HETEROCYCLES, Vol. 95, No. 2, 2017, pp. 1159-1166. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 30th August, 2016, Accepted, 14th November, 2016, Published online, 1st February, 2017
DOI: 10.3987/COM-16-S(S)55

PREPARATION AND OPTICAL AND ELECTROCHEMICAL PROPERTIES OF DIPHTHALOCYANINE LINKED WITH A TTF UNIT

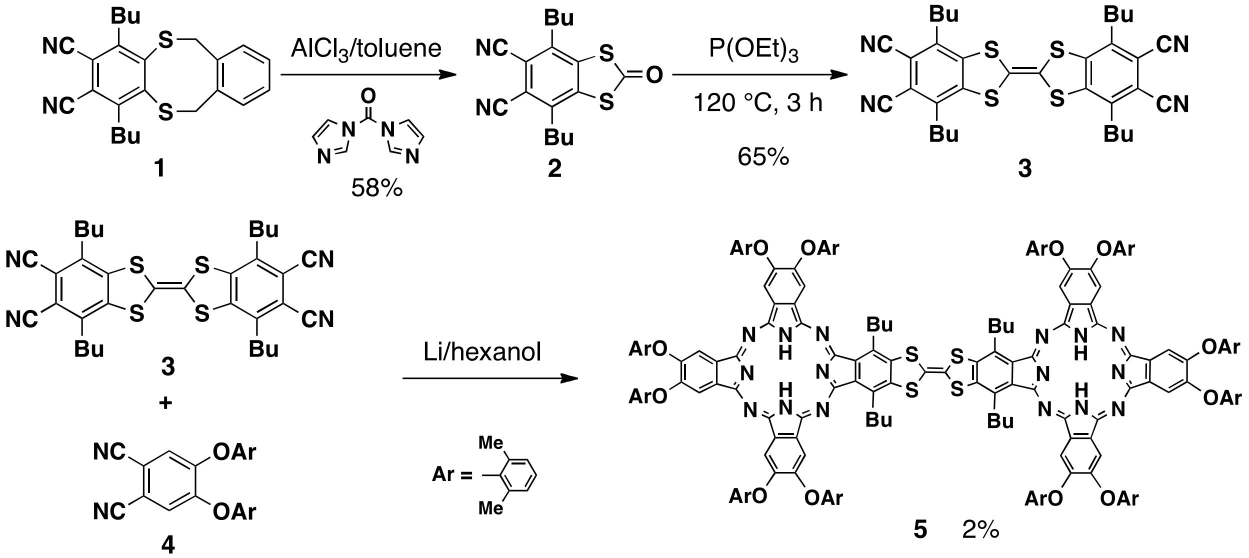
Takeshi Kimura,* Shomu Sasaki, and Shiduko Nakajo

Center for Instrumental Analysis, Iwate University, Morioka, Iwate 020-8551, Japan, E-mail: kimura@iwate-u.ac.jp

Dedicated to Prof. Dr. Masakatsu Shibasaki on the occasion of his 70th birthday

Abstract – 4,4’,7,7’-Tetrabutyl-5,5’,6,6’-tetracyano-2,2’-bis(benzo-1,3-dithiol-2-ylidene) (**3-Bu**) was prepared and mixed with 4,5-bis(2,6-dimethylphenoxy)-phthalonitrile (**4**), which was treated with lithium alkoxide at 120 °C to produce diphthalocyanine linked with a TTF unit. The structure of the product was determined by NMR and MALDI-TOF-MS. The optical and electrochemical properties were examined by UV-vis spectra and cyclic voltammetry.

Functionalized phthalocyanines and related compounds have been prepared and their optical and electrochemical properties explored, to develop actual and potential applications of them to catalysts, photovoltaic cells, organic semiconductors, and sensitizers for photodynamic therapy of cancer.[1] The prominent Q-band absorption of phthalocyanines, which lies at the near infrared region, is important for the application of these dyes to new photoactive materials. Furthermore, phthalocyanine’s Q-band absorption can be tuned by attaching electron donating or withdrawing substituents at α or β-positions, expanding a π-conjugation system, and introducing a central metal atom with several ligands.[2] Tetrathiafulvalene (TTF) is an excellent electron donor and can be utilized as a functional substance in supra-molecular systems.[3] In a field of functionalized dye’s chemistry, there are many reports of porphyrin,[4] tetraazaporphyrin,[5] phthalocyanine,[6] and calixpyrrole[7] derivatives linked with one or more TTF units. For example, Becher reported porphyrin and calixphyrin derivatives bearing one through four TTF units,[4,7] while Decurtins and we prepared phthalocyanines fused with four TTF scaffolds.[6] Recently, several metallated diporphyrin derivatives, linked with a dibenzotetrathiafulvalene unit, were prepared by the condensation reaction of four amino groups, substituted on dibenzotetrathiafulvalene, with two molecules of 2,3-dioxotetraphenylchlorin.[8] To prepare diphthalocyanine linked with a tetrathiafulvalene unit, we prepared tetracyanodibenzotetrathiafulvalene and cyclized it with diaryloxyphthalonitrile in the presence of lithium alkoxide at 120 °C. This paper reports the preparation, structural determination, and optical and electrochemical properties of β-dodecakis-(2,6-dimethylphenoxy)diphthalocyanine (**5**) connected with the tetrathiafulvalene unit as a linker.



Scheme 1. Preparation of diphthalocyanine **5**

As a starting compound, 4,5-(xylylenedithio)-3,6-dibutylphthalonitrile (**1**) was prepared from 1,4-dibutyltetrabromobenzene *via* four step reactions by the procedure reported previously.[9] Compound **1** was treated with aluminum chloride in toluene at room temperature for 2 h and then with carbonyldiimidazole at 100 °C for 1 h, which gave 4,5-dicyano-3,6-dibutylbenzo-1,3-dithiol-2-one (**2**) in 58% yield (Scheme 1). Then, 4,4’,7,7’-tetrabutyl-5,5’,6,6’-tetracyano-2,2’-bis(benzo-1,3-dithiol-2-ylidene) (**3-Bu**) was prepared by the condensation reaction of **2** in triethylphosphite at 120 °C for 3 h (65%).[6d,e] While the corresponding ethyl and octyl derivatives **3-Et** and **3-Oc** were obtained by the method reported previously,[9b] **3-Et** was insoluble in chloroform.

Prevention of aggregation of π-expanded phthalocyanines is a significant subject to analyze their optical and electrochemical characteristics. As reported by Whöle and other researchers, 4,5-bis(2,6-dimethyl-phenoxy)phthalonitrile (**4**) and its analogous compounds could be useful building blocks to construct unsymmetric phthalocyanines.[10,11] Therefore, we prepared phthalonitrile (**4**) and mixed with **3-Bu** in a 6 : 1 ratio; the mixture was then treated with lithium alkoxide in 1-hexanol at 120 °C for 3 h (Scheme 1). The blue-green solid, precipitated in the solution, was filtered and purified by silica gel column chromatography and Biobeads column chromatography. The reaction gave diphthalocyanine (**5**) linked with the TTF unit in 2% yield together with β-octakis(2,6-dimethylphenoxy)phthalocyanine (**6**). Although the reaction mixture seemed to contain other structural isomers containing two or more TTF units, we could not isolate such products by repeated column chromatography using silica gel and

Biobeads. Related compounds **3-Et** and **3-Oc** were similarly reacted with **4** in the presence of lithium alkoxide in 1-hexanol at 120 °C, respectively; however, we could not isolate desired diphthalocyanine derivatives from either of the reactions, although the octyl derivative was observed in the NMR spectrum of the reaction mixture.

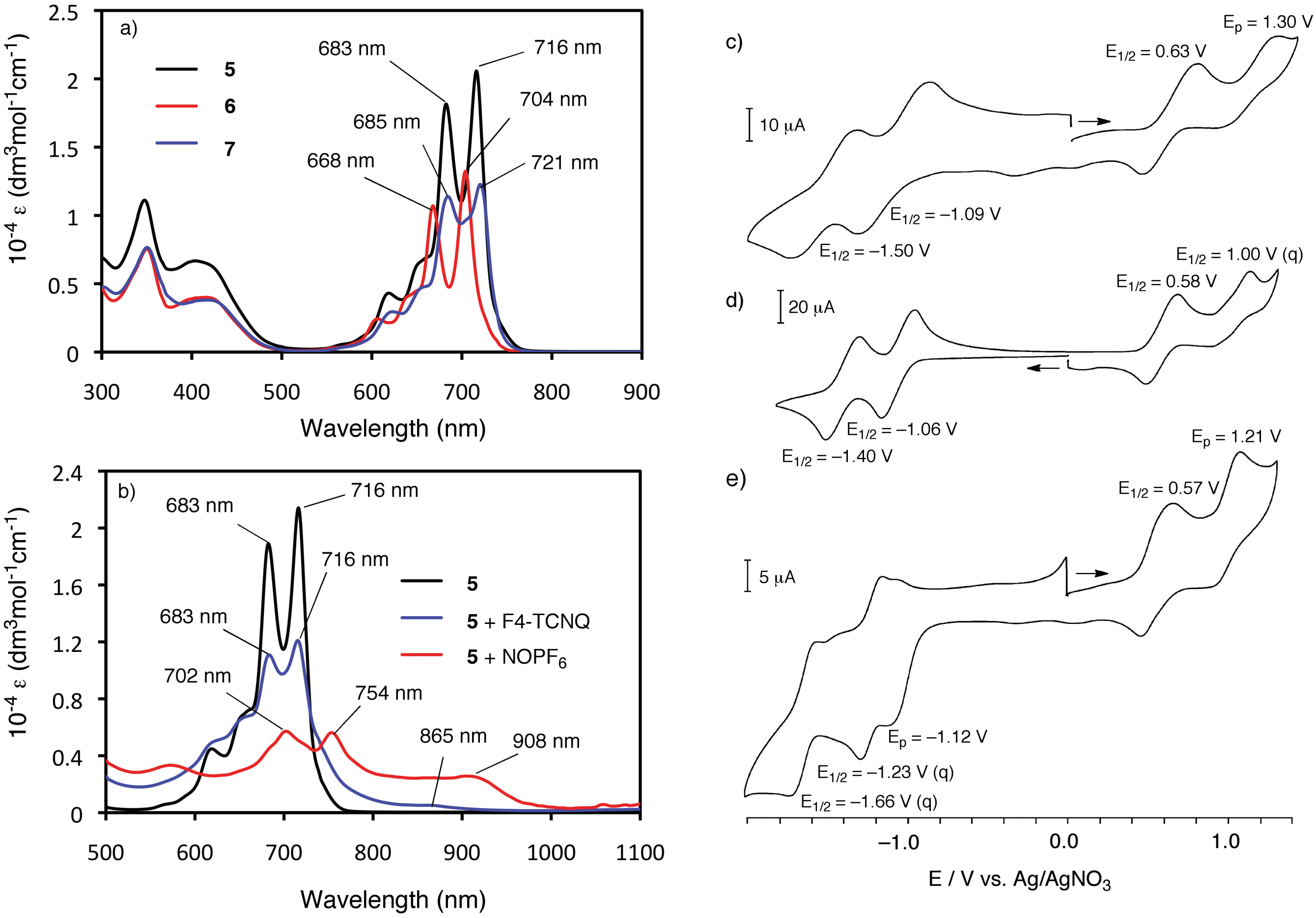
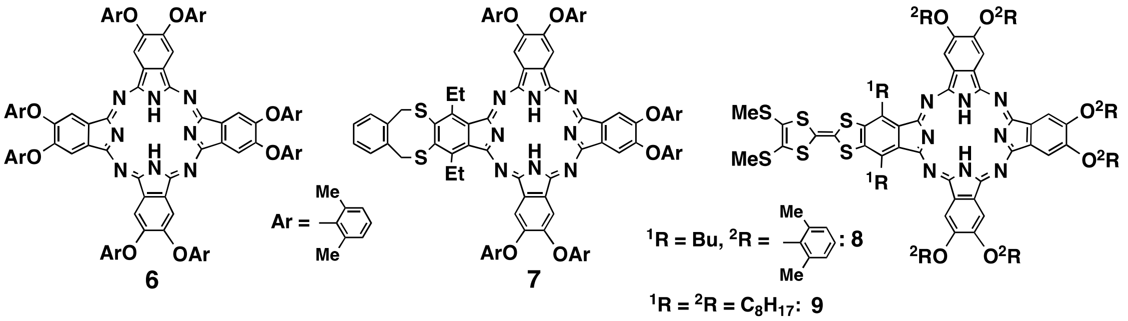


Figure 1. UV-vis spectra (measured in $CHCl_3$) of a) **5** and related compounds **6** and **7**; b) **5**, **5** + F4-TCNQ, and **5** + $NOPF_6$; cyclic voltammograms of c) **7**, d) **6**, and e) **5**

The ^1H NMR spectrum of **5** showed two broadened triplet signals for CH_3 and CH_2 groups at δ = 0.96 and 3.90 ppm, respectively, together with broadened quintet and multiplet signals for CH_2 groups (Supporting Information). A singlet peak for central NH groups (δ = –0.66 ppm) and three singlet peaks for aromatic protons at α-positions of phthalocyanine (δ = 8.17, 8.22, and 8.29 ppm) were observed together with the methyl and aromatic signals for 2,6-dimethylphenoxy groups. Since the four inner NH protons are observed as the sharp singlet peak, **5** exists as the tautomer. In the MALDI-TOF-MS measurement, compound **5** showed a molecular ion peak at 2841.42 [M^+]. Compound **5** is a little unstable and gradually decomposed under ambient condition. To compare the optical and electrochemical properties, phthalocyanine (**7**) was prepared by the reaction of **1** and **4** in the presence of lithium alkoxide in 1-hexanol at 120 °C. In addition, although we attempted to prepare phthalocyanine (**8**) linked with a bis(methylthio)TTF unit and six 2,6-dimethylphenoxy groups, the product was more unstable than **5** and decomposed under air.

The UV-vis spectrum of **5** shows split Q-band absorption at λ_{max} = 683 and 716 nm, which are longer wavelength than those of **6** (λ_{max} = 668 and 704 nm) while slightly shorter than those of **7** (λ_{max} = 685 and 721 nm) (Figure 1a). β-Dodecakis(2,6-dimethylphenoxy)diphthlocyanine linked with a benzene ring, reported by Whöle, showed large red-shift of the Q band absorption (λ_{max} = 853 nm) compared with that of **6**.[10] The λ_{max} value of compound **5** is much shorter than that of Whöle's diphthalocyanine and the lowest excitation energy of **5** is similar to that of **6** and **7**, suggesting that the π-conjugated system of **5** has weak interaction between two phthalocyanine parts.



6

7

Table 1. Oxidation and reduction potentials of phthalocyanines (V vs. Ag/$AgNO_3$)

Compound	3rd redn	2nd redn	1st redn	1st oxid	2nd oxid	ΔE (V)	Q (nm)
5	–1.66^a	–1.23^a	–1.12^b	0.57^a	1.21^a	1.69	716
6		–1.40	–1.06	0.58	1.00^a	1.64	704
7		–1.50	–1.09	0.63	1.30^b	1.72	721
9	–1.47^a	–1.27^a	–0.78^a	0.41^a	0.72^a	1.19	705
3-Oc			–1.36^a	0.81	1.10	2.17	

^{a}Quasi-reversible, ^{b}irreversible, ΔE = (1st oxid) – (1st redn); Since compound **8** is unstable, compound **9** was shown to compare the redox potentials instead of **8**.[9c]

The electrochemical properties were determined by cyclic voltammetry with Ag/$AgNO_3$ as a reference electrode. As shown in Figure 1 and Table 1, compound **5** exhibited two quasi-reversible couples ($E_{1/2}$ = 0.57 and 1.21 V) during oxidation and two quasi-reversible couples and one irreversible peak ($E_{1/2}$ = –1.66 and –1.23, E_p = –1.12 V) during reduction. While the first oxidation potential of **5** is slightly lower than that of **6** and **7** but higher than that of **9**, the first reduction potential of **5** is lower than that of **6**, **7**, and **9**.[9c] In the thin-layer cyclic voltammetry experiments of diporphyrin derivatives linked with the dibenzotetrathiafulvalene unit,[8] three oxidation couples were observed in the voltammogram, which consist of the first two-electron oxidation of the two porphyrin parts, the second one-electron oxidation of the TTF unit, and the third two-electron oxidation of the two porphyrin radical cations. Therefore, the first and the second oxidation couples of **5** could contain the two-electron oxidation of the phthalocyanine parts, respectively, and the one-electron oxidation peak may exist between the first and the second oxidation couple.

In a previous paper, when β-hexa(octylthio)phthalocyanine fused with one TTF unit [1st oxidation potential, $E_{1/2}$ = 0.38 V (quasi-reversible)] was treated with tetrafluorotetracyanoquinodimethane (F4-TCNQ) as an electron acceptor, we observed new absorption at 865 nm in the UV-vis spectrum and the solution showed a broadened ESR signal (g = 2.0056).[12] Based on these results, the UV-vis spectrum of **5** was measured in the presence of excess amounts of F4-TCNQ, which showed that the intensity of the Q band absorption decreased and weak absorption appeared at λ_{max} = 865 nm in the spectrum (Figure 1b). Compound **5** and F4-TCNQ would produce a trace amount of an electron transfer complex in the solution. The solution of this complex was then measured by ESR at room temperature; however, no signal was found in the spectrum. By the similar treatment with F4-TCNQ, **6** and **7** showed weak absorption at λ_{max} = 865 nm (Supporting Information). Next, we treated compound **5** with nitrosonium hexafluorophosphate ($NOPF_6$). By this treatment, the green colored solution changed to light brown and the Q band absorption showed a red-shift (λ_{max} = 702 and 754 nm) and new broadened absorption appeared at λ_{max} = 908 nm. The Q band absorption of **6** and **7** shifted to the longer wavelength by the similar treatment. While the results could show that radical cationic or dicationic species are generated in the solution, the species are unstable and decomposed in a few minutes.

In conclusion, tetracyanodibenzotetrathiafulvalene (**3-Bu**) was prepared from **1** by two step reactions and mixed with **4** in a 1 : 6 ratio. The mixture was treated with lithium alkoxide in 1-hexanol at 120 °C to produce diphthalocyanine **5** linked with the TTF unit. The NMR and MALDI-TOF-MS data supported the structure of the product and the optical and electrochemical properties were measured by UV-vis spectroscopy and cyclic voltammetry. In the UV-vis spectrum, the λ_{max} value of compound **5** is extremely shorter wavelength than that of Whöle's diphthalocyanine.[10] It appeared that compound **5** produced radical cationic or a dicationic species by treatment with $NOPF_6$, which showed new broadened absorption at λ_{max} = 908 nm.

EXPERIMENTAL

General

NMR spectra were measured by a Bruker AVANCE-500 spectrometer. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded with a JASCO Ubest V-570 spectrometer. IR spectrum was obtained employing a JASCO FT/IR-4200 spectrometer. A Hokuto Denko Co. Model HAB-151 apparatus was applied to measurements of redox potentials. Biobeads (SX-1) for column chromatography was purchased from Nippon Bio-Rad Laboratories. All measurements for redox potentials were performed by cyclic voltammetry, using Ag/$AgNO_3$ (0.01 mol/L) as a reference electrode, glassy carbon as a working electrode, and Pt wire as a counter electrode (scan rate: 200 mV/s). A solution of n-Bu_4NClO_4 in CH_2Cl_2 (0.1 mol/L) was used as an electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2}$ = 0.09 V by the apparatus without any correction.

Preparation of 4,4’,7,7’-tetrabutyl-5,5’,6,6’-tetracyano-2,2’-bis(benzo-1,3-dithiol-2-ylidene) (3-Bu).

Compound **2** (445.0 mg, 1.36 mmol) was dissolved in triethylphosphite (6 mL) and stirred at 120 °C for 3 h. The reaction mixture was cooled to rt and $CHCl_3$ was added. The solution was separated by column chromatography ($CHCl_3$) to produce oily yellow product. MeOH was added to the oily product, and the solid precipitated was filtered and washed with MeOH. Finally, compound (**3-Bu**) was obtained in 70% yield (301.6 mg); **3-Bu**: yellow powder; mp > 300 °C (decomposed); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, J = 7.4 Hz, 12H, CH_3), 1.43-1.52 (m, 8H, CH_2), 1.61-1.70 (m, 8H, CH_2), 2.82 (t, J = 8.0 Hz, 8H, CH_2Ar); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.7, 22.6, 30.5, 35.4, 110.3, 114.1, 114.5, 138.7, 143.0; IR (KBr) ν 2227 cm^{-1} (CN).[6e]

Preparation of phthalocyanine 5.

Lithium (41.8 mg, 6.0 mmol) was placed in a glass reactor and 1-hexanol (2.5 mL) was added under Ar. The solution was stirred at 120 °C until lithium was dissolved and then added to a mixture of **3-Bu** (107 mg, 0.17 mmol) and **4** (628 mg, 1.7 mmol), which was then stirred at 120 °C for 3 h. After cooling the reaction mixture, MeOH was added, and a green precipitate was filtered out. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$/hexane and then $CHCl_3$) and then (Biobeads, $CHCl_3$) to produce **5** in 2% yield (8.8 mg); green powder; ^{1}H NMR (500 MHz, $CDCl_3$) δ = –0.66 (s, 4H, NH), 0.96 (t, J = 7.4 Hz, 12H, CH_3), 1.38-1.47 (m, 8H, CH_2), 2.03 (quint, J = 7.6 Hz, 8H, CH_2), 2.39-2.51 (m, 72H, CH_3), 3.90 (t, J = 7.6 Hz, 8H, CH_2), 7.29-7.42 (m, 48H, ArH), 8.17 (s, 4H, ArH), 8.22 (s, 4H, ArH), 8.29 (s, 4H, ArH); UV-vis ($CHCl_3$) λ_{max} (ε) = 348 nm (111000), 683 nm (182000), 716 nm (206000); MALDI-TOF-MS (m/z) 2841.42 [M^+] (reflectron mode); Calcd for $C_{178}H_{160}N_{16}O_{12}S_4$ m/z = 2841.13.

Preparation of phthalocyanine 7.

Lithium (73 mg, 10.1 mmol) was placed in a glass reactor and 1-hexanol (3 mL) was added under Ar. The solution was stirred at 120 °C until lithium was dissolved and then added to a mixture of

4,5-(xylylenedithio)-3,6-diethylphthalonitrile (**3-Bu**) (175 mg, 0.5 mmol) and **4** (580 mg, 1.5 mmol). The reaction mixture was then stirred at 120 °C for 2 h. After cooling the reaction mixture, MeOH was added, and a green precipitate was filtered out. The residue was purified by column chromatography (Wakogel C-300HG, $CHCl_3$/hexane and then $CHCl_3$) to produce **5** in 7.7% yield; green powder; ^1H NMR (500 MHz, $CDCl_3$) δ = –0.76 (s, 2H, NH), 1.52 (t, *J* = 7.0 Hz, 6H, CH_3), 2.37-2.55 (m, 36H, CH_3), 4.37 (brq, *J* = 7.0 Hz, 4H, CH_2), 4.67 (s, 4H, CH_2), 6.66-6.71 (m, 2H, ArH), 6.98-7.04 (m, 2H, ArH), 7.29-7.45 (m, 18H, ArH), 8.17 (s, 2H, ArH), 8.18 (s, 2H, ArH), 8.27 (s, 2H, ArH); Fast atom bombardment mass spectrometry (FABMS) (*m/z*) 1457.6 [M^+].

REFERENCES

1. a) H. Lu and N. Kobayashi, *Chem. Rev.*, 2016, **116**, 6184; b) T. Tanaka and A. Osuka, *Chem. Soc. Rev*., 2015, **44**, 943; c) S. Singh, A. Aggarwal, N. V. S. D. K. Bhupathiraju, G. Arianna, K. Tiwari, and C. M. Drain, *Chem. Rev.*, 2015, **115**, 10261; d) M. Urbani, M. Grätzel, M. Nazeeruddin, and T. Torres, *Chem. Rev.*, 2014, **114**, 12330.
2. a) J. Mack and N. Kobayashi, *Chem. Rev.*, 2011, **111**, 281; b) V. N. Nemykin and E. A. Luk'yanets, 'Handbook of Porphyrin Science', Vol. 3, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, World Scientific, Singapore, 2010, pp. 1-324; c) T. Fukuda and N. Kobayashi, 'Handbook of Porphyrin Science', Vol. 9, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, World Scientific, Singapore, 2010, pp. 1-644.
3. a) J. O. Jeppesen and J. Becher, *Eur. J. Org. Chem.*, 2003, 3245; b) M. Iyoda, M. Hasegawa, and Y. Miyake, *Chem. Rev*., 2004, **104**, 5085; c) N. Martín, L. Sánchez, M. Á. Herranz, B. Illescas, and D. M. Guldi, *Acc. Chem. Res*., 2007, **40**, 1015.
4. a) J. Becher, T. Brimert, J. O. Jeppesen, J. Z. Pedersen, R. Zubarev, T. Bjørnholm, N. Reitzel, T. R. Jensen, K. Kjaer, and E. Levillain, *Angew. Chem. Int. Ed.*, 2001, **40**, 2497; b) K. A. Nielsen, E. Livillain, V. M. Lynch, J. L. Sessler, and J. O. Jeppesen, *Chem. Eur. J.*, 2009, **15**, 506; c) A. Jena, H. Gobeze, M. Ishida, T. Mori, K. Ariga, J. P. Hill, and F. D'Souza, *Dalton Trans*., 2015, **44**, 359.
5. a) T. Chen, C. Wang, H. Qui, L. Jin, B. Yin, and K. Imafuku, *Heterocycles*, 2007, **71**, 549; b) F. Leng, R. Hou, L. Jin, B. Yin, and R.-G. Xiong, *J. Porphyrins Phthalocyanines*, 2010, **14**, 108.
6. a) C. Loosli, C. Jia, S.-X. Liu, M. Haas, M. Dias, E. Levillain, A. Neels, G. Labat, A. Hauser, and S. Decurtins, *J. Org. Chem*., 2005, **70**, 4988; b) C. A. Donders, S.-X. Liu, C. Loosli, L. Sanguinet, A. Neels, and S. Decurtins, *Tetrahedron*, 2006, **62**, 3543; c) S. Delahaye, C. Loosli, S.-X. Liu, S. Decurtins, G. Labat, A. Neels, A. Loosli, T. R. Ward, and A. Hauser, *Adv. Funct. Mater*., 2006, **16**, 286; d) T. Kimura, D. Watanabe, and T. Namauo, *Heterocycles*, 2008, **76**, 1023; e) T. Kimura, T. Namauo, K. Amano, N. Takahashi, Y. Takaguchi, T. Hoshi, and N. Kobayashi, *J. Porphyrins*

Phthalocyanines, 2011, **15**, 547; f) T. Kimura, *Heterocycles*, 2013, **87**, 245.

7. a) K. A. Nielsen, J. O. Jeppesen, E. Livillain, and J. Becher, *Angew. Chem. Int. Ed.*, 2003, **42**, 187; b) C. M. Davis, J. M. Lim, K. R. Larsen, D. S. Kim, Y. M. Sung, D. M. Lyons, V. M. Lynch, K. A. Nielsen, J. O. Jeppesen, D. Kim, J. S. Park, and J. L. Sessler, *J. Am. Chem. Soc.*, 2014, **136**, 10410; c) S. Bähring, L. Martín-Gomis, G. Olsen, K. A. Nielsen, D. S. Kim, T. Duedal, Á. Sastre-Santos, J. O. Jeppesen, and J. L. Sessler, *Chem. Eur. J.*, 2016, **22**, 1958.
8. H. Jia, B. Schmid, S. Liu, M. Jaggi, P. Monbaron, S. V. Bhosale, S. Rivadehi, S. J. Langford, L. Sanguinet, E. Levillan, M. E. El-Khouly, Y. Morita, S. Fukuzumi, and S. Decurtins, *Chem. Phys. Chem.*, 2012, **13**, 3370.
9. a) T. Kimura, T. Suzuki, Y. Takaguchi, A. Yomogita, T. Wakahara, and T. Akasaka, *Eur. J. Org. Chem.*, 2006, 1262; b) T. Kimura, D. Watanabe, and T. Namauo, *Heteroat. Chem.*, 2011, **22**, 605; c) T. Kimura, N. Takahashi, T. Tajima, and Y. Takaguchi, *Heterocycles*, 2012, **84**, 333.
10. S. Makarov, C. Litwinski, E. A. Ermilov, O. Suvorova, B. Röder, and D. Wöhrle, *Chem. Eur. J.*, 2006, **12**, 1468.
11. T. Ikeuchi, S. Mori, N. Kobayashi, and M. Kimura, *Inorg. Chem.*, 2016, **55**, 5014; H. Pan, C. Chen, K. Wang, W. Li, and J. Jiang, *Chem. Eur. J.*, 2015, **21**, 3168.
12. T. Kimura, J. Kang, and S. Nakajo, *Heterocycles*, 2016, **93**, 762.