Novel polycarboxylated EDTA-type cyclodextrins as ligands for lanthanide binding, study of their luminescence, relaxivity properties of Gd(III) complexes, and PM3 theoretical calculations

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Supplementary Data

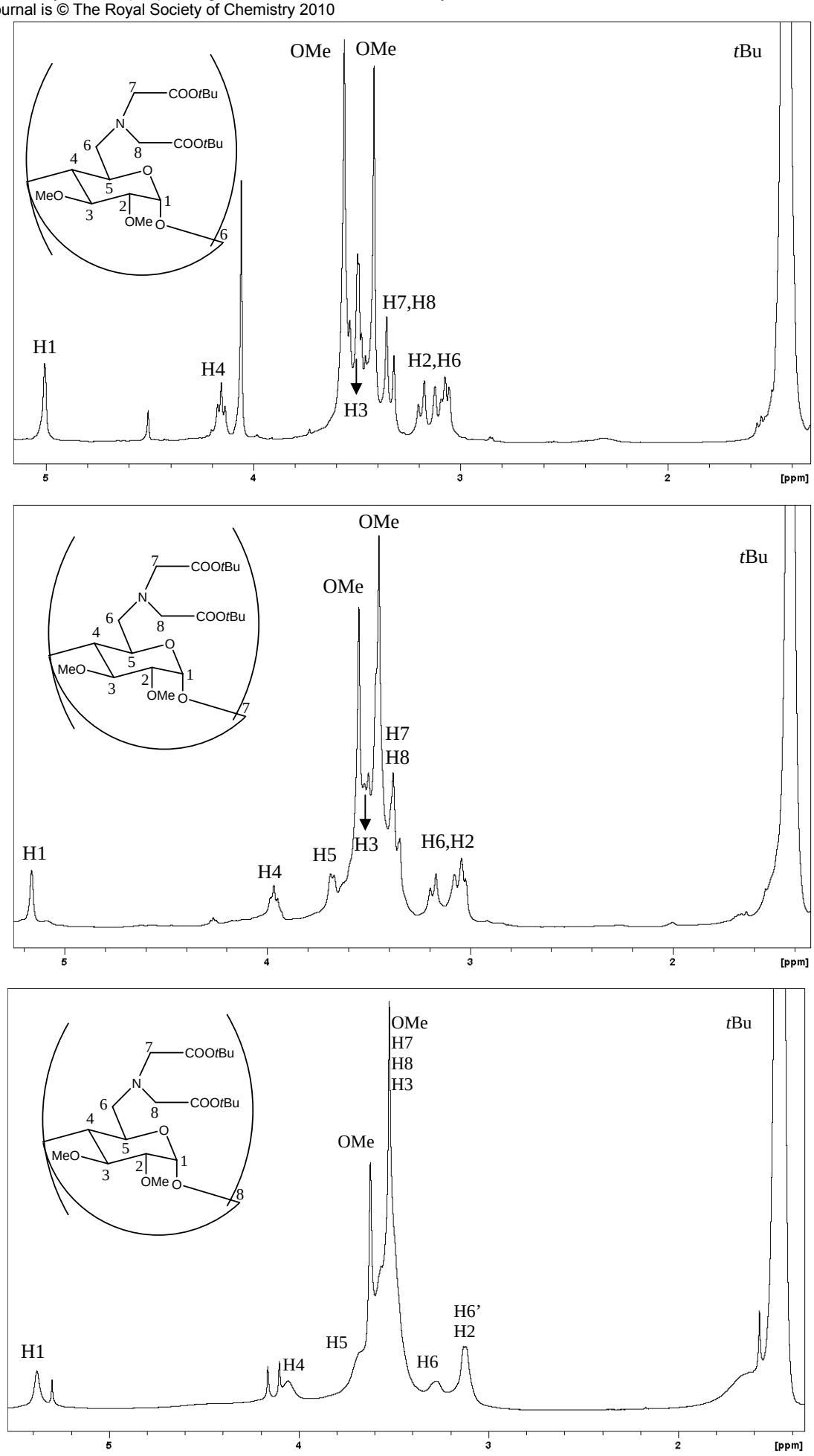


Figure S1a. ^{1}H NMR spectra of the *t*-Bu esters **5** of **AEDTA**, **BEDTA** and **GEDTA** (500 MHz, $CDCl_3$, 298K)

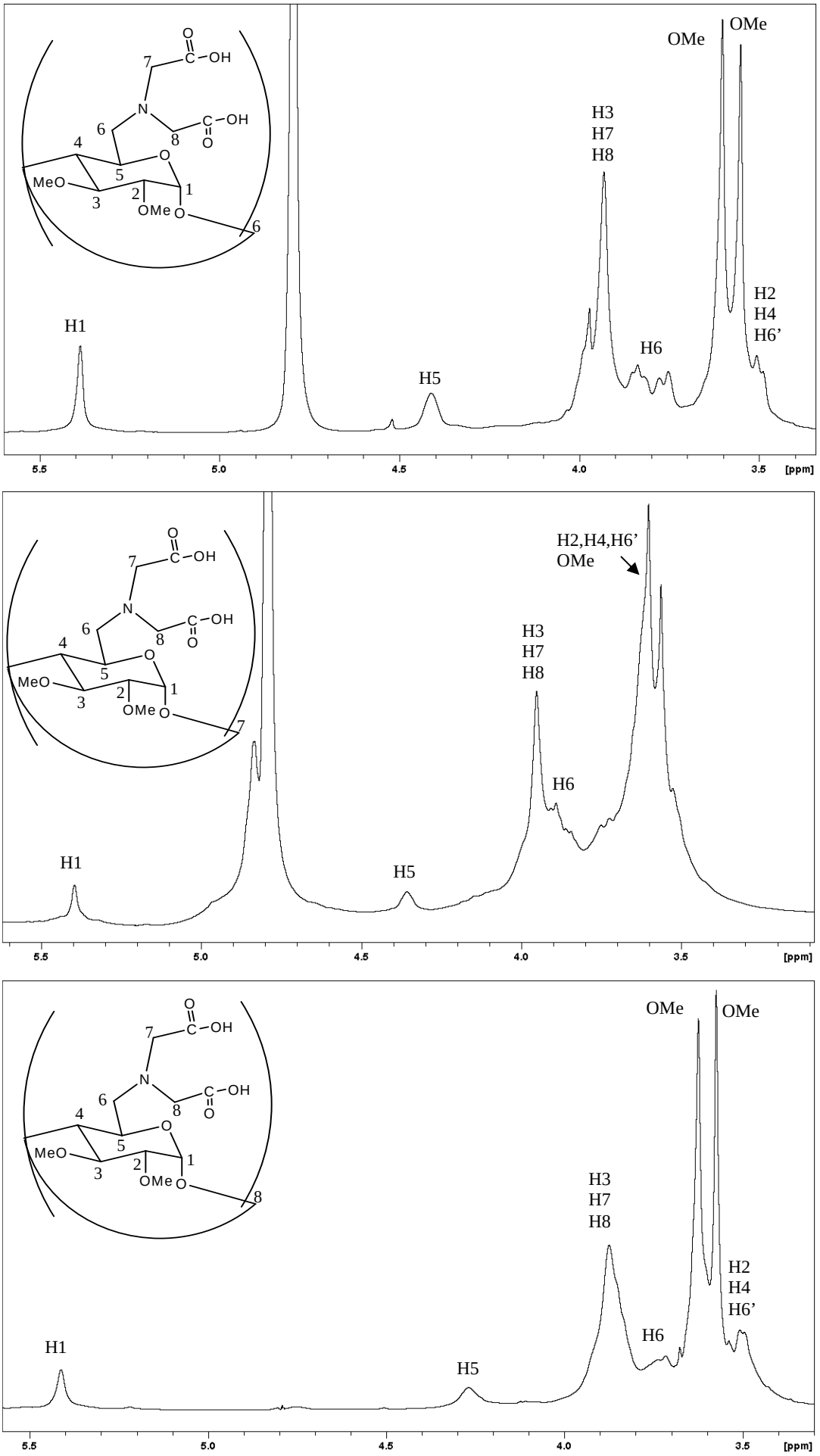


Figure S1b. ^{1}H NMR spectra of the products **6**, **AEDTA**, **BEDTA** and **GEDTA** (500 MHz, D_2O, 298K)

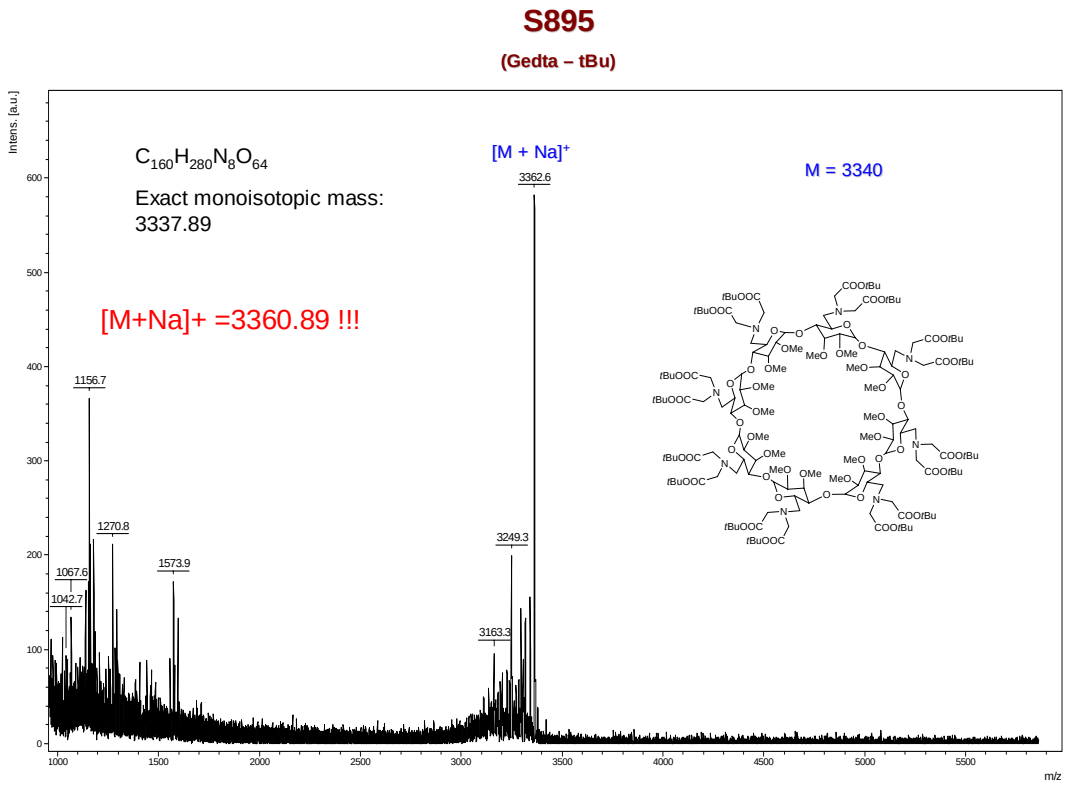
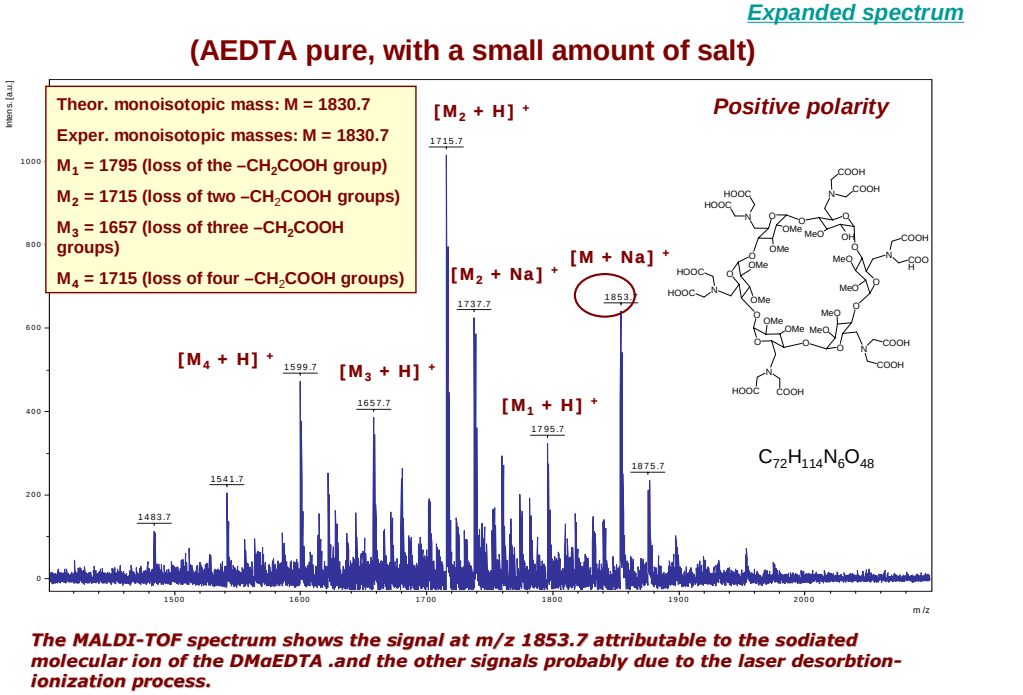
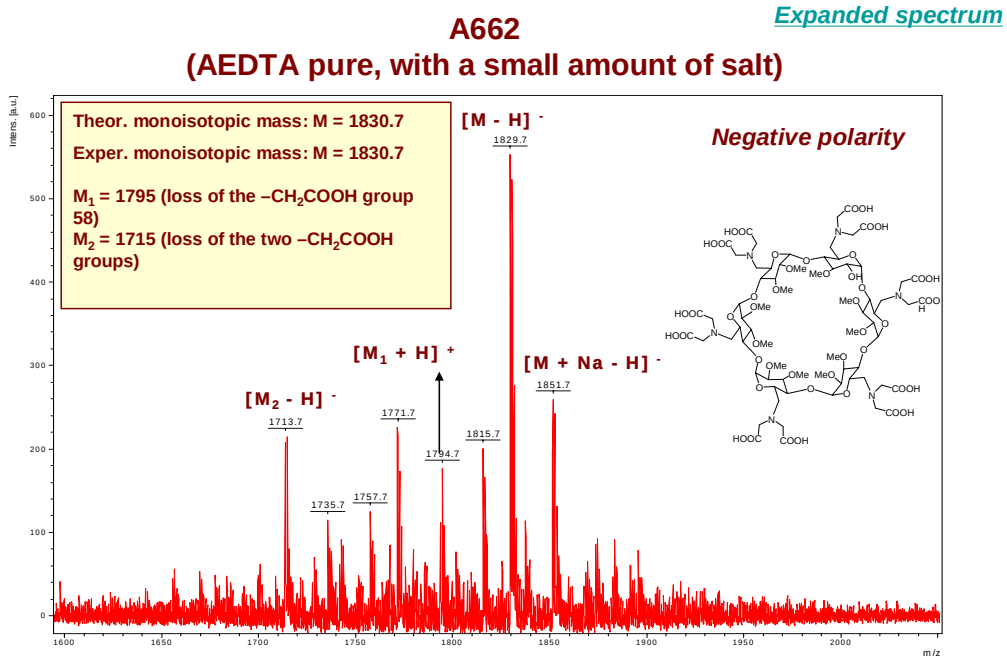


Figure S2. MALDI-TOF spectra (reflectron mode, positive polarity) of **5a** (top) and **5c** (bottom). Matrix solution: 2,5-dihydroxybenzoic acid in EtOH 80%.



The MALDI-TOF spectrum shows the signal at m/z 1853.7 attributable to the sodiated molecular ion of the DMaEDTA .and the other signals probably due to the laser desorbtion-ionization process.



The spectrum recorded in negative polarity shows the same signals with lower fragmentation during the laser desorbtion/ionization analysis .

Figure S3**.** MALDI-TOF spectra (reflectron mode) of **AEDTA** in positive polarity (top), and negative polarity (bottom). Matrix solution: 2,5-dihydroxybenzoic acid in EtOH 80%.

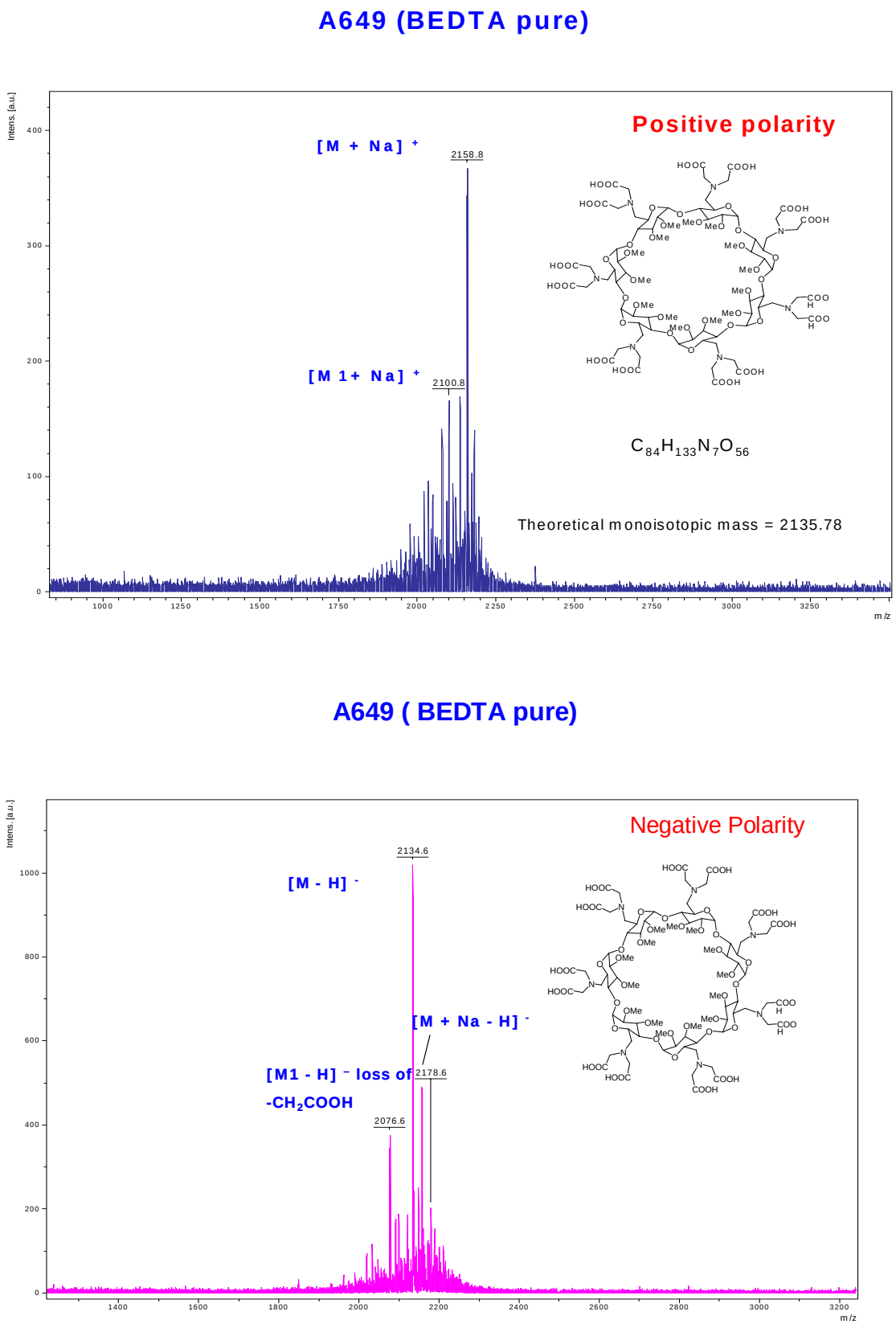


Figure S4**.** MALDI-TOF spectra (reflectron mode) of **BEDTA** in positive polarity (top), and negative polarity (bottom). Matrix solution: 2,5-dihydroxybenzoic acid in EtOH 80%.

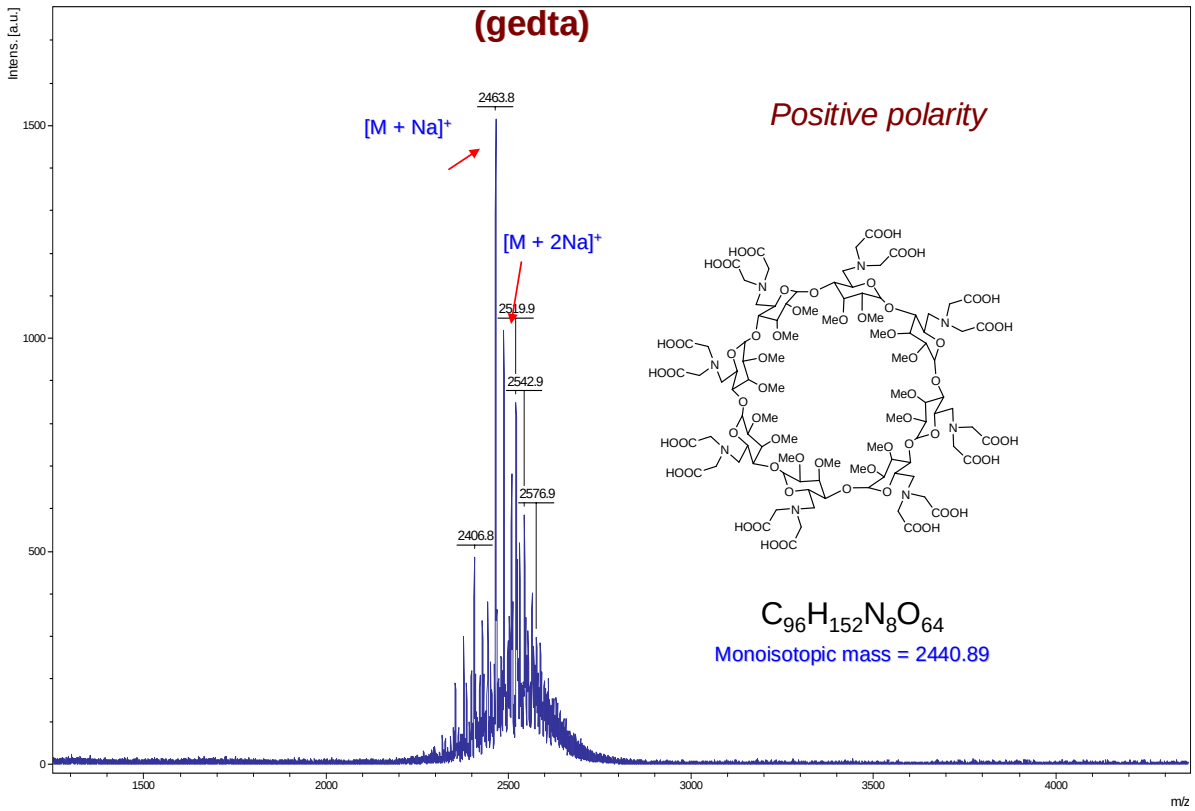


Figure S5. MALDI-TOF spectra (reflectron mode) of **GEDTA** in positive polarity. Matrix solution: 2,5-dihydroxybenzoic acid in EtOH 80%.

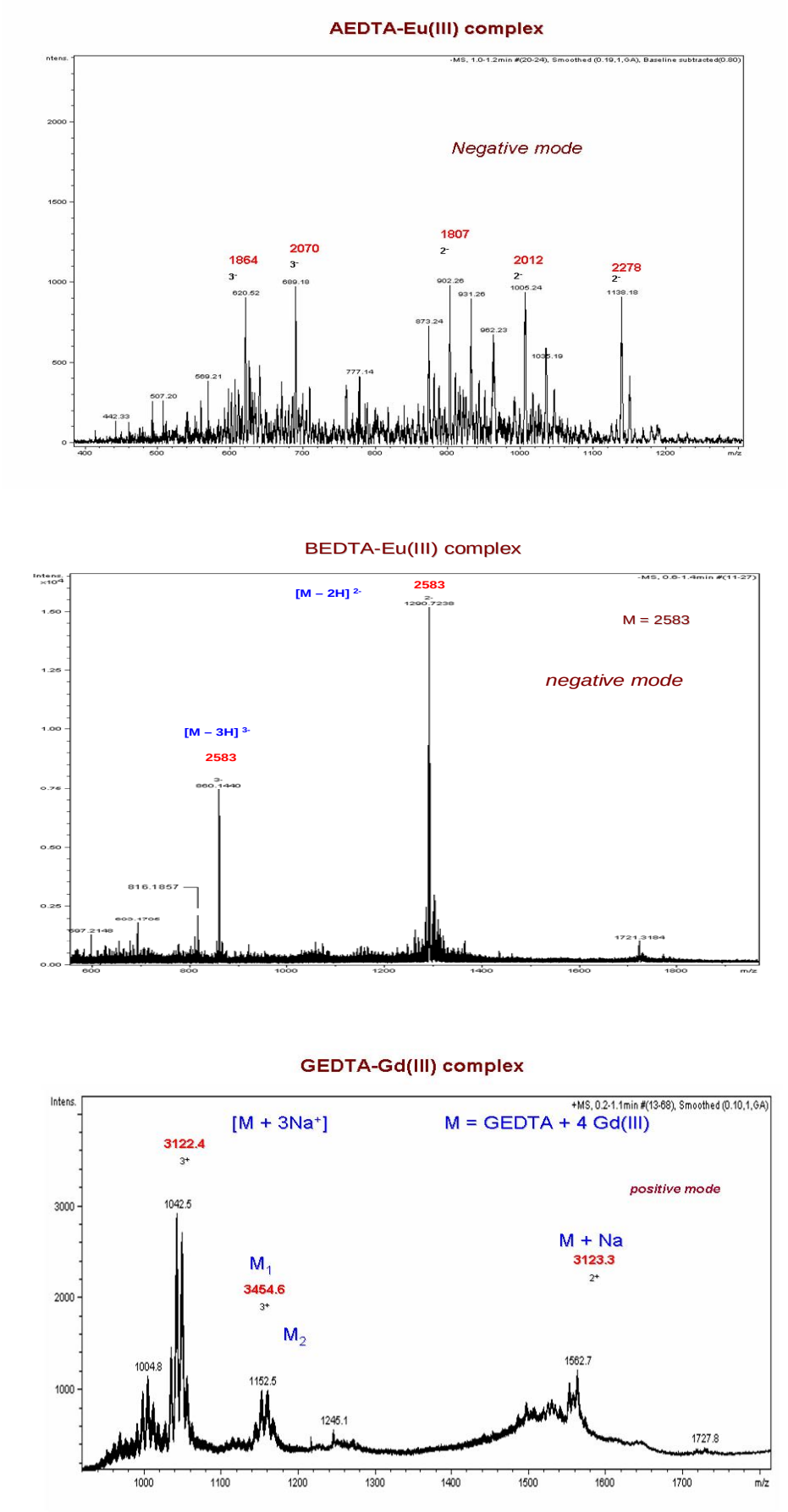


Figure S6**.** ESI-TOF spectra of EDTA-CDs with lanthanide ions.

Table S1. Binding energies (in kJ mol^{-1}) between lanthanide cations and anions of model ligands, calculated by PM3 and DFT (B3P86/3-21G*_Ln11eECP).

		PM3	DFT
La	**EDTA**	4564.0	6062.0
	NLIG	4379.4	5848.8
Eu	**EDTA**	4749.2	6303.6
	NLIG	4570.0	6085.4
Gd	**EDTA**	5303.0	6339.9
	NLIG	5085.3	6120.7
Tb	**EDTA**	4914.5	6401.4
	NLIG	4745.4	6140.2
Lu	**EDTA**	5061.2	6724.2
	NLIG	4895.1	6464.8

Table S2. Total binding energies (in kJ mol^{-1}) for the successive complexation of n = 1 - 4 lanthanide cations by fully deprotonated anions of substituted cyclodextrins, calculated at the PM3 level of theory. Numbers in parentheses indicate the stepwise binding energies of single lanthanide cations.

	n	AEDTA	BEDTA	GEDTA
Eu	1	7130.5 (7130.5)	7501.8 (7501.8)	7703.1 (7703.1)
	2	12930.6 (5800.1)	13993.7 (6491.9)	14520.1 (6817.0)
	3	17897.9 (4967.3)	19513.6 (5519.9)	20685.6 (6165.5)
	4		23312.4 (3798.8)	25795.4 (5109.8)
Gd	1	7749.1 (7749.1)	8090.0 (8090.0)	8333.1 (8333.1)
	2	14131.9 (6382.8)	15246.8 (7156.7)	15785.8 (7452.7)
	3	19726.5 (5594.5)	21368.2 (6121.4)	22574.3 (6788.6)
	4		25411.7 (4043.5)	28316.0 (5741.7)
Tb	1	7300.6 (7300.6)	7674.1 (7674.1)	7874.9 (7874.9)
	2	13272.7 (5972.1)	14338.2 (6664.1)	14863.5 (6988.6)
	3	18412.0 (5139.3)	20026.2 (5688.0)	21204.8 (6341.4)
	4		24058.8 (4032.6)	26481.1 (5276.2)

Table S3. Average values for the distances (in Å) between lanthanide atoms and coordinated heteroatoms (O, N,) for substituted cyclodextrins, calculated by PM3. The distances with two different types of oxygen atoms coordinated (in carboxyl group and glucopyranose ring, respectively) are shown separately.

		Ln-O (Carboxyl)	Ln-O (Glucopyranose)	Ln-N
	AEDTA	2.433	2.540	2.603
Eu	**BEDTA**	2.432	2.526	2.607
	GEDTA	2.433	2.533	2.613
	AEDTA	2.372	2.496	2.578
Gd	**BEDTA**	2.370	2.493	2.574
	GEDTA	2.372	2.490	2.582
	AEDTA	2.391	2.500	2.598
Tb	**BEDTA**	2.390	2.492	2.603
	GEDTA	2.391	2.493	2.600