Supramolecular squares of porphyrazines†

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The design, self-assembly, and characterization of discrete arrays of porphyrazine (Pz) squares are presented to illustrate the supramolecular chemistry of these macrocycles, and to highlight that these arrays have physical chemical properties that are different from similar arrays of porphyrinic systems.

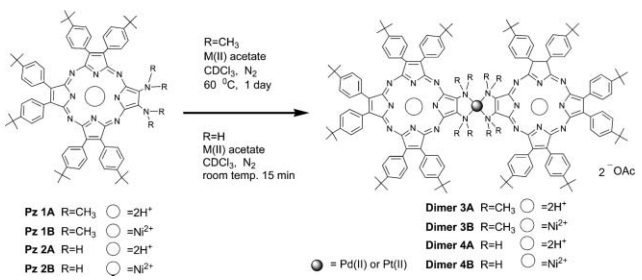
Porphyrins are widely studied because of their relevance to photosynthesis and numerous other biological systems that harvest light, transfer energy or electrons, or serve as redox catalysts.[1] Nature exploits only a small fraction of the rich electrochemical and photochemical properties of porphyrins and metalloporphyrins. Even after more than a century of research, the number of state-of-the-art publications on these macrocycles is astounding, which attests to many applications and potential applications—from redox catalysts to therapeutics.[2] Initially inspired by the photosynthetic systems, there has been a growing number of publications on the design, synthesis, and characterization of supramolecular porphyrin arrays in the last decade.[3,4] Early supramolecular systems using electrostatics,[5] hydrogen bonding,[6,7] and coordination chemistry[8,9] demonstrated the fundamental design principles, and later generations of these arrays have found applications as sensors, catalysts, and other photonic materials.[3,4,10]

In contrast, there is paucity of published work on the design and self-assembly of discrete supramolecular arrays of the other porphyrinoid dyes or pigments: corroles, phthalocyanines (Pc), and porphyrazines (Pz). There are examples of aggregates of Pz and Pc formed by electrostatic interactions,[11] and these systems are of interest because their rich photonic and structural properties are significantly different to those of the porphyrins.[2] Notably, high spin metals in the Pz macrocycle can be strongly coupled to auxiliary high spin metals complexed by exocyclic geminal ligands on the pyrrole moieties.[12] These photonic and magnetic properties, in turn, can impart new functionalities to supramolecular systems of Pz that are unobtainable with similar arrays of porphyrins. Herein we present an initial foray into the supramolecular chemistry of Pz. Though simple metal-linked Pz dimers, using exocyclic geminal ligands such as thiols are known,[13] the strength of this assembly motif likely precludes it from being used to form discrete higher ordered arrays *via* self-assembly. The design, self-assembly, and characterization of a series of supramolecular squares of porphyrazines illustrates that these macrocycles are also versatile molecular tectons for the creation of a variety of nanoarchitectures.

The modified Cook and Linstead[14] magnesium alkoxide templated macrocyclization reaction developed by Barrett, Hoffman *et al.*[13,15–19] uses bis substituted maleonitriles, is quite versatile, and is the basis for the synthesis of the Pz building blocks herein. All Pz macrocycles and their Ni(II) complexes (**1A**, **1B**, **2A**, **2B**, **5A** and **5B**) have ^{1}H NMR, UV-visible, and mass spectra† consistent with the expected structure and with previous reports.[13,15] These compounds are somewhat labile towards dioxygen[16,17] so inert atmospheres are used at all times.

In order to systematically develop the supramolecular chemistry and to understand the physical chemical properties of the assemblies, we initially characterize simple dimers (Scheme 1) as a basis for the formation and characterization of the square tetramer arrays of Pz (Scheme 2). The unambiguous spectroscopic signatures of the dimers serve as guideposts for the characterization of higher order arrays.[8,9,19]

The geminal dimethylamino groups on the pyrroles coordinate to Pt(II) and Pd(II), resulting in Pt(II) complexes that are generally more stable than the Pd(II) complexes.[19,20] In terms of supramolecular chemistry, this generally indicates that the Pt(II) complexes are harder to form in high yields but may be sufficiently robust for mass spectrometry analysis and for incorporation into materials, while the Pd(II) complexes are suitable for examining the self-assembly processes in solution *via* titration experiments.[8,9] However, the steric crowding of the methyl groups upon Pt(II) or Pd(II) coordination induces a twist in the coordination geometry of these otherwise square planar metals.[18] These trends are observed for both the Pz dimers and squares. Though the dimethylamino Pz derivatives are more chemically stable, the free primary amine analogues afford advantages such as lower barriers to metal ion binding, faster complex formation, and reduced steric interactions upon assembly. The latter reduces distortions in the square arrays.



Scheme 1 Pz dimers

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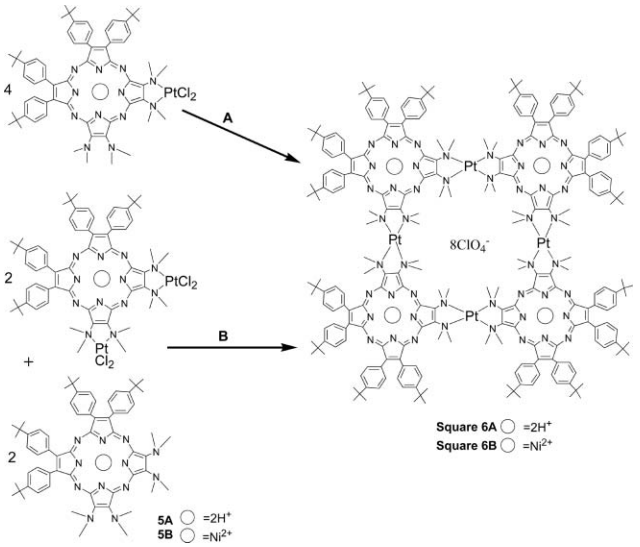

Scheme 2 Formation of squares **6A** and **6B** can be accomplished in two ways under an inert atmosphere. (A) The mono $PtCl_2$ adduct of **5A** or **5B** is formed using one equivalent of $PtCl_2$(benzonitrile)$_2$, followed by purification by chromatography. The square forms upon removal of the chlorides with four equivalents of $AgClO_4$ and heating at 60 °C for 8 h (~30% yield). (B) After the formation and purification of the bis $PtCl_2$ adduct, four equivalents of $AgClO_4$ are added to remove the chlorides, followed by addition of an equivalent of **5A** or **5B**, and heating at 40–50 °C for 3 h. The advantage of the latter strategy is that two different metallo-Pzs can be used to yield a predictable checkerboard-type tetramer, but the isolated yields are only ~15%.

The formation of Pz dimers **3A**, **3B**, **4A** and **4B** *via* reversible metal ion coordination chemistry is straightforward, as is the characterization.† As expected, the Pd(II) linked arrays form in greater yields (Table 1), which facilitates ^{1}H NMR and UV-visible titration studies, but are more labile, which makes mass spectral analysis and isolation more difficult. Conversely, the Pt(II) linked arrays are more robust, so can be isolated by chromatography, albeit in lower yields, and ^{1}H NMR and mass spectral analysis confirm the structures. The chemical shift changes observed for the methyl groups on the amines are diagnostic of the coordination, and the two observed resonances indicate that one points towards the metal ion center and one towards the macrocycle; computational studies confirm this interpretation. The electrospray ionization mass spectra (ESI-MS) of the Pt(II) dimers also confirm the structures. The primary, geminal diamino Pzs, **2A** and **2B**, are prepared just prior to use[20] and kept under an inert atmosphere under low light conditions. After the exocyclic ligands are complexed to Pt(II) or Pd(II), they are significantly more stable. Thus UV-visible titrations indicate the clean formation of the Pd(II) and Pt(II) linked dimers, **4A** and **4B**, using the primary amines. Only small shifts are observed for the orthogonal *tert*-butylphenyl groups in the ^{1}H NMR spectra, and the amine NH resonances are shifted and broadened. MALDI-MS are consistent with the structures indicated, but show some degradation. The Ni(II)Pz complex and the supramolecular arrays using Ni(II)Pz are more robust.

Table 1 Yields of dimers and squares (% ± 5)

Array	Yield Pd(II)[a]	Yield Pt(II)[b]
Dimer **3A**	60	55
Dimer **3B**	65	60
Dimer **4A**	80	65
Dimer **4B**	85	65
Square **6A**	35	30
Square **6B**	40	35

[a] Spectroscopic and [b] isolated yields.

The formation of the exocyclic Pd(II) or Pt(II) adducts of all Pz macrocycles significantly alters the electronic spectra for two general reasons: (1) since the exocyclic ligands are conjugated to the macrocycle metal binding diminishes n–π* transitions and (2) the metal ion orbitals are electronically coupled to the macrocycle *via* the ligand.[12–20] The electronic spectra of the dimers are also significantly different to both of the Pz monomers and their adducts because the two macrocycles are electronically coupled *via* the conjugated ligands bridged by the metal ion.

The formation of the tetrameric square arrays *via* simply adding four equivalents of Pt(II) to Pz **5A** or **5B** results in disappointing, ~5%, isolated yields, but isolated yields improve to >30% using the two-step strategy outlined in Scheme 1. UV-visible titrations indicate squares from the free geminal amine compounds are formed in ~80% yields but a significant fraction of these decomposed during purification and their lability hampers MS analysis. These results are consistent with the above data for the dimers.† The ^{1}H NMR spectra for squares Pt–**6A** and Pt–**6B** exhibit multiple resonances for the methylamino groups with shifts consistent with those of the dimers, and indicate that the twisting about the linking metal ions results in non-planar supramolecular squares. Similar to the dimers, only small changes in the *tert*-butyl group chemical shifts are observed upon formation of the squares, but these resonances are ~50% broader due to the ~4.5 fold increase in mass and supramolecular conformational dynamics. MALDI-MS also demonstrates the formation of squares Pt–**6A** and Pt–**6B**.†

The UV-visible spectra of square arrays Pt–**6A** and Pt–**6B** are also consistent with those of the dimers in that there is a broadening and red shift of both the Pz Soret bands and the Q bands compared to the exocyclically ligated Pd(II) and Pt(II) adducts, and the dimers (*e.g.* Fig. 1).† The UV-visible spectra of the monomers and adducts are qualitatively explained by the Gouterman 4-orbital model.[21] The observed changes upon

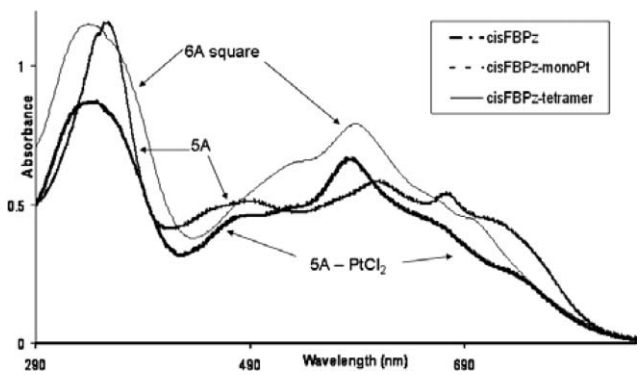

Fig. 1 UV-visible spectra in toluene at 20 μM of **6A** and the precursors show the substantial changes in the electronic spectra upon coordination by an exocyclic metal ion and by formation of the tetrameric square. Spectra are of similar concentrations in terms of total Pz content.

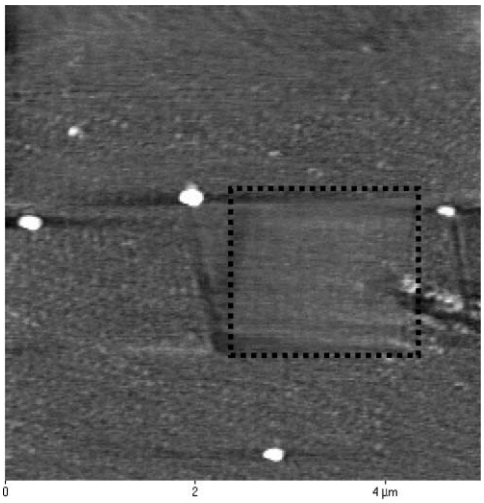

Fig. 2 5 µm × 5 µm tapping-mode AFM image of porphyrazine squares **6A** deposited on a mica surface from a ~100 µM toluene solution. A uniform film is observed with few discernable features. The outlined region shows part of a 2 µm × 2 µm area previously scanned by AFM. Partial removal of molecular species in this region shows that the film layer is somewhat mobile on the surface and can be easily modified with the AFM tip. The film thickness is ~0.5 nm as determined by nanoshaving in contact mode.†

formation of the dimers and square arrays are qualitatively explained in terms of Kasha's rules for transition dipoles,[22] which predict that the absorption bands should broaden or split, and red-shift compared to the monomers, both of which are observed.

With the exception of homogeneous catalysis, most applications of supramolecular materials will require that they be deposited on surfaces as either thin films or crystals. However, the deposition process and/or the interactions between the supermolecule and the substrate oftentimes significantly alter the supramolecular structure.[3,4] Therefore, drop cast films of arrays **6A** and **6B** on mica were examined by AFM. These cationic arrays were expected to interact well with the anionic surface of mica, and we found that they do indeed form uniform monolayer films (~0.6 nm in thickness) on mica (Fig. 2) that are weakly bound to the substrate. The height indicates the supramolecular array is parallel to the surface. UV-visible spectra indicate the array is intact. Control experiments with **5A** and **5A**–$PtCl_2$ result in amorphous films of varied heights. The mobility likely arises from several factors which weaken the surface–macrocycle interaction: (1) the methylamino and *tert*-butylphenyl groups are orthogonal to the supramolecular macrocycle pointing toward the mica surface, (2) the twist about the four Pt(II) ions results in a non-planar supramolecular square, and (3) the square tetramers are conformationally dynamic.

In conclusion, the dimethylamino groups impart stability to the Pz arrays, aid in ^{1}H NMR characterization, but inhibit chelating metal ions and distort the arrays. The geminal diamino groups make better ligands and thus facilitate self-assembly and characterization of the arrays *via* UV-visible titrations, but render the Pz and the arrays more labile. Also, Pt(II) imparts stability but at a cost in yield, and with Pd(II) yields are greater but with a cost in stability. The design and supramolecular synthesis of Pz arrays can use many of the architectural strategies widely employed in the construction of, for example, porphyrin (Por) squares. The photo physical properties of the arrays discussed herein are substantially different to the monomers and are complementary to similar Por arrays in terms of the absorption and luminescence. Similarly to the supramolecular chemistry of porphyrins, versatility in the design described herein can lead to a plethora of nanoarchitectures of Pz. By analogy to Por arrays, the properties of supramolecular arrays of Pz can also afford systems in which the rich physical chemical and coordinative properties depend on the specific nanoarchitecture.[23,24]

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