Cross-Linked Polymers based on 2,5-disubstituted tetrazoles for Unsaturated Hydrocarbons detection

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Contents

1. Instruments

The thermogravimetric analysis (TGA) was performed using a Netzch Sta 449c thermal analyzer system at the heating rate of 10^{o} C/min in air atmosphere. The FTIR spectra were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The nitrogen adsorption isotherm was measured on an Autosorb iQ2 adsorptometer, Quantachrome Instruments. The XRD was performed by a Riguku D/MAX2550 diffractometer using CuKα radiation, 40 kV, 200 mA with scanning rate of 0.4^{o} /min. TEM micrographs was recorded using a FEI Tecnai G2F20 s-twin D573 with an acceleration voltage of 300 kV. SEM micrographs were performing on JEOL JXA-840 under an accelerating voltage of 15 kV. The ^{1}H-NMR spectra were recorded at 400 MHz in DMSO-d_6 as internal standard with TMS, and the Solid-state ^{13}C NMR spectra were recorded at 5KHz. Photoluminescence spectra were recorded on a Perkin-Elmer LS55 spectrofluorometer.

2. Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted.

3. Synthesis

Synthesis of Tetrakis[(4-cyanophenoxy)methyl]methane

Tetrakis[(4-cyanophenoxy)methyl]methane was synthesized according to a procedure described.[S1]

Synthesis of Tetrakis[(4-tetrazoleophenoxy)methyl]methane (TTZM)

Tetrakis[(4-tetrazoleophenoxy)methyl]methane (TTZM) was synthesized according to a procedure described.[S2] A mixture of tetrakis[(4-cyanophenoxy)methyl]methane (0.162 g, 0.3 mmol), NaN$_3$ (0.24 g, 3.6mmol), and triethylamine hydrochloride(0.5 g, 3.6 mmol) in toluene (5 mL) and methanol (1 mL) was heated at reflux in a 50 mL round-bottomed flask for 4 d. Upon cooling to room temperature, an aqueous solution of NaOH (5 mL, 1m) was added, and the mixture was stirred for 30 min. The aqueous layer was treated with dilute HCl (ca. 10 mL, 1M) until no further precipitate formed. The precipitate was then collected by filtration, dried in air, and dissolved in aqueous NaOH (1M). The resulting clear, colorless solution was titrated with dilute HCl (ca. 4mL, 1m) until the pH of the solution was 4. The ensuing precipitate was washed with distilled water (3#150 mL) and dried in air to afford 0.16 g (75%) of product as a white powder.^{1}H NMR ([D$_6$]DMSO, 300 MHz): d=7.95 (d, 8H, J=8.8 Hz), 7.25 ppm(d, 8H, J=8.8 Hz)

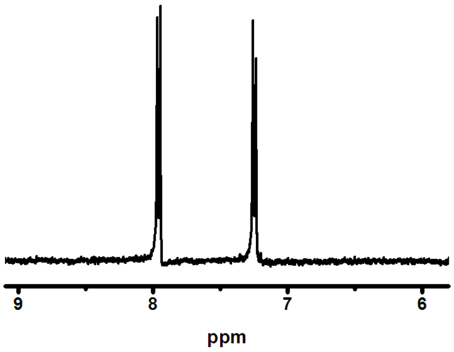

Figure S1. ^{1}H NMR spectra for TTZM.

Synthesis of TTZ-1

Into a 50 ml Schlenck tube was added Tetrakis[(4-tetrazoleophenoxy)methyl]methane (0.224mmol, 0.16g), benzene-1,4-diboronic acid (0.448mmol, 0.074 g), Cu$_2$O (5mol%, 0.0112mmol, 0.0016g) and DMSO (4mL). The reaction mixture was stirred under oxygen atmosphere at 100°C for 72 h to afford a brown precipitate and washed with 5mL of 1M aqueous HCl, 5mL of brine (four times), and ethyl acetate (40 mL).

The reaction of TTZ-1 with unstaturated hydrocarbons

A solution containing TTZ-1 (20 mg) and of alkenes or alkynes (5.0 equiv) in 6 mL EtOAc was irradiated with a hand-held 254-nm UV lamp for 4 h. The solvent and excess reagent were removed by filtration.

4. TGA trace

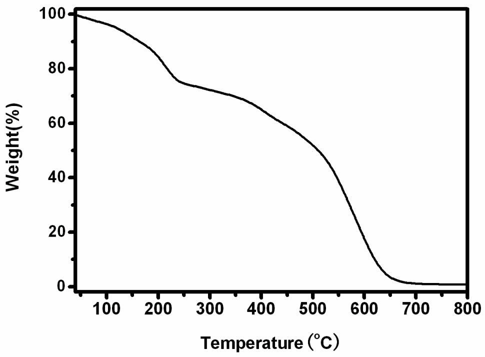

Figure S2. TGA curves of TTZ-1.

5. FTIR spectra

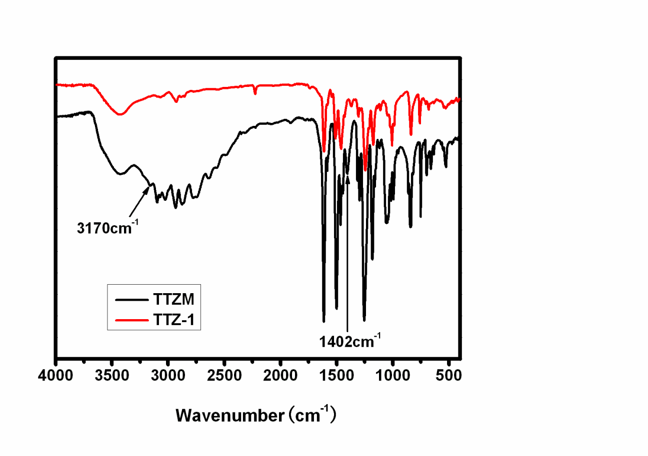

Figure S3. FT-IR spectra of TTZM (black) and TTZ-1 (red).

6. Powder X-ray diffraction patterns

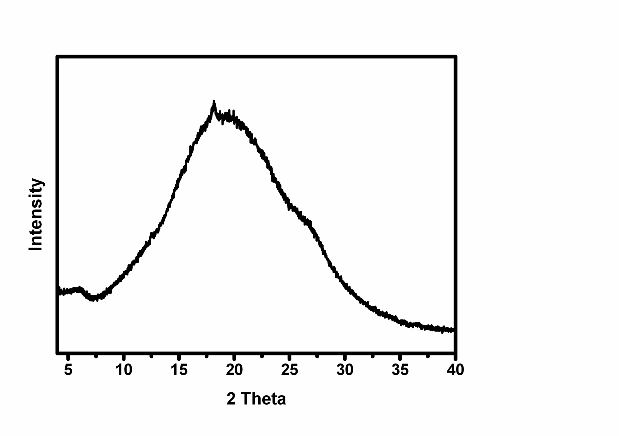

Figure S4. PXRD patterns for TTZ-1.

7. Nitrogen adsorption-desorption isotherms

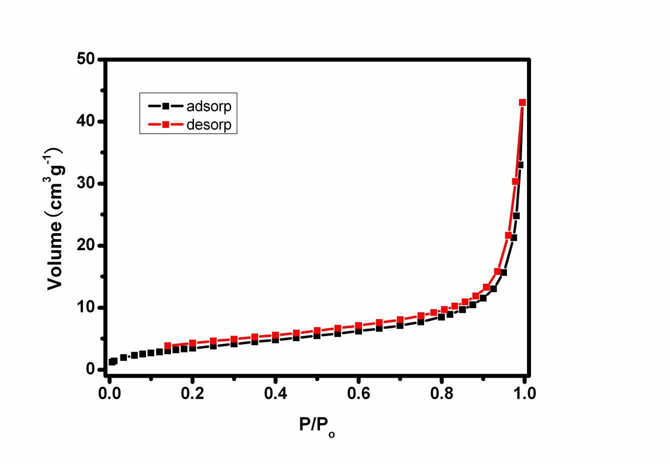

Figure S5. Nitrogen adsorption-desorption isotherms of TTZ-1measured at 77 K.

8. Solid-state ^{13}C NMR spectra

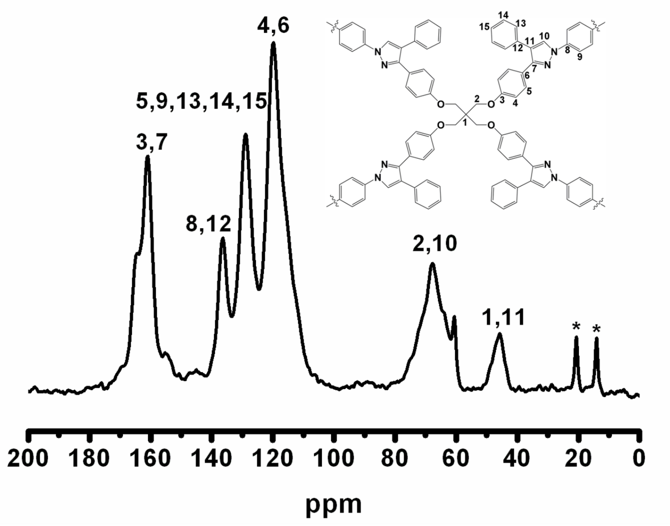

Figure S6. Solid-state ^{13}C CP/MAS NMR spectrum of Styrene-TTZ-Pyr product. Signals with * symbols are side peaks.

9. Absorption and fluorescence spectra

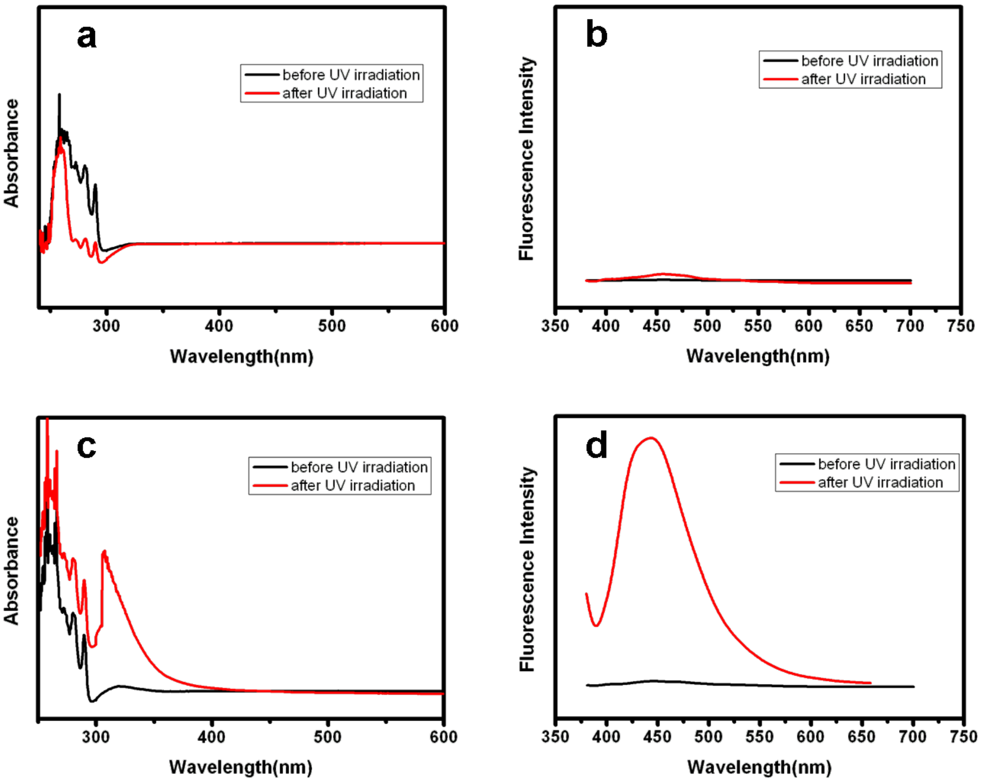

Figure S7. (a) Absorption and (b) fluorescence spectra of styrene in EtOAc before and after UV irradiation at 25 °C; (c) Absorption and (d) fluorescence spectra of the mixture of TTZ-1 and styrene in EtOAc before and after UV irradiation at 25 °C.

10. Photo images

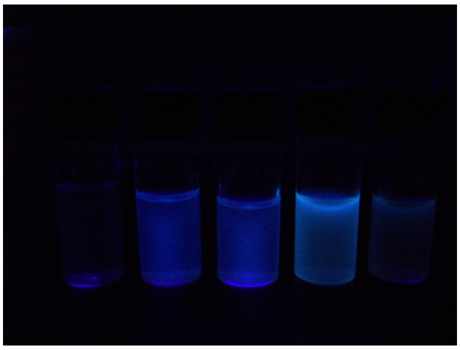

Figure S8. Photo images of TTZ-1 and TTZ-Pyr products dispersed in EtOAc under a handy UV light. From left to right are: TTZ-1, TTZ- Methylmethacrylate products, TTZ- Styrene products, TTZ- Ethene products and TTZ- Ethynyltrimethylsilane products.

11. Supporting references

S1. Dominic Laliberté, Thierry Maris, and James D. Wuest. *J. Org. Chem.* 2004, 69, 1776-1787.
S2. Mircea Dincã, Anne Dailly, and Jeffrey R.Long. *Chem.Eur.J.* 2008, 14, 10280-10285.