Supramolecular Assemblies of a Series of 2-Arylbenzimidazoles at the Air/Water Interface: In Situ Coordination, Surface Architecture and Supramolecular Chirality

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Abstract: The spreading behavior and supramolecular assemblies of some arylbenzimidazoles with 2-substituted aromatic groups such as phenyl, naphthyl, anthryl and pyrenyl on water surface and the subphase containing $AgNO_3$ were investigated. It was observed that although these compounds lack long alkyl chains, they showed surface activity when spread from chloroform solution on water surface and formed the supramolecular assemblies. When $AgNO_3$ was present in the subphase, a coordination between the imidazole group of the compounds and Ag^I occurred in situ in the spreading film, which was verified by the surface pressure/area (π–A) isotherms and UV/Vis absorption spectra. Both the spreading films from water and the aqueous $AgNO_3$ subphase were transferred onto solid substrates and their surface morphologies as well as properties were characterized by AFM, UV/Vis absorption and CD spectra. Various surface morphologies such as nanoparticles, block domains and nanoutensils were observed depending on the substituted aromatic groups. Interestingly, although all of these compounds were achiral, supramolecular chirality was obtained for some of the arylbenzimidazole films assembled from either the water surface or the subphase containing $AgNO_3$. It was revealed that chiral assemblies could be obtained from water surface for the benzimidazoles which have pyrenyl or α-naphthyl groups. For benzimidazole derivative with anthryl group, chiral assemblies could be obtained when spreading on the aqueous $AgNO_3$ subphase. For the benzimidazoles with phenyl or β-naphthyl groups, no chirality was obtained. It was suggested that both the overcrowded stacking of the aromatic groups and the cooperative arrangement of the molecules on water surface or aqueous $AgNO_3$ subphase play a crucial role in forming the chiral supramolecular assemblies.

Keywords: arylbenzimidazole · chirality · coordination modes · interfaces · supramolecular chemistry

Introduction

Air/water interface provides an important two-dimensional platform where various kinds of molecules can vividly act on.[1] Amphiphiles are one of the most investigated molecular systems that can be organized into a well-defined monolayer. In the typical monolayer on water surface, the hydrophilic groups immerse into the aqueous subphase and the hydrophobic alkyl chains extrude out into the air.[1,2] Through a lateral compression, the orientation of the functional groups and the molecular packing can be controlled. Recently, besides typical amphiphiles, many other molecules have been used to form organized structures at the air/water interface.[3] Simple water-insoluble molecules can also be spread, but they usually favor the formation of crystallites or multilayers with one to several layers thick.[4] Some bolaamphiphiles, in which two headgroups were covalently linked by the alkyl spacers, were reported to form various conformations and 3D nanoarchitectures at the air/water interface.[5] More complicated nanostructures can be generated through the interfacial interactions between different components.[6] Our group has been investigating the interfa-

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cial behaviors of various kinds of non-typical amphiphiles and found some new features.[7] For example, through the in situ coordination at the air/water interface, we obtained monolayers for 2-alkylbenzimidzazoles with short alkyl chains and got ultrathin films of metal ion coordinated bismuthiol at the air/water interface.[7] In addition, we obtained interesting nanoarchitectures through an interfacial coordination of a 1,20-octadecanedicarboxylic acid with $EuCl_3$ in the subphase.[8] These results clearly revealed that the air/water interface not only provides a place for monolayer formation, which is a main focus in the research, but also gives the possibility to construct more complicated and even 3D architectures using simple molecules. This latter case greatly expands our vision on the study of the surface ultrathin films.

Benzimidazoles, which are analogues of imidazole contained in histidine, are an important class of the biologically active compounds.[9,10] Besides, they are excellent organic ligands of many metal ions.[11] Previously, we have investigated the supramolecular assemblies of a series of benzimidazole-containing derivatives with or without long alkyl chains at the air/water interface and found a strong coordination ability of benzimidazoles with Ag^I ion at the air/water interface.[7a–d] Furthermore, we have found that an amphiphilic 2-heptadecyl naphtha[2,3]imidazole could form chiral molecular assemblies through an in situ coordination with Ag^I ion although the ligand was achiral.[12] In this paper, in order to get further insight into how the molecular packing was related to the chirality and how the molecular structure will affect the chirality of the molecular assemblies, we have made a systematic investigation on the interfacial behaviors of a series of arylbenzimidazoles (Figure 1) at the air/water interface and the subphase containing $AgNO_3$.

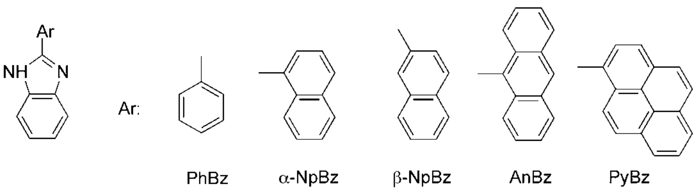

Figure 1. Molecular structures and abbreviations of the arylbenzimidazoles used in this work.

We selected the benzimidazoles, which have different ring sizes in the 2-position of the benzimidazole, for several reasons. First, these compounds, although can not be spread as a true monolayer due to the lack of alkyl chain, are potential to form some new nanostructures. It is helpful to understand the surface behaviors of non-amphiphile and further construct new nanoarchitectures. Second, in situ coordination provided an effective way in regulating the surface properties and fabricating functional ultrathin film.[13–22] Benzimidazole derivatives could serve as a good type of organic ligand and their coordination with Ag^I will give some clues to design new functional materials. Third, the chirality of supramolecular assemblies from achiral or chiral molecules is currently attracting great interest.[23–33] In our previous study we have found that chiral molecular assemblies could be obtained from achiral amphiphilic benzimidazole[12] and other achiral molecules.[34] In these cases, a steric hindrance between the neighboring assembling molecules played a key role. However, it is not clear if our findings are applicable to those molecules without alkyl chains. The object of this paper is to explore the film forming ability of these arylbenzimidazoles without any alkyl chains and further investigate the effect of the bulkiness or size of the aromatic substituents on the chirality of the assembled supramolecular films.

Systematic characterizations by using π–A isotherms, UV/Vis absorption and CD spectra, and AFM measurements were performed to reveal the surface properties, surface morphologies or nanoarchitectures and the chirality of the assembled molecular films.

Results and Discussion

Surface pressure–area isotherms of the spreading films: Although all the benzimidazole derivatives used have no alkyl chains, they showed surface activity when spread on water surface. Such surface activity could be investigated by measuring the π–A isotherm. Figure 2 shows the π–A isotherms of the spreading films of 2-arylbenzimidazoles on the water surface. Surface pressures were observed for all the benzimidazole derivatives on water surface. However, the molecular areas for the spreading films on water surface are too small to be regarded as true monolayers. On the other hand, the isotherms can be reproduced. This case was reported in other non-amphiphilic systems and in bolaamphiphiles.[5,8] It was suggested that the compounds formed multilayers or three-dimensional structures on water surface due to the lack of certain long alkyl chains. On the other hand, when there existed $AgNO_3$ in the subphase, a larger molecular area was obtained for all the isotherms in comparison with those on water surface. In addition, the isotherms showed a dependence on the concentration of $AgNO_3$. On increasing the concentration of the $AgNO_3$, there is an increment in the molecular area. When the concentration increased over 10 mM, no significant changes were observed for the isotherms. The present phenomena are essentially the same as those reported previously in the benzimidazole systems.[7a–d] Therefore, it can be suggested that all these 2-arybenzimidazole coordinated with Ag^I in situ at the air/aqueous $AgNO_3$ interface and monolayers might be formed. The limiting molecular areas extrapolated from the linear part of the isotherms of the spreading films on a higher concentration of $AgNO_3$ were obtained as 0.3, 0.3, 0.4 and 1.4 $nm^2 molecule^{-1}$ for α-NpBz, β-NpBz, PyBz and AnBz, respectively. Based on the CPK models and the molecular areas on aqueous $AgNO_3$, it was reasonable that monolayers were formed. However, whether the films were in a molecular thickness or not needs further confirmation by the AFM of the transferred monolayers and will be discussed later. Among these films, AnBz showed the largest molecular area. In AnBz, the anthryl moiety is attached to the 2-position of the benzimidazole through the 9-position. When the two nitrogen atoms of benzimidazole coordinated with Ag^I, the anthryl group is suggested to align with its long axis parallel to the water surface and showed the largest molecular area.

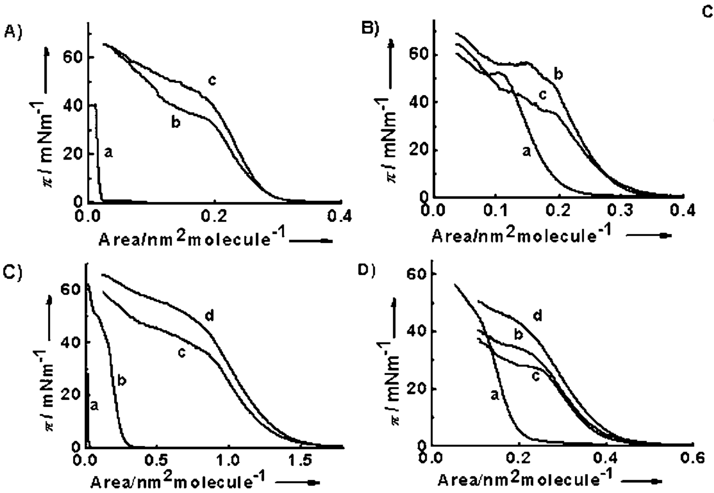

Figure 2. Surface pressure-area isotherms of the spreading films of A) α-NpBz; B) β-NpBz; C) AnBz and D) PyBz on aqueous subphases containing various concentration of $AgNO_3$ at 20°C: a) 0; b) 0.1 mм; c) 1.0 mм; d) 10 mм.

UV/Vis absorption spectra of the transferred multilayer films: The spreading films of the arylbenzimidazoles could be transferred onto solid substrates by a horizontal lifting method or Langmuir–Schaefer (LS) method similar to the previous study. Although the spreading films on water surface were not true monolayers, they could also be transferred onto solid substrates through the LS deposition. Figure 3 shows the UV/Vis absorption spectra of the dilute solutions and the LS films. Two distinct features are observed for the films. First, in comparison with the UV/Vis spectra in methanol solutions, all the spectra of the transferred films from water surface showed a bathochromic shift in the absorption maxima, indicating the ordered packing of the aromatic benzimidazoles in the transferred films. For example, α-NpBz shows three main absorption bands at 205, 225 and 305 nm in methanol, which can be ascribed to the n–π*, π–π* and charge transfer bands, respectively. For the multilayer film from water surface, both the π–π* and charge transfer bands showed a larger red shift to 234 and 331 nm, respectively. Similar cases are found for the other compounds. Second, clear spectral changes were observed for the films transferred from the aqueous $AgNO_3$ subphase in comparison with those from water surface. The band at around 250 nm diminished greatly for the films transferred from aqueous $AgNO_3$ surface. The spectral characteristic is similar to those Ag^I-coordinated benzimidazoles, suggesting that the aromatic benzimidazoles really coordinated with Ag^I in the subphase at the air/water interface. Therefore, from these spectra, we can conclude that although aromatic benzimidazoles could not form monolayers on water surface they could be orderly arranged. When spread on aqueous $AgNO_3$ subphase, in situ coordination occurred between the benzimidazoles and Ag^I at the interface.

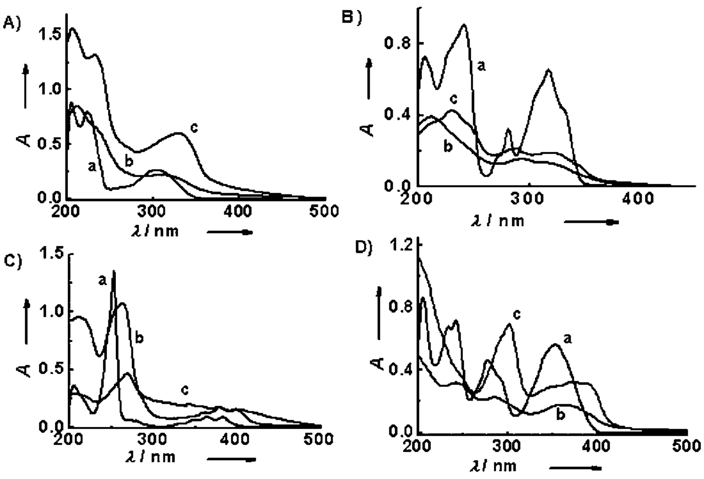

Figure 3. Absorption spectra of A) α-NpBz; B) β-NpBz; C) AnBz; and D) PyBz in different conditions: a) in methanol solution; b) multilayer film transferred from the subphases containing 1.0 mм $AgNO_3$; and c) from water surface.

Investigations on the surface morphologies of the spreading films: AFM technique is a powerful method to detect the surface morphologies and the film thickness. To investigate the film structures formed on water surface and the subphase of $AgNO_3$, we have transferred one-layer of spreading film from both water surface and the subphase containing $AgNO_3$ onto mica substrates and recorded the AFM pictures.

AFM images of one-layer LB films from pure water surface: Figure 4 shows the AFM pictures of the one-layer LB films transferred from the water subphase at 10 mN m^{-1}. Distinct morphologies were observed for the four films spread on water surface. Regular blocks were observed for α-NpBz film. From the height profiles, it was found that these blocks were flat and constructed from some flat steps. The smallest step was in a thickness of about 1.0 nm. From the CPK model, the length of the α-NpBz molecule is estimated to be 1.1 nm. This indicated that the blocks found in the α-NpBz film was composed of the multilayer. When α-NpBz was spread on a water surface, it might form a monolayer at the beginning due to the weak hydrophilicity of the nitrogen atoms in the benzimidazole. When compressed, however, the neighboring molecules can easily overlap to form the multilayers due to the lack of long alkyl chain, which could be served as a barrier for the molecules to overlap. For β-NpBz, a flat film with some holes was obtained. The height profile indicated that the hole was about 2 nm in depth, which is twice as the molecular length of β-NpBz, suggesting a double layer formed in the case of β-NpBz on water surface. The surface morphology of PyBz is like a rotten wood. The height profiles indicated that the thickness was about 2.8 nm. Since the molecular length of PyBz is estimated to be 1.4 nm, it can be concluded that a double layer structure was formed for PyBz on water surface. For AnBz, granular net-like aggregates are observed. The average height of the aggregates was 7 nm. These results indicated that multilayer or molecular aggregates were formed on water surface for the compounds and the size of the substituted aromatic groups have a great influence on the surface morphologies of the spreading films on water surface.

AFM images of one-layer LB films from aqueous $AgNO_3$ solution: Figure 5 shows the AFM pictures of the one-layer LB film transferred from the subphase containing $AgNO_3$. Uniform flat film or dotted domains were observed for the PyBz and α-NpBz films and flat domains with some pinholes for the film of β-NpBz. The thickness of the film or the holes was about 1 nm, indicating the monolayer formation of these compounds on aqueous $AgNO_3$ subphase. In the case of AnBz, interesting circular disk-like domains were observed. Underneath these domains, there are still layers which were composed of nano-sized particles. Further enlargement on the circular domains indicated that the domains are made of small nanoparticles. These particles gathered together to form the circular disks. On analyzing the height profiles, it was found that the height of the edge of the disk was about 7–8 nm, while that of the center was 4–4.5 nm. It indicated that a nanoutensil was actually formed, as clearly seen in the three-dimensional image of the AFM picture (Figure 5f). Although from the π–*A* isotherms AnBz showed a larger molecular area, in fact, it was not a monolayer from the AFM. This particular property of AnBz film was suggested to be due to the strong π–π interaction of the adjacent anthryl groups.

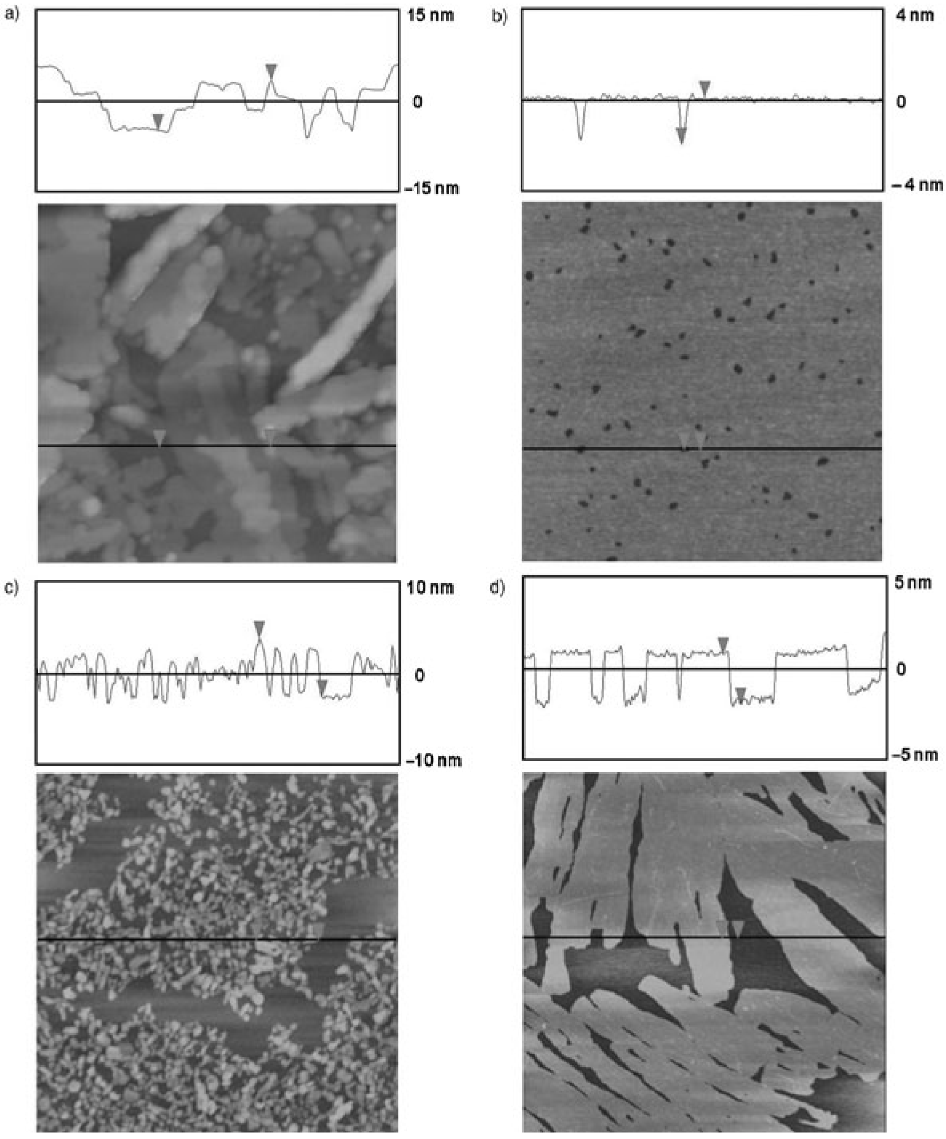

Figure 4. AFM images of one-layer a) α-NpBz; b) β-NpBz; c) AnBz and d) PyBz LB films from water surface at a surface pressure of 10 mN m^{-1}. The scan size is 2×2 μm for all of the pictures.

Supramolecular chirality

CD spectra: Previously, we have found that a long-chain 2-heptadecyl naphtha-[2,3]imidazole derivative could coordinate with Ag^I in situ in the monolayer and ex situ in solid substrates, and formed a chiral supramolecular assemblies although the long chain compound itself was achiral.[12] It was suggested that the formation of supramolecular chirality was due to the overcrowded stacking of the aromatic groups in the monolayers. In that case, such stacking was realized due to a steric hindrance between the adjacent naphtha-[2,3]imidazole group and the hydrophobic interaction between the alkyl chains. In addition, we have further found that long chain derivatives of benzimidazoles could not show chirality due to the small size of the benzimidazole ring. Herein, we used the benzimidazoles with larger substituted aromatic groups in the 2-position of the benzimidazole ring and without any alkyl chain. These compounds can be used to verify

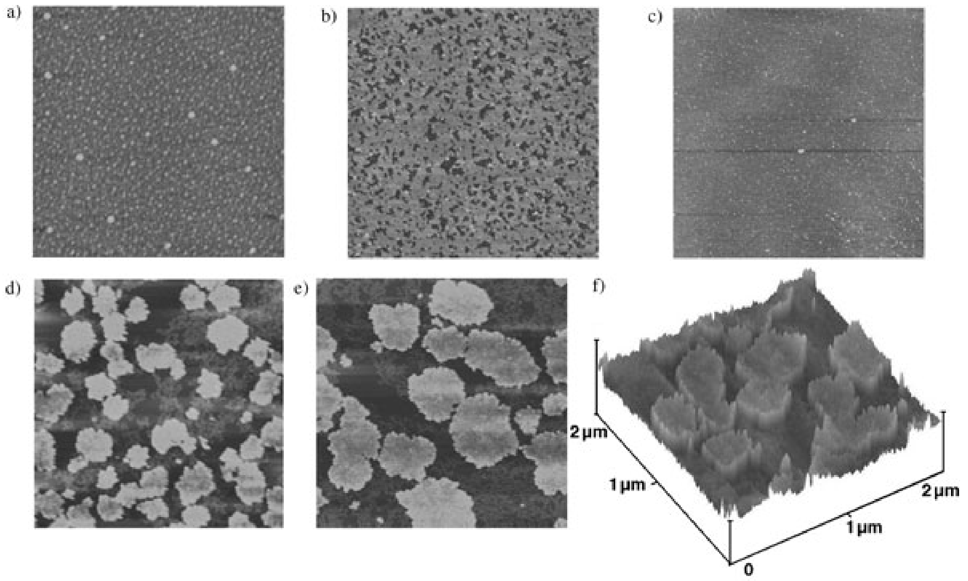

Figure 5. AFM images of one-layer LB films from 1 mм aqueous $AgNO_3$ solution at a surface pressure of 10 mNm^{-1}: a) α-NpBz; b) β-NpBz; c) PyBz; d) 10 mNm^{-1}, AnBz; e) 20 mNm^{-1}, AnBz; and f) 3D images of the AnBz LB film. Scan size is 2×2 µm for all of the pictures.

our previously results and further disclose the nature of the supramolecular chirality. We have measured the CD spectra of all the films deposited from water surface and the subphase containing $AgNO_3$, as shown in Figure 6. Three important features are observed. First, CD signals are observed only for the films of α-NpBz, PyBz and AnBz, while no CD signals were detected for PhBz and β-NpBz films. Second, CD signals are found for the films deposited from water surface in the case of α-NpBz and PyBz, while it appeared in the case of AnBz coordinated with Ag^I ions. Third, depending on the fabrication batches, the sign of the CD signals could be opposite although we can always observe the signals. Particularly, complicate CD spectra were found in the case of Ag^I-coordinated AnBz films.

For the CD spectrum of α-NpBz film, as shown in Figure 6a, a negative and positive Cotton effect was observed at 342 and 311 nm, with a crossover at 328 nm. Considering the fact that the α-NpBz film showed the absorption maximum at 328 nm, such CD signals can be ascribed to the exciton couplet between the chromophores.[35]

For PyBz, two distinct negative Cotton effects were found at about 380 and 305 nm. The positions of the Cotton effect were at the same absorption peak maxima of the film in the UV/Vis spectrum. It indicated that PyBz also formed chiral molecular assembly in the film. However, in this case, no exciton couplet existed.

For AnBz, no CD signal appeared for the film transferred from the water surface. However, CD signals were obtained when the film coordinated with Ag^I. However, CD spectra appeared in different manners in different deposition batches and even in different places although we got the same UV spectra for the AnBz film. Totally, we have got four types of CD spectra for the Ag^I-coordinated AnBz films, as shown in Figure 6c–f. These different CD spectra reflected subtle differences in the molecular arrangement of the transferred LS films. The details of the CD spectra and their explanation are as follows. In case one, a negative Cotton effect was at 257 nm and a split appeared at 216 nm (Figure 6c). Considering the fact that the AnBz film showed two strong broad absorption bands at around 260 nm (axis A transition) and 213 nm (axis B transition), as illustrated in Figure 7, it can be suggested that there a strong exciton couplet in the axis B transition band though no couplet in the axis A transition band existed.[35] In case two as shown in Figure 6d, split Cotton effect was both observed at around 264 and 211 nm. This suggested that exciton couplet existed in both the A and B axis transitions. Accordingly, we can ascribe the

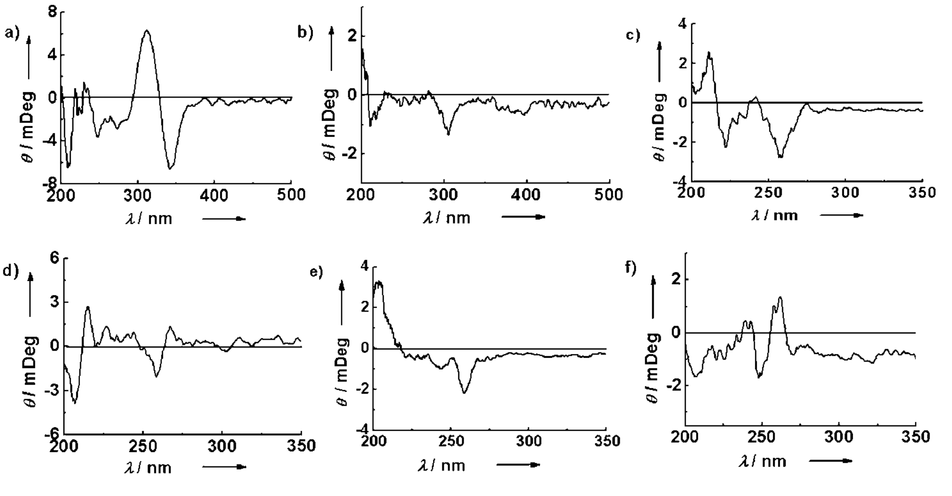

Figure 6. Circular dichroism spectra of various multilayer films: a) α-NpBz film transferred from water surface (10 mN m^{-1}); b) PyBz film from pure water surface, and c–f): Ag^I-coordinated AnBz films transferred from 1 mм aqueous $AgNO_3$ surface in different fabrication batches.

	exciton couplet (ca. 255 nm, axis A)	exciton couplet (ca. 213 nm, axis B)
Fig. 6c	No	Yes
Fig. 6d	Yes	Yes
Fig. 6e	No	No
Fig. 6f	Yes	No

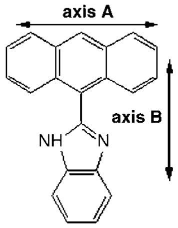

Figure 7. Direction of the transition moment in AnBz molecule and possible combination of the exciton couplet in relation to the CD spectra of the Ag^I-AnBz films.

Cotton effect observed in the Figure 6e and f to the couplet or ordinary CD signals of the A and B axis transitions. These four cases are all observed in the transferred films from different batches indicated that the subtle different chromophore arrangement could occur in different fabrication batches. It was in agreement with the AFM observations of Ag^I-coordinated AnBz film, dotted nanoparticles and aggregated nanoutensils were observed. It should be further noted that the sign of the CD signals could also be different in different batches, however, the combination between the couplet and non-couplet CD signals are all included in the above four kinds of CD spectra.

Discussion on the supramolecular chirality: It is clear from the results described above that only the benzimidazole derivatives with α-Np, An and Py could show chirality when forming the spreading films either on water surface or $AgNO_3$ subphase. Previously, we have found that for the long chain alkyl imidazole derivatives, although the naphtha[2,3]imidazole could form chiral molecular assemblies, other benzimidazole derivatives with alkyl chains in the 2-position could not show the chirality. In the present case, all the benzimidazole groups are the same, however, the 2-substituted aromatic groups were different. It seems that the larger aromatic groups favored for the formation of the supramolecular chirality although a further work is necessary in order to make clear the relationship between the molecular structure and the chirality of the molecular assemblies.

It should be noted that although α-NpBz and β-NpBz have the same-sized unit, no CD signal was observed for the film of β-NpBz. This further indicated that the orientation of the side group, which may affect slightly on the packing of the molecules, will influence the formation of chirality.

On the other hand, it is noted that CD spectra were obtained for the films of α-NpBz or PyBz from water surface and no CD signals could be obtained for these compounds spread on $AgNO_3$ subphase. Situation was just opposite for AnBz. This can be explained by the different interaction between the aromatic groups, as illustrated in Figure 9.

When these aromatic benzimidazoles aggregated on water surface, the hydrogen bonding between the benzimidazole groups[36] and the π–π stacking of the aromatic groups are responsible for the ordered assemblies. AnBz has a larger rectangle anthryl group and inhibited the hydrogen bond between the neighboring benzimidazole groups, while the π–π stacking between the anthryl groups predominates in the molecular assemblies. The opposite is for α-NpBz and PyBz and the hydrogen bond between the benzimidazole predominated. The intermolecular hydrogen bond for benzimidazole is in a linear way and such aggregation manner is favored for the aromatic groups with larger steric hindrance to stack in a cooperative way to form the chirality. Therefore, we observed the CD spectra for α-NpBz and PyBz film from water surface. When coordinating with Ag^I, linear structure could also form as in the case of naphtha[2,3]imidazole. However, in this case of α-NpBz and PyBz, an overcrowded stacking is not necessary for these two molecules and no CD was detected. For AnBz, the larger anthryl group caused an overcrowded and cooperative stacking and CD appeared. In addition, due to the larger anthryl group, the coordination between AnBz and Ag^I could be incomplete, which caused the subtle different stacking of the aromatic groups in the films. Therefore, we observed four kinds of CD spectra where different couplets were observed, which were due to the subtle interaction between the neighboring chromophores.

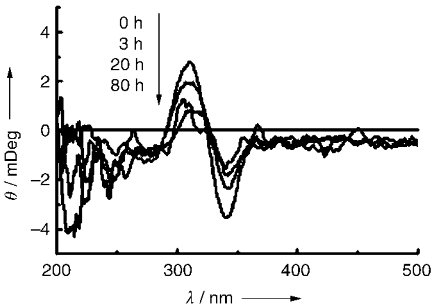

Figure 8. CD spectral changes of a α-NpBz LS film transferred from water surface with the immersion time in 1 mM aqueous $AgNO_3$ solution. The soak time was 0, 3, 20 and 80 h.

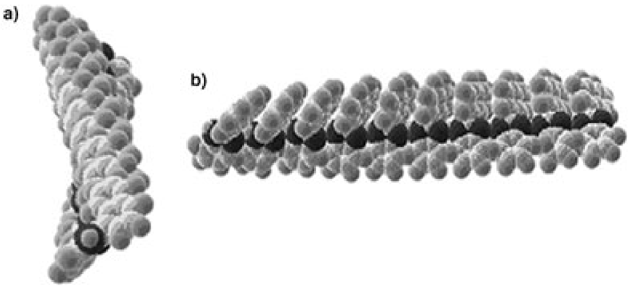

Figure 9. Schematic illustration of the chiral supramolecular assemblies from the achiral arylbenzimidazoles. The neighboring arylbenzimidazole was connected through the hydrogen bond in the case of α-NpBz and PyBz films, while it was through the coordination with Ag^I in the case of AnBz film: a) side view; b) front view.

Dynamic breaking of the supramolecular chirality: From the above discussion, it is clear that the supramolecular chirality of these assemblies was due to a sterically overcrowded stacking of the aromatic groups in the ordered assemblies. If the ordered stacking was destroyed, then the supramolecular chirality should disappear. In order to confirm this we selected the α-NpBz film as an example and studied the dynamic changes of CD spectra upon reacting with Ag^I ex situ in the solid films. Because the α-NpBz film was highly ordered, it can only react a little when the film was immersed in the aqueous $AgNO_3$ solution. However, the dynamic breaking of the chirality can still be clearly seen in the CD spectral changes, as shown in Figure 8. When the immersing time increased, the CD signals decreased continuously due to the partial reaction of α-NpBz film with Ag^I.

It is further noted that when both the film of α-NpBz and PyBz were exposed to HCl gas, the CD signals disappeared completely due to the collapse of the ordered structure of the film. These spectral changes clearly indicated that the formation of supramolecular chirality was due to the sterically regular stacking of the aromatic groups in the film, but not from the chirality of the molecules or any possible impurity, and gave a clear difference of the supramolecular chirality from molecular chirality.

Conclusion

A series of arylbenzimidazoles have been synthesized and their interfacial behaviors investigated. All benzimidazoles described formed aggregates on water surface even though they did not contain any alkyl chain. Depending on the molecular structures, layered and circular aggregated particles are formed on water surface. The easy aggregation behavior of these benzimidazoles on water surface is suggested to be due to the lack of long alkyl chain, which causes the neighboring molecules to slip onto each other and formed multilayer or circularly aggregated particles. When there existed $AgNO_3$ in the subphase, in situ coordination between the imidazole group of the arylbenzimidazoles and Ag^I ion could occur, which caused the changes in the interfacial properties of film. Supramolecular chirality could be obtained in the assemblies of α-NpBz, PyBz and AnBz molecules. While the films from water surface showed chirality for α-NpBz and PyBz, only Ag^I-coordinated film showed chirality for AnBz. It was suggested that both the overcrowded stacking of the side groups and the cooperative arrangement of the molecules are necessary in forming the supramolecular chirality. Interesting surface morphologies could be observed for all compounds. For AnBz on $AgNO_3$ subphase, a nanoutensil was observed. The nanoutensils were formed owing to a three-dimensional aggregation of the compound. These results indicated that molecules without any alkyl chains can also form ordered nanostructures at the air/water interface and their surface properties can be further regulated through an in situ reaction. Thus, the research on the classical amphiphile can be extended to the non- amphiphilic molecules and the research scope can be enlarged.

Experimental Section

Materials: The compounds studied in this work were 2-phenylbenzimidazole(PhBz), 2-(α-naphthyl)benzimidazole (α-NpBz), 2-(β-naphthyl)benzimidazole(β-NpBz), 2-anthrylbenzimidazole (AnBz) and 2-pyrenylbenzimidazole(PyBz). The molecular structures and the abbreviations are shown in Figure 1. The compounds were synthesized through the condensation of the corresponding aromatic aldehyde with *o*-phenylenediamine[37] and their structures were confirmed by NMR spectroscopy and elementary analysis. Example of the typical syntheses procure is as follows: 9-anthraldehyde (0.412 g, 2 mmol) and *o*-phenylenediamine (0.238 g, 2.2 mmol) were carefully mixed and placed into a round bottom flask under a nitrogen gas atmosphere, the mixture was stirred with THF (10 mL) in an oil bath at 60°C for 3–4 h and then filtered. After separated from brown-red solution, washed with dried diethyl ether and dried in vacuum to yield a light yellow powder (0.230 g, 38.9%). The final product was recrystallized from ethanol. Other compounds were synthesized in a similar way. 2-Phenylbenzimidazole (PhBz) was from Tokyo Kasei and purified by recrystallization from ethanol.

Procedures: The spreading ultrathin films of these compounds were formed by spreading a chloroform solution (ca. 1 mM) on aqueous subphases containing various concentrations of $AgNO_3$. Deionized water from a Milli-pore Q system (18 mΩ cm) was used in all the cases. The surface pressure–area isotherms were measured with a KSV film balance with a compression speed of 10.5 $cm^2 min^{-1}$. For UV/Vis absorption spectral measurements, the spread films on 5 mM aqueous $AgNO_3$ subphase were transferred at 20 mm^{-1} onto quartz plates, respectively by a horizontal lifting method. The UV/Vis spectra were recorded by a JASCO UV-560 system. In order to observe the surface morphology, one layer of film was deposited on a mica surface at different surface pressures and the AFM pictures were measured with a Digital Instrument Nanoscope III Multimode system (Santa, Barbara, CA) with a silicon cantilever using the tapping mode. All the AFM images are shown in the height mode without any image processing except flattening. Circular dichroism (CD) spectra of the films were recorded on a JASCO J-810 CD spectrometer. In the process of measuring CD spectra of the films, the films were placed perpendicular to the light path and rotated within the film plane to avoid polarization-dependent reflections and eliminate the possible angle dependence of the CD signals.[12,38]

Acknowledgements

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