Contents

Experimental

Measurements

The ultraviolet-visible (UV-Vis) absorption spectra of the solid samples were acquired using a conventional optical microscope equipped with an optical fibre connected to a spectrometer (Ocean Optics USB4000) and a temperature-controlled stage (Linkam THMS600). The transmitted light was guided from a Xe light source (Asahi Spectra LAX-103) through a custom-made adaptor, and the incident light was guided from a high-pressure Hg lamp via a 330–380 nm bandpass filter. The samples were prepared by growing thin-plate crystals on a glass slide by molten recrystallisation or by depositing thin-plate crystals obtained by solution recrystallisation on a glass slide. The spectra was captured with an acquisition time of 100 ms, and averaged over 10 runs (namely, the total acquisition time of 1.0 s). To capture the spectra of photospecies, the sample was irradiated with a Hg lamp through a dichroic mirror cube, and after the spectral change was saturated the dichroic mirror cube was replaced with a half-mirror cube that intercepts the UV irradiation. The solution-state UV-Vis absorption spectra of the compounds were measured in methylcyclohexane or ethanol (1×10^{-4} M) with a JASCO V-630 spectrophotometer. Powder X-ray diffraction patterns were obtained on a Rigaku RINT-2100 diffractometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer (400 MHz for ^{1}H) for samples in deuterated chloroform. The chemical shifts were measured relative to tetramethylsilane (0 ppm for ^{1}H) or chloroform (77.16 ppm for ^{13}C) as an internal standard. Mass spectra were recorded on a JEOL JMS-600H and 3-nitrobenzyl alcohol was used as matrix for FAB-MS spectra. IR spectra were measured by a JASCO FT/IR-420 spectrometer. Melting point was determined as the onset of endothermic peak recorded on a differential scanning calorimetry (Perkin-Elmer Pyris 1 DSC).

Synthesis

The Schiff base compounds **1Cn** (n = 13–18) and **1BN** were prepared according to a typical procedure for condensation of salicylaldehyde and amine. In a typical example, a dichloromethane solution (3.5 mL) of 5-bromosalicylaldehyde (201 mg, 1.0 mmol) was added to 1-aminotridecane (202 mg, 1.0 mmol) and allowed to stand for 19 h in ambient temperature (25°C). The mixture was desiccated with sodium sulfate and concentrated to a viscous brown liquid which was refrigerated to afford a yellow crystalline solid. The product was recrystallised from hot methanol. All the chemicals and solvents were purchased from Tokyo Chemical Industry and used without further purification.

1C13 Yellow needles (yield 79%); m.p. 43°C; Analysis for $C_{20}H_{32}BrNO$ C, 62.82; H, 8.44; N, 3.66; found C, 62.80; H, 8.41; N, 3.66; FAB(+) MS *m/z* calcd. for $[M+H]^+$ 382.2, 384.2, found 382.0, 384.1; IR (KBr) 2948, 2918, 2845, 1631, 1482 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.26 (m, $-CH_2-$, 20H), 1.69 (quint, *J* = 7.2 Hz, $-CH_2-$, 2H), 3.59 (t, *J* = 6.8, $N-CH_2-$, 2H), 6.85 (d, *J* = 8.6 Hz, ArH, 1H), 7.35 (m, ArH, 2H), 8.25 (s, -CH=N-, 1H), 13.73 (br, -OH, 1H); ^{13}C NMR δ 14.27, 22.83, 27.28, 29.46, 29.50, 29.68, 29.74, 29.78, 29.81, 30.87, 32.06, 59.63, 109.88, 119.25, 120.28, 133.33, 134.83, 160.74, 163.33.

1C14 Colourless plates (Yield 84%); m.p. 37°C; Analysis for $C_{21}H_{34}BrNO$ C, 63.63; H, 8.65; N, 3.53; found C: 63.72, H: 8.68, N: 3.57; FAB(+) MS *m/z* calcd. for $[M+H]^+$ 396.2, 398.2, found 396.3, 398.3; IR (KBr) 2957, 2914, 2851, 1639, 1470 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.0 Hz, CH_3, 3H), 1.25 (m, $-CH_2-$, 22H), 1.69 (quint, *J* = 7.3 Hz, $-CH_2-$, 2H), 3.59 (t, *J* = 6.8, $N-CH_2-$, 2H), 6.85 (d, *J* = 8.5 Hz, ArH, 1H), 7.35 (m, ArH, 2H), 8.25 (s, -CH=N-, 1H), 13.72 (br, -OH, 1H); ^{13}C NMR δ 14.26, 22.83, 27.28, 29.45, 29.50, 29.67, 29.74, 29.78, 29.80, 29.82, 30.87, 32.06, 59.63, 109.88, 119.25, 120.28, 133.33, 134.83, 160.74, 163.33.

1C15 Yellow needles (yield 85%); m.p. 53°C; Analysis for $C_{22}H_{36}BrNO$ C, 64.38; H, 8.84; N, 3.41; found C, 64.67; H, 8.75; N, 3.44; FAB(+) MS *m/z* calcd. for $[M+H]^+$ 410.2, 412.2, found 410.4, 412.3; IR (KBr) 2953, 2919, 2851, 1635, 1482 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.2 Hz, CH_3, 3H), 1.25 (m, $-CH_2-$, 24H), 1.69 (quint, *J* = 7.2 Hz, $-CH_2-$, 2H), 3.59 (t, *J* = 6.8, $N-CH_2-$, 2H), 6.85 (d, *J* = 8.4 Hz, ArH, 1H), 7.35 (m, ArH, 2H), 8.25 (s, -CH=N-, 1H), 13.72 (br, -OH, 1H); ^{13}C NMR δ 14.27, 22.84, 27.29, 29.46, 29.50, 29.68, 29.75, 29.80, 29.83, 30.88, 32.07, 59.64, 109.89, 119.27, 120.30, 133.34, 134.85, 160.75, 163.34.

1C16 Colourless plates (Yield 82%); m.p. 47°C; Analysis for $C_{23}H_{38}BrNO$ C, 65.08; H, 9.02; N, 3.30; found C: 65.18, H: 8.76, N: 3.29; FAB(+) MS *m/z* calcd. for $[M+H]^+$ 424.2, 426.2, found 424.4, 426.4; IR (KBr) 2960, 2915, 2850, 1634, 1469 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.1 Hz, CH_3, 3H), 1.25 (m, $-CH_2-$, 26H), 1.69 (quint, *J* = 7.1 Hz, $-CH_2-$, 2H), 3.59 (t, *J* = 7.1, $N-CH_2-$, 2H), 6.85 (d, *J* = 8.5 Hz, ArH, 1H), 7.35 (m, ArH, 2H), 8.25 (s, -CH=N-, 1H), 13.73 (br, -OH, 1H); ^{13}C NMR δ 14.27, 22.84, 27.29, 29.45, 29.51, 29.68, 29.74, 29.80, 29.84, 30.87, 32.07, 59.64, 109.89, 119.26, 120.29, 133.34, 134.84, 160.75, 163.34.

1C17 Yellow needles (yield 85%); m.p. 59°C; Analysis for $C_{24}H_{40}BrNO$ C, 65.74; H, 9.19; N, 3.19; found C, 65.61; H, 9.21; N, 3.22; FAB(+) MS *m/z* calcd. for $[M+H]^+$ 438.2, 440.2, found 438.3, 440.3; IR (KBr) 2948, 2915, 2847, 1634, 1481 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.0 Hz, CH_3, 3H), 1.25 (m, $-CH_2-$, 28H), 1.69 (quint, *J* = 7.0 Hz, $-CH_2-$, 2H), 3.59 (t, *J* = 7.0, $N-CH_2-$, 2H), 6.85 (d, *J* = 8.7 Hz, ArH, 1H), 7.35 (m, ArH, 2H), 8.25 (s, -CH=N-, 1H), 13.74 (br, -OH, 1H); ^{13}C NMR δ 14.27, 22.84, 27.28, 29.45, 29.51, 29.68, 29.74, 29.80, 29.83, 30.86, 32.07, 59.63, 109.88, 119.27, 120.30, 133.34, 134.84, 160.75, 163.33.

1C18 Colourless plates (Yield 82%); m.p. 54°C; Analysis for $C_{25}H_{42}BrNO$ C, 66.36; H, 9.36; N, 3.10; found C: 66.55, H: 9.44, N: 3.01; FAB(+) MS *m/z* calcd. for $[M+H]^+$ 452.3, 454.3, found 452.2, 454.2; IR (KBr) 2951, 2921, 2847, 1637, 1476 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.3 Hz, CH_3, 3H), 1.25 (m, $-CH_2-$, 30H), 1.69 (quint, *J* = 7.0 Hz, $-CH_2-$, 2H), 3.59 (t, *J* = 7.0, $N-CH_2-$, 2H), 6.85 (d, *J* = 9.3 Hz, ArH, 1H), 7.35 (m, ArH, 2H), 8.25 (s, -CH=N-, 1H), 13.74 (br, -OH, 1H); ^{13}C NMR δ 14.27, 22.84, 27.28, 29.46, 29.51, 29.68, 29.74, 29.78, 29.80, 29.84, 30.87, 32.07, 59.63, 109.88, 119.25, 120.27, 133.33, 134.84, 160.74, 163.33.

1BN Yellow plates (yield 100%); m.p. 70 °C; Analysis for $C_{14}H_{12}BrNO$ C, 57.95; H, 4.17; N, 4.83; found C, 58.10; H, 4.22; N, 4.98; FAB(+) MS *m/z* calcd. for $[M]^+$ 289.0, 291.0, found 289.0, 290.9, calcd. for $[M+H]^+$ 290.0, 292.0, found 290.0, 292.0; IR (KBr) 2908, 2848, 1631, 1569, 1478, 1454, 1367 cm^{-1}; ^1H NMR δ 4.82 (s, $N-CH_2-$, 2H), 6.86 (m, ArH, 1H), 7.35 (m, ArH, 7H), 8.35 (s, -CH=N-, 1H), 13.43 (br, -OH, 1H); ^{13}C NMR δ 63.24, 110.18, 119.23, 120.32, 127.70, 127.99, 128.91, 133.66, 135.15, 137.75, 160.34, 164.45.

Crystallography

For X-ray diffraction of single crystals, data were collected on a VariMax DW with Saturn CCD diffractometer, λ(Mo-Kα) = 0.71075 Å or λ(Cu-Kα) = 1.54187 Å. The structures were solved by direct method (SHELXS-2013[1]) and refined on F^2 by full-matrix least-square techniques (SHELXL-2016).[2] The crystal of 1C17 was twinned, and the twinning was resolved by PLATON.[3] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1566472 to 1566478 for **1C13**, **1C15**, **1C17**, and **1BN** (including different measuring temperatures). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

[1] G. M. Sheldrick, *Acta Crystallogr. A* 2008, **64**, 112-122.
[2] G. M. Sheldrick, Acta Cryst. 2015, C71, 3-8.
[3] A. L. Spek, Acta Cryst 2009, D65, 148–155.

1C13: $C_{20}H_{32}BrNO$, M_w =382.37, monoclinic, *a* = 9.834(9), *b* = 5.686(5), *c* = 35.79(3) Å, β = 93.958(11), *V* = 1996(3) $Å_3$, D_{calc} = 1.272 g/cm^3, *T* = 93(2) K, space group $P2_1/c$ (#14), *Z* = 4, μ(Mo–

K_{α}) =20.64 cm^{-1}, 19457 reflections measured and 4538 unique ($2\theta_{max}$ = 54.8°, R_{int} = 0.068) which were used in all calculations. R = 0.054, R_w =0.102.

1C13 (253 K): $C_{20}H_{32}BrNO$, M_w = 382.37, monoclinic, a = 9.9934(16), b = 5.7714(8) c = 35.925(5) Å, β = 93.957(8), V = 2067.1(5) $Å^3$, D_{calc} = 1.229 g/cm^3, T = 253(2) K, space group $P2_1/c$ (#14), Z = 4, μ(Mo–K_{α}) = 19.94 cm^{-1}, 10536 reflections measured and 2676 unique ($2\theta_{max}$ = 44.9°, R_{int} = 0.053) which were used in all calculations. R = 0.044, R_w = 0.107.

1C15: $C_{22}H_{36}BrNO$, M_w = 410.43, monoclinic, a = 9.769(12), b = 5.613(7), c = 39.16(5) Å, β = 96.05(5)°, V = 2135(5) $Å^3$, D_{calc} = 1.277 g/cm^3, T = 93(2) K, space group $P2_1/c$ (#14), Z = 4, μ(Cu–K_{α}) = 26.75 cm^{-1}, 21491 reflections measured and 3760 unique ($2\theta_{max}$ = 136.3, R_{int} = 0.088) which were used in all calculations. R = 0.067, R_w = 0.194.

1C15 (253 K): $C_{22}H_{36}BrNO$, M_w = 410.43, monoclinic, a = 9.912(8), b = 5.689(4), c = 39.13(3) Å, β = 95.81(2)°, V = 2195(3) $Å^3$, D_{calc} = 1.242 g/cm^3, T = 253(2) K, space group $P2_1/c$ (#14), Z = 4, μ(Cu–Kα) = 26.02 cm^{-1}, 25186 reflections measured and 3965 unique ($2\theta_{max}$ = 136.4°, R_{int} = 0.12) which were used in all calculations. R = 0.082, R_w = 0.255.

1C17: $C_{24}H_{40}BrNO$, M_w = 438.48, monoclinic, a = 9.739(9), b = 5.587(5), c = 42.62(4) Å, β = 96.40(2)°, V = 2305(4) $Å^3$, D_{calc} = 1.264 g/cm^3, T = 93(2) K, space group $P2_1/n$ (#14), Z = 4, μ(Cu–Kα) = 25.10 cm^{-1}, 25576 reflections measured and 4424, unique ($2\theta_{max}$ = 140.3°, R_{int} = 0.13) which were used in all calculations. R = 0.107, R_w = 0.321.

1BN: $C_{14}H_{12}BrNO$, M_w = 290.16, monoclinic, a = 14.100(11), b = 5.993(4), c = 29.53(2) Å, β = 102.576(7)°, V = 2435(3) $Å^3$, D_{calc} = 1.583 g/cm^3, T = 93(2) K, space group $P2_1/n$, (#14), Z = 8, μ(Mo–Kα) = 33.57 cm^{-1}, 16441 reflections measured and 4252 unique ($2\theta_{max}$ = 50.8°, R_{int} = 0.07) which were used in all calculations. R = 0.054, R_w = 0.127.

1BN (293 K): $C_{14}H_{12}BrNO$, M_w = 290.16, monoclinic, a = 14.730(6), b = 6.093(2), c = 14.524(7) Å, β = 102.290(8)°, V = 1273.7(9) $Å^3$, D_{calc} = 1.513 g/cm^3, T = 293(2) K, space group $P2_1/c$, (#14), Z = 4, μ(Mo–Kα) = 32.10 cm^{-1}, 8727 reflections measured and 2299 unique ($2\theta_{max}$ = 50.6°, R_{int} = 0.05) which were used in all calculations. R = 0.051, R_w = 0.138.

Supplementary figures

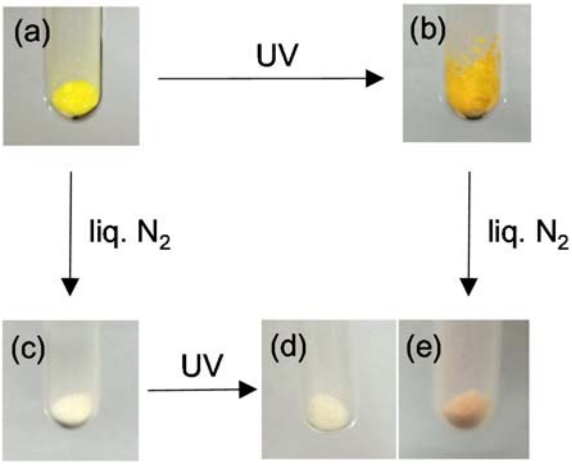

Figure S1 Photographs of **1BN** during various cooling and irradiation pathways. (a) at 25 °C, (b) irradiated with UV lamp at 25 °C, (c) cooled with liquid nitrogen, (d) irradiated with UV light during cooling with liquid nitrogen, (e) irradiated with a UV lamp at 25 °C and then cooled with liquid nitrogen.

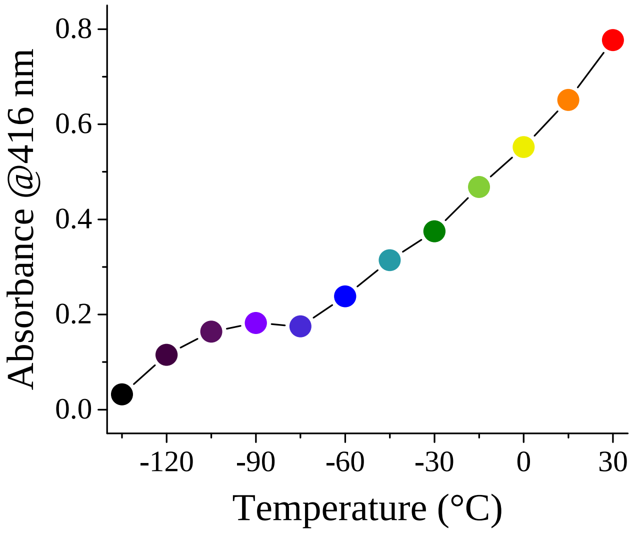

Figure S2 Plot of the absorbance at 416 nm picked up from temperature-dependent UV-Vis absorption spectra measured for a single crystal of **1C15** under microscope. The colour code is the same as in Figure 2.

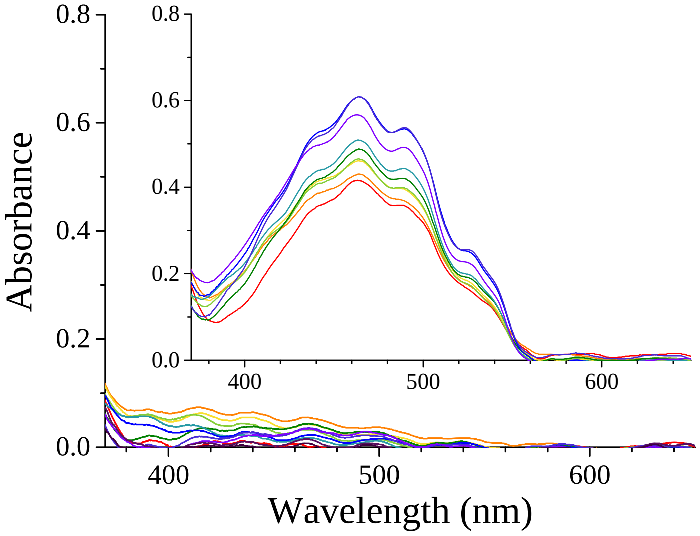

Figure S3 Temperature-dependent UV-Vis absorption spectra measured for the single crystal of **1C14** under microscope. Inset: the spectra measured immediately after UV irradiation with Hg lamp. The colour code is the same as in Figure 2.

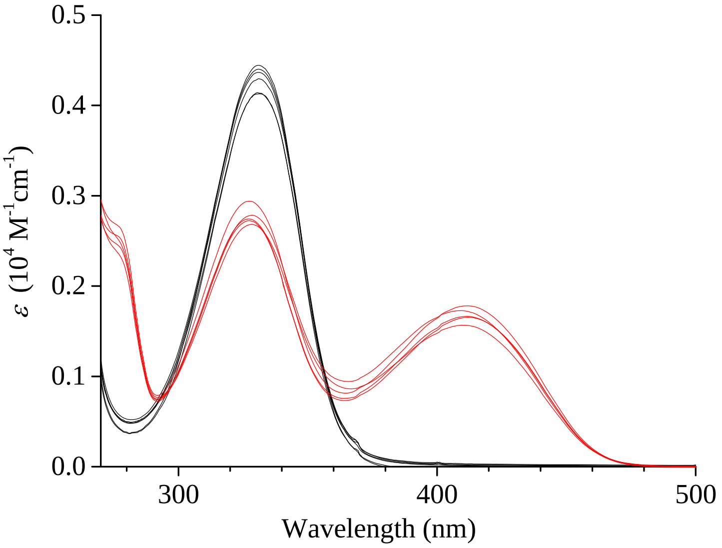

Figure S4 Solution UV-Vis spectra of **1Cn** (n = 13–18) overlaid in one graph: (black lines) in methylcyclohexane, 1×10^{-4} M, (red lines) in ethanol, 1×10^{-4} M. The data of ethanol solutions shows an absorption band around 410 nm, attributable to *cis*-keto tautomer, due to the effect of a protic solvent.

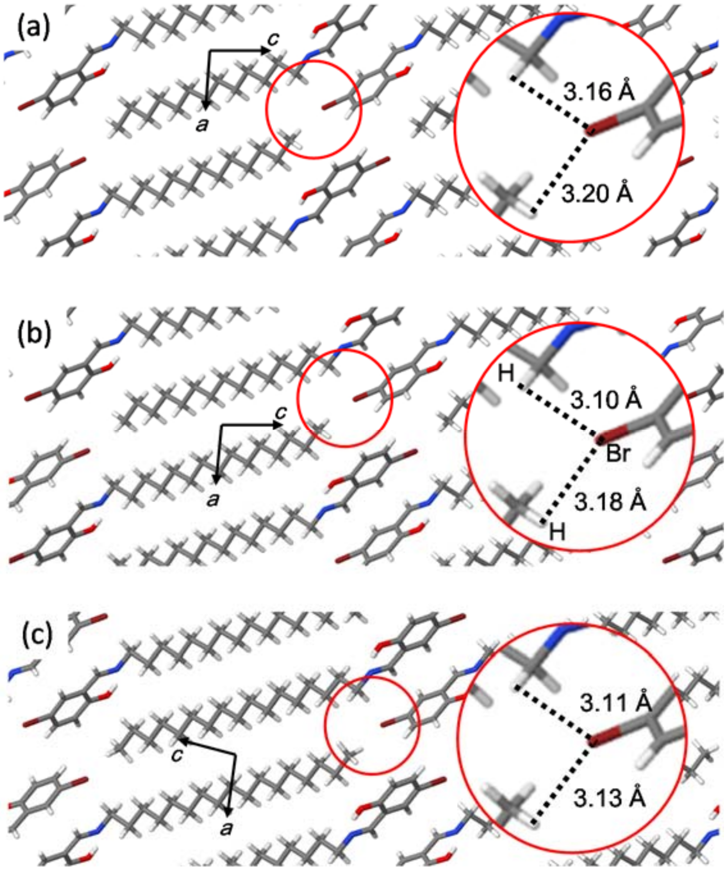

Figure S5 Molecular packing structure of (a) **1C13**, (b) **1C15**, and (c) **1C17** viewed along the crystallographic *b*-axis. The centroid–centroid distance between phenyl rings are (a) 5.318 and 6.281 Å, (b) 5.291 and 6.214 Å, (c) 5.302 and 6.157 Å.

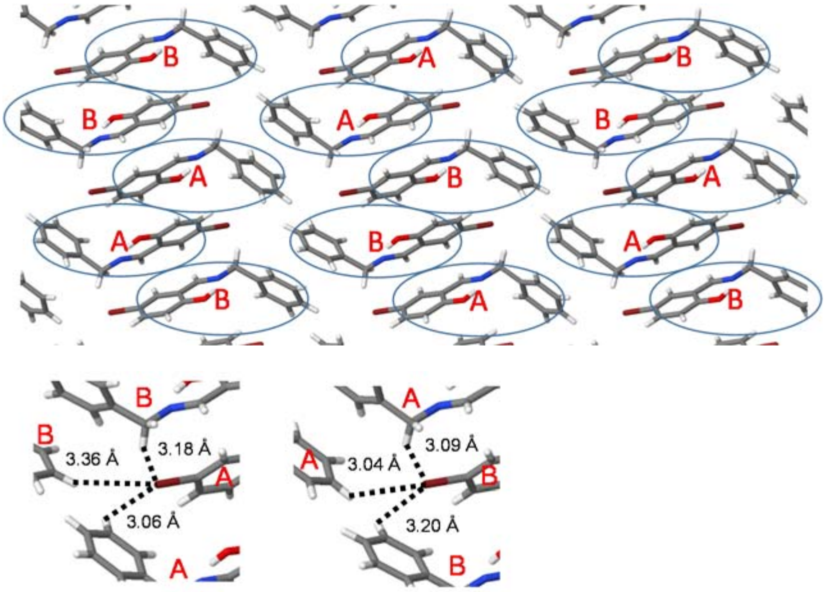

Figure S6 Molecular packing structure of **1BN** viewed along the crystallographic *b*-axis. At 93 K, the unit cell contains two asymmetric units A and B, which become nearly identical at 298 K and hence the unit cell halves in dimension.

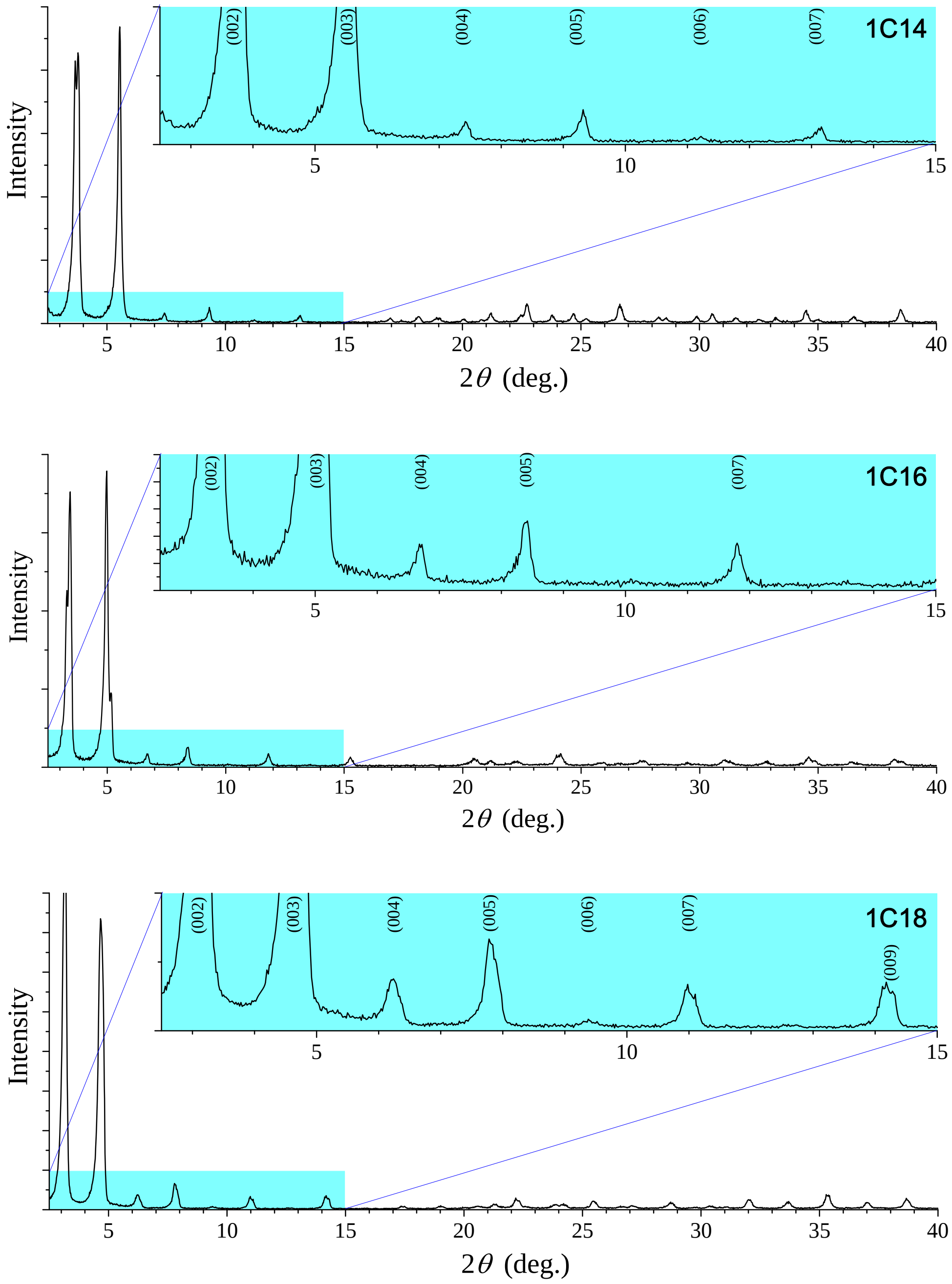

Figure S7 Powder X-ray diffraction patterns measured for **1C14**, **1C16**, and **1C18** with a tentative indexing of (00*l*) for a series of equally-spaced peaks.

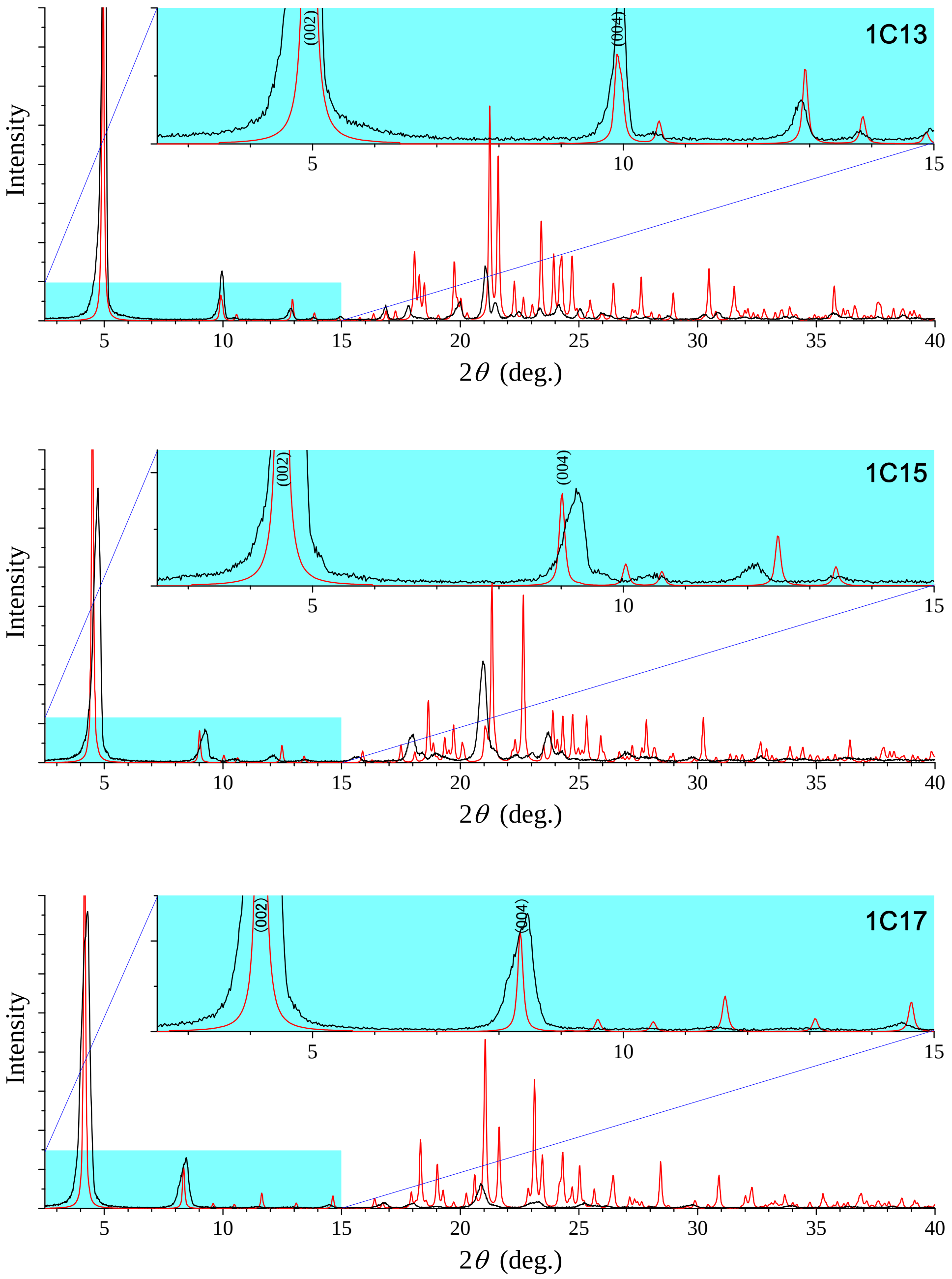

Figure S8 Powder X-ray diffraction patterns measured for **1C13**, **1C15**, and **1C17** (black lines) with those simulated from the corresponding single crystal data (red lines).

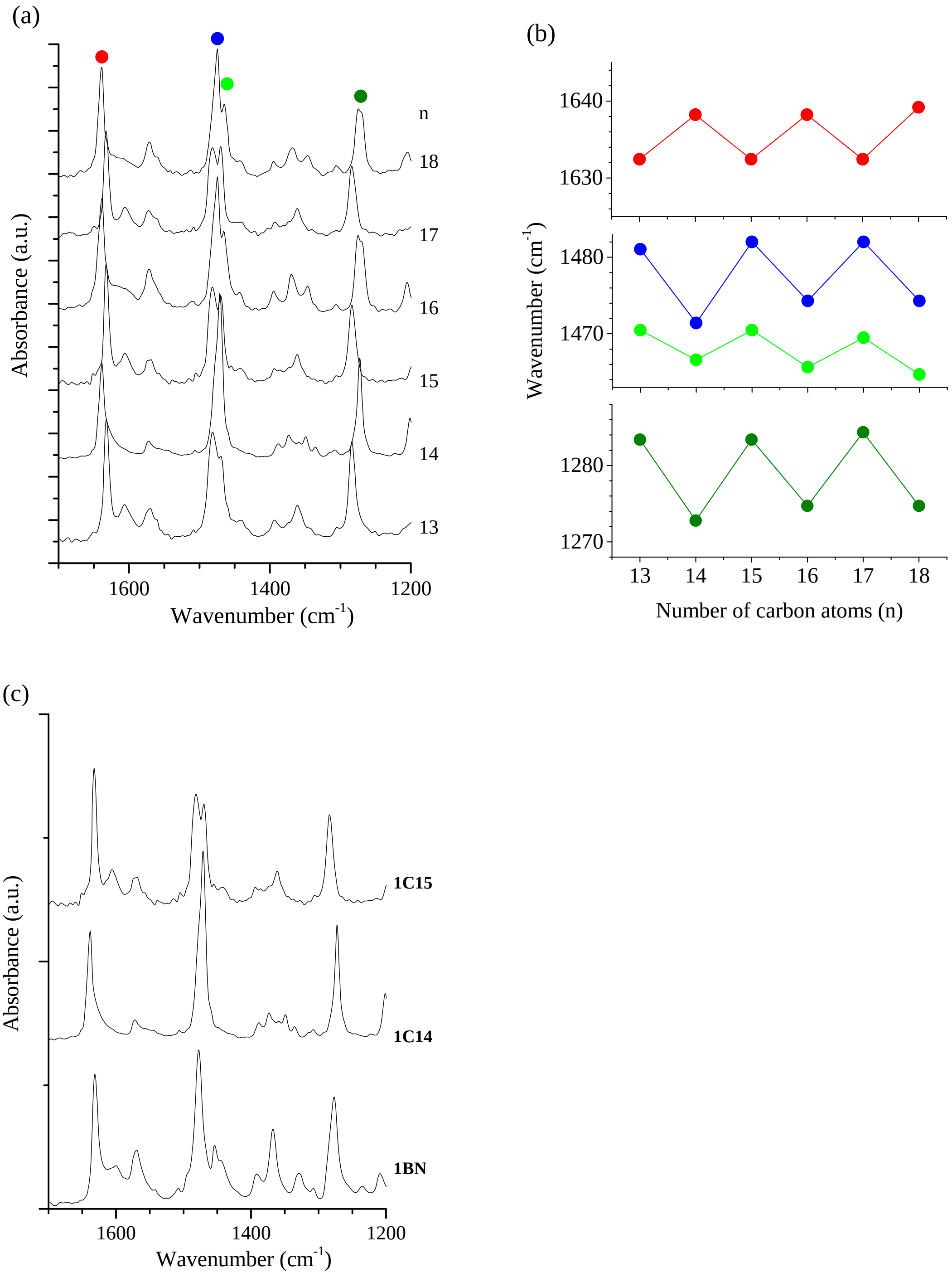

Figure S9 (a) Comparison of infrared spectra of **1Cn**. (b) Wavenumbers for some peaks indicated in (a). These peaks can be tentatively assigned to $\nu_{C=N}$ (1630–1640 cm^{-1}), $\nu_{C–C(aromatic)}$ (1460–1480 cm^{-1}), $\nu_{C–O}$ (1270–1290 cm^{-1}). (c) Infrared spectra of **1BN** compared with **1C14** and **1C15**.

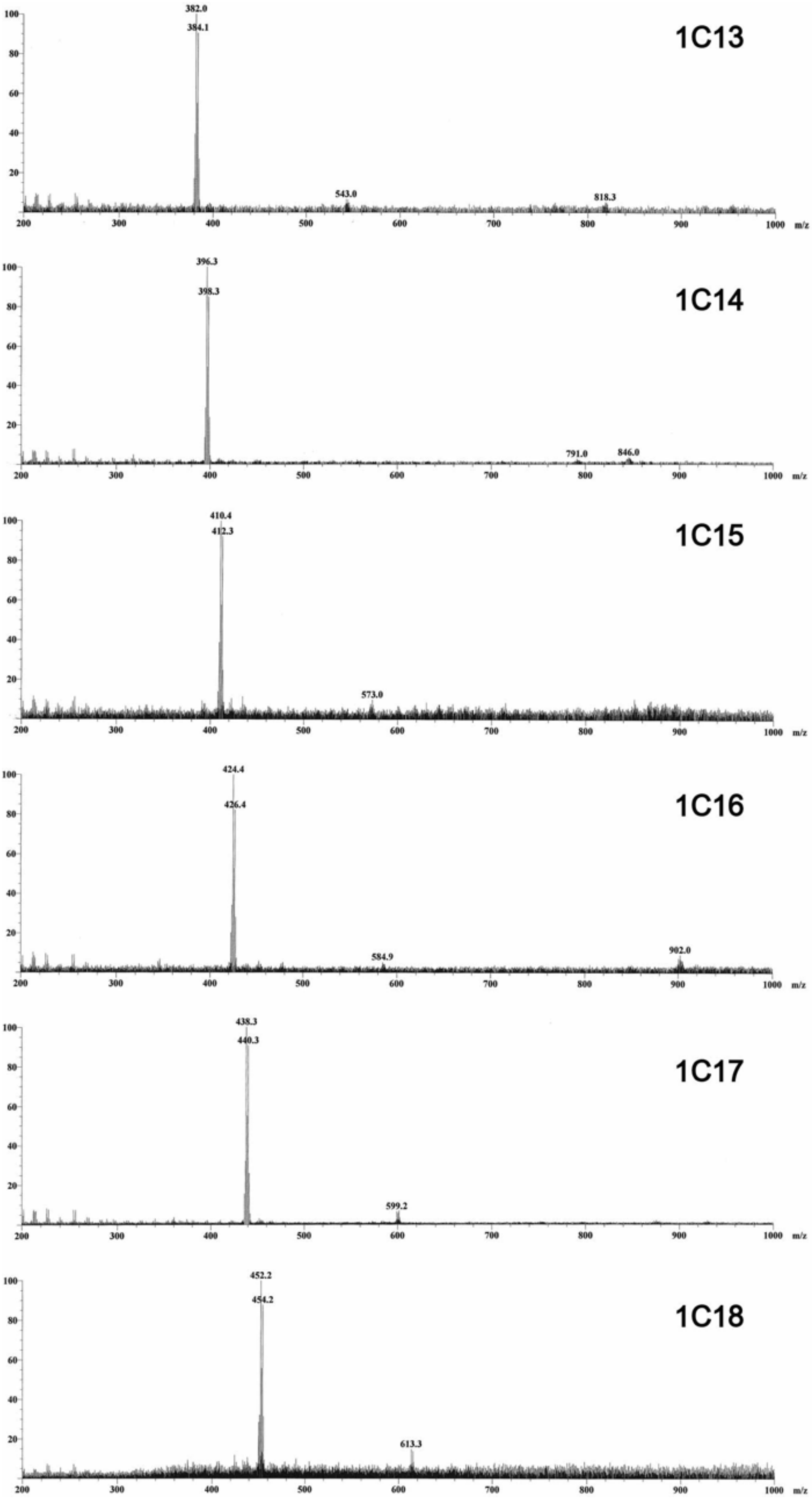

Figure S10 MS spectra of **1Cn** (n = 13–18).

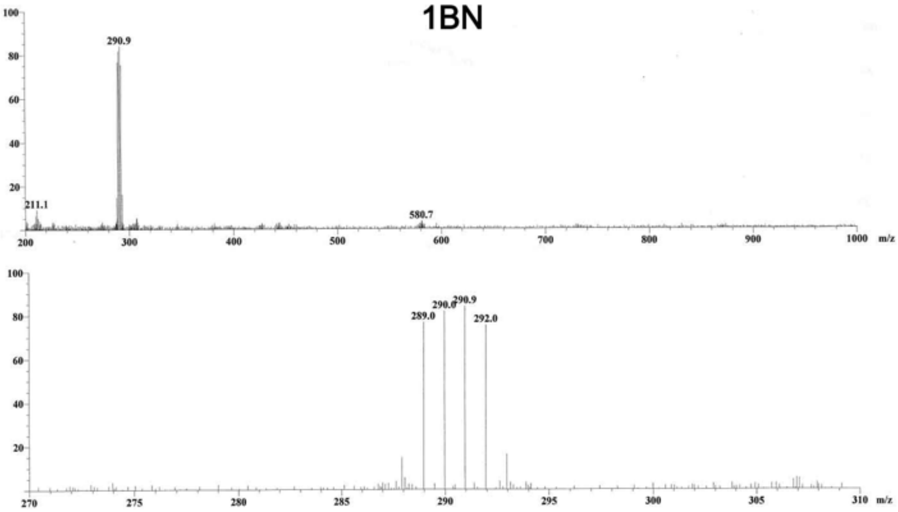

Figure S10 (continued) MS spectra of **1BN**.