Supplementary Information for

Crystal Melting and Glass Formation in Copper Thiocyanate based Coordination Polymers

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Experimental section

Materials. All reagents and chemicals were obtained from commercial sources, of reagent grade, and used without further purification. These ligands were newly synthesized according to the modified literature procedures.[1-4]

ESI-MS spectra were recorded on a Thermo Fisher Scientific EXACTIVE spectrometer. FT-IR were measured using a Nicolet ID5 ATR operating at ambient temperature between 4000 to 500 cm^{-1}.

Liquid state NMR: ^{1}H NMR spectra were obtained using JNM-ECS400 and JNM-ECZ500R spectrometers operating at 400 and 500 MHz, respectively. ^{13}C NMR spectra were obtained using JNM-ECS400 and JNM-ECZ500R spectrometers operating at 101 and 126 MHz, respectively.

Single crystal X-ray diffraction: Single crystal X-ray diffraction measurements were performed using a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF / VariMax rotating-anode X-ray generator with confocal monochromated Mo$K\alpha$ radiation. The structures were solved by a direct method (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97). The hydrogen atoms were positioned geometry and refined using a riding model. OLEX2 software was used to generate publication materials.[5]

X-ray powder diffraction (XRPD): XRPD patterns were collected on a Rigaku RINT 2000 Ultima diffractometer with CuK_α radiation. Variable temperature XRPD were recorded at Spring-8 synchrotron facility Japan, BL02B2 beamline on powder samples with heating rate of 10 °C min^{-1} in temperature range RT to 200 °C.

Thermal property measurements: Thermogravimetric analysis (TGA) was performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 25 °C and 500 °C in a N_2 atmosphere and at a heating rate of 10 °C min^{-1}. The differential scanning calorimetry (DSC) was carried out with Hitachi High-Tech Science Corporation model DSC7020 at the heating rate of 10 °C min^{-1} under a N_2 atmosphere using a sealed aluminum pan. The melting points and glass transition temperature was determined by using a software TA7000 Standard Analysis (Ver. 5.0).

X-ray absorption spectroscopy (XAS): The sample were prepared by mixing with appropriate amounts of boron nitride (BN) and pressed in to pellet. X-ray absorption spectra were collected at the Aichi Synchrotron Radiation Center (Aichi SR) on beamlines BL5S1. The data was processed using the IFEFFIT library.[6] Fourier transformation was k^3-weighted in the k range from 3-14 $Å^{-1}$. Cu foil internal energy

calibration was measured simultaneously with each sample. The energy was defined by assigning the first inflection point of the Cu foil spectrum to 8980.168 eV.

Solid state NMR: All the NMR experiments were carried out at ambient temperature (~25 °C) on a 600 MHz NMR spectrometer (JEOL JNM-ECZ600R) equipped with a 1 mm double resonance ultrafast MAS probe (JEOL RESONANCE Inc., Japan) at a magnetic field of 14.1 T. Approximately 1 mg of **1** and $\mathbf{1}_g$ are packed separately in zirconia rotors and MAS rate was set to 70 kHz. $^{1}H/^{13}C$ correlation spectra were measured by ^{1}H detected CP-HSQC experiments (Fig. S7a).[7] While a long contact time of 2 ms is used for the first CP transfer to maximize the ^{13}C magnetization, contact times of the second CP were reduced to 0.5-1 ms to selectively observe covalently ^{1}H-^{13}C pair. Thus no signal of quaternary carbons was observed. 10 kHz WALTZ heteronuclear decouplings were employed both for ^{1}H and ^{13}C decouplings during t_2 and t_1 evolution time, respectively. ^{1}H double quantum (DQ) / single quantum (SQ) correlation spectra were observed with BABA-xy16 DQ recoupling sequences (Fig. S7b).[8] ^{1}H-^{63}Cu RESPDOR[9] build up curve is observed with SR4 ^{1}H-^{63}Cu heteronuclear dipolar recoupling sequence,[10] irradiated on the ^{1}H channel. The ^{63}Cu magnetization was saturated by rotor synchronized phase-modulated saturation pulse[11] on the ^{63}Cu channel. The saturation pulse length of 657 μs was used.

Synthesis:

Ligands

Preparation of 4-ethyl-4, 4'-bipyridyl thiocyanate (C_2bpySCN):[1] 4,4'-bipyridine (9.00 g, 57.6 mmol) and bromoethane (4.28 ml, 57.7 mmol) were dissolved in acetonitrile (200 mL). The resulting solution was refluxed for 20 h and then evaporated. The crude product (13.1 g, 86%) and KSCN (4.78 g, 2.53 mmol) were dissolved in acetonitrile (250 mL). The resulting solution was stirred at 50 °C for 24 h and the formed precipitate was filtered and discarded. The filtrate was evaporated in vacuo and then C2bpySCN was obtained as pale yellow powder (9.62 g, 69%). ^{1}HNMR (400 MHz, DMSO-D6) δ 9.24 (d, J = 7.1 Hz, 2H), 8.86 (dd, J = 4.4, 1.6 Hz, 2H), 8.63 (d, J = 7.0 Hz, 2H), 8.03 (dd, J = 4.4, 1.6 Hz, 2H), 4.66 (q, J = 7.3 Hz, 2H), 1.58 ppm (t, J = 7.3 Hz, 3H); ^{13}CNMR (101 MHz, DMSO-D6) δ 152.75, 151.53, 145.67, 141.44, 130.07, 125.92, 122.46, 56.59, 16.85 ppm; IR (KBr) ν = 3025, 2051, 1644, 1600, 1549, 1531, 1497, 1470, 1440, 1412, 1362, 1227, 1184, 1092, 1080, 878, 870, 819, 737, 725, 706, 590, 561 cm^{-1}; HRMS-ESI (m/z): calcd for $[M-SCN]^+$ ($C_{12}H_{13}N_2$), 185.1073; found, 185.1069.

Preparation of 4-butyl-4, 4'-bipyridyl thiocyanate (C_4bpySCN):[2] This compound was prepared in 61% yield as pale yellow powder from the reaction of 4,4'-bipyridine, 1-bromobutane and KSCN according to a procedure similar to that described for C2bpySCN. ^{1}H NMR (400 MHz, DMSO-D6) δ 9.24 (d, J = 7.0 Hz, 2H), 8.85 (dd, J = 4.6, 1.6 Hz, 2H), 8.63 (d, J = 6.8 Hz, 2H), 8.04 (dd, J = 4.5, 1.7 Hz, 2H), 4.64 (t, J = 7.4 Hz, 2H), 1.90-1.97 (m, 2H), 1.32 (td, J = 15.0, 7.4 Hz, 2H), 0.92 ppm (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-D6) δ 152.24, 150.98, 145.29, 140.87, 129.53, 125.41, 121.93, 60.18, 32.64, 18.80, 13.35 ppm; IR (KBr) ν = 3028, 2957, 2053, 1644, 1548, 1532, 1464, 1412, 1226, 1181, 815, 751, 735, 718, 593, 566 cm^{-1}; ESI-MS: m/z = 213.1380 [C14H17N2$^+$], 57.9743 [SCN$^-$]. HRMS-ESI (m/z): calcd for $[M-SCN]^+$ ($C_{14}H_{17}N_2$), 213.1386; found, 213.1380.

Preparation of Zincke salt: This compound was synthesized according to the literature.[3] 4,4'-bipyridine (7.01 g, 44.9 mmol) and 2,4-dinitrochlorobenzene (6.05 g, 29.9 mmol) were dissolved in acetone (50 mL). The solution was refluxed for 13 h, during which time a pale gray precipitate formed. The precipitate was collected by filtration and washed several times with dichloromethane. The product was dried in vacuo to yield Zincke salt as a gray powder (7.14 g, 74%). ^{1}HNMR (500 MHz, D2O) δ 9.25 (d, J = 2.4 Hz, 1H), 9.10 (d, J = 6.7 Hz, 2H), 8.79 (dd, J = 8.5, 2.4 Hz, 1H), 8.69 (dd, J = 4.6, 1.5 Hz, 2H), 8.54 (d, J = 6.7 Hz, 2H), 8.12 (d, J = 8.5 Hz, 1H), 7.88 ppm (dd, J = 4.7, 1.7 Hz, 2H).

Preparation of 4-phenyl-4,4'-bipyridyl thiocyanate (PhbpySCN):[4] Zincke salt (1.44 g, 4.0 mmol) was dissolved with aniline (460 μL, 5.0 mmol) in ethanol (12 mL). The resulting solution was refluxed for 24 h and the formed precipitate was filtered and discarded. The filtrate was evaporated in vacuo and the crude product was refluxed with acetone (300 mL) for 2 h, filtered, and dried in vacuo to yield PhbpyCl as a very pale green powder (0.73 g, 55%). PhbpyCl (0.35 g, 1.3 mmol) and KSCN (0.13 g, 1.3 mmol) were dissolved in acetonitrile (100 mL). The resulting solution was stirred at 50 °C for 24 h and the formed precipitate was filtered and discarded. The filtrate was evaporated in vacuo and then PhbpySCN was obtained as yellow powder (0.30 g, 44%). ^{1}HNMR (400 MHz, DMSO-D6) δ 9.51 (dt, J = 7.2, 1.9 Hz, 2H), 8.90 (dd, J = 4.5, 1.7 Hz, 2H), 8.79 (dt, J = 7.1, 1.8 Hz, 2H), 8.15 (dd, J = 4.6, 1.6 Hz, 2H), 7.92-7.95 (m, 2H), 7.77 ppm (dd, J = 5.3, 1.8 Hz, 3H); ^{13}CNMR (126 MHz, DMSO-D6) δ 153.18, 151.10, 145.42, 142.31, 140.56, 131.31, 130.20, 129.50, 125.27, 124.77, 122.08 ppm; IR (KBr) *ν* = 3025, 2050, 1633, 1590, 1537, 1489, 1445, 1405, 1235, 1221, 870, 862, 847, 815, 761, 739, 720, 706, 688, 614, 574 cm^{-1}; HRMS-ESI (m/z): calcd for $[M-SCN]^+$ ($C_{16}H_{13}N_2$), 233.1067; found 233.1067.

Preparation of 3,1':4',4''-Terpyridinium thiocyanate (3-pybpySCN): This compound was newly prepared in 41% yield as a brown powder from the reaction of Zincke salt, 3-aminopyridine and KSCN according to a procedure similar to that described for PhbpySCN. ^{1}HNMR (400 MHz, DMSO-D6) δ 9.57 (d, J = 7.0 Hz, 2H), 9.13 (d, J = 2.6 Hz, 1H), 8.90-8.93 (m, 3H), 8.86 (d, J = 7.0 Hz, 2H), 8.42 (dq, J = 8.3, 1.4 Hz, 1H), 8.17 (dd, J = 4.4, 1.6 Hz, 2H), 7.83 ppm (dd, J = 8.2, 4.8 Hz, 1H); ^{13}CNMR (126 MHz, DMSO-D6) δ 153.64, 152.00, 151.13, 145.72, 145.54, 140.47, 138.95, 132.99, 129.51, 125.27, 124.54, 122.10 ppm; IR (KBr) *ν* = 3036, 2055, 1639, 1597, 1532, 1480, 1457, 1428, 1412, 1322, 1273, 1228, 1196, 1067, 1025, 1006, 993, 868, 853, 824, 805, 738, 728, 721, 707, 667, 630, 612, 576 cm^{-1}; HRMS-ESI (m/z): calcd for $[M-SCN]^+$ ($C_{15}H_{12}N_3$), 234.1026; found, 234.1020.

Coordination polymers

Synthesis of $[Cu_2(SCN)_3(C_2bpy)]$ (1), $[Cu_2(SCN)_3(C_4bpy)]$ (2) and $[Cu_8(SCN)_{12}(Phbpy)_4]$ (3): Copper (I) thiocyanate (CuSCN, 109 mg, 0.89 mmol) and C_2bpySCN (109 mg, 0.45 mmol) were added to THF (50 mL) in a 110 mL vessel. After the vessel was sealed, it was heated at 90 °C for 48 h. Crystalline powder samples thus produced were washed with THF (30 mL × 3) and the solvent was removed under vacuum at 70 °C. The same procedure was applied for **2** and **3**, using C_4bpySCN (122 mg, 0.45 mmol) and PhbpySCN (131 mg, 0.45 mmol) respectively instead of C_2bpySCN.

Syntheses of $[Cu(SCN)_2(3\text{-pybpy})]$ (4):

CuSCN (12 mg, 0.10 mmol), 3-pybpySCN (58 mg, 0.20 mmol), and KSCN (9.7 mg, 0.10 mmol) were added to THF (2 mL) in a 4 mL glass vessel. After the vessel was sealed, it was heated at 90 °C for 48 h. Crystalline powder samples thus produced were washed with THF (30 mL × 3) and the solvent was removed under vacuum at 70 °C.

CCDC reference numbers for CPs are 1899561 (**1**); 1899562 (**2**); 1899563 (**3**) and -1899564 (**4**).

Figures and Tables:

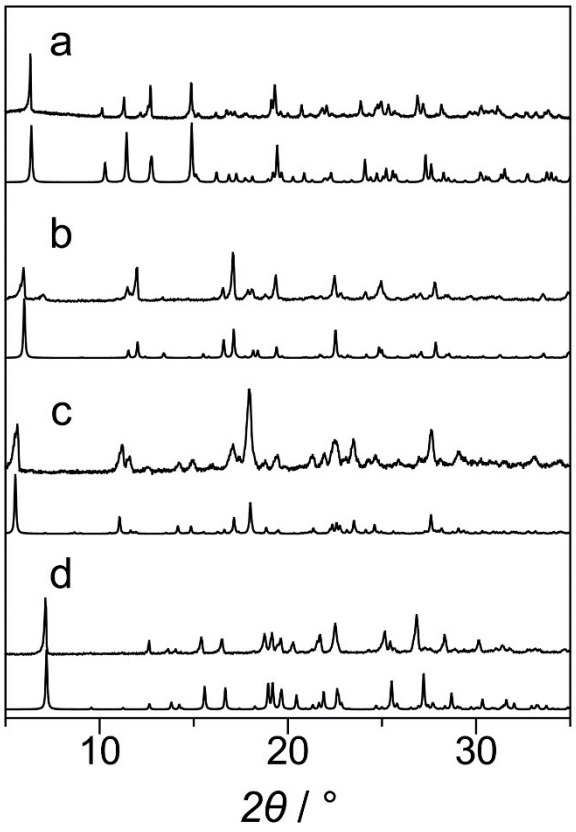

Figure S1. Simulated and As-synthesized X-ray Powder diffraction (XRPD) profiles of (a) **1**, (b) **2**, (c) **3** and (d) **4**.

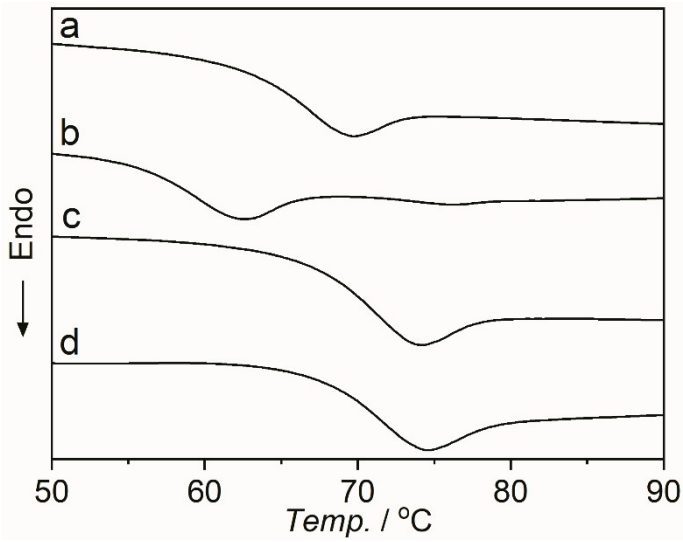

Figure S2. Second differential scanning calorimetry (DSC) heating up-scans of (a) **1**, (b) **2**, (c) **3** and (d) **4** under the N_2 atmosphere with heating rate of 10 °C min^{-1}.

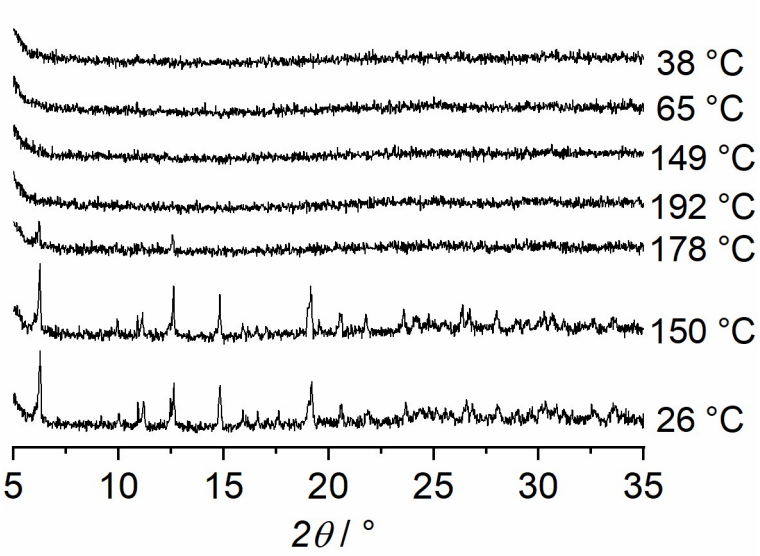

Figure S3. Variable temperature X-ray powder diffraction (XRPD) profiles of **1**. Sample was heated from 26 (from bottom) to 192 °C, and cooled to 38 °C (upper).

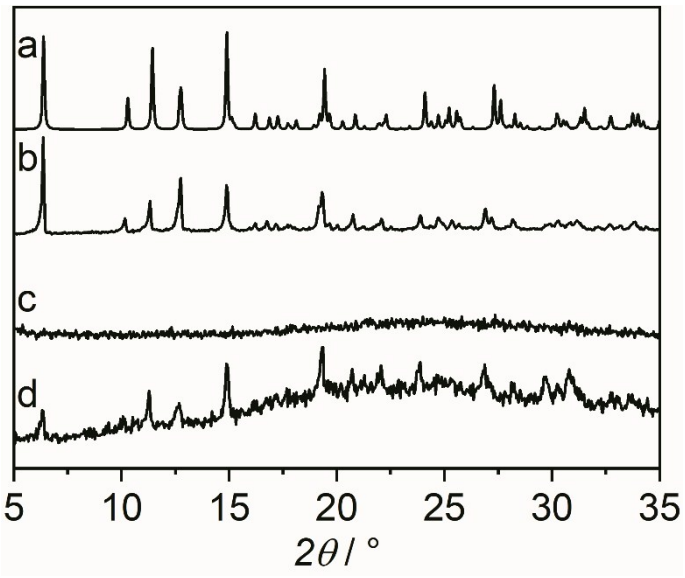

Figure S4. X-ray powder diffraction (XRPD) profiles of (a) Simulated (b) **1**, (c) $\mathbf{1}_g$ and (d) $\mathbf{1}_r$.

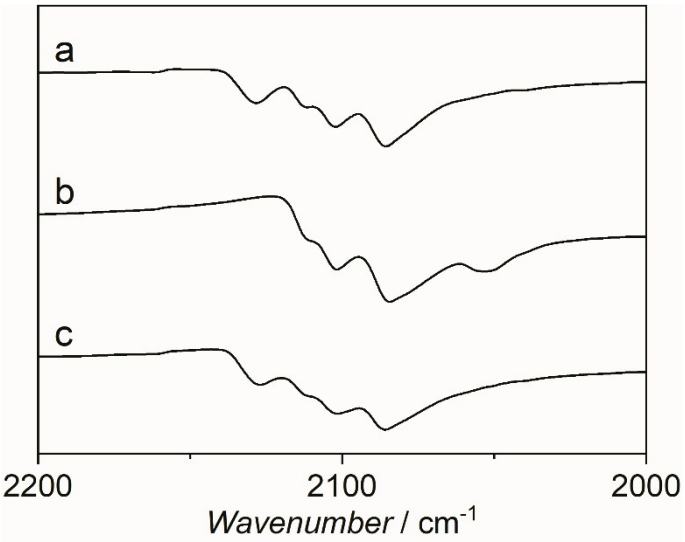

Figure S5. FT-IR spectra of (a) **1**, (b) $\mathbf{1}_g$ and (c) $\mathbf{1}_r$.

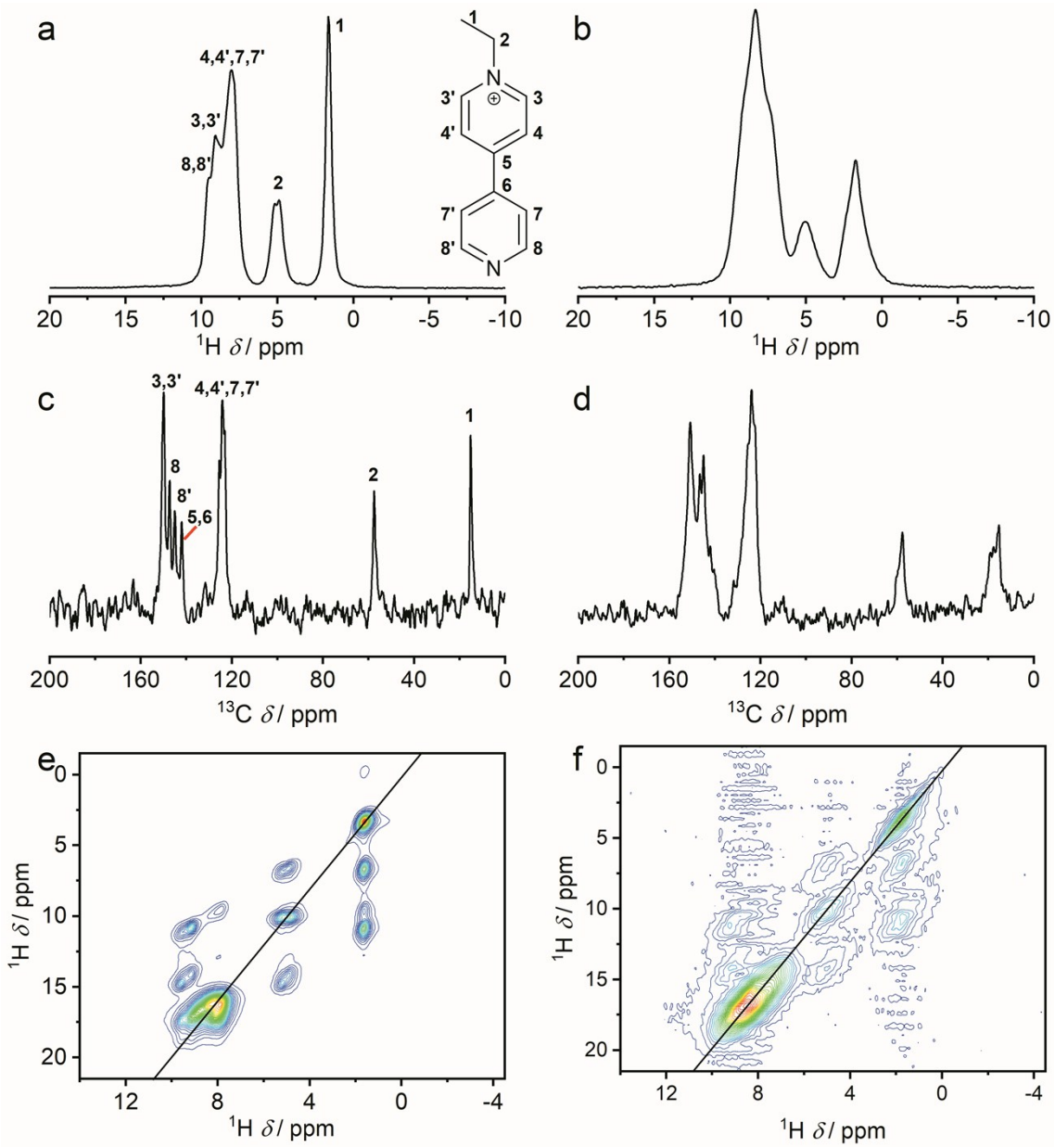

Figure S6. (a, b) ^{1}H spin echo, (c, d) ^{13}C CPMAS, and (e, f) 2D ^{1}H DQ/SQ correlation solid-state NMR spectra of **1** and $\mathbf{1}_g$.

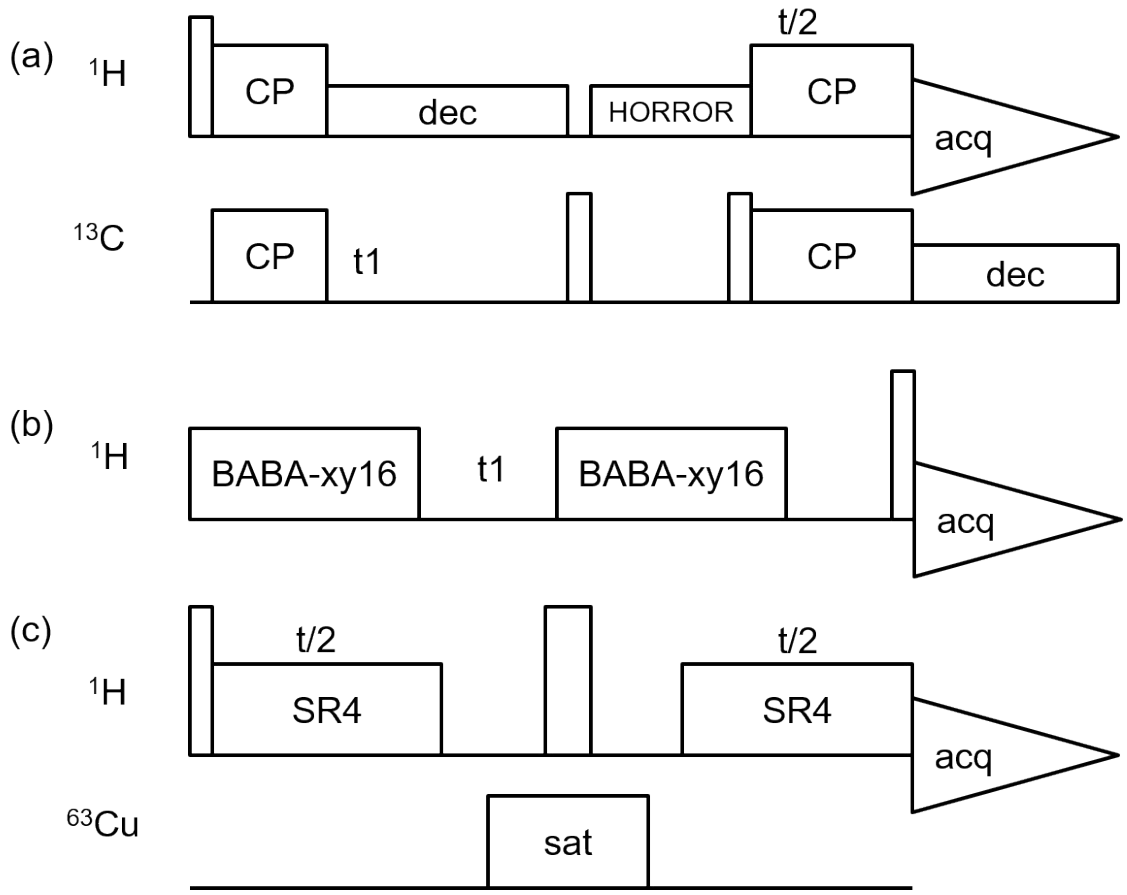

Figure S7. Pulse sequences used for (a) $^{1}H/^{13}C$ correlation, (b) ^{1}H DQ/SQ correlation and (c) ^{1}H-^{63}Cu RESPDOR experiments.

Table S1. Melting temperature (T_m), Glass transition (T_g), Enthalpy (ΔH_m) and Entropy (ΔS_m) of melting for CPs determined by DSC. Heating rates are 10 °C min^{-1}.

Entry	T_m / °C	T_g / °C	ΔH_f / kJ mol^{-1}	ΔS_f / J mol^{-1} K^{-1}
1	187	68	40	87
2	138	59	32	75
3	224	71	50	100
4	203	72	55	116

Table S2. ^1H T_1 relaxation time of **1** and $\mathbf{1}_g$. Saturation recovery method was used.

	Aromatic[a]	Methylene	Methyl
1	6.3 s	5.1 s	4.2 s
$\mathbf{1}_g$	5.3 s (monoexp.) 11 s, 0.9 s (biexp.)	4.8 s	2.8 s

[a] While the mono-exponential function fits well with the recovery curve of **1**, mono-exponential function gives poor fitting for $\mathbf{1}_g$. For better fitting, bi-exponential fitting was also applied on $\mathbf{1}_g$.

Table S3. ^1H T_2 relaxation time of **1** and $\mathbf{1}_g$. Spin echo method was used.

	Aromatic	Methylene	Methyl
1	1.3 – 1.8 s	1.3 s	2.5 s
$\mathbf{1}_g$	2 – 2.4 s	1.5 s	2.8 s

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