**Electronic Supporting Information**

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

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## Contents

**Table S1**. B3LYP and ωB97X-D3 excitation/emission energies in DMSO for [Ga($Br_2$-HQ)$_3$].

| Transition | B3LYP | | ωB97X-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 ωB97X-D3 energy comparison of the *mer*- and *fac*-isomers of [Ga($Br_2$-HQ)$_3$] in DMSO and vacuum (kJ/mol).

| Isomer | B3LYP-D3 DMSO | B3LYP-D3 vac | ωB97X-D3 DMSO | ωB97X-D3 vac |
|---|---|---|---|---|
| *mer* | 0 | 0 | 0 | 0 |
| *fac* | 5.3 | 26.3 | 7.8 | 30.8 |

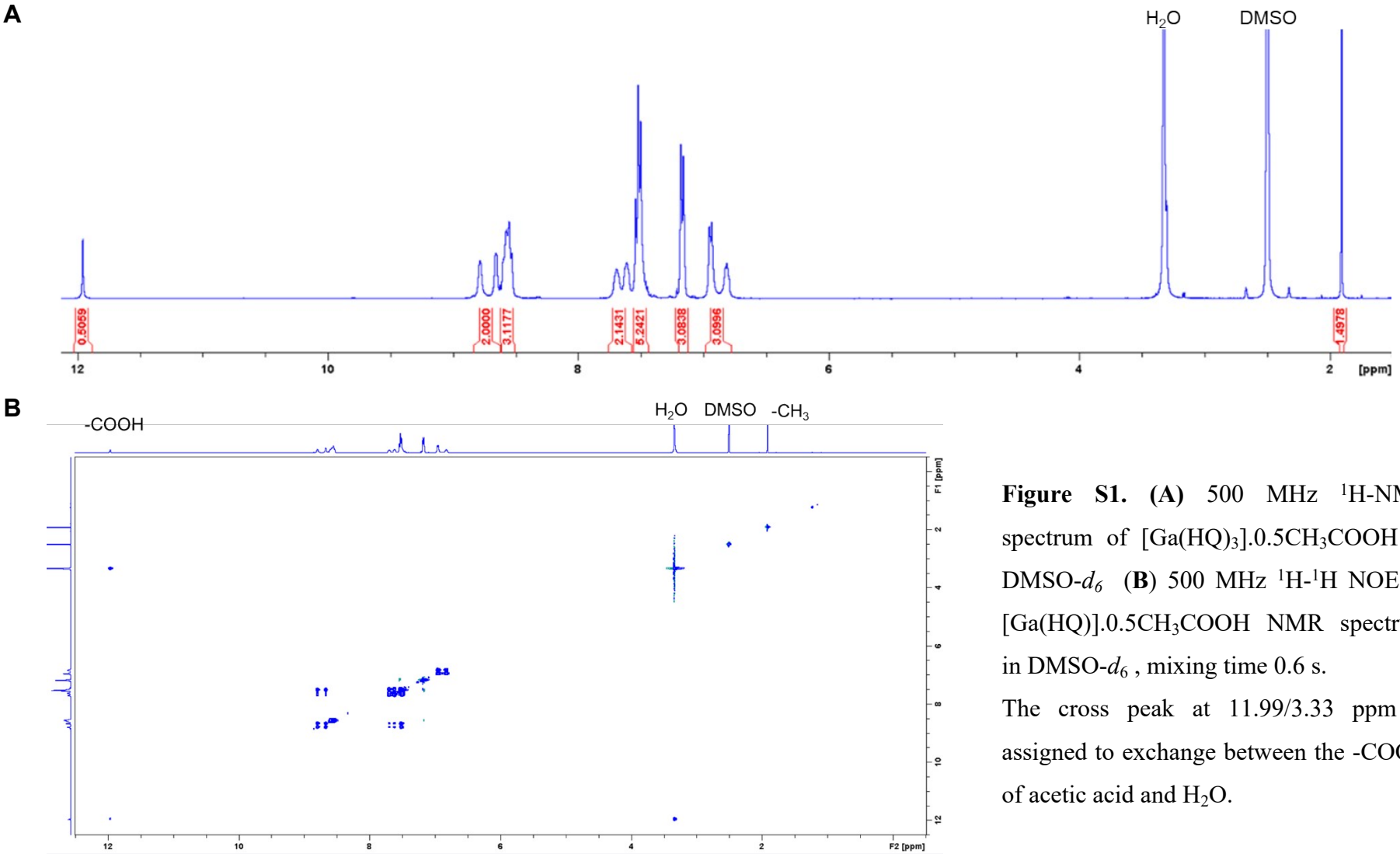


**Figure S1. (A)** 500 MHz $^{1}$H-NMR spectrum of $[Ga(HQ)_3].0.5CH_3COOH$ in DMSO-$d_6$ (**B**) 500 MHz $^{1}$H-$^{1}$H NOESY $[Ga(HQ)].0.5CH_3COOH$ NMR spectrum in DMSO-$d_6$ , mixing time 0.6 s.

The cross peak at 11.99/3.33 ppm is assigned to exchange between the -COOH of acetic acid and $H_2O$.

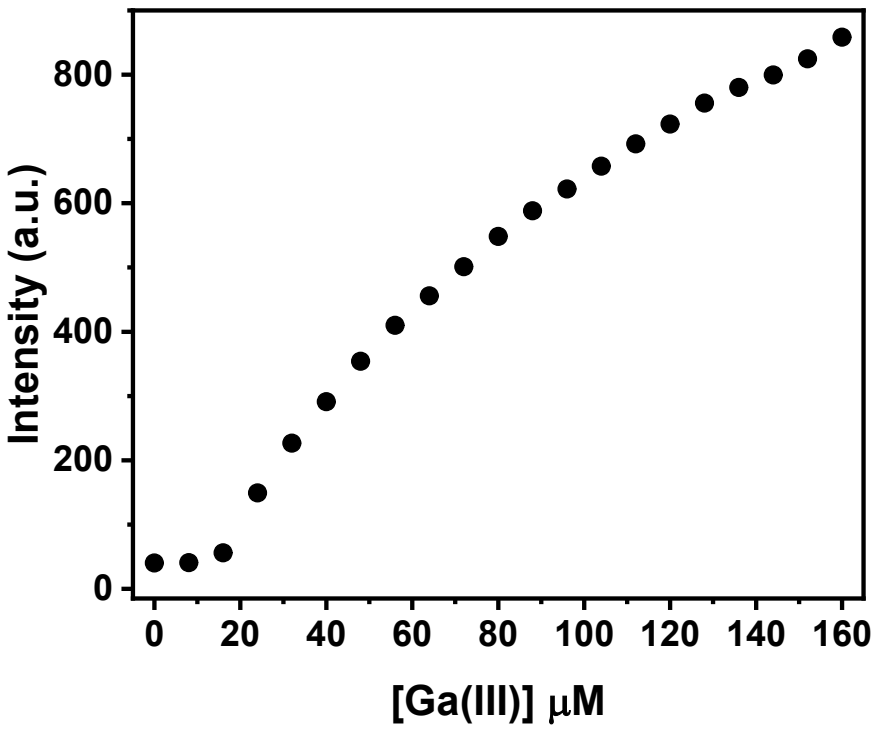


**Figure S2.** Variation of the intensity of emission at 550 nm on excitation at 400 nm with increasing Ga concentration on addition of aliquots of 0.6 μL $Ga(NO_3)_3$ in water (0.065 mol equiv, 8 μM) to $Br_2$-HQH (1 mol equiv, 0.16 mM) in 99.6% DMSO/ 0.4% DMF (v/v). See Figure 2B.

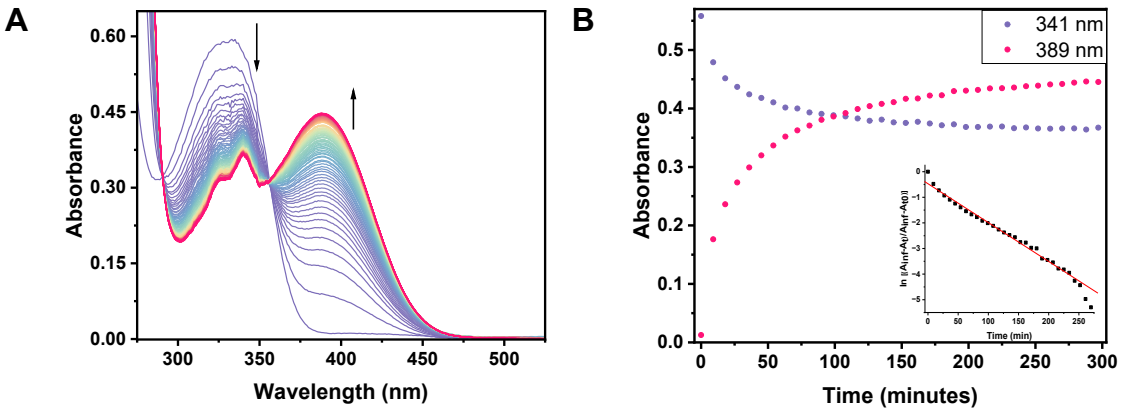


**Figure S3.** (**A**) Time-dependent changes in the UV-vis absorption spectrum after addition of $Ga(NO_3)_3$ (0.67 mol equiv, 0.10 mM) in water to $Br_2$-HQH (1 mol equiv, 0.15 mM) solution in 99.6% DMSO/ 0.4% DMF (v/v). (**B**) Changes in absorbance at 341 nm from $Br_2$-HQH and the new band at 389 nm from [$Ga(Br_2\text{-}HQ)_3$]. The inset shows the best fit of log A *vs.* time (red line), giving the first-order rate constants in Table 1.

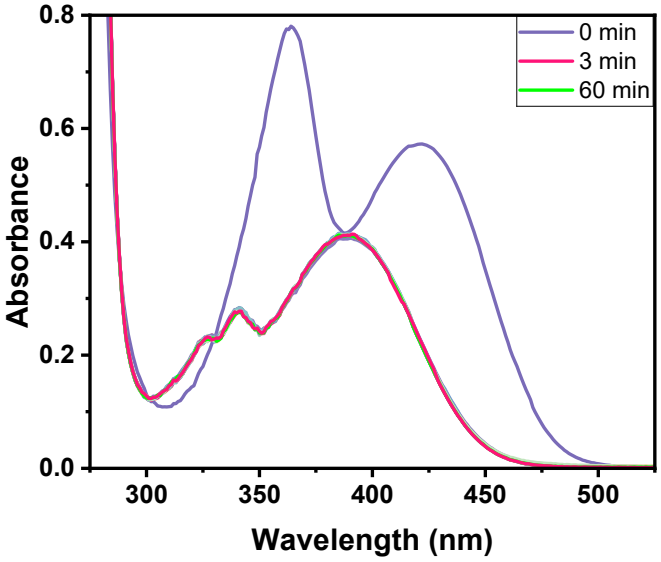


**Figure S4**. Time-dependent changes in the UV-vis absorption spectrum for $Ga(NO_3)_3$ (0.33 mol equiv, 0.05 mM) in water after addition of $Br_2$-HQ (1 mol equiv, 0.15 mM) in DMSO (0.4% DMF (v/v)).

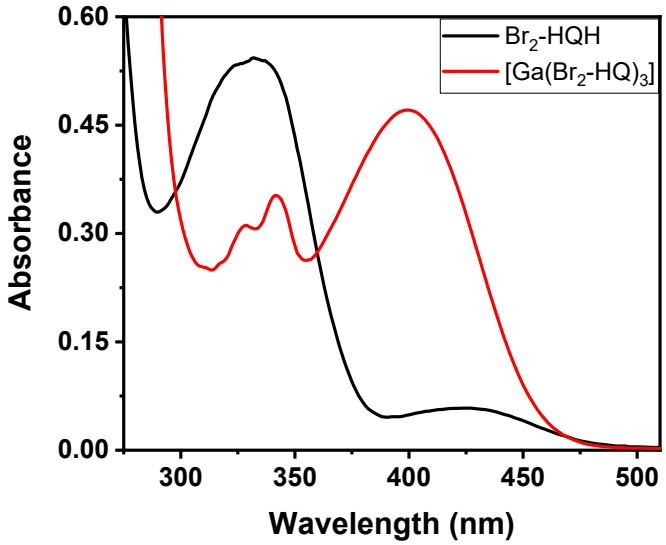


**Figure S5.** UV-vis spectra of $Br_2$-HQH (0.15 mM in 99.6% DMSO/ 0.4% DMF (v/v)) and synthesised [Ga($Br_2$-HQ)$_3$] (0.045 mM) in DMSO.

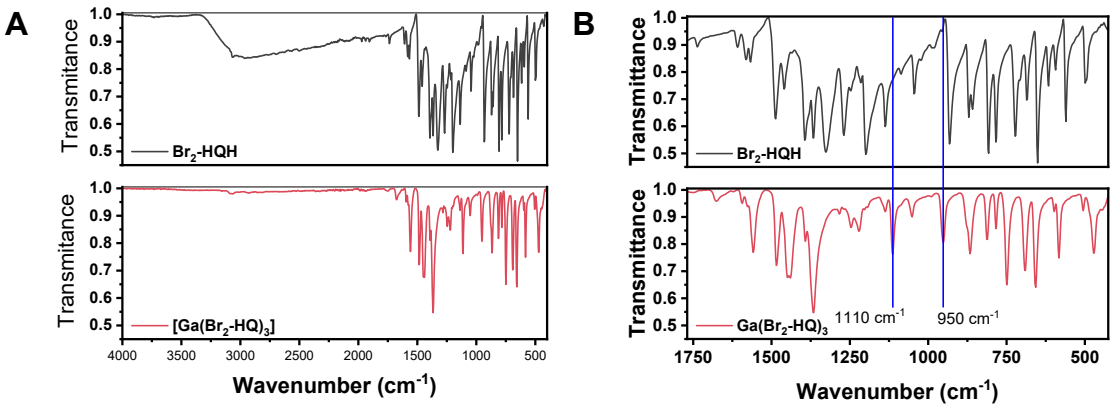


**Figure S6.** FT-IR comparison of $Br_2$-HQH and [Ga($Br_2$-HQ)$_3$] between (**A**) 4000 to 450 $cm^{-1}$; the band assignable to the phenolic -OH disappears upon coordination. (**B**) Finger print region between 1800 to 450 $cm^{-1}$ where two new peaks at 950 and 1110 $cm^{-1}$ assignable to Ga(III)–O bonds appear.

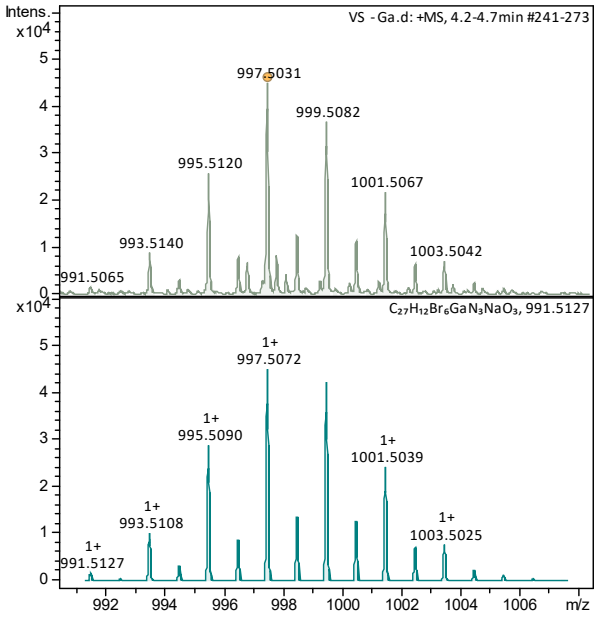


**Figure S7.** Observed (top) and calculated (bottom) HR-MS for $\{[Ga(Br_2\text{-}HQ)_3] + Na]\}^+$

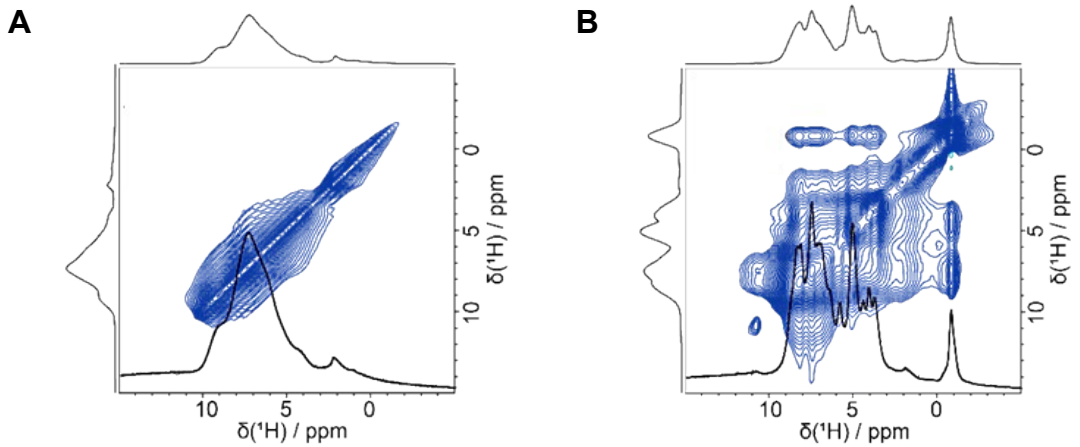


**Figure S8.** 850 MHz $^{1}$H-$^{1}$H NOESY 2D solid state MAS NMR spectra of (**A**) [Ga($Br_2$-HQ)$_3$] and (**B**) [Ga(HQ)$_3$]·0.5 $CH_3CO_2H$ (mixing time of 5 ms).

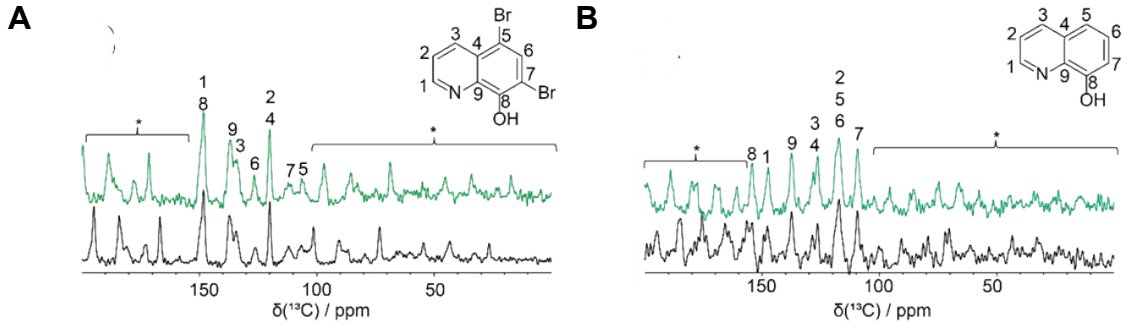


**Figure S9.** $^{13}C$ CPMAS NMR spectra of $Br_2$-HQH (**A**) and HQH (**B**) at spinning rates at 10 kHz (black) and 11 kHz (green). Peaks assigned to the ligands have chemical shifts independent of spinning rate. * = Spinning side bands.

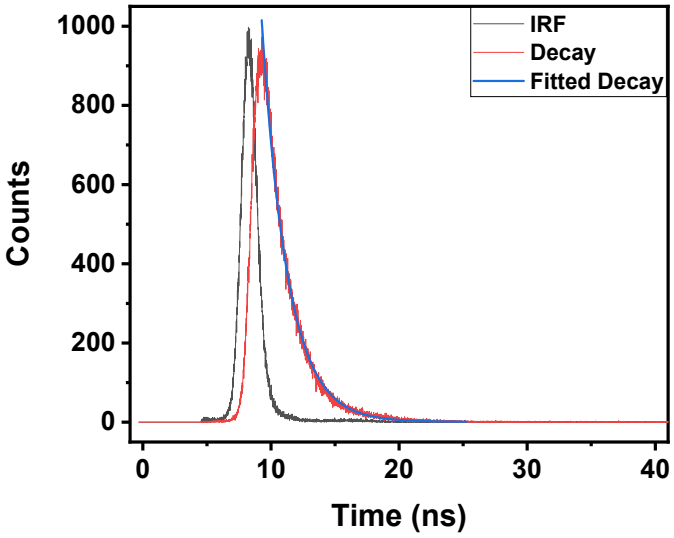


**Figure S10.** Lifetime decay of [Ga($Br_2$-HQ)$_3$] (1 μM) in DMSO with $\lambda_{ex}$= 405 nm. The decay was fitted to a monoexponential function with decay constant of 1.32 ns.

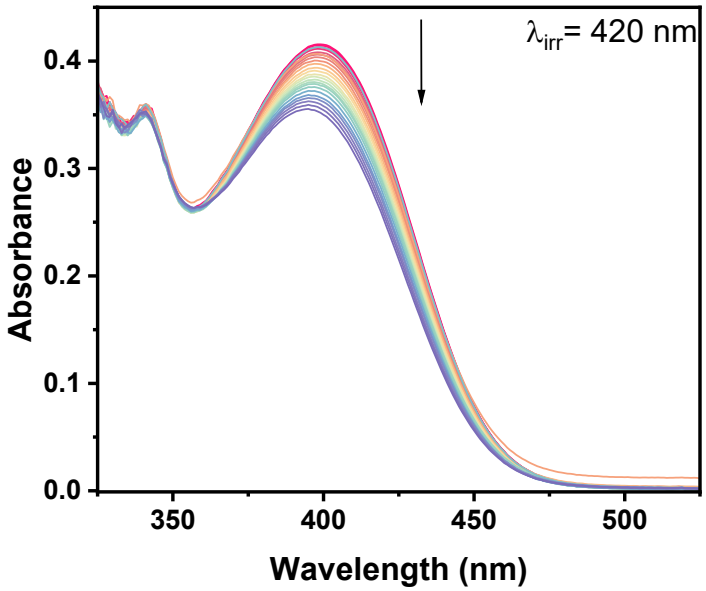


**Figure S11.** Photostability of [Ga($Br_2$-HQ)$_3$] (0.03 mM) in DMSO under irradiation for 15 min using blue light (420 nm) followed by UV-vis spectroscopy. A decomposition of 13% was observed.

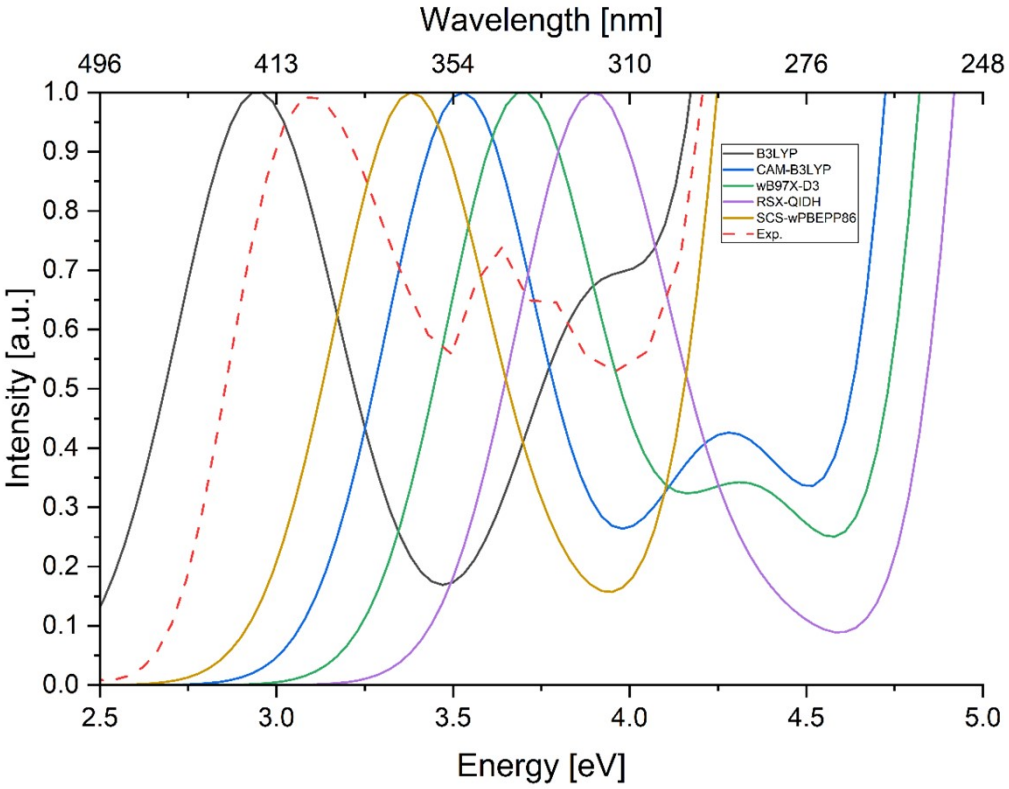


**Figure S12.** Comparison of the UV-vis absorption spectrum of $[Ga(Br_2\text{-}HQ)_3]$ in DMSO with those calculated using the DFT functionals B3LYP, CAM-B3LYP, ωB97X-D3, RSX-QIDH and SCS-ωPBEPP86 (see section 2.11). While all functionals show the right intensity pattern of the experimental absorption spectrum, excitation energies vary, with B3LYP giving the best fit to experiment.

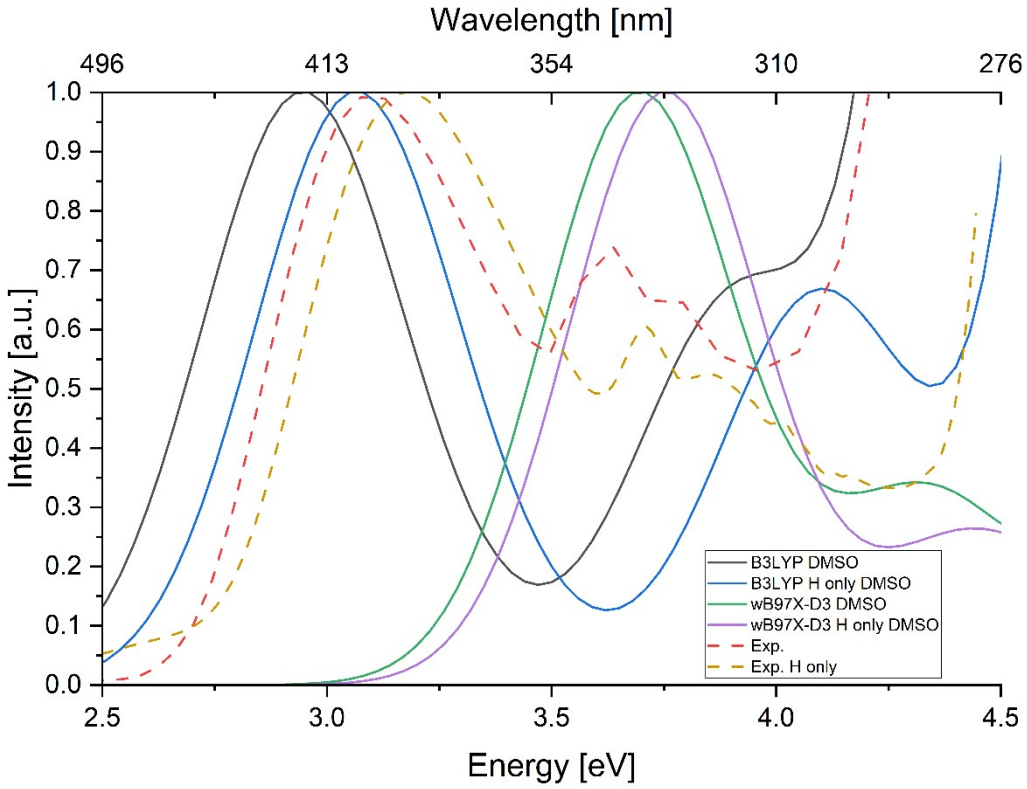


**Figure S13.** Comparison of the observed UV-vis absorption spectra for $[Ga(HQ)_3]$ (yellow hashed line) and $[Ga(Br_2\text{-}HQ)_3]$ (red hashed line) in DMSO with those calculated for $[Ga(Br_2\text{-}HQ)_3]$ using the B3LYP and ωB97X-D3 functionals. Both functionals reproduce the experimentally observed hypsochromic shift when replacing Br with H. Again, B3LYP is the best fit to experiment.