Supporting Information for

# Fluorination of Supramolecular Liquid Crystals – Tuning Tool and Analytical Probe

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## 1. Materials and Methods

All Commercially available compounds and solvents were used as received from suppliers without further purification. $^{1}$H-, $^{19}$F-, and $^{13}$C-NMR-Spectra of the compounds were collected in deuterated solvents ($CDCl_3$, DMSO-$d_6$ or MeOD-$d_4$) with a Bruker DRX 300 (300 MHz), Bruker 400sp (400 MHz), or a Bruker DRX 600 (600 MHz). Mass spectra were obtained with a Bruker Esquire~LC (LR-MS) and a Waters/Micromass LCT TOF-MS (HR-MS). IR-spectra were recorded with a *Perkin Elmer* Frontier FT-IR -spectrometer.

Polarized optical microscopy (POM) images/videos were taken on an Olympus BX41 microscope equipped with crossed polarizers, a hot stage, and an OptixCam Summit KZ OCS-SK2-52X microscope camera. The photo-response was investigated in-situ by irradiating the samples under the POM with a laser pointer (5 mW, 405 nm). DSC data were obtained using a *Perkin Elmer* STA 6000 with a heating/cooling rate of 5 K/min (sample weight ~5 mg). UV-visible spectroscopy was performed using a Thermo Fisher Evolution 201 spectrophotometer. The samples were measured as thin films of their isotropic melt between quartz slides heated by a Huber Unistat Tango thermostat.

## 2. Experimental Section

### 2.1 Synthesis of 2-fluoro-1,3,5-trihydroxybenzene (F-PHG)

**PHG-OMe**

A solution of anhydrous phloroglucinol (6.00 g, 0.047 mol), dimethyl sulphate (13.3 mL, 17,70 g, 0.140 mol), and potassium carbonate (33.50 g, 0.242 mol) in acetone (90 mL) was refluxed in the presence of molar sieves (4 Å ) for 19 h at 60 °C. The acetone phase was isolated by filtration and the solvent was removed from the filtrate under reduced pressure. The residue was purified by column chromatography with cyclohexane and ethyl acetate (Cy : EA [95:5]; $R_f$ = 0.3) to yield the product 1,3,5-trimethoxybenzene as a colourless solid (Yield: 7.06 g, 0.038 mol, 88%). The compound is literature[1] known and was characterized by $^{1}$H and $^{13}$C only.

MP: 50 – 51 °C

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.09 (s, 3H), 3.77 (s, 9H).

$^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 6.08 (s, 3H), 3.70 (s, 9H).

$^{13}$C NMR (75 MHz, $CDCl_3$) δ 162.1, 93.5, 55.9.

**F-PHG-OMe**

Finely powdered Selectfluor® (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane-bis(tetrafluoroborate); 9.78 g, 27.6 mmol) was added portion-wise to a cooled (ca. – 40 °C) solution of 1,3,5-trimethoxybenzene (4.22 g, 25.1 mmol) in acetonitrile (50 mL). The partially frozen reaction mixture was gradually warmed to ambient temperature and then stirred for 48 h. The solvent was removed under reduced pressure and $CH_2Cl_2$ (50 mL) was added. The residual solid was filtered off and the filtrate was concentrated under vacuo. Purification by column chromatography (Cy : EA [8:2], $R_f$ = 0.3) gave 2-fluoro-1,3,5-trimethoxybenzene as a colorless liquid (Yield: 2.43 g,13.1 mmol, 52%).

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.16 (d, $J$ = 6.2 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 2H).

$^{19}$F NMR (282 MHz, $CDCl_3$) δ -168.38 (t, $J$ = 6.1 Hz)

$^{13}$C NMR (75 MHz, $CDCl_3$) δ 156.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 149.2 (d, $J_{C\text{-}F}$ = 9.1 Hz), 138.4 (d, $J_{C\text{-}F}$ = 236.1 Hz, 92.9, 57.1, 56.3.

MS (ESI): m/z (%): positive: 187.0 (100, $[M+H]^+$, $C_9H_{11}FO_3+H^+$).

IR: ν (cm-1) = 3151, 2727, 1633, 1539, 1494, 1410, 1316, 1283, 1188, 1151, 1060, 1002, 838, 802, 778.

**F-PHG**

A solution of 2-fluoro-1,3,5-trimethoxybenzene (2.20 g, 11.8 mmol,1 eq.) in $CH_2Cl_2$ (10 mL) was stirred at room temperature and $BBr_3$ (9.5 mL, 25.12 g, 70.9 mmol, 6 eq.) was added dropwise over 20 min. The resulting reaction mixture was stirred at room temperature for 48 h and the reaction was monitored by TLC (Cy : EA [3:7] $R_f$ = 0.4). Due to incomplete conversion, additional $BBr_3$ (0.15 mL ,0.39 g, 1.6 mmol; 0.14 eq) was added after 24 h. The reaction mixture was then cooled to 0 °C, carefully quenched with deionized water (50 mL), and the resulting mixture was stirred until complete dissolution of the formed precipitate. The resulting mixture was extracted with $Et_2O$ (3 × 50mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $Na_2SO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Cy :EA [1 : 2] $R_f$ = 0.3) to provide 2-fluoro-1,3,5-trihydroxybenzene (**F-PHG**) as a pale brown solid (Yield: 1.29 g, 9.0 mmol, 76%). According to $^{19}F$ NMR experiments, the obtained product was contained impurities of di- (12.5%) and trifluorinated byproduct (0.3%), which could not be removed after methoxy deprotection. The di- and tri- fluorinated derivatives should be completely removed during reaction workup after fluorination.

MP: >216°C (decomposition)

$^1H$ NMR (600 MHz, DMSO-$d_6$,) δ 9.37 (s, 2H), 8.87 (s, 1H), 5.80 (d, $J$ = 6.5 Hz, 2H).

$^{19}F$ NMR (565 MHz, DMSO-$d_6$) δ -172.09 (t, $J$ = 6.4 Hz).

$^{13}C$ NMR (151 MHz, DMSO-$d_6$) δ 152.8 (d, $J_{C\text{-}F}$ = 2.3 Hz), 145.9 (d, $J_{C\text{-}F}$ = 10.5 Hz), 134.9 (d, $J_{C\text{-}F}$ = 226.4 Hz, 95.0.

MS (ESI): m/z (%): negative: 143.0151 (100, $[M\text{-}H]^-$, $C_6H_5FO_3\text{-}H^+$).

IR: ν (cm-1) = 3436, 3149, 2719, 1631, 1540, 1492, 1411, 1316, 1281, 1189, 1151, 1061, 1002, 939, 801, 779.

## 2.2 Synthesis of Azopyridyl-Derivatives (Ap-6 – 12).

### General procedure used for the synthesis of Ap-N, Ap3F-N, Ap3'F-N, and Ap3'5'F-N

The synthesis of the Aps was performed by a modifying a literature known procedure.[2] 4-Aminopyridine (2.00 g, 21.2 mmol, 1.2 eq.) was dissolved in 15 mL of 7 M $HCl_{(aq)}$ and cooled to -20 °C (acetone/dry ice). A solution of 2-fluorophenol (1.99 g, 17.7 mmol, 1.0 eq.) and sodium nitrite (1.34 g, 19.5 mmol, 1.1 eq.) in 10 mL of $NaOH_{(aq)}$ (10%) was slowly added dropwise to the cooled solution over the duration of 60 minutes. During the addition of the phenol solution, the reaction temperature was increased to -15 °C to prevent freezing. Subsequently, the solution was stirred until it exceeded 5°C, the cooling bath was removed, and the mixture was stirred for another 15 minutes at room temperature. Adjusting the pH to 6 by addition of base yielded a dark precipitate, which was filtered off, washed with water, (50 mL) and *n*-hexane (30 mL), and carefully rinsed with acetone (10 mL), to remove the main part of byproducts and impurities.

The crude product was subsequently used for alkylation without further purification. The azo compound (1 eq) and $K_2CO_3$ (1.5 eq) were dissolved in DMF (20 mL). After addition of the corresponding halide (1 eq) the mixture was heated to 90 °C for 3 h. The hot solution was poured into 50 mL deionized water yielding a dark violet precipitate which was extracted with ethyl acetate (5 × 50 mL). The organic layers were combined and washed once with 5% $NaHCO_{3(aq)}$ (50 mL) and once with saturated brine (50 mL). After drying over $Na_2SO_4$, the solvent was removed under reduced pressure. The obtained residue was purified by column chromatography (Cy : EA [2:1]) to yield a red solid.

### Ap-6

Yield: 28 %

$^1H$ NMR (400 MHz, MeOD-$d_4$) δ 8.71 (dd, $J$ = 4.7, 1.6 Hz, 2H), 8.01 – 7.94 (m, 2H), 7.78 (dd, $J$ = 4.7, 1.6 Hz, 2H), 7.09 (d, $J$ = 9.1 Hz, 2H), 4.10 (t, $J$ = 6.5 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.56 – 1.46 (m, 2H), 1.44 – 1.33 (m, 4H), 0.94 (t, $J$ = 7.1 Hz, 3H).

$^{13}C$ NMR (101 MHz, MeOD-$d_4$) δ 163.40, 158.04, 150.4, 146.7, 125.4, 116.3, 114.7, 68.3, 31.4, 28.8, 25.4, 22.3, 13.0.

IR: ν ($cm^{-1}$) = 3031, 2935, 2858, 1602, 1583, 1501, 1470, 1406, 1297, 1253, 1039, 1025, 988, 923, 838, 794, 728.

**Ap-8**
Yield after two steps: 32 %
MP: 80°C
$^{1}$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.56 – 1.46 (m, 2H), 1.44 – 1.26 (m, 8H), 0.91 (t, *J* = 6.9 Hz, 3H).
$^{13}$C NMR (101 MHz, MeOD-*d*$_4$, *C8*) δ 163.4, 158.1, 150.4, 146.7, 125.4, 116.3, 114.7, 68.3, 31.6, 29.1, 29.0, 28.9, 25.7, 22.3, 13.0.
IR: ν (cm$^{-1}$) = 3036, 2918, 2853, 1601, 1583, 1502, 1467, 1408, 1318, 1297, 1255, 1040, 1021, 999, 925, 846, 794, 724.

**Ap-9**
Yield after two steps: 37 %
MP: 71°C
$^{1}$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.09 (d, *J* = 9.0 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.55 – 1.45 (m, 2H), 1.43 – 1.25 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H).
$^{13}$C NMR (101 MHz, MeOD-*d*$_4$,) δ 163.4, 158.0, 150.4, 146.7, 125.4, 116.3, 114.7, 68.2, 31.7, 29.3, 29.1, 29.0, 28.9, 25.7, 22.3, 13.0.
IR: ν (cm$^{-1}$) = 3040, 2920, 2851, 1604, 1582, 1501, 1470, 1407, 1297, 1256, 1038, 1013, 986, 922, 846, 793, 726.

**Ap-10**
Yield after two steps: 25 %
$^{1}$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.5 Hz, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 7.80 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.57 – 1.48 (m, 2H), 1.44 – 1.29 (m, 12H), 0.92 (t, *J* = 6.9 Hz, 3H).
$^{13}$C NMR (101 MHz, MeOD-*d*$_4$) δ 163.4, 158.0, 150.4, 146.7, 125.4, 116.3, 114.7, 68.2, 31.7, 29.3, 29.3, 29.1, 29.1, 28.9, 25.7, 22.3, 13.0.
IR: ν (cm$^{-1}$) = 3035, 2918, 2850, 1604, 1583, 1499, 1468, 1407, 1297, 1253, 1034, 1015, 987, 923, 844, 794, 724.

**Ap-11**
Yield after two steps: 30 %
MP: 66°C
$^{1}$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.09 (d, *J* = 9.1 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.55 – 1.45 (m, 2H), 1.44 – 1.21 (m, 14H), 0.89 (t, *J* = 6.9 Hz, 3H).
$^{13}$C NMR (101 MHz, MeOD-*d*$_4$) δ 163.4, 158.0, 150.4, 146.7, 125.4, 116.3, 114.7, 68.2, 31.7, 29.3, 29.3, 29.3, 29.1, 29.0, 28.9, 25.7, 22.3, 13.0.
MS (ESI): m/z (%): positive: 354.2544 (100, $[M+H]^+$, $C_{22}H_{31}N_3O+H^+$, calc.: m/z = 354.2540).
IR: ν (cm$^{-1}$) = 3032, 2919, 2849, 1601, 1581, 1498, 1465, 1404, 1297, 1254, 1046, 1011, 986, 922, 844, 796, 719.

**Ap-12**
Yield after two steps: 25 %
MP: 69°C
$^{1}$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.55 – 1.46 (m, 2H), 1.42 – 1.26 (m, 16H), 0.89 (t, *J* = 6.9 Hz, 3H).
$^{13}$C NMR (101 MHz, MeOD-*d*$_4$) δ 163.4, 158.0, 150.4, 146.7, 125.4, 116.3, 114.7, 68.2, 31.7, 29.4, 29.4, 29.3, 29.3, 29.1, 29.1, 28.9, 25.7, 22.3, 13.0.
MS (ESI): m/z (%): positive: 368.2696 (100, $[M+H]^+$, $C_{23}H_{33}N_3O+H^+$, calc.: m/z = 368.2540)
IR: ν (cm$^{-1}$) = 3030, 2918, 2850, 1601, 1582, 1498, 1468, 1405, 1300, 1252, 1041, 1004, 920, 846, 796, 725.

## 2.3 Synthesis of Monofluorinated Azopyridyl-Derivatives (Ap-3F-6, Ap3'F-6 to 12)

### Ap3F-6

Yield after two steps: 20 %
MP: 64-65°C
$^{1}$H NMR (300 MHz, MeOD-*d4*) δ 8.67 (d, *J* = 2.7 Hz, 1H), 8.47 (d, *J* = 5.3 Hz, 1H), 7.98 (d, *J* = 9.1 Hz, 2H), 7.61 (dd, *J* = 6.6, 5.3 Hz, 1H), 7.09 (d, *J* = 9.1 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 1.90 – 1.74 (m, 2H), 1.65 – 1.17 (m, 6H), 0.93 (t, *J* = 7.1 Hz, 3H).
$^{19}$F NMR (282 MHz, MeOD-*d4*) δ -141.76 (dd, *J* = 6.4, 2.4 Hz).
$^{13}$C NMR (75 MHz, MeOD-*d4*) δ 165.2, 156.8 (d, *J* = 263.7 Hz), 148.5, 147.4 (d, *J* = 5.8 Hz), 147.0 (d, *J* = 5.8 Hz), 141.1 (d, *J* = 23.4 Hz), 127.2, 116.2, 113.0, 69.7, 32.7, 30.2, 26.8, 23.7, 14.4.
MS (ESI): m/z (%): positive: 302.1637 (100, $[M+H]^+$, $C_{17}H_{20}FN_3O+H^+$, calc.: m/z = 302.1663).
IR: ν ($cm^{-1}$) = 3022, 2944, 2919, 2855, 1599, 1578, 1499, 1448, 1410, 1298, 1251, 1223, 1193, 1157, 1024, 994, 922, 844, 802, 776, 730.

### Ap3F-8

Yield after two steps: 23 %
MP: 53-54°C
$^{1}$H NMR (300 MHz, MeOD-$d_4$) δ 8.68 (d, *J* = 2.7 Hz, 1H), 8.48 (d, *J* = 5.3 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 2H), 7.63 (dd, *J* = 6.4, 5.4 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 2H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.90 – 1.76 (m, 2H), 1.57 – 1.25 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H).
$^{19}$F NMR (282 MHz, MeOD-$d_4$) δ -141.71 (dd, *J* = 6.2, 2.1 Hz).
$^{13}$C NMR (75 MHz, MeOD) δ 165.2, 156.8 (d, *J* = 263.6 Hz), 148.5 (s), 147.4 (d, *J* = 5.8 Hz), 147.0 (d, *J* = 5.6 Hz), 141.1 (d, *J* = 23.2 Hz), 127.2, 116.2, 113.1, 69.7, 33.00, 30.5, 30.4, 30.3, 27.1, 23.7, 14.4.
MS (ESI): m/z (%): positive: 320.1978 (100, $[M+H]^+$, $C_{19}H_{24}FN_3O+H^+$, calc.: m/z = 330.1976).
IR: ν ($cm^{-1}$) = 3102, 3041, 2938, 2920, 2849, 1600, 1580, 1499, 1472, 1406, 1299, 1245, 1135, 1106, 1040, 999, 921, 839,776, 722.

### Ap3'F-6

Yield after two steps: 21 %
MP: 56-57°C
$^{1}$H NMR (400 MHz, MeOD-*d4*) δ 8.72 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.87 (ddd, *J* = 8.7, 2.2, 1.3 Hz, 1H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.70 (dd, *J* = 12.0, 2.3 Hz, 1H), 7.27 (t, *J* = 8.7 Hz, 1H), 4.16 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.56 – 1.46 (m, 2H), 1.44 – 1.30 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H).
$^{19}$F NMR (377 MHz, MeOD-$d_4$) δ -134.29 (ddd, *J* = 12.0, 8.5, 0.8 Hz).
$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 157.6), 152.8 (d, $J_{C-F}$ = 239.4 Hz), 151.5 (d, $J_{C-F}$ = 2.0 Hz), 150.47, 146.1 (d, $J_{C-F}$ = 5.5 Hz), 124.6 (d, $J_{C-F}$ = 2.8 Hz), 116.4, 113.5 (d, $J_{C-F}$ = 2.2 Hz), 107.0 (d, $J_{C-F}$ = 19.6 Hz), 69.2, 31.3, 28.7, 25.3, 22.3, 13.0.
MS (ESI): m/z (%): positive: 302.1670 (100, $[M+H]^+$, $C_{17}H_{20}FN_3O+H^+$, calc.: m/z = 302.1663).
IR: ν ($cm^{-1}$) = 3096, 2952, 2930, 2857, 2601, 1613, 1585, 1501, 1465, 1414, 1322, 1261, 1212, 1098, 1021, 991, 878, 840, 802, 724.

**Ap3'F-8**
Yield after two steps: 23 %
MP: 54 – 55 °C
$^{1}$H NMR (400 MHz, MeOD-$d_4$) δ 8.72 (dd, *J* = 4.8, 1.5 Hz, 2H), 7.87 (ddd, *J* = 8.7, 2.1, 1.2 Hz, 1H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.71 (dd, *J* = 12.0, 2.3 Hz, 1H), 7.28 (t, *J* = 8.6 Hz, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.57 – 1.45 (m, 2H), 1.44 – 1.28 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 3H).
$^{19}$F NMR (377 MHz, MeOD-$d_4$) δ -134.23 (ddd, *J* = 11.7, 8.4, 1.2 Hz).
$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 157.64, 152.8 (d, *J* = 240.1 Hz), 151.5 (d, *J* = 2.5 Hz), 150.47, 146.1 (d, *J* = 5.4 Hz), 124.6 (d, *J* = 2.7 Hz), 116.4, 113.5 (d, *J* = 2.1 Hz), 107.0 (d, *J* = 19.6 Hz, 69.2, 31.6, 29.0, 29.0, 28.7, 25.6, 22.3, 13.0.
MS (ESI): m/z (%): positive: 330.1987 (100, $[M+H]^+$, $C_{19}H_{24}FN_3O+H^+$, calc.: m/z = 330.1976).
IR: ν ($cm^{-1}$) = 3084, 2954, 2915, 2853, 2606, 1612, 1585, 1513, 1470, 1419, 1327, 1262, 1215, 1104, 990, 876, 829, 802, 717.

**Ap3'F-9**
Yield after two steps: 26 %
MP: 55°C
$^{1}$H NMR (400 MHz, MeOD-$d_4$) δ 8.75 (dd, *J* = 4.7, 1.5 Hz, 2H), 7.91 (ddd, *J* = 8.7, 2.2, 1.3 Hz, 1H), 7.81 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.75 (dd, *J* = 12.0, 2.3 Hz, 1H), 7.32 (t, *J* = 8.7 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 2H), 1.94 – 1.80 (m, 2H), 1.60 – 1.48 (m, 2H), 1.47 – 1.25 (m, 10H), 0.92 (t, *J* = 6.9 Hz, 3H).
$^{19}$F NMR (377 MHz, MeOD-$d_4$) δ -134.29 (ddd, *J* = 12.1, 8.6, 1.3 Hz).
$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 157.67, 152.8 (d, *J* = 240.8 Hz), 151.5 (d, *J* = 3.5 Hz), 150.5, 146.1 (d, *J* = 5.4 Hz), 124.6 (d, *J* = 2.9 Hz), 116.4, 113.6 (d, *J* = 2.1 Hz), 107.0 (d, *J* = 19.6 Hz), 69.2, 31.6, 29.3, 29.1, 29.0, 28.7, 25.6, 22.3, 13.0.
MS (ESI): m/z (%): positive: 344.2123 (100, $[M+H]^+$, $C_{20}H_{26}FN_3O+H^+$, calc.: m/z = 344.2133).
IR: ν ($cm^{-1}$) = 3082, 3054, 2956 2916, 2852, 2592, 1616, 1585, 1513, 1471, 1403, 1326, 1283, 1211, 1102, 1039, 1012, 979, 876, 825, 802, 715.

**Ap3'F-10**
Yield after two steps: 28 %
MP: 56 °C
$^{1}$H NMR (400 MHz, MeOD-$d_4$) δ 8.73 (dd, *J* = 4.7, 1.5 Hz, 2H), 7.88 (ddd, *J* = 8.7, 2.2, 1.2 Hz, 1H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.72 (dd, *J* = 12.0, 2.3 Hz, 1H), 7.29 (t, *J* = 8.7 Hz, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 1.91 – 1.78 (m, 2H), 1.58 – 1.47 (m, 2H), 1.43 – 1.25 (m, 12H), 0.90 (t, *J* = 6.9 Hz, 3H).
$^{19}$F NMR (377 MHz, MeOD-$d_4$) δ -134.26 (ddd, *J* = 12.0, 8.7, 1.3 Hz).
$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 157.7, 152.8 (d, *J* = 240.8 Hz), 151.5 (d, *J* = 3.4 Hz), 150.5, 146.1 (d, *J* = 5.4 Hz), 124.6 (d, *J* = 2.7 Hz), 116.38, 113.5 (d, *J* = 2.2 Hz), 107.0 (d, *J* = 19.6 Hz), 69.2, 31.7, 29.3, 29.3, 29.1, 29.0, 28.7, 25.6, 22.3, 13.0.
MS (ESI): m/z (%): positive: 358.2289 (100, $[M+H]^+$, $C_{21}H_{28}FN_3O+H^+$, calc.: m/z = 358.2289).
IR: ν ($cm^{-1}$) = 3087, 3054, 2954, 2916, 2852, 2592, 2071, 1948, 1864, 1615, 1586, 1514, 1420, 1407, 1327, 1284, 1214, 1105, 1026, 1015, 991, 876, 827, 802, 716.

**Ap3'F-11**
Yield after two steps: 20 %
MP: 54 °C
$^{1}$H NMR (400 MHz, MeOD-$d_4$) δ 8.73 (dd, *J* = 4.7, 1.5 Hz, 2H), 7.89 (ddd, *J* = 8.7, 2.1, 1.2 Hz, 1H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 2H), 7.73 (dd, *J* = 12.0, 2.3 Hz, 1H), 7.30 (t, *J* = 8.7 Hz, 1H), 4.18 (t, *J* = 6.4 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.57 – 1.46 (m, 2H), 1.43 – 1.24 (m, 14H), 0.89 (t, *J* = 6.8 Hz, 3H).
$^{19}$F NMR (377 MHz, MeOD-$d_4$) δ -134.28 (ddd, *J* = 11.8, 8.6, 1.4 Hz).
$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 157.67, 152.80 (d, *J* = 241.3 Hz), 151.5 (d, *J* = 3.9 Hz), 150.48, 146.1 (d, *J* = 5.3 Hz), 124.6 (d, *J* = 2.8 Hz), 116.4, 113.5 (d, *J* = 2.2 Hz), 107.0 (d, *J* = 19.6 Hz), 69.2, 31.7, 29.4, 29.4, 29.3, 29.3, 29.1, 29.0, 28.7, 25.6, 22.3, 13.0.
MS (ESI): m/z (%): positive: 372.2447 (100, $[M+H]^+$, $C_{22}H_{30}FN_3O+H^+$, calc.: m/z = 372.2446).
IR: ν ($cm^{-1}$) = 3084, 3054, 2953, 2915, 2852, 2599, 2075, 1864, 1616, 1585, 1513, 1470, 1406, 1326, 1282, 1209, 1102, 1023, 977, 875, 827, 802, 716.

**Ap3'F-12**
Yield after two steps: 27 %
MP: 54 °C
$^{1}$H NMR (400 MHz, MeOD-$d_4$) δ 8.73 (dd, $J$ = 4.6, 1.6 Hz, 2H), 7.90 (ddd, $J$ = 8.7, 2.2, 1.3 Hz, 1H), 7.80 (dd, $J$ = 4.7, 1.6 Hz, 2H), 7.74 (dd, $J$ = 12.0, 2.3 Hz, 1H), 7.31 (t, $J$ = 8.7 Hz, 1H), 4.19 (t, $J$ = 6.4 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.57 – 1.47 (m, 2H), 1.43 – 1.26 (m, 16H), 0.89 (t, $J$ = 6.9 Hz, 3H).
$^{19}$F NMR (377 MHz, MeOD-$d_4$) δ -134.30 (ddd, $J$ = 11.7, 8.4, 1.2 Hz).
$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 157.7, 152.8 (d, $J$ = 241.5 Hz), 151.5 (d, $J$ = 3.9 Hz), 150.5, 146.1 (d, $J$ = 5.4 Hz), 124.6 (d, $J$ = 2.7 Hz), 116.4, 113.6 (d, $J$ = 2.2 Hz), 107.0 (d, $J$ = 19.6 Hz), 69.2, 31.7, 29.4, 29.4, 29.3, 29.3, 29.1, 29.0, 28.7, 25.6, 22.3, 13.0.
MS (ESI): m/z (%): positive: 386.2606 (100, $[M+H]^+$, $C_{23}H_{32}FN_3O+H^+$, calc.: m/z = 386.2602).
IR: ν ($cm^{-1}$) = 3083, 3053, 2956, 2916, 2851, 2601, 2070, 2000, 1865, 1615, 1585, 1513, 1471, 1407, 1325, 1282, 1209, 1102, 1025, 975, 875, 825, 803, 715.

## 2.4 Synthesis of Difluorinated Azopyridyl-Derivatives (Ap3'5'F-6 + 8).

**Ap3'5'F-6**
Yield after two steps: 10 %
MP: >20 °C
$^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.83 (d, $J$ = 6.0 Hz, 2H), 7.82 - 7.64 (m, 4H), 4.25 (t, $J$ = 6.3 Hz, 2H), 1.77 - 1.62 (m, 2H), 1.50 – 1.16 (m, 6H), 0.86 (t, $J$ = 6.9 Hz, 3H).
$^{19}$F NMR (282 MHz, DMSO-$d_6$) δ -126.34 (d, $J$ = 8.7 Hz).
$^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 156.01, 155.2 (dd, $J_{C-F}$= 248.6, 6.8 Hz), 151.6, 145.9 (t, $J_{C-F}$ = 8.4 Hz), 138.6 (t, $J_{C-F}$ = 14.5 Hz*)* 115.9, 107.8 (dd, $J_{C-F}$ = 24.9, 8.1 Hz), 74.6 (t, $J_{C-F}$ = 3.3 Hz), 30.8, 29.3, 24.7, 22.0, 13.8.
MS (ESI): m/z (%): positive: 320.1569 (100, $[M+H]^+$, $C_{17}H_{19}F_2N_3O+H^+$, calc.: m/z = 320.1574).
IR: ν ($cm^{-1}$) = 2986, 2954, 2931, 2816, 1587, 1496, 1469, 1435, 1330, 1300, 1242, 1101, 1036, 988, 901, 870, 827, 732.

**Ap3'5'F-8**
Yield after two steps: 10 %
MP: 29-30 °C
$^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.82 (d, $J$ = 6.1 Hz, 2H), 7.82 - 7.60 (m, 4H), 4.23 (t, $J$ = 6.4 Hz, 2H), 1.78 - 1.60 (m, 2H), 1.48 - 1.09 (m, 10H), 0.83 (t, $J$ = 6.6 Hz, 3H).
$^{19}$F NMR (282 MHz, DMSO-$d_6$) δ -126.37 (d, $J$ = 8.6 Hz).
$^{13}$C NMR (75 MHz, DMSO-$d_6$) δ 156.0, 155.1 (dd, $J_{C-F}$ = 248.6, 6.7 Hz), 151.6, 145.9 (t, $J_{C-F}$ = 8.3 Hz), 138.6 (t, $J_{C-F}$ = 14.5 Hz), 115.8, 107.7 (d, $J_{C-F}$ = 24.9, 8.0 Hz), 74.5 (t, $J_{C-F}$ = 3.3 Hz), 31.1, 29.4, 28.6, 28.5, 25.0, 22.0, 13.9.
MS (ESI): m/z (%): positive: 348.1886 (100, $[M+H]^+$, $C_{19}H_{23}F_2N_3O+H^+$, calc.: m/z = 348.1887).
IR: ν ($cm^{-1}$) = 3032 (w), 2958, 2919, 2854, 1583, 1499, 1470, 1431, 1388, 1343, 1297, 1247, 1102, 1033, 983, 864, 835, 725.

## 2.5 Synthesis of the HBAs with phloroglucinol (PHG)as core unit

**General procedure:**
**PHG** (1.0 eq.) and the corresponding side chain (**Ap-N, Ap3F-N, Ap3'F-N, or Ap3'5'F-N)** (3.0 eq.) were weighed and separately dissolved in acetone. The solvent was removed under reduced pressure and the desired aggregates were formed in quantitative yields.

**PHG(Ap-6)$_3$**
MP: 103 °C
$^{1}$H NMR (400 MHz, MeOD-$d_4$) δ 8.70 (dd, $J$ = 4.7, 1.5 Hz, 6H), 7.97 (d, $J$ = 9.0 Hz, 6H), 7.77 (dd, $J$ = 4.6, 1.6 Hz, 6H), 7.08 (d, $J$ = 9.0 Hz, 6H), 5.79 (s, 3H), 4.09 (t, $J$ = 6.5 Hz, 6H), 1.87 – 1.76 (m, 6H), 1.57 – 1.45 (m, 6H), 1.43 – 1.32 (m, 12H), 0.93 (t, $J$ = 7.1 Hz, 9H).
IR: ν ($cm^{-1}$) = 3036, 2935, 2858, 2648, 1592, 1581, 1499, 1408, 1298, 1256, 1071, 1003, 927, 840, 794, 724, 696, 725.
Elemental Analysis: calc. (%) $C_{57}H_{69}N_9O_6$: C 70.13, H 7.12, N 12.91; found (%): C 70.03, H 7.19, N 12.71

## **PHG(Ap-8)**$_3$

MP: 97 °C

$^1$NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.97 (d, *J* = 9.0 Hz, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.09 (d, *J* = 9.1 Hz, 6H), 5.79 (s, 3H), 4.09 (t, *J* = 6.5 Hz, 6H), 1.87 – 1.76 (m, 6H), 1.56 – 1.45 (m, 6H), 1.43 – 1.28 (m, 24H), 0.91 (t, *J* = 6.9 Hz, 9H).

IR: ν (cm$^{-1}$) = 3048, 2952, 2935, 2919, 2867, 2852, 2632, 1594, 1584, 1499, 1408, 1322, 1303, 1250, 1141, 1000, 927, 835, 794, 718, 696.

Elemental Analysis: calc. (%) $C_{63}H_{81}N_9O_6$: C 71.36, H 7.70, N 11.75; found (%): C 71.24, H 7.89, N 11.84.

## **PHG(Ap-9)**$_3$

MP: 91 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.97 (d, *J* = 9.0 Hz, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.09 (d, *J* = 9.0 Hz, 6H), 5.79 (s, 3H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.75 (m, 6H), 1.56 – 1.45 (m, 6H), 1.42 – 1.25 (m, 30H), 0.90 (t, *J* = 6.9 Hz, 9H).

IR: ν (cm$^{-1}$) = 3048, 2955, 2929, 2919, 2852, 2635, 1593, 1585, 1499, 1408, 1322, 1303, 1248, 1142, 1000, 927, 837, 794, 718, 688.

Elemental Analysis: calc. (%) $C_{66}H_{87}N_9O_6$: C 71.90, H 7.95, N 11.43; found (%): C 71.75, H 8.04, N 11.28.

## **PHG(Ap-10)**$_3$

MP: 97 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.72 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.99 (d, *J* = 9.0 Hz, 6H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.11 (d, *J* = 9.1 Hz, 6H), 5.81 (s, 3H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.89 – 1.78 (m, 6H), 1.57 – 1.47 (m, 6H), 1.42 – 1.28 (m, 36H), 0.92 (t, *J* = 6.9 Hz, 9H).

IR: ν (cm$^{-1}$) = 3046, 2917, 2850, 2642, 1593, 1585, 1499, 1408, 1322, 1303, 1252, 1141, 1003, 925, 837, 794, 718.

Elemental Analysis: calc. (%) $C_{69}H_{93}N_9O_6$: C 72.41, H 8.19, N 11.01; found (%): C 72.21, H 8.39, N 10.86.

## **PHG(Ap-11)**$_3$

MP: 93 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.72 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.99 (d, *J* = 9.0 Hz, 6H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.11 (d, *J* = 9.1 Hz, 6H), 5.81 (s, 3H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.89 – 1.78 (m, 6H), 1.57 – 1.47 (m, 6H), 1.42 – 1.28 (m, 36H), 0.92 (t, *J* = 6.9 Hz, 9H).

IR: ν (cm$^{-1}$) = 3046, 2944, 2919, 2850, 2647, 1603, 1585, 1499, 1408, 1322, 1298, 1253, 1142, 1000, 924, 837, 794, 718, 688.

Elemental Analysis: calc. (%) $C_{72}H_{99}N_9O_6$: C 72.88, H 8.41, N 10.62; found (%): C 72.62, H 8.63, N 10.51.

## **PHG(Ap-12)**$_3$

MP: 97 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.97 (d, *J* = 9.0 Hz, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.09 (d, *J* = 9.0 Hz, 6H), 5.79 (s, 3H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.87 – 1.76 (m, 6H), 1.55 – 1.45 (m, 6H), 1.40 – 1.26 (m, 48H), 0.89 (t, *J* = 6.9 Hz, 9H).

IR): ν (cm$^{-1}$) = 3046, 2951, 2917, 2850, 2640, 1594, 1584, 1499, 1408, 1322, 1298, 1253, 1139, 1000, 924, 838, 794, 720, 688.

Elemental Analysis: calc. (%) $C_{75}H_{105}N_9O_6$: C 73.31, H 8.61, N 10.26; found (%): C 73.11, H 8.85, N 10.07.

## **PHG(Ap3F-6)**$_3$

MP: 104 °C

$^1$H NMR (300 MHz, MeOD-*d*$_4$) δ 8.67 (d, *J* = 2.7 Hz, 3H), 8.47 (d, *J* = 5.3 Hz, 3H), 7.98 (d, *J* = 9.1 Hz, 6H), 7.62 (dd, *J* = 6.4, 5.4 Hz, 3H), 7.09 (d, *J* = 9.1 Hz, 6H), 5.79 (s, 3H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.74 (m, 6H), 1.58 – 1.29 (m, 18H), 0.93 (t, *J* = 7.0 Hz, 9H).

$^{19}$F NMR (282 MHz, MeOD-*d*$_4$) δ -141.76 (dd, *J* = 6.2, 2.2 Hz).

IR: ν (cm$^{-1}$) = 3080, 2944, 2918, 2854, 2669, 1598, 1578, 1500, 1408, 1250, 1135, 1009, 1007, 838, 817, 776, 724, 678.

## **PHG(Ap3F-8)**$_3$

MP: 99 °C

$^1$H NMR (300 MHz, MeOD-*d*$_4$) δ 8.69 (d, *J* = 2.7 Hz, 3H), 8.49 (d, *J* = 5.3 Hz, 3H), 8.00 (d, *J* = 9.1 Hz, 6H), 7.63 (dd, *J* = 6.5, 5.4 Hz, 3H), 7.11 (d, *J* = 9.1 Hz, 6H), 6.05 (d, *J* = 158.7 Hz, 5H), 4.12 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.78 (m, 6H), 1.55 – 1.28 (m, 30H), 0.91 (t, *J* = 6.7 Hz, 9H).

$^{19}$F NMR (282 MHz, MeOD-*d*$_4$) δ -141.78 (dd, *J* = 6.3, 2.2 Hz).

IR: ν (cm$^{-1}$) = 3072, 2921, 2851, 2677, 1597, 1580, 1498, 1471, 1407, 1246, 1134, 998, 837, 776, 721, 677.

## **PHG(Ap3'F-6)**$_3$

MP: 91 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.74 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.89 (ddd, *J* = 8.8, 2.2, 1.3 Hz, 3H), 7.80 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.73 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.30 (t, *J* = 8.7 Hz, 3H), 5.81 (s, *J* = 2.7 Hz, 3H), 4.18 (t, *J* = 6.4 Hz, 6H), 1.92 – 1.80 (m, 6H), 1.59 – 1.48 (m, 6H), 1.46 – 1.33 (m, 12H), 0.95 (t, *J* = 7.1 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.29 (ddd, *J* = 12.1, 8.5, 1.1 Hz).

IR: ν (cm$^{-1}$) = 3052, 2918, 2850, 2620, 1593, 1500, 1465, 1408, 1332, 1298, 1260, 1143, 1107, 1003, 846, 819, 768, 724, 689.

Elemental Analysis: calc. (%) $C_{57}H_{66}F_3N_9O_6$: C 66.46, H 6.46, N 12.24; found (%): C 66.34, H 6.50, N 12.21.

## **PHG(Ap3'F-8)**$_3$

MP: 88 °C

$^1$NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.89 (ddd, *J* = 8.8, 2.2, 1.3 Hz, 3H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.73 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.30 (t, *J* = 8.7 Hz, 3H), 5.79 (s, *J* = 3.4 Hz, 3H), 4.18 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.80 (m, 6H), 1.57 – 1.45 (m, 6H), 1.45 – 1.25 (m, 24H), 0.91 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.30 (ddd, *J* = 12.1, 8.8, 1.2 Hz).

IR: ν (cm$^{-1}$) = 3062, 2922, 2845, 2618, 1593, 1503, 1467, 1413, 1324, 1271, 1145, 1102, 1000, 889, 818, 769, 724, 690.

Elemental Analysis: calc. (%) $C_{63}H_{78}F_3N_9O_6$: C 67.90, H 7.06, N 11.31; found (%): C 68.00, H 7.13, N 11.23.

## **PHG(Ap3'F-9)**$_3$

MP: 88 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.72 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.88 (ddd, *J* = 8.8, 2.2, 1.2 Hz, 3H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.72 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.29 (t, *J* = 8.7 Hz, 3H), 5.79 (s, 3H), 4.17 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.78 (m, 6H), 1.57 – 1.46 (m, 6H), 1.45 – 1.22 (m, 30H), 0.90 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.26 (ddd, *J* = 12.1, 8.8, 1.1 Hz).

IR: ν (cm$^{-1}$) = 3069, 2922, 2853, 2619, 1593, 1503, 1466, 1412, 1330, 1296, 1214, 1155, 1102, 1002, 885, 819, 805, 770, 723, 686.

Elemental Analysis: calc. (%) $C_{66}H_{84}F_3N_9O_6$: C 68.55 H 7.32, N 10.90; found (%): C 68.33, H 7.36, N 10.89.

## **PHG(Ap3'F-10)**$_3$

MP: 87 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.75 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.90 (ddd, *J* = 8.7, 2.2, 1.3 Hz, 3H), 7.81 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.74 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.31 (t, *J* = 8.7 Hz, 3H), 5.81 (s, 3H), 4.19 (t, *J* = 6.4 Hz, 6H), 1.93 – 1.81 (m, 6H), 1.60 – 1.47 (m, 6H), 1.46 – 1.23 (m, 36H), 0.92 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.27 (ddd, *J* = 12.0, 8.7, 1.3 Hz).

IR: ν (cm$^{-1}$) = 3058, 2920, 2851, 2619, 1597, 1503, 1465, 1410, 1298, 1279, 1217, 1155, 1105, 1001, 979, 881, 815, 719, 694.

Elemental Analysis: calc. (%) $C_{69}H_{90}F_3N_9O_6$: C 69.15, H 7.57, N 10.52; found (%): C 69.07, H 7.66, N 10.52.

## **PHG(Ap3'F-11)**$_3$

MP: 87 °C

$^1$H NMR (400 MHz, MeOD-*d4*) δ 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.89 (ddd, *J* = 8.7, 2.2, 1.2 Hz, 3H), 7.79 (dd, *J* = .7, 1.6 Hz, 6H), 7.72 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.29 (t, *J* = 8.7 Hz, 3H), 5.79 (s, 3H), 4.18 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.77 (m, 6H), 1.57 – 1.46 (m, 6H), 1.46 – 1.19 (m, 42H), 0.89 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d4*) δ -134.26 (ddd, *J* = 12.0, 8.7, 1.1 Hz).

IR: ν (cm$^{-1}$) = 3083, 3052, 2918, 2916, 2851, 2619, 1585, 1512, 1470, 1409, 1325, 1272, 1210, 1160, 1102, 1876, 826, 808, 767, 716.

Elemental Analysis: calc. (%) $C_{72}H_{96}F_3N_9O_6$: C 69.71, H 7.80, N 10.16; found (%): C 69.66, H 8.02, N 10.14.

## **PHG(Ap3'F-12)**$_3$

MP: 90 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.90 (ddd, *J* = 8.7, 2.2, 1.3 Hz, 3H), 7.80 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.74 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.31 (t, *J* = 8.7 Hz, 3H), 5.79 (s, 3H), 4.19 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.81 (m, 6H), 1.59 – 1.48 (m, 6H), 1.44 – 1.21 (m, 48H), 0.89 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.26 (ddd, *J* = 12.1, 8.8, 1.1 Hz).

IR): ν (cm$^{-1}$) = 3066, 2920, 2852, 2623, 1594, 1502, 1468, 1412, 1324, 1270, 1155, 1104, 1002, 885, 806, 768, 721, 686.

Elemental Analysis: calc. (%) $C_{75}H_{102}F_3N_9O_6$: C 70.23, H 8.02, N 9.83; found (%): C 70.23, H 8.16, N 9.86.

## **PHG(Ap3'5'F-6)**$_3$

MP: 85 °C

$^1$H NMR (300 MHz, DMSO-d$_6$) δ 8.93 (s, 3H), 8.83 (dd, *J* = 4.6, 1.4 Hz, 6H), 7.92 - 7.57 (m, 12H), 5.65 (s, 3H), 4.24 (t, *J* = 6.3 Hz, 6H), 1.69 (quint, *J* = 6.7 Hz 6H), 1.49 - 1.16 (m, 18H), 0.85 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (282 MHz, DMSO-d$_6$) δ -126.35 (d, *J* = 8.6 Hz).

IR: ν (cm$^{-1}$) = 3076, 2953, 2926, 2868, 2645, 2114, 1591, 1498, 1470, 1435, 1413, 1390, 1337, 1298, 1242, 1148, 1109, 1042, 1042, 1003, 897, 873, 830, 734, 693, 632, 565.

Elemental Analysis: calc. (%) $C_{57}H_{63}F_6N_9O_6$: C 63.15, H 5.86, N 11.63; found (%): C 62.93, H 5.79, N 11.28.

## **PHG(Ap3'5'F-8)**$_3$

MP: 81 °C

$^1$NMR (300 MHz, DMSO-*d*$_6$) δ 8.92 (s, 3H), 8.83 (dd, *J* = 4.5, 1.6 Hz, 6H), 7.81 - 7.65 (m, 12H), 5.65 (s, 3H), 4.25 (t, *J* = 6.4 Hz, 6H), 1.77 - 1.63 (m, 6H), 1.49 - 1.12 (m, 30H), 0.84 (t, *J* = 6.7 Hz, 9H).

$^{19}$F NMR (282 MHz, DMSO-*d*$_6$) δ -126.37 (t, *J* = 15.1 Hz).

IR: ν (cm$^{-1}$) = 3075, 2954, 2920, 2854, 1645, 1591, 1498, 1470, 1435, 1413, 1390, 1341, 1299, 1242, 1163, 1148, 1109, 1040, 1003,983, 962, 872, 723, 692.

Elemental Analysis: calc. (%) $C_{63}H_{75}F_6N_9O_6$: C 64.77, H 6.47, N 10.79; found (%): C 64.72, H 6.41, N 10.65.

### 1.1 Synthesis of the HBAs with 2-fluoro-1,3,5-trihydroxybenzene (F-PHG) as core unit

**General procedure:**

**F-PHG** (1.0 eq.) and the corresponding side chain (**Ap-N, Ap3F-N, Ap3'F-N, or Ap3'5'F-N)** (3.0 eq.) were weighed and separately dissolved in acetone. The solvent was removed under reduced pressure and the desired aggregates were formed in quantitative yields.

## **F-PHG(Ap-6)**$_3$

MP: 105 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.70 (dd, *J* = 4.7, 1.4 Hz, 6H), 8.01 – 7.92 (m, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.08 (d, *J* = 9.0 Hz, 6H), 5.87 (d, *J* = 6.5 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 6H), 1.87 – 1.75 (m, 6H), 1.55 – 1.43 (m, 6H), 1.43 – 1.31 (m, 12H), 0.93 (t, *J* = 7.1 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -175.12 (t, *J* = 6.4 Hz).

IR: ν (cm$^{-1}$) = 3036, 2935, 2858, 2857, 2648, 1730, 1592, 1499, 1406, 1255, 1141, 1071, 1001, 928, 839, 794, 769, 724.

Elemental Analysis: calc. (%) $C_{57}H_{68}FN_9O_6$: C 68.86, H 6.89, N 12.68; found (%): C 68.84, H 7.08, N 12.81.

## **F-PHG(Ap-8)**$_3$

MP: 98 °C

$^1$NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.97 (d, *J* = 9.0 Hz, 6H), 7.77 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.09 (d, *J* = 9.1 Hz, 6H), 5.86 (d, *J* = 6.4 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.88 – 1.76 (m, 6H), 1.57 – 1.45 (m, 6H), 1.43 – 1.29 (m, 24H), 0.91 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -175.14 (t, *J* = 6.4 Hz).

IR: ν (cm$^{-1}$) = 3053 (mbr), 2922, 2852, 2634, 1583, 1498, 1469, 1408, 1254, 1137, 1065, 1000, 836, 795, 724.

Elemental Analysis: calc. (%) $C_{63}H_{80}FN_9O_6$: C 70.17; H 7.48, N 11.69; found (%): C 70.33, H 7.62, N 11.90.

## **F-PHG(Ap-9)**$_3$

MP: 94 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.72 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.98 (d, *J* = 9.0 Hz, 6H), 7.78 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.09 (d, *J* = 9.1 Hz, 6H), 5.89 (d, *J* = 6.4 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 6H), 1.88 – 1.75 (m, 6H), 1.57 – 1.46 (m, 6H), 1.43 – 1.27 (m, 30H), 0.92 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -175.10 (t, *J* = 6.4 Hz).

IR: ν (cm$^{-1}$) = 3051, 2954, 2919, 2857, 2852, 2639, 1584, 1500, 1406, 1255, 1141, 1001, 925, 839, 794, 775, 718.

Elemental Analysis: calc. (%) $C_{66}H_{86}FN_9O_6$: C 70.75, H 7.74, N 11.25; found (%): C 71.16, H 8.00, N 11.55.

## **F-PHG(Ap-10)**$_3$

MP: 98 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.97 (d, *J* = 9.0 Hz, 6H), 7.77 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.09 (d, *J* = 9.0 Hz, 6H), 5.87 (d, *J* = 6.4 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 6H), 1.87 – 1.76 (m, 6H), 1.55 – 1.45 (m, 6H), 1.41 – 1.26 (m, 36H), 0.90 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -175.13 (t, *J* = 6.4 Hz).

IR: ν (cm$^{-1}$) = 3047, 2917, 2850, 2641, 1584, 1498, 1408, 1251, 1143, 1002, 925, 836, 795, 774, 718.

Elemental Analysis: calc. (%) $C_{69}H_{92}FN_9O_6$: C 71.29, H 7.98, N 10.84; found (%): C 71.21, H 8.10, N 10.91.

## **F-PHG(Ap-11)**$_3$

MP: 89 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.98 (d, *J* = 9.0 Hz, 6H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.09 (d, *J* = 9.1 Hz, 6H), 5.86 (d, *J* = 6.5 Hz, 2H), 4.10 (t, *J* = 6.4 Hz, 6H), 1.86 – 1.78 (m, 6H), 1.55 – 1.45 (m, 6H), 1.41 – 1.26 (m, 42H), 0.90 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -175.15 (t, *J* = 6.4 Hz).

IR: ν (cm$^{-1}$) = 3051, 2918, 2850, 2644, 1582, 1499, 1406, 1255, 1138, 1004, 928, 839, 794, 720.

Elemental Analysis: calc. (%) $C_{72}H_{98}FN_9O_6$: C 71.79; H 8.20, N 10.46; found (%): C 71.92, H 8.30, N 10.58.

## **F-PHG(Ap-12)**$_3$

MP: 96 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.71 (d, *J* = 6.1 Hz, 6H), 7.97 (d, *J* = 8.9 Hz, 6H), 7.78 (d, *J* = 6.0 Hz, 6H), 7.09 (d, *J* = 8.9 Hz, 6H), 5.87 (d, *J* = 6.4 Hz, 2H), 4.09 (t, *J* = 6.3 Hz, 6H), 1.89 – 1.73 (m, 6H), 1.56 – 1.17 (m, 54H), 0.89 (t, *J* = 6.7 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -175.14 (t, *J* = 6.3 Hz).

IR): ν (cm$^{-1}$) = 3046, 2918, 2851, 2643, 1583, 1498, 1408, 1251, 1137, 1002, 922, 836, 795, 769, 724.

Elemental Analysis: calc. (%) $C_{75}H_{104}FN_9O_6$: C 72.26, H 8.41, N 10.11; found (%): C 72.54, H 8.55, N 10.13.

## **F-PHG(Ap3F-6)**$_3$

MP: 99 °C

$^1$H NMR (300 MHz, MeOD) δ 8.68 (d, *J* = 2.7 Hz, 3H), 8.48 (d, *J* = 5.3 Hz, 3H), 8.00 (d, *J* = 9.1 Hz, 6H), 7.63 (dd, *J* = 6.5, 5.4 Hz, 3H), 7.11 (d, *J* = 9.1 Hz, 6H), 5.86 (d, *J* = 6.4 Hz, 2H), 4.11 (t, *J* = 6.4 Hz, 6H), 1.89 – 1.76 (m, 6H), 1.58 – 1.31 (m, 18H), 0.94 (t, *J* = 7.0 Hz, 9H).

$^{19}$F NMR (282 MHz, MeOD) δ -141.77 (dd, *J* = 6.4, 2.3 Hz, 2F), -175.15 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3076, 2942, 2919, 2855, 2669, 1597, 1578, 1499, 1409, 1251, 1134, 1022, 923, 838, 7759, 767.

## **F-PHG(Ap3'F-6)**$_3$

MP: 88 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.89 (ddd, *J* = 8.7, 2.2, 1.3 Hz, 3H), 7.80 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.73 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.30 (t, *J* = 8.7 Hz, 3H), 5.87 (d, *J* = 6.4 Hz, 2H), 4.18 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.80 (m, 6H), 1.59 – 1.47 (m, 6H), 1.46 – 1.32 (m, 12H), 0.95 (t, *J* = 7.1 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.31 (ddd, *J* = 11.9, 8.6, 1.1 Hz, 3F), -175.13 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3055, 2953, 2929, 2857, 2659, 2605, 1612, 1588, 1501, 1464, 1410, 1323, 1274, 1213, 1173, 1152, 1101, 1053, 1000, 885, 869, 838, 802, 768, 725.

Elemental Analysis: calc. (%) $C_{57}H_{65}F_4N_9O_6$: C 65.31, H 6.25, N 12.03; found (%): C 65.63, H 6.25, N 12.21.

## F-PHG(Ap3'F-8)$_3$

MP: 81 °C

$^1$NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.88 (ddd, *J* = 8.8, 2.2, 1.3 Hz, 3H), 7.79 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.72 (dd *J* = 12.0, 2.3 Hz, 3H), 7.29 (t, *J* = 8.7 Hz, 3H), 5.86 (d, *J* = 6.4 Hz, 2H), 4.17 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.79 (m, 6H), 1.57 – 1.45 (m, 6H), 1.43– 1.29 (m, 24H), 0.91 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.28 (ddd, *J* = 12.5, 8.8, 1.1 Hz, 3F), -175.13 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3056, 2918, 2854, 2604, 1593, 1503, 1467, 1412, 1325, 1272, 1214, 1179, 1149, 1103, 999, 886, 829, 801, 771, 724.

Elemental Analysis: calc. (%) $C_{63}H_{77}F_4N_9O_6$: C 66.82, H 6.85, N 11.13; found (%): C 67.38, H 7.02, N 11.34.

## F-PHG(Ap3'F-9)$_3$

MP: 81 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.88 (ddd, *J* = 8.7, 2.2, 1.2 Hz, 3H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.72 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.29 (t, *J* = 8.7 Hz, 3H), 5.86 (d, *J* = 6.4 Hz, 2H), 4.17 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.80 (m, 6H), 1.56 – 1.45 (m, 6H), 1.43 – 1.27 (m, 30H), 0.90 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.27 (ddd, *J* = 12.0, 8.5, 1.0 Hz, 3F), -175.14 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3056, 2953, 2920, 2853, 2662, 1594, 1505, 1466, 1412, 1325, 1278, 1212, 1177, 1151, 1103, 1067 1003, 874, 811, 838, 807, 771, 723.

Elemental Analysis: calc. (%) $C_{66}H_{83}F_4N_9O_6$: C 67.50, H 7.12, N 10.73; found (%): C 67.92, H 7.21, N 10.93.

## F-PHG(Ap3'F-10)$_3$

MP: 81 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.72 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.88 (ddd, *J* = 8.7, 2.2, 1.3 Hz, 3H), 7.78 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.72 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.29 (t, *J* = 8.7 Hz, 3H), 5.86 (d, *J* = 6.4 Hz, 2H), 4.17 (t, *J* = 6.4 Hz, 6H), 1.90 – 1.79 (m, 6H), 1.56 – 1.45 (m, 6H), 1.42 – 1.27 (m, 36H), 0.89 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.24 (ddd, *J* = 12.2, 8.8, 1.1 Hz, 3F), -175.12 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3067, 3054, 2917, 2851, 1591, 1503, 1471, 1406, 1338, 1271, 1212, 1175, 1153, 1102, 1000, 886, 828, 800, 768, 721.

Elemental Analysis: calc. (%) $C_{69}H_{89}F_4N_9O_6$: C 68.13, H 7.37, N 10.36; found (%): C 68.86, H 7.50, N 10.52.

## F-PHG(Ap3'F-11)$_3$

MP: 92 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$) δ 8.73 (dd, *J* = 4.7, 1.5 Hz, 6H), 7.89 (ddd, *J* = 8.7, 2.2, 1.2 Hz, 3H), 7.79 (dd, *J* = 4.7, 1.6 Hz, 6H), 7.73 (dd, *J* = 12.0, 2.3 Hz, 3H), 7.30 (t, *J* = 8.7 Hz, 3H), 5.87 (d, *J* = 6.4 Hz, 2H), 4.18 (t, *J* = 6.4 Hz, 6H), 1.91 – 1.80 (m, 6H), 1.57 – 1.46 (m, 6H), 1.43 – 1.26 (m, 42H), 0.90 (t, *J* = 6.9 Hz, 9H).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.25 (ddd, *J* = 12.0, 8.7, 1.0 Hz, 3F), -175.14 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3253, 3059, 2953, 2917, 2851, 2660, 2604, 1613, 1586, 1496, 1470, 1409, 1326, 1277, 1210, 1176, 1139, 1103, 1074, 1051, 1008, 875, 801, 767, 717.

Elemental Analysis: calc. (%) $C_{72}H_{95}F_4N_9O_6$: C 68.71, H 7.61, N 10.02; found (%): C 69.18, H 7.75, N 10.09.

## F-PHG(Ap3'F-12)$_3$

MP: 92 °C

$^1$H NMR (400 MHz, MeOD-*d*$_4$, *F-PG_2F-C12*) δ 8.73 (dd, *J* = 4.7, 1.6 Hz, 6H, C*H*$_{pyr}$), 7.89 (ddd, *J* = 8.8, 2.1, 1.2 Hz, 3H, C*H*$_{ar}$), 7.79 (dd, *J* = 4.7, 1.6 Hz, 6H, C*H*$_{pyr}$), 7.73 (dd, *J* = 12.0, 2.3 Hz, 3H, C*H*$_{ar}$), 7.30 (t, *J* = 8.7 Hz, 3H, C*H*$_{ar}$), 5.86 (d, *J* = 6.4 Hz, 2H, C*H*$_{F\text{-}PG}$), 4.18 (t, *J* = 6.4 Hz, 6H, C*H*$_2$), 1.91 – 1.80 (m, 6H, C*H*$_2$), 1.57 – 1.47 (m, 6H, C*H*$_2$), 1.41 – 1.25 (m, 48H, C*H*$_2$), 0.89 (t, *J* = 6.8 Hz, 9H, C*H*$_3$).

$^{19}$F NMR (377 MHz, MeOD-*d*$_4$) δ -134.25 (ddd, *J* = 11.9, 8.9, 1.4 Hz, 3F), -175.14 (t, *J* = 6.4 Hz, 1F).

IR): ν (cm$^{-1}$) = 3246, 3074, 3053, 2956, 2916, 2856, 2602, 1613, 1587, 1497, 147, 1409, 1326, 1273, 1210, 1175, 1139, 1103, 1074, 998, 876, 801, 767, 716.

Elemental Analysis: calc. (%) $C_{75}H_{101}F_4N_9O_6$: C 69.26, H 7.83, N 9.69; found (%): C 69.68, H 8.09, N 9.82.

## F-PHG(Ap3'5'F-6)$_3$

MP: 99 °C

$^1$H NMR (300 MHz, DMSO-d$_6$) δ 9.37 (s, *J* = 8.5 Hz, 2H), 8.87 (s, 1H), 8.83 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.84 - 7.63 (m, 12H), 5.79 (d, *J* = 6.5 Hz, 2H), 4.25 (t, *J* = 6.4 Hz, 6H), 1.78 - 1.61 (m, 6H), 1.50 - 1.17 (m, 18H), 0.85 (t, *J* = 7.0 Hz, 9H).

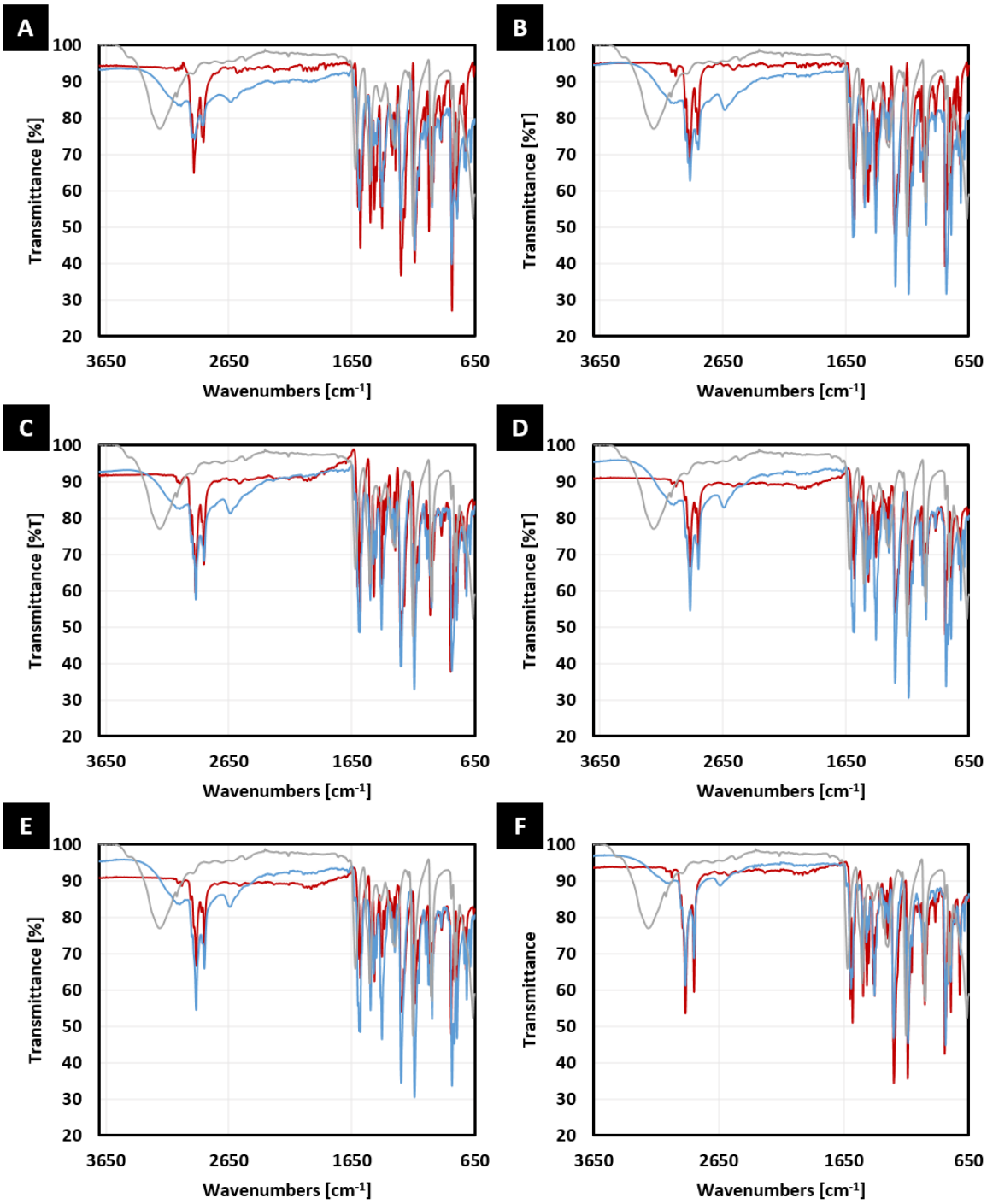
$^{19}$F NMR (282 MHz, DMSO-d$_6$) δ -126.34 (d, *J* = 8.7 Hz, 6F), -172.13 (t, *J* = 6.4 Hz, 1F).

IR: ν (cm$^{-1}$) = 3301, 3063, 2955, 2923, 2859, 2623, 2587, 1593, 1496, 1433, 1328, 1295, 1239, 1180, 1139, 995, 876, 812, 770, 729.

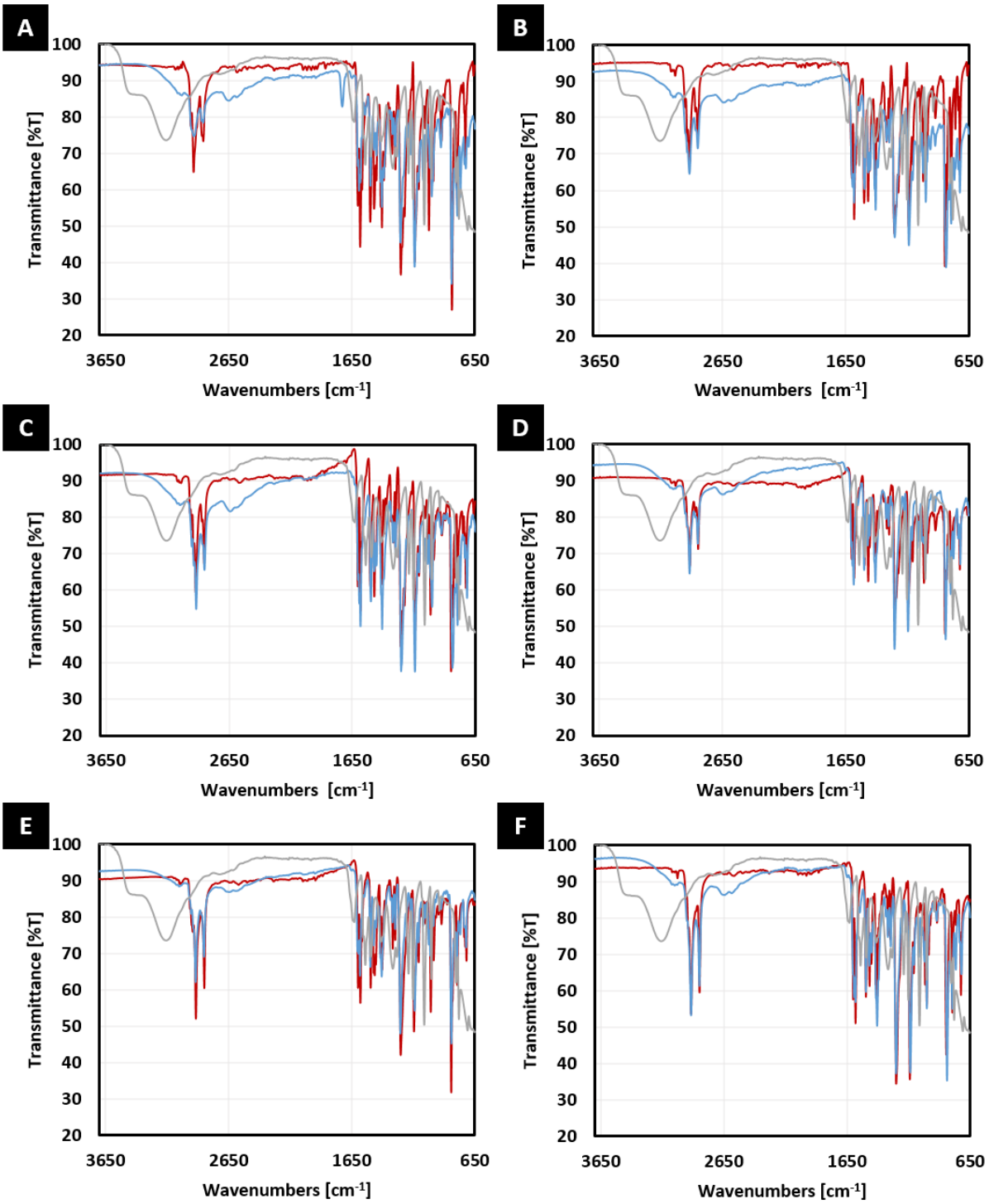
Elemental Analysis: calc. (%) $C_{57}H_{62}F_7N_9O_6$: C 62.12, H 5.67, N 11.44; found (%): C 62.14, H 5.78, N 11.45.

**F-PHG(Ap3'5'F-8)$_3$**
MP: 86 °C
$^1$NMR (300 MHz, DMSO-$d_6$) δ 9.36 (s, 2H), 8.86 (s, 1H), 8.82 (dd, *J* = 4.7, 1.4 Hz, 6H), 7.82 - 7.61 (m, 12H), 5.79 (d, *J* = 6.5 Hz, 2H), 4.23 (t, *J* = 6.4 Hz, 6H), 1.79-1.62 (m, 6H), 1.51 - 1.11 (m, 30H), 0.83 (t, *J* = 6.7 Hz, 9H).
$^{19}$F NMR ((282 MHz, DMSO-$d_6$) δ -126.36 (d, *J* = 8.6 Hz, 6F), -172.12 (t, *J* = 6.2 Hz, 1F).
IR: ν (cm$^{-1}$) = 3382, 3074, 2935, 2923, 2855, 2670, 1591, 1496, 1435, 1334, 1297, 1241, 1180, 1150, 1107, 1038, 1004, 873, 806, 773, 725.
Elemental Analysis: calc. (%) $C_{63}H_{74}F_7N_9O_6$: C 63.78, H 6.29, N 10.63; found (%): C 63.74, H 6.32, N 10.65.

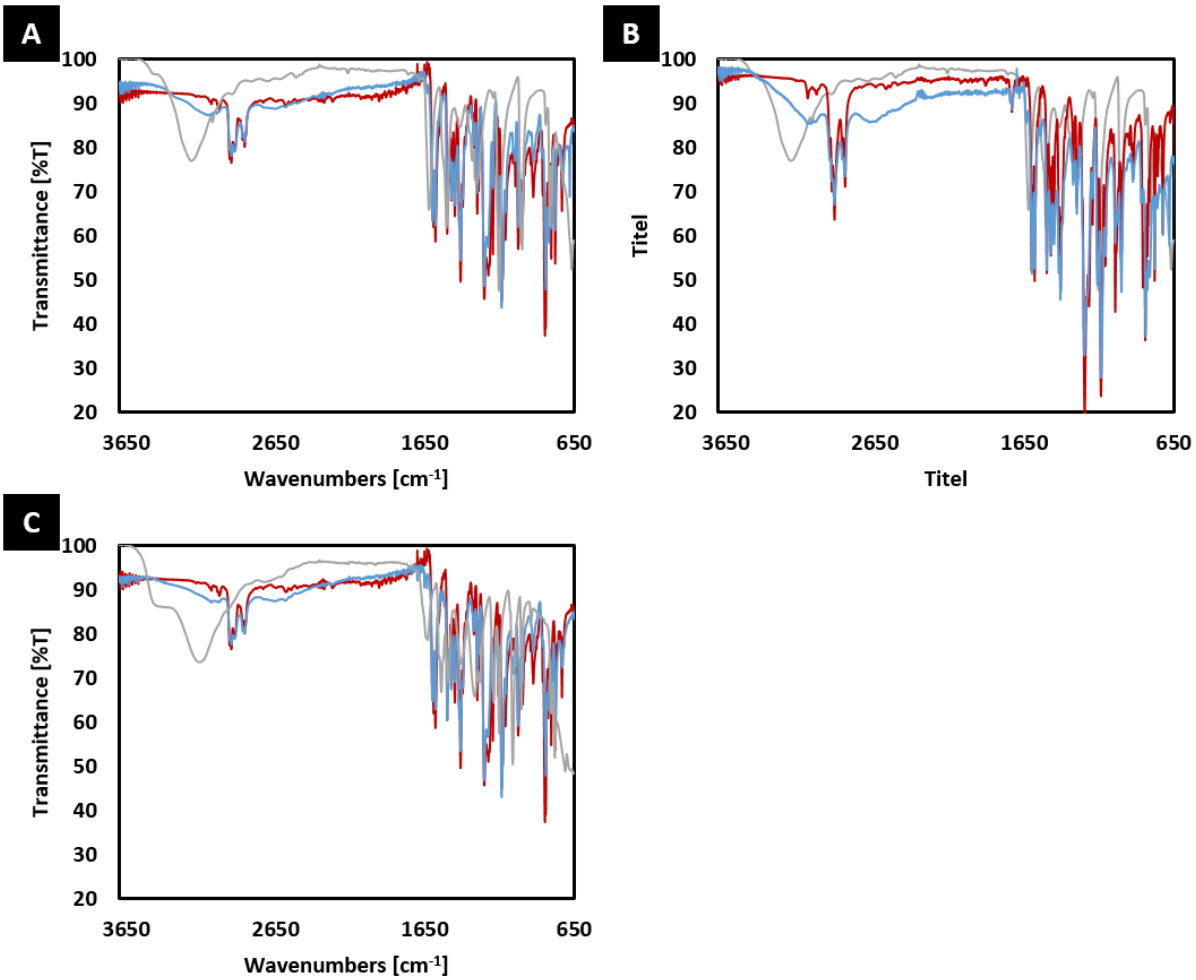
## 3. Characterization of the mesomorphic properties of the hydrogen-bonded assemblies



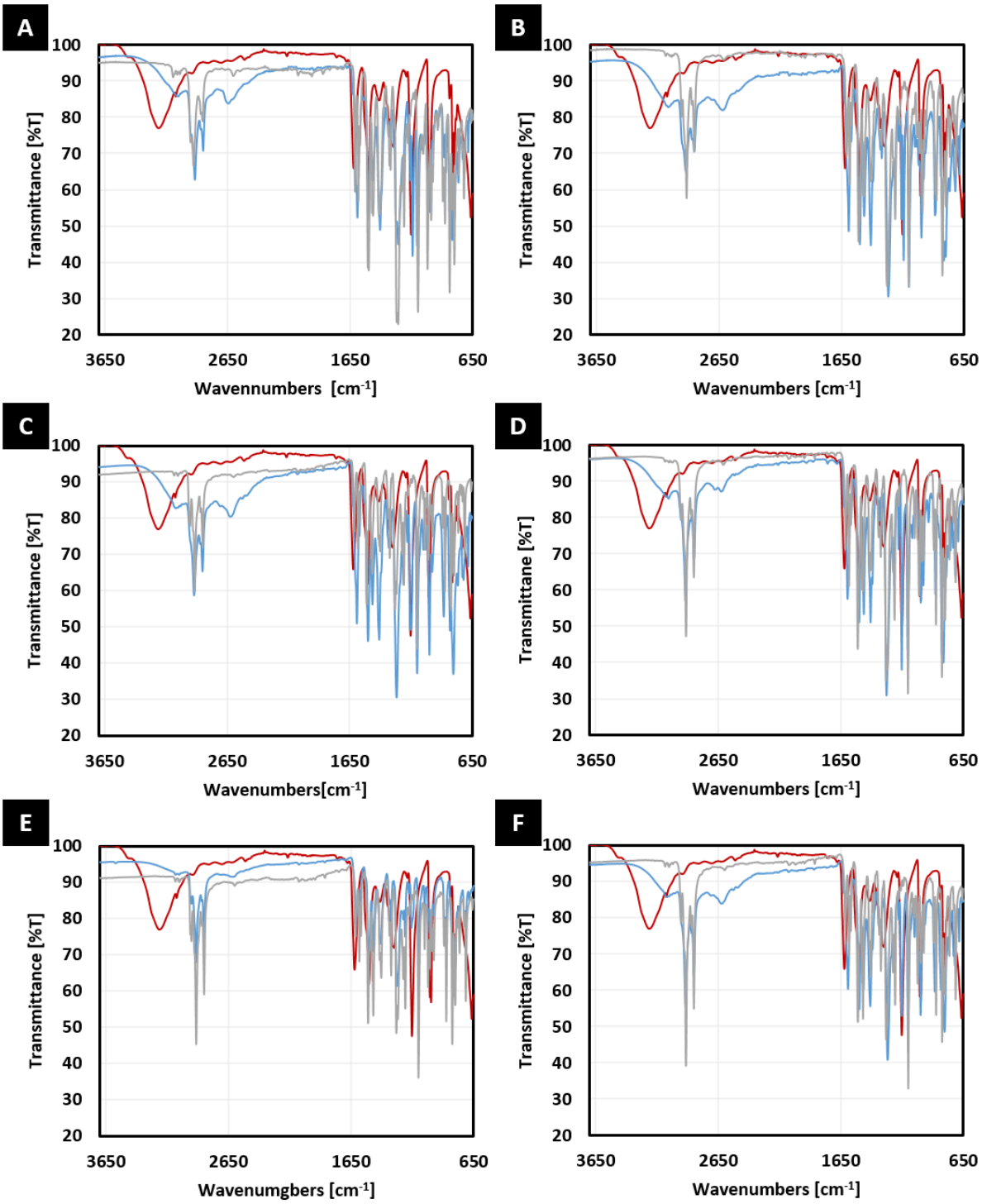

**Supporting Figure S1.** IR spectra of **PHG(Ap-6)$_3$** (A), **PHG(Ap-8)$_3$** (B), **PHG(Ap-9)$_3$** (C), **PHG(Ap-10)$_3$** (D), **PHG(Ap-11)$_3$** (E), **PHG(Ap-12)$_3$** (F).



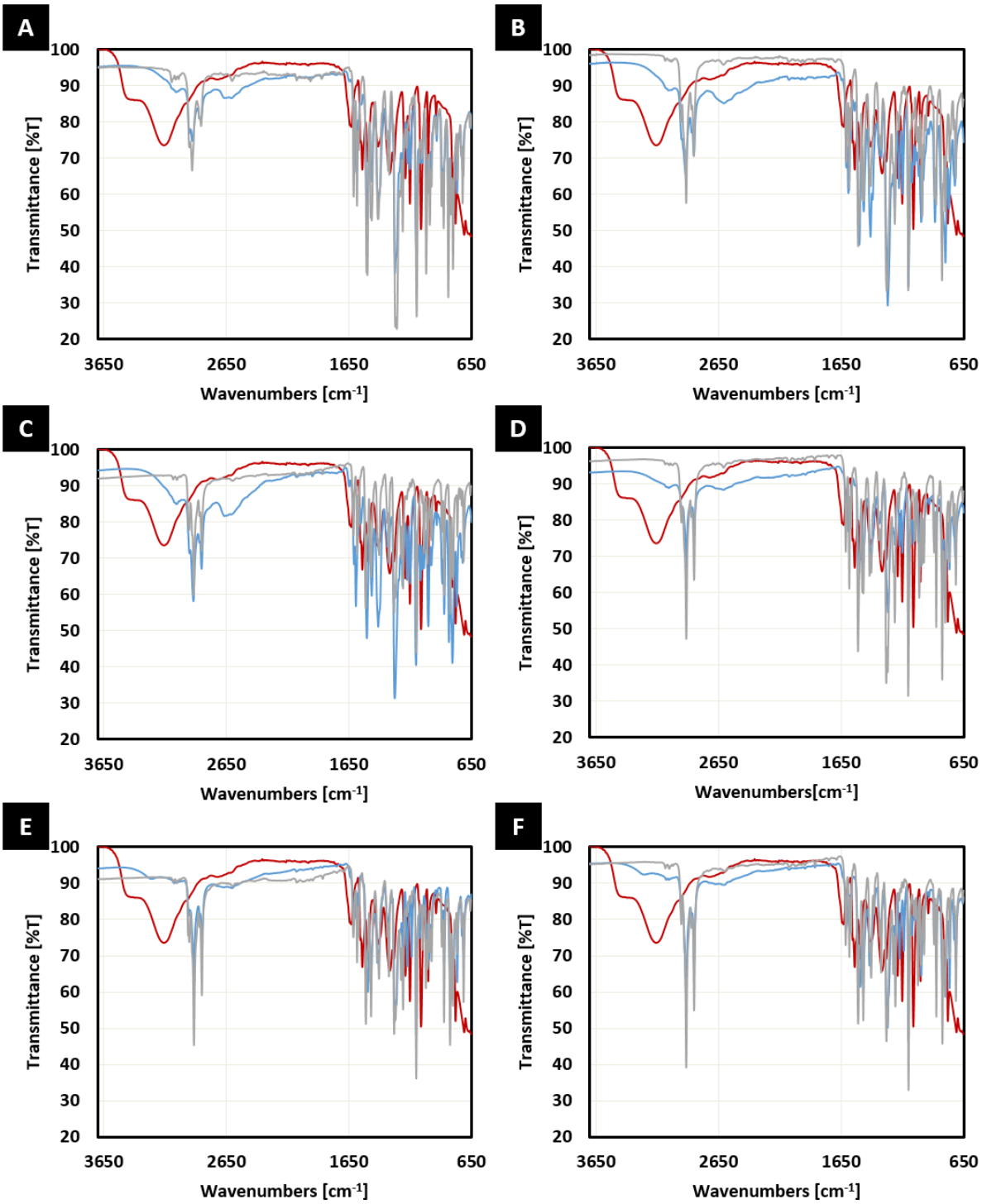

**Supporting Figure S2.** IR spectra of **F-PHG(Ap-6)**$_3$ (A), **F-PHG(Ap-8)**$_3$ (B), **F-PHG(Ap-9)**$_3$ (C), **F-PHG(Ap-10)**$_3$ (D), **F-PHG(Ap-11)**$_3$ (E), **F-PHG(Ap-12)**$_3$ (F).



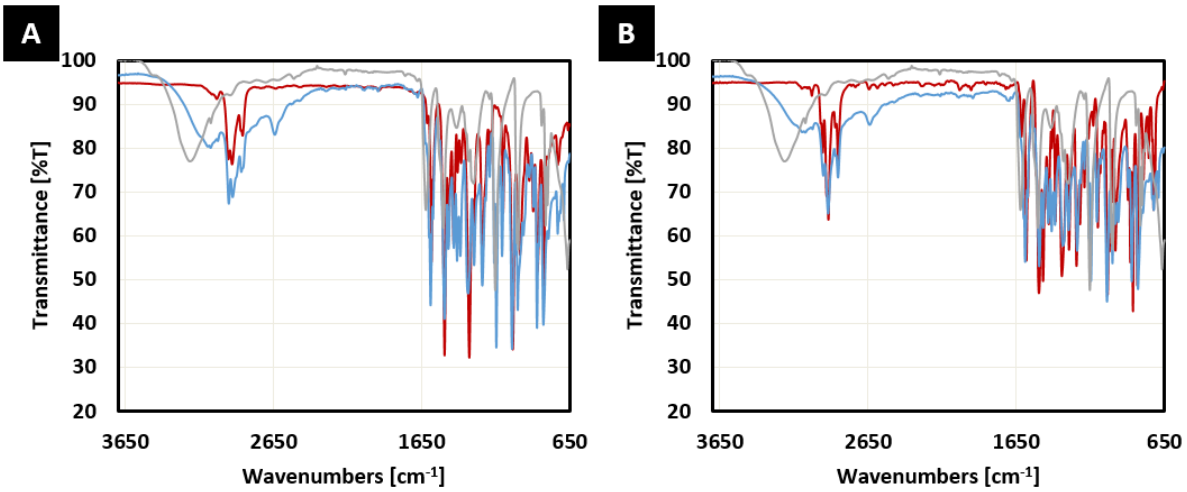

**Supporting Figure S3.** IR spectra of **PHG**(**Ap3F-6**)$_3$ (A), **PHG**(**Ap3F-8**)$_3$ (B), **F-PHG**(**Ap3F-6**)$_3$ (C).



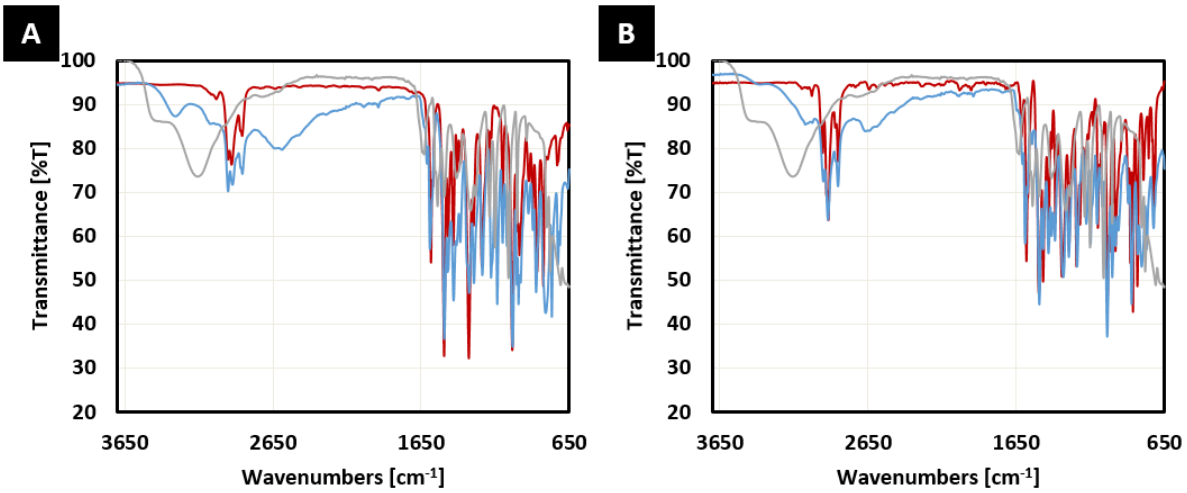

**Supporting Figure S4.** IR spectra of **PHG(Ap3'F-6)**$_3$ (A), **PHG(Ap3'F-8)**$_3$ (B), **PHG(Ap3'F-9)**$_3$ (C), **PHG(Ap3'F-10)**$_3$ (D), **PHG(Ap3'F-11)**$_3$ (E), **PHG(Ap3'F-12)**$_3$ (F).



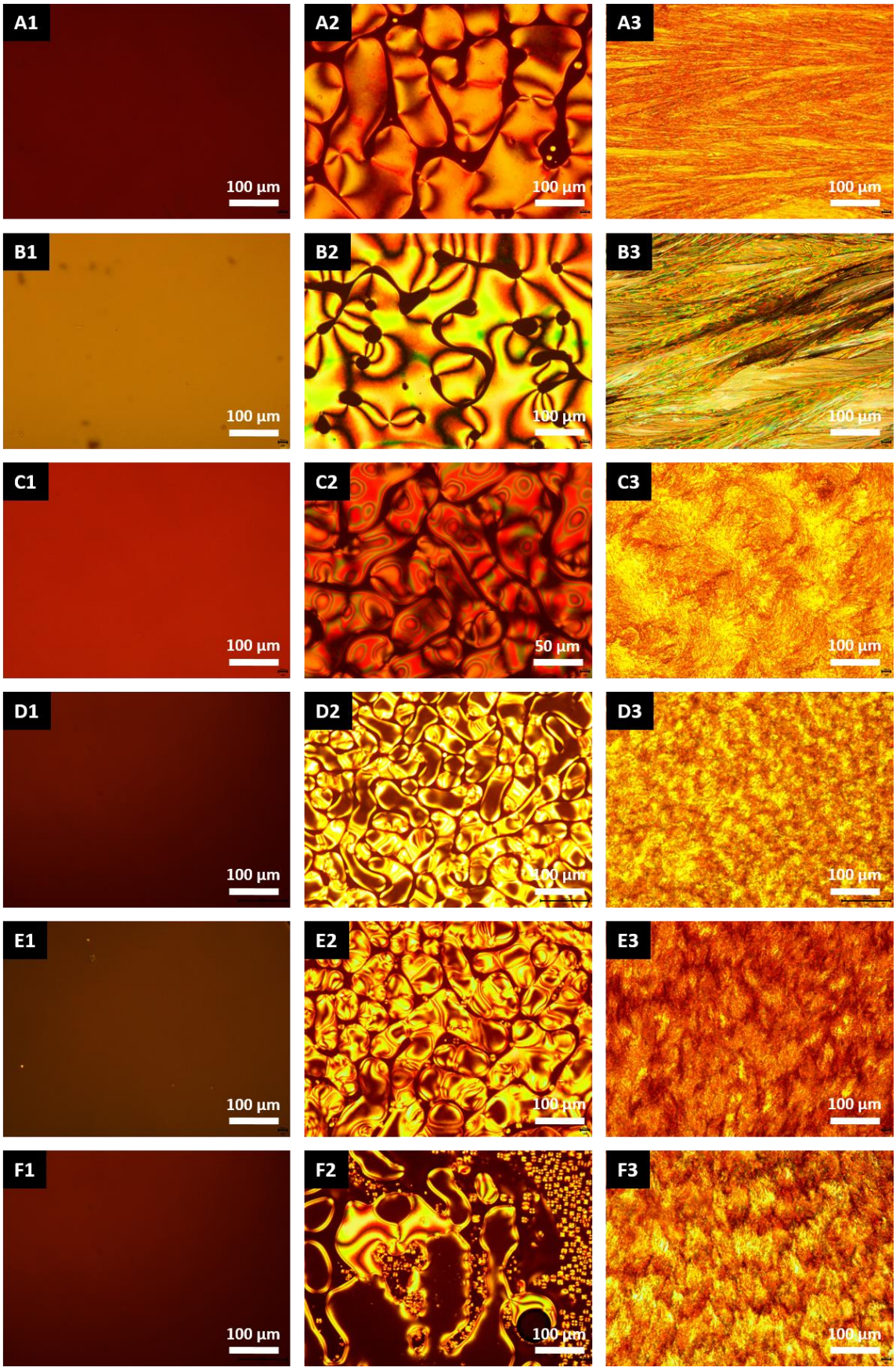

**Supporting Figure S5.** IR spectra of **F-PHG(Ap3'F-6)**$_3$ (A), **F-PHG(Ap3'F-8)**$_3$ (B), **F-PHG(Ap3'F-9)**$_3$ (C), **F-PHG(Ap3'F-10)**$_3$ (D), **F-PHG(Ap3'F-11)**$_3$ (E), **F-PHG(Ap3'F-12)**$_3$ (F).



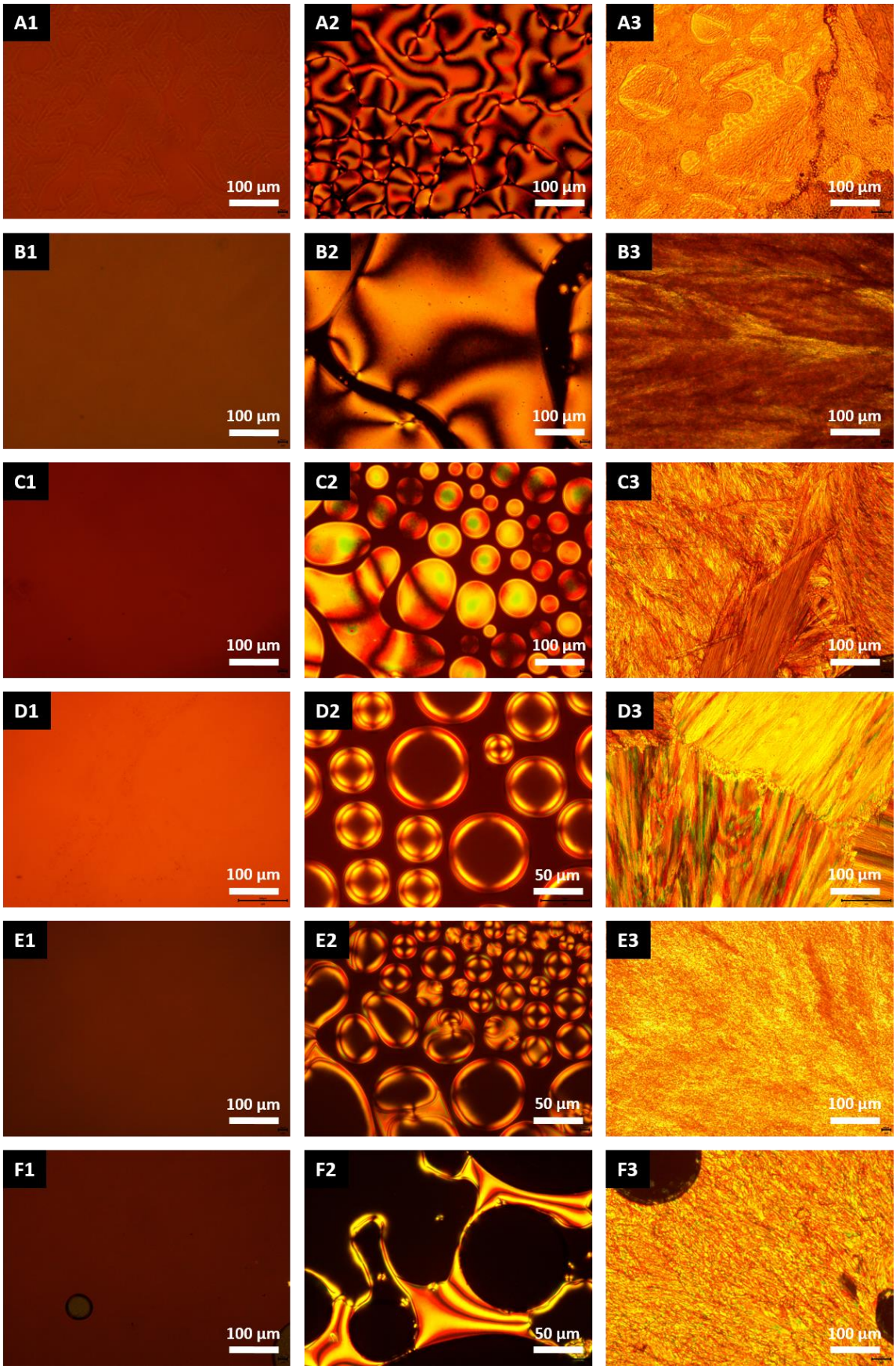

**Supporting Figure S6.** IR spectra of **PHG(Ap3'5'F-6)**$_3$ (A), **PHG(Ap3'5'F-8)**$_3$ (B).



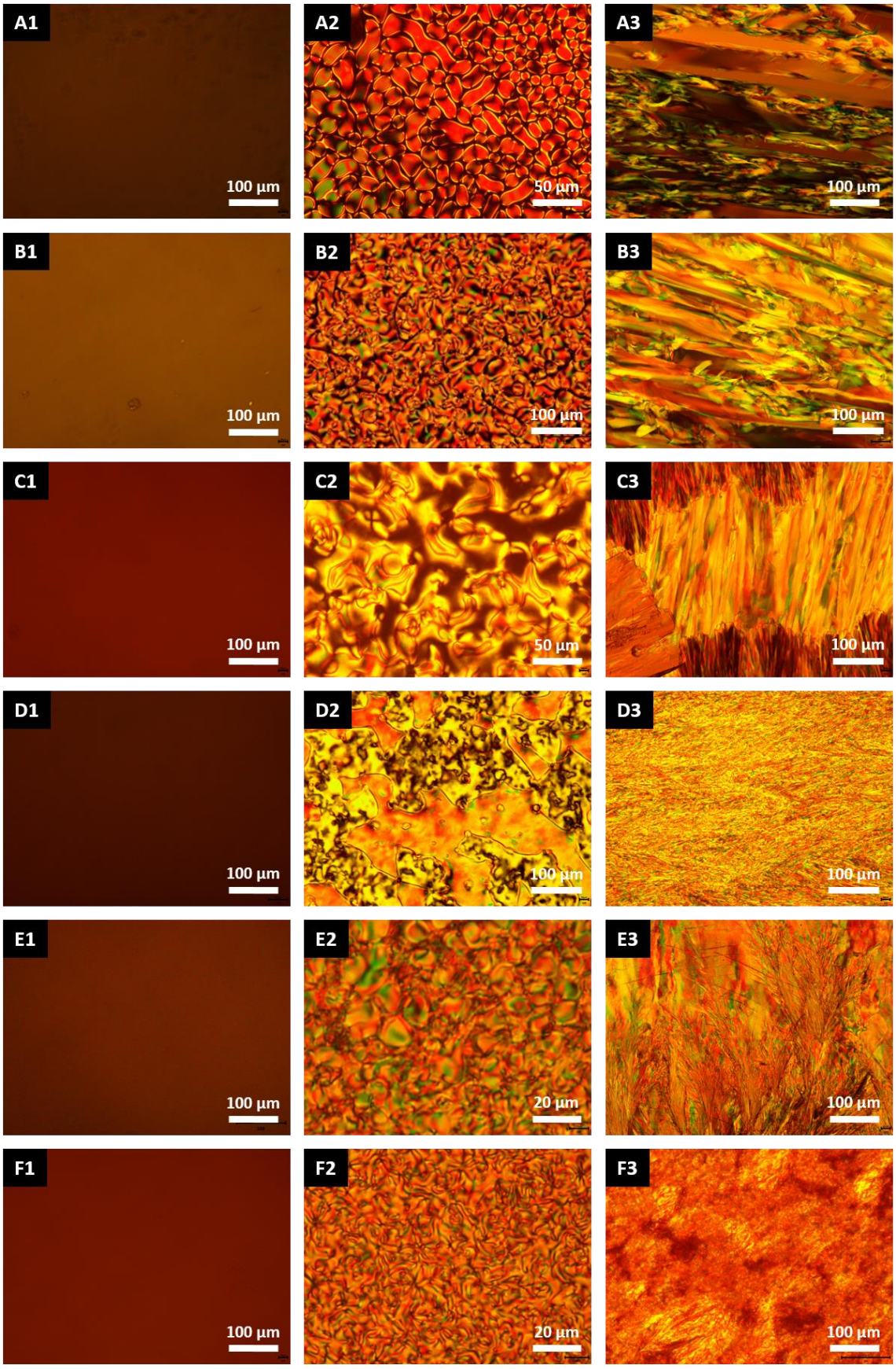

**Supporting Figure S7.** IR spectra of **F-PHG(Ap3'5'F-6)**$_3$ (A), **F-PHG(Ap3'5'F-8)**$_3$ (B).



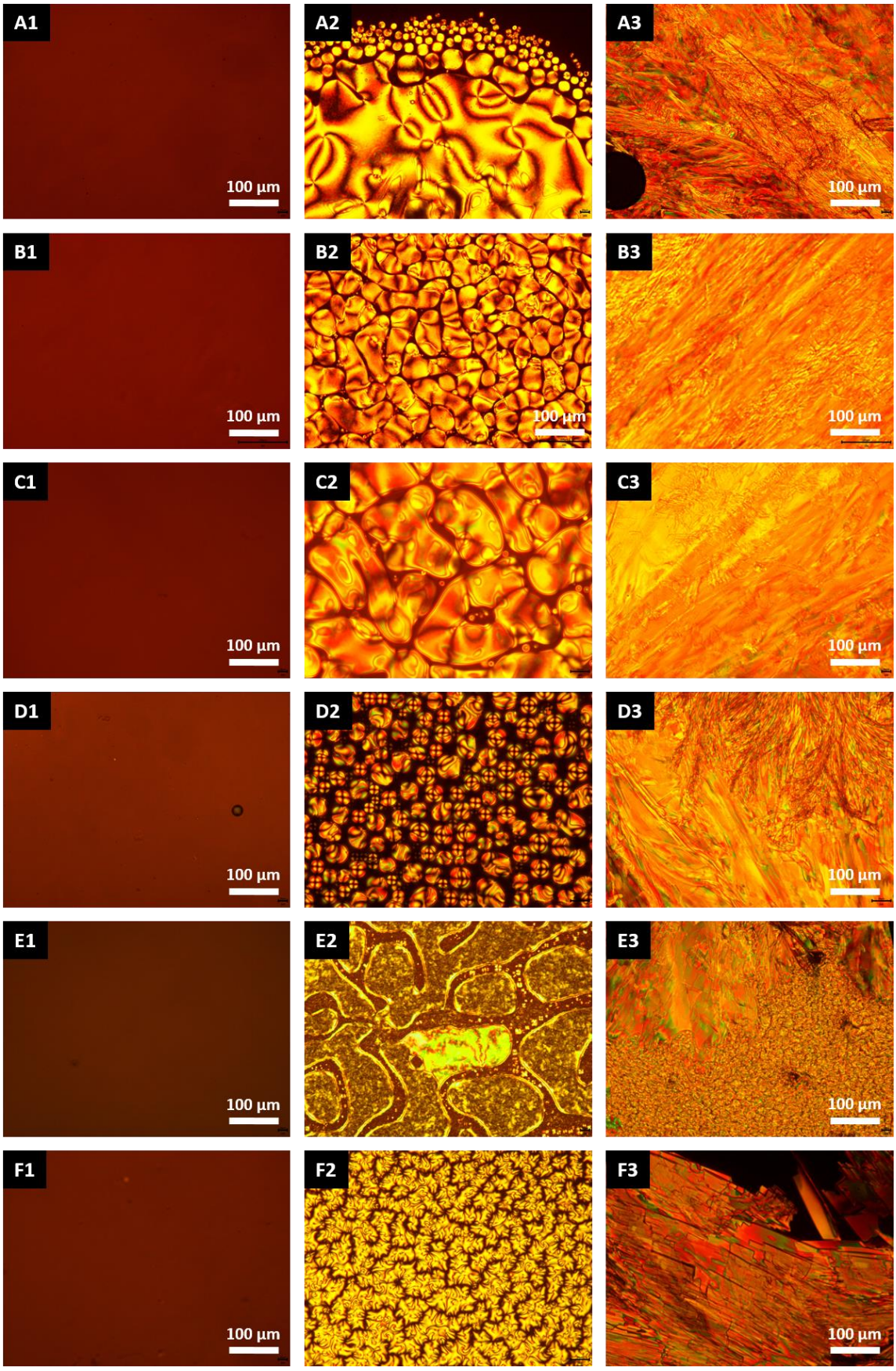

**Supporting Figure S8.** POM images of the **PHG**(**Ap-N**)$_3$ assemblies in their isotropic (1), nematic (2) and crystalline phase (3) under crossed polarizers. Representative micrographs of **PHG**(**Ap-6**)$_3$ (A), **PHG**(**Ap-8**)$_3$ (B), **PHG**(**Ap-9**)$_3$ (C), **PHG**(**Ap-10**)$_3$ (D), **PHG**(**Ap-11**)$_3$ (E), **PHG**(**Ap-12**)$_3$ (F) are shown.



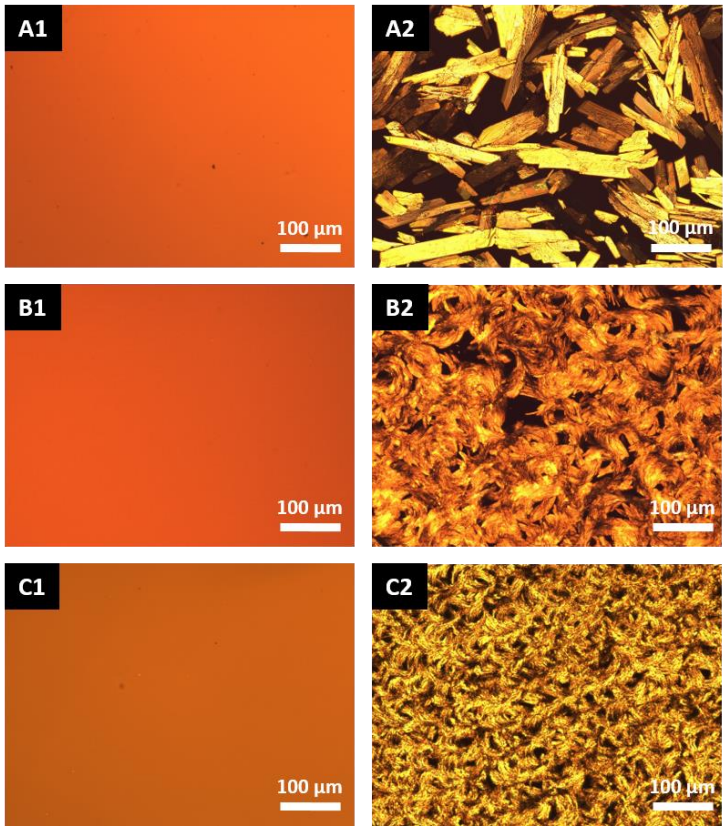

**Supporting Figure S9.** POM images of the **F-PHG(Ap-N)**$_3$ assemblies in their isotropic (1), nematic (2) and crystalline phase (3) under crossed polarizers. Representative micrographs of **F-PHG(Ap-6)**$_3$ (A), **F-PHG(Ap-8)**$_3$ (B), **F-PHG(Ap-9)**$_3$ (C), **F-PHG(Ap-10)**$_3$ (D), **F-PHG(Ap-11)**$_3$ (E), **F-PHG(Ap-12)**$_3$ (F) are shown.



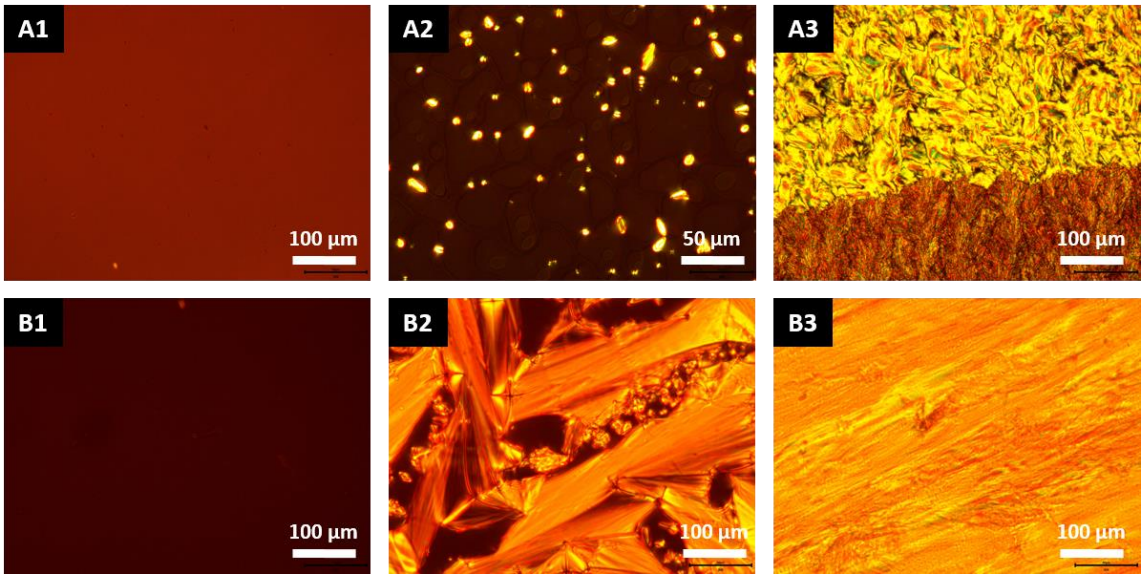

**Supporting Figure S10.** POM images of the **PHG**(**Ap3'F-N**)$_3$ assemblies in their isotropic (1), nematic (2) and crystalline phase (3) under crossed polarizers. Representative micrographs of **PHG**(**Ap3'F-6**)$_3$ (A), **PHG**(**Ap3'F-8**)$_3$ (B), **PHG**(**Ap3'F-9**)$_3$ (C), **PHG**(**Ap3'F-10**)$_3$ (D), **PHG**(**Ap3'F-11**)$_3$ (E), **PHG**(**Ap3'F-12**)$_3$ (F) are shown.



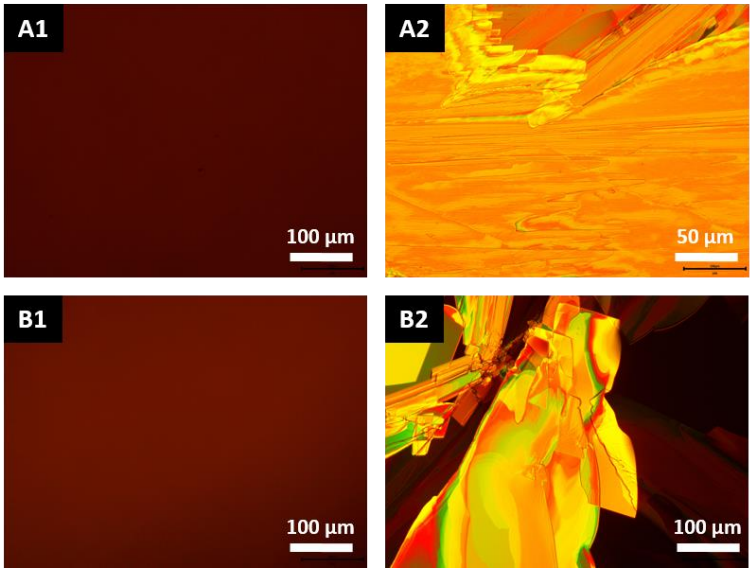

**Supporting Figure S11.** POM images of the **F-PHG(Ap3'F-N)**$_3$ assemblies in their isotropic (1), nematic (2) and crystalline phase (3) under crossed polarizers. Representative micrographs of **F-PHG(Ap3'F-6)**$_3$ (A), **F-PHG(Ap3'F-8)**$_3$ (B), **F-PHG(Ap3'F-9)**$_3$ (C), **F-PHG(Ap3'F-10)**$_3$ (D), **F-PHG(Ap3'F-11)**$_3$ (E), **F-PHG(Ap3'F-12)**$_3$ (F) are shown.



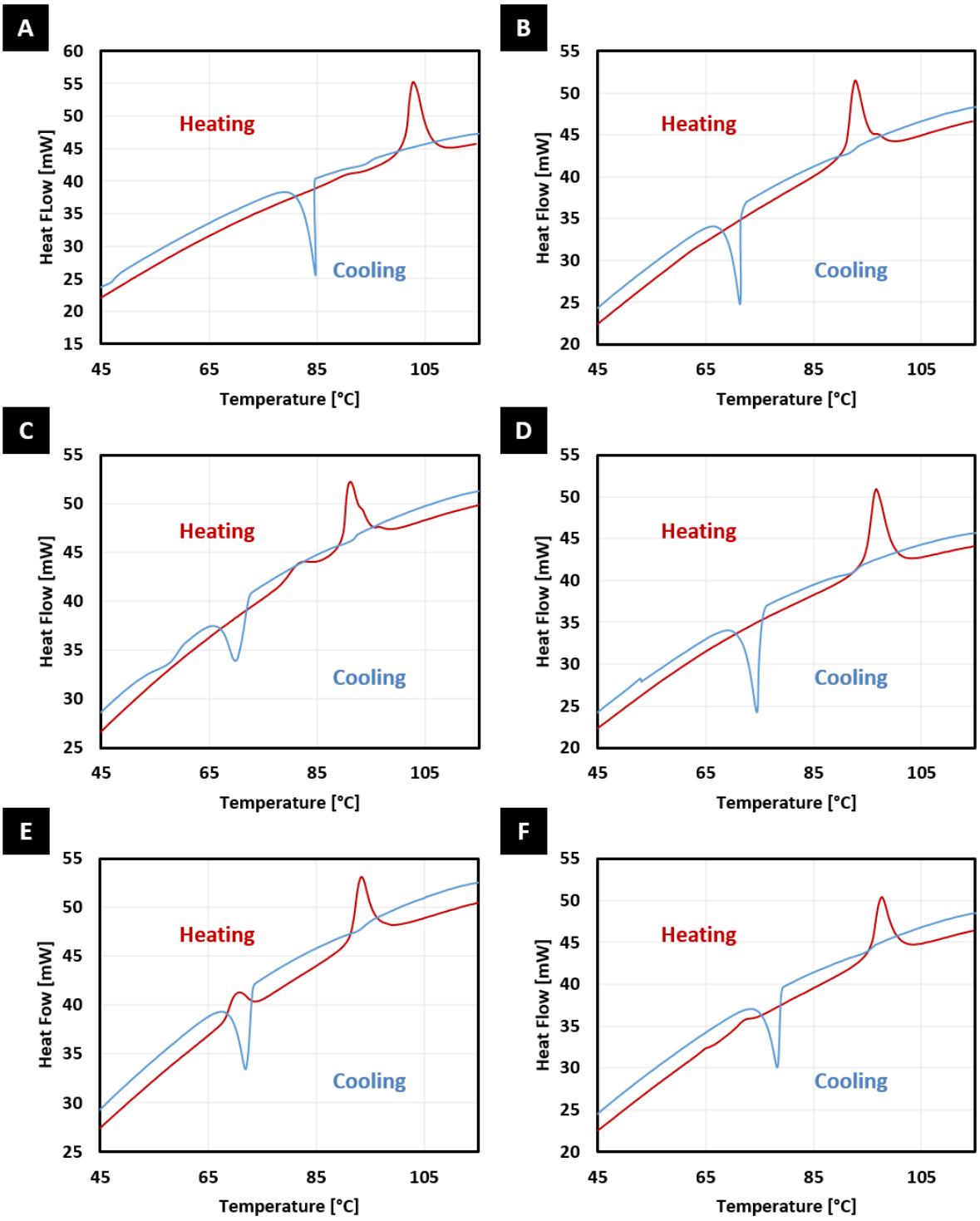

**Supporting Figure S12.** POM images of the **Ap3F-N** assemblies in their isotropic (1), crystalline phase (2) under crossed polarizers. Representative micrographs of **PHG**(**Ap3F-6**)$_3$ (A), **PHG**(**Ap3F-8**)$_3$ (B) and **F-PHG**(**Ap3F-6**)$_3$ are shown.



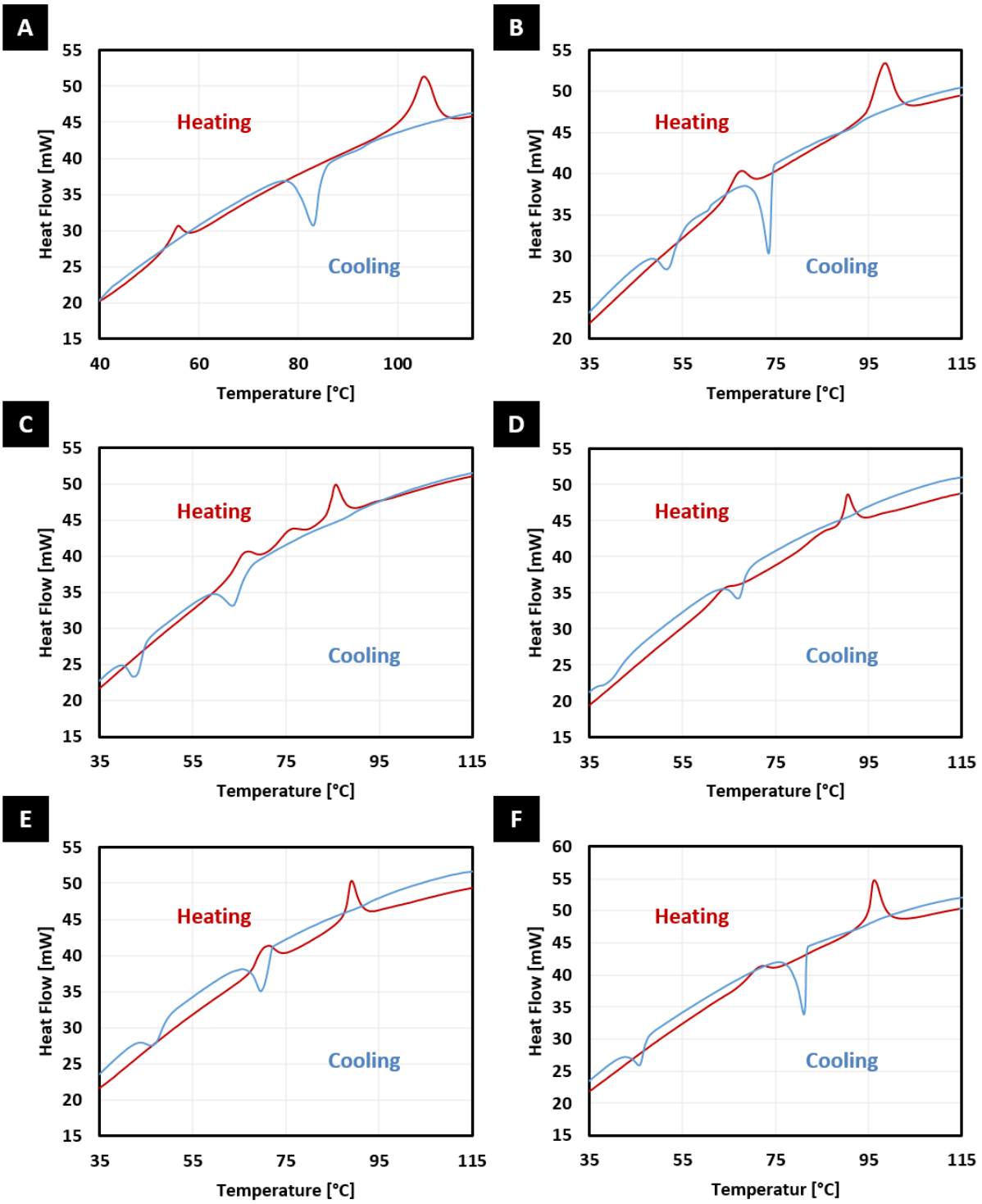

**Supporting Figure S13.** POM images of the **PHG**(**Ap3'5'F-N**)$_3$ assemblies in their isotropic (1), smectic (2) and crystalline phase (3) under crossed polarizers. Representative micrographs of **PHG**(**Ap3'5'F-6**)$_3$ (A) and **PHG**(**Ap3'5'F-8**)$_3$ (B) are shown.



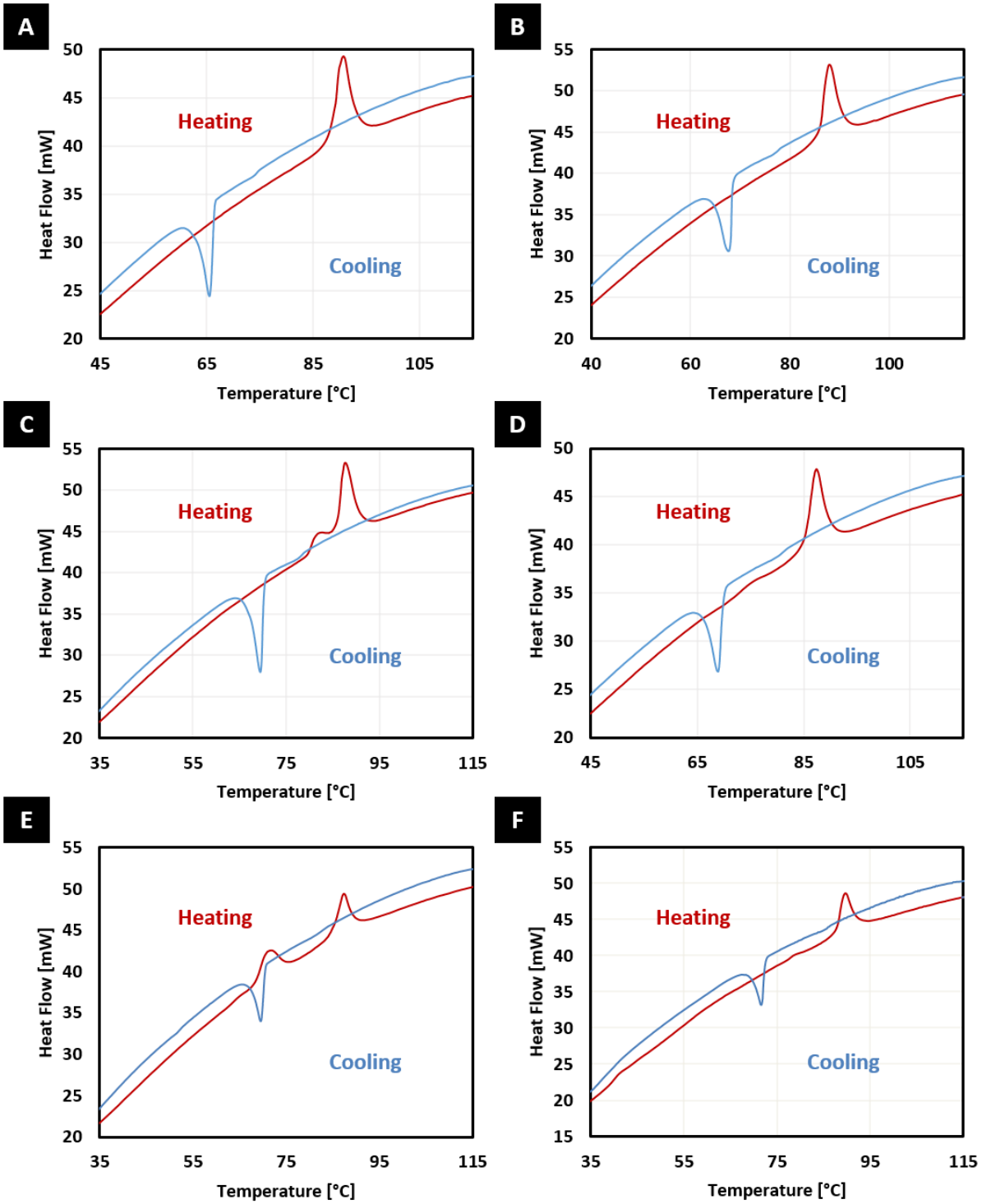

**Supporting Figure S14.** POM images of the **F-PHG(Ap3'5'F-N)$_3$** assemblies in their isotropic (1) and crystalline phase (2) under crossed polarizers. Representative micrographs of **F-PHG(Ap3'5'F-6)$_3$** (A) and **F-PHG(Ap3'5'F-8)$_3$** (B) are shown.



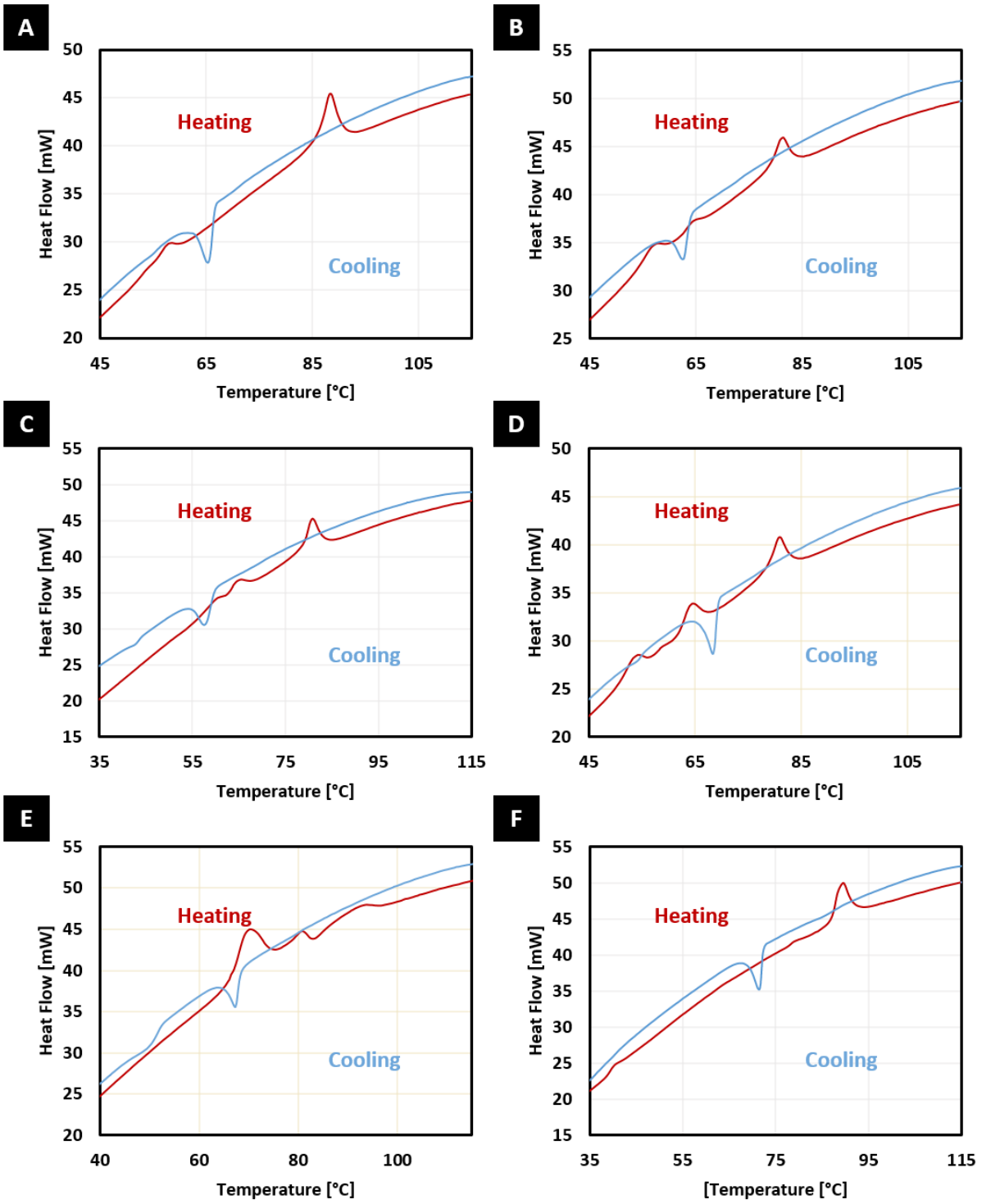

**Supporting Figure S15.** DSC profiles of **PHG**(**Ap-6**)$_3$ (A), **PHG**(**Ap-8**)$_3$ (B), **PHG**(**Ap-9**)$_3$ (C), **PHG**(**Ap-10**)$_3$ (D), **PHG**(**Ap-11**)$_3$ (E), and **PHG**(**Ap-12**)$_3$ (F) obtained a heating/cooling rate of 5 K/min.



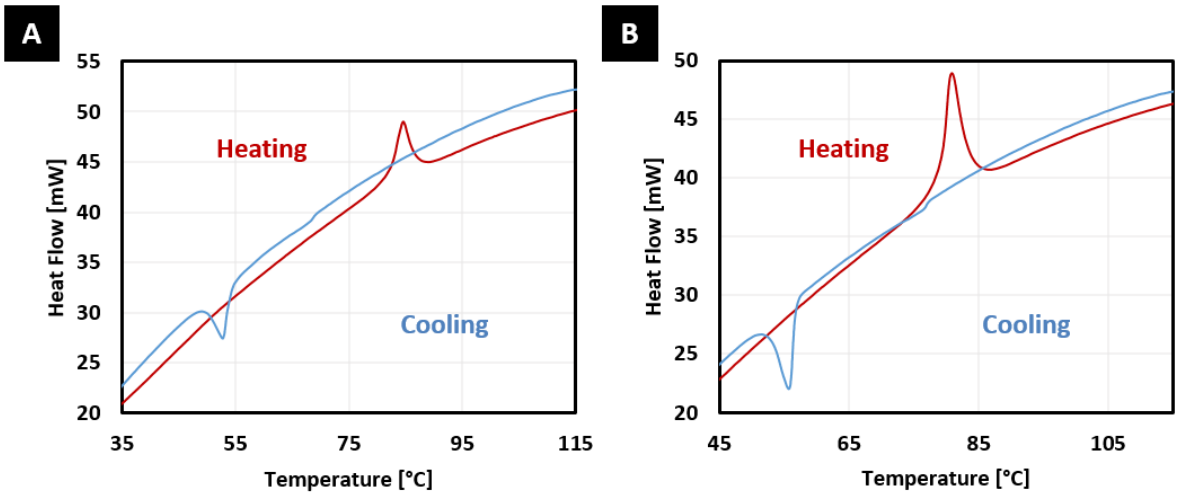

**Supporting Figure S16.** DSC profiles of **F-PHG(Ap-6)**$_3$ (A), **F-PHG(Ap-8)**$_3$ (B), **F-PHG(Ap-9)**$_3$ (C), **F-PHG(Ap-10)**$_3$ (D), **F-PHG(Ap-11)**$_3$ (E), and **F-PHG(Ap-12)**$_3$ (F) obtained a heating/cooling rate of 5 K/min.



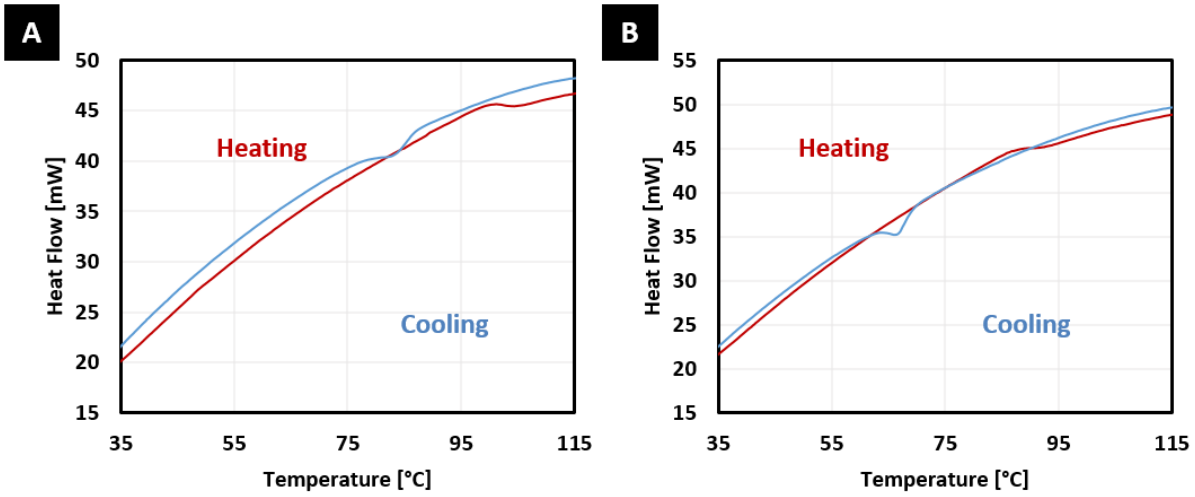

**Supporting Figure S17.** DSC profiles of **PHG**(**Ap3'F-6**)$_3$ (A), **PHG**(**Ap3'F-8**)$_3$ (B), **PHG**(**Ap3'F-9**)$_3$ (C), **PHG**(**Ap3'F-10**)$_3$ (D), **PHG**(**Ap3'F-11**)$_3$ (E), and **PHG**(**Ap3'F-12**)$_3$ (F) obtained a heating/cooling rate of 5 K/min.




**Supporting Figure S18.** DSC profiles of **F-PHG(Ap3'F-6)**$_3$ (A), **F-PHG(Ap3'F-8)**$_3$ (B), **F-PHG(Ap3'F-9)**$_3$ (C), **F-PHG(Ap3'F-10)**$_3$ (D), **F-PHG(Ap3'F-11)**$_3$ (E), and **F-PHG(Ap3'F-12)**$_3$ (F) obtained a heating/cooling rate of 5 K/min.




**Supporting Figure S19.** DSC profiles of **PHG(Ap3'5'F-6)**$_3$ (A) and **PHG(Ap3'5'F-8)**$_3$ (B) obtained a heating/cooling rate of 5 K/min.




**Supporting Figure S20.** DSC profiles of **F-PHG(Ap3'5'F-6)**$_3$ (A) and **F-PHG(Ap3'5'F-8)**$_3$ (B) obtained a heating/cooling rate of 5 K/min.

**Supporting Table S1.** Thermal properties of **PHG(Ap-N)**$_3$ as obtained by DSC (heating/cooling rate: 5 K/min).

| Compound | Thermal Properties | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **PHG(X)$_3$** | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] |
| **Ap-6** | I → N | 93.61 | -2.488 | N → Cr1 | 84.73 | -50.996 | Cr1 → Cr2 | 46.89 | -1.463 |
| **Ap-6*** | Cr2 → Cr1 | 90.36 | 2.350 | Cr1 → I | 102.83 | 79.804 | - | - | - |
| **Ap-8** | I → N | 91.47 | -2.298 | N → Cr | 71.37 | -47.202 | - | - | - |
| **Ap-8*** | | | | Cr → I | 92.69 | 67.943 | - | - | - |
| **Ap-9** | I → N | 91.07 | -2.404 | N → Cr1 | 70.10 | -47.478 | Cr1 → Cr2 | 57.67 | -7.443 |
| **Ap-9*** | Cr2 → Cr1 | 81.62 | 11.254 | Cr1 → I | 91.18 | 58.610 | - | - | - |
| **Ap-10** | I → N | 91.88 | -2.737 | N → Cr | 74.53 | -55.544 | - | - | - |
| **Ap-10*** | | | | Cr → I | 96.62 | 68.927 | - | - | - |
| **Ap-11** | I → N | 92.88 | -3.045 | N → Cr1 | 71.95 | -49.005 | Cr1 → Cr2 | 41.84 | -8.344 |
| **Ap-11*** | Cr2 → Cr1 | 70.34 | 17.395 | Cr1 → I | 93.36 | 57.888 | - | - | - |
| **Ap-12** | I → N | 91.88 | -2.737 | N → Cr | 74.53 | -55.544 | - | - | - |
| **Ap-12*** | | | | Cr → I | 96.62 | 68.927 | - | - | - |

X = **Ap-N**, *thermal data upon heating

**Supporting Table S2.** Thermal properties of **F-PHG(Ap-N)$_3$** as obtained by DSC (heating/cooling rate: 5 K/min).

| Compound | Thermal Properties | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **F-PHG(X)$_3$** | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] |
| **Ap-6** | I → N | 92.34 | -0.587 | N → Cr1 | 83.03 | -38.658 | - | - | - | - | - | - |
| **Ap-6*** | | | | Cr2 → Cr1 | 55.78 | 10.128 | Cr1 → I | 105.18 | 51.026 | - | - | - |
| **Ap-8** | I → N | 90.66 | -2.280 | N → Cr1 | 73.52 | -35.907 | Cr1 → Cr2 | 60.34 | -0.872 | - | - | - |
| **Ap-8*** | | | | Cr2 → Cr1 | 63.15 | 18.013 | Cr1 → I | 98.26 | 47.726 | - | - | - |
| **Ap-9** | I → N | 87.32 | -1.590 | N → Cr1 | 63.68 | -24.076 | Cr1 → Cr2 | 42.79 | -22.347 | -- | - | - |
| **Ap-9**** | Cr3 → Cr2 | 65.95 | 16.656 | Cr2 → Cr1 | 75.86 | 8.830 | Cr1 → N | 85.65 | 21.524 | N → I | 94.20 | 0.635 |
| **Ap-10** | I → N | 90.98 | -1.928 | N → Cr1 | 67.13 | -26.158 | Cr1 → Cr2 | 39.94 | -10.213 | - | - | - |
| **Ap-10**** | Cr3 → Cr2 | 63.82 | 16.114 | Cr2 → Cr1 | 84.41 | 4.142 | Cr1 → N | 90.45 | 22.140 | N → I | 97.20 | 2.445 |
| **Ap-11** | I → N | 81.49 | -1.402 | N → Cr1 | 69.68 | -45.246 | Cr1 → Cr2 | 46.87 | -25.373 | - | - | - |
| **Ap-11*** | | | | Cr2 → Cr1 | 70.46 | 30.585 | Cr1 → N | 89.09 | 40.810 | - | - | - |
| **Ap-12** | I → N | 92.47 | -2.154 | N → Cr1 | 82.09 | -49.782 | Cr1 → Cr2 | 45.82 | -23.226 | - | - | - |
| **Ap-12*** | | | | Cr2 → Cr1 | 71.27 | 15.281 | Cr1 → I | 96.16 | 56.249 | - | - | - |

X = **Ap-N**, *thermal data upon heating, **mesophase upon heating

**Supporting Table S3.** Thermal properties of **PHG(Ap3'F-N)$_3$** as obtained by DSC (heating/cooling rate: 5 K/min).

| Compound | Thermal Properties | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PHG(X)$_3$** | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] |
| **Ap3'F-6** | I → N | 73.67 | -0.950 | N → Cr1 | 65.55 | -48.347 | - | - | - | - | - | - |
| **Ap3'F-6*** | - | - | - | | | | - | - | - | Cr → I | 90.64 | 64.462 |
| **Ap3'F-8** | I →N | 76.39 | -1.740 | N → Cr1 | 67.77 | -57.093 | | | | - | - | - |
| **Ap3'F-8*** | - | - | - | | | | - | - | - | Cr → I | 87.91 | -79.123 |
| **Ap3'F-9** | I → N | 77.34 | -1.546 | N → Cr | 69.47 | -49.174 | - | - | - | - | - | - |
| **Ap3'F-9*** | | | | | | | Cr2 → Cr1 | 81.68 | 5.936 | Cr1 → I | 87.61 | 42.869 |
| **Ap3'F-10** | I → N | 80.05 | -1.605 | N → Cr1 | 68.94 | -44.809 | - | - | - | - | - | - |
| **Ap3'F-10*** | - | - | - | - | - | - | Cr2 → Cr1 | 75.26 | 2.038 | Cr → I | 87.35 | 60.332 |
| **Ap3'F-11** | I → N | 81.40 | -1.406 | N → Cr1 | 69.58 | -34.098 | Cr1 → Cr2 | 51.55 | -0.493 | - | - | - |
| **Ap3'F-11*** | | | | Cr3 → Cr2 | 64.90 | 0.513 | Cr2 → Cr1 | 70.99 | 30.800 | Cr1 → I | 87.33 | 37.830 |
| **Ap3'F-12** | I → N | 84.79 | -1.919 | N → Cr1 | 71.55 | -36.553 | - | - | - | - | - | - |
| **Ap3'F-12*** | Cr4 → Cr3 | 40.46 | 3.706 | Cr3 → Cr2 | 63.63 | 0.677 | Cr2 → Cr1 | 78.92 | 1.142 | Cr → I | 89.50 | 49.625 |

*thermal data upon heating, X = **Ap3'F-N**

**Supporting Table S4.** Thermal properties of **F-PHG(Ap3'F-N)$_3$** as obtained by DSC (heating/cooling rate: 5 K/min).

| Compound | Thermal Properties | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **F-PHG(X)$_3$** | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] |
| **Ap3'F-6** | I → N | 69.98 | -0.383 | N → Cr1 | 65.37 | -29.210 | Cr1 → Cr2 | 54.76 | -0.633 | - | - | - |
| **Ap3'F-6*** | | | | Cr2 → Cr1 | 57.82 | 5.281 | Cr1 → I | 88.24 | 34.280 | - | - | - |
| **Ap3'F-8** | I → N | 74.48 | -0.477 | N → Cr | 63.62 | -28.162 | - | - | - | - | - | - |
| **Ap3'F-8*** | Cr3 → Cr2 | 57.81 | 10.592 | Cr2 → Cr1 | 64.56 | 4.919 | Cr1 → I | 81.56 | 28.088 | - | - | - |
| **Ap3'F-9** | I → N | 72.50 | -0.650 | N → Cr1 | 62.48 | -25.024 | Cr1 → Cr2 | 47.36- | -2.218 | - | - | - |
| **Ap3'F-9*** | Cr3 → Cr2 | 60.02 | 4.413 | Cr2 → Cr1 | 64.79 | 6.745 | Cr1 → I | 80.79 | 32.746 | - | - | - |
| **Ap3'F-10** | I → N | 76.29 | -0.146 | N → Cr1 | 68.45 | -24.357 | Cr1 → Cr2 | 54.17 | -1.522 | - | - | - |
| **Ap3'F-10*** | Cr4 → Cr3 | 53.40 | 9.737 | Cr3 → Cr2 | 58.53 | 0.273 | Cr2 → Cr1 | 64.46 | 14.270 | Cr1 → N | 80.84 | 22.692 |
| **Ap3'F-11** | I → N | 78.44 | -0.308 | N → Cr1 | 67.25 | -21.850 | Cr1 → Cr2 | 49.65 | -12.034 | - | - | - |
| **Ap3'F-11*** | Cr3 → Cr2 | 69.84 | 59.170 | Cr2 → Cr1 | 80.52 | 6.594 | Cr1 → I | 91.94 | 25.767 | - | - | - |
| **Ap3'F-12** | I → N | 82.79 | -1.9189 | N → Cr1 | 71.49 | -36.533 | - | - | - | - | - | - |
| **Ap3'F-12*** | Cr4 → Cr3 | 40.46 | 3.7060 | Cr3 → Cr2 | 63.63 | 0.6796 | Cr2 → Cr1 | 78.92 | 1.1420 | Cr1 → I | 89.30 | 49.625 |

X = **Ap3'F-N,** *thermal data upon heating,

**Supporting Table S5.** Thermal properties of **PHG(Ap3'5'F-N)$_3$** as obtained by DSC (heating/cooling rate: 5 K/min).

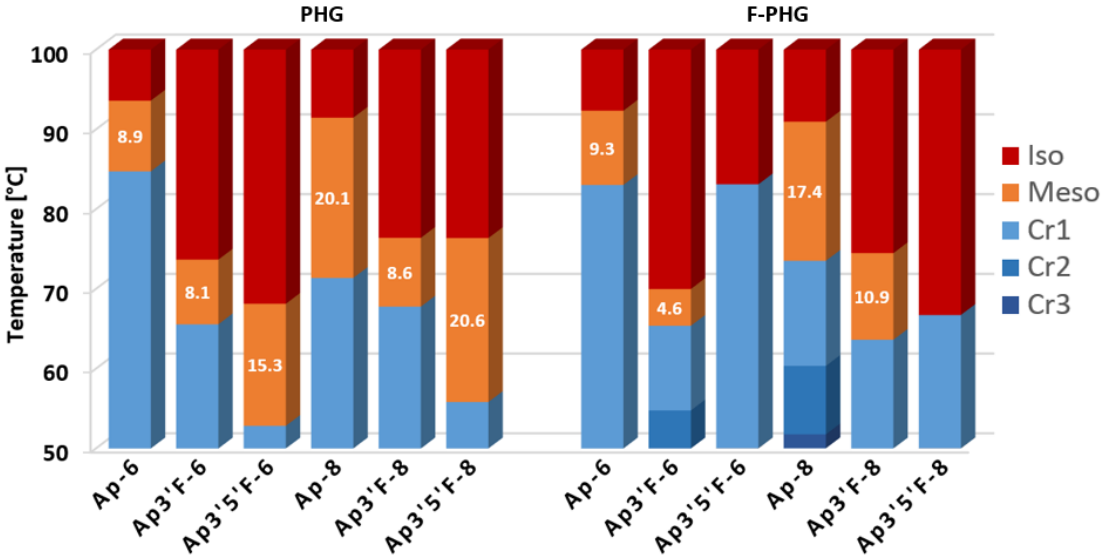
| Compound | Thermal Properties | | | | | |
|---|---|---|---|---|---|---|
| **PHG(X)$_3$** | | T [°C] | ΔH [J·g$^{-1}$] | | T [°C] | ΔH [J·g$^{-1}$] |
| **Ap3'5'F-6** | I → Sm | 68.13 | -2.200 | Sm → Cr | 52.82 | -26.507 |
| **Ap3'5'F-6*** | | | | Cr → I | 84.56 | 37.779 |
| **Ap3'5'F-8$_3$** | I → Sm | 76.37 | -2.136 | Sm → Cr | 55.81 | -26.141 |
| **Ap3'5'F-8*** | | | | Cr → I | 80.85 | 54.564 |

*thermal data upon heating, X = **Ap3'5'F-N**

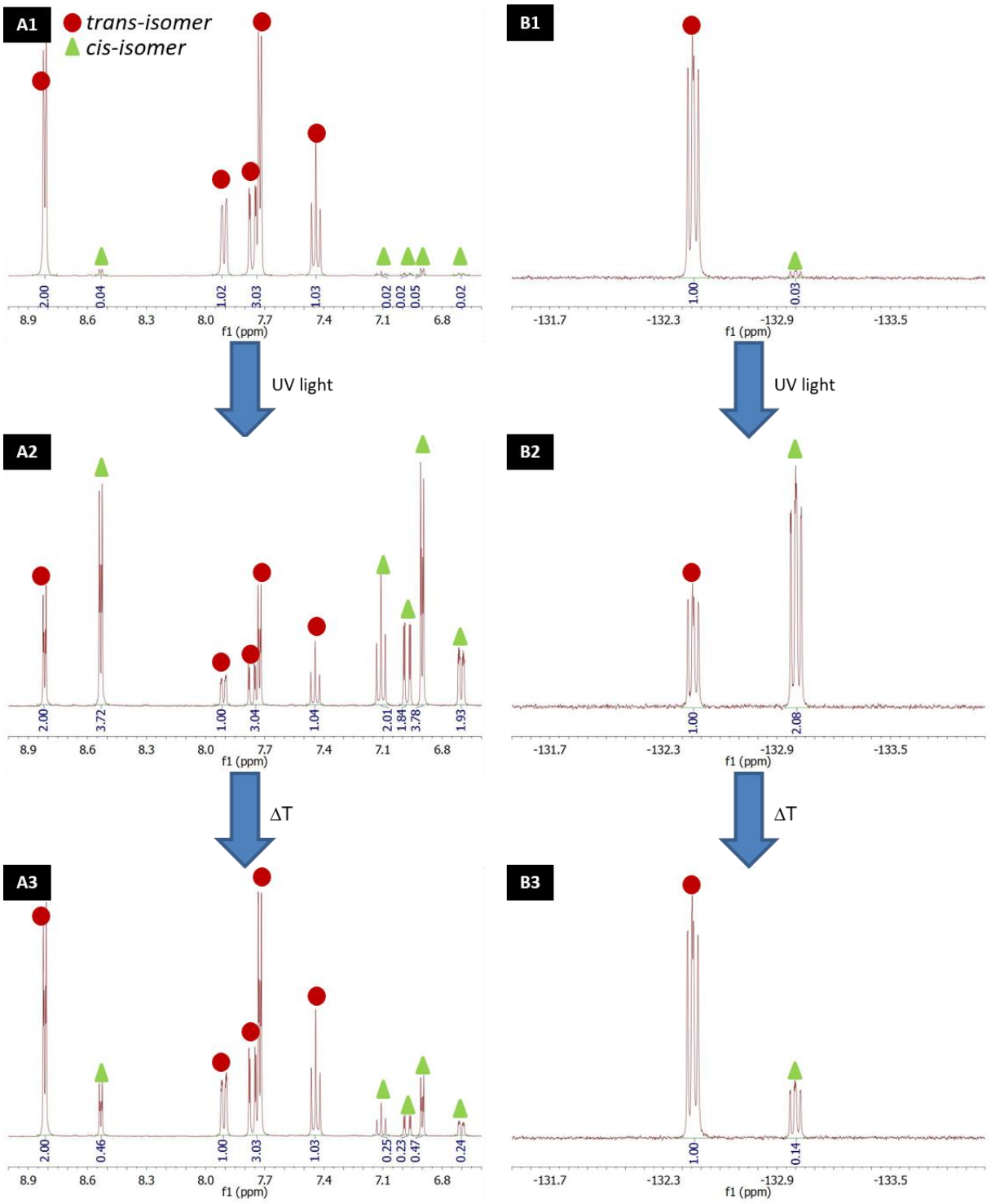
**Supporting Table S6.** Thermal properties of **F-PHG(Ap3'5'F-N)$_3$** as obtained by DSC (heating/cooling rate: 5 K/min).

| Compound | Thermal Properties | | |
|---|---|---|---|
| **F-PHG(X)$_3$** | | T [°C] | ΔH [J·g$^{-1}$] |
| **Ap3'5'F-6** | I → Cr | 83.11 | -9.424 |
| **Ap3'5'F-6*** | Cr → I | 99.09 | 18.246 |
| **Ap3'5'F-8$_3$** | I → Cr | 66.72 | -8.096 |
| **Ap3'5'F-8*** | Cr → I | 85.94 | 9.139 |

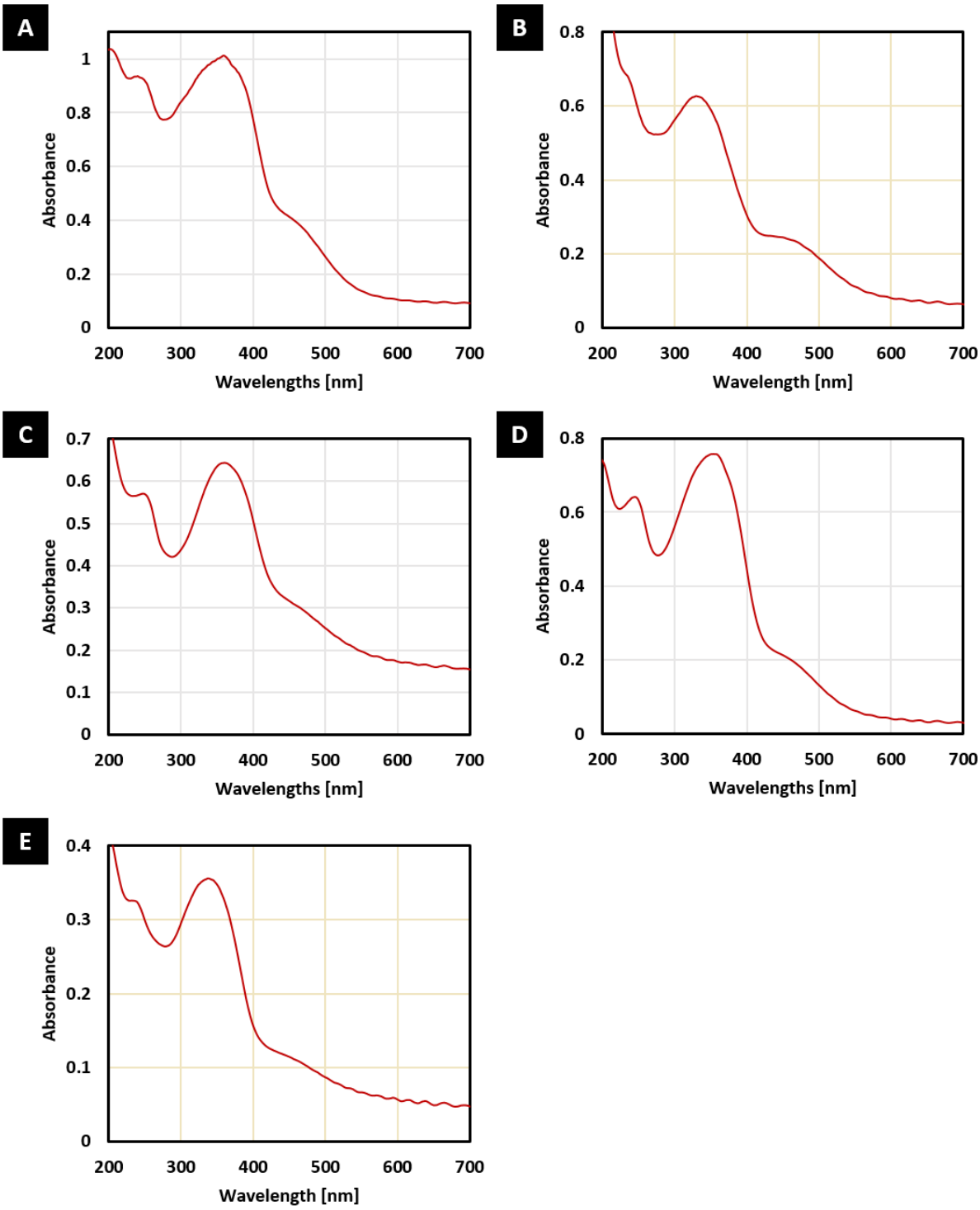
*thermal data upon heating, X = **Ap3'5'F-N**



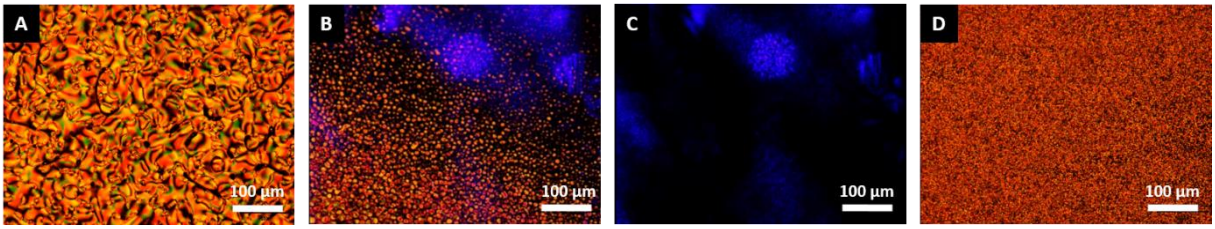

**Supporting Figure S21.** Graphical representation of the thermal behaviour the **PHG** (left) and **F-PHG** assemblies (right) of the difluorinated side chains **Ap3‘5’F-6** and **Ap3‘5’F-8** compared to the respective **Ap-N** and **Ap3’F-N** assemblies.



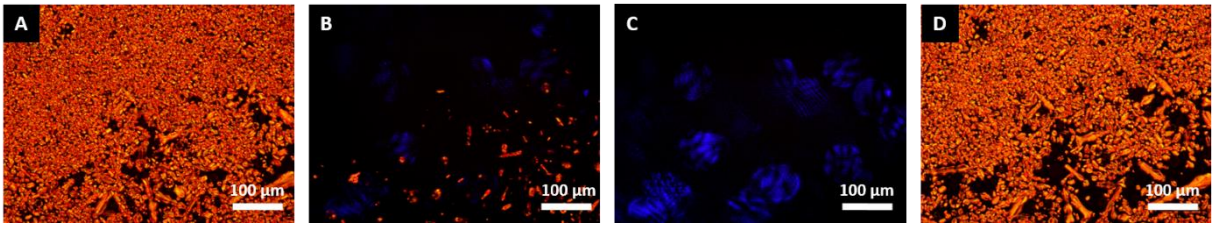

**Supporting Figure S22.** Graphical representation of the thermal behaviour the **PHG** (left) and **F-PHG** assemblies (right) of the difluorinated side chains **Ap3‘5’F-6** and **Ap3‘5’F-8** compared to the respective **Ap-N** and **Ap3’F-N** assemblies.




**Supporting Figure S23.** Representative UV/Vis spectra of **PHG(Ap3'F-6)**$_3$ (A), **PHG(Ap3'5'F-6)**$_3$ (B), **F-PHG(Ap-6)**$_3$ (C), **F-PHG(Ap3'F-6)**$_3$ (D), **F-PHG(Ap3'5'F-6)**$_3$ (E).



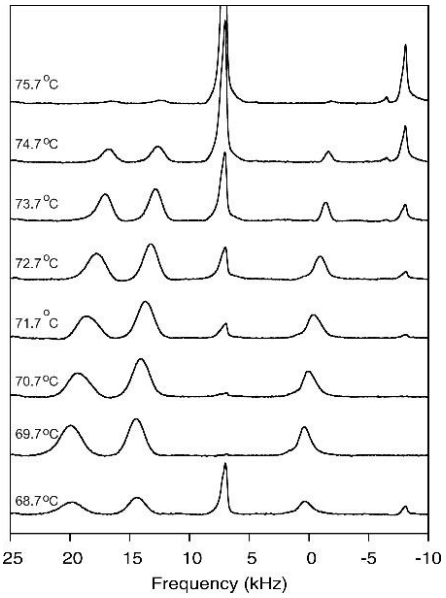

**Supporting Figure S24.** Photo-responsive behavior **PHG(Ap3'F-8)$_3$** @ 75 °C under irradiation with a laser pointer (405 nm, 5 mW). The Schlieren texture of the nematic phase (A) vanishes immediately within 1s upon irradiation (B) and the isotropic phase is observed (C), which is recovered within 8s after the irradiation is stopped.



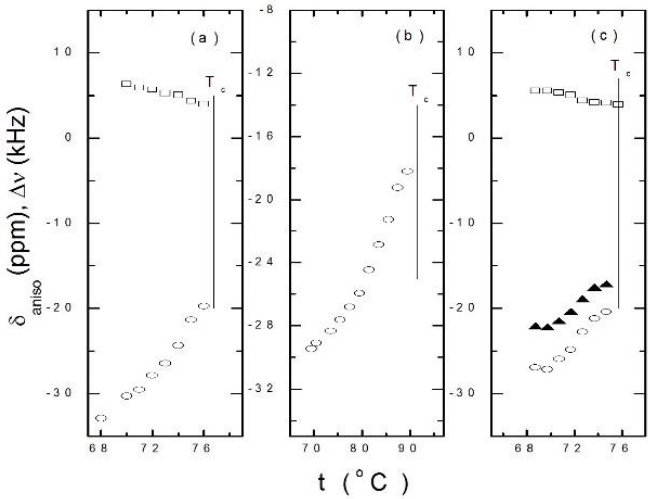

**Supporting Figure S25.** Photo-responsive behavior **PHG(Ap3'F-8)$_3$** @ 75 °C under irradiation with a laser pointer (405 nm, 5 mW). The Schlieren texture of the smectic phase (A) vanishes upon irradiation within 3-9s (B) and the isotropic phase is observed (C), which is recovered within 10-16s after the irradiation is stopped (D).

### 4. $^{19}$F Solid State NMR Results

Solid-state NMR experiments were carried out on a Varian Unity Inova 400 NMR spectrometer. $^{19}$F MAS spectra of powdered samples were collected with $^{1}$H decoupling and cross-polarization using radiofrequency field strengths of ca. 40 kHz in a Varian/Chemagnetics 4 mm T3-HXY MAS probe. Chemical shifts were measured relative to Bloch decay spectra of an external PTFE standard at -39 ppm,[3] collected with 8 and 8.5 kHz spinning rates in order to distinguish the isotropic shift. Variable temperature $^{19}$F spectra of the fluorinated azopyridine PG/ApC8 samples were collected using a Varian ASW high-resolution probe using 3 µs, ca. 15$^{o}$ pulses. $^{19}$F NMR spectra of three different PG/ApC8 samples were obtained by cooling from the isotropic melt to the columnar nematic phase. Typical spectra for **F-PHG(Ap3'F-8)$_3$** are shown in supporting Fig. S26. Experimental dipolar splitting and/or anisotropic chemical shift of **F-PHG(Ap-8)$_3$**, **PHG(Ap3'F-8)$_3$** and **F-PHG(Ap3'F-8)$_3$** versus temperature are shown in supporting Fig. S27.

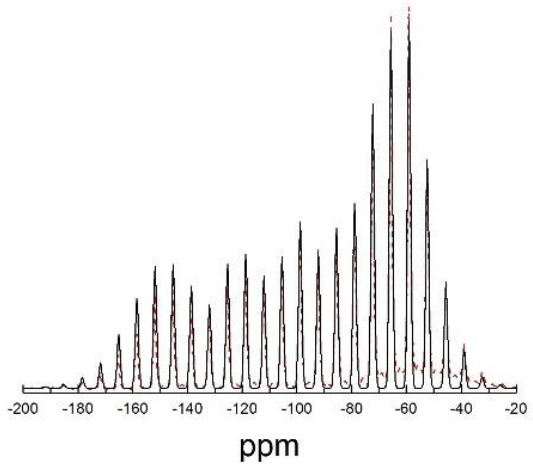



**Supporting Figure S26.** $^{19}$F NMR spectra of **F-PHG(Ap3'F-8)$_3$** obtained by cooling from the isotropic melt.

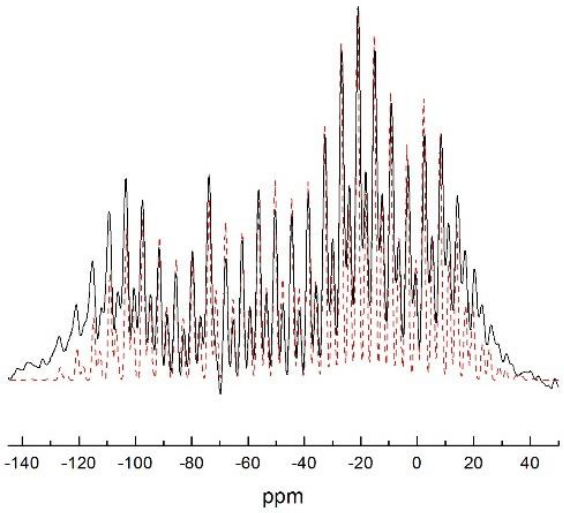



**Supporting Figure S27.** Experimental F-H splitting and chemical shift anisotropy versus temperature (a) **PHG**(**Ap3'F-8**)$_3$, (b) **F-PHG**(**Ap-8**)$_3$, and (c) **F-PHG**(**Ap3'F-8**)$_3$. Positive vertical scale is for F-H splitting, while negative scale is for $\delta_{aniso}$ (solid symbols denote values of **F-PHG**).

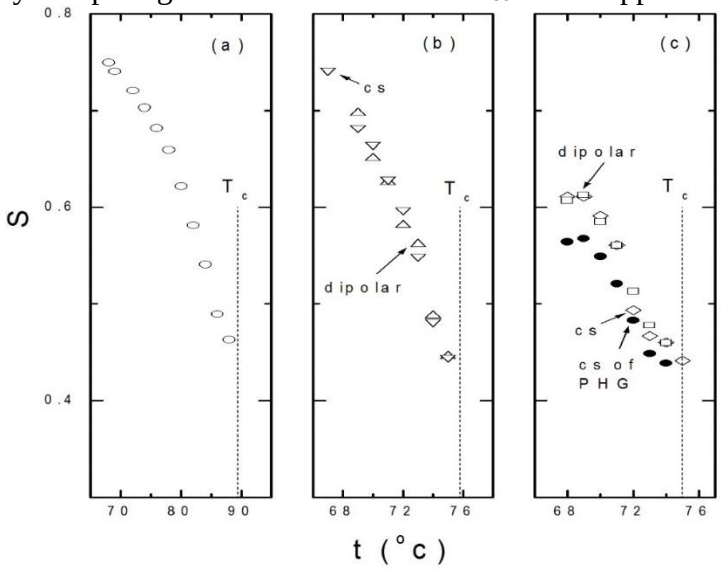
To determine the fluorine chemical shielding tensor (CST) elements, we make use of the sideband analysis[4] of the MAS spectra for the two fluorinated sites in two separate powder samples: **F-PHG**(**Ap-8**)$_3$ and **PHG**(**Ap3'F-8**)$_3$. The simulation of these spectra (Fig. S28 for **F-PHG**(**Ap-8**)$_3$ and Supporting Fig. S29 for **PHG**(**Ap3'F-8**)$_3$) are performed making use of WSOLIDS.[5] As shown by the above crystal structure, there are two fluorine sites for the latter sample and in the simulation, the relative intensities are 2:1 as expected and these sites have the same $\eta$ and $\Delta\delta$, but differ in $\delta_{iso}$. The measured $\delta_{iso}$, and the derived $\Delta\delta$ and $\eta$ are summarized in Supporting Table S7 for these powder samples. However, the orientations of the CST of these two sites cannot be obtained experimentally here.




**Supporting Figure S28.** MAS spectrum collected from **F-PHG**(**Ap-8**)$_3$ spinning at 2.5 kHz. Simulation using WSOLIDS with Gaussian broadening of 500 Hz.




**Supporting Figure S29.** MAS spectrum collected from **PHG**(**Ap3'-8**)$_3$ spinning at 2.2 kHz. Simulation using WSOLIDS with Gaussian broadening of 500 Hz. Site 2 has $\delta_{iso}$ = -36 ppm and half the intensity comparing to that of site 1 whose $\delta_{iso}$ = -38.3 ppm.




**Supporting Figure S30.** Nematic order parameter S *versus* temperature in the $N_{col}$ phase of (a) **PHG(Ap3'F-8)$_3$**, (b) **F-PHG(Ap-8)$_3$**, and (c) **F-PHG(Ap3'F-8)$_3$** (Down-triangles denote values of **F-PG**). Vertical line indicates $N_{col}$/I transition temperature ($T_c$).

**Supporting Table S7.** CST determined for two solid samples using simulation of MAS sideband pattern.

| Compound | $\delta_{iso}$[a] | $\Delta\delta$ | $\eta$ |
|---|---|---|---|
| **F-PHG(Ap-8)$_3$** | -92.3 ppm | -118 ppm | 0.25 |
| **PHG(Ap3'F-8)$_3$** | -38.3 ppm; -36ppm | -120 ppm | 0.5 |

[a] $\delta_{iso}$ is found by comparing spectra obtained at spin rate of 8 and 8.5 kHz, and calibrated with Poly(tetrafluoroethylene) $\delta_{iso}$ = -39 ppm[3]

**Supporting Table S8.** The $\gamma$ angle between the PAS z axis of $^{19}$F CST and the para axis of the phenyl ring. First column is determined in the present work by equating S from the dipolar splitting and the observed chemical shift anisotropy of the phenyl ring.

| Close to H and O atoms | Close to only H[a] | Close to ester group[b] |
|---|---|---|
| $\gamma = 32.1^o$ | $\gamma \approx 0$ | $\gamma \approx 65^o$ |

[a] [6] [b] [7]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