



Influence of size and nature of the aryl diborate spacer on the intrinsic microporosity of Iron(II) clathrochelate polymers



Noorullah Baig^a, Suchetha Shetty^a, Saleh Al-Mousawi^b, Fakhreia Al-Sagheer^b, Bassam Alameddine^{a,*}

^a Department of Mathematics and Natural Sciences, Gulf University for Science and Technology, Kuwait

^b Department of Chemistry, University of Kuwait, Kuwait

ARTICLE INFO

Article history:

Received 17 June 2018

Received in revised form

22 July 2018

Accepted 26 July 2018

Available online 27 July 2018

Keywords:

Polymer synthesis

Molecular engineering

Polycondensation

Polymers of intrinsic microporosity

Iron(II) clathrochelate

Adsorption

ABSTRACT

New polyclathrochelate derivatives were obtained using the mild one-step polycondensation reaction of an iron(II) center chelated to three polar furil dioxime side groups and doubly capped with various aryl diborate central spacers. Nitrogen adsorption measurements of the polyclathrochelates (**PCL1–4**) reveal a strong correlation between the intrinsic microporosity and the nature of aryl diborate spacer whose small size (**PCL1**) or contorted structure (**PCL2**) afford polymers with Brunauer-Emmett-Teller (BET) surface areas of $\sim 396 \text{ m}^2/\text{g}$ and $\sim 275 \text{ m}^2/\text{g}$, respectively. On the other hand, the BET surface area of the polymer diminishes either when the aryl diborate spacer has free rotation axes (**PCL3**) or a laterally extended aromatic structure (**PCL4**).

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Porous materials have gained interest as promising devices in future energy storage technologies, such as, i) natural gas adsorbents for vehicles, ii) hydrogen gas tanks for fuel cells, and iii) vessels for CO₂ separation/sequestration from flue gas [1–5]. Therefore, the field of porous materials has seen a noticeable surge in the development of organic and inorganic networks, from these we note, microporous organic polymers (MOPs) [1,6,7], metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs), with high porosity properties and large surface areas [8–18].

Based on their design and properties, microporous organic polymers have been classified into four conventional groups: covalent organic frameworks (COFs) [19–23], hyper-cross linked polymers (HCPs) [24,25], conjugated microporous polymers (CMPs) [26–35], and polymers with intrinsic microporosity (PIMs) [36–41]. MOPs have shown auspicious results for applications in several fields, like, batteries and capacitors [31–34,42–46], gas separation [12,24,47–52], catalysis [53], pesticides detection [54],

and drug delivery [55]. It is worth noting that some MOPs have revealed good metal ions encapsulation properties following their functionalization with heterocyclic aromatic units [27,56].

Clathrochelate-based organometallic derivatives have been known since more than three decades to be air- and moisture-resistant [57,58]. Clathrochelate iron(II) tris-dioximates are robust complexes easily made from a one-step coordinative condensation reaction of an iron(II) center with three vicinal dioxime derivatives, which are end-capped with boron Lewis acid moieties. Changing the structures of the dioxime and boronic acid offers the possibility to design a myriad of functional iron(II) clathrochelate derivatives [59–61], which can undergo several substitution and cross-coupling reactions [62–65]. Recently, our group reported a one-pot polycondensation reaction of iron(II) chloride with various nonpolar alkyl and aryl dioximes end-capped with benzene-1,4-diboronic acid, where some of the resulting polymers reveal promising microporous properties [66]. Interestingly, when benzene-1,4-diboronic acid spacer was replaced by fluorene diboronic acid derivatives with long alkyl chains, the subsequent highly soluble polymers form organogel in solvents of low and medium polarity [67]. We present herein four new iron(II) polyclathrochelates bearing polar furil dioximate side groups. We also study the influence of changing the longitudinal and lateral size of the end-

* Corresponding author.

E-mail address: alameddine.b@gust.edu.kw (B. Alameddine).

capping diboronic acid groups on microporosity.

2. Experimental section

2.1. General

All experiments were performed under argon atmosphere. The chemicals, notably, phenylboronic acid, benzene-1,4-diboronic acid, 4,4'-biphenyldiboronic acid, 4,4'-(acetylene-1,2-diyl)bis(phenylboronic acid pinacol ester), furil dioxime, iron(II) chloride were purchased from Sigma-Aldrich. Solvents were dried and bubbled with argon gas for 30 min. Thin layer chromatography was developed on aluminum sheets coated with silica gel 60 F254 and revealed using a UV lamp.

^1H - and ^{13}C NMR were recorded in CD_2Cl_2 on Bruker AVANCE II 600 MHz Fourier-transform nuclear magnetic resonance spectroscopy (FT-NMR), and data was processed using MestReNova software. The solution absorption spectra were recorded on VWR UV1600PC spectrophotometer. Matrix Assisted Laser Desorption/Ionization-Time of Flight Mass (MALDI-TOF) was recorded on a FT/ICR Bruker 4.7 T BioApex II spectrometer. MALDI spectra used DCTB as a matrix with a 337 nm nitrogen laser. X-ray Photoelectron spectroscopy (XPS) data were recorded with a Thermo ESCALAB 250 Xi using a monochromatic Al K-radiation source (1486.6 eV) with a spot size of 850 μm . Spectra acquisition and processing were carried out using the software Thermo Advantage Version 4.87. The base pressure in the XPS analysis chamber was in the range 10^{-10} to 10^{-9} torr. The analyzer was operated with a pass energy of 20 eV, dwell time of 50 min and with a step size of 0.1 eV. FTIR spectra were recorded on FT/IR-6300 type A instrument using a KBr matrix. Brunauer–Emmett–Teller (BET) surface area and porosity measurements were evaluated using a Surface Area and Pore Size Analyzer (Gemini-V, Micromeritics, USA) at the boiling point of liquid nitrogen (-196°C). Samples were degassed in VacuPrep 061 sample degassing system at a temperature of 105°C for overnight, before the experiments. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) model of isotherms, and the adsorption of N_2 at small relative pressures. Total pore volume (V_t) was determined from the specific adsorption of N_2 at a $p/p^0 = 0.99$. The t-plot method was used to estimate micropore volume (V_{mic}) and external surface area (S_{ext}). Thermogravimetric Analysis (TGA) were recorded on Shimadzu TGA-60H (Kyoto, Japan) analyzer was used to measure the thermal stability of composites. TGA was carried out from room temperature to 800°C . The heating rate was kept at $10^\circ\text{C}/\text{min}$ under inert atmosphere using pure nitrogen.

2.2. Synthesis of monomer

2.2.1. Preparation of (CL1)

To a stirring solution of phenyl boronic acid (0.140 g, 1.15 mmol) in chloroform (10 mL), furil dioxime (0.330 g, 1.5 mmol) and iron(II) chloride (0.065 g, 0.5 mmol) were added under argon and the reaction mixture was allowed to reflux for 24 h. After the reaction completion, the solvent was evaporated and the desired purple solid was precipitated using dichloromethane/hexane. The resulting purple color precipitate was filtered and washed with hexane followed by diethyl ether. Yield: 0.435 g (98%); UV–vis: (THF, 10^{-6}M), λ_{max} [nm]: 307, 510. ^1H NMR (CD_2Cl_2 , 600 MHz, ppm): δ 7.77 (br, 4H, ArH), 7.44–7.37 (m, 18H, ArH), 6.62 (br, 6H, ArH); ^{13}C NMR (CD_2Cl_2 , 150 MHz, ppm): δ 145.66, 143.08, 142.84, 131.45, 127.58, 127.30, 118.59, 111.77; MALDI-TOF; Calcd. for $(\text{M})^+$ $\text{C}_{42}\text{H}_{28}\text{B}_2\text{FeN}_6\text{O}_{12}$: 886.1301; found 886.1305. FTIR (KBr, cm^{-1}): 1646 (C=N), 1585 (C=C), 1224 (B-O), 1021(C-O), 980, 928 (N-O), 759 (C-H).

2.3. Synthesis of polymers

2.3.1. Preparation of PCL1

A solution of benzene 1,4-diboronic acid (0.422 mmol, 1 eq.), furil dioxime (1.266 mmol, 3 eq.) and iron(II) chloride (0.422 mmol, 1 eq.) in 7 mL of degassed chloroform was refluxed under argon for two days in a Schlenk tube. Benzene boronic acid (2 mg, 5 mol %) was then added to the reaction mixture and allowed to react for 2 h. The solvent was concentrated, and the red solid was precipitated from petroleum ether. The precipitate was washed thoroughly with hexane and diethyl ether then allowed to dry in air affording the desired product as a purple solid. Yield: 0.340 g (99%); UV–vis: (THF, 10^{-6}M), λ_{max} [nm] = 314, 516. FTIR (KBr, cm^{-1}): 1582 (C=N), 1504 (C=C), 1228 (B-O), 1021(C-O), 972, 925 (N-O), 884 (C-H), 750 (C-H).

2.3.2. Preparation of PCL2

This compound was prepared following the procedure adopted for polymer PCL1 but using 4,4'-biphenyldiboronic acid (0.367 mmol, 1 eq.), furil dioxime (1.180 mmol, 3 eq.), iron(II) chloride (0.367 mmol, 1 eq.) and benzene boronic acid (2 mg, 5 mol %). Yield: 0.310 g (95%); red solid; UV–vis: (THF, 10^{-6}M), λ_{max} [nm] = 307, 510. FTIR (KBr, cm^{-1}): 1600 (C=N), 1222 (B-O), 1015(C-O), 980, 936 (N-O), 887 (C-H), 754 (C-H).

2.3.3. Preparation of PCL3

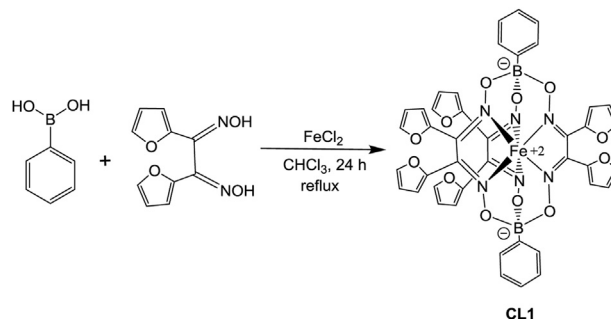
This compound was prepared following the procedure adopted for polymer PCL1 but using 4,4'-(acetylene-1,2-diyl)bis(phenylboronic acid pinacol ester) (0.350 mmol, 1 eq.), furil dioxime (1.046 mmol, 3 eq.), iron(II) chloride (0.350 mmol, 1 eq.) and benzene boronic acid (2 mg, 5 mol %). Yield: 0.305 g (96%); red solid; UV–vis: (THF, 10^{-6}M), λ_{max} [nm] = 307, 520. FTIR (KBr, cm^{-1}): 1601 (C=N), 1218 (B-O), 1015(C-O), 976, 936 (N-O), 887 (C-H), 754 (C-H).

2.3.4. Preparation of PCL4

This compound was prepared following the procedure adopted for polymer PCL1 but using 9,10-anthracenediboronic acid bis(pinacol) ester (0.5 mmol, 1 eq.), furil dioxime (1.5 mmol, 3 eq.), iron(II) chloride (0.5 mmol, 1 eq.) and benzene boronic acid (2 mg, 5 mol %). Yield: 0.487 g (90%); red powder; UV–vis: (THF, 10^{-6}M), λ_{max} [nm] = 294, 510; ^1H NMR (CD_2Cl_2 , 600 MHz, ppm): δ 7.39 (br, 18H, ArH), 6.65 (br, 8H, ArH); FTIR (KBr, cm^{-1}): 1582 (C=N), 1213 (B-O), 1023(C-O), 941 (N-O), 883 (C-H), 750 (C-H).

3. Results and discussion

Scheme 1 shows the synthesis of the model clathrochelate monomer CL1 which was prepared by reacting FeCl_2 (0.5 eq.) in refluxing chloroform with phenyl boronic acid (1.15 eq.) and furil dioxime (1.5 eq.). The desired product was isolated in quantitative



Scheme 1. Synthesis of monomer CL1.

Download English Version:

<https://daneshyari.com/en/article/7818894>

Download Persian Version:

<https://daneshyari.com/article/7818894>

[Daneshyari.com](https://daneshyari.com)