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Functionalization of zinc oxide nanorods with diarylethene-based photochromic compounds

Sandrine Remy, Syed Mujtaba Shah, Cyril Martini, Guillaume Poize, Olivier Margeat*, Arnault Heynderickx, Jörg Ackermann, Frédéric Fages

CINaM, UPR 3118 CNRS – Aix Marseille Université, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France

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ABSTRACT

Two diarylethene molecules functionalized with a carboxylic acid function were grafted onto the surface of zinc oxide nanorods. Photochromic studies based on electronic absorption spectroscopy in solution showed that the switching units operate in a bidirectional mode, allowing both ring closure and ring-opening processes to take place successively in photochemical sequences combining irradiations of the open species at 300 nm and the closed ones at 500 nm. Depending on the molecular structure, some losses were observed presumably due to photodegradation. Compound **2** containing a terminal phenyl unit provides a longer conjugation pathway, thus offering red-shifted electronic absorption and better photochemical stability.

1. Introduction

Nanosciences and nanotechnologies are fostering the search for new strategies that enable the facile implementation of functional elements into nanodevices. To this end, inorganic nanorods (NRs) and nanowires are the subject of a tremendously increasing interest because their anisotropic shape and properties and their large surface-to-volume ratio offer far-reaching perspectives in electronics, optics, photovoltaics and sensing [1–7]. Functionalization of 1D nanostructures with organic molecules was shown to enable the generation of functional hybrids with tunable properties in which organic and inorganic components operate in synergy [7–13]. In contrast to the case of spherical nanoparticles [14], surface functionalization of NRs and nanowires is still poorly investigated.

Recently, fluorescent molecules performing logic functions were attached to silicon nanowires in order to produce stimuli-sensitive nanostructures for nanosized memories and computing devices [15]. In that connection, we report here the light-induced switching of a series of dithienylethene derivatives anchored to zinc oxide nanorods as a first approach toward photo-switchable nanorods. Perhaps one of the most widespread phenomenon which underspins light-induced switching at the molecular level is photochromism [16,17]. Anchoring photochromic molecules to metallic [18] or semiconducting [19] quantum dots has allowed the translation of this fundamental molecular function into the nanoscopic world. In the search for inorganic nanorods as building-blocks for the construction of logic and memory circuit elements performing directional information processing and transport, it occurred to us that zinc oxide nanorods could represent a candidate of choice [20]. First, zinc oxide is a cheap, nontoxic material with versatile properties and the large-scale synthesis of ZnO nanorods is easy [12,21,22]. Second, surface functionalization of zinc oxide is straightforward and is based on the known ability of carboxylic acid derivatives to tightly bind the surface of metal oxide semiconductors, TiO_2 being the archetypal example [23]. In this study, we opted for dithyenylethene derivatives as photochromic units because they were already proven to possess a range of versatile properties [24]. Since the electronic properties of zinc oxide are very sensitive to surface properties [25], and given the high surface-to-volume ratio in such nanocolloids, the implementation of photochromic effect might represent an approach toward photo-modulating semiconducting properties of the nanohybrids. For example, functionalizing inorganic surfaces with azobenzene ligands has led to the development of photomagnetic nanomaterials [26].

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* Corresponding author. Tel.: +33 491829341; fax: +33 491829301.
E-mail address: olivier.margeat@univmed.fr (O. Margeat).

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In this paper, we report a study of the photochromic properties in solution of two dithienylethene derivatives, **1** and **2** (Scheme 1), tethered to zinc oxide NRs via two different spacers. Compound **2** has a π conjugation extended on one side of the central switching unit, which is expected to provide better photochromic properties in the visible region.

2. Experimental

2.1. General

Zinc oxide NRs were synthesized according to a procedure published recently [27]. We used ZnO NRs having an aspect ratio around 6 with an average diameter of 8 ± 1 nm and length of 50 ± 5 nm, as determined by TEM (Fig. 1). Compound **2** has been obtained according to literature [28].

2.2. Synthesis

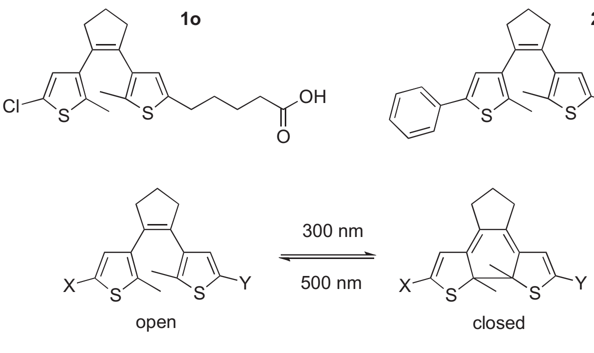
2.2.1. 1-(5-Chloro-2-methylthien-3-yl)-2-[5-(4-cyanobutyl)-2-methylthien-3-yl]cyclopentene

To a solution of 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene [29] (300 mg, 0.91 mmol) in THF (20 mL) cooled to −78 °C was added tert-butyllithium (0.56 mL of a 1.7 M solution in pentane, 0.95 mmol) slowly under argon. The mixture was stirred for 90 min and 1,4-diiodobutane (0.84 g, 0.027 mol) was added in one portion. This solution was allowed to warm to room temperature and stirred for a further 8 h, then quenched with H_2O (10 mL). The water layer was extracted with diethyl ether (2 × 15 mL) and the combined organic phases were dried ($MgSO_4$), filtered and the solvent was evaporated in vacuum. Subsequent purification by silica gel column chromatography (hexane) afforded a mixture of 1-(5-Chloro-2-methylthien-3-yl)-2-[5-(4-iodobutyl)-2-methylthien-3-yl]cyclopentane with 1,4-diiodobutane.

The mixture was dissolved in acetonitrile (20 mL). Potassium cyanide (1.76 g, 0.027 mol) and 18-crown-6 (450 mg, 1.7 mmol) was added, and the solution was stirred overnight at room temperature [30]. The reaction mixture was poured into water (40 mL) and extracted with ethyl acetate. The extract was washed successively with water and brine, and dried over anhydrous $MgSO_4$. The ethyl acetate solution was evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography (cyclohexane/dichloromethane/ether; 5/2/1) to give 1-(5-Chloro-2-methylthien-3-yl)-2-[5-(4-cyanobutyl)-2-methylthien-3-yl]cyclopentene as an oil (249 mg, 73%).

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.52{-}1.71$ (m, 4H), 1.76 (s, 3H), 1.87 (s, 3H), 1.90–1.98 (m, 2H), 2.19–2.29 (m, 2H), 2.60–2.69 (m, 6H), 6.30 (s, 1H), 6.49 (s, 1H) ppm.

^{13}C NMR (63 MHz, $CDCl_3$) $\delta = 13.86$, 14.03, 16.74, 22.76, 24.24, 26.74, 28.72, 30.07, 38.06, 119.38, 124.54, 125.35, 126.74, 132.30, 132.91, 133.11, 134.73, 135.08, 135.47, 139.25 ppm.



Scheme 1. Molecular structures used in this study and photoisomerization reaction between open and closed forms.

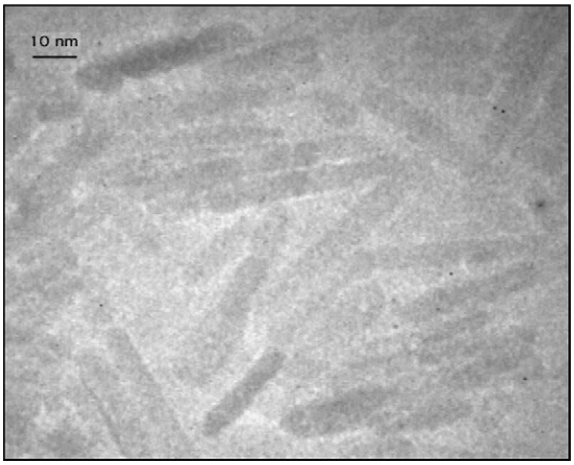


Fig. 1. Transmission electron microscopy (TEM) image of the dithienylethene-functionalized ZnO nanorods.

2.2.2. 1-(5-Chloro-2-methylthien-3-yl)-2-[5-(4-carboxybutyl)-2-methylthien-3-yl]cyclopentene (*1o*)

To a solution of 1-(5-Chloro-2-methylthien-3-yl)-2-[5-(4-cyanobutyl)-2-methylthien-3-yl]cyclopentene (249 mg, 0.66 mmol) in ethanol (3 mL) was added KOH (111 mg, 2 mmol) in water (2 mL) at room temperature with stirring. The reaction mixture was refluxed for 3 h then acidified to a pH of 1 with concentrated HCl and extracted with ethyl acetate. The extract was washed successively with water and brine, and dried over anhydrous $MgSO_4$. The ethyl acetate solution was evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography (ethyl acetate/Cyclohexane, 1/3) to give pure **1o** (213 mg, 0.54 mmol, 82%).

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.52{-}1.62$ (m, 4H), 1.74 (s, 3H), 1.85 (s, 3H), 1.86–1.99 (m, 2H), 2.24–2.34 (m, 2H), 2.55–2.72 (m, 6H), 6.31 (s, 1H), 6.50 (s, 1H), 10.08 (b, 1H, CO_2H) ppm.

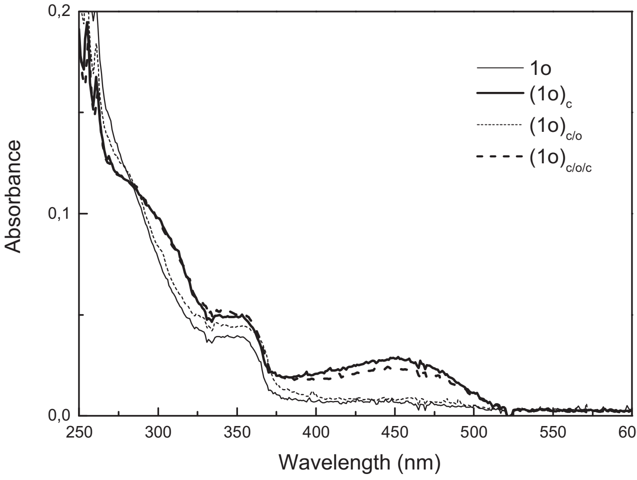


Fig. 2. Electronic absorption spectrum of compound **1** in THF (room temperature, 10^{-5} M) subjected to irradiations cycles using first UV light (300 nm), then visible light (500 nm). Irradiations periods are 30 min in order to reach the photostationnary state.

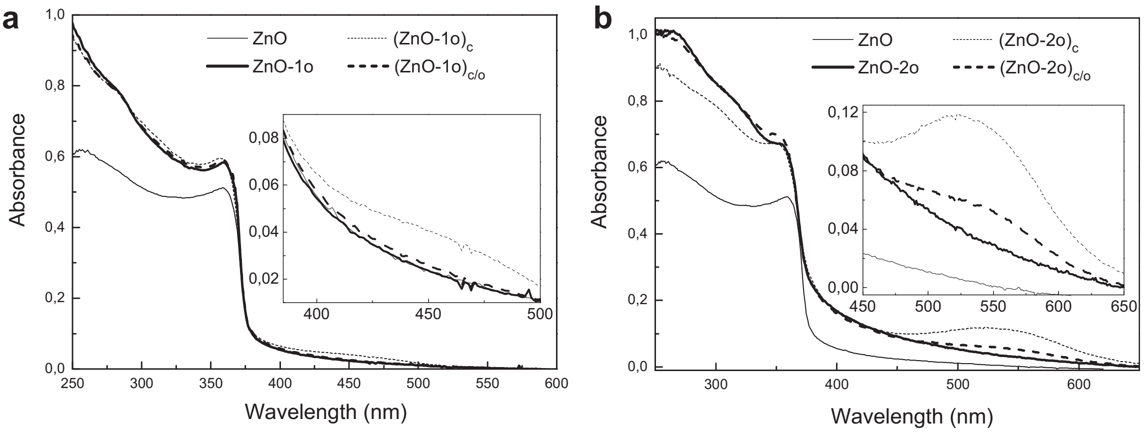


Fig. 3. Electronic absorption spectra of zinc oxide NRs grafted with (a) **1o** and (b) **2o** species before and after 300-nm and 500-nm irradiations.

^{13}C NMR (63 MHz, CDCl$_3$) $\delta = 13.96$, 14.13, 22.87, 23.79, 29.41, 30.74, 33.73, 38.19, 38.25, 124.70, 125.13, 126.80, 132.16, 133.05, 133.07, 134.75, 135.20, 135.64, 140.27, 180.18 ppm.

2.2.3. *Dithienylethene grafting on ZnO nanorods*

ZnO nanoparticles (5 mg) obtained after centrifugation were suspended in 5 mL tetrahydrofuran (THF) as solvent and to this suspension was added a THF solution (2×10^{-4} M) of the photochromic compounds **1** or **2**. The solution was kept standing in the dark for about 12 h then two precipitation steps for washing were done by centrifugation followed by dispersion in 5 mL THF. The final solution was then diluted ten times for spectroscopic studies. Using these conditions, the ZnO nanorods surface covering by the photochromic compounds was estimated at 40%, without taking in count the loss due to the washing steps.

3. Results and discussion

Fourier transform infrared spectroscopy (FT-IR) of a solid sample of grafted ZnO NRs obtained after solvent evaporation showed the presence of strong and broad carboxylate asymmetric at ca. 1600 cm^{-1} n(-COOas) and symmetric 1385 cm^{-1} n(−COOs) bands. The presence of these carboxylate bands in the IR spectra confirm that the carboxylic acid groups are adsorbed on the ZnO surface in a dissociated form, as classically observed in the case of TiO$_2$ [31].

In this study, **1o** and **1c** denote the open and closed forms of compound **1**, respectively. Upon irradiation of the open form **1o**, a ring closure reaction occurs (Scheme 1) leading to the colored closed form which is noted as **(1o)c**. Conversely, irradiation of **1c** leads to **(1c)o**. In the case of a multiple irradiation sequence, the letter **c** or **o** is added at the end of the symbol of the initial species in order to indicate the final state. For example, photo-induced ring closure of **(1c)o** leads to **(1c)o/c**. The same holds for compound **2**.

Fig. 2 shows the changes in electronic absorption spectra of compound **1o** in solution (THF, 10^{-5} M) when submitted to irradiation periods of 10 min with successively 300-nm or 500-nm light. Upon UV exposure, one notes the building of a new, broad absorption band centered at 450 nm, corresponding to the formation **(1o)c**, leading to a solution orange in color. Upon visible-light irradiation, a photobleaching is observed upon formation of the open species **(1o)c/o**, consistently with the known behavior of dithienylethene derivatives. The original absorption spectrum is almost reached, indicating the reversibility of the electrocyclic process in compound **1** is not fully complete, probably due to some photochemical degradation upon irradiation with such long time periods under UV light. Upon subsequent UV exposure, the formation of **(1o)c/o/c** takes place in the solution.

Grafting of compound **1o** onto ZnO NRs resulted in the hybrid nanostructure **ZnO-1o**. Its absorption spectrum is a superposition of the spectral bands of compound **1o** and zinc oxide (Fig. 3a). Upon irradiation with light of 300 nm, the formation of the closed isomer

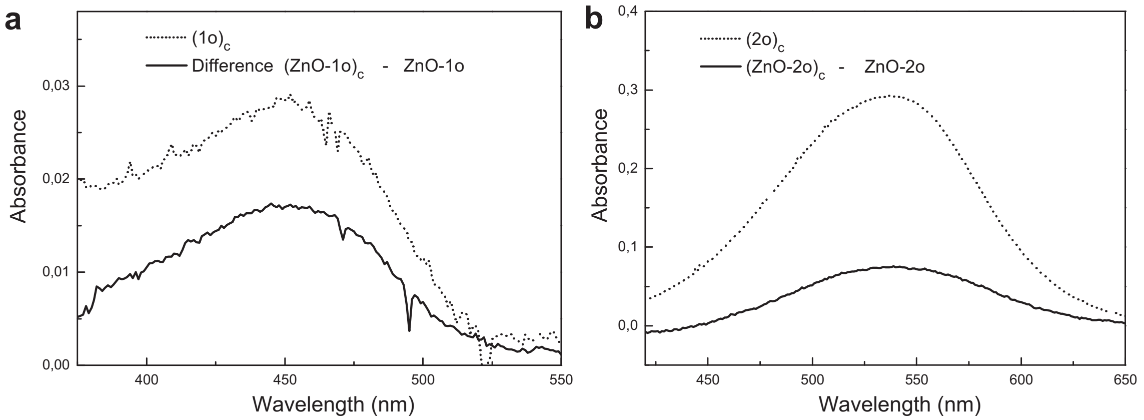


Fig. 4. Electronic absorption spectra of **(ZnO-1o)c** and **(Zn-2o)c** in THF obtained after subtraction of the spectra of **ZnO-1o** and **ZnO-2o**, respectively, in order to eliminate the contribution of light scattering, and compared to those of the corresponding unbound species.

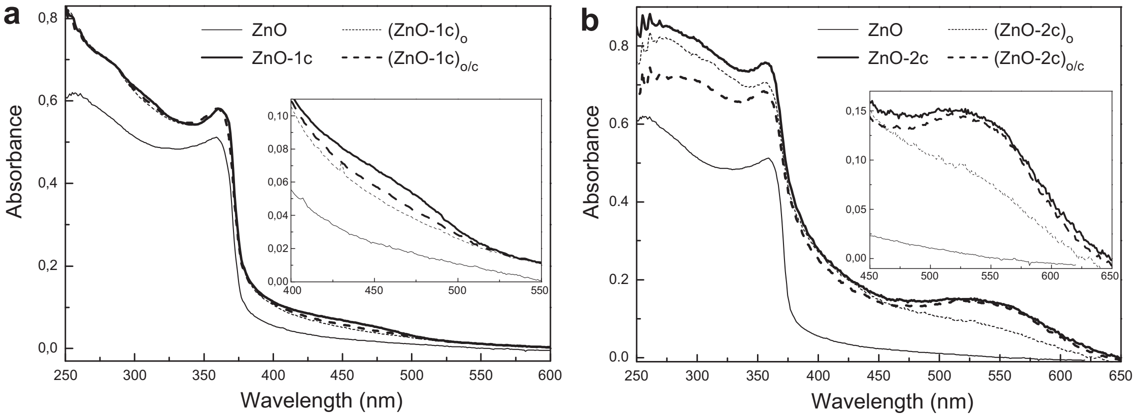


Fig. 5. Electronic absorption spectra of zinc oxide NRs grafted with (a) **1c** and (b) **2c** species and before and after 500-nm and 300-nm irradiations.

(ZnO-1o)c was observed. As the photostationary state was not reached under these conditions, because of part of the incident light was absorbed by ZnO NRs, only the qualitative study of the band position is useful and for **(ZnO-1o)c** it matched that obtained for the free corresponding molecules (Fig. 4a). Ring-opening was also observed to be effective (Fig. 3a) showing that the switch operates in a bidirectional mode. This indicates that zinc oxide does not quench significantly the excited state of the photochromic system. When **1c** was instead grafted onto the surface of zinc oxide, its ring-opening reaction to **(ZnO-1c)o** was observed to be efficient but not the subsequent transformation into **(ZnO-1c)o/c** (Fig. 5a), in contrast to the previous sequence. Although this behavior remains yet unclear, photochemical degradation cannot completely be ruled out because using **1c** implies the occurrence of an extra irradiation step in the process.

The same sequence of experiments was carried out using compound **2** grafted on zinc oxide nanorods. From Fig. 3b, it can be seen that grafting is accompanied by a large increase of light scattering relative to the solution of bare nanorods, which was not the case when compound **1** was used. This would mean that **ZnO-2o** is less soluble than **ZnO-1o**, which could stem from the shorter tether and the presence of the terminal phenyl unit in **2** relative to **1**. Upon UV light irradiation, **ZnO-2o** undergoes a change in color, leading to the purple **(ZnO-2o)c** hybrid (Fig. 3b). Here again, grafting of the photochromic molecule on zinc oxide does not hamper the ring-closure process. It is noteworthy that, as expected, the absorption maximum of the ring-closed hybrid is red-shifted as compared to **(ZnO-1o)c**, being consistent with the extended conjugation in **2** relative to **1** (Fig. 4b). Remarkably, it can also be seen that grafting the closed species **2c** leads to **ZnO-2c** that can undergo readily ring-opening followed by ring closure upon irradiation with visible and UV light, respectively. Compound **2** allows the generation of hybrid nanostructures **ZnO-2o** and **ZnO-2c** that both operate in a bidirectional mode. Ring-closing/ring-opening cycles can be carried out several times with minimal observable degradation, which indicates the better photochemical stability of compound **2**.

4. Conclusions

We have investigated the photochromic behavior of two dithienylethenes derivatives linked to zinc oxide nanorods via a carboxylic acid function. It is shown that not only both opening and closing of the switching unit take place at the surface of zinc oxide, but also bidirectionality of switching is observed. Depending on the molecular structure, however, some losses are observed presumably due to photodegradation. Therefore, zinc oxide offers an attractive surface to implement switching processes with this important class of photochromic compounds. Another appeal of the approach based on zinc oxide is that elongated nanocrystals such as nanorods can be used. One might envisage extending this strategy to nanowires for the generation of multistate nanostructures with tunable electronic or photonic properties.

Acknowledgments

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