

Supplementary material for

A Spectroscopic and DFT study of Alizarin Red S Complexes of Ga(III) in Semi-Aqueous Solution

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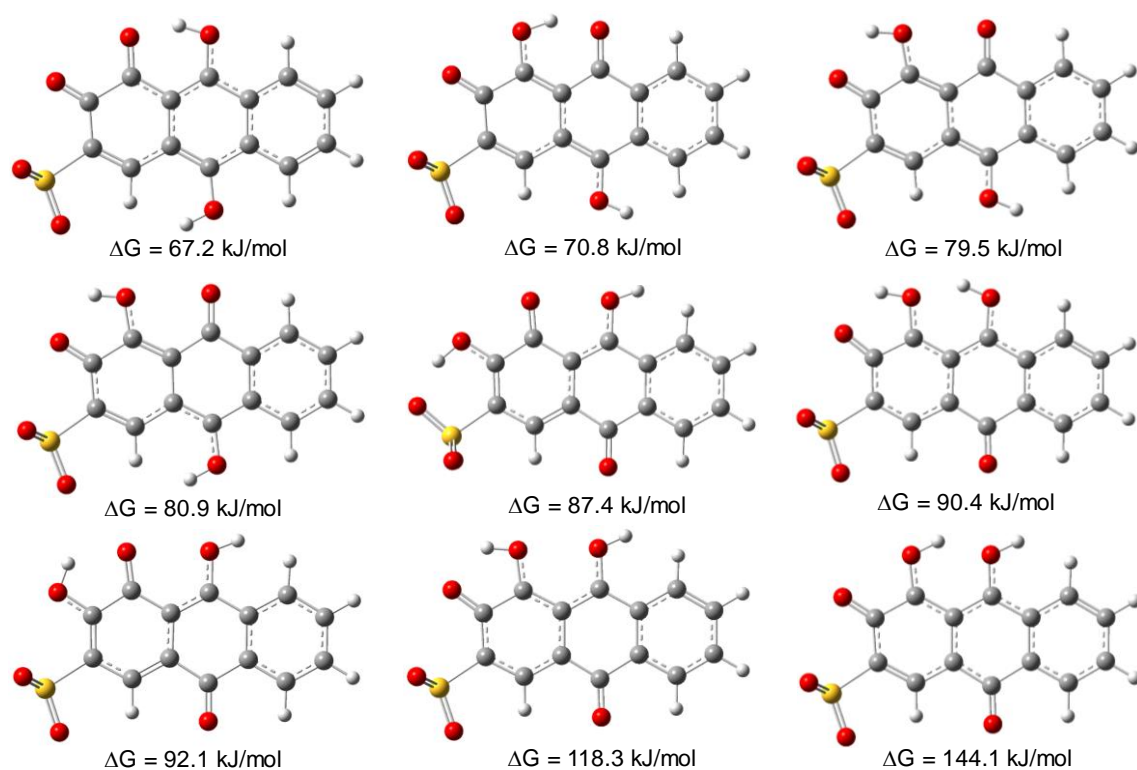


Figure S1. B3LYP/6-311++G(2d,2p) optimized geometries of additional tautomers of the monoanionic structure of ARS, considering the bulk effects of the solvent water (Gibbs energies are given relative to the lowest energy conformer **I**).

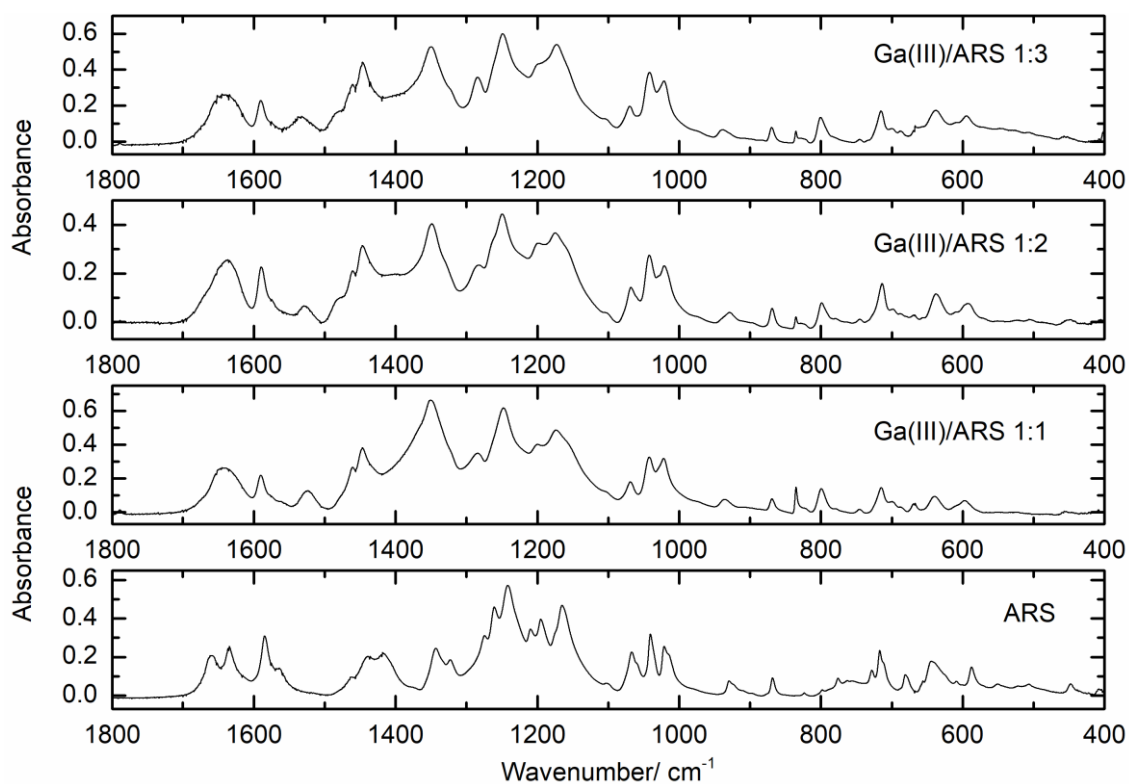


Figure S2. ATR-FTIR spectra ($1800\text{--}400\text{ cm}^{-1}$) of the solid powder samples obtained from the Ga(III):ARS 1:3 (top), 1:2 (middle top) and 1:1 (middle bottom) molar ratio solutions at pH=4, compared with the solid ARS (bottom).

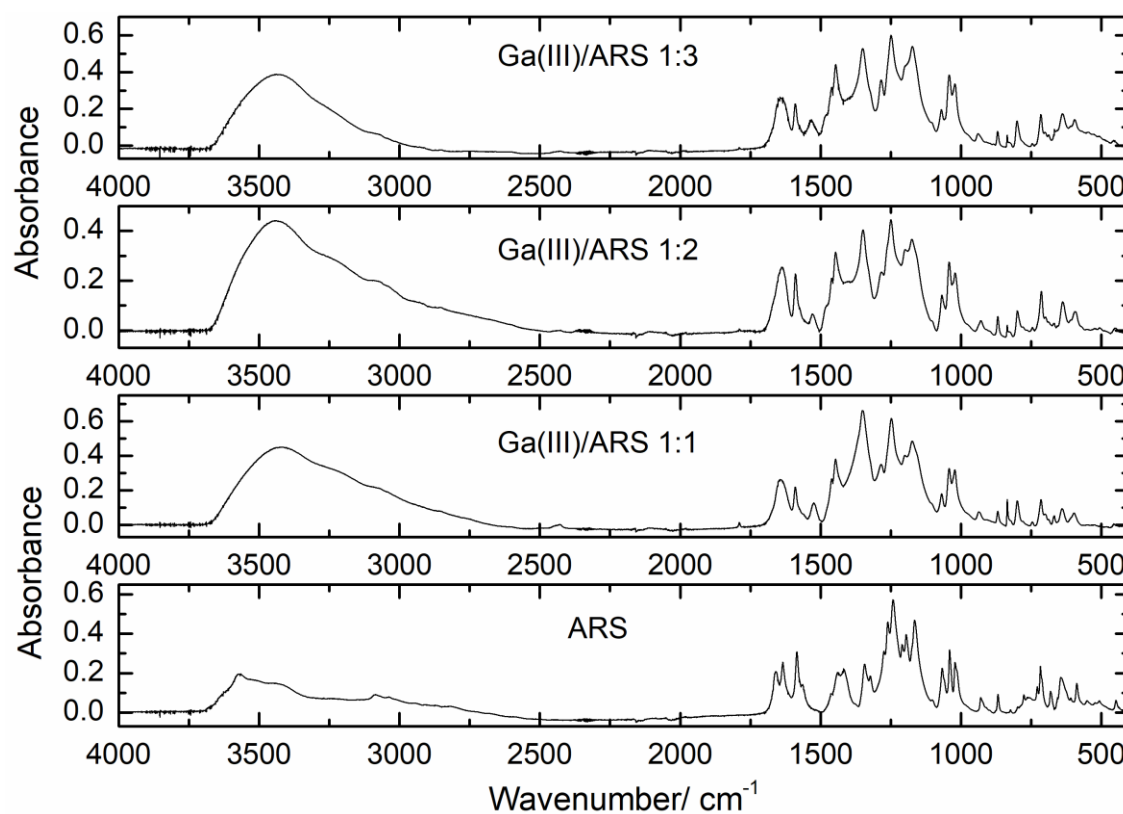


Figure S3. ATR-FTIR spectra of the solid powder samples obtained from the Ga(III):ARS 1:3 (top), 1:2 (middle top) and 1:1 (middle bottom) molar ratio solutions at pH=4, compared with the solid ARS (bottom).

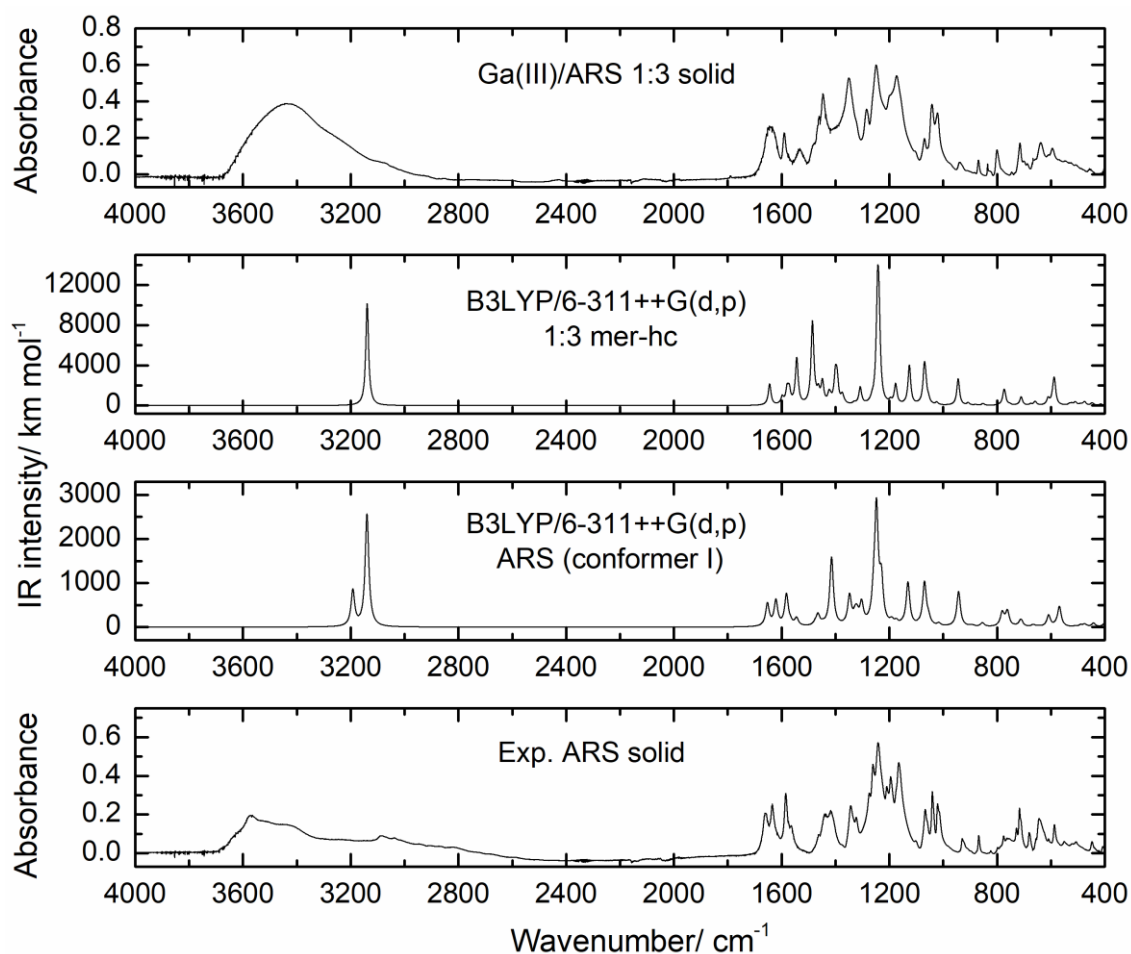


Figure S4. ATR-FTIR spectra ($4400\text{--}400\text{ cm}^{-1}$) of the solid powder samples of ARS and of the 1:3 Ga(III)/ARS sample (bottom and top spectra, respectively), compared with the B3LYP/6-311++G(d,p) calculated spectra for conformer **I** of ARS (middle bottom) and for the 1:3 *mer* structure (middle top). The calculated spectra were simulated using Lorentzian functions with a full-width-at-half-maximum (FWHM) of 6 cm^{-1} , centred at the scaled calculated frequencies.

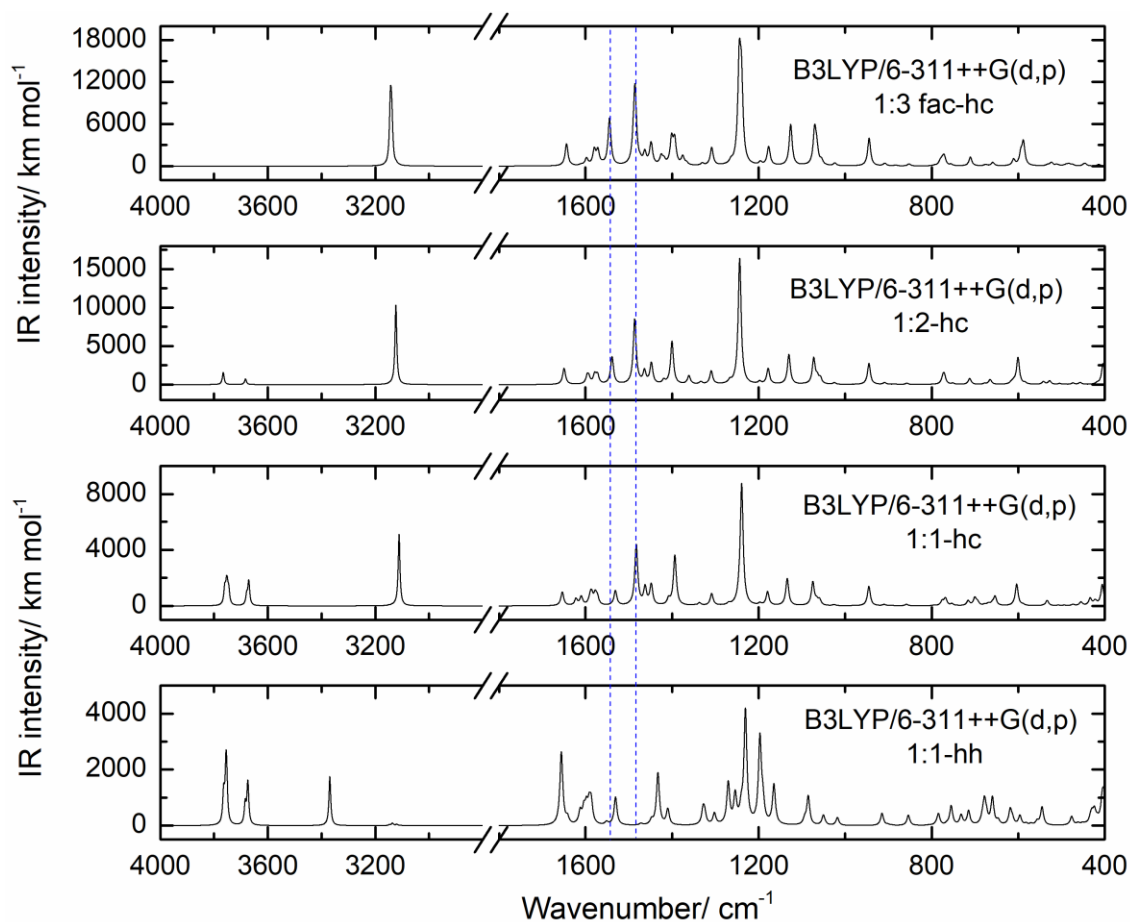


Figure S5. ATR-FTIR spectra (4400-400 cm⁻¹) calculated at the B3LYP/6-311++G(d,p) level of theory for the 1:3-fac-hc (top), the 1:2-anti-hc (middle top), the 1:1-hc (middle bottom) and the 1:1-hh (bottom) structures. The calculated spectra were simulated using Lorentzian functions with a full-width-at-half-maximum (FWHM) of 6 cm⁻¹, centred at the scaled calculated frequencies.

Table S1. ^1H and ^{13}C NMR chemical shifts (δ / ppm) for the free ligand ARS (experimental data in $\text{D}_2\text{O}/\text{CD}_3\text{OD}$, pH* 3,96 and calculated at the B3LYP/GIAO/6-311++G(d,p) level in water; the numbering is in accordance with Scheme 1).

	$\delta ^1\text{H RMN (exp.)}^a$	$\delta ^1\text{H RMN (calc.)}^a$		$\delta ^{13}\text{C RMN (exp.)}$	$\delta ^{13}\text{C RMN (calc.)}$
H ₁	--^b	--^c	C ₁₀	190,21	--^c
H ₂	--^b	--^c	C ₉	183,66	--^c
H ₈	8,15	8,72	C ₁	152,58	162,38
H ₅	8,08	8,69	C ₂	150,82	158,30
H ₄	7,98	8,28	C ₃	134,86	145,18
H ₇	7,82	8,10	C ₆	136,94	143,18
H ₆	7,82	8,09	C ₇	136,16	142,29
			C ₁₁	134,51	140,34
			C ₁₂	134,33	140,23
			C ₈	128,54	134,69
			C ₅	128,31	134,59
			C ₁₄	124,81	129,25
			C ₄	120,71	126,73
			C ₁₃	118,46	122,69

^a The numbering is based on the carbon atom to which the H atom is attached. ^b Not observed in this solvent (observed in DMSO at 11.47 and 12.64, respectively for H₁ and H₂). ^c The calculation for the isolated molecule does not give a realistic prediction of the ^1H NMR shifts of the OH protons nor of the ^{13}C shifts of the carbonyl groups, since these groups are strongly affected by hydrogen bonding established with the solvents and with neighbouring molecules.