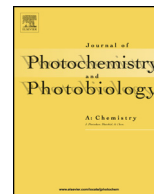




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Photoinduced processes in macrocyclic isoalloxazine–anthracene systems



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ABSTRACT

Two new macrocyclic structures containing 8-hydroxyisoalloxazine and 1,5-dihydroxyanthracene moieties linked by aliphatic chains of different lengths ($n=4$ and 6) were designed and synthesized in order to study photoinduced electron transfer (PET) processes from the anthracene unit towards the isoalloxazine singlet excited state induced by structural changes due to different intrachromophoric distances and orientations. The compounds have been fully characterized by NMR spectroscopy and the X-ray solid state structures of both macrocycles have been elucidated. Photophysical measurements, including continuous wavelength photoinduced absorption (cw-PIA), at room temperature and 77 K have been carried out in order to investigate the influence of the close contacts between the aromatic groups (π - π stacking) on the photophysical properties of the macrocycles.

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1. Introduction

Flavoenzymes are enzymes that contain as coenzymes, vitamin B2 derivatives such as, FAD (flavin adenine dinucleotide) and FMN (flavin mononucleotide). Both contain an isoalloxazine ring bound to a ribityl adenine diphosphate (FAD) or a ribityl phosphate chain, respectively (FMN) [1–5]. The isoalloxazine moiety is an

electroactive and photoactive unit that has the ability to accept one or two electrons and one or two protons to its central pyrazine unit and is responsible for the catalytic activity of flavoenzymes [6]. These particular chemical properties allow flavoenzymes to play an important role in many biological events such as cell apoptosis [7], oxygen activation [8], dehydrogenation of metabolites [9], light driven DNA repair [10], blue light photoreceptors (BLUF) [11,12] redox reactions [13] and halogenation of aromatic substrates [14]. The modulation of their reactivity is strongly dependent on the chemical environment and weak interactions such as hydrogen bonding [15–18], π - π stacking [16,19], steric effects [20] and charge transfer processes [21,22] play a key role in modulating such reactivity (Scheme 1).

A large number of studies on photoinduced electron transfer processes in flavoproteins are available in the literature [23]. A number of flavoproteins show a significant fluorescence quenching [24], where tryptophan (Trp) and/or Tyr residue(s) in the neighbourhood of the alloxazine ring of the flavoprotein are involved [25]. There are many studies available in the literature where [26,27], the factors that influence PET in flavoproteins are investigated, among them, interchromophoric distance [28], π - π stacking [29] and electrostatic interactions with aminoacids

Abbreviations: FAD, flavin adenine dinucleotide; FMN, flavin mononucleotide; BLUF, blue light photoreceptors; CRY, cryptochrome; NMR, nuclear magnetic resonance; PLQY, photoluminescence quantum yield; cw-PIA, continuous wavelength photoinduced absorption; PET, photoinduced electron transfer.

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in the isoalloxazine ring proteic environment play a major role and their contribution to the photophysical properties must be taken into account.

For instance, blue light sensors using FAD (BLUF) proteins and cryptochromes (CRYs), regulate diverse biological activities in response to blue light. Blue-light excitation causes a small spectral red shift of the S_0 – S_1 absorption band due to protein–flavin hydrogen-bond rearrangement which is mediated by photoinduced reductive electron transfer from an adjacent tyrosine to the flavin [30]. This flavin cofactor photoexcitation leads to changes in redox and protonation states that ultimately rearrange protein conformation and change molecular interactions [31].

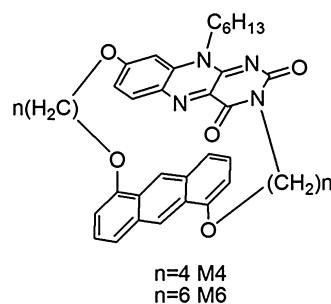
The photochemistry of flavins was first studied by Weber [32] and MacCormick and subsequently the fluorescence quenching of the flavin fluorescence by the indole ring was reported with isoalloxazine– $(\text{CH}_2)_n$ –indole diads.

We have previously reported naphthalene–isoalloxazine [33] and anthraquinone [34] systems with different chromophoric orientations due to the flexibility of the aliphatic chain linkers. Anthracene moieties were chosen in this occasion due to its robust photophysical properties and because of their ability to donate electrons. In particular, spectroscopic and photophysical properties of dialkoxyanthracenes [35,36] are very sensitive to various parameters (solvent, concentration, substitution, quenchers) and they have been used as components of photoswitches, conjugated polymers and supramolecular assemblies [37]. They can act as very powerful probes able to reveal weak molecular interactions such as π – π stacking, donor–acceptor, etc. When compared to unsubstituted anthracene, the spectroscopic properties of the dialkoxyanthracenes are significantly different. They undergo intramolecular conformational changes in the excited state that give rise to a reshaping of the fluorescence spectrum on the nanosecond timescale. A recent example of complexation of anthracene by an organic macrocycle led to significant changes in the energy transfer rates due to orientation of donor and acceptors [38].

A milestone in the field of PET of model systems was the seminal work of Closs and Miller [39] where photoinduced electron transfer (PET) in organic donor–acceptor systems linked by aliphatic and aromatic spacers was studied. Borkent et al. [40] were among the first to report the influence of geometry and solvent polarity on the charge-transfer fluorescence from electron donor–acceptor macrocycles. Since then many examples of covalently linked chromophores included in a macrocyclic structure can be found in the literature [41–44].

Anthracene–isoalloxazine systems were first studied by Staab et al. [45,46] in systems where two isoalloxazine molecules were linked by naphthalene or anthracene molecules or more flexible aliphatic chains, in order to quantify the effect of π – π stacking in the electrochemistry of the isoalloxazine ring.

With the intention to contribute to the understanding of flavin coenzyme functions we tried to synthesize models meeting these requirements. Aromatic stacking is one of two classes of non-covalent interactions known to govern redox and recognition properties in flavins (hydrogen bonding is the other one). Many studies have been devoted to understand such interactions, especially from the electrochemical point of view [46,47]. We are particularly interested in aromatic π – π interactions and their role in isoalloxazine photophysical behaviour because of their implications in biological systems and in view of designing new artificial systems capable of emulating them. In order to gain a deeper understanding and control of these effects, simple model compounds containing two chromophores, 8-hydroxyisoalloxazine and 1,5-dihydroxyanthracene, (Scheme 1) locked in a macrocyclic architecture were synthesized and their photophysical properties evaluated.



Scheme 1. Macrocycles under study containing 1,5-dialkoxyanthracene and 8-alkoxyisoalloxazine units.

2. Experimental

2.1. Materials and equipment

All chemicals and solvents were purchased from Aldrich and used as received. Melting Points were determined using a ThermoGalen hot stage microscope. Unless otherwise stated, column chromatography was performed on silica gel (Merck 60, 70–230 mesh). The R_f values were measured on aluminium coated silica gel 60 F254 TLC plates (Merck, 0.2 mm) with the indicated eluent. Mass spectra were performed in a FAB Waters VG Autospec (UAM-SIDI) using *m*-nitrobenzyl alcohol as matrix. Elemental analysis for carbon, hydrogen and nitrogen were carried out by the CAI-UCM Microanalytical Service on a PerkinElmer 240 Analyser. Spectra were recorded in a Bruker DRX 400 (9.4T, 400.13 MHz for ^1H and 100.62 MHz for ^{13}C NMR) spectrometer. Chemical shifts (δ in ppm) are given from internal CHCl_3 (7.26 ppm) for ^1H NMR, CDCl_3 (77 ppm) for ^{13}C NMR. Coupling constants (J in Hz) are accurate to ± 0.2 Hz for ^1H .

2.1.1. Spectroscopic measurements

Absorption spectra were recorded with a PerkinElmer $\lambda 9$ spectrophotometer in CH_2Cl_2 solvent. For luminescence experiments in the same solvent, the samples were placed in fluorimetric 1-cm path cuvettes. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm). An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained via a calibration curve supplied with the instrument. Luminescence quantum yields (ϕ_{em}) in solution obtained from the integration of the spectral area on a wavelength scale (nm) were calculated according to the approach described by Crosby and Demas [48] air-equilibrated $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ in water solution ($\phi_{\text{em}} = 0.028$) [49] as standard.

Emission lifetimes were determined with the single photon counting technique by means of the same Edinburgh FLS980 spectrometer using a laser diode as excitation source (1 MHz, $\lambda_{\text{exc}} = 407$ nm, 57 ps pulse width and ~ 30 ps time resolution after deconvolution) and a Hamamatsu MCP R3809U-50 (time resolution 20 ps) as detector. To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz Dewar, filled up with liquid nitrogen. Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime determinations, $\pm 20\%$ for emission quantum yields, ± 2 nm and ± 5 nm for absorption and emission peaks, respectively.

In continuous wavelength (cw) photo-induced absorption (PIA) an on/off monochromatic continuum laser source provides the excitation flux while a white light probes the photo-generated species. Formation and recombination of charge carriers is monitored in the ns–ms time domain. Setup detailed description is reported elsewhere [50].

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