Control on the organized structure of monoalkylethylenediamine copper(II) coordinated bilayer membranes by counter ions

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The organized structure of Cu^{2+}-coordinated bilayer membranes formed by monoalkyl derivatives of ethylenediamine can easily be modulated by varying the counter ions, and their physical properties change correspondingly.

The design and construction of supramolecular organized assemblies utilizing non-covalent intermolecular interactions, such as hydrogen bondings, metal–ligand interactions, van der Waals interactions, π–π stackings *etc.* has become a topic of increasing interest in recent years, due to their fascinating structures and novel functionalities.[1–4] It is well-known that the structure and properties of these aggregates are determined not only by the chemical structures of the component molecules, but also by environmental factors, including pH variation, metal-ion complexation, heat, light *etc.* Recently, much work has focused on the control of the macroscopic morphology and microscopic structure of self-organized materials by changing physical or chemical environments.[5]

In our previous papers, we have reported that complexed bilayer membranes are formed from a series of single-chain amphiphiles $C_nH_{2n+1}NHC_2H_4NH_2$ dispersed in dilute aqueous $Cu(NO_3)_2$.[6] In the present work, our investigation has been concentrated on the control of the organized structure of monoalkylethylenediamine in dilute aqueous CuX_2 by changing the counter ions ($X^- = Cl^-$, Br^-, NO_3^- and ClO_4^-).†

Fig. 1 shows the typical transmission electron micrographs for amphiphilic aggregates of $C_nH_{2n+1}NHC_2H_4NH_2$ ($n = 12$,

Fig. 1 Typical TEM morphologies of complexed bilayer membranes of $[Cu(C_nH_{2n+1}NHC_2H_4NH_2)_2]X_2$: (a) $X^- = Cl^-$, $n = 14$; (b) $X^- = ClO_4^-$, $n = 14$.

14, 16, 18) in aqueous CuX_2 ($X^- = Cl^-$, Br^-, NO_3^- and ClO_4^-), which all revealed the presence of vesicular morphologies. However, there are drastic differences between the samples with Cl^-, Br^- on the one hand and NO_3^-, ClO_4^- on the other as counter ions in the appearance of the dispersion. In the former case the aggregates are blue while the latter are purple. Obviously for these four systems, the only difference lies in the X^- anion type and size, therefore, it can be inferred that the type of counter ion is of vital importance to the determination of the organized structures, and the amphiphilic aggregates can be categorized into two structurally differing types.

The differences between the two kinds of assemblies in solution colour and in their solid-state electronic spectra reveal configurational diversities in the structures of the Cu^{2+}-coordinated headgroups. Typical results ($n = 14$) are shown in Table 1. For asymmetric derivatives of ethylenediamine, ML_2 type complexes of Cu^{2+}-coordinated amphiphiles usually adopt planar CuN_4 structures with *cis-* and *trans-*isomers.[7] It has been established that complexes with *cis-*configuration show higher σ–σ* transition energies than those with *trans-*arrangement.[8] Aditionally, square-coplanar CuN_4 complexes show d–d transition energies in the range $(18–20) \times 10^3$ cm^{-1} while the range for tetrahedral CuN_4 is $(12–16) \times 10^3$ cm^{-1}.[9] From the d–d and σ–σ* transition energies in Table 1, it can be deduced that when $X = Cl^-$ or Br^-, the Cu^{2+}-coordinated headgroups adopt a *trans-*configuration which give a compressed tetrahedral CuN_4 environment, and the two tails in the $[Cu(C_nH_{2n+1}NHC_2H_4NH_2)_2]X_2$ ($X^- = Cl^-$, Br^-, $n = 12–18$) complexes adopt an approximately diagonal position [see Fig. 3(a)]; while for $X^- = NO_3^-$ or ClO_4^- ions, a *cis-*configuration is adopted with the copper square-coplanar, with the two tails located at the same side of the plane and parallel to each other [see Fig. 3(b)]. Clearly the headgroup structures greatly influence the packing fashion of the hydrocarbon tails in the organized aggregates.

It has been demonstrated by many experiments that in cast films the self-aggregated structure of the amphiphiles in dilute aqueous dispersions is well preserved.[10] In order to elucidate the structural features of the assemblies in aqueous solution, small-angle XRD was applied to study the long spacing of the cast bilayer membranes. Powder diffraction experiments carried out on cast films of the complexed aggregates showed periodic peaks corresponding to bilayers with ordered structures, which are similar to those reported in the literature.[10] Fig. 2(a) shows
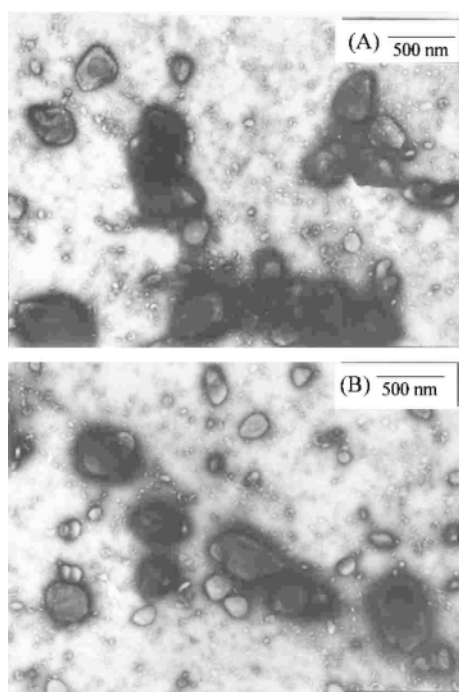
Table 1 The appearance of $C_{14}H_{29}NHC_2H_4NH_2$ aggregates in aqueous CuX_2, along with electronic transitions of their cast films

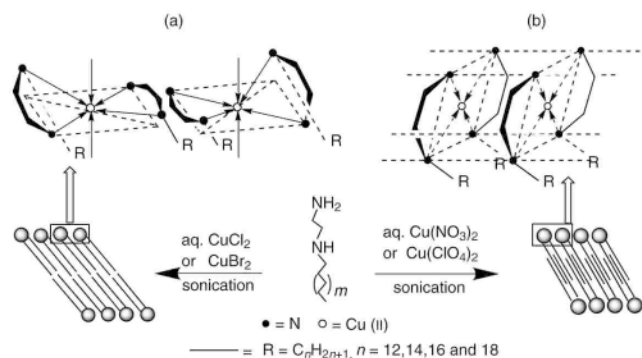| Counter ion (X^-)	Solution appearance	d–d Transition (10^{-3} $\bar{v}$/cm^{-1})	σ–σ* Transition (10^{-3} $\bar{v}$/cm^{-1})	
			I	II
Cl^-	Emulsion, blue	16.78	35.21	42.37
Br^-	Emulsion, blue	17.48	33.33	42.78
NO_3^-	Emulsion, purple	18.05	35.71	44.44
ClO_4^-	Emulsion, purple	19.23	36.50	43.10

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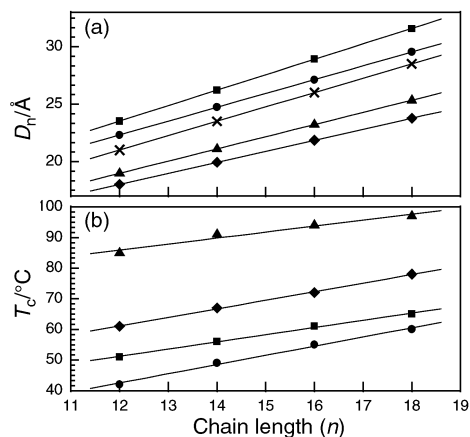
Fig. 2 (a) Bilayer thickness (D_n) values and the evaluated molecular length (L_n) as function of the tail length (n); (b) phase transition temperature (T_c) dependence on the tail length (n): $X^- = (\bullet)$ Cl^-; ($\blacksquare$) Br^-; ($\blacktriangle$) NO_3^-; ($\blacklozenge$) ClO_4^-; ($\times$) L_n.

the tail length (n) dependence of the bilayer thickness, *i.e.* the long spacing (D_n) of the cast bilayer membranes. As can be seen for each system the bilayer thickness shows good linearity with tail length ($n = 12, 14, 16$ and 18):

$$D_n (Cl^-) = 1.34n + 7.39$$
$$D_n (Br^-) = 1.21n + 7.83$$
$$D_n (NO_3^-) = 1.06n + 6.24$$
$$D_n (ClO_4^-) = 0.97n + 6.24$$

The cast bilayer thickness, for $X^- = Cl^-$, Br^- ions, falls between the monomolecular and bimolecular length of the amphiphile, while for $X^- = NO_3^-$, ClO_4^- ions the bilayer thickness is smaller than the corresponding evaluated molecular length (L_n) (CPK model). These results indicated that the amphiphilic molecules probably assume either a tail-to-tail chain packing mode or an interdigitated packing mode in the bilayer membranes.

Differential scanning calorimetry experiments of the complexed bilayer dispersions showed endothermic peaks (not shown here), indicating gel-to-liquid crystal phase transitions, one of the basic physicochemical properties of bilayer membranes. The value of the phase transition temperature (T_c) for each system exhibits fairly good linearity with n, as depicted in Fig. 2(b), indicating similar lateral packing in the membrane structure of each system. It is clear from Fig. 2(b), for $X^- =$ Cl^-, Br^- samples, the T_c values are $< 65\ °C$, which are similar to those of bilayer membranes showing tail-to-tail packing reported in the literature.[11] By contrast, for $X^- = NO_3^-$, ClO_4^-, the T_c values are $> 60\ °C$. It has been shown that in many cases the extensively tilted tail-to-tail type bilayer assemblages possess relatively fluid chain packing and exhibit relatively low T_c, whereas interdigitated type bilayer membranes have tighter chain packing and display higher T_c values than tail-to-tail ones.[11] Thus, by combining XRD and DSC results, it can be inferred that for $X^- = NO_3^-$, ClO_4^- dispersions the amphiphiles adopt the partially interdigitated chain packing mode in the bilayer membranes. Two quite different structures in cast films from complexed bilayer membranes with different counter ions are thus observed. Based on the packing model of aliphatic chains in the bilayer membranes, the chain tilt angles (with respect to the bilayer normal) for each system, calculated from the slope of the linear equations[12] are $58.2°$ (Cl^-), $61.6°$ (Br^-), $33.4°$ (NO_3^-) and $40.2°$ (ClO_4^-).

In summary, this study shows a very simple method, changing the counter ion can modulate the headgroup configuration and packing mode of the aliphatic chains in synthetic bilayer membranes formed by monoalkylethylenediamines $C_nH_{2n+1}NHC_2H_4NH_2$ ($n = 12$–18) in dilute aqueous CuX_2 (Fig. 3). Furthermore, this molecular-level modification arising from the change of counter ions is amplified by the self-assembly process through cooperative effects of metal–ligand interactions and van der Waals interactions, on their macroscopic properties leading to variations in appearance and gel-to-liquid transition temperatures of the dispersions.

Notes and references

† Samples were prepared and characterized as described in the literature.[6]

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Fig. 3 Schematic representation of bilayer formation from $C_nH_{2n+1}NHC_2H_4NH_2$ ($n = 12, 14, 16$ and 18) in aqueous CuX_2: (a) $X = Cl^-$ or Br^-; bilayer showing tail-to-tail packing mode, coordinated headgroups adopt a *trans*-configuration in a compressed tetrahedral CuN_4 environment with two tails in the $[Cu(C_nH_{2n+1}NHC_2H_4NH_2)_2]X_2$ complexes located at approximately diagonal positions. (b) $X = NO_3^-$ or ClO_4^-; bilayer showing a partially interdigitated chain packing mode, coordinated headgroups adopt a *cis*-configuration in a square-coplanar environment with the two tails located at the same side of the plane and parallel to each other.