

Rudolf Holze

## Fundamentals and applications of near infrared spectroscopy in spectroelectrochemistry

Received: 9 January 2004 / Accepted: 25 February 2004 / Published online: 11 August 2004  
© Springer-Verlag 2004

**Abstract** Near infrared spectroscopy as a tool for in situ spectroelectrochemical investigations of electrochemical systems is reviewed with particular attention to experimental approaches and typical results from all parts of chemistry and applied chemistry.

**Keywords** Spectroelectrochemistry · Near infrared spectroscopy

### Introduction

Near infrared spectroscopy (NIR-spectroscopy) deals with absorption of electromagnetic radiation by matter which occurs in the range of wavelengths extending from 700 nm to 3000 nm ( $14,300$  to  $3300\text{ cm}^{-1}$ ) [1, 2]. The limits of this range often fluctuate, and since many UV-Vis-spectrometers operate up to 1000 nm. This is thus often taken as the lower wavelength limit. Nevertheless and sometimes leading to confusion, data obtained in the range 800 to 1000 nm are also often assigned to NIR. Whereas UV-Vis-spectroscopy below 1000 nm is widely used for quantitative analysis and—to some extent—also for qualitative analysis, infrared spectrometry above 3000 nm is frequently used for qualitative analysis including molecular structure identification of a broad range of samples and systems. The NIR range occurring in between is generally less frequently investigated. Its current focus of application is on quantitative analysis of a fairly narrow selection of samples [3, 4] and on process and quality control in the chemical industry and related areas [5, 6, 7, 8, 9]. More recently this spectral range has attracted attention because of the requirements of dyes and other materials for optical data

storage operating preferably in this spectral range [10, 11].

Basically the same arguments are valid with respect to the applications of these spectroscopic tools in electrochemistry. Both UV-Vis- and infrared spectroscopy are frequently used; numerous reviews are available [12, 13, 14]. NIR-spectroscopy has been applied only infrequently, no review has been provided so far [15]. This apparent lack of interest is presumably caused by the fact, that NIR-spectra contain mainly overtone and combination bands of absorptions by infrared active modes (mainly those involving bonds between any given atom in a molecule and a hydrogen atom) already observed in most cases in the mid IR range. In addition, solvated rare earth element ions and transition metal ions and their metal complexes show NIR absorption caused by electronic transitions and charge transfer processes. These electronic transitions may involve charge transfer between the metal ion and the ligand or between two metals of different valencies in multinuclear complexes (intervalence transition). These bands show absorptivities one or two orders of magnitude smaller than the fundamental bands. Together with the inherent problems of spectroelectrochemical methods applied *in situ*, i. e. in the presence of an electrolyte solution or melt, which might be a good NIR-radiation absorber itself, this has seriously limited the interest of researchers.

More recently investigations of e.g. transition metal complexes showing a complex redox chemistry, studies of intrinsically conducting polymers with mobile charge carriers showing pronounced absorption spectra and measurements at complex organic molecules and oligomers showing electrochemical activity, have stimulated a renewed interest in spectroelectrochemical investigations in the NIR-range. As indicated, the investigated species may be present in various states and phases. In the case of metal complexes the investigated species are mostly dissolved, only infrequently are they attached to a solid phase via covalent bonds. This might exclude their discussion from the scope of this journal. The advent of

R. Holze  
AG Elektrochemie, Institut für Chemie,  
Technische Universität Chemnitz,  
09107 Chemnitz, Germany  
E-mail: rudolf.holze@chemie.tu-chemnitz.de

nanostructured surfaces (and electrodes) and the concepts of supramolecular chemistry combined with modified electrodes might cause surprising combinations of substances previously studied only in solution with solid electrodes; thus the relevant results are included here. Basically the same argument applies to organic molecules, those which are reviewed here are in most cases of still sufficient solubility. For the reasons given above they are nevertheless included. Intrinsically conducting polymers are mostly solid substances., Thus they form a special focus of interest for NIR-spectroelectrochemistry. Their precursors and reaction intermediates are nevertheless mostly soluble. Because of their obvious importance, their spectroelectrochemistry is included here. Electrochromic materials showing a constantly growing application potential beyond obvious uses in the UV-V is are obviously always solid materials; they are treated last.

The term spectroelectrochemistry has been used in a fairly general manner including all applications of spectroscopic methods coupled with electrochemical systems and processes. Although most frequently the electrochemical measurement and the spectroscopic measurement are done in the same cell, sometimes the electrochemical cell and the spectroscopic cell are coupled only somehow. Thus a product formed in the cell is subsequently transferred into the spectrometric setup. No attempt is made in the following review to distinguish between the various possibilities of establishing this connection. Thus studies with a spectroelectrochemical setup where the optically transparent electrode is situated in the light beam of the spectrometer as well as studies where electrolysis products formed *extra muros* are transferred to the cuvette of the spectrometer are collected. Strictly speaking only the former setup is correctly designated *in situ* whereas the latter is *ex situ*. In some investigations NIR spectroscopy is used as an analytical tool for the characterization of electrochemically as well as chemically formed products. These studies are not reviewed exhaustively here; they are only briefly touched upon when the results seem to bear importance for a better understanding of other (in situ) studies or of further work in progress.

### Instrumentation and experimental aspects

Various types of NIR-spectrometer are currently available [16]. Basically these can be grouped into dispersive and Fourier Transform FT systems. Because the general technical requirements for sources, monochromators and detectors used in the NIR, are rather similar to those for dispersive UV-Vis-spectrometers, NIR-spectrometers of the dispersive type are fairly similar to common UV-Vis-spectrometers. This includes the use of fiber optics and related optical devices; for further technical details see [15]. FT-spectrometers in the UV-Vis-range are not common. Consequently FT-based NIR-spectrometers are more closely related to the

already well established FTIR-instruments. Independently of the type of NIR-spectrometer used, major changes of the spectrometer are generally not required for spectroelectrochemical measurements. This is particularly true when fiber optics are used to couple the electrochemical setup with the spectrometer. In the latter case the spectroelectrochemical cell as will be described hereafter is simply inserted between the ends of the fiber cables running from the light source and to the monochromator/detector with necessary collimator lenses inserted between the fiber ends and the cell. The following considerations apply both to studies of dissolved species or species adsorbed/deposited onto the working electrode surface provided so that a change of electrode potential will affect these species. With electrolyte solvents of low optical density a standard UV-Vis-cuvette made of synthetic silica without optical absorption in the spectral region of interest (e. g. SUPRASIL 300 by Heraeus) can be employed as an electrochemical cell. Subsequently only experiments involving electrolyte solutions are discussed. Essentially the same arguments and considerations are valid for systems with molten salt electrolytes. So far NIR-spectroelectrochemistry with molten salts has not been reported. As a working electrode a glass plate preferably of a similar NIR-transparent material coated with an optically transparent but electrically conducting layer such as e. g. indium doped tin oxide (ITO) or sputtered gold or platinum can be used. A metal wire loop serves as counter electrode, the reference electrode is connected to the electrolyte solution via a solution filled plastic tube. A typical setup is shown in Fig. 1. If needed the cell can be fitted with a gas-tight lid to allow measurements under a controlled atmosphere (e. g. with exclusion of oxygen or moisture).

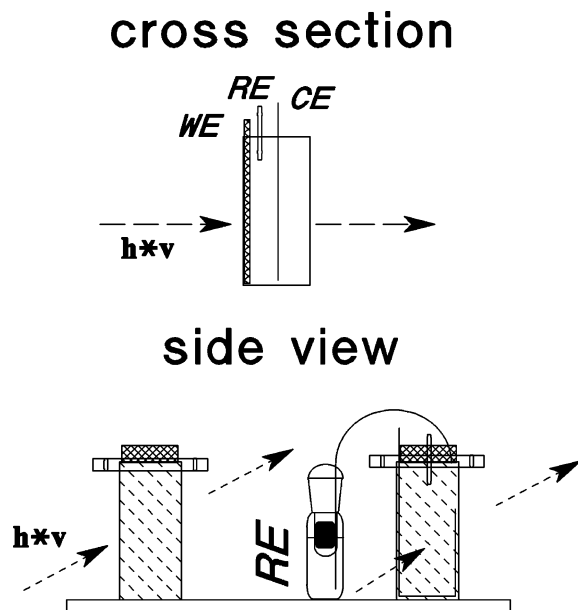
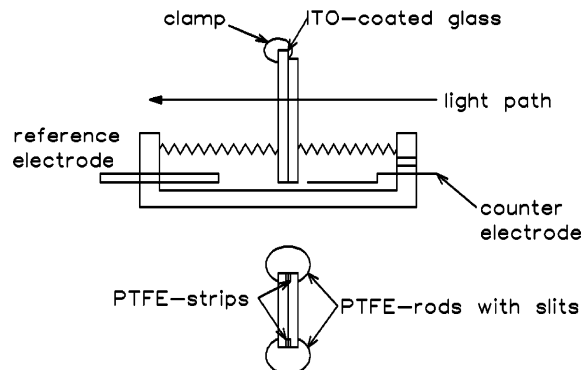


Fig. 1 Typical setup for NIR-spectroelectrochemical experiments, for details see text

Filling of this cell has to be performed in a glove box or otherwise under controlled ambient conditions. A similar setup with a metal grid working electrode mounted in the cuvette slightly above the optical beam path has also been used frequently. Optical response is somewhat slower because any reaction product has to diffuse downwards before being detected.

With strongly absorbing solvents such as e. g. water (for details see below) a thin layer setup is preferable. At first glance this might be considered unnecessary because only the relative changes of the absorbance of the medium inside the electrochemical cell are measured. Because many NIR-spectrometers are essentially single beam instruments, this means that initially a single beam spectrum of the electrochemical cell at a selected electrode potential (subsequently called  $E_r$ ), is collected. Subsequently, single beam spectra collected at different electrode potentials  $E_m$  are expressed as a ratio as compared to this initial spectrum. Thus all absorptions by the electrolyte solution etc. that are not affected by the changed electrode potential, are canceled out. Strong absorptions at any wavelength will nevertheless cause a poor signal to noise ratio in the resulting difference spectrum in this region. Thus thinner layers of electrolyte solution might be required. Thin layer cells for applications with UV-Vis-spectroscopy have frequently been described. For a review see [15]. A compromise between the simple design as depicted in Fig. 1 and the desired thin solution layer thickness can be achieved by using cuvettes of short optical path length (1 to 2 mm). Mounting the transparent working electrode and the counter electrode inside the cell tends to be a mechanically complicated process. An alternative setup successfully employed in the author's lab is depicted below. In its most basic version (not depicted here) two glass sheets sufficiently transparent in the NIR are clamped together with narrow strips of PTFE-tape acting as spacer. One glass sheet serves as a working electrode; consequently it has to be coated with a transparent, electrically conductive layer such as e. g. ITO. The lower edge of this sandwich is immersed into the electrolyte solution; a platinum wire acting as counter electrode and a reference electrode are also placed in the lower vessel. The electrolyte solution is sucked into the gap between the glass sheets by capillary action; generally vacuum has now to be applied at the upper edge. The NIR light passes via fiber optics and suitable collimator lenses through the glass plates. Typical results obtained with this setup are shown below. In the case of spectrometers operating with optical choppers, experiments can be conducted without the need of excluding ambient light. In a more sophisticated setup (see Fig. 2) the glass sheets are mounted in PTFE-rods with slits acting as holders which in turn fit into the bottom of a cell body as shown.

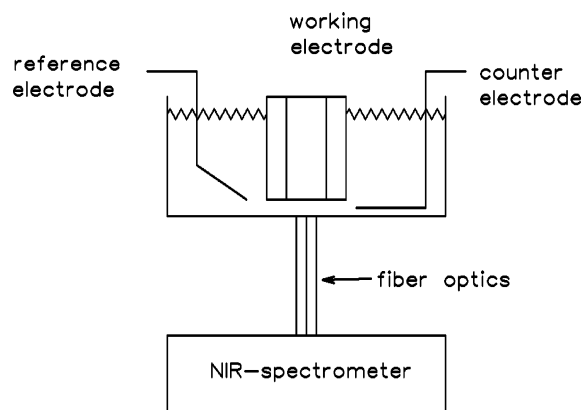
The gap between the two glass plates (one plate is coated with ITO and serves as a working electrode) is filled with electrolyte solution upon immersion into the solution pool in the bottom part of the cell. The gap between the glass plates is determined by the thickness of



**Fig. 2** Thin layer setup for NIR-spectroelectrochemical experiments, top: vertical cross section of cell setup, bottom: horizontal cross section of glass assembly, for details see text

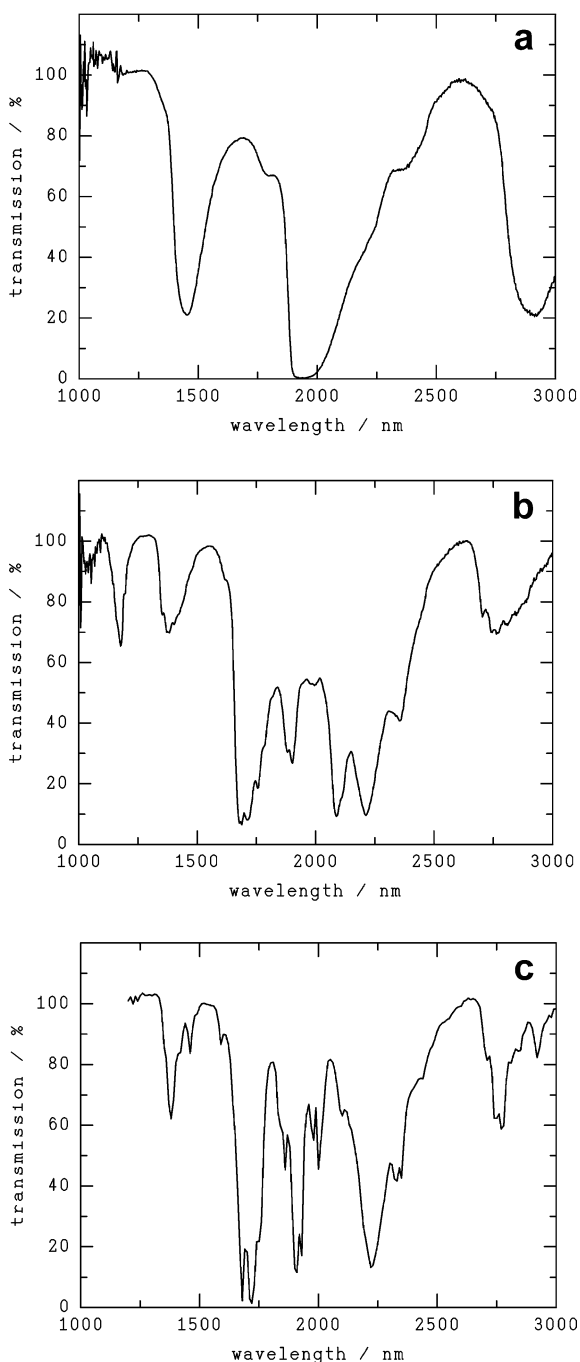
the strips of PTFE-tape inserted at the edges of the plates. Electrical contact is made with a brass clamp at the top edge of the ITO-coated glass sheet. This cell design can be modified for experiments under a controlled atmosphere by attaching the glass sheets to a suitably modified holder mounted on top of a vessel acting as electrochemical cell. For details see [15].

A setup suitable for work with highly reflecting solid electrodes (e. g. platinum, gold or glassy carbon discs) has been described by Salbeck [17]. As shown in the cross section in Fig. 3 the polished electrode surface is mounted close to the NIR-transparent cell bottom, leaving only a thin layer of electrolyte solution in the narrow gap. Connection to the NIR-spectrometer is accomplished with a fiber optic cable containing bundled cables from the light source and to the detector. The light coming via one fiber from the source passes the window and the solution. It is externally reflected at the electrode surface back into the fiber leading to the detector. The cell can be thermostatically brought down to  $-40\text{ }^{\circ}\text{C}$ . It shows both thin layer and semi-infinite diffusion behavior and can be used most easily for experiments under controlled atmosphere.



**Fig. 3** Thin layer setup for NIR-spectroelectrochemical experiments with solid electrodes in external reflection according to [17]

As a reference for selection of a suitable cell design and of the accessible range of wavelength, NIR-spectra of commonly employed electrolyte solvents are helpful as displayed below [18]. The NIR-spectrum of water as displayed in Fig. 4a, is dominated by several broad band absorptions. The O-H-stretching modes are easily identified at 1400 and 2000 nm [5]. Despite the short optical



**Fig. 4** a NIR-spectrum of water, 1 mm path length, NIR-spectrometer Guided Wave 200. b NIR-spectrum of propylene carbonate, 1 mm path length, NIR-spectrometer Guided Wave 200. c NIR-spectrum of acetonitrile, 1 mm path length, NIR-spectrometer Guided Wave 200

path length, absorption around the latter band is almost complete. Any additional spectral information in further spectroelectrochemical experiments around this position will be hampered by severe noise. The spectrum of propylene carbonate (Fig. 4b) is considerably more complicated in addition to C-H-mode bands caused by the methyl group can be assigned [5]. The spectrum of acetonitrile (Fig. 4c) is even more complicated despite the fairly simple molecular structure. With all displayed spectra the need for a thin layer arrangement is evident because of the strong absorption even with the thin layer of the liquid employed.

## Applications

Experimental results obtained with one of the experimental setup's described above can be grouped roughly into the following areas:

- 1 spectroelectrochemistry of
  - inorganic or organometallic transition metal compounds (including molecules of biochemical importance)
  - conjugated organic molecules (neutral and radical)
  - intrinsically conducting polymers
- 2 investigation of electrochromic compounds

## NIR-spectroelectrochemistry of inorganic or organometallic transition metal compounds

In the NIR electronic transitions, involving transition metal ions being coordinated in complexes of widely varying structure and complexity, can be observed. In addition charge transfer absorptions of these species can be found. They can be caused by charge transfer between the metal center and the ligand (MLCT) or—in the case of multinuclear complexes—between various metal centers (MMCT). If the participating metal centers have different oxidation states, this transfer is equal to an intervalence charge transfer (abbreviated IVCT). Both terms are in most cases of equal meaning. Thus they are not used consistently.

Polynuclear metal complexes showing multiple redox reactions have recently attracted increasing interest as multielectron transfer reagents in synthetic chemistry and as photo(electro)chemical energy collectors in renewable energy research. A theoretical approach towards electronic communication between carbon chain bridged ligands has been reported by Belanzoni et al. [19]. These complexes include linear metal polymers, supramolecular species and dendrimers. A tetranuclear species which might be considered as a core of a dendrimer has been reported by Haga et al. [20]. Their di- and tetranuclear ruthenium complexes show intervalence metal-metal charge transitions becoming evident easily

by their typical NIR-absorption. In case of the former species two closely spaced electron transfers starting with  $[(2,2'\text{-bipyridine})_2\text{Ru}(2,6\text{-bis}(2\text{-pyridyl})\text{-}2,2':6,6'\text{-thiazoo}[4,5\text{-}d]\text{benzothiazole})\text{Ru}(2,2'\text{-bipyridine})_2]^{4+}$  and ending with  $[(2,2'\text{-bipyridine})_2\text{Ru}(2,6\text{-bis}(2\text{-pyridyl})\text{-}2,2':6,6'\text{-thiazoo}[4,5\text{-}d]\text{benzothiazole})\text{Ru}(2,2'\text{-bipyridine})]^{6+}$  are expected. In case of the latter species starting with  $\{[(2,2'\text{-bipyridine})_2\text{Ru}(2,2'\text{-bis}(1\text{-methyl-benzimidazo-}2\text{-yl)-}4,4'\text{-bipyridine})]_3\text{Ru}\}^{8+}$  four closely spaced electron transfers are expected. The actual CV shows a first small wave ascribed to the oxidation of the central Ru(II) ion, subsequently the three peripheral Ru(II) ions are oxidized within potential intervals as small as 30 mV based on the results of numerical simulation. In the starting species four Ru(II) species are present, in the final four Ru(III) species. In between the respective mixed valence complexes are expected. In order to construct the correct absorption spectrum of every compound the authors proposed a mathematical separation procedure. The NIR-absorption around 1300 nm was indeed observed once the first oxidation peak was passed. It disappeared once the potential range wherein oxidation of the peripheral Ru(II) ions occurs was left.

A strong IVCT band around 1460 nm was observed upon oxidation of  $[(2,2'\text{-bipyridine})_2\text{ClRu}(\text{benzotriazole})\text{RuCl}(2,2'\text{-bipyridine})_2]^{+}$  by Rocha and Toma [21]. A dinuclear ruthenium complex containing as a bridging tetraoxolene ligand, 9-phenyl-2,3,7-trihydroxy-6-fluorone  $\{[\text{Ru}(2,2'\text{-bipyridine})_2]_2(\mu\text{-}(9\text{-phenyl-}2,3,7\text{-trihydroxy-}6\text{-fluorone}))\}^{+}$  was synthesized by Barthram and Ward [22]. All oxidized species (2+, 3+, 4+) showed NIR absorption bands assigned to metal-ligand and metal-metal charge transfers. Using ZINDO calculations these bands could be predicted approximately. Although the predicted energies were consistently too high, the relative order and intensity were roughly observed demonstrating the qualitative correctness of these calculations.

The MMCT can be influenced by the nature of the bridging ligand as observed by Bayly et al. [23] in a variety of dinuclear molybdenum complexes. McWhinnie et al. [24] reported on an oxygen-bridged bimetallic molybdenum complex  $\{[\text{Mo}(\text{NO})\text{L}(\text{CL})]_2(\mu\text{-O})\}$  with  $\text{L} = \text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3$  showing a fast one-electron reduction. Two weak NIR-bands with little or no solvent dependence were found implying, that the reduced species is delocalized and described best as class III species in the Robin and Day classification [25] This classification pertains to the degree of electronic communication between the metal centers in a bi- or polynuclear complex. In class I species both metals behave completely independently; there is no communication at all. Class II species show some communication evident in shifts of electrooptical properties assigned to one center after a change of redox state (valency) at the other center. A class III species shows considerable changes of the electrooptical properties assigned to both centers (as compared to their properties in the absence of this interaction in e. g. mononuclear units) even before any

change of valence has occurred; this may be related to a high degree of electronic delocalisation. Binuclear iron complexes  $[\text{NC}]_4\text{Fe}(2,2'\text{-bipyrimidine})\text{Fe}(\text{CN})_4]^{n-}$  and  $[(\text{NC})_4\text{Fe}(3,6\text{-bis}(2\text{-pyridyl})\text{-}1,2,4,5\text{-tetrazine})\text{Fe}(\text{CN})_4]^{n-}$  have been studied with respect to the influence of the bridging ligand on the intramolecular electronic communication [26]. Contrary to expectation the longer bridge in the latter complex supports a stronger interaction. This was evidenced from the absence of intervalence charge transfer bands upon oxidation of the starting with the Fe(II)/Fe(II) species. Thus the correct description would be  $\text{Fe}_2^{2.5}$ . In case of the former complex IVCT bands were observed in the NIR around 2200 nm, indicating a correct description of Fe(II)/Fe(III). The topology of bridging ligands has been studied with binuclear Mo(V)-complexes with various isomers of dihydroxynaphthalene as the bridging ligand [27]. Besides a ligand-metal charge transfer absorption in the NIR, in some cases depending on the degree of electronic delocalization between the metal centers afforded by the ligand, an additional intervalence charge transition could be observed.

Dinuclear oxomolybdenum(V) complexes with bisphenolate bridging ligands incorporating various spacers between the phenolate units have been studied [28, 29]. Based on NIR spectra the first oxidation was found to be metal-centered, the intense phenolate-metal ligand metal charge transfer band is indicative. The second oxidation results in the formation of an oxidized ligand (quinone like species) with both molybdenum ions being back in their initial oxidation state V.

Kowallick et al. [30] have studied mononuclear molybdenum complexes with substituted borate, NO,  $\text{Cl}^-$  and substituted pyridines as ligands. With strongly electron withdrawing substituents in position 3 of the pyridine ligand (which in turn was attached to the molybdenum via its nitrogen atom) a metal-to-ligand charge transfer band around 1514 nm was observed after reduction of the complex to formally Mo(0). These transitions in the reduced complexes with 3-substituted pyridines are of special significance for the development of electrochromic dyes to be used for electrooptic switching in the NIR. Ruthenium bipyridine complexes linked to a porphyrin core via a dioxolene system (semiquinone form of 1,2-dihydroxybenzene) have a similar switchable behavior in the NIR around 940 nm assigned to the  $\text{Ru}(d\pi) \rightarrow \text{semiquinone}(\pi^*)$  transition [31] making these complexes also promising candidates for optoelectronic devices requiring switchable NIR dyes and further electrochromic applications [32, 33]. The mononuclear ruthenium(III) complex with a tetradentate ligand composed of two *N,O*-chelating sites based on 3-(2-hydroxyphenyl)pyrazole with an *o*-xylyl spacer studied by Frey et al. [34] showed NIR absorptions at about 1100 and 1550 nm upon oxidation towards Ru(IV). Although a definite assignment was not yet possible the redox-switchable absorption makes this complex a potentially useful NIR electrochromic dye.

Dinuclear ruthenium complexes with the redox-active bridging ligand bis-dioxolene were investigated in a range of electrode potentials wherein the ruthenium ions do not change their state of oxidation in order to study the effect of changes of the redox state of the ligand on the intramolecular electronic communication [35]. By comparing UV-Vis-NIR spectra of the binuclear complexes in various states of oxidation with their respective mononuclear analogs the valence localization could be identified.

Pt(II) complexes with bipyridine and pyridine in various combinations including their substituted derivatives were studied by Braterman et al. [36]. Understanding the arguments proposed by the authors is hampered somewhat by the confusing use of the terms “neutral” and “reduced” species. In doubly reduced species with a Pt(I) ion the characteristic  $\pi^* \rightarrow \pi^*$ -transitions of ligand anion radicals were observed. Within a larger study of the spectroelectrochemistry of binuclear mixed-valence ruthenium and osmium complexes and mononuclear platinum complexes MacGregor et al. [37] have observed a reversible one-electron reduction with the Pt(bipyridyl)Cl<sub>2</sub> complex. The term “reversible” is used in this review consistently not in its (correct) thermodynamical sense but in a different meaning indicating a process which can go back and forth on the same mechanistic pathway such as in the redox process  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  at a relatively high rate (in term of heterogeneous electrode kinetics i. e. exchange current density). The electronic character of the semi occupied molecular orbital (SOMO) of [Pt(bipyridyl)Cl<sub>2</sub>] was investigated with EPR and the UV-Vis-NIR spectroelectrochemistry; it was found to be primarily bipyridine based.

Richter and Brewer have reported on mixed valence Os/Os and Os/Ru complexes [38, 39] showing both osmium- and ruthenium-based redox processes. The obtained NIR-spectra showed bands assigned to intervalence and to metal-ligand charge transfer processes and allowed assignment of the species to class II in the Robin and Day classification [25]. Results provided information about spin-orbit state energy separation. In a binuclear ruthenium complex  $[(\text{NH}_3)_4\text{Ru}(\mu\text{-}3,6\text{-bis}(2\text{-pyridyl})\text{-}1,2,4,5\text{-tetrazine})\text{Ru}(\text{NH}_3)_4]^{5+}$  a weak NIR transition around 1490 nm was assigned to an intervalence transition [40]. The surprising low intensity was ascribed to a particular chelate arrangement in the complex. Mixed valence osmium and ruthenium complexes as studied by Beley et al. [41] showed NIR-bands assigned to intervalence transitions occurring despite the relatively long distance (1.1 nm) between the metal centers afforded by the used bridging ligand. In a study of binuclear manganese(III)-manganese(IV)-complexes Brewer et al. [42] observed a tail of an extreme absorption around 650 nm extending into the NIR which was assigned to an intervalence transition. Trinuclear complexes containing Ru/Os/Ru were studied by Richter and Brewer [43]. Depending on the type of bridging ligand NIR absorptions around 966 to 1059 nm were

found after *in situ* electrooxidation of the Os(II)-ion in a spectroelectrochemical cell; they were assigned to metal-ligand charge transfer transitions. Heath and Raptis used NIR spectroscopy at low temperatures (208 K) to identify and study various binuclear rhenium complexes with quadruple metal-metal bond [44]. A tetranuclear rhenium complex  $[(\mu_4\text{-}(7,7,8,8\text{-tetracyano-}p\text{-quinodimethane}))\{fac\text{-Re}(\text{CO})_3(2,2'\text{-bipyridine})\}_4]^{4+}$  showed a NIR band upon a first one-electron reduction at 1020 nm [45]. It is assigned to a slightly perturbed TCNQ<sup>\*-</sup> chromophore.

Marvaud and Launay have prepared oligomers of ruthenium porphyrins coupled via azopyridines [46]. NIR spectroscopy revealed a band around 966 nm assigned to a charge transfer between the ruthenium cation and the axial (coupling) ligand. A study of porphyrin dimers with conjugated butadiyne bridges has been reported by Arnold et al. [47]. NIR-spectra of the anions and dianions (of mixed valence type) showed bands which were assigned to long-axis polarized  $\pi \rightarrow \pi^*$  transitions within the newly occupied upper manifold of the two-porphyrin eight-orbital framework. The one-electron reduction product of the octaethylporphyrin dimer  $\{[\text{M}(\text{OEP})](\text{buta-}1,3\text{-diyne})[\text{M}(\text{OEP})]\}$  with  $\text{M}_2 = \text{H}_4, \text{Co}_2, \text{Ni}_2, \text{Cu}_2, \text{Zn}_2, \text{Pd}_2, \text{Pt}_2, \text{Co/Ni}, \text{Ni/Zn}$  showed an NIR-absorption around  $4500 \text{ cm}^{-1}$  (2222 nm) which was assigned to an electronic promotion within the  $\pi$ -system of the intermediate valence diporphyrin [48].

Tetraphenylporphyrin systems showing reversible two-electron-one-proton ring-centered oxidation of metalloporphyrins bearing secondary amide-linked superstructures were reported by El-Kasmi et al. [49]. Based on spectroelectrochemical data including NIR-bands around 1000 nm appearing upon formation of the two-fold oxidized species formation of an isoporphyrin instead of a di-cation was concluded.

Buchler et al. [50] have studied tetraphenyl complexes  $\text{NBu}_4[\text{Me}(\text{III})(5,10,15,20\text{-tetraphenylporphyrin})_2]$  with  $\text{Me} = \text{Y}, \text{La-Lu}$  except Pm. With NIR-spectroscopy linear correlations between band positions and metal ion size were found for both oxidation products  $\text{M}(\text{TPP})_2$  and  $[\text{M}(\text{TPP})_2]^+$ . This was interpreted based on qualitative MO diagrams describing the  $\pi\pi$ -interactions of the four frontier orbitals of the two macrocyclic systems in the “double decker” molecule.

Tran-Thi et al. [51] have reported a systematic study of gadolinium and cerium double- and triple-decker tetraphenylporphyrin-phthalocyanine complexes. For mixed double- and triple-decker (Pc-M-TPP and TPP-M-Pc-TPP) where the metal could not be oxidized, obviously the Pc-moiety is oxidized. The resulting hole in the Pc-unit causes NIR-transitions around 1200–1300 nm with the double-decker and around 1800–2300 nm for the triple-decker. In Ru/Ru complexes with three chloride anions acting as bridging ligands the absence of NIR-bands reported by Batista et al. [52] was taken as evidence of the absence of intervalence charge-transfer which in turn implies a localized

valence type of complex. Laine et al. have attached two pentaammineruthenium(II) complexes to dicyanonorbadiene [53]. Upon oxidation to the Ru(II)/Ru(III)-state an intervalence charge transition band was observed between 1000 and 1600 nm. Mononuclear complexes of ruthenium(II) with three substituted bipyridine ligands showed striking NIR-absorptions around 1600 nm strongly dependent on the formal oxidation state of the central ion [54]. Whereas the complex with Ru(II) showed almost no absorption at the formal state  $-1$  a very strong absorption assigned tentatively to inter- or intra-ligand charge transfer transitions was recorded. Heath et al. [55] have reported on the reduction products in the series  $(\text{Ru}(\text{bipyridyl})_3)^{2+/1+/0/1-}$ . Tetranuclear pentaammineruthenium complexes wherein the four ruthenium ions are coordinated with amino groups and are attached to  $\pi$ -conjugated tetracyano ligands (similar to TCNE) have been studied by Moscherosch et al. [56]. According to the number of metal centers the available oxidation states of the complex are numerous. The species incorporating TCNQ and having ionic charge  $10+$  and  $7+$  show intense NIR absorption at 1170 nm and 1561 nm respectively. These bands can be rationalized in an extended MO-scheme.

A NIR-band observed with the species  $(\text{Ru}(\text{bipyridyl})_3)^{1+}$  and  $(\text{Ru}(\text{bipyridyl})_3)^0$  was assigned to a  $\pi \rightarrow \pi^*$  transition of the bipyridyl $^-$  species. The series of subsequent oxidation products of the iridium bipyridyl complex  $[\text{Ir}(\text{bipyridyl})_3]^{3+/2+/1+/0}$  showed NIR-absorptions decreasing with increasing anion state of oxidation, consequently iridium stays in oxidation state III whereas oxidation affects the ligands [57].

In a study of oxo/arylamido complexes of molybdenum(VI) Lee et al. [58] observed changes in NIR spectra during *in situ* electrooxidation of a ferrocene substituted system. A decrease of the band around 615 nm caused by a ferrocenyl-based metal-ligand charge transfer is replaced by a band around 890 nm characteristic of the ferrocenium moiety. Bimetallic molybdenum complexes with a  $\mu$ -oxygen bridge were studied by McWhinnie et al. [59]. Upon electroreduction of the complex a weak NIR-band around 840 nm appeared which was taken as evidence of a high degree of delocalization in the reduced species which was subsequently assigned to a class III species within the Robin and Day [25] classification. Metal-metal interactions in dimolybdenum-(0,0)- and -(I,0)-complexes were studied by Kaim et al. [60]. Results obtained with *in situ* NIR spectroelectrochemistry indicate metal-metal intervalence charge transfer bands with the Mo(0)-Mo(0) complexes only. The redox electrochemistry and the electrochemical conditioning of vanadium(V) pentoxide xerogel films ( $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) has been studied by Anaissi et al. [61]. NIR bands around 1400 nm were ascribed to V(IV)  $\rightarrow$  V(V) intervalence charge transitions. Binuclear complexes containing molybdenum(0) and tungsten(0) in (trialkylphosphane)tricarbonyl ligands bridged with a variety of different nitrogen containing ligands showed in nonpolar

solvents intense and very narrow charge transfer bands in the NIR suggesting small geometrical changes only between ground and excited metal-to-ligand-charge transfer state [62].

Lucas et al. [63] have investigated a family of tetrahedral group 6 iridium clusters. A detailed spectroelectrochemical investigation of the exhaustive one-electron oxidation ( $0 \rightarrow 1^+$ ) of  $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)_2$  significant changes in the range between  $40,000\text{ cm}^{-1}$  and  $8000\text{ cm}^{-1}$  (250–1250 nm) were observed. Taking into account local density functional theory the band around  $8000\text{ cm}^{-1}$  was assigned primarily to a  $\sigma(\text{W-W}) \rightarrow \sigma^*(\text{W-W})$  transition despite the fact, that other transitions involving iridium are also conceivable. Accordingly a metal-specific redox process with retention of the tetrahedral core geometry was concluded. The isosbestic disappearance of bands centered at  $21,500$  and  $35,000\text{ cm}^{-1}$  (465–285 nm) and the simultaneous appearance of bands at  $18,000$  and  $37,000\text{ cm}^{-1}$  (555–270 nm) was not interpreted further. In a study of related pseudooctahedral mixed-metal monocluster compounds wherein two iridium atoms are linked to two other atoms and the linked di- and tricluster compounds no NIR-absorption bands indicative of low energy transitions associated with intervalence charge-transfer were found [64].

Dimesitylplatinum complexes with unsaturated chelate ligands were studied by Klein and Kaim [65]. The monoanions of all complexes (with different bipyrazine and bipyrimidine type ligands) showed NIR-absorptions around 1390 nm which were not assigned further.

Metalla-supramolecular rectangle ions have been studied by Kaim et al. [66] as electron reservoirs for multielectron redox processes. In case of  $[\text{PtII}_4(\text{PET}_3)_8(\mu\text{-anthracene-1,8-diyl}^{2-})_2(\mu\text{-L})^{4+}]$  (with L = 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethene) NIR-absorption around 1050 nm were observed, but not assigned.

Intervalence charge transfer bands in the NIR were reported for mixed valence heteropolyanions  $[\text{HAS}_2\text{Mo}_{18}\text{O}_{62}]^{n-}$  by Zhang et al. [67]. The redox transitions of the heteropolyanion  $\text{VMo}_{12}\text{O}_{40}^{3-}$ , which undergoes three reversible one-electron reductions, into the mixed-valence heteropolyanions  $[\text{VMo}_{12}\text{O}_{40}^{n-}]$  ( $n=4,5,6$ ) was monitored with NIR-spectroscopy, also [68]. Cheng et al. [69] have studied multiple reductions of a series of undecatungstozincates monosubstituted by first-row transition metals  $[(\text{ZnW}_{11}\text{M}(\text{H}_2\text{O})\text{O}_{39})^{n-}]$  ( $\text{M}=\text{Cr, Mn, Fe, Co, Ni, Cu}$  or  $\text{Zn}$ ). In the case of the Fe-containing compound no NIR band indicative of IVCT caused by mixed valences is observed. Consequently no W-centered reduction has occurred. According to the displayed spectrum the same applies to the Mn-containing compound. The NIR-spectrum of the heteropolyanion  $[\text{PMo}_{12}\text{O}_{40}]^{4-}$  [70] showed a mixed-valence type behavior of class II type in the Robin and Day classification. Undecatungstozincates  $[\text{ZnW}_{11}\text{M}(\text{H}_2\text{O})\text{O}_{39}]^{n-}$  ( $\text{M}=\text{Cr, Mn, Fe, Co, Ni, Cu}$  or  $\text{Zn}$ ) monosubstituted by first-row transition metals were characterized with NIR-spectroscopy by Cheng et al. [71]. The mixed-valence

isopolyanion  $[\text{Mo}_6\text{O}_{19}]^{3-}$  has been investigated in aprotic media using a host of spectroelectrochemical techniques [72]. It was formed by electroreduction of  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and identified by characteristic absorptions at 500; 900 and 1100 nm in the UV-Vis-NIR and at  $940\text{ cm}^{-1}$  in the IR [73].

The temperature dependence of the  $\text{Cu}_A$  site in carbon monoxide inhibited cytochrome *c* oxidase has been studied by observing the relatively weak NIR absorption around 820 nm [74]. The obtained results together with those related to the absorption at 604 nm caused by  $\text{Fe}_a$  indicate, that the interaction between both redox centers causes a downshift of the reduction potential of one site once the other site has been reduced. The temperature dependence itself allowed calculation of the standard entropy of reduction of  $\text{Cu}_A$  at  $\Delta S^{\circ} = -48.7 \pm 2.3$  eu.

Geskes et al. [75] have observed a NIR-band between 927 nm and 974 nm for the anions of a series of transmetalated bacteriochlorophyll *a* molecules which they proposed to be a  $\pi$ -anion-state-marker band.

In glyoxal oxidase from *Phanerochaete chrysosporium* a free radical-coupled copper complex has been identified as the catalytic structure in the active system [76]. Upon oxidation a UV-Vis absorption extending into the NIR was observed without specific features in the latter range.

### NIR-spectroelectrochemistry of conjugated organic molecules

Organic molecules show absorption in the NIR once they have hydrogen atoms bound. Thus practically all molecules will show at least some absorption. In investigations of electrochemically generated radical anions of a broad selection of aromatic compounds containing several imide and quinone groups Rak et al. [77] have observed strong NIR-absorptions which were assigned to  $\pi \rightarrow \pi^*$  and  $\pi^* \rightarrow \pi^*$  transitions. Structural information pertaining to charge delocalization and the action of various structural moieties (electrophores as defined in [78]) involved in the electrooptical properties was obtained. In a study of diquinone anion radicals Almlöf et al. [79] obtained evidence for  $\pi^* \rightarrow \pi^*$  transitions of delocalized anions. Hünig et al. [80] reported absorptions between 700 and 1200 nm typical of violene radical cations obtained electrochemically. Lenhard and Cameron have studied a variety of cyanine dye radicals [81]. Weak absorptions found in NIR-spectra of most cyanine radical dications showed a systematic relationship to the polymethine chain length. Intervalence charge-transfer bands in the NIR have been observed with bistriarylamine systems containing two redox centers by Lambert and Nöll [82]. During electrooxidation of an oligotriarylamine a strong NIR-absorption around 1620 nm developed [83]. It was assigned to a one-dimensional intervalence charge transfer between the two redox centers of the molecules being at different states of oxidation. NIR-absorptions around  $7000\text{ cm}^{-1}$

as observed with oxidized forms of various substituted hexakis[4-(*N,N*-diarylamino)phenyl]benzene derivatives were assigned to intervalence charge-transfer excitations [84].

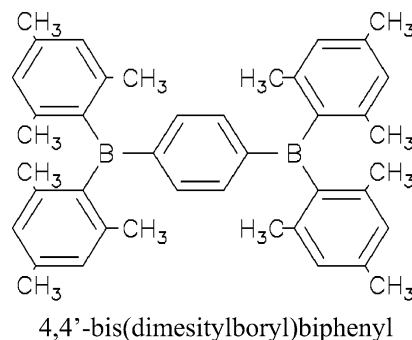
Diads composed of strong  $\pi$ -donors and  $\pi$ -acceptors (substituted tetrathiafulvalene derivatives and substituted polynitrofluorene derivatives) linked via a saturated  $\sigma$ -spacer have been synthesized and characterized [85]. Their reversible multielectron transfer capability includes strong NIR-absorptions around 1200 nm assigned to an intramolecular charge transfer transition. In  $\sigma$ -coupled tetrathiafulvalene-polynitrofluorene diads Peregichka et al. [86] have observed very small HOMO-LUMO gaps as small as 0.3 eV and an electrochromic behavior in the NIR.

Schiff base cryptands studied by Demol et al. [87] showed striking similarity of spectroelectrochemical data obtained with chemically and electrochemically reduced species implying identity of the products obtained via both ways. The cryptand **I** ( $[\text{N}[(\text{CH}_2)_2\text{N-CH-meta-C}_6\text{H}_4\text{-CH}=\text{N}(\text{CH}_2)_2]_3\text{N}]$ ) and its strand **II** ( $(\text{CH}_3)_2\text{CH-N}=\text{CH-meta-C}_6\text{H}_4\text{-CH}=\text{N-CH}(\text{CH}_3)_2$ ) were reduced electrochemically and with alkali metal [88]. **I**<sup>-</sup> and **I**<sup>2-</sup> showed the same UV-Vis-NIR spectrum. The electroreduction products **II**<sup>-</sup> and **II**<sup>2-</sup> are similar to **I**<sup>-</sup> and **I**<sup>2-</sup>.

Viologen radical cations studied by Lee et al. [89] showed NIR-absorptions around 1100 nm depending on the viologen concentration, the temperature and the concentration of added surfactants. They were ascribed to dimeric species.

Benzene and biphenyl carrying dimesitylboryl substituents show a complex redox behavior as reported by Fiedler et al. [90].

The radical anion of 4,4'-bis(dimesitylboryl)biphenyl



showed an intense absorption at 1305 nm which was assigned to a transition  $b_{3u}(\text{SOMO}) \rightarrow b_{2g}(\text{LUMO})$ .

In a comparative study of the four isomeric bidiazines 2,2'-bipyrazine, 3,3'-bipyridazine, 2,2'-bipyrimidine and 4,4'-bipyrimidine [91] some weak NIR bands assigned to forbidden electronic transitions were observed for the anion radicals of some isomers.

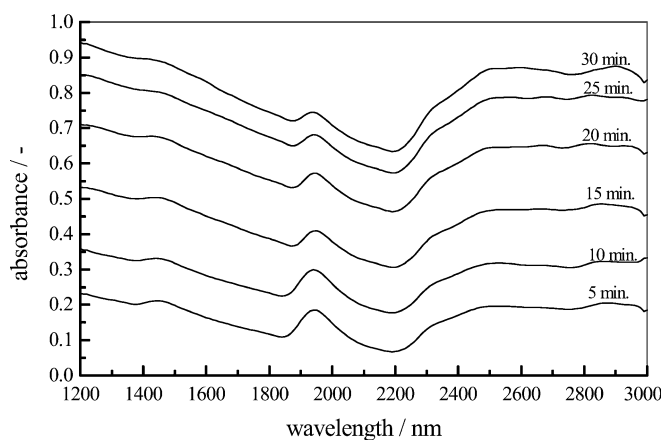
Higher carbon modifications like  $\text{C}_{60}$  or related molecules have attracted large attraction because both their most unusual properties and a rich choice of potential application. Kadish et al. have proposed NIR



spectroscopy to distinguish electrogenerated mono- and dianions of differently substituted fullerenes [92]. The state of oxidation of  $C_{76}$  fullerenes could be distinguished based on their NIR-absorption bands [93]. Rapta et al. have studied the electrochemistry of  $C_{120}O$  [94]. Using a combination of *in situ* EPR and UV-Vis-NIR spectroelectrochemistry they have observed a broad NIR-band around  $\lambda_{\max} = 940$  nm and simultaneously an EPR line in the potential range of the first reduction peak. Beyond the second reduction wave, where presumably  $C_{120}O^{3-}$  and  $C_{120}O^{4-}$  anions are formed, further EPR lines were found. NIR-bands in this potential region indicate the formation of  $C_{60}O^-$  and  $C_{60}O^{2-}$  as decomposition products of the highly charged  $C_{120}O^{x-}$ .

### NIR-spectroelectrochemistry of intrinsically conducting polymers

Frequently NIR-spectroscopy has been employed *in situ* as well as *ex situ* in investigations of intrinsically conducting polymers (ICP). These macromolecular materials show frequently strong absorptions in the NIR caused by the respective molecular moieties but also by mobile charge carriers (polarons or bipolarons, for an overview see [95, 96]). Frequently the assigned absorptions start in the long wavelength UV-Vis range and extend well into the NIR; consequently this phenomenon appearing as a broad absorption or even only an apparently tilted baseline has been called the “free carrier tail”. Optical properties (i. e. absorption) in this range are of particularly practical importance when employing NIR illumination for Raman (especially resonance Raman) spectroscopy [97, 98]. A typical example is shown in Fig. 5. NIR-spectra recorded during electropolymerization of polyaniline on an ITO-glass in a setup similar to the one depicted in Fig. 2 show a sloped line indicative of the free charge carriers being present within the freshly formed polymer. This is in its oxi-



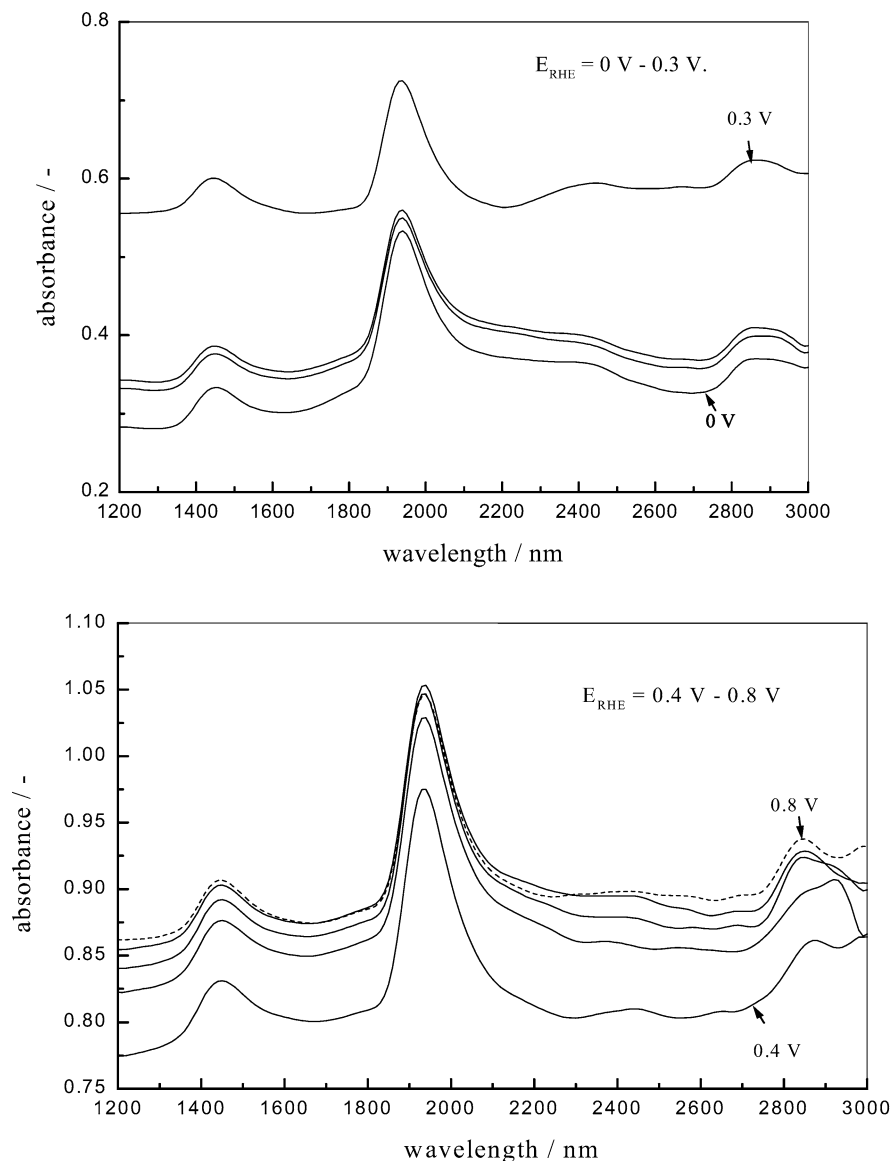
**Fig. 5** NIR-spectra recorded during polyaniline growth at  $E_{RHE} = 1$  V, Guided Wave 200, single beam spectrum at  $t = 0$  min as reference

dized, i. e. conducting state at  $E_{RHE} = 1$  V. The bands can be assigned to the first overtone of the N-H-stretch in an aromatic amine (1500 nm) and to the transition from the valence band into the lower polaron band (binding polaron band) of the benzoid polaron type [99]. The rather featureless absorption between 2400 nm and 3000 nm might be related to mobile charge carriers, its correlation with the electrical conductivity measured *in situ* is currently under investigation.

The effects of changes in the electrode potential can be discerned in Fig. 6. A polyaniline film formed potentiostatically at  $E_{RHE} = 1$  V in an aqueous solution of 0.1 M aniline and 1 M  $HClO_4$  is successively oxidized. Those absorptions already observed during the electropolymerization are obvious. The spectra are dominated by these bands, any subtle change of the absorption of the film is hard to detect. Using the reduced polymer film as a reference provides a clearer picture as seen in Fig. 7. The broad and structureless increase of absorption indicative of the “free carrier tail” is easily discerned. Further structures in particular at long wavelength cannot yet be assigned definitely.

Sabatani et al. [100] have used various spectroelectrochemical methods to study the influence of preparation conditions on the morphology and electrooptical properties of polyaniline. Application of a temporary negative electrode potential bias resulted in polymer film “annealing”. NIR data of these films showed a shift of the peak associated with polarons to lower energies implying an increased long-range order of the polymer. An electrochemical pretreatment (essentially exposure to a sulfuric acid solution under potential control at more or less reducing electrode potentials) results in an increase of the electrical conductivity of up to one order of magnitude [101]. In NIR-spectra collected *in situ* the significantly increased absorption between 1000 and 3000 nm implies an increase in the concentration of mobile charge carrier. The general improvement of electrochemical properties of PANI prepared by template synthesis employing inorganic (sol-gel silica) as well as organic (poly(vinylidene fluoride)) templates has been reported by Neves et al. based on the results of various methods including NIR-spectroscopy [102]. Attempts to obtain processable PANI via using specific dopant/solvent combinations reported by Rannou et al. [103] have yielded NIR spectra of polymer solutions showing changes in charge delocalization effected by the use of various phosphoric acid diesters. Relationships between the efficiency to induce charge delocalization and acid structure were established and explained by invoking different degrees of steric matching between polymer and dopant acid. When using organic acids like 4-phthalosulfonic acid or sulfosuccinic acid Dufour et al. [104] have obtained processible polymers with a supramolecular architecture. NIR data of the latter polymer obtained *ex situ* showed evidence of low temperature thermochromism. Polyaniline prepared by electrooxidation of anilinium electrostatically bound on top of a self assembled monolayer was studied by Sfez

**Fig. 6** Polyaniline spectra at various electrode potentials, Guided Wave 200, cuvette with supporting electrolyte solution as reference



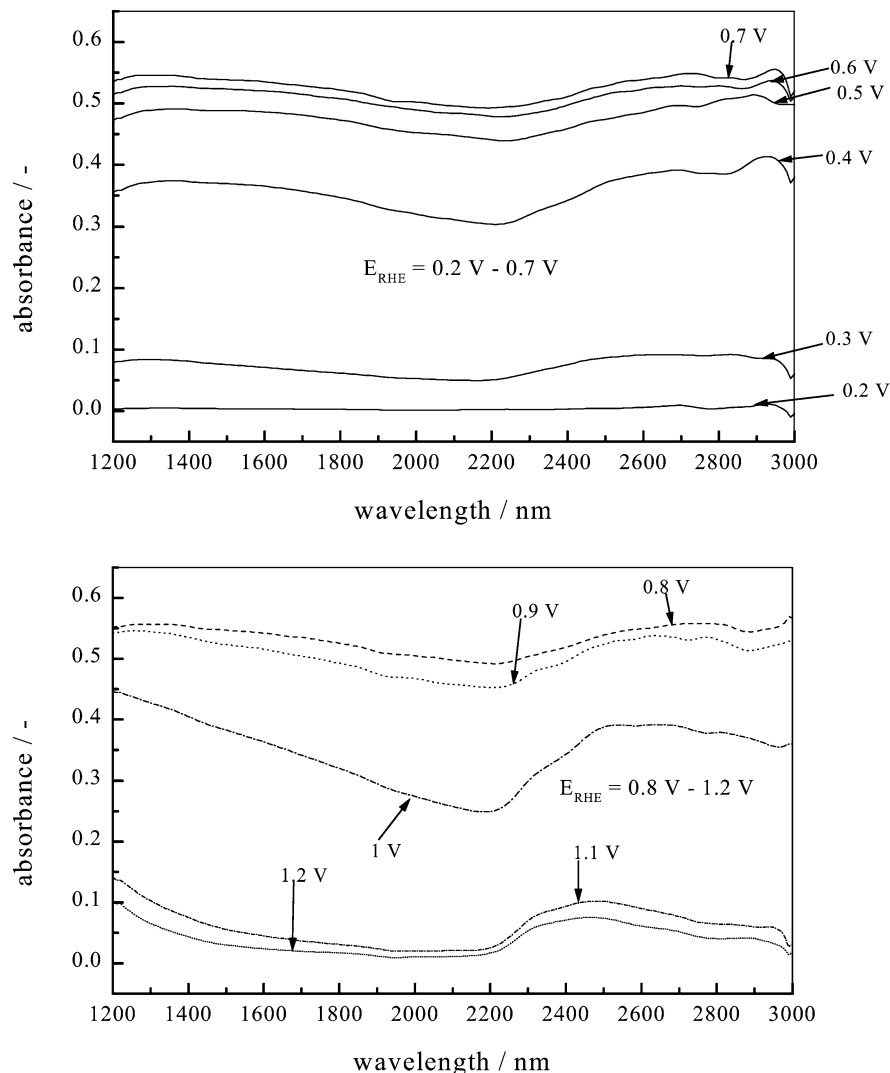
et al. [105]. NIR spectra showed a broad and poorly structured absorption extending to 1700 nm, the part between 800 and 1000 nm was assigned to polaron band transitions based on rather dated literature without further discussion. Considering the essentially two-dimensionality of the polymer this assignment (which at first glance is in contradiction to the generally assumed bipolaron transitions in this wavelength region) may be correct when taking into account, that no bipolarons might evolve in this environment, but rather long conjugated units (as opposed to those causing the absorption around 550 nm in this report) supporting low energy polarons [106].

Barbero et al. have studied sulfonated polyaniline (SPAN) as a potential battery material [107]. Spectroelectrochemical data in the NIR showed the absence of a band around 1600 nm found with non sulfonated PANI. It was concluded, that the corresponding band expected for SPAN was blue shifted and merged with a band

around 850 nm assigned to an absorption by metallic polarons. Pomfret et al. [108] have compared NIR-absorption data for polyaniline and a phenyl-capped tetramer. The strong similarity of spectra was taken as evidence of similar electronic structures. Hanly et al. [109] have reported spectroelectrochemical data on poly-*N*-methylisindole. A broad absorption around 1400 nm found upon oxidation of the polymer could not be explained by invoking polaron or bipolaron states in the band gap. A concept based on transitions between localized states was tentatively proposed.

The effect of vapors of *m*-cresol on camphorsulfonic acid doped polyaniline in its emeraldine salt form was studied by Xia et al. [110]. Changes in the NIR and the UV-Vis indicate a change from localized polarons into a delocalized polaron band. NIR-absorption around 1.4 eV (860 nm) for various substituted polythiophenes with ethyne bridges were assigned to transitions into polaron bands by Ng et al. [111]. Quillard et al. [112]

**Fig. 7** Polyaniline spectra at various electrode potentials, Guided Wave 200, reduced polymer film as reference



have reported some NIR-data on polyaniline which were used as a basis for the interpretation of Raman spectra recorded with NIR-excitation. Conformational changes and evidence of secondary doping (see [95, 96]) of polyaniline composites have been studied with *in situ* NIR-spectroscopy by Xie et al. [113].

In a study of various polythiophenes based on thiophene monomers with different alkyl- and aryltype substituents Kaeriyama et al. have reported NIR-spectra obtained *in situ* [114]. In the neutral (reduced, poorly conducting) state only one absorption band assigned to the transition between valence and conduction band is found. From a molecular point of view this corresponds to the  $\pi \rightarrow \pi^*$  transition in the single repeat unit. Upon oxidation two additional bands attributed to two different polaron bands from the valence into different polaron bands were observed. The position of the band at lower energies moved to higher values upon increased degree of doping whereas the band at higher energies only increased in intensity without any shift in position. The band caused by the valence band to conduction band transition decreased

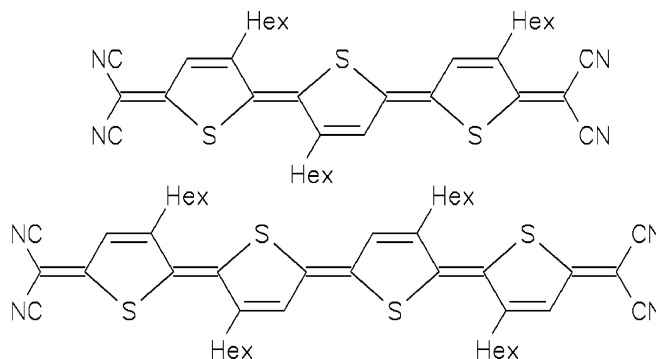
in intensity and shifted to lower energies (red shift). The latter observation was stated to be in contradiction with results of thorough theoretical calculations implying a blue shift reported by Brédas et al. [115]. For further details pertaining to other polymers see more recent reviews [95, 96]. The shift has been assigned to a change in transition energy caused by the change from the benzoid into the quinoid form of the benzene ring in the aniline unit, a similar argument seems to be valid with polythiophene. The assignment of both bands at lower energies to transitions from the valence into bipolaron bands (presumably the lower, binding one, and the upper, antibinding one) may require reexamination in view of recent evidence pertaining to the general validity of the polaron-bipolaron model [106]. In a related investigation Lapkowski et al. [116] have studied NIR-spectra of substituted quaterthiophene and its dimer. The monomer was capped at one end with a chlorine substituent preventing polymerization. The band found at 395 nm was again assigned to the  $\pi \rightarrow \pi^*$  transition of the repeat thiophene unit. Upon oxidation of the soluble oligomer the dimer

is formed. Two bands around 810 nm and 1420 nm were found. The former band was assigned to the radical cation of the octameric dimer, the latter band was assigned to its dication (bipolaron). Somewhat surprisingly the authors claimed the latter species to be a radical in disagreement with the literature on bipolarons in ICPs. Levillain and Roncali [117] have observed reversible dimerization of  $\pi$ -conjugated cation radicals of diversely substituted tetrathienylvinylenes. UV-Vis- and NIR-spectra showed two bands of the monomeric radical cation and two additional, hypsochromically shifted bands confirming this dimerization to occur already at room temperature. In a study of terthiophenes and their dimers used as precursor molecules for polythiophene a doublet band observed around 850–1000 nm after chemical oxidation was assigned to an absorption of the dication of the hexamer by Kankare et al. [118]. Guay et al. [119] have studied reduced and oxidized  $\alpha,\alpha$ -coupled oligothiophenes of different chain-length. The energies of the sharp absorption bands found in the NIR scaled linearly with the oligomer size. Extrapolation to infinite chain-length resulted in energies agreeing with those observed with neutral polymethylthiophene whereas with the oxidized oligomers results differing from those for oxidized polymers were found. Poly-3-alkylthiophene usually shows a rather low degree of regioregularity. Highly regioregular polymers could be obtained in recent years via chemical ways of synthesis; they could even be fractionated into samples of significantly different molecular weight [120]. NIR-absorption bands observed *in situ* showed the usual free carrier tail. In case of the fraction showing the highest molecular weight a polaronic band appears at rather low degrees of oxidation already around 1000 nm. Accordingly the sample with the highest molecular weight and the highest average conjugation length shows the most well defined separation of two separate oxidation processes; the latter is characteristic of regioregular poly(3-alkylthiophenes), but observed only infrequently. In a comparison of regioregular poly(3-octylthiophene) and nonregioregular one, Trznadel et al. [121] observed a NIR band around 1150 nm not assigned to any particular species. Its onset appears at lower electrode potential with the regioregular polymer.

Raimundo et al. have reported on steric effects in the reversible dimerization of short-chain oligothiophenes [122]. According to results obtained with various spectroelectrochemical techniques including NIR-spectroscopy it was found in the investigated series of end-capped 2,5''-dihexylterthiophenes, that the radical cation without any further substituent at the middle thiophene unit dimerizes already at room temperature whereas any alkyl substitution at this unit results in a dramatic decrease in the dimerization propensity. A general review of the use of *in situ* spectroelectrochemistry including in particular NIR-spectroscopy for studies of dimerization of electrogenerated radical anions has been provided [123]. Besides dimerization

via  $\pi$ -system interaction the reversible formation of  $\sigma$ -dimers is conceivable. In a study of fluoranthenopyracylene oligomers with different monomer unit length Dunsch et al. [124] have observed very broad NIR bands between 1200 and 1800 nm upon reduction of the monomers. Whereas for the shortest (one repeat unit) monomer dimerization is significant already with two repeat units the radical anion is sufficiently stabilized without dimerization.

Two bis(dicyanomethylene) oligothiophenes with hexylsubstituted quaterthiophene and terthiophene



central units have been studied with *in situ* spectroelectrochemistry and theoretical calculations [125].

The radical cation of the quaterthiophene showed a weak NIR band at 1404 nm (0.88 eV). It was expected at 0.87 eV and assigned to an electronic transition into the first excited state ( $1^2A_u \rightarrow 1^2B_g$ ). It can be described as a one-electron transition from the singly occupied HOMO to the LUMO with an important contribution from the HOMO-1  $\rightarrow$  HOMO excitation.

In an attempt to obtain low bandgap systems Hanack et al have electropolymerized a large family of arenemethylenes [126]. NIR-spectra of the obtained polymer film in their oxidized form showed broad featureless absorptions not discussed further presumably caused by mobile charge carriers.

Levillain and Roncali have studied the reversible dimerisation of various  $\pi$ -conjugated oligomeric cation radicals derived by chemical or electrochemical oxidation of variously substituted tetrathienylenevinylenes [127]. With only some dimers a NIR-band around 1500 nm was found; it was assigned to a sub gap transition of lowest energy. Cyclic voltammetry of polythiophene usually shows only a single broad oxidation wave and two reduction waves. Chen and Inganäs could resolve a three step redox process of a polymer based on 3,4-ethylenedioxythiophene (PEDOT) based on NIR-data recorded *in situ* [128]. Because of the still poor processability of PEDOT alkyl chain substituted PEDOT has been proposed. In an investigation of  $C_{14}$ -alkyl derivative of PEDOT [129] NIR spectra revealed a drastic decrease of the absorption assigned to the  $\pi \rightarrow \pi^*$  transition and a concurrent increase of two bands located at 1000 nm and 1800 nm in a very narrow range of electrode

potentials where in a CV a current increase towards an oxidation peak is observed. At more positive electrode potentials a featureless absorption (free carrier tail) is observed extending into the NIR beyond 1600 nm (the wavelength limit in this study) obviously indicative of the highly conductive state of the polymer.

Poly[4,4'-bis(butylsulphanil)-2,2'-bithiophene] has been studied by Ballarin et al. [130]. This polymer can be *p*- and *n*-doped. Both in the reduced and oxidized state absorptions in the NIR range were observed which were absent in the neutral state. Although the absorptions were strikingly different (broad and featureless increase towards longer wavelength in the oxidized state, maximum around 1420 nm and sharp peak around 1900 nm in the reduced state) no assignment was attempted.

Copolymers of e. g. thiophene and aniline [131] have attracted recently considerable attention because they show promise of providing combinations of desirable advantages of the respective homopolymers. In a spectroelectrochemical study of poly(alkylthiophene)-oligoaniline-2,5-thienylene hybrid polymer Dufour et al. [132] have observed a particularly broad absorption extending into the NIR (i. e. in this case up to 1100 nm) with the protonated form suitable for e. g. plastic photovoltaic cells. Using UV-Vis-NIR spectroscopy Seshadri et al. [133] could prove, that electrochemical copolymerisation of thieno[3,4-*b*]thiophene (T34bT) and 3,4-ethylenedioxythiophene (EDOT) yielded a true copolymer (instead of a mix of the respective homopolymers) based on the shifted onset of the  $\pi \rightarrow \pi^*$  transition in the NIR (around 1040 nm for the copolymer) and the occurrence of a single absorption peak assigned to this transition instead of two peaks as observed when homopolymers were deposited subsequently on top of each other. Demadrille et al. [134] have studied an alternate copolymer of 3,3'-di-*n*-octyl-2,2'-bithiophene and fluoren-9-one. Using among other spectroelectrochemical techniques *in situ* NIR-spectroscopy they could distinguish between doping-induced changes of the bithiophene and the fluoren-9-one subunit.

A conjugated ladder polymer polybenzimidazobenzophenanthroline (BBL) has been reported by Yaohannes et al. [135]. This polymer shows four reversible redox processes during *n*-doping. Only a very weak absorption increasing slightly with negative going electrode potential was found in the NIR range (between 900 and 1000 nm) during *in situ* measurements; no assignment was proposed.

An amide polymer of 1,4-bis[[*p*-phenylamino(phenyl)]amido-]benzene and -ferrocene was formed via electrochemical oxidation [136]. Broad NIR-bands observed with both polymers were assigned to intermolecular  $\pi$ -stacking of the protonated diphenylbenzidinium cations.

The absorption bands observed in the NIR and assigned to charge carriers can be taken as evidence of the state of oxidation because the state is closely related to the existence and the concentration of these species. This

has been employed in a characterization of nucleobase-functionalized polythiophene where shifts in the polymer oxidation potential caused by molecular interactions were observed with cyclic voltammetry and NIR spectroelectrochemistry [137].

---

### NIR-spectroelectrochemistry of electrochromic compounds

Electrochromism is the change of the color of a material caused by transfer of an electrical charge or application of an electrical field [32, 33]. In electrochemical systems it is mostly connected with a reduction or oxidation of a species caused by a charge transfer. Changes of color, i.e. shifts of absorption maxima, as well as changes in absorptivity, i. e. bleaching vs. coloration, have been reported. Applications like e. g. displays or smart windows and mirrors are obvious. With respect to thermal management of buildings and systems exposed to sunlight the fact is noteworthy, that about 50% of the solar power are delivered in the NIR. Consequently systems used for blocking or transmitting solar energy will always be tested for their NIR absorption characteristics. Jelle et al. [138, 139, 140, 141, 142, 143, 144] used a smart window containing both an inorganic electrochromic material WO<sub>3</sub> or Prussian blue and polyaniline to modulate sunlight with only 1.5 V applied to the device. Polypyrrole and WO<sub>3</sub> were used in an electrochromic device employing both liquid or solid electrolytes described by Rocco, de Paoli et al. [145, 146]. Pages et al. [147] reported corresponding data for a device based on polydiphenylamine and a substituted polythiophene. NIR absorption data demonstrating the capabilities of the system were provided. NIR-data of a system also based entirely on ICPs (polypyrrole and polythiophene) have been reported by Gazotti et al. [148]. Electrochromism of mixed Nb(V) and Cr(V) oxides has been studied by Cogan et al. [149, 150]. Data of an electrochromic device similar in application to the one described above based solely on inorganic compounds operating at a cell voltage of 2 V were reported. Optical absorption in the NIR is predominantly caused by WO<sub>3</sub>. An electrochromic system based on metal-metalphthalocyanato complexes showing NIR absorption around 850 nm was described by Takeshita and Ashida [151]. NIR-data of WO<sub>3</sub> lithiated electrochemically have been used by Arntz et al. [152] to calculate the Drude parameters of the obtained material. The electrochromism of WO<sub>3</sub>-based amorphous sol-gel coatings containing in addition variable amounts of Li, Ti, Nb or Ta resulting in different electrochemical performances has been studied by Avellaneda and Bulhoes [153]. A reversible change of transmission (10 to 90%) extending into the NIR associated with Li<sup>+</sup> insertion was observed. Polymerization of 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene and 2,9-dibromobenzo[*c*]thiophene-*N*-2'-ethylhexyl-4,5-dicarboxyimide yielded a donor-acceptor polymer showing electrochromism in the

NIR, but not in the UV-Vis-range implying application in NIR-devices [154].

**Acknowledgements** Help in retrieving the used documents by E. Rahm and financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Gaduiertenkolleg GRK 829/1) are gratefully appreciated.

## References

- Crandall EW (1987) *J Chem Educ* 64:466
- Hildrum KI (1992) *Near Infra-Red Spectroscopy* (Ellis Horwood Series in Analytical Chemistry), Ellis Horwood, New York
- Lin J, Brown CW (1994) *Tract. Trends Anal Chem* 13:320
- Woo YA, Ahn JW, Chun IK, Kim HJ (2001) *Anal Chem* 73:4964
- Osborne BG, Fearn T, Hindle PH (1993) *Practical NIR Spectroscopy with Applications in Food and Beverage Analysis*, Longman, Essex
- Burns DA, Ciurczak EW (eds) (2001) *Handbook of Near-infrared Analysis (Practical Spectroscopy)*, vol. 27. Marcel Dekker, New York
- Murray I, Cowe IA (eds) (1992) *Making light work: Advances in Near Infrared Spectroscopy*. VCH, Weinheim
- Siesler HW, Heise HM, Ozaki Y, Kawano S (2001) *Near-Infrared Spectroscopy: Theory, Instruments, and Applications*. Wiley, New York
- Raghavachari R (ed) (2001) *Near-Infrared Applications in Biotechnology (Practical Spectroscopy, vol. 25)*. Marcel Dekker, New York
- Emmelius M, Pawlowski G, Vollmann HW (1989) *Angew Chem Int Ed* 28:1445
- Fabian J, Zahradnik R (1989) *Angew Chem Int Ed* 28:1
- Gale RJ (ed) (1988) *Spectroelectrochemistry*. Plenum Press, New York
- Raghavachari HD (ed) (1991) *Electrochemical Interfaces*. VCH, New York
- Wieckowski A (ed) (1999) *Interfacial Electrochemistry*. Marcel Dekker, New York
- For an introductory textbook including applications of NIR-spectroscopy in electrochemistry see: Holze R, *Spectroscopic and surface analytical methods in electrochemistry—A toolbox*. Springer, Berlin Heidelberg New York, in preparation
- Lindon JC, Tranter GE, Holmes JL (eds) (2000) *Encyclopedia of Spectroscopy and Spectrometry*. Academic Press, San Diego
- Salbeck J (1992) *J Electroanal Chem* 340:169
- For a collection of NIR-spectra see: Buback M, Vögel HP *FT-NIR Atlas*, VCH, Weinheim 1993
- Belanzoni P, Re N, Scamellotti A, Floriani C (1998) *J Chem Soc Dalton Trans* 1825
- Haga MA, Ali MM, Sato H, Monjushiro H, Nozaki K, Kano K (1998) *Inorg Chem* 37:2320
- Rocha RC, Toma HE (2003) *Polyhedron* 22:1303
- Barthram AM, Ward MD (2000) *New J Chem* 24:501
- Bayly S, McCleverty JA, Ward MD, Gatteschi D, Totti F (2000) *Inorg Chem* 39:1288
- McWhinnie SLW, Charsley SM, Jones CJ, McCleverty JA, Yellowlees LJ (1993) *J Chem Soc Dalton Trans* 413
- Robin MB, Day P (1967) *Adv Inorg Radiochem* 10:247
- Glöckle M, Kaim W, Katz NE, Posse MG, Cutin EH, Fiedler J (1999) *Inorg Chem* 38:3270
- Bayly S, McCleverty JA, Ward MD, Gatteschi D, Totti F (2000) *Inorg Chem* 39:1288
- Bayly SR, Humphrey ER, de Chair H, Paredes CG, Bell ZR, Jeffery JC, McCleverty JA, Ward MD, Totti F (2001) *J Chem Soc Dalton Trans* 1401
- Harden N, Humphrey ER, Jeffery JC, Lee M, Marcaccio M, McCleverty JA, Rees LH, Ward MD (1999) *J Chem Soc Dalton Trans* 2417
- Kowallick R, Jones AN, Reeves ZR, Jeffery JC, McCleverty JA, Ward MD (1999) *New J Chem* 23:915
- Shukla AD, Ganguly B, Dave PC, Samanta A, Das A (2002) *Chem Commun* 22:2648
- For an introduction see: Rosseinsky DR, Mortimer RJ (2001) *Adv Mater* 13:783; Mortimer RJ (1997) *Chem Soc Rev* 1997 (1997) 147; Mortimer RJ (1999) *Electrochim Acta* 44:2971
- Scrosati B (ed) (1982) *Electrochromism and Electrochromic Displays*. University of Rome, Rome
- Frey GD, Bell ZR, Jeffery JC, Ward MD (2001) *Polyhedron* 20:3231
- Vicsek A Jr (1994) *Chemtracts: Inorg Chem* 6:227
- Braterman PS, Song JI, Wimmer FM, Wimmer S, Kaim W, Klein A, Peacock RD (1992) *Inorg Chem* 31:5084
- MacGregor SA, McInnes E, Sorbie RJ, Yellowlees LJ (1993) *NATO ASI Series, Series C* 385:503
- Richter MM, Brewer KJ (1993) *Inorg Chem* 32:2827
- Richter MM, Brewer KJ (1993) *Inorg Chem* 32:5762
- Poppe J, Moscherosch M, Kaim W (1993) *Inorg Chem* 32:2640
- Beley M, Collin JP, Sauvage JP (1993) *Inorg Chem* 32:4539
- Brewer KJ, Calvin M, Lumpkin RS, Otvos JW, Spreer LO, *Inorg Chem* 28 (1989) 4446
- Richter MM, Brewer KJ (1993) *Inorg Chem* 32:5762
- Heath GA, Raptis RG (1991) *Inorg Chem* 30:4106
- Hartmann H, Kaim W, Hartenbach I, Schleid T, Wanner M, Fiedler J (2001) *Angew Chem Int Ed* 40:2842
- Marvaud V, Launay JP (1993) *Inorg Chem* 32:1376
- Arnold DP, Heath GA, James DA (1999) *J Porphyrins Phthalocyan* 3:5
- Arnold DP, Heath GA (2003) *J Am Chem Soc* 115:12197
- El-Kasmi A, Lexa D, Maillard P, Momenteau M, Saveant JM (1991) *J Am Chem Soc* 113:1586
- Buchler JW, Hammerschmitt P, Kaufeld IE, Löffler J (1991) *Chem Ber* 124:2151
- Tran-Thi T-H, Mattioli TA, Chabach D, Decian A, Weiss R (1994) *J Phys Chem* 98:8279
- Batista AA, Porcu OM, Nascimento OR, Barbosa VM, Oliva G (1993) *J Coord Chem* 30:345
- Laine P, Marvaud V, Gourdon A, Launay JP, Argazzi R, Bignozzi CA (1996) *Inorg Chem* 35:711
- Elliott CM (1980) *J Chem Soc-Chem Commun* 261
- Heath GA, Yellowlees LJ, Braterman PS (1981) *J Chem Soc Chem Commun* 1981:287
- Moscherosch M, Waldhör E, Binder H, Kaim W, Fiedler J (1995) *Inorg Chem* 34:4326
- V.T. Coombe, Heath GA, MacKenzie AJ, Yellowlees LJ (1984) *Inorg Chem* 23:3423
- Lee S-M, Kowallick R, Marcaccio M, McCleverty JA, Ward MD (1998) *J Chem Soc Dalton Trans* 1998:3443
- McWhinnie SLW, Charsley SM, Jones CJ, McCleverty JA, Yellowlees LJ (1993) *J Chem Soc Dalton Trans* 413
- Kaim W, Bruns W, Kohlmann S, Krejčík M (1995) *Inorg Chim Acta* 229:143
- Anaissi FJ, Demets GJF, Toma HE (1999) *ElectroChem Commun* 1:332
- Bruns W, Kaim W, Waldhor E, Krejčík M (1995) *Inorg Chem* 34:663
- Lucas NT, Blitz JP, Petrie S, Stranger R, Humphrey MG, Heath GA, Otieno-Alego V (2002) *J Am Chem Soc* 124:5139
- Lucas NT, Notaras EGA, Cifuentes G (2003) *Organometallics* 22:284
- Klein A, Kaim W (1995) *Organometallics* 14:1176
- Kaim W, Schwederski B, Dogan A, Fiedler J, Kuehl CJ, Stang PJ (2002) *Inorg Chem* 41:4025
- Zhang SY, Sun HR, Yang GY, Xu JQ (1997) *Gaodeng Xuexiao Huaxue Xuebao* 18:772
- Zhang SY, Sun HR, Xu JQ, Shi TS (1997) *Chinese Chem Lett* 8:909

69. Cheng L, Sun H, Liu B, Liu J, Dong S (1999) *J Chem Soc Dalton Trans* 1999:2619
70. Sun HR, Zhang SY, Xu JQ, Yang GY, Shi TS (1998) *J Electroanal Chem* 455: 57
71. Cheng L, Sun H, Liu B, Liu J, Dong S (1999) *J Chem Soc* :2619
72. Sun HR, Yang GY, Xu JN, Xu JQ (1995) *Chinese Chem Lett* 6:1059
73. Sun H, Yang G, Xu J, Xu JQ (1996) *Gaodeng Xuexiao Huaxue Xuebao (Chemical Research in Chinese Universities)* 12:6
74. Wang H, Blair DF, Ellis WR Jr, Gray HB, Chan SI (1986) *Biochemistry* 25:167
75. Geskes C, Hartwich G, Scheer H, Mäntele W, Heinze J (1995) *J Am Chem Soc* 117:7776
76. Whittaker MM, Kersten PJ, Nakamura N, Sanders-Loehr J, Schweizer ES, Whittaker JW (1996) *J Biol Chem* 271:681
77. Rak SF, Jozefiak TH, Miller LL (1990) *J Org Chem* 55:4794
78. Miller LL, Jacoby LJ (1969) *J Am Chem Soc* 91:1130
79. Almlöf JE, Feyerisen MW, Jozefiak TH, Miller LL (1990) *J Am Chem Soc* 112:1206
80. Hünig S, Kemmer M, Wenner H, Perepichka IF, Bäuerle P, Emge A, Gescheid G (1999) *Chem Eur J* 5:1969
81. Lenhard JR, Cameron AD (1993) *J Phys Chem* 97:4916
82. Lambert C, Nöll G (1999) *J Am Chem Soc* 121:8434
83. Lambert C, Nöll G (1998) *Angew Chem Int Ed Engl [Angew Chem]* 37[110], 2107[2239]
84. Lambert C, Nöll G (2002) *Chemistry* 8:3467
85. Perepichka DF, Bryce MR, Batsanov AS, McInnes EJJ, Zhao JP, Farley RD (2002) *Chemistry* 8 (2002) 4656
86. Perepichka DF, Bryce MR, McInnes EJJ, Zhao JP (2001) *Org Lett* 3:1431
87. Demol F, De Backer MG, Levillain E, Sauvage FX (2001) *Spectrochim Acta A* 57:1611
88. Demol F, De Backer MG, Levillain E, Sauvage FX (2001) *Spectrochim Acta A* 57:1611
89. Lee C, Lee YM, Moon MS, Park SH, Park JW, Kim KG, Jeon S.H. Park (1996) *J Electroanal Chem* 416:139
90. Fiedler J, Zali ST, Klein A, Hornung F, Kaim W (1996) *Inorg Chem* 35:3039
91. Krejciak M, Zalis S, Ladwig M, Matheis W, Kaim W (1992) *J Chem Soc Perkin Trans* 2:2007
92. Kadish KM, Gao X, Caemelbecke van E, Suenobu T, Fukuzumi S (2000) *J Phys Chem A* 104:3878
93. Gao XA, Caemelbecke van E, Kadish KM (1998) *Electrochem Solid State Lett* 1:222
94. Rapta P, Stasko A, Gromov AV, Bartl A, Dunsch L (2000) *Proceedings of the Electrochemical Society* 2000–10:10
95. Holze R (2000) *Spectroelectrochemistry of Conducting Polymers*. In: Nalwa NS (eds) *Handbook of Electronic and Photonic Materials and Devices* vol 8. Academic Press, San Diego, p 209
96. Holze R (2001) In: Nalwa NS (ed) *Handbook of Advanced Electronic and Photonic Materials*, vol 2. OPA N.V. and Gordon&Breach, Singapur, p 171
97. Santos JR, Malmonge JA, Silva AJGC, Motheo AJ, Mascarenhas YP, Mattoso LHC (1995) *Synth Met* 69:141
98. do Nascimento GM, da Silva JEP, SIC de Torresi, Temperini MLA (2002) *Macromolecules* 35:121
99. RP McCall, Ginder JM, Leng JM, Ye HJ, Manohar SK, Masters JG, Asturias GE, MacDiarmid AG (1990) *Phys Rev B* 41:5202
100. Sabatani E, Redondo A, Rishpon J, Rudge A, Rubinstein I, Gottesfeld S (1993) *J Chem Soc Faraday Trans* 89:287
101. Han CC, Hong SP (2001) *Macromolecules* 34:4937
102. Neves S, Fonseca CP, Zoppi RA, de Torresi SIC (2001) *J Solid State Electrochem* 5:412
103. Rannou P, Dufour B, Travers JP, Pron A (2001) *Synth Met* 119:441
104. Dufour B, Rannou P, Djurado D, Zagorska M, Kulszewicz-Bajer I, Pron A (2003) *Synth Met* 135:63
105. Sfez R, Dezhong L, Turyan I, Mandler D, Yitzchaik S (2001) *Langmuir* 17:2556
106. Brandl V, Holze R (1997) *Ber Bunsenges Phys Chem* 101:251
107. Barbero C, Miras MC, Schnyder B, Haas O, Kötz R (1994) *J Mater Chem* 4:1775
108. Pomfret SJ, Rebourt E, Monkman AP (1996) *Synth Met* 76:19
109. Hanly NM, Bloor D, Monkman AP, Bonnett R, Ribo JM (1993) *Synth Met* 60:195
110. Xia YN, MacDiarmid AG, Epstein AJ (1994) *Macromolecules* 27:7212
111. Ng SC, Ong TT, Chan HSO (1998) *J Mater Chem* 8:2663
112. Quillard S, Berrada K, Louarn G, Lefrant S, Lapkowski M, Pron A (1995) *New J Chem* 19:365
113. Xie HQ, Ma YM, Guo JS (2001) *Synth Met* 123:47
114. Kaeriyama K, Sato M, Tanaka S (1987) *Synth Met* 18:233
115. Brédas JL, Thémans B, Fripiat JG, André JM, Chance RR (1984) *Phys Rev B* 29:6761
116. Lapkowski M, Gullierez S, Bidan G, Chauvet O (2001) *J Electroanal Chem* 501:166
117. Levillain E, Roncali J (1999) *J Am Chem Soc* 121:8760
118. Kankare J, Lukkari J, Pasanen P, Sillanpaa R, Laine H, Harmaa K, Visy C (1994) *Macromolecules* 27:4327
119. Guay J, Kasai P, Diaz A, Wu RL, Tour JM, Dao LH (1992) *Chem Mater* 4:1097
120. Trznadel M, Pron A, Zagorska M, Chrzaszcz R, Pielichowski J (1998) *Macromolecules* 31:5051
121. Trznadel M, Zagorska M, Lapkowski M, Louarn G, Lefrant S, Pron A (1996) *J Chem Soc Faraday Trans* 92:1387
122. Raimundo JM, Levillain E, Gallego-Planas N, Roncali J (2000) *Electrochem Commun* 2:211
123. Tarabek J, Petr A, Rapta P, Dunsch L (2001) *GDCh-Monographie* 23:275
124. Dunsch L, Rapta P, Schulte N, Schlüter AD (2002) *Angew Chem Int Ed* 41:2082
125. Casado J, Miller LL, Mann KR, Pappenfus TM, Higuchi H, Orti E, Milián B, Pou-Amerigo R, Hernandez V (2002) *J Am Chem Soc* 124:12380
126. Hanack M, Mangold KM, Röhrig U, Maichle-Mössmer C (1993) *Synth Met* 60:199
127. Levillain E, Roncali J (1999) *J Am Chem Soc* 121:8760
128. Chen XW, Inganäs O (1996) *J Phys Chem* 100:15202
129. Garreau S, Louarn G, Froyer G, Lapkowski M, Chauvet O (2001) *Electrochim Acta* 46:1207
130. Ballarin B, Costanzo F, Mori F, Mucci A, Pigani L, Schenetti L, Seeber R, Tonelli D, Zanardi C (2001) *Electrochim Acta* 46:881
131. Pekmez-Ozcicek N, Pekmez K, Holze R, and Yildiz A (2003) *J Appl Polym Sci* 89:862
132. Dufour B, Rannou P, Travers JP, Pron A, Zagorska M, Korc G, Kulszewicz-Bajer I, Quillard S, Lefrant S (2002) *Macromolecules* 35:6112
133. Seshadri V, Wu L, Sotzing GA (2003) *Langmuir* 19:9479
134. Demadrille R, Divisiablohorn B, Zagorska M, Quillard S, Rannou P, Travers JP, Pron A (2003) *New J Chem* 27:1479
135. Yohannes T, Neugebauer H, Luzzati S, Catellani M, Jenekhe SA, Sariciftci NS (2001) *Synth Met* 119:319
136. Wang L, Wang QQ, Cammarata V (1998) *J Electrochem* 145:2648
137. Bäuerle P, Emge A (1998) *Adv Mater* 3:324
138. Jelle BP, Hagen G, Odegard R (1992) *Electrochim Acta* 37:1377
139. Jelle BP, Hagen G, Sunde S, Odegard R (1993) *Synth Met* 54:315
140. Jelle BP, Hagen G, Nodland S (1993) *Electrochim Acta* 38:1497
141. Jelle BP, Hagen G (1993) *J Electrochem Soc* 140:3560
142. Jelle BP, Hagen G (1998) *J Appl Electrochem* 28:1061
143. Jelle BP, Hagen G (1999) *J Appl Electrochem* 29:1103
144. Jelle BP, Hagen G (1999) *Solar Energy Mater Solar Cells* 58:277
145. Rocco AM, De Paoli MA, Zanelli Z, Mastragostino M (1996) *Electrochim Acta* 41:2805

146. De Paoli MA, Zanelli Z, Mastragostino M, Rocco AM (1997) *J Electroanal Chem* 435:217
147. Pages H, Topart P, Lemordant D (2001) *Electrochim Acta* 46:2137
148. Gazotti WA, Depaoli MA, Casalbore-Miceli G, Geri A, Zotti G (1999) *J Appl Electrochem* 29 (1999) 753
149. Cogan SF, Rauh RD, Nguyen NM, Plante TD, Westwood JD (1993) *J Electrochem Soc* 140:112
150. Rauh RD, Cogan SF (1993) *J Electrochem Soc* 140:378
151. Takeshita K, Ashida M (1992) *J Electrochem Soc* 139:285
152. Arntz FO, Goldner RB, Morel B, Hass TE, Wong KK (1990) *J Appl Phys* 67:3177
153. Avellaneda CO, Bulhoes LO (2000) *Proceedings of SPIE-The International Society for Optical Engineering* 4104:57
154. Meng H, Tucker D, Chaffins S, Chen YS, Helgeson R, Dunn B, Wudl F *Advan Mater* 15