

Electronic Supplementary Information

Dinuclear Au(I) N-heterocyclic carbene complexes derived from unsymmetrical azolium cyclophane salts: potential probes for live cell imaging applications

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Unit cell contents for the crystal structures of the azolium cyclophane salts

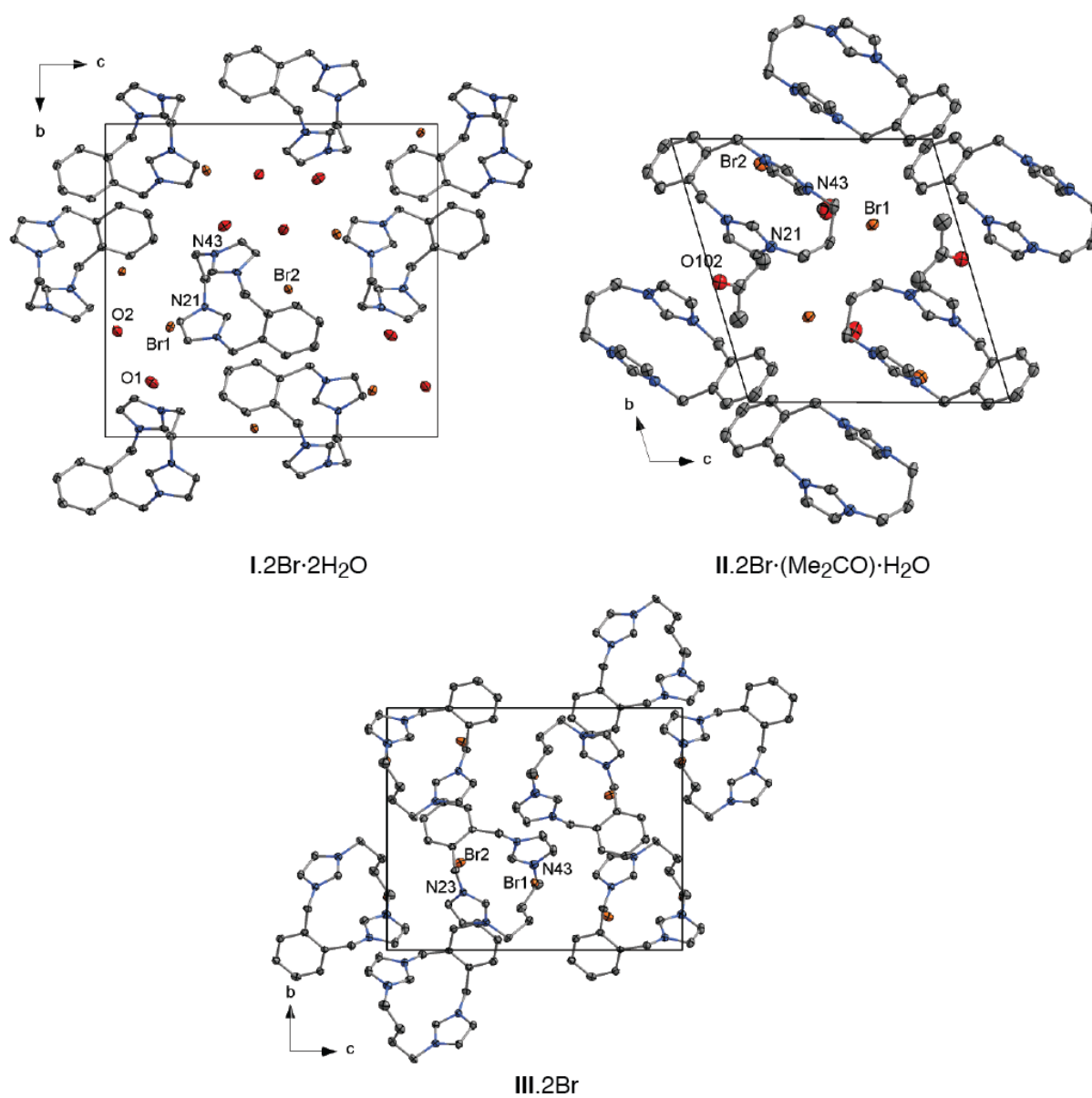


Fig. S1 Unit Cell contents for the crystal structures of the imidazolium cyclophane compounds I.2Br·2H₂O, II.2Br·(Me₂CO)·H₂O and III.2Br.

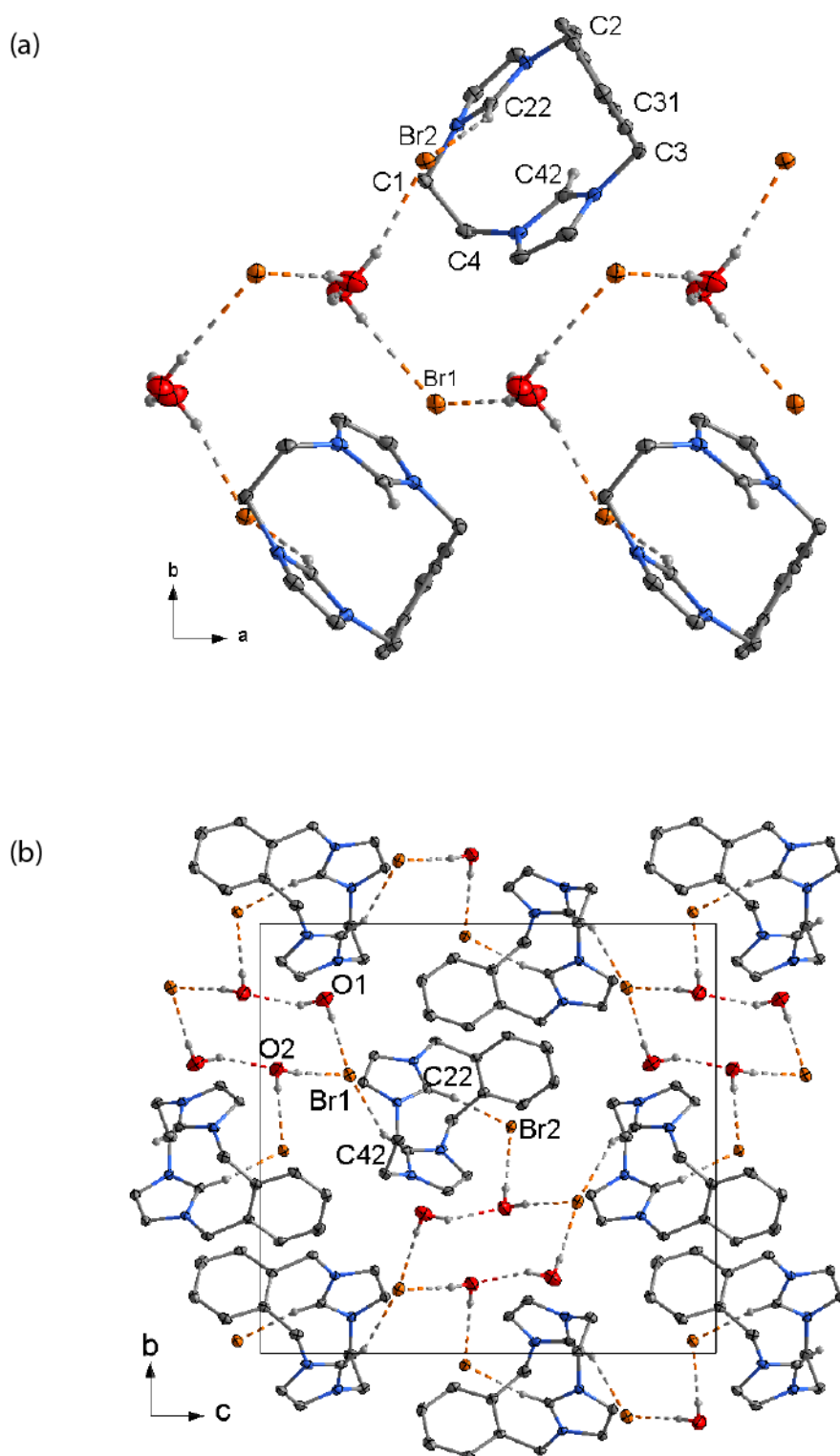


Fig. S2 (a) structure of the one-dimensional hydrogen-bonded polymer formed by $I_2Br \cdot 2H_2O$, showing the interaction between H(22) and Br(2), and the hydrogen bonds between the water molecules and bromide ions; (b) the three-dimensional hydrogen-bonded polymer formed by the weak interaction between H(42) and Br(1) which links sheets of the one-dimensional polymer shown in (a).

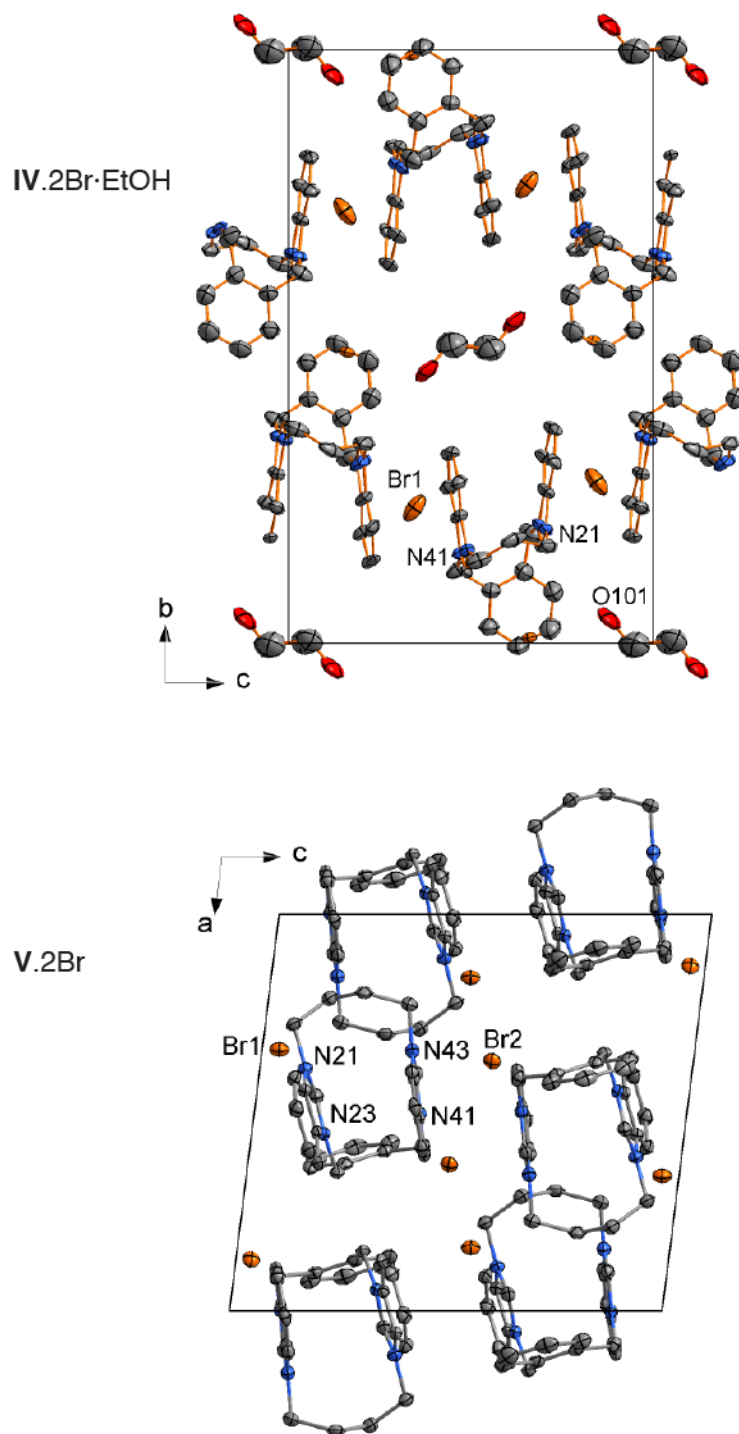


Fig. S3 Unit cell contents for the benzimidazolium cyclophane compounds **IV.2Br·(EtOH)** and **V.2Br**. For **IV.2Br·(EtOH)**, ethanol (solvent) molecules are shown and significant twisting of the cation structure can be seen. For **V.2Br**, it is clearly shown that the benzimidazolium units of the cation **V**²⁺ are not coplanar.

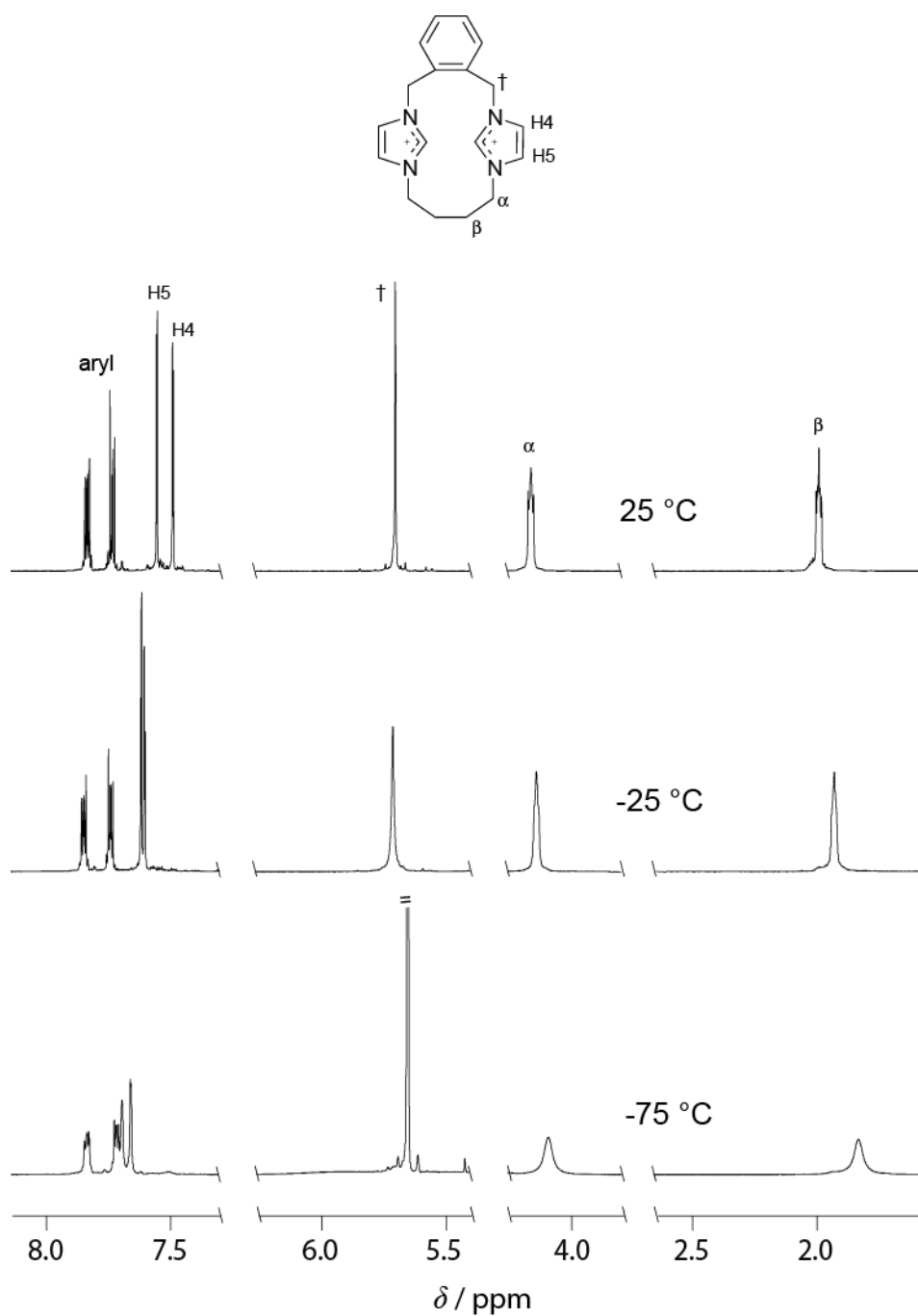
Variable Temperature ^1H NMR Spectra for III.2Br and V.2Br

Fig. S4 ^1H NMR spectra (500.1 MHz, CD_3OD) of III.2Br at 25, -25, and -75 °C. In the -75 °C spectrum, the signal due to the benzyl protons cropped for clarity.

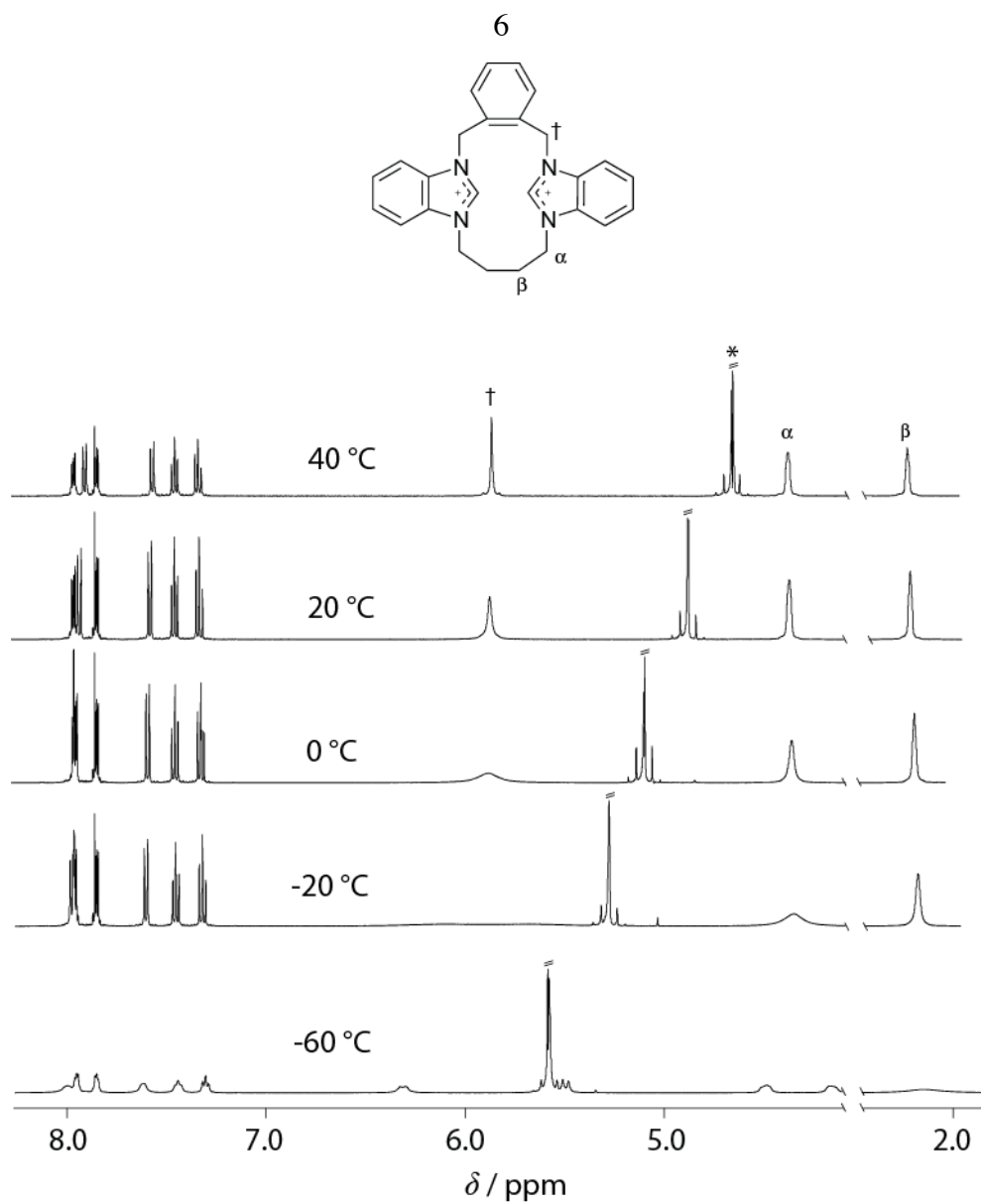


Fig. S5 ^1H NMR spectra (500.1 MHz, CD_3OD) of **V.2Br** at 40, 20, 0, -20, and -60 °C. The signal due to adventitious water is labelled with an asterisk (*) and has been cropped for clarity.

Unit cell contents and packing diagrams for the crystal structures of the Au(I) complexes

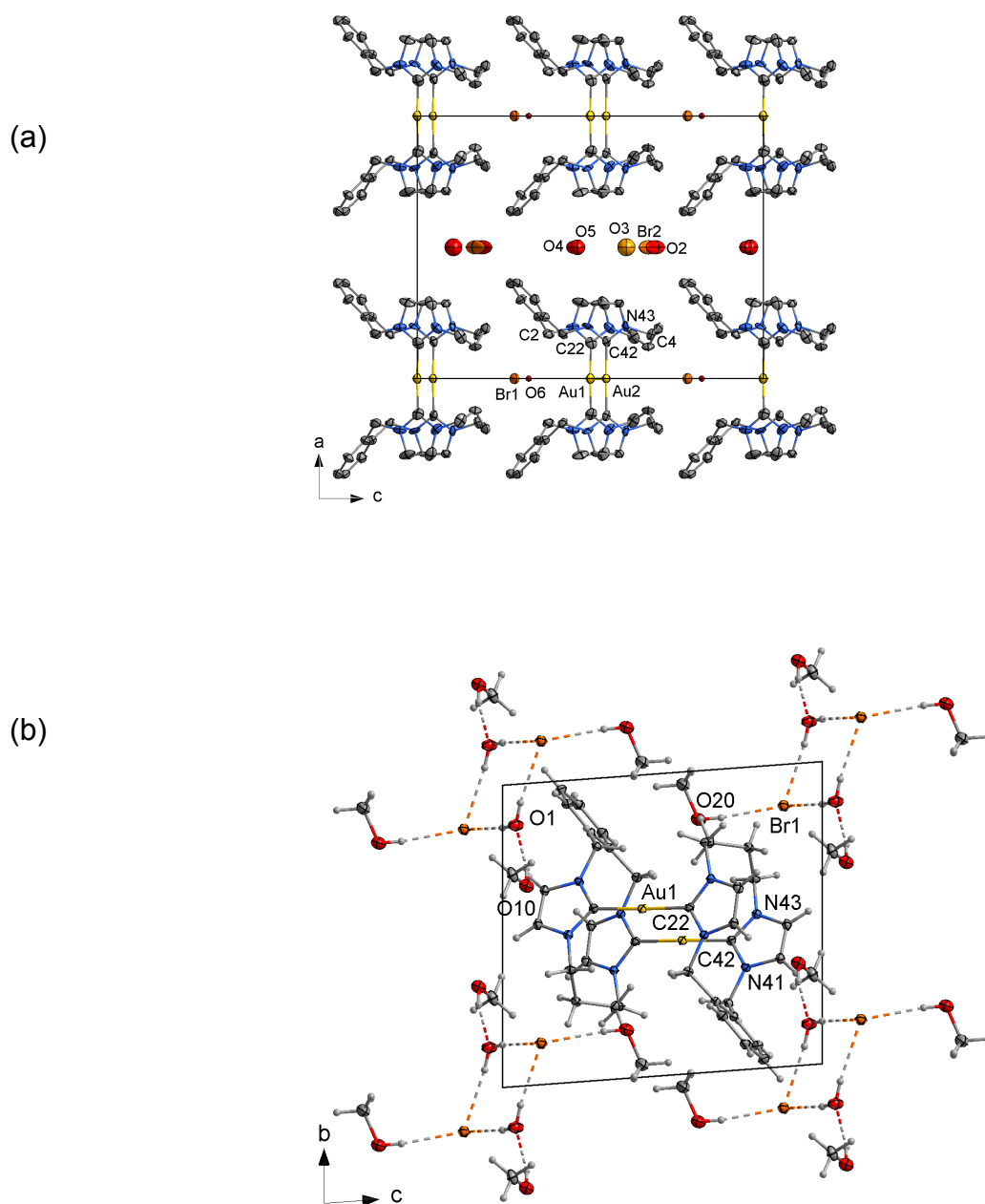


Fig. S6 Unit cell contents for the Au(I) complexes bearing C_4 -linked imidazolium-derived ligands, showing:

- (a) *cis-2*.BrCl. The cation $cis-2^{2+}$ is situated on a crystallographic mirror plane perpendicular to the crystallographic a axis, and the cations lie parallel to the ac plane, alternating with planes containing counter ions and water molecules.
- (b) *trans-2*.BrCl. Solvent (methanol) and water molecules form a hydrogen bonded cluster around the cell origins.

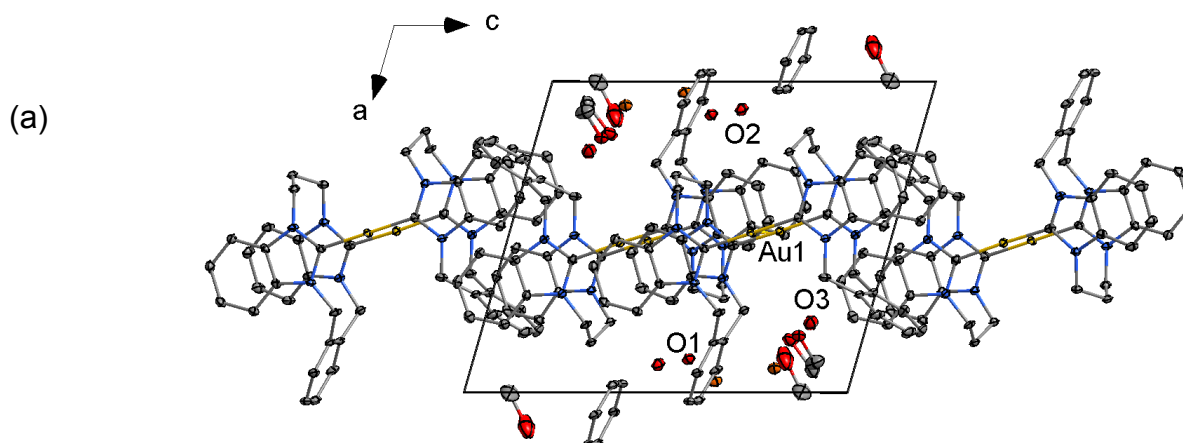


Fig. S7 Unit cell contents for the Au(I) complexes bearing benzimidazolium-derived ligands.

(a) *cis*-**3**·2Br·2CH₃OH·3H₂O. The cations lie in sheets parallel to the *bc* plane, and alternate with sheets containing bromide ions, methanol and water molecules.

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(b) *cis*-**4**·2Br·2CH₃OH. Note the interaction between the Br(1) and the neighbouring Au(1) atoms of adjacent *cis*-**4**²⁺ cations, which are related by a crystallographic two-fold along the *b* axis. The *cis*-**4**²⁺ cations pack in layers perpendicular to the *a* axis, with pairs of cations arranged in a herringbone manner.

(c) *trans*-**4**·2Br·3CH₃OH. The counter bromide ions are disordered over five sites in the structure, with the sum of their occupancy factors constrained to be 2.

Fig. S7(b)

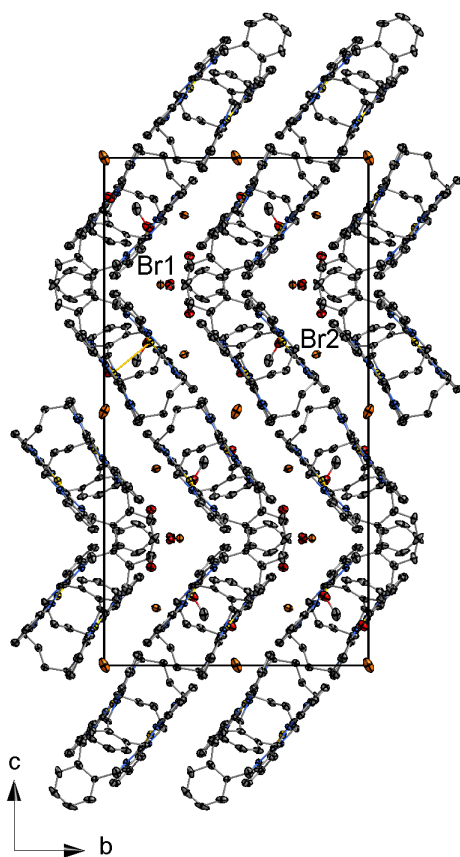
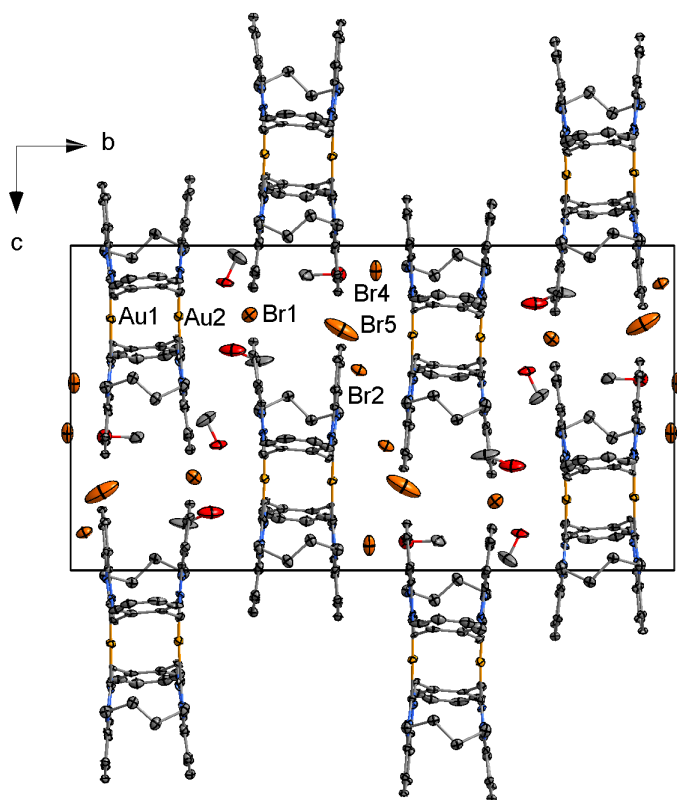


Fig. S7(c)



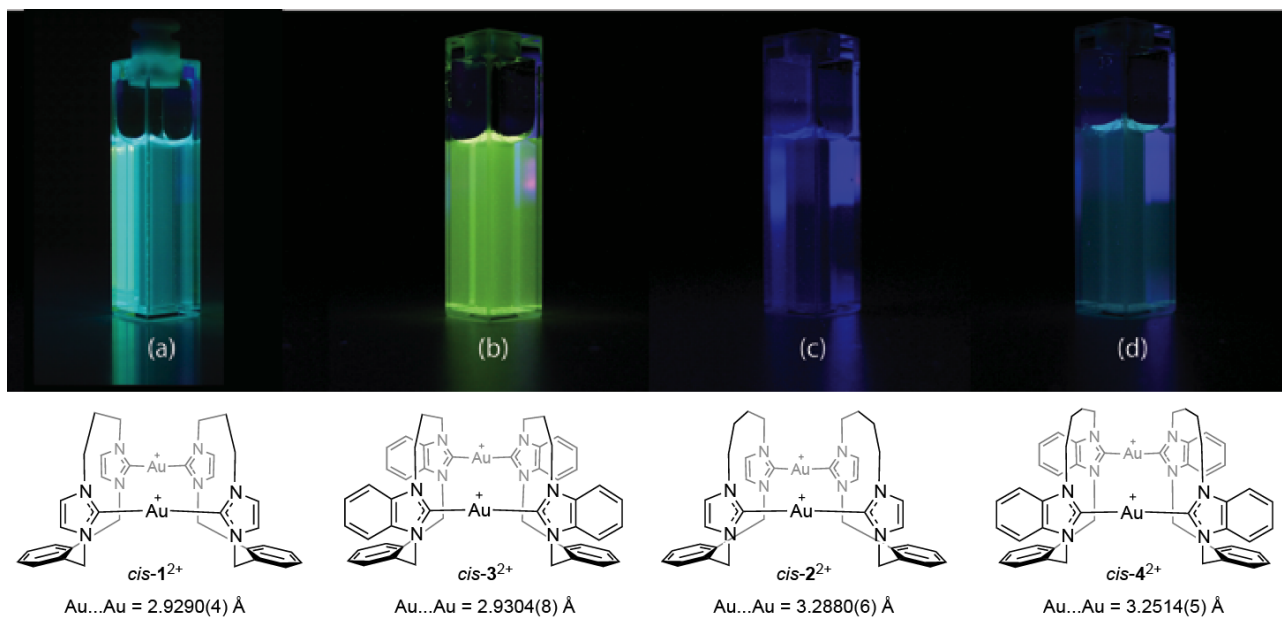


Fig. S8 Aqueous solutions of halide salts of (a) *cis*-[1]²⁺ (10 mM), (b) *cis*-[3]²⁺ (1 mM), (c) *cis*-[2]²⁺ (10 mM) and d) *cis*-[4]²⁺ (10 mM), under irradiation with UV light (TLC lamp, 254 nm) and the corresponding intramolecular Au(I)...Au(I) distances for the dinuclear Au-NHC cations determined in the solid state.

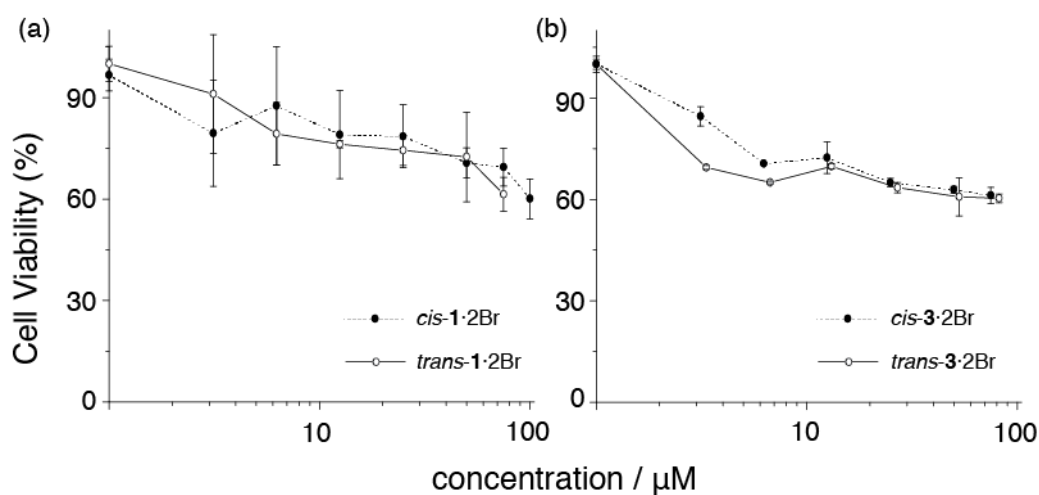


Fig. S9 Viability of HeLa cells measured using a cell titre assay 24 h after treatment with various concentrations of (a) *cis*- or *trans*-1·2Br and (b) *cis*- or *trans*-3·2Br. Data are expressed relative to controls not treated with Au-NHC complexes and are means \pm SD of three independent experiments.

Movie S1 (separate file). Development of luminescence from MDA-MB-231 (MDA) breast cancer cells after treatment with *cis*-3·2Br (final concentration 26.2 μM). Cells were imaged using a luminescence microscope for 6 h (UV illumination, BP 340-380 nm filter, emission recorded via one image every 30 s, LP 425 nm filter).