Peripherally η^1-Platinated Organometallic Porphyrins as Building Blocks for Multiporphyrin Arrays

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The modification of peripherally metalated *meso*-η^1-platiniometalloporphyrins, such as *trans*-[PtBr(NiDAPP)(PPh_3)$_2$] (H_2DAPP = 5-phenyl-10,20-bis(3′,5′-di-*tert*-butylphenyl)porphyrin), leads to the analogous platinum(II) nitrato and triflato electrophiles in almost quantitative yields. Self-assembly reactions of these *meso*-platinioporphyrin tectons with pyridine, 4,4′-bipyridine, or various *meso*-4-pyridylporphyrins in chloroform generate new multicomponent organometallic porphyrin arrays containing up to five porphyrin units. These new types of supramolecular arrays are formed exclusively in high yields and are stable in solution or in the solid state for extended periods. They were characterized by multinuclear NMR and UV−visible spectroscopy as well as high-resolution electrospray ionization mass spectrometry.

Introduction

The rich photochemical and redox properties of porphyrins have made them attractive targets for incorporation into oligomeric and polymeric assemblies that may exhibit useful photonic or electronic properties. Thus, there has been much interest recently in the design, synthesis, and properties of discrete ordered arrays of porphyrins and metalloporphyrins, and the work has spanned many disciplines of science.[1−3] Generally, multiporphyrin arrays have been considered as biomimetic models of several natural systems or as materials for the transport of energy, electrons, and ions and as potential catalytic species. Thus, these arrays are useful whenever a specific arrangement of porphyrins and/or metalloporphyrins with low conformational freedom is desired for the most efficient operation. A large range of molecular entities has been synthesized and studied, and these have provided much valuable knowledge of how electron transfer is affected by factors such as the separation distance, mutual orientation, nature of the insulating spacer group, energy gap, solvent polarity, and nature of the participating donors/acceptors.[1−3] To increase control over solution and solid-state structural characteristics, most supramolecular multiporphyrin arrays take advantage of coordination or covalent bonds, instead of hydrogen bonds with proteins as found in natural porphyrin-containing systems. Substitution of weaker hydrogen bonds or van der Waals forces with stronger chemical bonds has been successfully utilized to ensure the efficient electronic coupling in either ground or excited states between the individual components of the supramolecular system.[1−3]

The self-assembly of complementary components via noncovalent interactions such as metal−ligand coordination offers a popular synthetic methodology for the controlled synthesis of large supramolecular entities. These arrays usually possess well-defined and predictable architectures. By this approach and by choosing complementary components, elaborate multicomponent arrays may be constructed in a single step from a stoichiometric combination of the individual tectons.[4] Porphyrins represent ideal building blocks for the synthesis of oligomeric and polymeric arrays via the self-assembly technique. They are fairly rigid and prefer planarity, are easily modified and functionalized, and are able to coordinate a large number of metals and pseudometals within their central cavity. There are numerous examples of supramolecular porphyrinic arrays assembled through coordination of phosphine groups,[5] coordination to centrally bound Ru(II)[6,7] or Zn(II),[8] and coordination to external metal centers such as Pd(II) and Pt(II)[9−15] or other metals.[16,17] The vast majority of the systems prepared so far have utilized a "linker" (often a pyridyl moiety) between the porphyrin macrocycle and the coordinating metal center. Due to steric constraints between the porphyrin's β-hydrogens and the pyridyl ring, the aromatic group will often lie perpendicular to the plane of the porphyrin ring. This conformation reduces the amount of ground-state electronic communication within the molecule, which is often desirable to control the properties. However, it may also be useful to have linkers that modify the redox properties of the porphyrin(s) by more direct interactions. One way of combining redox control and array construction is to

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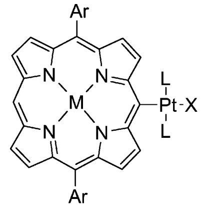
have the metal fragment directly η^1bonded to the porphyrin macrocycle.

Several types of organometallic porphyrins are known. The vast majority of examples in this area usually incorporate the organometallic bond between the *centrally* bound metal in the porphyrin and an organic fragment.[18] The recent discovery and investigation of modified porphyrin macrocycles such as inverted or "N-confused" porphyrins[19] and azuliporphyrins[20] have somewhat increased the number of examples in this area; however, the centrally coordinated metal still participates in the organometallic character of the molecule. There are also limited examples of porphyrins with an externally bound organometallic fragment, which include examples of both σ- and π-bonded organometallic moieties.[21]

Apart from the examples of organometallic porphyrins discussed above, there is another group of η^1-organometallic porphyrins that has been synthesized recently. Our publications have been the only reports of isolated η^1-organopalladio- and η^1-organoplatinioporphyrins.[22−24] This particular version of late-transition-metal chemistry leads to the compounds of type **1**, whose palladium(II) analogues are involved in the catalytic couplings of *meso*-bromoporphyrins with simple terminal alkynes, alkynylstannanes or alkynylzincs, and alkenyl organometallics.[25] It has been assumed in these examples that the key step in the coupling reactions is the oxidative addition of the *meso*-carbon-to-bromine bond to a zerovalent palladium species, usually a bis(phosphine) moiety. Several years ago, we serendipitously isolated the resulting *meso*-η^1-organopalladium(II) porphyrin



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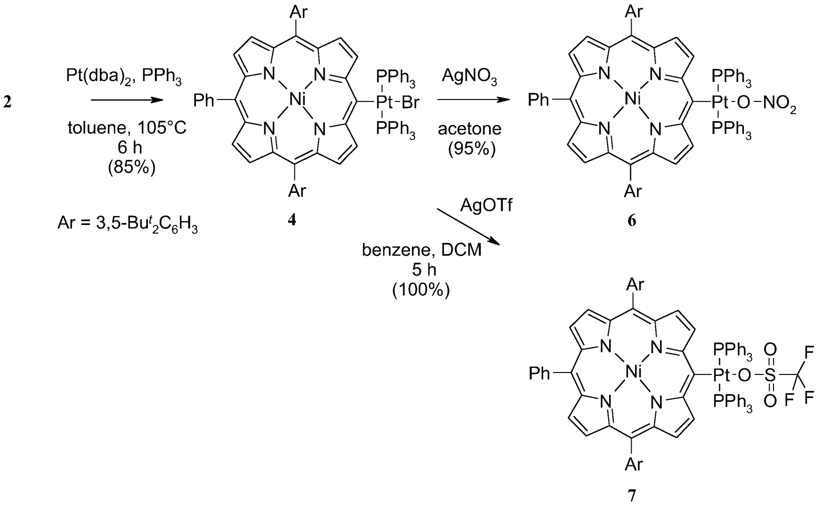
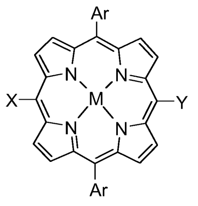
Scheme 1



from one of these reactions.[24] Because such compounds had not previously been studied in their own right, we embarked on a systematic study of this type of palladium compound and have also studied their more robust organoplatinum(II) analogues. Apart from our reports, there appear to be no other examples of isolated compounds with direct transition-metal to porphyrin M−C σ-bonds. The present paper reports the results of our recent work on (i) substitution reactions at the Pt(II) by various nucleophiles and (ii) coordination for the first time of these Pt(II) centers to various pyridyl moieties. Investigation of this pyridine coordination has allowed us to prepare and characterize several novel self-assembled multiporphyrin arrays using the direct porphyrin−platinum bond as a new construction principle.

Results and Discussion

Syntheses of Porphyrin Starting Materials. The base porphyrin chromophore chosen for this investigation was the readily synthesized **2**, and its transformations are shown in Scheme 1. This haloporphyrin is easily prepared from the diarylporphyrin (Ar = 3′,5′-di-*tert*-butylphenyl) via a simple phenylation, bromination, metalation scheme in multigram quantities and in high yields (ca. 75% over three steps from **3**).[23,26] One of the major advantages stemming from the use of this building block is that it is very soluble in many common organic solvents ($CHCl_3$, CH_2Cl_2, THF, DMSO, acetone, ether, toluene, benzene; partly soluble in cyclohexane). The inherent solubility of this macrocycle avoids the problems that have plagued other multiporphyrin arrays with[3,7,10,12,13,15,17] and without[2,27,28] coordinating metal centers. The η^1-organometallic porphyrin **4** has been previously prepared by the oxidative addition of the zerovalent platinum complex $Pt(PPh_3)_3$ to the appropriate bromoporphyrin **2** in degassed toluene at 105 °C.[23] It has since been found that a more attractive way of preparing such platinioporphyrins is to use $Pt(dba)_2$[29] (dba = dibenzylideneacetone) in combination with triphenylphosphine to generate the desired zerovalent platinum complex in situ. The very reactive $Pt(PPh_3)_2$



Ar = 3,5-Bu$^t_2$C$_6$H$_3$

Compound	M	X	Y
2	Ni	Ph	Br
3	H_2	H	H
4	Ni	Ph	*trans*-$Pt(PPh_3)_2Br$
5	Ni	Ph	*trans*-$Pt(PPh_3)_2Cl$

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or Pt(dba)$(PPh_3)_2$ then undergoes oxidative addition with the haloporphyrin. The initial product of the oxidative addition is the cis isomer, which with continued heating slowly isomerizes (over ca. 6 h) to furnish the desired trans isomer in a high yield. This method has the distinct advantage over the previous method in that it avoids the use of air-sensitive $Pt(PPh_3)_3$, which if not freshly prepared may be of unknown or dubious quality. The platinum-functionalized porphyrin **4** is an air- and moisture-stable entity, in line with other η^1-organometallic platinio- and palladioporphyrins. However, some Br/Cl exchange is known to occur in chlorinated solvents.[22-24]

Bromide abstraction with silver nitrate in acetone/CH_2Cl_2 proceeded smoothly to give the platinum nitrate **6** in 95% yield. The reaction was easily followed by TLC, and the product was isolated by filtration to remove the silver bromide byproduct, and the residue was washed with water to remove excess silver nitrate. The platinionitrate **6** was also found to be very soluble in common organic solvents and is air- and moisture-stable. Moreover, the compound is stable in solution for several weeks, with no detectable NO_3/Cl exchange (as measured by ^1H NMR) when dissolved in chlorinated solvents, and stable for over one year in the solid state. This complex was fully characterized, as outlined in the Experimental Section, by ^1H and ^{31}P NMR, UV−visible spectroscopy, high-resolution ESI mass spectrometry, and elemental analysis. Understandably, the proton NMR of **6** is similar to that of its parent compound; however, small (ca. 0.2 ppm) upfield shifts are seen for the porphyrin β-protons nearest the organometallic fragment (i.e. 2,3,7,8-β-H). The ^{31}P NMR of **6** shows no change of the chemical shift of the equivalent triphenylphosphine groups when compared to **4**, indicating similar polarity of the Pt−Br and Pt−ONO_2 bonds. The high-resolution ESI mass spectrum of **6** (calibrated against an internal standard of NaI clusters) shows a peak at m/z 1622.5124, which corresponds to the sodium adduct of $[M]^+$ (calculated m/z 1622.5034). Similarly, another cluster is seen at m/z 1537.5221 corresponding to the organometallic fragment after the loss of nitrate, $[M - NO_3]^+$.

It was also of interest to prepare the triflato platinioporphyrin, due to the more electrophilic nature of the Pt center. Initially, it was found that treatment of **4** with silver triflate in dichloromethane led to the rapid decomposition of the organometallic species and formation of a green product. Decomposition of the organometallic species was also encountered by Stang et al.[30] in studying their anthracene “molecular clip” system. This observation is in line with the recent work of Osuka and co-workers in their preparation of *meso*−*meso* linked porphyrin arrays by Ag(I) oxidation of the porphyrin macrocycle.[28,31] From this it can be seen that the higher redox potential of Ag^+ in dichloromethane (+0.65 V vs SCE)[32] favors oxidation of the porphyrin macrocycle, rather than inducing metathesis. This problem was overcome by carrying out the bromide abstraction reaction of **4** in benzene, rather than dichloromethane, where the redox potential of the system is apparently low enough to avoid porphyrin oxidation and hence achieve the anion exchange reaction. The simple workup of filtering off the silver bromide byproduct and washing the porphyrin residue with water furnished the desired triflate-exchanged product **7** in an almost quantitative yield. Inspection of the ^1H and ^{31}P NMR spectra of **7** showed that, unless the sample was rigorously dried under high vacuum, it preferred to exist as the cationic platinum complex with a water molecule as the coordinated ligand. This gave rise to broadened peaks in both the ^1H and ^{31}P NMR spectra. The coordinated water peak can be seen at approximately 5.5 ppm as a slightly broadened singlet. The identity of this peak was confirmed by the addition of 1−2 μL of D_2O to the NMR sample, after which the singlet at 5.5 ppm further broadened, diminished in size, and moved upfield to about 4.7 ppm. Even in the most thoroughly dried sample the aqua species can be seen in the ^1H NMR spectrum in approximately a 1:3 ratio with the triflato product. The ^{31}P NMR spectrum of **7** demonstrates the effect of the bonded triflate on the equivalent neighboring triphenylphosphine groups in **7**. The phosphine resonance occurs at 18.2 ppm (flanked by ^{195}Pt satellites, $^1J(^{31}P-^{195}Pt) = 2958$ Hz), considerably upfield of the analogous resonance in the parent compound **4** that occurs at 23.0 ppm. The high-resolution ESI mass spectrum supports the assigned structure and mainly consists of the parent ion of **7** at m/z 1686.4776 (calculated m/z 1686.4776) and $[M - OTf]^+$ at m/z 1537.5234.

Self-Assembly with Pyridyl Moieties. With the η^1-organometallic platinioporphyrin tectons **6** and **7** in hand, the coordination of pyridines was investigated (Scheme 2). This was initially attempted with the parent platinioporphyrin bromide **4** in $CHCl_3$ and pyridine. It was found that even after stirring at elevated temperatures with an excess of pyridine the desired cationic platinum complex was not formed. The reaction was repeated with the nitratoplatinum complex **6** with a stoichiometric amount of pyridine. It was found that elevated temperatures were also required for this reaction. Under these conditions, it was seen by both ^1H and ^{31}P NMR that the desired cationic platinum complex with coordinated pyridine was contaminated with the NO_3/Cl-exchanged product **5**. To avoid the use of chlorinated solvents, the reaction was repeated in acetone at 50 °C with a stoichiometric amount of pyridine. The reaction progress was monitored by ^1H NMR, and the conversion progressed smoothly and was considered complete after approximately 5 h. The product **8a** was obtained as the hexafluorophosphate salt by the addition of an excess of KPF_6. This procedure was repeated with $^1/_2$ equiv of 4,4′-bipyridine to furnish the bipyridine-linked dimer **9a**, which too was formed almost quantitatively. It was also found that, with the more electrophilic platinum triflate tecton **7**, the reactions with both pyridine (to form **8b**) and 4,4′-bipyridine (to form **9b**) proceeded smoothly and were complete within 3 h at room temperature (as monitored by ^1H NMR). The products did not require treatment with KPF_6, as they were quite stable as the triflate salts. This allowed the use of chlorinated solvents for these simple self-assembly reactions as the reaction proceeded relatively

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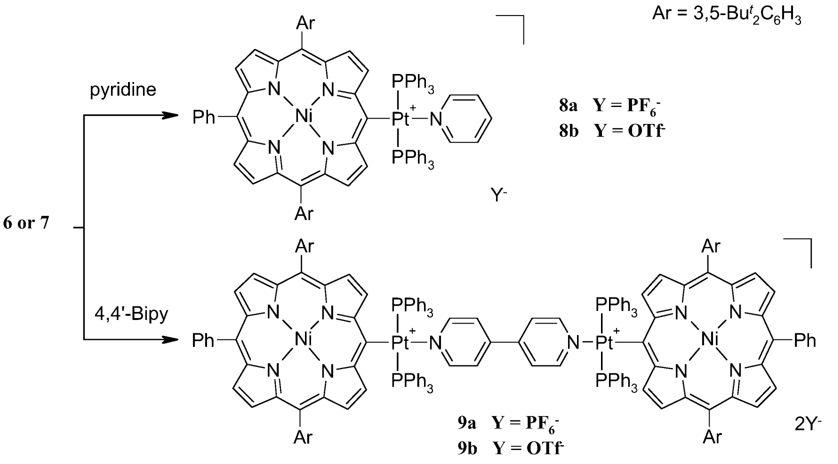
(30) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.

(31) (a) Aratani, N.; Osuka, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1361. (b) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed.* **1997**, *36*, 135. (c) Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3023.

(32) Connelly, N. G.; Geier, W. E. *Chem. Rev.* **1996**, *96*, 877.

Scheme 2



quickly (ca. 3 h) at room temperature, thus avoiding complications from the production of the triflate/chloro-exchanged product **5**.

NMR spectroscopy (^{1}H and ^{31}P) provides a convenient means of characterizing these products. The resonances of the pyridine and 4,4′-bipyridine moieties are all shifted from the usual positions of the free ligands, indicating that the desired coordination to the metal center has occurred. The spectrum of **8b** displays resonances from the ortho protons of the pyridine ring (H_o-py) as a broad doublet at 8.54 ppm ($J = 5.1$ Hz), indicating that they are equivalent and have shifted upfield. Other signals arising from the pyridine moiety are found as multiplets at 6.95 and 7.36 ppm, corresponding to the *m*- (H_m-py) and *p*-pyridyl (H_p-py) protons, respectively. These two resonances too are shifted upfield from corresponding resonances in the free ligand, supporting the conclusion of coordination to platinum. Usually the resonances arising from the pyridyl moiety are shifted somewhat downfield after coordination to a cationic metal center;[10,15,30,33] however, these systems are usually lacking coordinated phosphine groups or utilize less sterically demanding and magnetically isotropic trialkylphosphines. This effect was demonstrated by Stang and co-workers[33] by the synthesis and comparison of self-assembled phosphine-coordinated Pt and Pd cationic molecular squares with either Et$_3$P or dppp (1,3-bis(diphenylphosphino)propane) ligands. It has been proposed in this example and others[12−14,33] that the significant shielding effects of the bulky phenylphosphine groups offset the effect of the cationic metal center to give an overall moderate upfield shift of the pyridyl resonances. These assignments are supported by significant cross-peaks in DQF-COSY NMR experiments. Inspection of the ^{1}H NMR spectrum of the bipyridine-linked dimer **9b** suggests a structure with high symmetry. The bridging 4,4′-bipyridine group is seen as a pair of coupled resonances ($J = 6.2$ Hz) at 8.55 and 7.36 ppm, indicative of the bipyridyl ortho and meta protons, respectively. The symmetry of this 4,4′-bipyridine group demonstrates that the proposed dinuclear array **9b** exists as the exclusive coordinated species in solution. These 4,4′-bipyridine resonances are also significantly shifted upfield by 0.3−0.4 ppm from the respective signals of the free ligand, supporting the assigned structure. The resonances arising from the porphyrin β-hydrogens nearest the organometallic fragment (2,3,7,8-β-H's) are understandably affected most by the presence of a cationic platinum moiety. These signals are shifted downfield from that of triflate **7** by approximately 0.3−0.4 ppm. The triphenylphosphine signals (6.8−7.0 ppm) also experience a slight upfield shift after coordination of a pyridyl moiety. The symmetry of compounds **8b** and **9b** is also reflected in the corresponding ^{31}P NMR spectra, which consist of a single resonance at approximately 19 ppm that is flanked by ^{195}Pt satellites with a corresponding ^{195}Pt−^{31}P coupling constant of about 2900 Hz. This coupling constant is slightly diminished from that of noncationic η^1-organometallic platinioporphyrins by about 50−100 Hz, reflecting the different cis influences of pyridine and bromide.[22−24]

The ESI high-resolution mass spectra of the cationic complexes **8b** and **9b** gave excellent agreement with the predicted isotopic patterns. The mass spectrum of **8b** displayed a strong peak at *m*/*z* 1616.5786 corresponding to the cationic fragment, $[M - OTf]^+$ (calculated *m*/*z* 1616.5681). The bipyridine-bridged dimer **9b** also displayed a significant cluster at *m*/*z* 1616.0803, which corresponds well with the calculated pattern for the dication after loss of both the triflate anions, namely $[M - 2OTf]^{2+}$ (calculated *m*/*z* 1616.0603). This cluster displayed a line separation of half a mass unit in the isotopic pattern, demonstrating that it is indeed the dication that is being detected.

Self-Assembly of Multiporphyrin Arrays. With a basic methodology for the coordination of pyridyl moieties to η^1-organometallic *meso*-platinioporphyrins established, we wished to extend this to incorporate coordination to a range of pyridylporphyrins (see Scheme 3). When triflate **7** was reacted with 1 equiv of 5-(4-pyridyl)-10,15,20-tri-*p*-tolylporphyrin (**10**) in CDCl$_3$ at room temperature, formation of the new species **11** was observed by ^{1}H NMR. Likewise, the bis(pyridyl)porphyrin **12** and tetrakis(pyridyl)porphyrin **14**, when reacted with respective stoichiometric amounts of **7** (CDCl$_3$, room temperature, 5−24 h), gave rise to multiporphyrin arrays **13** and **15**, respectively. From the ^{31}P and ^{1}H NMR spectra of **11**, **13**, and **15** it was clearly evident that the reactions were quite selective, with only

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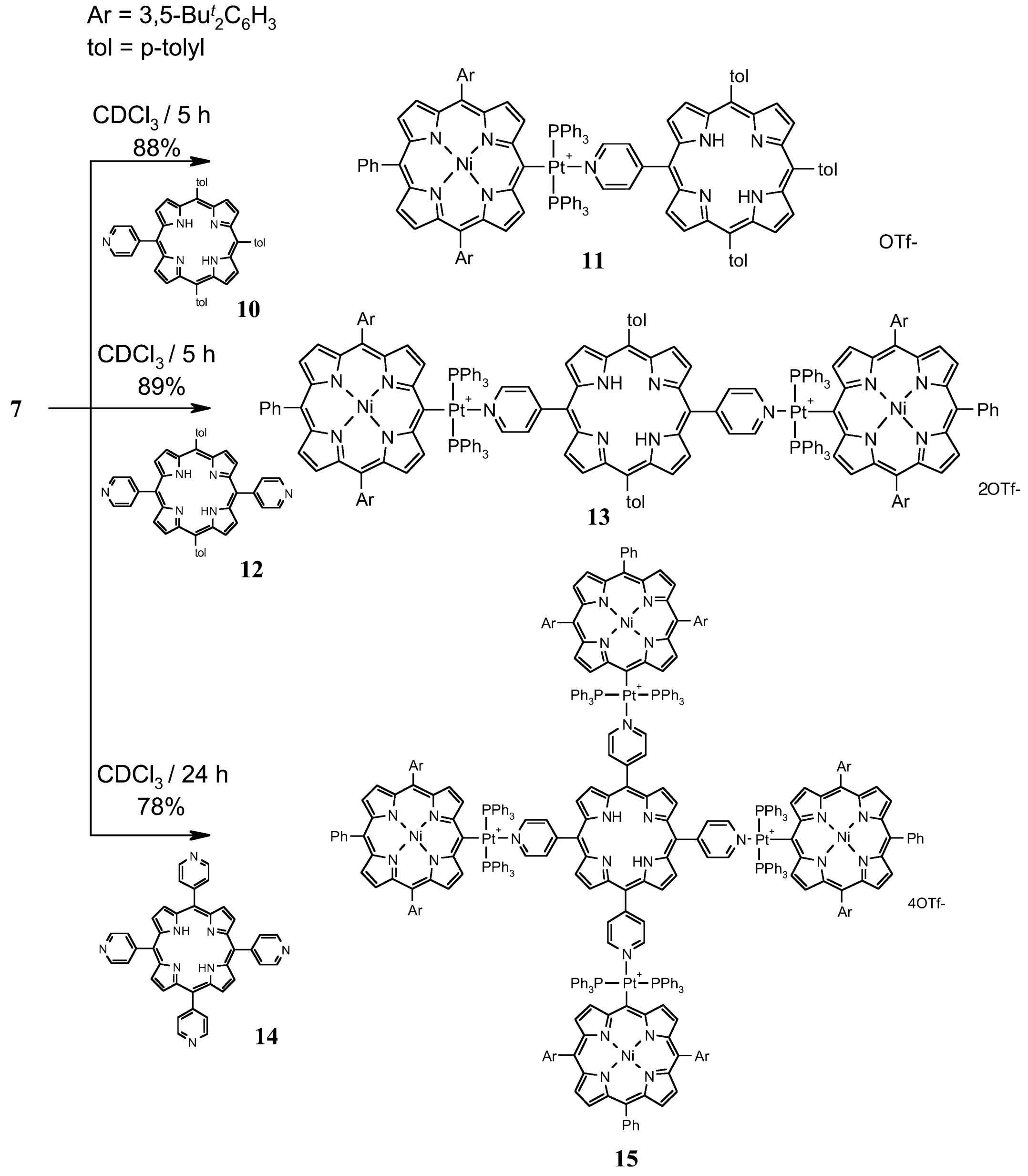
[33] Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

Scheme 3



one new species being produced in each case. The ^{31}P NMR spectra of these multiporphyrin arrays supported the assigned structures and showed a single resonance at around 20 ppm flanked by ^{195}Pt satellites with a $^1J_{Pt-P}$ coupling constant of approximately 2900 Hz. Peak shifts seen in the ^{1}H NMR spectra of **11**, **13**, and **15** indicate moderate changes to the pyridine-appended porphyrins after coordination to the η^1-platinioporphyrins. These changes include upfield shifts of approximately 0.2 ppm of the *o*-pyridyl protons closest to the coordinating metal centers of **11**, **13**, and **15**. This suggests moderate shielding from nearby triphenylphosphine groups. On the other hand, the *m*-pyridyl protons, those closest to the porphyrin macrocycle, underwent substantial downfield shifts (ca. 0.3 ppm) compared to the parent porphyrin due to coordination of the pyridyl group to a metal. These shifts of pyridyl *o*- and *m*-H are in line with those previously reported for self-assembled arrays and squares that contain coordinating metal centers in conjunction with porphyrin macrocycles.[10,12,15,17]

The ^{1}H NMR spectrum of **15** is, at first sight, not very informative, because it displays broadened peaks for all of the resonances. This is most likely to the slow rotation of the macrocycles relative to each other in this large array comprising bulky ligands. Despite the unattractive appearance of the 1D spectrum, the connectivity of the newly formed array was demonstrated by 2D NMR experiments (DQF-COSY and NOESY) (see the Supporting Information). For example, the COSY experiment showed the integrity of the Ni(II) and free base porphyrin portions and showed that the 2,8-β-H signal lies upfield of that for the remote 12,13,17,18-β-H's. In this pentanuclear array, the β-H's of the central free base pyridyl porphyrin are seen as a single resonance at 8.60 ppm, indicative of a highly symmetrical structure. The NOESY spectrum indicated the connection of the core with the peripheral porphyrins through the Pt linker by the presence of strong nOe's between the pyridyl protons of the central free base porphyrin macrocycle and the protons of the triphenylphosphine groups on the metalated porphyrin (Figure 1). The

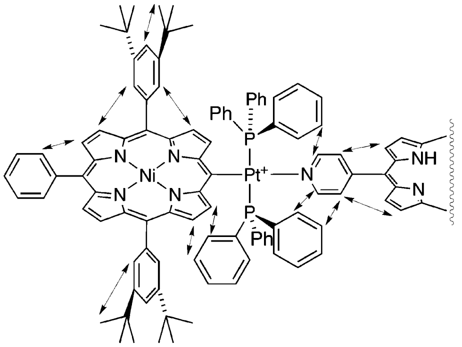


Figure 1. Through-space correlations revealed by the NOESY spectrum of pentanuclear array **15**.

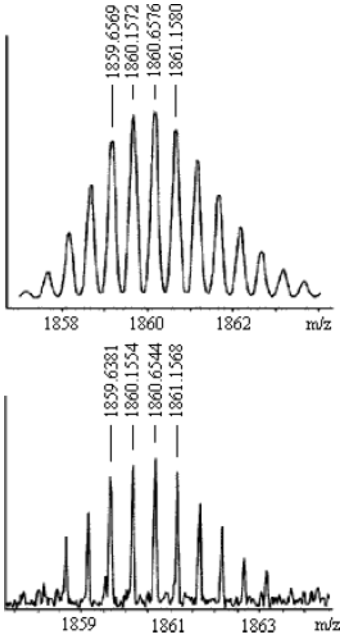


Figure 2. Experimental high-resolution ESI (bottom) and predicted (top) mass spectral patterns for the ion $[M - 2OTf]^{2+}$ for trinuclear array **13**.

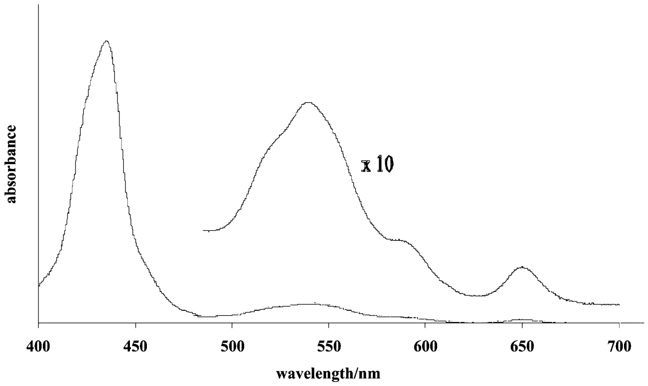


Figure 3. Absorption spectrum of **13** in CH_2Cl_2.

changes in ^{1}H and ^{31}P NMR spectra and nOe's relating the two types of macrocycles indicate that the desired conjugate is indeed exclusively formed and that it is not just a stoichiometric mixture of the individual tectons. For all three complexes **11**, **13**, and **15**, the inner NH protons appear as single broad resonances at approximately −3 ppm, indicating that these arrays comprise a single structure in solution and that the free base porphyrin is intact.

Arrays **11** and **13** displayed high-resolution positive ion mass spectra that agreed extremely well with those predicted for the assigned structures. Both of these mass spectra show strong parent ion peaks, which correspond to the mass of the array after the loss of the triflate counterions. For example, **13** displayed a strong peak at m/z 1860.6544 ($[M - 2OTf]^{2+}$), the cluster abundances corresponding well with the calculated isotopic pattern and the most intense ion matching at m/z 1860.6576 (Figure 2). This isotopic pattern of **13** displayed the desired half mass unit separation between neighboring peaks, indicating that it is indeed the assigned dication that is being detected. Unfortunately, no peaks that were assignable to the molecular ion of pentad **15** were detected by ESI, FAB, or MALDI-TOF mass spectrometric techniques. All mass spectra of **15** displayed the singly charged fragment assignable to the individual porphyrin macrocycle with the platinum phosphine fragment attached at m/z 1537.2 (calculated m/z 1537), indicating that considerable fragmentation of the molecule occurs under all these conditions. Elemental analyses returned carbon percentages that are about 1% low, which fits a solvate containing one molecule of chloroform from the recrystallization solvent. The presence of the one proton from this solvent is difficult to detect under the large, broad phosphine phenyl signal. However, the formulation of this array as **15** is strongly supported by the NMR spectra. Unfortunately, we have so far been unable to grow crystals suitable for X-ray analysis for any of these arrays, perhaps as a consequence of using the solubilizing *tert*-butyl groups on the peripheral aryl substituents.

Electronic Absorption Spectra. The electronic absorption spectra of the η^1-organometallic platinioporphyrins display some changes after coordination with the various pyridyl moieties. The Soret band of the Ni(II) porphyrin (ca. 430 nm) is slightly red-shifted by approximately 1−5 nm after coordination to the pyridine fragment. Larger shifts are seen from the complexes that involve coordination to free-base pyridyl porphyrins i.e. complexes **11**, **13**, and **15**. There is a decrease in the extinction coefficient per porphyrin (or per Ni(II) porphyrin) for these arrays. This suggests that there is some through-space electronic coupling between the porphyrin chromophores. However, the platinum fragment acts more as a structural component than a conjugative linking group. These observations are in line with those of other groups.[11−15] The coordinated free base pyridyl porphyrins show moderate changes in their electronic absorption spectra after coordination to platinum centers. The bands stemming from the free base porphyrins that are visible and not overlapped by those of the Ni(II) η^1-organometallic platinioporphyrins show larger 8−12 nm red shifts. The largest of these shifts is seen in the Q band (IV) at highest energy for complexes **11** and **13**. The spectrum of **13** is shown in Figure 3. However, in pentanuclear array **15** band IV was obscured by those of the Ni(II) porphyrins.

Conclusion

This report demonstrates that η^1-organometallic platinioporphyrins may be incorporated into multiporphyrin arrays and that predetermined structural characteristics of the individual tectons may be used to control the architecture of the newly self-assembled multicomponent systems. These meso organometallic porphyrins form stable conjugates with various pyridine ligands and pyridyl-substituted porphyrins that are very stable in solution for extended periods and in the solid state indefinitely. These conjugates self-assemble selectively in high yields when the individual components are reacted in stoichiometrically equivalent ratios. The newly formed arrays are highly soluble in common organic solvents, a property that stems from the use of trisubstituted parent monomers, and this avoids solubility problems that have plagued other similar assemblies. High-resolution mass spectral data and single- and multidimensional NMR experiments have unambiguously established their structures in solution. This fundamental design approach will allow for the possible incorporation of a large number of versatile components tailored to the specific requirements of the assembly. Various attractive components such as different metalloporphyrins and various electron-donor or -acceptor fragments may be included as either substituents on a η^1-organometallic platinioporphyrin or as the pyridine-substituted moiety, which is directly coordinated to an organometallic porphyrin. The ability to tailor the surface properties by the use of other substituents on the aryl rings and alternative phosphine or other ligands on the Pt(II) cationic center is an advantage. This methodology should make it possible to attach individual porphyrin macrocycles to surfaces via the appropriately substituted pyridyl ligand in combination with an organometallic porphyrin. For example, a η^1-organometallic platinioporphyrin coordinated to an isonicotinic fragment will allow for attachment to a nanoporous, nanocrystalline TiO_2 film. Preparation of these and other supramolecular assemblies that utilize bis(*meso*-η^1-organometallic)porphyrins and studies of their electrochemical and photophysical properties are in progress.

Experimental Section

General Procedures. Syntheses involving zerovalent metal precursors were carried out in an atmosphere of high-purity argon using conventional Schlenk techniques. Porphyrin starting materials 5,15-bis(3′,5′-di-*tert*-butylphenyl)porphyrin (**3**),[34] 5-bromo-10,20-bis(3′,5′-di-*tert*-butylphenyl)-15-phenylporphyrin (**2**),[23] 5-(4-pyridyl)-10,15,20-tri-*p*-tolylporphyrin (**10**), and 5,15-bis(4-pyridyl)-10,20-di-*p*-tolylporphyrin (**12**)[15] and the platinum precursor $Pt(dba)_2$[29] were synthesized by literature methods. All other reagents and ligands were used as received from Sigma-Aldrich. Toluene was AR grade, stored over sodium wire and degassed by heating and purging with argon at 90 °C. All other solvents were AR grade, and dichloromethane and chloroform were stored over anhydrous sodium carbonate. Analytical TLC was performed using Merck silica gel 60 F_{254} plates, and column chromatography was performed using Merck silica gel (230−400 mesh). NMR spectra were recorded on Bruker Avance 400 MHz or Varian Unity 300 MHz instruments in $CDCl_3$ solutions, using $CHCl_3$ as the internal reference at 7.26 ppm for ^1H spectra and external 85% H_3PO_4 as the reference for proton-decoupled ^{31}P spectra. UV−visible spectra were recorded on a Cary 3 spectrometer in dichloromethane solutions. High-resolution ESI mass spectra were recorded on a Bruker BioApex 47e FTMS fitted with an Analytica electrospray source. The samples were dissolved in dichloromethane and diluted with either dichloromethane/methanol (1:1) or methanol, and solutions were introduced into the source by direct infusion (syringe pump) at 60 μL/h, with a capillary voltage of 80 V. The instrument was calibrated using internal NaI. Positive ion FAB mass spectra were recorded on a Kratos Concept instrument at the Central Science Laboratory, University of Tasmania. Samples were dissolved in dichloromethane and dispersed in a 4-nitrobenzyl alcohol matrix. In the data below, masses given are for the strongest observed peak in the molecular ion cluster. The Microanalytical Service, The University of Queensland, provided the elemental analyses.

***trans*-[PtBr(NiDAPP)(PPh_3)$_2$] (4).** Toluene (250 cm^3) was added to a Schlenk flask and degassed by bubbling argon through the solution at 90 °C. Bromoporphyrin **2** (300 mg, 0.33 mmol) was added, and the mixture was stirred for 5 min. Pt(dba)$_2$ (328 mg, 0.50 mmol) and triphenylphosphine (262 mg, 1.0 mmol) were added, and the solution was stirred at 90 °C for 6 h. The residue after removal of the solvent (now air stable) was purified by column chromatography, with 50% $CHCl_3$/hexane as eluent, and the residue from the major red fraction was recrystallized from $CHCl_3$/hexane to give **4** (460 mg, 85%) as dark red crystals. The spectroscopic data (^1H and ^{31}P NMR) of this compound agreed well with those of a sample prepared previously using $Pt(PPh_3)_3$.[23]

***trans*-[Pt(NO_3)(NiDAPP)(PPh_3)$_2$] (6).** To a solution of platinioporphyrin **4** (200 mg, 0.12 mmol) dissolved in CH_2Cl_2 (10 cm^3) and acetone (50 cm^3) was added silver nitrate (210 mg, 1.2 mmol). The solution was protected from light and stirred at room temperature. After 3 h the reaction appeared to be complete by TLC analysis (100% CH_2Cl_2), and the solution was filtered through a fine glass frit to remove suspended silver bromide and undissolved silver nitrate. The solvent was removed in vacuo and the residue thoroughly washed with water. After recrystallization from CH_2Cl_2/pentane the product **6** (188 mg, 95%) was collected as bright red crystals. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.51 (s, 36H, *tert*-butyl H on 10,20-aryl), 6.70−6.90 (m, 18H, PPh_3), 6.90−7.00 (m, 12H, PPh_3), 7.60−7.70 (m, 3H, *m*,*p*-H on 15-phenyl), 7.67 (t, 2H, $J = 1.8$ Hz, 4′-H on 10,20-aryl), 7.71 (d, 4H, $J = 1.8$ Hz, 2′,5′-H on 10,20-aryl), 7.95−8.05 (m, 2H, *o*-H on 15-phenyl), 8.10, 8.54, 8.57, 9.47 (each d, 2H, $J = 4.7$ Hz, β-H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 22.1 (s, $^1J_{Pt-P}$ 3064 Hz). UV−vis (λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})): 429 (227), 537 (16.3), 571 sh (4.4) nm. High-resolution ESI MS: $[M + Na]^+$, accurate mass calculated for $C_{90}H_{85}N_5NiO_3P_2PtNa$ (+1), 1622.5034; found, 1622.5124. Anal. Calcd for $C_{90}H_{85}N_5NiO_3P_2Pt$: C, 67.54, H, 5.35; N, 4.38. Found: C, 67.60; H, 5.41; N, 4.30%.

***trans*-[Pt(OTf)(NiDAPP)(PPh_3)$_2$] (7).** Silver triflate (158 mg, 0.6 mmol) was added to a solution of platinum bromide **4** (200 mg, 0.12 mmol) in benzene (50 cm^3). The reaction mixture was stirred at room temperature for 5 h with protection from light. Silver bromide was removed by filtration, and the residue after solvent removal was washed thoroughly with water and dried in vacuo. After recrystallization from CH_2Cl_2/pentane, the product **7** was collected as a red solid (208 mg) in quantitative yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.47 (s, 36H, *tert*-butyl H on 10,20-aryl), 6.70−6.80 (m, 18H, PPh_3), 7.10−7.20 (m, 12H, PPh_3), 7.60−7.70 (m, 3H, *m*,*p*-H on 15-phenyl), 7.68 (t, 2H, $J = 1.8$ Hz, 4′-H on 10,20-aryl), 7.70 (d, 4H, $J = 1.8$ Hz, 2′,5′-H on 10,20-aryl), 7.95−8.05 (m, 2H, *o*-H on 15-phenyl), 8.16, 8.54, 8.56, 9.36 (each d, 2H, $J = 4.7$ Hz, β-H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 18.2 (bs, $^1J_{Pt-P} = 2958$ Hz). UV−vis (λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})): 429 (215), 537 (17.4), 568 (5.6) nm. High-resolution ESI MS: $[M]^+$, accurate mass calculated for $C_{91}H_{85}F_3N_4NiO_3P_2PtS$ (+1), 1686.4776; found, 1686.4204.

In solution, **7** was found to be in equilibrium with the cationic aquated analogue, namely *trans*-[Pt(NiDAPP)(H_2O)(PPh_3)$_2$](OTf), in an approximate 3:1 ratio, and ^1H NMR spectroscopic data of the latter are as follows. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.47 (s, 36H, *tert*-butyl H on 10,20-aryl), 5.57 (s,

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[34] Manka, J. S.; Lawrence, D. S. *Tetrahedron Lett.* **1989**, *30*, 6989.

2H, coordinated H_2O) 6.80−6.90 (m, 18H, PPh_3), 7.00−7.10 (m, 12H, PPh_3), 7.60−7.70 (m, 3H, *m*,*p*-H on 15-phenyl), 7.68 (t, 2H, J = 1.8 Hz, 4′-H on 10,20-aryl), 7.70 (d, 4H, J = 1.8 Hz, 2′,5′-H on 10,20-aryl), 7.95−8.05 (m, 2H, *o*-H on 15-phenyl), 8.17, 8.52, 8.54, 9.52 (each d, 2H, J = 4.7 Hz, β-H).

General Procedure for the Preparation of Compounds 8b, 9b, 11, 13, and 15. To a solution of **7** (20.0 mg, 0.012 mmol) in $CDCl_3$ (3 cm^3) was added a stoichiometric amount of the pyridyl-containing ligand as a $CDCl_3$ solution. The vessel was sealed and stirred at room temperature. Afterward an aliquot was removed via syringe and transferred to an NMR tube for monitoring of the reaction progress by ^{1}H and ^{31}P NMR. Once the reaction was considered complete (3−24 h), the NMR sample was recombined with the bulk reaction sample and the solvent removed in vacuo. The residue was recrystallized to yield the appropriate cationic platinum complex as a red solid. Where required, the product was recrystallized again as noted and dried thoroughly under high vacuum at 80 °C in order to obtain a sample for elemental analysis.

***trans*-[Pt(NiDAPP)(py)(PPh$_3$)$_2$](OTf) (8b**). Recrystallized from CH_2Cl_2/pentane, to give **8b** (21 mg) in 97% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.47 (s, 36H, *tert*-butyl H on 10,20-aryl), 6.70−6.90 (m, 18H, PPh_3), 6.95 (m, 2H, *m*-H on pyridine (signal overlapped by PPh_3)), 6.90−7.00 (m, 12H, PPh_3), 7.36 (m, 1H, *p*-H on pyridine), 7.60−7.70 (m, 3H, *m*,*p*-H on 15-phenyl), 7.71 (t, 2H, J = 1.8 Hz, 4′-H on 10,20-aryl), 7.75 (d, 4H, J = 1.8 Hz, 2′,5′-H on 10,20-aryl), 7.95−8.05 (m, 2H, *o*-H on 15-phenyl), 8.54 (d, 2H, J = 5.1 Hz, *o*-H on pyridine), 8.49, 8.58, 8.62, 9.70 (each d, 2H, J = 4.7 Hz, β-H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 19.2 (s, $^1J_{Pt-P}$ = 2906 Hz); UV−vis: λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1}) 429 (197), 538 (15.6), 574 (3.8) nm; High-resolution ESI MS: [M − OTf]$^+$, accurate mass calculated for $C_{95}H_{90}N_5NiP_2Pt$ (+1), 1616.5681; found, 1616.5786, Anal. Calcd for $C_{96}H_{90}F_3N_5NiO_3P_2PtS$: C, 65.27; H, 5.14; N, 3.96. Found: C, 65.00; H, 4.88; N, 4.02%.

{[*trans*-Pt(NiDAPP)(PPh$_3$)$_2$]$_2$(4,4′-bipyridine)}(OTf)$_2$ (9b). Recrystallized from CH_2Cl_2/pentane, to give **9b** (19 mg) in 93% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.48 (s, 72H, *tert*-butyl H on 10,20-aryl), 6.70−6.90 (m, 36H, PPh_3), 6.90−7.00 (m, 24H, PPh_3), 7.36 (d, 4H, J = 6.2 Hz, *m*-H on 4,4′-bipyridine), 7.60−7.70 (m, 6H, *m*,*p*-H on 15-phenyl), 7.74 (t, 4H, J = 1.8 Hz, 4′-H on 10,20-aryl), 7.78 (d, 8H, J = 1.8 Hz, 2′,5′-H on 10,20-aryl), 7.95−8.05 (m, 4H, *o*-H on 15-phenyl), 8.55 (d, 4H, J = 6.2 Hz, *o*-H on 4,4′-bipyridine), 8.40, 8.58, 8.63, 9.67 (each d, 4H, J = 4.7 Hz, β-H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 18.9 (s, $^1J_{Pt-P}$ = 2894 Hz). UV−vis (λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})): 430 (387), 538 (35.4), 578 sh (9.4) nm. High-resolution ESI MS: [M − 2OTf]$^{2+}$, accurate mass calculated for $C_{190}H_{178}N_{10}Ni_2P_4Pt_2$ (+2), 1616.0603; found, 1616.0803. Anal. Calcd for $C_{192}H_{178}F_6N_{10}Ni_2O_6P_4Pt_2S_2$: C, 65.31; H, 5.08; N, 3.97. Found: C, 65.04; H, 4.86; N, 3.93.

***trans*-[Pt(NiDAPP)(H$_2$PyTTP)(PPh$_3$)$_2$](OTf) (11).** Recrystallized from $CHCl_3$/pentane, to give **11** (26 mg) in 88% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −2.80 (bs, 2H, NH), 1.47 (s, 36H, *tert*-butyl H on 10,20-aryl), 2.70 (s, 3H, 4′-CH_3 on 15-tolyl), 2.80 (s, 6H, 4′-CH_3 on 10,20-tolyl), 6.80−7.0 (m, 18H, PPh_3), 7.15−7.30 (m, 12H, PPh_3), 7.57 (m, 6H, *m*-H on 10,15,20-tolyl), 7.66 (m, 3H, *m*,*p*-H on 15-phenyl), 7.75 (t, 2H, J = 1.8 Hz, 4′-H on 10,20-aryl), 7.79 (d, 4H, J = 1.8 Hz, 2′,5′-H on 10,20-aryl), 7.84 (m, 2H, *m*-H on 5-pyridyl), 8.00−8.05 (m, 2H, *o*-H on 15-phenyl), 8.10 (m, 6H, *o*-H on 10,15,20-tolyl), 8.18, 8.60, 8.62, 8.65 (each overlapping d, 2H, J = 4.7 Hz, β-H on free base porphyrin), 9.27 (m, 2H, *o*-H on 5-pyridyl), 8.42, 8.62, 8.64, 9.90 (each d, 2H, J = 4.7 Hz, β-H on Ni porphyrin). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 19.5 (s, $^1J_{Pt-P}$ = 2907 Hz). UV−vis (λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})): 430 (367), 453 sh (111), 522 sh (22.4), 536 (25.9), 587 (7.1), 647 (3.5) nm. High-resolution ESI MS: [M − OTf]$^+$, accurate mass calculated for $C_{136}H_{120}N_9NiP_2Pt$ (+1), 2195.8170; found, 2195.8270.

{[*trans*-Pt(NiDAPP)(PPh$_3$)$_2$]$_2$(H$_2$DPyDTP)}(OTf)$_2$ (13). Recrystallized from $CHCl_3$/pentane, to give **13** (22 mg) in 89% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.10 (bs, 2H, NH), 1.50 (s, 72H, *tert*-butyl H on 10,20-aryl), 2.72 (s, 6H, 4′-CH_3 on 10,20-tolyl), 6.80−7.0 (m, 36H, PPh_3), 7.10−7.20 (m, 24H, PPh_3), 7.64 (d, 4H, J = 8.1 Hz, *m*-H on 10,20-tolyl), 7.67 (m, 6H, *m*,*p*-H on 15-phenyl), 7.73 (t, 4H, J = 1.8 Hz, 4′-H on 10,20-aryl), 7.78 (d, 8H, J = 1.8 Hz, 2′,5′,-H on 10,20-aryl), 7.85 (m, 4H, *m*-H on 5,15-pyridyl), 8.00−8.05 (m, 2H, *o*-H on 15-phenyl), 8.10 (d, 4H, J = 8.1 Hz, *o*-H on 10,20-tolyl), 8.16, 8.88 (each d, 4H, J = 4.7 Hz, β-H on free base porphyrin), 9.20 (d, 4H, *o*-H on 5,15-pyridyl), 8.42, 8.61, 8.63, 9.90 (each d, 2H, J = 4.7 Hz, β-H on Ni porphyrin). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 19.5 (s, $^1J_{Pt-P}$ = 2895 Hz). UV−vis (λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})): 433 (601), 519 sh (34.4), 357 (43.3), 586 (13.5), 648 (7.3) nm. High-resolution ESI MS: [M − 2OTf]$^{2+}$, accurate mass calculated for $C_{201}H_{202}N_{14}Ni_2P_4Pt_2$ (+2), 1860.6576; found, 1860.6544.

{[*trans*-Pt(NiDAPP)(PPh$_3$)$_2$]$_4$(H$_2$TPyP)}(OTf)$_4$ (15). Recrystallized twice from $CHCl_3$/cyclohexane, to give **15** (18 mg) in 78% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −3.2 (bs, 2H, NH), 1.50 (s, 144H, *tert*-butyl H on 10,20-aryl), 6.75−7.10 (m, 48H, PPh_3), 7.10−7.30 (m, 72H, PPh_3), 7.60−7.70 (m, 12H, *m*,*p*-H on 15-phenyl), 7.78 (bs, 8H, 4′-H on 10,20-aryl), 7.82 (bs, 16H, 2′,5′-H on 10,20-aryl), 7.98 (bd, 8H, J = 5.2 Hz, *m*-H on 5,10,15,20-pyridyl), 8.00−8.10 (m, 8H, *o*-H on 15-phenyl), 8.60 (bs, 8H, β-H on free base porphyrin (overlapped by β-H on Ni porphyrin)), 9.48 (bd, 8H, J = 5.2 Hz, *o*-H on 5,10,15,20-pyridyl), 8.46, 8.61, 8.63 (overlapping), 9.92 (each d, 8H, J = 4.7 Hz, β-H). ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 20.3 (s, $^1J_{Pt-P}$ = 2954 Hz). UV−vis (λ_{max} ($\epsilon/10^3$ M^{-1} cm^{-1})): 434 (768), 538 (80.1), 587 sh (20.1), 646 (4.4) nm. FAB MS: [Pt(NiDAPP)(PPh$_3$)$_2$]$^+$ fragment, 1537.2; mass calculated for most intense peak of cluster $C_{90}H_{85}N_4NiP_2Pt$ (+1), 1537.5. Anal. Calcd for $C_{404}H_{366}F_{12}N_{24}Ni_4O_{12}P_8Pt_4S_4\cdot CHCl_3$: C, 64.95, H, 4.97; N, 4.49. Found: C, 64.87; H, 4.85; N, 4.50.

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Supporting Information Available: Figures giving 1D, DQF-COSY, and NOESY ^{1}H NMR spectra of the pentanuclear array **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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