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Classification of novel thiazole compounds for sensitizing Ru–polypyridine complexes for artificial light harvesting

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ABSTRACT

A systematic study of the Förster resonance energy transfer (FRET) efficiency between thiazole dyes and a ruthenium–polypyridine complex is presented. While ruthenium–polypyridines are conventionally used in artificial light harvesting systems as primary electron donors, their application suffers from rather low extinction coefficients in the visible spectral range and an absorption gap between the $\pi\pi^*$ transitions of the ligands and the MLCT transitions. In this paper it is shown how thiazoles might help to circumvent theses issues. The absorption and emission spectra of the thiazole can be synthetically adjusted to fall into the absorption gap of the Ru dye and to efficiently overlap with the ^{1}MLCT absorption of the complex, respectively. Thereby, the thiazoles might serve as antenna structures to funnel energy to the Ru-polypyridine unit, which finally can act as a photoactivated primary electron donor. Systematic investigations of the Förster radii of representative thiazole Ru-polypyridine dye pairs corroborate this potential quantitatively.

1. Introduction

Artificial photosynthesis presents a current intensely discussed approach to cope with the looming energy crisis which stems from limited resources of fossil fuels and an increasing demand for environmentally clean energy solutions [1–5]. The concept of artificial photosynthesis aims at adopting natural strategies of harvesting sunlight and converting it into chemical energy for the production of environmentally clean energy and – ideally – fuels in terms of, e.g., reduction of protons and production of molecular hydrogen [6,7]. In following its natural benchmark, artificial photosynthesis generally employs a modular approach in which photoactive centers are combined via molecular electron relays with catalytically active centers. The latter are activated upon photoinduced electron transfer. Being in their photoreduced state, these catalytically active centers can catalyze, e.g., the reduction of protons or CO_2 [8–11].

Ru-polypyridine complexes or Ru-polypyridine complex fragments are widely employed as possible primary electron donors. In such systems absorption of a photon causes a metal-to-ligand charge-transfer (MLCT) transition, upon which the electron density is reduced at the metal ion and enhanced on the ligands [12–14]. Such MLCT states can further transfer their electronic excitation within a supramolecular assembly [15–17] to a catalytically active center or across an interface into a wide-band-gap semiconductor (Graetzel cell). Despite their beneficial electron transfer properties, the use of Ru-polypyridine complexes as primary electron donors in artificial photosynthetic systems is complicated by the rather low extinction coefficients of the MLCT transition in the visible spectral range. Furthermore, such systems typically exhibit an absorption gap between the $\pi\pi^*$ transitions of the ligands (for bipyridine at around $\lambda = 290$ nm) and the MLCT transitions (typically at around $\lambda = 450$ nm), which limits the light-harvesting efficiency of the supramolecular assembly. These pitfalls can be improved by dressing the photoactive primary electron donor with an antenna structure—in very much the same fashion in which the natural photosystems are equipped with antenna structures.

In this contribution, the potential of using tailor-made thiazoles as antenna structures to efficiently absorb light within the absorption gap of Ru-polypyridine complexes is elicited. While the capability of absorbing light can be directly judged from the extinction coefficient, the potential of the antenna molecule to transfer (a fraction of) the absorbed photon energy to the primary electron donor also needs to be taken into account. Such an

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energy transfer is central for the functionality of the antenna structure and – in the limit of weak coupling between the antenna and the photoactive center – its efficiency can be estimated by the theory of Förster resonance energy transfer (FRET). Therefore, in order to investigate the potential of thiazole Ru-polypyridine complexes as antenna–photoactive center pairs a systematic study of Förster radii for such systems is presented. The Förster radius of a donor–acceptor pair for energy transfer is a metric that determines the effective range of the transfer process and thereby determines the quality of the pair of molecules to act as donor–acceptor unit. For optimized FRET pairs commonly used in fluorescence microscopy such as Cy3–Cy5 or Cy5–Cy5.5 Förster radii as large as 50 and 80 Å can be achieved [18]. In this paper, the Förster radii for selected pairs of thiazoles–ruthenium dye are quantified and the consequences for the implementation of thiazoles as antenna structures in artificial photosynthetic units are discussed. As a benchmark system for mimicking the photoactive center the well known tris (2,2′-bipyridine) ruthenium (II) hexafluorophosphate (Ru(bpy)$_3$) complex is employed.

2. Material and methods

In FRET, which presents a long-range-interaction mechanism, the energy of a donor is transferred by a nonradiative interaction of electrical dipoles to the energy acceptor [19]. The efficiency E and the transfer rate k_{FRET} of this process depend on the molecular electronic properties of both the donor and acceptor given by Eqs. (1) and (2), respectively:

$$E = \frac{1}{1+(R/R_0)^6} \tag{1}$$

$$k_{FRET}(R) = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6 \tag{2}$$

Here, R represents the distance between an energy donor and acceptor. τ_D is the donor luminescence lifetime in the absence of the energy acceptor and R_0 is the Förster radius. As can be seen from Eq. (1), R_0 describes the distance between donor and acceptor at which the energy transfer efficiency has dropped to 50% and, consequently, presents a convenient metric for judging the quality of a donor–acceptor pair for FRET. R_0 (in Å) can be expressed as [20]

$$R_0 = 0.211(\kappa^2 n^{-4} Q_D J(\lambda))^{1/6} \tag{3}$$

As can be seen from Eq. (3), the Förster radius is determined by the emission quantum yield of the donor Q_D and the index of refraction of the solvent (in this study we used acetonitrile as solvent, i.e., $n=1.34411$). The mutual orientation of the electronic transition dipole moments is expressed by the orientation factor κ^2. In the calculations the orientation factor κ^2 is assumed to be 2/3 [21]. Finally, the overlap integral $J(\lambda)$, given by Eq. (4), enters the formula for the Förster radius. In order to calculate the value of the Förster radius for a given pair of donor and acceptor according to Eq. (3), the overlap integral $J(\lambda)$ needs to be computed based on the donor emission F_D and the molar extinction coefficient ε_A of the acceptor according to Eq. (4) where J is expressed in unit of $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}\,(\mathrm{nm})^4$:

$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \tag{4}$$

All calculations were performed with in-house written scripts in Matlab.

3. Experimental

Measurements of the fluorescence intensity were carried out on a Perkin Elmer lambda16 UV/Vis spectrometer in the perpendicular excitation–emission geometry, while the absorbance in the most red-shifted absorption maximum was <0.05. The calculation of fluorescence quantum yields was done according to the following equation [22]:

$$\Phi = \Phi_r \frac{I}{I_r}\frac{A_r}{A}\frac{n^2}{n_r^2},$$

where Φ is the quantum yield, I is the corrected integrated emission intensity, A is the absorbance at the excitation wavelength and n is the refractive index of the solvent, i.e., acetonitrile in this study. The subscript r refers to a reference fluorophore of known quantum yield. Here we used quinine sulfate ($\Phi=0.55$) [22]. All thiazoles were excited in their absorption maximum and at the excitation wavelength of the reference chininsulfat (347 nm). Thus, the experimental protocol gives rise to a mean value of the quantum yield.

The fluorescence lifetimes of the thiazoles were obtained by time-correlated single photon counting (TCSPC) after excitation with either a frequency-doubled or a frequency-tripled Ti–sapphire laser (Tsunami, Newport Spectra-Physics GmbH), i.e., $\lambda_{ex}=420$ or 290 nm, respectively. Frequency tripling was achieved by sum-frequency-mixing of the fundamental with the second harmonic of the Ti-sapphire laser in a setup described in Ref. [23]. The repetition rate of the laser was adjusted to 0.8 MHz by a pulse selector (Model 3980, Newport Spectra-Physics GmbH). The emission of the thiazoles was detected using a PMC-140-photon-counting module from Becker and Hickel. To determine the lifetimes the software SPCImage 2.8 (Becker and Hickl) was used for fitting a monoexponential function to the experimental fluorescence decay curves.

The Ru(bpy)$_3$ complex was prepared by following a standard protocol [24]. After heating ruthenium (III) chloride with excess 2,2′-bipyridine in a 1:1 mixture of ethanol/water to reflux for 3 h, the complex was precipitated with NH_4PF_6 as the hexafluorophosphate salt. Further purification was achieved by two times recrystallization by ether diffusion in a CH_3CN solution of the complex. The synthesis of the thiazoles used in this study has been published elsewhere [25–27].

4. Results

The thiazoles presented in this study constitute potential energy donors for Ru(bpy)$_3$—a benchmark model for Ru–polypyridine complexes, which might serve as primary electron donors in artificial photosynthetic systems. As shown in Fig. 1 the λ_{max} of the absorption of the thiazoles is located in the gap between the $\pi\pi^*$ transition of the Ru-ligand and the ^{1}MLCT state of the Ru(bpy)$_3$ complex. Therefore, using the thiazoles as randomly orientated antennas in the vicinity of the complex, the absorption spectrum of the artificial photocatalytic system becomes broadened, which finally increases the energy available to excite the photoactive electron donor to the MLCT state. The requirement for funnelling the energy absorbed by the antennas to the ^{1}MLCT state is the overlap (according to Eq. (4)) of absorption and emission spectra between the ^{1}MLCT band of the Ru-complex and the emission spectra of the dyes. This condition is generally fulfilled from the used thiazoles. As an exemplification, the absorption spectra of two selected thiazoles and Ru(bpy)$_3$ are shown in Fig. 1. The photophysical properties of the thiazoles investigated are summarized in Table 1, while the chemical structures of all thiazoles investigated in this study are comprised in Fig. 2.