Synthesis and Characterisation of First Row Transition Metal Complexes of Functionalized 1,2,4-Benzothiadiazines
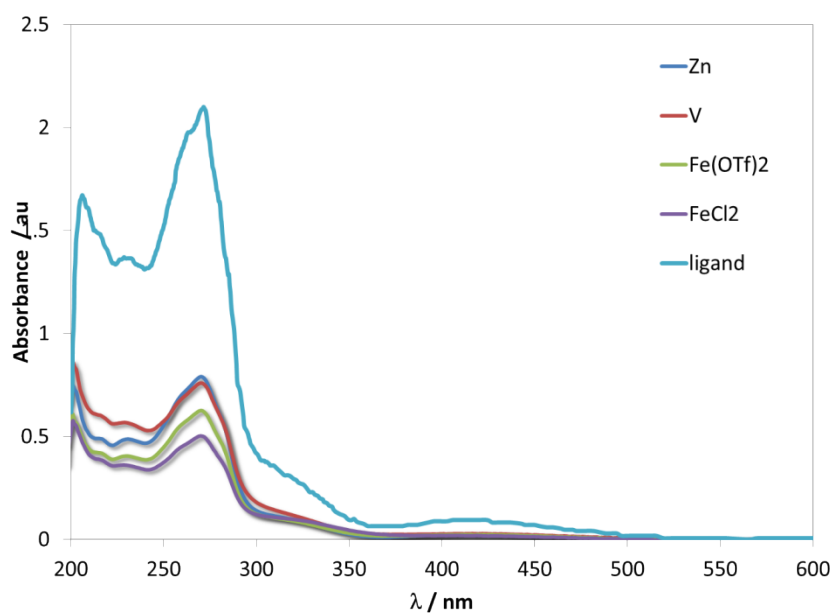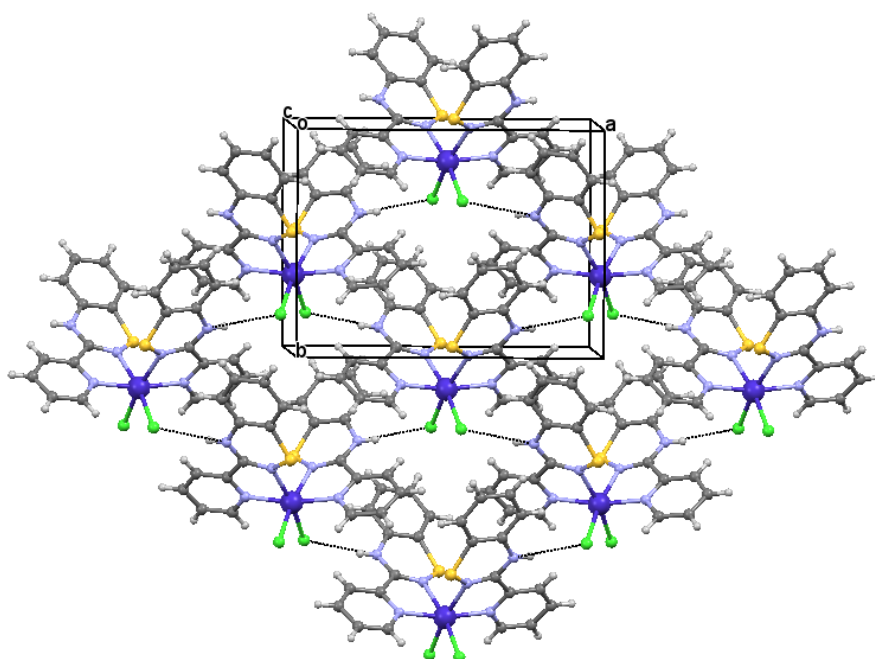
E. R. Clark, M. U. Anwar, B. J. Leontowicz, Y. Beldjoudi, J. J. Hayward, W. Chan, E. L. Gavey, M. Pilkington, E. Zysman-Colman and J. M. Rawson*
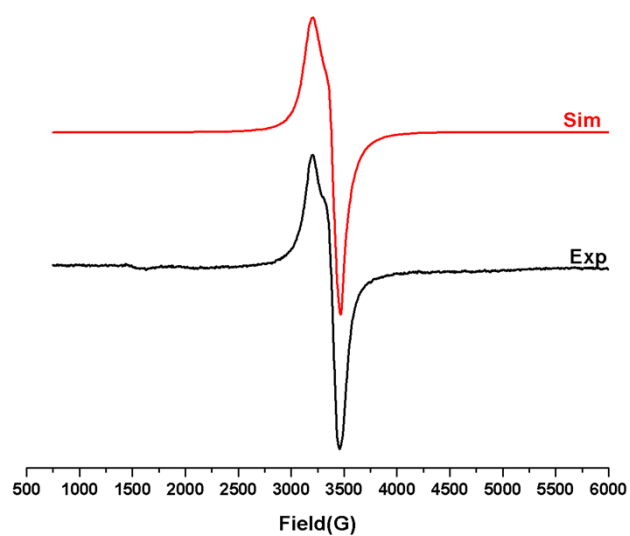
Supplementary Information

Fig. S1   Solution UV/vis spectra of selected derivatives of **1**, along with **3** and **4** as well as the parent ligand **L** to emphasise the ligand-based nature of the spectroscopic properties.

Fig. S2   Crystal packing of **1** in the *ab* plane revealing the two dimensional nature of the hydrogen-bonded motif.

Fig. S3   Experimental and simulation EPR spectra of **2** in solid-state at room temperature (295K); $g_{xx} = g_{yy} = 2.054$, $g_{zz} = 2.200$ ($<g> = 2.103$), $a_{xx} = a_{yy} = a_{zz} = 25G$, $\Delta H_{xx} = 175$, $\Delta H_{yy} = 25$, $\Delta H_{zz} = 75$ G.

Fig. S4   Curie-Weiss behaviour of **2** (left) ($C = 0.416$ emu.K.mol^{-1}, g= 2.103) and M *vs* H plot for **2** at 5 K (right) with the dotted line representing the fit to the Brillouin function for an S = ½ paramagnet (g = 2.103).

Fig. S5   Magnetic response of **3** in the region 5 K – 300 K.

Fig. S6   X-band EPR spectrum of **4** cast in a thin film of *p*-ClC$_6$H$_4$CN measured at room temperature. Simulation parameters were: $g_{11} = 1.950$, $g_{22} = g_{33} = 1.994$, $a_{V(11)} = 172$ G and $a_{V(22)} = a_{V(33)} = 66$ G, $\Delta H_{pp(11)} = 55$ G, $\Delta H_{pp(22)} = \Delta H_{pp(33)} = 42$ G (Lorentzian lineshape).
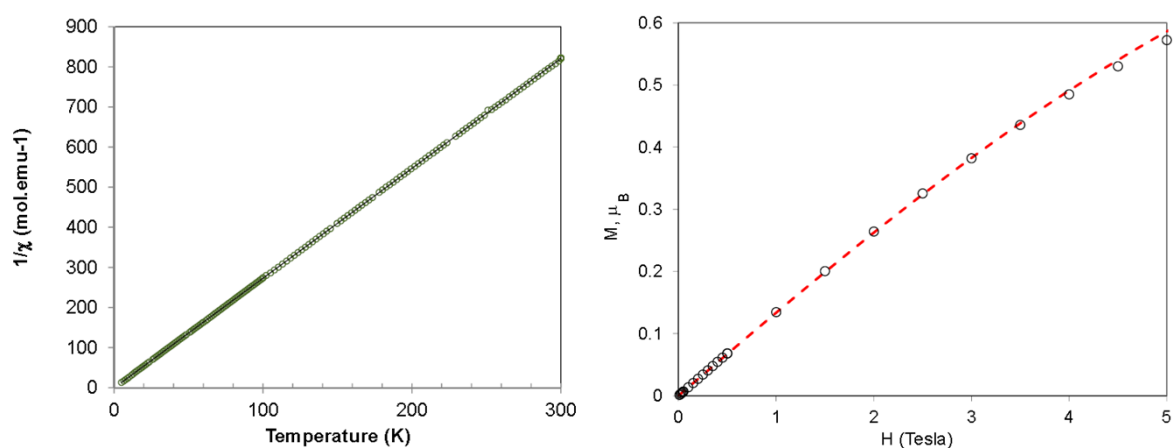
Fig. S1: Solution UV/vis spectra of selected derivatives of **1**, along with **3** and **4** as well as the parent ligand **L** to emphasise the ligand-based nature of the spectroscopic properties.

Fig. S2 Crystal packing of **1** in the *ab* plane revealing the two dimensional nature of the hydrogen-bonded motif.

Fig. S3 Experimental and simulation EPR spectra of 2 in solid-state at room temperature (295K); g_{xx} = g_{yy} = 2.054, g_{zz} = 2.200 (<g> = 2.103), a_{xx} = a_{yy} = a_{zz} =25G, ΔH_{xx} = 175, ΔH_{yy} = 25, ΔH_{zz} = 75 G.

Fig. S4 Curie-Weiss behaviour of **2** (left) (C = 0.416 emu.K.mol^{-1}, g= 2.103) and M *vs* H plot for **2** at 5K (right) with the dotted line representing the fit to the Brillouin function for an S = ½ paramagnet (g = 2.103).

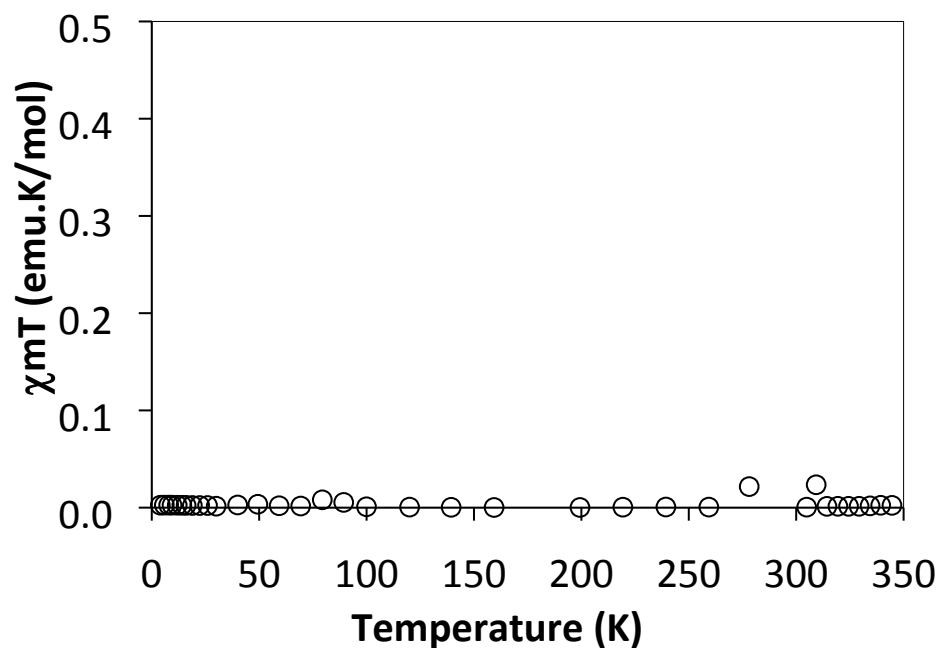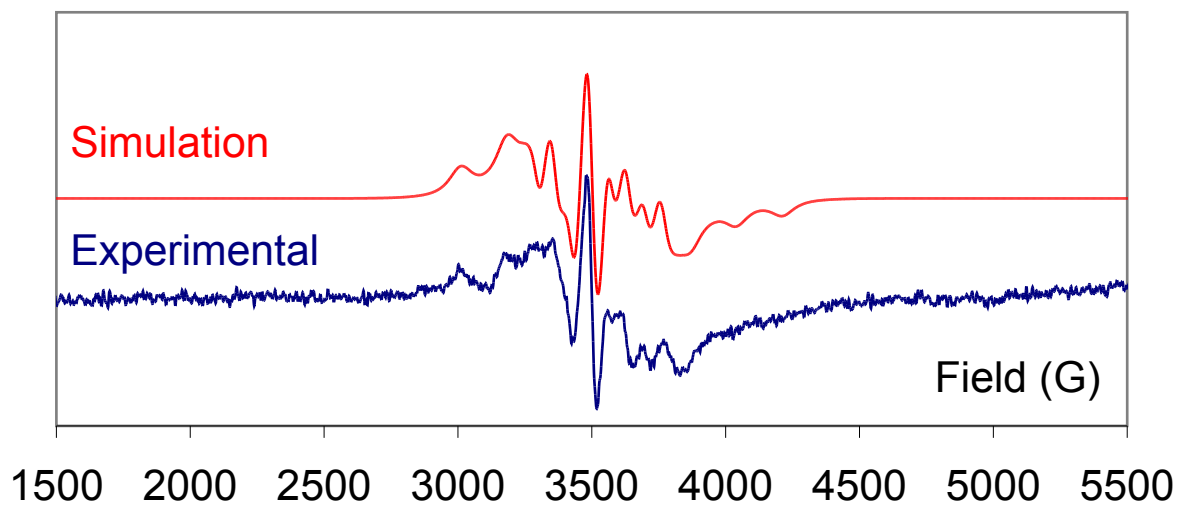**Fig. S5** Magnetic response of **3** in the region 5 K – 300 K.

Fig. S6 X-band EPR spectrum of **4** cast in a thin film of p-ClC$_6$H$_4$CN measured at room temperature. Simulation parameters were: $g_{11} = 1.950$, $g_{22} = g_{33} = 1.994$, $a_{V(11)} = 172$ G and $a_{V(22)} = a_{V(33)} = 66$ G, $\Delta H_{pp(11)} = 55$ G, $\Delta H_{pp(22)} = \Delta H_{pp(33)} = 42$ G (Lorentzian lineshape).