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Porphyrin-based nanoporous network polymers

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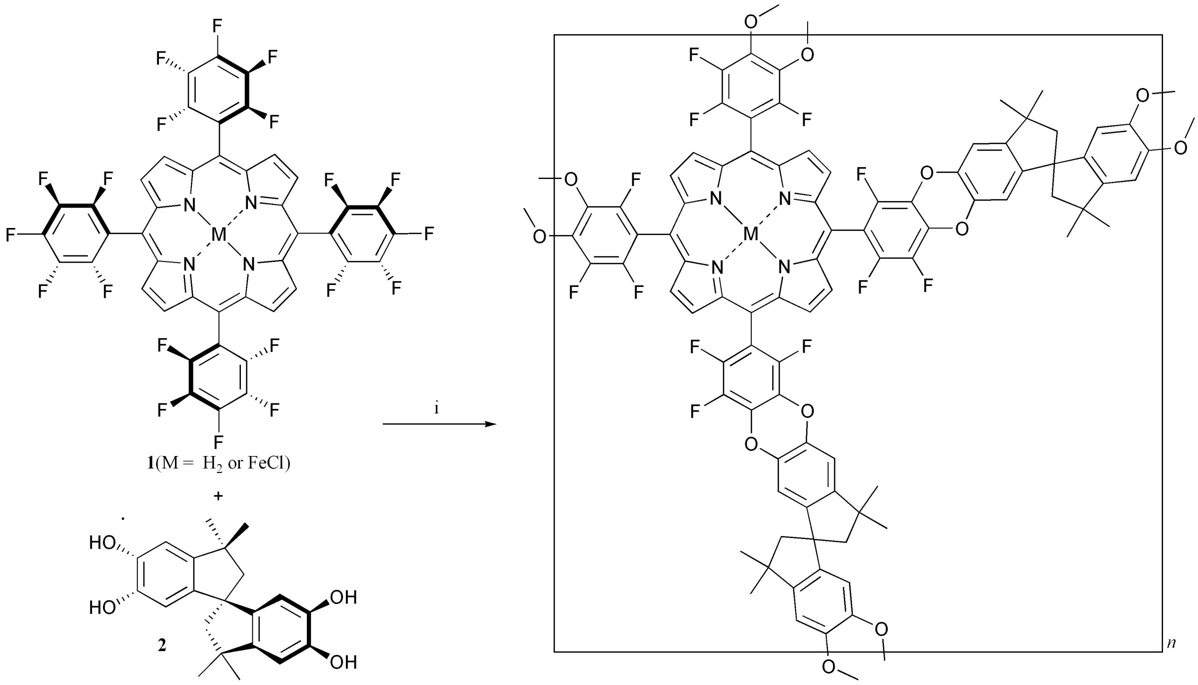
Network polymers exhibiting large surfaces areas (900–1000 $m^2\ g^{-1}$) are prepared by the highly efficient dibenzodioxane-forming reaction between *meso*-tetrakis(pentafluorophenyl)porphyrin and a rigid bis(catechol) monomer.

Porphyrins facilitate some of Nature's most important chemical processes including photosynthesis, oxygen transport and catalytic oxidations.[1] Attempts to mimic the remarkable catalytic activity of cytochrome P450 enzymes, has led to a number of useful homogeneous porphyrin catalysts.[2] For example, porphyrins with halogenated phenyl groups at the four *meso*-positions, such as *meso*-tetrakis(pentafluorophenyl)porphyrin **1** (M = FeCl), efficiently catalyse alkene epoxidation and hydrocarbon hydroxylation.[3,4] These reactions are achieved using environmentally benign oxidants (*e.g.* hydrogen peroxide), without rapid concurrent self-oxidation.

Generally, heterogeneous catalysts offer the advantages of ease of recovery and reusability over homogeneous catalysts and are better suited to the automated, high-throughput processes required by industry.[5] However, an effective heterogeneous catalyst requires a high surface area. Thus, there continues to be a considerable effort to support porphyrins within, or on the surface of, microporous or mesoporous (*i.e.* nanoporous) materials.[2,6] The desire for useful heterogeneous catalysts is also the motivation for the intense current interest in the direct self-assembly of porphyrin nanoporous materials using non-covalent interactions such as hydrogen bonding or coordination to metal centres.[7] Many derivatives of *meso*-tetraphenylporphyrin provide crystals with large void space, as determined by X-ray diffraction, and some of these are stable to the removal of the crystallisation solvent. However, none of these materials have demonstrated a high surface area by the reversible adsorption of gas.[8]

In the preceding contribution, a novel type of organic nanoporous material was described based upon phthalocyanine macrocycles, some of which exhibit surface areas approaching 1000 $m^2\ g^{-1}$. These nanoporous network polymers are prepared by the phthalocyanine-forming reaction of a bis(phthalonitrile) containing a rigid linking group composed of fused rings with a single spiro-centre. The spiro-centre ensures that adjacent phthalocyanine units within the polymer network are orthogonal to each other and, therefore, the material cannot fill space efficiently. In view of their well-established catalytic behaviour, it was of interest to determine whether similar nanoporous network polymers could be derived from porphyrin derivatives.

Generally, even optimised methods of porphyrin preparation, from the reaction between pyrrole and a suitable aldehyde in dilute solution, give only moderate yields and is accompanied by significant tar production.[9] Thus porphyrin formation, unlike phthalocyanine formation, is an unsuitable reaction for network assembly. Therefore, a synthetic strategy based on the reactivity of preformed porphyrin **1** was devised. For the preparation of the bis(phthalonitrile) precursor to the phthalocyanine network polymers, a facile reaction between 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane **2** and 4,5-dichlorophthalonitrile was used. This involves the formation of rigid dibenzodioxane units *via* an aromatic nucleophilic substitution



Scheme 1 Nanoporous network polymer formation. *Reagents and conditions*: (i) K_2CO_3, *N*-methyl pyrrolidone (NMP), 200 °C, 6 h.

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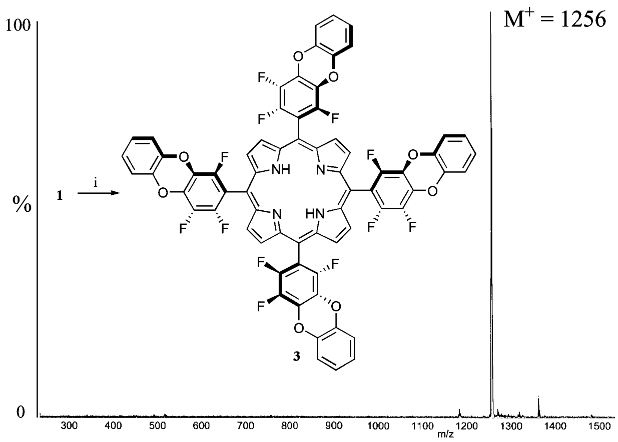

Scheme 2 *Reagents and conditions*: (i) catechol, K_2CO_3, *N*-methyl pyrrolidone, 100 °C, 6 h. The scheme is superimposed on the MALDI MS of the crude product mixture.

mechanism (S_NAr).[10] Previously, it has been established that the most distant fluorine atom on each of the four *meso*-pentafluorophenyl groups of **1** (*i.e. para* to the porphyrin core) is readily substituted by nucleophiles such as amines, thiols or phenolate anions.[11] This reaction involves a conventional S_NAr mechanism. Therefore, in order to investigate the possibility of preparing porphyrin network polymers directly from **1** and **2**, *via* dibenzodioxane formation (Scheme 1), a model S_NAr reaction between four molar equivalents of catechol and porphyrin **1** (M = H_2) was performed (Scheme 2). A MALDI mass spectrum of the crude reaction mixture shows that the only significant product was the desired low molar mass porphyrin **3**, which contains a single benzodioxane unit fused to each of the four *meso*-phenyl substituents. Therefore, it appears that the expected initial substitution of the *para*-fluorine atoms of **1** is followed rapidly by the intramolecular substitution of a neighbouring fluorine.

The highly efficient nature of this reaction (isolated yield = 80–90%) encouraged its use for the formation of porphyrin network polymers. A solution of porphyrin **1** (M = H_2; 1 equiv.) and bis(catechol) **2** (2 equiv.) was heated in NMP at 200 °C with K_2CO_3 as base (Scheme 1). Within 1 h, a solid precipitate formed which was collected by filtration. The resulting purple powder was washed for several days by Soxhlet extraction using MeOH, acetone and THF, and then dried in a vacuum oven. The efficiency of network formation can be demonstrated by the high yield obtained after purification (> 90% yield) and by C, H, N, F elemental analysis.† The latter agrees remarkably well (within ~ 0.5% for each element) with that expected for the idealised structure shown in Scheme 1—if the small amount (3%) of adsorbed water lost during thermal gravimetric analysis, prior to decomposition at 350 °C, is taken into consideration.

Nitrogen adsorption (Fig. 1) shows that the network polymers derived from **1** and **2** have reproducibly high surface areas in the range 900–1000 $m^2\ g^{-1}$ (BET; multi-point calculation using data obtained with a Coulter SA 3100 surface analyser). An analogous material, of high surface area (910 $m^2\ g^{-1}$), and with potential for heterogeneous catalysis, was obtained from the reaction between **1** (M = FeCl) and **2**. The shape of the isotherms and their marked hysteresis are similar to those obtained for the phthalocyanine network polymers.

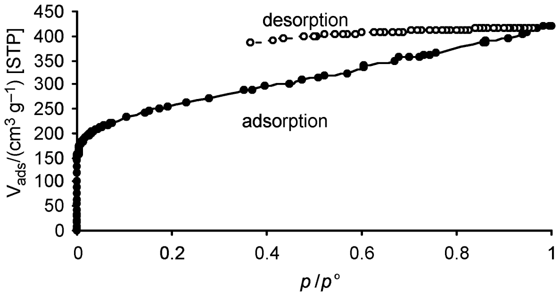

Fig. 1 Nitrogen adsoption/desorption isotherm for the porphyrin network derived from **1** and bis(catechol) **2** of BET surface area = 980 $m^2\ g^{-1}$.

It should be emphasised that the robust nanoporous materials described in this communication are easily and rapidly prepared from readily available monomers. Work is in progress to explore their catalytic and adsorption behaviour. A particularly exciting aspect of the benzodioxane forming reaction is the large number of suitable fluorine and catechol-containing monomers that can be envisaged to provide network polymers. It is likely that many combinations of these monomers will form nanoporous organic materials and this will also be explored.

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Notes and references

† Found: C, 66.45; H, 3.18; N, 3.62; F, 14.67. $C_{86}H_{50}F_{12}N_4O_8.H_2O$(3%) requires C, 67.00; H, 3.60; N, 3.63; F, 14.71%.

1 L. R. Milgrom, *The Colours of Life*, OUP, Oxford, 1997.
2 B. Meunier, *Acc. Chem. Res.*, 1992, **92**, 1411.
3 D. Dolphin, T. G. Traylor and L. Y. Xie, *Acc. Chem. Res.*, 1997, **30**, 251.
4 For catalysis reactions of porphyrin **1**: C. K. Chang and F. Ebina, *J. Chem. Soc., Chem. Commun.*, 1981, 778; A. J. Castelllino and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 158; A. J. Castelllino and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 7512; Y. Watanabe and Y. Ishimura, *J. Am. Chem. Soc.*, 1989, **111**, 8047.
5 M. Bowker, *The Basis and Applications of Heterogeneous Catalysis*, OUP, Oxford, 1998.
6 For heterogeneous porphyrin catalysts see: P. Battioni, E. Cardin, M. Louloudi, B. Schollhorn, G. A. Spyroulias, D. Mansay and T. G. Traylor, *Chem. Commun.*, 1996, 2037 and references therein.
7 I. Goldberg, *Crystengcomm*, 2002, 109 and references therein.
8 M. E. Kosal and K. S. Suslick, *J. Solid State Chem.*, 2000, **152**, 87.
9 J. S. Lindsey, I. C. Schreimann, H. C. Hsu, D. C. Keanney and A. M. Marguerettuz, *J. Org. Chem.*, 1987, **52**, 827.
10 K. Msayib, S. Makhseed and N. B. McKeown, *J. Mater. Chem.*, 2001, **11**, 2784.
11 P. Battioni, O. Brigaud, H. Desvaux, D. Mansay and T. G. Traylor, *Tetrahedron Let.*, 1991, **32**, 2893; D. Bouy-Debec, O. Brigaud, P. Leduc, P. Battioni and D. Mansay, *Gazz. Chim. Ital.*, 1996, **125**, 233.