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Molecular Design and Supramolecular Assemblies of Novel Amphiphiles with Special Molecular Structures in Organized Molecular Films

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1. Introduction

It is well known that supramolecular chemistry has played a major role in progressing research in nanoscience and nanotechnology, leading to novel classes of materials which are capable of light or electrically stimulated chemistry and long-range organized assembly (Lehn, 1995). Interfacial supramolecular assemblies use well-characterized amphiphiles as building blocks to create assemblies on surfaces that are purposefully structured on the molecular level, while at the same time extending over supramolecular distances (Kuhn et al., 2000). Creating organized structures is an important goal in interfacial supramolecular chemistry. The Langmuir-Blodgett technique is important for the production of macroscopic materials that are organized on the molecular length scale. This approach allows amphiphilic molecules to be oriented at the air-water interface and then transferred sequentially onto a solid support.

The flexibility of molecular design is one of the most significant advantages of supramolecular assembly, allowing organic, inorganic and biological components to be used as building blocks. Organized molecular films deposited on solid surfaces are of great conceptual interest because their small thickness makes them 'quasi-ideal' two-dimensional systems. They constitute a novel 'bottom-up' approach to creating nanoscale structures. This approach contrasts with 'top-down' approaches that entail making existing devices so small that they eventually finish up as nanosized objects, with dimensions of no more than a few hundred nanometers.

On the other hand, amphiphiles are organic molecules that have the ability to adsorb at interfaces, thereby altering significantly the physical properties of those interfaces. Numerous variations are possible within the structure of both the head and tail group of amphiphiles (Holmberg, 1998). The head group can be charged or neutral, small and compact in size, or a polymeric chain. The tail group is usually a single or double, straight or branched hydrocarbon chain, but may also be a fluorocarbon, or a siloxane, or contain aromatic groups. Since the hydrophilic part normally achieves its solubility either by ionic interactions or by hydrogen bonding, the simplest classification is based on amphiphile

head group type, with further subgroups according to the nature of the lyophobic moiety. Four basic classes therefore emerge as: the anionics and cationics, which dissociate in water into two oppositely charged species (the surfactant ion and its counterion); the non-ionics, which include a highly polar (non charged) moiety, such as polyoxyethylene or polyol groups; the zwitterionics (or amphoteric), which combine both a positive and a negative group. With the continuous search for improving amphiphile properties, new structures have recently emerged that exhibit interesting synergistic interactions or enhanced surface and aggregation properties. These novel amphiphiles have attracted much interest, and include the catanionics, bolaforms (Fuhrhop et al., 1986; Fuhrhop et al., 2006), gemini surfactants (Menger et al., 2000; Zana, 2002), polymeric and polymerisable surfactants. Characteristics and typical examples are shown in Table 1.

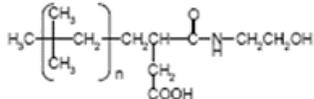
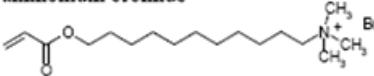
Classes	Structural characteristics	Example
Catanionic	Equimolar mixture of cationic and anionic surfactants (no inorganic counterion)	<i>n</i> -dodecyltrimethylammonium <i>n</i> -dodecyl sulfate (DTADS) $C_{12}H_{25} (CH_3)_3 N^+ O_4 S C_{12}H_{25}$
Bolaform	Two charged headgroups connected by a long linear polymethylene chain	Hexadecanediy1-1,16-bis(trimethyl ammonium bromide) $Br^- (CH_3)_3 N^+ - (CH_2)_{16} - N^+ (CH_3)_3 Br^-$
Gemini (or dimeric)	Two identical surfactants connected by a spacer close to or at the level of the headgroup	Propane-1,3-bis(dodecyl dimethyl ammonium bromide) $C_3H_8 -1,3-bis[(CH_3)_2 N^+ C_{12}H_{25} Br^-]$
Polymeric	Polymer with surface active properties	Copolymer of isobutylene and succinic anhydride 
Polymerisable	Surfactant that can undergo homopolymerisation or copolymerisation with other components of the system	11-(acryloyloxy)undecyltrimethyl ammonium bromide 

Table 1. Structural features and examples of some amphiphiles classes.

In our research, some special amphiphiles, including bolaamphiphiles, gemini and amphiphiles with functional substituted groups, have been designed and synthesized, and their organized supramolecular assemblies at the air/water interface have also been investigated, which may broaden the traditional research areas about LB film and give some perspectives and clues for the relative research in the future. In addition, some of the analytical methods, theoretical treatments and synthetic tools, which are being applied in the area of interfacial supramolecular chemistry and are driving its rapid development, will be highlighted. In this chapter, we summarize our main research contributions in recent years in three sections: (1) design and investigation of some series of bolaform amphiphiles with distinct structures; (2) supramolecular assemblies of some series of gemini amphiphiles with distinct structures; (3) design and interfacial characterization of some series of amphiphiles with functional substituted groups.

2. Design and investigation of some series of bolaform amphiphiles with distinct structures

Firstly, the spreading behavior and nano-architectures of a bolaamphiphilic diacid, 1,13-tridecandicarboxylic acid (TDA) on water surface and the subphase containing Eu(III) ion were investigated (Jiao et al., 2005a). It was found that although TDA itself could not spread on water surface, it could form an ultrathin film on the aqueous subphase containing Eu(III) ion. In addition, interesting nano-architectures were observed for the transferred film on mica surface. It was found that the formation and change of the nano-architectures were depended on the surface pressure and concentration of Eu(III) ion in the subphase. A rectangular slide morphology was observed for the film spread on an aqueous subphase containing lower concentration of Eu(III), while a walnut-like nano-architectures were observed for the film spread on a higher pressure and concentration of Eu(III) ion. Flower structure was observed at a higher surface pressure. The nano-architecture can be further regulated through mixing TDA with octadecylamine (OA) in which linear fiber nanostructure was obtained. It was revealed that while the nano-architectures were formed mainly through a three dimensional aggregation in the case of TDA/Eu(III) films, a two-dimensional aggregation occurred when TDA was mixed with OA. A series of methods such as atomic force microscope, scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction were used to characterize the supramolecular structures. A possible mechanism for the formation of these nanoarchitectures was discussed, as shown in Fig. 1. This provides an important clue to construct ordered 3D nano-architectures by utilizing the Langmuir-Blodgett technique at the air/water interface. In addition, the nano-architecture can be regulated between 2D and 3D dimension by adding other appropriate amphiphiles into the bolaamphiphiles.

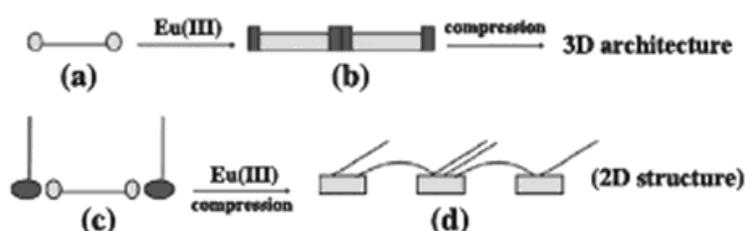


Fig. 1. Schematic illustrations on the formation of the nanoarchitectures in TDA/Eu(III) and TDA/OA films. (a) Bolaamphiphile (TDA); (b) TDA coordinated with Eu(III) to form floating "blog" on water surface, upon compression, these "blogs" will experience a three-dimensional aggregation to form a 3D nano-architecture; (c) mixed film of OA and bolaamphiphile; (d) spreading on the subphase of EuCl₃ caused the formation of fiber structure, the aggregation was limited in a two dimension (Reproduced from Jiao et al., 2005a, *Thin Solid Films*, 479, 269-276).

In addition, a bolaform Schiff base, *N,N'*-bis(salicylidene)-1,10-decanediamine (BSC10), has been synthesized and its interfacial hydrogen bond formation or molecular recognition with barbituric acid was investigated in comparison with that of a single chain Schiff base, 2-hydroxybenzaldehyde-octadecylamine (HBOA) (Jiao et al., 2005; 2011d). It has been found that while HBOA formed a monolayer at the air/water interface, the bolaform Schiff base formed a multilayer film with ordered layer structure

on water surface. When the Schiff bases were spread on the subphase containing barbituric acid, both of the Schiff bases could form hydrogen bonds with barbituric acid in situ in the spreading films. For example, one-layer HBOA LB film deposited from the water surface showed the dotted domains at a surface pressure of 5 mN/m and showed some large ribbon structures at a surface pressure over the plateau region, as shown in Fig. 2. On the other hand, when HBOA was spread on the BA subphase, plank-like morphology with a clear boundary was observed, indicating a complex monolayer formation between HBOA and BA at the air/water interface. As a result, an increase of the molecular areas in the isotherms was observed. The in situ H-bonded films could be transferred onto solid substrates, and the transferred multilayer films were characterized by various methods such as UV-vis and FT-IR spectroscopies. Spectral changes were observed for the films deposited from the barbituric acid subphase, which supported the hydrogen bond formation between the Schiff bases and barbituric acid. By measuring the MS-TOF of the deposited films dissolved in CHCl_3 solution, it was concluded that a 2:1 complex of HBOA with barbituric acid and a 1:2 complex of BSC10 with barbituric acid were formed. Such a complex mode can be regarded as related to the molecular structures of the Schiff bases, which is illustrated in Fig. 3. For the BSC10/BA films, BSC10 molecule, having two Schiff base headgroups, can act as a tweezers and two BA molecules are embedded in the BSC10 molecule. In this case, the alkyl spacer curved at the air/water interface and the two BA molecules formed intermolecular hydrogen bonding and were encapsulated under the alkyl chain. On the other hand, when the multilayer films of both Schiff bases were immersed in an aqueous solution of barbituric acid, a similar molecular recognition through the hydrogen bond occurred. A clear conformational change of the alkyl spacer in the bolaform Schiff base was observed during the complex formation with the barbituric acid. Now we provided a new hydrogen bonding system at the air/water interface. In addition, a continuous conformational change of the alkyl spacer was clearly shown experimentally in the LB film.

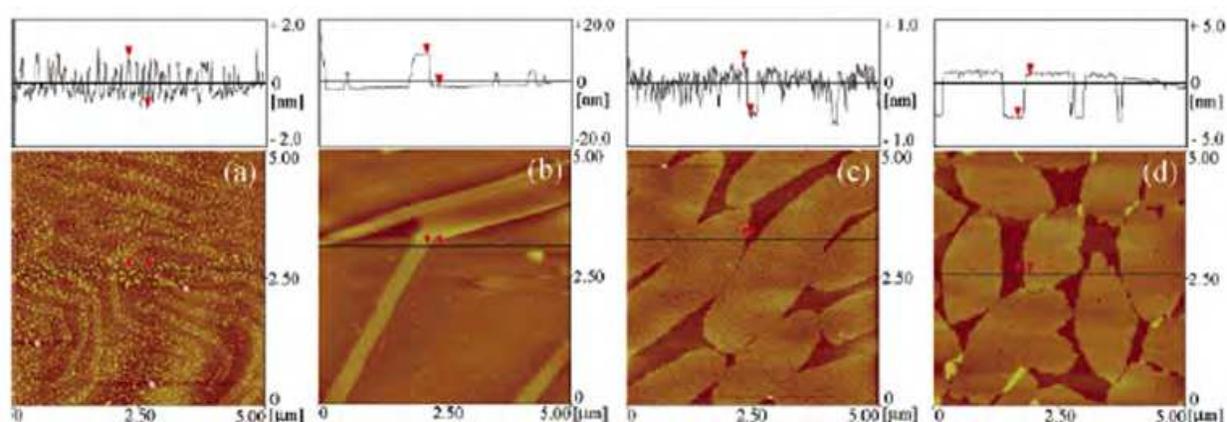


Fig. 2. AFM images of one-layer HBOA LB films from pure water at surface pressures of 5 (a) and 25 mN/m (b), respectively, and from 1.0 mM aqueous BA subphase at surface pressures of 5 (c) and 25 mN/m (d), respectively (Reproduced from Jiao et al., 2005, *The Journal of Physical Chemistry B*, 109, 2532-2539).

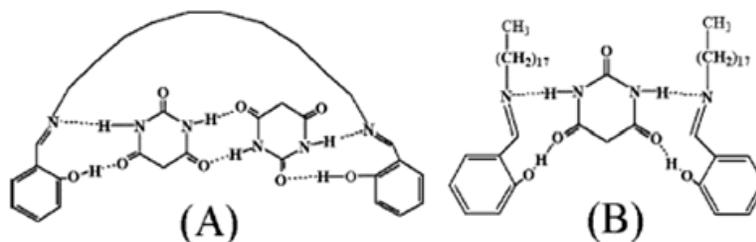


Fig. 3. Schematic Illustration of Structures of BSC10/BA (A) and HBOA/BA (B) Complexes (Reproduced from Jiao et al., 2005, *The Journal of Physical Chemistry B*, 109, 2532-2539).

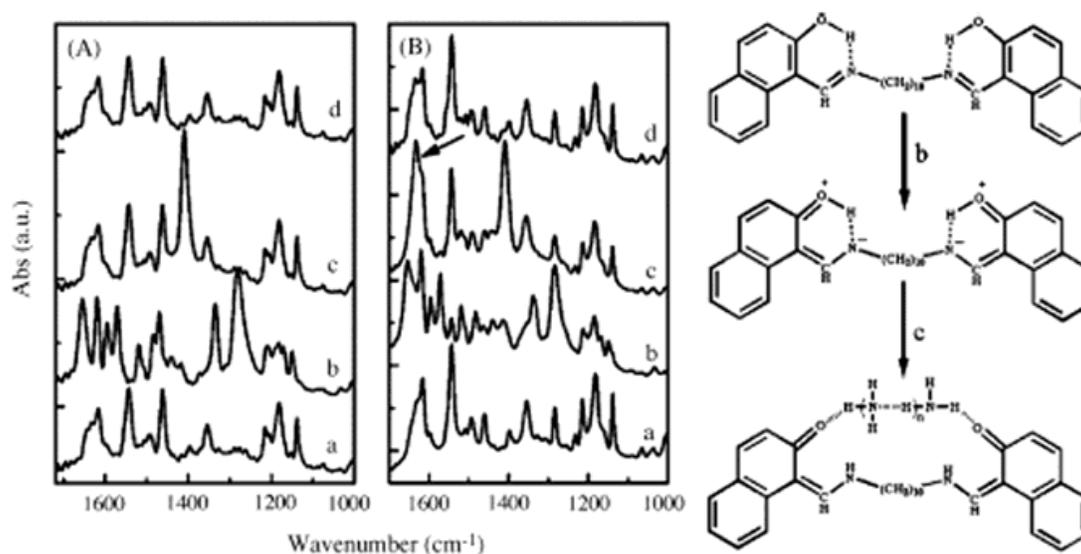


Fig. 4. FT-IR spectra of HNOA (A) and BNC10 (B) and acidochromism mechanism of BNC10: (a) LB film before gas exposure; (b) after exposure in HCl gas; (c) after exposure “b” in NH₃ gas; (d) after washing by water (Reproduced from Yin et al., 2007, *Chinese Chemical Letters*, 18, 30-32).

Nextly, a bolaform (BNC10) and single-headed (HNOA) amphiphilic Schiff bases containing naphthyl group were designed and their Langmuir-Blodgett films were investigated. It was found that both the LB films show acidochromism, i.e. a reversible color change upon alternatively exposing the films to HCl and NH₃ gases, respectively (Yin et al., 2007). It was further found that the bolaform Schiff bases film could trap NH₃ gas during the acidochromic process. Such difference between the single-headed and bolaform Schiff base can be explained as follows. The as-deposited films exist predominantly in the enol form, as verified by the FT-IR spectra. When the films were exposed to HCl gas, the intramolecular H-bond was destroyed and the keto form will be predominant. Upon exposing to NH₃ gas, the keto form returned to enol form for the HNOA, and thus the color changed reversibly. However, for the BNC10, when the film was exposed to NH₃ gas, NH₃ gas molecules were suggested to be trapped into the BNC10 molecules through intramolecular H-bonds, as shown in the mechanism scheme in Fig. 4. The trapped NH₃ was stabilized by the two keto form Schiff base headgroup, which is similar to the “chelating of metal ions by ligand”. In conclusion, we have shown the acidochromism in the LB films of Schiff bases containing

naphthyl group. The bolaform Schiff base can additionally trap NH_3 gas during the acidichromic process.

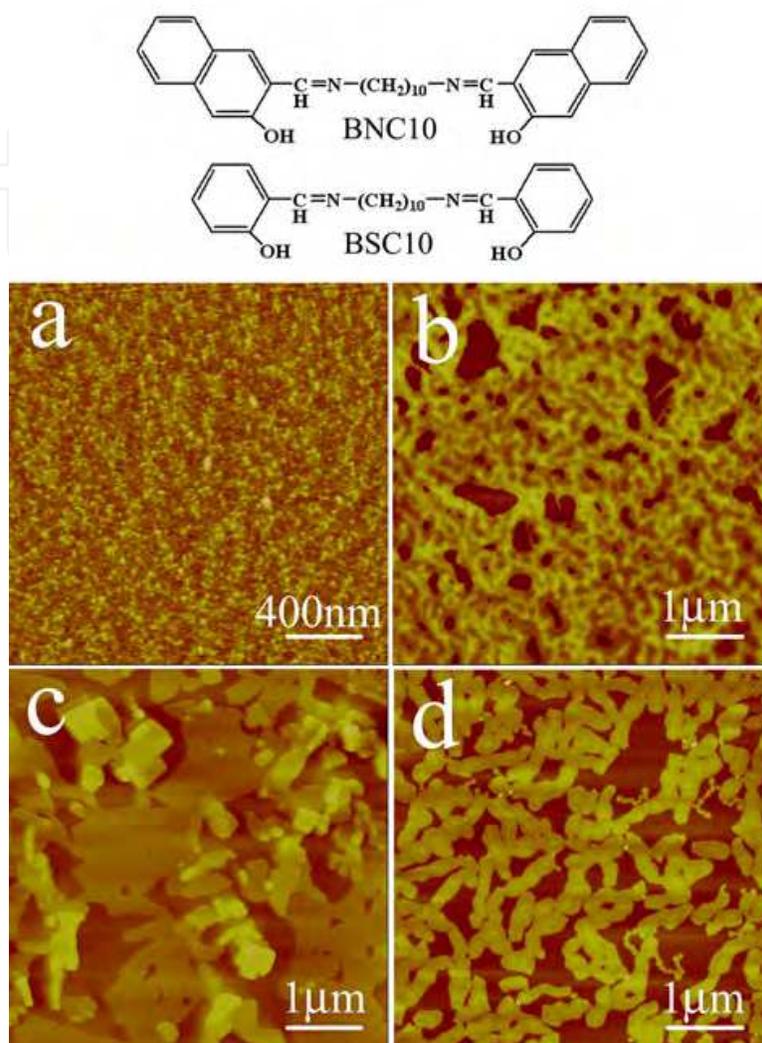


Fig. 5. Molecular structures and AFM images of one-layer BSC10 and BNC10 LB films from pure water (a, c) and aqueous 1.0 mM $\text{Cu}(\text{Ac})_2$ (b, d) at 20 mN/m, respectively (Reproduced from Jiao, et al., 2011f, *Journal of Dispersion Science and Technology*, 32, in press).

In addition, two bolaform Schiff bases derivatives with different substituted headgroups have been designed and their interfacial phase behaviors and coordination with $\text{Cu}(\text{II})$ ions were investigated (Jiao et al., 2011f). It has been found that while one molecule with benzene headgroup formed dotted aggregations at the air/water interface, another with naphthyl moiety as headgroup formed crystalline multilayer films on water surface. When on the subphase containing $\text{Cu}(\text{II})$ ions, both of the Schiff bases can coordinate with $\text{Cu}(\text{II})$ in situ in the spreading films with the obvious conformational change of alkyl chains. For the BSC10 film transferred from aqueous $\text{Cu}(\text{II})$ ions, a rigid superstructure with many hole was observed, as shown in Fig. 5. This indicated that BSC10 formed a multilayer film upon reaction with $\text{Cu}(\text{II})$ ions. On the other hand, as for the BNC10 LB films deposited from the water surface or $\text{Cu}(\text{II})$ subphase, different morphologies were observed. The distinct morphologies suggested the different aggregation modes in both cases, which agreed well

with the results of other sections. In comparison, the *ex situ* coordination process at the liquid/solid interface have also been investigated by continuous spectral measurement. Depending on the different headgroups, these amphiphiles showed different aggregation behaviors in the Langmuir-Blodgett films. Particularly, during the coordination process of ligand with Cu(II) ions in organized molecular films, great conformational change of the alkyl chains was observed. At the same time, a rational explanation about the headgroup effect on regulating the aggregation behaviors was discussed. The present work may give some insight to design and character the relationship between the molecular structures and supramolecular aggregation of bolaamphiphiles in organized molecular films.

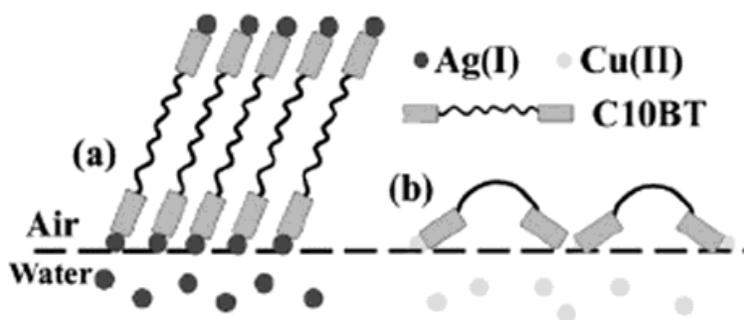


Fig. 6. Cartoon illustration of the packing modes for C10BT complex films on different subphases (Reproduced from Jiao et al., 2006b, *Thin Solid Films*, 503, 230-235).

Furthermore, the interfacial assemblies at the air/water interface from a newly designed tyrosine-based bolaamphiphile, 1,10-bis(*O*-*l*-tyrosine)-decane (C10BT), were investigated (Jiao et al., 2006b; 2011e). This bolaform compound could be spread on water surface and form organized ultrathin film. It was interesting to find that metal ions such as Ag^+ and Cu^{2+} in the subphase can greatly modulate the molecular packing of C10BT and the morphology of the subsequently deposited Langmuir-Blodgett (LB) films. Atomic force microscopic measurements revealed that C10BT LB film from the subphase containing Ag^+ ion showed well-ordered layered nanofibers, while Cu^{2+} ion coordinated C10BT film demonstrated dense cross-linked network. It was suggested that both the strong chelating property to the carboxylate and the different packing mode of hydrocarbon chain resulted in the distinct nanostructures. Fourier transform infrared spectra reveal the difference between the Ag-C10BT complex film and that of Cu^{2+} ion, and the mechanism of the packing mode of hydrocarbon chain was discussed. Furthermore, the X-ray diffraction and X-ray photoelectron spectra also verified the orderly layer structure and the relative molar ratios compared with different metal ions. Considering the coordinating orientation of the two metal ions and the conformation of the alkyl spacer, it is rational that in the case of Cu(II), the molecules were linked through coordination with a bended spacer and formed a polymeric compound and aggregate to construct the network morphology, while in the case of Ag(I), the molecules was aligned orderly via the cooperative interaction such as coordination with Ag(I) ions, hydrophobic force between the alkyl spacers and/or the π - π stacking interaction between the benzene moieties, as shown in Fig. 6. While many efforts have been devoted to manipulation of the nanostructures and functions of sophisticated bolaform amphiphiles, we provided a simple method of modulating the organization and morphology of C10BT films through metal ions.

3. Supramolecular assemblies of some series of gemini amphiphiles with distinct structures

Firstly, aggregations of cationic amphiphiles containing one, two and four positive charges with an anionic TPPS at the air/water interface were investigated (Zhang et al., 2006). The positive charge centers in these amphiphiles were separated by a rigid spacer. It was found that TPPS in the subphase could aggregate onto the spreading films as J-aggregate. Although the amphiphiles and the TPPS were achiral, CD signals were detected for the complex films. A possible helical sense of the TPPS stacked in the complex film was suggested to be responsible for the supramolecular chirality of the multilayer films. The charge distributions and spacers have great influence on the CD intensity as well as their split and the surface morphologies. AFM measurements revealed nanofiber structures in the surface morphologies for the complex films of TPPS with amphiphiles having one or two positive charges, while nanorod morphologies were observed for that with four positive charges. It was suggested that the charge centers in the amphiphiles limited the aggregation of TPPS and the interactions between the adjacent J-aggregates. Such effect and the differences from simple amphiphiles reported can be explained as illustrated in Fig. 7. The results provided a clue in regulating the surface morphologies and chirality of TPPS assemblies.

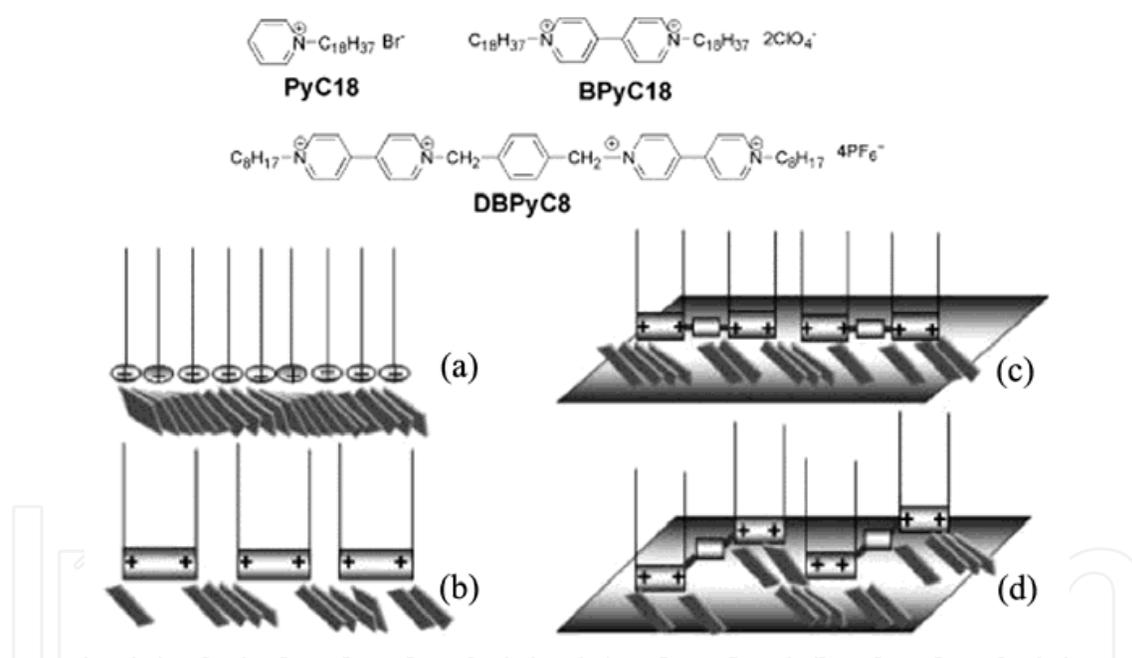


Fig. 7. Molecular structures and illustration of the possible structures of the complex film of TPPS with amphiphiles (a) PyC18, (b) BPyC18, (c and d) DBPyC8 with different conformations (Reproduced from Zhang et al., 2006, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 284-285, 130-134).

In addition, the designed gemini-type amphiphile containing Schiff base groups can form stable monolayers at the air/water interface. They can coordinate with Cu(II) ions in situ at the air/water interface and form an intramolecular complex between the ligand and the metal ion (Jiao et al., 2006). For BisSBC18C2, an additional intermolecular dimerlike complex could be formed. The series of amphiphiles shows a strong spacer effect on both the interfacial properties and the assemblies. Maximum limiting molecular areas are observed

for the monolayers of the gemini amphiphiles with spacer lengths of C6 and C8 on water and aqueous $\text{Cu}(\text{Ac})_2$, respectively, which is due to the formation of the upward-curved conformation of the hydrophobic spacer. Such an effect of the spacer leads to different morphologies such as nanonail and wormlike nanoarchitectures, depending on the spacer length and the subphases, as shown in Fig. 8. Because of the covalent connection of the Schiff base groups by the alkyl spacer, the π - π^* absorption of the localized aromatic rings split into two bands that could be assigned to H and J aggregation, respectively. With the spacer length increased, the J aggregation of the aromatic ring seems to be preferred. An interdigitated bilayer structure is formed in the multilayer films both for the film from water and from the aqueous $\text{Cu}(\text{Ac})_2$ subphase, as shown in Fig. 9. The present work provided new insight into the design and interfacial assembly of the gemini amphiphiles.

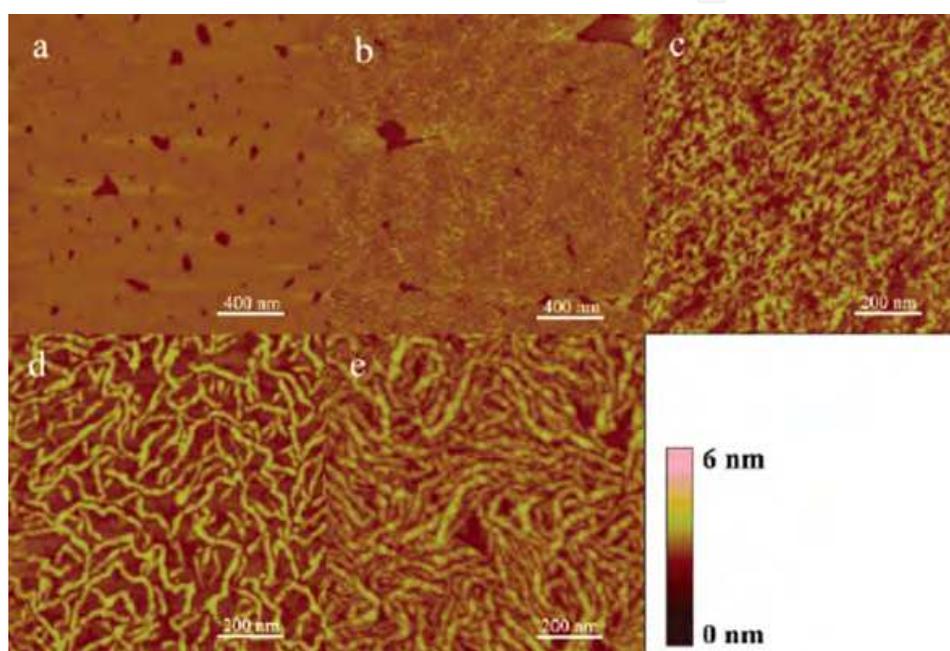


Fig. 8. AFM images of one-layer BisSBC18C_n LB films deposited from the subphase of a 1.0 mM $\text{Cu}(\text{Ac})_2$ solution at 20 mN/m: (a) BisSBC18C₂, (b) BisSBC18C₄, (c) BisSBC18C₆, (d) BisSBC18C₈, and (e) BisSBC18C₁₀ (Reproduced from Jiao et al., 2006, *Langmuir*, 22, 5005-5012).

Furthermore, a series of new gemini amphiphiles with hydrophilic spacers, GN_n (n=1-3), have been designed and they can form stable monolayers on water subphase with various pH values (Jiao et al., 2007). On strong alkaline and acidic subphase, the headgroup and the spacer of the gemini amphiphiles underwent dissociation and protonation, respectively, resulting in the enlargement of the molecular areas. Flat and uniform domains were obtained for the monolayers from nearly neutral subphase; flower-like or dendritic domains were observed for the films transferred from strong acidic subphase, as shown in Fig. 10. On the other hand, when an anionic tetrakis(4-sulfonatophenyl)porphine (TPPS) was added into an acidic subphase, an in situ complex formation between the gemini amphiphiles and TPPS occurred. The complex monolayers were transferred onto solid substrate and TPPS existed predominantly as J-aggregate in the complex films. Due to the multisited positive charges in the spacer on acidic subphase, the complex films of gemini amphiphiles with TPPS appeared as short fiber or nanorod structures and formed two-dimensional (2D)

conglomerate chiral domains, as shown in Fig. 11. Compared with the features of those conventional or gemini-type amphiphiles with hydrophobic spacer, the introduction of the hydrophilic spacer in the present work provides a pH regulated interfacial properties of the film.

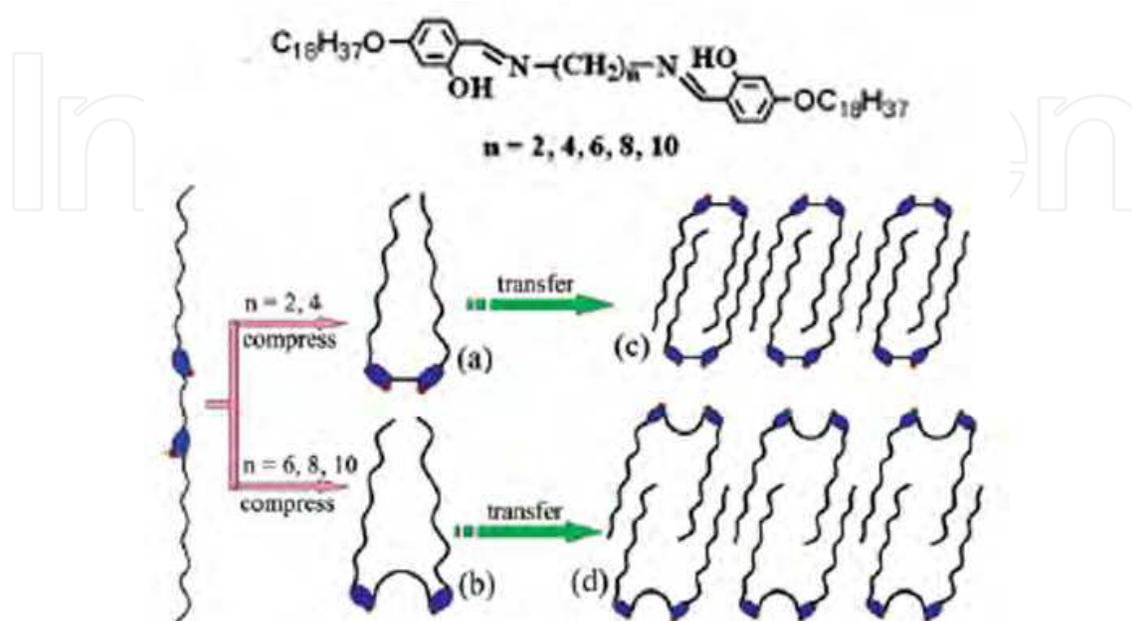


Fig. 9. Molecular structures and schematic illustration of the packing modes of BisSBC18Cn in organized films: when compressed at the air/water interface, the spacers are parallel to the water surface for a short spacer (a) and have an upwardcurved conformation with a longer spacer (b). During the transfer process, the overturning of the film leads to the formation of interdigitated films

(Reproduced from Jiao et al., 2006, *Langmuir*, 22, 5005-5012).

In addition, hybrid multilayer films based on a series of gemini amphiphiles BisBC18Nn ($n=1,2,3$) with different hydrophilic spacer lengths with phosphomolybdic acid (PMo_{12}) were constructed through the LB technique (Jiang et al., 2008). The hybrid monolayers could be deposited as multilayer films and all the hybrid films exhibited a well-defined layer structure. When exposed to UV light, the BisBC18Nn/ PMo_{12} hybrid films changed from pale yellow to cyan, as shown in Fig. 12. The reverse reaction occurred in air or O_2 with the help of heat. Repeatability of coloration-decoloration proved the excellent photochromic reversibility of the hybrid films. Such characteristics of absorption bands may be attributed not only to the coexistence of PMo_{12} and BisBC18Nn molecules, but also to the ordered arrangement of the molecules. Although the spacer length of the gemini amphiphiles has an obvious effect on the monolayer property, it affects the photochromic properties only slightly. The spacer length causes slight differences in the maximum absorption position of the coloured species, which may be due to subtle change of the environment around the POM. By analyzing changes in the position and relative strength of Mo-O_d and P-O_a stretching band, it was revealed that BisBC18N1/ PMo_{12} hybrid films with the shortest spacer showed the best photochromic ability. The present results prove that an appropriate selection of the polyoxometalate and amphiphiles could lead to the preparation of hybrid LB films that exhibit good photochromic properties.

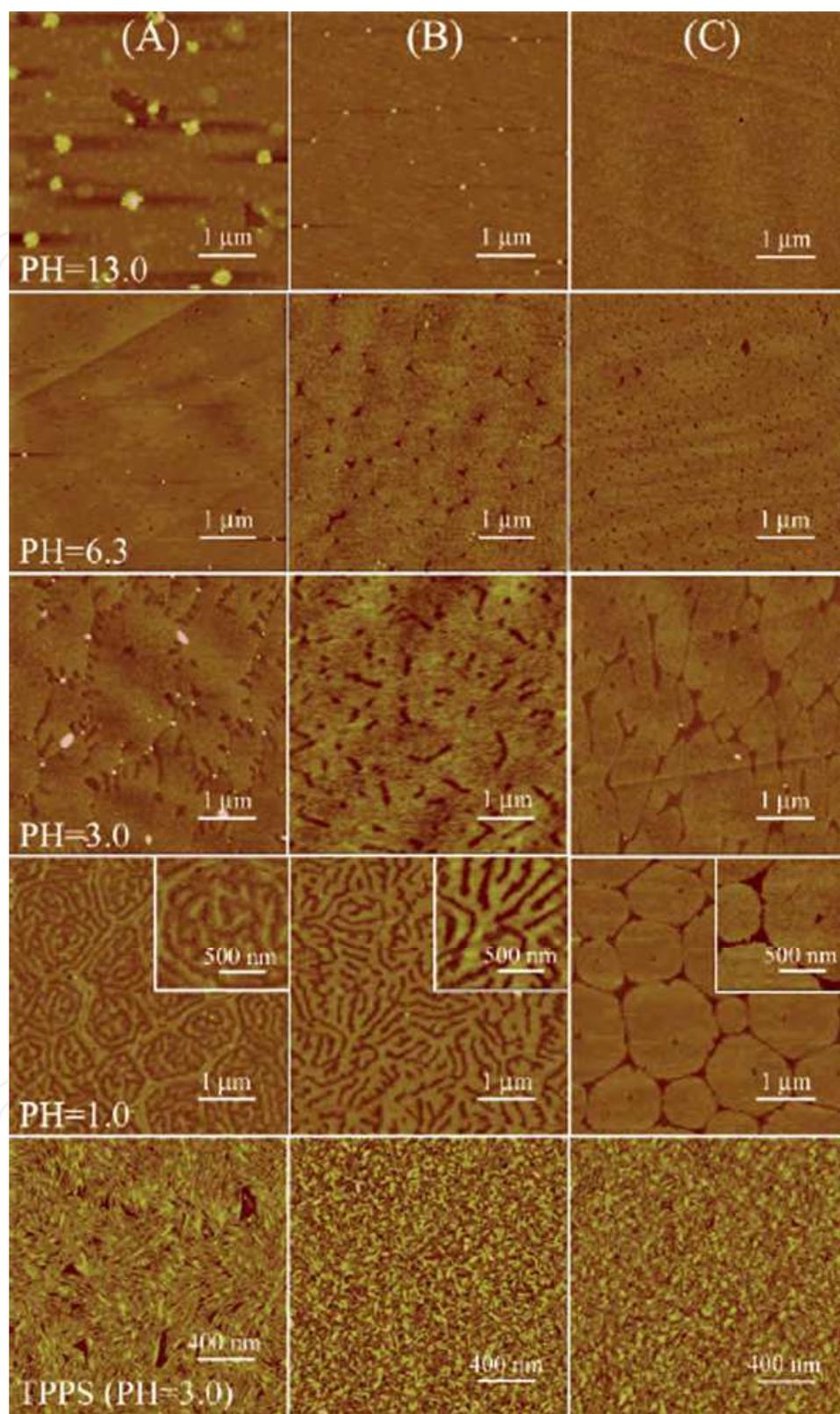


Fig. 10. AFM pictures of one-layer LB films of GN1 (A), GN2 (B), and GN3 (C) transferred from aqueous subphases with various pH values and aqueous TPPS (0.01 mM) at 20 mN/m (Reproduced from Jiao et al., 2007, *The Journal of Physical Chemistry B*, 111, 3090-3097).

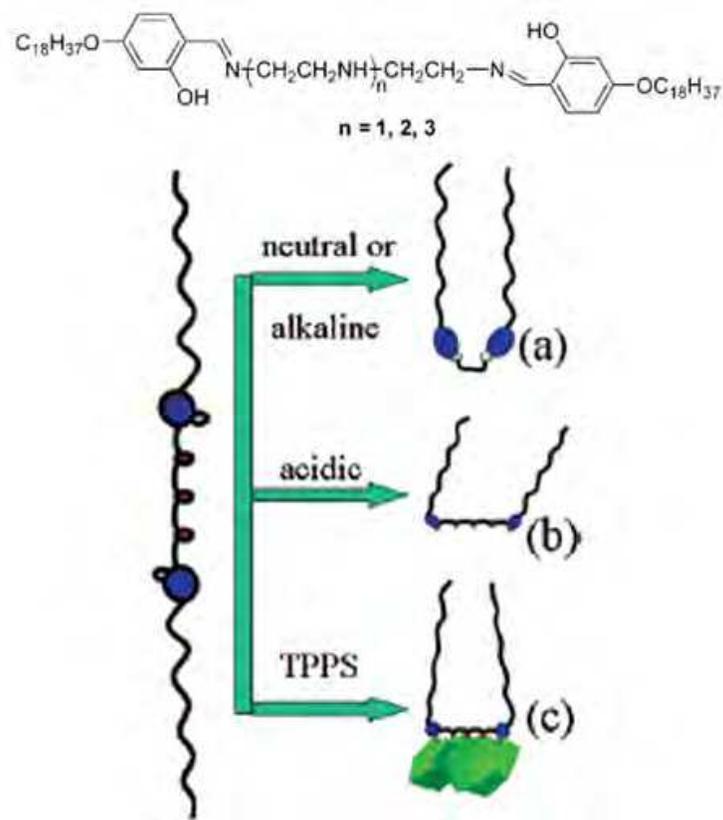


Fig. 11. Molecular structures of gemini amphiphiles and illustration on the packing of the gemini amphiphiles with their spacers on water surface. Part a, on neutral or alkaline subphase: the spacers were immersed into the subphase. Part b, on acidic subphase: the spacers were protonated and stayed on water surface. Part c, complex film with TPPS: the spacers were protonated and interacted with TPPS through electrostatic interaction (Reproduced from Jiao et al., 2007, *The Journal of Physical Chemistry B*, 111, 3090-3097).

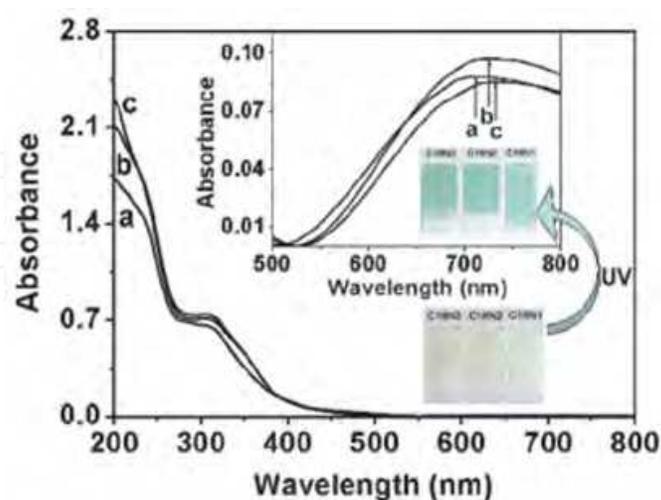


Fig. 12. UV-Vis absorption spectra of 70-layer multilayer films transferred at a constant pressure of 20 mN/m: (a) BisBC18N1/PMO₁₂, (b) BisBC18N2/PMO₁₂, (c) BisBC18N3/PMO₁₂. The inset shows UV-Vis spectra of the corresponding films after irradiation (Reproduced from Jiang et al., 2008, *New Journal of Chemistry*, 32, 959-965).

Nextly, this series of gemini amphiphiles in the organized molecular films were used to investigate the generation and assembly of gold nanostructures (Zhong et al., 2008). The chloroauric acid, dissolved in the aqueous subphase, was incorporated into the monolayers of the gemini amphiphiles containing ethyleneamine spacers through an interfacial assembly. The in situ formed complex monolayers were transferred onto solid substrates, and gold nanoparticles were generated in the film by a chemical or photochemical reduction, which is illustrated in Fig. 13. Discrete gold nanoparticles with an absorption maximum at 550 nm were generated in the films by photoirradiation, while different gold nanostructures were obtained by chemical reduction. Depending on the chemical reductant, various shape and assembly of gold nanostructures were obtained. When reduced by hydroquinone, a tree-branched assembly of the nanoparticles was obtained and the film showed a broad band centered at around 900 nm. When NaBH_4 was applied, crooked nanowires or assembly of nanoparticles were obtained, depending on concentration, and the film showed absorption at 569 or 600 nm. Furthermore, by combining the photochemical and chemical reduction methods, i.e., the chloroaurate ion-incorporated film was initially irradiated with UV light and then subjected to chemical reduction, the optical absorption of the formed gold nanostructures can be regulated. This study extends the research on the synthesis of metallic particles in films from conventional amphiphiles to other special amphiphiles and provides a very convenient method to modulate the optical properties in a large wavelength range, which will be important in designing optical devices based on different gold nanostructures.

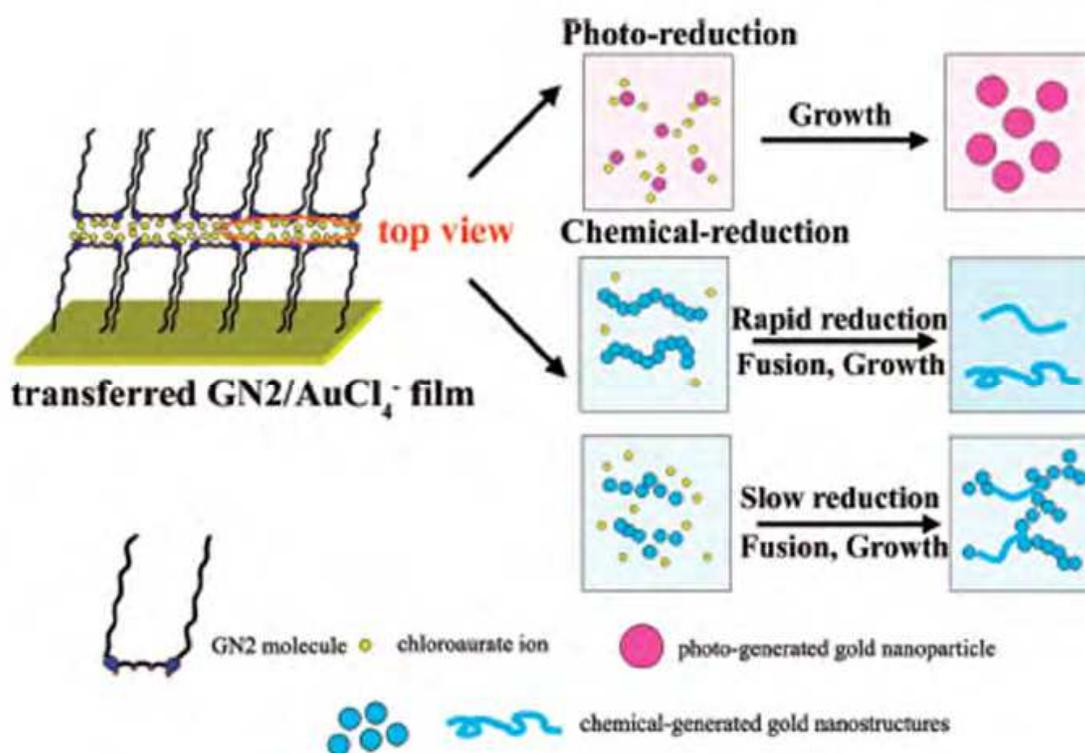


Fig. 13. Schematic illustration on the generation of gold nanoparticles by photochemical and chemical reduction in GN2/AuCl₄⁻ complex film (Reproduced from Zhong et al., 2008, Langmuir, 24, 11677-11683).

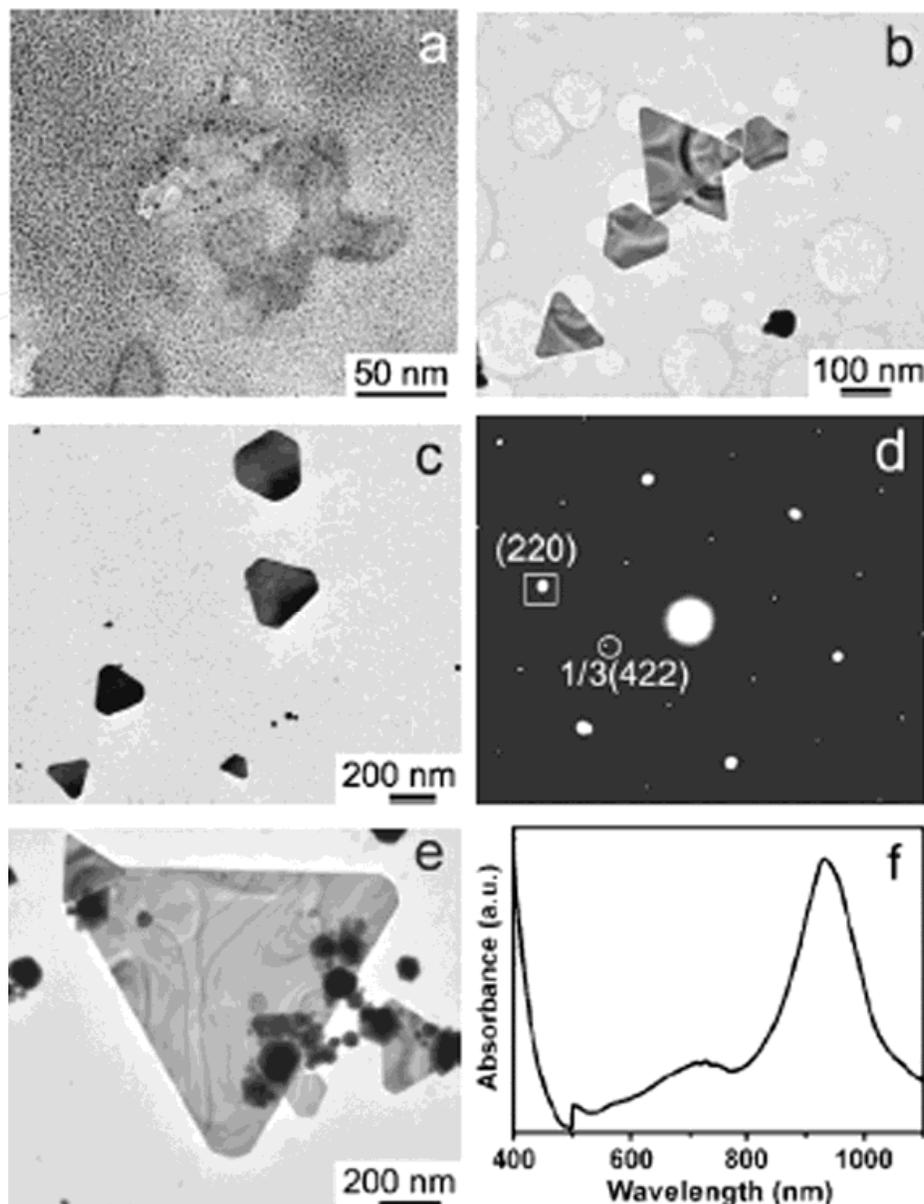


Fig. 14. TEM images of gold nanoparticles with GN2 to chloroaurate ions ratio of 1:2 after 3 hours (a), 7 hours (b), 15 hours (c) and 75 hours (e). SAED analysis of a single gold nanoprism after 7 hours on a single gold nanoprism (d). UV-vis spectrum of reduced gold nanoprisms by GN2 after 15 hours of reaction (f) (Reproduced from Zhong et al., 2009, *Journal of Nanoscience and Nanotechnology*, 9, 2726-2730).

On the other hand, this series of gemini amphiphiles with different lengths of hydrophilic ethyleneamine spacers can also be used to synthesize gold nanostructures at a liquid-liquid interface (Zhong et al., 2009). By stirring the aqueous solution containing AuCl_4^- ions with the chloroform solution of gemini amphiphiles, AuCl_4^- ions were transferred into the oil phase and reduced to gold nanostructures. UV-vis and Fourier Transform Infrared spectral measurements indicated that the gemini amphiphiles could serve as both capping and reducing agents. Crystalline gold nanoprisms were predominantly obtained if the gemini amphiphiles with appropriate spacer length and concentration were applied, as shown in Fig. 14. Thus the formation of the nanoprism can be possibly suggested as follows. First,

gemini amphiphile reduced AuCl_4^- ions to zerovalent Au or Au clusters. Next, the gemini amphiphiles selectively adsorbed on certain plane and nanoprism could be finally obtained. Thus appropriate spacer and concentration are both important for fabrication of anisotropic nanostructures. It is predicted that gold and other novel metal nanostructures may be produced by gemini amphiphiles, whose properties can be well-controlled by designing different headgroups, spacers or alkyl chains.

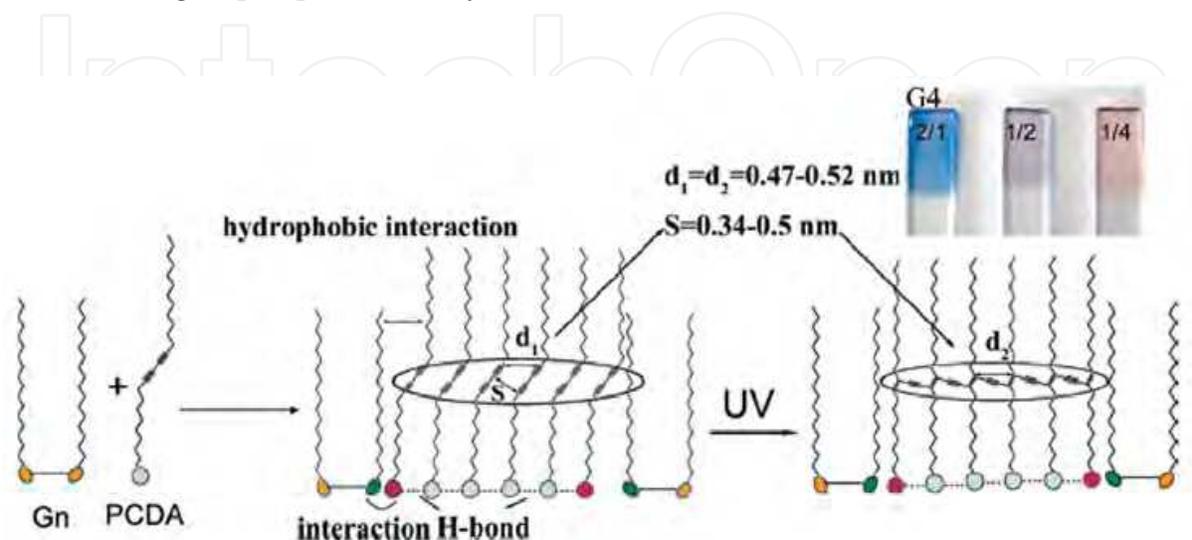


Fig. 15. Illustration of molecular packing in mixed PCDA/Gn film. The inset shows the color of the photopolymerized PCDA/G4 films with different ratios (Reproduced from Zhong et al., 2009a, *The Journal of Physical Chemistry B*, 113, 8867-8871).

In addition, we have investigated the photopolymerization of an amphiphilic diacetylene, 10,12-pentacosadiynoic acid (PCDA), in organized molecular films in the presence of this series of gemini amphiphiles with different spacer lengths (Zhong et al., 2009a). It has been found that, when gemini amphiphiles were mixed with the diacetylene, the film-forming properties were greatly improved and the photopolymerization could be regulated by the gemini amphiphiles. Miscibility and Fourier transform infrared spectroscopy (FT-IR) investigations revealed that the polymerization of PCDA in a mixed film was regulated by the mixing ratio and spacer length of the gemini amphiphiles. Although a slight amount of gemini amphiphile did not make the PCDA polymerize into blue films, the increment of the gemini amphiphile with the short spacer length in the mixed film caused the formation of a red film, and the intensity of red phase to blue phase can be modulated by changing the mixing ratios. When gemini amphiphiles with longer spacer lengths were mixed, blue films were predominantly obtained in all mixing ratios. A mechanism including the interaction between the headgroup of the gemini amphiphiles and the diacetylene and the regulation of the spacer was proposed, as shown in Fig. 15. It was suggested that the ionic interaction between the headgroups of geminis and diacetylene played an important role in causing such differences. The strong ionic interaction deviated the packing of PCDA molecules from the one with their carboxylic acid groups H-bonded and tended to form red film when the spacer length was short, while a longer spacer in the gemini can weaken the ionic interaction and keep the film packing in favor of the blue film. The present work provides an efficient way of regulating the photopolymerization of diacetylene through simple mixing with gemini amphiphiles.

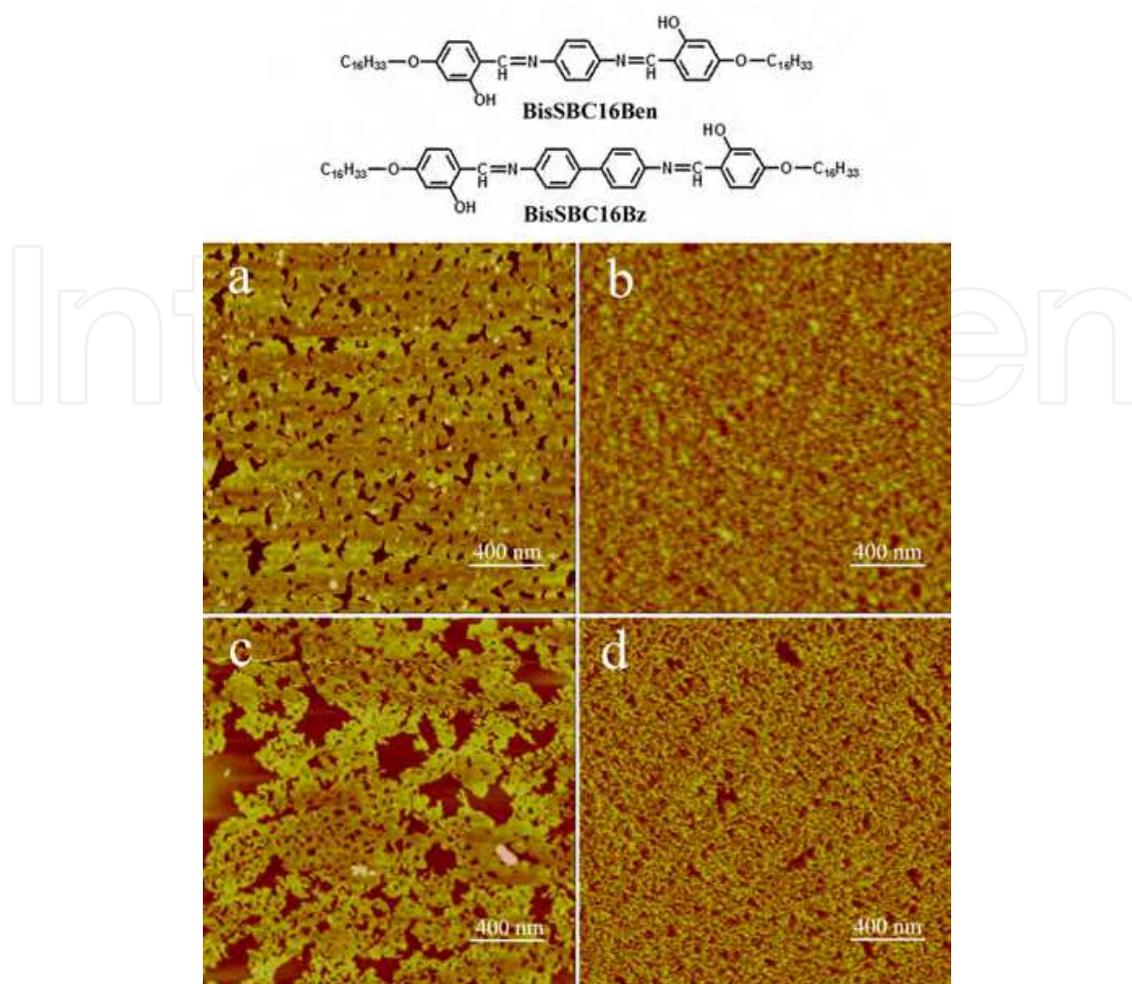


Fig. 16. Chemical structures and AFM images of one-layer LB films of BisSBC16Ben and BisSBC16Bz on pure water surface (a and c, respectively) and the aqueous 1 mM $\text{Cu}(\text{Ac})_2$ subphase (b and d, respectively) at surface pressures of 20 mN/m (Reproduced from Jiao et al., 2011g, unpublished results).

Recently, two gemini-type Schiff base amphiphiles containing aromatic spacers have been synthesized and characterized in LB films (Jiao et al., 2011g). These compounds could form stable multilayer films and show distinct phase behaviors on water surface and ion subphase. When the compounds were spread on $\text{Cu}(\text{II})$ ions subphase, an in situ coordination can occur for both ligands, while there have different morphologies and molecular rearrangement, as shown in Fig. 16. For both process, the aromatic spacers in gemini amphiphiles have predominant effect in regulating the aggregation mode and spectral changes in organized molecular films. The present work may give some insight to design and character the relationship between the molecular structures and supramolecular aggregation of gemini amphiphiles in organized molecular films.

4. Design and interfacial characterization of some series of amphiphiles with functional substituted groups

Firstly, diblock copolymer of $\text{PMMA}_{291}\text{-b-PEO}_{114}$ and triblock copolymer of $\text{PMMA}_{120}\text{-b-PEO}_{227}\text{-b-PMMA}_{120}$ were synthesized and their interfacial properties at the air-water

interface were investigated, where both blocks of polyethylene oxide (PEO) and poly(methyl methacrylate) (PMMA) are surface active but the former is soluble in water while the latter is not (Cheng et al., 2005). Both the block copolymers could form monolayers with two obvious transition regions. The first transition point is around 10 mN/m, which could be assigned to the pancake-brush change of the PEO chains. The other is around 18 mN/m, which could be ascribed to the condensed packing of PMMA. The surface morphological changes during the compression of the Langmuir monolayers are investigated by measuring the AFM and SEM pictures for the films deposited at difference surface pressure or molecular areas. At a lower surface pressure, morphology typical of PEO-containing lipopolymers is observed. Upon compression, sphere-dominant morphologies were observed, as shown in Fig. 17. While the diblock copolymer is easy to folding, the triblock copolymer is in favor of formation of circular domains through vesiculation.

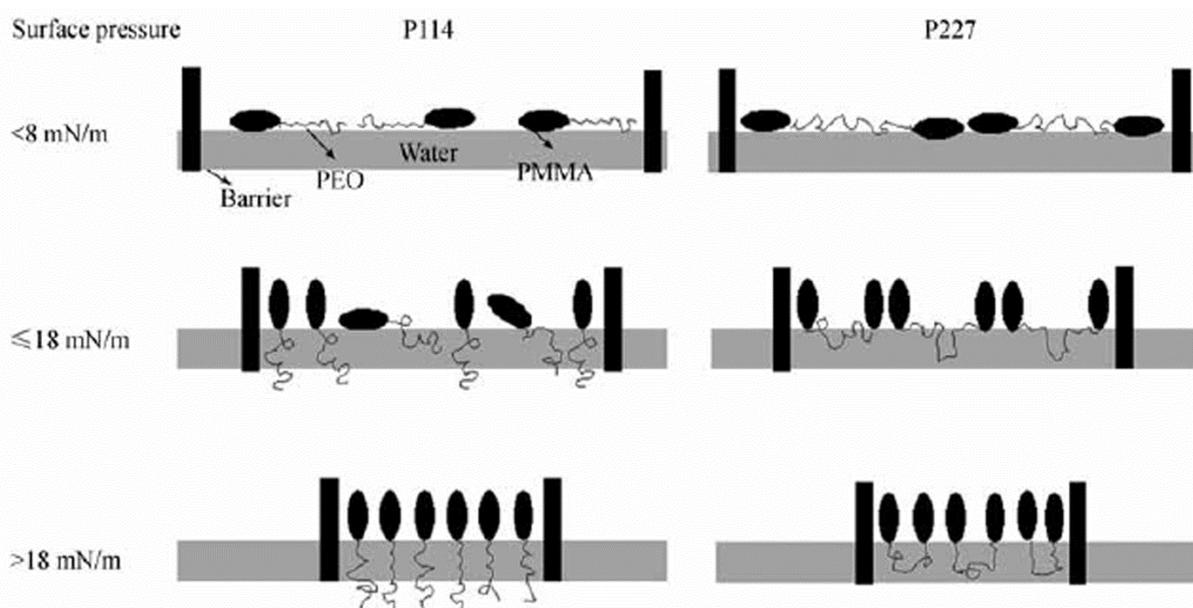


Fig. 17. Schematic drawing of possible PEO chain conformation from diblock and triblock copolymer at air/water interface (Reproduced from Cheng et al., 2005, Science in China Series B-Chemistry, 48, 567-573).

In addition, we have investigated the interfacial behavior of a novel ABC of PEO₄₅-b-PDMA₆₉ at various compression stages by the LB balance and morphology study (Cheng et al., 2006). Accompanied by a pancake-to-brush transition of PEO conformation, the wormlike surface micelles are compression induced. The micelles as the building blocks can be arrayed parallel to generate a long-range ordered structure, further bended and twisted upon compression, as shown in Fig. 18. Unusual 3D large aggregates of "springs" and "disks" appear when the LB film completely collapses. Such a rich phenomenon of hierarchical nanostructure evolution should be attributed to the coil-semirod architecture of the diblock and the unique assembly ability of the Percec-type dendronized PDMA. This provides a clue in designing block copolymers to control the nanostructures at the air/water interface.

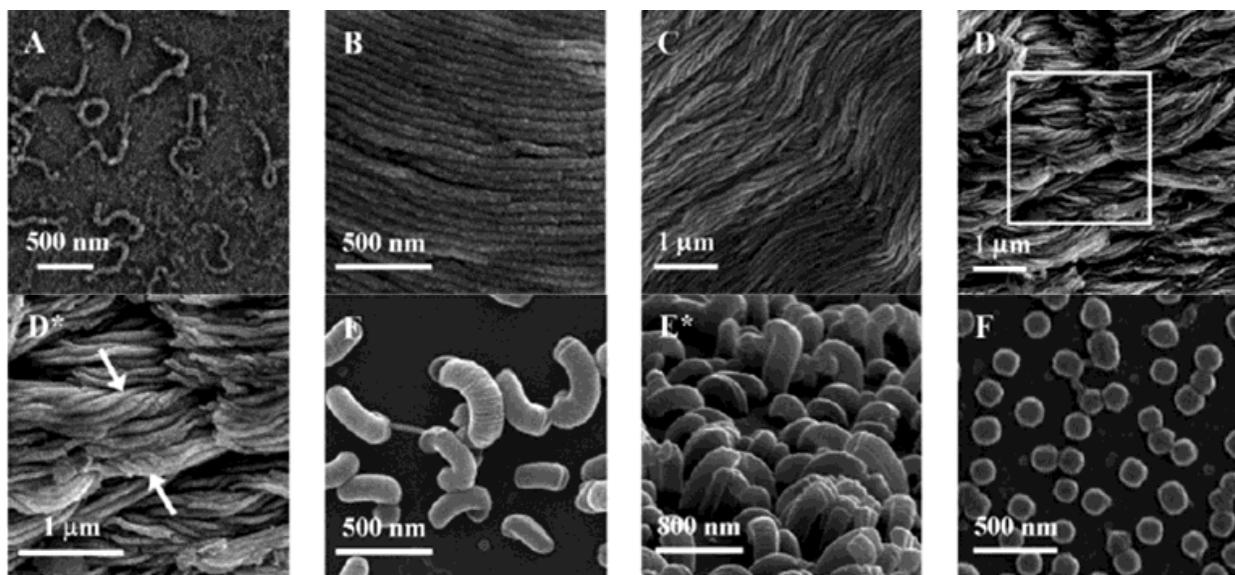


Fig. 18. A set of SEM images of the LB films at various molecular areas. The images A-F correspond to the points A-F. D* is the enlarged image of the area indicated by the square in D, where the twisted micelles are pointed by the arrows. E* shows the “springs” at point E with a viewing angle (Reproduced from Cheng et al., 2006, *Macromolecules*, 39, 6327-6330).

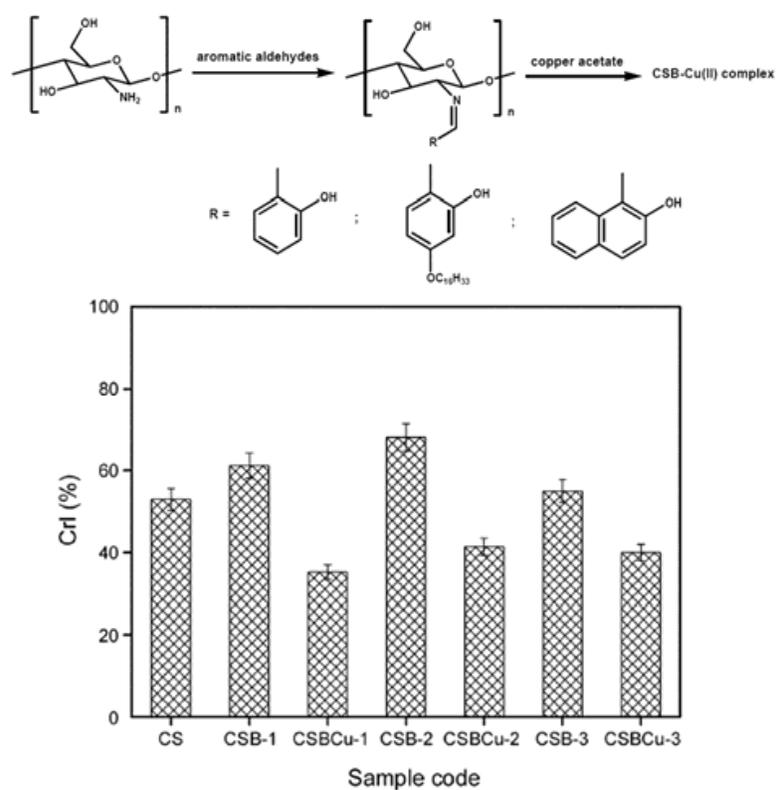


Fig. 19. The synthetic route and variation of crystallinity of chitosan-based Schiff bases and their copper (II) complexes (Reproduced from Jiao et al., 2011, *Iranian Polymer Journal*, 20(2), 123-136).

It is well known that Chitosan is the product of *N*-deacetylation of chitin. For its innocuous, renewable, biocompatible property chitosan is applied in many fields e.g., pharmaceutical, food, catalysis, material. In this work, three chitosan-based Schiff-based (CSB) compounds with aromatic substituent groups were synthesized from the reaction of chitosan with different aromatic aldehydes i.e., salicylaldehyde, 4-hexadecyloxy-2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde (Jiao et al., 2011). The chitosan-based Schiff base copper (II) complexes (CSBCu) were subsequently obtained through the reaction of relative Schiff bases with copper acetate. Generally, elemental analysis data may confirm the formation of chitosan-Schiff base as well as the coordination reaction of CSB with copper ions. FTIR analysis indicated that Schiff base and coordination reaction take place in Schiff base skeleton. Moreover, with the difference in substituent groups and spacer, FTIR spectra showed the clear variety. Thermal analysis showed that the thermal stability of CSB increased slightly, while that of the copper complexes was reduced significantly in comparison with chitosan. The XRD results demonstrated the appearance of a new crystallization peak of CSB in the vicinity of five degree and the lower crystallinity of CSBCu, as shown in Fig. 19. The change of crystallinity is mainly dependent on the formation of Schiff base and to some extent on other factors, such as spacial hindrance, hydrophobic force and π - π stacking. In the present case, these chitosan-based Schiff base compounds have different aromatic substituent groups and/or long hydrophobic alkyl chain. Thus, it seems that the crystallinity and designed structures can be regulated by the modification of substituent groups in chitosan molecule. The present results show that the specific properties of chitosan-based Schiff base derivatives can be altered by modifying the molecular structures of objective compounds with proper substituent groups.

In another case, three amphiphilic Schiff bases containing naphthylidene group (abbreviated as HNOA-1, HNOA-2, and HNOA-3) were designed and their interfacial assemblies were investigated (Jiao et al., 2006a; 2011a). These amphiphiles have different substitution groups in the Schiff base moiety. It was observed that HNOA-1, being in lack of second aromatic ring, formed multilayer films at the air/water interface, while the other two compounds, with another aromatic ring and some hydrophilic groups, can be spread as monolayers on water surface. All of Schiff bases could coordinate with $\text{Cu}(\text{Ac})_2$ in situ in the spreading films. Both the spreading films from water and aqueous $\text{Cu}(\text{Ac})_2$ subphases were transferred onto solid substrates and their surface morphologies as well as molecular packing modes were investigated by a series of methods such as atomic force microscopy, Fourier transform infrared spectra and X-ray diffraction. Depending on the different substitutions, these amphiphiles showed different orientations in the Langmuir-Blodgett films, as shown in Fig. 20. Particularly, during the process of complex formation at the air/water interface, great conformational change of the alkyl chain was observed for HNOA-2 in comparison with that of other compounds. In addition, nanofiber structures were observed for the $\text{Cu}(\text{II})$ -complexed HNOA-1 and HNOA-2 films. It was concluded that both the molecular orientation and the resulted nanostructures in the films could be controlled by modifying the molecular structure through the substitution groups.

The phenomena of self-sorting, defined as the ability to high efficiently distinguish between self and non-self within complex mixtures, has drawn more attention in recent years because of its commonality in biological system and potential applications in fields such as chemical sensors, artificial regulatory systems, and synthetic self-organizing systems, as well with biomimetic devices. To date, research about self-sorting has mainly focused on the

systems with different functional groups in bulk solution, especially from H-bonded aggregates, which is easily identified by nuclear magnetic resonance (NMR) measurement. In our present system, a series of Cu(II)-coordinated Schiff base complexes with alkyl or aromatic spacers have been synthesized and characterized by utilizing monolayer and LB techniques (Jiao et al., 2010a). It is found that the substitutional spacer in complexes play an important role in the morphological regulation and spectral change, which will provide distinct clue for designing similar organic/inorganic hybrid compounds at air/water interface. In addition, the self-sorting appears when the binary or ternary complexes mixtures were spread onto air/water interface. The situation of complex mixture with alkyl/aryl spacers shows more distinct interfacial morphologies than the case with only aromatic spacers, as shown in Fig. 21. The present work demonstrates the high versatility in designing similar hybrid organic-inorganic systems and investigating supramolecular assembly.

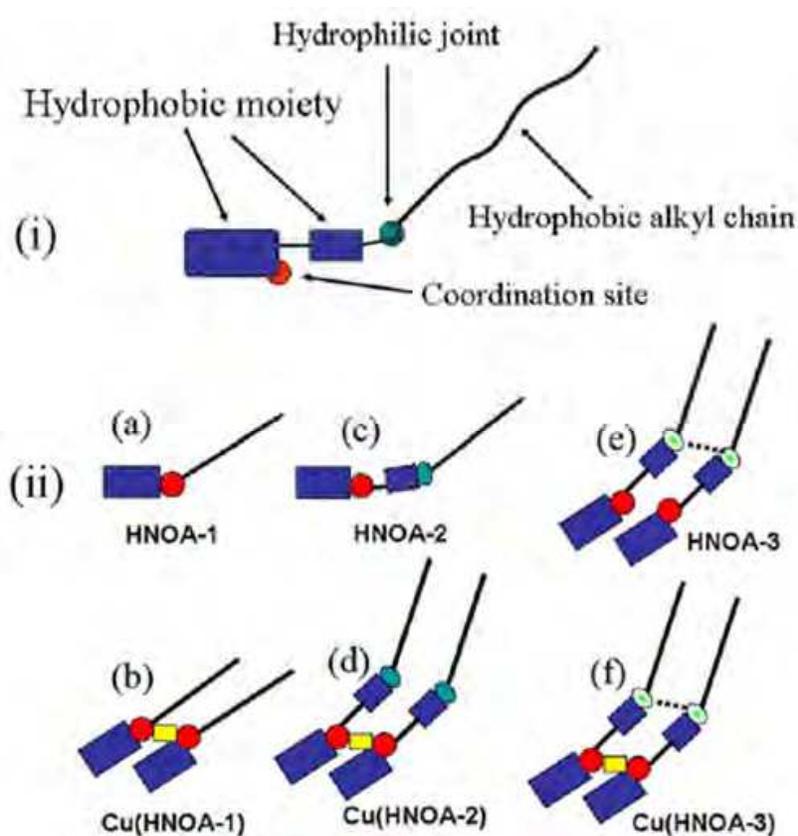


Fig. 20. Schematic illustrations on the designed common molecular structure and aggregation modes of the amphiphilic Schiff bases at air/water interface. (i) The illustrated molecular structure with the depicted function for each moiety; (ii) the detailed aggregation modes for different compounds: (a) for HNOA-1 with simple long alkyl chain, there was no distinct conformational change between water and $\text{Cu}(\text{Ac})_2$ surface (b); as for HNOA-2 (c), due to the hindrance of aromatic moiety and coordination matching, the long alkyl chain became more vertical to the surface distinctly (d); because of the intermolecular hydrogen bonding, the molecular skeleton of HNOA-3 was almost not changed both on water surface (e) and on the subphase of $\text{Cu}(\text{Ac})_2$ solution (f) (Reproduced from Jiao et al., 2006a, *Journal of Colloid and Interface Science*, 299, 815-822).

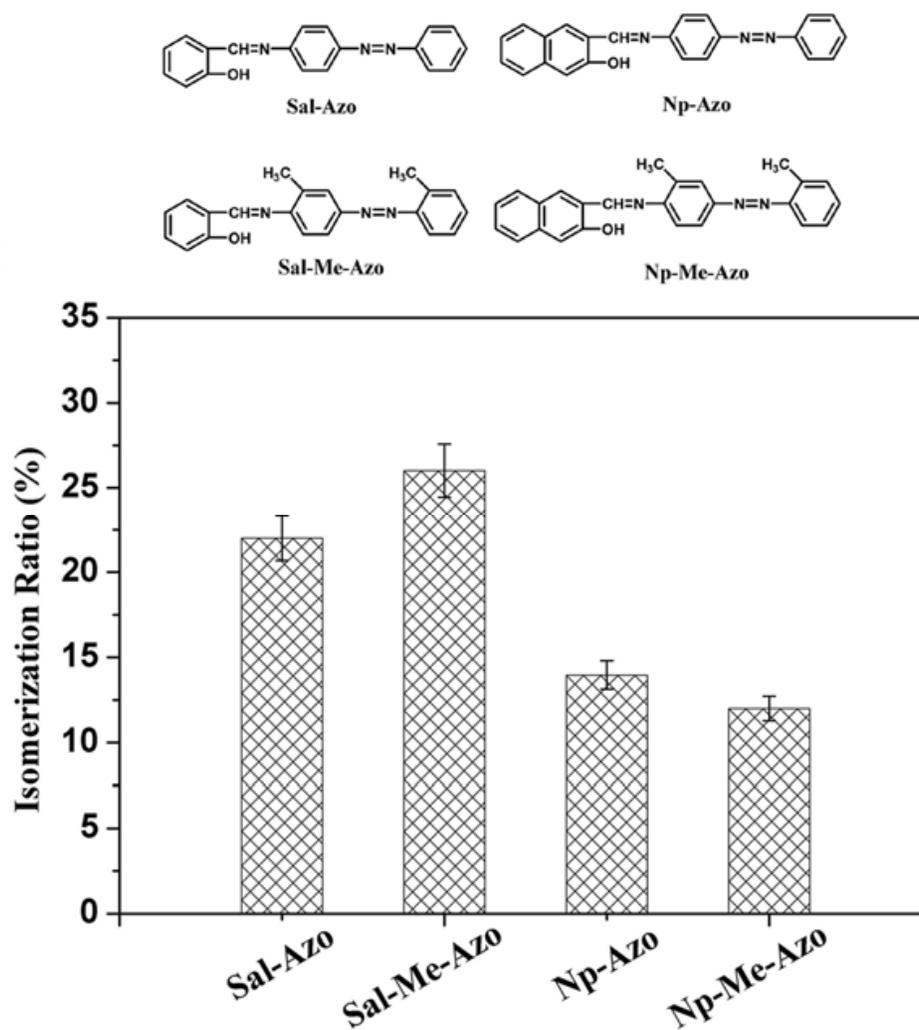


Fig. 23. Chemical structures and isomerization ratio of azobenzene derivatives in ethanol solution upon UV light irradiation (Reproduced from Jiao et al., 2011h, Applied Mechanics and Materials, in press).

Some functional azobenzene derivatives with aromatic substituted groups have been synthesized and their photoisomerization have also been investigated (Jiao et al., 2011). It has been found that depending on different substituted groups, such as phenyl or naphthyl segments, the formed azobenzene derivatives showed different properties, indicating distinct regulation of molecular skeletons. Spectral data confirmed commonly the characteristic absorption of substituted groups and aromatic segments in molecular structures. In addition, the photoisomerization of all compounds in solution can show *trans*-to-*cis* photoisomerization by UV light irradiation, and demonstrate distinct isomerization ratio depending on effect of different substituted headgroups, as shown in Fig. 23. The difference is mainly attributed to the aromatic substituted headgroups and methyl group in molecular structure. The present results have showed that the special properties of azobenzene derivatives could be effectively turned by modifying molecular structures of objective compounds with proper substituted groups, which show potential application in sensor and functional material field.

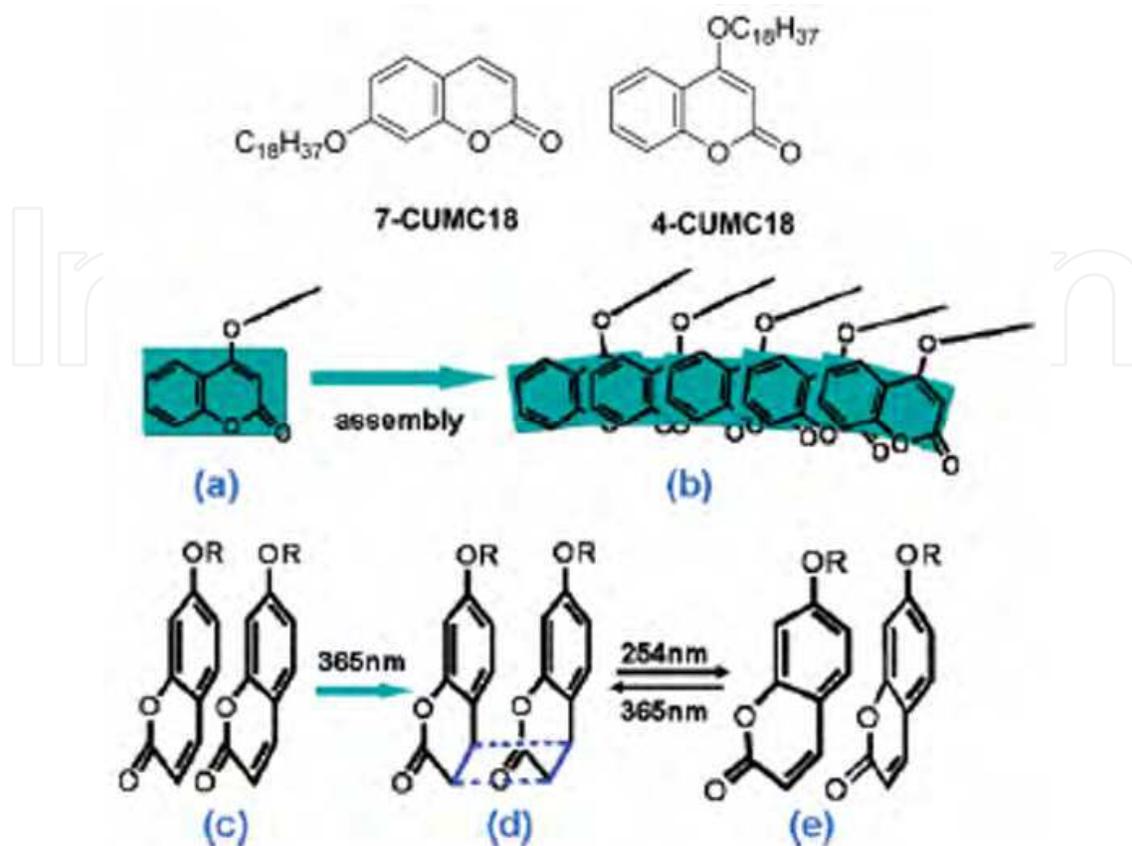


Fig. 24. Molecular structures and illustration of the possible packing and photoreaction in the LS films. Only one layer is presented in the scheme. The top part illustrates the possible orientation of 4-CUMC18 on the water surface (a) and in films (b). The bottom part shows the packing of as-deposited 7-CUMC18 film (c) and the reversible reaction between the dimer (d) and monomer (e) (Reproduced from Guo et al., 2007, *Langmuir*, 23, 1824-1829).

Coumarin is one of the important parent compounds found in many plants and could be used as the important component of various functional materials. In this work, the Langmuir and Langmuir-Schaefer (LS) films of two coumarin derivatives, 4-octadecyloxy coumarin (4-CUMC18) and 7-octadecyloxy coumarin (7-CUMC18) were newly synthesized, and their interfacial assemblies were investigated (Guo et al., 2007). Owing to the different substituent position of the long octadecyloxy chain in the coumarin parent, the two compounds showed completely different behaviors in the interfacial assemblies. When they were spread at the air/water interface, 7-CUMC18 formed a monolayer while 4-CUMC18 formed a multilayer film on the water surface. The spreading films on the water surface were transferred onto solid substrates by a Langmuir-Schaefer method, and the transferred films were characterized by UV-vis, Fourier transfer infrared, X-ray diffraction, circular dichroism, and atomic force microscopy spectra. Different packing of the molecules in the multilayer films was observed, as shown in Fig. 24. Furthermore, distinct properties of the multilayer films were observed. It is revealed that a reversible [2+2] photodimerization and photocleavage could be induced in the LS film of 7-CUMC18 under photoirradiation with UV light of 365 and 254 nm, respectively. Although 4-CUMC18 was achiral, it showed supramolecular chirality in the transferred films due to the formation of macroscopic 2D

conglomerates or chiral racemates. These results provided a way of regulating the properties of the molecular assemblies by precisely designing the molecules with subtle substituent position.

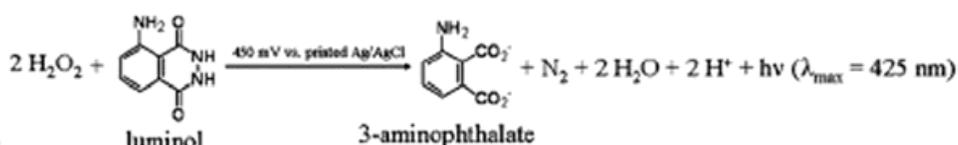


Fig. 25. Luminol electrochemiluminescence (ECL) reaction in the presence of H_2O_2 (Reproduced from Jiao et al., 2008a, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 321, 143-146).

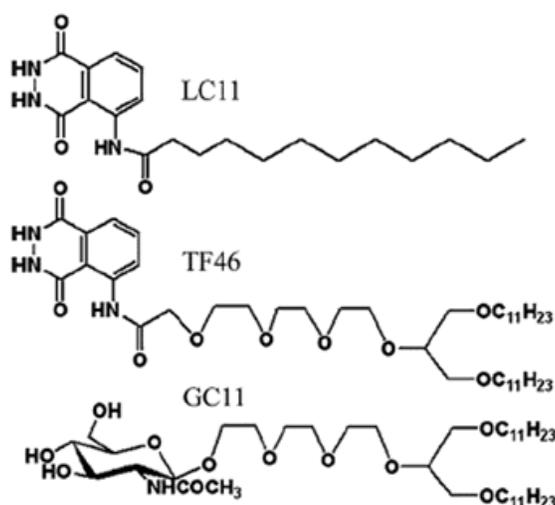


Fig. 26. Chemical structures of luminol derivatives (LC11, TF46) and glycolipid (GC11) (Reproduced from Jiao et al., 2008, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 321, 137-142).

It is well-known that luminol ECL in the presence of hydrogen peroxide can be produced through the action of a chemical catalyst like ferricyanide or a biocatalyst such as peroxidase, as shown in Fig. 25. The application of a potential to oxidize luminol can successfully replace a catalyst to provoke luminol electrogenerated chemiluminescence (ECL) with inherent high sensitivities and wide linear working ranges. The possibility to insert amphiphilic luminol derivatives in LB films as supports for ECL detection could give the opportunity to develop reagentless biomimetic nanosensors.

Firstly, two new synthetic luminol derivatives with different substituted chains, LC11 and TF46, as shown in Fig. 26, were mixed with glycolipid GC11 to form monolayers at the air-water interface (Jiao et al., 2008). The pure and mixed interfacial Langmuir films were studied by measuring the surface pressure-molecular area isotherms and their morphologies were characterized by Brewster angle microscopy (BAM). The surface pressure-area isotherms showed differences between both luminol compounds. LC11 (single strand acyl chain) displayed a condensed isotherm with a kink point and a high collapse pressure, whereas TF46 (double strand hydrocarbon chains connected to a triethylene glycol (TEG) moiety) displayed a typical liquid-expanded (LE) curve with a low collapse pressure. Dot-

like domains were observed by BAM for TF46 Langmuir films, contrariwise to some strip-like aggregated domains in the case of LC11, as shown in Fig. 27. These different morphologies may be attributed to distinct aggregation modes induced by differences in molecular structure. These results clearly demonstrate that changes of molecular structure induce different aggregation modes that markedly influence the interfacial phase behavior of their Langmuir films.

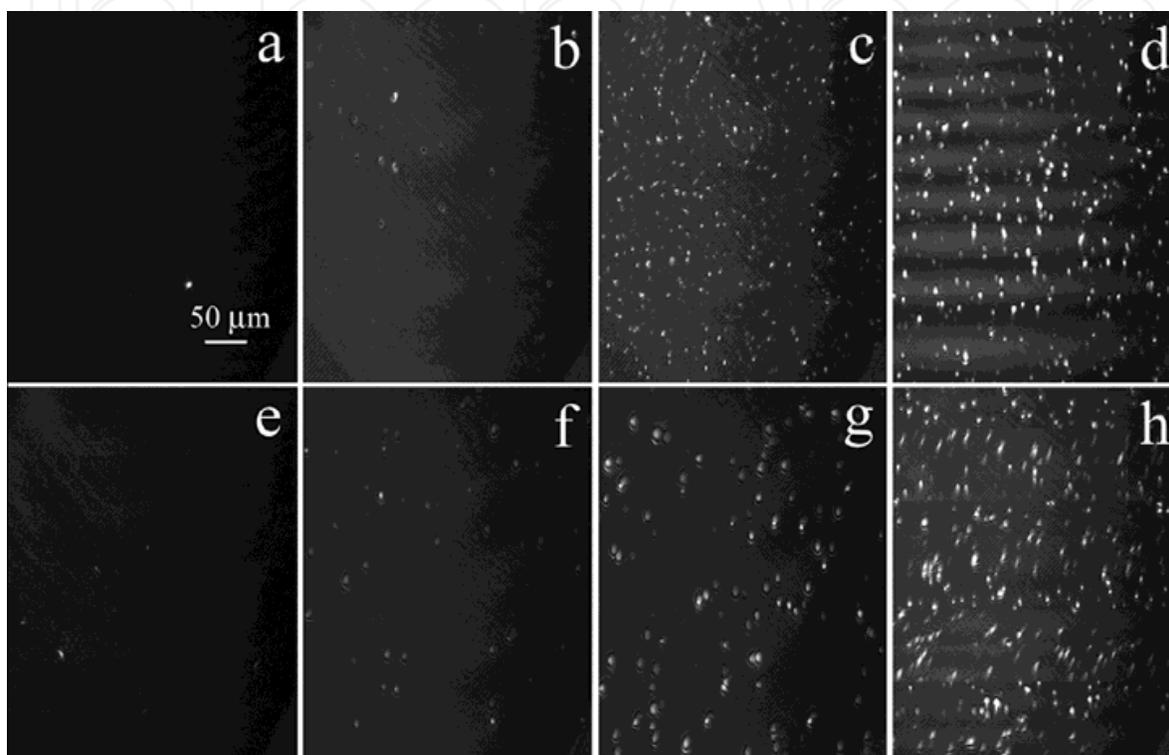


Fig. 27. BAM images of TF46 and mixed TF46/GC11 monolayers at different surface pressures. For TF46 monolayer: (a) 2 mN/m; (b) 12 mN/m; (c) 24 mN/m; (d) 28 mN/m. For mixed TF46/GC11 monolayer: (e) 25 mN/m; (f) 30 mN/m; (g) 32 mN/m; (h) 35 mN/m. The scale bar is 50 μ m (Reproduced from Jiao et al., 2008, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 321, 137-142).

In addition, both amphiphilic luminol derivatives have been evaluated for electrochemiluminescence (ECL) measurements with a view to develop new lipid membranes as sensing element of nanobiosensors (Jiao et al., 2008a). The design and synthesis of new biospecific luminol derivatives with various substitution groups have been then undertaken. In a first approach, the possibility to use polarized screen-printed electrodes to trigger ECL in a buffer solution containing luminol derivatives and hydrogen peroxide has been studied, as shown in Fig. 28. The ECL response to H_2O_2 in the presence of these luminescent derivatives has been investigated taking into account crucial factors such as the applied potential value, concentration of luminol derivatives and the substitution group in molecular structures. The lower hydrogen peroxide concentration detected varied from 1×10^{-7} M to 5×10^{-5} M, depending on the substitution group in the luminol derivative structures. Finally, the effect of acyl group in the molecular structure displayed better ECL performances with TF46 (dialkylchain and TEG spacer) than with LC11 (single alkyl chain).

The present results allow to consider the insertion of the luminol derivatives in a lipid-sensing layer, and to develop new optoelectronic devices based on ECL detection.

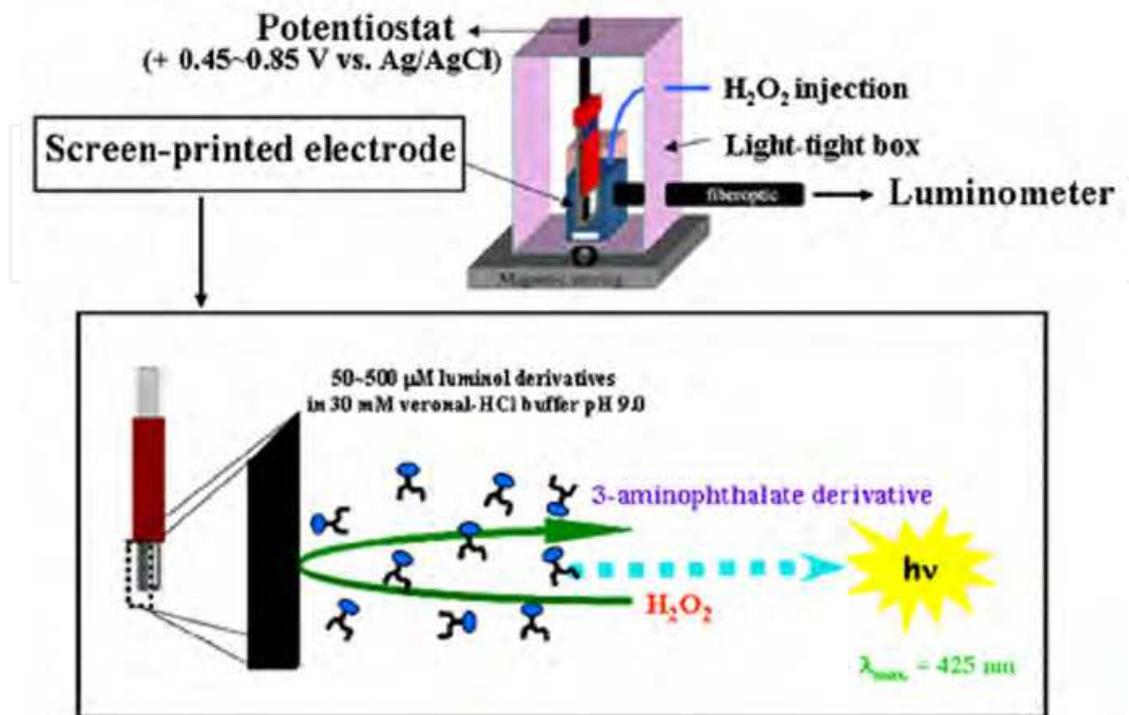


Fig. 28. Schematic representation of the measurement device for ECL detection using a screen-printed electrode. The potential poised at a fixed value between 0.45V and 0.85V vs. printed Ag/AgCl reference electrode allows triggering ECL in the presence of H_2O_2 (Reproduced from Jiao et al., 2008a, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 321, 143-146).



Fig. 29. Reagentless detection principle of choline oxidase activity by ECL reaction triggered directly in the sensing layer (Reproduced from Jiao et al., 2010, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 354, 284-290).

Nextly, this work explores the potentiality of two neosynthesized amphiphilic luminol derivatives to form a lipid bilayer serving as a matrix used for both antibody insertion and ECL detection in order to develop a newsensing layer allowing a reagentless detection (Jiao et al., 2010). As a model, choline oxidase activity has been detected, as shown in Fig. 29. After enzyme immobilization at the surface of the luminol derivative LB bilayer by the way of specific recognition of a non-inhibitory antibody, *in situ* catalytic generation of hydrogen peroxide is able to trigger ECL reaction in the sensing layer interfaced with an optoelectronic device leading to a reagentless detection of choline oxidase activity. Since the sensing layer is based on self-molecular organization of luminol derivatives, it is designed on the nanoscale, and hence, the detection area can be further miniaturized. In this sense, luminol derivative sensing layers exhibit great potentialities for further development toward sensor miniaturization. The main accomplishment of this work was the demonstration of a reagentless detection of oxidase activity based on electrochemiluminescent reaction. This can be regarded as a new achievement in the exploration of signal transduction of complex membrane structures. To our knowledge, only few enzyme biocatalysis studies have been achieved using LB films. The results reported in this paper are thus promising not only to perform new developments in the field of biomimetic miniaturized sensors but also to investigate biological processes involving oxidase activities.

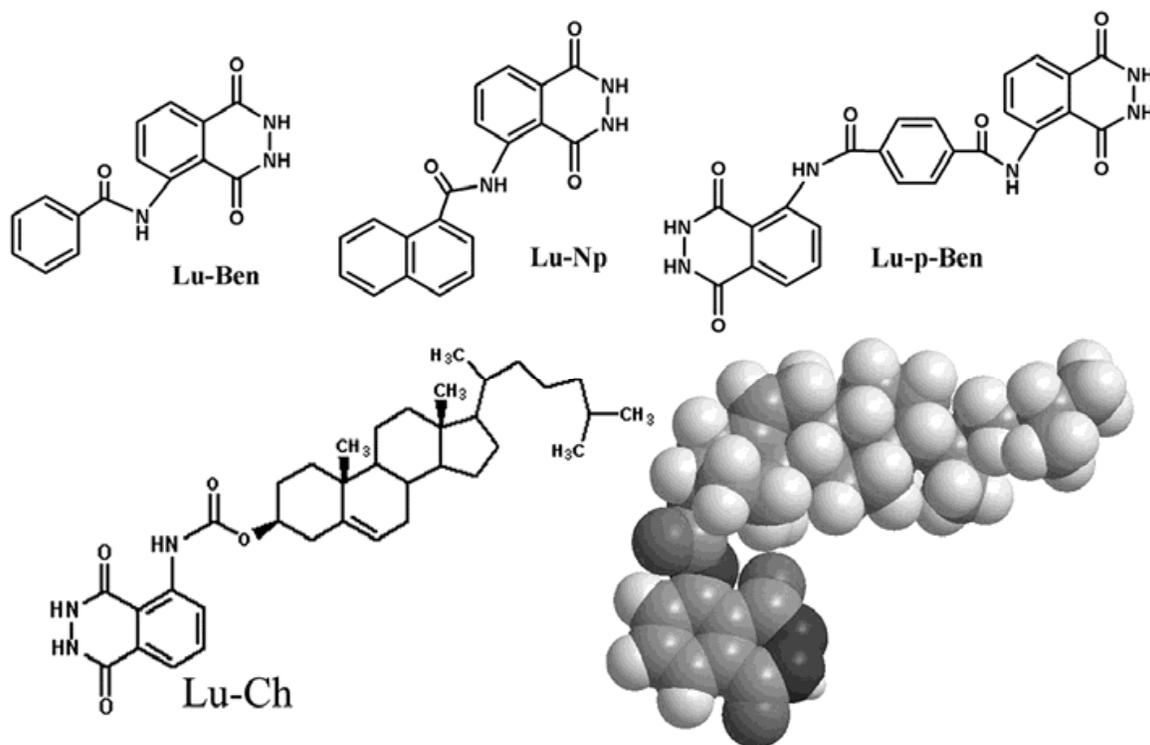


Fig. 30. Chemical structures and abbreviations of new luminol-based derivatives (Reproduced from Jiao et al., 2011b, *Advanced Materials Research*, 197-198, 606-609; 2011i, *Materials Science Forum*, 694, 565-569.).

Some functional luminol derivatives with cholesteryl or aromatic substituted groups have been designed and synthesized from the reaction of the corresponding aromatic acyl chloride precursors with luminol (Jiao et al., 2011b; 2011i). It has been found that depending on the size of aromatic groups, the formed luminol derivatives showed different properties, indicating distinct regulation of molecular skeletons. UV and IR data confirmed commonly the formation of imide group as well as aromatic segment in molecular structures. Thermal analysis showed that the thermal stability of luminol derivatives with p-phthaloyl segment was the highest in those derivatives. The difference of thermal stability is mainly attributed to the formation of imide group and aromatic substituent groups in molecular structure. The present results have demonstrated that the special properties of luminol derivatives can be turned by modifying molecular structures of objective compounds with proper substituted groups, which show potential application in functional material field and ECL sensor.

5. Present situation and future prospects

We are working on molecular design and supramolecular assemblies of novel amphiphiles with special molecular structures in organized molecular films. In this chapter, various kinds of amphiphiles, including bolaamphiphiles, gemini and amphiphiles with functional substituted groups, have been designed and synthesized, and their organized supramolecular assemblies at the air/water interface have also been investigated. First, some series of bolaform amphiphiles with distinct structures have been designed, and their interfacial assembling behaviors were investigated. Various factors, such as coordination mode, spacer length, and headgroup size, can distinctly influence the conformation of spacer, showing stretched or U-shaped arrangement. Second, some special gemini amphiphiles without charge have been also designed. It was found that the length, rigidity/flexibility and hydrophobicity/hydrophilicity of spacer, as well as the components in subphase (metal ions, dyes, and nanoparticles), can regulate the assembly mode and spectral characters, and induce the distinct interfacial morphologies. Moreover, we have done some groping research work about the interfacial behaviors of amphiphiles with functional substituted groups. The above work may give the potential perspective for the fabrication of nano-materials and biosensors. The present work may broaden the traditional research areas about LB film and give some perspectives and clues for the relative research in the future.

In closing, supramolecular assembly at interface is a key physical chemistry subject due to its close relationship to many fundamental and application scientific questions like catalysis, chirality, electron and energy transfer, single molecule science, and organic electronics. With the development of nanoscience and nanotechnology, supramolecular assembly is increasingly being recognized as a representative approach in "bottom-up" technique for the fabrication of organized nanostructure. The detailed understanding of the driving force for the assembly process makes it possible to tailor the assembly process. The sophisticated nanostructures with multiple components have deepened the insight of supramolecular assembly and enriched the content of supramolecular chemistry. The results mentioned here only provide a cursory browse of some progress on supramolecular assemblies of novel amphiphiles in organized molecular films. The input from other fields, such as theoretical modeling and surface spectroscopic techniques, is highly demanded to help us get quantitative information of the supramolecular assembly. It can be predicted that as the

growth of understandings of the rules in the nanoscale, our dream to manipulate molecules could be realized in future.

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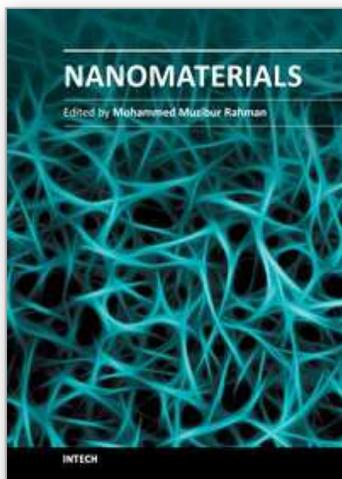
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