Articles

The Fe^{III}/Fe^{II} vs $Fe_2^{2.5}$ Formulation in Mixed-Valent Species $[(NC)_4Fe(BL)Fe(CN)_4]^{3-}$, BL = 2,2′-Bipyrimidine and 3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine. Distance and Size Do Not Always Matter

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Two molecule-bridged bis(tetracyanoiron) complexes $[(NC)_4Fe(BL)Fe(CN)_4]^{n-}$, BL = 2,2′-bipyrimidine (bpym) and 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), were studied by EPR, UV/vis/near-IR and IR spectroelectrochemistry ($n = 2-5$) in aprotic media. Following these results, the $Fe_2^{2.5}$ formulation is the correct valence description for the metal centers in the bptz-bridged trianion ($K_c = 10^{14.6}$ in CH_3CN), whereas the localized Fe^{III}/Fe^{II} formulation is appropriate for the bpym-bridged system ($K_c = 10^{5.4}$ in CH_3CN and $10^{6.4}$ in CH_2Cl_2). In contrast to common perception, the larger tetrazine-bridged system with the longer metal−metal distance exhibits much stronger metal−metal coupling than the bpym-bridged analogue, a consequence of the very low lying π^* LUMO of tetrazines with high MO coefficients at the coordinating nitrogen centers.

Introduction

Molecule-bridged mixed-valent dimers $L_kM^n(\mu\text{-BL})M^{n+1}L_k$ with $M^n = Ru^{II}$ and π conjugated bridging ligands BL are numerous and well-researched, e.g., with respect to intramolecular electron transfer and its spectroscopic consequences.[1−3] Due to the lower kinetic stability in solution, the number of corresponding diiron(III,II) complexes is much smaller. However, we have recently presented an example, $[(NC)_4Fe(bmtz)Fe(CN)_4]^{3-}$ (**1**$^{3-}$), bmtz = 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine, with a large comproportionation constant $K_c = 10^{14.1}$ in acetonitrile and delocalized valences on the vibrational time scale.[4]

$$K_c = 10^{\Delta E/59\text{mV}} = [X^{(n+1)}]^2/[X^n][X^{(n+2)}] \qquad (1)$$

$$X^n + X^{(n+2)} \rightleftharpoons 2X^{(n+1)}$$

The partial localization of valences in compound $[(NC)_5Fe(pz)Fe(CN)_5]$,$^{5-}$ pz = pyrazine, in aprotic solution[5] has now prompted us to extend these studies to compounds with less effectively bridging ligands[8] in terms of mediating metal−metal interaction. Such a ligand is the widely used[8−14] 2,2′-bipyrimidine (bpym) bis-chelating π system which can hold two metal centers in fixed orientation at about a 5.5 Å distance.[9−11] However, bpym is a weaker coupling bridge than functionalized tetrazines such as bmtz or 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) which keep the metals apart at about a 6.5−7.0 Å distance.[8,15] We have thus prepared and studied the redox systems $[(NC)_4Fe(BL)Fe(CN)_4]^{n-}$, BL = bptz (**2**$^{n-}$), n = 5, 4, 3, 2, and bpym (**3**$^{n-}$), n = 4, 3, 2, in aprotic media (CH_2Cl_2, CH_3CN) to determine their spectroelectrochemical response (UV/vis/IR, EPR) and thus the proper formulation of the mixed-valent intermediates (n = 3).

Experimental Section

Materials. $(NEt_4)_4$(2). A suspension of 1.07 g (8.44 mmol) of anhydrous $FeCl_2$ in 30 mL of CH_3OH was treated under argon with a suspension of 252 mg (1.07 mmol) of bptz in 30 mL of CH_3OH. After 40 min of stirring at room temperature a solution of 5.29 g (33.85 mmol)

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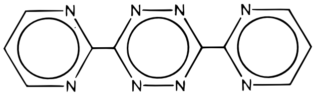
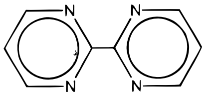
Table 1. Data[a] of Mixed-Valent Complexes $[(NC)_4Fe(BL)Fe(CN)_4]^{3-}$ and of Other Oxidation States $[(NC)_4Fe(BL)Fe(CN)_4]^{n-}$

complex	E_{ox}[b]	E_{red}[b]	K_c	λ_{IVCT} (ϵ)[c]	λ (ϵ)[c]	ν_{CN}[d]
$\mathbf{1}^{3-}$ [e]	+0.52	−0.32	$10^{14.1}$	2245 (750)	613 (12 300)	2116 w
$\mathbf{1}^{4-}$ [e]					300 sh, 831 (19 900), 489 (7400)	2085 s
$\mathbf{1}^{5-}$ [e]					675 (20 600), 525 (8200)	2064 s
$\mathbf{2}^{2-}$					656 (8260), 467 (1950), 413 (2740)	2127 sh, 2123
$\mathbf{2}^{3-}$	+0.35	−0.51[f]	$10^{14.6}$	2210 (750)	610 (10 530), 397 sh	2118 sh, 2113
$\mathbf{2}^{4-}$					1085 sh, 885 sh, 796 (14 950), 447 (5950)	2080
$\mathbf{2}^{5-}$					767 sh, 656 (8510), 496 (6940), 379 (2860)	2071, 2053
$\mathbf{3}^{3-}$	−0.23	−0.54[g]	$10^{5.4}$	nd	nd	nd
$\mathbf{3}^{3-}$ [h]	−0.18	−0.50	$10^{5.4}$	nd	nd	nd
$\mathbf{3}^{4-}$					880 (2770), 778 (2160), 517 (10 390)	nd
$\mathbf{3}^{2-}$ [j]					528 (1070), 487 (1300), 457 (1590), 400 sh	2119
$\mathbf{3}^{3-}$ [j]	−0.14	−0.51[k]	$10^{6.4}$	*i*	974 (1180), 599 sh, 552 (5040), 437 (1440), 399 (1370)	2117, 2091, 2077
$\mathbf{3}^{4-}$ [j]					854 (3140), 758 (2420), 507 (10820)	2080, 2064

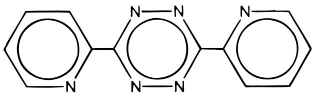
[a] Acetonitrile solutions, except where noted; nd: not determined. [b] Potentials in V vs $Fc^{+/0}$; 0.1 M Bu_4NPF_6 solutions, cyclic voltammetry with 100 mV/s. [c] Wavelengths in nm, molar extinction coefficients in M^{-1} cm^{-1}. [d] CN stretching frequencies in cm^{-1}. [e] From refs 4 and 5. [f] Further reversible reduction (1e) at −1.67 V. [g] Irreversible reduction at −2.36 V peak potential. [h] From studies of $K_4[(NC)_4Fe(bpym)Fe(CN)_4]$ solubilized with [2.2.2] cryptand. [i] Not observed. [j] In CH_2Cl_2/0.1 M Bu_4NPF_6. [k] Reversible reduction at −2.18 V for scan rates ≥500 mV/s, 0.2 M Bu_4NPF_6 solution.



bmtz



bpym



bptz

of Et_4NCN in 40 mL CH_3OH was added slowly. The resulting mixture was stirred for 20 h, the volume was reduced to 50 mL, and 200 mL of acetone and 150 mL of diethyl ether was added. The almost colorless solid was filtered off and discarded, and the filtrate was then treated with 150 mL of diethyl ether to yield a darkly colored precipitate. This second precipitate was purified by repeated chromatography on Sephadex LH 20 with methanol as eluent to yield about 10% of pure dark green complex. As was observed by others,[18] the elemental analyses of this class of compounds tend to be unreliable except for the H values and the C/N ratio. Anal. Calcd for $C_{52}H_{88}Fe_2N_{18}$: H, 8.24; C/N, 0.346. Found: H, 8.39; C/N, 0.345. ^1H NMR (CD_3OD): δ = 9.47 (d, 2H, $H^{6,6'}$), 8.81 (d, 2H, $H^{3,3'}$), 7.97 (dt, 2H, $H^{4,4'}$), 7.56 ppm (m, 2H, $H^{5,5'}$); $J^{4,6} = J^{3,5} = 1.4$ Hz, $J^{3,4} = 7.4$ Hz, $J^{4,5} = 7.7$ Hz, $J^{5,6} = 5.2$ Hz. EPR (CH_3CN, 3.7 K): $g_1 = 2.605$, $g_2 = 2.426$, $g_3 = 1.760$ for $\mathbf{2}^{3-}$; $\langle g \rangle = 2.0005$ for $\mathbf{2}^{5-}$.

$(NEt_4)_4(3)$. A suspension of 1.07 g (8.44 mmol) of anhydrous $FeCl_2$ in 30 mL of CH_3OH was treated under argon with a solution of 222 mg (1.404 mmol) of bpym in 30 mL of CH_3OH. After 45 min of heating under reflux and subsequent cooling to room temperature, a solution of 5.29 g (33.85 mmol) of Et_4NCN in 50 mL of CH_3OH was added slowly. The resulting mixture was stirred for 16 h at ambient temperature, the volume was reduced to 30 mL, and 130 mL of acetone and 100 mL of diethyl ether were added. The almost colorless solid was filtered off after 10 h and discarded, and the filtrate was then treated with another 100 mL of diethyl ether to yield a bluish precipitate. This second precipitate was purified by repeated chromatography on Sephadex LH 20 with methanol as eluent to yield about 5% of pure purple complex. The second filtrate contained predominantly mononuclear complex, which was precipitated by adding still more diethyl ether (150 mL). As was described,[18] the elemental analyses of iron cyanide complexes tend to be unreliable except for the H values and the C/N ratio. Anal. Calcd for $C_{48}H_{86}Fe_2N_{16}$: H, 8.68; C/N, 0.333. Found: H, 8.36; C/N, 0.330. ^1H NMR (CD_3CN): δ = 9.40 (d, 4H, $H^{4,4',6,6'}$), 7.20 ppm (t, 2H, $H^{5,5'}$); $J^{4,5} = J^{5,6} = 5.5$ Hz. EPR (CH_2Cl_2, 3.4 K): $g_\perp = 2.597$, $g_\parallel = 1.459$ for $\mathbf{3}^{3-}$.

$(NEt_4)_2[(bpym)Fe(CN)_4]$. Purification was by chromatography on Sephadex LH 20 with methanol (yield: 35%). Anal. Calcd for $C_{28}H_{46}FeN_{10}$: H, 8.01; C/N, 0.357. Found: H, 8.00; C/N, 0.356. ^1H NMR (CD_3CN): δ = 9.96 (dd, 2H, $H^{6,6'}$), 8.72 (dd, 2H, $H^{4,4'}$), 7.35 (dd, 2H, $H^{5,5'}$); ppm; $J^{4,6} = 2.2$ Hz, $J^{4,5} = 4.6$ Hz, $J^{5,6} = 5.8$ Hz. Absorption data (CH_2Cl_2): λ_{max} (ϵ) 730 (2140), 693 sh, 478 nm (7440 M^{-1} cm^{-1}). Infrared data (CH_2Cl_2): ν_{CN} 2081, 2062, 2055 sh cm^{-1}. Cyclic voltammetry (CH_2Cl_2/0.2 M Bu_4NPF_6, 100 mV/s, Pt): $E_{ox} = -0.51$ V, $E_{red} = -2.17$ V vs $Fc^{+/0}$. EPR (CH_2Cl_2, 3.5 K): $g_\perp = 2.593$, $g_\parallel = 1.512$ for $[(bpym)Fe(CN)_4]^-$.

$K_4(3)$ was prepared following the literature procedure.[18]

For comparison with the spectroelectrochemically generated mixed-valent ion $\mathbf{2}^{3-}$ a small amount of $(NEt_4)_3(\mathbf{2})$ was prepared by chemical oxidation: A solution of 10.4 mg (0.038 mmol) of *p*-fluorobenzenediazonium hexafluorophosphate[19] in 14 mL of CH_3CN was slowly added to 39.6 mg (0.037 mmol) of $(NEt_4)_4(\mathbf{2})$, dissolved in 20 mL of acetonitrile. After 30 min the solvent was removed under vacuum and the residue washed with 10 mL of acetone. Precipitation from an CH_3CN solution with diethyl ether yielded 34 mg of a dark blue solid, which exhibited identical UV/vis/NIR and IR spectra as obtained from spectroelectrochemistry.

Instrumentation. EPR spectra were recorded for glassy frozen solutions at 4 K in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ^1H NMR spectra were taken on a Bruker AC 250 spectrometer, and infrared spectra were obtained using a Perkin-Elmer Paragon 1000 PC FTIR instrument. UV/vis/NIR absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at a 100 mV/s scan rate in solutions 0.1 M in Bu_4NPF_6, using a three-electrode configuration (glassy carbon or Pt electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[16] for UV/vis and IR spectra and a two-electrode capillary for EPR studies.[17]

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Results and Discussion

The dinuclear complex ions [(NC)$_4$Fe(BL)Fe(CN)$_4$]$^{n-}$ were obtained in the Fe$_2^{\mathrm{II,II}}$ forms **2**$^{4-}$ and **3**$^{4-}$ as well soluble tetraethylammonium salts. Alternatively, the easier obtained potassium compounds[18] can be solubilized using ion-encapsulating agents such as [2.2.2] cryptand.[20,21] Not unexpectedly, the tetrazine-bridged complexes **1**$^{n-}$ and **2**$^{n-}$ exhibit similar behavior (Table 1), the Fe$_2^{\mathrm{III,III}}$ state being more stable in the case of **2**$^{2-}$ (bptz is more basic than bmtz). (Spectro)electrochemistry[16] for the mixed-valent species **1**$^{3-}$ and **2**$^{3-}$ reveals large K_c values ($>10^{14}$), long-wavelength intervalence charge transfer (IVCT) absorptions at ca. 2230 nm, and valence delocalization on the vibrational time scale, i.e., only one (intermediate) CN stretching band in the infrared spectra (Figures 1, and 2, Table 1).[4] The small energy difference between the four expected CN stretching bands in such *cis*-[Fe(X−X)(CN)$_4$] complexes[18,21] usually causes band overlap and thus only one observable feature in the IR spectrum. Strong solvation of these polyanionic species is probably responsible for the not symmetrically averaged frequency of the mixed-valent intermediate **2**$^{3-}$. On the other hand, the study of redox system **3**$^{n-}$ in CH$_2$Cl$_2$ shows a much lower[22] though still appreciable[23] comproportionation constant of $10^{6.4}$ (Tab. 1), no detectable IVCT absorption,[24] and the appearance of slightly shifted CN stretching bands for both separate (NC)$_4$Fe$^{\mathrm{II}}$ and (NC)$_4$Fe$^{\mathrm{III}}$ entities (Figures 1 and 3, Table 1). Reversible oxidation to the Fe$_2^{\mathrm{III,III}}$ state **3**$^{2-}$ removed the metal-to-ligand charge transfer bands in the visible and the intense low-energy CN stretching bands of the (NC)$_4$Fe$^{\mathrm{II}}$ group (Figures 1 and 3). The assignments of CN stretching bands are supported by the following, relating to the complication by the [Fe(CN)$_6$]$^{3-/4-}$ pair[5] formed during chromatographic separation as an impurity (Figure 1): Typically, the intensity of the IR bands from cyanoiron(III) species is lower than those of iron(II) analogues, which explains the difference also for the hexacyanoferrate pair. Cyclic voltammetry confirms that the amount of this impurity is always much less than 5%. In addition, the mononuclear [(bpym)Fe(CN)$_4$]$^{2-}$ does not produce the hexacyanoferrate impurity, as evident from both cyclic voltammetry and the total absence of an IR band at 2101 cm^{-1}.

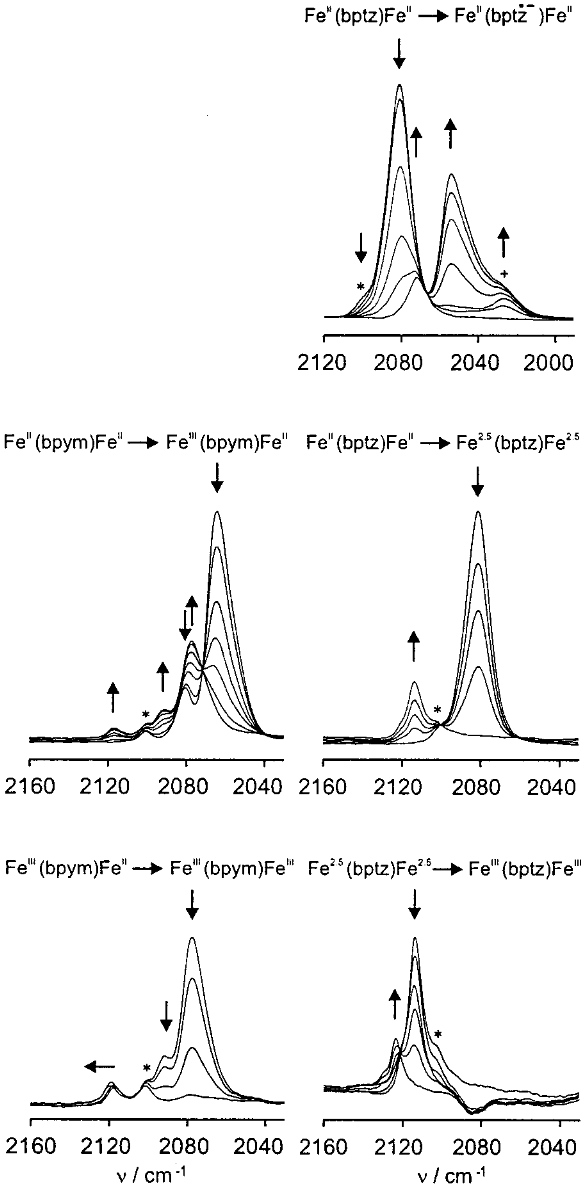

Figure 1. IR-spectroelectrochemical response of the transitions **2**$^{(4-)\to(5-)}$ (top right), **2**$^{(4-)\to(3-)}$ (center right), **2**$^{(3-)\to(2-)}$ (bottom right), **3**$^{(4-)\to(3-)}$ (top left), and **3**$^{(3-)\to(2-)}$ (bottom left) in CH$_3$CN/0.1 M Bu$_4$NPF$_6$ (**2**^{n}) or CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ (**3**^{n}). The bands at 2101 cm^{-1} (*) and 2025 cm^{-1} (+) are attributed to [Fe(CN)$_6$]$^{3-/4-}$ according to comparison with an authentic sample of (NEt$_4$)$_3$[Fe(CN)$_6$] (ref 5).

Unfortunately, the apparently very low intensity[24] of the IVCT band of **3**$^{3-}$ does not allow a corresponding comparison of electronic interaction parameters for the metal−metal coupling. For **2**$^{3-}$ the approximation $H_{AB} = \nu_{\max}/2 = 2260$ cm^{-1} is justified because of the class III behavior with a narrow and unsymmetrical band;[1−3] the experimental bandwidth at half-height ($\Delta\nu_{\exp} = 1660$ cm^{-1}) and the value calculated from $\Delta\nu = (2310\ \nu_{\max})^{1/2} = 3230$ cm^{-1} are very different. While **2**$^{3-}$ exhibits a rhombic EPR signal ($g_1 = 2.605$, $g_2 = 2.426$, $g_3 = 1.760$) similar to that of **1**$^{3-}$,[4] the dinuclear **3**$^{3-}$ with higher local symmetry (C_{2v}) at the iron centers shows an axial EPR response ($g_\perp = 2.597$, $g_\parallel = 1.459$) in glassy frozen solution. The close similarity to the EPR signal ($g_\perp = 2.593$, $g_\parallel = 1.512$) of the mononuclear iron(III) species [(bpym)Fe(CN)$_4$]$^-$ suggests valence localization on the time scale of the EPR experiment. The one-electron-reduced form **2**$^{5-}$ of the Fe$_2^{\mathrm{II,II}}$ state **2**$^{4-}$ exhibits a radical-type EPR signal at $g = 2.000$, hypsochromically shifted MLCT absorption (Figure 2), and a low-energy shift and splitting of the cyanide stretching band (Figure 1). That state could not be reached reversibly for the bpym-bridged system **3**$^{n-}$ (Table 1) because of the higher lying π* MO of that bridging ligand.[25]

IR spectroelectrochemical effects as reported here (Figure 1) were observed by Geiger and co-workers for organometallic

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(20) Waldhör, E.; Kaim, W.; Olabe, J. A.; Slep, L. D.; Fiedler, J. *Inorg. Chem.* **1997**, *36*, 2969.

(21) Waldhör, E.; Poppe, J.; Kaim, W.; Cutin, E.; Garcia Posse, M.; Katz, N. E. *Inorg. Chem.* **1995**, *34*, 3093.

(22) Cf. bis(tetraammineruthenium) complexes of bpym ($K_c = 10^{5.1}$ in CH$_3$CN) and bptz ($K_c = 10^{15.0}$ in H$_2$O): ref 13 and Poppe et al. (Poppe, J.; Moscherosch, M.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 2640). See also: Roche, S.; Yellowlees, L. J.; Thomas, J. A. *Chem. Commun.* **1998**, 1429.

(23) Cf. the Creutz−Taube ion with $K_c = 10^{7.3}$ in acetonitrile: Creutz, C.; Chou, M. H. *Inorg. Chem.* **1987**, *26*, 2995.

(24) Very weak but still detectable IVCT features were observed (refs 12 and 13) at 2700 cm^{-1} for [(R$_3$P)$_2$(OC)$_2$Mo(μ-bpym)Mo(CO)$_2$(PR$_3$)$_2$]$^+$ and at about 3200 cm^{-1} for [(H$_3$N)$_4$Ru(μ-bpym)Ru(NH$_3$)$_4$]$^{5+}$; no corresponding electronic absorption band was detected for **3**$^{3-}$ between 1300 and 7000 cm^{-1}.

(25) Kaim; W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.

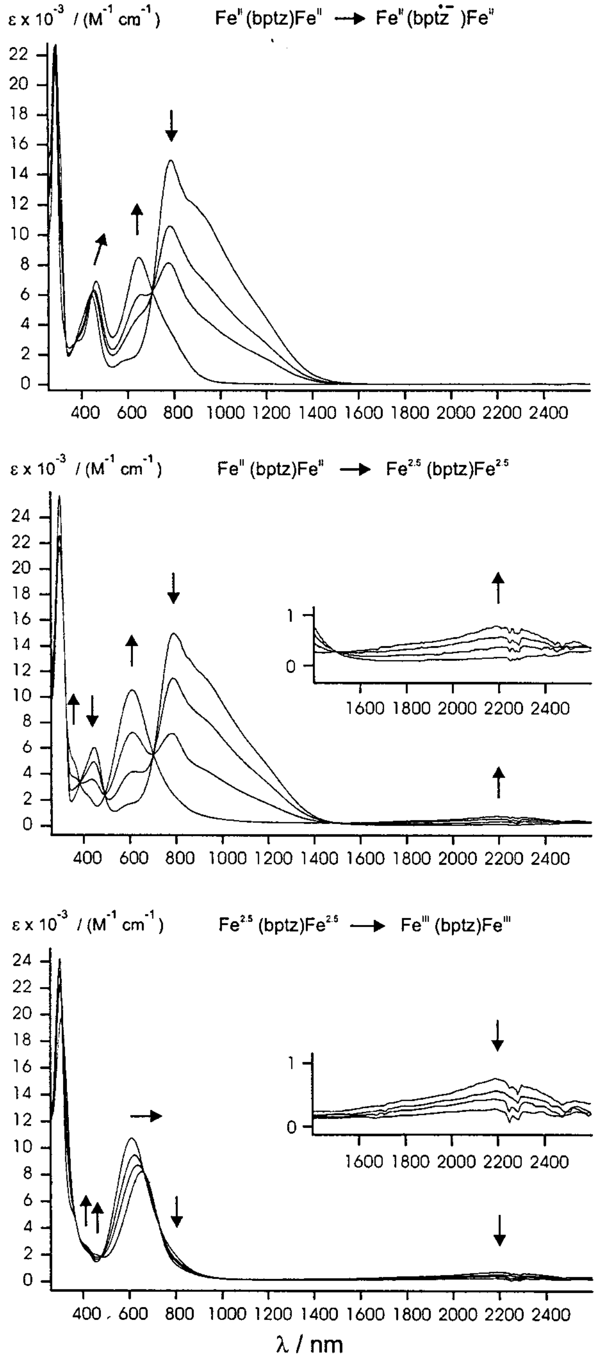


Figure 2. UV/vis/NIR-spectroelectrochemical response of the transitions $\mathbf{2}^{(4-)\to(5-)}$ (top), $\mathbf{2}^{(4-)\to(3-)}$ (center), and $\mathbf{2}^{(3-)\to(2-)}$ (bottom) in CH_3CN/0.1 M Bu_4NPF_6.

species, e.g., bimetallocenes.[26,27] The results on systems $\mathbf{1}^{3-}$–$\mathbf{3}^{3-}$ illustrate clearly that smaller metal–metal distances do not necessarily imply stronger metal–metal interaction. Several series of mixed-valent compounds with increasing ligand size and metal–metal distance had seemingly demonstrated that larger π systems with spatially more separated metal centers lead to rapidly decreasing metal–metal coupling.[1–3,28–31] In contrast to those experiments which could not differentiate

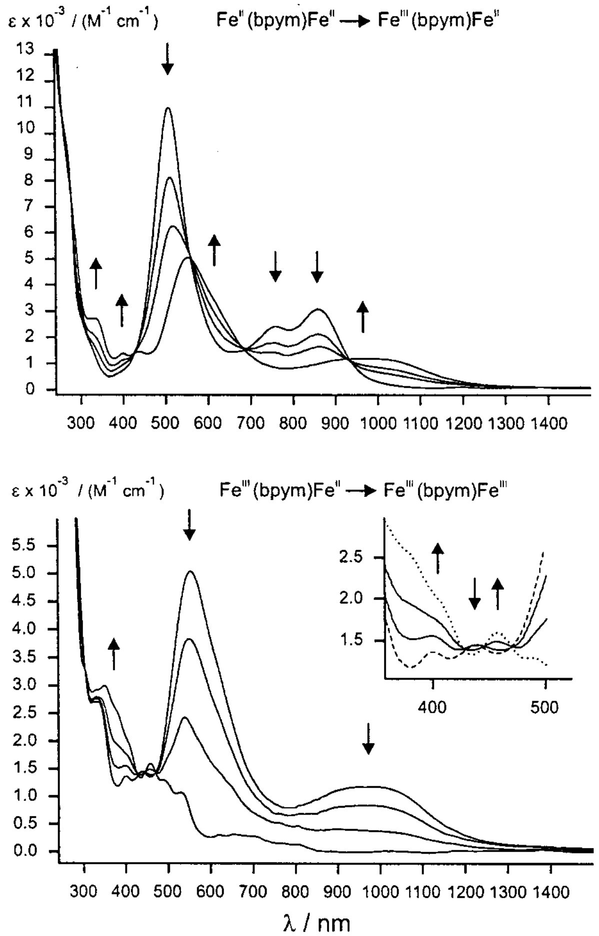
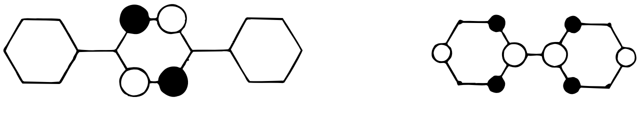


Figure 3. UV/vis/NIR-spectroelectrochemical response of the transitions $\mathbf{3}^{(4-)\to(3-)}$ (top) and $\mathbf{3}^{(3-)\to(2-)}$ (bottom) in CH_2Cl_2/0.1 M Bu_4NPF_6.

between distance and orbital effects, the bptz/bpym pair of conjugated bridging ligands is particularly instructive:

Despite the smaller size of the π system and the shorter metal–metal distance in corresponding dinuclear compounds, the 2,2′-bipyrimidine bridging ligand induces a localized valence situation and a much smaller K_c value than the tetrazines. Thus, on the time scale of vibrational spectroscopy, the delocalized Fe$_2^{2.5}$ description is appropriate for $\mathbf{2}^{3-}$, while the Fe^{III}/Fe^{II} formulation is valid for $\mathbf{3}^{3-}$. The origin of this difference lies in the π^* MO properties which are essential for the electron transfer alternative of exchange in mixed-valent systems.[32] Tetrazines like bptz have a lower lying LUMO with higher MO coefficients at the coordinating nitrogen centers (the "metal–ligand interface") than bpym.[8,25] (See Chart 1.)

Chart 1



A similar note of caution concerns the relation between the comproportionation constant and the (de)localization of valence: While $K_c \geq 10^{14}$ certainly supports delocalized states for $\mathbf{1}^{3-}$ and $\mathbf{2}^{3-}$, the lower value of $K_c = 10^{6.4}$ for $\mathbf{3}^{3-}$ does not

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necessarily imply localization (as indeed observed here). In contrast, the species $[(R_3P)_2(OC)(H)ClOs(\mu\text{-pz})OsCl(H)(CO)(PR_3)_2]^+$ ($K_c = 10^{4.3}$ in CH_2Cl_2)[33] and the Creutz−Taube ion $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ ($K_c = 10^{7.3}$ in CH_3CN)[23] are delocalized on the vibrational time scale.[34] The overall charge in conjunction with effects from the environment thus plays a decisive role in valence (de)trapping, as is similarly known from solid state studies.[35]

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