

## Supporting information for

# Design and Characterization of Fe(II) Complexes with Tetradentate Ligands Exhibiting Spin-Crossover Near Room Temperature

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## Experimental Section

### General

All reagents obtained from commercial sources were used without further purification. Safety Note: Perchlorate salts are potentially explosive, and caution should be taken when dealing with such materials.

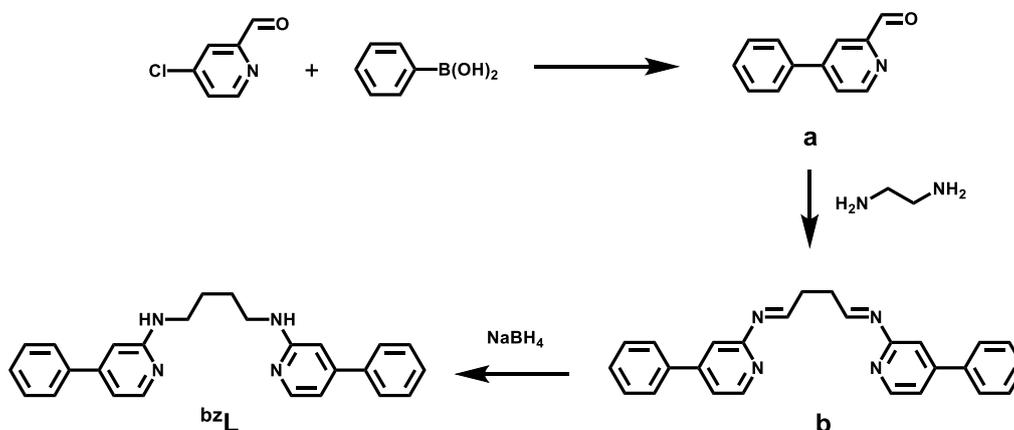
### Physical characterization

**Magnetic susceptibility measurements** were recorded with a Quantum Design PPMS-9, operating with an applied field of 1000 Oe between 10 and 300 K for  $\alpha$ -form, and between 10 and 380 K for  $\beta$ -form, in both cooling and heating modes at a temperature scan rate of 2 K min<sup>-1</sup>. **Elemental analyses** were performed using an Elementar Vario EL Elemental Analyser. **IR spectra** were recorded by the attenuated-total-reflectance (ATR) technique in the range of 4000–525 cm<sup>-1</sup> with THERMO FISHER NICOLET IS20. **DSC** measurements were performed on NETZSCH DSC 300 instrument under a nitrogen atmosphere at a scan rate of 10 K min<sup>-1</sup> in both heating and cooling modes. **PXRD** patterns were recorded on a D8 ADVANCE X-ray diffractometer (CuK $\alpha$  radiation,  $\lambda = 0.154056$  nm). **TG** curves were recorded on a Mettler-Toledo TGA / SDTA851<sup>o</sup> thermoanalyzer by filling the sample into alumina crucibles under a Ar atmosphere within the temperature range of 30–800 °C at a heating rate of 10 K min<sup>-1</sup>. Room temperature **<sup>1</sup>H NMR** spectra were recorded on Bruker AVANCE III 500MHz.

**Single crystal X-ray diffraction.** Single-crystal X-ray data were collected on a Bruker D8 Quest diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A multi-scan absorption correction was performed (SADABS, Bruker, 2016). The structures were solved using direct method (SHELXS) and refined by full-matrix least-squares on  $F^2$  using SHELXL<sup>1</sup> under the graphical user interface of Olex2<sup>2</sup>. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. CCDC 2333208-2333211 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Synthetic Procedures.

### Synthesis of *N,N'*-bis(4-Phenyl-2-pyridylmethyl)ethane-1,2-diamine (<sup>bz</sup>L).



**Scheme S1.** Synthesis of *N,N'*-bis(4-Phenyl-2-pyridylmethyl)ethane-1,2-diamine (<sup>bz</sup>L).

**4-Phenyl-2-pyridinecarboxaldehyde (a).** A solution of 1,4-dioxane and H<sub>2</sub>O (4:1, 100 mL) was degassed with N<sub>2</sub> for 10 min. Under N<sub>2</sub>, 4-chloropicolinaldehyde (1.415 g, 10 mmol), K<sub>2</sub>CO<sub>3</sub> (1.656 g, 12 mmol), phenylboronic acid (1.463 g, 12 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.365 g, 0.5 mmol) were combined in the solution and stirred at 25 °C for 1 h, then heated at 110 °C for 24 h. The solution was filtered through Celite and washed with MeOH until the washings went colorless. The solution was then reduced to dryness by rotary evaporation yielding a black solid, which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×30 mL). Combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum to get crude residues as brown solid. The crude residues were purified by silica gel column chromatography (ethyl acetate/petroleum ether (15:1)) to afford the product as a white powder (Yield: 0.933 g, 51%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51 (dq, *J* = 7.1, 14.3 Hz, 3H), 7.70 (d, *J* = 7.0 Hz, 2H), 7.75 (dd, *J* = 1.8, 5.0 Hz, 1H), 8.21 (s, 1H), 8.84 (d, *J* = 5.1 Hz, 1H), 10.15 (s, 1H).

***N,N'*-Bis(4-Phenyl-2-pyridinylmethylene)ethanediamine (b).** A solution of **a** (0.4 g, 2.18 mmol), and 1,2-ethanediamine (0.065 g, 1.08 mmol) in MeOH (80 mL) was heated at reflux for 24 h with stirring. The solution was reduced to dryness by rotary evaporation and washed with MeCN, filtered to obtain the filter residue as yellow solid in 70% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) δ 8.66 (d, *J* = 5.2 Hz, 2H), 8.50 (s, 2H), 8.23 (s, 2H), 7.69 (d, *J* = 7.4 Hz, 4H), 7.53 (d, *J* = 6.3 Hz, 2H), 7.47 (dt, *J* = 13.0, 7.0 Hz, 6H), 4.12 (s, 4H).

***N,N'*-bis(4-Phenyl-2-pyridylmethyl)ethane-1,2-diamine (<sup>bz</sup>L).** A solution of **b** (0.294g, 0.752mmol) in MeOH (30ml) was cooled to 0 °C, NaBH<sub>4</sub> (0.142 g, 3.753 mmol) was then added slowly to the cooled solution and the mixture was stirred for a further 24 hours. The solution was then reduced to dryness by rotary evaporation yielding a

white solid, which was dissolved in water (50 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (3×30 mL). Combined organic phase was dried over  $\text{Na}_2\text{SO}_4$  and evaporated under vacuum to get yellow liquid in 92% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 8.58 (d,  $J = 5.1$ , 2H), 7.62 – 7.65 (m, 4H), 7.56 (s, 2H), 7.45 (dt,  $J = 7.0, 14.1$ , 6H), 7.38 (dd,  $J = 1.7, 5.2$ , 2H), 4.01 (s, 4H),  $\delta = 2.91$  (s, 4H),

**Synthesis of  $[\text{Fe}(\text{b}^z\text{L})(\text{NCSe})_2]$ .** Because of the air-sensitivity of Fe(II) and the  $\text{b}^z\text{L}$  ligand, the synthesis of the complex was carried out under a nitrogen atmosphere. Two different crystals ( $\alpha$ ,  $\beta$ ) were prepared under different conditions.

**Selective Synthesis of  $\alpha$ -form (single crystals).** The synthesis of the complex was carried out at – 6 to 6 °C.  $[\text{Fe}(\text{SeCN})_2]$  was prepared in situ by reacting an Fe(II) salt with a thiocyanate anion. A solution of  $\text{KSeCN}$  (0.026 g, 0.2 mmol) in MeOH (5 mL) was added to a MeOH (5 mL) solution containing  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.036 g, 0.1 mmol) and a small amount of ascorbic acid (0.03 g) as a reducing agent. The solution was stirred for 10 min and the resulting white precipitate ( $\text{KClO}_4$ ) was filtered. The colorless solution of  $[\text{Fe}(\text{SeCN})_2]$  was mixed with a solution of  $\text{b}^z\text{L}$  (0.040 g, 0.1 mmol) in MeOH (8 mL), and the color of the solution changed to yellow. The resulting reaction mixture was stirred for 2 min, then transfer to glass bottles (3 mL), yellow massive crystals precipitated out after 12 h in 48% yield. Elemental analyses. Calcd: C, 50.93; H, 3.97; N, 12.73. Found: C, 50.12; H, 4.02; N, 12.39.

**Selective Synthesis of  $\beta$ -form (single crystals).** The colorless solution of  $[\text{Fe}(\text{SeCN})_2]$  was mixed with a solution of  $\text{b}^z\text{L}$  (0.040 g, 0.1 mmol) in MeOH (8 mL), and the color of the solution changed to yellow. The resulting reaction mixture was stirred for 3 min, and the yellow precipitate was recrystallization from hot MeOH/DMF (40:1, 82 mL) gave yellow needle-like hollow crystals in 54% yield. Elemental analyses. Calcd: C, 50.93; H, 3.97; N, 12.73. Found: C, 50.01; H, 3.94; N, 12.46.

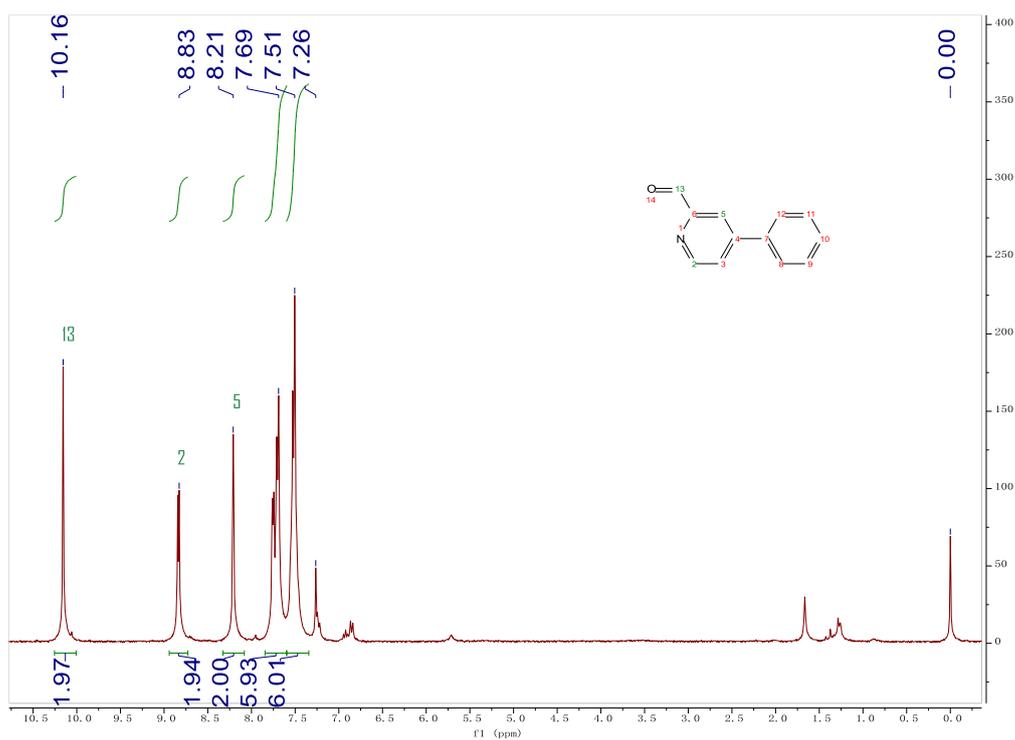


Figure S1.  $^1\text{H}$  NMR spectrum of 4-Phenyl-2-pyridinecarboxaldehyde (**a**) in  $\text{CDCl}_3$  (500 MHz, room temperature).

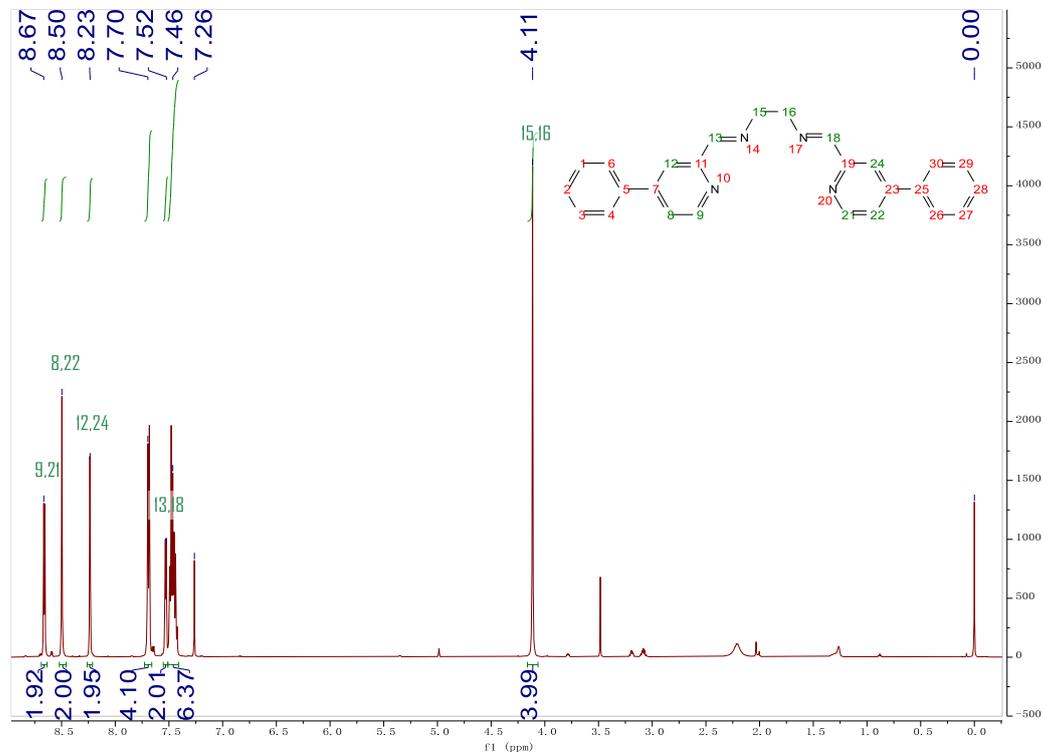
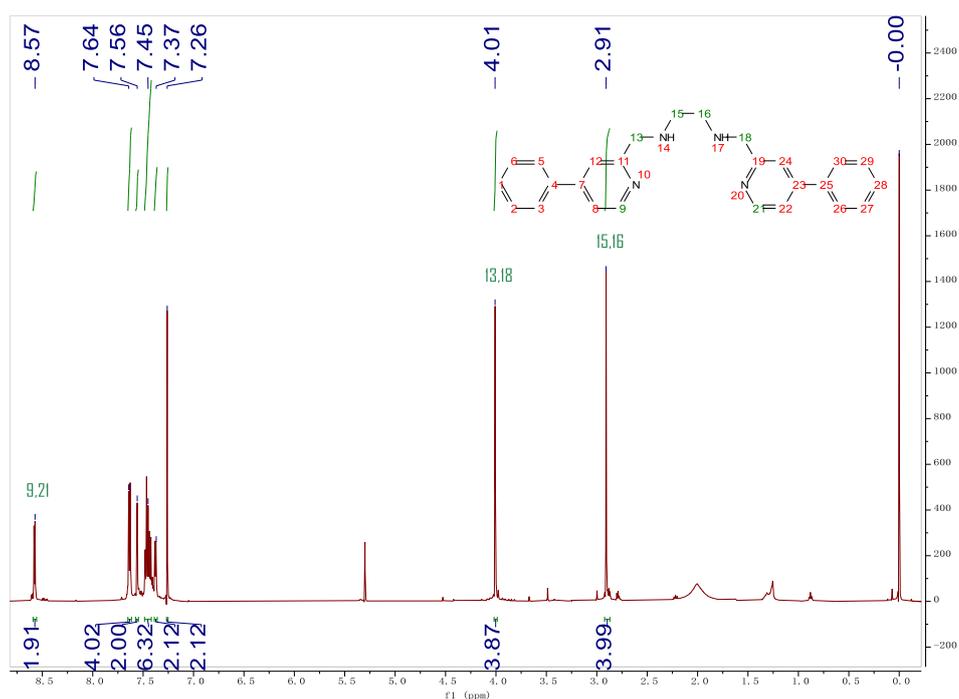
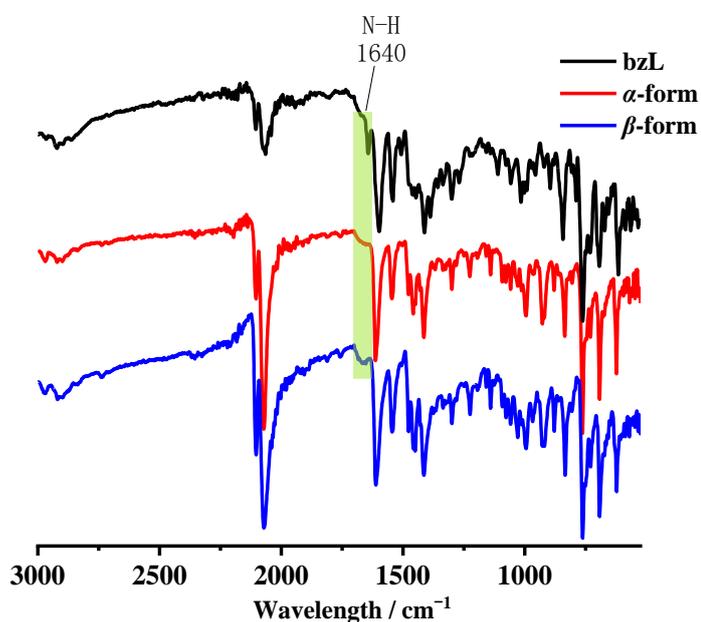


Figure S2.  $^1\text{H}$  NMR spectrum of *N,N'*-Bis(4-phenyl-2-pyridinylmethylene)ethanediamine (**b**) in  $\text{CDCl}_3$  (500 MHz, room temperature).



**Figure S3.**  $^1\text{H}$  NMR spectrum of *N,N'*-bis(4-Phenyl-2-pyridylmethyl)ethane-1,2-diamine (**bzL**) in  $\text{CDCl}_3$  (500 MHz, room temperature).



**Figure S4.** IR spectra for  $\alpha$  form (blue),  $\beta$  form (orange) and **bzL** (black) in the region of  $3500\text{--}525\text{ cm}^{-1}$  at room temperature. The IR spectra of the two polymorphs was found to be similar. The disappearance of the characteristic spectral bands of N-H ( $1640\text{ cm}^{-1}$ ) is due to the involvement of coordination.

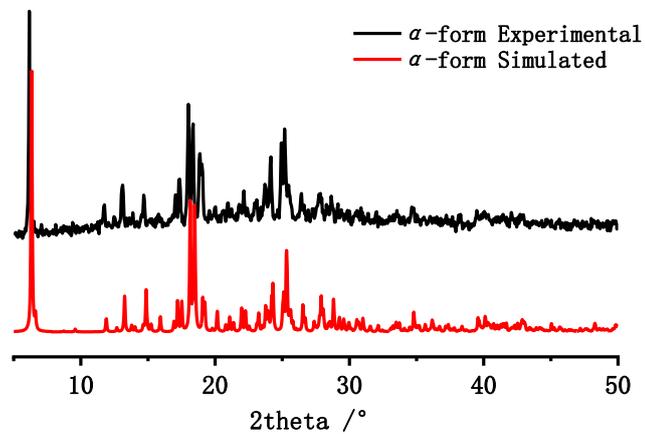


Figure S5. Experimental and simulated PXR D patterns of  $\alpha$ -form.

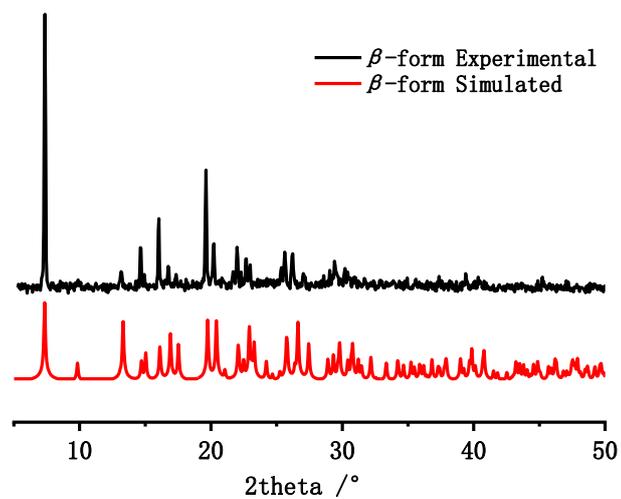
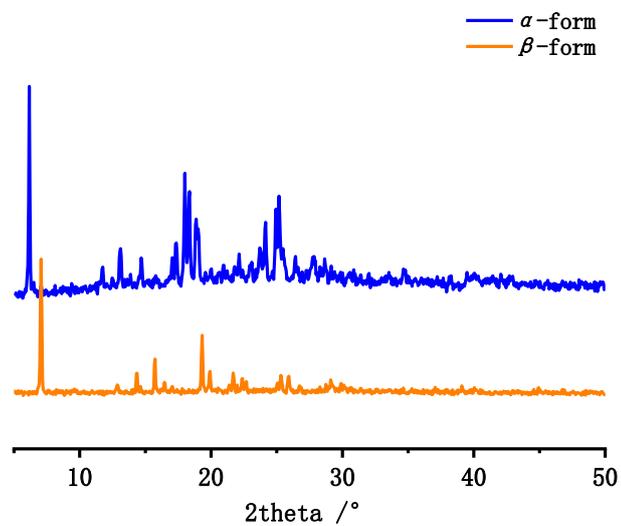
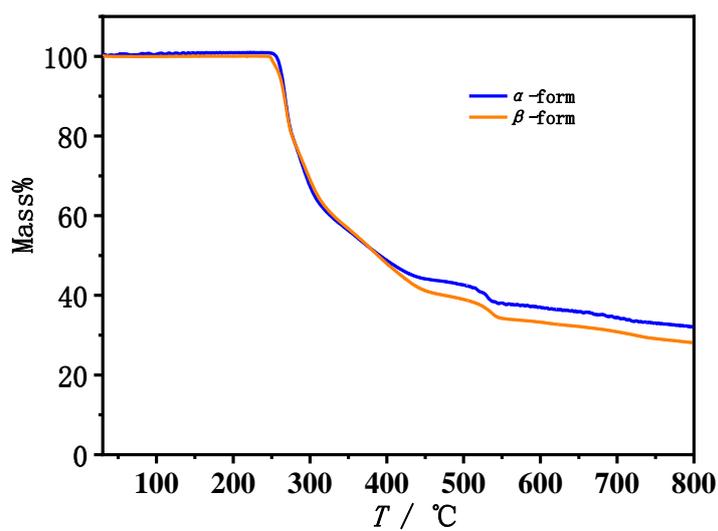


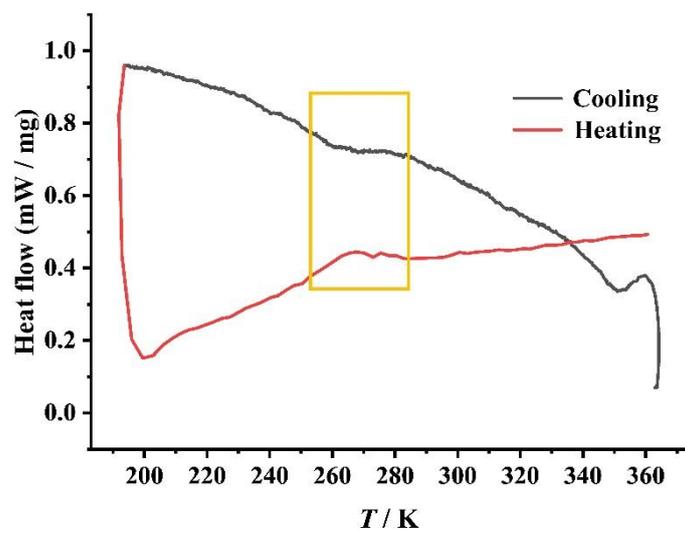
Figure S6. Experimental and simulated PXR D patterns of  $\beta$ -form.



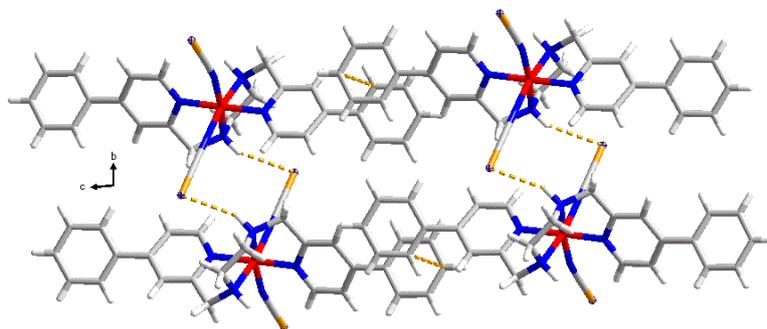
**Figure S7.** Experimental PXRD patterns of  $\alpha$ - (blue) and  $\beta$ - (orange) forms.



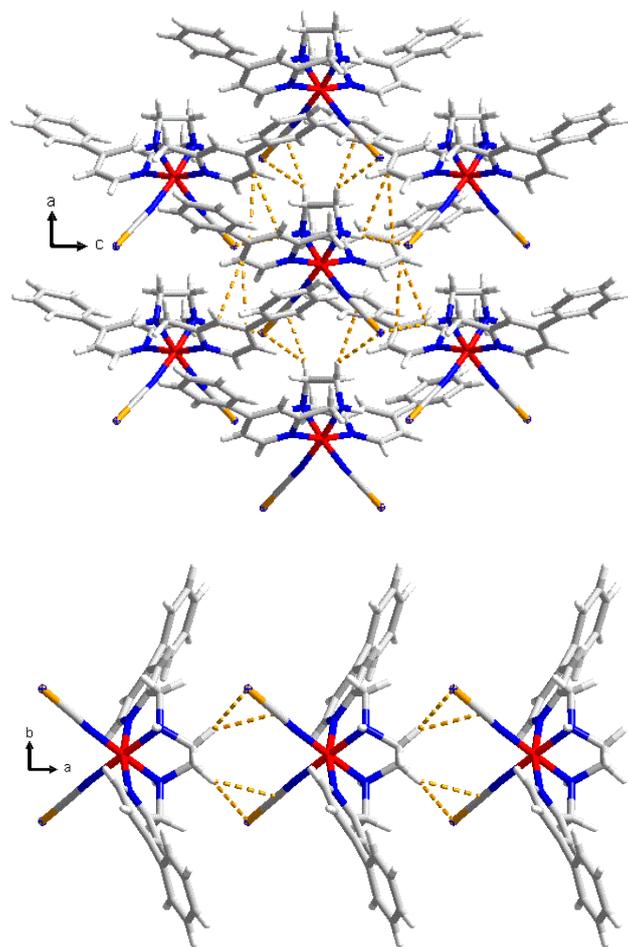
**Figure S8.** Thermogravimetric analysis (TGA) curves for  $\alpha$  (blue) and  $\beta$  (orange) forms from 30 to 800 °C at a 10 K min<sup>-1</sup> temperature rate under Ar atmosphere. The thermal weight loss performance of the two polymorphs was found to be similar.



**Figure S9.** DSC curves of  $\beta$ -form. An inconspicuous peak of second-order transitions<sup>3</sup> was observed near 270 K.



**Figure S10.** Packing between *bc* layers for  $\alpha$ -form at 123 K.



**Figure S11.** Packing between *ac* (above) and *ab* (below) layers for  $\beta$ -form at 123 K.

## Crystal data and refinement details

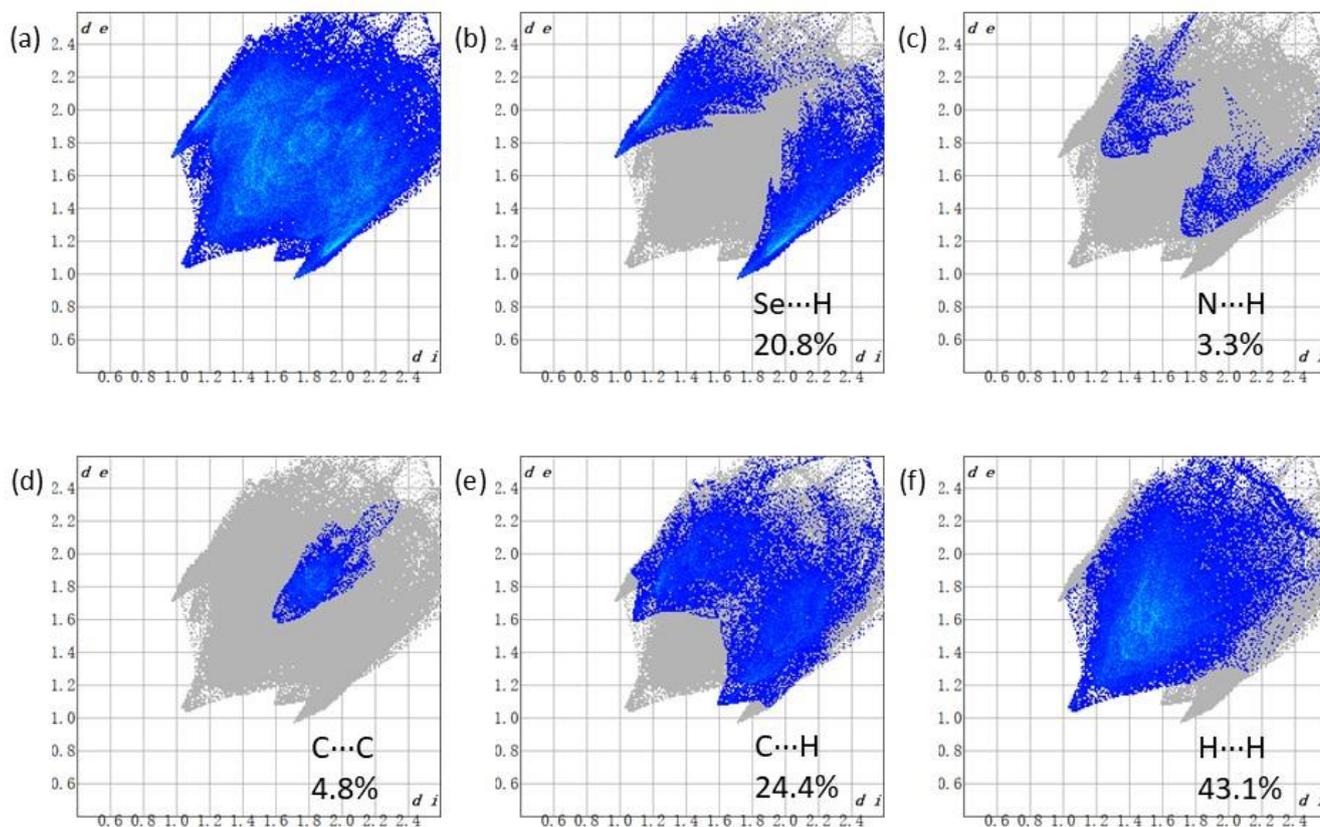
**Table S1.** Crystal data and refinement details for  $\alpha$  and  $\beta$  forms, respectively.

	$\alpha$		$\beta$	
CCDC number	2333209	2333208	2333211	2333210
Temperature / K	123	298	123	298
Empirical formula	$C_{28}H_{26}FeN_6Se_2$		$C_{28}H_{26}FeN_6Se_2$	
Formula weight	660.32		660.32	
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Aea2$	$Aea2$
$a / \text{\AA}$	7.2699(4)	7.4622(3)	13.5008(18)	13.6833(12)
$b / \text{\AA}$	13.4476(7)	13.4258(6)	24.067(3)	24.3553(19)
$c / \text{\AA}$	13.6246(7)	14.0208(5)	8.0492(11)	8.2423(7)
$\alpha / ^\circ$	94.7632(15)	95.0903(12)	90	90
$\beta / ^\circ$	93.6896(15)	92.7699(12)	90	90
$\gamma / ^\circ$	93.9047(16)	93.8097(12)	90	90
Volume / $\text{\AA}^3$	1321.01(12)	1393.98(10)	2615.4(6)	2746.8(4)
$Z$	2	2	4	4
$\rho_{\text{calc}} / \text{mg mm}^{-3}$	1.660	1.573	1.677	1.597
$\mu / \text{mm}^{-1}$	3.356	3.18	3.39	3.228
$F(000)$	660.0	660	1320	1320
Reflections collected	20202	16961	12765	13504
Independent reflections	6059	6257	2935	3130
$R_{\text{int}}$	0.0261	0.0255	0.0356	0.0554
Goodness-of-fit on $F^2$	1.024	1.033	1.044	1.010
Final $R$ indexes <sup>a</sup>	$R_1 = 0.0223$	$R_1 = 0.0390$	$R_1 = 0.0272$	$R_1 = 0.0409$
$[I \geq 2\sigma(I)]$	$wR_2 = 0.0527$	$wR_2 = 0.0803$	$wR_2 = 0.0477$	$wR_2 = 0.0596$
Final $R$ indexes [all data]	$R_1 = 0.0267$	$R_1 = 0.0634$	$R_1 = 0.0364$	$R_1 = 0.0919$
	$wR_2 = 0.0545$	$wR_2 = 0.0882$	$wR_2 = 0.0496$	$wR_2 = 0.0648$
Largest diff. peak/hole / $e\text{\AA}^{-3}$	0.35/-0.45	0.71/-0.85	0.46/-0.41	0.34/-0.28
Flack parameter	Null	Null	0.032(13)	0.034(17)

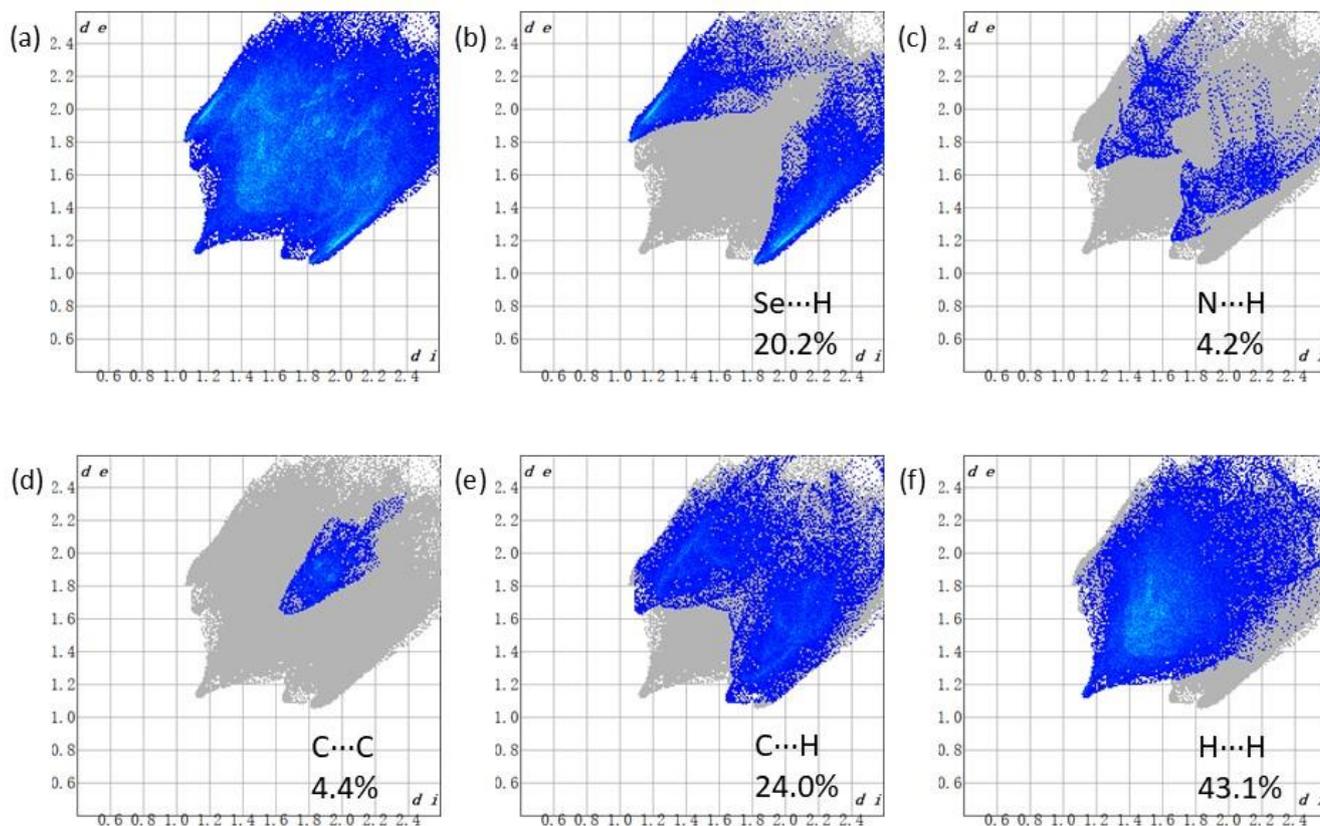
**Table S2.** Selected bond lengths and structural parameters for  $\alpha$  and  $\beta$  forms, respectively.

	$\alpha$		$\beta$	
$T / \text{K}$	123	298	123	298
Spin state	LS	HS	LS	HS
Fe-N <sub>Ncx</sub> / $\text{\AA}$	1.9567(15)	2.113(3)	1.943(2)	2.0820(15)
Fe-N <sub>pyridine</sub> / $\text{\AA}$	1.9797(14)	2.187(2)	1.980(2)	2.1869(14)
Fe-N <sub>amine</sub> / $\text{\AA}$	2.0231(14)	2.234(2)	2.002(2)	2.2660(14)
Fe-N <sub>average</sub> / $\text{\AA}$	1.98	2.17	1.97	2.17
$\Sigma \text{Fe} / ^\circ$	52.0(2)	85.4(3)	43.0(4)	79.8(2)
$\theta$	113.6(5)	189.5(7)	68.4(6)	220.4(5)
N-C-E / $^\circ$	177.84(18)	179.7(3)	178.4(2)	178.06(17)
Fe-N-C <sub>NCE</sub> / $^\circ$	168.97(14)	165.7(2)	173.6(2)	164.87(15)

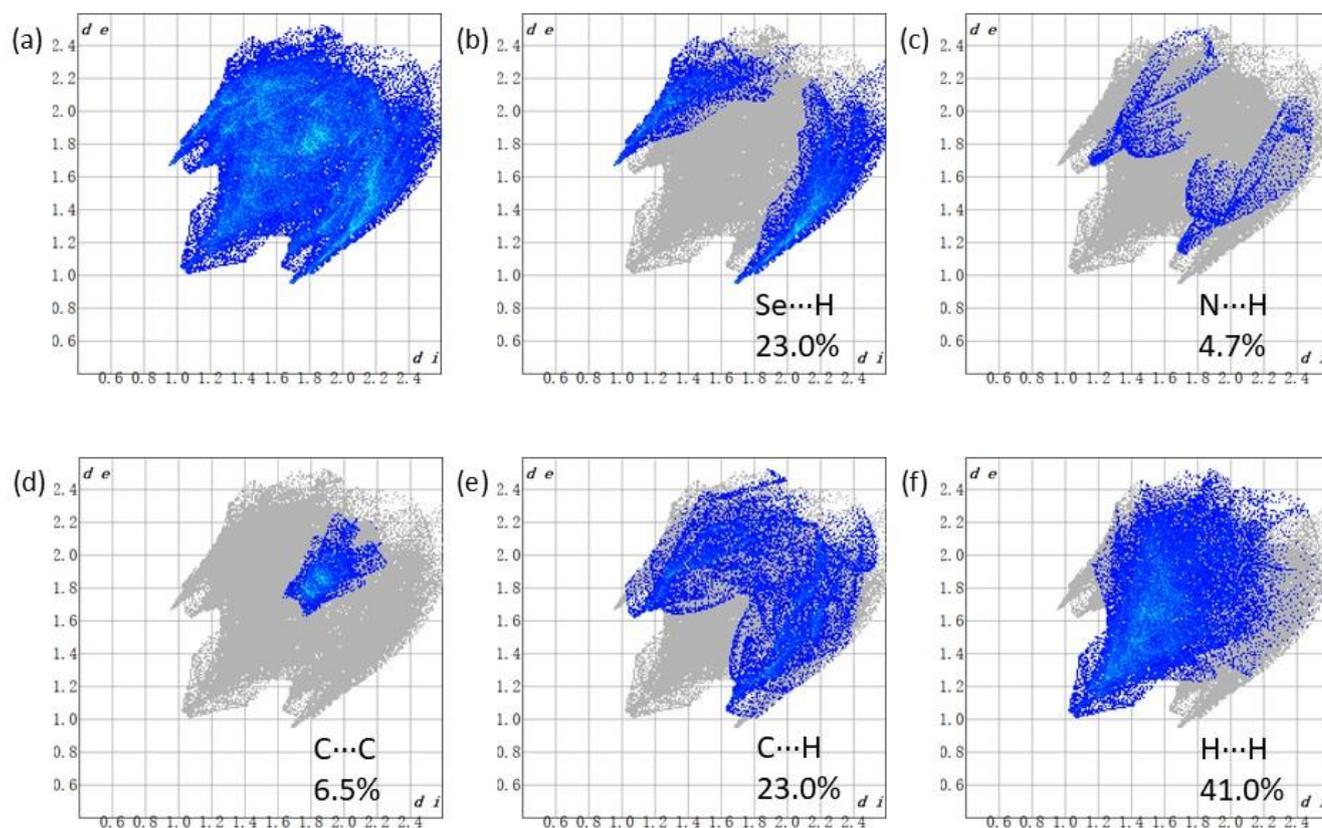
## Hirshfeld surface analysis of $\alpha$ and $\beta$ forms



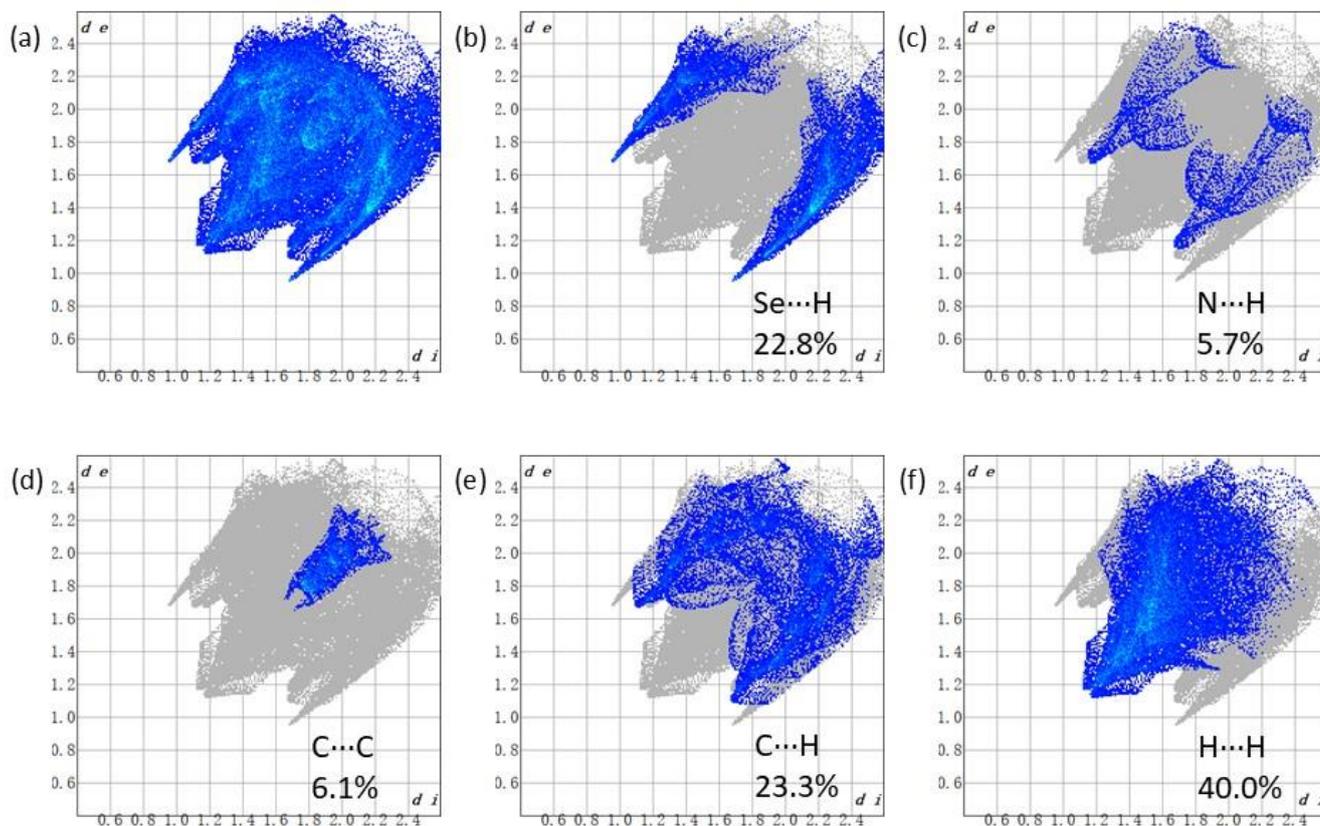
**Figure S12.** (a) Hirshfeld surface model and ball-and-stick morphology of  $\alpha$ -form at 123 K. Contribution of each type of interactions (b)  $\text{Se}\cdots\text{H}$ , (c)  $\text{N}\cdots\text{H}$ , (d)  $\text{C}\cdots\text{C}$ , (e)  $\text{C}\cdots\text{H}$ , (f)  $\text{H}\cdots\text{H}$ , derived from the fingerprint plot. The outline of the full fingerprint contribution is shown in gray.



**Figure S13.** (a) Hirshfeld surface model and ball-and-stick morphology of  $\alpha$ -form at 298 K. Contribution of each type of interactions (b) Se...H, (c) N...H, (d) C...C, (e) C...H, (f) H...H, derived from the fingerprint plot. The outline of the full fingerprint contribution is shown in gray.



**Figure S14.** (a) Hirshfeld surface model and ball-and-stick morphology of  $\beta$ -form at 123 K. Contribution of each type of interactions (b)  $\text{Se}\cdots\text{H}$ , (c)  $\text{N}\cdots\text{H}$ , (d)  $\text{C}\cdots\text{C}$ , (e)  $\text{C}\cdots\text{H}$ , (f)  $\text{H}\cdots\text{H}$ , derived from the fingerprint plot. The outline of the full fingerprint contribution is shown in gray.



**Figure S15.** (a) Hirshfeld surface model and ball-and-stick morphology of  $\beta$ -form at 298 K. Contribution of each type of interactions (b) Se...H, (c) N...H, (d) C...C, (e) C...H, (f) H...H, derived from the fingerprint plot. The outline of the full fingerprint contribution is shown in gray.

## References

1. G. M. Sheldrick, *Acta Crystallographica Section A: Foundations of Crystallography*, 2008, **64**, 112-122.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *Journal of applied crystallography*, 2009, **42**, 339-341.
3. C. Leyva-Porras, P. Cruz-Alcantar, V. Espinosa-Solís, E. Martínez-Guerra, C. I. Piñón-Balderrama, I. Compean Martínez and M. Z. Saavedra-Leos, *Polymers*, 2019, **12**, 5.