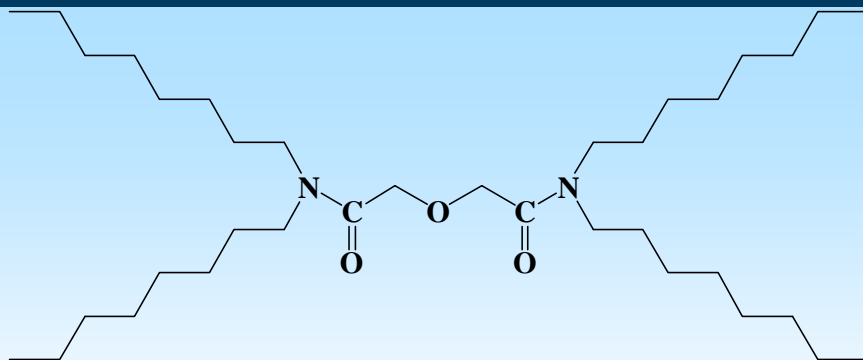




Calixarenes functionalized with phosphine oxide and diamide functions as extractants and ionophores for rare-earth metals.

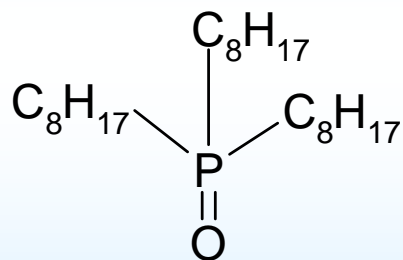
Alyapyshev M.Yu., Babain V.A., Eliseev I.I., Smirnov I.V.,
Boyko V.I., Klimchuk O.V. Rodik R.
Legin A.V., Kirsanov D.O. Mikhailina E.S., V.,

*Khlopin Radium Institute,
The Institute of Organic Chemistry, N AS of Ukraine,
St. Petersburg University, Laboratory of Chemical Sensors,*

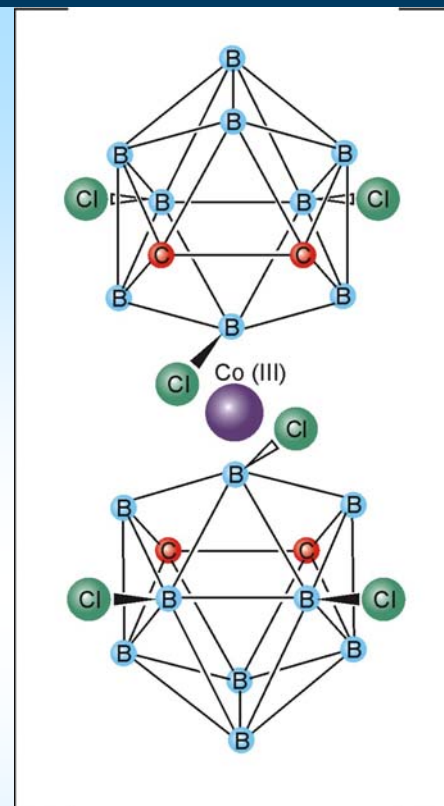


Tetraoctyl-3-oxapentanediamide

(TODGA)

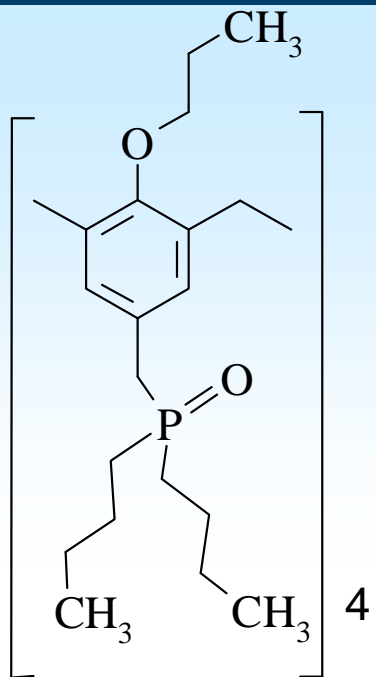


Trioctylphosphine oxide **(TOPO)**



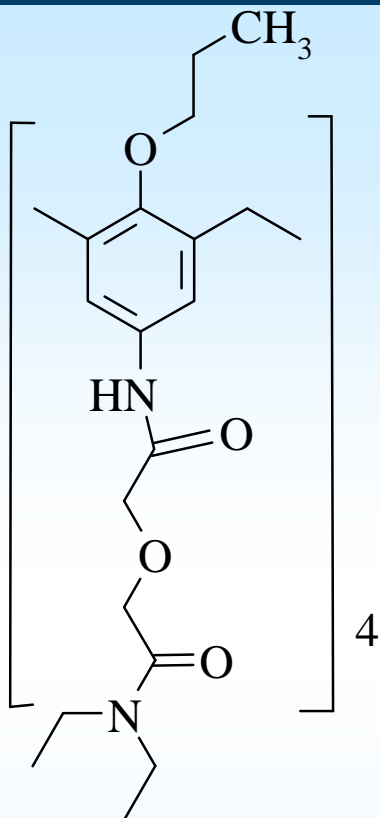
Hexachlorodicyclopolyborate
anion **(CCD)**

Calixarene ligands



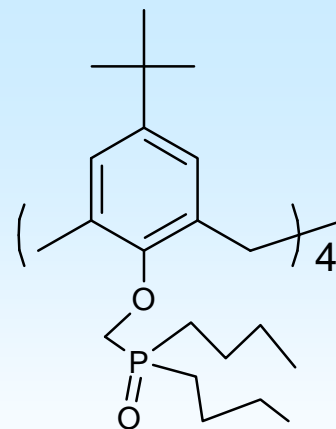
5,11,17,23-tetrakis-
dibutylphosphinylmethyl-
25,26,27,28-tetrapropoxy-
calix[4]arene (cone
conformer)

(CIP 2)



5,11,17,23-tetra(diethylcarbamoyl-
ethoxymethyl-carboxamido)-
25,26,27,28-tetrapropoxy-
calix[4]arene

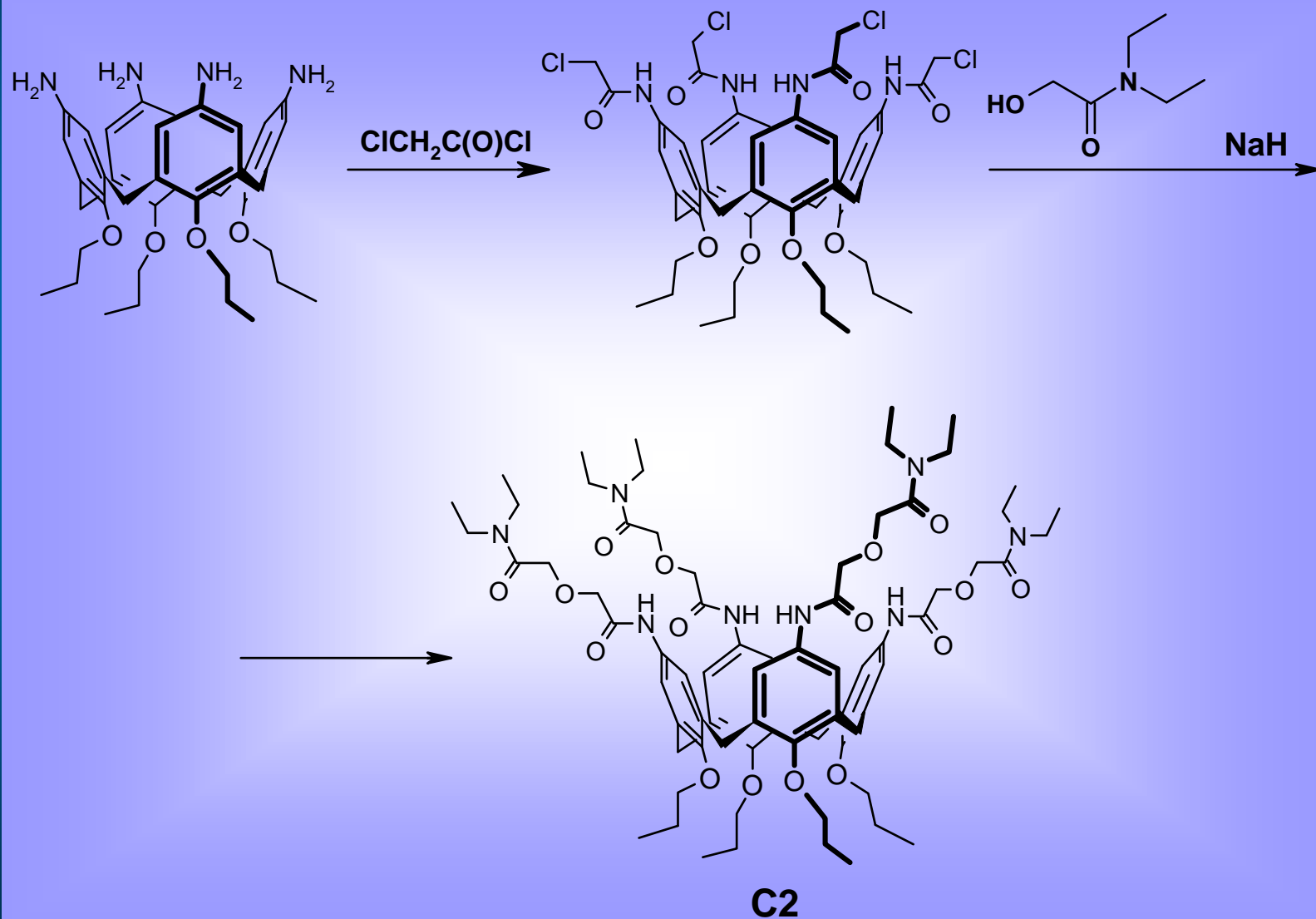
(CIP 146)



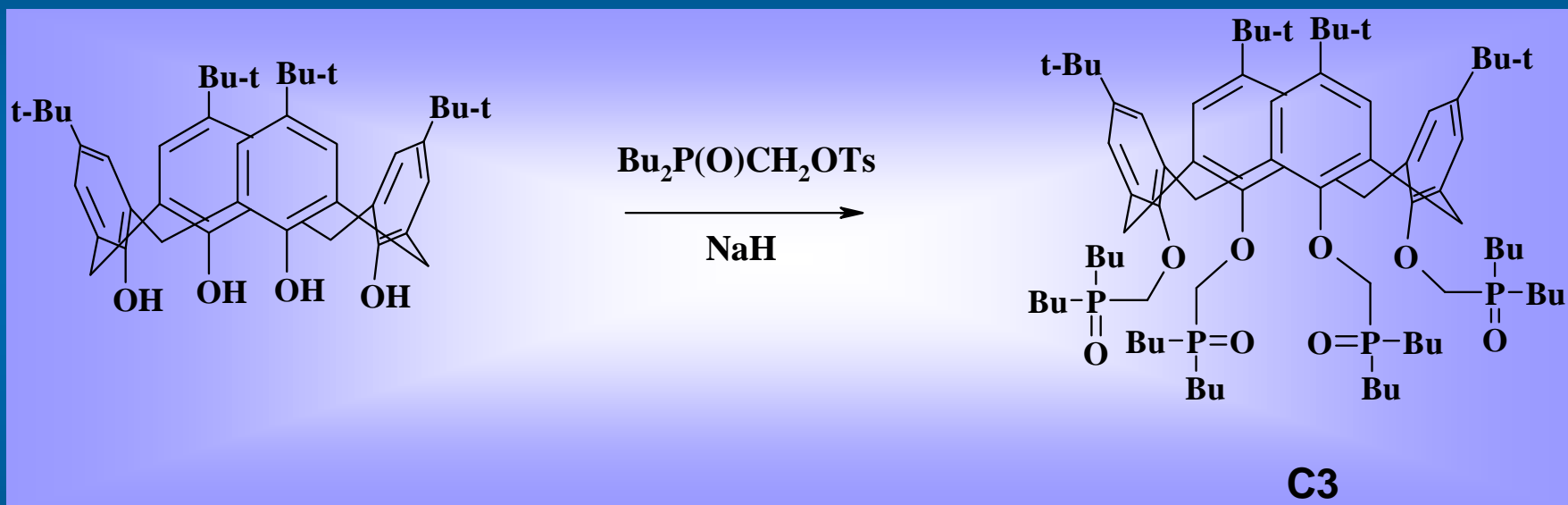
5,11,17,23-tetra-tert-butyl-
25,26,27,28-tetrakis-
[dibutylphosphinylmethyl-
oxy]-calix[4]arene
(cone conformer)

(CIP 48)

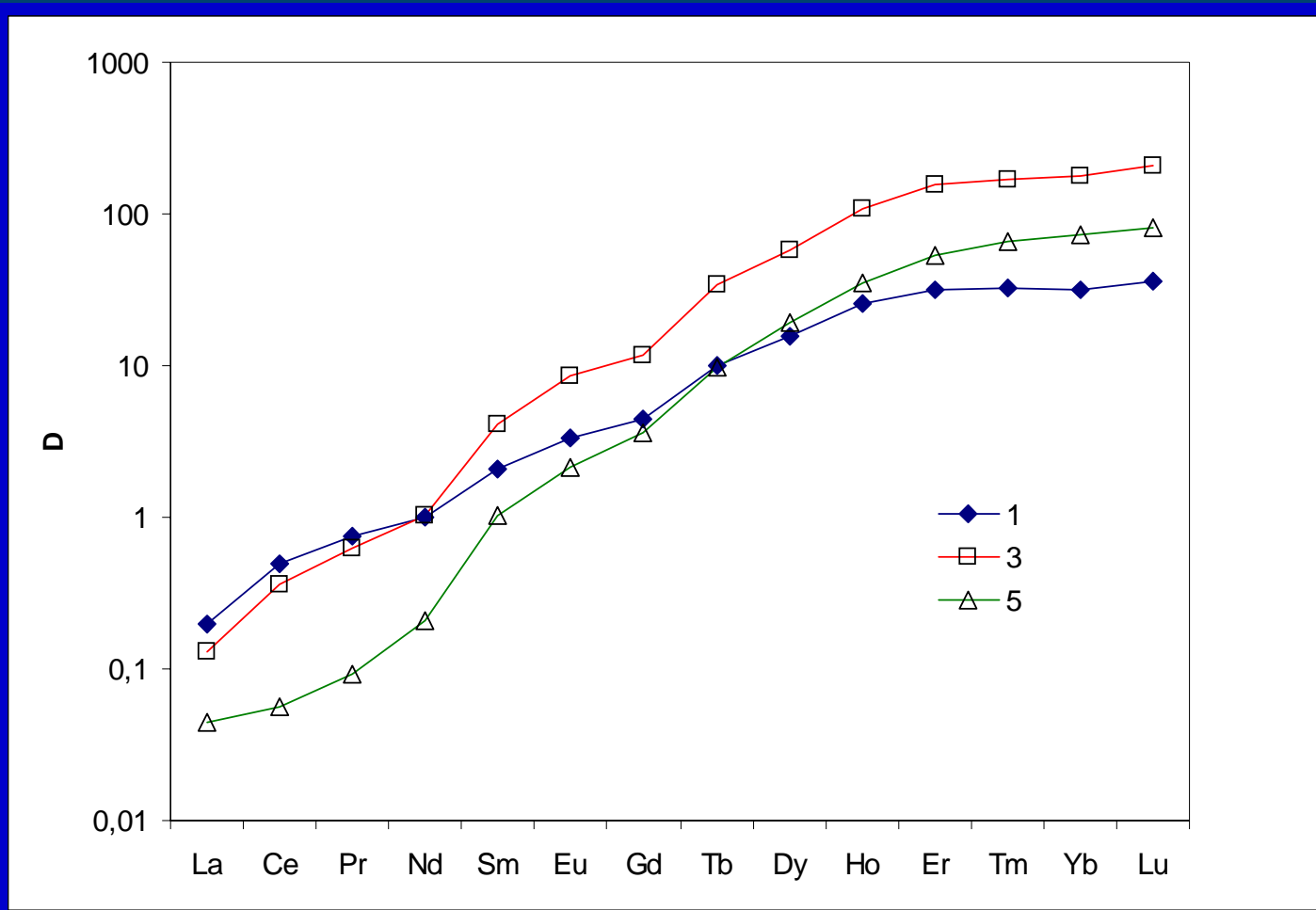
Synthetic way for CIP 146



Synthetic way for CIP 48

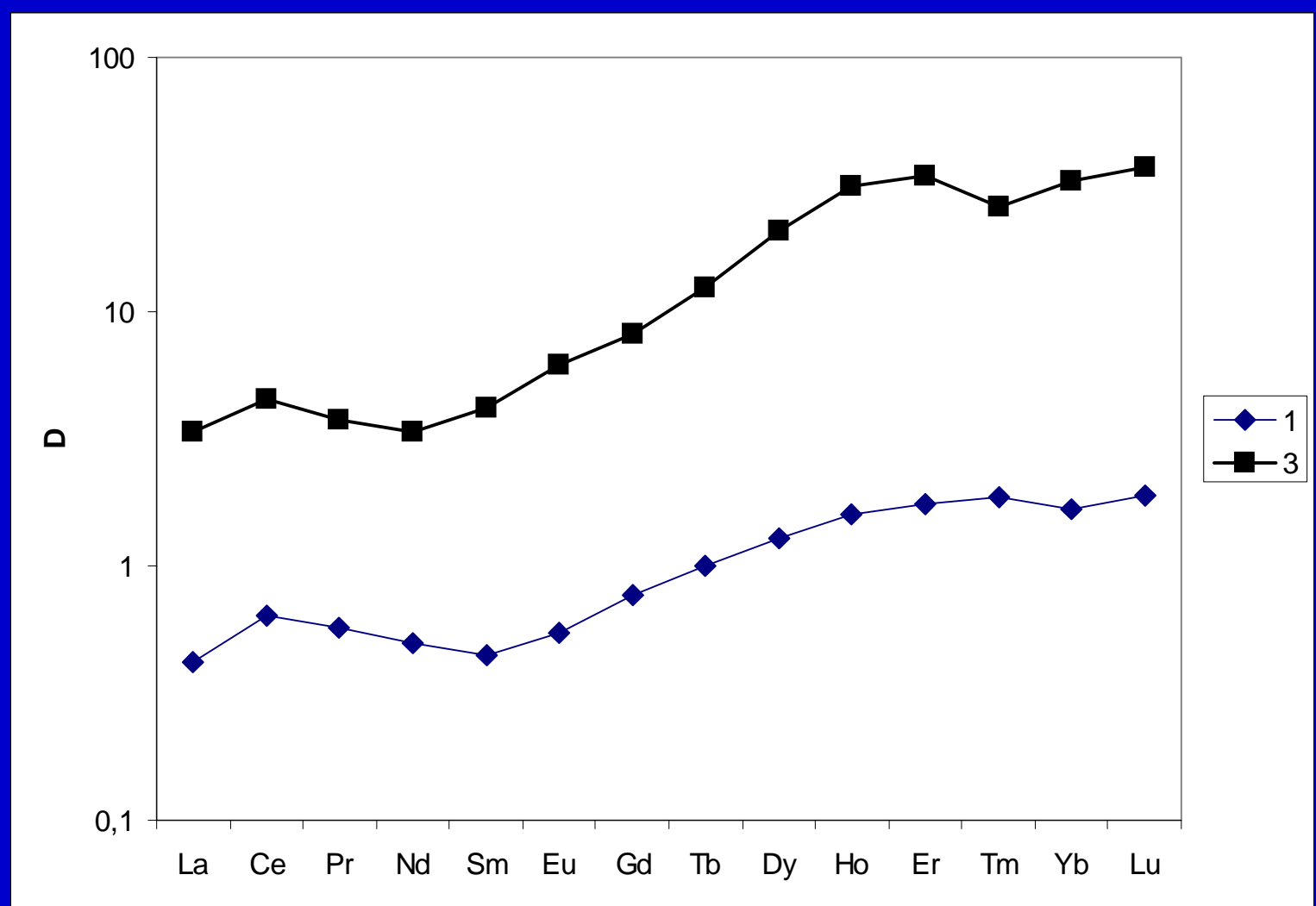


Lanthanides extraction



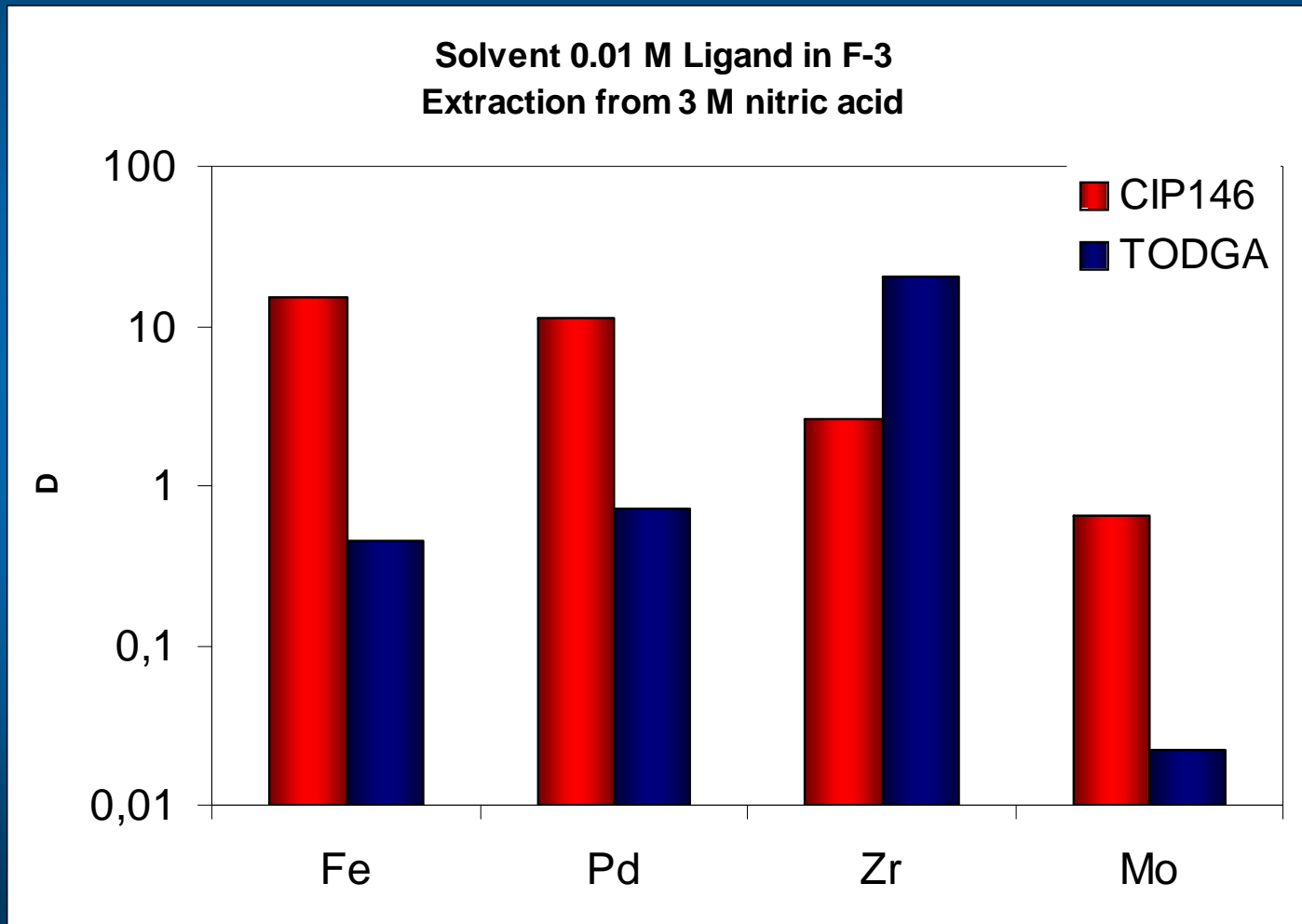
Org. phase: 0.01 M TODGA in m-nitrobenzotrifluoride (F-3)
aqueous phase: nitric acid solutions(1- 1M, 3- 3M, 5 – 5M HNO3)

Lanthanides extraction

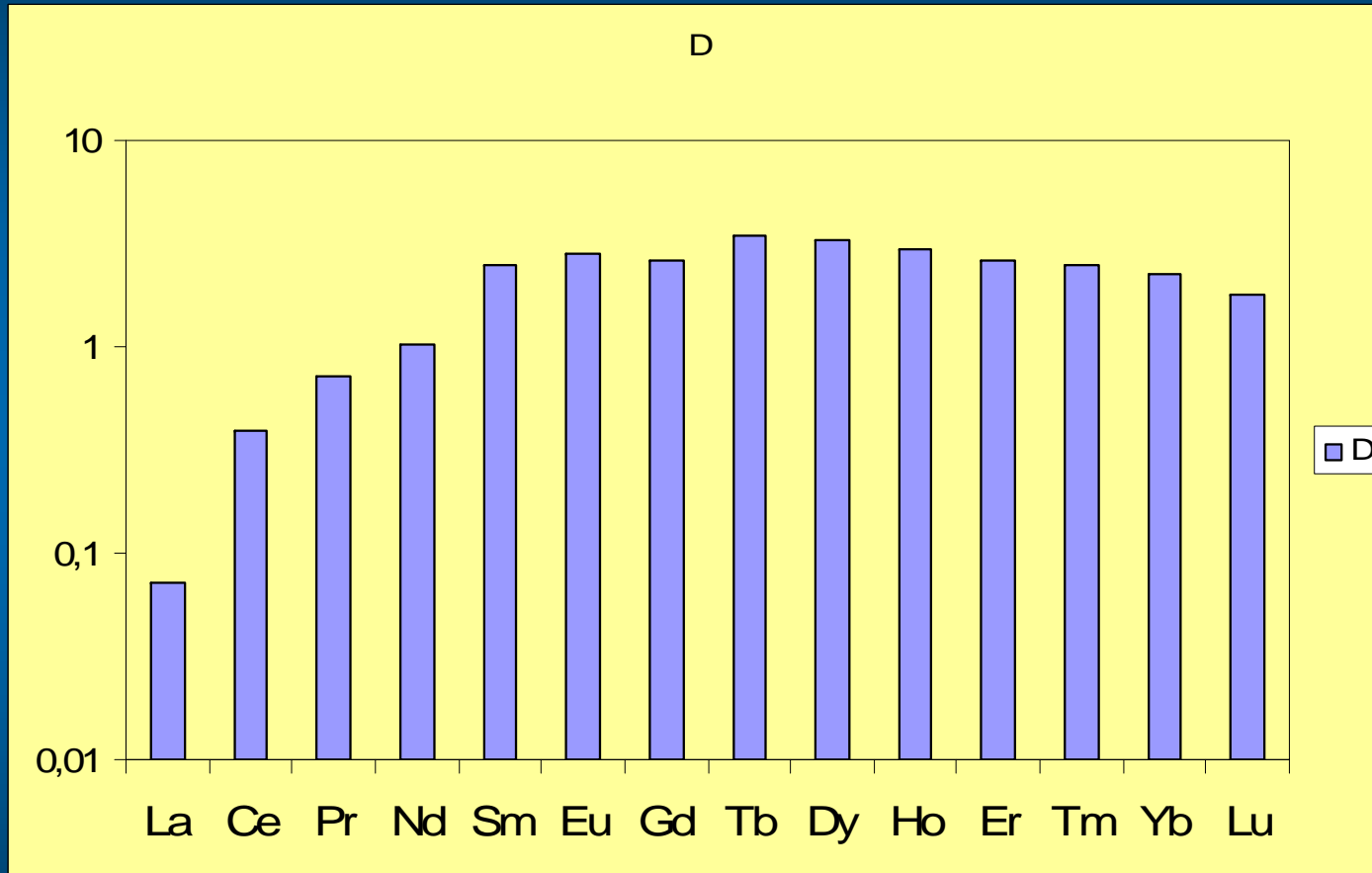


Org. phase: 0.01 M C2 in m-nitrobenzotrifluoride (F-3)
aqueous phase: nitric acid solutions(1- 1M, 3- 3M, HNO3)

Other metals extraction



Lanthanides extraction



Org. phase: 0.01 M CIP2 in m-nitrobenzotrifluoride (F-3)
aqueous phase: nitric acid solutions(0.3M HNO₃)

What are the sensors?

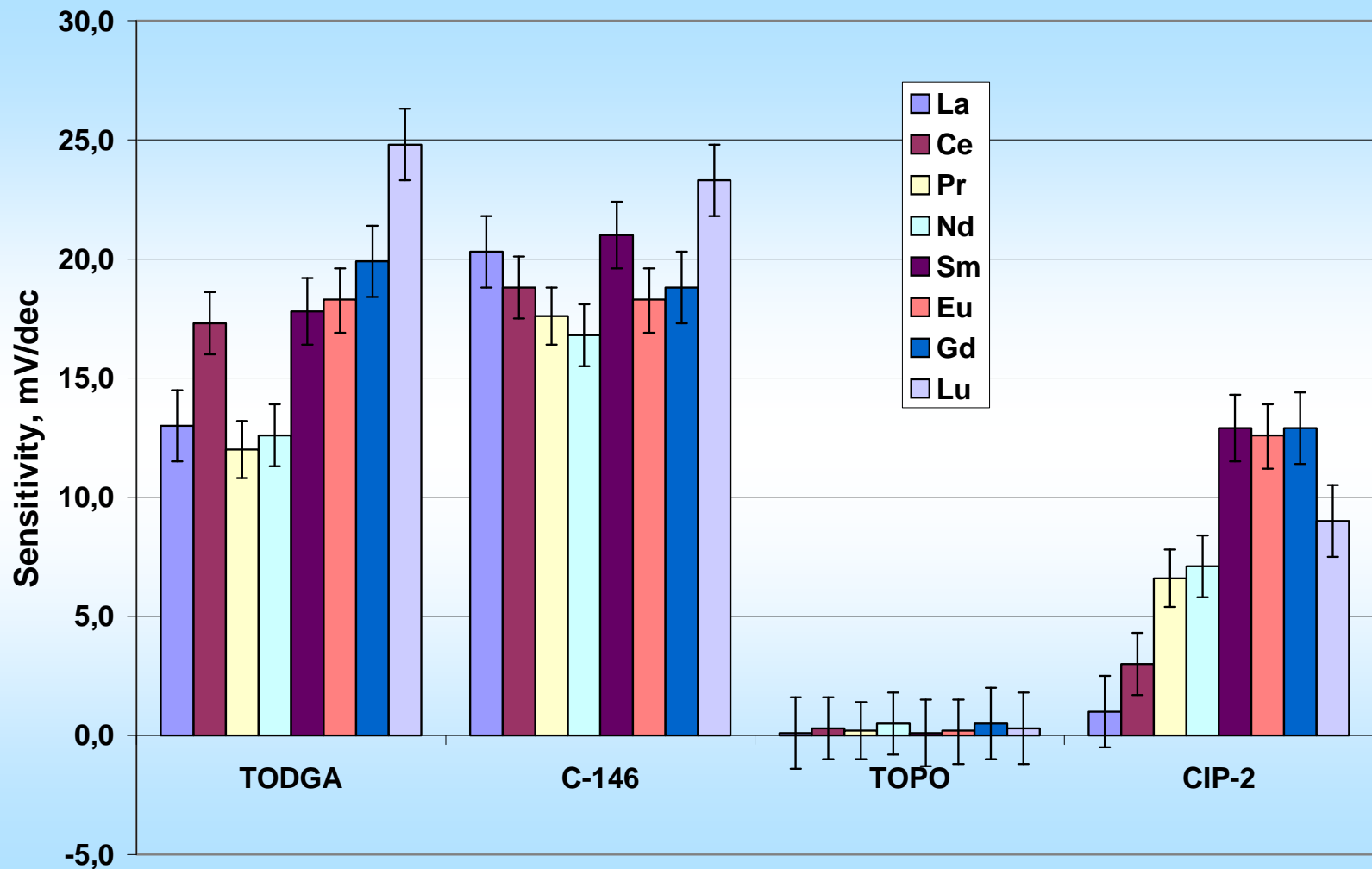


Sensor membrane composition

Sensor	Components	Mass, g	Molality (mol/kg)
TOPO	PVC	0.1073	
	NPOE	0.2146	
	TOPO	0.0064	0.050
	CCD	0.0018	0.010
TODGA	PVC	0.1062	
	NPOE	0.2124	
	TODGA	0.0096	0.050
	CCD	0.0018	0.010
CIP2	PVC	0.1020	
	NPOE	0.2040	
	C1	0.0210	0.050
	CCD	0.0018	0.010
CIP 146	PVC	0.1020	
	NPOE	0.2040	
	C2	0.0220	0.050
	CCD	0.0018	0.010
C3	PVC	0.1020	
	NPOE	0.2040	
	C3	0.0220	0.050
	CCD	0.0018	0.010

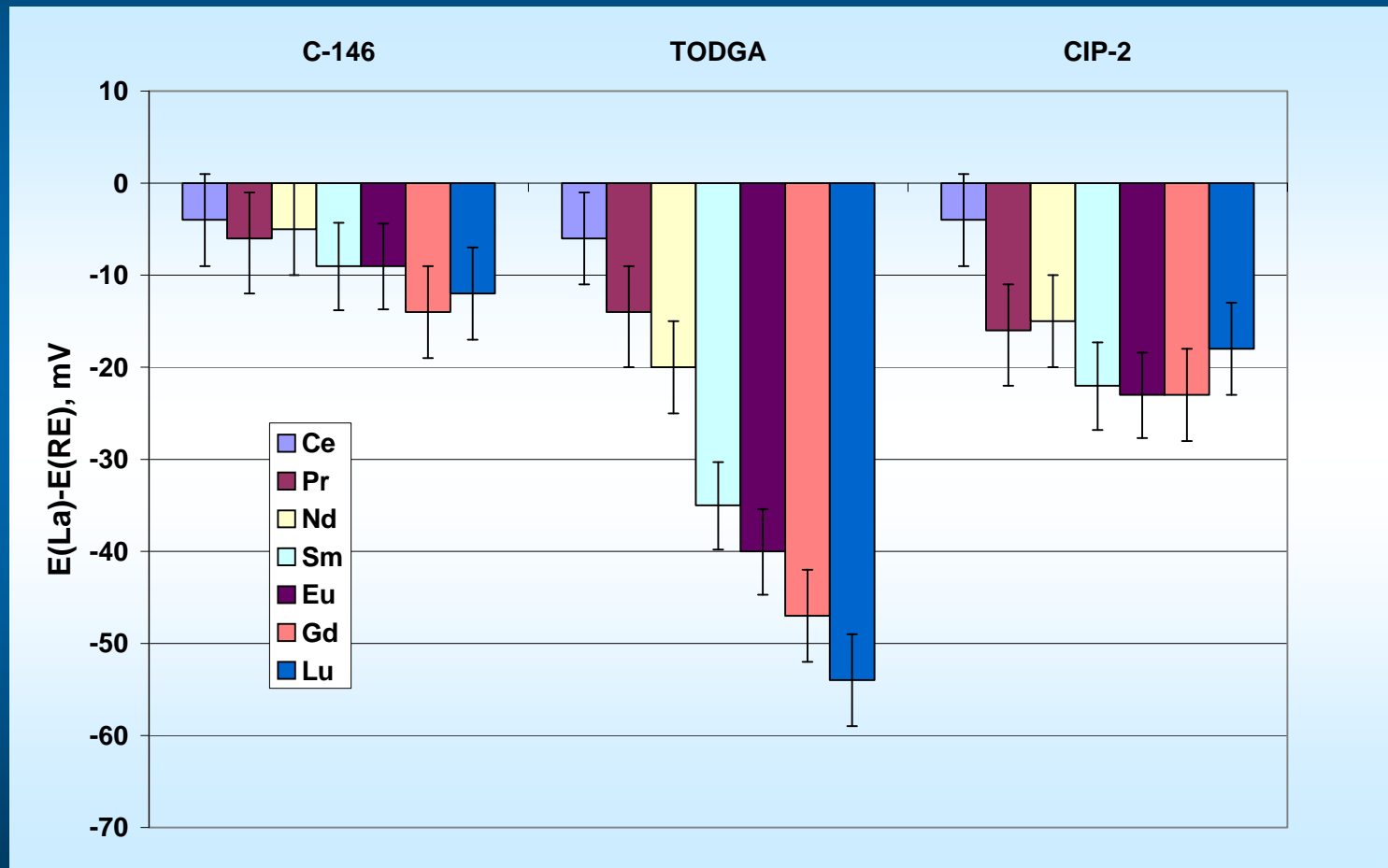
Molality for membrane active compounds is presented as mol/kg of membrane.

Polymeric sensors sensitivities



RE metal solutions with pH 2

Selectivity of the developed sensors to lanthanides



Selectivity was determined by bi-ionic potentials method method

CONCLUSION

Extraction and electrochemical sensing properties are influenced in a similar way when comparing calixarene and mono-analogues.

Extraction properties are a good basis for selection of ionophores to be used in polymeric electrochemical sensors, but no direct projection of these properties can be done due to the obvious differences in extraction and sensor systems