

ORIGINAL PAPER

Synthesis and properties of macrocyclic diazene switch with binaphthalene unit attached via acrylamide linkers

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

2,2'-Diiodo-1,1'-binaphthalene undergoes a tandem Heck reaction with methyl acrylate to afford methyl 2-(7*H*-dibenzo[*c,g*]fluoren-7-ylidene)acetate. As a consequence, the target macrocyclic diazene with binaphthalene unit attached via acrylamide linker was prepared by the stepwise building of acrylamide at a binaphthalene moiety, including the Doebner modification of the Knoevenagel condensation, and completed by oxidative macrocyclisation of aniline end-groups. Despite being an equimolar mixture of monomer and dimer, it exhibited remarkable changes in CD spectra due to reversible (*E/Z*) isomerisation of N=N diazene bonds upon irradiation at 365/465 nm. Although the dimer isomerises from (*E*) to (*Z*) isomer 7.4 times faster than the monomer, the latter's contribution to the change in ellipticity at 307 nm in the photostationary state is 2.4 times greater. © 2012 Institute of Chemistry, Slovak Academy of Sciences

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Introduction

Light-driven molecular machines have attracted a great deal of attention due to their potential applications in the field of optical data processing and storage. An alternative strategy for non-destructive read-out entails utilisation of their chiroptical properties. Chiroptical switches (Feringa & Browne, 2011) undergo photochemically-induced conformational changes that result in modification of either the molecular chiroptical characteristics or collective behaviour, such as chiral nematic phase-switching, due to a change in the helical twisting power of the photochromic chiral dopant.

The photochromic diaryldiazene unit undergoes a significant change in molecular geometry upon (*E/Z*) isomerisation which has been successfully explored for construction of macrocyclic chiroptical switches in combination with the binaphthalene moiety as

the conformation-sensitive chiral unit (changing the dihedral angle between naphthalene units). Macrocyclic cyclophanes of this type (Fig. 1, structures A–C) have the photochromic di-(*ortho* or *meta*)-phenyldiazene unit attached to the binaphthalene moiety at positions 2 and 2' (Kawamoto et al., 2007, 2010; Takaishi & Kawamoto, 2011; Takaishi et al., 2009, 2011a, 2011b, 2012), or 7 and 7' (Takaishi & Kawamoto, 2011; Takaishi et al., 2009, 2011a), via relatively flexible (oligomethylene)dioxy linkers (most often via propane-1,3-diyl dioxy linkers). Switching of these macrocyclic diazenes is accompanied with a reversible change in the molecular chiroptical characteristics or induced changes of the nematic liquid-crystalline host (Kawamoto et al., 2007). However, changes in the binaphthalene dihedral angle upon switching are not dramatic due to the flexibility of (oligomethylene)dioxy linkers and, therefore, relative and absolute changes in ellipticity (θ) in CD spectra

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