

Porous networks based on iron(II) clathrochelate complexes

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Microporous networks based on boronate ester-capped iron(II) clathrochelate complexes are described. The networks were obtained by covalent cross-linking of tetrabrominated clathrochelate complexes via Suzuki-Miyaura polycross-coupling reactions with diboronic acids, or by Sonogashira-Hagihara polycross-coupling of clathrochelate complexes with terminal alkyne functions and 1,3,5-tribromobenzene. The networks display permanent porosity with apparent Brunauer-Emmett-Teller surface areas of up to $S_{\text{ABET}} = 593 \text{ m}^2 \text{ g}^{-1}$. A clathrochelate complex based on an enantiopure dioximate ligand was used to prepare chiral networks. One of these networks was shown to preferentially absorb D-tryptophan over L-tryptophan.

Introduction

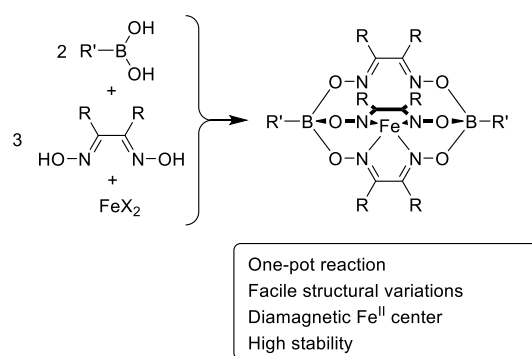
Metal-catalyzed carbon-carbon coupling reactions of rigid, polyfunctional monomers can give rise to microporous polymers.¹ Different types of reactions have been used in this context, including the Yamamoto coupling of polybrominated monomers,² the Pd^{II}/Cu^I-catalyzed homo-coupling of polyethynylbenzenes,³ the Suzuki-Miyaura cross-coupling of polyhalogenated compounds with polyarylboronic acids,⁴ and the Sonogashira-Hagihara cross-coupling of polyhalogenated compounds with monomers featuring two or more terminal alkyne groups.⁵ Direct C-H arylation reactions in the presence of Pd catalysts have also been explored.⁶ The resulting polymers are classified as “porous aromatic frameworks” (PAFs)^{1b,f} or “conjugated microporous polymers” (CMPs), depending on the nature of the polyfunctional monomer.^{1c,g} PAFs and CMPs are obtained as amorphous solids. The lack of crystallinity and structural homogeneity is a disadvantage over other materials with permanent porosity such as porous molecular crystals,⁷ covalent organic frameworks (COFs)⁸ or metal-organic frameworks (MOFs).⁹ On the other hand, PAFs and CMPs typically show high chemical and thermal stability, which is a critical feature for many applications.

The nature of the polyfunctional monomers is of central importance for the properties of the resulting polymer. Typically, purely organic monomers are employed, but the utilization of inorganic monomers represents an interesting alternative. Catalytically active porous polymers were obtained by covalent cross-linking of metalloporphyrins,¹⁰ organometallic Ir complexes,¹¹ or salen complexes.¹² Inorganic monomers can

also be used to obtain polymers with unusual topologies. For example, functionalized silsesquioxanes were employed to prepare porous polymers with 8-connected links.¹³

In order to use inorganic monomers for the synthesis of PAFs or CMPs, they need to be stable under polymerization conditions. The stability can be a critical point, because metal-catalyzed C-C coupling reaction are often performed under harsh reaction conditions. Furthermore, it should be noted that the synthesis of functional inorganic monomers can be challenging, costly and time-consuming. In view of these difficulties, it is not surprising that PAFs and CMPs are generally prepared from organic monomers.¹

Herein, we report the synthesis and the characterization of robust microporous networks based on boronate ester-capped iron(II) clathrochelate complexes. Cage complexes of this kind are easily accessible by one-pot reactions involving a boronic acid, a dioxime ligand, and an iron(II) salt (Scheme 1).¹⁴ The scope of this reaction is large, and structural modifications of the boronic acid and/or the dioxime ligand are well tolerated.



Scheme 1 General reaction scheme for the synthesis of boronate ester-capped iron(II) clathrochelate complexes.

Iron(II) clathrochelate complexes have been used in the context of medicinal inorganic chemistry,¹⁵ and as catalyst precursors

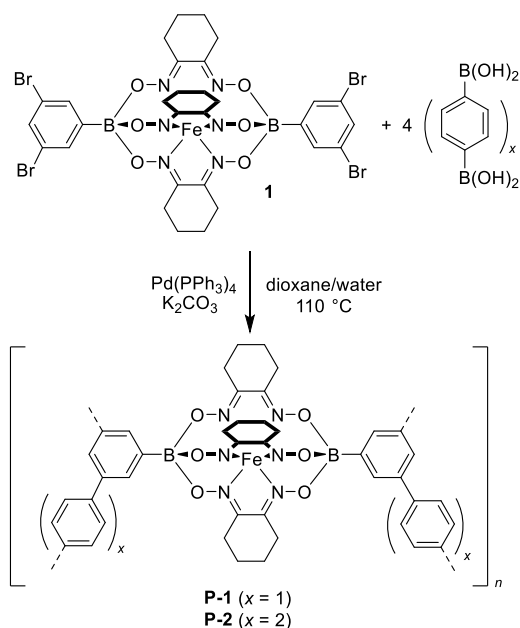
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

for electrochemical hydrogen evolution.¹⁶ Furthermore, they can show interesting magnetic behavior.¹⁷ Our group has examined the utilization of functionalized clathrochelate complexes as metalloligands in supramolecular coordination chemistry.^{18,19} A preliminary study had shown that a *dinuclear* Fe(II)/Fe(III) cage complex can be used to make a cross-linked polymer with permanent porosity.²⁰ This finding prompted us to examine if *mononuclear* Fe(II) clathrochelates complexes, which are easier to access, can also be employed to prepare porous polymer networks. The results of these investigations are summarized below.

Results and discussion

Recently, we have reported the synthesis of clathrochelate complex **1** (Scheme 2).^{18b} It can be obtained by a one-pot reaction from commercially available materials, namely (3,5-dibromophenyl)boronic acid, nioxime, and iron chloride. Complex **1** features four bromo substituents which are arranged in a divergent fashion. Suzuki-Miyaura-type cross-coupling reactions are possible, as evidenced by the successful coupling of **1** with pyridylboronic acid.^{18b} The fact that complex **1** can be coupled with boronic acids may seem surprising, because the clathrochelate complex itself contains boronate ester linkages. However, the latter are highly inert, and they do not interfere with the coupling chemistry.



Scheme 2 Synthesis of the clathrochelate networks **P-1** and **P-2**.

In order to prepare a polymeric network, we have investigated the polycross-coupling reaction of **1** with 1,4-benzenediboronic acid or 4,4'-biphenyldiboronic acid, respectively. The reaction conditions were optimized using the porosity of the final polymer as main criteria (for details see ESI). The utilization of dioxane/water (6:1) as solvent was found to be advantageous. As catalyst precursor, we have employed $\text{Pd(PPh}_3)_4$ (7.5 mol% with respect to the boronic

acid) in combination with K_2CO_3 as base. A molar ratio of 4:1 between the diboronic acid and the brominated clathrochelate was found to give polymers with the highest porosity. Most likely, the excess of boronic acid is needed to compensate for protodeboronation reactions.²¹ Using these optimized conditions, we prepared the porous clathrochelate polymers **P-1** and **P-2** by heating the reaction mixtures at $110\text{ }^\circ\text{C}$ for 24 h (Scheme 2).

The covalent linkage of the clathrochelates via phenylene and diphenylene spacers is expected to give large macrocyclic structures if fully connected 2D networks are formed. However, the formation of 3-dimensional network structures is conceivable as well.

P-1 and **P-2** were characterized by solid-state ^{13}C NMR spectroscopy, thermogravimetric analysis (TGA), and sorption measurements. Furthermore, **P-1** was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy. EDX revealed only minor amounts of residual bromine ($\sim 1.15\%$ of the initial amount), indicating efficient conversion of the bromo functions during the cross-coupling process. We were also able to detect Pd, the concentration of which varied depending on the precise location of the measurement on the polymer sample (0.31–0.47 Pd per Fe). Most likely, Pd nanoparticles are formed from the catalyst precursor $\text{Pd(PPh}_3)_4$ during the polymerization process. The presence of Pd has been observed for other polymers, which were obtained by Suzuki-Miyaura polycross-coupling reactions.²²

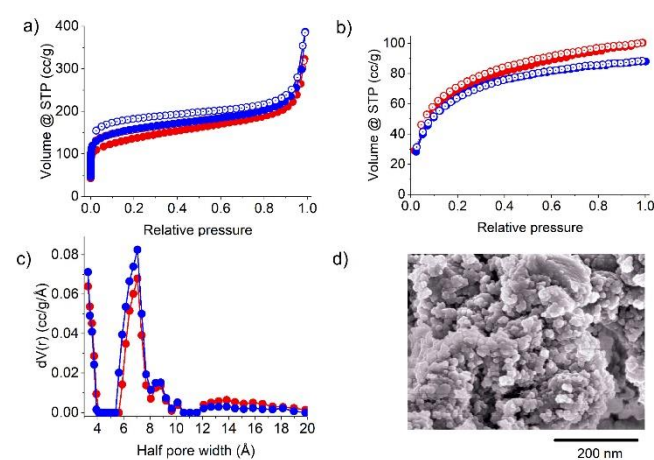


Fig. 1 Characterization of **P-1** (red symbols) and **P-2** (blue symbols) by sorption measurements and SEM. a) N_2 adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K; b) H_2 adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K; c) Pore size distribution; d) SEM image of **P-1**.

The polymer networks **P-1** and **P-2** were characterized by N_2 physisorption measurements at 77 K and the pore size distribution was calculated from nonlocal density functional theory (Figure 1 and Table 1). The sorption measurements revealed an apparent Brunauer-Emmett-Teller (BET) surface area of $S_{\text{BET}} = 550\text{ m}^2\text{ g}^{-1}$ for **P-1**. The BET surface of **P-2** is only slightly higher ($593\text{ m}^2\text{ g}^{-1}$), despite the fact that clathrochelates are connected by significantly longer diphenylene spacers. The

micropores of both polymers have a diameter of around 1.4 nm. CO₂ and H₂ uptakes were measured up to 1 bar at 273 K and 77 K, respectively. The corresponding values (CO₂: 58 cm³ g⁻¹ (**P-1**), 48 cm³ g⁻¹ (**P-2**); H₂: 101 cm³ g⁻¹ (**P-1**), 90 cm³ g⁻¹ (**P-2**)) are within the expected range for microporous polymers of the given porosity (for details see ESI).¹ The SEM image of **P-1** (Fig. 1d) shows agglomerates of irregular spherical nanoparticles, which are typical for porous cross-linked polymers.

Iron clathrochelate complexes are chemically and physically very stable. Accordingly, we expected a high stability for the networks **P-1** and **P-2**. Indeed, TGA measurements revealed a good thermal stability, with decomposition occurring between 250 and 300 °C (see ESI). Heating suspensions of **P-1** in water at 80 °C for 6 h resulted in no significant loss of porosity.

It is worth noting that Fe-templated polycondensation reactions of dioximes with diboronic acids can also give polymers with permanent porosity (*S*_{BET} of up to 412 m² g⁻¹).²³ For these linear polymers, the porosity in the solids state is due to inefficient packing of the polymer chains.

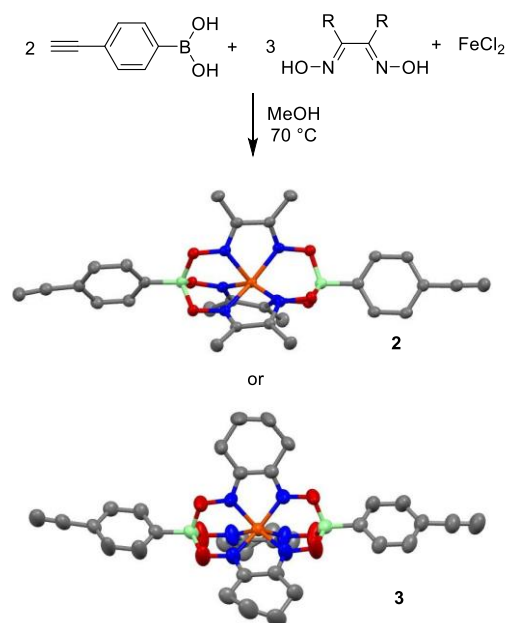
Table 1 – Results of N₂ sorption measurements at 77 °C.

polymer	<i>S</i> _{BET} [m ² g ⁻¹]	<i>S</i> _{Lang} [m ² g ⁻¹]	pore vol. [cm ³ g ⁻¹]	pore diam. [nm]
P-1	550	691	0.38	1.40
P-2	593	670	0.25	1.39
P-3	235	318	0.30	1.35
P-4	360	525	0.28	1.33
P-5	548	634	0.24	1.38
P-6	417	493	0.31	1.41

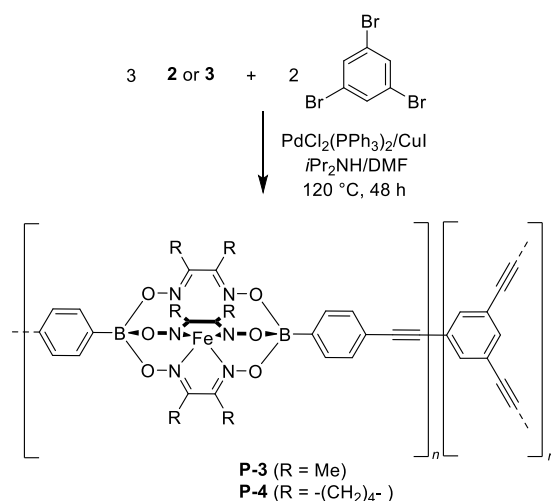
Next, we studied the preparation of clathrochelate polymers with a higher degree of cross-linking. Using triboronic acid instead of diboronic acids as coupling partners in Suzuki-Miyaura polycross-coupling reactions gave rise to porous polymers, but the surface area of these polymers was lower (see ESI). More detailed investigations were therefore not undertaken.

Sonogashira-Hagihara polycross-coupling reactions are frequently employed to prepare porous polymer networks.⁵ In order to examine if this coupling chemistry is compatible with clathrochelate complexes, we have synthesized the monomers **2** and **3**, featuring terminal alkyne functions (Scheme 3). The complexes were characterized by NMR spectroscopy, high resolution mass spectrometry, and single crystal X-ray diffraction.

The clathrochelate complexes **2** and **3** were then cross-linked by Pd-catalyzed reactions with 1,3,5-tribromobenzene (Scheme 4). As catalyst precursor, we used PdCl₂(PPh₃)₂ (3.5 mol% with respect to the **2/3**) and CuI, and the reactions were carried out at 120 °C for 48 h in DMF/*i*Pr₂NH (1:1).



Scheme 3 Synthesis of the clathrochelate complexes **2** and **3**. The graphic representations of the structures of **2** and **3** are based on crystallographic analyses. Color coding: C (gray), Fe (orange), N (blue), O (red), and B (green). Hydrogens are not shown for clarity.



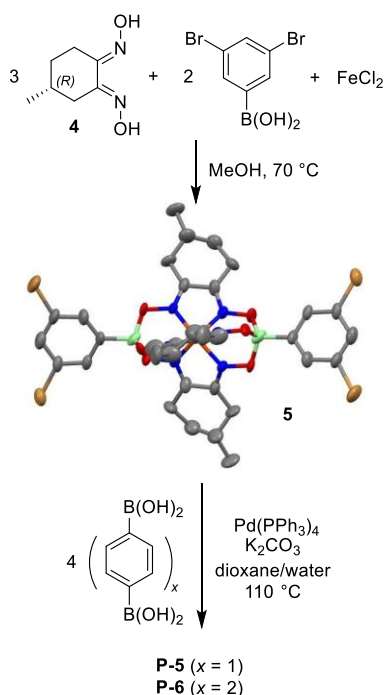
Scheme 4 Synthesis of the clathrochelate networks **P-3** and **P-4**.

The polymers **P-3** and **P-4** were characterized by the same analytical techniques used for **P-1** and **P-2**. N₂ sorption measurements at 77 K gave apparent BET surface areas of 205 and 360 m² g⁻¹, respectively (Table 1). We have briefly investigated the utilization of other brominated ligands such as complex **1** and 1,3,5-tris(4-bromophenyl)benzene (see ESI), but the resulting polymers displayed a lower porosity, and a more detailed characterization of these polymers was not undertaken.

One interesting feature of clathrochelate complexes is the fact that the lateral side chains can easily be varied by using a different dioxime during the synthesis. We wanted to explore if we could use a dioxime with a stereogenic center in order to prepare chiral clathrochelate complexes. The latter could then

be used for the synthesis of chiral networks. It is worth noting that homochiral materials with permanent porosity and high thermal stabilities are of interest for applications in enantiomeric separation and catalysis.^{1a,24}

(R)-Pulegone is a commercially available compound, which can be converted into the corresponding diketone by ozonolysis.²⁵ Subsequent reaction with hydroxylamine hydrochloride in water gave the dioxime **4** in 64% yield. The reaction between **4**, FeCl₂, and 3,5-dibromophenylboronic acid in MeOH at 70 °C under N₂ atmosphere provided the chiral clathrochelate **5** in 61% yield.



Scheme 5 Synthesis of the clathrochelate networks **P-5** and **P-6**. The graphic representation of the structure of **5** is based on a crystallographic analysis. Only one of the two isomers is shown. Color coding: C (gray), Fe (orange), N (blue), Br (yellow) O (red), and B (green). Hydrogens are not shown for clarity.

Complexes **5** was obtained as a mixture of two isomers, which differ by the relative orientation of the chiral methyl groups with respect to the B...Fe...B axis.^{14a} These isomers cannot be distinguished by NMR spectroscopy, but they co-crystallize, and one can observe disorder for the position of the methyl groups on the dioximato ligand. TLC tests revealed very similar *R_f* values for the two isomers, and a chromatographic separation was not attempted.

Complex **5** was then used for polycross-coupling reactions with 1,4-benzenediboronic acid or 4,4'-biphenyldiboronic acid, respectively (Scheme 5 and ESI) to yield the chiral polymers **P-5** and **P-6**. The reaction conditions were analogous to what was used for the networks **P-1** and **P-2**.

Sorption measurements for the homochiral networks **P-5** and **P-6** gave apparent BET surface areas of 548 and 417 m² g⁻¹, respectively (Table 1), and H₂ and CO₂ uptakes in the expected range (Figure 2 and ESI). As in the case of **P-1** and **P-2**, the

polymers are thermally robust and not susceptible to hydrolytic degradation.

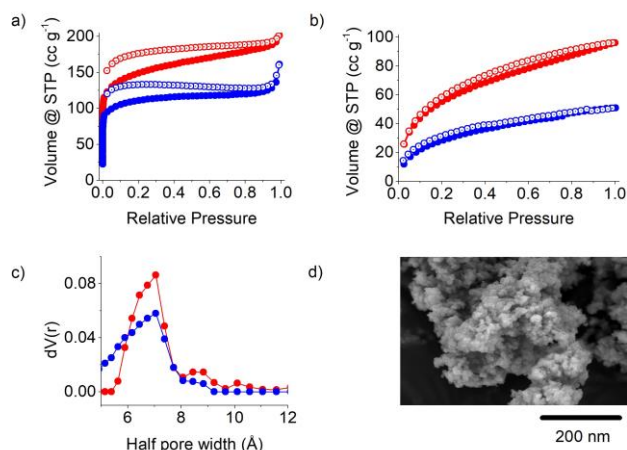


Fig. 2 Characterization of **P-5** (blue symbols) and **P-6** (red symbols). a) N₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K; b) H₂ adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K; c) Pore size distribution; d) SEM image of **P-6**.

Inspired by a study by Hosseini,²⁶ we have then studied the adsorption of L- and D- tryptophan. Before the measurements, the polymers were dried for 10 hours at 120 °C under vacuum. The activated polymers (4 mg) were suspended in a solution of either L- or D- tryptophan (2 mL, 120 μM). The mixtures were sonicated for 30 s, mixed with a vortex mixer for 1 min, and then stirred at room temperature. The concentration of the amino acid in solution was determined by measuring the absorption at 280 nm as a function of time. All measurements were performed in triplicates.

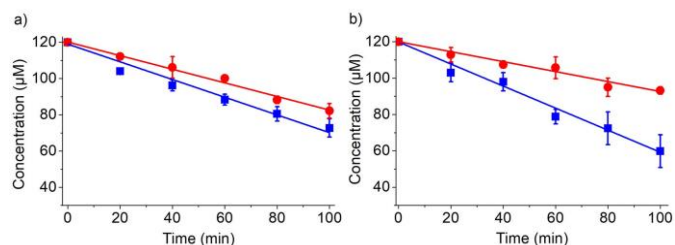


Fig. 3 D-Tryptophan (blue symbols) and L-tryptophan (red symbols) concentration as a function of time in the presence of the polymers **P-5** (a) or **P-6** (b).

For polymer **P-5**, the adsorption kinetics for L- and D-tryptophan were very similar (Figure 3a). Polymer **P-6**, on the other hand, preferentially adsorbed D-Tryptophan: after 100 minutes the concentration of D-tryptophan was reduced to 57 μM, whereas the L-tryptophan concentration was still at 91 μM (Figure 3b).

The preferential adsorption of D-tryptophan shows that chiral clathrochelate networks are capable of enantioselective recognition. The selectivity is not sufficient for a batch separation of enantiomers, but the differentiation might be augmented when the polymers are used as a stationary phase in liquid chromatography.

Conclusions

Boronate ester-capped Fe(II) clathrochelate complexes are easily accessible coordination compounds with high thermal and chemical stability. We have employed functionalized clathrochelate complexes as monomers for the preparation of microporous polymers. Two distinct coupling reactions were investigated: a) the covalent cross-linking of a tetrabrominated clathrochelate complex via a Suzuki-Miyaura polycross-coupling reaction with diboronic acids, and b) the Sonogashira polycross-coupling of alkyne-substituted clathrochelate complexes with tribromobenzene. The resulting polymers display permanent porosity, with apparent surface areas of up to 593 m² g⁻¹. The thermal stability of the materials is good (decomp. > 250 °C), and they are not susceptible to hydrolytic degradation.

The modular synthesis of clathrochelate complexes allows for facile structural modifications. For the present project, we have used the boronate ester caps to introduce bromo- and alkyne functions, which enable the cross-coupling reactions. The lateral groups, on the other hand, are not involved in the polymerization process. These groups will decorate the walls of the polymer pores, and they can thus be employed to change the material properties. In principle, different modifications can be envisioned. For example, one could use the lateral side chains to alter the polarity of the pores, or to attach additional functional groups. We have focused on a different aspect, namely the introduction of chirality. A dioxime derived from (R)-pulegone was used to prepare a chiral clathrochelate complex, which was then polymerized via Suzuki-Miyaura reactions. The resulting porous polymers are capable of chiral recognition, as evidenced by the selective adsorption of D-tryptophan. However, a real application would likely require further optimization.

Overall, our results demonstrate that Fe(II) clathrochelate complexes are interesting building blocks for the preparation of porous polymer networks. These complexes are rigid, robust, and easy to synthesize. A key advantage is their structural and functional variability, which facilitates the preparation of polymer networks with tailor-made properties.

Acknowledgements

The work was supported by the Swiss National Science Foundation, by the Ecole Polytechnique Fédérale de Lausanne (EPFL).

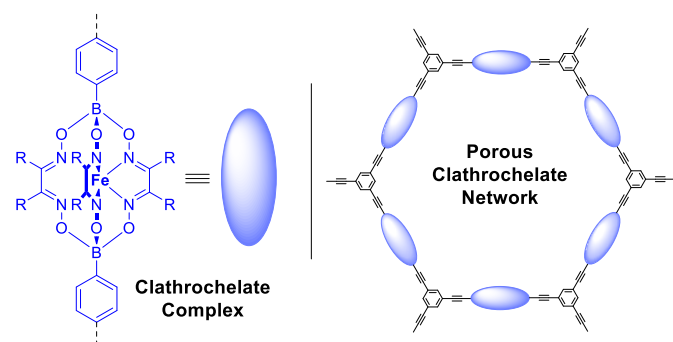
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Graphic for the TOC



Iron clathrochelate complexes were used for the preparation of microporous polymers. The networks display permanent porosity with apparent Brunauer-Emmett-Teller surface areas of up to $SA_{\text{BET}} = 593 \text{ m}^2 \text{ g}^{-1}$, and they are not susceptible to hydrolytic degradation.