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# Photo-induced charge separation in molybdenum–mononitrosyl–ferrocenyl–stilbene

Massimo Marcaccio[a], Jon A. McCleverty[a], Walther Akemann[b],
Céline Fiorini–Debuisschert[b], Jean-Michel Nunzi[c,*]

[a] *School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 ITS, UK*
[b] *DRT-LIST/DECS/SE2M, Composants Organiques, CEA Saclay, 91191 Gif-sur-Yvette, France*
[c] *POMA, UMR-CNRS 6136, Université d'Angers, 2 Boulevard Lavoisier, 49045 Angers, France*

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## Abstract

The excited state spectrum of molybdenum–mononitrosyl–ferrocenyl–stilbene in DMF is studied using time resolved Kerr ellipsometry with a pump wavelength of 532 nm in resonance with the $S_0$ (ground state) to $S_1$ (lowest excited state) transition. Photoexcitation forms a transient charge separated state with photoreduction of the molybdenumnitrosyl group. The induced dipole change derived from six-wave-mixing (SWM)using 1064 and 532 nm wavelengths is $\Delta\mu = 3.9$ D (Debye). The life time of the transient state is estimated to be at least 200 ps.

*Keywords:* Photo-induced charge transfer; Long-lived charge separation; Non-linear spectroscopy; Kerr ellipsometry; Six-wave-mixing

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## 1. Introduction

Organic materials are becoming increasingly attractive for optoelectronics. Indeed, competitive device efficiency is achieved and new applications take advantage of the universal variability in organic molecular design and easy processability in rigid as well as flexible structures [1–3]. A group of materials particularly interesting is based on chromophoric molecules of general A–B–D structure where A and D are eligible acceptor and donor groups and B is an interlinking bridge containing conjugated bonds [4]. Molecules of this kind have intensively been studied as model systems for intramolecular charge transfer [5] (CT) and as active media for quadratic non-linear optics [6–8].The intriguing material engineering aspect consists in the possibility to tailor the optical properties by adapting the potential energy surface of electrons in the semiconducting bridge through an adequate choice of the terminal A and D groups. In the particular case of bisubstituted stilbene, a large range of A and D functional molecules has been investigated with regard to optical non-linearity [9]. However, existing studies rarely involved organometallic functional groups [10], presumably because of difficult synthesis procedures and limited stability.

The present communication reports on a stilbene derivative containing two organometallic compounds, namely molybdenum (Mo)–mononitrosyl as an acceptor and ferrocenyl as a donor group [11], (see Fig. 1). The particular interest in this molecule, abbreviated MNFCS, stems from a pronounced redox behavior as observed in cyclic voltammetry. Voltammetric data in dry $CH_2Cl_2$ solution [12] show two quasi reversible current waves at −0.74 and 0.58 V versus SCE. Since the latter potential is close to the potential of the ferrocene/ferrocenium equilibrium in the same solution, the respective redox couple at 0.58 V is likely to involve the neutral and the oxidized donor group. By analogy the process at −0.74 V may represent the interconversion of the neutral and the reduced acceptor. This would mean that the molecule is capable of sustaining molecular stability in either redox state with the additional charge residing in one of the terminal redox centers. Such a rigid redox behavior, in fact, represents an essential prerequisite for various photonic applications. We keep particularly in mind the photovoltaic application [13]. However, in order to validate the utility of the molecule, for example as a dye sensitizer in photonic charge transfer devices, it is necessary to study the optical properties with focus on the internal photo-induced charge displacement and efficiency of extramolecular charge transfer.

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[*] Corresponding author. Tel.: +33-241735364; fax: +33-241735216.
*E-mail address:* jean-michel.nunzi@univ-angers.fr (J.-M. Nunzi).

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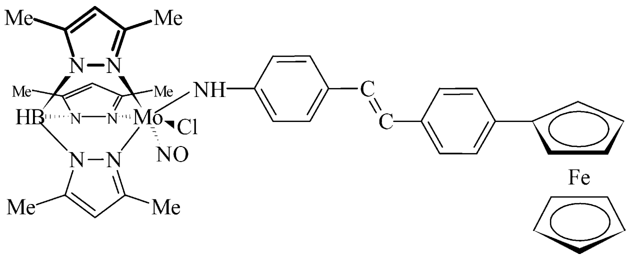

Fig. 1. Structure of the investigated molybdenum–mononitrosyl–ferrocenyl–stilbene (MNFCS).

As a first step into this direction, we studied the optical spectra of the ground and the first excited (transient) state of MNFCS in solution. Our approach to analyze the excited state spectrum is based on a comparison of the spectra of the neutral and the reduced compound. By chemical reduction of the molecule we intend to transfer an electron into the lowest unoccupied orbital of the acceptor group and quench the pathway of the internal photo-induced charge transfer. Hence, the difference of the optical spectra of the neutral and the reduced compound is expected to provide valuable information concerning the intermolecular charge separation process.

## 2. Experimental

The molecule (Fig. 1) ($m = 836.87$ g) was synthesized according to a procedure given elsewhere [12]. The compound is well soluble in common solvents, for example in dry DMF which is used as a solvent in this work. The optical measurements are performed using a fused silicon optical cuvette of 1 mm path length. The absorption of the dye in solution is measured by means of a commercial two-path photometer in the range 280–1200 nm. The absorption spectra are deconvoluted into Gaussian absorption bands and the dipolar transition moments are calculated from the standard oscillator strength expression within the quantum mechanical two-level-model [14]. As a check for stability of the sample solution, we verified that the optical density remains identical during the course of the experiments (about 4 h). The absorption spectrum of the excited state is derived from Kerr ellipsometry measurements [15]. Briefly, the method uses a high intensity (0.5 GW/cm$^2$), linearly polarized laser pulse in resonance with the lowest electronic transition of the molecule in order to produce an optical index anisotropy with respect to the axes parallel and perpendicular to the pump polarization. This transient anisotropy is probed by a second, time-delayed white light pulse of lower intensity polarized 45° to the polarization axis of the pump beam. Since the induced anisotropy in general is composed of a real (birefringent) and an imaginary (dichroic) part, the probe beam will become elliptically polarized on traversing the sample medium. The resulting polarization ellipsoid is immediately related to the transient index anisotropy $\Delta n$. The molar differential absorption coefficient $\Delta\alpha$, in particular, is given by (for small values of the dichroic angle $\phi_{\text{Kerr}}$):

$$\Delta\alpha(\lambda) = 6\frac{\phi_{\text{Kerr}}(\lambda)}{cl} \tag{1}$$

where $\phi_{\text{Kerr}}$ is measured as the angular deviation of the ellipsoid's main axis from the initial polarization direction, $c$ the concentration of the dye in the solution and $l$ the interaction length (length of pump and probe beam overlap inside the sample volume).

The measurements reported here are performed using an automated set-up based on a 40 ps mode-locked YAG laser. As a pump we use the second harmonic of the YAG at 532 nm and as a probe, a spectral continuum obtained by frequency conversion of the 1064 nm pulses in deuterated water. The polarization of the probe beam after interaction with the sample is analyzed by means of a crystal polarizer followed by a grating spectrometer and a diode array detector. For each wavelength we determine $\phi_{\text{Kerr}}$ as the angular deviation in the polarizer setting of minimum probe beam transmission (with respect to the isotropic case without pump). In this way, we reconstruct the spectrum $\phi_{\text{Kerr}}(\lambda)$ which is equivalent to the differential optical absorption according to the equation given above. Life time of the excited state is determined by fitting with an exponential law the decay of $\phi_{\text{Kerr}}$ with respect to pump-probe delay [15].

As a supplementary tool, we use the six-wave-mixing (SWM) technique [16] to gain an estimate of the molecular hyperpolarizabilty and permanent dipole change $\Delta\mu$ (charge transfer). The method is based on the measurement of the second harmonic generation efficiency by an ensemble of homopolar molecules in solution selected by a phase matched polar optical field which is generated by the dual frequency interference between laser beams at 1064 and 532 nm wavelength inside the sample. Within the framework of the two-level model the second harmonic yield in SWM is given by:

$$\sqrt{I_{2\omega}^{\text{SWM}}} \propto \frac{\Delta\mu^2\mu_{01}^2}{\Gamma(\omega_{01}^2 - (2\omega)^2)} \tag{2}$$

with $\Gamma$ the total decay corresponding to the sum of electronic and orientation decay rates. This latter decay arises from the loss of alignment of the transition moments following the thermal motion and rotation of the molecules in solution. Using the expression above together with values of $I_{2\omega}$ from SWM and $\mu_{01}$ and $\omega_{01}$ from the absorption spectrum we derive an experimental value for $\Delta\mu$.

## 3. Results and discussion

In the case that only one singlet system of the molecule is involved in optical excitation and deexcitation and the pump energy is resonant with the lowest energy transition

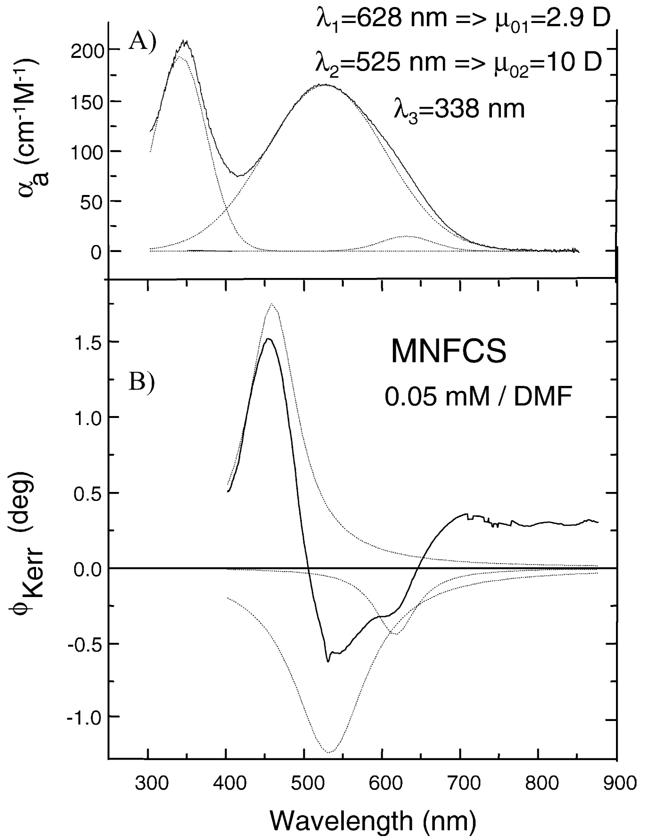

Fig. 2. (A) Stationary absorption spectrum (solid curve) of MNFCS in DMF ($5 \times 10^{-5}$ M) and its deconvolution (dotted curves). (B) Kerr spectrum of the same solution as in (A) using an excitation wavelength of 532 nm and 0.5 GW/cm$^2$ pump intensity (solid curve) and deconvolution into bands of Lorentz-shape (dotted curves).

from the $S_0$ (ground state) to $S_1$ (lowest excited state), the differential molar absorption $\Delta\alpha$ becomes [17]:

$$\Delta\alpha(\lambda, t) = [\alpha_{a1}(\lambda) - \alpha_{a0}(\lambda) - \alpha_{e1}(\lambda)]\,\frac{c_1(t)}{c} \qquad (3)$$

where $\alpha_{a1}$ is the coefficient of absorption in the first excited state, $\alpha_{a0}$ the coefficient of absorption in the ground state, $\alpha_{e1}$ the coefficient of stimulated fluorescence and $c_1$ the density of molecules in the first excited state $S_1$. Note that $\alpha_{a0}$ enters with a negative sign which reflects the fact that the $S_0$ to $S_1$ absorption is diminished (bleached) because of an increased population of the $S_1$ state. For observation times $t$ greater than the pulse duration $\Delta\alpha$ depends on the pump intensity only through the initial population $c_1(0)$. $\alpha_{a0}(\lambda)$ is immediately obtained from the absorption spectrum (see Fig. 2A), and yields two major absorption bands at 338 nm (FWHM 100 nm) and at 525 nm (FWHM 160 nm). In the case of the second band, one notices a slight asymmetry of the band shape in the form of a weak shoulder on the long wavelength tail. This inhomogeneous broadening of the visible absorption band principally complicates the assignment of the $S_0$ to $S_1$ transition in the case of MNFCS. The observed inhomogeneity could indicate the occurrence of two principal electronic transitions with a large difference in the dipole transition moment $\mu_{01}$, namely 2.9 D (1 D = 3.335 10–30 cm) for the 628 nm transition versus 10 D for the dominant transition centered at 525 nm. The inhomogeneity, however, may also arise from the vibrational sub-structure of the $S_0$ to $S_1$ transition. In spite of this ambiguity it is assumed a priori that the 532 nm laser line used in the Kerr as well as in the SWM experiment is indeed in resonance with the principal electronic transition in the visible frequency range.

Fig. 2B displays the spectrum between 400 and 850 nm of the excited state referring to a pump wavelength of 532 nm and zero delay. Apparently, the spectrum is composed of four distinct bands, which may conveniently be recovered by a deconvolution into a sum of Lorentz-functions, see Fig. 2B. The devonvolution reveals two transient absorption bands ($\Delta\alpha > 0$), one band centered at 460 nm (FWHM 80 nm) and a second, considerably broader band, covering the red and infrared range with FWHM of at least 500 nm, as well as two gain bands ($\Delta\alpha < 0$) at 530 nm (FWHM 120 nm) and 620 nm (FWHM 65 nm). The phenomenological interpretation of these observations is based on the different contributions entering Eq. (3): the two transient absorption bands are attributed to the optical absorption in the excited state, different from the ground sate. The dominant gain band at 530 nm, on the other hand, fairly resembles the visible absorption band in the stationary spectrum (see Fig. 2A), and is therefore assigned to the bleaching of the $S_0$ to $S_1$ transition. By analogy, the second gain peak at 620 nm could result from the bleaching of a second transition corresponding to the 628 nm feature in the ground state absorption spectrum. An alternative assignment would involve a stimulated emission from the $S_1$ state, with the peak of the fluorescence band being red shifted by 90 nm from the absorption band. The transient absorption decays uniformly at all wavelength according to a monoexponential decay law with a lifetime of 200 (±10) ps (see Fig. 3). This value should not be too much affected by orientational randomization. Indeed, an estimation of the orientation time $\tau_{or}$ can be inferred from

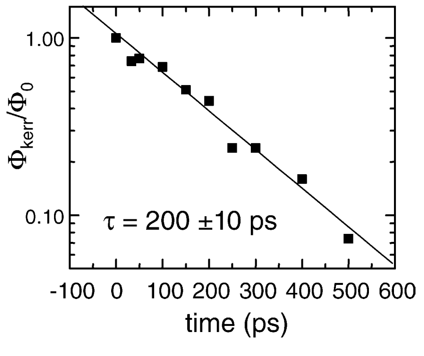

Fig. 3. Decay of the normalized dichroic angle at 460 nm as a function of the delay time. An excited state life time of $200 \pm 10$ ps is found.

the Debye–Stokes–Einstein relation [18,19]: $\tau_{\mathrm{or}} = \eta V/kT$, where $\eta$ is solvent viscosity (0.8 cp in DMF), $V$ the molecular volume, $T$ the temperature, and $k$ the Boltzman constant. For the dye under study we estimate $\tau_{\mathrm{or}}$ in the order of 1 ns in DMF. Consequently, the lifetime of 200 ps should reflect essentially the excited state electronic lifetime ($\tau_{\mathrm{exc}} \approx$ 250 ps). Such quite long electronic lifetime for a singlet state of charge transfer character can be attributed to an ultra-fast internal geometrical reorganization (twist) of the molecule following charge transfer excitation.

In order to advance further in the interpretation of the excited states we investigated the spectra of the compound after chemical reduction using Cobalt(cp)$_2$ as a reducing agent. Upon introduction of Cobalt(cp)$_2$ into the dye solution, the reaction is observed as a color change from deep violet to light blue. Care was taken to prevent oxidation of the cobalt–complex in air. It is inferred that the final solution consists of the quantitatively reduced dye together with an excess of unreacted cobaltcenyl. The absorption spectrum of the reduced MNFCS is obtained upon using a cobaltcenyl/DMF solution as a reference. However, the reference is not critical since cobaltcenyl does not show a considerable absorption in the spectral range above 400 nm. The resulting spectrum (see Fig. 4A), exhibits a major absorption band at 420 nm with 165 nm FWHM together with a small background absorption in the red spectral range. The excited state spectrum given in Fig. 4B is composed of a broad absorption covering the whole visible range and a small gain region between 460 and 540 nm. Note that in the case of reduced MNFCS, the pump at 532 nm is not fully resonant with the main visible absorption band. Evidently, the deconvolution into single bands is less obvious than in the case of the neutral compound. However, two observations are worth to be emphasized: the two absorption bands in the transient spectrum of the neutral compound are not reproduced in the transient spectrum of the reduced compound, in particular the peak at 460 nm, which is the dominant feature in the former spectrum, does not occur in the spectrum of the same compound after reduction. On the other hand, however, the excited state spectrum matches much better with the stationary absorption spectrum of the reduced compound. In particular, the 460 nm band resembles the major absorption band of the reduced MNFCS. Similarly, does the transient absorption in the red spectral range seem to have a correspondence in the stationary absorption of the reduced molecule.

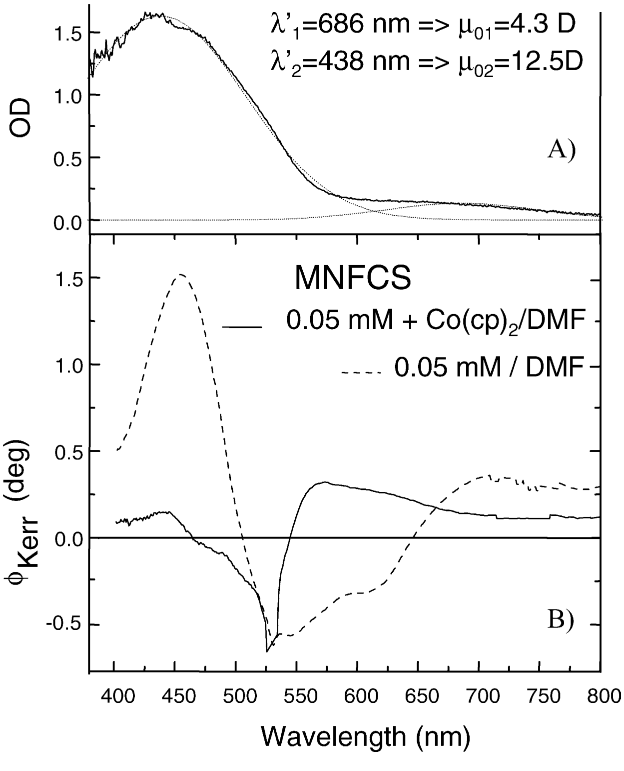

Fig. 4. (A) Stationary absorption spectrum of MNFCS ($5 \times 10^{-5}$ M) and Co(cp)$_2$ in DMF, see text. (B) Kerr spectrum of MNFCS ($5 \times 10^{-5}$ M) and Co(cp)$_2$ in DMF (solid curve) and of MNFCS ($5 \times 10^{-5}$ M) in DMF (broken curve), taken from Fig. 2A.

This spectral similarity in optical absorption between the excited state of MNFCS and the ground state of the MNFCS anion radical is a central result of our investigation since it provides spectroscopic evidence for a zwitterionic configuration in the excited state involving the photoreduced acceptor Mo-complex. Since this intramolecular charge separation is equivalent to the formation of a dipole in the excited state, we applied SWM to determine the dipole change $\Delta\mu$. Since the second harmonic wave at 532 nm is fully resonant with the absorption band of MNFCS centered at 525 nm we can make use of the two level approximation. Thus, from the measured SH intensity and by assuming $\omega_{01} = 2.36$ eV and $G = 5 \times 10^{-9}\,\mathrm{s}^{-1}$, we finally obtain $\Delta\mu = 3.9$ D. This value appears amazingly small in comparison with other stilbene compounds, as for instance DMANS with $\Delta\mu = 19$ D [20], and indeed indicates only a weak optical non-linearity of MNFCS (at 1064 nm wavelength). Actually, the small value of $\Delta\mu$ excludes the possibility that a full electronic charge is transferred in one-step by photoexcitation from the donor to the acceptor with a rigid (*trans*) stilbene bridge in between. The observation may be rationalized in different ways: the CT process may still involve the two terminal A and D groups, but either the ground state already exhibits a considerable dipole moment which means that charge is permanently transferred from D to A, or a full charge is transferred but the CT is coupled to an isomerization process reducing the excited state dipole. However, both explanation seem not very likely. The first explanation would be in disagreement with our interpretation of the excited state spectra where we have argued that the S$_1$ state involves the photoreduction of the acceptor group. On the other hand, do we fail to find any spectroscopic trace of a *trans–cis* isomerization of MNCFS which probably would be characterized by two ground states as in the case of the stilbene molecule [21]. An alternative explanation therefore might be that the reduction of the acceptor complex by 532 nm excitation does not involve a charge donation from the terminal ferrocenyl complex in the first place but from a donor center in greater proximity to the acceptor. A primary candidate for a possible donor would be the amino group linking the molybdenum complex to the stilbene. Within this conception of a dual-donor functional configuration the ambiguity in the assignment of the $S_1$ state, as discussed above, appears no longer surprising. In particular, it might be possible that the two bands resulting from the deconvolution of the visible absorption band represent the two different CT transitions consisting of charge donation from the ferrocenyl and from the amino group, respectively. In this case, the weaker band at 628 nm would be attributed to the charge transfer from the ferrocenyl. However, the 532 nm laser line used as an excitation source in our experiment is out of resonance with this band.

## 4. Conclusion

This first and preliminary study of a new stilbene compound carrying two organometallic redox centers revealed a combination of interesting properties in view of potential applications in optoelectronics. Most remarkably the molecule supports long-lived charge separation in the excited state and, according to the observations so far, stable redox states. Note that the lack of chemical stability in the ionic state represents a serious shortcoming of many chromophores with respect to photonic charge transfer applications. On the other hand, further work is needed to discriminate and confirm the different charge transfer processes in MNFCS, in particular concerning the transfer from the ferrocenyl group. A detailed understanding of the charge separation process certainly will allow to optimize the inner charge separation coordinate and the $\Delta\mu$ value of this compound. The present study also opens up another interesting perspective of a more general nature. This refers to the use of external redox processes in order to manipulate the charge distribution in a molecule and to modify the internal chromatic charge transfer. Obviously, the use of chemical redox reactions is of limited value because of the presence of a second, optically active compound. This obstacle may be elegantly excluded in future work by the use of electrochemical oxidation/reduction of the chromophore in an electrolytic solution. Such experiment would permit in particular to study both the reduced and the oxidized states.

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