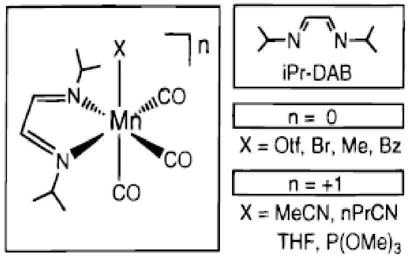
Applications of the OTTLE Cells in the Reading Spectro-Electrochemical Laboratory and by Our Customers Elsewhere (Selected Examples)

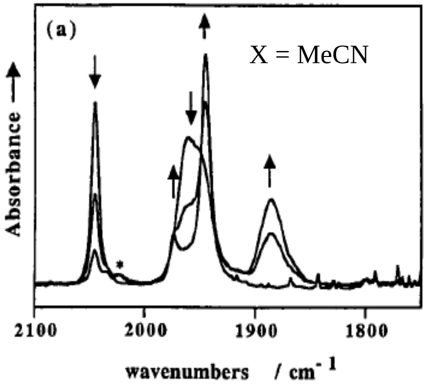
The *Room-Temperature OTTLE Cell* is completely air-tight. It requires a small sample volume and offers a rapid and reliable performance, easy handling and cleaning. This cell has been widely used in UV-Vis-NIR, IR, luminescence and Raman spectroelectrochemistry. Special applications include combination with fibre optics (UV-Vis absorption, time-resolved luminescence and streak camera), microscopes (resonance Raman and epifluorescence microscopy) and telescopic IR beam path reduction (FIR absorption). The cell has also been modified for vibrational circular dichroism (VCD) and laser spectroscopy (including 2D-IR) requiring no light scattering. It can be employed conveniently in studies of extremely air- and moisture-sensitive samples in a glove box.

UV-Vis-NIR and IR Spectroelectrochemistry

(a) Redox Behaviour of Transition Metal Complexes

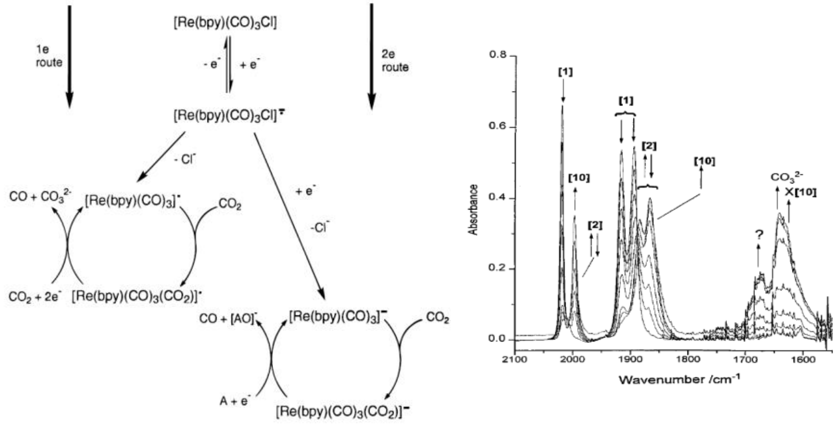
The method of UV-Vis-NIR and IR spectroelectrochemistry within RT OTTLE cells has been employed by **Frantisek Hartl** (University of Reading, UK) in investigations of redox properties, reactivity of redox intermediates and redox pathways of a wide range of transition metal complexes (*Inorg. Chem.*, **2009**, *48*, 1887; *Angew. Chem. Int. Ed.*, **2009**, *48*, 3104; *Dalton Trans.*, **2009**, *38*, 3993; *Inorg. Chem.*, **2006**, *45*, 8326; *Inorg. Chem.*, **2003**, *42*, 4442; *New J. Chem.*, **2002**, *26*, 145; *Inorg. Chim. Acta*, **2001**, *318*, 143; *Dalton Trans.*, **2000**, 4323; *Organometallics*, ***1997***, *16*, 4675). As shown below, IR spectral changes in the *v*(CO) region accompanying the reduction of the complex $[Mn(MeCN)(CO)_3(iPr\text{-}DAB)]^+$ at room temperature reveal dissociation of the axial ligand from the radical product and formation of the dimer $[Mn(CO)_3(iPr\text{-}DAB)]_2$ via an ECEC mechanism involving the 2e$^-$ reduced anion $[Mn(CO)_3()iPr\text{-}DAB)]^-$.





(b) Electrocatalytic Reduction of CO_2

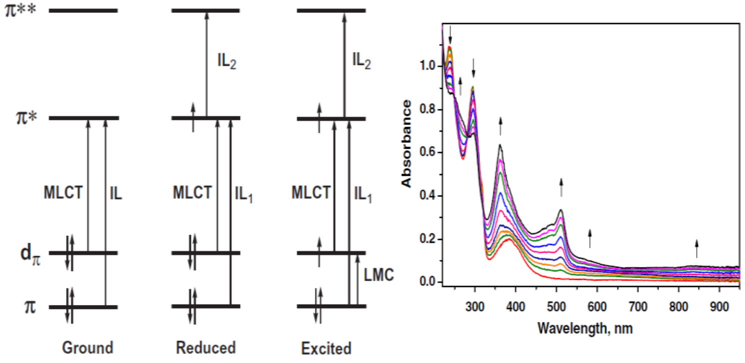
A pioneering application of the IR OTTLE technique jn the in situ investigation of electrocatalytic reduction of carbon dioxide using the complex $[Re(CO)_3(bpy)Cl]$ as a catalyst precursor was published by **Frantisek Hartl** (University of Reading, UK) and **Michael W. George** (University of Nottingham) in 1996. The electrocatalytic mechanism was shown to involve one- and two-electron pathways based on $[Re(bpy)(CO)_3]^{\bullet}$ and $[Re(bpy)(CO)_3]^{-}$, respectively.



The IR spectral changes in the ν(CO) region accompanying the reduction of $Re(bpy)(CO)_3Cl$] (**1**) in CO_2-saturated THF solution within the RT OTTLE cell are shown in the Figure above. The one-electron reduction of $[Re(bpy)(CO)_3Cl]$ (**1**) initially produces $[Re(bpy)(CO)_3Cl]^{\bullet-}$ (**2**) and reactive $[Re(bpy)(CO)_3]^{\bullet}$ which induces slow reduction of CO_2 to CO. As the CO_2 reduction progresses, $[Re(bpy)(CO)_3Cl]^{\bullet-}$ (**2**) is converted into $[Re(bpy)(CO)_3(O_2CH)]^{\bullet-}$ (**10**). This behaviour is evidenced by the shoulder marked X on the low-frequency side of the absorption due to the HCO_3^- side product, assigned to the ν_{as}(COO) band of the coordinated formate in **10**. The much more efficient two-electron path operates in acetonitrile (*Organometallics*, ***1996***, *15*, 3374).

(c) Excited States of Transition Metal Complexes

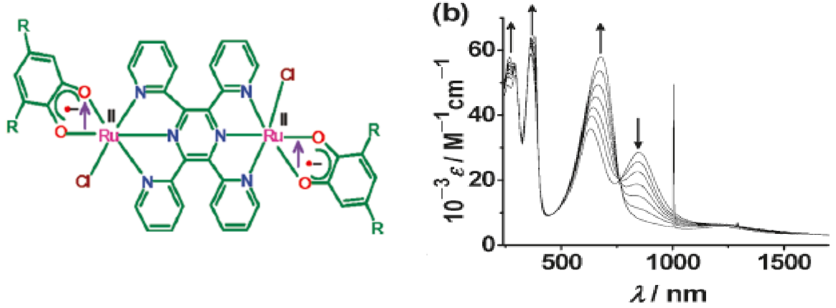
As documented by **Antonín Vlček, Jr.** (Queen Mary University of London, UK) and **František Hartl** (University of Reading, UK) in a series of articles, both charge-transfer and highly π-delocalized excited states of α-diimine metal complexes can conveniently be characterized by transient UV-Vis-NIR and IR spectroscopies in combination with UV-Vis-NIR and IR spectroelectrochemistry, using the RT OTTLE cell.



As shown above, one-electron reduction of the complex $[Re(bpy)(CO)_3Cl]$ generates the anion $[Re(bpy^{\bullet -})(CO)_3Cl]^-$ and results in appearance of the characteristic intraligand $\pi\pi^*$ and $\pi^*\pi^{**}$ absorption (IL_1 and IL_2) of the reduced $bpy^{\bullet -}$ ligand in the 300-1000 nm region. The UV-Vis absorption spectra of the reduced-state complexes can be compared with those of the photogenerated transients to aid the assignment of the nature of the lowest excited states. (*Inorg. Chim. Acta*, **2011**, *374*, 578; *Chem. Eur. J.*, **2008**, *14*, 6912; *J. Am. Chem. Soc.*, **2006**, *128*, 4253; *J. Phys. Chem. A*, **2005**, *109*, 6149; *Inorg. Chem.*, **2004**, *43*, 4523; *Inorg. Chim. Acta*, **2001**, *318*, 143).

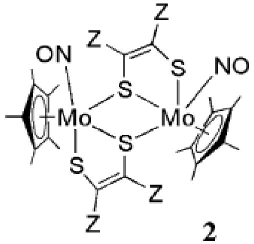
(d) Redox Intermediates

Wolfgang Kaim (University of Stuttgart, Germany) and **Jan Fiedler** (J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic) have been the most frequent users of our cells. A large number of their studies dealt with identification and characterisation of unusual redox intermediates of mononuclear and mixed-valence dinuclear transition metal complexes. For example, the bridged diruthenium complex below features two *o*-semiquinone (one-electron-reduced dioxolene) ligands. Combined with theoretical calculations and electron paramagnetic resonance measurements, UV-Vis-NIR spectroelectrochemistry documents dioxolene-based redox activity and variable intra- and intermolecular spin-spin interactions. As addressed in the following Figure, the predominant Ru(II) oxidation results in diminished intensity and a hypsochromic shift of the NIR band, suggesting largely metal-based spin and mixed MLCT/LMCT charge transfer transitions. (Recent papers: *Inorg. Chem.*, **2011**, *50*, 7090; *Inorg. Chem.*, **2011**, *50*, 4753; *Eur. J. Inorg. Chem.*, **2011**, *33*, 1436; *Dalton Trans.*, **2011**, *40*, 2757; *Organometallics*, **2010**, *29*, 5511; *Inorg. Chem.*, **2010**, *49*, 6565; *Inorg. Chim. Acta*, **2010**, *363*, 3070; *Inorg. Chim. Acta*, **2010**, *363*, 163; *Inorg. Chem. Commun.*, **2010**, *13*, 1160; *J. Organomet. Chem.*, **2010**, *695*, 1052.)



A dinuclear complex $[Cp^*Mo(NO)(S_2C_2Z_2)]_2$ (Z = COOMe) was prepared and characterized by **Masatsugu Kajitani** (Sophia University, Japan). The electrochemical reduction of the dimer indices a shift of the N-O stretching frequency from 1653 to 1506 cm^{-1} and the ester C=O stretching absorptions at 1701 and 1732 cm^{-1} are replaced by a single band at 1711 cm^{-1}. The first observation reflects the higher electron density at the NO group of the reduced form and the latter one indicates the formation of a monomeric dithiolene complex, $[Cp^*Mo(NO)(S_2C_2Z_2)]^-$. Interestingly, this complex exhibits significant reversibility of structural interchange between the monomer and dimer upon redox cycling (*J. Organomet.*

Chem., **2006**, *691*, 3274). In this study, the RT OTTLE cell was kindly lend by our customer, **Masa-aki Haga** (Chuo University, Tokyo, Japan).



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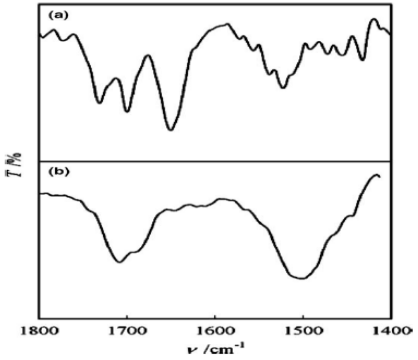
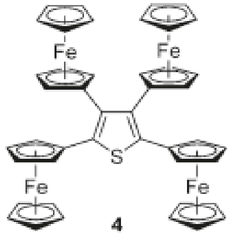


(e) *Electronic Properties of Mixed-Valence Complexes*

Heinrich Lang and co-workers (Technische Universität Chemnitz, Germany) utilize UV-Vis-NIR spectroelectrochemistry within the RT OTTLE cells to analyze the electron-transfer properties of redox-active thiophene- and fulvalenediyl-bridged homo- and heterodi- and multi-metallic complexes. In particular, the selected Figures show the structure of supercrowded *2,3,4,5*-tetraferrocenylthiophene and several UV-Vis-NIR absorption bands appearing between 280 and 3000 nm when the ferrocenyl terminals in the complex are oxidized in a slow and stepwise fashion. This observation reveals that the positive charges are localized on the Fc^+ terminals in the mixed-valent partially oxidized intermediates. No intervalence charge transfer bands of significant intensity could be detected. *(Organometallics*, ***2010***, *29*, 4900; *J. Organomet. Chem*., ***2009***, *694*, 655; *J. Organomet. Chem*., ***2009***, *694*, 3542*)*.



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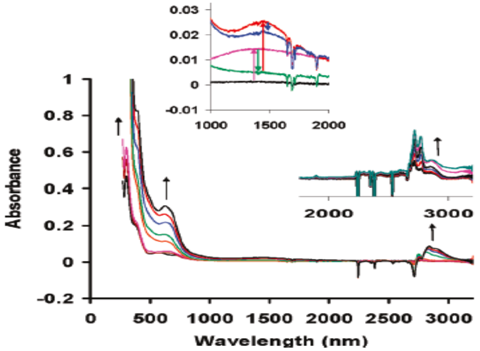
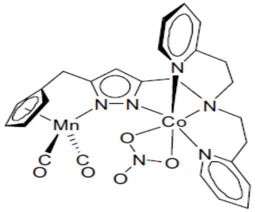


Franc Meyer's group (Georg-August-Universität, Göttingen, Germany) has reported a series of bimetallic complexes featuring organometallic and Werner-type coordination sites. IR and UV-Vis spectro-electrochemistry was employed to identify the redox-active sites and characterise the electronic coupling. For example, ν(CO) IR spectral changes during the oxidation of a heterodinuclear Mn-Co complex (see Figures below) reveal that the oxidation is largely localized at the manganese dicarbonyl site (*Eur. J. Inorg. Chem*., **2007**, *29*, 4679; *J. Organomet. Chem*., **2007**, *692*, 2956; *Inorg. Chem*., **2005**, *44*, 3863; *Chem. Eur. J*., **2003**, *9*, 2636; *J. Organomet. Chem*., **2002**, *641*, 113).



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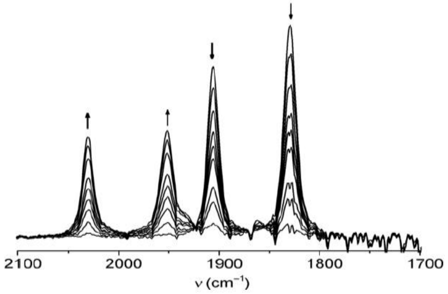
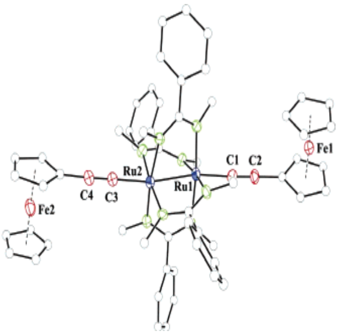
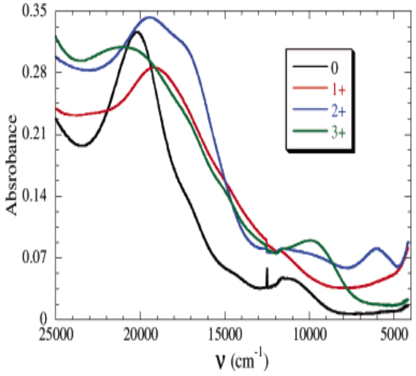
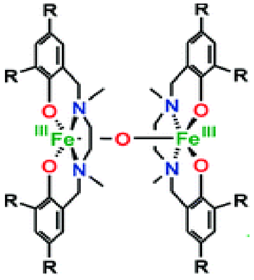


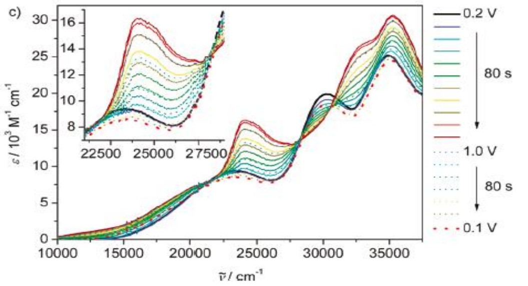
As reported by **Robert J. Crutchley** (University of Ottawa, Ontario, Canada), a wide range of Ru based mononuclear mixed-ligand complexes bearing the azoimine ligand and multinuclear mixed-valence metal-alkynyl complexes were prepared and their electronic structures and absorption properties studied using the OTTLE cell. UV-Vis-NIR spectroelectrochemistry of the complex shown below indicates that broad low-energy band extending from the NIR into IR region and the band centred at 6040 cm^{-1}, emerging upon 1e^{-} and 2e^{-} oxidation, respectively, are associated with the intervalence charge-transfer (IVCT) transitions (*Inorg. Chem*., **2009**, *48*, 5187; *Polyhedron*, **2008**, *27*, 2698; *Polyhedron*, **2007**, *26*, 3675; *Inorg. Chim. Acta*, **2006**, *359*, 1458; *J. Am. Chem. Soc*.,**2005**, *127*, 13354; *Inorg. Chem*., **2004**, *43*, 1770; *J. Am. Chem. Soc*.,**2004**, *126*, 3728; *J. Am. Chem. Soc*.,**2003**, *125*, 10057).





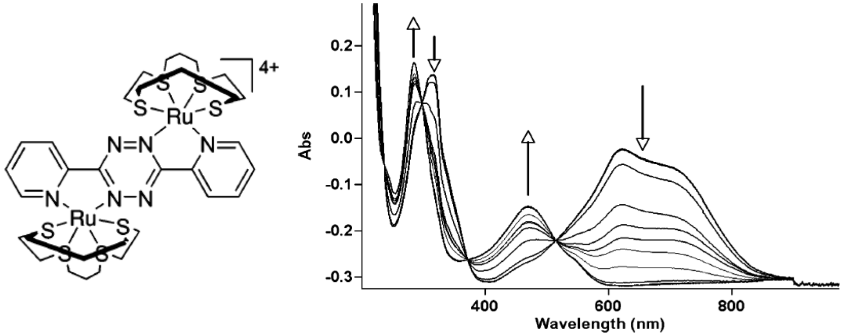
UV-Vis spectroelectrochemistry conducted with our OTTLE cells has been also employed by **Thomas Glaser** and co-workers, (Universität Bielefeld, Germany) to describe molecular and electronic structures of oxidized forms of dinuclear iron complexes incorporating strongly electron-donating ligands. For the complex of [L$^{t\text{-}Bu2}$Fe(μ-O)FeL$^{t\text{-}Bu2}$] (see the structure below), UV-Vis spectra recorded during a chronoamperometric measurement exhibit a strong absorbance intensity increase at 24100 cm^{-1}. Further, the absorbance decreases at 30100 cm^{-1} and increases at 35200 cm^{-1}. These features are consistent with the stepwise generation of the monocation and dication of the parent complex (*Inorg. Chem*., **2011**, *50*, 155).



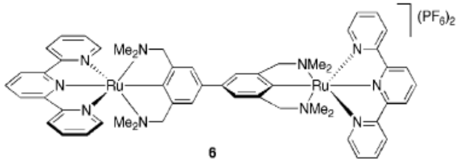


The Creutz-Taube mixed-valence complexes containing the dppz and dioxolene/dithiolate ligands have been prepared and characterized by the research group of **Michael Ward** (University of Sheffield, UK). Using UV-Vis and IR spectroelectrochemistry, electronic structures of these complexes have also been resolved, suggesting that the electronic delocalization in these complexes is modulated by the coordinated thiacrown, dithiolate, and dioxolene ligands. One-electron reduction of the dinuclear complex [{Ru^{II}([n]aneS$_4$)}(bpta)]] (see below) results in a collapse of low-energy MLCT bands and growth of a higher-energy band centred at

472 nm, indicating this anodic process is based on the bpta/bpta$^{\bullet -}$ couple. (*Inorg. Chem.*, **2010**, *49*, 10041; *Dalton Trans.*, **2010**, *39*, 200; *Inorg. Chem.*, **2008**, *47*, 11633; *Inorg. Chem.*, **2006**, *45*, 821; *Inorg. Chem.*, **2006**, *45*, 7877; *Dalton Trans.*, **2006**, 2900).



In collaboration with **Frantisek Hartl** (University of Reading, UK), **Gerard van Koten** (Utrecht University, The Netherlands) has also investigated electronic communication in diverse mixed-valence oligonuclear metal complexes through diverse bridging cyclometalated, pincer and photochromic ligands. For example, UV-Vis-NIR spectroelectrochemical measurements were employed to characterize the different redox states of the dinuclear Ru complex featuring the bridging bis(NCN) pincer ligand (see Figure above). The one-electron oxidized mixed-valence complex (class II-III) exhibits a very intense band centred at 747 nm. (*Chem. Eur. J.*, **2010**, *16*, 14322; *Inorg. Chem.*, **2009**, *48*, 1711; *Inorg. Chem.*, **2009**, *48*, 5685; *Inorg. Chem.*, **2007**, *46*, 11133; *Eur. J. Inorg. Chem.*, **2007**, *29*, 2111)



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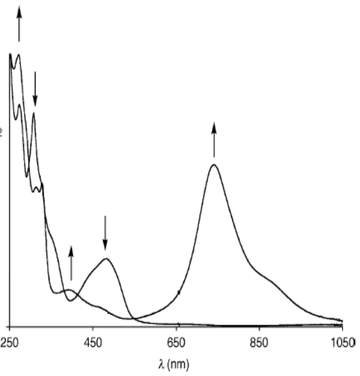
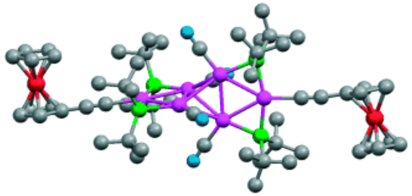
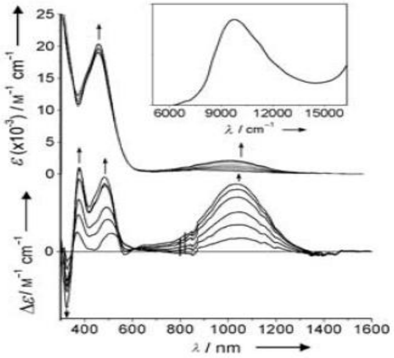


(f) Electron Transfer in Transition Metal Clusters

Recently, **Piero Leoni** (Università di Pisa, Italy) has demonstrated light-induced platinum-cluster-to-iron charge transfer in ferrocenylethynyl substituted multinuclear platinum derivatives by using IR and UV-Vis-NIR spectroelectrochemistry.

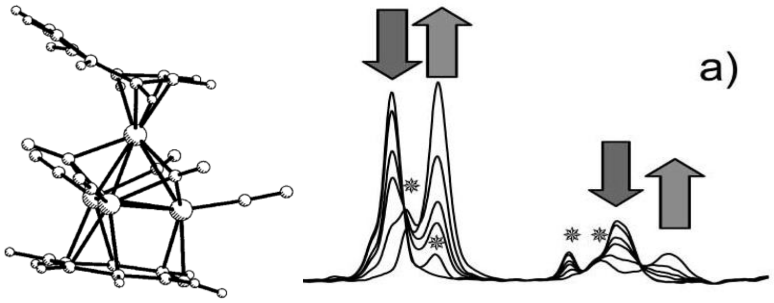


$[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(C{\equiv}C\text{-}Fc)_2]$ (**1**)

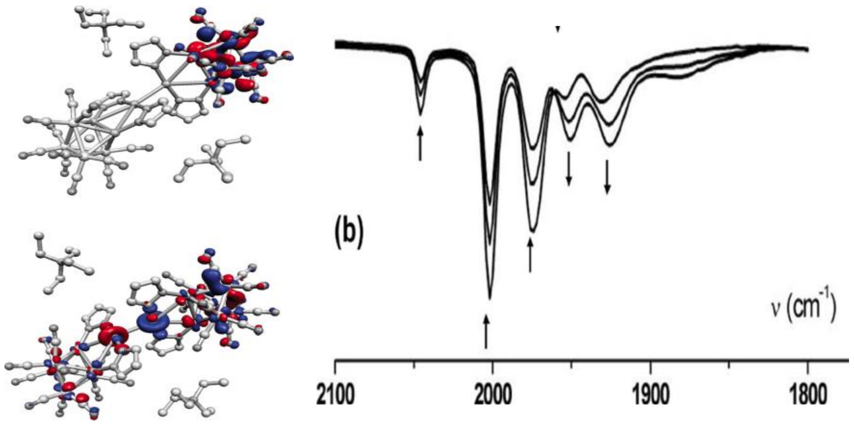


As shown in the Figures above, the absorption in the UV-Vis region does change upon stepwise two-electron oxidation of the cluster; however, a broad band in the NIR region appears progressively, suggesting consecutive metal-to-metal charge transfers (MMCT) from the Pt_6 cluster to the peripheral ferrocenium subunits. (*Inorg. Chem.*, **2010**, *49*, 3714; *Inorg. Chem.*, **2009**, *48*, 10126).

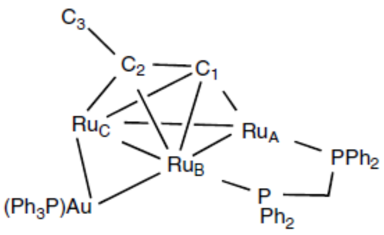
Carlo Nervi (Dipartimento di Chimica IFM, Università di Torino, Italy) reports the use of IR spectroelectrochemistry in combination with theoretical calculations in a study of the electronic structures and redox properties of dodecahedral transition metal clusters featuring the cyclooctatetraene ligand. Selected Figures show the spectral changes of $[Co_4(CO)_6(C_8H_8)_2]$ in the region of carbonyl stretching during the one-electron reduction, which leads partial decomposition of the bis(cyclooctatetraene) system, as marked with stars. (*Chem. Eur. J.*, **2009**, *15*, 3130; *Organometallics*, **2005**, *24*, 1284; *Dalton Trans.*, **2002**, 3705).

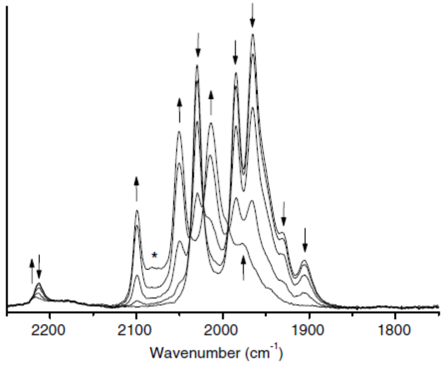


Piero Zanello (Università di Siena, Italy) and co-workers have studied electron transfer and bonding properties in mixed-valence transition metal clusters. Concerning the IR spectroelectrochemical investigation of $[\{Fe_4Cu_3C(CO)_{12}(\mu\text{-pz})_2\}_2]^{2-}$ displayed in Figure below, the one-electron cathodic process causes the original bands in the terminal ν_{CO} region at 2002 cm^{-1} and 1975 cm^{-1} to halve in magnitude in favour of the new bands rising at 1952 and 1926 cm^{-1}. This observation is in agreement with the theoretical calculations, confirming that the two electrons simultaneously enter a single Fe_4C unit and these two units are not electronically communicating. (*Dalton Trans.*, **2011**, *40*, 5464; *Dalton Trans.*, **2010**, *39*, 5286; *Eur. J. Inorg. Chem.*, **2010**, *30*, 4831; *Organometallics*, **2009**, *28*, 2707; *Inorg. Chem.*, **2007**, *46*, 10659).



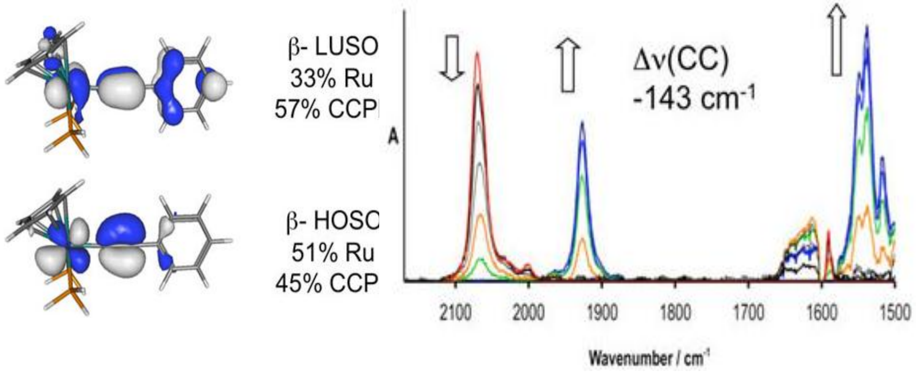
Paul Low (Durham University, UK) and **František Hartl** (University of Reading) investigated the electronic interaction between a remote substituent and the organometallic end-caps in mixed metal clusters. IR spectral changes in the C≡C and C≡O stretching region observed during the oxidation of the cluster shown below indicate clearly a cluster core based oxidation. The oxidation does not induce any CO dissociation reaction and the geometry of the triruthenium-carbonyl moiety remains largely preserved after the oxidation process. (*Dalton Trans*., **2010**, *39*, 1222; *Inorg. Chim. Acta*., **2008**, *361*, 1646; *Phys. Chem. Chem. Phys*., **2006**, *8*, 151; *Dalton Trans*., **2003**, 4084; *Chem. Eur. J*., **2002**, *8*, 1741; *J. Organomet. Chem*., **1999**, *573*, 121).



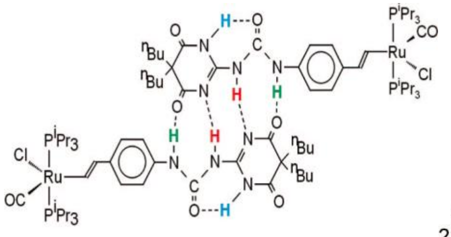


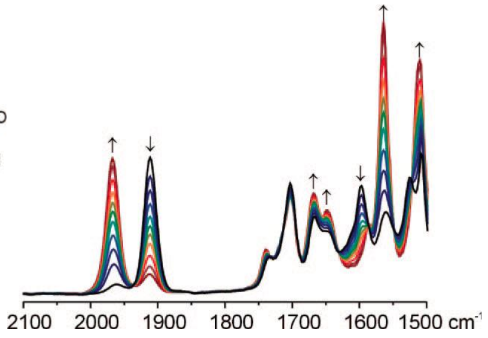
(g) Organometallic Compounds with Carbon-Rich Chains

Paul Low (Durham University, UK), partly in collaboration with our laboratory, has also wide interests in the systems of organometallic mixed-valence complexes featuring unsaturated carbon-rich bridges, such as butatrienylidene, diynyl, diyndiyl, cyanoacetylide and cyanovinylidene. A combination of UV-Vis-NIR and IR spectroelectrochemistry and theoretical calculations serve conveniently to localize the redox steps on the metal centres and the non-innocent ligand bridge. The sample Figures depicted below characterize the one-electron oxcidation of the mononuclear acetylide complex [RuCp(dppe)(C≡CPh)]. (*Dalton Trans*., **2011**, *40*, 1267; *Organometallics*, **2011**, *30*, 3763; *Organometallics*, **2011**, *30*, 1852; *Organometallics*, **2011**, *30*, 884; *Inorg. Chim. Acta*, **2011**, *374*, 461; *Dalton Trans*., **2010**, *39*, 11605; *Organometallics*., **2010**, *29*, 1261; *Inorg. Chem*., **2010**, *49*, 9101; *Organometallics*., **2009**, *28*, 5266; *J. Am. Chem. Soc*.,**2008**, *130*, 3566; *Chem. Commun*., **2008**, 5845; *Dalton Trans*., **2008**, *37*, 6763; *J. Organomet. Chem*., **2007**, *692*, 3277; *Inorg. Chim. Acta*, **2006**, *359*, 946).



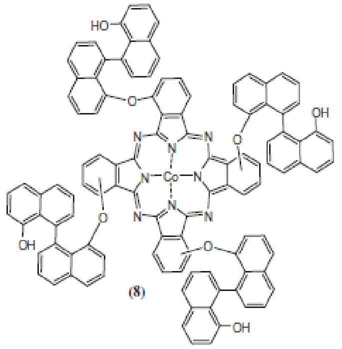
Rainer Winter (Universität Konstanz, Germany) also investigates in details intervalence charge transfer and electron delocalization in mixed-valence oligonuclear complexes through the vinybenzoate, vinylpyridine, vinyl, styryl, (ethynyl)(vinyl)phenylene, vinylpyrenyl, heteroaryl bridges and ligands linked by multiple hydrogen bonds. As shown below, oxidation of the dinuclear Ru complex induced numerous IR spectral changes, in particular the shift of the carbonyl stretching frequency from 1912 to 1967 cm^{-1}; in addition to slight red-shifts and intensity changes of the multiple NH bands due to the hydrogen-bonded imine groups. Importantly, significant changes in the region below 1600 cm^{-1} provide clear evidence for the close proximity of the CNH stretching and bending modes with the C=C stretch of the ruthenium styryl moiety. Moreover, IR spectroelectrochemistry aided by quantum chemical calculations suggests that the urea-pyrimidinedione hydrogen-bonding motif does not support electron transfer. (*Organometallics*, **2010**, *29*, 5912; *Dalton Trans*., **2010**, *39*, 8000; *J. Am. Chem. Soc*., **2009**, *131*, 4892; *Dalton Trans*., **2009**, *38*, 2940; *Organometallics*, **2009**, *28*, 4196; *J. Organomet. Chem*., ***2009***, *694*, 1041; *Eur. J. Inorg. Chem*., **2009**, *31*, 4069; *J. Am. Chem. Soc*.,**2008**, *130*, 259; *Chem. Eur. J*., **2007**, *13*, 10257)



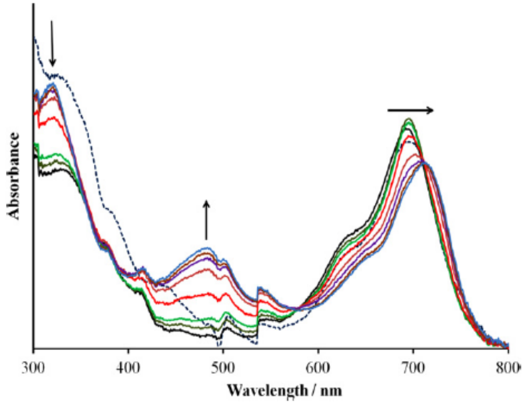


(h) Transition Metal Complexes with Macrocyclic Ligands

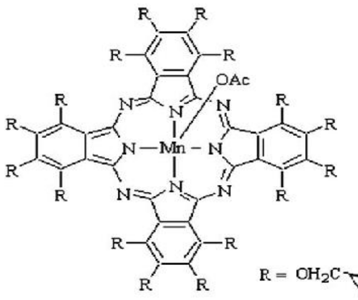
Aimed at diverse applications in molecular electronics, non-linear optics, gas sensors and in electrocatalysis, a wide range of metallophthalocyanines based on Co, Mn, Ni, Fe, Ta, Ti and V have been prepared and studied by **Tebello Nyokong** (Rhodes University, South Africa). Spectroelectrochemistry offers excellent opportunities to identify and understand the redox processes in these complexes. Upon one-electron reduction at –0.5 V, the UV-Vis spectrum of a cobalt phthalocyanine (see the structure below) shows a shift of the Q-band from 693 to 708 nm and a new absorbance appears centred at 480 nm, which is associated with the reduction of the metal centre (Co^{II} to Co^{I}). Co^{I} exhibits low binding affinity to the axial ligand, and the secondary reactions may be reflected in lacking isosbestic points. (*Polyhedron*, **2011**, *30*, 2132; *Polyhedron*, **2011**, *30*, 508; *Synth. Met*., **2011**, *161*, 241; *Inorg. Chem. Commun*., **2011**, *14*, 330; *Inorg. Chim. Acta*, **2010**, *363*, 3662; *Inorg. Chim. Acta*, **2010**, *363*, 3229; *Polyhedron*, **2010**, *29*, 2352; *Polyhedron*, **2010**, *29*, 1257; *Polyhedron*, **2009**, *28*, 2831)

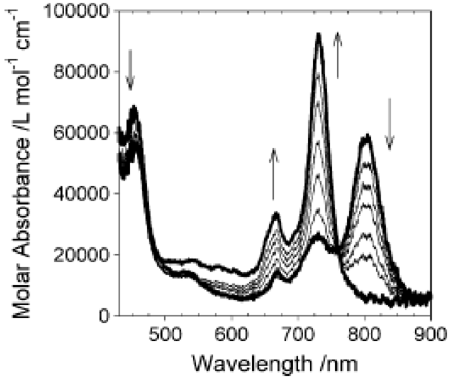


(8)

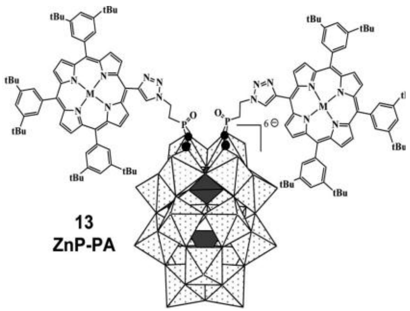


Barry Lever (York University, Ontario, Canada) presented a hexadecaalkoxyphthalocyanine ligand in transition metal complexes of Mg, Mn and Ru). In these studies, spectroelectro-chemistry was used to characterize the products of the metallophthalocyanine oxidation or reduction. The first reduction process of the sample complex below results in a shift of the Q-band around 810 nm to a higher energy region, revealing a metal centre based redox process (Mn^{III} to Mn^{II}) (*Inorg. Chim. Acta*, **2006**, *359*, 2690; *J. Porphyr. Phthalocyanines*, **2005**, *9*, 626).

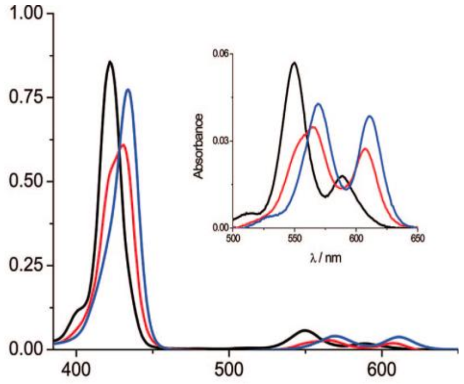




Anthony Harriman (Molecular Photonics Laboratory, Newcastle University, UK) studied charge delocalization in metalloporphyrins and clarified the intermolecular electron transfer in Dawson-type polyoxometalates (POM) covalently linked to porphyrin residues by UV-Vis and IR spectroelectrochemistry. Two-electron reduction of the POM results in a pronounced effect on absorption spectrum of ZnP-PA and leads to formation of the ZnP radical anion. The red-shift of both Soret and Q bands may have its origin in replacement of the weakly coordinated DMF molecule with a stronger coordinating ligand (*J. Org. Chem*., **2010**, *75*, 2018; *J. Phys. Chem. C*, **2009**, *113*, 5834).

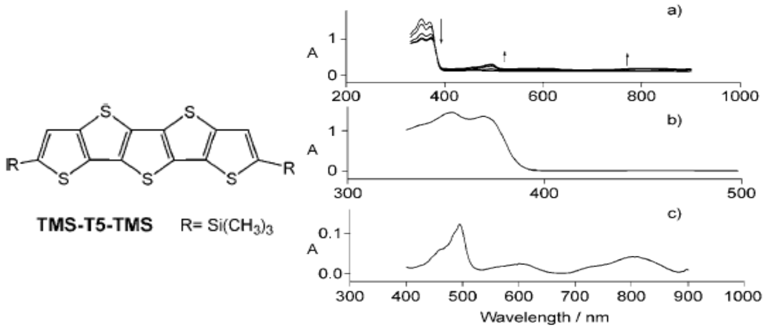


13
ZnP-PA



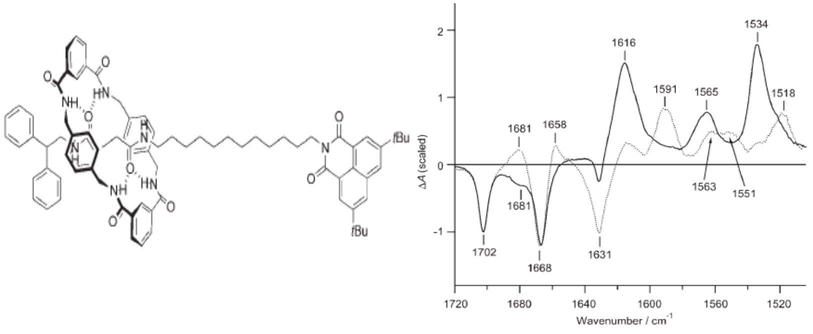
(i) Characterization of Redox-Active Chain Molecules

Victor Hernandez (Universidad de Malaga, Spain) has studied, recently also in close collaboration with our laboratory, π-dimerization of oxidized π-conjugated oligothienoacenes by in situ UV-Vis-NIR spectroelectrochemistry. As evidenced by spectro-electrochemical measurements, neutral TMS-T5-TMS (Figure b) showing the π-π* transition at 369 nm converts to oxidized species characterised by new bands at 492, 603 and 805 nm (Figure c). Specifically, the bands at about 500 and 800 nm are assigned to the corresponding radical cation and the band at about 600 nm to the corresponding dimer dication. (*Chem. Eur. J.*, **2010**, *16*, 5481; *Chem. Eur. J.*, **2009**, *15*, 12346)



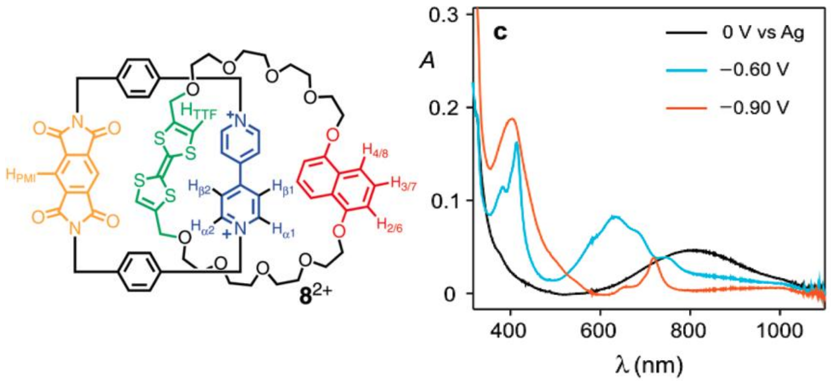
(j) Supramolecular Chemistry

Fred Brouwer (University of Amsterdam, The Netherlands) and **Frantisek Hartl** (University of Reading, UK) used IR spectroelectrochemistry to demonstrate a redox triggered molecular motion in a bistable rotaxane supramolecule, where the macrocycle is hydrogen-bonded to the neutral succinamide, but it can move toward the naphthalimide site when the former is reduced.



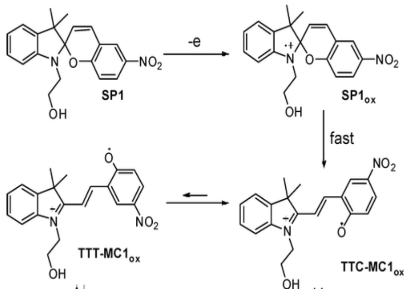
The conformational switching upon the one-electron reduction of the binding site can be monitored by the hydrogen-bond-dependent shifts of the amide *v*(CO) and *v*(NH) frequencies. These red shifts are due to the hydrogen bonding between the NH groups of the macrocycle and the carbonyls of the radical anion suggesting the translational movement of the macrocycle for the succinamide to the naphthalimide radical anion (*Chem. Eur. J.*, **2008**, *14*, 1935).

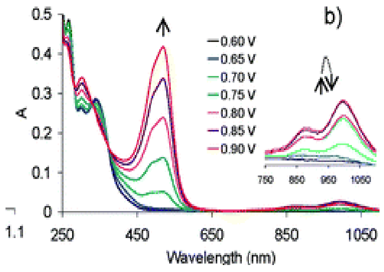
Margarita Venturi (Universita di Bologna, Italy) investigated a series of redox-active rotaxanes and catenanes. UV-Vis-NIR OTTLE measurements show that the ring components of these supramolecules undergo reversible shuttling driven by the electrochemical reaction of the thread molecules. The first one-electron reduction of the catenane below is assigned to the 4,4′-bipyridinium dication (MV)-localized process and the second one is bielectronic and ascribed to the simultaneous reduction of the MV and PMI (pyromellitic diimide) linkers. (*J. Am. Chem. Soc.*, **2010**, *132*, 1110; *J. Am. Chem. Soc.*,**2007**, *129*, 12159; *PNAS*, **2006**, *103*, 1178).



(k) *Electrochromism*

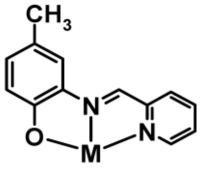
Klaudia Wagner (University of Wollongong, Australia) has reported colour changes accompanying oxidative transformation of electroactive nitrospiropyran incorporated into a polymer backbone, polyterthiophene, into strongly coloured isomeric merocyanine forms. Parent spiropyran can be regenerated photochemically. The irreversible oxidative opening of the spiropyran ring (not bound to the polymer chain) within the OTTLE cell was monitored by UV-Vis-NIR spectroscopy (see below). In this unique multichromophoric and multiswitchable system the planar merocyanine form causes a smoother polymer film. (*J. Am. Chem. Soc.* **2011**, *133*, 5453).



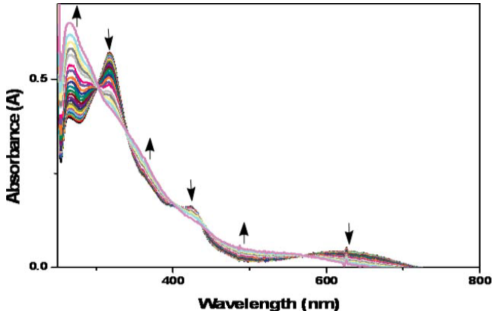


(l) *Biochemistry and Biocatalysis*

A square planar complex [Pt(pyrimol)Cl] with the tridentate ligand 4-methyl-2-*N*-(2-pyridylmethylene)aminophenolate (pyrimol, see below) cleaves oxidatively supercoiled double-stranded DNA in a non-specific manner without any external oxidant added. UV-Vis spectroelectrochemistry is particularly useful in this case to monitor the 1e$^-$ oxidation of the neutral complex, revealing formation of the phenoxyl radical derived from pyrimol, which absorbs between 400 and 600 nm. Based on this assignment **Jan Reedijk** (Leiden University, The Netherlands) and **Frantisek Hartl** (University of Reading, UK) have argued that the formation of the phenoxyl radical is responsible for the DNA cleavage. This observation may be useful for the development of novel antitumor drugs (*Dalton Trans*., **2009**, *38*, 10846).



M-pyrimol

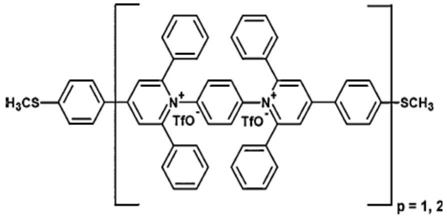


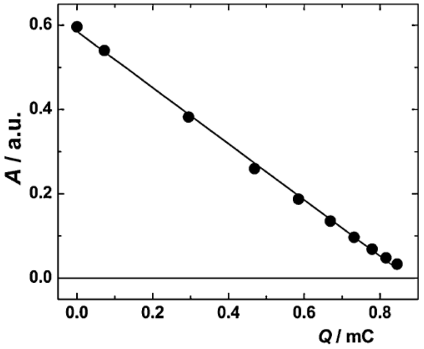
A related square-planar compound [Cu(pyrimol)Cl] was described by the same authors as a biomimetic model of the enzyme galactose oxidase (GOase). This copper(II) compound is capable of stoichiometric aerobic oxidation of activated primary alcohols in acetonitrile/water to the corresponding aldehydes. Evidence for the dominant Cu^{II}–$L^{\bullet}$ chromophore ($L^{\bullet}$ = phenoxyl radical) in the oxidized catalyst was obtained from spectroelectrochemistry in the visible spectral region that revealed electronic absorption having a mixed $\pi\rightarrow\pi^*(L^{\bullet})$ intraligand and $Cu–Cl\rightarrow L^{\bullet}$ charge transfer character. (*Inorg. Chim. Acta*, **2011**, *374*, 406.)

Special Applications

(m) Thin-Layer Coulometry

Lubomír Pospíšil (UOCHB, Prague) and **Magdalena Hromadová** (J. Heyrovsky Institute of Physical Chemistry, Czech Republic) have reported electron transfer in extended viologen-type wires and further investigated their chemical stability after multiple one-electron reduction by UV-Vis spectroelectrochemical monitoring (*Phys. Chem. Chem. Phys.*, **2011**, *13*, 11422). ***Importantly,*** the apparent number of consumed electrons was determined first time by combining thin-layer coulometry with UV-Vis spectroelectrochemistry. The rapid coulometry in a small volume is a reliable and highly convenient method with many envisaged future applications. In the Figure below, the reduction of methyl viologen in the OTTLE cell results in a linear decay of the absorbance at 265 nm with increasing consumed charge Q. In particular, the intercept value of 0.88 mC corresponds to the exhaustion of the reduced viologen in the optical path. Further, this value can be assigned to the concentration of methyl viologen in the thin solution layer, giving the charge consumption of 0.484 $Cmol^{-1}L^{-1}$ that can be used as a standard value to determine the number of electrons consumed by the new compound (see below). (*Anal. Chim. Acta*, **2011**, *697*, 23)



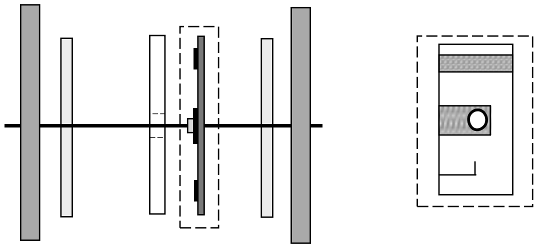


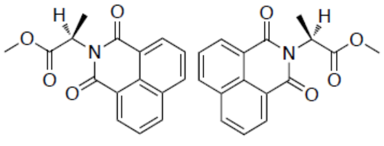
(n) Vibrational Circular Dichroism

Vibrational Circular Dichroism (VCD), the infrared circular dichroism associated with vibrational transitions of chiral molecules, is a relatively new and potentially very useful technique for investigating molecular configuration and conformation in solution, in particular, for the molecules ranging from helical chiral polymers, helical peptides to transition metal complexes and metalloproteins.

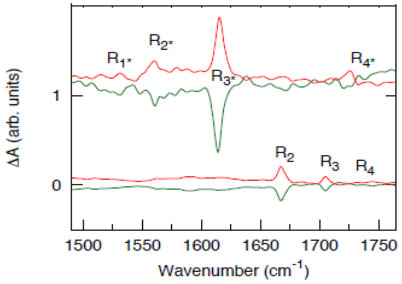
Herein, **Sérgio Domingos**, **Sander Woutersen** and **Wybren Jan. Buma** (University of Amsterdam, The Netherlands) and **Frantisek Hartl** (University of Reading, UK) reported the first VCD measurements on an electrochemically generated radical anion species (*Chem. Commun*., **2012**. *48*, 353).

Customized OTTLE cell for VCD measurements





(R)-**1** (S)-**1**

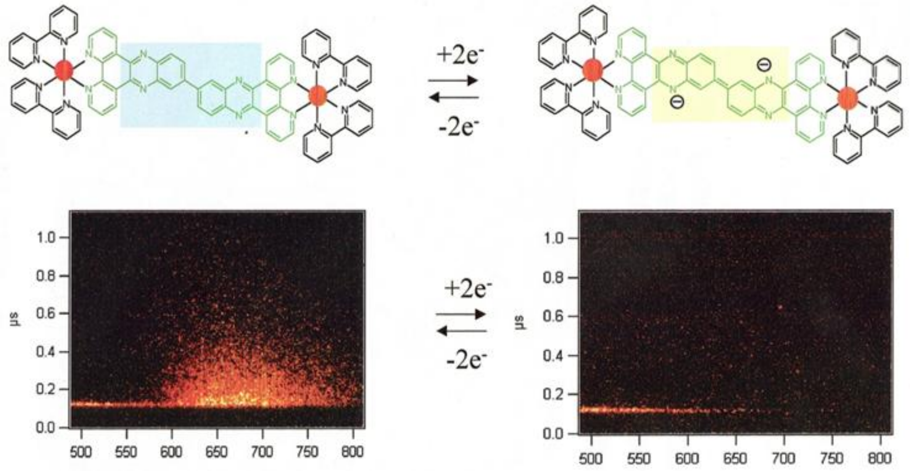


The schematic drawing of the VCD OTTLE cell (© Sérgio R. Domingos)

Spectroelectrochemistry of the chiral molecules (R)-**1** and (S)-**1** was carried out within a customized infrared optically transparent thin-layer electrochemical (IR OTTLE) cell. The primary modification of the cell involved the polyethylene electrode spacer, into which the three electrodes are melt-sealed. A small cut was made in the centre of the Pt mini-grid, resulting in a cylindrical protrusion in the centre of the working electrode. Further, a 1 mm thick PTFE spacer with a circular aperture of 4 mm sits on top of this construction, giving an increased optical path length. Compared to the neutral forms of (R)-**1** and (S)-**1**, the radical anions show a red shift of the mirror image features R_2, R_3 and R_4 and a strong increase in the signal intensities of the VCD spectra. The latter observation is attributed to a strong vibronically induced mixing of low-lying electronic excited states with the ground state in the electrochemically generated radical anion species.

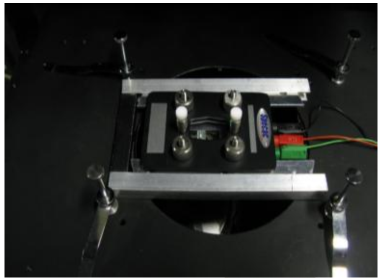
(o) Redox Controlled Time-Resolved Luminescence

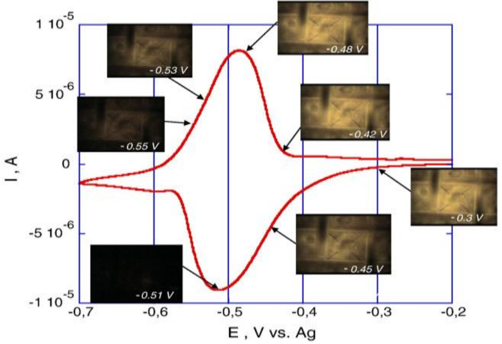
Luisa De Cola (Universität Münster, Germany) and **Frantisek Hartl** (University of Reading) employed the RT OTTLE cell for measurements of emission spectra and emission lifetimes during electrochemical quenching experiments with a diruthenium complex featuring a bridging bis(dipyridylphenazine) ligand.



In these experiments, the emission spectra were recorded using optical fibres connected to an Nd-YAG laser and a *streak camera*. As shown below, the parent complex (in acetonitrile) exhibits an intense luminescence at 650 nm with a lifetime of 130 ns. This phosphorescence becomes completely quenched upon the two-electron reduction. This observation is due to efficient electron transfer from the electrochemically reduced bridging ligand to the excited metal centre. Protonation of the reduced ligand may recover and modify the emission. (*Eur. J. Inorg. Chem*., **2002**, *24*, 335).

(p) Coupling OTTLE with Epifluorescence Microscopy

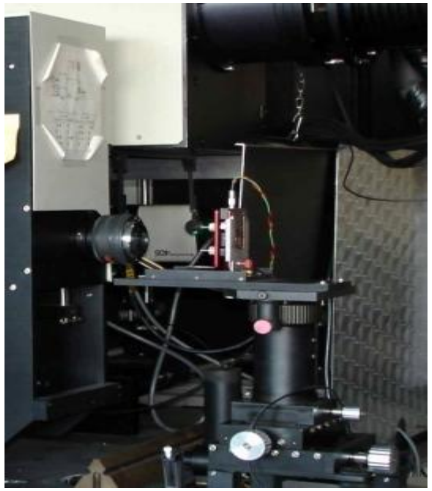


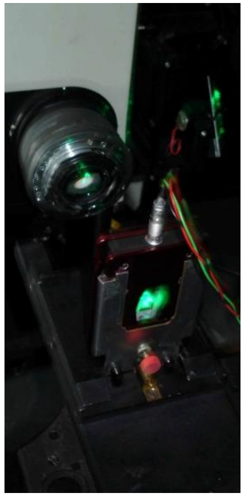


Fabien Miomandre and **Pierre Audebert** (Ecole Normale Supérieure de Cachan, France) and **František Hartl** (University of Reading) reported the first example of RT OTTLE spectroelectrochemical cell coupled to epifluorescence microscopy in the total internal reflectance mode and the application in the study of electrochemically modulated fluorescence of an organic dye (*p*-chloromethoxytetrazine) in solution. In this approach, the OTTLE cell was placed on the microscope stage and connected to a potentiostat. The laser beam was focused on a thin solution layer above the Pt mini grid working electrode. The thin-layer cell allows generating fully reversible fluorescence based on the reversible redox switch of the dye and offers the advantage of an exhaustive redox conversion that avoids any residual fluorescence in the dark state. The lifetime of the fluorescence was shown to decrease progressively with the conversion of the neutral dye to the corresponding radical anion due to the electron transfer quenching of the emissive exctited state. (*Electrochem. Commun*., **2011**, *13*, 574)

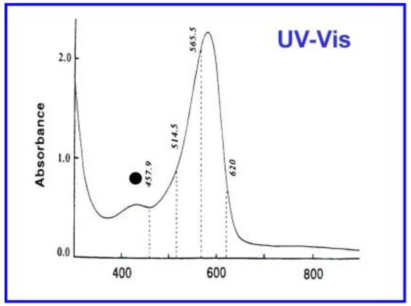
(q) Resonance Raman Spectroelectrochemistry

Barry Lever (York University, Ontario, Canada) and **Frantisek Hartl** (University of Reading, UK) published a resonance Raman spectroelectrochemical study of the $[(bpy)_2Ru(\mu\text{-}Q\text{-}Q)Ru(bpy)_2]^{4+}$ (Q = quinonediimine, bpy = 2,2'-bipyridine) complex and its one-, two- and four-electron reduced products. The spectroelectrochemical investigation of the redox series was carried out by using a Raman spectrometer in a ***back-scattering mode***. The OTTLE cell was placed in the beam path and the laser beam was carefully focused in the thin solution layer at the surface of the minigrid working electrode. The set up is shown in the following Figure.



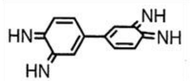


Careful analysis of the Raman spectra recorded at different excitation wavelengths allowed to attribute the visible absorption bands to particular electronic transition (see below). The presence of separate RuQ and RuSQ (SQ = semiquinone diimine) chromophores in the 1e reduced product revealed a persistent twist angle between the bridging ligand halves. In contrast, the SQ-SQ ligand is planar, thereby promoting electronic communication between the Ru(II) centres. The ultimate 4e reduced product could only be studied within the superior OTTLE cell. Slow decomposition prevents its isolation. (*Inorg. Chem*., **1995**, *34*, 3887).

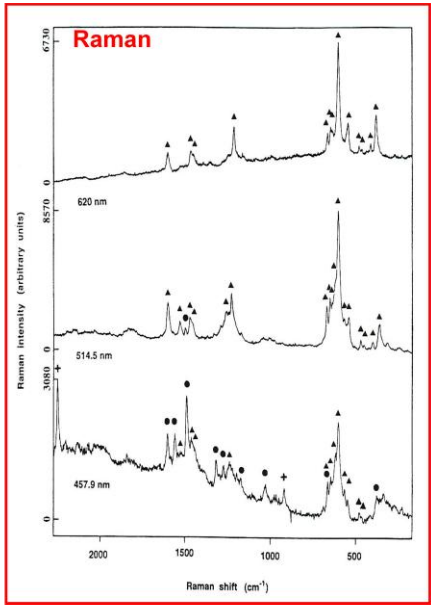


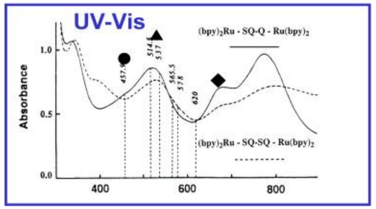
Electronic transitions

- ● d(Ru) → π*(bpy) MLCT
- ▲ π(Ru-Q) → π*(Ru-Q)



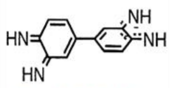
Ru-Q-Q-Ru



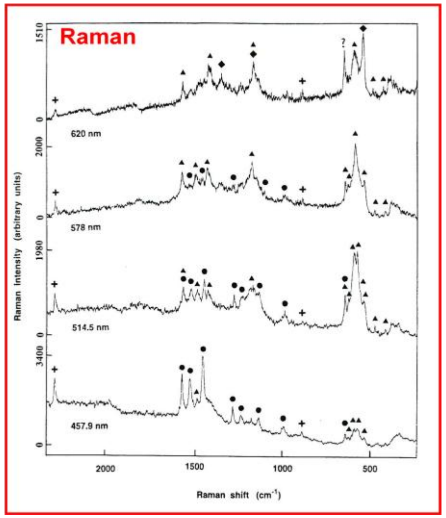


Electronic transitions

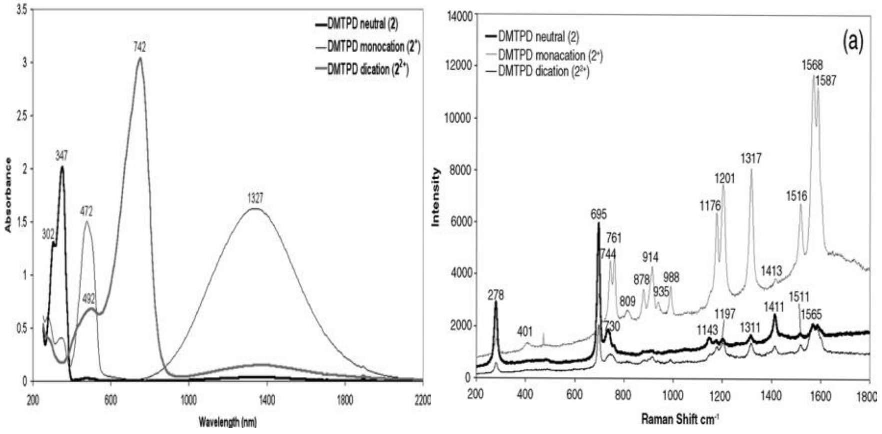
- ● d(Ru) → π*(bpy) MLCT
- ▲ π(Ru-Q) → π*(Ru-Q)
- ◆ π(Ru-SQ) → π*(Ru-SQ)

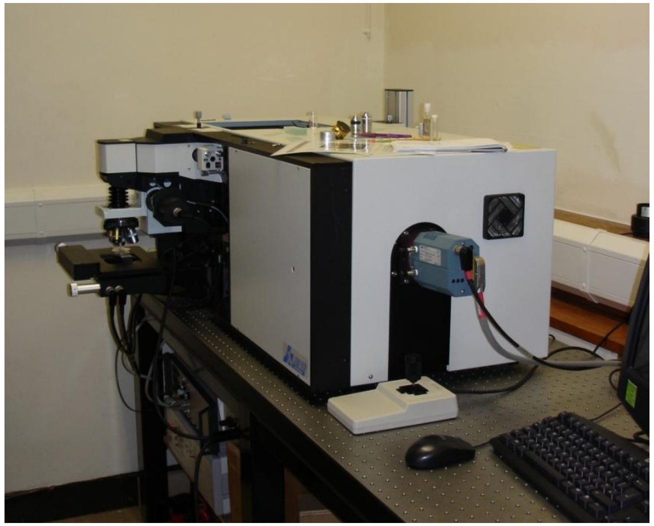


Ru-Q-SQ-Ru



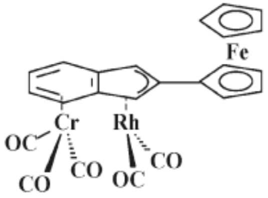
The OTTLE cell combined with a ***Raman microscope*** system also provides an effective way to study the electronic properties of redox active compounds, for example poly(aryl)amine based charge transfer materials such as DMTPD (*N,N'*-diphenyl-*N,N'*-bis(2,4-dimethylphenyl)(1,1'-biphenyl)-4,4'-diamine). In this case, the laser beam was focused with precision onto a pore within the Pt minigrid working electrode. Using this setup, **Paul Low** (Durham University, UK) and **Ewen Smith** (University of Strathclyde, UK) presented significant discrimination of Raman scattering from the mono- and dications due to resonance enhancement associating with the dominant absorptions at 472 nm (monocation, excited at 514.5 nm) and 742 nm (dication, excited at 632.7 nm), see below, (*Phys. Chem. Chem. Phys.*, **2004**, *6*, 3257).



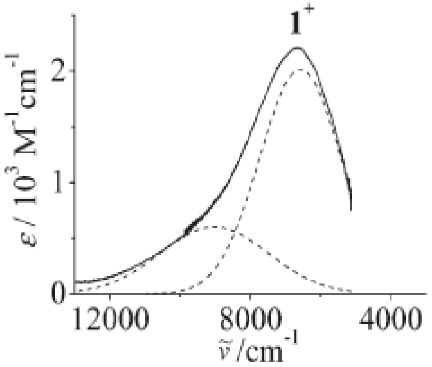


Keeping advantages of RT OTTLE cell, our *Low-Temperature OTTLE cell* is designed to be user-friendly and to facilitate operation from 298-175 K for temperature dependent mechanistic redox studies and for characterisation of thermally unstable transient redox products in the UV-Vis-NIR-IR region.

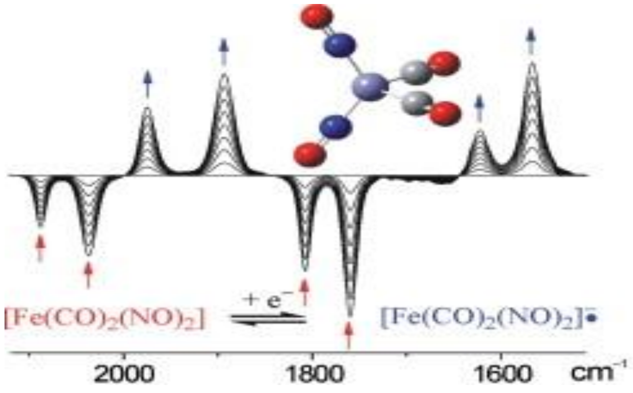
Low-temperature spectroelectrochemistry in the UV-Vis-NIR region was employed by **Saverio Santi** (Universita degli Studi di Padova, Italy) to study the electronic features and coupling of a series of mixed-valence complexes. In particular, for the complex below, the stable mixed-valence cation is obtained at -45 ˚C and shows a strong absorption band centred at 6650 cm^{-1} and a weak should around 9450 cm^{-1}. By Gaussian deconvolution, these bands are associated with multiple through-bridge interactions of mixed-valence Fe-Cr transition and Rh-Fe transition, respectively. (*Organometallics*, **2010**, *29*, 2046; *Organometallics*, **2009**, *28*, 3319; *Organometallics*, **2007**, *26*, 5867; *Chem. Eur. J.*, **2007**, *13*, 7933; *Chem. Eur. J.*, **2007**, *13*, 1955)



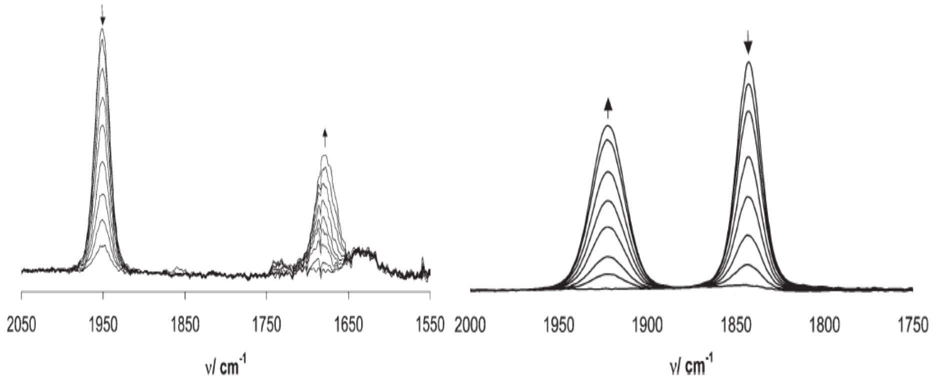
(1)



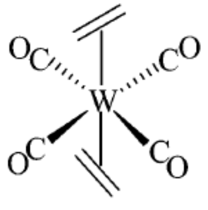
Axel Klein (Universität Köln, Germany) reported the applications of UV-Vis-NIR and IR spectroelectrochemistry in studies of electronic structures and electronic coupling reactions of transition mono/poly-metallic complexes and metalloporphyrins at both room temperature (*Chem. Eur. J.*, **2011**, *17*, 4765; *Dalton Trans.*, **2007**, *36*, 3427; *Eur. J. Inorg. Chem.*, **2007**, *29*, 965; *Organometallics*, **2006**, *25*, 635; *Inorg. Chem.*, **2003**, *42*, 7018) and low temperature (*Polyhedron*, **2010**, *29*, 2553; *Inorg. Chem.*, **2009**, *48*, 9947). For example, the first one-electron reduction of $[Fe(CO)_2(NO)_2]$ at -25 ˚C results in the formation of the radical anion, $[Fe(CO)_2(NO)_2]^{\bullet -}$. This process has been monitored by IR spectroelectrochemistry, displaying new features at 1974 and 1894 cm^{-1} (both ν_{CO}), 1622 and 1565 cm^{-1} (both ν_{NO}). Comparing to the parent complex, the decrease for the vibration energy is resulted from the reduction of the complex leading to higher back-bonding to the acceptor ligands CO and NO^+ which reduces the E≡O bond order.



Wolfgang Kaim (Universität Stuttgart, Germany) has applied the LT OTTLE cell to the studies of the electronic structures of imidazole ligand (*Inorg. Chim. Acta*, **2010**, *363*, 3070) or nitrosyl ligand (*Inorg. Chem.*, **2008**, *47*, 7106; *Inorg. Chem.*, **2006**, *45*, 4602; *Dalton Trans.*, **2008**, *37*, 868; *Dalton Trans.*, **2004**, *33*, 1797) containing transition metal complexes at both room and low temperatures in UV-Vis-NIR and IR regions. As shown below, a reversible NO-centred reduction (left Figure) and a reversible metal centre based oxidation (right Figure) were observed by IR spectroelectrochemistry at -40 ˚C in PrCN for $K[Cl_5Ir(NO)]$ and $(Bu_4N)_2[Cl_5Ru(NO)]$, respectively. In these cases, a large low-energy shift of the NO stretching arises from the formation of metal-bonded $NO^{\bullet}$ and a high-energy shift of the NO stretching is caused by weakening the π donor ability of the metal toward NO^+ and strengthening the σ donor component of NO^+ towards the metal due to the oxidation of the metal centre. Moreover, under this condition, redox reactions do not result in significant decomposition of the complexes.



Frantisek Hartl (University of Reading, UK) and co-workers reported the stable redox intermediates of some transition metal complexes monitored by LT FTIR spectroelectrochemistry (*Organometallics*, **2007**, *26*, 4066; *Chem. Eur. J.*, **2002**, *8*, 1741). For the *trans*-tetracarbonyl olefin tungsten complex below, it displays one strong ν_{CO} at 2035 cm^{-1} with a shoulder at 2055 cm^{-1} and a medium-intensity band at 2125 cm^{-1} upon one-electron oxidation at room temperature. This observation corresponds to the formation of *cis*-isomer, which is probably due to a fast *trans*-*cis* isomerisation of the radical cation following the one-electron oxidation of the *trans*-complex at room temperature. While at 243 K (the following Figure), the IR spectrum significantly differ from the band pattern obtained at room temperature indicating IR spectroscopic detection of the initially formed cation *trans*-1$^+$.



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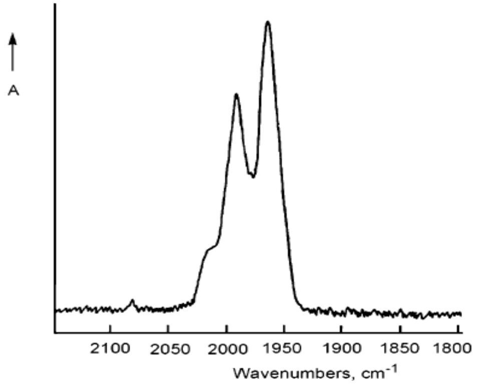

LT UV-Vis-NIR and IR spectroelectrochemistry was also employed to help characterize electronic transition and lowest-lying excited states of α-diimine metal complexes (*Inorg. Chim. Acta*, **2011**, *374*, 578; *Inorg. Chem.*, **2004**, *43*, 4523) by **Antonin Vlcek Jr.**

APPLICATIONS OF OTTLE CELLS

(Queen Mary University of London, UK) in collaboration with our laboratory. For example, at room temperature IR spectroelectrochemistry of $[Re(bopy)(CO)_3(bpy)]^+$ shows an electrode-catalyzed substitution of the bopy ligand by the solvent of PrCN. However, at low temperature of 233 K the first reduction leads that IR bands shift to 2022, 1919, 1905 and 1624 cm^{-1}. In particular, the band at 1624 cm^{-1} is resulted from the disappearance of the parent ketone *v*(C=O) stretching of the bopy ligand suggesting that the first reduction is bopy-localized.