



Triazine-based conjugated microporous polymers constructing triphenylamine and its derivatives with nitrogen as core for iodine adsorption and fluorescence sensing I₂

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ABSTRACT

Three new triazine-based conjugated microporous polymers with nitrogen as cores containing triphenylamine (TPA), 4,4',4''-tris(N,N-diphenylamino)triphenylamine (TDATA) and 4,4',4''-tri[phenyl(*m*-tonyl)amino]triphenylamine moieties (TMDATA) (TPPA, TTDATA and TTMDATA) were constructed via Friedel-Crafts reaction catalysed by methanesulfonic acid. The resulting CMPs possess high BET surface area of over 308, 491 and 456 m² g⁻¹, large pore volumes, good stability, and display efficient and reversible guest uptake of 4.92, 4.72 and 4.49 g g⁻¹ in iodine vapour which are higher than that of the CMPs with benzene as core. Two ways to release the adsorbed iodine were explored: either slow release into ethanol or quickly release upon heating (with a high degree of control). Spectral studies make us known that the strong affinity for I₂ is mainly due to large porosity, a conjugated π -electron aromatic system, C–N bonds, and propeller-like twisted structures. Furthermore, luminescent study indicated that TPPA exhibits high sensitivity to electron-deficient I₂ via fluorescence quenching. TPPA shows the largest amount of iodine adsorption and was the first CMP used fluorescence sensing iodine.

1. Introduction

Conjugated microporous polymers (CMPs) are a charming class of porous solid materials and have attracted tremendous research attention because of their designable structures, tunable properties and potential applications in gas storage and separation, adsorption, separation, luminescence, heterogeneous catalysis, supercapacitors, light harvesting, encapsulation, hydrogen production, electrodes, superhydrophobic separation, etc [1]. Recently the multifunctionalization [2,3] of CMPs have become one of the principal focuses of polymer and material chemistry because multiple physical properties may coexist and even synergetically interact [4]. Nevertheless, most of the reported multifunctional CMPs are focused on gas absorption and fluorescence sensing [5–9], while other studies about multifunctional CMPs (such as iodine adsorption and fluorescence sensing) are a few [2,10].

It has been revealed that there are the same mechanism and influence factor of CMPs between the adsorption of iodine and fluorescent sensing. For example, they both belong to the charge transfer mechanism. Conjugate effects can promote the electron transfer from CMPs to electron deficient compounds, and the heteroatoms can

enhance the interaction between CMPs and guest molecules (iodine, sensing molecules), hence the adsorption performance for iodine and fluorescence sensing sensitivity for nitro-aromatic compounds (NACs) can be enhanced. However, the study of CMPs with iodine adsorption and fluorescence sensing dual function is rare [10].

For decades, with the increased use of nuclear energy to meet our needs, an urgent issue of concern for safety associated with nuclear energy is appropriate the disposal of nuclear wastes [11,12] produced at each stage of the nuclear fuel cycle, which can limit its growth [13]. The radioactive wastes are classified as solid (high-level), liquid (low-level), and gases. Gaseous radioactive waste presents an immediate threat to general population and the environment because of the ease of dispersal through the atmosphere. Particularly challenging is the capture of volatile gaseous fission products from nuclear fuel reprocessing or inadvertent environmental release. These radionuclides include ¹²⁹I and ¹³¹I, ³H, ¹⁴CO₂, and ⁸⁵Kr. Of these, radiological iodine poses exceptional issues. As an important radioisotope in nuclear waste, radioactive iodine isotopes produced during the fission of ²³⁵U, is a highly mobile gas [11]. The γ -ray emitter of ¹²⁹I is dangerous for health, because it is a highly mobile and volatile contaminant with a half-life of

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1.52×10^7 years, and bioaccumulates concentrating in the thyroid gland affecting biometabolism [13–15]. Whereas ^{131}I is another radiotoxic isotope of iodine, which has low half-life period 8.02 d, due to its volatility and directly involvement in human metabolic processes despite its relatively short half-life [11,12]. Therefore, efficient I_2 capture has attracted a great deal of attention in recent years.

Triphenylamine (TPA) and its derivatives are an important class of building blocks because they are able to form stable aminium radical cations (such as, the oxidized radical cation and dication states of triarylamines) with low ionization potentials and relatively high mobility [16]. Moreover, TPA is capable of forming a rigid propeller-like geometry with an electron-rich, central electroactive nitrogen atom which is linked to three electron-rich phenyl groups [17]. Meanwhile, the TPA in the networks can improve the hole transporting ability of the materials and the bulky volume of TPA also can prevent the aggregation of the materials [18]. The selection of TPA and its derivatives as the luminescent units are driven by the low cost of TPA sources and excellent properties of TPA-containing functional materials, including efficient light emission, high photoreactivities and photo-conductivities [19,20]. Many of the CMPs based-triphenylamine exhibited excellent fluorescent properties [21,22] and fluorescent sensing properties for NACs [21–26], temperature [18], humidity [27], and bioimaging [28]. However, the TPA-based CMPs used for iodine adsorption got little attention [10,29].

Covalent triazine based frameworks (CTFs) consist of s-triazine cores connected to each other by three conjugated organic struts, which are typically microporous, display fluorescence, generally have very high surface areas, and high thermal stability [30], derived from the structural symmetry of 1,3,5-triazine units. Recently, much attention has been paid to 1,3,5-triazine containing π -conjugated systems. Because they have the properties of high spatial coplanarity, π -conjugated structures, and good π -electron mobility, amorphous CTFs have been applied in fluorescence sensors for NACs [3,9,25,31,32], Fe^{3+} [7,33], mercury ions [34], H_2S [35], and ammonia gas sensor [36]. However, the triazine-based CMPs used for the iodine adsorption and fluorescent sensing property has seldom been explored [10,37].

In our previous works, triazine- and TPA-based CMPs with benzene as cores were synthesized. Although these CMPs exhibit high properties of fluorescence sensing for NACs and iodine adsorption, their fluorescence sensing performance for iodine are very poor [10,38]. In addition, the specific surface area and properties of iodine adsorption of the triazine-based CMPs of TPA derivatives with benzene as cores are small [38]. In this work, a series of novel fluorescent triazine-based CMPs of TPA derivatives with nitrogen as cores were synthesized using methane-sulfonic acid-catalysed Friedel–Crafts reaction of 2,4,6-trichloro-1,3,5-triazine (TCT) with triphenylamine (TPA), 4,4',4''-tris(N,N-diphenylamino)triphenylamine (TDATA) and 4,4',4''-tri[phenyl(m-onyl)amino]triphenylamine (TMDATA) (Scheme 1). The influence of ratio triazine units with TPA units and methyl on the properties were investigated.

2. Results and discussion

The synthesis of CMPs (TTPA, TTDATA and TTMDATA) were accomplished by a straightforward Friedel–Crafts reaction (Scheme 1) with well-defined para-substituted inferred via the model product [39], which were simple and convenient [10,38–40]. As a liquid catalysts, methane-sulfonic acid is miscible in all proportions with the monomers, which can substantially improve the reaction efficiency and has tremendous potential for scaled-up commercial production [39,40]. Moreover, the benefits of utilizing a liquid Lewis acid catalyst are clear considering its high thermal stability, relatively low toxicity, and the absence of hazardous volatile compounds, even at high concentrations. Furthermore, the porous networks can simply be recovered by washing the liquid acid from the final mixture with water [40]. Thus, these advantages make methane-sulfonic acid become an ideal choice for the catalyst in this work [39]. In order to study the influence of building

blocks on the pore properties, the adsorption performance and fluorescence sensing property for iodine, we chose TPA and its derivatives with nitrogen as cores (TDATA and TMDATA) which are different from the triazine-based CMPs of TPA derivatives with benzene as cores in our previous study [38]. To maximize the specific surface area and uptake capacity for iodine molecules, we optimized the polymerization time for constructing CMP networks. However, the reaction time of TDATA and TMDATA are longer (72 h for TDATA and 48 h for TMDATA) than that of TPA (24 h), which can possibly be ascribed to the hindering effect of TTDATA and TTMDATA. Surprisingly, the reaction time of TCT with TDATA is longer than that of TCT with TMDATA, which may be that electronic effect is greater than the steric effect for the methyl on TMDATA [10]. The yield of the catalytic reaction for TTPA, TTDATA and TTMDATA after 24, 48 and 72 h are 73.86%, 68.51% and 93.25%, respectively.

The successful preparation of CMPs were confirmed by Fourier-transform infrared (FT-IR), solid state ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopies, solid-state ultraviolet–visible (UV–vis) and elemental analysis [41]. FT-IR spectra of TTPA, TTDATA and TTMDATA are shown in Fig. S1. Typical vibration depletion of the intense C–Cl stretching at 847 cm^{-1} almost disappears, indicating the complete conversion of C–Cl [34,39,42,43]. Strong characteristic absorption peaks at $1596\text{--}1642\text{ cm}^{-1}$ (C=N) and $1382\text{--}1388\text{ cm}^{-1}$ (C–N) prove the existence of the triazine ring [40,43]. Further evidence of the formation of the target networks are given by the intense bands at $1450\text{--}1490\text{ cm}^{-1}$ (in-plane deformation vibration of triazine ring) and $812\text{--}814\text{ cm}^{-1}$ (out-of-plane deformation vibration) [41]. The presence of the absorption at $3437\text{--}3446\text{ cm}^{-1}$ are originated from the moisture adsorbed by KBr or the CMPs, which are due to porosity of the CMPs and the hydrogen bonds to form between the nitrogen atom in networks and H_2O [40]. Fig. 1 shows the ss ^{13}C CP/MAS NMR spectra of the three CMP solid samples. The chemical shifts at about 171.5 ppm are observed in the NMR spectra, which are assigned to the carbon atom in the triazine rings [40,42]. The peaks observed at 146 and 136 ppm could be assigned to the substituted aromatic carbon bonded to nitrogen atom and substituted aromatic carbon of aromatic ring connected with triazine ring, respectively. Another major peaks at about 127 ppm are correspond to the unsubstituted phenyl carbon atoms [39,42–44]. The C, H and N contents of the TTPA, TTDATA and TTMDATA were determined by elemental analysis (Table S1). The resulting C and H contents of CMPs were in reasonable agreement with the theoretically calculated values, further confirming the polymer structures [40]. UV-vis absorption spectra were used to compare the electronic properties of TTPA, TTDATA and TTMDATA against the starting materials (TCT, TPA, TDATA and TMDATA) (Fig. S2). The broad absorption were observed in about 424, 666, and 644 nm for TTPA, TTDATA and TTMDATA, which were red shifted relative to those in TCT, TPA, TDATA and TMDATA (256, 321, 390, and 347 nm). These results indicate the extended π -conjugation in TTPA, TTDATA and TTMDATA [41,45].

Powder X-ray diffraction (PXRD) patterns of the three CMP materials (Fig. S3) show the characteristic broad peaks and indicate their amorphous nature [46]. Scanning electron microscopy (SEM) images show that the obtained CMPs adopted large block morphology (Figs. 4a–c) [47–49]. Thermogravimetric analysis (Fig. S5) under N_2 was measured to investigate the structural stability of the three CMPs. There are only less 5–10% weight loss between 120 and 250°C for the three CMPs, suggesting the removal of guests completely by the supercritical activation. The thermal stability of the three CMPs were excellent, pyrolysis temperature are at 585, 567, and 527°C for TTPA, TTDATA, and TTMDATA networks, respectively. The thermal stability of TTPA is highest, which may be that it has high triazine units, while the thermal stability of TTMDATA is lowest, which could be due to methyl in its structure. Furthermore, these polymer networks also exhibit chemical stability, which are verified by the lack of dissolution or decomposition in common organic solvents such as THF, acetone,

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