

Supplementary Information for

Self assembled liquid crystal polymers on photo-irradiated alignment surfaces for tailoring response properties of liquid crystal molecules

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S.1 Calibration of sum-frequency vibrational spectrum. We acquired the reflected sum-frequency (sf) spectra from a sample with *ssp* and *ppp* polarization combinations, where the letters indicate the polarizations of the sf, visible, and ir beams, respectively. All spectra were calibrated to the *ssp* signal from a z-cut LiNbO₃ at the same condition. The sum-frequency reference field is proportional to an effective second-order nonlinear optical susceptibility of

$$c_{eff}^{(2)} = c_{xzx}^{(2)} \sin q \cos^2 f + c_{yyy}^{(2)} \cos q (\sin^2 f - 2 \cos^2 f \sin f) . \quad (S-1)$$

Here f is the azimuthal angle between the incident plane and the x-axis of LiNbO₃.

By examining the azimuthal pattern, we can fix the z-cut LiNbO₃ crystal at $f = p/2$

to yield $c_{eff}^{(2)} = 2 \times 10^{-12} \text{ m/V}$ with an incident angle of $q = p/4$. The sum-frequency

reference field is generated by a surface layer with a thickness of coherence length. In

a reflective geometry, the coherence length $d = p/(k_{vis,z} + k_{ir,z} + k_{sf,z})$ is estimated

to be 50 nm . The resulting second-order nonlinear optical polarization

$$P_{sf}^{(2)} = e_0 [c_{eff}^{(2)} d] E_{vis} E_{ir} = e_0 c_s^{(2)} E_{vis} E_{ir} = \epsilon_s^{(2)} E_{vis} E_{ir} \text{ serves as the radiation source}$$

for the observed sum-frequency reference signal $I_{sf}/(I_{vis} I_{ir}) \propto |\epsilon_s^{(2)}|^2$, which can be

conveniently expressed as $|\epsilon_s^{(2)}(\text{LiNbO}_3)|^2 = 8000 \times 10^{-64} \text{ m}^2 \text{C}^2 / \text{V}^4 \text{ Å}^2$.

For the measured SFVS spectra shown in Fig. 6(b), we found the signal at

1515 cm^{-1} from the 90-nm thick LCP film to be about 1/30 of the reference signal. The SFVS spectra can be calibrated and presented in the unit of $10^{-64} \text{ m}^2 \text{C}^2 / \text{V}^4$, which are shown in Fig. S1.

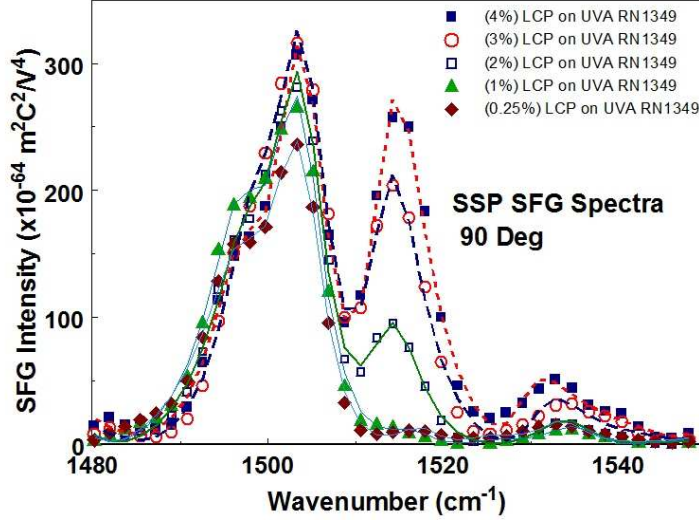


FIG. S1: Calibrated *ssp* SFVS spectra of LCP films spin coated with 0.25%, 1%, 2%, 3% and 4% LCP solutions. The polarization of the LPUV light E_{UV} was oriented at 90° relative to the incident plane of SFVS measurement.

We noticed that Masahito Oh-e, *et al.* had studied PMDA-ODA (poly[4,4'-oxydiphenylenepyromellitimide]) with SFVS and found the phenylene skeleton C–C stretch of the film at 1515 cm^{-1} yielding an intensity of

$$3.8 \times 10^{-42} \text{ m}^4 / \text{V}^2 \quad (: \quad 3 \times 10^{-64} \text{ C}^2 \text{m}^2 / \text{V}^4).^{S1}$$

For an isotropic medium such as PMDA-ODA, the SFVS signal shall originate from the surface polar layer, whose thickness was estimated to be about 5 nm. Assuming the packing density of phenyl ring is similar in PMDA-ODA and LCP, a 45-nm thick LCP layer with a polar structure can produce a SFVS intensity of $240 \times 10^{-64} \text{ C}^2 \text{m}^2 / \text{V}^4$ in a reflection geometry. The layer thickness needed is about one coherence length in a reflection geometry. This result supports the concept that the LCP is grown epitaxially to form a uniaxial structure, which yields an intense SFVS signal from the bulk.








S.2 Calculation of the vibrations of the biphenyl carbonate moiety. The calculation was

carried out with a DMol3 software package, which can model the electronic structure and energetics of molecules using density functional theory (DFT). The DFT calculation was implemented with the Perdew-Wang (PW91) generalized gradient approximation (GGA) in a double numerical plus polarization (DNP) basis set. The SCF convergence quality was better than 1×10^{-6} .

We first optimized the geometry of biphenyl carbonate moiety to an SCF convergence of energy $\leq 10^{-5}$ Ha, force ≤ 0.002 Ha/Å, and displacement ≤ 0.005 Å. The optimized structure reveals that the two phenyl rings connected to the carbonate group are in a trans configuration. The result of vibrational analysis is summarized in Table S1, which presents the normal modes relevant to the core segment with frequencies lying between 1400-1800 cm^{-1} and IR strength larger than 30 km/mol. The ring stretching modes with frequency below 1500 cm^{-1} are antisymmetric with IR transition moments perpendicular to the molecular long axis. Between 1500-1600 cm^{-1} , there are two symmetric ring distortions, which are mixed with C-H wag, with IR transition moments parallel to the molecular long axis. Other normal modes with purer symmetric stretch characteristics have vibrational frequencies higher than 1600 cm^{-1} . For SFVS study, we focused on the two symmetric ring distortions between 1500-1600 cm^{-1} in viewing that these two modes not only have an IR transition moment parallel to the molecular long axis, but also possess the character of C-H wags, which may produce significant dynamic dipoles and Raman tensors to yield intense sum frequency generation-active vibrations.

Table S1: Summary of the Vibrational Analysis of biphenyl carbonate moiety

Frequency	IR	Comment	Mode Pattern
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(cm ⁻¹)	Strength (km/mol)		
1436	45	AntiSym. \perp	 1436cm-1 mode.wmv
1440	32	AntiSym. \perp	 1440cm-1 mode.wmv
1503	128	Sym. \parallel	 1503cm-1 mode.wmv
1512	94	Sym. \parallel	 1512cm-1 mode.wmv
1615	188	Sym. \parallel	 1615cm-1 mode.wmv
1618	31	Sym. \parallel	 1618cm-1 mode.wmv
1735	235	C=O	 1735cm-1 mode.wmv

Supplementary References

- S1. Oh-e, M.; Kim, D.; Shen, Y. R. *J. Chem. Phys.* **2001**, 115, 5582-5588.