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Porous Polymers

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Soluble Conjugated Microporous Polymers**

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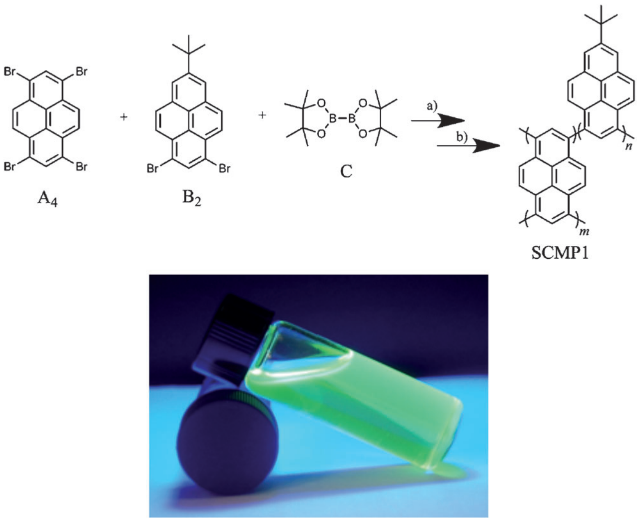
In memoriam Jon Weaver

In the last five years, conjugated microporous polymers (CMPs)[1] and other polymer networks formed by carbon–carbon coupling chemistry[2] have emerged as an important platform in amorphous porous materials. CMPs are the first synthetic networks that combine permanent microporosity (pores <2 nm) with extended π-conjugation. Building on reports of tunable pore sizes,[1a,c] structural modularity,[1e] record surface areas (5000–6500 $\mathrm{m^2\,g^{-1}}$),[2b,c] and exceptional physicochemical stability,[2b] new materials have been developed for applications such as catalysis,[1h,i,2e] light harvesting,[1g] carbon dioxide capture,[1k,2d] superhydrophobic separations,[1m] luminescence,[1l] sensors,[1n] and supercapacitors.[1j] All of these materials are insoluble networks. This insolubility limits the range of processing options for some of the more interesting applications of CMPs that seek to exploit the unique combination of porosity, conjugation, and synthetic diversity. Indeed, processability and device integration were highlighted as a challenge of "paramount importance" in a recent review of this area.[10]

Unlike CMP networks, some other porous polymers are solution processable. In particular, rigid and contorted "polymers of intrinsic microporosity" (PIMs)[3] can be dissolved in organic solvents and fabricated, for example, into microporous membranes.[3,4] To date, however, soluble linear PIMs have been prepared by condensation chemistry that introduces heteroatoms into the polymer chain and that does not introduce extended π-conjugation. Processing of microporous polymers has been described as an important target.[5] However, the closest reported step towards soluble CMPs have been solution-dispersible CMP nanoparticles formed by emulsion techniques.[6]

Here, we report the first example of a soluble conjugated microporous polymer (SCMP). The synthesis is based on hyperbranching, as used previously, for example, to prepare soluble hyperbranched polyphenylenes.[7] Initially, we focused on 1,3,6,8-tetrabromopyrene as an A_4 monomer, building on our studies of insoluble pyrene CMP networks.[8] Here, a *tert*-butyl-functionalized B_2 monomer is introduced to limit the molecular weight of the material and to incorporate solubilizing alkyl groups. To prepare the soluble CMPs, a two-step ($A_4 + B_2$)-type Suzuki-catalyzed aryl–aryl coupling copolymerization was performed (Scheme 1). In the first step, palladium acetate ($\mathrm{Pd(OAc)_2}$)[9] catalyzes an aryl halide/diboron coupling to generate arylboronates of both the A_4 monomer, 1,3,6,8-tetrabromopyrene, and the B_2 monomer, 1,3-dibromo-7-*tert*-butylpyrene,[10] in a one-pot "prepolymerization" reaction. Without isolating the arylboronate species, statistical copolymerization of the two monomers was then carried out in a second step by addition of $\mathrm{Pd(PPh_3)_4}$ and $\mathrm{K_2CO_3}$. After purification by antisolvent reprecipitation, the polymer was isolated as a deep yellow film. These materials were dissolved in common organic solvents such as tetrahydrofuran (THF), $\mathrm{CH_2Cl_2}$, and toluene to give homogeneous green-luminescent solutions (Scheme 1 and Table S1 in the Supporting Information).



Scheme 1. Two-step, one-pot synthesis of a soluble conjugated microporous polymer, SCMP1. The resulting material is a statistical hyperbranched copolymer that is soluble in common organic solvents. A solution of SCMP1 in THF shows green luminescence under UV irradiation ($\lambda = 254$ nm; image below the scheme). Reagents and conditions: a) bis(pinacolato)diboron, $\mathrm{Pd(OAc)_2}$, KOAc, anhydrous DMF, 90 °C and b) $\mathrm{Pd(PPh_3)_4}$, $\mathrm{K_2CO_3}$, anhydrous DMF, 110 °C.

SCMP1 is porous and the porosity depends on the method by which the material is isolated from solution. In particular, the porosity was different for materials precipitated rapidly in antisolvents in comparison with films prepared by slow solvent evaporation. A wide range of conditions and solvents were investigated (see the Supporting Information), but here

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we discuss two examples: antisolvent precipitation in a poor solvent (petroleum ether) and solution casting from a good solvent (dichloromethane, DCM). In both cases, SCMP1 was dissolved initially in DCM. For antisolvent precipitation, this DCM solution was added dropwise into excess petroleum ether. The rapidly precipitated SCMP1 powder was then removed by centrifugation (Figure 1 a). For solvent casting, the DCM was simply allowed to evaporate slowly on a glass slide, leaving the solid SCMP1 as a transparent, yellow film (Figure 1 b). Scanning electron microscope (SEM) images reveal the rapidly precipitated powder is comprised of fused spheres of around 100 nm in diameter (Figure 1 c), while the DCM-cast film has a smooth and uniform surface (Figure 1 d). The film is uniform and coherent but does not, in this first example, have sufficient mechanical strength to be self-supporting upon removal.

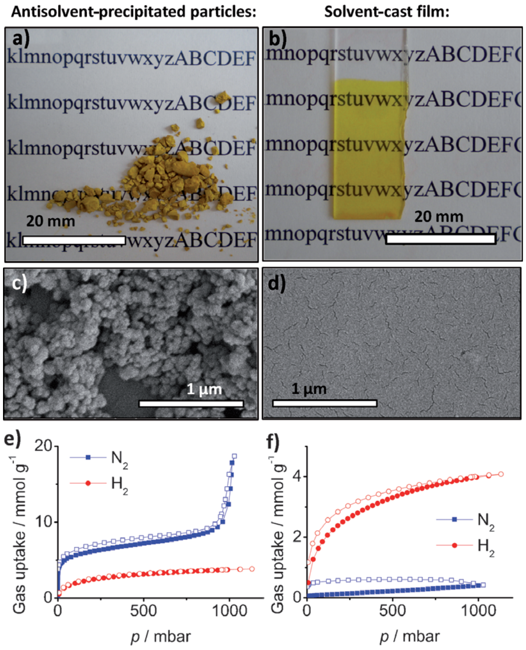

Figure 1. a) Photograph of antisolvent-precipitated SCMP1 powder. b) Photograph of a SCMP1 film prepared by slow evaporation. c) SEM image showing fused nanospheres in the precipitated polymer. d) SEM image showing the smooth surface of a cast SCMP1 film. e) Gas sorption isotherms for the precipitated powder, measured at 77 K, for nitrogen (blue) and hydrogen (red); desorption curves shown as open symbols. f) Equivalent gas sorption isotherms for the solvent-evaporated film. Note different vertical scales in (e) and (f).

The nitrogen and hydrogen sorption isotherms for SCMP1 are shown in Figure 1 e and 1 f. The rapidly precipitated SCMP1 shows a type II nitrogen isotherm and a clear micropore step at low relative pressures. The Brunauer–Emmett–Teller surface area (SA_{BET}) is 505 m^2 g^{-1}; that is, at the low end of the range for our first generation of insoluble CMP networks.[1a] The upturn in the nitrogen isotherm at higher relative pressures indicates meso/macroporosity, presumably from the nanoscopic particles (Figure 1 c) and associated interparticle voids.

By contrast, the solvent-cast SCMP1 film is effectively nonporous to nitrogen at 77 K (BET surface = 12 m^2 g^{-1}). Both materials, however, have a similar H_2 uptakes (about 4 mmol g^{-1} at 1 bar, 77 K), although greater desorption hysteresis is observed for the solvent-cast film. The difference in gas selectivity for the two samples may arise from the packing of the polymer molecules in the solid state, with the rapidly precipitated SCMP1 sample vitrifying into a less densely packed molecular structure. The solvent-evaporated SCMP1 sample forms a film that is selectively porous to hydrogen, suggesting potential in applications as coatings for gas separations. The solvent-cast SCMP1 film also adsorbs significant quantities of other gases such as CO_2, methane, and xenon at 273 K (Figure 2).

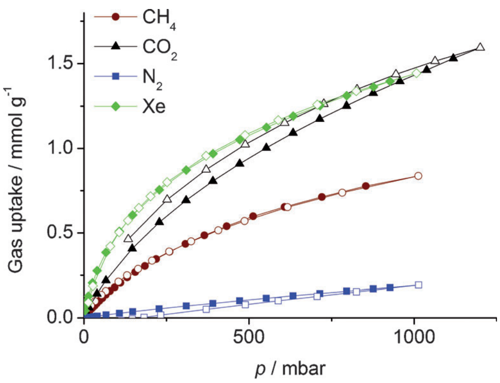

Figure 2. Nitrogen, methane, xenon, and carbon dioxide isotherms, recorded at 273 K, for DCM-cast SCMP1 films. Adsorption/desorption curves are shown as closed/open symbols, respectively.

The weight-averaged molecular weight of SCMP1, as measured by gel permeation chromatography (GPC) was 5.316 g mol^{-1}. However, accurate molecular weight determination for highly branched polymers is challenging using GPC, which uses linear polymers as calibration standards. To address this, two pyrene dendrimers[10] were synthesized as control molecules with defined mass and structure. This also allowed comparison of the sorption properties of SCMP1 with those of analogous branched molecules with precisely controlled composition and mass. Two hybrid polyhedral oligomeric silsesquioxane (POSS)–polypyrene dendrimers were synthesized with peripheral dendrons that reflect the structure of the hyperbranched copolymer, SCMP1 (Figure 3). These dendrimers were synthesized by a convergent cross-metathesis pathway using Grubb's catalyst[11] (see details in the Supporting Information).

POSS-dend-1 (Figure 3 a) has a calculated molecular weight, confirmed by mass spectrometry, of 5952 g mol^{-1}. POSS-dend-2 has additional bulky groups in the dendrons (shown in pink Figure 3 b) and a higher mass of 10.053 g mol^{-1} relative to POSS-dend-2. The dendrimers were dissolved in DCM and precipitated into petroleum ether in identical manner to the SCMP1 antisolvent process. POSS-dend-1 shows low nitrogen porosity in comparison to SCMP1, with an apparent BET surface area of 28 m^2 g^{-1} (Figure 3 c). POSS-dend-1 does adsorb H_2 at 77 K, but the isotherm shows

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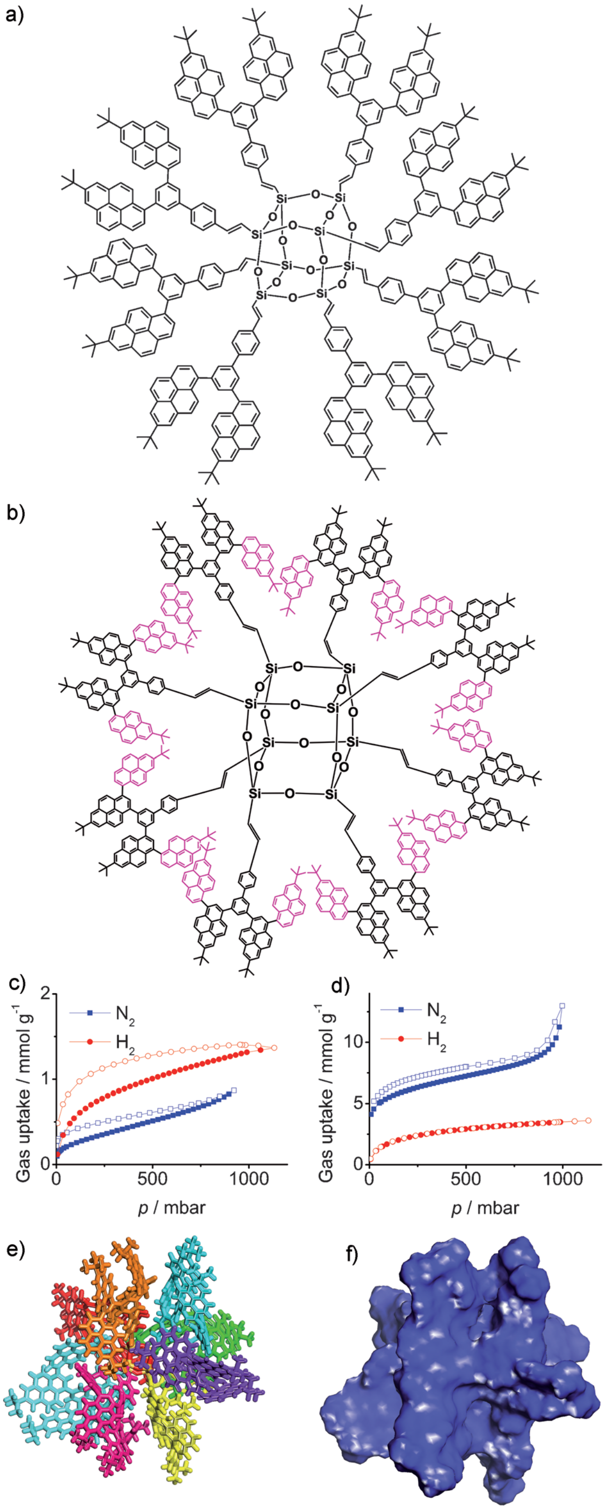

Figure 3. a) Structure of POSS-dend-1. b) Structure of POSS-dend-2, additional bulky groups shown in pink. c) Nitrogen and hydrogen isotherms, measured at 77 K, for POSS-dend-1. d) Comparable nitrogen and hydrogen isotherms for POSS-dend-2. Note different vertical scales in (c) and (d). e) Molecular model for POSS-dend-2. f) Model with Connolly surface shown in blue, probe radius = 1.82 Å.

hysteresis. POSS-dend-2, however, is much more porous with nitrogen sorption similar to SCMP1, with an apparent BET surface area of $498\ m^2 g^{-1}$ and no hysteresis in the hydrogen isotherm (Figure 3 d). We suggest that POSS-dend-2 is less interpenetrated in the solid state than POSS-dend-1 as a result of the additional bulky pyrene groups (Figure 3 b), leading to a significant enhancement in microporosity. A structural model for POSS-dend-2 was constructed (Figure 3 e). A Connolly surface for the dendrimer (Figure 3 f) highlights its irregular shape and the existence of cavities extending deep within the dendrimer. It is likely that these cavities contribute to the permanent porosity of the rigid dendrimer in the solid state. An analogous type of microporosity can be envisaged in SCMP1, but the latter material is more difficult to simulate because it is not possible to define a single molecular building block.

The GPC elution curves for SCMP1 and the two pyrene dendrimers are shown in Figure 4 and the data are summarized in Table 1. The molecular weight distribution for SCMP1 is, unsurprisingly, broader than the dendrimers which are single-molecule species. GPC underestimates the true molecular weights of the dendrimers. Overall, the GPC data suggest that the molecular weight for SCMP1 falls in the same range as the two dendrimers. The porous properties of antisolvent-

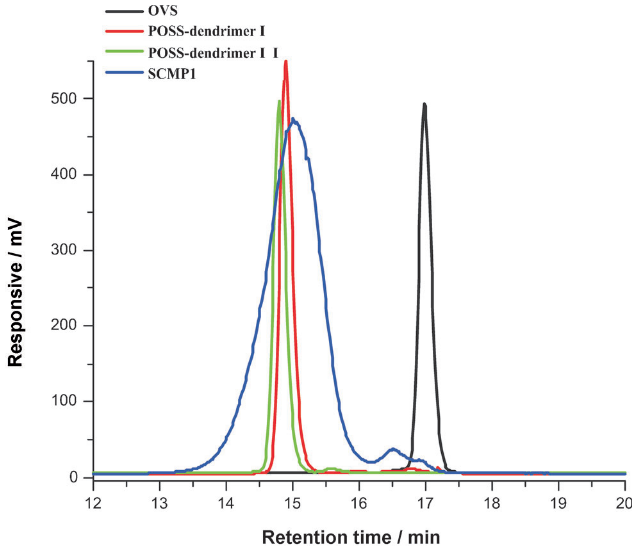

Figure 4. GPC chromatograms of octavinylsilsesquioxane (OVS), POSS-dend-1, POSS-dend-2, and SCMP1.

Table 1: Molecular weight and sorption properties for SCMP1 and pyrene dendrimers.[a]

Sample	M_w [g mol^{-1}]	M_n [g mol^{-1}]	PDI	BET[b] [m^2 g^{-1}]	N$_2$,[c] H$_2$[d] [mmol g^{-1}]
SCMP1	5316	4340	1.22	505	5.6, 3.8
OVS	560	551	1.01	–	–
POSS-dend-1	4709	4651	1.01	28	0.3, 1.3
POSS-dend-2	6115	6040	1.01	498	5.5, 3.5

[a] Sorption data given for the antisolvent precipitated form. [b] Apparent BET surface area calculated over the range $P/P_0 = 0.01$–0.1. [c] N$_2$ uptake at $P/P_0 = 0.1$, 77 K. [d] H$_2$ uptake at 1 bar, 77 K.

precipitated POSS-dend-2 and SCMP1 are also very similar, and their N_2 sorption isotherms overlay almost exactly (Figure S4 in the Supporting Information).

Both POSS-dend-1 and POSS-dend-2 display strong blue luminescence when their solutions are irradiated by UV light (Figure S5 in the Supporting Information).[12] Solutions of SCMP1 are also photoluminescent because of the conjugated structure of the polymer (Scheme 1). Absorption and emission spectra are included in Figures S6–S8 in the Supporting Information. It was shown previously, for pyrene-based dendrimers and polymers, that an increase in extended conjugation causes a red-shift in fluorescence.[8,10]

Here, fluorescence in SCMP1 is more red-shifted because the POSS core breaks the conjugation in the dendrimers. The larger red-shift in fluorescence for POSS-dend-1 with respect to POSS-dend-2 is not at present understood, but could stem from reduction in conjugation arising from steric constraints in the larger dendrimer.

To conclude, we have demonstrated for the first time that soluble conjugated microporous polymers, SCMPs, can be prepared by adapting the synthesis conditions to form discrete hyperbranched chains rather than extended networks. These materials can be processed from solution to form films, and the resultant porosity is a function of the processing conditions. Soluble conjugated dendrimers can also exhibit microporosity, and we suggest that the structural origin of microporosity—rigidity combined with non-interpenetrating cavities—is probably similar in both cases. From a practical viewpoint, however, SCMPs are preferable to dendrimers because they can be prepared in a simple two-step, one-pot procedure. Our first SCMPs involve pyrene monomers and Suzuki cross-coupling chemistry, but it is likely that analogous hyperbranching strategies can be developed for the wide range of insoluble CMP networks,[1] as well-related, non-conjugated porous networks,[2] that have been reported recently.

Experimental Section

Synthesis of SCMP1: Step 1 (pre-polymerization): To an oven-dried 500 mL round-bottom flask equipped with a reflux condenser were added 1,3,6,8-tetrabromopyrene (A_4, 2.58 g, 5.0 mmol), 1,3-dibromo-7-*tert*-butylprene[10] (B_2, 4.16 g, 10.0 mmol), bis(pinacolato)diboron (C, 8.00 g, 31.5 mmol), palladium acetate, $Pd(OAc)_2$ (240 mg, 1.07 mmol), potassium acetate, KOAc (5.80 g, 59.10 mmol), and anhydrous dimethylformamide, DMF (275 mL) under a nitrogen atmosphere. After the mixture was degassed, it was heated and stirred at 90 °C for 22 h.

Step 2 (polymerization): The pre-polymerized mixture was cooled down to room temperature and $Pd(PPh_3)_4$ (680 mg, 0.59 mmol), K_2CO_3 (4.80 g, 34.73 mmol), and H_2O (25 mL) were added and the solution was degassed. The mixture was then heated to 120 °C and stirred for five days under a nitrogen atmosphere.

Purification of SCMP1: Step 1: The resulting deep green mixture was diluted with DCM (500 mL), washed with a 20 % HCl solution followed by brine until the green organic layer changed to brown; it was then washed with water and dried over $MgSO_4$. The clear solution was concentrated at reduced pressure and any Pd-black particles were removed by passing through a short silica gel column, followed by elution with THF. The organic solution was then concentrated and precipitated twice from DCM (40 mL) into MeOH (320 mL). The polymer product was isolated by centrifugation and dried in vacuum at 120 °C to give 3.2 g of a light yellow powder.

Step 2: This light yellow powder was dissolved in DCM (20 mL) and absorbed on 10 g silica gel and air dried, followed by Soxhlet extraction with hot hexane, a poor solvent for the SCMP, for three days. The hexane solution was replaced with THF, a good solvent for the SCMP, to extract the polymer from the silica gel over two days. THF was removed by rotary evaporation to give 2.6 g of the product, SCMP1, as a deep yellow film (yield = 81 % by weight). GPC analysis: $M_w = 5316\ \text{g mol}^{-1}$, $M_n = 4340\ \text{g mol}^{-1}$, PDI = 1.22 ($M_w$ = weight-averaged molecular weight, M_n = number-averaged molecular weight, and PDI = polydispersity index). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.1$–7.3 (br, -pyrenyl) and 1.9–0.3 ppm (br, $-CH_3$). Assuming no end groups, a ratio of aromatic/*tert*-butyl groups of 1.11:1 would be expected. For SCMP1, an integration of 0.625:1 is found. After hydrolysis of boronic ester end groups using BBr_3, a ratio of 1.08:1 was measured, close to the theoretical value. Hence, the feed ratio is maintained, but the polymer also contains a significant number of end groups, as expected from the relatively low molecular weight.

Typical antisolvent reprecipitation conditions: SCMP1 was dissolved in CH_2Cl_2 (1 mL) at $80\ \text{mg mL}^{-1}$ concentration and added dropwise to petroleum ether (10 mL, b.p. 40–60 °C). The resulting precipitated material was separated by centrifugation for 5 minutes at 5000 revolutions per minute (r.p.m.) before decanting the supernatant.

Film casting: SCMP1 was dissolved in CH_2Cl_2 (1 mL) at $80\ \text{mg mL}^{-1}$ concentration. The CH_2Cl_2 was subsequently allowed to evaporate under nitrogen flow, leaving the polymer as a coherent film on the glass surface of the containment vessel.

Dendrimers: The syntheses and purification processes of POSS-dend-1 and POSS-dend-2 are detailed in the Supporting Information.

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