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Supporting Information

Multi-functional switches of ditopic ligands with azobenzene central bridge at a molecular scale

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1. STM results



Figure S1. (a) Scheme of bpy-azo-bpy trans to CIS conformation transformation. STM images (1-heptanoic acid/HOPG interface) of trans organization after 20-40 min of UV irradiation at a wave length of 365nm, $I_t = 15\sim30$ pA, $U_s = -0.4\sim-0.6$ mV. (b) 190×177 nm², (c) 170×160 nm², (d) 216×172 nm², (e) 162×147 nm².

The bpy-azo-bpy molecules self-assemble at 1-heptanoic acid/HOPG interface as a long range ordered zig-zag structure, as shown by the STM images in Figure 2. Single bpy-azo-bpy molecules uniformly adopt a trans conformation (Figure S1a) at the bipyridine terminals^{1,2} where the central azo unit is in a planar TRANS state. After 20-40 min of UV light irradiation, some of the TRANS conformers are switched to their CIS states at the central azobenzene units and half of molecules protrude out of surface plane. The CIS conformers are observed as bright spot from large area STM images as shown in FigureS1 b,c,d,e whereas the unswitched TRANS molecules remains as dark organizations.



Figure S2. High resolution STM images (1-heptanoic acid/HOPG interface) of transorganization after 20-40 min of UV irradiation at a wave length of 365nm, $I_t = 20 \sim 30$ pA, $U_s = -0.4 \sim -0.6$ mV (a) 87×76 nm² (b) 18×18 nm² (c) 51×51 nm²

STM image in FigureS2a shows that individual molecules switched to CIS states are observed decorating the planar TRANS organizations after UV radiation. A high resolution STM image

shows that a few molecules in CIS states are observed where the surrounding TRANS zig-zag self-assembly is clearly visible.



Figure S3. (a) Scheme of bpy-azo-bpy cis to CIS conformation transformation. (b) STM image (1-octanol/HOPG interface) of cis organization after 40 min of UV irradiation a wave length of 365nm, 99×72 nm², $I_t = 50$ pA, $U_s = -350$ mV.

The bpy-azo-bpy show cis state at their bipyridine terminal groups at the non-acidic solid liquid interface.^{1,2} STM image in Figure S3 shows that different domains of the bpy-azo-bpy molecules are observed at the 1-octanol/HOPG interface. The HOPG surface is not fully covered due to a controlled low molecular concentration from the depositing solution. Bright spots in corresponding to the CIS azobenzene units are observed in contrary to the planar cis stripe organization. The molecules have been visualized switching from the cis-TRANS to their cis-CIS states after UV radiation.

The four different conformers of bpy-azo-bpy molecules: *cis-TRANS, trans-TRANS, cis-CIS* and *trans-CIS*, are all observed under STM and can be controlled for the switching by protonation or by light irradiation.



Figure S4. (a) Scheme and STM image of bpy-fluo-bpy cis conformation with gear-chain organization. $16 \times 15 \text{ nm}^2$, $I_t = 12 \text{ pA}$, $U_s = -580 \text{ mV}$. (b) Scheme and STM image of bpy-PE₂P-bpy (1-octanol/HOPG interface) cis conformation and the organization. $10 \times 9 \text{ nm}^2$, $I_t = 15 \text{ pA}$, $U_s = -450 \text{ mV}$.

The molecular system bpy-X-bpy (X spacer can vary as phenyl-fluorene-phenyl or phenylbiEDOT-phenyl) have been investigated by STM both at the non-acidic solvent conditions such as 1-phenyloctane (1-octanol)/HOPG interface. High resolution STM image in Figure.S4a shows that the bpy-fluo-bpy molecules adapt a cis conformation and the conformers form a gear-chain organization. High resolution STM image in Figure.S4b shows that a second molecules bpy-PE₂P with the same ditopic bipyridine terminal groups adapt a similar cis conformation although the center units have changed into bi-EDOT. The molecules investigated in this article in Figure.1 belong to the same bpy-X-bpy family and our results have suggested that the molecules bpy-azo-bpy are in cis conformations as well at the 1-octonal/HOPG interface.

2. UV-vis results



Figure S5. Absorption spectral changes upon light irradiation of the bpy-azo-bpy: The spectra of the initial solution, after irradiation with UV light (15 minutes, λ_{irrad} =365nm) and after irradiation of Vis light (1 minute, λ_{irrad} =435nm) are shown in red, blue and green colors, respectively. (a) 2×10⁻⁵M in DMF, (b) 1×10⁻⁵M in 1-heptanoic acid.

UV-Vis spectroscopy.

Figure S5 shows the absorption spectral changes observed upon light irradiation in DMF (FigureS5a) and 1-heptanoic acid (FigureS5b) solutions, containing **bpy-azo-bpy** compound. The initial UV-vis absorption spectrum of the non-acidic solution (red solid curve) presents the characteristic absorption bands at 280 nm and at 358 nm, respectively attributed to the π - π * transition of the bipyridine ending groups and of the azobenzene central bridge. The band centered at 455 nm correspond to the transition n- π * assigned to the azobenzene part. Their modifications after a few minutes of irradiation under UV light (bleu solid curve) are consistent with the TRANS-CIS isomerization of the benzene group.³ For the π - π * transition, the shift of the absorption wavelength towards blue and the decrease of the molecular extinction coefficient can be explained by the difference in structure between

the TRANS and CIS isomers. Whereas for the $n-\pi^*$ transition which is due to the nonbinding doublet of the nitrogen atom constituting the N = N double bond, this transition is forbidden in the TRANS isomer and allowed in the CIS isomer. As a result, the molecular extinction coefficient is higher in CIS than in TRANS isomer. Upon visible light irradiation, a complete recovery of the original spectral characteristics has been observed (green dotted curve). These latter observations confirm the reversibility of the isomerization of the bpy-azo-bpy, which is a typical behavior of azobenzene-based compounds. The same behaviors and reversibility have been proven also in the acidic environment (FigureS5b). Nonetheless, the different absorption peaks are a slightly shifted towards the longer wavelengths due to the acidity effects.

References

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