Electronic Supplementary Material (ESI) for CrystEngComm.


**Electronic Supplementary Information**

# Modulating the assembly of *N*-benzylideneaniline by halogen bonding: crystal, cocrystal and liquid crystals

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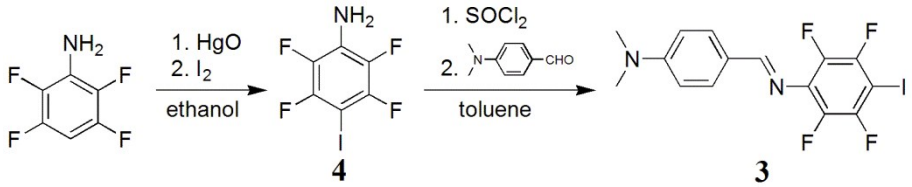
## Synthetic procedure

Synthesis route of *N*-(4-(dimethylamino)benzylidene)-2,3,5,6-tetrafluoro-4-iodoaniline (**3**)



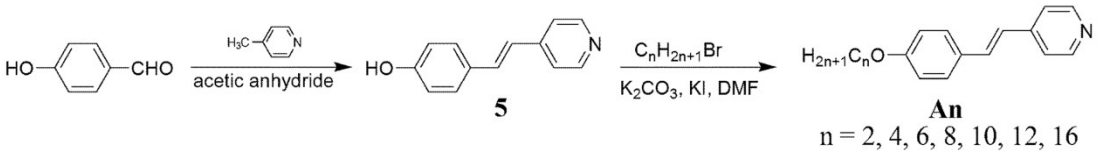

**Synthesis of 2,3,5,6-tetrafluoro-4-iodoaniline (4)**

0.40 g (1.84 mmol) of yellow HgO was added to the solution of 0.45 g (2.45 mmol) of 2,3,5,6-tetrafluoroaniline in 20 mL of ethanol. Mixture was stirred for 30 minutes, and then 0.62 g (2.44 mmol) of $I_2$ was added. Mixture was stirred overnight and then filtered over celite. Solvent was removed on rotary evaporator. Then product was redissolved in DCM and washed several times with saturated $Na_2S_2O_3$ solution and dried over $MgSO_4$. After that, the filtrate was removed solvent in vaccum and dark red needle-like product was obtained, (0.60 g, yield 82%). $^1$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 4.10 (s, 2H).

**Synthesis of *N*-(4-(dimethylamino)benzylidene)-2,3,5,6-tetrafluoro-4-iodoaniline (3)**

0.60 g (2.06 mmol) of 1-iodo-2,3,5,6-tetrafluoroaniline was stirred under reflux in 10 mL of $SOCl_2$ . The resulting dark red solution was cooled to room temperature after gas evolution stopped. The remaining solvent was fully removed in vacuum. 10 mL of toluene and 0.31 g (2.08 mmol) of 4-dimethylaminobenzaldehyde were added and stirred under reflux for 12 h. The solvent was removed in vacuum, and product was purified on $Al_2O_3$ column, using hexane : ethyl acetate = 5 : 1 gradient solvent system. The resulting solid was recrystallized from acetone, (0.31 g, yield 37%). $^1$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.41 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 3.09 (s, 6H); $^{13}$C-NMR (126MHz, $CDCl_3$) δ/ppm = 167.51, 153.49, 131.40, 123.13, 111.41, 40.12 [*Note*: Carbon signals of the pentafluorobenzene ring are not present, due to C-F coupling]; Anal. Calcd for $C_{15}H_{11}F_4IN_2$: C, 42.68; H, 2.63; N, 6.64. Found: C, 42.80; H, 2.53; N, 6.68; MS: m/z = 422.3; M. p.: 155 ℃.

Synthesis route of 4-alkoxystilbazole (A2-16)




**Synthesis of 4-hydroxystilbazole (5)**

9.33 g (0.10 mol) of 4-methylpyridine and 12.20 g (0.10 mol) of 4-hydroxybenzaldehyde were dissolved in 25.72 g (0.25 mol) of acetic anhydride, and the mixture was refluxed at 130 ℃ for 10 hours. After cooling the reaction mixture, solvent was removed by vacuum filtration and the solid was recrystallized from ethanol. Then 6.67 g of product and 3.32 g (0.06 mol) KOH were refluxed in the ethanol for 6 hours. After that, the reaction mixture was cooled to room temperature and filtered under reduced pressure. The filtrate was added to water, and turned pH to 6-7 by 1 mol $L^{-1}$ HCl. The resulting solid was obtained by vacuum filter, (2.50 g, yield 46 %). $^1$H-NMR (500 MHz, DMSO-$d_6$) δ/ppm = 9.74 (s, 1H), 8.49 (d, *J* = 5.7 Hz, 2H), 7.49 (d, *J* = 6.1 Hz, 4H), 7.43 (d, *J* = 16.4 Hz, 1H), 7.00 (d, *J* = 16.4 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 2H).

**General procedure for the synthesis of 4-alkoxystilbazole (An)**

0.49 g (2.50 mmol) of 4-hydroxystilbazole, 1.73 g (12.50 mmol) of $K_2CO_3$, 0.0025 g (0.015 mmol) of KI, 2.50 mmol of bromoalkane and 10 mL of DMF were added into a round-bottomed flask, and the mixture was stirred at 87 °C for 7 h. After cooled, the reaction mixture was poured into water with intense stirring. The precipitate was washed with water and purified by silica gel column chromatography with ethyl acetate as the eluent to obtain light yellow solid.

**4-ethoxystilbazole (A2)**: yield 76%. $^1$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.55 (d, *J* = 5.8 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 5.6 Hz, 2H), 7.27 (d, *J* = 16.1 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 16.5 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H).

**4-butoxystilbazole (A4)**: yield 80%. $^1$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.54 (d, *J* = 6.1 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 6.1 Hz, 2H), 7.26 (d, *J* = 16.3 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 16.3 Hz, 1H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.79 (dt, *J* = 14.4, 6.5 Hz, 2H), 1.57-1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

**4-hexyloxystilbazole (A6)**: yield 90%. $^1$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.55 (d, *J* = 5.1 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 5.3 Hz, 2H), 7.26 (d, *J* = 16.2 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 16.4 Hz, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.88-1.69 (m, 2H), 1.57-1.18 (m, 6H), 0.92 (t, *J* =

6.8 Hz, 3H).

**4-octyloxystilbazole (A8)**: yield 92%. $^{1}$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.54 (d, *J* = 5.4 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 5.3 Hz, 2H), 7.29 (d, *J* = 16.3 Hz, 1H), 6.90 (t, *J* = 13.3 Hz, 3H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.85-1.73 (m, 2H), 1.39 (ddd, *J* = 25.6, 17.5, 9.8 Hz, 10H), 0.89 (t, *J* = 6.9 Hz, 3H).

**4-decyloxystilbazole (A10)**: yield 91%. $^{1}$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.55 (d, *J* = 5.9 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 5.9 Hz, 2H), 7.26 (d, *J* = 16.1 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 16.3 Hz, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.85-1.72 (m, 2H), 1.52-1.17 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).

**4-dodecyloxystilbazole (A12)**: yield 76%. $^{1}$H-NMR (500 MHz, $CDCl_3$) δ/ppm =8.55 (d, *J* = 6.0 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 6.0 Hz, 2H), 7.26 (d, *J* = 16.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 16.3 Hz, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.84-1.74 (m, 2H), 1.51-1.16 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).

**4-hexadecyloxystilbazole (A16)**: yield 42%. $^{1}$H-NMR (500 MHz, $CDCl_3$) δ/ppm = 8.54 (d, *J* = 4.3 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 5.7 Hz, 2H), 7.26 (d, *J* = 16.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 16.3 Hz, 1H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.83-1.75 (m, 2H), 1.54-1.13 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 3H).

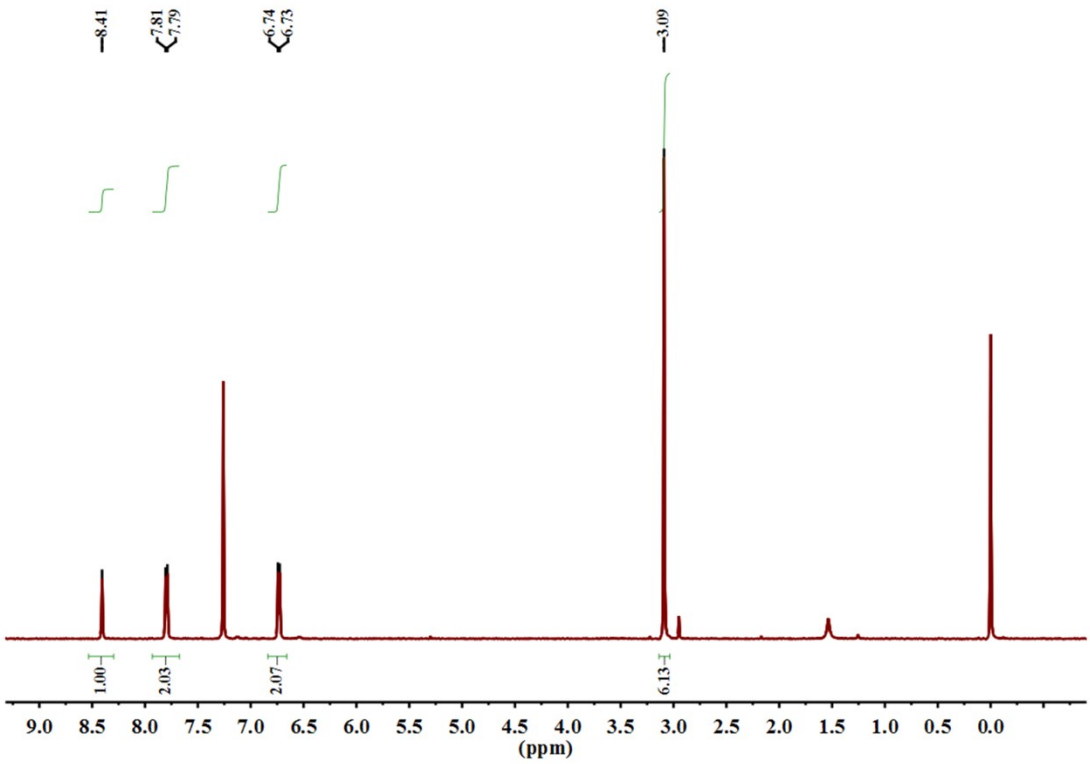



**Fig. S1** $^{1}$H-NMR spectrum of molecule **3** in $CDCl_3$.

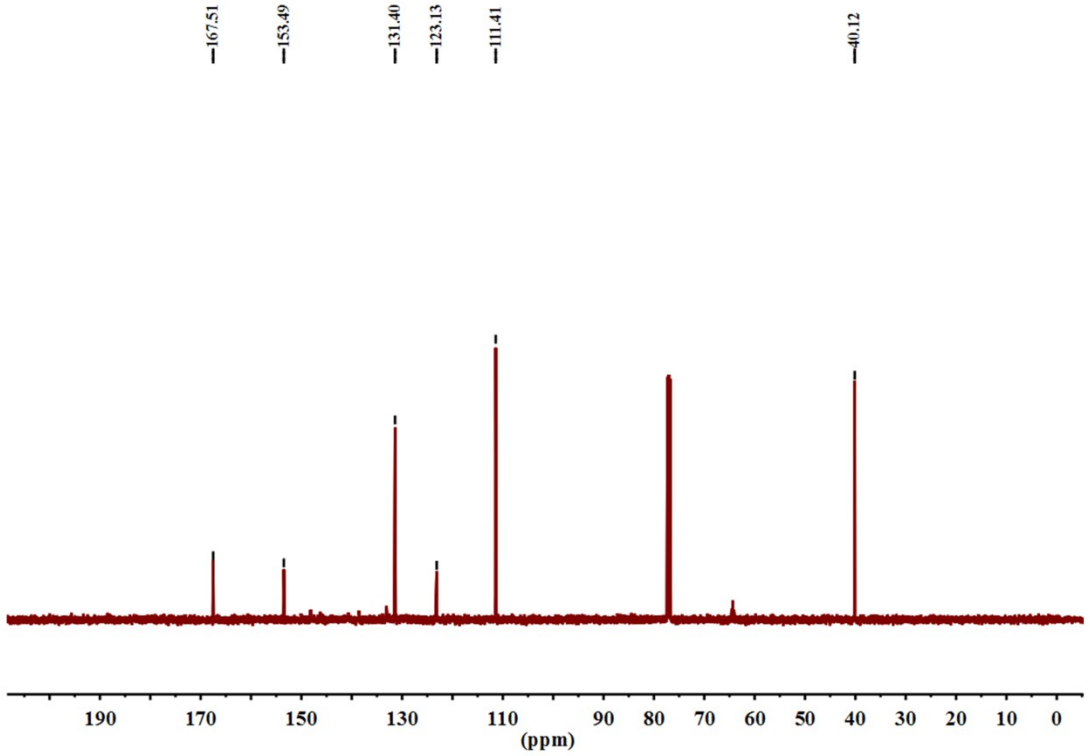



**Fig. S2** $^{13}$C-NMR spectrum of molecule **3** in $CDCl_3$.

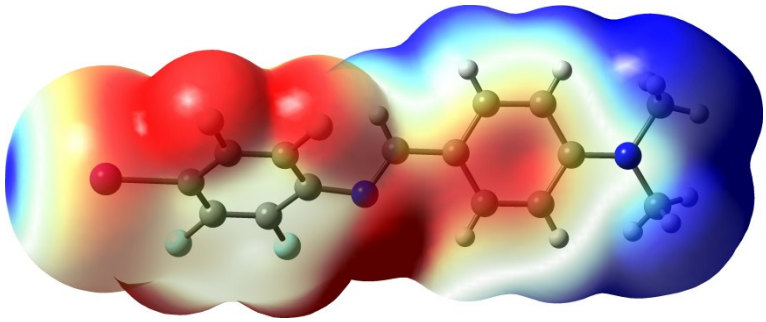


**Fig. S3** Plot of the electrostatic potential of the **3**. Potentials are mapped on the isosurfaces (0.001 a.u.) of the electron density. Values of electrostatic potential range from -0.02 (red) to 0.02 (blue) a.u. Atom color scheme: C, gray; H, light gray; N, dark blue; F, sky blue; I, magenta.

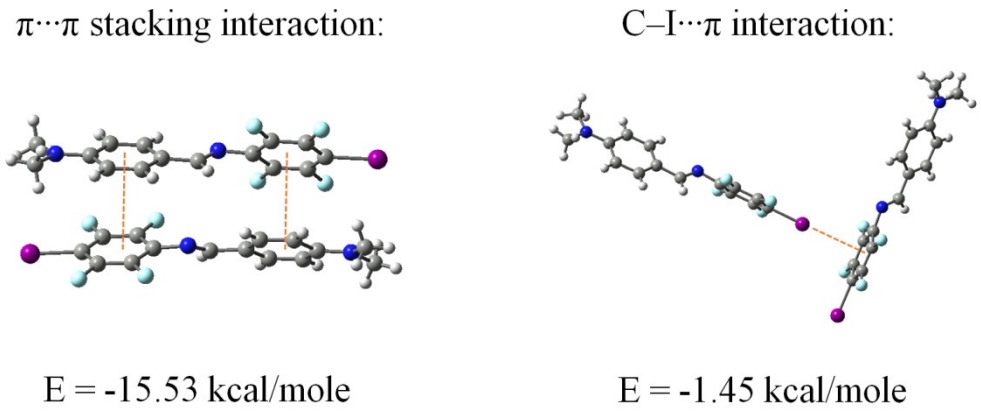



**Fig. S4** The interaction energy of π···π and C–I···π interactions.

**Table S1** Crystal data for **3** and **3**-BiPy

| Compound | **3** | **3**-BiPy |
|---|---|---|
| Empirical formula | $C_{15}H_{11}F_4IN_2$ | $C_{40}H_{30}F_8I_2N_6$ |
| Formula weight/g mol$^{-1}$ | 422.16 | 1000.50 |
| $T$/K | 293(2) | 293(2) |
| $\lambda$/Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1$ | $C2/c$ |
| Unit cell dimensions/Å | $a$ = 6.296(13)<br>$b$ = 10.568(2)<br>$c$ = 22.978(5) | $a$ = 27.217(5)<br>$b$ = 10.277(2)<br>$c$ = 14.795(3) |
| Unit cell angles/° | $\alpha$ = 90<br>$\beta$ = 92.70(3)<br>$\gamma$ = 90 | $\alpha$ = 90<br>$\beta$ = 110.06(3)<br>$\gamma$ = 90 |
| Volume/Å$^3$ | 1527.3(5) | 3887.1(14) |
| $Z$ | 4 | 4 |
| $\rho$(calculated)/Mg m$^{-3}$ | 1.836 | 1.710 |
| Absorption coefficient/mm$^{-1}$ | 2.136 | 1.695 |
| $F$(000) | 816 | 1960 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.10 | 0.13 × 0.12 × 0.10 |
| $\theta$ range for data collection/° | 3.24 to 27.48 | 3.06 to 27.48 |
| Index ranges | -6 <= $h$ <= 8, -13 <= $k$ <= 13, -29 <= $l$ <= 29 | -35 <= $h$ <= 35, -12 <= $k$ <= 13, -19 <= $l$ <= 29 |
| Reflections collected | 14169 | 18093 |
| Independent reflections | 6660 [$R$(int) = 0.0635] | 4445 [$R$(int) = 0.0258] |
| Completeness to $\theta$ = 27.48 | 98.3 % | 99.8 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8148 and 0.7687 | 0.8488 and 0.8098 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6660 / 1 / 401 | 4445 / 0 / 254 |
| Goodness-of-fit on $F^2$ | 1.058 | 1.086 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0569, w$R_2$ = 0.1261 | $R_1$ = 0.0285, w$R_2$ = 0.0742 |
| $R$ indices (all data) | $R_1$ = 0.0784, w$R_2$ = 0.1366 | $R_1$ = 0.0358, w$R_2$ = 0.0762 |
| Largest diff. peak and hole/e Å$^{-3}$ | 0.609 and -0.699 | 0.626 and -0.377 |

**Table S2** Selected FT-IR spectroscopy of **3**, A10 and their halogen-bonded complex

| | **3** | **3**-A10 | A10 |
|---|---|---|---|
| Pyridine $\nu_{C-H}$ stretching | | 3030 | 3022 |
| Pyridyl ring breathing | | 1593 | 1590 |
| Pyridyl ring breathing | | 1513 | 1512 |
| Pyridyl ring breathing | | 1421 | 1412 |
| Fluorophenyl $\nu_{C-F}$ stretching | 1474 | 1469 | |
| Fluorophenyl $\nu_{C-F}$ bending | 940 | 936 | |
| Fluorophenyl $\nu_{C-F}$ bending | 804 | 797 | |

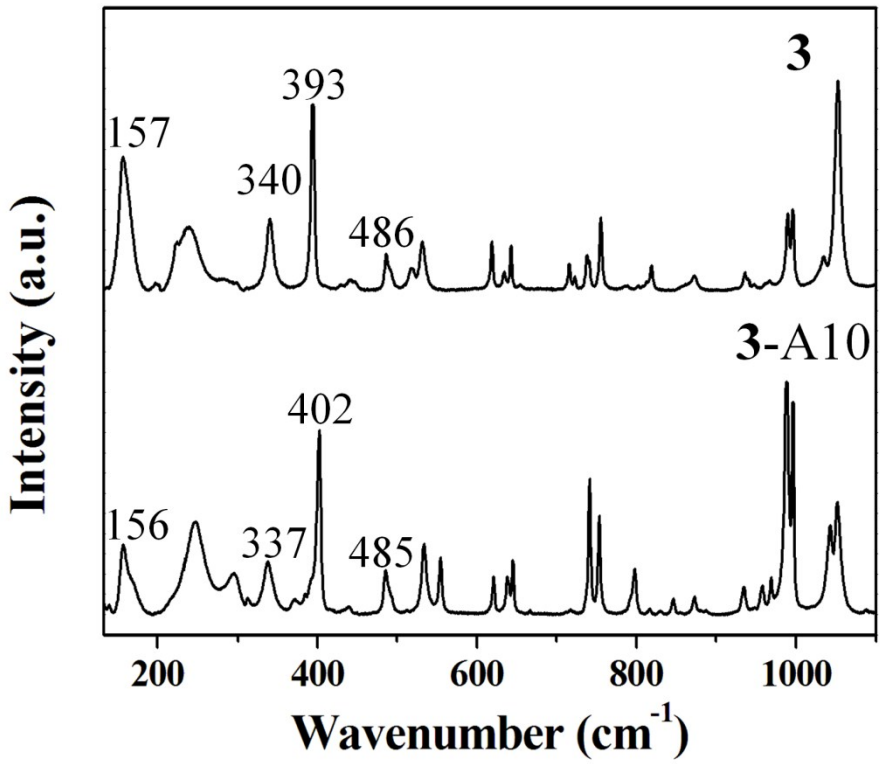



**Fig. S5** Raman spectrum of **3** and the complex **3**-A10.

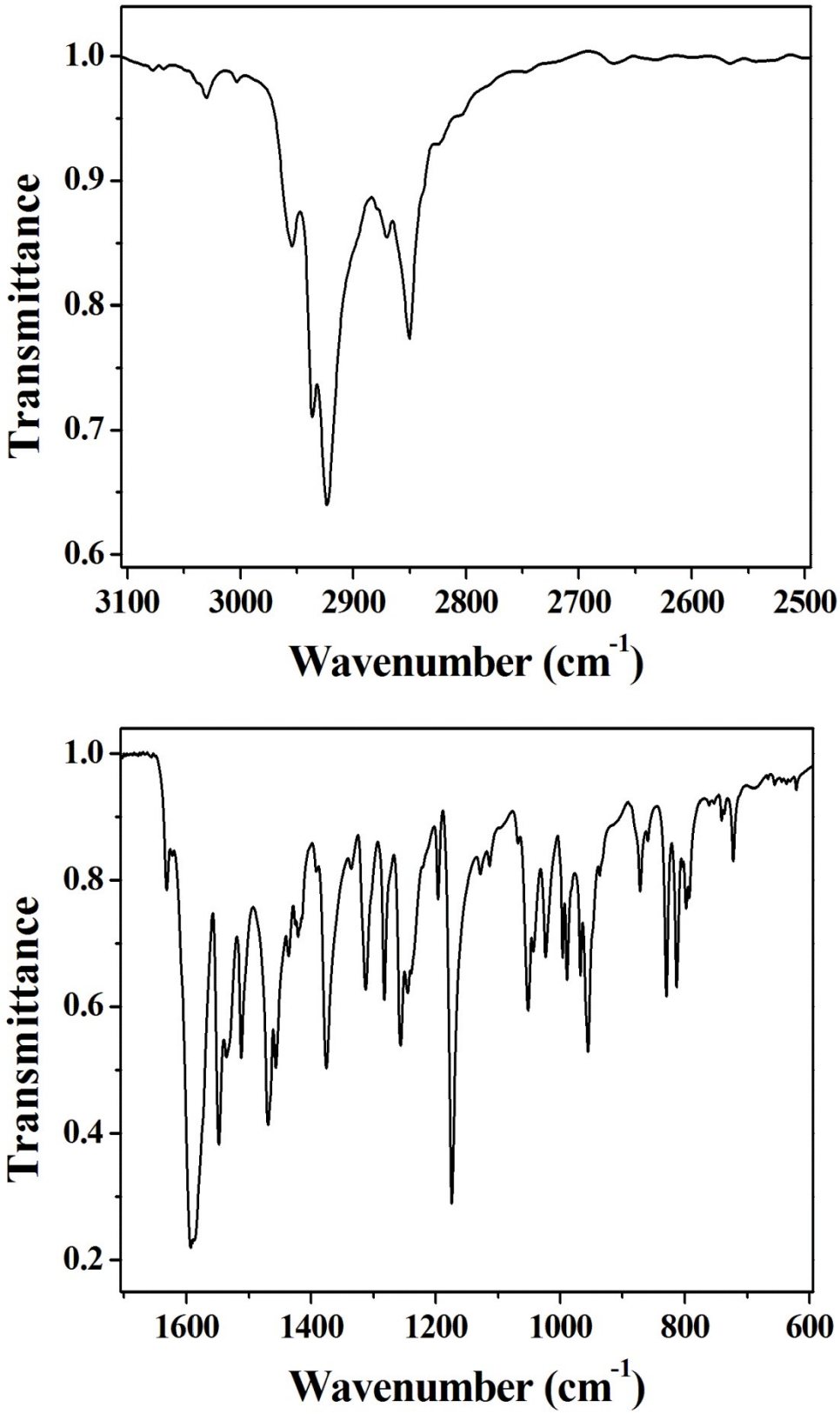



**Fig. S6** FT-IR spectrum of **3**-A10. Top: region between 3100-2500 $cm^{-1}$; bottom: region between 1700-600 $cm^{-1}$.

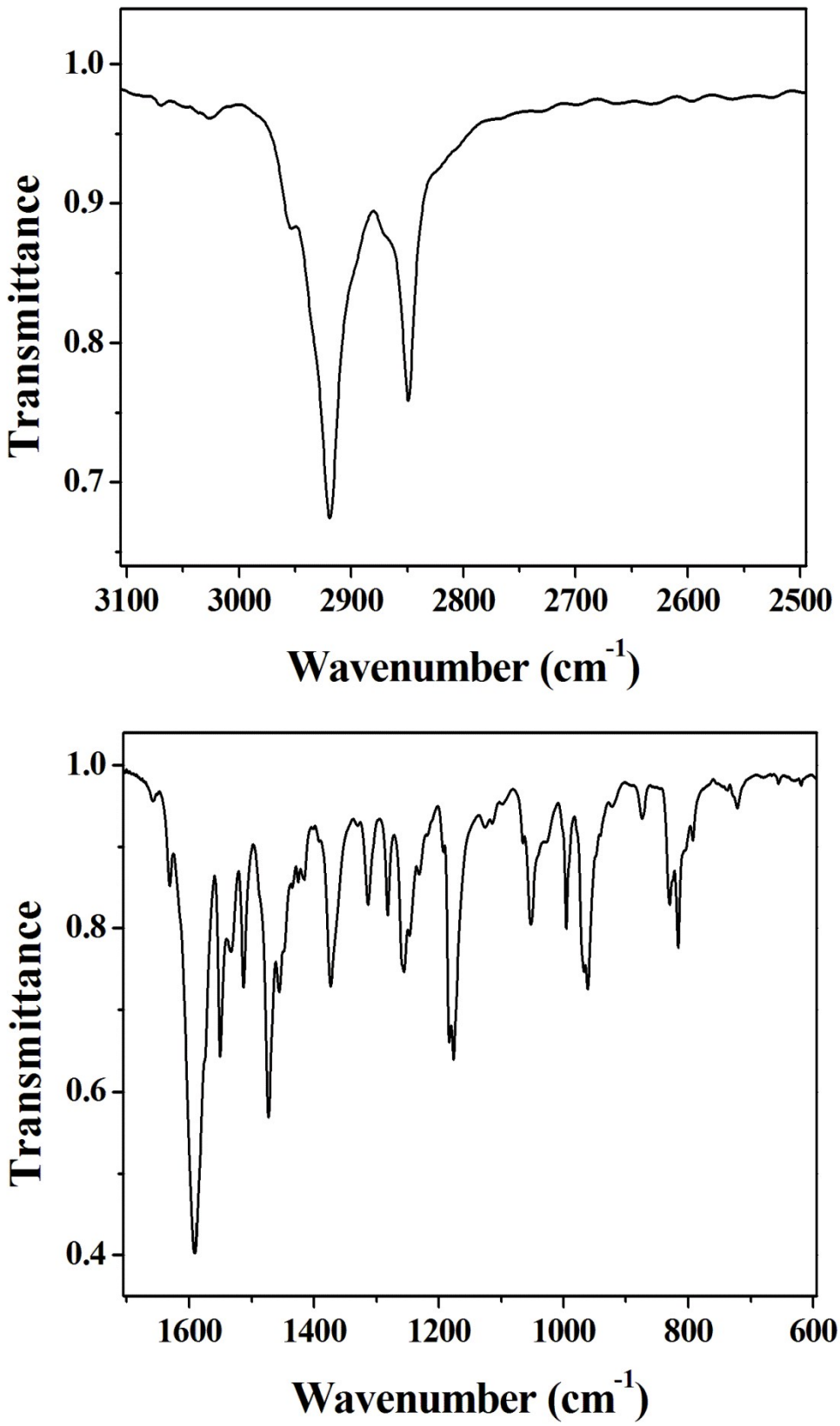



**Fig. S7** FT-IR spectrum of **3**-A12. Top: region between 3100-2500 $cm^{-1}$; bottom: region between 1700-600 $cm^{-1}$.

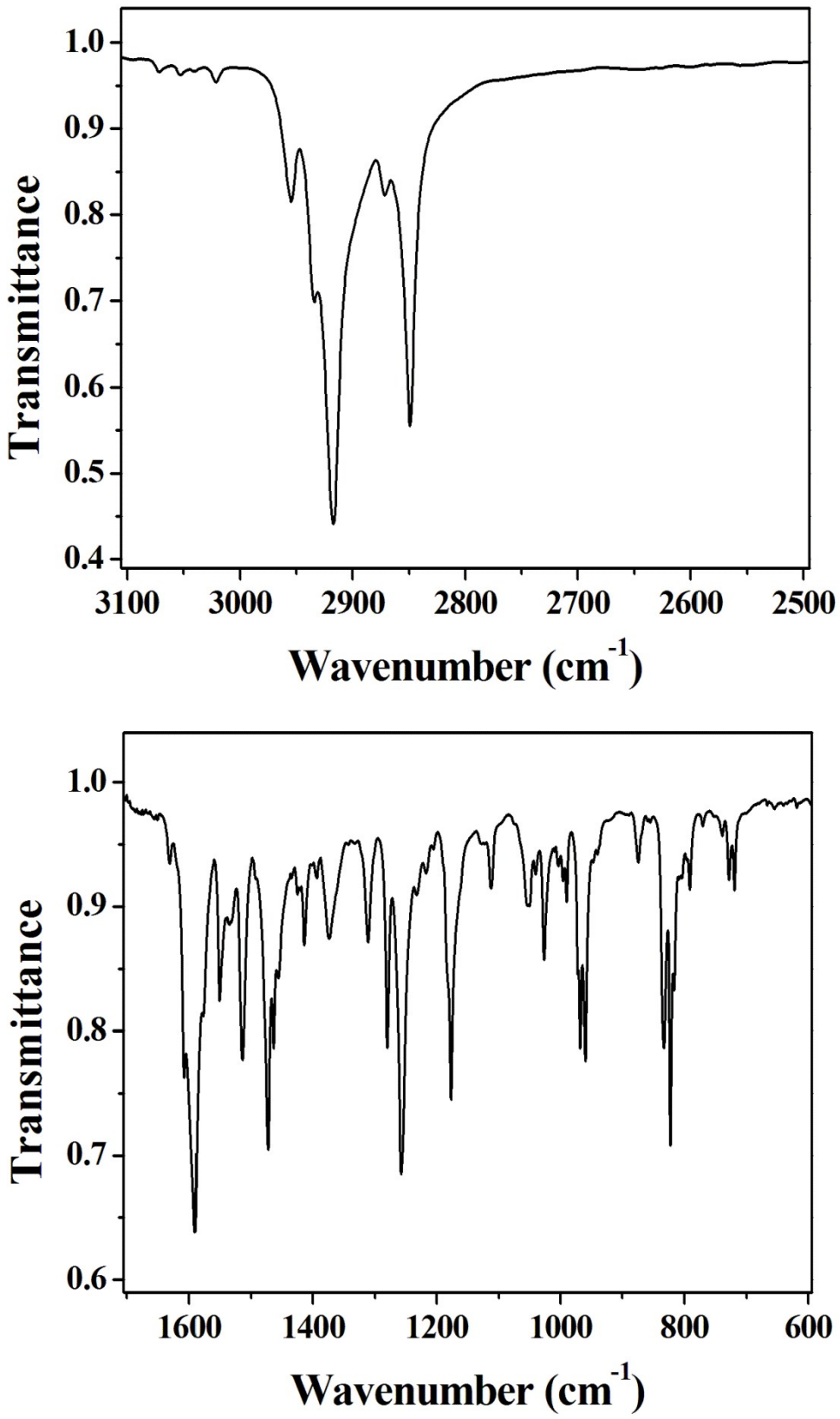



**Fig. S8** FT-IR spectrum of **3**-A16. Top: region between 3100-2500 $cm^{-1}$; bottom: region between 1700-600 $cm^{-1}$.

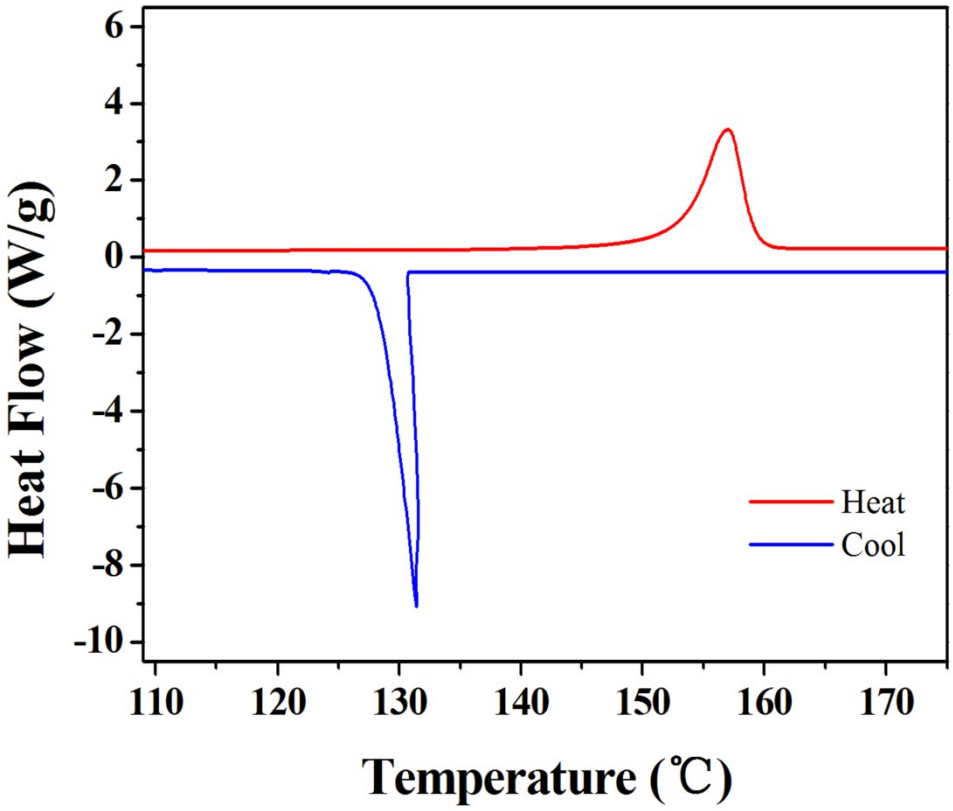



**Fig. S9** DSC trace of **3**-A2 (10 ℃ min$^{-1}$).

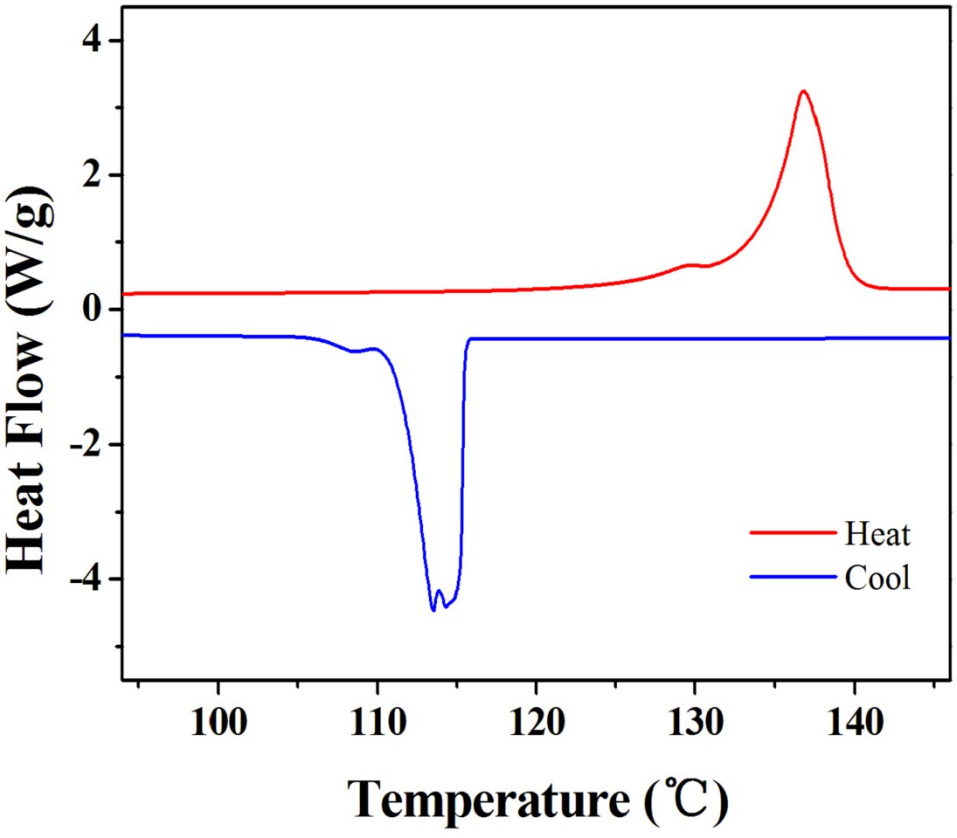



**Fig. S10** DSC trace of **3**-A6 (10 ℃ min$^{-1}$).

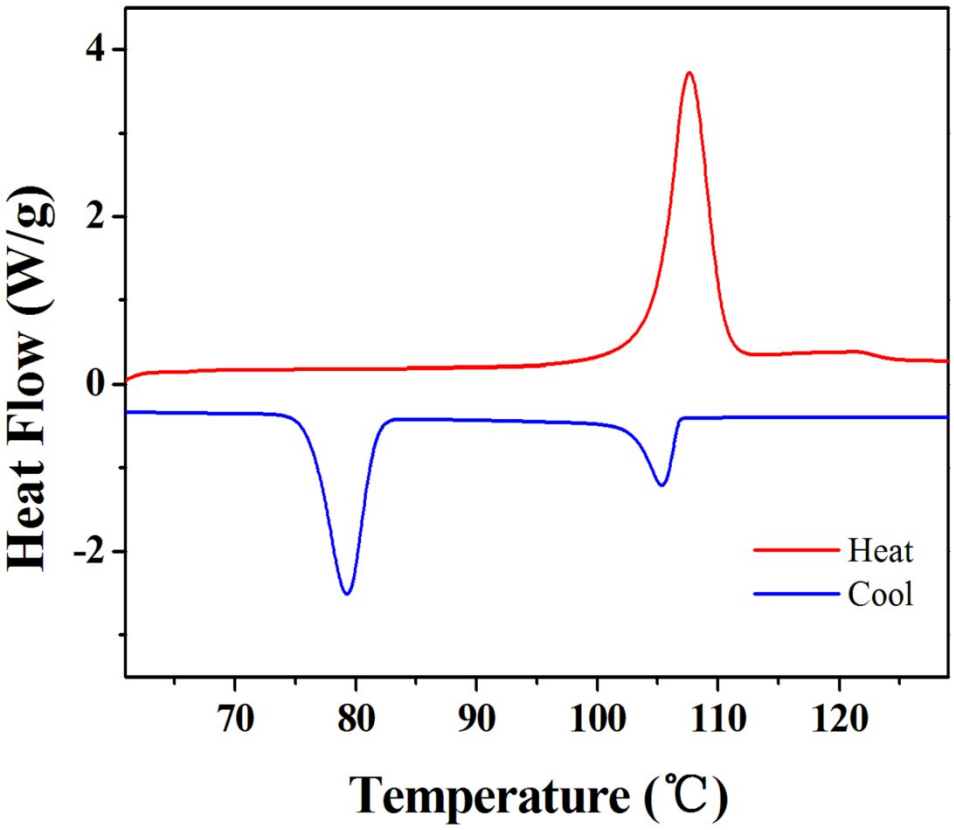



**Fig. S11** DSC trace of **3**-A10 (10 ℃ $min^{-1}$).

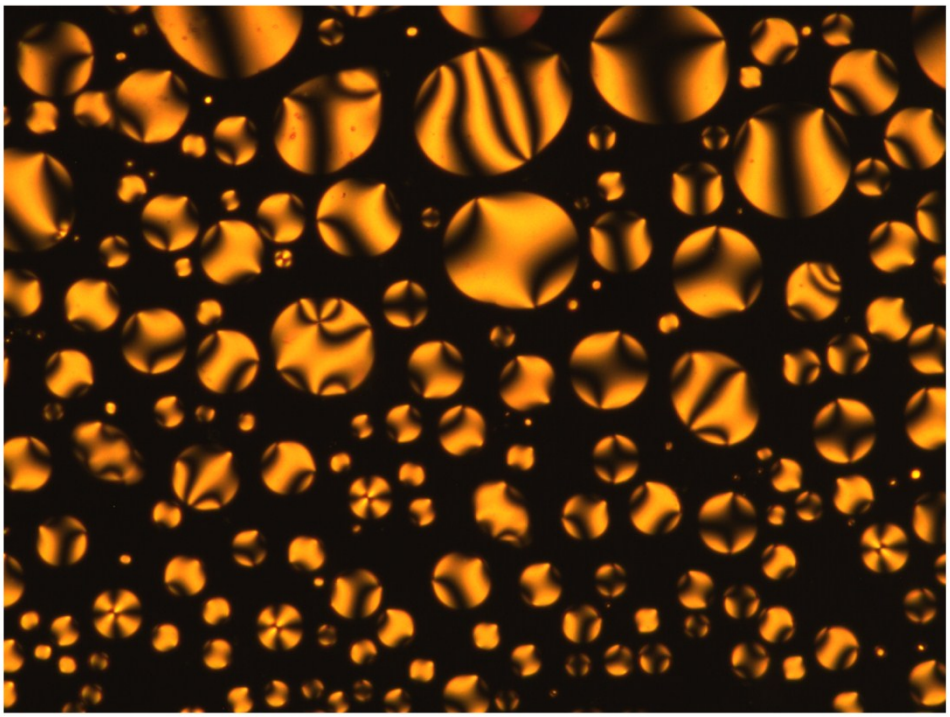


**Fig. S12** Optical texture of the nematic phase of **3**-A6 at 115 ℃ on cooling from isotropic.