Sol-gel organic-inorganic hybrid materials, containing lanthanide complexes with polydentate acyclic and cyclic ligands: synthesis and spectral-luminescent properties

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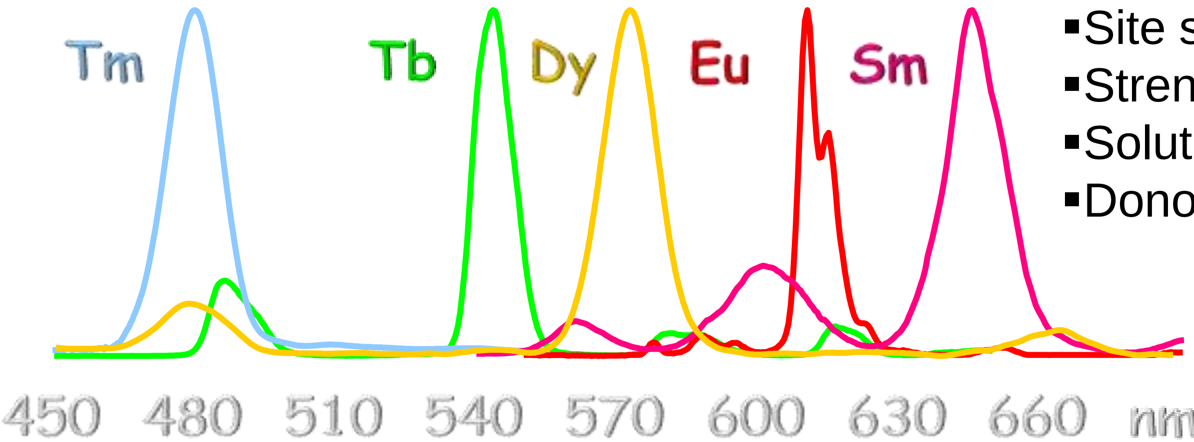
Lanthanide luminescence

Emission spectra:
- ➢atom-like, cover the entire visible/NIR range
- ➢long lived excited states

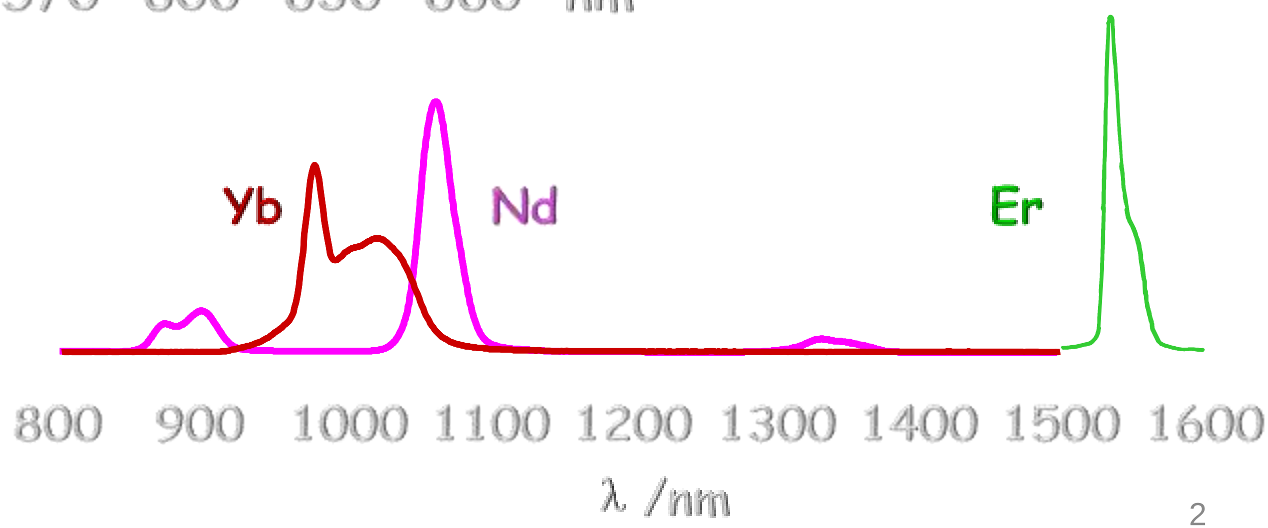
Information:
- ▪Number of metal-ion sites
- ▪Composition of the 1st coordination sphere
- ▪Site symmetry
- ▪Strength of the Ln-L bond
- ▪Solution state of the Ln(III) ion
- ▪Donor – acceptor distance



Main problems are:

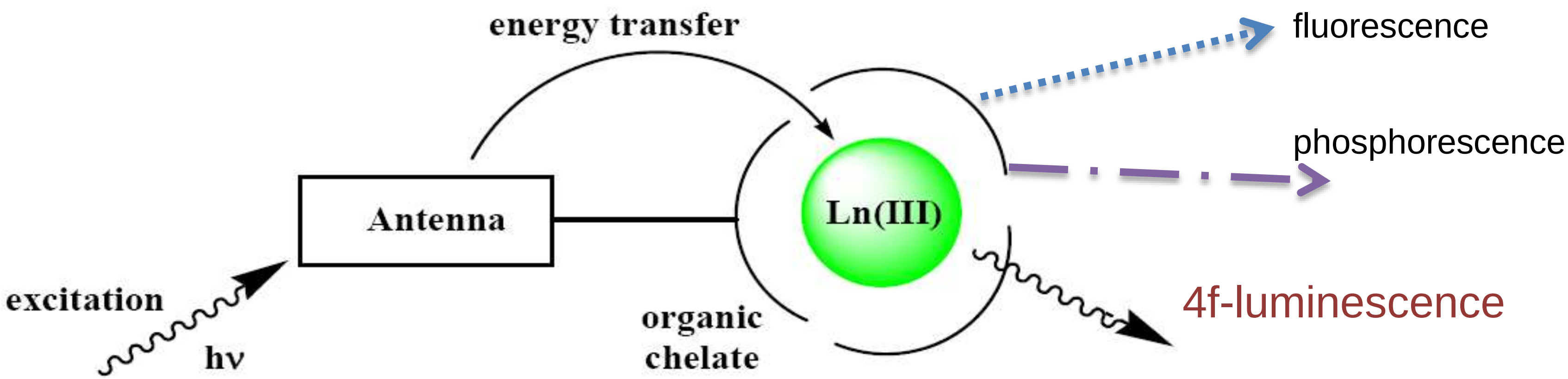
•weak 4f-absorption – sensitization by organic ligand needed

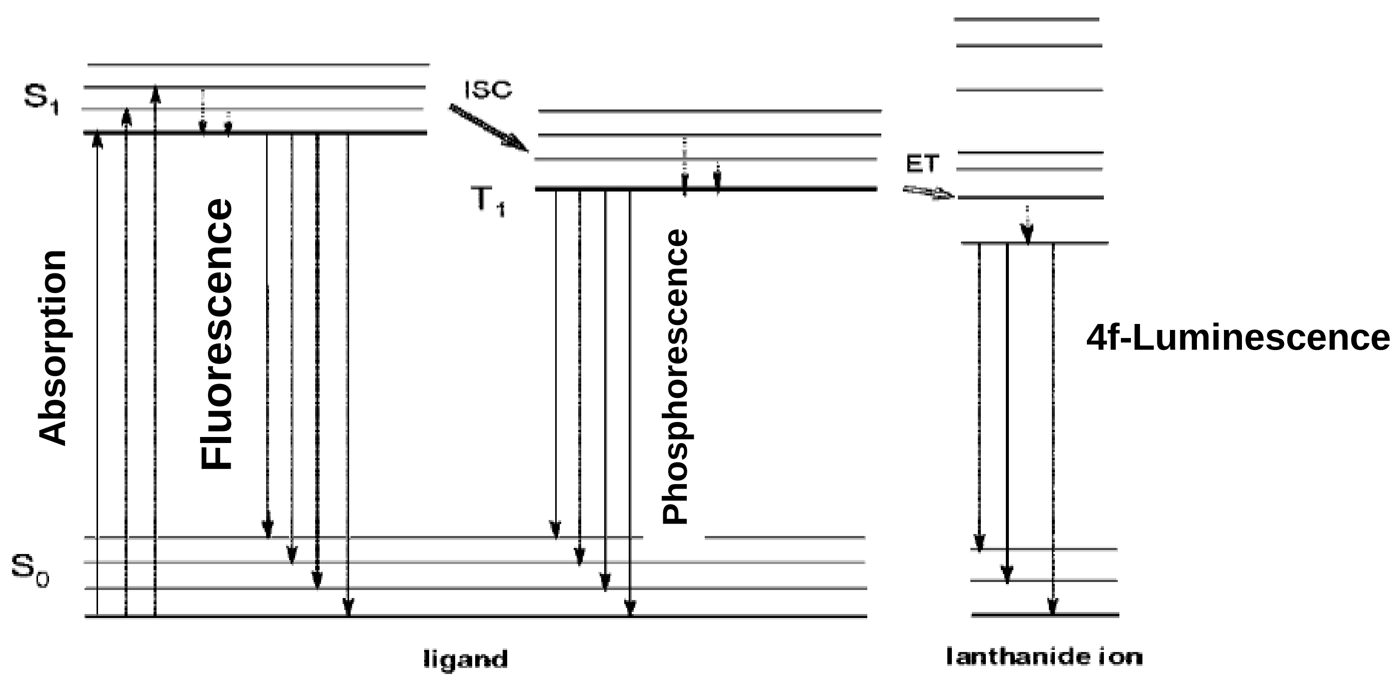
•quenching processes, particularly high-energy vibrations (O-H, C-H)

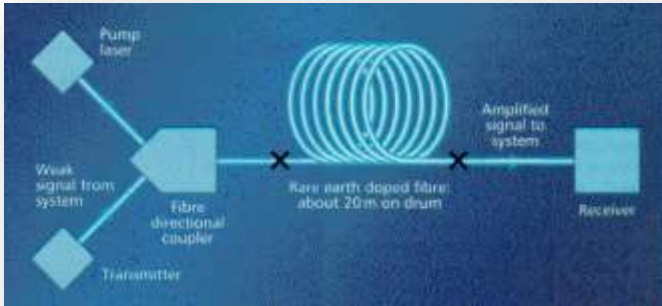


Sensitized lanthanide luminescence

Organic ligand acts as a sensitizer, transfers excitation energy to the Ln(III) ion and provides protection from quenching solvent interactions, thermodynamic and kinetic stability







Optical waveguides

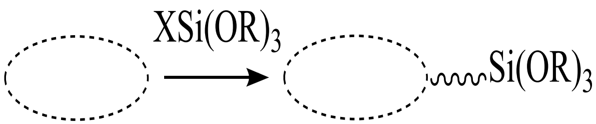
Applications of
luminescent lanthanide complexes

Optical amplifiers

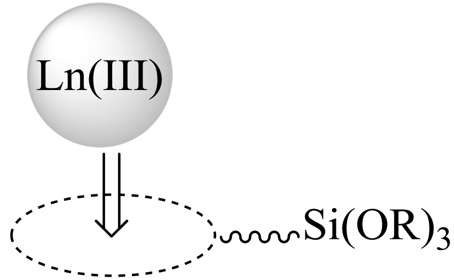
Organic light emitting diodes

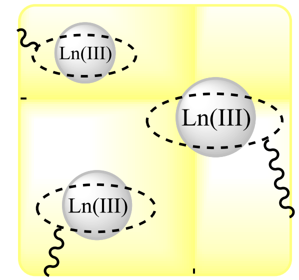
Time-resolved fluoroimmunoassays

The strategy for luminescent Ln(III)-based organic-inorganic hybrid materials preparation



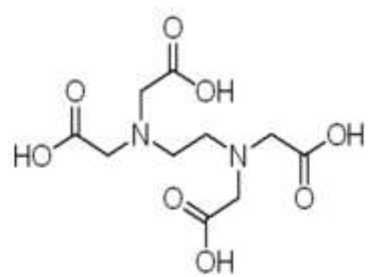
X contains reactive group
(-NH_2, -$CONH_2$, -NCO, =CH_2 etc)



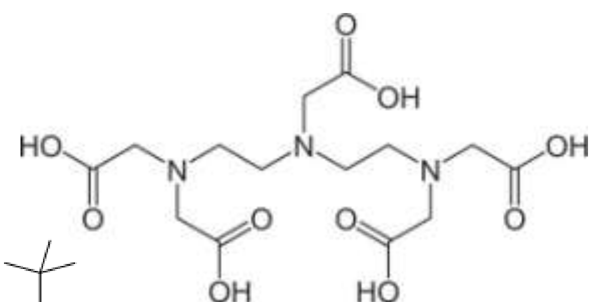


Modification of organic ligand → Formation of Ln(III) complex → Sol-gel synthesis of hybrid material

Aminopolycarboxylic acids:
- ethylenediaminetetraacetic acid (Edta)
- diethylenetetraminepentaacetic acid (Dtpa)

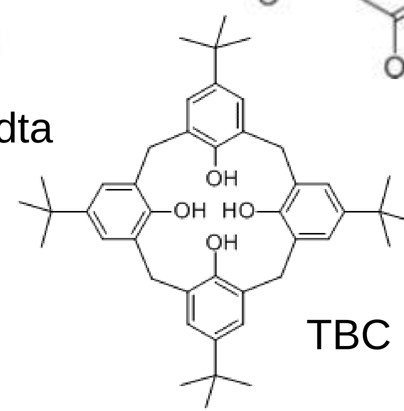


Edta



Dtpa

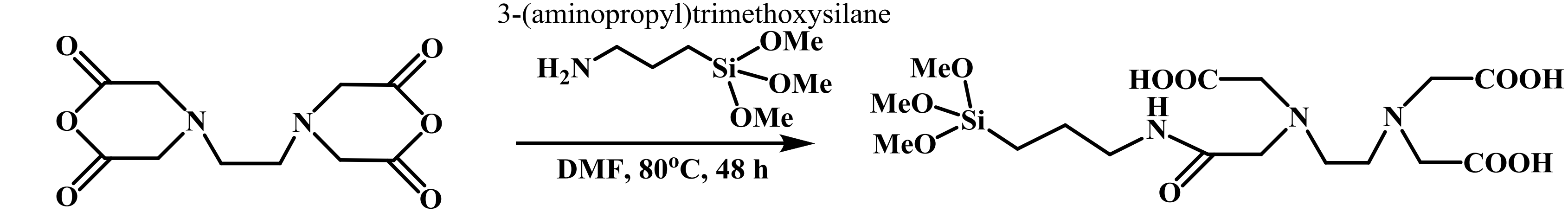
Calix[n]arenes:
-p-tert-butylcalix[4]arene (TBC)



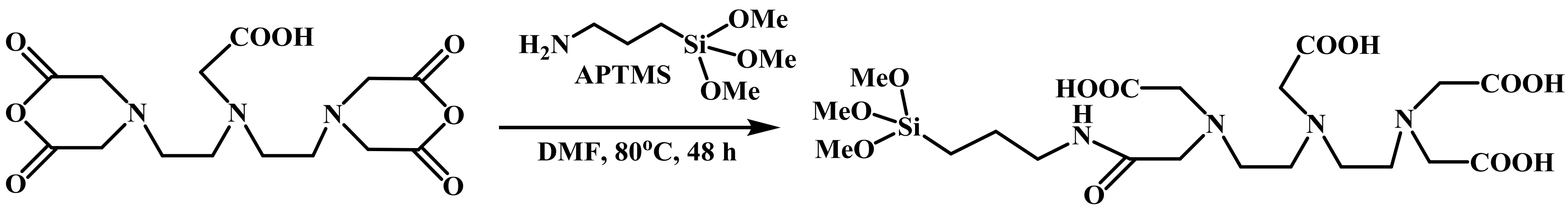
TBC

Modification of aminopolycarboxylic acids

Aminopolycarboxylic acid dianhydride



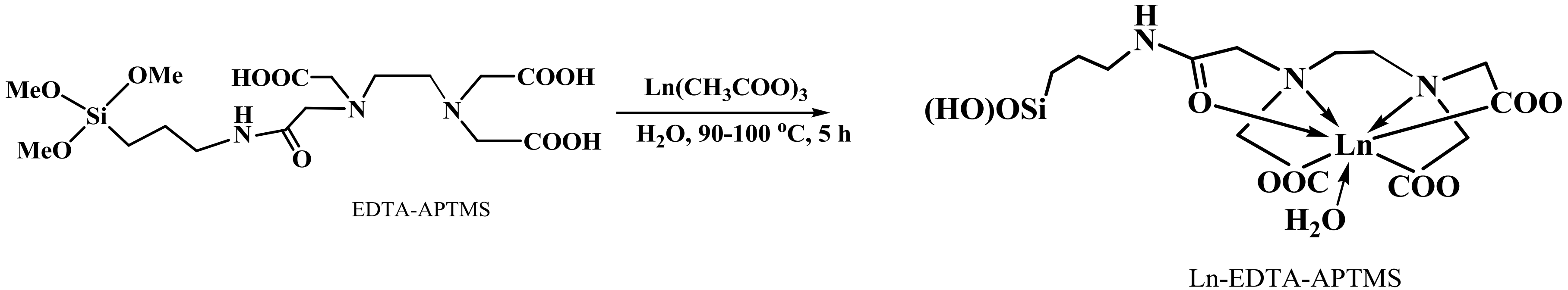
EDTA-APTMS

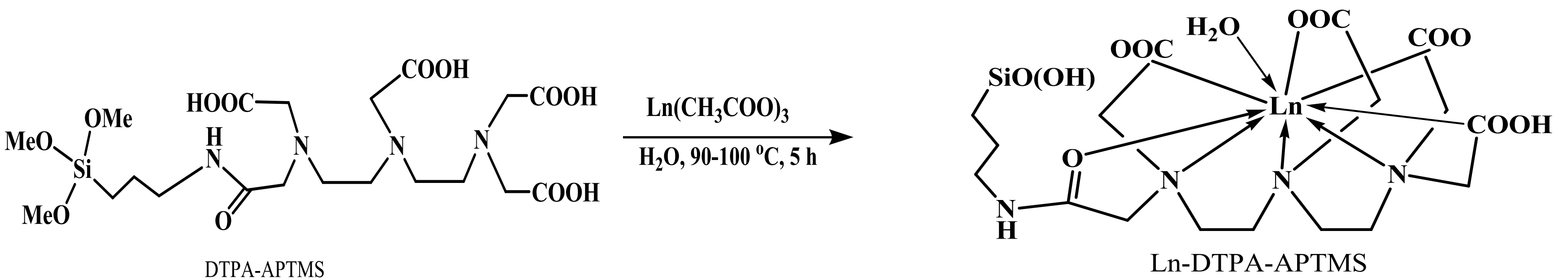


DTPA-APTMS

Compound	^{1}H NMR δ, ppm (D_2O, pH>10)			ESI-MASS, $[M]^-$
	$-CH_2-$ (Gly)	$-CH_2-$ (En)	$-CH_2-$ (n-Pr)	
EDTA-APTMS	3.08 (2 H) s 3.52 (6 H) s	3.15-3.35 (4 H) m	0.73 (2 H) t 1.77 (2 H) m 3.00 (2 H) t	392
DTPA-APTMS	3.33 (8 H) s 3.49 (2 H) s	2.97 (4 H) t 3.09 (4 H) t	0.59 (2 H) t 1.67 (2 H) m 2.90 (2 H) t	493

Complexation with Ln(III) ions



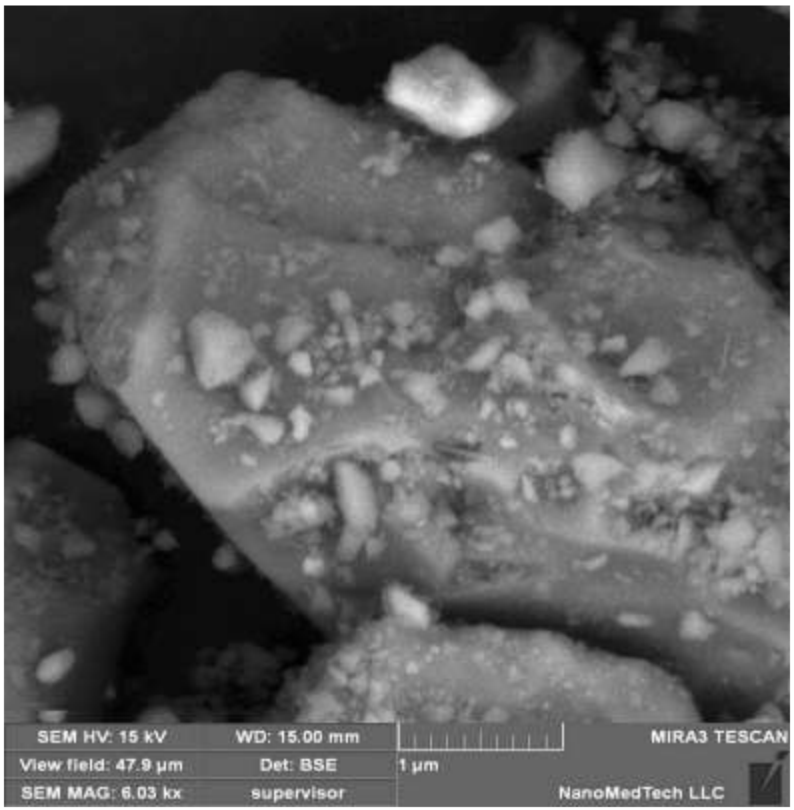


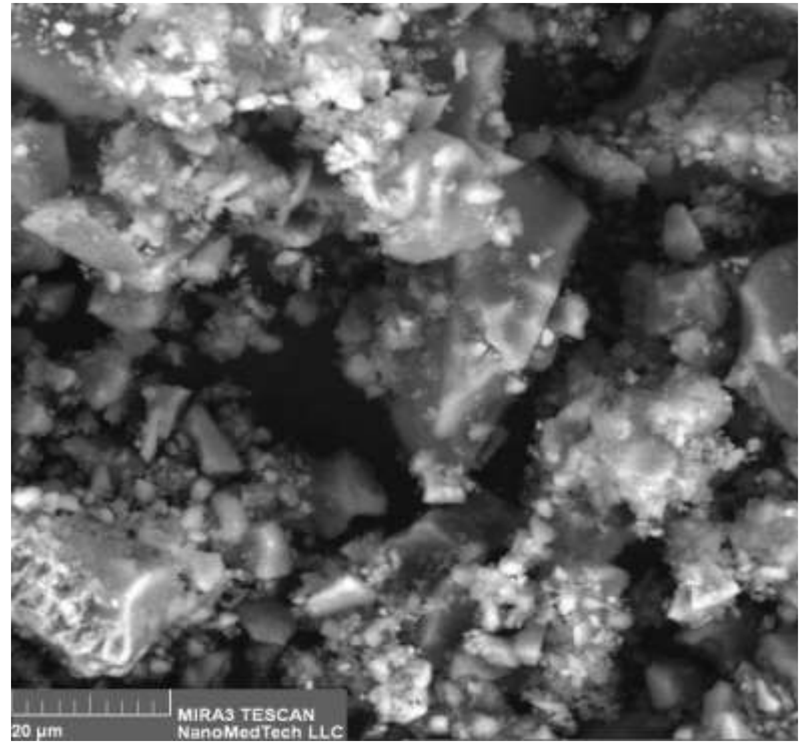
Complex	^1H NMR δ, ppm (D_2O, pH>10)			ESI-MASS, $[M]^-$	Complex	ESI-MASS, $[M]^-$
	$-CH_2-$ (Gly)	$-CH_2-$ (En)	$-CH_2-$ (n-Pr)			
Lu-EDTA-APTMS	3.23-3.68 (8 H) m	3.01 (2 H) t 3.14 (2 H) t	0.79(2 H) t 1.81 (2 H) m 3.04 (2 H) t	564	Tb-EDTA-APTMS	548
Lu-DTPA-APTMS	3.29-3.70 (10 H) m	2.55 (2 H) t 2.72 (2 H) t 2.94 (2 H) t 2.97 (2 H) t	0.71 (2 H) t 1.71 (2 H) m 3.01 (2 H) t	665	Tb-DTPA-APTMS	649

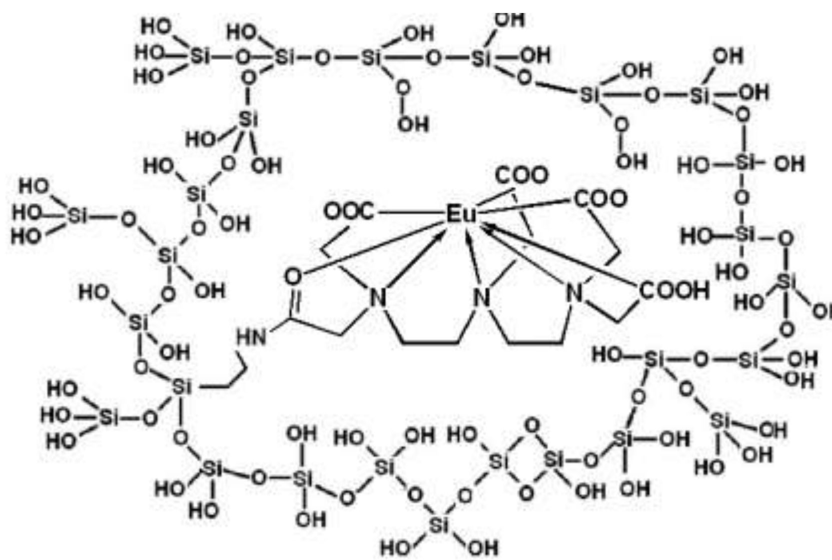
Sol-gel synthesis of Ln(III)-based hybrid materials

Ln-L-APTMS $\xrightarrow[\text{H}_2\text{O-EtOH, 25 }^{o}\text{C}]{\text{Si(OEt)}_4\text{; 1. HCl; 2. NH}_4\text{OH}}$

Ln = Eu, Tb, Yb, Lu
L = EDTA, DTPA

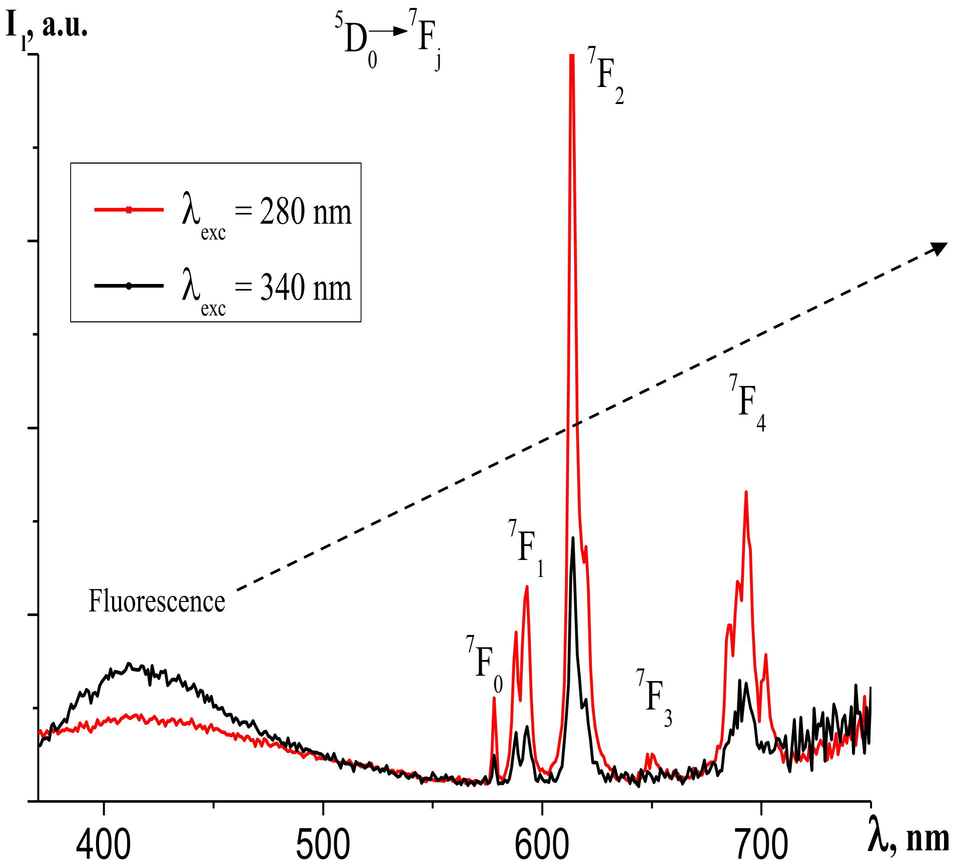




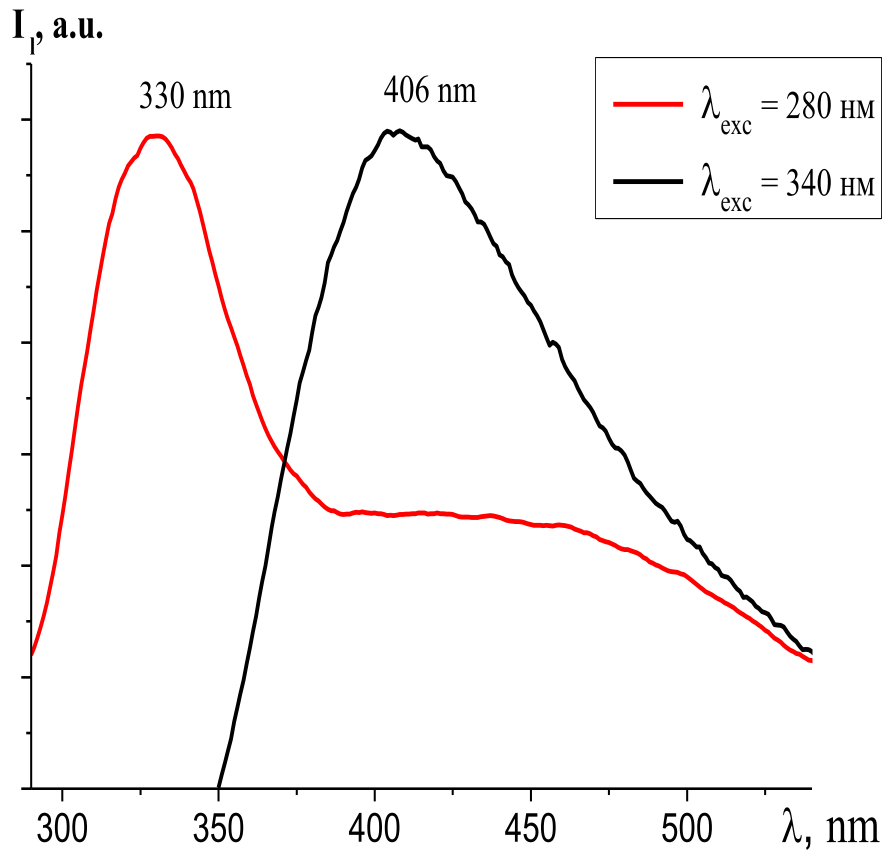


SEM-images of Eu-DTPA-APTMS/SiO_2 sample

Luminescent properties of Eu-DTPA-APTMS/SiO_2

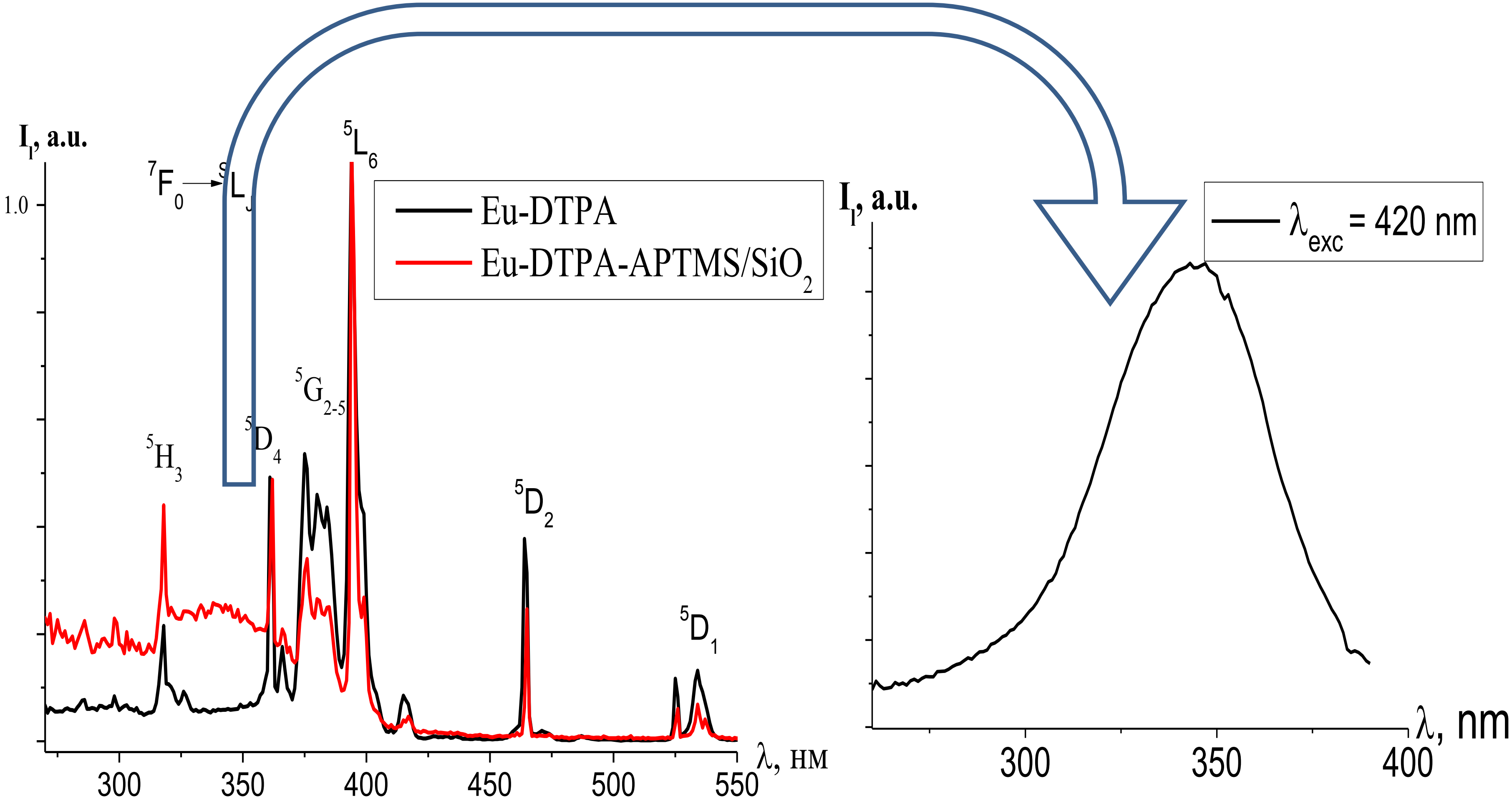


Emission spectra of Eu-DTPA-APTMS/SiO_2



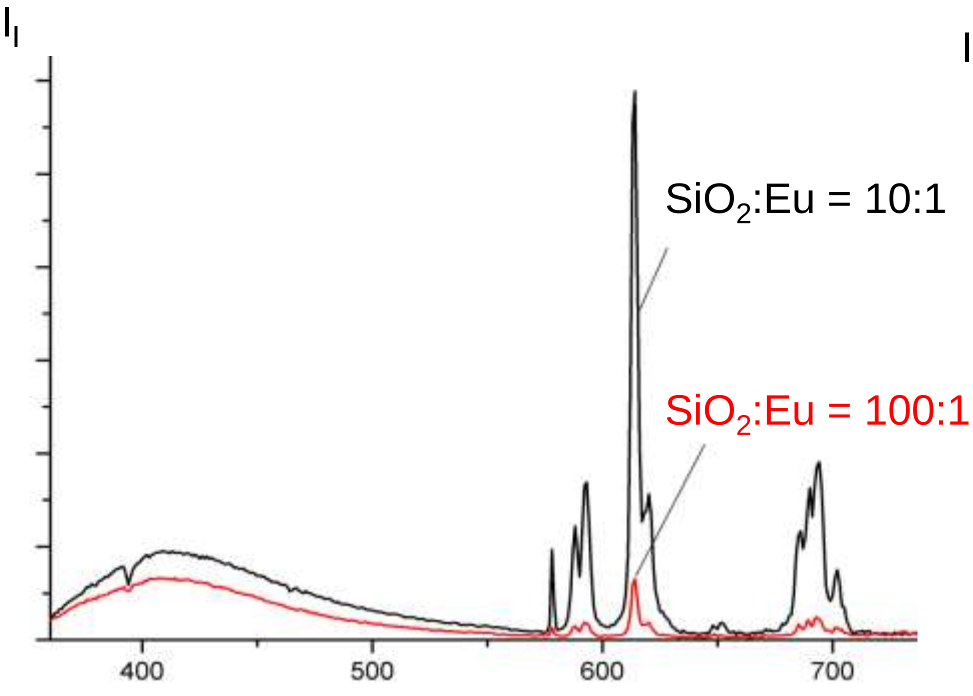
Fluorescence spectra of Ln-free sample

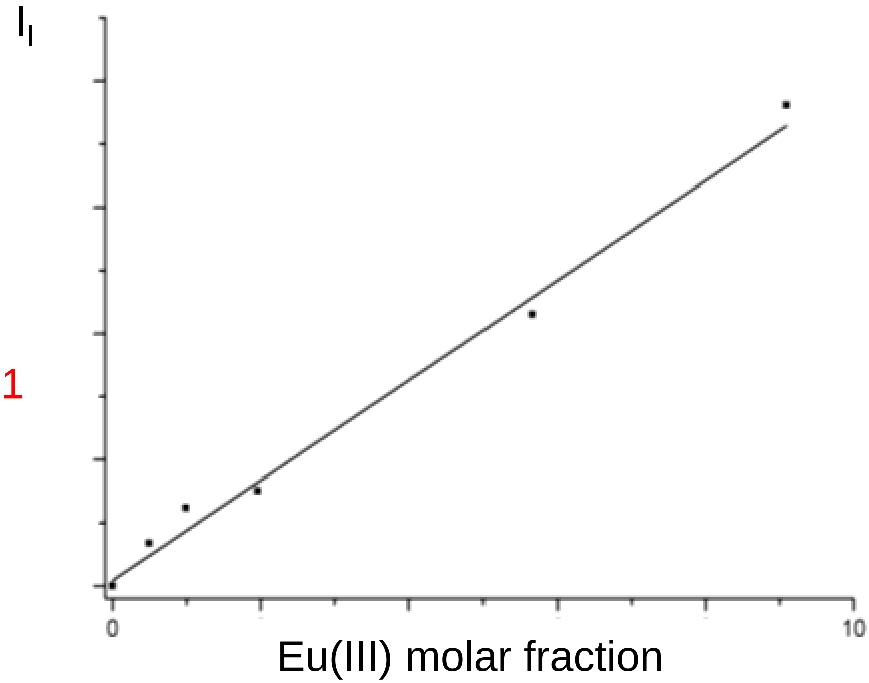
Luminescent properties of Eu-DTPA-APTMS/SiO_2



Excitation spectra of Eu-DTPA and Eu-DTPA-APTMS/SiO_2 (λ_{em} = 615 nm)

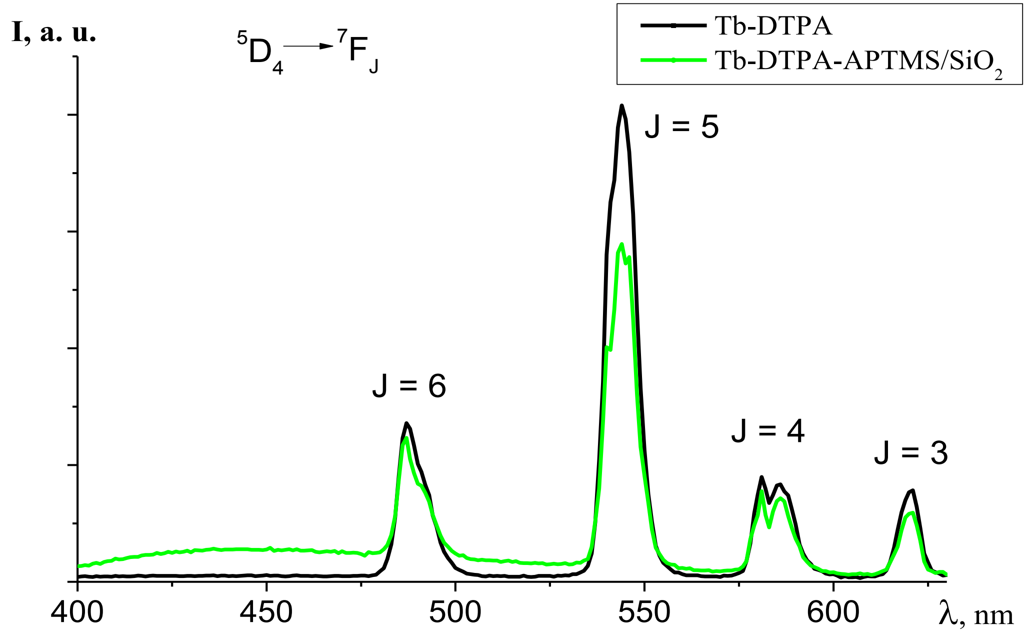
Concentration effects





Ratio SiO_2/EuL	Molar fraction of EuL	Fluorescence intensity, a.u.	4f-Luminescence intensity, a.u.
200:1	0.50	1.26	0.81
100:1	0.99	1.31	1.50
50:1	1.96	1.67	1.81
25:1	5.66	1.86	4.52
10:1	9.09	3.47	9.40
$EuCl_3$ 50:1	--	1.00	1.00

Luminescence of Tb(III)-based hybrid materials

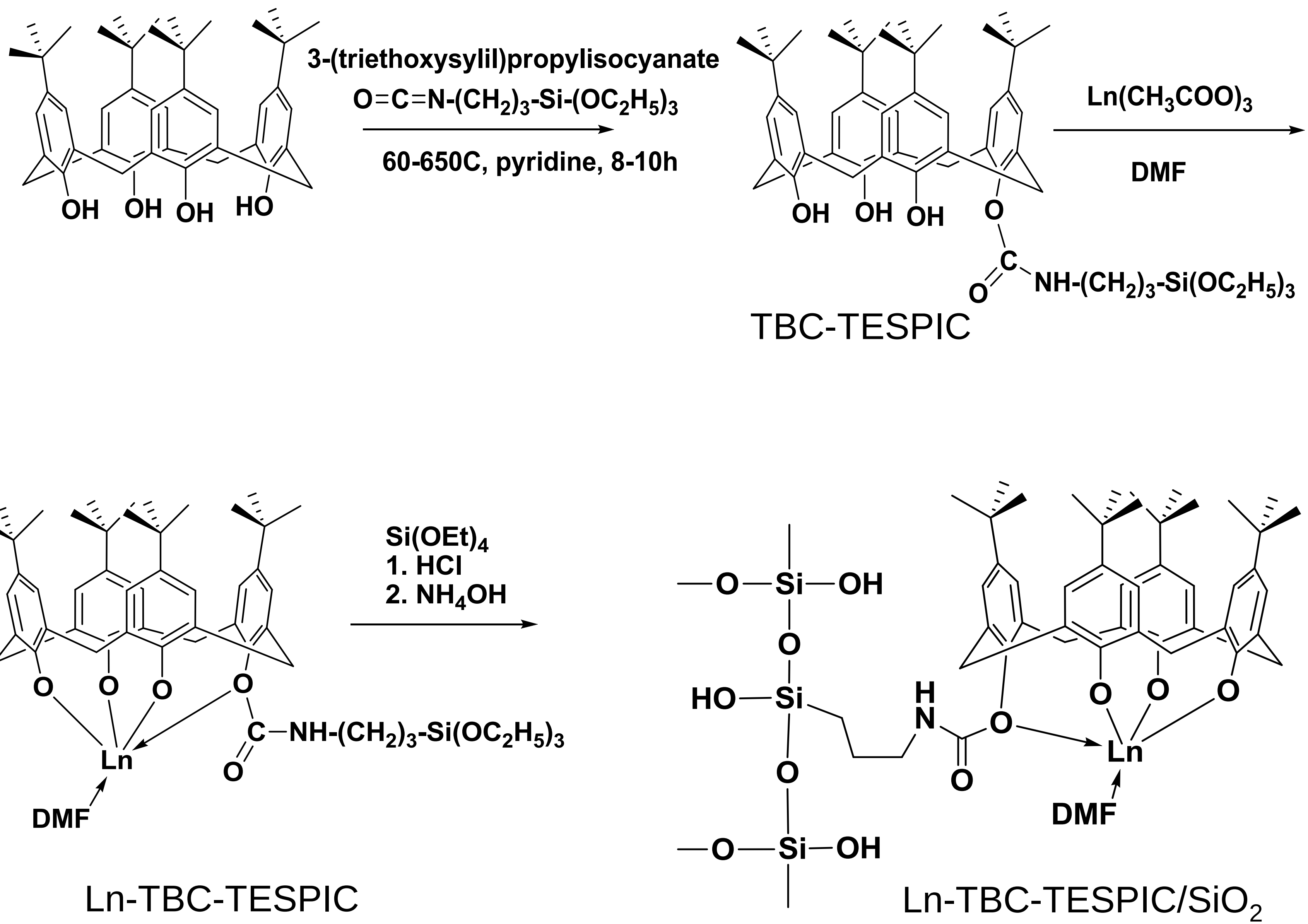


Emission of Tb-Dtpa and Tb-Dtpa-Aptms/SiO_2 (λ_{exc} = 340 nm)

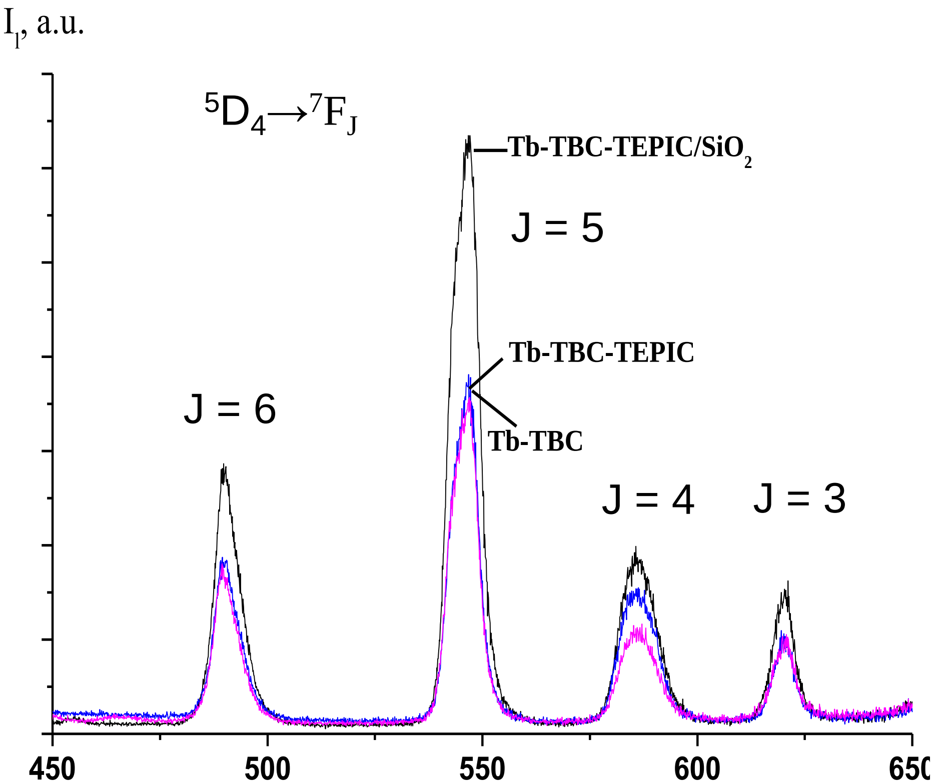
Compound	I_{4f}, %	Compound	I_{4f}, %
Eu-EDTA	91	Tb-EDTA	89
Eu-DTPA	100	Tb-DTPA	100
Eu-EDTA-APTMS-SiO_2	78	Tb-EDTA-APTMS-SiO_2	67
Eu-DTPA-APTMS-SiO_2	83	Tb-DTPA-APTMS-SiO_2	71

Ln:SiO_2 = 1:50 (applies to the APTMS-SiO_2 rows)

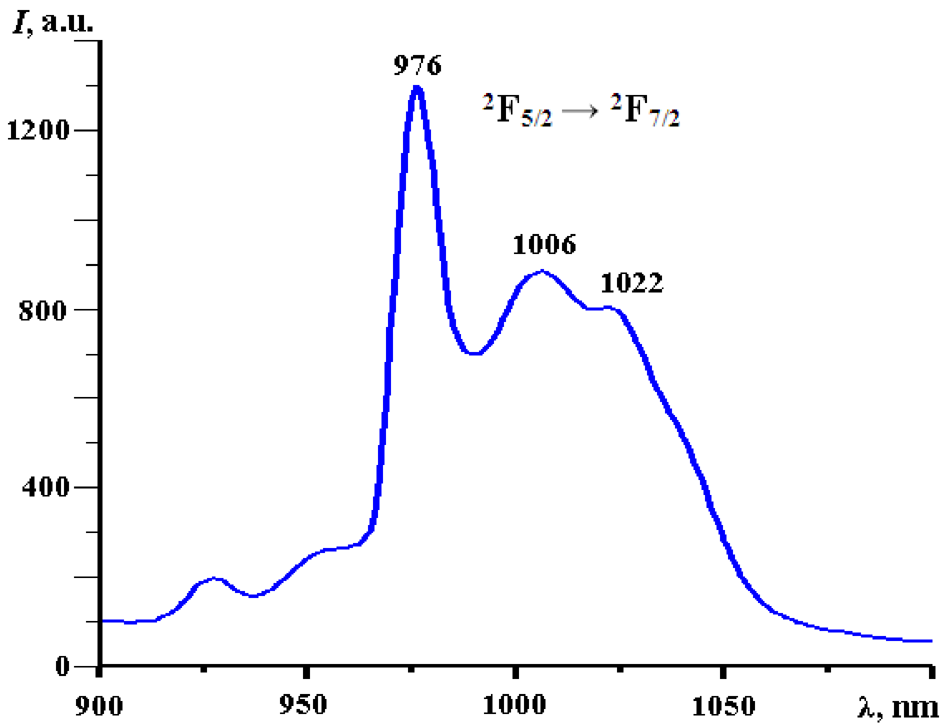
Functionalization of p-tert-butylcalix[4]arene



Luminescence of Ln-TBC-based hybrid materials



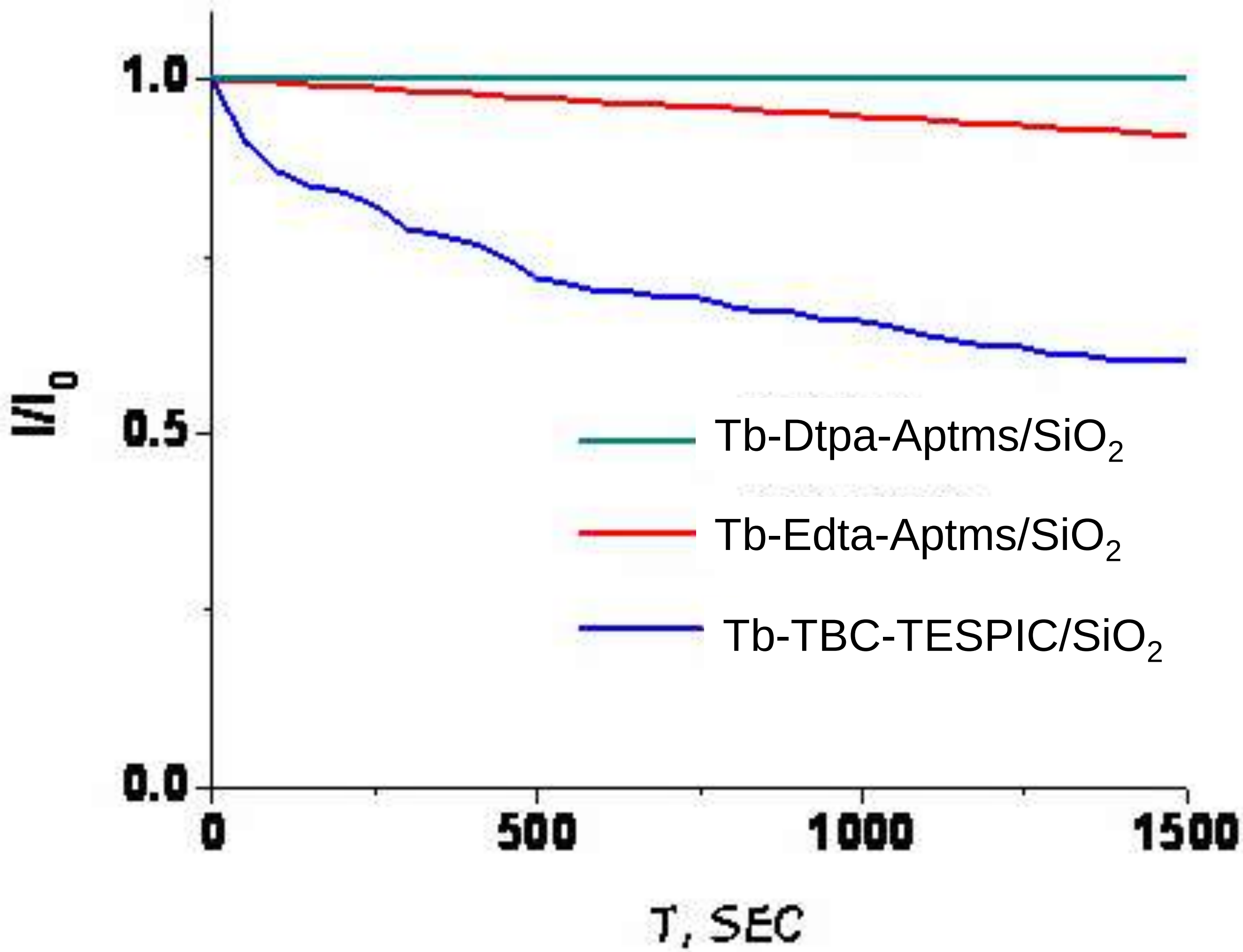
Emission spectra of Tb-containing compounds (λ_{exc} = 310 nm)



Emission spectrum of Yb-TBC-TESPIC/SiO_2 (λ_{exc} = 310 nm)

Compound	τ, μsec	Compound	τ, μsec
Eu-TBC	350	Tb-TBC	370
Eu-TBC-TESPIC/SiO_2	192	Tb-TBC-TESPIC/SiO_2	650

Photostability of Ln(III)-containing hybrid materials



Acknowledgements

Dr. E. Trunova, Dr. O. Berejnytskaya
V.I. Vernadsky Institute of General and Inorganic Chemistry of NAS of Ukraine

A. Rogovtsov, TOV NanoMedTech

Financial support

National Academy of Sciences of Ukraine