

# Positive Cooperativity in Dinuclear Spin-Crossover Complexes

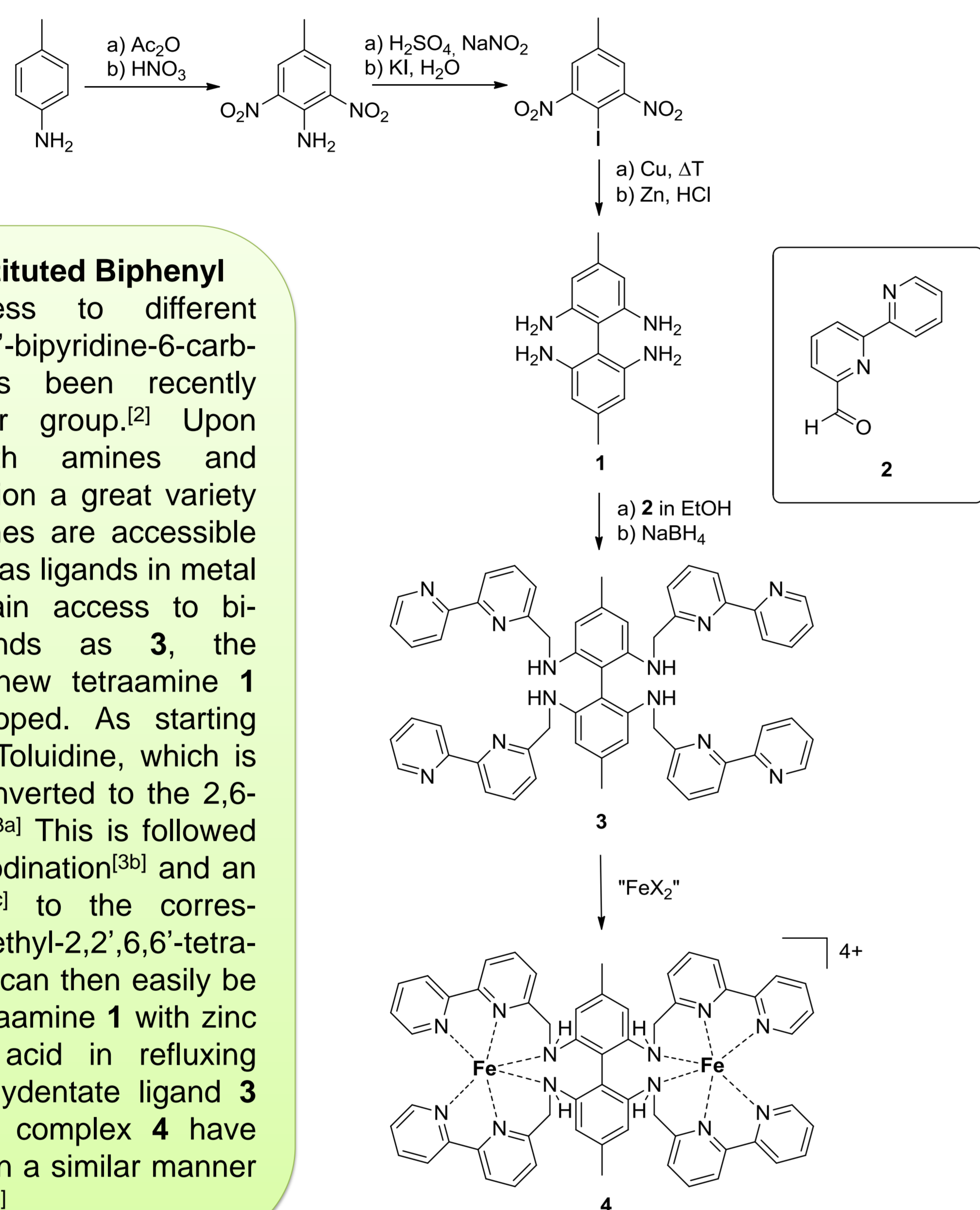
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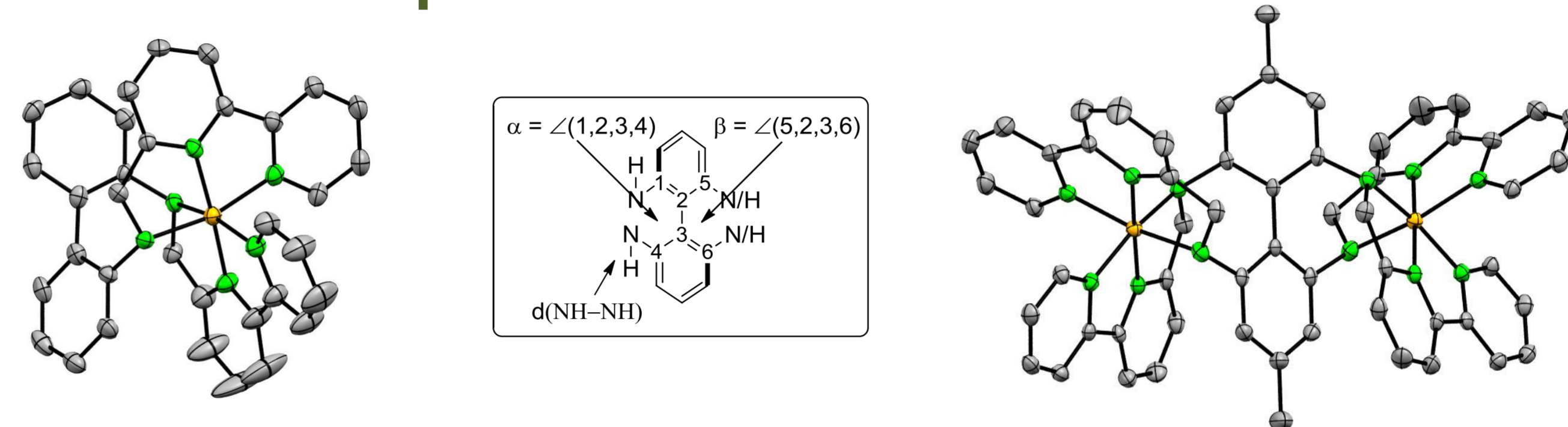
## Introduction

Due to their  $d^6$  electron configuration octahedral  $Fe^{2+}$  complexes can exist in a diamagnetic low-spin or a paramagnetic high-spin form. In the last 50 years a lot of complexes have been studied, which can change their spin state and accompanied with this also their magnetic behaviour and e.g. their colour upon change of external stimuli like temperature, pressure, light irradiation etc.<sup>[1]</sup> These so called Spin-Crossover (SCO) complexes have ever since been promising candidates for several applications as data storage, new displaying devices or for sensors. Recently we found a facile synthesis of a new group of  $Fe^{2+}$  SCO complexes and we could show the influence of several substitution patterns to the SCO transition temperature in solution.<sup>[2]</sup> As the next step we wanted to expand this ligand system to the coordination of two  $Fe^{2+}$  ions in a symmetrical fashion, because we believe that this ligand scaffold will allow a positive cooperativity of the SCO centres. This would indeed be the first example where a positive cooperativity in a dinuclear SCO complex would be achieved in solution. By investigation of these SCO complexes in solution packing effects and other difficulties can be avoided allowing the clear tracking of the interaction pathway.

## Synthesis of New Ligand Scaffold for Dinuclear Complexes



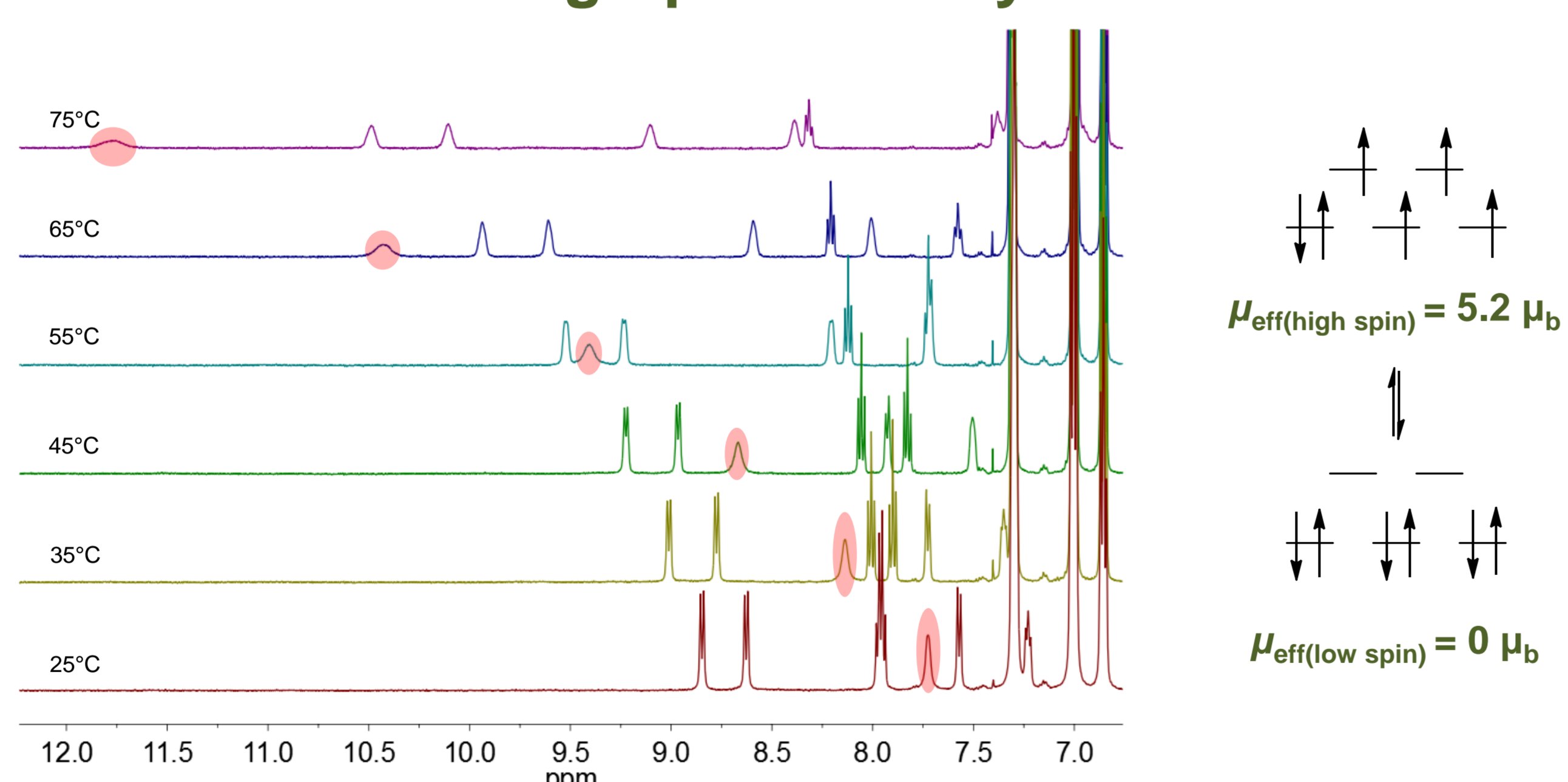
## Comparison of Solid State Structures



| Complex                               | Fe-N (Å)<br>(solid @ 110K) | d(NH - NH) (Å)<br>(solid @ 110K) | $ \Delta(\alpha-\beta) $<br>(solid @ 110K) | Spin State<br>(solid @ 110K)         |
|---------------------------------------|----------------------------|----------------------------------|--|--------------------------------------|
| [4][BPh <sub>4</sub> ] <sub>4</sub>   | 1.8884(17) – 2.0553(17)    | 2.9629(27)                       | 0°   | Low-Spin                             |
| [5][Cl] <sub>2</sub>                  | 1.883(4) – 2.059(4)        | 3.0068(62)                       | 2.8(10)°                                   | Low-Spin                             |
| [5-Zn][PF <sub>6</sub> ] <sub>2</sub> | 2.0621(16) – 2.3123(17)    | 3.3255(26)                       | 1.3(4)°                                    | Model for High-Spin Fe <sup>2+</sup> |

In the solid state structures several indicators for the low spin state can be found. First, the Fe-N bond lengths of ca 1.9 to 2.1 Å clearly demonstrate the low spin configuration of these complexes. Due to changing the spin state from low spin to high spin the  $Fe^{2+}$  ion is enlarged which results in elongation of Fe-L bond lengths. To have a qualitative glance on the structure of the respective high spin complex of **5**, the  $Zn^{2+}$  complex akin to **5** was investigated by X-Ray analysis (radii of  $Zn^{2+}$  and  $Fe^{2+}_{hs}$  are very similar). The most striking change is the elongation of the M-N bond length by ca 0.3 Å and subsequent increasing N-N distance of the amino nitrogens by 0.3 Å. The difference of the torsion angles ( $\alpha$ ,  $\beta$ ) can be used as a measure for the steric strain. In an unstrained biphenyl bridge  $\Delta(\alpha-\beta)$  should be zero. We have recently shown that placing substituents R in the 6,6'-positions can increase this steric strain and hence lower the spin transition temperature  $T_{1/2}$  according to size (R = H, Me, Br;  $T_{1/2}$  = 403K, 375K, 341K;  $\Delta(\alpha-\beta)$  = 2.8(10)°, 5.0(4)°, 7.8(4)°).<sup>[2]</sup> Subsequently replacing the R groups by a second complex fragment should yield a positively coupled dinuclear  $Fe^{2+}$  SCO complex.

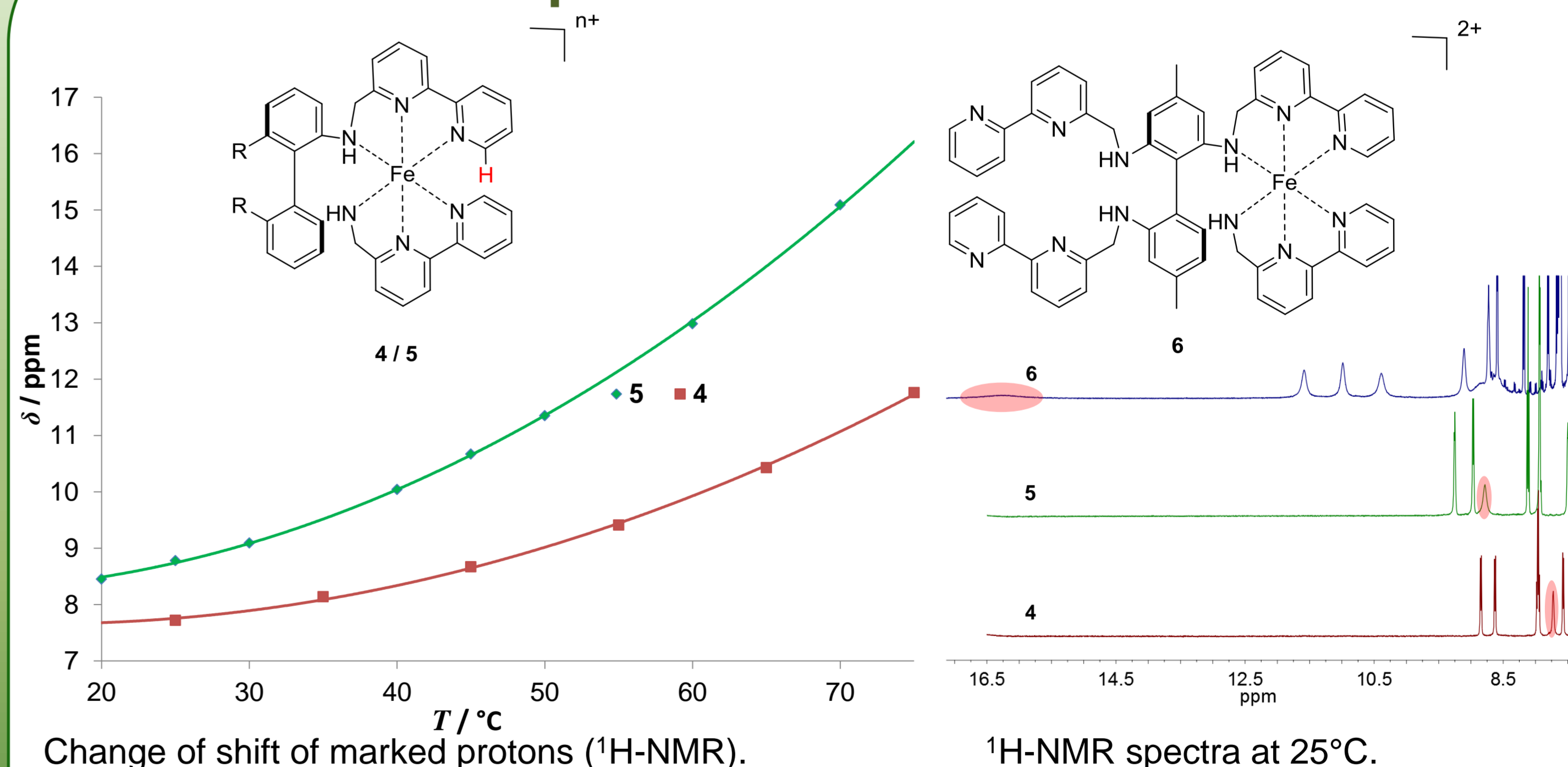
## Probing Spin State by <sup>1</sup>H-NMR



<sup>1</sup>H-NMR spectra of [4][BPh<sub>4</sub>]<sub>4</sub> at different temperatures in CD<sub>3</sub>CN.

The measurement of NMR spectra at different temperatures is an easy and fast tool for observing the occurrence of a spin transition. As can be seen above, with rising temperature the signal half-width and also the shift region increases. This is attributed to the temperature dependent equilibrium between low spin and high spin form of the corresponding complex. With increasing temperature this equilibrium is shifted towards the high spin configuration which originates the observed changes in the <sup>1</sup>H-NMR spectra. Therefore Variable-Temperature NMR experiments proved the existence of an SCO occurring in **4** above room temperature in CD<sub>3</sub>CN solution.

## Comparison of SCO Behaviour



Change of shift of marked protons (<sup>1</sup>H-NMR).

<sup>1</sup>H-NMR spectra at 25°C.

A similar behaviour as for **4** was also found for mononuclear complexes like **5** or **6**. As the structural motifs with bipyridine "arms" and a biphenyl "backbone" are similar, the chemical shifts of the terminal *ortho*-Hydrogens – marked in red above – can directly be used for means of comparison of the SCO properties. Complex **6** shows the already reported behaviour,<sup>[2]</sup> that substituents R (NHCH<sub>2</sub>bipy) in the biphenyl backbone increase the magnetic moment at room temperature according to their size. For the dinuclear complex **4** the magnetic moment is clearly reduced at room temperature. Obviously the SCO centres influence each other by reducing the steric strain in the biphenyl bridge. The two  $Fe^{2+}$  ions are forced to have the same spin state.

## Conclusion

We have been able to synthesize the first dinuclear SCO complex in which two octahedrally coordinated  $Fe^{2+}$  ions are ligated by a single ligand. Additionally, the two centres are interacting, which can be understood as "steric coupling". We could prove this cooperativity with temperature dependent <sup>1</sup>H-NMR and X-Ray structure analyses. For the moment complex **4** lacks stability at high temperatures, that hampers the exact determination of the thermodynamic parameters  $\Delta H$  and  $\Delta S$  for the SCO. We are currently under way to tune **2** by introduction of substituents for decreasing the SCO temperature and increasing the stability of the resulting dinuclear complex.

## References

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