Chem. Rev. 2009, 109, 1630–1658

# Self-Organized Porphyrinic Materials

Charles Michael Drain,*,[†],[‡] Alessandro Varotto,[†] and Ivana Radivojevic[†]

Department of Chemistry and Biochemistry, Hunter College and Graduate Center of the City University of New York, 695 Park Avenue, New York, New York 10065, and The Rockefeller University, 1230 York Avenue, New York, New York 10065

Received November 11, 2007

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## 1. Introduction

"Anything that exists must be possible." is often referred to as K. E. Boulding's First Law.[1] For example, nanoscale photonic devices exist that harvest light and convert it to electrochemical potential energy with near quantum efficiency, the photosynthetic apparatus; therefore it must be possible to construct nanoscale quantum-efficient photonic devices. At present, no man-made device comes even close to this efficiency. Self-assembled nanoscale motors such as helicases, isomerases, and kinesins exist, so nanoscale motors must be possible. Self-organized microscale bacteria with nanoscale components such as chloroplasts and mitochondria exist, so nanoscale powerhouses must be possible. Photodriven nanoscale ion pumps such as those in bacteriorhodopsin exist, so nanoscale pumps must be possible. Combined, these illustrate the vast potential for molecular electronics, nanomachines, and nanodevices.

Nanoscale biological devices such as those mentioned above are self-organized and function remarkably efficiently, with the caveat that they can have limited stability.[2] Conversely, machines on this scale composed only of conventional inorganic materials, such as metals, ceramics, glasses, and other rigid composites or polymers, are very unlikely to be able to accomplish similar tasks. For example, photosynthetic antenna complexes, reaction centers, and chloroplasts rely on precise hierarchical self-organization of the molecular components to accomplish their respective functions.

So what are the differences, in terms of molecular engineering, that allow biological systems to accomplish these tasks but not ceramic materials? For all devices, function dictates form, but there are several differences that can be heuristically divided into (1) solvent and (2) dynamics. Because of space limitations, one comparative relevant example is given. Photosynthetic antenna complexes consist of self-assembled arrays of porphyrinic and carotenoid pigments on self-assembled protein scaffolds and can harvest light with near quantum efficiencies.[3,4] The solar energy is funneled to reaction centers, wherein the chromophores are also self-assembled in a protein matrix and which convert the excited-state energy to a potential gradient with similar

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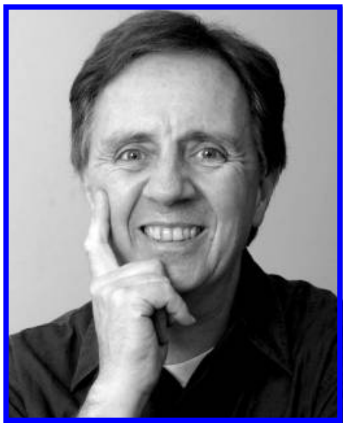
* To whom correspondence should be addressed. E-mail: cdrain@hunter.cuny.edu.
[†] Hunter College.
[‡] Rockefeller University.

10.1021/cr8002483 CCC: $71.50



Charles Michael Drain was born in St. Louis, Missouri, and he received his bachelors degree from the University of Missouri at St. Louis. His doctoral thesis was on porphyrin chemistry, and he received his Ph.D. from Tufts University in 1989 under the supervision of Dr. Barry B. Corden. While doing his postdoctoral work at Rockefeller University with David Mauzerall on exploiting membrane electrostatics and porphyrin assemblies as molecular electronics, he also published a paper with R. Bruce Merrifield on enantiomeric peptide antibiotics. During this time, he was invited by Jean-Marie Lehn to join his laboratory in Strasburg, so he took off for France where he continued his work on the supramolecular chemistry of porphyrins. Upon returning to the United States, he worked with Dewey Holten at Washington University in St. Louis on the excited-state dynamics of distorted porphyrins before joining the faculty at Hunter College of the City University of New York and as an adjunct faculty at the Rockefeller University. Needless to say, he likes porphyrin chemistry. He began rock and ice climbing and mountaineering as a teenager and has climbed mountains on four continents. Chemistry runs in the family since he is the great, great, great grandson of Dr. Antoine Saugrain, noted physician and chemist.

Alessandro Varotto was born in Venice, Italy. In 2004, he received his Laurea in Chemistry at Universita' degli Studi di Padova working on the synthesis of porphyrin dyads as molecular sensors in Professor Tommaso Carofiglio's laboratory. After spending a semester at Boston University, he moved to New York in 2005. He is currently a doctoral student at The City University of New York in Professor Charles M. Drain's laboratory. His research interests include the synthesis of new porphyrinoid derivatives and their supramolecular assembly for the preparation of photonic devices.

Ivana Radivojevic received her Diploma in Chemical Engineering from Faculty of Technology and Metallurgy, University of Belgrade, Serbia, in 2003. She is currently pursuing her doctoral studies in Chemistry at Hunter College, The City University of New York. She is working with Professor Charles M. Drain in his Nanotechnology and Material Science Laboratory. Her primary research interest is based on testing new porphyrin dyes as sensitizers for photovoltaic solar cell devices. She is also working on self-assembly of porphyrin derivatives on surfaces for light-harvesting materials.

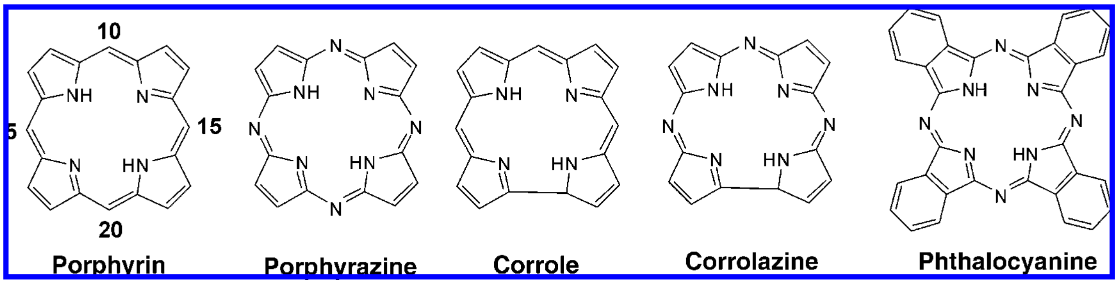
efficiencies.[5] The efficiencies arise from the precise nanoarchitecture of both components of the photosynthetic apparatus mediated by intermolecular interactions between the chromophores and between the protein scaffolds. Just as importantly, there are a myriad of small, local vibrations and conformational changes that constitute the system dynamics that come from both $kT$ energy and the vibrational energy released as the chromophores traverse from the initially formed excited state to the first excited state.[6−8] All the while, this electron pump is operating in a lubricating solvent, water and lipids, which also tunes the dynamics. Thus, the dynamics of specific solute−solvent interactions are also key components of the function. On the other hand, the efficiencies of light harvesting and charge separation by covalently synthesized porphyrin arrays and porphyrin compounds on surfaces or in a matrix are much less than the natural systems. These covalent materials have taught us much in terms of the fundamental photonic principles of multichromophore systems,[9] including the importance of conformational/vibrational dynamics and solvent reorganization energetics.[10]

The corollary of Boulding's law is "Not everything that is possible exists."[1] For example, tetraphenylporphyrin did not exist, that we know of, before it was synthesized in the laboratory. As in nature, self-assembly and self-organization may provide the means to economically construct highly efficient, robust photonic materials.[11] However, there remain keystone issues of local and global dynamics, solvent interactions and dynamics, and asymmetric interactions with substrates that natural machines exploit to accomplish their function.[12−14] Brownian motion, for example, ratchets, and $kT$ energy are also essential features of many biological motors. These dynamics and interactions are difficult to design a priori. In this latter respect, computational efforts may yield insights into experimental results and supramolecular design. What can be learned from a natural machine that processes along DNA and progress in porphyrin-containing mechanical devices are discussed in section 9.

## 1.1. Definitions

There are discussions about the usage of "self-organization," "self-ordering," and "component or molecular assembly" that are based both on the information content of the components or molecules that results in organizational algorithms and on the number of different components.[15] However, the following definitions are used in this review to aid in the presented concepts and perspectives.[11,16,17] There are overlapping areas, and hierarchically organized systems possess different architectures at different size scales, for example, self-assembled porphyrin squares (ca. 4 nm) that organize into liquid crystals or thin films that are a few nanometers thick and cover many square millimeters. **Self-assembly** results in discrete systems with exact geometries,

**Scheme 1. Different Types of Porphyrinoid Structures**



albeit with varying yields, where a missing component is a defect that alters the structure and properties of the system. These are often topologically closed systems. Examples include the self-assembly of supramolecular porphyrin squares. Self-assembly is a subset of self-organization. **Self-organization** results in nondiscrete systems with varying sizes, where a missing component does not alter the structure and the properties are not affected below a critical defect density. These are often topologically open systems, for example, coordination polymers, aggregates, crystals, and monolayers. **Specific intermolecular interactions** are directional motifs designed to recognize complementary components to yield predictable intermolecular interactions, such as H-bonds, metal ion coordination, and dipolar interactions. These generally lead to predictable self-assembled architectures in solution. For example, the coordination of metal ions by 2,2′-bipyridines. **Nonspecific intermolecular interactions** are generally nondirectional, such as dispersion forces and ionic interactions. These generally lead to structures that are difficult to predict; for example, the interactions between pyridinium and sulfonate ions on porphyrins yield many different structures depending on the methods used. **Self-complementary** indicates specific intermolecular interactions between copies of the same groups, for example, the H-bonds between a carboxylic acid dimer. **Heterocomplementary** indicates specific intermolecular interactions between two different groups, for example, Watson−Crick base pairs. **Closed topologies** are squares, rings, cages, spheres, etc., wherein all of the available specific intermolecular interactions are used to form the structure. The formation of closed topologies may or may not be cooperative. **Open topologies** are linear or distorted tapes, wires, tubes, rods, etc., wherein the ends have recognition motifs that are not used in structural organization. **Hierarchical organization**, though there is some confusion in the literature, a priori, involves structures that have *different molecular organization* at different length scales. For example, 3 nm self-assembled porphyrin arrays can be crystallized (ca. millimeter objects), aggregated into 100 nm nanoparticles, or cast into differently organized structures (nanometers high by micrometers wide) on surfaces. Tessellation of two-dimensional arrays, monolayers, and crystalline materials of simple, symmetric porphyrins are generally not hierarchically organized.

## 1.2. Porphyrins

Stable organic chromophores that absorb visible light well and/or, luminesce with high efficiency are good candidates as components of photoelectronic materials, such as sensors, electronics, photosensitized solar cells, and organic light-emitting devices. Porphyrinoids and their metallo derivatives can be used in such devices due to their unique aromatic structure and excellent photochemical and photophysical properties.[18−21] In addition to the molecular structure, the photonic properties are highly dependent on the architectural arrangement of the chromophores and the environment. The structures of key synthetic porphyrinoids are given in Scheme 1. The rigid, planar macrocycles are amenable to appending a variety of auxiliary moieties, such as H-bonding motifs and exocyclic ligands, at predefined geometries for the synthesis of designed supramolecular systems.[22] The core porphyrinoid is stable under a wide range of temperatures, pH, and other environmental conditions. The oxidation and reduction potentials, and therefore the chemical and photonic activities, can be tuned by appending a variety of exocyclic organic motifs and by choice of metal ion chelated in the center of anionic porphyrinoid. Axial ligation of the metalated compounds affords an additional means for assembly or organization. Most of the supramolecular chemistry of these macrocycles focuses on porphyrins because of their well-developed chemistry. While liquid crystalline phthalocyanine materials are common, there is a paucity of reported work on discrete self-assembled structures of phthalocyanines, porphyrazines, coroles, and corolazines. In addition to their chemical and photophysical similarities to the hemes and chlorophylls, porphyrins can be considered as ideal molecules for the construction of photonic systems.

Porphyrins are tetrapyrrolic macrocycles that are ubiquitous in nature.[23] In general, porphyrins have very strong absorption bands around 400−430 nm (Soret band) with absorptivities, $\varepsilon$, on the order of $10^5$ $M^{-1}$ $cm^{-1}$ and several Q-bands between 500 and 650 nm with $\varepsilon$ 10−20 times less. The electronic spectra depend on the exocyclic modifications and coordinated metal ion and are well explained by the Gouterman four-orbital model.[24] The other porphyrinoids also have strong absorptions, generally to the red of the porphyrins.[18] The fluorescence quantum yield of typical free base porphyrins and some of their metalloderivatives (e.g., $Zn^{2+}$, $Mg^{2+}$) range from ca. 1% to 15%, with corresponding lifetimes between ca. 1 and 15 ns. For these systems, a substantial percentage of the molecules in the excited state intersystem cross to the triplet state, such that the phosphorescence quantum yield in matrices can be over 90%, for example, for Pd and Pt derivatives used in oxygen pressure sensing.[25] For many open-shell metal ions such as Ni(II), the excited-state energy is shunted to a metal-centered excited d,d state in a few picoseconds,[26−28] or charge transfer complexes may form.[20] Distortion of the nominally planar porphyrin results in substantial shifts in the electronic spectra and the excited-state properties.[29,30] The highly distorted Ni(II) 5,10,15,20-tetra-*tert*-butylporphyrin is an excellent example of the interrelated effects of substituents, macrocycle conformation, chelated metal ion, and environmental factors on the ground-state and excited-state energy landscapes. The excited-state lifetime of this metalloporphyrin can be tuned over 6 orders of magnitude, picoseconds to microseconds, by choice of solvent properties, because of the conformational dynamics available to the metal-centered d,d state.[26] Axial ligands to metalloporphyrins can also have a profound effect on excited-state dynamics.[27]

## 1.3. Supramolecular Porphyrin Materials

For some applications, such as solar energy harvesting,[31] several chromophores are needed to collect light from the entire solar spectrum and to maximize optical density.[32] Therefore as in nature, construction of multichromophoric systems or materials is important to ensure maximum use of solar energy. Arrays containing different kinds of dyes can be engineered in several ways. (1) To ensure vectoral energy and electron transfer, the architectural organization of the chromophores must be specifically designed such that molecules with the greatest HOMO−LUMO gap can funnel energy/electrons to those with the lowest HOMO−LUMO gap next to the electrode. Supramolecular systems afford a viable means to accomplish this. (2) Spatially separated chromophores in patterns with periodicity less than ca. 400 nm may ensure maximal charge injection into the electrode without competing energy and electron transfer to neighboring dyes with different electronic properties. The latter strategy can be accomplished by adsorbing the dyes onto different nanoparticles and by nanolithography. The former strategy is employed in natural light-harvesting systems in photosynthesis,[3,4,33,34] wherein the photonic properties of the antenna systems are controlled by the spatial arrangement and orientation of the various chromophores self-assembled on a protein scaffold.

Given the potential applications and the need for better theoretical frameworks, the design and construction of novel multiporphyrin architectures by self-assembly and self-organization continues to be an active research area. The self-organization of a single type of porphyrin into crystalline materials using nonspecific intermolecular interactions and homocoordination has a long rich history.[21,35−39] More recent efforts have incorporated exocyclic moieties for specific intermolecular interactions that direct the organization of a given porphyrin into more ordered or more robust crystalline systems.[40,41] An early example of discrete porphyrin arrays are those self-assembled using electrostatic interactions in the liquid crystalline matrix of lipid bilayers, which functioned as photogated ion conductors.[42−44] Later, arrays assembled by specific intermolecular interactions such as by H-bonds[45−47] and by metal ion coordination were reported.[46,48−50] Linear tapes assembled with H-bonds and with coordination chemistry placed in lipid bilayers exhibit photogated electronic conductivity wherein the function of the device relies on the hierarchical structure: molecule, tape, alignment of the tapes in the bilayer, and the organization of the device itself.[11] Self-organized systems with different topologies can be formed using designed intermolecular interactions, but additionally, long chain hydrocarbons can be used for the formation of liquid crystals. Covalent attachment to surfaces results in self-assembled monolayers, and packing forces in crystalline materials can be designed. New venues toward the crystal engineering of porphyrins into lattices include iodopyridyl and iodophenyl halogen bonding, but the robustness of these interactions needs to be further investigated.[51,52]

Supramolecular synthetic methods and strategies have developed rapidly, and porphyrins are particularly amenable to the design of complex and robust architectures because of their rigid framework. One-, two-, and three-dimensional materials are now routinely accessible. Strategies to make hierarchically organized porphyrinic materials, wherein the local structure is different than the global organization,[50] are now a research focus. These porphyrin assemblies are of fundamental importance not only as models for the study of light-harvesting antenna and photosynthetic reaction centers, but also as building blocks for the construction of variety of functional photonic devices.[32]

## 1.4. Supramolecular Dynamics

*Thermodynamics* are important considerations in the design and function of self-assembled or -organized materials[53−55] and for comparison and understanding of these processes in natural systems.[15] One of the issues in terms of definitions is the relative energetics needed to self-assemble or self-organize a system. In the laboratory, we use thermal energy, at room temperature or refluxing in a solvent, to improve yields of self-assembled or -organized systems or to reduce the time needed to reach equilibrium or both. Biological systems use ambient temperature and the local chemical and thermal energy obtained from chemical reactions. The often cited hallmark of self-assembly or self-organization is spontaneity, yet whether or not a reaction is spontaneous depends on the temperature or energy input. ATP hydrolysis in biological systems provides both chemical and thermal energy. A second issue is one of equilibrium: Must all self-organized systems be at equilibrium? The answer to these questions must be relative to the energetics and time scale of interest.[15] Any man-made material eventually decomposes to more thermodynamically stable products. The majority of self-assembled or -organized systems discussed herein are spontaneously formed within a narrow temperature window of ca. 100 °C and short times of less than a few weeks. Photoinduced conformational changes are one means of supplying an internal driving force, and internal conversion of photoexcited states to heat allows some control of the degree of aggregation.[56−58] Sonication has been used for decades in the formation of liposomes and more recently for self-organization of porphyrin nanorods.[59]

*Conformational dynamics* of both the constituent porphyrins and the intermolecular interactions in supramolecular systems are important considerations in the use of these macrocycles in photonic materials because this strongly affects the function. Dynamics are more complex in hierarchically organized materials. In meso aryl porphyrins, the rotation barrier about the porphyrin−phenyl bond is 20−30 kcal/mol depending on the nature of the ortho substituents and other factors such as chelated metal ion.[60] The rotation barrier of a coordinated axial pyridyl ligand or pyridyl coordination to a metal ion is ca. 18 kcal/mol.[60] The dynamics are proportional to the strength of the interaction and the environment. For photonic materials, the local heating of the materials upon light absorption can transiently diminish the intermolecular interactions, thereby reducing the electronic coupling of the chromophores and diminishing energy or electron transfer. Thus, the function of supramolecular photonic materials may decrease with increasing light flux.

Conversely, the flexibility of molecular and supramolecular constructs can be exploited, especially in terms of host−guest chemistry. The preorganization of the host to chemically and topologically bind a guest significantly increases the binding, but an appropriate degree of flexibility in the host can further enhance the intermolecular interactions by an induced fit mechanism.[61] This concept is illustrated by the reports on using porphyrins as “molecular tweezers”; for example,

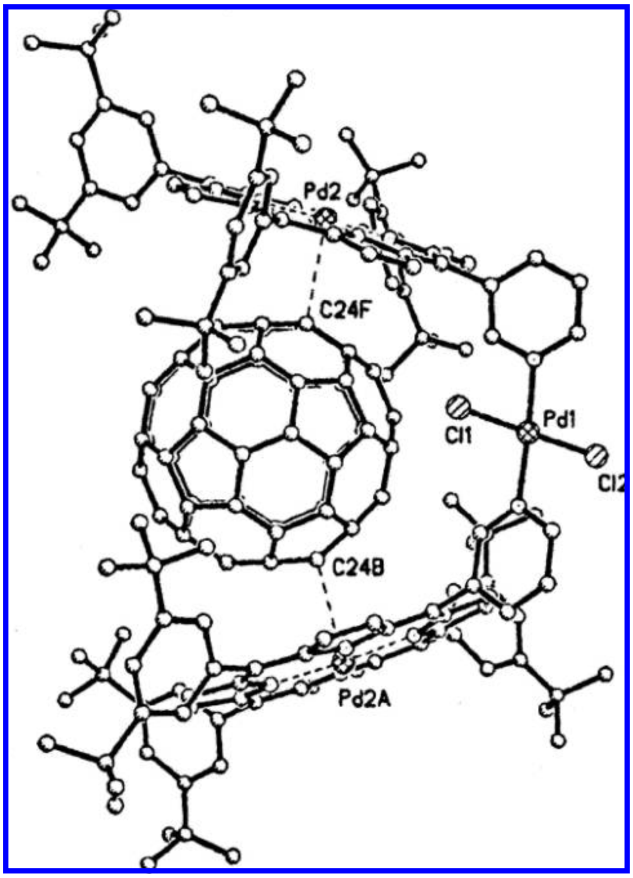


**Figure 1.** X-ray crystal structure of a porphyrin dyad with encapsulated $C_{60}$. The Pd2···C24F distance is 2.856(10) Å. A combination of $\pi-\pi$ interactions and electrostatic forces between the porphyrins in the tweezers allow the complexation of the fullerene. Reproduced from ref 62. Copyright 2002 American Chemical Society.

covalently bound porphyrins tethered with flexible hydrocarbons can bind $C_{60}$ (Figure 1) better than the individual unit or those with rigid tethers.[62,63] An additional consequence of supramolecular dynamics and equilibriums is that there is no a priori correspondence between the supramolecular structure in solution and in the solid state.

## 2. Scope

Covalently linked porphyrin architectures have advantages in terms of characterization and can be organized into materials[9,64−67] but have disadvantages in terms of synthetic scalability and complexity, and thus are beyond the present scope and are reviewed elsewhere.[9] Because of the versatility and structural stability afforded by coordination chemistry, this is perhaps the most studied aspect of supramolecular materials of porphyrins,[22,48,49,68−72] and metalloporphyrin constructs are covered in the adjacent review. This review will focus on the formation and function of supramolecular porphyrinic materials assembled, organized, or both by intermolecular interactions other than coordination chemistry. Coordination assemblies with analogous topologies to specific examples discussed will be included to compare how the different intermolecular interactions impact function. Some systems self-assembled by coordination chemistry that subsequently organize into solid state materials by other forces are included, for example, films and crystals.[41,50] In some instances, materials composed of one of the other porphyrinoids are included to compare the chemistry and properties of the porphyrin system. The emphasis will be on recent developments (since 2004) in the context of some of the initial concepts in porphyrin materials design and organization. There are several previous reviews on porphyrin organization by coordination chemistry,[72−74] and other intermolecular interactions.[22,68−70] There have been several reviews on supramolecular capsules as reactors,[75] nanoarchitectures by self-assembly,[55] assembly of extended aromatic systems,[76] molecular rods,[77] and rotors[60] that include sections on porphyrins and related macrocycles.

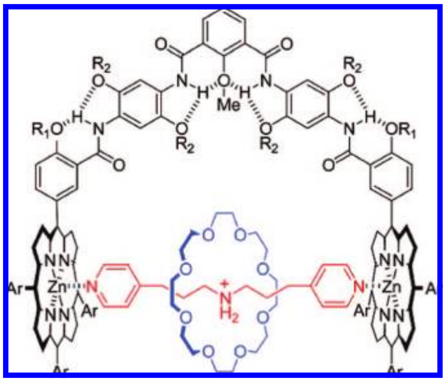


**Figure 2.** Intramolecular hydrogen bonds help to preorganize a porphyrin dimer to bind and cap a rotaxane, as well as stabilize the final structure. Reproduced from ref 86. Copyright 2007 American Chemical Society.

## 3. Self-Organization by Hydrogen Bonds

H-bonding can be a remarkably diverse driving force for the self-assembly and self-organization of materials. The exact nature of H-bonds, for example, the degree of electrostatic character, remains a topic of considerable interest.[78,79] H-bonds are commonly used for the fabrication of supramolecular assemblies because they are directional and have a wide range of interaction energies that are tunable by adjusting the number of H-bonds, their relative orientation, and their position in the overall structure.[80−82] H-bonds in the center of protein helices can be ca. 20 kcal $mol^{-1}$ due to cooperative dipolar interactions.[83,80]

### 3.1. Intramolecular H-Bonding

There are several porphyrinic systems where intramolecular H-bonds of a backbone or linking component helps to preorganize the molecular geometry so that it can bind a guest,[84] reversibly position the chromophores to switch photonic properties,[85] or lock in the ends of a rotaxane.[86] Control of intramolecular H-bonds in the oligoamide spacer of a Zn porphyrin dimer allows control of the molecular conformation so that it preorganizes the metalloporphyrins to bind the pyridyl ends of a rotaxane to form a three-component system. The binding of the guest reinforces the nanoarchitecture of the host (Figure 2).[86]

### 3.2. Intermolecular H-Bonding

Porphyrins bearing multiple H-bonding donor and acceptor groups are being investigated as components of new materials for a diverse array of applications[87] and to study the fundamental photophysics of these systems.[88] Because the porphyrin macrocycle is rigid, the placement of rigid H-bonding moieties and their relative orientation allows the design of a variety of specific architectures. For example, H-bond groups directed along the plane of the macrocycle and on the 5,10-meso positions afford a molecule with a rigid right angle topology,[89,90] whereas when these groups are on opposite sides, the 5 and 15 positions, a linear topology results. Alternatively, the H-bond groups can be directed above or below the plane of the macrocycle to organize structures vertically.[90] The variety of supramolecular structures using H-bonds as a primary driver of nanoarchitecture range from open to closed topologies, films on surfaces, tubes, wires, rods, and more complex 3D architectures. As with other supramolecular systems, the structure of solid state materials is also mediated by other nonspecific or designed intermolecular interactions. The synergistic combination of different intermolecular interactions such as metal ion coordination and $\pi$-stacking with H-bonding allows formation of more robust materials and diversifies the possible structural orientation of the chromophores.[87,91,92] These self-assembled structures can be used in sensors, molecular sieves, photonics, and catalysis.[69]

### *3.2.1. Open Structures*

The carboxyphenyl group is one of the most used functionalities for the formation of supramolecular porphyrin materials driven by H-bonding because these compounds are easy to make. Many different solid-state porphyrin structures exploit the two H-bonds in the self-complementary interactions of meso carboxyphenyl groups as the primary means of organization.[87] Since H-bonds are reversible intermolecular interactions, varying the solvent of crystallization or using them for casting onto surfaces can result in significantly different structures.[93] The commercially available tetra-(4-carboxyphenyl)porphyrin (TCPP), for example, can form many different porphyrin structures depending on crystal growth conditions such as pH, auxiliary interactions with metal ions such as lanthanide ions,[94] and other auxiliary motifs. Two-dimensional square grid arrays are formed when the porphyrin units form H-bonds with each other through their carboxylic acid groups.[87] Alternatively, 2D and 3D arrays are generated by intermolecular H-bonding moieties between the carboxyl groups and hydroxyl ligand substituents.[87,95]

Supramolecular systems with structures directed by H-bonds using heterocomplementary interactions between different exocyclic substituents allow construction of more complex systems. This strategy allows the construction of materials with two different porphyrins, thereby increasing the diversity and the potential properties of the resultant materials.[70,89] For example, the carboxy groups on two Zn(II)5-(4-carboxyphenyl)-10,15,20-(triphenyl)porphyrins combine with the amino groups of *trans*-1,2-diaminocyclohexane to form a ternary system organized by H-bonding and Coulombic interactions, which can accept various diamine guests[96] When the recognition motifs are rigidly attached to the porphyrin, the formation of the linear or cyclic arrays depends on the positions of these motifs, but when flexible spacers tether the recognition motifs, the topology is largely directed by the nature of the spacer.[97] Triazines are a versatile scaffold for porphyrin arrays.[45,69,98] Supramolecular network structures can be formed by a porphyrin dimer using triazine as a spacer that works both as a scaffold for the porphyrin and as a source of H-bonds for the construction of the array.[99]

Mashiko and co-workers reported self-organization of TCPP on a Au(111) surface via H-bonding wherein supramolecular wires are formed first, and as the surface density increases, thin films result.[100] In acidic solutions, the organization of porphyrins with H-bonding groups on the surface of Au(111) electrodes can be controlled by changing the number of carboxy groups and the applied electrochemical potential.[101] Reaction of the Pd, Ru, and Cu complexes of TCPP with a Lewis base such as pyridine or DMSO induces the formation of different structural motifs with different H-bonding patterns mediated by the Lewis bases.[77,102] The formation of a homodimer mediated by the four H-bonds of a 2-ureidopyrimidin-4(1*H*)-one group on a zinc porphyrin allows the selective recognition of diamine guests (Figure 3).[78,79,103]

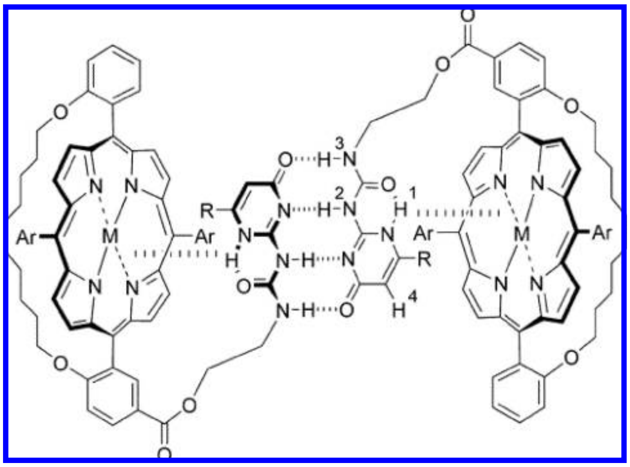


**Figure 3.** Intermolecular self-complementary hydrogen-bonding groups mediate the assembly of an open porphyrin dimer. Note that intramolecular hydrogen bonds help to orient the recognition motifs, and the atropisomerization is minimized by the strap between the meso aryl groups. Reproduced from ref 103. Copyright 2004 American Chemical Society.

The vast majority of crystalline materials of porphyrins possess a center of symmetry, but crystals lacking a center of symmetry have the greatest potential as nonlinear optical materials. Goldberg et al. have shown that noncentrosymmetric supramolecular structures can be formed by free-base 5-(3′-pyridyl)-10,15,20-tris(4′-carboxyphenyl)porphyrin and 5-(2′-quinolyl)-10,15,20-tris(4′-hydroxyphenyl)porphyrin molecules.[104] In both cases, the porphyrin building block is connected to neighboring species in a cooperative but asymmetric manner by a combination of O−H···O and O−H···N interporphyrin H-bonds, where optimal O−H···N interactions involve molecules related by 2-fold screw symmetry and the formation of two-dimensional arrays (Figure 4).[104]

Goldberg et al. refer to the exocyclic motifs on porphyrins as converging if they tend toward formation of closed systems and diverging if they tend to form open lattices; thus Zn-5-(3′-pyridyl)-10,15,20-tris(4′-hydroxyphenyl)porphyrin bears a converging pyridyl moiety and three diverging phenolic H-bonding sites. This molecule forms a tetrameric square architecture that is further organized in hierarchical structure in the solid state.[36,37,92,93,105]

Depending on the coordination chemistry of the metal ion, the one or two axial positions of metalloporphyrins can provide secondary motifs for the organization of materials. Though most structures exploit axial coordination by organic ligands, H-bonding by axial hydroxyl groups to water or other molecules can facilitate the organization of new materials. Several solid-state supramolecular structures can be formed by the interaction of dihydroxy tin(IV)tetra(4-pyridyl)porphyrin, $(OH)_2Sn(IV)(TPyP)$, with water. H-bond-

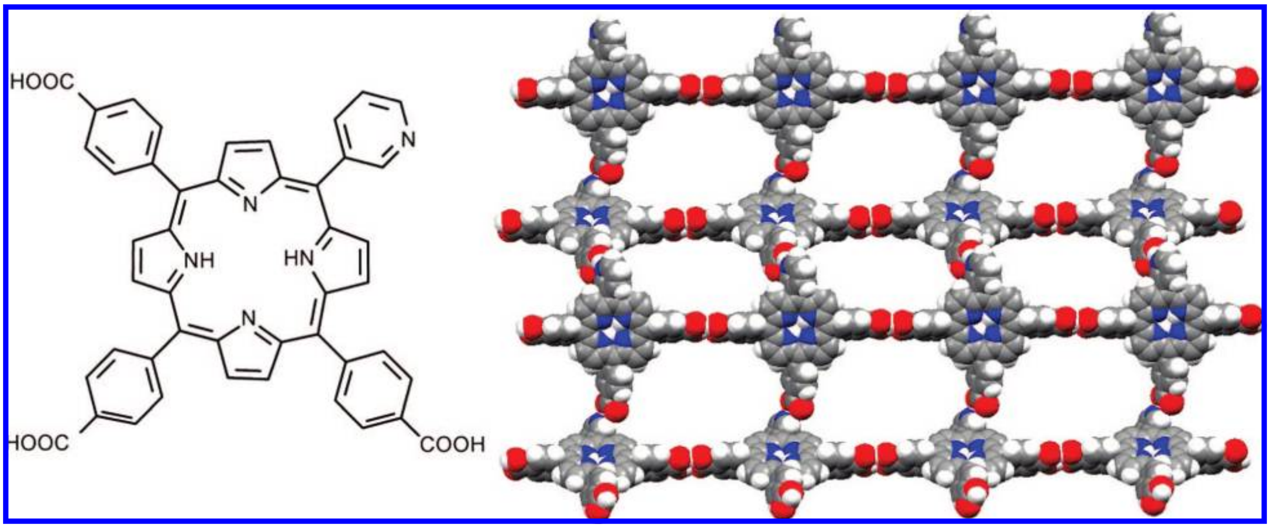


**Figure 4.** Mono-(3-pyridyl)-tris-(4-carboxyphenyl)porphyrin forms a noncentrosymmetric space group *P*21 with a 2-fold screw axis running in the vertical direction driven by the COOH···N(py) hydrogen bonds wrapped around in a helical manner. (Courtesy of I. Goldberg).[104]

ing between neighboring water molecules results in a helical arrangement, and this modulates the formation of alternating planes of $(OH)_2Sn(IV)(TPyP)$ and water.[106,107] Since the topology of the molecule often dictates the molecular organization, using a different disposition of exocyclic recognition motifs results in a different structure. H-bonding between the axial hydroxyl ligands of a dihydroxy tin(IV)5-pyridyl-10,15,20-(triphenyl)porphyrin molecule and the pyridyl group of an adjacent molecule via a bridging water molecule, along with hydrophobic forces and $\pi-\pi$ interactions, results in the formation of nanosheets of the molecules in a square arrangement.[85,86,108] Other examples of H-bonding between axial ligands are metalloporphyrins inclusion materials.[109] H-bonding interactions between four para phenolic protons on tetra(3,5,-dimethyl-4-hydroxyphenyl)porphyrin and neighboring pyrrole imino nitrogen atoms can result in formation of linear arrays of molecules in hatch-like structures.[110] The two methyl groups on each phenol moiety likely participate in dictating the structure by steric interactions, both in the crystal structure and in the organization of these molecules into cyclic trimers, arrays, and lattice structures on surfaces.[110]

### *3.2.2. Closed Structures*

Supramolecular porphyrin arrays assembled with H-bonds into closed topologies can have different functionalities as receptors, capsules, and photonics.[45,69,70] For example, Inouye and co-workers have reported a supramolecular cage consisting of two porphyrins self-assembled using self-complementary aminopyrimidinone moieties with spacers large enough to accommodate $C_{60}$ as a guest.[88] Here, H-bonding groups are also important for interactions with $C_{60}$ guest.

Complementary H-bonded melamine–barbituric acid motifs can form rosettes or tapes with porphyrins appended to the melamine[45] or to the barbituric acid.[111] More robust structures can be formed by introduction of a strapped porphyrin unit to the cyanuric acid moiety, and this can be used as supramolecular receptors for binding large molecules.[103,111] Another example of a self-assembled capsule results from the four H-bonds formed between a tetracarboxylcalixarene and *meso*-tetra(2-pyridyl)porphyrin.[112] The flexibility of the host allows it to encapsulate various small guest molecules ranging in size from methane to THF (Figure 5). A similar approach uses four cucurbiturils to host four pyridinium moieties on $TPyP^{4+}$ in nonpolar solvents.[113] Supramolecular capsules are proposed to be suitable molecule storage containers, as a method for separation, sensors, as catalyst for some chemical reactions,[75,112] as well as in therapeutic applications.[113] Different atropisomers of a 5,15-meso-substituted methyluracyl porphyrin derivative and an alkylated melamine form different supramolecular structures. The αα isomer forms a face to face dimer, whereas the $\alpha\beta$ isomer takes a zigzag structure (Figure 6).[114] The conformation of a covalent porphyrin dimer can be switched from a cofacial to a linear arrangement by choice of solvent, thereby the photophysical properties of the system can be tuned by the relative position and the spacing of the chromophores and by the solvent.[114]

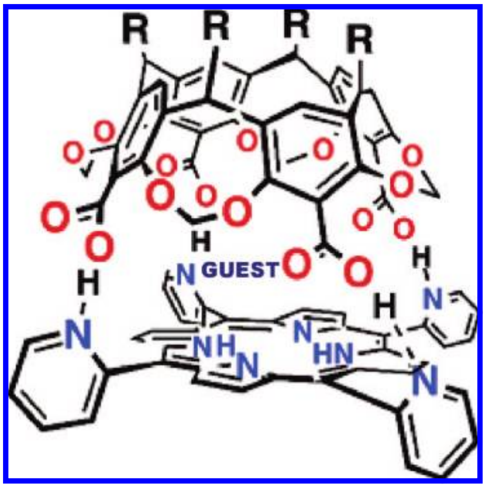


**Figure 5.** Reversible self-assembly of host capsule formed by hydrogen bonding to a calixerane allows it to discriminate between possible guests. Reproduced from ref 112. Copyright 2006 American Chemical Society.

## 3.3. Energy Transfer in Systems Organized by Hydrogen Bonds

Arrays of porphyrins assembled by covalent[9] and noncovalent[115] interactions are used as model systems to mimic natural photosynthesis. Supramolecular systems are used to understand the mechanism of electron transfer through

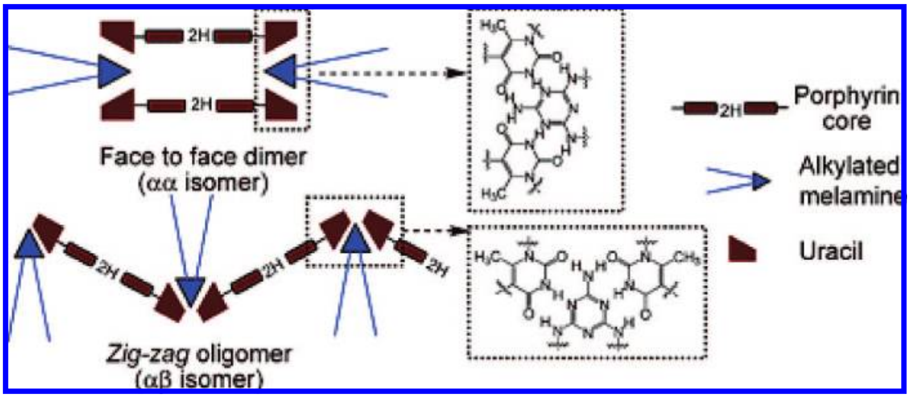


**Figure 6.** Atropisomers of uracyls on the 5 and 15 positions of a porphyrin dictate the formation of closed, face-to-face dimers or open zigzag chains when the complementary melamine is added. Reproduced from ref 114. Copyright 2007 American Chemical Society.

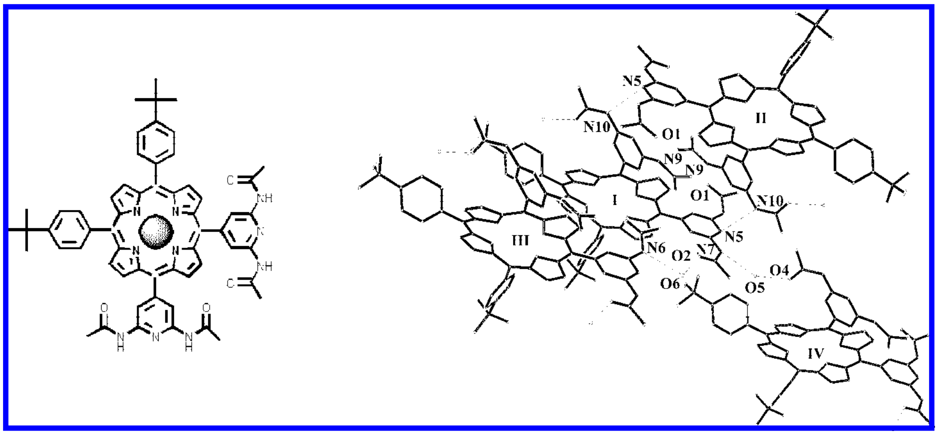


**Figure 7.** Self-assembly of square helix by self-complementary hydrogen-bonding motifs. The recognition groups are attached directly to the meso positions of the porphyrins. Thus, the optimal positioning minimizes the dynamics that would decrease the structural fidelity of the assembled systems. Reproduced from ref 89. Copyright 2001 American Chemical Society.

intermolecular interactions. Nearly isoenergetic covalent porphyrin multimers on surfaces have electron transfer kinetics complicated by reverse reactions,[116] thus systems with different porphyrins or combinations of porphyrinoids arranged from greatest to least HOMO−LUMO energy gaps may afford better vectoral electron transfer. Beyond donor−acceptor dyads, it is difficult to design and precisely assemble in high yields multiple component structures with different dyes that possess energetic gradients (HOMO−LUMO gaps). Good yields with high structural fidelity are needed to examine the kinetics of electron or energy transfer down the energy gradient. However, recent work done using H-bonds and coordination chemistry to assemble arrays of porphyrins shows that efficient energy transfer may occur across the intermolecular bonds.[97,117] Meijer et al. report the observation of energy transfer from two oligo(*p*-phenylenevinylene) groups to a free base porphyrin assembled with cyanuric acid and complementary diaminotriazine motifs. This trimer then organizes into a helical structure by $\pi-\pi$ stacking and H-bonds.[118] A similar covalent, amide-linked system with a central porphyrin surrounded by four phenylenevinylene groups organizes into H-aggregates mediated by $\pi$-stacking and H-bonds. The organization of this material into H aggregates facilitates energy transfer along the stack direction.[118,119] Other examples of H-bond-mediated structures include the self-assembly of a porphyrin dimer by carboxyl−amino interactions and by other H-bonding interactions, which result in systems that may allow electron transfer from a metalloporphyrin donor to a porphyrin acceptor.[103,105]

H-bonding moieties directly attached to the meso positions result in rigid topologies that favor formation of organized structures. Similar to the coordination arrays, the use of heterocomplementary H-bond recognition units, such as 2,6-diacetamidopyridyl and uracyl, at specified geometries allows assembly of porphyrin dimers, tapes, tetrameric squares, and two-dimensional sheets with various yields.[69,70,89,120] The right angle disposition of 5,15-(3,5-diacetamido-4-pyridyl) groups results in self-complementary interactions between porphyrins to form a square structure in solution, but in crystals of this array, one of the porphyrins cants at an angle to form a square helical structure that allows denser packing (Figure 7).[89,120] This illustrates the differences that can be found between solution and solid-state structures. Steady-state fluorescence of some of these square arrays indicates energy transfer across the H-bonding groups,[90,120] but not reported are lifetime and electron transfer measurements analogous to those on the recent square array assembled by coordination chemistry.[121]

However, the synthesis of many of the porphyrins described in this section is challenging for several reasons, such as difficulties in preparing the precursor aldehydes and separation of statistical mixtures of compounds and isomers after condensation with the pyrrole. The synthesis of porphyrins with meso aryl groups appended with a saturated tether terminated in similar recognition motifs is significantly easier, but the dynamics of the tether result in the formation of nondiscrete aggregates of varying sizes.[97] Nonetheless, self-assembly of these systems into dimers and self-organization into nanoaggregates results in systems where electron transfer rates can be measured. Notably, these rates are different depending on the direction across the asymmetric H-bond moieties.[97]

## 3.4. Summary

H-bonding interactions can result in stable supramolecular systems of porphyrins. The one-, two-, and three-dimensional arrays of porphyrins are used to mimic and study photosynthetic antenna systems and energy/electron transfer. The formation of capsule and cavity hosts that are tailored to a given guest is reported, but the exploitation of the reversibility of the H-bonding interactions to reversibly bind, transport, and release a guest remains to be demonstrated. An alternative mode of operation might be to form crystals or solids that bind a gaseous guest at one partial pressure or temperature and release it at a lower partial pressure or temperature. Materials relying primarily on weak H-bonding interactions between small molecules for structural integrity may have problems with stability in real-world applications. However, from another standpoint these materials may be self-healing to damage or may be reannealed. Considering that proton coupled electron transfer reactions can be more efficient, it may be that systems self-assembled and self-organized using H-bonds may be more efficient mediators of electron transfer than heretofore appreciated,[122−124] which may be akin to photogated charge sensitive ion conducting systems in bilayers.[11,42]

## *4. Self-Assembly and Self-Organization of Porphyrin Thin Films on Surfaces*

Because of the potential applications of porphyrinic nanomaterials in areas such as molecular electronics or photonics and for semiconductor sensitization, there has been a great interest in utilizing supramolecular chemistry as a means to fabricate components for nanoscale devices. However, in order to make stable and useful solid nanoarchitectures, the self-assembled and self-organized systems have to be transferred from solution onto a surface while maintaining the same or at least predictable structure and function. Deposition onto surfaces can be challenging since the equilibriums and therefore structures in supramolecular systems can significantly change upon altering the environment. These factors include solvent, concentration, temperature, moisture, and evaporation rate. For weakly interacting molecules deposited from solvents (drop cast, spin cast, and dipping), solvent dynamics, in terms of microscopic flow and shear, play a crucial role in the morphology of the resultant film. Microscale and nanoscale rings, rods, and fibers can be formed as a consequence of both intermolecular interactions and solvent dynamics.[125,126] The angle of the substrate during deposition, whether it is held horizontal or vertical, can make significant differences. Since surface energetics and surface structure can have a significant influence on the organization of molecules on surfaces, from a different standpoint, surface properties can be used as another design tool. Matching surface chemistry to linking groups, for example, gold and thiols, and energetics to molecules, for example, HOPG and large aromatic molecules, can yield highly organized monolayers. Additionally, useful nanomaterials should be long lasting and resistant to environmental influences like humidity, dioxygen, or redox chemistry.[22,68]

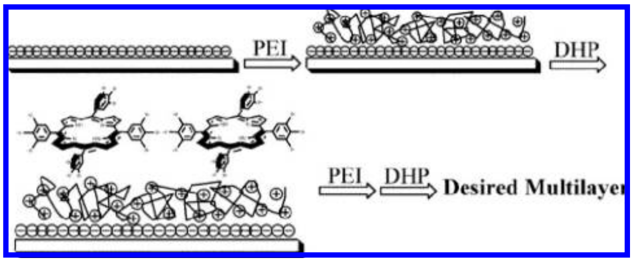


**Figure 8.** Electrostatic self-assembly of multilayers on quartz can result in porphyrinic films with good NLO properties. Reproduced from ref 141. Copyright 2005 American Chemical Society.

There have been many reports on self-assembled and self-organized porphyrinic systems deposited on surfaces.[68] Recent work using H-bonds between stereogenic centers probed the role of chiral centers on surface assembly in two dimensions, where it was found by STM that only one of the two porphyrin faces is oriented toward the HOPG surface.[127] We focus on multicomponent, two-dimensional porphyrin materials, self-organized into multilayer thin films, as well as 2D ordering of molecules on solid surfaces. Various degrees of molecular organization can be obtained through several deposition methods.[22,68,69] (1) Multilayer thin films on surfaces can be fabricated by layer-by-layer and sequential dipping methods that rely on noncovalent electrostatic, ionic, coordination, or H-bonding interactions,[68] and (2) self-assembled monolayers (SAMs) bind to surfaces via covalent or coordination bonds or by absorption. Scanning probe microscopy (AFM or STM) are key tools in examining the structure of these materials on a surface.

## 4.1. Layer-by-Layer Methods

Generally, layer-by-layer (LBL) methods consist of dipping a charged substrate into a solution containing a molecule or polyelectrolyte of the opposite charge, resulting in the formation of a layer of material on the surface.[128,129] After annealing and rinsing, the substrate is immersed into a second solution containing a molecule or polyelectrolyte of opposite charge than that in the first solution. Thus, each dipping results in a film electrostatically absorbed onto the surface. The films are not a priori complete, and often they interdigitate. This method enables formation of multilayer films since the same procedure can be repeated many times. A large number of layers is possible, but the fidelity and structure of the films can change, usually decrease, with an increasing number of layers.[22,68−70] While charged supports such as mica allow more rapid development of the initial layers, polar oxide surfaces such as glass and ITO can be used, but several dipping cycles are usually necessary to form complete films of charged molecules.

There are many reports on LBL porphyrin materials for use as sensors[130−137] for modification of electrodes,[69] for photovoltaics,[138−140] and for nonlinear optic (NLO) materials.[130,141] Here we point out several examples of thin films composed of porphyrins and other diverse components. The electrostatic deposition of 20 bilayers of 5,10,15,20-tetrakis(3,4,5-trihydroxyphenyl)porphyrin and an oppositely charged polyethylenimine polymer results in a film with strong NLO properties.[141] A periodic donor−acceptor layered system using the same anionic dodecahydroxy porphyrin as a donor and a water-soluble fullerene derivative with two quaternary ammonium moieties as the acceptor results in another NLO material with a nonlinear absorption coefficient of $-7 \times 10^{-6}$

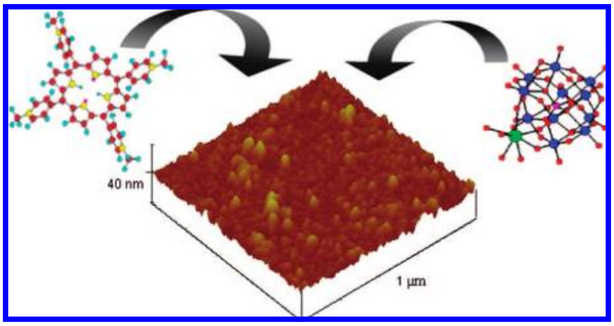


**Figure 9.** Films fabricated by electrostatic interaction from tetra-*N*-methylpyridiniumporphyrin$^{4+}$ and $[EuPW_{11}O_{39}]^{4-}$ polyoxometalate using a sequential dipping method on an ITO surface, an example of multilayered architecture created from small molecules. Reproduced from ref 147. Copyright 2007 American Chemical Society.

m/W (Figure 8).[130,141] These results are notable considering that the materials are noncrystalline, layered systems.

Multilayered electrocatalysts can be fabricated using electrostatic assembly of porphyrins and phthalocyanines[126,141−143] and porphyrins with other materials.[141] A notable example of electrostatic assembly of porphyrins with polymers uses anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and polycationic polyallylamine where the optical properties are controlled by the pH (J-aggregates form below pH 1.5, while above pH 3.0 H-aggregates are observed).[144] Interestingly, tetrakis(4-sulfonatophenyl)porphyrin forms J-aggregates in ionic liquids of 1-butyl-3-methyllimidazolium tetrafluoroborate, suggesting an ionic assembly mechanism.[145]

Supramolecular thin films fashioned from sequential dipping of substrates into a solution of a cationic porphyrin followed by dipping into a solution of an anionic polyoxometalates (POM) (or vice versa) can have properties that are a result of both components. Like porphyrins, POMs are stable and have a diverse array of properties that make them suitable for an array of applications as catalysts, sensors, and electron conduits.[146] For example, robust thin films can be formed by electrostatic interactions between cationic porphyrins such as tetra-*N*-methylpyridiniumporphyrin ($TPyP^{4+}$) and anionic POM $[EuPW_{11}O_{39}]^{4-}$ on mica or ITO substrates[69,147] (Figure 9). The important findings in this system are that both components can be small molecules, that the number of dipping cycles it takes to make a complete film depends on surface energetics, and that the order of the two components in the film can increase with the number of layers. Other porphyrin−POM films on electrodes have been reported to have catalytic activities.[148−150]

Thin films can also be assembled using ionic interactions[151] or H-bonding interactions,[134] where the ionic interactions organize the material so that the components can be covalently cross-linked by UV irradiation to produce films of greater stability that can have increased photoelectric properties. H-bond interactions between *meso*-carboxyphenyl-substituted porphyrins on Au(111) initially organize into 2D ribbon and 3D wire-like structures, but after more deposition cycles, thin films result.[100] Similar step-by-step methodologies can be used to create porphyrin/$TiO_2$/$C_{60}$ trilayers films that are photoactive materials that exhibit electron transfer from the porphyrins, such as TCPP, to the fullerene mediated by a nanometer thick layer of $TiO_2$.[152]

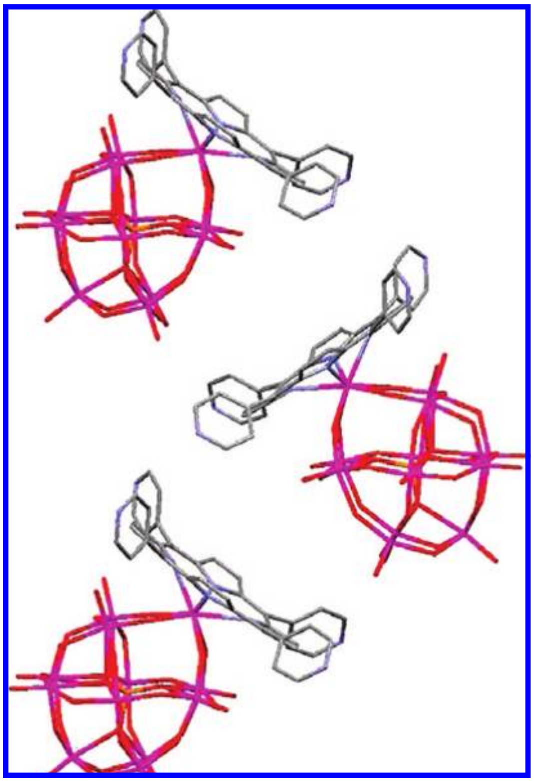


**Figure 10.** Crystal packing of the $[(TPyP)Hf(PW_{11}O_{39})]^{-5}$ complex shows formation of the zigzag pattern along the *a*-axis, solvent omitted, where the top surface of one porphyrin approaches the side of the POM of an adjacent complex. The structure is reinforced by H-bonds between water and the pyridyl moeieties.[153]

### *4.1.1. Porphyrin−Metal−Polyoxometalate Complexes*

Discrete, ternary porphyrin−metal−polyoxometalate (Por−M−POM) complexes, where M is a Hf(IV) or Zr(IV) metal ion bound both to the porphyrin core and to the lacunary site of a Keggin POM, $PW_{11}O_{39}{}^{-7}$, can be nearly quantitatively prepared.[153] The seven to eight coordination and large size of the metal ions forces them to reside outside the plane of the porphyrin macrocycle and protrude from the Keggin POM, thus enabling the simultaneous coordination to both. The physical properties of the $(TPP)Hf(PW_{11}O_{39})[TBA]_5$, $(TPyP)Hf(PW_{11}O_{39})[TBA]_5$, and $(TPP)Zr(PW_{11}O_{39})[TBA]_5$ complexes are similar. The crystal structure of $(TPyP)Hf(PW_{11}O_{39})[TBA]_5$ (Figure 10) is organized by H-bonding of water to the pyridyl moieties. This architecture couples the photonic properties of the porphyrin to the POM because the metal ion is incorporated into both frameworks. Thus the ternary complexes can serve as a basis for the characterization of Hf(IV) and Zr(IV) porphyrins bound to oxide surfaces via these metal ions. The Hf(Por) and Zr(Por) were found to bind strongly to $TiO_2$ nanoparticles and indium tin oxide (ITO) surfaces but significantly less bind to crystalline $SiO_2$ or $TiO_2$. The strong binding of the metalloporphyrins to the POM, $TiO_2$ nanoparticles, and ITO surfaces, together with the paucity of binding to crystalline surfaces, suggests that the three to four open coordination sites on the Hf(Por) and Zr(Por) are predominantly bound at surface defect sites. Whether this is a good means to bind porphyrins to sensitize the $TiO_2$ remains to be seen.

Hafnium(IV) metalloporphyrins have also been assembled into dimers with a variety of other multitopic oxygen-containing ligands, such as sulfate and phosphate, which bind to the open coordination sites of the metal ion.[154] Using metal

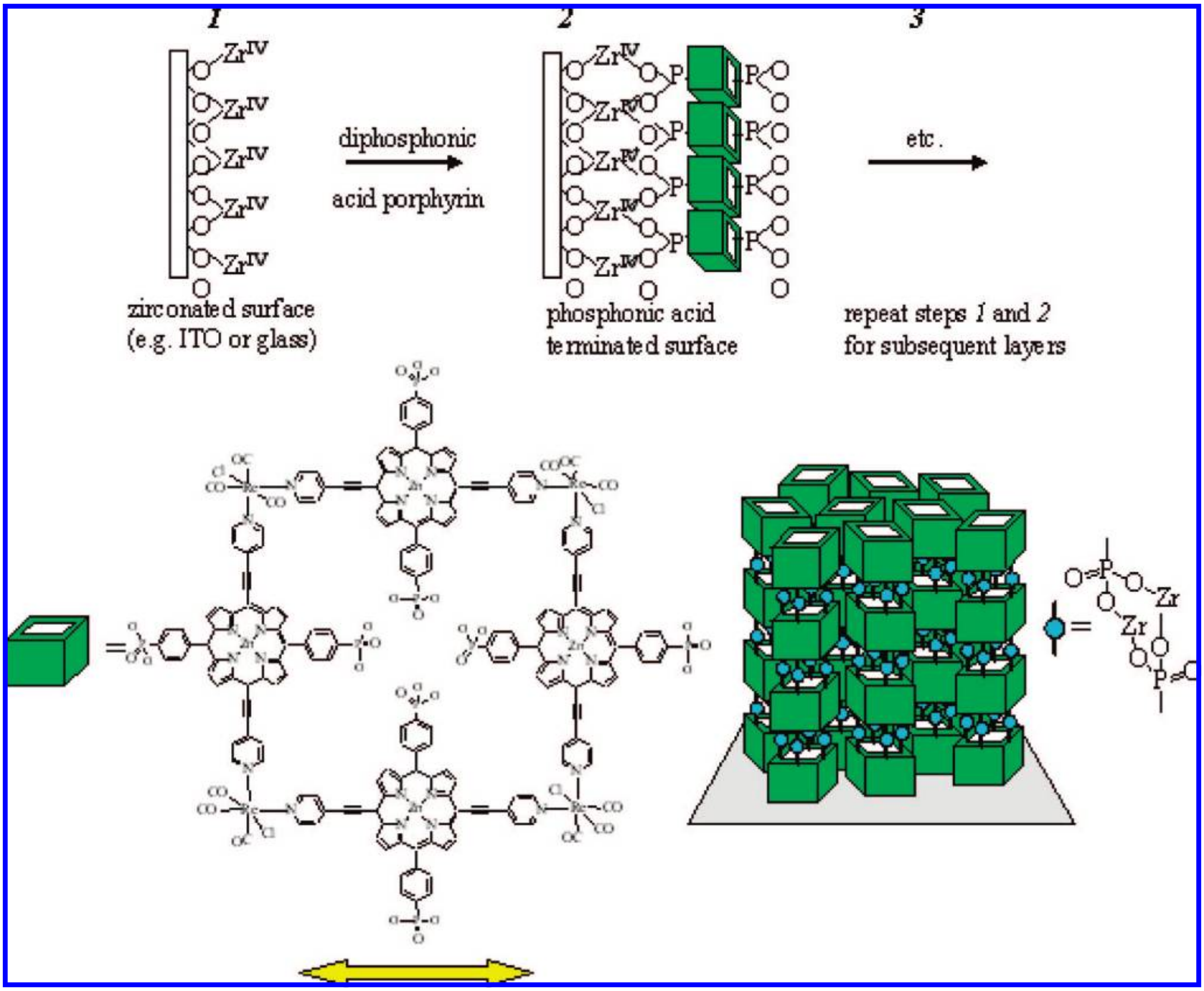


**Figure 11.** Hierarchically organized thin film materials. Films of molecular squares are formed by layer-by-layer deposition (Courtesy of J. T. Hupp). Adapted with permission from ref 72. Copyright 2006 Elsevier.

ions that reside outside the plane of the macrocycle with multitopic counterions represents a new strategy for porphyrinoid assembly, and new photonic properties may emerge from these constructs and materials.

### *4.1.2. Zirconium Phosphonate Chemistry*

Hupp and co-workers have demonstrated simple fabrication of ultrathin porous films of porphyrin of precise thickness by employing a layer-by-layer technique that combines a porphyrin with arylphosphonate moieties on the opposite sides of the macrocycle and zirconium chemistry.[136,155−157] For example, an ITO substrate is first phosphorylated and alternately immersed in an aqueous solution of $ZrOCl_2$ and a solution of a 5,15-bisarylphosphonate-functionalized porphyrin to form a layer assembled by coordination chemistry (Figure 11). Each layer has a thickness of about 1.9 nm.[72] The development of hierarchically organized systems can be achieved using similar chemistry but using a preassembled supramolecular square in the sequential dipping process, which also gives rise to films with precise porosities.[157]

The zirconium phosphonate work builds upon the formation of multilayers by pyridyl porphyrins and transition metals such as Cd, Pd, and Hg.[158−160] These latter sequentially organized films have a greater degree of order than films created using weak intermolecular interactions or nonspecific electrostatic interactions.[69] The rigidity of these sequentially layered films is greater than discotic liquid crystals, and the structural organization has shown to be responsive to external fields. Most of these thin films are quite stable, have applications as sensitizers for photovoltaics,[161,135−137,140,162] and can have properties similar to molecular sieves[155,163,164] and active catalysts.[165−169]

Some of these layered films have been shown to be chemically and photonically active. Mn(III) porphyrins are known catalysts for olefin epoxidation. Incorporation of Mn(III)bis-arylphosphonate porphyrin derivatives into multilayer films on ITO using the aforementioned zirconium−-phosphonate chemistry results in a catalytic system with longer lifetimes and higher turnover numbers for the epoxidation of styrene compared with the metalloporphyrins in solution.[170] In terms of electroactive materials, the film’s pores can be electrochemically filled with a conductive polymer such as polyaniline.[140] Other reports on metal/phosphonate driven assembly of porphyrin films on ITO[135−137,171] demonstrate that $Hf^{4+}$ or $Y^{3+}$ can be used in place of the $Zr^{4+}$. The advantages of the multilayer strategy to form thin films include the rapid development of materials with uniform thicknesses, achievement of multiple functions by varying the choice of metal ion in the porphyrin and as the linker, robustness, and organization of the chromophore molecules into different geometries. Both monolithic and porous films made to date have resulted in a linear arrangement of the porphyrins. Considering the wealth of geometries afforded by transition metal ion ligation by the numerous types of exocyclic ligands available, the formation of thin films of porphyrins with architectures similar to those found in highly porous porphyrin crystals should be achievable. These later films would greatly expand the repertoire of potential hosts and therefore applications.

### 4.1.3. Organic−Inorganic Films

Layer-by-layer techniques can be used for fabricating composite films composed of organic molecules and inorganic nanoparticles, thereby adding potential functions to the photonic systems. Robust inorganic−organic films consisting of up to 20 bilayers are formed on a quartz substrate by alternating between 5,10,15,20-tetra-(4-trimethylaminophenyl)porphyrin copper iodide and CdSe nanoparticles.[132,172] This hybrid porphyrin−nanoparticle system has significantly different electronic properties compared with the individual components, and photonic studies show electron transfer and energy migration between layers. Notably, citrate-stabilized platinum nanoparticles and tetrakis(*N*-methylpyridyl)porphyrinato cobalt were deposited through electrostatic interactions onto ITO surfaces to form a 3D nanostructured material that can serve as a catalyst for oxygen reduction.[141,167,173]

## 4.2. Self-Organized Adsorbed Monolayers on Surfaces: STM Studies

The spontaneous absorption of porphyrins on a surface using controlled or designed surface−molecule interactions and 2D organization on the surface using weak intermolecular interactions represent an alternative to the covalent chemistry used to make SAMs.[174] The adsorbed organized monolayers tend to have the chromophore parallel to the surface, while with the chemically bonded SAMs, the porphyrin is at an angle to the surface.[175] STM has been widely used to characterize the structure and the electronic properties of films and has contributed to our understanding of both intermolecular interactions and substrate−molecule interactions. STM also enables the manipulation of single atoms or molecules on a conductive surfaces in ultrahigh vacuum.[176]

Hipps and co-workers reported ordered two-dimensional self-organized arrays of common porphyrin structures on highly ordered pyrolytic graphite (HOPG) and gold substrates. STM studies identified the structure and orientation of the molecules and compared different deposition methods on different substrates.[177] For example, simple immersion of a graphite substrate into a benzene or chloroform solution of Ni(II)octaethylporphyrin (NiOEP) at ambient conditions yields stable thin films. The two-dimensional monolayers of this open-shell metalloporphyrin sit flat on the surface with very similar lattice constants for films cast from both solvents. On the other hand, UHV vapor deposition of NiOEP on Au(111) gives layers with different lattice constants. STM bias measurements of tunneling through the HOMO and LUMO are shown to be independent of the deposition method on both HOPG and Au surfaces.[177] An important discovery by Hipps et al. is that the STM can be used to make patterned architectures of NiOEP molecules from a benzene solution onto HOPG at room temperature. One can create molecule-free regions in the surface patterned with a NiOEP monolayer by using high current set points and low tunneling resistance below 120 MΩ.[176] This current-gated nanoshaving method may be applicable to the nanolithography of other systems.

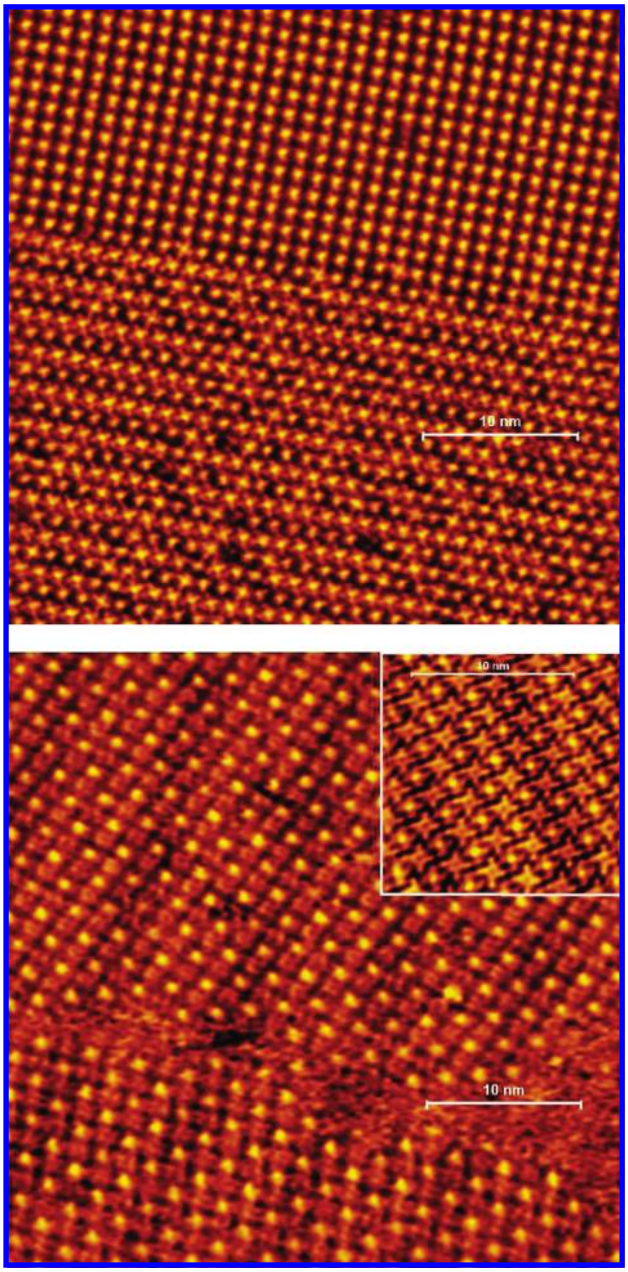


**Figure 12.** STM constant current image of Co(II)TPP/Co(II)Pc (top) and Co(II)TPP/$F_{16}$Co(II)Pc (bottom) on gold illustrates how weak intermolecular hydrogen bonding between the components in the system with the fluorinated dye results in significantly different two-dimensional order.[172] Courtesy of K. W. Hipps. See refs 174 and 176−178.

The formation of multicomponent films on gold substrates by vapor deposition was also recently reported.[178] Self-organization driven by H-bonding interactions between the fluorines on a perfluorinated cobalt(II)phthalocyanine and hydrogens on Ni(II)TPP yield densely packed 2:1 films (Figure 12) where each fluorinated Co(II)phthalocyanine is surrounded by four Ni(II)TPP.[174] While 2:1 films of cobalt(II)phthalocyanine and Co(II)TPP also result in an ordered 2D structure, STM images show that these films are less densely packed and somewhat disordered (Figure 12). To study the effect of central metal ions on the frontier orbitals in porphyrins by STM, Miyake et al. used ocatethylporphyrin (OEP) systems because they are simple with regular symmetry and they lack orthogonal aromatic substituents that can project from the plane of the macrocycle and hinder interactions between substrate and molecule. Recent examples include STM studies of 2D crystals of vanadyl and cobalt OEP on HOPG.[179]

Among the various STM studies of porphyrins on a variety of substrates, it is worth noting that 5,10,15,20-tetrapyridylporphyrins (TPyP) can form highly ordered chiral domains on Ag(111) surfaces by vapor deposition over a wide temperature range.[180] STM analysis reveals that packing in the layer is controlled by intermolecular interactions, while porphyrin−substrate coupling directs the orientation of porphyrin molecules relative to the surface. Also, porphyrins with aliphatic or polar groups such as tetrakis(3,5-ditertiary-butylphenyl)porphyrin and 5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(4-cyanophenyl)porphyrin, respectively, show different arrangements on gold substrates.[181] In this case the two di-*tert*-butylphenyl substituents diminish the $\pi$-interactions with the surface, but the $\pi$-interactions remain strong enough to rotate the meso aryl groups, which usually have a nominal 90° dihedral angle to the macrocycle, to a more coplanar arrangement. When the four meso substituents are the same, these molecule−surface interactions direct the formation of a hexagonal film. In this case, the 180° geometry of the cyanophenyl groups directs the assembly of these porphyrins into a single molecule wide wire-like structure.

Porphyrin−fullerene systems can be self-organized using the attraction between the large $\pi$ systems or by adding substituents for designed interactions and are of interest because of the great range of tunable electronic and photonic characteristics that can be designed into these materials. An early STM study of a porphyrin−fullerene material by Bonifazi et al.[182] shows a 2D structure of a preadsorbed layer of tetraphenylporphyrin on Ag(100) treated with $C_{60}$. The fullerene molecules are weakly adsorbed onto the porphyrin and can be easily rearranged using the STM tip without altering the underlying porphyrin layer. Different porphyrin structures allow control of the intermolecular interactions with $C_{60}$, thereby allowing control of the architecture of the materials on surfaces.

## 4.3. Summary

Since there is a wide interest in making stable porphyrin nanomaterials for various applications, two important factors that impact commercial viability are the costs of synthesizing the molecules and the costs of fabrication. With LBL methods, one can easily blend together various components (porphyrins, POMs, phthalocyanines, and polymers) into films of appropriate thickness or optical density via electrostatic, H-bond, or ionic interaction. These constructs can be quite stable. While the structure of rigid molecules such as the porphyrins and POMs are known, the precise architecture of these components in the film is difficult to ascertain, so that success or failure of the material is most easily determined by the function. As with other self-organized materials, the function of these films may change with changes in the environment.

Scanning tunneling and atomic force microscopy continue to be excellent tools for understanding interactions between molecules and interactions between molecules and surfaces. SPM methods allow exquisite control and manipulation of molecules in terms of fabrication of patterned nanostructures.[176] Given that large aromatic macrocycles have a good affinity for electron-rich substrates such as HOPG and gold, it is not surprising that deposition conditions can be found that result in well-ordered monolayers of porphyrinoids on highly ordered surfaces even with minimal intermolecular interactions. Using porphyrins with more substantial intermolecular interactions generally gives rise to more densely packed, high-fidelity arrays.

Given the ease of forming ordered layers on HOPG and Au, fundamental studies of the effects of surfaces, intermolecular interactions, and chelated metal ions on the frontier molecular orbitals or porphyrinoids have yet to be systematically evaluated. For example, since porphyrins and phthalocyanines bind nearly every metal in the periodic table, systematic comparison of electron distributions of different metalated OEP and TPP can be compared with the calculated molecular orbitals. Closed-shell, open-shell, high-spin, and low-spin metals alter the optical properties and can interact with the surfaces. These electron density maps may then be correlated to the degree of intermolecular interactions and thus the packing/order observed on these surfaces. Comparisons between surfaces may reveal differences in the HOMO and LUMO driven by molecule−surface interactions. Combined, these studies will yield both a better understanding of the chromophores and the role of surfaces on the photonic properties.

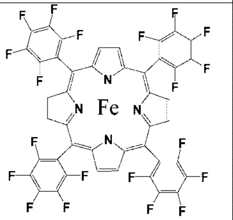
# *5. Supramolecular Porphyrin Catalysts*

## 5.1. Porphyrin Catalysts

The discovery by Groves and co-workers[183,184] that iron porphyrins (Fe-Por) in organic solvents with oxygen sources such as iodosylbenzene can mimic the oxidative catalysis observed for cytochrome P-450 led to a huge amount of research on the reactivity and mechanism of this reaction.[185−190] It was quickly realized that different metals exhibited different chemical reactivities, which included different products or product ratios.[191] Other major findings included (a) appropriate modification of the porphyrin macrocycle with bulky substituents alters reactivity in terms of site selectivity,[19,192] (b) substituent halogenation generally makes the metalloporphyrins more robust to oxidative degradation or increases the activity,[193−197] (c) axial ligands can alter reactivity,[198−202] (d) the solvent can also affect the reactivity, and (e) other oxygen sources such as $H_2O_2$, but seldom $O_2$,[203] can be used with some systems. Various metalloporphyrins are now used in laboratory scale reactions.

Many reaction types are catalyzed by metalloporphyrins including electrocatalytic and photocatalytic processes, but perhaps the most well-known are oxidation reactions. Especially for oxidative transformations, the solution-phase systems generally exhibit modest catalytic turnover numbers because of degradation of the metalloporphyrin. Several strategies have been employed to enhance the catalytic activity of metalloporphyrins. Heterogeneous porphyrin systems[19] include those in lipid bilayers, micelles, or zeolites[204,205] or on supports such as silica[206,207] and Montmorillonite clay.[208] For example, $FeTPPF_{20}$ linked to polystyrene catalyzed the oxidation of ethylbenzene with dioxygen at elevated temperatures (∼100 °C) to give three major products—the ketone, alcohol, and hydroperoxide.[209] This example shows that the synthetic modification (fluorination)

**Table 1. Catalytic Epoxidation of Cyclohexene by a Homogeneous Solution of $FeTPPF_{20}$ versus a Solution of Self-Organized Organic Nanoaggregates of the Same Porphyrin[a]**

| Porphyrin | | Solution | 35 nm NP PhIO[b] | 10 nm NP $O_2$[c] |
|---|---|---|---|---|
|  | % yield | 68.9 | 73.5 | 70 |
| | % epoxide | 99 | 73.5 | <1 |
| | % ketone | <1 | 15.7 | 70 |
| | % alcohol | <1 | 10.7 | 30 |
| | TON | 300 | 16511 | 3500 |

[a] Reaction conditions: Homogeneous reaction conditions were carried out in $CH_3CN$/methanol using $H_2O_2$ at room temperature for 24 h. Nanoparticles were prepared using DMF for 35 nm NP or THF for 10 nm NP as host solvent, water as guest solvent, and tetraethyleneglycol monomethylether as stabilizer. [b] A catalyst/iodobenzene (PhIO)/alkene molar ratio of 1:2527:405555, was used and pinene was added as the external standard, yields based on PhIO. [c] Catalyst:cyclohexene 1:30,000 with excess $O_2$ based on toluene internal standard. Ketone = cyclohexen-3-one in product, alcohol = cyclohexen-3-ol in product, TON = Turn over numbers. Product identification was confirmed by GC-MS. Adapted from reference.[215]

of the porphyrin and selection of the appropriate metal (iron) combined with a solid support (polystyrene) can lead to a rather powerful catalyst that oxidizes C−H bonds with $O_2$.

Other metalloporphyrinoids such as phthalocyanines, which are also +2 ligands, are also catalysts[210] (especially as sensitizers for the catalytic formation of singlet oxygen), but solubility issues have hindered the solution-phase studies and applications of these systems. The oxidative catalytic activity of metallophthalocyanines adsorbed onto various supports can affect the reduction of $CO_2$.[211,212] An advantage of these pigments is that many are, or can be, made on commercial scales.

## 5.2. Self-Organized Catalytic Systems

### 5.2.1. Nanoparticles

The enhanced catalytic activity of metalloporphyrins self-organized into 10−100 nm diameter nanoscale aggregates was reported.[213] These organic nanoparticles (ONPs) are formed by adding a guest solvent, in which the porphyrinoid is insoluble, to a solution of the macrocycle in a host solvent with a small percentage of poly(ethylene glycol) as a stabilizer and vigorous mixing. Particle size and chromophore organization depend on the molecule and the conditions used to form the nanoparticles.[214] The photonic and chemical properties of porphyrinoid nanopartices are different from the solvated molecule, the crystal, or the amorphous solid state. For example, it was found that nanoparticles of several metalloporphyrins have significantly better catalytic properties in terms of turnovers than the same solvated metalloporphyrin.[213,215] In general for nanoparticles composed of iron and manganese porphyrins there is a 10−30-fold increase in turnover number with only a 2−10-fold decrease in rate. One of the most interesting discoveries is that nanoparticles of Fe(III)perfluorophenyl porphyrin, $FeTPPF_{20}$, activate $O_2$ toward the oxidation of cyclohexene (Table 1) to exclusively yield cyclohexene-3-one and cyclohexene-3-ol rather than the epoxide and with ca. 15-fold greater turnover numbers[215] than the completely solvated species, which requires $H_2O_2$ or other synthetic oxygen sources.[193,197,216] This reactivity is quite nonintuitive because the metalloporphyrins are in close proximity in the nanoparticles and so their oxidative degradation should be enhanced, thus causing a significant *decrease* in catalytic turnovers. Furthermore, the allylic products suggest a different oxidative mechanism compared with that of the solvated metalloporphyrins.

Most methods to make nanoaggregates of small organic molecules have their historical roots in the formation of colloidal dispersions of organic systems.[217] The methods to make nanoscale aggregates of dyes such as porphyrinoids[69,70,213,214,218] include (a) the rapid exchange of solvent, (b) host/guest solvents whereby aggregation occurs by mixing of solutions containing the chromophoric molecules with miscible solvents in which they are not soluble (e.g., THF/$H_2O$) and stabilized by surfactants or amphipathic molecules, (c) interfacial precipitation, and (d) the rapid expansion of supercritical solvents. The former two methods result in dispersions in solution and the latter two methods result in many types of nanostructures that are kinetically trapped from further aggregation by deposition on surfaces. There is considerable interest in understanding the intermolecular processes governing formation of organic colloids and ONPs.[218] For example, formation of ONPs of porphyrinoids and other chromophoric systems offers the potential to enhance or modulate the photonic properties of the molecules through quantum mechanical effects.[219−221]

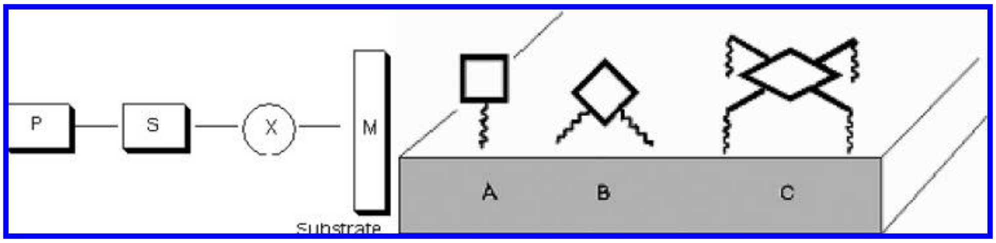
### 5.2.2. Self-Assembled Monolayers

Metalloporphyrins bearing appropriate exocyclic functional groups matched to the reactivity of a surface can be induced to form self-assembled monolayers (SAMs) on a variety of surfaces such as gold, silicon, and other electrodes. The structure of the monolayers depends on the macrocycle, the intervening tether, and the surface chemistry. The surface density can be controlled by addition of diluents, such as alkanes, with the same reactive group for surface attachment.[175] The structure and photonic properties of SAMs of porphyrins can be characterized by SPM, X-ray photoelectron spectroscopy (XPS), UV−visible and fluorescence spectroscopy, and optical methods.[175,222]

A generalized scheme of the components of porphyrin molecules for the formation of SAMs includes a reactive group for surface attachment, a spacer, and the chromophore (Scheme 2). [68,166,168] The number and relative orientation of the reactive groups on the macrocycle can dictate the relative orientation to the planar surface; from nearly perpendicular to nearly parallel (Scheme 2).[223−225] The photonic and catalytic properties of the SAMs are significantly influenced by the relative orientation and degree of aggregation of the porphyrins on the surface.[68] These properties can be fine-tuned by chemical properties of the porphyrin and the linkers. Since the focus of this section is on catalytic activity, metalloporphyrins are emphasized, the most common being Mn, Fe, Co, and Ni.

The spacer can be an additional design element in the architecture of the molecules because it can have a significant role in the activity of the SAM and therefore in the applications. For example, increasing the spacer length allows more highly ordered free base porphyrin SAMs to be formed on gold electrodes, and the relative orientation depends on the presence of an even or an odd number of methylene groups. Photoelectrochemical studies of the same SAMs using methylviologen show that the quantum yield increases with increasing spacer length up to six methylene groups.

**Scheme 2. Porphyrin Macrocycles P (Left) Can Be Attached to a Metal Substrate M through a Spacer S Having a Reactive Linking Group X That Is Matched to the Chemical Reactivity of the Surface and the Number, Direction, and Relative Positions of the Linking Groups (Right) Can Determine the Relative Geometry of the Macrocycles on a Surface**



The quantum yield also depends on the relative orientation of the porphyrins.[224,225]

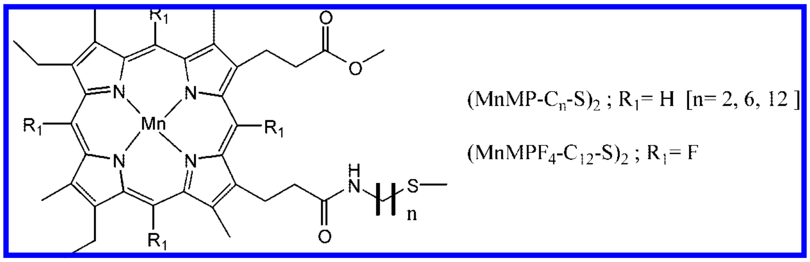
Rigid aromatic spacers can reduce the dynamics and dictate the orientation of SAMs of zinc porphyrin derivatives on metal oxide surfaces and thereby facilitate photo- or electrochemical-induced electron transfer between the chromophores and the electrodes.[224] When all four meta positions on tetraarylporphyrins bear carboxylate moieties, the porphyrin−aryl dihedral angle results in a roughly parallel binding (Scheme 2C) to metal oxide surfaces ($TiO_2$, ZnO, $ZrO_2$), whereas the corresponding para substitution results in SAMs with nonparallel orientations (Scheme 2A).[68]

Because the synthetic chemistry can be more direct, much of the work on porphyrinic SAMs uses tethers attached to meso tetraaryl moieties, but similar monolayers can be formed when the spacer is attached to the pyrrole. In this latter regard, protopophyrin (IX) and other naturally occurring porphyrins can provide easy access to a diverse array of derivatives of surface attachment with either monopodal or bipodal tethers. SAMs of a manganese porphyrin (Figure 13) on gold electrode surfaces with various spacer chain lengths were reported.[226] Consistent with the quantum yield for the photoelectrochemistry noted above, the rate constant for the electron transfer process from and to the manganese porphyrin on the gold surface increases as the length decreases. In this system, there are six atoms in the linker backbone and no intervening aryl group. As expected, the substituents on the macrocycle also dictate the electrochemical potentials and, therefore, influence the electron transfer rate constants. A decrease in the above rate constant was observed with the fluorination of the meso substituents on the porphyrin relative to the nonfluorinated derivatives. This is consistent with observations of electron transfer rate constants for tetraphenylporphyrin and its halogenated derivatives.[226]

Another approach to improve the activity of metalloporphyrin catalysts is to self-assemble them into a structure that inhibits self- or interporphyrin oxidation and degradation. SAMs of CoTPP appended with four thiols on gold surfaces are organized mostly parallel to the surface. These cobalt porphyrin films have better catalytic activity with turnover numbers about 100 times greater than similar homogeneous phase systems because of the reduced deactivation and decomposition of the metalloporphyrin.[166] In addition to porphyrin oxidation, the deactivation of the metalloporphyrins during the catalytic reaction also can be due to formation of an unreactive metal oxide (or oxidation state). Hupp and co-workers reported that inactive, oxidized manganese porphyrin rings can be reactivated by the addition of anthracene or related compounds to the reaction mixture.[227] The inactive oxidized porphyrins react with anthracene to produce the active catalyst and anthraquinone. This method increases the TON by about a factor of 10, and the lifetime for the catalyst can be extended from minutes to greater than 24 h.

SAMs of metalloporphyrins can be used in applications as sensors, in reduction of $O_2$,[228] in oxidation of unsaturated organic compounds such as styrene and olefins, and in alkane hydroxylation reactions.[206−208] An interesting alternative use of the porphyrin macrocycle is to use them as bulky steric protecting groups on active metallocatalysts. Porphyrins have been used to encapsulate an active rhodium−phosphine catalyst wherein the single phosphine is substituted with three pyridyl moieties that axially coordinate three zinc porphyrins around the multitopic ligand to form a shell.[169] The resulting encapsulated monoligated rhodium metal complexes catalyze hydroformylation of 1-octene with a 10-fold increase in activity and an increased yield of the branched aldehyde.

There is a substantial body of work by the Lindsey and Bocian team and other groups on the chemistry and function of porphyrin SAMs on semiconducting surfaces.[116,229−241] Applications include redox-based memory, molecular electronics, and solar energy conversion.[229] For example, metalloporphyrin derivatives photolithographically patterned on a chip can act as memory cells. The basic design strategy for information storage molecules includes a redox active unit that specifically binds to an electroactive surface through a tether bearing a terminal functional group. The information is stored in discrete molecules by taking advantage of their multiple stable oxidation states. Zn porphyrins serve as redox active species with alkane or aryl-alkane spacers using



$(MnMP\text{-}C_n\text{-}S)_2$ ; $R_1$= H [n= 2, 6, 12 ]

$(MnMPF_4\text{-}C_{12}\text{-}S)_2$ ; $R_1$= F

**Figure 13.** Molecular structures of sulfide-linked manganese porphyrin derivatives with different methylene spacer lengths. SAMs based on protoporphyrin IX can be used as a model to study the electron transfer to the electrode as a function of the different tethers, length, and molecular orientation.[226]

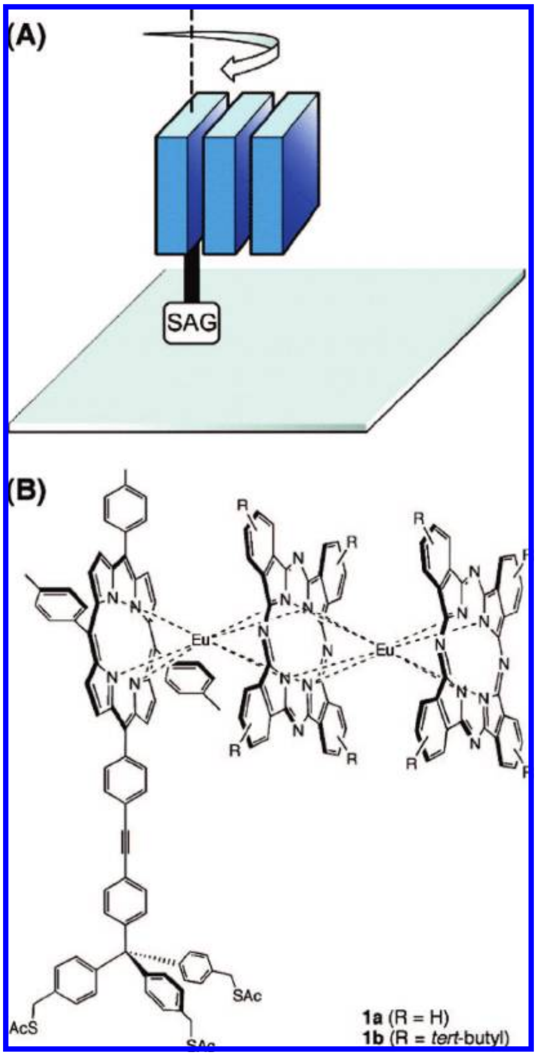


**Figure 14.** Triple decker sandwich compounds have been proposed as building blocks for molecular electronics because of their multiple reversible oxidation/reduction processes: (A) schematic representation of the camshaft rotation of the triple decker with surface attachment group (SAG); (B) example of molecular structure of a phthalocyanine−phthalocyanine−porphyrin triple decker sandwich. Reproduced from ref 230. Copyright 2006 American Chemical Society.

attachment chemistry appropriate for the surface, X = O, S, Se, to form monolayers on Si(100) or Au(111). Both single porphyrin units and sandwich complexes consisting of both porphyrins and phthalocyanines are reported (Figure 14).[230] The work of Galoppini et al. also has probed the roles of attachment and linker chemistry on the efficiency of sensitizing $TiO_2$ for solar energy harvesting.[224,242]

Significant work has revealed the role of each molecular component on the packing efficiency of the SAMs and on electrochemical performance. In addition to the electrochemistry of the porphyrin part of the molecule, these studies included examining (1) the effect of attachment group X (O, S, Se, acetylene, vinyl) on electron transfer kinetics,[226,232,238,239] (2) the single or tripodal topology of the linker,[234,236] (3) spacer length, composition, and structure,[233,236] and (4) the effect of surface charge density of the monolayers.[238] In addition to the expected dependence on distance, linker moiety, and chromophore, several nonintuitive results were found. First, the maximum charge transport is observed at significantly less than the maximum surface density of the redox-active SAM, after which the transport properties of the monolayer actually decrease with increasing surface density of the porphyrinic system. This is attributed to space charge[243] and is akin to the space charge limited transport properties observed for electrostatically assembled porphyrins in lipid bilayers.[42−44] Second, short alkane spacers are better than aryl or alkyne-aryl spacers.[229]

## 5.3. Summary

The catalytic properties of metalloporphyrin derivatives can be significantly changed depending on the morphology of the material in which they are incorporated. For example, catalytic porphyrins in SAMs or as nanoparticles can be more active than the corresponding solvated molecules. The catalytic properties of SAMs of metalloporphyrins on surfaces also depend upon the length of the spacer that joins the macrocycle to the surface. Electrochemical and photochemical reactions of SAMs on electrodes depend on the spacer as well, with ca. six carbon atoms providing the optimum balance between flexibility and distance to the surface. The catalytic processes can also depend upon the electronegativity of substituents on the porphyrin. The mechanistic differences in the catalytic properties of self-assembled and self-organized metalloporphyrin catalysts versus those in solution are not clearly understood. The large inventory of organic tethers, spacers, and functional groups used to attach porphyrins to surfaces studied to date also indicates that alternative modes of attachment need to be designed and developed. Attachment of porphyrins and other porphyrinoids to oxide surfaces via metal ions with large ionic radii that protrude out of the plane of the macrocycle, see section 4.1.1, may represent an attractive alternative to organic tethers studied to date.

## 6. Porphyrin and Fullerene Architecture

The primary focus of this review is on supramolecular porphyrinic materials, so it will not extensively cover the substantial literature on covalently bonded porphyrin−fullerene systems. Examples wherein the fullerene is coordinated to metalloporphyrins via a ligand will be discussed. Great efforts have been devoted to the preparation and the study of complexes formed between porphyrins and fullerenes because these constructs and materials can exhibit efficient charge separation.[244] Thus porphyrin−fullerene architectures have been studied as photovoltaic devices and proposed to be viable components for the conversion and utilization of solar energy.[245−247]

The nature of the bonding between the porphyrin and fullerene is an important director of the photonic properties of materials composed of these molecules, so the complexes are grouped according to bonding. Constructs that use covalent bonds to link the porphyrin to the fullerene, which may or may not include a functional linker or spacer, are widely studied. In supramolecular porphyrin−fullerene materials, the components are spontaneously self-assembled and self-organized by noncovalent interactions.[248,249] There are nondirectional interactions such as $\pi-\pi$ interactions and van der Waals forces as found in cocrystallized materials. There are also specific intermolecular interactions mediated by coordination chemistry, for example, the axial coordination of a substituted fullerene to a metalloporphyrin. In solid-state materials, a combination of several intermolecular interactions dictate the arrangement of the molecules in the material.

## 6.1. Covalent Bonding

There are numerous studies on porphyrins covalently bound to $C_{60}$.[250−258] The nature of covalent bonds to the fullerene and to the porphyrin, for example, the functional groups used, can be exploited as a means to fine-tune the properties of the dyads. The linking moiety also can provide a versatile handle to impart additional functions to covalently linked dyads. The synthetic chemistry of these systems is well developed, can proceed in good yields, and facilitates characterization of the molecule by a variety of spectroscopic techniques. One significant disadvantage of the covalent approach includes the modification of the fullerene to form a covalent bond, which decreases the spherical orbital symmetry and causes an increase in the reorganization energy to be overcome in the formation of charge transfer species with an electron donor. The decreased efficiency is generally deleterious to the function of the materials, but these dyads can have better charge separation than other donor−spacer−acceptor systems.[259]

Many of these covalent structures have been deposited on surfaces in the form of chemisorbed or physisorbed materials.[260] Some porphyrin−fullerene compounds can self-organize into ordered arrays, and some are further modified to allow the formation of SAMs on solid surfaces such as gold electrodes or ITO.[261−263] Considering the chemical differences in the covalently bound systems, it is difficult to discern which mode of surface binding (adsorption or SAM) results in the more efficient charge injection into band gap materials.

## 6.2. Dispersion Forces

Fullerenes and porphyrins are spontaneously attracted to each other via $\pi-\pi$ intermolecular interactions between the curved surface of a fullerene and the center of a porphyrin. There are also electrostatic interactions between the electropositive center of the porphyrin or some metalloporphyrin macrocycles and fullerenes such as $C_{60}$.[264,265] The combination of these two attractive forces shortens the distance between the $C_{60}$ and the center of the porphyrin compared with the distance expected from the $\pi-\pi$ interactions alone. This supramolecular motif is used for the design of a variety of new solid-state porphyrin−fullerene nanoarchitectures.[264−267]

Fullerenes such as $C_{60}$ are efficient electron acceptors and differ from other widely used electron acceptor molecules because of the spherical shape, large size, polarizability, and lack of a dipole.[244,268] These properties result in small molecular and solvent reorganization energies upon accepting electron(s) from metallo- and free-base porphyrin electron donors.[244] Though much of this work has been done on the covalently bonded dyads, supramolecular porphyrin−$C_{60}$ constructs can also lead to the formation of long-lived charge-separated states, which exhibit desirable electronic and photophysical properties.[244] Consequently, porphyrin−$C_{60}$ systems can be used as dyes that serve to photosensitize charge transport in band gap materials such as $TiO_2$ and ITO using solar light.[269,270] Photoelectronic applications and dye-sensitized solar cells are well reviewed.[271]

Depending on the environment, the peripheral substituents on the macrocycle, and the mode of assembly, several different nano- to microscaled structures have been made. These structures range from nanotubes,[272,273] nanoporous networks,[260] and host−guest complexes[274−278] to highly ordered framework solids.[133,182,279−287] Varying the conditions used to self-organize these materials can lead to the formation of different architectures using the same starting compounds. For instance, Imahori and co-workers demonstrated that altering the ratio of porphyrin/$C_{60}$ results in different structures of the composite clusters, which display different photoelectrochemical properties.[277] Two important considerations in the supramolecular synthesis of host−guest complexes containing porphyrins and fullerene are the size of the chromophores and the separation between them. For example, crystal structure analysis shows the approach of a fullerene $C_{60}$ to the center of the porphyrin mean molecular plane to be ca. 0.27 nm,[264] so a minimum of ca. 1.2 nm between the two porphyrins is needed to host the fullerene (Figure 15).[62] It has been shown that shorter or greater values lower the binding constants, in the former case because there is not enough space to accommodate the buckyball and in the latter because of an increased flexibility.

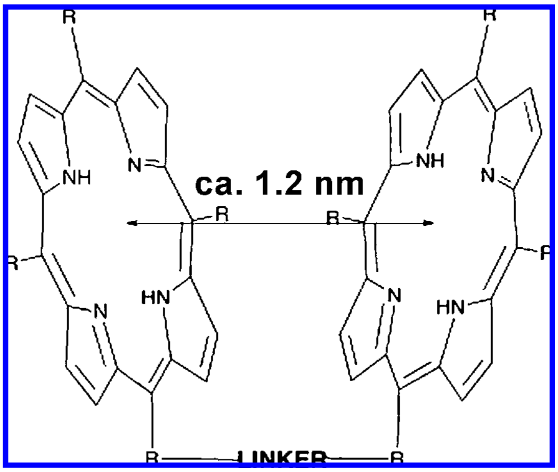


**Figure 15.** The correct separation of two porphyrins in a dyad should be about 1.2 nm in order to host a fullerene $C_{60}$.[62]

To assemble porphyrins and fullerenes into architectures more complex than discrete host−guest systems such as into nanotubes, other specific intermolecular interactions are used. For instance, Naruta et al.[272] described a tubular structure formed between a cyclic porphyrin dimer and $C_{60}$ that takes full advantage of several noncovalent interactions. The porphyrin nanotubes are self-organized by both the formation of nonclassical H-bonds between the pyrrole $\beta$-H and the nitrogen of a pyridyl group and weak $\pi-\pi$ interactions between the pyridyl groups. The $C_{60}$ molecules are held within the tubular structure by $\pi-\pi$ and $C-H\cdots\pi$ interactions. In this case, the host reinforces the structure of the guest. Recently, a rotaxane−porphyrin conjugate has been used as a molecular tweezers to host $C_{60}$ through $\pi-\pi$ interactions.[288] This assembly is interesting because the scaffold can be immobilized onto a gold surface through a thio-terminated linker to create a functionalized electrode for photoelectrochemical applications. In another report, porphyrins have been attached to a cellulose motif designed to encapsulate $C_{60}$, and films of this material fabricated by a LB technique exhibited photocurrents.[289] Mixtures of $C_{60}$ with simple tetraphenylporphyrins and those appended with long alkyl chains cast on ITO surfaces do not form films and often separate into the two components because the $\pi-\pi$ interactions are insufficient to maintain an organized structure. However, perfluoro alkanes appended on the para positions of tetrakis-(tetrafluorophenyl)porphyrin drive the formation of thin films containing $C_{60}$ (Figure 16).[290] The films are organized by the low surface energy due to the

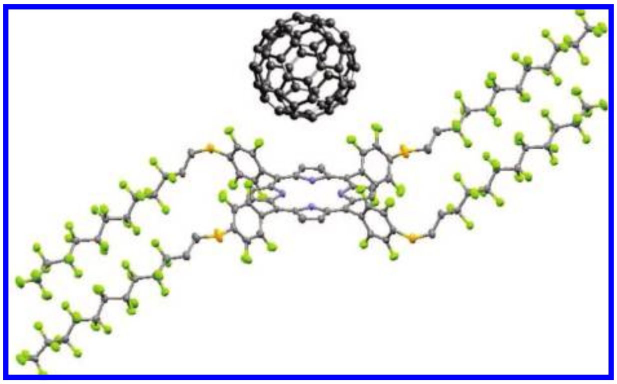


**Figure 16.** Films of a highly fluorinated porphyrin and $C_{60}$ form when cast on ITO due to both $\pi-\pi$ interactions and the additional van der Waal's interactions between the fluorous alkanes and the fullerene.[290]

fluorous alkanes, and fullerene $C_{60}$ is held in the film through a combination of $\pi-\pi$ interactions and C−F···$\pi$ interactions.[266,267,290]

## 6.3. Axial Coordination

There are numerous reports on the formation of porphyrin−$C_{60}$ architectures mediated by axial coordination of a ligand substituent on the fullerene to the metal center of a metalloporphyrin.[131,281,291−303] The nature of the ligand is matched to the binding and geometry of the target metal ion. Moreover, it is possible to place more than one ligand on the $C_{60}$ core, thereby increasing the topological diversity of self-assembled structures and affording a compound that can be in the backbone of a coordination polymer or assembled into a triad with two different donor molecules.[304]

Axial coordination offers a versatile approach to the rapid preparation and photophysical characterization of self- assembled porphyrin−$C_{60}$ structures in solution. While some supramolecular systems are not very stable in solution and may reorganize when deposited onto surfaces, the stability and solid state structure can be modulated by designing ligands with greater binding constants or different topologies. As anticipated above, in many cases the self-organization of porphyrin−$C_{60}$ complexes takes advantages of more than one kind of designed interaction simultaneously. An elegant example of a supramolecular structure assembled by a set of designed intermolecular interaction is offered by D'Souza et al.[293] In this work, two zinc-porphyrins bearing four substituent crown ethers are preassembled into a cofacial dimer upon binding four potassium ions, and then a fullerene bisubstituted with a pyridyl and alkylammonium groups is added to the porphyrin assembly. The 2 × 2 array forms when the pyridyl moieties bind the zinc ion center and the ammonium groups electrostatically interact with the crown ether cation binding centers (Figure 17).

## 6.4. Cocrystals

As a result of the chemical properties of the two chromophores, it is often possible to obtain cocrystallized porphyrin−$C_{60}$ materials. A number of examples are reported in which porphyrins cocrystallize with $C_{60}$ at various ratios. These cocrystals have been shown to form ordinate arrays of various shapes, ranging from tapes to sheets and other 3D architectures that are largely dictated by the size of the $C_{60}$ and the substituents on the porphyrin. Preassembled porphyrins arrays can be used as well.[266,267,279,284,305] The photonic properties of these materials depend on the electronic interactions between the two components, which arise from the solid-state architecture. While the cofacial separation at the interface of two porphyrins is usually greater than 0.32 nm and the distance between a porphyrin and an arene system ranges from 0.30 to 0.35 nm, the distance between a $C_{60}$ carbon atom and the center of a porphyrin plane can be as little as 0.27 nm.[264−266] This shorter separation has been attributed to an additional interaction between the electron density of a 6:6 ring juncture of the fullerene and the electropositive center of the porphyrin. Moreover, DFT calculations have shown that in the case of TPP the *ortho*-C−H··· $\pi$ interactions increase $\pi-\pi$ interactions by as much as 20% when four C−H bonds are involved.[266] Fullerenes are known to encapsulate various species, and the cocrystallization of a metal oxide cluster inside an icosahedral $C_{80}$ fullerene with Ni OEP was recently reported by Balch et al.[306]

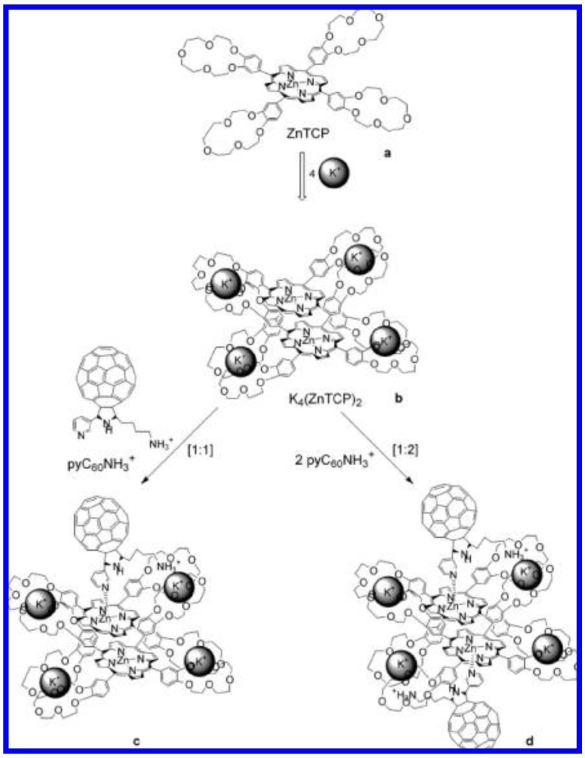


**Figure 17.** Self-assembly of porphyrin−fullerene materials can be mediated by synergic interactions using metal ion coordination and ionic recognition. First, the tetra-crown ether substituted porphyrin (a) preassembles into a cofacial arrangement where the potassium ion is sandwiched between crown ethers (b). Second, a fullerene, bis-substituted with a pyridyl and alkylammonium groups, coordinates to the Zn and one of the crown ether entities yielding the formation of a triad if the ratio is 1:1 (c) or tetrad if the ratio is 1:2 (d). Reproduced from ref 293. Copyright 2007 Wiley.

Increased interaction energies can be accomplished by using perfluorinated phenyl groups on the macrocycle as reported by Olmstead et al.[267] In these cocrystals, a combination of C−F···$C_{60}$, C−F···H, and C−F···$\pi$ interactions lead to the formation of structures wherein the fullerene is encapsulated between three porphyrins. Another structure by Hosseini et al.[266] finds that C−F···H−C interactions between the perfluorophenyl groups on one porphyrin and the pyrrole $\beta$-H on a neighboring porphyrin result in several nanoarchitectures such as sheets, tapes, and prisms (Figure 18). This builds upon earlier work on the formation perfluorphenylporphyrin−$C_{60}$ cocrystals.[264] The literature on porphyrin−

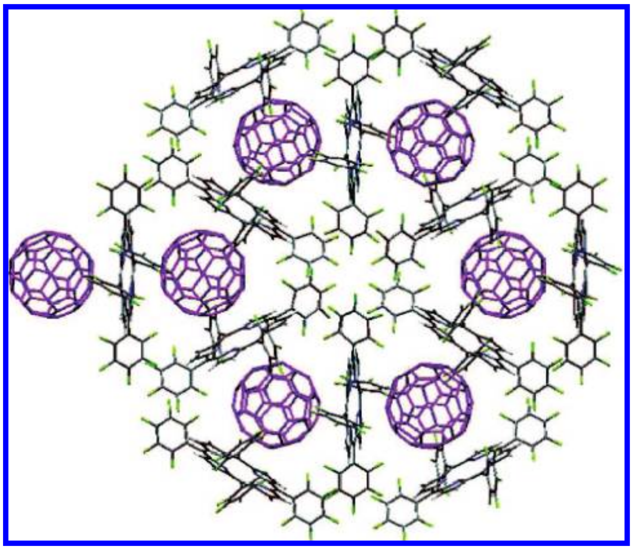


**Figure 18.** Honeycomb array of $C_{60}$ cocrystallized with perfluorophenylporphyirn. The porphyrin$-C_{60}$ arrangement is dictated by $\pi-\pi$ and electrostatic interactions, whereas the proximity of the porphyrins is due to $C-F\cdots H-C$ interactions between some F atoms and the pyrrole $\beta$-H on a neighboring molecule. Reproduced from ref 266. Copyright 2006 American Chemical Society.

fullerene cocrystals demonstrates that the choice of solvents, temperature, ratio of the chromophores, and rate of evaporation affect the crystal lattice dramatically and that it is possible to obtain a variety of different crystal structures by changing these parameters. Nevertheless, from these examples, it seems difficult to extrapolate a blueprint for the formation of a specific crystalline structure. The information yielded by these cocrystals is of fundamental importance for the design of new supramolecular adducts, but the photonic properties of these materials are not well characterized.

## 6.5. Summary

Because porphyrin−fullerene materials can form long-lived charge-separated states, they represent an excellent system for components of organic electronics and photoactive devices. Reduction or elimination of complex synthetic and purification methods are a significant advantage of self-organization, yet more work needs to be done in order to establish whether supramolecular chemistry is a preferable strategy over the fabrication of covalently bound constructs. As mentioned above, how stable are these supramolecular materials to commercially viable applications? Crystallographic data have yielded several important design criteria on the cooperative formation of lattices containing fullerenes and porphyrins. Second, there is a paucity of detailed photophysical data on the supramolecular arrays in solution or as a material. Recent literature has shown that the combination of more than one specifically designed noncovalent interaction can increase the stability and prevent the degradation of order of the molecules in the material.[307,308] Porphyrins,[309] $C_{70}$,[310] and porphyrin$-C_{60}$ compounds[311] have been organized into lipid bilayers or vesicles where photoinduced charge transfer reactions resulted in observable currents and pumps. The self-organizing properties of lipids into bilayers also allow the active photonic molecules, electron donors, and electron acceptors to partition into the appropriate places by choice of the hydrophobicity.[42] These systems represent functional materials that use light to drive proton or electrical currents. One of the design principles learned from the latter systems is that the relative orientation of a collection of molecules or supramolecular systems can be accomplished in a self-organizing matrix. These also show that hierarchical organization can lead to more complex functions.

## 7. Porphyrin Nanostructures Driven by $\pi-\pi$ Interactions

Large, planar aromatic macrocycles such as the porphyrinoids are prone to aggregation by $\pi$-stacking and these interactions for porphyrins can be ca. 5 kcal mol$^{-1}$ per face.[312] The $\pi-\pi$ interactions can be face-to-face (H aggregates) or edge-to-edge (J aggregates), each having distinctive absorption and emission properties. There are a large number of crystal structures of simple porphyrins and metalloporphyrins organized by $\pi-\pi$ interactions and dispersion forces.[35] Conversely, the tendency of porphyrins to spontaneously aggregate and precipitate into amorphous materials has been the bane of many researchers. Historically, one way to purify hydrophobic porphyrins was to pour the reaction mixture or a solution in a solvent miscible in water into a large amount of water to cause the precipitation of the macrocycle while the byproducts remain in the mixed solvent solution.[313] An initial report exploiting this host solvent/guest solvent process showed that control of the aggregation process can be used to kinetically trap the aggregates as nanoscale dispersions by using a stabilizing agent such as a short poly(ethylene glycol) (see section 5.2.1).[213] These suspensions can be stable for over a year, but since these organic nanoparticles are organized by dispersion forces, they can disaggregate or further aggregate into amorphous solids by changing the environment of the particles. These porphyrin nanoparticles are not crystalline, and both J and H interactions are indicated by electronic spectra. The size, stability, and macrocycle organization of the nanoparticles are highly dependent on the intermolecular forces between the porphyrins, the solvents, and the stabilizer.[214]

The design of predefined nanoarchitectures usually requires additional specific intermolecular interactions because $\pi-\pi$ interactions of simple porphyrins generally are not specific or topologically modifiable. The organization of porphyrins bearing large aromatic substituents such as pyrene directly attached to the meso position has not been reported. $\pi$-Stacking of perylene−dicarboximides on the *para* position of TPP drives the formation of nanoaggregates because the perylenes are coplanar with the porphyrin (Figure 19).[314] These exhibit interesting photonic properties in that the charge delocalizes in the nanoparticles. Other localized interactions such as dipolar and electrostatic interactions can be exploited to develop ordered structures on ordered surfaces. Recently, complex architectures using $\pi$ interactions combined with electrostatic interactions, coordination chemistry, and H-bonds have been reported. Many different self-organized architectures have been fabricated, such as elongated nanorods,[315−320] nanotubes,[321−324] nanowires,[73,325] spherical structures such as micelles,[319,326] and rings[126,327] (e.g., Figure 20). Other ordered 2D or 3D structures containing porphyrins with J- and H-aggregates are also reported.[32,108,125,260,314,328−332]

Molecular design principles allow the incorporation of moieties for specific intermolecular interactions with specific topologies that can lead to targeted structures in solution and in the solid state. The substituents on the porphyrin core also play a crucial role in modifying the photophysical properties.

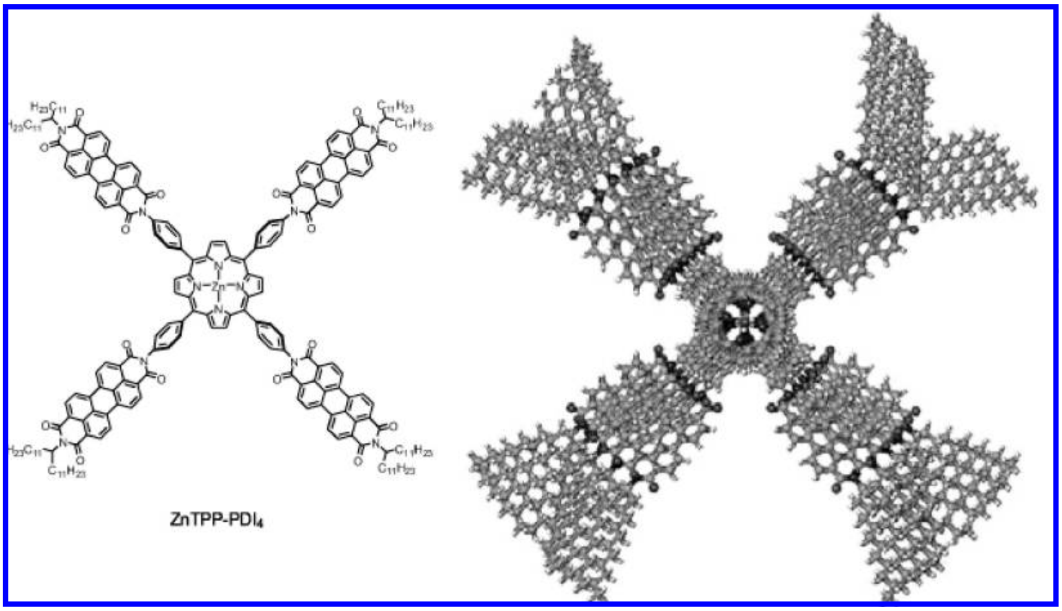


**Figure 19.** Zinc-TPP surrounded by four perylene-3,4,9,10-bis(dicarboximide) $(ZnTPP-PDI)_4$: left, molecular structure; right, side view of MM+ geometry-optimized structure. The perylene units are electron acceptors and promote the electronic communication between the adjacent porphyrin allowing energy or charge transfer. Self-assembly of the $(ZnTPP\text{-}PDI)_4$ is driven primarily by $\pi-\pi$ interactions between the adjacent PDI and yields columnar stacks of an average of five cofacial molecules. Reproduced with permission from ref 314. Copyright 2007 Royal Society of Chemistry.

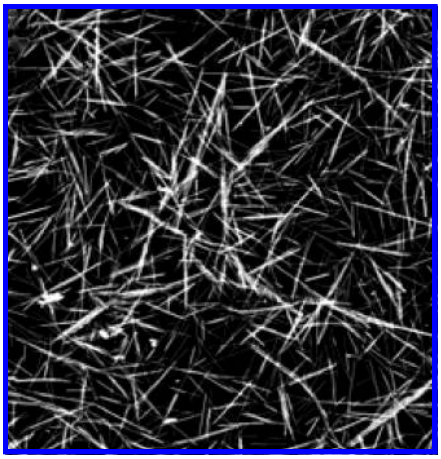


**Figure 20.** AFM image of $H_4TPPS_4^{2-}$ bundles of nanorods formed from acidic solution deposited on mica. The nanorods form by self-assembly of J-aggregates of porphyrins in HCl aqueous solution. The substrate was immersed in 5 $\mu$M solution of porphyrin in 0.3 M HCl. The density of the nanorod bundles increases with immersion time. Reproduced from ref 320. Copyright 2003 American Chemical Society.

The choice of specific assembly conditions is also a factor to be considered, such as temperature, concentration, time, and solvents. Balaban and co-workers[139] have shown that several architectures can be organized with porphyrins bearing 5,15-meso-substituted anchoring groups that are mediated by both H-bonds and metal ion coordination. Depending on the conditions used, either a tetragonal or a layered structure of porphyrin stacks can be formed. This work continues with studies of 5,15-meso-substituted zinc porphyrins with electron donor or acceptor moieties assembled by $\pi$-interactions.[333] In the work of Hu et al.,[329] the length and the aspect ratio of porphyrin nanoprisms can be tuned by controlling the stoichiometric ratio of porphyrin to a cetyltrimethylammonium bromide surfactant. In both cases, it is clear that the crystallization solvents and the surfactants play a crucial role in the formation of targeted structures. Some progress has been made in understanding the mechanism of formation of these aggregates and crystalline systems,[73,317] but more needs to be done.

In some cases, peripheral substitution can be used to force the nominally planar macrocycle to adopt a dome-shaped or saddle-shaped conformation, and this topology can be used to direct the formation of hierarchical structures. For example, Mo(IV)dodecaphenylporphyrins have been used as tectons to make a variety of structures such as tubes (Figure 21).[321] Again, a number of noncovalent interactions are acting synergistically: the dodecaphenylporphyrin exhibits a large saddle distortion that makes it suitable as a building block for the growth of nanotubes; the phenyl groups provide additional sites for intermolecular $\pi-\pi$ interactions, the aqua ligand stabilizes the assembly by formation of H-bonds, and the toluene molecules of crystallization work as a glue to bring the tubes together via $\pi-\pi$ and CH$-\pi$ interactions.

## 7.1. Summary

The self-assembly of porphyrins and $C_{60}$ driven by $\pi-\pi$ interactions is widely described in literature. It is still difficult to predict both the local structure (order of the molecules) and the global morphology (e.g., shape of the crystal) of these materials; thus the mechanism of growth is under investigation. It is clear that in addition to molecular structure, the growth conditions play a pivotal role in determining the mechanism of formation and the structure of the material. H-bonds from solvent molecules such as water have long been recognized as important players in determining structure as mediators of intermolecular interactions or as competitors for H-bonding moieties on the molecule. In general, this cannot be said of aromatic solvents, where in crystal structures the solvent molecules can be rationalized once they are found.

The combination of several different types of molecule can lead to hierarchically structured materials on surfaces. For example, the initial porphyrin tectons can interact to form

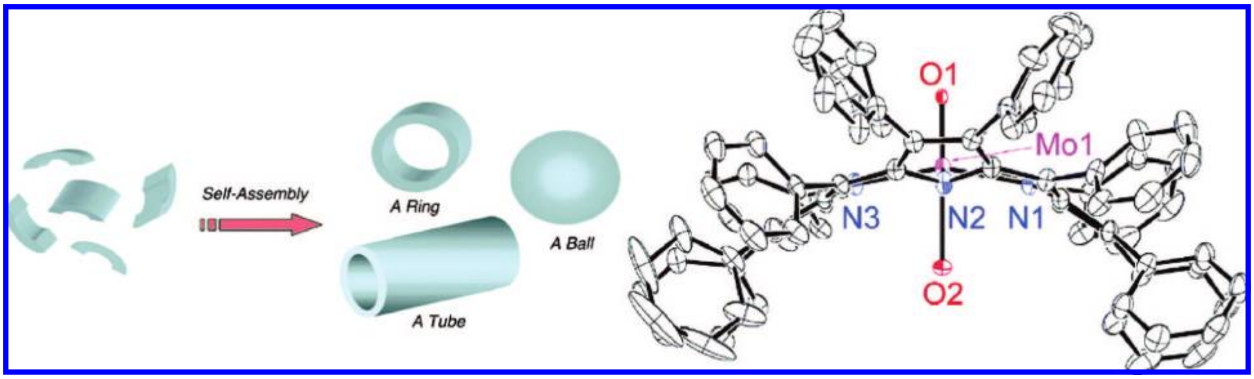


**Figure 21.** Saddle-distorted porphyrins and metalloporphyrins are tectons for self-assembly with curved surfaces and so are useful in the fabrication of tubular and circular nanostructures based on noncovalent interactions. For example, Mo(V)dodecaphenylporphyrin has an ideal shape to yield curved structures. Reproduced from ref 321. Copyright 2007 American Chemical Society.

a secondary structure, which then packs into a solid state material via supramolecular interactions with $C_{60}$ to form a tertiary structure. When this material is placed on a functional surface such as $SnO_2$ it forms a hierarchically organized photonic material.[245] The formation of photonic materials of the other porphyrinoids, especially phthalocyanines and porphyrazines, is becoming a research focus. If more than one chromophore is to be absorbed onto a semiconducting material, the organization of the dyes relative to each other and the surface is important to ensure vectoral energy or electron transfer. In this regard, the self-assembly of a tetramer containing two porphyrins and two porphyrazines was reported to show good energy transfer from the former to the latter.[71] AFM studies reveal that these tetramers form uniform thin films with the arrays parallel to mica surfaces. An older method that is enjoying a renaissance is the formation of materials at liquid−liquid interfaces. The liquid−liquid interface has unique features for the self-organization and growth of porphyrinic materials because the mobility of molecules and particles at the fluid interface affords a rapid means to reach an equilibrium and the ability to use components that are soluble in different nonmiscible solvents.[334] Sequential dipping methods to prepare multilayers of porphyrins through metal−porphyrin coordination bonds[99,158−160,173] or by electrostatic interactions (see section 4.1) are also a means to achieve the hierarchical organization of porphyrin systems. In all of these materials, the secondary $\pi$ interactions are an essential feature of the structure.

## 8. Porphyrin Liquid Crystals

There are numerous reports on the self-assembly of porphyrin arrays and crystal structures mediated by coordination chemisty.[72] For these materials to interact with the macroscopic world, an emerging emphasis is the hierarchical organization of these systems on surface.[22] An early investigation into the hierarchical organization of porphyrins compared the structure of films of Pd(II) and Pt(II) self-assembled porphyrin squares appended with *tert*-butylphenyl groups to the structure of the same squares appended with dodecyloxphenyl groups.[46,50] It was found that the different alkyl groups mediated the supramolecular conformation and dynamics of the porphyrin squares and directed different organizaiton on surfaces. The *tert*-butylphenyl-substituted porphyrin squares using Pt(II) form discrete columnar stacks, which assemble in a vertical direction via $\pi$-stacking interactions among the marcocycles. The corresponding tetrameric porphyrin array with dodecyloxyphenyl groups forms a continuous film via van der Waals interactions among the peripheral hydrocarbon chains. The squares with liquid crystal-forming moieties also form three-dimensional crystalline structures at higher deposition concentrations. The conclusions are that hierarchical organizaiton is dictated by (1) the number, position, and nature of the peripheral groups, (2) the supramolecular structure and dynamics, and (3) the energetics of interactrions with the surface. Similarly, self-assembled porphyrin arrays can be inserted into lipid bilayer membraines, which causes the array to orient perpendicular to the bilayer−water interface.[11] Placement of electron donors on the opposite side of the membrane as electron acceptors allows the formation of photogated transistors wherein the function depends on the hierarchical organization of the material.

An alternative route to the fabrication of self-organized materials of porphyrins is based on the synthesis of mesogenic substances. Liquid crystalline materials composed of porphyrinoids can be made with the proper exocyclic functionalities. This is well developed for phthalocynines.[142,335] The porphyrin core confers distinctive photophysical properties, and the liquid crystal forming moieties provide a means for the fabrication of large areas of defect-free monodomain films. These materials are especially promising alternatives to the other liquid crystalline materials because the luminescence properties can be tuned in terms of lifetime and to a lesser extent color by the nature of the chelated metal or the free base. For example, the fluorescence lifetimes of typical free base, Mg(II), and Zn(II) porphyrin are ca. 12, 5, and 2 ns, respectively. Pt(II) and Pd(II) porphyrins can have phosphorescence quantum yields near unity. The porphyrin core is the mesogen, that is, the rigid part that aligns molecules in the axial direction, and long alkyl chains orient the material equatorially and impart fluidity. The optimum balance between the mesogen and the flexible parts determine the suitability of the material as a liquid crystal. The position, the lengths, and number of alkyl chains on the porphyrin determine the specific properties of the materials, such as melting point, solubility, and phase. To strengthen the equatorial interactions and modulate the $\pi-\pi$ interactions, *meso*-3,5-dialkyphenyl moieties are often used. A number of reports on the synthesis and characterization of new mesogenic porphyrinic materials, including those with fullerene, have appeared since 2003.[125,336−347]

Nolte and co-workers synthesized a mesogenic material by mounting three porphyrins bearing liquid crystal-forming substituents on a central benzene ring (Figure 22).[125] By

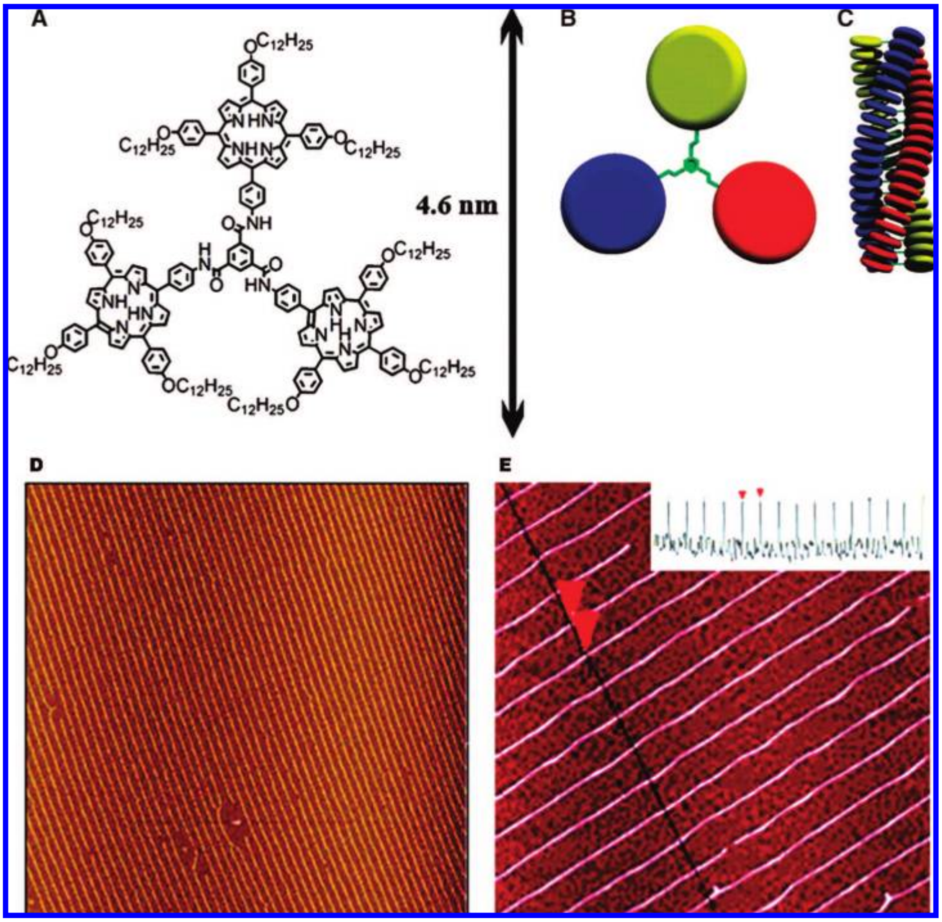


**Figure 22.** Porphyrin liquid crystal patterning. Both the presence of nine dodecyl groups and intramolecular hydrogen-bonding contribute to the organization of a porphyrin trimer on mica: (A) molecular structure; (B) schematic representation; (C) columnar stack of the liquid crystal; (D) AFM image (scan size = 25 × 25 $\mu m^2$) of a pattern formed on mica; (E) zoomed AFM image (scan size = 10 × 10 $\mu m^2$). Reproduced with permission from ref 125. Copyright 2006 AAAS.

simple drop casting of a solution onto a surface, large domains form containing highly ordered patterns as a result of a synergy between the mesogenic properties and the H-bonding interaction of the amide linking groups. It is asserted that the complex topological arrangement and features of the molecule lead to the hierarchically organized patterns such as lines, yet as shown above (e.g., in section 7), it is likely that by utilization of both axial and equatorial intermolecular interactions, many porphyrins can be induced to form similar complex structures on surfaces under the appropriate deposition conditions. Replacement of the *n*-alkyl chains with those containing a chiral center also results in supramolecular polymers in solution via H-bonding and $\pi-\pi$ interactions, but a different organization was observed after deposition on surfaces.[348]

A unique structure from Sessler's group is prepared by expanding the porphyrin core to a 32 $\pi$-electron system.[346] The interest for the expansion of the porphyrin macrocycle relies on the fact that these molecules show unusual optical properties and can coordinate metal cations including those in the lanthanide and actinide series. In this case, these features have been combined with the properties of a liquid crystal creating a new class of materials (Figure 23).

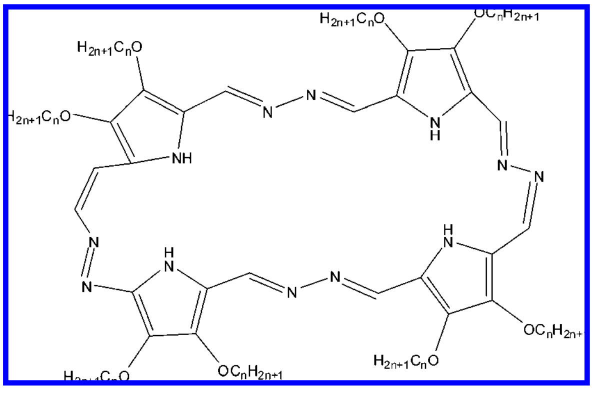


**Figure 23.** Hydrazinoporphyrin liquid crystal, $n$ = 1, 6, 10, or 14. This is the first example of an expanded porphyrin as a core of a liquid crystal.[346]

## 8.1. Summary

Because porphyrin liquid crystal-forming and mesogenic molecules are easy to prepare, form macroscopic domains, and are robust, these organic materials show significant potential in opto-electronics and perhaps in the fabrication of photovoltaic devices. In the latter arena, in addition to chemical stability, one of the challenges for the uses of self-organized organic molecules is the stability of these materials under long-term use, that is, possible reorganization induced by environmental conditions such as light, temperature, and humidity. The approach afforded by liquid crystals may meet these latter challenges because they have a good mechanism for self-repair. It may be possible to build in additional functions into these systems.

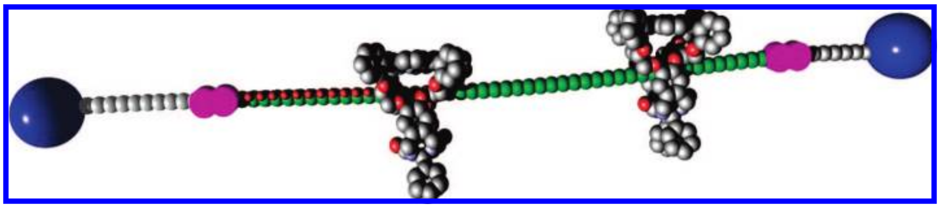


**Figure 24.** The direction of a supramolecular catalyst threaded on a butadiene polymeric substrate is driven by the differences in binding affinities for the diene compared with the epoxide product (courtesy of R. J. M. Nolte). Adapted with permission from ref 357. Copyright 2003 Nature Publishing Group.

## 9. Toward Mechanical Devices

Existing biological motors, pumps, and devices still have much to teach us. Because of both mechanical and tribological considerations, nanoscale motors, pumps, and other mechanical devices require controlled dynamics on several length scales. Global conformational changes must be in tune with local dynamics and intermolecular interactions to maximize device efficiency. Specific solvent interactions and dynamics can be exploited to tune the tribology.[349,350] The design criteria de facto mean that individual devices will need to be self-assembled into discrete structures, which then may self-organized into larger scale materials as long as the individual units are oriented into arrays where they can perform cooperatively, for example, aligned in the same direction. Additionally, in order for unidirectional motion of a supramolecular motor on a polymer or molecules through a pump, there must be built-in asymmetries in the device.[11,43,44]

One biological example is given. Helicases are ubiquitous in all living systems because they are essential proteins that unwind DNA and RNA for replication and transcription; estimates indicate that ~15% of the human genome codes for this class of enzyme.[12−14] Many are ring-shaped hexamers that are ca. 10 nm in diameter. The likely mechanism of these molecular motors involves the ring surrounding one strand of duplex DNA and forcing the strands apart as it moves along the double helix using both energy from the hydrolysis of ATP and thermal energy from the reaction and the bath ($kT$) acting on both the nucleic acid strands and the helicase. During this process there are several conformational changes in the hexamer that are largely governed by the three-dimensional structure, which is of course dictated by the protein sequence, the organization of the monomers, and the system's dynamics. The helicase machine is designed to not interact too strongly with the substrate or it would not be processive. Note that base pair fraying and enzyme−substrate interactions are modulated due to $kT$ as an essential part of the mechanism.

There are several notable examples of supramolecular systems that can function as a component of a mechanical device such as a motor.[351−353] There has been several decades of study and design of molecular rotors, such as the aryl moieties on tetraarylporphyrins and the axially coordinated groups on metalloporphyrins.[60] Stochastic devices or those without directional control, for example, rotors that go in either direction, can act as a bearing. A priori mechanical/dynamic properties of molecular systems are temperature dependent. Device dynamics or structures can be photogated thermally,[27] by electron transfer,[354] or by groups that isomerize reversibly.[67,355,356] In terms of photoisomerization, individual molecules can be cycled but populations will eventually reach an equilibrium because the quantum yields of the photoisomerization processes are not 100%. Second, populations of molecular rotors and mechanical devices that are gated by chemical stimuli, such as metal ion binding or recognition of a given motif, eventually reach an equilibrium because neither the recognition of the stimuli nor the release of this agent are achieved with 100% yields. These equilibriums can be pushed using large concentration differences, long irradiation times, and long incubation times but at the cost of diminishing the usefulness of the functional ensemble. Nature addresses these issues in several ways. Global and local asymmetries in the supramolecular complex and asymmetries in the interactions with substrates are modulated by numerous weak intermolecular interactions rather than a few strong interactions, thereby exploiting microscopic reversibilities. In turn, the sum of the small asymmetries in the interactions and dynamics can result in unidirectional movements.

An attractive example of unidirectional movement is a strapped porphyrin catalyst threaded by a polymeric substrate (Figure 24).[357] As the catalyst moves along the polymeric substrate it oxidizes polybutadiene to the epoxide, and the movement of the catalysts is then driven by asymmetric interactions with the substrate. Though the analogy has limitations, the authors compared the catalytic system to a T4 DNA polymerase. The rotational dynamics of porphyrin zirconium and cerium sandwich complexes have been shown to be gated by the binding of appropriate substrates to recognition groups on the porphyrins.[358] The position of the ring in a rotaxane can be reversibly shuttled from one position to another by photoinduced electron transfer from a porphyrin to a $C_{60}$ and subsequent redox chemistry.[359] Other rotaxanes, some including porphyrins, reversibly change their length in response to binding of different metal ions in rough analogy to muscle contraction.[360,361]

## 10. Conclusions and Outlook

### 10.1. Design

The design and implementation of motifs that direct the self-organization of chromophores has facilitated the development porphyrin-based photonic materials. Materials composed of porphyrins that are difficult or cumbersome to synthesize may have limited commercial potential because of the costs related to the synthesis; nevertheless these molecules are useful in developing the design principles needed to form complex architectures and understand the physical properties of these materials. The optimization of the chemical and photonic properties of the materials arises from the nanoarchitecture, and these studies have revealed much in terms of both the function and the principles of supramolecular chemistry. The versatility of a building-block approach for the bottom-up fabrication of materials, especially hierarchical organization on surfaces, extends to a plethora of other dyes and functional molecules. These studies have led to a deeper understanding of the chemical, electrochemical, and photochemical properties of supramolecular systems and the multiple roles the recognition motifs play in both structure and function.

Future directions toward practical utilization of self-organized multiporphyrin nanoarchitectures will focus on several areas. The photonic function(s) of many systems will require hierarchical organization on length scales of nanometers (molecule), to tens of nanometers (e.g., film heights), to centimeters (e.g., films), perhaps with different chromophores in analogy to photosynthesis to ensure the directional flow of photonic energy. The assembly of molecules (primary structure) into supramolecular systems (secondary structure) has been well developed, and organization of these into crystalline materials (tertiary structure) is rapidly developing. However the hierarchical organization into materials that interact in predetermined ways with surfaces (quaternary structure) remains a keystone issue.[11]

### 10.2. Intermolecular Interactions

The design and implementation of porphyrin molecules bearing two or more different recognition motifs that can be systematically, either simultaneously or sequentially, used to construct ordered materials is affording the next generation of supramolecular photonic materials. Controlled use of nonspecific interactions, in addition to H-bonding and different types of coordination chemistry, can result in more complex architectures. Note that the moieties used to assemble or organize the chromophores may bring a function in themselves or modulate the function of the system.[32,314] The role of the recognition motifs in photoinduced energy and electron transfer is not well understood. For example, energy transfer rates from donors to acceptors have been shown to depend on the direction across the intervening H-bonding groups used for self-assembly.[97]

### 10.3. Dynamics

The role of molecular dynamics in covalent electron donor−acceptor systems is well appreciated.[10] There are a few reports on photoinduced conformational changes in systems containing porphyrins, and some are reversible for a limited number of cycles.[353] Considering the substantial vibrational energy imparted to chromophores upon light absorption,[26−28] the intermolecular forces holding supramolecular photonic materials together may weaken or break transiently or result in a reorganization of the nanoarchitecture. For example, in porphyrinic assemblies mediated by axial coordination to chelated metal ions, the axial ligands may transiently deligate in the excited state.[27] There is little work on the precise role of supramolecular dynamics in both the ground state and the excited state in the photonic properties of self-organized systems. A better understanding of these dynamics will afford additional design criteria. Combinations of time-resolved transient optical spectroscopy and time-resolved photoaccoustic analysis[362] of supramolecular porphyrinoid materials can probe the excited-state dynamics.

### 10.4. Combinations of Different Chromophores

There remains a paucity of self-assembled systems containing different chromophores, such as porphyrins and phthalocyanines, in precise architectures that can serve as efficient light-harvesting materials wherein energy flows in a predictable direction. Therefore new design algorithms are needed to assemble and organize two or more different types of dye into specific architectures before functional evaluation of these systems can lead to the design of new materials. In addition to added stability relative to the porphyrins, the extended $\pi$-systems in phthalocyanine and naphthalocyanines bring new photonic properties to the design palette, but it can be difficult to synthesize specific molecules. Rational synthetic methods of Pc and NPc, similar to those developed for the porphyrins,[363] are needed to develop the supramolecular chemistry of these systems. Covalently attached arrays can more readily organize the photonic moieties.[2,9,364]The formation of hybrid materials, such as porphyrins with fullerenes or with polyoxometalates, is developing rapidly as well. The supramolecular approaches to forming these hybrid systems aim to synergistically exploit the useful properties of each. These burgeoning efforts have yielded catalysts, but the detailed photonic properties are not well studied. Porphyrins adsorbed or organized onto conducting or semiconducting surfaces, either crystalline or nanoparticle, are yielding information on the transport properties in terms of molecular photonic and molecular electronic materials.[175] The majority of the well-characterized materials are self-assembled monolayers or crystals. The organized deposition of discrete self-assembled arrays onto surfaces remains a challenge, and as a result, the transport properties between these structures and conducting or semiconducting materials are poorly understood. Therefore, many exciting challenges remain in understanding the fundamental chemistry and physics of supramolecular photonic materials composed of porphyrins and other chromophores on surfaces.

With a ca. 3.5 billion year head start, Nature is still better able to construct complex functional materials ordered from nanometers to meters. We have developed a good understanding of the organic chemistry to design molecules and the supramolecular chemistry to organize them into small arrays or simple films and can sometimes form crystals with hierarchical order. Our ability to self-assemble and self-organize porphyrins and related macrocycles into complex three-dimensional architectures is limited. Though systems with designed conformational changes have been made, these are necessary but not sufficient for the design of systems with dynamic properties that function as motors, pumps, and other directional mechanical devices gated chemically or photochemically, so these are yet to come. These nanodevices exist, so they are possible.

## 11. Abbreviations

| | |
|---|---|
| CoPc | cobalt(II) phthalocyanine |
| $F_{16}$CoPc | perfluorinated cobalt(II) phthalocyanine |
| H-bond | hydrogen bond |
| HOPG | highly ordered pyrolitic graphite |
| ITO | indium tin oxide |
| LB | Langmuir−Blodgett |
| LBL | layer-by-layer |
| NiOEP | nickel ocatethylporphyrin |
| NLO | nonlinear optics |
| POM | polyoxometalate |
| SAM | self-assembled monolayer |
| TCPP | *meso*-tetra-4-carboxyphenylporphyrin |
| THF | tetrahydrofuran |
| TON | turn over number |
| TPP | tetraphenylporphyrin |
| TPPS | *meso*-tetra(4-sulfonatophenyl)porphyrin |

| | |
|---|---|
| TPyP | *meso*-tetra-4-pyridylporphyrin |
| $TPyP^{4+}$ | *meso*-tetra-4-*N*-methylpyridiniumporphyrin |
| UHV | ultrahigh vacuum |
| porphyrinic | adjective meaning containing porphyrins |
| porphyrinoid | tetrapyrrole macrocycle such as porphyrins, phthalocyanines, corroles, porphyrazines, and corrolazines |

## 12. Acknowledgments

We thank the other member of our groups for contributing to this work: Sunanina Singh, Amit Aggarwal, and Mikki Vinodu. This work was supported by the NSF (Grant CHE-0554703) and the NIH SCORE program (Grant GM60654) to C.M.D. Support for infrastructure and instrumentation in the sciences at Hunter College comes from the National Science Foundation, National Institutes of Health, including the RCMI program (Grant RR-03037), and The City University of New York. Dedicated to Professor Klaus Grohmann, friend and colleague, on the occasion of his retirement.

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CR8002483