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1,4-Phenylene-bridged *meso–meso* linked diporphyrin array

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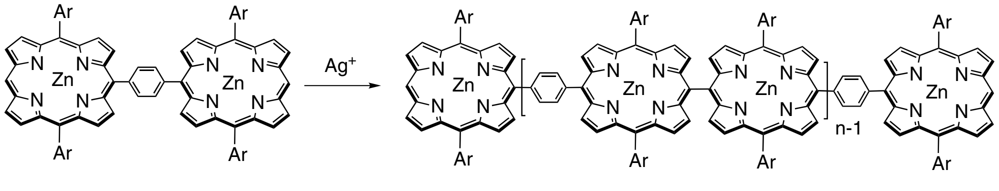
Abstract—1,4-Phenylene-bridged zinc(II) *meso–meso* linked diporphyrin arrays were prepared by Ag(I)-promoted coupling reaction in a regioselective manner.

In recent years, a variety of covalently-linked porphyrin arrays have been explored in light of their uses as biomimetic models of photosynthetic systems, photonic materials, and functional molecular devices.[1] Among these, we reported the Ag(I)-promoted coupling reaction of a 5,15-diaryl Zn(II)porphyrin that enabled the synthesis of very long yet discrete porphyrin arrays. These porphyrin arrays are attractive as a molecular wire owing to the linear shape, the small HOMO–LUMO gap of a constitutional porphyrin, and the ample electronic interaction between neighboring porphyrin subunits arising from the direct linkage.[2] Here we report Ag(I)-promoted coupling reaction of 1,4-phenylene-bridged diporphyrin **ZB** as a prototype of the coupling reaction of spacer-bridged 5,15-diaryl Zn(II) diporphyrins. If this type of coupling reaction is feasible, the overall molecular shape and the magnitude of the electronic interaction of porphyrin arrays can be controlled by the design of a spacer, thus enhancing the synthetic potential of this coupling reaction (Scheme 1).

Diporphyrins **ZB** was prepared from Suzuki coupling of boronate **1** with 1,4-diiodobenzene (Scheme 2).[3,4] To a solution of **ZB** (0.2 mM) in $CHCl_3$ was added $AgPF_6$ (1.0 equiv) and the resulting mixture was stirred for 6 h at room temperature. Progress of the reaction was monitored by MALDI-TOF mass spectroscopy. After the usual workup, the products were separated over size-exclusion chromatography to give porphyrin tetramer **2ZB** (18%), hexamer **3ZB** (8%), and octamer **4ZB** (3%) (Scheme 3).[5] Similar coupling reaction of **2ZB** gave **4ZB** (20%), **6ZB** (10%), and **8ZB** (4%), and that of **4ZB** gave **8ZB** (19%), **12ZB** (9%), and **16ZB** (3%). As is the case for *meso–meso* linked porphyrin arrays,[2] these porphyrin



ZB

***n*ZB**

Scheme 1. A modular approach to the construction of *meso–meso* linked porphyrin oligomers using Ag(I) promoted coupling method.

Keywords: Porphyrin; Porphyrin arrays; Coupling reaction.

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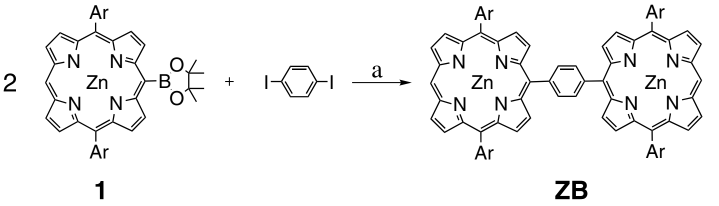
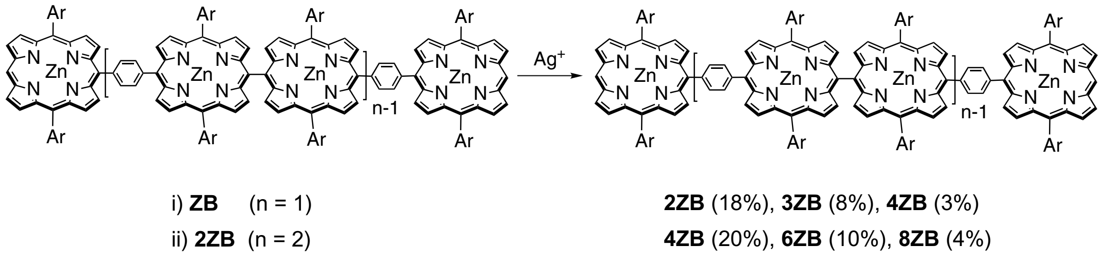


Scheme 2. Synthesis of **ZB**. Ar = *p*-dodecyloxyphenyl. Reagents and conditions: (a) Cs_2CO_3, $PdCl_2(PPh_3)_2$, $AsPh_3$, DMF, 64%.



Scheme 3. Synthesis of 1,4-phenylene-bridged *meso–meso* linked diporphyrin arrays. Ar = *p*-dodecyloxyphenyl.

products have sufficient solubility in $CHCl_3$ and THF and the separation of long arrays were aided by a large difference in molecular size over preparative GPC–HPLC. Molecular length of **16ZB**, a porphyrin 32-mer, is estimated to be 33 nm. All these products have been fully characterized by ^1H NMR, mass, UV–vis, and fluorescence spectra.[6] The coupling regio-selectivity is very high, only occurring at *meso–meso* positions.

The absorption spectrum of **ZB** shows a split Soret band caused by weak exciton coupling between the porphyrins bridged by a 1,4-phenylene spacer, while more distinct exciton coupling prevails in the absorption spectra of the arrays over **2ZB** owing to the presence of *meso–meso* direct connection (Fig. 1). Low-energy Soret bands and Q-bands become intensified with respect to high-energy Soret bands with increasing number of porphyrins. This trend can be explained as follows; the two end porphyrins are escaping from the strong exciton coupling of *meso–meso* linked diporphyrin but are merely involved in a weaker exciton coupling over a 1,4-phenylene spacer, thus mainly contributing to the absorbance around 410–420 nm,[6] while the intervening *meso–meso* linked diporphyrin subunits are contributing to the absorbances around 410–420 and 465 nm. Therefore, the longer the arrays, the larger the contribution of *meso–meso* linked porphyrin arrays, hence leading to increasing absorbance around 465 nm.

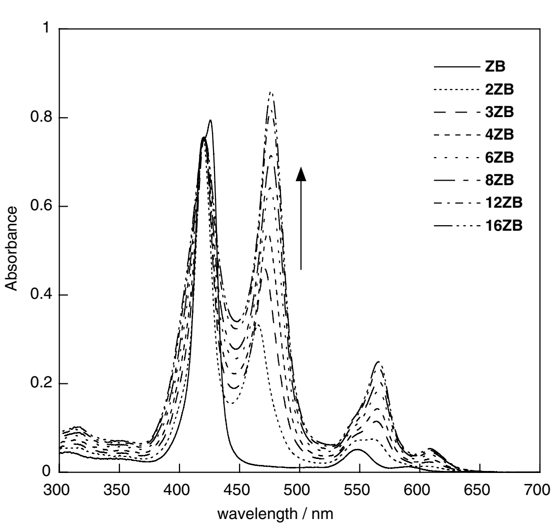


Figure 1. UV–vis absorption spectra of ***n*ZB** in toluene. Absorbances at 420 nm were normalized.

The steady-state fluorescence spectrum of **ZB** exhibits an emission with peaks at 599 and 646 nm that is characteristic of Zn(II) porphyrin,[2] while the arrays **2ZB**, **3ZB**, and **4ZB** exhibit only the emission from the *meso–meso* linked diporphyrin subunits, clearly indicating efficient excitation energy transfer from the end monomeric porphyrin fragments to the *meso–meso* linked diporphyrin fragments.[2b,c] Interestingly, the relative fluorescence intensity becomes gradually increased in order of **ZB** < **2ZB** < **4ZB** (Fig. 2a) and then decreases in order of **4ZB** > **6ZB** > **8ZB** > **12ZB** > **16ZB** (Fig. 2b). The octamer **4ZB** is the most fluorescent. This feature is similar to that of the *meso–meso* linked porphyrin arrays, in which the maximum fluorescence intensity is observed for a hexadecamer.[2e] This feature may be ascribed to the delocalization nature of the single excited state over several porphyrins (coherent length) and the conformational heterogeneity of the arrays.[7] Judging from the observed fluorescence intensities, the coherent length may be estimated to be around 8 for the 1,4-phenylene-bridged array. When the arrays becomes more longer than **4ZB**, the conformational heterogeneity becomes more serious, which leads to the reduction of fluorescence quantum yields.

In summary, the Ag(I)-promoted oxidative coupling of the 1,4-phenylene-bridged diporphyrin **ZB** proceeds

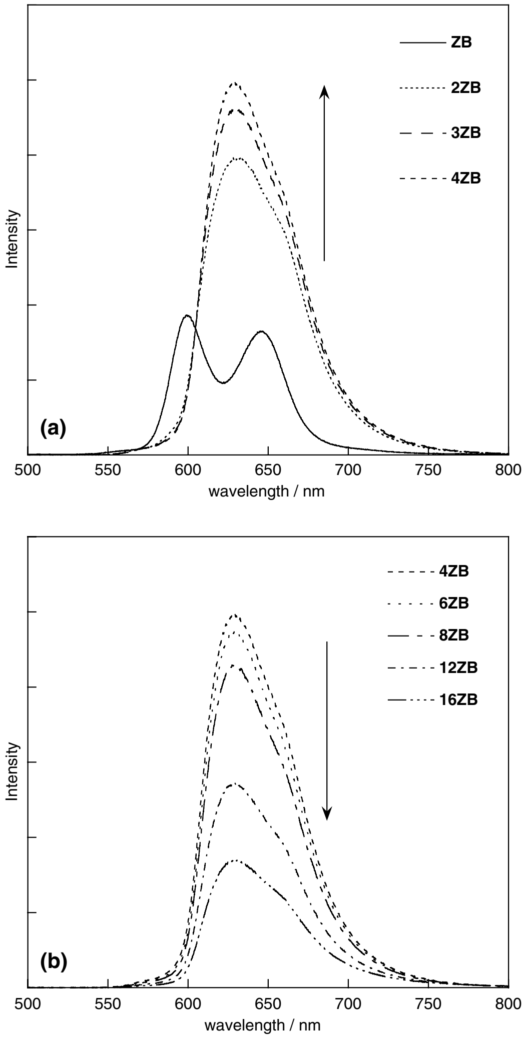


Figure 2. Fluorescence spectra of (a) **ZB**–**4ZB** and (b) **4ZB**–**16ZB** in toluene, taken for excitation at 420 nm. Absorbances at 420 nm were adjusted at 0.75.

with high *meso–meso* regio-selectivity to give long linear porphyrin arrays. This reaction has been extended for long arrays. Incorporation of other aromatic spacer is now actively investigated in this laboratory.

Acknowledgements

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4. Boronate porphyrin **1** (140 mg, 0.137 mmol) was mixed with 1,4-diiodinebenzene (22.7 mg, 0.0687 mmol), Cs_2CO_3 (116 mg), $PdCl_2$ $(PPh_3)_2$ (16 mg) and $AsPh_3$ (4.1 mg) in DMF. The mixture was degassed three times by freeze-pump thaw cycles and stirred at 80 °C for 6 h. Then the mixture was washed with water, extracted with $CHCl_3$, dried over $MgSO_4$ and evaporated. The residue was recrystallized with $CHCl_3$/acetonitrile. After passed through a short silica gel column and evaporated, the residue was loaded in GPC. The first fraction is **ZB** (82 mg, 64%). **1**: ^1H NMR ($CDCl_3$, 600 MHz): δ 10.30 (s, 1H), 9.92 (d, $J = 4.6$ Hz, 2H), 9.40 (d, $J = 4.6$ Hz, 2H), 9.15 (d, $J = 4.56$ Hz, 2H), 9.11 (d, $J = 4.56$ Hz, 2H), 8.13 (d, $J = 8.2$ Hz, 4H), 7.29 (d, $J = 8.2$ Hz, 4H), 4.28 (t, 4H), 2.01 (m, 4H), 1.85 (s, 12H), 1.65 (m, 4H), 1.50–1.30 (br m, 32H), and 0.90 (t, 6H). MALDI-TOF MS found *m/z* 1019, calcd for $C_{62}H_{79}N_4O_4BZn$, *m/z* 1019; UV–vis($CHCl_3$); $\lambda_{max} = 414$, and 542 nm. **ZB**: ^1H NMR ($CDCl_3$, 600 MHz): δ 10.25 (s, 2H), 9.44 (d, $J = 4.6$ Hz, 4H), 9.41 (d, $J = 4.6$ Hz, 4H), 9.22 (d, $J = 4.1$ Hz, 4H), 9.17 (d, $J = 4.1$ Hz, 4H), 8.60 (s, 4H), 8.20 (d, $J = 8.2$ Hz, 8H), 7.34 (d, $J = 8.3$ Hz, 8H), 4.30 (t, 8H), 2.02 (m, 8H), 1.66 (m, 8H), 1.50–1.30 (br m, 64H), and 0.90 (t, 12H). MALDI-TOF MS found *m/z* 1863, calcd for $C_{118}H_{138}N_8O_4Zn_2$, *m/z* 1863; UV–vis($CHCl_3$); $\lambda_{max} = 420$, 425, 548, and 590 nm.
5. To a solution of **ZB** (100 mg, 0.0536 mmol) in $CHCl_3$ was added a solution of $AgPF_6$ in acetonitrile (0.1 M, 0.0536 mmol). After stirring for 6 h, the mixture was diluted with water, and the porphyrin products were extracted with $CHCl_3$. Combined organic extract was washed with water and dried over anhydrous Na_2SO_4. After the zinc metallation with $Zn(OAc)_2$, the products were passed through short silica gel column, and evaporated. Separation by GPC–HPLC allowed the isolation of four major fractions: tetramer **2ZB** (18 mg, 18%), hexamer **3ZB** (8 mg, 8%), octamer **4ZB** (3 mg, 3%), and recovery of **ZB** (42 mg, 42%). **2ZB**: ^1H NMR ($CDCl_3$, 600 MHz): δ 10.22 (s, 2H), 9.52 (m, 8H), 9.41 (d, $J = 4.6$ Hz, 4H), 9.39 (d, $J = 4.6$ Hz, 4H), 9.27 (m, 8H), 9.17 (d, $J = 4.1$ Hz, 4H), 8.80 (d, $J = 5.0$ Hz, 4H), 8.71 (d, $J = 7.3$ Hz, 4H), 8.68 (d, $J = 7.3$ Hz, 4H), 8.21 (m, 20H), 7.34 (d, $J = 8.8$ Hz, 8H), 7.23 (d, $J = 8.8$ Hz, 8H), 4.28 (t, 8H), 4.17 (t, 8H), 2.01 (m, 8H), 1.91 (m, 8H), 1.60-1.26 (br m, 144H), 0.90 (t, 12H), and 0.84 (t, 12H). MALDI-TOF MS found *m/z* 3721, calcd for $C_{236}H_{274}N_{16}O_8Zn_4$, *m/z* 3724; UV–vis($CHCl_3$); $\lambda_{max} = 420$, 465, 555, and 609 nm. **3ZB**: ^1H NMR ($CDCl_3$, 600 MHz): δ

10.28 (s, 2H), 9.51–9.58 (m, 12H), 9.44 (d, $J = 4.6$ Hz, 4H), 9.30–9.26 (m, 12H), 9.20 (d, $J = 4.14$ Hz, 4H), 8.79–8.81 (m, 12H), 8.73–8.68 (m, 8H), 8.22–8.25 (m, 32H), 7.36 (d, $J = 8.8$ Hz, 8H), 7.7.25–7.27 (m, 16H), 4.29 (t, 8H), 4.20 (m, 16H),2.03 (m, 8H), 1.93 (m, 16H), 1.70–1.26 (br m, 216H), 0.91 (t, 12H), and 0.84 (m, 24H). MALDI-TOF MS found m/z 5579, calcd for $C_{354}H_{410}N_{24}O_{12}Zn_6$, m/z 5586; UV–vis($CHCl_3$); $\lambda_{max} = 420$, 471, 566, and 612 nm. **4ZB**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.31 (s, 2H), 9.58–9.46 (m, 20H), 9.29–9.21 (m, 20H), 8.82–8.72 (m, 28H), 8.26–8.21 (m, 44H), 7.37 (d, $J = 8.8$ Hz, 8H), 7.27 (m, 24H), 4.32 (t, 8H), 4.22 (m, 24H), 2.04 (m, 8H), 1.94 (m, 24H), 1.60–1.26 (br m, 288H), 0.91 (t, 12H), and 0.84–0.90 (m, 48H). MALDI-TOF MS found m/z 7442, calcd for $C_{472}H_{546}N_{32}O_{16}Zn_8$, m/z 7447; UV–vis($CHCl_3$); $\lambda_{max} = 420$, 474, 568, and 612 nm. **6ZB**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.30 (s, 2H), 9.56–9.45 (m, 28H), 9.28–9.21 (m, 28H), 8.79–8.67 (m, 44H), 8.25–8.16 (m, 68H), 7.36 (d, $J = 8.8$ Hz, 8H), 7.26–7.29 (m, 40H), 4.32 (t, 8H), 4.22 (m, 40H), 2.05 (m, 8H), 1.94 (m, 40H), 1.60–1.26 (br m, 432H), and 0.84–0.92 (m, 72H). MALDI-TOF MS found m/z 11241, calcd for $C_{708}H_{818}N_{48}O_{24}Zn_{12}$, m/z 11169; UV–vis($CHCl_3$); $\lambda_{max} = 420$, 475, 568, and 612 nm. **8ZB**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.32 (s, 2H), 9.58–9.47 (m, 36H), 9.30–9.22 (m, 36H), 8.82–8.67 (m, 60H), 8.25–8.16 (m, 92H), 7.36 (d, $J = 8.8$ Hz, 8H), 7.25–7.29 (m, 56H), 4.32–4.20 (m, 64H), 2.05–1.94 (m, 64H), 1.60–1.26 (br m, 576H), and 0.84–0.92 (m, 96H). MALDI-TOF MS found m/z 15121, calcd for $C_{944}H_{1090}N_{64}O_{32}Zn_{16}$, m/z 14891; $\lambda_{max} = 420$, 476, 568, and 612 nm. **12ZB**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.32 (s, 2H), 9.56–9.46 (m, 52H), 9.29–9.21 (m, 52H), 8.81–8.66 (m, 92H), 8.25–8.17 (m, 140H), 7.36–7.25 (m, 96H), 4.32–4.20 (m, 96H), 2.05–1.94 (m, 96H), 1.60–1.26 (br m, 864H), and 0.84–0.92 (m, 144H). MALDI-TOF MS found m/z 22616; calcd for $C_{1416}H_{1634}N_{96}O_{48}Zn_{24}$, m/z 22336; $\lambda_{max} = 420$, 476, 568, and 613 nm. **16ZB**: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.31 (s, 2H), 9.56–9.46 (m, 68H), 9.29–9.21 (m, 68H), 8.81–8.66 (m, 124H), 8.25–8.17 (m, 188H), 7.36–7.25 (m, 128H), 4.32–4.20 (m, 128H), 2.05–1.94 (m, 128H), 1.60–1.26 (br m, 1152H), and 0.84–0.92 (m, 192H). $\lambda_{max} = 420$, 476, 568, and 613 nm.

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