Photochromic nanocomposite films of mononitrosyl complexes embedded in polymer matrices

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ABSTRACT

New photochromic nanocomposite films based on mononitrosyl ruthenium complex [RuCl(NO)py4]2+ have been synthesized by dispersion in polymer matrices. Infrared study under irradiation reveals that the composites present very high population of metastable state (~45%). Nanoparticles of molecular complex stabilized in different matrices have been observed by transmission electron microscopy.

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Research devoted to new generations of data storage devices has recently explored the use of new photoactive materials [1–4]. Materials based on molecules that can be switched between two discrete states, may show storage capacities similar to DNA, i.e. in the order of the terabyte/cm3. Photochromic complexes bearing the nitrosyl ligand exhibit long-lived metastable states upon irradiation and have been extensively studied in this field [5–7]. Photorefractive and photosensitive devices are also of high interest for applications such as real-time holography [8,9].

Upon specific conditions of irradiation and temperature, the conformation of the nitrosyl ligand (GS) switches reversibly towards the isonitrosyl (MS1) and the bent (MS2) forms. The metastable linkage isomers MS1 or MS2 are identified by the decay temperature (Td) which is the temperature of the peak in the heat flow curve of a DSC experiment. This reversible change can also be evidenced by the νNO IR shift. Even though not general [10], it is most often shifted towards lower wave numbers. The nitrosyl ligand interconversion leads to a significant change of the refractive index of the compound [6]. Previous studies have shown that the photoinduced structural change observed on the sodium nitroprussiate salt (SNP), is large enough to allow data writing and reading [7]. In order to be incorporated into optical devices, photochromic complexes have to be processed, more likely as films, and their properties should be retained after processing. Polymer and silica matrices are the most popular for inclusion of photochromic materials. Recently, photoswitchable hybrid materials were successfully prepared by embedding nitrosyl complexes in sol–gel matrices [11,12].

Transparent thin films may be also processed through the inclusion of an active material within a polymer matrix. Numerous examples have been reported with biological compounds [13], photochromic materials [1,14–16] or NLO materials [17]. Polymer:spiroinanes and polymer:diarylethenes composites show only slight changes in photochromic properties compared to the single crystals ones [18]. These composites appear as homogeneous distributions of the active materials (haemoglobin, chromophores . . . ) as nano-sized objects.

During the last decade, we have focused on the study of ruthenium analogues of SNP, in particular on the [RuCl(NO)py4]Br2H2O (1) and [RuCl(NO)py4]2[Pf6]·1/2H2O (2) complexes (py = pyridine) because of their outstanding photochromic properties, (Td = 246 K, 76% MS1,Td = 161 K, 56%MS2 for 2) [19]. A schematic illustration of the photoinduced processes occurring in these salts is shown in Fig. 1 with the wavelengths generating the MS1 (470–514 nm) and MS2 states (successive irradiation at 470–514 nm and at 980–1064 nm).

More recently, we have studied the inclusion of these complexes into composites, by selecting polymers that fit the requirements for optical data storage, i.e. leading to transparent films: polyvinylalcool (PVA), poly(4-vinylpyridine) (PVP), polyvinylphenoil (PVPb), and nitrocellulose (NC). All these polymers but nitrocellulose are water or ethanol soluble. NC:complex composites are prepared in acetonitrile. The photochromic polymer compos-
ites are processed as thin films and contain nanoparticles of 1 and 2. Infrared spectroscopy upon irradiation and transmission electron microscopy evidence the photochromic properties of the composites and the morphology of the included materials, respectively.

Films of 1 and 2 are made from deposition on glass plates and drying of 6 drops of the polymer/complex solutions. These solutions are obtained from mixing of complexes 1 or 2 in polymer matrices dispersed in the appropriate solvent (water for PVA, ethanol for PVP and PVPh; acetonitrile for NC) [20].

In these conditions, the films deposited are transparent (Figs. 2 and 3) and offer a good adhesion on the substrate. The colour of the films is uniformly orange meaning that the photochromic complex is equally distributed within the polymer matrix. The colour intensifies with increasing concentrations of ruthenium complex. The films show a rather uniform thickness ranging from 70 μm to 180 μm for polyvinyl polymers and 40 μm for nitrocellulose with a slightly higher one (<10%) at the periphery. In order to avoid it, deposits can also be obtained by spin-coating [21] with a thickness around 150 nm for polyvinyl polymers (75 nm for PVA and 250 nm for PVP) and 550 nm for nitrocellulose. Increasing amounts of inserted complex is also evidenced by the intensity of the ν(NO) band relative to the IR bands of the polymer. Indeed, infrared spectroscopy under irradiation at low temperature is an excellent and easily handled technique to identify the isomerisation.

The existence of metastable states is associated with the nitrosyl ligand interconversion which is easily observable by the shift of the ν(NO) vibration frequency upon irradiation. On powdered samples of photochromic complexes 1 and 2, 17% and 76% of the molecules switch to MS1 state, respectively. Infrared data of the composite films, collected at 100 K before and after irradiation are reported in Figs. 4 and 5 [22].

In both spectra, the intensity of the ν(NO) vibration characteristic of the photochromic complex in the ground state (GS: 1910 cm⁻¹) decreases after irradiation. This feature is accompanied with the appearance of the ν(NO) vibration characteristic of the MS1 state (MS1: 1777 cm⁻¹). The GS peak area ratio before and after irradiation in the absorbance spectra allows evaluating the population of the MS1 state. In all cases, the process is reversible. There is no decomposition and no evidence of NO release. MS1 population in PVA:1 and PVP:1 reaches 34% and 32% respectively, a value larger than that of 1 alone (vs. 17%). The increase in photoconverted molecules is supported by the increase in the surface of photochromic material exposed to the light beam. Surface increase results from the size reduction of the particles, occurring when they are produced within the polymer matrix. The photoconversion amount is much lower (8%) when PVPh is used, probably because the OH groups of the polymer create strong interactions that help the GS of the photochromic complexes to be stabilized. In contrast, the photoconversion for NC:2 composite material is almost as high as for 2 alone (62% vs. 76%). The nitrosyl ability to rotate is weakly affected by interactions between the NC polymer and 2.
The organisation of the ruthenium complexes in the matrix has been observed by transmission electron microscopy [23]. The polymer:complex composites were directly produced on the microscope copper-grids. The film should not be too thick to get good quality images. Micrographs of PVP:1 and NC:2 composites are shown on Figs. 6 and 7.

Dark nanoparticles dots are observed on both micrographs. These nanoparticles are spherical and their diameter ranges from 10 to 40 nm in the case of polyvinyl composites. Their size and distribution are similar in the other two polymers PVA and PVPh. For NC composites, we obtained nanorods ranging between 10 × 10 nm and 50 × 15 nm. The shape and the size of the nanoparticles are independent on complex concentration variation. Nano-objects appear as dark dots uniformly distributed within the polymer. Considering that the preparation of films is performed from 2 pure reactants (polymer and complex) and that the infrared spectra of the composites exhibit the IR vibrations of both the complex and the polymer without significant changes, we can assume that the photochromic complex is stabilized as nanoparticles. Moreover, EDX analyses of the particles confirm the presence of RuCl(NO)py4[2]: the 3 signals at 2.6, 19.2 and 2.8 keV in 1 and 2 are characteristic of the Lxα, Kxα lines of ruthenium and Kxα lines of chlorine atoms, respectively. In addition, the signals for 2 at 0.68 and 2.05 keV corresponds to the Kxα line of fluorine and phosphorous, respectively. An intense line at 8.04 keV is attributed to ½RuCl that the photochromic complex is stabilized as nanoparticles.

In conclusion, we have prepared transparent photochromic nanocomposite films by inclusion of two mononitrosyl complexes [RuCl(NO)py4]Br2H2O (1) and [RuCl(NO)py4][PF6]2·2H2O (2), in polymer matrices. The photochromic property of the ruthenium complexes in the composites is supported by the shift of their characteristic VNO vibration due to ligand inversion upon irradiation. 1 and 2 are embedded as nanoparticles within the polymer matrices. This feature is rarely observed on molecular complexes. Inert polymer matrices as PVA and PVP favour the increase of the photoconverted population. On the other hand, the metastable MS1 states of 1 and 2 are differently reached in PVC and NC matrices, because of intermolecular interactions driven by the polymer. Nevertheless, the amount of photo-generated states is quite large in all films. Note that, the NC:2 composite shows a conversion value as high as that of a SNP single crystal. Thus, this study demonstrates that photochromic complexes can be embedded within polymer matrices and retain their optical properties. Such polymer:photochromic complex composites may therefore be evaluated as photoactive media for applications with a short lifetime of the refractive or photochromic response, as it was shown that this type of linkage isomers can be generated by short laser pulses at room temperature [24].

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References

[20] The complex 2 is prepared as previously reported [13]. 1 is synthesized from 2 and excess of NBu4Br in acetonitrile. Polymer powders are dispersed in appropriate solvents: water for PVA, ethanol for PVP and PVPh; acetonitrile for NC. PVA, PVP, PVPh and NC were purchased from Aldrich. 1 is embedded in water soluble polymer (PVA, PVP, PVPh) while nitrucellose is used for the water insoluble complex 2. Different concentrated films are prepared with a weight ratio Polymer/Complex in the range from 50/1 to 57/1 for a maximum concentration in ruthenium complex of 90 nmol L–1. Thickness is estimated by Bausch and Lomb microscope (model StereoZoom 7).
[21] Homogeneous deposits are spin-coated on dry-clean glass plate of 1 cm2 by TP1100 SET Spin-coater at 4000 rpm and an acceleration of 4000 rpm s–1 during 30 s. The thickness is measured with a TENCOR-P2 Long Scan profiler.
[22] IR Measurements under irradiation are performed with monochromatic light from a diode laser (λ = 473 nm). Infra red spectra are detected with a PERKIN ELMER CX2000 spectrophotometer. The films are cooled down to 100 K in a cryostat (Specac/P/N 20000). KBr windows allow the irradiation at 473 nm.
30 mW cm⁻² for 180 min. In case of PVA:1 sample, IR pellets are prepared from grated dried films mixed in KBr (1/100) because of the solubility of PVA in H₂O. Otherwise the solubility of PVP and NC in ethanol and acetonitrile, respectively, allows deposition of drops of solution on the pure KBr pellets.

[23] A JEOL-1011 TEM and a JEOL-2100F/EDX TEM equipment is used for the observations of the composites morphologies.