

Porphyrin–Azobenzene–Bodipy Triads: Syntheses, Structures, and Photophysical Properties

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(5) Supporting Information



ABSTRACT: Cyclic and acyclic azobenzene bridged porphyrin–dipyrrin derivatives were successfully prepared via Suzuki– Miyaura coupling reaction of α, α' -diborylated dipyrromethane with bromoazophenyl porphyrin or reaction of borylated porphyrin with dibromoazophenyl dipyrrin, and the corresponding porphyrin–Bodipy derivatives were obtained by subsequent boron complexation. The cyclic porphyrin–dipyrrin compound **3Ni** was confirmed by X-ray diffraction. The low fluorescence quantum yields of azobenzene bridged porphyrin–Bodipy can be ascribed to the presence of the intramolecular charge transfer state.

The design and synthesis of photosensitizers capable of harvesting a large fraction of solar light has attracted a great deal of interest.^{1,2} Porphyrin derivatives have been widely employed as energy capturing antenna or electron donor units in artificial model compounds due to their structural resemblance to natural chlorophylls.^{3,4} Porphyrin derivatives have an intense absorption in 400-450 nm region and relative weak absorptions in 500-700 nm region. However, porphyrin derivatives exhibit insufficient absorption property in blue-green region, so they are not ideally suited for broadband solar harvesting. In order to improve the broadband light harvesting properties of porphyrin derivatives, one strategy involves coupling green absorbing chromophores to it and creating donor-acceptor array complexes.⁵⁻¹² Boron-dipyrrins (Bodipys) absorb strongly in blue-green region and have a number of favorite properties such as large molar absorption coefficients, high fluorescence yields, relatively long excited state lifetimes, and excellent photo-stability.^{9,13–18} Bodipys are widely used in the fields of luminescent devices,¹⁹ biological labeling,²⁰ chemical sen-sors,^{21–25} fluorescent probes,²⁶ artificial photosynthetic systems, and molecular wires.^{27,28} In order to enhance the light-harvesting efficiency throughout the solar spectrum, many Bodipyporphyrin conjugate dyads have been reported in the literature taking advantage of Bodipy's ability to act as an antenna molecule.^{29–36} Azobenzene and its derivatives are very important organic pigments, owning to their reversible cis/trans photo-isomerization.³⁷⁻⁴¹ Azobenzene and its derivatives are considered to be useful materials in the field of photoresponsive conjugated molecules such as liquid crystal, light-driven

switches,^{42,43} and image storage.⁴⁴ Recently, we reported the synthesis of azobenzene bridged porphyrin nanorings and found one Azo-linker of trimer exhibits cis/trans isomerization with external stimuli.⁴⁵ To the best of our knowledge, azobenzene bridged porphyrin–Bodipy has rarely been reported. As an extension of our research, we describe the synthesis, structures, and photophysical properties of cyclic and acyclic azobenzene bridged porphyrin–Bodipy derivatives in this letter.

We found the Suzuki-Miyaura cross coupling of $\alpha_{,}\alpha'_{-}$ diborylated dipyrromethane 1, which was prepared by iridiumcatalyzed selective borylation of mesityldipyrromethane, with bromoazophenyl nickel porphyrin 2Ni⁴⁵ in the presence of a [Pd₂(dba)₃]/PPh₃ catalyst and cesium bases gave the cyclic azobenzene bridged porphyrin-dipyrrin compound 3Ni in 14% yield, whereas no cyclic 3Ni was separated when cross coupling of 5 with borylporphyrin monomer. The ¹H NMR and highresolution ESI-TOF spectra of 3Ni confirm its expected structure. Freebase precursor 3H was also obtained in 10% yield by this way. Compound 3H was converted into 3Zn upon treatment with $Zn(OAc)_2$ in quantitative yield. We also examined the Suzuki-Miyaura coupling of 1 with dibromoazobenzene 4, which provided dibromoazophenyl dipyrrin 5; further Suzuki-Miyaura coupling of 5 with meso-borylated nickel porphyrin 6Ni or free base porphyrin 6H gave the acyclic azobenzene bridged porphyrin-dipyrrin compounds 7Ni and 7H in 30% and 28% yields, respectively. Compound 7H was converted into 7Zn upon

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Scheme 1. Synthesis of 3M, 7M, 8M, and 9M



treatment with $Zn(OAc)_2$ in quantitative yield. The subsequent boron complexation of **3M** and **7M** (M = Ni, 2H) with BF₃.OEt₂ afforded corresponding porphyrin–Bodipy derivatives **8M** and **9M** (M = Ni, 2H) all in decent yields. Compounds **8H** and **9H** were all converted into **8Zn** and **9Zn** upon treatment with $Zn(OAc)_2$ in quantitative yields (Scheme 1). All these newly synthesized azobenzene bridged porphyrin–Bodipy derivatives **8M** and **9M** and the precursors **3M** and **7M** were fully characterized by high-resolution mass spectrometry, ¹H NMR, UV/vis absorption, and fluorescence spectroscopy (see the Supporting Information).

Single crystal of **3Ni** was obtained by the slow diffusion of *i*-PrOH vapor into its PhCl solution. The molecular structure of **3Ni** was unambiguously confirmed by X-ray crystallography study (Figure 1). The porphyrin ring is nearly parallel to the plane defined by the dipyrrin. The porphyrin core is slightly ruffled, as is often seen for nickel porphyrins. The maximum displacement of the β -carbons from the porphyrin mean plane, which is composed of carbon and nitrogen atoms, is 0.39 Å. The two azobenzene moieties adopt trans conformations, and the azobenzene moieties



Figure 1. X-ray structure of **3Ni**: (a) Top view and (b) side view. The thermal ellipsoids are 50% probability level. *tert*-Butyl and methyl groups are omitted for clarity.

are tilted by 42.7° and 54.7° relative to the adjacent pyrrole rings of porphyrin, while the tilted angles of the azobenzene moieties relative to the adjacent pyrrole rings of dipyrrin are 2.6° and 27.7°, implying that $\pi - \pi$ conjugation exists between the benzene rings and the dipyrrin moiety. The dihedral angles between the two benzene rings in the same azobenzene are 23.2° and 36.2°, respectively, while the dihedral angle between the two benzene rings in different linkages adjacent to the porphyrin is 88.7°, and that adjacent to the dipyrrin is 38.4°. The optimized structures of 3Zn, 7Zn, 8Zn, and 9Zn were obtained at CAM-B3LYP/6-31G(d) level (Figure S36) displaying dihedral angles between units. Unlike similar dihedral angles between porphyrin and azobenzene units in 3Zn to 8Zn and 7Zn to 9Zn, dihedral angles between azobenzene and Bodipy in 8Zn and 9Zn are almost 20° larger than those between azobenzene and dipyrrin units in 3Zn and 7Zn. This difference seems to originate from steric hindrance between hydrogen atom in benzene and fluoride atom in Bodipy unit, which in turn can relatively obstruct through-bond interaction between Bodipy and azobenzene unit. The most important difference is that the dihedral angle between porphyrin and azobenzene unit is relatively large in 7Zn and 9Zn compared with those in 3Zn and 8Zn.

The UV/vis absorption spectra of **3Zn**, **7Zn**, **8Zn**, and **9Zn** were measured in toluene (Figure 2). The acyclic compounds **7Zn** and **9Zn** show Soret bands at 424 and 421 nm, respectively, and when compared to porphyrin monomer,⁴⁶ slightly extended Q bands ranging from 518 to 646 nm appear. In contrast to **7Zn** and **9Zn**, the cyclic compounds **3Zn** and **8Zn** exhibit broader and red-shifted Soret bands than **7Zn** and **9Zn** centered at 430 nm. The broadened Soret bands of the cyclic compounds imply there is larger electronic interaction between porphyrins and dipyrrins or Bodipys than that in the acyclic compounds. The higher extinction coefficients of Soret bands of **7Zn** and **9Zn** are attributable to two factors: (1) the number of porphyrin moieties; **7Zn** and **9Zn** have one more porphyrin moiety than **3Zn** and **8Zn** definitely leading to the higher extinction coefficient; and (2) conformational heterogeneity; **3Zn** and **8Zn** seem to exist in a



Figure 2. (a) UV/vis absorption and (b) fluorescence ($\lambda_{ex} = 550 \text{ nm}$) spectra of **3Zn** (black), **8Zn** (green), **7Zn** (red), and **9Zn** (blue) in toluene.

range of conformation on account of broader Soret band features in line with stronger electronic communication between porphyrin and azobenzene unit. Remarkably, complex 8Zn and 9Zn do not show any characteristic absorption of Bodipy and its derivatives, which have high extinction coefficient in the visible region.^{9,47} This rare phenomenon indicates that two azobenzene and dipyrrin (or Bodipy) units are not independent, rather, these two units behave as an unit; hence, we will mention only two units, hereinafter, porphyrin and azobenzene units. Furthermore, from the sharp Soret bands of 7Zn and 9Zn considering that 7Zn and 9Zn are in a condition where these complexes are not locked in as 3Zn and 8Zn of cyclic structure, we may assume that porphyrin moiety in 7Zn and 9Zn possesses a highly independent character despite their plausible conformational heterogeneities. On the contrary, porphyrin and azobenzene units in 3Zn and 8Zn are relatively more strongly coupled to each other, which could be understood by their much smaller dihedral angles between porphyrin and azobenzene units than those of 7Zn and 9Zn. Thus, their absorption spectra can be more influenced by conformational factor. No distinct feature was observed from the fluorescence spectra (Figure 2) except for the quantum yield (OY) that all the complexes exhibit very low OY, less than 1%, which can be ascribed to the intramolecular charge transfer (ICT) process upon photoexcitation as Zn porphyrin monomer or Bodipy showed much stronger fluorescence.^{9,46,47}

To understand their radiative properties, we carried out timecorrelated single-photon counting (TCSPC) measurements in toluene as shown in Figure S39. Compounds **3Zn** and **8Zn** decayed with double exponential functions, which are 100 (95%) and 620 ps (5%) for **3Zn** and 22 (76%) and 48 ps (24%) for **8Zn**, respectively. However, **7Zn** and **9Zn** decayed with single exponential functions, which are 490 ps for **7Zn** and 340 ps for **9Zn**. Double exponential decay in **3Zn** and **8Zn** may be due to the conformational heterogeneities in line with the above discussion in the steady-state absorption spectra. Despite of their low quantum yields, complexes with Bodipy (**8Zn** and **9Zn**) showed clear tendencies to have decreased lifetimes and increased radiative and nonradiative rates compared with complexes with dipyrrin (**3Zn** and **7Zn**). Their optical properties are listed in Table S1.

In order to get further information on excited state dynamics of the complexes, femtosecond transient absorption (fs-TA) measurements were carried out (Figure S40). All experiments were conducted with excitation wavelength of 555 nm in toluene. Compounds **3Zn** and **8Zn**, where π - π interaction between

moieties seems to play an important role in electronic structure, decay with double exponential functions, lifetimes of 103 (96%) and 609 ps (4%) for 3Zn and 20 (65%) and 48 ps (35%) for 8Zn, respectively. Since their lifetimes and coefficients well correspond to the fluorescence lifetimes obtained from TCSPC, and they did not display any spectral shift or change in shape of excited state absorption (ESA), we may conclude that they exist in a range of conformation and also their lifetimes of singlet excited state are lying in some range of time scale. Therefore, decay profiles were fitted with double exponential functions, and ICT state of 3Zn and 8Zn is directly populated by excitation. The excited state dynamics of 7Zn and 9Zn, however, lies in a more complex manner than those of 3Zn and 8Zn. A contrasting feature in TA spectra of 7Zn and 9Zn was observed that the excited state dynamics cannot be explained only by the fluorescence process from the lowest electronic excited state unlike the cases of 3Zn and 8Zn. TA spectra of 7Zn and 9Zn evolves to relaxed S₁ state with additional component. (ICT process in 7Zn and 9Zn is not full-charge transfer or electron transfer as discussed in absorption spectra.)

Therefore, we analyzed the excited state dynamics of 7Zn and 9Zn by extracting decay-associated spectra (DAS) using global fitting method (Figure S40e,f).⁴⁸ In both compounds, three decay components were found: lifetimes of 1.2, 425, and 1525 ps for 7Zn and 5, 330, and 933 ps for 9Zn, respectively. These components seem to originate from ICT, charge recombination (CR), and relaxation of porphyrin triplet state, respectively, since a fast decrease of stimulated emission (SE) was observed around 600 to 650 nm, which is indicative of ICT process.^{47,49} Furthermore, electron density difference map (EDDM) for the lowest electronic transition also implies that ICT process may occur after population of Franck-Condon (FC) state (Figure S41). Interestingly, 7Zn showed very strong ESA signal compared to 9Zn even overwhelming the ground state bleaching (GSB) signal, which can be ascribed to many possible transitions from the lowest excited state to the higher states in line with timedependent density functional theory (TDDFT) calculations showing a number of states around 350 nm (Figure S42).

In summary, we have achieved the synthesis of cyclic and acyclic azobenzene bridged porphyrin–Bodipy derivatives via Suzuki– Miyaura coupling and boron complexation. The structures of these compounds were characterized by high-resolution mass spectrometry, ¹H NMR, UV/vis absorption, and fluorescence spectroscopy. The structure of **3Ni** was confirmed by X-ray diffraction analyses, and optimized structures of **3Zn**, **7Zn**, **8Zn**, and **9Zn** were analyzed focusing on the dihedral angle. Timecorrelated single-photon counting (TCSPC), femtosecond transient absorption (fs-TA) measurements, and electron density difference map (EDDM) indicate that, while CT state is directly populated in **3Zn** and **8Zn**, CT state is populated via additional ICT process from FC state in **7Zn** and **9Zn** upon photoexcitation. Investigations of other elegant Bodipy–porphyrin conjugated systems are underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00988.

Detailed synthetic procedures and spectroscopic characterization, ¹H (¹³C ¹¹B) NMR spectra, computational results of **3Zn**, **7Zn**, **8Zn**, and **9Zn** (PDF)

Crystallographic files for compound 3Ni (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Hagfeldt, A.; Boschloo, G.; Sun, L. C.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.

(2) Yum, J. H.; Baranoff, E.; Wenger, S.; Nazeeruddin, M. K.; Gratzel, M. *Energy Environ. Sci.* **2011**, *4*, 842–857.

(3) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198. (b) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. *8*, pp 153–190.

(4) (a) Fukuzumi, S.; Guldi, D. M. In *Electron Transfer in Chemistry*; Balzani, V., Eds.; Wiley-VCH, Weinheim, 2001; Vol. 2, pp 270–337.
(b) Fukuzumi, S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 8, pp 115–151.
(c) Fukuzumi, S. *Phys. Chem. Chem. Phys.* 2008, 10, 2283–2297.

(5) Whited, M. T.; Djurovich, P. I.; Roberts, S. T.; Durrell, A. C.; Schlenker, C. W.; Bradforth, S. E.; Thompson, M. E. J. Am. Chem. Soc. **2011**, 133, 88–96.

(6) Koepf, M.; Trabolsi, A.; Elhabiri, M.; Wytko, J. A.; Paul, D.; Albrecht-Gary, A. M.; Weiss, J. Org. Lett. **2005**, *7*, 1279–1282.

(7) Warnan, J.; Buchet, F.; Pellegrin, Y.; Blart, E.; Odobel, F. Org. Lett. **2011**, *13*, 3944–3947.

(8) Lee, C. Y.; Jang, J. K.; Kim, C. H.; Jung, J.; Park, B. K.; Park, J.; Choi,

W.; Han, Y. K.; Joo, T.; Park, J. T. Chem. - Eur. J. 2010, 16, 5586-5599.

(9) Loudet, A.; Burgess, K. Chem. Rev. 2007, 107, 4891-4932.

(10) Liu, J.-Y.; El-Khouly, M. E.; Fukuzumi, S.; Ng, D. K. P. *Chem. - Eur. J.* **2011**, *17*, 1605–1613.

(11) Jiao, C.; Zhu, L.; Wu, J. Chem. - Eur. J. 2011, 17, 6610-6614.

(12) Lazarides, T.; Charalambidis, G.; Vuillamy, A.; Reglier, M.; Klontzas, E.; Froudakis, G.; Kuhri, S.; Guldi, D. M.; Coutsolelos, A. G. *Inorg. Chem.* **2011**, *50*, 8926–8936.

(13) Coskun, A.; Akkaya, E. U. J. Am. Chem. Soc. 2005, 127, 10464–10465.

(14) Ziessel, R.; Ulrich, G.; Harriman, A. New J. Chem. 2007, 31, 496–501.

(15) Ulrich, G.; Ziessel, R.; Harriman, A. Angew. Chem., Int. Ed. 2008, 47, 1184–1201.

(16) Boens, N.; Leen, V.; Dehaen, W. Chem. Soc. Rev. 2012, 41, 1130–1172.

(17) Bessette, A.; Hanan, G. S. Chem. Soc. Rev. 2014, 43, 3342-3405.

- (18) Frath, D.; Massue, J.; Ulrich, G.; Ziessel, R. Angew. Chem., Int. Ed. 2014, 53, 2290–2310.
- (19) Lai, R. Y.; Bard, A. J. J. Phys. Chem. B 2003, 107, 5036-5042.
- (20) Kobayashi, H.; Ogawa, M.; Alford, R.; Choyke, P. L.; Urano, Y. *Chem. Rev.* **2010**, *110*, 2620–2640.

(21) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. J. Am. Chem. Soc. 2000, 122, 968–969.

(22) Turfan, B.; Akkaya, E. U. Org. Lett. 2002, 4, 2857-2859.

(23) Baruah, M.; Qin, W.; Vallée, R. A. L.; Beljonne, D.; Rohand, T.; Dehaen, W.; Boens, N. Org. Lett. **2005**, *7*, 4377–4380.

(24) Atilgan, S.; Ozdemir, T.; Akkaya, E. U. Org. Lett. 2010, 12, 4792-4795.

(25) Baruah, M.; Qin, W.; Basarić, N.; De Borggraeve, W. M.; Boens, N. J. Org. Chem. **2005**, 70, 4152–4157.

(26) Hiruta, Y.; Koiso, H.; Ozawa, H.; Sato, H.; Hamada, K.; Yabushita, S.; Citterio, D.; Suzuki, K. *Org. Lett.* **2015**, *17*, 3022–3025.

(27) Erten-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. Org. Lett. **2008**, *10*, 3299–3302.

(28) Cakmak, Y.; Akkaya, E. U. Org. Lett. 2009, 11, 85-88.

(29) Khan, T. K.; Bröring, M.; Mathur, S.; Ravikanth, M. Coord. Chem. Rev. 2013, 257, 2348–2387.

(30) Erwin, P.; Conron, S. M.; Golden, J. H.; Allen, K.; Thompson, M. E. *Chem. Mater.* **2015**, *27*, 5386–5392.

(31) Eggenspiller, A.; Takai, A.; El-Khouly, M. E.; Ohkubo, K.; Gros, C.

P.; Bernhard, C.; Goze, C.; Denat, F.; Barbe, J.-M.; Fukuzumi, S. J. Phys. Chem. A 2012, 116, 3889–3898.

(32) Zhang, T.; Zhu, X.; Wong, W.-K.; Tam, H.-L.; Wong, W.-Y. Chem. -Eur. J. **2013**, *19*, 739–748.

(33) Lee, C. Y.; Hupp, J. T. Langmuir 2010, 26, 3760-3765.

(34) Gu, Z.-Y.; Guo, D.-S.; Sun, M.; Liu, Y. J. Org. Chem. 2010, 75, 3600–3607.

(35) Leonardi, M. J.; Topka, M. R.; Dinolfo, P. H. *Inorg. Chem.* **2012**, *51*, 13114–13122.

(36) Kursunlu, A. N. RSC Adv. 2014, 4, 47690-47696.

(37) Loudwig, S.; Bayley, H. J. Am. Chem. Soc. 2006, 128, 12404-12405.

(38) Bossi, M. L.; Murgida, D. H.; Aramendia, P. F. J. Phys. Chem. B 2006, 110, 13804–13811.

(39) Yagai, S.; Iwashima, T.; Kishikawa, K.; Nakahara, S.; Karatsu, T.; Kitamura, A. *Chem. - Eur. J.* **2006**, *12*, 3984–3994.

(40) Takamatsu, D. T.; Yamakoshi, Y.; Fukui, K.-i. *J. Phys. Chem. B* **2006**, *110*, 1968–1970.

(41) Harbron, E. J.; Vicente, D. A.; Hadley, D. H.; Imm, M. R. J. Phys. Chem. A 2005, 109, 10846–10853.

(42) Liu, Z. F.; Hashimoto, K.; Fujishima, A. Nature **1990**, 347, 658–660.

(43) Sekkat, Z.; Dumont, M. Appl. Phys. B: Photophys. Laser Chem. 1992, 54, 486–489.

(44) Ikeda, T.; Tsutsumi, O. Science 1995, 268, 1873-1875.

(45) Huang, W.; Peng, F.; Yin, B.; Ma, M.; Chen, B.; Liu, S.; Kim, D.; Song, J. *Chem. - Eur. J.* **2015**, *21*, 15328–15338.

(46) (a) Seybold, P. G.; Gouterman, M. J. Mol. Spectrosc. **1969**, 31, 1– 13. (b) Kim, D.; Osuka, A. Acc. Chem. Res. **2004**, 37, 735–745. (c) Kim,

D.; Osuka, A. J. Phys. Chem. A **2003**, 107, 8791–8816.

(47) (a) Lazarides, T.; Kuhri, S.; Charalambidis, G.; Panda, M. K.;
Guldi, D. M.; Coutsolelos, A. G. *Inorg. Chem.* 2012, *51*, 4193–4204.
(b) Yan, Y.; Wu, F.; Qin, J.; Xu, H.; Shi, M.; Zhou, J.; Mack, J.; Fomo, G.;
Nyokong, T.; Shen, Z. *RSC Adv.* 2016, *6*, 72852–72858.

(48) van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R. Biochim. Biophys. Acta, Bioenerg. 2004, 1657, 82–104.

(49) (a) Easwaramoorthi, S.; Shin, J. Y.; Cho, S.; Kim, P.; Inokuma, Y.; Tsurumaki, E.; Osuka, A.; Kim, D. *Chem. - Eur. J.* **2009**, *15*, 12005– 12017. (b) Whited, M. T.; Patel, N. M.; Roberts, S. T.; Allen, K.; Djurovich, P. I.; Bradforth, S. E.; Thompson, M. E. *Chem. Commun.* **2012**, *48*, 284–286. (c) Vauthey, E. *ChemPhysChem* **2012**, *13*, 2001–2011.

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