Nonlinear absorption reversing between an electroactive ligand and its metal complexes

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Abstract: We present the nonlinear absorption investigation of an electroactive ligand and two ruthenium and iron metal complexes under 532 nm, 30 ps laser excitation, by the "open aperture" Z-scan technique. Significant nonlinear optical parameters have in all cases been measured, while the nonlinear attribute has been found to change from saturable to reverse saturable absorption between the initial ligand and its complexes.

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1. Introduction

Recently the possibility to employ the tetrathiafulvalene (TTF) unit in photonic applications has been widely investigated [1–6]. This is due to the enhanced charge transfer resulting from the electron donating ability of the TTF moiety, when it is properly connected to an electron accepting group [7,8]. The TTF unit has also been combined with different coordinating heteroatom based ligands leading to transition metal complexes with specific electronic properties [9]. Pyridine and 2,2'-bipyridine based ligands have been extensively used for the preparation of such metal complexes [10,11]. In addition to these ligands, the 2,2':6',2"-Terpyridine is also known to coordinate a large series of metal ions and to form very stable metal complexes [12], however only one system where this ligand is associated with an electroactive TTF moiety has been published so far [10].

Concerning the nonlinear absorption, the efficiency of TTF derivatives in general, and the TTF based ligands in particular has not yet been widely investigated. In a previous work carried out in our laboratory [3] the nonlinear absorption efficiency of some orthogonal TTF-derivatives has been studied. In that work the systems have been found to exhibit Reverse Saturable Absorption (RSA) character, while the magnitude of the nonlinear absorption has been strongly dependent upon the metal ion which was positioned in the corner position of the system. In the same direction and as a continuation of these findings, in the present work we investigate the nonlinear absorption of three novel TTF based systems (see Fig. 1). The system S1 is the electroactive EDT-TTF-Terpy ligand and the systems S2, S3 are its corresponding ruthenium and iron metal complexes respectively. The primary goal of the present study is to characterize these novel systems in terms of their nonlinear absorption parameters and in this way to check and analyse the difference between the free and the metal coordinated EDT-TTF-Terpyridine ligand, and the impact of the presence of the metal ion on the nonlinear optical response.

2. Synthesis/preparation of samples

The ligand S1 [13] was prepared by a condensation reaction between EDT-TTF acid chloride [14] and the 4'-amino-2,2':6', 2"-terpyridine [15,16]. Reaction of the ligand S1 with the terpyridine-ruthenium-trichloride precursor followed by an anion exchange reaction afforded
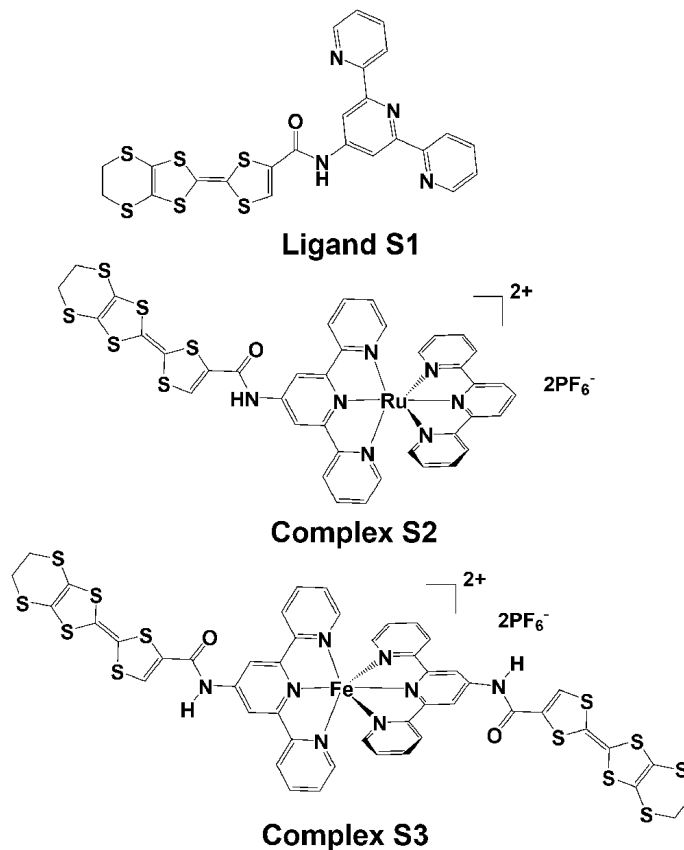

Fig. 1. Chemical structures of the investigated compounds.

complex S2 in 72% yield as an orange dark solid. The complex S3 has been obtained by the complexation reaction of the ligand S1 with iron(II) chloride followed by an anion exchange to afford the hexafluorophosphate complex in 65% yield as a violet solid. UV-visible electronic absorption spectra of S1 in (chloroform) are characterized by a λ_{max} value of 443 nm (Fig. 2), whereas λ_{max} values of 486 nm and 576 nm are observed for metal complexes S2 (in dimethylformamide) and S3 (in acetonitrile) respectively. These transitions in complexes S2, S3 are related to the Metal to Ligand Charge Transfer (MLCT).
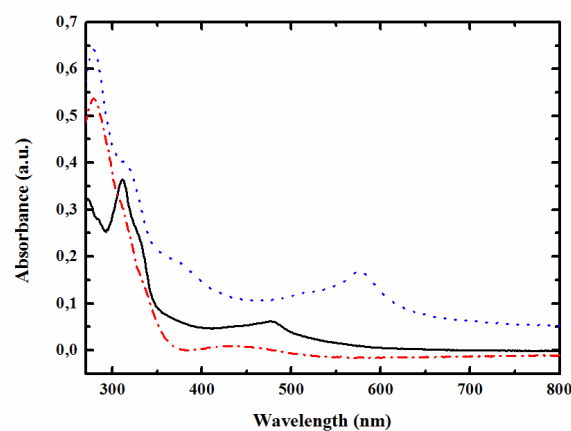
Fig. 2. UV-Visible absorption spectra of the ligand S1 (red/dash-dot line), the complex S2 (black/solid line) and the complex S3 (blue/dot line), corresponding to 3×10^{-5} M in choloform, 4×10^{-5} M in DMF, 4×10^{-5} M in acetonitrile, respectively.

3. Results and discussion

For the determination of the nonlinear absorption of the samples the "open aperture" Z-scan has been employed using the frequency doubled exit (532 nm) of a 30 ps diode pumped
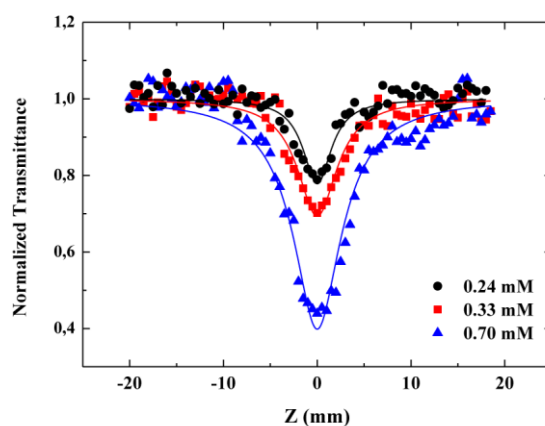

Fig. 3. "Open-aperture" Z-scans obtained for the S1 system for different sample concentrations.

passively mode-locked Nd:YVO$_4$ laser with a repetition rate of 10 Hz. In this way the imaginary part of the third order nonlinear susceptibility (Im$\chi^{(3)}$), as well as of the second hyperpolarizability (Imγ) have been determined. The details concerning the "open aperture" Z-scan technique as well as the equations in order to determine the nonlinear optical parameters from the experimental data will not be given here, as detailed information can be found in the literature [17]. For the needs of the measurements, solutions of different concentrations of all three systems have been prepared. For solubility reasons, ligand S1 was dissolved in chloroform, while the ruthenium metal complex S2 and the iron complex S3 were dissolved in dimethylformamide (DMF) and acetonitrile respectively. The utilized range of concentrations for all investigated molecules has been carefully chosen to allow high NLO signals, without formation of molecular aggregations in the solutions. The samples have been

introduced into 1 mm thick cells in order to be studied by the "open aperture" Z-scan technique. In all cases for the laser energies used the contribution of the solvents has been found to be negligible, so the total response can be attributed to the metal complexes.

The transmittance of the samples has been measured by moving them along the transmission axis of the laser beam and the normalized curves (i.e. the "open aperture" Z-scans) have been obtained. In Fig. 3, characteristic curves for the ligand S1, which correspond to different concentrations in chloroform and under the same experimental conditions, can be seen. It is obvious that around the focal plane of the lens (z = 0), where the laser intensity is maximum, there is a strong transmittance minimum for all investigated concentrations indicating RSA type behaviour, which is associated with optical limiting action. It can be also seen that the dip increases by increasing the concentration of the ligand S1, as expected for third order nonlinearity. "Open aperture" Z-scans have been also measured for the ruthenium and iron metal complexes (S2, S3). The fact that the normalized transmittance exhibited maximum around the focal plane, as it can be seen in Fig. 4(a), 4(b) for the two compounds respectively, indicates Saturable Absorption (S.A.) behaviour, opposing the nonlinear absorption attribute of the initial ligand S1.

From a plethora of "open-aperture" Z-scan curves, obtained under several different laser excitation intensities in order to verify that no saturation of the nonlinearity takes place, the
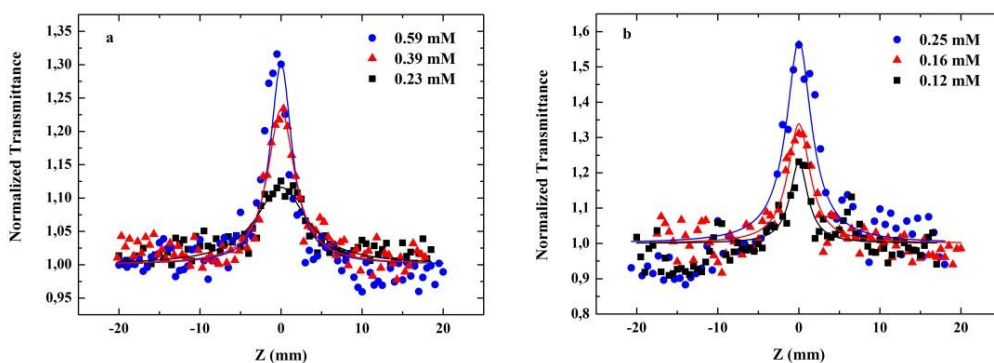

Fig. 4. "Open-aperture" Z-scans obtained for the (a) S2 and (b) S3 systems.

nonlinear optical parameters of the systems have been determined and can be seen in Table 1. More specifically the nonlinear absorption coefficient (β), as well as the $Im\chi^{(3)}$ are tabulated for similar concentrations of the S1-S3 molecules. Also the concentration independent $Im\gamma$ value, which is characteristic of each molecule has been obtained and is shown in the same table. The negative sign in the nonlinear optical parameters of the systems S2, S3 indicates an S.A. behavior. In all cases, high $Im\gamma$ values have been found reaching 0.57×10^{-30} esu and -0.33×10^{-30} esu for the R.S.A. and S.A. respectively. Comparison between the complexes S2, S3 shows that the imaginary part of the second hyperpolarizability is larger in the case of S3 by about 16 times. This significant enhancement can be attributed to the presence of the additional TTF group in S3 and also to the different nature of the metal ion.

The reversing of the nonlinear absorption character of the molecular systems studied here reflects that the introduction of the metal cations can drastically change the energy levels of the systems, and this includes also the introduction of the metal to ligand charge transfer states. So the S.A. character of the systems S2, S3 can be attributed to the fact that the excited-state absorption cross-section in these Ru, Fe complexes is lower compared with that of the ground state absorption cross-section, while the inverse is taking place in the case of the S1 system. Consequently the higher, positive γ value of the S1 molecule can be attributed to excited state enhancement of the third order nonlinear absorption, which is well known to

affect the third order nonlinearities under the ps regime and has been described in details elsewhere [18].

Table 1. Nonlinear optical parameters determined from the Z-scan measurements (30 ps, 532 nm).

Sample	β $\times 10^{-11}$ [m/W]	$Im\chi^{(3)}$ $\times 10^{-13}$ [esu]	γ $\times 10^{-30}$ [esu]
S1 (0.24 mM)	6.36 ± 1.34	3.53 ± 0.74	0.57 ± 0.11
S2 (0.23 mM)	-0.20 ± 0.03	-0.11 ± 0.02	-0.021 ± 0.003
S3 (0.25 mM)	-3.80 ± 0.68	-1.90 ± 0.34	-0.33 ± 0.05

The SA character found for the systems S2, S3 is in very good agreement with the results of Konstantaki *et al.* [19]. In their work, the authors have shown that Ru and Os complexes exhibit S.A. character under 0.5 ps laser pulses at 497 nm, while they attribute this behaviour to the fact that the duration of the pulse is much shorter than the lifetime of the triplet state.

The reversing of the nonlinear absorption attribute has been previously investigated in the literature, while the origins of the effect can be various depending on the nature of the system. Cassano et al [20] for example have observed such an effect using the Z-scan technique with nanosecond laser pulses. Actually they studied two metal dithiolenes (Pt and Pd) and they have found S.A and R.S.A. for the Pd-based and the Pt-based system respectively. Such switching behaviour has been also found to be dependent upon the pulse duration and the laser excitation wavelength [21,22].

4. Conclusion

In conclusion, the nonlinear absorption properties of an electroactive ligand, as well as of a ruthenium and iron metal complexes have been investigated. It has been found that although the initial ligand S1 exhibits RSA attribute, the S2 and S3 complexes exhibit exactly the opposite response (i.e. SA). The γ values have been found to be 0.57×10^{-30} esu, -0.021×10^{-30} esu and -0.33×10^{-30} esu for the systems S1, S2, S3 respectively. This reversing of the nonlinear absorption found in our work is highly desirable for nonlinear optics, as the combination of the S.A. and R.S.A. action of the systems can be employed in several different ways, covering a large field of photonic applications.

Acknowledgment