TUTORIAL REVIEW

Photoswitchable mixed valence

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5 For a molecular electronics technology to be fully serviceable, switching functions will be indispensable. Specifically, it will be desirable to control the conductivity of a given molecule using an external stimulus. Photoswitchable mixed valence systems are comprised of a reversibly photoisomerizable bridging unit connecting two redox-active moieties, and as such represent some of the most simple chemical systems in which switching of charge delocalization can be explored. As photoisomerizable

10 units, dithienylethenes have received much attention in the context of photoswitchable mixed valence, but there are also more exotic examples such as norbornadiene- and dimethyldihydropyrene-based switchable systems. As redox-active units responsible for the mixed valence phenomenon, both metal-containing as well as purely organic moieties have been employed. Typical investigations in this area involve the comparison of cyclic voltammograms and (near-infrared) optical absorption spectra of the two isomeric

15 forms of a given system. The magnitude of the comproportionation constant and evaluation of intervalence absorption bands using appropriate theoretical models yield information regarding the extent of charge delocalization in the two isomeric forms. In several of the compounds investigated so far, the light stimulus induces a substantial increase of charge delocalization, or in the terminology commonly used in mixed valence chemistry, a changeover from class I to class II or even class III behavior.

1. Introduction

20 Mixed valence species contain two chemically identical units that are formally in different oxidation states.[1] These redox-active units may contain metals,[2-4] or they may be entirely organic.[5-6,60] Although there are exceptions to this rule,[7] the two redox-active

25 centers typically differ in oxidation state formally by one unit, and consequently there is usually one unpaired electron in mixed valence systems.[1-6] This odd electron may be localized entirely on one of the two redox centers, or it may be partially or even fully delocalized between them. Depending on which of the three

30 possible scenarios is encountered, the mixed valence species is categorized as a class I, class II or class III system.[4-5, 8] To which class a newly synthesized mixed valence compounds belongs is usually one of the key questions. The issue of charge delocalization is interesting in its own right, but it is also

35 important in the context of long-range electron transfer and, possibly, for a future molecular electronics technology. When attempting to build molecular systems that can mediate charge transport over long distances, one is usually interested in materials which permit charge delocalization over many atoms,

40 and it may even be desirable to influence the extent of charge delocalization or conductivity of a given molecule by applying an external stimulus. Photoswitchable systems are particularly attractive in this respect because light can selectively and rapidly address specific molecular units.[9] Mixed valence compounds with

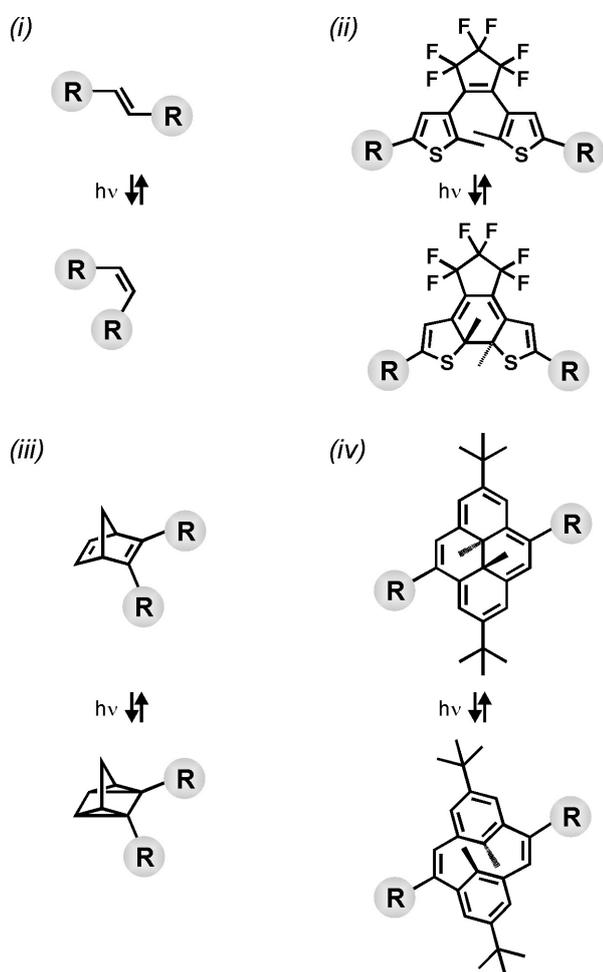45 molecular bridges comprised of units that can undergo reversible

photoisomerization reactions are well suited, simple model systems for investigating how charge delocalization can be affected with light. The first three reports on photoswitchable mixed valence appeared in 1996 and 2000,[10-12] but then this field

50 of research has been dormant until 2006, when it finally experienced a revival.[13] ~~This *tutorial review* reports on the most significant findings from this emerging field, with particular focus on the contributions made by the groups of Launay, Akita, Nishihara, and the author's own research team.~~

55 The control of electron transfer by light is of long-standing interest. Recent advances in the field of photoswitchable mixed valence are highly relevant in this context, and this provided the motivation for this *tutorial review*. At this point, the field of photoswitchable mixed valence is yet a rather young area of

60 research, and the current article provides a comprehensive review on this particular sub-discipline of electron transfer chemistry. The *tutorial review* begins with a section discussing the design principles for photoswitchable mixed valence compounds, introducing the most common types of photoisomerizable units

65 used for the construction of photoswitchable mixed valence systems. A subsequent section (no. 3) gives a brief introduction to two key measures for quantification of mixed valence phenomena; this section on electrochemical and optical spectroscopic measurements is kept to minimum length because

70 the theory of mixed valence chemistry has been reviewed many times before.[1-2, 4, 14-16] Sections 4 – 7 represent the core part of the review, discussing specific case studies from the field of photoswitchable mixed-valence. A summary and conclusions

section puts the findings from sections 4 – 7 into greater context and mentions some chemical and technical challenges associated with this emerging field of research.

2. Design principles for photoswitchable mixed valence compounds

The key feature of a photoswitchable mixed valence system is a covalent linker between two redox-active units that can be converted back and forth between two isomeric states using light as an energy input. To the best of the author's knowledge, four types of photoisomerizable linkers have been used so far as bridges in photoswitchable mixed valence compounds (Scheme 1): (i) alkene linkers that can undergo E-Z isomerization; (ii) dithienylethenes which exhibit ring-closure and ring-opening reactions, (iii) norbornadiene spacers which isomerize to quadricyclane units, (iv) dimethyldihydropyrene units which photoisomerize to cyclophanediene forms. In this *tutorial review*, a separate section will be dedicated to each of these four types of photoisomerizable units, discussing the key studies in each case.

If one aims to elucidate what photoisomerizable units could potentially provide the most efficient switching functions in a molecular electronics technology, the photoswitchable unit represents the most important component of a photoswitchable mixed valence system.

From this viewpoint, the choice of redox-active units is secondary. Organometallic complexes represent a popular choice because they tend to exhibit clean and reversible electrochemistry, a fact that can greatly simplify the determination of comproportionation constants (section 3). Purely organic redox-active centers appear particularly attractive for detection of intervalence bands by optical absorption spectroscopy (section 3). A researcher's choice of redox-active units may therefore be geared in large part by the experimental technique that he or she has in mind for investigation of the mixed valence phenomenon. However, even if the choice of the redox-active unit may be secondary, this does not mean at all that this choice is unimportant: There are usually clear advantages and disadvantages associated with a given redox-active unit, and where appropriate, these aspects will be specifically mentioned in later sections of this article. Since this *tutorial review* is structured according to photoswitchable bridging units, most of the sections 4 – 7 contain systems with a variety of different redox-active units; no particular preference was given to certain specific redox-active moieties. The current article simply reflects what in the author's view represents the current state-of-the-art in the field of photoswitchable mixed valence.

An important aspect in mixed valence chemistry is the distance dependence of electron transfer: The shorter the electron transfer distance, the more spectacular the mixed valence phenomenon is likely to manifest. [1-2, 4, 14-16] Therefore, one usually has a strong interest in linking two redox-active moieties to the photoswitchable spacer in the closest way possible.

Regarding design of photoswitchable mixed valence compounds, the field still has great potential for further creative development. The four photoisomerizable bridges mentioned above are by no means the only promising photoswitchable moieties that could be incorporated into mixed valence species. What is more, in several instances reported below the switching functions are actually rather modest, sometimes because of a suboptimal choice of redox-active units, sometimes because the redox-active units seem to be too far apart from each other.

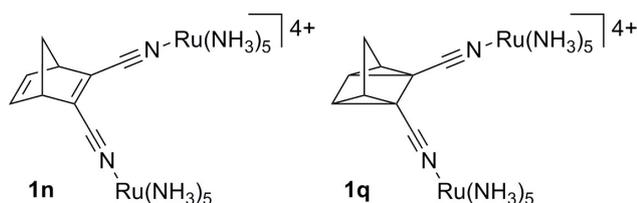## 3. Comproportionation constant and electronic coupling factor

There are several reviews treating the theory of mixed valence in considerable depth.[1-2, 4, 14-16] Here, only two aspects that are especially pertinent to the experimental case studies presented in the following sections are briefly reviewed. One important experimental observable in many of the systems discussed below is the electrochemical potential for oxidation of the redox-active centers (R). In cases where cyclic voltammograms or differential pulse voltammograms exhibit a splitting (ΔE) between the redox waves associated with the two oxidizable units of a given molecule, it is possible to calculate the equilibrium constant for the comproportionation reaction $R^{n+}\text{-}R^{n+} + R^{(n+1)+}\text{-}R^{(n+1)+} \leftrightarrows 2\ R^{n+}\text{-}R^{(n+1)+}$.[3] The comproportionation constant ($K_c = 10^{\Delta E/0.059V}$) is frequently used as a measure for the extent of electronic communication between the two redox-active centers of a given mixed valence species.[3] There can be significant electrostatic contributions to K_c,[17] and hence it is usually desirable to obtain complementary information on electronic communication from

other experiments. Analysis of intervalence charge transfer (IVCT) bands by Hush theory or more elaborate three-state models is frequently the preferred method.[15-16, 18] The key outcome of such analyses is the electronic coupling factor (H_{AB}) which is a useful measure for the electronic interaction between the two redox-active units.[19-21] Although it is the interplay between H_{AB} and the reorganization energy (λ) accompanying intramolecular charge transfer in a mixed valence compound that defines to which class a given system belongs,[1, 4-6, 15-16] it may be useful to note that typical H_{AB} values are below 100 cm^{-1} for weakly coupled systems, between 100 cm^{-1} and 1000 cm^{-1} for systems with intermediate coupling strengths, and above 1000 cm^{-1} for strongly coupled systems.[2, 4, 14] K_c values range from the statistical lower limit of 4 for class I species up to values around 10^{15} for class III systems.[3]

Both methods for characterizing mixed valence behavior mentioned here have their limitations. To name just two specific issues, calculation of K_c relies on the assumption that the solvation energies of the R^{n+}-$R^{(n+1)+}$ and $R^{(n+1)+}$-$R^{(n+1)+}$ species are the same, but this does not necessarily have to be the case. H_{AB} is often estimated using geometrical distances between redox-active units (see below), but in some cases this is not an appropriate method.[22]

4. Norbornadiene as a bridging photoswitchable unit

The first example of a photoswitchable mixed valence compound ever reported is also the one bearing most chemical resemblance to the prototype of a designed mixed valence species, the Creutz-Taube ion.[1] In 1996, Launay, Bignozzi and coworkers reported on a molecule containing two pentaammineruthenium moieties coordinated to the cyano-groups of a central 2,3-dicyanonorbornadiene unit (1n).[10] Irradiation of this molecule with UV or visible light induces photoisomerization of the bridging unit from its in initial norbornadiene (n) form to the so-called quadricyclane (q) form, resulting in molecule 1q.
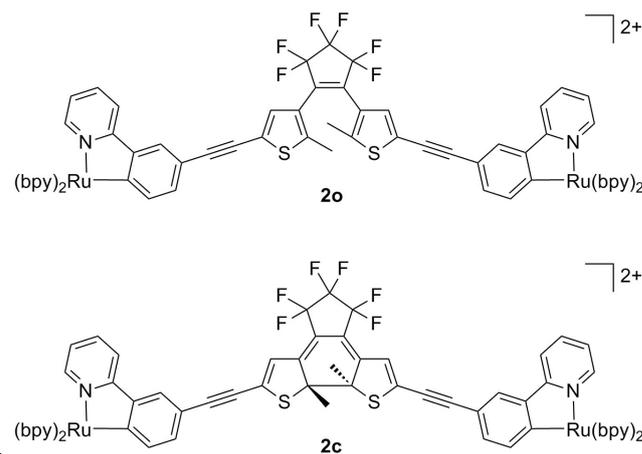

Depending on the exact excitation wavelength, photoisomerization quantum yields (ϕ) range from $(8.3\pm0.6)\cdot10^{-4}$ to $(2.2\pm0.2)\cdot10^{-2}$, with the higher values obtained for UV excitation. A substantial increase of the CN vibrational frequency indicates that the extent of metal-nitrile back-bonding is reduced in 1q compared to 1n, and this interpretation is consistent with the observation of a significant cathodic shift of the electrochemical potential for ruthenium(II) oxidation upon converting 1n to 1q. A splitting into two Ru(II/III) oxidation waves, as frequently observed for strongly interacting di-ruthenium species,[1, 3] was not reported, and the comproportionation constant (K_c) for the equilibrium Ru(II)-Ru(II) + Ru(III)-Ru(III) $\leftrightarrows$ 2 Ru(II)-Ru(III) could be determined for neither of the two isomeric forms of molecule 1. However, direct evidence for metal-metal interaction

in the mixed-valence form of 1n came from optical absorption spectroscopy:[10] Upon oxidizing 1n to 1n$^+$ with tetrabutylammonium tribromide, a weak ($\epsilon < 100$ M^{-1} cm^{-1}) and broad absorption band with a maximum near 1400 nm became detectable. Consistent with the assignment of this near-infrared absorption to an intervalence charge transfer (IVCT) band, it disappeared again upon reducing 1n$^+$ back to 1n with zinc amalgam. Analysis of the IVCT band with Hush theory lead to the conclusion that the electronic coupling (H_{AB}) between metal centers amounts to 185 cm^{-1} in 1n$^+$. By contrast, for 1q$^+$ no near-infrared absorption could be detected, and it was concluded that metal-metal coupling in the quadricyclane form is insignificant.

A later study reported on similar results for a mixed valence system in which two Ru(bpy)$_2$(pp)$^{2+}$ (bpy = 2,2'-bipyridine; pp = 2-phenylpyridine) units are bridged by a photoisomerizable norbornadiene spacer.[11]

5. Dithienylethenes as photoswitchable units

The one-electron oxidized form of molecule 2 was the first example of a designed mixed valence compound incorporating a photoswitchable dithienylethene spacer.[11] As long as the dithienylethene (DTE) bridge is in its open form (2o), there is no evidence for any interaction between the two ruthenium units, but upon photoisomerization to the closed DTE form (2c), an intervalence absorption band becomes detectable.

Analysis of the IVCT band with Hush theory yields $H_{AB} = 200$ cm^{-1}, which is a relatively high value given the large spatial separation (> 23 Å) between the two redox-active metal centers. In this context it appears appropriate to mention that the effective electron transfer distance in mixed valence systems is frequently much shorter than the spatial separation between the atoms which are formally oxidized or reduced. Extended Hückel calculations yield $H_{AB} = 170$ cm^{-1} for 2c$^+$ and $H_{AB} = 24$ cm^{-1} for 2o$^+$. Both of these calculated values are compatible with experiment and suggest that electronic coupling increases by a factor of 7 upon photochemical ring closure.

Akita and coworkers explored two related systems in which ethynyl-substituents, attached at both sides of a central DTE spacer, directly coordinate to iron and ruthenium metal centers (M).[23-24] As additional ligands, pentamethylcyclopentadienyl (η^5-Cp*) and a chelating 1,2-bis(diphenylphosphino)ethane (dppe) coordinate to Fe(II) or Ru(II). In the iron compound (3o), the

metal-metal distance is 15.22 Å according to X-ray crystal structure analysis.

For both systems, cyclic voltammetry provides clear evidence for an increase in the comproportionation constant upon photoinduced closure of the DTE spacer (Figure 1): In the iron compound K_c increases from 13 (3o) to 510 (3c),[23] in the ruthenium compound from 17 (4o) to 71 (4c).
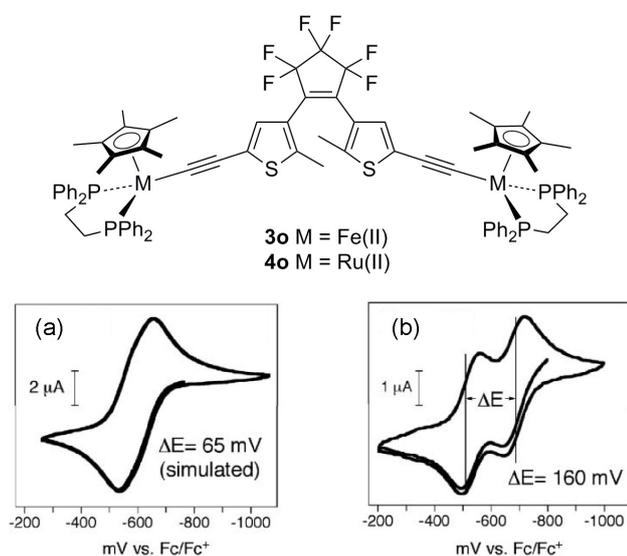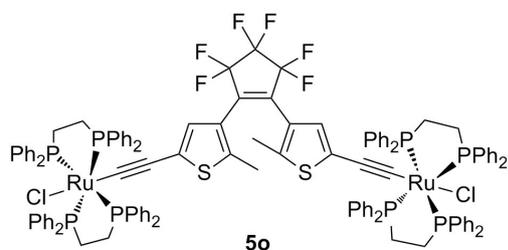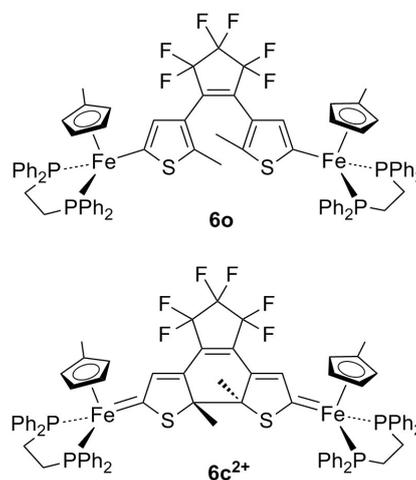

3o M = Fe(II)
4o M = Ru(II)

The DTE-closed forms of both mixed valence species (3c$^+$, 4c$^+$) exhibit complicated near-infrared (NIR) absorption spectra due to the occurrence of a ligand-to-metal charge transfer (LMCT) band at ~12000 cm^{-1} and additional NIR bands between 6000 and 10000 cm^{-1} which were attributed to electronic transitions occurring on the ethynyl-disubstituted DTE unit. This complicated situation with several overlapping transitions permits unambiguous detection of an IVCT band exclusively in the case of the iron compound (3c$^+$). Its analysis leads to a conflict which is not without precedent in the field of mixed valence:[4] The lack of a significant solvent dependence of the IVCT band as well as its shape point towards class III, but this seems incompatible with $K_c = 510$. Consequently, 3c$^+$ was interpreted as a class II species, and in this framework $H_{AB} = 380$ cm^{-1} was obtained.[24]

Depending on how DTEs are substituted, electrochemical ring-closure or ring-opening can be induced.[25-28] This type of electrochromism is also observed for 4o, giving 4c^{2+} as the main two-electron oxidation product.[24]
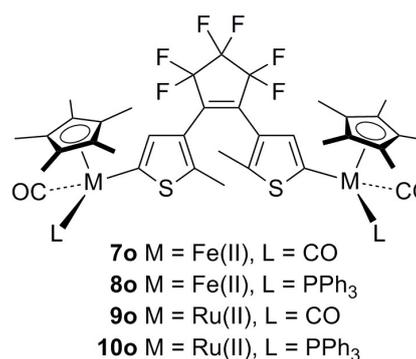

5o

A French research group employed exactly the same ethynyl-

disubstituted DTE unit as a bridging ligand between two [Cl(dppe)$_2$Ru]$^+$ moieties (5o).[29] As for 3c$^+$ and 4c$^+$, the NIR absorption spectra of 5c$^+$ are complicated due a multitude of overlapping transitions. Consequently, like in the case of 4c$^+$, an IVCT band cannot be identified unambiguously. The only evidence for an enhancement of metal-metal communication upon photochemical DTE ring-closure therefore comes from cyclic voltammetry: K_c is found to increase from a value of 28 for 5o to 108 for 5c. As in the case of molecule 4o, two-electron oxidation of 5o is accompanied by DTE ring-closure.

6o

6c^{2+}

Building on molecules 3o/3c and 4o/4c, Akita and coworkers recently disclosed a second generation of DTE-bridged metal complexes (6o, 7o, 8o, 9o, 10o) which differ from the first generation in that the iron and ruthenium centers are now attached directly to the thiophenes of the DTE unit.[30-31] This shortens the metal-metal distance from 15.22 Å in 3o to 10.95 Å in 6o, according to crystal structure analyzes. The impact of Fe-Fe distance shortening on switching of the metal-metal communication can be followed most directly by comparison of the nearly homologous molecules 3o and 6o: While photoisomerization of 3o to 3c increases the comproportionation constant by a factor of 39 (see above), K_c increases from 85 for 6o to $7.5 \cdot 10^4$ for 6c.

7o M = Fe(II), L = CO
8o M = Fe(II), L = PPh$_3$
9o M = Ru(II), L = CO
10o M = Ru(II), L = PPh$_3$

The highest switching factor (SF) between K_c-values for open and closed isomers was found for 10o/10c (5400), the lowest for 6o/6c (880). The general trend is that K_c increases as the ancillary ligands on Fe(II) and Ru(II) become more electron-donating (Table 1): 7c has two carbonyl ligands and $K_c = 4.5 \cdot 10^3$, 8c bears

one carbonyl and one triphenylphosphine leading to $K_c = 1.6·10^4$, and 6c has a dppe chelating agent and $K_c = 7.5·10^4$. An analogous trend is observed for the ruthenium compounds 9c and 10c. IVCT bands were not reported for any of the one-electron oxidized forms of these molecules, hence the K_c-values are the only available measures of charge delocalization in these systems.

Table 1. Comproportionation constants (K_c) and electronic coupling matrix elements (H_{AB}) for the two isomers of each photoswitchable mixed valence system considered in this *tutorial review*.
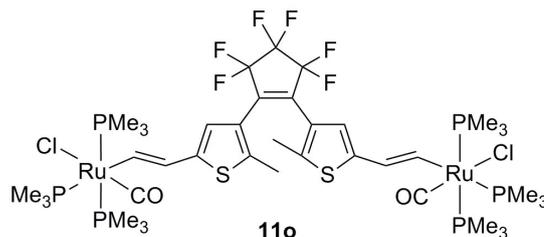
isomer	K_c	H_{AB} [cm^{-1}]	isomer	K_c	H_{AB} [cm^{-1}]
1n			1q		185[a]
2o		24[b]	2c	12[d]	200[d]
3o	13[c]		3c	510[c]	380
4o	17[c]		4c	71[c]	
5o	28[c]		5c	108[c]	
6o	85[c]		6c	7.5·10^4 [c]	
7o	~4[c]		7c	4.5·10^3 [c]	
8o	~4[c]		8c	1.6·10^4 [c]	
9o	6.2[c]		9c	7.2·10^3 [c]	
10o	~4[c]		10c	2.2·10^4 [c]	
11o			11c	349[c]	
12o	< 25[d]		12c	7.9·10^3 [d]	5550[d]
13o	< 25[d]		13c	349[d]	599[d,e]
E-14	15[c]		Z-14	7[c]	
E-15	18[c]	534[c]	Z-15	12[c]	529[c]
16_DHP	57[f]		16_CPD	~4[f]	

[a] In CD$_3$OD. [b] Calculated based on extended Hückel theory, see text. [c] In CH$_2$Cl$_2$. [d] In CH$_3$CN. [e] Average value of the upper and lower limit mentioned in the text. [f] In 1,3-dichloropropane.

There are remarkable differences in photoisomerization efficiencies between the iron and ruthenium molecules 6 – 10.[31] When irradiating THF solutions of the iron compounds 6o and 8o at wavelengths shorter than 360 nm there is essentially no photoisomerization, while for the iron compound 7o a photostationary state containing only 17% of 7c can be attained. By contrast, under identical experimental conditions the ruthenium compounds evolve to photostationary states containing 73% of 9c and 92% of 10c. Analysis with time-dependent density functional theory suggested that in the ruthenium systems the lowest triplet excited state is DTE-localized.[31] Thus, initial singlet-singlet photoexcitation is ensued by intersystem crossing promoted by the metal, and this can be followed by energy transfer to the lowest triplet excited state of DTE from where ring-closure is known to be efficient. In the iron compounds the lowest triplet excited state is metal-localized, hence after intersystem crossing the excitation energy dissipates on the metal center,[32] and the DTE triplet state is not populated.[31]

Molecules 6 – 10 exhibit ring-closure upon two-electron oxidation, and this process seems to be even more efficient than in the case of the DTE-systems with ethynyl linkers (3o and 4o). For the dications $6c^{2+}$ – $10c^{2+}$ it is possible to draw resonance structures in which there is a formal metal-carbon double bond,[31] and this may help understanding why electrochemical ring-closure proceeds with relative ease in these compounds. Direct evidence for the double bond character of the Fe-C bond in $8c^{2+}$ comes from X-ray crystal structure analysis. In $8c^{2+}$ the two determined Fe-C distances are 1.852(5) Å and 1.871(6) Å, while in the neutral molecule 8o an Fe-C distance of 1.979(4) Å was found.[30]

Starting from the twofold ethynyl-substituted DTE bridge employed in molecules 3o, 4o, and 5o, Liu and coworkers synthesized a DTE linker with two pendant vinyl groups that can ligate to ruthenium centers.[33] A series of four ruthenium complexes with different ancillary ligands was investigated, all of which show similar photophysical and electrochemical properties. Molecule 11o is a representative example. For its isomer 11c $K_c = 349$ was determined, whereas the cyclic voltammogram of 11o exhibits no noticeable splitting of the relevant redox waves, hence K_c is presumably < 25 in this case. Replacement of the hexafluoropentene backbone in the DTE by an ordinary cyclopentene unit had no significant impact on the comproportionation constants, and IVCT bands were not reported.[33]

11o

Although frequently associated with coordination compounds and organometallic complexes, the phenomenon of mixed valence is very common in purely organic substances.[5-6,60] Building on the numerous studies of mixed valence in bis(triarylamine) radical cations,[6, 34-35] the DTE-bridged systems 12o/12c and 13o/13c were investigated in the context of photoswitchable mixed valence.[22] Both of these compounds contain redox-active tertiary amino-groups. In the case of 12o/12c the nitrogen atoms are attached directly to the thiophene rings, while in molecules 13o/13c there are *p*-xylene spacers between the N-atoms and the thiophenes. The estimated through-bond N-N distances are 9.3 Å for 12c and 17.6 Å for 13c.
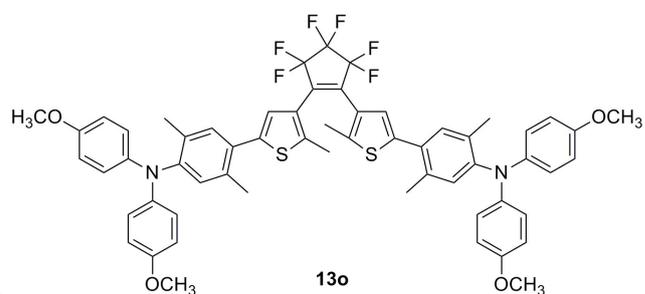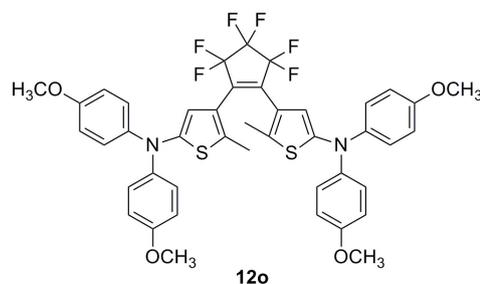
12o

13o

Figure 2a shows that in molecule 13c the redox waves

associated with one-electron oxidation of the two triarylamine units are separated by 150 mV. Figure 2b exhibits an analogous cyclic voltammogram for molecule 12c, but in this case the respective potential splitting (ΔE) is 230 mV. These ΔE-values yield comproportionation constants of 349 for molecule 13c and $7.9 \cdot 10^3$ for 12c.[22] For the open isomers of both molecules (12o, 13o) K_c is estimated to be < 25 due to lack of any noticeable splitting between triarylamine-based one-electron oxidations in cyclic voltammetry.
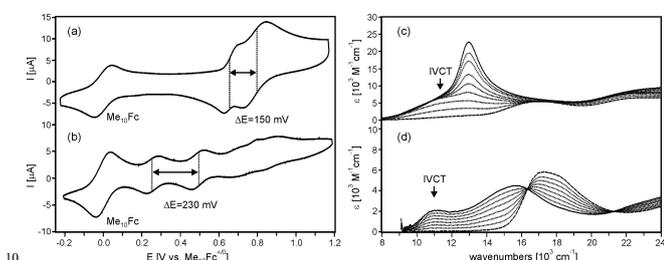

Figure 2. Cyclic voltammograms of molecule 13c (a) and molecule 12c (b) in CH$_3$CN. Changes in optical absorption of CH$_3$CN solutions of molecule 13c (c) and molecule 12c (d) following addition of Cu(ClO$_4$)$_2$ oxidant. The dashed lines show the initial spectra, the solid lines are the final spectra obtained after addition of 1 eq. of Cu(ClO$_4$)$_2$. B. He, O. S. Wenger, *J. Am. Chem. Soc.* 2011, **133**, 17027-17036. Copyright 2011 American Chemical Society.
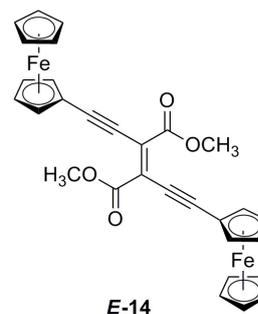
Titration of acetonitrile solutions of the open and closed forms of molecules 12 and 13 with copper(II) perchlorate permits systematic investigation of the oxidation sequence from neutral 12/13 molecules to 12$^+$/13$^+$ monocations and, finally, to 12^{2+}/13^{2+} dications. For the closed forms of the monocations (12c$^+$, 13c$^+$) near-infrared absorptions appear (Figure 2c/2d) and some of them can be identified as IVCT bands. In the case of 13c$^+$ (Figure 2c), the IVCT band shows up as a broad and relatively weak feature centered around 11250 cm^{-1} which is somewhat hidden below a more intense, triarylamine-based absorption maximizing at 12900 cm^{-1}. Analysis of the IVCT band in the framework of Hush theory yields H$_{AB}$ = 476 cm^{-1} when taking the geometrical N-N distance (d$_{NN}$) of 17.6 Å as an effective electron transfer distance (d$_{AB}$). However, prior work on bis(triarylamine) radical monocations demonstrated that d$_{AB}$ is frequently only roughly two thirds of d$_{NN}$ in mixed valence systems of this type.[5,6,60] On the basis of d$_{AB}$ = 2/3·17.6 Å one obtains H$_{AB}$ = 722 cm^{-1}. It appears reasonable to consider the values of 476 cm^{-1} and 722 cm^{-1} as lower and upper limits of H$_{AB}$ in 13c$^+$.[22]

In the case of 12c$^+$ (Figure 2d), an absorption centered at 11100 cm^{-1} was identified as an IVCT band. Due to its solvent independence and narrow width, this band was analyzed in the framework of class III mixed valence. This approach yields H$_{AB}$ = 5550 cm^{-1}, a value close to those obtained for four chemically related bis(triarylamine) mixed valence systems with non-photoswitchable bithiophene bridges and comparable N-N distances.[59] No IVCT bands can be observed for the open forms 12o$^+$ and 13o$^+$.
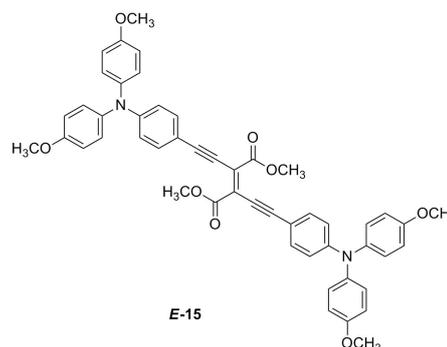
The conclusion from this work on bis(triarylamine) systems is that photoisomerization of the DTE linker from the open to the closed form induces a changeover from class I mixed valence behavior to class II in the case of 13c$^+$ and to class III in the case of 12c$^+$.[22]

6. Photoswitching based on E-Z isomerism in diethynylethenes

E-Z photoisomerization reactions have been explored to considerable extent in stilbene and azobenzene derivatives. Initial efforts to analyze the mixed-valence interaction in cis-azoferrocene in a quantitative manner were not successful,[36] and therefore Nishihara and coworkers turned their attention to photoinduced E-Z isomerization in diethynylethene systems with attached ferrocene or triarylamine units as redox-active centers.[37-38] Irradiation of molecule E-14 in dichloromethane with yellow (578 nm) or green (546 nm) light leads to a photostationary state comprised of 89% Z-14 and 11% E-14.

E-14

Both isomers exhibit an intense absorption band in the visible spectral range which is assigned to a charge transfer transition from ferrocene d-orbitals to ethynylethene π^* orbitals, i. e., in a sense it is an MLCT band. IVCT absorptions could not be detected, and consequently the only experimental evidence for changes in ferrocene-ferrocene interaction upon photoisomerization comes from electrochemistry. Indeed, the cyclic voltammograms of E-14 and Z-14 are slightly different, and Nishihara and coworkers extracted potential splittings (ΔE) of 70 mV (E-14) and 48 mV (Z-14) from these data.[37] These ΔE-values translate to comproportionation constants of 15 (E-14) and 7 (Z-14). The higher K$_c$ value in the E-form is consistent with the expectation of weaker π-conjugation in the Z-isomer. This experimental finding also indicates that direct (through-space) interaction between the two ferrocene units in Z-14 over the (crystallographically determined) Fe-Fe distance of 6.17 Å is insignificant.
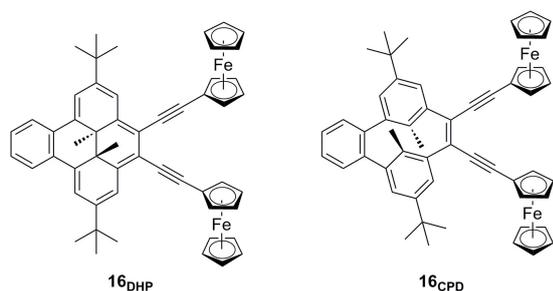

E-15

Molecule 15 represents an all-organic counterpart to molecule 14. In several respects, the triarylamine-based system 15 exhibits more favorable properties for investigation of photoswitchable mixed valence than the ferrocene-based molecule 14:[38] (i) The

quantum yield for E-Z photoisomerization is more than 3 orders of magnitude higher for the organic system because it has no energetically low lying metal-based (triplet) states through which the excitation energy can dissipate rather than being used for photoisomerization; (ii) an IVCT band can be detected for 15^+ but not for 14^+; (iii) redox potential splittings in cyclic voltammetry are somewhat larger in the all-organic compound. Unfortunately, the differences between E-15 and Z-15 are minor, both regarding K_c and H_{AB}: The comproportionation constant decreases from a value of 18 for E-15 to a value of 12 for Z-15, while H_{AB} changes from 534 cm^{-1} for the E-isomer to 529 cm^{-1} in the Z-isomer.[38] Given the large uncertainties in d_{AB} (see above), the variations in H_{AB} between E- and Z-forms reported here are insignificant. In conclusion, the diethynylethene systems investigated so far provide much less spectacular evidence for photoswitchable mixed valence than the DTE- or norbornadiene-based systems presented in the prior sections.

7. Dimethyldihydropyrene as a photoswitchable spacer

Aside from the norbornadiene/quadricyclane study from section 3 (1n, 1q), the most exotic example of a photoswitchable mixed valence system investigated so far is Nishihara's ferrocene-disubstituted dimethyldihydropyrene molecule 16_{DHP}.[39] When irradiating a THF solution of 16_{DHP} with yellow (578 nm) light, the dimethyldihydropyrene (DHP) core of the molecule is excited into a π-π^* transition. This is followed by isomerization of the DHP moiety into a cyclophanediene (CPD) form (16_{CPD}). Continued irradiation at 578 nm ultimately results in a photostationary state containing 97% of 16_{CPD} and 3% of 16_{DHP}, as determined by ^{1}H NMR spectroscopy. The CPD form is significantly less π-conjugated than the DHP isomer, consequently one might expect stronger ferrocene-ferrocene interaction in 16_{DHP} than in 16_{CPD}. Indeed, the cyclic voltammogram of 16_{DHP} in 1,3-dichloropropane exhibits a noticeable splitting between the waves associated with one-electron oxidation of the two ferrocene units, leading to a comproportionation constant of 57 for 16_{DHP}.[39] By contrast, there is no evidence for separation of the respective oxidation waves in 16_{CPD}, hence K_c is assumed to be close to the statistical value of 4. IVCT bands were not reported.

16_{DHP}   **16_{CPD}**

8. Summary and conclusions

Among the four types of photoisomerizable units investigated so far in the context of photoswitchable mixed valence, dithienylethenes (DTEs) lead by far to the most pronounced switching properties. The two most spectacular cases reported to date include molecule 10 in which DTE ring closure increases K_c by a factor of 5400,[30-31] and molecule 12 in which photocyclization of the DTE spacer induces a changeover from class I to class III mixed valence behavior with H_{AB} on the order of 5550 cm^{-1} for $12c^+$.[22]

Until now, ferrocene or related organometallic (Fe(II) or Ru(II)) complexes have been used very frequently as redox-active units in the field of photoswitchable mixed valence.[13, 23-24, 30-31, 33, 37-41] An advantage of these systems is their clean electrochemistry and hence relatively facile determination of comproportionation constants. The disadvantage is that K_c-values are often the only experimentally accessible measure of electronic interaction between such redox centers because IVCT bands usually remain unobserved. Purely organic mixed valence systems represent an attractive alternative in this respect: Selected triarylamines exhibit very clean electrochemistry while at the same time can give rise to fairly intense IVCT absorptions. Purely organic mixed valence systems offer the additional advantage that there are usually no energetically low-lying triplet excited states on the redox-active centers that can negatively affect the quantum yield for photoisomerization of the bridging unit.[32, 42-43] Experimental investigations of electronic communication between redox-active units bridged by a photoisomerizable bridge are so far mostly limited to electrochemical studies (cyclic voltammetry, differential pulse voltammetry) and optical absorption spectroscopy. EPR spectroscopy would appear to be a promising additional tool, particularly in view of recent investigations of mixed valence phenomena in organic systems.[44-45,59]

The general concept of investigating electronic communication mediated by a photoswitchable molecular unit through exploring mixed valence phenomena is clearly a very successful approach. When attempting to explore photoinduced electron transfer in donor-bridge-acceptor compounds containing a photoisomerizable bridge, one is often confronted with the problem that the photoexcitation required to trigger the charge transfer event can also induce photoisomerization.[42-43, 46-49] This undesired situation may arise either through direct excitation of the isomerizable bridge or via energy transfer from the donor (or the acceptor) to the bridge.[32, 42-43, 46-49] Since IVCT bands usually occur in the NIR spectral range while shorter wavelengths are required for bridge photoisomerization, this problem is much less prone to occur in mixed valence compounds.

While there is considerable room for improvement of the mixed valence properties of photoswitchable systems, it seems clear that much future work will be geared at direct measurement of the conductance of photoisomerizable molecules. Although the scope of this *tutorial review* is limited to photoswitchable mixed valence, it appears appropriate to mention in this context that there have already been several investigations of light-induced conductance switching.[50-58] To name just one specific example, the direct measurement of the resistance of the two isomers of a DTE molecule incorporated into a break junction circuit yielded 526±90 MΩ for the open form and 4±1 MΩ for the closed isomer.[50] The switching factor of 132 is in line with the switching factors determined for some of the mixed valence systems discussed above.

With some broad-mindedness, photoswitchable mixed valence

may be considered as a form of light-controlled conductance switching. It is likely that future investigations of photoswitchable mixed valence will continue to provide information on charge transfer phenomena that is complementary to the results obtained from studies of light-controlled conductance switching in molecules which are integrated in real electronic circuits.

Notes and references

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