



Supramolecular FRET modulation by pseudorotaxane formation of a ditopic stilbazolium dye and carboxylato-pillar[5]arene



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ABSTRACT

In this paper we introduce a new approach towards the modulation of fluorescence resonance energy transfer (FRET). Two stilbazolium dyes (**A**, **D**) exhibiting opposite fluorescence responses upon complexation with anionic, water soluble carboxylato-pillar[5]arene (**WP5**) were covalently linked via click chemistry, yielding a FRET-capable ditopic indicator (**G**). The pseudorotaxane formation of **G** with **WP5** in pure water induced fluorescence enhancement combined with the modulation of the FRET process due to the interaction of the macrocycle with the two fluorophore units.

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1. Introduction

Förster resonance energy transfer (or fluorescence resonance energy transfer, FRET) is an energy transfer mechanism occurring between an excited donor and a ground state acceptor fluorophore through non-radiative dipole-dipole interactions [1,2]. The efficiency of the FRET process depends on the distance between the donor and acceptor units, on their alignment, on the spectral overlap between the donor emission and the acceptor absorbance and on the fluorescence quantum yield of the donor, thereby providing versatile ways of FRET modulation [3]. FRET is widely used in fluorescence sensing and imaging, utilizing the inherent advantage of ratiometric measurements [4–6]. FRET-related techniques are particularly important in biomedical research, exploiting

that FRET is sensitive in the 1–10 nm distance range that matches the dimensions of proteins, polynucleotides, or the thickness of cell membranes [7–9]. FRET is also popular in the design of chemical sensors, in which the modulation of FRET is achieved by a chemical reaction: the analyte binds covalently or coordinatively to the sensor, induces the splitting of a chemical bond in their donor/acceptor units or induces the cleavage of the donor-acceptor bond [10,11].

In principle, FRET can also be modulated by supramolecular interactions, in the presence of a macrocyclic host that forms an inclusion complex with the FRET sensor. Stimuli-responsiveness, i. e. photoresponsive supramolecular systems are widely studied [12,13], especially in the case of interlocked structures [14–16]. A few studies have been published on the effect of cyclodextrins on the fluorescence behavior of FRET dyads in aqueous solutions [17,18], however the modulation of FRET in covalently linked donor-acceptor pairs by supramolecular interactions is virtually

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unexplored. In the present work we studied this effect on the example of a complex formed by a stilbazolium dyad (**G**) and a pillararene macrocycle. Since the fluorophore components of **G** are strongly solvatochromic, this could be exploited to modulate the overall FRET process by the changes in optical properties upon interaction with a macrocyclic host. To our knowledge, neither FRET systems containing stilbazolium fluorophores was compiled previously nor the modulation of the intramolecular FRET process was attained by the complexation of a FRET dyad by a pillararene. It was hoped that the results on such a model system can be helpful in the application of solvatochromic FRET-based sensors in complex matrices of biological origin.

Although pillar[*n*]arenes (**Pns**) are a relatively new class of macrocycles [19], they have soon become one of the most popular targets in host-guest chemical studies [20–27]. Especially, the discovery of water soluble derivatives (**WPns**) have further extended their applications in various biological systems. Mostly ionic (carboxylate [28–30], ammonium [31,32], imidazolium [33]) pillararenes, in particular carboxylate-**Pns** have been used in binding studies performed in aqueous medium. Carboxylate-pillar[5]arene (**WP5**), first synthesized by Ogoshi in 2010 [28] is an ideal host for ammonium-containing and electron-deficient guests [34–36]. It is worth mentioning that only a few papers describe the complexation of fluorescent guests by **WP5** [37,38] and the observation of FRET on sophisticated supramolecular systems containing pillararenes was reported only in two recent articles [39,40]. Recently, we described the complexation of **WP5** with three stilbazolium dyes, of which 4-dimethylaminostyryl-*N*-methylpyridinium iodide (**DAST**) produced a colorimetric response and a large fluorescence enhancement upon binding to **WP5** [41]. In the present paper, we report the complexation of two simple pyridinium dyes (**A**, **D**) and their covalently linked, FRET-capable

derivative (**G**), with **WP5** (Fig. 1).

2. Results and discussion

2.1. Synthesis

4-Methoxystyryl-*N*-methylpyridinium iodide (**D** as donor), 4-dimethylaminostyryl-*N*-phenylpyridinium chloride (**A** as acceptor) and **WP5** were synthesized using standard literature methods [42–44]. In order to efficiently link these fluorophores, we turned to click chemistry which is often used to yield FRET-capable dyads [45–48]. The covalently linked ditopic compound was therefore achieved by the click reaction of the *O*-propargyl-analogue of **D** (**4**) and the azide-containing analogue of **A** (**2**) and fully characterized by NMR and HRMS measurements (Fig. 2). The starting materials **2** and **4** were prepared in the same manner as **D** and **A**, namely by the Knoevenagel condensation of the corresponding benzaldehydes **1** and **3**, respectively, in ethanol or methanol using piperidine as catalyst.

2.2. Complexation of **D** and **A** with **WP5**

The effects of the inclusions of **D** and **A** by **WP5** on their fluorescence are illustrated schematically in Fig. 3a. The variations of the absorption and fluorescence spectra of **D** and **A** upon the addition of **WP5** are shown in Fig. 3b–e. They both are negative solvatochromic dyes, accordingly, their absorption bands are shifted to the red when the dyes are included in the pillararene cavity, as an environment of lower polarity (see Fig. 3b and d). The shifts of the fluorescence bands upon complexation are less pronounced, the intensities, however, show a spectacular change (see Fig. 3c and e). Interestingly, despite the virtually small structural differences between **A** and **D**, their fluorescence responses to the complexation are opposite: turn off in case of **D**, turn on in the cases of **DAST** [41] and **A** (see Table 1 for spectroscopic details). The relatively weak fluorescence of uncomplexed **A** can be explained with its deactivation via a low energy twisted intramolecular charge transfer state [49,50], which is blocked when **A** is confined in the cavity of **WP5**. The fluorescence quenching of **D** upon complexation may be related with an electron transfer between the pyridinium unit in the excited state of dye and a carboxylate group of the **WP5** host. A photoinduced electron transfer within the contact pair of **DAST** with I^- ion had been described [51]. The theoretically calculated ground state dipole moments for **D** and **A** have close values, but in excited state **D** has a higher dipole moment, which may indicate a higher local positive charge on its pyridinium unit, favoring for electron acceptance [52].

The expected 1:1 stoichiometries of the **D**-**WP5** and **A**-**WP5** complexes were verified by Job's method (see Supporting Information, Figs. S8 and S9). A least-square fitting to the absorption spectra of the dye-pillararene mixtures yielded the values of $K_a(\mathbf{D}\cdot\mathbf{WP5}) = 1.64 \cdot 10^6 \text{ M}^{-1}$ and $K_a(\mathbf{A}\cdot\mathbf{WP5}) = 6.63 \cdot 10^6 \text{ M}^{-1}$ for the association constants. It is clear, that there is no significant difference in the magnitude of the two K_a values.

The complexation of **D** and **A** was further examined by ^1H NMR spectroscopy in D_2O (Fig. 4). As can be seen on Fig. 4, almost all signals deviate in the spectra of the complexes. The splitting of the proton signals of **WP5** shows the inclusion-induced restriction of rotation (as previously observed with **DAST** and paraquat [21,32]) of the constituent units. Significant upfield shifts and signal broadening can be observed both in the cases of **D** and **A**, that indicate the threading and thereby the shielding effect.

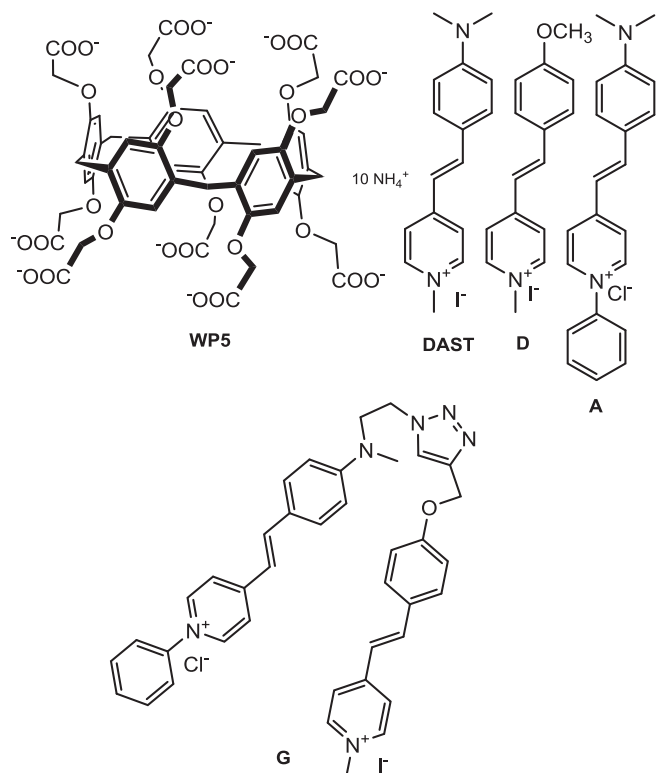


Fig. 1. Structures of **WP5**, **DAST**, **D**, **A** and **G**.

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