Supplementary information S1

A. Synthesis of AZOTAB.

Materials: 4-butylanilin (M=149.23 g.mol^{-1}), phenol (M=94.11 g.mol^{-1}), sodium nitrite (M=69.00 g.mol^{-1}), dibromopropane (M= 201.9 g.mol^{-1}), 35% trimethylamine solution in ethanol (M=59.1 g.mol^{-1}) were purchased from Aldrich and used without purification.

Method: AzoTAB was synthesized by the following stepwise procedure: 1) diazoic coupling, 2) substitution of a bromoalkane by the phenate to introduce the propyloxy spacer, and 3) Menschutkin's reaction to form the ammonium bromide.

1) Synthesis of 4-butyl-(4'hydroxy)azobenzene (I): 25 g of 4-butylanilin (0.16 mol.L^{-1}) were dissolved and thoroughly stirred in 100 ml of HCl (5 mol.L^{-1}) at 0°C. Then 25 ml of sodium nitrite (6.67 mol.L^{-1} in water) was added (i.e. 1 eq). The reaction mixture was left to react for 1h at 0°C. Then 84 ml of phenol in 2.5eq sodium carbonate was added. When the medium became basic, the product precipitated as a brown solid. The reaction mixture was filtered, and dried under vacuum overnight. This product was purified by recristallisation in a minimum amount of n-hexane (91 % yield).

2) Synthesis of 4-butyl-(4'-(3-bromopropyloxy)phenyl)azobenzene (II): An excess (8 g) of 1,3-dibromopropane and 2.7 g of KOH (1.2 eq) were placed in 50 ml THF. Total dissolution of KOH was achieved by addition of a minimum amount of water. 10g of 4-butyl-(4'-hydroxy) azobenzene (1 eq) were dissolved in 50ml of THF and introduced dropwise in the reaction mixture, brought to reflux and thoroughly stirred overnight. The advancement of reaction was followed by TLC (Silica gel, CH2Cl2/n-Hexane 75/15). The crude was filtered to remove KBr, evaporated down to an oily solution that was resuspended in n-hexane for precipitation at low temperature (about 50 % yield).

3) Synthesis of azoTAB: 13g of C_4AzoOC_3Br was dissolved in 200mL of ethyl acetate and 300mL of ethanol at 70°C. A cold solution of 35% trimethylamine in ethanol (33mL – 4 equivalents) was introduced dropwise in the reacting bath. The mix was kept in reflux for 48h. Upon cooling to room T, a precipitate of azoTAB forms. After

filtration, the precipitate was recristallized twice in 90:10 v/v solution of ethyl acetate:ethanol and finally drying under vacuum overnight. (about 53% yield).

B. Measurement of the cis/trans composition using UV spectrophotometry

In order to get the reference 100% trans state, solutions of predominantly trans AzoTAB (as obtained just after hydration of the powder) were incubated, for on week, in the dark. It was checked that the spectrum of this "trans" state was unchanged even after three weeks of relaxation. Then, the spectra of mixtures were recorded under exposure of the same solution to light with various wavelengths. Absorbances are considered to vary in proportion to the composition, to calculate theoretical extinction coefficients as follows:

$$\varepsilon_{mix}(\lambda) = R_{trans}\varepsilon_{trans}(\lambda) + R_{cis}\varepsilon_{cis}(\lambda).$$ Where $R_{trans} = \dfrac{c_{trans}}{c_{tot}}$ $R_{cis} = \dfrac{c_{cis}}{c_{tot}}$ are the ratio of each

conformer in the solution prepared for a given wavelength of stimulation. To obtain the values of extinction coefficient of the cis form, and in turn the composition index of trans R_{trans}, it was necessary to implement an iterative process. Briefly, the spectrum of the trans isomer weighted by a dummy value of $R_{trans(UV)}$, was substracted from the spectrum of the mixture obtained under UV to give a putative spectrum of the cis. Self-consistency is reached by matching the values of $R_{trans(blue)}$ calculated from the spectrum of blue-adapted sample using extinction coefficients of the cis at different wavelengths. At the end of the process, the two calculated spectra of the cis, obtained from UV-adapted (respectively blue-adapted) experimental spectra diminished of the spectrum of trans weighted by the respective R_{trans} (UV or blue) converge to a single one shown on Fig A.
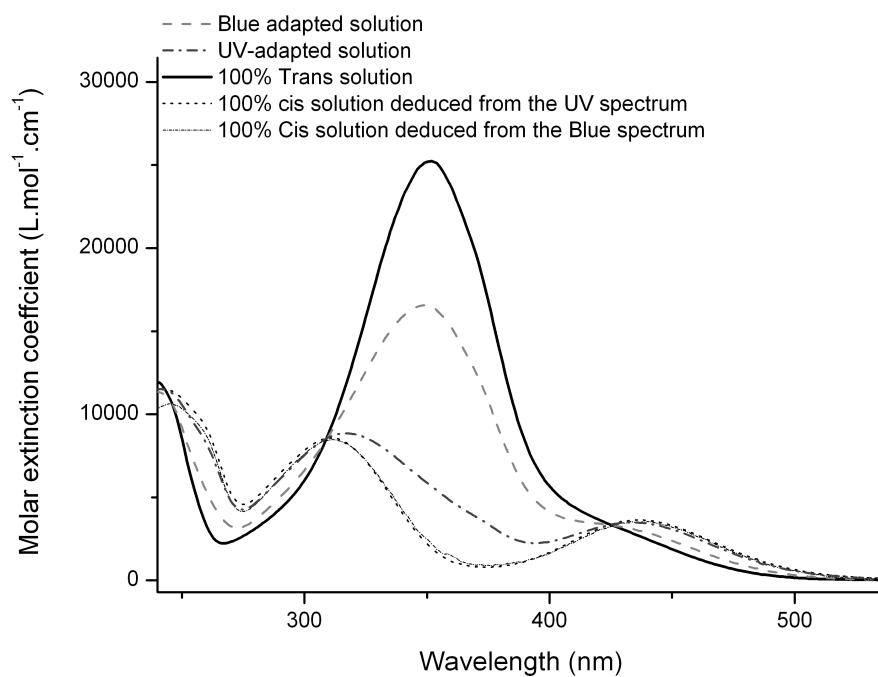
Fig A : Uv-vis spectra of solutions for different compositions : blue-adapted and UV-adapted solutions and a dark-adapted solution accounting for a pure solution of trans. The spectra of the pure cis are deduced either from the blue-adpted spectra or the Uv-adapted one.