# The materials chemistry of porphyrins and metalloporphyrins

KENNETH S. SUSLICK*, NEAL A. RAKOW, MARGARET E. KOSAL and JUNG-HONG CHOU

*School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Goodwin Avenue, Urbana, IL 61801, USA*

**ABSTRACT:** Porphyrins and metalloporphyrins provide an extremely versatile nanometer-sized building block for the control of materials properties. Films, solids and microporous solids have been explored as field-responsive materials (i.e. interactions with applied electric, magnetic or electromagnetic fields) and as 'chemo-responsive' materials (i.e. interactions with other chemical species as sensors or for selective binding or catalysis). Copyright © 2000 John Wiley & Sons, Ltd.

**KEYWORDS:** non-linear optics; photonic materials; microporous solids; conductive polymers; sensors

## INTRODUCTION

Porphyrins and metalloporphyrins provide an extremely versatile synthetic base for a variety of materials applications [1]. During the past decade, metalloporphyrin assemblies have been increasingly explored as building blocks for tailored materials properties. The fundamental properties of materials come from their response to macroscopic effects (i.e. mechanical properties), their interaction with applied electric, magnetic or electromagnetic fields (i.e. field responsive properties) or their interaction with other chemical species (i.e. 'chemo-responsive' properties). The materials chemistry of porphyrins falls primarily into the latter two categories.

Porphyrins and metalloporphyrins have been broadly studied as field-responsive materials, particularly for potential optoelectronic applications. For example, the facile substitution of the periphery of various porphyrins has generated a series of unusual liquid crystalline materials. The porphyrin ligand serves as a platform on which one can erect desirable molecular and materials properties, including very large dipole moments, polarizabilities and hyperpolarizabilities. The non-linear optical properties of these materials are of special interest, in part for energy transfer with molecular control, and in part for potential applications in optical communications, data storage and electro-optical signal processing. The stability of mono- and dication porphyrin $\pi$-radicals makes these systems especially interesting for photoionization and photoconductive processes, closely related to the so-called special-pair reaction center of photosynthesis and the photogeneration of electron transfer. As another example, various polymeric porphyrins have been examined for their unusual low-dimensional conductivity.

In contrast to their interaction with applied fields, porphyrins and metalloporphyrins can also interact with other chemical species. One might view such interactions as chemo-responsive rather than field-responsive. The development of chemo-responsive materials based on porphyrins, however, has been somewhat less development. As an example of such applications, porphyrin solids are often highly porous and the intentional development of molecularly based molecular sieves or shape-selective solid catalysts is currently under development. Porphyrins and metalloporphyrins have also been examined for a variety of sensor applications, which clearly represent an important class of chemo-responsive materials.

## FIELD-RESPONSIVE MATERIALS

Most of the work on field-responsive porphyrins has centered on photonic materials: mesogenic (i.e. liquid crystalline) systems, non-linear optical response and nanoscale optoelectronic materials (e.g. 'molecular electronics'). Appending long alkyl chains to the periphery of a rigid tetrapyrrolic core has proved to be a general methodology for the synthesis of liquid crystalline materials. Liquid crystals show properties of both the liquid and solid phases, possessing order over intermediate distances but retaining many of the rheological properties of liquids. Phthalocyanine derivatives have been widely investigated as thermotropic mesogenic materials [2], whereas porphyrins and metalloporphyrins have received only cursory examination. The larger phthalocyanines tend to have high melting points; porphyrins offer a similar geometrical structure and a greater ease of functionalization, while having a smaller inner core and therefore lower, more usable melting points. The majority of porphyrin mesogenic

*Correspondence to: K. S. Suslick, School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Goodwin Avenue, Urbana, IL 61801, USA.
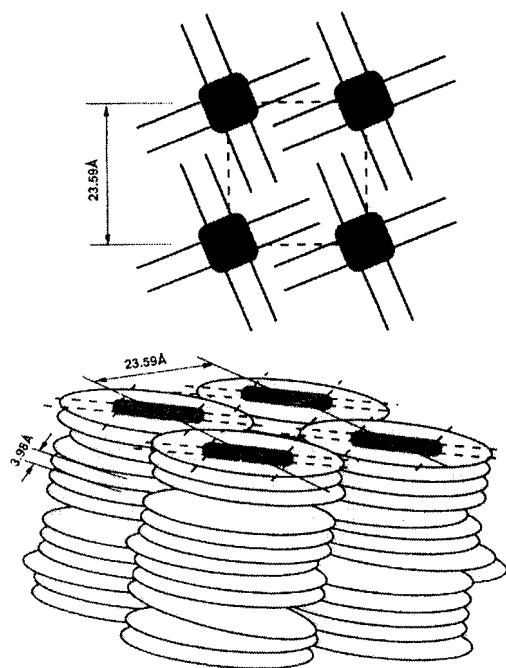E-mail: ksuslick@uiuc.edu

**Fig. 1.** Schematic representation of columnar arrangement of discotic zinc *n*-decyl ether octa-substituted porphyrin stacks. (Reprinted with permission from Ref. [3].).



**Fig. 2.** Structure of 3,5-dicarboxyphenylporphyrin.

materials have a discotic columnar nature in which the porphyrins stack like saucers along their short axis (Fig. 1).

As one example, Fox, Bard and co-workers have synthesized and investigated the physical properties of a series of octyl-ether and octyl-ester porphyrin materials, e.g. the free base and metalated derivatives of 2,3,7,8,12,13, 17,18-octakis($\beta$-*n*-alkoxy)ethylporphyrin, $H_2((OC_nH_{2n+1})$ OEP). The molecules were found to structurally order in columns such that the macrocyclic planes tilt significantly with respect to the columns with interfacial porphyrin–porphyrin distances of $\sim$4 Å. This structure has been suggested as a one-dimensional 'molecular wire' motif for electronic conduction [3].

Thin films of the zinc octakis($\beta$-decoxyethyl)porphyrin material included in indium tin oxide (ITO) electrodes were explored as an electro-optical data storage system. Capillary filling of the porphyrin into the ITO cell provided the physical construction of the photoconductive system. A scanning tunneling microscope (STM) was used to initiate charge trapping ('writing') and measurement ('reading'). A storage density of $\sim$3 Gbits cm$^{-2}$ was maintained over 2000 h of continual subjection to charge, and greater than 60% of the current signal was still 'readable' after $\sim$1500
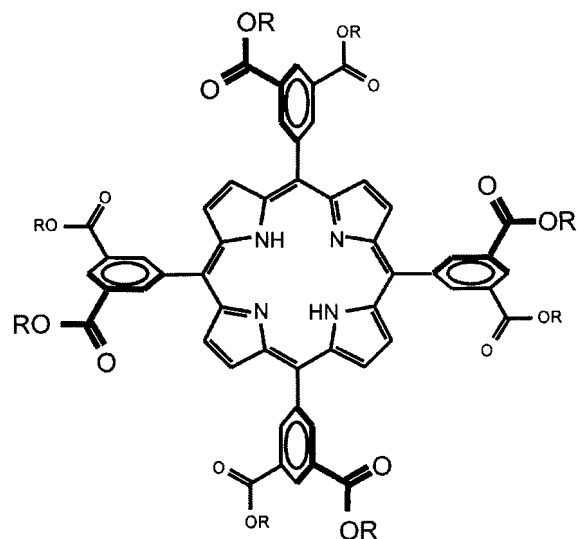
readings. Subsequent work demonstrated 1.5 billion 'writing' and 'reading' sequences of the material without substantial change in output signal [4].

As another recent example, Patel and Suslick reported [5] the synthesis and properties of a series of mesogenic 'bispocket' porphyrins (Fig. 2). These materials possess liquid crystalline phases that are stable over an extremely wide temperature range (Fig. 3), greatly increasing their potential utility. In addition, they isolated novel metalloporphyrin mesogens that permitted axial ligation to the metal, including one novel phase possessing a permanent dipole moment. Hexagonal columnar discotic liquid crystals of the *n*-alkyl esters of free base 5,10,15,20-tetrakis(3,5-dicarboxyphenyl)porphyrin ($H_2(T(3,5-CO_2R)PP)$, $R \equiv n$-$C_nH_{2n+1}$, $n = 10$, 12, 14, 16, 18, 20, 22) displayed a narrowing range of mesogenic behavior as the alkyl chain length increased. These porphyrins feature pocketed sites on both faces of the porphyrin macrocyclic ring, due to the relative rotation of the phenyl groups. The presence of these protected pockets for axial ligation was utilized to construct a unique five-coordinate vanadyl derivative with dodecyloxyl chains. This approach produced both a liquid crystalline range of over 246 °C and a substantial dipole moment perpendicular to the porphyrin plane.

The synthesis and chemistry of non-linear optical (NLO) porphyrin-based materials have been examined in some detail. Porphyrins have several desirable properties for use in optoelectronics: they have greater thermal and photochemical stability than typical organic chromophores; their



Ken Suslick received his B.S. from Cal Tech in 1974, his Ph.D. from Stanford in 1978, and is presently the *William H. and Janet Lycan* Professor of Chemistry and Professor of Material Science & Engineering at the University of Illinois at Urbana-Champaign. He has received the ACS Nobel Laureate Signature Award, the MRS Medal, an NIH RCDA, a Sloan Foundation Research Fellowship, and the Silver Medal of the Royal Society for the Arts, Manufactures and Commerce.
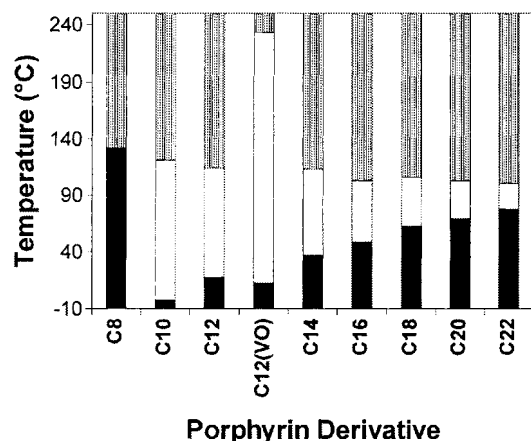
**Fig. 3.** Histogram of differential scanning calorimetry results for T(3,5-COOR)PP materials: black, solid phase; white, meso-phase; gray, isotropic. (Reprinted with permission from Ref. [5].).

extended $\pi$-conjugated macrocyclic ring gives large NLO effects [6]; and subtle variation in their physical properties can be made easily through chemical modification of their periphery. Recent developments in this area describe some second- and third-order non-linear optical properties.

Suslick *et al.* [7] measured the first hyperpolarizabilities ($\beta$) of porphyrins having electron donor (amino) and acceptor (nitro) groups in the *para* position of 5,10,15,20-substituted tetraphenylporphyrins using the electric-field-induced second-harmonic generation (EFISH) technique. The dipole moment ($\mu$) and $\beta$ values were affected by the position of donor and acceptor groups. In these cases the amino group 'pushes' electron density onto the macrocycle, while the nitro groups 'pull', increasing the hyperpolarizability substantially. The well-aligned charge transfer gives rise to large $\beta$ values. Since this first report, a number of other 'push–pull porphyrins' have been produced by several other groups [8–10].

Since second-order NLO response occurs only in a non-centrosymmetric environment, the incorporation of porphyrins into a polar (in the sense of poled or asymmetric) array is mandatory for most optoelectronic applications. Langmuir–Blodgett (LB) films are an extremely effective means of providing the necessary asymmetric environment for good NLO response. Suslick and co-workers incorporated similar 'push–pull' porphyrin derivatives into Langmuir–Blodgett films in order evaluate the bulk response of the material [11]. They found that good films could be created from these push–pull porphyrins simply by conjugating a long-chain fatty acid to the free phenylamine functionalities. The mean molecular area of these LB films depended strongly on the number of alkyl chains, which did not change the porphyrin orientation, but rather altered the packing density of the porphyrins.

As with phthalocyanines, the third-order non-linear optical susceptibility ($\chi^{(3)}$) of porphyrins can be manipulated by chemical substitution. The third-order NLO properties of several tetraphenylporphyrin compounds were first reported by Meloney *et al.* [12]. $\chi^{(3)}$ was measured by the degenerate four-wave mixing technique from toluene solutions of free base, zinc- and cobalt-containing TPPs. The effective $\chi^{(3)}$ values of these materials were estimated from the thermally induced refractive index changes. All porphyrin derivatives showed $\chi^{(3)}$ values on the order of $10^{-11}$ esu.

Optical limiting properties of fullerenes, porphyrins and phthalocyanines have attracted much attention since they have applications in passive solid state sensors and in human eye protection from high-intensity visible light sources [13]. Although metallophthalocyanines have been studied in detail, there are few reports on optical limiting properties of porphyrins. Su and Cooper [14] reported optical limiting properties of free base octabromotetra-phenylporphyrin ($H_2(Br_8TPP)$) and its metal-containing derivatives. The non-linear optical absorption efficiency was measured at 532 nm. The efficiency data showed a trend as $Zn(Br_8TPP) > Cd(Br_8TPP) > H_2(Br_8TPP) > Pb(Br_8TPP) > Cu(Br_8TPP) \approx Cd(Br_8TPP)$ which was related to the spin state of the central metal atom. Comparable to phthalocyanines, $Zn(Br_8TPP)$ showed the strongest non-linear absorption efficiency observed among porphyrins.

An ultimate goal in microelectronics is the design of electronic switches, wires, transistors and gates made of single molecules. Approaches to this goal borrow heavily from the photosynthetic reaction center, both in their physics and in their chemistry. In principle, porphyrin arrays connected with conducting or insulting molecular wires could be converted into such molecular photoelectronic devices. In practice, however, the majority of the models have yet to function as electronic switching devices or molecular wires. Among others, the groups of Wasielewski [15], Lindsey [16], Crossley [17], Osuka [18] and Drain [19] have explored various strategies to produce multi-porphyrin arrays for studies of molecular photonics. Some of these systems extend as 'molecular photonic wires' with lengths of 90 Å or more (Fig. 4).

Studies in the areas of conductive polymers and ferroelectric materials constitute a relatively small subset of porphyrin materials research. Nonetheless, the versatility of porphyrins has allowed for some interesting and useful results in these areas. A variety of approaches have been made towards the creation of porphyrin-based conductive polymers and ferroelectric materials.

Electrical conductivity of polymers continues to be one of the most important research areas for materials science. Porphyrins constitute a versatile building block for the preparation of conductive polymers. The large $\pi$ system of porphyrins and metalloporphyrins yields a HOMO and LUMO which are generally separated by only 2 eV. This gap can be narrowed via polymerization or additional
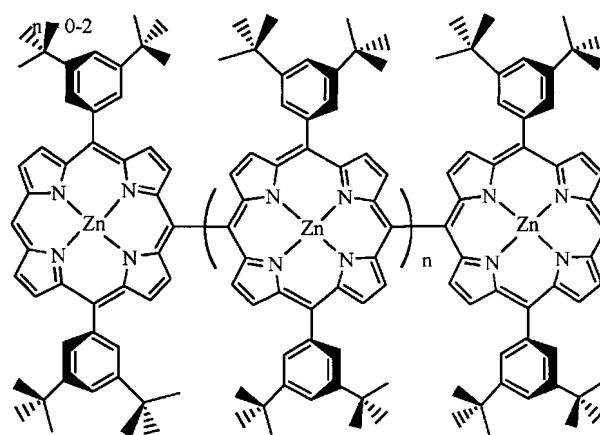


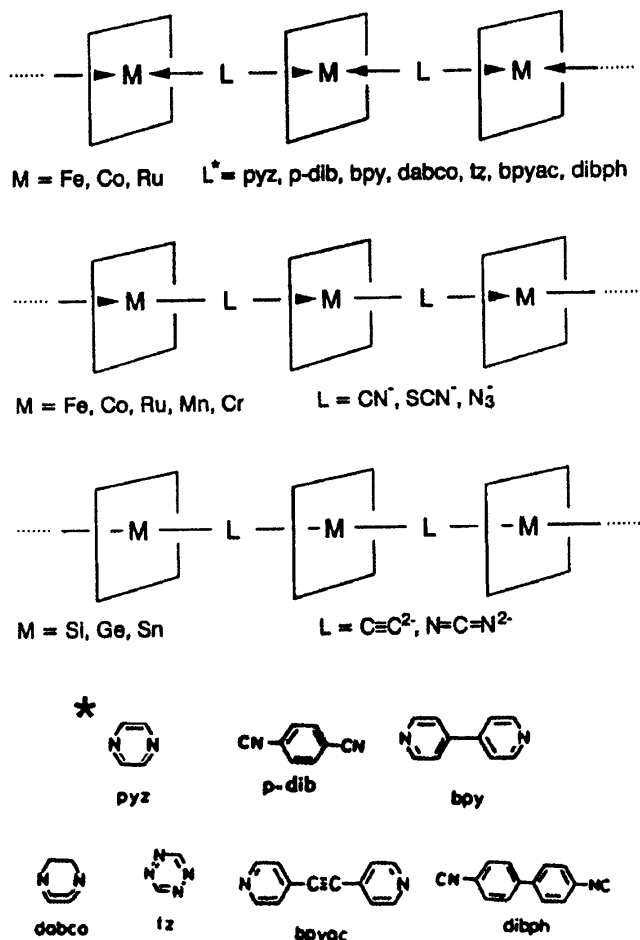**Fig. 4.** 5,10,15,20-Linked porphyrin arrays. (Reprinted with permission from Ref. [18].).

**Fig. 5.** Various 'shish kebab' one-dimensional coordination polymers.



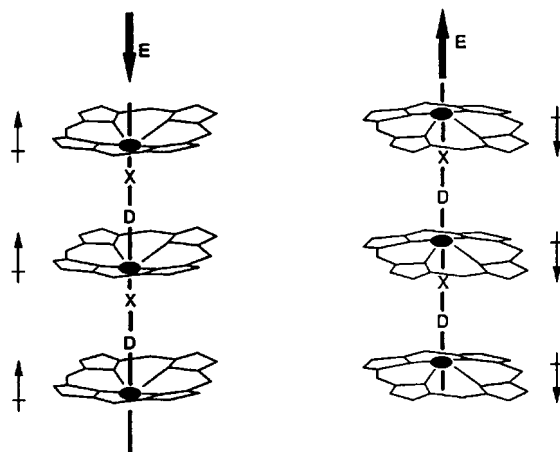**Fig. 6.** Schematic representation of a ferroelectric coordination polymer and dipole moment switching in response to an external field.

conjugation, leading to interesting conductivity possibilities. In addition to conduction through the $\pi$ system, metal–metal conductivity is possible within a chain of metalloporphyrins. Because porphyrins are able to coordinate a wide range of metals, conductivity is readily tunable in these cases.

The 'shish kebab' approach [20–22] yields a class of coordination polymers based on stacked macrocyclic metal complexes (Fig. 5). Here, macrocyclic complexes are linked together by axial coordination of bridging ligands. Until recently, 'shish kebab' polymers with bridging ligands larger than a single atom were rare. In the late 1970s, Hanack *et al.* [21] started to prepare a large family of such polymers employing phthalocyanines of the type $[M(Pc)(L\text{-}L)]_\infty$.

Collman *et al.* [22, 23] have reported similar 'shish kebab' polymers of the type $[M(OEP))(L\text{-}L)]_\infty$ (M $\equiv$ Fe, Ru, Os; L-L $\equiv$ pyz, bpy, dabco) and examined their conductivities. Many of the these 'shish kebab' coordination polymers can be doped with iodine, which drastically increases their conductivity (e.g. $\sigma_{300\ K} = 1 \times 10^{-6}\ \Omega^{-1}$ cm$^{-1}$ for $[Fe^{II}(Pc)(pyz)]_\infty$; $\sigma_{300\ K} = 2 \times 10^{-1}\ \Omega^{-1}$ cm$^{-1}$ for $[Fe^{II}(Pc)(pyz)I_{2.54}]_\infty$). The conductivity of these doped 'shish kebab' polymers depends on the interaction of the metal $d_\pi$ orbitals with the $\pi^*$ level of the bridging ligand. Collman *et al.* found that the metal–metal communication is greater for the better $\pi$-bonding metals (e.g. Os > Ru > Fe) and the more $\pi$-acidic bridging ligands (e.g. pyz > bpy dabco).

Porphyrins linked with conjugated organic bridges form another subclass of conductive porphyrin materials. Work toward such polymers was done by Crossley and Burn, who synthesized a linearly conjugated porphyrin system [24]. Spectroscopic data on this system indicated a significant decrease in the HOMO–LUMO gap (by *ca* 0.8 eV) compared with the porphyrin monomer. In related studies, Yu and co-workers used the Heck coupling reaction to synthesize conjugated porphyrinic polymers [25]. A series of polymers were generated with $M_w$ values of 5000–46 000. The polymers were soluble in a range of organic solvents and were cast as optical films onto glass slides. Their conductivities were studied, showing a steady increase in current upon photoirradiation.

Very little work has been done on the development of coordination polymers as molecularly based ferroelectric materials. Ferroelectrics carry a permanent, macroscopic electric dipole moment (i.e. polarization) in the absence of electric field. Furthermore, the polarization of ferroelectric materials can be switched with the application of an external electric field. Ferroelectrics have unusual electro-optical, photorefractive and pyroelectric properties. They can be fabricated into electronic oscillators, high-frequency filters, electroacoustic converters, pyroelectric radiant energy receivers and non-linear capacitive elements. Most ferroelectrics are metal oxides, such as $BaTiO_3$ and $LiNbO_3$. In a further development of the 'shish-kebab' class of polymers, metalloporphyrin coordination polymers have been suggested as possible ferroelectric materials [20]. Coordination polymers of non-planar metalloporphyrins with *non-symmetrical* bridging ligands carry an aligned dipole moment along the stacking axis. The dipole moment originates from the charge separation between the bowl-shaped porphyrinato core and the metal atom. The metal atom tends to be pulled out of the porphyrin plane by strong axial ligands. If the metalloporphyrin has two different axial ligands, the metal atom will be pulled toward one side, depending on relative ligation strength and steric demands. By analogy to metal oxide ferroelectrics, the direction of the bulk polarization in such coordination polymers may respond to an external field (Fig. 6). Suslick and Chen have prepared several one-dimensional coordination polymers of metalloporphyrins with non-symmetric bridging ligands as candidates for molecular ferroelectric materials [20, 26]. Metalloporphyrin complexes of Fe(II), Fe(III) and Sn(IV) were examined.

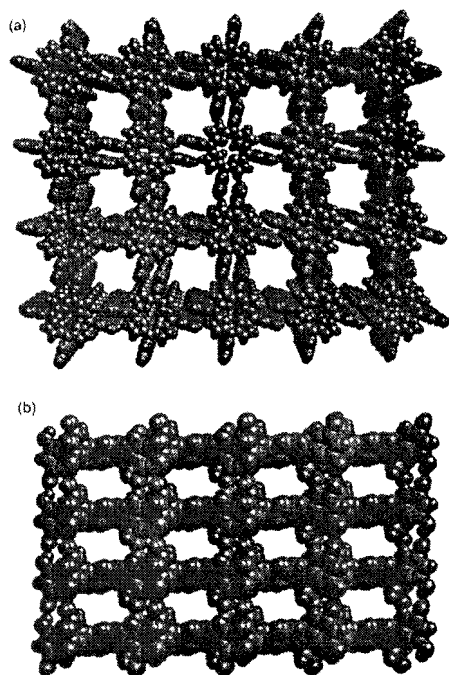**Fig. 7.** Molecular packing diagrams of $H_2(T(3',5'-DHP)P) \cdot 5EtOAc$ showing (a) channels between porphyrin columns and (b) channels perpendicular to columns. (Reprinted with permission from Ref. [33].).

# CHEMO-RESPONSIVE MATERIALS

In order to generate selective chemo-responsive materials, molecularly sized binding sites or pores must be created. A number of researchers have explored synthetic strategies for the construction of porphyrinic solids that contain molecularly sized cavities or channels. Porphyrin macrocycles can be envisioned as flat, rigid, geometrically square building blocks approximately 1 nm wide. Out-of-plane twisting by the 5,10,15,20-substituted phenyl rings (as necessitated by steric constraints) provides a route to construct structures extending beyond the porphyrin macrocycle plane. Chemical modification of the perimeter is facile in many cases. Additionally, the thermal stability makes them an attractive precursor for potential use at elevated temperatures. Furthermore, metalloporphyrins have demonstrated catalytic ability in a wide variety of reactions [27, 28]; thus porous metalloporphyrin networks have the potential to act as shape- and size-selective catalysts.

Strouse and coworkers [29–31] examined the extensive crystal structure library of free base and metalated porphyrin lattice clathrates in which the predominant intermolecular bonding interactions were of a very weak nature. In addition to $H_2(TPP)$, their database included simple substituted porphyrins such as o-amino- ($H_2(T(o-NH_2)PP)$), p-methoxy- ($H_2(T(p-OCH_3)PP)$) and p-bromo- ($H_2(T(p-Br)PP)$) tetraphenylporphyrins. While the most commonly metalloporphyrin studied was the Zn(II) species, at least 11 other metalloporphyrins were examined. They realized that the large majority of these structures contained a high concentration of solvates and were in effect 'porphyrin sponges'. These TPP derivative materials were held together by van der Waals forces and found to exhibit comparable packing modes generalized as the simple body-centered cubic (BCC) arrangement. The driving force for

clathrate formation was identified as the efficient packing of the porphyrin moieties in two dimensions. A third dimension is accessible for inclusion of guest molecules. The dominant interaction is described as 'porphyrin–porphyrin interactions' between perpendicularly oriented phenyl groups on adjacent molecules. Similar packing modes were observed for over 65 different TPP species [29, 30].

In an effort to synthesize more robust frameworks, hydrogen-bonding interactions have been explored as basis for linking porphyrin molecules. Hydrogen bonds offer the additional advantages of directionality and selectivity. While hydrogen bonding is certainly a stronger interaction than the van der Waals interactions that hold the 'porphyrin sponge' solids together, even multiple hydrogen bonds per porphyrin still provide only modest stabilization of the solids in the absence of their solvates. For example, Goldberg et al. have explored a number of substituted tetraphenylporphyrins as building blocks for clathrate solids [32]. Supramolecular networks based on hydrogen bonding between symmetrically substituted octahydroxyporphyrins were explored by Suslick and co-workers [33, 34]. Both ortho- and meta-dihydroxyphenylporphyrins and their Zn(II) and Mn(III) derivatives were developed as molecular building blocks for nanoporous materials. The position of the peripheral hydroxyl groups, the choice of metalated or free base porphyrin and the nature of the solvate dramatically influence structural features. These materials featured significant void volumes, as high as 67% calculated channel volume from X-ray crystal structures. For example, a one-dimensional hydrogen-bonding structure was found for $H_2(T(3',5'-DHP)P) \cdot 5EtOAc$ in which porphyrin macrocycles stack in a columnar fashion. These columns of porphyrins align parallel to one another, forming a porous three-dimensional network with channels of 6.5 Å × 6.5 Å between them and 3.4 Å × 3.4 Å running perpendicular to the columns (Fig. 7). These columns are held together by weak van der Waals interactions.

In the last decade, significant progress toward the rational construction of three-dimensional solids constructed from metal cations and organic molecules has been described [35]. Of particular interest have been metal–organic coordination networks possessing nanoscale pores [36]. Metal–ligand interactions are often quite strong and should therefore provide a more robust framework than those based on van der Waals, hydrogen bond or π–π interactions. The most interesting of these have come from Robson and co-workers, who have explored metal-to-ligand coordinative bonding as a means to build more robust porphyrinic materials. They reported a structure in which Pd(TPyP) molecules are interconnected by Cd(II) centers [37]. Each porphyrin is coordinated by two trans-pyridyl donor porphyrin molecules and by two cis donor porphyrin molecules (Fig. 8). The overall neutral framework $[Pd(TPyP) \cdot Cd(NO_3)_2 \cdot 8.6H_2O]$ features infinite interwoven layers of the porphyrin network.

In subsequent work, Robson and co-workers [38] reported three-dimensional network solids using the copper porphyrin complexes of 5,10,15,20-tetra-4'-pyridylporphyrin, Cu(TPyP), and 5,10,15,20-tetra-4'-cyanophenylporphyrin, Cu(TCNPP). Large extended channels (10–20 Å) were observed in which tetrahedral Cu(I) ions (as opposed to the square planar Cu(II) ions bound to the center of the porphyrin ring) coordinate to pyridyl or cyano groups on the periphery of four porphyrin molecules. While the cationic frameworks were reported to occupy less than half the
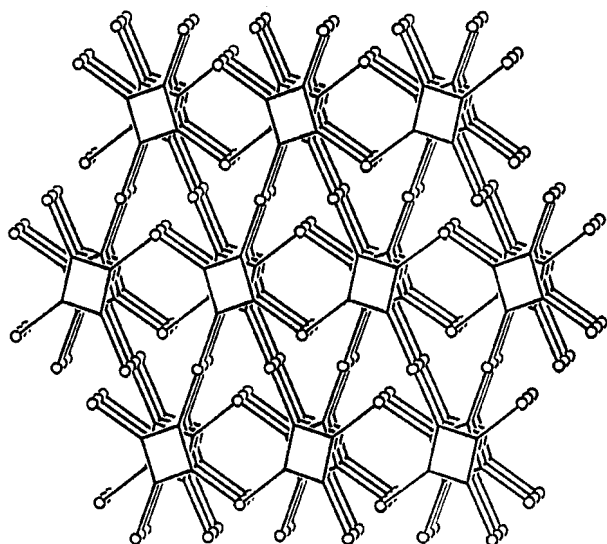
**Fig. 8.** Schematic illustration of three-dimensional porphyrin network in Pd(TPyP)·Cd(NO$_3$)$_2$·8.6H$_2$O in which porphyrins are represented as squares and cadmium ions as circles. Solvent molecules are omitted for clarity. (Reprinted with permission from Ref. [37].).



**Fig. 10.** Collman's picnic-basket porphyrins.

volume of the crystal, the void spaces were occupied by non-coordinating anions (BF$_4^-$) and highly disordered solvent molecules (acetonitrile/nitrobenzene); upon removal of the anions, crystallinity was lost. In the tetrapyridyl system a single infinite PtS-like network (Fig. 9) was revealed.

Because of their inherent stability, unique optical properties and synthetic versatility, porphyrins and metalloporphyrins are excellent candidates for a variety of sensing materials applications. Research in this area has focused on incorporation of synthetic porphyrins and metalloporphyrins into a variety of material matrices, such as polymers, glasses and Langmuir–Blodgett films. Substantial work has been done in the areas of solution and gas phase sensing.

Considering the well-understood ability of heme to bind a variety of gases, such as NO, CO$_2$ and O$_2$, porphyrins would indeed seem a suitable choice for the detection of gaseous species. During the 1990s, much work has been done involving the porphyrin-based detection of a series of gases, such as oxygen, ammonia and chlorine. In addition, recent work has entailed utilization of metalloporphyrin arrays for the detection of organic odorants, such as amines, thiols and
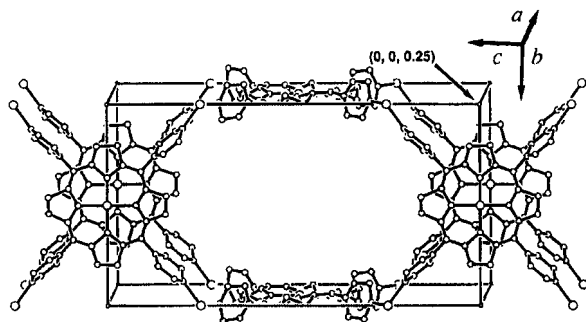


**Fig. 9.** Packing arrangement in [Cu(TPyP) · Cu]$_n^{n+}$ framework. Larger circles represent copper ions. Solvent and non-coordinating anions are omitted for clarity. (Reprinted with permission from Ref. [38].).
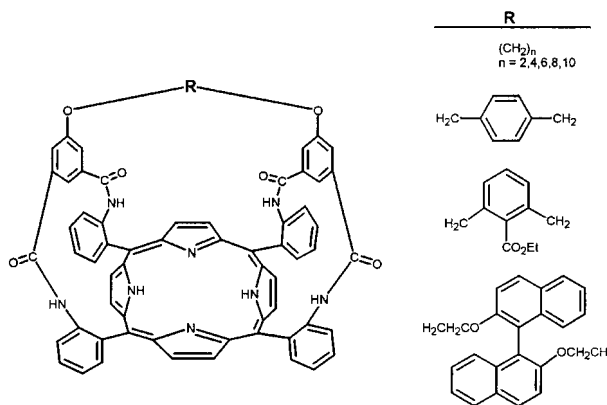
phosphines. Many gas sensors take advantage of analyte binding to the porphyrin metal center, which gives a detectable optical change. Other methods, such as the use of piezoelectric substrates coated with porphyrin films, have also been utilized for gas detection.

The use of metalloporphyrin-based materials for the detection of molecular oxygen is well developed. One approach that has been employed extensively involves the well-known phenomenon of quenching of metalloporphyrin phosphorescence by O$_2$. Owing to their high phosphorescence quantum yields and short triplet lifetimes, platinum and palladium porphyrins were originally suggested as probes for oxygen by Eastwood and Gouterman [39]. Lee and Okura have utilized sol–gels to make optically transparent glasses containing Pt(OEP) [40]. This approach is aimed at creating chemically inert, photostable materials which can be used in a variety of environments. Mills and Lepre have also employed Pt(OEP) and Pd(OEP) in a variety of different encapsulating matrices for the detection of molecular oxygen [41].

Reversible binding of oxygen to thin films of cobalt porphyrins forms the basis for another series of oxygen sensors. Systems involving cobalt porphyrins have employed a variety of signal transduction techniques. Work by Oglesby, Leighty, Collman and co-workers has utilized synthetic cobalt porphyrins for surface acoustic wave (SAW) sensing of oxygen [42]. The SAW sensor, which registers a resonance frequency decrease upon adsorption of an analyte, is coated with the porphyrin, both in the presence and absence of an imidazole- or pyridine-containing copolymer. Porphyrins used for the study were the cobalt(II) picket-fence porphyrin and cobalt(II) picnic-basket porphyrins [43] (Fig. 10). The sensor response to oxygen is reversible, although some hysteresis is noted, which is due to slow diffusion of O$_2$ out of the polymer matrix. The picnic-basket porphyrins are particularly interesting because they allow easy tailoring of the oxygen binding constant, either by changing the central metal ion or by altering the length of the bridge or 'handle'. This allows for sensing over a wide range of oxygen concentrations.

Detection of nitric oxide has become particularly important in light of its regulatory role in many physiological processes. In an example of NO detection via porphyrin-based sensors, Malinski and Taha have used microelectrode sensors consisting of layers of a polymeric porphyrin and Nafion deposited on a thermally sharpened carbon fiber [44]. Tetrakis(3-methoxy-4-hydroxyphenyl)

porphyrinatonickel(II) was polymerized onto the fiber electrochemically from a solution of 0.1 M NaOH containing the monomer. The resulting sensor operates based on the electrochemical oxidation of NO at the porphyrin-doped electrode. A 10 ms response time and a detection limit of 10 nM have been observed, and the sensor has been used for NO analysis from single endothelial cells in the pulmonary artery, as well as for NO quantitation in the blood.

## CONCLUSIONS

Porphyrins and metalloporphyrins have provided an extremely versatile nanometer-sized building block for the control of materials properties. A wide range of such properties have been explored, including various non-linear optical behavior and low-dimensional electric conduction. Porphyrinic films, solids and microporous solids have been explored as field-responsive materials (i.e. interactions with applied electric, magnetic or electromagnetic fields) and as 'chemo-responsive' materials (i.e. interactions with other chemical species as sensors or for selective binding or catalysis).

## Acknowledgements

## REFERENCES AND NOTES

1. Chou J-H, Kosal ME, Nalwa HS, Rakow NA, Suslick KS. In *Porphyrin Handbook*, vol. 6. Kadish K, Smith K, Guilard R (eds). Academic Press: New York, 2000; 43–131.
2. Lezznoff CC, Lever ABP (eds). *Phthalocyanines: Properties and Applications*, vol. 1–4. VCH: New York, 1992–1996.
3. Liu CY, Pan HL, Tang H, Fox MA, Bard AJ. *J. Phys. Chem.* 1995; **99**: 7632.
4. Liu C-Y, Pan HL, Fox MA, Bard AJ. *Chem. Mater.* 1997; **9**: 1422.
5. Patel BR, Suslick KS. *J. Am. Chem. Soc.* 1998; **120**: 11802.
6. Nalwa HS. In *Nonlinear Optics of Organic Molecular and Polymeric Materials*. Nalwa HS, Miyata S (eds). CRC Press: Boca Raton, FL, 1997; 611.
7. Suslick KS, Chen CT, Meredith GR, Cheng LT. *J. Am. Chem. Soc.* 1992; **114**: 6928.
8. Sen A, Ray PC, Das PK, Krishnan VJ. *J. Phys. Chem.* 1996; **100**: 19611.
9. Karki L, Vance FW, Hupp JT, LeCoers SM, Therien MJ. *J. Am. Chem. Soc.* 1998; **120**: 2606.
10. Peng Z, Bao Z, Yu L. *J. Am. Chem. Soc.* 1994; **116**: 6003.
11. Chou H, Chem C-T, Stork KF, Bohn PW, Suslick KS. *J. Phys. Chem.* 1994; **98**: 383.
12. Meloney C, Byrne H, Dennis WH, Blau W, Kelly JM. *Chem. Phys.* 1988; **121**: 21.
13. Perry JW. In *Nonlinear Optics of Organic Molecules and Polymers*. Nalwa HS (ed). CRC Press: Boca Raton, FL, 1997; 813–840.
14. Su W, Cooper TM. *Chem. Mater.* 1998; **10**: 1212.
15. Debreczeny MP, Svec WA, Wasielewski MR. *Science* 1996; **274**: 584.
16. Wagner R, Lindsey JS. *J. Am. Chem. Soc.* 1994; **116**: 9759.
17. Crossley M, Burn PL. *J. Chem. Soc., Chem. Commun.* 1991; 1569.
18. Osuka A, Shimidzu H. *Angew. Chem. Int. Ed. Engl.* 1997; **36**: 135.
19. Drain CM, Nifiatus F, Vasenko A, Batteas JD. *Angew. Chem. Int. Ed. Engl.* 1998; **37**: 2344.
20. Chen CT, Suslick KS. *Coord. Chem. Rev.* 1993; **128**: 293.
21. Hanack M, Deger S, Lange A. *Coord. Chem. Rev.* 1988; **83**.
22. Collman JP, McDevitt JT, Yee GT, Leidner CR, McCullough LG, Little WA, Torrance JB. *Proc. Natl. Acad. Sci. USA* 1986; **83**: 4581.
23. Collman JP, McDevitt JT, Leidner CR, Yee GT, Torrance JB, Little WA. *J. Am. Chem. Soc.* 1987; **109**: 4606.
24. Crossley MJ, Burn PL. *J. Chem. Soc., Chem. Commun.* 1991; 1569.
25. Bao Z, Chen Y, Yu L. *Macromolecules* 1994; **27**: 4629.
26. Chen C-T. *Porphyrins and Metalloporphyrins as Field Responsive Materials*. University of Illinois at Urbana-Champaign: Urbana, IL, 1992.
27. Suslick KS, Van Deusen-Jeffries S. In *Comprehensive Supramolecular Chemistry; Bioinorganic Systems*, vol. 5. Suslick KS (ed.). Elsevier: Oxford, 1996; 733.
28. Meunier B. In *Metalloporphyrins Catalyzed Oxidations*. Monanari F, Casella L (eds). Kluwer: Boston, MA, 1994; 1.
29. Byrn MP, Curtis CJ, Khan SI, Sawin PA, Tsurumi R, Strouse CE. *J. Am. Chem. Soc.* 1990; **112**: 1865.
30. Byrn MP, Curtis CJ, Goldberg I, Hsiou Y, Khan SI, Sawin PA, Tendick SK, Strouse CE. *J. Am. Chem. Soc.* 1991; **113**: 6549.
31. Byrn MP, Curtis CJ, Hsiou Y, Khan SI, Sawin PA, Tendick SK, Terzis A, Strouse CE. *J. Am. Chem. Soc.* 1993; **115**: 9480.
32. Goldberg I, Krupitsky H, Stein Z, Hsiou Y, Strouse CE. *Supramol. Chem.* 1995; **4**: 203.
33. Bhyrappa P, Wilson SR, Suslick KS. *J. Am. Chem. Soc.* 1997; **119**: 8492.
34. Bhyrappa P, Suslick KS. *Supramol. Chem.* 1998; **9**: 169.
35. Robson R. In *Infinite Frameworks*, vol. 6. MacNicol DD, Toda F, Bishop R (eds). Pergamon: New York, 1996; 733.
36. Yaghi OM, Li H, Davis C, Richardson D, Groy TL. *Acc. Chem. Res.* 1998; **31**: 474.
37. Abrahams BF, Hoskins BF, Robson R. *J. Am. Chem. Soc.* 1991; **113**: 3606.
38. Abrahams BF, Hoskins BF, Michall DM, Robson R. *Nature* 1994; **369**: 727.
39. Eastwood D, Gouterman M. *J. Mol. Spectrosc.* 1970; **35**: 359.
40. Lee S, Okura I. *Analyst* 1997; **122**: 81.
41. Mills A, Lepre A. *Anal. Chem.* 1997; **69**: 4653.
42. Oglesby DM, Upchurch BT, Leighty BD, Collman JP, Zhang X, Herrmann PC. *Anal. Chem.* 1994; **66**: 2745.
43. Collman JP, Brauman JI, Fitzgerald JP, Hampton PD, Naruta Y, Sparapany JW, Ibers JA. *J. Am. Chem. Soc.* 1988; **110**: 3477.
44. Malinski T, Taha Z. *Nature* 1992; **358**: 676.