

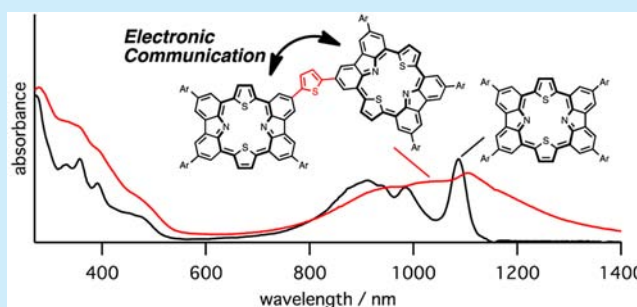
## Intramolecular Electronic Coupling in the Thiophene-Bridged Carbazole-Based Diporphyrin

Chihiro Maeda,\*<sup>1</sup> Mototsugu Takata, Asami Honsho, and Tadashi Ema\*

Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

## Supporting Information

**ABSTRACT:** The Glaser coupling reaction of ethynyl-substituted carbazole-based isophlorins provided butadiyne-bridged dimers, which were transformed into the thiophene-bridged dimers via the annulation reaction. Oxidation of these isophlorin dimers afforded carbazole-based diporphyrins. Notable electronic interactions in the diporphyrins have been confirmed by means of UV/vis–near-infrared (NIR) absorption spectroscopy, cyclic voltammetry (CV) measurements, and density functional theory (DFT) calculations.

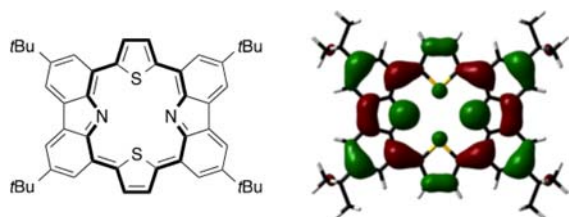


Porphyrin arrays have been extensively studied with the aim of mimicking natural photosynthesis since the structures of light harvesting complexes were determined.<sup>1,2</sup> In particular, various porphyrin dimers have been synthesized to investigate the electronic communications between the chromophores.<sup>3</sup> Direct connections and butadiyne linkages have often been employed because the strong electronic interactions have been observed. In addition, such interactions in the diporphyrins depend on the connecting positions (*meso* or  $\beta$ ). Development of novel porphyrinoids such as core-modified porphyrins,<sup>4</sup> ring-expanded porphyrins,<sup>5</sup> and fused porphyrins<sup>6</sup> is intriguing because of the unique and unexpected properties. Oligomerization of such porphyrinoids has also been investigated.<sup>7</sup> Such  $\pi$ -extended porphyrins often show near-infrared (NIR) absorption and are useful for photodynamic therapy (PDT) and solar energy conversion, while organic dyes absorbing light in wavelength of around 1200 nm or more are very few.

Previously, we reported the synthesis of carbazole-based porphyrins as novel fused porphyrinoids. These porphyrins exhibited strong NIR absorption due to the quadruple benzo-fusion effects (Figure 1).<sup>8,9</sup> The highest occupied molecular orbital (HOMO) exhibits large electronic coefficients on both thiophene and carbazole moieties, and efficient substituent effects

have been observed at the  $\beta$ -positions of thiophene and 3,6-positions of carbazole units.<sup>8c,f,g</sup> Here, we report the synthesis of carbazole-based diporphyrins with the butadiyne or thiophene linkages at the thiophene or carbazole moieties. This is the first example of carbazole-based diporphyrins. The photophysical properties of the diporphyrins were investigated by UV/vis/NIR absorption spectroscopy and DFT calculations. The electronic interactions between the chromophores depend on both the connecting positions and spacers, and the diporphyrin with thiophene spacer at the carbazole moieties was found to show the strong electronic communications.

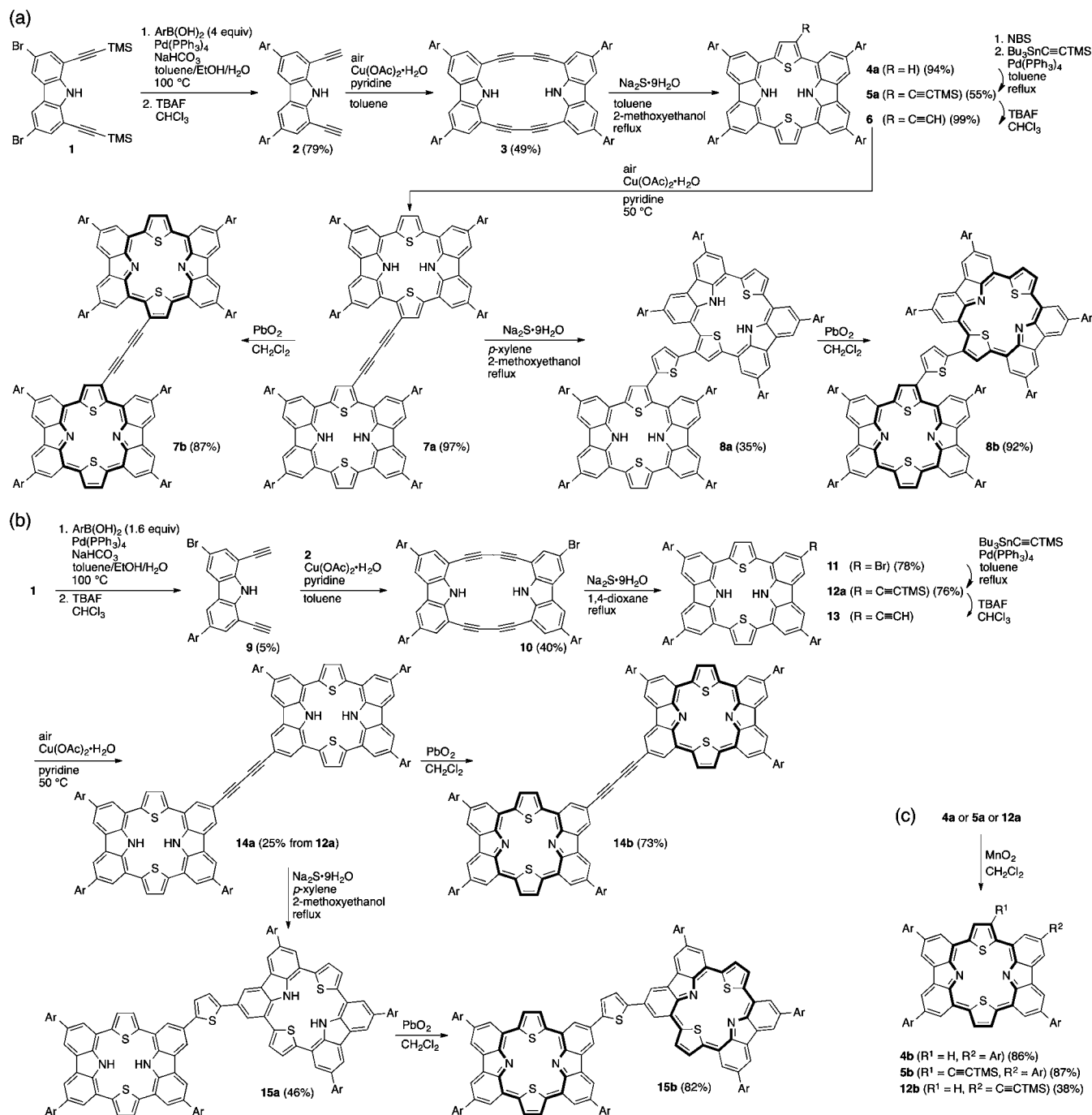
Synthetic routes to the diporphyrins are shown in Scheme 1. Here, 3,5-di-*tert*-butylphenyl groups were newly introduced into the carbazole moieties as a solubilizing group. The Suzuki–Miyaura coupling reaction of 3,6-dibromo-1,8-bis-(trimethylsilylethynyl)carbazole (**1**) with 4 equiv of the arylboronic acid and the subsequent trimethylsilyl deprotection provided diethynylcarbazole **2**. The Glaser coupling reaction of **2** provided cyclic carbazole dimer **3**. Annulation reaction of **3** with Na<sub>2</sub>S produced carbazole-based isophlorin **4a**. The bromination of **4a** with 1.3 equiv of NBS and the subsequent Stille coupling reaction provided trimethylsilylethynyl substituted isophlorin **5a** in 55% yield. The trimethylsilyl deprotection of **5a**, followed by the Glaser coupling reaction of **6** afforded butadiyne bridged isophlorin dimer **7a**. The oxidation of **7a** produced the diporphyrin **7b**. Alkyne moieties can be converted into various heterocycles<sup>10</sup> so that we tried the annulation reaction of butadiyne-bridged dimer **7a**. The reaction of **7a** with Na<sub>2</sub>S and the subsequent oxidation of **8a** afforded thiophene-bridged diporphyrin **8b**.



**Figure 1.** Structure and HOMO (calculated at the B3LYP/6-31G\* level) of the carbazole-based diporphyrin.

**Received:** October 11, 2016

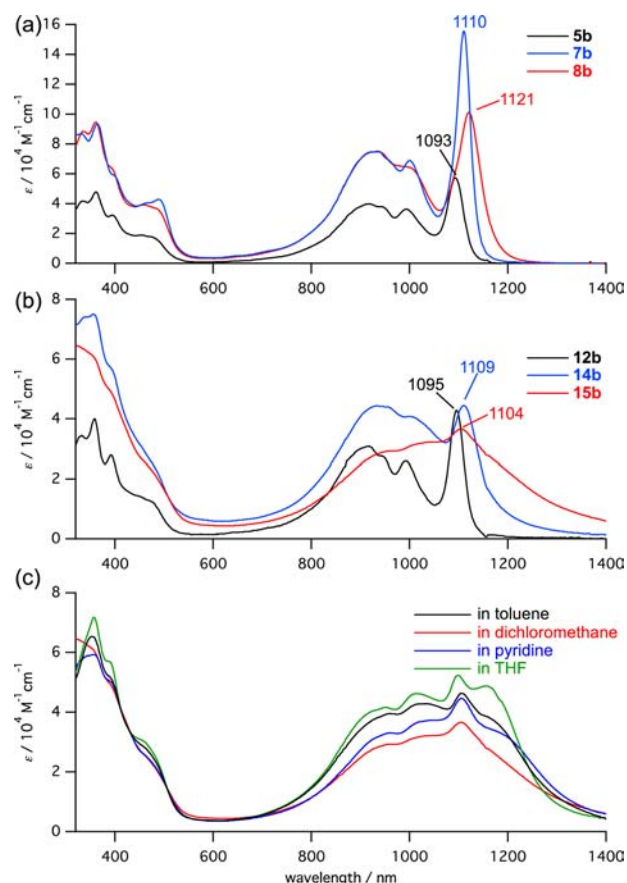
**Published:** November 16, 2016

Scheme 1. Synthesis of Carbazole-Based Porphyrins (a) 7b and 8b, (b) 14b and 15b, and (c) 4b, 5b, and 12b<sup>a</sup>

However, diporphyrins connected at the 3,3'-positions of the carbazole moieties were prepared as follows (Scheme 1b). The Suzuki–Miyaura coupling reaction of **1** with 1.6 equiv of the arylboronic acid and the subsequent TMS deprotection provided unsymmetrical carbazole **9**. The Glaser coupling reaction of the mixture of **2** and **9** provided carbazole dimer **10**, which was converted into bromo-substituted isophlorin **11** via the annulation with Na<sub>2</sub>S. The bromo moiety was transformed into ethynyl group via the Stille coupling reaction of **11** and the subsequent TMS deprotection of **12a**. The Glaser coupling reaction of **13** afforded butadiyne bridged isophlorin dimer **14a**. Thiophene-bridged dimer **15a** was obtained from **14a** via the

annulation reaction. The oxidation of **14a** and **15a** produced **14b** and **15b**, respectively. Additionally, monomers **4b**, **5b**, and **12b** were also prepared for comparison via the oxidation of **4a**, **5a**, and **12a**, respectively (Scheme 1c).

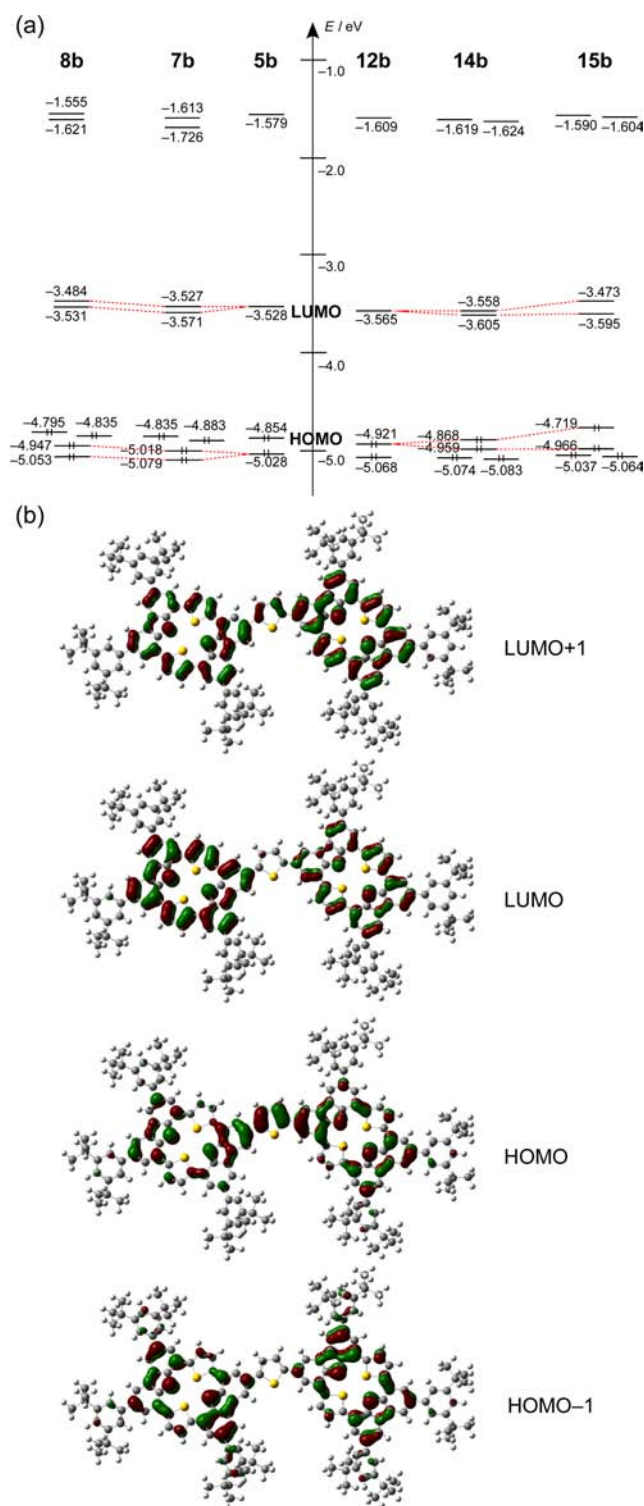
The UV/vis/NIR absorption spectra are shown in Figure 2. As previously reported, carbazole-based porphyrin monomer **5b** exhibited red-shifted Q-like bands in the NIR region due to the extended  $\pi$ -conjugation as compared to regular porphyrins. In addition, the spectra of dimers **7b** and **8b** are more intensified and red-shifted (Figure 2a). However, the spectral forms of **7b** and **8b** are similar to that of **5b**, suggesting weak intramolecular electronic interactions in **7b** and **8b**. However, the spectra of dimers **14b** and



**Figure 2.** UV/vis/NIR absorption spectra of (a) **5b**, **7b**, and **8b**, (b) **12b**, **14b**, and **15b** in dichloromethane, and (c) **15b** in several solvents.

**15b** showed extremely broadened NIR bands and are different from that of **12b**, which suggests the strong electronic communications between the two carbazole-based porphyrins (Figure 2b). The broad NIR bands were also observed in other solvents such as toluene, pyridine, and THF (Figure 2c). It should be noted that the absorption terminal wavelengths of **14b** and **15b** exceed 1300 and 1400 nm, respectively. Therefore, such dyes with broad NIR absorption bands as **14b** and **15b** may be applied to photoconversion of solar energy.

DFT calculations were conducted at the B3LYP/6-31G\* level to investigate the electronic states (Figures 3 and S22–23).<sup>11</sup> Since the lowest unoccupied molecular orbitals (LUMOs) of monomers **5b** and **12b** are significantly stabilized by 1.9–2.0 eV, we can consider that the NIR absorption bands are related to the HOMO–LUMO and HOMO–1–LUMO transitions. Similarly, the NIR absorption bands of the dimers are related to the transitions from the HOMO–3–HOMO to the LUMO or LUMO+1, which was supported by TD-DFT calculations (Figure S24). Interestingly, **7b** and **8b** showed somewhat large gap between the HOMO–3 and HOMO–2, while **14b** and **15b** showed the gap between the HOMO–1 and HOMO. These results are in good agreement with the ethynyl substituent effects on the monomer previously reported: Ethynyl groups at the thiophene moiety perturbed the HOMO–1, while those at the carbazole moiety perturbed the HOMO.<sup>8f,h</sup> It is noteworthy that **15b** shows the largest HOMO–1–HOMO gap and LUMO–LUMO+1 gap, and that these four orbitals exhibit delocalized electronic coefficients at both porphyrin moieties (Figure 3b). Such nondegenerated energy levels contribute to multiple or



**Figure 3.** (a) Energy diagrams of **5b**, **7b**, **8b**, **12b**, **14b**, and **15b**. (b) Selected molecular orbitals of **15b**.

broad absorption bands. In other words, the porphyrin units in **15b** are electronically coupled to each other. In addition, existence of rotational isomers and aggregates may also contribute to the broad NIR absorption bands.

Redox potentials of the diporphyrins along with the monomers were measured by cyclic voltammetry (Figure S21). Compounds **5b**, **7b**, and **8b** showed first oxidation waves at 0.469, 0.391, and 0.379 V, respectively, and reduction waves at –0.461, –0.530, and



−0.491 V, respectively. Such similar values suggest weak electronic interactions between the porphyrin units in **7b** and **8b**. In fact, the oxidation and reduction process of **7b** occur simultaneously at the porphyrins. However, **12b**, **14b**, and **15b** showed oxidation waves at 0.305, 0.264, and 0.159 V, respectively, and reduction waves at −0.502, −0.497, and −0.580 V, respectively. The electrochemical HOMO–LUMO gaps of **12b**, **14b**, and **15b** are 0.807, 0.761, and 0.739 eV, respectively. Diporphyrin **15b** showed the smallest electrochemical HOMO–LUMO gap, which is consistent with the results of absorption spectroscopy and DFT calculations.

In summary, we have synthesized butadiyne-bridged carbazole-based diporphyrins **7b** and **14b** via the Glaser coupling reaction. Furthermore, thiophene-bridged carbazole-based diporphyrins **8b** and **15b** were prepared via the annulation reaction. Diporphyrins **7b** and **8b** linked at the thiophene moieties showed similar properties with the corresponding monomer **5b**, indicating weak electronic intramolecular interactions. However, the absorption spectra, CV measurements, and DFT calculations indicated that diporphyrins **14b** and **15b** linked at the carbazole moieties had strong intramolecular electronic interactions within the diporphyrins. Further investigations on the synthesis of longer carbazole-based porphyrin arrays are currently in progress in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03054.

Experimental procedures and compound data (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: cmaeda@okayama-u.ac.jp.

\*E-mail: ema@cc.okayama-u.ac.jp.

### ORCID

Chihiro Maeda: 0000-0003-4370-3905

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Number 15K05427. We thank Prof. A. Osuka, Prof. H. Yorimitsu, and Dr. T. Tanaka (Kyoto University) for mass measurements, Prof. S. Suga and Prof. K. Mitsudo (Okayama University) for CV measurements, and Dr. K. Takaishi (Okayama University) for DFT calculations.

## ■ REFERENCES

- (1) (a) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517. (b) Roszak, A. W.; Howard, T. D.; Southall, J.; Gardiner, A. T.; Law, C. J.; Isaacs, N. W.; Cogdell, R. J. *Science* **2003**, *302*, 1969.
- (2) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40. (b) Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.* **2002**, *35*, 57. (c) Satake, A.; Kobuke, Y. *Tetrahedron* **2005**, *61*, 13. (d) Maeda, C.; Kamada, T.; Aratani, N.; Osuka, A. *Coord. Chem. Rev.* **2007**, *251*, 2743. (e) Aratani, N.; Osuka, A. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1. (f) Tanaka, T.; Osuka, A. *Chem. Soc. Rev.* **2015**, *44*, 943.
- (3) (a) Lin, V. S.-Y.; DiMaggio, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105. (b) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.

- (c) Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676. (d) Aratani, N.; Osuka, A. *Org. Lett.* **2001**, *3*, 4213. (e) Locos, O. B.; Arnold, D. P. *Org. Biomol. Chem.* **2006**, *4*, 902. (f) Ikeue, T.; Furukawa, K.; Hata, H.; Aratani, N.; Shinokubo, H.; Kato, T.; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6899. (g) Bringmann, G.; Götz, D. C. G.; Gulder, T. A. M.; Gehrke, T. H.; Bruhn, T.; Kupfer, T.; Radacki, K.; Braunschweig, H.; Heckmann, A.; Lambert, C. *J. Am. Chem. Soc.* **2008**, *130*, 17812. (h) Tokuji, S.; Yorimitsu, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 12357.
- (4) (a) Latos-Grażyński, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol 2, Chapter 14. (b) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795. (c) Gupta, I.; Ravikanth, M. *Coord. Chem. Rev.* **2006**, *250*, 468. (d) Lash, T. D. *Eur. J. Org. Chem.* **2007**, 5461. (e) Misra, R.; Chandrashekar, T. K. *Acc. Chem. Res.* **2008**, *41*, 265. (f) Matano, Y.; Imahori, H. *Acc. Chem. Res.* **2009**, *42*, 1193.
- (5) (a) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267. (b) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134. (c) Stępień, M.; Sprutta, N.; Latos-Grażyński, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4288. (d) Saito, S.; Osuka, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 4342.
- (6) (a) Fox, S.; Boyle, R. W. *Tetrahedron* **2006**, *62*, 10039. (b) Lewtak, J. P.; Gryko, D. T. *Chem. Commun.* **2012**, 48, 10069. (c) Roznyatovskiy, V. V.; Lee, C.-H.; Sessler, J. L. *Chem. Soc. Rev.* **2013**, *42*, 1921. (d) Mori, H.; Tanaka, T.; Osuka, A. *J. Mater. Chem. C* **2013**, *1*, 2500.
- (7) (a) Gupta, I.; Ravikanth, M. *J. Org. Chem.* **2004**, *69*, 6796. (b) Toganoh, M.; Takayama, T.; Ritesh, N.; Kimizuka, N.; Furuta, H. *Chem. Lett.* **2011**, *40*, 1021. (c) Matano, Y.; Fujii, D.; Shibano, T.; Furukawa, K.; Higashino, T.; Nakano, H.; Imahori, H. *Chem. - Eur. J.* **2014**, *20*, 3342. (d) Kral, V.; Andrievsky, A.; Sessler, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 2953. (e) Hata, H.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 932. (f) Misra, R.; Kumar, R.; Chandrashekar, T. K.; Suresh, C. H. *Chem. Commun.* **2006**, 4584. (g) Inokuma, Y.; Ono, N.; Uno, H.; Kim, D. Y.; Noh, S. B.; Kim, D.; Osuka, A. *Chem. Commun.* **2005**, 3782. (h) Davis, N. K. S.; Thompson, A. L.; Anderson, H. L. *Org. Lett.* **2010**, *12*, 2124. (i) Fukui, N.; Yorimitsu, H.; Lim, J. M.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 4395.
- (8) (a) Maeda, C.; Yoneda, T.; Aratani, N.; Yoon, M.-C.; Lim, J. M.; Kim, D.; Yoshioka, N.; Osuka, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5691. (b) Maeda, C.; Yoshioka, N. *Org. Lett.* **2012**, *14*, 2122. (c) Maeda, C.; Yoshioka, N. *Org. Biomol. Chem.* **2012**, *10*, 5182. (d) Masuda, M.; Maeda, C. *Chem. - Eur. J.* **2013**, *19*, 2971. (e) Masuda, M.; Maeda, C.; Yoshioka, N. *Org. Lett.* **2013**, *15*, 578. (f) Maeda, C.; Masuda, M.; Yoshioka, N. *Org. Lett.* **2013**, *15*, 3566. (g) Maeda, C.; Masuda, M.; Yoshioka, N. *Org. Biomol. Chem.* **2014**, *12*, 2656. (h) Maeda, C.; Kurihara, K.; Masuda, M.; Yoshioka, N. *Org. Biomol. Chem.* **2015**, *13*, 11286.
- (9) (a) Piatek, P.; Lynch, V. M.; Sessler, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 16073. (b) Arnold, L.; Norouzi-Arasi, H.; Wagner, M.; Enkelmann, V.; Müllen, K. *Chem. Commun.* **2011**, 47, 970. (c) Arnold, L.; Baumgarten, M.; Müllen, K. *Chem. Commun.* **2012**, 48, 9640. (d) Azarias, C.; Jacquemin, D. *J. Phys. Chem. A* **2016**, *120*, 2824.
- (10) (a) Arnold, D. P.; Nitschinsk, L. *J. Tetrahedron* **1992**, *48*, 8781. (b) Fletcher, J. T.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 4298. (c) Maeda, C.; Shinokubo, H.; Osuka, A. *Org. Lett.* **2010**, *12*, 1820.
- (11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *GAUSSIAN 09*, revision E.01; Gaussian, Inc.: Wallingford CT, 2013.