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Invited paper

Synthesis, photochemical and luminescent properties of *ortho*-hydroxystyrylquinazolinone-linked benzocrown ethers



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ABSTRACT

Photoinduced transformations of (*E*)-2-(2-hydroxystyryl)quinazolinone-linked benzo[15(18)]crown-5(6) ethers in solutions have been studied by using UV–vis absorption and NMR spectroscopy. These crown ethers were found to have dual emission at 520 and 650 nm, associated with proton-transfer tautomer emission (ESIPT-luminescence) as a rare case of excited-state proton-transfer reaction in the non-pseudocyclic chromophoric systems. It was established also, that the organic bases affect the luminescence intensity of solutions of these compounds in the 550–650-nm wavelength range. An X-ray crystallography analysis of molecular structures of crown ethers and their complexes in crystals has been carried out. The fact of reversible photo/thermal *E*-*Z* isomerization in DMF and Et₃N for these macroheterocyclic compounds has been confirmed. An opportunity to control the photochemical isomerization rate of quinazolinone 2-(hydroxyphenyl)ethenyl derivatives by changing pH of the medium has been demonstrated.

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1. Introduction

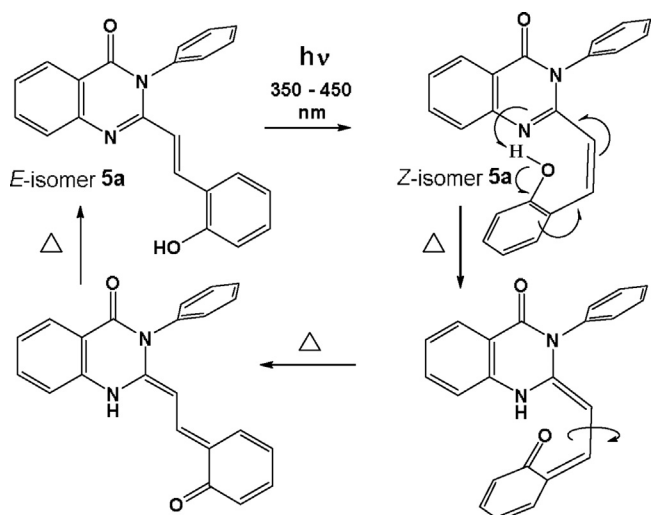
Diaryl substituted ethenes and their heterocyclic analogues are considered to be one of the basic groups of modern electroluminescent and photochromic materials, widely used in nonlinear optics, lasers with tunable frequency, optoelectronic devices for recording and storage of information, and molecular photoswitches [1,2]. In the series of hetaryl substituted stilbenes, their unsymmetrical derivatives [3,4] are of particular interest. Due to the contribution of the n,π^* -state, the presence of an acceptor azine (azinone) core, in addition to electron-donating aryl fragment in stilbene derivatives might be of considerable influence on photochemical and photophysical behavior of these luminophores [5]. Indeed, there are several publications concerning the synthesis of (*E*)-2-styrylquinazolin-4(3*H*)-ones and studying of their photophysical properties [4,6–10]. It should be noted that compounds of this push-pull type, having a specific emission ability and a profound tendency to a photoinduced *E*-*Z*-

isomerization [9,10] are quite promising for development of pH-sensitive photochromic materials. Recently, we have first established the ability of *ortho*-hydroxystyrylquinazolinone **5a** (Scheme 1, 2) to undergo a reversible photo/thermal switch in solutions [11]. The process of *E*-*Z*-isomerization is initiated by irradiation with a light in the 300 – 400 nm range, while the reverse *Z*-*E*-inversion is a dark process, which is accelerated significantly at elevated temperatures. It has been shown that both photochromic and luminescent properties of such compounds can be regulated by changing pH of the medium.

As a rule, successful application of organic photoswitches depends on light absorption in a visible area by their chromophoric fragments, and it is besides determined by the presence of noticeable fluorescence in an initial compound or a photoproduct [2]. Hydroxystyrylquinazolinones are potential photoacids, namely, compounds with increasing acidity in an electronically excited state [12]. A dual emission connected with excited-state intra- or intermolecular proton-transfer reaction is distinctive feature of the certain photoacids [13]. One of approaches to improve photophysical and photochemical properties appears to be ionization of pH-sensitive groups of photochromic frameworks. It is known, that the crown ethers are able to activate such groups through the

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Scheme 1. Reversible photo/thermal *E-Z-E* isomerization of *ortho*-hydroxystyrylquinazolinone **5a**.

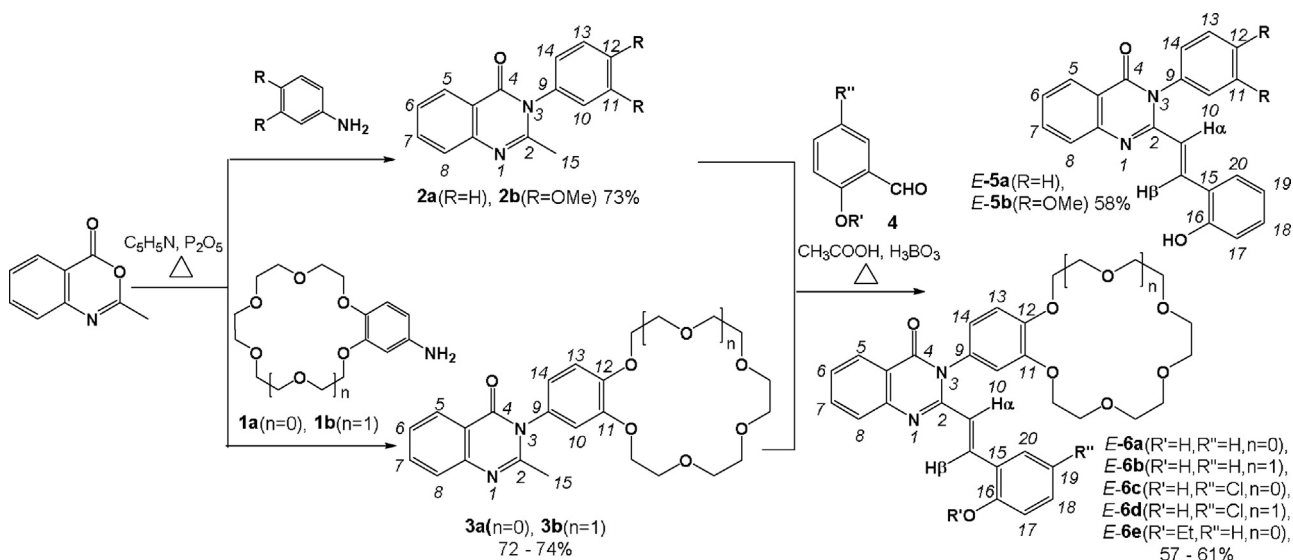
formation of inter- and intramolecular hydrogen bonds (H-bonds) with their polyether macrocyclic cavity [14–17]. Besides that, the self-assembling/hetero-assembling ability of crown ethers in different media is the important factor in supramolecular chemistry [3,18]. In this communication we wish to report photophysical and photochemical behavior of (*E*)-2-(2-hydroxystyryl)quinazolinone-linked benzo[15(18)]crown-5(6) ethers **6a-d** by comparison of their properties with those of the ethoxy substitution derivate *E*-**6e** and acyclic analogues *E*-**5a,b** (Scheme 2).

2. Experimental

2.1. General methods and measurements

IR spectra were recorded on a Perkin Elmer Spectrum One IR Fourier transform spectrometer using a diffuse reflectance sampling accessory (DRA). Electron absorption spectra were recorded on a UV-2600 PC double-beam spectrophotometer (Shimadzu, Japan) in the range of 190–700 nm with the wavelength setting accuracy of ± 0.3 nm using a Shimadzu Scan

standard program. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer with mutually perpendicular beams, the wavelength setting accuracy of 0.5 nm. The measurements were carried out in the range of 190–800 nm in SUPRASIL 111-QS 10 quartz cells at 298 K (Hellma, Germany), the bandwidth around the stationary point of excitation/emission was 10 nm. The wavelength of the excitation stationary point was assigned based on the maximum in absorption and emission spectra each time, the wavelength of the emission stationary point, based on the maximum in excitation spectra. The PEM bias was 700 V. The solvent luminescence was taken into account in the spectra. The relative quantum yields of solutions were measured at 22 ± 1 °C according to the procedure, given at www.jyhoriba.co.uk (Jobin Yvon Ltd. 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ UK). The control samples were fluorescein [19] ($\Phi_{\text{abs}} = 0.85$) in 0.1 N aqueous solution of KOH and quinine bisulfate [19] ($\Phi_{\text{abs}} = 0.55$) in 0.1 N aqueous solution of H_2SO_4 . ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400 and 100 MHz) and Bruker AVANCE-500 (500 and 126 MHz) spectrometers in $\text{DMSO}-d_6$ at 295 K, using TMS and $\text{DMSO}-d_6$ ($\delta_{\text{C}} = 39.5$ ppm) as references. ^1H and ^{13}C signals in the NMR spectra were assigned using 2D experiments $^1\text{H}-^1\text{H}$ COSY, $^1\text{H}-^1\text{H}$ NOESY, $^1\text{H}-^{13}\text{C}$ HSQC, and HMBC. The mass analyzer was a Bruker Daltonics MicroTOF-Q II mass spectrometer with an electrospray ionization source, a 6-port divert valve and syringe pump kd Scientific with flow rate 180 $\mu\text{L}/\text{h}$. The instrument controls were performed with HyStar 3.2 and microTOF control 2.3 patch 1 (Bruker Daltonics) software. The nominal resolution of the instrument was 17,500. The instrument was operated in positive ion mode with m/z range of 50–800. The capillary voltage was 4500 V, and the capillary exit was 166 V. The nebulizer gas pressure was 0.4 bar, and the drying gas flow was 4 L/min. The drying temperature was 250 °C. The spectra average was set to 3, and the summation was 5000, corresponding to 1 s sample time. The transfer time was 70 microseconds, and the hexapole RF was 100 Vpp. A 6-point external instrument mass scale calibration was performed before each sequence with lithium formate clusters by infusing 10 mmol L^{-1} lithium hydroxide in isopropanol/0.2% formic acid (1:1, vol/vol). Melting points were measured on a Boetius heating microstage. Thin layer chromatography was carried out on Silufol UV-254 plates. Spots were visualized under the light of a low-pressure mercury lamp (6 W) or in iodine vapors. Column chromatography was performed over silica gel (Merck, 230–400 mesh).



Scheme 2. Synthesis of substituted quinazolinones **2-6**.

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