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Pincer-Porphyrin Hybrids

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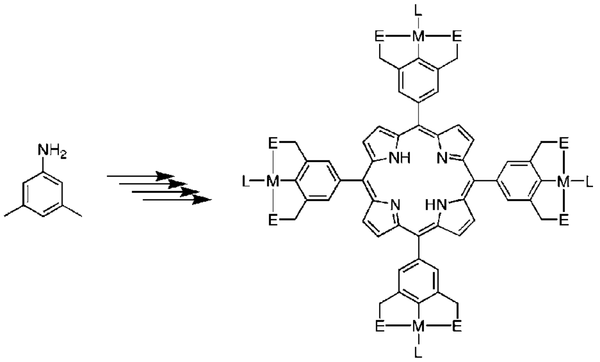
ABSTRACT



Starting from tetrakis(3,5-bis(bromomethyl)phenyl)porphyrin, pincer-porphyrin hybrid molecules (tetrakis(ECE-pincer)porphyrin; E = N, P, S) based on a tetraphenylporphyrin skeleton have been prepared in high yields. These multi-ligand site compounds could be selectively metalated at their peripheries, which was shown by X-ray crystallography.

Inspired by Nature's use of macrocyclic, tetrapyrrolic molecules in processes such as oxygen transport and the conversion of light energy into chemical potential, porphyrins are widely used in chemical research.[1] These photoactive molecules have been employed in systems ranging from artificial photosynthetic model systems[2] and hemoglobin and myoglobin mimics[3] to building blocks in supramolecular multicomponent systems.[4] In addition, porphyrins containing a covalently or noncovalently attached extra-annular metal center have been shown to be interesting for, e.g., molecular electronic devices[5] and supramolecular architectures. Several porphyrin systems containing peripheral ligand sites have been constructed to date,[6,4a,7−9] and the corresponding metal complexes were extensively studied. However, with the exception of metallocene derivatives,[5,10] few examples have

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(1) (a) *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978. (b) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000.

(2) (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198−205. (c) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849−866. (d) Harriman, A.; Sauvage, J. P. *Chem. Soc. Rev.* **1996**, 41−48. (e) Gust, D.; Moore, T. A.; Moore, A. L. *Pure Appl. Chem.* **1998**, *70*, 2189−2200. (f) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48.

(3) Collman, J. P.; Fu, L. *Acc. Chem. Res.* **1999**, *32*, 455−463.

(4) (a) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133−156. (b) Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113−171.

(5) Boyd, P. D. W.; Burrell, A. K.; Campbell, W. M.; Cocks, P. A.; Gordon, K. C.; Jameson, G. B.; Officer, D. L.; Zhao, Z. *Chem. Commun.* **1999**, 637−638.

(6) (a) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. *Chem. Eur. J.* **1998**, *4*, 1744−1754. (b) Uyeda, H. T.; Zhao, Y.; Wostyn, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *125*, 13806−13813.

(7) (a) Prodi, A.; Indelli, M. T.; Kleverlaan, C. J.; Alessio, E.; Scandola, F. *Coord. Chem. Rev.* **2002**, *229*, 51−58. (b) Iengo, E.; Zangrando, E.; Alessio, E. *Eur. J. Inorg. Chem.* **2003**, *13*, 2371−2384.

(8) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168−6179 and references therein.

(9) (a) Märkl, G.; Reiss, M.; Kreitmeier, P.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2230−2233. (b) Darling, S. L.; Stulz, E.; Feeder, N.; Bampos, N.; Sanders, J. K. M. *New J. Chem.* **2000**, *24*, 261−264. (c) Stulz, E.; Scott, S. M.; Ng, Y.-F.; Bond, A. D.; Teat, S. J.; Darling, S. L.; Feeder, N.; Sanders, J. K. M. *Inorg. Chem.* **2003**, *42*, 6564−6574.

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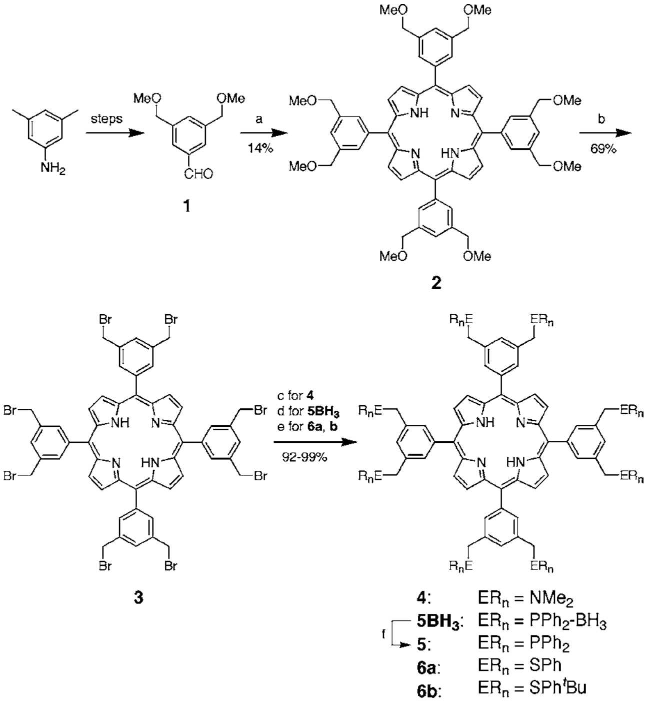
been reported concerning metal atoms directly attached to the (tetraphenyl)porphyrin skeleton via a metal-to-carbon σ bond. Notable examples include direct *meso*-metalation[11] and *ortho*-metalation of a pyridylporphyrin.[12] In search of novel peripherally metalated porphyrins, we anticipated that a robust metal−ligand system would be highly desirable as the extra-annular metal site. If this metal−ligand system, in addition, were to have other interesting properties, this would only add to the impetus of connecting such a system to a porphyrin. Hence, the metallo-ECE-pincer system (with ECE pincer being the monoanionic, potentially tridentate ligand $[2,6\text{-}(ECH_2)_2C_6H_3]^-$ (E = NR_2, SR, PR_2)) was selected because it is known to be chemically robust and because of its catalytic and physicochemical properties.[13,14] Linear, Hammett-type relations are known between substituents at the *para* position with respect to the metal in metallopincers and both the electron density at the metal and the catalytic activity of the complexes.[15] Since the electronic properties of a porphyrin can be fine-tuned by the introduction of a metal, metallopincer-metalloporphyrin hybrid systems might provide an interesting and novel entry into catalyst modulation. Taking these facts into account, we sought for a way to combine both (metallo)porphyrin chemistry and metallopincer chemistry and, hence, to construct a molecular hybrid of both. Because these materials can, in theory, incorporate a plethora of different metals in both coordination moieties, we anticipated that their synthesis would provide access to interesting homo- and heteromultimetallic systems.

Since several pincer ligand systems are known (i.e., SCS, NCN, and PCP), we were interested in synthesizing a common hybrid ligand precursor. Most of the synthetic routes to these types of ligands involve nucleophilic substitution of a benzylic bromine atom by the desired heteroatom-containing nucleophile. Hence, a tetraphenylporphyrin derivative containing benzyl bromide moieties at all of its 3,5-phenyl positions would be highly desirable. Thus, starting from 3,5-dimethylaniline, 3,5-bis(methoxymethyl)benzaldehyde **1** was obtained in a 29% overall yield (4 steps) and subsequently used in an Adler-type condensation reaction with pyrrole to yield 12% of 5,10,15,20-tetrakis(3,5-bis(methoxymethyl)phenyl) porphyrin **2** (see Scheme 1).

Scheme 1[a]



[a] (a) pyrrole, propionic acid, reflux; (b) HBr/HOAc, CH_2Cl_2, rt; (c) $HNMe_2$, CH_2Cl_2, rt; (d) $LiPPh_2-BH_3$, THF, −40° C; (e) thiophenol or 4-*tert*-butylthiophenol, K_2CO_3, 18-C-6, THF, rt; (f) Et_2NH, THF, reflux.

The structure of porphyrin **2** was confirmed by ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography (see Supporting Information, Figure S1). Following a modified literature procedure,[16] treatment of **2** with HBr/AcOH in CH_2Cl_2 gave 5,10,15,20-tetrakis(3,5-bis(bromomethyl)phenyl) porphyrin **3** in 67% yield.

This compound proved to be an excellent general ligand precursor for the syntheses of tetrakis(ECE-pincer)porphyrins **4**, **5**, **6a**, and **6b** (E = N, P, and S, respectively; see Scheme 1). Nucleophilic replacements of the bromine atoms by the appropriate nucleophiles proceeded smoothly under standard conditions under exclusion of light and molecular oxygen. Tetrakis(NCN)porphyrin **4** was obtained after treatment of **3** with an excess of dimethylamine in CH_2Cl_2 as a purple, crystalline solid in 96% yield. Its structural composition was confirmed by X-ray crystallography; however, the disorder in the crystal was too high to warrant publication. Notably, in contrast to most porphyrins, **4** dissolves in solvents ranging from polar (MeCN, MeOH) to nonpolar (pentane, hexane) at room temperature.

Using $LiPPh_2-BH_3$ in THF as a nucleophile, borane-protected tetrakis(PCP)porphyrin **$5BH_3$** was obtained in 99% yield. Deprotection with Et_2NH quantitatively yielded tetrakis(PCP)porphyrin **5**. Fourfold platination of **5** by a transcyclometalation (TCM) reaction[17] with NCN−PtCl was

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(10) For selected examples, see: (a) Wang, H. J. H.; Jaquinod, L.; Nurco, D. J.; Vicente, M. G. H.; Smith, K. M. *Chem. Commun.* **2001**, 2646−2647. (b) Gryko, D. T.; Zhao, F.; Yasseri, A. A.; Roth, K. M.; Bocian, D. F.; Kuhr, W.; Lindsey, J. S. *J. Org. Chem.* **2000**, 65, 7356−7362. (c) Gogan, N. J.; Siddiqui, Z. U. *Can. J. Chem.* **1972**, *50*, 720−725.

(11) (a) Arnold, D. P.; Sakata, Y.; Sugiura, K.; Worthington, E. I. *Chem. Commun.* **1998**, 2331−2332; Arnold, D. P.; Healy, P. C.; Hodgson, M. J.; Williams, M. L. *J. Organomet. Chem.* **2000**, *607*, 41−50. (c) Hodgson, M. J.; Healy, P. C.; Williams, M. L.; Arnold, D. P. *J. Chem. Soc., Dalton Trans.* **2002**, 4497−4504. (d) Hartnell, R. D.; Arnold, D. P. *Organometallics* **2004**, *23*, 391−399. (e) Hartnell, R. D.; Arnold, D. P. *Eur. J. Inorg. Chem.* **2004**, *6*, 1262−1269.

(12) Darling, S. L.; Goh, P. K. Y.; Bampos, N.; Feeder, N.; Montalti, M.; Prodi, L.; Johnson, B. F. G.; Sanders, J. K. M. *Chem. Commun.* **1998**, 2031−2032.

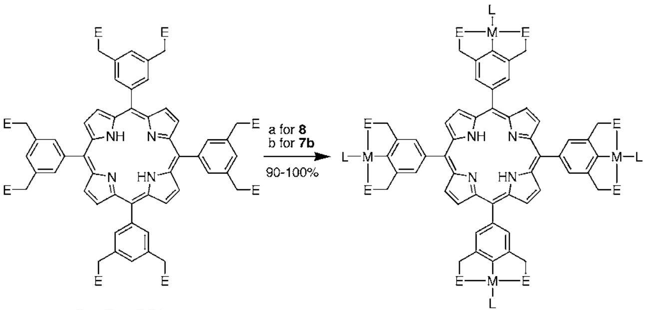
(13) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *40*, 3750−3781.

(14) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837−1857.

(15) (a) van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468−477. (b) Slagt, M. Q.; Rodríguez, G.; Grutters, M. P.; Klein Gebbink, R. J. M.; Klopper, W.; Jenneskens, L. W.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **2004**, *10*, 1331−1344.

(16) Jux, N. *Org. Lett.* **2000**, *2*, 2129−2132.

Scheme 2[a]



5: E = PPh_2
6b: E = SPh^tBu

8: E = PPh_2, M = Pt, L = Cl
7b: E = SPh^tBu, M = Pd, L = Cl

[a] (a) NCN−PtCl, toluene, reflux; (b) (1) $[Pd(NCMe)_4](BF_4)_2$, CH_2Cl_2/MeCN, rt, (2) LiCl, MeCN.

then performed in toluene (see Scheme 2). Addition of a clear, colorless solution of NCN−PtCl in toluene to a clear, dark-red solution of **5** in toluene gave a voluminous purple precipitate and a colorless supernatant within minutes. This precipitate was not further analyzed but most probably consisted of a coordination compound in which the phosphorus atoms of **5** had replaced the nitrogen atoms of NCN−PtCl in coordinating to platinum.[17b] Heating this suspension for 72 h at 110 °C did not visibly change the reaction mixture, which still consisted of a purple precipitate in a colorless supernatant. However, when analyzing the supernatant, it consisted solely of a solution of the free NCN ligand in toluene. The purple precipitate was collected and washed with toluene, pentane, and finally CH_2Cl_2. The compound is not soluble in pentane, toluene, or benzene and is only sparingly soluble in solvents such as THF, CH_2Cl_2, and $CHCl_3$. The resulting product **8** was fully characterized (^{1}H and ^{31}P NMR, UV−vis, MALDI-TOF, and elemental analysis), and all analyses showed that we succeeded in selectively metalating the porphyrin at its extra-annular pincer sites.

Finally, the introduction of four SCS pincer ligands around a mutual porphyrin core was undertaken. Allowing **3** to react with 8 equiv of thiophenol in THF in the presence of 18-crown-6 and K_2CO_3 furnished tetrakis(SCS)porphyrin **6a** in 88% yield. Unfortunately, 4-fold palladation of this compound using $[Pd(MeCN)_4](BF_4)_2$ in a mixture of CH_2Cl_2 and acetonitrile[18] led to a product that was insufficiently soluble for proper characterization. Hence, *tert*-butyl derivative **6b** was synthesized similarly in 93% yield using commercially available 4-*tert*-butylthiophenol as the nucleophile. Compound **6b** was palladated according to the procedure used for **6a**, and after exchange of acetonitrile for chloride in the palladium coordination environments, **7b** was obtained in 90% yield (see Scheme 2). Palladation was spectroscopically confirmed by the disappearance of the ^{1}H NMR resonance belonging to the hydrogen atom connected to C_{ipso}, which was previously situated at $\delta = 7.68$ ppm. In addition, a downfield shift of the AB pattern of the *tert*-butylphenylsulfido protons from $\delta = 7.37$ and 7.33 ppm to $\delta = 7.95$ and 7.49 ppm, respectively, was observed in combination with an upfield shift of the hydrogens positioned *meta* with respect to C_{ipso}.

5,10,15,20-Tetrakis(3,5-bis((4-*tert*-butylphenylsulfido) methyl)-4-chloropalladio(II)phenyl)porphyrin (**7b**) was fully characterized (^{1}H, ^{13}C NMR, UV−vis, mass spectrometry, and elemental analysis), and all analyses consistently showed a quantitative and selective introduction of palladium at the extra-annular SCS sites, without affecting the inner tetradentate *N*,*N*′,*N*″,*N*‴ coordination site. Similar selective palladation was also observed for a related SCS-pincer-substituted porphyrin by Reinhoudt and co-workers.[19]

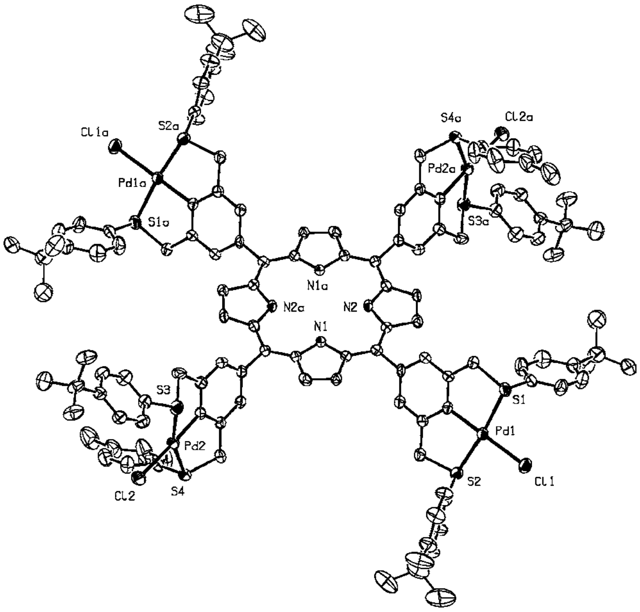


Figure 1. Crystal structure of **7b**. Hydrogen atoms and co-crystallized molecules of toluene have been omitted for clarity. Only the major disorder component of the *tert*-butyl groups is shown. Selected distances [Å] and dihedral angles [deg]: Cl(1)−Cl(1a) 24.2734(19), Pd(1)−Cl(1) 2.3925(12), Pd(1)−S(1) 2.2916(14), Pd(1)−S(2) 2.2804(14), Pd(1)−C_{ipso} 1.988(4); porphyrin−pincer-(Pd(1)) 56.5(7), porphyrin−pincer(Pd(2)) 67.7(7).

Selective palladation was corroborated by X-ray crystallography. The molecular geometry of **7b** in the solid state shows a molecule with C_{2v} symmetry (see Figure 1). A slightly distorted porphyrin core is surrounded by four diorganosulfide moieties (dihedral angles between porphyrin

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(17) (a) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317−11318. (b) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 11822−11833. (c) Dijkstra, H. P.; Albrecht, M.; van Koten, G. *Chem. Commun.* **2002**, 126−127.

(18) Dijkstra, H. P.; Meijer, M. D.; Patel, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Canty, A. J.; van Koten, G. *Organometallics* **2001**, *20*, 3159−3168.

(19) Huck, W. T. S.; Rohrer, A.; Anikumar, A. T.; Fokkens, R. H.; Nibbering, N. M. M.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *New J. Chem.* **1998**, 165−168

and *meso*-phenyl groups are 56.5(7)° and 67.7(7)°, each of which is cyclopalladated at the position between the CH_2SPh^tBu groups. This affords square planar Pd(II) centers with a ligand environment that comprises tridentate *S,C,S′* coordination by the organic moiety with a chloride ligand trans to the metal-bonded aromatic carbon atom (C_{ipso}). Two identical pincer groups opposite to each other (around palladium atoms Pd(2) and Pd(2a), Figure 1) show a distorted ligand environment, wherein the two *tert*-butylphenyl groups do not point away from each other in an *anti* way but rather adopt a quasi *syn* geometry.

The introduction of metal atoms in the periphery of the porphyrin affects the electronic spectra of the hybrid molecules, which are completely dominated by the porphyrin part (see Figure 2).

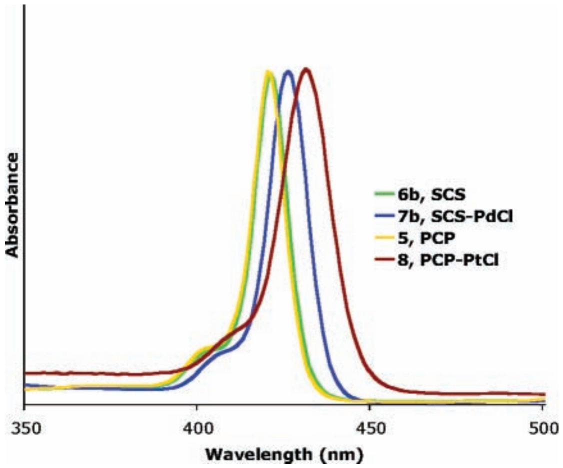

Figure 2. Soret region of the electronic spectra of pincer-porphyrin hybrids **5**−**8**. The Soret peaks are normalized.

The B- and Q-bands of free ligands **5** (420, 514, 550, 588, and 643 nm) and **6b** (420, 516, 549, 591, and 645 nm) shift bathochromically to 426, 522, 557, 596, and 650 nm, respectively, for **7b** and to 431, 522, 561, 600, and 654 nm for **8** upon peripheral metalation (for the Q-band region, see Supporting Information Figure S2). In addition, the Soret bands broaden upon peripheral metalation from a full width at half-maximum (fwhm) of 12 nm for **5** and **6b** to 14 and 18 nm for **7b** and **8**, respectively. This observation is not uncommon for peripherally metalated porphyrins but nonetheless emphasizes that there is electronic communication between the metallo-pincer and porphyrin parts of the molecule in the excited state.[20] Moreover, fluorescence measurements ($\lambda_{exc} = 516$ nm) of **6b** and **7b** revealed a 74% quenching of the fluorescence of the latter with respect to the former, which further supports an intramolecular communication in the excited state. We believe that the fluorescence quenching is caused by a singlet to triplet intersystem crossing, which can be mediated by heavy metal atoms.

In conclusion, a new class of pincer ligand-functionalized porphyrins has been developed. Starting from a general ligand precursor, 5,10,15,20-tetrakis(3,5-bis(bromomethyl)-phenyl)porphyrin (**3**), tetrakis-NCN-, -PCP-, and -SCS-porphyrins were synthesized in high yields. The tetrakis-SCS- and PCP-porphyrins were selectively metalated at their peripheral ligand sites, as judged from NMR spectrometry and X-ray crystallography. Thus, we have shown that organometallic moieties comprising an exceedingly stable metal-to-carbon σ bond can be fitted onto a porphyrin core, yielding multiligand systems. In addition, UV−vis and fluorescence spectroscopy provide evidence for an appreciable amount of electronic communication between the subunits of the hybrid in the excited state. We are currently focusing on the metalation chemistry of the reported tetrakis-(ECE)porphyrins, i.e., the selectivity of metal incorporation in- or outside the porphyrin core, and on potential catalytic and physicochemical applications.

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Supporting Information Available: Synthetic procedures and spectroscopic characterization for compounds **1**−**8** and crystallographic data for compounds **2** and **7b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Dixon, I. M.; Collin, J.-P. *J. Porphyrins Phthalocyanines* **2001**, *5*, 600−607.