Carbon parity affecting the packing state of azobenzene–urea monolayers

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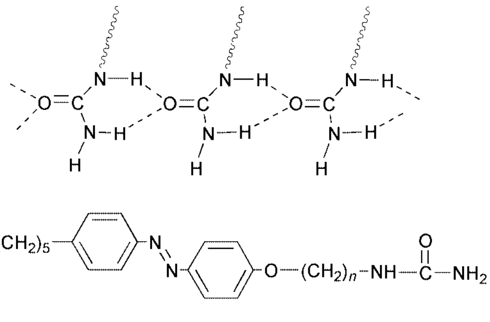
The monolayers of azobenzene (Az)-containing urea amphiphiles show clear odd–even effects of the alkylene spacer length in respect of the spreading behavior on water and the packing state of the Az chromophore on a quartz substrate.

The urea moiety is very simple in structure but provides a particularly useful building block[1] in supramolecular chemistry.[2,3] Urea derivatives associate *via* intermolecular bifurcated NH···O=C hydrogen bonds (see Fig. 1) and these paired hydrogen bonds afford a robust and highly directional intermolecular joint. On the surface of water, the monolayers of long chain alkylureas are known to exhibit a unique thermally-induced area change.[4] The monolayer of alkylureas, unlike other amphiphiles, exhibits a sudden contraction at an intrinsic transition temperature on heating. It is assumed that the rupture of the bifurcated hydrogen bonds among the urea heads is responsible for this thermal change in the molecular packing.

Our recent work using an azobenzene (Az)-containing long chain urea showed that this monolayer on the surface of water adopts a characteristic packing structure in which the *trans*-to-*cis* photoisomerization is completely prevented.[5] More interestingly, when the monolayer is transferred onto a hydrophilic substrate, the atmospheric humidity change sharply switches the assembled state and hence the photoreactivity of Az in the assembly.[6] We report herein a new aspect of the molecular design of the Az–urea monolayer system. It is found here that the carbon parity (odd/even number) of the alkylene spacer connecting the urea and the Az unit obviously results in the alternation of the spreading behavior and the molecular packing nature. Examples of odd–even effects affecting the thermal properties in thermotropic liquid crystals are widely known.[7] In two dimensional monolayer or bilayer assembly systems, various surface-mediated phenomena, such as wetting of liquid,[8] ice nucleation,[9] liquid crystal alignment[10] and electrochemical properties[11] are altered by the carbon parity. This paper presents a new example involving the photochromic monolayer.

The family of Az–urea compounds, *N*-(5-{4-[(4-hexylphenyl)azo]phenoxy})alkylurea (**1**, *n* = 3–7), used in this work are shown in Fig. 1. These compounds were synthesized in a similar manner to that described in ref. 5 for *n* = 10. The corresponding Az-containing carboxylic acid derivatives, the starting compounds, were converted to isocyanates and then a subsequent reaction with ammonia gas was performed.[12] The spreading behavior of Az-containing monolayers was evaluated on pure water (Milli-Q grade, 18 MΩ cm^{-1}, pH = 5.8) using a Lauda FW1 film balance in subdued red light. After evaporation of the solvent, monolayers were compressed at a speed of 30 cm^2 min^{-1}, and the surface pressure was recorded *versus* the molecular area. The absorption spectra were taken on a JASCO MAC-1 spectrophotometer, which was principally designed for low absorbance measurements.



1 (*n* = 3, 4, 5, 6 and 7)

Fig. 1 Schematic representation of the bifurcated hydrogen bonds between the urea units (above), and the chemical structure of the Az–urea amphiphiles used in this study (below).

Surface pressure–area (*π*–*A*) isotherms of **1** (*n* = 3–7) in the *trans* form obtained at 20 ± 0.5 °C are shown in Fig. 2. As indicated, the limiting area per molecule, which was estimated by extrapolating the steepest slope to zero pressure, indicated systematic alternation with *n* (see Fig. 2 inset). For the compounds with an odd number of carbons in the spacer (*n* = 3, 5 and 7), the limiting area was in the range 0.29–0.30 nm^2. On the other hand, the monolayers of **1** having an even numbered spacer (*n* = 4 and 6) showed significant area expansions with higher compressibility. Since the cross section of vertically aligned Az is 0.25 nm^2, as estimated from the X-ray diffraction data of crystals,[13] it can be thus interpreted that the molecules in these monolayers are tilted with respect to the surface normal. The degree of molecular tilting for the even numbered carbon spacers should be greater than that of the odd numbered ones.

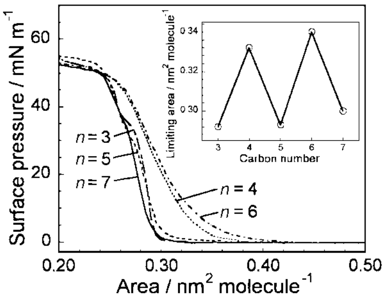


Fig. 2 Surface pressure–area isotherms of monolayers of **1** (*n* = 3–7) on pure water at 20 °C. In the inset, the limiting occupying area is plotted against the alkylene spacer length (*n*).

The shape of *π*–*A* curves also showed regular changes with *n*. The even numbered (*n* = 4 and 6) compounds gave a continuous smooth slope in the *π*–*A* curves. In contrast, monolayers of the odd carbon series (*n* = 3, 5 and 7) showed a sharper increase in the curve, indicative of lower compressibility. Furthermore, a characteristic inflecting region around 33 mN m^{-1} was observed for the odd numbered series only. We have not yet elucidated the process involved in this phase transition.

Single layers of **1** (*n* = 3–7) on water were deposited onto a clean quartz plate by the vertical lifting procedure at 20 mN m^{-1}. The transfer ratio was 1.0 ± 0.1 in all cases. Fig. 3 displays the transmission UV–vis absorption spectra of the monolayers of **1** on both sides of the quartz plate measured in the dry state. From these spectral features, the effect of the carbon parity of

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the spacer on the packing state of Az can be evaluated as follows.

Firstly, the aggregation state of Az was altered by the carbon number. The peak position of the π–π* band attributed to the long axis transition of Az (λ_{max}), which indicates the aggregation state of the chromophore,[14] showed a zigzag change with increasing *n* (open circles in Fig. 3 inset). The Az units in the transferred monolayers formed H-aggregates in all cases, judging from the considerable hyprochromic shifts of λ_{max} (317–327 nm) from the value in chloroform solution (352 nm).[5] As a general tendency, λ_{max} shifted to shorter wavelengths with increasing spacer length, indicating that a stronger H-type aggregation is formed in the monolayer with the longer spacers, due to stronger van der Waals interactions. Among these, λ_{max} for the odd numbered series showed significant hypsochromic shifts.

Secondly, the molecular orientation was altered. The absorption ratios of the two π–π* bands, *i.e.* the absorption intensity of the short-axis transition (peaking below 250 nm) relative to that of the long-axis transition (300–400 nm) (A_{short}/A_{long}), are plotted as a function of *n* (filled squares in Fig. 3 inset). The value of A_{short}/A_{long} was less than 1.0 for the even numbered series, whereas it exceeded 1.0 for the odd numbered series. This absorbance ratio can be related to the degree of molecular tilting. In the transmission mode measurements, the smaller value of A_{short}/A_{long} indicates a larger molecular tilt from the surface normal. Therefore, the monolayers of **1** with the even numbered spacers should be tilted to a greater extent than those of the odd numbered series. This observation is in good agreement with the above mentioned results of (i) the larger expansion in the spreading behavior on water (Fig. 2) and (ii) the less hypsochromic shifts of the π–π* band in the absorption spectrum (open circles in Fig. 3 inset) for the even numbered series.

We assume the origin of the odd–even effects observed here is as follows. The formation of the bifurcated hydrogen bonds fixes the head groups firmly and molecular motion is thereby strongly hindered. When the alkylene spacer chain takes the all-*trans* zigzag conformation, then the orientation of the Az moiety should be affected alternately by the carbon parity. A precise understanding of the packing state requires further exploration using techniques such as X-ray analysis, Fourier transform infrared spectroscopy and microscopy observations, which will be the subject of future investigations.

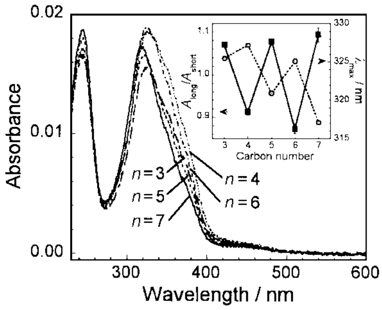

Fig. 3 UV–Vis absorption spectra of monolayers of **1** (n = 3–7) transferred at 20 mN m^{-1} onto both sides of a quartz plate. The inset shows λ_{max} (open circles) and A_{short}/A_{long} (filled squares, see text for definition) plotted against the alkylene spacer length (n).

In conclusion, this work revealed a new carbon parity effect observed in the packing state of photochromic Az units in a monolayer assembly. Since the packing state of Az governs the *trans*-to-*cis* photoisomerization behavior,[5] the findings observed here may have implications for the design of various photochromic functions.

Notes and references

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12 Detailed procedures and analytical data for this series will be reported elsewhere. Only the melting points and elemental analysis data are listed here. *N*-(3-{4-[(4-Hexylphenyl)azo]phenoxy})propylurea (n = 3): mp = 163–165 °C; found: C: 68.70; H: 7.80; N: 14.57; calcd for $C_{22}H_{30}N_4O_2$: C: 69.08; H: 7.91; N: 14.65%. *N*-(4-{4-[(4-Hexylphenyl)azo]phenoxy})butylurea (n = 4); mp = 154–156 °C; found: C: 69.80; H: 7.85; N: 14.30; calcd for $C_{23}H_{32}N_4O_2$: C: 69.67; H: 8.13; N: 14.13%. *N*-(5-{4-[(4-Hexylphenyl)azo]phenoxy})pentylurea (n = 5): mp = 148–149 °C; found: C: 70.09; H, 8.62; N: 13.60; calcd for $C_{24}H_{34}N_4O_2$: C: 70.24; H: 8.29; N: 13.66%. *N*-(6-{4-[(4-Hexylphenyl)-azo]phenoxy})hexylurea (n = 6): mp = 154–155 °C; found: C: 70.64; H: 8.69; N: 13.22; calcd for $C_{25}H_{36}N_4O_2$: C: 70.72; H: 8.55; N: 13.20%. *N*-(7-{4-[(4-Hexylphenyl)azo]phenoxy})heptylurea (n = 7): mp = 141–143 °C; found: C: 71.05; H: 8.67; N: 12.81; calcd for $C_{26}H_{38}N_4O_2$: C: 71.20; H: 8.73; N: 12.77%.

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