Diiron dithiolate complexes containing intra-ligand $NH \cdots S$ hydrogen bonds: [FeFe] hydrogenase active site models for the electrochemical proton reduction of HOAc with low overpotential[†]

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Four diiron dithiolate complexes containing *ortho*-acylamino-functionalized arenethiolato ligands, $[(\mu-S-2-RCONHC_6H_4)_2Fe_2(CO)_6]$ (R = CH₃, 1; CF₃, 2; C₆H₅, 3; 4-FC₆H₄, 4), were synthesized and well characterized as biomimetic models of the Fe–Fe hydrogenase active site. The molecular structures of **3** and **4** were determined by X-ray crystallography. The intra-ligand NH ··· S hydrogen bonds were studied by the X-ray analysis and by the ¹H NMR spectroscopy. The contribution of the NH ··· S hydrogen bonds to the reduction potentials of complexes **1–4** was investigated by electrochemistry. The first reduction potentials of complexes **1–4** exhibit large positive shifts, that is, 220–320 mV in comparison to that of the analogous complex $[(\mu-SPh)_2Fe_2(CO)_6]$ and 370–470 mV to that of $[(\mu-pdt)_2Fe_2(CO)_6]$ (pdt = propane-1,3-dithiolato). Complex **4** is capable of electrocatalysing proton reduction of acetic acid at relatively low overpotential (*ca*. 0.2 V) in acetonitrile.

Introduction

Although the complexes of the general formula $[(\mu-SR)_2Fe_2(CO)_6]$ have been known for over 70 years,1 the chemistry of diiron dithiolate complexes did not attract extensive attention until the striking resemblance in structure between the Fe-Fe hydrogenase active site and the well-known complexes $[(\mu -$ SR)₂Fe₂(CO)₆] was disclosed.^{2,3} In recent years, a great progress has been achieved in structurally biomimicking the $[Fe_2S_2]$ subunit of Fe-Fe hydrogenase active site. A large number of diiron dithiolate complexes, either with the alkylene bridges, e.g. pdt (propane-1,3-dithiolato)⁴ and edt (ethane-1,2-dithiolato),⁵⁻⁷ or an adt (2-azopropane-1,3-dithiolato) bridge,8-11 were prepared and characterized. Most reported structural models, such as [(µpdt)Fe₂(CO)₆],¹² [(μ -pdt){Fe(CO)₃}{Fe(CO)₂L}](L = P(NC₄H₈)₃, N-heterocyclic carbene (NHC)),^{13,14} $[(\mu-pdt){Fe(CO)_2L}_2]$ (L = PMe₃, 1,3,5-triaza-7-phosphaadamantane (PTA)),¹² and [(µ-pdt)-{Fe(CO)₃}{Fe(CO)(η^2 -L)}] (L = 1-methyl-3-(2-pyridyl)imidazole-2-ylidene $(NHC_{MePy}))$,¹⁵ can electrocatalyse the proton reduction with 0.5 to 1.0 V overpotential in the presence of weak acid (HOAc) in CH₃CN.¹⁶ Some diiron dithiolate complexes, $[(\mu-pdt){Fe(CO)_2(CN)}{Fe(CO)_2(PMe_3)}]$,^{17,18} $[(\mu-pdt)-$ {Fe(CO)₃}{Fe(CO)(η^2 -I_{Me}-CH₂-I_{Me})}](I_{Me} = 1-methylimidazol-2ylidene),¹⁹ [{(μ -SCH₂)₂N(CH₂C₆H₄-4-Br)}Fe₂(CO)₆],²⁰ and [{(μ - $SCH_2_2NCH_2(2-C_4H_3S)$ Fe₂(CO)₆]²¹ were reported active for

electrocatalytic proton reduction with relatively large overpotential *ca.* (0.75 to 1.22 V) after protonation on the iron atoms or on the bridged-N atom by moderate to strong acids, HOTs, HBF₄·Et₂O, H₂SO₄, and HClO₄ in CH₃CN. The native Fe–Fe hydrogenase can catalyse the reversible reduction of protons to molecular hydrogen at neutral pH and at an incredibly low potential (*ca.* -0.4 V *vs.* NHE).^{22,23} Biomimic of the property and reactivity of the Fe–Fe hydrogenase at such a low potential in aqueous medium is undoubtedly a challenge and an arduous task.

While much effort has focused on adjusting the redox potential, the protophilicity, and the water solubility of diiron dithiolate model complexes by CO-displacement with various ligands, such as cyanide,²⁴⁻²⁶ tertiary phosphines and phosphites,²⁷⁻³¹ isocyanides,^{32,33} and N-heterocyclic carbenes,^{14,34} little work has been reported on tuning the reactivity and the electrochemical property of the diiron center by varying the dithiolato part. It was reported that in the presence of HOAc diiron complexes containing μ -SEt bridges displayed similar activity for electrocatalytic proton reduction as the analogous pdt-bridged complex at almost identical reduction potentials.³⁵ The alkyl in the μ -SR bridge and the alkylene in the μ -SRS bridge have little effect on the redox potential of the diiron center.³⁶ Introduction of the functionalized R group to the dithiolato bridge may give an additional approach to adjust the redox property of the diiron center.

The crystallographic and spectroscopic studies have shown that the NH···S hydrogen bonds are biologically important for the activity of electron transfer metalloenzymes, *e.g.* rubredoxins,³⁷ ferredoxins,³⁸ and high-potential iron-sulfur proteins.³⁹ It has been reported that the number and extent of the NH···S hydrogen bonds in rubredoxin and ferredoxin peptide model complexes,^{40,41} as well as in molybdenum oxotransferase models,^{42,43} can effectively control the redox potentials of the metal centers. Enlightened by these reports, we designed and prepared the diiron complexes containing *ortho*-acylamino-functionalized arenethiolato ligands, on the purpose to tune the redox potential of the diiron center

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[†] Electronic supplementary information (ESI) available: Fig. S1 and S2: packing geometry and the NH \cdots S data for complexes **3** and **4**; Fig. S3: cyclic voltammograms of **3**, **4** and [(μ -SPh)₂Fe₂(CO)₆](1.0 mM) in CH₂Cl₂. CCDC reference numbers 655667 and 655668. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715990k

by forming the intra-ligand NH ··· S hydrogen bond. Herein we report the preparation and spectroscopic characterization of diiron dithiolate complexes, $[(\mu-S-2-RCONHC_6H_4)_2Fe_2(CO)_6]$ (1, $R = CH_3$; 2, CF_3 ; 3, C_6H_5 ; 4, 4-FC₆H₄). Complexes 3 and 4 were structurally characterized, which shows that these complexes contain the intra-ligand NH ··· S hydrogen bond. As expected, complexes 1-4 display considerable positive shifts (370-470 mV) for the reduction potentials of the diiron centers as comparison to that displayed by the well-known diiron complex [(µpdt)Fe₂(CO)₆], and complex 4 exhibit relatively low overpotential (0.2 V) for electrochemically catalysed proton reduction of acetic acid in CH_3CN . The result drops a hint that the possible $NH \cdots S$ hydrogen bond between the amido group in protein and the sulfur bridge in the H-cluster may have a contribution to the low reduction potential and the possible proton pathway of the Fe-Fe hydrogenase active site.

Results and discussion

Preparation and spectroscopic characterization of complexes 1-4

The preparation of diiron dithiolate complexes with the general formula $[(\mu-SR)_2Fe_2(CO)_6]$ by reactions of various disulfides and iron(0) carbonyl compounds can be traced back to the 1960s.^{44,45} Complexes 1–3 were prepared using this traditional protocol (Scheme 1). Treatment of Fe₃(CO)₁₂ with 1 equiv of bis(2-acylaminophenyl) disulfide in toluene at 70 °C afforded the predesigned diiron complexes 1–3 as red crystalline solid in moderate yields. Owing to the poor solubility of bis(2-(4-fluorobenzoylamino)phenyl) disulfide in toluene, complex 4 was prepared in refluxing THF following the essentially identical procedure in 46% yield. To make a comparison with 1–4, the known complex $[(\mu-SPh)_2Fe_2(CO)_6]$ was also prepared according to the literature procedure.⁴⁶





Complexes 1–4 were characterized by IR, ¹H NMR spectroscopy and elemental analysis. The IR data of v_{CO} bands for 1–4 are listed in Table 1, together with the v_{CO} data of $[(\mu-pdt)Fe_2(CO)_6]$ and $[(\mu-SPh)_2Fe_2(CO)_6]$ for a ready comparison. Complexes 1–4 each show one moderate and two strong v_{CO} bands in the region of 1990–2080 cm⁻¹. The average v_{CO} bands of 1 and 3 move by 4–8 cm⁻¹ to higher wavenumbers as comparison to the average v_{CO} bands of $[(\mu-pdt)Fe_2(CO)_6]$ and $[(\mu-SPh)_2Fe_2(CO)_6]$, implicating a certain decrease of the electron density in the diiron center of complexes 1 and 3. Introduction of an electron-withdrawing group CF₃ or 4-FC₆H₄ to the acylamino substituent caused the further blue-shift of the v_{CO} bands of complexes 2 and 4.

The proton signal for the NH group was studied to detect the intramolecular hydrogen bonds in the diiron complexes obtained. Complexes 1–4 display the signals for the hydrogen of the amido

Table 1 The v_{CO} bands of **1–4**, and related diiron dithiolate complexes^{*a*}

Complex	$v_{\rm CO}/{\rm cm}^{-1}$	
1	2074 (m), 2037 (s), 1998 (s)	
2	2077 (m), 2042 (s), 2003 (s)	
3	2075 (m), 2038 (s), 1999 (s)	
4	2076 (m), 2040 (s), 2001 (s)	
$[(\mu-SPh)_2Fe_2(CO)_6]$	2073 (m), 2032 (s), 1994 (s)	
$[(\mu-pdt)Fe_2(CO)_6]$	2072 (m), 2028 (s), 1987 (s)	
^{<i>a</i>} In CH ₂ Cl ₂ .		

group at δ 7.6–9.0, which are relatively sharp and shifted to downfield compared with the corresponding signal of acetanilide in the same solvent (CDCl₃), giving a hint to the formation of hydrogen bonds for the amido hydrogen (NH).⁴⁷ The chemical shifts of the signals for the NH group in complexes **1–4** did not change as the concentration of the complexes was increased up to eightfold. The insensitivity of the NH chemical shift toward variation of the complex concentration provides an indirect proof for the intramolecular hydrogen bonds in solution between the amido hydrogen and the adjacent sulfur atom in complexes **1– 4**.⁴⁷ The intramolecular hydrogen bonds in the obtained diiron complexes were further proved by the X-ray studies on the crystal structures of complexes **3** and **4**.

Crystal structures of complexes 3 and 4

The molecular structures of 3 and 4 are shown in Fig. 1 and 2, and selected bond lengths and angles are listed in the captions. Complex 3 exists as two conformational isomers in the crystalline state, while only one conformation was found for complex 4. The central $[Fe_2S_2]$ structures of **3** and **4** are in the familiar butterfly framework, and each Fe atom is coordinated in the square-based pyramidal geometry as those in previously reported [Fe₂S₂] models.^{4,25-29} The Fe–Fe distances (2.4994(8)–2.5123(4) Å) fall in the normal range of the Fe-Fe bond length (2.49-2.57 Å) found in the analogous diiron complexes.²⁵⁻²⁹ Viewing along the Fe-Fe bond, we can find that the basal CO ligands are eclipsed with each other in 3 and 4. Complexes 3 and 4 both possess an axial/equatorial (a/e) configuration for the two thiolate ligands. It is reasonable that the preparation of 1-4 either at 70 °C in toluene or in refluxing THF afforded thermodynamically more stable a/e isomers. We did not observe the conversion of the a/e isomer to the e/e isomer in CDCl₃ by ¹H NMR spectroscopy, which is consistent with the fact reported for $[(\mu-SPh)_2Fe_2(CO)_6]^{48}$

For conformational isomer **3**a the N(2) \cdots S(2) distance (3.17 Å) is relatively long as the N(2)–H bond is directed opposite to the S(2) atom, indicating there is no N(2)H \cdots S(2) hydrogen bond (Fig. S1), while the short N(1) \cdots S(1) distance (2.94 Å) suggests the presence of the N(1)H \cdots S(1) hydrogen bond. The N(2)H group in the equatorial μ -SR ligand of conformational isomer **3**a forms the N(2)H \cdots O(7)=C(13) (N(2) \cdots O(7) 2.87 Å) intermolecular hydrogen bond. For conformational isomer **3**b, there also exist one NH \cdots S hydrogen bond and one NH \cdots O=C bond (Fig. 3). The location of the hydrogen atom of the N(4)H group is close to the adjacent arenethiolate S(4) atom (N(4) \cdots S(4) 2.93 Å) in the equatorial μ -SR ligand of **3**b, favoring the formation of the N(4)H \cdots S(4) hydrogen bond, while the N(3)H group in the axial μ -SR ligand forms the N(3)H \cdots O(8)=C(26)



Fig. 1 Molecular structure of the two conformational isomers of **3**, with thermal ellipsoids at 30% probability. Hydrogen atoms except for those on nitrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **3**a: Fe(1)-Fe(2), 2.4998(7); Fe(1)-S(1), 2.2742(10); Fe(1)-S(2), 2.2661(10); Fe(2)-S(1), 2.2629(10); Fe(2)-S(2), 2.2579(10); Fe(1)-C(1), 1.811(5); Fe(1)-C(2), 1.778(4); Fe(1)-C(3), 1.787(5); N(1) \cdots S(1), 2.9389, N(2) \cdots S(2), 3.1721; Fe(1)-S(1)-Fe(2), 66.87(3); Fe(1)-S(2)-Fe(2), 67.09(3); S(1)-Fe(1)-S(2), 79.96(4); S(1)-Fe(2)-S(2), 80.37(4); C(7)-S(1)-Fe(1), 111.81(12); C(20)-S(2)-Fe(1), 114.56(12); C(1)-Fe(1)-S(1), 104.57(12); C(1)-Fe(1)-S(2), 100.08(11). For **3**b: Fe(3)-Fe(4), 2.4994(8); Fe(3)-S(3), 2.2969(12); Fe(3)-S(4), 2.2511(11); Fe(4)-S(3), 2.2666(12); Fe(4)-S(4), 2.2733(11); Fe(3)-C(33), 1.811(5); Fe(3)-C(34), 1.789(5); Fe(3)-C(35), 1.766(5); N(3) \cdots S(3), 2.9380, N(4) \cdots S(4), 2.9263; Fe(3)-S(3)-Fe(4), 66.42(3); Fe(3)-S(4)-Fe(4), 67.07(3); S(3)-Fe(3)-S(4), 78.65(4); S(3)-Fe(4)-S(4), 78.82(4); C(39)-Fe(3), 114.39(13); C(52)-S(4)-Fe(3), 118.08(13); C(33)-Fe(3)-S(3), 114.31(13); C(33)-Fe(3)-S(4), 95.07(13).



Fig. 2 Molecular structure of 4, with thermal ellipsoids at 30% probability. Hydrogen atoms except for those on nitrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(2), 2.5123(4); Fe(1)–S(1), 2.2818(6); Fe(1)–S(2), 2.2738(6); Fe(2)–S(1), 2.2679(6); Fe(2)–S(2), 2.2730(6); Fe(1)–C(1), 1.812(2); Fe(1)–C(2), 1.790(3); Fe(1)–C(3), 1.792(2); N(1) \cdots S(1), 2.9989, N(2) \cdots S(2), 2.9741; Fe(1)–S(1)–Fe(2), 67.034(19); Fe(1)–S(2)–Fe(2), 67.084(18); S(1)–Fe(1)–S(2), 80.33(2); S(1)–Fe(2)–S(2), 80.65(2); C(7)–S(1)–Fe(1), 116.20(7); C(20)–S(2)–Fe(1), 119.15(7); C(1)–Fe(1)–S(1), 98.33(8); C(1)–Fe(1)–S(2), 109.90(8).

 $(N(3) \cdots O(8) 2.88 \text{ Å})$ intermolecular hydrogen bond. Fig. 4 shows the intramolecular hydrogen bonds in the solid state of complex **4**. The N(2) \cdots S(2) distance (2.97 Å) in the axial arm of complex **4** is short enough for the formation of the N(2)H \cdots S(2) hydrogen bond (Fig. 4).⁴² The oxygen atom O(7) in the equatorial arm of **4** forms intermolecular hydrogen bonds with both the hydrogen atom of the N(1)H group and one of the *ortho*-Hs of the 4-FC₆H₅ group, forming a 7-membered ring (Fig. S2).[†]



Fig. 3 The N(4)H \cdots S(4) and N(3)H \cdots O(8) hydrogen bonds in the solid state of complex 3.



Fig. 4 The $N(2)H\cdots S(2)$ hydrogen bond in the solid state of complex 4.

Electrochemistry of complexes 1–4 and electrocatalytic property of 4

Cyclic voltammograms (CVs) of complexes 1-4, shown in Fig. 5, were recorded in anhydrous CH₃CN with 0.05 M nBu_4NPF_6 as





Fig. 5 Cyclic voltammograms of (top) complexes 1 and 2, and (bottom) 3, 4 and $[(\mu$ -SPh)₂Fe₂(CO)₆] (1.0 mM) in CH₃CN with 0.05 M *n*Bu₄NPF₆ at a scan rate of 100 mV s⁻¹.

electrolyte. The redox potentials of **1–4** and the related complexes, *e.g.* $[(\mu-pdt)_2Fe_2(CO)_6]$ and $[(\mu-SPh)_2Fe_2(CO)_6]$, were given in Table 2. Complexes **1–4** each display an irreversible reduction peak at –1.19 to –1.29 V and a weak peak at –1.66 to –1.73 V *vs.* Fc/Fc⁺. In light of the previously reported electrochemical and spectroelectrochemical studies on the all-CO complex $[(\mu-pdt)Fe_2(CO)_6]$,^{12,35,49,50} the current height in the CVs of complexes **1–4** is compared with that in the CV of $[(\mu-pdt)Fe_2(CO)_6]$ with identical concentration and under the same measuring condition. The approximately equal current height in the CVs of complexes

Table 2 The redox potentials of 1–4 and the related diiron complexes in CH_3CN^{α}

Complex	$E_{\rm pa}/{ m V}^b$	$E_{\rm pcl}/{ m V}$	$E_{ m pc2},{ m V}$
1	+0.74	-1.29	-1.73
2	+0.88	-1.22	-1.68
3	+0.75	-1.24	-1.71
4	+0.77	-1.19	-1.66
$[(\mu-SPh)_2Fe_2(CO)_6]$	+0.72	-1.51	-2.24
$[(\mu-pdt)_2Fe_2(CO)_6]^c$	+0.82	-1.66	-2.27

^{*a*} In 0.05 M nBu_4NPF_6/CH_3CN at a scan rate of 100 mV s⁻¹. ^{*b*} All potentials are *versus* Fc/Fc⁺. ^{*c*} Ref. 35 and 36.

1–4 and $[(\mu-pdt)Fe_2(CO)_6]$ suggests that the primary reduction of complexes 1–4 is a one-electron process (Fe¹Fe¹/Fe¹Fe⁰). The control experiment showed that the second reduction peak did not disappear in CO-saturated CH₃CN solution, indicating that it does not result from the CO-displaced species of the diiron complexes. Introduction of the electron-withdrawing group, *e.g.* CF₃ (2) and 4-FC₆H₄ (4), to the acylamino substituent results in a small anodic shift (50–70 mV), compared with the corresponding potentials of 1 and 3, respectively.

The reduction potentials of 1-4, having an amide NH group at the ortho position of an arenethiolato ligand, are positively shifted by 220-320 mV in comparison to that of their analogous complex $[(\mu-SPh)_2Fe_2(CO)_6]$ (-1.51 V vs. Fc/Fc⁺), and by 370–470 mV to that of the familiar diiron complex $[(\mu-pdt)Fe_2(CO)_6](-1.66 \text{ V vs.})$ Fc/Fc⁺).^{35,36} To exclude the possible influence of the intermolecular hydrogen bonds between the amido NH group and solvent on the reduction potentials, the cyclic voltammograms of 3, 4 and $[(\mu SPh_{2}Fe_{2}(CO)_{6}$ were measured in $CH_{2}Cl_{2}$, and the first reduction potentials move to -1.57, -1.43, and -1.88 V vs. Fc/Fc⁺ (Fig. S3[†]), respectively. The large positive shifts (310-450 mV) of reduction potentials of 3 and 4 relative to that of the analogous complex $[(\mu-SPh)_2Fe_2(CO)_6]$ in CH₂Cl₂ suggest that the shifts of the reduction potentials of diiron dithiolate complexes containing the ortho-amido NH group could result from the formation of the intra-ligand NH ···· S hydrogen bonds as reported for other ironsulfur and molybdenum-sulfur complexes.^{40–43} The intermolecular NH ··· O hydrogen bonds, which is far away from the iron center, cannot display important influence on the reduction potential of the iron center. And considering the large steric hindrance for the ortho-amido group in complexes 1-4, the intermolecular NH ··· S hydrogen bonds between two diiron complexes in a dilute solution (1.0 mM) should be much less favored as comparison to the intra-ligand NH ···· S hydrogen bonds. A puzzling phenomenon is found that complexes 1-4 display the relatively large shifts in reduction potentials but the small shifts of the average v_{co} bands in comparison to those of $[(\mu-pdt)Fe_2(CO)_6]$ and $[(\mu-SPh)_2Fe_2(CO)_6]$. Similar phenomena were also reported for the diiron dithiolate complexes with different μ -SR and $(\mu$ -S)₂R bridges.^{35,36} It is noteworthy that the diiron dithiolate complexes with different ligands, such as cyanide, tertiary phosphines, isocyanides and N-heterocyclic carbenes, often display quite sympathetic shifts for the v_{co} frequencies and reduction potentials, while the allcarbonyl diiron dithiolate complexes with different µ-SR and (µ- S_2R bridges sometimes display the relatively small shift of the v_{co} frequencies compared with the large shift in reduction potentials. The plausible explanation for this phenomenon might be that the R group and the $NH \cdots S$ hydrogen bond, which are far away from the CO ligand, have indirectly influences on the CO electron density. Another alternate explanation is also possible. The greater interaction of the bridging-S atom and the amido group involves the reduced complex, resulting in the apparent shift of the reduction events to the positive potential, while the neutral complexes show only small shifts of the ν_{CO} bands in the IR spectra.

The behavior of catalytic proton reduction by 4 was investigated by cyclic voltammograms in the presence of weak acids (HOAc) in CH₃CN. The blank electrochemical scan for acetic acid (40 mM) in the absence of electrocatalyst was made and the obtained CV curve is presented in Fig. 6 for a convenient comparison. The



Fig. 6 Cyclic voltammograms of 4 (1.0 mM) and HOAc (0–40 mM) in CH₃CN.

addition of 0-40 mM HOAc does not affect the current height and the potential of the first reduction peak of 4, while the current height of the second reduction peak grows apparently with increase of the HOAc concentration (Fig. 6). Such observation in the CVs indicates that complex 4 is electrocatalytic active at the second reduction potential (-1.66 V) for reduction of protons from HOAc. The electrocatalytic property of 4 in the presence of weak acid is quite similar to those of $[(\mu-pdt)_2Fe_2(CO)_6]$ and [(µ-SEt)₂Fe₂(CO)₆] reported by Darensbourg and co-worker,^{12,35} which also shows that the first reduction peak is inert and the second one at ca. -2.27 V vs. Fc/Fc⁺ is electrocatalytic active with addition of 0-100 mM HOAc. It is noteworthy that the overpotential for electrochemical reduction of protons from weak acid catalysed by the well-known diiron complexes [(µ $pdt_{2}Fe_{2}(CO)_{6}$ and $[(\mu-SEt)_{2}Fe_{2}(CO)_{6}]$ is ca. 0.8 V,¹⁶ while the overpotential for catalysed proton reduction of HOAc based on complex 4 is dramatically reduced to ca. 0.2 V. To the best of our knowledge, it is the lowest overpotential so far reported for electrochemically catalysed proton reduction of a weak acid based on bio-inspired diiron dithiolate model complexes.

Conclusions

Four diiron complexes containing ortho-acylamino functionalized arenethiolato ligands were prepared as a new type of model complexes for the Fe-Fe hydrogenase active site. The presence of the NH ···· S hydrogen bond in the solid state was established by X-ray crystallographic analyses of complexes 3 and 4, and the evidence of ¹H NMR spectra suggests the existence of the intramolecular hydrogen bonds in solution. The reduction peaks of complexes 1-4 show large positive shifts in comparison to complexes [(µ-SPh)₂Fe₂(CO)₆] and [(µ-pdt)Fe₂(CO)₆], attributed to the fact that the formation of the intra-ligand NH · · · S hydrogen bond reduces the electron donating capability of the sulfur atom. Complex 4 can electrocatalyse the proton reduction of acetic acid with a considerably low overpotential (*ca.* 0.2 V) in CH₃CN. The results show that it is effective to tune the redox potential of the $[Fe_2S_2]$ complexes by formation of the intramolecular NH · · · S hydrogen bonds. The efforts to introduce electron-withdrawing groups to the benzene ring of the ortho-acylamino functionalized

arenethiolate are under way to further improve the electrocatalytic property of $[Fe_2S_2]$ model complexes.

Experimental

All procedures were carried out under dry nitrogen atmosphere with standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use. Bis(2-aminophenyl) disulfide,⁵¹ bis(2-acetylaminophenyl) disulfide,⁵² bis(2-(trifluoroacetylamino)phenyl) disulfide,⁴² bis(2-benzoylaminophenyl) disulfide,⁵² bis(2-(4-fluorobenzoylamino)phenyl) disulfide,⁴⁰ and [(µ-SPh)₂-Fe₂(CO)₆] were prepared according to the literature procedures.⁴⁶ Infrared spectra were recorded on a JASCO FT/IR 430 spectrophotometer. Proton NMR spectra were collected on a Varian INOVA 400 NMR spectrometer with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer.

General procedure for preparation of diiron dithiolate complexes 1–4, [(µ-S-2-RCONHC₆H₄)₂Fe₂(CO)₆]

Iron carbonyl compound $Fe_3(CO)_{12}$ (3.0 g, 5.95 mmol) was suspended in toluene (80 mL) followed by the addition of 1 equiv of bis(2-acetylaminophenyl) disulfide (1.98 g, 5.95 mmol). The reaction mixture was stirred at 70 °C until the color of the solution changed from deep green to dark red (*ca.* 10 h). The reaction mixture was cooled to room temperature and filtered. The red filtrate was evaporated to dryness under vacuum. The residue was subjected to silica gel chromatography and eluted with *n*hexane/dichloromethene to give pure complex 1 as red powder. Complexes **2–4** were prepared with the essentially identical procedure.

[(μ -S-2-CH₃CONHC₆H₄)₂Fe₂(CO)₆] (1). Yield: 1.87 g (51%). ¹H NMR (CDCl₃): δ = 2.17 (s, 3H), 2.27 (s, 3H), 6.94 (t, 1H) 7.02 (t, 1H), 7.09 (d, 1H), 7.19 – 7.41 (m, 3H), 7.62 (s, 2H), 8.06 (d, 1H), 8.15 (d, 1H). IR (CH₂Cl₂): v_{max} /cm⁻¹ 2074 (m), 2037 (s), 1998 (s) (CO). Found: C 43.41; H 2.79; N 4.63. Calc. for C₂₂H₁₆Fe₂N₂O₈S₂: C 43.16; H 2.63; N 4.58%.

[(μ-S-2-CF₃CONHC₆H₄)₂Fe₂(CO)₆] (2). Yield: 1.67 g (39%). ¹H NMR (CDCl₃): δ = 7.05–7.22 (m, 3H), 7.31–7.48 (m, 3H), 8.10 (d, 1H), 8.20 (t, 1H), 8.53 (s, 2H). IR (CH₂Cl₂): ν_{max}/cm^{-1} 2077 (m), 2042 (s), 2003 (s) (CO); Found: C 36.52; H 1.46; N 3.74. Calc. for C₂₂H₁₀F₆Fe₂N₂O₈S₂: C, 36.69; H, 1.40; N, 3.89%.

[(μ-S-2-PhCONHC₆H₄)₂Fe₂(CO)₆] (3). Yield: 2.32 g (53%). ¹H NMR (CDCl₃): δ = 6.94 (br, 1H), 7.08 (br, 2H), 7.30–7.80 (m, 9H), 7.94–8.12 (br, 3H), 8.27 (br, 1H), 8.57 (br, 2H), 8.95 (s, 2H). IR (CH₂Cl₂): ν_{max}/cm^{-1} 2075 (m), 2038 (s), 1999 (s) (CO). Found: C 52.38; H 2.81; N 3.84. Calc. for C₃₂H₂₀Fe₂N₂O₈S₂: C, 52.20; H, 2.74; N, 3.80.

[{**μ-S-2-(4-FC₆H₄CONHC₆H₄)**}₂**Fe**₂(**CO**)₆] (4). Yield: 2.11 g (46%). ¹H NMR (CDCl₃): δ = 6.94 (s, 1H), 7.07 (s, 2H), 7.34 (br, 5H), 7.72 (br, 2H), 7.99 (br, 3H), 8.21 (s, 1H), 8.46 (s, 2H), 8.82 (S, 2H). IR (CH₂Cl₂): *v*_{max}/cm⁻¹ 2076 (m), 2040 (s), 2001 (s) (CO). Found: C 49.72; H 2.41; N 3.65. Calc. for C₃₂H₁₈F₂Fe₂N₂O₈S₂: C, 49.77; H, 2.35; N, 3.63.

 Table 3
 Crystallographic data and processing parameters for complexes 3 and 4

Complex	3	4	
Formula	$C_{32}H_{20}Fe_2N_2O_8S_2$	$C_{32}H_{18}F_2Fe_2N_2O_8S_2$	
$M_{ m w}$	736.32	772.30	
Crystal system	Monoclinic	Monoclinic	
Space group	P2(1)/n	P2(1)/c	
a/Å	11.4255(13)	15.3983(3)	
b/Å	20.178(2)	9.8861(2)	
c/Å	27.909(3)	24.0297(4)	
β/deg	98.886(6)	120.090(1)	
$V/Å^3$	6357.2(12)	3165.06(10)	
Ζ	8	4	
$D_{\rm calcd}$ /g cm ⁻³	1.539	1.621	
μ/mm^{-1}	1.098	1.115	
Crystal size/mm	$0.22 \times 0.15 \times 0.08$	$0.48 \times 0.22 \times 0.15$	
θ range/deg	1.79–25.80	1.96-27.94	
Refins collected/indep refins	31825/11738	39178/7384	
R _{int}	0.0460	0.0382	
Refins with $I > 2\sigma(I)$ /parameters	7448/845	5460/441	
GOF on F^2	1.003	1.013	
$R1^a [I > 2\sigma(I)]/wR2^b$	0.0447/0.1000	0.0347/0.0797	
Residue electron density/e Å ⁻³	0.519/-0.337	0.331/-0.264	
^{<i>a</i>} $R1 = \sum F_o - F_c $. ^{<i>b</i>} $wR2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum$	$[w(F_o^2)^2]^{1/2}$.		

Crystal structure determination[†] of complexes 3 and 4

The crystals of 3 and 4 suitable for X-ray analysis were obtained by recrystallization in hexane/CH₂Cl₂ (2:1 v/v). The single-crystal X-ray diffraction data were collected with SMART APEXII diffractometer for 3 and 4 with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 273 K using the ω -2 θ scan mode. Data processing was accomplished with the SMART and SAINT software package of Siemens Energy & Automation Inc. (Madison, Wisconsin). Intensity data were corrected for absorption by the SADABS program. The structures were solved by direct methods and refined on F^2 against full-matrix leastsquares methods using the SHELXTL97 program.53 All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed on the calculated positions except for the hydrogen atoms of the amides, which were located by Fourier difference maps and adjusted by taking into account of the N-H bond distance. Crystal data and parameters for data collections and refinements of complexes 3 and 4 are listed in Table 3.

Electrochemistry studies of complexes 1–4

Acetonitrile (Aldrich, spectroscopy grade) used for electrochemical measurements was dried with molecular sieves and then freshly distilled from CaH₂ under nitrogen. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV s⁻¹. A solution of 0.05 M *n*Bu₄NPF₆ (Fluka, electrochemical grade) in CH₃CN was used as electrolyte, which was degassed by bubbling with dry argon for 10 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 µm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (0.01 M AgNO₃ in CH₃CN) and the auxiliary electrode was a platinum wire. All potentials are reported relative to the Fc/Fc^+ potential.

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