The chromophore in Photoactive Yellow Protein PYP is a simple donor-acceptor substituted benzene derivative, the thioester of 1, yet it shows a remarkable spectral tuning of its absorption in response to the surrounding protein environment [1, 2]. Also the photochemical activity (trans-cis isomerization around the double bond) is influenced by the medium and by variation of the substituents. Photochemical activity (here twisting around bonds) is not only expected for the double bond but also for the single bonds (see e.g. the well-known class of TICT-forming molecules [3]). Recent theoretical and experimental work showed that the character of single and double bonds can even be interchanged with sufficiently strong donor-acceptor substituents [4,5]. In order to get a clearer idea of the photochemical mechanism in PYP and to continue the few literature studies with bridged compounds [6], we synthesized and investigated the selectively bridged model compound 2 of the PYP-chromophore and also varied the donor-acceptor strength.

The results show that there are unexpected nonradiative decay channels and that the spectral tuning in PYP can be understood on the basis of the polymethinic theory [4,7].


