Hydrophobic tail length in spin crossover active iron(II) complexes predictably tunes $T_{1/2}$ in solution and enables surface immobilisation

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ELECTRONIC SUPPORTING INFORMATION

Contents

S1. NMR spectra and solvent dependent tautomerism	2
S2. Variable temperature Evans method ¹ H-NMR spectra for all complexes	. 20
S3. Calculation and fitting of $\chi_M T$ vs T data from VT Evans method NMR spectra	. 29
S4. Infrared spectra of all complexes	. 36
S5. Monolayer surface deposition of [Fe ^{II} (L ^{H-OC18})(NCBH ₃) ₂] by the Langmuir Blodgett technique .	. 42
S6 ESI Mass spectra:	. 44
S7. References:	. 50



S1. NMR spectra and solvent dependent tautomerism

Figure S1: Comparison of the ¹H NMR spectra of HL^{H-OH} in CDCl₃ versus D₆-DMSO.



Figure S2: ¹H NMR spectrum of HL^{H-OH} in D₆-DMSO.



Figure S3: ¹³C NMR spectrum of HL^{H-OH} in D₆-DMSO.



Figure S4: Possible ring-chain tautomeric equilibrium of compound L^{H-OH} in CDCl₃ solvent, which is not observed in D₆-DMSO, analogous to that reported for a similar system studied by Crumbie.¹



Figure S5: gCOSY NMR spectrum of HL^{H-OH} in D₆-DMSO.



Figure S6: ¹H NMR spectrum for L^{H-oc10} in D₆-DMSO.



Figure S7: ¹³C NMR spectrum for L^{H-OC10} in D₆-DMSO.



Figure S8: gCOSY NMR spectrum for L^{H-OC10} in D₆-DMSO.



Figure S9: ¹H NMR spectrum for L^{H-OC16} in D₆-DMSO.



Figure S10: ¹³C NMR spectrum for L^{H-OC16} in D₆-DMSO.



Figure S11: ¹H NMR spectrum for L^{H-OC18} in D₆-DMSO.



Figure S12: ¹³C NMR spectrum for L^{I-OC18} in D₆-DMSO.



Figure S13: gCOSY NMR spectrum for L^{H-OC18} in D₆-DMSO.



Figure S14: ¹H NMR spectrum for L^{H-OC20} in D_6 -DMSO.



Figure S15: ¹³C NMR spectrum for L^{H-C20} in D₆-DMSO.



Figure S16: ¹H NMR spectrum for L^{H-OC22} in D₆-DMSO.



Figure S17 : ¹³C NMR spectrum for L^{H-C22} in D₆-DMSO.



Figure S18: gCOSY NMR spectrum for L^{H-OC22} in D₆-DMSO.

S2. Variable temperature Evans method ¹H-NMR spectra for all complexes

Variable temperature solution magnetic susceptibility data were measured using the Evans ¹H NMR spectroscopy method,² on a Varian 500 MHz VNMRS spectrometer, for all six complexes in CD₃CN (298-343 K), and for the $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ complex also in CD₃NO₂ (298-343 K) and $(CD_3)_2CO$ (243-303 K).

In all cases the samples were prepared by dissolving a precisely known mass in 0.500 mL of the appropriate solvent, to give a 5.00×10^{-3} M solution of complex. Pure solvent was placed in a special capillary NMR tube, which is located inside the outer tube that contains the paramagnetic solution in the same solvent.

The NMR spectrometer probe temperature is displayed to one decimal place and is accurate to \pm 0.5 K. Herein, T was considered 'settled' when it remained unchanged at the target T, to one decimal place, on the display for a 'wait' time of 2 minutes (except for the thermal hysteresis studies where the wait time was 5 minutes), at which point the Evans NMR spectrum was obtained, before ramping to the next target T and repeating the protocol.



Figure S19: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(HL^{H-OH})(NCBH_3)_2]$ in CD₃CN. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).



Figure S20: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-OC10})(NCBH_3)_2]$ in CD₃CN. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).



Figure S21: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-C16})(NCBH_3)_2]$ in CD₃CN. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).



Figure S22: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ in CD₃CN. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).



Figure S23: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-OC20})(NCBH_3)_2]$ in CD₃CN. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).



Figure S24: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-OC22})(NCBH_3)_2]$ in CD₃CN. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).



Figure S25: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ in CD₃NO₂. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).

308 K		~								* 1	k J	k		-
303 K										м				
298 K										л			Л	
293 K		,								ı			J	
288 K		^								A			J	
283 K													L	
278 K													J	
273 K													J	
268 K													J	
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258 K		۸												
253 K		^											J	
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243 K		۱								*		¢		
10.0 9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0	5.5	5.0	4.5 4.0 f1 (ppm)	3.5	3.0	2.5	2.0

Figure S26: Stacked spectra, obtained by the Evans ¹H NMR method, for $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ in $(CD_3)_2CO$. The red stars indicate the solvent peaks for the inner capillary (pure solvent) vs outer solution (containing complex).

S3. Calculation and fitting of $\chi_M T$ vs T data from VT Evans method NMR spectra

The methodology to calculate $\chi_M T$ from Evans ¹H NMR method data at a range of temperatures has been previously described.²⁻⁴

The modelling of each dataset (using OriginPro version 9.1.0 software from the OriginLab Corporation) as a gradual and complete SCO, using the regular solution model, equation (1) below,⁴⁻⁶ resulted in good fits (see Figures 3 and 6 also Figures S27-S31 and Tables S1 and S2). For each data set, the fit gives Δ H and Δ S, the thermodynamic enthalpy and entropy values associated with the spin crossover. From these two values the T_{1/2} value can be calculated, simply by dividing Δ H/ Δ S, as Δ G = 0 at T_{1/2} (and Δ G = Δ H – T Δ S). The derived parameters are reported in Tables S1 and S2.

 $\chi_{M}T(T) = \chi_{M}T(max) / 1 + e^{((-\Delta H/RT) + (\Delta S/R))}$ (1) ^{refs 4-6}

Where:

 $\chi_M T(T)$ is $\chi_M T$ measured at temperature T,

 $\chi_M T(max)$ is the maximum $\chi_M T$ value, which herein was set to 3.5 emu K mol⁻¹ as this value falls within the expected literature range for iron(II) complexes.⁷⁻⁹

R is the ideal gas constant (8.314 J mol⁻¹ K^{-1})

Note:

The Evans method has a relative error of 5%,¹⁰ therefore significant errors are associated with the data fitting.

Table S1: Solution $\chi_M T$ vs T data for 5.00 X 10⁻³ M CD₃CN solutions of all six complexes, [Fe^{II}(HL^{H-OR})(NCBH₃)₂] (where **R** = **H**, **C10**, **C16**, **C18**, **C20** and **C22**), measured in the heating mode from 298.0 to 343.0 ± 0.5 K, at 5 K intervals (see section 2 for more details).

Temperature (K)	н	C10	C16	C18	C20	C22
298.0	0.33635	0.10063	0.16166	0.49335	0.32257	0.23220
303.0	0.33908	0.12326	0.16982	0.53029	0.38310	0.24742
308.0	0.34069	0.14880	0.23510	0.58437	0.47088	0.30128
313.0	0.34025	0.16292	0.31862	0.66107	0.87399	0.39685
318.0	0.34971	0.17795	0.40197	0.76611	1.10112	1.23729
323.0	0.36508	0.20251	0.60360	0.92722	1.86394	1.61069
328.0	0.36650	0.25140	0.73603	1.15827	2.21178	2.13663
333.0	0.36694	0.26656	0.87326	1.35711	2.44895	2.48208
338.0	0.38633	0.34258	0.95319	1.39584	2.53728	3.16988
343.0	0.38338	0.41158	1.08325	1.59063	2.68986	3.27169

Table S2: Solution $\chi_{M}T$ vs T for a 5.00 X 10⁻³ M solution of $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ in different solvents, measured in the heating mode in the appropriate temperature range for the respective solvent (starting safely above the freezing and ending safely below the boiling point), in 5 K intervals (see section 2 for more details).

Temperature (K)	CDNO₂	CDCN	(CD ₃) ₂ CO		
243.0			2.13581		
248.0			2.32961		
253.0			2.4987		
258.0			2.70915		
263.0			2.92706		
268.0			3.13750		
273.0			3.18584		
278.0			3.33177		
283.0			3.39136		
288.0			3.45236		
293.0			3.49912		
298.0	0.18601	0.37813	3.55952		
303.0	0.20108	0.45163	3.57463		
308.0	0.22430	0.46318			
313.0	0.23197	0.49138			
318.0	0.27255	0.58494			
323.0	0.41901	0.77414			
328.0	0.44262	0.98119			
333.0	0.49531	1.15126			
338.0		1.27528			
343.0		1.34547			



Figure S27: Plot of $\chi_M T vs T$ for a 5.00 X 10⁻³ M CD₃CN solution of [Fe^{II}(L^{H-OC18})(NCBH₃)₂], at 5 K intervals from 298.0 to 343.0 to 298.0 to 298.0 K (error on T is ± 0.5 K), confirming reproducibility of the small thermal hysteresis, and that it is due to the complex not instrument lag as the heating and cooling data points outside the loop overlay almost perfectly). Dots (first cycle) and stars (second cycle) are the data points; the lines just join the data points as a guide for the eye. See section 2 for the detailed protocol used.



Figure S28: Plot of $\chi_M T vs T$ for 5.00 X 10⁻³ M in CD₃CN solution of $[Fe^{II}(L^{H-C20})(NCBH_3)_2]$ at 5 K intervals from 298.0 to 343.0 K to 298.0 K (error on T is ± 0.5 K). Dots are the data points whereas the lines just join the data points as a guide for the eye. See section 2 for the detailed protocol used.



Figure S29: Plot of $\chi_M T vs T$ for 5.00 X 10⁻³ M in CD₃CN solutions of [Fe^{II}(**L**^{H-C22})(NCBH₃)₂] at 5 K intervals from 298.0 to 343.0 K to 298.0 K (error on T is ± 0.5 K). Dots are the data points whereas the line is just a guide for the eye and not a fitting. See section 2 for the detailed protocol used.



Figure S30: Plot of $\chi_M T vs T$ for 5.00 X 10⁻³ M in CD₃CN solution of $[Fe^{II}(L^{H-C20})(NCBH_3)_2]$ at 2 K intervals from 298.0 to 343.0 K to 298.0 K (error on T is ± 0.5 K). Dots are the data points whereas the line is just a guide for the eye and not a fitting. See section 2 for the detailed protocol used.



Figure S31: Plot of $\chi_M T$ vs T for 5.00 X 10⁻³ M in CD₃CN solution of $[Fe^{II}(L^{H-C18})(NCBH_3)_2]$ at 5 K intervals from 298.0 to 343.0 to 298.0 K (error on T is ± 0.5 K). No hysteresis is seen. Dots are the data points whereas the line is just a guide for the eye and not a fitting. See section 2 for the detailed protocol used.

S4. Infrared spectra of all complexes



Figure S32: ATR Infrared spectrum of [Fe^{II}(HL^{H-OH})(NCBH₃)₂]



S37



Figure S34: ATR Infrared spectrum of [Fe^{II}(L^{H-OC16})(NCBH₃)₂]



Figure S35: ATR Infrared spectrum of [Fe^{II}(L^{H-OC18})(NCBH₃)₂]



Figure S36: ATR Infrared spectrum of [Fe^{II}(L^{H-OC20})(NCBH₃)₂].



Figure S37: ATR Infrared spectrum of [Fe^{II}(L^{H-OC22})(NCBH₃)₂]

S5. Monolayer surface deposition of $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ by the Langmuir Blodgett technique



Figure S38: Pressure area isotherms on an air/water interface at 298 K for: (red) $[Fe^{II}(L^{H-OC10})(NCBH_3)_2]$, (brown) $[Fe^{II}(L^{H-OC16})(NCBH_3)_2]$, (blue) $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$, (pink) $[Fe^{II}(L^{H-OC20})(NCBH_3)_2]$ and (green) $[Fe^{II}(L^{H-OC22})(NCBH_3)_2]$.



Figure S39: Surface deposition of 20 μ L of a 1:1 mixture of stearic acid and [Fe^{II}(L^{H-OC18})(NCBH₃)₂] in a 9:1 mixture of chloroform and methanol at a concentration of 1 mg/mL onto a hydrophilic quartz slide. After carefully adding the 20 μ L aliquot onto the water subphase and leaving it 30 minutes for the organic solvents to evaporate the barriers were compressed at a speed of 5 mm min⁻¹ to a point at which the surface pressure was 40 mN m⁻¹. The surface pressure was then set to be maintained at 40 mN m⁻¹ as the slide was brought up through the surface from the subphase. The area of the trough was monitored throughout the deposition process. Successful deposition of a monolayer on the slide was indicated by the decrease in total trough area from 6389 to 5609, i.e. 780 mm² (a decrease in area is required in order to maintain the surface pressure at 40 mN m⁻¹), which is close to that of the area of the quartz slide (900 mm²), giving a transfer ratio of 0.9 (ideal transfer ratio = 1).

The transfer ratio (TR) is calculated by the simple formula:

 $TR = A_i/A_s$

Where A_i is the decrease in the monolayer area and A_s is area of the substrate (18 mm x 25 mm rectangular quartz slide = 450 mm² per side = 900 mm² in total as both sides are coated in the deposition process)

So the TR for this 1:1 mixture of stearic acid and $[Fe^{II}(L^{H-OC18})(NCBH_3)_2]$ is

 $A_i = 780 \text{ and } A_s = 900$

TR = 780/900 = 0.9.

S6. ESI mass spectra



Figure S40: Mass spectrum of HL^{H-OH}.



Figure S41: Mass spectrum of L^{H-OC10}.



Figure S42: Mass spectrum of L^{H-OC16}.



Figure S43: Mass spectrum of L^{H-OC18}.



Figure S44: Mass spectrum of L^{H-OC20}.



Figure S45: Mass spectrum of L^{H-OC22}.



Figure S46: Mass spectrum of [Fe^{II}(HL^{H-OH})(NCBH₃)₂].



Figure S47: Mass spectrum of $[Fe^{II}(L^{H-OC10})(NCBH_3)_2]$.



Figure S48: Mass spectrum of $[Fe^{II}(L^{H-OC16})(NCBH_3)_2]$.



Figure S49: Mass spectrum of [Fe^{II}(L^{H-OC18})(NCBH₃)₂].



Figure S50: Mass spectrum of [Fe^{II}(L^{H-OC20})(NCBH₃)₂].



Figure S51: Mass spectrum of [Fe^{II}(L^{H-OC22})(NCBH₃)₂].

S7. References

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