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SUPPORTING INFORMATION

Tuning the Photonic Properties of Chiral Nematic Mesoporous Organosilica with Hydrogen-Bonded Liquid-Crystalline Assemblies

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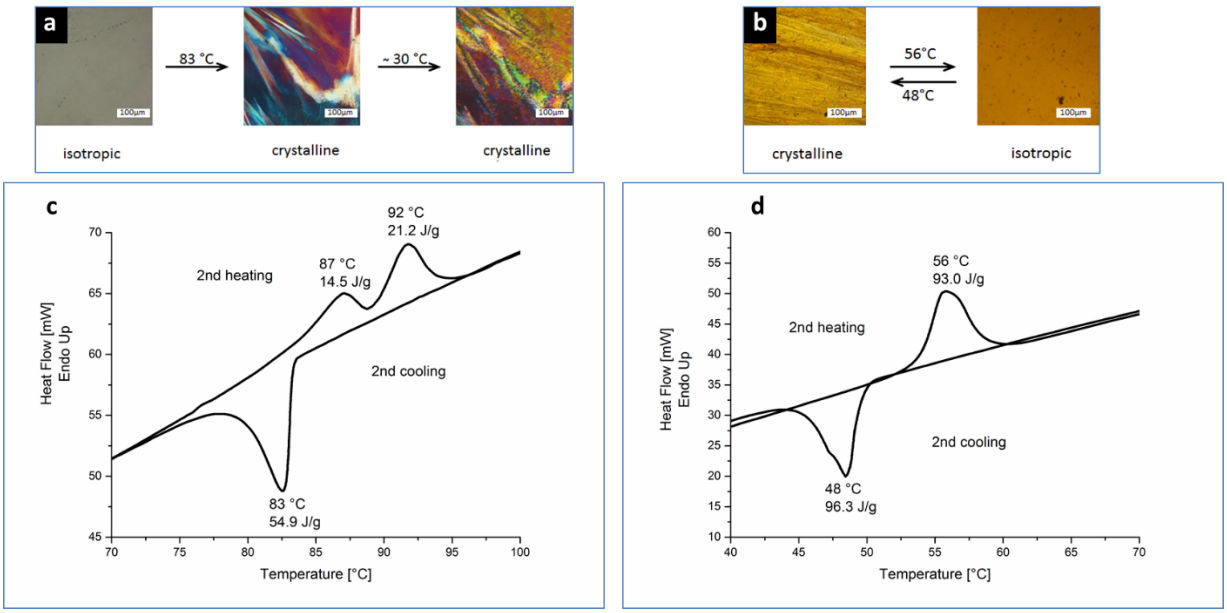

Fig. S1 Polarized optical micrographs of **1** (a) and **2b** (b) upon cooling from the isotropic melt reveal no liquid crystalline phase. (c,d) DSC profiles of **1** and **2b** for both heating and cooling cycles. Literature assigns the two signals upon heating as the melting transitions of two different crystalline states.[1,2]

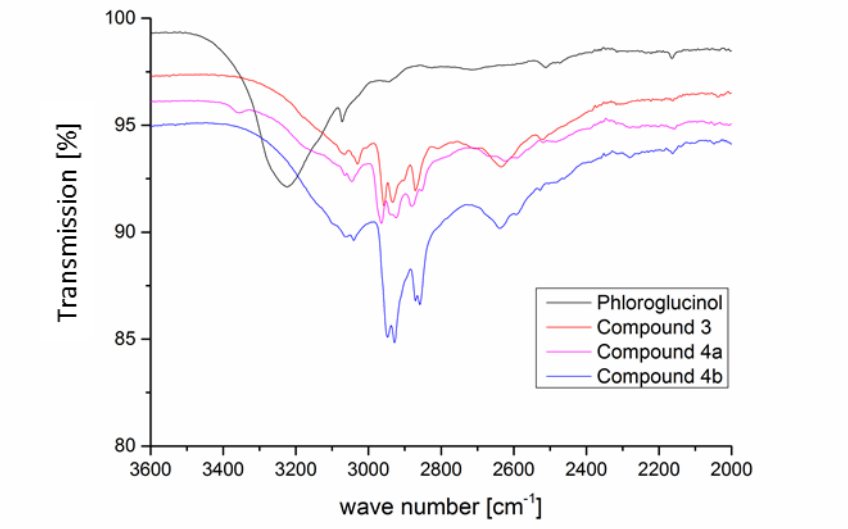

Fig. S2 IR data of compounds **3**, **4a** and **4b** verifying the hydrogen bonding as the OH absorption bands shift to lower energy.

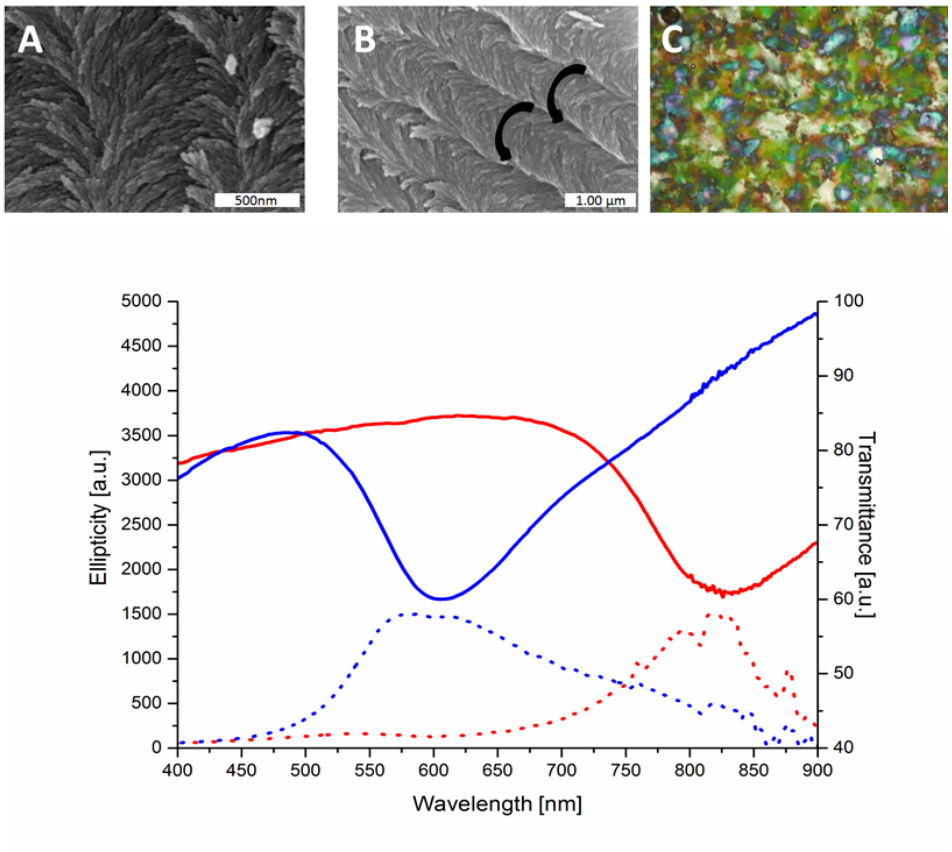

Fig. S3 SEM data of the CNMO films (a,b). Both images clearly depict the helical twist of the material. (c) POM observation showing the birefringence of the material between crossed polarizers. (d) Optical properties of CNC@CNMO films (red lines) and organosilica films upon acidic removal of the CNC (blue lines) are shown in the bottom row. Solid lines represent UV-vis spectra measured in transmittance mode, while the dotted lines represent CD spectroscopic data.

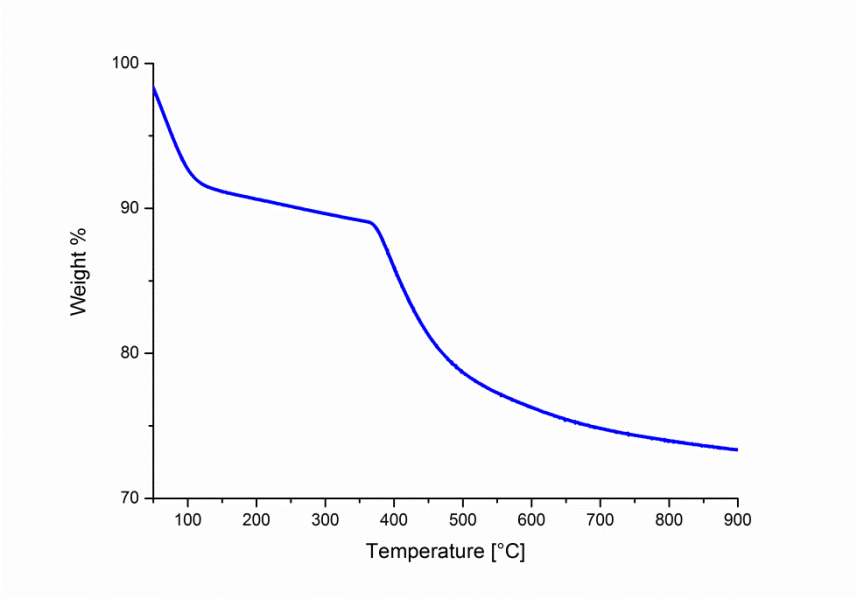

Fig. S4 TGA results of the CNMO films. The films are stable until reaching 380 °C. The weight loss up to 100 °C is due to moisture loss.

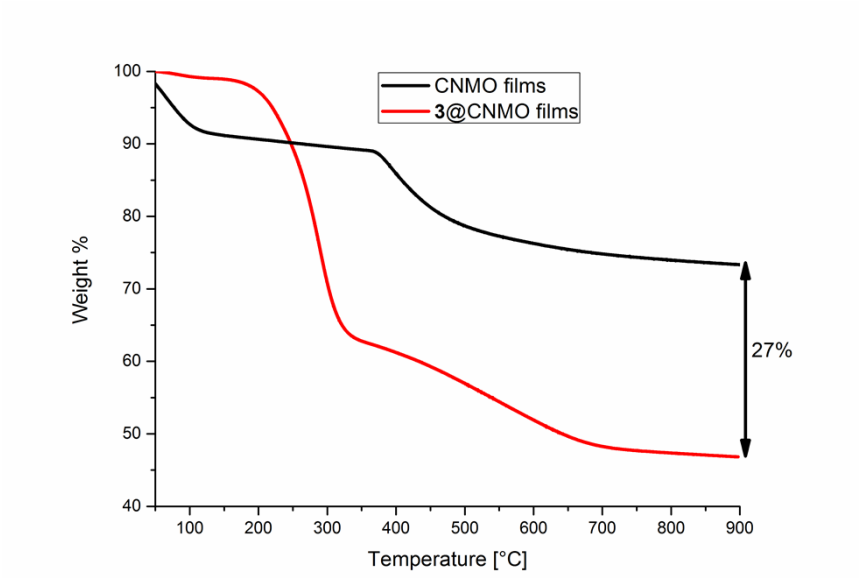

Fig S5 TGA data of CNMO films and composite **3**@CNMO films. The first weight loss of 3@CNMO films at ~ 200 °C to 350 °C corresponds to the decomposition of the LC guest 3. The second weight loss resembles the loss related to the organic spacer groups of the host material. This weight loss, starting between ~ 350 °C to 700 °C, can also be observed in the black curve for the pristine host material.

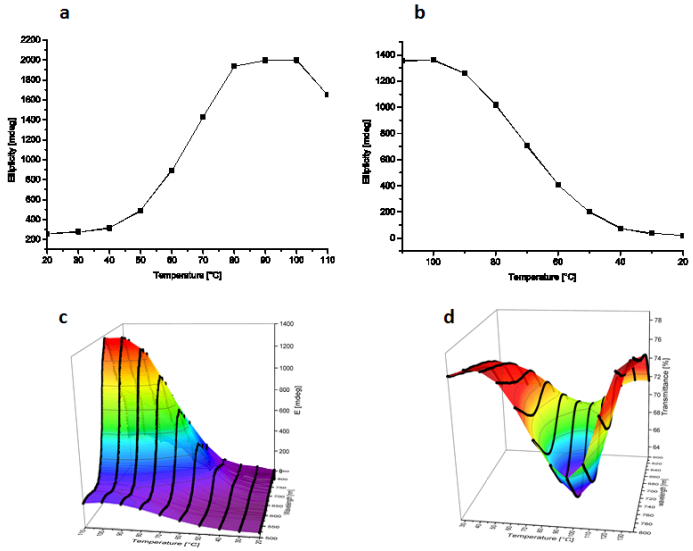

Fig S6 Variable-temperature CD spectra of **3**@CNMO upon heating (a) and cooling cycles (b); (c) variable-temperature CD spectra of **3**@CNMO upon cooling; (d) variable-temperature UV-vis spectra of **3**@CNMO upon heating. The CD graphs (a,b) were extracted from the full datasets at 727 nm at each temperature, corresponding to the maximum in the full spectra.

References

(1) Li, X.; Hong Goh, S.; Hing Lai, Y. *Liq. Cryst.* **2003**, *30*, 811–821.

(2) Bruce, D. W.; Metrangolo, P.; Meyer, F.; Pilati, T.; Präsang, C.; Resnati, G.; Terraneo, G.; Wainwright, S. G.; Whitwood, A. C. *Chemistry* **2010**, *16*, 9511–9524.

Single Crystal X-ray Diffraction

For compound **3**

Data Collection

A yellow tablet crystal of $C_{57}H_{63}N_3O_6$ having approximate dimensions of 0.11 x 0.17 x 0.43 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of -183.0 ± 0.1°C to a maximum 2θ value of 50.9°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 30.0-second exposures. The crystal-to-detector distance was 37.73 mm.

Data Reduction

Of the 73811 reflections that were collected, 17878 were unique (R_{int} = 0.050); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.78 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[2]), with minimum and maximum transmission coefficients of 0.914 and 0.991, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[3]. The material crystallizes with two crystallographically independent molecules in the asymmetric unit. In one formula unit one amine is disordered in two orientations. The disorder is essentially a 180° rotation about the C45—C46 bond. All non-hydrogen atoms were refined anisotropically. All OH hydrogen atoms were located in difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 17878 reflections and 1270 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \sum ||Fo| - |Fc|| \,/\, \sum |Fo| = 0.089$$

$$wR2 = [\sum (w\,(Fo2 - Fc2)2)\,/\,\sum w(Fo2)2]1/2 = 0.143$$

The standard deviation of an observation of unit weight[5] was 1.01. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.61 and –0.32 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf" were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All refinements were performed using the SHELXL-2012[10] via the OLEX2[11] interface.

For compound **4a**

Data Collection

A red prism crystal of $C_{48}H_{51}N_9O_6$ having approximate dimensions of 0.16 x 0.22 x 0.31 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of -183.0 ± 0.1°C to a maximum 2 θ value of 60.3°. Data were collected in a series of ϕ and ω scans in 0.5° oscillations using 2.0-second exposures. The crystal-to-detector distance was 40.09 mm.

Data Reduction

Of the 79647 reflections that were collected, 12704 were unique (R_{int} = 0.035); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.88 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[2]), with minimum and maximum transmission coefficients of 0.910 and 0.986, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[3]. All non-hydrogen atoms were refined anisotropically. All OH hydrogen atoms were located in difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 12704 reflections and 583 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \sum ||Fo| - |Fc|| / \sum |Fo| = 0.058$$

$$wR2 = [\sum (w (Fo2 - Fc2)2) / \sum w(Fo2)2]1/2 = 0.117$$

The standard deviation of an observation of unit weight[5] was 1.03. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.43 and –0.23 $e^-/Å^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf" were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All refinements were performed using the SHELXL-2012[10] via the OLEX2[11] interface.

References

(1) SAINT. Version 8.27A Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2012).

(2) SADABS. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2012).

(3) SIR97 - Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. (1999) J. Appl. Cryst. 32, 115-119.

(4) Least Squares function minimized:

$$\sum w(Fo2 - Fc2)2$$

(5) Standard deviation of an observation of unit weight:

$$[\sum w(Fo2 - Fc2)2 / (N_O - N_V)]^{1/2}$$

where: N_O = number of observations

N_V = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) SHELX-2012 Sheldrick, G. M.; Acta Cryst., A64, 112-122 (2008).
(11) OLEX2 – V1.2.2 Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341.

A. Crystal Data	Compound **3**	Compound **4a**
CCDC Number	1033683	1033684
Empirical Formula	$C_{57}H_{63}N_3O_6$	$C_{48}H_{51}N_9O_6$
Formula Weight	506.33	849.97
Crystal Colour, Habit	yellow, tablet	red, prism
Crystal Dimensions	0.11 x 0.17 x 0.43 mm	0.16 x 0.22 x 0.31mm
Crystal System	triclinic	monoclinic
Lattice Type	Primitive	Primitive
Lattice Parameters	a = 11.3178(10) Å	a = 12.4651(11) Å
	b = 21.3745(18) Å	b = 14.1037(12) Å
	c = 21.9731(18) Å	c = 24.879(2) Å
	α = 70.045(4)°	α = 90°
	β = 76.206(5)°	β = 98.502(2)°
	γ = 88.942(5)°	γ = 90°
	V = 4840.8(7) Å^3	V = 4325.8(6) Å^3
Space Group	*P*-1 (#15)	$P2_1/n$ (#14)
Z value	4	4
D_{calc}	1.216 g/cm3	1.305 g/cm3
F_{000}	1896.00	1800.00
μ(Mo-Kα)	0.78 cm^{-1}	0.88 cm^{-1}
B. Intensity Measurements		
Diffractometer	Bruker APEX DUO	Bruker APEX DUO
Radiation	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)
Data Images	1539 exposures @ 30.0 seconds	1626 exposures @ 2.0 seconds
Detector Position	37.73 mm	40.09 mm
$2\theta_{max}$	50.9°	60.3°
No. of Reflections Measured	Total: 73811	Total: 79647
	Unique: 17878 (R_{int} = 0.050)	Unique: 12704 (R_{int} = 0.035)
Corrections	Absorption (T_{min} = 0.914, T_{max}= 0.991)	Absorption (T_{min} = 0.910, T_{max}= 0.986)
	Lorentz-polarization	Lorentz-polarization
C. Structure Solution and Refinement		
Structure Solution	Direct Methods (SIR97)	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Function Minimized	Σ w (Fo^2 - Fc^2)^2	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	w=1/(σ^2(Fo^2)+(0.0658P) ^{2}+ 2.1772P)	w=1/(σ^2(Fo^2)+(0.0583P) ^{2}+ 1.1770P)
Anomalous Dispersion	All non-hydrogen atoms	All non-hydrogen atoms
No. Observations (I>0.00σ(I))	17878	12704
No. Variables	1270	583
Reflection/Parameter Ratio	14.08	21.79
Residuals (refined on F^2, all data): R1; wR2	0.089; 0.143	0.058; 0.117
Goodness of Fit Indicator	1.01	1.03
No. Observations (I>2.00σ(I))	12415	9981
Residuals (calculated on F^2): R1; wR2	0.052; 0.124	0.041; 0.106

Max Shift/Error in Final Cycle	0.00	0.00
Maximum peak in Final Diff. Map	0.61 $e^-/Å^3$	0.43 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.32 $e^-/Å^3$	-0.23 $e^-/Å^3$