

SHORT COMMUNICATION

Properties of singlet- and triplet-excited states of hemicyanine dyes

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The fluorescence emission spectra and fluorescence quantum yields of hemicyanine dyes LDS 698, LDS 722, and LDS 730 were measured in different media. No transient species was detected in the laser flash-photolysis experiments performed with Ar-saturated solutions of the dyes in methanol. However, in the presence of 0.08 M potassium iodide, the absorption of the triplet states was clearly observed. Oxygen consumption measurements in the absence and presence of a chemical trap (furfuryl alcohol) in MeOH : H₂O ($\varphi_r = 1 : 1$) solutions of the dyes containing KI confirmed the generation of singlet molecular oxygen.

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Commercially available hemicyanine dyes, such as LDS 698, LDS 722, and LDS 730 (HMCs) (Fig. 1), have potential applications in non-linear optics (Shim et al., 2006), optoelectronics (Ashwell et al., 2004), information-processing (Qin et al., 2010), and biophotonics (Yamaguchi et al., 2006). These dyes in liquid media are able to lase with high efficiencies, despite their low fluorescence quantum yields (Φ_f) (Cerdán et al., 2012).

HMCs are aromatic compounds containing electron-donor and acceptor groups in the same system, thus exhibiting solvent-dependent emission properties due to the charge-transfer process from donor to acceptor in the excited state. Fluorescent amphiphilic hemicyanine dyes contain donor and acceptor groups in the same molecule linked by methylene groups. The photophysical properties of some of these dyes have been investigated (Cerdán et al., 2012; Görner & Gruen, 1985; Fromherz & Heilemann, 1992; Strehmel et al., 1997; Cao et al., 1998; Kim & Lee, 1999). Upon excitation of the dyes to the singlet-excited state, charge-transfer takes place from the styryl group to the pyridinium moiety. This results in a large change

in the dipole moment between the ground and the excited state (Sczepan et al., 2001). This intra-molecular charge-transfer (ICT) process may be followed by:

a) Internal rotation around the single bond, leading to the formation of a twisted intra-molecular charge-transfer (TICT) state. For hemicyanine dyes, this state is usually non-fluorescent. With the increasing solvent polarity, the activation barrier of the TICT state decreases, leading to a decrease in the fluorescence quantum yield. However, the solvent viscosity restricts the TICT state formation (Mishra & Haram, 2004).

b) The electronic coupling between the donor (D) and acceptor (A) leading to a complete charge separation. The dipolar state (ICT) is fluorescent and the fluorescence shows solvatochromic behaviour.

As a result, the fluorescence lifetimes of these dyes are affected by the solvent polarity and viscosity and the intra-molecular charge transfer process leads to large Stokes shifts, mainly in polar solvents. For this type of dyes, the main deactivation process of the singlet-excited state is formation of the non-fluorescent TICT state.

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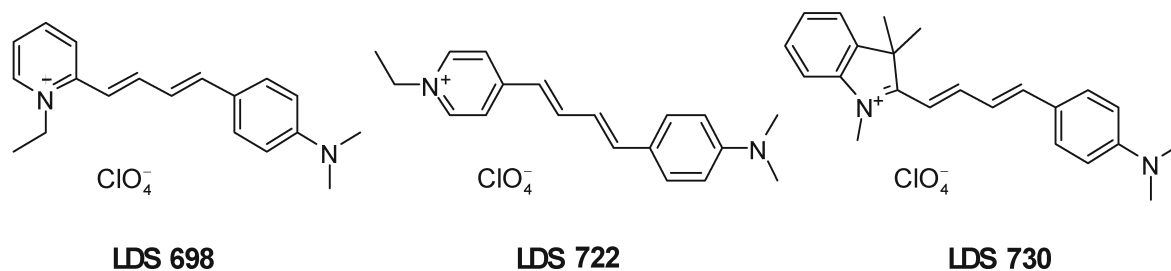


Fig. 1. Chemical structures of hemicyanine dyes under study.

Table 1. Absorption and fluorescence properties of LDS 722 in different solvents

Solvent	Solvent viscosity at 20 °C	$\lambda^{\max a}$	$\lambda^{\text{em} b}$	Φ_f^c
	mPa s	nm	nm	
Acetone ^d	0.36	493.0	720.5	0.088
Metanol	0.59	476.0	688.0	0.075
Methanol + 0.1 M KI	0.59	476.0	687.0	0.075
Glycerol	945	480.4	675.0	0.23

a) Absorption maxima; b) fluorescence maxima; c) fluorescence quantum yield; d) data from Cerdán et al. (2012).

Although the singlet-state properties of the hemicyanine dyes in solution were widely investigated in the literature, the spectroscopic and kinetic features of their longer-lived triplet states, as well as the ability of these dyes to generate or react with singlet molecular oxygen, $\text{O}_2(^1\Delta_g)$, remain almost unexplored. Since this information is useful for predicting the possible photodegradation routes of the dyes in solution, laser flash-photolysis experiments and time-resolved $\text{O}_2(^1\Delta_g)$ phosphorescence experiments (both with $\lambda^{\text{exc}} = 532$ nm) were performed in this work.

Fluorescence measurements were made using a Jobin-Yvon SPEX Fluorolog spectrofluorometer (model FL3-11) (Analytical Technologies, Singapore) equipped with a steady-state Xe lamp as the excitation source.

A Spectron SL400 Nd:YAG laser (532 nm, 18 ns pulse width) (Quantel, Les Ulis, France) was used as the excitation source. The laser beam was defocused in order to cover all the path length (10 mm) of the analysing beam from a 150 W Xe lamp. The detection system comprised a monochromator (Photon Technology International, LASEROPTICS, Buenos Aires, Argentina) coupled to a photomultiplier R666 (Hamamatsu, Bridgewater, NJ, USA). The signal, acquired by a digitising scope (Hewlett-Packard 54504) (Agilent Technologies, Santa Clara, CA, USA), was averaged and then transferred to a computer. The experiments were carried out in HPLC-grade methanol from Sintorgan. Solutions were de-aerated by purging with argon for 20 min.

The phosphorescence emission of singlet oxygen $\text{O}_2(^1\Delta_g)$ was determined using a system previously reported (Criado et al., 1997). To achieve a good signal-to-noise ratio, the decay curve was obtained from the

average of 16 shots. Air-equilibrated solutions were employed in all cases.

The oxygen uptake was measured in water with a 97-08 electrode (ORION, Beverly, MA, USA).

The spectroscopic properties of the LDS 722 dye in different media are detailed in Table 1.

The LDS 722 dye shows low Φ_f values in solvents of low viscosity. Higher values are obtained in glycerol. Similar results were obtained for the HMCs LDS 698 and LDS 730.

The low Φ_f values of LDS 722 in solution and the very low triplet-yield (if any, see below) indicate that the probability of non-radiative deactivation of the excited singlet state is very high. This is probably related to deactivation involving isomerisation of the double bonds of the conjugated chain. This type of deactivation is present in dyes with fluorescence quantum yields strongly dependent on medium viscosity (Valeur, 2002), as demonstrated here for the higher value of Φ_f measured in glycerol (Table 1).

The compound KI was employed to enhance the intersystem-crossing process to the triplet state. Table 1 shows that, for LDS 722, the addition of KI to the methanol solutions had almost no effect on the fluorescence yield. The addition of KI to a dye solution may have the heavy atom effect promoting intersystem-crossing to the triplet state with a concomitant decrease in the fluorescence yield (Chmyrov et al., 2010) but, in the case of cationic dyes, it may have other effects due to the formation of ion pairs. This was reported by Görner & Gruen (1985) who proposed, for other hemicyanine dyes in the presence of iodide ion, the population of an excited-state ion pair, which by intersystem-crossing may yield the ion pair in a triplet-excited state. The ion

pair should have a somewhat shorter lifetime than that of the isolated HMC singlet-excited state, due to the intersystem-crossing process. The fluorescence rate constant (k_f) value still being low in the complex and the values of the quotient $k_f/\Sigma k_{\text{singlet}}$ for the isolated HMC and for the complex could be similar, as experimentally observed for all three HMCs studied, due to a compensation effect between the competitive ISC and non-radiative pathways in the latter.

These authors also observed that, in polar solvents and in the absence of iodide ions, where the ion pair mechanism does not take place, the triplet-excited state is not populated. A similar mechanism may be invoked to explain why it was not possible to detect a decrease in the fluorescence yield with the increasing iodide concentration.

No transient species was detected in the laser flash photolysis (LFP) experiments performed with Ar-saturated solutions of the dyes in methanol. This is an important result for laser applications of these dyes, because losses by reabsorption laser emission from any triplet state should be negligible. However, in the presence of potassium iodide (KI, ≥ 99.0 mass %) ca 0.08 M, the absorption of transient species was clearly observed. The absorption spectra of the transient species (Fig. 2) are similar to the triplet states of other hemicyanine dyes and are thus assigned to these species (Görner & Gruen, 1985; Fromherz & Heilemann, 1992; Strehmel et al., 1997; Cao et al., 1998; Kim & Lee, 1999).

The triplet–triplet absorption spectra of hemicyanine dyes exhibit large negative peaks caused by depletion of the ground state. In all cases, the negative absorption of the difference transient spectra is very similar to the ground-state absorption band of the corresponding dye, revealing the lack of photo-product generation under the laser experimental conditions selected. This assumption is endorsed by analysing the similarity between the time profiles obtained at wavelengths of maximal positive and negative signals, respectively (inset, Fig. 2).

Solutions of the HMCs + KI in deuterated methanol exhibited a significant generation of $\text{O}_2(^1\Delta_g)$, comparable with that of Rose Bengal, which is used as reference (Wilkinson et al., 1993). However, due to quenching by I^- , the lifetime of $\text{O}_2(^1\Delta_g)$ was reduced from ca 30 μs to ca 5–6 μs in the absence and presence of 0.08 M KI, respectively. This result is in line with the value reported for the rate constant of the quenching of $\text{O}_2(^1\Delta_g)$ by I^- ($1.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in water : MeOH ($\varphi_r = 40 : 60$) solution) (Wilkinson et al., 1995).

Further confirmation of $\text{O}_2(^1\Delta_g)$ generation by solutions of the HMCs containing KI was provided for LDS 722 by means of oxygen consumption measurements, upon continuous photo-irradiation, in the absence and presence of the recognised $\text{O}_2(^1\Delta_g)$ -

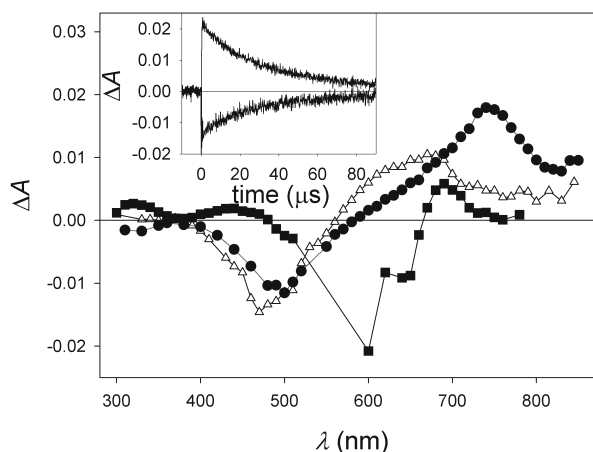


Fig. 2. Triplet–triplet absorption spectra in Ar-saturated methanol solutions in the presence of 0.08 M KI for: LDS 730 (■), LDS 722 (●), and LDS 698 (△). Inset: Time profile of ground-state ($\lambda = 500$ nm, lower signal) and triplet state ($\lambda = 740$ nm, upper signal) of LDS722.

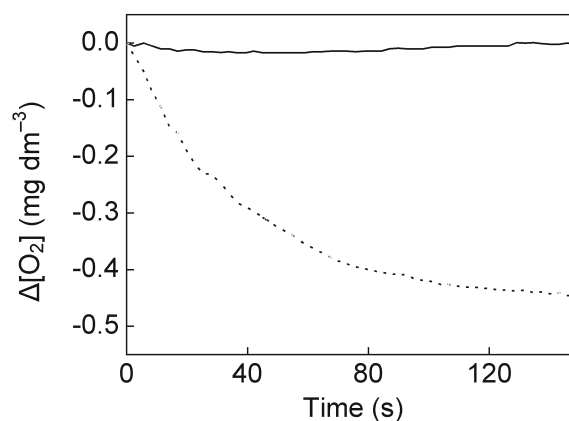


Fig. 3. Oxygen uptake measured with aqueous LDS 722 solutions in the presence of 0.04 M KI (solid line) or in the presence of 0.04 M KI and 0.8 mM FFA (dotted line).

chemical trap furfuryl alcohol (FFA), in MeOH : H_2O mixture ($\varphi_r = 1 : 1$). FFA has a reported pH-independent reactive quenching rate constant value of $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Wilkinson et al., 1995) and the oxygen uptake in water was monitored with a polarographic electrode.

Fig. 3 shows that, at relatively short times, a photo-irradiated solution of LDS 722 containing KI with light of a wavelength greater than 360 nm does not consume oxygen, while it does in the presence of 0.8 mM FFA.

Although KI as an additive was needed to obtain measurable absorbance of the triplet states in the present experiments, very low concentrations of these species may be sufficient to generate $\text{O}_2(^1\Delta_g)$, which may lead to the dye photo-degradation (expected to be very slow from the results shown in Fig. 3). Thus,

the very slow degradation of the HMCs upon laser irradiation in a polymeric medium (García-Moreno et al., 2009) may be due to self-photo-oxidation mediated by $O_2(^1\Delta_g)$. The diene central structure of these dyes appears to be an appropriate target for the well-known singlet oxygen reaction with rate constants in the order of 10^5 – 10^6 $M^{-1} s^{-1}$ (Wilkinson et al., 1995).

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References

- Ashwell, G. J., Tyrrell, W. D., & Whittam, A. J. (2004). Molecular rectification: Self-assembled monolayers in which donor-(π -bridge)-acceptor moieties are centrally located and symmetrically coupled to both gold electrodes. *Journal of the American Chemical Society*, *126*, 7102–7110. DOI: 10.1021/ja049633u.
- Cao, X., Tolbert, R. W., McHale, J. L., & Edwards, W. D. (1998). Theoretical study of solvent effects on the intramolecular charge transfer of a hemicyanine dye. *The Journal of Physical Chemistry A*, *102*, 2739–2748. DOI: 10.1021/jp972190e.
- Cerdán, L., Costela, A., García-Moreno, I., Bañuelos, J., & López-Arbeloa, I. (2012). Singular laser behavior of hemicyanine dyes: unsurpassed efficiency and finely structured spectrum in the near-IR region. *Laser Physics Letters*, *9*, 426–433. DOI: 10.7452/lapl.201210019.
- Chmyrov, A., Sandén, T., & Widengren, J. (2010). Iodide as a fluorescence quencher and promoters: Mechanisms and possible implications. *The Journal of Physical Chemistry B*, *114*, 11282–11291. DOI: 10.1021/jp103837f.
- Criado, S., Bertolotti, S. G., Soltermann, A. T., & García, N. A. (1997). Kinetics studies on the photosensitized oxidation ($O_2(^1\Delta_g)$ -mediated) of tryptophan-alkyl esters in Triton X-100 micellar solutions. *Journal of Photochemistry and Photobiology B: Biology*, *38*, 107–113. DOI: 10.1016/s1011-1344(96)07447-7.
- Fromherz, P., & Heilemann, A. (1992). Twisted internal charge transfer in (aminophenyl)pyridinium. *The Journal of Physical Chemistry*, *96*, 6864–6866. DOI: 10.1021/j100196a004.
- García-Moreno, I., Costela, A., Martín, V., Pintado-Sierra, M., & Sastre, R. (2009). Materials for a reliable solid-state dye laser at the red spectral edge. *Advanced Functional Materials*, *19*, 2547–2552. DOI: 10.1002/adfm.200900112.
- Görner, H., & Gruen, H. (1985). Photophysical properties of quaternary salts of 4-dialkylamino-4'-azastilbenes and their quinolinium analogues in solution: IX. *Journal of Photochemistry*, *28*, 329–350. DOI: 10.1016/0047-2670(85)85036-x.
- Kim, J. H., & Lee, M. Y. (1999). Excited-state photophysics and dynamics of a hemicyanine dye in AOT reverse micelles. *The Journal of Physical Chemistry A*, *103*, 3378–3382. DOI: 10.1021/jp984167e.
- Mishra, A., & Haram, N. S. (2004). New push-pull type dendritic stilbazolium dyes: synthesis, photophysical and electrochemical investigation. *Dyes and Pigments*, *63*, 191–202. DOI: 10.1016/j.dyepig.2004.02.011.
- Qin, C. X., Tang, R. C., Chen, B., Chen, D. W., Wang, X. M., & Chen, G. Q. (2010). Study on the dyeing properties of hemicyanine dyes. I. Acrylic fabrics. *Fibers and Polymers*, *11*, 193–198. DOI: 10.1007/s12221-010-0193-7.
- Szczepan, M., Rettig, W., Tolmachev, A. I., & Kurdyukov, V. V. (2001). The role of internal twisting in the photophysics of stilbazolium dyes. *Physical Chemistry Chemical Physics*, *3*, 3555–3561. DOI: 10.1039/b102779b.
- Shim, T. K., Kim, D. S., Lee, M. H., Rhee, B. K., Cheong, H. M., Kim, H. S., & Yoon, K. B. (2006). Determination of the hyperpolarizability components of hemicyanine dyes by measuring the anisotropic fluorescence and second harmonic of the dyes uniformly aligned within zeolite channels. *The Journal of Physical Chemistry B*, *110*, 16874–16878. DOI: 10.1021/jp062859u.
- Strehmel, B., Seifert, H., & Rettig, W. (1997). Photophysical properties of fluorescence probes. 2. A model of multiple fluorescence for stilbazolium dyes studied by global analysis and quantum chemical calculations. *The Journal of Physical Chemistry*, *101*, 2232–2243. DOI: 10.1021/jp962835v.
- Valeur, B. (2002). *Molecular fluorescence: Principles and applications*. Weinheim, Germany: Wiley-VCH.
- Wilkinson, F., Helman, W. P., & Ross, A. B. (1993). Quantum yields for the photosensitized formation of the lowest electronically excited singlet state of molecular oxygen in solution. *Journal of Physical and Chemical Reference Data*, *22*, 113–262. DOI: 10.1063/1.555934.
- Wilkinson, F., Helman, W. P., & Ross, A. B. (1995). Rate constants for the decay and reactions of the lowest electronically excited singlet state of molecular oxygen in solution. An expanded and revised compilation. *Journal of Physical and Chemical Reference Data*, *24*, 663–1021. DOI: 10.1063/1.555965.
- Yamaguchi, A., Nakano, M., Nochi, K., Yamashita, T., Morita, K., & Teramae, N. (2006). Longitudinal diffusion behavior of hemicyanine dyes across phospholipid vesicle membranes as studied by second-harmonic generation and fluorescence spectroscopies. *Analytical and Bioanalytical Chemistry*, *386*, 627–632. DOI: 10.1007/s00216-006-0470-x.