

Monolayers and Langmuir–Blodgett films of optically active macrocyclic poly(esters) containing the 1,1'-bi-2-naphthol moiety at the air/water interface

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In order to fabricate chiral Langmuir–Blodgett (LB) films and expand the range of monolayer-forming materials, a new type of macrocyclic poly(aryl ester) containing the optically active 1,1'-bi-2-naphthol group, and which have no substituted alkyl chains, were investigated. The spreading behaviors and the fabrication of ultrathin films of the compounds were studied. Stable monolayers were formed with collapse surface pressures up to 40 mN m⁻¹ at the air/water interface, although these compounds have no substituted alkyl chains. It is suggested that in the monolayers the macrocyclic rings lie flat on the surface of the water, while the aromatic rings extended upwards out of the water surface. The monolayers can be transferred onto solid substrates uniformly using the horizontal lifting method. Transferred LB films were characterized by UV, polarized UV and circular dichroism (CD) spectra. In comparison with the corresponding solutions, the ¹B_g and ¹L_a bands of the compounds in LB films show a red shift. Both the UV and polarized UV spectra indicate a J-like aggregation of the chromophores in the LB films. In the CD spectra, splitting of the Cotton effect is observed both in solution and in LB films, indicating that interactions between the neighboring naphthalene chromophores take place. In the LB films, the exciton couplet shows a red shift in comparison with those in solution due to aggregation.

1 Introduction

Organized molecular assemblies such as monolayers, bilayers and Langmuir–Blodgett films are attracting much interest due to their potential applications in molecular electronics and the mimicry of biological systems.¹ Traditionally, amphiphiles or compounds substituted with long alkyl chains are usually necessary in order to form stable monolayers at the air/water interface. There are fewer reports on monolayers and LB films fabricated from compounds without such chains. In order to expand the range of molecules with which to assemble organized molecular films, we are systematically investigating the formation of monolayers and LB films of simple molecules which have no alkyl substituents. Previously, we have found that some benzimidazole compounds which have short or no alkyl chains can form stable monolayers at the air/water interface induced by Ag(I) ions in the subphase.² It has been confirmed that these monolayers are formed through *in situ* coordination at the air/water interface between the benzimidazole moiety and Ag(I) ion in the subphase. Other simple compounds seem to be difficult to form into stable monolayers at the air/water interface. On the other hand, many macrocyclic compounds, such as porphyrins,³ phthalocyanines⁴ and calixarenes,⁵ have been reported to form stable monolayers and their properties have been widely investigated. This suggests that it may be possible for macrocyclic compounds which have no alkyl chains to form stable monolayers at the air/water interface.

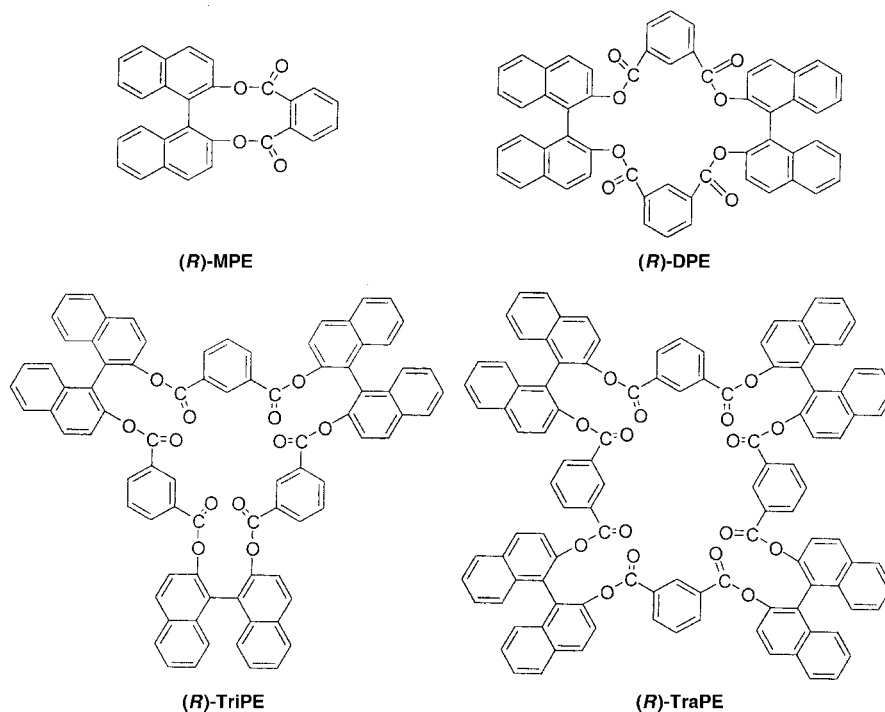
The chirality of molecules plays an important role in biology and materials science. Recently, there has been

increasing interest in supramolecular assemblies of chiral molecules. LB films of chiral molecules are attracting attention due to their unique capability of discriminating between chiral substrates or biomaterials.^{1a,b,6} So far, LB films of chiral molecules have mostly been associated with amphiphilic chiral molecules.^{7,8} Recently, Miyashita's group reported the formation of LB films of optically active macrocycloamides.⁹ 1,1'-Binaphthol is an inherently dissymmetric chromophore,¹⁰ the study of this system has been mostly related to chiral recognition and asymmetric organic synthesis.¹¹ This chromophore has been widely used as a chiral unit to construct chiral molecules or assemble chiral supramolecular systems.^{12–14} While the properties of these macrocyclic compounds have been widely investigated, their ability to form monolayers was not studied. In this paper, we report monolayer formation with a new type of chiral macrocyclic compound containing the 1,1'-bi-2-naphthol moiety and the fabrication of chiral LB films from these macrocyclic compounds.

2 Experimental

2.1 Materials

Four optically active macrocyclic poly(aryl ester)s: monocyclic, dimeric, trimeric and tetrameric compounds, abbreviated as MPE, DPE, TriPE and TraPE, respectively, were synthesized by reacting chiral 1,1'-bi-2-naphthol with phthalyl chloride, isophthalyl chloride as reported in a previous paper.¹⁵ Their structures are shown in Scheme 1.



Scheme 1 Compounds used in the work and their abbreviations.

2.2 Procedures

The monolayer and Langmuir–Blodgett experiments were performed using a KSV 1100 Teflon-coated LB trough (KSV Instruments, Helsinki, Finland), with which a surface of 240 cm² could be obtained. Milli-pore-Q water (18 mΩ cm) produced by the Institute of Semiconductors (Beijing, CAS) was used in all the cases. The monolayers were formed by spreading chloroform solutions (1×10^{-3} mol L⁻¹) onto the surface of the water. After waiting 15 min for the solvent to evaporate, surface pressure–area isotherms were recorded on a computer with a compression speed of 5 mm min⁻¹ at 20 °C.

Quartz plates (5 × 1 cm) were cleaned in mixed chromic acid and washed thoroughly with Milli-Q water. After the plates had been dried, they were rubbed with ferric stearate to make the surface hydrophobic. Langmuir–Blodgett films were fabricated by transferring the monolayers at the air/water interface onto hydrophobic quartz slides at 15 mN m⁻¹ by the horizontal lifting or Langmuir–Schäfer methods. UV-visible spectra of the transferred LB films were measured with a JASCO UV-530 spectrophotometer. CD spectra of the transferred films on quartz substrates were recorded with a JASCO-720 system. Polarized UV spectra were recorded with the UV-530 spectrophotometer by adding polarizers on to the apparatus.

3 Results and discussion

3.1 Monolayers at the air/water interface

Chloroform solutions of poly(aryl ester)s were spread at the air/water interface and surface pressures were measured. Fig. 1(a) shows the compression surface pressure–area (π – A) isotherms of the spread Langmuir films of poly(aryl ester)s on the surface of pure water at 20 °C. All of the compounds are found to be surface active, as elucidated from their surface pressure–area isotherms. The isotherm for DPE is of the condensed type, while those of TriPE and TraPE are somewhat expanded. For MPE, the surface pressure appears at a relatively small molecular area. The collapse pressures for DPE, TriPE and TraPE are 50, 41 and 42 mN m⁻¹, respectively. The molecular areas where the surface pressures begin to appear

are found at 1.8, 2.25 and 3.4 nm² molecule⁻¹ for the Langmuir films of DPE, TriPE and TraPE, respectively. By extrapolating the linear part of the isotherms to zero surface pressure, molecular areas of 0.14, 0.72, 1.0 and 1.40 nm² molecule⁻¹ can be obtained for MPE, DPE, TriPE and TraPE, respectively. Considering the fact that in these macrocyclic compounds only the ester groups are hydrophilic and the other groups are hydrophobic, it is reasonable to consider that the hydrophilic ester groups are immersed in the water, while the aromatic rings protrude out of the surface, as illus-

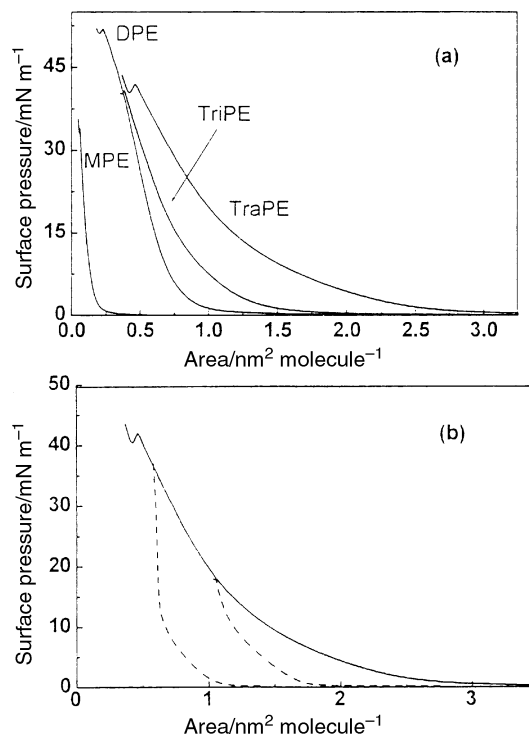
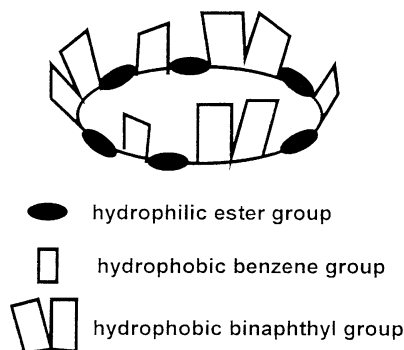


Fig. 1 Surface pressure–area isotherms of monolayers of the four compounds at the air/water interface at 20 °C: (a) compression isotherms for (R)-MPE, (R)-DPE, (R)-TriPE and (R)-TraPE; (b) expansion isotherms for (R)-TraPE.



Scheme 2 Possible molecular arrangement of the monolayers at the air/water interface.

trated in Scheme 2. Based on these considerations, the molecular areas, which correspond to the ring sizes, can be estimated to be 0.79, 1.04–1.54 nm² molecule⁻¹ for DPE, TriPE and TraPE, respectively. These values are smaller than the onsets of the monolayers and are very close to the limiting areas of the monolayers of the macrocyclic compounds, suggesting that monolayers are formed for DPE, TriPE and TraPE on the water surface. In the case of MPE, the molecular area is so small that it can not be regarded as a “true” monolayer. For the other three compounds, due to the symmetrically distributed binaphthyl and benzene groups, a balance can be obtained to ensure the formation of a stable monolayer. In the case of MPE, however, because there is only one binaphthyl and one benzene group, and the benzene group is not as hydrophobic as the binaphthyl group, such weak hydrophobicity and an unbalance in the surface activity causes the difficulty in forming stable monolayers. Therefore, we could not obtain a “true” stable monolayer for MPE.

On the other hand, the monolayers of DPE, TriPE and TraPE all show hysteresis. Fig. 1(b) shows, for example, the expansion isotherms for the TraPE monolayer expanded from different surface pressures or molecular areas. When expanded from 37 mN m⁻¹, the surface pressure initially shows a large decrease. While when expanded from 18 mN m⁻¹, a relatively slow decrease in the surface pressure is observed. In both cases, the expansion isotherms are different from the compression isotherms, indicating that the compression and expansion processes for the monolayers are irreversible. Similar phenomena were found for the monolayers of the other compounds.

Stability is very important in judging the properties and the quality of the monolayer. We have investigated the stabilities of these monolayers by monitoring the decrease in the molecular areas while keeping the surface pressure at 15 mN m⁻¹. This revealed that the decreases in the molecular area were within 6% in the initial 30 min, suggesting that the monolayers are fairly stable.

In classical concepts, amphiphiles are usually needed in order to form stable monolayers at the air/water interface. It is interesting to note that these macrocyclic compounds, which have no alkyl chains, can nevertheless form stable monolayers on the surface of water. This adds a new family of macrocyclic compounds, besides the well-studied porphyrins and phthalocyanines, to the list of those able to form monolayers.

3.2 Langmuir–Blodgett films

3.2.1 UV spectra. In contrast to those monolayers formed from typical amphiphiles, the monolayers of these macrocyclic compounds with no alkyl substituents could not be deposited by vertical dipping. However, using the horizontal lifting or Langmuir–Schaefer method, the monolayers of DPE, TriPE and TraPE were successfully transferred onto solid substrates.

Fig. 2(a)–(c) shows the UV absorption spectra of the LB films with various numbers of deposited layers in comparison with methanol solutions. Similar spectra are obtained for all

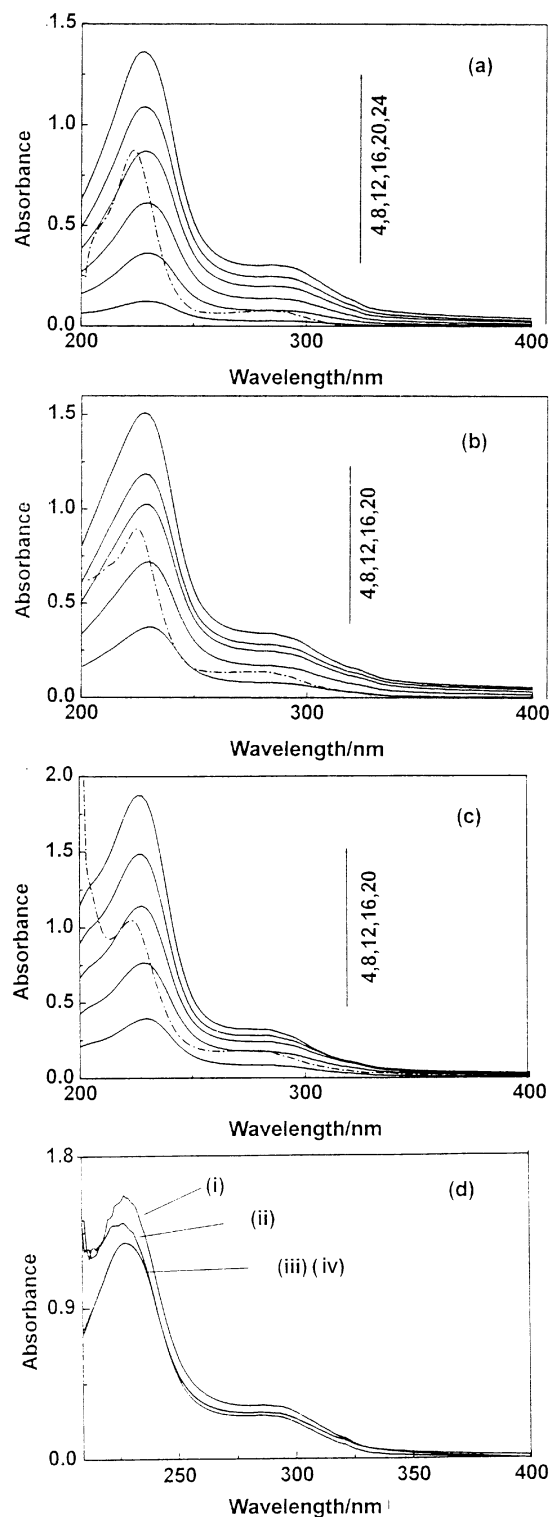


Fig. 2 Absorption spectra of the transferred LB films (solid lines) with different layer numbers: (a) (R)-DPE, (b) (R)-TriPE and (c) (R)-TraPE. Absorption spectra in methanol solution (dashed lines): (d) (R)-TraPE, (i) *p*-polarized, 45° incidence; (ii) *s*-polarized, 45° incidence; (iii) *s*-polarized, 0° incidence; and (iv) *p*-polarized, 0° incidence.

the compounds. In methanol solution, the spectra show absorption bands at 223 and 283 nm, respectively, which can be assigned as the ¹B_b and ¹L_a bands due to the binaphthyl group.¹⁶ In the LB films, the ¹B_b and ¹L_a bands are observed at 228 and 290 nm, respectively. The slight red shift of the bands for the LB films can be attributed to the organized aggregation of the binaphthyl chromophore. Because the ¹B_b band corresponds to the long axis of the naphthyl group, while the ¹L_a band corresponds to the short axis, this red shift

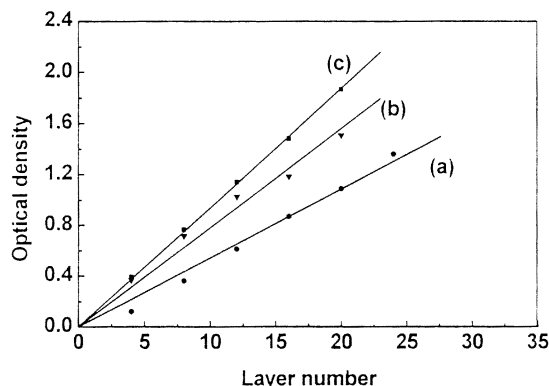


Fig. 3 Plots of the optical densities of the transferred LB films at 228 nm as a function of layer number: (a) (R)-DPE, (b) (R)-TriPE and (c) (R)-TraPE.

of the two bands indicates that the naphthyl groups undergo J-like aggregation in the LB films.

In order to further clarify the kind of aggregation in which the naphthyl groups are involved, polarized UV spectra of the LB films were measured. Fig. 2(d) shows an example for the case of DPE. Although no anisotropy is observed at an incidence angle of 0° , anisotropy is observed with an incidence

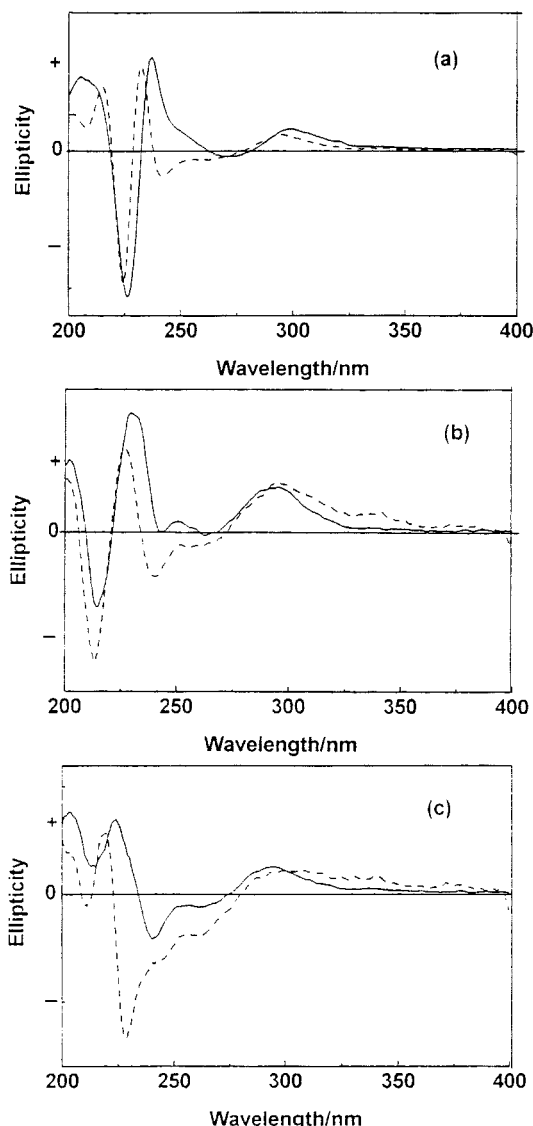


Fig. 4 CD spectra of (R)-DPE (a), (R)-TriPE (b) and (R)-TraPE (c) transferred LB films (solid lines) and methanol solutions (dashed lines).

angle of 45° , where stronger absorption is found with *p*-polarized light. The dichroic ratio of A_p to A_s (where A_p and A_s are the absorbance at 228 nm for the LB films observed with *p*- and *s*-polarized light, respectively) are estimated to be 1.12 for DPE, and 1.05 for TriPE and TraPE LB films. According to Yoneyama's equation,¹⁷ and assuming the refractive index (*n*) of the films is 1.5,¹⁸ the angles between the chromophores in the LB films and the substrate were estimated to be 49° for DPE, and 41° for TriPE and TraPE. This indicates that the naphthyl groups undergo J-like aggregation in the LB film, supporting the above deduction from comparison of the UV spectra of the solutions and LB films. Moreover, dissolution of the LB film in methanol reproduced the solution absorption spectra. This result further verifies that the red shift of the 1B_b and 1L_a bands in the LB film was indeed due to the aggregation.

The absorbances of the LB films at 228 and 290 nm increased with increasing layer number. Plots of the optical densities at 228 nm and the number of transferred layers are shown in Fig. 3. Good linear relationships are obtained, suggesting the uniform transfer of the monolayers onto the solid substrates.

3.2.2 CD spectra of the LB film. Since these compounds are optically active, circular dichroism (CD) spectra are useful to characterize the LB films. Fig. 4 shows the CD spectra of the LB films in comparison with those in methanol solutions. In the case of DPE, two exciton couplets (zero crossing) are observed at 230 and 277 nm in methanol solution. This spectrum is typical of a compound in *R*-configuration and indicates that strong interactions exist for both the 1B_b and 1L_a bands.^{19,20} For the LB film, the shape of the CD spectrum is essentially the same, but the crossovers show a slight red shift, where corresponding couplets are observed at 233 and 281 nm. This shift is regarded as being due to the aggregation in the LB film. Similar spectra are observed for the TriPE and TraPE LB films. These results indicate that the chirality of the compounds is essentially maintained in the LB films, although there are some differences due to the aggregation.

Conclusions

The monolayer formation and Langmuir–Blodgett films of a series of chiral macrocyclic poly(aryl ester)s containing the binaphthol moiety at the air/water interface were investigated, in order to expand the choice of molecules with which to form organized molecular films. It reveals that, although MPE, which has only one unit, could not form stable monolayers, other compounds with larger macrocyclic rings could form stable monolayers on the surface of water. This shows that a macrocyclic compound without alkyl chains can still be a good candidate for monolayer formation. Uniform LB films can be fabricated by transferring the monolayers at the air/water interface using the horizontal lifting method. The chirality based on the binaphthol moiety is maintained in the transferred LB films.

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References

- (a) J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; (b) K. Kurihara, K. Ohto, Y. Tanaka, Y. Aoyama and T. Kunitake, *J. Am. Chem. Soc.*, 1991, **113**, 444; (c) Y. Honda, K. Kurihara and T. Kunitake, *Chem. Lett.*, 1991, 681.

- 2 M. H. Liu, A. Kira and H. Nakahara, *Langmuir*, 1997, **13**, 4807; J. F. Cai, M. H. Liu, D. Chen, J. Tang, J. R. Li and L. Jiang, *Colloids Surf. A*, 2000, **175**, 165.
- 3 D. G. Whitten, *J. Am. Chem. Soc.*, 1976, **98**, 1584; M. Vandevyer, A. Barraud, A. Ruaudel-Teixier, P. Maillard and C. Gianotti, *J. Colloid Interface Sci.*, 1982, **85**, 571; G. A. Schick, I. C. Schreiman, R. W. Wagner, J. S. Lindsey and D. F. Bocian, *J. Am. Chem. Soc.*, 1989, **111**, 1344.
- 4 S. Baker, M. C. Petty, G. G. Roberts and M. V. Twigg, *Thin Solid Films*, 1983, **99**, 53; W. H. Ko, C. W. Fu, H. Y. Wang, D. A. Batzel, M. E. Kenny and J. B. Lando, *Sens. Mater.*, 1990, **2**, 39.
- 5 M. A. Markowitz, V. Janout, D. G. Castner and S. L. Regen, *J. Am. Chem. Soc.*, 1989, **111**, 8192; Y. Ishikawa, T. Kunitake, T. Matsuda, T. Otsuka and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1989, 763; W. C. Moreira, P. J. Dutton and R. Aroca, *Langmuir*, 1995, **11**, 3137.
- 6 J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley, New York, 1982.
- 7 E. M. Arnett, N. G. Harvey and P. L. Rose, *Acc. Chem. Res.*, 1989, **22**, 131; E. M. Arnett and J. M. Gold, *J. Am. Chem. Soc.*, 1982, **104**, 636; N. G. Harvey, D. Mirajovsky, P. L. Rose, R. Verbiar and E. M. Arnett, *J. Am. Chem. Soc.*, 1989, **111**, 1115; J. G. Heath and E. M. Arnett, *J. Am. Chem. Soc.*, 1992, **114**, 4500.
- 8 S. Pathirana, W. C. Neely, L. J. Myers and V. Vodyanoy, *J. Am. Chem. Soc.*, 1992, **114**, 1404.
- 9 F. Feng, T. Miyashita, H. Okubo and M. Yamaguchi, *J. Am. Chem. Soc.*, 1998, **120**, 10166.
- 10 K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *J. Am. Chem. Soc.*, 1962, **84**, 1455.
- 11 C. Rosini, L. Franzini, A. Raffaelli and P. Salvadori, *Synthesis*, 1992, 503; L. Pu, *Chem. Rev.*, 1998, **98**, 2405.
- 12 R. C. Helgeson, J. M. Timko and D. J. Cram, *J. Am. Chem. Soc.*, 1973, **95**, 3023; R. C. Helgeson, J. M. Timko, P. Moreau, S. C. Peacock, J. M. Mayer and D. J. Cram, *J. Am. Chem. Soc.*, 1974, **96**, 6762.
- 13 E. P. Kyba, K. Koga, L. R. Sousa, M. G. Siegel and D. J. Cram, *J. Am. Chem. Soc.*, 1973, **95**, 2692.
- 14 X. X. Zhang, J. S. Bradshaw and R. M. Lzatt, *Chem. Rev.*, 1997, **97**, 3336.
- 15 A. J. Gong, W. H. Liu, Y. M. Chen, X. Zhang, C. F. Chen and F. Xi, *Tetrahedron: Asymmetry*, 1999, **10**, 2079.
- 16 H. B. Kleven and J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 470; J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 484.
- 17 M. Yoneyama, M. Sugi and M. Saito, *Jpn. J. Appl. Phys.*, 1985, **25**, 961.
- 18 *Handbook of Chemistry & Physics*, 78th edn., ed. D. R. Lide, CRC Press, Boca Raton, FL, 1997.
- 19 L. D. Bari, G. Pescitelli and P. Salvadori, *J. Am. Chem. Soc.*, 1999, **121**, 7998.
- 20 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*, University Science Books, Oxford, 1983.