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# Tuning the optical properties of Prussian blue-like complexes

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**The rational design of the organic ligand allows to finely tune the degree of delocalization of mixed-valence Prussian blue-like molecules.**

One of the important issues in modern molecular chemistry is the ability of chemists to influence the electronic properties of molecules. Among the electronic properties worth modifying at will are those of mixed-valence polynuclear species, wich can serve for instance as models for electron-transfer reactivity[1] or can play a major role in molecular electronics.[2] One of the most known and the oldest mixed-valence compound is Prussian blue ($Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}15H_2O$).[3] This three-dimensionnal cyanide-bridged compound has intervalence band centered at 14080 $cm^{-1}$ ($\varepsilon$ = 9800 L $mol^{-1}$ $cm^{-1}$) responsible for its intense blue colour.[4] It is considered as the archetype of mixed-valence class II compounds in the classification of Robin and Day.[5]

In 1980, N. Lewis stated: 'The problem with complexes (*sic*) like Prussian blue is that discrete molecular units cannot be isolated. (...) [That] limits the amount of useful chemical information which may be obtained for such a system.'[6] We have recently overcome this problem,[7,8] using a molecular step-by-step approach. The reaction of $K_4[Fe^{II}(CN)_6]$ with six equivalents of $[Fe^{III}(L_2)Cl]$ ($H_2L_2$ is the pentadentate ligand bis(3-salicylideneaminopropyl)methylamine) leads to the formation of a mixed-valence, mixed-spin heptanuclear complex $[Fe^{II}\{(CN)Fe^{III}(L_2)\}_6]Cl_2$ that reproduces all the electronic characteristics of Prussian blue.

Vahrenkamp and coworkers showed recently that the energy of the metal-to-metal transition in cyanide bridged trimers with phtalocyanine iron centers depends on the nature of the external metal units: for electron rich metal, the MMCT band shifts to high energy.[9] Here we show that we are able to tune the position of the intervalence band of Prussian blue-like molecules without changing the nature of the metal, just playing with the reduction potential of the peripheral $Fe^{III}$ by a judicious choice of the organic ligand, the more easily reducible the peripheral $Fe^{III}$ are, the lower in energy the intervalence transition is.

Three different pentadentate ligands $H_2L_1$ (*N*,*N*′-bis(2-methylphenol)-*N*-(2-methylpyridine)-1,2-diaminoethane), $H_2L_2$ (bis(3-salicylideneaminopropyl)methylamine) and $HL_3$ (*N*,*N*-bis(2-methylpyridine)-*N*′-salicylidene-1,2-diaminoethane) were synthetized (see Graphical Abstract).

The corresponding mononuclear $Fe^{III}$ complexes were prepared: $[Fe^{III}(L_1)Cl]$ **1**, $[Fe^{III}(L_2)Cl]$ **2** and $[Fe^{III}(L_3)Cl][B(C_6H_5)_4]$ **3**.† The single crystal structure studies‡ show that the sixth position is occupied by a chloride for the three complexes.[10]

Cyclic voltammetry studies were carried out to compare quantitatively the reduction potential of $Fe^{III}$ in these three complexes. In order to obtain reversible (or quasi-reversible) reduction waves, we added about 5000 equivalents of water so that the species present in solution are in fact $[Fe^{III}(L_1)(H_2O)]^+$ **1′**, $[Fe^{III}(L_2)(H_2O)]^+$ **2′** and $[Fe^{III}(L_3)(H_2O)]^{2+}$ **3′**.§

The reduction peaks from $Fe^{III}$ to $Fe^{II}$ are observed at −0.354, −0.145 and +0.053 V/SCE for **1′**, **2′** and **3′**, respectively (Fig. 1). This evolution of the reduction potential of $Fe^{III}$ in these complexes can be rationalized, following qualitatively the ideas developed by Lever.[11] First, since the phenolate group is a strong π-donor ligand, it should stabilize $Fe^{III}$. We can thus justify that, in **1′** and **2′**, $Fe^{III}$ is more difficult to reduce than in **3′** because the metal is linked to two phenolate groups in the former two and to only one in the latter compound. Secondly, since imine and pyridine goups (which we consider as equivalent in this rough approach) are π-acceptor ligands wheras amines are only σ-donor, the reduced $Fe^{II}$ state must be more accessible in **2′** than in **1′**, and this is what is experimentally observed. Finally, the presence of two pyridine and one imine π-acceptor groups in **3′** is in line, as well, for the stabilisation of the reduced $Fe^{II}$ state in **3′**.

The corresponding Prussian blue-like molecules have then been synthetized following the strategy already used for the synthesis of $[Fe^{II}\{(CN)Fe^{III}(L_2)\}_6]Cl_2$ hereafter denoted **B**.[7,8] Starting from **1**, we obtained $[Fe^{II}(CN)_2\{(CN)Fe^{III}(L_1)\}_4]$ **A**¶ and starting from **3**, we obtained $[Fe^{II}\{(CN)Fe^{III}(L_3)\}_6][B(C_6H_5)_4]_8$ **C**.‖ UV–vis spectra of these compounds were measured in solution (5 × $10^{-5}$ M)** and compared to the spectrum of the corresponding $Fe^{III}$ monomer. Subtracting the spectrum of the mononuclear $Fe^{III}$ complex from that of the polynuclear measured in the same solvent, leads to the spectra shown in Fig. 2. The spectra corresponds to the intervalence band associated to the electron transfer from low spin $Fe^{II}$ to high spin $Fe^{III}$.

Assuming gaussian shapes, we can extract the Hush parameters from the intervalence spectra, which indicate the degree of localization in those complexes, compared to those of Prussian blue (Table 1).[12]

The localization rates $\tau$ are rather high compared to those obtained for other cyanide bridged systems,[9] but are of the same order of magnitude as for Prussian blue itself. The electronic coupling between donor and acceptor centers are rather small compared to those previously reported by Pfenning *et al.*[13] for heteronuclear cyanide bridged trimers, but still of the same

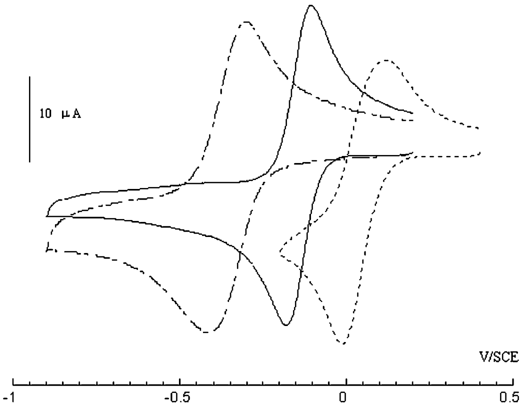

**Fig. 1** Cyclic voltammograms for **1′** (–·–), **2′** (—), and **3′** (---).

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**Table 1** Analysis of the intervalence spectra (Hush model)

| Compound | $\nu_{max}$/cm$^{-1}$ | $\varepsilon_{max}$/M$^{-1}$ cm$^{-1}$ | $\Delta_{1/2}{}^{a}$/cm$^{-1}$ | $n^{b}$ | $H_{ab}{}^{c}$/cm$^{-1}$ | $\tau^{d}$ (%) |
|---|---|---|---|---|---|---|
| **A** | 18500 | 5500 | 6100$^{e}$ | 4 | 1590 | 99.26 |
| **B** | 14950 | 7800 | 4500 | 6 | 1190 | 99.36 |
| Prussian blue | 14100 | 9800 | 5100 | 6 | 1380 | 99.04 |
| **C** | 13400 | 10400 | 6050 | 6 | 1510 | 98.72 |

[a] Full width at half-maximum. [b] Number of acceptor sites. [c] Magnitude of the electronic coupling calculated as $H_{ab} = (0.0206/R)[(\varepsilon_{max}\nu_{max}\Delta_{1/2})/n]^{1/2}$ with $R$ = 5.1 Å. [d] Localization rate calculated as $\tau = 1 - \{4.24 \times 10^{-4}[(\varepsilon_{max}\Delta_{1/2})/(n\nu_{max}R^2)]\}$. [e] This value for $\Delta_{1/2}$ is over-estimated (leading to $H_{ab}$ over-estimated and $\tau$ under-estimated) because of obscuration of the IT band by the LMCT transition on Fe$^{III}$ which prevents precise measures.

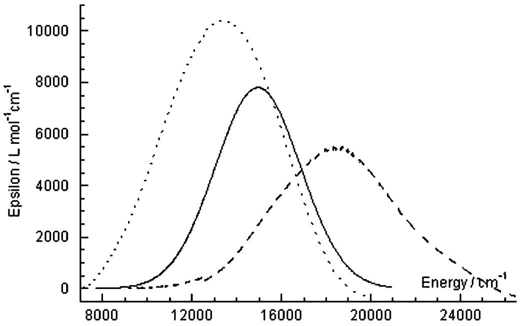

**Fig. 2** Intervalence spectra for **A** (---) in $CH_3OH$, **B** (—) in $CH_2Cl_2$ and **C** (···) in $CH_3CN$.

order of magnitude. This justifies the treatment of those true Prussian blue molecules as mixed valence class II systems.

We have shown previously that **B** presents ferromagnetic coupling between Fe$^{III}$ which is related to the presence of a low lying intervalence excited state.[7] We are currently investigating the relation between the energy of the MMCT transition in these Prussian blue molecules and the amplitude of the ferromagnetic coupling.

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## Notes and references

† Anal. Found (calc.) for **1**·$C_2H_5OH$, $C_{24}H_{29}N_3O_3ClFe$: C, 57.31(57.70); H, 5.73(5.80); N, 8.47(8.42); Cl, 7.30(7.10); Fe, 10.60(11.20). Anal. Found (calc.) for **2**, $C_{21}H_{25}N_3O_2ClFe$: C, 56.79(56.96); H, 5.68(5.65); N, 9.41(9.49); Cl, 8.01(8.06); Fe, 12.60(12.51). Anal. Found (calc.) for **3**, $C_{45}H_{41}N_4OClBFe$: C, 71.05(71.50); H, 5.52(5.47); N, 7.29(7.42); Cl, 4.70(4.63); B, 1.46(1.46); Fe, 7.18(7.41)%.

‡ *Crystal data* for **1**: $C_{22}H_{22}N_3O_2ClFe$, $M$ = 451.73, monoclinic, $a$ = 13.889(2), $b$ = 7.6512(11), $c$ = 18.908(3) Å, $\beta$ = 97.809(3)°, $U$ = 1990.7(5) Å$^3$, $T$ = 150 K, space group $P2_1/n$, $Z$ = 4. The data were collected on Station 9.8 at Daresbury Synchrotron Radiation Source ($\lambda$ = 0.6884 Å),[14] 13653 reflections measured, 5496 unique ($R_{int}$ = 0.1140), 3269 with $I = 2\sigma(I)$. The structure was solved and refined with SHELXTL.[15] The final conventional $R$ factor (on $F$) was 0.0599 [$wR2$ = 0.1248].

*Crystal data* for **2**: $C_{21}H_{25}N_3O_2ClFe$, $M$ = 442.75, monoclinic, $a$ = 7.864(5), $b$ = 22.044(5), $c$ = 11.560(5) Å, $\beta$ = 98.140(5)°, $U$ = 1983.8(16) Å$^3$, $T$ = 150 K, space group $P2_1/c$, $Z$ = 4, Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å), 4971 reflections measured, 3959 unique ($R_{int}$ = 0.0212), of which 2967 were considered observed [$I = 2\sigma(I)$]. The final conventional $R$ factor (on $F^2$) was 0.0435 [$wR2$ = 0.1195 (all data)].

*Crystal data* for **3**: $C_{45}H_{41}N_4OBClFe$, $M$ = 755.93, monoclinic, $a$ = 28.149(7), $b$ = 10.622(3), $c$ = 26.677(6) Å, $\beta$ = 106.912(4)°, $U$ = 7631(3) Å$^3$, $T$ = 150 K, space group $C2/c$, $Z$ = 8, Bruker SMART APEX diffractometer operating with Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å), 21351 reflections measured, 7789 unique ($R_{int}$ = 0.0369) ), of which 5924 had $I = 2\sigma(I)$. The structure was solved using SIR97[16] and refined with SHELXTL.[15] The final conventional $R$ factor (on $F^2$) was 0.0385 [$wR2$ = 0.0947 (all data)].

CCDC reference numbers 182432–182434. See http://www.rsc.org/suppdata/cc/b2/b202288e/ for crystallographic data in CIF or other electronic format.

§ Because of partial substitution of the chloride ligand in solution when linked to Fe$^{III}$, and mainly because of the instability of the reduced species when the chloride is coordinated,[17] it was not possible to obtain reversible waves, even at high scan rates (up to 2 V s$^{-1}$). The addition of an excess of water leads to complete substitution of the chloride by a water molecule: the waves are then reversible and shift towards positive potentials by about 200 mV relative to the irreversible process with chloride. Experiments were carried out using a standard three-electrode (C/Au/SCE) configuration, in $CH_3CN$ ($10^{-3}$ M) in the presence of tetraethylammonium perchlorate (0.1 M), at 20 °C and at a scan rate of 100 mV s$^{-1}$. Potentials are reported *vs.* saturated calomel electrode, SCE.

¶ For solubility reasons, we had to work in water, so the neutral compound precipitated, corresponding to the formula $[Fe^{II}(CN)_2(CNFe^{III}(L_1))_4]$.

‖ Anal. Found (calc.) for **A**·$6H_2O$, $C_{138}H_{150}N_{24}O_{18}Fe_5$: C, 57.68(57.75); H, 5.09(5.12); N, 12.87(12.90); Fe, 14.16(14.30). Anal. Found (calc.) for **C**, $C_{324}H_{286}N_{30}O_{68}Fe_7$: C, 74.77(75.18); H, 5.45(5.57); N, 8.33(8.12); B, 1.9(1.7); Fe, 8.01(7.57)%.

** For solubility reasons, we had to work with a different solvent for each Prussian blue molecule. Although one expects solvent dependence of the intervalence band for mixed-valence class II compounds, we only measured a small dependence for our compounds (even though we were strongly limited in the choice of solvent by the solubility). This is probably due to the spherical symetry of the compounds, and to the fact that the electron can be delocalized onto four or six acceptor centers. In any case, in considering the quantitative interpretation of the spectra, one must keep in mind that they are not recorded in the same solvent, even though the changes in the ligands seem to be the dominant factor.

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