Noncovalent Surface Grafting of Uranium complexed Cucurbit[5]uril Oligomer onto Palm Shell Powder: A Novel Approach for selective Uranyl ion Extraction

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Experimental.

Synthesis of Ion Imprinted oligomer and Grafted Ion Imprinted oligomer.

The U2CB[5] complex was synthesized as reported earlier. After complexation, hydroxylation and allylation of the complex was done according to a reported procedure [46] to form the monomer. Polymerisation was performed by refluxing 25mg monomer, 10mg AIBN (initiator) and 10mL methanol (porogen) under nitrogen atmosphere in a three neck flask at 55°C in thermostatically controlled oil bath with constant stirring for 10h. After completion of reaction, excess methanol was distilled off under reduced pressure and dried under reduced pressure in vaccum oven for 12h to obtain ion imprinted oligomer (IU2CB[5]). IU2CB[5] was then grafted to, palm shell powder (PSP) by dry impregnation method for 12h to get PGIU2CB[5].
Control oligomer (CCB[5]) and PSP grafted control oligomer (CPGCB[5]) were similarly prepared in the absence of the template $(UO_2)^{2+}$.

Leaching of the template.

The imprint ion UO_2^{2+} was leached from IU2CB[5] and PGIU2CB[5] by sonication with 10 mL of 1N $HClO_4$ for 6h. The resultant material was dried in a vacuum oven at 60^0C to obtain leached imprinted (LIU2CB[5]) and leached grafted imprinted oligomer (LPGIU2CB[5]). Leaching of imprint ion was tested for two cycles by ICP-AES.

Selectivity Studies.

The selectivity of IU2CB5, PGIU2CB5, CU2CB5, CPGIU2CB5for uranium over other inorganic ions was determined by shaking 20 mg of polymer particles with 25 ppm of Cu^{2+},

Cd^{2+}, Zn^{2+}, Cr^{6+}, Fe^{3+}, Cs^{+} and U^{6+}present in 10 mL of deionized water at pH1 adjusted using HNO_3. The selectivity coefficient ($S\ UO_2^{2+}/M^{n+}$) is defined as

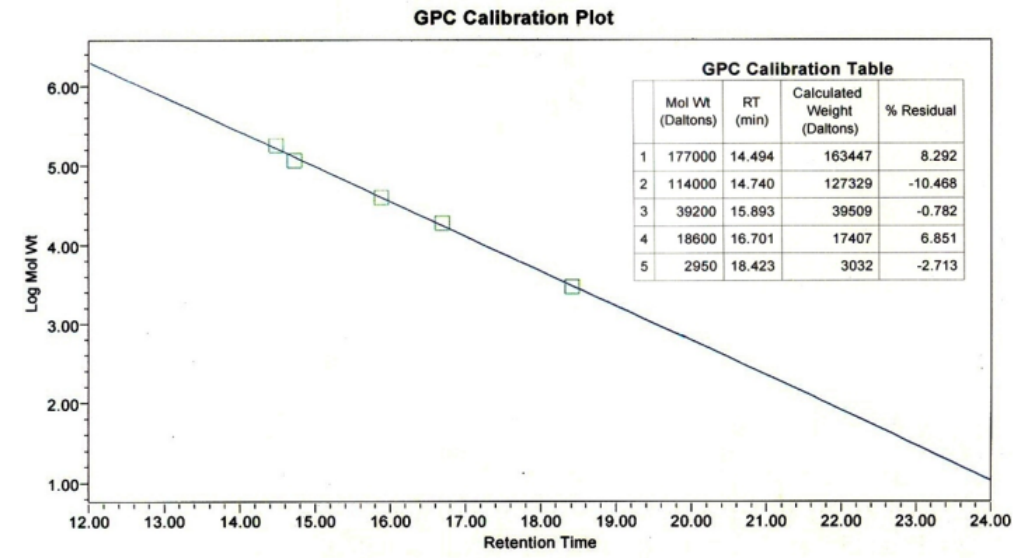
$$S_{UO_2^{2+}/M^{n+}} = \frac{D_{UO_2^{2+}}}{D_{M^{n+}}}$$

where DUO_2^{2+} and DM^{n+} are the distribution ratios of the uranyl ion and other inorganic species, respectively, with polymer particles (CU2CB5 or IU2CB5). These distribution ratios were calculated using the formula

$$D_{M^{n+}} = \frac{C^i_{M^{n+}} - C^f_{M^{n+}}}{C^f_{M^{n+}}} \times \frac{v}{m}$$

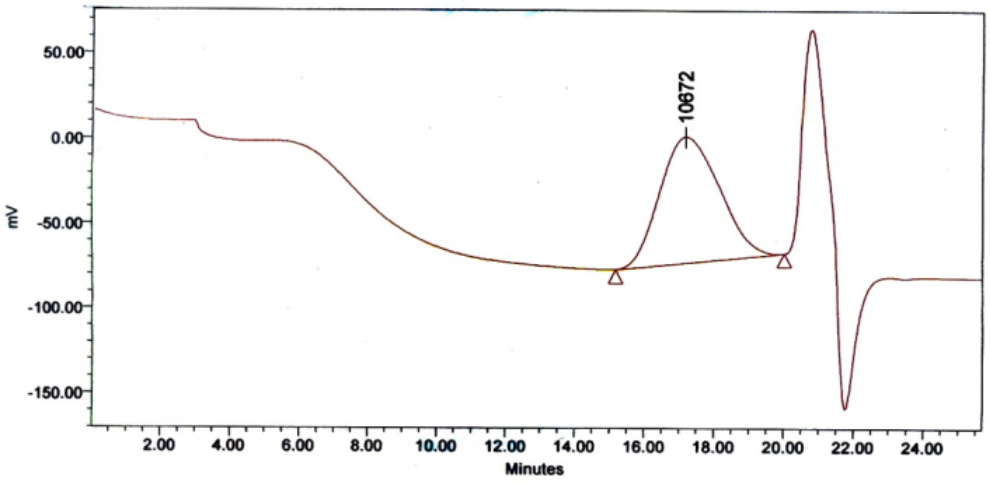
where $C_i\ M^{n+}$ and $C_f\ M^{n+}$ are the concentrations of inorganic ions in aqueous phase before and after extraction, v is the volume of the solution, and m is the mass of the polymer. The percent extraction (%E) of inorganic ion is defined as

$$\%E = \frac{C^i_{M^{n+}} - C^f_{M^{n+}}}{C^i_{M^{n+}}} \times 100$$



GPC Calibration Table

	Mol Wt (Daltons)	RT (min)	Calculated Weight (Daltons)	% Residual
1	177000	14.494	163447	8.292
2	114000	14.740	127329	-10.468
3	39200	15.893	39509	-0.782
4	18600	16.701	17407	6.851
5	2950	18.423	3032	-2.713



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6712	11968	10672	18765	25910		1.783096		

Figure S1. GPC calibration and experimental results for IU2CB5

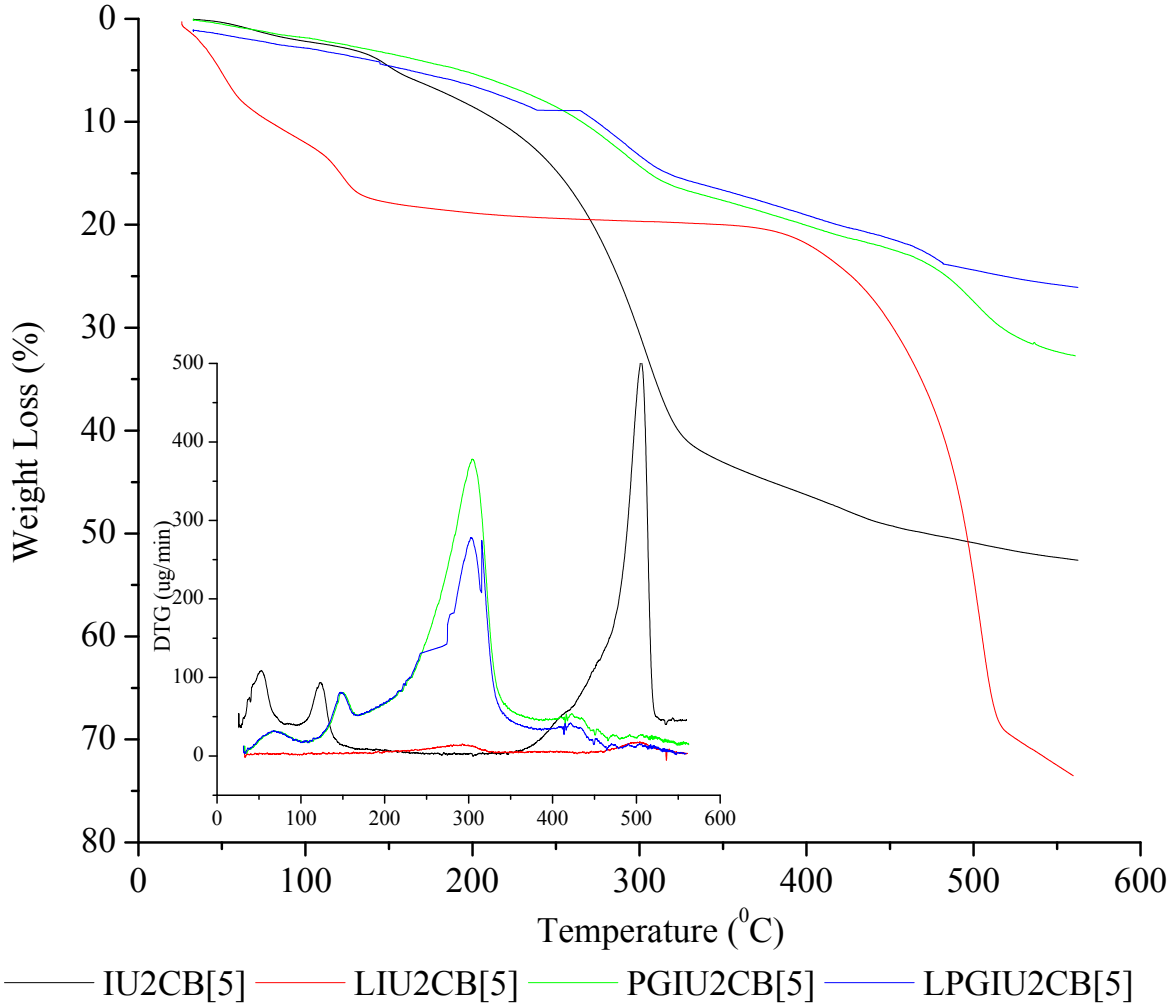


Figure S2. Thermal analysis TGA and DTG of IU2CB[5], PGIU2CB[5], LIU2CB[5] and LPGIU2CB[5]

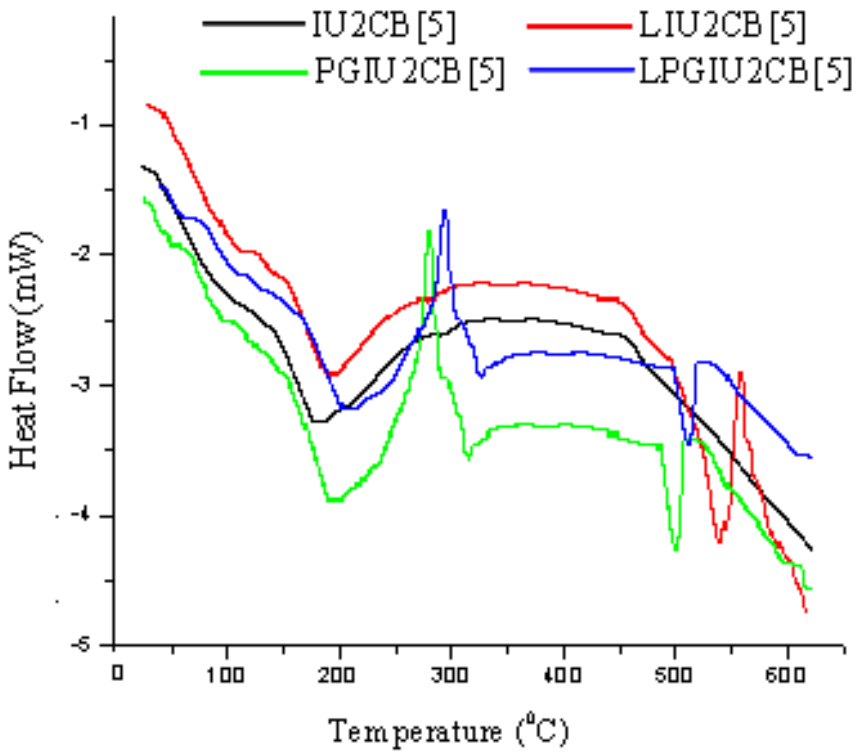
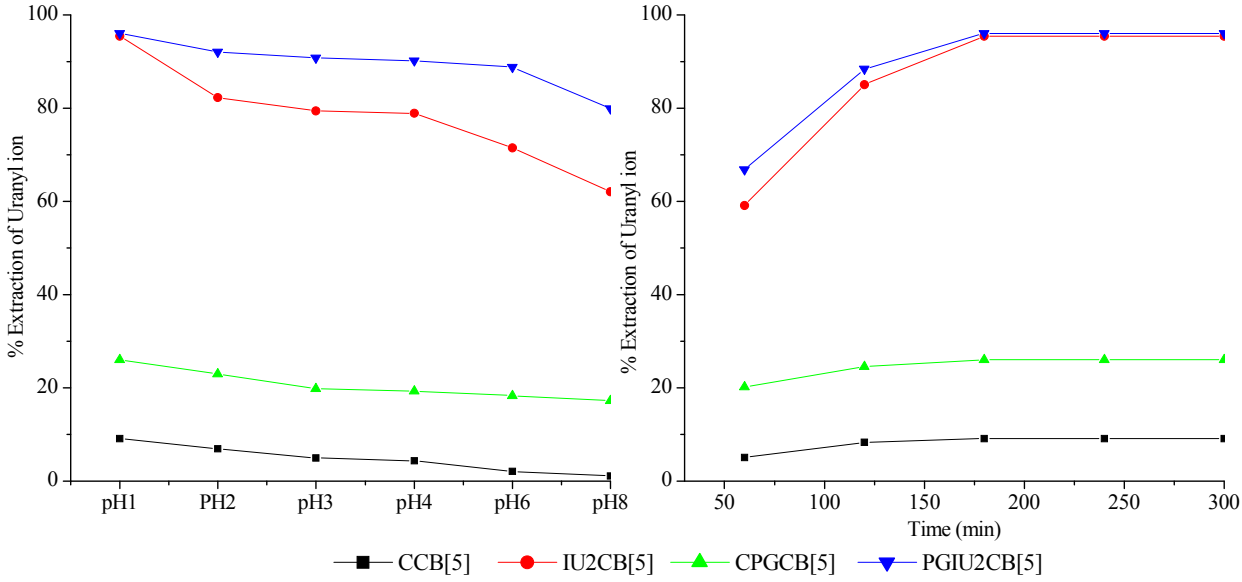


Figure S3. DSC analysis of IU2CB[5], PGIU2CB[5], LIU2CB[5] and LPGIU2CB[5]



Operating parameters: pH: 1.0-9.0, 20 mg dosage, 30 ^{0}C, 180 rpm; 180 min, 1000 ppm of M^{2+}

Figure S4. Extraction of uranyl ion with respect to pH and time

Table S1. FTIR spectral assignments

Functional groups	CB5	U2CB [5]	CCB[5]	IU2CB[5]	LIU2CB [5]	PSP	CPGCB[5]	PGIU2CB [5]	LPGIU2CB [5]
-C=O Stretch	1738	1766	1745	1759	1750	1732	1742	1764	1732
-CH Stretching & bending	3002 2941 1485 1382	3020 2924 2830 1381	2989 2915 2827 1380	2930 2915 2827 1380	2994 2932 2825 1390	2959 2895 1454 1430 1373	2991 2940 2833 1390	2991 2928 2832 1385	2959 2895 1454 1373
Stretching & bending of H_2O	3439 1636	3445 1695 1653	3429 1680	3396 1692	3401 1642 1670	1648	3402 1640 1670	3402 1639 1669	3391 1648
-OH stretching & bending	-	-	-	-	-	3361	-	3402	3391
-C-O- bending	-	-	1044	1256 1044	1235 1052	1250 1049	1051	1215 1057	1254 1059
-C-H bending	959 793 630	964 788 624	-	-	964 788 624	893 809	-	962 878 ~710	-
U-O Stretch	-	579 480 445 948 859	-	580 481 448 951 864	-	-	-	583 483 450 952 859	-

Table S2. EDX analysis of leached and unleached oligomers

Elements	IU2CB[5]	PGIU2CB[5]	LIU2CB[5]	LPGIU2CB[5]
C	19.37 %	26.24 %	28.89 %	35.75 %
H	2.89 %	3.12 %	3.97 %	3.32 %
N	19.11 %	11.09 %	23.76 %	13.17 %
O	35.16 %	40.39 %	43.18 %	47.43 %
U	22.94 %	19.16 %	-	-

Elemental analysis was carried out using JSM 5610 LV combined with INCA instrument for EDX analyzer for the quantitative identification of the elements on gold coated sample holders.