Supplementary Information

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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Contents

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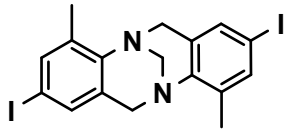
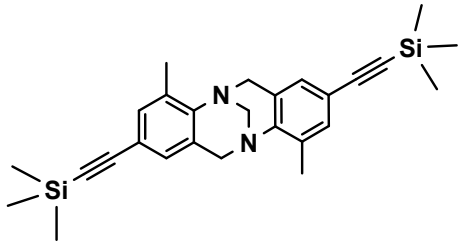
i). Synthesis of 2,8-diiodo-4,10-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine:



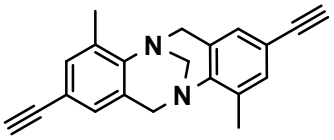
2-methyl-4-Iodoaniline (2.32 g, 1mmol) was dissolved in trifluoroacetic acid (20 ml) and cooled in an ice bath. Dimethoxymethane (2.28 ml, 3 mmol) was added dropwise, and the reaction was stirred for 24 h. The reaction mixture was poured slowly into an aqueous ammonia solution (100 ml) and stirred thoroughly. The resulting precipitate was filtered and washed with water (500ml). The crude product was purified by column chromatography on silica gel with ethyl acetate/ petroleum ether (4:1, v/v) as an eluent to yield a white solid; yield 98%; mp. 218-20 ºC; Anal. Calcd for $C_{17}H_{16}I_2N_2$: C, 40.66; H, 3.21; N, 5.58; I, 50.55. Found: C, 40.63; H, 3.23; N, 5.57; I, 50.56; EI-HRMS: m/z calculated for ($M^{\cdot+}$) $C_{17}H_{16}I_2N_2$ 501.9396 found 501.9397; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.38 (s, 2H, ArH), 7.16 (s, 2H, ArH), 4.43 (d, 2H, J = 18.0 Hz, methylene-CH), 4.18 (s, 2H, methylene-CH), 3.95 (d, 2H, J = 18.0 Hz, methylene-CH), 2.28 (s, 6H, methyl-CH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 145.4, 137.7, 135.3, 132.8, 130.9, 87.8, 66.4, 53.5,

ii)*. Synthesis of 4,10-dimethyl-2,8-bis((trimethylsilyl)ethynyl)-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine*



A Schlenk tube containing 2,8-diiodo-4,10-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (5.02 g, 1 mmol), bis(triphenylphosphine)-palladium dichloride (0.35 g, 0.03 mmol), copper(I) iodide (0.19 g, 0.1 mmol), anhydrous triethylamine (10 ml) was deoxygenated and backfilled with argon. Then anhydrous toluene (100 ml) was added and backfilled with argon. Finally, under the flow of argon, trimethylsilylacetylene (1.068 ml, 1.2 mmol) was added drop wise and the mixture was stirred at room temperature for 24 hours. The crude product was purified by column chromatography on silica gel with ethyl acetate/ petroleum ether (4:1, v/v) as an eluent to yield a white solid; yield 56%; mp. 177-79 ºC; Anal. Calcd. for $C_{27}H_{34}N_2Si_2$: C, 73.25; H, 7.74; N, 6.33; Si, 12.69. Found: C, 73.27; H, 7.72; N, 6.30; Si, 12.71; EI-HRMS: m/z calculated for ($M^{\cdot+}$) $C_{27}H_{34}N_2Si_2$ 442.2255 found 442.2258; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.12 (s, 2H, ArH), 6.93 (s, 2H, ArH), 4.44 (d, 2H, J = 12.0 Hz, methylene-CH), 4.20 (s, 2H, methylene-CH), 3.97 (d, 2H, J = 12.0 Hz, methylene-CH), 2.29 (s, 6H, methyl-CH), 0.16 (s, 18H, methyl-CH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 146.51, 132.82, 131.52, 128.53, 128.02, 116.78, 105.42, 92.75, 66.69, 53.89, 16.47, 0.07.

iii)*. Synthesis of 2,8-diethynyl-4,10-dimethyl-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine (3a)*



4,10-dimethyl-2,8-bis((trimethylsilyl)ethynyl)-6,12-dihydro-5,11-methanodi-benzo[b,f][1,5]diazocine (4.42 g, 1 mmol) was dissolved in methanol (20 ml). Potassium carbonate (5.48 g, 4 mmol) was added, and the reaction mixture was stirred for 24 h. The mixture was poured slowly into ice cold water and stirred thoroughly. The precipitate was collected by filtration and purified by column chromatography on silica gel with ethyl acetate/ petroleum ether (4:1, v/v) as an eluent to yield a white solid; yield 95%; mp. 185-56 ºC; Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.55; H, 6.10; N, 9.39; EI-HRMS: m/z calculated for ($M^{\cdot+}$) $C_{21}H_{18}N_2$ 298.1464 found 298.1465; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.18 (s, 2H, ArH), 6.92 (s, 2H, ArH), 4.54 (d, 2H, J = 18.0 Hz, methylene-CH), 4.27 (s, 2H, methylene-CH), 3.96 (d, 2H, J = 18.0 Hz, methylene-CH), 3.01 (s, 2H, acetylene-CH) 2.36 (s, 6H, methyl-CH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 146.86, 133.26, 132.44, 128.18,116.96, 83.44, 75.95, 67.31, 54.69, 16.64.

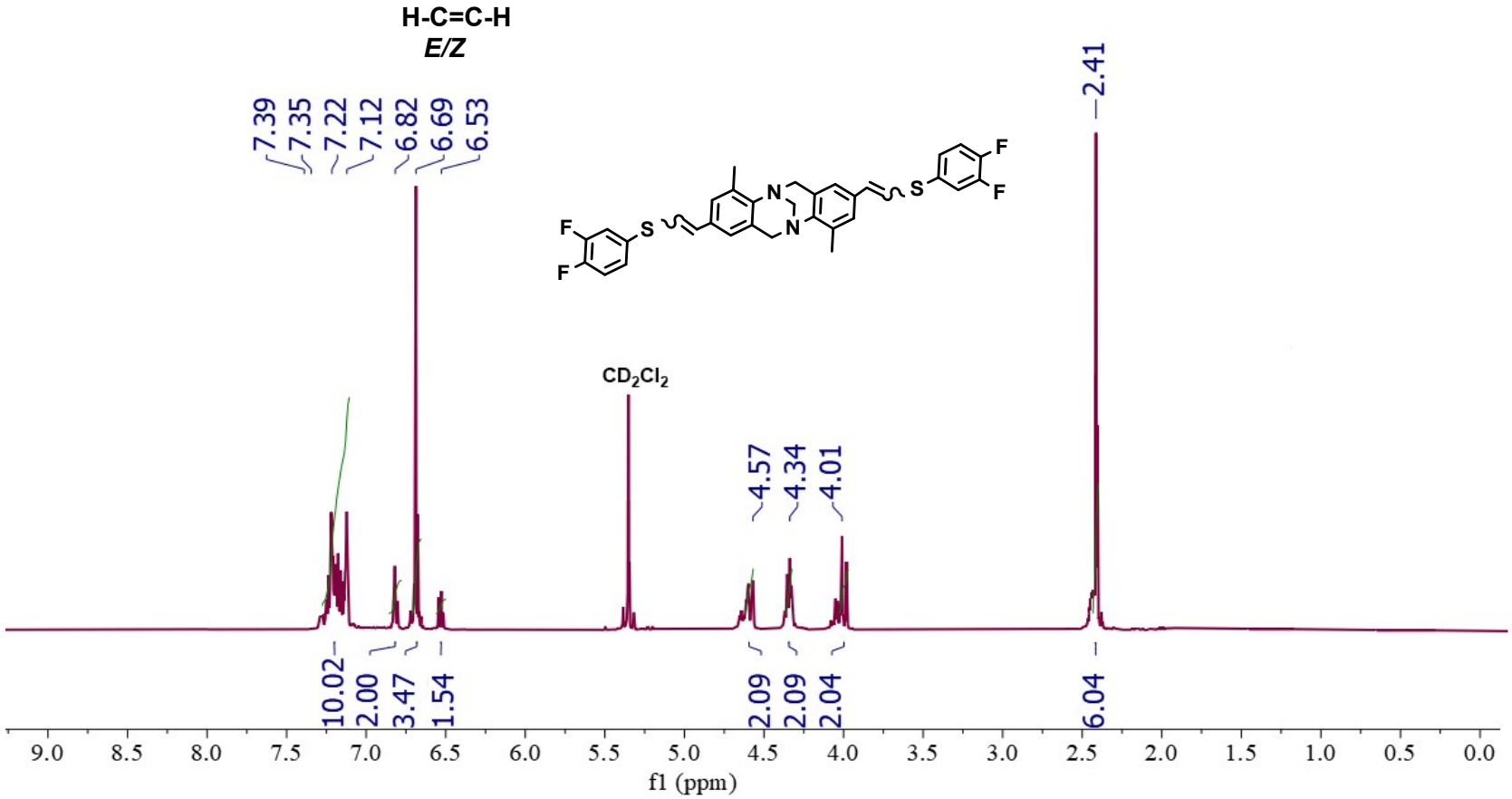


Figure S1: ^{1}H NMR spectrum of **TB-S** (CD_2Cl_2, 600 MHz)

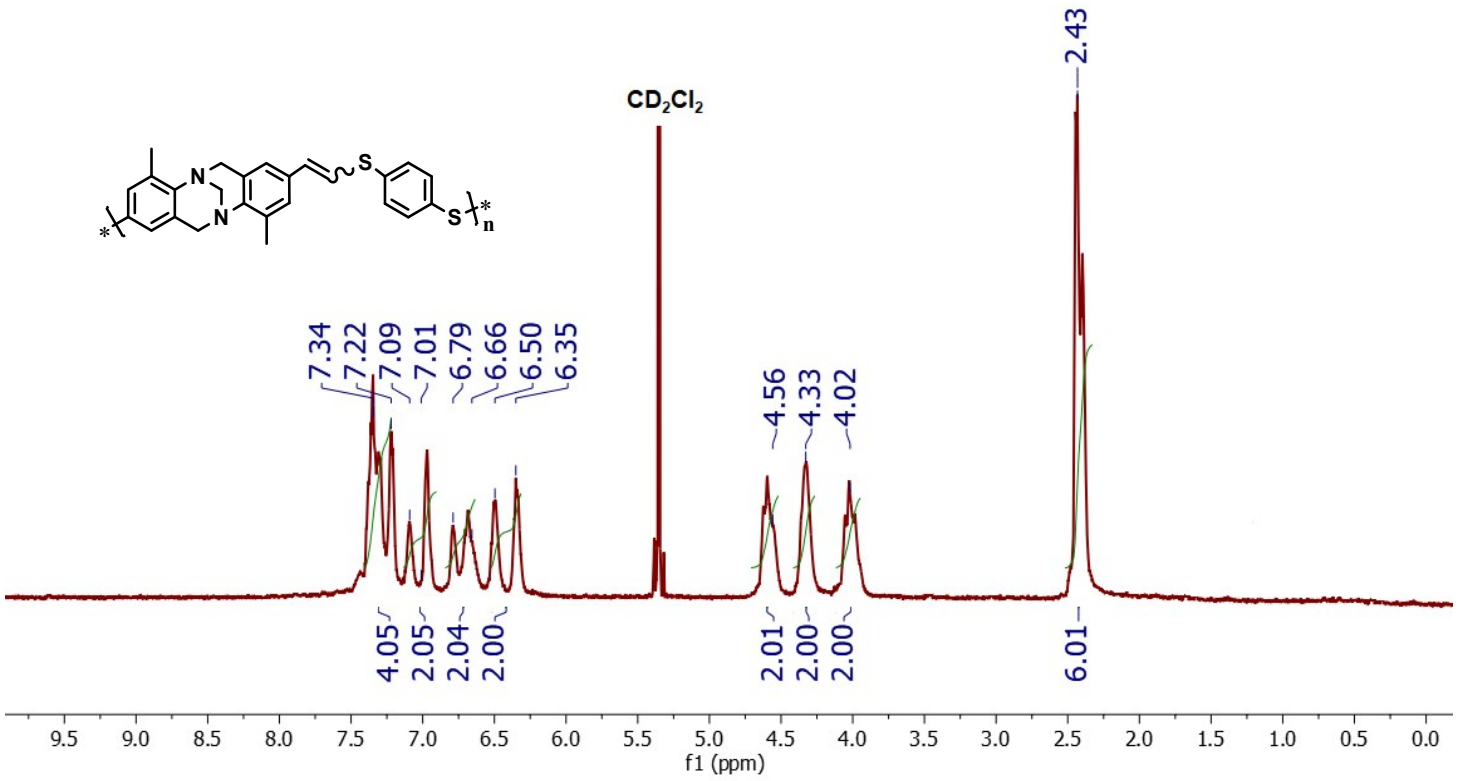


Figure S2: ^{1}H NMR spectrum of **TCP1** (CD_2Cl_2, 600 MHz)

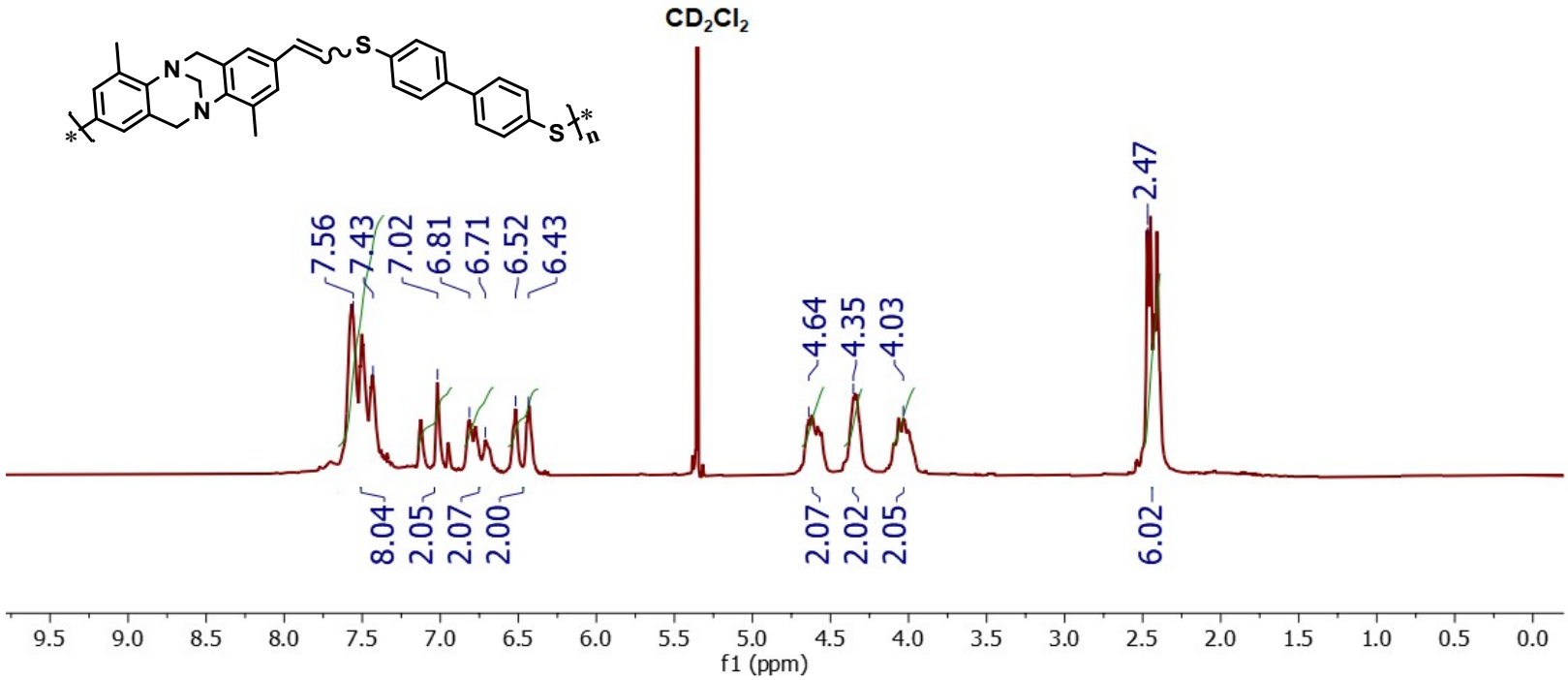


Figure S3: ^{1}H NMR spectrum of **TCP2** (CD_2Cl_2, 600 MHz)

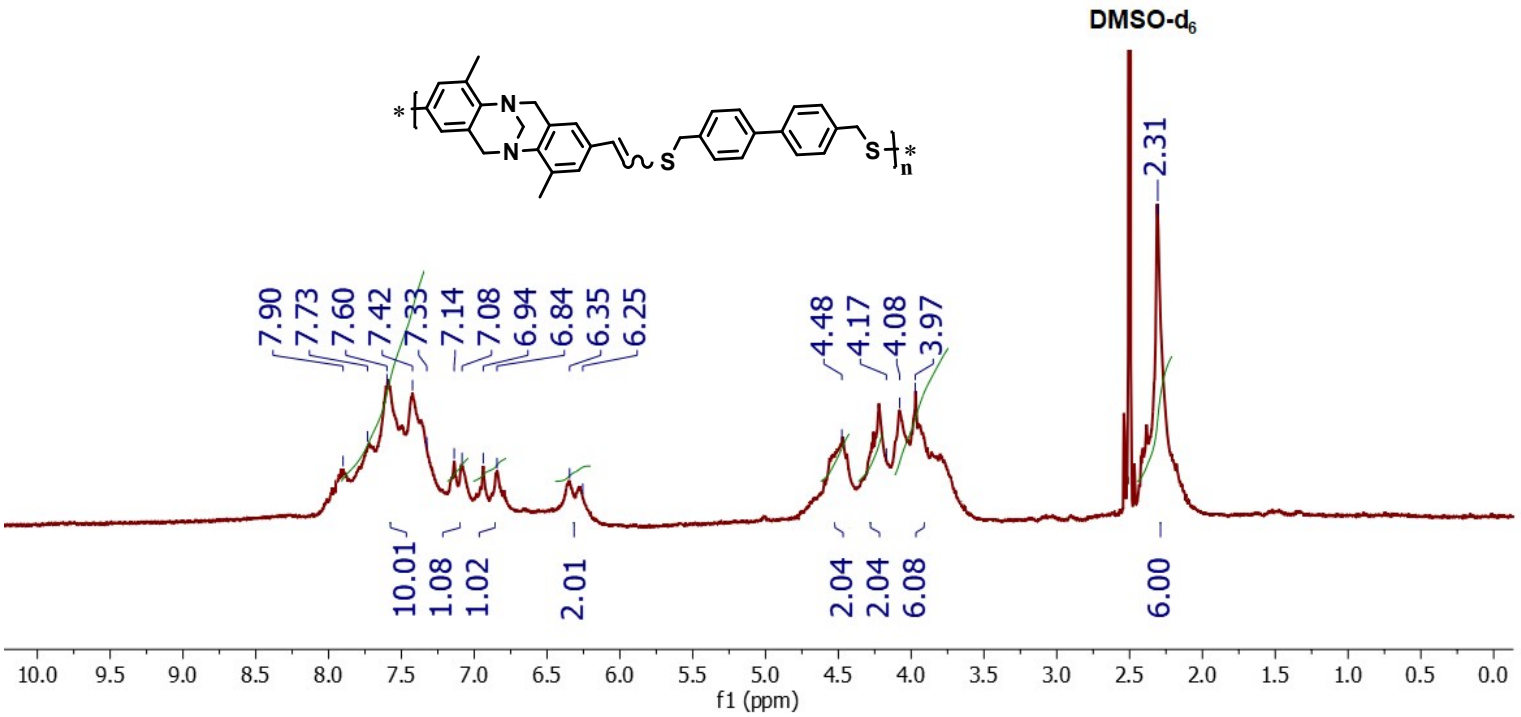


Figure S4: ^{1}H NMR spectrum of **TCP3** (DMSO-d_6, 600 MHz)

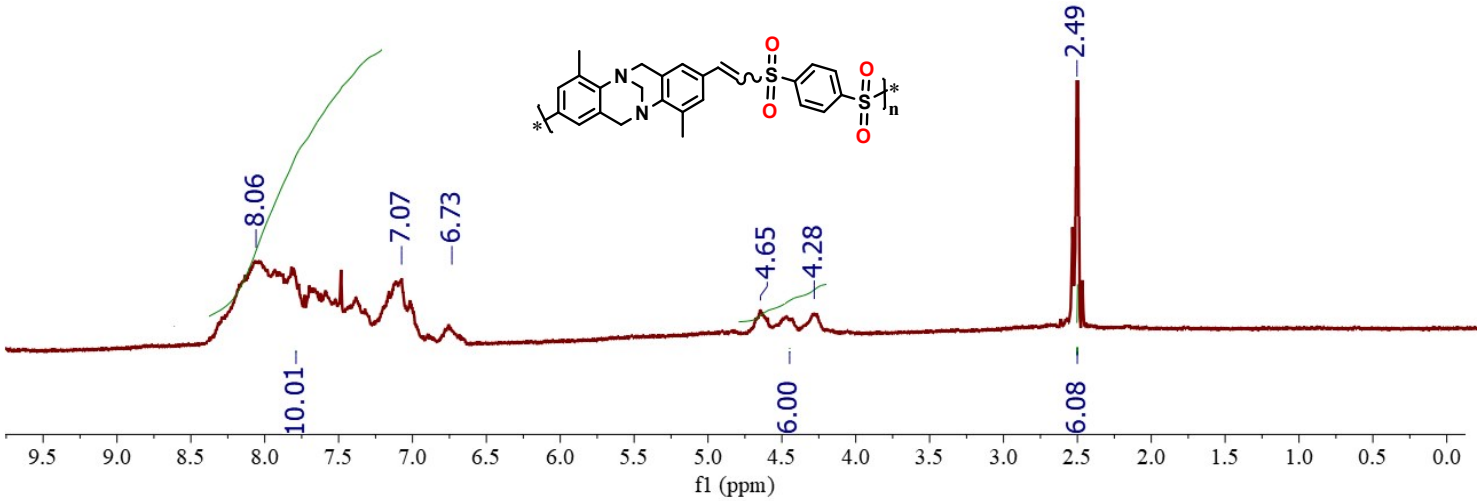


Figure S5: ^{1}H NMR spectrum of **TCP4** (DMSO-d_6, 600 MHz)

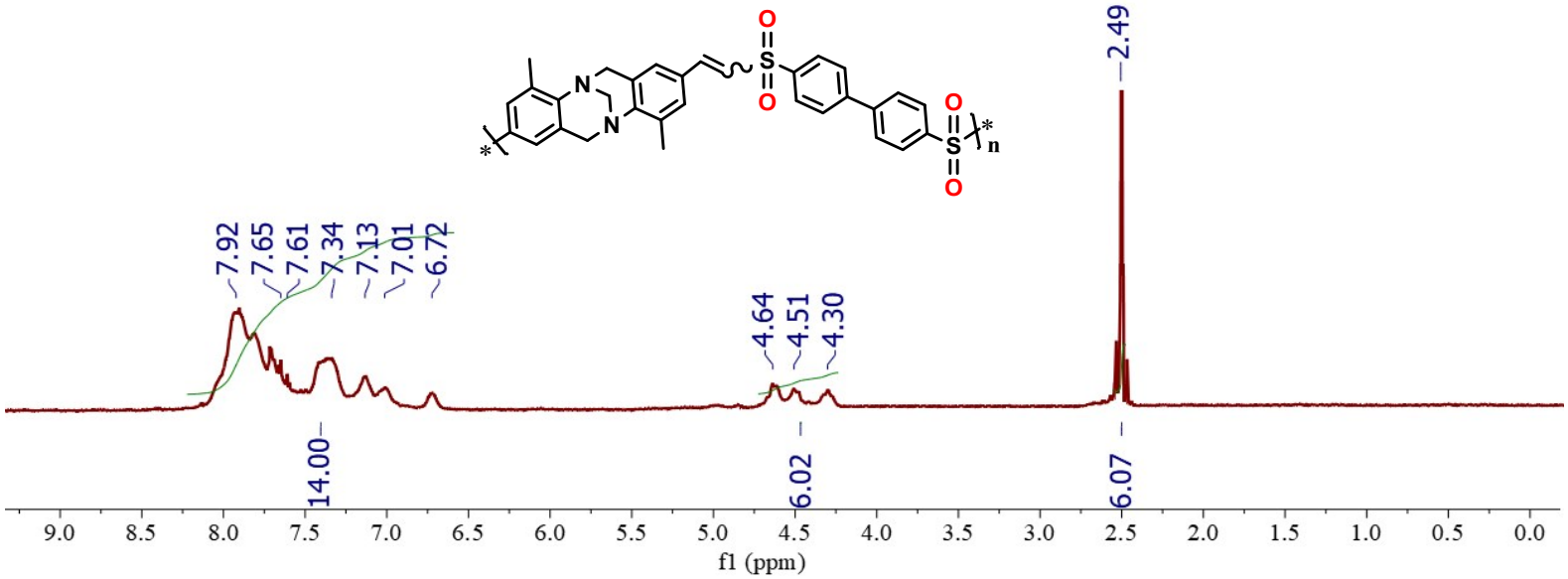


Figure S6: ^{1}H NMR spectrum of **TCP5** (DMSO-d_6, 600 MHz)

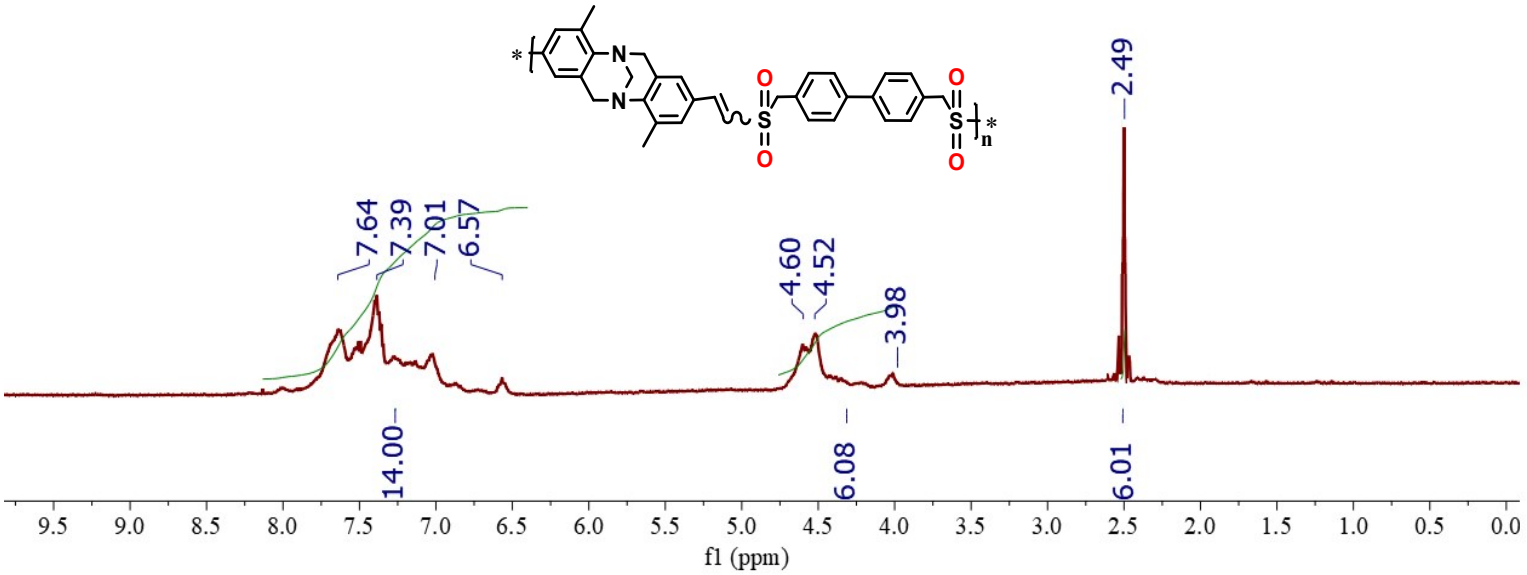


Figure S7: ^{1}H NMR spectrum of **TCP6** (DMSO-d_6, 600 MHz)

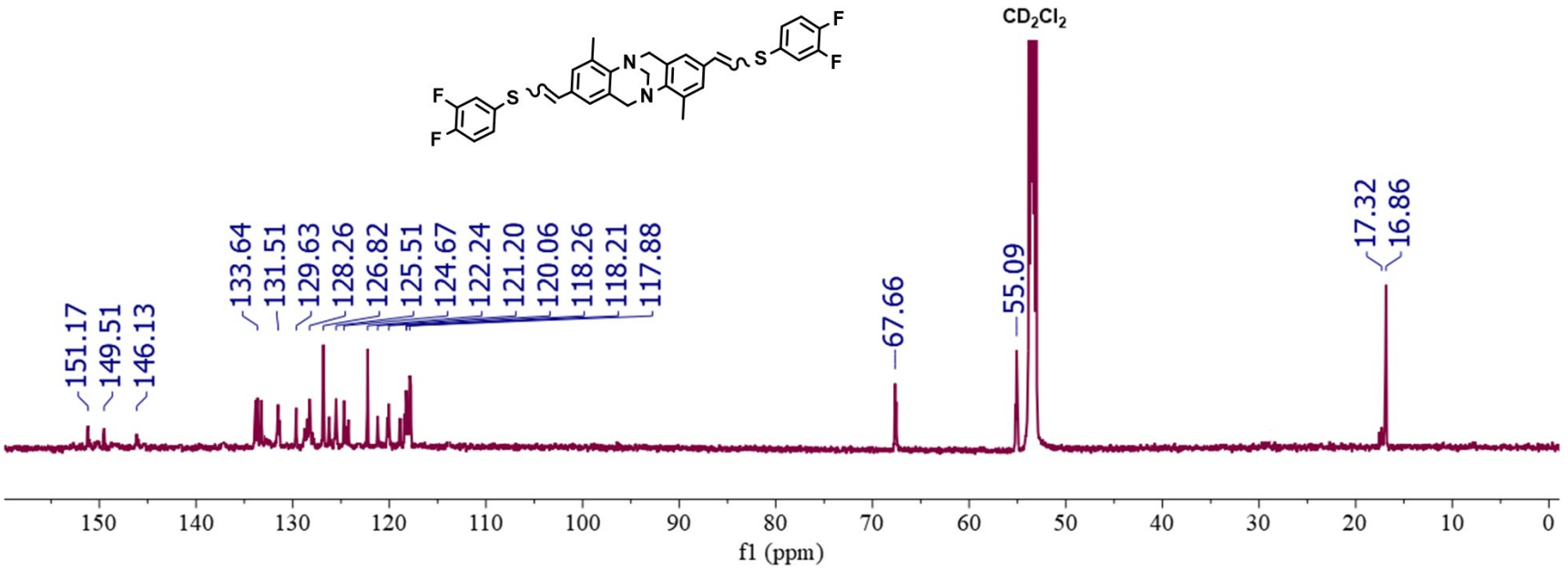


Figure S8: ^{13}C NMR spectrum of **TB-S** (CD_2Cl_2, 150 MHz)

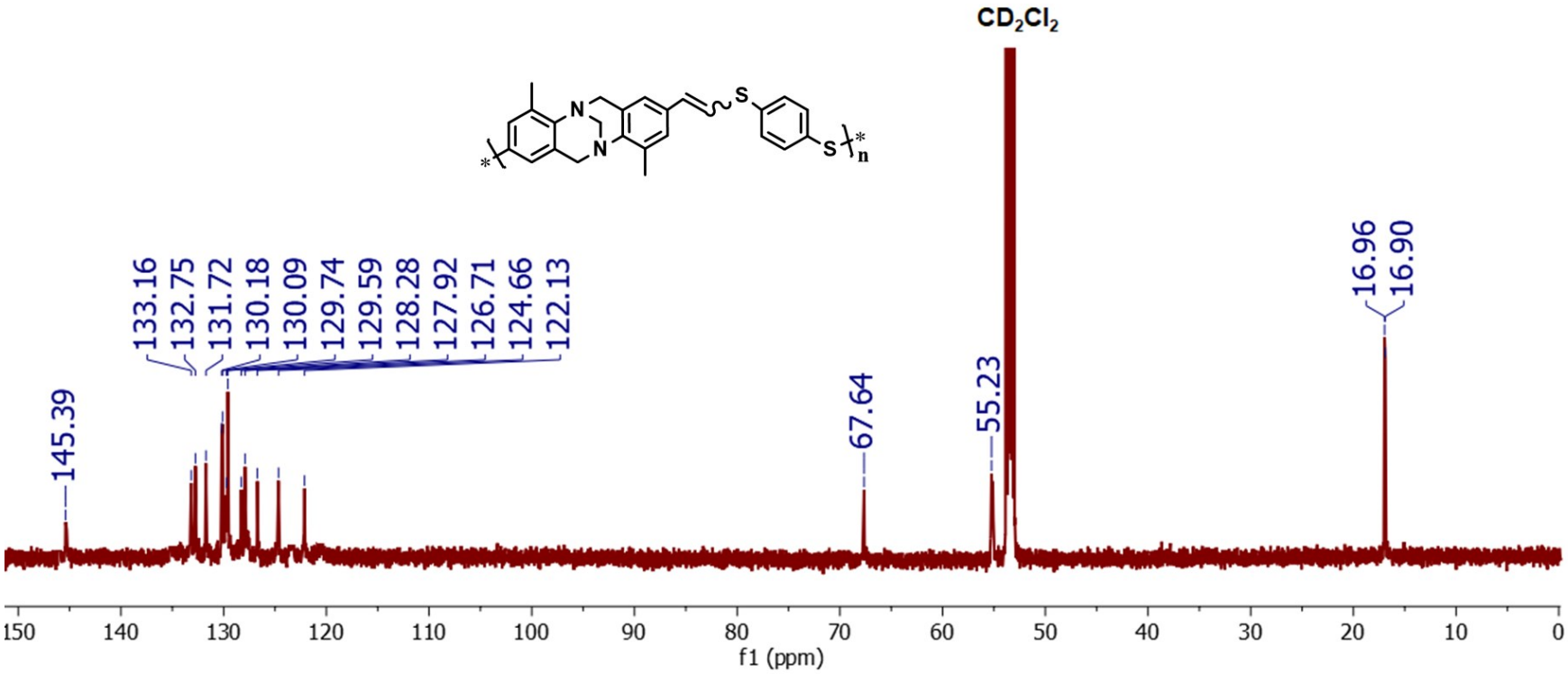


Figure S9: ^{13}C NMR spectrum of **TCP1** (CD_2Cl_2, 150 MHz)

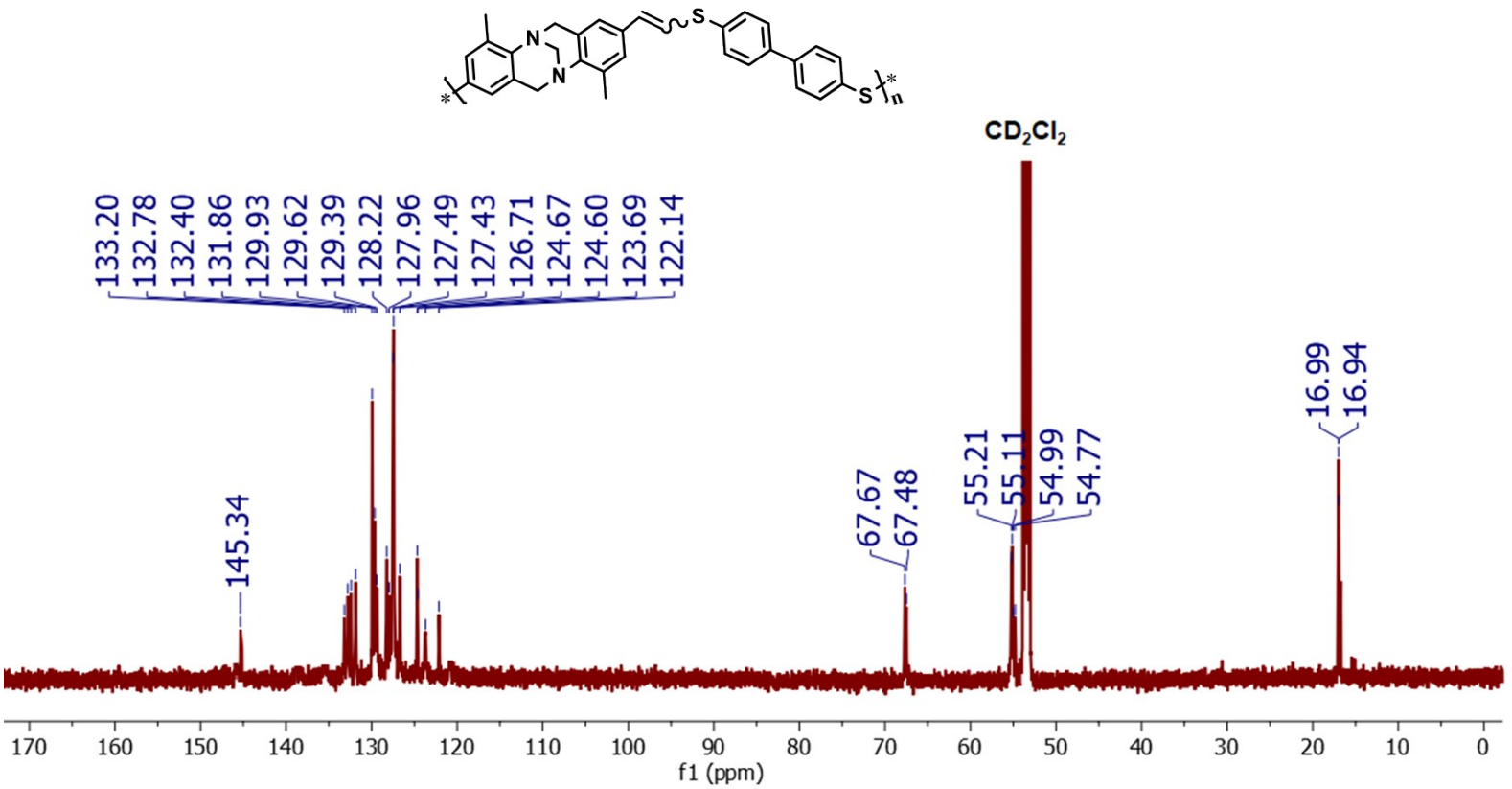


Figure S10: ^{13}C NMR spectrum of **TCP2** (CD_2Cl_2, 150 MHz)

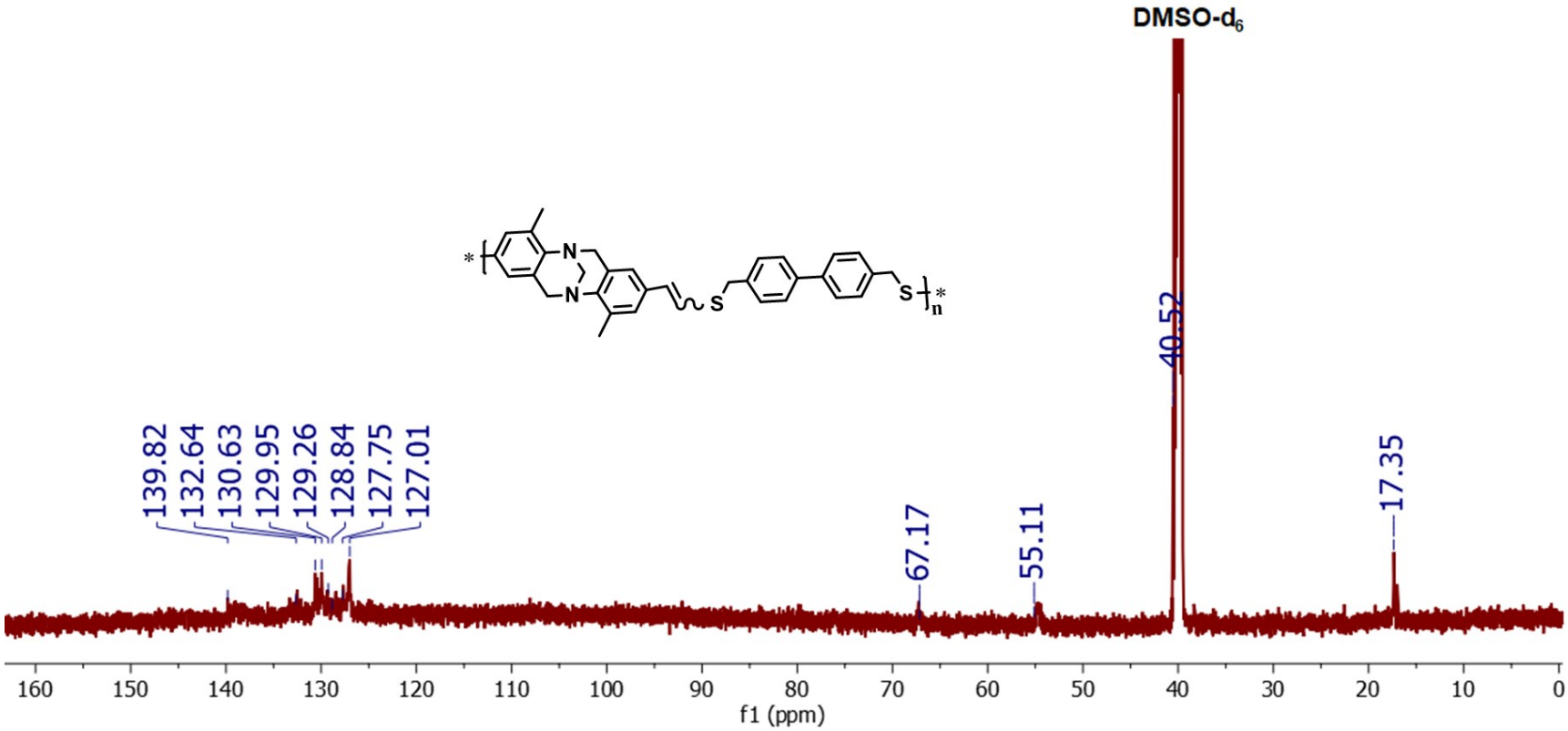


Figure S11: ^{13}C NMR spectrum of **TCP3** (DMSO-d_6, 150 MHz)

Mn = 2840
Mw = 8675
Đ = 3.0

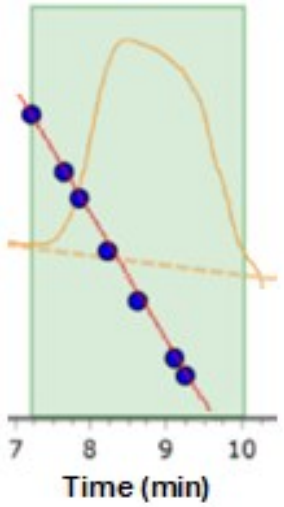


Figure S12: GPC of **TCP1**

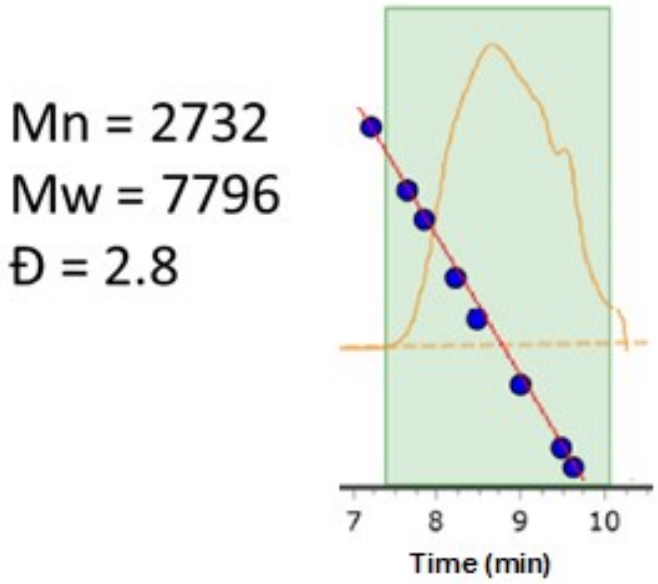


Figure S13: GPC of **TCP2**

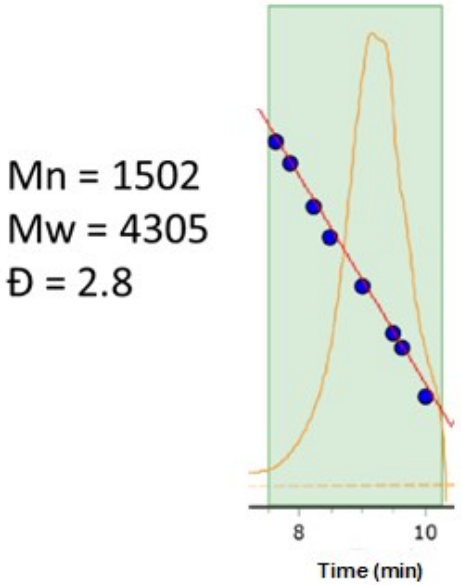


Figure S14: GPC of **TCP3**

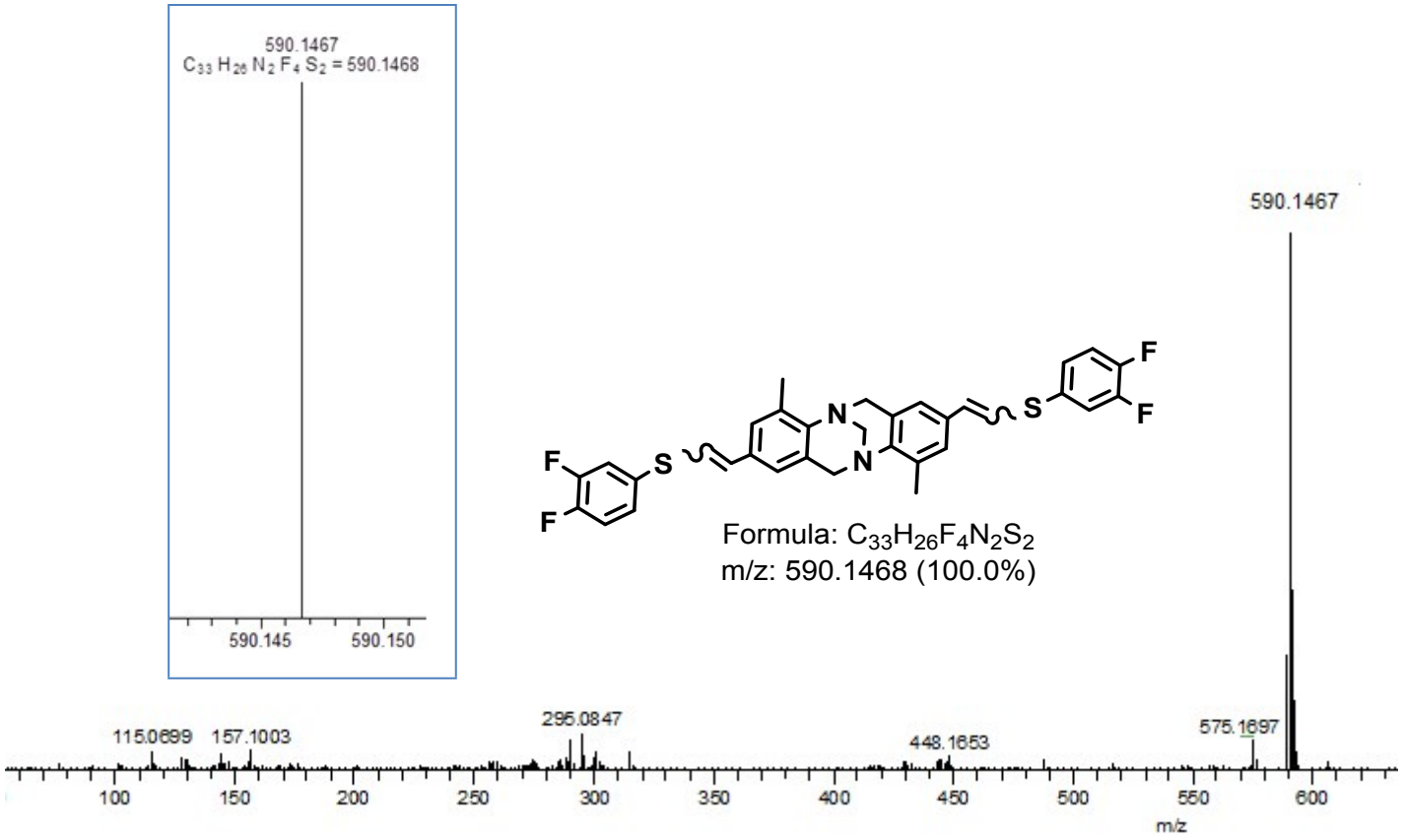
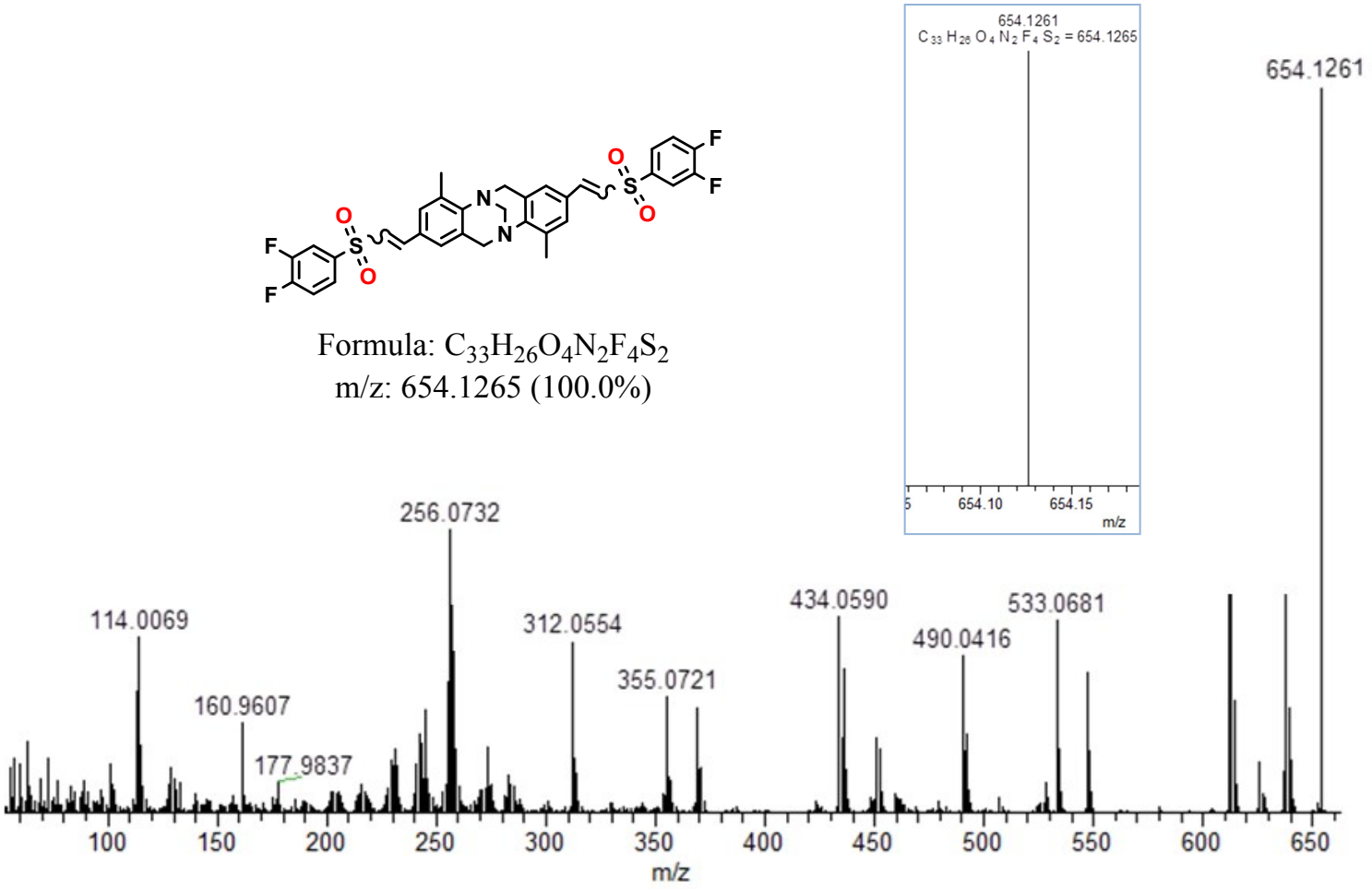


Figure S15: EI-HRMS of **TB-S**



Formula: $C_{33}H_{26}O_4N_2F_4S_2$
m/z: 654.1265 (100.0%)

Figure S16: EI-HRMS of **TB-SO2**

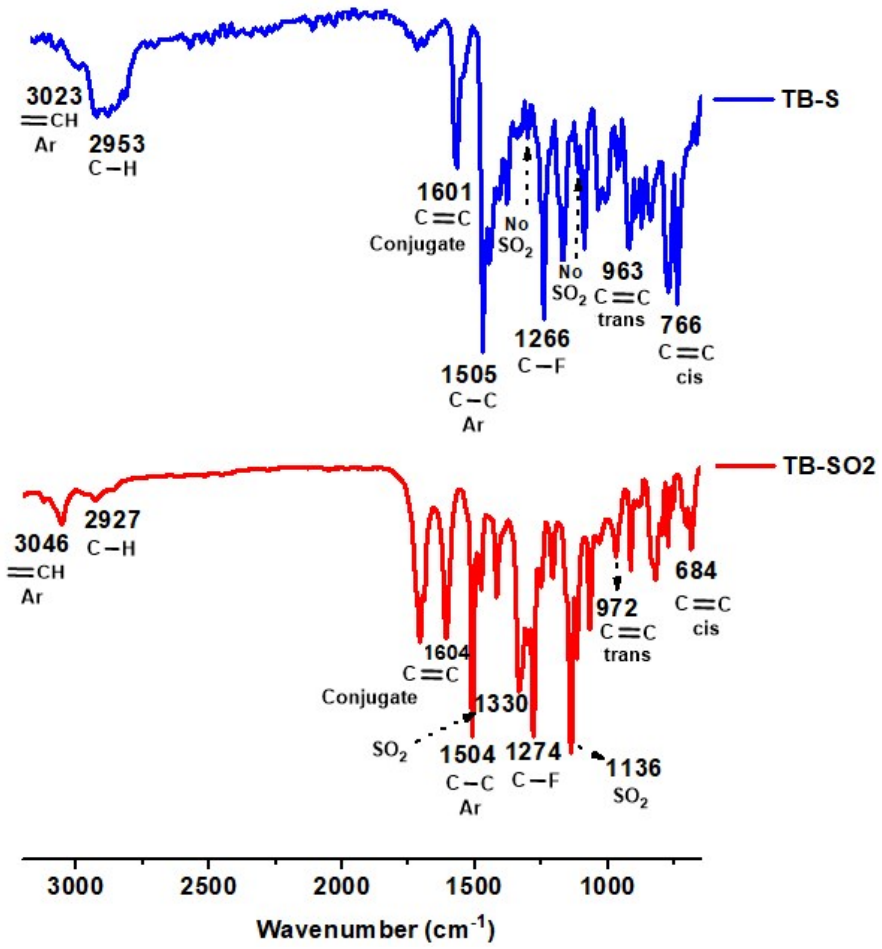


Figure S17: Comparative FT-IR spectra of **TB-S** and **TB-SO2**

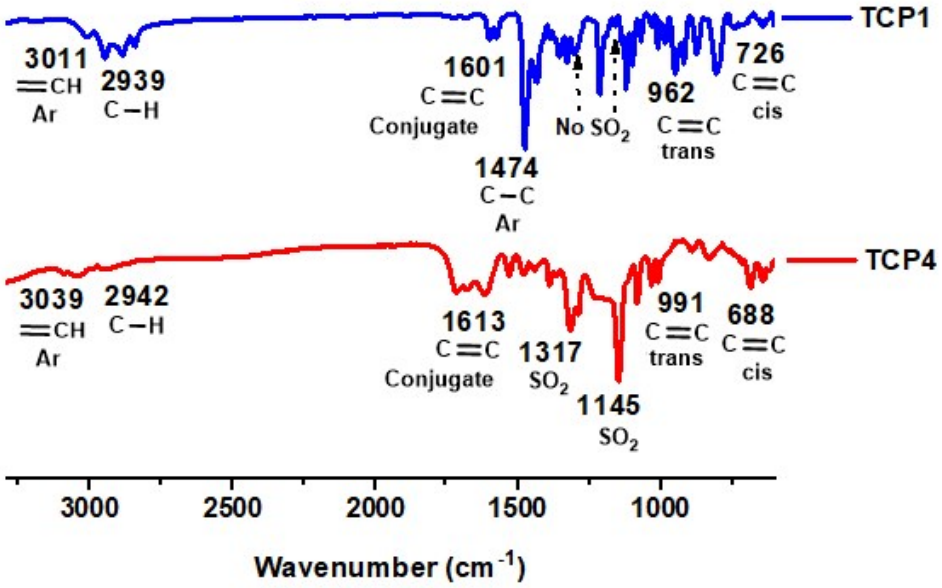


Figure S18: Comparative FT-IR spectra of **TCP1** and **TCP4**

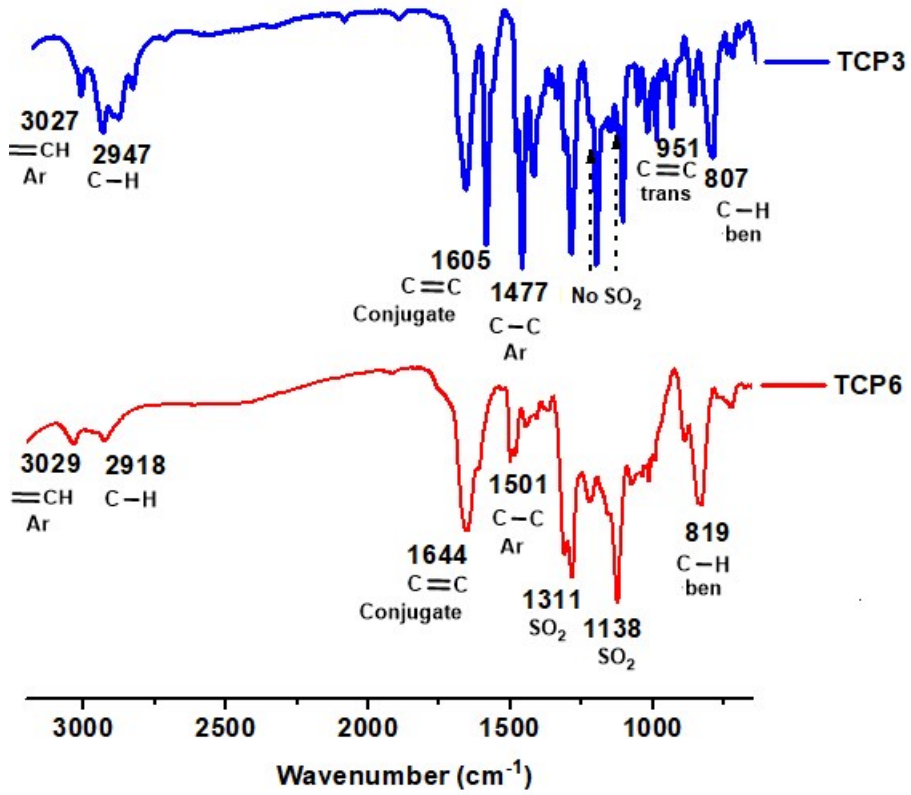


Figure S19: Comparative FT-IR spectra of **TCP3**,**6**

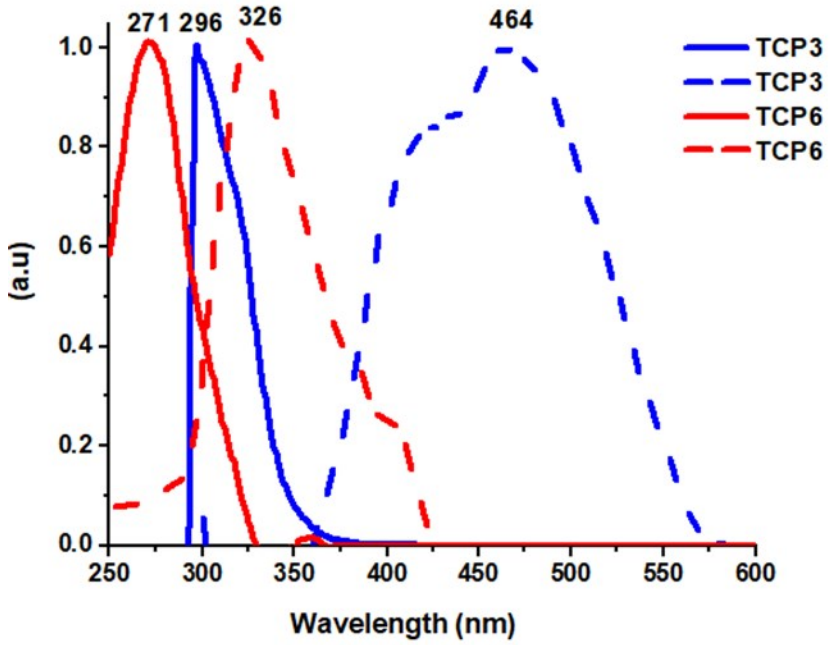


Figure S20: Normalized UV-VIS absorption ($C_M = 10^{-7}$ M in THF, solid lines) and emission ($C_M = 10^{-8}$ M in THF, dotted lines) spectra of **TCP3,6** (absorption maxima were used as the excitation wavelengths).

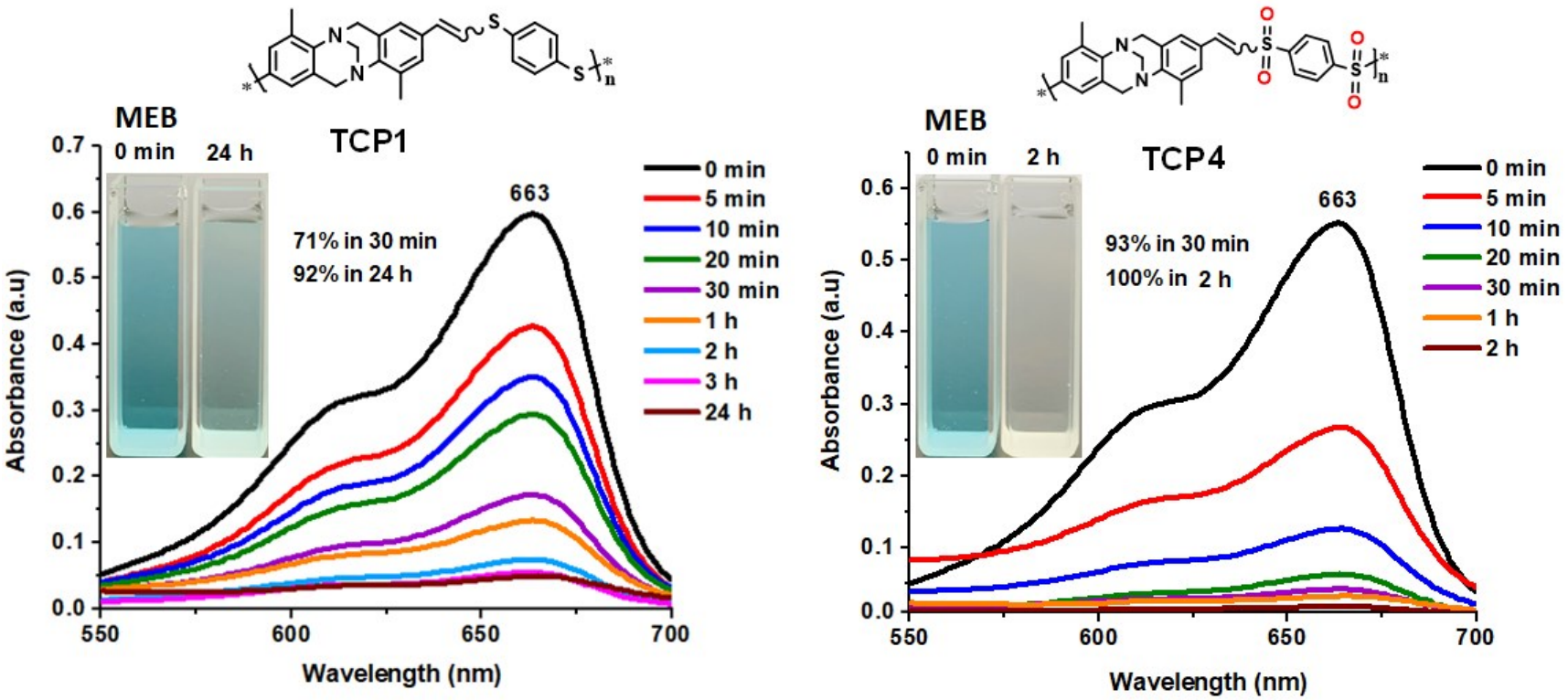


Figure S21: Methylene blue (MEB) dye adsorption by **TCP1,4** at various time intervals

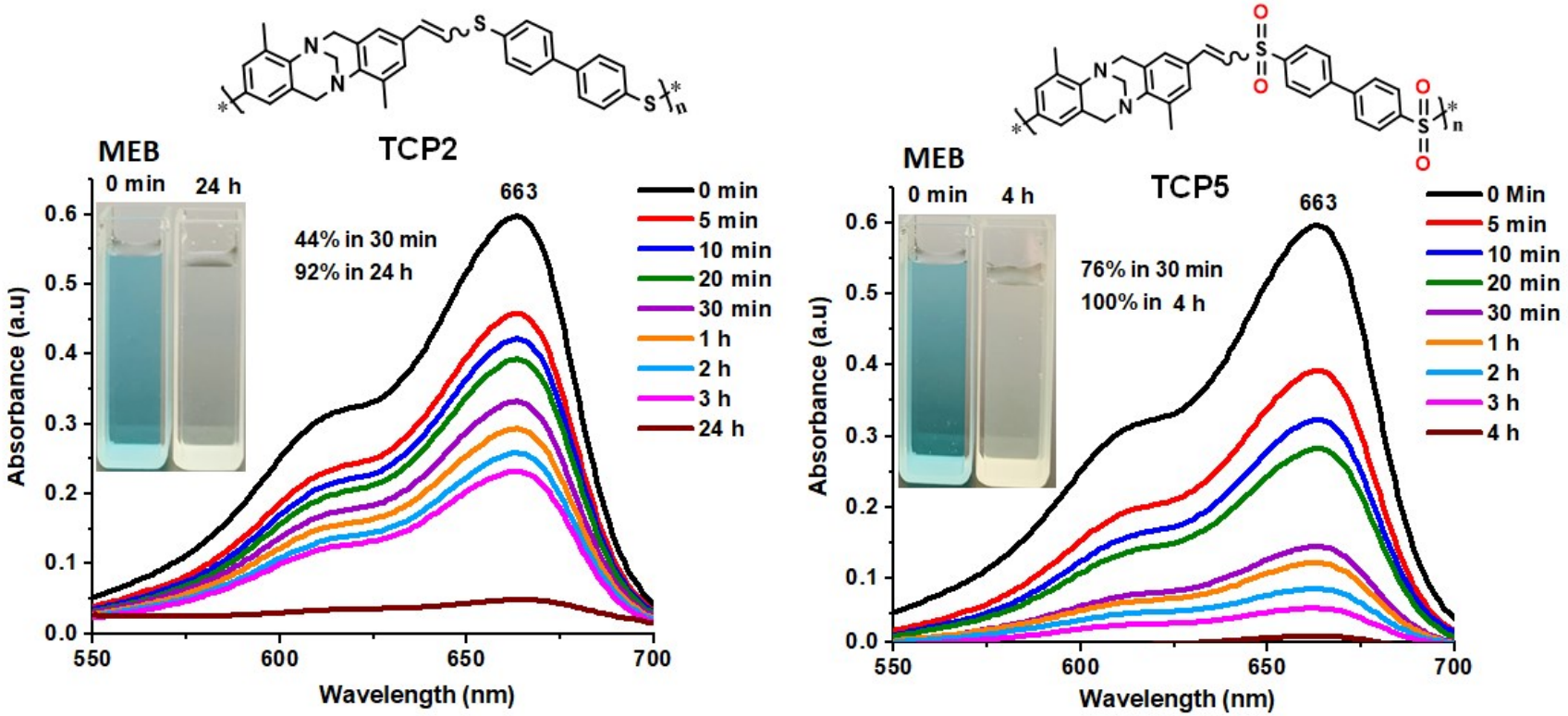


Figure S22: Methylene blue (MEB) dye adsorption by **TCP2,5** at various time intervals

Table S1 Summary of dye adsorption by copolymers **TCP1-6**

Entry	Adsorbent	Dye	% Adsorption	Time
1	TCP1	CR	27	24 h
2	TCP1	MO	5	24 h
3	TCP1	MB	45	24 h
4	TCP1	MEB	71	30 min
5	TCP1	MEB	92	24 h
6	TCP2	MEB	44	30 min
7	TCP2	MEB	92	24 h
8	TCP3	MEB	25	30 min
9	TCP3	MEB	45	24 h
10	TCP4	MEB	93	30 min
11	TCP4	MEB	100	2 h
12	TCP5	MEB	76	30 min
13	TCP5	MEB	100	4 h
14	TCP6	MEB	84	30 min
15	TCP6	MEB	100	4 h

Table S2 Comparison of percentage removal of MEB with different adsorbents

Entry	Adsorbent	% Removal	Ref
1	Tröger Base-Containing Sulfone Copolymers	100	This work
2	GO-HBE/PES membrane	85.9	M. Mahmoudian *et. al.*, *Polymer*, 2021, **224**, 123693.
3	Chitosan cross-linked graphene oxide/lignosulfonate composite	>99	M. Yan, *et. al.*, *International Journal of Biological Macromolecules*, 2019, **136**, 927-935.
4	Chitosan-derived three-dimensional porous carbon	>93.4	Q. Jin, *et. al.*, *RSC Advances*, 2018, **8**, 1255-1264.
5	PSf/GO membrane	84	L. Badrinezhad, S. *et. al.*, *Polymer Bulletin*, 2018, **75**, 469-484.
6	GO-PDADMC/PSf membrane	63	M. G. Kochameshki, *et. al.*, *Chemical Engineering Journal*, 2017, **309**, 206-221.

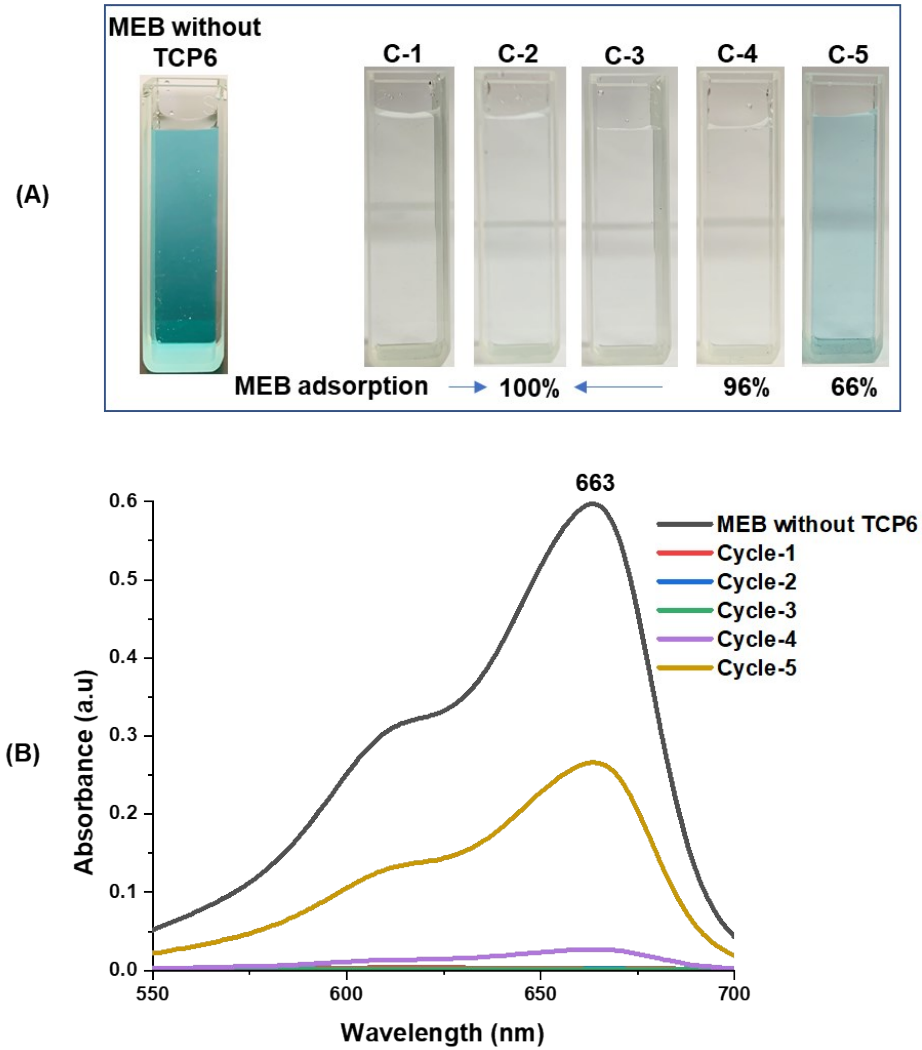


Figure S23: Reusability of **TCP6** on Methylene blue (MEB) dye adsorption up to 5 cycles(C1-5): (A) photographs showing the color change up on each cycle (B) UV-Vis spectrum after each cycle