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Ordering transitions in micrometer-thick films of nematic liquid crystals driven by self-assembly of ganglioside GM_1

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ABSTRACT

We report an investigation of the self-assembly of the monosialoganglioside (GM_1) at interfaces formed between aqueous solutions of 10 μM GM_1 (at 25 °C) and micrometer-thick films of the nematic liquid crystal (LC) 4′-pentyl-4-cyanobiphenyl (5CB). We observe the process of spontaneous transfer of GM_1 onto the interfaces to be accompanied by continuous ordering transitions within the micrometer-thick films of the LC. At saturation coverage, the GM_1 orders the LC in an orientation that is perpendicular to the interface, an orientation that is similar to that caused by phospholipids such as dilauroylphosphatidylcholine (DLPC). This result suggests an interaction between the LC and GM_1 that is dominated by the hydrophobic tails of the GM_1. Relative to DLPC, however, we observe the dynamics of the LC ordering transition driven by GM_1 to be slow (2 h for DLPC versus 100 h for GM_1). To provide insight into the origins of the slow dynamics of the GM_1-induced ordering transition in the LC, we performed two additional measurements. First, we quantified the time-dependent adsorption of GM_1 at the LC interface by using fluorescently-labeled GM_1. Second, we used the Langmuir–Schaefer method to transfer preorganized monolayers of GM_1 from an air–water interface to the aqueous-LC interface. Results obtained from these two experiments are consistent with a physical picture in which the final stages of spontaneous adsorption/ordering of GM_1 at the aqueous-LC interface dictate the dynamics of the LC ordering transition. This rate limiting process underlying the ordering transition was substantially accelerated by heating the system above the phase transition temperature of GM_1(26 °C), suggesting that the phase state of the GM_1 micellar aggregates in bulk solution strongly influences the kinetics of the final stages of ordering/adsorption of GM_1 at the LC interface. Overall, these results and others presented in this manuscript reveal that it is possible to decorate interfaces of a nematic LC with GM_1, and that the assembly of GM_1 at these interfaces impacts the dynamic and equilibrium ordering of the LC.

1. Introduction

A series of recent studies have reported on ordering transitions induced in micrometer-thick films of liquid crystals (LC) that are caused by the self-assembly of amphiphiles at aqueous interfaces of LC films [1–13]. Of the various different amphiphiles explored in these studies (which includes surfactants, phospholipids, macromolecular amphiphiles), the ordering of nematic LCs by the interfacial self-assembly of the phospholipid L-α-dilauroylphosphatidylcholine (L-DLPC) has been particularly well characterized [3,5,6,9–13]. Specifically, equilibration of aqueous dispersions of unilamellar vesicles formed from L-DLPC has been shown to lead to formation of monolayers of DLPC at the interfaces of the LC. The formation of the monolayer of L-DLPC has in turn been demonstrated to cause the LC to adopt a perpendicular (homeotropic) ordering at the aqueous interface. Additional experiments have also revealed that (i) the phase behavior of monolayers of DLPC formed at the interfaces of the nematic LC is substantially different from that observed in the absence of the nematic ordering of the LC, and (ii) that binding of proteins (such as phospholipases) to these lipid-laden LC interfaces leads to easily visualized ordering transitions in the LCs [5,6]. Whereas an increasingly complete understanding of the assembly of phospholipids at aqueous interfaces of LCs is emerging, in this paper, we move to report on the assembly of glycolipids at aqueous-LC interfaces. In particular, as a prototypical example of the wide range of glycolipids found in biological systems, we focus on the self-assembly of the monosialoganglioside GalBeta1-3GalNAcBeta1-4(NeuAcAlpha2-3)GalBeta1-4GlcBeta1-1′-ceramide (GM_1) at aqueous interfaces of thermotropic

Abbreviations: 5CB, 4′-pentyl-4-cyanobiphenyl; L-DLPC, L-α-dilauroylphosphatidylcholine; DPPC, 1,2-dipalmitoyl-*sn*-Glycero-3-phosphocholine; GM_1, monosialoganglioside GalBeta1-3GalNAcBeta1-4(NeuAcAlpha2-3)GalBeta1-4GlcBeta1-1′-Ceramide; BODIPY FL-GM_1, BODIPY FL-GalBeta1-3GalNAcBeta1-4(NeuAcAlpha2-3)GalBeta1-4GlcBeta1-1′-Ceramide.

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LCs. We note that GM_1 binds the bacterial toxin produced by *Vibrio cholerae* and, consequently, that the biophysical properties of GM_1 have been studied in detail within Langmuir monolayers and lipid bilayers.

Gangliosides, in general, are lipids with head groups comprised of oligosaccharides containing one or more *N*-acetylneuraminic acid (sialic acid) residues [14]. GM_1 contains a pentasaccharide (Fig. 1). As noted above, the self-organization of gangliosides with *in vitro* mimics of biological membranes have been widely studied [15–22] as have the interactions of protein toxins with these models of cell membranes [23–35]. In the context of the former investigations, the physicochemical characteristics of GM_1-laden interfaces have been investigated with atomic force microscopy (AFM) [16,19–21,24], light scattering techniques [17,18], surface plasmon resonance (SPR) [25], and fluorescence microscopy [36]. In this paper, we report the results of an investigation that sought to create a new class of GM_1-decorated interfaces that are prepared by self-assembling GM_1 at the interfaces of LCs. By analogy to phospholipid-decorated LCs, we hypothesized that the orientational ordering of the LC would be closely coupled to the formation of the GM_1-decorated interface, and thus that the LC ordering behavior could be used to report on the interfacial behavior of the GM_1. Although certain similarities in the orientational ordering of the LC in the presence of phospholipids and GM_1 are noted in our paper, the results of our study also reveal striking differences in the dynamics of these two systems. We end our introduction by noting that the development of methods that lead to formation of GM_1-laden interfaces of LCs, and an understanding of the equilibrium and dynamic properties of the interfaces, is a prerequisite to exploring their potential use as biomolecular interfaces at which protein toxin interactions with GM_1 can be reported via ordering transitions in LCs. In future studies, we will investigate the influence of protein toxins on the ordering of GM_1-decorated interfaces of LCs.

2. Materials and methods

2.1. Materials

GalBeta1-3GalNAcBeta1-4(NeuAcAlpha2-3)GalBeta1-4GlcBeta1-1′-Cer (GM_1) was obtained from Avanti Polar Lipids, Inc. (Alabaster, AL). Trizma-hydrochloride (Tris[hydroxymethyl]-aminomethane hydrochloride, Tris HCl), sodium azide, ethylenediaminetetraacetic acid (EDTA), and chloroform were obtained from Sigma–Aldrich (St. Louis, MO). Octadecyltrichlorosilane (OTS), sodium chloride, methanol, methylene chloride, sulfuric acid, hydrogen peroxide (30% w/v), 2-propanol, and heptane were obtained from Fisher Scientific (Pittsburgh, PA). BODIPY FL C_5-GalBeta1-3GalNAcBeta1-4(NeuAcAlpha2-3)GalBeta1-4GlcBeta1-1′-Cer (BODIPY FL-GM_1) was purchased from Molecular Probes (Eugene, OR). Sodium hydroxide was obtained from LabChem Inc. (Pittsburgh, PA). The LC 4′-pentyl-4-cyanobiphenyl (5CB) was obtained from EM Sciences (New York, NY). All chemicals were used as obtained. Deionization of a distilled water source was performed with a Milli-Q system (Millipore, Bedford, MA) to give water with a resistivity of 18.2 MΩcm. Glass microscope slides were Fisher's Finest Premium Grade obtained from Fisher Scientific. Gold specimen grids (20 μm thickness, 50 μm wide bars, and 283 μm grid spacing) were obtained from Electron Microscopy Sciences (Fort Washington, PA).

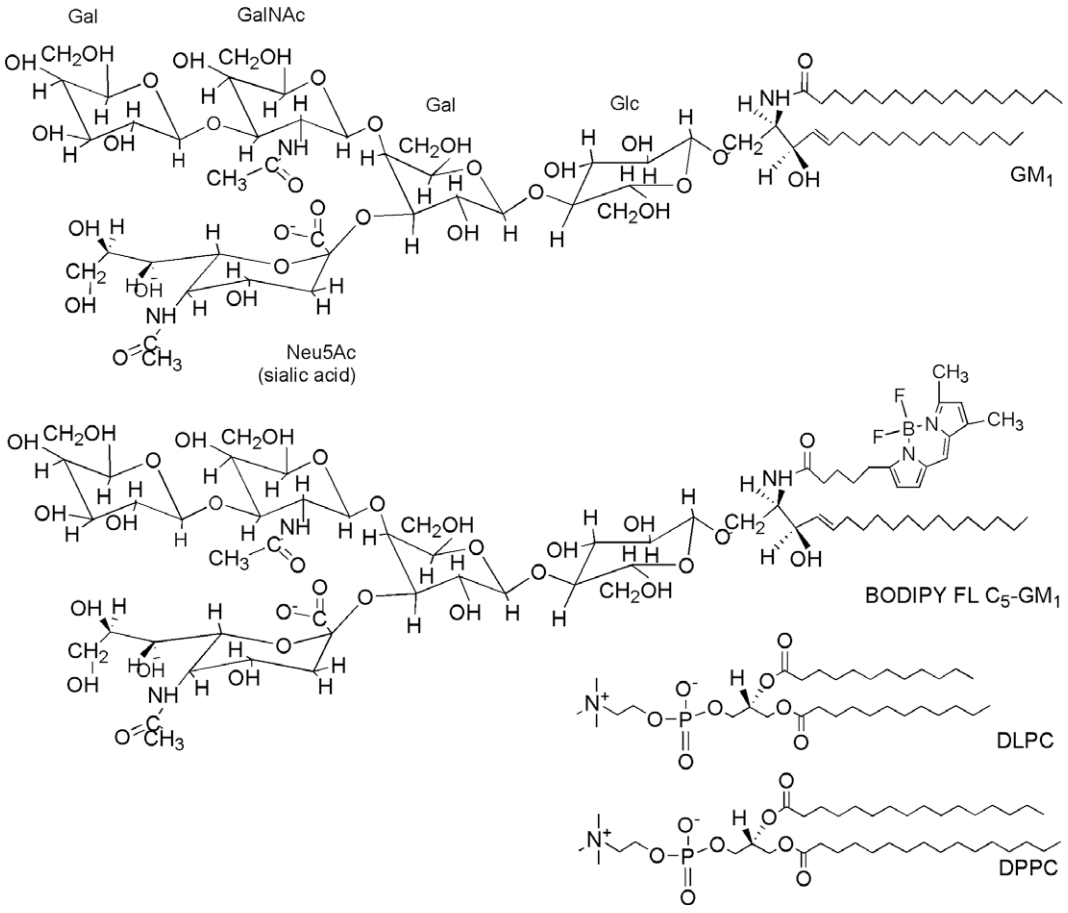

Fig. 1. Structures of GM_1, BODIPY FL-GM_1, DLPC and DPPC. Gal, galactose; Glc, glucose; GalNAc, *N*-acetylgalactosamine; Neu5Ac, *N*-acetylneuraminic acid.