Supplementary Information for

Organised structures of flexible bolaamphiphiles with trisiloxane spacers: three- and two-dimensional molecular assemblies with different molecular conformation

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1. Polarised UV/Vis Spectra of the LB Films of 2

UV/Vis spectroscopy measurements for the LB films of **2** indicated that no in-plane anisotropy was induced by polarised UV or visible light irradiation. Figure S1 show the UV/Vis spectra of the LB film of **2** transferred at the surface pressure of 30 mN m^{-1} onto a quartz substrate. After the film deposition from the water surface by vertical dipping method, the azobenzene moieties show no in-plane order (Fig. S1a). The film was exposed to polarised visible light (436 nm, 1000 mJ cm^{-2}, the electric field vector is perpendicular to the dipping direction) and then preserved at room temperature for 2 days to complete the thermal *cis–trans* isomerisation. Figure S1b presents the polarised UV/Vis spectra of the visible light-irradiated LB film, which shows no dichroism. Moreover, we checked the isomerisation behaviour of the azobenzene cores during the polarised light irradiation. The LB film with no in-plane order was exposed to 30 mJ cm^{-2} of polarised UV light (365 nm). For this irradiation energy, the monolayer film consists of ca. 40% *trans* form and 60% *cis* form. If the in-plane motion of the core is restricted, azobenzene cores aligned parallel to the polarised UV light are selectively excited and thereby dichroism in UV/Vis spectra should be observed. However, as shown in Fig. S1c, the absorbances in the directions parallel and perpendicular to the dipping direction were almost the same. These results indicate that the core parts have high molecular motions and thus the anisotropic core distributions induced by polarised light irradiation are not preserved because of the active in-plane motions.

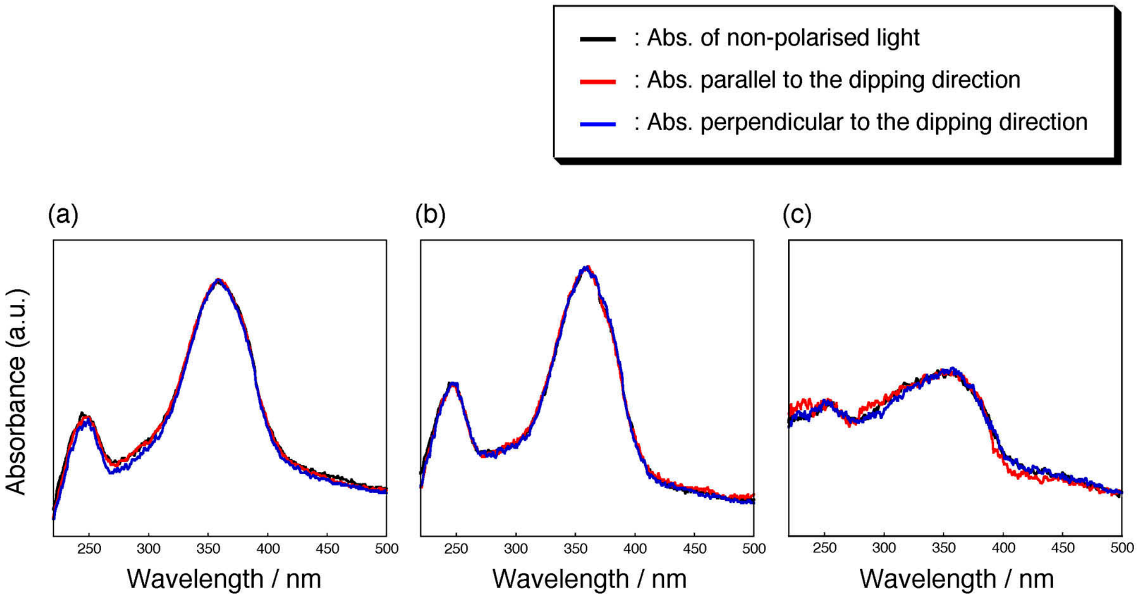

Fig. S1 UV/Vis spectra of the LB film of **2** transferred at the surface pressure of 30 mN m^{-1} onto a quartz substrate: (a) after deposition from the water surface; (b) LB film exposed to polarised visible light (436 nm, 1000 mJ cm^{-2}); (c) LB film exposed to 30 mJ cm^{-2} of polarised UV light (365 nm).

2. Atomic Force Microscopy to Measure Film Thickness

The film thickness of the LB films deposited onto mica substrates was measured by atomic force microscopy (AFM). To obtain the height profile of the cross section of the films, we mainly performed two methods. One is to mechanically remove a part of the films by scratching the film surface with an AFM tip. Although we attempted the film removal on tapping mode and contact mode, scratching on the contact mode is more effective to remove the films. As an example, an AFM image of the LB film of compound **1** prepared at 5 mN m^{-1} was shown in Fig. S2a. Another method is to seek some holes or partially unsticked parts for the LB films. Fortunately, we could find such a part for the film of compound **2** (Fig. S2b). In these cases, the films thickness is estimated to be 1.0–1.2 nm as described in the main text.

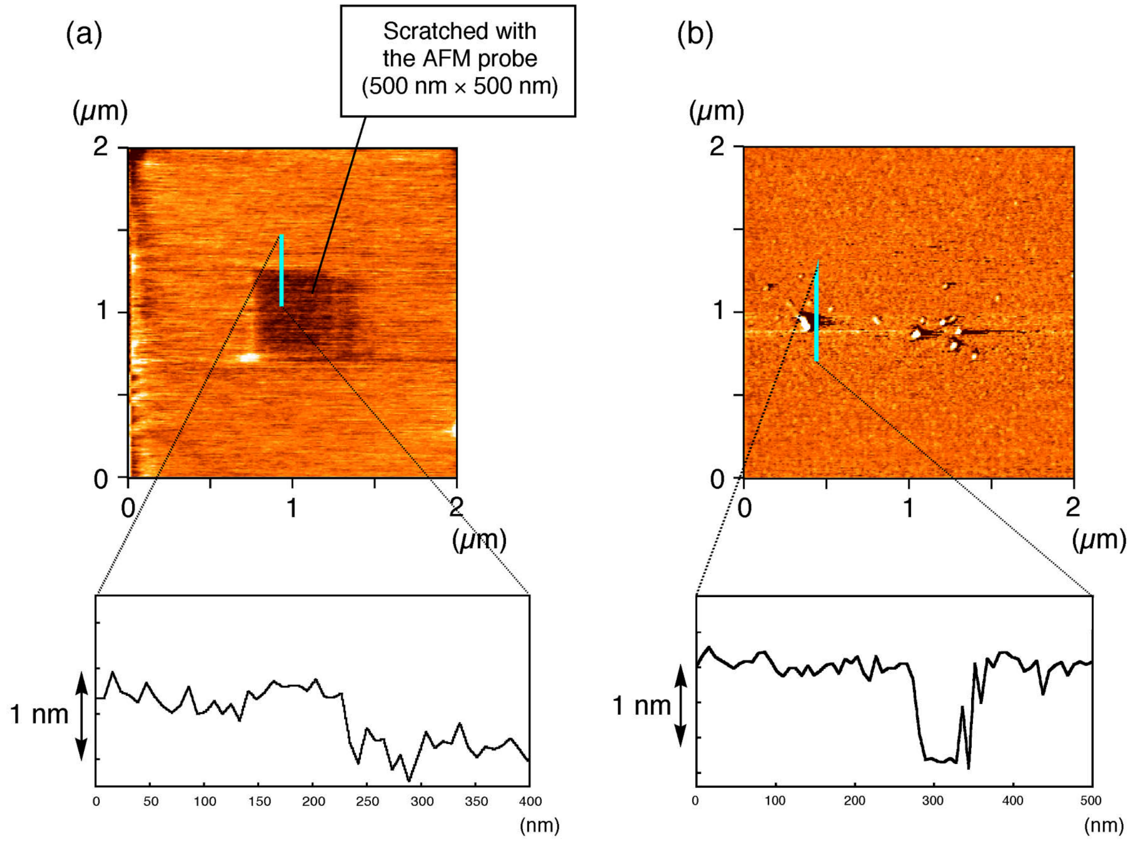

Fig. S2 Examples of the AFM images used to examine the film thickness: (a) compound **1** transferred at 5 mN m^{-1}; (b) compound **2** transferred at 10 mN m^{-1}.