Recognition of f-elements by phosphorylated calixarenes

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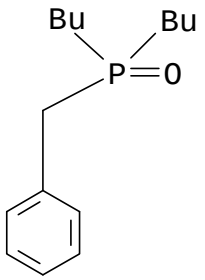
1. Calixarenes substituted with phosphine oxides

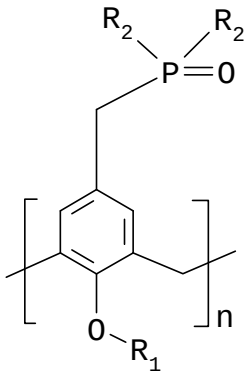
Upper rim derivatives
Lower rim derivatives

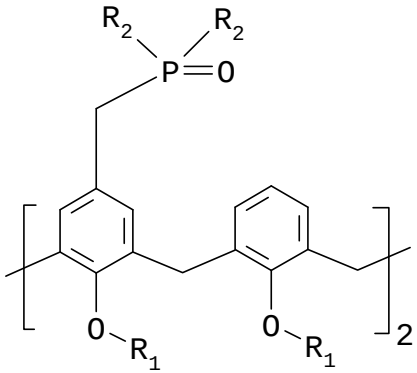
2. Calix[4]arenes substituted with phosphonates

Structures of the upper rim calixarenes substituted with phosphine oxides and one related monomer (**C36)**.



C36





R_1=Pr, R_2=Pr **C131**

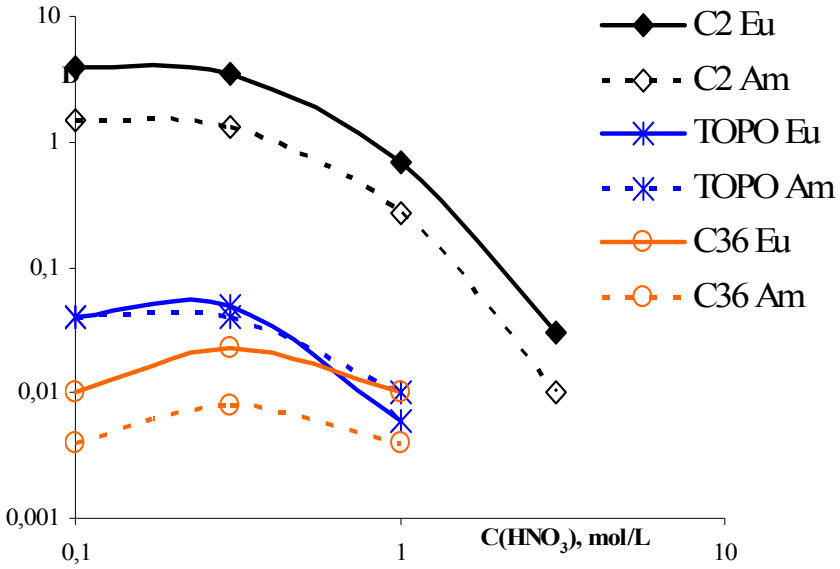
n=4

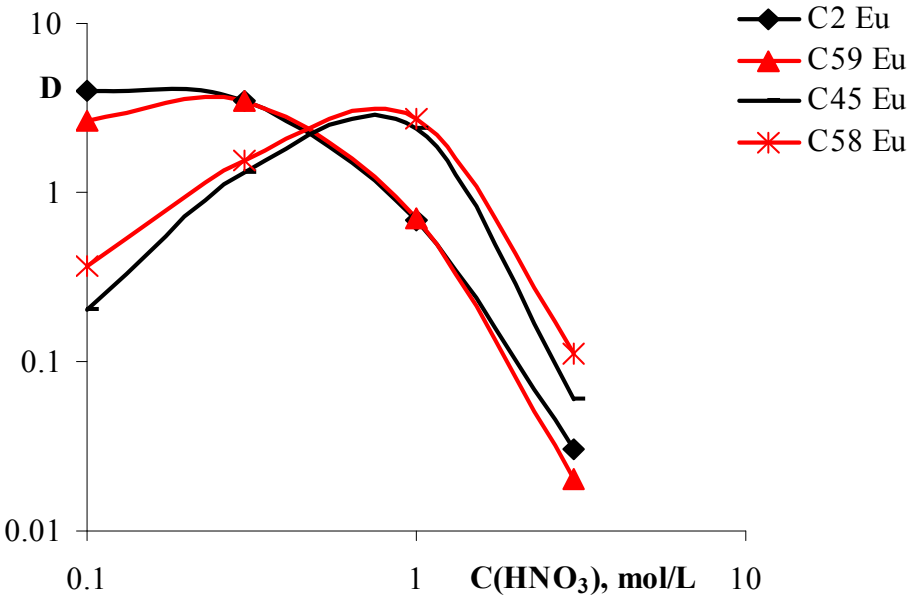
R_1=Pr	R_2=Me	**C57**
	R_2=Et	**C45**
	R_2=Pr	**C67**
	R_2=i-Pr	**C75**
	R_2=Bu	**C2**
	R_2=Ph	**C69**
R_1=Hex	R_2=Et	**C58**
	R_2=Bu	**C59**
	R_2=Ph	**C60**

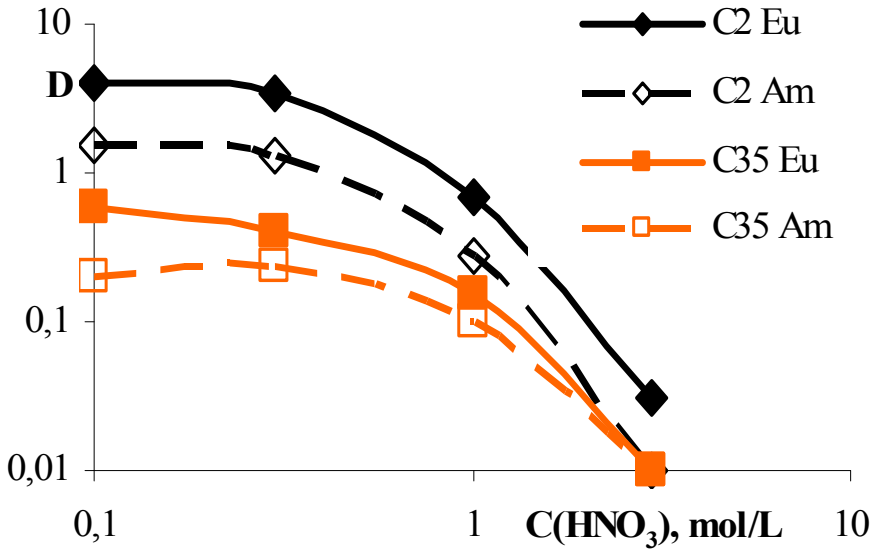
n=6

R_1=Me	R_2=Et	**C68**
	R_2=Bu	**C35**
	R_2=Ph	**C14**
	R_2=Bu, Ph	**C15**

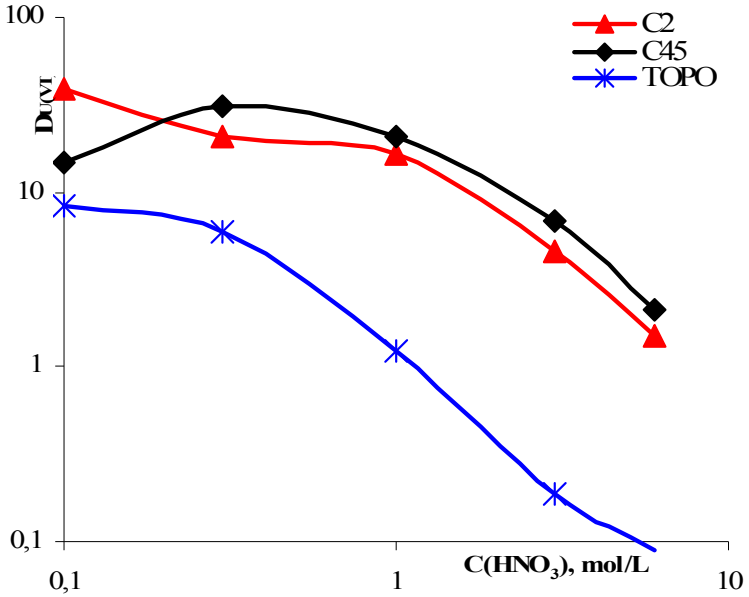
Extraction of ^{241}Am and ^{152}Eu (m-NBTF)

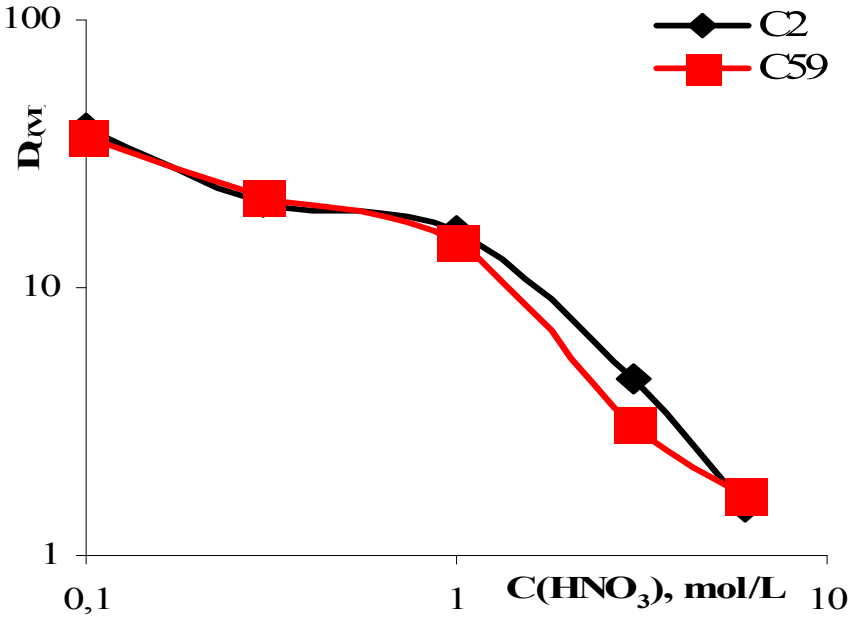


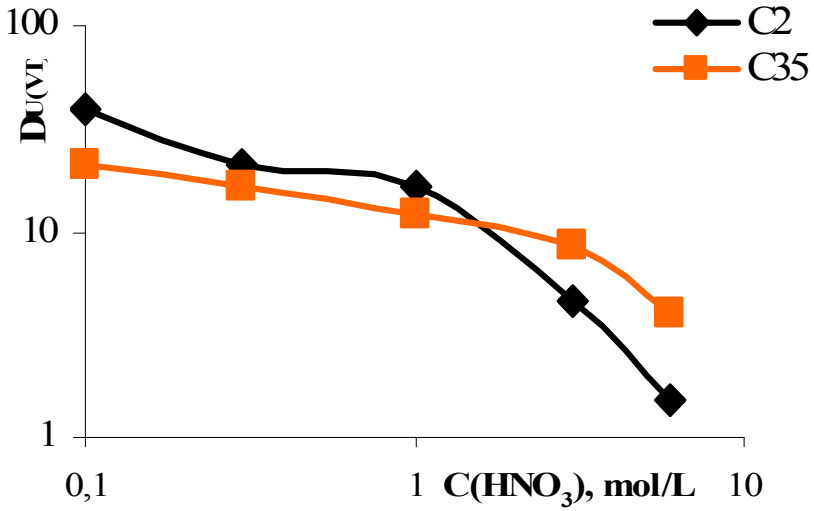




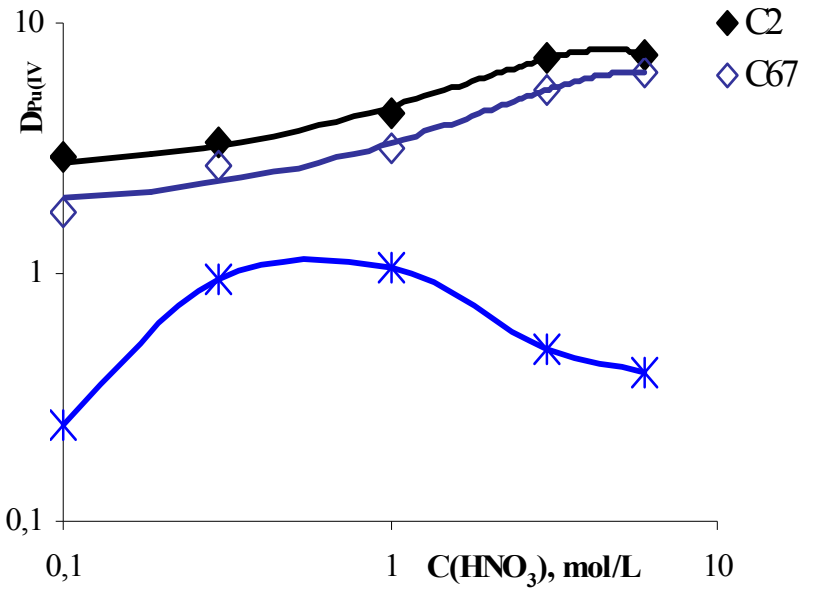
Extraction of ^{233}U (m-NBTF)

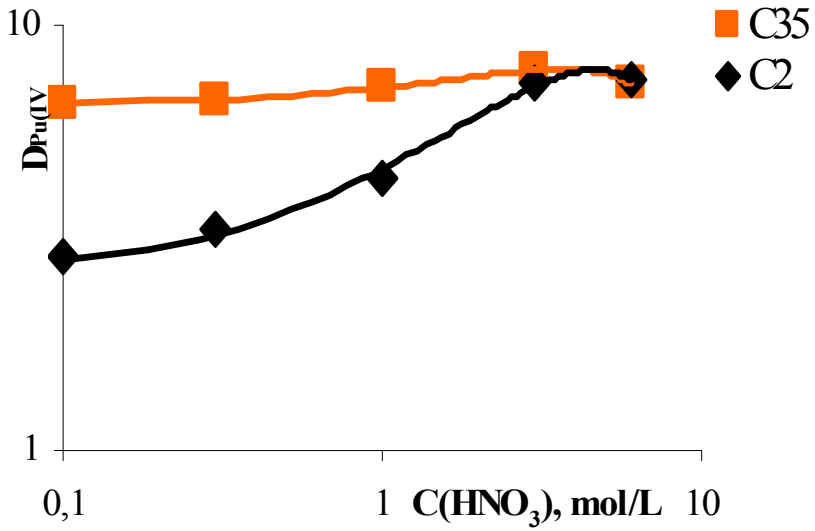


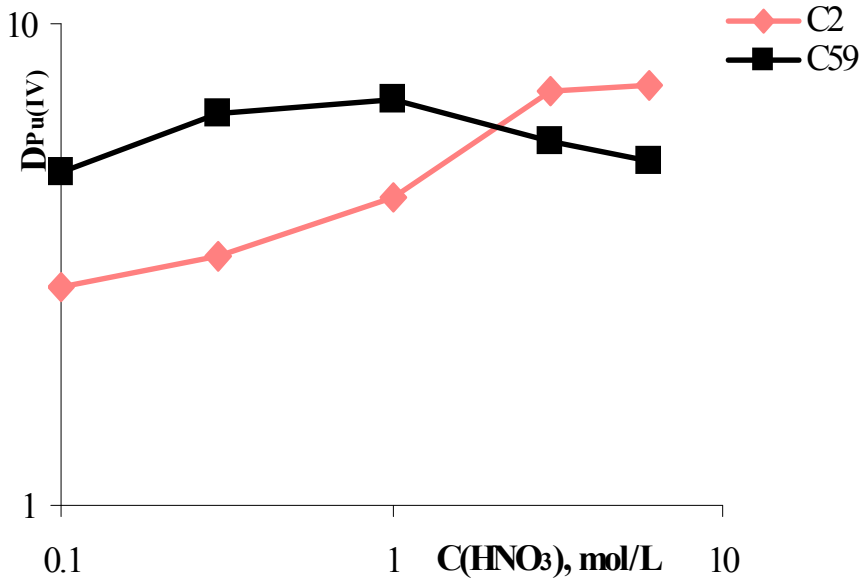




Extraction of ^{239}Pu (m-NBTF)

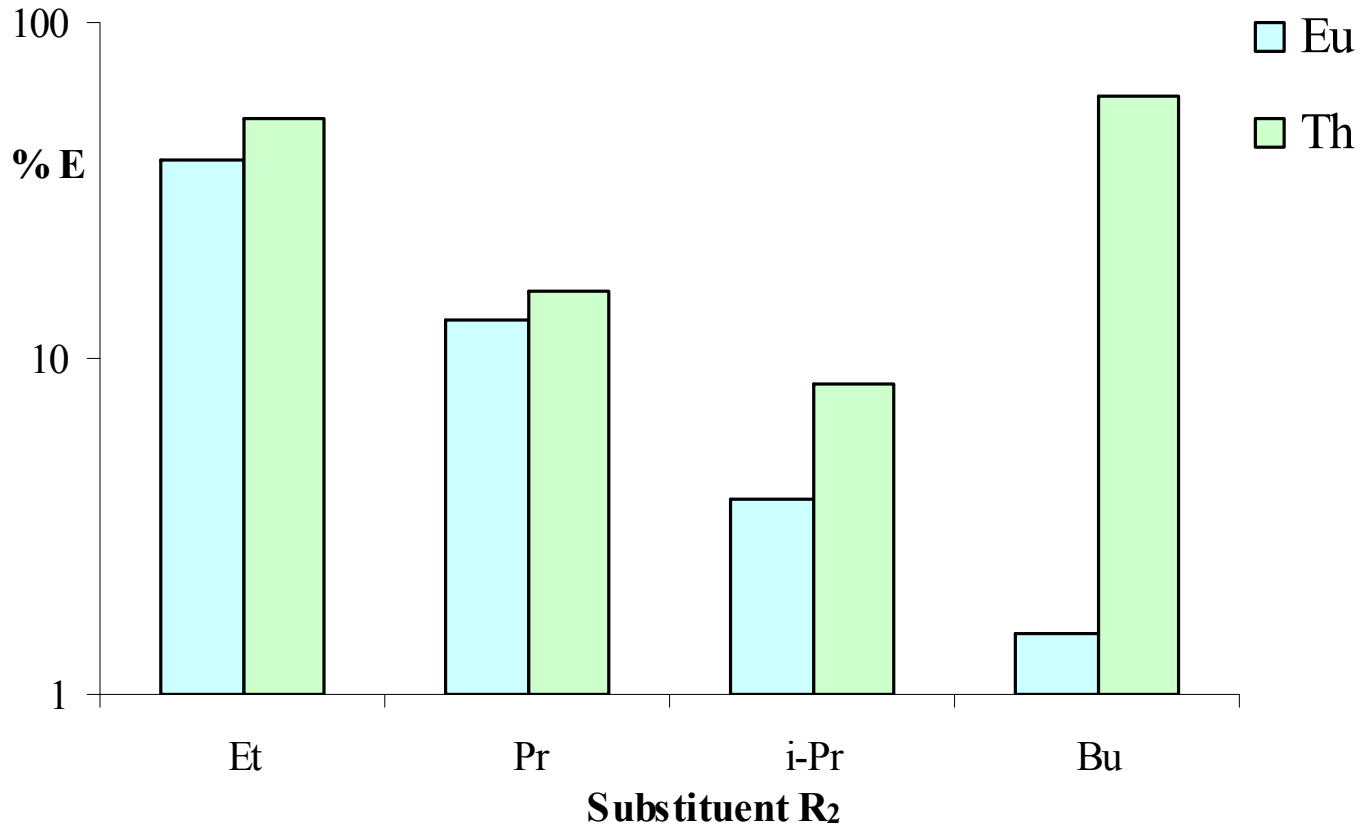






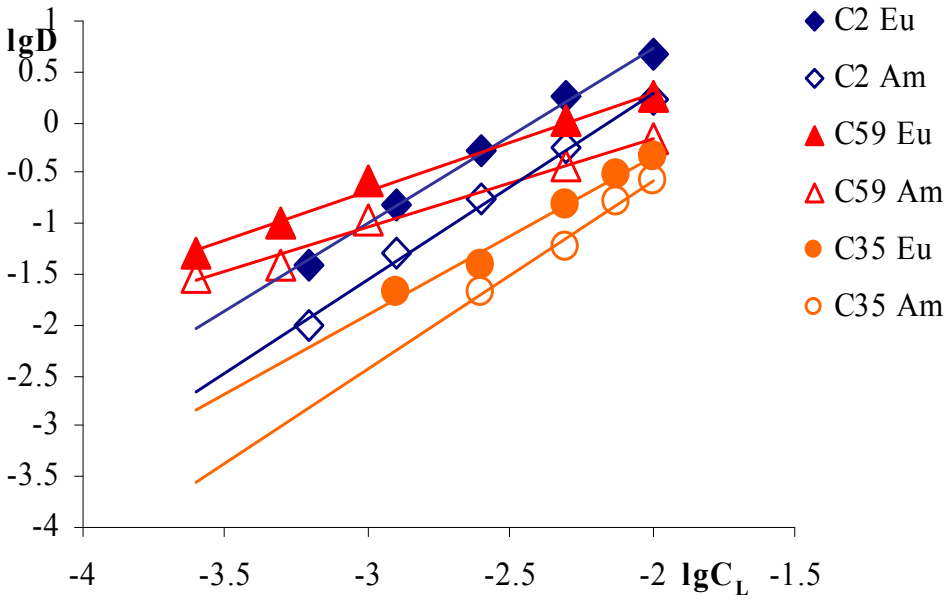
Influence of the length of alkyl substituent R_2 (CH_2Cl_2)

C (HNO_3) = 1 mol/L



C45 (R_2 = Et), **C67** (R_2 = Pr), C**75** (R_2 = i-Pr), **C2** (R_2 = Bu)

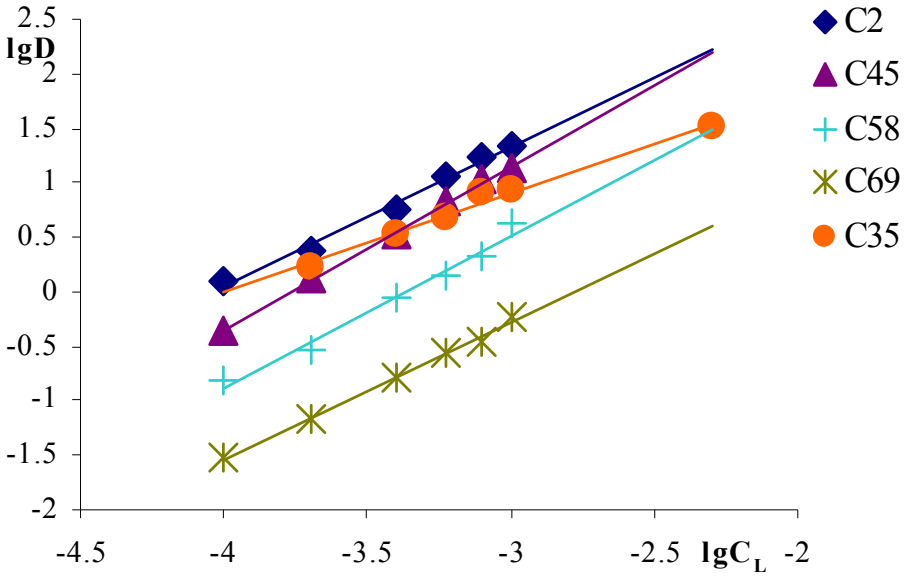
Extracted complex stoichiometry: apparent solvate numbers
m-NBTF



^{241}Am and ^{152}Eu

C2 (R_1 = Pr, R_2 = Bu, n = 4)
C35 (R_1 = Me, R_2 = Bu, n = 6)
slope: 1.5 – 1.8 ⇨ ML + ML2

C59 (R_1 = Hex, R_2 = Bu, n = 4)
y = 0.9 ⇨ ML

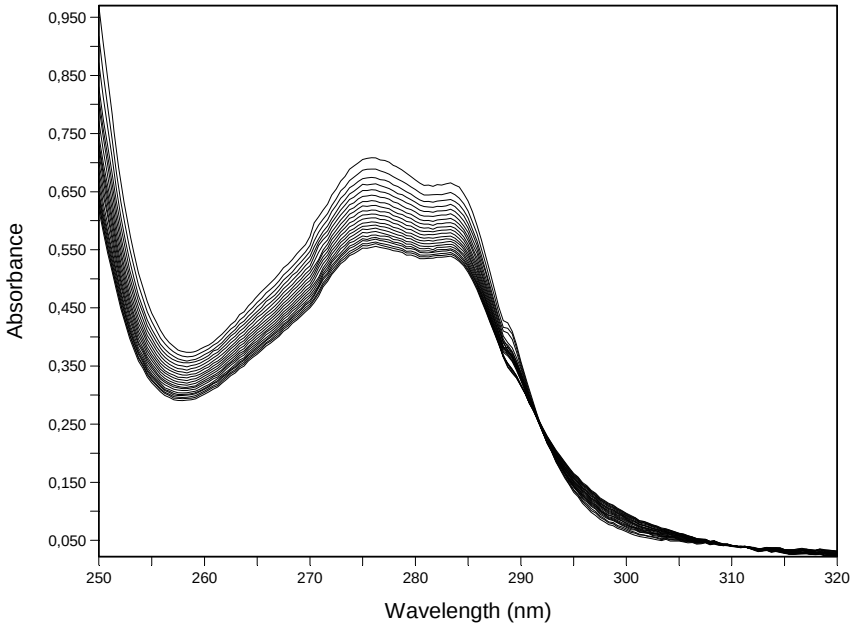


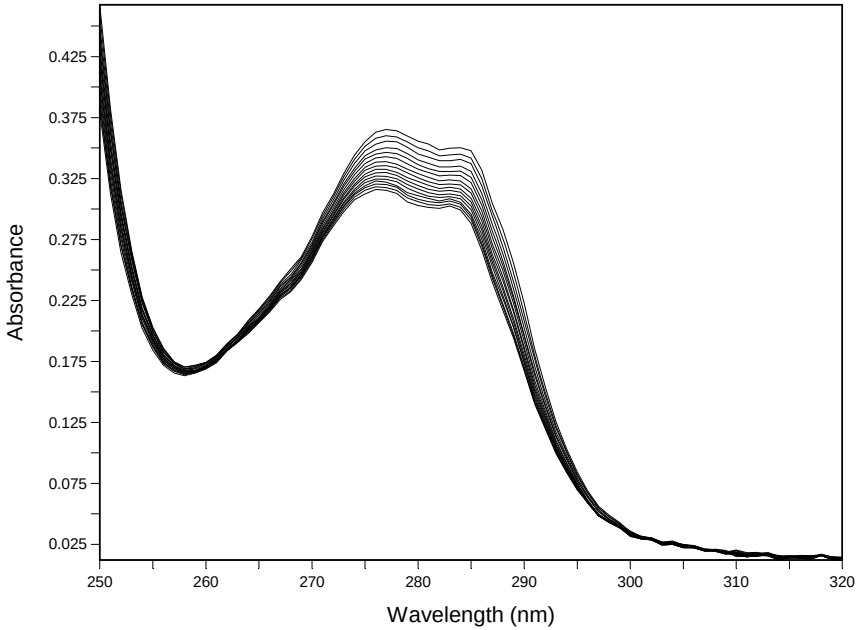
^{233}U

C2 (R_1 = Pr, R_2 = Bu, n = 4)
C45 (R_1 = Pr, R_2 = Et, n = 4)
C58 (R_1 = Hex, R_2 = Et, n = 4)
C35 (R_1 = Me, R_2 = Bu, n = 6)
slope: 1.5 – 1.8 ⇨ ML + ML2

C69 (R_1 = Pr, R_2 = Ph, n = 4)
slope: 0.9 ⇨ ML

UV-spectrophotometric titrations





Titrations of **C67** by $La(NO_3)_3$

in methanol

$C_L = 2.25 \times 10^{-4}$ mol/L

$0 \leq R = C_M/C_L \leq 23$

in acetonitrile

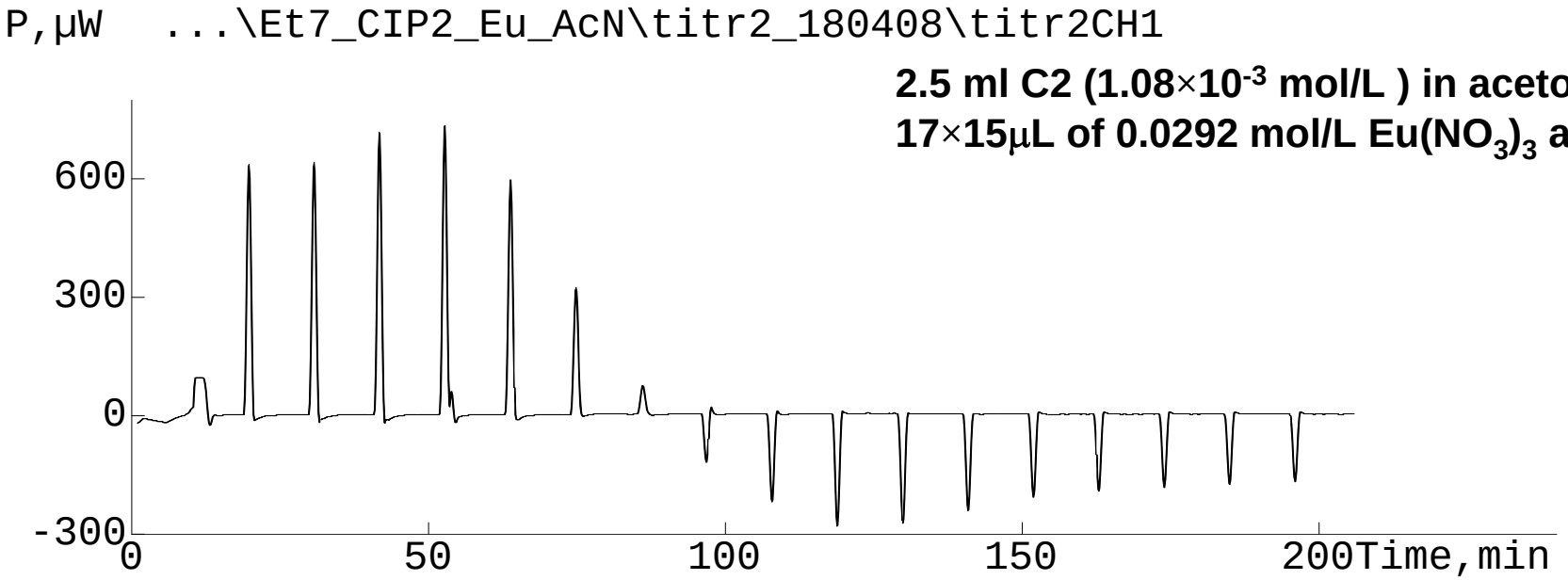
$C_L = 1.04 \times 10^{-4}$ mol/L

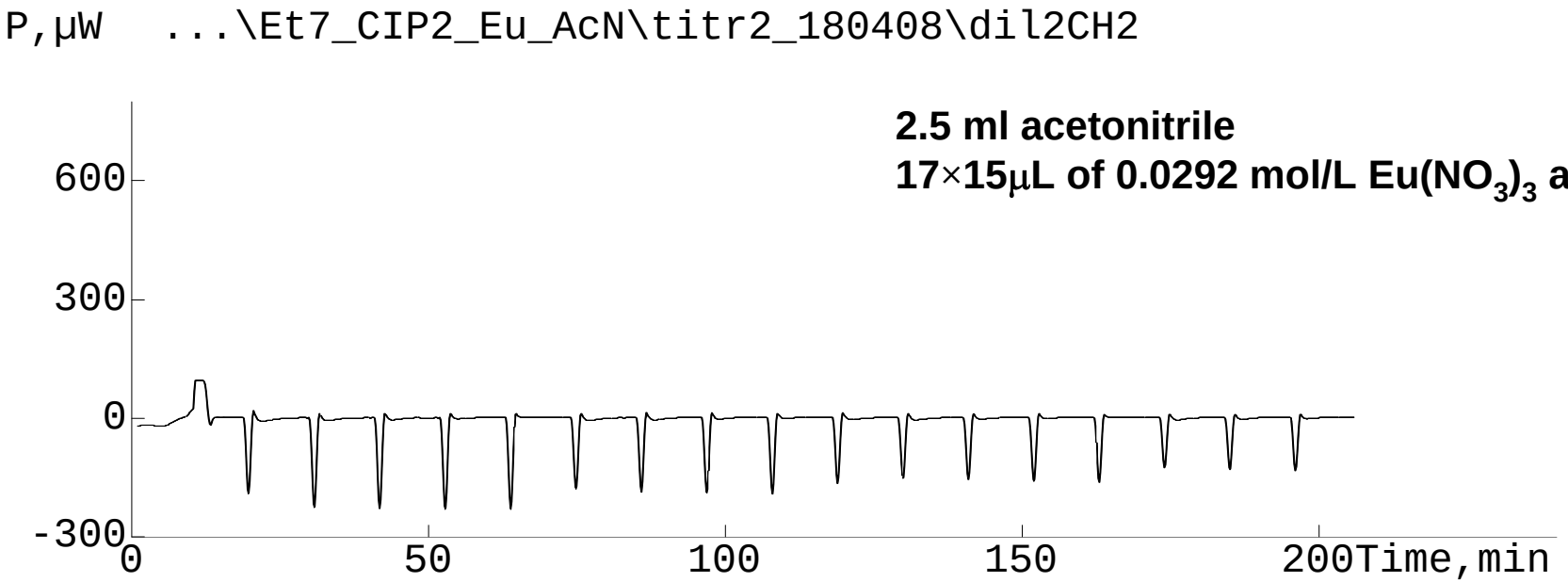
$0 \leq R = C_M/C_L \leq 1$

Stability constants (log β)

Cations	Ligands			
	Complexes (M : L)	C67 (R_2 = Pr)	C2 (R_2 = Bu)	C35 (n = 6, R_2 = Bu)
Methanol, I = 10^{-2} mol/L (Et_4NNO_3), T = 25°C				
La^{3+}	1 : 1	3.3	3.5	undetermined
Eu^{3+}	1 : 1	3.9	4.4	3.9
Yb^{3+}	1 : 1	4.8	3.8	undetermined
Th^{4+}		precipitation	-	precipitation
UO_2^{2+}	2 : 1	7.4	7.45	undetermined
Acetonitrile, I = 10^{-2} mol/L (Et_4NNO_3), T = 25°C				
La^{3+}	1 : 1	3.84	3.8	
Yb^{3+}	1 : 1	3.8	4.0	
Th^{4+}		precipitation	precipitation	
UO_2^{2+}	2 : 1	undetermined	undetermined	

Microcalorimetric titration

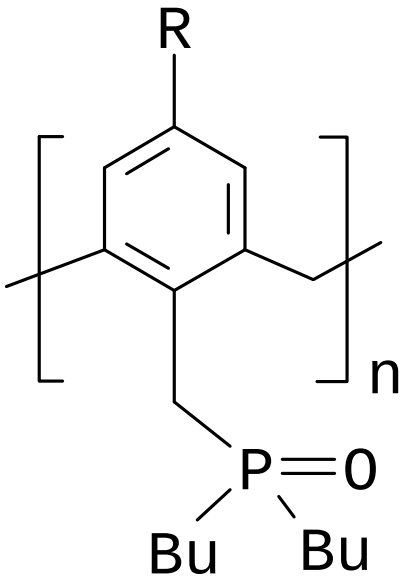




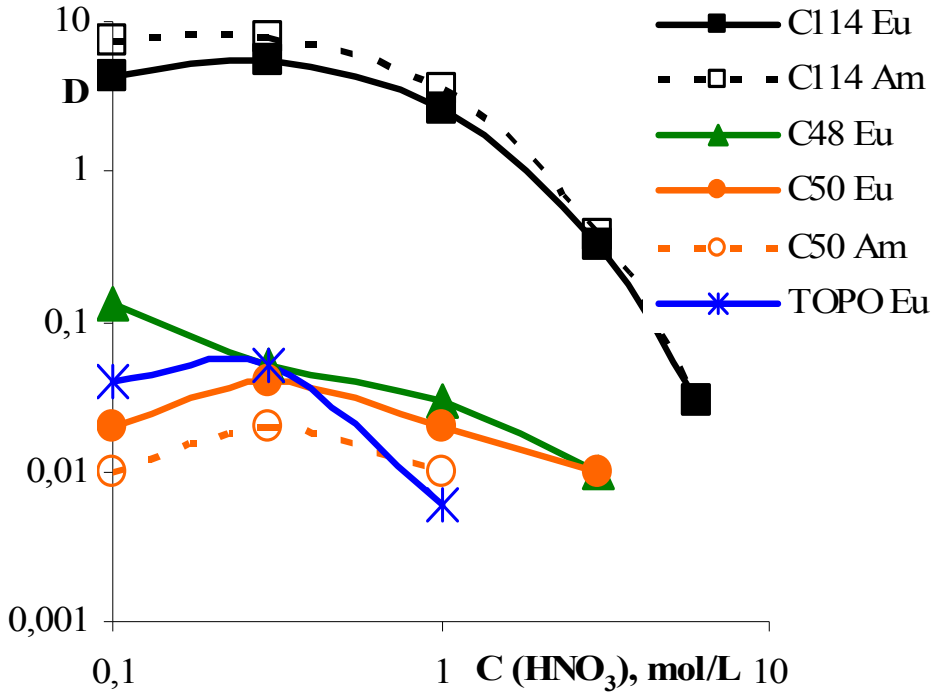
Thermodynamic complexation parameters for $UO_2(NO_3)_2$ with C67, C75 and C2 in acetonitrile at 25 °C

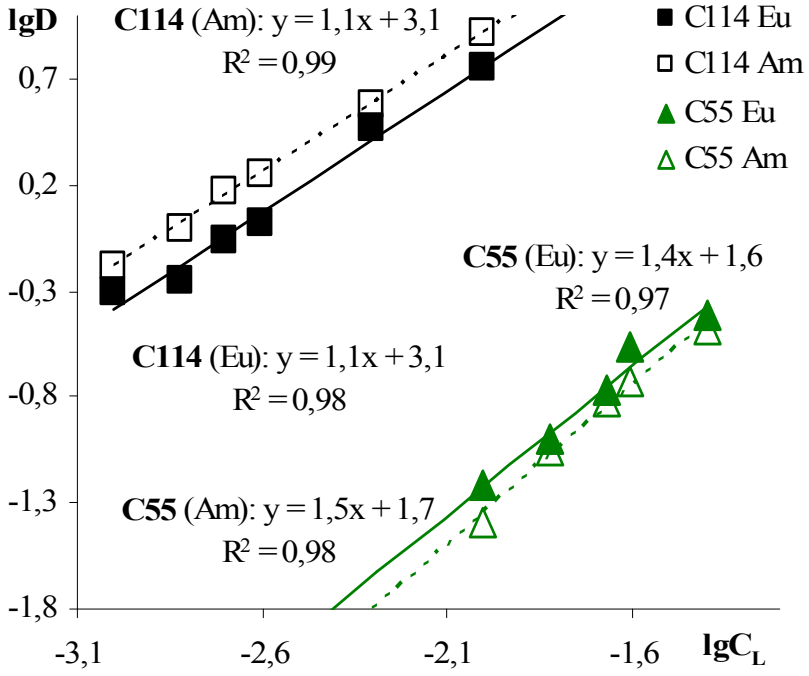
Ligands	Complexes	logβ	- ΔG kJ mol^{-1}	- ΔH kJ mol^{-1}	TΔS kJ mol^{-1}
C67	1 : 1	4.2	23.9	96	-72
C75	1 : 1	6.2	35	85.7	-50
	2 : 1	10.6	63	125	-62
C2	1 : 1	5.9	34	97	-63
	2 : 1	10.6	60	105	-44

Structures of the lower rim substituted calixarenes studied



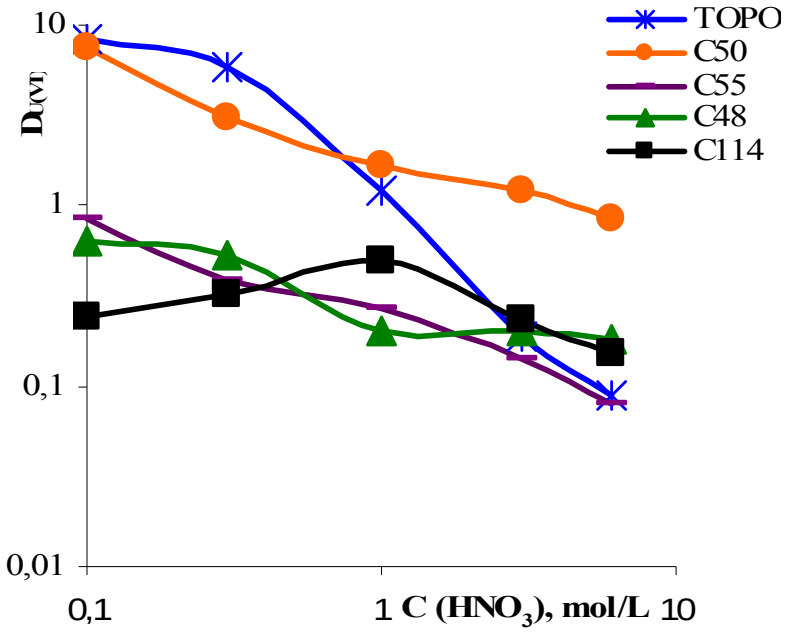
n=4	R=H	**C55**
n=4	R=t-Bu	**C48**
n=5	R=t-Bu	**C114**
n=6	R=H	**C50**



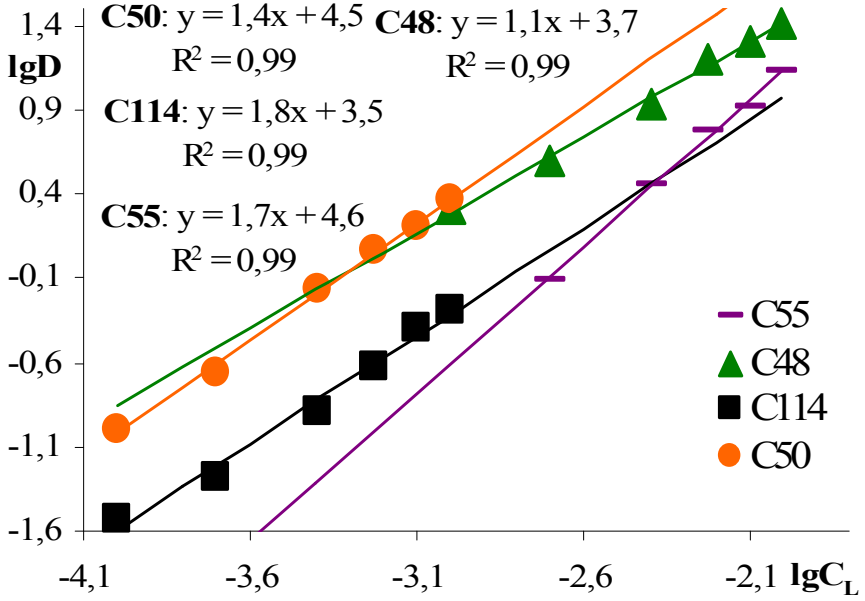


Extraction of ^{241}Am and ^{152}Eu in m-NBTF

log – log plots of ^{241}Am and ^{152}Eu From 0.3 mol/L HNO_3 into m-NBTF



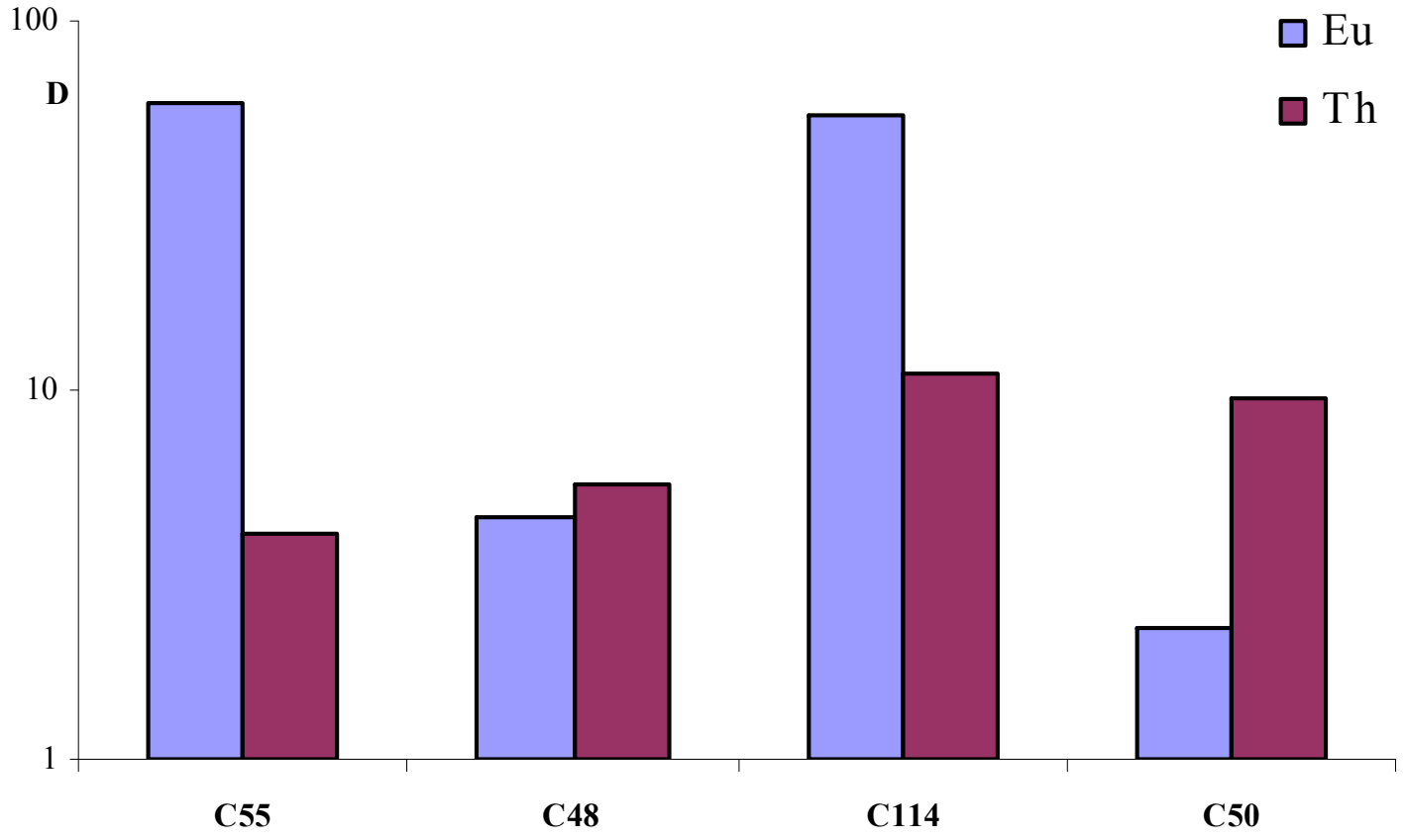
Extraction of ^{233}U in m-NBTF



log – log plots of ^{233}U from 0.3 mol/L HNO_3 into m-NBTF.

Influence of the condensation degree n and *p*-dealkylation on the extraction properties of C55 (R = H, n = 4), C48 (R = t-Bu, n = 4), C114 (R = t-Bu, n = 5), 50 (R = H, n = 6).

C (HNO_3) = 1 mol/L. Diluent – CH_2Cl_2.

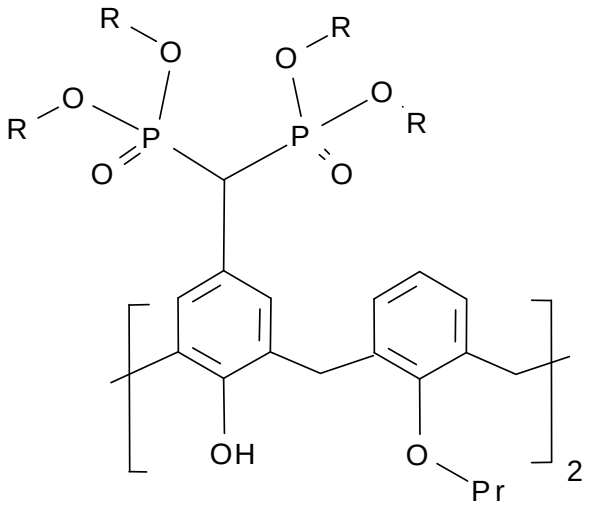


Thermodynamic complexation parameters of $Eu(NO_3)_3$ with C55, C48, C114 and C50 in methanol at 25 °C

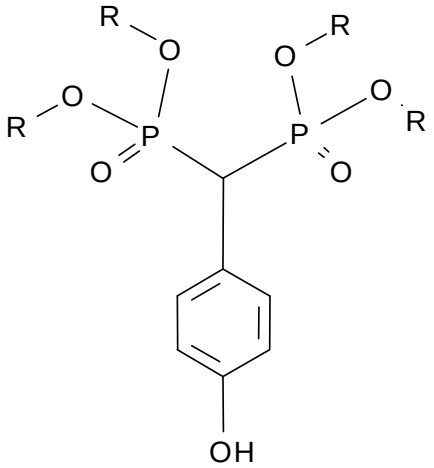
Ligands	Complexes	Log β	- ΔG kJ mol^{-1}	- ΔH kJ mol^{-1}	TΔS kJ mol^{-1}
C55	1 : 1	4.5 (3.8)*	26	15	11
C48	1 : 1	4.55 (3.9)*	25.9	10.7	15.2
	1 : 2	7.72	44.0	-1.6	45.6
C114	1 : 1	4.8	27	5	22
C50	1 : 1	2.9	17	-6	23

* - spectrophotometric results

Structures of the calixarene phosphonate derivatives studied and of related monomeric subunits

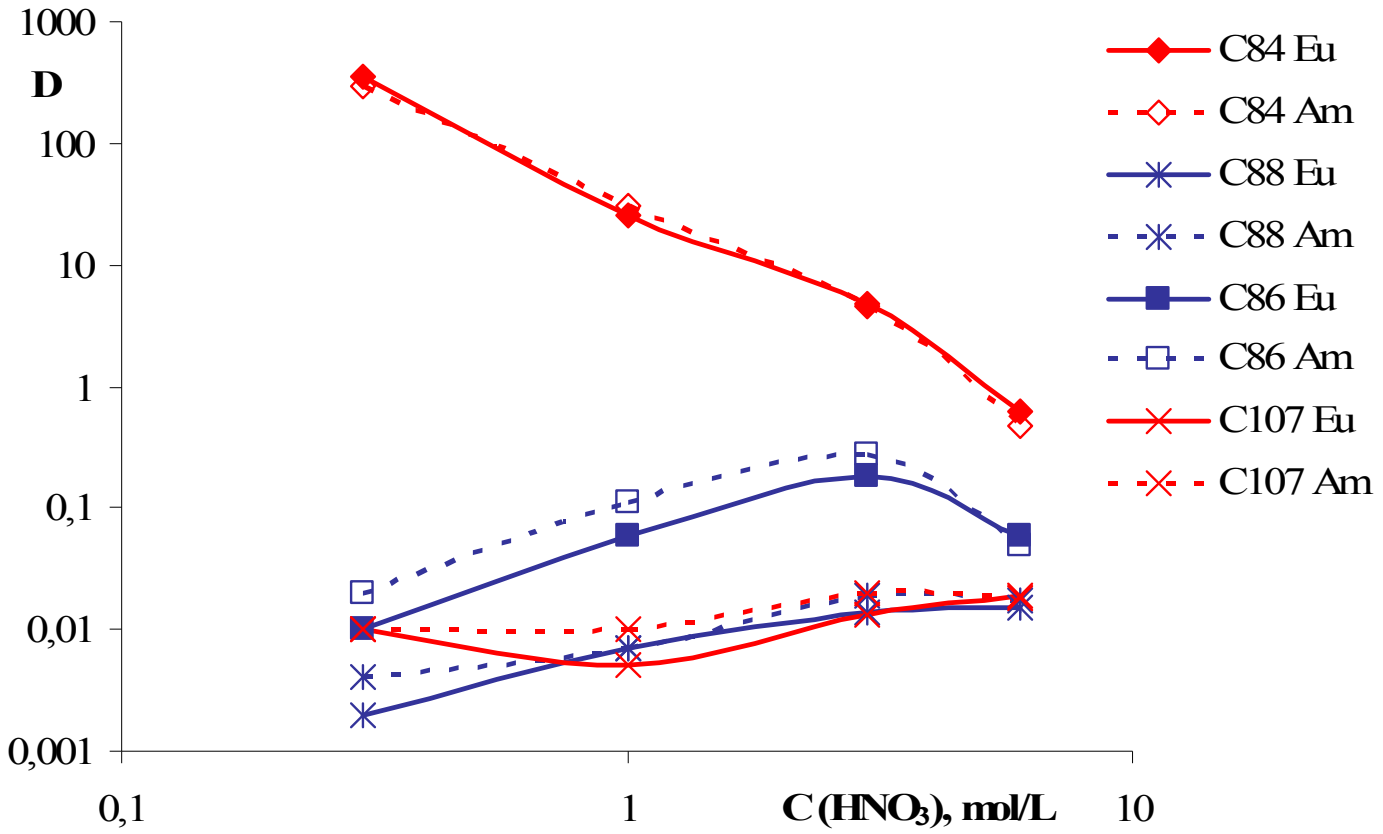


R=Me	**C83**
R=Et	**C82**
R=Pr	**C84**
R=i-Pr	**C85**
R=Bu	**C86**

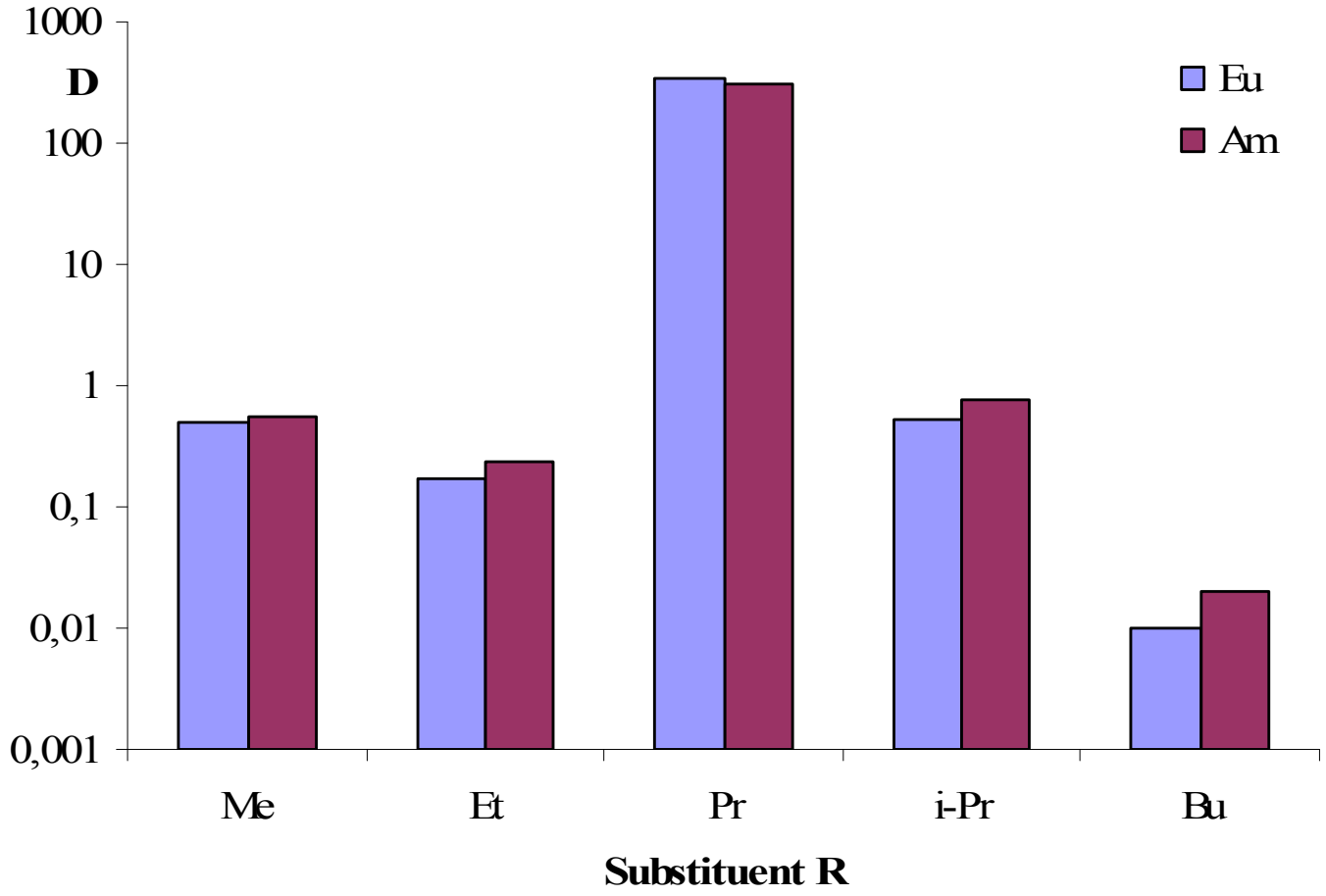


R=Et	**C87**
R=Pr	**C88**
R=Bu	**C107**

Extraction of ^{241}Am and ^{152}Eu by phosphonate derivatives (m-NBTF)

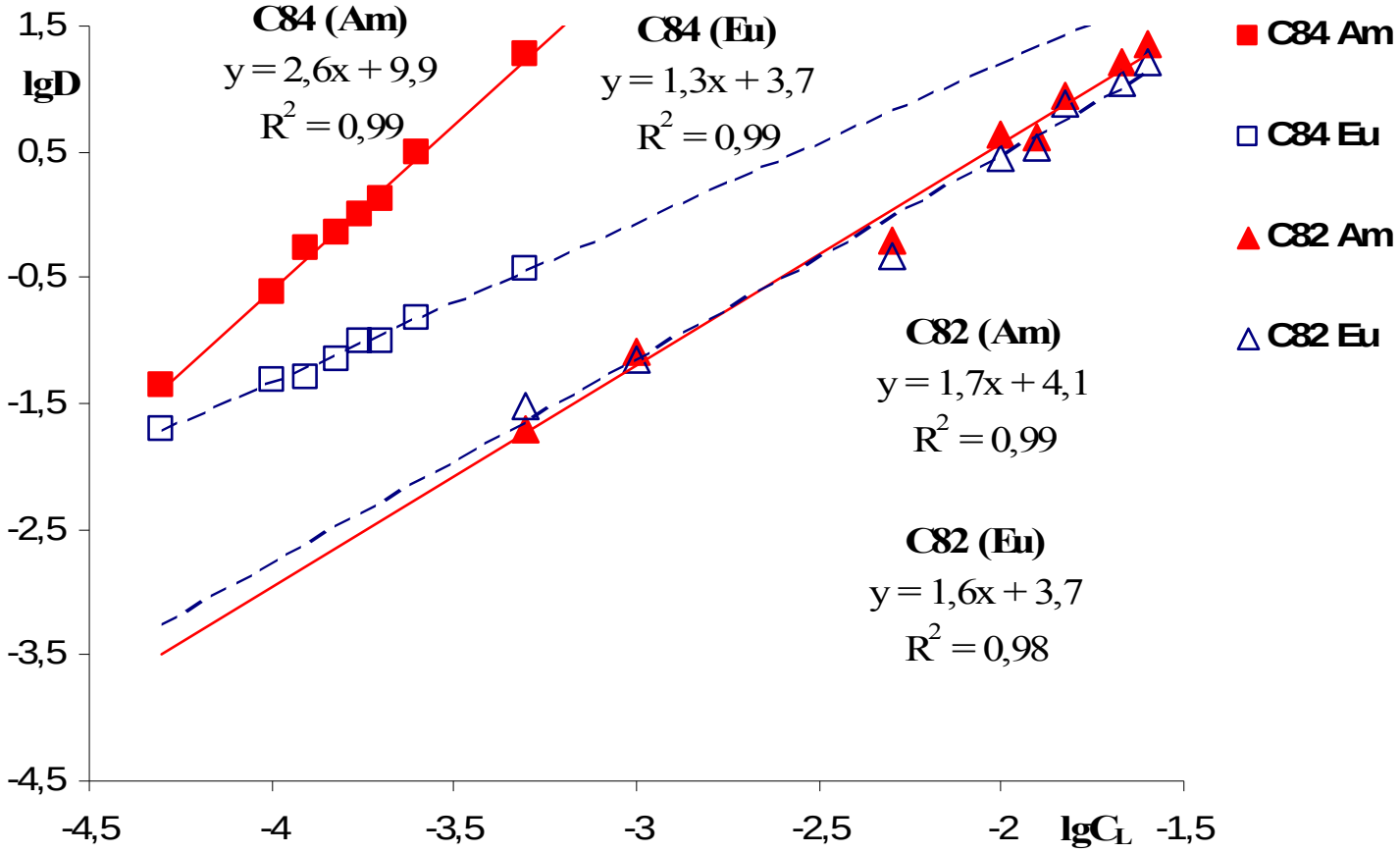


Influence of alkyl substituent R on the extraction properties of C83 (R = Me), C82 (R = Et), C84 (R = Pr), C85 (R = i-Pr) and C86 (R = Bu).
C (HNO_3) = 0.3 mol/L. Diluent – m-NBTF.



log – log plots of ^{241}Am and ^{152}Eu extraction by C82 (R = Et) and C84 (R = Pr)

from 0.3 mol/L HNO_3 into m-NBTF



Thermodynamic parameters of the complexation for $Eu(NO_3)_3$ and $UO_2(NO_3)_2$ with C84 and C86 in methanol at 25 °C

Ligands	Cations	Complexes	log β	-ΔH kJ mol^{-1}
C84	Eu^{3+}	ML_2	6.2	-6
	UO_2^{2+}	ML_2	6.0	18.8
C86	Eu^{3+}	ML	3.30 (3.9)*	-3
	UO_2^{2+}	ML_2	5.77	19

* - spectrophotometric results

Thermodynamic parameters for $Eu(NO_3)_3$ and $UO_2(NO_3)_2$ with C84 and C86 in acetonitrile at 25 °C

Ligands	Cations	Complexes	log β	-ΔH kJ mol^{-1}
C84	Eu^{3+}	ML	5.46	55
	UO_2^{2+}	M_2L	10.0	51
C86	Eu^{3+}	ML	6.5	58
	UO_2^{2+}	M_2L	11.7	56

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