

Supporting Information for:

Tessellation of Porphyrazines with Porphyrins by Design

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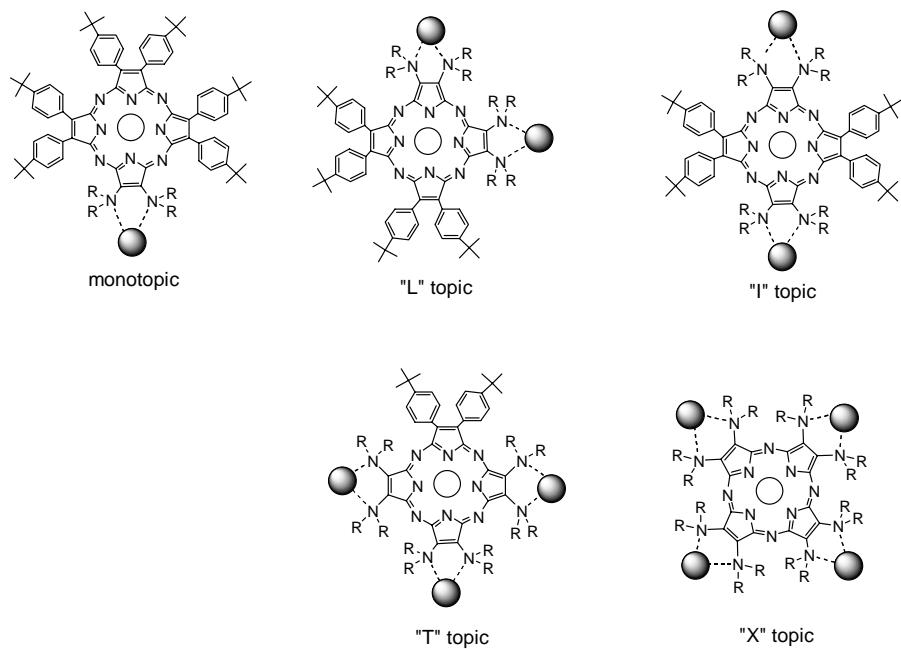
Porphyrin & Porphyrazine Synthesis:

The synthesis of the component Por and Pz, or similar compounds, were previously described and use a mixed aldehyde^[1] Adler^[2] synthesis and a mixed maleonitrile^[3-5] Linstead^[6] synthesis, respectively. These procedures are used because all of the products can be used as reference compounds and/or to make supramolecular constructs, and are amenable to scale-up.

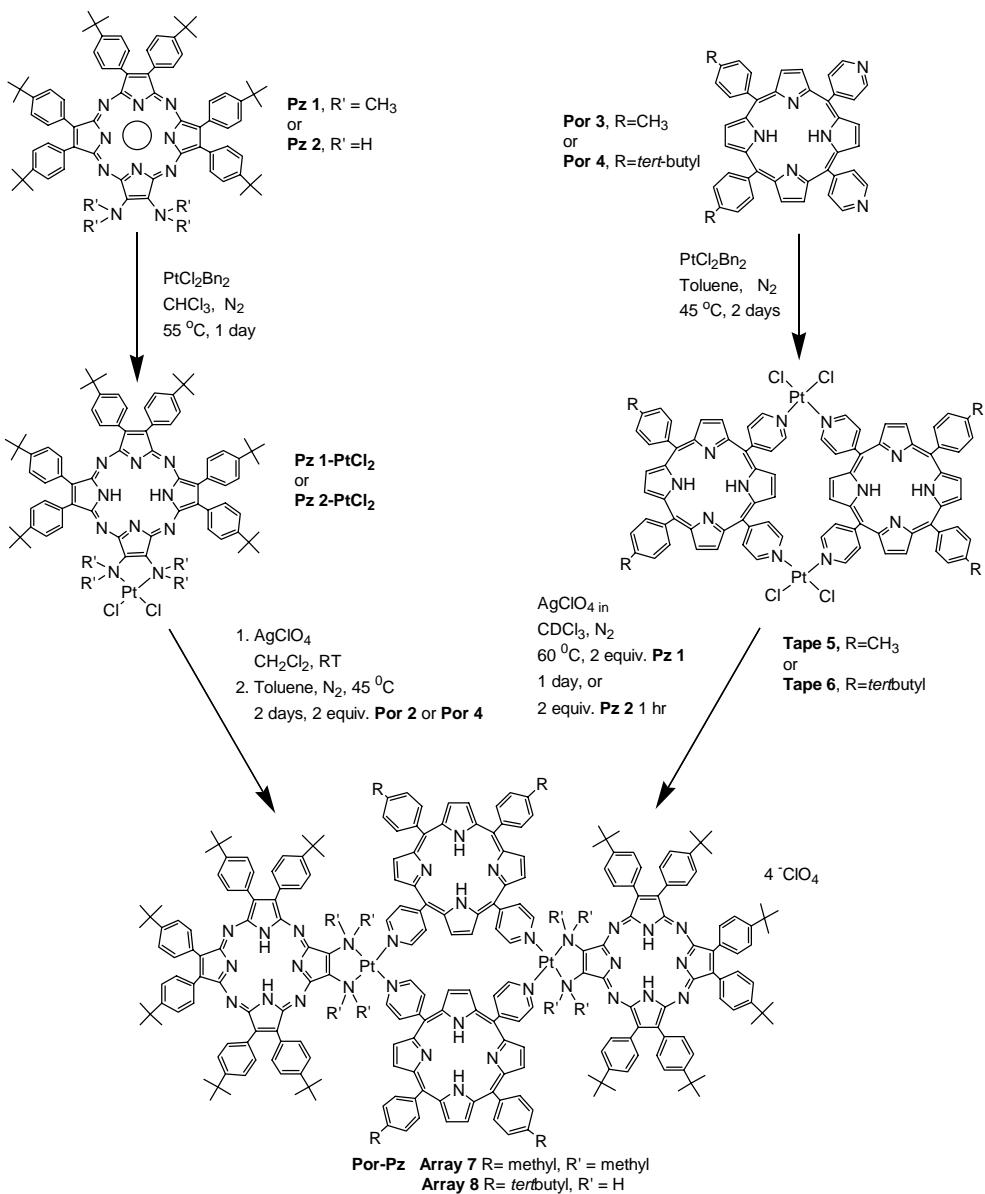
The use of stable di-substituted maleic dinitriles in Linstead magnesium alkoxide template macrocyclization reactions results in a variety of octa-substituted porphyrazines in good yield.^[3, 5, 7-10] Similar to a porphyrin synthesis with two aldehydes,^[1, 11, 12] the crossover macrocyclization of equimolar quantities of two different maleonitrile derivatives produce a mixture of six different Pz molecules which are easily purified by flash chromatography. The modifications of the Linstead magnesium alkoxide templated macrocyclization reaction developed by Barret and Hoffman^[13] 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 – in this case using 3,4-bis(4-*tert*-butylphenyl)pyrroline-2,5-diimine and bis(dimethylamino)maleonitrile^[7] – 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. All Pz, Por, Ni(II)Pz, Zn(II)Por and the supramolecular tapes have ¹H NMR, UV-visible, and mass spectra consistent with the given structures, and with previous reports.^[7, 13, 14] Typical spectra for the assemblies are presented below. The starting materials are all readily characterized by ESI-MS, but the assemblies are usually not observed by this method. In general for the MALDI, we find a variety of counter ions associated with the tetracationic arrays, but the spectra below are representative

of several repeated preparations and several different instrumental parameters. Pz are somewhat labile to dioxygen^[15] so are manipulated under an inert atmosphere and stored as solids in the dark. The NMR spectra indicate that the assemblies are distorted such that there are two resonances for the methyl groups – one pointing toward the porphyrin and one tilting toward the porphyrazine. Also, the porphyrazines are likely distorted as the phenyl resonances are more complex than expected for a completely planar system.

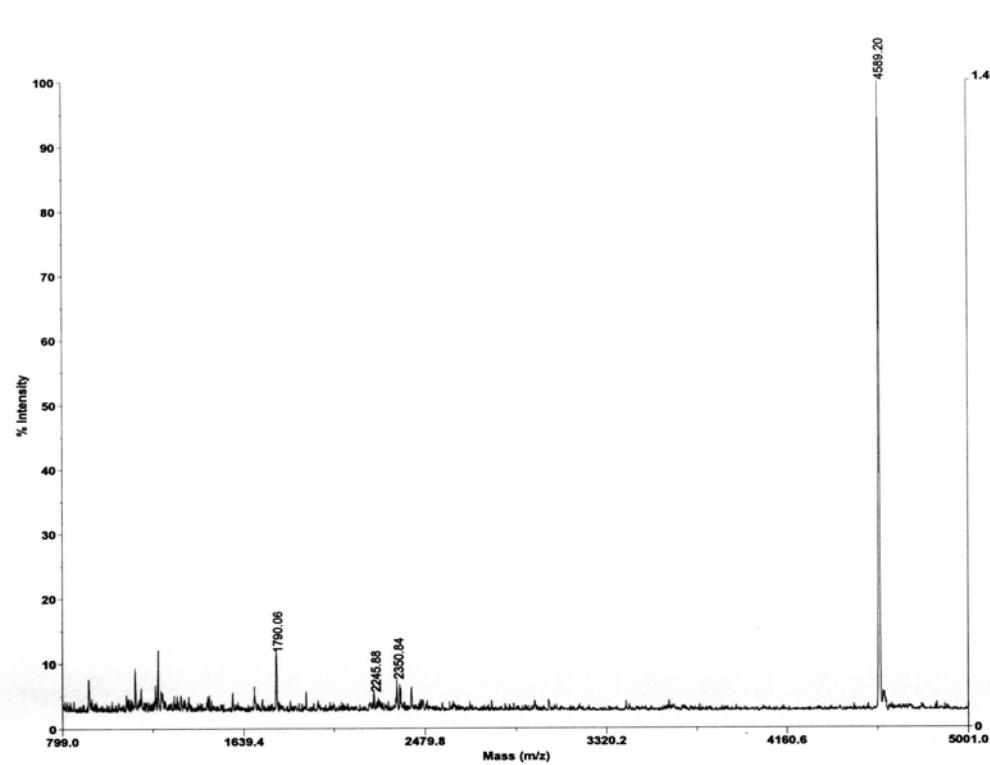
Dynamic light scattering (DLS) of the purified assemblies, Precision Detectors MiniDawn in batch mode, indicate only particles with a hydrodynamic diameter of ~5 nm, which corresponds well to the structures assigned to these assemblies. DLS of the reaction mixtures indicate that major side products are not large oligomers. This latter is consistent with thin-layer chromatography data monitoring the formation of the products



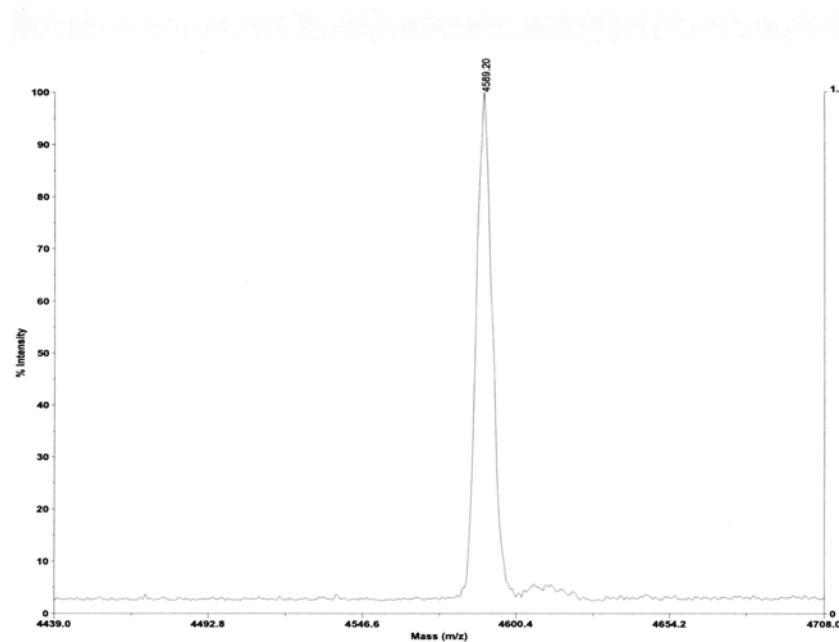
Scheme SI-1. Topologies of simple porphyrazines, R= methyl, or R=H,
●= metal ion auxiliary for self-assembly, ○ 2H⁺, or metal ion^{X⁺} (x-2)anion⁻



Scheme SI-2. At right, the porphyrazine-porphyrin tetramer was prepared by dechlorination of the Pt-planar tape (10 μ M in toluene), with silver perchlorate and then reacted with two equivalents the Pz in toluene at room temperature (\sim 23 °C) for 24 hrs in the dark under nitrogen. The Pt tape was formed through the coordination of two equivalents 5,10-bis(4-pyridyl)-15,20,-bis(4-*tert*-butylphenyl)porphyrin to two trans platinum dichloride in toluene with concentration of 10 μ M in boiling toluene for 24 hrs in the dark. Purification of the porphyrin dimer is accomplished on flash silica gel using a toluene-to-chloroform gradient. An alternative synthesis of arrays 7 and 8, shown on the left, results in ca. half the yield of the method illustrated on the right.

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**Figure SI 1.** MALDI MS of porphyrazine-porphyrin array $[8(\text{ClO}_4)_3\text{AgAc}]^+$.

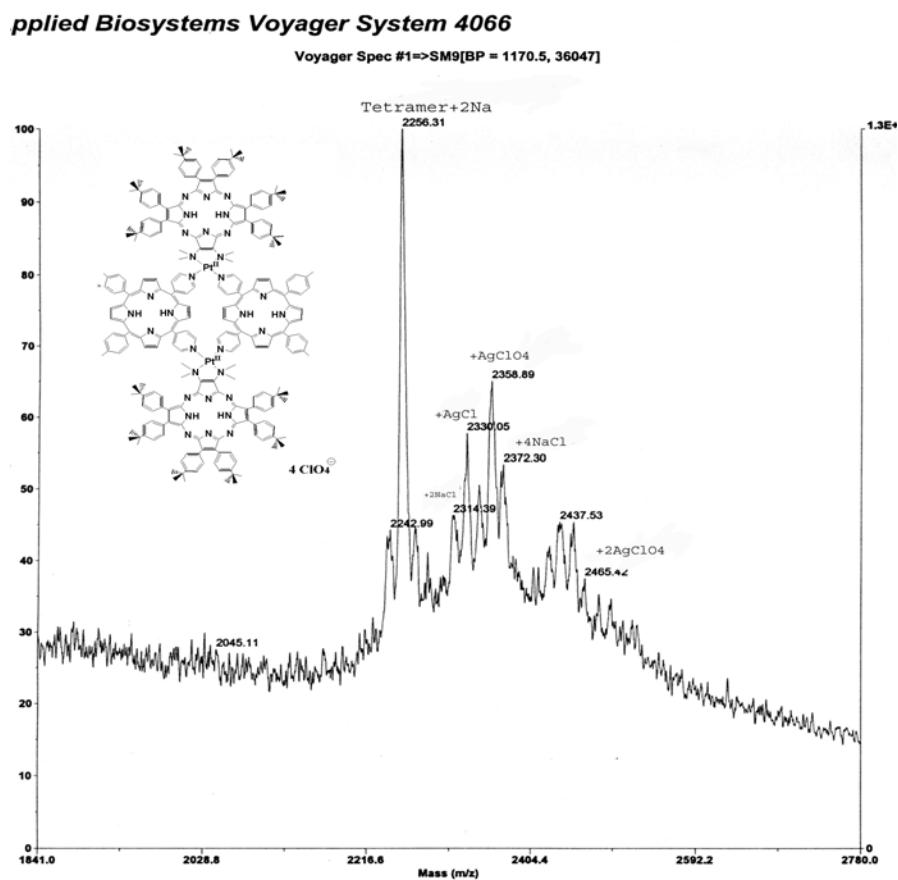


Figure SI-2. MALDI MS of array 7 shows a variety of counter ions. The peak at 2256 is assigned as $[7 (\text{ClO}_4^-)_4 (\text{Na}^+)_2]^{2+}$

UV-visible spectra of Array 8 & its components

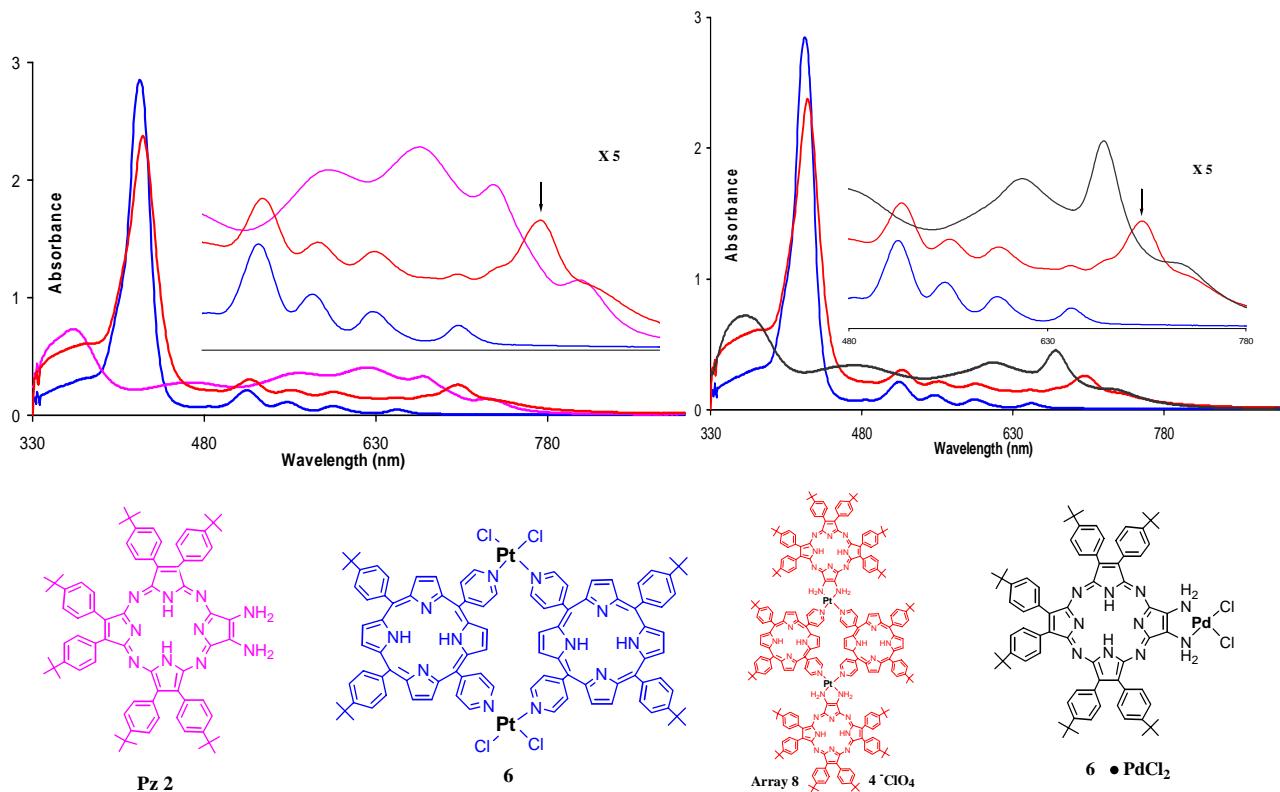
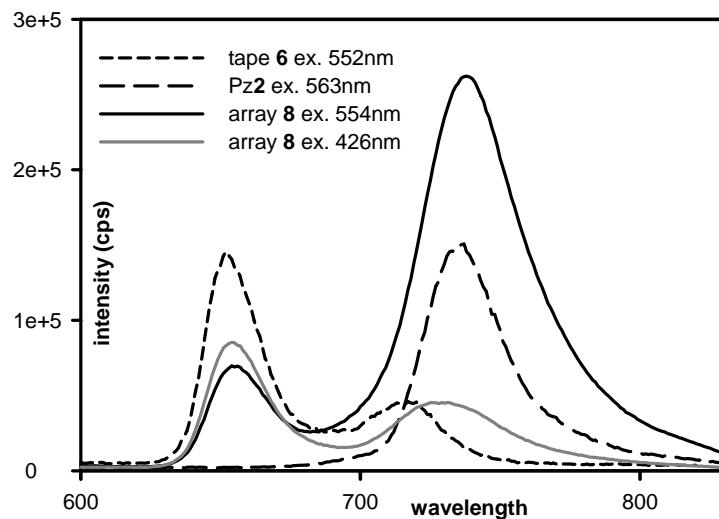
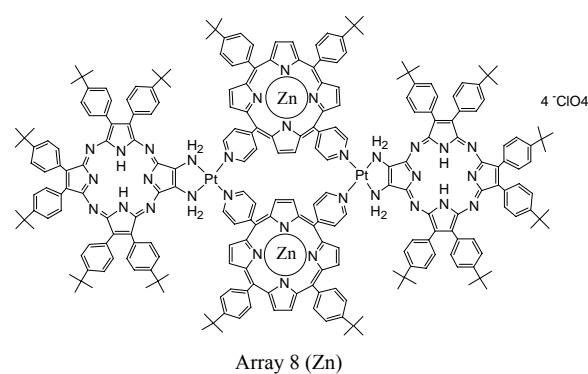
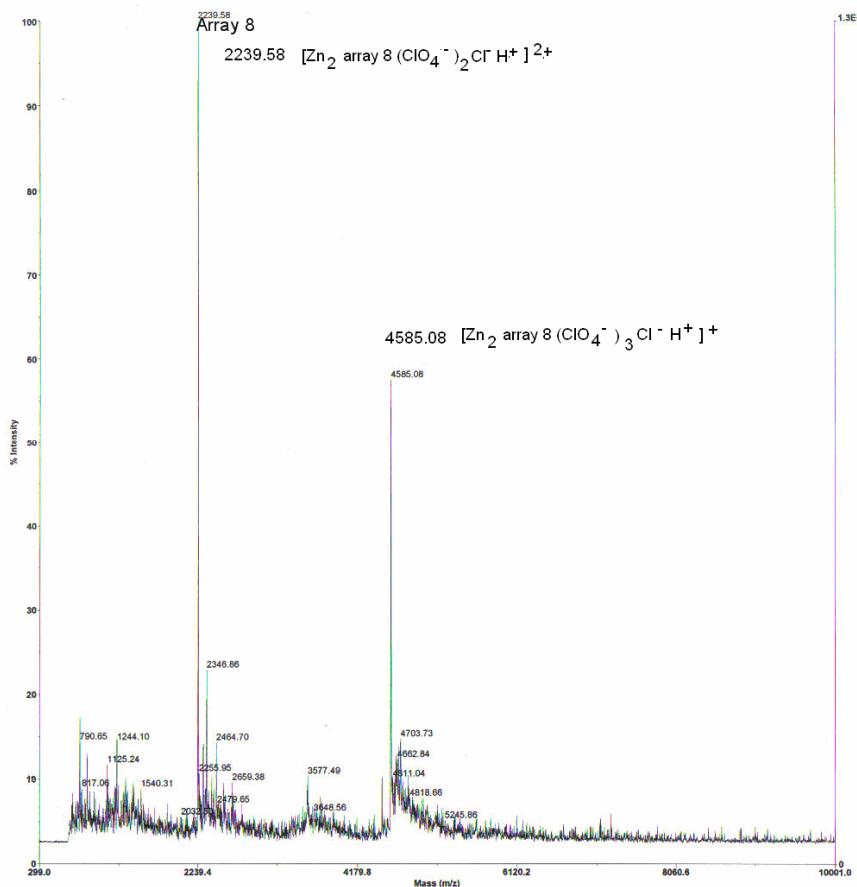


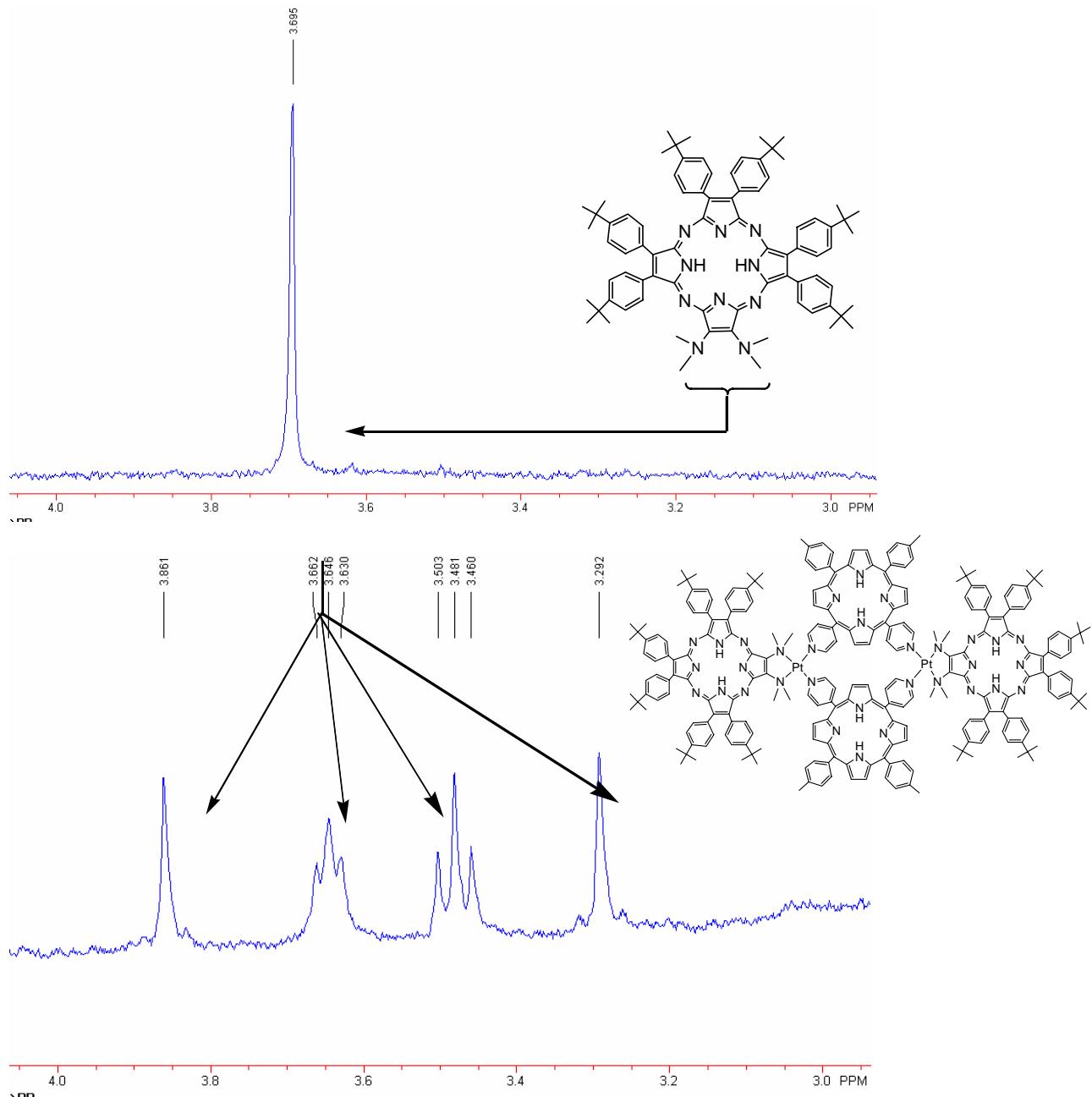
Figure SI-3. The UV-visible spectra of array **8** and its components are shown. The colors of the compounds in the scheme correspond to the colors in the spectra. Note the new band near 775 nm (arrow) that is unique to the array. All spectra are 5 μM in toluene with 1 cm cells at room temperature.



SI Figure 4. Comparison of the fluorescence spectra of array **8** with free base chromophores, $\sim 2 \mu\text{M}$ in degassed toluene, to Por tape **6** (---) and to Pz **2** (—) indicates electronic coupling of the chromophores. At 426 nm the optical cross section of the Por moieties of array **8** is ~ 11 times that of the Pz subunits, but the emission bands (—) from the Por are diminished and that of the Pz enhanced. At 554 nm the Pz absorbs 2-3 times that of the Por, and Pz emission dominates the spectrum (—). As expected from the lower energy band in the electronic spectra of the Pz, energy transfers from the Por tiles to the Pz tiles.



SI Figure 5. MALDI MS of array **8** wherein the two porphyrin moieties are metalated with Zn(II). $[(\text{ZnPor})_2 \mathbf{8} (\text{ClO}_4^-)_2 \text{Cl}^-, \text{H}^+]^{2+}$ at $m/z = 2239.58$ and $[\mathbf{8} (\text{ClO}_4^-)_3 \text{Cl}^-, \text{H}^+]^{+}$ $m/z = 4585.08$. The “HCl” likely comes from the CHCl₃ solvent.



Scheme SI 6. ^1H NMR (300 MHz in CDCl_3) of Pz 1 and Array 7 in the dimethylamino region.

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