

Publication

A New Class of Rigid Multi(azobenzene) Switches Featuring Electronic Decoupling: Unravelling the Isomerization in Individual Photochromes

JournalArticle (Originalarbeit in einer wissenschaftlichen Zeitschrift)**ID** 4529468**Author(s)** Galanti, Agostino; Santoro, Jasmin; Mannancherry, Rajesh; Duez, Quentin; Diez-Cabanes, Valentin; Valasek, Michal; De Winter, Julien; Cornil, Jerome; Gerbaux, Pascal; Mayor, Marcel; Samori, Paolo**Author(s) at UniBasel** [Mayor, Marcel](#) ; [Mannancherry, Rajesh](#) ;**Year** 2019**Title** A New Class of Rigid Multi(azobenzene) Switches Featuring Electronic Decoupling: Unravelling the Isomerization in Individual Photochromes**Journal** Journal of the American Chemical Society**Volume** 141**Number** 23**Pages / Article-Number** 9273-9283

We report a novel class of star-shaped multiazobenzene photoswitches comprising individual photochromes connected to a central trisubstituted 1,3,5-benzene core. The unique design of such C₃-symmetric molecules, consisting of conformationally rigid and pseudoplanar scaffolds, made it possible to explore the role of electronic decoupling in the isomerization of the individual azobenzene units. The design of our tris-, bis-, and mono(azobenzene) compounds limits the π -conjugation between the switches belonging to the same molecule, thus enabling the efficient and independent isomerization of each photochrome. An in-depth experimental insight by making use of different complementary techniques such as UV-vis absorption spectroscopy, high performance liquid chromatography, and advanced mass spectrometry methods as ion mobility revealed an almost complete absence of electronic delocalization. Such evidence was further supported by both experimental (electrochemistry, kinetical analysis) and theoretical (DFT calculations) analyses. The electronic decoupling provided by this molecular design guarantees a remarkably efficient photoswitching of all azobenzenes, as evidenced by their photoisomerization quantum yields, as well as by the Z-rich UV photostationary states. Ion mobility mass spectrometry was exploited for the first time to study multiphotochromic compounds revealing the occurrence of a large molecular shape change in such rigid star-shaped azobenzene derivatives. In view of their high structural rigidity and efficient isomerization, our multiazobenzene photoswitches can be used as key components for the fabrication of complex stimuli-responsive porous materials.

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