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Near infrared detection by means of coordination complexes

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Abstract

We report on the detection of near infrared (NIR) radiation in the range 900-1600 nm by means of coordination complexes such as $[M(R,R'timdt)_2]^{x-}$ (M = Ni, Pd, Pt; R,R'timdt = formally monoreduced disubstituted imidazolidine-2,4,5-trithione; x = 0, 1), and $[\{Ru(bipy)_2\}_2(\mu\text{-}L)]^{x+}$ (H_3L = 9-phenyl-2,3,7-trihydroxy-6-fluorone; x = 1, 3). By exploiting these stable coordination complexes absorbing in the visible and NIR region, the poor stability to air and light usually found in low band-gap organic semiconductors can be overcome. $[M(R,R'timdt)_2]$ and $[\{Ru(bipy)_2\}_2(\mu\text{-}L)]^{1+}$ complexes show π-π* transitions in the range 700-1000 nm, which can be bathochromically shifted by changing their oxidation state. Taking profit of this feature, we prepared photodetecting devices operating in the NIR region up to 1600 nm, thus reaching the appealing spectral range of telecommunications. NIR quantum efficiencies of these preliminary photodetectors, made by simple casting from solution, are comparable to those in the visible of most devices based on pristine organic materials. We succeeded in detecting train pulses with a repetition frequency of about 200 kHz at 960 nm and 80 kHz at 1450 nm, to our knowledge an unprecedented result that demonstrates the possibility to enter the NIR region by organic molecular-based devices.

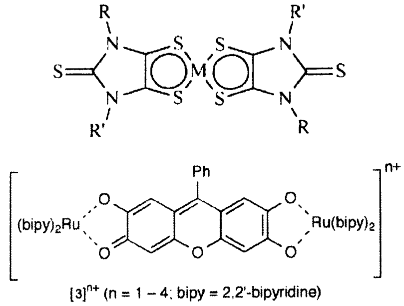
Keywords: detectors, photoconductivity, semiconducting films, organic semiconductors based on conjugated molecules (not polymers)

1. Introduction

Light harvesting devices based on organic semiconductors experienced a fast development in last few years, leading to the demonstration of efficient photo-conversion both in solid state and in photo-electrochemical cells [1,2]. This technology is also promising for light signal photodetectors. In fact, the possibility to easily deposit the active materials from solution on a substrate of ideally any kind and shape [3], allows to prepare a photodetector on prefabricated active substrates. In addition, the possibility to obtain flexible devices, and to easily cover large areas, might open a vast range of applications from which devices based on inorganic semiconductors are excluded.

Only few realizations can be found in the field of light signal detection by organic materials [4,5] and most of them show a spectral sensitivity suited to the detection of visible light pulses, while the highly appealing range of wavelengths of telecommunication interest remained unexplored, mainly because of the poor thermal and chemical stability of common organic materials showing low HOMO-LUMO energy gaps [6].

To overcome this problem we adopted transition metals coordination complexes, namely dithiolenes [7] and dioxolenes, which show both strong low energy transitions and good thermal and photochemical stabilities. Moreover, the possibility to electrochromically shift the positions of their absorption maxima towards longer wavelengths allowed the realization of prototype detectors responsive in all three optical fiber windows.



$[3]^{n+}$ (n = 1 – 4; bipy = 2,2'-bipyridine)

Fig. 1. Scheme of $[M(R,R'timdt)_2]$ dithiolenes (top) and $[\{Ru(bipy)_2\}_2(\mu\text{-}L)]^{n+}$ (n=1-4) dioxolenes (bottom).

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2. Experimental

2.1. Materials

Neutral [M(R,R'timdt)$_2$] dithiolenes (Fig. 1 top, M = Ni, Pd, Pt; R,R'timdt = monoanion of disubstituted imidazolidine-2,4,5-trithione) were synthesized and characterized as previously reported: they show a very intense absorption in the NIR region at about 1000 nm, with extinction coefficient as high as 120000 $M^{-1}cm^{-1}$ in toluene solution [8,9]. Here we report on two particular complexes belonging to this class, namely [Pt(Et$_2$timdt)$_2$] (**1**) and [Pt(Et,Pent-timdt)$_2$] (**2**). [Bu$_4$N][**1**], containing the monoanionic dithiolene [Pt(Et$_2$timdt)$_2$]$^-$, synthesized according to the procedure recently reported using 1,4-phenilenediamine as reducing agent [10].

Dinuclear ruthenium complex (see Fig. 1 bottom) [{Ru(bipy)$_2$}$_2$(μ-L)][PF$_6$] ([3][PF$_6$]; H$_3$L = 9-phenyl-2,3,7-trihydroxy-6-fluorone) was prepared as described earlier [11] and converted to [3][PF$_6$]$_3$ as follows. A mixture of [3][PF$_6$] (50 mg, 0.0388 mmol) and two equivalents of acetylferrocenium hexafluorophosphate (29 mg, 0.077 mmol) dissolved in CH_2Cl_2 was stirred under N_2(g) for 30 minutes. The solvent was then removed *in vacuo* and [3][PF$_6$]$_3$ was recrystallized from CH_2Cl_2/hexane to remove the acetylferrocene by-product.

2.2. Devices realization and photocurrent measurements

Devices were prepared by casting a solution of the active material on a hot SiO_2 substrate where a chromium micro-lithography was previously provided: a low capacitive planar metal-semiconductor-metal configuration was obtained (Fig. 2) with interelectrode spacings of few microns (3 to 12 μm). This structure, besides increasing signal-to-noise ratio with respect to a vertical one thanks to its low intrinsic capacitance [12], allows also to avoid the potentially critical step of the evaporation of a metal onto the active material.

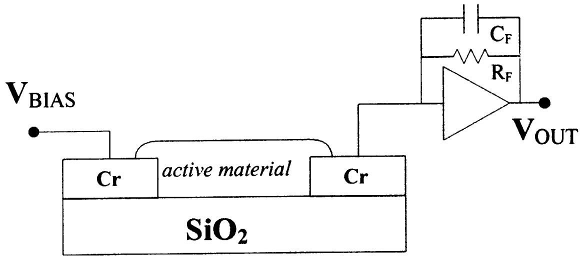
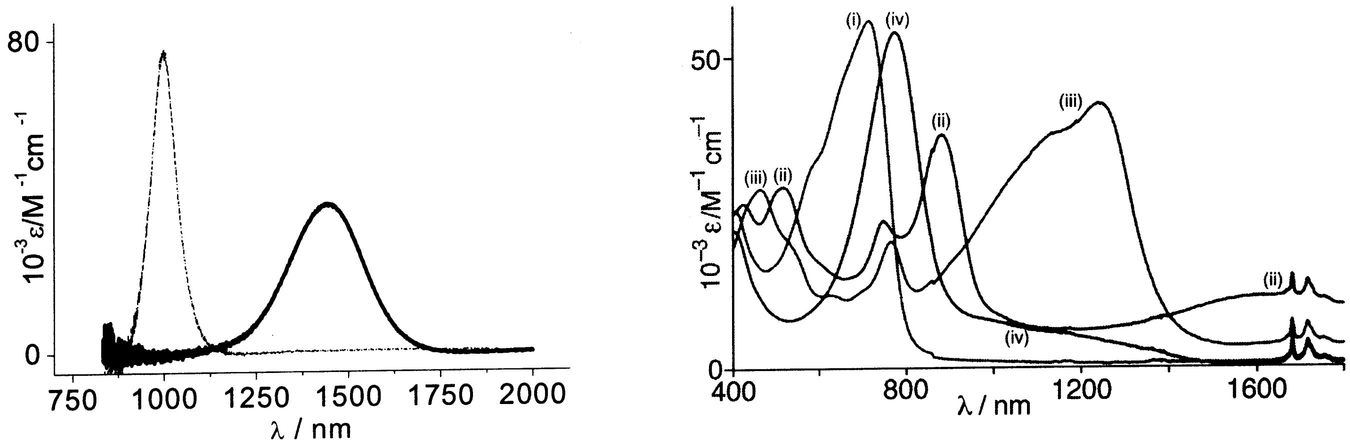


Fig. 2. Schematic representation of the planar configuration adopted for the photodetector, biased and connected to a transimpedance amplifier.

We irradiated our prototype photodetectors with a set of light emitting diodes; photocurrents were measured by biasing the device with a voltage source and connecting it to a transimpedance amplifier, as shown in Fig. 2. All measurements were performed in vacuum at a pressure of about 10^{-5} mbar. The light intensity of each LED was measured by means of a silicon photodiode for the visible range and by means of a GaInAsSb:GaSb photodiode for the infrared region of the spectrum. For the measurement of short light pulses the Signal to Noise ratio of the amplifying chain was enhanced by means of a band pass SILENA 7614 amplifier.

3. Results and Discussion

Both dithiolenes and dioxolenes, besides showing good chemical and thermal stabilities, are characterized by low energy π→π* transitions due to a high degree of electronic delocalization over the entire molecules [8,11]. Moreover, they are soluble in common organic solvents, thus allowing a simple deposition by casting. By adopting complex **2** as



(a) (b)

Fig. 3. UV-Vis-NIR molar extinction coefficient spectra of **1** (dotted line, a) in $CHCl_3$ and [Bu$_4$N][**1**] (continuous line, a) in CH_2Cl_2. and of complex **3** in MeCN in the oxidation states from +1 to +4 (i to iv, b).