Photochemical and Photobiological Sciences

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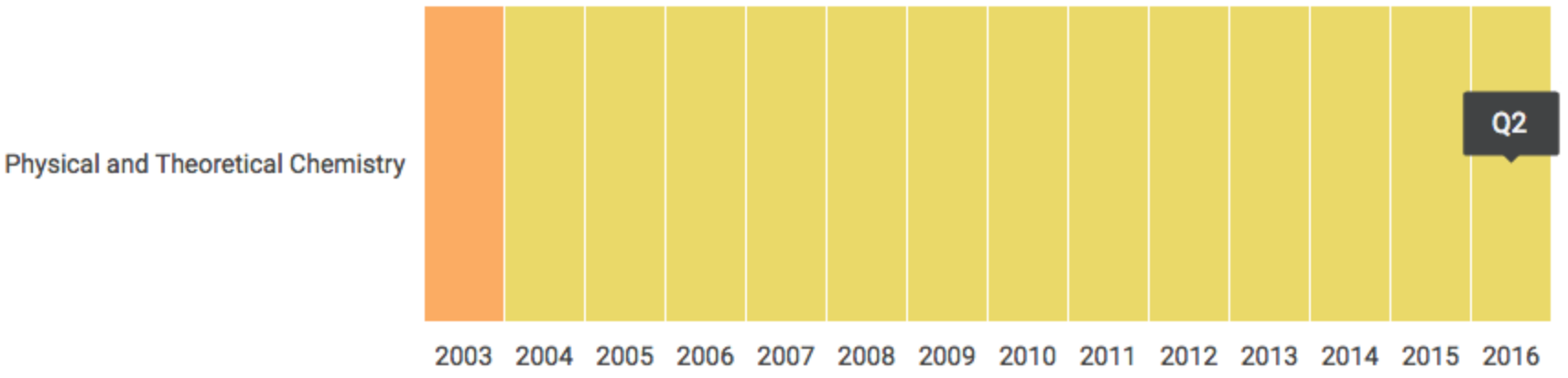

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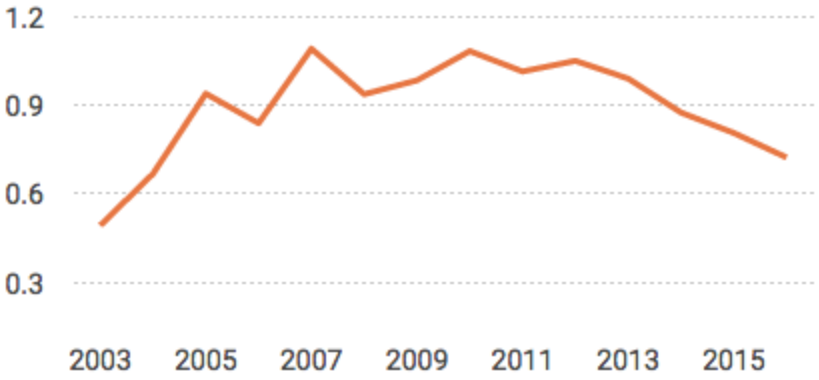

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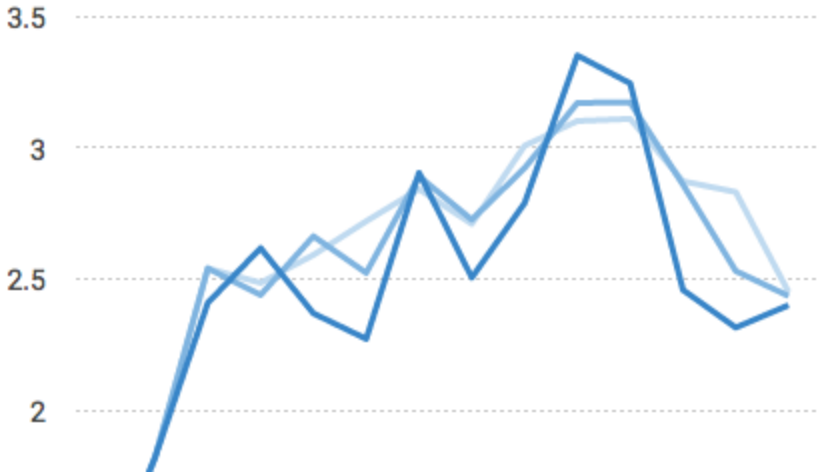

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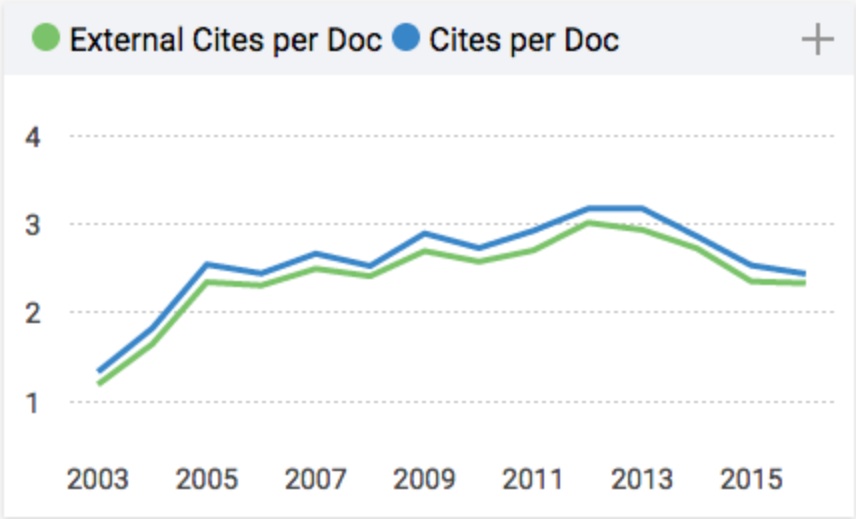
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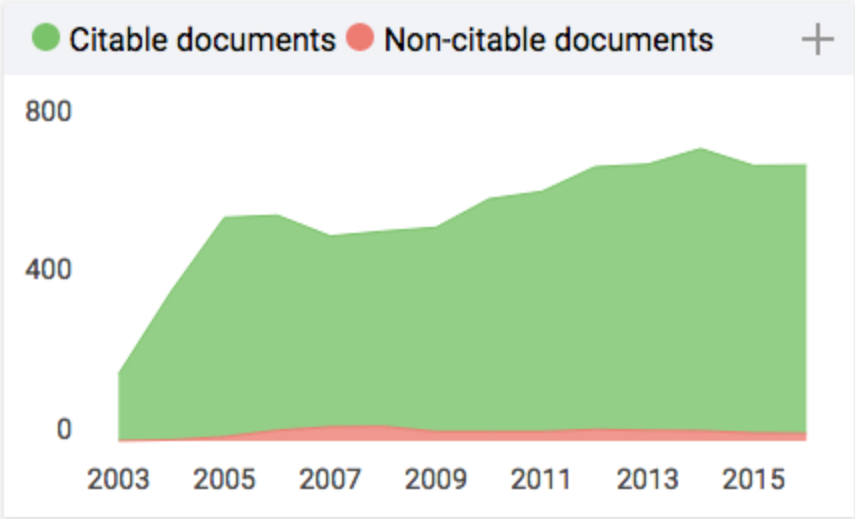

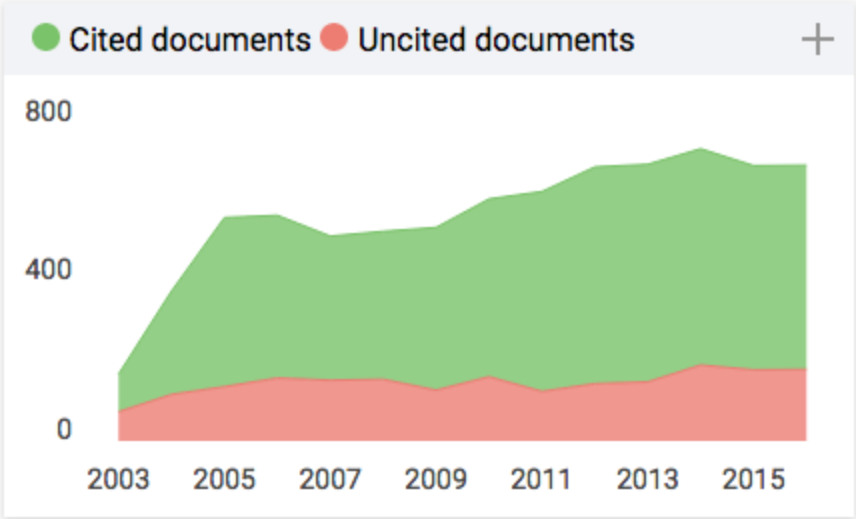

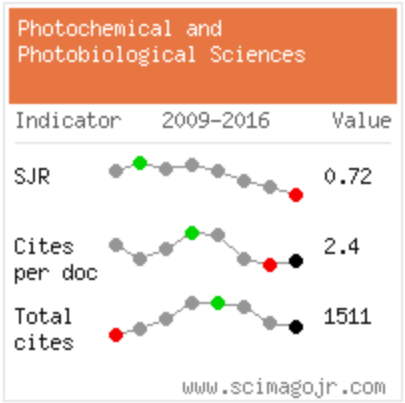

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Azobenzene photoisomerization quantum yields in methanol redetermined†

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The quantum yields of azobenzene photoisomerization in methanol solution were redetermined using newly obtained molar absorption coefficients of its *cis*- and *trans*-isomers. The results differ substantially from those published previously, especially in the range of the nπ* absorption band. Besides actinometry, these findings are relevant for applications of azobenzene derivatives in optical switching.

Introduction

Azobenzene is widely used as an actinometer, because it is readily available, not degraded by prolonged irradiation, and because its isomeric distribution can be conveniently and accurately monitored by absorption spectroscopy.[1] The quantum yields (QYs) of azobenzene photoisomerization were characterized for a variety of solvents[2–4] as a function of temperature[5–9] and also in rigid environments.[5–9] Gauglitz has characterized the QYs of *cis* → *trans* and *trans* → *cis* photoisomerization in methanol solution for various wavelengths.[10–12] The literature on the photoisomerization of azobenzene and its derivatives[13,14] and of its numerous applications[15–17] has been reviewed.

We have employed both azobenzene and ferrioxalate as actinometers to measure photon fluxes. During these measurements we found significant inconsistencies between the photon fluxes determined by these two actinometers. Similar problems were mentioned also in the recent literature.[18,19] As described in the accompanying paper, we carefully redetermined the molar absorption coefficients of *cis*- and *trans*-azobenzene in methanol and found that previously reported absorption spectra were somewhat distorted in the range from 250 to 550 nm due to incomplete separation of the isomers.[20] Here we redetermine the QYs of azobenzene photoisomerization in methanol using the revised molar absorption coefficients. QYs are fundamental physico-chemical characteristics of azobenzenes and their dependence on the wavelength and on the environment is key for their function in various photoswitching applications. Furthermore, the azobenzene isomerization QYs have been a touchstone for theoretical approaches aimed at characterizing the isomerization mechanism.[21–23]

Experimental

Chemicals

For measurements of the QYs freshly recrystallized azobenzene (Reachim, pure) was used as in the accompanying paper.[20] 1,10-Phenanthroline monohydrate (Lachema, p. a.), sodium acetate trihydrate (Penta, p. a.), sulphuric acid (Lachner, p. a.), and methanol (Merck, Uvasol® for spectroscopy) were used without further purification. Demineralized water was used to prepare aqueous solutions. Ferrioxalate was prepared and thrice recrystallized according to the standard procedure.[12,24]

Instrumentation

The optical bench used for the determination of the azobenzene photoisomerization QYs consisted of a monochromator (MSH 150, LOT), a cuvette holder with stirrer, and either a Xe lamp, XBO 450 W, Osram, or a high-pressure Hg lamp, HBO 202 W/4, Osram. The light beam passing through the cuvette was collimated by quartz lenses. The spectra of the irradiation beam were measured by an Ocean Optics USB 2000 portable spectrophotometer behind the empty cuvette holder for calculation of the azobenzene absorption spectrum overlap with the irradiation beam to account for the particular spectral distribution during each irradiation: molar effective absorption coefficients for the actual irradiation spectrum were calcu-

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†Electronic supplementary information (ESI) available: Matlab programs to calculate the QYs of reversible photoreaction, trial data and a representative figure of the fit; calculated isomers' ratios in the photostationary state. See DOI: 10.1039/c7pp00315c

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