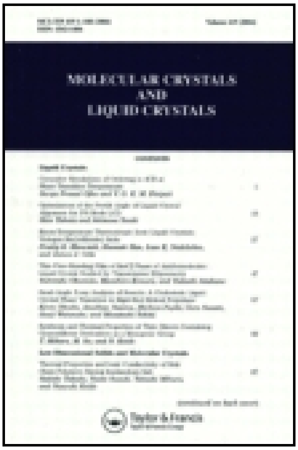


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mimicking the Dye Processes of Sensory Photoreceptors

Jörg Daub [a], Christian Trieflinger [a], Oleg Kushnir [a] & Roman Procházka [a]

[a] Institut für Organische Chemie, Universität Regensburg, Regensburg, Germany

Version of record first published: 31 Aug 2006

To cite this article: Jörg Daub, Christian Trieflinger, Oleg Kushnir & Roman Procházka (2005): Mimicking the Dye Processes of Sensory Photoreceptors, Molecular Crystals and Liquid Crystals, 430:1, 115-122

To link to this article: http://dx.doi.org/10.1080/15421400590946244

Mol. Cryst. Liq. Cryst., Vol. 430, pp. 115–122, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590946244

Mimicking the Dye Processes of Sensory Photoreceptors

Jörg Daub
Christian Trieflinger
Oleg Kushnir
Roman Procházka
Institut für Organische Chemie, Universität Regensburg,
Regensburg, Germany

Photochromism describes the dye-based events of sensory photoreceptors initiating the signalling cascades in living organisms. Research on synthetic dye conjugates related to these primary processes are presented. Isoalloxazine(flavin)-borondipyrromethene **1a** *and its photoredox switching with 1,3-propanedithiol parallels in some aspects the flavin-based blue-light photoreceptors. Dihydroazulene/vinylheptafulvene (DHA/VHF) photochromism resembles the retinal-type photoreceptors. They both proceed by a photochemical "on" and a thermal "off" switching. Details on the electronically excited state properties of DHA/VHF photochromism are reported.*

Keywords: boron-dipyrromethene (BODIPY); dihydroazulene photochromism; flavin; flavin-thiol photochromism; molecular switching; photochromism; photophysics; sensory photoreceptors; ultrafast processes

INTRODUCTION

Growth and development of organisms in Nature are regulated by solar energy. The incoming light signals are either transformed into chemical energy by the photosynthetic reaction centers or transformed

We gratefully acknowledge cooperations with the groups of H. Görner (MPI, Mülheim), C. Kryschi (Universität Erlangen-Nürnberg), E. Riedle/V. De Waele (LMU München/Université Paris Sud), and K. Rurack, Bundesanstalt für Materialforschung und –prüfung, Berlin). This work is financially supported by Deutsche Forschungsgemeinschaft (Graduate college "Sensory Photoreceptors", Regensburg University, GRK 640). Christian Trieflinger is recipient of a fellowship of Studienstiftung des Deutschen Volkes.

Address correspondence to Jörg Daub, Institut für Organische Chemie, Universität Regensburg, Regensburg, D-93040, Germany. E-mail: joerg.daub@chemie.uni-regensburg.de

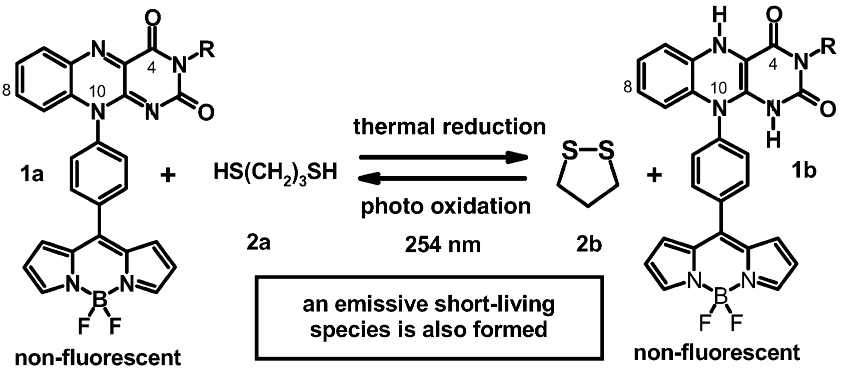
into signal information by light-sensing proteins [1]. Important progress in the understanding of the photobiological processes has been achieved recently, especially due to structure analysis by x-ray or electron diffraction methods which provide information on reaction centers [2], antenna [3], sensory photoreceptor proteins [4,5], or photolyases [6]. Functional dyes are the molecules' operational units for the handling of the incoming light pulses. Embedded as cofactors in the proteins they are the primary targets and accomplish signal transduction and transformation. Supramolecular chemistry and molecular switching meet in these sensory photoreceptors and the dye components evolved into various functions among which are a) the specificity of the protein-dye interaction, b) the efficiency of absorption in the spectral range of the solar light and c) the transformation of the electromagnetic energy (information) into chemical or structural energy. Here photochromism comes into play in particular if photochromism is comprehended as a light-driven reversible A $\leftrightarrows$ B switching leading to a change of the electronic and structural state of matter which may be imprinted either on molecular, supramolecular or even larger dimension [7]. The outcome of the primary light activation may then be structural reorganization, photoinduced electron transfer, a photochemical reaction or the life processes driven by signalling pathways.

In recent work we reported on the mimicking of the photoinduced electron transfer by a pyrene-isoalloxazine(flavin)-phenothiazine triad [8,9]. Here we refer on the following two topics.

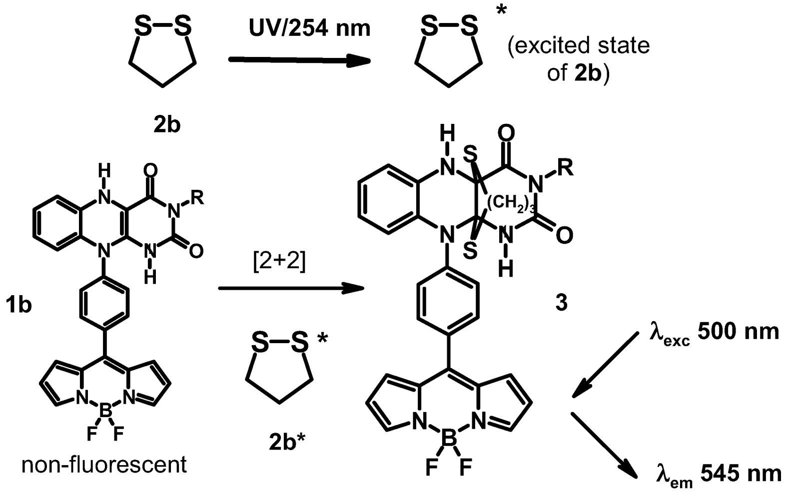
- The photochromism and switching of a flavin-borondipyrromethene/thiol system which relates to the flavin (FMN)/cysteine reaction of blue-light photoreceptors like phototropin.
- The dynamics of the dihydroazulene/vinylheptafulvene photochromism which has some aspects of retinal type photosensory systems.

PHOTO REDOXSWITCHING OF A FLAVIN-BORONDIPYRROMETHENE

Phototropins are members of the blue-light sensory photoreceptor family which use flavin mononucleotide (FMN) and the C-4a-flavin-cysteinyl photoadduct as the primary signalling state in order to mediate light responses in plants like phototropism, chloroplast movement, stomatal opening, or inhibition of hypocotyl growth [10,11]. The flavin-borondipyrromethene dyad **1a** was synthesized by subsequent design of the flavin and borondipyrromethene subunits. Its photoprocesses in the presence of thiols were investigated. NMR studies confirm the twisted structure of **1a**, electrochemical and spectroscopic studies show that the phenylene bridge electronically decouples the flavin(isoalloxazine) and the borondipyrromethene chromophores. Almost unperturbed individual spectral and electrochemical properties are obtained. It is well established that under photochemical conditions flavin(isoalloxazine) and thiols may either react under C4a-adduct formation [12,13] or under the formation of dihydroflavin [14]. In our approach the borondipyrromethene chromophore is supposed to be the fluorescent signalling unit [15]. Both forms **1a** (oxidized form) and **1b** (reduced form) are non-fluorescent which is assumed to be due to the internal photoinduced electron transfer (PET effect) in the excited state (Scheme 1) [16]. In the oxidized form **1a** the isoalloxazine operates as the electron acceptor whereas in the reduced form **1b** the dihydroisoalloxazine acts as electron donor. Rehm-Weller calculations support these conclusions. The results of the phototriggering are given in schemes 1 and 2. Propane-1,3-dithiol **2a** reduces compound **1a** to the dihydroform **1b** in a fast thermal process. In a photochemical back reaction induced by 254 nm irradiation reoxidation to **1a** is observed. Equilibrium **1a**/**1b** represents therefore a non-emissive silent interconverting system. The interesting finding however was that irradiation at 254 nm also causes strong emission of the borondipyrromethene at 540 nm which slowly decays after switch-off. A short-living fluorescent intermediate must have been formed (Scheme 2) lacking the PET effect and leading to the emissive local excited state of the borondipyrromethene (Fig. 1). Tentatively, we assign the structure **3** to the emissive species resulting from photochemical [2 + 2]-cycloaddition of dithiane **2** and the dihydroflavin **1b**. The modified flavin subunit in **3** may be both a weaker electron donor and a weaker electron acceptor.



SCHEME 1 The photochromism of the flavin-borondipyrromethene dyads **1a**/**1b**.



SCHEME 2 Proposed chemistry of generating the fluorescent species **3**.

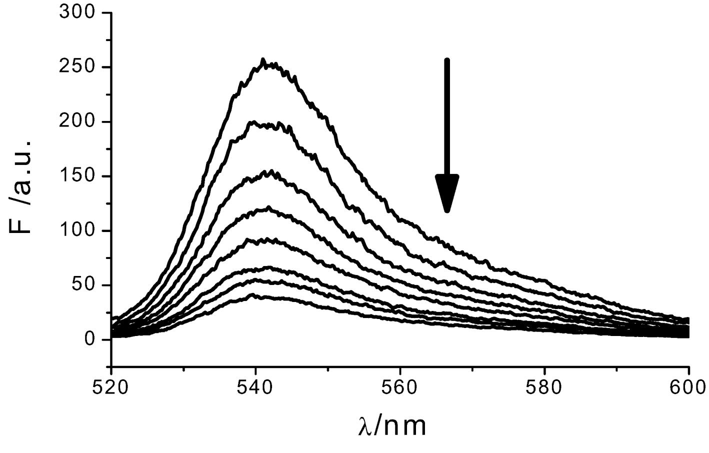


FIGURE 1 Decrease of the emission of the photochemically produced species with the proposed structure **3** after switch-off of illumination at 254 nm.

DIHYDROAZULENE/VINYLHEPTAFULVENE PHOTOCHROMISM

Despite mechanistic differences in the structural reorganization the retinal-type trans-cis photoisomerization [17] and dihydroazulene/vinylheptafulvene photochromism [18] have some aspects in common.

Both rely on a photochemical forward and a thermal back reaction and both are either directly or indirectly related to the terpenoids as natural products. The 1,8a-dihydroazulene skeleton evolved as a structural building block of sesquiterpenes [19].

Dihydroazulene/vinylheptafulvene photochromism emerged as an independent photochromic principle based on switching between the alternant π-DHA and the non-alternant π-VHF [20,21]. This distinctive change in the electronic structure made it useful for multifold switching starting from the first experiments on photoelectroswitching [22–24]. In order to learn more on the photoprocesses detailed photophysical studies were undertaken recently. By femtosecond-resolved transient absorption spectroscopy it was found that DHA → VHF photorearrangement sensitively depends on the structural motif. 1,2,3,8a-Tetrahydro-9H-cyclopent[a]azulene-9,9-dicarbonitrile(CP-DHA) **4a** ringopens to CP-VHF **4b** in a highly efficient and ultrafast photochemical process with a quantum yield of nearly one and with a single exponential decay within 600 fs [25] (Scheme 3). Theoretical studies predicted a conical intersection for this ultrafast interconversion [26]. On the contrary the phototransformation of the "free-rotating" 1,1-dicyano-2-(4-cyanophenyl)-1,8a-dihydroazulene (CN-DHA) **5a** to CN-VHF **5b** occurs with much lower quantum yield and in a stepwise deactivation cascade along the excited-state potential energy surface as shown by sub-30 fs spectroscopy [27] (Scheme 3). The Franck-Condon state deactivates in an ultrafast process to a dihydroazulene in the first excited state (CN-DHA-S_1) which leads to s-cis-CN-VHF-S_1 (1.2 ps) followed by the internal conversion to the s-cis-CN-VHF ground state in 13 ps. The rearrangement of s-cis-CN-VHF-S_0 to s-trans-CN-VHF-S_0 **5b** proceeds within 10 μs. s-trans-CN-VHF-S_0 **5b** reverts to CN-DHA-S_0 **5a** thermally with a lifetime of 1.2 hr (room temperature in acetonitrile). The topology of the excited state and ground state energy surfaces of CN-DHA/CN-VHF **5a**/**5b** enables reversible short-cut photochemical interconversion between CN-DHA **5a** and s-cis-CN-VHF in an all-photochemical bidirectional switch [28,29].

Further information on the excited state regime comes from dihydroazulene derivative (DT-DHA) **6a** composed of the photoswitchable DHA and the diamidotriazine (DT) receptor designed for probing supramolecular interaction. Compound **6a** shows the expected photochromic behaviour expressing an efficient photochemical forward and a thermal-only back reaction (Fig. 2). DT-DHA **6a** shows weak fluorescence at room temperature whereas DT-VHF **6b** is absolutely non-emissive at room temperature.

The photochemical/photophysical/thermal behaviour of DT-DHA/DT-VHF significantly changes on protonation with trifluoroacetic acid. The absorption spectrum of DT-DHA shifts from 379 nm to 435 nm on

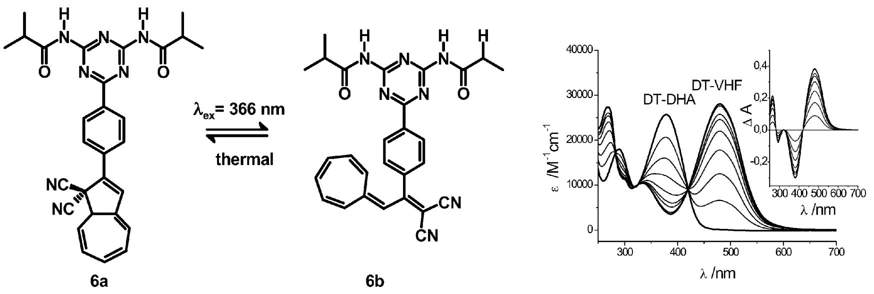


FIGURE 2 Photochromism of DT-DHA/DT-VHF (**6a**/**6b**) (left side); spectral response on irradiation of **6a** at $\lambda = 366\,\text{nm}$ (right side), insert: plot of the difference spectra.

protonation which is an indication of a more extended π-system in the protonated form **6a•H**$^+$ and the emission ($\lambda_{\text{ex}} = 380\,\text{nm}$; $\lambda_{\text{em}} = 585\,\text{nm}$) strongly increases and is red shifted in comparison to DT-DHA **6a**. Additionally, the quantum yield of the photochemical forward reaction decreases on protonation and the rate of the thermal back reaction (DT-VHF•**H**$^+ \rightarrow$DT-DHA•**H**$^+$) increases. These results corroborate the previous assumption of a heterolytic ring opening on the excited state energy surface [30]. The protonation must increase the energy barrier (Fig. 3).

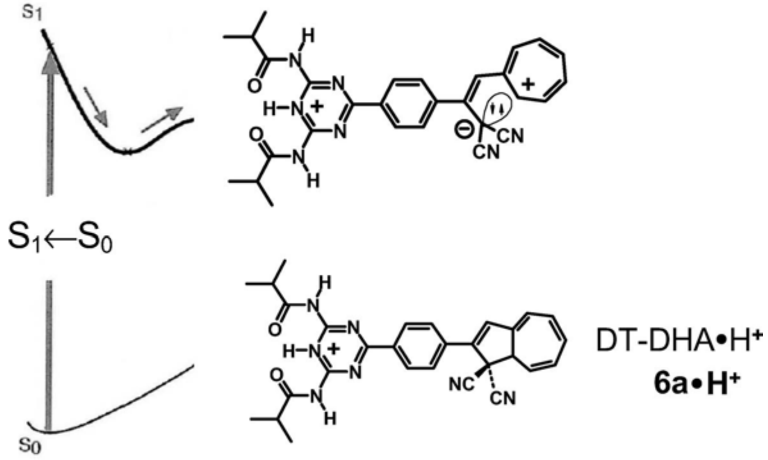
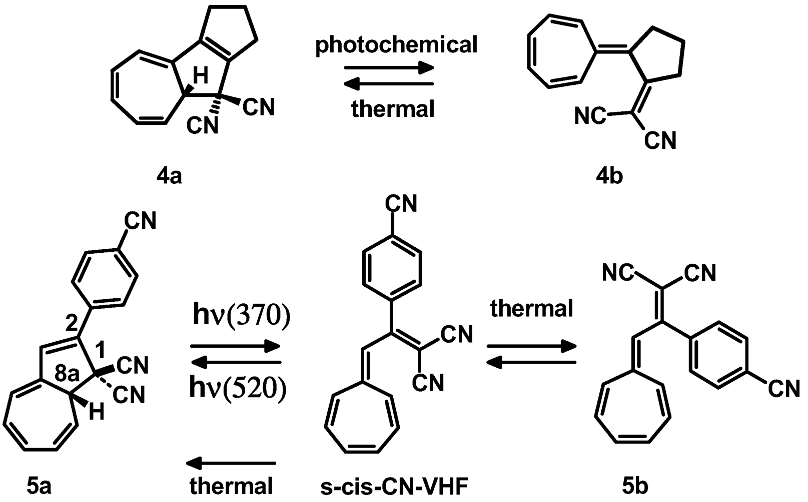


FIGURE 3 Schematic representation of the energetics of photochemical ring opening of protonated DT-DHA (**6a•H**$^+$).



SCHEME 3 Structural representation of the photochromic systems **4a**/**4b** and **5a**/**5b**.

In summary, DHA/VHF photochromism can specifically and sensitively be tuned for environmental recognition and multiple input treatment by structural modification and is therefore a good candidate for the implementation of logic functions on the molecular level.

REFERENCES

[1] van der Horst, M. A. & Hellingwerf, K. J. (2004). *Accounts of Chemical Research*, *37*, 13.

[2] Deisenhofer, J., Epp, O., Miki, K., Huber, R., & Michel, H. (1984). *J. Mol. Biol.*, *180*, 385.

[3] Ben-Shem, A., Frolow, F., & Nelson, N. (2003). *Nature (London, United Kingdom)*, *426*, 630.

[4] Fedorov, R., Schlichting, I., Hartmann, E., Domratcheva, T., Fuhrmann, M., & Hegemann, P. (2003). *Biophysical Journal*, *84*, 2474.

[5] Crosson, S. & Moffat, K. (2001). *Proc. Natl. Acad. Sci. U.S.A.*, *98*, 2995.

[6] Park, H. W., Kim, S. T., Sancar, A., & Deisenhofer, J. (1995). *Science*, *268*, 1866.

[7] Kennis, J. T. M., Van Stokkum, I. H. M., Crosson, S., Gauden, M., Moffat, K., & Van Grondelle, R. (2004). *J. Am. Chem. Soc.*, *126*, 4512.

[8] Shen, Z., Strauss, J., & Daub, J. (2002). *Chem. Commun.*, *460*.

[9] Shen, Z., Procházka, R., Daub, J., Fritz, N., Acar, N., & Schneider, S. (2003). *Physical Chemistry Chemical Physics*, *5*, 3257.

[10] Huala, E., Oeller, P. W., Liscum, E., Han, I.-S., Larsen, E., & Briggs, W. R. (1997). *Science*, *278*, 2120.

[11] Crosson, S., Rajagopal, S., & Moffat, K. (2003). *Biochemistry*, *42*, 2.

[12] Salomon, M., Christie, J. M., Knieb, E., Lempert, U., & Briggs, W. R. (2000). *Biochemistry*, *39*, 9401.

[13] Schleicher, E., Kowalczyk, R. M., Kay, C. W. M., Hegemann, P., Bacher, A., Fischer, M., Bittl, R., Richter, G., & Weber, S. (2004). *J. Am. Chem. Soc.*, *126*, 11067.

[14] Ishikawa, M., Fukuzumi, S., & Tanii, K. (1989). *Chemistry Letters*, 2189.

[15] Toele, P., Zhang, H., Trieflinger, C., Daub, J., & Glasbeek, M. (2003). *Chemical Physics Letters*, *368*, 66.

[16] Kollmannsberger, M., Rurack, K., Resch-Genger, U., & Daub, J. (1998). *J. Phys. Chem. A*, *102*, 10211.

[17] Hampp, N. (2000). *Chem. Rev.*, *100*, 1755.

[18] Daub, J., Knoechel, T., & Mannschreck, A. (1984). *Angew. Chem.*, *96*, 980.

[19] Takeda, R. & Katoh, K. (1983). *J. Am. Chem. Soc.*, *105*, 4056.

[20] Daub, J., Gierisch, S., Klement, U., Knöchel, T., Maas, G., & Seitz, U. (1986). *Chem. Ber.*, *119*, 2631.

[21] Daub, J., Fischer, C., Gierisch, S., & Sixt, J. (1992). *Molecular Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals*, *217*, 177.

[22] Daub, J., Salbeck, J., Knöchel, T., Fischer, C., Kunkely, H., & Rapp, K. M. (1989). *Angew. Chem. Int. Ed.*, *28*, 1494.

[23] Mrozek, T., Daub, J., & Ajayaghosh, A. (2001). In: *Molecular Switches*, Feringa, B. L. (Ed.), Wiley-VCH: Weinheim.

[24] Gobbi, L., Seiler, P., Diederich, F., Gramlich, V., Boudon, C., Gisselbrecht, J.-P., & Gross, M. (2001). *Helv. Chim. Acta.*, *84*, 743.

[25] Ern, J., Petermann, M., Mrozek, T., Daub, J., Kuldová, K., & Kryschi, C. (2000). *Chemical Physics*, *259*, 331.

[26] Boggio-Pasqua, M., Bearpark, M. J., Hunt, P. A., & Robb, M. A. (2002). *J. Am. Chem. Soc.*, *124*, 1456.

[27] De Waele, V., Beutter, M., Schmidhammer, U., Riedle, E., & Daub, J. (2004). *Chem. Phys. Lett.*, *390*, 328.

[28] De Waele, V., Schmidhammer, U., Mrozek, T., Daub, J., & Riedle, E. (2002). *J. Am. Chem. Soc.*, *124*, 2438.

[29] Schmidhammer, U., De Waele, V., Buntinx, G., & Riedle, E. (2004). In: *Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science*, Martin, M. M. & Hynes, J. T. (Eds.), Elsevier B.V.: Amsterdam.

[30] Görner, H., Fischer, C., Gierisch, S., & Daub, J. (1993). *J. Phys. Chem.*, *97*, 4110.