

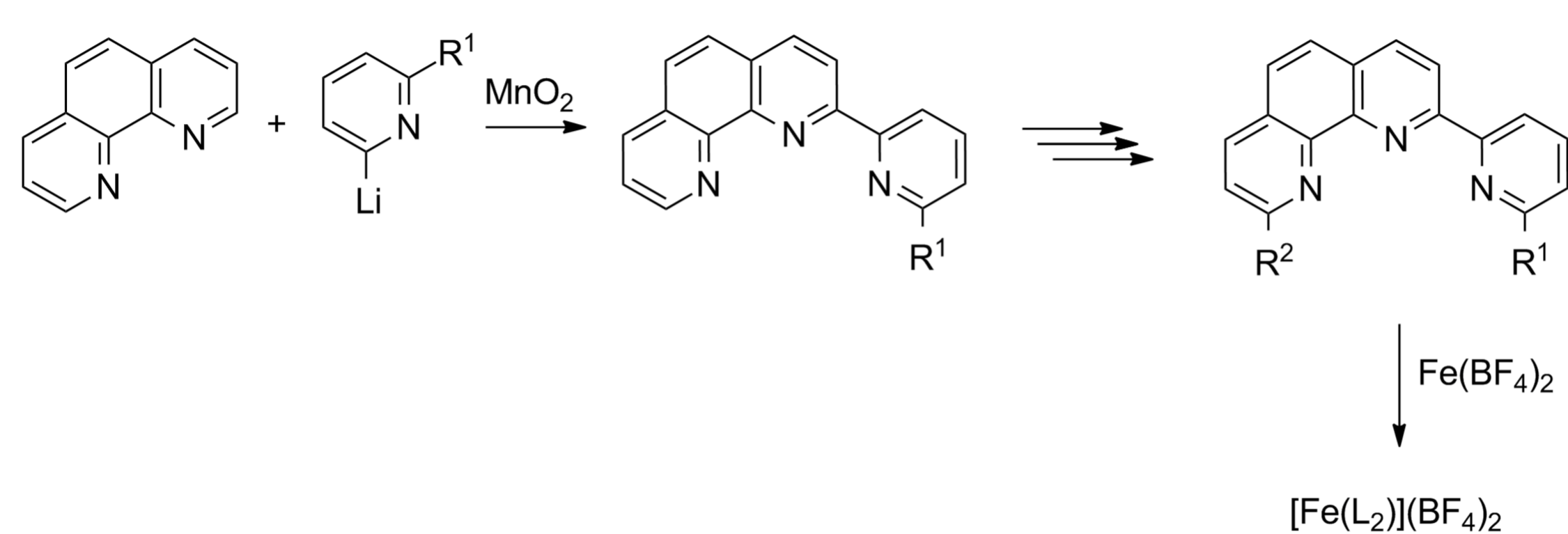
Synthesis of novel terpy-analogous ligands and their application in Fe²⁺ Spin Crossover complexes

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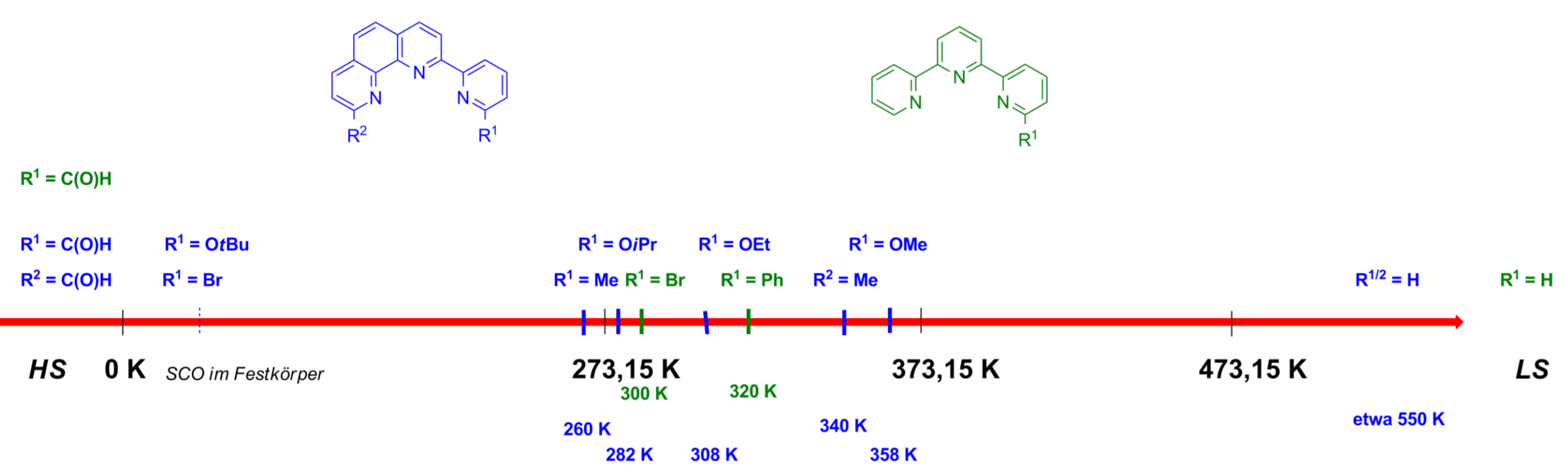
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Fe²⁺ spin crossover (SCO) complexes are of interest due to their unique magnetic and photophysical properties. Whereas in the last decades SCO research was focused on finding wide hysteresis loops around room temperature nowadays the LIESST-effect becomes more and more attractive.[1] Both effects lead to bistable systems which can be exploited as molecular memories or switches. The LIESST-effect is a molecular property and therefore is also observable in other matrixes, large hysteresis loops are often found in crystals as a consequence of intermolecular interactions. It was shown that terpy analogous tridentate ligands can show both high LIESST temperatures as well as wide hysteresis loops.[2] We recently started to elaborate syntheses of terpy analogous ligands that are readily prepared in a few-step synthesis route and which can be easily tuned. The 2-(pyridin-2-yl)-1,10-phenanthroline motif has yet been unused in Fe²⁺-SCO complexes but meets the two requirements. Most of the complexes [(L₂Fe)²⁺] are indeed SCO-systems. The 6-position (R¹) on the pyridine or the 9-position (R²) in the phenanthroline part can be easily substituted. Most of the transformations are simple. We have found that all complexes bearing substituents that have no donor ability to the metal center are SCO systems with T_{1/2} spanning from 600 K to < 170 K in solution. Substituents that are able to act as donors to the metal center lead to pure HS systems. The R¹ position has greater influence on T_{1/2} than the R² position and analogous terpy complexes show transitions that are 100-200 K higher.

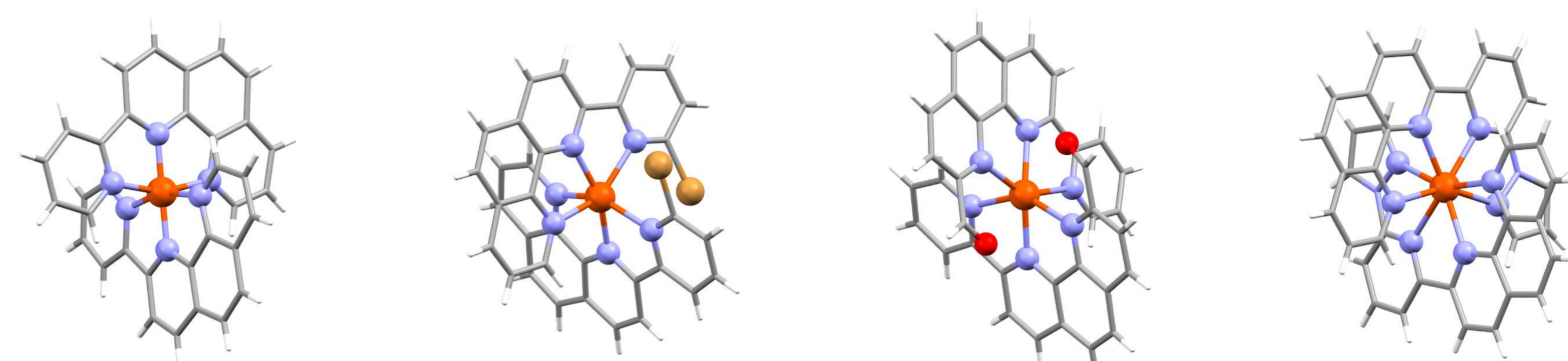
Syntheses and T_{1/2}



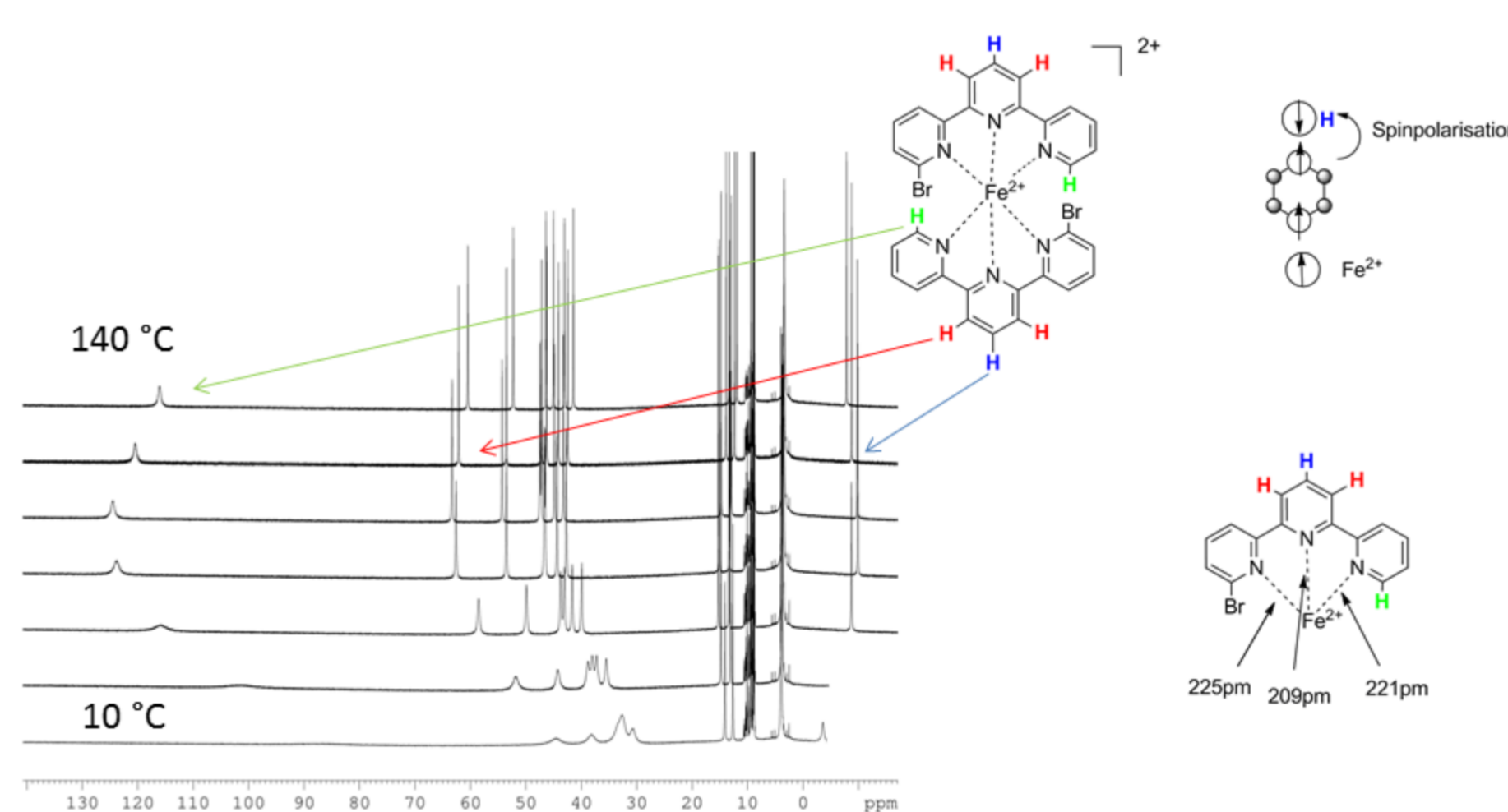
The Key step in the syntheses of 2-(pyridin-2-yl)-1,10-phenanthrolines is the nucleophilic attack of a *ortho*-lithio pyridine on phenanthroline. Due to the conjugation with the anellated aromatic ring system this reaction proceeds smoothly. Further transformations allow the synthesis of a broad number of 2-(pyridin-2-yl)-1,10-phenanthroline derivatives. The corresponding Fe²⁺-complexes are obtained by treatment with Fe²⁺ salts, like [Fe(H₂O)₆](BF₄)₂. Nearly all of the Fe²⁺ complexes are SCO systems with a wide range of transition temperatures spanning from <170 K (R¹ = Br) to 550 K (parent complex). Below are the transition temperatures given found in solution.



Molecular Structures

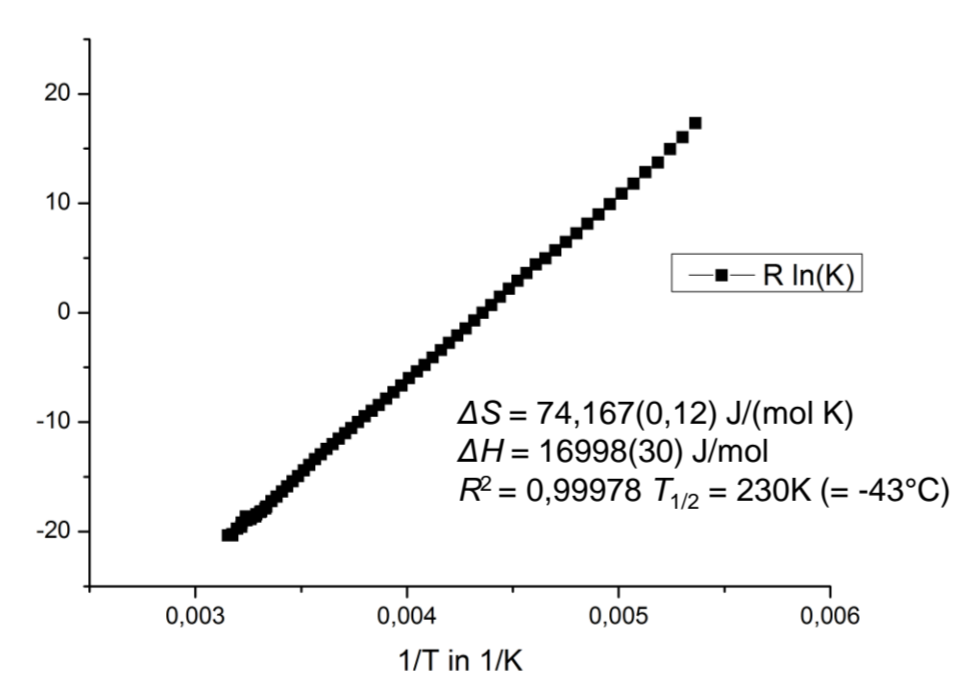
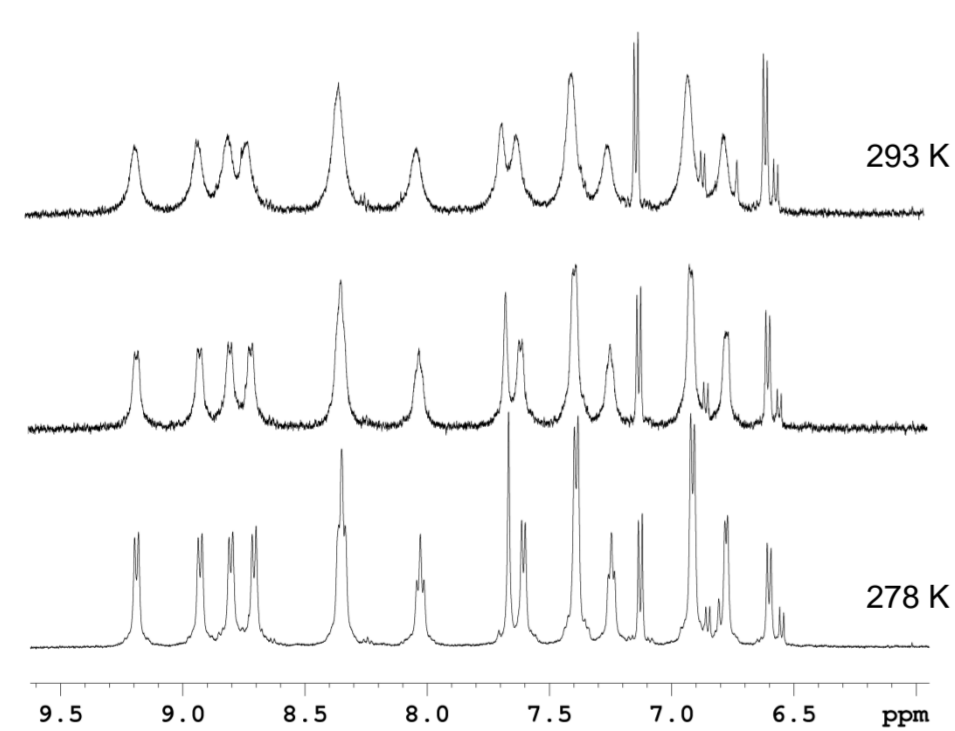
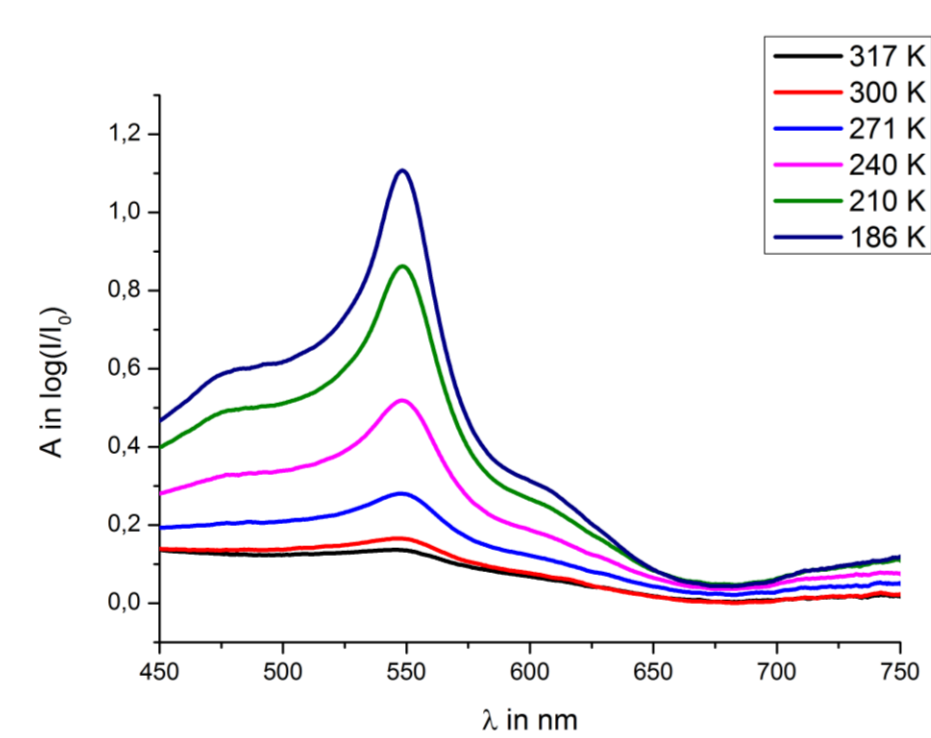
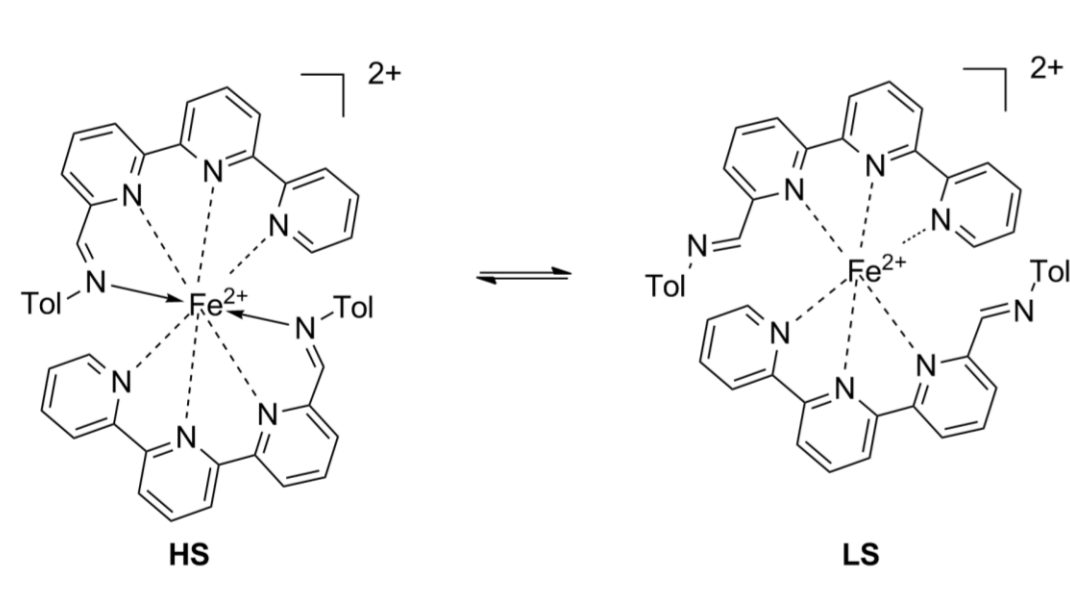


parent	R ¹ = Br	R ² = C(O)H	R ¹ = N-pyrazol
1.962 (LS)	2.63 (110 K/LS)	8.45 (HS)	18.25 (HS)
1.88-2.0 Å	6.22 (RT/HS) 1.89-2.07 Å (LS) 2.09-2.25 Å (HS)	2.15-2.41 Å	2.28.2.42 Å



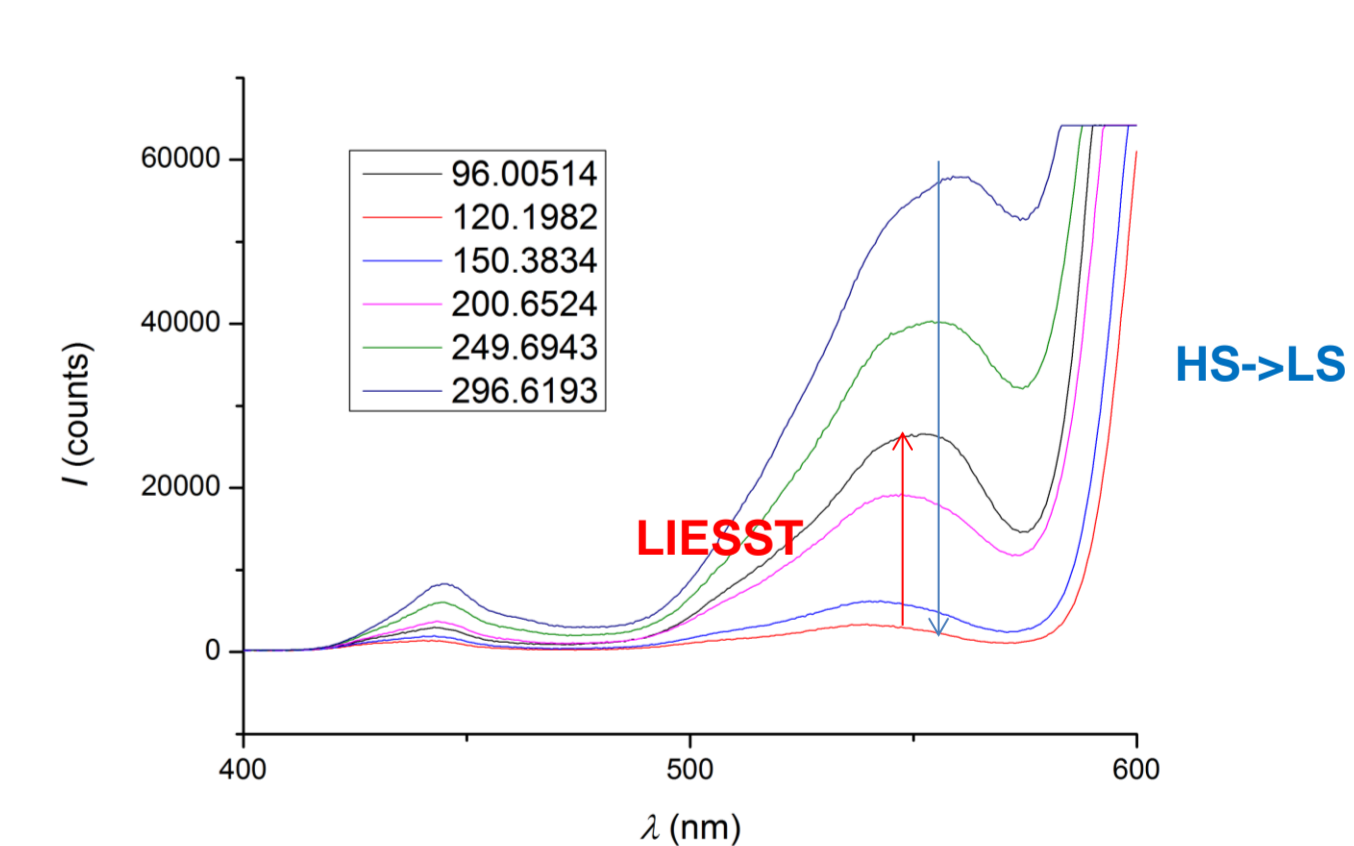
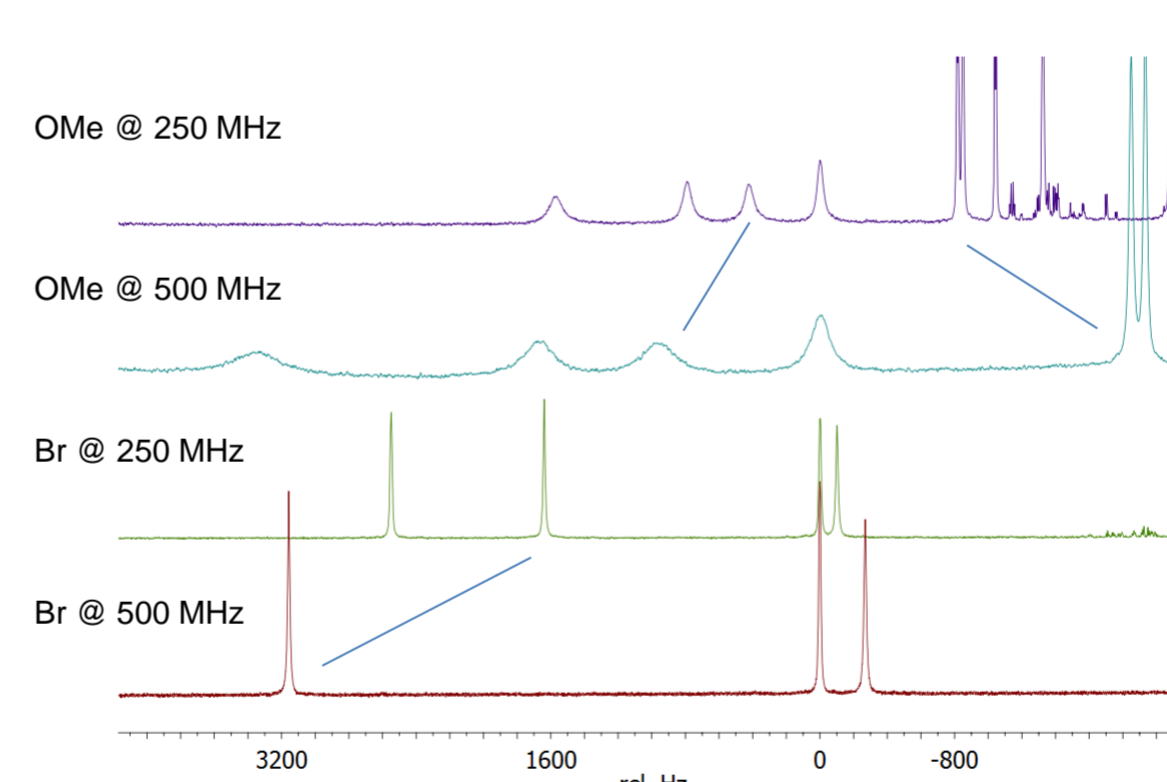
The distortion of a coordination environment and the bond length differences play an important role as they determine the anisotropy of HS-LS transition and the activation barrier. In this series of complexes the distortion of N6 octahedron spans over a large range. Starting with the parent complex to the N8 complex with *N*-pyrazol in the R¹ position. Below the molecular structures from x-ray analysis the constant **symmetry measure values (csm)** [4] are given. Also the **Fe-N bond length** differ by more the 0.3 Å. Our next aim is to find complexes that are in a constant equilibrium between the left and right side. All complexes can be conveniently investigated by ¹H NMR spectroscopy

Extremely Slow HS-LS Equilibrium



Substituents that are able to act as 7th or even 8th donor lead to stable HS complexes hence no SCO is observed. To get back a SCO system that work between a N6-LS state and (N6+X)-HS state the donor ability must be reduced. This is achieved by replacing the well coordinating aldehyde by the weakly coordinating imine, this sounds odd, but in this case "size matters". Still in this system the spin state is associated with large structural change and therefore the equilibrium is unusual slow (in the Fe²⁺-SCO world). In this system the low temperature NMR Spectra aren't characterized by a averaging over LS and HS chemical shift, instead the LS state becomes resolved and the rate constant for LS to HS transition reflects in the line broadening.

LIESST Effect for Everyone



Take home your LIESST-Stipe

The purple compound is a complex from this series R¹ = OiPr. This complex shows a T_{1/2} around RT which is observable by gentle heating or cooling in liquid N₂. Moreover it can be excited to the HS-State with a green laser pointer. Dip the stripe in liquid N₂ and take it out and quickly point over it by a green laser pointer. You can see a bleaching that vanishes after the N₂ is evaporated.



to the clip

It was already shown by Letard and Halcrow groups that terpy analogue complexes show high activation barriers between LS and HS state.[1-3] This also reflects in line broadening that is strongly field dependent and only observed in SCO region. (upper left) Moreover this allows trapping of the metastable HS state near liquid nitrogen temperatures. The metastable HS state can be generated by irradiation with light, this process is very efficient with almost unity quantum yield. This is a molecular property hence it is also observed e. g. in polymer matrix. (upper right) In combination with the intensive CT bands observed in this compounds the excitation can be achieved by weak light sources like laser pointers.

Conclusion

The 2-(pyridin-2-yl)-1,10-phenanthroline and terpy analogue ligands allow fine tuning of Fe²⁺ SCO complexes and still are attractive subjects for developing new concepts in SCO research. Starting with strong field ligands allows observation of interesting substituent effects. Expansion of the coordination environment from N6 to N6+X is a possible mean of increasing anisotropy as well as the activation barrier between the HS and LS-state. The complexes show high T(LIESST) values and intensive charge transfer bands (CT bands) in the visible region which allow Light Induced HS-State Trapping by laser pointers.

References

- [1] J.-F. Letard, G. Chastanet, P. Guionneau, C. Desplanches, in *Spin-Crossover Mater.* (Ed.: M.A. Halcrow), Wiley & Sons, 2013, pp. 475–506.
- [2] J.-F. Letard, G. Chastanet, P. Guionneau, C. Desplanches, in *Spin-Crossover Mater.* (Ed.: M.A. Halcrow), Wiley & Sons, 2013, pp. 475–506.
- [3] J.-F. Letard, *J. Mater. Chem.* 2006, 16, 2550–2559.
- [4] <http://www.csm.huji.ac.il/new/>

Acknowledgement

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