



Contents lists available at ScienceDirect

# Microporous and Mesoporous Materials

journal homepage: [www.elsevier.com/locate/micromeso](http://www.elsevier.com/locate/micromeso)

## The synthesis and fluorescence detection properties of benzoquinone-based conjugated microporous/mesoporous polymers

Tong-Mou Geng<sup>a,\*</sup>, Deng-Kun Li<sup>a</sup>, Zong-Ming Zhu<sup>a</sup>, Ye-Bin Guan<sup>a</sup>, Yu Wang<sup>b</sup><sup>a</sup> Collaborative Innovation Center for Petrochemical New Materials, Anhui Key Laboratory of Functional Coordination Compounds, School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, PR China<sup>b</sup> School of Resource and Environmental Science, Anqing Normal University, Anqing 246133, PR China

### ARTICLE INFO

#### Article history:

Received 25 January 2016

Received in revised form

1 May 2016

Accepted 15 May 2016

Available online 17 May 2016

#### Keywords:

Conjugated microporous/mesoporous polymer

Chemosensor

Miniemulsion polymerization

Picronic acid

Benzoquinone

### ABSTRACT

The benzoquinone-based conjugated microporous/mesoporous polymers were synthesized through Sonogashira–Hagihara cross-coupling with tetrabromo-1,4-benzoquinone (TBrBQ) and 1,4-diethynylbenzene (DEB) by both solution polymerization (DBQP) and miniemulsion polymerization (DBQN). The Brunauer–Emmett–Teller (BET) surface areas of these polymers were 356 and 25 m<sup>2</sup> g<sup>-1</sup> and pore average diameter were concentrated at around 2.12 and 3.84 nm for DBQP and DBQN, respectively. The two dimensional  $\pi$ -conjugated polymer frameworks could be combined with permanent microporous/mesoporous, luminescent properties and abundant oxygen atoms in the skeleton. Fluorescence studies found that both DBQP and DPQN could be utilized as fluorescent chemosensors for picronic acid (PA) in acetone suspension.

© 2016 Elsevier Inc. All rights reserved.

### 1. Introduction

Conjugated polymers are attractive materials for the detection of chemicals, especially nitroaromatic explosives, because of their remarkable  $\pi$ -conjugation and their enhanced sensitivity through fluorescent signal amplification [1–3]. However, owing to their rigid conformation, they have a high tendency to aggregate in solution and the solid state. To resolve this issue, molecular approaches based on site isolations with bulky polymeric matrices have been developed to prevent the aggregation of conjugated polymers. These approaches provide highly luminescent polymers, but at the price of a loss in interchain electronic communications [4–7].

Conjugated microporous polymers (CMPs) are a class of porous organic polymers (POPs) with a conjugated network structure [8–10], which display a lot of advantages, such as their skeletons are strong covalent bonds between organic units, display higher stability to air and atmospheric moisture and much more severe conditions, for example, high temperature, strong acid and base.

Furthermore, one of the most attractive aspects is the promise of tuning structures, properties and functionalities through rational chemical design and intensive selection of organic building blocks [8,9]. In contrast to the site isolation approach, the porous network strategy is unique in that it not only enhances luminescence but also promotes  $\pi$ -electronic interactions via the conjugated network scaffolds [10–13]. Moreover, they possess large surface areas, three dimensional  $\pi$ -conjugated polymer framework and provide a broad interface for analytes interaction [8,9,14]. Therefore, CMPs are attractive candidates for sensing materials. Nevertheless, most studies on CMPs to date have focused on the development of synthetic approaches for the control of pore size, surface area and gas storage [15]. Until 2011 there are no reports for sensing property of CMPs [8,16–18]. In recent years, the most of the research on sensing of performance of CMPs are inclined to nitroaromatic explosives [8,19–26], other organic compounds, such as dopamine [26], chiral amino alcohols [27], fluoride anions [28], hypochlorous acid [26], and transition metal ions, such as Fe<sup>3+</sup> [24,26], Co<sup>3+</sup> [26], Ag<sup>+</sup> [26], and Hg<sup>2+</sup> [29].

The 2,4,6-trinitrophenol (PA, i.e. 2,4,6-trinitrophenol, TNP) is one of nitroaromatic derivatives, which is widely used in dyes, fireworks, glass and leather industries. During commercial production and use, PA is released into the environment, leading to the

\* Corresponding author. School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, PR China.

E-mail address: [gengtongmou@sina.com.cn](mailto:gengtongmou@sina.com.cn) (T.-M. Geng).

contamination of soil and aquatic biosystems. Thus, there is an urgent need to develop an efficient and reliable sensor for detection of PA, owing to their serious pollution and potential threats to security [30]. Recently, there are several forms of CMPs emerging in fluorescent sensing field as PA chemosensors. Most of them are insoluble bulk powders, which are synthesized by solution polymerization [17,18,20–22,24,30–37]. The nanoparticles as chemosensors are easily dispersed in organic solvents, which are fabricated in miniemulsion polymerization [36]. The soluble conjugated hyperbranched polymers may be soluble in common organic solvents, which are prepared with both solution and miniemulsion polymerization [25]. The film as a chemosensor [19] is the desired form, which can be prepared by not only miniemulsion and the soluble conjugated hyperbranched polymers [38] but also by direct way, such as electrochemical method [23]. In some case, despite starting from the same monomer and comonomer, the insoluble bulk powders and nanoparticles are obvious difference in optical and fluorescent sensing property [25]. Moreover, the most conjugated POPs are microporous materials, such as CMPs, while the investigation for conjugated microporous/mesoporous polymers are rather few [16].

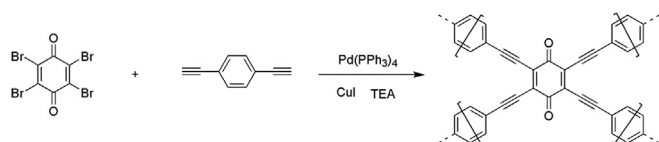
In general, the building units play a crucial role in designing and controlling the structures and properties of CMPs. Synthesis of novel polymers is very interesting in the field using new building blocks. Quinones are provided with both conjugated structure and oxygen atoms, hence, they are fit for as the building units of CMPs used for sensing [39,40]. In this contribution, we designed and synthesized benzoquinone-based conjugated microporous/mesoporous polymers through the Pd-catalyzed Sonogashira-Hagihara cross-coupling reactions of tetrabromo-1,4-benzoquinone (TBrBQ) and 1,4-diethynylbenzene (DEB) by both solution polymerization in DMF and miniemulsion polymerization technique. Then, we comparatively investigated the porous, fluorescent, and sensing performance for picronic acid (PA) in acetone suspension of obtained both conjugated microporous/mesoporous polymers (see Scheme 1).

## 2. Experimental

### 2.1. Materials and nonoptical characterization

Tetrabromo-1,4-benzoquinone (TBrBQ), 1,4-diethynylbenzene (DEB), copper (I) iodide (CuI) ( $\geq 99.5\%$ ), tetrakis(triphenylphosphine)palladium ( $\text{Pd}(\text{PPh}_3)_4$ ) and sodium dodecylsulfate (SDS,  $\geq 98\%$ ) were purchased from Aladdin Chemistry Co. Ltd. N,N-dimethylformamide (DMF, 99.0%), methanol, tetrahydrofuran (THF), chloroform, acetone, toluene, hydrochloric acid, sodium hydrate, triethylamine (TEA), picronic acid (PA), 4-nitrotoluene (NT), phenol and p-dichlorobenzene were obtained commercially, and used without further purification. Reactions were carried out under a nitrogen atmosphere.

The solid-state  $^{13}\text{C}$  NMR spectra were collected from a 9.4 T Bruker DSX NMR 400 MHz spectrometer equipped with a 4 mm HXY triple-resonance MAS probe (in double resonance mode) [8]. Fourier transform infrared (FTIR) spectra were recorded on a FTIR spectrophotometer (model Nicolet Neus 8700) with KBr



**Scheme 1.** Synthesis of the DBQP and DBQN by Sonogashira–Hagihara cross-coupling.

compressing tablet. Elemental analyses (C, H and N) were carried out on an analyzer (model VarioELIII). Wide angle X-ray diffraction (XRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta = 5^\circ$  up to  $60^\circ$  with  $0.02^\circ$  increment. Scanning electron microscopy (SEM) was performed on a model JEOL-3400LV (Japan) operating at an accelerating voltage of 5.0 kV. The sample was prepared by drop-casting a THF suspension onto mica substrate and then coated with gold. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at  $150^\circ\text{C}$  for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The Saito-Foley (SF) method was applied for the estimation of pore size and pore size distribution. Thermogravimetric analysis (TGA) data were obtained on a ATA409PC instrument (Germany), with a heating rate of  $10^\circ\text{C min}^{-1}$  under flowing  $\text{N}_2$ .

UV–vis spectra were obtained using a PerkinElmer Lambda 950 UV–vis spectrophotometer running the UV probe software, version 2.34. All spectra were obtained as absorbance measurements from 200 to 800 nm, with scan speed set to fast and using a slit width of 5 nm. Solid powdered samples were analyzed using the ISR-2200 integrating sphere attachment with a quartz solid sample holder as diffuse reflection measurement. Emission spectra were obtained on a Shimadzu RF-5301PC spectra fluorophotometer. Spectra were obtained using a fast scan speed and with sensitivity set to high. Slit widths were adjusted so as to maximize the signal-to-noise for each sample. Suspension liquid was analyzed in a quartz cuvette with the standard cell holder attachment [13].

### 2.2. Detection of arene derivatives

All Fluorescence studies were done using Shimadzu Spectrofluorimeter (model RF 5301PC) with 1 cm quartz cuvettes. A standard stock solution of PA, NT, phenol and p-dichlorobenzene ( $1.00\text{ mol L}^{-1}$ ) was prepared by dissolving an appropriate amount of the arene derivatives in tetrahydrofuran (THF), chloroform, acetone, or absolute ethyl alcohol and adjusting the volume to 100.00 mL in a volumetric flask. This was further diluted to  $0.10\text{ mol L}^{-1}$ . For all measurements of fluorescence spectra, excitation was fixed at 365 nm with the emission recorded over the wavelength range of 375–600 nm. The excitation and the emission slit widths were 10.0 nm and 5.0 nm, respectively. The detection limit was calculated with the equation: detection limit =  $3S/\rho$ , where S is the standard deviation of blank measurements and  $\rho$  is the slope between relative fluorescent intensity versus sample concentration [24,37].

### 2.3. General synthetic procedure of DBQP and DBQN

All of the networks were synthesized by Sonogashira-Hagihara cross coupling reaction of arylhalides and aryethynyls [12,41]. The molar ratio of ethynyl to bromo functionalities in the monomer feed was set at 1.5:1 [9,42–45].

### 2.4. Polymerization in a solution state

A mixture of TBrBQ (212 mg, 0.50 mmol), DEB (189 mg, 1.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (20 mg, 0.0173 mmol) and CuI (10 mg, 0.053 mmol) was placed in a round bottom flask equipped with a magnetic stirring bar and a reflux condenser. The solids were dissolved in a mixture of anhydrous DMF (8.4 mL) and anhydrous TEA (4.2 mL). After degassing the mixture for 30 min, the reaction was carried out at  $90^\circ\text{C}$  for 72 h under a nitrogen atmosphere with

Download English Version:

<https://daneshyari.com/en/article/71983>

Download Persian Version:

<https://daneshyari.com/article/71983>

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