

## Novel Conjugated Multi-Azobenzene Photochromic Rigid Systems

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Multichromophoric molecules are unique building blocks for opto-electronics and photonics since they integrated multiple functions in a single component. A fundamental question which arises is how the different chromophores electronically cross-talk. Here we have designed and synthesised a novel C<sub>3</sub>-symmetric branched molecule containing three azobenzene units attached in *meta*-position of the same benzene core. The decoration with external carboxylic acid moieties enables the use of H-bonding to control the self-assembly of such rigid molecules at surfaces and interfaces.<sup>1-3</sup> The reciprocal connection of the azobenzenes to the *meta*-position on the central phenyl ring yields a partial interruption of the electronic communication between the photoactive units, but keeping the system sufficiently rigid for allowing its self-assembly in 2D. Breaking the electronic coupling was seen to be fundamental in order to retain the photoresponsive properties of multi-chromophoric systems.<sup>4-6</sup>

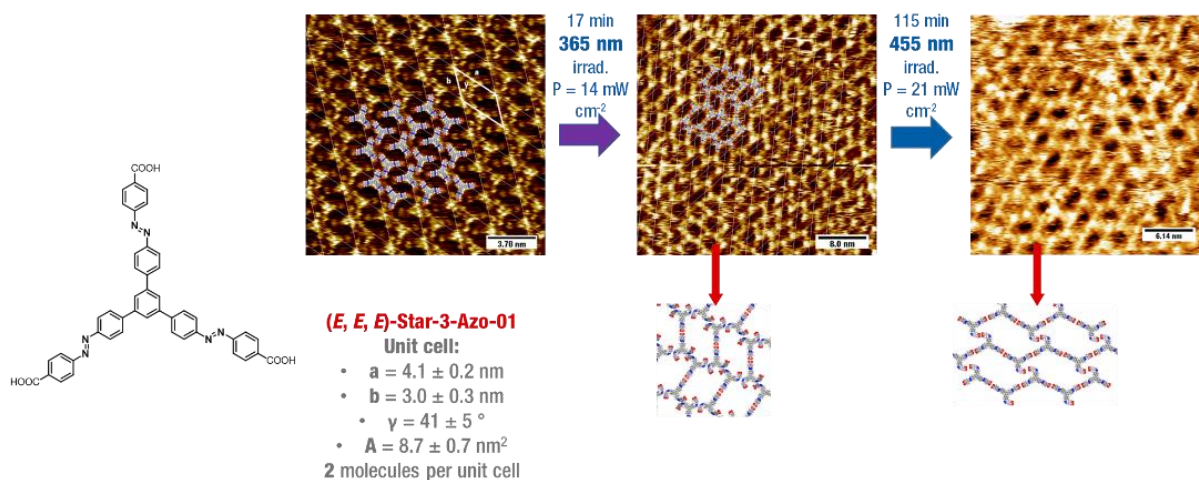


Figure 1. Scanning tunnelling microscopy images of the self-assembly of **Star-3-Azo-01** on the basal plane of highly ordered pyrolytic graphite at the solid-liquid interface. The occurrence of the desired photochemical isomerisation is evident from the change in packing geometry upon variation of the isomeric composition of the solution by UV (365 nm) and visible (455 nm) irradiation at the respective photostationary states.

The occurrence of photochemical isomerisation of our azobenzenes was demonstrated by means of UV-Vis absorption spectroscopy, moreover all the four possible isomers were

separated using HPLC. Self-assembly in 2D hydrogen-bonded patterns on highly ordered pyrolytic graphite was observed by STM at the solid-liquid interface. We were also able to show that the photochromic behaviour was retained in such 2D assemblies, by observing a disappearance of ordered patterns, or an apparent change in molecular packing. Following the demonstration of switching occurrence of the three azobenzene-containing **Star-3-Azo-01**, an important question remained open: upon photoswitching and change in morphology of the molecular layer, it was not clear whether the ordered domains were composed by one single or more isomers, and which isomer was present. Since isolation of the single isomers is not a feasible operation due by thermal instability of Z-isomer of azobenzene, we synthesized new derivatives with similar shape and dimensions, but containing less photochromic moieties, by progressive substitution of the azobenzenes with tolane groups. Photochromism of such derivatives with either two (**Star-2-Azo-01**) and one (**Star-1-Azo-01**) azobenzene moieties was again demonstrated by means of UV-Vis absorption spectroscopy and HPLC. Occurrence of similar hydrogen bond-directed self-assembly to the already known **Star-3-Azo-01** was confirmed in the same experimental conditions without irradiation. Moreover, with the help of theoretical simulations (MM/MD) we were able to reproduce the molecular packing seen experimentally and to get insight into the thermodynamics of adsorption and self-assembly of the system. The synthesis of photoresponsive, nanoporous materials (MOFs) with the use of our C<sub>3</sub>-symmetric branched tri-azobenzene system is currently under investigation.

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