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N,*N*′-Bis(2,2′-bipyridine-6-ylmethyl)-2,2′-biphenylenediamines: A Tuneable Ligand Scaffold for Room Temperature Fe^{2+} SCO Complexes

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Keywords: Iron / Spin crossover / N ligands / Steric effects / Solution studies

Condensation and subsequent reduction of 2,2′-diaminobiphenyls **5** with 6′- and 5′-substituted 6-carbaldehyde-2,2′-bipyridines **4** yielded *N*,*N*′-bis(2,2′-bipyridine-6-ylmethyl)-2,2′-biphenyl-enediamines **7**, which were employed as hexadendate ligands with N6 donor sets in the synthesis of dicationic [Fe^{2+}(**7**-κ^6N)] complexes **8**. Dependent on the substitution pattern the respective complexes are found in the HS state (**8b** and **8c**) or show SCO behaviour. By means of temperature-dependent susceptibility measurements, using Evans′ method, the thermodynamic parameters ΔH, ΔS and $T_{1/2}$ for the SCO have been determined. $T_{1/2}$ as well as ΔH are remarkably susceptible to substitution next to the central C–C bond of the biphenyl bridge.

Introduction

Since the first discovery and interpretation of spin crossover (SCO) systems in the last century,[1] this class of complexes has attracted much interest because of its possible applications, for example, in data storage, molecular switches or sensors.[2] Promising candidates are iron(II) complexes as they show the most significant changes in their properties upon SCO from a high-spin state (HS), which is paramagnetic, to a low-spin state (LS), resulting in a diamagnetic complex. Pairing of four electrons and subsequent depopulation of all antibonding e_g orbitals in an octahedral Fe^{2+} complex goes along with substantial shortening of the metal ligand bonds, when comparing the LS with the HS.[3,4] These large changes can be transported to neighbouring complexes in the crystal lattice. Therefore, most research on Fe^{2+} SCO complexes is focused on SCO in the solid state, mainly aimed to find hysteresis.[5] Compared with the number of investigations in the solid state, the spin crossover behaviour of complexes in solution is seldom investigated.[6–9] This is because most SCO systems lack the required stability in diluted solutions, especially in the presence of air and/or water. As SCO complexes can only have a well-defined ligand field and consequently stabilisation energy, they are substitution labile. To prevent these systems from ligand substitution and oxidation, complexes are often designed using chelating ligands.[4,10–12] To obtain SCO complexes the ligand has to be tuned precisely and even more sophisticated tuning is necessary to obtain SCO in a defined temperature range. Synthesis of multidentate ligand systems that allow this fine tuning is not trivial. Here we wish to report on our strategy to design Fe^{2+} SCO complexes with N6 chelate ligands that show spin crossover near room temperature in solution.

Results and Discussion

In order to have a useful flexibility for tuning the ligand field of the resulting complexes we decided to build up the potential ligands with an AB_2 structure, where A is a 2,2′-diaminobiphenyl (**5**) and B a 2,2′-bipyridine-6-carbaldehyde (**4**) that was first used by Constable et al.[13] to obtain N6 chelating ligands for transition metal complexes. Moreover, it was reported that the hydrazones derived from **4** react with Fe^{2+} salts to yield SCO complexes.[14] The two building blocks A and B can be combined together by condensation and subsequent reduction of the formed Schiff bases **6** (Scheme 2), which is a commonly employed strategy to prepare substituted 2,2′-diaminobiphenyls.[15]

The flexibility of this ligand system depends on the flexibility of the substitution pattern of the building blocks A and B, respectively. We found that Negishi cross-coupling[16] of **1** with a 2-bromopyridine derivative gives efficient access to a broad range of different building blocks B (**4**) (Scheme 1). The advantages of our synthetic strategy, over commonly employed methods,[17] are that the formed zinc complexes[18] can be isolated in high purity since they are insoluble in tetrahydrofuran (THF). Therefore column chromatography for means of purification is not necessary. Secondly, with our strategy it is possible to introduce different 2-bromopyridine derivatives in a late step of the synthesis, which enables one to convert expensive pyridine de-

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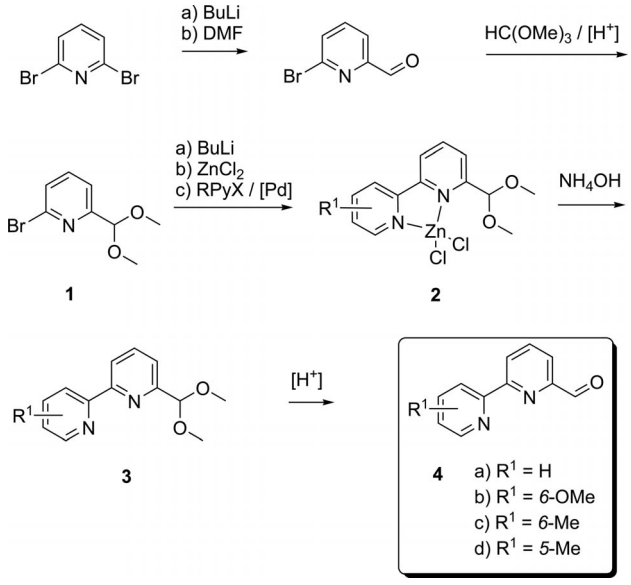
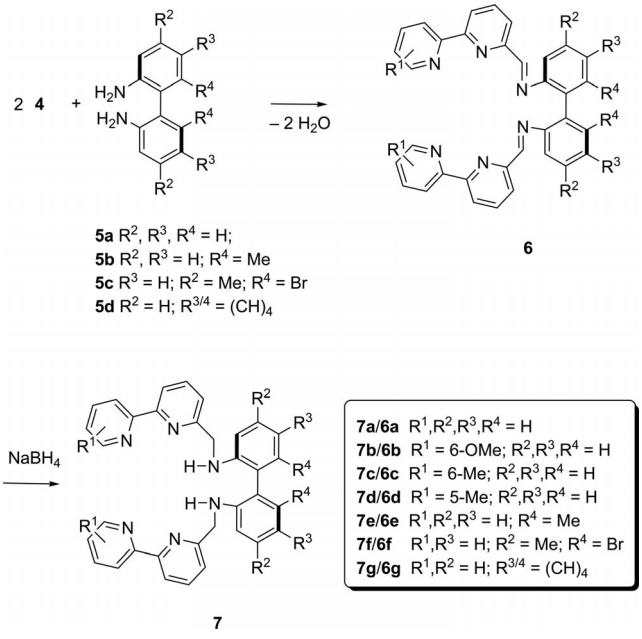
rivatives very economically (Scheme 1). Moreover, **1** can be prepared on a large scale and in good yield. Suitable biphenyl building blocks A are commercially available or can be easily prepared by Ullmann coupling.[19,20]



Scheme 1. Synthesis of **4a**–**d** by a Negishi cross-coupling reaction (DMF = dimethylformamide).

Diimines **6** can simply be prepared by stirring **4** and **5** in a 2:1 ratio in anhydrous ethanol (or diethyl ether) without any addition of water binding additives or catalytic amounts of acids. In contrast to the starting materials the formed Schiff bases **6** (Scheme 2) are insoluble in ethanol and are best isolated by centrifugation. The imines are generally well soluble in chlorinated solvents like dichloromethane but tend to hydrolyse rapidly if any traces of water are present. The obtained colourless solids have been used without further purification. Treatment of the Schiff bases with $NaBH_4$ in ethanol/NMP(*N*-methyl-2-pyrrolidone) afforded amines **7** (Scheme 2). These compounds are isolated in 60–80% yield in good purity as oily substances that are difficult to crystallize. The presented derivatives **7** crystallize upon treatment with a suitable cocrystallizing solvent [MeOH (**7a**, **7e**), EtOH (**7b**–**7d**, **7g**), CH_2Cl_2 (**7f**)] as crystalline materials with excellent purity making further purification unnecessary. Crystallization of **7c** from hot [D_6]DMSO allowed the isolation of single crystals suitable for X-ray structure analysis. Part a of Figure 1 shows the molecular structure of **7c** in the solid state, interestingly the crystals include no solvent molecules even though the crystallization requires a cocrystallizing solvent. The packing is dominated by π stacking of the bipyridyl moieties that are completely flattened and adopt a typical *trans* arrangement of the pyridine nitrogen atoms. One of the two amino groups of the 2,2′-biphenylenediamine bridge forms a weak hydrogen bond to the adjacent amino nitrogen [N1–H···N4: 2.9670(17) Å], while the other one forms a shorter hydrogen bond to the nearby pyridine nitrogen [N4–H···N5: 2.6205(15) Å].



Scheme 2. Synthesis of the hexadentate molecules **7** with AB_2 structure by condensation of 2,2′-diaminobiphenyls (**5**) with 2,2′-bipyridine-6-carbaldehydes (**4**) and subsequent reduction with $NaBH_4$.

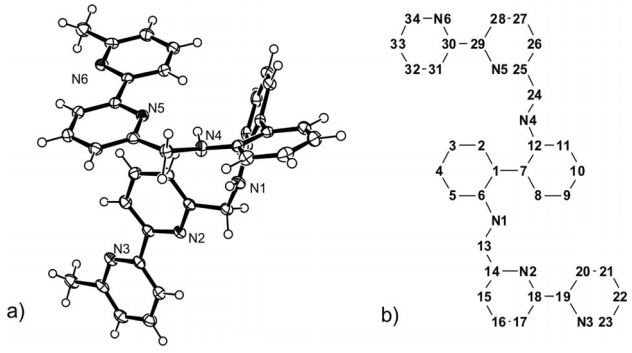
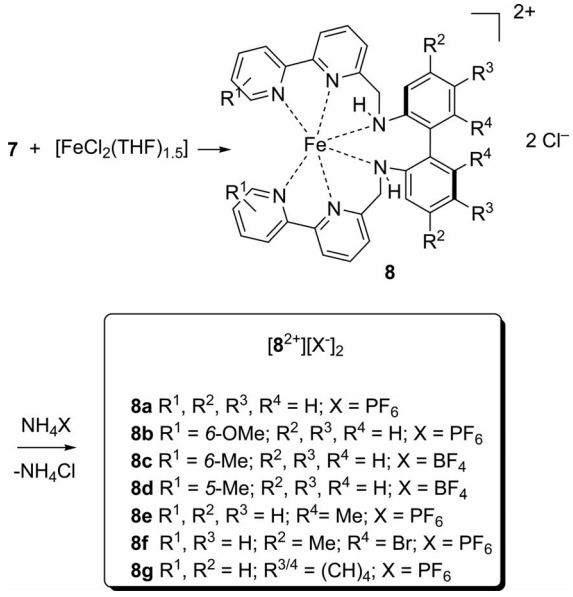


Figure 1. ORTEP diagram of the molecular structure of **7c** in the solid state and the applied numbering scheme for amines **7** and complexes **8**.

In order to obtain the complexes **8a**–**c** the amines **7a**–**c** have been treated with [$FeCl_2(THF)_{1.5}$] or [$Fe(H_2O)_7(SO_4)$] in ethanol (Scheme 3). After appropriate workup and exchange of the counterions Cl^- or SO_4^{2-} by BF_4^- or PF_6^-, complexes **8** could be isolated as deep red to purple solids. The parent complex **8a** is found to be a low spin Fe^{2+} complex. Marginal broadening of proton resonances of the protons near to the Fe^{2+} ion indicates a small paramagnetic contribution (vide infra). The PF_6^- and BF_4^- salts of **8** are very soluble in acetonitrile and DMF but only sparingly soluble in diethyl ether, dichloromethane and THF; they partially decompose by decomplexation in dmso solution. Upon exposure to air all complexes **8** are oxidized to the corresponding imine compounds over a period of several days, this process is much slower for the HS than for the LS complexes.[21] This oxidation is even more severe if an excess of Fe^{2+} or Fe^{3+} ions are present, for example, during the synthesis. We used a large excess of ascorbic acid and a

small amount of sodium borohydride to establish a reducing environment as well as NH_4Cl to prevent deprotonation of the amino groups – initial step for oxidation – by applying slightly acidic conditions. Precipitation of the complexes by the addition of an NH_4PF_6 solution in water allowed an easy and efficient separation of **8a**,**d**–**g** from an excess of $Fe^{2+/3+}$ remaining in solution. Once "free $Fe^{2+/3+}$" has been removed the complexes are stable against oxidation in solution and in the solid state but should best be stored as solids at low temperature to prevent oxidation.[21]



Scheme 3. Synthesis of complexes **8** by treatment of the amines **7** with $[FeCl_2(THF)_{1.5}]$.

By diffusion of diethyl ether vapour to a solution of the chloride salt in methanol dark crystals of **8a** suitable for X-ray structure analysis were obtained. Figure 2 (a) shows the molecular structure of dicationic **8a**. In the solid state **8a** forms layers that are connected by π stacking of the bipyridyl moieties and that are separated by the chloride ions and several disordered solvent molecules. The arrangement of the donor atom set around the Fe^{2+} ion is slightly distorted octahedral with a *mer* arrangement of the two arms. Because of the better coordination ability of the bipyridine moiety the Fe–N bond lengths to the pyridyl nitrogen atoms are shorter than those to the amine nitrogen atoms by 0.1–0.2 Å (for details see Table S2).

In a similar manner to **8a**, complexes **8b** and **8c** were obtained. The less intense red colour points to a HS of the Fe^{2+} ion in both transition metal complexes. Indeed, determination of the susceptibility by Evans' method[22] revealed that **8b** [μ_{eff}(25 °C) = 4.9 μ_b] and **8c** [μ_{eff}(25 °C) = 5.1 μ_b] are HS complexes at room temperature in solution with μ_{eff} close to the spin only value, resembling the lower C_2 symmetry. Both complexes **8b** and **8c** have been investigated at 153 K by single-crystal X-ray structure analysis [Figure 2 (b) and S1d in the Supporting Information]. The molecular structures of **8b** and **8c** exhibit a distorted octahedral coordination sphere with significant deviations of the N–Fe–N

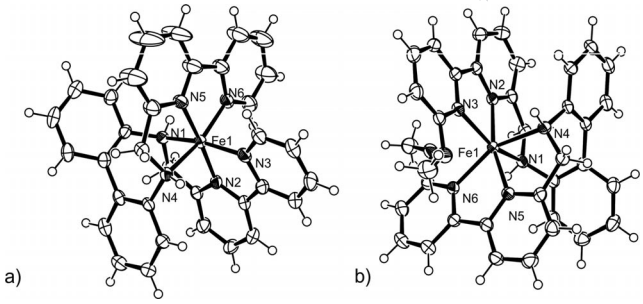


Figure 2. Molecular structures of complexes **8a** and **8b** in the solid state. Counter ions and solvent molecules are omitted for clarity; probability level is 50%.

angle from the ideal angle of 90°. The angles N3–Fe–N5 [**8b**: 109.89(7)°; **8c**: 118.43(6)°] and N2–Fe–N6 [**8b**: 118.69(7)°; **8c**: 117.19(6)°] are remarkably large. The increased angles are caused by the steric influence of substituents at the 6′ position bound to C23 and C34 of the bipyridyl moiety.[4] The Fe–N bond lengths agree well with the determined spin states, i.e. high-spin in the cases of **8b** and **8c**, while low-spin for the other Fe^{2+} complexes at 153 K (also see Table 1). As expected from known SCO systems the differences in the metal–ligand distances in HS vs. LS complexes are 0.18–0.25 Å.[4,11–13]

Table 1. Magnetism at room temperature and thermodynamic data of the SCO of selected complexes.

Complex	μ_{eff} (25 °C)[a]	ΔH	ΔS	$T_{1/2}$	$\Delta(\alpha-\beta)$[b]
	[μ_B]	[kJ mol^{-1}]	[J K^{-1} mol^{-1}]	[K]	[°]
8a (SCO)	0.45	22.5	56	403	2.8(10)
8b (HS)	4.90	–	–	–	1.1(4)
8c (HS)	5.10	–	–	–	1.6(3)
8d (SCO)	0.50	n.d.[c]	n.d.	n.d.	n.d.
8e (SCO)	0.82	20.6	55	375	5.0(4)
8f (SCO)	1.43	19.1	56	341	7.8(4)
8g (SCO)	1.20	n.d.	n.d.	n.d.	n.d.

[a] Determined by Evans' Method[22] as described in the Supporting Information. [b] Difference of torsion angles in biphenyl moiety, expressing steric strain. Determined by X-ray crystallography at 153 K. [c] n.d.: not determined.

Large substituents in the 6′ position (bound to C23 and C34) should push the other donor atoms (N1–N6) surrounding the Fe^{2+} ion together. But on closer look at the biphenyl bridge (Part A) an elongation of about 0.34 Å of the intramolecular distance N1···N4 – the two amino nitrogens of the biphenyl moiety – is found; obviously the expansion of the Fe^{2+} ion upon SCO from a LS to a HS overcompensates the steric demand of the methyl or methoxy group and is large enough to allow all donor atoms to gain more space. The larger distance N1···N4 (3.355 Å) is found in **8b**, with respect to **8c**, due to the smaller size of the methoxy group.

Substituents with size – based on the van der Waals radii – between the methoxy group and hydrogen atom (1.5 Å vs. 1.1 Å) should result in SCO behaviour but unfortunately the necessary substitution patterns are not easily accessible. Therefore, we tested a modification of the bridge part A in

order to directly influence the distance N1···N4 and subsequently the spin state of the Fe^{2+} ion. Substitution of building block A biphenyl-2,2′-diamine (**5a**) by 6,6′-dimethylbiphenyl-2,2′-diamine (**5b**), 6,6′-dibromo-4,4′-dimethylbiphenyl-2,2′-diamine (**5c**) or 1,1′-binaphthyl-2,2′-diamine (**5d**) results in the formation of complexes **8e**, **8f** and **8g**, respectively, which show SCO behaviour near room temperature, indicated by broad and shifted signals in the ^{1}H NMR spectra (Figure 3).

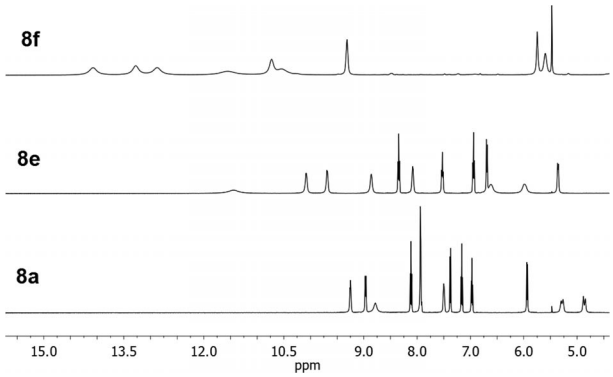


Figure 3. Downfield region of ^{1}H NMR spectra of complexes **8a**, **8e** and **8f** at 25° in CD_3CN solution.

In order to gain more information on the influence of bridge A on the SCO behaviour of the Fe^{2+} complexes, temperature-dependent measurements of the susceptibility have been performed on **8a**, **8e** and **8f** in acetonitrile using Evans' method.[22] Fitting of measured μ_{eff} versus T to a regular solution model with the assumption that $\mu_{eff}(HS) = 5.2\ \mu_b$ and $\mu_{eff}(LS) = 0\ \mu_b$ yielded $T_{1/2}$, ΔH and subsequently ΔS for the SCO (Figure 4, Table 1). $T_{1/2}$ is 341 K for **8f** and is the lowest among the investigated complexes; for **8e** this temperate is 375 K; finally for **8a** $T_{1/2}$ is calculated to be 403 K. Interestingly ΔS is equal for all three complexes with calculated values of 56 $J K^{-1} mol^{-1}$, 55 $J K^{-1} mol^{-1}$ and 56 $J K^{-1} mol^{-1}$ for **8f**, **8e** and **8a**, respectively. The values for ΔH are markedly different with 19.1 $kJ mol^{-1}$ (**8f**), 20.6 $kJ mol^{-1}$ (**8e**) and 22.5 $kJ mol^{-1}$ (**8a**). The ΔS values fall in the lower range from 30–130 $J K^{-1} mol^{-1}$[4,7,9,23] of reported data, which is not unexpected for complexes with rigid ligands. The successive population of the HS results in large shifts of the ^{1}H NMR signals. Most susceptible for changes in the spin state are the protons in the 6′ positions of the bipyridyl moiety bound to C23 and C34, closest to the paramagnetic Fe^{2+} centre.[8] As complexes **8a**,**e**–**g** only differ in the bridge A, far away from the protons in the 6′ positions and the influence of the nearby methyl group in **8d** is small, the chemical shift of these protons without paramagnetic contribution should be similar and hence this shift can be used to compare the SCO behaviour of the complexes **8**. Figure 5 shows a plot of the chemical shifts over the temperature range for **8a**,**d**–**g**. Recently, it was shown that the use of chemical shifts instead of volume susceptibility has some advantages in terms of errors and necessary corrections, especially if sensitive compounds have to be handled.[7] Although in this particular case where the lack of suitable values for the isotropic shifts hampers accurate fits, the qualitative correlation of mol fraction γ(HS) and extent of paramagnetic contribution to the chemical shift is obvious. Comparing the curves of **8a**, **8d** and **8e** underlines the different influence of additional methyl groups bound to C23 and C34 of the biphenyl moiety compared to methyl groups placed at C8 and C2 of the bridge A that approximately differ by a factor of 5. The two additional methyl groups in **8d** have a minor influence on $T_{1/2}$ with respect to **8a**; although they are separated from the iron atom by only four bonds in contrast to those in **8e** that are separated by five bonds.

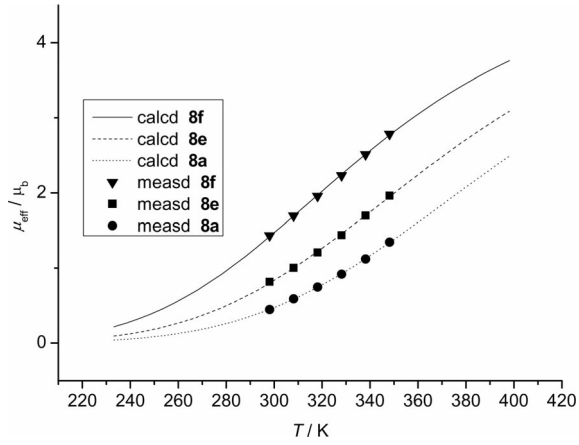


Figure 4. The μ_{eff} versus T plot of the measured (measd) values in the range 25–75 °C with a 10 K step width and the calculated curves using a regular solution model with best fit parameters given in the text.

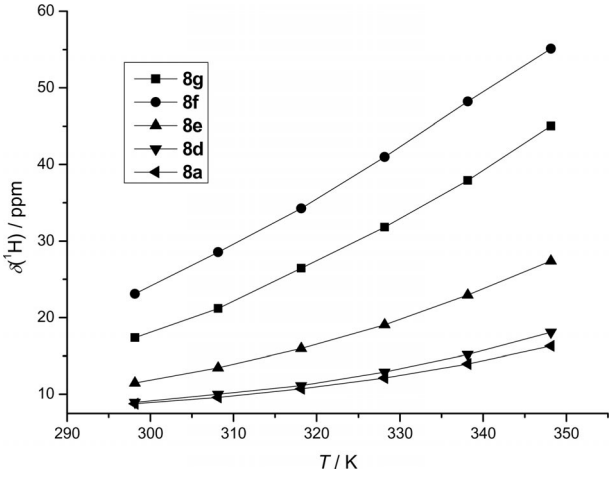


Figure 5. Plot of the chemical shift of protons bound to C23 and C34 versus T for complexes **8a**,**d**–**g**.

The obtained results raise the question which factors influence $T_{1/2}$ and ΔS. Growing single crystals by diffusion of diethyl ether vapour into a solution of **8e** and **8f** in acetonitrile allowed us to perform an X-ray structure analysis on single crystals at 153 K, which shows Fe^{2+} complexes in the low spin state (see Figures S1e and S1f in the Supporting Information).

If the molecular structures of **8a**, **8e** and **8f** are compared, only minor changes in the Fe–N distances are found. Even the distances N1···N4 directly bound to the biphenyl bridge vary only slightly: 3.0068(62) Å in **8a**, 3.0304(32) Å in **8e** and 3.0607(31) Å in **8f**. Even though the differences in N1···N4 are on the verge of significance they correlate well with the order found for $T_{1/2}$ and ΔH. A similar correlation is found for other structure parameters, for example, strains in the biphenyl bridge can be estimated by differences among the torsion angles C6–C1–C7–C12 and C2–C1–C7–C8, which should be zero in unstrained biphenyls but differ by 2.8(10)° in **8a**, 5.0(4)° in **8e** and 7.8(4)° in **8f**. This shows that repulsion of the substituents placed on C8 and C2, separated by four bonds to the donating amine nitrogens N1 and N4, influence the spin state of the Fe^{2+} ion. One would expect that the methyl groups and bromine atoms in **8e** and **8f**, respectively, are very close; indeed with a distance of 3.24 Å the two methyl substituents in **8e** are closer then the sum of van der Waals radii (2×2.0 Å), while in contrast the distance Br1···Br2 (3.71 Å) in **8f** is larger than the sum of the van der Waals radii (2×1.8 Å). The electronic influence on $T_{1/2}$ of different substitution patterns in the bridges A in **8e**–**g** is expected to be rather low as bromine and methyl groups show only small inductive and mesomeric effects; moreover there is no correlation between electronic properties with respect to +/–M nor +/–I effects of R^2 – R^4 on the SCO temperature $T_{1/2}$.

Conclusions

In summary we have gained access to a new ligand system that allows fine tuning of the ligand field strength in Fe^{2+} complexes. The design is very flexible and allows various substitution arrangements, either in the biphenyl or in the bipyridyl moieties, or in both of them. With the help of this variable pattern we were able to achieve precise control of the Fe^{2+} SCO and the corresponding SCO temperature $T_{1/2}$ in these systems. Most susceptible for substitution effects are the positions on C8 and C2, because of the induced steric strains in the biphenyl bridge A. If substituents on C8 and C2 can control the spin state of the Fe^{2+} ion through the spatial arrangement of the donor atoms N1 and N4 then the spin state of the Fe^{2+} ion should also effect donor atoms bound to C8 and C2, therefore it is our aim to expand this ligand system to dinuclear complexes.

Experimental Section

CCDC-786979 (for **7c**), -786980 (for **8a**), -786981 (for **8b**), -786982 (for **8c**), -786983 (for **8e**) and -786984 (for **8f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the X-ray structure analyses (Table S1) on **7c**, **8a**–**c**,**e**,**f**, ORTEP diagrams (Figure S1), table of selected bond lengths and angles (Table S2), as well as experimental details for the synthesis of aldehydes **4**, amines **7** and complexes **8** and details of the susceptibility measurements.

Acknowledgments

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