

Efficient mercury removal in 30 seconds by designing a dithiocarbamate-based organic polymer with customizable functionalities and tuneable properties

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Table of Contents

1. Materials and Methods.....	S2
2. Synthesis of building block (chloroacetylated diamides)	S2
3. Synthesis of DTC-OP	S4
4. Characterization of DTC-OP	S5
4.1 EDAX spectrum.....	S5
4.2 Elemental analysis	S7
4.3 Physisorption studies	S8
4.4 SEM analysis	S9
4.5 XRD studies.....	S10
4.6 Differential scanning calorimetry analysis	S11
4.7 Elasticity studies	S11
5. Hg ²⁺ adsorption studies.....	S12
5.1 SEM analysis	S12
5.2 EDAX spectrum.....	S12
5.3 Hg ²⁺ adsorption studies by ICP-OES	S12
5.4 Competitivity studies	S13
5.5 pH studies.....	S13
5.6 Adsorption studies using spin column	S13
5.6.1 Removal of 400 ppm Hg ²⁺	S13
5.6.2 Hg ²⁺ removal from real water samples	S14

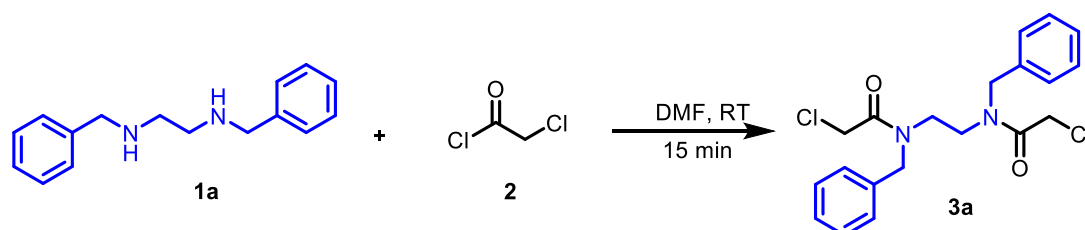
1. Materials and Methods

All the chemicals were purchased from Sigma Aldrich, Alfa Aeser, Spectrochem and TCI and used without further purification. ^1H NMR spectra were recorded on Bruker AV III 500 MHz and the data were analyzed by MestReNova (version 8.1.1). ^1H NMR shifts are reported in units of ppm relative to tetramethyl silane. Fourier Transformed IR Spectroscopy (FT-IR) was recorded in Shimadzu IR Tracer 100 in KBr pellet method and spectra were plotted in OriginPro 8.5.1. SEM images were taken using Carl Zeiss - Gemini SEM 300 with 2000000 X magnification. The quantitative analysis of mercury was done using inductively coupled plasma-optical emission spectroscopy (ICP-OES) instrument (Perkin Elmer Optima 5300 DV). Thermal gravimetry analysis was carried out in Perkin Elmer Inc Thermal Analyzer STA 8000, Differential scanning calorimetry was performed in NETZSCH DSC 204F1 Phoenix. X-Ray diffraction studies were carried out in Rigaku XRD Smart lab, 9 kW system. The rheometric analysis was carried out in Ares G2, TA instruments. Physisorption analysis was carried out in Quantachrome ASi Qwin , version 5.21.

2. Synthesis of building block (chloroacetylated diamides)

Chloroacetylated diamides (**3a** and **3b**) were synthesized from the reaction of diamines (**1a** and **1b**) and chloroacetyl chloride in the solvent DMF under room temperature. The reaction was monitored by TLC in 7:3 system of ethyl acetate and hexane and visualized under UV light. After completion of reaction (15 min), the excess chloroacetyl chloride was quenched by the addition of sodium bicarbonate solution until the evolution of CO_2 ceased. The reaction mixture was extracted by ethyl acetate and water and the organic layer was passed through anhydrous Na_2SO_4 . The solvent was removed under low pressure and the product was obtained with high purity (98 %).

Based on the above procedure:



Scheme S1. Synthesis of **3a**.

N, N'-dibenzylethylene 1,2 diamine, **1a** was taken in 15 ml DMF and chloroacetyl chloride was added very slowly to afford **3a**; white solid (Yield = 770 mg, 98 %). ^1H NMR (500MHz, CDCl_3) spectrum of **3a**: δ (ppm) 3.63 (s, 4H), 4.07 (s, 4H), 4.68 (s, 4H), 7.16-7.42 (m, 10H) and '*' represents the residual solvent peak of internal standard tetramethyl silane.

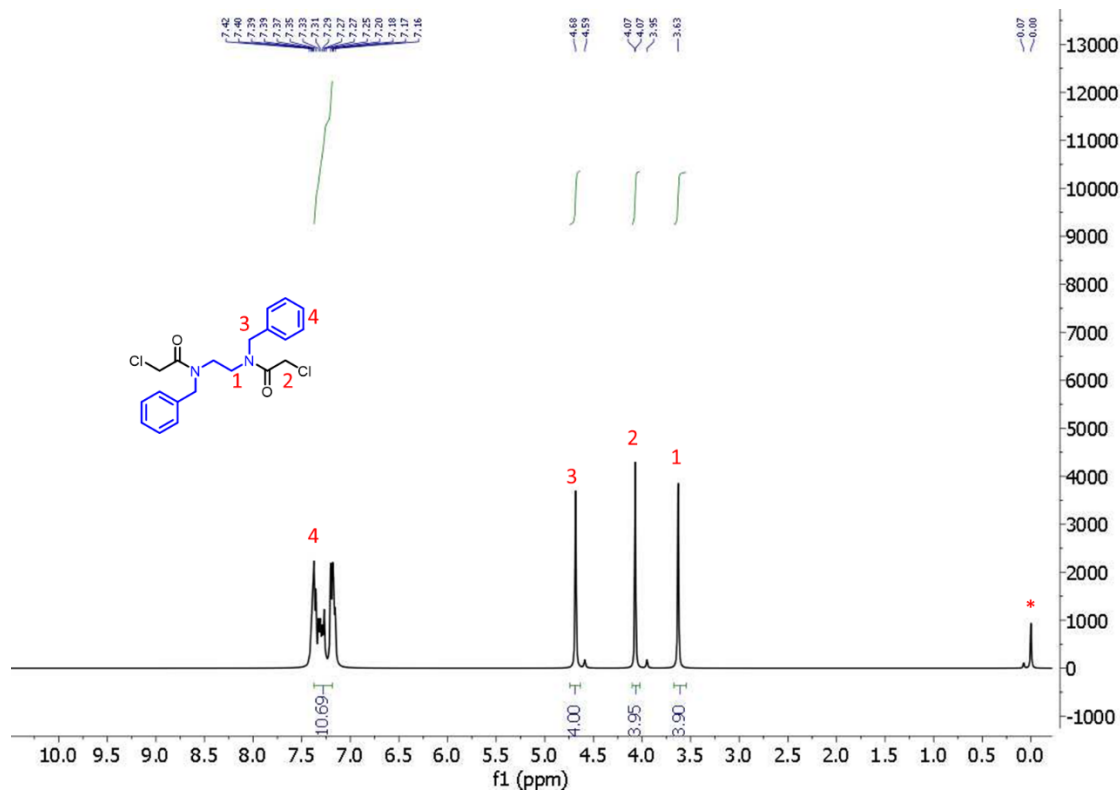
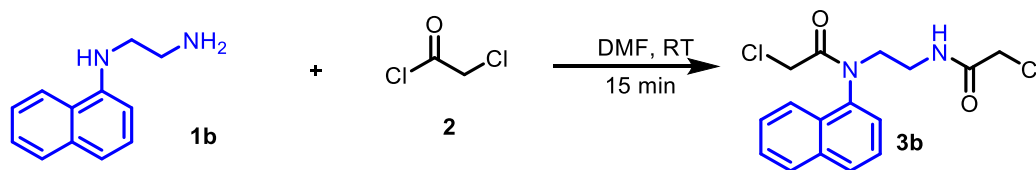


Figure S1. ^1H NMR (500MHz, CDCl_3) spectrum of **3a**.



Scheme S2. Synthesis of **3b**.

N-naphthyl ethylene diamine, **1a** was taken in 15 ml DMF and chloroacetyl chloride was added very slowly to afford **3b**; white solid (Yield = 800 mg, 96 %). ^1H NMR (400MHz, CDCl_3) spectrum of **3b**: δ (ppm) 3.71 (t, 2H), 3.88 (t, 3H), 4.10 (s, 4H), 7.35-7.98 (m, 7H) and ‘*’ represents the residual solvent peak of internal standard tetramethyl silane.

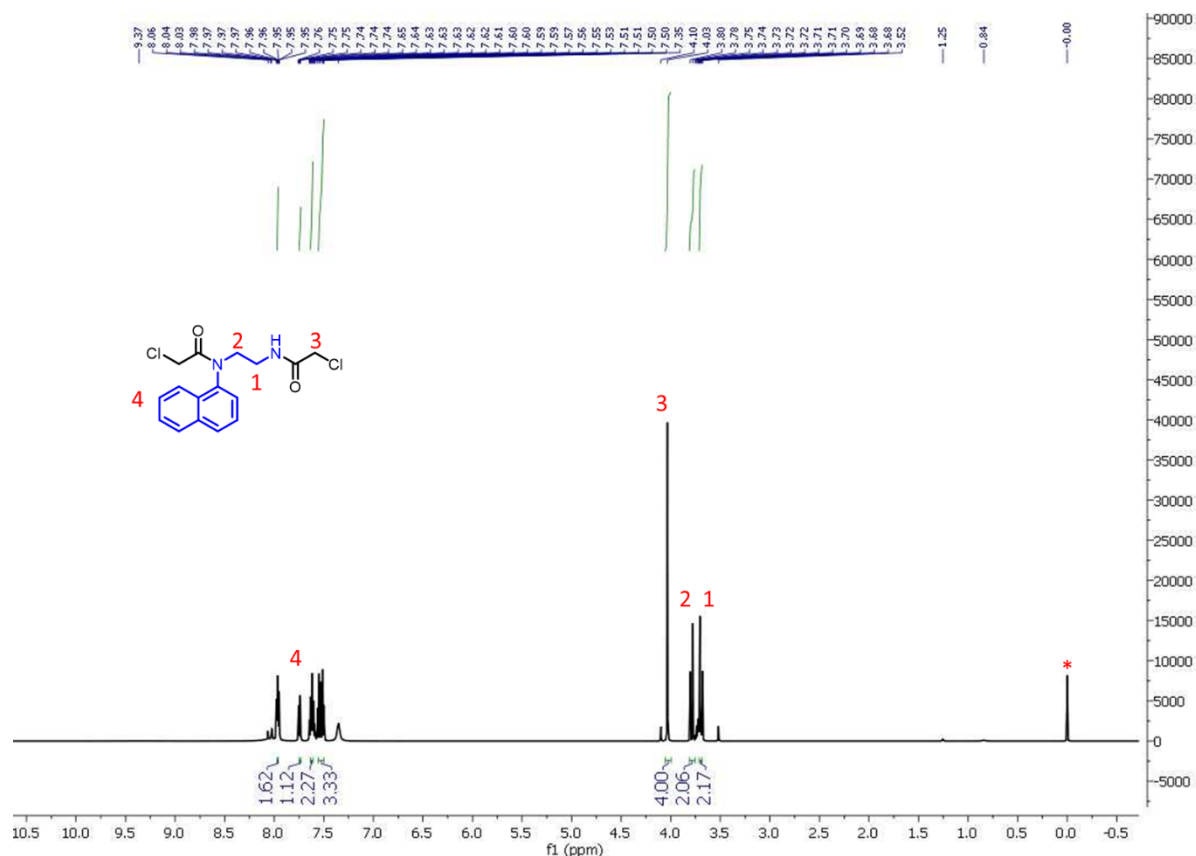


Figure S2. ¹H NMR (500MHz, CDCl₃) spectrum of **3b**

3. Synthesis of DTC-OP

The chloroacetylated diamides (**3a** and **3b**) were dissolved in the solvent PEG-200 and carbon disulfide followed (8 mmol, 8 eq.) by diamines (**5**) was added very slowly. The reaction is exothermic. After 15 minutes, the consumption of chloroacetylated diamide was confirmed by TLC eluted in 70% ethyl acetate and water. The reaction was quenched with water and ethyl acetate was added to this. A precipitate of DTC-OP was formed and was filtered through Whatman filter paper and washed many times with water and ethyl acetate until the organic layer is free from any compounds. The product is dried in hot air oven to give the DTC-OP.

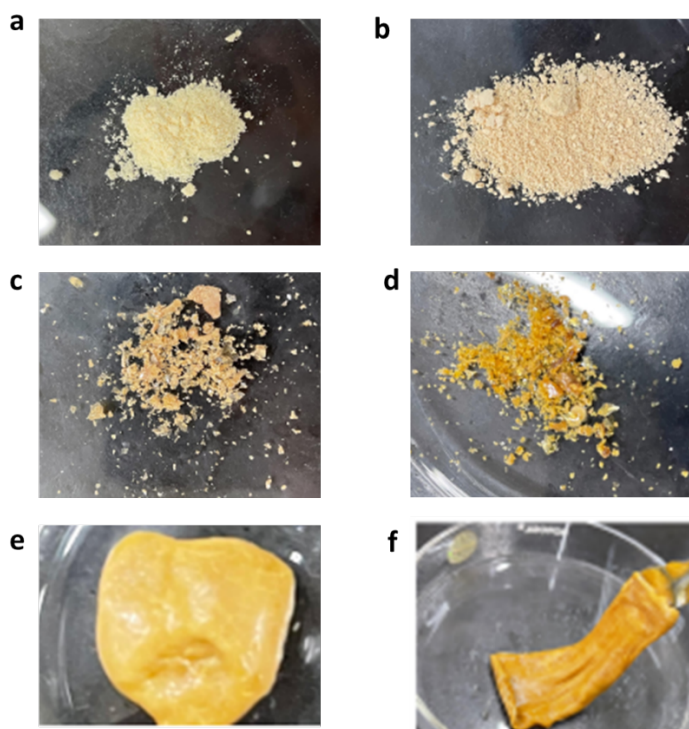
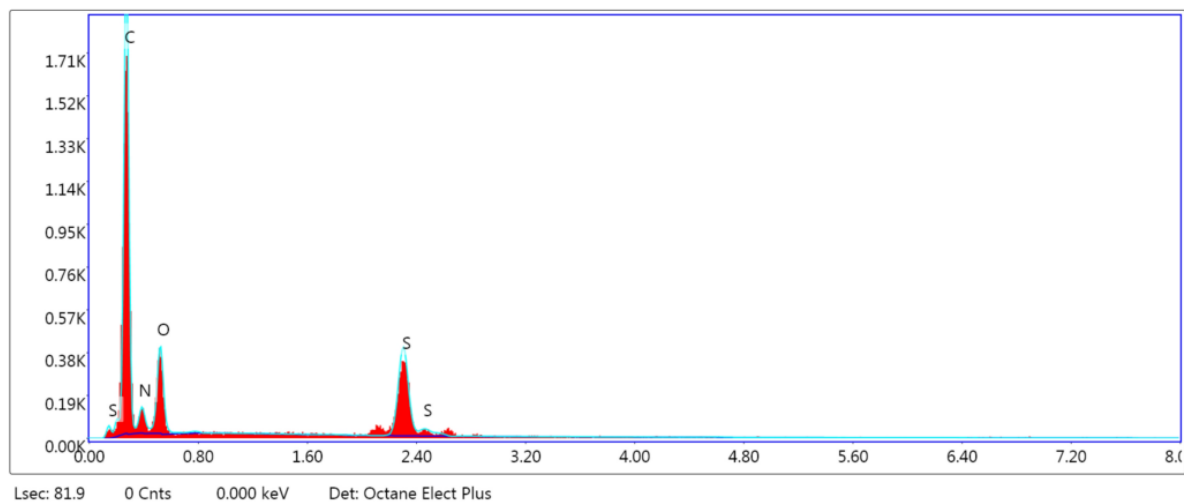


Figure S3. Photographs of a) DTC-OP1 b) DTC-OP2 c) DTC-OP3 d) DTC-OP4 e) DTC-OP3 before drying and f) DTC-OP4 before drying

4. Characterization of DTC-OP

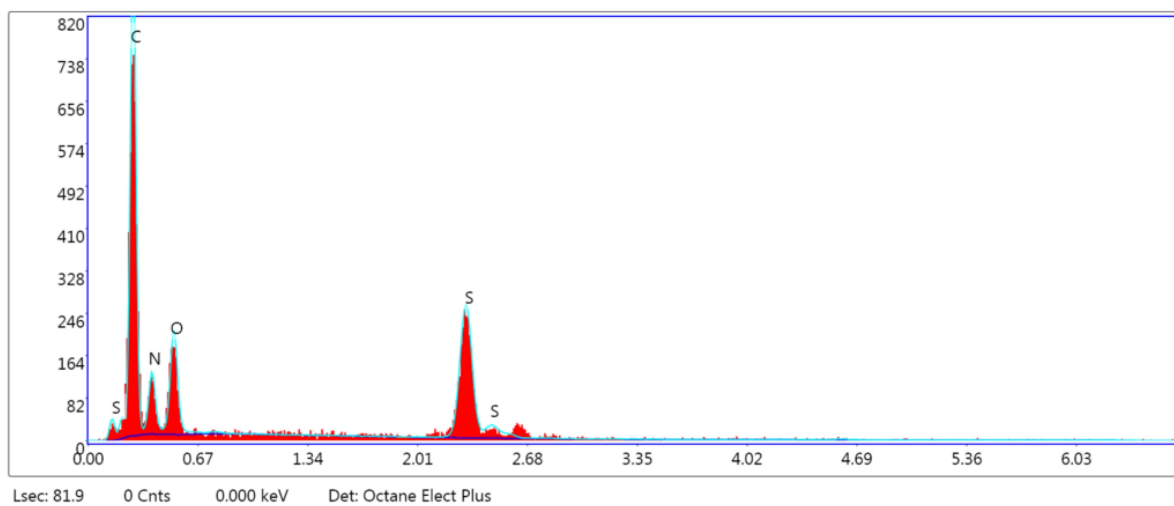
4.1 EDAX spectrum



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	66.77	75.85	122.40	8.51	0.2875	1.0298	0.4181	1.0000
N K	8.06	7.85	5.80	25.54	0.0113	1.0004	0.1405	1.0000
O K	13.09	11.16	23.70	14.16	0.0325	0.9751	0.2547	1.0000
S K	12.08	5.14	45.80	4.20	0.1031	0.8469	1.0029	1.0049

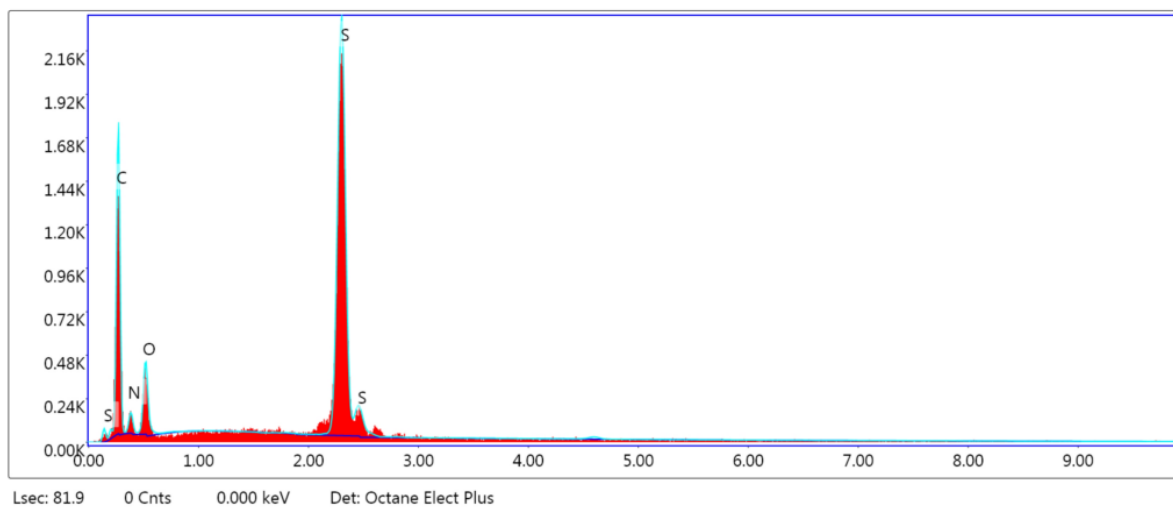
Figure S4. EDAX spectrum of DTC-OP1.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	57.87	69.30	54.10	9.67	0.2335	1.0457	0.3859	1.0000
N K	12.44	12.77	6.90	18.75	0.0263	1.0143	0.2088	1.0000
O K	10.25	9.21	12.40	14.76	0.0344	0.9873	0.3403	1.0000
S K	19.45	8.72	30.40	5.06	0.1664	0.8512	1.0021	1.0033

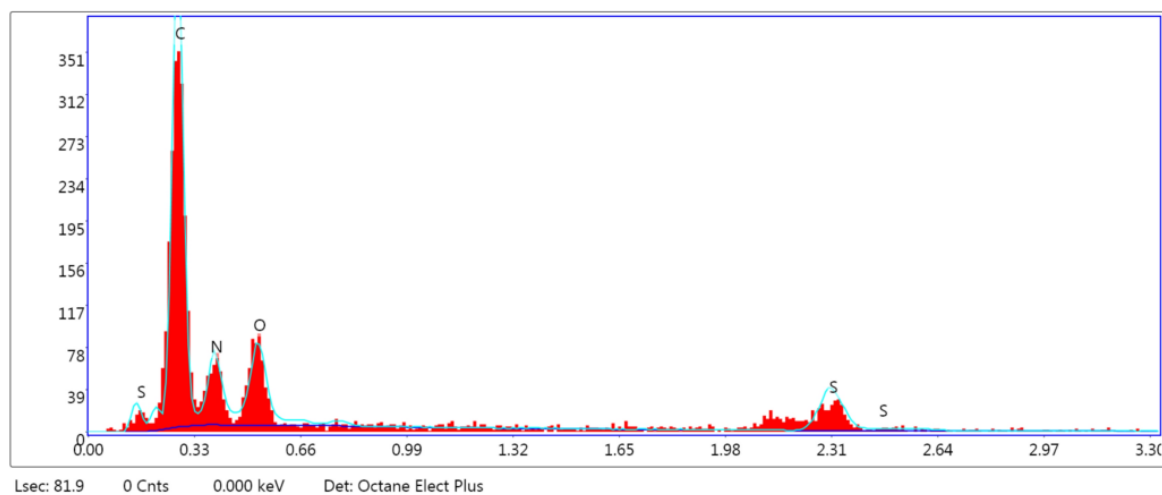
Figure S5. EDAX spectrum of DTC-OP2.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	58.32	72.54	85.00	10.85	0.1133	1.0478	0.1854	1.0000
N K	6.48	6.91	6.30	20.36	0.0065	1.0206	0.0981	1.0000
O K	8.86	8.28	23.00	13.65	0.0158	0.9971	0.1784	1.0000
S K	26.34	12.27	256.10	2.30	0.2320	0.8759	1.0034	1.0024

Figure S6. EDAX spectrum of DTC-OP3.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
CK	55.44	69.79	27.70	10.14	0.3648	1.0742	0.6125	1.0000
NK	9.77	10.54	3.80	22.22	0.0515	1.0352	0.5089	1.0000
OK	6.88	6.50	4.40	22.47	0.0465	1.0022	0.6744	1.0000
SK	27.91	13.16	4.50	15.80	0.2342	0.8358	1.0016	1.0022

Figure S7. EDAX spectrum of DTC-OP4.

4.2 Elemental analysis

Table S1. Elemental analysis (EA) of DTC-OP. (There is a deviation in the elemental %, which is expected for such polymers due to the change in elemental % because of the trapped adsorbates including gases and water (Liu, G., Wang, Y., Shen, C., Ju, Z., & Yuan, D. *Journal of Materials Chemistry A*, **2015**, 3(6), 3051-3058.)

Material	Element	Expected %	Observed % by EA
DTC-OP1	N	7.54	5.3
	C	64.6	55.3
	S	17.26	8.55
DTC-OP2	N	9.05	9.27
	C	58.22	54.3
	S	20.72	18.2
DTC-OP3	N	9.48	16.98
	C	56.92	38.47
	S	21.7	35.6
DTC-OP4	N	10.44	10.72
	C	53.7	51.79
	S	23.89	22.05

4.3 Physisorption studies

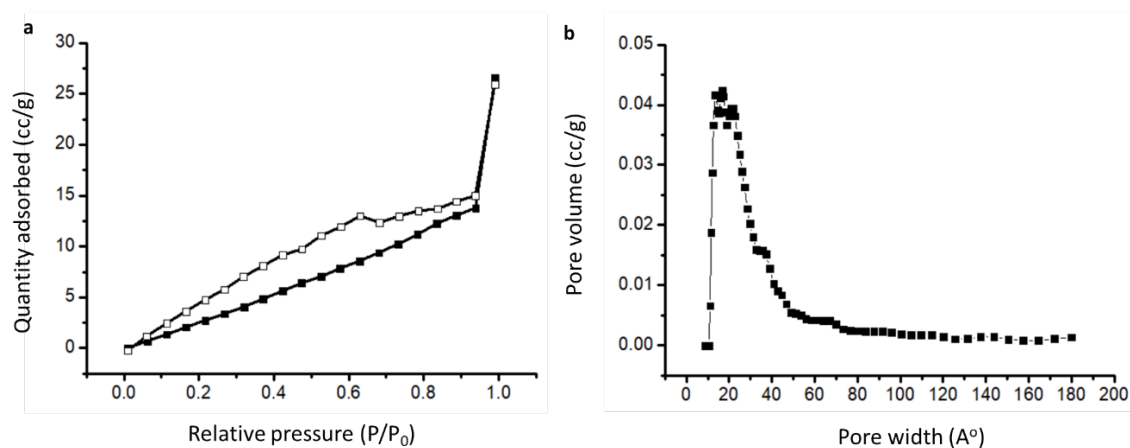


Figure S8. a) Nitrogen sorption isotherm of DTC-OP2 at 77 K. The solid shapes represent adsorption, and the hollow shapes represent desorption. b) NLDFT pore size distribution of DTC-OP2.

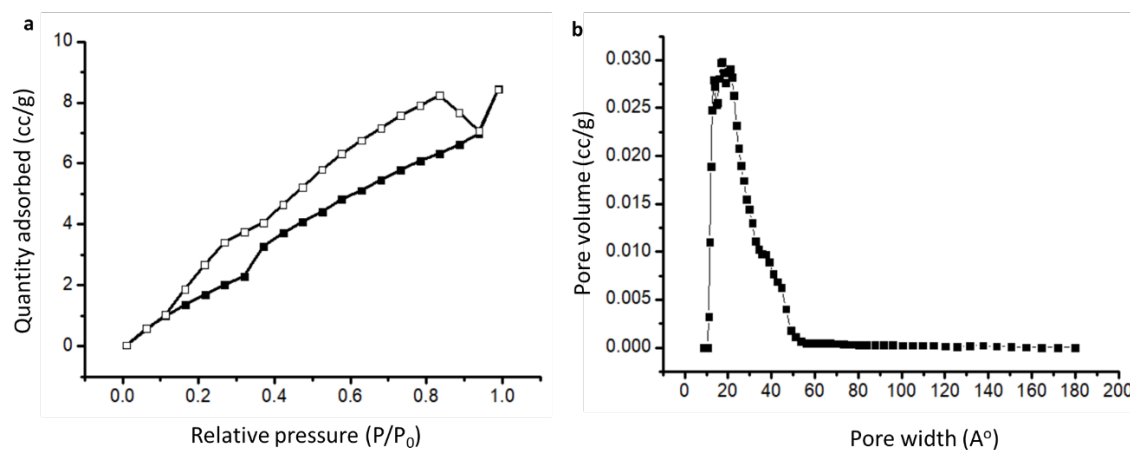


Figure S9. a) Nitrogen sorption isotherm of DTC-OP3 at 77 K. The solid shapes represent adsorption, and the hollow shapes represent desorption. b) NLDFT pore size distribution of DTC-OP3.

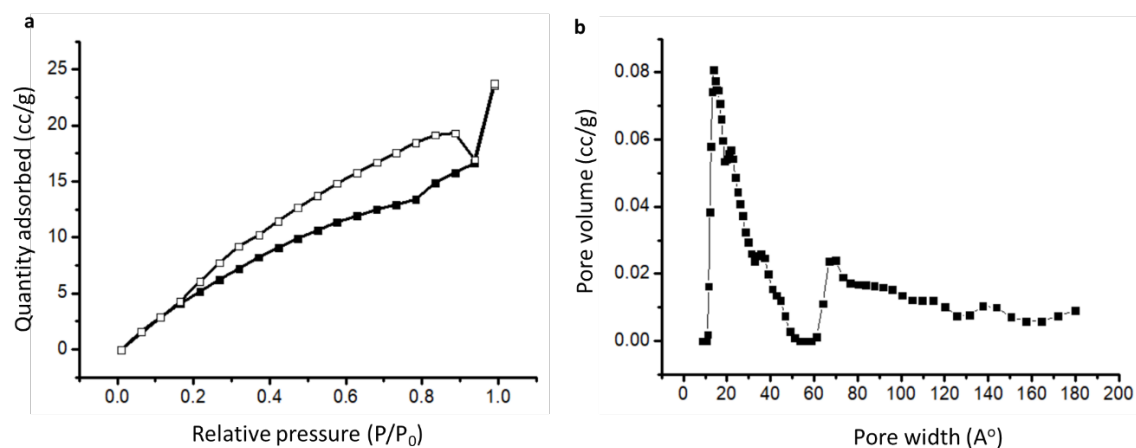


Figure S10. a) Nitrogen sorption isotherm of DTC-OP4 at 77 K. The solid shapes represent adsorption, and the hollow shapes represent desorption. b) NLDFT pore size distribution of DTC-OP1.

4.4 SEM analysis

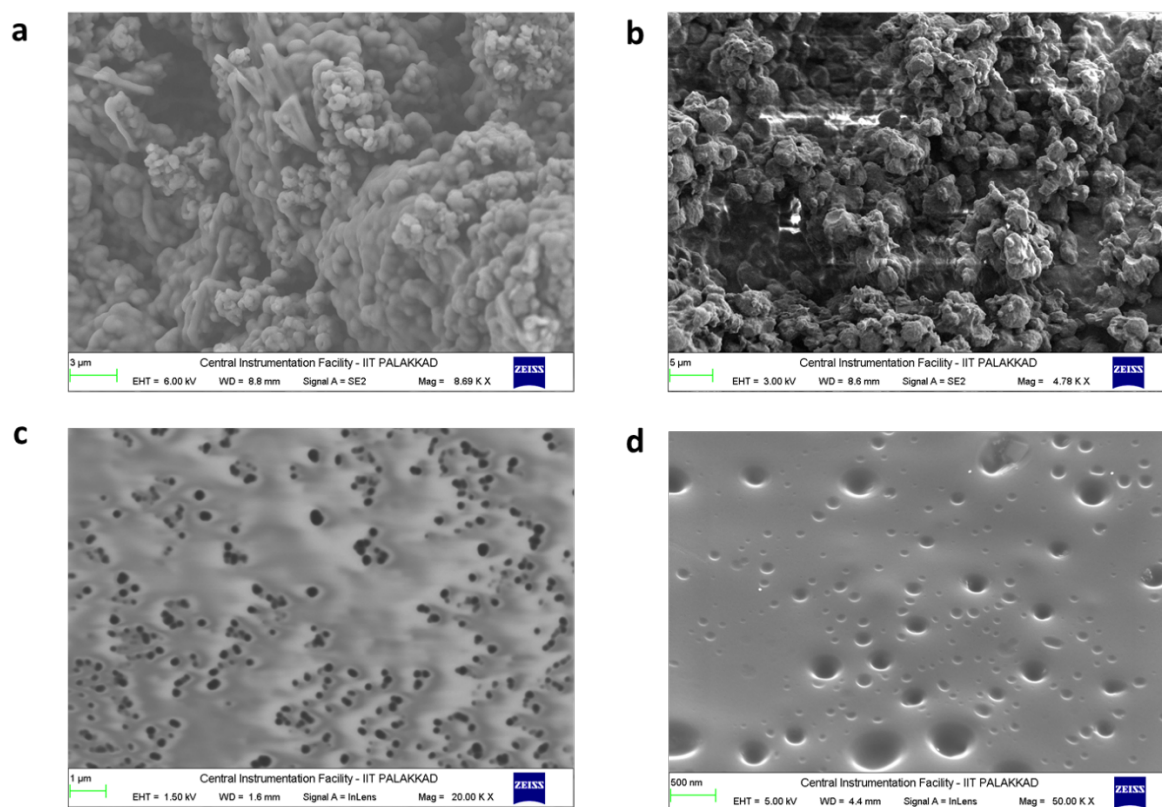


Figure S11. SEM images of a) DTC-OP1 b) DTC-OP2 c) DTC-OP3 and d) DTC-OP4

4.5 XRD studies

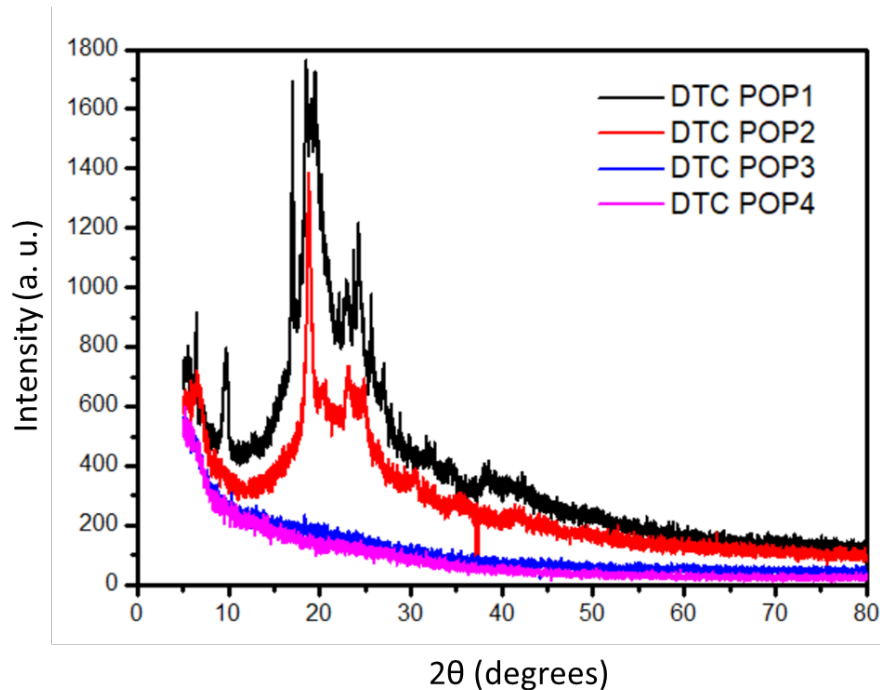


Figure S12. X-ray diffraction patterns of DTC-OP. DTC-OP1 and DTC-OP2 showed semi-crystalline nature and DTC-OP3 and DTC-OP4 showed amorphous properties.

The crystallinity index of each material was calculated by the equation below and the values are tabulated.

$$\text{Crystallinity index} = \frac{\text{Area of crystalline peaks}}{\text{Area of all the peaks}}$$

Table S2. Crystallinity index of DTC-OP based on the XRD data

Polymer	Crystallinity index
DTC-OP1	37.99
DTC-OP2	32.78
DTC-OP3	19.68
DTC-OP4	20.62

4.6 Differential scanning calorimetry analysis

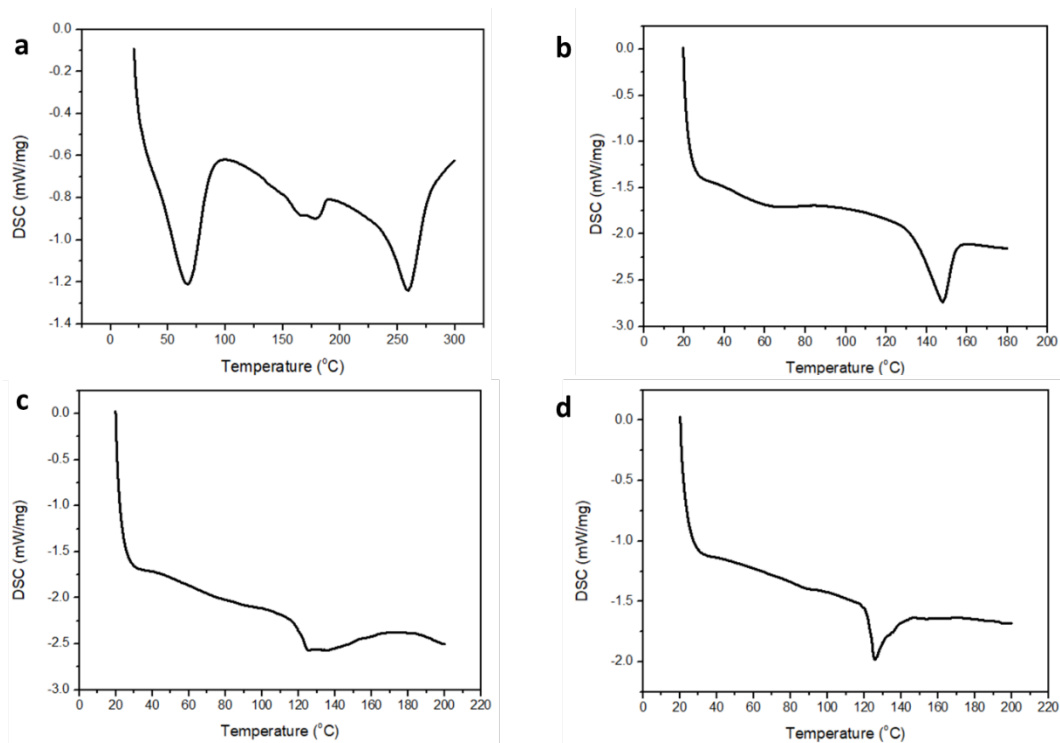


Figure S13. Differential scanning calorimetry plot of **a)** DTC-OP1 **b)** DTC-OP2 **c)** DTC-OP3 and **d)** DTC-OP4

4.7 Elasticity studies

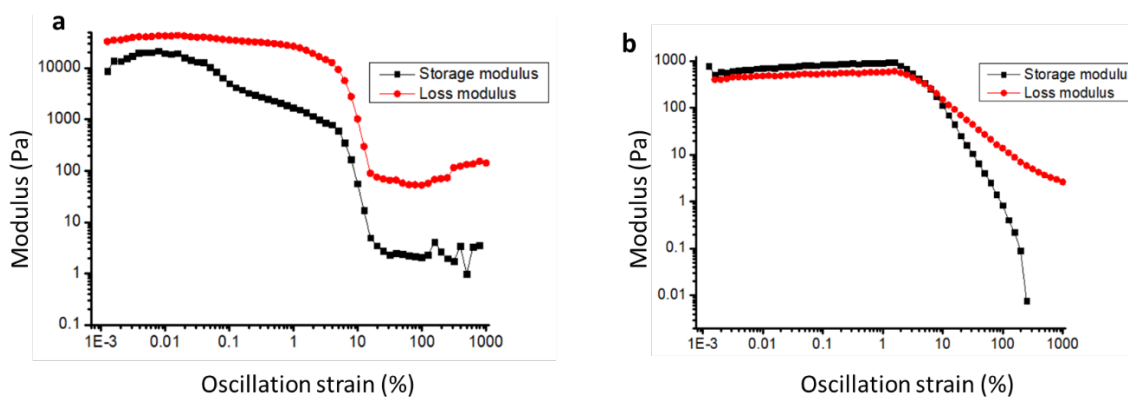


Figure S14. Elasticity properties of **a)** DTC-OP3 (5.01 % and 5.79 % are the oscillation strain at the breakdown point of loss modulus and storage modulus respectively) and **b)** DTC-OP4 (2.21 % and 1.81 % are the oscillation strain at the breakdown point of loss modulus and storage modulus respectively)

5. Hg²⁺ adsorption studies

5.1 SEM analysis

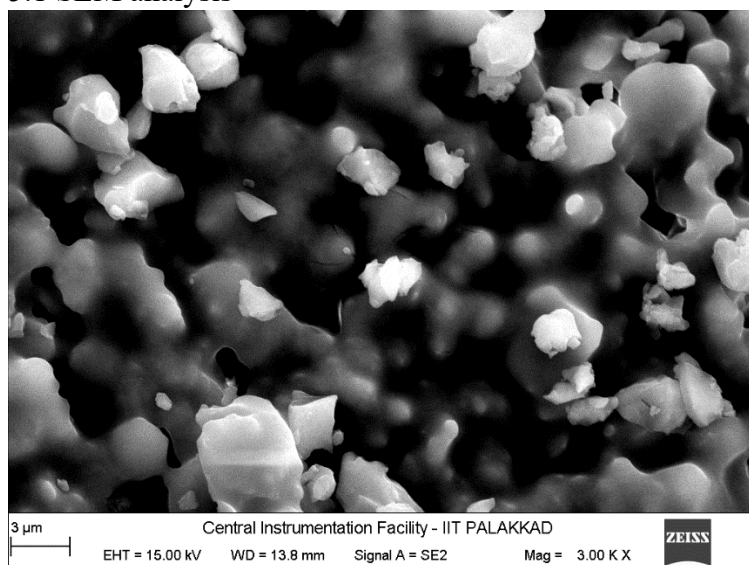
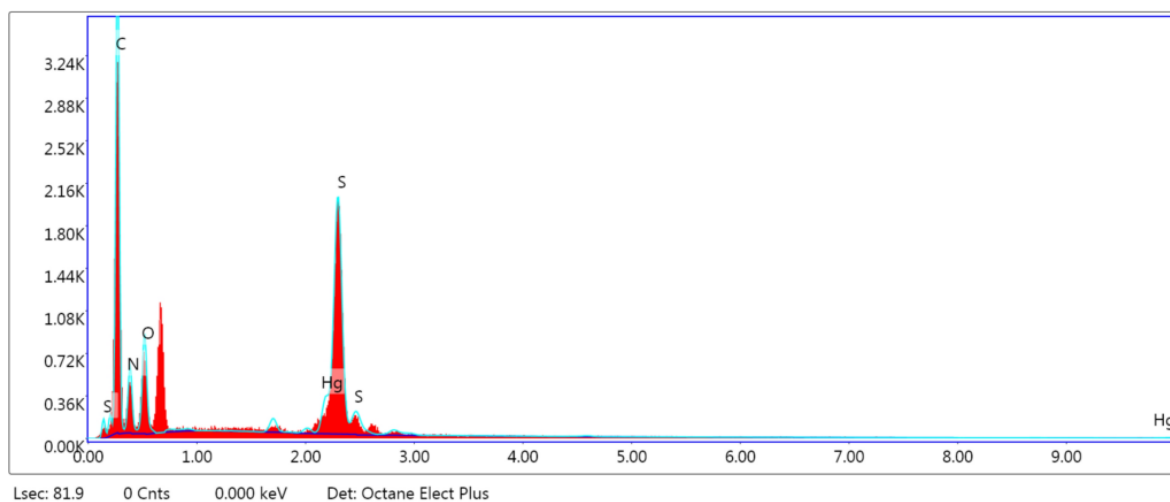


Figure S15. SEM image of DTC-OP2 with Hg²⁺ adsorbed. (Ref: *a*) Duan, Y., Zhang, Y., Wang, F., Sun, Y., Chen, M., Jing, Z., ... & Peng, W. *Photonic Sensors*, **2022**, *12*(1), 23-30. *b*) Jose, A., Nanjan, P., & Porel, M. *Polymer Chemistry*, **2021**, *12*(36), 5201-5208.

5.2 EDAX spectrum



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
CK	54.38	66.22	211.70	9.00	0.1763	1.0512	0.3083	1.0000
NK	15.82	16.52	30.10	14.10	0.0193	1.0241	0.1192	1.0000
OK	11.81	10.80	49.10	12.66	0.0210	1.0007	0.1776	1.0000
HgM	4.55	0.33	31.10	9.46	0.0373	0.5623	1.3027	1.1192
SK	13.43	6.13	205.70	2.63	0.1165	0.8802	0.9870	0.9986

Figure S16. EDAX spectrum of Hg²⁺ adsorbed DTC-OP2.

5.3 Hg²⁺ adsorption studies by ICP-OES

Table S2. % removal of Hg^{2+} by 5 mg of DTC-OP2 at various concentrations

Concentration of Hg^{2+} ions used (ppm)	% removal
50	99
100	99.68
200	99.85
300	99.15
400	99.92
500	94.66
800	64.65

From the above data, it was inferred that if 1 ppm Hg^{2+} was used with 5 mg of the material, the remaining concentration will be 1.5 ppb (approved for drinking purpose) which is not under the detection limit of the instrument. The approved maximum level of Hg^{2+} in the water can be achieved even in higher contaminated level water by increasing the load of material for adsorption.

5.4 Competitivity studies

Table S3. Competitivity of DTC-OP2 with various essential metals

Metal	% removal
Hg^{2+}	99.9%
Ca^{2+}	0%
K^{+}	2.8%
Na^{+}	0%

5.5 pH studies

Table S4. Hg^{2+} adsorption by DTC-OP2 in various pH

pH	% removal
4	99.8%
7	99.9%
11	99.9%

5.6 Adsorption studies using spin column

5.6.1 Removal of 400 ppm Hg^{2+}

% removal by DTC-OP2= 99.91 % (Calculated by ICP-OES)

% removal by DTC-OP1= 99.41 % (Even the least efficient among the 4 candidates showed good removal efficiency by spin column.



Figure S17. Photograph of the spin column apparatus loaded with DTC-OP2 and Hg²⁺ contaminated water

5.6.2 Hg²⁺ removal from real water samples

Table S5. Hg²⁺ removal from real water samples with DTC-OP2 using spin column

Sample	% removal
Lake water	98.1
Tap water	99.4