Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Detection and Selective Sample Clean up of Beryllium(II) through {extractor-HOMO} (:) $\{Be_3O(OH)_2\}^{2+}$ 'ion pair complexation' amidst Aluminum(III) and Uranium(VI) by employing Fluorescent Assisted Resin: Resin's HOMO Amount, a Quantitative descriptor of BTC

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File S1. DFT optimization of the synthesized extractor: The geometrical optimization and energy calculation of different aqua-hard acids $\{Be(H_2O)_6\}^{2+}$ (HOMO: -23.35 eV; LUMO: -3.74 eV; η: 19.61 eV), $\{Al(H_2O)_6\}^{3+}$ (HOMO: -29.24 eV; LUMO: -8.76 eV; η: 20.48 eV) and $\{UO_2(H_2O)_6\}^{2+}$ (HOMO: -19.49 eV; LUMO: -7.13 eV; η: 12.36 eV) and PAN compound (HOMO: -7.78 eV; LUMO: 1.66 eV; η: 9.44 eV) (Fig. S1 and File S1) was performed by employing Gaussian 09 Revision D.01 package. All the necessary computations were carried out with RHF using SDD basis set and neutral bond order (NBO) calculations were performed to obtain the molecular orbitals. The energies of all the optimized structures have been computed after the ZPE (zero point energy) and thermal corrections. [1]

File S2. Instrumentation: Fourier transforms infrared (FT-IR) spectra of FSG-PAN and its metal loaded (FSG-PAN-Metal) complexes in KBr pellets were recorded (400−4000 cm^{-1}) on

Shimadzu FTIR spectrophotometer (Model no. FTIR-8400S) to investigate the bonding interactions appear inside the adsorbent. The thermal stability and composition of the extracted species was employed by thermo gravimetric analysis (TGA) over the temperature range 40°C to 900°C (at a heating rate of 25°C min^{-1} under the flow of nitrogen, 20 $ml.min^{-1}$) using Perkin Elmer (STA 6000) Simultaneous Thermal Analyzer. Elemental composition and surface morphology were conducted with EDX and SEM using a Scanning Electron Microscope (ZEISS Supra 55). Luminescence spectra of nano FSG-PAN and its Be (II) complex in DMSO were recorded on Perkin Elmer LS-55 spectrofluorometer over the extractor concentrations (0.63×10^{-6} – 2.5×10^{-5} $mol.L^{-1}$). UV visible spectra of Be(II) in solution were recorded by UV-1800 spectrophotometer having 1 cm quartz cell path length. A digital Elico L1-120 pH meter combined with glass electrode was used for pH measurements of different analyte solutions.

File S3. Materials: Double distilled water and high purity reagents were used for all preparations of the standard and sample solutions. All the chemicals except silica gel and DMDCS (BDH, Mumbai, India) were purchased from Merck Chemicals, Mumbai, India. For the introduction of aromatic nitro group silica gel (SG) (60-120 Mesh) was functionalized with *m*-nitroaniline using dimethyldichlorosilane (DMDCS) as a new silane coupling reagent (FSG). 1-(2-Pyridylazo)-2-naphthol (PAN) (Merck, Mumbai, India) is an alkali soluble azo dye comprising phenolic –OH groups was covalently immobilized on FSG through diazo coupling reaction. Standard stock solutions of Be(II), Al(III) and U(VI) (10^{-2} $mol.L^{-1}$) were prepared by dissolving an appropriate amount of metal salts (viz., $BeSO_4.7H_2O$, $Al_2(SO_4)_3$ and $UO_2(NO_3)_2$) in double distilled water. Solutions pH of different analytes was adjusted by adding hexamine or ammonium chloride / ammonia buffer solution (NH_4Cl-NH_3 (17.3 g: 142 $mL.L^{-1}$)). Unless specified otherwise all the reagents / chemicals were prepared from reagent of analytical grade chemicals.

File S4. Preparation of ion exchange material: SG (A) (60-120 mesh) and *m*-nitroaniline (B) were taken in toluene in a round bottom flask and DMDCS (C) was added slowly at 300K. *m-nitroaniline* (NA) binds with SG through DMDCS with the formation of Si-O-Si(Me)$_2$-NH-$C_6H_4NO_2$ bonding (D) by an instantaneous reaction. Subsequently, diazo salt (Functionalized Silica gel: FSG) (E) was made by using the literature method. Finally, the resin (FSG-PAN) (F) was synthesized by diazo coupling reaction[2] between PAN and FSG. The synthesized resin (FSG-PAN, a deep brown colored mass) was sequentially washed with 6M HNO_3 followed by distilled water. It was dried at room temperature till constant weight. The whole synthesis (Scheme 1) needs only 45-60 minutes. The corresponding nano-FSG-PAN was synthesized by using nano-silica gel in replace of normal size silica gel. Yields were found to be quantitative.

References:

(1) Gaussian 09, Revision D.01,

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria; M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci; G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian; A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada; M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima; Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.; J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers; K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand; K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi; M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross; V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann; O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski; R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth; P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels; O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski; and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

2. Clayden, Greeves, Warren, Wothers, Organic Chemistry, Oxford. University Press, first ed., oxford, 2001, 597-600.

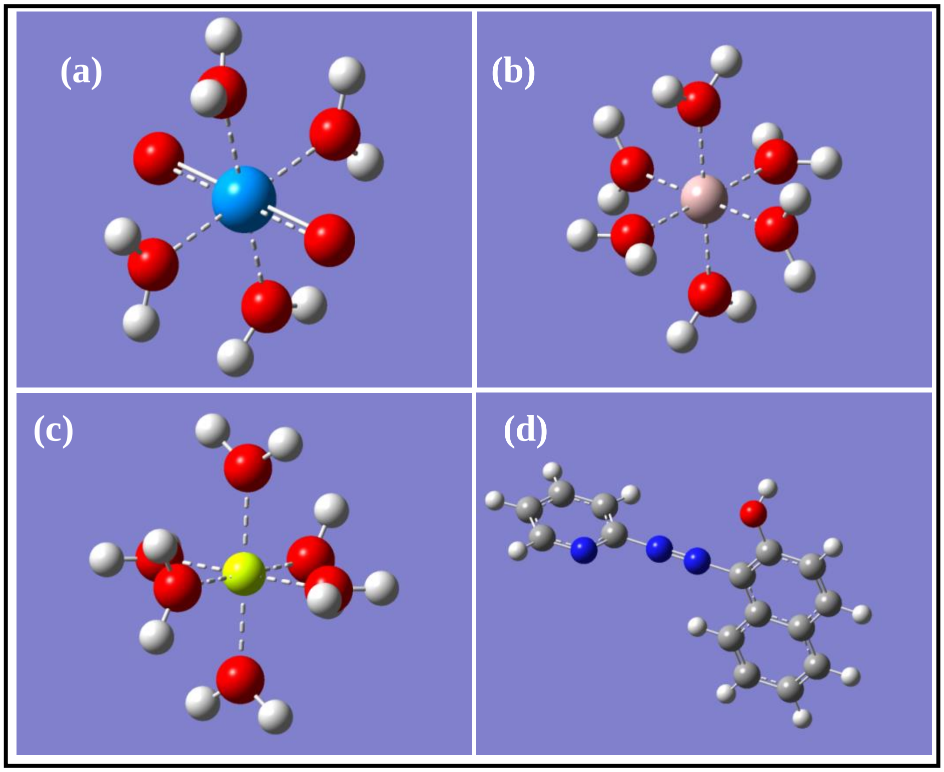

Fig. S1 Optimized structures (calculation method: RHF; Basis set: SDD) **(a)** of aqua uranyl ion (HOMO: -19.49 eV; LUMO: -7.13 eV; η: 12.36 eV) **(b)** aqua aluminum ion (HOMO: -29.24 eV; LUMO: -8.76 eV; η: 20.48 eV) **(c)** aqua beryllium ion (HOMO: -23.35 eV; LUMO: -3.74 eV; η: 19.61 eV) and **(d)** pure PAN: (HOMO: -7.78 eV; LUMO: 1.66 eV; η: 9.44 eV)

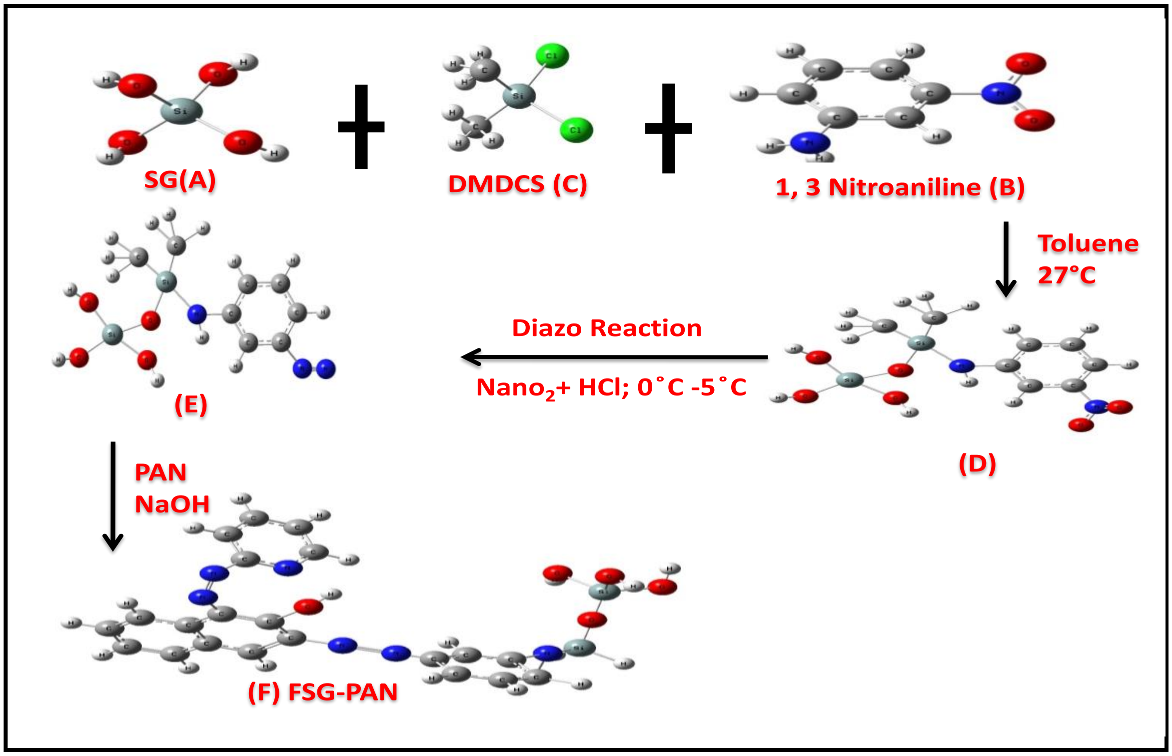

Fig. S2 Preparation of FSG Followed by Ligand (PAN) Immobilization (can be assessed with naked eye as deep red mass)

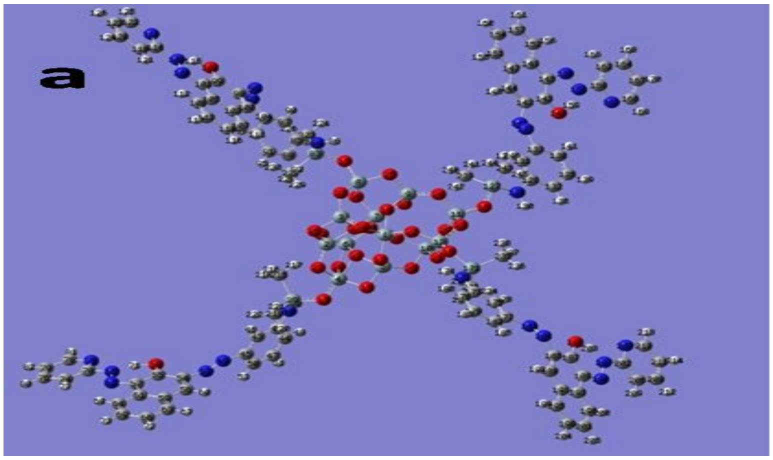

Fig. S3 Tetrahedrally disposed 3D optimised structure of FSG-PAN; extractor contains four PAN units (ligand) at each hand of the tetrahedra

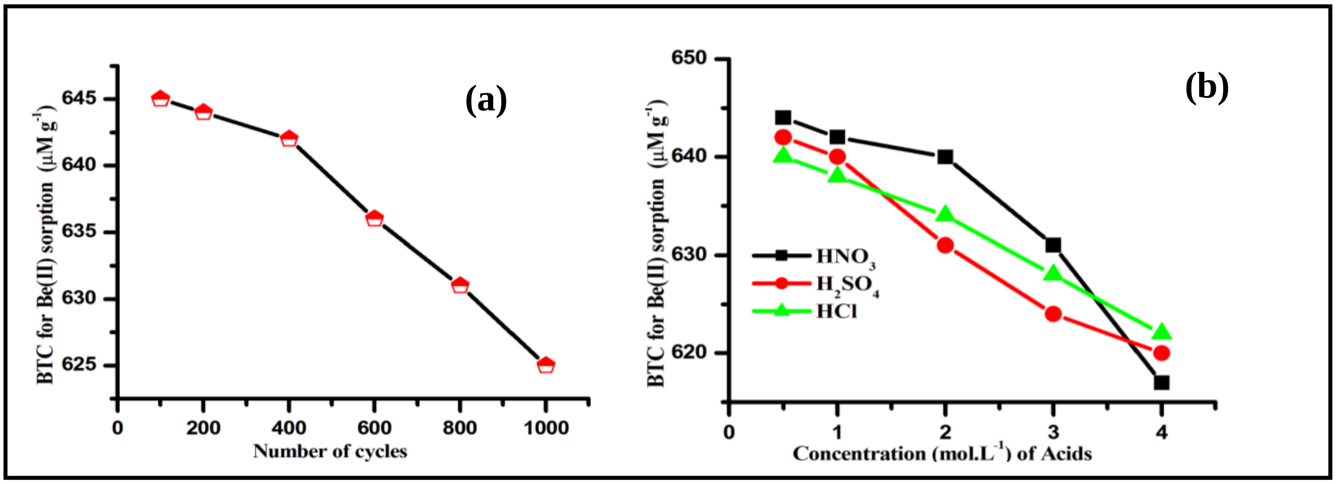

Fig. S4 (a) 'Breakthrough capacity (BTC) for Be(II) sorption' versus reusability (i.e., number of cycles used) relationship of FSG-PAN and **(b)** BTC for Be(II) sorption of FSG-PAN, treated with HCl / H_2SO_4 / HNO_3 acids at their range of concentrations 0.05-4.5 mol.L^{-1}.

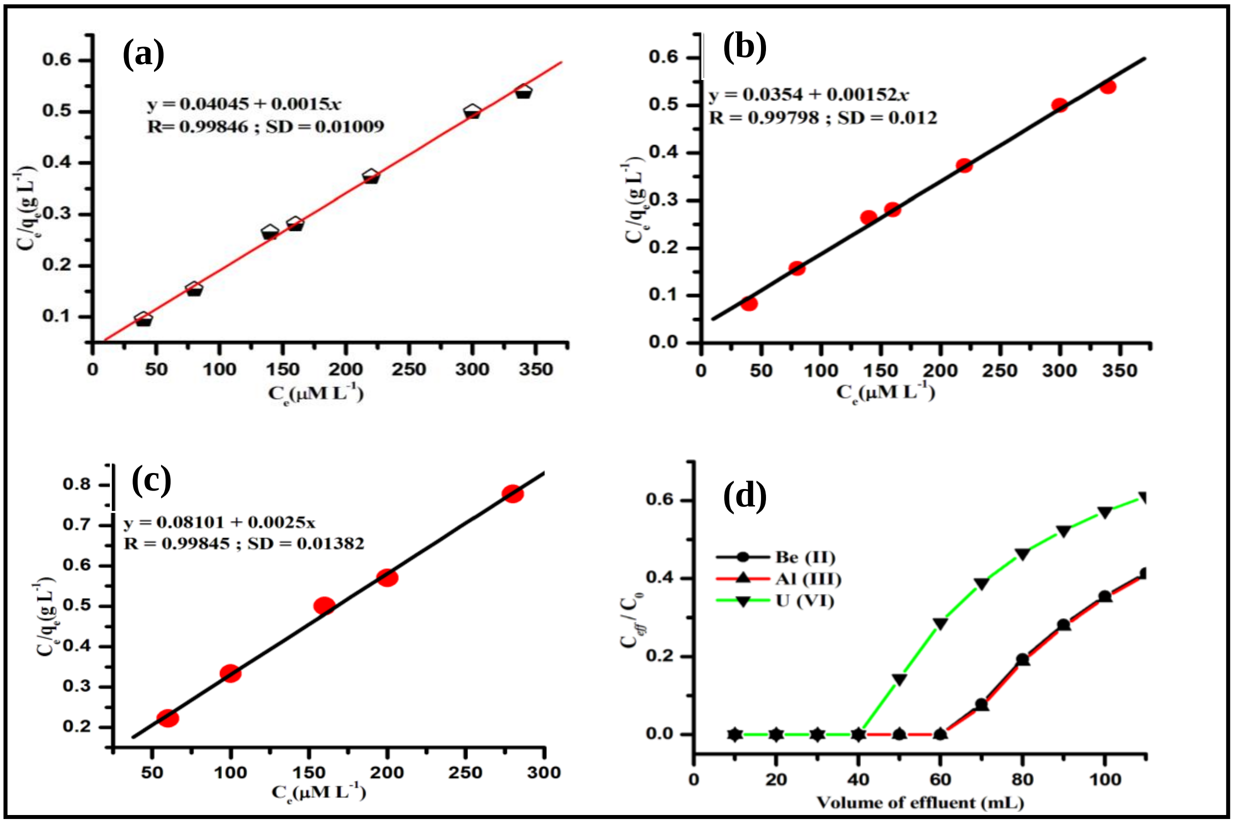

Fig. S5 Langmuir Sorption isotherms of **(a)** Be(II) **(b)** Al(III) **(c)** U(VI) **(d)** Breakthrough curve for the sorption of the respective metal ions (Be(II), Al(III), and U(VI)).

Table S1 Analytical characteristics of the extractors so far been reported

^{a}**Inert support** ^{b} **Immobilized Ligand** ^{c} **Immobilization condition**	**Highlights of the extractor**		**Limitations**
	^{x} **Equilibrium time $t_{1/2}$ (min/sec)** ^{y} **Sorption condition (pH) {foreign ion tolerance}** ^{z} **Desorption condition in**	^{p} **PF** ^{q}**Max. sorption (μmol g^{-1})** ^{r} **LOD** ^{s}**RSD (%)** ^{t} **Reusability (cycles) & stability**	
^{a} Octadecyl silica gel [65] ^{b}Aurin tricarboxylic acid (ATCA) (aluminon) ^{c} Octadecyl silica gel was modified with aurin tricarboxylic acid (aluminon)	^{x}------- ^{y} pH 6.1 {100 times of Be(II) conc} ^{z} 0.05 mol.L^{-1} 5 mL of HNO$_3$	^{p} 330 ^{q}----------- ^{r}0.1 μg.L^{-1} ^{s}2.1–10.8 ^{t}-----------	1. Max. sorption capacity was not investigated. 2. Actual species of Be(II), sorbed on the exchanger was not mentioned. 3. in presence of Zr(IV) the method was not selective 4. stability and reusability of the extractor not at all studied
^{a} MCM-41[66] ^{b} 2,4-dihydroxybenzaldehyde (4-OHsal) ^{c} MCM-41 was modified by refluxing it with 3aminopropyltriethoxysilane (APS) , filtered, washed with dichloromethane and ethanol and dried. Then it was suspended in methanol and x's 4-OHsal adeed.	^{x} 1 min ^{y} Sorption pH = 7.2 and at a conc. of beryllium:0.002–100 μg.L^{-1} ^{z} 1 mL of 1mol.L^{-1} HNO$_3$	^{p}100 ^{q} 34 mg.g^{-1} ^{r} <2.4 ^{s}99% ^{t} more than 6 cycles.	1. Needs 20h refluxing for functionalization of SG. 2. 32 h for the whole synthesis process. 3. Quantitative recovery was obtained up to sample volume of 100 mL only. It may results an enrichment of 100 times. 4. Actual species of Be(II), sorbed on the exchanger was not mentioned
^{a} Sephadex DEAE A-25 and Sephadex QAE A-25 anion exchangers in its chloride form [5] ^{b} aurintricarboxylic acid (ATCA) ^{c} Mechanical stirring of ATCA and Resin in NaOH+thiel buffer (at pH 4.5–6.5) containing Be(II) for 30 min	^{x} 30 min ^{y} pH = 4.5–6.5 and need of EDTA to mask foreign ions {.015-.375mg.L^{-1}} ^{z}------------	^{p} ------- ^{q} -------- ^{r}--------- ^{s} 5 ng.L^{-1} ^{t} <2.4	1. Exchanger suffers for selectivity and need EDTA; The metal ions which form weak complex with EDTA may appear on the exchanger 2. Loss of exchanger for every cycle of estimation 3. No mention of de -sorption condition

[a] OH-form strong base anion exchange resin [21] [b]-------- [c] -------------------	[x]-------- [y]At pH 6–8 Be(II) in aqueous solution makes complex with CAS [z] 4 ml of 1.5 mol.L^{-1} HCl	[p]125 [q] ------------ [r] 1.2-3.2 [s] 95–102.5% [t] ------------	1. The exchanger was not developed. 2. No specific path for exchanger-metal ion sorption was described. 3. stability and reusability of the extractor not at all been studied
[a] Polyethylene powder (PE) [67] [b] Chrome azurol S (CAS) [c] Chrome azurol S (0.6% w/v in water) was continuously passed through PE in a saline medium (0.1 tool/1 KCI) at pH 4 (using succinate buffer). This adsorbed phase was used as the sorbent.	[x]----------------------- [y] pH 6–8 [z] CAS-Be(II) complex was eluted with ethanol containing nitric acid (0.3%).	[p] 20 [q] --------- [r] 40-400 µg.L^{-1} [s] ------------ [t] Not reusable	1. The adsorbent material is prepared by just adsorption of the ligand. The ligand-metal complex was eluted from column. So, it was not reusable. 2. The material floats on aqueous solution. So adsorption isotherms experiment through batch method was not possible. 3. preconcentration factor for Be(II) was poor, only 20 4. Influent sample size (100 mL) for preconcentration studies was poor
[a] No inert support[68] [b] Sodium 2-propylpiperidine-1-carbodithioate [c] Carbon disulphide was slowly added to a solution of 2-propyl-piperidine in 25 ml of water at 0-5°C with constant stirring in sodium hydroxide to form sodium 2-propylpiperidine-1-carbodithioate.	[x] 30 Sec [y] Sorbed at (pH 5.0±0.2) [z] eluted with 7 mL 3mol.L^{-1} HCl	[p]14.5 {100 mL sample is converted to 7 mL} [q] --------- [r]0.30 µg.L^{-1} [s] ------------ [t] 0.11%	1. The efficiency of recovery decreased when the sample volume was more than 60 ml. So, PF is very low. 2. Stability and reusability of the extractor not at all studied. 3. The maximum sorption capacity was also not investigated. 4. method is not applicable for sample size of more than 100 mL

Table S2 Tolerance limits of electrolytes on the sorption of Be(II), Al(III) and U(VI) on resin. [Sample volume: 100 mL; pH 6.0 ± 0.2 (Al(III), U(VI),) and *4.0 ± 0.2 (Be(II), Th(IV)); Stock solution Concentration: 5 μmol.mL^{-1}; Flow-rate: 2.5 mL.min^{-1}; Temperature: 27 °C; Amount of FSG-PAN: 1 g; Column height: 3 cm]

Metal ion 10 μmol.L^{-1}	**Electrolytes [(Cl^-, F^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-salts of Na/K of Concentration: 0.25-2.0 mmol.mL^{-1}) and Cl^- salts of Ca^{2+}/Mg^{2+} of Concentration: 0.25-2.0 mmol.mL^{-1} (Values in the parenthesis)]^{b} are present in 100 mL sample**							
	I^-	Cl^-	Br^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	CH_3COO^-
Be(II)	160	200 (180)	120	180	180	180	75	240
Al(III)	140	260 (200)	140	220	230	160	70	250
U(VI)	60	240 (220)	80	160	200	125	70	200

Table S3 Binary separation of diverse metal ions from their synthetic solutions [Sample volume: 80 mL; pH 6.0 ± 0.2 (Al(III), U(VI),) and *4.0 ± 0.2 (Be(II), Th(IV)); Stock solution Concentration: 5 µmol.mL^{-1}; Flow-rate: 2.5 mL.min^{-1}; Eluent volume: 8 mL; Temperature: 27 °C; Amount of FSG-PAN: 1 g; Column height: 3 cm]

Cations	**Amount of Cations (µmol)**		**Recovery (%)**	**Relative Error (%)**	**Eluent Used (mol.L^{-1})**
	Added	**Recovered**			
Al(III) *Be(II)	200 200	195.4 194.8	97.7 97.4	2.3 2.6	0.1 mol.L^{-1} HNO_3 1 mol.L^{-1} CH_3COOH
Al(III) U(VI)	200 200	193.2 192.2	96.6 96.1	3.4 3.9	0.1 mol.L^{-1} HNO_3 0.05 mol.L^{-1} HNO_3
Al(III) *Th(II)	200 200	191.7 193.2	95.8 96.6	4.15 3.4	0.1 mol.L^{-1}HNO_3 0.01 mol.L^{-1} HNO_3
*Be (II) U (VI)	150 200	143.4 195.4	95.6 97.7	4.4 3.3	1 mol.L^{-1} CH_3COOH 0.05 mol.L^{-1} HNO_3
*Be (II) Ce(IV)	150 200	142.8 191.7	95.2 95.85	4.8 4.15	1 mol.L^{-1} CH_3COOH 1 mol.L^{-1} HCl
*Be (II) *Th (IV)	150 200	143.2 192.8	95.4 96.4	4.5 3.6	1 mol.L^{-1} CH_3COOH 0.01 mol.L^{-1} HNO_3