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# Selective removal of toxic organic dyes using Tröger base-containing sulfone copolymers made from a metal-free thiol-yne click reaction followed by oxidation†

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Three copolymers TCP1–3 bearing Tröger's base (TB) units intercalated with various thioether groups were synthesized using a catalyst-free thiol-yne click reaction. TCP1–3 display excellent solubility in common organic solvents allowing for their structural, and photophysical characterization. The thioether groups in TCP1–3 were selectively oxidized into their respective sulfone derivatives under mild oxidation reaction conditions affording the postmodified copolymers TCP4–6. Investigation of organic dye uptake from water by TCP1–6 proved their efficiency as selective adsorbents removing up to 100% of the cationic dye methylene blue (MEB) when compared to anionic dyes, such as Congo red (CR), methyl orange (MO) and methyl blue (MB). The sulfone-containing copolymers TCP4–6 display superior and faster MEB removal efficiencies with respect to their corresponding synthons TCP1–3.

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## 1. Introduction

Organic dyes, which could be either anionic such as methyl orange (MO), methyl blue (MB) and Congo red (CR) or cationic like methylene blue (MB) are widely used in pharmaceutical, food, textile, and paper industries.<sup>1</sup> Most ionic organic dyes are water-soluble, non-biodegradable, and biologically active revealing mutagenic and carcinogenic properties.<sup>2,3</sup> Consequently, the aforementioned dyes are classified as pollutants causing adverse environmental impacts and are also considered highly toxic due to their bioaccumulation, and skin and eye irritation, besides being potential allergens causing various respiratory complications.<sup>4,5</sup> Consequently, removal of toxic organic dyes from freshwater resources using viable and efficient techniques is deemed crucial. Among the various techniques that have been developed to remove organic dyes from water,<sup>6–8</sup> adsorption proved to be promising because it is usually employed under ambient conditions and is highly efficient, cost-effective, and simple.<sup>9,10</sup>

Tröger's base (TB)<sup>11</sup> is a bowl-shaped heterocyclic compound which has been thoroughly investigated as a chiral building block, particularly in supramolecular systems.<sup>12–16</sup> Since the last decade, there has been a growing interest in the synthesis of

copolymers with TB units for applications in gas storage and separation materials.<sup>12,17–19</sup> The introduction of TB in the copolymer's structure bestows the latter with better gas selectivity and enhanced microporosity properties. The intricate structure of TB allows for trapping acidic gases more efficiently, whereas its rigid bicyclic bridge with a twist angle of 117° leads to zigzag copolymer chains with a high fractional free volume (FFV).<sup>20,21</sup> These interesting features have prompted researchers to employ TB in the synthesis of solution-processable polymers of intrinsic microporosity (PIMs) for gas separation membranes.<sup>22–29</sup> PIMs bearing Tröger's base (PIM-TBs) units reveal enhanced separation properties for several gas pairs, such as, O<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub>, where Robeson's upper bounds for permeability and selectivity had to be redefined.<sup>30–32</sup> Although there are numerous reports on TB-containing materials for gas separation applications, other properties have been scarcely investigated. For instance, the optical and electrochemical properties have been reported for some TB-containing polymers,<sup>33</sup> whereas the adsorption of picric acid from water was evaluated for other derivatives.<sup>34</sup> Recently, covalent organic polymers containing TBs were employed for the removal of acid dyes from aqueous media.<sup>35</sup>

Click chemistry dates back to the early work of Sharpless *et al.*<sup>36</sup> and was since then considered to be a conspicuous synthetic tool<sup>37</sup> because of several advantages, among others, mild reaction conditions, fast reaction rates, versatility, stereospecificity, and high yields.<sup>38–40</sup> Click reactions have been employed in various fields, namely, pharmaceuticals, bio-conjugated products, materials, and polymers.<sup>41</sup> Amongst the

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wide range of click reactions reported in the literature, nucleophilic ring opening, Michael addition, Diels–Alder, and azide-ene are the most prominent.<sup>42–46</sup> Recently, thiols click reactions have seen a noticeable surge and were employed under several reaction conditions *e.g.* metal catalysts, radical initiators, and UV-irradiation.<sup>47–49</sup> Thiol-ene click reactions have been reported in the synthesis of functional materials for various applications,<sup>13,41,50,51</sup> notably, to make conjugated polymers<sup>52</sup> where sulfur atoms act as bridging groups between the aromatic building blocks which, consequently, leads to a superior conductivity.<sup>39,53</sup>

The oxidation of thioether copolymers into their corresponding sulfone derivatives has proven to be an effective technique to increase the polarity of the resulting copolymers<sup>53</sup> and bestow them with improved thermal, mechanical, and electrical properties.<sup>54–56</sup> Copolymers bearing sulfone groups are widely utilized in fuel cells,<sup>57</sup> organic light emitting diodes (OLEDs),<sup>54,58</sup> chemosensors,<sup>59</sup> proton exchange,<sup>60</sup> organic solvent nanofilters,<sup>61</sup> and gas separation membranes.<sup>62</sup> Typically, thioether groups can be oxidized into sulfones either by employing oxone<sup>63</sup> or hydrogen peroxide.<sup>64</sup>

Tröger's base copolymers connected by thioether units **TCP1–3** were synthesized *via* a metal free thiol-ene click polymerization reaction under mild reaction conditions. **TCP1–3** were subsequently oxidized into their corresponding sulfone target copolymers **TCP4–6** using the environmentally friendly hydrogen peroxide. Dye adsorption properties of **TCP1–6** were tested using various organic dyes, revealing a higher affinity for the Tröger's base containing sulfone copolymers to adsorb cationic dyes when compared to their thioether synthons.

## 2. Experimental

### 2.1 General

All the reactions were carried out under inert atmosphere using dry Argon. All chemical reagents were used without further purification as purchased from Aldrich, Merck, Alfa Aesar, CDH, and HiMedia unless otherwise specified. Anhydrous solvents, namely, hexane, DCM, THF, methanol, diethyl ether, and acetone were further dried over molecular sieves and deoxygenated by bubbling with argon gas for 30 minutes. The Tröger's Base derivative **TB** was synthesized using a reported procedure in the literature<sup>65</sup> which was slightly changed (*cf.* the ESI file†). Thin layer chromatography was performed on aluminum sheets coated with silica gel 60 F254 and revealed using a UV lamp. NMR (<sup>1</sup>H: 600 MHz, <sup>13</sup>C: 150 MHz) spectra were recorded on Bruker BioSpin GmbH 600 MHz spectrometer using CD<sub>2</sub>Cl<sub>2</sub> or DMSO-*d*<sub>6</sub> as a solvent with the chemical shifts ( $\delta$ ) given in ppm and referred to tetramethylsilane (TMS). Electron impact high-resolution mass spectra (EI-HRMS) were recorded on a Thermo (DFS) with a standard PFK (perfluorokerosene) as lock mass. The analyzed data is converted to accurate mass employing X-Calibur accurate mass calculation software. UV-vis spectra were recorded on Shimadzu UV1800 spectrophotometer. Photoluminescence spectra were recorded on an Agilent G9800 Cary Eclipse Fluorescence spectrophotometer. Agilent Gel Permeation Chromatography (GPC/SEC)

equipped with two columns (PL mixed-C) and calibrated against twelve monodisperse polystyrene (PS) standards, using THF as eluent at a flow rate of 1.0 mL min<sup>-1</sup>, was employed to determine the relative weight-average ( $M_w$ ), number-average ( $M_n$ ) molecular weights, and polydispersity index ( $D = M_w/M_n$ ) of all the reported copolymers. FTIR spectra were recorded on FT/IR-6300 type A instrument using a KBr matrix.

### 2.2 Synthesis

**2.2.1 Synthesis of monomer TB-S.** Diethynyl Tröger's base **TB** (149 mg, 0.5 mmol, 1 eq.) and 3,4-difluorobenzenethiol **1** (0.110 mL, 1.0 mmol, 2 eq.) in THF (5.0 mL) were charged in a Schlenk tube under argon. The reaction mixture was heated at 50 °C overnight and the resulting solution was evaporated under reduced pressure. The desired product was isolated using silica gel column chromatography with ethyl acetate/hexane (10 : 90 v/v) as the eluent affording a pale-yellow solid (215 mg, 73%). <sup>1</sup>H-NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  7.39–7.12 (m, 10H, ArH), 6.82 (m, 2H, alkene-CH), 6.69 (m, 4H, alkene-CH), 6.53 (m, 2H, alkene-CH), 4.57 (d, 2H,  $J = 16$  Hz, methylene-CH), 4.34 (m, 2H, methylene-CH), 4.01 (d, 2H,  $J = 16$  Hz, methylene-CH), 2.41 (s, 6H, methyl-CH); <sup>13</sup>C-NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  151.17, 149.51, 146.13, 133.64, 131.51, 129.63, 128.26, 126.82, 125.51, 124.67, 122.24, 121.20, 120.06, 118.26, 118.21, 117.88, 67.66, 55.09, 17.32; EI-HRMS:  $m/z$  calculated for ( $M^+$ ) C<sub>33</sub>H<sub>26</sub>F<sub>4</sub>N<sub>2</sub>S<sub>2</sub> 590.1468 found 590.1467; FTIR (KBr, cm<sup>-1</sup>): 3023 (=C–H str), 2953 (–C–H str), 1601 (conjugated alkene C=C str), 1505 (Ar C–C str), 1266 (C–F str), 963 (*trans*; C=C ben), 766 (*cis*; C=C ben).

**2.2.2 Synthesis of copolymer TCP1 (procedure A).** Diethynyl **TB** (149 mg, 0.5 mmol, 1 eq.) and 1,4-benzenedithiol **2a** (71 mg, 0.5 mmol, 1 eq.) in THF (20 mL) were reacted in a Schlenk tube under argon at 50 °C for 24 hours. The resulting solution was further diluted with THF (20 mL) and added dropwise to 250 mL of hexane while stirring. The precipitate was filtered off and washed successively with hexane (20 mL), acetone (20 mL), and methanol (20 mL). Pale yellow solid (175 mg, 85%). <sup>1</sup>H-NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  7.34–7.22 (bm, 4H, ArH), 7.09 (brd, 2H, ArH), 6.79 (brd, 2H, alkene-CH), 6.50 (brd, 2H, alkene-CH), 4.56 (br, 2H, methylene-CH), 4.33 (br, 2H, methylene-CH), 4.02 (br, 2H, methylene-CH), 2.43 (s, 6H, methyl-CH); <sup>13</sup>C-NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  145.39, 133.16, 132.75, 131.72, 130.18, 130.09, 129.74, 129.59, 128.28, 127.92, 126.71, 124.66, 122.13, 67.64, 55.23, 16.96; GPC (THF);  $M_w$  (g mol<sup>-1</sup>): 8675  $M_n$  (g mol<sup>-1</sup>): 2840,  $D$ : 3.0; FTIR (KBr, cm<sup>-1</sup>): 3011 (=C–H str), 2939 (–C–H str), 1601 (conjugated alkene C=C str), 1474 (Ar; C–C str), 962 (*trans*; C=C ben), 726 (*cis*; C=C ben); UV-vis: (THF, 10<sup>-7</sup> M),  $\lambda_{max}$  [nm] = 325.

**2.2.3 Synthesis of copolymer TCP2.** **TCP2** was prepared following procedure A with: **TB** (149 mg, 0.5 mmol, 1 eq.), biphenyl-4,4'-dithiol **2b** (105 mg, 0.5 mmol, 1 eq.) in THF (20 mL). Pale yellow solid (195 mg, 80%). <sup>1</sup>H-NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  7.56–7.43 (bm, 8H, ArH), 7.02 (bm, 2H, ArH), 6.81–6.71 (m, 2H, alkene-CH), 6.52 (brd, 2H, alkene-CH), 4.64 (br, 2H, methylene-CH), 4.35 (br, 2H, methylene-CH), 4.03 (br, 2H, methylene-CH), 2.47 (s, 6H, methyl-CH); <sup>13</sup>C-NMR (150



MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta$  145.34, 133.20, 132.78, 132.40, 131.86, 129.93, 129.62, 129.39, 128.22, 127.96, 127.49, 127.43, 126.71, 124.67, 124.60, 123.69, 122.14, 67.67, 55.21, 16.99; GPC (THF);  $M_w$  (g mol<sup>-1</sup>): 7796  $M_n$  (g mol<sup>-1</sup>): 2732,  $D$ : 2.8; FTIR (KBr, cm<sup>-1</sup>): 3021 (=C-H str), 2941 (-C-H str), 1605 (conjugated alkene C=C str), 1476 (Ar; C-C str), 969 (*trans*; C=C ben), 807 (C-H ben), 716 (*cis*; C=C ben); UV-vis: (THF, 10<sup>-7</sup> M),  $\lambda_{max}$  [nm] = 330.

**2.2.4 Synthesis of copolymer TCP3.** TCP3 was prepared following procedure A with: **TB** (149 mg, 0.5 mmol, 1 eq.), 4,4'-bis(mercaptomethyl)biphenyl **2c** (123 mg, 0.5 mmol, 1 eq.) in THF (20 mL). Pale-yellow solid (225 mg, 87%). <sup>1</sup>H-NMR (600 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  7.90–7.33 (bm, 10H, ArH), 7.14 (brd, 1H, ArH), 7.08 (brd, 1H, ArH), 6.35 (brd, 2H, alkene-CH), 4.48 (br, 2H, methylene-CH), 4.17 (br, 2H, methylene-CH), 4.08–3.97 (br, 6H, benzyl & methylene-CH), 2.31 (s, 6H, methyl-CH); <sup>13</sup>C-NMR (150 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  139.82, 132.64, 130.63, 129.95, 129.26, 128.84, 127.75, 127.01, 67.17, 55.11, 40.52, 17.35; GPC (THF);  $M_w$  (g mol<sup>-1</sup>): 4305  $M_n$  (g mol<sup>-1</sup>): 1502,  $D$ : 2.8; FTIR (KBr, cm<sup>-1</sup>): 3027 (=C-H str), 2947 (-C-H str), 1605 (conjugated alkene C=C str), 1477 (Ar; C-C str), 951 (*trans*; C=C ben), 807 (C-H ben); UV-vis: (THF, 10<sup>-7</sup> M),  $\lambda_{max}$  [nm] = 296.

**2.2.5 Synthesis of the sulfone monomer TB-SO<sub>2</sub>.** To a stirring suspension of **TB-S** (50 mg, 0.08 mmol) in acetic acid (2.5 mL), was added dropwise 1 mL of aqueous hydrogen peroxide (aq. H<sub>2</sub>O<sub>2</sub>, 30 wt%). The reaction mixture was stirred at 80 °C for 15 min. The resulting pale-yellow precipitate was filtered off and washed with deionized water (20 mL) and diethyl ether (20 mL) then dried under vacuum to yield **TB-SO<sub>2</sub>** as a pale-yellow solid (54 mg, 98%). EI-HRMS:  $m/z$  calculated for (M<sup>+</sup>) C<sub>33</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>F<sub>4</sub>S<sub>2</sub> 654.1265 found 654.1261; FTIR (KBr, cm<sup>-1</sup>): 3046 (=C-H str), 2927 (-C-H str), 1604 (conjugated alkene C=C str), 1504 (Ar; C-C str), 1330 (O=S=O as-str), 1274 (C-F str), 1136 (O=S=O s-str), 972 (*trans*; C=C ben), 684 (*cis* C=C ben).

**2.2.6 Synthesis of TCP4 (procedure B).** To a stirring solution of **TCP1** (50 mg, 0.12 mmol) in acetic acid (2.5 mL), was added dropwise 1 mL of a 30 wt% aqueous solution H<sub>2</sub>O<sub>2</sub>. The reaction mixture was stirred at 80 °C for 15 min. The precipitate was filtered off and washed with deionized water (20 mL) and diethyl ether (20 mL) then dried under vacuum to yield **TCP4** as

a pale-yellow solid (57 mg, 100%). <sup>1</sup>H-NMR (600 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  8.06–6.73 (bm, 10H, ArH & alkene-CH), 4.65–4.28 (m, 6H, methylene-CH), 2.49 (s, 6H, methyl-CH); FTIR (KBr, cm<sup>-1</sup>): 3039 (=C-H str), 2942 (-C-H str), 1613 (conjugated alkene C=C str), 1317 (O=S=O as-str), 1145 (O=S=O s-str), 991 (*trans*; C=C ben), 688 (*cis* C=C ben); UV-vis: (THF, 10<sup>-6</sup> M),  $\lambda_{max}$  [nm] = 297.

**2.2.7 Synthesis of TCP5.** TCP5 was prepared following procedure B with: **TCP2** (50 mg, 0.1 mmol), acetic acid (2.5 mL), and 30 wt% of aq. H<sub>2</sub>O<sub>2</sub> (1 mL). Pale-yellow solid (52 mg, 93%). <sup>1</sup>H-NMR (600 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  7.92–6.72 (bm, 14H, ArH & alkene-CH), 4.64–4.30 (m, 6H, methylene-CH), 2.49 (s, 6H, methyl-CH); FTIR (KBr, cm<sup>-1</sup>): 3050 (=C-H str), 2918 (-C-H str), 1605 (conjugated alkene C=C str), 1476 (Ar; C-C str), 1313 (O=S=O as-str), (1148 O=S=O s-str), 995 (*trans*; C=C ben), 819 (C-H ben), 722 (*cis* C=C ben); UV-vis: (THF, 10<sup>-6</sup> M),  $\lambda_{max}$  [nm] = 281.

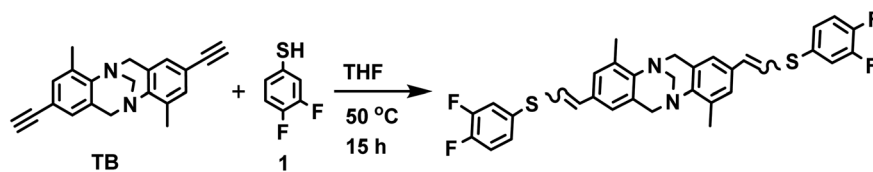
**2.2.8 Synthesis of TCP6.** TCP6 was prepared following procedure B with: **TCP3** (50 mg, 0.1 mmol), acetic acid (2.5 mL), and 30 wt% of aq. H<sub>2</sub>O<sub>2</sub> (1 mL). Pale-yellow solid (53 mg, 95%). <sup>1</sup>H-NMR (600 MHz, DMSO-d<sub>6</sub>, ppm):  $\delta$  7.64–6.57 (bm, 14H, ArH & alkene-CH), 4.60–3.98 (m, 6H, methylene-CH), 2.49 (s, 6H, methyl-CH); FTIR (KBr, cm<sup>-1</sup>): 3029 (=C-H str), 2918 (-C-H str), 1644 (conjugated alkene C=C str), 1501 (Ar; C-C str), 1311 (O=S=O as-str), 1138 (O=S=O s-str), 819 (C-H ben); UV-vis: (THF, 10<sup>-6</sup> M),  $\lambda_{max}$  [nm] = 271.

## 3. Results and discussion

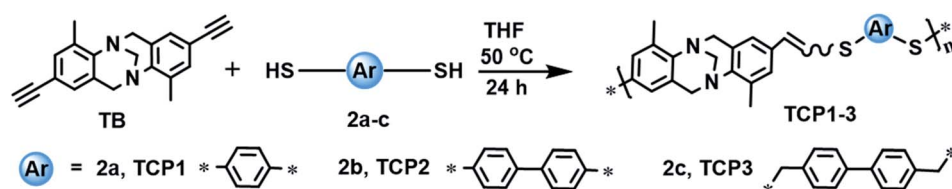
### 3.1 Synthesis

The feasibility of the metal-free thiol-yne click reaction was tested by preparing the prototypical monomer **TB-S** from the reaction of diethynyl Tröger's base **TB** with two equivalents of 3,4-difluorobenzenethiol **1** in THF at 50 °C, and which afforded the desired monomer in 73% yield (Scheme 1). The structure of **TB-S** was confirmed by <sup>1</sup>H- and <sup>13</sup>C-nuclear magnetic resonance (NMR), high-resolution mass spectroscopy (HRMS), and FTIR spectroscopy (see Fig. S1, S8, S15 and S17 in the ESI file†).

Synthesis of the Tröger's base containing copolymers **TCP1–3** (Scheme 2) was carried out following similar reaction conditions to those described above to make **TB-S**, but which were



Scheme 1 Synthesis of monomer TB-S.



Scheme 2 Synthesis of copolymers TCP1–3.



**Table 1** Effect of temperature on thiol-yne click polymerization reaction of TB and 2a<sup>a</sup>

Entry	Product	T (°C)	M <sub>w</sub> (g mol <sup>-1</sup> )	M <sub>n</sub> (g mol <sup>-1</sup> )	D
1	TCP1	30	5125	2050	2.5
2	TCP1	50	8675	2840	3.0
3	TCP1	70	7535	2485	3.0

<sup>a</sup> Reaction conditions: equimolar amount of TB (0.025 M) and 2a in THF.**Table 2** Effect of monomer concentration on polymerization reaction of TB and 2a<sup>a</sup>

Entry	Product	C <sub>M</sub> × 10 <sup>-2</sup> [M]	M <sub>w</sub> (g mol <sup>-1</sup> )	M <sub>n</sub> (g mol <sup>-1</sup> )	D
1	TCP1	5.0	6655	1564	4.2
2	TCP1	2.5	8675	2840	3.0
3	TCP1	1.0	4900	1800	2.7

<sup>a</sup> Reaction conditions: equimolar amount of TB and 2a in THF at 50 °C.**Table 3** Effect of reaction time on thiol-yne click polymerization of TB and 2a<sup>a</sup>

Entry	Product	Time	M <sub>w</sub> (g mol <sup>-1</sup> )	M <sub>n</sub> (g mol <sup>-1</sup> )	D
1	TCP1	60 min	5687	1820	3.1
2	TCP1	2 h	6475	2290	2.8
3	TCP1	4 h	7100	2595	2.7
4	TCP1	6 h	7160	2450	2.9
5	TCP1	24 h	8675	2840	3.0
6	TCP1	4 d	7535	2485	3.0

<sup>a</sup> Reaction conditions: equimolar amount of TB (0.025 M) and 2a in THF at 50 °C.

optimized by studying the effect of changing the medium temperature, reactants' concentration, and reaction time. Consequently, the four-day reaction of TB and 2a at room temperature (30 °C) afforded copolymer TCP1 with an average weight molar mass  $M_w \approx 5.1$  kDa and a polydispersity index  $D = 2.5$ . When the temperature of the reaction medium was raised to 50 °C,  $M_w$  increased to  $\sim 8.6$  kDa ( $D = 3.0$ ). Nevertheless, a further increase of the reaction temperature to 70 °C led to a drop in the molar mass ( $M_w$ ) of TCP1 to  $\sim 7.5$  kDa ( $D = 3.0$ , Table 1).

The monomer's concentration effect on the copolymer chain growth was also investigated. Table 2 depicts that when the reactants' concentration in the medium is  $5 \times 10^{-2}$  M, a molar mass  $M_w$  of 6.6 kDa was recorded for TCP1 (Table 2, entry 1). The target copolymer TCP1 was obtained in a higher weight average molar mass,  $M_w$ , when the reactants' concentration in THF was diluted to  $2.5 \times 10^{-2}$  M (Table 2, entry 2). Further dilution of the reactants' concentration to  $1 \times 10^{-2}$  M afforded TCP1 with a lower  $M_w$  of 4.9 kDa.

Table 3 summarizes the effect of changing the reaction time on TCP1 chain growth where a 60 minute reaction yielded the target copolymer with an average weight molar mass  $M_w = 5.6$  kDa (Table 3, entry 1). The prolongation of the reaction time to six hours afforded TCP1 with  $M_w$  of 7.1 kDa (Table 3, entry 3) and a further duration extension to 24 hours increased  $M_w$  to  $\sim 8.6$  kDa (Table 3, entry 5). Nevertheless, when the reaction was left for three additional days, the target copolymer TCP1 was isolated in a lower yield ( $\square$ ) with reduced average molar mass values, which could be explained by the formation of insoluble copolymer networks when the reaction is left for a prolonged period (Table 3, entry 6).

Copolymers TCP2–3 were synthesized by applying the optimized reaction conditions described above to make TCP1. It is noteworthy that all the target copolymers TCP1–3 were obtained

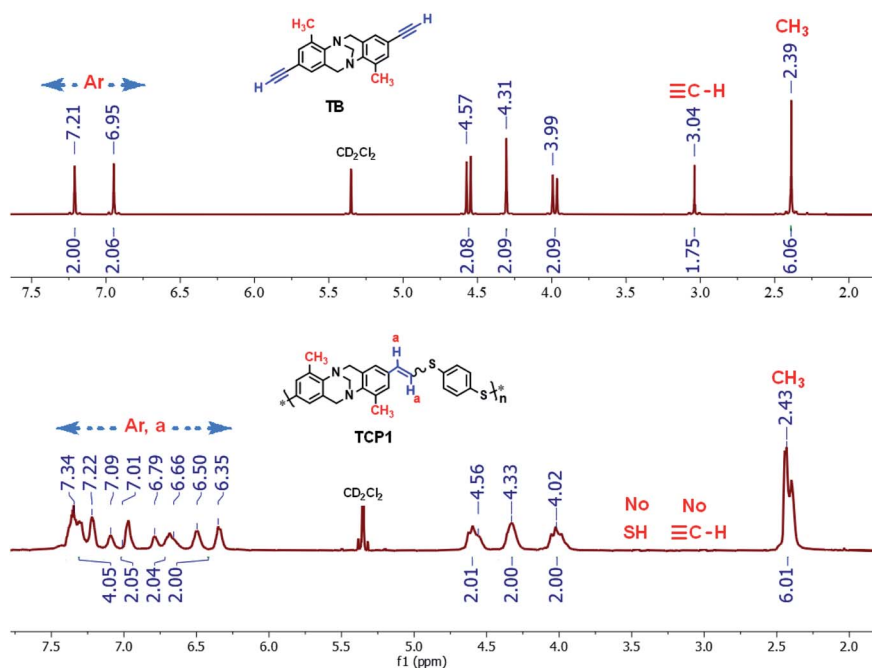
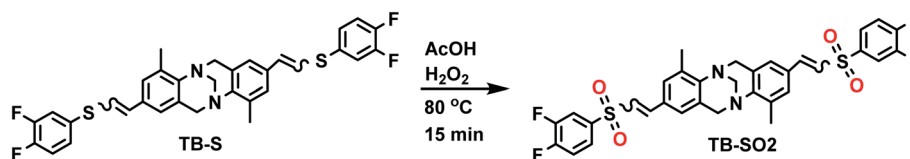
**Fig. 1** Comparative <sup>1</sup>H-NMR of TB (up) and TCP1 (down).

Table 4 Summary of GPC results of copolymers TCP1–3<sup>a</sup>

Entry	Co-monomers	Copolymer	Yield (%)	$M_w$ (g mol <sup>-1</sup> )	$M_n$ (g mol <sup>-1</sup> )	$D$
1	2a	TCP1	85	8675	2840	3.0
2	2b	TCP2	80	7796	2732	2.8
3	2c	TCP3	87	4305	1502	2.8

<sup>a</sup> Reaction conditions: TB, [M] = 0.025 M, 50 °C, 24 hours.



Scheme 3 Synthesis of monomer TB-SO2.

in very good yields (80–87%) and found to be highly soluble in common organic solvents, like, chloroform, dichloromethane, and tetrahydrofuran, which allowed for their structural characterization by instrumental analysis, namely, <sup>1</sup>H- and <sup>13</sup>C-NMR, gel permeation chromatography (GPC), FTIR, UV-vis and emission spectroscopy (see Fig. 2–4 and the related figures in the ESI file†).

Fig. 1 portrays the comparative <sup>1</sup>H-NMR spectra of synthon TB and target copolymer TCP1. The chemical shifts of the terminal alkyne in the former, detected at 3.04 ppm, completely disappeared in the <sup>1</sup>H-NMR spectrum of TCP1. In addition, the chemical shifts observed in the region ranging from 7.34 ppm to 6.35 ppm can be attributed to vinylic and aromatic protons whereas the protons located at 2.43 ppm are assigned to the methyl (–CH<sub>3</sub>) group. It is noteworthy that the proton of the thiol group detected at 3.39 ppm in the <sup>1</sup>H-NMR spectrum of monomer 2a was not found in that of TCP1, and therefore, indicating the successful formation of the latter copolymer and complete consumption of both monomers TB and 2a (see Fig. 1 and S2 in the ESI file†).

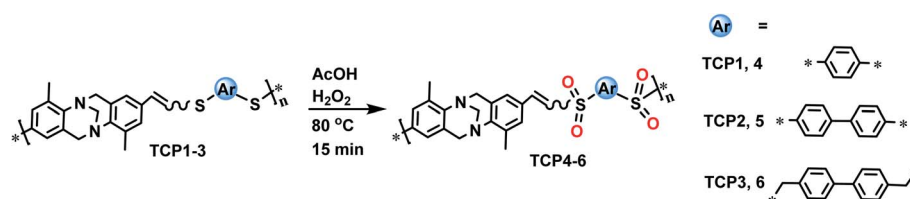
Gel permeation chromatography (GPC) analyses of TCP1–3 reveal the formation of copolymers with a weight average molar mass  $M_w$  ranging from ~4.3 kDa to ~8.6 kDa with a polydispersity index ( $D = M_w/M_n$ ) of 2.8–3.0 (Table 4).

Selective oxidation of the thioether groups into their corresponding sulfones was carried out using the prototypical monomer TB-S which underwent a reaction with hydrogen peroxide in acetic acid at 80 °C for 15 minutes (Scheme 3). The desired product TB-SO2 was isolated quantitatively by simple

filtration from the reaction mixture and its formation was confirmed by EI-HRMS and FTIR absorption spectra (see Fig. S16 and S17 in the ESI file†).

Hence, selective oxidation reactions of the thioether groups of copolymers TCP1–3 into their corresponding sulfone moieties were carried out using the same reaction condition applied to make TB-SO2, which afforded the sulfone-bearing copolymers TCP4–6 (Scheme 4). These latter were found to be insoluble in common organic solvents (*e.g.* THF, DCM, and CHCl<sub>3</sub>) and were only sparingly soluble in polar aprotic solvents, namely, DMF and DMSO. The structures of TCP4–6 were confirmed by <sup>1</sup>H-NMR, FTIR, UV-visible and emission spectroscopy (see Fig. 3, 4 and the related figures in the ESI file†).

Fig. 2 divulges the comparative FTIR absorption spectra of the thioether containing copolymer TCP2 and its corresponding sulfonated compound TCP5. The asymmetric and symmetric stretching vibrations peaks of the sulfone (O=S=O) moiety in TCP5 were detected at 1313 cm<sup>-1</sup> and 1148 cm<sup>-1</sup>, respectively. It is noteworthy that subtle shifts could be noticed in the stretching vibration peaks of the aromatic =C–H groups of TCP2 and TCP5, at 3021 cm<sup>-1</sup> and 3050 cm<sup>-1</sup>, respectively. On the other hand, the stretching vibration peaks of the aliphatic –C–H groups of TCP2 and TCP5, were detected at 2941 cm<sup>-1</sup> and 2918 cm<sup>-1</sup>, respectively. FTIR absorption spectra of TCP4–6 disclose their fingerprint functional groups' stretching and bending vibration peaks. The aromatic (=C–H) and aliphatic (–C–H) stretching vibrations were detected in the range of ~3029–3050 cm<sup>-1</sup> and 2918–2942 cm<sup>-1</sup>, respectively. Similarly, the absorption bands observed in the regions of 1605–



Scheme 4 Synthesis of copolymer TCP4–6.



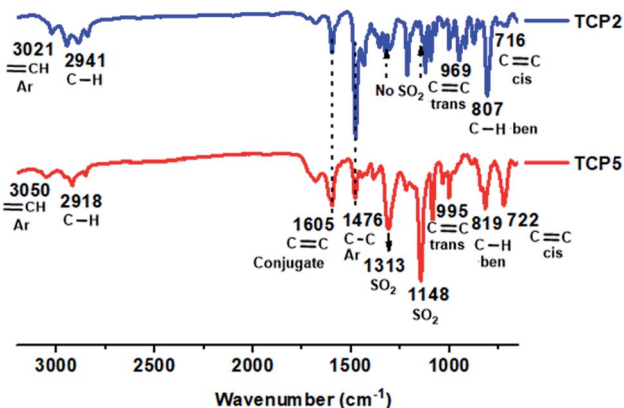


Fig. 2 Comparative FT-IR spectra of TCP2 (blue) and TCP5 (red).

1644  $\text{cm}^{-1}$ , 991–995  $\text{cm}^{-1}$ , and 688–722  $\text{cm}^{-1}$ , could be attributed to the characteristic *trans* and *cis* conjugated alkenes, respectively. Moreover, the distinctive asymmetric and symmetric stretching vibrations of sulfone ( $\text{O}=\text{S}=\text{O}$ ) were identified in the range of 1311–1317  $\text{cm}^{-1}$ , and 1138–1148  $\text{cm}^{-1}$ , respectively. The typical aromatic C–C and C–H bending vibrations were also found at 1476–1501  $\text{cm}^{-1}$  and  $\sim 819$   $\text{cm}^{-1}$ , respectively. It is worthwhile to note that the FTIR absorption peak of sulfoxide usually detected at  $\sim 1030$   $\text{cm}^{-1}$  was not observed in any of the sulfonated copolymers TCP4–6 (see Fig. 2 and S18, S19 in the ESI file<sup>†</sup>), hence, confirming the complete oxidation of the thioethers moieties of TCP1–3 into their sulfone groups in TCP4–6.

Fig. 3 portrays the UV-vis absorption and emission spectra of the thioether containing copolymers TCP1–3 and their corresponding sulfonated ones TCP4–6. TCP1 shows a strong UV absorption band detected at 325 nm but which is blue shifted to 297 nm for its sulfonated derivative TCP4. The same feature is encountered in copolymers TCP2,5 and their respective compounds TCP3,6 (see Fig. 3 and S20 in the ESI file<sup>†</sup>). The emission spectra of TCP1, which contains phenyl spacers between the thioethers, displays a broad spectrum with an intensity maximum at 395 nm whereas its corresponding sulfonated copolymer TCP4 illustrates a  $\sim 19$  nm bathochromic shift with an emission peak detected at 414 nm. Interestingly,

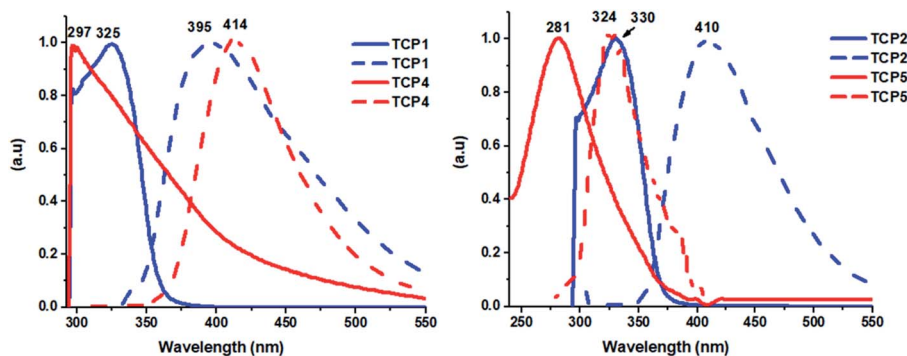


Fig. 3 Normalized UV-vis absorption ( $C_M = 10^{-7}$  M in THF, solid lines) and emission ( $C_M = 10^{-8}$  M in THF, dotted lines) spectra of: (A) TCP1,4 (left) TCP2,5 (right) (absorption maxima were used as the excitation wavelengths).

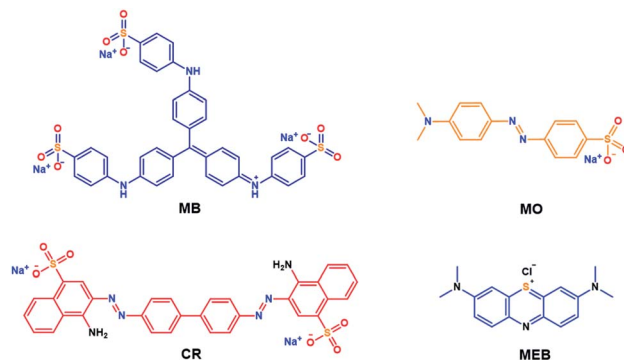


Fig. 4 Structures of methyl blue (MB), methyl orange (MO), congo red (CR), and methylene blue (MEB).

copolymers TCP2 and TCP3, which contain biphenyl spacers, reveal emission maxima at 410 and 464 nm, respectively. Nevertheless, the sulfonated derivatives of these latter, namely, TCP5 and TCP6 disclose emission peaks at 324 and 326 nm, respectively, thus, revealing hypsochromic shifts of with respect to their synthons TCP2 and TCP3 by  $\sim 86$  and 138 nm, respectively (see Fig. 3 and S20 in the ESI file<sup>†</sup>).

### 3.2 Dye adsorption studies

The thioether containing copolymers were investigated as possible adsorbents of organic dyes (Fig. 4). Therefore, TCP1 was soaked in aqueous solutions of three anionic dyes, precisely, Congo red (CR), methyl orange (MO), and methyl blue (MB) in addition to methylene blue (MEB) which is cationic. The adsorption efficiency of TCP1 towards CR, MO, MB, and MEB from water was monitored by recording the UV-visible absorbance spectra of the aqueous solutions after the addition of the target copolymer at different time intervals. The dyes removal experiments were carried out by stirring at room temperature a 5 mL aliquot of a 5  $\text{mg L}^{-1}$  aqueous solution of the hitherto mentioned dyes in presence of 5 mg of TCP1 (in Fig. 5).

A noticeable decrease in the absorbance intensity of MEB was observed, revealing a  $\sim 71\%$  removal efficiency after 30 minutes of TCP1 addition at room temperature, and which reached 92% after 24 h. On the other hand, TCP1 disclosed lower adsorption efficacies towards the anionic dyes CR, MO,



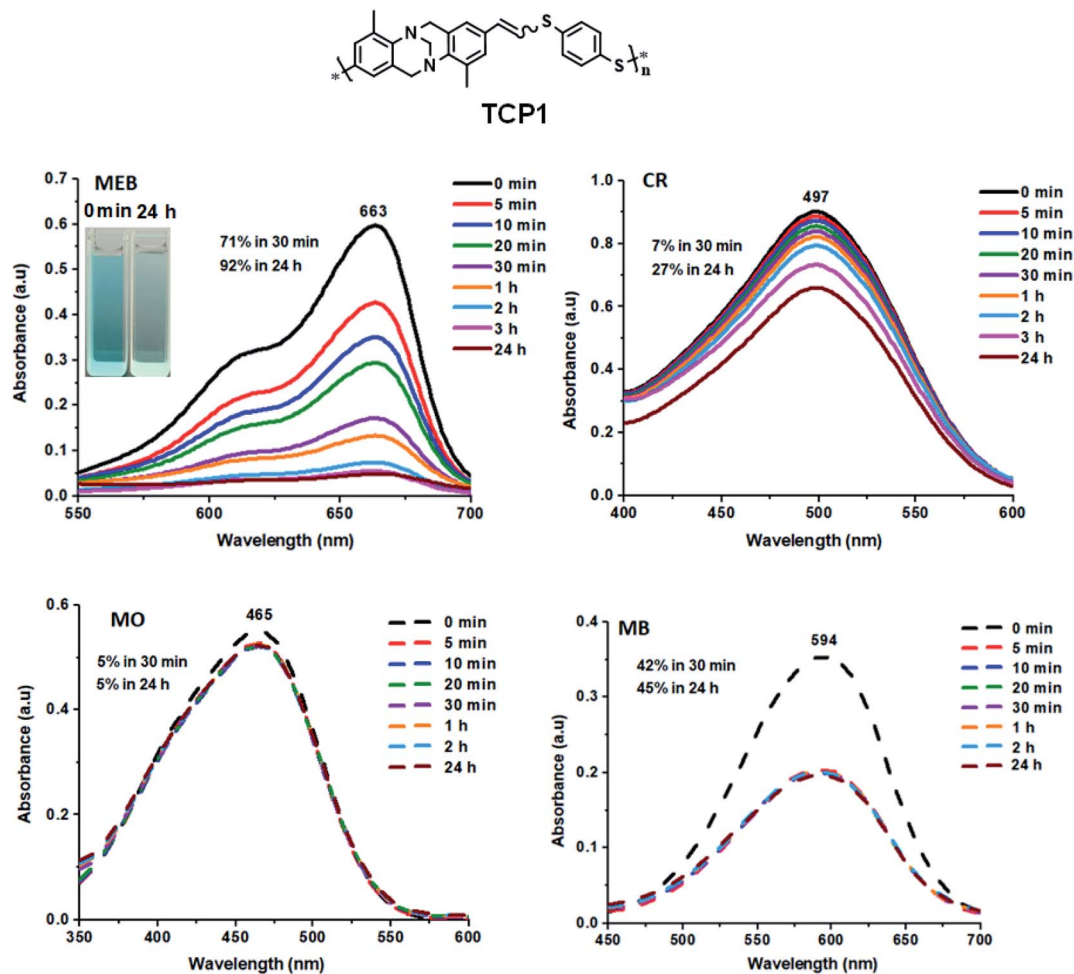


Fig. 5 TCP1 adsorption of methylene blue (MEB), Congo red (CR), methyl orange (MO), and methyl blue (MB) at various time intervals (inset: photographs showing the color change upon dye adsorption).

and MB with 27%, 5%, and 45%, respectively (Fig. 5). Similar results were obtained when thioether containing copolymers TCP2–3 were tested as adsorbents.

Interestingly, sulfonated copolymers TCP4–6 displayed superior adsorption efficiencies towards MEB when compared to their corresponding thioether copolymer synthons TCP1–3

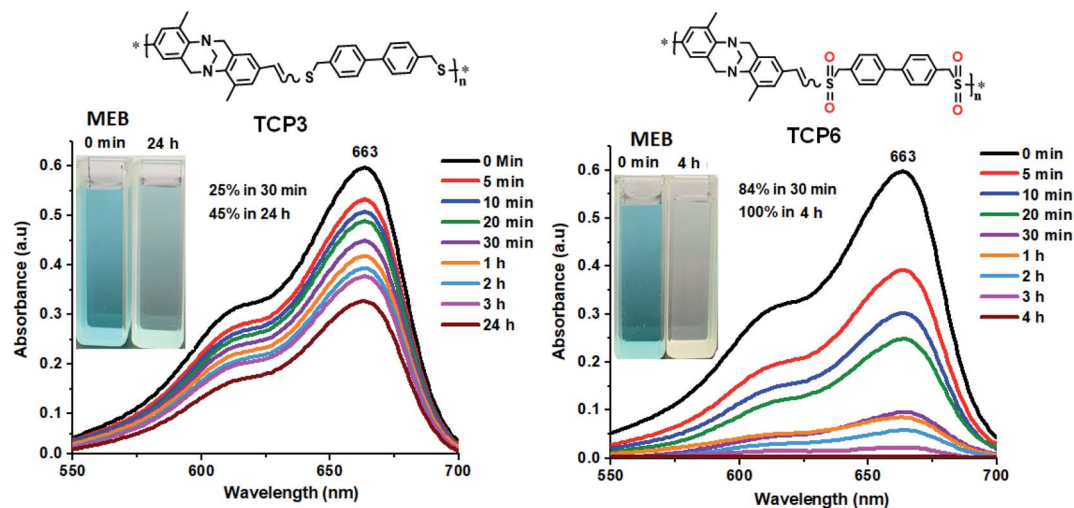


Fig. 6 Methylene blue (MEB) dye adsorption by TCP3,6 at various time intervals (insets: photographs showing the color change upon dye adsorption).



(see Fig. 6 and S21, S22 in the ESI file†). **TCP1–3** revealed **MEB** ~25–71% uptake efficiencies from water after 30 min which increased to ~45–92% after 24 h. Nevertheless, the sulfonated copolymers **TCP4–6** portrayed enhanced and faster **MEB** uptake efficacies ranging from ~76% to 93% after 30 min and reached quantitative adsorption (~100%) after 2–4 h (see Table S1 in the ESI file† which summarizes the dye adsorption properties of **TCP1–6**). The noticeable improvement in **MEB** dye adsorption properties for **TCP4–6** could be explained by the presence of sulfone groups, which are more polar when compared to thioether units, hence, resulting in a more pronounced charge separation, and therefore, enhancing the electrostatic attraction between the adsorbent and adsorbates.<sup>66</sup> Recyclability tests of the sulfonated copolymers to **MEB** were investigated using **TCP6** as a model adsorbent which revealed a 100% efficiency for three successive cycles that slightly dropped to 96% uptake in the fourth cycle (see Fig. S23, in the ESI file†). It is noteworthy that, to the best of our knowledge, these results are either superior or equivalent to the adsorption capacities reported in the literature.<sup>67–71</sup>

## 4. Conclusion

Three novel poly(vinylene sulfone)s containing Tröger's base units, **TCP4–6**, were synthesized in very good yields *via* a metal-free click thiol-yne reaction affording copolymers **TCP1–3** and which underwent post-modification of their thioether units into sulfones using green oxidation reaction conditions. It is worthwhile to mention that copolymers **TCP4–6** disclose fast and selective adsorption of methylene blue with uptake efficiencies reaching ~93% after 30 minutes of adding the target materials to the aqueous solutions. The facile catalyst-free synthetic methodology to make these copolymers and their excellent selective dye adsorption properties promote them as potential materials for water treatment.

## Data availability

The raw data required to reproduce these findings are available upon request.

## Conflicts of interest

The authors declare no conflict of interests.

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