

Supplementary Information for:

Concerted mitigation of O...H and C(π)...H
interactions prospects sixfold gain in optical
nonlinearity of ionic stilbazolium derivatives

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Supporting Information

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SI1: The process by which crystal structure data and second-harmonic-generation powder test data of subject DAST derivative were sourced according to a workflow of selection criteria

One of the challenges of this analysis is the search for structural data and Kurtz powder SHG results of all DAST-derivatives published in literature. However, in order that our results are meaningful, we need to apply quality control criteria to select only suitably reliable data for our analysis: every candidate compound must have both good structural data and a reliable powder SHG value reported in literature. In the footnote a of Table 1 of the manuscript, we briefly explain how the final subject compounds were chosen for this analysis, while below is the step-by-step search criteria that we employed for this work:

A. Use the DAST cation molecular backbone to search for all organic compounds in the Cambridge Structural Database (version 5.35 updates Nov. 2013). The requirements for

acceptance are: R factor ≤ 0.075 , no errors, not disordered and not polymeric. We found in total 64 unique compounds at this stage.

B. 46 out of the total 64 compounds we found in Step-A crystallize in centrosymmetric space groups. These compounds are only suitable for thin-film NLO applications and do not show bulk SHG activity in single-crystal form. We therefore excluded these compounds from our list; this left only 18 compounds in our list.

C. In addition, one of these 18 candidates, Cambridge Structural Databased reference code, PUVKUN, is a co-crystal structure formed by the DAST-cation and $p\text{-N}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{CHO}$; the latter molecule is severely disordered, to the extent that the author had to model this compound using the SQUEEZE routine in the Platon program. We thus decided to eliminate this compound from our list for quality control purposes.

D. Next, we did a comprehensive search through the literature for the Kurtz Powder SHG results that correspond to these short-listed 17 compounds. This search revealed that only the eight compounds in this manuscript have trustworthy Kurtz powder SHG results available.

Thus, we arrive at the eight compounds that we have used for this reported analysis: these are the only possible DAST-derivatives that fulfill our requirements. As more structural data and powder SHG values continue to be published in the future, we are very interested to see how other compounds behave according to our model.

SI2: Considering the most appropriate value of β_0 to use for the subject study

Many independent measurements of β_0 have been determined for DAST, which have variable reliability and relevance to this subject study. Details and comments on these measurements are given in Table S1.

Table S1. A summary of various measurements of β for DAST (or its derivatives), experimental details and associated comments on their applicability to this case study.

Reference	Experimental	Static β_0 (10^{-30} esu)	Comments
Duan, 1995 (Ref A)	Compound: DAST; Method: Conventional HRS at $\lambda=1064$ nm in MeOH.	364	Value may have been largely overestimated due to uncorrected multi-photon fluorescence (MPF).
Clays, 1998 (Ref B)	Compound: DAST derivative $\Rightarrow$ C6-alkyl on pyridinium nitrogen; Method: High-frequency demodulation HRS at $\lambda \sim 800$ nm in DMSO.	<u>100</u>	This is a fluorescence-free data and can be taken as one of the reference values. But the effect of the C6-alkyl substitution is hard to quantify precisely.
Clays, 2000 (Ref C)	Compound: DAST derivative $\Rightarrow$ C18-alkyl on pyridinium nitrogen; Method: High-frequency demodulation HRS at $\lambda = 1300$ nm in chloroform.	36	This paper studies five DAST derivatives with different ethylene-bridge length ($n=1-5$). There is a sudden drop for 'n=1' compound, i.e. $\beta_{0,n=1} = 36$ compare to $\beta_{0,n=2} = 481$ and $\beta_{0,n=3} = 496$.
Günter, 2001 (Ref D)	Compound: DAST; Method: Conventional HRS at $\lambda = 1542$ nm in DMSO. MPF is partly corrected using quadratic fitting on the fundamental intensity.	210	The result may have been overestimated due to residual two-photon fluorescence (2PF) intensity. (2PF also has the same quadratic dependence on the fundamental intensity as SHG.)
Coe, 2002 (Ref E)	Compound: DAST cation, PF_6^- anion; Method: (A) High-frequency demodulation HRS at $\lambda = 1300$ nm in acetonitrile. (B) Stark spectroscopic method.	(A) 25 (B) <u>90</u>	The $\lambda=1300$ nm-HRS experimental set-up once again measured an unusual low β_0 (i.e. compared to the Ref C findings), whereas the Stark spectroscopic method shows comparable β_0 as the $\lambda=800$ nm-HRS measurement (Ref B).
Clays, 2003 (Ref F)	Compound: DAST cation, PF_6^- anion; Method: High-frequency demodulation HRS at $\lambda = 800$ nm in acetonitrile.	<u>110</u>	This report of β_0 derived from $\lambda=800$ nm-HRS is comparable with the other $\lambda=800$ nm-HRS findings, but much higher than the $\lambda=1300$ nm-HRS findings.

Coe, 2003 (Ref G)	Compound: DAST cation, PF ₆ ⁻ anion; Method: Stark spectroscopic method.	118	The reported β_0 here is comparable with the other $\lambda=800\text{nm}$ -HRS findings, but much higher than the $\lambda=1300\text{nm}$ -HRS findings.
Teshome, 2011 (Ref H)	Compound: DAST cation with three different anions (i, ii and iii) Method: High-frequency demodulation HRS at $\lambda = 800 \text{ nm}$ in DMSO, MeOH and CHCl ₃	(i) 138; (ii) 120; (iii) 110 Each value is the average of three measurements conducted in different solvents.	The three sets of data are in a fairly good agreement with the other $\lambda=800\text{nm}$ -HRS findings.

Reliability of β_0 . Overall, when comparing to the $\lambda=1300\text{nm}$ -HRS results, the fluorescence-free $\lambda=800\text{nm}$ -HRS and Stark spectroscopic methods seem to provide more reliable β_0 values for DAST and its derivatives. Furthermore, β_0 derived from these two methods ($\lambda=800\text{nm}$ -HRS and Stark) are also much closer to DFT or HF predictions ($\sim 150\text{-}200 \times 10^{-30}$ esu; see Ref. 15 in the main text).

Compatibility of the DAST β_0 experimental origins to other optical measurements in this study. Since the $\lambda=800\text{nm}$ -HRS method was also employed in this work to characterize BP3, use of β_0 derived from the $\lambda=800\text{nm}$ -HRS data for the DAST cation seems to be the appropriate choice.

Solvent and anion effects on β_0 for DAST. In references [F] and [H], the DAST cation has been characterized using the $\lambda=800\text{nm}$ -HRS method in four different solvents (MeCN, DMSO, MeOH, and CHCl₃) with four different anions ([PF₆]⁻, I⁻, [*p*-OTs]⁻ and 2-ONs). It is clear that both the solvents and the different anions affect β_0 in the $\lambda=800\text{nm}$ -HRS measurement. Four possible options were considered when selecting the appropriate β_0 value of the DAST-cation for this work:

1. Average all the reported DAST-cation data in Ref. F and H => **AVE. $\beta_0 = 123 * 10^{-30}$ esu.**
2. Average all DAST-cation data measured in MeOH from Ref. [F] and [H] (but with different anions) => **AVE. $\beta_0 = 135 * 10^{-30}$ esu.** *(This approach implies that we assume the solvent effect is more dominant than the anion effect for the measured β_0)*
3. Average all the data measured for the ‘DAST-cation plus [*p*-OTs]⁻ anion’ only (i.e. this combination forms the parent DAST compound) => **AVE. $\beta_0 = 120 * 10^{-30}$ esu.** *(This approach implies that we assume the anion effect is more dominant than the solvent effect for the measured β_0)*
4. Since both solvent and anion affect the β_0 of the DAST-cation, one can choose the data of the ‘DAST-cation plus *p*-OTs anion’ (the parent DAST compound) that is measured in MeOH (the same solvent used for BP3 HRS tests in this study); hence, **$\beta_0 = 125 * 10^{-30}$ esu** (data from Ref. [H]).

Note that the dielectric constants for the used solvents in Ref. [F] and [H] are as follows: DMSO=46.7, MeOH=33, CHCl₃=4.81 and MeCN=37.5.

Option 2 affords a β_0 value that deviates the most from that provided by the other three options. This stands to reason since it is clear that different anions do have certain effect on the measured β_0 from the data reported in Ref. [H] (e.g., for DMSO, $\beta_0 = 120, 100$, and 95 for the three different anions; for MeOH, $\beta_0 = 150, 125$, and 130 for the three different anions; for CHCl₃, $\beta_0 = 145$ and 135 for the two different anions). On this basis, this option was excluded.

The β_0 values offered by the three other options are similar to each other, so choosing any of these options should not significantly influence the findings in this paper. Option 3 was selected for the paper, since this largely corrects for solvent effects via use of the two-state model to generate individual β_0 values prior to their overall averaging.

SI3: Correlation between η_{inter} and the non-bonded contact effects

The principal cation-anion interactions for the subject DAST-derivatives are C-H...O and C-H...C(π) short-contacts. As shown in Table 1 (main text), all these non-bonded contacts with their strength have been identified and computed. A comprehensive correlating study has been attempted in order to establish the relationship (if any) between the strength of these contacts and η_{inter} ; however, only a very modest correlation between η_{inter} and contact-distance of H(2)...C(π) interaction has been identified as displayed in Figure S1. The geometries of the principal cation-anion interactions of compound [2]-[7] are shown in Figure S2 for reference.

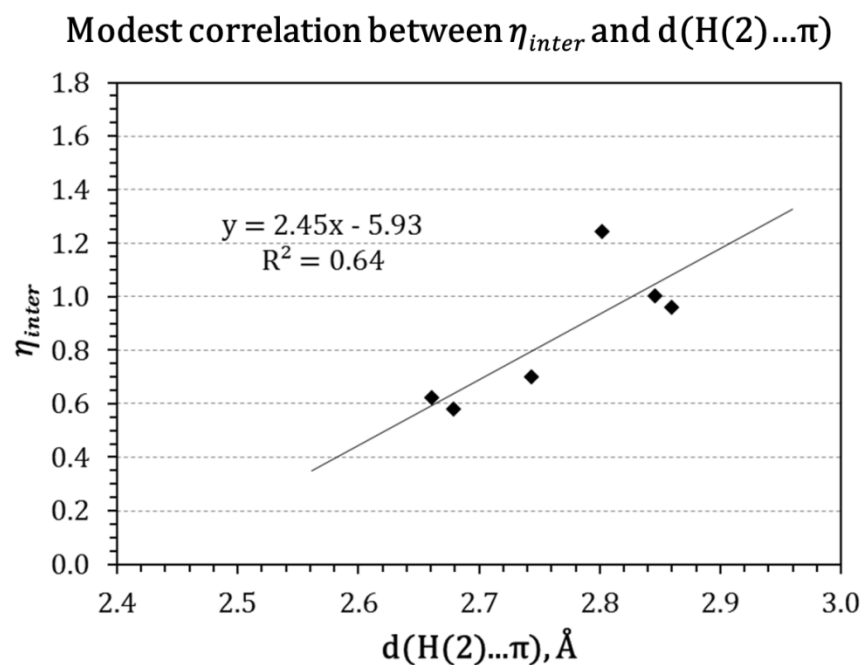


Figure S1. A modest correlation between η_{inter} and the distances of the H(2)... π contacts for compound [1]-[6].

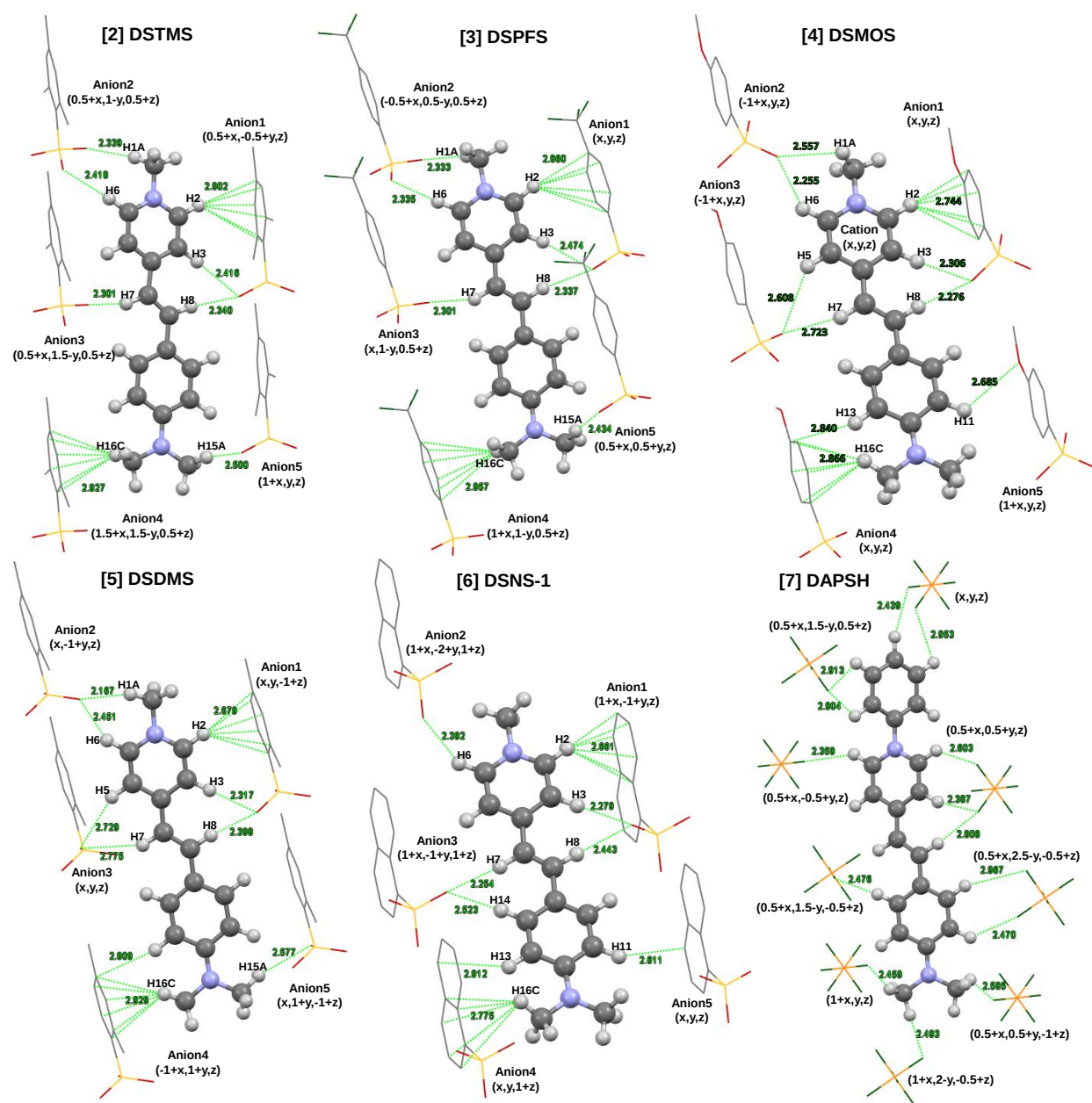


Figure S2. Cation-anion interactions in [2]-[7]. The hydrogen atoms of the anions are omitted for clarity. A comparable plot for [1,8] is given in Figure 2. Compound [4] contains four pairs of cations and anions in the asymmetric unit and therefore, the contact-distances shown here are the averaged values from the four cations.

As shown in Figure S2, compound [7] has a completely different anion to the other subject compounds [1]-[6] and [8] and therefore, [7] only shows one type of cation-anion interactions, C-

H...F. These C-H...F non-bonded contacts lie at similar positions as the other types of contacts in the subject compounds. Presumably, these C-H...F contacts exhibit analogous effects as C-H...O/C-H... C(π) short-contacts to the cations and this is evident from the correlating relationship shown in Figure S3.

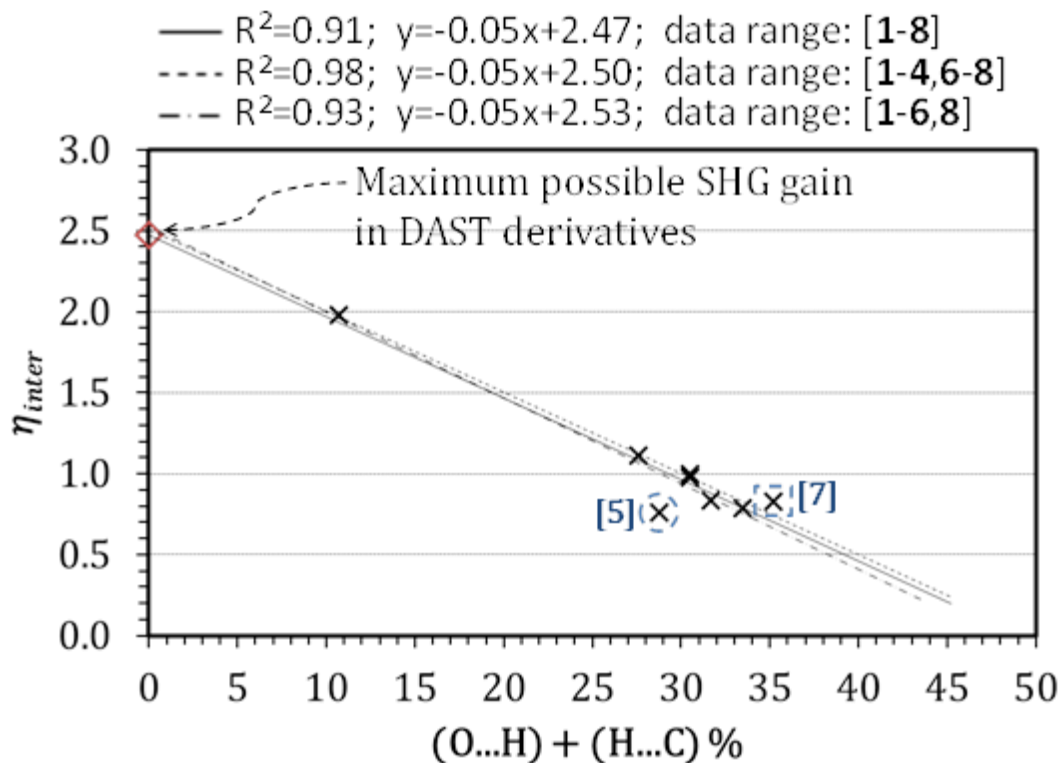


Figure S3. Linear correlations between η_{inter} and the total percentage of the Hirshfeld surface area coverage of H...O and H...C(π) contacts for compound [1]-[8] (solid-line), compound [1]-[4] and [6]-[8] (dash-line) and compound [1]-[6] and [8] (dash-dotted-line). The data for compound [5] and [7] are highlighted. The linear correlation coefficients (R^2) and the linear regression formula are given on the top of the plot.

A near-perfect ($R^2 > 0.91$) linear relationship between η_{inter} and the sum of the H...O and H...C(π) contact-surface percentages for all the subject compounds [1-8] is discovered, as shown in Figure S3. This excellent correlation indicates that these *two* contact-types, when taken together, have a dominating impact on η_{inter} , and therefore on the overall ICT processes ensuing in the DAST-derivatives.

Since the greatest deviation in the linear regression relates to compound [5] (highlighted in Figure S3), another correlation fit, excluding compound [5] was also calculated; this afforded an improved fit with $R^2 = 0.98$ for compound [1]-[4] and [6]-[8] (dashed line in Figure S3). It is observed that the molecular packing arrangement and the cation...anion interaction network for [5] are very similar to those of the other DAST-derivatives. One possible explanation of this deviation may be attributed to the uncertainty occurred during powder SHG measurement, which is known to be affected by a number of factors, such as the ground powder size and optical coherent length of a material (see Ref. [I]).

As mentioned earlier, compound [7] has a completely different type of counter-anion $[\text{PF}_6]^-$, causing H...O contact contributions to be replaced by those of H...F contacts. Interestingly, the correlation coefficient did not alter much when the data for compound [9] are added into the fit (*c.f.* the solid and dash-dotted fitting curves plotted in Figure S3).

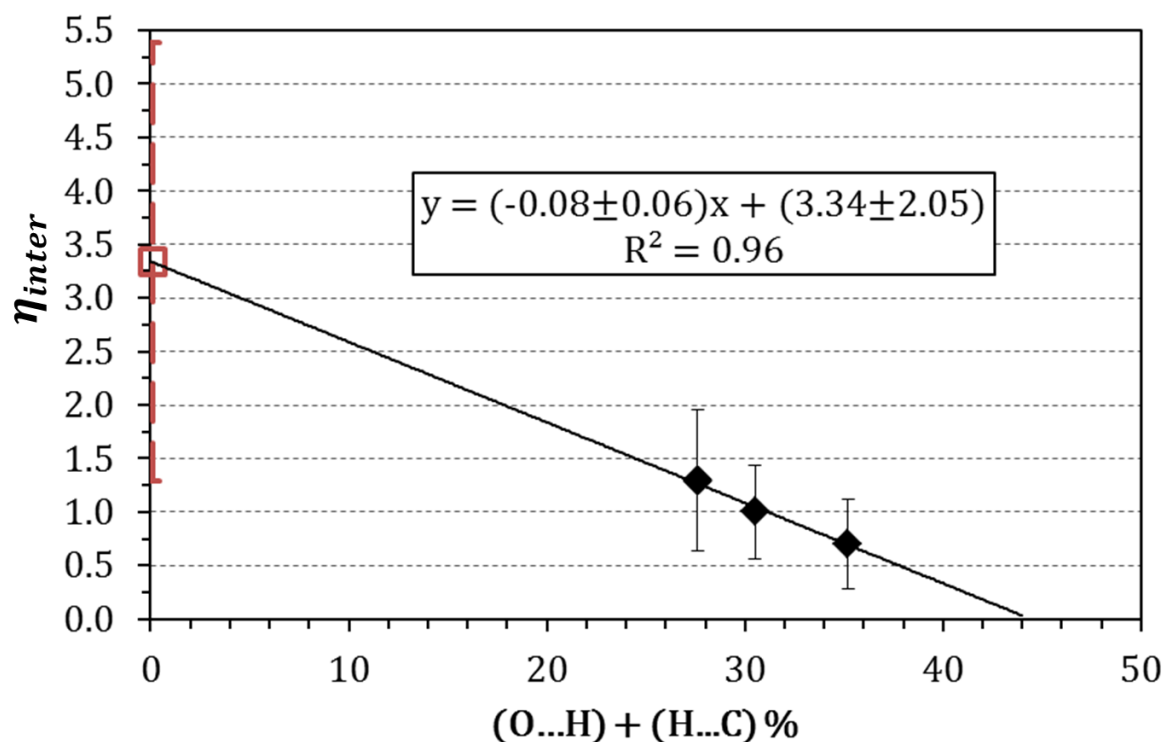


Figure S4. Linear correlations between η_{inter} and the total percentage of the Hirshfeld surface area coverage of H...O and H...C(π) contacts derived from Maker-Fringe SHG data (Ref J-N) for [1], [2] and [7]. Amongst all the subject compounds in this work, Maker-Fringe SHG data are only available for these three compounds. This correlation is almost perfectly linear, although it manifests over only a modest range and hence, the prediction in the zero limit features a notable statistical uncertainty. Nevertheless, the extrapolated range readily contains the zero-limit prediction made using SHG data; since this correlation analysis used completely independent experimental NLO data, this further corroborates the newly discovered trend shown in Figure 3 and S3.

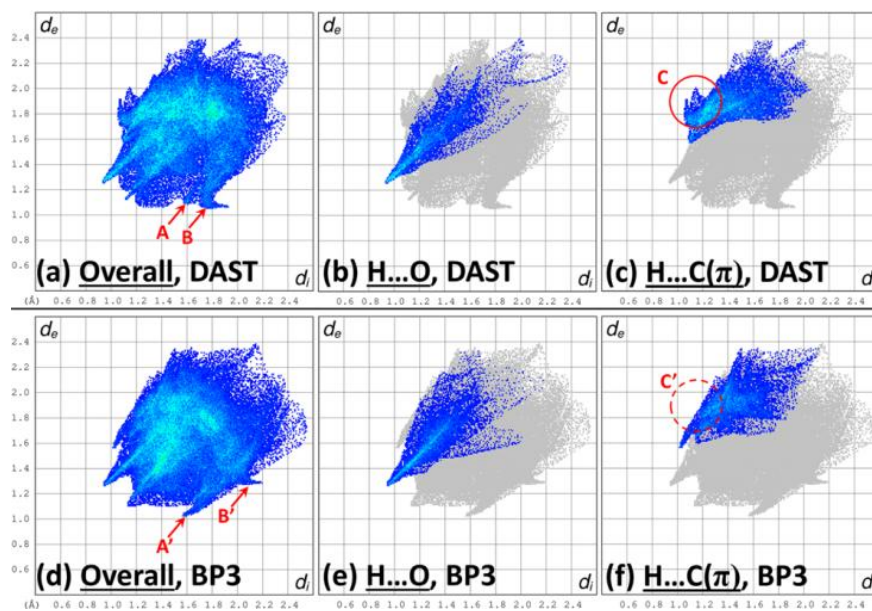


Figure S5. The fingerprint plots for [1]DAST and [8]BP3.

Corresponding fingerprint plots (Figure S5), that visually map all hydrogens inside the Hirshfeld surface of the cation to their O and C(π) hydrogen-bond acceptors on the outside, highlight distinct intermolecular features in [1] and [8]. Each compound bears similar H...O cation...anion interaction patterns, some of which are particularly short, as denoted by the sharp ‘spike’ in Figure S4 (b) and (e). A detailed examination of the 3-D Hirshfeld surfaces of [1]-[6] reveals that, this sharp spike area mainly represents the contact-surface coverage of H(2)/(3)...O contacts associated with Anion1 (Figure S2). Since Anion 1 is, in general, the closest anion which forms multiple strong interactions with [1]-[6] core-cations, the calculated fractional contact-surface area coverage of H...O contact-types is dominated by these two strong H...O hydrogen-bonds.

H...C(π) interactions in [1] and [8] are notably disparate: [1] exhibits the closest such interaction between the cation and anion1 (C in Figure S5(c)) while [8] lacks H...C(π) cation...anion interactions entirely (C' in Figure S5(f)); instead, it only features H...C(π) cation...cation interactions (A&B and A'&B' in Figures S5(a) and (d), respectively). Among all H... π contacts, H(2)... π contacts are commonly found in compounds [1]-[6]; these are much stronger than the other types of H... π contacts. This H(2)... π contact is also associated with the closest anion, Anion 1, and therefore, such contacts represent the largest contribution to the overall sum of H... π contact-surface area coverage.

SI4: REFERENCES

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