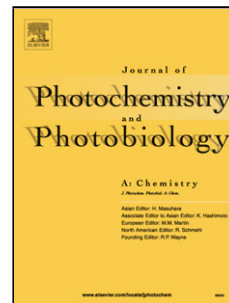


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PUMP-PROBE SPECTROSCOPY



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- Excitation of Ni(xan)<sub>2</sub> complex in CCl<sub>4</sub> leads to 0.6 ps relaxation to triplet state.
- Triplet state undergoes vibrational cooling and slowly decays to the ground state.
- In acetonitrile the processes follow the same pathway with a close times.

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# PHOTOPHYSICS OF BIS(ETHYLXANTHATO)NICKEL(II) [Ni(EtOCS<sub>2</sub>)<sub>2</sub>] COMPLEX STUDIED BY FEMTOSECOND PUMP-PROBE SPECTROSCOPY

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## Abstract

Femtosecond spectroscopy was applied to study the ultrafast relaxation dynamics for the excited state of xanthogenate Ni(S<sub>2</sub>COEt)<sub>2</sub> complex in acetonitrile and CCl<sub>4</sub>. The radiation of second harmonic (400 nm) of Ti:Sapphire laser transfers the Ni(S<sub>2</sub>COEt)<sub>2</sub> complex to excited LMCT state which in CCl<sub>4</sub> with time 0.76 ps decays to excited triplet state of (*d*, *d*<sup>\*</sup>) type. With the time 6.8 ps the triplet state undergoes vibrational relaxation and then it slowly decays during 550 ps to the ground state. In acetonitrile the processes of relaxation after femtosecond excitation follows the same pathway with a close times.

**Keywords:** Photophysics, photochemistry, fast processes, xanthogenate Ni(II) complex

## 1. Introduction

Dithiolate Ni(II) complexes, containing a coordination NiS<sub>4</sub> unit, are widely applied in analytical chemistry [1], organic synthesis [2] and biology [3]. Dithiolate ligands are used to extract metals [4], their complexes serve as precursors of sulfides in modern electronics [5-7]. The electronic structure of the dithiolate Ni(II) complexes is considered in [8]. However, the photophysics of these complexes is unavailable in the literature which is also concerned with the xanthogenate ones. Of interest is paper [9] which considers the photophysics and photochemistry of the Ni(mnt)<sub>2</sub><sup>2-</sup> complex (mnt = maleonitriledithiolate = S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>)<sup>2-</sup>) also containing a coordination NiS<sub>4</sub> unit with picoseconds time resolution in CH<sub>3</sub>CN and CHCl<sub>3</sub> mixtures. The authors demonstrate that the quantum yield of Ni(mnt)<sub>2</sub><sup>2-</sup> photolysis increases with increasing concentration of chloroform whose molecules are an electron acceptor. Besides, the quantum yield increases substantially with decreasing irradiation wavelength. This increase was assigned to the

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existence of weak bands of charge transfer to a solvent (CTTS) in the range 200-300 nm that are masked by the bands related to intraligand transitions ( $LL^*$ ) and ligand-metal charge transfer (LMCT). The picosecond excitation (355 nm, 30 ps) of  $Ni(mnt)_2^{2-}$  gives rise to a broad absorption band over the range 426-675 nm with a dip at 475 nm caused by the disappearance of absorption from the ground state of the complex [9]. The intermediate absorption is independent of the solvent ( $CH_3CN$  or  $CHCl_3$ ) and almost vanishes during 100 ps.

It is shown in [10] that the femtosecond excitation (100 fs, 400 nm) of the dithiocarbamate  $Cu(dtc)_2$  complex (with  $CuS_4$  unit) also gives a broad band of intermediate absorption in the visible spectrum region which vanishes in the process with biexponential kinetics with times 0.5 and 10 ps. Excitation transfers the  $Cu(dtc)_2$  complex into the excited LMCT state which converts during 0.5 ps to the vibrationally “hot” ground state with vibrational cooling during 10 ps.

In framework of the program to research the photochemistry and photophysics of dithiolate  $Ni(II)$  complexes the goal of present work is to study the fast photophysical processes for the xanthogenate  $Ni(S_2COEt)_2$  complex in acetonitrile and  $CCl_4$  solutions using the second harmonic (400 nm) of the Ti:Sapphire laser.

## 2. Experimental

A pump-probe spectroscopy was used to study transient absorption in femto- and picosecond time domains. The experimental setup was described in details elsewhere [11]. The samples were excited by  $\sim 60$  fs pulses at  $\sim 400$  nm (second harmonic of a Ti:Sapphire generator - amplifier system, CDP Ltd., Moscow, Russia). The excitation pulse repetition rate was 10 Hz, and 200 pulses were used to record a single time-resolved spectrum. The samples were placed in a 1 mm rotating cuvette to provide uniform irradiation of the sample and to avoid thermal effects from the heating of sample by the pumping pulse. The typically time-resolved spectra were collected with a delay displacement of 100 fs during the first 3 ps after excitation and with exponentially increasing delay times at longer delays. Usually, 60-70 spectra were collected for each sample. The fitting program performed corrections of the group velocity dispersion and calculated the response time of the instrument. The overall time resolution was 150-200 fs. All pump-probe measurements were carried out at room temperature.

The stationary irradiation of solutions was performed either with the pulses of YAG:Nd (355 nm), excimer XeCl lasers (308 nm), by the lines of high-pressure mercury lamp (290, 313, 365 nm) or using a set of light emitting diodes (275, 306, 375 and 405 nm). The optical absorption spectra were recorded using an HP 8453 spectrophotometer. When determining the quantum yield, the laser pulse energy was measured using a ferrioxalate actinometer and Gentec-EO system (Canada)

(SOLO-2 monitor and pyroelectric measuring QE25SP-H-MB head). Intensities of the mercury lamp light and the light emitting diode radiation were measured with the same system using a photodiode PH100-SiUV head. Solutions were prepared using spectrally pure solvents.

### 3. Results and discussion

#### 3.1. Structure, UV and visible spectra of $\text{Ni}(\text{S}_2\text{COEt})_2$ complex

The  $\text{Ni}(\text{S}_2\text{COEt})_2 = \text{Ni}(\text{xan})_2$  complex possesses a flat coordination  $\text{NiS}_4$  unit with a Ni-S distance of 2.216 Å [12-14]. The optical spectrum of the  $\text{Ni}(\text{xan})_2$  complex in acetonitrile (Figure 1 and Table 1) is in good agreement with that depicted in [15-17]. The spectrum of the  $\text{Ni}(\text{xan})_2$  complex in  $\text{CCl}_4$  almost coincides with that in acetonitrile except for both a small shift of bands towards the red section of the spectrum and an increase in band absorption coefficients in the visible region (Figure 1). For free ligand  $\text{Et-xan}^-$  the first strong band displays its maximum at 301-310 nm (Table 1).

A broad weak band of the  $\text{Ni}(\text{xan})_2$  complex with a maximum at 643 nm is determined by the forbidden d-d transitions. For the Ni(II) ion with electron configuration  $3d^8$ , the orbital  $d_{xy}$  is the low unoccupied molecular orbital (LUMO). Therefore, in the spectrum, four d-d transitions should be manifested. However, due to the overlapping of broad bands, only one maximum is observed. The stronger bands at 476 – 316 nm refer to the bands of charge transfer from ligand to metal (LMCT) [15]. The bands in the region shorter than 316 nm belong to intraligand excitation ( $\text{LL}^*$ ), because this region contains the absorption bands of the free  $\text{Et-xan}^-$  ligand [17-19].

The concentration of  $\text{Ni}(\text{xan})_2$  complex in femtosecond experiments was about 3 mM. The independence of general view of optical spectrum on concentration in range  $10^{-4} - 10^{-2}$  M (the spectra were recorded in optical cells with thickness 1 – 0.01 cm) shows the absence of the dimerisation or aggregation.

Photochemical activity of  $\text{Ni}(\text{xan})_2$  complex in such solvents as acetonitrile, benzene, toluene, alcohols is absent. Only the presence of an electron acceptor (for example,  $\text{CCl}_4$  molecules) leads to the disappearance of the  $\text{Ni}(\text{xan})_2$  complex under irradiation in UV spectral region. The quantum yield strongly depends on the wavelength of irradiation and even in pure  $\text{CCl}_4$  it is very small at 400 nm ( $\varphi \leq 10^{-5}$ ). The quantum yield starts to increase substantially only at  $\lambda < 300$  nm ( $\varphi = 0.024$  (306 nm) and  $\varphi = 0.22$  (266 nm)).

A similar behavior of quantum yield is characteristic of the dithiolate Ni(II) complexes display photochemical activity only in presence of the electron acceptors (chloroform or  $\text{CCl}_4$ ). Thus, e.g. for the  $[\text{Ni}(\text{mnt})_2]^{2-}$  complex, the quantum yield increases with increasing mole fraction of chloroform in a  $\text{CH}_3\text{CN} - \text{CHCl}_3$  mixture [9]. A similar dependence of quantum yield in the

$\text{CH}_3\text{CN} - \text{CCl}_4$  mixtures was recorded for the flat  $\text{Ni}(\text{dtc})_2$  complex ( $\text{dtc}^-$  = dithiocarbamate ion) [20]. The quantum yield of these complexes sharply increases in a short-wave region (300 - 250 nm) where the intraligand ( $\text{LL}^*$ ) absorption bands are located. It is typical for dithiolate complexes of other metal ions. In the photolysis of the  $\text{Cu}(\text{dtc})_2$  complex in  $\text{CCl}_4$ , the quantum yield drastically increases at  $\lambda < 370$  nm [10]. For the  $[\text{Ni}(\text{mnt})_2]^{2-}$  complex, the quantum yield in chloroform at 313 nm is 0.25, and decreases to 0.001 at 405 nm [21]. It is assumed then that the electron transfer to an acceptor occurs from the unbonding peripheral ligand orbitals.

Thus, the radiation of the second harmonic of the Ti:Sapphire laser (400 nm) excites the  $\text{Ni}(\text{xan})_2$  complex to the second LMCT state (the band maxima at 414 nm in acetonitrile and at 421 nm in  $\text{CCl}_4$ ). In both solvents, no photochemical processes are observable at this wavelength, therefore, the fast relaxation of excited states is likely to occur.

### 3.2. Femtosecond spectroscopy of the $\text{Ni}(\text{xan})_2$ complex in acetonitrile and $\text{CCl}_4$

In femtosecond experiments, the charge transfer band of the  $\text{Ni}(\text{xan})_2$  complex at 476 nm in acetonitrile is within the detection range 440-550 nm (Table 1). In these conditions it is expected that both the disappearance of absorption from the ground state and the dynamics of its recovery will be manifested in transient spectra. Figure 2a shows the kinetics of optical density change after the laser pulse for the  $\text{Ni}(\text{xan})_2$  solution in acetonitrile. A global treatment of all kinetics with regard to the instrument response indicates that the calculated curves are in good agreement with the experimental ones in the three-exponential approximation (solid lines in Figure 2a)

$$\Delta A(\lambda, t) = A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} + A_3(\lambda)e^{-\frac{t}{\tau_3}} \quad (1)$$

The characteristic times of the exponents of transient absorption disappearance are  $\tau_1 = 0.59 \pm 0.05$  ps,  $\tau_2 = 3.6 \pm 0.6$  ps, and  $\tau_3 = 540 \pm 50$  ps. The spectra of  $A_1(\lambda)$ ,  $A_2(\lambda)$  and  $A_3(\lambda)$  are presented in Figure 2b. The laser pulse is immediately followed by wide absorption over the entire spectral range from 440 to 550 nm (Figure 2c). Against the background the wide dip with minimum at 476 nm is due to the disappearance of absorption from the ground state of  $\text{Ni}(\text{xan})_2$ . The spectrum 7 in Figure 2c shows that the shapes of the dip and the absorption band of  $\text{Ni}(\text{xan})_2$  are the same. Absorption decreases considerably during 1 ps and the dip with the same depth moves to the negative region (bleaching of sample in region of 476 nm). The existence of dip with the conservation of its shape and size during time interval 0-3 ps indicates that the complex is in the excited state (no absorption recovery from the ground state). Due to the decrease of transient absorption the dip center (476 nm) reaches its maximal negative value at 3 ps. Thereafter, the dip

with negative optical density and positive absorption at other wavelengths are decreased with time  $\tau_3 = 540 \pm 50$  ps. So, the fast relaxation processes stop completely to 1-2 ns. It should be noted that the relative depth of the dip allows to estimate the concentration of photolysed  $\text{Ni}(\text{xan})_2$  complex ( $\sim 3.8 \times 10^{-4}$  M) and the absorption coefficient of transient absorption ( $\epsilon \approx 2100 \text{ M}^{-1}\text{cm}^{-1}$  at 515 nm and at zero time).

Figure 3a shows the kinetics of the absorption change after the laser pulse for the  $\text{Ni}(\text{xan})_2$  in  $\text{CCl}_4$ . In this case, the global treatment of kinetics was also performed in the three-exponential approximation (eq. 1). Figure 3b shows the spectra of  $A_1(\lambda)$ ,  $A_2(\lambda)$  and  $A_3(\lambda)$  amplitudes of exponents. The characteristic times of exponents in this case are  $\tau_1 = 0.76 \pm 0.08$  ps,  $\tau_2 = 6.8 \pm 0.9$  ps and  $\tau_3 \sim 550 \pm 150$  ps. The change of the transient absorption spectra are presented in Figures 3c. As in acetonitrile solutions, after the laser pulse a wide absorption band appears which contains a dip with minimum at 485 nm due to the disappearance of absorption from the ground state of the complex in this solvent. The dip center reaches its maximal negative value at 2.5-3 ps after the laser pulse.

### 3.3. Discussion

The assignment of  $\text{Ni}(\text{xan})_2$  optical spectrum in range 200-500 nm (without forbidden d-d transitions and assuming molecular symmetry of  $D_{2h}$ ) is presented in [15]. The first three bands (476, 414, 387 nm in  $\text{CH}_3\text{CN}$ ) were explained as the LMCT transitions (transitions from ligand  $\pi$ -orbitals to empty  $3d_{xy}$  metal orbital). The decomposition of the  $\text{Ni}(\text{xan})_2$  spectrum in  $\text{CCl}_4$  in a range  $27000 - 12500 \text{ cm}^{-1}$  (including d-d transitions) on a gaussian components is shown in Figure 4. The first four components (14990, 16010, 17330 and  $19100 \text{ cm}^{-1}$ ) are due to the forbidden d-d transitions (their intensities are multiplied by ten). The next four components (20700, 22150, 23700 and  $24950 \text{ cm}^{-1}$ ) can be explained as the LMCT transitions according to ref. [15]. The dispositions of  $\text{Ni}(\text{xan})_2$  molecular orbitals bears a strong resemblance to the positions of orbitals for dithioacetylacetone  $\text{Ni}(\text{II})$  complex with  $D_{2h}$  symmetry [22]. So, the femtosecond pulse with the wavelength at 400 nm ( $25000 \text{ cm}^{-1}$ ) falls in the region of an eighth gaussian component, therefore the  $\text{Ni}(\text{xan})_2$  complex is excited to the state which we denote as the  $S_8$  state.

Recent works on the femtosecond dynamics show that the fast intersystem crossing (ISC) in transition metal complexes can be exceedingly fast and the transitions  $^1\text{CT} \rightarrow ^3\text{CT}$  can occur with  $\tau < 30 - 100$  fs [23-26]. The role of low-lying ligand-field states as highly efficient deactivation pathways for higher-lying charge-transfer states was demonstrated in low-spin  $\text{FeII}$  polypyridyl

complexes. Following ground state (GS)  $\rightarrow$   $^1$ CT excitation, the ligand-field manifold is accessed with a time constant of  $\sim 100$  fs [23].

In accordance with these results in the photophysics of coordination compounds, we can assume that the first change of transient absorption ( $A_1(\lambda)$ ,  $\tau_1 = 0.6$ - $0.8$  ps) for the  $\text{Ni}(\text{xan})_2$  complex can be the sequence of fast processes involving internal conversion (IC) in the charge transfer manifold, the intersystem crossing  $^1$ LMCT to  $^3$ LMCT and the transfer to triplet ligand field manifold ( $^3$ LF). The alternative pathway is the transfer  $^1$ LMCT  $\rightarrow$   $^1$ LF and the following fast intersystem crossing in ligand field manifold ( $^1$ LF  $\rightarrow$   $^3$ LF). In both cases the triplet  $^3$ LF state is the final state of these processes.

The second ( $A_2(\lambda)$ ,  $\tau_2 = 3.6$ - $6.8$  ps) process can be determined by the vibration cooling of the “hot”  $^3$ LF state. In [23] it was found that the vibration relaxation for the  $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$  complex in the  $^5\text{T}_2$  ligand field state takes about 8 ps. For  $\text{Cr}(\text{acac})_3$  the vibration cooling in the  $^2\text{E}$  excited LF state having a time constant of 1.1 ps. The vibration relaxation of  $^3(d, d^*)$  state for the  $\text{Ni}(\text{II})\text{Pc}$  (Pc – phthalocyanine) complex which contains a flat coordination  $\text{NiN}_4$  unit takes 20 ps [27]. For the popular  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex it is shown that the excited singlet  $^1$ MLCT state changes due to the fast intersystem crossing to the vibrationally excited triplet  $^3$ MLCT state whose vibrational cooling takes 10 ps [28]. The vibrationally excited triplet state of the  $\text{W}(\text{CO})_5(4\text{-cyanopyridine})$  complex cools off during 1-10 ps depending on excitation wavelength, solvent and oscillation frequency of CO and CN groups [29]. In the  $[\text{W}(\text{CO})_5(\text{solvent})]$  complex, the vibrationally excited CO group cools off for 16-22 ps through an anharmonicity of vibration which provides a communication with low-frequency vibration modes [29]. So, the times of vibration cooling for the  $\text{Ni}(\text{xan})_2$  complex in  $^3$ LF state ( $\tau_2 = 3.6$ - $6.8$  ps) fall in the region is quite normal for the triplet states of different coordination compounds.

In this mechanism of photophysical processes for the  $\text{Ni}(\text{xan})_2$  complex the third slow ( $A_3(\lambda)$ ,  $\tau_3 \approx 550$  ps) process is the decay of triplet  $^3$ LF state to the ground state. It is worth noting that the excited triplet  $^3(d, d^*)$  state for the  $\text{Ni}(\text{II})\text{Pc}$  complex converts, rather slowly, for 300 ps, to the ground state [28]. The time of  $^3$ LF  $\rightarrow$   $^1$ GS transition can vary over a wide range from hundreds of picoseconds to nano- and microseconds. For the  $\text{Ni}(\text{II})$  octaethyl porphyrin (OEP), the  $(d, d^*)$  excited state was formed in  $< 350$  fs [30]. The relaxation of the  $(d, d^*)$  state was found to be biexponential. The first component of this decay,  $\tau_1 \approx 10$  ps, was attributed to the equilibration of  $(d, d^*)$  excited states. The second component,  $\tau_2 = 250$  ps, accounted for the decay of the excited state to the ground state [30]. It can be noted that for the transition  $^3$ MLCT  $\rightarrow$   $^1$ GS the times also



varies in a wide region. For the  $[\text{Ru}(\text{bpy})_2(\text{dppp})]^{2+}$  complex in  $\text{CH}_3\text{CH}_2\text{OH}$  it takes about 1.7 ns, in  $\text{CH}_3\text{CN}$  – 35 ns, and in  $\text{CH}_2\text{Cl}_2$  – 273 ns [31]. Thus, the  $\tau_3 \approx 550$  ps in the  $\text{Ni}(\text{xan})_2$  complex can be satisfactorily explained by the  $^3\text{LF} \rightarrow ^1\text{GS}$  transition.

Figure 5 schematically depicts the relaxation processes for the excited  $\text{Ni}(\text{xan})_2$  complex and is shown similarly to the figure presented in ref. [23]. It is presented the fast internal conversion in the charge transfer manifold, then the transfer to ligand field manifold and the next transfer to triplet  $^3\text{LF}$  state with the following vibration cooling. The final process is the transition of triplet  $^3\text{LF}$  state to ground state.

#### 4. Conclusions

The kinetic and spectroscopic femtosecond measurements have shown that the excitation of the  $\text{Ni}(\text{xan})_2$  complex in the region of the high-frequency slope of the second LMCT band (400 nm) causes the fast relaxation ( $\tau_1 = 0.6\text{-}0.8$  ps) of the  $^1\text{LMCT}$  state to triplet  $^3(d, d^*)$  excited state. With the time  $\tau_2 = 3.6\text{-}6.8$  ps the triplet state undergoes vibrational relaxation and then it slowly decays ( $\tau_3 \sim 540\text{-}550$  ps) to the ground state.

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### Figure Captions

**Fig. 1.** The optical spectra of the  $\text{Ni}(\text{xan})_2$  complex in  $\text{CCl}_4$  (1) and acetonitrile (2) solutions.

**Fig. 2.** Fast photophysical processes for the  $\text{Ni}(\text{xan})_2$  complex in acetonitrile ( $C = 3 \times 10^{-3} \text{ M}$ ,  $l = 1 \text{ mm}$ ) after the femtosecond pulse (100 fs, 400 nm). **a** – kinetics at 440, 476 and 510 nm; **b** – 1-3 – spectra of  $A_1(\lambda)$ ,  $A_2(\lambda)$  and  $A_3(\lambda)$  amplitudes of exponents (eq.1); **c** – 1-6 – transient spectra at 0, 0.3, 1, 3, 10, 300 ps after the laser pulse; 7 – spectrum of the  $\text{Ni}(\text{xan})_2$  complex in acetonitrile.

**Fig. 3.** Fast photophysical processes for the  $\text{Ni}(\text{xan})_2$  complex in  $\text{CCl}_4$  ( $C = 3 \times 10^{-3} \text{ M}$ ,  $l = 1 \text{ mm}$ ) after the femtosecond pulse (100 fs, 400 nm). **a** – kinetics at 440, 480 and 590 nm; **b** – 1-3 – spectra of  $A_1(\lambda)$ ,  $A_2(\lambda)$  and  $A_3(\lambda)$  amplitudes of exponents (eq.1); **c** – 1-6 – transient spectra at 0, 0.3, 1, 3, 10, 300 ps after the laser pulse; 7 – spectrum of the  $\text{Ni}(\text{xan})_2$  complex in  $\text{CCl}_4$ .

**Fig. 4.** The decomposition of  $\text{Ni}(\text{xan})_2$  spectrum in  $\text{CCl}_4$  on gaussian components. 1-4 – forbidden d-d transitions, 5-8 – LMCT transitions.

**Fig. 5.** The scheme of photophysical processes for the  $\text{Ni}(\text{xan})_2$  complex upon the femtosecond excitation at 400 nm. This scheme is close to the scheme presented in ref. [23].

**Table 1.** Position of absorption bands maxima and absorption coefficients of the Ni(xan)<sub>2</sub> complex, free xan<sup>-</sup> ligand and the origin of absorption bands.

Molecule Solvent	$\lambda_{\max}$ / nm ( $\epsilon$ / M <sup>-1</sup> cm <sup>-1</sup> ), origin of band							Ref.
Ni(Et-xan) <sub>2</sub> CH <sub>3</sub> CN	218 (48400) d→Sπ*	251 (25980) Sπ→Sπ*	316 (41250) Sσ→dσ*	387sh (1140) Sp→dσ*	414 (2390) Sp→dσ*	476 (1260) Sn→dσ*	643 (43.4) d-d	[15]
Ni(Et-xan) <sub>2</sub> Benzene				389sh (1440)	417 (3055)	480 (1725)		[16]
Ni(Et-xan) <sub>2</sub> CHCl <sub>3</sub>			316 (25000)		418 (2700)	480 (1500)	642 (50)	[17]
Ni(Et-xan) <sub>2</sub> CCl <sub>4</sub>		253 (21870)	318.5 (28500)	387sh (1140)	421 (2860)	484.5 (1700)	643 (50)	This work
Et-xan <sup>-</sup> CH <sub>3</sub> CN	212 (12000) CTTS?	227 (11120) CTTS?	262 (2190)	310 (21500) π→π*	396 (43.5) n→π*			[15]
Et-xan <sup>-</sup> H <sub>2</sub> O		226 (8750)		301 (17600) π→π*	380 (50) n→π*			[18]
Et-xan <sup>-</sup> H <sub>2</sub> O		226 (9332) n→σ*		301 (17000) π→π*	380 (55) n→π*			[17]
Me-xan <sup>-</sup> Methanol		224 f = 0.1062		302 f = 0.2042				[19]

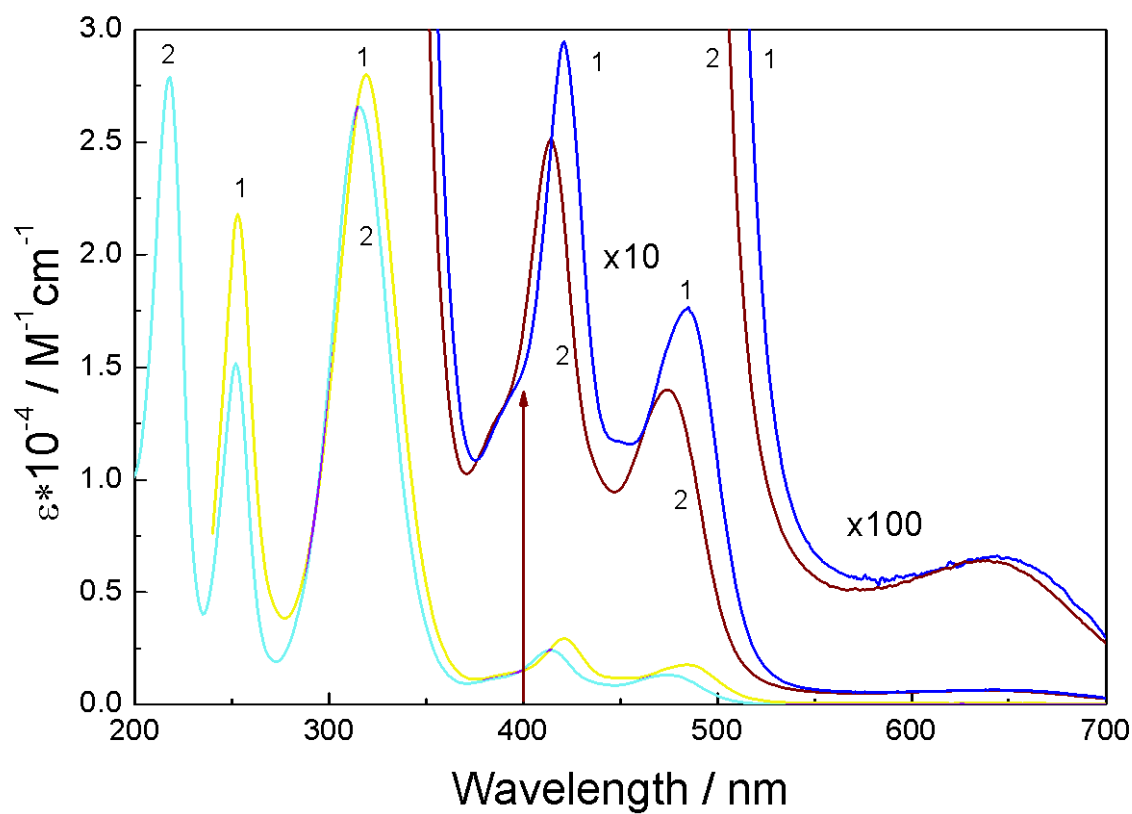


Figure 1

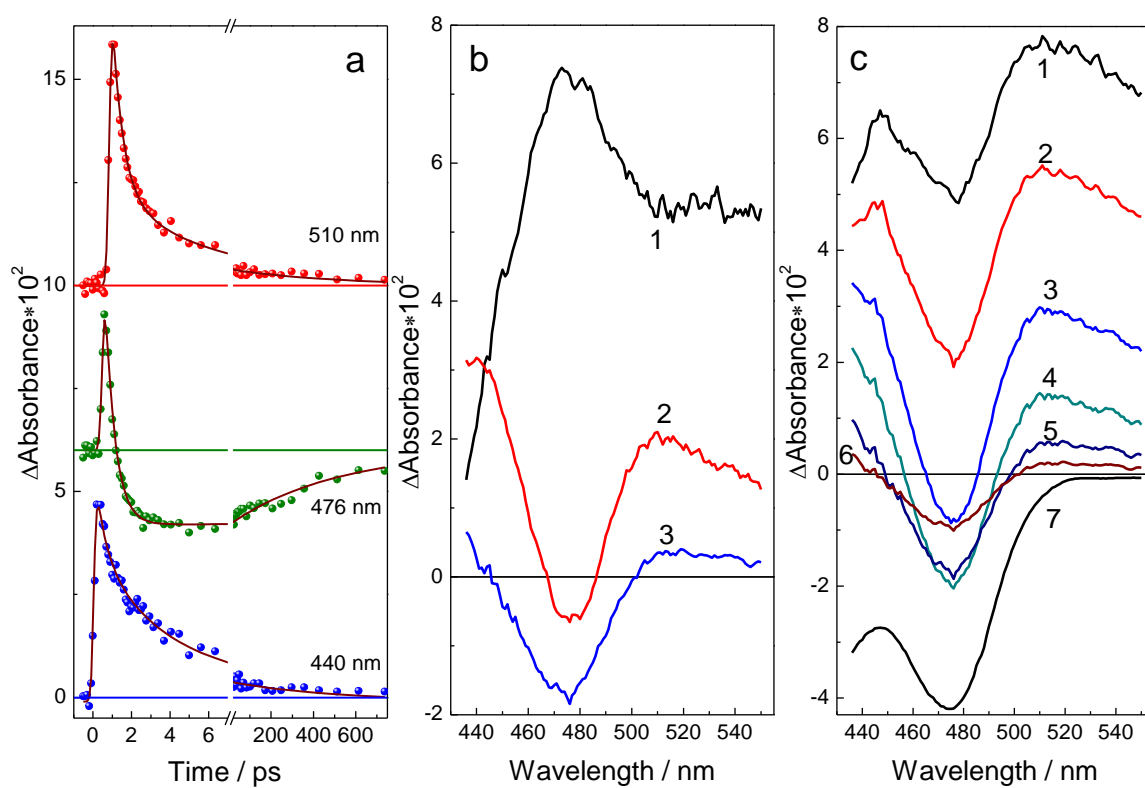


Figure 2

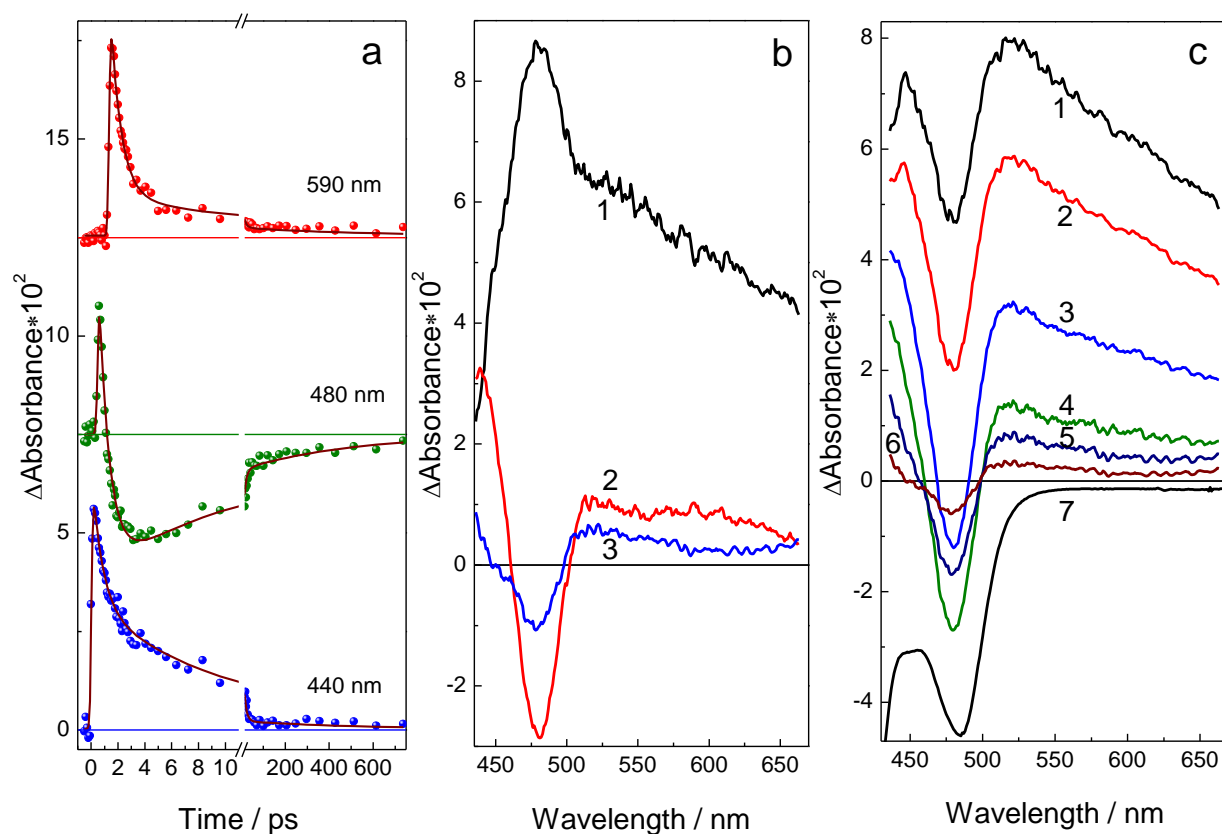


Figure 3

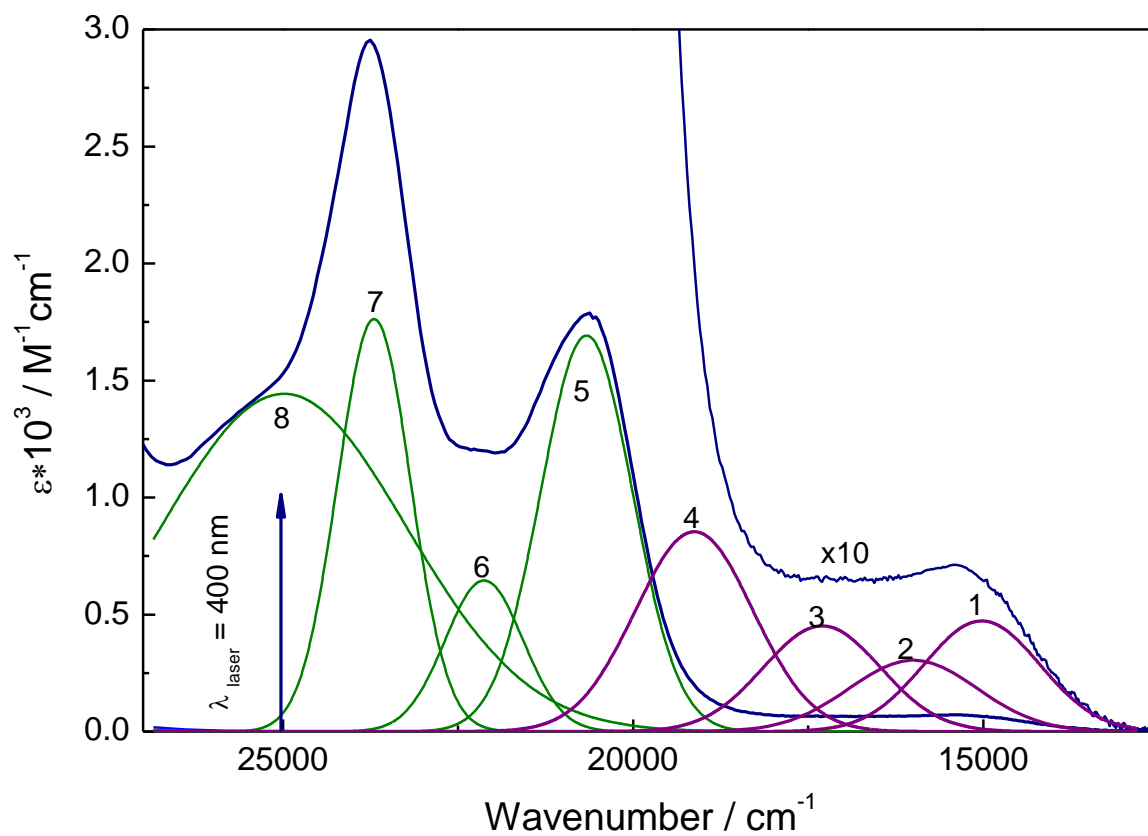


Figure 4



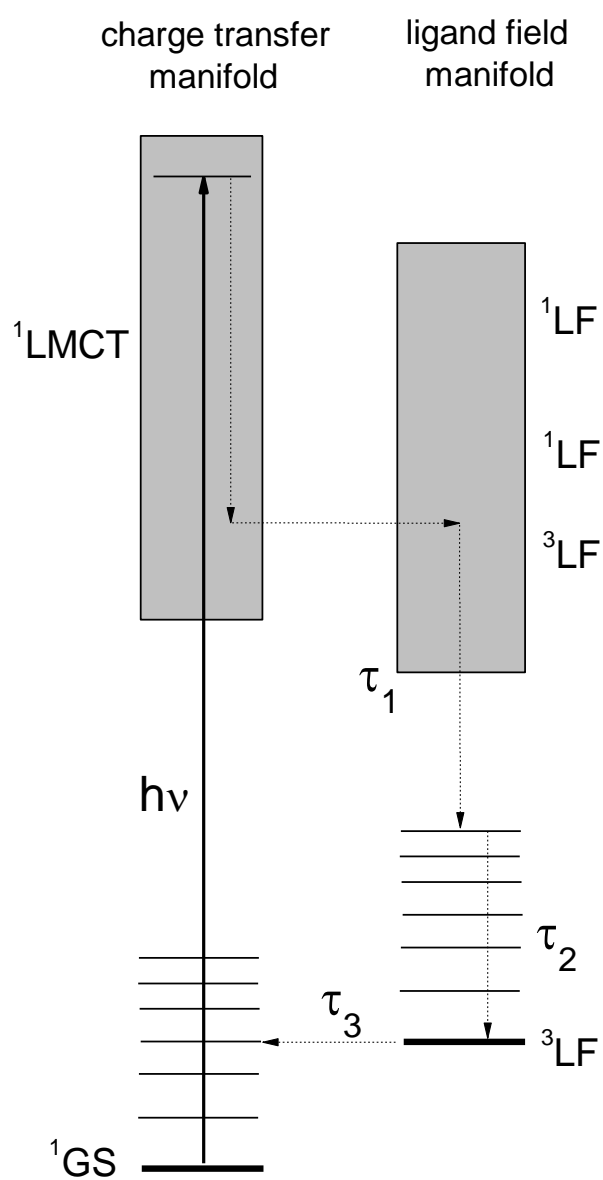


Figure 5

