited fast decay components of  $\sim 30$  ps for **1** and  $\sim 45$  ps for **2** when monitored near the onset of the fluorescence (670 and 710 nm, respectively) and the corresponding rise components at longer wavelengths (820 and 840 nm, respectively), followed by the singlet excited-state lifetimes of 870 and 550 ps, respectively (See Table S1 in ESI for the fitted decay parameters). This suggests that upon photoexcitation, one conformer with a twisted geometry, which originally fluoresces at red wavelengths in the visible region, undergoes conformational change into a more planar conformer that emits at near-infrared region within several tens of picoseconds.<sup>6d</sup> The exact time constants for the shorter components were confirmed by femtosecond transient absorption (TA) measurements in the visible region (Fig. S1 in ESI) and were in excellent agreement with those acquired in the time-resolved fluorescence experiments. Furthermore, we could observe spectral shifts of the ground-state bleaching (GSB) signals in the TA spectra of both molecules; the Q bands with peaks at  $\sim 670$  (**1**) and 690 nm (**2**) at shorter time delays evolved into blue-shifted Q bands whose peaks are located at  $\sim 635$  (**1**) and 665 nm (**2**), as previously seen in the steady-state absorption spectra. The fluorescence decay profiles measured in paraffin oil (Fig. S2 in ESI) were also fitted into a biexponential decay, but the faster components became significantly slower (300 and 150 ps, respectively) without much affecting the singlet excited-state lifetimes, indicating that the conformational dynamics is hindered. It is worthwhile to note that whereas the fast decay and rise components of **1** became almost tenfold ( $\sim 30$  to  $\sim 300$  ps) longer, those of **2** were less affected (45 to 150 ps). This again points to our previous finding that the existence of bulky substituents at the beta positions already imposes some steric hindrance and therefore restriction on the free rotation of the molecule.

While the conformational change by the rotational dynamics was merely slowed down with the increase in viscosity, it was found out that the molecules were completely frozen into certain dominant conformations at low temperature (Fig. S3 in ESI). **1** and **2** shared the overall spectral changes as the temperature was lowered from 297 to 77

K, in which progressive red-shifts and sharpening of the lower-energy Soret and Q bands were observed along with blue-shifts of the fluorescence bands, giving rise to the extremely reduced Stokes shift values of 480 and 517  $\text{cm}^{-1}$ , respectively. It is notable that the fluorescence emission spectra recover their vibronic structures at low temperature, which is in sharp contrast to the broad structureless fluorescence spectra observed at 297 K.

Despite these similarities, **2** revealed one striking difference from **1** in that a new absorption peak at  $\sim 900$  nm appeared along with an unprecedented sharp Soret band at 510 nm. Moreover, a corresponding weak fluorescence peak at  $\sim 950$  nm (See Fig. S4 in ESI for enlarged spectra) was resolved from the main emission band at 650 – 900 nm. This is presumably due to the coexistence of two dominant conformers depending on whether the two beta substituents are situated close to or apart from each other,<sup>5b</sup> even at sufficiently low temperatures.<sup>4</sup> Regardless of the observing wavelengths, the fluorescence decay profiles (insets in Fig. S3) of both **1** and **2** at 77 K were fitted into a monoexponential decay with the time constants of 1.5 and 1.4 ns, respectively, suggesting that the rotational motion around the double bond was completely blocked at 77 K.

In order to further elucidate the photophysical differences between the two conformers of **2**, we have examined the TA spectra at the near-infrared ( $\sim 850 - 1400$  nm) region at 77 K (Fig. 2), which enables us to directly probe the NIR fluorescence which is appreciably present only at low temperature. Two pump wavelengths of 490 nm and 510 nm were employed for selective excitation of each conformer.



**Fig. 2** Near-infrared TA spectra of **2** measured in 2-mTHF at 77 K using the pump wavelength of 490 (left) and 510 nm (right), respectively. Insets show the fitted decay profiles probed at 1100 (blue) and 1210 nm (red).

The spectra showed negative stimulated emission (SE) signals up to  $\sim 1000$  nm and strong excited-state absorption (ESA) signals with two moderately broad peaks at 1100 and 1210 nm without any spectral shifts, which is in sharp contrast to the TA spectra at 297 K (Fig. S5 in ESI). Interestingly, when the pump wavelength was changed from 490 to 510 nm, the relative intensities of the ESA signals at 1100 and 1210 nm were reversed at 77 K, accompanied by the great difference in the fitted time constants at each peak (350 ps at 1210 nm and 1.2 ns at 1100 nm). From these results, we can conclude that the primary excited species at 510 nm is the more planar, or more conjugated, conformer of **2** with smaller HOMO-LUMO energy gap and thus shorter lifetime,<sup>10</sup> and this is the origin of the extraordinary Q band at  $\sim 900$  nm.

For a more elaborate control of the dihedral angles between the two porphyrin rings under ambient conditions, **1** and **2** were titrated with *n*DA (Fig. 3) and the UV/Vis absorption and fluorescence emission spectra of the resultant complexes (**1-nDA**, **2-nDA**) were recorded. Job's plot indicates a 1:1 molecular ratio for the formation of the complexes (Fig. S6 in ESI). Interestingly, completely different trends

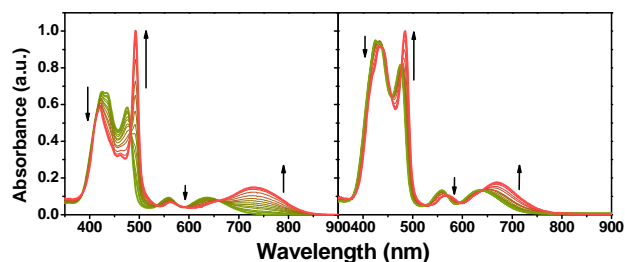


Fig. 3 UV/Vis titration of **1** with 1,7-diaminoheptane (**7DA**, left) and 1,10-diaminodecane (**10DA**, right).  $[1] = 2.06 \times 10^{-6}$  M,  $[7DA] = [10DA] = 2.1 \times 10^{-6}$  M.

were observed depending on the length of the diamine ligands (Figs. S7-8 and Table S2 in ESI).

The most remarkable spectral changes were observed for coordination with **7DA** for both **1** and **2**. The absorption spectra much resembled their UV/Vis spectra measured at low temperature: the lower-energy Soret bands were greatly sharpened and red-shifted with considerable increase in intensity, and the Q bands were also prominently red-shifted by 2081 and 2000  $\text{cm}^{-1}$ , respectively. On the contrary, for shorter ligands ( $n = 3 - 6$ ), the overall absorption exhibited no significant change except for only slight red-shifts, which might be the result of only one-side complexation of the ligands.<sup>6b, 11</sup> A similar trend was observed for longer ligands ( $n = 9, 10$  and  $12$ ). In the case of **2**, upon complexation with **5-**, **6-**, and **7DA** ligands, a gradual growth in a previously unseen Q-like band in the near-infrared region was observed, just as in the absorption spectrum at 77 K (Fig. S8 in ESI). This can be interpreted as an enforced formation of a more conjugated conformer by the steric confinement induced by the diamine ligands.

Meanwhile, the fluorescence emission spectra of the diamine-coordinated complexes could be analyzed in a very similar fashion to their absorption spectra. Overall, the spectra were red-shifted to the infrared region and the Stokes shifts were gradually decreased in all species upon coordination with **nDA**, converging to the most decreased values observed for **7DA** complexes (1850  $\text{cm}^{-1}$  for **1** and 1261  $\text{cm}^{-1}$  for **2**). From this result we can assume that the dihedral angles between the two porphyrin moieties are confined to a certain extent, and the optimal length of the diamine ligand for an effective control of their conformational dynamics is seven methylene groups for both **1** and **2**. On the other hand, considering that the Stokes shift values for  $n = 3 - 6$  had only very little difference (less than 300  $\text{cm}^{-1}$ ) from those of uncoordinated species, we can conjecture that these diamines are too short in length and therefore not suitable for imposing conformational confinements unless the dimers are in an extremely twisted, almost *cis*-like conformation. Similarly, relatively large Stokes shift values were maintained for **9-**, **10-** and **12DA** complexes, suggesting that these long ligands are still able to bind to the two zinc metal centers without exerting sufficient conformational inhibition on them.

In summary, we have illustrated the control of the conformations in two *meso-meso* vinylene-linked Zn(II)porphyrin dimers induced by the rotation around the vinylene bridge. Steady-state and time-resolved spectroscopic results strongly indicate that there exists a fast excited-state dynamics involving the facile rotational motion around the vinylene bridge. Also, it is revealed that the dihedral angles of these flexible dimers can easily be modulated by simple chemical modification without going to rather extreme conditions by employing a viscous medium or lowering the temperature.

The work at Yonsei was financially supported by the Mid-career Researcher Program (2005-0093839) and Global Research Laboratory (2013K1A1A2A02050183) administered through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST). The work at Kyoto was supported by Grant-in-Aid from MEXT (grant number 25220802 (S)) for Scientific Research. S.T. acknowledges a JSPS fellowship for Young Scientists.

## Notes and references

<sup>a</sup> Department of Chemistry, Yonsei University, Seoul 120-749, Korea.

E-mail: dongho@yonsei.ac.kr; Fax: +82 2-2123-2434;

Tel: +82 2-2123-2652

<sup>b</sup> Department of Chemistry and Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.

E-mail: osuka@kuchem.kyoto-u.ac.jp; Fax: +81-75-753-3970;

Tel: +81 75-753-4008

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

- (a) B. I. Greene, R. M. Hochstrasser and R. B. Weisman, *Chem. Phys. Lett.*, 1979, **62**, 427; (b) D. H. Waldeck, *Chem. Rev.*, 1991, **91**, 415.
- (a) D. Holten, D. F. Bocian and J. S. Lindsey, *Acc. Chem. Res.*, 2002, **35**, 57; (b) T. Hirose, F. Helmich and E. W. Meijer, *Angew. Chem. Int. Ed.*, 2013, **52**, 304.
- (a) *Handbook of Porphyrin Science Vol. 1-25*, ed. K. M. Kadish, K. M. Smith and G. Guilard, World Scientific, Singapore, 2010; (b) *Multiporphyrin Arrays. Fundamentals and Applications*, ed. D. Kim, Pan Stanford Publishing Pte. Ltd., Singapore, 2012.
- O. Locos, B. Bašić, J. C. McMurtrie, P. Jensen and D. P. Arnold, *Chem. Eur. J.*, 2012, **18**, 5574.
- (a) M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, J. E. Slagle, P. A. Fleitz, M. Drobizhev, A. Rebane and H. L. Anderson, *Org. Lett.*, 2005, **7**, 5365; (b) S. Tokuji, H. Awane, H. Yorimitsu and A. Osuka, *Chem. Eur. J.*, 2013, **19**, 64.
- (a) N. Yoshida, T. Ishizuka, A. Osuka, D. H. Jeong, H. S. Cho, D. Kim, Y. Matsuzaki, A. Nogami and K. Tanaka, *Chem. Eur. J.*, 2003, **9**, 58; (b) H. Shinmori, T. K. Ahn, H. S. Cho, D. Kim, N. Yoshida and A. Osuka, *Angew. Chem. Int. Ed.*, 2003, **42**, 2754; (c) S. Cho, M.-C. Yoon, J. M. Lim, P. Kim, N. Aratani, Y. Nakamura, T. Ikeda, A. Osuka and D. Kim, *J. Phys. Chem. B*, 2009, **113**, 10619; (d) M. U. Winters, J. Kärnbratt, M. Eng, C. J. Wilson, H. L. Anderson and Bo Albinsson, *J. Phys. Chem. C*, 2007, **111**, 7192.
- (a) M. Nappa and J. Valentine, *J. Am. Chem. Soc.*, 1978, **100**, 5075; (b) C. A. Hunter, M. N. Meah and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1988, **11**, 694.
- M. Kasha, H. R. Rawls and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371.
- (a) M. Chachisvilis, V. S. Chirvony, A. M. Shulga, B. Källebring, S. Larsson and V. Sundström, *J. Phys. Chem.*, 1996, **100**, 13857; (b) M. Chachisvilis, V. S. Chirvony, A. M. Shulga, B. Källebring, S. Larsson and V. Sundström, *J. Phys. Chem.*, 1996, **100**, 13867.
- R. Englman and J. Jortner, *Mol. Phys.*, 1970, **18**, 145.
- B. R. Danger, K. Bedient, M. Maiti, I. J. Burgess and R. P. Steer, *J. Phys. Chem. A*, 2010, **114**, 10960.