Electronic Supplementary Material (ESI) for Chemical Communications

Unexpected isotopic effect of deuteriumed countercation on the spin-Peierls-type transitions in quasi-one-dimensional bis-(maleonitriledithiolato)nickelate monoanion spin systems

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Experimental section

Chemicals and materials. All reagents and chemicals were purchased from commercial sources and used without further purification.

General Methods. The starting material, Na_2mnt, was prepared by means of the literature approach.[1] The compounds [X-BzPy-d_5]X and [X-BzPy-d_5]$_2$[Ni(mnt)$_2$] (X = Br or Cl) were synthesized utilizing a similar procedure for preparation of [X-BzPy]X and [X-BzPy]$_2$[Ni(mnt)$_2$] [2] instead of Py by Py-d_5.

Preparation of [Br-BzPy-d_5][Ni(mnt)$_2$] (Br-Py-d5). A methanol solution (10 cm^3) of I_2 (150mg, 0.59mmol) was slowly added to a methanol solution (20 cm^3) of [R-BzPy-d_5]$_2$[Ni(mnt)$_2$] (823 mg, 1.0 mmol), the mixture was stirred for 15 min and allowed to stand overnight, and then 500mg of black microcrystal was filtered off, wished with Methanol, and dried under vacuum. Yield: 85%. Anal. Calcd for $C_{20}H_6D_5N_5BrNiS_4$: C, 40.46; H and D, 1.87; N, 11.80. Found: C, 40.45; H and D, 2.03; N, 12.24.

Preparation of [Cl-BzPy-d_5][Ni(mnt)$_2$] (Cl-Py-d_5). The same procedure used for preparing **Br-Py-d5** was also used to synthesize **Cl-Py-d_5**. Yield: 86%. Anal. Calcd for $C_{20}H_6D_5N_5ClNiS_4$: C, 43.74; H and D, 2.02; N, 12.76. Found: C, 43.63; H and D, 2.07; N, 13.16.

The single crystals suitable for X-ray structure analyses were obtained by evaporation of the solutions of **Br-Py-d_5** or **Cl-Py-d_5** in MeCN at ambient temperature for 6-8 days.

Physical Measurements. Elemental analyses for C, H and N were performed with an Elementar Vario EL III analytic instrument. Vacuum IR spectra were recorded on a Bruker Vertex 80 Fourier Transform Infrared Spectrometer (KBr disc). Magnetization measurements were carried out with a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer, and the diamagnetic corrections of a sample for the constituent atoms were made with Pascal's constants. Differential

scanning calorimetry (DSC) were carried out on a Q2000 V24.9 Build 121 instrumental in the temperature range of -180 to 20 °C (93-293 K) with a rate of 20 °C·min^{-1}.

X-ray Crystallography. The crystal structures of **Br-Py-d$_5$** and **Cl-Py-d$_5$** were determined at 293 and 273 K in high-temperature phase, with a CCD area diffractometer, respectively. The structures were solved by direct method and refined on F^2 by the full matrix least-squares method using SHELXL-97 software packages.[3] All non-hydrogen atoms were refined anistropically. Hydrogen and deuterium atoms were placed in their calculated positions and only their coordinates were refined. Other details of crystal data collection and refinement for **Br-Py-d$_5$** and **Cl-Py-d$_5$** are listed in Table S1 and Table S2.

References

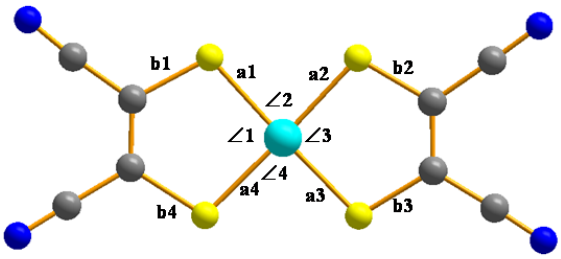
1. A. Davison, H. R. Holm, *Inorg. Synth.* 1967, **10**, 8-26.
2. X. M. Ren, Q. J. Meng, Y. Song, C. S. Lu, C. J. Hu, X. Y. Chen, *Inorg. Chem.* 2002, **41**, 5686-5692.
3. G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.

Table S1 Crystallographic data and refinement parameter for **Br-Py-d$_5$** and **Cl-Py-d$_5$** in HT-phase

compound	**Br-Py-d$_5$**	**Cl-Py-d$_5$**
Temperature (K)	293(2)	273(2)
Wavelength (Å)	0.71073	
Empirical formula	$C_{20}H_6D_5BrN_5NiS_4$	$C_{20}H_6D_5ClN_5NiS_4$
Formula weight	593.23	548.77
CCDC no.	808975	808974
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a (Å)	12.0244(17)	12.0783(13)
b (Å)	26.253(4)	26.163(3)
c (Å)	7.4047(10)	7.3540(8)
α (°)	90.00	90.00
β (°)	102.646(3)	102.526(2)
γ (°)	90.00	90.00
V (Å^3)/Z	2280.8(5)/4	2268.6(4)/4
ρ (g·cm^{-1})	1.728	1.607
F(000)	1172	1100
Abs. coeff. (mm^{-1})	2.987	1.360
θ Ranges (data collection °)	1.90- 25.99	1.89- 26.00
Index ranges	-11 ≤ h ≤ 14 -30 ≤ k ≤ 32 -8 ≤ l ≤ 9	-12 ≤ h ≤ 14 -32 ≤ k ≤ 32 -9≤ l ≤ 9
R_{int}	0.1290	0.1047
Reflections measured	12169	12081
Independent reflections/restraints/parameters	4458/0/317	4438/0/281
Refinement method	The least square refinement on F^2	
Goodness of fit on F^2	1.006	1.067
R_1, wR_2[a] [$I>2\sigma$(I)]	0.0715, 0.1626	0.0516, 0.1277
R_1, wR_2[a] [all data]	0.0931, 0.1722	0.0595, 0.1320
Residual (e·nm^{-3})	1.345/-1.130	0.633/-0.602

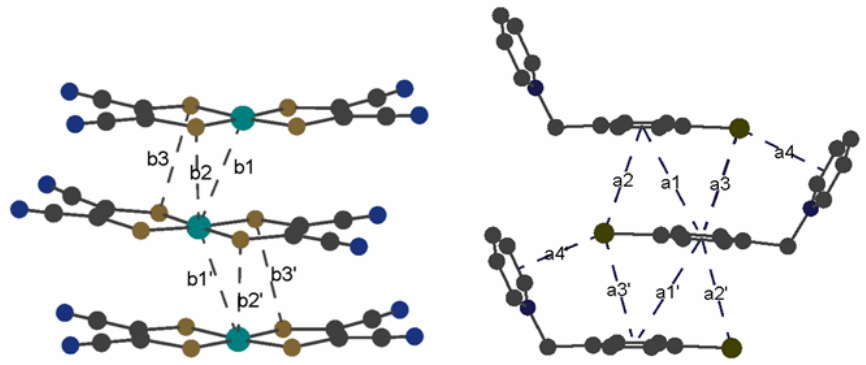
[a] $R_1 = \sum||F_o| - |F_c||/|F_o|$, $wR_2 = [\sum w(\sum F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2 Characteristic bond lengths and angles in $[Ni(mnt)_2]^-$ moiety of **Br-Py-d$_5$**, **Br-Py**, **Cl-Py-d$_5$** and **Cl-Py** at room temperature.



	Br-Py-d$_5$	**Br-Py**	**Cl-Py-d$_5$**	**Cl-Py**
∠1	92.44(6)	92.426(90)	92.46(3)	92.173(45)
∠2	85.94(6)	85.865(90)	89.31(3)	89.403(45)
∠3	92.09(6)	92.111(89)	92.24(3)	92.372(46)
∠4	89.48(6)	89.570(89)	85.96(3)	86.015(46)
a1	2.1274(16)	2.1518(23)	2.1338(9)	2.1447（11）
a2	2.1316(15)	2.1483(22)	2.1353(9)	2.1509（12）
a3	2.1344(15)	2.1409(23)	2.1386(9)	2.1395（12）
a4	2.1420(15)	2.1403(23)	2.1481(9)	2.1391（12）
b1	1.701(5)	1.7541(78)	1.713(3)	1.7063（40）
b2	1.707(5)	1.7029(82)	1.720(3)	1.7253（41）
b3	1.726(6)	1.7208(78)	1.705(3)	1.7122（40）
b4	1.715(6)	1.7049(81)	1.711(3)	1.7165（41）

Table S3 R···π interactions between substituent X (Br or Cl) atoms and phenyl/pyridyl rings for **Br-Py-d$_5$**, **Br-Py**, **Cl-Py-d$_5$** and **Cl-Py** at room temperature



distance/Å	**Br-Py-d$_5$**	**Br-Py**	**Cl-Py-d$_5$**	**Cl-Py**
a1	4.2613(5)	4.2817(13)	4.1233(4)	4.1334(9)
a1’	4.2613(5)	4.2817(13)	4.1233(4)	4.1334(9)
a2	3.8076(9)	3.8321(18)	3.7935(12)	3.8070(18)
a2’	3.8076(9)	3.8321(18)	3.7935(12)	3.8070(18)
a3	3.9537(9)	3.9656(19)	3.9727(12)	3.9823(18)
a3’	3.9537(9)	3.9656(19)	3.9727(12)	3.9823(18)
a4	3.4522(9)	3.4703(12)	3.3946(11)	3.4020(8)
a4’	3.4522(9)	3.4703(12)	3.3946(11)	3.4020(8)
b1	3.9071(12)	3.9267(21)	3.9020(7)	3.9131(14)
b1’	3.9071(12)	3.9267(21)	3.9020(7)	3.9131(14)
b2	4.4648(17)	4.2999(30)	4.4232(11)	3.6291(19)
b2’	4.4648(17)	4.2999(30)	4.4232(11)	3.6291(19)
b3	3.9142(22)	4.0536(35)	3.8990(13)	4.0677(21)
b3’	3.9142(22)	4.0536(35)	3.8990(13)	4.0677(21)

Table S4 IR Data and assignments for **Br-Py-d$_5$**, **Br-Py**, **Cl-Py-d$_5$** and **Cl-Py**

Br-Py-d$_5$	**Br-Py**	**Cl-Py-d$_5$**	**Cl-Py**	assignment	reference
	3126.0m		3128.3m		
3095.1w*	3097.0sh	3097.5w	3097.5sh		
3081.6w	3083.6m	3085.1w	3084.4m	ν_{C-H} in	
3046.9w	3066.2m	3051.6w	3066.0m	phenyl or	3-7
3027.6w	3029.6sh	3028.1w	3030.7w	pyridyl ring	
3000.6w	3002.5w	3001.8w	3001.2w		
2971.7w	2971.7w	2972.9w	2967.7w		
2917.7w	2923.5w	2920.5w	2926.6w	ν_{C-H} in	
2900.4w	2892.6w	2902.1w	2893.0w	-CH_2-	
	2854.0w	2857.6w	2855.6w		
2215.7sh	2215.8sh	2215.7sh			
2205.2vs	2202.3vs	2204.1vs	2204.4vs	ν_{CN} of C≡N	8
2186.9sh	2186.9sh	2152.4sh	2153.9sh		
1645.3w	1667.4w	1643.1w	1669.0w		
1623.1w	1652.0sh				
1602.5w	1628.7s	1582.9vs	1630.6vs		
1583.2s	1603.9w	1549.6m	1592.9w		
1550.5m	1583.0w		1581.5w		
1482.9m	1497.4m	1485.8m			
1463.0s	1480.8s	1462.1s			
1406.0s	1451.7s	1404.2s	1453.9s		
1370.4s	1403.0s	1370.1s	1407.1s		
1331.6w	1342.5w	1335.3w	1345.1w		
1316.4w	1320.3w	1318.8w	1318.4w		
1296.8w	1294.2m	1298.8w	1298.8w		
1272.1m	1273.4m	1279.3m	1278.9m		
1155.4s	1155.4s	1154.1s	1158.4vs	ν_{C-C} + ν_{C-S} in anion	8
1114.8s	1104.7m	1117.4s	1108.1s		
1101.9m	1095.1sh	1103.4m		π_{C-CN} in anion	8
1070.1m	1070.7m	1090.8m	1090.6s	ν_{C-C} + ν_{C-S} in anion	8
1012.1s	1015.1w	1015.8s	1015.8s		
985.2m	1009.9m	984.7m	976.2w		
886.5m	887.5m	885.6m	885.5m	ν_{C-H} in anion	8
867.0m	852.9s	865.6m	855.4s		
850.3s		851.9s			

840.4s		842.5s	
800.7s	821.2s	806.1s	826.4s
782.2s	786.7vs	783.0s	792.1vs
752.4s	761.1vs	754.7s	764.1vs
705.4w	710.5vs	711.6w	718.6vs
669.6m	676.9vs	668.9m	678.7vs
659.6m			655.3m
612.0s	631.1s	627.3m	
563.9s	577.0s	568.5s	587.0s
532.2vs	530.4w	531.7vs	530.7w
516.9w	516.9w	515.0w	517.4w
501.8s	500.9s	500.6s	501.6s
473.4s	473.4s	482.1s	488.0s

*Abbreviations: vs, very strong; s, strong; m, medium; w, weak and sh, shoulder. ν, stretching; δ, in-plane bending; γ, out-of-plane bending.

References

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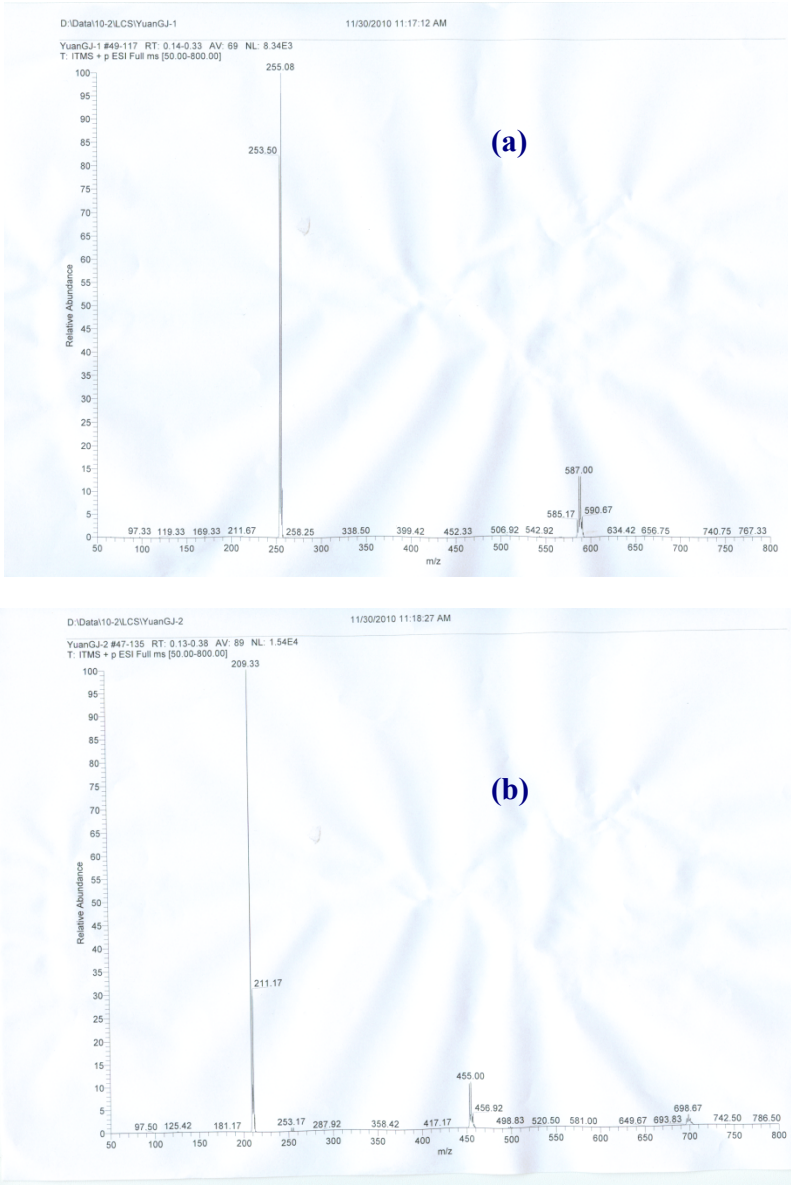

Figure S1. Electric spray ionization mass spectra of (a) (4-Br-BzPy-d_5)Br and (b) [4-Cl-BzPy-d_5]Cl. The peaks assignments: M/Z = 253.50, 255.08 correspond to 4-Br-BzPy-d_5^+ and the peaks at M/Z = 585.17, 587.00, 590.67 contribute from $[(4\text{-Br-BzPy-}d_5)_2\text{Br}]^+$ for the compound (4-Br-BzPy-d_5)Br; M/Z = 209.33, 211.17 correspond to 4-Cl-BzPy-d_5^+ and the peaks at M/Z = 455.00, 456.92 contribute from $[(4\text{-Cl-BzPy-}d_5)_2\text{Cl}]^+$ for the compound (4-Cl-BzPy-d_5)Cl.

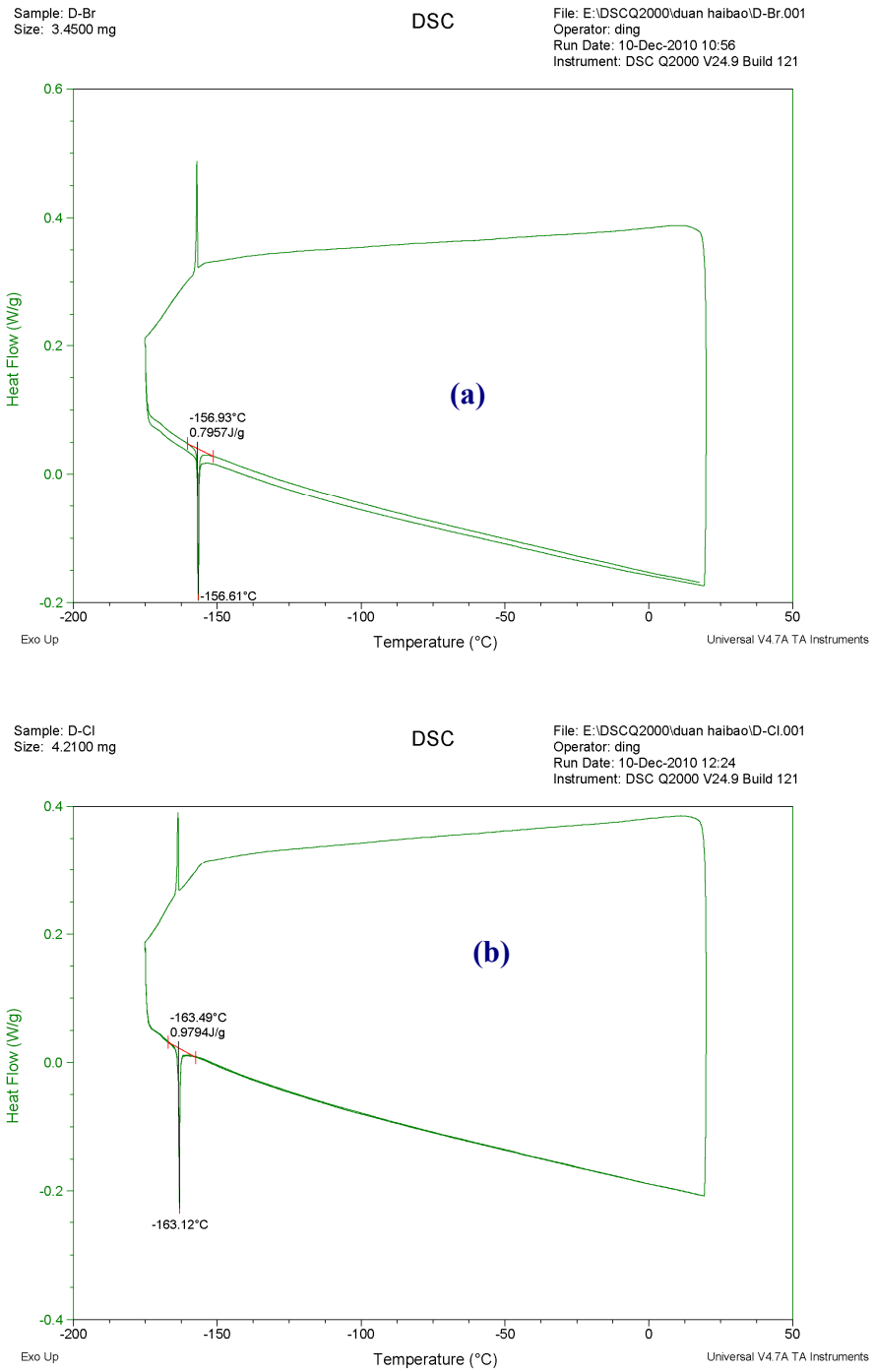

Figure S2. DSC plots for (a) **1** and (b) **2** in the -180 to 20 °C (93-293 K)) range.

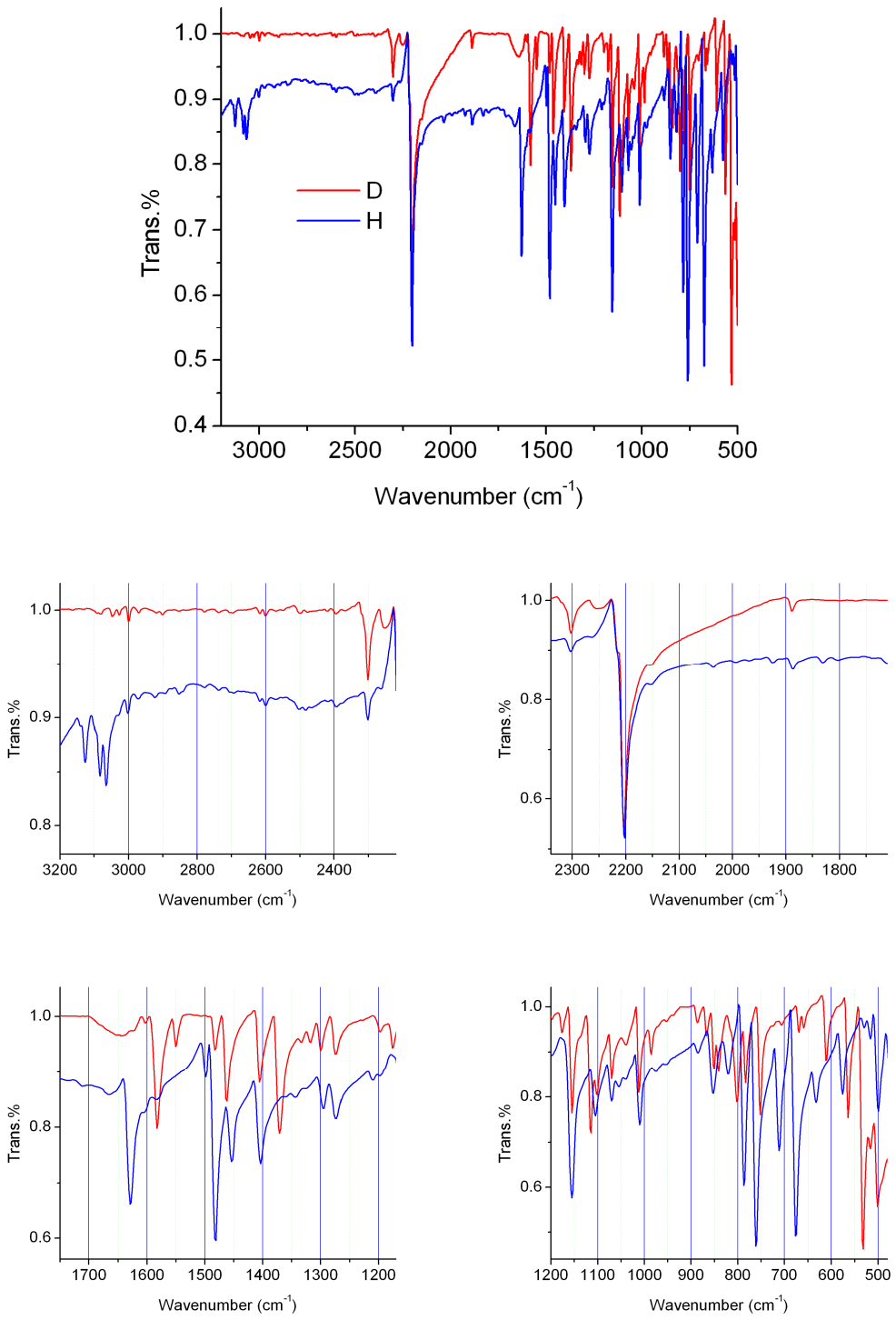

Figure S3. Infrared spectra of **Br-Py-d$_5$** and **Br-Py** (three bands centered at 3083.6, 3066.2 and 3029.6 cm^{-1} in **Br-Py** attributed to $\nu_{C\text{-}H}$ of pyridyl or phenyl rings, the relative

intensities of these bands becomes weaker in the IR spectrum of **Br-Py-d6** since the hydrogen atoms in pyridyl ring were substituted by deuterium atoms; the relative intensity of the vibration band centered at ca. 2300 cm^{-1} in **Br-Py** become stronger in the **Br-Py-d6**, and the band can be assigned to the contributions from both ν_{C-H} of $-CH_2-$ and ν_{C-D} of -py-d5; and the reference: J. Chem. Phys. 1953, 21, 1170; J. Mol. Spectroscopy 1984, 104, 129).

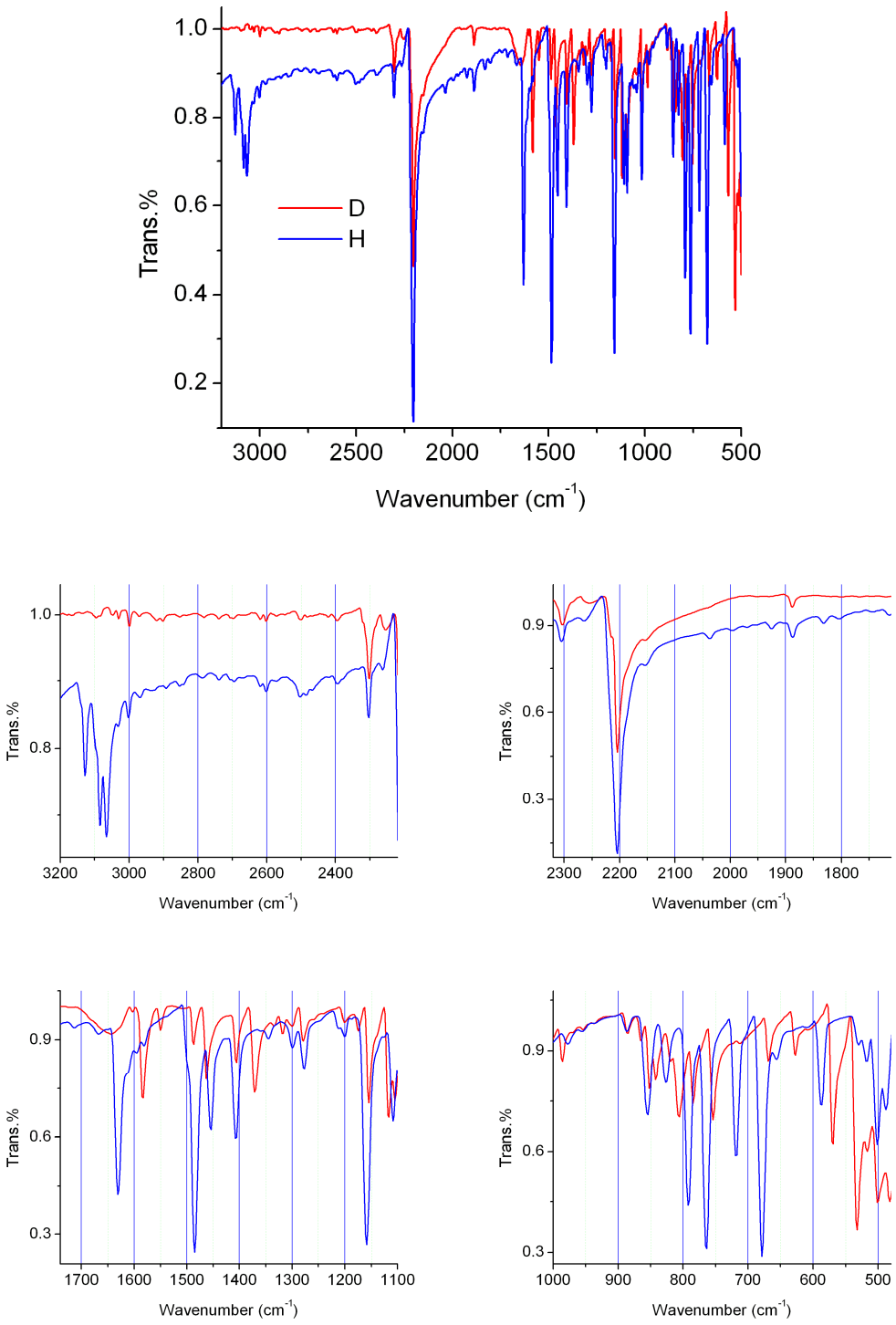

Figure S4. Infrared spectra of **Cl-Py-d$_5$** and **Cl-Py** (three bands centered at 3097.5, 3084.4 and 3066.0 cm^{-1} in **Cl-Py** attributed to $\nu_{C\text{-}H}$ of pyridyl or phenyl rings, the relative

intensities of these bands becomes weaker in the IR spectrum of **Cl-Py-d6** since the hydrogen atoms in pyridyl ring were substituted by deuterium atoms; the relative intensity of the vibration band centered at ca. 2300 cm^{-1} in **Cl-Py** become stronger in the **Cl-Py-d6**, and the band can be assigned to the contributions from both ν_{C-H} of $-CH_2-$ and ν_{C-D} of -py-d5; and the reference: J. Chem. Phys. 1953, 21, 1170; J. Mol. Spectroscopy 1984, 104, 129).

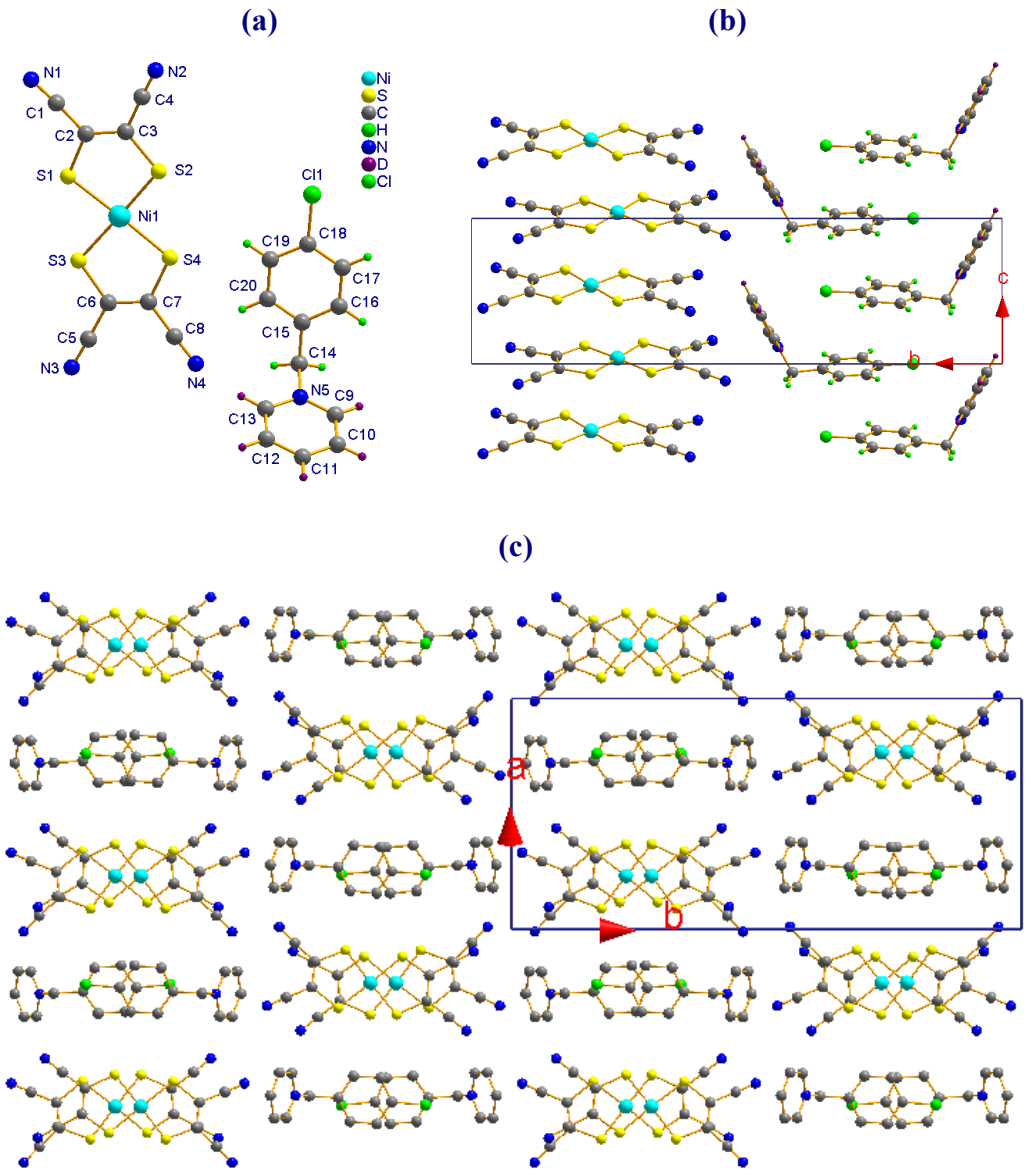

Figure S5. (a) Molecular structure with non-hydrogen atom labeling (b) and (c) pack diagrams viewed along crystallographic a-axis and c-axis for **Cl-Py-d$_5$** in HT-phase, respectively, which show the segregated stacks of anions and cations.