**Supporting information**

**Experimental Section**

***Synthesis.***

**4CB**: To a dichloromethane solution (3ml) of 4-chlorosalicylaldehyde (2.04 mmol, 320 mg), 4-bromoaniline (356 mg, 2.07 mmol) was added and stirred for 5 hours. To remove water in the mother liquid, dehydrated sodium sulfate was added and filtered off. Methanol was added and the solution was stored in refrigerator for a day. Yellow crystals were collected by filtration, and dried under reduced pressure. Yield: 523 mg (84%).

**4BB**, **4BC**: To a methanolic solution (5ml) of 4-bromosalicylaldehyde (1.00 mmol, 201 mg), 4-bromoaniline (1.01 mmol, 173 mg) or 4-chloroaniline (1.00 mmol, 128mg) was added, and stored for a day. Yellow crystals were collected by filtration, and dried under reduced pressure. Yield: **4BB**: 323 mg, (91%), **4BC**: 278 mg (90 %).

**4BB**: Elemental Analysis for $C_{13}H_9Br_2NO$: Calcd. C, 43.98; H, 2.56; N, 3.95. Found: C, 44.16; H, 2.34; N, 4.10. FAB MS(+) m/z 354.0, 356.1, 358.1 (calcd. 353.9, 355.9, 357.9 for M + $H^+$). $^1$H NMR ($CDCl_3$): δ 7.09 (1H, dd, J = 8.2, 1.8 Hz, ArH), 7.16(2H, m, ArH), 7.22 (1H, d, J = 1.8 Hz, ArH), 7.24 (1H, d, J = 8.2Hz, ArH), 7.55 (2H, m, ArH), 8.57 (1H, s, N=CH-), 13.28 (1H, br, OH), $^{13}$C NMR ($CDCl_3$): δ = 118.1, 120.8, 120.9, 122.8, 122.9, 127.9, 132.7, 133.4, 147.2, 161.9, 162.2.

**4BC**: Elemental Analysis for $C_{13}H_9BrClNO$: Calcd. C, 50.28; H, 2.92; N, 4.51. Found: C, 50.26; H, 2.85; N, 4.63. FAB MS(+) m/z 310.2, 312.1 (calcd. 310.0, 312.0 for M + $H^+$). $^1$H NMR ($CDCl_3$): δ 7.09 (1H, dd, J = 8.2, 1.8 Hz, AH), 7.2-7.26 (3H, m, ArH), 7.16 (2H, m, ArH), 7.32 (1H, d, J = 8.2 Hz, ArH), 7.40 (2H, m, ArH), 8.56 (1H, s, N=CH-), 13.30 (1H, br, OH), $^{13}$C NMR ($CDCl_3$): δ = 118.1, 120.8, 122.6, 122.8, 127.9, 129.8, 133.0, 133.4, 146.7, 161.9, 162.2.

**4CB**: Elemental Analysis for $C_{13}H_9BrClNO$: Calcd. C, 50.28; H, 2.92; N, 4.51. Found: C, 50.17; H, 2.85; N, 4.64. FAB MS(+) m/z 310.1, 312.1 (calcd. 310.0, 312.0 for M + $H^+$). $^1$H NMR ($CDCl_3$): δ 6.93 (1H, dd, J = 8.3, 1.9 Hz, A-H), 7.04 (1H, d, J = 1.9 Hz, ArH), 7.16 (2H, m, ArH), 7.32 (1H, d, J = 8.2 Hz, ArH), 7.55 (2H, m, ArH), 8.57 (1H, s, N=CH-), 13.31 (1H, br, OH), $^{13}$C NMR ($CDCl_3$): δ = 117.8, 117.8, 119.9, 120.8, 122.9, 132.7, 133.3, 139.4, 147.2, 162.0, 162.1.

**Table S1** Crystallographic parameters of 4XY

| | m-4BB | o1-4BB | o2-4BB | 4BC | 4CB | 4CC-y† | 4CC-o† |
|---|---|---|---|---|---|---|---|
| crystal habit | plate | plate | plate | plate | plate | plate | plate |
| crystal color | yellow | yellow | yellow | yellow | yellow | yellow | orange |
| crystal system | monoclinic | orthorhombic | orthorhombic | monoclinic | orthorhombic | monoclinic | monoclinic |
| space group | *I*2/*a* | *Pca*2$_1$ | *Pccn* | *P*2$_1$/*c* | *Pccn* | *I*2/*c* | *P*2$_1$/*c* |
| *a* / Å | 6.1745(3) | 6.0569(1) | 56.5791(10) | 27.8584(9) | 55.8702(10) | 6.140(5) | 10.004(6) |
| *b* / Å | 6.8716(3) | 6.9330(1) | 6.8940(1) | 6.8627(3) | 6.9161(2) | 6.848(6) | 4.688(3) |
| *c* / Å | 28.3078(12) | 28.5038(3) | 6.1018(1) | 6.1547(2) | 6.1083(1) | 27.39(2) | 11.919(7) |
| *β* / ° | 96.189(4) | 90 | 90 | 95.840(3) | 90 | 95.26(2) | 93.2393(10) |
| *V* / Å3 | 1194.06(9) | 1196.95(3) | 2380.05(7) | 1170.57(7) | 2360.27(9) | 1146.8(16) | 558.1(6) |
| $D_{calcd}$ | 1.975 | 1.970 | 1.982 | 1.762 | 1.748 | 1.541 | 1.584 |
| *Z* | 4 | 4 | 8 | 4 | 8 | 4 | 2 |
| *Z′* | 0.5 | 1 | 1 | 1 | 1 | 0.5 | 0.5 |
| *T* / K | 93 | 93 | 103* | 93 | 153* | 93 | 93 |
| *R* | 0.0410 | 0.0306 | 0.054 | 0.0662 | 0.1145 | 0.0447 | 0.0504 |
| $R_w$ | 0.0958 | 0.0843 | 0.1194 | 0.1299 | 0.2599 | 0.1002 | 0.1208 |

†: ref. 1, *: due to a temperature controller condition, we could not collect the data at 93K.

**Table S2** Geometric parameters of 4XY crystals

| | C-O (Å) | C=N (Å) | $\varphi_1$ (°) | $\varphi_2$ (°) | $\theta$ (°) |
|---|---|---|---|---|---|
| m-4BB | 1.356(6) | 1.29(2) | 4(3) | 39(2) | 45.91 |
| o1-4BB | 1.340(9) | 1.29(1) | -8(1) | -36(1) | 46.82 |
| o2-4BB | 1.352(8) | 1.277(8) | -7.9(9) | -35.8(9) | 46.08 |
| 4BC† | 1.358(6) | 1.28(1) | -10(2) | -33(1) | 45.91 |
| 4CB | 1.36(1) | 1.28(1) | 7(2) | 35(2) | 46.31 |
| 4CC-Y | 1.368(4) | 1.28(1) | -7.8(9) | -35.0(8) | 46.13 |
| 4CC-O | 1.310(6) | 1.27(2) | 2(2) | -4(2) | 0 |

$\varphi_1$: dihedral angle of $C_{2'}$-$C_{1'}$-C=N, $\varphi_2$: dihedral angle of $C_2$-$C_1$-N=C (Aniline side), $\theta$: angles between the normal vectors of two benzene rings, †: major part

**Table S3** Crystallographic parameters of 5XY

| | 5BB | 5BC | 5CB | 5CC-y | 5CC-o |
|---|---|---|---|---|---|
| crystal system | orthorhombic | monoclinic | orthorhombic | monoclinic | monoclinic |
| space group | *Pccn* | $P2_1/c$ | *Pccn* | $P2_1/c$ | $P2_1/c$ |
| *a* / Å | 56.4542(12) | 27.652(11) | 6.9964(15) | 27.419(7) | 20.427(6) |
| *b* / Å | 6.9020(2) | 7.011(3) | 55.786(12) | 6.901(2) | 4.5728(13) |
| *c* / Å | 6.10530(10) | 6.219(3) | 6.1443(14) | 6.137(1) | 12.101(4) |
| *β* / ° | 90 | 96.38(2) | 90 | 95.57(2) | 92.301(5) |
| *V* / Å3 | 2378.91(9) | 1198.2(8) | 2398.1(9) | 1155.75 | 1129.4(6) |
| $D_{calcd}$ | 1.983 | 1.722 | 1.72 | 1.529 | 1.565 |
| *Z* | 8 | 4 | 8 | 4 | 4 |
| *Z′* | 1 | 1 | 1 | 1 | 1 |
| *T* / K | 93 | 296 | 298 | 190 | 93 |
| *R* | 0.0391 | 0.031 | 0.054 | 0.034 | 0.0333 |
| $R_w$ | 0.0976 | 0.078 | 0.128 | 0.0905 | 0.083 |
| Reference | This work | ref. 2 | ref. 3 | ref. 4 | ref. 1 |

**Table S4** Geometric parameters of 5XY crystals

| | C-O (Å) | C=N (Å) | $\varphi_1$ (°) | $\varphi_2$ (°) | $\theta$(°) |
|---|---|---|---|---|---|
| 5BB | 1.356(4) | 1.293(4) | 5.5(4) | 36.0(4) | 44.45 |
| 5BC | 1.341(3) | 1.274(4) | -4.6(4) | -35.6(4) | 43.90 |
| 5CB | 1.352(5) | 1.276(5) | 5.4(6) | 35.8(6) | 44.27 |
| 5CC-y | 1.352(3) | 1.280(3) | -5.4(4) | -35.9(3) | 44.55 |
| 5CC-o | 1.353(2) | 1.287(2) | 3.3(2) | -6.0(2) | 2.85 |

$\varphi_1$: dihedral angle of $C_{2'}$-$C_{1'}$-C=N, $\varphi_2$: dihedral angle of $C_2$-$C_1$-N=C (Aniline side), $\theta$: angles between the normal vectors of two benzene rings

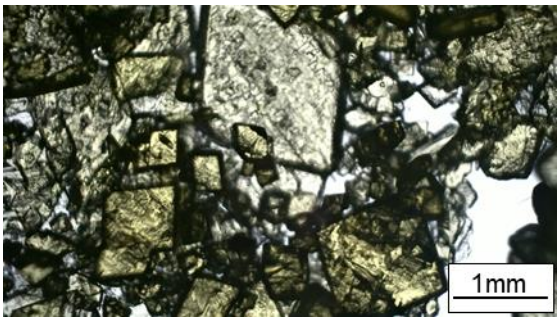


**Figure S1** 4BB crystals obtained from a mixed solution of dichloromethane and hexane. The crystals were a conglomerate of several polymorphs, all similar yellow platelets.

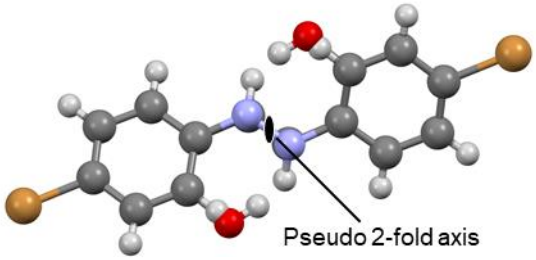


**Figure S2** Static disorder in m-4BB. The ratio of 1:1 for opposite orientations caused pseudo 2-fold axis on the center of imine bond.

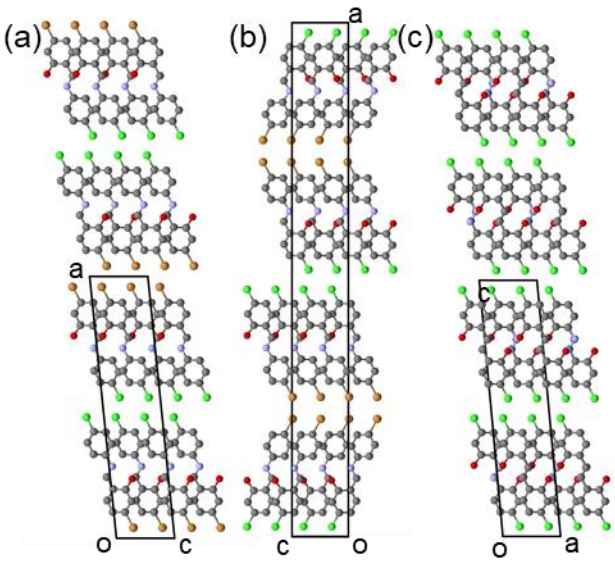


**Figure S3** Crystal packing of a) 4BC (major part), b) 4CB and c) 4CC-y.

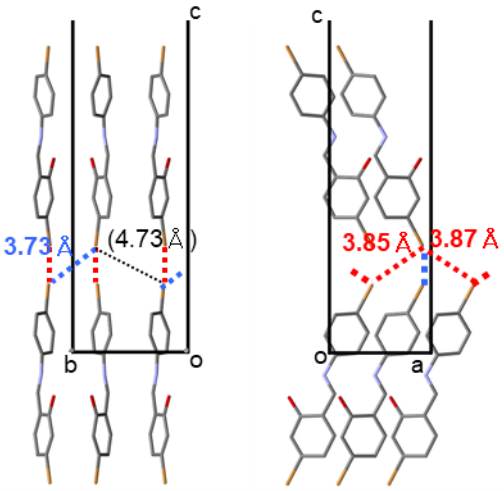


**Figure S4** Type-II halogen bond network along a-axis (red) and additional type-I halogen bond along b-axis (blue) in $o_1$-4BB crystal.

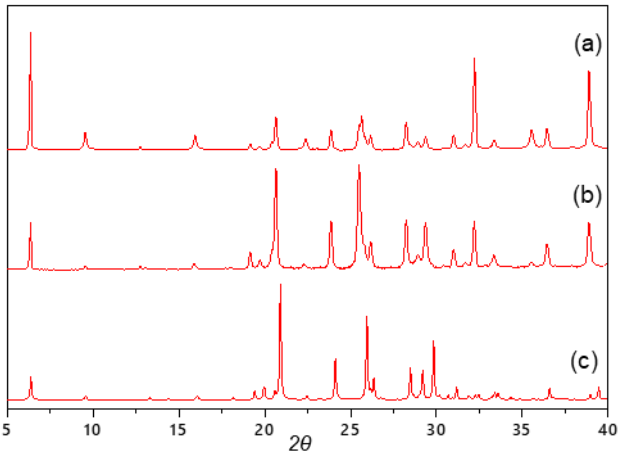


**Figure S5** Powder X-ray diffraction patterns of 4BC measured for the samples recrystallized from solution (a) and from melt (b), with simulated pattern for 4BC crystal (c).

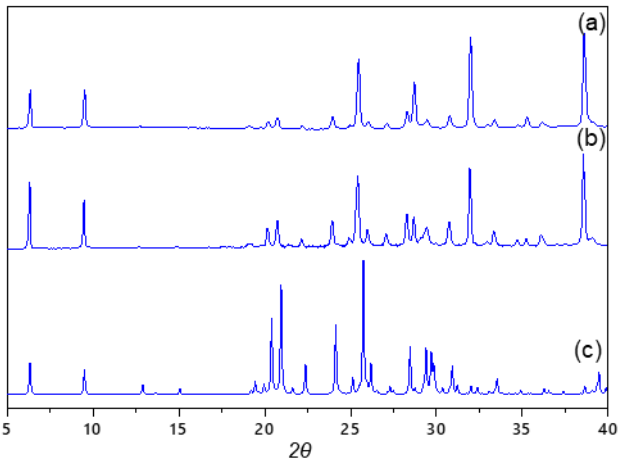


**Figure S6** Powder X-ray diffraction patterns of 4CB measured for the samples recrystallized from solution (a) and from melt (b), with simulated pattern for 4CB crystal (c).

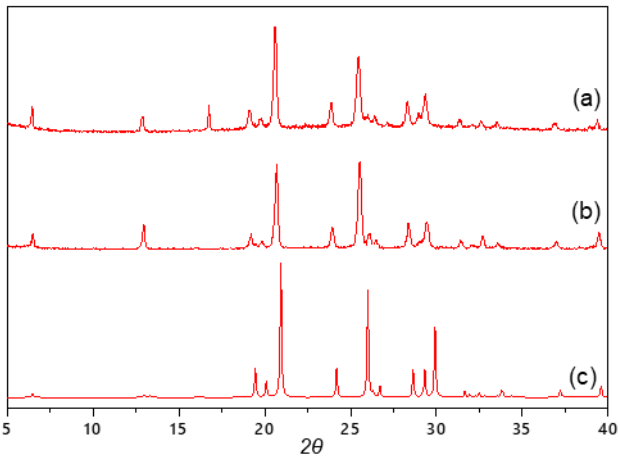


**Figure S7** Powder X-ray diffraction patterns of 4CC measured for 4CC recrystallized from solution (a) and from melt (b), with simulated pattern for 4CC-y crystal (c).

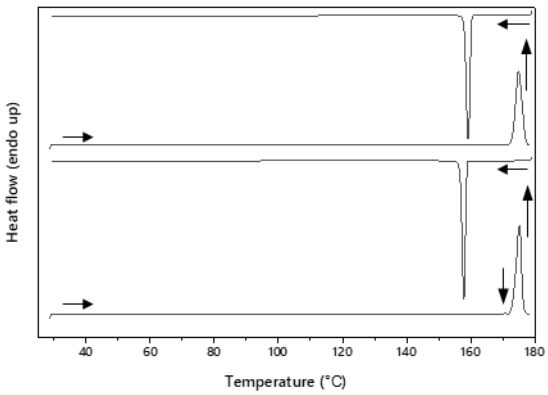


**Figure S8** DSC curves of 4BB.

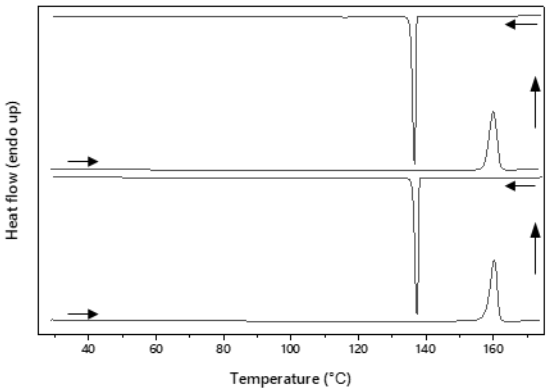


**Figure S9** DSC curves of 4BC

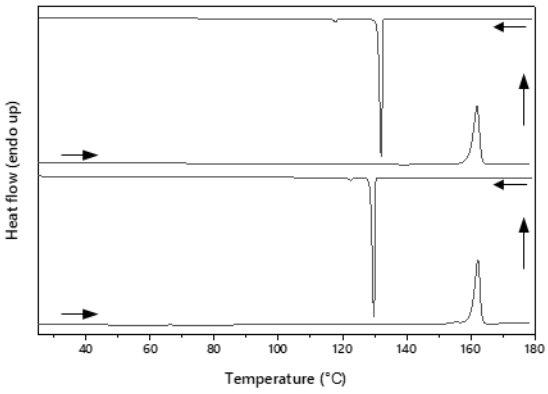


**Figure S10** DSC curves of 4CB

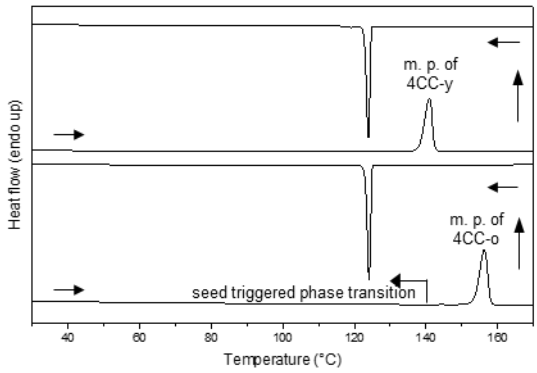


**Figure S11** DSC curves of 4CC-Y. Contamination of small amount of 4CC-o caused a seed-triggered phase transition to 4CC-o below the melting point of 4CC-y in the first heating curve.

**References for supporting information**

(1) Z. Zhang, M. Suzuki, Y. Yang, I. Yoshikawa, Q. Yin, and H. Houjou, *CrystEngComm* 2020, **22**, 4903–4913.

(2) A. A. Ardakani, R. Kia, H. Kargar, and M. N. Tahir, *Acta Crystallogr. Sect. E Struct. Reports Online* 2011, **67**, o597–o597.

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