

Rapid Intramolecular Hole Hopping in *meso*–*meso* and *meta*-Phenylene Linked Linear and Cyclic Multiporphyrin Arrays

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Abstract: A series of zinc porphyrin arrays comprised of a *meso*–*meso* linked porphyrin dimer, a *meta*-phenylene linked dimer, gable-like tetramers consisting of the *meso*–*meso* linked dimers bridged via a *meta*-phenylene linker, and a dodecameric ring composed of this alternating dimeric pattern were singly oxidized, and intramolecular hole hopping between the porphyrin moieties was probed using electron paramagnetic resonance (EPR) spectroscopy. Electron nuclear double resonance (ENDOR) spectroscopy was also used to probe hole hopping within the dimers. Rapid hole hopping occurs between both porphyrins within both dimers and among three porphyrins of the tetramers with rates $>10^7$ s⁻¹ at 290 K. Additionally, the hole hops among 8–12 porphyrins in the dodecameric ring with a rate that is $>10^7$ s⁻¹ at 290 K, but hopping is slow at 180 K. These results show that hole hopping is rapid even though the *meta*-phenyl bridges and direct *meso*–*meso* linkages do not provide optimal electronic coupling between the porphyrins within these multiporphyrin arrays. This greatly expands the scope of possible structures that can be employed to tailor the design of long distance charge transport systems.

Introduction

The photosynthetic proteins in green plants and photosynthetic bacteria have long provided the inspiration for developing synthetic architectures to explore the energy and electron transfer functions of these natural solar energy conversion systems.^{1,2} Porphyrin building blocks have been used in the quest to build large circular chromophore arrays similar to those found in the light-harvesting antenna complexes (LH1 and LH2) of photosynthetic purple bacteria^{3–6} largely because of their synthetic accessibility relative to the natural chlorophylls, photochemical stability, and similar optical and redox properties. Numerous covalently linked^{7–17} and self-assembled^{18–21} multiporphyrin cyclic arrays have been prepared previously. The covalently

linked array systems typically connect the porphyrins using phenylene, phenylene-ethynylene, and butadiyne linkers. Peng

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- Wasielewski, M. R. *J. Org. Chem.* **2006**, *71*, 5051–5066.
- Choi, M. S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150–158.
- Cogdell, R. J.; Gall, A.; Kohler, J. *Q. Rev. Biophys.* **2006**, *39*, 227–324.
- Freer, A.; Prince, S.; Sauer, K.; Papiz, M.; Hawthornthwaite-Lawless, A.; McDermott, G.; Cogdell, R.; Isaacs, N. W. *Structure* **1996**, *4*, 449–462.
- Koepke, J.; Hu, X. C.; Muenke, C.; Schulten, K.; Michel, H. *Structure* **1996**, *4*, 581–597.
- McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517–521.

- Nakamura, Y.; Aratani, N.; Osuka, A. *Chem. Soc. Rev.* **2007**, *36*, 831–845.
- Nakamura, Y.; Hwang, I. W.; Aratani, N.; Ahn, T. K.; Ko, D. M.; Takagi, A.; Kawai, T.; Matsumoto, T.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 236–246.
- Hoffmann, M.; Karnbratt, J.; Chang, M. H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4993–4996.
- Hoffmann, M.; Wilson, C. J.; Odell, B.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3122–3125.
- Mongin, O.; Schuway, A.; Vallot, M. A.; Gossauer, A. *Tetrahedron Lett.* **1999**, *40*, 8347–8350.
- Li, J. Z.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927–8940.
- Wagner, R. W.; Seth, J.; Yang, S. I.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1998**, *63*, 5042–5049.
- Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1714–1715.
- Aratani, N.; Osuka, A. *Chem. Commun.* **2008**, 4067–4069.
- Vidal-Ferran, A.; Clyde-Watson, Z.; Bampos, N.; Sanders, J. K. M. *J. Org. Chem.* **1997**, *62*, 240–241.
- Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2255–2267.
- Fujisawa, K.; Satake, A.; Hirota, S.; Kobuke, Y. *Chem.—Eur. J.* **2008**, *14*, 10735–10744.
- Kuramochi, Y.; Satake, A.; Kobuke, Y. *J. Am. Chem. Soc.* **2004**, *126*, 8668–8669.
- Jensen, R. A.; Kelley, R. F.; Lee, S. J.; Wasielewski, M. R.; Hupp, J. T.; Tiede, D. M. *Chem. Commun.* **2008**, 1886–1888.
- Metselaar, G. A.; Ballester, P.; Mendoza, J. d. *New J. Chem.* **2009**, *33*, 777–783.

et al.²² prepared the first cyclic array that uses a direct *meso-meso* linkage between two porphyrins. Six *meso-meso* linked porphyrin dimers were coupled using a *meta-phenylene* bridge in an alternating fashion to form a rigid dodecameric ring with an ~ 35 Å diameter. Efficient energy migration within this cyclic array is attributed to its rigid structure and strong dipole-dipole interactions between neighboring subunits.^{23–25} However, ground-state intramolecular hole hopping and/or charge delocalization have yet to be explored in such systems, a property which could render these materials useful in a variety of applications as electronic materials.

Electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopies are well-established probes of charge hopping in both chemical and biological systems.^{12,26–30} Notably, these techniques provide convincing evidence that the oxidized primary electron donor in the bacterial photosynthetic reaction center consists of a bacteriochlorophyll (BChl) “special pair” over which the positive charge is delocalized. The single-line, inhomogeneously broadened EPR spectrum of the BChl₂⁺ special pair narrows by a factor of $1/\sqrt{2}$ over the signal obtained from monomeric BChl⁺, while ENDOR spectroscopy shows a 2-fold reduction of the isotropic hyperfine coupling constants (hfcc’s) of BChl₂⁺ relative to those of BChl⁺.^{31–33} Prior studies of radical cation hopping and/or delocalization in mono-oxidized multiporphyrin systems have examined dimers connected by phenylene, diphenylethyne, and ethyne linkages.^{12,34–38} In one case, hole delocalization over at least seven porphyrins has been observed in long linear arrays on the EPR time scale (10^7 s⁻¹),³⁸ which is set by the hyperfine coupling between the hole (unpaired electron) and the nitrogen and hydrogen nuclei in the porphyrins. Other small two- or three-dimensional porphyrin architectures such as boxes, stars,

and rings, generally consisting of 4–6 porphyrins, also exhibit hole hopping phenomena as probed by EPR.^{12,35,39}

In this study, we have used EPR and ENDOR spectroscopies to explore hole hopping in a series of mono-oxidized multiporphyrin systems, including the *meso-meso* linked porphyrin dimer, **Z2B**, the *meta-phenylene* linked dimer, **MPD**, gable-like tetramers comprised of the *meso-meso* linked dimers bridged by a *meta-phenylene* linkage (**4ZA** and **4ZB**), and a dodecameric ring (**C12Z**) comprised of this alternating pattern (Figure 1). In these solution phase studies we found rapid hole hopping between the two porphyrins within both dimers and among three porphyrins within the tetramers. Additionally, hole hopping within the dodecameric ring was observed among 8–12 porphyrins on the EPR time scale ($>10^7$ s⁻¹). These results give further insight into how *meta-phenyl* bridges and direct *meso-meso* linkages influence hole mobilities in multiporphyrin arrays. This is important for designing extended molecular charge transport arrays.

Experimental Section

Synthesis. The synthesis of **MPD**⁴⁰ and **C12Z**^{22,41,42} has been described previously, while that of the model compounds **Z2B**, **4ZA**, and **4ZB** is detailed in the Supporting Information and is minimally modified from literature procedures^{41,42} by adding phenyl groups at the terminal *meso* positions of each acyclic array to preclude oligomerization upon chemical oxidation with AgClO₄/I₂. Briefly, *N*-bromosuccinimide was used to dibrominate the *meso-meso* linked diporphyrin or H-terminated tetramers. A Suzuki coupling between the dibromo compounds and phenylboronic acid gave the phenyl-terminated oligomers **Z2B**, **4ZA**, and **4ZB** in 84, 89, and 85% yields, respectively.

Optical Spectroscopy. Steady-state absorption measurements were performed on a Shimadzu 1601 UV-vis spectrometer. A 1.0 mm quartz cuvette was used, and all measurements were performed at room temperature. Nonstabilized HPLC grade dichloromethane (DCM) from Fischer and inhibitor-free HPLC grade tetrahydrofuran (THF) from Aldrich were dried using a Glass Contour solvent purification system.

EPR and ENDOR Spectroscopy. EPR and ENDOR spectra were acquired with a Bruker Elexsys E580 spectrometer, fitted with the DICE ENDOR accessory, EN801 resonator, and an ENI A-500 RF power amplifier. Applied RF powers ranged from 250 to 300 W across the 4 MHz scanned range, and the microwave power ranged from 0.6 to 100 mW. The sample temperature was controlled by a liquid nitrogen flow system. Solutions of **ZnTPP**⁺, **MPD**⁺, **Z2B**⁺, **4ZA**⁺, **4ZB**⁺, and **C12Z**⁺ ($(0.25 - 1.0) \times 10^{-4}$ M) in CH₂Cl₂/THF (9:1, v:v) were generated by addition of a solution of I₂ and AgClO₄ dissolved in acetonitrile. The oxidation process was monitored using UV-vis absorption spectroscopy to maximize the production of the singly oxidized species. Oxidized samples were loaded into 2.35 mm I.D. quartz tubes and sealed under vacuum following several freeze-pump-thaw cycles. A spline fit baseline correction was applied to the ENDOR spectra following integration.

Results and Discussion

Steady-State Spectroscopy. The normalized UV-vis absorption spectra of all neutral species in CH₂Cl₂/THF (9:1, v:v) are

- (22) Peng, X.; Aratani, N.; Takagi, A.; Matsumoto, T.; Kawai, T.; Hwang, I. W.; Ahn, T. K.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2004**, *126*, 4468–4469.
- (23) Park, M.; Yoon, M. C.; Yoon, Z. S.; Hori, T.; Peng, X.; Aratani, N.; Hotta, J. I.; Uji-i, H.; Sliwa, M.; Hofkens, J.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2007**, *129*, 3539–3544.
- (24) Yang, J.; Park, M.; Yoon, Z. S.; Hori, T.; Peng, X. B.; Aratani, N.; Dedecker, P.; Hotta, J. I.; Uji-i, H.; Sliwa, M.; Hofkens, J.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2008**, *130*, 1879–1884.
- (25) Hwang, I. W.; Ko, D. M.; Ahn, T. K.; Yoon, Z. S.; Kim, D. H.; Peng, X. B.; Aratani, N.; Osuka, A. *J. Phys. Chem. B* **2005**, *109*, 8643–8651.
- (26) Srivatsan, N.; Norris, J. R. *J. Phys. Chem. B* **2001**, *105*, 12391–12398.
- (27) Muresan, A. Z.; Thamnyongkit, P.; Diers, J. R.; Holten, D.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem.* **2008**, *73*, 6947–6959.
- (28) Baumgarten, M.; Huber, W.; Müllen, K. *Adv. Phys. Org. Chem.* **1993**, *28*, 1–44.
- (29) Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 6462–6463.
- (30) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508–515.
- (31) Norris, J. R.; Uphaus, R. A.; Crespi, H. L.; Katz, J. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 625–628.
- (32) Norris, J. R.; Druyan, M. E.; Katz, J. *J. Am. Chem. Soc.* **1973**, *95*, 1680–1682.
- (33) Feher, G.; Hoff, A. J.; Isaacson, R. A.; Ackerson, L. C. *Ann. N.Y. Acad. Sci.* **1975**, *244*, 239–259.
- (34) Huber, M.; Kurreck, H.; Vonmaltzan, B.; Plato, M.; Mobius, K. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1087–1094.
- (35) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578–10592.
- (36) Seth, J.; Palaniappan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194–11207.
- (37) Thamnyongkit, P.; Muresan, A. Z.; Diers, J. R.; Holten, D.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2007**, *72*, 5207–5217.
- (38) Susumu, K.; Frail, P. R.; Angiolillo, P. J.; Therien, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 8380–8381.

- (39) Li, J. Z.; Diers, J. R.; Seth, J.; Yang, S. I.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 9090–9100.
- (40) Cho, S.; Yoon, M. C.; Kim, C. H.; Aratani, N.; Mori, G.; Joo, T.; Osuka, A.; Kim, D. *J. Phys. Chem. C* **2007**, *111*, 14881–14888.
- (41) Hori, T.; Aratani, N.; Takagi, A.; Matsumoto, T.; Kawai, T.; Yoon, M. C.; Yoon, Z. S.; Cho, S.; Kim, D.; Osuka, A. *Chem.—Eur. J.* **2006**, *12*, 1319–1327.
- (42) Hori, T.; Peng, X.; Aratani, N.; Takagi, A.; Matsumoto, T.; Kawai, T.; Yoon, Z. S.; Yoon, M. C.; Yang, J.; Kim, D.; Osuka, A. *Chem.—Eur. J.* **2008**, *14*, 582–595.

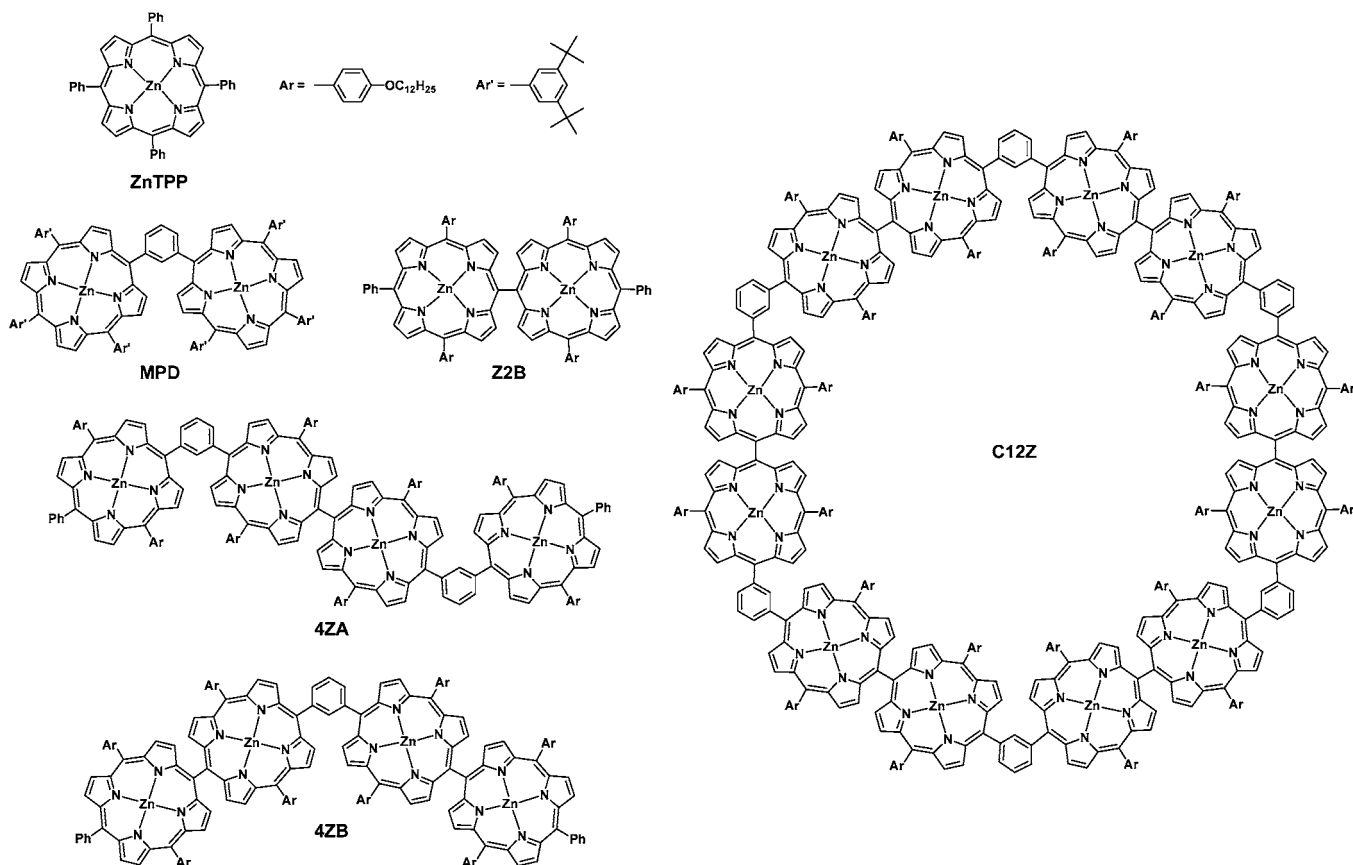


Figure 1. Molecular structures.

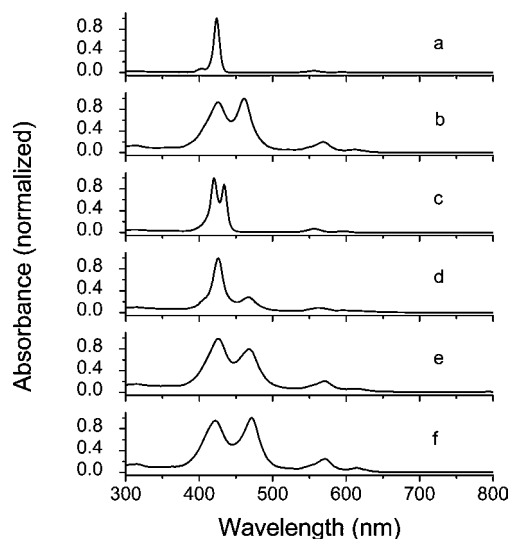


Figure 2. UV-vis absorption spectra of ZnTPP (a), Z2B (b), MPD (c), 4ZA (d), 4ZB (e), and C12Z (f) in CH₂Cl₂/THF (9:1).

presented in Figure 2. It is well established that there is a relatively large energy separation in metalloporphyrin monomers, such as ZnTPP, between the S₂ (B or Soret band) and S₁ (Q-band) states, absorbing at 424 nm (B band) and 556 and 595 nm (Q bands). The UV-vis spectra of the dimers exhibit perturbations in the B-bands due to strong excitonic interactions between the two zinc porphyrins.⁴³ The Soret band of the zinc porphyrin monomer has two degenerate perpendicular components B_x and B_y. However, as previously reported for the

meso-meso linked dimer Z2B,^{44,45} only the parallel B_x transitions couple effectively, while the other dipole interactions should be nearly zero for an averaged perpendicular conformation between the two zinc porphyrins. This results in a split of the Z2B Soret band into a red-shifted B_x component at 461 nm and unperturbed B_y and B_z components at 426 nm. The Q-band of Z2B is also slightly red-shifted to 569 and 612 nm. Due to the gable geometry of MPD,⁴⁰ both *H*- and *J*-type exciton interactions are present, which results in a split B-band that is both red- and blue-shifted to 420 and 434 nm, respectively. In the tetramers 4ZA and 4ZB the gable geometry is formed by combining the *meta*-phenylene linkage in MPD and the directly *meso-meso* linked zinc porphyrin geometry in Z2B in an alternating fashion, such that in 4ZA there is one *meso-meso* linkage and in 4ZB there are two. Thus, the intensity of the red-shifted B_x band is larger in 4ZB than 4ZA. The absorption spectra of the tetramers and C12Z are also further red-shifted compared to that of Z2B, which is indicative of strong excitonic coupling between the diporphyrin Z2B subunits.²³

Upon partial chemical oxidation of the zinc porphyrin species (Figures 3 and S1–S6), absorption changes are observed across the spectrum that are consistent with those observed previously for *meso*-substituted Zn porphyrin radical cations.⁴⁶ In the case of the exciton coupled dimers, tetramers, and cyclic array, a decrease in the red-shifted B band is observed, as seen in the

(43) Kasha, M.; Rawles, H. R.; El-Bayoumi, M. L. *Pure Appl. Chem.* **1965**, *11*, 371–392.

(44) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458–1462.

(45) Kim, D.; Osuka, A. *J. Phys. Chem. A* **2003**, *107*, 8791–8816.

(46) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451–3459.

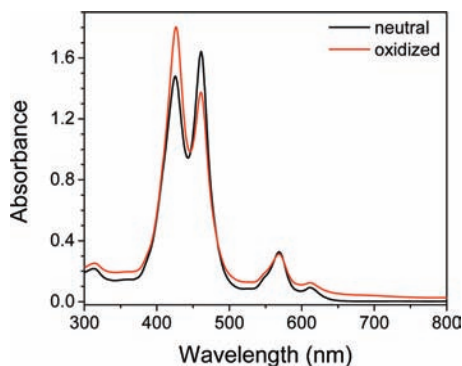


Figure 3. UV-vis absorption spectra of neutral **Z2B** (black) and partially oxidized **Z2B⁺** (red) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (9:1).

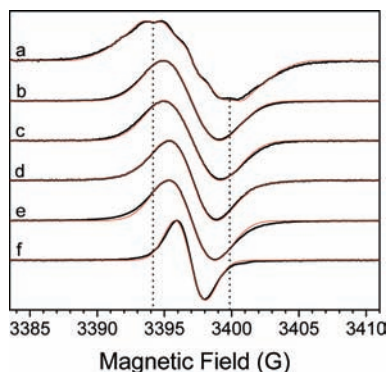


Figure 4. CW-EPR spectra of **ZnTPP⁺** (a), **MPD⁺** (b), **Z2B⁺** (c), **4ZA⁺** (d), **4ZB⁺** (e), and **C12Z⁺** (f) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (9:1) at 290 K. Microwave power was 0.6 mW (a), 20 mW (b, c, f), or 60 mW (d, e) with a modulation amplitude of 0.1 G (a) or 1 G (b–f) at 25 kHz. Simulations are shown in red, and the simulation parameters are presented in Table S1.

UV-vis spectra of **Z2B⁺** (Figure 3), as the exciton coupling is lost upon the formation of the mono-oxidized species. The degree of oxidation was maintained well under 50, 25, and 8% for the dimers, tetramers, and dodecamer, respectively, to ensure that each species contains a single radical cation.

EPR and ENDOR Spectroscopy. The EPR spectrum of **ZnTPP⁺** shown in Figure 4a is typical of a porphyrin π -cation radical in the $^2A_{2u}$ ground state, exhibiting the characteristic nine hyperfine lines due to the interaction of the unpaired spin with the four pyrrole nitrogens and broadening of these lines from the interaction of the unpaired spin with the phenyl protons. The EPR spectra of **MPD⁺**, **Z2B⁺**, **4ZA⁺**, **4ZB⁺**, and **C12Z⁺** are inhomogeneously broadened into single unresolved lines owing to the large number of electron–nuclear hyperfine interactions within each molecule. At the same time, rapid hopping or delocalization will reduce the magnitude of each hyperfine interaction.³¹ As seen in Figure 4, the peak-to-peak EPR line width decreases from 5.8 to 2.1 G as the number of porphyrins increases from just a single **ZnTPP** to 12 porphyrins in **C12Z**. The measured peak-to-peak line widths, ΔH , are summarized in Table 1. While both dimers exhibit Gaussian EPR line shapes, the line shapes of the larger systems **4ZA⁺**, **4ZB⁺**, and **C12Z⁺** show ~20–30% deviations from a pure Gaussian (see below). All radical cations have measured g -values of 2.0022 ± 0.0002 , which is typical for organic aromatic molecules.⁴⁷

Table 1. EPR Line Widths (ΔH), Line Width Ratios of **ZnTPP⁺** Monomer to Porphyrin N -mers ($\Delta H_M/\Delta H_N$), and Number of Porphyrins over Which the Radical Cation Is Shared (N_S) Based on Eq 1

molecule	ΔH (G)	$\Delta H_M/\Delta H_N$	N_S
ZnTPP⁺	5.8	—	—
MPD⁺	4.2	1.4	1.9
Z2B⁺	4.3	1.3	1.8
4ZA⁺	3.5	1.7	2.7
4ZB⁺	3.4	1.7	2.9
C12Z⁺	2.1	2.8	7.6

The number of sites over which the radical cation is shared by either hole hopping or delocalization can be estimated from the narrowing of Gaussian EPR lines using the equation of Norris et al.,³¹

$$\Delta H_N = \left(\frac{1}{\sqrt{N_S}} \right) \Delta H_M \quad (1)$$

which relates the line width of the monomer, ΔH_M , to the line width when an unpaired spin is shared over N_S molecular sites, ΔH_N . The ratios of ΔH_M to ΔH_N are reported in Table 1 along with the number of hopping sites N_S , according to eq 1, over which the charge is rapidly hopping on the EPR time scale ($>10^7$ s⁻¹). More specifically, the EPR time scale is governed by the hyperfine interactions between the unpaired spin and the nitrogen and hydrogen nuclei of the porphyrins, such that a typical porphyrin nitrogen hfcc of 1.54 G corresponds to a frequency of 4.3×10^6 s⁻¹, the rate at which charge hopping between porphyrins must exceed in order to observe EPR line narrowing. The unpaired spin is fully shared by the two porphyrins in the **MPD⁺** and **Z2B⁺** dimers. However, in both tetramers, **4ZA⁺** and **4ZB⁺**, the unpaired spin is only rapidly hopping among three porphyrins. This could be due to the fact that the oxidation potentials (HOMO energies) of the four porphyrins in the tetramers are not sufficiently similar to allow thermally activated hopping among all four porphyrins at room temperature. In this case, the hole would spend more time on the two inner porphyrins which have a slightly lower oxidation potential than the two outer porphyrins, such that the overall charge hopping process, as revealed by EPR line width narrowing, becomes slow.^{48,49} According to eq 1, which assumes a Gaussian line shape, the unpaired spin is rapidly hopping among nearly eight porphyrins in **C12Z⁺**.

These results were analyzed further by simulating the EPR spectra using WinSIM.⁵⁰ The four nitrogen and eight *ortho*-phenyl hydrogen isotropic hfcc's of **ZnTPP⁺** were obtained by fitting the EPR spectrum using a Gaussian line shape, which gave nitrogen (a_N) and proton (a_H) coupling constants consistent with the literature value, $a_N = 1.54$ G and $a_H = 0.28$ G.^{46,51} Spectra of the multiporphyrin arrays were then simulated by adding the appropriate number of extra nuclei and dividing the isotropic hfcc by the additional number of porphyrins, while keeping the line width parameter constant. In the case of **Z2B⁺** for example, eight nitrogens were used (four for each porphyrin) with $a_N = 0.77$ G and 12 *ortho*-phenyl hydrogens were used

(48) Wilson, T. M.; Tauber, M. J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2009**, *131*, 8952–8957.

(49) Muller, U.; Baumgarten, M. *J. Am. Chem. Soc.* **1995**, *117*, 5840–5850.

(50) Duling, D. R. *J. Magn. Reson., Ser. B* **1994**, *104*, 105–110.

(51) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 197–256.

(47) Gerson, F.; Huber, W. *Electron spin resonance spectroscopy of organic radicals*; Wiley-VCH: Weinheim, 2003.

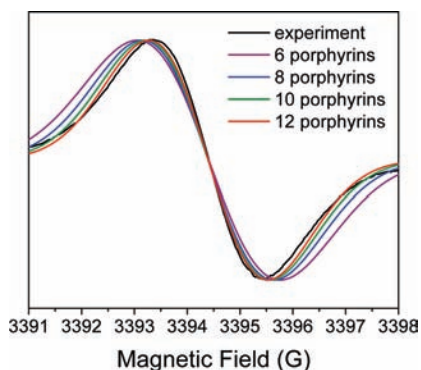


Figure 5. Experimental CW-EPR spectrum of **C12Z⁺⁺** and simulated spectra based on the extent of charge hopping between porphyrin units within the ring on the EPR time scale. Simulation parameters are reported in Table S1.

from the six *meso*-substituted aryl groups with $a_H = 0.14$ G. The simulated spectra are shown in red overlaying the experimental data in Figure 4, and the simulation parameters are reported in Table S1. Again, the dimer spectra were well simulated by a spectrum having parameters consistent with hole hopping between both porphyrins within the dimer, while the tetramer spectra were best simulated with hole hopping among only three porphyrins (Figures S7 and S8). However, assuming a Gaussian line shape for the simulation of **C12Z⁺⁺** does not yield a particularly good fit (Figure 5). Nonetheless, curve fitting using a Gaussian line shape provides the best agreement with the EPR spectrum of **C12Z⁺⁺** if the hole is hopping rapidly among all 12 units of the cyclic array at a rate $>10^7$ s⁻¹. Simulations performed using either a pure Lorentzian (Figures S9 and S10, Table S2) or a mixed Gaussian/Lorentzian (Voigt) line shape (not shown) also indicated hole hopping among 10–12 porphyrins. In view of these simulations and the measured ΔH values, it is concluded that the hole hops between 8 and 12 porphyrins in **C12Z⁺⁺** at a rate $>10^7$ s⁻¹. The observation of mixed Gaussian/Lorentzian (Voigt) line shapes has also been reported in other large multiporphyrin³⁸ arrays and multi-BChl proteins.^{52–54} One possibility for the emergence of Lorentzian line shapes along with narrowing is spin exchange; however we consider this unlikely with the dilute oxidation conditions used in these experiments. Instead, we hypothesize that the hopping rate lies in an intermediate motion regime, in which EPR line shapes have been shown to deviate from their Gaussian shape observed at either the fast or slow hopping limits.⁵⁵

Upon lowering the temperature to 180 K, near the freezing point of the solvent, the CW-EPR spectra of all radical cation species broadened to approximately the width of the **ZnTPP⁺⁺** monomer (Figure S11). The samples neither showed signs of broadening until the temperature decreased below 250 K nor exhibited narrowing upon heating to 310 K, except for **4ZB⁺⁺** and **C12Z⁺⁺**, which showed slight narrowing from 3.4 to 3.2 G and from 2.1 to 2.0 G, respectively. This indicates that hole hopping between *meso*–*meso* linked and *meta*-phenylene linked

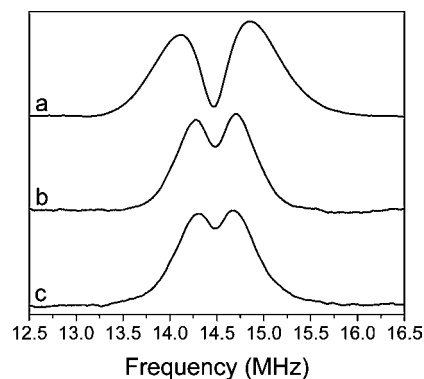


Figure 6. ¹H-ENDOR spectra of **ZnTPP⁺⁺** (a), **MPD⁺⁺** (b), and **Z2B⁺⁺** (c) at 290 K in CH₂Cl₂/THF. Microwave powers were 20–100 mW, and RF power was 240–400 W with a modulation frequency of 100 kHz.

porphyrins is a thermally activated process, likely dependent upon torsional motion between the porphyrin planes. Localization of the radical cation in singly oxidized multiporphyrin systems when the sample temperature is lowered to near the freezing point or below has also been observed with diphenylethyne bridging units.^{12,35,36} However, porphyrins linked at their *meso* positions to an ethyne group exhibited temperature independent charge motion, which in fact may indicate that the charge is fully delocalized within a HOMO that extends over the entire multiporphyrin π system of this array.³⁸ Counterions and solvent polarity often play a decisive role as to whether a charge will migrate throughout a molecule. The ClO₄⁻ counterion used in these studies is considered to be a weakly complexing ion with respect to its interactions with porphyrins;^{51,56} however, it is still likely that the hole localization observed at low temperatures is a result of the inability of the counterion to move between the porphyrins sufficiently fast to accommodate charge hopping on a $>10^7$ s⁻¹ time scale.

ENDOR spectroscopy is often used to obtain individual isotropic hfcc's that cannot be easily resolved from inhomogeneously broadened EPR spectra. However, ¹H-ENDOR spectra for the systems larger than the **Z2B** and **MPD** dimers could not be obtained. We suspect this may be due to changes in (nuclear) relaxation times of the larger systems, in addition to anticipated very small hyperfine splittings. Isotropic hfcc's for **ZnTPP⁺⁺**, **Z2B⁺⁺**, and **MPD⁺⁺** were obtained from ENDOR spectroscopy in liquid CH₂Cl₂/THF (9:1, v:v) using the ENDOR resonance condition $\nu_{ENDOR}^{\pm} = |\nu_n \pm a_H/2|$, where ν_{ENDOR}^{\pm} are the ENDOR transition frequencies and ν_n is the proton Larmor frequency.⁵⁷ The 0.79 MHz hyperfine splitting of **ZnTPP⁺⁺** shown in Figure 6 is assigned to the phenyl protons.⁵¹ Both **Z2B⁺⁺** and **MPD⁺⁺** show essentially identical spectra with a hyperfine splitting of 0.42 MHz (Figure 6), nearly half that of the monomer **ZnTPP⁺⁺** spectrum. This indicates that rapid hole hopping is occurring in both dimers at a rate $>10^7$ s⁻¹. While these results are in agreement with previous studies on **MPD**,³⁴ they contradict earlier results of Segawa and co-workers on mono-oxidized *meso*–*meso* linked porphyrins.^{58,59} These investigators used NaAuCl₄ as the oxidant in CHCl₃, a combina-

(52) Kolbasov, D.; Srivatsan, N.; Ponomarenko, N.; Jager, M.; Norris, J. R. *J. Phys. Chem. B* **2003**, *107*, 2386–2393.

(53) Srivatsan, N.; Kolbasov, D.; Ponomarenko, N.; Weber, S.; Ostafin, A. E.; Norris, J. R. *J. Phys. Chem. B* **2003**, *107*, 7867–7876.

(54) Srivatsan, N.; Weber, S.; Kolbasov, D.; Norris, J. R. *J. Phys. Chem. B* **2003**, *107*, 2127–2138.

(55) Tang, J.; Dikshit, S. N.; Norris, J. R. *J. Chem. Phys.* **1995**, *103*, 2873–2881.

(56) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 349–364.

(57) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH: New York, 1988.

(58) Nakazaki, J.; Senshu, Y.; Segawa, H. *Polyhedron* **2005**, *24*, 2538–2543.

(59) Segawa, H.; Machida, D.; Senshu, Y.; Nakazaki, J.; Hirakawa, K.; Wu, F. P. *Chem. Commun.* **2002**, 3032–3033.

tion that results in stronger ion pairing. Using these same experimental conditions, we also observed charge localization onto one of the porphyrins of **Z2B**⁺ (Figure S12). These findings exemplify how important the surrounding environment is toward facilitating charge hopping.

The porphyrin *meso* positions have large spin densities, so that despite the nearly orthogonal orientation of the porphyrin planes, which limits electronic coupling, charge hopping still occurs. Other examples of charge hopping in orthogonally linked molecular arrays include those of oligo(9,10-anthrylene)s, in which both hole and electron hopping are observed,⁴⁹ and our recent findings of electron hopping in *N-N* linked perylene-3,4:9,10-bis(dicarboximide) (PDI) oligomers.⁴⁸ The PDI oligomers differ from the *meso-meso* linked porphyrins in that the PDI LUMO has nodes at its imide nitrogen atoms, while the porphyrin HOMO has large orbital coefficients at the *meso* positions. This suggests that the degree of electronic coupling between adjacent π systems necessary to achieve rapid charge hopping between them is relatively modest.

The dodecameric porphyrin array **C12Z** is to our knowledge the largest artificial cyclic light-harvesting array in which EPR experiments have been performed to probe charge migration within the ring. In singly oxidized B880 light-harvesting proteins isolated from photosynthetic bacteria, EPR line width narrowing was interpreted as hole hopping or delocalization over ~ 12 BChls.^{60,61} Further studies on B880⁺ explored in detail the mechanisms and temperature dependence of the EPR line narrowing, finding that at extremely low temperatures charge transport becomes slower so that the hole is localized on one or two BChls.^{53,54} In the larger cyclic array of BChls within the LH1 protein, which contains about 32 BChls, charge hopping was found to occur over ~ 11 BChls with a rate constant of 10^8 – 10^9 s⁻¹.⁵² Again, the EPR line shapes were of mixed Gaussian/Lorentzian character, and charge localization was observed upon lowering the temperature. One of the primary differences between the natural light-harvesting arrays and cyclic porphyrin dodecamer **C12Z** is structural. **C12Z** is entirely covalently linked with large dihedral angles between the π systems of several of its porphyrins, while the natural systems are self-assembled and have continuous networks of cofacially overlapping BChls. Despite this large structural difference, the rigidity of **C12Z** results in a system having porphyrins with very similar oxidation potentials, which allows for hole hopping

among 8–12 porphyrins, nearly the same extent observed among BChls in the natural light-harvesting systems.

Conclusions

Hole transfer among two different sets of singly oxidized porphyrin dimers, either directly connected with a *meso-meso* linkage or bridged by a *meta*-phenylene linkage, and larger arrays comprised of these subunits, including two gable-like tetramers and a cyclic dodecamer, were studied using EPR and ENDOR spectroscopies. Thermally activated hole hopping at rates faster than 10^7 s⁻¹ was found to occur in both of the dimers at 290 K. In the case of the tetramers, it was found that rapid hole hopping occurs only between three porphyrin molecules, likely due to small energetic differences in the HOMOs between the outer and inner porphyrins. In the cyclic array, hole hopping among 8–12 porphyrins was observed at 290 K (but not at 180 K), which is a step closer toward reaching the extent of charge hopping observed in cyclic BChl arrays within natural photosynthetic light-harvesting systems. Our results expand upon the initial studies of charge transfer in *meta*-phenylene linked porphyrins³⁴ and demonstrate for the first time that charge hopping occurs readily in nearly orthogonal *meso-meso* linked porphyrins. Hole hopping is rapid in these systems, even though the *meta*-phenyl bridges and direct *meso-meso* linkages do not provide optimal electronic coupling between the porphyrins within these multiporphyrin arrays. This greatly expands the scope of possible structures that can be employed to tailor the design of long distance charge transport systems.

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Supporting Information Available: Details regarding the synthesis and characterization of the molecules presented in this study, and additional EPR/ENDOR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(60) Gingras, G.; Picorel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 3405–3409.

(61) Picorel, R.; Lefebvre, S.; Gingras, G. *Eur. J. Biochem.* **1984**, *142*, 305–311.