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Tessellation of Porphyrazines with Porphyrins by Design

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The efficient self-assembly and functional characterization of arrays containing multiple types of chromophores will provide a basis for the design and applications of functional photonic materials that are unobtainable using only one type of molecule. The design, synthesis, and characterization of supramolecular systems bearing two different types of porphyrinic chromophores, porphyrins and porphyrazines, are reported. Because the porphyrins and porphyrazines bear different exocyclic ligands for self-assembly by metal ion coordination, these systems require new supramolecular synthetic strategies wherein reactants are added in a specific order. These arrays display unique photophysical properties derived from the component chromophores, the metal geometry, and the supramolecular nanoarchitecture.

Introduction

A variety of applications of chromophoric materials, such as solar energy harvesting, energy transfer, and photonics, require more than one type of functional molecule to cover a wider range of the solar spectra, ensure excited-state energy flow is vectoral, and provide diverse ground-state and excited-state redox properties. For most of the aforementioned applications, the supramolecular nanoarchitecture of the chromophores is as important as the photophysical properties of the molecular components.

Though first synthesized more than 50 years ago,[1] porphyrazines (Pz) are considerably less studied than other porphyrinoids; however, new synthetic strategies have paved the way for further exploration of their physical properties and potential applications.[2−6] The nitrogens in the meso positions of these tetraazaporphyrins modulate the properties such that the electron-rich Pz macrocycle has substantially different photophysical and chemical properties than porphyrins (Por), yet still bind most metals.[6−8] A variety of Pz derivatives functionalized at both β positions of one to four of the pyrroles have been made,[2−9] including derivatives that have geminal Lewis bases, such as dimethylamino and thiol groups. Because these exocyclic ligands are conjugated to the macrocycle, metal ion binding can significantly alter the electronic and therefore physical properties of the Pz.[3,4,6,7,9−13] The meso nitrogen can also participate in exocyclic metal binding. An example of the properties arising from a

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bimetallic Pz system is the elegant report on the magnetic coupling of high-spin metalloporphyrazines to high-spin metals coordinated at exocyclic positions.[7,14] Architecturally, Pz can be monotopic, "L"-shaped 90° ditopic, "I"-shaped 180° ditopic, or have "T"- or "X"-shaped topologies[15] which makes them suitable for a diverse array of supramolecular materials self-assembled by coordination chemistry.[16] As such, Pz can be topologically complementary to Por bearing meso ligands such as pyridyl moieties.

Because their chemical, photophysical, and architectural properties are complementary to porphyrins, Pz are logical building blocks for the construction of supramolecular arrays containing *both* chromophores. Since the first publication of discrete porphyrin arrays assembled by coordination chemistry,[17] the supramolecular chemistry of Pors[18−20] remains a rapidly growing field. Conversely, the supramolecular chemistry of Pz remains virtually unexplored beyond self-assembled squares.[16] We present herein the design, synthesis, and characterization of a series of robust, discrete Por−Pz tetramers self-assembled via coordination chemistry. While aggregates containing mixtures of two oppositely charged porphyrinoids (phthalocyanines, Por, and Pz) have been reported,[21−23] as have Pz dimers irreversibly assembled via geminal thiol coordination to metal ions such as Ni(II),[2,6] the systems presented here constitute premier investigations into the formation of discrete supramolecular arrays containing both chromophores. Unique functionality arises from significant electronic coupling of the macrocycles mediated by the metal ion linker.

Experimental Section

Reagents and Physical Measurements. All solvents were HPLC grade from Fisher Scientific. Silica gel (Selecto Scientific, 32−63 μm average particle size) was used for flash column chromatography (FCC). MALDI-MS were done as a service by the facility at the University of Illinois at Urbana−Champaign. ^{1}H 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. A Spex tau-3 fluorometer was used in right-angle mode on samples degassed with N_2.

Typical Electrospray Ionization Mass Spectroscopy (ESI-MS) Method. Solutions (∼0.05 mM) 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. The supramolecular arrays were deposited on the freshly cleaved mica surface via the drop-dry method, subsequently rinsed with toluene, and dried under a stream of N_2. Even in tapping mode, sufficient shear of the molecules at the surface occurs for displacement to be observed.

Results and Discussion

Arrays Synthesis. The coordination chemistry of exocyclic pyridyl Por,[15,17,24−26] and geminal dimethylamino Pz[4,5,11] to Pt(II) and Pd(II) is already established, and the coordination chemistry of the assemblies described herein is consistent with these motifs. Specifically, the solution-phase yields are greater and there are lower barriers to complex formation with Pd(II) linkers, thus allowing various titration experiments that yield information on the stoichiometry and the self-assembly process. Conversely, Pt(II) arrays are less labile, affording greater isolated yields. The presence of the two methyl groups on the exocyclic nitrogens of the Pz increases the kinetic barrier to metal binding and induces deformations in the otherwise planar geometries of these metals due to steric interactions but impart oxidative stability to the Pz macrocycles.

Several supramolecular architectures of "2 + 2" Por−Pz arrays can be envisioned such as in Scheme 1, and several synthetic strategies can be employed for their fabrication. Merely mixing the appropriate stoichiometries of the Por, Pz, and M(II) (2:2:2) does not produce significant quantities of the desired array since the binding geometries of the building blocks are not predisposed to form discrete, closed, supramolecular systems[18,19,25] such as squares[17] or grids,[15] and there are significant differences in the binding constants for the geminal diamino chelates versus the pyridines to the square planar metals. The arrays can, however, be synthesized in two steps in ∼75% spectroscopic yields for the Pd(II)-linked systems and ∼60% yields when Pt(II) is the linker (Scheme 1). In addition to the free base components, the Ni(II)Pz and Zn(II)Por derivatives can also be successfully used. An alternative route that first makes the Pt(II) adducts of **Pz 1** or **Pz 2** and then adds **Por 3** or **Por 4** yields the same arrays, albeit at ∼30% yields, which further supports the proposed nanoarchitecture of the tessellated arrays. Because of the aforementioned robustness, the Pt(II) arrays are described in detail herein.

We previously reported the formation of Pt(II)-linked Por dimers and squares,[17] as well as the 3 × 3 tessellation of nine porphyrins and longer tapes using the same strategies

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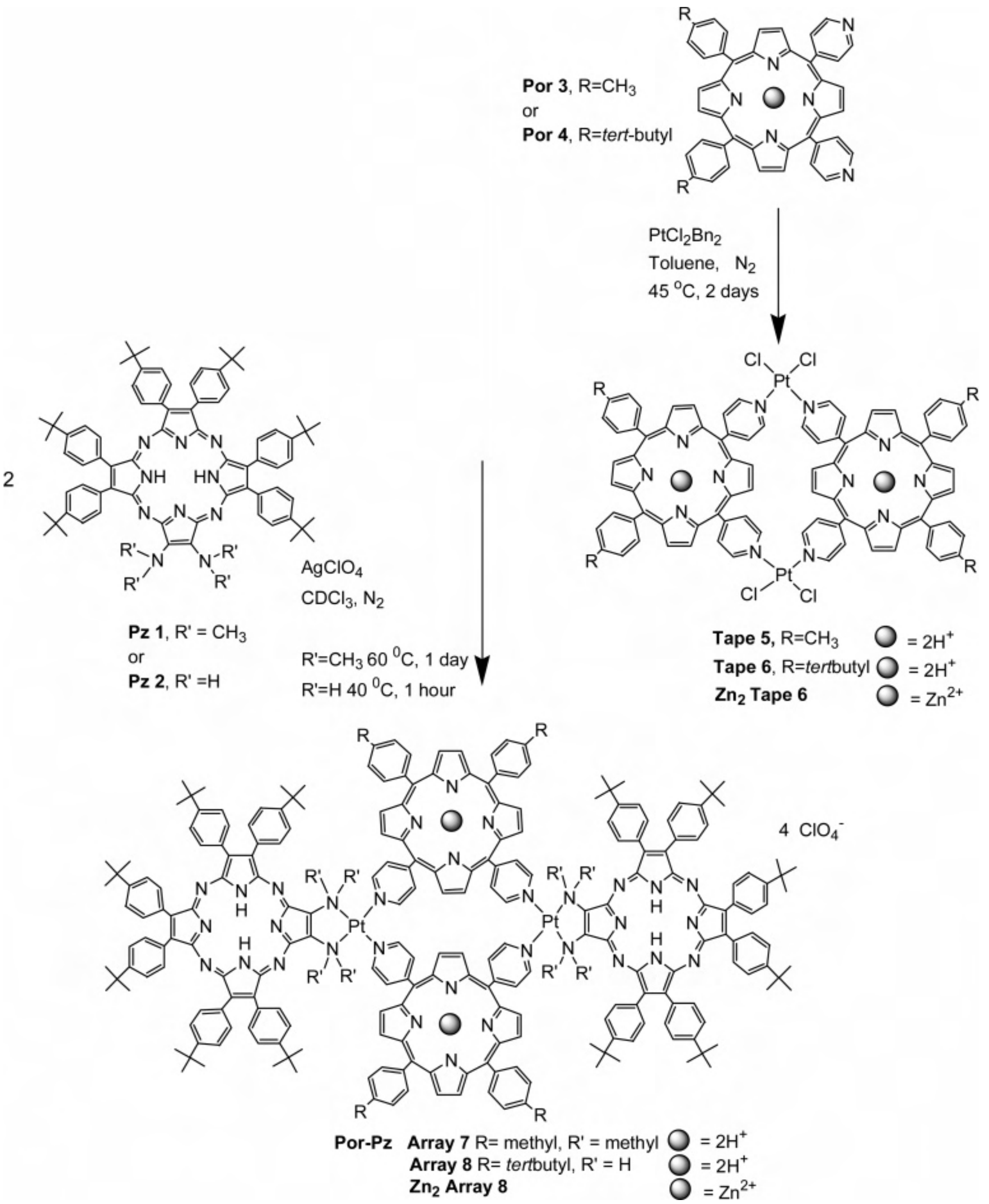
Scheme 1



in the context of higher-order arrays.[15] Both of these reports have served as the conceptual bases for a large number of 1- and 2-dimensional porphyrinic constructs.[18−20] The formation of the dimer moieties **5** and **6** proceeds in high yields because the binding topology of the monomers favors formation of the closed supramolecular system. The removal of the chloride counterions on the tapes with Ag(ClO$_4$) facilitates the coordination of the remaining two sites by the exocyclic geminal amino groups on the Pz to yield the tetrameric arrays **7** and **8**. MALDI-MS of the reaction mixture resulting from the stoichiometric addition of Ag(ClO$_4$), Pd(ClO$_4$)$_2$, or Pt(ClO$_4$)$_2$ to the 1:1 mixture of Pz and Por indicates that the yield of the Pz$_2$−Por$_2$ array is only ca. 5% and there is a plethora of uncharacterized oligomeric materials.

The characterization of these arrays is straightforward (Supporting Information). MALDI mass spectra indicate the formation of arrays **7** and **8**. The ^{1}H NMR of arrays bearing the dimethylamino groups, e.g. **7**, indicate formation of the tetrameric array since the chemical shift changes observed for the methyl groups are diagnostic of coordination to the square planar metal (3.7 to 3.9 and 3.3 ppm). Computational studies suggest that the two observed resonances result from one methyl tilting toward the porphyrin and one toward the porphyrazine; similar to the twisting about the metal center observed for Pt(II)-linked Pz dimers.[4,16] There is an ∼50% broadening of both the *N*-methyl and the *tert*-butyl resonances; indicating a higher-molecular-weight species. The ^{1}H NMR of array **8** exhibits a broad peak for the NH and a similar broadening of the *tert*-butyl group resonances as observed for array **7**.

Optical Properties. The observed complex photophysical properties of the arrays arise from both the chromophores and the nanoarchitecture. The electronic absorption spectra of Por and Pz depend on the substitution pattern and nature of the peripheral groups and are generally described by the Gouterman four-orbital model.[27] Since the pyridyl groups on **Por 3** and **4** are nominally orthogonal to the macrocycle,

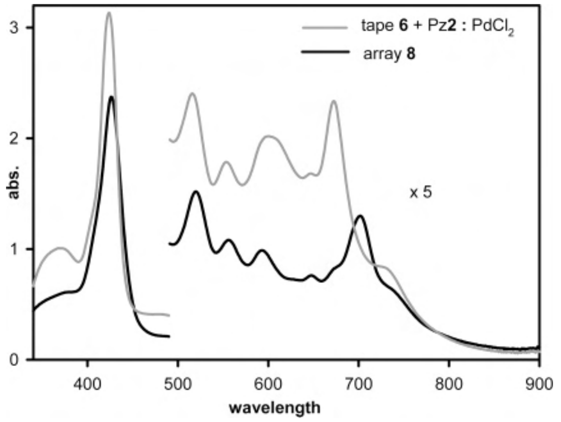


Figure 1. UV−visible spectra of a 5 μM solution of array **8** in toluene (black), compared to the added spectra of 5 μM tape **5** and 5 μM of the PdCl$_2$ adduct of Pz **2** in the same solvent (gray).

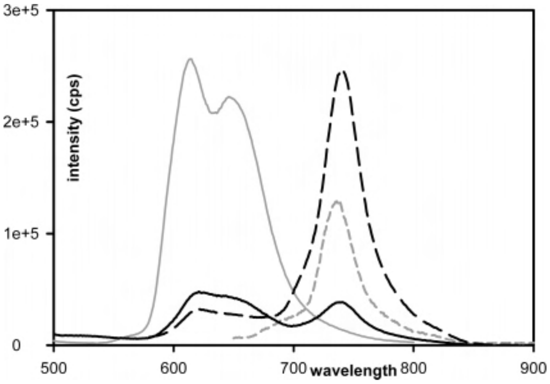


Figure 2. Fluorescence emission spectra of array Zn$_2$**8**, wherein the porphyrins are both metalated with Zn(II), indicates significant energy transfer from the porphyrin tiles to the porphyrazine tiles. Excitation at 432 nm, black lines —, where the porphyrin optical density is ca. 11 times that of the Pz shows a substantial Pz emission and a quenched emission of the porphyrin tape. Excitation at 565 nm, black − − −, where the Pz absorbs ca. 2 times the Por, results in predominantly a Pz emission peak. The fluorescence spectra of the starting components are shown for comparison: the bis Zn(II) tape **6** (grey line, − excitation at 429 nm); and Pz **2** (gray line, − − − excitation at 623 nm).

only small changes in the UV−visible spectra are observed upon formation of the intermediate tapes, e.g., a red-shift and broadening of the Soret band. Compared to tetraarylporphyrins, Pz such as **1** and **2** have more intense *Q*-bands that are to the red, and a blue-shifted Soret band that is significantly diminished because the lone pairs of electrons on the exocyclic amino nitrogens are conjugated to the aromatic macrocycle and the n → p* transitions.[4,5] Thus metal ligation by the exocyclic nitrogens has a significant impact on the electronic spectra of Pz. For example, the significantly sharpened and blue-shifted Pz *Q*-bands are highly diagnostic for the chelation of Pt(II) by the geminal amino groups on **1** or **2**. The UV−visible spectra of arrays **7** and **8** (Figure 1) are diagnostic in terms of changes in both the Por and Pz spectral components. As with other coplanar Por arrays, the Soret bands of the Por in **7** and **8** further red-shift and broaden compared to the tapes. The complex changes in the Pz *Q*-bands are consistent with both chelation of the metal ion and with interactions with the porphyrin tiles; notably, the lowest energy *Q*-band red-shifts and gains intensity. The red-shifted absorption bands arise from the edge-to-edge electronic interactions between chromophores.[28,29] The electronic spectra are also affected by the electronic structure of the Pt(II) linkers, which are 'conjugated' to the Pz π system and the pyridyl moieties, providing effective mediation of electronic coupling between the chromophores.[30] Thus, the electronic spectra are indicative of substantial electronic communication between all four chromophores, and that they are in a nominally coplanar arrangement.

The red-shifted fluorescence emission spectra (Figure 2) are consistent with the optical spectra and reveal that there is substantial energy migration from the porphyrins to the porphyrazines. When a solution of array **Zn$_2$ 8** (with two Zn(II) Por) is excited at 432 nm in the porphyrin Soret band, where the Por absorption is ~11 times that of the Pz, the emission from the Por tiles is significantly diminished and the emission from the Pz tiles is enhanced. When the excitation light is centered at 565 nm where the Pz absorbs ~3 times the Por, the Pz emission at 740 nm dominates the spectrum. These observations are consistent with previous reports on electronic coupling mediated by Pt(II).[30]

Surface Deposition. A conundrum for supramolecualr chemistry—especially for discrete self-assembled arrays such as those discused herein—is that many applications of these materials require deposition onto surfaces, but the deposition process oftentimes signifigantly changes the supramolecular structure or results in disassembly.[19,24,26] Since the nanoarchitecture of photonic materials dictates the photophysical properties, it is essential to investigate the supramolecular structure of arrays such as **7** and **8** on surfaces relevent to the intended application. Initial studies of drop-cast films of arrays **7** and **8** on mica were examined by AFM. These cationic arrays were expected to interact well with the anionic surface of mica, and we find that they indeed form uniform ultrathin films (Figure 3). Both UV−visible and fluorescence studies indicate the array remains intact on mica. The diaphanous films can be manipulated by an AFM tip, and nanoshaving experiments reveal a thickness of ca. 2−3 nm. The mobility of the supramolecular systems on mica likely arises from several factors which weaken the surface−supermolecule interactions:[31] (1) the methylamino and *tert*-butylphenyl groups are orthogonal to the plane of the supramolecular tiles and present bulky, hydrophobic groups to the mica surface, (2) the deviations from the square planar geometry about the four Pt(II) results in a nonplanar supramolecular array (especially for array **7**), and (3) as with all self-assembled systems, supramolecular conformational dynamics diminish surface−supermolecule interactions.

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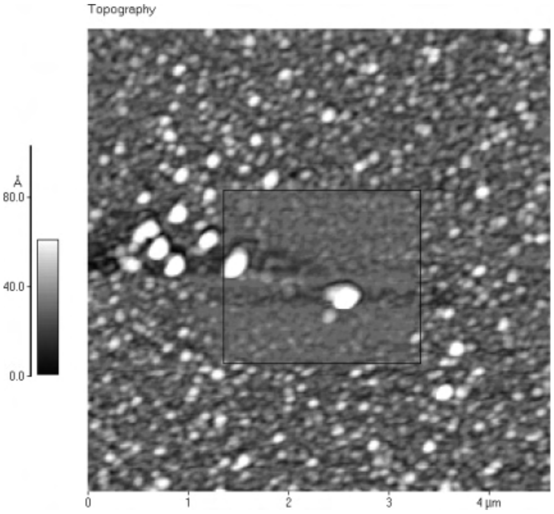

Figure 3. 5 μm × 5 μm tapping mode AFM image of tiled array **8** deposited on a mica surface. A uniform film of small molecular aggregates is observed. The outlined region shows a 2 μm × 2 μm area previously scanned by AFM. Removal of molecular aggregates in this region shows that the supramolecular layer is still somewhat mobile on the surface and is easily modified with the AFM tip even in tapping mode.

Conclusions

The topological design principles that have been used to make a myriad of porphyrinic arrays and materials can be similarly applied to the creation of discrete arrays composed of two different porphyrinoid chromophores, but the latter require new supramolecular synthetic strategies. The photophysical properties of arrays such as **7** and **8** are due to both the component porphyrins and porphyrazines and to the exact nanoarchitecture of the arrays. The supramolecular synthetic principles described herein, as well as the ability to fine-tune the physical properties of these arrays via metalation of one or both chromophores with virtually any transition metal(s), indicates a rich variety of supramolecular materials with predictable functionalities can be designed. For example, the properties of these materials can be exploited for sensors, catalysts, and solar energy harvesting.

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Supporting Information Available: Other supramolecular synthetic schemes, scheme of Pz topologies, selected UV−visible, mass-spectral, and fluorescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

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