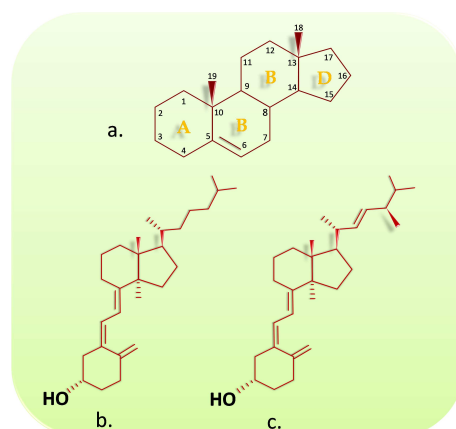**SUPPLEMENTARY INFORMATION**

FIG. 1: Chemical structure of the steroid core (a), cholecalciferol (b), and ergocalciferol (c).
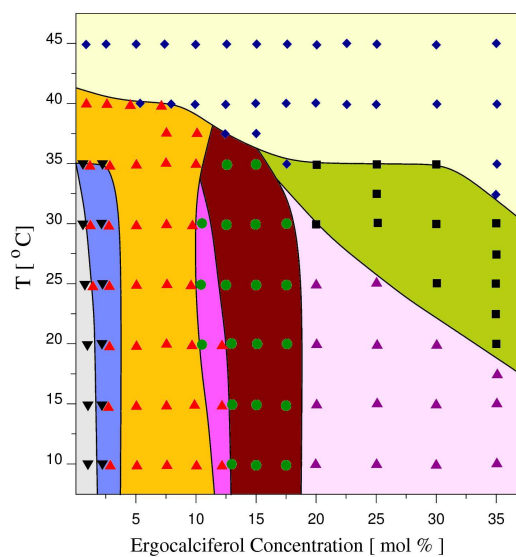

FIG. 2: Partial phase diagram of DPPC-ergocalciferol binary mixtures at 98 ± 2 % relative humidity. Only the L_α phase (♦) occurs above the chain-melting transition temperature over the whole composition range shown, whereas a variety of phases are observed at lower temperatures. As a function of increasing ergocalciferol concentration, these are: $L_{\beta'}$ (▼), $P_{\beta'}$ (▲), P_β (●), $P_{\beta'}^*$ (▲) and RC (■). Ergocalciferol was found to phase separate out of the membrane for $\phi_{ec} > 35$ mol%.

TABLE I: Diffraction data from the RC phase used to calculate the electron density profile. I denotes the relative intensity of the reflections after geometric corrections. The phases of the reflections were obtained using the pattern recognition method described in the text. $\phi_{cc} = 50$ mol%, T $= 12.5°$C.

hk	I	Phase
20	100.0	-
40	42.2	-
60	1.3	+
80	2.5	-
31	0.5	-
51	5.3	-
71	2.1	+

TABLE II: Diffraction data from the $P_{\beta'}^*$ phase used to calculate the electron density profile. I denotes the relative intensity of the reflections after geometric corrections. The phases of the reflections were obtained using the pattern recognition method described in the text. $\phi_{cc} = 25$ mol%, T $= 10.0°$C.

hk	I	Phase
10	100.0	-
20	28.7	-
30	0.2	+
40	10.9	-
11	1.1	-
2$\bar{1}$	2.2	-
21	2.3	-
3$\bar{1}$	2.9	-
31	1.3	+
4$\bar{1}$	3.1	+

TABLE III: Temperature dependence of the lamellar periodicity d (in Å) in different phases of DPPC-cholecalciferol membranes. The cholecalciferol concentration in the bilayer, ϕ_{cc}, is in mol%. Typical error in d is $\pm$ 0.03 Å.

T°C	40.0	37.5	35.0	30.0	27.5	25.0	22.5	20.0	17.5	15.0	10.0
$P'_{\beta}(\phi_{cc}=7.5)$	62.5	62.6	63.3	65.3	-	65.6	-	67.0	-	67.6	68.2
$P_{\beta}(\phi_{cc}=12.5)$	-	-	62.5	65.4	65.8	65.8	-	68.5	-	68.1	68.1
$P_{\beta'}^*(\phi_{cc}=20.0)$	-	-	-	61.0	-	61.5	-	62.5	-	62.2	62.5
$RC(\phi_{cc}=50.0)$	-	-	-	-	53.2	53.9	56.8	59.0	59.9	60.4	-

TABLE IV: Temperature dependence of the lamellar periodicity d (in Å) in different phases of DPPC-ergocalciferol membranes. The ergocalciferol concentration in the bilayer, ϕ_{ec}, is in mol%. Typical error in d is $\pm$ 0.03 Å.

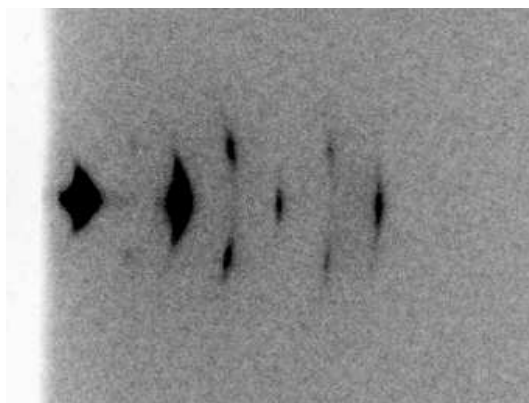| T°C	40.0	37.5	35.0	30.0	27.5	25.0	22.5	20.0	15.0	10.0
$P'_{\beta}(\phi_{ec}=7.5)$	60.2	63.4	64.2	66.2	-	68.0	-	68.9	69.6	70.2
$P_{\beta}(\phi_{ec}=15.0)$	-	-	62.2	64.2	-	66.2	-	67.4	68.0	68.6
$P_{\beta'}^*(\phi_{ec}=20.0)$	-	-	-	-	-	64.2	-	65.6	65.4	65.8
$RC(\phi_{ec}=35.0)$	-	-	-	57.0	57.6	57.9	59.4	61.4	-	-

FIG. 3: Diffraction pattern of the RC phase in DPPC-cholecalciferol membranes showing a weak [31] off-axis reflection. ϕ_{cc} = 50 mol%, T = 12.5°C.
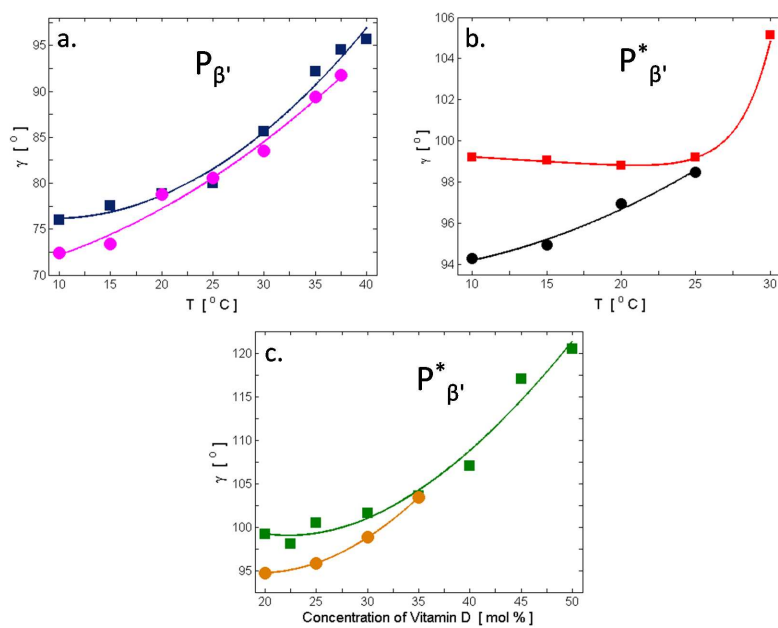

FIG. 4: Variation of the lattice parameter γ with temperature in the $P_{\beta'}$ (a) and $P^*_{\beta'}$ (b) phases of DPPC-cholecalciferol (■) and DPPC-ergocalciferol(●) bilayers. Variation of γ with secosteroid concentration in $P^*_{\beta'}$ phase (c). Secosteroid concentration is 7.5 mol% in (a) and 20 mol% in (b). T = 10°C in (c). The smooth lines are merely guides to the eye.
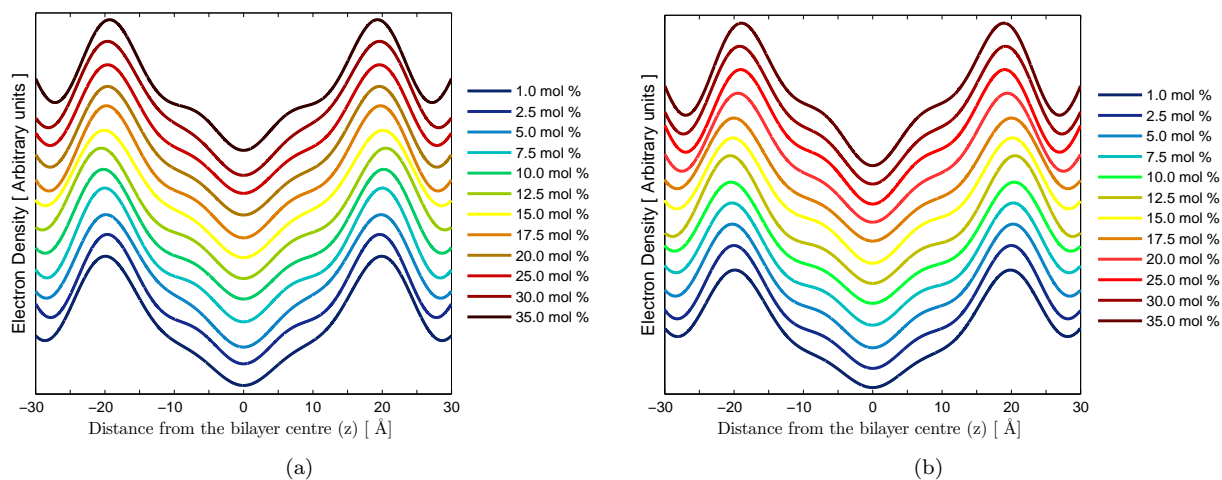
(a)

(b)

FIG. 5: Variation of the bilayer electron density profile with secosteroid concentration at $45°C$ in the L_α phase of DPPC-cholecalciferol (a) and DPPC-ergocalciferol (b) bilayers. Phases of the [h0] reflections in all cases are $(- \; - \; + \; -)$ for h going from 1 to 4.
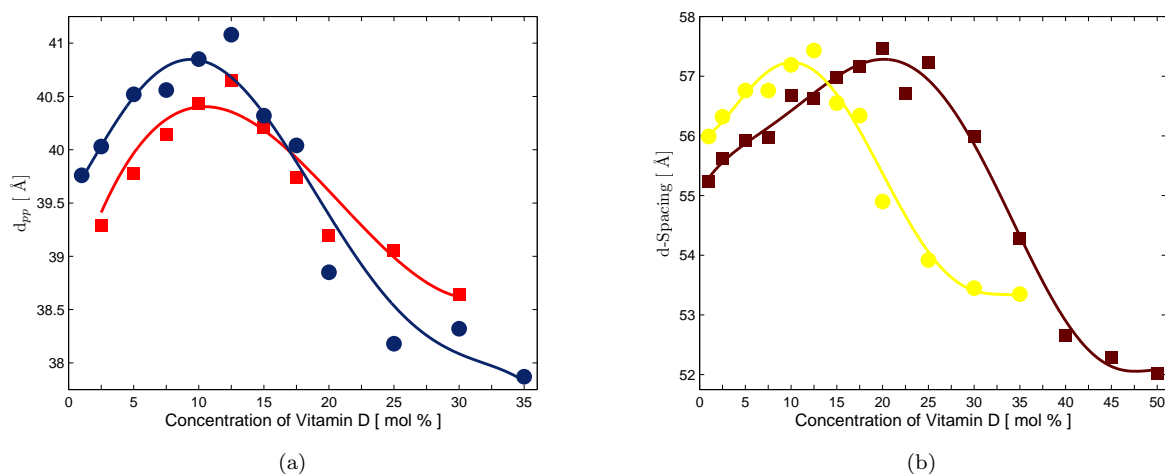

(a)

(b)

FIG. 6: Variation of the bilayer thickness (d_{pp}) (a) and d-spacing (b) with secosteroid concentration at $45°C$ in the L_α phase of DPPC-cholecalciferol (■) and DPPC-ergocalciferol(●) bilayers. The smooth lines are merely guides to the eye.
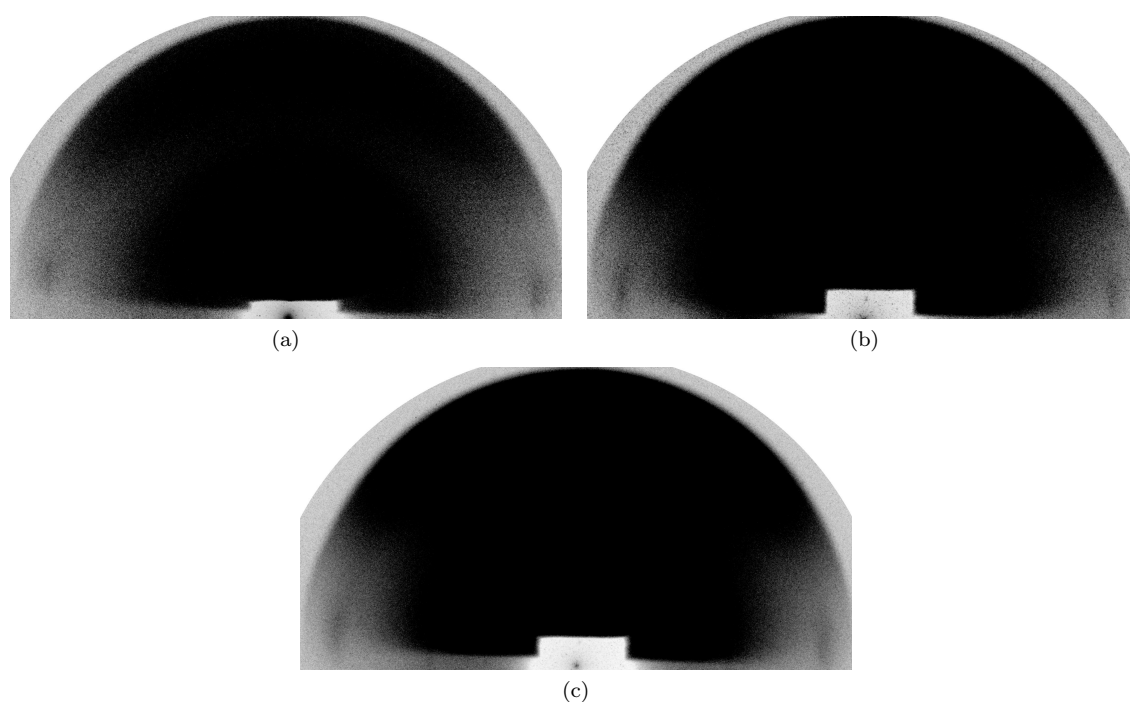
FIG. 7: WAXS patterns of the (a) P_β [$\phi_{ec} = 15.0$ mol%, T = 15.0°C], (b) $P^*_{\beta'}$ [$\phi_{ec} = 35.0$ mol%, T = 15.0°C], and (c) RC [$\phi_{ec} = 35.0$ mol%, T = 22.5°C] phases showing the equatorial reflection from in-plane chain ordering.
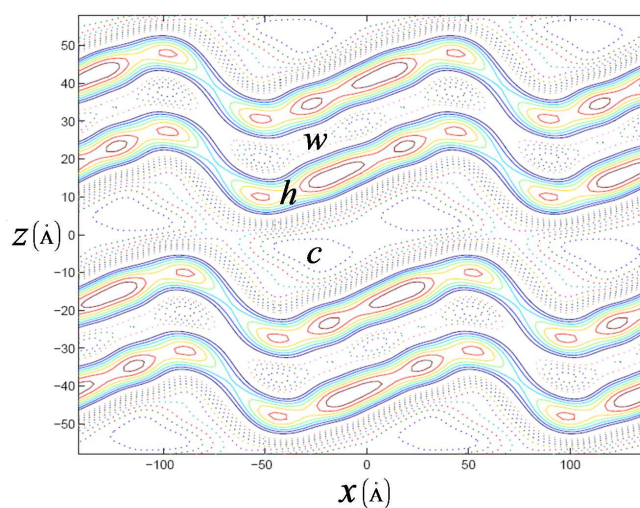

FIG. 8: Typical electron density map of the $P_{\beta'}$ phase of DPPC bilayers. Bands labeled w and h correspond to the water and head group regions, whereas that labeled c corresponds to the bilayer mid-plane. Note the much longer modulation wavelength and higher amplitude compared to the $P^*_{\beta'}$ phase of DPPC-secosteroid bilayers.