

Electronic Supporting Information

New insights into bioactive Ga(III) hydroxyquinolate complexes from UV-vis, fluorescence and multinuclear high-field NMR studies

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Table S1. B3LYP and ω B97X-D3 excitation/emission energies in DMSO for [Ga(Br₂-HQ)₃].

Transition	B3LYP		ω B97X-D3	
	Energy [eV]	Wavelength [nm]	Energy [eV]	Wavelength [nm]
S1 vert Exc	2.90	428	3.69	336
S1 vert Em	2.05	605	2.81	442
T1 vert Exc	2.33	532	2.74	453
T1 vert Em	1.64	758	1.60	774

Table S2. B3LYP and ω B97X-D3 energy comparison of the *mer*- and *fac*-isomers of [Ga(Br₂-HQ)₃] in DMSO and vacuum (kJ/mol).

Isomer	B3LYP-D3 DMSO	B3LYP-D3 vac	ω B97X-D3 DMSO	ω B97X-D3 vac
<i>mer</i>	0	0	0	0
<i>fac</i>	5.3	26.3	7.8	30.8

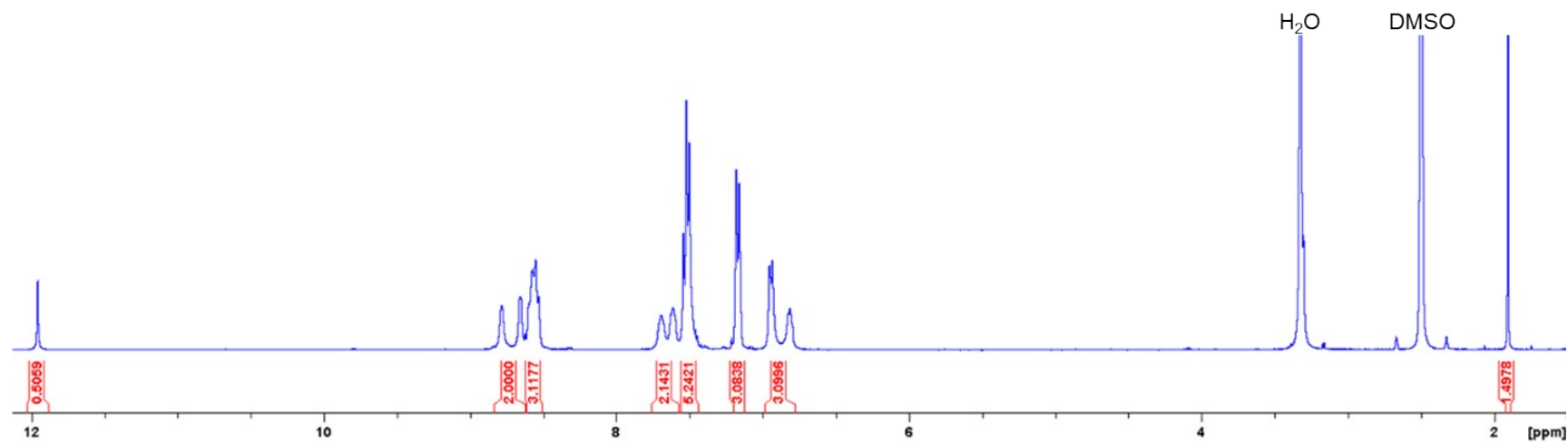
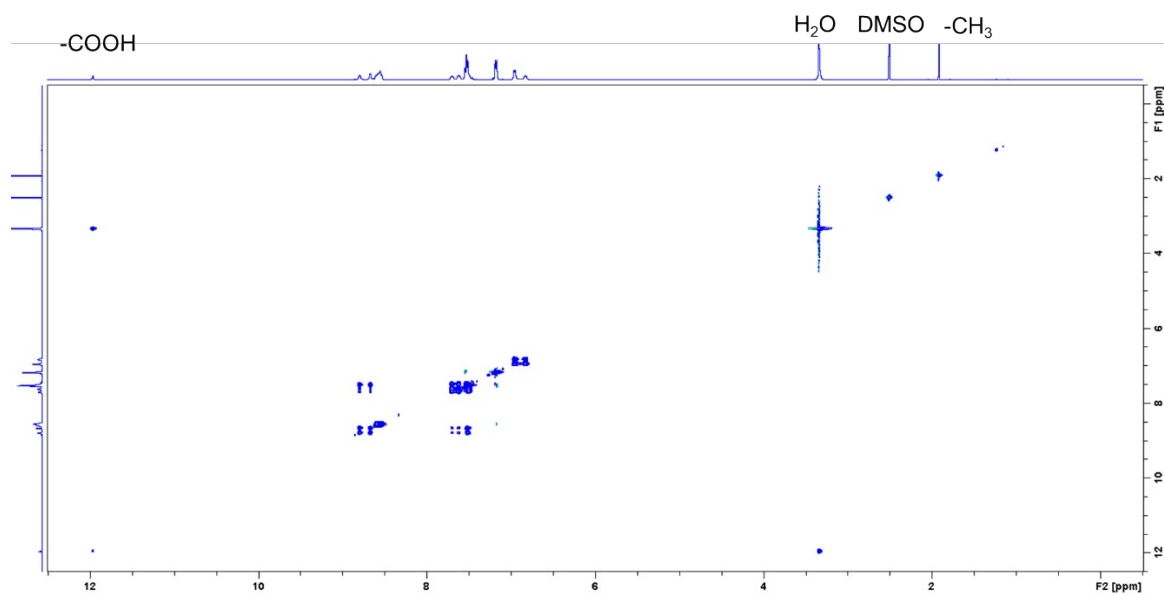
A**B**

Figure S1. (A) 500 MHz ¹H-NMR spectrum of [Ga(HQ)₃].0.5CH₃COOH in DMSO-*d*₆ (B) 500 MHz ¹H-¹H NOESY [Ga(HQ)].0.5CH₃COOH NMR spectrum in DMSO-*d*₆, mixing time 0.6 s.

The cross peak at 11.99/3.33 ppm is assigned to exchange between the -COOH of acetic acid and H₂O.

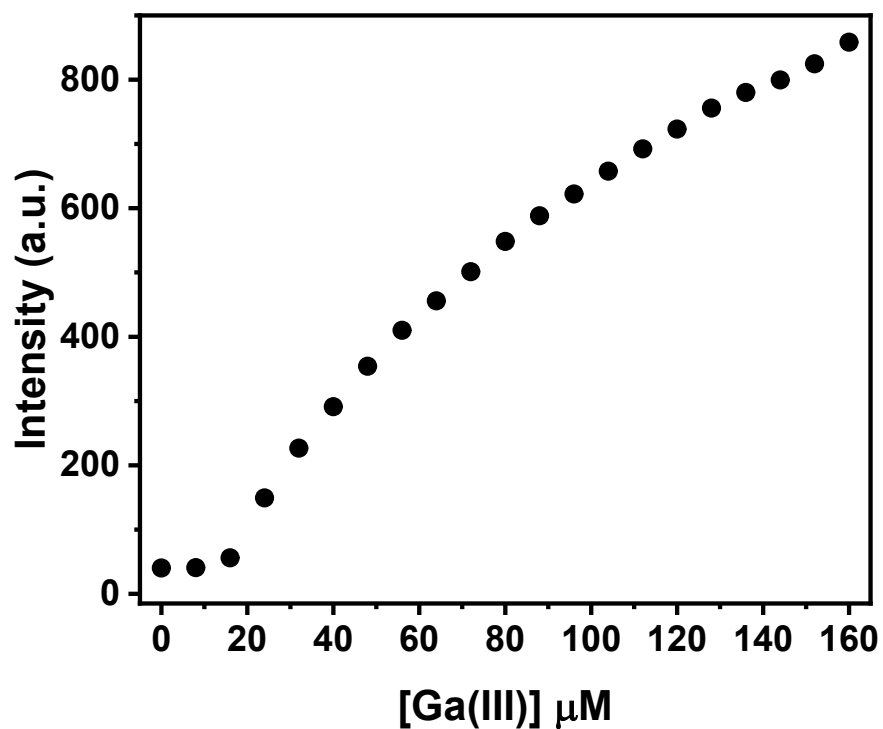


Figure S2. Variation of the intensity of emission at 550 nm on excitation at 400 nm with increasing Ga concentration on addition of aliquots of 0.6 μL $\text{Ga}(\text{NO}_3)_3$ in water (0.065 mol equiv, 8 μM) to $\text{Br}_2\text{-HQH}$ (1 mol equiv, 0.16 mM) in 99.6% DMSO/ 0.4% DMF (v/v). See Figure 2B.

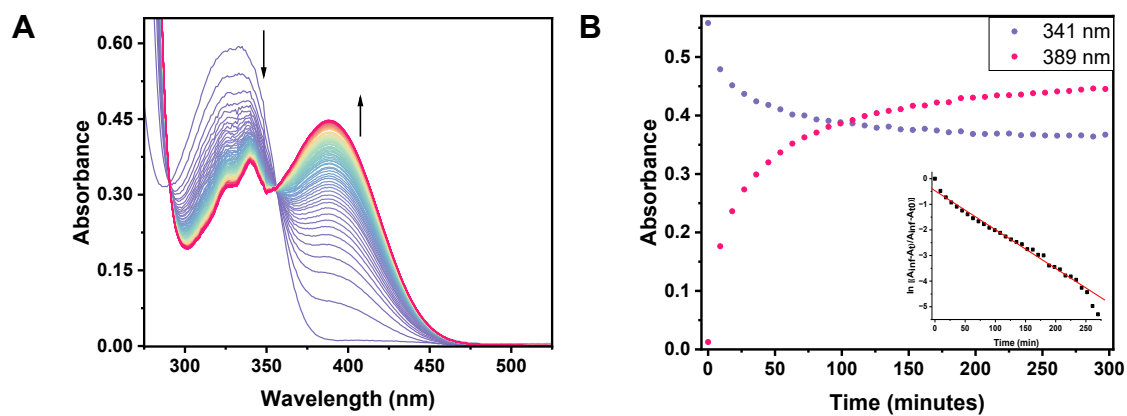


Figure S3. (A) Time-dependent changes in the UV-vis absorption spectrum after addition of $\text{Ga}(\text{NO}_3)_3$ (0.67 mol equiv, 0.10 mM) in water to $\text{Br}_2\text{-HQH}$ (1 mol equiv, 0.15 mM) solution in 99.6% DMSO/ 0.4% DMF (v/v). (B) Changes in absorbance at 341 nm from $\text{Br}_2\text{-HQH}$ and the new band at 389 nm from $[\text{Ga}(\text{Br}_2\text{-HQ})_3]$. The inset shows the best fit of $\log A$ vs. time (red line), giving the first-order rate constants in Table 1.

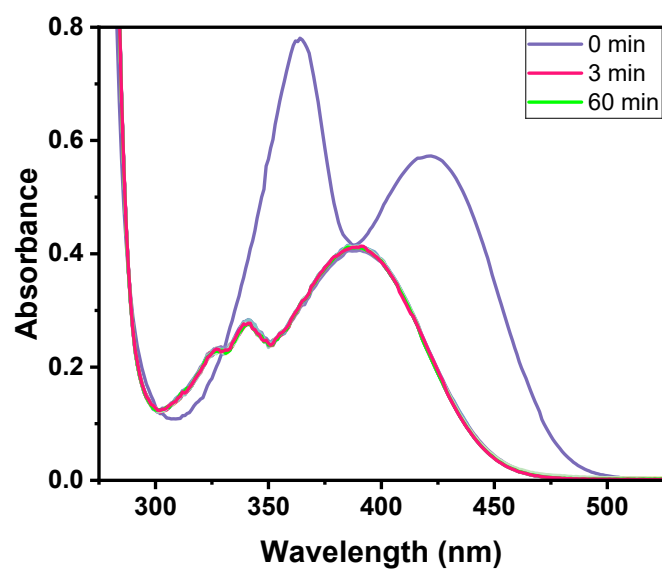


Figure S4. Time-dependent changes in the UV-vis absorption spectrum for Ga(NO₃)₃ (0.33 mol equiv, 0.05 mM) in water after addition of Br₂-HQ (1 mol equiv, 0.15 mM) in DMSO (0.4% DMF (v/v)).

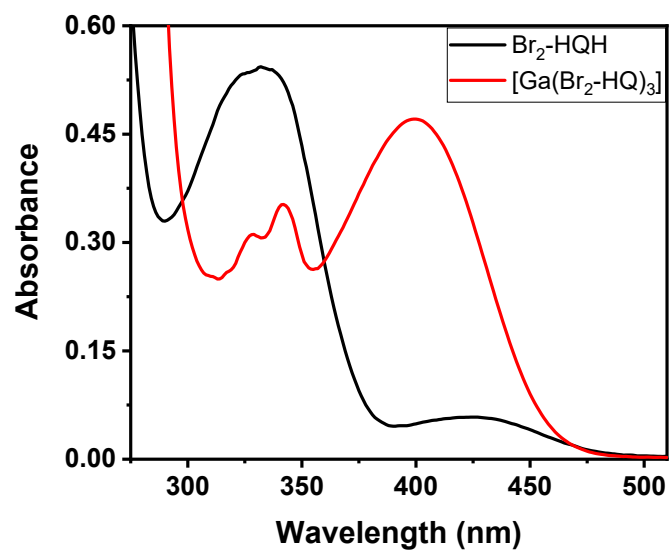


Figure S5. UV-vis spectra of $\text{Br}_2\text{-HQH}$ (0.15 mM in 99.6% DMSO/ 0.4% DMF (v/v)) and synthesised $[\text{Ga}(\text{Br}_2\text{-HQ})_3]$ (0.045 mM) in DMSO.

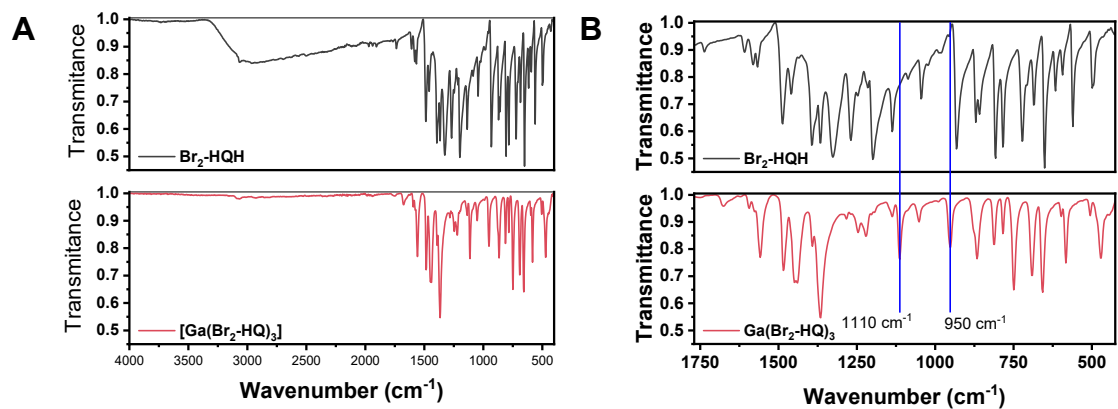


Figure S6. FT-IR comparison of Br₂-HQH and [Ga(Br₂-HQ)₃] between (A) 4000 to 450 cm⁻¹; the band assignable to the phenolic -OH disappears upon coordination. (B) Finger print region between 1800 to 450 cm⁻¹ where two new peaks at 950 and 1110 cm⁻¹ assignable to Ga(III)-O bonds appear.

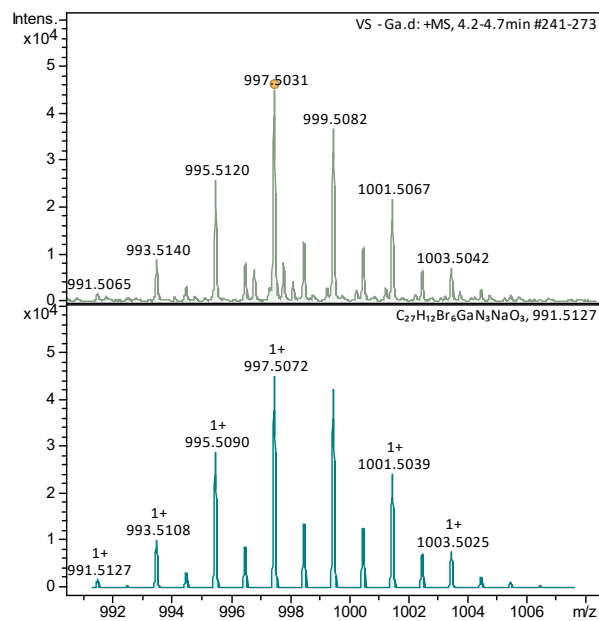


Figure S7. Observed (top) and calculated (bottom) HR-MS for $\{[\text{Ga}(\text{Br}_2\text{-HQ})_3] + \text{Na}\}^+$

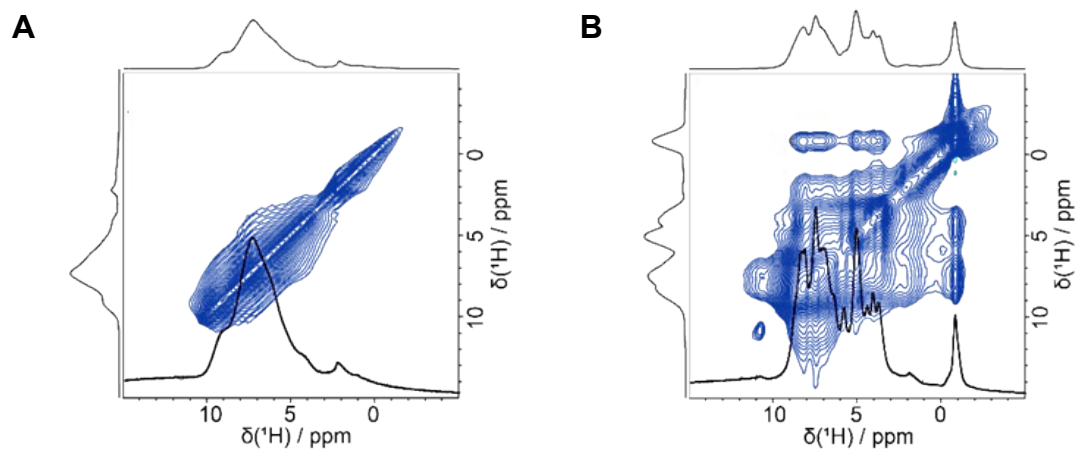


Figure S8. 850 MHz ^1H - ^1H NOESY 2D solid state MAS NMR spectra of (A) $[\text{Ga}(\text{Br}_2\text{-HQ})_3]$ and (B) $[\text{Ga}(\text{HQ})_3] \cdot 0.5 \text{CH}_3\text{CO}_2\text{H}$ (mixing time of 5 ms).

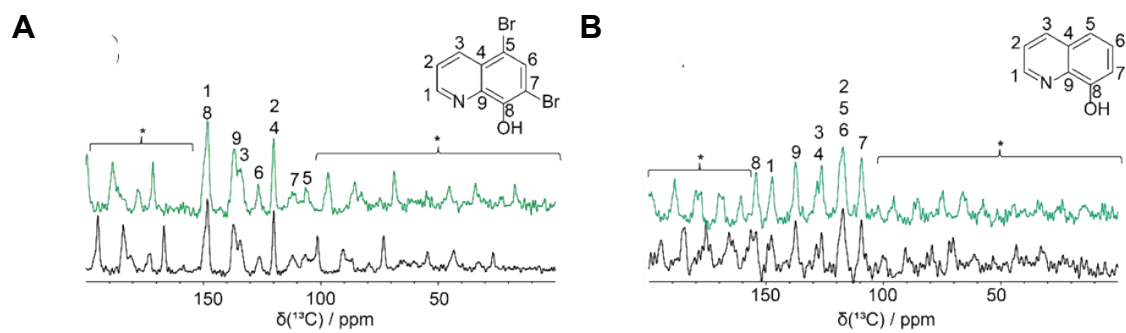


Figure S9. ^{13}C CPMAS NMR spectra of $\text{Br}_2\text{-HQH}$ (A) and HQH (B) at spinning rates at 10 kHz (black) and 11 kHz (green). Peaks assigned to the ligands have chemical shifts independent of spinning rate. * = Spinning side bands.

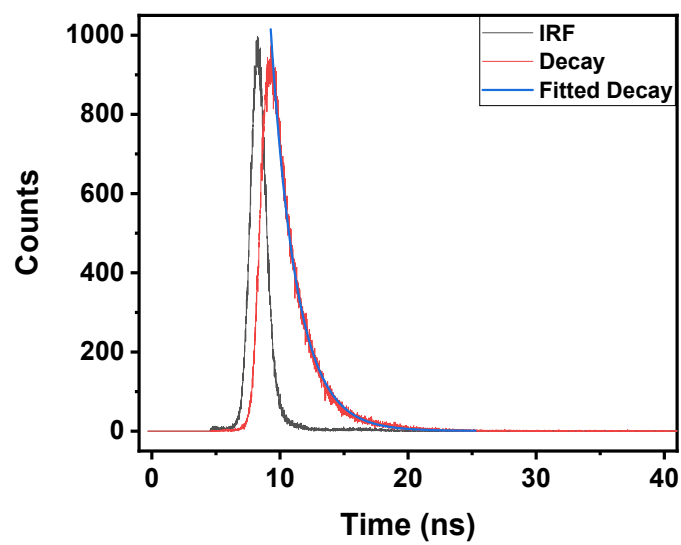


Figure S10. Lifetime decay of [Ga(Br₂-HQ)₃] (1 μM) in DMSO with $\lambda_{\text{ex}}=405$ nm. The decay was fitted to a monoexponential function with decay constant of 1.32 ns.

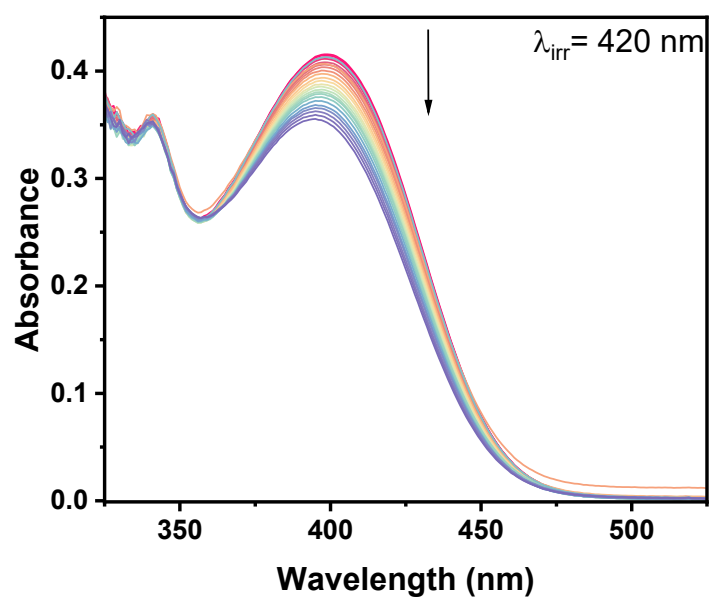


Figure S11. Photostability of [Ga(Br₂-HQ)₃] (0.03 mM) in DMSO under irradiation for 15 min using blue light (420 nm) followed by UV-vis spectroscopy. A decomposition of 13% was observed.

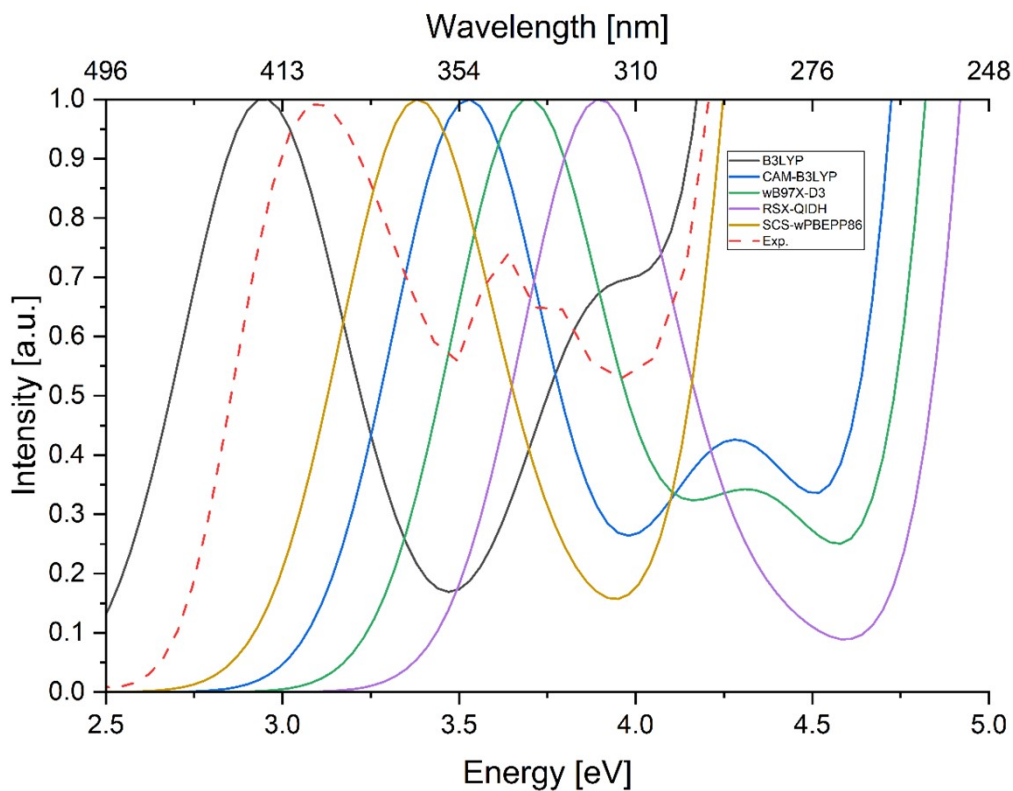


Figure S12. Comparison of the UV-vis absorption spectrum of $[\text{Ga}(\text{Br}_2\text{-HQ})_3]$ in DMSO with those calculated using the DFT functionals B3LYP, CAM-B3LYP, $\omega\text{B97X-D3}$, RSX-QIDH and SCS- ωPBEP86 (see section 2.11). While all functionals show the right intensity pattern of the experimental absorption spectrum, excitation energies vary, with B3LYP giving the best fit to experiment.

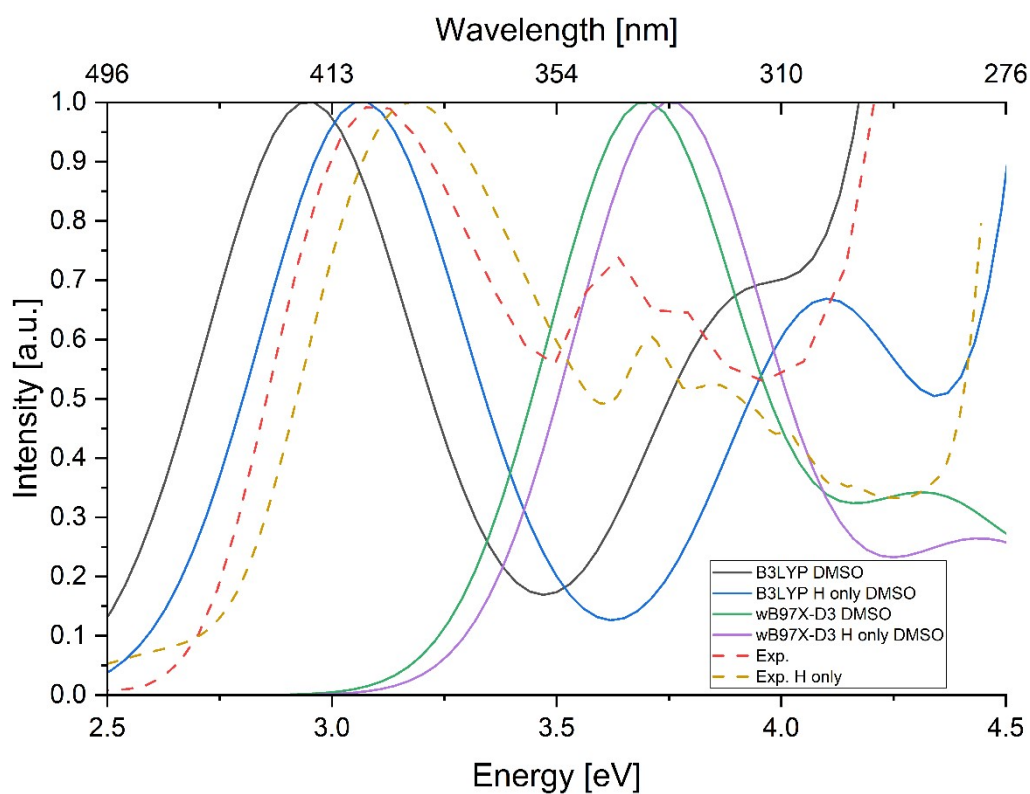


Figure S13. Comparison of the observed UV-vis absorption spectra for $[\text{Ga}(\text{HQ})_3]$ (yellow hashed line) and $[\text{Ga}(\text{Br}_2\text{-HQ})_3]$ (red hashed line) in DMSO with those calculated for $[\text{Ga}(\text{Br}_2\text{-HQ})_3]$ using the B3LYP and $\omega\text{B97X-D3}$ functionals. Both functionals reproduce the experimentally observed hypsochromic shift when replacing Br with H. Again, B3LYP is the best fit to experiment.