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A silver(I) coordinated phenanthroline-based polymer with high ethylene/ethane adsorption selectivity†

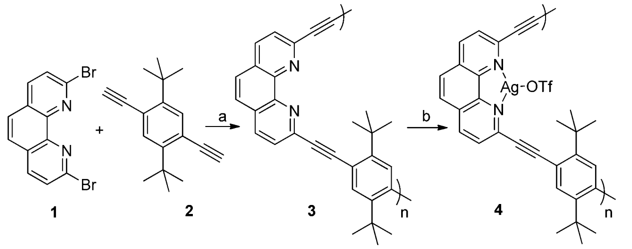
Chao Yu,[a] Matthew G. Cowan,[b] Richard D. Noble[b] and Wei Zhang*[a]

We report a non-porous silver(I) coordinated phenanthroline-based polymer, which exhibits a high ideal ethylene/ethane adsorption selectivity (15/1) and high ethylene uptake (5.0 mmol g^{-1}) at ambient temperature and pressure. Both silver(I) coordination and polymer structures are important for the high uptake of ethylene.

Ethylene and ethane are usually obtained as a mixture from cracking processes used in the petroleum industry.[1] Separation of these two gases in an energy-efficient way is challenging due to the similarities in their molecular sizes and physical properties.[2] The current industrial practice is to use cryogenic distillation, which is a highly energy-intensive process.[3] Recently, selective adsorption on porous solid adsorbents has emerged as a promising, energy-efficient and environmentally benign alternative for ethylene/ethane separation. Various porous solids, mainly molecular sieve zeolites[4] and metal–organic frameworks (MOFs),[2,5,6] have been developed for selective adsorption of ethylene over ethane. Porous organic polymers[7–9] are another important class of porous materials. However, they have barely been explored in ethylene/ethane separation. One recent example is that of the copper(catecholate)-decorated porous organic polymer, which exhibits an ideal adsorbed solution theory (IAST) selectivity of 3.8/1 for ethylene/ethane adsorption.[10] Herein, we report the synthesis of a robust, silver(I) coordinated, phenanthroline-based polymer, which shows a high ideal selectivity (15/1, v/v) for the adsorption of ethylene over ethane at ambient temperature and pressure.

Most of the selective adsorption of olefins over paraffins is based on the reversible formation of π-complexes of olefins with transition-metal cations.[11–16] Among the first and second row transition metals, silver(I) and copper(I) ions have been the most popular choices of metal ions for selective adsorption of olefins.[17] We envisioned that phenanthroline-based polymers can readily coordinate with silver(I) ions and serve as solid adsorbents for ethylene/ethane separation. The phenanthroline-containing polymer (**3**) was synthesized from two readily accessible monomers, 2,9-dibromophenanthroline (**1**) and 1,4-di-*tert*-butyl-2,5-diethynylbenzene (**2**), in 1 : 1 stoichiometric ratio *via* Sonogashira cross-coupling (Scheme 1). The polymer product **3** was purified through simple filtration and washing to give a brown precipitate in 77% yield. The *t*-butyl group was introduced into monomer **2** to enhance the solubility of short oligomers and prevent their premature precipitation. It was also anticipated that the presence of bulky *t*-butyl groups would minimize the aggregation between phenanthroline and phenyl moieties, thus producing more void space between polymer backbones and facilitating the transport of gas within the polymers.

The phenanthroline moiety has been widely used as a coordinating ligand in supramolecular chemistry to form complex molecular entities, owing to its capability of binding various metal ions and also its unique structural and electronic properties (planarity, rigidity and electron-deficient conjugated ring).[18,19] Therefore, metal ions are expected to be readily incorporated into polymer **3** through the coordination with phenanthroline moieties. We chose silver(I) as the metal cation



Scheme 1 Synthesis of phenanthroline-based polymer **3** and its metallated analogue **4**: (a) Pd(PPh$_3$)$_2$Cl$_2$, CuI, triethylamine, THF, 70 °C, 77%; (b) AgOTf, acetone, CH$_2$Cl$_2$, 95%.

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[a] *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA. E-mail: wei.zhang@colorado.edu*

[b] *Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309, USA*

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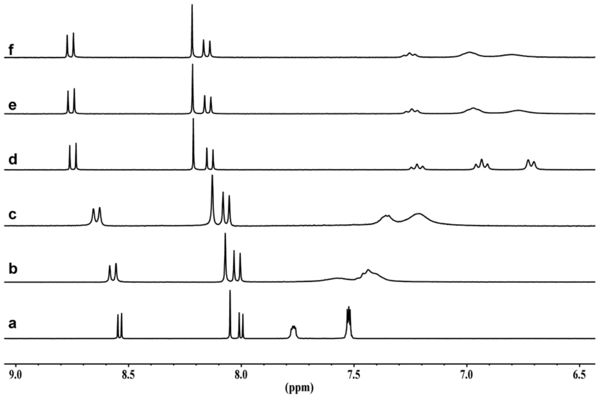


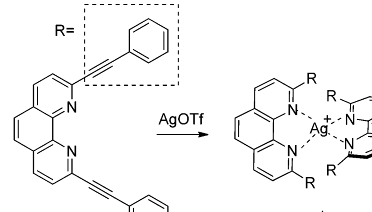
Fig. 1 ^{1}H NMR spectra of titration study of AgOTf and **5**: (a) compound **5**; (b) after the addition of 0.1 equiv. AgOTf; (c) after the addition of 0.25 equiv. AgOTf; (d) after the addition of 0.5 equiv. AgOTf; (e) after the addition of 1.0 equiv. AgOTf; (f) after the addition of 1.5 equiv. AgOTf.

since it can form π-complexes with olefins and the reaction can be easily reversed by pressure and temperature swings.[17] A simple model compound (**5**) was used to study the coordination of the phenanthroline moiety to the silver(I) cation. Upon the addition of increasing amounts of AgOTf in acetone (0.1 equiv. → 0.5 equiv.) to the solution of compound **5** in dichloromethane, we observed the gradual downfield shifting of phenanthroline protons in the ^{1}H NMR spectrum of the complex (Fig. 1). With the addition of 0.5 equiv. AgOTf, the system reached the saturation point, and further addition of excess silver(I) triflate (up to 1.5 equiv.) did not lead to any significant changes in the ^{1}H NMR spectrum. The resulting silver(I) complex was further characterized using ESI-MS and IR-spectroscopy. High-resolution ESI-MS of the silver(I) complex displays peaks at *m*/*z* of 487.0376 and 869.1687, which correspond to the monomeric complex [**5**·Ag$^+$] and the dimeric complex [**5**·Ag$^+$·**5**], with relative intensities of 10% and 100%, respectively. Based on this result, we tentatively assigned the silver(I) complex to the dimer [**5**·Ag$^+$·**5**] (Scheme 2). In the IR spectra of [**5**·Ag$^+$·**5**] (Fig. S2, ESI†), we observed new intensive peaks at 1294 cm^{-1}, 1228 cm^{-1}, 1164 cm^{-1}, 1022 cm^{-1} and 634 cm^{-1}, and slight blue shifts of a few peaks (*e.g.*, 1537 cm^{-1} to 1542 cm^{-1}, 1496 cm^{-1} to 1504 cm^{-1}, and 1357 cm^{-1} to 1365 cm^{-1}), indicating the successful coordination of silver(I), which is in agreement with the literature report.[20]

Silver(I) coordinated polymer **4** was then prepared following the same procedure as the model system. The suspension of polymer **3** in a mixture of acetone and dichloromethane was treated with 1 equiv. AgOTf per phenanthroline unit (Scheme 1). The metallated polymer product **4** was obtained as a black solid after successive washing with acetone to get rid of excess AgOTf. Polymers **3** and **4** were characterized using IR, solid state NMR, elemental analyses, and TGA. Similar to the model system described above, the IR spectrum of polymer **4** shows new peaks at 1268 cm^{-1}, 1232 cm^{-1}, 1140 cm^{-1}, 1025 cm^{-1} and 636 cm^{-1}, and slight blue shifts of a few peaks (*e.g.*, 1537 cm^{-1} to 1543 cm^{-1}, 1496 cm^{-1} to 1502 cm^{-1}, and 1361 cm^{-1} to 1367 cm^{-1}) in comparison to that of polymer **3** (Fig. S1, ESI†). Solid-state ^{13}C CP-MAS NMR spectra show that the two broad signals from ethynylene carbons of polymer **3** merge into a single broad peak upon metallation, which is consistent with the observed changes in the ^{13}C NMR spectra of the model complex (Fig. S3, ESI†). ICP-MS analysis has been used to estimate silver(I) ion loadings in polymer **4**. We determined that 75% of phenanthroline units were coordinated with silver(I) ions, which is 1 : 0.75 molar ratio of phenanthroline to silver(I). Although the model study indicated that phenanthroline moieties prefer to form dimer complexes (2 : 1 binding of phenanthroline : Ag^{I}), we assumed that the majority of phenanthrolines in polymer **4** form the 1 : 1 binding complex with silver(I), considering the poor mobility of polymer chains in the solid state. The TGA analyses show that polymer **3** and the Ag(I) coordinated polymer **4** have high thermal stability at the decomposition onset temperature of 350 °C (Fig. S9, ESI†).

With such a high loading of silver(I) ions in polymer **4**, selective adsorption of ethylene over ethane was anticipated. We therefore performed single component adsorption experiments under ambient conditions (room temperature, 0.9 bar) to explore the gas adsorption properties of the polymers. All the samples were ground using a mortar and pestle, and activated at 25 °C under high vacuum (< 0.5 torr) for 18 hours to remove the residual solvent and water molecules. The Brunauer–Emmett–Teller (BET) surface area measurements showed that polymer **4** is non-porous, with a BET specific surface area of <10 m^2 g^{-1}. However, this apparently non-porous polymer showed impressively high ideal selectivity in the adsorption of ethylene over ethane (15/1), with C_2H_4 and C_2H_6 uptakes of 5.04 mmol g^{-1} and 0.34 mmol g^{-1}, respectively (Table 1). To the best of our knowledge, this ethylene/ethane selectivity is among the highest reported values obtained so far in the literature.[6,10,21–23] It is not unprecedented that non-porous or low surface area materials show high gas adsorption selectivities either through selective binding or the molecular sieving effect.[24–30]

The observed high selectivity and high uptake of ethylene over ethane in non-porous polymer **4** is mainly attributed to the binding of ethylene molecules with the silver(I) ions.



5

[5·Ag$^+$·5]

Scheme 2 Metallation of model compound **5** to form [**5**·Ag$^+$·**5**].

Table 1 Ag^{I} loading and gas adsorption capacities of **3**, **4**, and [**5**·Ag$^+$·**5**]

Adsorbent	Ag$^+$ loading (%)	C_2H_4 uptake (mmol g^{-1})	C_2H_6 uptake (mmol g^{-1})	Ideal selectivity
3	n/a	0.41	0.45	0.9/1
4	13.3	5.04	0.34	15/1
[**5**·Ag$^+$·**5**]	21.0	0.20	0.015	13/1

As a control experiment, we studied the gas adsorption properties of the metal-free polymer **3**. Our study shows that polymer **3** does not discriminate between C_2H_4 and C_2H_6, exhibiting no apparent selectivity in uptakes. This is in great contrast to the silver(I) coordinated polymer **4** that exhibits much higher uptake of C_2H_4 than C_2H_6. Such a result clearly shows that the coordination of silver(I) ions is crucial for selective adsorption of ethylene over ethane.[6] The slight decrease in ethane uptake in polymer **4** could be due to the increase in the molecular weight of the adsorbent after metallation. In order to probe the importance of the polymer structure to the high gas uptake in polymer **4**, we studied the gas adsorption behavior of the silver(I) containing dimer complex [**5**·Ag$^+$·**5**] as another control experiment. Not surprisingly, the compound [**5**·Ag$^+$·**5**] shows a high selectivity (13/1) in the adsorption of ethylene over ethane due to the formation of π-complexation between the silver(I) ion and ethylene. However, 25-fold lower ethylene uptake (0.20 mmol g^{-1}) compared to polymer **4** was observed, indicating that the polymer structure plays an important role in the increased uptake of gas molecules. Presumably, the rigidity of the polymer backbone and the bulkiness of the *t*-butyl group restrict the close stacking of the polymer backbones, which promotes transport of gases within the polymers.

In summary, we report a readily accessible silver(I) coordinated phenanthroline-based polymer, which shows high adsorption selectivity of ethylene over ethane at ambient temperature and pressure. Both the polymer structure and the silver(I) complexation account for the high gas uptake and high selectivity in ethylene/ethane adsorption. Currently, design and synthesis of metal coordinating polymers with high porosity and their use in composite membrane fabrication are being pursued in our labs and will be reported in due course.

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