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Molecular structure design of conjugated microporous poly(dibenzo[*b*,*d*]thiophene 5,5-dioxide) for optimized photocatalytic NO removal

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A B S T R A C T

Conjugated microporous polymers with high BET surface areas and a tunable bandgap are promising candidates for photocatalytic NO removal in the solid–gas phase reaction system. Herein, we report that three conjugated microporous poly(dibenzo[*b*,*d*]thiophene 5,5-dioxide) (B-DT-1,3,5; B-DT-1,2,4; B-DT-1,2,4,5) consisting of alternating electron-rich and electron-deficient units with ethynyl linker have been synthesized, and optical bandgaps varied from 2.29 eV to 2.79 eV by adjusting the position and number of C≡C connected to the 3D center benzene. Combined with intrinsic merits including facile tunable bandgap and high BET surface areas, the synthesized CMP(B-DT) proved to be good photocatalysts for photocatalytic NO removal. The NO removal efficiency of B-DT-1,3,5 reached up to 56% with good stability. Active species scavenger experiments and other characterizations indicated that the superior photocatalytic NO removal ability of B-DT-1,3,5 may arise from the synergistic effect of stronger hole oxidation ability, greater amounts of $\cdot O_2^-$ and $^1O_2$, and higher BET surface area. Thus, our proof-of-concept design of conjugated microporous polymers was used for a highly efficient photocatalytic NO removal in the solid-gas phase.

1. Introduction

With the rapid development of urbanization, smog has been a serious global concern, especially for some developing countries. One main contributor to smog is nitric oxide (NO), which is a byproduct emitted from the combustion of petroleum fuels such as gasolines used in vehicles. Selective catalytic reduction (SCR) proves to be an effective strategy for reducing NO concentration [1]; however, some intrinsic drawbacks limit their further application, such as high reaction temperature. Similar to the mechanism of light driven energy conversion, the use of renewable energy such as solar power is also considered as one of the most promising strategies for eliminating NO [2]. Over the past several decades, there have been increasing progress in the exploration for an efficient photocatalyst for energy conversion and removing pollutants. However, there are further improvements that can be made for fabricating photocatalysts in specific fields. Until now, TiO_2-based semiconductor photocatalysts are still the most promising solution for the photocatalytic removal of NO due to their high photoredox ability and photocorrosion resistance. However, their practical application is still limited by their inability to absorb visible light [3–9]. As a result, other types of suitable metal-based photocatalyst have also been explored such as Bi-based semiconductors [10–15] and perovskite oxides (ABO_3) [16–18].

Since the initial application of the metal-free polymeric carbon nitride (C_3N_4) in photocatalytic water splitting in 2009 [19], interest in its use for photocatalytic conversion has risen tremendously due to its suitable bandgap (2.7 eV), porous properties, and abundant functional amine residue. Hundreds of pure C_3N_4 and modified C_3N_4 have been fabricated to enhance its photocatalytic performance [20–23], and the porous property of C_3N_4 makes it ideal for the photocatalytic removal of NO [6,24–28]. Since polymeric C_3N_4 are prepared via thermal condensation at high temperatures, chemical structure of very often C_3N_4-like co-monomer such as heteroatoms than nitrogen with optimized bandgap is very difficult to be characterized in the light of organic synthesis. In this respect, researchers are directing their attention to other pure organic semiconductors such as conjugated microporous polymers (CMP), which are also promising photocatalytic candidates [29,30]. CMPs have been used in various applications since its first use for gas absorption and separation in 2007 [31]. Their fully π conjugated backbones are useful for photocatalytic organic transformation [32–38], photocatalytic hydrogen and oxygen generation [39–43], molecular recognition [44–47], and photocatalytic organic pollutant degradation [43,48,49].

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Conjugated microporous polymers consist of alternate electron-deficient acceptors and electron-rich donors with bridge linkers, wherein efficient intramolecular charge transfer occurs under irradiation. In comparison to inorganic semiconductors and a state-of-the-art example C_3N_4, the redox potential of CMP can be easily tailored by changing the donor and acceptor monomers, bridge linker, or 3D network. Moreover, CMP can be prepared in a solution-phase synthesis at ambient temperatures via transition-metal catalyzed cross-coupling reaction with easily predictable chemical structures [50–52]. It should be noted that the intrinsic high BET surface areas of CMP should have made it a suitable photocatalyst for a photocatalytic reaction carried out in the solid-gas phase state in terms of molecular level. However, linear conjugated polymers with low surface areas performed better than corresponding CMP in photocatalytic hydrogen evolution, and it was inferred that the photocatalytic reaction was normally conducted with the photocatalyst in liquid-swollen state while BET measurement was measured in solid-gas state [39,41,42,53].

Herein, based on the geometry design strategy to tune the HOMO and LUMO potential levels of 3D network structure, three conjugated microporous polymer networks (B-DT-1,3,5; B-DT-1,2,4; and B-DT-1,2,4,5) were synthesized via Sonogashira cross-coupling polycondensation (Scheme 1). With benzene as the electron donating moiety, the strong electron acceptor dibenzo[*b*,*d*]thiophene 5,5-dioxide was connected to 1,3,5-, 1,2,4-, and 1,2,4,5-cross-linked positions of the phenyl position with C≡C as linkers. Similar to other reported CMP, the cross-linked poly(dibenzo[*b*,*d*]thiophene 5,5-dioxide) (B-DT) were insoluble in common organic solvents and water. Comprehensive characterizations of the synthesized products were carried out, and it was found that they showed different HOMO and LUMO potential levels and bandgaps. The photocatalytic mechanism of NO removal with the three synthesized CMP was proposed, and the main impact factors on the NO removal efficiency were further analyzed. To the best of our knowledge, this is the first time that controlled fabricated conjugated microporous polymers were applied in the field of NO removal in the solid-gas phase state.

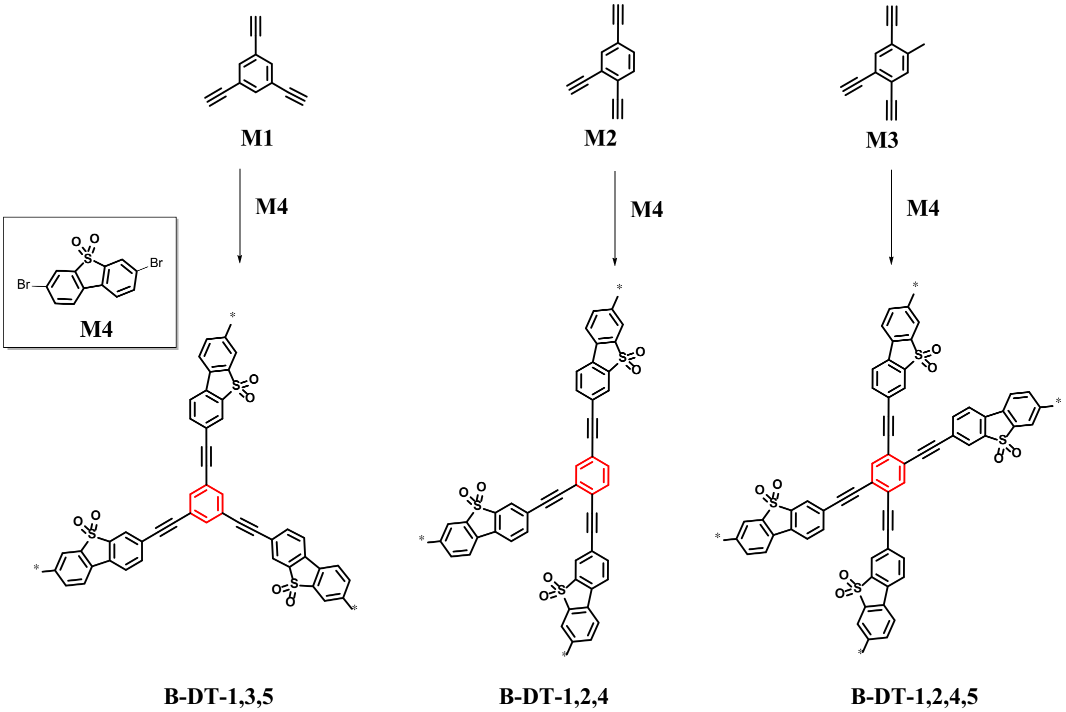
2. Experimental

2.1. Materials

All commercially available chemicals were analytical grade without further purification unless otherwise specified. Monomers 1,3,5-triethynylbenzene, 1,2,4-triethynylbenzene, and 1,2,4,5-tetraethynylbenzene were been synthesized via Sonogashira cross-coupling polycondensation and trimethylsilyl deprotection steps [36] 3,7-dibromodibenzo[*b*,*d*]thiophene 5,5-dioxide was synthesized based on our previous work [43].

2.2. Characterization

The functional groups of the three synthesized insoluble CMP were characterized by Fourier transform infrared spectroscopic (FT-IR, Nicolet Inc., USA) after being mixed with KBr and pressed into pellets. The chemical structures were confirmed via solid state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy (Bruker Avance 400 MHz). Thermogravimetric analysis (TGA) was employed under atmospheric conditions at a heating rate of 10 °C/min (NETZSCH TG209) to evaluate the thermal stability of the photocatalyts. With Cu Kα as the radiation source, an X-ray powder diffractometer (XRD, D8 advance Bruker Inc., Germany) was utilized to measure the crystalline structures at 40 kV. The morphological properties were determined using transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN). Visible light absorption ability was assessed by UV–Vis diffuse reflectance spectroscopy (DRS, Shimadzu UV-3100), and the optical bandgap was calculated by Kubelka–Munk function based on DRS. The specific Brunauer-Emmett-Teller (BET) surface area and pore volumes were determined by the N_2 sorption isotherms methods (Micrometrics ASAP 2040), and size distributions were calculated by the Density Functional Theory (DFT) method. Cyclic voltammetry (CV) on a CHI 660E workstation was employed to determine the photocurrent and LUMO reduction potential. A glassy carbon electrode, Ag/Ag^+ electrode, and platinum plate were used as the working electrode,



Scheme 1. Structures of monomers and synthesis of CMP photocatalysts by Sonogashira cross-coupling polycondensation. Condition: $Pd(PPh_3)_2Cl_2$, CuI, DMF/TEA, 80 °C. The "*" indicates repeating units.