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Electronic Supplementary Information

Selective Recovery of Rare Earth Elements Using Chelating Ligands Grafted on Mesoporous Surfaces

Justyna Florek[a,b #], Ambreen Mushtaq[a,c#], Dominic Larivière[a,c *], Gabrielle Cantin[a,c], Frédéric-G. Fontaine[a,c *]and Freddy Kleitz[a,b *]

a) Department of Chemistry, Université Laval, Quebec City, G1V 0A6, QC, Canada.
b) Centre de Recherche sur les Matériaux Avancés (CERMA), Université Laval, Quebec City, G1V 0A6, QC, Canada.
c) Centre en Catalyse et Chimie Verte (C3V), Université Laval, Quebec City, G1V 0A6, QC, Canada.
d) # Contributed equally to this work.

E-mails: freddy.kleitz@chm.ulaval.ca; dominic.lariviere@chm.ulaval.ca; frederic.fontaine@chm.ulaval.ca

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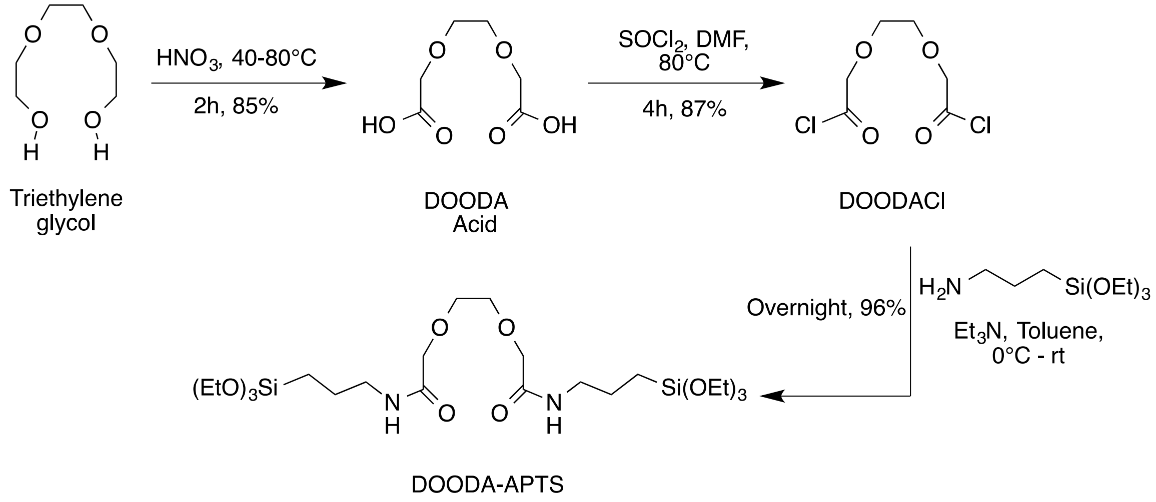
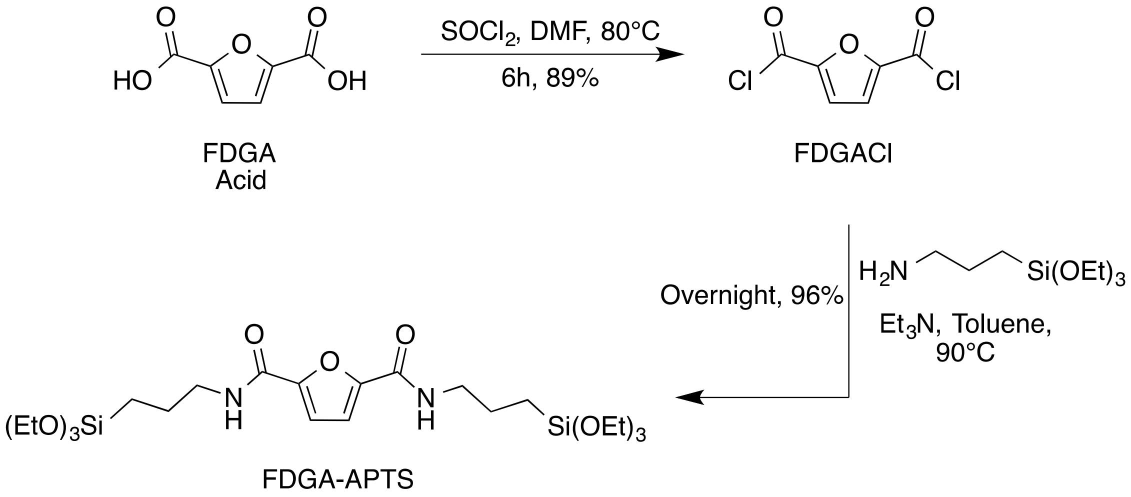
1. Ligands synthesis

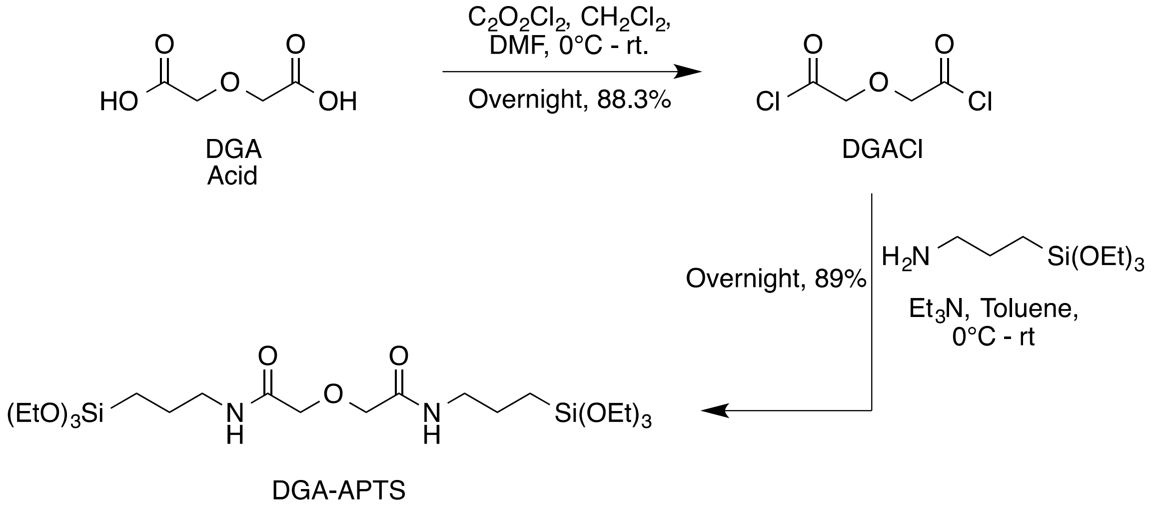
General Procedures. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in nitrogen filled gloveboxes, unless specified otherwise. The glassware was dried overnight prior to use. All solvents were dried prior to use. Deuterated benzene-*d*$_6$ was distilled under reduced pressure from a Na/K alloy. Deuterated chloroform and acetone were used as received. Triethylene glycol, 2,5-furandicarboxyllic acid, thionyl chloride ($SOCl_2$), oxaallyl chloride $(COCl)_2$ and aminopropyltriethoxysilane (APTS) were purchased from Sigma Aldrich and used without further purification. NMR spectra were recorded on an Agilent Technologies NMR spectrometer at 500 MHz (^1H), 125.758 MHz (^{13}C) and on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^1H), 100.580 MHz (^{13}C). ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to residual solvent signals in deuterated solvent. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad (br). Chemical shifts are reported in ppm.



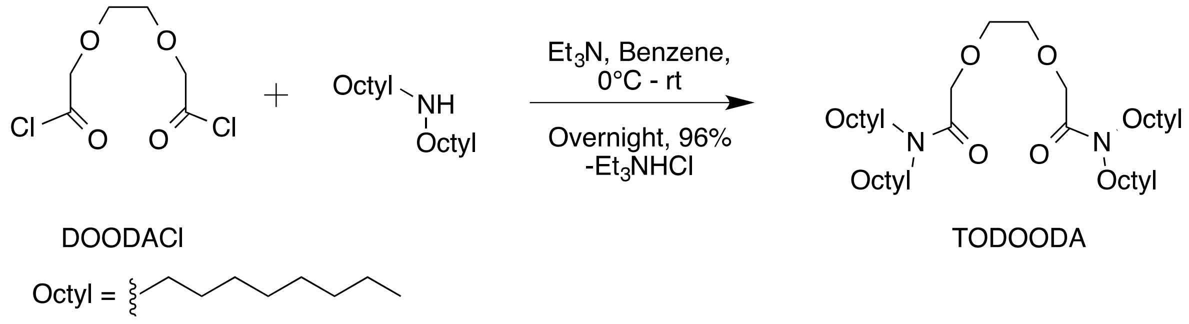
Scheme 1: Synthesis of 3,6-dioxaoctanediamido-propyltriethoxysilane ligand (DOODA-APTS) from triethylene glycol.



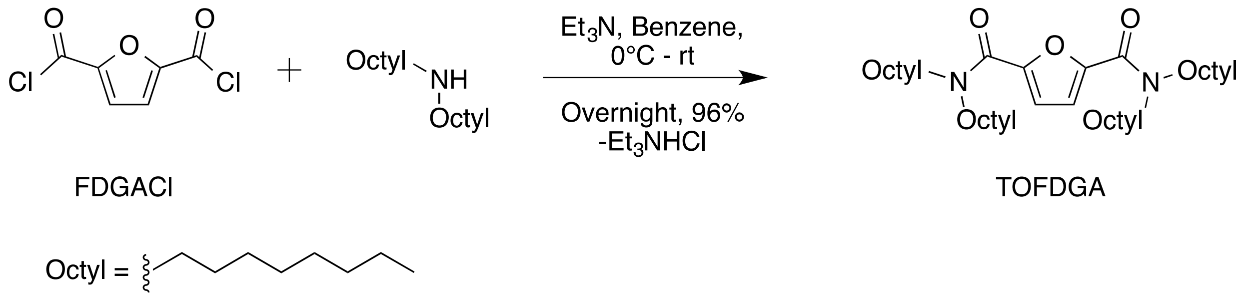
Scheme 2: Synthesis of furan-2,4-diamido-propyltriethoxysilane ligand (FDGA-APTS) from 2,5-furandicarboxyllic acid.



Scheme 3: Synthesis of diglycol-2,4-diamido-propyltriethoxysilane ligand (DGA-APTS).



Scheme 4: Synthesis of N, N-dioctyl-3, 6-dioxaoctanediamide ligand (TODOODA).



Scheme 5: Synthesis of N, N-dioctylfuran-2, 4-diamide (TOFDGA).

2. Ligands NMR characterization

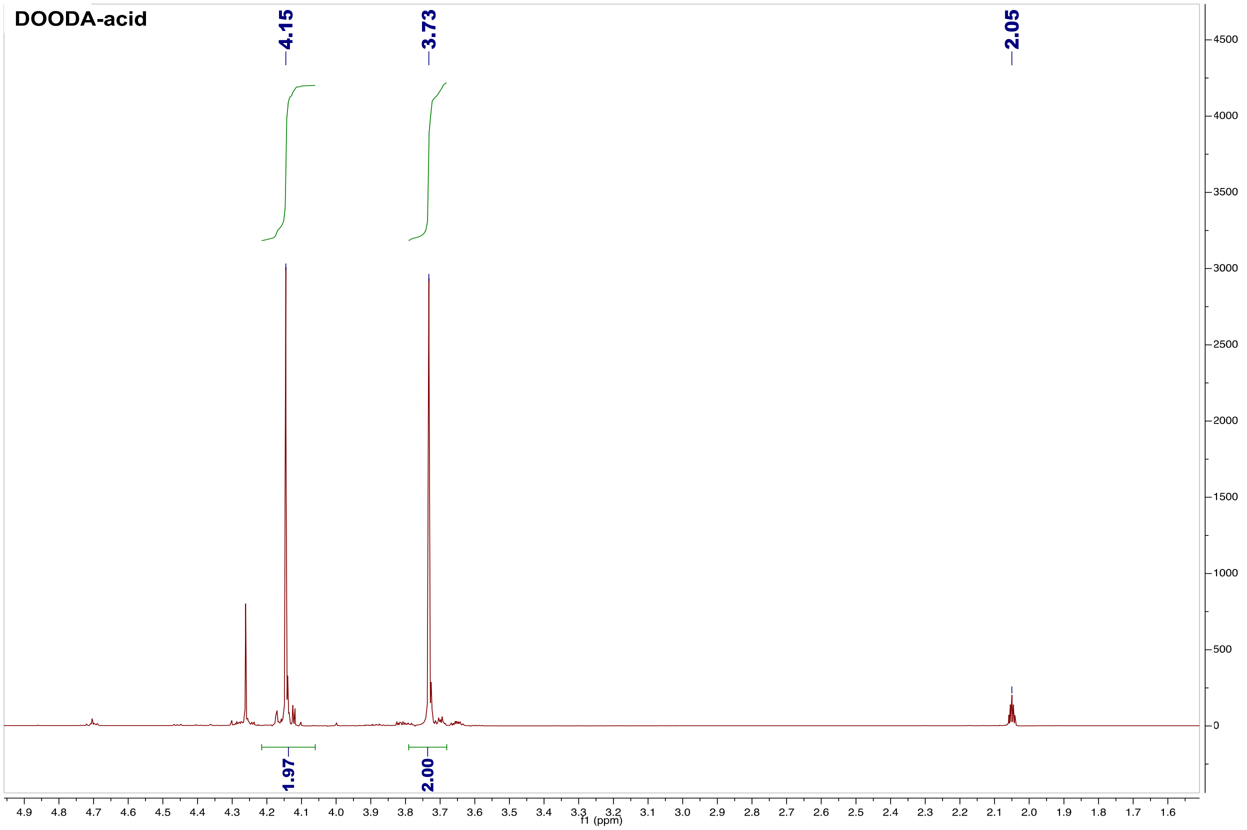


Figure S1. ^{1}H NMR of **DOODA acid** (*acetone-d_6*, 400 MHz).

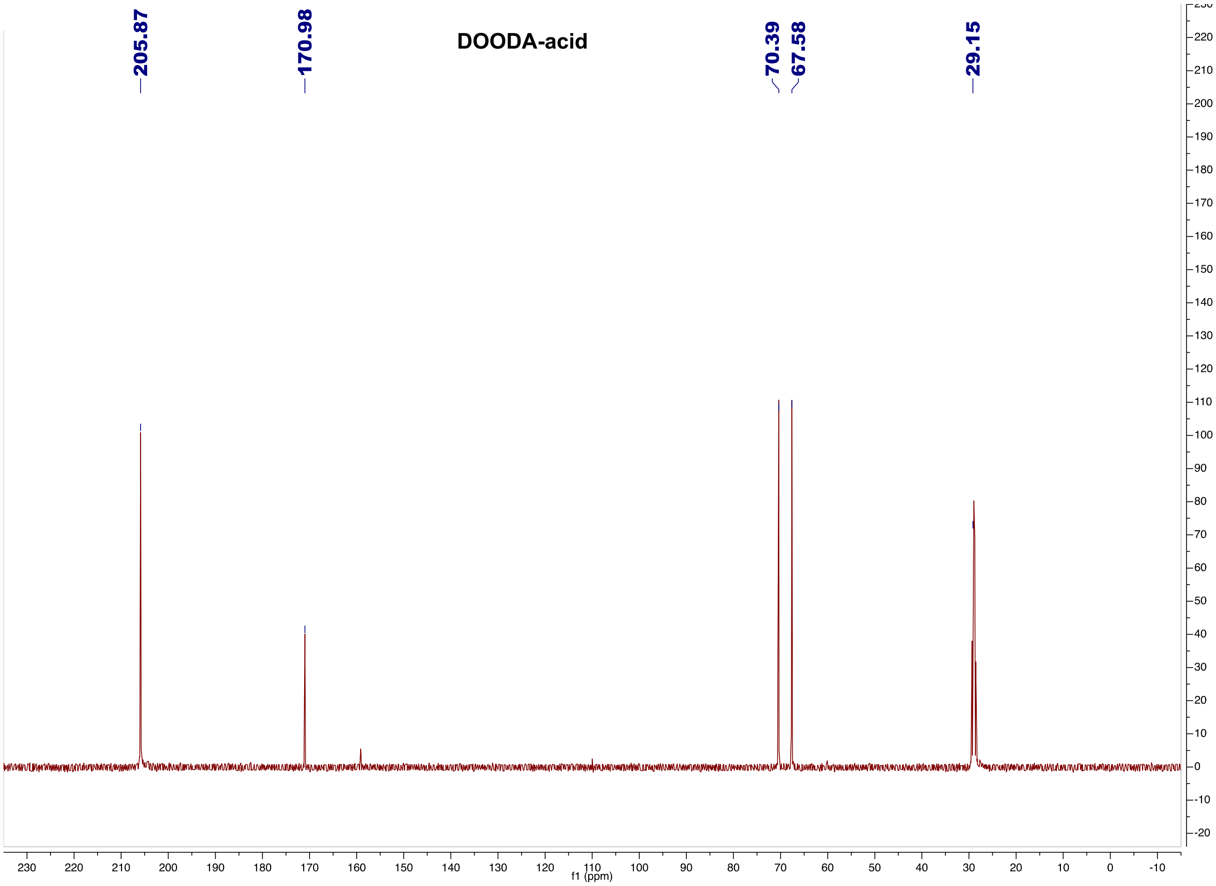


Figure S2. $^{13}C\ \{^1H\}$ NMR of **DOODA acid** (*acetone-d_6*, 100.58 MHz).

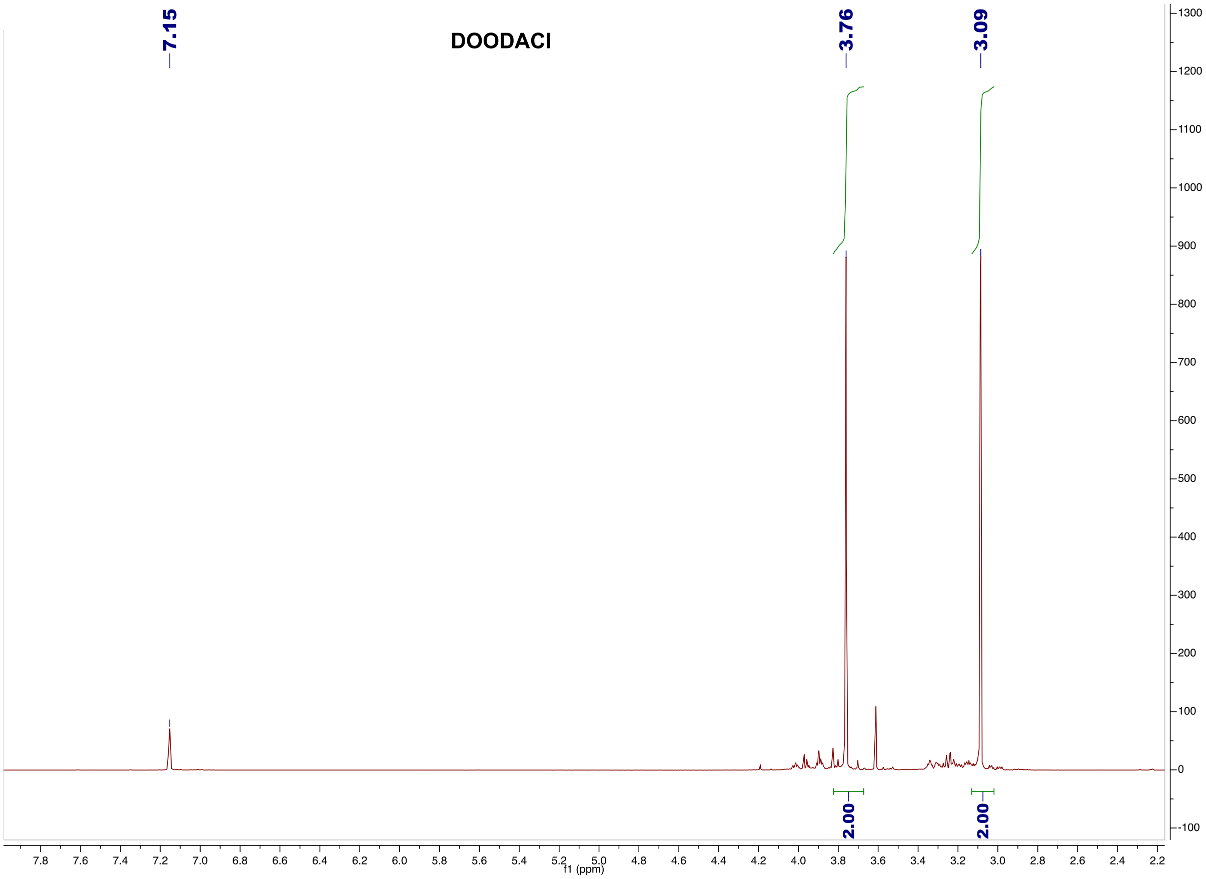


Figure S3. ^{1}H NMR of **DOODA**-**Cl** (*benzene-d$_6$*, 400 MHz).

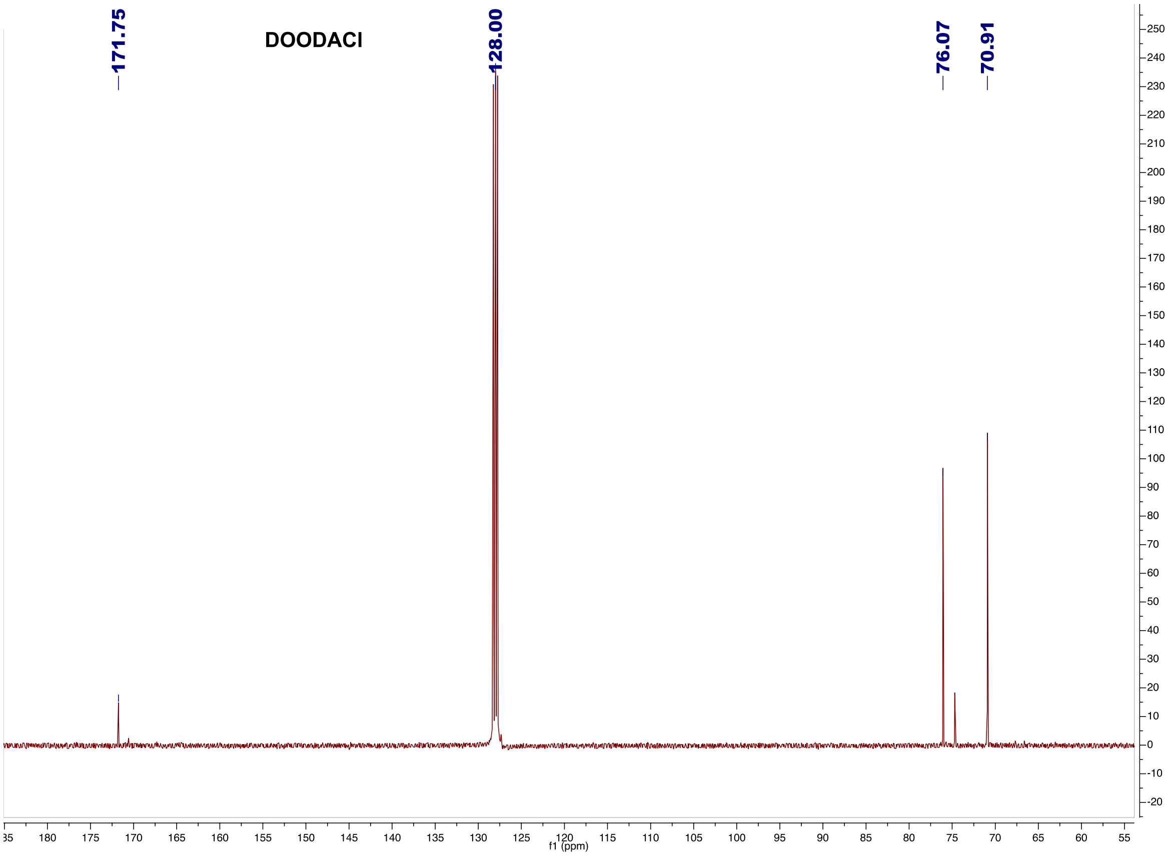


Figure S4. $^{13}C\{^1H\}$ NMR of **DOODA-Cl** (*benzene-d*$_6$, 100.58 MHz).

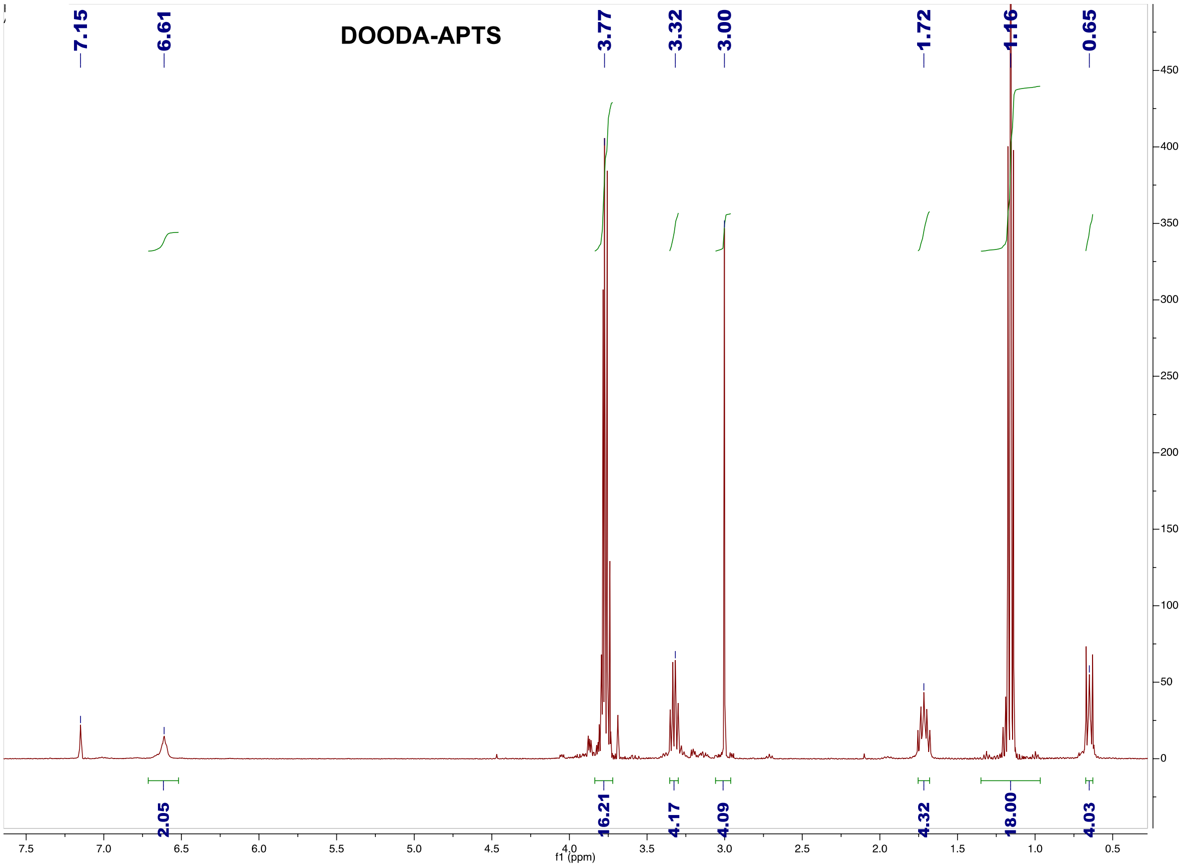


Figure S5. ^{1}H NMR of **DOODA-APTS** (*benzene-d$_6$*, 400 MHz).

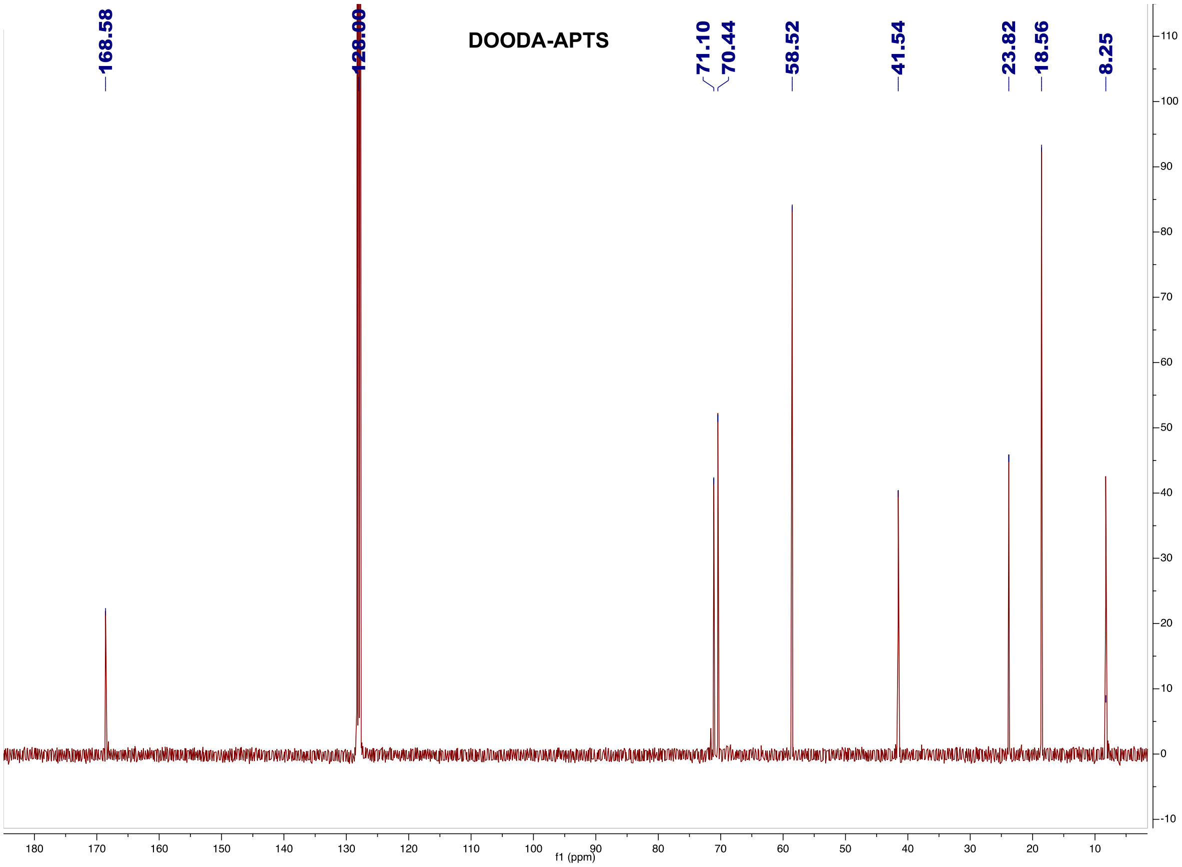


Figure S6. $^{13}C\{^{1}H\}$ NMR of **DOODA-APTS** (*benzene-d_6*, 100.58 MHz).

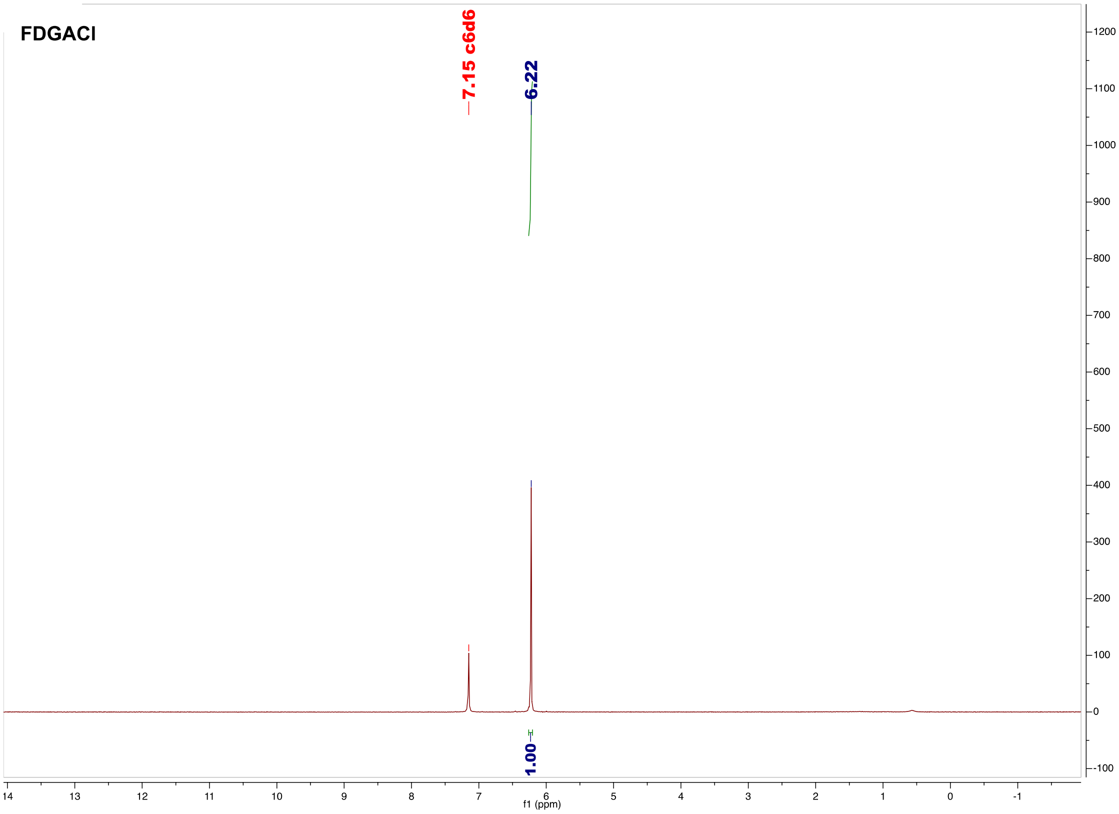


Figure S7. ^{1}H NMR of **FDGA-Cl** (*benzene-d$_6$*, 400 MHz).

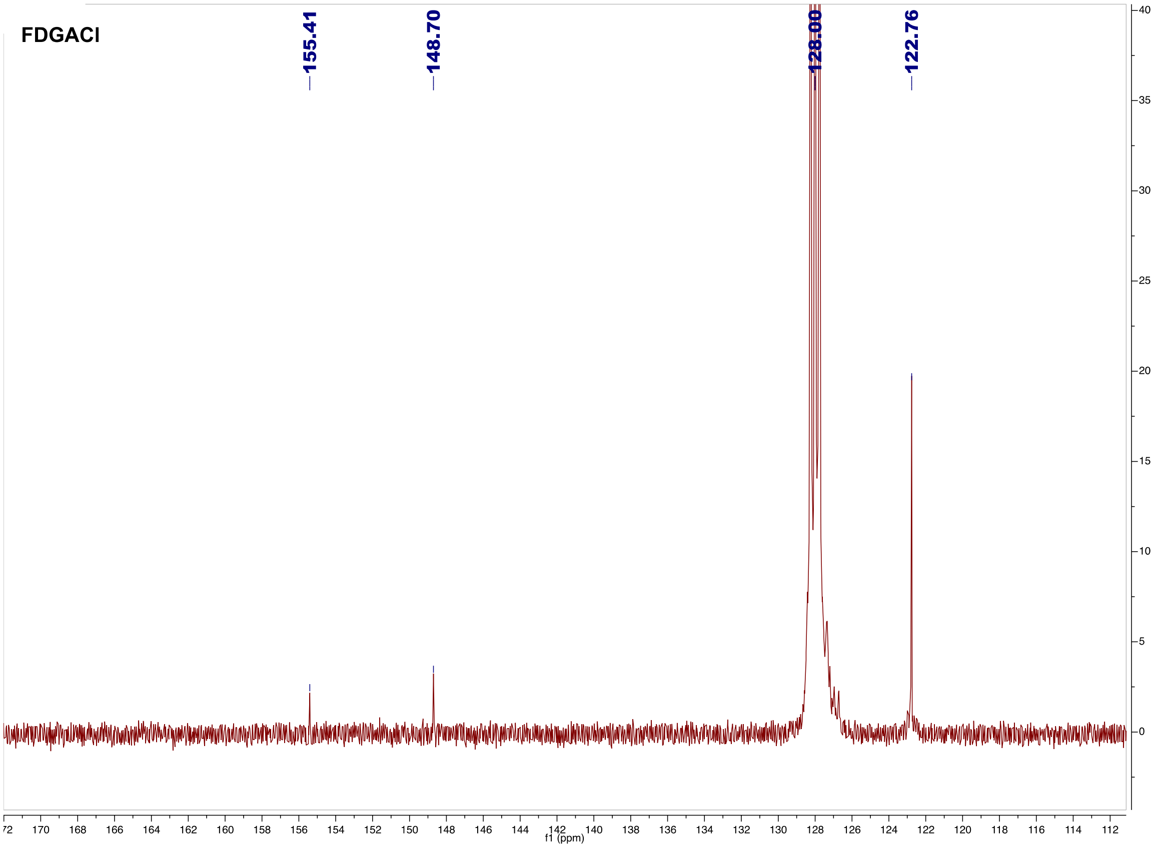


Figure S8. $^{13}C\{^{1}H\}$ NMR of **FDGA-Cl** (*benzene-d*$_6$, 100.58 MHz).

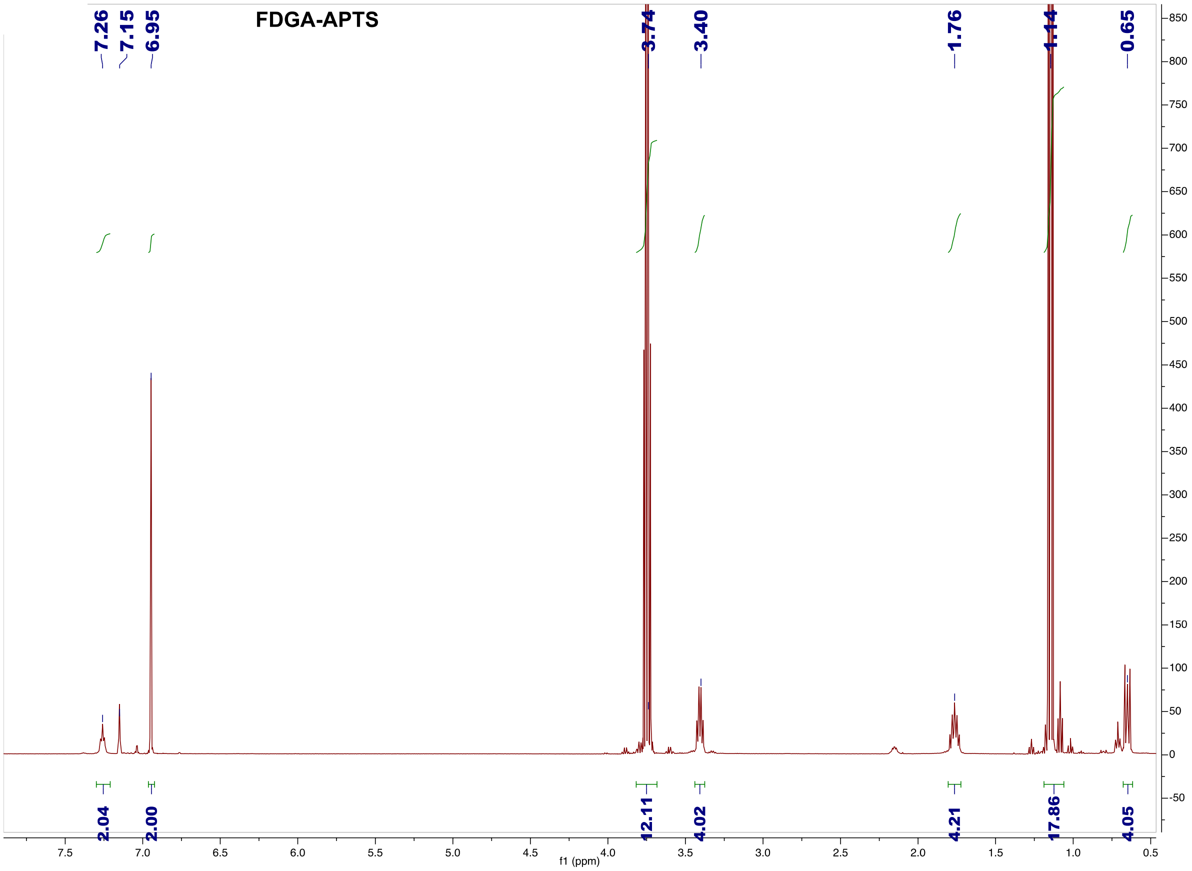


Figure S9. ^{1}H NMR of **FDGA-APTS** (*benzene-d$_6$*, 400 MHz).

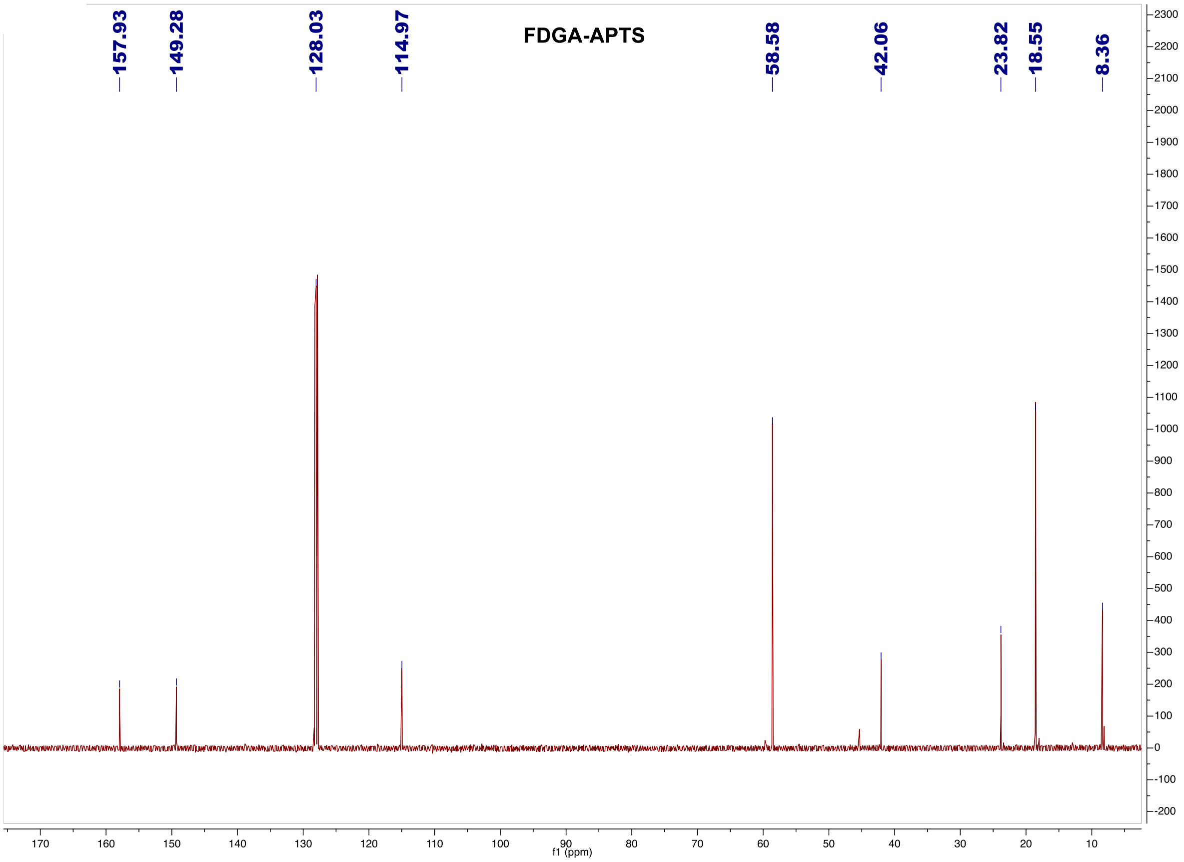


Figure S10. $^{13}C\{^{1}H\}$ NMR of **FDGA-APTS** (*benzene-d$_6$*, 100.58 MHz).

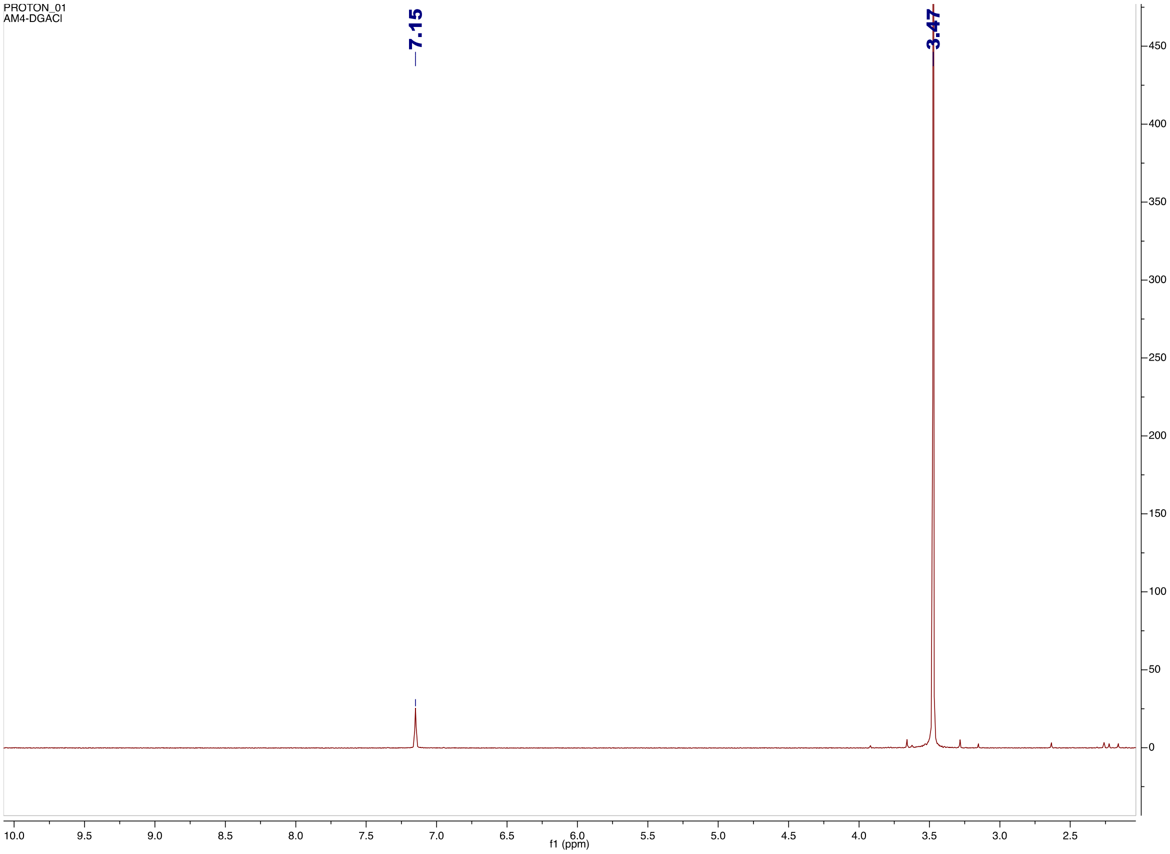


Figure S11. ^{1}H NMR of **DGA-Cl** (*benzene-d$_6$*, 400 MHz).

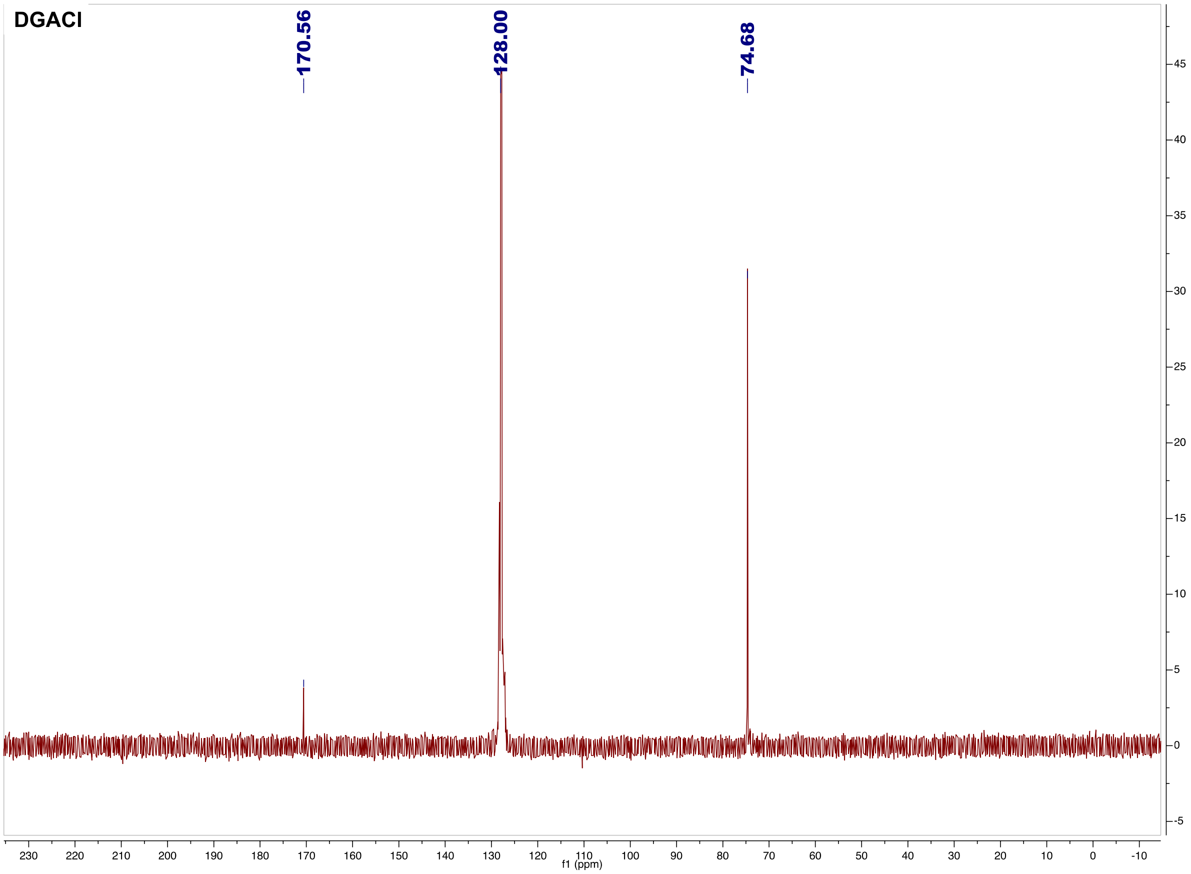


Figure S12. $^{13}C\{^{1}H\}$ NMR of **DGA-Cl** (*benzene-d*$_6$, 100.58 MHz).

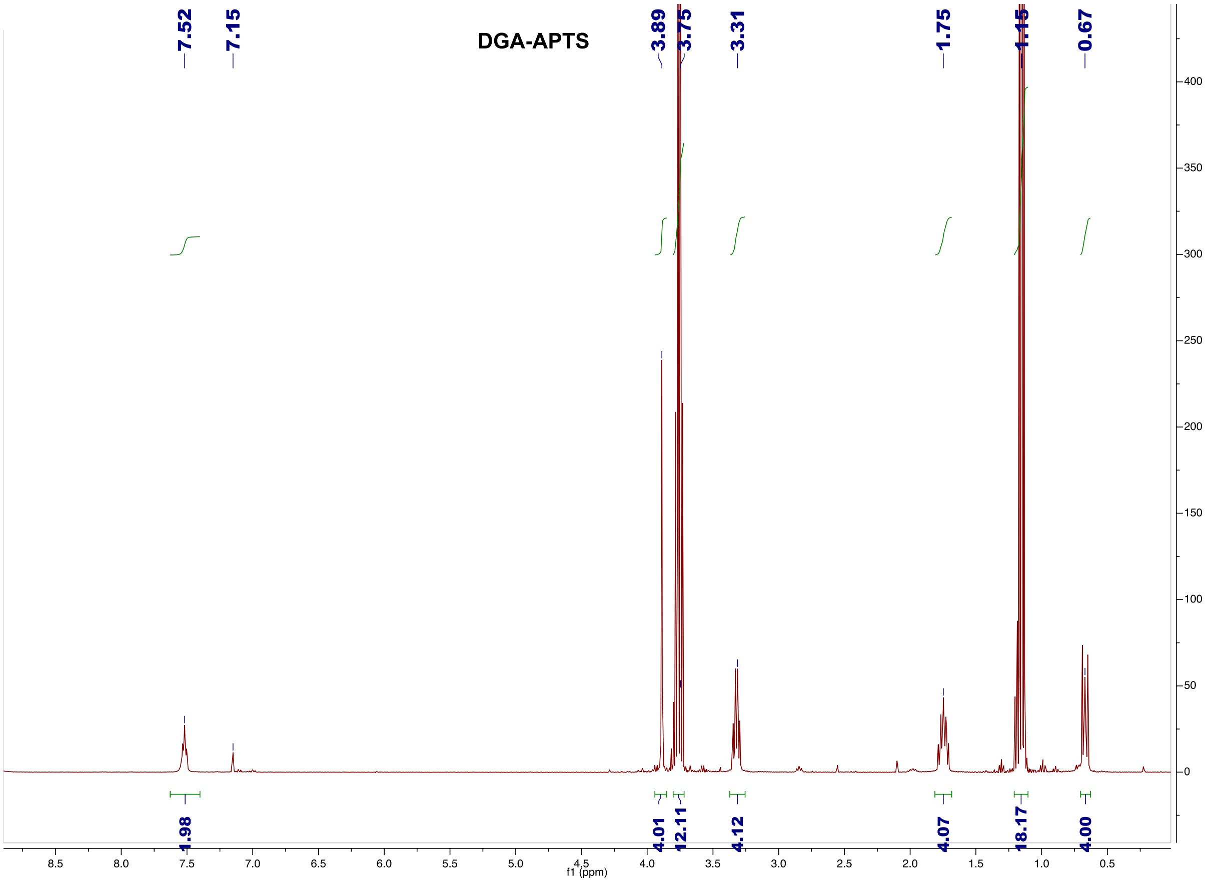


Figure S13. ^{1}H NMR of **DGA-APTS** (*benzene-d_6*, 400 MHz).

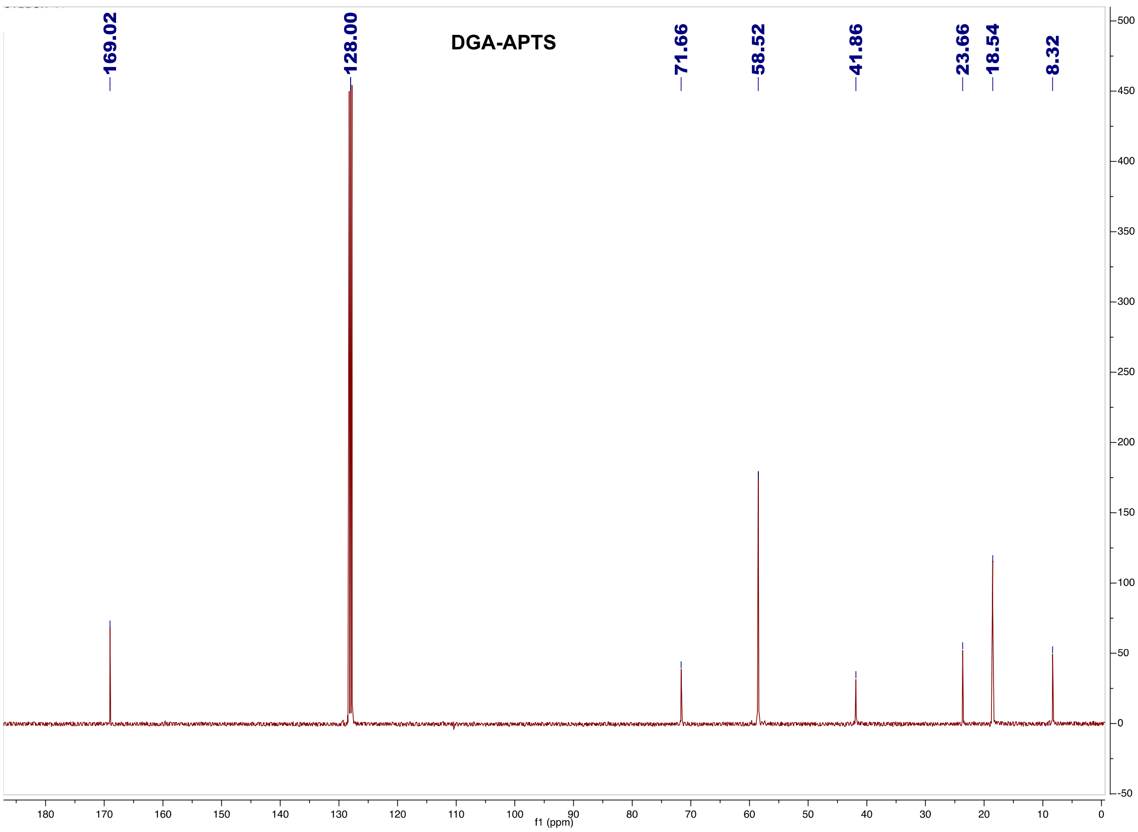


Figure S14. $^{13}C\{^{1}H\}$ NMR of **DGA-APTS** (*benzene-d_6*, 100.58 MHz).

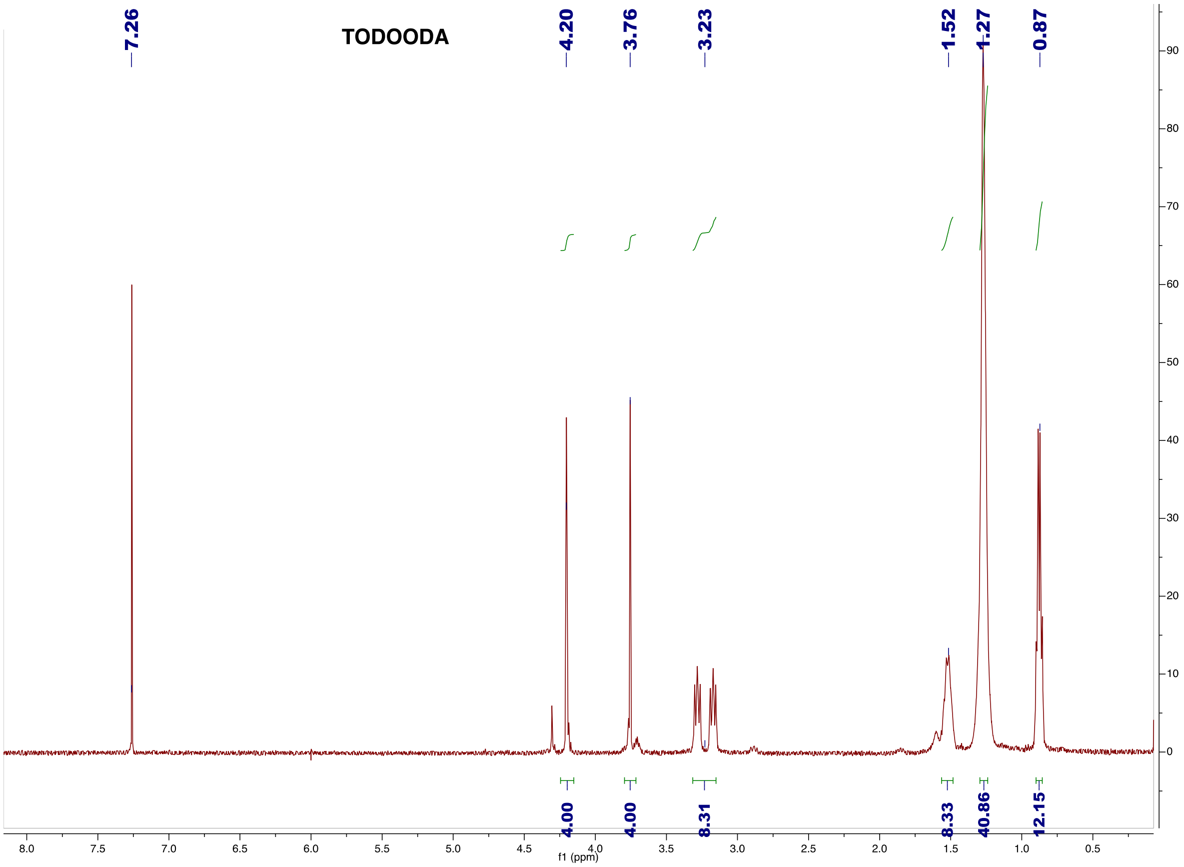


Figure S15. ^{1}H NMR of **TODOODA** (*chloroform-d*, 500 MHz).

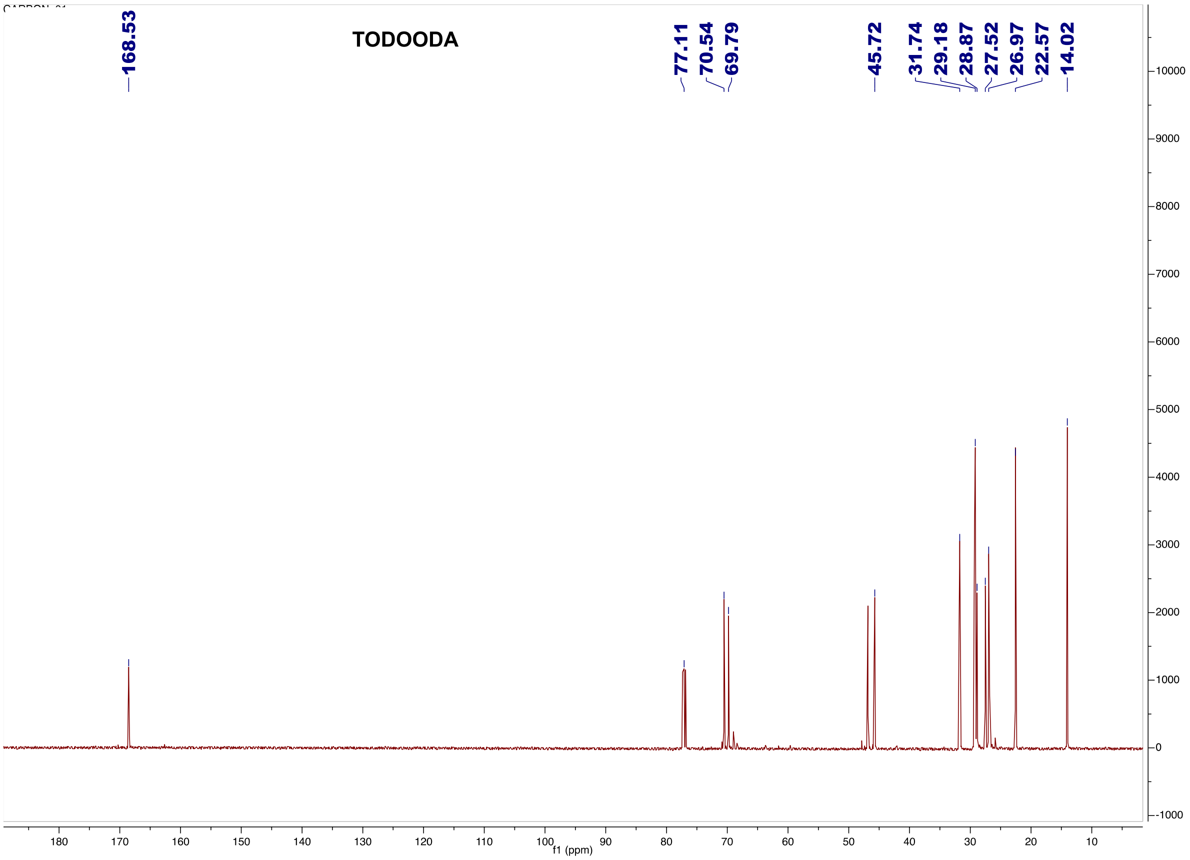


Figure S16. $^{13}C\{^{1}H\}$ NMR of **TODOODA** (*chloroform-d*, 125 MHz).

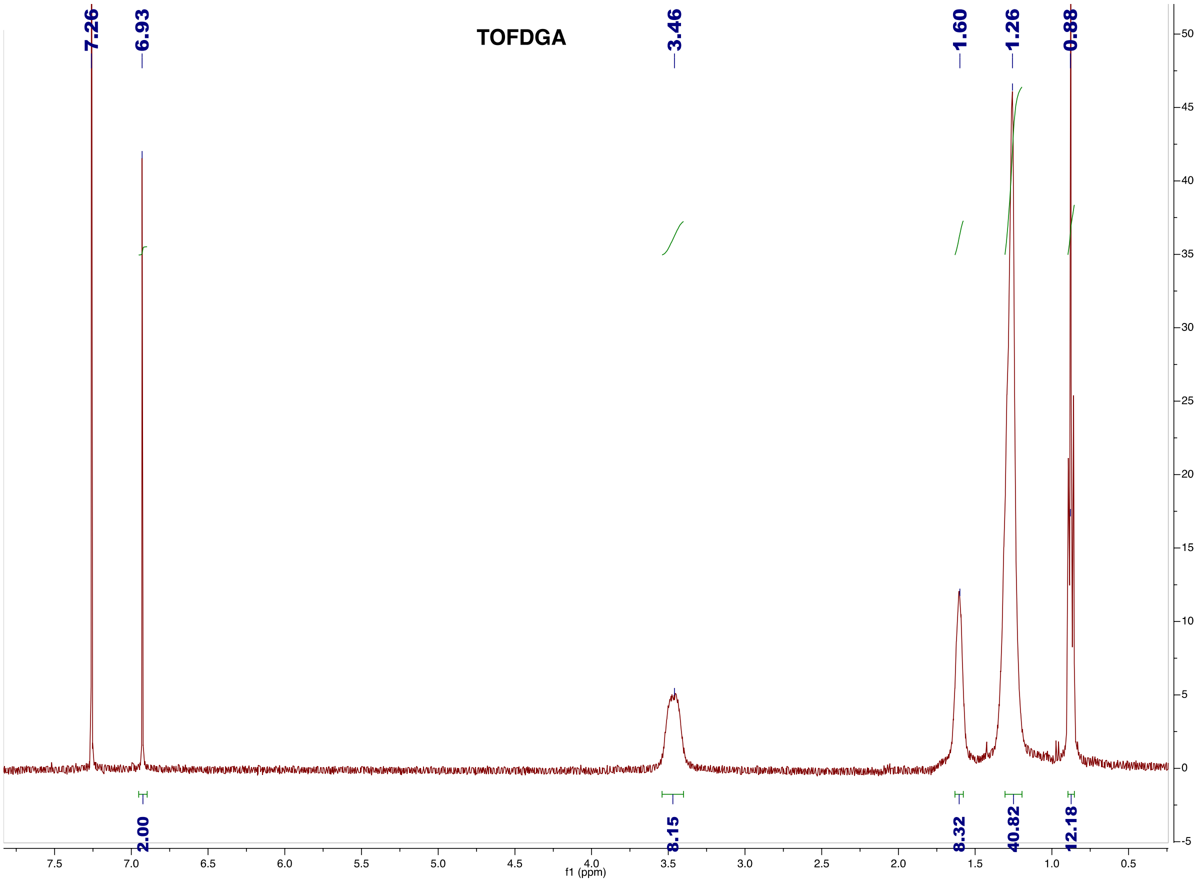


Figure S17. ^{1}H NMR of **TOFDGA** (*chloroform-d*, 500 MHz).

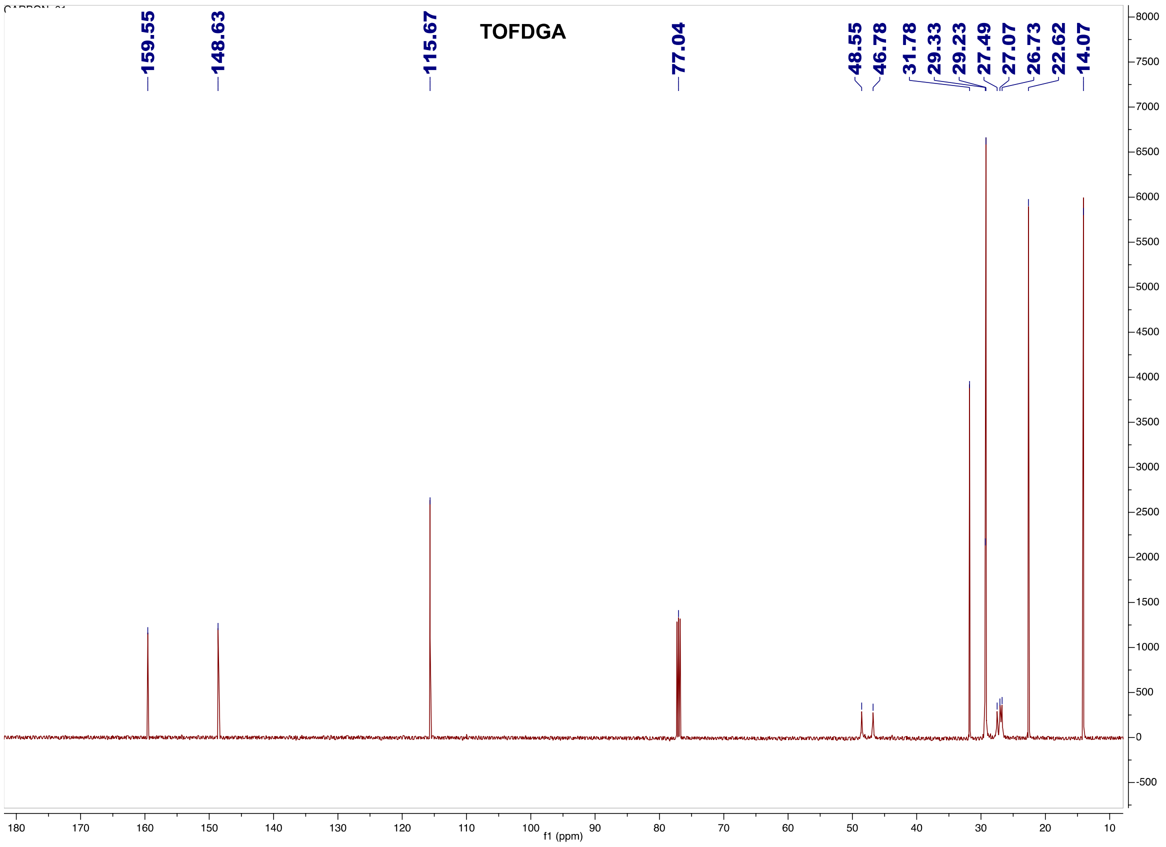


Figure S18. $^{13}C\{^{1}H\}$ NMR of **TOFDGA** (*chloroform-d*, 125 MHz).

3. Material characterization

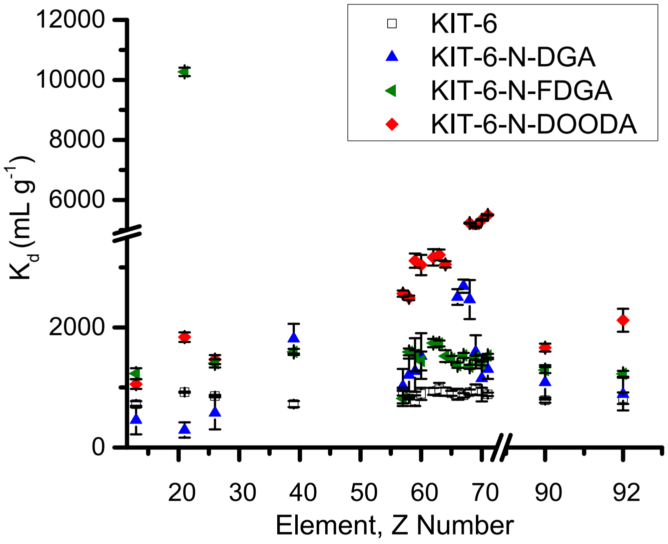


Figure S19. Distribution coefficients (K_d) values and corresponding standard deviations for the modified silica materials for the mixture of the lanthanides and competitive elements, i.e., aluminum, iron, thorium and uranium in the extraction mixture, as a function of the atomic number Z.

Table S1. Chemical shifts (ppm) of the characteristic peaks for the mesoporous sorbents in solid state NMR (^{13}C and ^{29}Si).

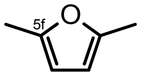
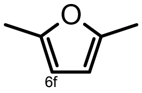
Functional group	KIT-6-N-DGA	KIT-6-N-DOODA	KIT-6-N-FDGA
$\underline{C}H_3$-$\underline{C}H_2$-Si-	61.14	58.04; 16.99	60.06; 19.01
-Si-$\underline{C}H_2$-CH_2-CH_2-	9.24	9.24	10.40
-Si-CH_2-$\underline{C}H_2$-CH_2-	21.58	22.19	24.20
-Si-CH_2-CH_2-$\underline{C}H_2$-	41.77	41.77	43.02
O=$\underline{C}$-CH2-	171.12	171.19	160.75
O=C-$\underline{C}$H2-O-	67.33	71.21	-
-CH2-O-$\underline{C}$H2-	-	71.21	-
	-	-	150.68
	-	-	115.83
T^1 species ($RSi(OH)_2(OSi)$	-	-48.71	-52.35
T^2 species ($RSi(OH)(OSi)_2$	-58.91	-58.93	-
T^3 species ($RSi(OSi)_3$	-67.54	-	-

Table S2. Tabulated distribution coefficients (K_d) values.

Element	LLE			SPE (KIT-6 material)		
	TODGA	TODOODA	TOFDGA	DGA	DOODA	FDGA
Sc	27.46	0.13	0.08	291.65	1839.00	10268.00
Y	88.30	0.86	0.69	2812.58	3561.00	1593.00
La	2.54	2.16	2.13	1021.47	2564.00	817.00
Ce	2.60	1.90	2.02	1206.91	2493.00	1592.00
Pr	3.65	1.83	2.16	1273.09	3112.00	1544.00
Nd	6.32	1.33	2.03	1523.08	3040.00	1442.00
Sm	30.72	0.90	1.15	3543.36	3167.00	1740.00
Eu	80.58	0.88	1.11	4282.13	3209.00	1733.00
Gd	53.61	0.66	0.82	4619.63	3051.00	1522.00
Tb	116.86	0.82	0.79	4490.05	3716.00	1476.00
Dy	147.45	0.90	0.69	2506.50	3726.00	1370.00
Ho	137.88	0.97	0.76	2687.73	4891.00	1534.00
Er	231.51	0.98	0.77	2465.22	5230.00	1345.00
Tm	188.17	1.12	0.64	1593.39	5106.00	1495.00
Yb	149.91	1.01	0.71	1153.33	5339.00	1400.00
Lu	148.97	0.99	0.70	1306.39	5503.00	1529.00

Table S3. A comparison of the separation factors for LLE and SPE with the different ligand systems.

Separation factor	LLE		SPE (KIT-6 hybrids)		SPE/LLE	
	DOODA	FDGA	DOODA	FDGA	DOODA	FDGA
Ce/La	0.8	0.9	1.0	1.9	1.25	2.11
Gd/La	0.3	0.4	1.2	1.9	4.00	4.75
Lu/La	0.5	0.3	2.1	1.9	4.20	6.33