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Microporous Network Polymers Based on Cobaltphthalocyanines

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Summary: A series of microprous Co-phthalocyanine based plolymers were prepared in good yield (>90%) by the polymeric tetramerisation reaction of nonplanar bisphthalonitrile monomers with cobalt acetate. The resulting free-flowing polymers are dark green in apperance with good stability towards a range of solvents and temperature. High Resolution Transmission Electron Microscopy image clearly shows the presence of micropores (<2 nm). Nitrogen adsorption/desorption measurements show that these materials have high surface areas in the range of 500–600 m^2g^{-1} along with high concentration of pores in the range of 0.6–0.7 nm.

Keywords: catalysts; microporous; networks; phthalocyanines; polymers

Introduction

Phthalocyanine (Pc) and its analogues are a class of organic functional materials broadly studied and with wide range of technological applications.[1–4] The metallophthalocyanines have been used as efficient catalysts for oxidation and reduction process.[5] However cofacial aggregation of the hydrophobic Pc unit limits their activity to a great extent and other disadvantage associated with retrieval of the catalysts from the reaction mixture. Recent work on porous materials demonstrated that microporous polymer networks of high surface area (500–1000 m^2g^{-1}) can be constructed.[6,7] These materials consist of phthalocyanine macrocycles, which are excellent catalysts for a number of important reactions, linked by a molecular scaffold. The highly rigid scaffold is designed to arrest both positional and rotational movement of Pc units and efficiently prohibit their cofacial aggregation. Pcs are generally immobilised onto polymer substrates or encapsulated within zeolites. Such supported catalysts offer improved recoverability and, for some systems, enhanced activity. Unfortunately, in such systems the major concerns include hindered access of large reactant molecules to the transition metal bearing Pcs, poor compatibility of the host with organic reactants and formation of aggregates. Consequently, this work aiming a successful strategy involves the incorporation of cobaltphthalocyanine (CoPc) within a rigid polymer network structure, to mimic the phthalocyanines immobilized zeolites[8] and polymer supported systems.[9] The commercial applications of these cobalt based catalysts are continually expanding and the promising technological areas in this category are catalysis for the industrially important sweetening of crude petrochemicals (merox process)[10,11] and the oxidation of phenols.[12]

Experimental Part

Materials and Methods

The dry solvents DMF purchased from Aldrich co, and the potassium carbonate obtained locally. The solvent quiniline was used after distillation. ^{1}H NMR spectra (400 MHz) were recorded using Bruker

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DPX 400. IR spectra were recorded on a Perkin Elmer System 2000 FTIR. Elemental analyses were carried out using LECO Elemental Analyzer CHNS 932. Mass analysis were done on a VG Autospec-Q. TGA and DSC analyses were carried out on Shimadzu TGA-50 and Shimadzu DSC-50. Microscopic techniques employed are Scanning Electron Microscopy (SEM: JEOL Model 6300) and High Resolution Transmission Electron Microscopy (HRTEM: JEOL Model JEM- 3010). Surface area analysis was carried out at liquid nitrogen temperature using ASAP 2010 Micromeritics Sorptometer equipped with an outgassing platform, an online data acquisition and handling system.

Synthesis

The biscatechols A_1[12] and A_2[13] were synthesised and characterised according to the literature procedure. 4,5-Dicholorophthalonitrile (B) was synthesised from commercially available materials in a five steps reaction.[14]

Bisphthalonitrile: (A_1B)

Yield: 75%; m.p. 365 °C; 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.82$ (d, 2H), 7.44(m, 2H), 7.34 (d 4H) 7.18 (s, 2H), 7.11 (s, 2H), 6.87 (d, 2H) 6.79 (d, 2H) 6.71 (d, 2H); IR (KBr) υ/cm^{-1}: 2232 (CN); MS (EI) m/z (100): 630 (M^+); Elemental analysis calcd for $C_{41}H_{18}N_4O_4$ requires %C 78.09, %H 2.88, %N 8.88; found C 77.80, %H 2.9, %N 9.04.

Bisphthalonitrile: (A_2B)

Yield 80%. m.p. 330 °C; 1H NMR (400 MHz, DMSO-d_6): $\delta = 7.77$ (s, 4H), 6.90 (s, 4H), 1.80 (s, 6H) and 1.51 (s, 4H); IR (KBr) υ/cm^{-1}: 2229 (CN); MS (EI) m/z (100): 546 (M^+) Elemental analysis calcd for $C_{34}H_{18}N_4O_4$ requires %C 74.72, %H 3.32, %N 10.25; found C 74.53, %H 3.49%N 10.11.

CoPc-PIMA$_1$B

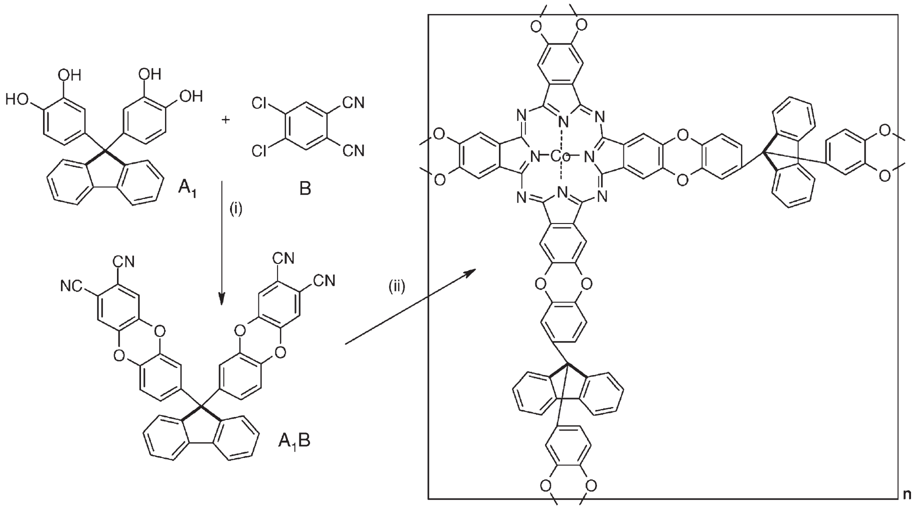
Yield >90%; m.p. >400 °C; IR (KBr) υ/cm^{-1}: 3059 (ArH); 1645 (C=N); Elemental analysis calcd (%) for the repeat unit $C_{82}H_{36}N_8O_{12}Co$ requires: C 71.14, H 2.6, N 8.10; found: C 69.90, H 3.02, N 8.80; XPS/eV: 794 (Co2p1), 779 (Co2p3).

CoPc-PIMA$_2$B

Yield >90%; m.p. >400 °C; IR (KBr) υ/cm^{-1}: 3062 (ArH); 1637 (C=N); Elemental analysis calcd (%) for the repeat unit $C_{68}H_{36}N_8O_{12}Co$ requires: C 67.15, H 2.96, N 9.22; found: C 67.28, H 3.46, N 9.03; XPS/eV: 795 (Co2p1), 780 (Co2p3).

Results and Discussion

The starting bisphthalonitrile monomers (A_1B and A_2B) are prepared in good yield by dioxane forming reactions (Scheme 1 and 2). The reactions are highly efficient and an elegant route to prepare the newly target ladder monomers. Spectroscopic analyses of A_1B and A_2B were consistent with their expected structure. Each compound gave a satisfactory elemental analysis. Metal- containing Pcs are readily prepared by the template cyclotetramerisation reaction of the corresponding phthalonitrile. Following the reported strategy[6] we have synthesised high surface area network polymers, by the Pc-forming reaction of nonplanar bisphthalonitriles. All the attempted Polymeric cyclotetramerisations of bisphthalonitriles were carried out at 200 °C in quinoline under nitrogen atomosphere using cobalt acetate (Scheme 1 and 2). The crude product obtained was wahsed with deionised water and methanol. Further purification was achieved by using soxhlet extraction in methanol, acetone and THF. After grinding the green solids were dried under vacuum at 120 °C for 24 h to give free-flowing dark green powder (yield >90%). The IR spectrum clearly confirms the formation of phthalocyanine macrocyles through the isoindole links and the absence corresponding nitrile groups. Elemental analysis of CoPc-PIMA$_1$B and CoPc-PIMA$_2$B were consistent with their proposed repeat units. XPS spectra clearly exhibit characteristic peaks for divalent cobalt with binding energies ranging from 779–795 eV. Thermogravimetric analyses (TGA) showed that the



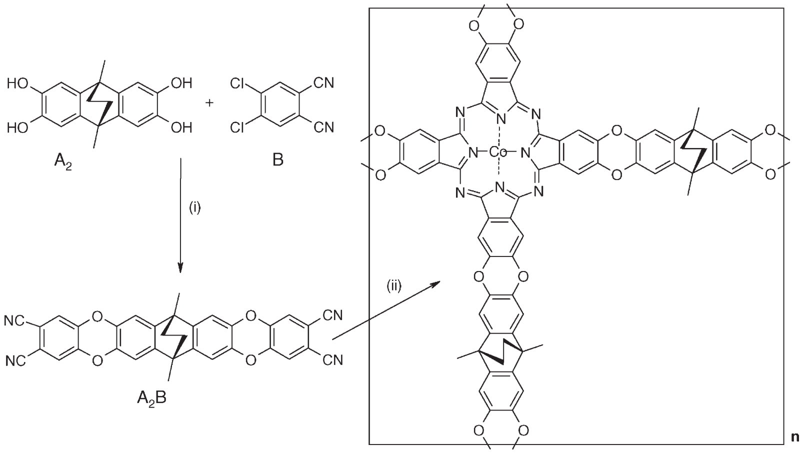
Scheme 1.

The preparation of Cobalt phthalocyanine-based microporous network polymer CoPc-PIMA$_1$B, from spirocyclic monomer (A$_1$B). Reagents and conditions: (i) K_2CO_3, dimethylformamide, 80 °C; (ii) Cobalt acetate, quinoline, 200 °C.

green network materials exhibit a 10% loss in the temperature range of 400–500°C. Considering other high surface area materials, these materials can also tolerate harsh conditions, which promote the potential applications.

Morphology

Scanning Electron Microscopic images show that materials are comprised of irregular particles of dimensions ranging from 0.5–1.5 μm. Figure 1 gives a typical SEM image of CoPc-PIMA$_1$B. The high resolution transmission electron microscopy (HRTEM) operating at 300 kV (Figure 2) was used to confirm the porous structure of the network polymers. The pore structure in CoPc-PIMA$_1$B gave no evidence for an ordered structure. The cobaltphthalocyanine network organiza-



Scheme 2.

Synthesis of Cobalt phthalocyanine-based microporous network polymer (CoPc-PIMA$_2$B), from a nonplanar rigid ladder monomer (A$_2$B). Reagents and conditions: (i) K_2CO_3, dimethylformamide, 80 °C; (ii) Cobalt acetate, quinoline, 200 °C.

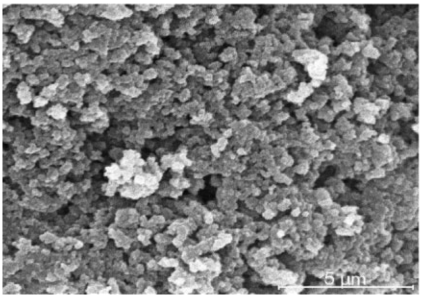


Figure 1.
SEM image of CoPc-PIMA$_1$B.

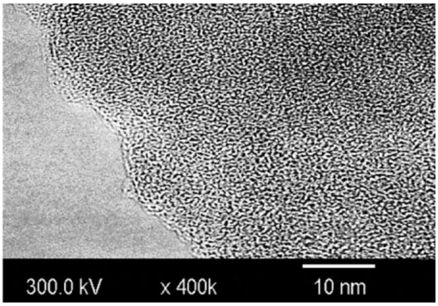


Figure 2.
HRTEM image of CoPc-PIMA$_1$B.

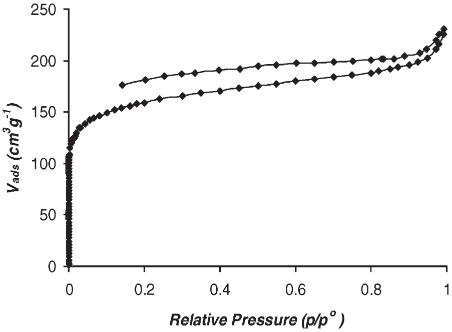


Figure 3.
N_2 adsorption/desorption isotherm of CoPc-PIMA$_2$B.

tion leads to worm hole type pore structures. The result surprisingly shows the structural homogeneity of the prepared organic network polymer which we report for the first time. In the case of CoPc-PIMA$_2$B also the HRTEM image clearly shows nano porous structures. Overall, this is a fairly unique nanoporous structure that dramatically enhances catalytic process selectivities. Like other porous materials (e.g. activated carbons) our prepared network polymers were found to be stable under the experimental condition (300 kV) as an additional indication of the high stability.

Microporosity and Pore Size Distribution

Analysis of the isotherms using BET theory results in spatial maping of the specific surface area, and the pore size distribution. Figure 3 gives the nitrogen adsorption/desorption isotherm for CoPc-PIMA$_2$B. The measuments give BET surface areas in the range of 500–600 m^{2}g^{-1}. The adsorption/desorption isotherms clearly exhibit remarkable hysterisis up to low partial pressures. Table 1 gives adsorption analysis data for the network polymers. The shape of the isotherm and the large volume of nitrogen adsorbed at low relative pressure indicate microporosity.[6] The high surface areas of both polymers can be illustrated by its rigid architecture which is due to the restricted rotation as a result of the dioxane-ladder linkages. The spirocenter present in the A$_1$B nonplanar skeleton present in the A$_2$B creates the nonlinearity by propagating the polymer chain in three dimensional irregular fashion producing a polymer chain that can prevent the dense packing which provided enough internal surface area. The overall structure itself is considered as a network system constructed with phthalocyanine repeat units which are connected each other by the double stranded strong covalent bonds (Scheme 1 and 2). These molecular structures that cannot pack efficiently in the solid state and therefore trap a large amount of free volume, which may be regarded as having

Table 1.
Adsorption analysis data for the network polymers.

Polymer	BET Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Micropore diameter (nm)
CoPc-PIMA$_1$B	538	0.325	0.6–0.7
CoPc-PIMA$_2$B	554	0.324	0.6–0.7

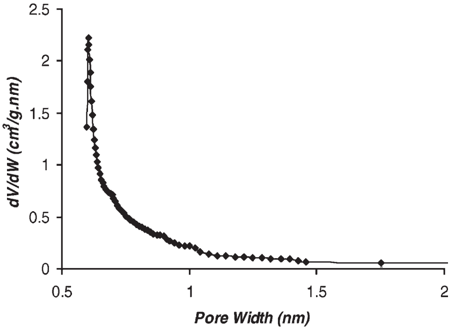


Figure 4.
Pore size distribution curve for the CoPc-PIMA$_2$B.

intrinsic microporosity (effective pore diameter $<$ 2nm). Polymers of intrinsic microporosity have rigid backbones (e.g., ladder-like sequences) and sites of contortion, that force the backbone to twist and turn randomly[15]. Control of pore diameter at the nano level makes it possible to modify separation or catalytic process selectivities by several orders of magnitude.

Figure 4 shows the typical pore size distribution curve for CoPc-PIMA$_2$B as calculated by the Horvath-Kawazoe (HK) method. The HK method is suitable for microporous materials and this equation relates the adsorption potential with the micropore size and allows each amount adsorbed at a relative pressure to be expressed in terms of the width of a slit shape pore. Our analyses show that both PIMs have maximum pore size in the range of 0.6–0.7 nm.

Conclusion

This work summarises the effective use of highly rigid and nonlinear linking groups between the planar phthalocyanine subunits that would ensure their space-inefficient packing, thus preventing structural relaxation and consequent loss of microporosity. Considering its proven structural features, stability towards a range of solvents and temperature the prepared cobalt phthalocyanine network polymers have greater interest in the field of smart high surface area materials that provide a mechanism to encapsulate the sample rapidly on a short time scale or rapidly process the large volume of reactants. This material offers other attractive features such as high thermal and structural stability. Further studies on catalysis are in progress to evaluate their potential to act as a catalyt.

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