Supplementary Information

Comparative studies of electronic, binding and photophysical properties of a new nona-dentate hemi-cage tripodal HQ pendant trizaza-macrocycle with unfilled, half-filled and completely filled lanthanide ions

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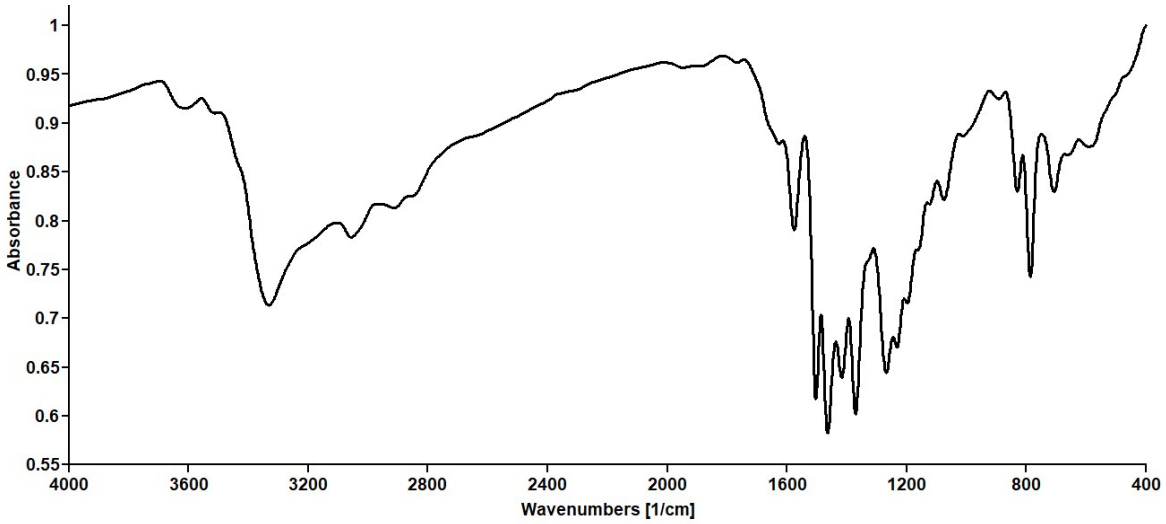


Fig. S1 Experimental FTIR spectra of 9N3Me5Ox in KBr.

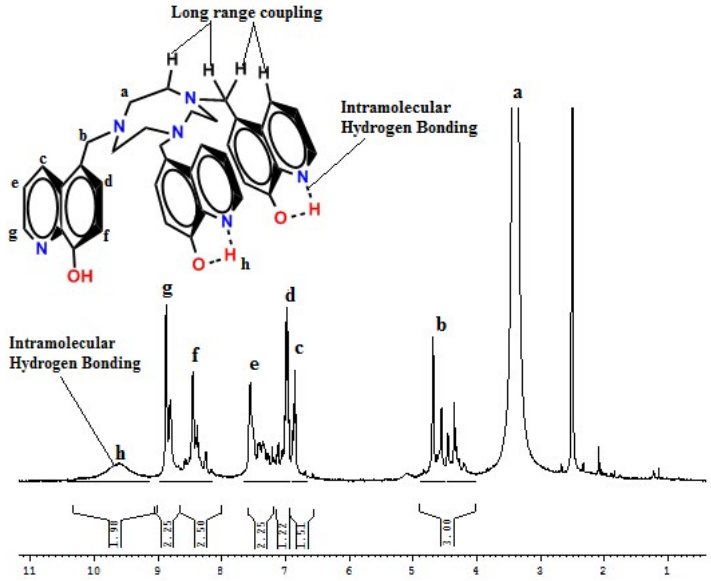


Fig. S2 Experimental ^{1}H NMR spectra of 9N3Me5Ox in DMSO-d_6 solution.

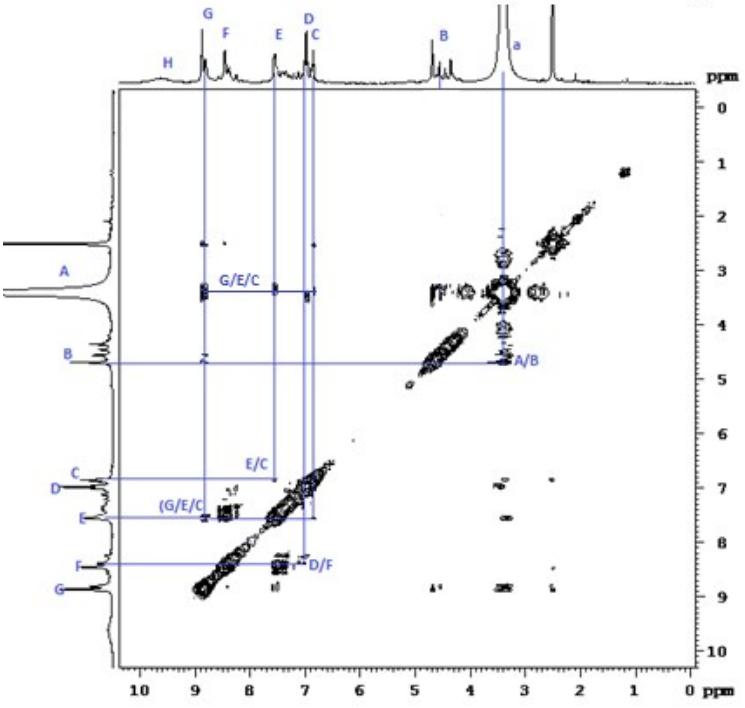


Fig. S3 Experimental ^{1}H-^{1}H COSY spectra of 9N3Me5Ox in DMSO-d_6.

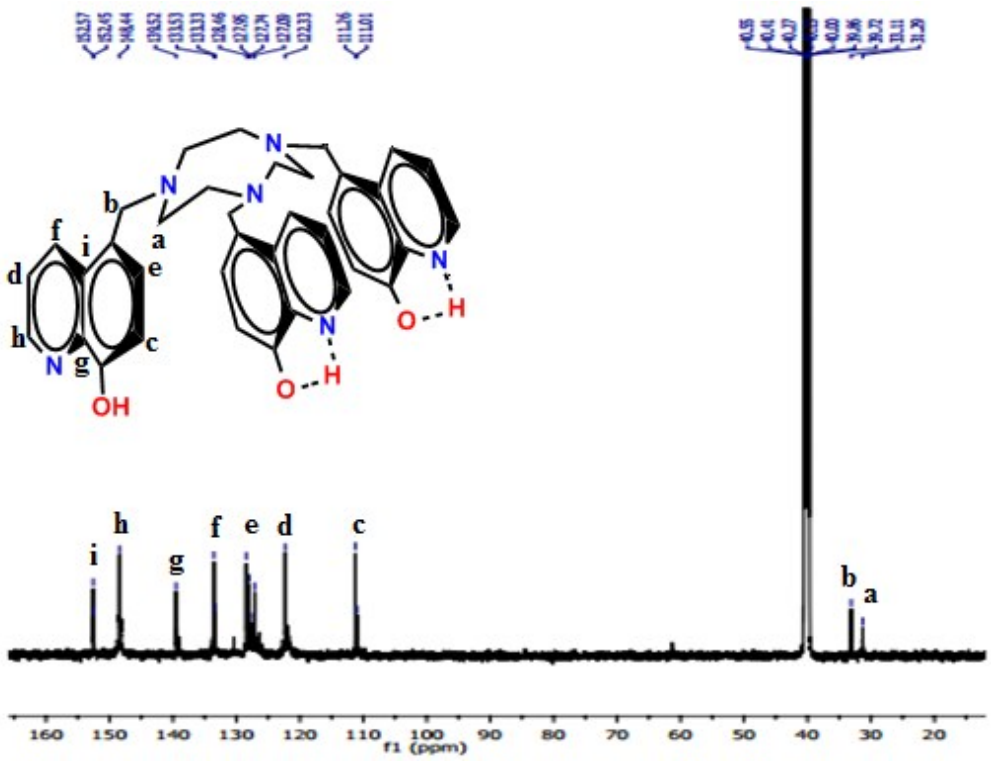


Fig. S4 Experimental ^{13}CNMR of 9N3Me5Ox in DMSO-d_6.

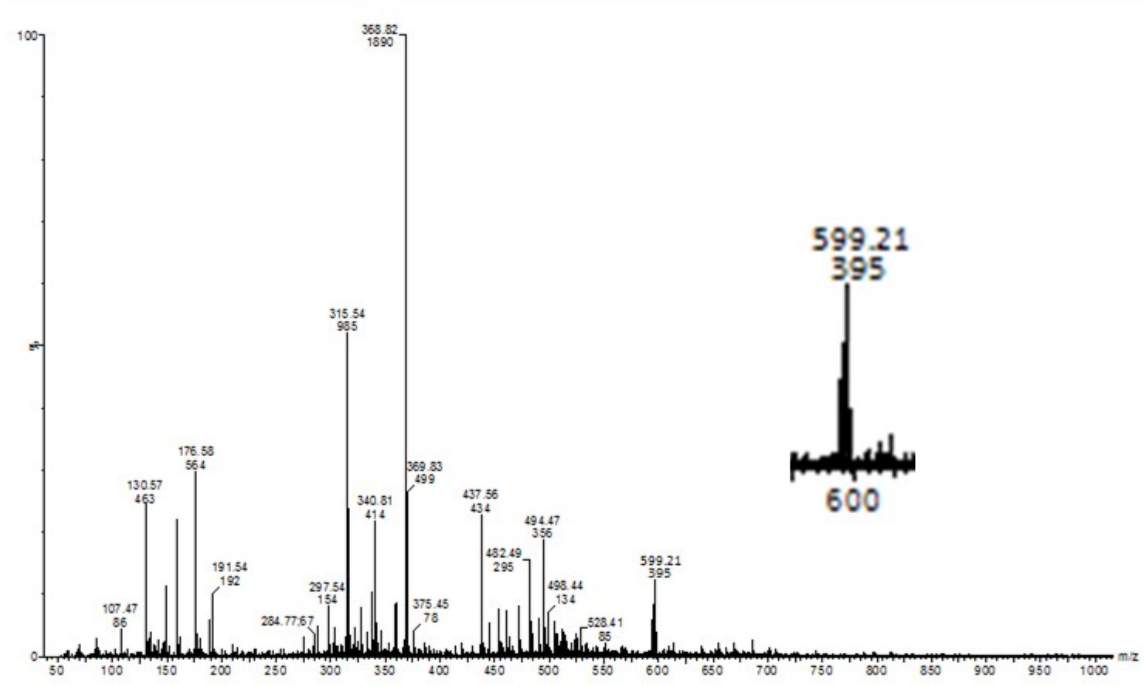
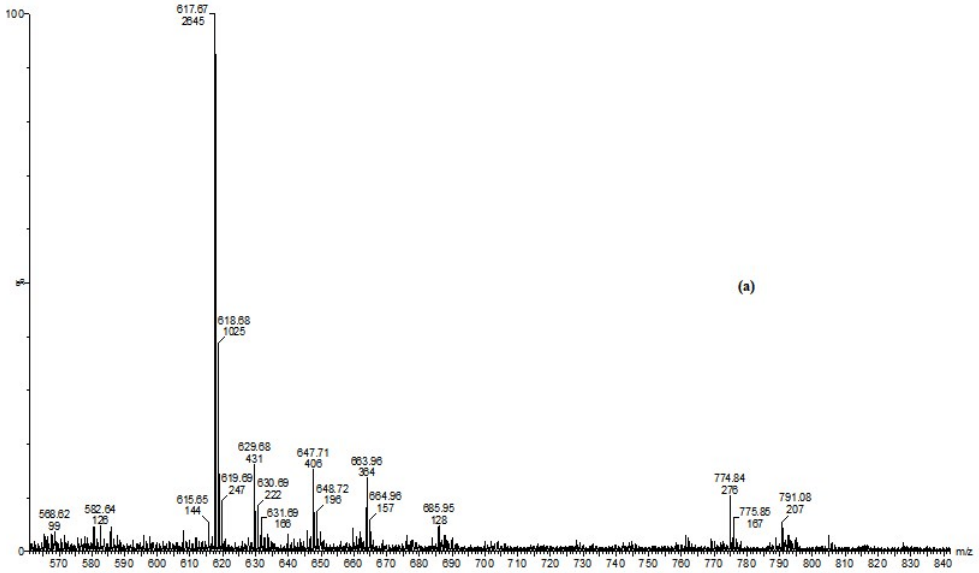


Fig. S5 Mass (ES^+) spectra of 9N3Me5Ox.



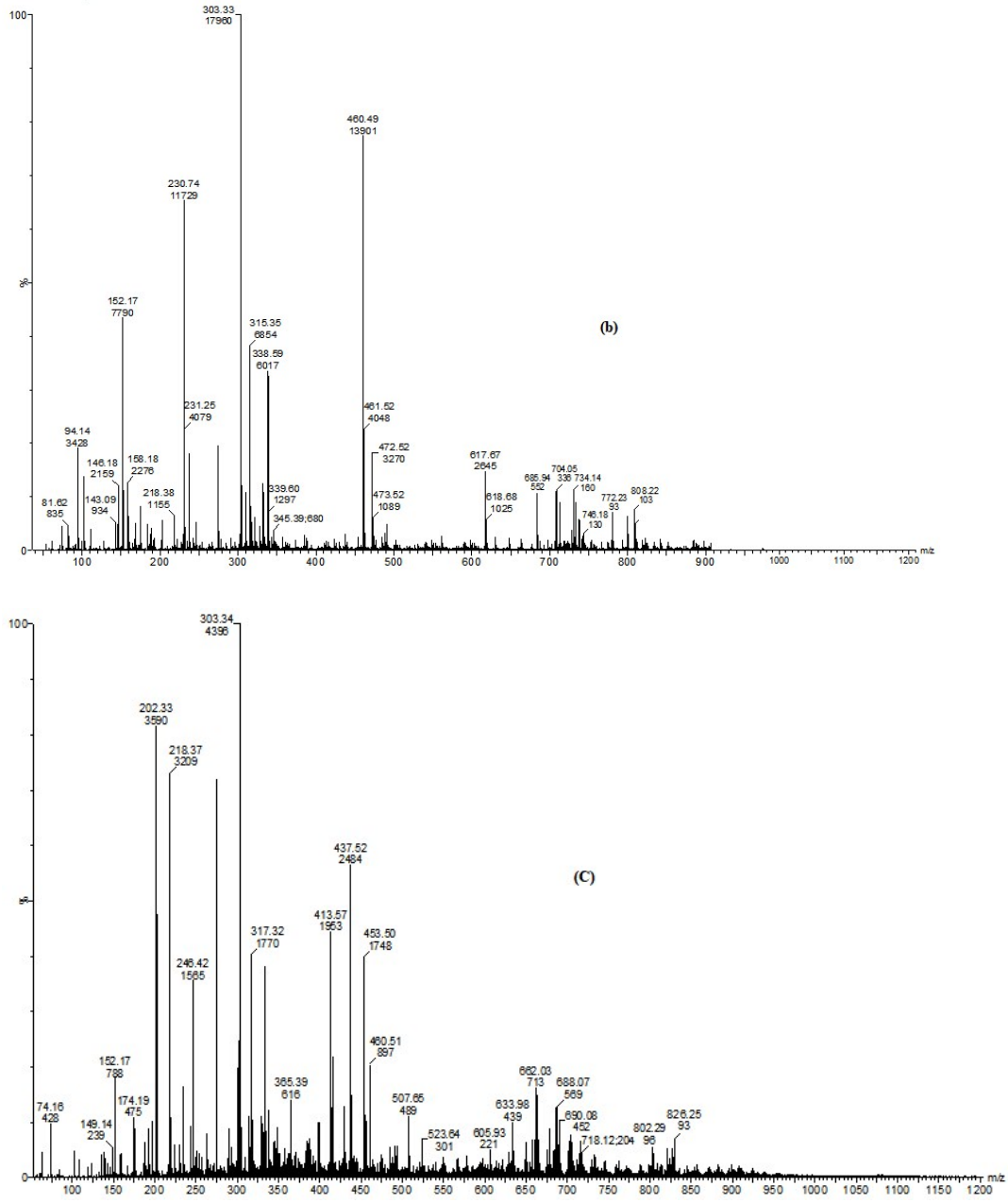


Fig. S6 MS(ES$^+$) mass spectra of (a) [La(9N3Me5Ox)(H_2O)$_3$] (b) [Gd(9N3Me5Ox)(H_2O)$_3$] and (c) [Lu(9N3Me5Ox)(H_2O)$_3$].

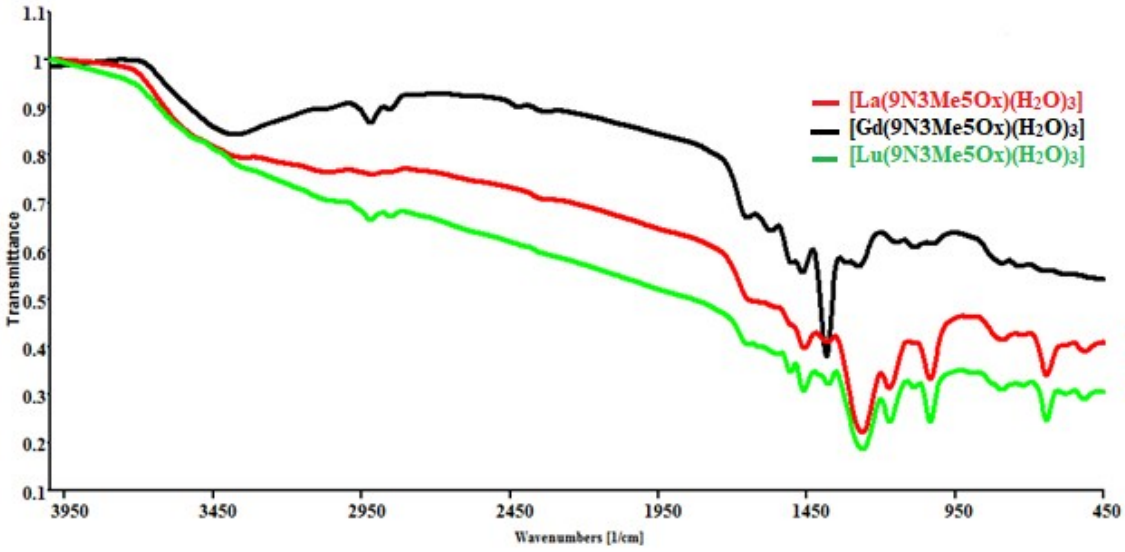
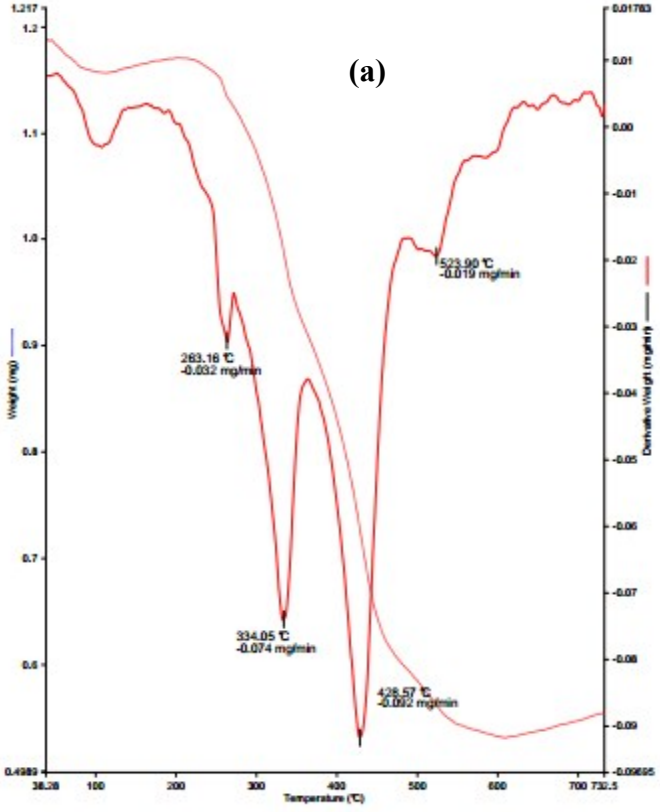


Fig. S7 Experimental IR spectra of [La(9N3Me5Ox)(H_2O)$_3$], [Gd(9N3Me5Ox)(H_2O)$_3$], and [Lu(9N3Me5Ox)(H_2O)$_3$] in KBr.



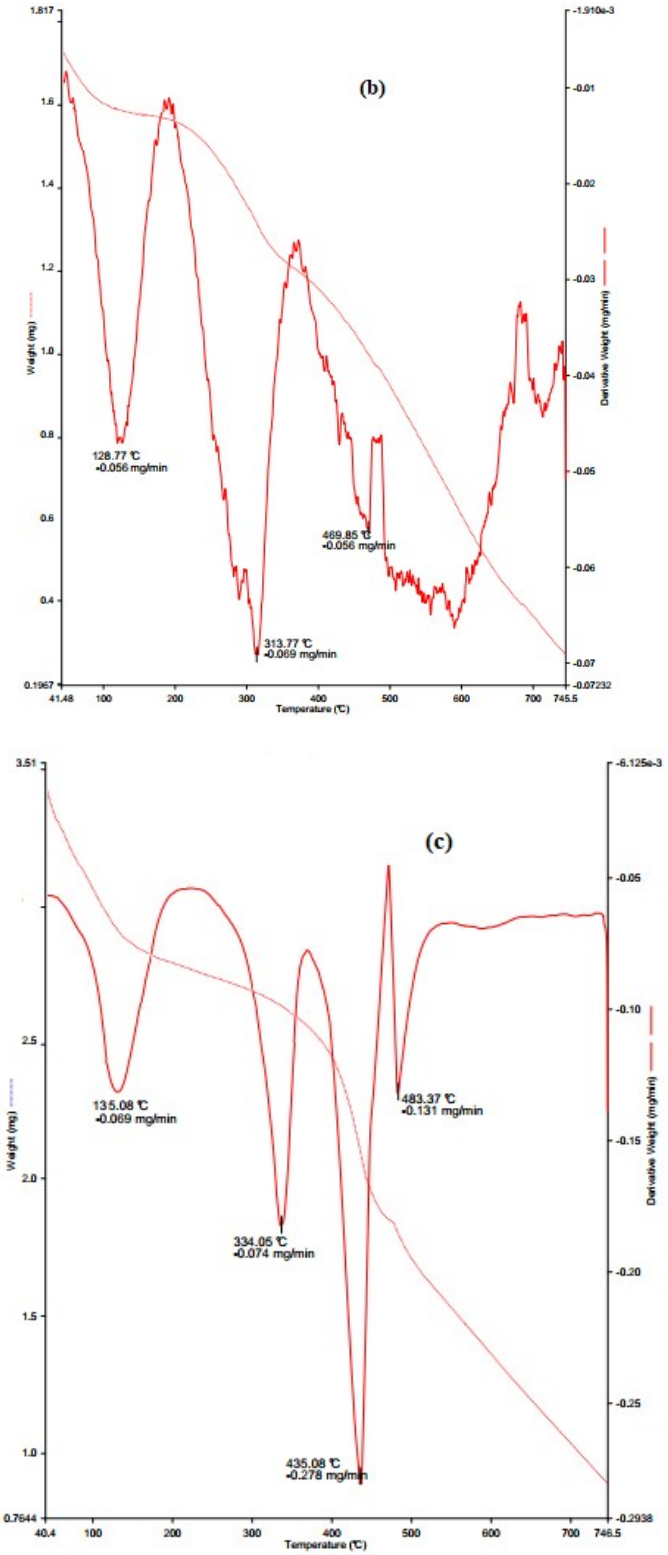


Fig. S8 TG-DTG analysis of (a) [La(9N3Me5Ox)$(H_2O)_3$], (b) [Gd(9N3Me5Ox)$(H_2O)_3$] and (c) [Lu(9N3Me5Ox)$(H_2O)_3$] metal complex, heat from 40.0 ^oC and 750 ^oC temperature at 20.00 ^oC/min.

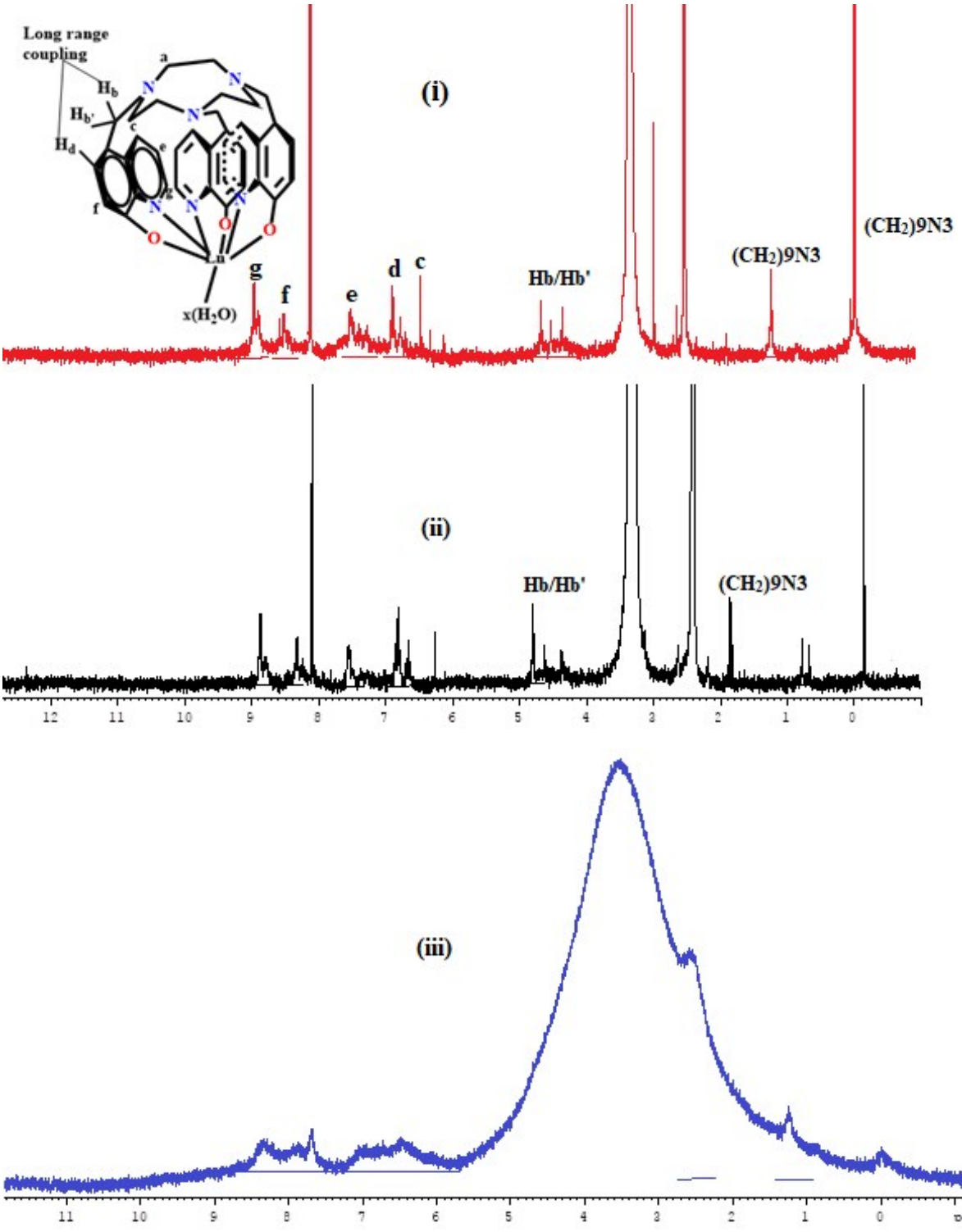


Fig. S9 Experimental ^{1}H NMR spectra of 9N3Me5Ox metal complexes (i) [La(9N3Me5Ox)$(H_2O)_3$], (ii) [Lu(9N3Me5Ox)$(H_2O)_3$], and (iii) [Gd(9N3Me5Ox)$(H_2O)_3$].

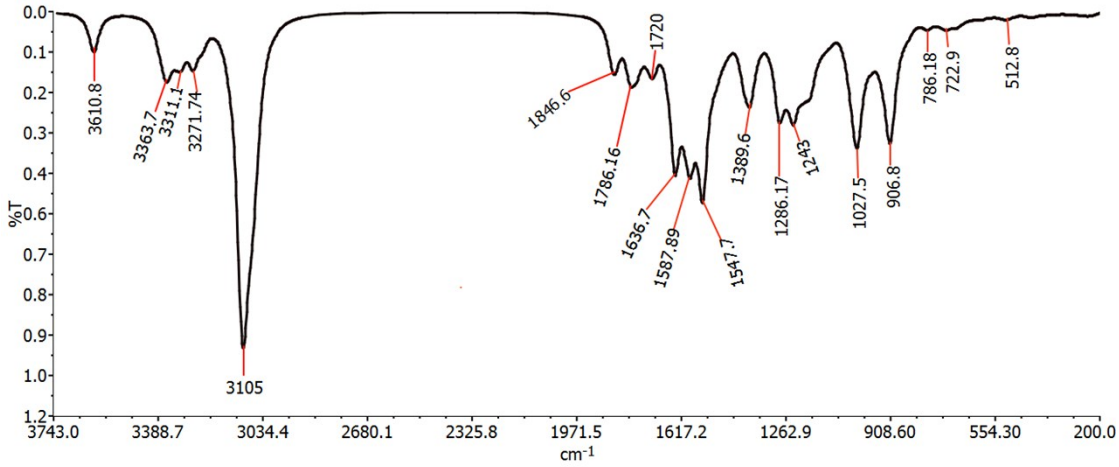


Fig. S10 Theorectical FTIR spectra of the 9N3Me5Ox ligand, calculated with GGA/BLYP method.

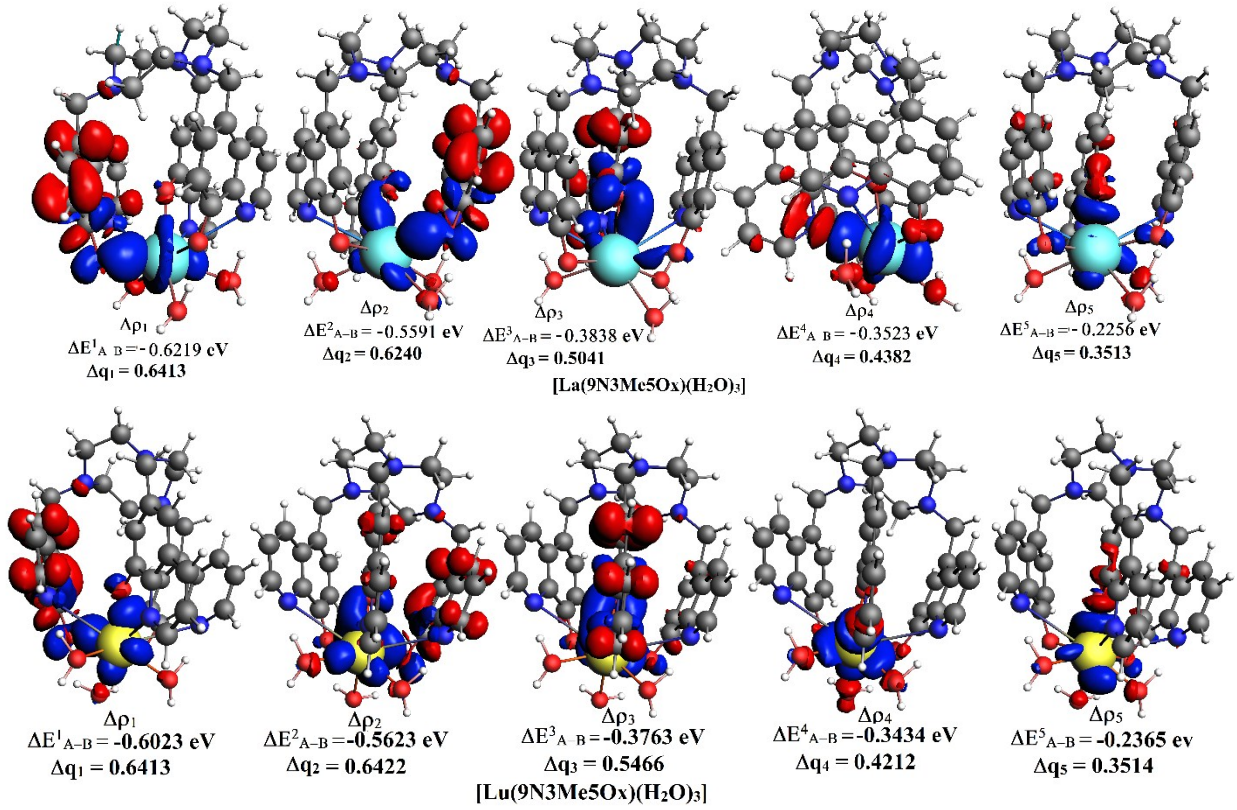


Fig. S11. Contours of deformation density channels, $\Delta\rho i$ describing donation {A ([9N3Me5Ox] $^{3-}$) - B (Ln^{3+}) }together with the corresponding energies, $\Delta E^{orb}{}_{A-B}$, obtained from the ETS-NOCV method. The isovalue of the contours is 0.007 a.u.

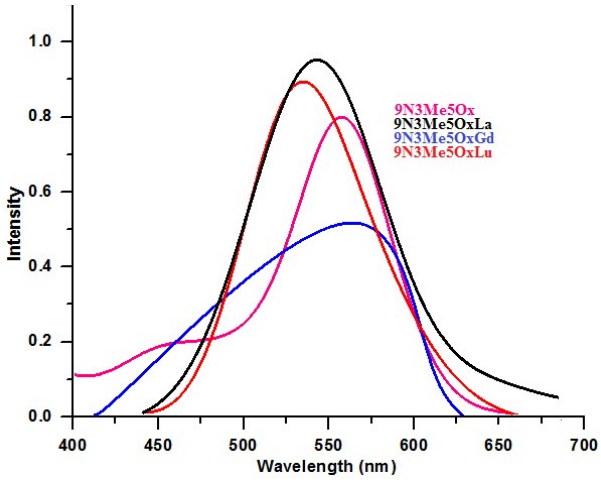


Fig. S12 Calculated Emission spectra of 9N3Me5Ox ligand and [Ln(9N3Me5Ox)(H_2O)$_3$].

Table 1. Frontier molecular orbital (FMOs) composition based on atomic orbitals (AOs) contribution and their relative energies (eV) for all [Ln(9N3Me5Ox)(H_2O)$_3$].

Closed Shell						Open Shell		
[La(9N3Me5Ox)(H_2O)$_3$]			[Lu(9N3Me5Ox)(H_2O)$_3$]			[Gd(9N3Me5Ox)(H_2O)$_3$]		
MO	**E(ev)**	**AOs(%)**	**MO**	**E(ev)**	**AOs(%)**	**MO**	**E(ev)**	**AOs(%)**
192a	-6.133	p_xC(87.9)	199a	-6.235	p_xC(77.3)	192α	-6.417	p_xC(77.3)
		p_xN(1.44)			p_zC(3.35)			p_zC(3.35)
193a	-6.032	p_yO(44.8)	200a	-5.891	p_zO(65.3)	195β	-6.128	p_xO(59.0)
		p_zO(34.6)			p_zC(8.02)			p_xC(23.7)
		p_yC(4.55)			d_{xy}Lu(1.26)			d_{xy}Gd(1.35)
194a	-5.782	p_zO(69.0)	201a	-5.767	p_yO(38.1)	199α	-5.853	p_yO(39.1)
		p_zC(8.39)			p_zO(27.6)			p_xO(34.4)
		d_{yz}La(1.92)			d_{yz}Lu(1.92)			p_xC(5.65)
195a	-5.642	p_yO(45.5)	202a	-5.646	p_yO(45.9)	202β	-5.783	f_zGd(60.9)
		p_zO(26.8)			p_zO(27.8)			f_{z2y}Gd(12.0)
		p_yC(4.37)			p_yC(4.37)			f_xGd(11.8)
								f_{xyz}Gd(10.5)
196a	-4.968	p_xC(27.8)	203a	-4.852	p_xC(31.7)	204α	-5.023	f_xGd(40.0)
		p_yN(16.7)			p_xO(14.5)			f_{z2y}Gd(28.0)
		p_xN(10.5)			p_zN(13.5)			f_{z3}Gd(13.5)
								f_yGd(8.10)
197a	-4.840	p_xC(27.0)	204a	-4.797	p_xC(43.5)	206β	-4.813	f_{z2x}Gd(56.2)
		p_zN(16.7)			p_xO(17.6)			f_xGd(22.4)
		p_yN(9.46)			p_yO(3.45)			f_{z3}Gd(8.48)
								f_yGd(4.59)
198a	-4.722	p_xC(49.0)	205a	-4.741	p_xC(18.7)	200α	-4.694	f_{xyz}Gd(70.6)

		p_xO(20.7) p_zN(4.60)			p_zN(18.3) p_yN(12.1)			f_zGd(12.7) f_{z2x}Gd(4.64) f_{z3}Gd(4.30)
199a	-4.567	p_zN(26.4) p_yN(18.7) p_xC(14.2)	206a	-4.603	p_xC(43.1) p_xO(23.4) p_yC(4.24)	203β	-4.671	f_{z2y}Gd(43.5) f_{z2x}Gd(22.0) f_zGd(16.0) f_xGd(7.05)
200a	-4.529	p_xC(42.3) p_xO(19.7) p_yN(11.9)	207a	-4.543	p_zN(35.8) p_yN(26.1) sH(12.7)	207β	-4.396	f_{z3}Gd(44.8) f_yGd(21.1) f_xGd(7.65) f_{xyz}Gd(6.47)
201a	-4.260	p_zN(38.4) p_yN(20.9) $_s$ H (14.2)	208a	-4.371	p_zN(40.9) p_yN(19.7) $_s$ H (17.2)	201α	-3.690	p_xN(64.3) p_xC(20.7) p_xN(19.2)
202a HOMO	-2.810	p_xC(63.6) p_xN(20.3) p_yN(11.9)	209a HOMO	-2.638	p_xC(61.8) p_xN(19.3) p_yN(13.2)	205β SOMO	-2.782	p_xC(61.8) p_xN(19.2) p_yC(12.4)
203a LUMO	-2.518	p_xC(64.2) p_xN(20.9) d_{xy}La(2.34)	210a LUMO	-2.580	p_xC(58.1) p_xN(19.45) d_{xy}Lu(1.38)	210β SOMO	-2.572	p_xC(58.9) p_xN(16.8) d_{xy}Gd(1.38)
204a	-2.340	p_xC(70.3) p_xN(19.2) p_yO(1.43)	211a	-2.451	p_xC(57.7) p_xN(17.4) p_yC(8.29)	214α	-2.499	p_xC(49.7) p_xN(14.2) p_yC(13.7)
205a	-1.451	p_xC(90.8) f_yLa(1.12)	212a	-1.501	p_xC(83.3) p_yC(7.32)	209α	-1.713	p_xC(87.6) p_yC(8.94) sH(1.13)
206a	-1.391	p_xC(82.8) f_{xyz}La(1.19)	213a	-1.445	p_xC(81.8) p_yC(7.95)	218β	-1.524	p_xC(83.9) p_yC(17.4)
207a	-1.341	p_xC(88.4) f_xLa(1.74) f_{z2x}La(1.49) f_{xy}La(1.44)	214a	-1.374	p_xC(85.6) p_yC(11.8)	220α	-1.462	p_xC(79.9) p_yC(19.7)
208a	-1.261	f_{z2y}La(60.7) f_yLa(8.07) f_zLa(6.88)	215a	-0.570	p_xC(85.6) sH(40.6) d_{yz}Lu(1.39)	215β	-1.190	dz^2Gd(40.8) sH(18.8) sGd(15.1) p_xGd(7.84)
209a	-1.172	fz^3La(53.1) f_zLa(21.3) f_{z2y}La(8.11)	216a	-0.501	sH(48.9) p_xC(26.9) dz^2Lu(3.09)	212α	-0.739	p_xC(26.3) sH(25.9) d_{yx}Gd(10.2) dx^2Gd(8.67) sGd(15.1)
210a	-1.154	f_{xy}La(43.0)	217a	-0.464	p_xC(58.9)	222α	-0.627	p_xC(35.7)

		f_{z2x}La(32.3) f_{y}La(15.2)			p_{y}C(13.5) d_{xy}Lu(1.26)			d_{xy}Gd(16.7) d_{yx}Gd(3.54) $dx^2 - y^2$Gd(2.37)
211a	-1.124	f_{y}La(37.5) fz^3La(26.4) f_{z2y}La(20.0)	218a	-0.395	p_{x}C(67.8) $p_{x}N$(5.41) d_{xz}Lu(1.02)	219β	-0.547	p_{x}C(54.0) $p_{x}N$(4.56) d_{xy}Gd(3.10) d_{yx}Gd(1.47)

Optimized coordinates of metal complex using GGA-BLYP-D3

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La        3.32861950        7.35082750       -3.89026689
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