Investigation of thermodynamics in melting Cu^{2+}-based 1D coordination polymers

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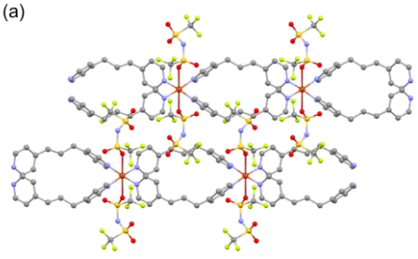
Keywords: Coordination polymer; Melting; Crystal structures; Thermodynamics; Entropy

Liquid and glassy states of coordination polymers (CPs) or metal-organic frameworks (MOFs) have gained attention as a new class of amorphous materials.[1] To expand the structural libraries and functions, design principles for crystal structures with low melting points (T_m) before reaching decomposition is desired. T_m can be predicted by analyzing thermodynamic parameters described by enthalpy of fusion (ΔH) and entropy of fusion (ΔS) according to the equation $T_m = \Delta H/\Delta S$. Recent studies in ionic liquids have revealed that a large ΔS deriving from conformational and configurational entropy is critical for decreasing T_m.[2] However, for CPs it has been challenging to estimate T_m from thermodynamic parameters, especially for ΔS because of their complex, extended natures and the uncertainty of the liquid structures.

We observed molecular structure-dependent differences in melting behaviors of 1D ribbon-chain CPs, which consist of Cu^{2+}, bipyridine derivative linkers and monovalent anions (Fig).[3] The observed tendency of melting and non-melting structures indicates that the melting behaviors are governed by increasing ΔS deriving from conformational entropy, which is expected from the molecular structures of the linkers and anions. A further decrease in T_m was observed when the -CF_3 groups in bis(trifluoromethylsulfonyl)imide anion ($TFSI^-$) was changed to -CH_3 groups (Ms_2N^-). DFT calculations indicate that the latter compound has stronger interaction between 1D chains, which enlarges ΔS by suppressing the kinetic entropy in crystalline state. These studies suggest that ΔS in terms not only of multiple conformation of molecules but also of dynamics of crystals is important for understanding the melting of CPs.

(a)



(b)

Compounds	$Cu(TFSI)_2(bpp)_2$	$Cu(Ms_2N)_2(bpp)_2$	$Cu(BF_4)_2(bpp)_2$	$Cu(TFSI)_2(bpe)_2$
Linker (L)	bpp	bpp	bpp	bpe
Anion (A)	$TFSI^-$	Ms_2N^-	BF_4^-	$TFSI^-$
T_m / °C	196	171	No melting	No melting
ΔH / kJ mol^{-1}	44.6	44.0	--	--
ΔS/ J mol^{-1} K^{-1}	95.1	99.2	--	--

Fig. (a) The crystal structure of the representative 1D ribbon-chain CP $Cu(TFSI)_2(bpp)_2$ (b) T_m, ΔH, and ΔS of four isostructures measured in differential scanning calorimetry (DSC).

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