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Article

Excited-State Energy-Transfer Dynamics in Self-Assembled Triads Composed of Two Porphyrins and an Intervening Bis(dipyrrinato)metal Complex

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The synthesis and characterization of various triads composed of a linear array of two zinc porphyrins joined via an intervening bis(dipyrrinato)metal(II) complex are reported. The preparation exploits the facile complexation of dipyrrins with divalent metal ions to give bis(dipyrrinato)metal(II) complexes [abbreviated $(dp)_2M$]. Copper(II) and palladium(II) chelates of dipyrrins (available by oxidation of dipyrromethanes) were prepared in 50–80% yield. A one-flask synthesis of bis(dipyrrinato)zinc(II) complexes was developed by oxidation of a dipyrromethane with DDQ or *p*-chloranil in the presence of $Zn(OAc)_2 \cdot 2H_2O$ in THF (~80% yield). Three routes were developed for preparing porphyrin-dipyrrins: (1) Suzuki coupling of a boronate-substituted zinc porphyrin (ZnP) and bis[5-(4-iodophenyl)-dipyrrinato]Pd(II) to give the $(ZnP\text{-}dp)_2Pd$ triad (50% yield), followed by selective demetalation of the $(dp)_2Pd$ unit by treatment with 1,4-dithiothreitol under neutral conditions (71% yield); (2) oxidation of a porphyrin-dipyrromethane with *p*-chloranil in the presence of $Zn(OAc)_2 \cdot 2H_2O$ followed by chromatography on silica gel (71% yield); and (3) condensation of a dipyrrin-dipyrromethane and a dipyrromethane-dicarbinol under $InCl_3$ catalysis followed by oxidation with DDQ (10–16% yield). Four triads of form $(ZnP\text{-}dp)_2Zn$ were prepared in 83–97% yield by treatment of a porphyrin-dipyrrin with $Zn(OAc)_2 \cdot 2H_2O$ at room temperature. Free base dipyrrins typically absorb at 430–440 nm, while the bis(dipyrrinato)metal complexes absorb at 460–490 nm. The fluorescence spectra/yields and excited-state lifetimes of the $(ZnP\text{-}dp)_2Zn$ triad in toluene show (1) efficient energy transfer from the bis(dipyrrinato)zinc(II) chromophore to the zinc porphyrins (98.5% yield), and (2) little or no quenching of the resulting excited zinc porphyrin relative to the isolated chromophore. Taken together, these results indicate that bis(dipyrrinato)zinc(II) complexes can serve as self-assembling linkers that further function as secondary light-collection elements in porphyrin-based light-harvesting arrays.

Introduction

The preparation of light-harvesting arrays requires the organization of a large number of pigments in well-defined 3-dimensional architectures. Porphyrinic macrocycles have been widely employed in the construction of synthetic light-harvesting arrays owing to their desirable optical and photochemical features, as well as the desire to mimic the properties of photosynthetic light-harvesting antennas.[1] In the preceding paper, we described a series of porphyrinic light-harvesting arrays wherein the porphyrins were covalently linked via an imine motif. This motif is attractive because the arrays can be prepared using one-flask reactions. The imine motif was found to support highly efficient energy transfer between porphyrins.[2]

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(1) (a) Harvey, P. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2003; Vol. 18, pp 63−250. (b) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751−2796.

(2) Sazanovich, I. V.; Balakumar, A.; Muthukumaran, K.; Hindin, E.; Kirmaier, C.; Diers, J. R.; Lindsey, J. S.; Bocian, D. F.; Holten, D. *Inorg. Chem.* **2003**, *42*, 6616−6628.

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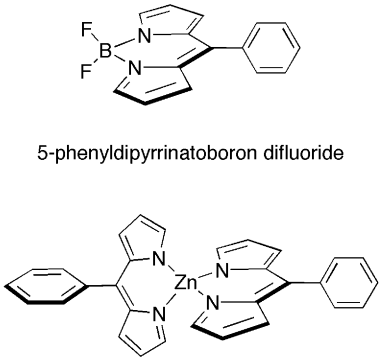
A general limitation of porphyrins for light-harvesting purposes is that porphyrins have strong absorption only in the blue region ($\lambda_{\max}$ ~420 nm), with weak absorption across the remainder of the visible spectrum. One approach to increase the spectral coverage of porphyrin-based light-harvesting arrays has been to include accessory pigments that absorb in regions where the porphyrins are relatively transparent and that funnel the resulting excited-state energy to the porphyrin. The ideal accessory pigment for use with porphyrins should have the following properties: (1) strong light absorption in the region between the porphyrin Soret and Q-bands, (2) a long-lived excited-state, (3) high stability, (4) high solubility, and (5) synthetic compatibility with a molecular building block approach.[3] Accessory pigments that have been used with porphyrins include boron-dipyrrin dyes,[4−7] carotenoids,[8] coumarin dyes,[9] cyanine dyes,[10] perylene-imide dyes,[7,11,12] and xanthene dyes.[13] Meeting all of the criteria for an ideal accessory pigment is a significant challenge, and no one class is superior in all aspects. The carotenoids absorb very strongly but have very short excited-state lifetimes, requiring very close juxtaposition for energy transfer to an acceptor. The cyanine dyes can be tuned for absorption across the visible region but, like the xanthene dyes, are positively charged, limiting solubility and typically causing difficulties in purification. The coumarins are neutral but absorb weakly, and the absorption band is in the vicinity of the porphyrin Soret band, affording little additional spectral coverage. The perylene-monoimide dyes have modest absorption intensity, undergo efficient energy transfer, and are nonpolar, but they require extensive substitution with bulky groups to achieve adequate solubility.[13,14] The boron-dipyrrin dyes have been widely used as fluorescent labels[15] in biological applications and provide a nice compromise of all features for use with porphyrins. While the synthesis of boron-dipyrrins is more straightforward than that of perylene-imides, the one type of boron-dipyrrin that was used in conjunction with porphyrins exhibited a biphasic excited-state decay, with a short component that limits the yield of energy transfer.[6] Accordingly, there remains a need for new types of dyes that can be used as accessory pigments with porphyrins.

Chart 1



5-phenyldipyrrinatoboron difluoride

bis(5-phenyldipyrrinato)zinc(II)

Dipyrrins provide the basis for the boron-dipyrrin dyes[16] and also have a rich chemistry with diverse transition metals. Free base dipyrrins react readily with a wide variety of metal salts, affording the corresponding bis(dipyrrinato)metal(II) (or tris(dipyrrinato)metal(III)) complexes. The bis(dipyrrinato)metal(II) complexes typically absorb quite strongly in the blue-green region ($\lambda_{\max}$ ~ 470−500 nm; $\epsilon_{\lambda\max}$ 50 000−100 000 M^{-1} cm^{-1}). However, the photochemical properties of bis(dipyrrinato)metal complexes have rarely been studied, with only anecdotal reports concerning fluorescence of the complexes.[17] The bis(dipyrrinato)metal complexes derived from a divalent metal such as zinc are fundamentally distinct from the dipyrrinatoboron difluoride complexes (Chart 1); the latter comprise only one dipyrrin ligand per boron and typically are quite fluorescent.

The chemistry of bis(dipyrrinato)metal complexes dates to the time of Hans Fischer, where dipyrrins (previously termed pyrromethenes or dipyrromethenes)[18] employed as precursors to naturally occurring porphyrins were found to form stable complexes with divalent metal ions such as iron, copper, cobalt, nickel, and zinc.[19] The dipyrrins, obtained by oxidation of dipyrromethanes, typically contained a full complement of substituents at the α- and β-positions of the chromophore. In the ensuing years, complexes of diverse divalent metals (Mg,[20] Ca,[21] Mn,[21] Fe,[22] Co,[23−31] Ni,[21,23−29,31−33]

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(3) (a) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.* **1996**, *68*, 1373−1380. (b) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.* **1998**, *70* (8), i.

(4) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759−9760.

(5) Ambroise, A.; Wagner, R. W.; Rao, P. D.; Riggs, J. A.; Hascoat, P.; Diers, J. R.; Seth, J.; Lammi, R. K.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *Chem. Mater.* **2001**, *13*, 1023−1034.

(6) Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, C. H., III; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001−10017.

(7) Ambroise, A.; Kirmaier, C.; Wagner, R. W.; Loewe, R. S.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 3811−3826.

(8) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 6, 198−205.

(9) Hecht, S.; Vladimirov, N.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2001**, *123*, 18−25.

(10) Lindsey, J. S.; Brown, P. A.; Siesel, D. A. *Tetrahedron* **1989**, *45*, 4845−4866.

(11) Just, E. M.; Wasielewski, M. R. *Superlattices Microstruct.* **2000**, *28*, 317−328.

(12) Tomizaki, K.-Y.; Loewe, R. S.; Kirmaier, C.; Schwartz, J. K.; Retsek, J. L.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 6519−6534.

(13) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941−8968.

(14) Loewe, R. S.; Tomizaki, K.-Y.; Youngblood, W. J.; Bo, Z.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 3438−3451.

(15) (a) Kim, H.; Burghart, A.; Welch, M. B.; Reibenspies, J.; Burgess, K. *Chem. Commun.* **1999**, 1889−1890. (b) Burghart, A.; Kim, H.; Welch, M. B.; Thoresen, L. H.; Reibenspies, J.; Burgess, K. *J. Org. Chem.* **1999**, *64*, 7813−7819. (c) Chen, J.; Burghart, A.; Derecskei-Kovacs, A.; Burgess, K. *J. Org. Chem.* **2000**, *65*, 2900−2906. (d) Burghart, A.; Thoresen, L. H.; Chen, J.; Burgess, K.; Bergström, F.; Johansson, L. B.-Å. *Chem. Commun.* **2000**, 2203−2204.

(16) Treibs, A.; Kreuzer, F.-H. *Liebigs Ann. Chem.* **1968**, *718*, 208−223.

(17) Granick, S.; Gilder, H. In *Advances in Enzymology*; Nord, F. F., Ed.; Interscience Publishers: New York, 1947; Vol. VII, pp 305−368.

(18) Moss, G. P. *Pure Appl. Chem.* **1987**, *59*, 779−832.

(19) (a) Fischer, H.; Schubert, M. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 610−617. (b) Fischer, H.; Klarer, J. *Justus Liebigs Ann. Chem.* **1926**, *448*, 178−193.

(20) Corwin, A. H.; Melville, M. H. *J. Am. Chem. Soc.* **1955**, *77*, 2755−2759.

(21) Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1970**, *9*, 1832−1839.

Cu,[20,22−25,27−29,31,34,35] Zn,[21−24,27,29−31,34] Pd,[23,27] Cd,[22,23] and Hg[23,27]) have been prepared from similarly substituted dipyrrins.

In the past decade, dipyrromethanes that bear one meso-substituent and lack any α- or β-substituents have become available via a simple one-flask synthesis.[36,37] Dolphin's group[38] found that exposure of such meso-substituted dipyrromethanes to DDQ or *p*-chloranil afforded the corresponding dipyrrins. Dolphin also showed that such dipyrrins could be converted to the corresponding bis(dipyrrinato)metal complex[38] $[(dp)_2M]$ or tris(dipyrrinato)metal complex[39] upon treatment with base and a divalent (M = Zn, Cu, Ni) or trivalent (Co, Fe) metal acetate. Dolphin subsequently showed that a variety of elegant structures could self-assemble from multimers of the fundamental dipyrrin motif.[40,41] Similar structures have been made by others.[42,43] The ready access to dipyrromethanes/dipyrrins and the facile self-assembly of bis(dipyrrinato)metal complexes prompted us to consider the use of this motif as the basis for linking porphyrins in a self-assembly process. Given the strong absorption in the blue-green region, we also sought to examine whether excited-state energy transfer would occur from the bis(dipyrrinato)metal unit to the attached porphyrin. Such a process, if viable, would afford a self-assembling accessory pigment for elaborating multiporphyrin light-harvesting arrays. This approach closely resembles the strategy employed by the groups of Collin, Flamigni, and Sauvage where a terpyridine-porphyrin reacts with a ruthenium (or iridium) reagent to give the array containing two porphyrins joined by a bridging bis(terpyridyl)ruthenium (or iridium) complex.[44−47] More generally, the self-assembly approach is inspired by a rich collection of self-assembled arrays composed of porphyrins and metal-coordinated ligands.[48]

In this paper, we describe the synthesis of a number of bis(dipyrrinato)metal complexes. We then investigate three routes for forming porphyrin-dipyrrins. The porphyrin-dipyrrins are used to create triads consisting of two zinc porphyrins joined by an intervening bis(dipyrrinato)metal complex. The spectroscopic properties of several all-zinc triads and their component parts have been characterized. This work provides the foundation for the use of bis(dipyrrinato)metal complexes as self-assembling chromophores in light-harvesting systems.

Results and Discussion

Synthesis. Preparation of 5-Substituted Dipyrromethanes. Dipyrromethanes bearing various substituents at the 5-position are readily available via condensation of the corresponding aldehyde + pyrrole under TFA catalysis.[36,37] The dipyrromethanes **1a**−**j** were prepared as shown in Scheme 1.

Preparation of Free Base Dipyrrins and Bis(dipyrrinato)metal Complexes. Brückner et al. reported that oxidation of 5-phenyldipyrromethane (**1a**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene at room temperature affords 5-phenyldipyrrin (**2a**) in 47% yield.[38] We performed the same reaction in THF, a solvent providing much higher solubility for quinones than benzene.[49] The reaction with DDQ for 40 min gave **2a** in 42% yield, while the milder oxidant *p*-chloranil for 18 h gave **2a** in 62% yield. Similarly, oxidation of **1b**, **1h**, and **1j** with DDQ in THF afforded the corresponding free base dipyrrins **2b**, **2h**, and **2j** in 51%, 57%, and 85% yields, respectively.

Brückner et al. reported two approaches for the formation of bis(dipyrrinato)metal complexes: (1) the traditional treatment of a purified dipyrrin with a metal acetate,[38] or (2) a two-step one-flask approach involving oxidation of a dipyr-

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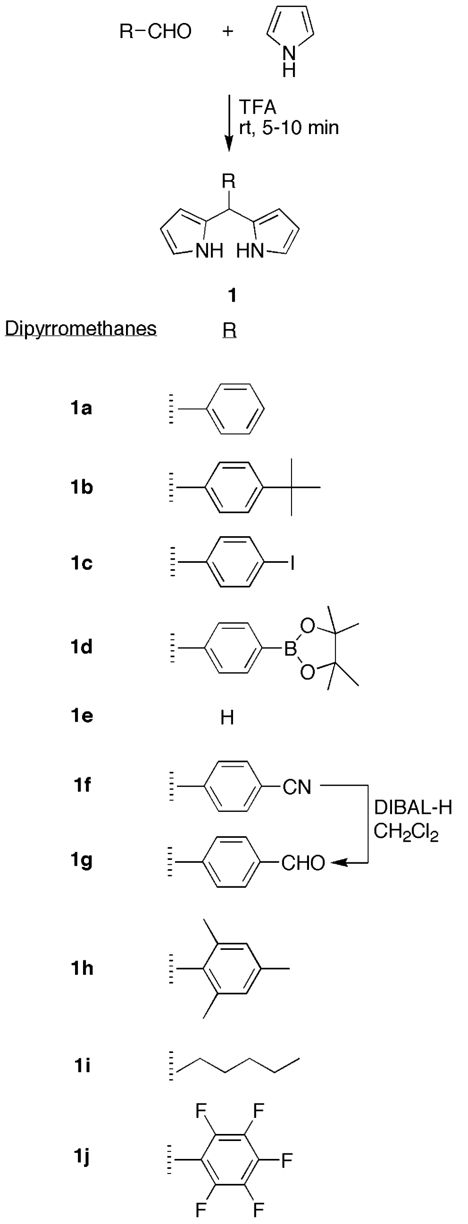
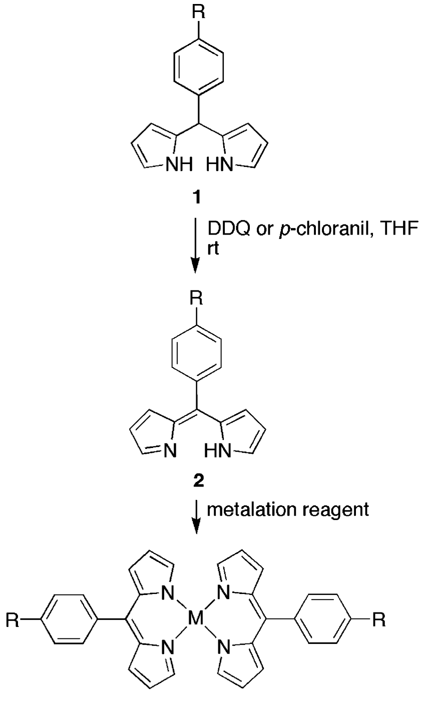
(22) Corwin, A. H.; Sydow, V. L. *J. Am. Chem. Soc.* **1953**, *75*, 4484−4486.
(23) Porter, C. R. *J. Chem. Soc.* **1938**, 368−372.
(24) Fergusson, J. E.; Ramsay, C. A. *J. Chem. Soc.* **1965**, 5222−5225.
(25) Murakami, Y.; Sakata, K. *Inorg. Chim. Acta* **1968**, *2*, 273−279.
(26) Murakami, Y.; Kohno, Y.; Matsuda, Y. *Inorg. Chim. Acta* **1969**, *3*, 671−675.
(27) March, F. C.; Couch, D. A.; Emerson, K.; Fergusson, J. E.; Robinson, W. T. *J. Chem. Soc. A* **1971**, 440−448.
(28) Murakami, Y.; Matsuda, Y.; Sakata, K. *Inorg. Chem.* **1971**, *10*, 1734−1738.
(29) Murakami, Y.; Matsuda, Y.; Sakata, K.; Martell, A. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1729−1734.
(30) Murakami, Y.; Matsuda, Y.; Kobayashi, S. *J. Chem. Soc., Dalton Trans.* **1973**, 1734−1737.
(31) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416−3424.
(32) Cotton, F. A.; DeBoer, B. G.; Pipal, J. R. *Inorg. Chem.* **1970**, *9*, 783−788.
(33) Ferguson, J.; West, B. O. *J. Chem. Soc. A* **1966**, 1565−1568.
(34) Murakami, Y.; Matsuda, Y.; Kanaoka, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 409−415.
(35) Murakami, Y.; Matsuda, Y.; Sakata, K. *Inorg. Chem.* **1971**, *10*, 1728−1734.
(36) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440.
(37) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.
(38) Brückner, C.; Karunaratne, V.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *74*, 2182−2193.
(39) Brückner, C.; Zhang, Y.; Rettig, S. J.; Dolphin, D. *Inorg. Chim. Acta* **1997**, *263*, 279−286.
(40) (a) Zhang, Y.; Thompson, A.; Rettig, S. J.; Dolphin, D. *J. Am. Chem. Soc.* **1998**, *120*, 13537−13538. (b) Thompson, A.; Rettig, S. J.; Dolphin, D. *Chem. Commun.* **1999**, 631−632. (c) Thompson, A.; Dolphin, D. *J. Org. Chem.* **2000**, *65*, 7870−7877.
(41) Thompson, A.; Dolphin, D. *Org. Lett.* **2000**, *2*, 1315−1318.
(42) Zhang, Y.; Ma, J. S. *Org. Prep. Proced. Int.* **2001**, *33*, 81−86.
(43) Zhang, Y.; Wang, Z.; Yan, C.; Li, G.; Ma, J. *Tetrahedron Lett.* **2000**, *41*, 7717−7721.
(44) (a) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Dixon, I. M.; Sauvage, J.-P.; Williams, J. A. G. *Coord. Chem. Rev.* **1999**, *190−192*, 671−682. (b) Harriman, A.; Sauvage, J.-P. *Chem. Soc. Rev.* **1996**, *25*, 41−48.
(45) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. *Chem. Eur. J.* **1998**, *4*, 1744−1754.
(46) Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L. *Inorg. Chem.* **2001**, *40*, 5507−5517.
(47) Flamigni, L.; Marconi, G.; Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P. *J. Phys. Chem. B* **2002**, *106*, 6663−6671.
(48) (a) Alessio, E.; Iengo, E.; Marzilli, L. G. *Supramol. Chem.* **2002**, *14*, 103−120. (b) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168−6179. (c) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219−221*, 545−572. (d) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483−3537. (e) Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. In *The Porphyrin Handbook*; Kadish, K. M.;, Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, pp 1−42. (f) Sanders, J. K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 3, pp 347−368. (g) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133−156. (h) Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113−171.
(49) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153−195.

Scheme 1



Scheme 2



M-2

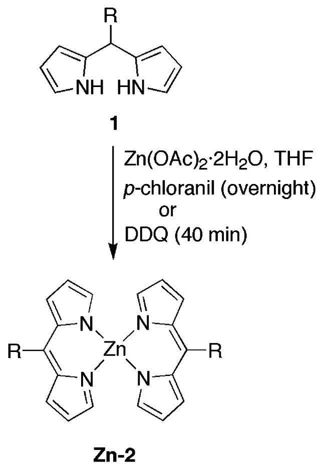
R	metalation reagent	compound	yield (based on **1**)
t-Bu	$Cu(OAc)_2 \cdot H_2O/MeOH$ CH_2Cl_2, rt, 10 min	**Cu-2b**	42%
t-Bu	$Pd_2(dba)_3/CHCl_3$ MeOH/TEA; rt, overnight	**Pd-2b**	43%
I	$Pd(OAc)_2/CH_2Cl_2$ rt, 20 min	**Pd-2c**	47%

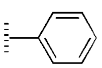
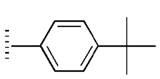
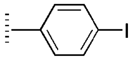
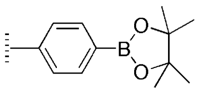
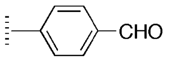
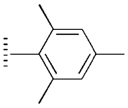
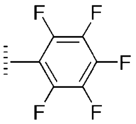
romethane yielding the dipyrrin followed by treatment of the crude dipyrrin with triethylamine (TEA) and a metal acetate.[39] Our application of the first approach with **2b** and $Cu(OAc)_2 \cdot H_2O$ in $CH_2Cl_2/MeOH$ at room temperature for 10 min afforded the bis(dipyrrinato)copper(II) species **Cu-2b** in 82% yield (42% from **1b**) after chromatographic purification (Scheme 2). Similar attempts to metalate **2b** using either $Pd(OAc)_2$ or $Pd(NO_3)_2$ in different solvents over a range of temperatures gave either a low yield (10%) or complicated product distributions. However, exposure of **2b** to tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) in $CHCl_3/MeOH/TEA$ at room temperature afforded **Pd-2b** after a simple chromatographic purification. The overall yield from dipyrromethane **1b** was 43%.

Similar attempts to prepare the desired bis[(5-(4-iodophenyl)dipyrrinato]palladium(II) complex **Pd-2c** by using $Pd_2(dba)_3$ were not successful. In a two-step approach, dipyrromethane **1c** was treated with *p*-chloranil, the crude reaction mixture was filtered to remove quinone species, and the crude dipyrrin was treated with $Pd(OAc)_2$ in CH_2Cl_2 to give **Pd-2c** in 47% overall yield upon filtration (Scheme 2). It is noteworthy that this method did not involve any chromatography.

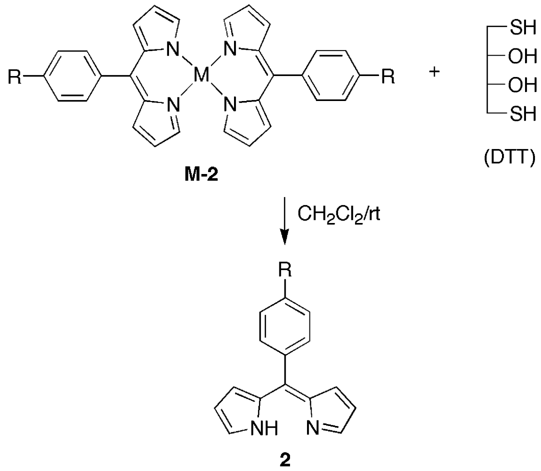
One-Flask Synthesis of Bis(dipyrrinato)zinc(II) Complexes. The facile formation of bis(dipyrrinato)zinc(II) complexes prompted us to investigate a one-flask synthesis. Thus, treatment of 5-phenyldipyrromethane (**1a**) with an equimolar amount of DDQ in THF for 30 min at room temperature in the presence of $Zn(OAc)_2 \cdot 2H_2O$ afforded bis(5-phenyldipyrrinato)zinc(II) (**Zn-2a**) in 78% yield after column chromatography (Scheme 3). With the milder oxidant *p*-chloranil, the oxidation/complexation of **1a** was complete in ~27 h but gave a cleaner reaction than that with DDQ. The product was obtained in 81% yield after column chromatography. Under the same conditions, **Zn-2b**, **Zn-2c**, **Zn-2d**, **Zn-2g**, **Zn-2h**, and **Zn-2j** were prepared in good yields. The same reaction of **1e** (no meso-substituent) or **1i** (containing a meso-alkyl substituent) with DDQ or *p*-chloranil failed to give the desired bis(dipyrrinato)zinc(II) complexes, though in both cases the starting dipyrromethane was completely consumed. The failure must originate in the

Scheme 3



R	oxidant	compound	yield
	DDQ *p*-chloranil	**Zn-2a**	78% 81%
	*p*-chloranil	**Zn-2b**	82%
	*p*-chloranil	**Zn-2c**	65%
	*p*-chloranil	**Zn-2d**	85%
	*p*-chloranil	**Zn-2g**	81%
	*p*-chloranil	**Zn-2h**	86%
	*p*-chloranil DDQ	**Zn-2j**	31% 55%

Scheme 4



reaction	M	R	time	yield
Zn-2a → 2a	Zn	H	30 min	80%
Cu-2b → 2b	Cu	*t*-Bu	10 min	95%
Pd-2b → 2b	Pd	*t*-Bu	overnight	79%
Zn-2c → 2c	Zn	I	30 min	85%
Pd-2c → 2c	Pd	I	overnight	89%
Zn-2g → 2g	Zn	CHO	60 min	31%

oxidation rather than the complexation process, because in each case, oxidation (DDQ or *p*-chloranil) alone failed to afford the expected free base dipyrrin.

The attempted metalation of 5-phenyldipyrrin (**1a**) with $CaCl_2$, $MgBr_2 \cdot OEt_2$, or $Cd(OAc)_2 \cdot 2H_2O$ was not successful as evidenced by UV−vis and ^1H NMR spectroscopic analysis of the crude reaction mixture (see Supporting Information). The failure in these cases was surprising, because each type of complex has been prepared from dipyrrins with a full complement of α- and β-substituents. The conditions for $MgBr_2 \cdot OEt_2$ were very similar to those used for magnesiation of porphyrins.[50]

Demetalation of Bis(dipyrrinato)metal Complexes. We investigated methods for the demetalation of bis(dipyrrinato)-metal complexes because we wanted to be able to (1) disassemble self-assembled structures, and (2) remove metals employed for protective purposes during specific synthetic transformations (vide infra). We first examined the acid-induced demetalation of **Zn-2a** to give 5-phenyldipyrrin (**2a**). However, only partial demetalation was observed with use of excess trifluoroacetic acid (TFA, 50 equiv) in CH_2Cl_2 for several hours. Even use of methanolic HCl did not afford complete demetalation. Because the complexes were resistant to acid hydrolysis, an alternative method of demetalation was explored.

Dithiothreitol (*threo*-1,4-dimercapto-2,3-butanediol, DTT) is a nonvolatile, thiol-containing ligand capable of coordinating a variety of metal ions. We examined the use of DTT to liberate the free base dipyrrins by displacement of the metal from the bis(dipyrrinato) complexes (Scheme 4). Treatment of **Cu-2b** in CH_2Cl_2 (5 mM) with 10 molar equiv of DTT at room temperature gave quantitative demetalation as observed by TLC and UV−vis spectroscopic analysis. The free base dipyrrin **2b** was obtained in 95% yield after chromatographic purification. Each zinc(II)−dipyrrin complex that was examined also was readily demetalated under the same conditions within 30 min. The bis(dipyrrinato)palladium(II) complexes **Pd-2b** and **Pd-2c** demetalated much more slowly (17 h) under the same conditions, yet the free base dipyrrins **2b** and **2c** were obtained in 79% and 89% yield, respectively. It is noteworthy that treatment of **Zn-1a** with ethylene glycol in place of DTT caused no demetalation, indicating that the thiols of DTT are essential for the demetalation process.

We examined an alternative method for removing the metal from the bis(dipyrrinato)metal complexes. Treatment of **Cu-2b** with $NaBH_4$ (20 molar equiv) in THF/MeOH (3:1) at room temperature for 20 min gave complete reduction,

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(50) Lindsey, J. S.; Woodford, J. N. *Inorg. Chem.* **1995**, *34*, 1063−1069.

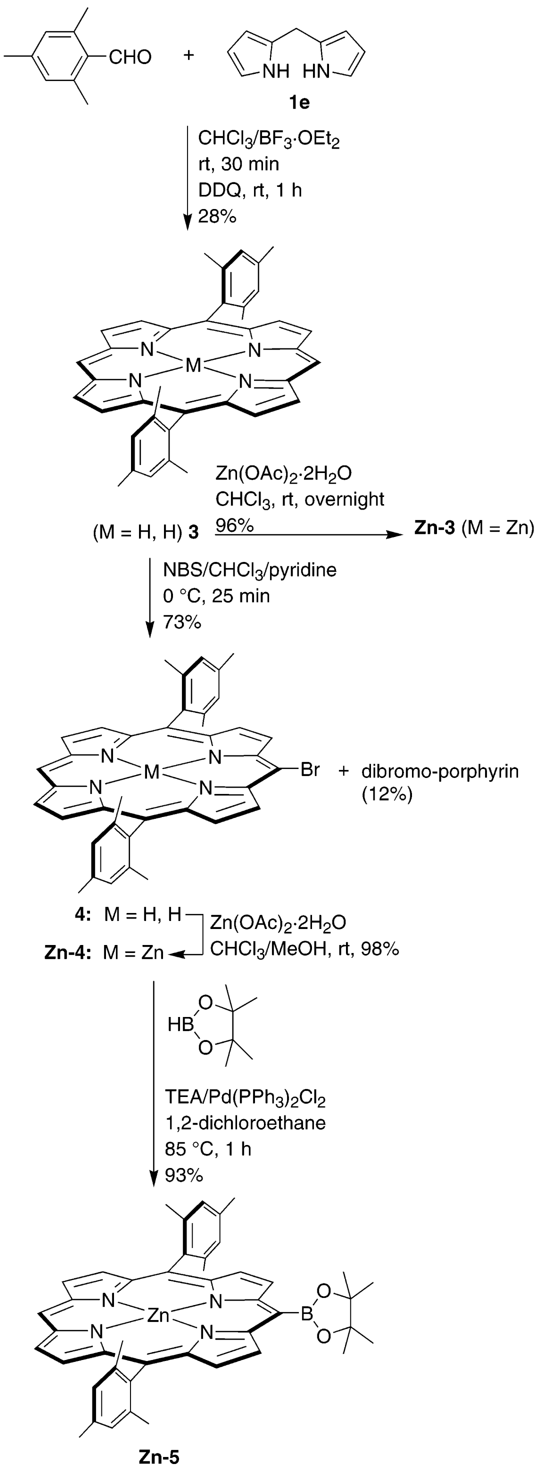
affording dipyrromethane **1b** in 88% yield after chromatographic purification. However, **Zn-2a** gave only a 50% yield of **1a** upon similar reduction. Dipyrrins are well-known to undergo reduction to give the dipyrromethane.[51] Indeed, Dolphin showed that meso-substituted dipyrrins could be converted to the dipyrromethanes upon reduction with $NaBH_4$.[38] Our results show that the bis(dipyrrinato)metal complexes undergo reduction to give the dipyrromethane.

Routes to Porphyrin-Dipyrrins. We developed three routes for the synthesis of porphyrin-dipyrrin systems. The first two routes employ a porphyrin building block, while the third route employs a dipyrrin in a porphyrin-forming reaction.

Route 1: Suzuki Coupling of a Porphyrin and a Bis(dipyrrinato)metal Complex. The synthesis of the key porphyrin building block for use in a Suzuki coupling reaction is shown in Scheme 5. Treatment of dipyrromethane **1e** and mesitaldehyde with BF_3−ethanol cocatalysis (achieved with $BF_3 \cdot OEt_2$ in $CHCl_3$ containing 0.75% ethanol)[52] for 0.5 h at room temperature followed by oxidation with DDQ afforded the target 5,15-dimesitylporphyrin (**3**) in 28% yield. No acidolytic scrambling leading to undesired porphyrin products was detected as evidenced by laser desorption-mass spectrometry (LD-MS) analysis of the crude reaction mixture. Metalation with $Zn(OAc)_2 \cdot 2H_2O$ afforded **Zn-3**. Following a standard procedure,[53] treatment of **3** with 1 molar equiv of NBS in $CHCl_3$/pyridine for 25 min at 0 °C gave the desired monobrominated product **4** in 73% yield, the dibrominated byproduct (12% yield), and the unreacted **3** (12%), which were readily separated by chromatography. No β-bromination was observed by ^1H NMR spectroscopic analysis. Metalation of **4** with $Zn(OAc)_2 \cdot 2H_2O$ afforded **Zn-4** in 98% yield. Following the conditions used previously for Suzuki coupling at the porphyrin meso-positions,[54,55] reaction of **Zn-4** and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane in the presence of TEA/$Pd(PPh_3)_2Cl_2$ in 1,2-dichloroethane at 85 °C for 1 h afforded the desired product **Zn-5** in 93% yield after column chromatography.

A number of approaches were explored for the Suzuki coupling of a porphyrin and a dipyrrin species. Attempts to couple boronate-porphyrin **Zn-5** and iodo-complex **Zn-2c**, or bromo-porphyrin **Zn-4** and boronate-complex **Zn-2d**, under standard Suzuki coupling conditions resulted in failure, which we attributed to the sequestration of palladium by the dipyrrins following transmetalation of zinc. A large number of control experiments showed that Suzuki reactions are poisoned by the presence of a free base dipyrrin, bis(dipyrrinato)zinc(II), or bis(dipyrrinato)copper(II), even if the dipyrrin has no functional groups to participate as a coupling partner (see Supporting Information). We turned to the use of **Pd-2c** for the Suzuki reaction.

Scheme 5



Reaction of **Zn-5** and **Pd-2c** under the conditions employed previously[56] gave the $(ZnP\text{-}dp)_2Pd$ triad **6** in only 6% yield. We examined the Suzuki coupling of **Zn-5** and **Pd-2c** under conditions similar to those employed by Therien et al. for attachment of substituents to the porphyrin meso-position:[57] $Pd[(PPh_3)]_4$ (15% mol relative to **Zn-5**); $Ba(OH)_2 \cdot$

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(51) Gossauer, A.; Engel, J. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. II, pp 197−253.

(52) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828−836.

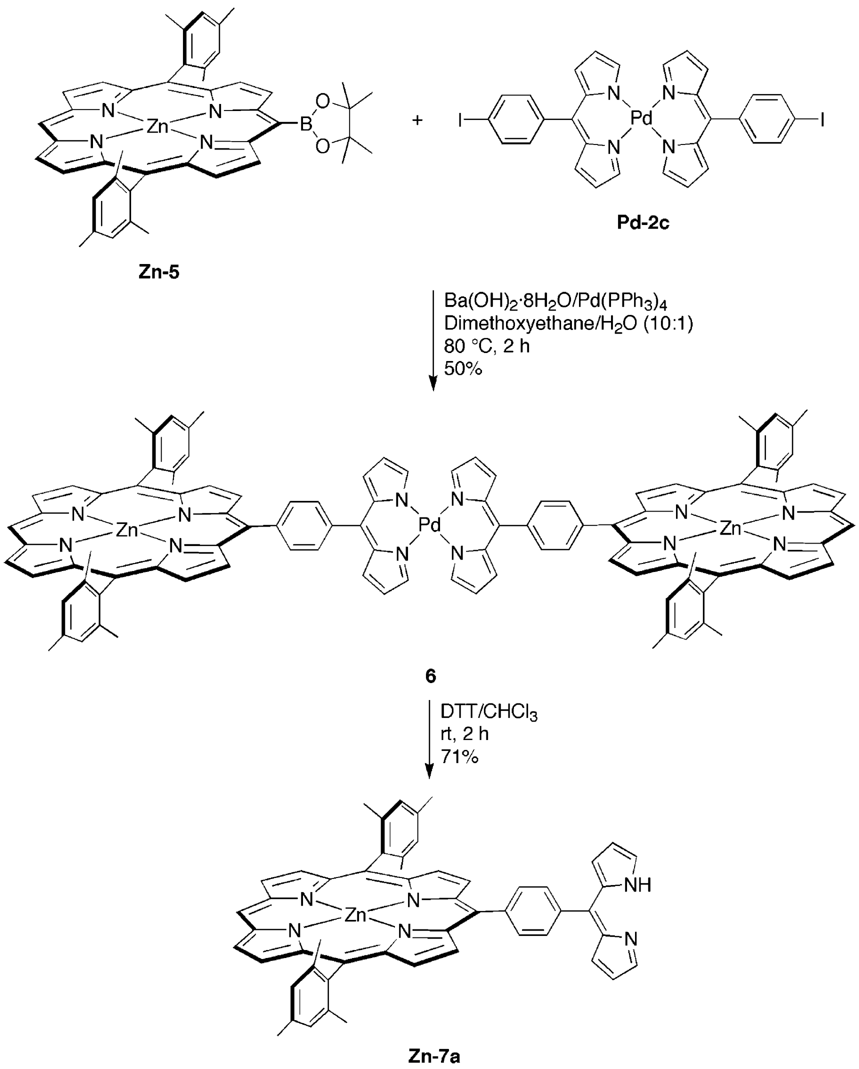
(53) (a) Nudy, L. R.; Hutchinson, H. G.; Schieber, C.; Longo, F. R. *Tetrahedron* **1984**, *40*, 2359−2363. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983−5993.

(54) Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676−12677.

(55) Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 6458−6459.

(56) Yu, L.; Lindsey, J. S. *Tetrahedron* **2001**, *57*, 9285−9298.

Scheme 6



$8H_2O$ (1 equiv relative to **Zn-5**); 1,2-dimethoxyethane/H_2O (10:1) at 80 °C under argon; [**Zn-5**] = 20 mM and [**Pd-2c**] = 10 mM. TLC analysis showed complete consumption of the starting porphyrin after 2 h. Analytical size exclusion chromatography (SEC) indicated the desired triad **6** was formed in ~50% yield, and a considerable amount of monomeric porphyrin species was present (~45%, as indicated by analytical SEC). LD-MS analysis of this latter product showed that deboronation and phenylation are the major side reactions in this Suzuki coupling. Purification by silica gel chromatography, preparative SEC, and silica gel chromatography afforded the desired $(ZnP\text{-}dp)_2Pd$ triad **6** in 50% yield (Scheme 6).

Treatment of **6** with DTT at room temperature resulted in selective demetalation of the bis(dipyrrinato)Pd complex, affording the Zn-porphyrin-dipyrrin **Zn-7a** in 71% yield. No demetalation of the Zn-porphyrin was observed by UV−vis absorption or LD-MS analysis.

Route 2: Formation and Oxidation of a Dipyrromethane-Substituted Porphyrin. The second route entails the synthesis of a porphyrin-dipyrromethane, which is then oxidized to the porphyrin-dipyrrin. The reaction of bromoporphyrin **4** and 4-formylphenylboronic acid under standard Suzuki coupling conditions afforded porphyrin **8a** in 91% yield (Scheme 7). Porphyrin-benzaldehyde **8b** was prepared via the reaction of a dipyrromethane bearing a carboxaldehyde group and a dipyrromethane-dicarbinol.[56] Porphyrins **8a** and **8b** were converted to the zinc chelates **Zn-8a** and **Zn-8b** (Scheme 8).

The availability of porphyrin-benzaldehydes prompted us to explore the conditions for preparing porphyrin-substituted dipyrromethanes, following the general method for preparing dipyrromethanes shown in Scheme 1. In this method, the aldehyde is dissolved in neat pyrrole and then treated with a catalytic amount of TFA at room temperature.[36,37] We modified this method slightly.[14,58] A solution of porphyrin-benzaldehyde **8a** or **8b** (~15 mM) in dichloromethane was treated with a large excess of pyrrole (300−400 molar equiv). When 0.1 equiv of TFA was employed, only a minor amount of porphyrin-dipyrromethane was formed, but increasing the

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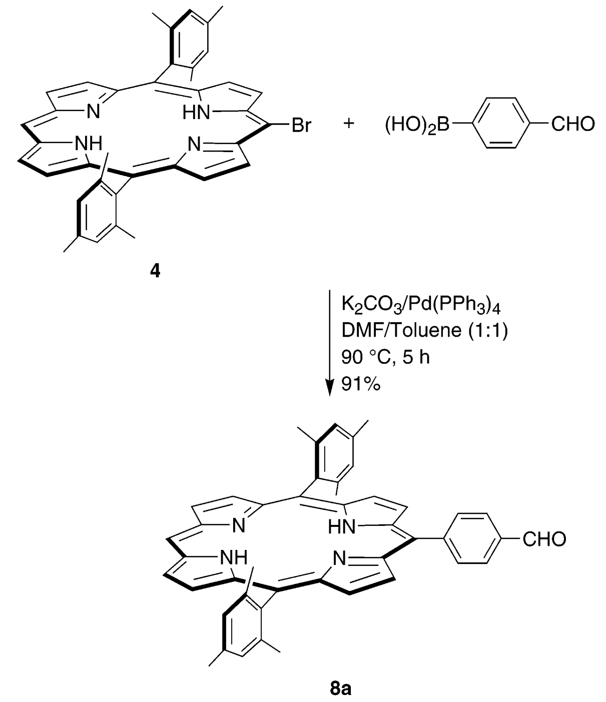
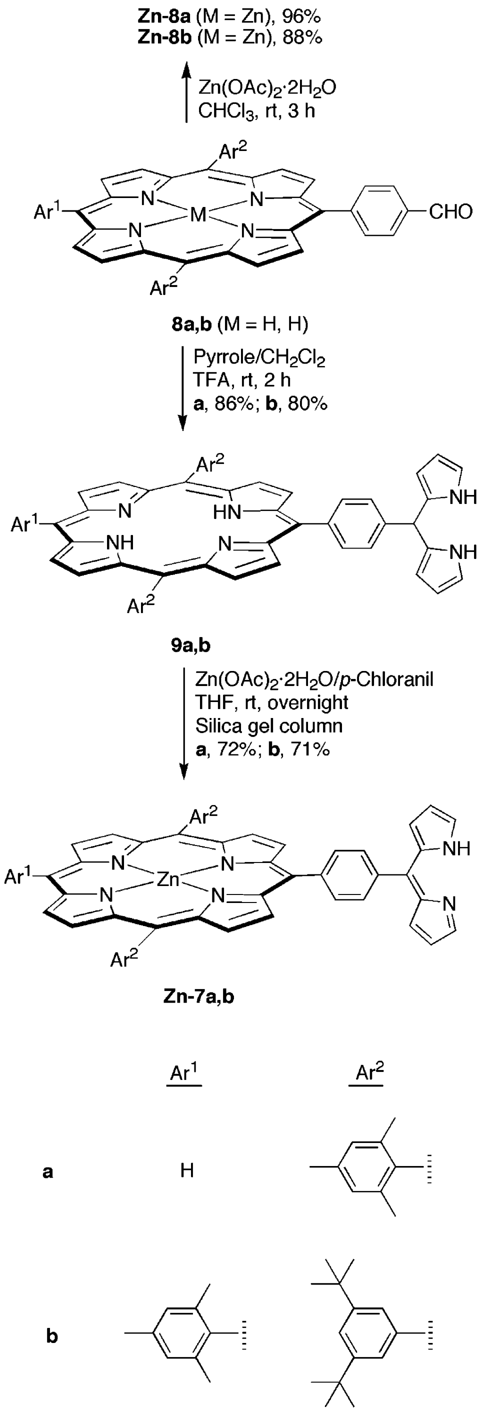
(57) Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *112*, 8717−8727.

(58) Speckbacher, M.; Yu, L.; Lindsey, J. S. *Inorg. Chem.* **2003**, *42*, 4322−4337.

Scheme 7



Scheme 8



amount of TFA to 1.1 equiv led to complete consumption of the porphyrin-benzaldehyde in 2 h. Chromatographic purification using an eluant containing 1% TEA [silica, $CHCl_3$/TEA (99:1)] to minimize acidolysis of the dipyrromethane afforded porphyrin-dipyrromethane **9a** (86%) or **9b** (80%) in good yield (Scheme 8).

The porphyrin-dipyrromethanes were treated under the conditions for dipyrrin formation, employing *p*-chloranil in the presence of $Zn(OAc)_2 \cdot 2H_2O$. The presumed product in this reaction is the triad composed of two Zn porphyrins attached to a central bis(dipyrrinato)zinc complex. However, such triads were not stable upon exposure to the silica chromatographic purification process, and the zinc porphyrin-free base dipyrrin compounds **Zn-7a** and **Zn-7b** were obtained in ~70% yield (Scheme 8).

Route 3: Formation of a Porphyrin from a Dipyrrin-Dipyrromethane. The reaction of a dipyrromethane and a dipyrromethane-dicarbinol provides a straightforward route to meso-substituted porphyrins.[59] This approach is compatible with diverse substituents, particularly upon attachment to the dipyrromethane moiety. We sought to employ this method using a dipyrromethane bearing a dipyrrin. Several routes are available for the preparation of the precursor dipyrrin-benzaldehyde **2g**. Oxidation of dipyrromethane-benzaldehyde **1g** with *p*-chloranil in the presence of $Zn(OAc)_2 \cdot 2H_2O$ afforded **Zn-2g** in 81% yield (Scheme 3); however, treatment with DTT gave the free base dipyrrin **2g** in only 31% yield (Scheme 4). For a more expedient synthesis, **1g** was treated with *p*-chloranil in THF at room temperature for 24 h, giving the free base dipyrrin in 60% yield (Scheme 9).

The condensation of **2g** (1 equiv) with pyrrole (50 equiv) in CH_2Cl_2 in the presence of TFA (1.2 equiv) afforded compound **10**. Analysis by ^{1}H NMR spectroscopy indicated the presence of an impurity, which gave signals consistent with that for the N-confused dipyrromethane. The ratio of **10** and the N-confused isomer was 96:4; the combined yield was 41% (Scheme 9). The mixture could not be separated and was used directly in subsequent condensations.

The condensation of **10** with dipyrromethane-dicarbinol **11a-diol** in the presence of TFA (30 mM) in CH_3CN for up to 30 min followed by oxidation with DDQ failed to give the porphyrin. We next examined the condensation of **10** and **11a-diol** under new catalysis conditions that employ mild

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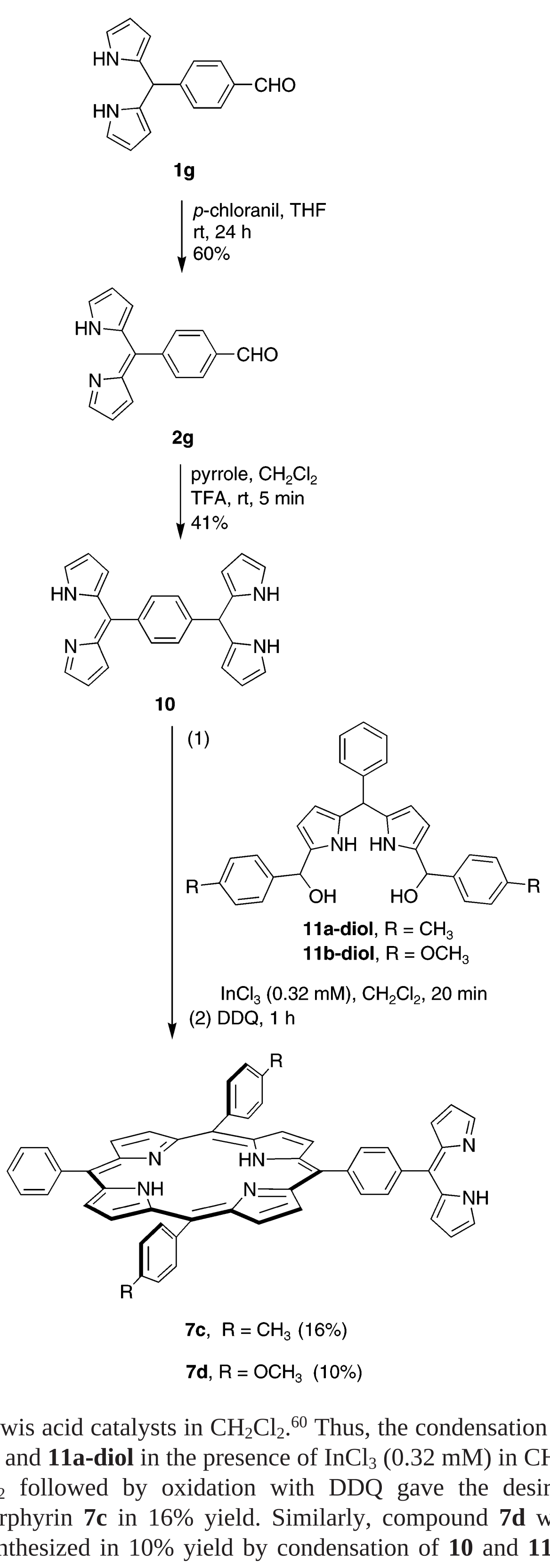
(59) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323−7344.

Scheme 9



Lewis acid catalysts in CH_2Cl_2.[60] Thus, the condensation of **10** and **11a-diol** in the presence of $InCl_3$ (0.32 mM) in CH_2Cl_2 followed by oxidation with DDQ gave the desired porphyrin **7c** in 16% yield. Similarly, compound **7d** was synthesized in 10% yield by condensation of **10** and **11b-diol**. Two points concerning this approach are noteworthy. (1) Reaction of a dipyrrin (**2a**) and a dipyrromethane-dicarbinol (**11a-diol**) showed only a 2.5% yield of porphyrin, while a competition experiment of a dipyrrin (**2b**) and a dipyrromethane (**1a**) in the reaction with a dipyrromethane-dicarbinol (**11a-diol**) gave the porphyrin derived by exclusive reaction with the dipyrromethane (see Supporting Information). (2) Syntheses employing a mixed condensation of **2g**, mesitaldehyde, and pyrrole with $BF_3{\cdot}OEt_2$/ethanol cocatalysis did not yield the porphyrin-dipyrrin, even with increased acid concentration and prolonged reaction time. The success of the dipyrromethane + dipyrromethane-dicarbinol condensation/oxidation in the presence of the dipyrrin highlights the mild conditions of this transformation and the greater reactivity of the dipyrromethane versus the dipyrrin toward electrophilic substitution.

Bis(porphyrin-dipyrrinato)metal Triads. Triads composed of two zinc porphyrins and one zinc-dipyrrin complex were prepared as shown in Scheme 10. Treatment of **Zn-7a**, **Zn-7b**, **7c**, or **7d** with $Zn(OAc)_2{\cdot}2H_2O$ afforded the desired $(ZnP\text{-}dp)_2Zn$ triad **12a**, **12b**, **12c**, or **12d** in 83−97% yield. In each case, the absorption spectral data indicated the reaction had gone to completion. Attempts to perform TLC analysis or column chromatography on silica, or SEC (analytical or preparative), however, resulted in disassembly of the bis(dipyrrinato)zinc unit and formation of the zinc porphyrin-free base dipyrrin. The LD-MS spectrum showed the expected molecule ion peak for the triad. Each triad was examined by fluorescence spectroscopy, which indicated the integrity of the zinc porphyrin.

Characterization. Chemical Characterization. The free base dipyrrins and metal derivatives were generally assessed for purity by TLC and characterized by absorption spectroscopy, ^1H NMR spectroscopy, ^{13}C NMR spectroscopy (except **Pd-2c**), and FAB-MS. Acceptable elemental analyses were obtained except for **2a**−**c**, **2g**, **2h**, **Pd-2b**, **Zn-2b**, **Zn-2g**, and **10**. The porphyrins and triads were characterized by absorption and fluorescence spectroscopy, ^1H NMR spectroscopy, and LD-MS. Note that the bis(dipyrrinato)zinc(II) complexes remained intact upon exposure to silica whereas the all-zinc containing triads $(ZnP\text{-}dp)_2Zn$ disassembled upon exposure to silica (see Supporting Information). The ^1H NMR spectra of all free base dipyrrins and their metal complexes display simple coupling patterns derived from the protons on the dipyrrin units. However, the ^1H NMR spectrum (in $CDCl_3$) of the free base dipyrrins showed no peak for the NH proton in the dipyrrin moiety, possibly due to hydrogen bonding.

The available crystal structure analyses for $(dp)_2M$ complexes include the following: (1) β-substituted dipyrrins where the metal is palladium[27] or nickel;[32] (2) bis[5-(4-nitrophenyl)dipyrrinato]nickel;[38] (3) zinc complexes of dipyrrin multimers;[40,43,61] and (4) a zinc complex in which each dipyrrin bears one meso-substituent and one α-substituent.[62] A single crystal suitable for X-ray analysis was obtained by slow evaporation of a solution of **Zn-2a** in $CHCl_3$/ethanol. A summary of the crystal data for **Zn-2a** is given in Table

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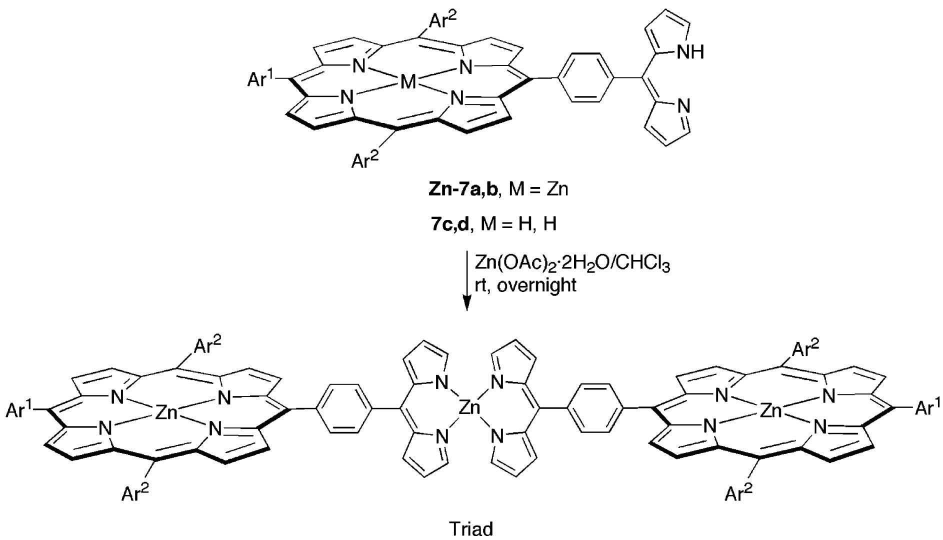
(60) Geier, G. R., III; Callinan, J. B.; Rao, P. D.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 810−823.

(61) Subramanian, J.; Fuhrhop, J.-H. In *The Porphyrins*; Dolphin, D. Ed., Academic Press: New York, 1978; Vol. II, pp 255−285.

(62) Hill, C. L.; Williamson, M. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1228−1229.

Scheme 10



Zn-7a,b, M = Zn

7c,d, M = H, H

Triad

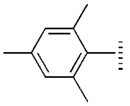
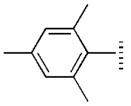
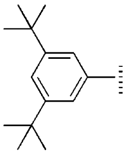
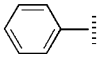
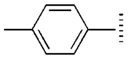
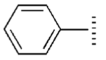
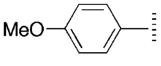
Porphyrin-dipyrrin	Ar^1	Ar^2	Triad	Yield
Zn-7a	H		**12a**	97%
Zn-7b			**12b**	87%
7c			**12c**	83%
7d			**12d**	85%

Table 1. Crystal Data for **Zn-2a·CHCl$_3$**

chemical formula	$C_{31}H_{23}Cl_3N_4Zn$
fw	623.28
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a/Å	25.478(5)
b/Å	10.9632(10)
c/Å	22.143(4)
β/deg	111.866(16)
V, Å^3	5740.0(16)
Z	8
T/°C	−125
λ/Å	0.71073
ρ/g cm^{-1}	1.443
μ/cm^{-1}	11.6
R^a	0.064
R_w	0.077

[a] Definitions of R and R_w: $R = \sum|F_o - F_c|/\sum F_o$; $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

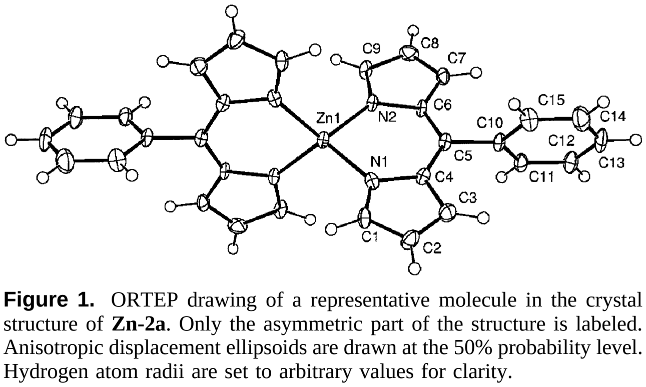


Figure 1. ORTEP drawing of a representative molecule in the crystal structure of **Zn-2a**. Only the asymmetric part of the structure is labeled. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Hydrogen atom radii are set to arbitrary values for clarity.

1. The asymmetric unit consists of two symmetry independent half molecules as well as a chloroform molecule occupying a general lattice position, giving a total of eight **Zn-2a** molecules per unit cell. Each molecule sits on a crystallographic 2-fold axis passing through the Zn atom positions, which gives rise to a columnar structure running along [010]. The Zn atom positions are separated on the 2-fold axis by approximately a half of the unit cell length along the *b* axis. A depiction of one of the molecules is given in Figure 1. Selected bond lengths and angles from the first coordination sphere are given in Table 2. In the ensuing

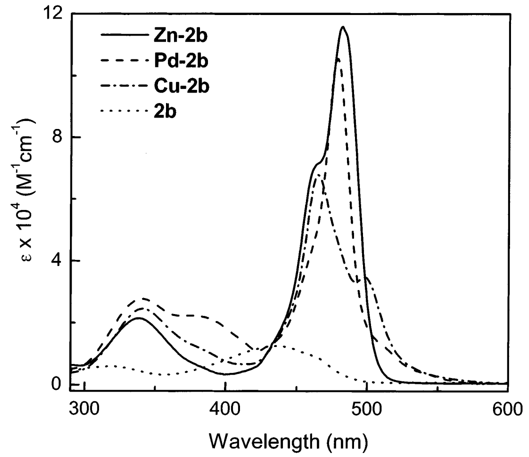


Figure 2. Absorption spectra in CH_2Cl_2 at room temperature of free base dipyrrin **2b** and its bis(dipyrrinato)metal complexes.

Table 2. Selected Bond Lengths and Angles (Å, deg)[a]

Zn1−N1	1.980(5)	Zn2−N1′	1.987(5)
Zn1−N2	1.972(5)	Zn2−N2	1.973(5)
N1−Zn1−N2	94.2(2)	N1′−Zn2−N2′	94.7(2)
N1−Zn1−N1*	120.3(2)	N1′−Zn2−N1′*	119.0(2)
N1−Zn1−N2*	114.6(2)	N1′−Zn2−N2′*	114.9(2)
N2−Zn1−N2*	121.0(2)	N2′−Zn2−N2′*	120.5(2)

[a] The asterisk indicates atoms related by the 2-fold crystallographic axis.

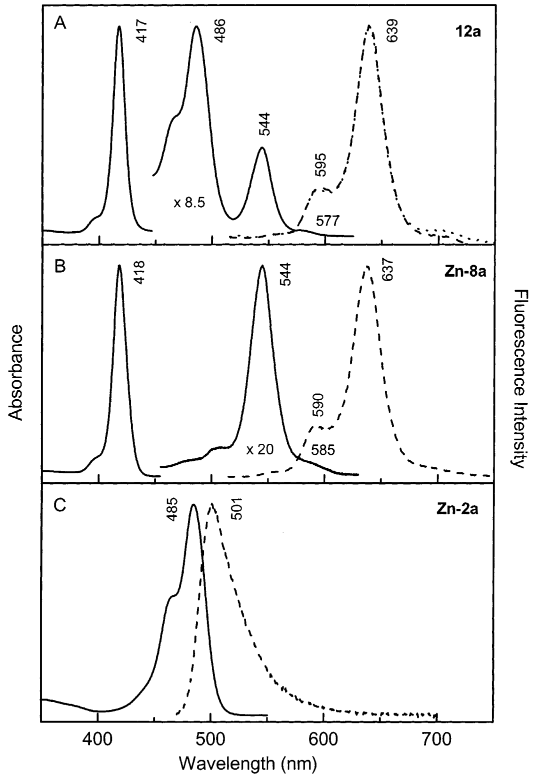


Figure 3. Electronic absorption spectra (—) and fluorescence spectra (— — and • • •) for the triad **12a** (A) and reference porphyrin **Zn-8a** (B) and bis(dipyrrinato)zinc **Zn-2a** (C) in toluene at room temperature. The absorption spectra in the 450−650 nm region in parts A and B have been multiplied by the factors shown. The triad emission in A and B was obtained using the predominant zinc porphyrin excitation (— —) at 400 nm or bis(dipyrrinato)zinc excitation (• • •) at 453 nm. Spectra in the respective regions have been normalized to the same peak intensity, and the maxima (±1 nm) indicated.

discussion, quantities for both symmetry independent molecules are reported with the quantities for the second molecule given in parentheses. The following features of the molecular structure of **Zn-2a** are pertinent: (1) Each dipyrrin unit deviates only slightly from planarity. The dihedral angle between the two pyrrolic rings in each dipyrrin is 1.2(3)° (4.3(3)°). As expected, owing to conjugation, the dipyrrin C−C bond lengths range between 1.349 and 1.428 Å. (2) The dipyrrin ligands are nearly perpendicular to one another with the dihedral angle between the N−Zn−N chelate planes being 85.1(3)° (86.0(3))°. (3) The phenyl ring is also roughly perpendicular to the dipyrrin moiety as evidenced by a dihedral angle of 77.8(3)° (74.1(3)°). (4) The Zn−N bond distances range from 1.972 to 1.987 Å.

Electrochemistry. The redox characteristics of a representative bis(dipyrrinato)metal complex, **Zn-2a**, were examined in the 0−1.5 V range using both square-wave and cyclic voltammetry. In this window, the complex exhibits oxidation waves at 0.81 and 0.94 V (vs Ag/Ag$^+$; $E_{1/2}$ (Fc/Fc$^+$) = 0.19 V). The cyclic voltammetric studies revealed, however, that the redox process is highly irreversible. In particular, the reductive waves for the two oxidation processes are completely absent in the voltammogram. Scans that were terminated at a potential between the two oxidation waves also failed to reveal the reduction analogue of the first oxidation wave. These results suggest that **Zn-2a** demetalates upon formation of either the mono- or dication. Bulk electrolysis studies of **Zn-2a** were further consistent with this view.

Absorption Spectra. Figure 2 shows the absorption spectra in CH_2Cl_2 of free base dipyrrin **2b** and its bis(dipyrrinato)metal(II) complexes with zinc, copper, or palladium. Most striking is the change from the broad-band absorption of the free base dipyrrin to the more intense, sharp feature for the metallo complexes. Similar comparisons apply for a wide variety of dipyrrins and their (dp)$_2$M complexes,[17,21,24,25,33] including those synthesized here.

The absorption spectra of (ZnP-dp)$_2$Zn triad **12a** and reference zinc porphyrin **Zn-8a** and bis(dipyrrinato)zinc complex **Zn-2a** in toluene are shown in Figure 3 (—). The spectrum of the triad is essentially the sum of the spectra of the component parts. The ultimate porphyrin absorption characteristics in the triad derive mainly from the addition of the aryl ring at the linker site to starting porphyrin **Zn-3** to give **Zn-8a**, with little change upon attachment of the dipyrrin to give porphyrin-dipyrrin **Zn-7a**, or upon self-assembly to produce (ZnP-dp)$_2$Zn triad **12a**. Similar results are found for triad **12b** and its reference compounds, except for spectral changes expected for porphyrins bearing four instead of three meso-aryl substituents (see Scheme 10). Similar findings were also obtained for the compounds in benzonitrile, except that metal coordination red shifts the zinc porphyrin absorption bands by 5−10 nm and alters the Q-band ratios; in contrast, the (dp)$_2$Zn features are unperturbed. The spectral comparisons are given in the Supporting Information. Thus, the (ZnP-dp)$_2$M triads display $S_0 \rightarrow S_1$ absorption of the bis(dipyrrinato)metal complex (~485 nm) sandwiched between the strong $S_0 \rightarrow S_2$ Soret band (410−

430 nm) and weaker $S_0 \rightarrow S_1$ Q vibronic manifold (480−610 nm) of the porphyrins.

Table 3. Photophysical Properties[a]

		zinc porphyrin excited-state decay			bis(dipyrrinato)zinc excited-state decay	
compd	solvent	Φ_f[b]	τ (ns)[c]	Φ_Q[d]	τ (ps)[e]	Φ_{EnT}[f]
		Triads				
12a	toluene	0.022 (0.025)	2.6	<0.1	1.4	0.97
	PhCN	0.010 (0.012)	~1[g]	~0.6	0.8	~0.8
12b	toluene	0.043 (0.037)	2.4	<0.1	1.4	0.97
	PhCN	0.030 (0.021)	~1[g]	~0.6	0.8	~0.8
		Reference Compounds				
Zn-7a	toluene	0.019	2.5			
	PhCN	0.010	1.5	0.45		
Zn-7b	toluene	0.030	2.4			
	PhCN	0.020	1.5	0.45		
Zn-3	toluene	0.024	2.6			
	PhCN	0.023	2.7			
Zn-8a	toluene	0.032	2.8			
	PhCN	0.032	2.7			
Zn-8b	toluene	0.033	2.8			
	PhCN	0.034	2.5			
Zn-2a[h]	toluene				9, 93	
	PhCN				6.5, 1000[i]	

[a] All data taken in toluene or benzonitrile (PhCN) at room temperature. [b] Porphyrin fluorescence yield (± 15%) for nondeoxygenated solutions relative to ZnTPP in toluene ($\Phi_f = 0.030$)[74] obtained with predominant porphyrin excitation in the Soret region (e.g., 400 nm for **12a** and **12b**). The values in parentheses are for predominant excitation of the bis(dipyrrinato)zinc subunit at 453 nm for **12a** and 487 nm for **12b**. [c] ZnP* lifetimes (±5%) were measured by fluorescence modulation spectroscopy using samples deoxygenated by bubbling with dry nitrogen. [d] The yield of quenching of ZnP* by a process such as charge transfer derived from the static and time-resolved optical spectroscopy. See Supporting Information for the analysis of the data for the triads in benzonitrile, which give yields of 0.6 ± 0.2. [e] $[(dp)_2Zn]^*$ lifetime determined by transient absorption spectroscopy (±0.2 ps for the triads). [f] Quantum yield of energy transfer from $[(dp)_2Zn]^*$ to ZnP in the [ZnP-dp]$_2$Zn triads, estimated from the combined fluorescence and transient absorption data. The results for the triads in benzonitrile are analyzed in the Supporting Information and give values of 0.8 ± 0.2. [g] The ZnP fluorescence profile for **12a** in benzonitrile is dual exponential with time constants of 0.9 ns (52%) and 2.2 ns (48%), and a time constant of 0.7 ns was obtained by transient absorption, giving the effective lifetime shown. For **12b** in benzonitrile, the respective values are 0.9 ns (50%), 2.1 ns (50%), and 0.7 ns. Effective time constants of ~1 ns are listed. [h] The fluorescence yield of **Zn-2a** is 0.007 in toluene and 0.002 in benzonitrile. [i] In addition to the fast (~6.5 ps) phase associated with $[(dp)_2Zn]^*$, and the slower decay phase (~1 ns) that may derive from the excited or other (e.g., charge-transfer) states, a considerable (~30%) contribution of long-lived state (>5 ns) is also observed (not seen in toluene).

Fluorescence Spectra, Quantum Yields, and Lifetimes. The emission spectra of (ZnP-dp)$_2$Zn triad **12a** and reference porphyrin **Zn-8a** and bis(dipyrrinato)zinc complex **Zn-2a** in toluene are shown in Figure 3 (− − and ···). The fluorescence from reference **Zn-2a** has rough mirror symmetry to the absorption with a rather large Stokes shift of ~660 cm^{-1}. The fluorescence quantum yield of **Zn-2a** is 0.007. The emission from the triad occurs only from the porphyrin(s), displaying Q(0,0) and Q(0,1) bands (~595 and ~640 nm) present in reference **Zn-8a**, using direct excitation of either the porphyrin (400 nm; − −) or the (dp)$_2$Zn complex (485 nm; · · ·). Furthermore, the porphyrin fluorescence yields of the triad are the same upon excitation of either type of subunit (0.022 or 0.025). These yields are comparable to those for the reference porphyrin, as are the lifetimes (~2.6 ns) of the excited zinc porphyrin (ZnP*) in the triad and isolated chromophores in toluene (Table 3). Similar results are obtained for triad **12b** (and its component parts), except for differences in emission profiles that parallel the absorption spectra. The results for **12a** and **12b** in toluene demonstrate the following. (1) Energy transfer from the excited bis(dipyrrinato)zinc complex, denoted $[(dp)_2Zn]^*$, to a zinc porphyrin to produce ZnP* is basically quantitative, as will be addressed further below using the transient absorption data. (2) There is minimal (<10%) quenching of ZnP* due to the presence of (dp)$_2$Zn in the triads.

Differences in the fluorescence behavior for the compounds in benzonitrile versus toluene are described in the Supporting Information and summarized as follows (Table 3). (1) The fluorescence spectra, yields, and lifetimes of the Zn porphyrin and the (dp)$_2$Zn complex are altered. The fluorescence yield of **Zn-2a** in benzonitrile is 0.002. (2) State $[(dp)_2Zn]^*$ in triads **12a** or **12b** may be modestly quenched by a process (e.g., charge transfer) competing with energy transfer to ZnP. (3) State ZnP* in the triads and ZnP-dp species (**Zn-7a** and **Zn-7b**) is substantially quenched relative to reference porphyrins (e.g., **Zn-8a**, **Zn-8b**). (3) More than one structural/ligated/electronic form likely contributes to the photophysics in the triads.

Time-Resolved Absorption Spectra. Triad **12a** and the benchmark bis(dipyrrinato)metal complex **Zn-2a** have been characterized by time-resolved absorption spectroscopy in toluene or benzonitrile. Transient absorption data for the bis(dipyrrinato)metal complexes will be described elsewhere. A finding pertinent to the (ZnP-dp)$_2$Zn triads is that the (dp)$_2$M complexes display multicomponent excited-state profiles. For **Zn-2a** in toluene, a fast (~9 ps) phase likely represents electronic/conformational/vibrational relaxation in the excited-state manifold while the slower (~93 ps) component reflects population decay of $[(dp)_2M^*]$. The latter phase is accompanied by substantial ground-state recovery, indicating little formation of longer-lived transients such as the triplet excited state. The situation changes to some extent in benzonitrile (Table 3).

Figure 4 shows representative transient absorption difference spectra for triad **12a** in toluene using primary excitation of the central (dp)$_2$Zn moiety with a 485 nm 130 fs flash. The spectrum at 0.5 ps can be assigned mainly to $[(dp)_2Zn]^*$ on the basis of the sharp trough in the 500−525 nm region. This feature primarily reflects excited-state stimulated (by the white-light probe pulse) emission that coincides with the red side of the spontaneous emission from reference complex **Zn-2a** (Figure 3C, − −). State ZnP* also contributes to the 0.5 ps spectrum on the basis of partial bleaching of the porphyrin Q(1,0) ground-state band at 545 nm and weak Q(0,1) stimulated emission at 640 nm. A contribution of ZnP* at early times likely derives from direct porphyrin excitation in a fraction of the arrays (in which (dp)$_2$Zn is not excited) and the early stage of energy transfer from $[(dp)_2Zn]^*$. By 6.2 ps (− −), the $[(dp)_2Zn]^*$ stimulated emission has decayed and is replaced by ZnP* excited-state absorption along with further development of the ZnP* features noted above.[63] The kinetic trace and fit in Figure 4b shows decay of $[(dp)_2Zn]^*$ stimulated emission and growth of ZnP* absorption; this time profile combined with

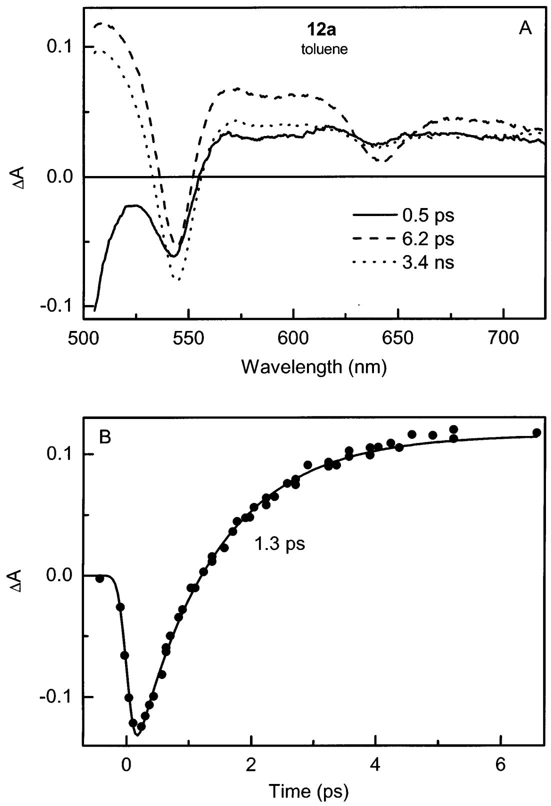


Figure 4. Representative time-resolved absorption spectra (A) and a kinetic profile at 508 nm (B) for the triad **12a** in toluene at room temperature using predominant excitation of the bis(dipyrrinato)zinc subunit with a 485 nm 130 fs flash. The 0.5 ps spectrum (—) was constructed from spectra at closely spaced time intervals in order to account for the time dispersion of wavelengths in the white-light probe pulse. The fit to the data in part B is the convolution of the instrument response with a dual exponential plus a constant, giving time constants of 1.3 ps and ~1 ns (inset). The average $(dp)_2Zn^*$ and ZnP* lifetimes, respectively, deduced from measurements at a number of probe wavelengths are given in Table 3.

those at other probe wavelengths gives a $[(dp)_2Zn]^*$ lifetime of 1.4 ps (Table 3).

The spectrum at 6.2 ps then evolves slowly to 3.4 ns, showing little remaining ZnP* stimulated emission while retaining porphyrin Q(1,0) bleaching at 550 nm at about the same amplitude (Figure 4a, • • •). These findings reflect the decay of ZnP* to give the triplet excited-state ZnP^T in high yield, as is found for reference porphyrins ($\Phi_T \sim 0.9$[64]). The subsequent spectral evolution for ZnP* decay (not shown) is in keeping with the 2.6 ns fluorescence lifetime (Table 3).

Similar results were obtained for triad **12b** in toluene, including the same $[(dp)_2Zn]^*$ lifetime of 1.4 ps found for **12a**, which is much shorter than the value of 93 ps for $(dp)_2Zn$ reference complex **Zn-2a** (Table 3). Using standard methods,[65] energy transfer from $[(dp)_2Zn]^*$ to a zinc porphyrin subunit has rate constant $k_{EnT} = (2 \cdot 1.4\ ps)^{-1} - (93\ ps)^{-1} = (2.8\ ps)^{-1}$ and yield $\Phi_{EnT} = [1-2 \cdot (1.4\ ps)/(93\ ps)] = 0.97$ (Table 3). The factors of 2 derive from the assumption that the excited state of the $(dp)_2Zn$ complex can transfer energy with equal probability to either of the two zinc porphyrin energy acceptors in each $(ZnP\text{-}dp)_2Zn$ triad.

The excited-state dynamics are more complex for **12a** or **12b** in benzonitrile (Supporting Information), as is also the case for $(dp)_2Zn$ reference complex **Zn-2a**, with more than one structural/ligated/electronic form probably contributing. For **Zn-2a** in benzonitrile, the dynamics are different with some uncertainty in the assignments: a fast (~6.5 ps) phase associated with $[(dp)_2Zn]^*$, followed by a slower decay phase (~1 ns) that may derive from the excited or other (e.g., charge transfer) states, followed by a considerable (~30%) contribution of a long-lived state (>5 ns) not seen in toluene. State $[(dp)_2Zn]^*$ in each triad has a lifetime of 0.8 ps, compared to 1.4 ps in toluene and 6.5 ps for the fast decay component in **Zn-2a**. Analysis of these lifetimes, the transient absorption spectra, and the fluorescence data suggests that energy transfer from $[(dp)_2Zn]^*$ to one of the zinc porphyrins in each triad has a yield of 80 ± 20% that competes with alternate routes such as charge transfer. The subsequent spectral evolution in combination with the fluorescence data indicates that ZnP* is 60 ± 20% quenched by a process such as charge transfer (Table 3). Thus, energy transfer in the self-assembled $(Zn\text{-}dp)_2Zn$ triads is somewhat less effective in polar, ligating solvents compared to the excellent behavior in nonpolar media.

Outlook. Dyes must meet a number of challenging criteria for use as accessory pigments with porphyrins. The bis(dipyrrinato)zinc complexes (1) are nonpolar (i.e., neutral), thereby facilitating chemical manipulations, (2) form by self-assembly from the free base dipyrrin, (3) provide spectral coverage in the blue-green, a region where porphyrins absorb poorly, and (4) can be synthesized by oxidation of dipyrromethanes with DDQ or *p*-chloranil in the presence of $Zn(OAc)_2 \cdot 2H_2O$. Three different routes to prepare porphyrin-dipyrrins were developed. Static emission spectroscopy and time-resolved absorption spectroscopy of two $(ZnP\text{-}dp)_2Zn$ triads indicated efficient energy transfer from the bis(dipyrrinato)zinc complexes to the zinc porphyrin. In comparison with the boron-dipyrrin complexes, the bis(dipyrrinato)zinc complexes have the distinct advantages of efficient self-assembly and the ability to serve a mechanical role in linking two porphyrins. Although the excited-state decay of bis(dipyrrinato)zinc complexes is shorter than that of boron-dipyrrin complexes, a high yield of energy transfer can be achieved in an appropriate architecture as shown herein.

The approach for preparing the self-assembled triads described herein was inspired by the work of Collin, Sauvage, and Flamigni aimed at preparing analogous triads based on

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(63) Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500−6506.

(64) (a) Gradyushko, A. T.; Sevchenko, A. N.; Solovyov, K. N.; Tsvirko, M. P.; *Photochem. Photobiol.* **1970**, *11*, 387−400. (b) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9−14. (c) Kajii, Y.; Obi, K.; Tanaka, I.; Tobita, S. *Chem. Phys. Lett.* **1984**, *111*, 347−349. (d) Kikuchi, K.; Kurabayashi, Y.; Kokubun, H.; Kaizu, Y.; Kobayashi, H. *J. Photochem. Photobiol. A: Chem.* **1988**, *45*, 261−263. (e) Bonnett, R. D.; McGarvey, D. J.; Harriman, A.; Land, E. J.; Truscott, T. G.; Winfield, U. J. *Photochem. Photobiol.* **1988**, *48*, 271−276.

(65) (a) Yang, S. I.; Lammi, R. K.; Seth, J.; Riggs, J. A.; Arai, T.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Phys. Chem. B* **1998**, *102*, 9426−9436. (b) Prathapan, S.; Yang, S. I.; Seth, J.; Miller, M. A.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Phys. Chem. B* **2001**, *105*, 8237−8248.

terpyridyl-metallo complexes bridging two porphyrins in a linear array.[44−47] The synthesis of the latter arrays can be done in a directed manner, affording unsymmetrical triads (M^1P-terpy)M(terpy-M^2P).[45,46] No such directed methods yet exist for the rational synthesis of unsymmetrical dipyrrin-metal complexes. On the other hand, the terpy-based triads generally have been designed to undergo photoinduced electron transfer among the three components, though some energy-transfer processes have been elicited with iridium-terpy complexes upon UV illumination.[47] The bis(dipyrrinato)zinc complexes undergo highly efficient energy transfer following excitation and thus constitute viable accessory pigments for the attached porphyrins.

Experimental Section

General. ^{1}H NMR spectra (300 or 400 MHz) and ^{13}C NMR spectra (75 or 100 MHz) were collected in $CDCl_3$. Absorption spectra and fluorescence spectra were collected in CH_2Cl_2 or toluene at room temperature. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) in the absence of an added matrix,[66] or by high-resolution fast atom bombardment mass spectrometry (FAB-MS). All reagents were obtained from Aldrich and were used as received. The known compounds **1a**−**c**,[37] **1d**,[56] **1e**,[37,67] **1f**,[59] **1g**,[59] **1h**,[37] **1i**,[68] **1j**,[37] **8b**,[56] **11a**,[59] **11b**,[59] **11a-diol**,[59] and **11b-diol**[59] were prepared according to literature procedures.

Solvents. All solvents were dried by standard methods. Toluene was distilled from CaH_2. Anhydrous DMF, 1,2-dimethoxyethane, CH_2Cl_2, and $CHCl_3$ (certified ACS grade stabilized with 0.8% ethanol) were used as received.

Chromatography. Adsorption column chromatography was performed using flash silica gel (Baker, 60−200 mesh). Preparative-scale size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1 in THF (HPLC grade). Analytical SEC[69] ($\lambda = 420$ nm) was performed to monitor the progress of the coupling reactions.

Synthesis of Dipyrrins by Oxidation of Dipyrromethane. 5-Phenyldipyrrin (2a). To a solution of **1a** (666 mg, 3.00 mmol) in THF (10 mL) was added dropwise a solution of DDQ (681 mg, 3.00 mmol, one molar equiv) in THF (10 mL). TLC analysis (silica, $CHCl_3$) indicated complete consumption of the starting materials after stirring for 1 h at room temperature. The mixture was poured into H_2O, extracted with $CHCl_3$, and dried (Na_2SO_4). Column chromatography [silica, $CHCl_3$/MeOH (99:1)] afforded a brown oil which partially solidified upon storage overnight at 0 °C (280 mg, 42%): mp 176−178 °C; ^{1}H NMR δ 6.39 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.2$ Hz, 2H), 6.60 (d, $J = 4.2$ Hz, 2H), 7.43−7.52 (m, 5H), 7.65 (s, 2H); ^{13}C NMR δ 117.5, 127.5, 128.9, 129.1, 130.7, 137.2, 140.5, 143.6; FAB-MS obsd 221.1068 ($M^+ + H$), calcd 221.1079 ($C_{15}H_{12}N_2$); λ_{abs} (CH_2Cl_2, log ϵ) 309 (3.84), 432 (4.28) nm. See ref 38.

5-(4-*tert*-Butylphenyl)dipyrrin (2b). Following the procedure described for the preparation of **2a**, a sample of **1b** (834 mg, 3.00 mmol) in THF (10 mL) was treated with a solution of DDQ (681 mg, 3.00 mmol) in THF (10 mL) for 1 h at room temperature. Removal of solvent and chromatography [silica, $CHCl_3$/MeOH (98:2)] afforded a brown-black solid (415 mg, 51%): mp 148−150 °C; ^{1}H NMR δ 1.39 (s, 9H), 6.39 (dd, $J^1 = 1.6$ Hz, $J^2 = 5.6$ Hz, 2H), 6.66 (d, $J = 5.6$ Hz, 2H), 7.44 (s, 4H), 7.64 (s, 2H); ^{13}C NMR δ 31.3, 34.7, 117.4, 124.5, 128.9, 130.7, 134.3, 140.9, 142.3, 143.3, 152.1; LD-MS obsd 274.8; FAB-MS obsd 277.1707 ($M^+ + H$), calcd 277.1705 ($C_{19}H_{20}N_2$). Anal. Calcd: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.15; H, 7.37; N, 9.93. λ_{abs} (CH_2Cl_2, log ϵ) 327 (3.97), 433 (4.36) nm.

5-(4-Formylphenyl)dipyrrin (2g). A solution of **1g** (1.15 g, 4.60 mmol) in THF (46 mL) was treated with *p*-chloranil (1.13 g, 4.60 mmol). The reaction mixture was stirred at room temperature for 24 h. The mixture was diluted with $CHCl_3$, washed with water, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford a dark residue. The dark residue obtained was chromatographed [silica, hexanes/ethyl acetate (3:1)], affording an orange oil (0.68 g, 60%). The analytical data were identical to those obtained for the product prepared by demetalation of **Zn-2g**.

5-Mesityldipyrrin (2h). Following the procedure described for the preparation of **2a**, a solution of **1h** (264 mg, 1.00 mmol) in THF (5 mL) was treated with a solution of DDQ (227 mg, 1.00 mmol) in THF (3 mL) for 30 min at room temperature. Removal of solvent and chromatography [silica, CH_2Cl_2/MeOH (98:2)] afforded a brown solid (150 mg, 57%): mp 114−116 °C; ^{1}H NMR δ 2.08 (s, 6H), 2.35 (s, 3H), 6.32 (d, $J = 4.4$ Hz, 2H), 6.40 (d, $J = 4.4$ Hz, 2H), 6.91 (s, 2H), 7.62 (s, 2H); ^{13}C NMR δ 19.9, 21.1, 117.6, 117.7, 127.3, 127.7, 133.4, 136.6, 137.4, 140.5, 140.9; LD-MS obsd 261.7, calcd av mass 262.4 ($C_{18}H_{18}N_2$). Anal. Calcd: C, 82.41; H, 6.92; N, 10.68. Found: C, 81.63; H, 6.97; N, 10.37. λ_{abs} (CH_2Cl_2) 431 nm.

5-(Pentafluorophenyl)dipyrrin (2j). Following the procedure described for the preparation of **2a**, a sample of **1j** (624 mg, 2.00 mmol) in THF (5 mL) was treated with a solution of DDQ (454 mg, 2.00 mmol) in THF (5 mL) at room temperature. TLC analysis [silica, hexanes/CH_2Cl_2 (1:1)] after 40 min showed incomplete oxidation; therefore, an additional amount of DDQ (91 mg, 0.40 mmol) in THF (2 mL) was added and stirred for another 20 min at room temperature. Removal of solvent and chromatography [silica, hexanes/CH_2Cl_2 (1:1)] afforded a brown-yellowish solid (530 mg, 85%): mp 116−117 °C; ^{1}H NMR δ 6.42 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.0$ Hz, 2H), 6.47 (d, $J = 4.0$ Hz, 2H), 7.66 (s, 2H); ^{13}C NMR δ 118.9, 123.8, 126.8, 140.3, 145.4. Anal. Calcd: C, 58.07; H, 2.27; N, 9.03. Found: C, 58.21; H, 2.19; N, 9.06 ($C_{15}H_7F_5N_2$). λ_{abs} (CH_2Cl_2) 430 nm.

Synthesis of Bis(dipyrrinato)metal Complexes by Metalation of Dipyrrins. Bis[5-(4-*tert*-butylphenyl)dipyrrinato]copper(II) (Cu-2b). A solution of **2b** (113 mg, 0.410 mmol) in CH_2Cl_2 (10 mL) was treated with a suspension of $Cu(OAc)_2 \cdot H_2O$ (204 mg, 1.02 mmol, 2.5 molar equiv) in methanol (∼3 mL). The mixture was stirred at room temperature for 10 min. UV−vis spectroscopic analysis showed no remaining free base dipyrrin. The reaction mixture was then diluted with CH_2Cl_2 (30 mL) and washed with H_2O. The organic layer was separated and dried (Na_2SO_4). Chromatography (silica, CH_2Cl_2) afforded a brown solid (104 mg, 82%): mp > 280 °C; LD-MS obsd 611.5, FAB-MS obsd 613.2408, calcd 613.2392 ($C_{38}H_{38}CuN_4$). Anal. Calcd: C, 74.30; H, 6.24; N, 9.12. Found: C, 74.19; H, 6.37; N, 8.91. λ_{abs} (CH_2Cl_2, log ϵ) 342 (4.38), 466 (4.83), 499 (4.54) nm.

Bis[5-(4-*tert*-butylphenyl)dipyrrinato]palladium(II) (Pd-2b). A solution of **2b** (28 mg, 0.10 mmol) in $CHCl_3$ (2.0 mL) and TEA (0.50 mL) was treated with $Pd_2(dba)_3$ (228 mg, 0.250 mmol) in methanol (1 mL) overnight at room temperature. The mixture was

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(66) (a) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291. (b) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99.

(67) Wang, Q. M.; Bruce, D. W. *SYNLETT* **1995**, 1267−1268.

(68) Hammel, D.; Erk, P.; Schuler, B.; Heinze, J.; Müllen, K. *Adv. Mater*. **1992**, *4*, 737−739.

(69) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166−11180.

diluted with $CHCl_3$ (5 mL) and filtered through a pad of silica gel ($CHCl_3$). Chromatography (silica, $CHCl_3$) afforded a red-orange solid (28 mg, 85%): mp > 280 °C; ^{1}H NMR δ 1.42 (s, 18H), 6.36 (dd, $J^1 = 1.6$ Hz, $J^2 = 4.4$ Hz, 4H), 6.77 (dd, $J^1 = 1.6$ Hz, $J^2 = 4.4$ Hz, 4H), 7.41 (s, 4H), 7.48 (d, $J = 8.0$ Hz, 4H), 7.52 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR δ 31.4, 34.8, 116.6, 124.3, 130.3, 131.3, 134.6, 137.2, 148.2, 151.5, 151.8; FAB-MS obsd 656.2166, calcd 656.2131 ($C_{38}H_{38}N_4Pd$). Anal. Calcd: C, 69.45; H, 5.83; N, 8.53. Found: C, 68.74; H, 6.00; N, 7.88. λ_{abs} (CH_2Cl_2, log ϵ) 342 (4.42), 376 (4.32), 479 (5.02) nm.

Bis[5-(4-iodophenyl)dipyrrinato]palladium(II) (Pd-2c). A solution of **2c** (140 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) was treated with $Pd(OAc)_2$ (90 mg, 0.40 mmol) at room temperature. UV−vis and TLC analysis (silica, $CHCl_3$) indicated complete metalation after 20 min. Removal of solvent and chromatography (silica, CH_2Cl_2) afforded a yellow-orange solid (80 mg, 50%): mp > 280 °C; ^{1}H NMR δ 6.37 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.0$ Hz, 4H), 6.69 (d, $J = 4.0$ Hz, 4H), 7.32 (d, $J = 8.4$ Hz, 4H), 7.39 (m, 4H), 7.83 (d, $J = 8.4$ Hz, 4H); LD-MS obsd 752.8, calcd 753.9 ($C_{30}H_{20}I_2N_4Pd$); Anal. Calcd: C, 45.22; H, 2.53; N, 7.03. Found: C, 45.26; H, 2.51; N, 6.78. λ_{abs} ($CHCl_3$, log ϵ) 333 (br, 4.19), 385 (br, 4.11), 482 (4.78) nm.

Bis[5-(4-iodophenyl)dipyrrinato]palladium(II) (Pd-2c). A solution of **1c** (5.27 g, 15.1 mmol) in THF (150 mL) was treated overnight with *p*-chloranil (3.71 g, 15.1 mmol) at room temperature. Solvent was removed, and the residue was collected in CH_2Cl_2 (150 mL), sonicated, and filtered to remove the quinone species. The filtrate was concentrated, affording a brown solid. This crude product was dissolved in CH_2Cl_2 (150 mL) and was treated with $Pd(OAc)_2$ (6.78 g, 30.2 mmol) at room temperature. TLC and UV−vis analysis indicated complete metalation after 20 min. The red-orange solid precipitated from the reaction mixture. Filtration and washing with CH_2Cl_2 afforded a red-orange solid (2.46 g, 43%). The analytical data were identical to those obtained for the product prepared by metalation of the dipyrrin. The one-flask oxidation/complexation process employed to form zinc-dipyrrin complexes applied to **1c** using *p*-chloranil and $Pd(OAc)_2$ in THF gave slow reaction and afforded the product **Pd-2c** in only 30% yield.

One-Flask Syntheses of Bis(dipyrrinato)zinc Complexes from the Dipyrromethane. Bis(5-phenyldipyrrinato)zinc(II) (Zn-2a). A mixture of **1a** (111 mg, 0.500 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (274 mg, 1.25 mmol) in THF (5 mL) was treated all at once with *p*-chloranil (123 mg, 0.500 mmol). TLC (silica, $CHCl_3$) showed no dipyrromethane remained after stirring for 27 h at room temperature. Solvent was removed, and the residue was dissolved in $CHCl_3$. The organic phase was washed with aqueous $NaHCO_3$ and H_2O and dried (Na_2SO_4). Chromatography [silica, $CHCl_3 \rightarrow CHCl_3$/MeOH (98:2)] afforded a yellow solid. ^{1}H NMR analysis of this product showed a mixture of the free base dipyrrin and the zinc(II)-dipyrrin complex. This mixture was dissolved in $CHCl_3$ (5 mL) and treated with $Zn(OAc)_2{\cdot}2H_2O$ (274 mg, 1.25 mmol) in methanol (1 mL) at room temperature. After stirring overnight, standard workup and chromatography (silica, $CHCl_3$) afforded a yellow solid (102 mg, 81%): mp 225−227 °C; ^{1}H NMR δ 6.40 (dd, $J^1 = 4.0$ Hz, $J^2 = 1.2$ Hz, 6H), 6.71 (d, $J = 3.6$ Hz, 6H), 7.44−7.50 (m, 4H), 7.55−7.58 (m, 6H); ^{13}C NMR δ 117.0, 127.1, 128.4, 130.6, 132.9, 139.0, 140.6, 148.7, 149.7; FAB-MS obsd 502.1172, calcd 502.1136 ($C_{30}H_{22}N_4Zn$). Anal. Calcd: C, 71.50; H, 4.40; N, 11.12. Found: C, 71.29; H, 4.56; N, 11.21. λ_{abs} (CH_2Cl_2, log ϵ) 322 (br, 4.14), 482 (5.06) nm. Alternatively, the same mixture of **1a** and $Zn(OAc)_2{\cdot}2H_2O$ in THF (5 mL) was treated dropwise with a solution of DDQ (114 mg, 0.500 mmol) in THF (1 mL) for 40 min at room temperature. The same workup procedure afforded a yellow solid (99 mg, 78%) with identical analytical data. See ref 38.

Bis[5-(4-*tert*-butylphenyl)dipyrrinato]zinc(II) (Zn-2b). A mixture of **1b** (115 mg, 0.413 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (227 mg, 1.03 mmol, 2.5 equiv) in THF (5 mL) was treated with *p*-chloranil (102 mg, 0.413 mmol) overnight at room temperature. The reaction mixture was poured into H_2O, extracted with $CHCl_3$, and dried (Na_2SO_4). The solvent was removed, and the residue was collected into $CHCl_3$ (5 mL) and was treated with $Zn(OAc)_2{\cdot}2H_2O$ (227 mg, 0.413 mmol) in methanol (1.0 mL) overnight at room temperature. Standard workup and chromatography (silica, CH_2Cl_2) afforded a yellow solid (105 mg, 82%): mp > 280 °C; ^{1}H NMR δ 1.41 (s, 18H), 6.39−6.41 (m, 4H), 6.76 (d, $J = 4.2$ Hz, 4H), 7.46 (d, $J = 8.4$ Hz, 4H), 7.50 (d, $J = 8.4$ Hz, 4H), 7.53 (s, br, 4H); ^{13}C NMR δ 31.4, 34.7, 116.8, 124.0, 130.6, 133.0, 136.1, 140.7, 149.2, 149.5, 151.6; FAB-MS obsd 614.2392, calcd 614.2388 ($C_{38}H_{38}N_4Zn$). Anal. Calcd: C, 74.08; H, 6.22; N, 9.09. Found: C, 73.43; H, 6.18; N, 8.96. λ_{abs} (CH_2Cl_2, log ϵ) 338 (br, 4.30), 482 (5.06) nm.

Bis[5-(4-iodophenyl)dipyrrinato]zinc(II) (Zn-2c). A mixture of **1c** (1.92 g, 5.51 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (3.02 g, 13.8 mmol, 2.5 equiv) in THF (75 mL) was treated with *p*-chloranil (1.35 g, 5.51 mmol). After stirring overnight at room temperature, the entire reaction mixture was filtered through a short pad of silica gel, which was then washed with THF. Solvent was removed, and the residue was collected in $CHCl_3$ (100 mL). $Zn(OAc)_2{\cdot}2H_2O$ (1.21 g, 5.51 mmol) in methanol (10 mL) was added, and the mixture was stirred overnight at room temperature. The reaction mixture was then washed with aqueous $NaHCO_3$ and H_2O and dried (Na_2SO_4). The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, $CHCl_3$), affording a yellow solid. The solid was washed (sonicated) with methanol (1.35 g, 65%): mp > 280 °C; ^{1}H NMR δ 6.42 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.4$ Hz, 4H), 6.69−6.70 (m, 4H), 7.30 (d, $J = 8.0$ Hz, 4H), 7.53 (s, br, 4H), 7.81 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR δ 117.4, 132.3, 132.7, 136.4, 138.4, 140.2, 147.2, 150.1; LD-MS obsd 756.9, calcd 753.9 ($C_{30}H_{20}I_2N_4Zn$). Anal. Calcd: C, 47.68; H, 2.67; N, 7.41. Found: C, 47.83; H, 2.71; N, 7.38. λ_{abs} (CH_2Cl_2, log ϵ) 333 (br, 4.29), 485 (5.08) nm

Bis[5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-dipyrrinato]zinc(II) (Zn-2d). A mixture of **1d** (348 mg, 1.00 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (549 mg, 2.50 mmol) in THF (14 mL) was treated overnight with *p*-chloranil (246 mg, 1.00 mmol) at room temperature. The mixture was poured into H_2O and extracted with $CHCl_3$. The organic layer was dried (Na_2SO_4) and chromatographed [silica, $CHCl_3 \rightarrow CHCl_3$/methanol (95:5)], affording a yellow solid. The solid was dissolved in $CHCl_3$ and precipitated with methanol (321 mg, 85%): mp 272 °C (dec); ^{1}H NMR δ 1.40 (s, 24H), 6.40 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.2$ Hz, 4H), 6.69 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.2$ Hz, 4H), 7.53 (br, s, 4H), 7.58 (d, $J = 8.4$ Hz, 4H), 7.90 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (100 MHz) δ 24.93, 84.01, 117.08, 129.98, 132.86, 133.42, 140.35, 141.80, 148.59, 149.78; LD-MS obsd 752.5, calcd exact mass 754.3 ($C_{42}H_{44}B_2N_4O_4Zn$). Anal. Calcd: C, 66.74; H, 5.87; N, 7.41. Found: C, 66.87; H, 5.78; N, 7.45. λ_{abs} (CH_2Cl_2, log ϵ) 323 (br, 4.26), 483 (5.07) nm.

Bis[5-(4-formylphenyl)dipyrrinato]zinc(II) (Zn-2g). A solution of **1g** (1.15 g, 4.60 mmol) in THF (46 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (2.52 g, 11.5 mmol) and *p*-chloranil (1.13 g, 4.60 mmol). The reaction mixture was stirred at room temperature for 20 h. The mixture was diluted with $CHCl_3$, washed with water, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to afford a dark residue. The dark residue obtained was chromatographed [silica, CH_2Cl_2/ethyl acetate (9:1)], affording an orange solid. The orange solid was washed with methanol (to remove any quinone species present) to afford an orange solid (1.05 g, 81%): mp 221−223 °C; ^{1}H NMR δ 6.44 (dd, $J^1 = 1.2$ Hz, $J^2 = 4.4$ Hz, 4H), 6.64 (dd, $J^1 = 0.8$ Hz, $J^2 = 4.4$ Hz, 4H), 7.58 (s, 4H), 7.75 (d, $J = 8.0$ Hz, 4H), 8.01 (d, $J = 8.0$ Hz, 4H), 10.16 (s, 2H); ^{13}C NMR δ 117.75, 128.69, 131.40, 132.75, 136.35, 140.00, 145.16, 146.77, 191.91. Anal. Calcd for $C_{32}H_{22}N_4O_2Zn$: C, 68.08; H, 3.87; N, 10.24. Found: C, 68.88; H, 3.95; N, 9.99. λ_{abs} (CH_2Cl_2) 486 nm.

Bis[5-mesityldipyrrinato]zinc(II) (Zn-2h). A mixture of **1h** (264 mg, 1.00 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (549 mg, 2.50 mmol) in THF (10 mL) was treated with *p*-chloranil (248 mg, 1.00 mmol) overnight at room temperature. Removal of solvent and chromatography (silica, CH_2Cl_2) afforded an orange solid. The orange solid was washed with methanol and dried giving an orange solid (253 mg, 86%): mp 254−256 °C; ^{1}H NMR δ 2.18 (s, 12H), 2.38 (s, 6H), 6.35 (d, $J = 4.0$ Hz, 4H), 6.58 (d, $J = 4.0$ Hz, 4H), 6.95 (s, 4H), 7.47 (s, 4H); ^{13}C NMR (100 MHz) δ 19.9, 21.1, 117.1, 127.6, 131.1, 135.4, 136.4, 137.1, 140.0, 148.2, 149.1; MALDI-MS (dithranol) obsd 586.5, calcd av mass 588.1 ($C_{36}H_{34}N_4Zn$). Anal. Calcd: C, 73.53; H, 5.83; N, 9.53. Found: C, 73.21; H, 5.78; N, 9.47. λ_{abs} (CH_2Cl_2) 345 (br), 485 nm.

Bis[5-(pentafluorophenyl)dipyrrinato]zinc(II) (Zn-2j). A mixture of **1j** (312 mg, 1.00 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (549 mg, 2.50 mmol) in THF (10 mL) was treated with DDQ (272 mg, 1.20 mmol) for 40 min at room temperature. The reaction mixture was filtered through a pad of silica and washed with CH_2Cl_2. The solvent was removed, and the residue was dissolved in CH_2Cl_2 (30 mL) and was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (549 mg, 2.50 mmol) in methanol (5.0 mL) overnight at room temperature. The reaction mixture was washed with aqueous $NaHCO_3$, H_2O and dried (Na_2SO_4). Chromatography [silica, hexanes/CH_2Cl_2 (1:1)] afforded an orange-red solid, which was washed with methanol (190 mg, 55%): mp 266−268 °C; ^{1}H NMR δ 6.46 (d, $J = 4.0$ Hz, 4H), 6.67 (d, $J = 4.0$ Hz, 4H), 7.59 (s, 4H); ^{13}C NMR δ 118.7, 130.4, 131.2, 139.5, 151.7. Anal. Calcd: C, 52.69; H, 1.77; N, 8.19. Found: C, 52.66; H, 1.73; N, 8.14 ($C_{30}H_{12}F_{10}N_4Zn$). λ_{abs} (CH_2Cl_2) 496 nm. Alternatively, the same mixture of **1j** (312 mg, 1.00 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (547 mg, 2.50 mmol) in THF (10 mL) was treated overnight with *p*-chloranil (297 mg, 1.20 mmol) at room temperature. The same workup procedure afforded an orange-red solid (105 mg, 31%) with identical analytical data.

Synthesis of Dipyrrins via DTT-Mediated Demetalation of Bis(dipyrrinato)metal Complexes. 5-Phenyldipyrrin (2a). A solution of **Zn-2a** (163 mg, 0.323 mmol) in CH_2Cl_2 (60 mL) was treated with DTT (498 mg, 3.23 mmol, 10 molar equiv) at room temperature. TLC and UV−vis analysis showed complete demetalation after 30 min. The reaction mixture was diluted with CH_2Cl_2, washed with H_2O, and dried (Na_2SO_4). Removal of solvent and chromatography [silica, ethyl acetate/hexanes (1:2)] afforded a slightly brown solid (114 mg, 80%). The analytical data were identical to those obtained for the product prepared by direct oxidation of the dipyrromethane.

5-(4-*tert*-Butylphenyl)dipyrrin (2b) from Demetalation of Cu-2b. A solution of **Cu-2b** (50 mg, 0.081 mmol) in CH_2Cl_2 (15 mL) was treated with DTT (125 mg, 0.81 mmol, 10 molar equiv) at room temperature. TLC and UV−vis analysis showed complete demetalation after 10 min. The reaction mixture was diluted with CH_2Cl_2, washed with H_2O, and dried (Na_2SO_4). Removal of solvent and chromatography [silica, ethyl acetate/hexanes (1:2)] afforded a slightly brown solid (43 mg, 95%). The analytical data were identical to those obtained for the product prepared by direct oxidation of the dipyrromethane.

5-(4-*tert*-Butylphenyl)dipyrrin (2b) from Demetalation of Pd-2b. A solution of **Pd-2b** (34 mg, 0.052 mmol) in CH_2Cl_2 (10 mL) was treated with DTT (80 mg, 0.52 mmol, 10 molar equiv) at room temperature. TLC and UV−vis analysis showed complete demetalation after 17 h. The reaction mixture was diluted with CH_2Cl_2, washed with H_2O, and dried (Na_2SO_4). Removal of solvent and chromatography [silica, ethyl acetate/hexanes (1:2)] afforded a slightly brown solid (23 mg, 79%). The analytical data were identical to those obtained for the product prepared by direct oxidation of the dipyrromethane.

5-(4-Iodophenyl)dipyrrin (2c) from Demetalation of Zn-2c. A solution of **Zn-2c** (227 mg, 0.300 mmol) in CH_2Cl_2 (30 mL) was treated with DTT (462 mg, 3.00 mmol, 10 equiv) at room temperature. UV−vis analysis indicated complete demetalation after 30 min. Then, the reaction mixture was washed with H_2O three times and dried (Na_2SO_4). Removal of solvent and chromatography (silica, CH_2Cl_2) afforded a brown solid (176 mg, 85%): mp 145 °C (dec); ^{1}H NMR δ 6.41 (dd, $J^1 = 1.6$ Hz, $J^2 = 4.4$ Hz, 2H), 6.58−6.59 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.67 (s 2H), 7.79 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 117.7, 130.5, 132.5, 136.9, 144.0; LD-MS obsd 345.6; FAB-MS obsd 347.0045 ($M^+ + H$), calcd 347.0053 ($C_{15}H_{11}IN_2$); λ_{abs} (CH_2Cl_2, log ϵ) 320 (3.98), 433 (4.33) nm.

5-(4-Iodophenyl)dipyrrin (2c) from Demetalation of Pd-2c. A suspension of **Pd-2c** (159 mg, 0.200 mmol) in CH_2Cl_2 (40 mL) was treated with DTT (308 mg, 2.00 mmol, 10 equiv) at room temperature. UV−vis analysis indicated complete demetalation after 18 h. Then, the reaction mixture was washed with H_2O three times and dried (Na_2SO_4). Removal of solvent and chromatography [silica, ethyl acetate/hexanes (1:2)] afforded a brown solid (124 mg, 89%). The analytical data were identical to those obtained for the product prepared from demetalation of **Zn-2c**.

5-(4-Formylphenyl)dipyrrin (2g) from Demetalation of Zn-2g. A solution of **Zn-2g** (0.750 g, 1.34 mmol) in CH_2Cl_2 (134 mL) was treated with DTT (2.06 g, 13.4 mmol) at room temperature. After 1 h, the TLC examination of the reaction mixture indicated that the Zn complex was completely consumed. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and concentrated. Chromatography (silica, $CHCl_3$) afforded a dark oil (204 mg, 31%): ^{1}H NMR δ 6.41 (dd, $J^1 = 1.6$ Hz, $J^2 = 4.4$ Hz, 2H), 6.52 (dd, $J^1 = 0.4$ Hz, $J^2 = 4.0$ Hz, 2H), 7.67−7.68 (m, 4H), 7.97−7.98 (m, 2H), 10.12 (s, 1H); ^{13}C NMR δ 118.20, 128.45, 129.01, 131.40, 136.50, 139.94, 140.55, 143.46, 144.32, 191.82. Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 76.95; H, 4.94; N, 10.95. λ_{abs} (CH_2Cl_2) 439 nm.

Synthesis of Porphyrins. 5,15-Dimesitylporphyrin (3). Following a published procedure,[70] a solution of dipyrromethane (**1e**) (1.75 g, 12.0 mmol) and mesitaldehyde (1.78 g, 12.0 mmol) in $CHCl_3$ (1200 mL) was flushed with argon for 5 min and treated with $BF_3 \cdot OEt_2$ (840 μL, 3.3 mM) at room temperature for 30 min under argon. DDQ (4.09 g, 18.0 mmol) was added, and the mixture was stirred for another 1 h. Triethylamine (920 μL, 3.3 mM) was added, and the entire reaction mixture was filtered through a pad of alumina. The alumina pad was washed with $CHCl_3$ until the eluent was colorless. Removal of solvent and chromatography [silica, $CHCl_3$/hexanes, (2:1)] afforded a purple solid (922 mg, 28%): ^{1}H NMR δ −3.08 (s, br, 2H), 1.84 (s, 12H), 2.66 (s, 6H), 7.32 (s, 4H), 8.88 (d, $J = 4.5$ Hz, 4H), 9.32 (d, $J = 4.5$ Hz, 4H), 10.22 (s, 2H); LD-MS obsd 544.9; FAB-MS obsd 546.2776, calcd 546.2783 ($C_{38}H_{34}N_4$); λ_{abs} (toluene) 407, 502, 532, 576, 632 nm; λ_{em} ($\lambda_{ex} = 500$ nm, toluene) 632, 701 nm.

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(70) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.

5,15-Dimesitylporphinatozinc(II) (Zn-3). A solution of free base porphyrin **3** (218 mg, 0.400 mmol) in $CHCl_3$ (30 mL) was treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (438 mg, 2.00 mmol) in methanol (5.0 mL) at room temperature. Standard workup and washing with methanol afforded a red-purple solid (235 mg, 96%): ^1H NMR δ 1.82 (s, 12H), 2.66 (s, 6H), 7.32 (s, 4H), 8.95 (d, $J = 4.5$ Hz, 4H), 9.37 (d, $J = 4.5$ Hz, 4H), 10.23 (s, 2H); LD-MS obsd 606.6; FAB obsd 608.1926, calcd 608.1918 ($C_{38}H_{32}N_4Zn$); λ_{abs} (toluene) 411, 538, 573 nm; λ_{em} ($\lambda_{ex} = 540$ nm, toluene) 578, 632 nm.

5-Bromo-10,20-dimesitylporphyrin (4). Following a known procedure,[53] a solution of **3** (328 mg, 0.600 mmol) in $CHCl_3$ (200 mL) and pyridine (250 μL) was treated with NBS (106 mg, 0.600 mmol) at 0 °C. After 25 min, the reaction was quenched with acetone (10 mL). Then, the reaction mixture was washed with H_2O and dried (Na_2SO_4). Chromatography [silica, $CHCl_3$/hexanes (1:2)] afforded three bands (in order of elution): the first band (purple) was dibrominated product (51 mg, 12%), the second band (purple) was the desired product, and the third band (purple) was the starting material **3** (42 mg, 12%). The second band was rechromatographed [silica, $CHCl_3$/hexanes (1:2)] affording a purple solid (274 mg, 73%). Data for the title compound follow: ^1H NMR δ -2.87 (s, br, 2H), 1.83 (s, 12H), 2.65 (s, 6H), 7.31 (s, 4H), 8.78 (d, $J = 4.4$ Hz, 4H), 9.22 (d, $J = 4.4$ Hz, 2H), 9.66 (d, $J = 4.4$ Hz, 2H), 10.08 (s, 1H); LD-MS obsd 624.7; FAB-MS obsd 624.1902, calcd 624.1889 ($C_{38}H_{33}BrN_4$); λ_{abs} (toluene) 417, 511, 543, 589, 646 nm; λ_{em} ($\lambda_{ex} = 515$ nm) 647, 711 nm. Data for the dibrominated porphyrin follow: ^1H NMR δ -2.54 (s, br, 2H), 1.82 (s, 12H), 2.64 (s, 6H), 7.29 (s, 4H), 8.69 (d, $J = 4.4$ Hz, 4H), 9.55 (d, $J = 4.4$ Hz, 4H); LD-MS obsd 702.5, calcd 702.1 ($C_{38}H_{32}Br_2N_4Zn$).

5-Bromo-10,20-dimesitylporphinatozinc(II) (Zn-4). A solution of **4** (240 mg, 0.383 mmol) in $CHCl_3$ (50 mL) was treated overnight with $Zn(OAc)_2{\cdot}2H_2O$ (421 mg, 1.92 mmol, 5 equiv) in methanol (2.0 mL) at room temperature. Standard workup gave a purple solid (259 mg, 98%): ^1H NMR δ 1.81 (s, 12H), 2.66 (s, 6H), 7.31 (s, 4H), 8.87 (d, $J = 4.5$ Hz, 4H), 9.30 (d, $J = 4.5$ Hz, 2H), 9.74 (d, $J = 4.5$ Hz, 2H), 10.14 (s, 1H); LD-MS obsd 688.0; FAB-MS obsd 686.1055, calcd 686.1024 ($C_{38}H_{31}BrN_4Zn$); λ_{abs} (toluene) 420, 548, 583 nm; λ_{em} ($\lambda_{ex} = 550$ nm, toluene) 639 nm.

5,15-Dimesityl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphinatozinc(II) (Zn-5). Following a literature procedure,[54] samples of **Zn-4** (482 mg, 0.700 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (122 μL, 0.840 mmol), TEA (780 μL, 5.60 mmol), and $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.0210 mmol, 3% mol) were loaded into a 100 mL Schlenk flask under argon. Then, 1,2-dichloroethane (35 mL) was added, and the mixture was stirred at 85 °C. TLC analysis [$CHCl_3$/hexanes (1:1)] after 1 h showed complete consumption of the starting porphyrin and the presence of a new, polar spot. The reaction mixture was cooled to room temperature, washed with water, and dried (Na_2SO_4). Chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a purple solid (479 mg, 93%): ^1H NMR δ 1.80 (s, 12H), 1.85 (s, 12H), 2.66 (s, 6H), 7.30 (s, 4H), 8.90 (d, $J = 4.5$ Hz, 2H), 8.96 (d, $J = 4.5$ Hz, 2H), 9.36 (d, $J = 4.5$ Hz, 2H), 9.87 (d, $J = 4.5$ Hz, 2H), 10.24 (s, 1H); LD-MS obsd 735.9; FAB-MS obsd 734.2794, calcd 734.2771 ($C_{44}H_{43}N_4O_2Zn$); λ_{abs} (toluene) 415, 543, 573 nm; λ_{em} ($\lambda_{ex} = 540$ nm, toluene) 581, 637 nm.

Bis[5-[4-(5,15-dimesitylporphinatozinc(II)-10-yl)phenyl]dipyrrinato]palladium(II) (6). Following a standard method,[57] samples of **Pd-2c** (16 mg, 0.020 mmol), **Zn-5** (29 mg, 0.040 mmol), $Ba(OH)_2{\cdot}8H_2O$ (13 mg, 0.040 mmol), and $Pd(PPh_3)_4$ (6.9 mg, 0.0060 mmol) were weighed into a 10 mL Schlenk flask. The flask was pump-purged with argon for three times. Dimethoxyethane (1.8 mL) and H_2O (0.2 mL) were added under argon, and the mixture was stirred at 80 °C. TLC analysis (silica, $CHCl_3$) indicated complete consumption of the starting porphyrin after 2 h. The solvent was removed, and the residue was chromatographed (silica, $CHCl_3$) affording a mixture of porphyrins. This mixture was purified by preparative SEC (THF) affording four major bands (in order of elution): (1) unidentified product ($t_R = 10.34$ min); (2) desired triad ($t_R = 10.89$ min); (3) monocoupled byproduct ($t_R = 11.52$ min, LD-MS obsd at $m/z = 1151$, calcd 1153.0 ($C_{68}H_{52}N_8PdZn$); and (4) monomeric porphyrin species ($t_R = 11.96$ min). The second fraction from the SEC column was chromatographed (silica, $CHCl_3$), affording a red-purple solid (18 mg, 50%): ^1H NMR δ 1.87 (s, 24H), 2.67 (s, 12H), 6.61$-$6.62 (m, 4H), 7.22$-$7.23 (m, 4H), 7.33 (s, 8H), 7.65 (s, 4H), 8.03 (d, $J = 8.0$ Hz, 4H), 8.40 (d, $J = 8.0$ Hz, 4H), 8.92 (d, $J = 4.4$ Hz, 4H), 8.95 (d, $J = 4.4$ Hz, 4H), 9.06 (d, $J = 4.4$ Hz, 4H), 9.38 (d, $J = 4.4$ Hz, 4H), 10.21 (s, 2H); LD-MS obsd 1758.6; calcd av mass 1761.0 ($C_{106}H_{82}N_{12}PdZn_2$); λ_{abs} (toluene, log ϵ) 419 (5.72), 483 (4.88), 544 (4.70) nm; λ_{em} ($\lambda_{ex} = 485$ nm, toluene) 531 (w), 590, 637 nm.

5,15-Dimesityl-10-[4-(dipyrrin-5-yl)phenyl]porphinatozinc(II) (Zn-7a) by Demetalation of Triad 6. A sample of triad **6** (14.5 mg, 8.23 μmol) in $CHCl_3$ (3.0 mL) was treated with DTT (13.0 mg, 82.3 μmol) at room temperature. UV$-$vis analysis indicated complete demetalation of the dipyrrin moiety (removal of palladium) after 2 h. The reaction mixture was washed with H_2O and dried (Na_2SO_4). Chromatography [silica, $CHCl_3 \rightarrow CHCl_3$/MeOH (98:2)] afforded a purple solid (9.6 mg, 70%): ^1H NMR δ 1.84 (s, 12H), 2.66 (s, 6H), 6.57 (d, $J = 3.6$ Hz, 2H), 7.04 (d, $J = 3.6$ Hz, 2H), 7.31 (s, 4H), 7.77 (s, 2H), 7.99 (d, $J = 8.0$ Hz, 2H), 8.33 (d, $J = 8.0$ Hz, 2H), 8.87 (d, $J = 4.4$ Hz, 2H), 8.93 (d, $J = 4.4$ Hz, 2H), 8.98 (d, $J = 4.4$ Hz, 2H), 9.36 (d, $J = 4.4$ HZ, 2H), 10.19 (s, 1H); LD-MS obsd 824.0; FAB-MS obsd 827.2864 ($M^+ + H$); calcd 827.2841 ($C_{53}H_{42}N_6Zn_4$); λ_{abs} (toluene) 417, 544 nm; λ_{em} ($\lambda_{ex} = 540$ nm, toluene) 590, 637 nm.

5,15-Dimesityl-10-[4-(dipyrrin-5-yl)phenyl]porphinatozinc(II) (Zn-7a) via Oxidation of 9a. A mixture of **9a** (49 mg, 0.064 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (70 mg, 0.32 mmol, 5 equiv) in THF (5 mL) was treated with *p*-chloranil (16 mg, 0.064 mmol) at room temperature. The mixture was stirred overnight. The standard workup and chromatography [silica, CH_2Cl_2/MeOH (99:1)] afforded a purple solid (38 mg, 72%). The characterization data were identical to those obtained for the product prepared from triad **6**.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-mesityl-20-[4-(dipyrrin-5-yl)phenyl]porphinatozinc(II) (Zn-7b). A mixture of **9b** (41 mg, 0.040 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (44 mg, 0.20 mmol, 5 equiv) in THF (3 mL) was treated overnight with *p*-chloranil (9.8 mg, 0.040 mmol) at room temperature. The standard workup and chromatography [silica, CH_2Cl_2/MeOH (99:1)] afforded a purple solid (31 mg, 71%): ^1H NMR δ 1.54 (s, 36H), 1.87 (s, 6H), 2.63 (s, 3H), 6.55$-$6.57 (m, 2H), 7.04$-$7.05 (m, 2H), 7.29 (s, 2H), 7.76 (s, 2H), 7.80$-$7.81 (m, 2H), 7.89 (d, $J = 8.1$ Hz, 2H), 8.13$-$8.14 (m, 4H), 8.34 (d, $J = 8.1$ Hz, 2H), 8.81 (d, $J = 4.5$ Hz, 2H), 8.97$-$9.05 (m, 6H); LD-MS obsd 1085.8; FAB-MS obsd 1085.5175 ($M^+ + H$), calcd 1085.5188 ($C_{72}H_{72}N_6Zn$); λ_{abs} (toluene) 425, 551, 590 nm; λ_{em} ($\lambda_{ex} = 550$ nm, toluene) 599, 648 nm.

5,15-Bis(4-methylphenyl)-10-[4-(dipyrrin-5-yl)phenyl]-20-phenylporphyrin (7c). Following a standard procedure,[60] a sample of diacyldipyrromethane **11a** (137 mg, 0.300 mmol) in THF/methanol (16 mL, 3:1) was treated with $NaBH_4$ (570 mg, 15.0 mmol). After 40 min (TLC showed reaction completion), the reaction was quenched with aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The resulting dicarbinol **11a-diol** and compound **10** (109 mg, 0.300 mmol) were dissolved in CH_2Cl_2

(120 mL) and treated with $InCl_3$ (8.4 mg, 0.038 mmol, 0.32 mM). The reaction mixture was stirred at room temperature for 20 min, then DDQ (204 mg, 0.900 mmol) was added, and the mixture was stirred for 1 h at room temperature. The mixture was filtered through a pad of silica [eluted with a mixture of CH_2Cl_2/methanol (95:5)], and the filtrate was concentrated. Chromatography [silica, CH_2Cl_2/methanol (98:2)] afforded a purple solid (38 mg, 16%): ^1H NMR δ −2.73 (s, 2H), 2.72 (s, 6H), 6.59 (dd, $J^1 = 0.8$ Hz, $J^2 = 4.0$ Hz, 2H), 7.06 (d, $J = 3.6$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 4H), 7.65−7.82 (m, 5H), 7.91 (d, $J = 7.6$ Hz, 2H), 8.12 (d, $J = 7.6$ Hz, 4H), 8.23 (dd, $J^1 = 1.6$ Hz, $J^2 = 7.2$ Hz, 2H), 8.32 (d, $J = 7.6$ Hz, 2H), 8.80−9.00 (m, 8H); LD-MS obsd 784.6; FAB-MS obsd 785.3379 ($M^+ + H$), calcd 785.3393 ($C_{55}H_{40}N_6$); λ_{abs} (toluene) 421, 516, 551, 593, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm, toluene) 652, 720 nm.

5,15-Bis(4-methoxyphenyl)-10-[4-(dipyrrin-5-yl)phenyl]-20-phenylporphyrin (7d). Following a standard procedure,[60] a sample of diacyldipyrromethane **11b** (147 mg, 0.300 mmol) in THF/methanol (16 mL, 10:1) was treated with $NaBH_4$ (228 mg, 6.00 mmol). After 40 min (TLC showed reaction completion), the reaction was quenched by with aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The resulting dicarbinol **11b-diol** and compound **10** (109 mg, 0.300 mmol) were dissolved in CH_2Cl_2 (120 mL) and treated with $InCl_3$ (8.4 mg, 0.038 mmol, 0.32 mM). The reaction mixture was stirred at room temperature for 20 min, then DDQ (204 mg, 0.900 mmol) was added, and the mixture was stirred for 1 h. The mixture was filtered through a pad of silica [eluted with a mixture of CH_2Cl_2/methanol (95:5)], and the filtrate was concentrated. Chromatography [silica, CH_2Cl_2/methanol (98:2)] afforded a purple solid (23 mg, 10%): ^1H NMR δ −2.72 (s, 2H), 4.11 (s, 6H), 6.60 (d, $J = 3.6$ Hz, 2H), 7.06 (d, $J = 4.0$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 4H), 7.72−7.83 (m, 5H), 7.91 (d, $J = 8.4$ Hz, 2H), 8.15 (d, $J = 8.0$ Hz, 4H), 8.23 (dd, $J^1 = 2.0$ Hz, $J^2 = 7.6$ Hz, 2H), 8.33 (d, $J = 7.6$ Hz, 2H), 8.82−8.98 (m, 8H); LD-MS obsd 815.7; FAB-MS obsd 817.3304 ($M^+ + H$), calcd 817.3291 ($C_{55}H_{40}N_6O_2$); λ_{abs} (toluene) 422, 517, 553, 593, 650 nm; λ_{em} ($\lambda_{ex} = 550$ nm, toluene) 656, 723 nm.

5,15-Dimesityl-10-(4-formylphenyl)porphyrin (8a). Following a standard procedure for Suzuki coupling,[56] samples of **Zn-4** (2.05 g, 3.28 mmol), 4-formylphenyl boronic acid (984 mg, 6.56 mmol), anhydrous K_2CO_3 (3.62 g, 26.2 mmol), and $Pd(PPh_3)_4$ (381 mg, 0.330 mmol, 10 mol %) were weighed into a Schlenk flask. The flask was pump-purged with argon three times. Toluene/DMF (164 mL, 1:1) was added, and the mixture was heated to 90 °C under argon. TLC analysis (silica, $CHCl_3$) after 5 h indicated complete consumption of the starting porphyrin and the formation of a new polar spot. Removal of the solvent and chromatography (silica, $CHCl_3$) afforded a purple solid (1.94 g, 91%): ^1H NMR δ −2.90 (s, br, 2H), 1.84 (s, 12H), 2.64 (s, 6H), 7.30 (s, 4H), 8.27 (d, $J = 8.0$ Hz, 2H), 8.41 (d, $J = 8.1$ Hz, 2H), 8.74−8.77 (m, 4H), 8.84 (d, $J = 4.8$ Hz, 2H), 9.29 (d, $J = 4.8$ Hz, 2H), 10.16 (s, 1H), 10.38 (s, 1H); LD-MS obsd 649.7, FAB-MS obsd 650.3058, calcd 650.3046 ($C_{45}H_{38}N_4O$); λ_{abs} (toluene) 415, 509, 540, 584, 640 nm; λ_{em} ($\lambda_{ex} = 510$ nm, toluene) 642, 709 nm.

10-(4-Formylphenyl)-5,15-dimesitylporphinatozinc(II) (Zn-8a). A solution of free base porphyrin **8a** (130 mg, 0.200 mmol) in $CHCl_3$ (10 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (220 mg, 1.00 mmol) in methanol (2.0 mL) for 3 h at room temperature. Standard workup afforded a purple solid (138 mg, 96%): ^1H NMR δ 1.82 (s, 12H), 2.65 (s, 6H), 7.30 (s, 4H), 8.27 (d, $J = 8.4$ Hz, 2H), 8.42 (d, $J = 8.4$ Hz, 2H), 8.84 (s, 4H), 8.93 (d, $J = 4.8$ Hz, 2H), 9.36 (d, $J = 4.8$ HZ, 2H), 10.21 (s, 1H), 10.38 (s, 1H); FAB obsd 712.2215, calcd 712.2181 ($C_{45}H_{36}N_4OZn$); λ_{abs} (toluene) 418, 544 nm; λ_{em} ($\lambda_{ex} = 540$ nm, toluene) 593, 640 nm.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-formylphenyl)-20-mesitylporphinatozinc(II) (Zn-8b). A solution of free base porphyrin **8b** (2.5 mg, 2.7 μmol) in $CHCl_3$ (1.0 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (3.0 mg, 14 μmol) in methanol (200 μL) for 3 h at room temperature. Standard workup afforded a purple solid (2.3 mg, 88%): ^1H NMR δ 1.53 (s, 36H), 1.86 (s, 6H), 2.63 (s, 3H), 7.28 (s, 2H), 7.79−7.80 (m, 2H), 8.09−8.10 (m, 4H), 8.28 (d, $J = 8.0$ Hz, 2H), 8.42 (d, $J = 8.0$ Hz, 2H), 8.81 (d, $J = 4.8$ Hz, 2H), 8.86 (d, $J = 4.8$ Hz, 2H), 8.96 (d, $J = 4.8$ Hz, 2H), 9.01 (d, $J = 4.8$ Hz, 2H), 10.39 (s, 1H); LD-MS obsd 970.6; FAB-MS obsd 970.4490, calcd 970.4528 ($C_{64}H_{66}N_4OZn$); λ_{abs} (toluene) 425, 551, 592 nm; λ_{em} ($\lambda_{ex} = 550$ nm, toluene) 601, 649 nm.

5,15-Dimesityl-10-[4-(dipyrromethan-5-yl)phenyl]porphyrin (9a). A mixture of **8a** (65 mg, 0.10 mmol) and pyrrole (2.7 g, 40 mmol) in CH_2Cl_2 (5.0 mL) was treated with TFA (9.6 μL, 0.11 mmol) for 2 h at room temperature. The reaction mixture was neutralized with TEA. The solvent and the excess pyrrole were removed under reduced pressure. Chromatography [silica, $CHCl_3$/TEA (99:1)] afforded a purple solid (66 mg, 86%): ^1H NMR δ −2.90 (s, br, 2H), 1.84 (s, 12H), 2.65 (s, 6H), 5.83 (s, 1H), 6.18−6.19 (m, 2H), 6.30−6.31 (m, 2H), 6.86−6.87 (m, 2H), 7.30 (s, 4H), 7.59 (d, $J = 8.4$ Hz, 2H), 8.17 (d, $J = 8.4$ Hz, 2H), 8.22 (s, br, 2H), 8.73 (d, $J = 4.4$ Hz, 2H), 8.82−8.84 (m, 4H), 9.27 (d, $J = 4.4$ Hz, 2H), 10.11 (s, 1H); LD-MS obsd 765.3, FAB-MS obsd 767.3866, calcd 767.3862 ($C_{53}H_{46}N_6$); λ_{abs} (toluene) 414, 508, 584, 640 nm; λ_{em} ($\lambda_{ex} = 510$ nm, toluene) 642, 710 nm.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-(dipyrromethan-5-yl)-phenyl]-20-mesitylporphyrin (9b). A solution of **8b** (227 mg, 0.250 mmol) and pyrrole (5.0 g, 75 mmol) in CH_2Cl_2 (12 mL) was treated with TFA (22 μL, 0.28 mmol, 1.1 equiv) at room temperature. TLC analysis [silica, $CHCl_3$/TEA (99:1)] showed complete consumption of the starting porphyrin-benzaldehyde after 2 h. The reaction mixture was neutralized with TEA. The solvent and the excess pyrrole were removed under reduced pressure. Chromatography [silica, $CHCl_3$/TEA (99:1)] afforded the desired product as a purple solid (205 mg, 80%): ^1H NMR δ −2.65 (br s, 2H), 1.53 (s, 36H), 1.86 (s, 6H), 2.62 (s, 3H), 5.84 (s, 1H), 6.18 (br s, 2H), 6.29−6.32 (m, 2H), 6.85−6.87 (m, 2H), 7.27 (s, 2H), 7.60 (d, $J = 8.1$ Hz, 2H), 7.78−7.79 (m, 2H), 8.08−8.09 (m, 4H), 8.18 (d, $J = 8.1$ Hz, 2H), 8.22 (br s, 2H), 8.69 (d, $J = 4.8$ Hz, 2H), 8.83−8.88 (m, 6H); LD-MS obsd 1024.8; FAB-MS obsd 1024.6115, calcd 1024.6131 ($C_{72}H_{76}N_6$); λ_{abs} (toluene) 421, 516, 550, 593, 649 nm; λ_{em} ($\lambda_{ex} = 515$ nm, toluene) 652, 720 nm.

5-[4-(Dipyrrin-5-yl)phenyl]dipyrromethane (10). Following a standard procedure[37] with slight modification,[14,58] a sample of **2g** (0.320 g, 1.30 mmol) in CH_2Cl_2 (4.6 mL) was mixed thoroughly with pyrrole (4.60 mL, 65.0 mmol). The mixture was treated with TFA (0.120 mL, 0.156 mmol). The reaction mixture was stirred at room temperature for 5 min and quenched with 0.1 N aqueous NaOH. The reaction mixture was extracted with ethyl acetate, dried (Na_2SO_4), and concentrated. The dark residue obtained was chromatographed [silica, hexanes/ethyl acetate (3:1)] to give dark oil. The dark oil was dissolved in hexanes/ethyl acetate (9:1), and the precipitate that formed was filtered off. The yellow filtrate was concentrated to afford an orange solid (196 mg, 41%): mp 129−130 °C; ^1H NMR δ 5.57 (s, 1H), 5.96 (s, 2H), 6.20−6.21 (m, 2H), 6.40 (dd, $J^1 = 4.0$ Hz, $J^2 = 1.2$ Hz, 2H), 6.63 (d, $J = 4.0$ Hz, 2H), 6.75−6.76 (m, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.64 (s, 2H), 8.02 (s, 2H). (In addition, signals consistent with that for the N-confused dipyrromethane were present in the ^1H NMR spectrum, indicating a 96:4 ratio of **10**/N-confused isomer. All data reported here were derived from this mixture.) ^{13}C NMR δ 43.9, 107.5, 108.6, 117.6, 117.7, 127.7, 129.0, 130.1, 131.3, 132.2, 143.7; FAB-MS obsd 365.1779 ($M^+ + H$), calcd 365.1766 ($C_{24}H_{20}N_4$); λ_{abs} 431 nm.

Bis[5-[4-(5,15-dimesitylporphinatozinc(II)-10-yl)phenyl]dipyrrinato]zinc(II) (12a). A solution of **Zn-7a** (9.60 mg, 0.0116 mmol) in $CHCl_3$ (3 mL) was treated overnight with $Zn(OAc)_2{\cdot}2H_2O$ (12.7 mg, 0.0579 mmol) in methanol (0.2 mL) at room temperature. UV−vis analysis showed complete metalation. The reaction mixture was washed with aqueous $NaHCO_3$ and H_2O. The organic layer was dried (Na_2SO_4) and concentrated, affording a purple solid (9.7 mg, 97%): ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 24H), 2.67 (s, 12H), 6.66 (d, $J = 4.4$ Hz, 4H), 7.23 (d, $J = 4.4$ Hz, 4H), 7.33 (s, 8H), 7.78 (s, 4H), 8.01 (d, $J = 7.6$ Hz, 4H), 8.39 (d, $J = 7.6$ Hz, 4H), 8.92 (d, $J = 4.4$ Hz, 4H), 8.95 (d, $J = 4.4$ Hz, 4H), 9.06 (d, $J = 4.4$ Hz, 4H), 9.38 (d, $J = 4.4$ Hz, 4H), 10.21 (s, 2H); LD-MS obsd 1720.1, calcd av mass 1720.4 ($C_{106}H_{82}N_{12}Zn_3$); λ_{abs} (toluene, log ϵ) 419 (5.72), 486 (4.93), 544 (4.58) nm; λ_{em} ($\lambda_{ex} = 485$ nm, toluene) 531 (w), 590, 637 nm.

Bis[5-[4-[5,15-bis(3,5-di-*tert*-butylphenyl)-10-mesitylporphinatozinc(II)-20-yl]phenyl]dipyrrinato]zinc(II) (12b). A solution of **Zn-7b** (31 mg, 0.028 mmol) in $CHCl_3$ (3 mL) was treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (22 mg, 0.10 mmol) in MeOH (0.5 mL) at room temperature. The standard workup and washing with methanol (sonication and filtration) afforded a purple solid (28 mg, 87%): ^{1}H NMR δ 1.49 (s, 72H), 1.81 (s, 12H), 2.57 (s, 6H), 6.58−6.60 (m, 4H), 7.16−7.17 (m, 4H), 7.22 (s, 4H), 7.72−7.74 (m, 8H), 7.94 (d, $J = 7.8$ Hz, 4H), 8.03−8.08 (m, 8H), 8.31 (d, $J = 7.8$ Hz, 4H), 8.73−8.76 (m, 4H), 8.86−8.95 (m, 6H), 9.01−9.02 (m, 6H); LD-MS obsd 2238.2, calcd av mass 2236.9 ($C_{144}H_{142}N_{12}Zn_3$); λ_{abs} (toluene, log ϵ) 423 (5.85), 486 (4.97), 551 (4.68), 590 (4.04) nm; λ_{em} ($\lambda_{ex} = 485$ nm, toluene) 597, 647 nm.

Bis[5-[4-[5,15-bis(4-methylphenyl)-10-phenylporphinatozinc(II)-20-yl]phenyl]dipyrrinato]zinc(II) (12c). A solution of **7c** (24 mg, 0.030 mmol) in $CHCl_3$ (3 mL) was treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (49 mg, 0.23 mmol) in MeOH (0.5 mL) at room temperature. The standard workup afforded a purple solid. The solid was washed with methanol, affording a purple solid (22 mg, 83%): ^{1}H NMR δ 2.74 (s, 12H), 6.68 (d, $J = 4.8$ Hz, 4H), 7.25 (d, $J = 4.4$ Hz, 4H), 7.59 (d, $J = 7.6$ Hz, 8H), 7.72−7.84 (m, 10H), 8.03 (d, $J = 8.0$ Hz, 4H), 8.15 (d, $J = 8.4$ Hz, 8H), 8.24−8.25 (m, 4H), 8.38 (d, $J = 8.0$ Hz, 4H), 8.92−9.14 (m, 16H); LD-MS obsd 1755.3; calcd 1754.4 ($C_{110}H_{74}N_{12}Zn_3$); λ_{abs} (toluene) 427, 486, 557, 597 nm; λ_{em} ($\lambda_{ex} = 485$ nm, toluene) 599, 648 nm.

Bis[5-[4-[5,15-bis(4-methoxyphenyl)-10-phenylporphinatozinc(II)-20-yl]phenyl]dipyrrinato]zinc(II) (12d). A solution of **7d** (15 mg, 0.018 mmol) in $CHCl_3$ (2 mL) was treated overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (30.0 mg, 0.135 mmol) in MeOH (0.5 mL) at room temperature. The standard workup afforded a purple solid. The solid was washed with methanol, affording a purple solid (14 mg, 85%): ^{1}H NMR δ 4.12 (s, 12H), 6.68 (d, $J = 4.0$ Hz, 4H), 7.22−7.38 (m, 12H), 7.72−7.84 (m, 10H), 8.03 (d, $J = 8.0$ Hz, 4H), 8.17 (d, $J = 8.0$ Hz, 8H), 8.25 (d, $J = 7.2$ Hz, 4H), 8.38 (d, $J = 7.6$ Hz, 4H), 8.97 (d, $J = 4.0$ Hz, 4H), 9.03 (d, $J = 4.4$ Hz, 4H), 9.09−9.10 (m, 8H); LD-MS obsd 1820.3, calcd 1818.4 ($C_{110}H_{74}N_{12}O_4Zn_3$); λ_{abs} (toluene) 426, 486, 551, 591 nm; λ_{em} ($\lambda_{ex} = 485$ nm, toluene) 600, 650 nm.

Characterization. Electrochemistry. The electrochemical measurements were made using instrumentation and procedures previously described.[71] The solvent was CH_2Cl_2 and 0.1 M Bu_4NPF_6 (Aldrich, recrystallized three times from methanol and dried under vacuum at 110 °C) served as the supporting electrolyte. The potentials were measured versus Ag/Ag^+; $E_{1/2}$ $Fc/Fc^+ = 0.19$ V. The scan rate was 0.1 V/s.

Static and Time-Resolved Optical Spectroscopy. The spectroscopic measurements were performed as described in the preceding article.[2]

X-ray Crystallography. Data Collection. All X-ray measurements were made on an Enraf-Nonius CAD4-MACH diffractometer at −125 °C. The unit cell dimensions were determined by a symmetry constrained fit of 25 well-centered reflections and their Friedel pairs with $30° < 2\theta < 36°$. A quadrant of unique data was collected using the ω scan mode in nonbisecting geometry. The adoption of a nonbisecting scan mode was accomplished by offsetting ψ by 20° for each data point collected. This was done to minimize the interaction of the goniometer head with the cold stream.

Structure Solution and Refinement. The data were reduced using routines from the NRCVAX set of programs.[72] The structure was solved using SIR92.[73] Most non-hydrogen atoms were recovered from the initial E-map. The hydrogen atom positions were introduced at idealized positions. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were allowed to ride on the parent carbon atoms. The calculated structure factors were fit to the data using full-matrix least-squares based on F. The calculated structure factors included corrections for anomalous dispersion.

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Supporting Information Available: Description of control experiments related to synthesis methodology development; ^{1}H NMR spectra for all new compounds; ^{13}C NMR spectra for all new non-porphyrin compounds except **Pd-2c**; LD-MS spectra for all new porphyrins; X-ray data for **Zn-2a**; static absorption and emission spectra and description for triads **12a** and **12b**, porphyrin-dipyrrins **Zn-7a** and **Zn-7b**, reference porphyrins **Zn-8a**, **Zn-8b**, and **Zn-3**, and bis(dipyrrinato)zinc complex **Zn-2a** in toluene and benzonitrile at room temperature; time-resolved absorption data and description for triad **12b** in toluene and **12a** and **12b** in benzonitrile. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(71) Seth, J.; Palanniapan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194−11207.

(72) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384−387.

(73) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(74) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1−13.