Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Using High Throughput Techniques to Identify Complexants for ^{137}Cs

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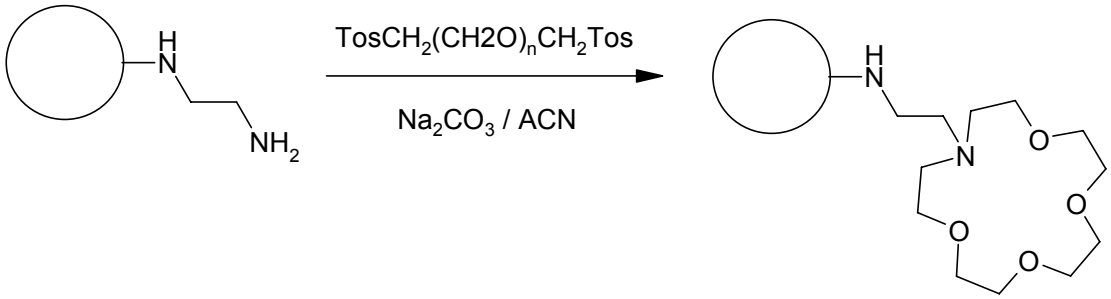
S1 Synthesis of Compound Library

Materials

Polystyrene (*Quadrapure™*) and Silica (*QuadraSil™*) supported materials were supplied by Sigma-Aldrich Chemical Company and used as supplied. All other materials were supplied by Sigma-Aldrich Chemical Company and used as supplied.

General Procedure for the preparation of Mono aza crown ether via reaction 1



The appropriate amine support (1 eqv) was suspended in anhydrous acetonitrile (100mls). Sodium carbonate (5 eqv) and the corresponding ethylene glycol ditosylate (1 eqv) were added. The suspension was then refluxed for 24 hours. After cooling the reaction mixture was poured into water (250mls). The suspension was filtered and the isolated beads washed with further portions of water, acetone and finally with dichloromethane. The isolated materials were dried under vacuum at 120^{o}C for 3 hours.

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Polystyrene Supported Materials

Compound 1 (loading 5.0mmol / g , average particle size 400-1100μm)

C 70.14 H 7.21 N 2.81 %, IR (KBr) 3108, 2900, 2830, 1520, 1110cm^{-1}, TGA 99.178 % weight loss at 600^{o}C

Compound 3 (2.0mmol / g , 500-800μm)

C 46.53 H 5.76 N 4.26 %, IR (KBr) 3111, 2901, 2834, 1521, 1119cm^{-1}, TGA 82.79% weight loss at 600^{o}C

Compound 7 (1.3mmol / g , 100-400μm)

C 69.71 H 6.97 N 3.31 %, IR (KBr) 3265, 3101, 2905, 2831, 1110cm^{-1}.

Compound 8 (1.3mmol / g , 100-400μm)

C 76.34 H 7.47 N 2.94 %, IR (KBr) 3268, 3100, 2903, 2831, 1109cm^{-1} TGA 98.60% weight loss at 600^{o}C

Compound 15 (2.0mmol / g , 500-800μm)

C 52.33 H 5.58 N 4.82 %, IR (KBr) 3101, 2901, 2831, 1523, 1115cm^{-1}, TGA 85.46% weight loss at 600^{o}C

Compound 16 (1.3mmol / g , 100-400μm)

C 74.81 H 7.60 N 4.16 %, IR (KBr) 3261, 3109, 2909, 2834, 1111cm^{-1} TGA 99.18% weight loss at 600^{o}C

Compound 19 (5.0mmol / g , 400-1100μm)

C 66.79 H 7.26 N 5.90 %, IR (KBr) 3100, 2907, 2838, 1527, 1111cm^{-1}.

Compound 21 (5.0mmol / g , 400-1100μm)

C 68.15 H 7.31 N 6.15 %, IR (KBr) 3102, 2911, 2840, 1531, 1111cm^{-1}, TGA 96.21% weight loss at 600^{o}C

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Silica Supported Materials

Compound 2 (loading 2.0mmol / g , average particle size 54μm)

C 13.35 H 5.76 N 4.26 %, IR (KBr) 3111, 2901, 2834, 1521, 1119cm^{-1}, TGA 82.79% weight loss at 600^{o}C

Compound 5 (1.5mmol / g, 54μm)

C 12.93 H 2.45 N 3.30 %, IR (KBr) 3327, 3281, 3108, 2911, 2841, 1112cm^{-1}.

Compound 12 (1.5mmol / g, 54μm)

C 14.21 H 2.92 N 3.70 %, IR (KBr) 3319, 3296, 3107, 2918, 2846, 1111cm^{-1}.

Compound 24 (1.5mmol / g, 54μm)

C 14.25 H 2.86 N 3.90 %, IR (KBr) 3322, 3294, 3105, 2917, 2839, 1117cm^{-1}

Compound 25 (2.0mmol / g , 54μm)

C 13.72 H 2.98 N 2.71 %, IR (KBr) 3104, 2900, 2851, 1521, 1101cm^{-1}.

Compound 26 (2.0mmol / g , 54μm)

C 12.78 H 2.58 N 2.74 %, IR (KBr) 3099, 2909, 2834, 1527, 1109cm^{-1}.

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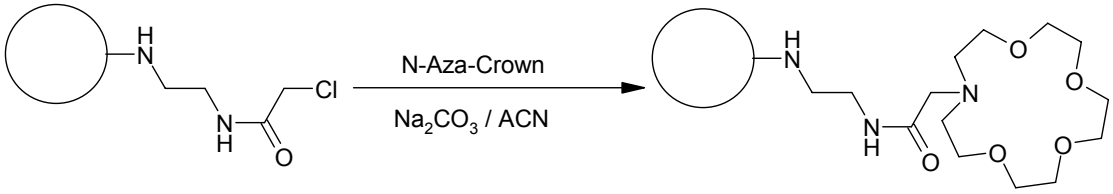
General Procedure for the preparation of Mono aza crown ether acetamide via reaction X



The appropriate chloroacetylamide support (1 Eqv) was suspended in anhydrous acetonitrile (100mls). Sodium carbonate (1.2 Eqv) and the corresponding N-Aza-Crown Ether (1 eqv) were added. The suspension was then refluxed for 24 hours. After cooling the reaction mixture was poured into water (250mls). The suspension was filtered and the isolated beads washed with further portions of water, acetone and finally with dichloromethane. The isolated materials were dried under vacuum at 120^{o}C for 3 hours.

Polystyrene Supported Materials

Compound 6 (loading 2.0mmol / g , average particle size 500-800μm)

C 56.88 H 6.20 N 5.46 %, IR (KBr) 3318, 3291, 3101, 2927, 2820, 1111cm^{-1} TGA 69.999% weight loss at 600^{o}C

Compound 9 (1.3mmol / g , 100-400μm)

C 73.97 H 7.44 N 4.21 %, IR (KBr) 3301, 3297, 3100, 2921, 2831, 1117cm^{-1}.

Compound 10 (5.0mmol / g , 400-1100μm)

C 68.18 H 6.71 N 6.88 %, IR (KBr) 3321, 3277, 2911, 2821, 1110cm^{-1}.

Compound 13 (1.3mmol / g , 100-400μm)

C 69.27 H 7.14 N 3.81 %, IR (KBr) 3308, 3281, 3108, 2909, 2834, 1111cm^{-1}.

Compound 14 (5.0mmol / g , 400-1100μm)

C 62.17 H 6.14 N 8.01%, IR (KBr) 3301, 3292, 3101, 2911, 2831, 1107cm^{-1}.

Compound 17 (1.3mmol / g , 100-400μm)

C 74.19 H 7.45 N 3.97 %, IR (KBr) 3300, 3296, 3101, 2911, 2822, 1110cm^{-1}.

Compound 18 (3.2mmol / g , 400-600μm)

C 62.90 H 5.60 N 8.31 S 6.70%, IR (KBr) 3287, 3102, 2909, 2834, 1357, 1111cm^{-1} TGA 95.307% weight loss at 600^{o}C

Compound 20 (5.0mmol / g , 400-1100μm)

C 74.81 H 7.35 N 4.07 %, IR (KBr) 3300, 3271, 3100, 2902, 2831, 1102cm^{-1}.

Compound 22 (2.0mmol / g , 500-800μm)

C 55.82 H 5.82 N 5.42 %, IR (KBr) 3322, 3294, 3104, 2921, 2822, 1107cm^{-1}.

Silica Supported Materials

Compound 4 (1.5mmol / g, average particle size 54μm)

C 12.19 H 1.18 N 1.97 %, IR (KBr) 3109, 2928, 2831, 1111cm^{-1}.

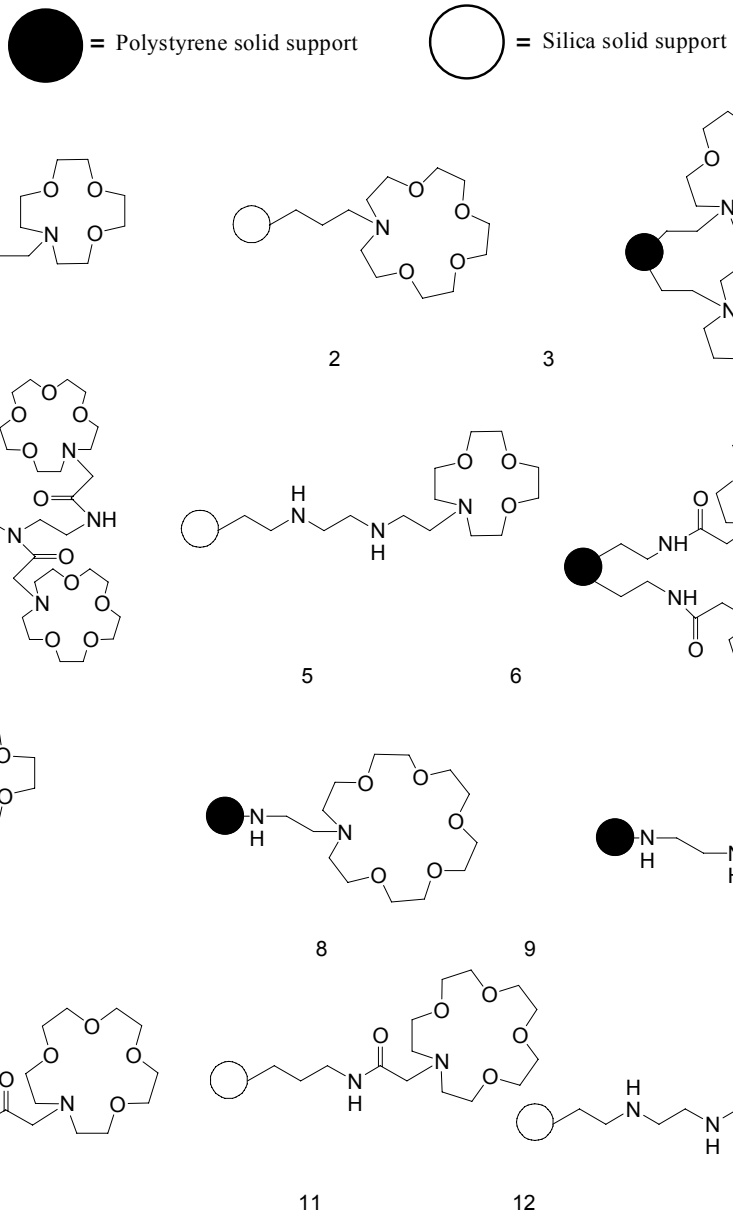
Compound 11 (2.0mmol / g, average particle size 54μm)

C 15.21 H 2.73 N 3.24 %, IR (KBr) 3318, 3277, 3101, 2922, 2838, 1110cm^{-1}.

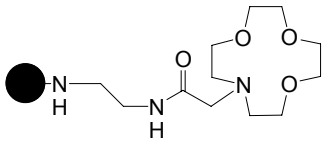
Compound 23 (1.5mmol / g, average particle size 54μm)

C 15.21 H 2.73 N 3.24 %, IR (KBr) 3109, 2922, 2838, 1110cm^{-1}.

S2 Library of Compounds



Supplementary Material (ESI) for Journal of Materials Chemistry



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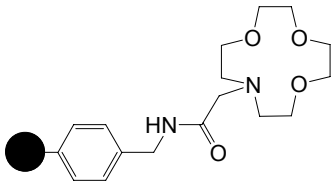

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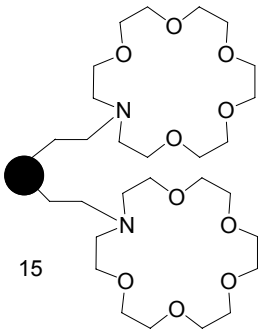

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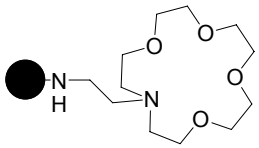

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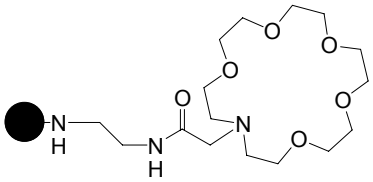

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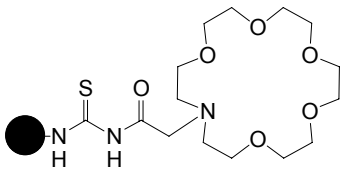

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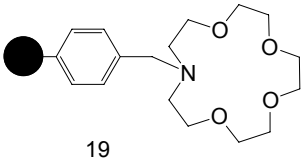

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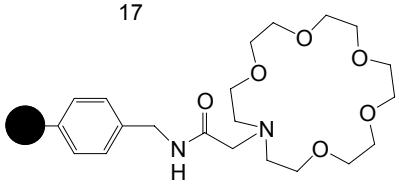

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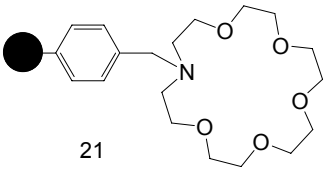

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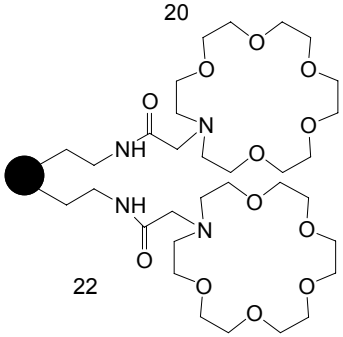

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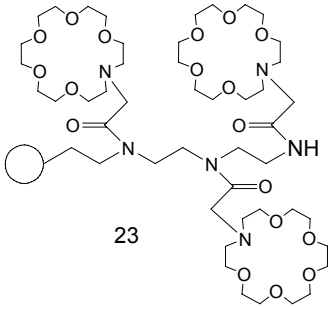

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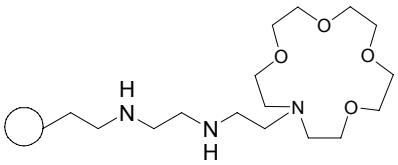

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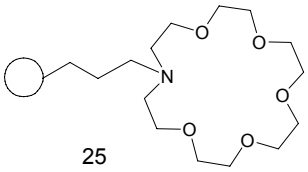

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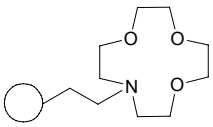
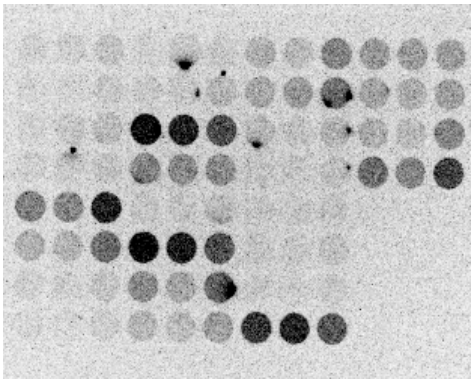


26

S3 Average Pixel Intensities

The average pixel intensities were determined from the autoradiography image using ImageQuant™ software. The higher the pixel intensity the better the compound is at binding the isotope the isotope.



	1	2	3	4	5	6	7	8	9	10	11	12
A		7			16			2			15	
B		1			19			4			12	
C		13			6			18			25	
D		14			3			17			23	
E		5			9			20				
F		26			6			8				
G		9			24			21				
H		10			11			22				

Average Pixel Intensities

Compound	^{137}Cs	Pre-treated with K^+	^{137}Cs and K^+
1	47.7	47.5	57.0
2	84.8	71.6	131.5
3	133.8	124.0	125.5
4	94.7	110.6	154.4
5	133.4	130.8	240.0
6	265.2	235.5	194.3
7	51.2	50.6	63.2
8	63.4	58.7	64.7
9	49.3	51.5	61.6
10	41.8	43.4	51.4
11	76.8	72.9	100.2
12	95.9	91.8	101.3
13	47.9	59.5	70.6
14	50.7	62.9	65.6
15	110.2	104.8	101.1
16	51.9	64.7	57.4
17	64.6	64.2	69.4
18	79.6	65.7	83.7
19	57.0	60.2	77.2
20	64.2	60.4	67.5
21	61.6	58.7	60.4
22	214.9	228.1	175.8
23	157.8	128.9	200.2
24	123.5	96.8	161.6
25	86.1	72.2	128.1
26	82.8	79.9	157.5

S4 Decontamination Experiments

Decontamination experiments were carried out with ^{137}Cs spiked tap water. Nine of our solid compounds (**1, 2, 3, 4, 6, 7, 11, 12, 23** in Fig. S2) were selected and put into solid phase extraction columns. The compounds were chosen based on autoradiography results, some chosen were good at binding ^{137}Cs and some were poor at binding.

The decontamination factors (DF), which were determined from the counts of the ^{137}Cs gamma peak at 654.22 keV (counts of standard solution/counts of filtrate = DF) are shown in the table below:

Compound	Decontamination Factor	% decrease in γ peak at 654.22 keV (i.e. % decontamination)	Average Pixel Intensities
1	1.02	1.8	47.7
2	1.22	17.8	84.8
3	6.77	84.7	133.8
4	2.84	65.5	94.7
6	2.48	59.5	265.2
7	1.03	2.2	51.2
11	2.4	57.5	76.8
12	4.47	77.9	95.9
23	6.18	84.2	157.8

S5 ^{60}Co Autoradiography Results

The radiometric screening data for our compounds with ^{60}Co is shown below. The same experimental procedure that was used for ^{137}Cs was followed here. Three wells were filled with each of the compounds. In the first column of each group (columns 1, 4, 7 and 10) only ^{60}Co (250 Bq) was added; in the second columns (2, 5, 8 and 11), the wells were pre-treated with Manchester tap water before adding 250 Bq of ^{60}Co. In the third group (columns 3, 6, 9 and 12), ^{60}Co and tap water were added simultaneously. All the solutions were adjusted to pH 2 before addition to the wells.

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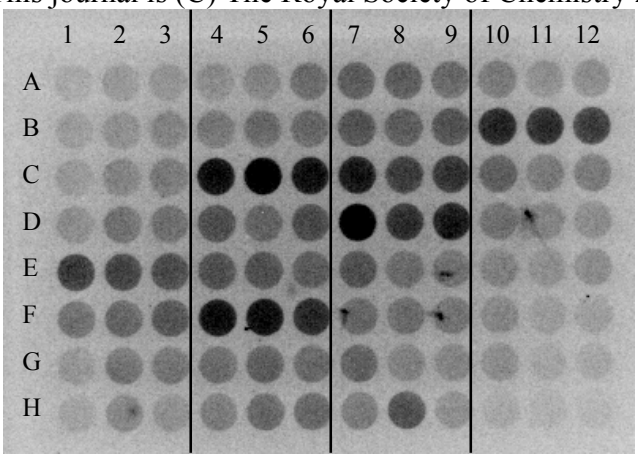

	1	2	3	4	5	6	7	8	9	10	11	12
A		7			16			2			15	
B		1			19			4			12	
C		13			6			18			25	
D		14			3			17			23	
E		5			9			20				
F		26			6			8				
G		9			24			21				
H		10			11			22				

Compound	^{60}Co	Average Pixel Intensities Pre-treated with Tap Water	^{60}Co and Tap Water
1	1199.2	1332.7	1497.5
2	**1969.8**	**1973.3**	**1803.9**
3	**2143.2**	**1907.9**	**2230.0**
4	**2093.3**	**1965.6**	**2104.4**
5	**2391.5**	**2285.7**	**2185.7**
6	**2965.2**	**3380.2**	**2931.8**
7	1034.9	1240.1	1297.6
8	1856.3	1806.7	1705.2
9	**2149.1**	**2134.3**	**2012.1**
10	1117.3	1449.5	1348.3
11	1588.4	1850.7	1848.2
12	**2660.6**	**2539.0**	**2344.0**
13	1246.0	1500.2	1608.4
14	1383.4	1719.7	1749.5
15	1620.2	1357.1	1364.2
16	1402.4	1497.4	1794.9
17	**3479.7**	**2550.8**	**2825.0**
18	**2846.5**	**2367.1**	**2498.5**
19	1669.9	1832.1	1853.0
20	**2149.9**	**1829.5**	**1729.4**
21	1943.9	1547.7	1497.4
22	1611.9	2108.4	1352.6

23	1736.3	1506.2	1389.4
24	1793.5	1964.9	1836.7
25	1951.4	1614.4	1593.8
26	1724.6	1859.7	2070.2

It can be seen from the images and the average pixel intensities that there are a number of compounds that bind ^{60}Co well and also bind Co^{2+} selectively over the tap water. Those compounds, which are good at binding Co^{2+} are highlighted in the table above.

S6 ^{60}Co Tap Water Decontamination Results

As for ^{137}Cs, decontamination experiments were carried out with ^{60}Co spiked tap water. The same compounds were chosen for ^{60}Co that were used for the ^{137}Cs experiments (**1, 2, 3, 4, 6, 7, 11, 12, 23**) and the same experimental procedure was followed. The gamma peak at 1159.99 keV was used to calculate the decontamination factor. These are shown in the table below and are compared to the average pixel intensities in the graph below:

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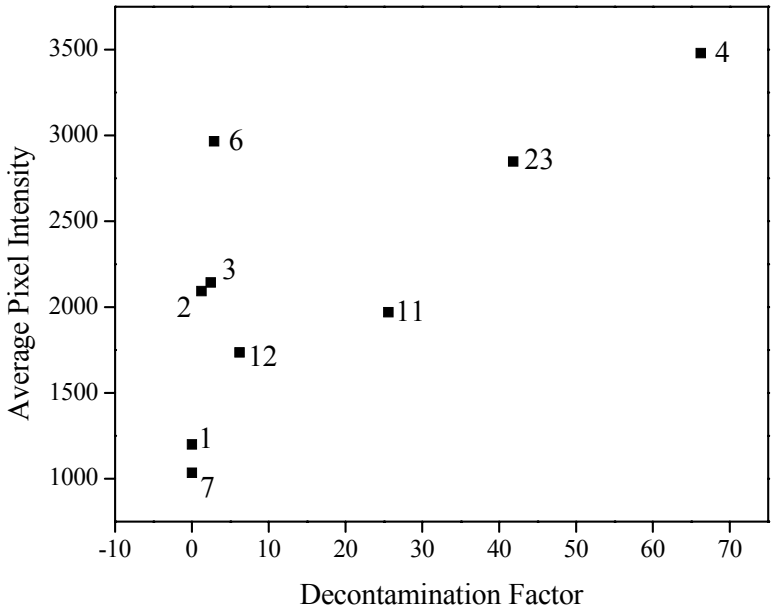
Compound	Decontamination Factor	% decrease in γ peak at 1159.99 keV (i.e. % decontamination)	Average Pixel Intensities
1	negligible	negligible	1199.2
2	1.28	21.7	2093.3
3	2.48	59.6	2143.2
4	66.25	97.4	3479.7
6	2.9	65.5	2965.2
7	negligible	negligible	1034.9
11	25.6	96.1	1969.8
12	6.21	83.9	1736.3
23	41.84	97.6	2846.5

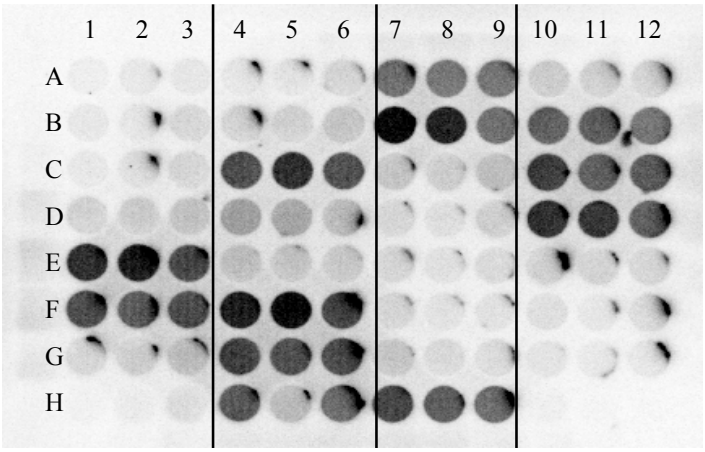


It can be seen from the table and the graph above that some of the decontamination factors for our compounds are good for ^{60}Co. There is good correlation for a number of the compounds between the average pixel intensities and DF, but there are a few compounds where the average pixel intensities are much higher than the decontamination factors. This may be due to experimental factors including the flow rate, contact time and the type of material (i.e. polystyrene or silica).

Supplementary Material (ESI) for Journal of Materials Chemistry

S7 ^{90}Sr Autoradiography Results

The radiometric screening data for our compounds with ^{90}Sr is shown below. The same experimental procedure that was used for ^{137}Cs and ^{60}Co was followed here. Three wells were filled with each of the compounds. In the first column of each group (columns 1, 4, 7 and 10) only ^{90}Sr (250 Bq) was added; in the second columns (2, 5, 8 and 11), the wells were pre-treated with a 1 mM Ca^{2+} solution before adding 250 Bq of ^{90}Sr. In the third group (columns 3, 6, 9 and 12), ^{90}Sr and Ca^{2+} were added simultaneously. All the solutions were adjusted to pH 7 before addition to the wells.



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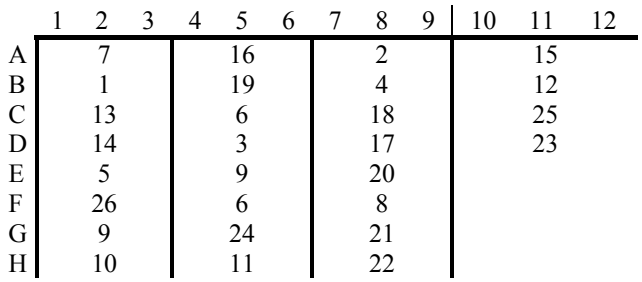

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A		7			16			2			15	
B		1			19			4			12	
C		13			6			18			25	
D		14			3			17			23	
E		5			9			20				
F		26			6			8				
G		9			24			21				
H		10			11			22				

Compound	Average Pixel Intensities		
	^{90}Sr	Pre-treated with Ca^{2+}	$^{90}Sr + Ca^{2+}$
1	203.5	243.5	349.9
2	**1315.6**	**1227.5**	**1250.6**
3	877.4	802.3	646.9
4	**2267.8**	**2010.2**	**1308.1**
5	**1900.7**	**2142.8**	**1675.9**
6	**2070.6**	**2272.6**	**1710.5**
7	137.9	206.4	210.8
8	384.7	266.1	275.0
9	374.2	446.8	623.3
10	114.5	173.0	298.8
11	1514.9	619.6	1315.5
12	**1447.2**	**1476.7**	**1233.6**
13	202.7	296.5	373.0
14	393.7	464.4	559.3
15	454.8	427.7	412.3
16	223.9	253.5	374.6
17	371.3	300.9	436.1
18	509.6	451.5	590.6
19	407.6	412.5	524.7
20	375.3	300.9	436.1
21	521.0	337.3	315.1
22	**1677.9**	**1416.1**	**1300.9**
23	**1897.8**	**1818.3**	**1459.9**
24	**1764.3**	**1601.9**	**1625.9**
25	**1777.5**	**1437.7**	**1493.9**
26	**1623.0**	**1486.7**	**1645.9**

It can be seen from the image and the average pixel intensities that there are a number of compounds that bind Sr^{2+} very well and they also bind the ion selectively over Ca^{2+} (highlighted compounds). All three sizes (12-crown-4, 15-crown-5 and 18-crown-6) bind Sr^{2+} equally well..