Typical data for the characterization of the porphyrazine dimers and squares is presented below. Note that the various free base porphyrazines and the corresponding exocyclic coordinated adducts are somewhat labile to oxidation so are stored and manipulated under an inert atmosphere. The synthesis, properties, and potential applications of Pz are reported.1-25 The detailed characterization of the dimers is presented as a basis for the characterization of the more complex squares, i.e. interpretation of the UV-Visible and NMR spectra. The MS of the dimers were consistent with the proposed structures.

Instrumentation.
MALDI-MS were done as a service by the facility at the University of Illinois at Urbana Champaign. 1H NMR spectra were recorded on JEOL 400 MHz, a Varian VXR-300 MHz, or a Varian 500 MHz instrument. Chemical shifts are reported in ppm relative to TMS. NMR assignments are consistent with those published previously. Agilent Technologies HP 1100 LC/MSD, and a Cary Bio-3 were used. Typical Electrospray Ionization Mass Spectroscopy (ESI-MS) method: ~0.05mM solutions in toluene were injected using acetonitrile/water (50:50 v:v) containing 1% trifluoroacetic acid, positive ion mode, and the fragmentor voltage between 100 and 350 V. AFM data were taken in tapping mode with a Park Scientific Instruments Auto Probe CP microscope under ambient conditions. Molecules were deposited on the freshly cleaved mica surface via drop-dry method, subsequently rinsed with toluene and dried under a stream of N2.

Figure ESI-1A. 1H NMR (300 MHz) spectra of free base 2,3-bis(dimethylamino)-7,8,12,13,17,18-hexakis(4-(tert-butyl)phenyl)porphyrazine (top), its palladium adduct (middle), and dimer Pd-3A (bottom). Arrows indicate the chemical shift changes of the methylamino groups and internal pyrrole NH.

Figure SI-1B 1H NMR (300 MHz) of the dimer using the Ni(II) Pz gives a clearer indication of the chemical shift changes upon formation of the dimer. Spectra of 2,3-bis(dimethylamino)-7,8,12,13,17,18-hexakis(4-(tert-butyl)phenyl)porphyrazine (top), its palladium adduct (middle), and dimer Pd-3B (bottom). Arrows indicate the chemical shift changes of methylamino groups.
Synthesis. The modifications of the Linstead magnesium alkoxide templated macrocyclization reaction developed by Barrett and Hoffman uses bis substituted maleonitriles, is quite versatile, and is the basis for the synthesis of the Pz building blocks herein. The use of two maleonitriles derivatives results in a statistical mixture of six Pz weighted by a variety of factors including stoichiometry, reactivity and solubility; nonetheless these compounds and isomers are readily separated and purified by flash chromatography. This strategy, in this case using 3,4-bis(4-tert-butylphenyl)pyrroline-2,5-diimine and bis(dimethylamino)-maleonitrile, is employed because all six of the products can be used as tectons or reference compounds and is easy to scale up. All Pz and the Ni(II) complexes (1A, 1B, 2A, 2B, 5A, 5B) have \(^1\)H NMR, UV-visible, and mass spectra consistent with the structure and previous reports (see below). Since the Pd(II) assemblies are less stable than the corresponding Pt(II) arrays the yields in table 1 are spectroscopic for the former and isolated for the latter. The purification of adduct 5A-PtCl\(_2\) and arrays 6A and 6B is accomplished using flash chromatography (silica gel purchased from Seleto Scientific, 32-63 µm average particle size) using 1% methanol in dichloromethane as eluents. The Rf on TLC plate (Silica Gel 60 with a 254 nm fluorescent indicator) for 5A-PtCl\(_2\), 6A, and 6B are 0.8, 0.4 and 0.5, respectively using the same eluents.

![Fig ESI-2. Simple sterics calculation using PC Model on the ligand binding sites of the monomer and dimer (for simplification the chromophores were replaced by the pyrrole rings) show the inequivalence of the methyl peaks in the Pt(II) dimers.](image)

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![Fig ESI-3. Formation of the Ni(II) porphyrazine palladium adduct 1B-PdAc\(_2\) and dimer Pd-3B via two different methods. \(^1\)H NMR, MS and UV-visible spectra indicate the products are the same compounds. The Pt(II) adducts can be formed similarly. The bottom method is precedence for the formation of the squares by a similar route.](image)

Figure ESI-3. Formation of the Ni(II) porphyrazine palladium adduct 1B-PdAc\(_2\) and dimer Pd-3B via two different methods. \(^1\)H NMR, MS and UV-visible spectra indicate the products are the same compounds. The Pt(II) adducts can be formed similarly. The bottom method is precedence for the formation of the squares by a similar route.
Figure ESI-4. Typical electrospray ionization mass spectra, in this case of the Pt-3B in positive-ion mode. 2729 (Pt-3B – Cl). NiPz 1B = 1249; 1B-PtCl+ = 1479; 3B-PtCl2 = 2764.

Figure ESI-5. Typical investigation of the self assembly processes. Formation of the dimer Pd-4A investigated by titration experiments, wherein aliquots of a Pd(OAc)2 solution were added to the porphyrizine solution (50µM in toluene), the mixture was stirred at room temperature for ~10 min, and spectra were recorded at ~20 °C. The isosbestic points are an indication of the formation of one product. Only with a >4-fold excess of Pd(OAc)2 does the dimer disassemble and the 1:1 adduct form.

Figure ESI-6. Comparison of the UV-visible spectra in toluene (20µM) of the Pd adducts of the Pz monomers with geminal dimethylamino and geminal amino ligands (left), and the Pz dimers (right). Colors of the structures correspond to the lines in the spectra.
The 1H NMR of the dimers show two resonances for the methyl groups due to a twisting about the metal, thus with the squares one expects the inner and outer methyl groups to be distinguishable and which would result in four peaks. With an asymmetric supramolecular conformation, eight peaks are expected – one for each methyl about the metal ion linker – which is observed (Figure ESI-7).

Figures ESI-7. 1H-NMR of tetrameric square 6A in the N-methyl group region indicates a substantial asymmetric twisting in the supramolecular square and that the inner methyl groups are differentiated from the outer methyl groups.

The UV-visible spectra of the monomers and adducts are qualitatively explained by the Gouterman 4-orbital model, and the observed changes upon formation of the dimers and square arrays are explained in terms of Kasha’s rules for transition dipoles as applied to porphyrins. This latter model predicts splitting of the Soret band and to a lesser extent the Q bands because of the coupling of the two orthogonal exitons of each chromophore. Edge-to-edge coupling should be manifested as a red shift in the electronic spectra compared to the monomers, the corresponding adducts, and the dimers, as is observed. Since the square arrangement means that each Pz is electronically coupled to two other Pz at right angles, Kasha’s model predicts that the absorptions band should broaden or split, which is also observed. Note that the Pt(II) and Pd(II) adducts are blue shifted relative to the free Pz because of the changes in the changes in the electron coupling of the nitrogen lone pairs to the π system, thus comparison of the adducts to the squares and dimers is appropriate.

UV-Vis peak maxima 20 µM in toluene nm (rel. abs): 5A: 356 (1.503), 450 (0.477), 486 (0.530), 606 (0.581), 672 (0.538), 721 (0.433); 5A-Pt(II): 343 (0.869), 480 (0.456), 532 (0.487), 583 (0.662), 664 (0.431), 736 (0.249); Square 6A: 340 (1.503), 528 (0.647), 586 (0.789), 662 (0.522), 695 (0.452), 5B: 344 (1.57), 436 (1.03), 462 (1.14), 588 (1.22), 635 (1.11), 718 (0.84); 5B–Pt(II): 346 (1.60), 425 (0.90), 458 (1.00), 597 (1.07), 630 (1.13), 685 (0.97); 6B: 345 (1.49), 459 (0.84), 492 (0.86), 622 (1.13), 690 (0.76), 738 (0.59). (Figure ESI-11)

Figure ESI-8. MALDI-MS of tetrameric square 6A from a chloroform solution is consistent with the structure. The water may be indicative of adducts or of oxidative reactions during the mass spectrometric analysis, and the reduction of the Pt(II) during MALDI analysis was also observed occasionally with the dimers. The Cl likely comes from traces of HCl in the CHCl₃. Inset: the low resolution calculated spectrum is for 6A with four ClO₄ counter ions.

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The compound may disassemble over time as this sample was about 6 months old when the MS was taken.

Figure ESI-9. MALDI-MS of tetrameric square 6B from a chloroform solution is consistent with the structure. The water may be indicative of adducts or of oxidative reactions during the mass spectrometric analysis. The [(NiPz)3Pt2]4+(ClO4)2 may be from decomposition in the MS or this compound may disassemble over time as this sample was about 6 months old when the MS was taken.

The preliminary AFM studies show that drop casting 6A onto mica results in a monolayer film that corresponds to the supramolecular Pz array laying flat on the surface. (See the line trace from the nanoshaving experiment SI-10.) Control experiments using only Pz 5A or 5A-PtCl2 result in amorphous films of varied thicknesses. UV-Visible spectra of 6A on mica are fundamentally similar to the solution phase spectra but with well understood and documented red shifts due to surface-molecule interactions and the “orientation” of the supermolecules. UV-Visible spectra of square 6A on mica is essentially simmilar to that in solution but with modest red-shifts arising from surface deposition – a well documented effect. This indicates the arrays are in tact on this surface.

Notes and references


