

SUPPORTING INFORMATION

Design and synthesis of tetralactam macrocycle-based porous organic polymers (POPs): application in the recovery of gold from e-waste

Ashish Kumar,^{†a} Gulshan Anjum^{†a} and Jarugu Narasimha Moorthy^{a,b*}

^a*Department of Chemistry, Indian Institute of Technology Kanpur, 208016, India*

^b*School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Trivandrum 695551, India*

[†]A. K. and G. A. contributed equally

*Corresponding Author; E-mail: moorthy@iitk.ac.in

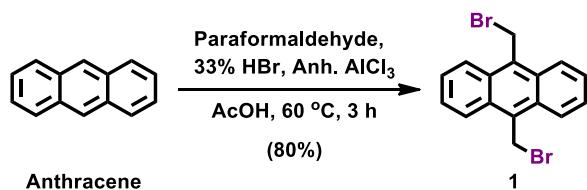
TABLES OF CONTENTS

1	General aspects	S2
2	Schemes S1-S10	S2-S10
3	pH Effect on gold adsorption	S10
4	Gold adsorption	S10
5	Metal selectivity	S11
6	Metal adsorption from electronic waste	S11
7	Recyclability	S12
8	¹ H NMR, ¹³ C NMR and HRMS spectra	S12-S20
9	Solid-state ¹³ C NMR of Mac-TMP	S21
10	Solid-state ¹³ C NMR of Mac-DMP	S21
11	DFT-optimized structure of Mac-TM and Mac-DM	S22
12	XPS plots of gold-loaded polymer Mac-TMP and Mac-DMP	S22-S23
13	TGA profiles of Mac-TMP and Mac-DMP ; Mac-TMP@Au and Mac-DMP@Au	S23
14	Langmuir and Freundlich isotherm models for adsorption of gold	S24
15	Comparison of the recovery of gold from e-waste with previously reported polymers.	S25
16	HRTEM images, interplanar spacing of Au particle and average size of the gold nanoparticles adsorbed on Mac-TMP@Au and Mac-TMP@Au	S26
17	Elemental mapping of Mac-TMP@Au and Mac-DMP@Au	S27
18	References	S27-S28

General aspects

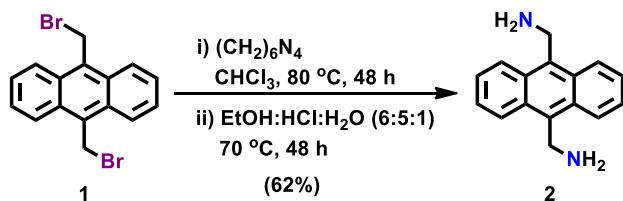
All the reagents were purchased from commercial sources and used without further purification. Freshly distilled solvents were used for the synthesis. Silica-gel column chromatography was performed for the purification of synthesized compounds. ^1H and ^{13}C NMR spectra were recorded on JEOL-Lambda spectrometers. Infrared (IR) spectra were recorded using a Bruker Vector 22 FT-IR spectrophotometer. High-resolution mass spectrometric (HR-MS) analyses carried out with ESI-QToF (Agilent 6546) instrument. Thermogravimetric analyses were performed with a heating rate of 10 °C/min through SDT-Q600TGA apparatus under N_2 atmosphere. Melting points were determined using a PERFIT melting point apparatus. Powder X-ray diffraction (PXRD) profiles were recorded on a PANalytical X'pert powder X-ray diffractometer. BET measurements were carried out with N_2 using Quantachrome Autosorb iQ automated gas sorption analyzer. The average pore size and average pore distributions were determined by NLDFT method using the N_2 sorption isotherms. Scanning electron microscope (SEM) images were recorded on a Nova Nano SEM 450. HR-TEM images were recorded on carbon-coated Cu grids with FEI Titan G2 60-300 HRTEM, operating at a voltage of 300 kV. XPS analyses were carried out with X-ray photoelectron spectroscopy module (PHI 5000 Versa Prob II, FEI Inc.).

Scheme S1. Synthesis of 9,10-Bis(bromomethyl)anthracene **1**¹



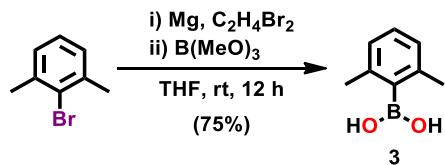
Anthracene (1.0 g, 5.6 mmol) and paraformaldehyde (0.674 g, 22.5 mmol) were dissolved in acetic acid (2.0 mL) in a round bottom flask. HBr (33.0%) in acetic acid (8.0 mL) was added dropwise over a period of 15 min followed by the addition of anhydrous AlCl_3 in a catalytic amount. The reaction mixture was heated at 60 °C for 3 h with constant stirring. After completion of the reaction, it was cooled to rt and quenched with ice. The resultant solid was filtered and washed thoroughly with distilled water and dried in vacuo. The product was recrystallized in toluene to afford a yellow solid, 1.6 g (yield, 80%). ^1H NMR (400 MHz, CDCl_3) δ 5.5 (s, 4H), 7.65-7.68 (m, 4H), 8.35-8.37 (m, 4H).

Scheme S2. Synthesis of 9,10-Bis(aminomethyl)anthracene **2**¹



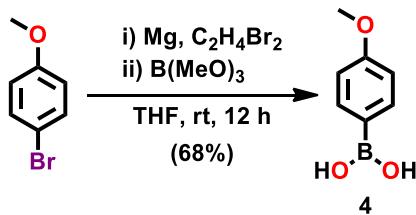
An oven-dried round-bottomed flask was charged with 9,10-bis(bromomethyl)anthracene (1.0 g, 2.7 mmol) and anhyd. CHCl_3 (100 mL). To the resultant solution was added hexamethylenetetramine (1.0 g, 7.1 mmol) in small portions, and the resulting reaction was heated at reflux for 48 h. At the end of this period, the reaction mixture was allowed to cool and the precipitate formed was collected by filtration, washed with chloroform and dried in open air. The air-dried precipitate was then suspended in a mixture of ethanol (130 mL), water (20 mL) and conc. HCl (25 mL), and it was heated at 70°C reflux for 48 h. Initially, the solid dissolved to afford a clear solution and slowly re-precipitated within 1.0 h. The mixture was cooled to room temperature, and the resulting precipitate was collected by filtration and washed with cold ethanol. The solid was suspended in aq. Na_2CO_3 (2.0 M, 25 mL) with stirring, and the diamine was extracted with chloroform 3 times. The organic extract was dried over Na_2SO_4 , and the solvent removed in vacuo. The desired 9,10-bis(aminomethyl)anthracene was isolated as a yellow solid, 0.402 g (yield, 62%). ^1H NMR (400 MHz, CDCl_3) δ 4.82 (s, 4H), 7.53-7.56 (m, 4H), 8.38-8.40 (m, 4H).

Scheme S3. Synthesis of (2,6-Dimethylphenyl)boronic Acid **3**



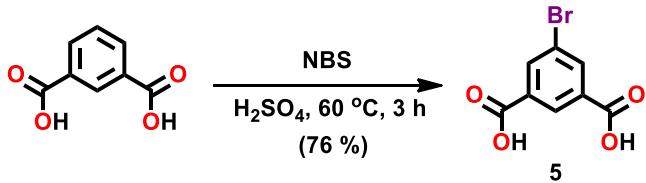
An oven-dried two-necked round bottom flask was charged, under N_2 atmosphere, with magnesium turnings (0.195 g, 8.1 mmol), dry THF (50 mL) and a catalytic amount of 1,2-dibromoethane, and the contents were stirred for 10 min at rt. Subsequently, 2,6-dimethylbromobenzene (1.0 gm, 5.4 mmol) was introduced over a period of 15 min slowly. The color of the solution turned slowly dark brown, and the reaction mixture was stirred at rt for additional 3 h. Afterward, trimethyl borate (1.08 mL, 9.72 mmol) was added dropwise after cooling the reaction mixture to 0°C . The resultant reaction mixture was stirred

for 12 h at rt, quenched subsequently with 10% HCl solution and allowed to stir for further 1.0 h. THF from the resultant reaction mixture was removed in vacuo, and the organic matter was extracted with diethyl ether (50 mL \times 3). The combined organic extract was stripped off solvent under reduced pressure to yield a semisolid material, which was washed with pet-ether with trituration to yield the boronic acid as white powder, 608 mg (yield, 75%). ^1H NMR (400 MHz, CDCl_3) δ 4.71 (s, 2H), 6.98 (d, J = 7.2 Hz, 2H), 7.14-7.16 (m, J = 7.2, 1H).



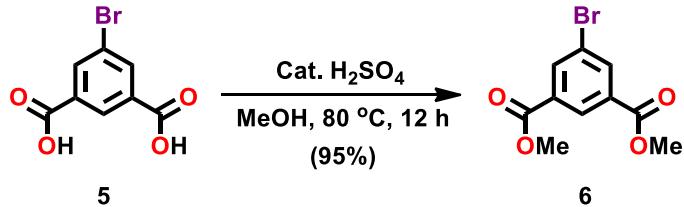
For the synthesis of 4-Methoxyphenylboronic acid **4**, procedure similar to that described was followed, yield 524 mg (68%). ^1H NMR (400 MHz, CDCl_3) δ 3.87 (s, 3H), 7.00 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H).

Scheme S4. Synthesis of 5-Bromoisophthalic Acid **5**²



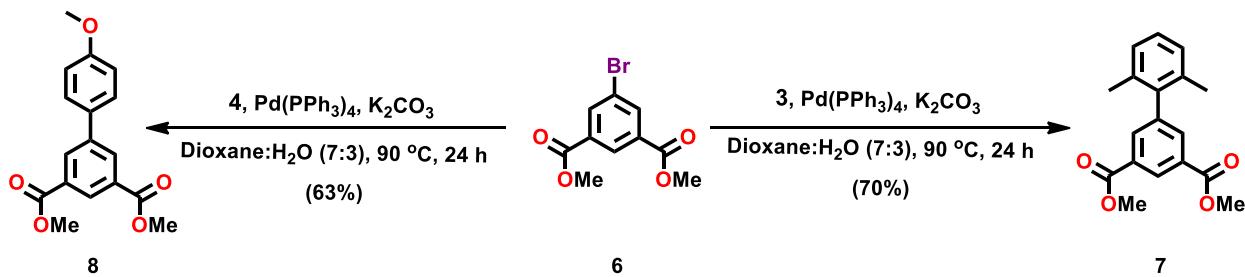
Isophthalic acid (0.5 g, 3.0 mmol) was dissolved in Conc. H_2SO_4 (2 mL) and heated at 60 °C. To this solution was added NBS (0.55 g, 3.1 mmol) in small portions over 10 min. The resulting reaction mixture was stirred for 3 h at 60 °C, and subsequently poured into crushed ice to obtain a white precipitate. The solid was filtered and washed thoroughly with distilled water to remove the acid, and dried in an oven at 80 °C to obtain 5-bromoisophthalic acid, 0.558 g (yield, 76%); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.20 (s, 2H), 8.36 (s, 1H), 13.57 (s, 1H).

Scheme S5. Synthesis of Dimethyl 5-Bromoisophthalate **6**



5-Bromoisophthalic acid (0.5 g, 2.0 mmol) was dissolved in 20 mL methanol in a 100 mL round bottom flask and the resultant solution was cooled to 5-10 °C. A catalytic amount of Conc. H_2SO_4 (0.5 mL) was added dropwise. The resultant reaction mixture was heated at reflux for 12 h at 80 °C. After completion of the reaction, the reaction mixture was cooled to rt, and was neutralized by adding 10% aq. NaHCO_3 solution. The solvent methanol was removed from the reaction mixture in vacuo and the organic matter was extracted with ethyl acetate (50 mL \times 3). The combined organic extract was dried over Na_2SO_4 and the solvent was reduced under vacuum. The resultant residue was purified by silica-gel column chromatography to obtain dimethyl 5-bromoisophthalate as a white solid material, 529 mg (yield, 95%); ^1H NMR (400 MHz, CDCl_3) δ 3.93 (s, 6H), 8.32 (d, $J = 2$ Hz, 2H), 8.57 (d, $J = 2$ Hz, 1H).

Scheme S6. Synthesis of Diethyl 2',6'-dimethyl-[1,1'-biphenyl]-3,5-dicarboxylate **7** and Diethyl 4'-methoxy-[1,1'-biphenyl]-3,5-dicarboxylate **8**

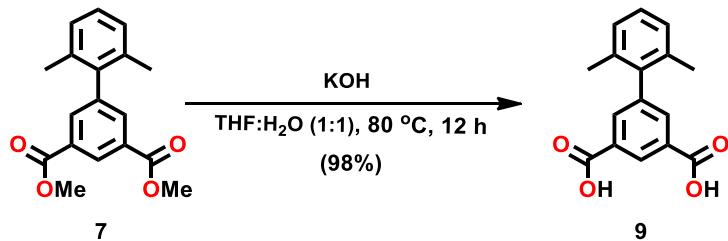


An oven-dried pressure tube was charged with dimethyl 5-bromoisophthalate (300 mg, 1.1 mmol), 2,6-dimethylphenyl boronic acid (197 mg, 1.32 mmol), K_2CO_3 (608 mg, 4.4 mmol), and dioxane:water (7:3 mL) and purged the nitrogen for 15 min, then freshly prepared $\text{Pd}(\text{PPh}_3)_4$ (63 mg, 5.0 mol %) was added into the reaction mixture and continuous purging of nitrogen for additional 10 min, heated the reaction

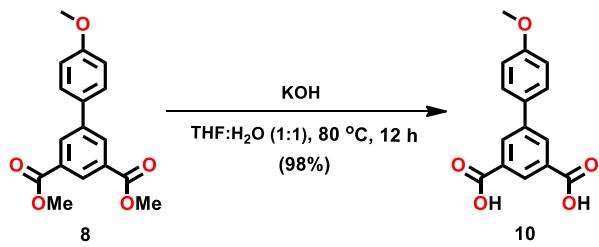
mixture at 90 °C for 24 h. The completion of the reaction was checked by TLC technique. Subsequently, system was removed from heating and leave it for cooling up to room temperature, pass the reaction mixture through celite and evaporated the dioxane/water under reduced pressure. The desired compound was extracted with ethyl acetate, and dried over anhydrous Na_2SO_4 , and the organic phase was evaporated under reduced pressure. The desired compound was purified through column chromatography using ethyl acetate and pet-ether (5:95) to obtain as white solid **7**, 229 mg (yield, 70%). ^1H NMR (400 MHz, CDCl_3) δ 1.98 (s, 1H), 3.93 (s, 6H), 7.11 (d, J = 7.6 Hz, 2H), 7.16-7.2 (m, 1H), 8.04 (d, J = 1.6 Hz, 2H), 8.67 (t, J = 1.6 Hz, 1H).

The synthesis of Diethyl 4'-Methoxy-[1,1'-biphenyl]-3,5-dicarboxylate **8** was carried out by following the procedure described for **7**. Yield, 0.410 g (63%). ^1H NMR (500 MHz, CDCl_3) δ 3.85 (s, 3H), 3.95 (s, 6H), 7.00 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 8.4 (d, J = 2 Hz, 2H), 8.58 (t, J = 2 Hz, 1H).

Scheme S7. Synthesis of 2',6'-Dimethyl-[1,1'-biphenyl]-3,5-dicarboxylic Acid **9** and 4'-Methoxy-[1,1'-biphenyl]-3,5-dicarboxylic Acid **10**

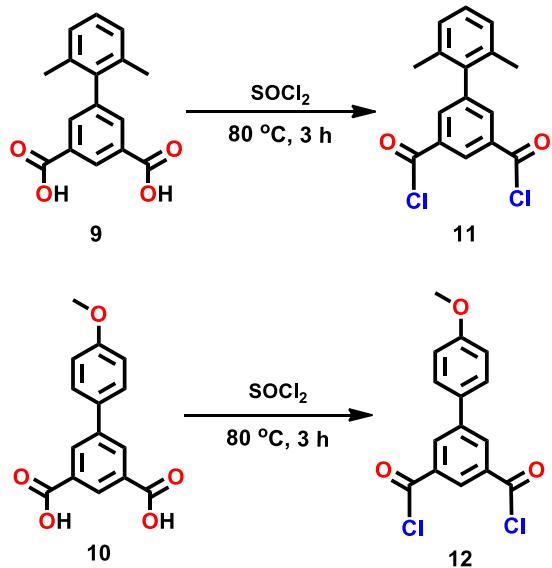


A round-bottomed flask was charged with compound **7** (298.3 mg, 1.0 mmol), mixture of THF/water in 1:1 (20 mL) as a solvent, and KOH (225 mg, 4.0 mmol). The reaction mixture was heated at 80 °C for 12 h. The progress of the reaction was monitored by TLC technique. After completion of the reaction, THF was removed under reduced pressure and 10% HCl was added dropwise to obtain a white precipitate. The precipitate was filtered, washed with water, and dried under vacuum to obtain product **9**. Yield 256.5 mg (95%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 1.93 (s, 6H), 7.15 (d, J = 7 Hz, 2H), 7.18-7.21 (m, 1H), 7.86 (d, J = 2 Hz, 2H), 8.47 (t, J = 2 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 20.94, 128.02, 128.22, 129.12, 132.32, 134.22, 135.63, 139.93, 141.63, 167.05.



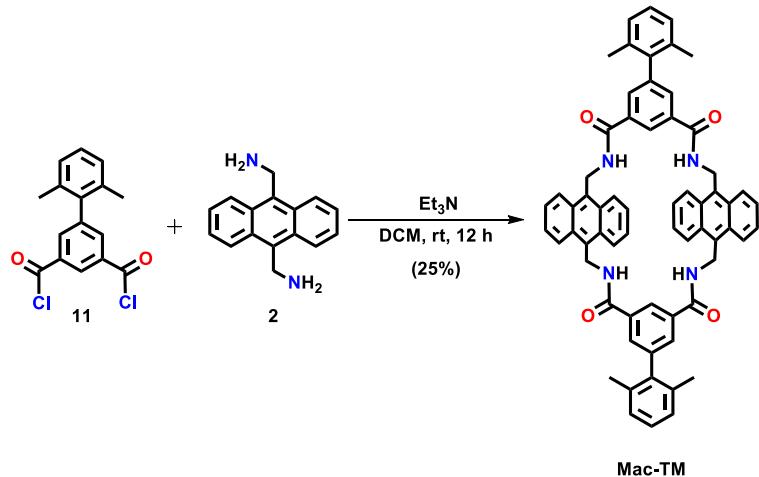
The synthesis of 4'-Methoxy-[1,1'-biphenyl]-3,5-dicarboxylic acid **10** carried in the same manner as that described above for compound **9**, 266.6 mg (yield, 98%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.81 (s, 3H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 8.32 (d, *J* = 2 Hz, 2H), 8.39 (t, *J* = 1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): 55.73, 115.14, 128.60, 131.23, 132.50, 141.25, 160.04, 167.114.

Scheme S8. Synthesis of 2',6'-Dimethyl-[1,1'-biphenyl]-3,5-dicarbonyl Dichloride **11** and 4'-Methoxy-[1,1'-biphenyl]-3,5-dicarbonyl Dichloride **12**



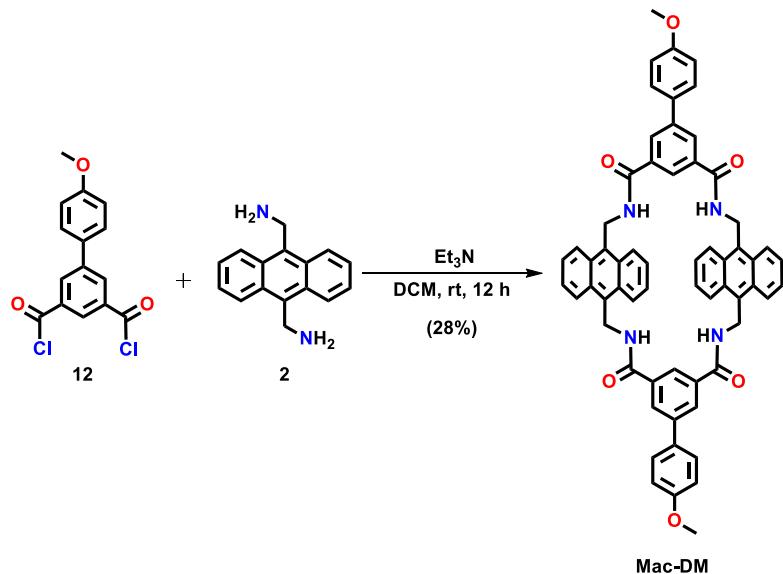
3,5-Dicarboxylic acid **9/10** (100 mg, 0.37 mmol) and 1.0 mL of SOCl₂ were taken in an oven-dried round bottom flask under nitrogen atmosphere and heated for 3.0 h at 80 °C. Thionyl chloride was removed from the reaction mixture in an inert condition to afford white solid 3,5-dicarbonyl dichloride derivatives (**11** and **12**), and the same was used without further purification for the synthesis of macrocycles (**Mac-TM** or **Mac-DM**).

Scheme S9. Synthesis of **Mac-TM** and **Mac-DM**³



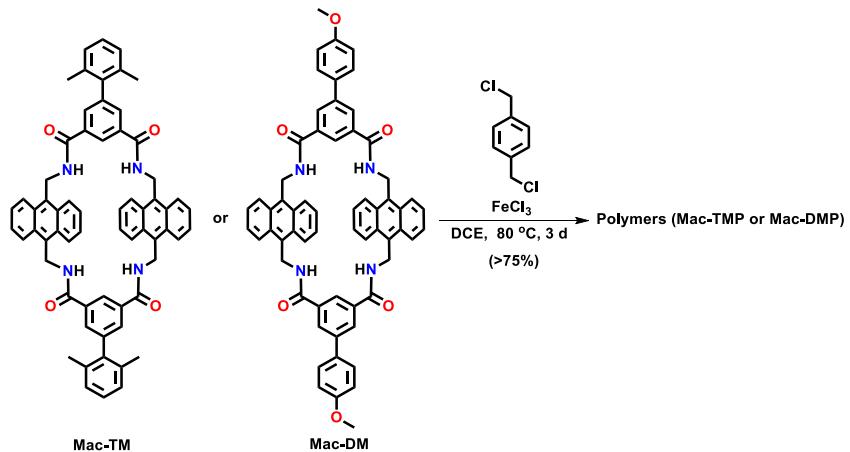
A three-necked oven-dried 500 mL round bottom flask was charged with 300 mL of anhyd. dichloromethane under nitrogen atmosphere. Two separate solutions were prepared separately; one was of 3,5-dicarbonyl dichloride derivative **11/12** (113 mg, 0.37 mmol) in dry DCM (25 mL), and the other was of 9,10-Bis(aminomethyl)anthracene (88 mg, 0.37 mmol) along with triethylamine (0.182 mL, 1.48 mmol) in dry DCM (25 mL). Both these solutions were added simultaneously dropwise over a period of 8.0 h, and the resultant solution was stirred for another 4.0 h at rt. At the end of this period, DCM was removed under reduced pressure and the residue was subjected to silica-gel column chromatography using chloroform and methanol (99:1%) to obtain the desired product.

Mac-TM: 87.0 mg (yield, 25%); Mp >250 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.02 (s, 12H), 5.47 (s, 8H), 6.21 (s, 4H), 7.11 (d, *J* = 6.0 Hz, 4H), 7.18 (m, 6H), 7.43-7.41 (m, 8H), 8.12 (d, *J* = 1.2 Hz, 2H), 8.18-8.16 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 21.0, 37.5, 123.4, 124.5, 126.8, 127.7, 127.9, 129.3, 130.3, 133.78, 133.9, 135.7, 139.7, 143.4, 166.1; HRMS (ESI) m/z: [M+H]⁺ calcd for C₆₄H₅₃N₄O₄ 941.4061; found, 941.4061.



Mac-DM: 97.9 mg (yield, 28%); Mp >250 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.88 (s, 6H), 5.49 (s, 8H), 6.26 (s, 4H), 7.03 (d, *J* = 8.8 Hz, 4H), 7.44 (m, 8H), 7.7 (d, *J* = 7.6 Hz, 4H), 8.19 (s, 8H), 8.5 (s, 4H); HRMS (ESI) m/z: [M+H]⁺ calcd for C₆₄H₄₉N₄O₆ 945.3647; found, 945.3649.

Scheme S10. Synthesis of the Polymers **Mac-TMP** and **Mac-DMP**



To a solution of the macrocycle **Mac-TM/Mac-DM** (100 mg, 0.11 mmol) in dry DCE (30 mL), *p*-Xylylene dichloride (38.5 mg, 0.22 mmol) and anhydrous FeCl₃ (142.7 mg, 0.88 mmol) were added. The reaction mixture was stirred for 3 d at 80 °C under inert atmosphere, the reaction mixture was cooled to rt and washed with distilled water and ethanol to remove unreacted FeCl₃ and other impurities. The polymer thus obtained was activated by treatment with several solvents such as methanol, THF, chloroform, etc. to remove dimers, oligomers, etc. After this process, the resultant material was dried in an oven at 100 °C

for 24 h to obtain the desired polymer **Mac-TMP/Mac-DMP**. The yield of **Mac-TMP** was 94.7 mg (yield, 78%), while that of **Mac-DMP** was 101.5 mg (yield, 80%).

Effect of pH on gold adsorption

A stock solution of HAuCl₄ was diluted to 500 ppm and the pH was adjusted to the values of 2, 4, 7, and 9 using dil NaOH and HCl (10%). One control sample and one experimental sample were prepared for each pH. To a one-mL stock solution of HAuCl₄ contained in a 5 mL round bottom flask was added 1.0 mg of the adsorbent, that is, **Mac-TMP/Mac-DMP**, and the suspension was stirred for 36 h. The polymer from each of the solutions was filtered off through a syringe filter, and the concentrations of gold ions in the control sample as well as all others were determined by ICP-MS.

Gold adsorption⁴

To determine the amount of gold uptake by the macrocycle adsorbent **Mac-TMP/Mac-DMP**, a stock solution of gold (III) chloride trihydrate was prepared and the same was diluted to various concentrations, that is, solutions with 20, 100, 200, 500, 1000 and 2000 ppm. In each study, one control and two experimental samples were prepared. To a one-mL solution of HAuCl₄ in a 5 mL round bottom flask was added 1.0 mg of the adsorbent. The same was also done for the experimental samples. The suspensions were stirred 36 h at rt. Subsequently, the insoluble polymeric materials were filtered off and the concentration of gold was determined in each case by ICP-MS. By comparing the concentration of gold the control and experimental samples, the amount of gold adsorbed by adsorbents was estimated. The Langmuir adsorption model and Freundlich adsorption model were used to fit the data for gold adsorption.

The equation of Langmuir model is shown below:

$$q_e = \frac{q_m K_L C_e}{1 + (K_L C_e)}$$

Where q_e (mg_{Au}/ mg_{Ads}) is the quantity of adsorbed metal ions at equilibrium, C_e (mg L⁻¹) is the equilibrium concentration, q_m (mg_{Au}/ mg_{Ads}) is the maximum uptake amount of the metal ion in a gram of adsorbent, and K_L is the Langmuir constant.

The equation of Freundlich model is as follows:

$$q_e = k_F C_e^{1/n}$$

Where q_e (mg_{Au}/ mg_{Ads}) refers to the quantity of adsorbed metal ions at equilibrium, K_F to Freundlich constant and n to the adsorption intensity.

Metal selectivity

The selectivity for gold was determined by using a standard solution containing several metal ions in 100 ppm concentration. Three control and three experimental samples (each 1 mL) were prepared, and to each of them was added 1.0 mg of the adsorbent, that is, **Mac-TMP/Mac-DMP** and the suspension was vigorously stirred at rt for 36 h. All the samples were filtered by using PVDF syringe filter of pore size 0.22 μ m. The concentration of metal ions after adsorption and before adsorption (standard sample) were determined by ICP-MS analysis. Based on the concentrations of the experimental group and the control group, the quantity of adsorption was determined.

$$\text{Uptake (\%)} = \frac{C_c - C_e}{C_c} \times 100 (\%)$$

Where C_c and C_e correspond to average concentrations of the control group and the experimental group, respectively.

Metal adsorption from electronic waste

Electronic waste was collected from a local computer repair store. The CPUs were primarily immersed in 10 M NaOH solution for 24 h at ambient temperature to remove the epoxy coating on the surface. Subsequently, it was removed from the NaOH solution and washed properly using water. Afterward, CPUs were soaked in 1.0 M HNO₃ and 1.0 M HCl (1:3) solution at rt for 2 days. The resultant solution was decanted and filtered to remove undissolved materials. The pH of the filtered e-waste solution was close to zero. Therefore, solution was made up to pH 2.0 by adding dil. solution of KOH. The metal content in the solution was determined by ICP-MS analysis. In general, the major components present in CPUs are Mg, Al, Ni, Cu, Zn, Sn, and Au. These metal ions were chosen to determine their concentrations. The adsorption of metal ions was performed according to metal selectivity test explained above.

Recyclability

To verify the recyclability of synthesized polymers, a stock solution of 500 ppm gold solution was prepared. To 10 mL of this stock solution was added 10 mg of the adsorbent. Extraction of the gold was performed as described above. An acidic solution of thiourea (0.1 M) in (0.1 M H_2SO_4) was used for leaching out gold. Gold-loaded polymer (10.0 mg) and 10 mL of thiourea solution were heated for 6 h at 80 °C. The concentration of the gold was determined after filtration of the polymer by ICP-MS analysis. For further adsorption, the polymer were washed properly with distilled water and organic solvents, and dried at 100 °C in an oven for 12 h. Four consecutive adsorption and desorption cycles were performed with the same polymer. At the end of these processes, each of the two polymers was found to be stable.

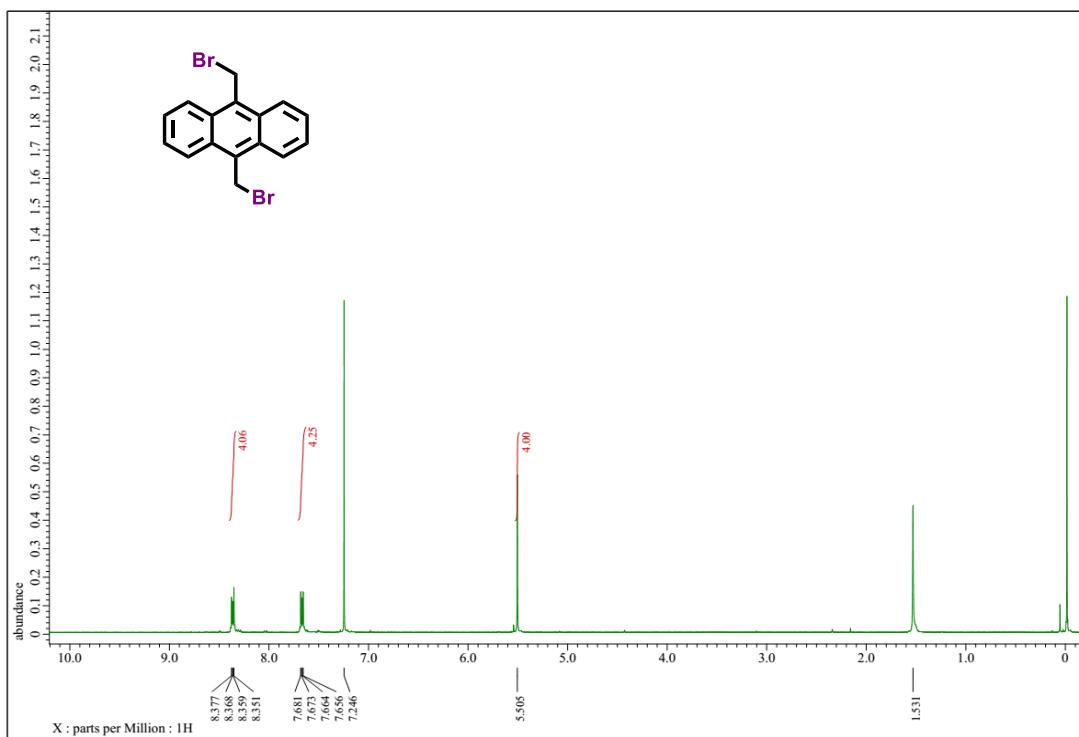


Fig. S1 ^1H NMR (400 MHz) spectrum of **1** in CDCl_3 .

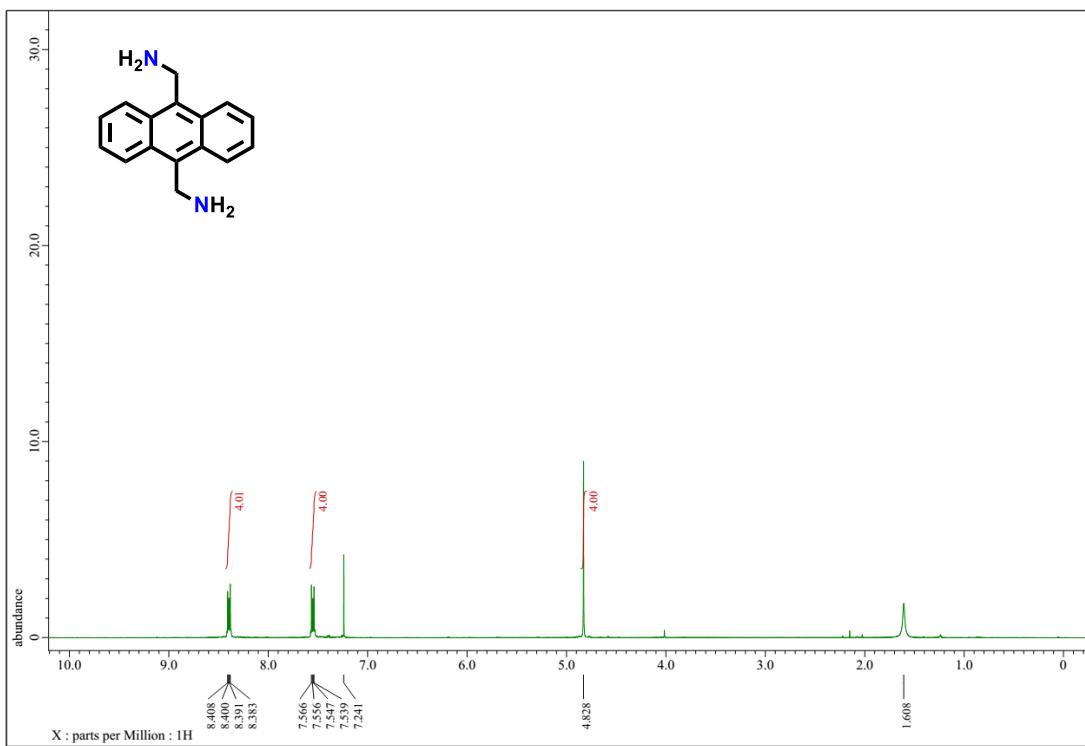


Fig. S2 ^1H NMR (400 MHz) spectrum of **2** in CDCl_3 .

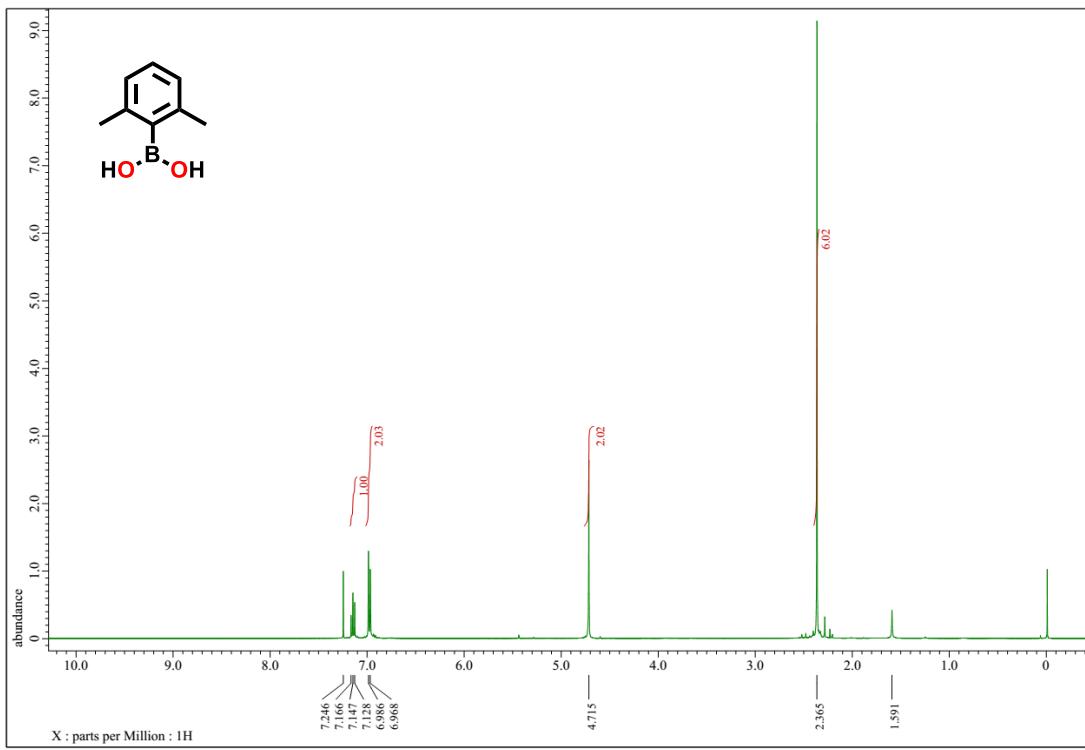


Fig. S3 ^1H NMR (400 MHz) spectrum of **3** in CDCl_3 .

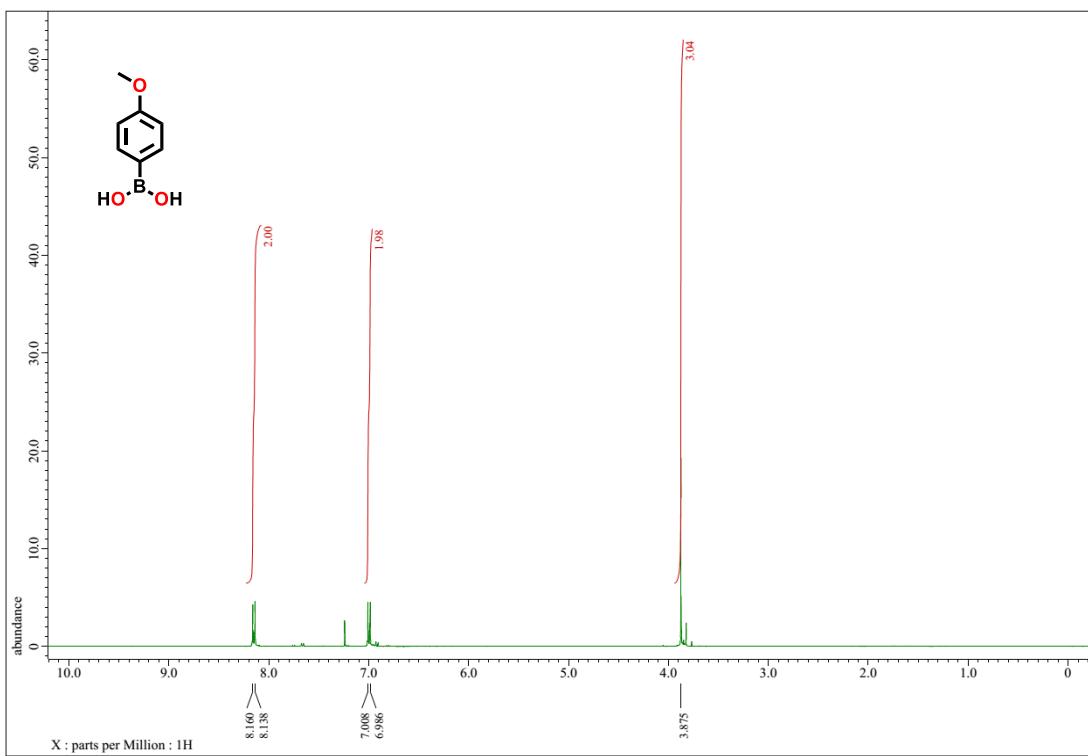


Fig. S4 ^1H NMR (400 MHz) spectrum of **4** in CDCl_3 .

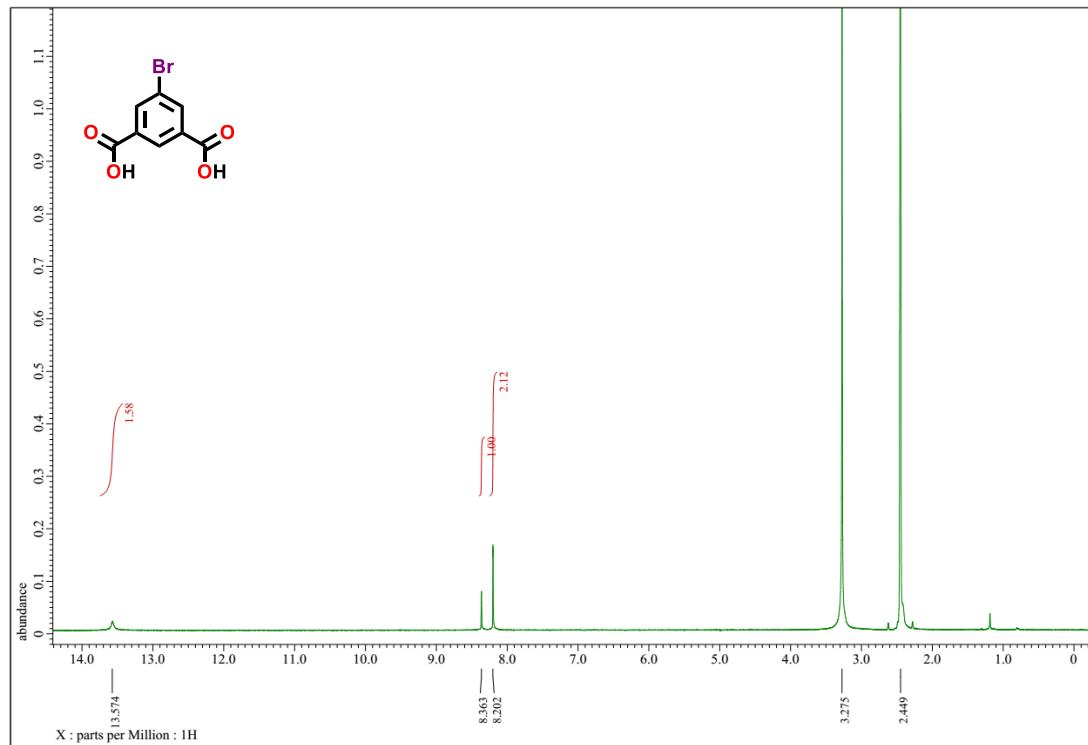


Fig. S5 ^1H NMR (400 MHz) spectrum of **5** in $\text{DMSO-}d_6$.

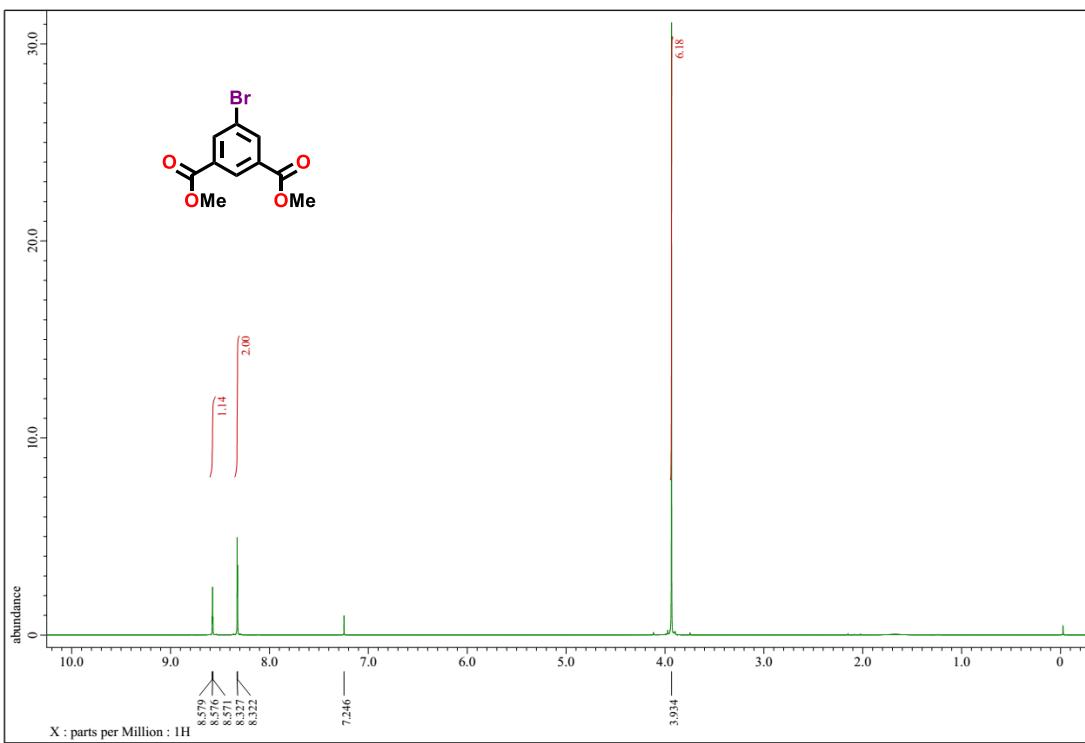


Fig. S6 ^1H NMR (400 MHz) spectrum of **6** in CDCl_3 .

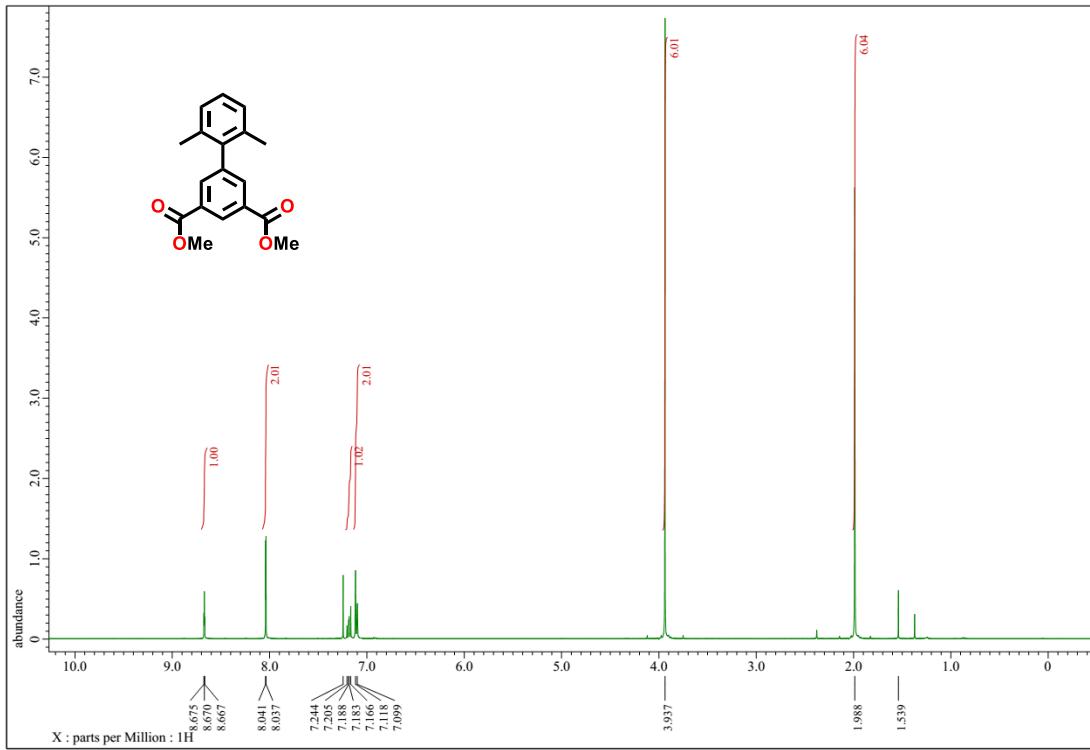


Fig. S7 ^1H NMR (400 MHz) spectrum of **7** in CDCl_3 .

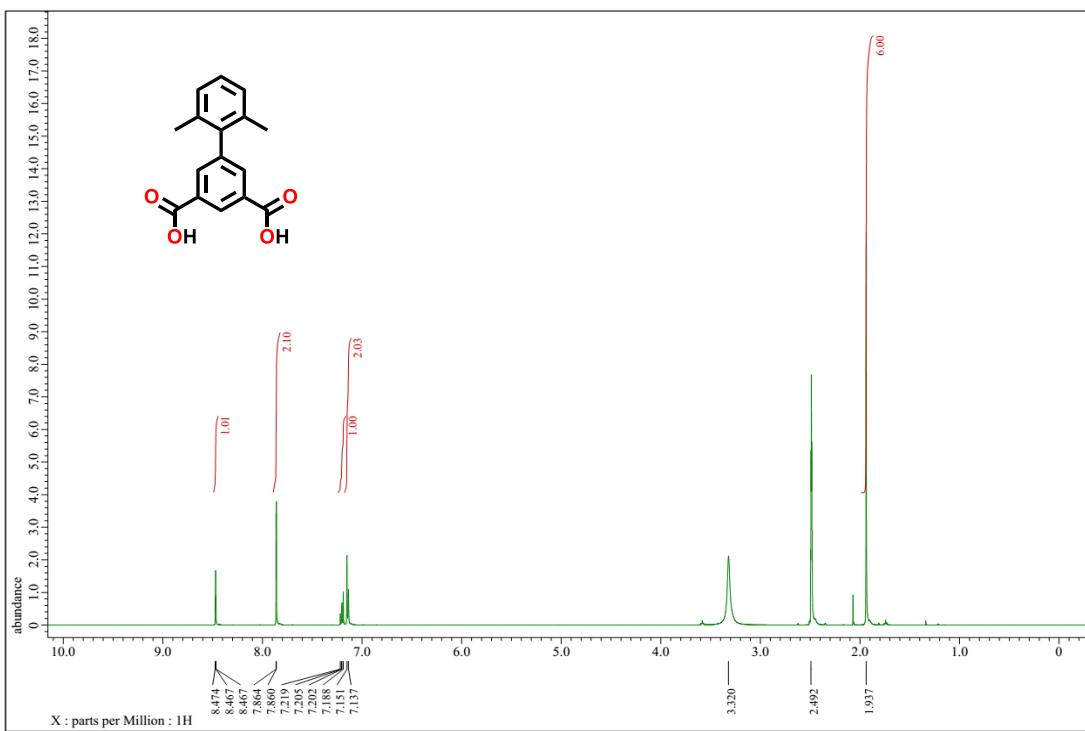


Fig. S8 ^1H NMR (500 MHz) spectrum of **9** in $\text{DMSO}-d_6$.

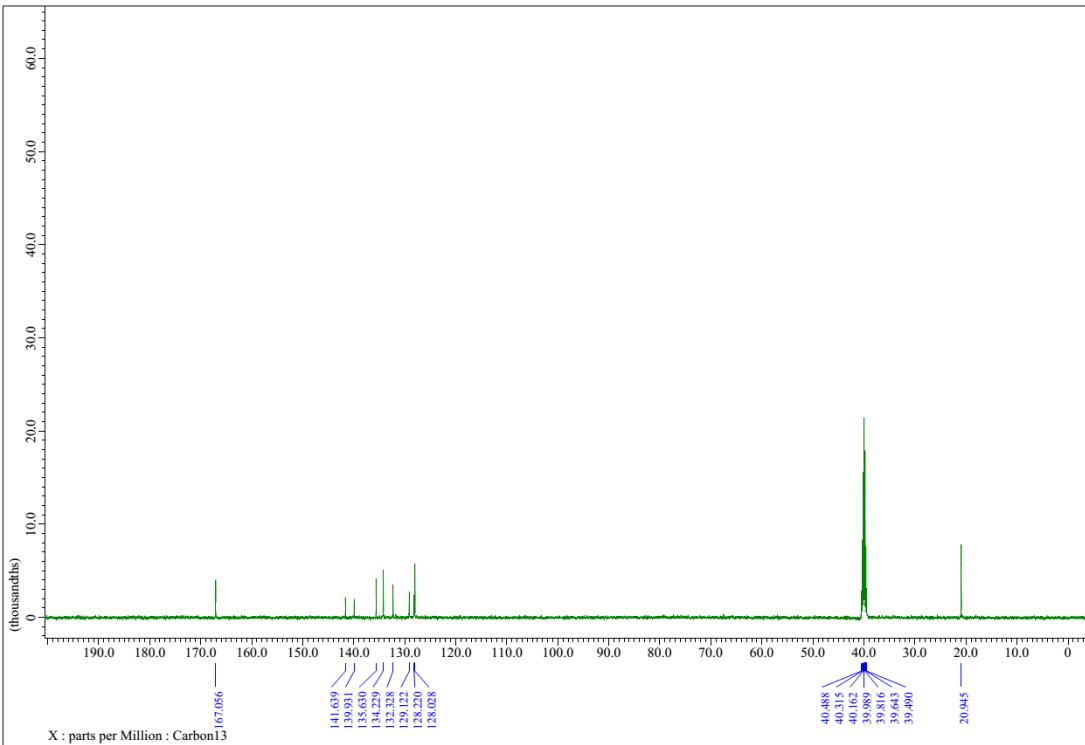


Fig. S9 ^{13}C NMR (125 MHz) spectrum of **9** in $\text{DMSO}-d_6$.

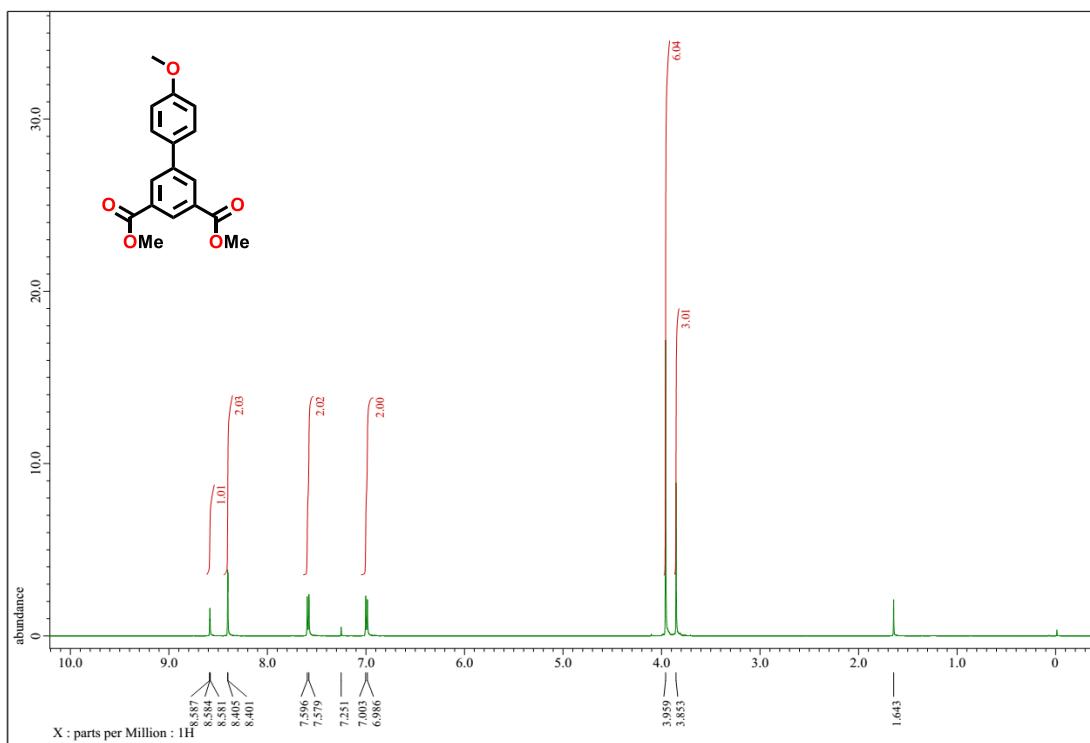


Fig. S10 ^1H NMR (400 MHz) spectrum of **8** in CDCl_3 .

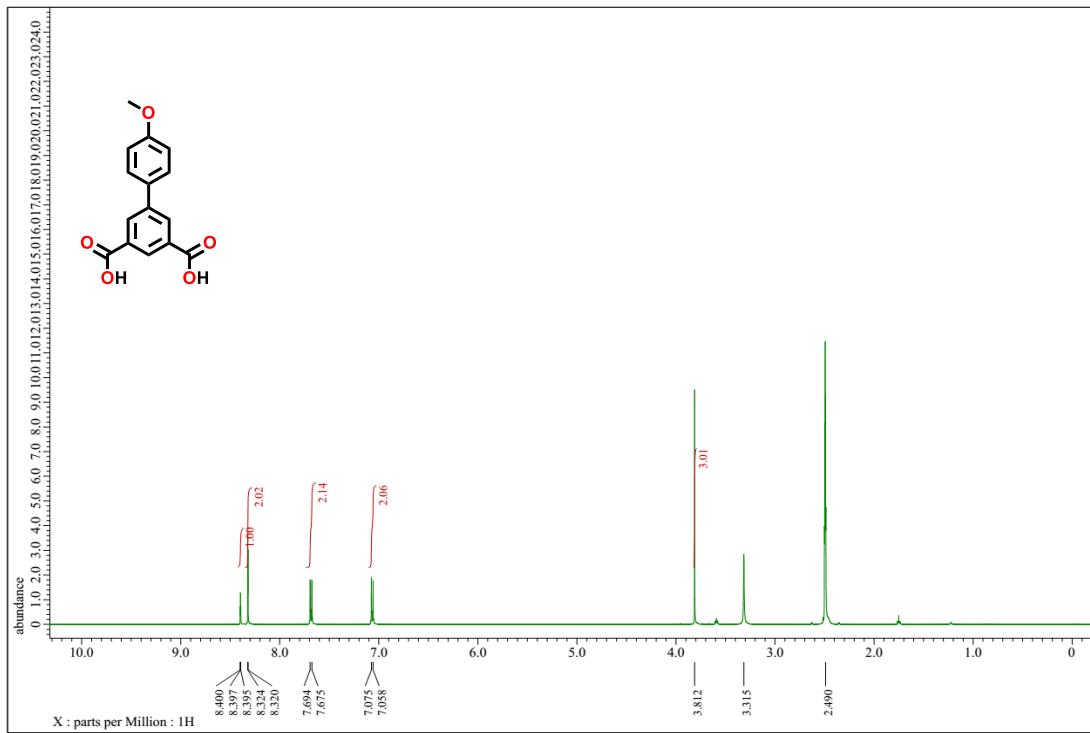


Fig. S11 ^1H NMR (500 MHz) spectrum of **10** in $\text{DMSO-}d_6$.

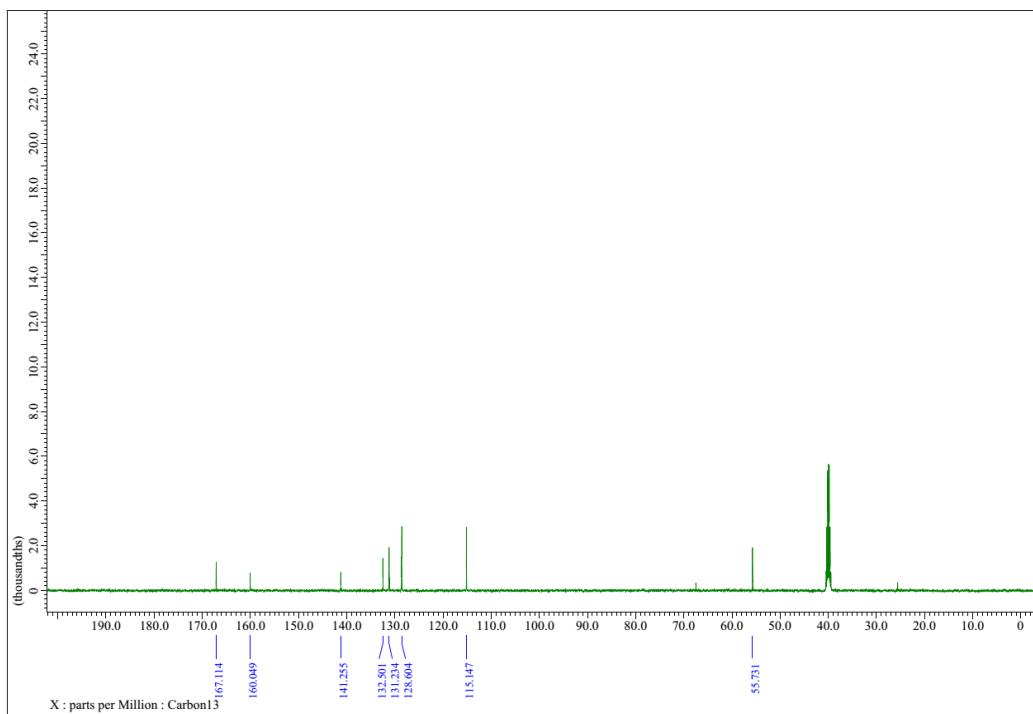


Fig. S12 ^{13}C NMR (125 MHz) spectrum of **10** in $\text{DMSO-}d_6$.

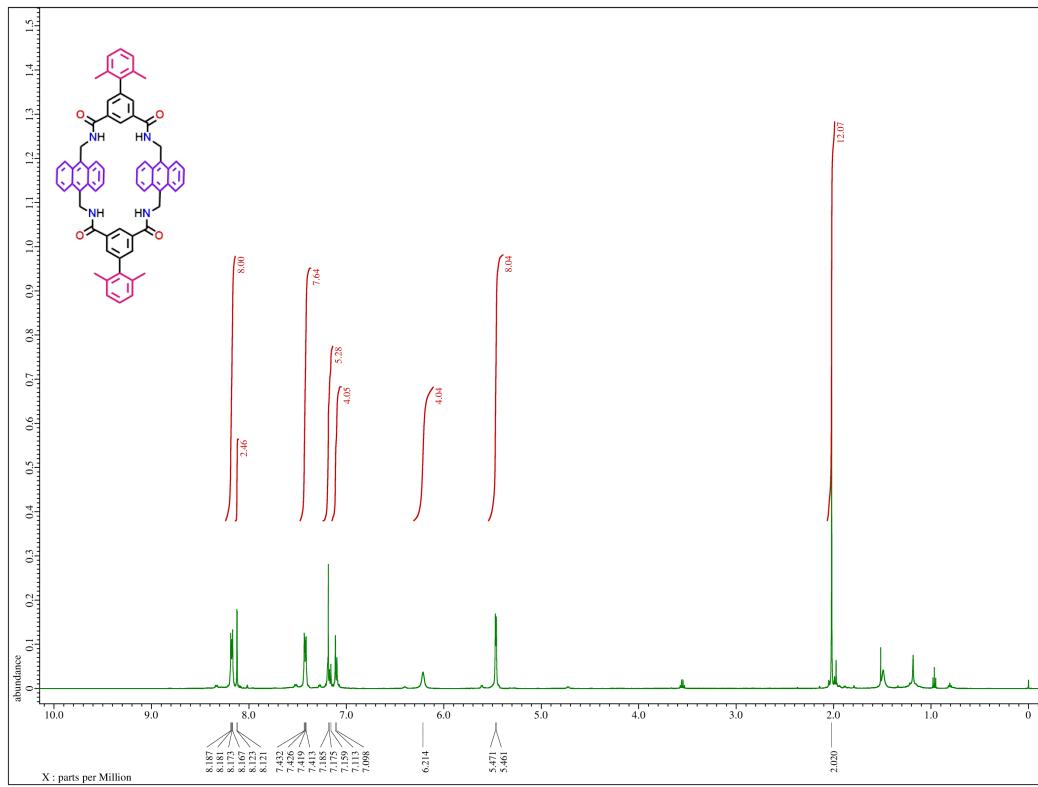


Fig. S13 ^1H NMR (400 MHz) spectrum of **Mac-TM** in CDCl_3 .

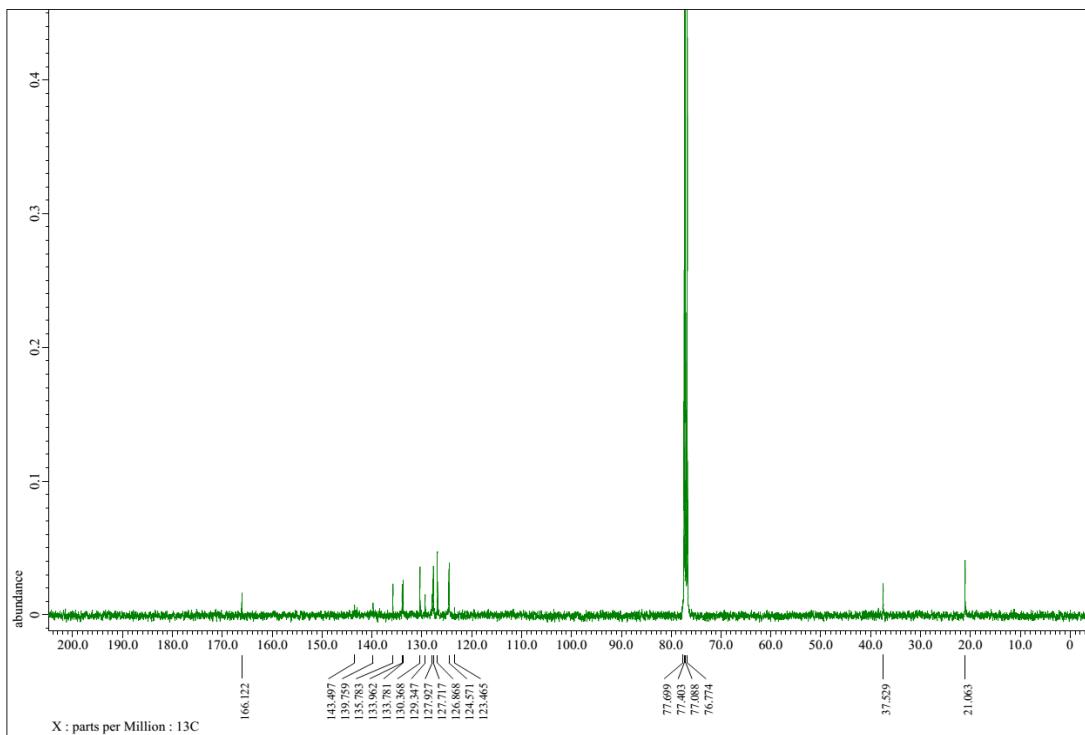


Fig. S14 ^{13}C NMR (100 MHz) spectrum of **Mac-TM** in CDCl_3 .

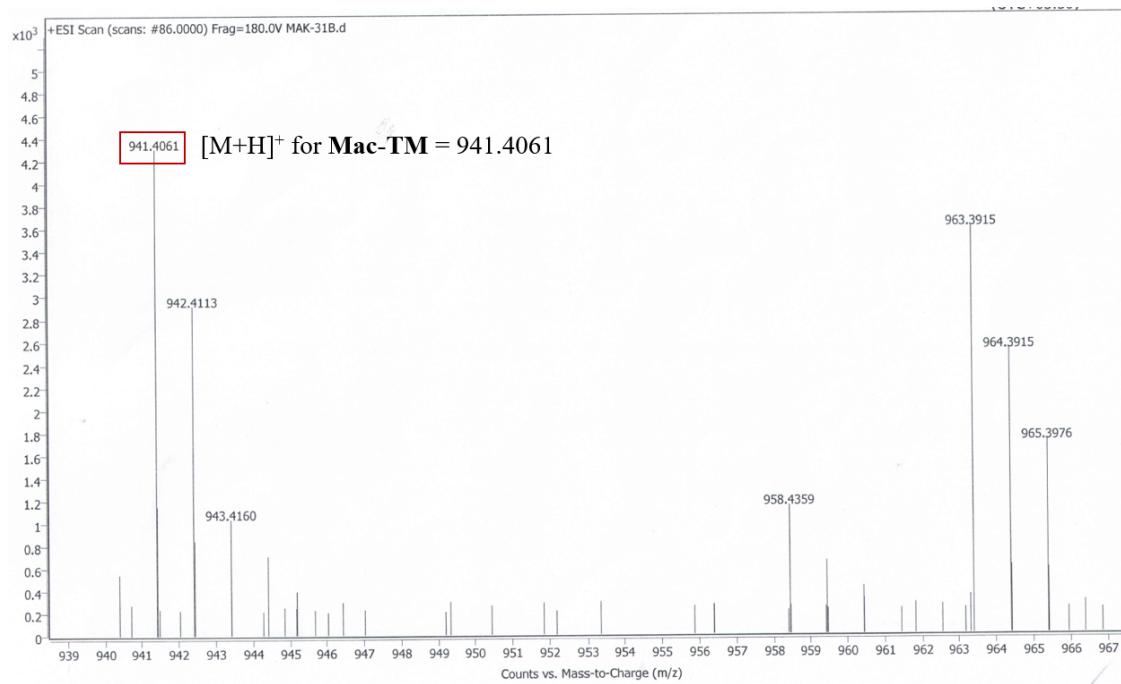


Fig. S15 HRMS(ESI) spectrum of **Mac-TM**.

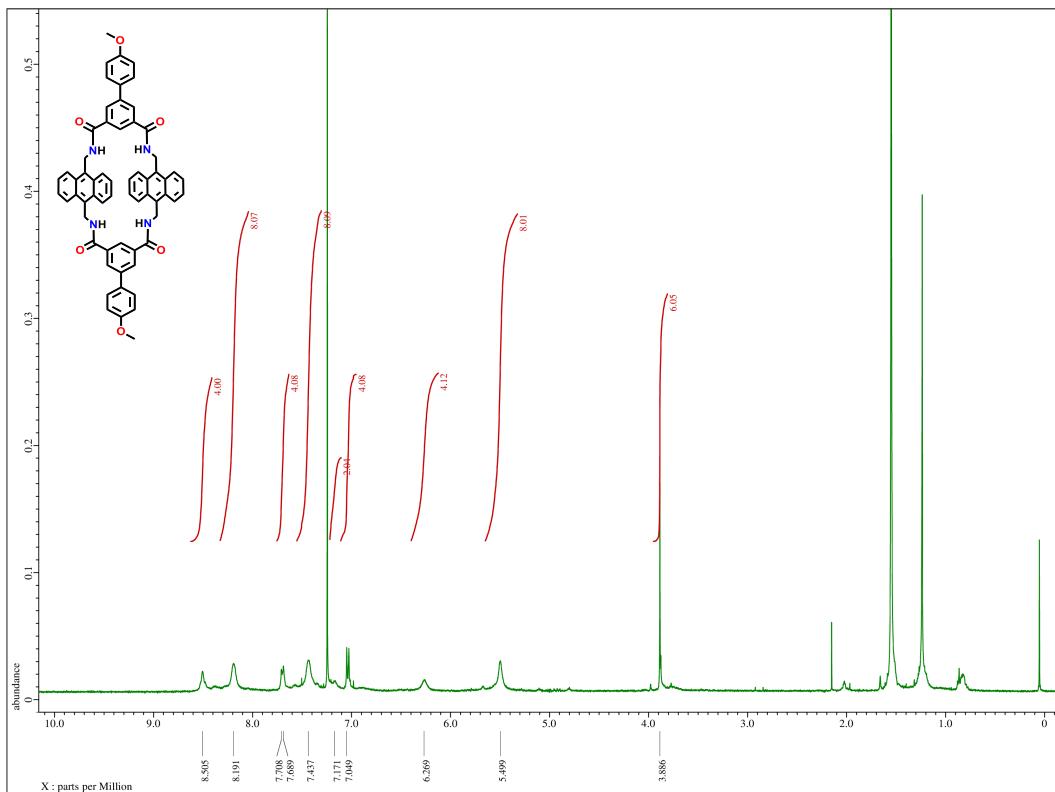


Fig. S16 ^1H NMR (400 MHz) spectrum of **Mac-DM** in CDCl_3 .

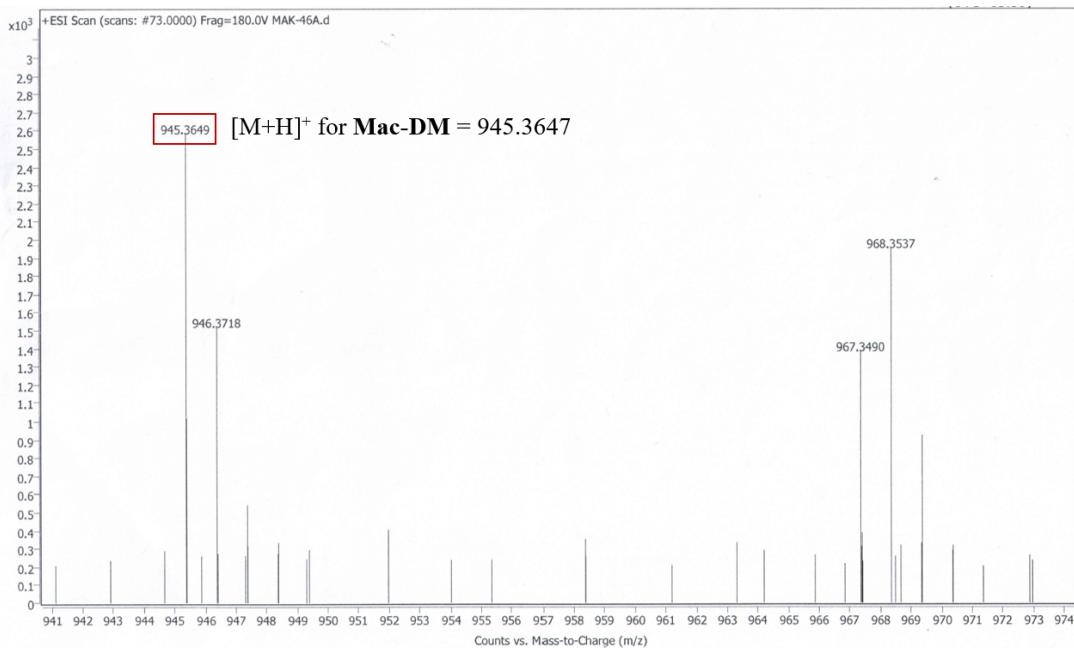


Fig. S17 HRMS(ESI) spectrum of Mac-DM.

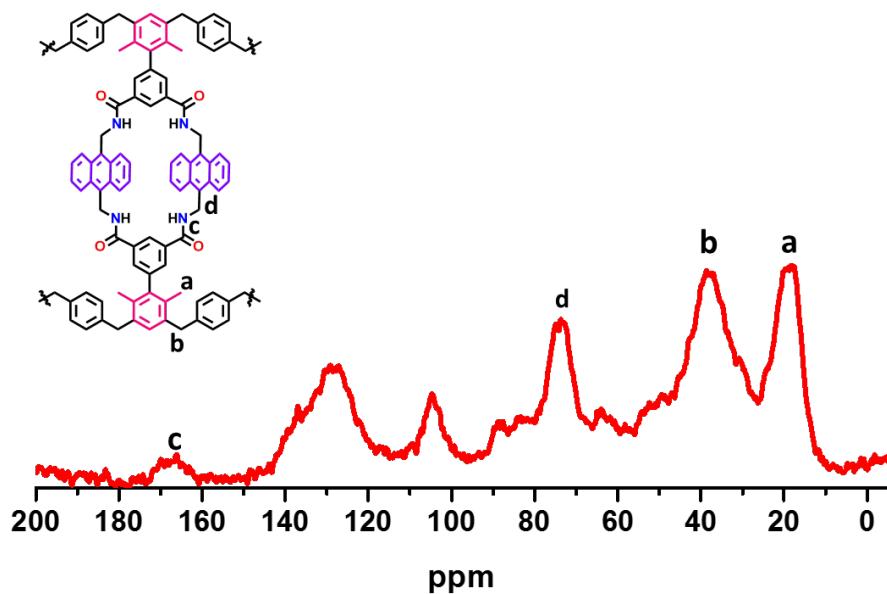


Fig. S18 Solid-state ^{13}C NMR spectrum of Mac-TMP.

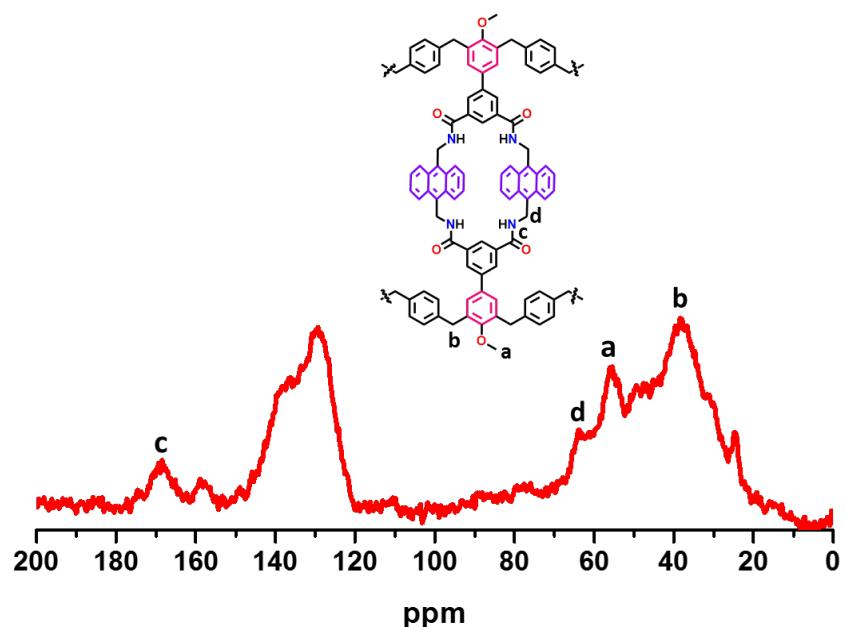


Fig. S19 Solid-state ^{13}C NMR spectrum of Mac-DMP.

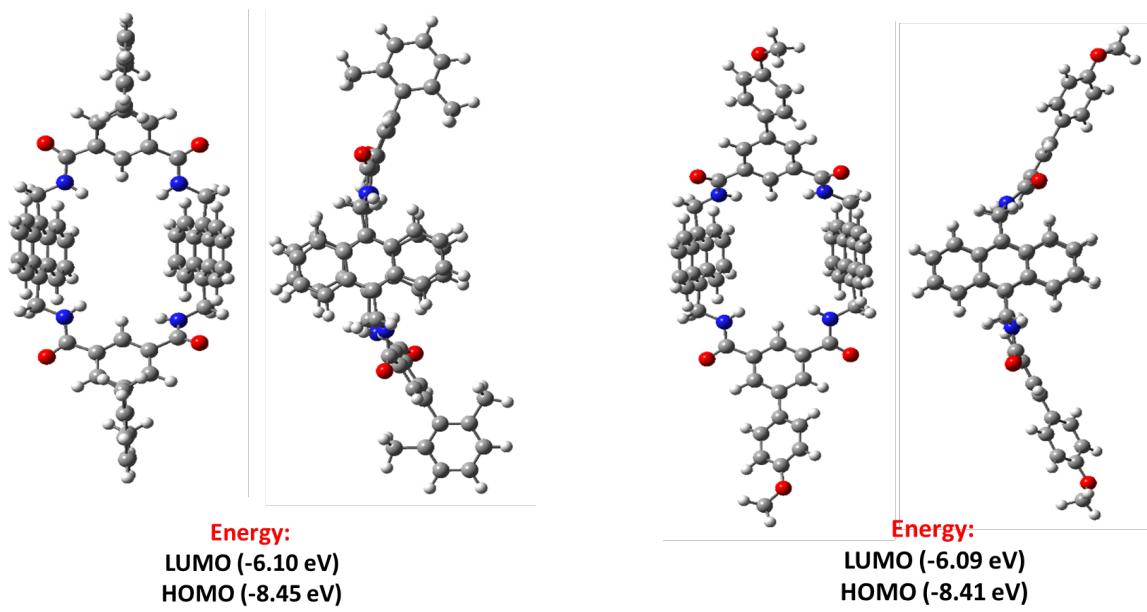


Fig. S20 Optimized DFT structures of **Mac-TMP** (left) and **Mac-DMP** (right).

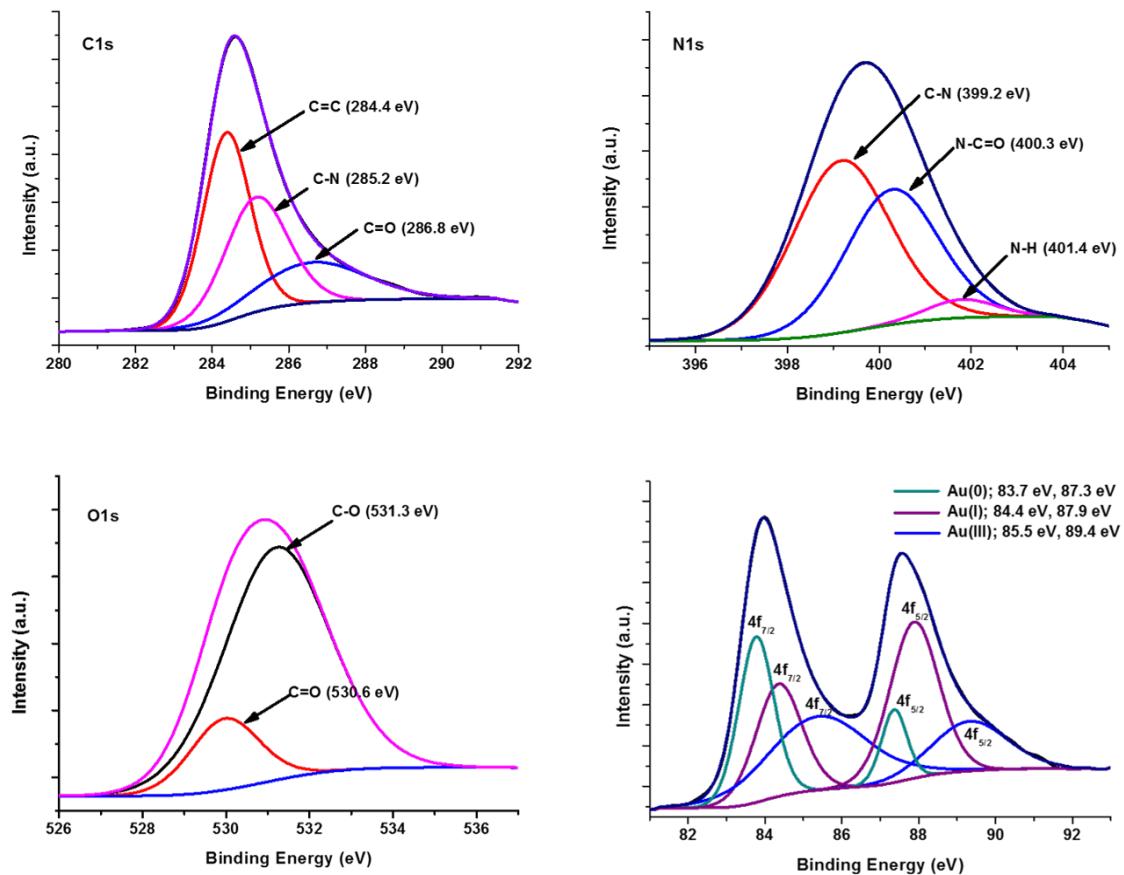


Fig. S21 XPS plots of gold loaded polymer **Mac-TMP**.

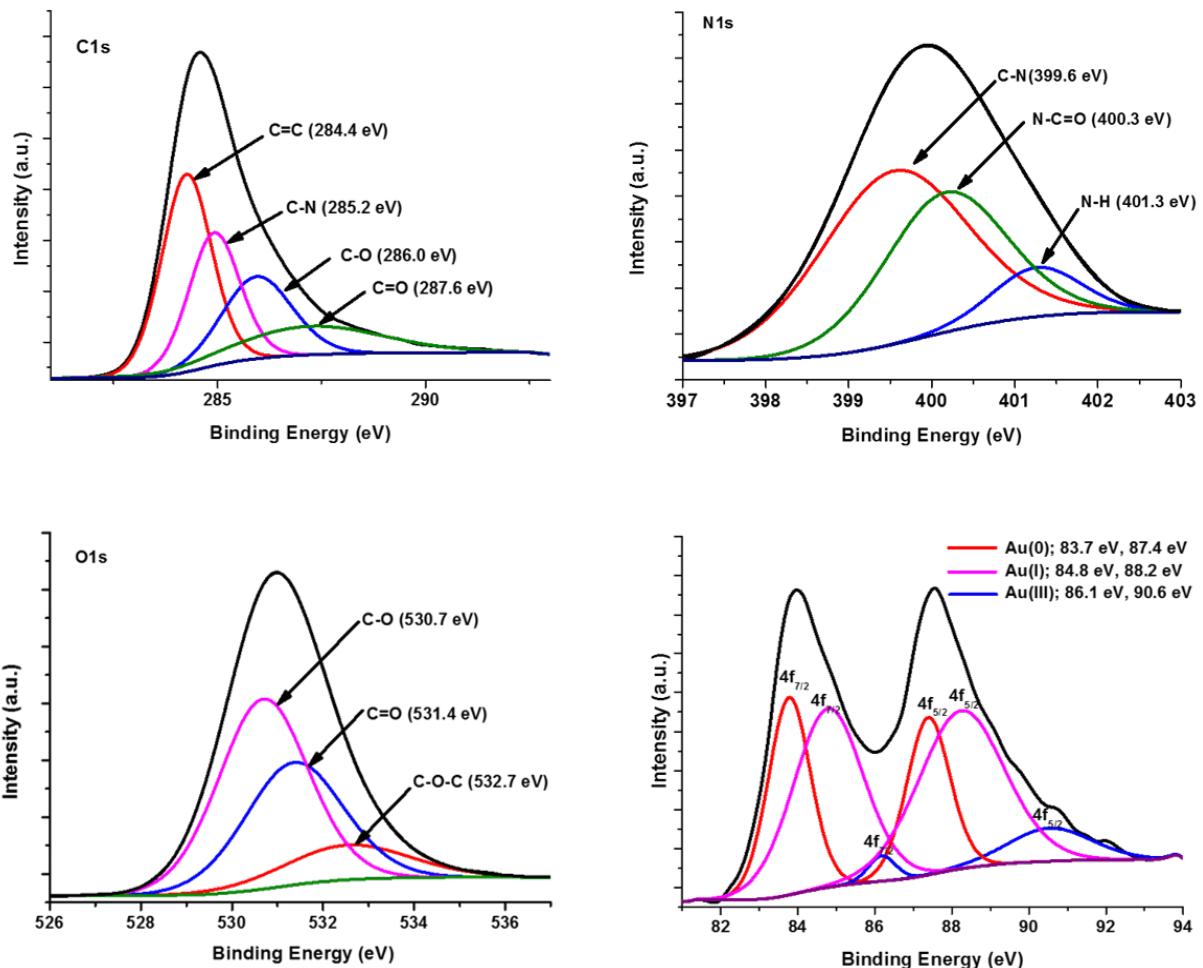


Fig. S22 XPS plots of gold loaded polymer **Mac-DMP**.

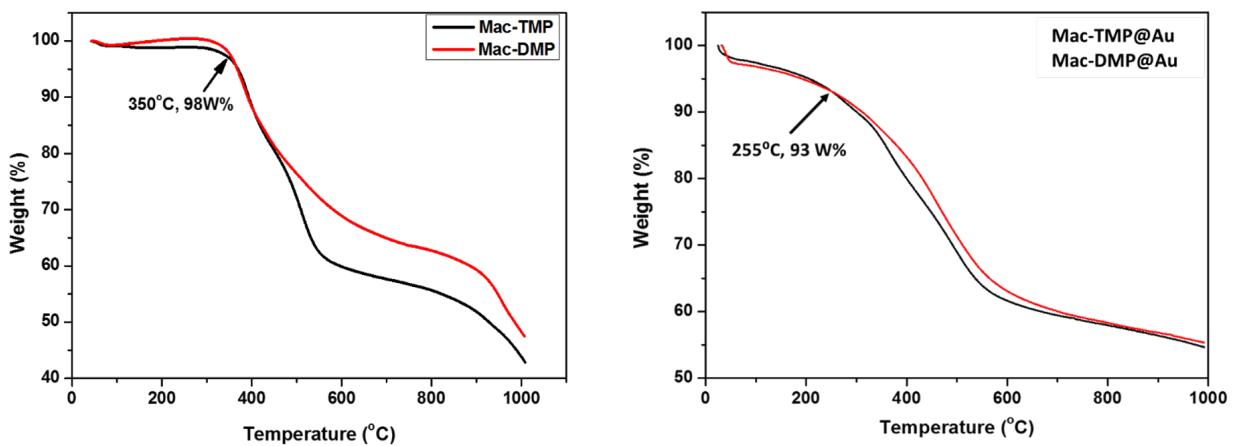


Fig. S23 TGA profiles of **Mac-TMP** and **Mac-DMP** (left side); **Mac-TMP@Au** and **Mac-DMP@Au** (right side).

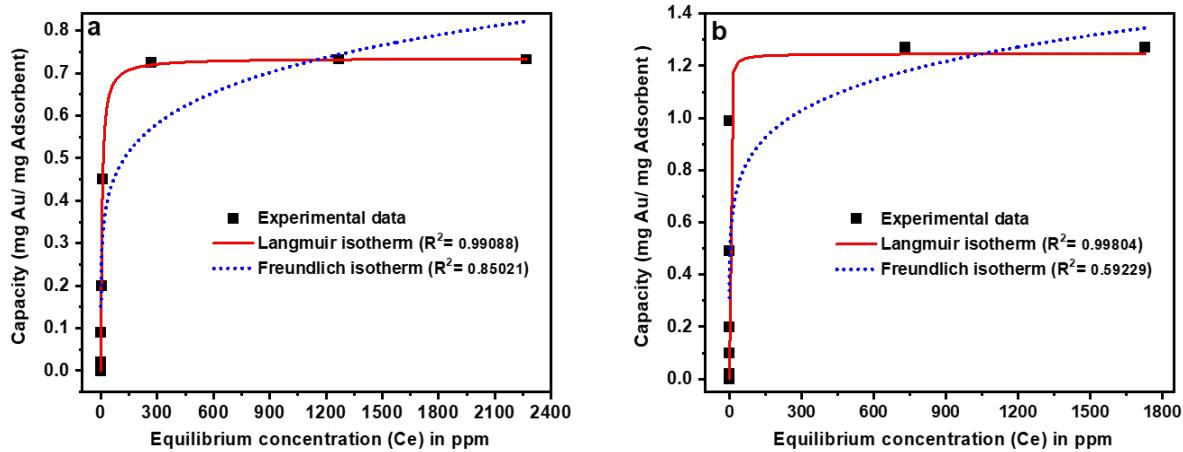


Fig. S24 (a and b) Fitting of the data of gold adsorption by **Mac-TMP** and **Mac-DMP**, respectively, to Langmuir and Freundlich isotherm models.

Table S1. Comparison of the recovery of gold from e-waste with previously reported polymers.

S.No.	Material	BET surface area (m ² g ⁻¹)	Recovery Amount (g/g)	Recyclability	Ref.
1	Se-polyurethane	–	0.802	7	5
2	COPs	685–856	0.901–1.250	3	6
3	Polyhedral oligomeric silsesquioxane (POSS-2)	–	1.486	5	7
4	Porphyrin and viologen-linked cationic porous organic polymer (V-PPOP-Br)	219	0.792	8	8
5	Silsesquioxane (SQ)-based hybrid network (PCS-PAA)	6.972	1.235	–	9
6	Cationic imidazolium and porphyrin functionalized POPs (Imi-PPOPs-Br)	15	1.543	8	10
7	Polyamine-functionalized porous organic polymers (Pc-POSS-POPs)	28	1.026	5	11
8	1,2,4-triazolium-based POP carbene adsorbent (Ptiaz-CN-A)	332	2.09	7	12
9	2D/3D porphyrin-based porous polyaniline derivatives (POP-1 and POP-2)	22.6 and 67.2	0.984 and 1.152	6	13
10	Covalent Porphyrin/Triphenylamine-Based Porous Polymer (Por-net)	836	1.25	7	14
11	Thiophene-functionalized covalent triazine frameworks (TD-TPTA and DBA-TPTA)	98.34 and 113.07	1.123 and 0.714	5	15
12	Mac-DMP and Mac-TMP	130 and 26	1.27 and 0.72	4	Present work

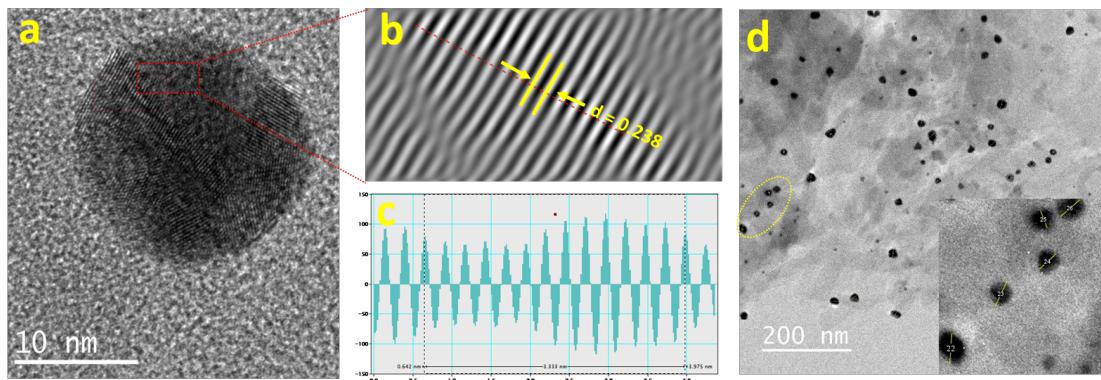


Fig. S25 (a) HRTEM image of gold adsorbed **Mac-TMP@Au**. (b and c) The interplanar spacing of the gold nanoparticles. (d) Average particle size determination of gold nanoparticles (16.34 nm) of **Mac-TMP@Au** by ImageJ software.

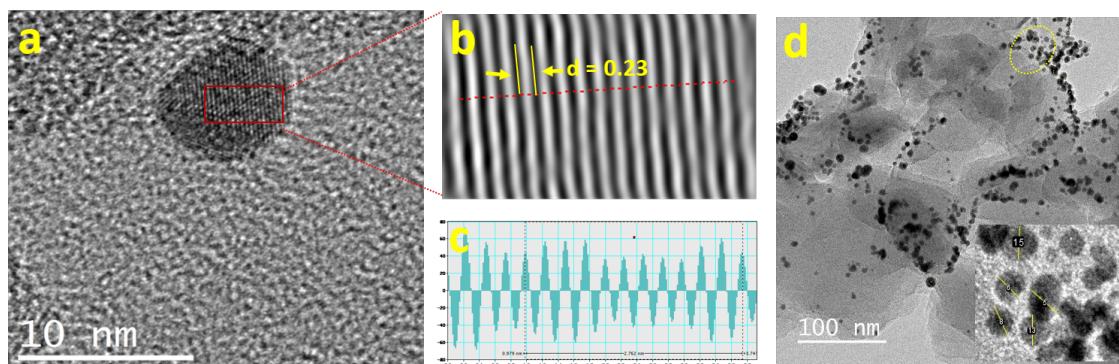


Fig. S26 (a) HRTEM image of gold adsorbed **Mac-DMP@Au**. (b and c) The interplanar spacing of the gold particles. (d) Average particle size determination of gold nanoparticles (7.28 nm) of **Mac-DMP@Au** by ImageJ software.

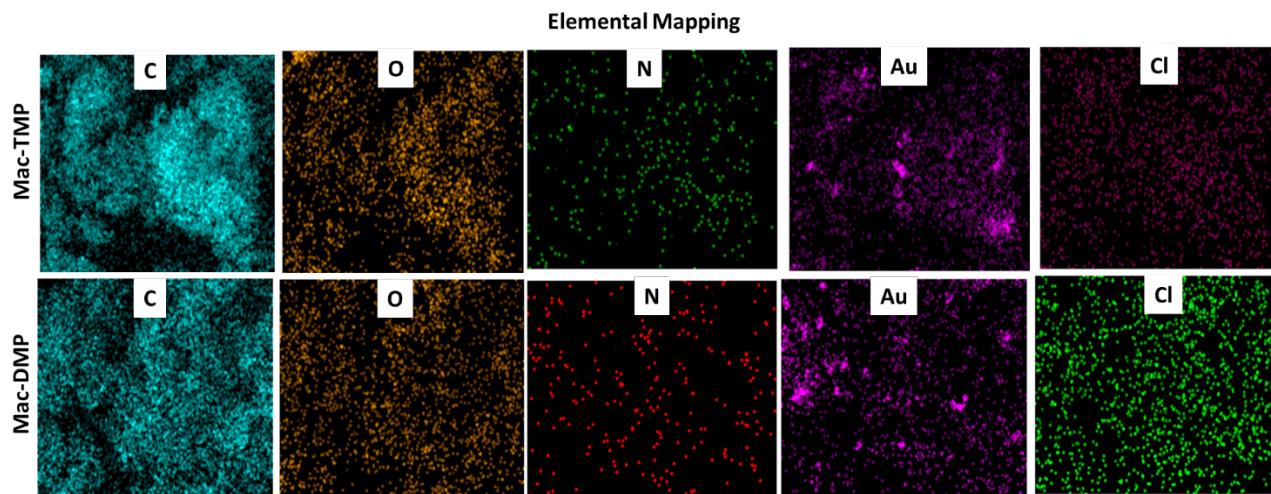


Fig. S27 Elemental mapping of **Mac-TMP@Au** (top) and **Mac-DMP@Au** (bottom)

References:

1. W. Liu, A. G. Oliver and B. D. Smith, *J. Am. Chem. Soc.*, 2018, **140**, 6810-6813.
2. K. Rajesh, M. Somasundaram, R. Saiganesh and K. K. Balasubramanian, *J. Org. Chem.*, 2007, **72**, 5867-5869.
3. J. J. Gassensmith, J. M. Baumes, J. Eberhard and B. D. Smith, *Chem. Commun.*, 2009, **18**, 2517-2519.
4. Y. Hong, D. Thirion, S. Subramanian, M. Yoo, H. Choi, H. Y. Kim, J. F. Stoddart and C. T. Yavuz, *PNAS*, 2020, **117**, 16174-16180.
5. Y. Dai, K. Zheng, Y. Tan, W. Xiang, B. Xianyu and H. Xu, *Adv. Sustain. Syst.* 2020, **4**, 2000072.
6. Y. Hong, V. Rozyyev and C. T. Yavuz, *Small Sci.* 2021, **1**, 2000078.
7. Z. Chen, D. Wang, S. Feng and H. Liu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 23592-23605.
8. Y. Chen, Z. Li, R. Ding, T. Liu, H. Zhao and X. Zhang, *J. Hazard. Mater.* 2022, **426**, 128073.
9. Q. Ge and H. Liu, *ACS Appl. Nano Mater.*, 2022, **5**, 9861-9870.
10. R. Ding, J. Liu, T. Wang and X. Zhang, *Chem. Eng. J.*, 2022, **449**, 137758.

11. R. Ding, Y. Chen, Y. Li, Y. Zhu, C. Song and X. Zhang, *ACS Appl. Mater. Interfaces*, 2022, **14**, 11803-11812.
12. X. Li, Y. L. Wang, J. Wen, L. Zheng, C. Qian, Z. Cheng, H. Zuo, M. Yu, J. Yuan, R. Li and W. Zhang, *Nat. Commun.*, 2023, **14**, 263.
13. Q. Lu, Z. Hu and J. Xia, *Sep. Purif. Technol.*, 2023, **327**, 124820.
14. A. Preetam, A. Modak, S. N. Naik, K. K. Pant and V. Kumar, *ACS Appl. Polym. Mater.* 2024, **6**, 3676-3689.
15. Y. Wu, S. H. Zeng, W. Xu, Y. R. Chen, K. Liu, Y. T. Dai, H. Y. Wu and W. R. Cui, *Sep. Purif. Technol.*, 2024, **345**, 127408.