

**Effect of metal coordination on the interaction of
substituted phenanthroline and pyridine ligands with
quadruplex DNA**

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Supplementary Information

1. X-ray crystallography.

The N–H and O–H protons in the structures of **L**¹ and **L**⁶ were found from ΔF maps and refined subject to an X–H distance constraint (0.90 Å). The N–H and O–H protons in **2** could not be located and so were not included. The O–H protons in **6** could not be located from ΔF maps and so were added in idealised positions and allowed to rotate about the associated C–O bonds (HFIX 147). The included solvent in **2** is highly disordered; in particular three orientations were identified for the dmso solvent. However, the indications are that this is merely a small subset of the orientations present for this molecule and so the hydrogen bonding interaction to this area need to be treated with caution.

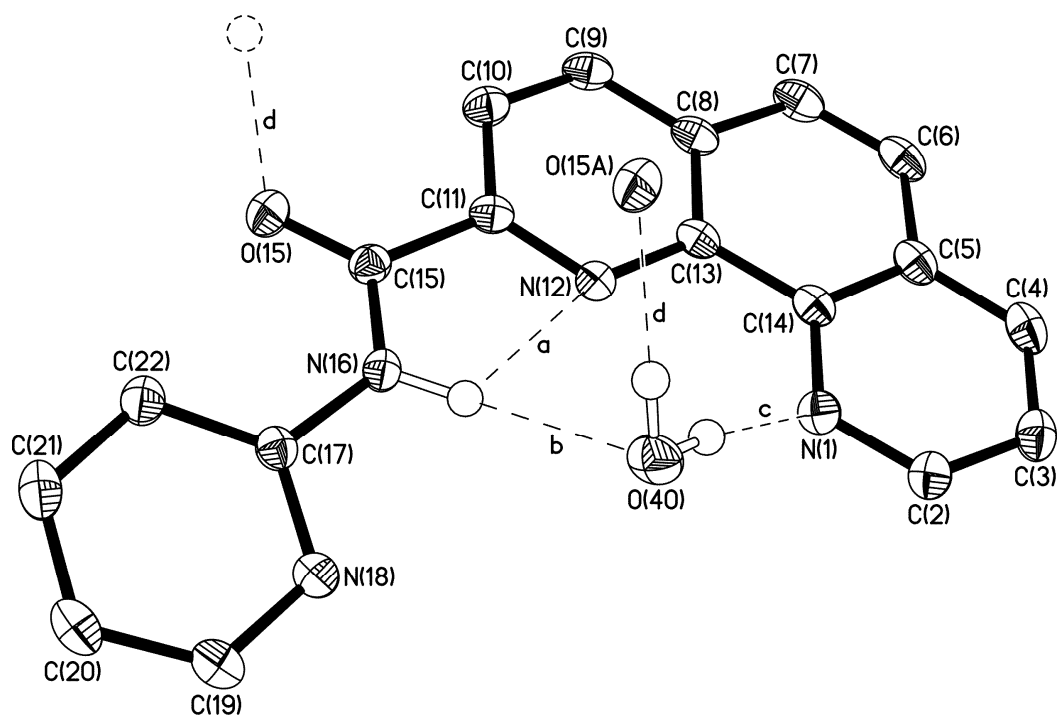


Fig. S1 The molecular structure of **L**¹ (50% probability ellipsoids).

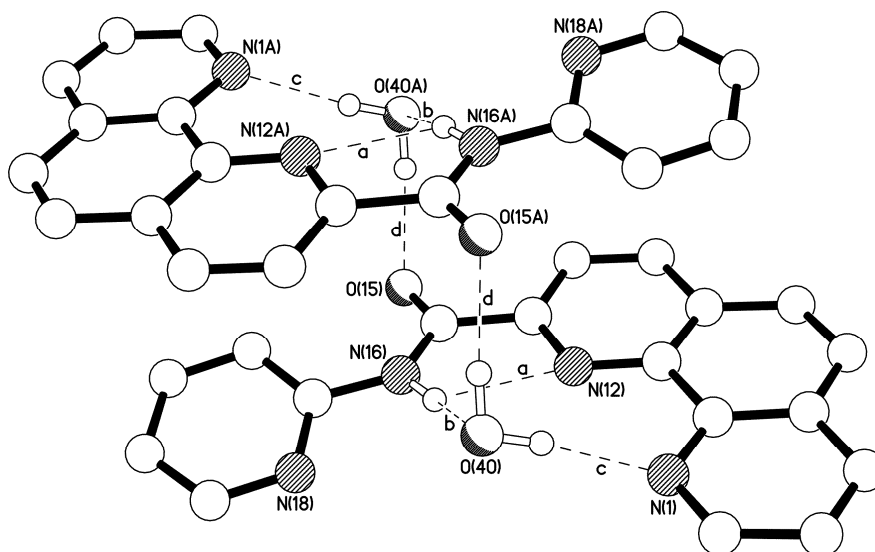


Fig. S2 One of the hydrogen-bonded dimers pairs present in the structure of **L¹**.

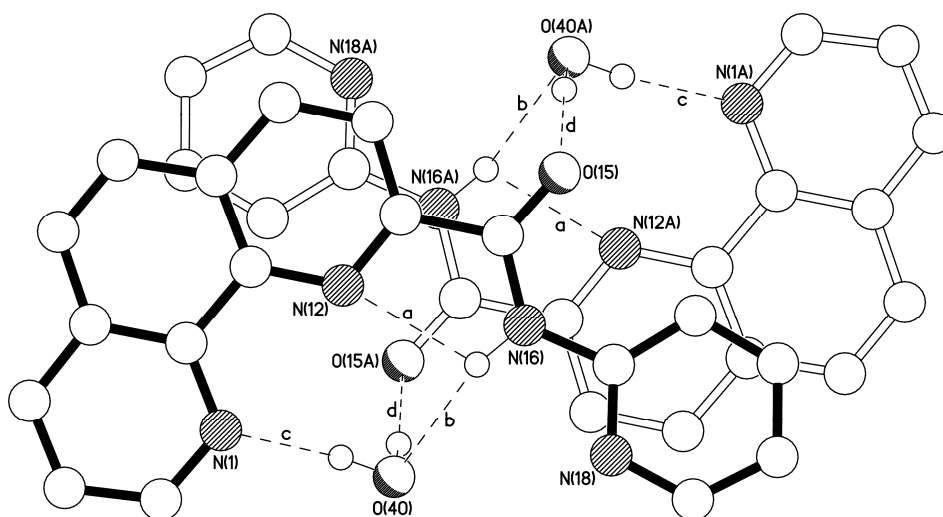


Fig. S3

Fig. S3 One of the hydrogen-bonded dimers pairs present in the structure of **L¹** viewed in parallel projection perpendicular to the mean plane of the molecule, showing the overlap between the N(12) aromatic ring in one molecule and the N(18) aromatic ring in its centrosymmetrically related counterpart. The centroid⋯centroid and mean interplanar separations for these C₅N rings are 3.74 and 3.43 Å respectively, the two rings being inclined by *ca.* 11°.

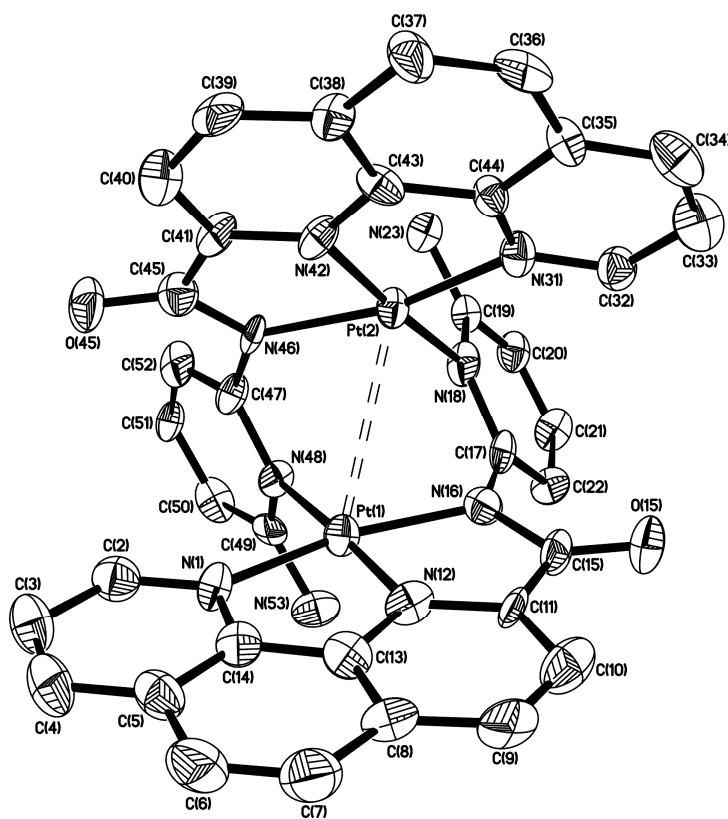


Fig. S4 The molecular structure of the dication in **2** viewed down the molecular C_2 axis. (50% probability ellipsoids).

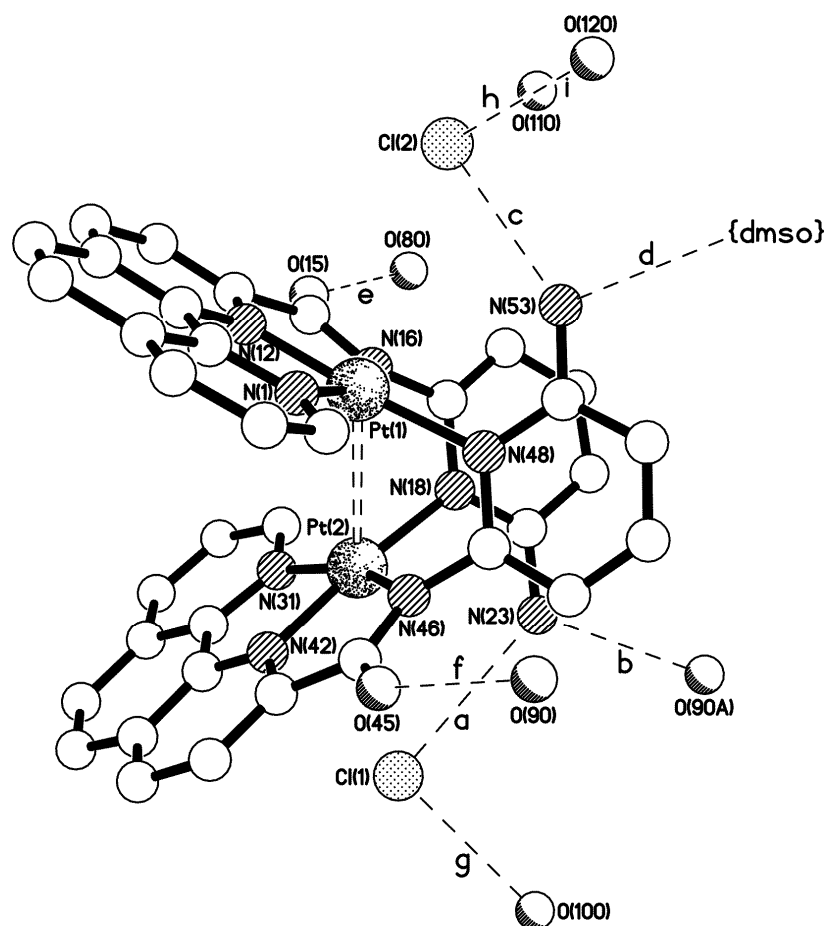


Fig. S5 The hydrogen bonding interactions involving the cation and anions in the structure of **2**. The hydrogen bonding geometries [X...Y Å] are **a**) 3.304(10); **b**) 2.885(13); **c**) 3.374(11); **d**) 2.73(3); **e**) 2.798(12); **f**) 2.877(11); **g**) 3.164(10); **h**) 3.193(15); **i**) 3.25(3). The dmsolvent molecule is highly disordered and so the contact distance for interaction **d** should be treated with caution. However, it is clear that there is some kind of interaction between the N(53) NH₂ unit and the area occupied by the dmsolvent.

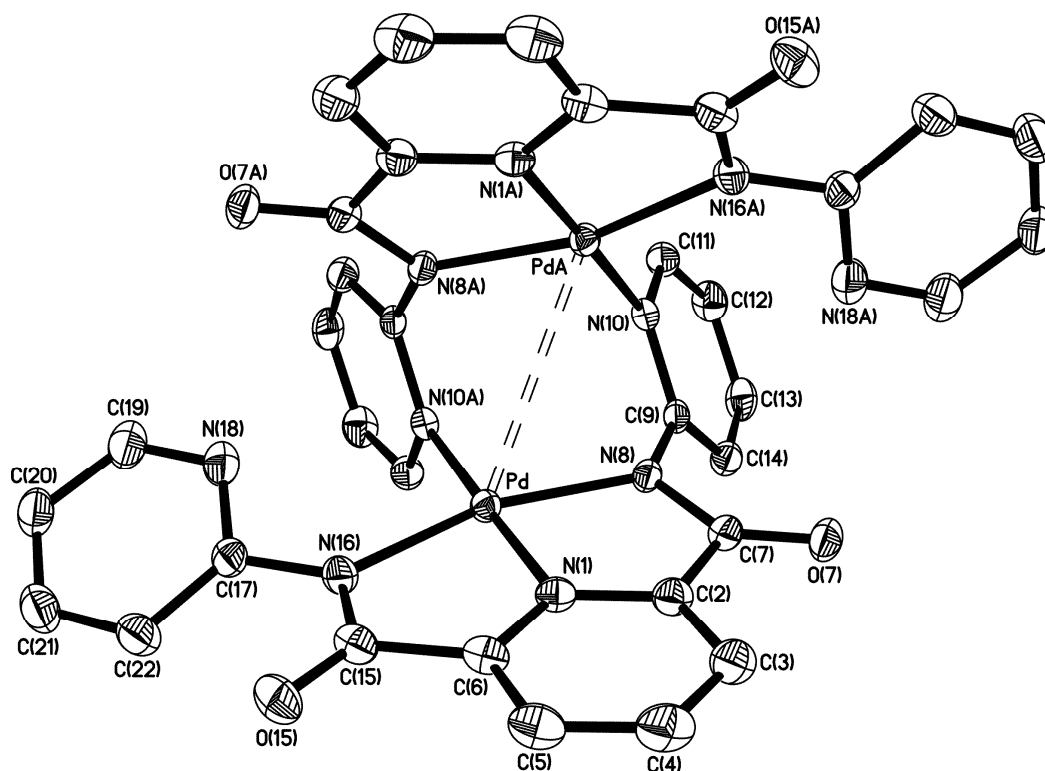


Fig. S6 The molecular structure of the C_2 -symmetric complex **6** viewed down the C_2 axis (50% probability ellipsoids).

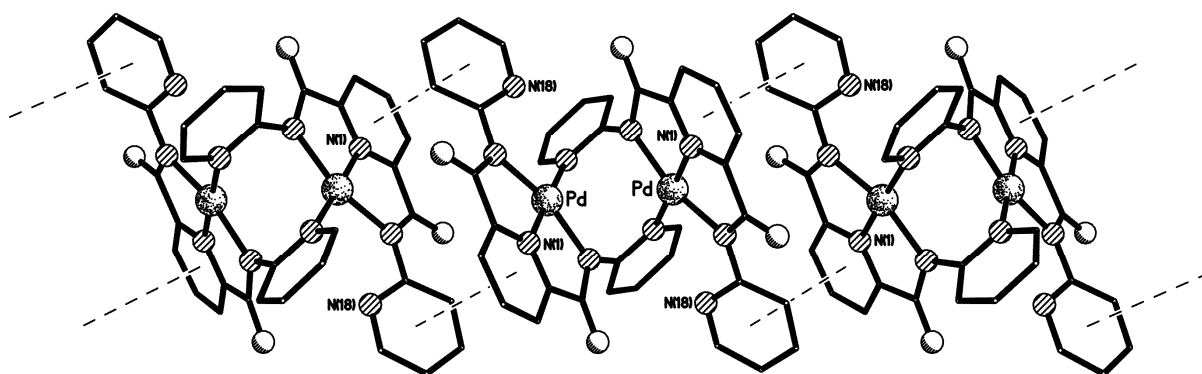


Fig. S7 Part of one of the extended chains of π - π stacked molecules along the a axis direction present in the crystals of **6** showing the stacking between the N(1) ring in one molecule and the N(18) ring in its centrosymmetrically related counterpart, and *vice versa*. The centroid...centroid and mean interplanar separations are *ca.* 3.81 and 3.65 Å respectively, the two rings being inclined by *ca.* 28°.

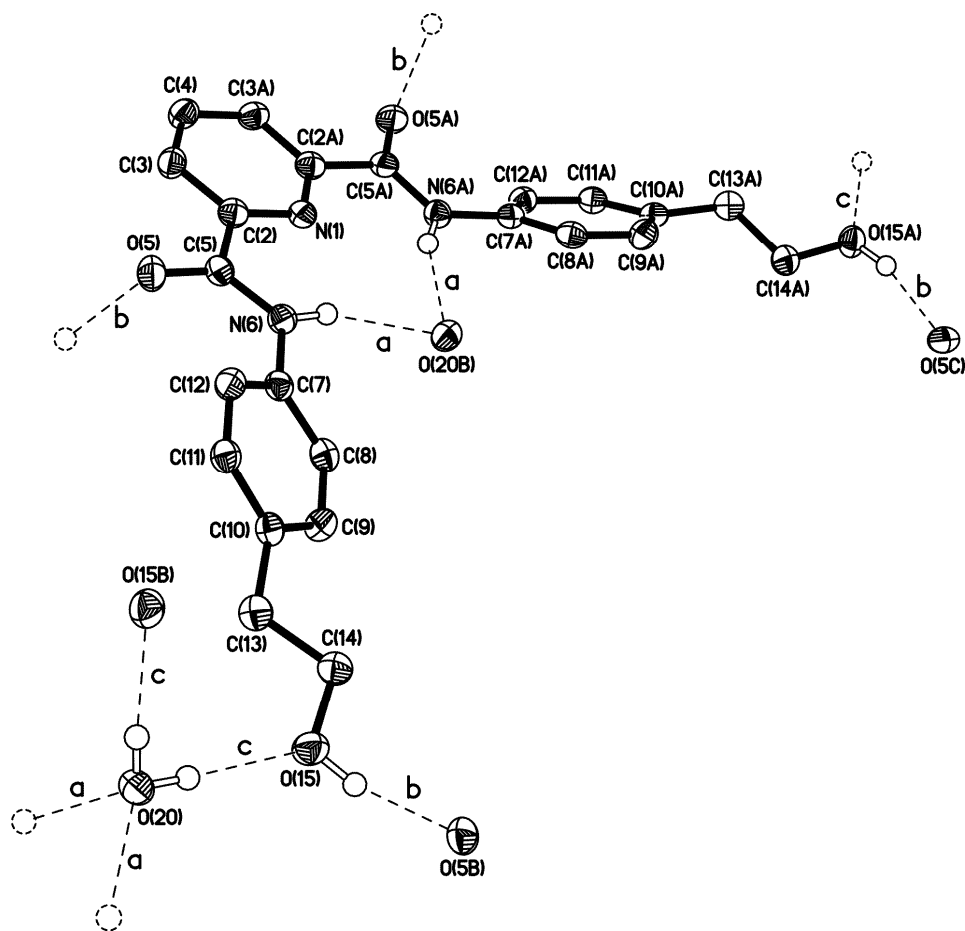


Fig. S8 The molecular structure of L^6 (50% probability ellipsoids).

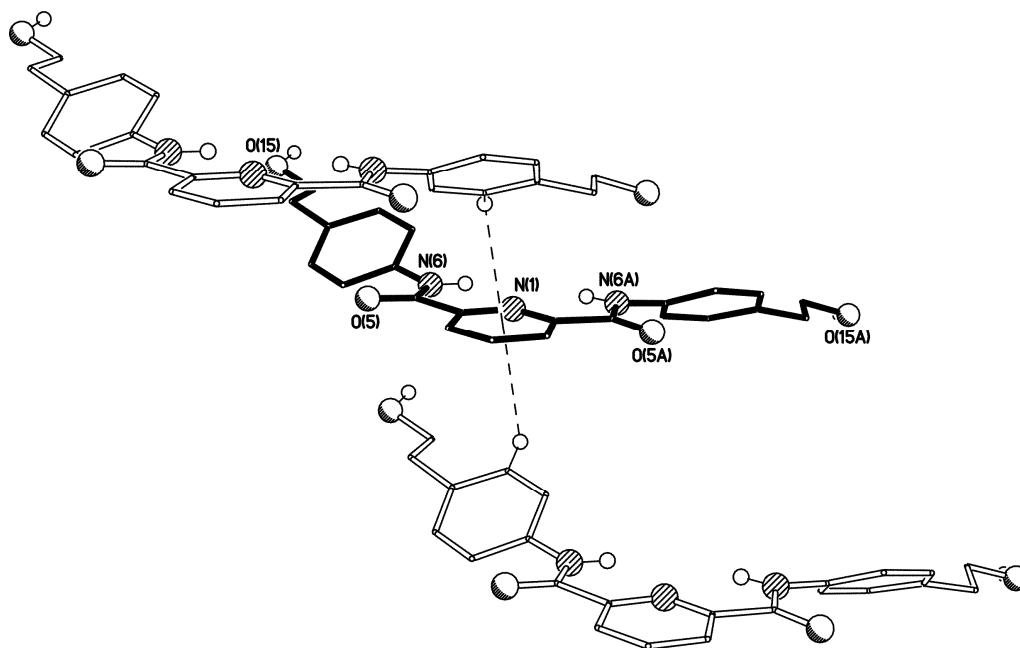


Fig. S9 Part of the packing in the structure of **L**⁶ showing the C–H··· π contacts to the N(1) pyridyl ring.

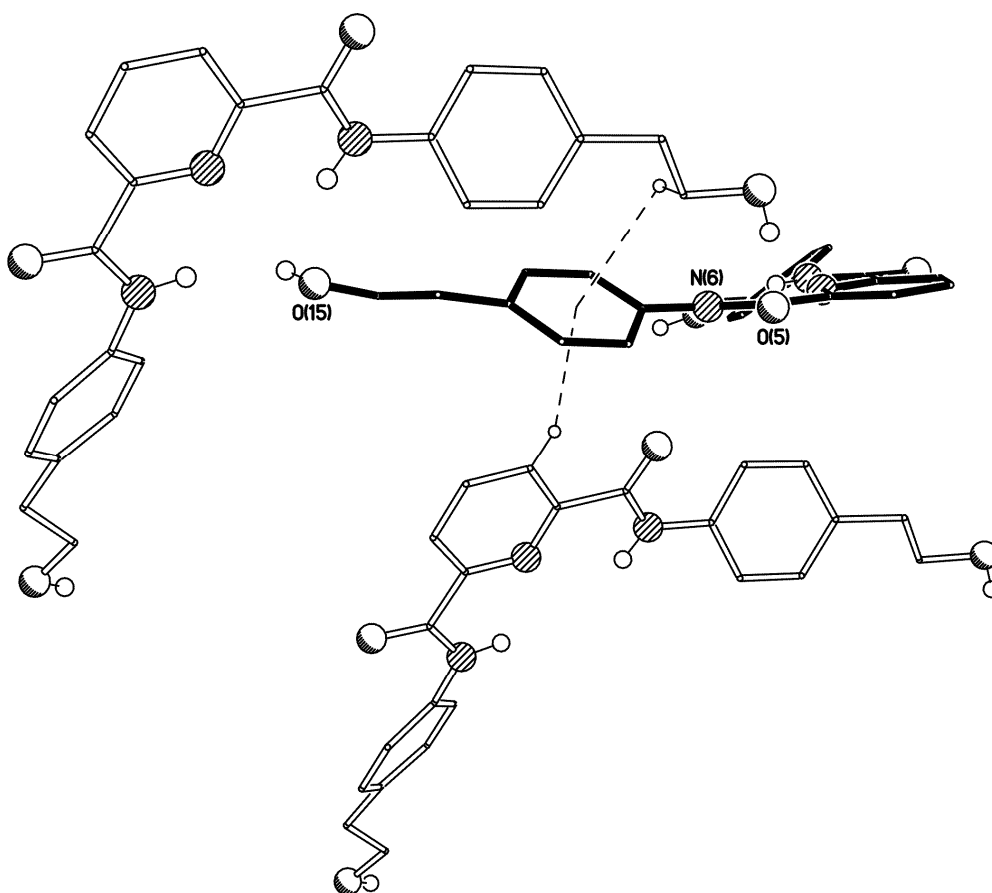


Fig. S10 Part of the packing in the structure of **L**⁶ showing the C–H··· π contacts to the N(6)-bound phenyl ring.

2. FRET studies

2.1 Quadruplex DNA melting curves determined by FRET

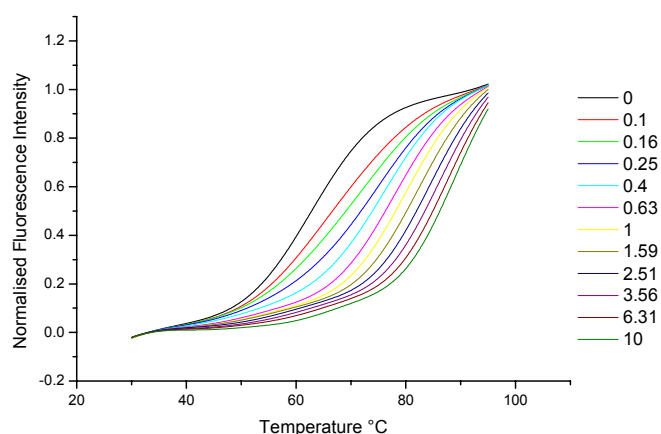


Fig. S11. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of complex **1**

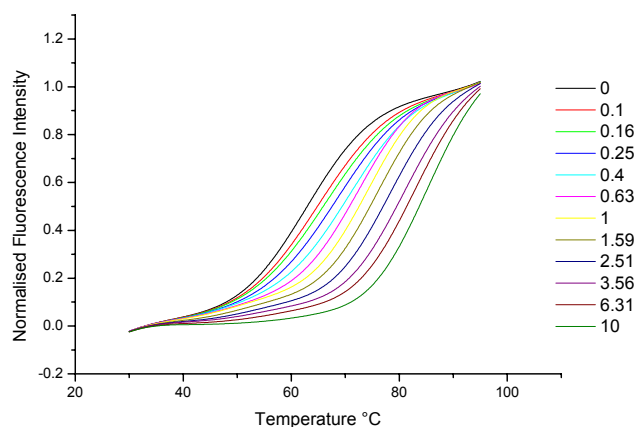


Fig. S12. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of complex **2**

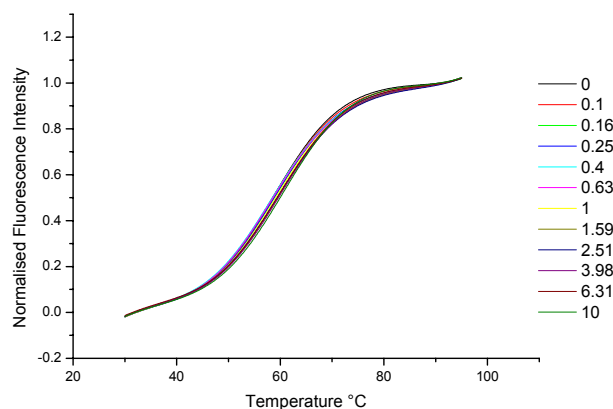


Fig. S13. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of **L3**

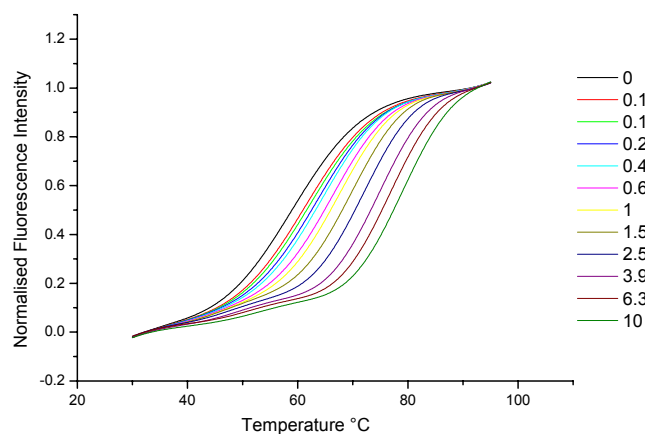


Fig. S14. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of **L4**

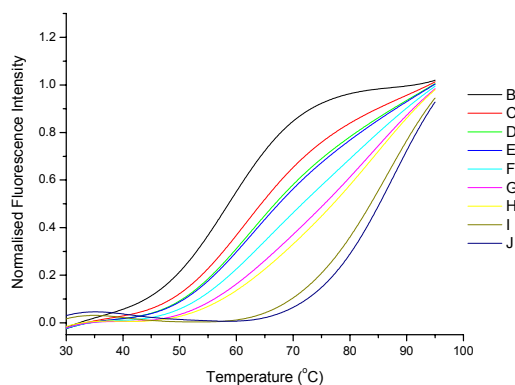


Fig. S15. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of complex **4**

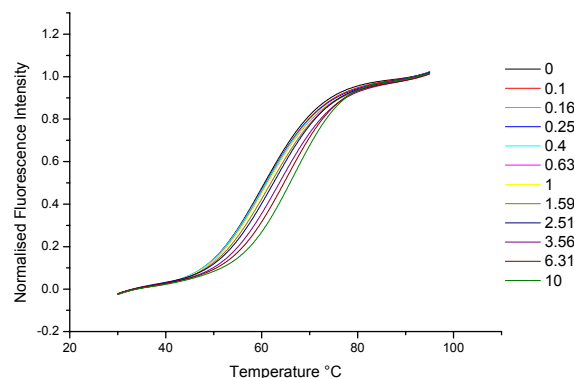


Fig. S16. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of **L6**

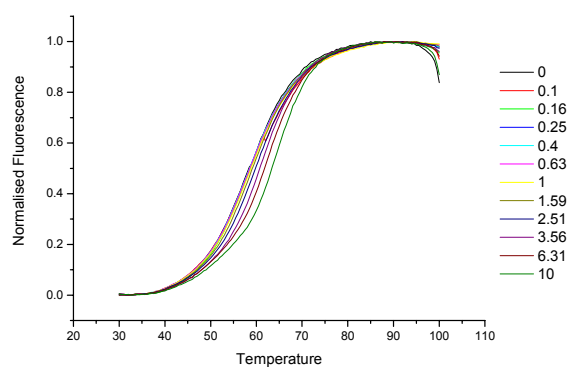


Fig. S17. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of **L7**

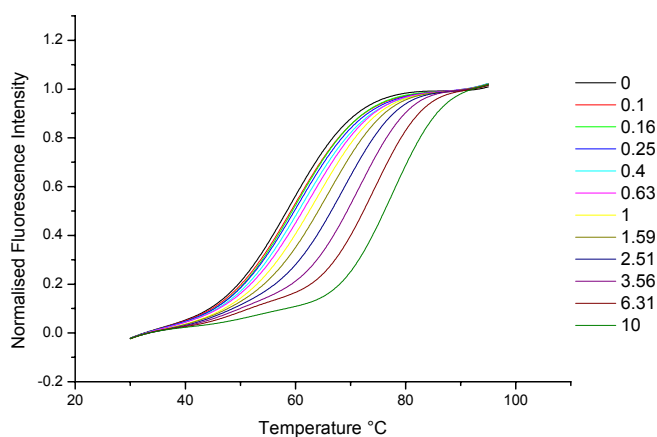


Fig. S18. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of **L8**

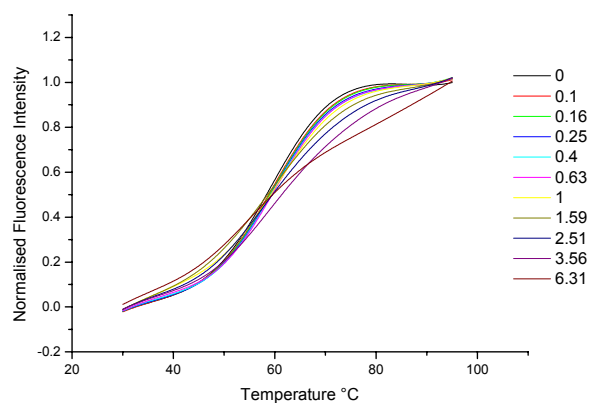


Fig. S19. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of complex **7**

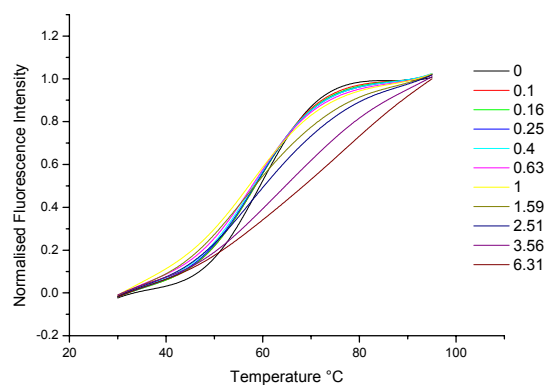


Fig. S20. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of complex **8**

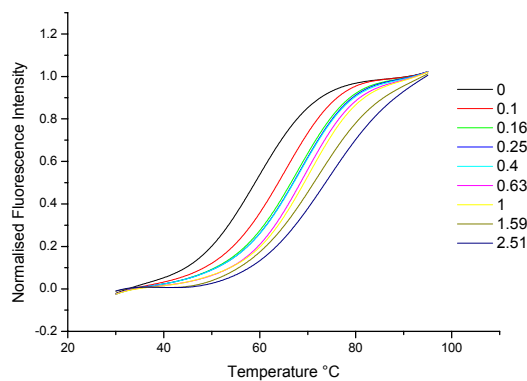


Fig. S21. Quadruplex DNA melting curves for different concentrations (values in plot given in μM) of complex **9**

2.2 Quadruplex DNA melting curves determined by FRET

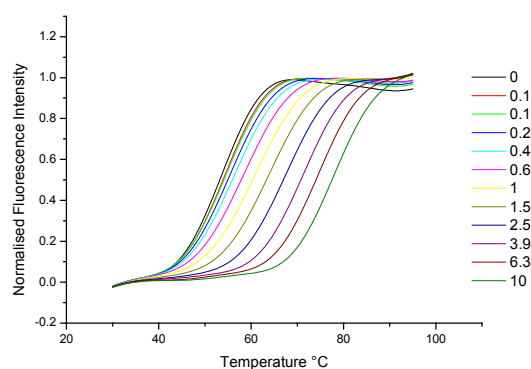


Fig. S22. Duplex DNA melting curves for different concentrations (values in plot given in μM) of complex **1**

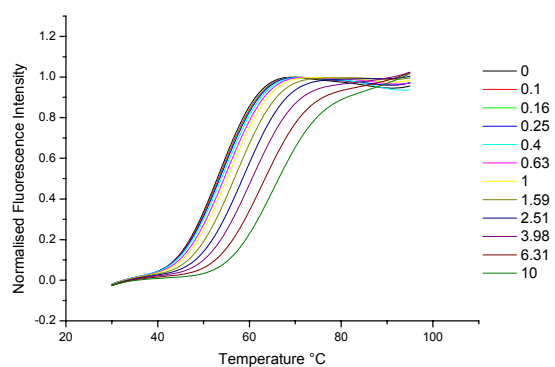


Fig. S23. Duplex DNA melting curves for different concentrations (values in plot given in μM) of complex **2**

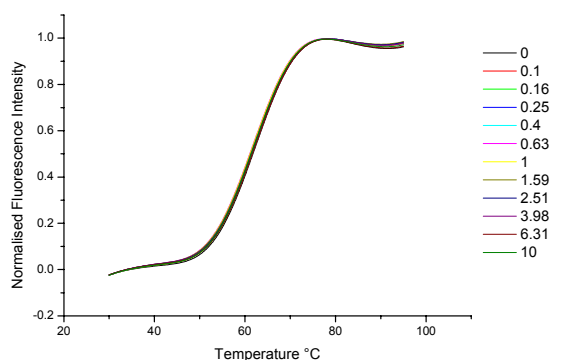


Fig. S24. Duplex DNA melting curves for different concentrations (values in plot given in μM) of **L3**

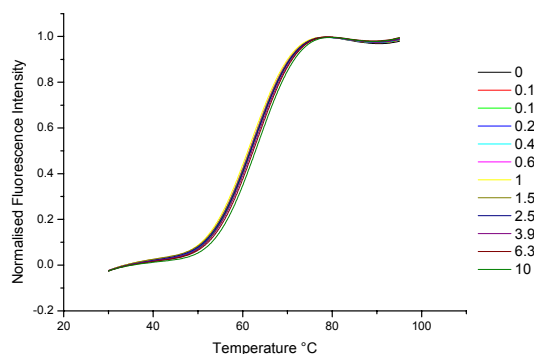


Fig. S25. Duplex DNA melting curves for different concentrations (values in plot given in μM) of **L4**

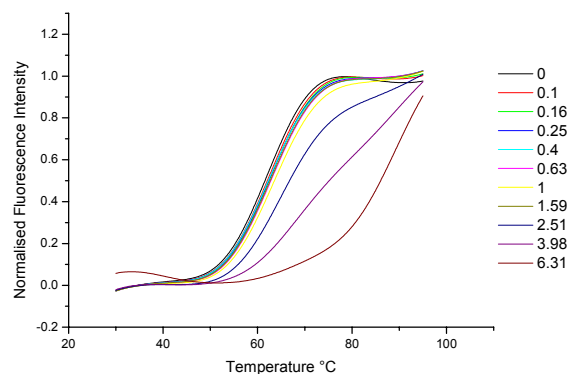


Fig. S26. Duplex DNA melting curves for different concentrations (values in plot given in μM) of complex **4**

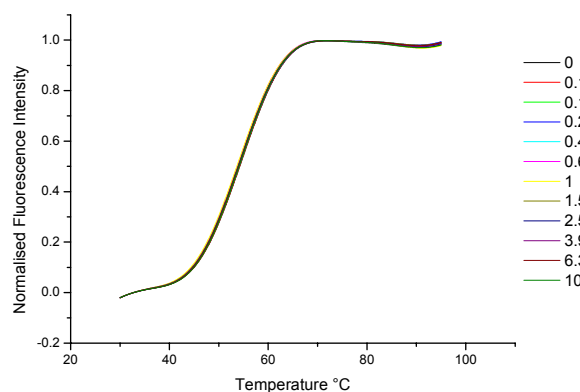


Fig. S27. Duplex DNA melting curves for different concentrations (values in plot given in μM) of **L6**

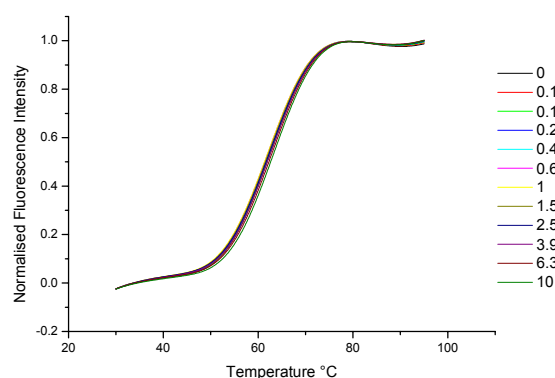


Fig. S28. Duplex DNA melting curves for different concentrations (values in plot given in μM) of **L8**

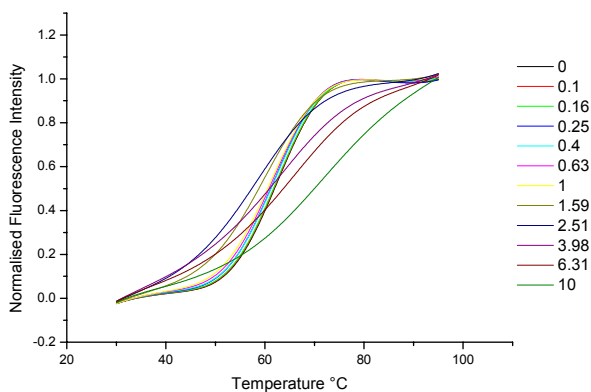


Fig. S29. Duplex DNA melting curves for different concentrations (values in plot given in μM) of complex **7**

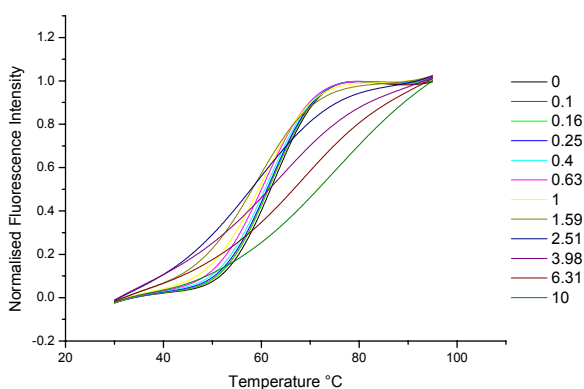


Fig. S30. Duplex DNA melting curves for different concentrations (values in plot given in μM) of complex **8**

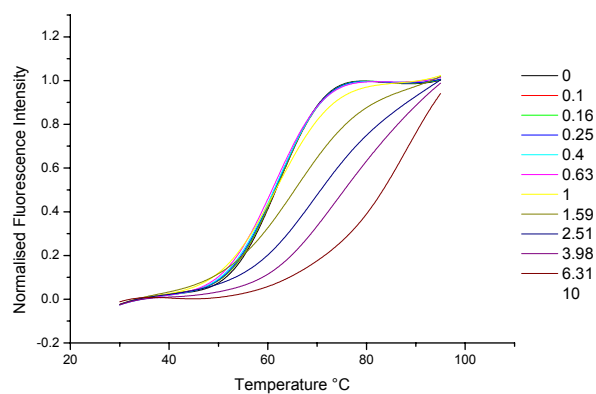


Fig. S31. Duplex DNA melting curves for different concentrations (values in plot given in μM) of complex **9**