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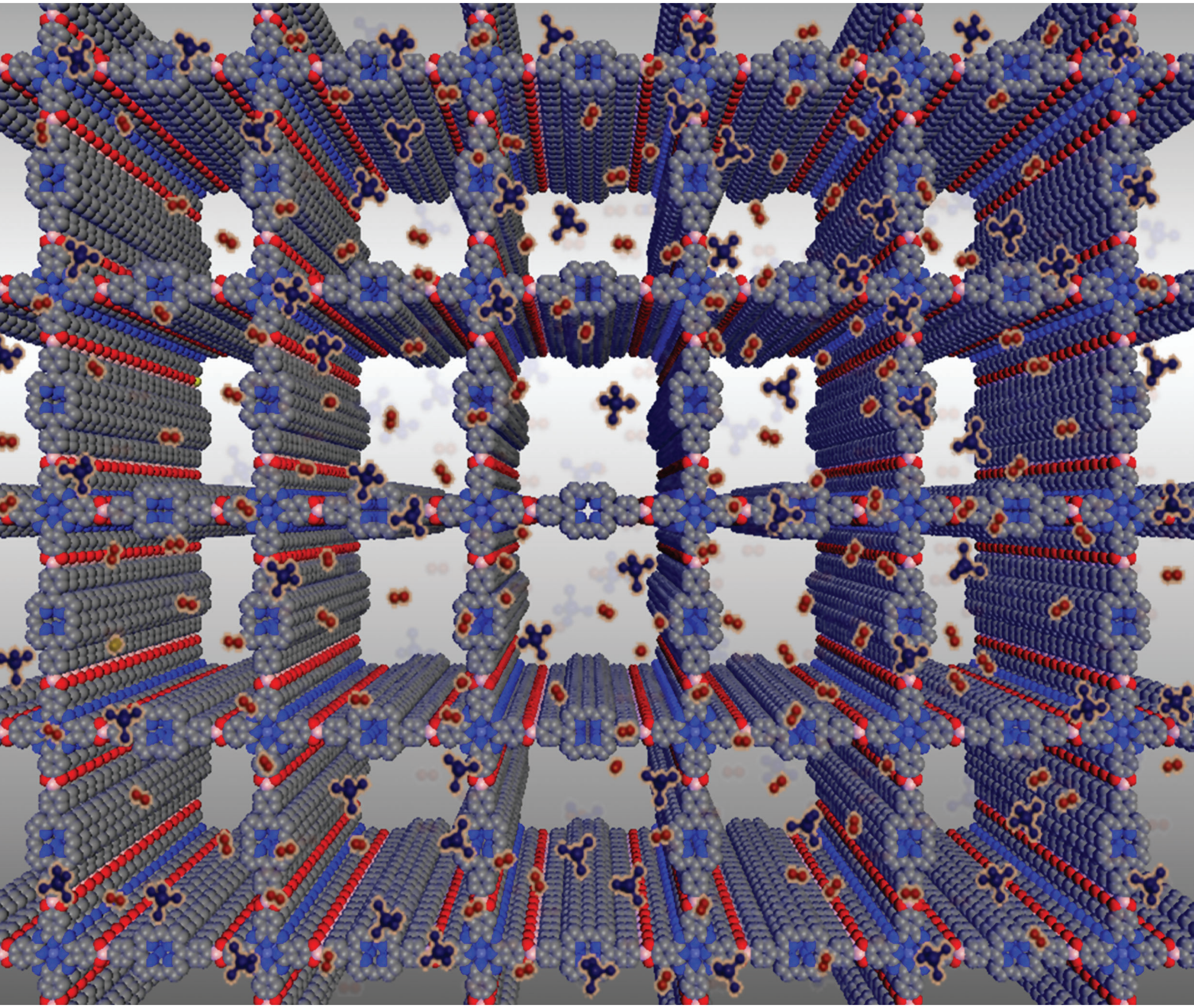

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Synthesis of a phthalocyanine and porphyrin 2D covalent organic framework†

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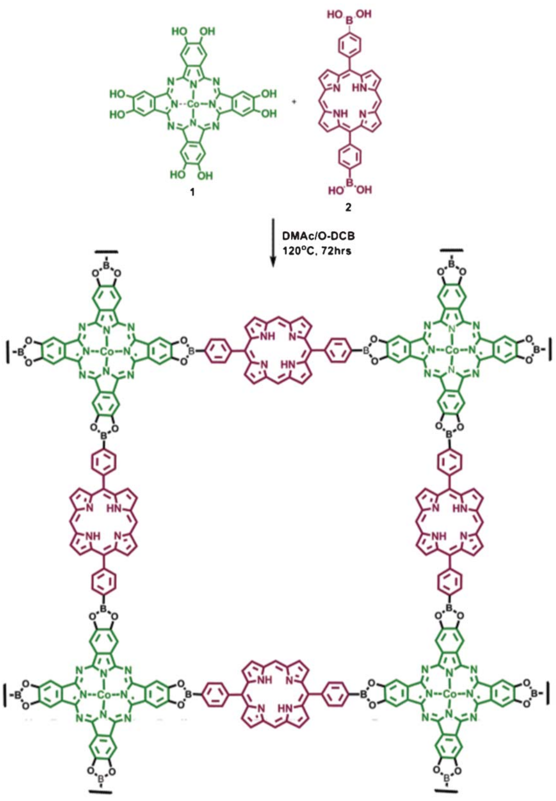
A new phthalocyanine and porphyrin based hybrid covalent organic framework, CoPc-PorDBA COF, has been synthesized and its gas storage properties have been measured. The CoPc-PorDBA COF crystallizes into 2D sheets with an eclipsed AA stacking motif, and it showed high surface area (S_{BET} = 1315 m^2 g^{-1}), and can store up to 0.8 wt% of H_2 at 77 K and 1 bar and 0.6 wt% of CH_4 at 298 K and 1 bar.

Phthalocyanine and porphyrin covalent organic frameworks[1] (COFs) have attracted considerable attention due to their photocurrent generation properties,[2] applications in optoelectronic devices[3] and their potential in organic photovoltaics (OPVs). In addition to these attractive applications, some 2D and 3D covalent organic frameworks[4] and metal organic frameworks[5] (MOFs), initially designed for gas storage applications, have achieved high storage capacities of H_2 and CH_4 at 77 K and 298 K within a pressure range of 0–100 bar. Preparation of COFs with high surface area with adjustable pore size through the rational design and incorporation of good electron donors into a framework to improve light absorption is a challenging problem. Phthalocyanines and porphyrins are highly stable and intensely colored aromatic macrocyclic compounds and can be found in many coordination complexes,[6] and luminescent devices.[7] Recently, several metallophthalocyanine COFs have been reported with Zn, Ni, and Co as central metal ions.[1,2] To date, the H_2 and CH_4 storage capacities of a phthalocyanine and porphyrin COF with a high surface area has not been reported. Here we report a new boronate ester based COF that exhibits a H_2 storage capacity of 0.8 wt% at 77 K, 1 bar and 0.6 wt% CH_4 at 298 K, 1 bar. This COF contains two very good electron donors which absorb in different regions of the UV-Vis spectra in a single framework. The COF is based on octahydroxy phthalocyanine Co(II) (**1**) and 5,15 porphyrin diboronic acid (**2**) (Scheme 1). The chemical connectivity and composition of the CoPc-PorDBA COF were determined by several methods such as Powder X-ray Diffraction (PXRD), infrared spectroscopy, solid-state ^{11}B and ^{13}C CP-MAS NMR, surface area measurements and elemental analysis. The CoPc-PorDBA COF was synthesized under solvothermal conditions in a mixture of dimethylacetamide and *o*-dichlorobenzene (2/1 v/v) in a sealed glass ampoule at 120 °C for 72 h (see ESI†).

The CoPc-PorDBA COF was isolated in 65% yield as a green powder that is totally insoluble in common organic solvents such



Scheme 1 Synthesis of CoPc-PorDBA COF from 5,15 porphyrin diboronic acid and $(OH)_8$Pc Co(II).

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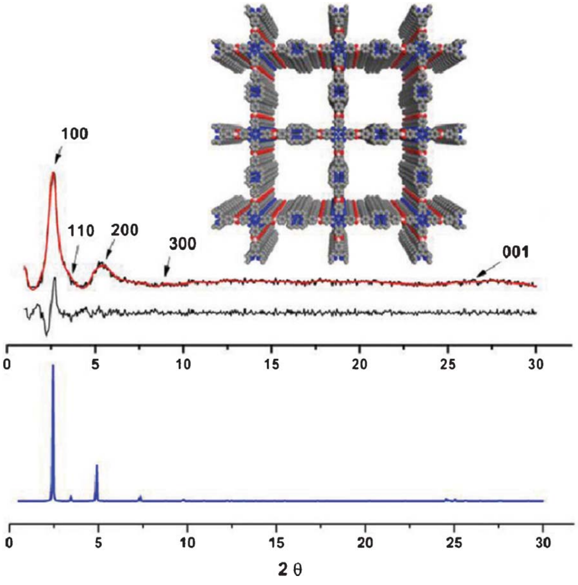

Fig. 1 XRD pattern of CoPc-PorDBA COF with the observed pattern in black, Pawley refined profile in red, and the difference plot in black (observed minus refined profiles). The calculated XRD pattern from the proposed models is shown in blue. Inset: eclipsed stacking representation of CoPc-PorDBA COF based on powder diffraction and modeling projected along the *c* axis (H atoms are omitted). C, B, and O are represented in turn as gray, purple, and red spheres.

as dimethylsulfoxide, dichloromethane, *N*,*N*-dimethylformamide, tetrahydrofuran *etc*. The solid state ^{13}C with (CP-MAS) NMR spectrum (Fig. S3, ESI†) of the CoPc-PorDBA COF shows nine signals at δ = 173.44, 157.86, 143.95, 134.64, 127.72, 115.23, 106.06, 100.94 and 97.11 ppm, which were assigned to the carbon atoms of the phthalocyanine and phenyl groups by comparison to the spectrum of octahydroxy phthalocyanine Co(II) (Fig. S4, ESI†). The ^{11}B magic angle spinning (MAS) NMR spectrum of the CoPc-PorDBA COF display similar features to those of other reported COFs and to those of the starting materials.[2a] PXRD (Cu Kα radiation) was used to determine the crystallinity of the synthesized CoPc-PorDBA COF. The CoPc-PorDBA COF displays an intense diffraction peak at a 2θ angle (*d*-spacing) of 2.63° (36.14 Å), less intense peaks at 3.52° (25.55 Å), 5.31 (18.07 Å), 7.74° (7.33 Å), and a broad peak at 25.3 (24.54 Å) (Fig. 1). This pattern was manually indexed into a primitive tetragonal unit cell with cell parameters a = 36.14 Å and c = 3.62 Å similar to other previously reported primitive tetragonal NiPc and ZnPc COFs.[1,2] Crystal models were generated using the Materials Studio modeling suite, using eclipsed sheets of CoPc-PorDBA COF (Fig. 1 inset) in a **sql** topology[8] in the space group *P4*/*mmm*, obtaining simulated cell parameters of a = 36.14 Å and c = 3.62 Å, which match well with the indexed values. Simulated PXRD pattern matched well the measured one (Fig. 1). Pawley refinement was subsequently performed to refine the unit cell parameters and to confirm the assignments of the observed diffraction peaks, obtaining values of a = 36.54 Å and c = 3.67 Å with good residuals (see ESI†).

In addition to PXRD, the Fourier-Transformed Infrared spectrum showed a stretching frequency at 1344 cm^{-1} which corresponds to the newly formed boronate ester linkage between **1** and **2** (see ESI†) including attenuation of peaks at 3400 cm^{-1} and 3140 cm^{-1}, which correspond to hydroxyl groups of the phthalocyanine and porphyrin diboronic acid, respectively. The layered structure of the COF was also observed by Field-emission scanning electron microscopy (FE-SEM). The SEM image revealed its layered sheet structure (Fig. 2) and flake-like morphology. To evaluate the porosity of the CoPc-PorDBA COF, N_2 adsorption isotherms were measured at 77 K. A Brunauer–Emmet–Teller (BET) surface area of 1315 m^2 g^{-1} was obtained with a type IV isotherm typical of mesoporous materials and with reversible sorption profiles (Fig. 3). The total pore volume was calculated to be 0.88 cm^3 g^{-1} and the average pore size was calculated using nonlocal density functional theory (NLDFT), and found to be approximately 3.5 nm (see ESI†).

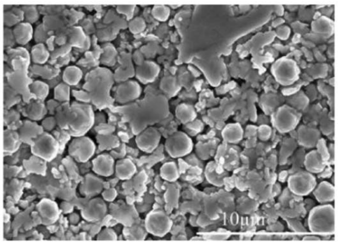

Fig. 2 Scanning electron microscope (SEM) image of the CoPc-PorDBA COF grown under solvothermal conditions.

Once the permanent porosity of CoPc-PorDBA COF was established, we evaluated its potential for H_2 and CH_4 storage. The hydrogen storage capacity of CoPc-PorDBA COF is 0.8 wt% at 77 K, 1 bar (Fig. 4a) which is comparable to other crystalline 2D COFs such as COF-10[2] (0.8 wt% at 1 bar). In direct contrast to the H_2 uptake, the CH_4 isotherm for CoPc-PorDBA revealed an uptake of only 0.6 wt% at 298 K, 1 bar (Fig. 4b). We believe that the lower uptake of methane compared to hydrogen may be due to the size difference and to the absence of metal–hydrogen interactions.

The UV-Vis diffuse reflectance powder spectra of CoPc-PorDBA COF (Fig. 5, ESI†) showed strong absorption bands at 220, 252, 282, 453, 590, 625 and 730 nm and CoPc showed absorption peaks

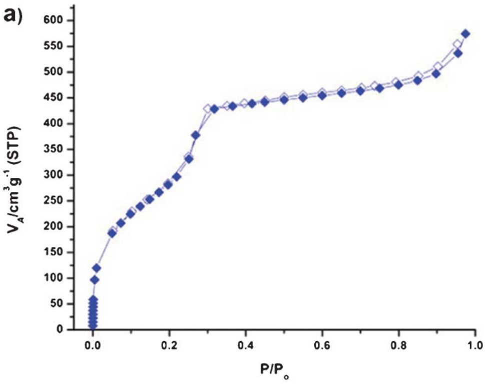

Fig. 3 Nitrogen adsorption (filled symbols) and desorption (empty symbols) isotherm curve and surface area.

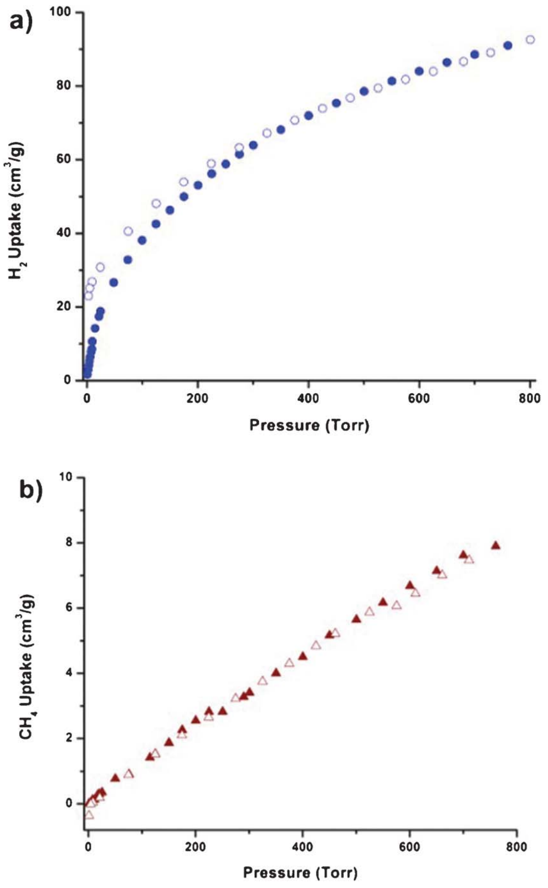

Fig. 4 (a) Hydrogen and (b) methane adsorption–desorption isotherm curves of CoPc-PorDBA COF.

at 280, 595, 650 and 735 nm. The CoPc electronic absorption spectrum (Fig. S5, ESI†) in dilute dichloromethane solution showed strong absorption bands at 295, 342, 443, 615 and 740 nm which are typical of metallophthalocyanines. As explained in other reports[1a] the blue shift of solid state CoPc-PorDBA (35 nm) of the B band when compared to that for CoPc(OMe)$_8$ in dichloromethane solution is due to the difference in aggregated phthalocyanines in the solution and in the solid state (liquid crystalline) while the red shift of the Q band is due to the differences in aggregation geometry as well as the electron-withdrawing nature of the boronate esters. The PorDBA solid-state diffuse reflectance spectrum (Fig. S6, ESI†) shows a low intensity band at about 415 nm, typical for the Soret band of the UV-Vis absorption spectra of porphyrins in homogeneous solutions (Fig. S5, ESI†). The low intensity of the Soret band may be due to stacking instead of aggregation of the porphyrins in the COF. The CoPc-PorDBA COF showed some similarities when compared to individual electronic absorption spectra of CoPc(OMe)$_8$ and PorDBA. Thermogravimetric analysis of the CoPc-PorDBA COF showed high thermal stability (see ESI†), retaining 90% of its mass at 300 °C.

Conclusions

In conclusion, we have synthesized and characterized a new cobalt based phthalocyanine and porphyrin covalent organic framework with a high surface area and reasonable H_2 and CH_4 storage capacities. We connected two very good electron donors which absorb in different regions of the UV-Vis spectrum. This COF is potentially useful in photovoltaic applications and is currently being evaluated as such.

Acknowledgements

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