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Phthalocyanine-based nanoporous network polymers

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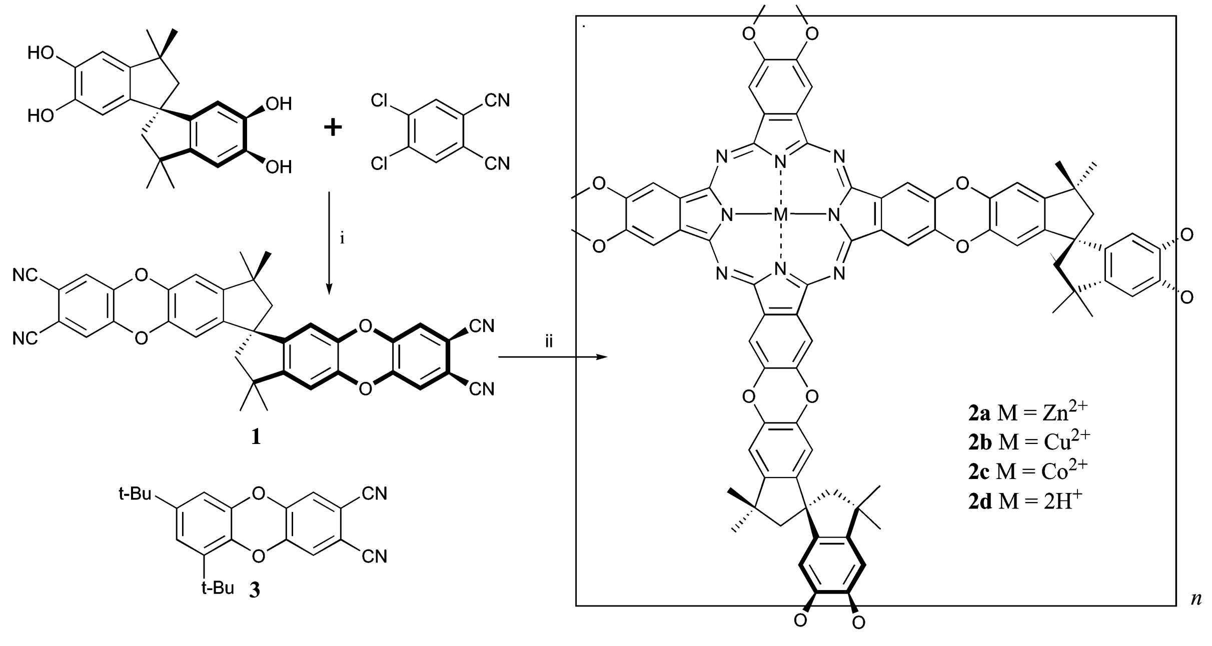
Received (in Cambridge, UK) 5th August 2002, Accepted 2nd September 2002
First published as an Advance Article on the web 31st October 2002

Network polymers exhibiting large surfaces areas (450–950 m^2 g^{-1}) are prepared by the phthalocyanine-forming reaction of a bis(phthalonitrile) monomer containing a rigid spirocyclic linking group.

Inorganic microporous and mesoporous (*i.e.* nanoporous) materials are of great technological importance as heterogeneous catalysts and adsorbents due to their high surface areas, typically between 300 and 1200 m^2 g^{-1}.[1] Presently, there is intense interest in the creation of nanoporous materials by the linking of rigid *organic* molecules by directional non-covalent interactions such as hydrogen bonding or coordination to metal centres.[2] Such systems can possess beautiful crystal structures and a growing number of examples, for example the remarkable organic–inorganic hybrid materials of Yaghi and co-workers,[3] have been shown to survive the removal of the included solvent and allow reversible gas adsorption. Clearly, it would be desirable to construct similar nanoporous materials using proven catalytic systems, such as metalloporphyrins or phthalocyanines. Many derivatives of *meso*-tetraphenylporphyrin provide crystals with large void space and some of these are stable to the removal of the crystallisation solvent.[4,5] To date, however, none have demonstrated a high surface area by the reversible adsorption of gas.[5] The design of analogous phthalocyanine-based nanoporous crystals presents an even greater challenge, due to the competitive non-covalent self-association of the phthalocyanine unit forcing a densely-packed arrangment.

It was anticipated that a nanoporous organic material could result from the *covalent* binding of large planar molecules *via* rigid, fused ring spacers that contain a spiro-centre. The spiro-centre would ensure that adjacent planar components are orthogonal and, therefore, the resulting network polymer should not fill space efficiently. Phthalocyanine is a particularly desirable planar component for evaluating this novel concept due to its size, rigidity and stability.[6] Also, it can play host to cations derived from over seventy elements and several metal phthalocyanines are well-established catalysts. For example, cobalt phthalocyanine is used as a homogeneous catalyst in the industrial desulfurisation of crude petroleum, the Merox process, which involves the oxidation of thiols under aerobic conditions.[7] In addition, iron phthalocyanine is a useful laboratory catalyst for several oxidation reactions—including hydrocarbon oxidations.[8] During the past thirty years, a number of research groups, especially that of Wöhrle, have examined phthalocyanine-based network polymers containing different linking groups.[9] Generally, they are prepared by the phthalocyanine-forming reaction of a bis(phthalonitrile). In one study, the surface area of a network was measured by nitrogen adsorption but found to be low (~ 1 m^2 g^{-1}).[10] As noted, phthalocyanines have a strong tendency to form dense solids composed of columnar stacks in which the cofacial intermolecular interactions (*e.g.* π–π interactions) are maximised and this arrangement is commonly observed for phthalocyanine network polymers. However, it was hoped that the phthalocyanine network polymer constructed using a rigid spirocyclic linker, such as the one provided by bis(phthalonitrile) **1**, would enforce an orthogonal orientation of adjacent phthalocyanine units and induce porosity.

Bis(phthalonitrile) **1**† is prepared in high yield (80–90%) using the aromatic nucleophilic substitution reaction between 4,5-dichlorophthalonitrile and 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane, both of which are commercially available (Scheme 1).[11] Metal-containing network poly-



Scheme 1 *Reagents and conditions*: (i) K_2CO_3, DMF, 70 °C; ii, metal salt, quinoline, 220 °C (**2a–c**) or lithium pentoxide, pentan-1-ol, reflux (**2d**).

DOI: 10.1039/b207642j

mers **2** (**a**, M = Zn^{2+}; **b**, M = Cu^{2+}; **c**, M = Co^{2+}) are formed by heating **1** in the presence of the appropriate metal acetate at temperatures in excess of 200 °C in quinoline solution. Within 0.25 h from the start of the reaction, **1** forms a darkly coloured precipitate and after 1 h stirring of the reaction, using a magnetic or mechanical stirrer, becomes impossible due to the conversion of the reaction mixture to a solid. Similar conditions give model, monomeric phthalocyanines derived from the related phthalonitrile, 1,3-di-*tert*-butyl-6,7-dicyanodibenzodioxane **3**,[11] in good yield (65–80%). The effectiveness of network formation is indicated by the weak absorption bands in the IR spectra of the products corresponding to unreacted nitrile and imide 'end-groups' and the absence of bands due to triazine by-products. The resulting blue or green material (the colour depends on the metal salt used in the reaction) was washed, initially by DMF, and then for several days by Soxhlet extraction using MeOH, acetone and THF. A metal-free network **2d** (M = $2H^+$) is prepared by heating **1** in a refluxing solution of lithium pentoxide dissolved in pentan-1-ol. This solid was stirred in acetic acid to remove the lithium cations from the central cavity of the phthalocyanine, prior to washing using the same solvent sequence employed for the metal containing materials. After washing, all network polymers are obtained in high yields (90–100%), as free-flowing powders. Electron microscopy shows that the materials are comprised of irregular particles of dimensions 10-50 μm.

Spectroscopic and structural characterisation of the network polymers confirms that the rigid spirocyclic linkages prevent close packing of the phthalocyanine components. For example, UV/Vis absorption spectra, with minimised scattering effects, are obtained using a suspension of the material in 1-chloronaphthalene (Fig. 1) and show that, for each network, the primary band in the visible region (Q-band) is unperturbed by exciton coupling between phthalocyanine units.

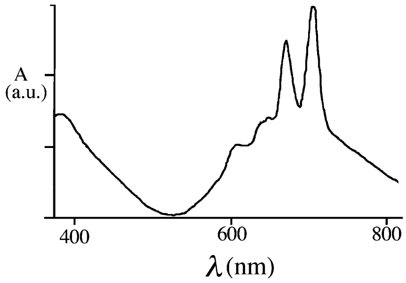


Fig. 1 The UV/Vis spectrum of phthalocyanine network **2d** from a suspension in 1-chloronaphthalene.

An EPR spectrum of network **2b** (M = Cu^{2+}) shows well-defined hyperfine splitting due to the interaction of the metal ion with the eight nitrogens of the phthalocyanine ligand (Fig. 2). This is consistent with the desired isolated arrangement of the phthalocyanines, as for most phthalocyanine materials cofacial association prohibits the observation of hyperfine splitting due to the strong electronic coupling between adjacent Cu^{2+} ions.[12] In addition, a wide-angle X-ray powder diffraction study of **2a** shows the absence of significant scattering corresponding to a repeat distance of 0.34 nm. This value represents the distance between the molecular planes of aggregated phthalocyanines and such scattering is commonly observed from the analysis of previously prepared phthalocyanine network polymers.[13]

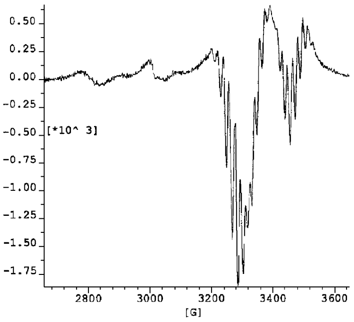


Fig. 2 The second derivative EPR spectrum of **2b** showing the hyperfine splitting characteristic of isolated copper phthalocyanine.

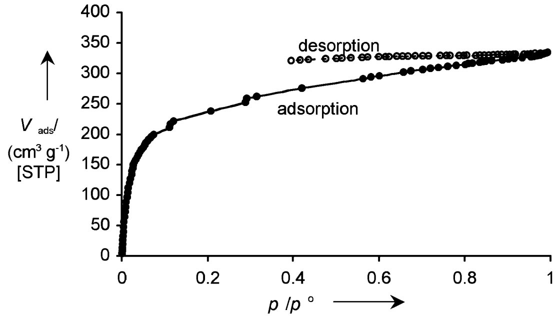


Fig. 3 Nitrogen adsoption/desorption isotherm for phthalocyanine network **2a** giving a BET surface area of 895 $m^2 g^{-1}$. Similar isotherms were obtained for **2b** (750 $m^2 g^{-1}$), **2c** (489 $m^2 g^{-1}$) and **2d** (535 $m^2 g^{-1}$).

Nitrogen adsorption measurements give BET values (multipoint) for the surface areas of the networks **2a–d** in the range 450–950 $m^2 g^{-1}$, Fig. 3. The shape of the isotherms and their marked hysteresis are consistent with a wide distribution of pore size, spanning the microporous (< 2 nm) and mesoporous (2–50 nm) range. Thermogravimetic analysis (TGA) of **2a** shows a gradual loss of mass (8–10%) up to 250 °C—consistent with the loss of water which is known to bind tightly to zinc phthalocyanine. Mass loss due to thermal degradation commences at 370 °C.

This preliminary study demonstrates the viability of the concept of preparing robust nanoporous materials by the covalent binding of planar molecules *via* a rigid spirocyclic linker. Furthermore, the phthalocyanine networks have potential technological applications as catalysts and adsorbents due to their proven stability towards low pressure, a range of solvents and elevated temperatures. The likely difficulties in achieving nanoporous phthalocyanine-based materials using non-covalent interactions adds to the significance of this result. Further studies are in progress to evaluate the potential of this novel method of preparing organic nanoporous materials.

This work was supported by grants from the EPSRC and Kuwait University. We thank Dr Eric McInnes of the EPSRC National EPR Service, University of Manchester, for assistance.

Notes and references

† *Spectroscopic data* for **1**: ^{1}H NMR (300 MHz, [D]$_6$-DMSO, 60 °C): δ 1.28 (s, 6H), 1.36 (s, 6H), 2.14 (d, 2H), 2.28 (d, 2H,), 6.39 (s, 2H), 6.98 (s, 2H), 7.75 (s, 2H), 7.82 (s, 2H); ES-MS *m/z*: 611 ($M^- + Na^+$), IR (KBr): ν = 2220 cm^{-1} (CN).

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