All-Liquid Crystal based High-performance Laser Protection System via Linear/Nonlinear Dual-mechanisms

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¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured in CDCl₃ on Bruker-ARX400 spectrometer at room temperature using tetramethylsilane (TMS) as internal standard. All MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer. The operation was performed at an accelerating potential of 20 KV by a linear positive ion mode with dithranol as a matrix. Elemental analysis was carried out with a Perkin-Elmer Analyzer 2400 with an accuracy of \pm 0.3%. UV-vis spectra were recorded on a Perkin /Elmer Lambda 950 UV-VIS-NIR spectrophotometer. Polarized optical microscope (POM) observations were performed with Zeiss Axio Scope A1 Microscope equipped with a hot stage. The small angle Xray scattering (SAXS) instrument used in this study was Nano-Viewer with a CCD camera (Rigaku Corp. Japan). The Z-scan measurement was carried out with a Nd: YAG laser (Pro-230, Spectra-Physics, 532 nm, 10 ns). A nanosecond laser beam was focused onto the LC cell samples through a lens and the samples moved along the optical axis near the focus, two power meters were used to record the open and closed aperture Z-scan signal through one collimation lens and a beam splitter (Fig. 2a). The OPL measurement was performed with a nanosecond Nd: YAG laser (Pro-230, Spectra-Physics, 532 nm, 10 ns). The beam intensity was controlled using neutral density filters and measured with a pyroelectrical energy meter (Coherent EMP 2000).

All reactions were carried out under Argon. Dichloromethane and acetonitrile were distilled from CaH₂. Toluene was distilled from sodium and benzophenone. All chemicals were purchased from commercial sources and used as received, unless stated otherwise.

Synthesis of Mesogenic [60] fullerenes F_A and F_B



Fig. S1 Synthetic route of the mesogenic fullerene derivative F_A .

Methyl 4-hydroxybenzoate (2): 4-Hydroxybenzoic acid (10 g, 72.4 mmol) and concentrated H₂SO₄ (5 mL) were added slowly to 150 mL CH₃OH. The mixture was refluxed for 12 h and, after cooling to r.t., excess methanol was distilled off. The solid was washed with aqueous sodium bicarbonate solution and then with cold water. The crude product was dried in an oven and further purified by column chromatography over silica gel using (ethyl acetate) as the eluent. The product **2** was isolated as a white solid (9.73 g, 88.3%). ¹H NMR (CDCl₃, 400 MHz): δ = 3.92 (3H, s), 6.37 (1H, s), 6.91 (2H, d, J = 8.0), 7.98 (2H, d, J = 8.0) ppm.

Methyl 4-((10-hydroxydecyl)oxy)benzoate (4): To a solution of methyl 4hydroxybenzoate **2** (9.6 g, 63.10 mmol), K_2CO_3 (26.4 g, 191.01 mmol) and trace amount of KI (0.8 g, 4.82 mmol) in 100 mL DMF, the 10-bromodecan-1-ol **3** (16.48 g, 69.48 mmol) was added dropwise The reaction mixture was heated at 100 °C for 20 h and then cooled to room temperature. The resulting mixture was washed with water (3×50 mL) and extracted with dichloromethane (3×50 mL). The combined organic extracts were dried with MgSO₄, and concentrated. The resulting precipitate was dried in an oven and used for the next procedure without further purification.

4-((10-Hydroxydecyl)oxy)benzoic acid (5): A solution of ester **4** (9 g, 29.18 mmol) in ethanol (200 mL) was refluxed for 5 h under nitrogen with 1 N NaOH (200 mL). The mixture was acidified with HCl and extracted with AcOEt (30 mL). The organic phase was washed with brine, dried (Na₂SO₄), filtered, and concentrated at reduced pressure. Flash chromatography on a short column of silica gel (ethyl acetate: petroleum ether = 1:2) afforded **5**, 7.30 g (85.0%), as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ = 1.36 (18H, m), 3.99 (2H, t), 4.28 (1H, t), 6.96 (2H, d, J = 8.4), 7.83 (2H, d, J = 8.4) 12.53 (1H, s) ppm.

4-((4-Hydroxyphenyl)diazenyl)benzonitrile (6): 4-Cyanoaniline (8.27 g, 70 mmol) was dissolved in a mixture of hydrochloric acid (16 mL) and water (16 mL). The

reaction mixture was then cooled in an ice bath with constant stirring and diazotised by slow addition of a solution of sodium nitrite (4.83 g, 70 mmol) in 20 mL of water (i.e. temperature below 5 °C). Phenol (6.59 g, 70 mmol) dissolved in 10% sodium hydroxide solution (45 mL) was cooled to 5 °C and the reaction mixture was stirred prior to the addition of cold diazonium salt solution. The mixture was kept in an ice bath for 30 min. Upon completion of the reaction, the mixture was poured into water (500 mL) and acidified with aqueous hydrochloric acid, where upon the orange colour product was obtained. The crude product was filtered through a Buchner funnel with gentle suction and washed with water. Purification of the solid by column chromatography over silica gel using (ethyl acetate: petroleum ether=1:3) as the eluent to give orange-red **6** (11.56 g, 74%). ¹H NMR (CDCl₃, 400 MHz): δ = 5.30 (1H, s), 6.98 (2H, d, J = 8.0), 7.80 (2H, d, J = 8.0), 7.93 (4H, t) ppm.

4-((4-Cyanophenyl)diazenyl)phenyl 4-((10-hydroxydecyl)oxy)benzoate (7): DMAP (2.98 g, 24.43 mmol) and DCC (8.11 g, 39.61 mmol) were added to a solution of **5** (7.00 g 23.78 mmol) and 4-((4-Hydroxyphenyl)diazenyl)benzonitrile **6** (5.42 g, 24.30 mmol) in dry CH₂Cl₂ (300 ml) at 0 °C . The mixture was slowly warmed up and stirred at room temperature for 24 h, and then evaporated to dryness. Purification of the solid residue by column chromatography over silica gel using (CH₂Cl₂: ethyl acetate=10:1) as the eluent to give pure orange **7** (9.38 g, 79%). ¹H NMR (CDCl₃, 400 MHz): δ = 1.33 (16H, m), 3.65 (2H, t), 4.06 (2H, t), 5.35 (1H, s), 6.99 (2H, d, J = 8.0), 7.41 (2H, d, J = 8.0), 7.83 (2H, d, J = 8.0), 8.00 (2H, d, J = 8.0), 8.04 (2H, d, J = 8.0), 8.16 (2H, d, J = 8.0) ppm.

Bis(10-(4-((4-((4-

cyanophenyl)diazenyl)phenoxy)carbonyl)phenoxy)decyl)malonate (8): A solution of malonyl dichloride (0.56 g, 3.97 mmol) in CH₂Cl₂ (10 mL) was added slowly to a dry CH₂Cl₂ (120 mL) solution of 7 (3.98 g, 7.97 mmol) and DMAP (0.97 g, 7.97 mmol) at 0 °C. The mixture was stirred at room temperature for 22 h, and evaporated to dryness. Purification of the solid residue by column chromatography over silica gel using (ethyl acetate: petroleum ether = 1:2) as the eluent to give pure orange 8 (2.63 g, 62%). ¹H NMR (CDCl₃, 400 MHz): δ = 1.44 (32H, m), 3.37 (2H, s), 4.05(4H, t), 4.15(4H, t), 6.98 (4H, d, J = 8.8), 7.40 (4H, d, J = 8.8), 7.81 (4H, d, J = 8.4), 7.98 (4H, d, J = 8.4), 8 (4H, d, J = 8.8), 8.15 (4H, d, J = 8.8) ppm.

Mesogenic [60]fullerene derivative F_A : Tetrabromomethane (0.41 g, 1.18 mmol) and DBU (0.36 g, 2.37 mmol) were added to an oxygen-free solution of **8** (1.27 g, 1.19 mmol) and C₆₀ (1.21 g, 1.67 mmol) in dry toluene (50 mL). The mixture was stirred at room temperature for 24 h under Ar and evaporated to dryness. Purification of the solid residue by column chromatography (first with toluene to eliminate unreacted C₆₀, and then with toluene: ethyl acetate = 10: 0.5) to give brown F_A (0.74 g, 35%). ¹H NMR (CDCl₃, 400 MHz): δ = 1.33 (36H, m), 4.06 (4H, t), 6.97 (4H, d, J = 8.0), 7.40 (4H, d, J = 8.0), 7.82 (4H, d, J = 8.0), 7.99 (4H, d, J = 8.0), 8.15 (4H, d, J = 8.0) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 26.04, 28.63, 29.16, 29.24, 29.40, 29.62, 29.66, 67.46, 68.38, 71.76, 80.19, 96.03, 100.01, 114.03, 114.46, 122.68, 123.38, 124.66, 132.44, 133.24, 138.90, 140.90, 141.94, 142.21, 143.01, 143.06, 143.13, 143.89, 144.64, 144.71, 145.21, 145.29, 145.43. 149.93, 154.18,

154.49, 163.78, 163.81, 164.48. Elemental analysis calcd (%) for $C_{123}H_{66}N_6O_{10}$ (1787.487): C 82.63, H 3.72, N 4.70, O 8.95; found: C 82.61, H 3.74, N 4.71, O 8.94.



Fig. S2 Synthesis route of the mesogenic fullerene derivative F_B .

4'-Cyano-[1,1'-biphenyl]-4-yl 4-((10-hydroxydecyl)oxy)benzoate (10): The synthesis of **10** used the same method as described for the preparation of **7** (9.04 g, 81%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 1.14$ (17H, m), 3.65 (2H, t), 4.05(2H, t), 6.99 (2H, d, J = 8.8), 7.33 (2H, d, J = 8.4), 7.64 (2H, d, J = 8.8), 7.69 (2H, d, J = 8.4), 7.74 (2H, d, J = 8.4), 8.16 (2H, d, J = 8.8) ppm.

Bis(10-(4-(((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)carbonyl)phenoxy)decyl) malonate (11): The synthesis of 11 used the same method as described for the preparation of 8 (3.04 g, 76%). ¹H NMR (CDCl₃, 400 MHz): δ = 1.32 (32H, m), 3.72 (2H, s), 4.05(4H, t), 4.14(4H, t), 6.98 (4H, d, J = 8.8), 7.32 (4H, d, J = 8.8), 7.63 (4H, d, J = 8.4), 7.68 (4H, d, J = 8.4), 7.74 (4H, d, J = 8.4), 8.15 (4H, d, J = 8.8) ppm.

Mesogenic [60]fullerene derivative F_B: The synthesis of F_B used the same method as described for the preparation of F_A (0.61 g, 30%). ¹H NMR (CDCl₃,): δ = 1.32 (32H, m), 4.05 (4H, t), 4.14(4H, t), 6.98 (4H, d, J = 8.0), 7.33 (4H, d, J = 9.0), 7.64 (4H, d, J = 9.0), 7.69 (4H, d, J = 9.0), 7.74 (4H, d, J = 8.0), 8.16 (4H, d, J = 9.0) ppm. ¹³C NMR (CDCl₃, 75MHz): δ = 26.04, 28.63, 29.15, 29.23, 29.33, 29.43, 29.52, 64.78, 67.54, 68.50, 71.78, 111.08, 114.41, 118.86, 121.33, 122.58, 127.71, 128.35, 132.38, 132.66, 136.65, 139.00, 140.98, 141.94, 142.21, 142.74, 143.00, 143.89, 144.61, 144.72, 144.91, 145.21, 145.29, 145.43, 151.65, 161.86, 163.86, 164.81. Elemental analysis calcd (%) for C₁₂₃H₆₆N₂O₁₀ (1731.85): C 85.30, H 3.84, N 1.62, O 9.24; found: C 85.27, H 3.85, N 1.62, O 9.26.





Fig. S3 (a) ¹H NMR, (b) ¹³C NMR, and (c) MALDI-TOF spectra of the mesogenic [60] fullerene derivative F_A .





Fig. S4 (a) ¹H NMR, (b) ¹³C NMR, and (c) MALDI-TOF spectra of the mesogenic [60]fullerene derivative F_B .



Fig. S5 POM image of focal-conic fan texture of semectic A phase for F_B at 183 °C during the cooling scan with a rate of 1 °C/ min.



Fig. S6 X-Ray diffraction pattern of $\mathbf{F}_{\mathbf{B}}$ recorded at 183 °C. q^* and $2q^*$ refer to the first and second order signals corresponding to the layer periodicity and the inset is the proposed model for the organization of $\mathbf{F}_{\mathbf{B}}$ within the smectic A phase.



Fig. S7 (a) The open aperture, (b) closed aperture Z-scan curves measured at 532 nm, 10 ns, 5.2 μ J laser and (c) optical-limiting behavior of LC E7.



Fig. S8 The open aperture (**a**) and closed aperture (**b**) Z-scan curves measured at 532 nm, 10 ns, 5.2 μ J laser for **F**_B (red-circle) and pristine C₆₀ (black-cross) in LC E7 at 25 °C (**F**_B: 20.0wt%; C₆₀: 0.1wt%).



Fig. S9 The open aperture (**a**, **c**) and closed aperture (**b**, **d**) Z-scan curves measured at 532 nm, 10 ns, 5.2 μ J laser for **F**_A and **F**_B with different concentrations in LC E7, the LC cell is 20 μ m thick.



Fig. S10 The nonlinearity parameters (a) β , (b) n_2 and (c) $\chi^{(3)}$ for F_A and F_B with different concentrations in LC E7 measured at 532 nm, 10 ns, 5.2 µJ laser.



Fig. S11 Time evolution of the UV-Vis absorption spectra of F_A in CH_2Cl_2 solution (a) from trans-PSS to cis-PSS under 365 nm light irradiation, (b) from cis-PSS back to trans-PSS in the dark.



Fig. S12 (a) Open-aperture and (b) closed-aperture Z-scan curves of F_A solution of CH_2Cl_2 in the cis and trans-states measured in the dark with the irradiation of 5.0 μ J, 10 ns, 532 nm laser light. The cis-state is obtained by irradiation with a 365 nm light from a xenon arc lamp prior to the Z-scan experiments.



Fig. S13 Optical-limiting behaviors of F_B with different concentrations in LC E7 measured at 532 nm, 10 ns laser. The insets show the nonlinear transmittance as a function of the input fluence for the samples with 20.0 wt% concentration.



Fig. S14 The UV-Vis transmittance spectra of (a) F_A and (b) F_B with different concentrations in LC E7 measured in 20 μ m thick LC cells.

- (a) Nematic LC SLC-1717 (Jiangsu Hecheng Display Co., Ltd.) Mixture of LCs with positive dielectric anisotropy ($n_0 = 1.519$, $n_e = 1.720$, $\Delta n = 0.201$)
- (b) Photo- polymerizable monomer C6M (Lab synthesized)



(c) Chiral dopant S811and R811(Merck Co. Ltd)



(d) Dye (Lab synthesized)

(e) Photo initiator 651(TCI Co., Ltd.)

Fig. S15 Chemical structures of the materials used

Table S1. The NLO parameters of FA in the trans-and cis-PSS in CH2Cl2 solution

States	β (10 ⁻¹⁰ m/W)	n ₂ (10 ⁻¹⁷ m ² /W)	Reχ ⁽³⁾ (10 ⁻¹¹ esu)	Imχ ⁽³⁾ (10 ⁻¹¹ esu)	χ ⁽³⁾ (10 ⁻¹¹ esu)
trans-PSS	2.16	-3.42	-2.00	5.36	5.72
cis-PSS	1.84	-2.72	-1.59	4.56	4.83

Table S2. NLO and OL parameters of F_A and F_B

	NLO Properties			OPL Properties		
Materials	β (10 ⁻⁸ m/W)	n ₂ (10 ⁻¹⁵ m ² /W)	χ ⁽³⁾ (10 ⁻⁹ esu)	F _{th} ^a (J/cm ²)	F _{cl} ^b (J/cm ²)	
FA	5.77	-5.25	3.40	0.31	0.06	
F _B	5.16	-5.14	3.27	0.42	0.06	

^a Limiting threshold, defined as the input fluence at which point the transmittance drops to 50% of

the linear transmittance (calculated from the insets of transmittance versus input fluence). ^bOptical clamping value. All the samples are doped in nematic LC E7 and measured in 20 µm thick parallel aligned LC cells.

Sample ^a	SLC-1717	C6M	S811	R811	Dye	F _A	651
i-L	71.7	15.0	10.0	0.00	1.50	1.50	0.30
i-R	71.7	15.0	0.00	10.0	1.50	1.50	0.30

Table S3. Formulas of the [60]fullerene-doped CLC complex samples

^aThe samples are polymerized with UV light (365 nm, 0.281 mW/cm²) for 30.0 min at 40 °C.

Sample manufacturing. Homogeneously aligned LC cells were prepared by putting together two ITO glass plates coated with alignment layer of polyimide. The alignment layer was spin-coated, thermally cured and subsequently unidirectionally buffered with a velvet cloth to ensure alignment of the LC director at the surfaces. The plates were cemented together and separated with spacers (20 μ m, 60 μ m) to assure a well-defined LC layer thickness. Subsequently, the empty cells were filled with the [60]fullerene-doped LC mixtures by capillary action.

Z-scan technique. Z-scan is a relatively simple experimental technique allowing for the third-order nonlinearity characterization. The nonlinear refractive index n_2 , the nonlinear absorption coefficient β , the real and imaginary parts of the third-order nonlinear susceptibility $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ and the third-order nonlinear susceptibility $\chi^{(3)}$ can be calculated as follows:

The normalized transmittance for the open aperture Z-scan can be written as:

$$T(z) = 1 - \frac{1 - T \quad (Z = 0)}{1 + Z^2 / Z_0^2}$$
(1)

Where z_0 is the diffraction length of the beam, and z is the sample position. The nonlinear absorption coefficient β can be obtained by the following:

$$\beta = \frac{2\sqrt{2}[1 - T(Z = 0)]}{I_0 L_{eff}}$$
(2)

Where $I_0 = \frac{E_0}{\pi \omega_0^2 \tau}$ is the intensity of laser beam at focus (Z = 0), E_0 is the laser energy, ω_0 is the radius at focus and $L_{eff} = \frac{|1 - \exp(-\beta_0 L)|}{\beta_0}$ is the effective thickness with β_0 as the linear absorption coefficient.

The normalized transmission for the closed aperture Z-scan can be written as:

$$T = 1 + \frac{4\Delta\Phi_0 x}{(x^2 + 9)(x^2 + 1)}$$
(3)

Where $x = Z/Z_0$, $\Delta \Phi = 2\pi n_2 I_0 L_{eff}/\lambda \Delta \Phi$ is on-axis phase change caused by the nonlinear refractive index of the sample

The nonlinear refractive index n_2 can be obtained by the following:

$$n_2 = \frac{\Delta T_{PV}}{0.406(1-S)^{0.25}kL_{eff}}$$
(4)

Where $k = 2\pi/\lambda$ is wave vector, λ is the laser wavelength and ΔT_{PV} is the transmittance difference between the curve peak and valley.

The third-order susceptibility $\chi^{(3)}$ can be obtained by the following:

$$|\chi^{(3)}| = \sqrt{|Re\chi^{(3)}|^2 + |Im\chi^{(3)}|^2} = \sqrt{\left|\frac{n_0^2 c}{120\pi^2}n_2\right|^2 + \left|\frac{c^2 n_0^2}{240\pi^2\omega}\beta\right|^2}$$
(5)

Where $\omega = 2\pi c/\lambda$, c is the speed of light and n_0 is the refractive index of the medium. **"Stacking" Method.** The mesogenic [60]fullerene-doped CLC complex samples were achieved by "stacking" method with the following procedure. At first, the homogeneously aligned LC cells were filled with the [60]fullerene-doped LC mixtures with left- and right-handed helical structures (LHHS, RHHS) at 70.0 °C, respectively. Following that, the cells were cooled to 40.0 °C at a rate of 1.0 °C/min and were irradiated with UV light (365 nm, 0.281 mW/cm²) for 30.0 min for bandwidth broadening purposes. Thus, the samples with LHHS and RHHS exhibiting broadband reflection were obtained. Then the upper glass slides of the two sample cells were peeled off. Finally, by layer stacking of the above two samples with LHHS and RHHS, the mesogenic [60]fullerene-doped CLC complex samples exhibiting broadband- and total-reflection were obtained.

Optical density measurement. An optical parametric oscillator (OPO, Innolas, 10 Hz repetition and 4-7 ns duration) pumped by the third-harmonic light of a Nd: YAG laser (Spitlight 1000, Innolas) was used as a light source for the optical density experiments. The beam intensity was controlled using neutral density filters and measured with a pyroelectrical energy meter (Ophir, NOVA II MeterAssy, PD10-C and PE10-C). The pump beam was focused into a spot of 2 mm diameter on the samples set perpendicularly to the laser incident direction. At each laser wavelength, data of incident and transmitted laser energy were collected, and optical density (OD) was calculated with the following equation:

$$OD = \log_{10} (1/T) = \log_{10} (E_{in}/E_{tr})$$

 E_{in} and E_{tr} were the incident and transmitted laser energy, respectively.