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COMMUNICATION

Synthesis and Sorption Properties of Hexa-(peri)-hexabenzocoronene-Based Porous Organic Polymers

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**In this communication, we report the synthesis of several novel hexa(peri)-hexabenzocoronene containing microporous polymers. These polymers exhibit good adsorption properties for H_2, N_2 and CO_2 gases. Based on fluorescence quenching studies, we have shown that the highly conjugated π-surfaces may be accessible by guests in solution.**

Porous organic materials have become an increasingly developed area of polymer chemistry over the past several years as potential storage matrices for the next generation of clean energy fuels. Porous polymers[1-3] are attractive materials for practical energy storage applications as they are structurally robust and resistant to degradation under harsh conditions. Tetraphenylmethane (TPM)-based polymers are an attractive subset of porous materials that can be easily synthesized using a variety of metal-catalyzed cross-[4, 5] or homocoupling[6, 7] reactions and remain permanently porous as a result of the rigid bulk of the TPM unit. The ease of synthesis and diverse functional groups that can be placed on the TPM unit make it amenable for use in combination with a wide variety of organic co-monomers that endow these polymers with a wide variety of functionality and sorption properties. Porous organic polymers (POPs) absorb gases such as H_2,[8] CH_4,[2] and CO_2,[9-11] selectively.

Polycyclic aromatic hydrocarbons (PAH) represent attractive targets for incorporation into porous polymers owing to their large π-conjugated surfaces[12] that can potentially act as sites for chemical sensing, gas storage and binding. HBC-structures have found use in energy-related applications such as photovoltaics,[13, 14] as well as in self-assembled materials.[15] Along with other large PAH compounds, HBC has been considered as an ideal model for graphitic systems[12, 16] because of its planarity, extended π-conjugation and its relatively straightforward chemical synthesis that is amenable to preparation on multi-gram scales. We consider HBC to be an
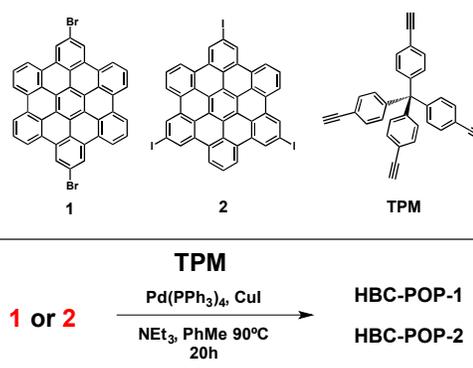

Figure 1. Monomers and synthetic conditions used to prepare the HBC-POPs discussed in this communication.

interesting target for incorporation into porous materials for these same reasons – its π-conjugation could endow HBC-POPs with improved gas sorption capability and supramolecular recognition properties.

In order to test these hypotheses and investigate HBC-based porous polymers, we have chosen two halide functionalized HBC structures (Figure 1). HBC compounds **1** and **2** can be prepared on gram scales using previously published procedures[17, 18] and provide different symmetries (two and three fold respectively). Previous reports[19, 20] have indicated that the bonding geometry can have significant effects on the pore size and surface area in porous polymer materials. As shown in Figure 1, either monomer can be polymerized under Sonogashira conditions[4] along with a tetrakis(4-ethynyl)tetra-phenylmethane (TPM) unit[21] to give brown powders that are insoluble in all organic solvents.

To determine the accessible surface areas and pore size distributions, these POPs (referred to as HBC-POP-1 and HBC-POP-2) were evaluated through nitrogen adsorption at 77K. The resulting isotherms and pore size distributions are shown in Figure 2. The BET surface areas were calculated to be 668 and 457 m^2/g for HBC-POP-1 and -2 respectively. Hydrogen

uptake isotherms were also obtained at 77K indicating that both POPs were capable of ~0.8 wt% storage (see ESI for details).
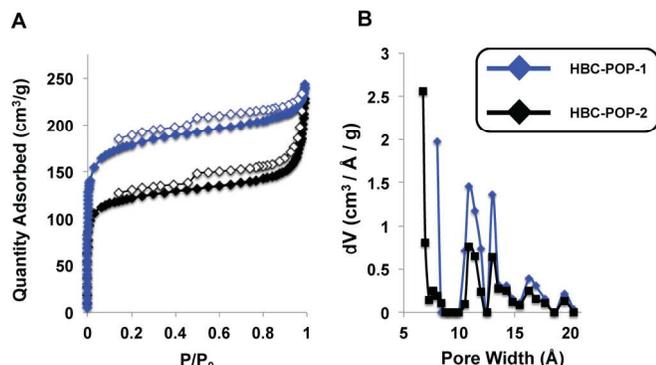
Figure 2. (**A**) Nitrogen gas isotherms taken at 77K. The filled diamonds represent the adsorption isotherm and open diamonds represent the desorption isotherm. (**B**) Pore size distributions for both HBC-POPs based on differential pore volumes.

The pore size distributions (Figure 2B) indicate that despite the higher surface area of HBC-POP-1 both compounds have similar pore sizes, with HBC-POP-2 actually having slightly smaller micropores (~7Å). Previous reports[20] have indicated that the linker angle, in this case the angle between each halide bonding site of **1** and **2** can greatly affect the surface area and pore characteristics of the POP. Considering geometry and symmetry concerns alone, we would expect a diamondoid net for HBC-POP-1 and a 4,3c net for HBC-POP-2. The theoretical surface area for a diamondoid net structure of HBC-POP-1 was calculated to be ~8000 m^2/g, indicating that this arrangement is not formed (see SI for details). Elemental analyses indicated that when compared with the corresponding monomers, approximately 6% and 19% by weight of the halides in HBC-POP-1 and 2, respectively, remained.

Carbon dioxide isotherms (Figure 3) were collected at 273 and 298K for HBC-POP-1 and -2. HBC-POP-1 adsorbed ~9 wt% CO_2 while HBC-POP-2 carried ~8 wt% at 273K. These storage capacities are comparable with other hydrocarbon based porous polymers[22] and better than some others despite comparatively low surface areas. COF-5, for example can adsorb 5.9 wt% with a BET surface area of 1670 m^2/g.[23] The higher storage capacity in HBC-POPs can potentially be attributed to the extended π-surfaces[22] accessible to the CO_2.
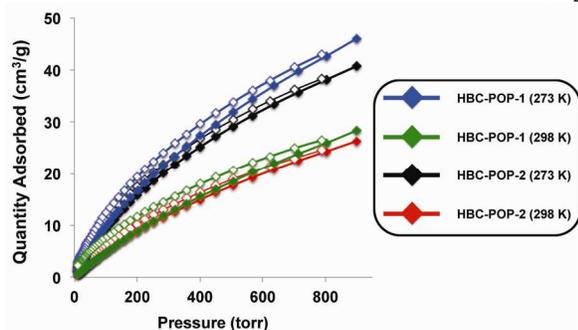
Figure 3. Carbon dioxide isotherms for both HBC-POPs at 273 and 298K. The filled diamonds represent the adsorption isotherm and open diamonds represent the desorption isotherm.

Heats of adsorption (HOA) for CO_2 were calculated from these data for both polymers (Figure 4A). The decreasing HOA with increasing amount of gas adsorbed is consistent with most porous materials and can be explained by the gas-POP interaction being stronger than gas-gas interaction. As the accessible surface becomes occupied at higher capacity, the HOA decreases. The adsorption enthalpies are relatively high for CO_2 compared with many porous polymers that lack polar functional groups such as alcohols or amines. Both polymers however have very similar HOA characteristics at low surface coverage despite different BET surface areas. Additionally, the less porous polymer HBC-POP-2 appears to maintain a higher HOA with increasing quantity of adsorption in comparison with HBC-POP-1. We hypothesize that this could be explained by the structure of HBC-POP-2 having more accessible and open HBC surface sites than HBC-POP-1 owing to the poorer symmetry match between the monomers of the former (3-fold symmetry of **2**) and the tetrahedral TPM versus the more symmetrical HBC **1**.
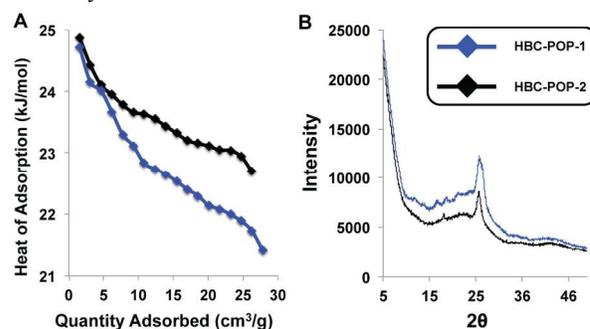

Figure 4. (**A**) CO_2 heat of adsorption measurements for HBC-POP-1 and -2. (**B**) Powder X-Ray diffraction patterns of HBC-POPs

In order to investigate this hypothesis and to characterize any potential π-stacking interactions and other long-range ordering in the POPs, powder X-Ray diffraction (pXRD) measurements were carried out (Figure 4B). Most porous polymers formed under kinetic polymerization conditions result in largely amorphous materials.[5] This is observed for the HBC-POPs discussed here with the exception of one major, discernible peak at 26°. Using Bragg's Law, this diffraction angle corresponds to a spacing of ~3.5 Å which is consistent with a face-to-face π-stacking interaction. The presence of this peak indicates that many of the HBC moieties could be involved in stacking interactions. As the strongest interactions between the gas and material are expected to come from the π-surface of the HBC, strong π-stacking between polymer chains may be detrimental to sorption. The lack of any other significant periodicity observed by pXRD further supports the conclusion that these materials do not contain any type of ordered net type structure.

Although it appears that π-stacking is a strong organizational force in the formation of HBC-POPs, we investigated the possibility of some HBC sites remaining open and accessible through the use of fluorescence spectroscopy. Previous studies involving HBC and its variants have shown

that close interaction with buckminsterfullerene (C_{60}) can result in quenching of the HBC fluorescence. Shown in Figure 5 are the fluorescence spectra of HBC-POP-1 (Figure 5A) and -2 (Figure 5B) and the effects of quenching upon addition of C_{60} (in concentrations up to 0.15 mM) to suspensions of each polymer in toluene. The fluorescence emissions at ~530 nm are consistent[17] with the HBC moieties in our POPs, confirming their presence in the polymer. While these experiments cannot give quantitative information about the exact number of accessible HBC sites, they do indicate that at least some of the HBC faces are open to interaction with C_{60}, which has a diameter of ~7 Å and is small enough to enter all but the smallest of the pores in both polymers.
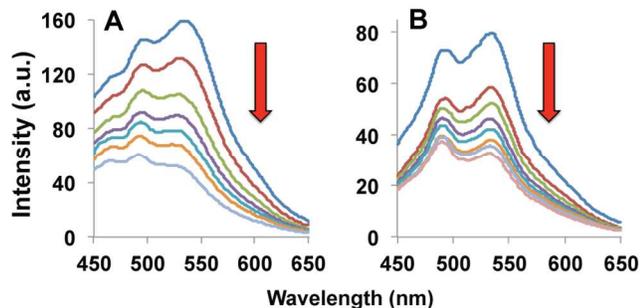
Figure 5. Fluorescence spectra of HBC-POP-1 (**A**) and HBC-POP-2 (**B**) and additional spectra that demonstrate the quenching behaviour upon addition of C_{60}. (See ESI for experimental details)

Conclusions

In conclusion, we have successfully prepared and evaluated the first permanently porous HBC containing polymers, which we have designated HBC-POPs, through a Sonogashira polymerization with tetrakis(4-ethynyl) TPM. These polymers have demonstrated permanent porosity and accessible surface area along with excellent adsorption enthalpies for CO_2, giving them the ability to adsorb high amounts of CO_2 relative to their surface areas. HBC-POPs have also been shown to exhibit strong π-stacking interactions despite the fact that the polymers are formed under kinetic conditions. The effect of the strong π-stacking interaction on the polymer structure may also explain why the difference in bonding angle between HBC-POP-1 and -2 does not result in as large a change in surface area as is seen in other systems. In other words, π-stacking, rather than monomer geometry, may be the major directing force in the structure of these polymers. Future work will be directed towards both utilizing the strong π-stacking properties of HBC monomers to develop more functional POPs as well as developing strategies to control the amount of π-aggregation in the material to improve their gas storage properties.

Notes and references

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