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Electronic Supplementary Information for

Hydrogen-Bonded Liquid Crystals with Broad-Range Blue Phases

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1 Materials and Methods

Compounds and solvents were used as obtained from suppliers without further purification. ^{1}H- and ^{13}C-NMR-Spectra of the intermediats and products were recorded in deuterated solvents ($CDCl_3$, DMSO-d6 or MeOD) with a Bruker DRX 300 or DRX 600. Mass spectra were taken with a Bruker amaZon (MS) and IR-spectra were recorded with a Jasco FT/IR-430, ATR, IR-spectrometer. Polarized optical microscopy (POM) images were taken on a Nikon Eclipse Ni microscope with crossed polarizers equipped with a Linkam hot stage. The images were recorded by an Imaging Source camera (DFK23UX174). DSC thermograms were received using a DSC 3+/700/866/Argon from Mettler Toledo with a heating/cooling speed of 10°C/min (sample weight ~5 mg). Solid-state NMR experiments were carried out on a Varian Unity Inova 400 spectrometer using a Varian ASW high-resolution probe with a 3 µs (ca. 15°) pulse. ^{19}F-NMR spectra were obtained for **F-PHG**···($Ap_{1.5}St^{*}_{1.5}$) by cooling from the isotropic melt to the BP and chiral nematic phase.

2 Experimental Procedure and Analytical Data

2.1 General Procedure of the Single Building Blocks

Ap and **Ap*** were synthesized using the synthetic pathway of Pfletscher *et al.*,[1] while **St** and **St*** were prepared based on the description reported from Giese *et al.*[2] Analytical data of **Ap** and **St** are given in the literatures.

(*S*, *E*)-4-(4-Citronellyloxyphenyl)azopyridine (**Ap***)

m.p: 45–46 °C (cyclohexane).

$[a]_D^{20}$ = -6.77°.

^{1}H-NMR (300 MHz, MeOD): δ = 8.77 (dd, *J* = 4.6, 1.6 Hz, 2H), 8.03 – 7.89 (m, 2H), 7.67 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.08 – 6.93 (m, 2H), 5.11 (dddt, *J* = 8.4, 5.5, 2.7, 1.3 Hz, 1H), 4.18 – 4.02 (m, 2H), 2.13 – 1.95 (m, 2H), 1.95 – 1.80 (m, 1H), 1.79 – 1.55 (m, 8H), 1.41 (dddt, *J* = 11.4, 8.6, 7.5, 3.8 Hz, 1H), 1.24 (qdd, *J* = 9.7, 7.1, 5.0 Hz, 1H), 0.98 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C-NMR (75 MHz, MeOD): δ = 163.06, 157.67, 151.24, 146.87, 131.55, 125.76, 124.69, 116.32, 115.04, 66.96, 37.23, 36.11, 29.65, 25.85, 25.58, 19.69, 17.81 ppm.

MS (ESI): m/z (%): positive: calc. $C_{22}H_{29}NO + H^+$: 338.2227, found: 338.2232.

FT-IR (ATR): ν (cm^{-1}) = 3078, 3046, 2965, 2949, 2932, 2903, 2874, 2845, 2625, 1597, 1584, 1564, 1499, 1472, 1452, 1418, 1408, 1379, 1352, 1333, 1319, 1310, 1296, 1281, 1254, 1227, 1177, 1142, 1101, 1070, 1053, 1028, 1005, 988, 962, 939, 924, 880, 839, 797, 787, 739, 718, 662, 631, 604.

(*S*, *E*)-4-(4-Citronellyloxystyryl)pyridine (**St***)

m.p: 43–45 °C (cyclohexane).

$[a]_D^{20}$ = -5.24°.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.54 (dd, *J* = 4.7, 1.5 Hz, 14H), 7.51 – 7.44 (m, 14H), 7.36 (d, *J* = 5.9 Hz, 14H), 7.27 (d, *J* = 16.3 Hz, 11H), 6.94 – 6.88 (m, 1H), 6.88 (d, *J* = 16.3 Hz, 1H), 5.11 (tdt, *J* = 7.0, 2.7, 1.3 Hz, 1H), 4.09 – 3.97 (m, 1H), 2.00 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.91 – 1.78 (m, 1H), 1.79 – 1.52 (m, 1H), 1.40 (dddd, *J* = 11.9, 9.3, 8.0, 5.9 Hz, 1H), 1.31 – 1.13 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 21H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 160.07, 149.55, 133.55, 131.50, 128.74, 128.63, 124.77, 123.49, 120.88, 115.05, 66.60, 37.27, 36.23, 29.69, 27.07, 25.86, 25.60, 19.71, 17.81 ppm.

MS (ESI): m/z (%): positive: calc. $C_{22}H_{29}NO + H^+$: 336.2322, found: 336.2330.

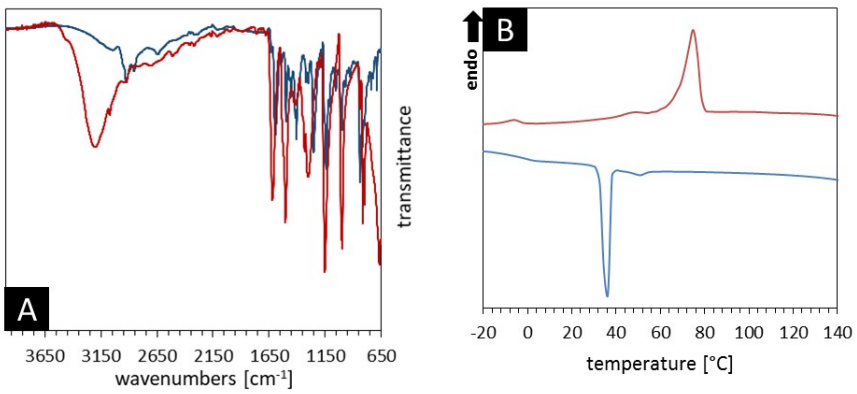
FT-IR (ATR): ν (cm^{-1}) = 3069, 3024, 2962, 2911, 2880, 2850, 1940, 1661, 1634, 1602, 1589, 1572, 1549, 1511, 1474, 1456, 1423, 1414, 1391, 1379, 1329, 1304, 1281, 1255, 1215, 1192, 1176, 1113, 1087, 1058, 1006, 989, 972, 936, 879, 833, 816, 803, 774, 739, 716, 688.

2.2 Analytic Data of the Chiral Hydrogen-bonded Assemblies

The hydrogen-bonded assemblies were obtained by dissolving the core moiety (1.0 eq. of **PHG** or **F-PHG**), the chiral (1.5 eq. of **St*** or **Ap***) and achiral side chains (1.5 eq. of **St** or **Ap**) separately in acetone. The solutions were subsequently combined and after stirring the mixture for 30 min the solvent was removed under reduced pressure at 40°C. The assemblies were then dried under vacuum for at least 10 h, yielding the desired assemblies in quantitative yields.

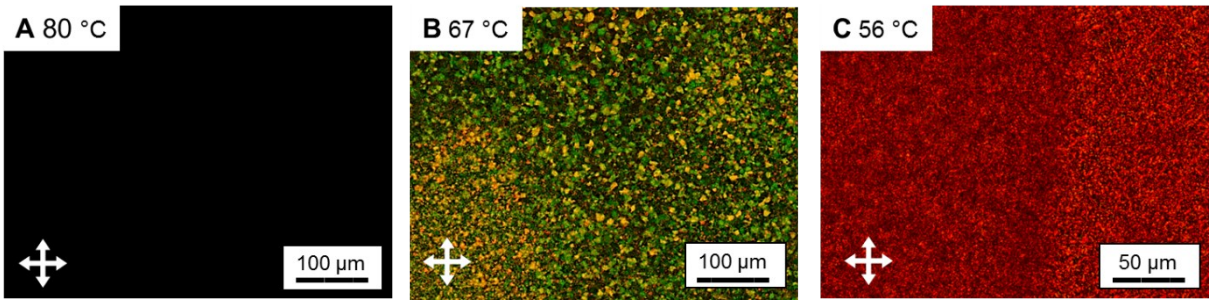
The formation of HB assemblies was confirmed by IR-spectroscopy. Typically, the broad vibration band of the OH group of the PHG (~3190 cm^{-1}) shifts to lower wavenumbers (~3050 cm^{-1}) when assembled with the pyridyl group of the side chain, with an additional signal at 2630 cm^{-1}. For the assemblies based on F-PHG, the IR signals at ~3200 and ~2690 cm^{-1} shifted to ~3020 and ~2630 cm^{-1} upon formation of the HB assemblies (Supporting Fig. 1–22).
The ideal molar ratio, which is 1(core):1.5(first side chain):1.5(second side chain) was established by ^{1}H NMR spectroscopy using methanol$_{d4}$ as solvent. Since all the assemblies feature a citronellyl side chain, we calibrated our spectra using the proton on the terminal C=C double bond, which is at 5.1 ppm in CD_3OD. This signal can be compared with those of the O-CH_2 protons, which are at 4 ppm (4 protons in total from the two different side chains). It can also be compared with the signal of the two protons in the FPHG core at 5.85 ppm (Ideal integral of 1.33) or that of the three protons in the PHG core at 5.8 ppm (Ideal integral of 2). In general, we observed a very good to an excellent agreement to our proposed 1:1.5:1.5 ratio and the error is in all cases below 5%.

[PHG/(*E*)-4-(4-Octyloxyphenyl)azopyridine/(*S*, *E*)-4-(4-Citronellyloxyphenyl)azopyridine]$_{1/1.5/1.5}$ PHG···($^{Ap}_{1.5}{}^{Ap^*}_{1.5}$)

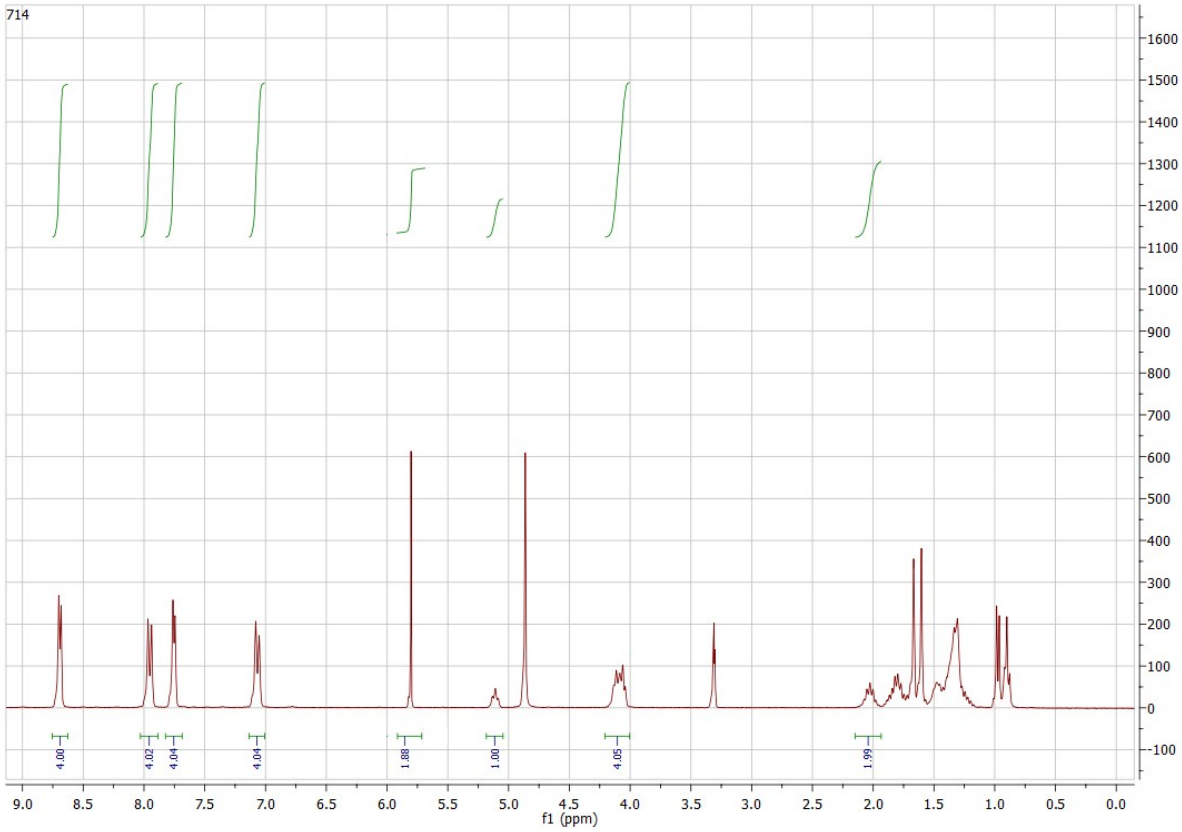


Supporting Figure 1. IR spectra (A) of **PHG** (red) and **PHG**···($^{Ap}_{1.5}{}^{Ap^*}_{1.5}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 2924, 2854, 2644, 2387, 2350, 2314, 2288, 2112, 1938, 1765, 1681, 1632, 1592, 1582, 1537, 1499, 1467, 1453, 1406, 1321, 1300, 1252, 1178, 1141, 1110, 1062, 1051, 1014, 1000, 970, 946, 926, 869, 836, 816, 797, 738, 721, 687 cm^{-1}.



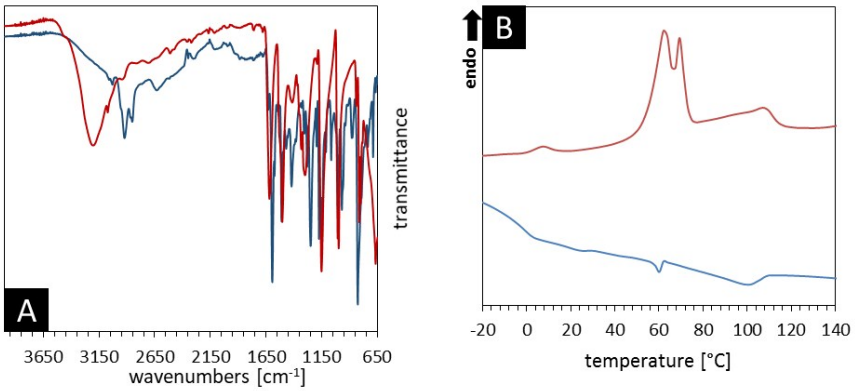
Supporting Figure 2. POM images taken upon cooling of **PHG**···($^{Ap}_{1.5}{}^{Ap^{*}}_{1.5}$) in its isotropic (A), blue phase I (B) and chiral nematic phase (C).



Supporting Figure 3. ^{1}H NMR spectrum of **PHG**···($^{Ap}_{1.5}{}^{Ap^{*}}_{1.5}$) in CD_3OD.

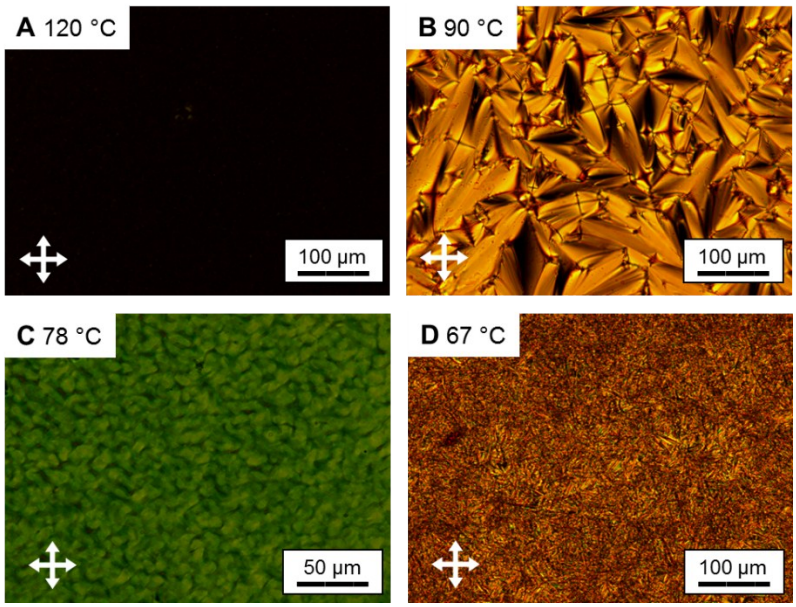
[PHG/(*E*)-4-(4-Octyloxystyryl)pyridine/(*S*, *E*)-4-(4-Citronellyloxystyryl)pyridine]$_{1/1.5/1.5}$

PHG···($St_{1.5}St^{*}_{1.5}$)

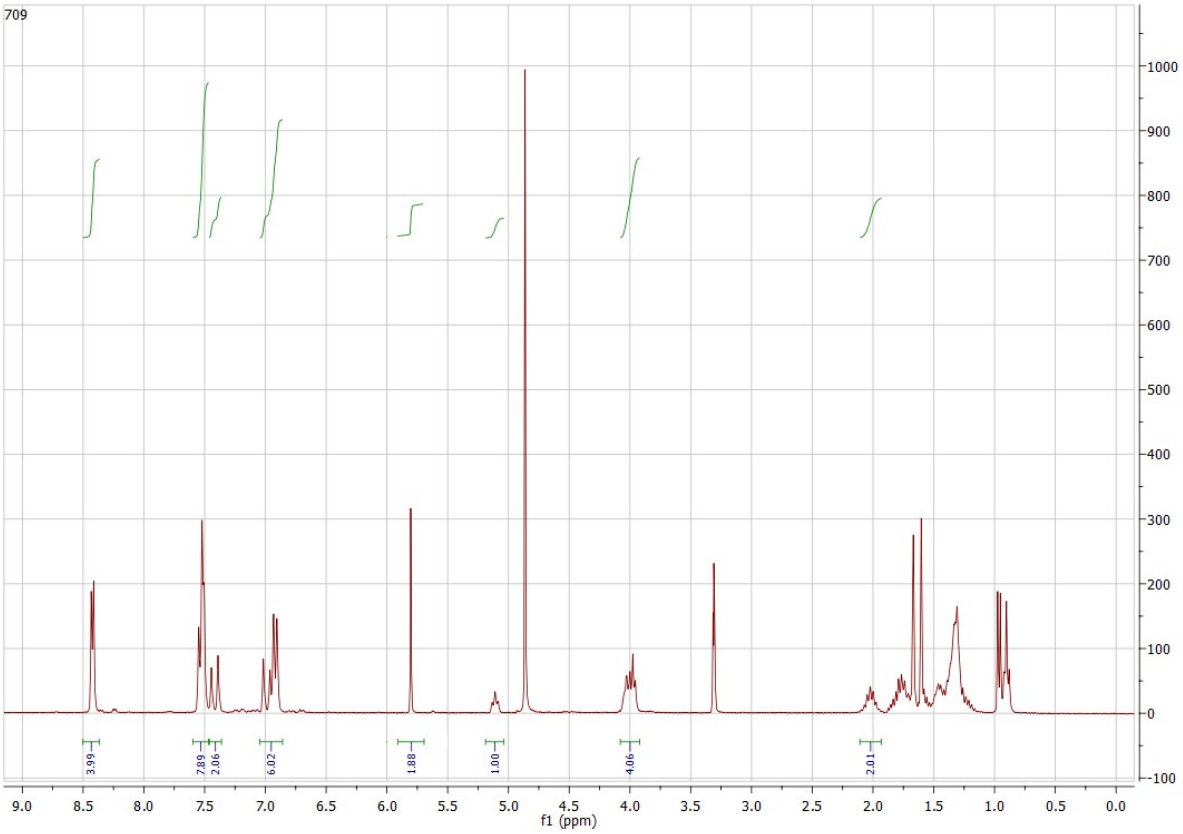


Supporting Figure 4. IR spectra (A) of **PHG** (red) and **PHG**···($St_{1.5}St^{*}_{1.5}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3030, 2962, 2924, 2914, 2877, 2646, 2358, 2343, 2322, 1632, 1594, 1575, 1552, 1525, 1511, 1474, 1418, 1380, 1306, 1282, 1251, 1195, 1175, 1162, 1149, 1113, 1092, 1065, 1000, 967, 936, 882, 827, 766, 735, 686, 668 cm^{-1}.

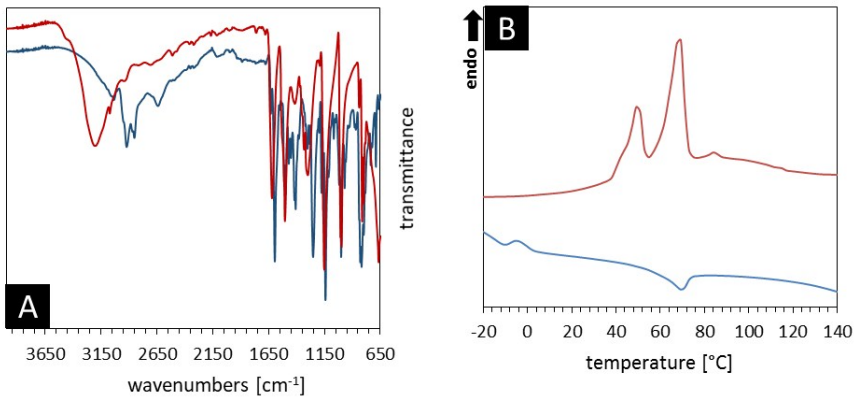


Supporting Figure 5. POM images taken upon cooling of **PHG**···($St_{1.5}St^{*}_{1.5}$) in its isotropic (A), chiral nematic (B), and oily-like TGBA (C) and chiral smectic A (D).



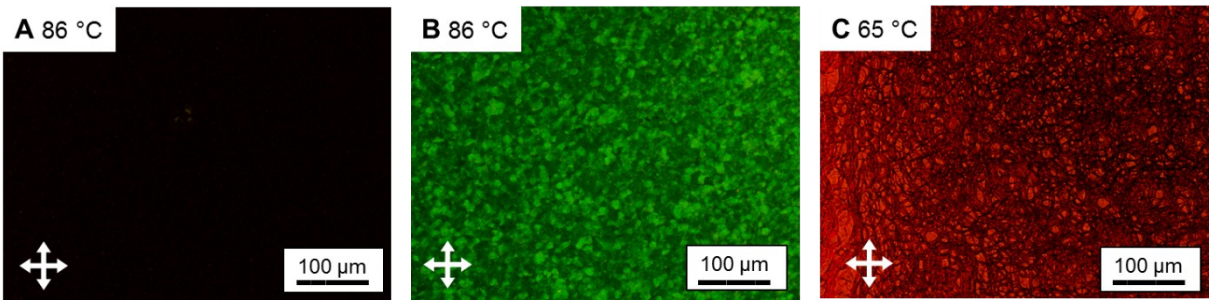
Supporting Figure 6. ^{1}H NMR spectrum of **PHG**···($St_{1.5}St^{*}_{1.5}$) in CD_3OD.

[PHG/(*E*)-4-(4-Octyloxyphenyl)azopyridine/(*S*, *E*)-4-(4-Citronellyloxystyryl)pyridine]$_{1/1.5/1.5}$ PHG···($Ap_{1.5}St^{*}_{1.5}$)

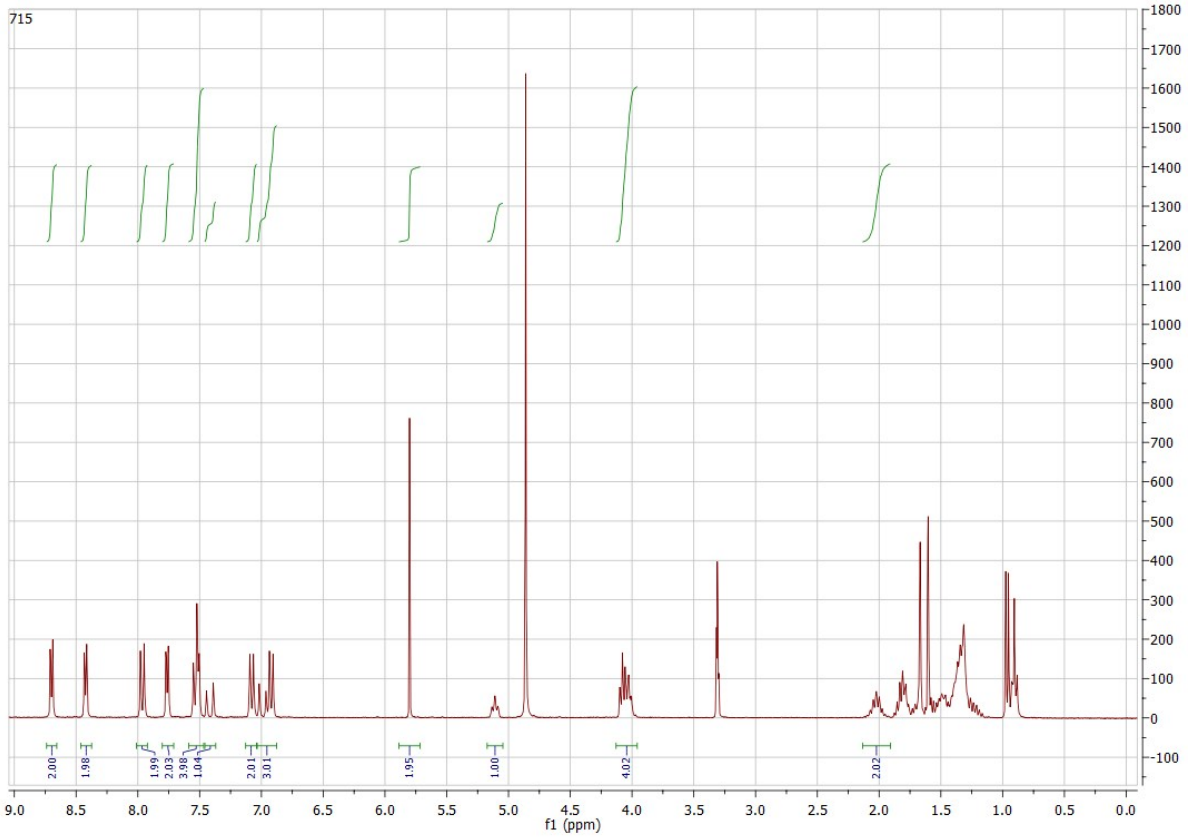


Supporting Figure 7. IR spectra (A) of **PHG** (red) and **PHG**···($Ap_{1.5}St^{*}_{1.5}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3036, 2922, 2869, 2852, 2639, 2395, 2350, 2322, 2114, 2000, 1887, 1679, 1630, 1595, 1552, 1512, 1498, 1470, 1450, 1418, 1408, 1380, 1301, 1282, 1252, 1196, 1177, 1160, 1141, 1114, 1067, 1050, 1018, 1000, 969, 932, 869, 829, 818, 798, 736, 723, 689, 666 cm^{-1}.

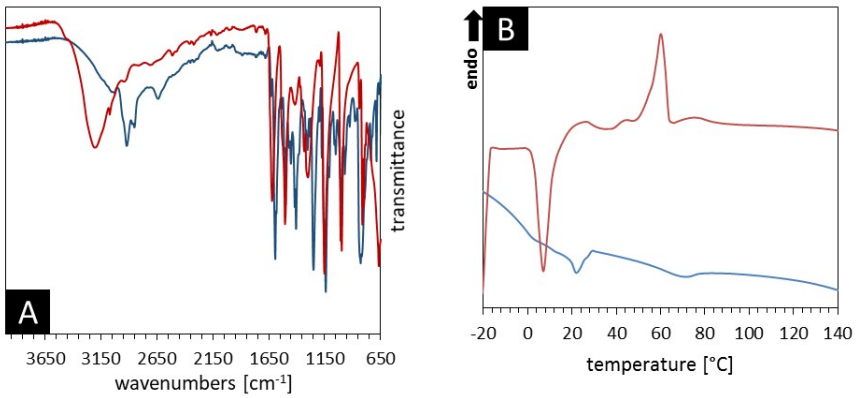


Supporting Figure 8. POM images taken upon cooling of **PHG**···($Ap_{1.5}St^{*}_{1.5}$) in its isotropic (A), blue phase I (B) and chiral nematic phase (C).



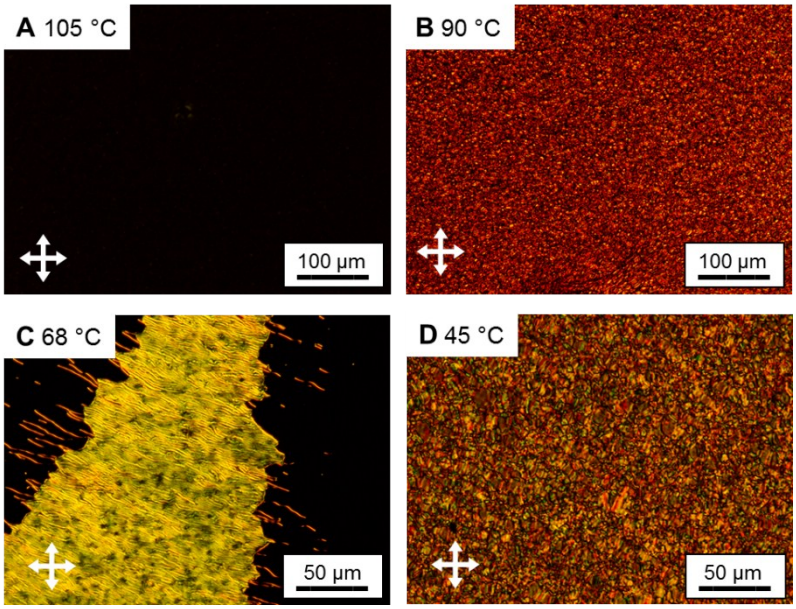
Supporting Figure 9. ^{1}H NMR spectrum of **PHG**···($Ap_{1.5}St^{*}_{1.5}$) in CD_3OD.

[PHG/(*S*, *E*)-4-(4-Octyloxystyryl)pyridine/(*E*)-4-(4-Citronellyloxyphenyl)azopyridine]$_{1/1.5/1.5}$ PHG···($^{St}_{1.5}Ap^{*}_{1.5}$)

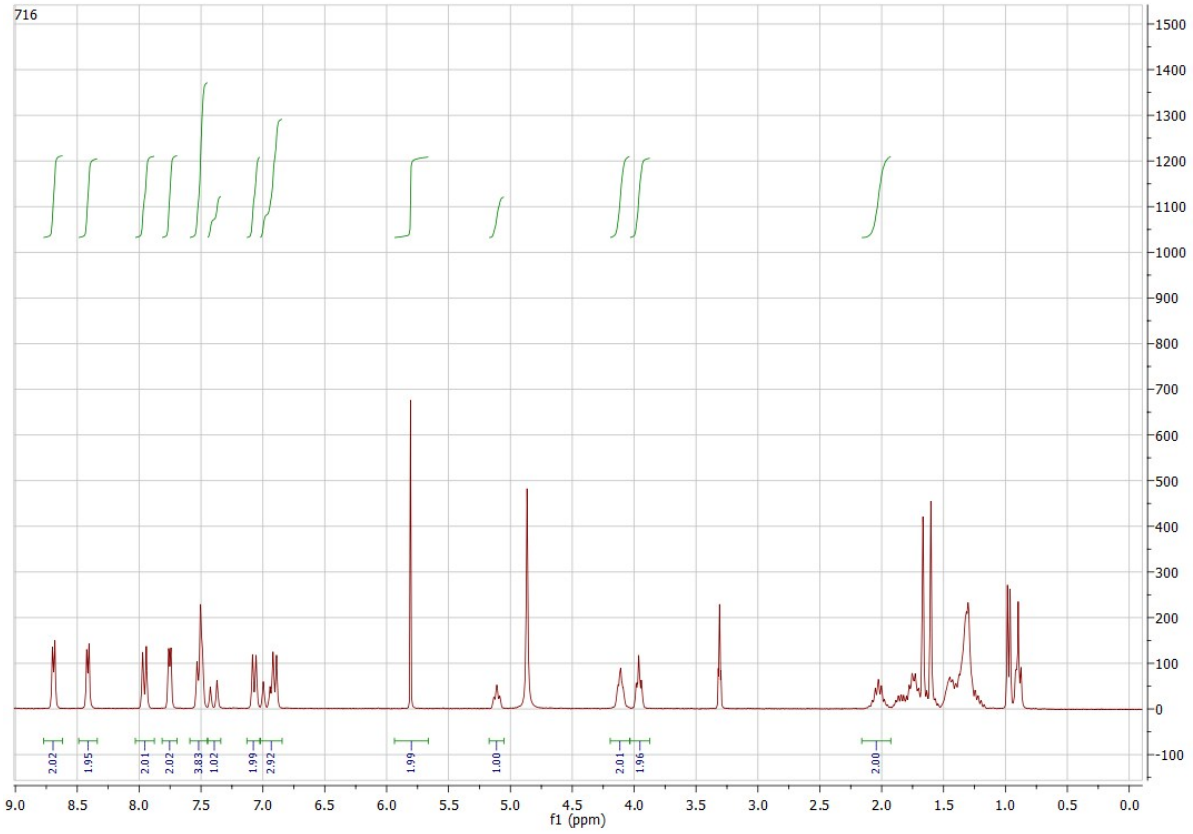


Supporting Figure 10. IR spectra (A) of **PHG** (red) and **PHG**···($^{St}_{1.5}Ap^{*}_{1.5}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3047, 2922, 2851, 2641, 2349, 2317, 2288, 2170, 2113, 1888, 1755, 1680, 1630, 1594, 1554, 1531, 1512, 1498, 1469, 1454, 1419, 1408, 1304, 1282, 1250, 1196, 1175, 1148, 1112, 1065, 1052, 1001, 969, 939, 877, 841, 826, 792, 734, 687, 665 cm^{-1}.

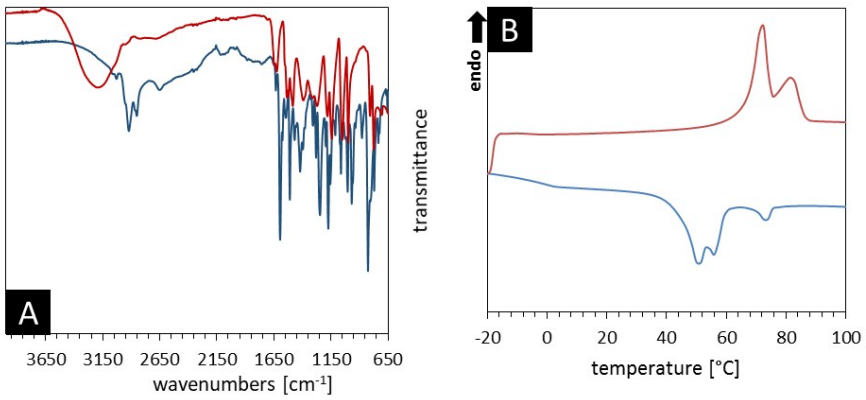


Supporting Figure 11. POM images taken upon cooling of **PHG**···($^{St}_{1.5}Ap^{*}_{1.5}$) in its isotropic (A), chiral nematic phase (B), TGBA (C) and chiral smectic A phase(D).



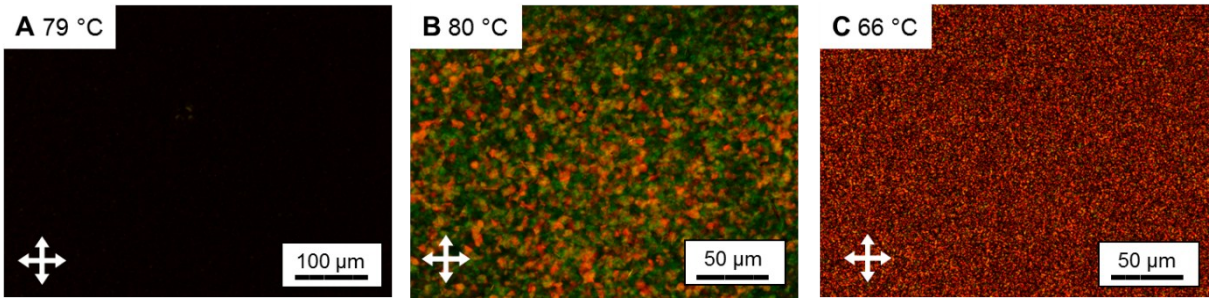
Supporting Figure 12. ^{1}H NMR spectrum of **PHG**···($^{St_{1.5}Ap^{*}_{1.5}}$) in CD_3OD.

[F-PHG/(*E*)-4-(4-Octyloxyphenyl)azopyridine/(*S*, *E*)-4-(4-Citronellyloxyphenyl)azopyridine]$_{1/1.5/1.5}$ F-PHG···($^{Ap_{1.5}Ap^{*}_{1.5}}$)

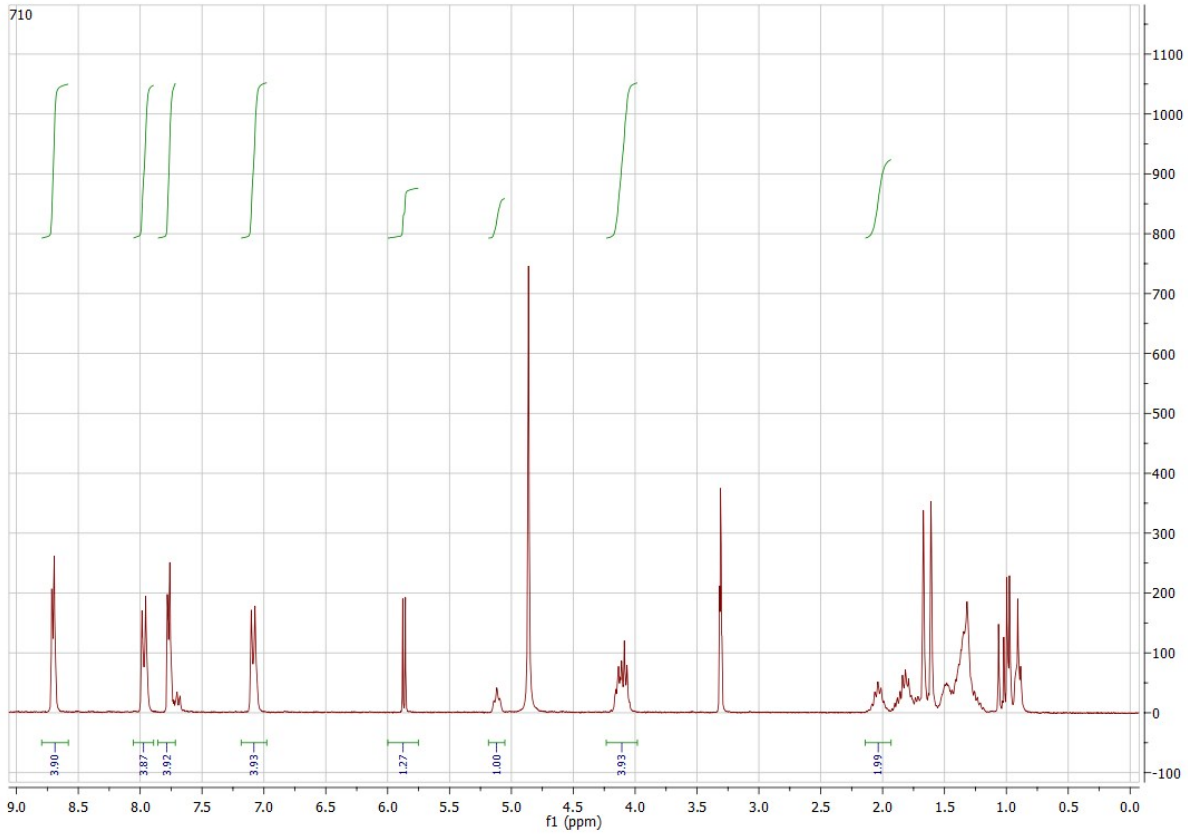


Supporting Figure 13. IR spectra (A) of **F-PHG** (red) and **F-PHG**···($^{Ap_{1.5}Ap^{*}_{1.5}}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3042, 2919, 2870, 2853, 2650, 2590, 2325, 2288, 1651, 1594, 1583, 1548, 1499, 1471, 1453, 1418, 1407, 1320, 1297, 1253, 1205, 1174, 1141, 1109, 1070, 1051, 1003, 971, 926, 838, 811, 796, 771, 738, 723, 652 cm^{-1}.

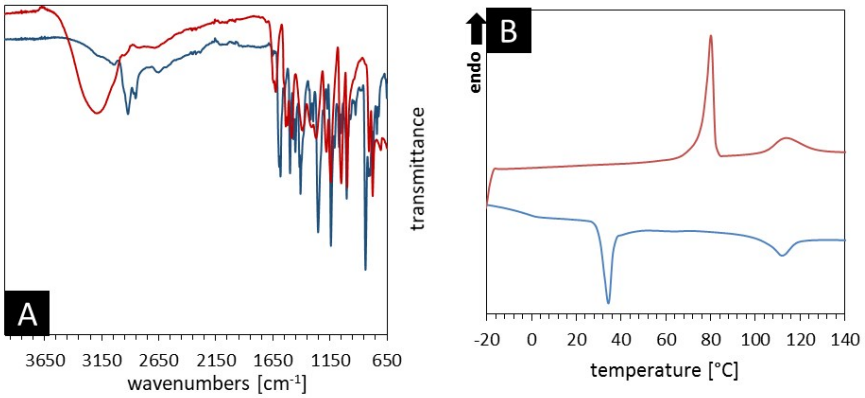


Supporting Figure 3. POM images taken upon cooling of **F-PHG**···($Ap_{1.5}Ap^{*}_{1.5}$) in its isotropic (A), blue phase I (B) and chiral nematic phase (C).



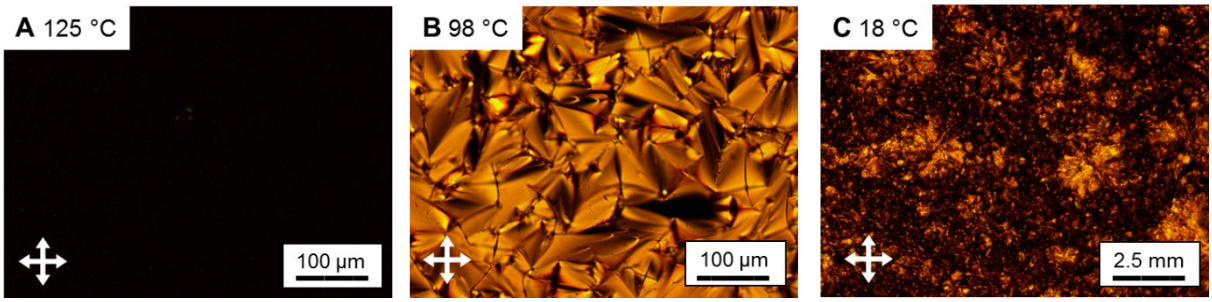
Supporting Figure 15. ^{1}H NMR spectrum of **F-PHG**···($Ap_{1.5}Ap^{*}_{1.5}$) in CD_3OD.

[F-PHG/(*E*)-4-(4-Octyloxystyryl)pyridine/(*S*, *E*)-4-(4-Citronellyloxystyryl)pyridine]$_{1/1.5/1.5}$ F-PHG$\cdots(^{St_{1.5}}St^{*}_{1.5})$

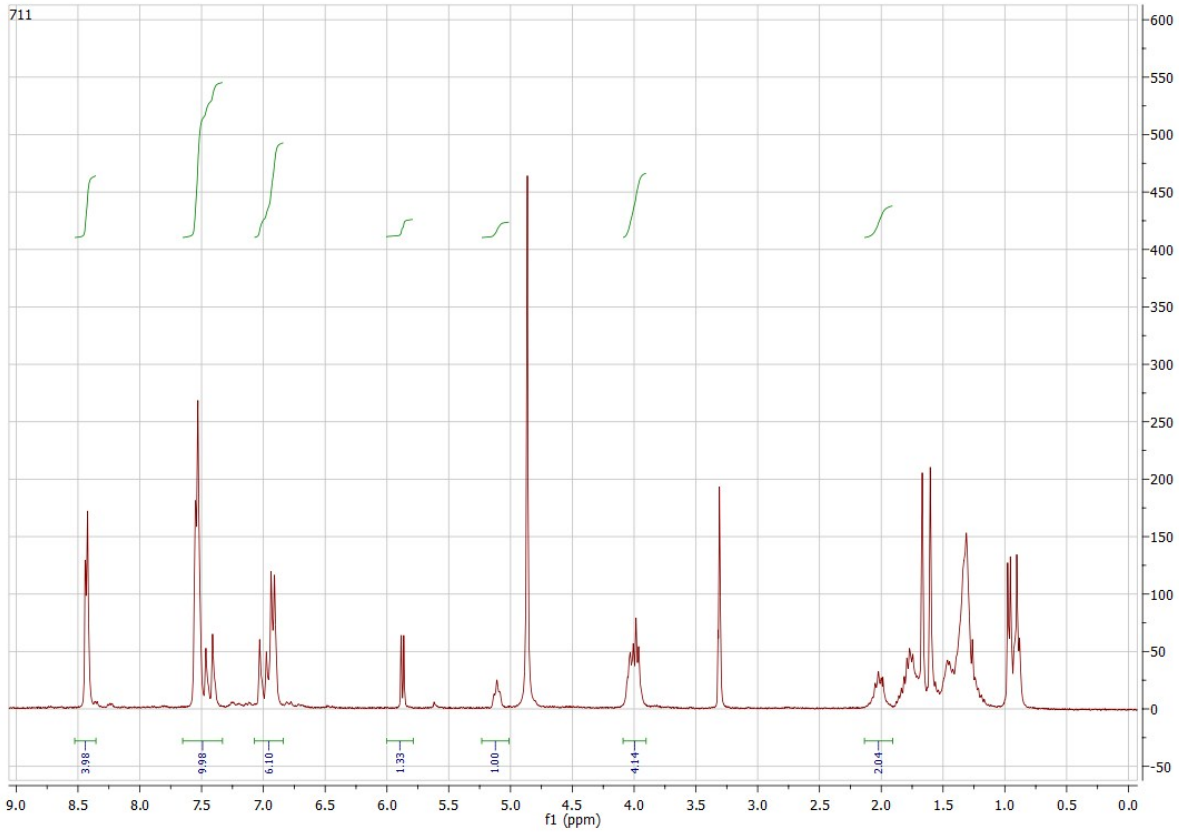


Supporting Figure 4. IR spectra (A) of **F-PHG** (red) and **F-PHG**$\cdots(^{St_{1.5}}St^{*}_{1.5})$ (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3029, 2921, 2852, 2650, 2355, 2116, 1885, 1759, 1633, 1596, 1575, 1545, 1510, 1468, 1420, 1396, 1329, 1308, 1280, 1246, 1195, 1173, 1156, 1112, 1062, 1021, 1004, 968, 936, 878, 825, 805, 771, 735, 666, 655 cm^{-1}.

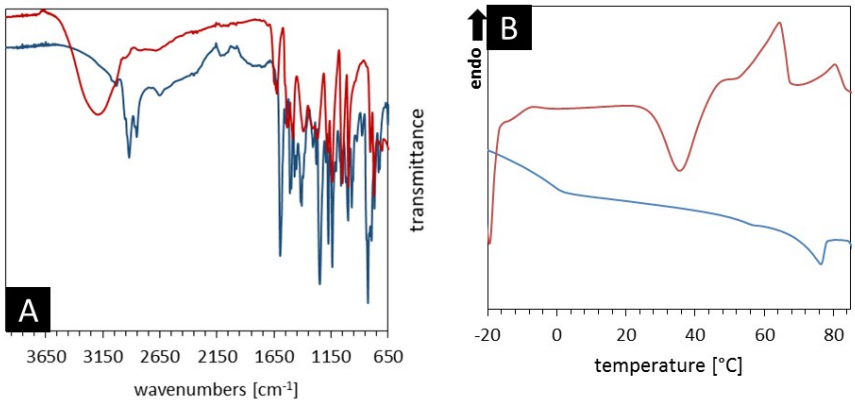


Supporting Figure 5. POM images taken upon cooling of **F-PHG**$\cdots(^{St_{1.5}}St^{*}_{1.5})$ in its isotropic (A), chiral nematic (B) and crystalline phase (C).



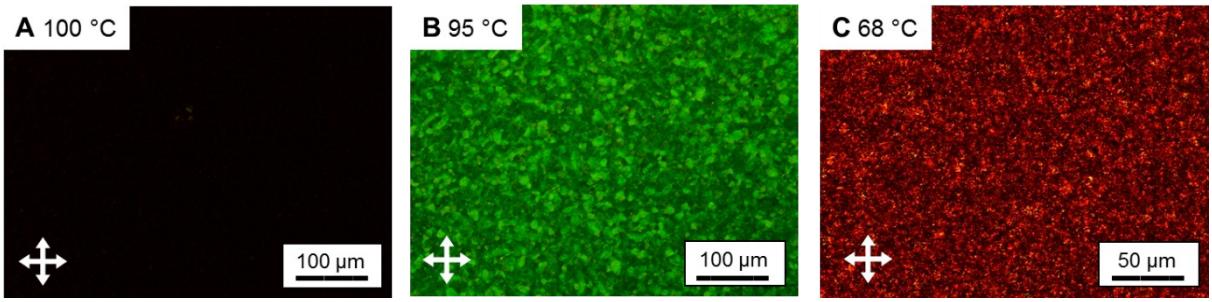
Supporting Figure 18. ^{1}H NMR spectrum of **F-PHG**···($St_{1.5}St^{*}_{1.5}$) in CD_3OD.

[F-PHG/(*E*)-4-(4-Octyloxyphenyl)azopyridine/(*S*, *E*)-4-(4-Citronellyloxystyryl)pyridine]$_{1/1.5/1.5}$ F-PHG···($Ap_{1.5}St^{*}_{1.5}$)

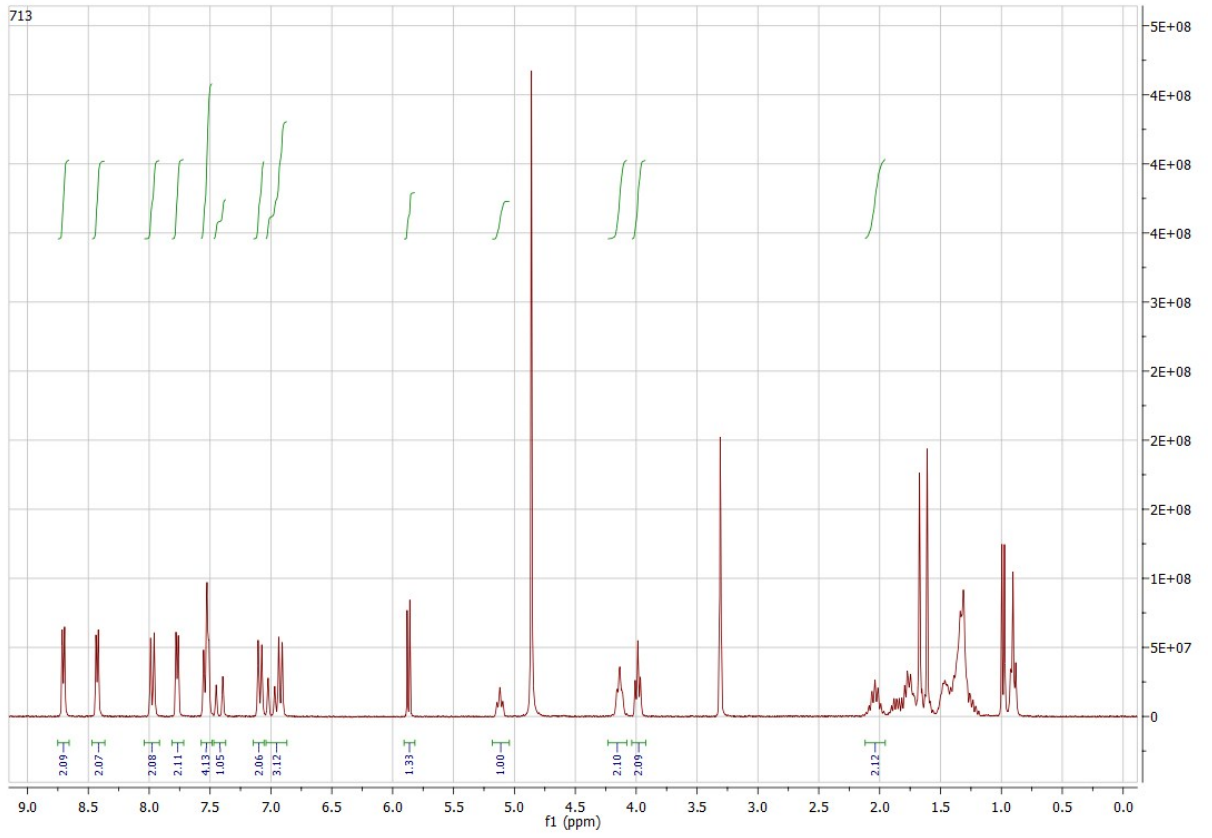


Supporting Figure 6. IR spectra (A) of **F-PHG** (red) and **F-PHG**···($Ap_{1.5}St^{*}_{1.5}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3030, 2921, 2852, 2644, 2355, 2114, 1882, 1759, 1632, 1596, 1542, 1511, 1499, 1469, 1454, 1418, 1408, 1309, 1282, 1249, 1197, 1175, 1139, 1110, 1077, 1063, 1044, 1002, 958, 927, 877, 840, 826, 805, 770, 734, 726, 654 cm^{-1}.

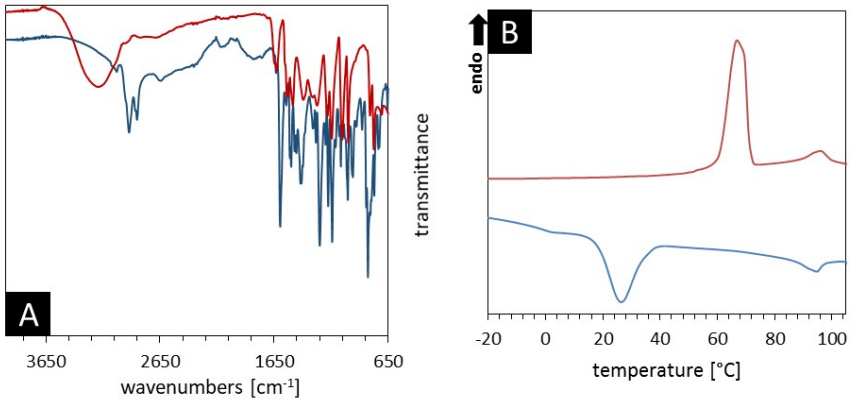


Supporting Figure 20. POM images taken upon cooling of **F-PHG**···($^{Ap}_{1.5}St^{*}_{1.5}$) in its isotropic (A), blue phase I (B) and chiral nematic phase (C).



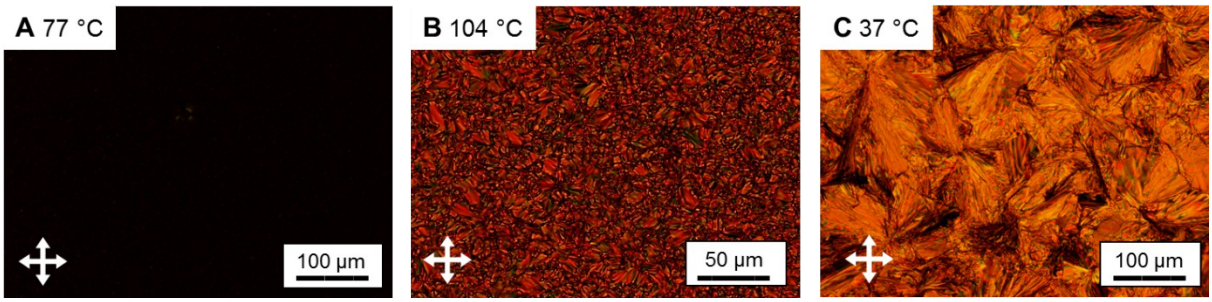
Supporting Figure 21. ^{1}H NMR spectrum of **F-PHG**···($^{Ap}_{1.5}St^{*}_{1.5}$) in CD_3OD.

[F-PHG/(*S*, *E*)-4-(4-Octyloxystyryl)pyridine/(*E*)-4-(4-Citronellyloxyphenyl)azopyridine]$_{1/1.5/1.5}$ F-PHG···($^{St}_{1.5}Ap^{*}_{1.5}$)

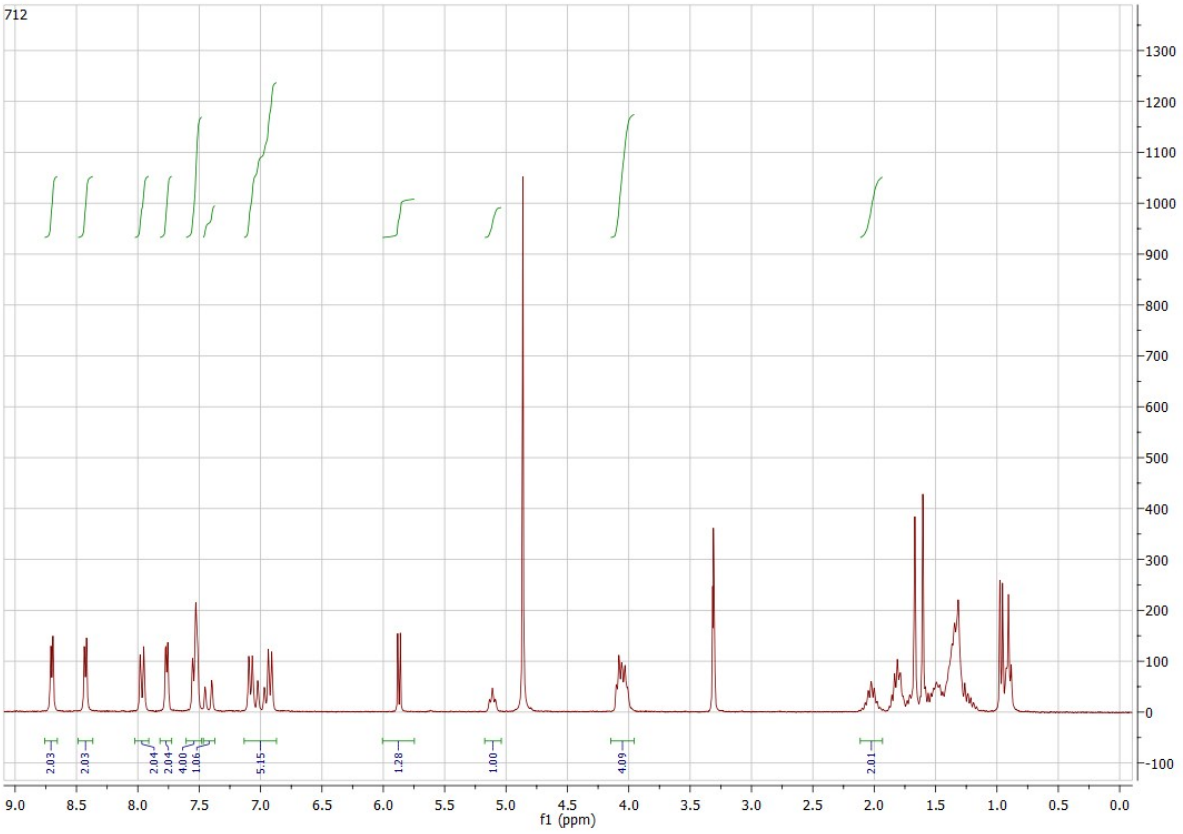


Supporting Figure 22. IR spectra (A) of **F-PHG** (red) and **F-PHG**···($^{St}_{1.5}Ap^{*}_{1.5}$) (blue) and DSC trace (B) of the corresponding assembly.

FT-IR (ATR): 3031, 2919, 2869, 2852, 2653, 2356, 2116, 1880, 1633, 1596, 1546, 1511, 1500, 1471, 1454, 1408, 1309, 1281, 1250, 1195, 1174, 1140, 1108, 1063, 1051, 1022, 1002, 970, 925, 880, 828, 815, 796, 771, 735, 724, 654 cm^{-1}.



Supporting Figure 23. POM images taken upon cooling of **F-PHG**···($^{St}_{1.5}Ap^{*}_{1.5}$) in its isotropic (A), chiral nematic (B) and crystalline phase (C).



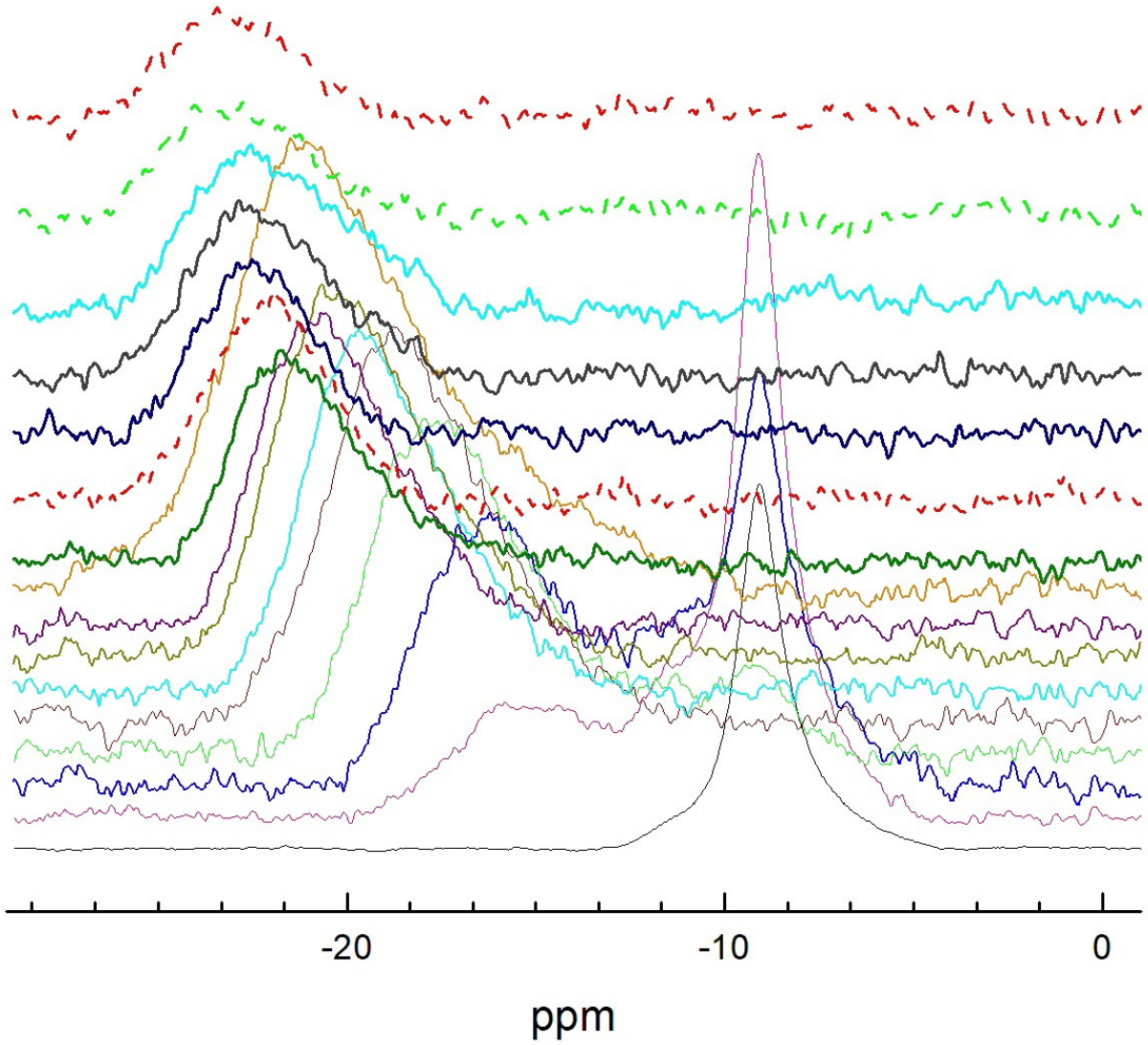
Supporting Figure 24. ^{1}H NMR spectrum of **F-PHG**···($St_{1.5}Ap^{*}_{1.5}$) in CD_3OD.

2.3 Thermal Data of the Chiral Hydrogen-bonded Assemblies

Supporting Table 1. Thermal properties of the chiral hydrogen-bonded liquid crystals as obtained by DSC (ΔT = 10 K/min).

PHG	Thermal Properties								
		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]		T [°C]	ΔH [J·g^{-1}]
$Ap_{1.5}Ap^{*}_{1.5}$	Cr → I	74.3	52.3	I → *N**	50.9	-1.37	*N** → Cr	35.8	-31.9
$St_{1.5}St^{*}_{1.5}$	glas → Cr	26.3	-9.92	Cr → Cr2	62.2	22.3	Cr → *N**	68.9	11.7
	*N** → I	106.4	14.0	I → *N**	100.3	-3.91	*N** → SmA*	60.2	-0.75
	SmA*→glas	2.78[a]	-	-	-	-	-	-	-
$Ap_{1.5}St^{*}_{1.5}$	Cr → Cr2	49.6	20.2	Cr2 → Cr2/*N**	68.0	39.1	Cr2/*N** → I	84.1	17.3
	BPI → *N**	69.6	-4.84	-	-	-	-	-	-
$St_{1.5}Ap^{*}_{1.5}$	glas → Cr	6.68	-14.8	Cr → *N**	60.1	9.69	*N** → I	74.9	1.01
	I → *N**	73.2	-3.39	*N** → SmA*	20.0	-2.40	SmA* → glas	0.73[b]	-
F-PHG									
$Ap_{1.5}Ap^{*}_{1.5}$	Cr → *N**	71.3	33.2	*N** → I	81.1	17.7	*BPI* → *N**	74.2	-2.55
	*N** → Cr	57.6	-12.5	Cr → Cr2	50.2	-17.3	-	-	-
$St_{1.5}St^{*}_{1.5}$	Cr → *N**	79.5	28.7	*N** → I	113.1	8.82	I → *N**	111.6	-9.94
	Cr → *N**	34.3	-20.2	-	-	-	-	-	-
$Ap_{1.5}St^{*}_{1.5}$	glas → Cr	34.5	-15.9	Cr → *N**	63.1	8.21	*N** → I	79.1	3.01
	I → *N**	76.6	-2.60	*N**→glas	3.57[c]	-	-	-	-
$St_{1.5}Ap^{*}_{1.5}$	Cr → *N**	67.9	37.3	*N** → I	95.3	4.59	-	-	-
	I → *N**	94.7	-3.48	*N** → Cr	26.22	-28.2	-	-	-

a: Δcp = 0.525 J(gK)$^{-1}$, b: Δcp = 0.399 J(gK)$^{-1}$, c: Δcp = 0.338 J(gK)$^{-1}$



3 Solid State ^{19}F-NMR Spectra

Supporting Figure 25. ^{19}F-NMR Spectra collected of the **F-PHG**···($St_{1.5}Ap^{*}_{1.5}$) upon cooling the isotropic phase beginning at 65 °C (bottom trace) with a decreasing increment of 2 °C, the top trace is at 35 °C.

4 References

[1] M. Pfletscher, C. Wölper, J. S. Gutmann, M. Mezger and M. Giese, *Chem. Commun* **2016**, *52*, 8549–8552.

[2] M. Giese, T. Krappitz, R. Y. Dong, C. A. Michal, W. Y. Hamad, B. O. Patrick and M. J. MacLachlan, *J. Mater. Chem. C* **2015**, *3*, 1537–1545.