Characterization of *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline and oriented crystallization of $CuSO_4 \cdot 5H_2O$ under its monolayer

Chaoyang Jiang, Ruikang Tang and Zihou Tai*

*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute,
Nanjing University, Nanjing, 210093, P.R. China*

A new amphiphilic ligand, *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline (HIHQ), has been synthesized in a convenient method and the characteristics of its monolayer on pure water and on a subphase containing copper ions investigated. LB films of HIHQ were studied by small angle X-ray scattering, UV–VIS and XPS spectra. An oriented crystallization was examined at the monolayer/water interface. A good selection of the (110) crystal face of $CuSO_4 \cdot 5H_2O$ occurred at the solid state of the monolayer due to the perfect match between this crystal face and the definite lattice structure of the monolayer.

Inspired by investigation of biomineralization, crystallization of minerals in biological systems, the study of oriented crystallization of inorganic compounds at inorganic/organic interfaces has received considerable attention and developed rapidly in recent years.[1–5] Various organized molecular films were used as templates, but monolayers, tailored by specific chemical modification, were always used as good organic substrates for controlled oriented inorganic crystallization.[6–9] Up to now, many papers about the nucleation and growth of inorganic crystals under monolayers have been published and the influences of some factors such as chemical binding, lattice matching and structural complementarity between crystals and monolayers have been discussed.[10–15]

8-Hydroxyquinoline and its derivatives readily form insoluble precipitates with many metal ions, and are available in the laboratory as analytical reagents and for the extraction of many metal ions,[16] incorporating 8-hydroxyquinoline or its derivatives in LB films; such films may have potential applications in biomineralization.[17,18] Here, a new amphiphilic ligand, *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline (HIHQ), was synthesized using a convenient method and characterized by elemental analysis, IR, and UV–VIS spectral studies. The coordination of HIHQ with copper ions at the air/water interface and the oriented crystallization of $CuSO_4 \cdot 5H_2O$ at a HIHQ monolayer were also investigated.

Experimental

Materials

8-Hydroxyquinoline (Shanghai Chemical Reagents Co.) and hexadecylamine (Fluka Chemical Co.) were used without any further purification. All solvents were purified by standard procedures. $CuSO_4$ was of A.R. grade, purchased from Shanghai Chemical Reagents Co. Water used in the experiments was doubly distilled and purified by ion exchange.

Synthesis

The synthesis procedure for the amphiphilic ligand, *N*-hexadecyl-5-iminomethyl-8-hydroxyquinoline (HIHQ) is illustrated in Scheme 1. This route involves the preparation of 5-formyl-8-hydroxyquinoline,[19] and its condensation reaction with a long chain alkylamine. This method is more convenient than that of *N*-hexadecyl-8-hydroxyquinolinecarboxamide (HHQ), which we have studied previously.[17] The product HIHQ is a yellow-green powder, Anal. Calc. for $C_{26}H_{40}N_2O$: C, 78.70; H, 10.11; N, 7.03. Found: C, 78.71; H, 10.11; N, 7.03%. The synthesis of HIHQ will be detailed elsewhere.

Apparatus

C,H,N analyses of HIHQ were performed using a Perkin-Elmer Model 240C elemental analyzer. UV–VIS spectra were measured with a Shimadzu Model 240 UV–VIS recording spectrophotometer. XPS spectra of the films were obtained on an X-ray photoelectron spectrometer (Escalab MK-II), which was operated at 15 kV–20 mA (300 W) using Al-Kα radiation. A Langmuir KSV5000 trough system was used in LB film preparation. The formed crystals were studied by optical microscopy and crystal faces examined by a rotating-anode X-ray diffractometer (D/Max-RA, Rigaku, Japan).

Isotherm measurement and fabrication of LB films

The surface pressure–area (π–*A*) isotherms were measured in the usual manner as reported elsewhere.[20] After the monolayer had self-organized for *ca.* 30 min, the LB films were fabricated at a surface pressure of *ca.* 30 mN m^{-1} by lifting–dipping cycling of the substrate. The speed of the slide for the first layer was 1 mm min^{-1}, then raised to 3 mm min^{-1}. All work was carried out in a dust-free box at 20 °C.

Crystal growth of $CuSO_4 \cdot 5H_2O$ at an HIHQ monolayer

$CuSO_4$ (20 g) was added to water (50 g) at 40 °C and the solution was filtered at 20 °C. The filtrate was heated to 30 °C and transferred into the KSV5000 minitrough. When the temperature was lowered to 22 °C, on the surface of the filtrate, the monolayer of HIHQ was carefully and slowly spread from a 1.0×10^{-3} mol dm^{-3} solution in chloroform. After the chloroform had been evaporated off, a stable monolayer was compressed into solid or other phases according to its π–*A* curve, meanwhile, the temperature was reduced to 20 °C and $CuSO_4 \cdot 5H_2O$ crystals were induced to form at the monolayer.

Results and Discussion

Formation of monolayers of HIHQ on aqueous subphase

Fig. 1 shows the surface pressure–area (π–*A*) isotherm of HIHQ monolayer on pure water and displays expanded, coexistent and condensed regions at different surface pressures. The plateau might indicate that a phase change or a change in orientation of the headgroup fragment of HIHQ, which occurs when the surface pressure is increased to 20 mN m^{-1}. A limiting area A_0 of *ca.* 60 Å^2 per molecule is obtained in the expansion region. However, with increase of surface pressure, two other values of A_0, 40 and 29 Å^2, were obtained in the compression region.
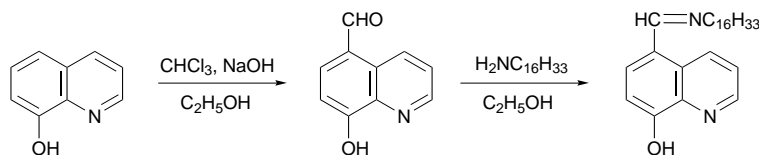
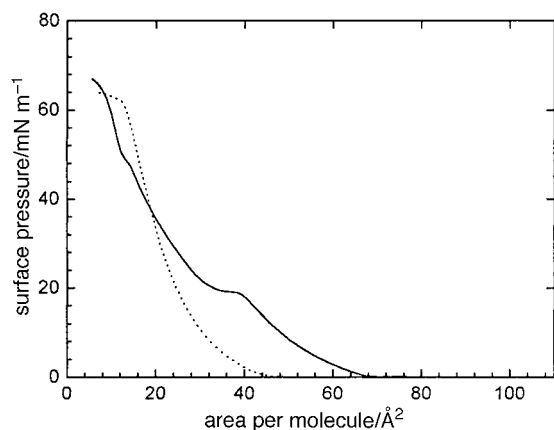Scheme 1 Synthesis of the amphiphilic molecule HIHQ

Fig. 1 Surface pressure–area isotherms of HIHQ on pure water (solid line), and a subphase containing 10^{-3} mol dm^{-3} CuSO$_4$ (dashed line)

The small-angle X-ray scattering profile of 13-layer LB films of HIHQ deposited from pure water is shown in Fig. 2. Only one broad Bragg peak ($2\theta = 2.282°$) is observed. The derived bilayer spacing (38.711 Å) is much smaller than twice the thickness of the length of molecule (2×23.4 Å). As Y-type bilayer structure was formed, the incline mode is proposed [Fig. 3(b)].

The area per molecule (60 Å^2) corresponds to a cross-sectional area of 8-hydroxyquinoline approximated by a rectangular block with dimensions $8.4 \times 7.4 \times 3.6$ Å^3 according to a space-filling molecular (CPK) model. The values, 40 and 29 Å^2, per molecule might correspond to the incline side area [$(8.4^2 + 7.4^2)^{1/2} \times 3.6$ Å^2] and the vertical side area (8.4×3.6 Å^2) of the 8-quinolinol ring of HIHQ. The thickness of a single monolayer of HIHQ estimated by SAXS is 19.50 Å corresponding to the structure in Fig. 3(b); we can deduce that the Y-type bilayer was formed during the deposition process of HIHQ and the molecular orientation in the LB film is of the structure shown in Fig. 3(b) rather than in Fig. 3(a) or (c).

Obviously, the HIHQ molecule has different oriented structures under various surface pressures. At lower surface pressure, the 8-quinoline ring lies on the surface [Fig. 3(a)]. With
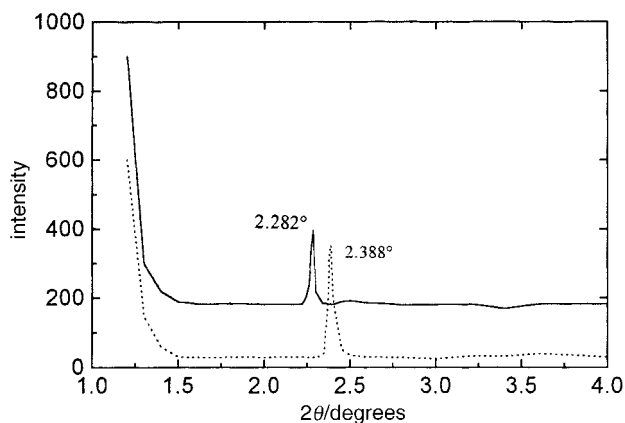

Fig. 2 Small X-ray scattering patterns of a 13-layer LB film of HIHQ obtained from pure water (solid line) and from a subphase containing copper ions (dashed line)
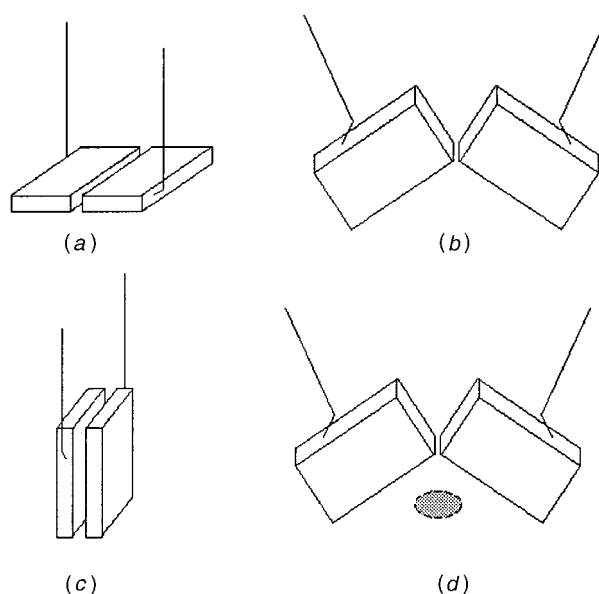

Fig. 3 Stacking modes of HIHQ molecules at the air/water interface. The dashed circle represents a copper ion.

increase of surface pressure, the orientation of the quinoline ring in the monolayer changes from a 'flat' to an 'edge on' structure, and when the surface pressure is > 50 mN m^{-1}, a 'stand up' structure is adopted. This molecular orientation of HIHQ in the monolayer can be ascribed to the hydrophilicity of the head group: phenolic hydroxy and tertiary amine. More evidence on these oriented structures will be collected by Brewster angle microscopy in the future.

Formation of monolayers of HIHQ on a subphase containing copper ions

In general, the π–A isotherm and the organization of the monolayer depend strongly on the composition of the sub-phase. The presence of metal ions in a subphase has a marked effect on the behavior of the monolayer, especially for mono-layers of amphiphilic molecules with coordinating head groups. When Cu^{2+} ions were added to the subphase, the character-istics of the HIHQ monolayer were changed remarkably. Fig. 1 also shows the surface pressure–area per molecule of a mono-layer of HIHQ on a subphase containing Cu^{2+}. The isotherm displays a typical condensed region. The limiting area per molecule on the Cu^{2+}-containing subphase is 20 Å^2 at a surface pressure of 30 mN m^{-1} (A_{30}).

Fig. 2 shows the SAXS profile of 13-layer LB films of HIHQ deposited from a subphase containing Cu^{2+} ions (dashed line). One broad Bragg peak at 2.388° is observed and the derived bilayer spacing is 37.008 Å. The slight change from 38.711 to 37.008 Å is evidence of an altered stacking mode of the HIHQ monolayer on different subphases. As the thickness of a single monolayer of HIHQ estimated by the CPK model is 18.67 Å in Fig. 3(d), we can deduce that this orientation is adopted.

UV–VIS spectra and XPS studies of monolayers

To confirm the interaction between the amphiphilic HIHQ monolayer and copper ions contained in the subphase, UV–VIS

spectra and XPS studies of the LB films of HIHQ deposited in pure water and in a copper containing subphase were investigated.

Fig. 4 shows UV–VIS spectra of HIHQ in ethanol, a 13-layer LB film on a quartz substrate deposited from pure water and from a subphase containing Cu^{2+} ions, respectively. Compared with the absorption of HIHQ in ethanol, the ^1L_a band of an HIHQ LB film deposited from pure water is bathochromically shifted from 400 to 410 nm, and that of the ^1B_b band in LB film is shifted from 240 to 245 nm. These red shifts might be attributed to a strong interaction between the molecules of HIHQ in the LB film. Similarly, different absorption spectra were obtained by constructing LB films on different subphases. Red shifts of ^1L_a (from 410 to 420 nm) and ^1B_b (from 245 to 257 nm) bands were observed in the LB film deposited from a subphase containing copper ions. In particular, a band at 203 nm, which is assigned to the n→π* transition of the long alkyl chain, was also red shifted and observable in the UV. All these indicated that interfacial coordination occurs immediately after spreading the HIHQ molecules on a subphase containing Cu^{2+} ions.

XPS is a technique which provides elemental and chemical information about a solid surface, and generally, the shift of binding energy usually provides a measurement of the electron density about the atom with the shift increasing with decrease in electron density.[21,22] In our experiment, two nitrogen atom signals (399.1, 400.1 eV) were observed for the HIHQ film deposited from pure water. A similar result (399.5, 400.1) was obtained for the HIHQ film deposited from a subphase containing copper ions. The 400.1 eV signal can be assigned to N 1s of nitrogen atoms near the alkyl chain. The shift of the binding energy of the nitrogen atom of the quinoline ring (from 399.1 to 399.5 eV) and that of oxygen (from 532.1 to 532.4 eV) show that the coordination bonds were formed in conjunction with electron transfer from N and O atoms of the monolayer to copper ions. The surface composition of the LB films constructed from the Cu^{2+} aqueous subphase was also determined by XPS. It is found that the Cu:N:C atomic ratio was *ca.* about 1:4:52; two HIHQ molecules appear to interact with one copper ion as shown in Fig. 3(*d*).

Oriented crystallization of CuSO₄·5H₂O under HIHQ monolayers

In the absence of the monolayer, the crystallization of $CuSO_4·5H_2O$ in the supercooled solution is uncontrolled. Nucleation occurred both at the air–water interface and at the bottom of the trough. These crystals were randomly aggregated and had a heterogeneous size distribution. However, nucleation of $CuSO_4·5H_2O$ was induced by the compressed HIHQ monolayer and was found to be oriented. X-Ray diffraction patterns

revealed that the favoured crystal face was (110). Just as the Cu ions induce HIHQ formation in the deposition of LB films in the presence of Cu^{2+}, so the HIHQ monolayer induces formation of $CuSO_4·5H_2O$ crystals at the monolayer in the crystallization process.

As already known, the influence of an inorganic–organic interface is important in the regulation of inorganic crystal growth and in the resulting specificity of crystal morphology and particle aggregation.[23–25] It is postulated that the localized chemical control, spatial localization and constraints, and molecular complementarity can influence the matching between the potential fields surrounding the inorganic and organic surfaces.

HIHQ is an amphiphilic ligand. According to the principle of coordination and HSAB (theory of hard and soft acids and bases), it coordinates preferably to soft acids such as Cu^{2+}. HIHQ is also a typical surface active agent and can increase the concentration of the solute in domains located under the monolayer. When the monolayer HIHQ is formed, the local concentration of $CuSO_4·5H_2O$, Cu^{2+} ions and the value of supersaturation ratio (S) at the interface are increased. On the other hand, the surface energy is decreased upon formation of the monolayer. The monolayer can be also considered as a different phase formed on the surface of the solution and can act as a site for heterogeneous nucleation; the Gibbs energy (G_1) of heterogeneous nucleation is much lower than G_1 for homogeneous nucleation. Thus, nucleation of $CuSO_4·5H_2O$ occurs initially at the interface between the monolayer and the solution.

In the period of crystal growth, since the crystals are attached to the monolayer, they are restricted in growing towards the monolayer. Some directions of crystal expansion are inhibited and a remarkable growth distortion along (110) at the monolayer is observed. Since the monolayer cannot bear too heavy masses when the crystal expands to a certain size its mass will overcome the support force of the monolayer and the crystal will separate from the monolayer and drop down to the bottom of the solution.

The most important aspect of the crystal growth under the monolayer is the oriented crystallization and the $CuSO_4·5H_2O$ crystal has a given face (110) attached to the monolayer corresponding to the interaction between the crystal and the monolayer. The key to specificity in nucleation is the presence of some forms of molecular complementarity between functional groups on the HIHQ monolayer and copper ions, which determines the specificity in nucleation and orientation of the crystals. In fact, the monolayer is an organized aggregation and has a definite lattice structure. If the lattice of the monolayer is similar to a certain crystal face of $CuSO_4·5H_2O$, then this crystal face will readily form under the monolayer.

We studied the lattice structure of the HIHQ monolayer on the subphase of Cu^{2+} by computer simulation[26,27] and results are shown in Fig. 6; the structural parameters of the monolayer are: $a = 7.0$, $b = 6.0$, $\theta = 72.5°$, with the area per molecule of $Cu^{2+}(HIHQ)_2$ on the monolayer being 40.0 Å². The corresponding lattice parameters of the (110) crystal face of
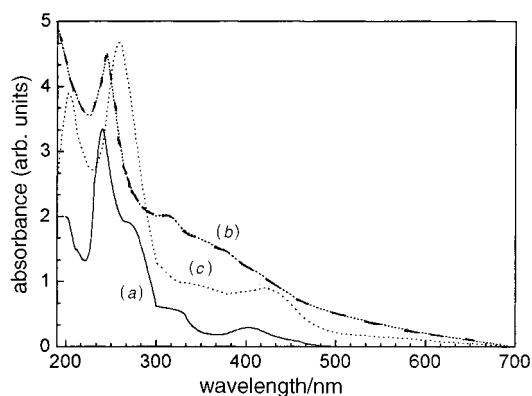

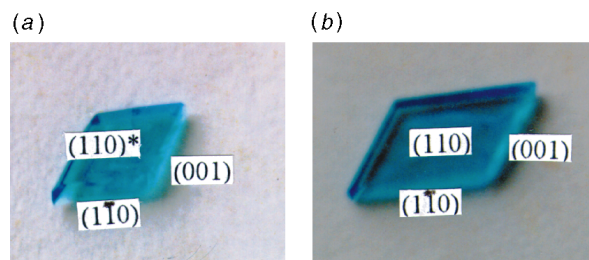**Fig. 4** UV–VIS absorption spectra of HIHQ in ethanol solution (*a*), HIHQ LB film deposited from pure water (*b*) and from a subphase containing Cu^{2+} ions (*c*)

Fig. 5 Topographies of the $CuSO_4·5H_2O$ crystals. A $CuSO_4·5H_2O$ crystal removed from the monolayer (*a*) is different from one grown without the monolayer (*b*).
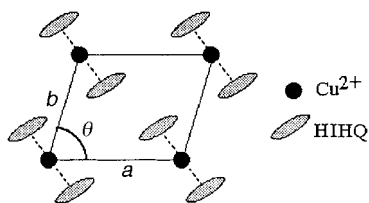
Fig. 6 The matching between $Cu^{2+}(HIHQ)_2$ and the (110) face of $CuSO_4 \cdot 5H_2O$. Each Cu^{2+} ion is coordinated by two HIHQ molecules and the arrangement of the Cu^{2+} under the monolayer is $a = 7.0$, $b = 6.0$ Å and $\theta = 72.5°$, which is similar to those on the (110) face of a $CuSO_4 \cdot 5H_2O$ crystal (6.97, 5.96 Å and 72.8°).

$CuSO_4 \cdot 5H_2O$ are: 6.97, 5.96 and 72.8° and the area per Cu^{2+} ion on the face is 39.68 Å^2 in good accord with the HIHQ monolayer.

Conclusions

Here, we have reported the synthesis and characterisation of a novel amphiphilic ligand HIHQ. The characterization of HIHQ monolayers shows that in a monolayer, HIHQ can coordinate with copper ions contained in the subphase. As a new kind of template, the HIHQ monolayer can induce oriented crystallization of $CuSO_4 \cdot 5H_2O$ and a good selection of the (110) crystal face occurs at the solid state of the monolayer.

References

1 H. A. Lowenstam and S. Weiner, *On Biomineralization*, Oxford University Press, Oxford, 1989.
2 *Biomineralization: Chemical and Biochemical Perspectives*, ed. S. Mann, J. Webb and R. J. P. Williams, VCH, New York, 1989.
3 A. Berman, L. Addad, A. Kuick, L. Leiserowitz and M. Nelson, *Science*, 1990, **250**, 664.
4 A. H. Heuer, D. J. Frind, V. J. Laraia, J. L. Arias, P. D. Calvert, K. Kendall, G. L. Messing, J. Blackwell, P. C. Rieke, D. H. Thompson, A. P. Wheeler, A. Veis and A. I. Caplan, *Science*, 1992, **255**, 1098.
5 L. Addadi and S. Weiner, *Angew. Chem., Int. Ed, Engl.*, 1992, **31**, 153.
6 S. Mann, *J. Chem. Soc., Dalton Trans.*, 1993, 1.
7 S. Mann, *Nature (London)*, 1993, **365**, 499.
8 X. K. Zhao, S. Baral, R. Rolandi and J. H. Fendler, *J. Am. Chem. Soc.*, 1988, **110**, 1012.
9 R. F. Ziolo, E. P. Giannelies, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrota, M. W. Russell and D. R. Huffman, *Science*, 1992, **257**, 219.
10 E. M. Landau, S. G. Wolf, M. Levanon, L. Leiserowitz, M. Lahav and J. Sagiv, *J. Am. Chem. Soc.*, 1989, **111**, 1436.
11 I. Weissbuch, F. Frolow, L. Addadi, M. Lahav and L. Leiserowitz, *J. Am. Chem. Soc.*, 1990, **112**, 7718.
12 S. Rajam, B. R. Heywood, J. B. A. Walker, S. Mann, R. J. Davey and J. D. Birchall, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 727.
13 X. K. Zhao, J. Yang, L. D. McCormick and J. H. Fendler, *J. Phys. Chem.*, 1992, **96**, 9933.
14 A. Berman, D. J. Ahn, A. Lio, M. Salmerson, A. Reichert and D. Charych, *Science*, 1995, **269**, 515.
15 S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum and N. J. Reeves, *Science*, 1993, **261**, 1286.
16 N. Zakareia, S. M. Khalifa, M. Fofal and H. F. Aly, *Radiochim. Acta*, 1989, **47**, 229.
17 J. Ouyang, Z. Tai, C. Jiang and W. Tang, *Spectrosc. Lett.*, 1996, **29**, 763.
18 J. Ouyang, Z. Tai and W. Tang, *J. Mater. Chem.*, 1996, **6**, 963.
19 G. R. Clemo and R. Howe, *J. Am. Chem. Soc.*, 1955, 3352.
20 J. Ouyang, Z. Tai and W. Tang, *Thin Solid Films*, 1996, **289**, 199.
21 K. Kurihara, T. Kawahara, D. Y. Sasaki, K. Ohto and T. Kunitake, *Langmuir*, 1995, **11**, 1408.
22 Y. Ikeura, K. Kurihara and T. Kunitake, *J. Am. Chem. Soc.*, 1991, **113**, 7342.
23 R. Tang, Z. Tai and Y. Chao, *J. Chem. Soc., Dalton Trans.*, 1996, 4439.
24 S. Mann, *Struct. Bonding (Berlin)*, 1983, **54**, 127.
25 S. Mann, *Nature (London)*, 1988, **332**, 119.
26 Q. Miao, R. Tang, Z. Tai and X. Qian, *Langmuir*, 1995, **11**, 1072.
27 M. V. Alfimov, A. A. Bangaturgants and K. Ya. Burshtein, *Thin Solid Films*, 1991, **200**, 165.