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Supramolecular tuning of energy transfer efficiency and direction in a bis(styryl) dye–crown ether conjugate

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ABSTRACT

The control of the energy transfer (FRET) in a novel bischromophoric styryl(pyridinium) dye bearing two different crown ether residues is presented. Complexation of the dye with metal cations allows to tune the FRET efficiency without changing the transfer direction or to switch the FRET off, whereas protonation launches the FRET process in the opposite direction relative to the molecular structure.

1. Introduction

Photoinduced resonance energy transfer (FRET) is one of the basic processes in Nature that ensures photosynthetic conversion of the solar energy into chemical bonds in living organisms [1]. In artificial systems, photoinduced energy transfer is widely used in solar energy harvesting elements, ratiometric sensors, and organic photovoltaics [2–6]. Most of these applications require a stringent control of the FRET rate, efficiency and, especially, the direction. Along these lines, it is highly desirable that the direction of the energy transfer can be switched on demand. For example, such switching has been realized by changing the complexed metal cations in homo- and heterodimers of metalloporphyrins [7], metallocyclodextrin assemblies [8] and [2]-catenates incorporating the $[Ru(tpy)_2]^{2+}$ fragment [9]. The control of the FRET direction can be also accomplished by protonation/deprotonation of the donor or acceptor unit as has been shown for oligophenylene-vinylene (OPV)–phenanthroline [10] and OPV–fullerene [11] dyads and for multichromophoric BODIPY systems [12,13]. In addition, several intriguing examples of switchable FRET directions have been reported that use site-specific solvent effects [14], temperature changes [15] or the electronic difference between cation-binding sites [16,17]. Nevertheless, molecules or molecule assemblies that enable the fine regulation of the energy transfer processes based on supramolecular interactions are still rare and their discovery and development remains a topical challenge.

Herein, we present a dye–crown ether conjugate whose energy transfer efficiency and direction is controlled by supramolecular complexation and protonation. The system is based on a novel bischromophoric styryl derivative **1** that is functionalized with benzo-15-crown-5 and azadithia-15-crown-5 ether units (Chart 1). Owing to the different affinity of the crown ether fragments towards metal ions or protons, the optical properties of each chromophore can be varied independently by introduction of appropriate metal cations or protonation, thus enabling the control of the energy transfer properties.

2. Results and discussion

2.1. Synthesis of bis(styryl) dye 1

The bis(styryl) dye **1** was obtained in 42% yield by condensation of the corresponding formylbenzocrown derivatives with γ-picoline and subsequent quaternization of the intermediate styryl(pyridine) species with 1,4-bis(bromomethyl)benzene (for details see ESI, Section 1). The parent monochromophoric dyes **2** and **3** were synthesized according to published protocols [18,19].

2.2. Steady-state optical spectroscopy

The absorption spectrum of bis(styryl) dye **1** exhibits two long-wavelength absorption bands centered at 420 and 486 nm (Fig. 1, Table 1). Comparison with the absorption spectra of the related monochromophoric dyes **2** (λ_{abs} = 395 nm) [18] and **3** (λ_{abs} = 474 nm)

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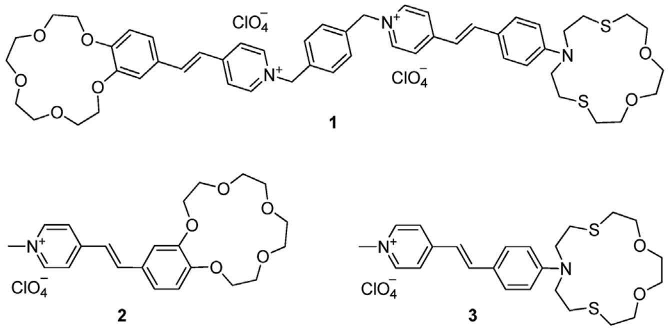

Chart 1. Chemical structures of styryl dyes **1–3**.

Table 1
Optical properties and stability constants of **1** and its complexes in acetonitrile.

Compound	λ_{abs}, nm	$\varepsilon \times 10^{-4}$, L mol^{-1} cm^{-1}	log *K*
1	420, 486	3.27, 3.63	–
1-Mg^{2+}	368, 486	3.12, 3.71	3.27 ± 0.03
1-Hg^{2+}	373, 393	3.37, 3.43	> 7[a]
1-H^{+}	404, 338	3.96, 3.07	3.38 ± 0.01

[a] The value is too high to be determined from spectrophotometric titration.

[19] in acetonitrile, respectively (Figs. S3 and S4, ESI), allowed to assign the band at 420 nm to the benzocrown-substituted styryl chromophore of dye **1** and the band at 486 nm to the azadithiacrown-substituted one. For the sake of clarity, the benzocrown-functionalized chromophore will be referred to as the O-chromophore and the azadithiacrown-functionalized one as the N-chromophore, to indicate that the respective electron-donating heteroatom of the crown ether, that is directly conjugated with the styryl(pyridinium) fragment, determines the photophysical properties of the chromophore.

Complexation of the crown ether functionalities of dye **1** with metal cations leads to a blue shift of the corresponding absorption bands. It is known that oxacrown ethers have a high affinity to alkali and alkali-earth metal ions [20], whereas the introduction of N or/and S atoms leads to higher affinity towards transition metal ions [21]. Based on this difference, the attachment of different crown ethers with diverse heteroatom substitution to the two chromophoric parts of **1** enables the independent regulation of the optical properties of each chromophore by complexation with appropriate cations. For the present study, we have selected Mg^{2+} and Hg^{2+} cations as they have the most effective interaction with the corresponding crown ethers [22,23]. The metal cations were used as perchlorate salts. To avoid introduction of different anions that may potentially influence complexation, we used perchloric acid for protonation of the azadithiacrown ether residue.

Addition of Mg(ClO$_4$)$_2$ to a solution of **1** results in a blue shift ($\Delta\lambda = 52$ nm) of the O-chromophore absorption whereas the N-chromophore absorption remains unaffected (Fig. 1A, Table 1). Conversely, the introduction of Hg(ClO$_4$)$_2$ and HClO$_4$ causes a blue shift of the N-chromophore absorption (Hg(ClO$_4$)$_2$: $\Delta\lambda = 124$ nm; HClO$_4$: $\Delta\lambda = 148$ nm) without significant changes of the O-chromophore absorption (Fig. 1B and C, Table 1). The stability constants of the complexes of **1** were obtained from the spectrophotometric titration data (Figs. S1 and S2, ESI) and are collected in Table 1.

According to the classical description of the Förster resonance energy transfer (FRET), an efficient energy transfer requires a spectral overlap between the emission of the donor and the absorption of the acceptor chromophores [24,25]. To estimate the potential for an intramolecular energy transfer in dye **1** and its complexes, the optical characteristics of each chromophore were assessed separately with parent monochromophoric dyes **2** and **3** and their complexes with Mg^{2+}, Hg^{2+} and H^{+}. The fluorescence of **2** overlaps significantly with the absorption of **3** (Fig. 2A). Therefore, within the bischromophoric dye **1**, the O-chromophore may act as an energy donor (ED), whereas the N-chromophore is an energy acceptor (EA). The blue shift of the fluorescence of **2** upon complexation with Mg^{2+} provides more pronounced spectral overlap between the fluorescence of the O-chromophore (ED) and the absorption of the N-chromophore (EA) (Fig. 2B), thus favoring energy transfer in complex **1**-Mg^{2+}. At the same time, the absorption and fluorescence spectra of dye **2** and complex **3**-Hg^{2+} do not overlap so that an energy transfer is not feasible in the complex of dye **1** with Hg^{2+} (Fig. S5, ESI). Protonation of dye **3** results in a sufficient spectral overlap of the fluorescence of **3**-H^{+} and the absorption of **2** which leads to a reversal of the donor and acceptor functions of the chromophores in the energy transfer process (Fig. 2C). Thus, in the bischromophoric system **1**-H^{+} the protonated N-chromophore acts as energy donor and the O-chromophore as energy acceptor.

2.3. Theoretical calculation of the energy transfer efficiency

To estimate the efficiency of the energy transfer in **1** and its complexes **1**-Mg^{2+} and **1**-H^{+}, we performed calculations according to Förster resonance theory (for details seeESI, Section 5) [25]. Taking into account the crucial influence of the interchromophoric distance on FRET efficiency, on one side, and high conformational lability of **1**, on the other side, we considered two extreme conformations of dye **1** with maximally close and maximally remote mutual positions of the chromophores (Fig. S11, ESI). After geometry optimization (MOPAC 2016, PM7), the corresponding interchromophoric distances were determined as $r_{max} = 15$ Å and $r_{min} = 9$ Å. Based on these values, we obtained the following theoretical intervals of the FRET efficiencies Φ_{FRET} (th): 97.4–99.9% for **1**, 93.7–99.7% for **1**-Mg^{2+} and 42.8–94.1% for **1**-H^{+}. Therefore, the expected FRET efficiencies in the studied species in most cases are very high. At the same time, the pronounced difference in the theoretical values Φ_{FRET} (th) for two extreme conformations of complex **1**-H^{+} arises from the relatively small value of the Förster radius $R_0 = 14$ Å, i.e. the distance at which the energy transfer efficiency is

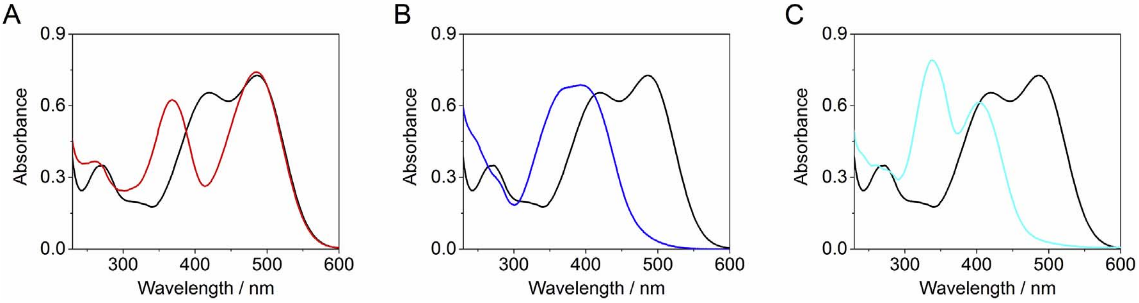

Fig. 1. Absorption spectra of **1** (black), (A) complex **1**-Mg^{2+} (red) with the Mg^{2+} cation bound to the benzocrown ether residue; (B) complex **1**-Hg^{2+} (blue) with the Hg^{2+} cation bound to the azadithia-crown ether residue; (C) protonated form **1**-H^{+} (cyan) with a proton bound to the crown ether nitrogen. In all cases $c = 20\,\mu$M, in acetonitrile, $T = 20$ °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)