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- 16 Figure S1: (a) Sorption-desorption cycles (n) Recovery (%) relationship (b) Plot of solution
- 17 pH vs distribution ratio, K_D (c) Contact time-sorption relationship.



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21 Figure S2: (a) 3-D structure of methylated surface; red balls (SiMe₂O₂ groups), gray balls 22 (SG unit cells), violet balls (cross linking sites) (b) long fatty acid chain of nCA is hooked at 23 hydrophobic SSG surface while its –COOH group is present in hydrophilic mobile phase as 24 hydrogen bonded dimeric metal trapping core (HBDMTC).

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30 Figure S3: TGA curve of (a) SSG (b) SSG-nCA (c) SSG-nCA-Th(IV)



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32 Figure S4: Systematic analysis on DFT optimization of unit cells comprising different number

33 of silicon atoms i.e. (a) 3 silicon (b) 6 silicon (c) 12 silicon (d) 16 silicon (e) 20 silicon



35 Figure S5: An Electrospray Ionization Tof derived mass spectrum of SSG along with possible



36 conversion of different fragments.

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38 Figure S6: XRD spectra (a) SSG (b) SSG-nCA and (c) SSG-nCA-Th(IV).







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42 Figure S8: (a) Plot of pH of the influent solution vs. extraction (%) of Th(IV)



44 Figure S9: DFT optimized configuration and the spatial distribution of electron population
45 (HOMO-LUMO) of (a) (nCA)₂-[Th(OH)₂]: -44521.56 eV (b) (nCA)₂-[Th₂(OH)₂]⁺⁴: -55533.7 eV
46 (c) (nCA)₂-[Th₂(OH)₂(H₂O)₂]⁺⁴: -59676.5 eV (d) (nCA)₂-[Th₂(OH)₂(H₂O)₄]⁺⁴: -63812.5 eV.

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51 Figure S10: DFT optimized (Method: HF; basis set: SDD) structures of different Th(IV)-aqua 52 species: (a) $[Th(OH)_2]^{2+}$: -15845.8 eV: HOMO: -24.32 eV; LUMO: -10.28 eV; η = 14.04 eV; (b) 53 $[Th_2(OH)_2]^{6+}$: -26103.6 eV; HOMO: -45.29 eV; LUMO: -32.14; η = 13.15 eV; Dipole moment: 54 2.44 Debye; Th-O: 237 pm (c) $[Th_2(OH)_2(OH_2)_2]^{6+}$: -30252.87 eV; HOMO: -40.96 eV; LUMO: 55 -27.47; η = 13.49 eV; Dipole moment: 2.47 Debye; Th-OH: 237.12 pm; Th-OH₂: 229 pm (d) 56 $[Th_2(OH)_2(OH_2)_4]^{6+}$: -34395.80 eV; HOMO: -39.27 eV; LUMO: -26.27; η = 13.0 eV; Dipole 57 moment: 4.90 Debye; Th-OH: 237.12 pm; Th-OH₂: 229 pm.



59 Figure S11: DFT optimized (Method: HF; basis set: SDD) structure of dimeric nCA: Energy:

60 - 29385.26 eV; HOMO: -11.5 eV; LUMO: 4.13 eV; η = 15.63 eV; OH-O: 1.73 pm

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63 Table S1: Comparison of sorption capacities of various solid phase extractors for Th(IV)

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	т. т	T 1.11 /•	Г	G		DE	DTC	D	D
Inert support	Ligand	Immobilization condition	Eq. time, t _{1/2} (min)	Sorption conditio n (pH) {foreign ion toleranc e: M}	Elution conditio n in M (mL)	PF	BTC (µmol g ⁻¹)	Reco v (%) & RSD (%)	Reuse (cycles) & stability
Cellulose	5- chloroqui no-line- 8-ol	1h refluxing in 60% NaOH and 8h stirring	5-30 min	5.0-7.0 {0.01}	1M HCl (5 mL)	200	86.21	 & 1.5	
AXAD-4	malonic acid	Amberlite XAD-4 was acylated in anhydrous $CaCl_2 \& AlCl_3$ with 8h stirring and finally diethyl malonate was immobilized by another 2h stirring in K ₂ CO ₃	< 0.5 min	6.0-8.0.	1M HCl (5 mL)	500	83.1	& 	30 & stable up to three months at ambient condition
AXAD-4 15	o-anillin- semicarb -azone	After 1h treatment of AXAD-4 with Conc nitric acid + sulfuric acid it was refluxed with Sn- HCl for 12h in ethanol. Diazotized and refluxed with o-vanillinsemi- carbazone for another 40h at 0-3°C	5 min	3.0-4.5 {0.5- 1.5M}	1.5N HCl (20 mL)	125	13.9	96– 98 & 2.2	10–12 &
AXAD-4 19	Octacarb oxymeth yl-C- methyl- calix[4]re sorcinare ne	6h refluxing under nitrogen and 24h stirring of AXAD-4 with ligand		3.0 {0.005- 0.15M}	2M HCl (10 mL)	105	290	96– 99 & 0.2- 0.5	10–12 & stable up to 2M HCl
AXAD- 2000 20	α- benzoin oxime	0.01M benzoin oxime in methanol was reacted with AXAD-2000 resin with 1h constant stiring		2.5-5.0 {0.035± 0.015M}	1 N HCl (5 mL)	100	14.2	98.5 & 3.7	
AXAD-4 21	bicine ligands	30h refluxing with acetic anhydride in AlCl ₃ for acylation of XAD-4; KMnO ₄ oxidation in NaOH followed by 1h refluxing with thionyl- chloride at 60°C and finally the intermediate was refluxed with ligand for 12h at 100°C.	10 min	4.5–9 {0.2- 0.3M}	1M HCl (10 mL)	50	250		

AXAD-16	Carminic acid	AXAD-16 was treated with 6M HCl for 12h and ligand impregnation need another 6h	5 min	3.5-5.75 {0.01-0.5 M}	2.25M HCl (10 mL)	250	832	97.85 ± 0.88 & 2.47	50 &
AXAD-4 23	Bacillus sp.	Bacteria was cultivated in pH 6.0 with constant shaking for 24h and centrifuged (10,000 rpm). Bacteria mass and AXAD-4 was taken in water, dried at 105°C. Wetting for 1h and drying steps were repeated to maximize the contact.		5.0 {5-500 μg mL ⁻¹ }	1 M HCl (5 ml)	100	74	99.8 ±0.3	10 &
AXAD-4 24	Humic acid (HA)	Dry XAD-4, contacted with 50mL (1.0% HA) in 1M NaOH-methanol (20 : 80) for 6 h until equilibrium		3.0-7.0 {100}	2 M HNO ₃ (10–15 mL)		151	96– 99 & 2.7	15 &
Styrenediv i-nyl benzene copolymer (XAD-4) ²⁵	p-tet- butyl- calix[8]ar ene	Method described in [8]	5 min	4.5-9 {0.05M}	0.1M HCl (10 ml)	50	750	98.4 & 0.01	Only several cycles
Merrifield chloro methylate d styrene– divinyl- benzene resin ²⁶	di-bis (2- ethyl- hexyl)ma lonamide (DB2EH M)	DB2EHM was refluxed with resin support for 12h in DMF at 60°C.	4.1 min	At 5M HNO ₃ {0.07- 0.82M}	1M amm. carbonate (10-15 mL)	250	164	99.5 & 5.2	15 & stable up to <4 M HCl
Merrifield chloro methylate d resin 27	calix[4]ar ene-o- vanillin semicarb azone	Heated at 75 °C tempera- ture for 8 h under N ₂ gas atmosphere. Repeated washing with the solvents dimethylfo - mamide and tetrahydrofuran	5 min	3.5-4.5	2.0N HCl or 0.1N HNO ₃ (6.5mL)	153	177	99.7 & 1.5	20 & Stable up to 5N HCl, 3N HNO ₃ and $3.5N$ H ₂ SO ₄
Merrifield peptide resin 28	11,23- Disemica rbazeno- 26,28- <i>n</i> - dipropox y-25,27- dihydrox y calix[4]ar ene	4h refluxing and 4 h stirring of Merrifield's resin with ligand in tetrahydrofuran– dimethylformamide (THF–DMF) medium (60ml, 5:1) for 24 h in an argon atmosphere.	6.5 min	2.5-4.5 {0.5- 2.0M}	2M HCl/ 0.15 M HNO ₃	102	12.2	98 & 2	10–12 & Stable up to 2.0 M HCl

Merrifield chloromet hylated resin 29	Thenoyl trifluoroa cetone (TTA)	12h refluxing at 60°C of Merrifield chloromethy- lated resin with TTA in tetrahydrofuran (THF) under anhydrous condi- tion using NaH	3.0 min	2.0-4.0 {0.1M- 0.4M}	4M HCl / 4M HNO ₃	300	117.2	99.5	30 & stable at high acid condition
Merrifield chloromet hylated resin ³⁰	N,N,N,N -tetra- hexylmal on-amide	Ligand was prepared by treating the reagents at 0°C for 4h in dry ether medium and finally was coupled with the support material in dry NaH and dry DMF at controlled temperature (70°C).	3.0 min	4M HNO ₃ {0.05- 0.06M}	0.5 M (NH ₄) ₂ C O ₃ (10 mL)	350	402	99.6	25 & Stable up to 4 M HNO ₃
Benzophe none ³¹	5,7- dichloro quinoline -8-ol	5,7-Dichloroquinoline- 8-ol and benzophenone (1:100) in acetone was reacted for 3h with constant stirring and was settled for 10 min.	15 min	6.0-6.5	Acetone (5 mL)	200	4.74	99.0 & 2.9	~ &
Duolite XAD761 32	9-phenyl- 3- fluorone chelates			4.0-6.0 {5- 5000 M}	2 N HCl (5 mL)	30		92±1 & 4.5	>300 &
mesoporo us silica (MCM- 41) ³³	5-nitro-2- furaldehy de (fural)	12 h refluxing under dry nitrogen atmosphere	0.5-3 min		1.0 N HNO ₃ (1mL)	100	211	97.5 & 2.6	>8 &
Chitosan/ bentonite (PMAA- g-CTS/B) ³⁴	Poly (methacr ylic acid)	SPE material was pre- pared through polymeri- zation reaction in N_2 atmosphere KPS as initiator and need 6-8h	120 min	5.0-6.0	0.1M HNO ₃ ; elution need 2h shaking		431	97.2	4 &
MCI GEL CHP20P 35	2- nitroso- 1- naphthol	MCI GEL CHP20P (2 g) in 25mL of 2-nitroso-1- naphthol (0.01M) was treated for 12 h with continuous stirring		6.0-8.0 {0.4- 0.1M }	1M HNO ₃ (5 mL)	20		95± 2 & 1.6- 3.2	20 &

67 Max. sorption capacity: BTC (μmol g⁻¹); Preconcentration factor: PF; Amberlite XAD: AXAD

77 TableS2: Correlation between the dimension of SG unit cell and required DMDCS to

- 78 silanised

i	n an unit <u>cell (n)</u> 12	6.023×10^{23}	$60 \times n$	0.025 × 10 × 1	$6.023 \times 10^{23} \times 4$
	12		00 ~ 11	$60 \times n$	$60 \times n \times 2$
		119.542×10-2	8.37×10 ²⁰	3.346×10 ²¹	1.67×10 ²¹
1	16	159.389×10 ⁻²	6.274×10 ²⁰	2.51×10 ²¹	1.25×10 ²¹
	20	199.236×10 ⁻²	5.02×10 ²⁰	2.01×10 ²¹	1.004×10 ²¹
1	28	278.931×10 ⁻²	3.585×10 ²⁰	1.434×10 ²¹	0.72×10^{21}
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112 Table S3: Correlation between the dimension of SG unit cell and required DMDCS to 113 silanised 114

Diameter, δ (pm)of	Number of unit cells	Wt. of a SG	No of SG	No of free-	Required number
DFT optimized unit	in one SG particle	particle	particle in	OH groups	of DMDCS
cell (pm) comprising	(100 Mesh : diameter	y =	$1g = \frac{1}{2}$	$q = \frac{4 \times x}{2}$	molecules for
"n" number of	10⁸(pm)); $x = \frac{10^8}{10^8}$	$\frac{60 \times n \times x}{3}g$	y y	y	silanization of 1g
silicon atoms	δ	6.023×10 ²³ °			dry SG = $\frac{q}{r}$
					2
390 pm for n =12	2.50×10 ¹⁵	2.99×10 ⁻⁶	3.34×10 ⁵	3.34×10 ²¹	1.67×10 ²¹
473 pm for n =20	2.11×10 ¹⁵	3.57×10 ⁻⁶	2.80×10 ⁵	2.36×10 ²¹	1.18×10 ²¹
647 pm for n =28	1.54×10 ¹⁵	4.30×10-6	2.33×10 ⁵	1.44×10 ²¹	0.72×10 ²¹
671 pm for n =30	1.50×10 ¹⁵	4.48×10 ⁻⁶	2.23×10 ⁵	1.34×10 ²¹	0.67×10 ²¹
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128 Table S4: Correlation of FT-IR peak position and peak assignments of various129 frameworks/functional groups present in SSG-nCA, the ion exchange material

group	Frequency (cm ⁻¹)	Remarks
Si-O-Si	1020-1095	broad strong peak [S1] found in all the compounds (SG, SSG, SSG-nCA,
		SSG-nCA-Th(IV))
Si-(CH ₃) ₂	798	Found in all the compound except SG [S2] which suggests the
		functionalization of SG through the formation of $Si-O-Si(CH_3)_2$ -
-OH and	3000-3700	Found in all the compounds except SSG. In SSG there is no such silanol
surface	(Broad & strong	-OH groups & suggests complete silanization (Si-O-SiMe ₂);-OH peak in
H ₂ O	peak)	SSG-nCA and SSG-nCA-Th(IV) is coming from –C(O)OH group and
		bridging μ -OH group between two Th(IV) centers respectively [S3].
		Intramolecular H-bonding and H ₂ O in these hydrophilic compounds
		suggest the peak broadening.
C-C	949	Found in both SSG-nCA and SSG-nCA-Th(IV) but missing in both
		SSG and SG
C-H (For	2990.9	Found in all the three compound (SSG, SSG-nCA and SSG-nCA-Th(IV))
Si-CH ₃)		but missing in SG
C-H (For	2862.1	Found in SSG-nCA and SSG-nCA-Th(IV) [S2,S4] but missing SSG
-CH ₂ of		& SG.
nCA)		
С=О	1701	Found in SSG-nCA is shifted to lower region at 1540 in SSG-nCA-Th(IV
		This is because, after metal chelate formation the bond order in C=O is
		decreased. This peak is missing in both SSG and SG [S4,S5]

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147 Table S5: Tolerance limits of electrolytes on quantitative sorption of Th(IV) on SSG-nCA

148 [Analyte concentration: 0.4 µM mL⁻¹]

Metal	Electr	olytes [(Cl ⁻ ,	F -, Br -, I	$NO_3^-, SO_4^{2-}, 1$	PO ₄ ³⁻ , CH ₃	COO ⁻ salts o	f Na/K of	Concentration:
ion	0.125-	-0.150 mM r	nL ⁻¹) and	l CI ⁻ salts of	[•] Ca ²⁺ /Mg ²⁺	of Concer	ntration: 0.	1-0.3 mM mL ⁻¹
80 µM	(Valu	es in the par	enthesis)]	are present	in 200 mL	sample		
	F-	Cl-	Br -	NO ₂ -	NO ₃ -	SO4 ²⁻	PO4 ³⁻	CH ₃ COO ⁻
Th(IV)	140	260 (40)	160	220	230	60	50	250
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50 51 52								

Single crystal XRD is an authenticated tool to have the 3-D structure of the material loaded with metal ions. 154 This would have been able to give the precise location of the metal ions and exact dimension of $[Th_2(\mu^2 -$ 155 OH)₂(H₂O)_{x = 2→4}]⁶⁺ (i.e., the precise value of x) in the extractor molecule. But, it is beyond of scope as SSG-156 157 nCA-Th(IV) is amorphous in nature (Fig. S6c). As an alternative to have the 3-D configuration and the spatial distribution of electron population (HOMO-LUMO) reliable density functional theory (DFT) computation was 158 made (Fig. S9 (a-d)). DFT computed binding energy of a mono-nuclear [Th(OH)₂]²⁺ {E_{nCA-Th(OH)2}-159 $E_{nCA} = -E_{Th(OH)2} = (-44521.56 \text{ eV}) - (-29385.26 \text{ eV} - 15845.8 \text{ eV}) = +709.5 \text{ eV} \text{ in } [(nCA)_2 - Th(OH)_2]$ 160 shows a huge instability for complex formation (Fig.S8a). The stabilization energy of DFT optimized 161 162 structure of (nCA)₂, [(nCA)₂-Th(OH)₂], [(nCA)₂-Th₂(OH)₂]⁴⁺, [(nCA)₂-Th₂(OH)₂(OH₂)₂]⁴⁺, [(nCA)₂-Th₂(OH)₂]⁴⁺, [(nCA)₂-Th₂(OH) $Th_2(OH)_2(OH_2)_4]^{4+}$, $[Th(OH)_2]^{2+}$, $[Th_2(OH)_2(OH_2)_2]^{6+}$, $[Th_2(OH)_2(OH_2)_4]^{6+}$ and H_2O was found to be 163 respectively E_(nCA): -29385.26 eV, E_{nCA-Th(OH)2}: -44521.56 eV, E_{nCA-Th2(OH)2}: -55533.7 eV, E_{nCA-} 164 Th2(OH)2(OH2)2: -59676.50, E_{nCA-Th2(OH)2(OH2)4}: -63812.5 eV, E_{Th(OH)2}: -15845.8 eV, E_{Th2(OH)2(OH2)2}: -165 30252.87 eV, E_{Th2(OH)2(OH2)4}: -34395.8 eV and E_{H2O}: -2068.35 eV (Fig. S8-S10). It results the much 166 higher binding energy for per mole of H₂O in [(nCA)₂-Th₂(OH)₂(OH₂)₂]⁴⁺ in DFT-optimized structure-c 167 168 (Fig.S9) $(\frac{1}{2}[E_{nCA-Th2(OH)2(OH2)2} - E_{nCA-Th2(OH)2} - 2 \times E_{H2O}] = -3.0 \text{ eV})$ than that found in $[(nCA)_{2}Th_{2}(OH)_{2}(OH_{2})_{4}]^{4+}, \text{ structure-d (Fig.S9)} (\frac{1}{4} [E_{nCA-Th_{2}(OH)_{2}(OH_{2})_{4}} - E_{nCA-Th_{2}(OH_{2})_{2}} - 4 \times E_{H_{2}O}] = -1.36$ 169 eV). Binding energy for $[Th_2(OH)_2(OH_2)_2]^{6+}$ entity $\{E_{nCA-Th_2(OH)_2(OH_2)_2} - E_{\{nCA\}_2} - E_{Th_2(OH)_2(OH_2)_2} - E_{(nCA+Th_2(OH)_2(OH_2)_2)_2} - E_{(nCA+Th_2(OH_2)_2)_2} - E_{(nCA+Th_2(OH_2)_2)_2$ 170 38.37 eV} in [(nCA)₂-Th₂(OH)₂ (OH₂)₂]⁴⁺ (Fig.S9c) was also found to be much higher than that of 171 $[Th_2(OH)_2(OH_2)_4]^{6+}$ entity $\{E_{nCA-Th_2(OH)_2(OH_2)_4} - E_{\{nCA\}_2} - E_{Th_2(OH)_2(OH_2)_4} = -31.44 \text{ eV}\}$ in $[(nCA)_2 - E_{nCA}_2 - E$ 172 Th₂(OH)₂(OH₂)₄]⁴⁺(Fig.S9d). Here, the hard base, the dimeric {nCA}₂ entity ($\eta = 15.63$ eV) 173 (Fig.S11) makes a more stable complex with the hard acid, $[Th_2(OH)_2(OH_2)_2]^{6+}$ ($\eta = 13.49 \text{ eV}$) 174 (Fig.S10c) in comparison to the relatively less harder center $[Th_2(\mu^2-OH)_2(OH_2)_4]^{6+}(\eta = 13.0 \text{ eV})$ 175 (Fig.S10d) [32]. 176

All these (experimental and DFT) results in unison, thus give a clear verdict and validity of Th₂(μ^2 -OH)₂(H₂O)_{x = 2}]⁶⁺ as sorbed species (Dipole moment: 20.2 Debye; LUMO:-12.43 eV; HOMO: -179 16.90 eV; $\eta = 4.47$ eV; C=O...Th(IV): 2.24A; Th(IV)... μ OH: 2.36A; Th(IV) μ OH₂: 2.47A; OThO: 180 57.5°; OHThOH: 64.7°; OThOH: 87.9°; Th(μ -OH)Th: 115.2°) and confirms its presence at the metal 181 trapping core (Fig.S2c; Fig.S11) as {nCA}₂[Th₂(μ^2 -OH)₂(H₂O)_{x=2}]⁴⁺ (Fig.S9c).

182 File S2:

The important factors that affect the preconcentration technique are the type, the concentration, and the volume of the eluent used for the release of the metal ions from the resin surface. Preconcentration factor (PF), the ratio of final concentration to initial concentration of an analyte, is an important parameter for sample clean up. Mathematically, it can be expressed as

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$$PF = \frac{C_f}{C_i} \quad \text{i.e.,} \quad PF = \frac{V_i}{V_f} \times re \operatorname{cov} ery(\%)$$
(S1)

It, thus, maximizes at a minimum volume of eluent (equivalent to V_{f}) of maximum recovery (%). 188 Furthermore, for selective stripping of an analyte, a selective eluent (here, it would be an acid; as stripping 189 190 is nothing but a reverse reaction of extraction, eq. 11) at its lowest possible level of concentration is urgent 191 to prevent the degradation of the resin [24]. The concentration of the eluent varied between 0.01 and 3.0 M in order to achieve enough protons to protonate the chelation sites (proton exchange mechanism, eq. 11). 192 Systematic analysis gave quantitative elution of Th(IV) with $H_2SO_4 \leq 0.05M$; 18 mL) HCl($\leq 0.1M$; 20 193 194 mL), HNO₃(≤ 0.5 M; 5 mL), HClO₄(≤ 0.1 M; 20 mL) and CH₃COOH(≤ 3.0 M; 40 mL) (Table 3). The elution process follows the reverse path of extraction, so the organic acid (CH₃COOH), being 195 weak electrolyte is less efficient than that of inorganic acids used. 196