



Table S1: Infrared intensities (in  $\text{km mol}^{-1}$ ) of the amide and C=C stretching modes calculated for the fragment molecules in Fig. 5 using various electronic structure methods and basis sets.

fragment	method	basis	Amide <sup>a</sup>			CC str.
			I	II	A	
$a_2/c_2$	B3LYP	cc-pVDZ	218	266	14	5
$a_2/c_2$	B3LYP	aug-cc-pVDZ	231	278	16	7
$a_2/c_2$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	239	277	16	6
$a_2/c_2$	B3LYP	(aug)-cc-pVTZ <sup>b</sup>	236	230	17	6
$a_2/c_2$	B3LYP	(aug)-cc-pVQZ <sup>b</sup>	235	233	17	6
$a_2/c_2$	BLYP	(aug)-cc-pVDZ <sup>b</sup>	219	206	9	7
$a_2/c_2$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	239	277	16	6
$a_2/c_2$	LC-BLYP	(aug)-cc-pVDZ <sup>b</sup>	267	386	36	5
$a_2/c_2$	MP2	(aug)-cc-pVDZ <sup>b</sup>	224	278	25	5
$a_1/c_1$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	287	215	24	0
$a_2/c_2$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	239	277	16	6
$a_3/c_3$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	213	260	19	16

<sup>a</sup> I, II, and A correspond to the CO stretching, NH bending, and NH stretching modes, respectively.

<sup>b</sup> Diffuse functions are added only to the amide atoms (N, H, C, and O) or to the double bonded carbons.

Table S2: Raman activities (in  $\text{\AA}^4$  amu) of the amide and C=C stretching modes calculated for the fragment molecules in Fig. 5 using various electronic structure methods and basis sets.

fragment	method	basis	Amide <sup>a</sup>			CC str.
			I	II	A	
$a_2/c_2$	B3LYP	cc-pVDZ	6	1	57	71
$a_2/c_2$	B3LYP	aug-cc-pVDZ	10	2	63	95
$a_2/c_2$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	12	2	63	85
$a_2/c_2$	B3LYP	(aug)-cc-pVTZ <sup>b</sup>	11	2	61	85
$a_2/c_2$	B3LYP	(aug)-cc-pVQZ <sup>b</sup>	11	2	61	87
$a_2/c_2$	BLYP	(aug)-cc-pVDZ <sup>b</sup>	15	4	76	96
$a_2/c_2$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	12	2	63	85
$a_2/c_2$	LC-BLYP	(aug)-cc-pVDZ <sup>b</sup>	11	1	50	70
$a_2/c_2$	MP2	(aug)-cc-pVDZ <sup>b</sup>	18	3	63	32
$a_1/c_1$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	12	2	77	40
$a_2/c_2$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	12	2	63	85
$a_3/c_3$	B3LYP	(aug)-cc-pVDZ <sup>b</sup>	11	1	52	102
$a_3/c_3$	MP2	(aug)-cc-pVDZ <sup>b</sup>	16	2	54	38

<sup>a</sup> I, II, and A correspond to the CO stretching, NH bending, and NH stretching modes, respectively.

<sup>b</sup> Diffuse functions are added only to the amide atoms (N, H, C, and O) or to the double bonded carbons.

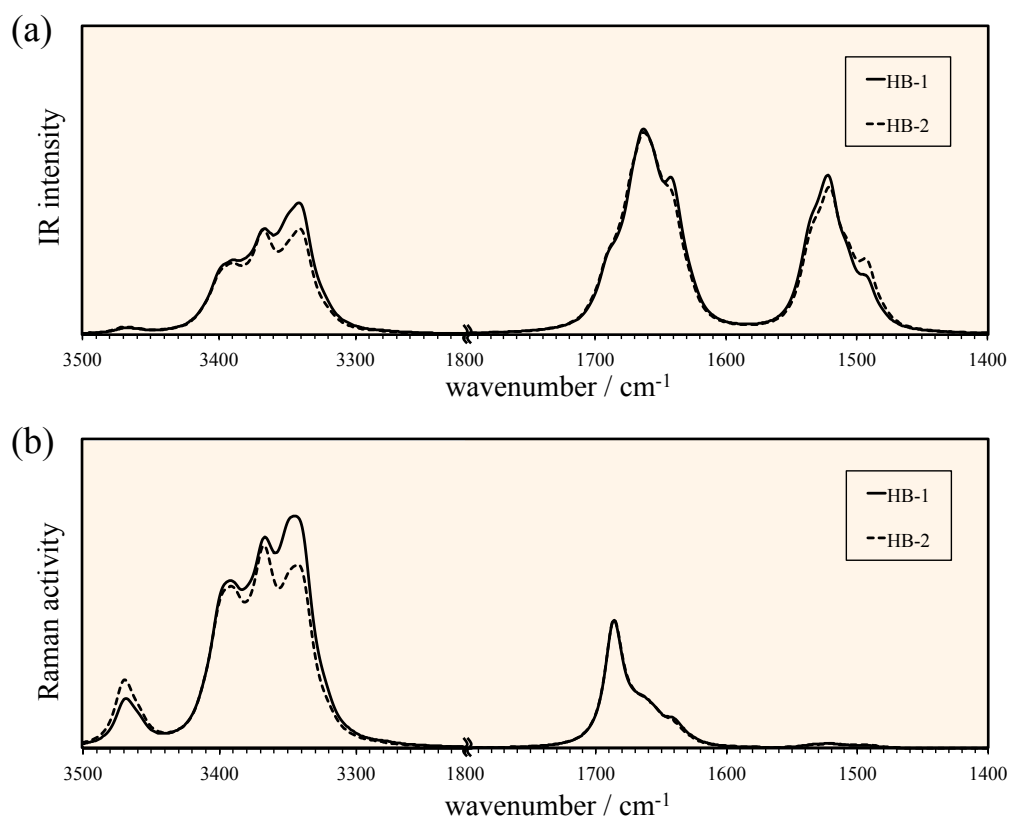


Figure S1: (a) IR and (b) Raman spectrum calculated by two different definitions of the hydrogen bond. (bold line) HB-1:  $r_{XY} < 3.5 \text{ \AA}$  and  $\theta_{HXY} < 30.0^\circ$ . (broken line) HB-2:  $r_{XY} < 3.2 \text{ \AA}$  and  $\theta_{XHY} > 150.0^\circ$ . HB-1 is the definition used in the main text.

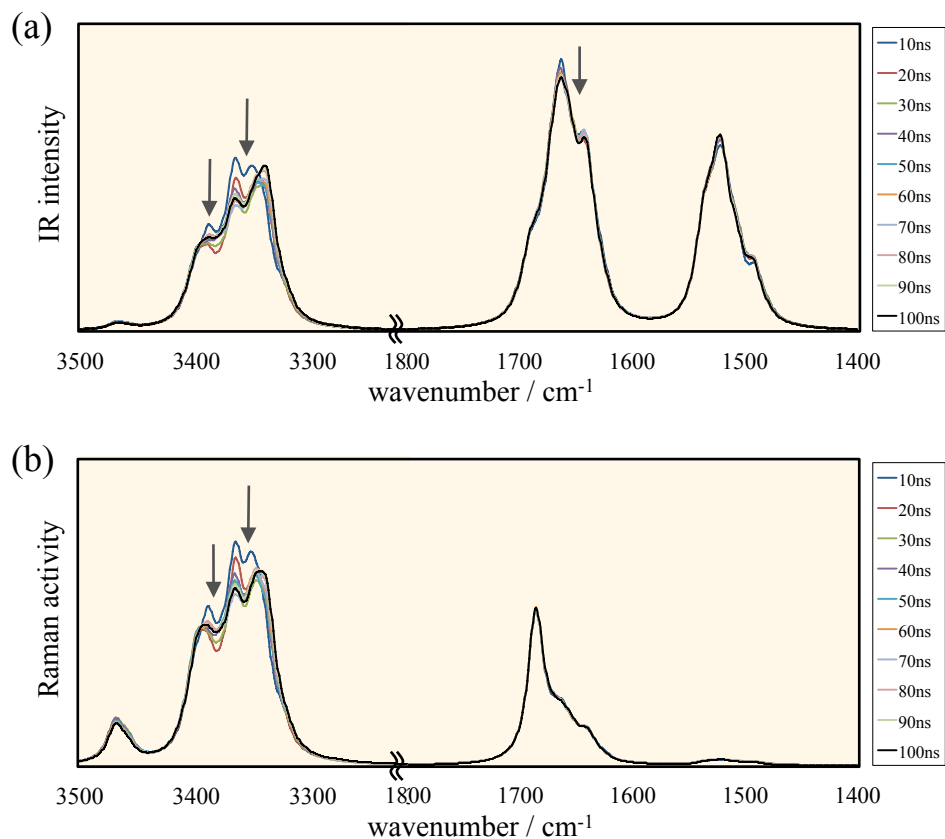


Figure S2: (a) IR and (b) Raman spectra of the SM bilayer in the gel phase obtained from different length of time average. The arrows guide the variation of the spectrum with respect to time length.

The IR and Raman spectra of the SM bilayer have been calculated by Eq. (4) performing the HB analysis and the DFT calculations every 10 ns and averaging the instantaneous spectrum up to 100 ns. Figure S4 demonstrates the convergence of the calculated spectra with respect to the length of time average. The low frequency bands corresponding to the amide I, II, and CC stretching modes are found to be hardly affected by the time-average except for a shoulder band near  $1640\text{ cm}^{-1}$  in the IR. In contrast, the amide A band in the high frequency region is more sensitive to the averaging. The spectrum, which initially shows spike and shaggy shape around  $3350 - 3400\text{ cm}^{-1}$ , is smoothed out in due course of time. The result shows that the overall shape of the spectrum is well converged after 100 ns.

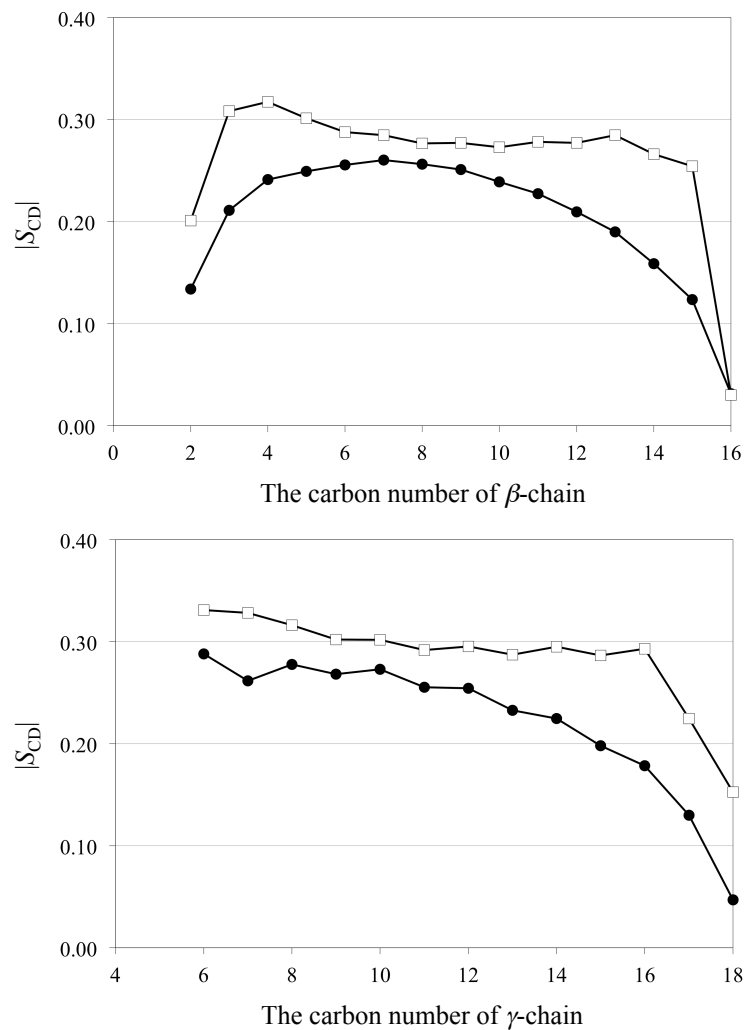


Figure S3: The order parameter ( $|S_{CD}|$ ) with respect to the carbon number in the acyl chain obtained from the simulation of the SM bilayer in the LC (filled circle) and gel (open square) phase.

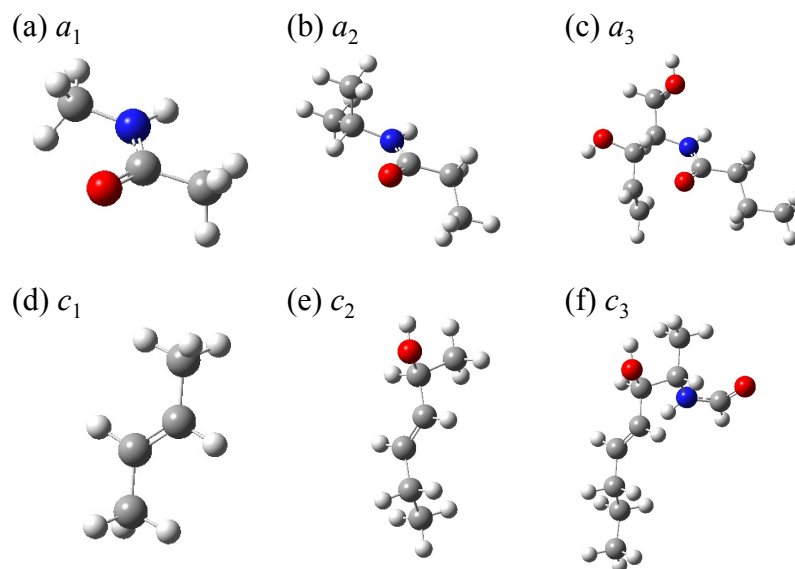


Figure S4: The geometry of the fragments of SM obtained by the DFT calculations at the level of B3LYP/(aug)-cc-pVDZ level of theory.