Synthesis, spectroelectrochemistry and electronic structure calculations of 4-(2-ferrocenylvinyl)-[2.2]-paracyclophane and 4,12-di-(2-ferrocenylvinyl)-[2.2]-paracyclophane

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ABSTRACT

4,12 di (2 ferrocenylvinyl) [2.2] paracyclophane **2** has been prepared and investigated with respect to its electrochemical and UV/Vis/NIR spectroelectrochemical properties. Cyclic and square wave voltammetric measurements show two consecutive one electron oxidations with a moderate redox splitting of 112(±3) mV for the individual Fc/Fc⁺ couples. In spite of this redox splitting, radical cation **2**^{•+} is a class I mixed valent system with no detectable electronic coupling between the individual redox sites as is shown by the comparison of the Vis/NIR spectra of **2**^{•+}, **2**²⁺ and the radical cation of 4 (2 ferrocenylvinyl) [2.2] paracyclophane, **4**^{•+}. The NIR bands observed for the oxidized forms have been assigned as ferrocene based d d transitions by quantum chemical calculations.

1. Introduction

Studies of intramolecular metal–metal electronic interactions (“electronic communication”) in mixed valent (MV) states of inorganic and organometallic compounds have attracted considerable attention [1]. Apart from being driven by purely academic motivation, progress in that area is, inter alia, stimulated by possible applications of MV compounds in opto electronic technologies [2] of the future and the design of novel redox responsive polymers [3]. Moreover, it has recently been found that the extent of electron delocalization in MV states of some organometallic compounds positively correlates with their anti cancer activity [4].

Derivatives with ferrocenyl end groups represent an abundant and still increasing class of MV compounds that have been extensively investigated with respect to their electronic structures. This is due to the high stabilities of the neutral and oxidized forms of the ferrocenyl moiety and the well developed synthetic chemistry of ferrocene itself [5]. In the simplest case of ferrocene, two ferrocenyl units are directly bonded to each other and strong

metal–metal interactions are observed that may be tuned by the interplanar angle between the interconnected rings or the identity and orientation of the counterion [6]. The challenging issue of long range metal–metal electronic interactions requires, however, that redox active ferrocenyl units are separated by π conjugated bridges that are able to strongly interact with and electronically couple the terminal ferrocenyl sites. This architecture leads to ferrocenyl capped compounds of class **A** (Fig. 1).

Such a kind of molecular architecture can be regarded as prototypical for a “molecular wire”. In compounds of class **A**, charge is transmitted between oxidized and reduced ferrocenyl end groups along the plane defined by the intervening π conjugated bridge. Apart from the influence of the outer solvation sphere, the extent of metal–metal interactions in MV states depends on the energy levels and the electronic structure of the bridge and the spatial distance between the redox centers. While five and six membered S, Se, O or N atom containing heterocycles are the most abundant class of bridges [7], there are also examples of di(ferrocenes) with π conjugated carbocyclic [8], polyenyl [9] or arylenevinylene bridges [10]. It has been claimed that oligophenylenevinylene bridges allow for electronic interactions between interconnected ferrocenyl units over distances of up to 40 Å [10a]. Interestingly, metal–metal electronic interactions have also been observed in compounds where two ferrocenyl groups were bridged by short saturated linkers [8c,11].

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Fig. 1. The general representations of classes A, B of complexes and the structure of pseudo-[2.2]paracyclophane C.

Complexes of class B (Fig. 1) represent a design where a planar one or two dimensional (1D or 2D) π conjugated bridge has been replaced by a three dimensional (3D) one. Such an arrangement offers complementary through space and through bond pathways for establishing electronic interactions between the individual redox sites via π stacking of the arene decks or via the saturated linkers. In this respect [2.2] paracyclophane (PCP) [12] (C; Fig. 1) appears as an attractive and commercially available 3D π conjugated bridging group. In [2.2] paracyclophane two benzene rings are tied together at their 1,4 positions by short ethylene linkers. As a consequence free rotation of the benzene rings is no longer possible. Moreover, the short ethylene straps force the two arene decks into a boat conformation which in turn decreases their aromaticity. Thus, the distance between the bottoms of the boat like rings is ca. 3.1 Å while the carbon atoms that are interlinked

by the $-\text{CH}_2\text{CH}_2-$ straps are only ca. 2.8 Å apart. The average distance between the arene decks in C is, however, shorter than that between isolated benzene rings (~ 3.5 Å), that in graphite (3.35 Å) and that between benzene rings in typical charge transfer complexes (> 3.2 Å).

There are several organometallic complexes in the literature where [2.2] paracyclophanes (PCPs) serve as 3D π conjugated bridges, η^6 ligands or simply as bulky substituents [13]. However, reports dealing with "electronic communication" in [2.2] paracyclophane bridged binuclear organometallic compounds are still scarce. The group of Akita reported electrochemical studies on the pseudo *meta* isomer of a binuclear $-\text{C}\equiv\text{C}-\text{FeCp}^*(\text{dppe})$ appended [2.2] paracyclophane [13d]. Based on the observation of two separate redox waves with a half wave splitting of ca. 100 mV they argued for some degree of electronic interactions between the Fe containing entities, yet without further investigation of its mixed valent radical cation. The group of Connick [13e] has utilized C as a bridge in binuclear rhenium and ruthenium complexes while some of us were able to quantify the degree of ground state delocalization in the radical cation of a divinyl [2.2] paracyclophane based diruthenium complex and to demonstrate the preference of the through space over the through bond pathway for establishing electronic communication in the MV state [13f]. Both groups employed a combination of spectroscopic and electrochemical methods in order to probe for metal-metal interactions. However, to the best of our knowledge, there are no reports addressing the problem of electronic interactions in complexes of class B where the redox active capping end groups are ferrocenyl moieties. Interestingly, related 1,8 naphthalenediyl bridged metallocenes of Heck et al. were found to display intramolecular magnetic interactions through space [14].

Taking into account the above mentioned reports and our continued interest in the field of "electronic communication" in binuclear organometallic compounds [4a,15] we here describe the synthesis, spectroelectrochemistry and quantum chemical calculations of 4,12 di (2 ferrocenylvinyl) [2.2] paracyclophane **2**. We also investigated the spectroelectrochemistry of the known 4 (2 ferrocenylvinyl) [2.2] paracyclophane (**4**; Fig. 2) [13a-c], while that of styrylferrocene (**5**; Fig. 2) has already been reported [16,17]. These compounds serve as reference systems where no Fc/Fc^+ (**4**) or arene-arene interactions (**5**) are possible.

2. Results and discussion

2.1. Synthesis and characterization

The primary objective of the investigations reported here was to introduce 2 ferrocenylvinyl electrophores into positions 4 and 12

Fig. 2. The structures of compounds **2**, **4** and **5**.

of the pseudopara [2.2] paracyclophane core. In our hands, the most efficient procedure involves the palladium catalyzed phase transfer Heck reaction of vinylferrocene with 4,12 dibromo [2.2] paracyclophane **1** at 70 °C over two days (Scheme 1; for an alternative, lower yielding two step procedure see the Supporting information).

Two products were isolated: binuclear complex **2** in 36% yield and trace amounts of 4 bromo 12-(2 ferrocenylvinyl) [2.2] paracyclophane **3**. The small amount of **3** allowed for its characterization by means of HRMS only. Extended reaction times, elevated temperatures or an excess of vinylferrocene led to even lower yields of **2**. After purification, **2** is an orange, crystalline, and air stable solid. It was characterized by standard spectroscopic methods including ^1H NMR, ^{13}C NMR, MS and elemental analysis. All analytical data confirm the proposed structure. The ^1H NMR spectrum of **2** shows a two proton singlet at δ 6.84 ppm for the H_4 protons, two doublets for the vinyl protons at δ 6.72 ppm and δ 6.68 ppm (H_6 and H_7), each integrating as two protons, and two two proton doublets for the phenyl protons H_3 and H_2 at δ 6.51 ppm and δ 6.44 ppm, respectively (see the Experimental section for atom numbering). Figure S1 of the Supporting information gives an extended view of the aromatic region of the ^1H NMR spectrum. The E stereochemistry in **2** has been unambiguously confirmed by the large $^3J_{\text{HH}}$ coupling constant of 16.2 Hz between the vinylic protons. As illustrated in Figure S2, the peaks for the α hydrogen atoms in the ferrocenyl groups are magnetically inequivalent and appear as two two proton singlets at δ 4.71 ppm and δ 4.56 ppm (H_8 and H_9). The signals at δ 4.43 and 4.21 ppm are assigned to the β hydrogen atoms of the ferrocenyl groups (H_{10}) and the hydrogen atoms of C_5H_5 groups (H_{11}). The ^1H NMR signals of the bridging $\text{CH}_2\text{-CH}_2$ groups resonate at δ 3.58 ppm, δ 3.13 ppm and δ 2.89–2.78 ppm (H_1 and H_5).

2.2. Electrochemistry

The electrochemical properties of **2**, **4** and **5** were determined by cyclic voltammetry (CV) and square wave voltammetry (SWV) in $\text{NBu}_4^+\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{3,5})_4^-/\text{CH}_2\text{Cl}_2$ at room temperature. The choice of this weakly coordinating anion containing supporting electrolyte [18] instead of the more commonly used $\text{NBu}_4^+\text{PF}_6^-$ was motivated by its ability to decrease the effects of ion pairing, to increase the redox splitting and to increase the solubility of the higher oxidized forms in solvents of low polarity. Table 1 lists the electrochemical data for **2**, **4** and **5** while Fig. 3 shows their voltammograms. Like in other supporting electrolytes [19–21], styrylferrocene **5** undergoes a single uncomplicated one electron redox process, which under the present conditions occurs at a half wave potential of 6 mV against the ferrocene/ferrocenium standard. Within the electrochemical window of the $\text{NBu}_4^+\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{3,5})_4^-$ supporting electrolyte complex **4** also oxidizes in

Table 1

Electrochemistry data for compounds **2**, **4** and **5** obtained at a scan rate of 0.1 V s^{-1} at 295 K in $\text{CH}_2\text{Cl}_2/\text{NBu}_4^+\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{3,5})_4^-$ (0.1 M) as the supporting electrolyte.

Compound	$E_{1/2}^{0/+}$ [V] ^a	$E_{1/2}^{+/2+}$ [V]	ΔE_p [V] ^b
4	−0.014		0.063
2	−0.034 ^c	0.078 ^c	
5	−0.006		0.065

^a All potentials are referenced to the ferrocene/ferrocenium redox couple. $E_{1/2}^{0/+} = (E_{p,a}^{0/+} + E_{p,c}^{0/+})/2$.

^b $\Delta E_p = |E_{p,a} - E_{p,c}|$.

^c Data from deconvolution of double peak in the square wave experiment.

a single Nernstian one electron process at a half wave potential $E_{1/2}^{0/+}$ of 14 mV against the Fc/Fc^+ couple. Complex **2**, on the other hand, undergoes two successive, closely spaced one electron oxidations that are assigned as the $2^{0/+}$ and $2^{+/2+}$ couples. Both oxidized forms are stable on the voltammetric time scale as is indicated by the reverse to forward peak current ratios of essentially unity. Half wave potentials $E_{1/2}$ for the two oxidations of **2** are 34 mV and +78 mV against the Fc/Fc^+ reference couple. The comproportionation constant K_c of $78(\pm 10)$ was calculated according to the equation $K_c = \exp[(n \cdot F)/(RT) \cdot \Delta E_{1/2}]$ [22] ($n = 1$, $F = 96,487$, $R = 8.3143$, $T = 298\text{ K}$, $\Delta E_{1/2} = 0.112(\pm 0.003)\text{ V}$, determined from digital simulation of the square wave voltammograms) and indicates that the radical cation $2^{+ \cdot}$ is moderately stable towards disproportionation.

Inspection of the half wave potentials of each member of this series reveals only slight cathodic shifts of the first oxidation potential upon replacement of the phenyl substituent by the [2.2] paracyclophane one and upon addition of the second vinyl ferrocene entity. Similarly small effects on changing the arene substituent have been documented for a series of arylolethynyl and arylolethynyl substituted ferrocenes [16] and traced to an only limited ground state delocalization between the redox active ferrocene nucleus and the pendant arylolethynyl or arylolethynyl substituent (*vide infra*).

2.3. UV/Vis spectroscopic and UV/Vis/NIR spectroelectrochemical measurements

Details pertaining to the electronic spectra of complexes **2**, **4** and **5** are collected in Table 2 and displayed in Fig. 4. The electronic spectrum of styrylferrocene **5** has already been scrutinized along with those of similar vinyl or ethynyl ferrocenes with more extended aryl substituents [16,23]. The prominent UV bands of **5** at 266 and 308 nm originate from the $\pi \rightarrow \pi^*$ transitions of the parent arene. The latter band has been observed to progressively red shift as the extension of the attached π perimeter increases. Additional, much weaker absorptions at 360 and 451 nm are due to ferrocene based d d bands. Complexes **4** and **2** are [2.2] paracyclophanes

Scheme 1. One-step synthesis of **2**.

Fig. 3. CVs of complexes **2**, **4** and **5** (0.1 M NBu₄⁺ B{C₆H₃(CF₃)₂-3,5}₄, ν 100 mV/s) and square wave voltammogram of **2** (step height 0.25 mV, ν 20 Hz) showing the resolution of the composite wave into individual peaks.

with extended π conjugation that can be envisioned as a bis(ethylene) fused dimer of styrylferrocene and its truncated form, respectively. Substituting the styryl by the [2.2] paracyclophanyl residue induces distinct spectroscopic changes in the UV. Thus, the 266 nm band of **5** experiences a strong red shift and appears as a shoulder at 299 nm while the main band also red shifts by ca. 1500 cm⁻¹ from 308 to 323 nm. Attachment of a second ferrocenylvinyl unit to the other deck has no effect on the UV part of the spectrum other than increasing the overall absorptivity of the composite band with respect to monoferrocene **4**. This shows that the π stacked arene ring of the [2.2] paracyclophane (PCP) skeleton increases electron delocalization with respect to

Table 3
Dihedral angles between the PCP and Fc moieties vs. the C—CH=CH—C plane of the vinyl moiety.

Species	Dihedral angle in deg
4	4.3
4 ^{•+}	2.3
2	23.7, 23.5
2 ^{•+}	22.1, 20.4
2 ²⁺ (singlet diradical)	15.7, 16.0

styrylferrocene through conjugative and inductive effects. A red shift of essentially the same magnitude has also been observed for the *p* stilbene/4,12 distyryl [2.2] paracyclophane pair of compounds [24]. The d d bands of **2** and **4** appear as an asymmetric peak with a main absorption at ca. 435 nm and a shoulder near 490 nm. In keeping with the ferrocene parentage of this band, its overall absorptivity in **2** is roughly twice of that in **4**.

Identical peak positions in the electronic spectra of **2** and **4** suggest a lack of ground state delocalization between the individual vinylferrocene moieties. This does, however, not exclude electronic interactions in the monooxidized, mixed valent state where the PCP framework may serve as a rigid 3D bridge facilitating intramolecular electron transfer between the (formally) reduced and the (formally) oxidized ferrocenium moieties. Such effects have been clearly demonstrated for vinyl ruthenium substituted [2.2] paracyclophanes [13f]. The observation of two separate one electron waves for **2** with a moderate splitting of ca. 110 mV may also be regarded as pointing into that direction. In fact, redox splittings of such magnitude are often viewed as a token for at least some degree of electronic interaction between mutually interconnected redox sites [13d]. Caution is, however, warranted because several factors like electrostatic interactions, inductive effects, magnetic exchange and a statistical factor all contribute to the observed redox splitting [25,26] with the Coulombic term often prevailing [18c]. The latter reflects the increase of electrostatic repulsion with every charge that is removed from an already charged system. The observation of some redox splitting is thus, *per se*, no proof of electronic communication between interlinked redox sites but needs to be backed by independent spectroscopic probes.

Intramolecular electron transfer between identical but differently charged redox sites usually manifests itself through a characteristic low energy absorption band in the low energy part of the visible or the near infrared (NIR) that is absent in similar systems with just one redox active moiety. The availability of complexes **5** and **4** thus allows us to directly probe for such interactions in **2**. The electronic spectrum of **5**^{•+} in CH₂Cl₂/NBu₄⁺ PF₆⁻ has already been reported [16,23]. For the sake of consistency with the measurements on **2**ⁿ⁺ and **4**ⁿ⁺ we measured the UV/Vis/NIR spectra of **5** and **5**^{•+} in the same 1,2-C₂H₄Cl₂/NBu₄⁺ B{C₆H₃(CF₃)₂-3,5}₄ supporting electrolyte. Changes of the electronic spectra observed upon gradual oxidation of **5** inside an OTTE (optically transparent thin layer electrolysis) cell are

Table 2
UV/Vis/NIR spectra of complexes **2**, **4**, and **5** in 1,2-C₂H₄Cl₂/NBu₄⁺ B{C₆H₃(CF₃)₂-3,5}₄ (0.1 M); λ_{max} in nm (ϵ in l mol⁻¹ cm⁻¹).

5	5 ^{•+}	4	4 ^{•+}	2	2 ^{•+}
266 (13,700)	262 (18,500)	299 (sh, 10,800)	303 (14,900)	299 (sh, 18,000)	306 (22,200)
308 (18,800)	273 (sh, 17,800)	323 (15,450)	381 (sh, 7450)	320 (23,000)	379 (sh, 10,800)
360 (3200)	302 (15,800)	347 (sh, 11,330)	427 (8000)	354 (sh, 14,500)	423 (10,400)
451 (1230)	367 (6700)	437 (2450)	498 (5450)	434 (4300)	497 (6440)
	400 (5800)	488 (sh, 2060)	558 (sh, 2870)	490 (sh, 3200)	555 (sh, 3860)
	477 (2250)		910 (sh, 1180)		915 (sh, 1500)
	513 (sh, 1300)		1057 (1700)		1055 (2000)
	585 (220)				
	890 (sh, 880)				
	941 (950)

Fig. 4. Changes in the electronic spectra during oxidation of complexes 2, 4 and 5 inside an OTTE cell (1,2- $\text{C}_2\text{H}_4\text{Cl}_2$, 0.1 M $\text{NBu}_4^+\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2-3,5)_4^-$).

displayed in the top panel of Fig. 4. Differences between the reported data and ours are expectedly small. The most conspicuous features in the electronic spectra of 5^{*+} are the weak, broad NIR band peaking at 941 nm, an even weaker band at 585 nm and a richly structured absorption that envelopes the spectroscopic region from 520 to 360 nm with discernible peaks at 477, 400 and 367 nm (see Table 2). Previous studies on 5 and 5^{*+} and similar arylolethynyl and arylolethynyl ferrocene derivatives have shown that the conjugated arene substituent strongly perturbs the frontier MOs of parent ferrocene by lifting

the degeneracy of the two $e_1(\pi)$ and the two $e_2(\delta)$ orbitals. One MO of each set (denoted as $e_1' a$ and $e_2' a$ in ref. [23]) has appropriate symmetry to interact with the π conjugated substituent and is raised in energy with respect to its non interacting counterpart $e_1' b$ and $e_2' b$. The FMO ordering and electronic configuration of such ferrocenes is thus $(e_1' b)^2 < (a_1)^2 < (e_1' a)^2 < (e_2' b)^2 < (e_2' a)^2$ [23]. The NIR band of 5^{*+} has been assigned as a transition between the $e_1' a$ (π) SOMO 2 orbital and the singly occupied $e_2' a$ (δ) SOMO. While both orbitals are delocalized across the entire ferrocene- $\text{CH}=\text{CH}$ -phenyl array, this transition is still associated with appreciable charge transfer from the styryl substituent to the ferrocenium nucleus as is, *inter alia*, indicated by its considerable negative solvatochromism. The weak band at 585 nm is the SOMO $\rightarrow$ SOMO + 1 transition while the richly structured visible band has been found to involve (an) other transition(s) between states that are likewise delocalized across the entire arenevinyl-ferrocenium chromophore. The rich structuring of that group of transitions is a likely consequence of the degeneracy lifting of the parent e states. A slight blue shift of the arene $\pi \rightarrow \pi^*$ bands in the UV is readily traced to the effect of changing the ferrocenyl donor into a ferrocenium acceptor.

Replacing the styryl substituent of 5^{*+} by vinyl[2.2]paracyclophane in 4^{*+} has the effect of red shifting and intensifying all electronic bands that receive contributions from the ferrocenium subunit (see Fig. 4, middle). Linear correlations between the HOMO energy (gas phase ionization potential), the oxidation potential of the parent arene and the energy of the NIR band of arylolethynyl and arenevinyl substituted ferrocenium ions have already been noted [16,23]. The position of the NIR band places 4^{*+} close to the radical cation of the 9 anthrylvinyl substituted ferrocene. This is despite the distinctly larger ionization potentials (8.1 eV vs. 7.45 eV) [27,28] and half wave potentials (1.57 V vs. ca. 1.26 V) [29,30] of [2.2] paracyclophane compared to anthracene. The effect of replacing the styryl by the [2.2] paracyclophanyl substituent is thus more complex to be accounted for by simple relations based on the energy levels of the parent arene alone. The red shift of all bands of 4^{*+} in the visible régime by 1000–1500 cm^{-1} with respect to the equivalent ones in 5^{*+} indicates that the paracyclophane tag is also involved in those transitions.

Spectra collected during the stepwise oxidation of bis(ferrocenylvinyl) [2.2]paracyclophane 2 to dication 2^{2+} inside an OTTE cell are depicted in the bottom panel of Fig. 4 (for pertinent data see Table 2). It immediately appears that the spectra of 4^{*+} and 2^{2+} are nearly superimposable and differ only by the somewhat larger extinction coefficients in 2^{2+} . The latter is readily explained by the presence of two identical chromophores instead of just one. Spectral comparison thus argues against any mutual interaction between the vinylferrocenium groups which mirrors the situation observed for their reduced forms. More importantly, however, our data also indicate the absence of any detectable electronic interactions between them at the level of the mixed valent radical cation. Slowly scanning the electrode potential through the regime where first the $2^{0/+}$ and then the $2^{+/2+}$ processes occur proceeds with clear isosbestic points, a continuous growth of all bands and without the intermittent formation of any new absorption that might be related to an IVCT band of 2^{*+} , even on an extended energy scale down to 2200 nm (not depicted in Fig. 4). The comproportionation constant of 78 ± 10 dictates that 2^{2+} reaches a maximum concentration of more than 80% of the initial concentration of 2 ($K_c = \frac{[2^{*+}]_{\text{max}}^2}{([2_0] - ([2^{*+}]_{\text{max}}/2))^2}$) with $[2_0]$ initial concentration of 2 during electrolysis. Any specific band associated with 2^{*+} should thus readily be discerned in the spectra collected during the conversion of 2 to fully oxidized 2^{2+} . From the absence of any such band and the maintenance of the same isosbestic points throughout the entire process we can therefore conclude that 2^{*+} constitutes a valence localized mixed

Fig. 5. Contour diagrams of the HOMO (left) and LUMO (right) of ferrocenes **2** (top) and **4** (bottom) as obtained by DFT calculations.

valent system of Class I according to the Robin and Day classification scheme [1c] in spite of the redox splitting of the two redox waves. This is in stark contrast to the radical cation of the similar 4,12 divinyl [2.2] paracyclophane bridged diruthenium complex $\{(\text{P}^i\text{Pr}_3)_2(\text{CO})\text{CIRu}-\text{CH}=\text{CH}-\}_2[2.2]$ paracyclophane, where “electronic communication” between the individual redox sites was clearly indicated by sequential shifts of the Ru–CO stretches following the individual one electron oxidation steps [13f]. The reason underlying the rather disparate behavior between the two related systems is probably due to the fact that the redox processes of styryl ruthenium complexes are strongly biased to the organic (“non innocent”) ligand [31] while they are much more metal centred for the ferrocenyl systems of the present study (*vide infra*) (Table 3).

2.4. Quantum chemical calculations

We have performed density functional theory (DFT) calculations on the electronic structures of compounds **2** and **4** using the ORCA computer package [32] and Perdew–Burke–Ernzerhof (PBE0) functional. Iron atoms were described by the effective core potential pseudo relativistic basis set [33] while for all other atoms the 6 31G(d) basis set was used. The molecular structures were fully optimized in the 1,2 dichloroethane solvent ($\epsilon = 10.3$) using COSMO solvation model [34]. Open shell systems were calculated

by the unrestricted Kohn–Sham approach (UKS). We have explored relative energies of possible staggered/eclipsed conformers of **2** and **4** and found that the staggered conformers have the lowest energy. Optimized geometries of **2** and **4** are shown as Figures S3 and S4 of the Supporting information. The staggered and eclipsed designations refer to the relative dispositions of the PCP and Fc units. The most significant structural parameter is the dihedral angle between the PCP and Fc planes as measured by the torsion angles between the PCP phenylene bond at the vinyl linkage and the adjacent C=CH bond of the ferrocenyl ring (C4–C3–C37–C38 for **4** and C4–C3–C41–C42 for **2**, for atomic numbering see Scheme S2). Deviation from coplanarity of the ferrocenyl and the PCP groups reduces π conjugation between them and would also attenuate the electronic coupling in 2^{*+} . Values of the calculated torsional angle for the various oxidation states are given in Table 2.

The calculated geometries (Table 2) show that in the mono ferrocene derivative **4** the PCP and Fc units are nearly coplanar. In diruthenium **2**, however, the dihedral angle is considerably larger but not to the degree of seriously impeding π conjugation. This more twisted ground state conformation of neutral **2** may also be related to the fact that the two α hydrogens of each ferrocenyl (Fc) unit in **2** differ with respect to their chemical shifts (Figure S2 of the Supporting information) while the anisotropy of their shifts in **4** is considerably smaller. Another interesting observation deduced from the calculations is that oxidation of **2** and **4** leads to a reduction of pertinent dihedral angles (“planarization”) which facilitates electron interactions (transfer) between the Fc and the PCP units.

Quantum chemical calculations (Fig. 5) indicate that the HOMO of **2** and of **4** is delocalized over the PCP and Fc units and receives large contributions from the (di)vinyl PCP ligand, particularly for **2**, while the respective LUMO is even more ligand based. This finding resembles those for similar arylvinyl and arylolethynyl substituted ferrocenes [16,17]. The lowest energy electron transition of 4^{*+} represented by the weak band in the NIR spectrum involves MOs that are localized on the ferrocene nucleus and can essentially be viewed as an iron centred d d transition between the a_1 (d_{z^2}) and e_2' (δ) orbital. The same obviously holds for radical cation 2^{*+} . Our calculations also indicate that dioxidized 2^{2+} has a singlet ground state and displays an open shell biradicaloid structure. This conclusion follows from the comparison of calculated and observed NIR transitions in the electronic spectra of that species. For the alternative triplet diradical and singlet closed shell structures agreement between calculated and observed spectra was much poorer. The NIR electronic transitions were calculated with ZINDO/S Hamiltonian [35] which represents the best compromise between accuracy and computational efficiency for the size of molecules studied in this work. Based on these calculations, the low energy electronic transitions in 2^{2+} are also purely metal based and

Fig. 6. MOs involved in the optical transitions of singlet diradical 2^{2+} .

involve Fe $3d_z^2$ and Fe $3d(\delta)$ orbitals. Details can be found in Fig. 6 and S5 and in Table 1 of the Supporting information. We also note that, while still considered unusual, there is a growing number of accounts where open shell singlet diradical ground states have been evoked or proven for the dioxidized forms of complexes featuring two bridged redox sites [14a,36].

3. Conclusions

We have prepared the new 4,12 bis(ferrocenylvinyl) substituted [2.2] paracyclophane **2** and compared its electronic and electrochemical properties to those of the closely related mono ferrocenylvinyl substituted [2.2] paracyclophane **4** and of styrylferrocene **5**. While the cofacial arrangement of two styryl groups has the expected consequences on the salient electronic features of the arene part of the structure resulting from through space and through bond interactions, no mutual interaction is seen between the two ferrocenyl subunits of **2** in both the reduced and the fully oxidized 2^{2+} state. Electronic spectra of **4** and **2** on one hand and of 2^{2+} and 4^{2+} are superimposable and the only difference between them is the somewhat higher extinction coefficient of 2^{n+} . Most importantly, this is also true for the mixed valent radical cation $2^{•+}$ where one of the redox active ferrocenyl tags is present in the oxidized and the other one in the reduced state. Despite the presence of discernible splitting of half wave potentials of 112 ± 3 mV corresponding to a K_c of 78 ± 10 and despite the presence of the NIR absorption, $2^{•+}$ constitutes a mixed valent system of Class I with mutually non interacting redox sites. The NIR absorptions of $4^{•+}$, $2^{•+}$ and $2^{•+}2^{•+}$ originate from d d transitions that are localized on the Fe atoms and may not be misinterpreted as IVCT bands for the mixed valent (MV) states. Our results are thus a caveat for studies on similar systems and a reminder that additional proof beyond simple electrochemical data and a low energy electronic transition of the MV form is necessary before any firm conclusion as to the presence and strengths of electronic interactions can be reached.

4. Experimental section

4.1. General remarks

All preparations were carried out using standard Schlenk techniques. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM), alumina (EcoChrom™ MP Biomedicals, 96 g Al_2O_3 :4 g water). CH_2Cl_2 was distilled over CaH_2 prior to use. Other solvents were of reagent grade and were used without prior purification. All other chemicals were purchased from the Aldrich Chemical Co. The NMR spectra were recorded on a Bruker 600 (600 MHz) spectrometer. Chemical shifts are reported in δ (ppm) using residual $CHCl_3$ (1H δ 7.26 ppm) as the reference. Mass spectra were recorded using EI methods on a Finnigan MAT 710A spectrometer. Microanalyses were determined by Analytical Services of the Polish Academy of the Sciences (Łódź). 4 (2 ferrocenylvinyl) [2.2] paracyclophane [13c] **2** was prepared according to the literature procedure. Electrochemical works were performed on a Princeton Applied Research VersaStat3 and Epsilon™ potentiostats from BASi (Bioanalytical Systems, Inc.) in home built vacuum tight one compartment cells using Pt electrodes as the working electrode, a platinum spiral as the counter electrode and a silver spiral as a pseudo reference electrode. Each of the spiral shaped electrodes was welded to Vycon wire and sealed into a glass tube. Counter and reference electrodes are introduced into the cell by appropriate fittings in the side wall and sealed via a Quickfit screw. CH_2Cl_2 for electrochemical use was distilled from CaH_2 , deoxygenated by saturation with argon and

briefly stored over molecular sieves. Potential calibration was performed by adding ferrocene or decamethylferrocene ($E_{1/2}$ 0.550 V vs $Cp_2Fe^{0/+}$) as an internal standard to the analyte solution. The amount of the reference system was adjusted until its peak currents were comparable to those of the analyte. Potentials are given against the ferrocene/ferrocenium couple.

4.1.1. Synthesis of 4,12 di (2 ferrocenylvinyl) [2.2] paracyclophane **2**

A deoxygenated mixture of vinylferrocene (636 mg, 3.0 mmol), K_2CO_3 (5.52 g, 40 mmol), tetrabutylammonium bromide (4.51 g, 14 mmol), 4,12 dibromo [2.2] paracyclophane (**1**, 366 mg, 1.0 mmol) and $Pd(OAc)_2$ (67 mg, 0.3 mmol) in DMF (43 mL) was heated at 70 °C for 2 days. After cooling to r. t. the dark reaction mixture was filtered, diluted with CH_2Cl_2 (~40 mL) and washed with brine (4×30 mL). The organic phase was dried with $MgSO_4$, filtered and the solvent was removed from the filtrate in vacuo. The residue was subjected to chromatography on deactivated Al_2O_3 (*n* hexane). Two fractions containing products were collected: a first one containing trace amounts of **3** and a second one containing **2**. Slightly impure **2** was subjected to column chromatography on silica gel with $CHCl_3$ followed by crystallization from a $CHCl_3$ /MeOH mixture. **2** was obtained as an orange solid in 36% (226 mg) yield. **3** HRMS: m/z 496.04921 (Calcd for $C_{28}H_{25}BrFe$: 496.04890).

1H NMR (600 MHz, $CDCl_3$): δ 6.84 (s, 2H, H_4), 6.72 (d, $^3J_{H,H}$ 16.2 Hz, 2H, H_6), 6.68 (d, $^3J_{H,H}$ 16.2 Hz, 2H, H_7), 6.51 (d, $^3J_{H,H}$ 7.8 Hz, 2H, H_3), 6.44 (d, $^3J_{H,H}$ 7.8 Hz, 2H, H_2), 4.71 (s, 2H, H_9), 4.56 (s, 2H, H_8), 4.43 (s, 4H, H_{10}), 4.21 (s, 10H, H_{11}), 3.58 (ddd, $^3J_{H,H}$ 12 Hz, $^3J_{H,H}$ 9 Hz, $^3J_{H,H}$ 0.07 Hz, 2H, H_5), 3.13 (ddd, $^3J_{H,H}$ 12 Hz, $^3J_{H,H}$ 9 Hz, $^3J_{H,H}$ 0.07 Hz, 2H, H_5), 2.89–2.78 (m, 4H, H_1).

^{13}C NMR (150 MHz, $CDCl_3$): δ 139.5, 137.1, 134.9, 131.0, 126.7, 126.0, 124.3, 69.5, 69.4, 69.2, 68.4, 65.5, 34.4, 34.3. MS (EI, 70 eV): m/z 628 (M^+), 314 (M^+ $C_{20}H_{18}Fe$). Anal. Calcd for $C_{40}H_{36}Fe_2$: C, 76.45; H, 5.77. Found: C, 76.62; H, 6.01.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jorganchem.2012.07.020>.

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