ChemComm
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Monoreduced $[M(R,R'timdt)_2]^-$ dithiolenes (M = Ni, Pd, Pt; R,R′timdt = disubstituted imidazolidine-2,4,5-trithione): solid state photoconducting properties in the third optical fiber window†

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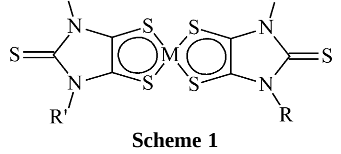
Received (in Cambridge, UK) 28th April 2004, Accepted 28th May 2004
First published as an Advance Article on the web 7th July 2004

Electrochemically monoreduced $[M(R,R'timdt)_2]^-$ dithiolenes, showing unprecedented wavelength selective photoconducting properties in the third optical fiber window (1500–1800 nm), fine-tunable through modifications in the chemical structure, allowed for the fabrication of a test photodetector with a bit rate of about 85 kbit s^{-1}.

The demand for photoactive materials combining the properties of photonic devices with those of standard semiconductors is continuously increasing, due to their possible applications in telecommunications as photodetectors and photo-switches, and in light harvesting systems as solar cells. While most devices operate in the visible region, the near infrared (NIR) is precluded, especially as far as photodetectors for signal applications are concerned.[1] In particular, even if few examples of molecular materials absorbing in the NIR region have been reported,[2] to the best of our knowledge none has been exploited in photodetectors operating in the NIR region. For several years we have studied the general class of neutral dithiolene complexes $[M(R,R'timdt)_2]$ (M = Ni, Pd, Pt; Scheme 1),[3] that feature a very intense absorption (up to 120000 M^{-1} cm^{-1} in toluene) in the range 990–1070 nm, depending on the central metal ion, on the nature of the substituents R and R′, and on the solvent.[3] This very intense absorption positioned close to the emission wavelengths of Nd-based lasers, along with the very high thermal and photochemical stabilities, ensures the candidacy of these dithiolenes as Q-switching dyes in solution.[4] Moreover, their photoconducting properties at the wavelengths corresponding to the NIR absorption maxima suggested a potential use as photodetectors in the first optical fiber window (850–1000 nm).[5] CV measurements performed in CH_2Cl_2 on a large number of dithiolenes of this type‡ show two monoelectronic (coulometrically tested) reversible reduction processes, leading to the monoanionic and dianionic species. Both species proved to be stable over the longer time-span of macroelectrolysis. While dianionic dithiolenes $[M(R,R'timdt)_2]^{2-}$ do not absorb in the NIR region, monoreduced species show absorption maxima falling between 1370 and 1440 nm, for Ni- and Pt-dithiolenes, and between 1670 and 1745 nm for Pd-dithiolenes. Thus, all the monoreduced dithiolenes show a strong bathochromic shift of the NIR absorption compared to the neutral ones (see Fig. 1a for the couple $[Pt(Et_2timdt)_2]^{0/-}$).§¶[6] EPR spectra, recorded on the triad of electrogenerated dithiolenes $[M(Et_2timdt)_2]^-$ [M = Ni(**1**), Pd(**2**), Pt(**3**)], feature a well resolved rhombic symmetry, typical of $S = \frac{1}{2}$ systems. In the case of $[\mathbf{3}]^-$ (Fig. 1b) the doublet derived from the interaction of the unpaired electron with the magnetically active Pt nucleus (^{195}Pt: $I = \frac{1}{2}$; natural abundance 33.8%) can be observed as satellite peaks. The $\langle g \rangle$ values [2.032(5), 2.012(5), 2.017(5) for $[\mathbf{1}]^-$, $[\mathbf{2}]^-$, and $[\mathbf{3}]^-$, respectively] significantly differ from the g_{electron} value (2.0023) indicating that the SOMO possesses a mixed metal–ligand character. The relatively small $\Delta g = g_l - g_h$ values [0.062(5), 0.065(5), 0.220(5) for $[\mathbf{1}]^-$, $[\mathbf{2}]^-$, and $[\mathbf{3}]^-$, respectively] testify to the delocalisation of the unpaired electron on the molecular frame. In all cases, at the glassy–fluid transition, the rhombic spectra collapse giving an unresolved isotropic signal. In the range 178–220 K, the primary geometries of the monoanions are retained, since the $\langle g \rangle$ and the $g_{\text{isotropic}}$ values are nearly identical. Rapid refreezing of the solutions quantitatively restores the original signals, indicating the stabilities of the monoanionic species. According to TD-DFT calculations,** performed on $[M(H_2timdt)_2]^{x-}$ model dithiolenes (M = Ni, Pd, Pt; x = 0, 1), the NIR transition is almost entirely (94.4, 94.0, 95.5%, for M = Ni, Pd, and Pt, respectively) due to a one-electron $91b_{2u}$–$92b_{1g}$ SOMO–LUMO transition (considering one α-electron added on reduction). The stability of the monoreduced forms allows their isolation as salts generated by macroelectrolysis on the preparative scale.‡



Scheme 1

Since the NIR-spectral features of the reduced dithiolenes are preserved in the solid state, it has been possible to prepare a test photodetector based on $[Bu_4N][\mathbf{3}]$, whose diffuse reflectance spectrum (Fig. 2) shows a maximum falling at 1550 nm, and therefore represents an ideal substrate for a device operating in the third window. The responsivity of the device and the diffuse reflectance spectrum of $[Bu_4N][\mathbf{3}]$ are in very good agreement (Fig. 2). At 1550 nm the obtained efficiency on a device biased at 3×10^4 V cm^{-1} is 0.5×10^{-3}%, at least an order of magnitude higher than

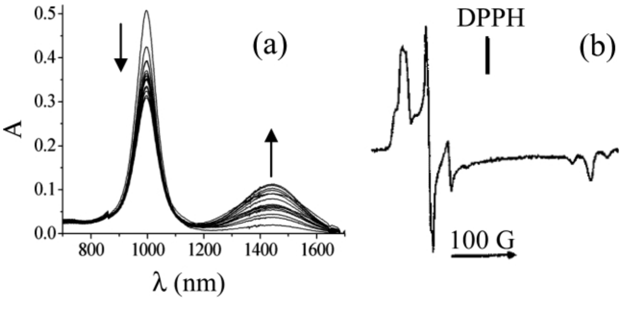


Fig. 1 (a) Spectroelectrochemical reduction of **3** and (b) EPR spectrum of $[\mathbf{3}]^-$ (first derivative; CH_2Cl_2, T = 100 K).

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† Electronic supplementary information (ESI) available: Kohn–Sham MO diagram for $[Pt(H_2timdt)_2]^{0/-}$. Scheme and specifications of the prototype photodetector. See http://www.rsc.org/suppdata/cc/b4/b406406b/

DOI: 10.1039/b406406b

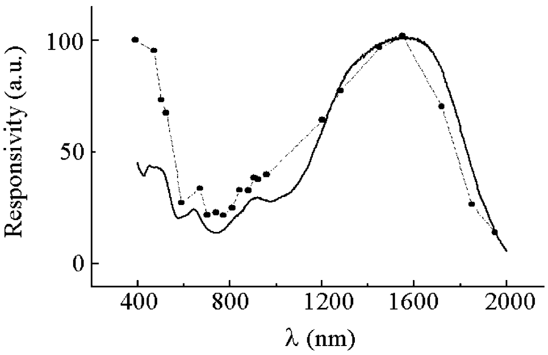

Fig. 2 Solid state diffuse reflectance spectrum (continuous line) and responsivity (circles and dashed line) of the photodetector based on [Bu$_4$N][**3**].

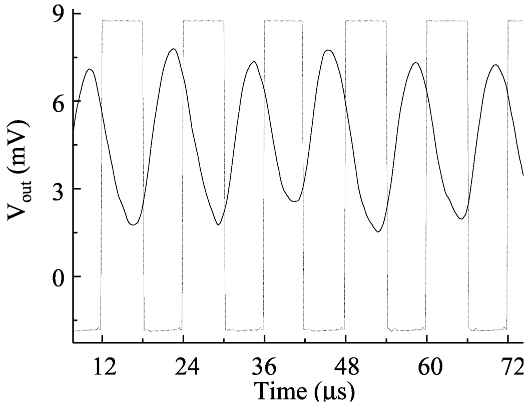

Fig. 3 Response (continuous line) of the photodetector based on [Bu$_4$N][**3**] to a train of light pulses (dotted line) at 1450 nm, 6 μs long, with a repetition period of 12 μs; signal has been averaged to filter noise. The device was connected to a transimpedance amplifier followed by a band pass filter.

the efficiency of any examined neutral dithiolene belonging to the general class [M(R,R′timdt)$_2$].[5] This value obtained in the NIR is comparable to the efficiency in the visible region of photodetectors based on pristine organic semiconductors.[7] The response of the photodetector irradiated with an impinging train of light pulses (λ = 1450 nm) results in the ability of the device to operate at a frequency of 85 kbit s^{-1} (Fig. 3). In conclusion, the unprecedented intense NIR absorption in the third optical fiber window, which can be fine-tuned through modifications in the chemical structure, the ease of deposition and the low cost, compared to that of typical inorganic materials, make monoreduced [M(R,R′timdt)$_2$]$^-$ dithiolenes the materials of choice for fabricating photodetectors operating in the third optical fiber window, which could be applied to optical telecom systems and large area sensor arrays.

Notes and references

‡ Symmetrically and unsymmetrically substituted Ni, Pd, and Pt neutral dithiolenes with different combinations of R and R′ substituents [R = Me, Et, ^{i}Pr, *p*-F–Ph; R′ = Et, naphthyl, *m*-CF$_3$–Ph, *m*-CF$_3$–Bz, *p*-F–Ph, *p*-NO$_2$–Ph, *m,m,p*-(CH$_3$O)$_3$–Ph] were synthesised as previously outlined.[3] Monoreduced dithiolenes were electrogenerated by controlled potential macroelectrolysis. [Bu$_4$N][**3**]: 30 mL of a CH$_2$Cl$_2$ suspension of **3** (50 mg) and Bu$_4$NBF$_4$ (988 mg) were introduced in a three-compartment electrolytic cell and maintained at −0.2 V under stirring in an argon atmosphere until the electrolysis current decayed to about 5% of the original value. The solution was concentrated under reduced pressure and the solid repeatedly washed with hot water to eliminate excess Bu$_4$NBF$_4$. Yield: 56 mg, 91%. C$_{30}$H$_{56}$N$_5$S$_6$Pt, calcd. C 41.22, H 6.46, N 8.01, S 22.00%; found C 41.50, H 7.16, N 7.83, S 20.94%. Mp 256 °C. IR ν_{max}/cm^{-1} 249m, 279m, 301w, 325w, 354w, 386s, 396s, 667w, 697w, 733w, 789w, 957w, 1081w, 1100w, 1350m, 1457m, 1507m, 1521w, 1636m, 1733w and 2959w. NIR λ_{max} = 1408 (MeCN), 1441 (CH$_2$Cl$_2$), 1505 (toluene) nm. CV potentials (*vs.* SCE), NIR maxima positions of all neutral and reduced dithiolenes, and EPR data for [M(Et$_2$timdt)$_2$]$^-$ (M = Ni, Pd, Pt) are available from the authors upon request.

§ Only the monoreduced dithiolene [Ni(^{i}Pr$_2$timdt)$_2$]$^-$, obtained by chemical reduction, has been reported so far in ref 6.

¶ $\varepsilon \approx$ 25000, 30000, and 40000 M^{-1} cm^{-1} for [**1**]$^-$, [**2**]$^-$, and [**3**]$^-$, respectively, in CH$_2$Cl$_2$.‖

‖ As was found for neutral [M(R,R′timdt)$_2$] dithiolenes, the positions of the NIR-absorption maxima recorded for monoreduced dithiolenes depend upon the nature of the substituents R and R′, but the effect is reversed compared to that found for the neutral ones. Aryl substituents cause a hypsochromic shift with respect to aliphatic substituents. All monoreduced dithiolenes undergo a remarkable solvatochromic effect: on passing from MeCN (dielectric constant 37.5) to toluene (2.4), the positions of the maxima undergo bathochromic shifts ranging between 41 (M = Pt; R = Naphthyl; R′ = Et) and 112 nm (M = Pd; R = R′ = Et).

** TD-DFT calculations on [M(H$_2$timdt)$_2$]$^{x-}$ (x = 0,1) model dithiolenes have been performed at hybrid-DFT level (functional mPW1PW; pVDZ Schafer *et al.* basis set for C,H,N, and S; LanL2DZ with ECP's for M). In agreement with the experiment, the transition is calculated to occur at similar energies for Ni- and Pt-dithiolenes, and at lower energies for Pd ones. A linear correlation holds (R = 0.984) between the π–π* transition energies calculated for [M(H$_2$timdt)$_2$]$^{x-}$ and [M(edt)$_2$]$^{x-}$ (M = Ni, Pd, Pt; edt = ethylenedithiolato; x = 0,1) dithiolenes and the experimental ones (average values in the case of [M(R,R′timdt)$_2$]$^{x-}$).

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Typeset and printed by Black Bear Press Limited, Cambridge, England