Supporting Information

Can Melting Point Trends Help Us Develop New Tools to Control the Crystal Packing of Weakly Interacting Ions?

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Materials:

Salicylic acid, tetrabutylammonium hydroxide solution (54-56 wt% in water) and tetrabutylphosphonium hydroxide solution (40 wt.% in water) were purchased from Sigma-Aldrich, Co. LLC (St. Louis, MO, USA). Dicamba free acid (> 95% purity) was provided by Monsanto Co. (St. Louis, MO, USA). Methanol was purchased from ACP Chemicals Inc. (Montreal, QC, Canada). All chemicals were used as obtained, otherwise noted.

Syntheses:

[N_{4444}][Dic] and [P_{4444}][Dic]: The salts of [N_{4444}][Dic] and [P_{4444}][Dic] were synthesized by acid-base reactions as reported earlier with slight modification.[1] Typically, dicamba free acid (2 mmol) was weighed in a 25 mL round bottom flask followed by the addition of 2 mL methanol. The mixture was stirred to obtain a homogeneous solution. To this stirring solution, aqueous tetrabutylammonium or tetrabutylphosphonium hydroxide (2 mmol) was added at once and allowed to stir (350 rpm) at 30 °C for 1 h. After 1 h, the reaction mixture was concentrated on the rotary evaporator (35 °C, 103 mbar) and then subjected to high vaccum for 12 h to obtain an off-white crystalline solid.

[P_{4444}][H(Dic)$_2$]: Dicamba free acid (4 mmol) was weighed in a 25 mL round bottom flask followed by the addition of 4 mL methanol. The mixture was stirred to obtain a homogeneous solution. To this stirring solution, aqueous tetrabutylphosphonium hydroxide (2 mmol) was added at once and allowed to stir (350 rpm) at 30 °C for 1 h. After 1 h, the reaction mixture was concentrated on the rotary evaporator (35 °C, 103 mbar) and then subjected to high vaccum for 12 h to obtain an off-white crystalline solid of [P_{4444}][H(Dic)$_2$].

[N_{4444}][Sal]: The salt [N_{4444}][Sal] was synthesized as reported earlier with slight modification.[2] A solution of tetrabutylammonium hydroxide (54-56% in H_2O) (5 mmol) was added dropwise to a solution of salicylic acid (5 mmol) in 20 mL of acetone and stirred for 15 min at room temperature. The solvent was evaporated and the remaining viscous liquid was dried at 0.1 mbar with stirring for 24 h to obtain tetrabutylammonium salicylate in quantitative yield as colorless crystals.

Differential Scanning Calorimetry (DSC):

DSC was performed using a TA Q2000 unit (New Castle, DE, USA) under nitrogen flow. Sample between 5 and 15 mg were placed in T_0 Aluminum Hermetic pans and sealed using a T_0 press. The protocol of DSC analysis was as follows: the sample was cooled from room temperature to -60 °C at a cooling rate of 5 °C/min, maintaining an isotherm at -60 °C for 5 min. Then, the sample was heated to 120 °C at a ramp rate of 5 °C/min, followed by an isotherm at 120 °C for 5 min and cooling to -60 °C at 5 °C/min. The above-mentioned cycle was repeated twice to reproduce the results. The data was analyzed using TA Universal Analysis software.

Single Crystal X-ray Diffraction (SCXRD):

SCXRD data for [N_{4444}][Dic] and [P_{4444}][H(Dic)$_2$] were collected on a Bruker D8 Advance diffractometer with a Photon 100 CMOS area detector and an IμS microfocus

X-ray source (Bruker AXS, Madison, WI, USA) using Mo-Kα radiation. Crystals were coated with Paraffin oil and cooled to 100 K under a cold stream of nitrogen using an Oxford cryostat (Oxford Cryosystems, Oxford, UK). SCXRD data for [P_{4444}][Dic] and [N_{4444}][Sal] were collected on a Bruker diffractometer equipped with a PLATFORM 3-circle goniometer and an Apex II CCD area detector (Bruker AXS) using graphite-monochromated Mo-Kα radiations, respectively. Hemispheres of data out to a resolution of at least 0.80 Å were collected by a strategy of φ and ω scans. Unit cell determination, data collection, data reduction, and correction for absorption were all conducted using the Apex2 software suite (Bruker AXS).[3] The crystal structure was solved by direct methods and refined by full matrix least squares (SHELXTL software package, Bruker AXS).[4]

Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms bonded to nitrogen and oxygen atoms were located from the difference map. Their coordinates were allowed to refine while their thermal parameters were constrained to ride on the carrier atoms. Hydrogen atoms bonded to carbon atoms were placed in calculated positions, and their coordinates and thermal parameters were constrained to ride on the carrier atoms. Short contact analysis and packing plots were made using Mercury[5] (Cambridge Crystallographic Data Center, Cambridge, UK).

The anions in [P_{4444}][Dic], [N_{4444}][Dic], and [N_{4444}][Sal] are disordered over two positions related by approximate 2-fold symmetry. The disorder has been refined using Part 1 and Part 2 instructions. Both conformations for the disordered molecules in [N_{4444}][Dic] and [N_{4444}][Sal] were located from the difference map. The site occupancy factors (SOFs) for both parts were manually adjusted until the isotropic thermal displacement parameters for both parts were approximately equal, and then they were fixed at those values. [P_{4444}][Dic] was refined using the exact coordinates and SOFs of the isomorphous [N_{4444}][Dic] structure, including disorder. Anomalous thermal ellipsoids for some of the carbon (C), oxygen (O), and chlorine (Cl) atoms in the [Dic]$^-$ anions, C and O atoms in the [Sal]$^-$ anions, and C atoms in the [P_{4444}]$^+$ cations, were found in [P_{4444}][Dic], [N_{4444}][Dic], [N_{4444}][Sal], and [P_{4444}][H(Dic)$_2$] salts respectively, possibly due to unresolvable disorder. A global restraint was added to keep the components of the thermal tensors of all atoms equal along the axes of covalent bonds. The [Dic]$^-$ and [Sal]$^-$

anions were located at two different sites with multiple occupancies with an ordered and a disordered anion in the [P$_{4444}$][Dic], [N$_{4444}$][Dic], and [N$_{4444}$][Sal] salts (Table S1). However, in [P$_{4444}$][H(Dic)$_2$], the [P$_{4444}$]$^+$ cation occupies two different sites with ordered (~50%) and disordered (~50%) occupancies. All details of the disorder refinement strategy are available as part of the deposited crystallographic information files.

Table S1. Percentage occupancies in case of positional disorders of anions in the 1:1 salts.

Salts	Ordered anion occupancies (%)	Disordered anion occupancies (%)
[P$_{4444}$][Dic]	~79	~21
[N$_{4444}$][Dic]	~80	~20
[N$_{4444}$][Sal]	~56	~44

Crystal Structures:

The disordered molecule of the dicamba anion in [P$_{4444}$][Dic] has pseudo 2-fold symmetry and the disorder has been omitted here for clarity (**Figure S1a**). The crystal structure of [P$_{4444}$][Sal] is adapted from reference 6 (**Figure S1b**). The crystal structure of [P$_{4444}$][Dic] is isomorphous with [N$_{4444}$][Dic], however, [N$_{4444}$][Sal] is not isomorphous with the reported [P$_{4444}$][Sal].[6]

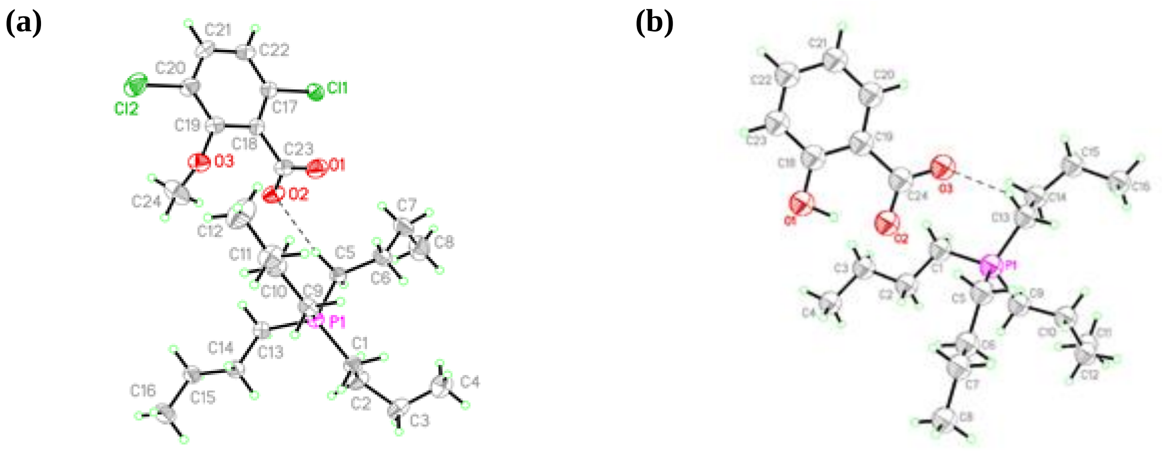


Figure S1. ORTEP (50% probability ellipsoids) diagram of (a) [P$_{4444}$][Dic] and (b) [P$_{4444}$][Sal]. The figure b was drawn from data in reference 6.

In the crystal structure of [P_{4444}][Dic], the dicamba anion is connected to four cations and another dicamba anion through various non-classical weak C–H···Cl and C–H···O hydrogen bonds (**Figure S2a**). However, the [P_{4444}]$^+$ cation is connected via two types of weak intermolecular interactions like C–H···Cl and C–H···O with four dicamba anions in the crystal structure of the salts (**Figure S2b**). There are no intermolecular interactions between cations.

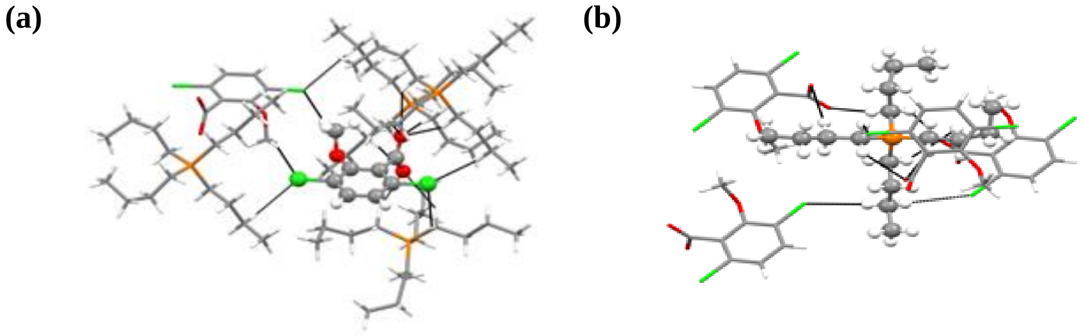


Figure S2. Interaction environments of the (a) anion and (b) cation of [P_{4444}][Dic].

The interaction environments of the cation and anion of [N_{4444}][Dic] are similar to [P_{4444}][Dic]. In [N_{4444}][Dic], the [Dic]$^-$ anions connect with six molecules, including five [N_{4444}]$^+$ and one [Dic]$^-$, however, the [N_{4444}]$^+$ cations connect with five [Dic]$^-$ through various non-classical weak C–H···Cl and C–H···O hydrogen bonds (**Figure S3**). Interestingly, in [P_{4444}][Dic], the [P_{4444}]$^+$ and [Dic]$^-$ connect to each other with one less cation and anion, respectively, compared to [N_{4444}][Dic].

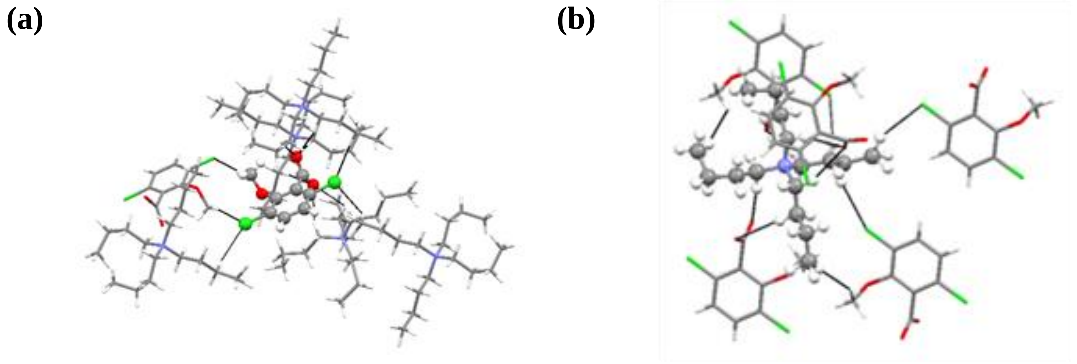


Figure S3. Interaction environments of the (a) anion and (b) cation of [N_{4444}][Dic].

No strong directional intermolecular interactions were observed in the crystal structure of $[P_{4444}][Sal]$ similar to $[P_{4444}][Dic]$ and $[N_{4444}][Dic]$. In $[P_{4444}][Sal]$, one $[Sal]^-$ anion is connected with four $[P_{4444}]^+$ cations via weak non-classical C–H···O hydrogen bond (**Figure S4a**). However, one $[P_{4444}]^+$ cation is also connected with four salicylate molecules via only weak C–H···O hydrogen bonds (**Figure S4b**). One alkyl chain of the cation is disordered.

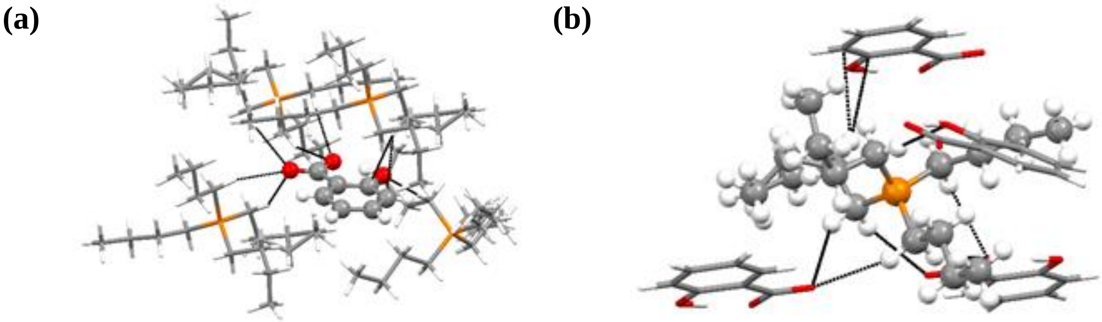


Figure S4. Interaction environments of the (a) anion and (b) cation of $[P_{4444}][Sal]$.

The crystal structure of $[N_{4444}][Sal]$ is similar to $[P_{4444}][Sal]$, where one $[Sal]^-$ anion is connected with four $[N_{4444}]^+$ cations via weak non-classical C–H···O hydrogen bonds (**Figure S5a**). However, one $[N_{4444}]^+$ cation is also connected with four salicylate molecules via only weak C–H···O hydrogen bonds (**Figure S5b**). There are no intermolecular interactions between the cations.

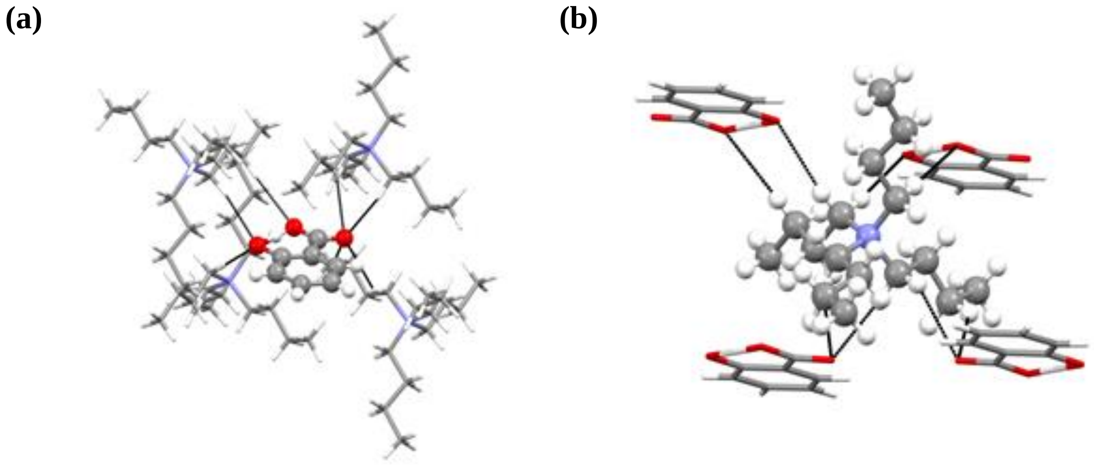
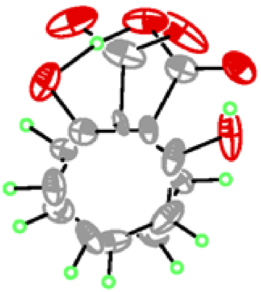


Figure S5. Interaction environments of the (a) anion and (b) cation of $[N_{4444}][Sal]$.

The anions in $[P_{4444}][Dic]$, $[N_{4444}][Dic]$, and $[N_{4444}][Sal]$ are disordered over two positions related by approximate 2-fold symmetry (**Figure S6**).

$[Dic]^-$ anion in $[P_{4444}][Dic]$ **$[Dic]^-$ anion in $[N_{4444}][Dic]$**



$[Sal]^-$ anion in $[N_{4444}][Sal]$

Figure S6. Disorder of the anions.

In the crystal structure of $[P_{4444}][H(Dic)_2]$, there are numerous weak C–H···O hydrogen bonds present between $[H(Dic)_2]^-$ anion and $[P_{4444}]^+$ cation (**Figure S7**). One anion is connected with two $[P_{4444}]^+$ cations and four $[H(Dic)_2]^-$ anions via weak C–H···O hydrogen bonds, however, each $[P_{4444}]^+$ cation is connected with two $[H(Dic)_2]^-$ anions only. One alkyl chain of the cation is disordered.

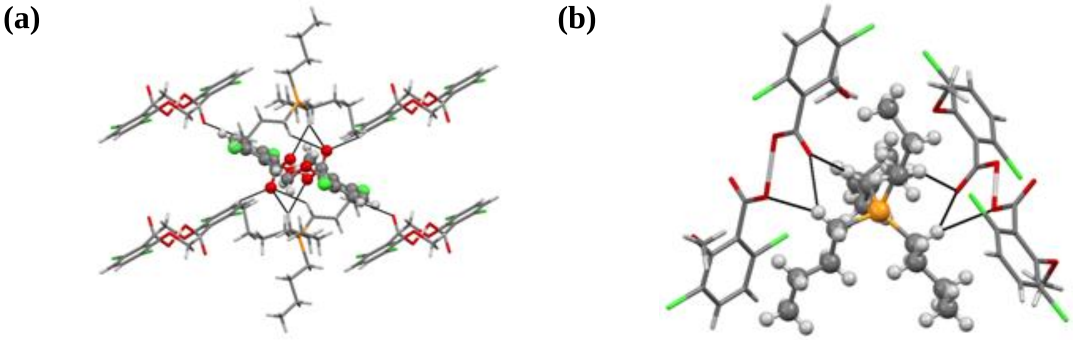


Figure S7. Interaction environments of the (a) anion and (b) cation of $[P_{4444}][H(Dic)_2]$.

Based on the first cycle of the DSC curve (black), the melting point of the $[P_{4444}][H(Dic)_2]$ salt is 112 °C (**Figure S8**). However, the compound did not crystallize during cooling, and thus, there is no melting peak in the second cycle (red). Instead, a glass transition was observed at -36 °C.

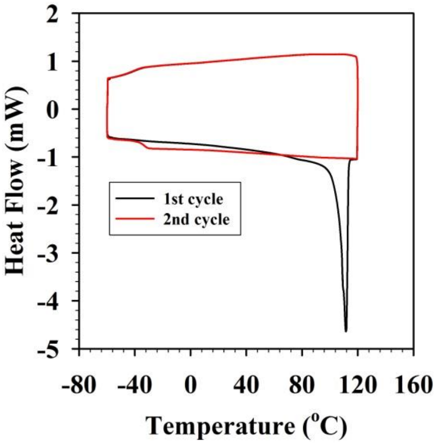


Figure S8. Differential scanning calorimetry (DSC) and melting point of $[P_{4444}][H(Dic)_2]$.

References:

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