Crystal Structure of 9-(Hexadecyl)imino-4,5-diazafluorene

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The molecular and crystal structures of a new bilayer-forming amphiphilic ligand containing π-conjugated diazafluorenone Schiff base as the head group, 9-(hexadecyl) imino-4,5-diazafluorene ($C_{27}H_{39}N_3$), were determined by the X-ray diffraction method.

Since the first report on totally synthetic bilayer membranes,[1] many artificial amphiphilic molecules have been extensively used to investigate the physicochemical properties of the biomimetic membrane.[2] For the better understanding of these properties and of the relation between the chemical structure of an amphiphile and its state of aggregation, it is essential to accumulate detailed information about preferred molecular and crystal structures of various types of bilayer-forming amphiphiles.[2,3]

Recently, we synthesized the title compound,[4] 9-(hexadecyl)imino-4,5-diazafluorene ($C_{27}H_{39}N_3$), **1**, a single-chain amphiphilic ligand composed of only two structural elements: a rigid diazafluorenone Schiff base segment containing two nitrogen atoms with lone pair electrons as hydrophilic head group and an alkyl chain containing sixteen carbon atoms as the hydrophobic tail. In the previously paper,[5] we reported that the synthetic amphiphile **1** can form stable bilayer membranes when dispersed in water. For the better understanding of the bilayer structure and its self-assembling properties, we succeeded in preparing the single crystal of **1** suitable for X-ray diffraction.

Amphiphilic ligand **1** was dissolved in aqueous ethanol (water/ethanol= 1: 4 by volume) and pale yellow grain crystals ($0.28\times0.26\times0.16$ mm^3) were obtained by keeping the solution for two weeks at room temperature.

The crystal structure was determined by Enraf-Nonius CAD-4 four-circle X-ray diffractometer.[6] The molecular conformation of **1** is shown in Figure 1 together with their atomic labelling. The C-C bond distances and C-C-C bond angles in the alkyl tail are in the range of 1.509(4) ~ 1.552(4)Å and 106.6(3) ~ 113.6(3)°. These values are in reasonable agreement with values previously found in other amphiphilic compounds with long hydrocarbon chains[7], and the dihedral angles indicate an all-*trans* conformation. Furthermore, the zigzag plane of the alkyl tail of **1** is linked through the Schiff base bond to diazafluorene plane with a small torsion angle, 179.76° [C(16)-N(1)-C(17)-C(18)] and -0.45° [C(16)-N(1)-C(17)-C(27)]. Consequently, the whole molecule looks like a "tadpole".

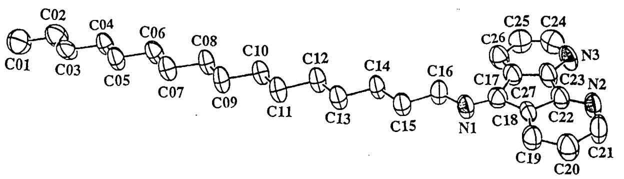

Figure 1. The structure of 9-(hexadecyl)imino-4,5-diazafluorene ($C_{27}H_{39}N_3$), **1**. Hydrogens are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°)

N1-C17	1.280(4)	C16-N1-C17	118.1(3)
N2-C22	1.317(4)	N1-C17-C18	120.9(3)
C17-C18	1.481(4)	C17-C18-C19	132.0(3)
C18-C19	1.366(4)	C17-C18-C22	108.5(3)
C18-C22	1.410(4)	C18-C22-N2	124.2(3)
C22-C23	1.469(5)	C21-N2-C22	116.4(3)

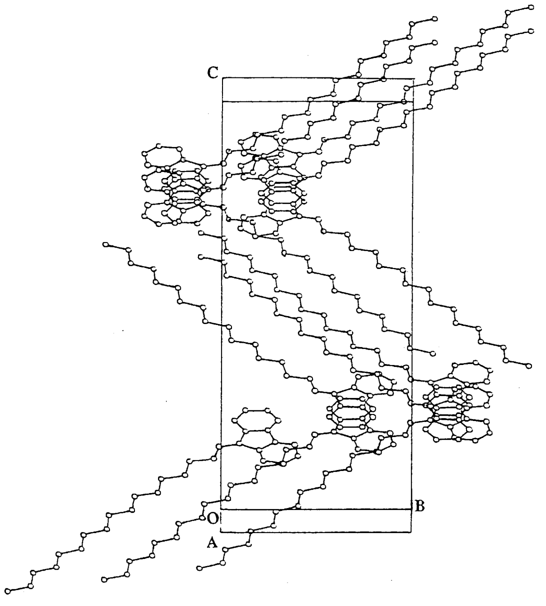

Figure 2. The crystal packing of 9-(hexadecyl)imino-4,5-diazafluorene ($C_{27}H_{39}N_3$), **1**.

The crystal packing scheme of **1** is shown in Figure 2. The structure can be seen as an alternation of the hydrophobic and hydrophilic layers stacked along *c* direction. In the hydrophobic layer, the molecular alkyl chains are interdigitated mutually. The tilted diazafluorenone Schiff base packing is in close agreement with the J-like aggregate formation in the bilayer membrane inferred from the red shift for the bilayer of **1** relative to the absorption of the isolated chromophore in ethanol.[4]

Figure 3 shows the perspective view of the head groups of **1** onto the *c*-plan, together with the molecular labelling. The head groups are overlapped by π-π interactions along the *c*-axis and

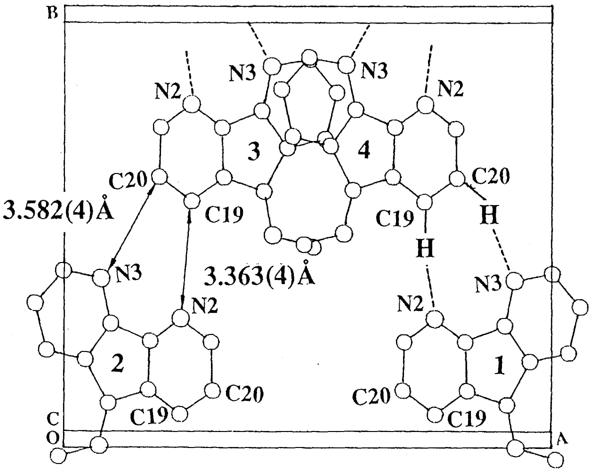

Figure 3. Perspective view of the head groups of 9-(hexadecyl)imino-4,5-diazafluorene ($C_{27}H_{39}N_3$), **1**. in the hydrophilic layer onto the *c*-plane (A=1, B=1, C=0.5).

the distance between the two head groups is 3.267(2) Å, while their alkyl chains are stretched in the different direction. As shown in Fig. 3, the distances of 3.363(4) Å (N2···C19) and 3.582(4) Å (N3···C20) between molecule 1(2) and the neighboring molecule 4(3) in the same plane fall in the normal range of hydrogen-bond distances. Molecular ribbons are formed *via* these hydrogen-bonds. The alkyl chains of two ribbons are interdigitated to form a double layer structure with a head-head tail-tail arrangement of the molecules. In addition, the head groups are overlapped by π-π interactions, and the shortest distance between non-hydrogen atoms of neighboring head groups(*e.g.* molecule 3 and 4) is 3.267(2).

Thus, the crystal structure of amphiphilic ligand **1** is stabilized by intermolecular (noncovalent) binding interactions which include π-π overlap along the *c*-axis and hydrogen-bonding interactions along the *b*-axis between the head groups, and hydrophobic interactions between the alkyl chains.[8]

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References and Notes

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6 Crystal data for 1: $C_{27}H_{39}N_3$, *M* 405.6, monoclinic, C 2/c, =14.544(4), b=12.322(3), c=27.947(5) Å, β=96.12(2)°, cell volume = 4979(1) Å^3, Z=8, D_X=1.082 g·cm^{-1}. λ(Mo-K$_\alpha$)= 0.71073 Å , R = 0.0697 , R_W = 0.0803 , 5670 measured reflections, 4892 independent reflections , 1574 refctions ($w=1/\sigma^2(F)$) for the structure solution(direct methods) and refinement (full-matrix least-squares). The little high R value dues to the vibration of the long alkyl chain .

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