Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Multimodal nanogels combining ZW800-1 as an optical absorber and gadolinium chelates for multispectral optoacoustic tomography (MSOT) and magnetic resonance imaging (MRI)

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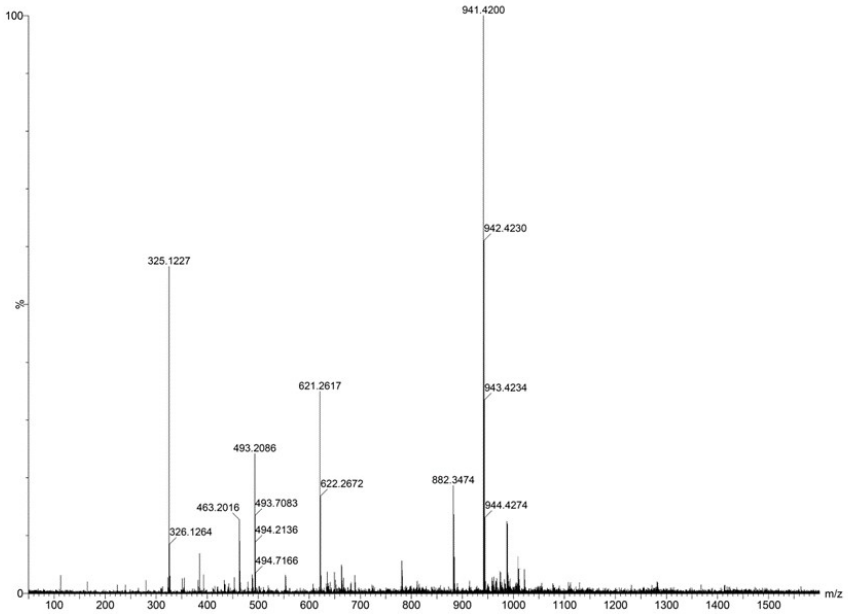

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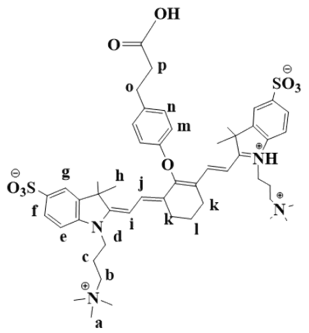


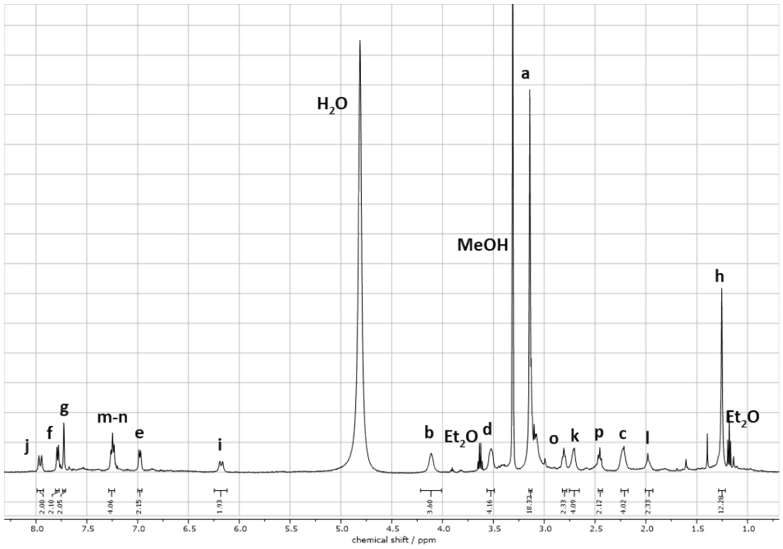
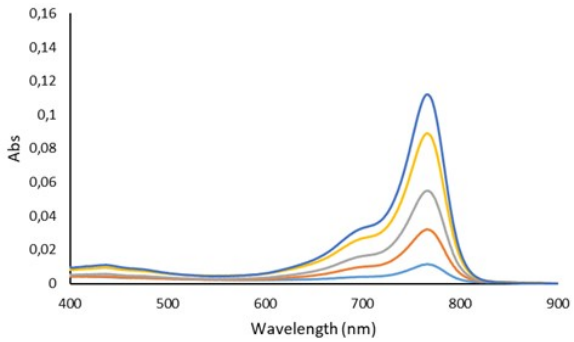
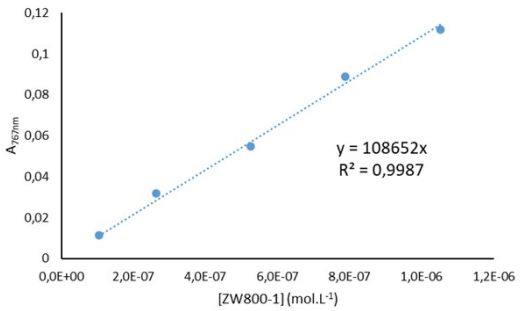


Fig. S1: a- HR-ESI-MS mass spectrum (negative mode, water), b- ^{1}H NMR spectrum of ZW800-1 (500 MHz, D_2O/MeOD)

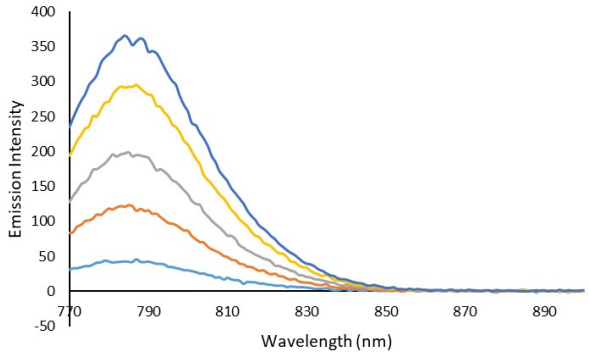
a

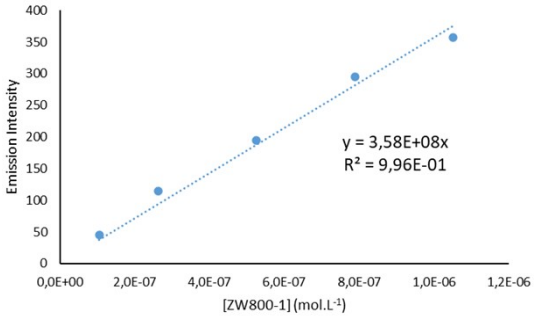




$\varepsilon_{767\ nm} = 108\ 652\ L.mol^{-1}.cm^{-1}$

b





$k_{ZW800,787\ nm} = 3.58 \times 10^{8}\ mol^{-1}L$

Fig. S2: a- Determination of ZW800-1 molar absorption coefficient $\varepsilon_{767\ nm}$ in acetate buffer. b- determination of $k_{ZW800,\ 787\ nm}$ (λ_{exc} = 760 nm, $\Delta\lambda_{exc} = \Delta\lambda_{exc}$ = 5 nm)

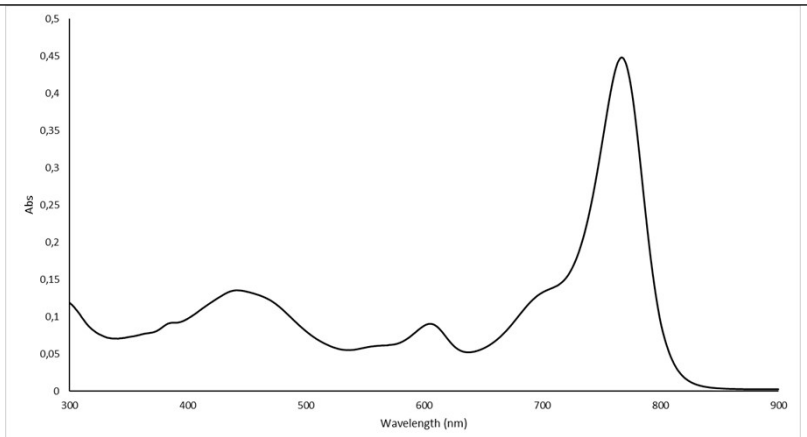


Fig.S3: UV-visible spectrum of CS-ZW800 before purification in acetic acid 1%

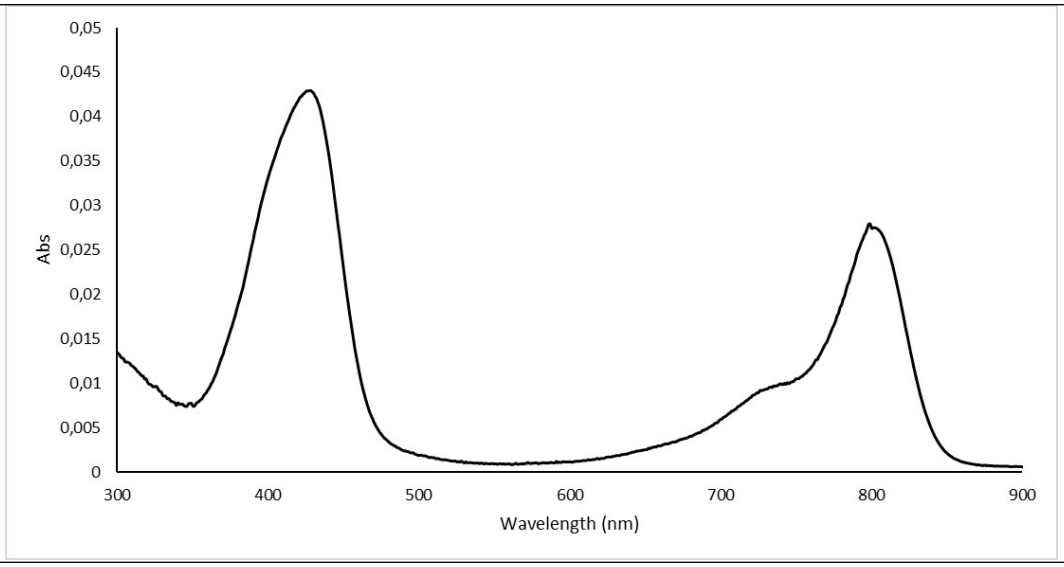


Fig.S4: UV-visible spectrum of chloro compound **1** in DMSO

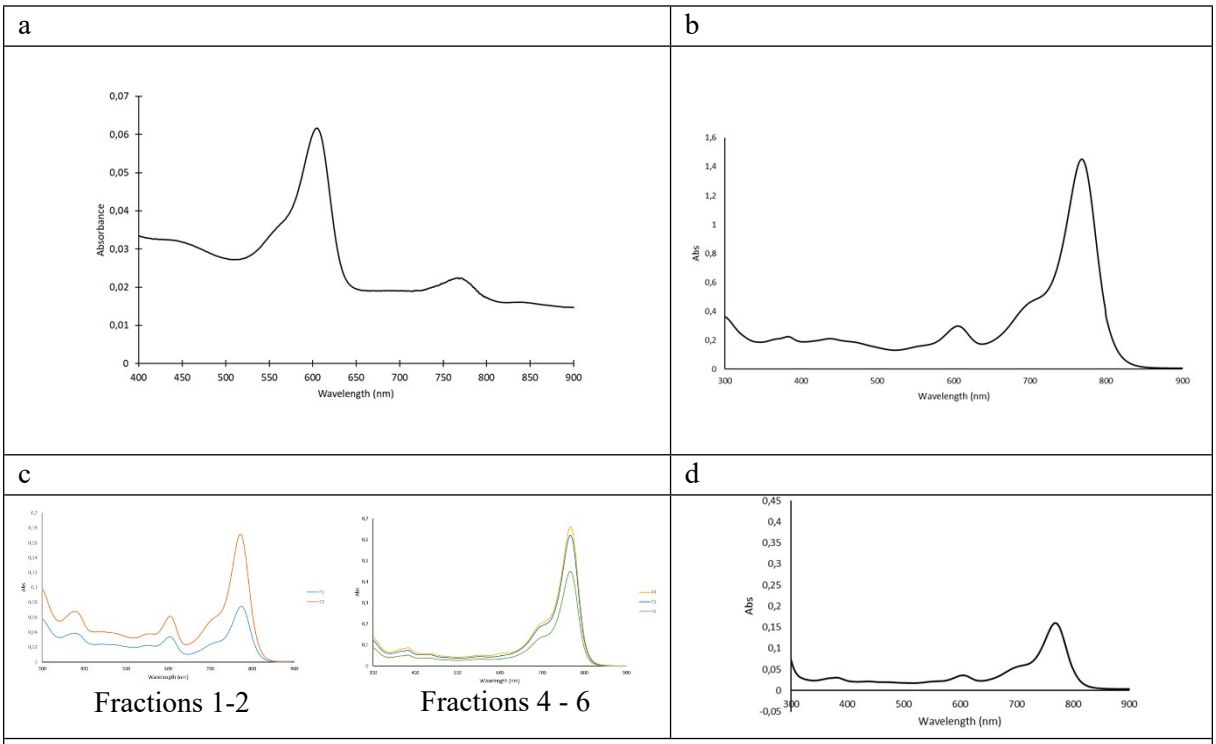


Fig. S5: Evolution of the UV-visible spectrum of CS-ZW800 according to purification procedures a- NaOH precipitation, b- dialysis against water, c- steric exclusion chromatography (LH60, elution with acetate buffer), d- cross-flow filtration (eluent: water)

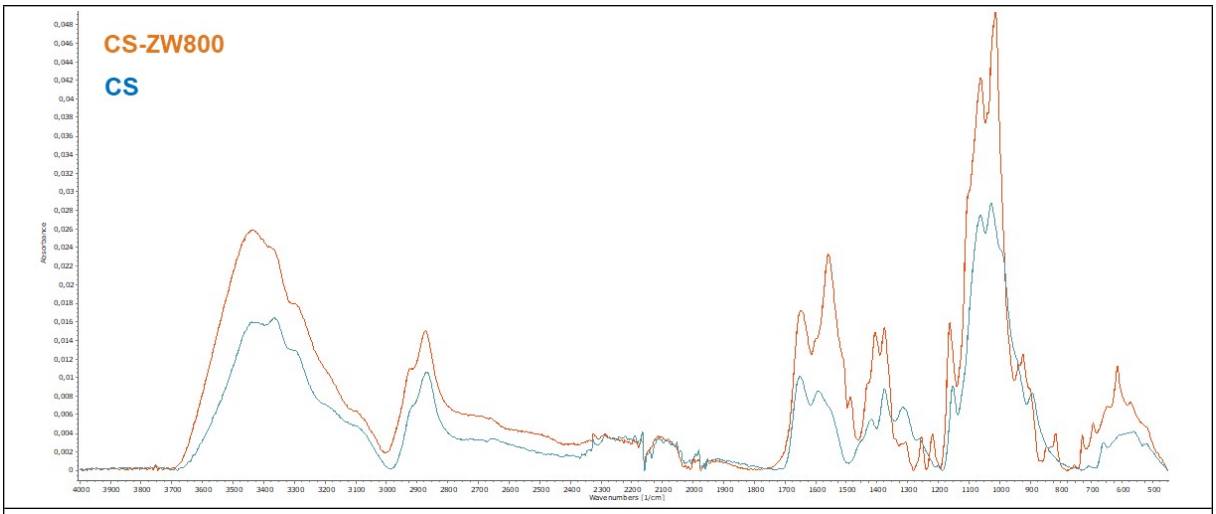


Fig. S6: FTIR spectra of CS, and CS-ZW800

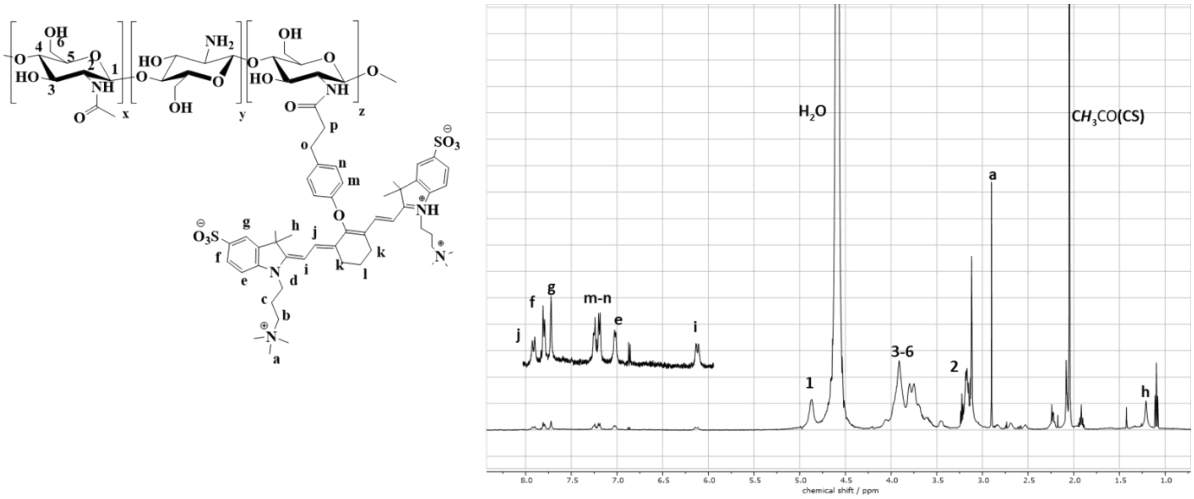


Fig. S7: ^{1}H NMR spectrum of CS-ZW800 (%mol $(ZW800\text{-}1/NH_2)_{initial}$ = 10%, 500 MHz, 318 K, D_2O/DCl (700/1, v/v))

Table S8: Evaluation of ZW800-1/$NH_{2\ (CS)}$ degree of association according to increasing ZW800-1/NH_2 CS initial ratios by a- absorption (λ_{abs} = 767 nm, ε = 108 652 L mol^{-1} cm^{-1}) and b- emission (λ_{abs} = 787 nm, $k_{787} = 3.58\times10^8$ L mol^{-1}) spectroscopies (mean values calculated from triplicates)

$(ZW800\text{-}1/NH_2)_{initial}$ [% mol]	**a**	**b**
10%	2.85%	2.66%
5%	1.16%	1.24%

Table S9: $(ZW800\text{-}1)_{Total}$/CS, $(ZW800\text{-}1)_{Grafted}$/($ZW800\text{-}1)_{Total}$ and $(ZW800\text{-}1)_{Grafted}$/CS ratios (mean values calculated from triplicates)

$(ZW800\text{-}1/NH_2)_{initial}$ [% mol]	**$(ZW800\text{-}1)_T$/CS [% mol] average**	**$(ZW800\text{-}1)_G$/ $(ZW800\text{-}1)_T$ [% mol] average**	**$DS_{CS}^{ZW800-1}$ = $ZW800\text{-}1_G$/ CS [% mol] average**
10	2.75	61	1.68
5	1.20	65	0.78

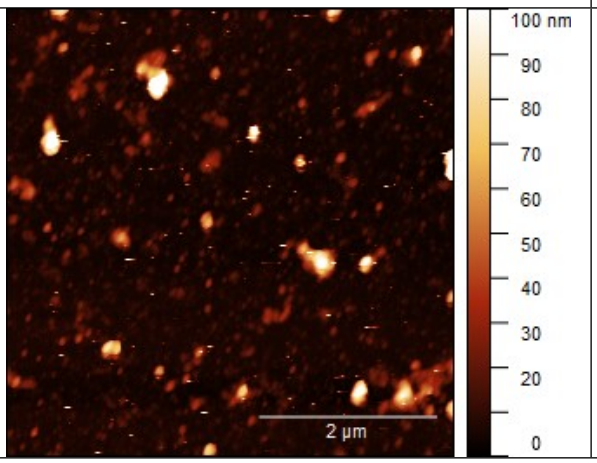
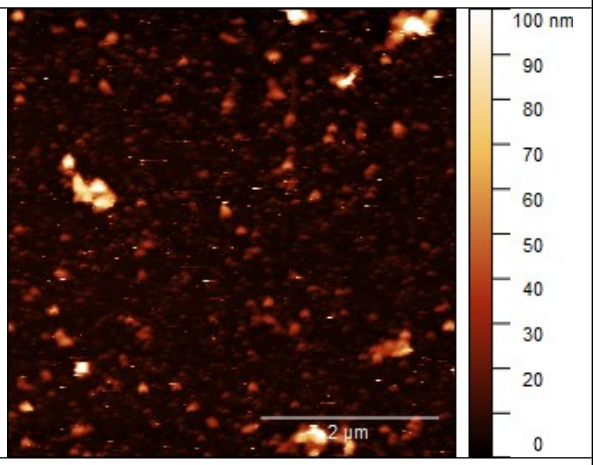
CS-ZW800-TPP/HA	**GdDOTA⊂CS-ZW800-TPP/HA**
	

Fig. S10: AFM images of CS-ZW800-TPP/HA and GdDOTA⊂CS-ZW800-TPP/HA NGs after purification

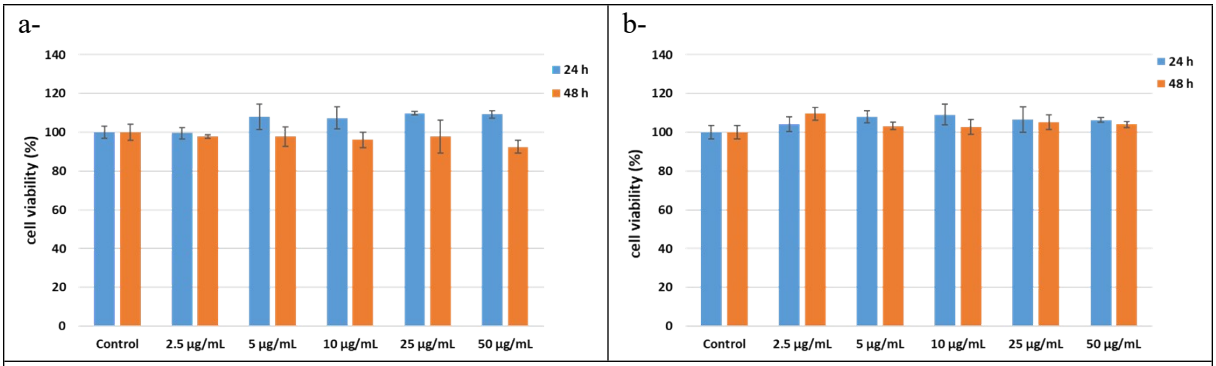


Fig. S11: Viability of RAW 264.7 cells after 24 and 48 hours of exposure to different concentrations of a- CS-ZW800-TPP/HA and b- GdDOTA⊂CS-ZW800-TPP/HA nanogels. Results are calculated as mean ± SD (n = 3) and expressed as percentage (%) of control

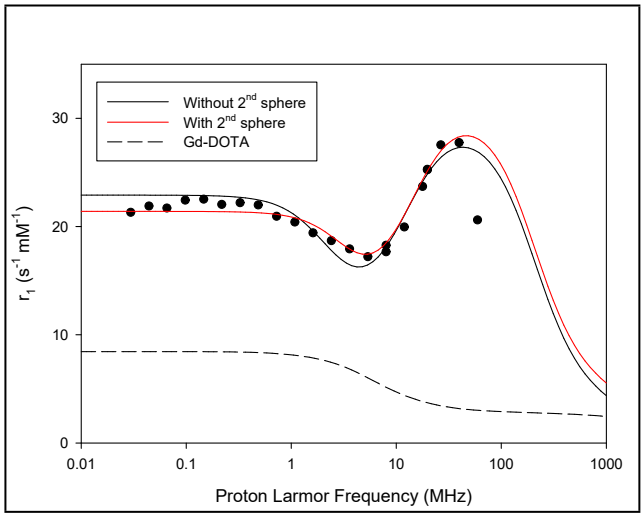


Fig. S12: Fit of the NMRD relaxivity profile of GdDOTA⊂CS-ZW800-TPP/HA nanogels at 37°C (black line = without second sphere, red line = with second sphere – dotted lines; GdDOTA control)

Table S13: Fitted parameters for the NMRD relaxivity profile of GdDOTA⊂CS-ZW800-TPP/HA nanogels

		SBM	SBM + SS
q(*)		1	
D	m^2s^{-1}	6.5×10^{-10}	
d(*)	nm	0.36	
r(*)	nm	0.31	
τ_R	ns	0.83	0.84
τ_V	ps	33.2	34.3
τso	ps	145	102
τ_M (*)	ns	100	
q_{ss}			2.4
τ_{ss} (*)	ps		40
r_{ss} (*)	nm		0.36

(*) = parameters fixed during the fit