



ELSEVIER

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Rapid Communication

Influence of aggregated morphology on carbon dioxide uptake of polythiophene conjugated organic networks

Shanlin Qiao^{a,b}, Zhengkun Du^a, Wei Huang^a, Renqiang Yang^{a,*}^a CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 21 October 2013

Received in revised form

16 December 2013

Accepted 28 December 2013

Available online 8 January 2014

Keywords:

Pore organic polymer

Polythiophene

Steric configuration

Aggregated morphology

Carbon dioxide adsorption

ABSTRACT

Two novel thiophene-based conjugated networks CMPs-TTT and CMPs-DTBT were designed and prepared with different steric configuration building blocks by FeCl₃ oxidative coupling polymerization. UV–vis spectra, FE-SEM and TEM images showed CMPs-TTT and CMPs-DTBT having the different aggregated morphologies. After porous analysis and gas adsorption test, the result showed CO₂ uptake capacity of CMPs-DTBT with amorphous aggregation model is 2.88 times and 2.66 times greater than that of CMPs-TTT with large lamellar structure model at 273 K and 298 K (1.0 bar), respectively. As a result, this communication proved that change the topological structure of the polymer can influence the CO₂ adsorption capacity significantly.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Rapid consumption of hydrocarbon fuels had caused CO₂ concentration increased quickly in the atmosphere. It is well known that CO₂ is probably the main contributor to the global-warming and climate change. Most countries had drawn much manpower and financial resources in this problem last few decades [1]. In a long-term, the best strategy to lower CO₂ emissions is to adopt new energy solutions which do not produce CO₂ as a byproduct, however, this envisaging is not practical nowadays, because there is no any new energy reserves combining with technology can substitute the low-price fossil fuel (coal, petroleum and natural gas). CO₂ capture and storage provides humanity a potential resolution to the fossil energy used continually without CO₂ release in the short-term until green energy technologies mature [2,3]. A wide range of CO₂ adsorbents have been reported including zeolites [4,5], carbons [6,7], metal organic frameworks (MOFs) [8,9] and microporous organic polymers (MOPs) [10,11].

Organic porous polymers skeleton comprised of light, non-metallic elements with high chemical and thermal stability had exhibited potential application in CO₂ uptakes. Various organic reactions have been exploited to synthesize microporous polymers such as hypercross-linked polymers (HCPs) [12,13], polymers of intrinsic microporosity (PIMs) [14,15], covalent organic frameworks (COFs) [16]. Conjugated microporous polymers (CMPs) [17–19] is a new class

of pore materials which are prepared by transition metal coupling chemistry, such as palladium-catalyzed Stilling, Suzuki, Sonogashira–Hagihara coupling condensation reaction and other oxidative coupling reaction. The unique feature of CMPs is that they combine the stiff pore structure and conjugated electron system in one bulk material which show good performance in gas storage and separation. Weber and Thomas [20], Yuan et al. [21], and Chen et al. [22] reported a series of polyfluorene microporous polymers with Brunauer–Emmett–Teller (BET) areas from 450 m² g⁻¹ to 1043 m² g⁻¹ and the highest CO₂ uptake reached to 12 wt% at 1.0 bar, 273 K. Schmidt et al. [23], reported the polythiophene microporous conjugated polymers with BET area up to 1056 m² g⁻¹, however, no CO₂ adsorption data was given. Recently, Chen et al. [24] reported the microporous polycarbazole CMPs with BET area up to 2220 m² g⁻¹ and the CO₂ uptake capacity as high as 21.2 wt% at 273 K, 1.0 bar. Kanatzidis [25–27] reported a series of new conjugated polymers for gas capture which CO₂ uptake can be up to 18 wt% near atmospheric pressure at 273 K. However, the relationship of steric structure of monomer with gas adsorption got little attention.

In this communication, we focused on the relationship between configuration of the building blocks (or starting monomers) with CO₂ adsorption capacity on the networks which has different aggregation morphology caused by the steric configuration of the building block. Two thiophene based networks CMPs-TTT and CMPs-DTBT have been prepared and with different aggregation morphology caused the CO₂ isosteric enthalpies has much discrepancy although the two networks with identical chemical component and similar BET areas and pore structure.

* Corresponding author. Tel.: +86 532 80662700; fax: +86 532 80662778.
E-mail address: yangrq@qibebt.ac.cn (R. Yang).

2. Results and discussion

Efficient CO₂ adsorption depends on the surface area, pore structure, and chemical functionality of the material [28]. The building blocks show great influence on the above three parameters, thus, design and/or selection of specific monomer is very important. In this work we chose thiophene as the chemical unit to structure the following reasons, (1) the electron-rich thiophene conjugated aromatic system (Lewis-base) may have the strong interaction with CO₂ molecules (electron-poorer, Lewis-acid), (2) the lone pair electrons of heterocyclic sulfur atom on the pore surface can provide dipole–quadrupole interactions sites with CO₂ [29]. The two core building blocks TTT (nonplanar propeller-like) and DTBT (right-angle) are made up of thiophene rings and show different steric configuration (Scheme 1). The single crystals structures show that each thiophene ring in the TTT unit is chiral due to a twist through the center thiophene plane, the three α -conjugated rings are quasi-coplanar (torsional angles = 21° and 15°), the other two thiophene rings in the β -positions of the central unit are nearly perpendicular to the average plane of the more conjugated sequence (93° and 80°) [30]. The crystallographic structure of DTBT represents a pseudo-tetrahedral 3D conjugated architecture, the two thiophene rings attached at the 3- and 3'-positions of bithiophene produce a dihedral angle close to 90° between the two thiophene rings that form the 2,2'-bithiophene [31]. The two thiophene-based networks CMP_s-TTT, CMP_s-DTBT were straightforward synthesized by FeCl₃ oxidative coupling polymerization at room temperature shown in Scheme 1. This method gave high yield and the single building block used in polymerization process can avoid the effect of other structure on the morphology. The crude polymers were washed with methanol and concentrated hydrochloric acid, then, Soxhlet extraction with methanol and tetrahydrofuran for 24 h gave yield more than 90% (CMP_s-TTT, dark red solid; CMP_s-DTBT, brownish solid). The insoluble solid was characterized by FT-IR (Fig. 1a) and ¹³C CP-MAS NMR (Fig. 1b). One can observe that the signal at 1663–1669 cm⁻¹ was assigned to the C=C stretching vibration in the thiophene ring and 1220 cm⁻¹, 1090 cm⁻¹ was the stretching vibration of C–S–C. The ¹³C CP-MAS NMR signals of carbon chemical shift in the range of 115–150 ppm are related to the thiophene carbon atoms of building block.

The porosity structural parameters of CMP_s-TTT and CMP_s-DTBT were measured by adsorption analysis using nitrogen as the probe molecule at 77 K. Fig. 2 shows the N₂ adsorption–desorption isotherms for the two polymers and they give similar BET surface area with 57.72 m² g⁻¹ and 62.97 m² g⁻¹, respectively. The building

blocks of CMP_s-TTT and polycarbazole network CPOP-1 have the similar propeller-like configuration, however, the BET surface area of CPOP-1 is up to 2220 m² g⁻¹, the much lower BET for CMP_s-TTT

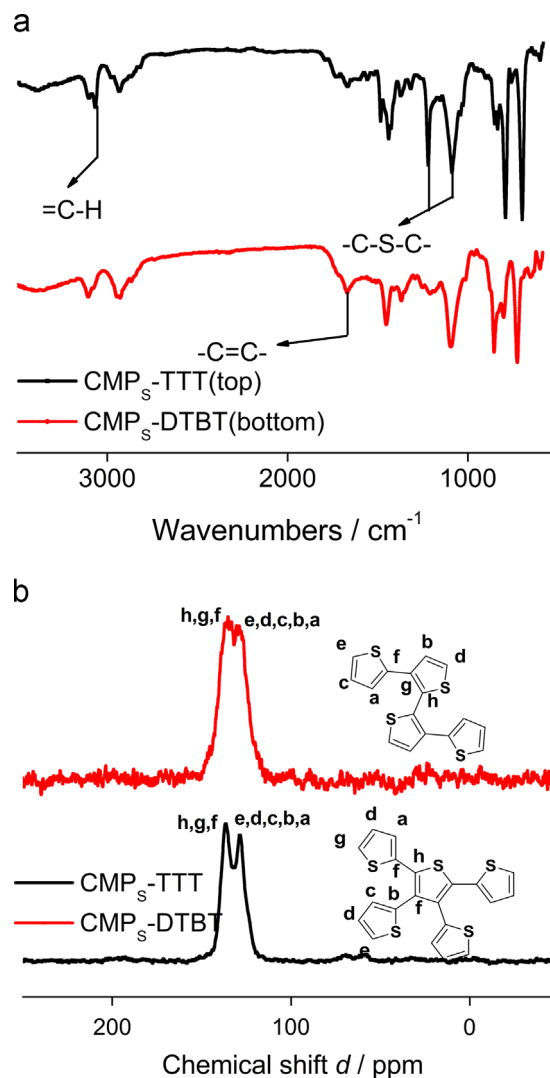
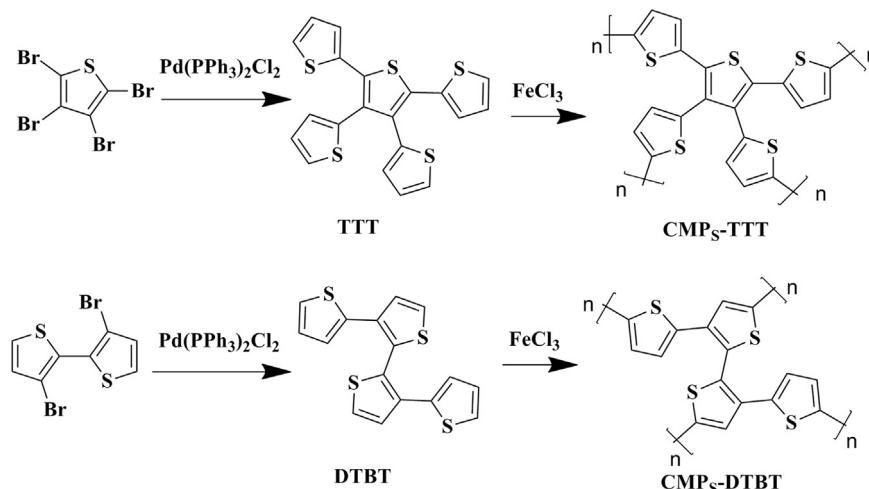


Fig. 1. (a) FT-IR spectra and (b) ¹³C CP-MAS NMR spectra of the two networks CMP_s-TTT and CMP_s-DTBT. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Synthetic pathway toward the polythiophene networks CMP_s-TTT and CMP_s-DTBT.

Download English Version:

<https://daneshyari.com/en/article/1329885>

Download Persian Version:

<https://daneshyari.com/article/1329885>

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