COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Electronic coupling in 6,6″-donor-substituted terpyridines: tuning of the mixed valence state by proton and metal ion complexation†

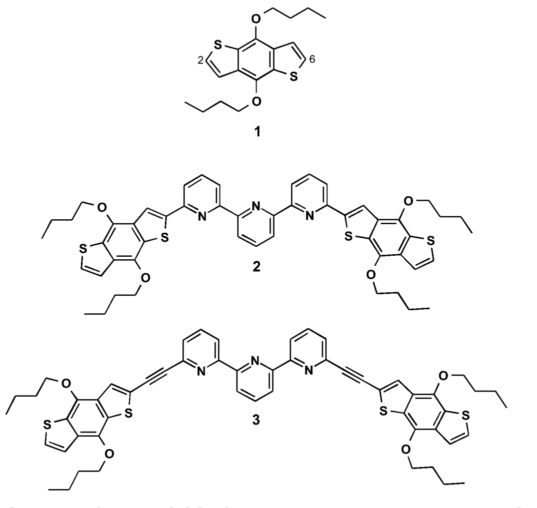
Michael Büschel, Markus Helldobler and Jörg Daub*
Institut für Organische Chemie, Universität Regensburg, D-93040 Regensburg, Germany.
E-mail: joerg.daub@chemie.uni-regensburg.de

Received (in Cambridge, UK) 12th November 2001, Accepted 30th April 2002
First published as an Advance Article on the web 22nd May 2002

6,6″-Terpyridyl-bishydroquinone conjugates are synthesised by Pd-catalyzed cross-coupling and their conformational switching, triggered by protons, zinc(II) or cobalt(II), is studied by cyclovoltammetry and *in situ* UV/Vis/NIR and FT-IR spectroelectrochemistry.

Terpyridines are found to be outstanding ligands leading to supramolecular structures upon metal ion assisted self-assembling.[1] They also inspired research in the field of molecular electronics[2] mainly due to their potential in forming metal ion coordinated terpyridine–bridge–terpyridine complexes enabling intramolecular energy or electron transfer.[3] Besides these fields of application 2,2′:6′,2″-terpyridines are candidates for studying mechanical switching triggered by metal ions. In the uncomplexed state an elongated conformation is prefered whereas upon complexation they adopt a U-shaped conformation.[4] Accordingly, metal ion or proton triggered conformational changes cause spatial reorientation as well as changes of electronic properties and interaction of attached functional units.

In the course of our studies on using charge transfer interaction and switchable intervalence states for controlling transmission in structurally extended systems,[5] we applied 6,6″-functionalized terpyridines as spacers in donor–spacer–donor systems, in order to study coupling of the donor units depending on complexation of the spacer. As donor units we engage dialkyl-bisthiophene-hydroquinone moieties as exemplified by compound **1** (Scheme 1) which unify several beneficial properties, such as (i) a low oxidation potential (420 mV *vs.* Fc^+/Fc in CH_2Cl_2),[6] (ii) completely reversible oxidation to the radical cation (which contrasts with alkylated benzohydroquinones, showing quasireversible redox behaviour,[7]) and (iii) an inherent structural symmetry which allows them to be linked at the C-2 and C-6 positions.



Scheme 1 Oligopyridyl-hydroquinone conjugates investigated.

Conjugates containing terpyridine, quinones or hydroquinones have been studied recently.[8] However, in all these systems the quinone or hydroquinone units are attached at 4′-position. Only minor effects on the properties of the quinone or hydroquinone groups were observed upon complexation indicating weak coupling.

Hydroquinone **1** was prepared according to known procedures.[9] The long chain alkyl groups are utilized to increase the solubility in organic solvents. Compounds **2** and **3** are synthetically accessible in high yields through Pd(0)-catalyzed cross-coupling methods using iodo and stannyl derivatives of **1** and bromo-oligopyridines.[10] For comparison, hydroquinone functionalized 6,6′-bipyridyl and 2,6-pyridyl systems were also studied.

In **3** ethynyl groups are used for bridging since recent work establishes that their geometric and electronic structure enables strong interaction between the attached functional groups.[10] Compounds **2** and **3** show fluorescence with rather high Stokes shifts as depicted in Fig. 1.

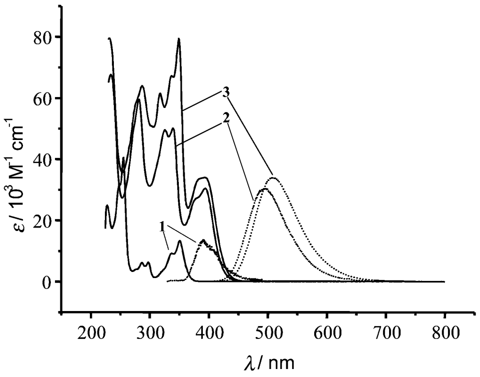


Fig. 1 Absorption and emission spectra of **1**, **2** and **3** in CH_2Cl_2.

All compounds have been investigated by electrochemical and spectroelectrochemical techniques.[11]

Anodic oxidation of compound **1** to its radical cation leads to a reversible wave at 420 mV *vs.* Fc^+/Fc in CH_2Cl_2 (Fig. 2). Compared to the parent compound **1** the oxidation of **2** occurs at 350 and 470 mV and of **3** at 440 and 540 mV *vs.* Fc^+/Fc, respectively. The feature of the oxidation wave of **2** and **3**,

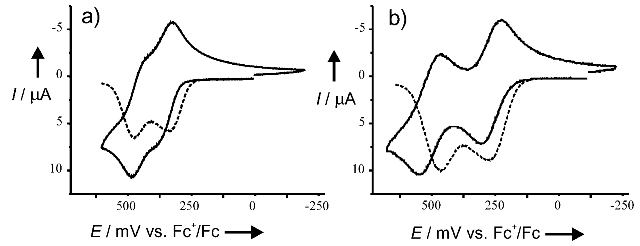


Fig. 2 Cyclo- (solid) and square-wave (dotted) voltammograms of **2** in CH_2Cl_2, 0.1 M $NBu^n{}_4PF_6$; (a) uncomplexed, (b) after addition of TFA.

---

† Electronic supplementary information (ESI) available: Job plots of UV and fluorescence titration of **3** with Zn^{2+}. See http://www.rsc.org/suppdata/cc/b1/b110289c/

DOI: 10.1039/b110289c

exhibiting weak splitting of the two-step oxidation indicates a weak coupling between the donor groups, as summarized in Table 1. In the NIR region a weak absorption at 1350 nm is an indication of a charge transfer interaction in the mono-oxidized forms of **2** (Table 1).

Table 1 Electrochemical data for the terpyridine conjugates

System	ΔE^a/mV	$K_c{}^b$	$\bar{\nu}_{max}$/cm^{-1}	V^c
2	120	100	8120	710
3	100	46	—^{d}	—^{d}
[**2**·2H$^+$]	240	10^4	7420	1540

[a] *vs.* Fc$^+$/Fc, obtained from square-wave voltammetry and simulation. [b] Calculated from the difference of the redox potentials. [c] Coupling according to Hush. [d] ε of intervalence band too small for determination of *V*.

FT-IR spectroelectrochemistry[11] provides information on the vibrational structure and alteration depending on charge distribution. Calculation of the IR absorption bands at DFT level using B3LYP functional and 6/31G* basis set permits tentative assignments of the normal modes. The parent compound **1**, as well as compounds **2** and **3**, exhibit similar changes of the IR bands upon oxidation as depicted in Fig. 3 for terpyridine **3**. Upon oxidation, the decrease of bands in the range of 1500–1400 cm^{-1}, originates from vibrations in the neutral hydroquinone moiety, and the increase of bands in the range of 1050–950 cm^{-1}, which is due to the hydroquinone radical cation, proves high localisation of the positive charges at the hydroquinone substructures leaving the terpyridyl spacer uncharged. The ethynyl-bridged system **3** has an even more sensitive probe for intramolecular charge distribution, due to the C≡C stretching vibration. The higher oxidation potential of **3** compared to the oxidation of the unsubstituted hydroquinone **1** itself indicates the electron withdrawing effect of the ethynyl spacer. FT-IR spectroelectrochemistry demonstrates that the weak C≡C stretching vibration is almost unaffected by oxidation. This finding is again an indication that the positive charge is localized on the hydroquinones. These observations suggest that there is no strong interference between complexation at the terpyridines and the oxidation of the hydroquinone subunits.

Upon the addition of trifluoroacetic acid, zinc(II), or cobalt(II) salts the electronic coupling is enhanced significantly, as cyclic voltammetry demonstrates in the case of protonation (Fig. 2(b)). In accordance with recent investigation by Drew *et al.* a diprotonated terpyridine complex is formed.[4] The formation of 1:1 complexes with zinc(II) and cobalt(II) is verified by fluorescence titrations, with complete quenching of emission upon metal ion complexation. It is also of interest that bipyridyl bridged bishydroquinone compounds do not show enhanced intramolecular coupling upon zinc(II) or cobalt(II) addition. UV/Vis/NIR spectroelectrochemistry of [**2**·2H$^+$] also provides evidence for enhanced coupling, showing a much higher intensity of the intervalence band in the NIR region (see Table 1). It is also found that upon complexation, IR spectra of the mixed valence states are mostly unchanged, suggesting that the electron transfer is restricted to the hydroquinone moieties leaving the terpyridyl bridge unaffected.

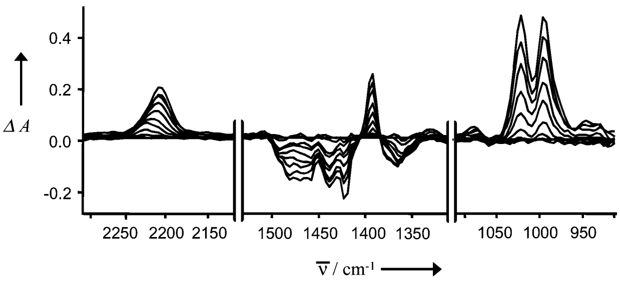


Fig. 3 Differential FT-IR spectroelectrochemistry of the consecutive oxidation of **3** to the radical cation and bisradical cation states (in methylene chloride, the neutral compound is used as reference). The absorption ranges of the supporting electrolyte at about 1650 and 1250 cm^{-1} are omitted.

We conclude from these studies that structural changes originating from protonation or metal ion complexation at the terpyridine subunits tunes the interaction between the hydroquinone subunits in their mono-oxidized state thus leading to a mixed-valence type absorption in the NIR region which signifies electron transfer interaction. This supplements reports on ethynylated polypyridine metal complexes[12] dealing with energy-transfer-based coupling.

It also follows from these studies that the complexation of **2** and **3** leads to a conformational change from a linear to a U-shaped geometry. This brings the redox centers in closer contact and enables increased coupling through space whereas through-bond coupling seems to be of minor extent.

In summary, hydroquinones of type **1** are promising candidates for use as reversibly oxidizable redox probes. Because of their low oxidation potentials they are likely not to electrochemically interfere with other redox processes in multifunctional, supramolecular systems. Complexation of the terpyridine spacer leads to a remarkable increase of electronic coupling which is attributed to enhanced coupling through space. Tuning the intervalence interaction may find potential application in mechanically triggered switching devices. Binding studies of other metal ions are presently in progress.

A fellowship of the 'Studienstiftung des Deutschen Volkes e.V.' for M. B. and of the 'Verband der Chemischen Industrie' for M. H. is gratefully acknowledged. This work is part of the Graduate College 'Sensory Photoreceptors' granted by the Deutsche Forschungsgemeinschaft (GRK 640/1).

Notes and references

1 V. G. Machado, P. N. W. Baxter and J.-M. Lehn, *J. Braz. Chem. Soc.*, 2000, **12**, 431–462.
2 *Molecular Electronics*, ed. J. Jortner and M. Ratner, Blackwell, Oxford, 1997.
3 M. Hissler, A. El-ghayoury, A. Harriman and R. Ziessel, *Angew. Chem. Int. Ed.*, 1998, **37**, 1717–1720; F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1–12; B. Schlicke, P. Belser, L. De Cola, E. Sabbioni and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 4207–4214.
4 M. G. B. Drew, M. J. Hudson, P. B. Iveson, M. L. Russell, J.-O. Liljenzin, M. Skålberg, L. Spjuth and C. Madic, *J. Chem. Soc., Dalton Trans.*, 1998, 2973–2980.
5 J. Daub, M. Beck, A. Knorr and H. Spreitzer, *Pure Appl. Chem.*, 1996, **68**, 1399–1404; M. Büschel, *PhD Thesis*, University of Regensburg, submitted.
6 The oxidation potential is comparable to those of tetrathiafulvalene (0.34 and 0.78 V *vs.* Fc$^+$/Fc in CH$_3$CN, see: A. J. Moore, M. L. Goldenberg, M. R. Bryce, M. C. Petty, J. Moloney, J. A. K. Howard, M. J. Joyce and S. N. Port, *J. Org. Chem.*, 2000, **65**, 8268–8276) and phenothiazine (0.32 V *vs.* Fc$^+$/Fc in THF, see: H. Spreitzer, *PhD Thesis*, 1995, University of Regensburg).
7 A. Zweig, W. G. Hodgson and W. H. Jura, *J. Am. Chem. Soc.*, 1964, **86**, 4124–4136.
8 G. D. Storrier, S. B. Colbran and D. B. Hibbert, *Inorg. Chim. Acta*, 1995, **239**, 1–4; M. Kimura, T. Horai, T. Muto, K. Hanabusa and H. Shirai, *Chem. Lett.*, 1999, 1129–1130.
9 D. W. Slocum and P. L. Gierer, *J. Org. Chem.*, 1976, **41**, 3668–3673.
10 V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 1491–1500; A. El-ghayoury and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 7757–7763 and references therein.
11 M. Büschel, Ch. Stadler, Ch. Lambert, M. Beck and J. Daub, *J. Electroanal. Chem.*, 2000, **484**, 24–32.
12 A. El-ghayoury, A. Harriman, A. Khatyr and R. Ziessel, *Angew. Chem., Int. Ed.*, 2000, **39**, 185–189.