# Electronic Supporting information (ESI)

# DFT and MD Simulations Supplemented Experiments for Isotopic Fractionation of Zinc Compounds Using Macrocyclic Crown Ether Appended Polymeric Resin

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**Table.S1. Non-bonded interaction parameters**

| | | σ [Å] | ε [kcal/mol] |
|---|---|---|---|
| **PMA-DB18C6** | C | 3.55 | 0.070 |
| | O | 3.17 | 0.155 |
| | CA | 3.40 | 0.109 |
| | N | 3.25 | 0.170 |
| | C | 3.75 | 0.105 |
| | O2 | 2.96 | 0.210 |
| | CT | 3.50 | 0.066 |
| | H | 2.50 | 0.016 |
| | HN | 2.65 | 0.016 |
| | HA | 2.42 | 0.030 |
| | HC | 1.00 | 0.000 |
| **Zn** | Zn | 1.96 | 0.013 |
| **Cl** | Cl | 4.42 | 0.118 |
| **$H_2O$** | Ow | 3.16 | 0.185 |
| | Hw | 1.00 | 0.000 |

**Table.S2. Bonded interaction parameters for Bonds and Angles**

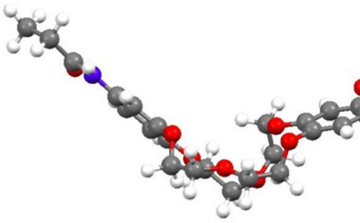
| **Bonds** | **Bond type** | **$l_0$** | **$K_{l0}$[kcal/mol-Å$^2$]** |
|---|---|---|---|
| **PMA-DB18C6** | C-C [DB18C6] | 1.526 | 260 |
| | C-O [DB18C6] | 1.425 | 320 |
| | C-H [DB18C6] | 1.098 | 340 |
| | CA-CA [DB18C6] | 1.400 | 469 |
| | CT-CT | 1.526 | 310 |
| | CA-N | 1.340 | 481 |
| | C2-N | 1.463 | 337 |
| | CA-HA | 1.080 | 367 |
| | N-HN | 1.010 | 434 |
| | CT-HT | 1.090 | 340 |
| | C-O2 | 1.250 | 656 |
| | C2-CT | 1.526 | 310 |
| | CA-C | 1.510 | 317 |
| **$H_2O$** | Ow-Hw | 0.9572 | 450 |

| **Angles** | **Angle type** | **$\Theta_0$** | **$K_{\Theta 0}$[kcal/mol-rad$^2$]** |
|---|---|---|---|
| **PMA-DB18C6** | O-C-C [DB18C6] | 109.5 | 80 |
| | C-O-C [DB18C6] | 111.8 | 100 |
| | C-C-H [DB18C6 | 109.5 | 35 |

|  |  |  |  |
|---|---|---|---|
|  | O-C-H [DB18C6] | 109.5 | 35 |
|  | H-C-H [DB18C6] | 109.5 | 35 |
|  | CA-CA-CA | 120.0 | 63 |
|  | CA-CA-HA | 120.0 | 35 |
|  | CA-N-C2 | 123.2 | 50 |
|  | CA-N-H | 120.0 | 35 |
|  | C2-N-H | 120.0 | 30 |
|  | CA-CA-N | 120.0 | 80 |
|  | CT-C2-N | 116.6 | 70 |
|  | O2-C2-N | 122.9 | 80 |
|  | CA-CA-C | 120.0 | 70 |
|  | CA-C-C | 114.0 | 63 |
|  | C-CA-HA | 120.0 | 35 |
|  | CT-CT-H | 109.5 | 50 |
|  | HT-CT-HT | 109.5 | 35 |
|  | CA-C-O | 109.5 | 50 |
|  | C2-CT-HT | 109.5 | 50 |
|  | O2-C2-CT | 117.0 | 70 |
|  | C2-CT-CT | 111.1 | 63 |
| **$H_2O$** | Hw-Ow-Hw | 55.0 | 104.52 |

**Table.S3. Interaction parameters for dihedrals in PMA-DB18C6**

| **Dihedral type** | **V1** | **V2** | **V3** | **V4** |
|---|---|---|---|---|
| O-C-C-O [DB18C6] | 0 | 0.25 | 0.07 | 0 |
| H-C-C-H [DB18C6] | 0 | 0 | 0.65 | 0 |
| H-C-C-O [DB18C6] | 0 | 0 | 0.65 | 0 |
| C-C-O-C [DB!8C6] | 0 | -0.1 | 0.19 | 0 |
| H-C-O-C [DB18C6] | 0 | 0 | 0.575 | 0 |
| CA-CA-CA-CA | 0 | 7.25 | 0 | 0 |
| HA-CA-CA-HA | 0 | 7.25 | 0 | 0 |
| HA-CA-CA-CA | 0 | 7.25 | 0 | 0 |
| HA-CA-CA-C | -0.209 | -0.627 | 0 | 0.837 |
| C-C-CA-CA | 0 | 0 | 0.3 | 0 |
| HT-CT-CT-C2 | 0 | 2.03 | 0 | 0 |
| HT-CT-CT-HT | 5.184 | 35.932 | -14.355 | -26.761 |
| CA-CA-N-H | 30.288 | -4.811 | -25.476 | 0 |
| CA-CA-NT-C2 | 25.476 | 0 | -25.476 | 0 |
| CA-N-C2-CT | 20.501 | 0 | -20.501 | 0 |
| CA-N-C2-O2 | 0 | 0 | 0 | 0 |
| H-N-C2-O2 | 0 | 7.25 | 0 | 0 |
| H-N-C2-CT | 0 | 0 | 2.2 | 0 |
| O-C-CA-HA | 0 | 0.25 | 0.07 | 0 |
| C-O-C-CA | 0 | 7.25 | 0 | 0 |
| CA-CA-O-C | 0 | 0 | 0 | 0 |
| CA-CA-C-O | 0 | 1.62 | 0 | -0.44 |
| HT-CT-C2-O2 | 0 | 0 | 0.575 | 0 |
| CA-CA-CA-N | -0.627 | 1.883 | -1.25 | 0 |
| N-C2-CT-CT | 5.487 | 0.027 | 0 | -5.514 |
| O2-C2-CT-CT | 4.878 | 0.0 | -4.878 | 0 |



a

b

**Fig. S1.:** Optimized structures of (a) PMA-DB18C6 resin (b) complexes of $Zn^{2+}$ ion withPMA-DB18C6 resin in gas phase.

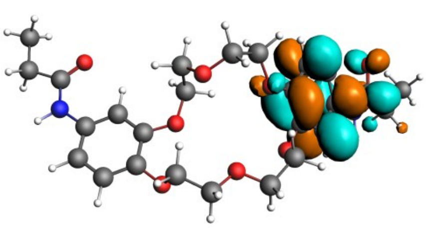


**Fig. S2.:** Calculated HOMO and LUMO of PMADB18C6 resin

**Table S4. Molecular descriptor for different ligand systems at the M06-2X level of theory. (data in the parentheses are using B3LYP/TZVP functional).**

| System | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) | η | χ | ΔN |
|---|---|---|---|---|---|---|
|  | GP/AP | GP/AP | GP/AP | GP/AP | GP/AP | GP/AP |
| $[Zn\text{-}(H_2O)^4]^{2+}$ | -21.66/-12.85<br>(-19.19/-10.39) | -9.17/-0.46<br>(-10.33/-1.55) | 12.48/12.38<br>(8.86/8.84) | 6.24/6.19<br>(4.43/4.42) | 15.41/6.65<br>(14.76/5.97) |  |
| PMADB18C6 | -6.87/-7.04<br>(-5.50/-5.67) | 0.61/0.35<br>(-0.37/-0.55) | 7.48/7.40<br>(5.13/5.10) | 3.74/3.70<br>(2.56/2.55) | 3.13/3.34<br>(2.93/3.12) | 0.61/0.16<br>(0.84/0.20) |

**Table S5. Calculated electron density, Laplacian of electron density, total energy density (H) at BCP of Zn-O bond for $[Zn\text{-}RCE]^{2+}$ system.**

| Molecular system | Bond | P | $\Delta^2\rho$ | H | Ave. ρ | Ave. $\Delta^2\rho$ | Ave. H |
|---|---|---|---|---|---|---|---|
| $[Zn\text{-}RCE]^{2+}$ | Zn-O | 0.057 | 0.26 | -0.0026 | 0.055 | 0.250 | -0.0025 |
|  | Zn-O | 0.055 | 0,25 | -0.0018 |  |  |  |
|  | Zn-O | 0.057 | 0.27 | -0.0019 |  |  |  |
|  | Zn-O | 0.056 | 0.26 | -0.0022 |  |  |  |
|  | Zn-O | 0.049 | 0.21 | -0.0011 |  |  |  |
|  | Zn-O | 0.049 | 0.22 | -0.0002 |  |  |  |

## Experimental Section

### Synthetic method

PMA-DB18C6 was prepared by condensation reaction between carboxylic (–COOH) group of PMA resin and amine (–$NH_2$) of 4,4'-diaminodibenzo-18-crown-6 (DADB16C6). The introduction of the amine on the DB18C6 was first carried out following already reported method with little modifications followed by the condensation step.

### Synthesis of dinitrodibenzo-18-crown-6 (DNDB18C6)

DNDB18C6 was prepared from DB18C6 (**Fig. S3**) following method reported in literature[1-2]. Briefly, 10 g of DB18C6 was dissolved in 200mL chloroform and 150mL glacial acetic acid was added to it. 7 mL of nitric acid in 20 mL of glacial acetic acid was added slowly to the solution in stirring condition. The reaction mixture was further stirred at room temperature for 24 hours. The solution was neutralized with $Na_2CO_3$solution followed by separation of the organic phase which was dried over $MgSO_4$. The clear chloroform phase was distilled in rotary evaporator producing a crude yellow colour product of DNDB18C6.

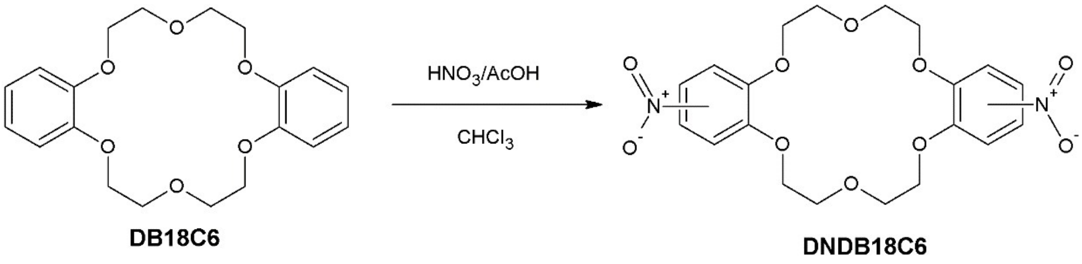


**Fig. S3.** Preparation step of DNDB18C6 from DB18C6 by nitration

## Synthesis of Diaminodibenzo-18-crown-6 (DADB18C6)

DNDB18C6 were reduced by amination of DNDB18C6 to prepare DADB18C6 (**Fig. S4**) following reported technique[1, 3]. 5 g of crude DNDB18C6 was dissolved in 300 mLethanol in reflux condition. To the solution, 1.2 g of 10% Pd/C catalyst was added followed by slow and drop wiseaddition of60mL of hydrazine hydrate wasadded. After refluxing the solution for 7 h, the resulting reaction mixture was filtered in hot condition through Whatman 541 filter paper. The precipitation of white DADB18C6 product (cotton like) was seen on the filtrate. The filtrate was kept overnight undisturbed.The white product was filtered off under vacuum through Whatman 541 and dried in vacuum oven at 60$^0$C.

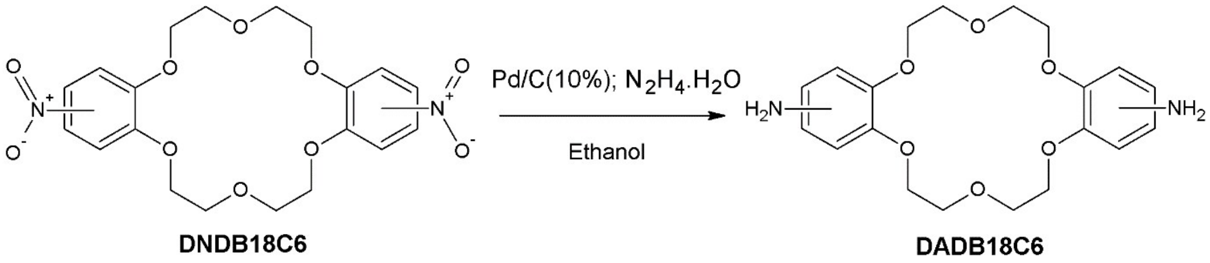


**Fig. S4.** Reduction step of DNDB18C6 to DADB18C6

## Preparation of DB18C6 functionalized PMA (PMA-DB18C6) resin

PMA-DB18C6 resin is prepared by theamidation coupling reaction using DCC coupling reagent and DMAP as additive (**Fig. S5**) [4]. 10 g of PMA resin, swelled overnight in DMF, was added to the solution containing 1 g of DADB18C6 dissolved in DMF. The reaction mixture is swirled in an orbital shaker at 400rpm. A solution of 0.25 g of DCC and 0.04 g of DMAP in DMF was added slowly drop wise to swirling reaction solution. The swirling was continued for 120 hours. The product was separated from the solution by filtration with several wash with DMF, hot ethanol, 1M HCl solution and ethanol. Finally, the DB18C6 grafted resin was dried overnight in vacuum oven at 80$^0$C.

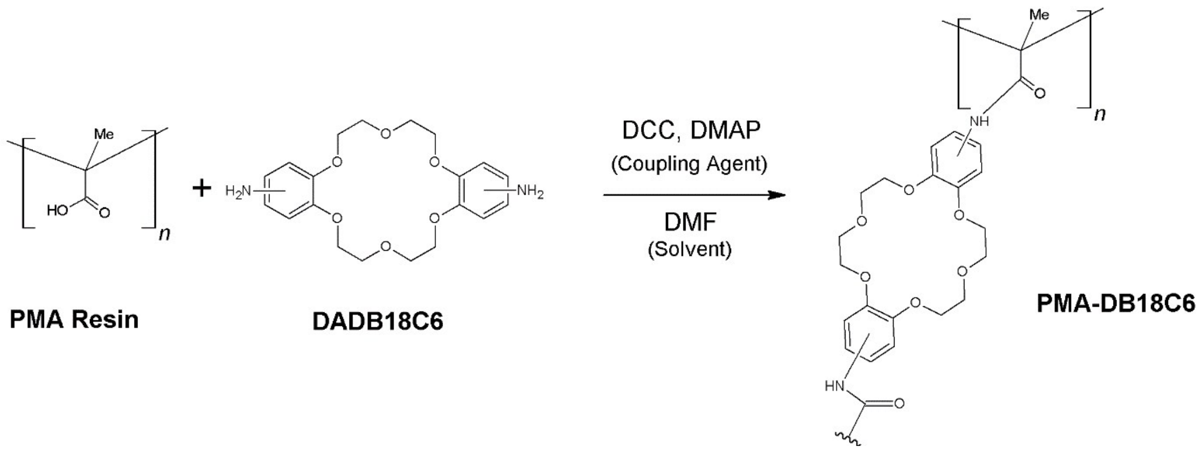


**Fig. S5.** Amidation coupling between PMA resin and DAAB18C6 to PMA-DB18C6

### Characterization

The nitration and amination steps were monitored by observing the FTIR (Bruker Invenio) and NMR ($^{13}$C-NMR, Bruker Avance 500) spectra of reactant and product. The grafting of DB18C6 with PMA resin through elemental analysis (Perkin Elmer series - II 2400 Elemental Analyzer), FTIR spectroscopy, and thermogravimetry(TGA, Netzsch-STA 449-Jupiter F3).

### Batch Adsorption Studies

Batch solid-liquid extraction of Zn(II) metal ions were conducted with the prepared PMADB18C6 as well as PMA resin in aqueous medium. The stock solutions of Zn(II) were prepared by dissolving appropriate amounts of zinc sulphate ($ZnSO_4$) in deionized water. Adsorption as a function of solutionpH, contact time, initial zinc ion concentration, temperature, and ionic strength were performed. The selectivity and regeneration performances were also investigation. In order to conduct the pH studies, solutions of 10 mg/L Zn(II) solution were prepared having pH between 2 to 8. The pH of the solutions was modified by using dilute solution of NaOH and HCl. After the addition of adsorbent to the prepared Zn solution of desired pH in a screw-capped glass sample bottle, the mixture is equilibrated by swirling at 300 rpm in an orbital shaker (model: IKA KS 4000) for a period of 2 hours. The supernatant solution was then separated and analysed for Zn metal ion concentration using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Horiba Scientific make, Ultima 2 model). Experiments were performed twice and average values were considered for the calculation. The adsorption capacity was determined using equation (S1) [16].

$$q_e = (C_0 - C_e) \times \frac{V}{m} \text{(S1)}$$

where $q_e$ (mg/g) is the equilibrium adsorption capacity. $C_0$ and $C_e$ (mol/L) refer to the initial and final zinc (II) concentration, respectively. $V$(mL) refers to the volume of solution, and $m$ (g) is the mass of the adsorbent. The percent removal of metals from the solution was calculated by the following equation (S2).

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad \text{(S2)}$$

## Effect of contact time

100 mL of 50ppm Zn(II) solution at pH6 was taken in 250mL stoppered conical flask. 0.5 g of the adsorbent (PMADB18C6 or PMA)was added tosolution upon shaking in the orbital shaker at 300rpm. After specific time interval from the adsorbent addition, 0.1 mL of aliquot was isolated and the concentration of Zn(II) was measured using ICP-OES. The time dependent adsorption data up to 250minutes were taken.

## Effect of initial concentration

Adsorption isotherms were determined by keeping the adsorbent amount constant and varying the initial concentrations of Zn(II) at pH 6. The initial concentrations were varied between 10 and 400 ppm. Similar batch adsorption technique and analysis was followed as above.

## Effect of temperature

Effect of temperature studies were carried out by varying the temperature from RT to $80^0$Cat pH 6. The adsorbent dose and initial metal ion concentration were kept constant in all the studied temperature. The adsorbate-adsorbent system was placed inside the incubator shaker, desired temperature was maintained and equilibrated for 2 hours. The aliquot was collected at the set temperature and analysed for Zn concentration.

## Desorption and regeneration studies

Desorption studies are performed for the reuse of the adsorbent by unloading adsorbate. In this study, desorption is done by using sulfuric acid as a desorbing agent. 1 M $H_2SO_4$was equilibrated withknown amount Zn(II) loaded PMADB18C6 or PMA adsorbent. The desorption percentagewas evaluated from the amount of Zn(II) leached out after the desorption and the initial loading using equation (S4)

$$\text{Desorption Percentage (\%)} = \frac{Amount\ of\ Zn(II)\ released\ in\ solution}{amount\ of\ Zn(II)\ adsorbed} \times 100 \qquad \text{(S3)}$$

For regeneration studies, the adsorbent after desorption was washed with 1M $H_2SO_4$followed by water and dried. The dried PMADB18C6 or PMA resin was again used for solid-liquid extraction of Zn(II) ions from aqueous solution using similar procedure mentioned in the previous section and adsorption efficiency was calculated. The desorption-adsorption cycles were repeated 5 cycles to check the reusability of the adsorbents.

## Fixed bed column studies

A plastic-coated glass column of 1.5 x 60 cm IDx L was used for the fixed bed column studies with influent flowing from top of the column and effluent is collected at the bottom. A flow rate of 4.5 mL/min was maintained by using a peristaltic pump. 1 L of Zn solution was passed through the column having 9.25g of PMADB18C6 adsorbent as the fixed bed of bed length 10cm. Effluent solution samples were collected for plotting the breakthrough curve. Ceramic plug and cloth filter was used to act as a membrane to pass the solution and hold the resin inside the column. A schematic diagram of the fixed bed setup is shown in the **Fig. S6.**

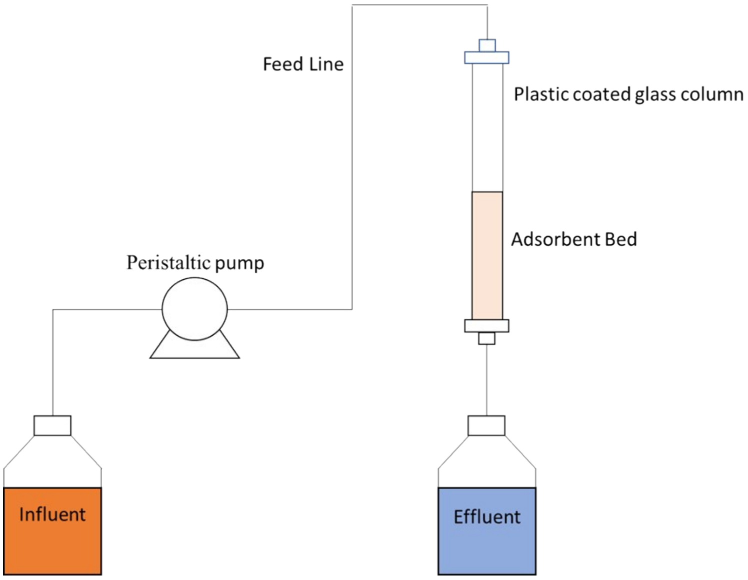


**Fig. S6.** Schematic diagram of the setup used for the fixed bed column separation of Zn(II) using PMADB18C6 or PMA as chromatographic bed.

The purpose of column studies is to acquire breakthrough curve which will eventually characterizes the kinetic adsorption performance of the fixed bed column studies. This kinetic study will help calculating the parameters like bed saturation point, inlet volume and maximum adsorption capacity of fixed bed column. These data are very useful of the scaling up of the process. The breakthrough curve is represented by the ratio of effluent concentration to influent concentration ($C_t/C_0$) as a function of volume (V) or time. The breakthrough point $t_b$ (min) where the effluent concentrationreaches arbitrarily at some low value was chosen at the time when$C_t/C_0 = 0.05$ and the exhaustion/saturation time $t_s$ (min) of the bedwas considered when Ct/C0 = 0.95.

The total quantity of adsorbate adsorbed ($Q_{tot}$) for a given feed concentration and flow rate is the area under the curve where $C_0$-$C_t$ is plotted against V and is given as

$$Q_{tot} = \int_0^{V_t} (C_0 - C_t) dV \quad \text{(S4)}$$

Where $V_t$ is the volume of effluent collected at time t. The equilibrium capacity of an adsorbent ($Q_e$, mg/g) is given as

$$Q_e = \frac{Q_{tot}}{M} \quad \text{(S5)}$$

Where M is the mass of the adsorbent present in the fixed bed column. The flow of influent fluid creates awave front as it flows through the packed adsorbent bed. Equilibrium takes place in this broad zone of the adsorbent bed called the mass transfer zone (MTZ) where the active adsorption takes place. The height of the mass transfer zone ($h_z$) can be calculated as

$$h_z = L \frac{t_e - t_b}{t_e} \qquad \text{(S6)}$$

Where L is the adsorbent bed height.

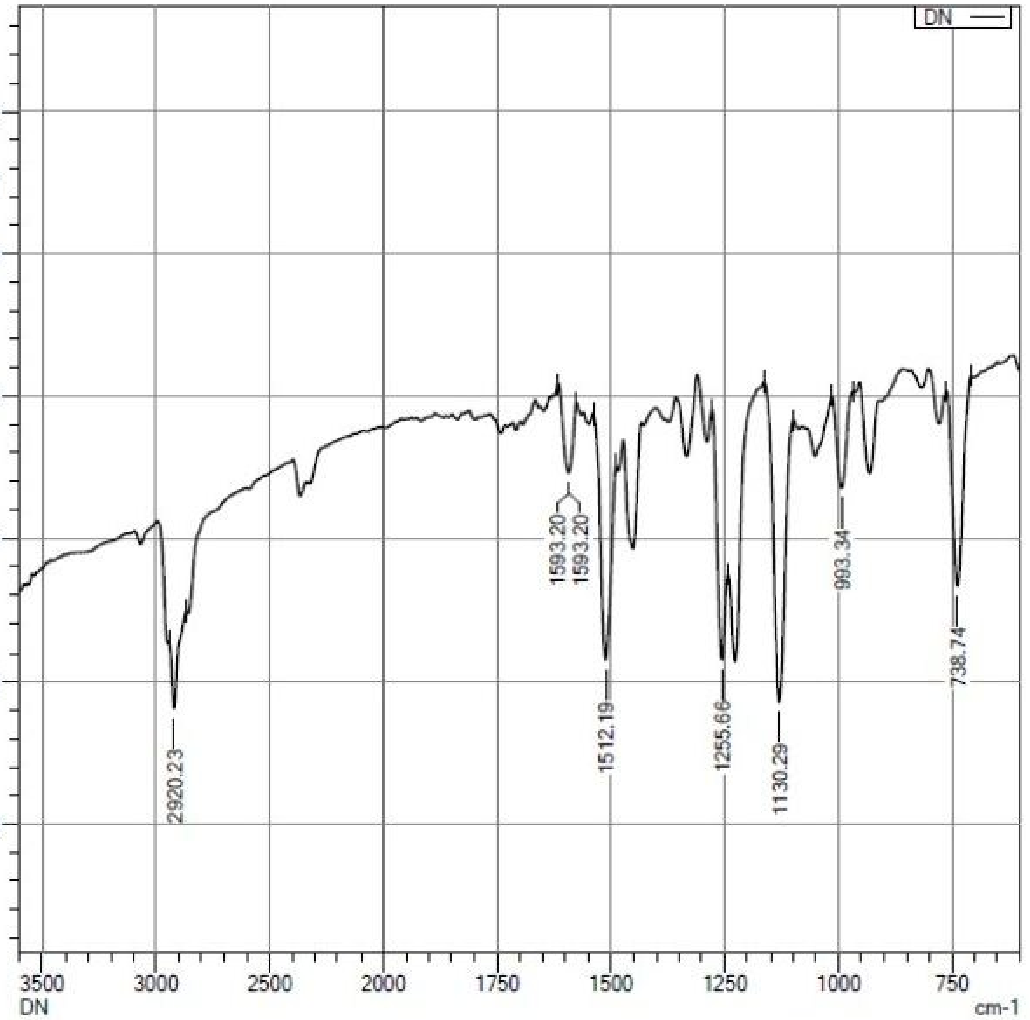
## Experimental results and discussion

### Characterization

### FTIR

The FTIR spectra of DNDB18C6 and DADB18C6 are shown in **Fig. S7(a-b).** The appearance of two sharp peaks of $-NO_2$ stretching vibration at 1330cm$^{-1}$ and 1512cm$^{-1}$ in the IR spectra of DNDB18C6 (Fig. S7(a)) indicates the nitration of DB18C6. The IR peaks of aromatic $-NH_2$ groups (N-H stretching vibration peaks between 3400-3500 cm$^{-1}$ along with the N-H bending peak at 1595cm$^{-1}$ ) are observed in the IR spectra of DADB18C6 (Fig. S7(b)) suggesting the amination of the DNDB18C6. The condensation of DADB18C6 on the surface of PMA resin can be attributed from theIR peaks amidic (-C(=O)-NH-, **Fig. S5**) linkages (N-H stretching, C=O stretching and N-H bending) and etheric peaks (1159 cm$^{-1}$) along with other PMA resin peaks, as shown in **Fig. S8**.

**(a)**


DN
105
%T
100
95
90
85
80
3500
3000
2500
2000
1750
1500
1250
1000
750
DN
cm-1
2920.23
1593.20
1593.20
1512.19
1255.66
1130.29
993.34
738.74

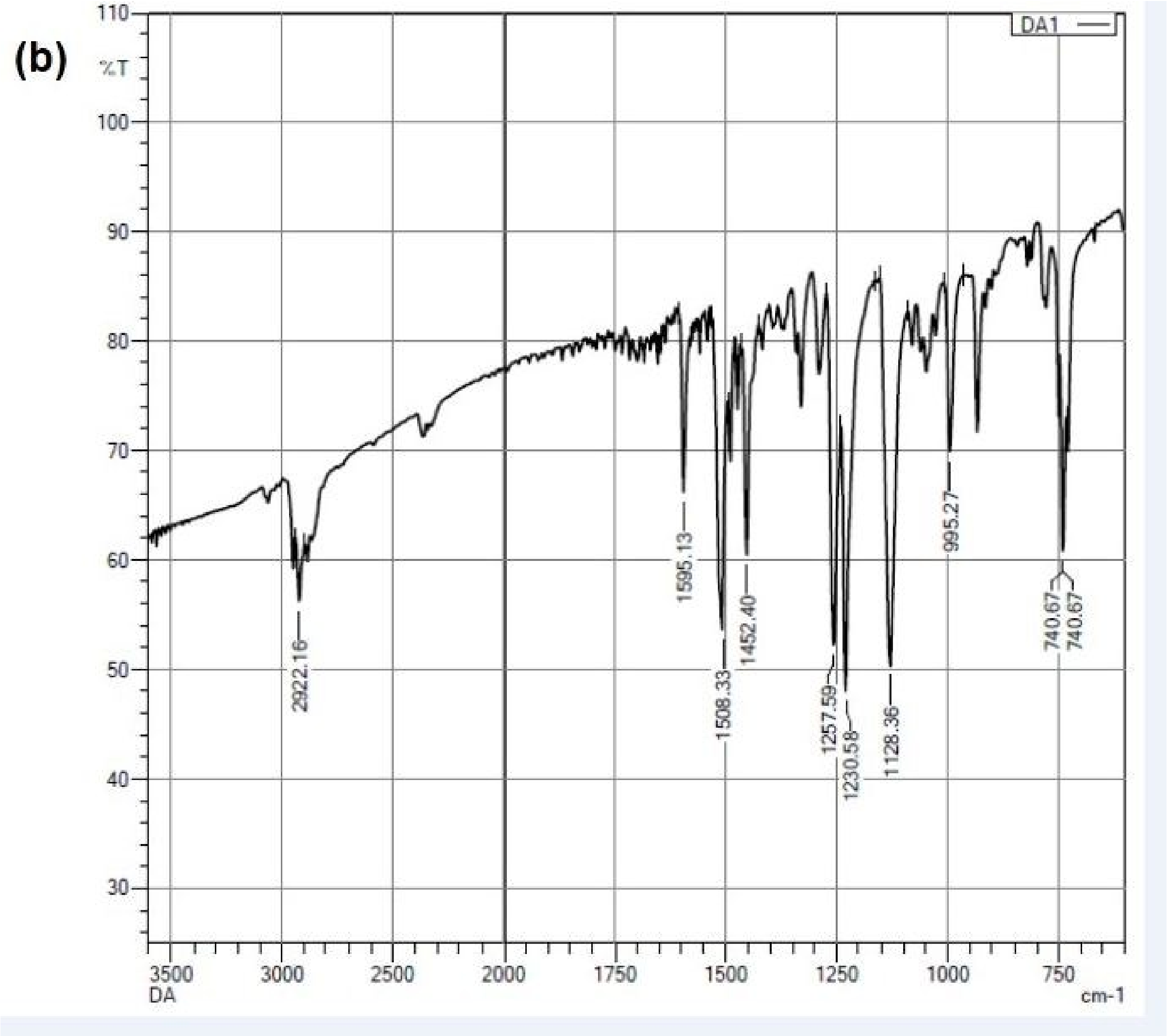


**Fig. S7.** Recorded FTIR spectra of (a) DNDB18C6 and (b) DADB18C6

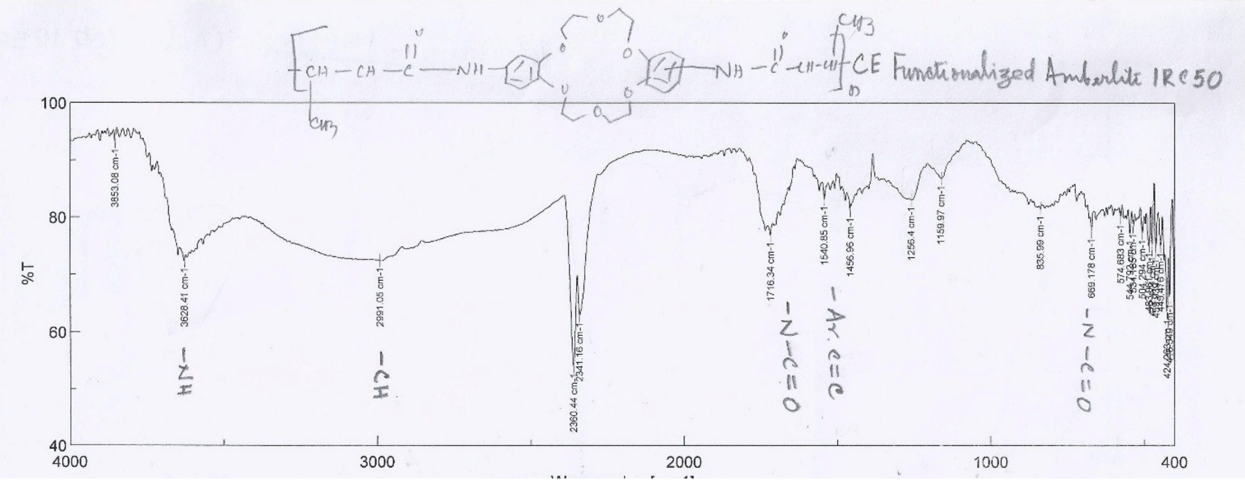


**Fig. S8.** Recorded FTIR spectrum of PMADB18C6

## NMR

The $^1$H NMR spectra of purchased DB18C6 and prepared DNDB18C6 and DADB18C6 are shown in Fig. S9 (a-c). The multiplate signals between 3.9 to 4.2 ppm are the chemical shift resonance of 16Hs of $–O-CH_2-CH_2-O-$ units of the basic crown ether system present in all the structures. The $^1$H NMR peaks within 6.8 – 7.4 ppm are attributed to protons of two benzene rings in all the three structures. The weak chemical shift of 4Hs of amine groups of DADB18C6 are seen in the Fig. S9(C).

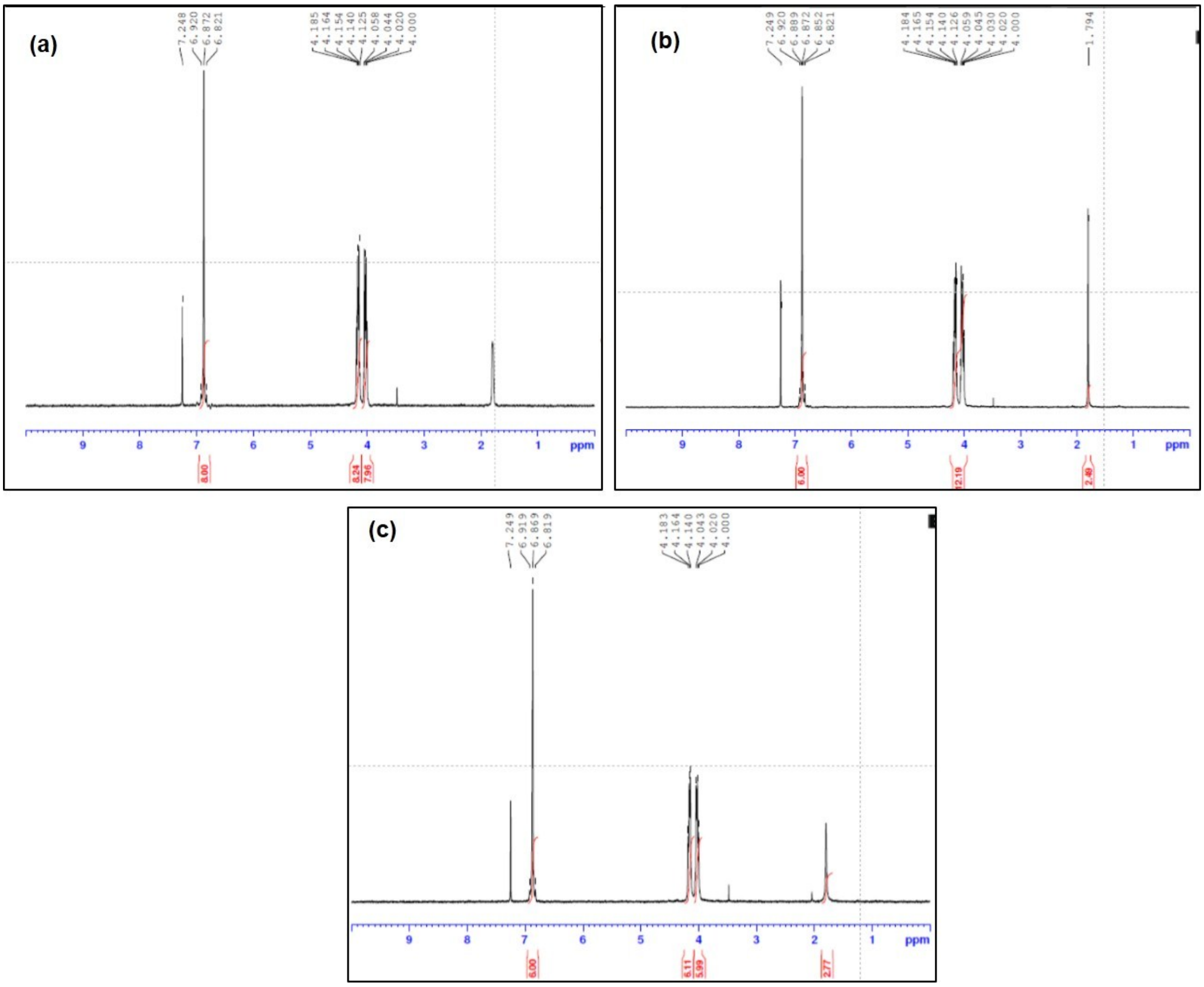


**Fig. S9.** 1H NMR spectra of (a) DB18C6 (b) DNDB18C6 and (c) DADB18C6

## Elemental Analysis

The CHNO elemental analysis of PMA and PMADB18C6 is shown Table S3. The introduction of DADB18C6 (chemical formula $C_{20}H_{26}N_2O_6$) in the structure of PMA (chemical formula $(C_4H_6O_2)n$) can easily be understood from the appearance of nitrogen (N) content and increase in the carbon (C) content in case of PMADB18C6 compared to PMA.

**Table S6. Elemental analysis data of PMA and PMADB18C6**

| Sample | C (%) | H (%) | N (%) | O (%) |
|---|---|---|---|---|
| **PMA** | 49.5 | 10 | - | 40.5 |
| **PMA-DB18C6** | 52.8 | 10.2 | 2.4 | 34.6 |

## TGA

The thermogravimetric scan of PMA and PMDB18C6 are shown in Fig. S10. It can be observed that the formulation of the weight loss is same which is based on the backbone structure of the PMA resin, except a sharp weight loss after 250$^0$C in case of functionalized PMA. The extra weight loss may be attributed to the thermal decomposition of the DB18C6 unit from the surface of the resin backbone.

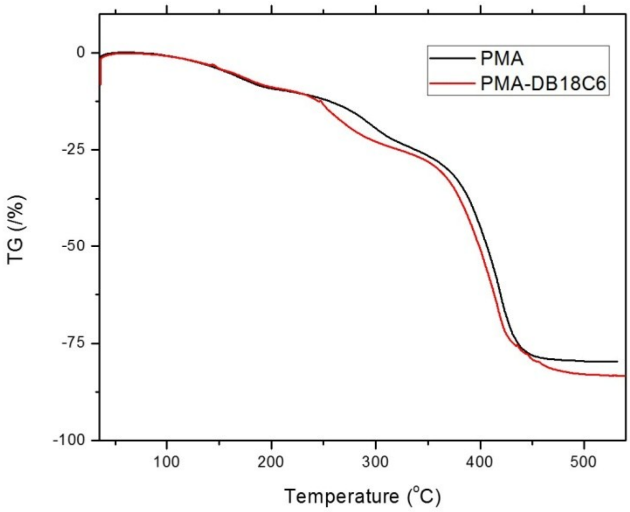


**Fig. S10.** Thermogravimetric analysis of PMA and PMADB18C6

## Adsorption studies

### Effect of pH

The pH value of Zinc (II) solution plays a very crucial role in the entire adsorption experiments. The adsorption of Zn (II) by PMA and PMADB18C6 resin as a function of pH was shown in **Fig. S11**. The highest adsorption of both of the adsorbent are found within pH 6-7. The adsorption capacity of the resin has increased after its DB18C6 functionalization as can be clearly seen from highest adsorption of PMA (0.56 mg/g) and PMADb18C6 (0.74 mg/g). The different pH of highest capacity of PMA and PMADB18C6 suggest the change in the surface functional groups on the resin. The variation of $q_e$ with pH is a result of tough competition between Zinc (II) and $H^+$ ions for the available and active adsorption sites on the PMA & DB18C6PMA resin surface.

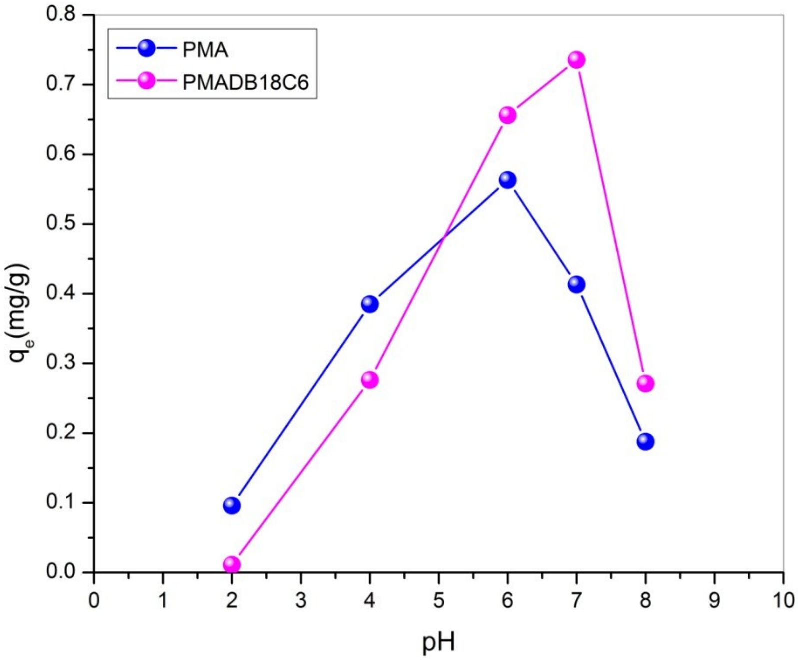


**Fig. S11.** Effect of pH on Zn(II) adsorption by PMA and PMADB18C6

At low pH, the surface of the PMA or PMADB18C6 will in protonated and binding of metal ions will be lower. When the pH increases, the surface covered $H^+$ leaves the resin surface, making more adsorption sites available for Zinc (II) and the sorption increases. The decrease of adsorption after pH 6 or 7, may be due to the formation of anionic species of the Zn(II) which would not bond strongly on the surface functional groups (carboxyl or crown ethers) containing electronegative oxygen.

### Isotherm modeling on equilibrium data

The equilibrium data of the Zn(II) adsorption by PMA and PMADB18C6 were fitted with Langmuir (equation S1) and Freundlich (equation S2) isotherm models.

$$q_e = \frac{q_m b C_e}{1 + bC_e} \quad \text{(S1)}$$

$$q_e = K_f C_e^{1/n} \quad \text{(S2)}$$

Where $q_m$ and b are the Langmuir isotherm parameters. $q_m$(mg/g) is the maximum possible amount of metal ion adsorbed per unit of weight of adsorbentand b (L/mg) is a constant related to the affinity of the bindingsites for the metals.$K_f$ and n are the Freundlich constants which measure the adsorption capacity and intensity, respectively.

**Table S7. Langmuir and Freundlich isotherm model parameters.**

| Isotherm Model | Parameters | PMA | PMADB18C6 |
|---|---|---|---|
| | Temperature ($^0$C) | 30 | |
| Langmuir | $q_{m,exp}$ (mg/g) | 1.129 | 3.276 |
| | $q_m$(mg/g) | 1.133 | 3.638 |
| | b(L/mg) | 0.082 | 0.017 |
| | $R^2$ | 0.942 | 0.947 |
| Freundlich | $K_f$ | 0.371 | 0.380 |
| | n | 5.189 | 2.736 |
| | $R^2$ | 0.911 | 0.851 |

## Effect of temperature

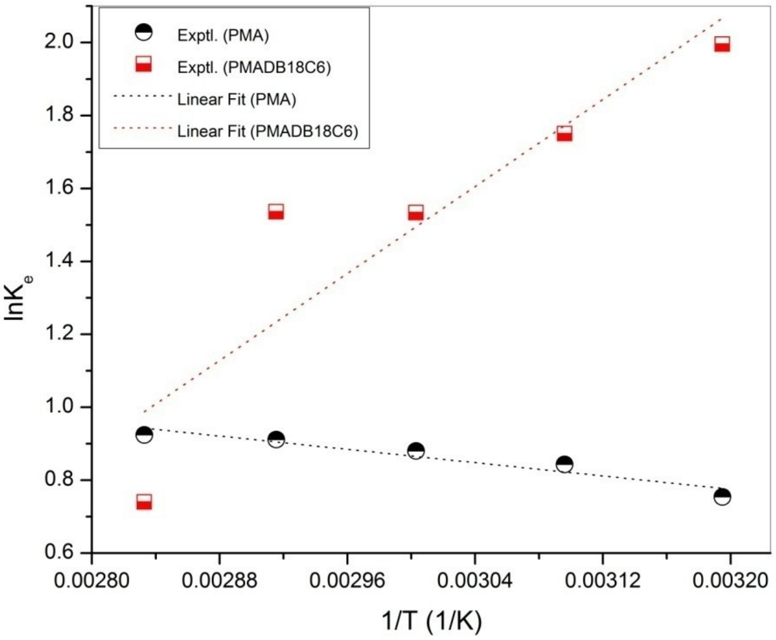


**Fig. S12.** Van't Hoff plot for the Zn(II) adsorption by PMA and PMADB18C6 resins

## Isotopic separation coefficients

The separation coefficients, ε's were calculated by using the isotopic enrichment curves of the front and rear boundaries according to the equation developed by Spedding et al. [5] and Kakihana and Kanzaki[6].

$$\varepsilon = \sum\left(\frac{q_j}{Qr_0}\right)\left[\frac{r_j - r_0}{1 - r_0}\right]$$

Here, q is the amount of Zn in the sample fraction, Q is the total amount of sorbed Zn in the resin packed in the column, $r_j$ is the isotopic ratio of $^{H}Zn/^{L}Zn$, and the subscripts j and o denote the fraction number and the feed, respectively.

**Table S8. Experimentally determined separation coefficient of Zn ion with PMA and PMADB18C6 resin in the column chromatography.**

| System | Separation coefficient | | |
|---|---|---|---|
| | $\varepsilon\times10^4$ ($^{66}Zn/^{64}Zn$ ) | $\varepsilon\times10^4$ ($^{68}Zn/^{64}Zn$ ) | $\varepsilon\times10^4$ ($^{68}Zn/^{66}Zn$ ) |
| PMA | 8.51 | 5.85 | 4.76 |
| PMA DB18C6 | 13.80 | 27.41 | 48.70 |

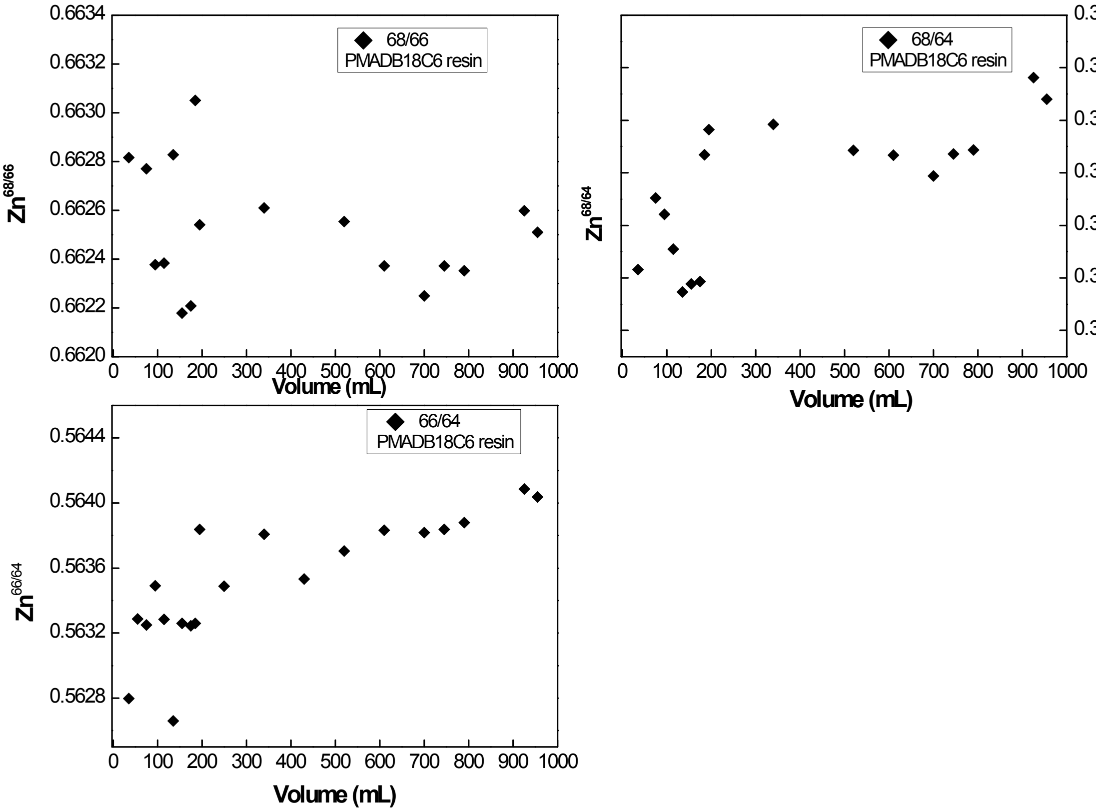


**Fig. S13**: The variation in the isotopic ratio of Zn with PMADB18C6 resin

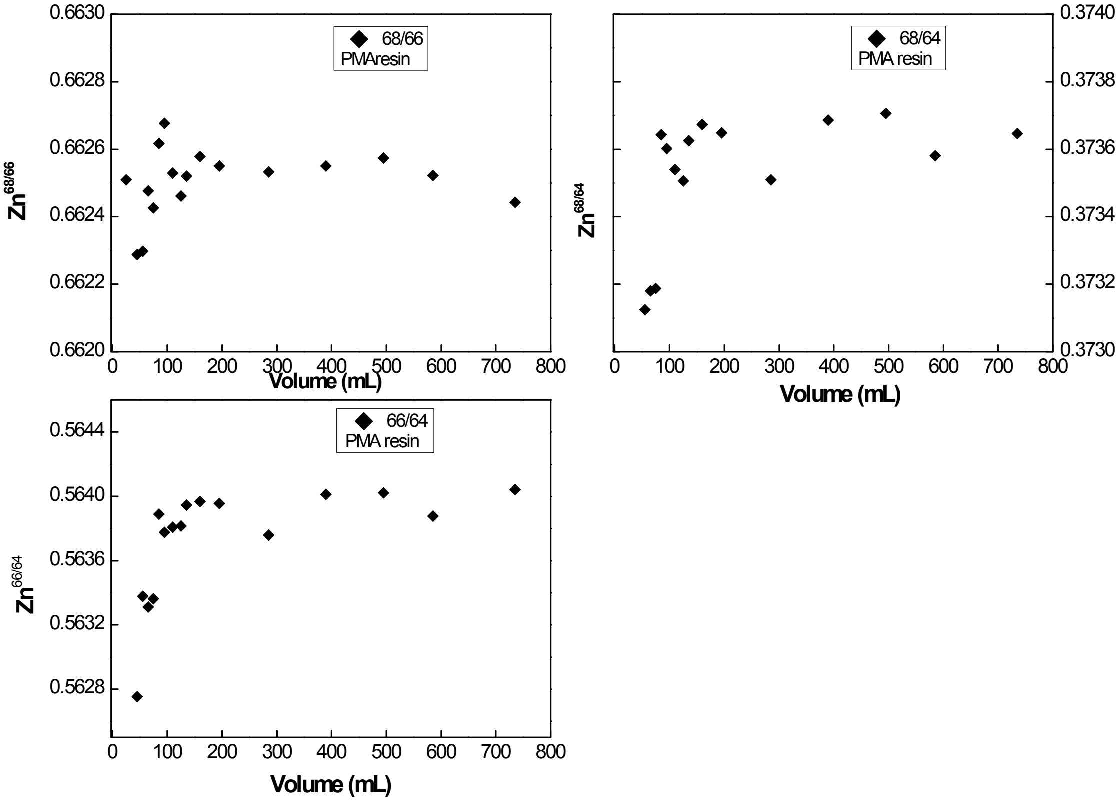


**Fig. S14**: The variation in the isotopic ratio of Zn with PMA resin

The profile of Zn isotopic fractions in the effluent fractions with PMADB18C6 and PMA resin are displayed in Figure 10 and 11 respectively. From the figure it is clear that the front end of the band is enriched with respect to heavier isotope and rear end is enriched with respect to lighter isotope with both PMA and PMADB18C6 resin. The calculated separation coefficients ($\varepsilon\times10^4$) were found to be 8.51,5.85 and 4.76 for 66/64, 68/64 and 68/66 respectively for PMA resin. Whereas, with PMADB18C6 resin the separation coefficient values for Zn were found to be 13.8,27.41 and 48.70 for 66/64, 68/64 and 68/66 respectively which are one order higher in magnitude compared to that of PMA resin. These values indicates that PMADB18C6 holds promise for the future isotopic enrichment technology.

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