Supporting Information

to the paper

Recent advances in anion−π interactions

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Table S1. Contact distances characterizing the anion-π interaction between a SbF_6^- and a 1,3,5-triazine ring. Represention (in space-filling mode) of the molecular structure of 1-fluoro-2,4,6-trimethoxy-1,3,5-triazinium hexafluoroantimonate (CSD refcode MACHAA).[1]

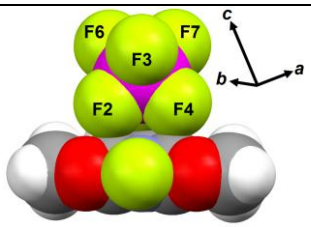
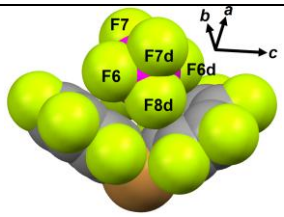
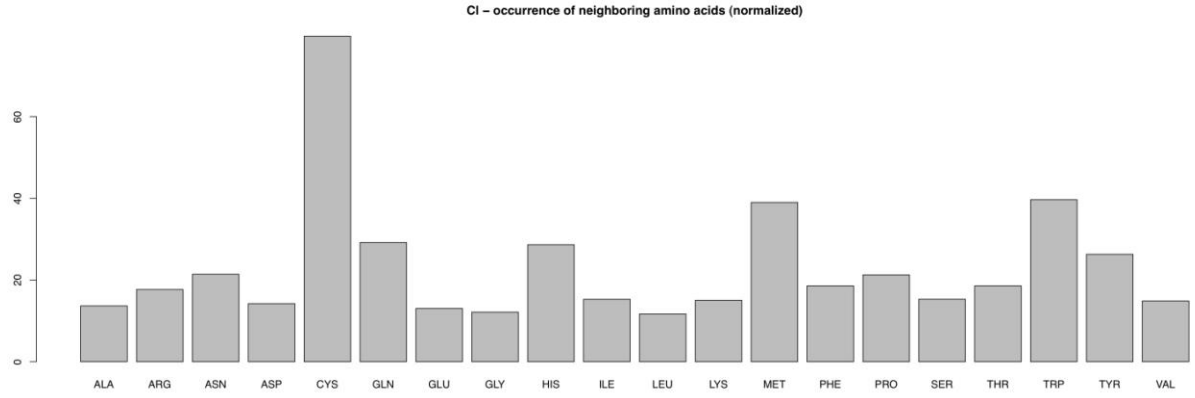
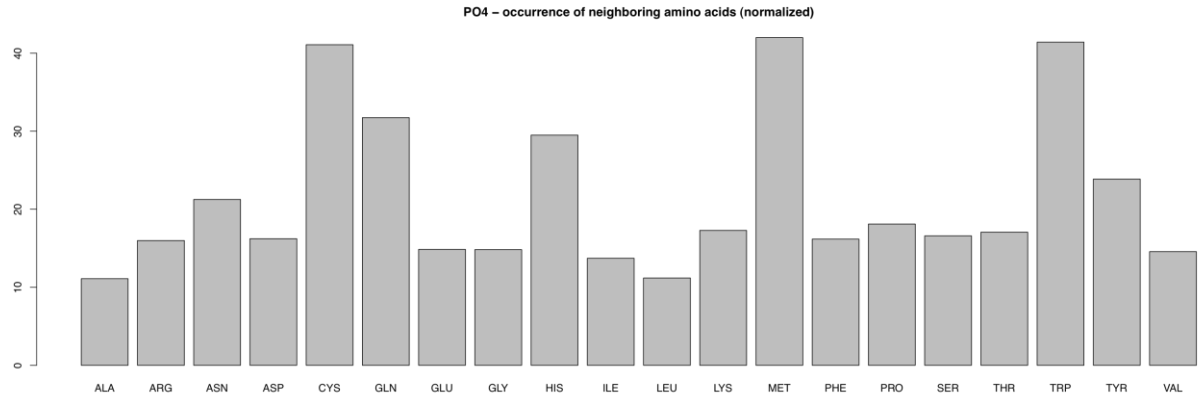
Anion-π contact	Distance (Å)	
F2−C3	2.831(5)	
F5−C2	2.886(5)	
F4−C1	2.858(6)	

Table S2. Contact distances characterizing the anion-π interaction between an AsF_6^- and a pentafluoro aromatic ring. Represention (in space-filling mode) of the molecular structure of bis(pentafluorophenyl)bromonium hexafluoroarsenate (CSD refcode HOHKAQ).[2] Symmetry operation: d = −1/2+x, 3/2−y, 7/4−z

Anion-π contact	Distance (Å)	
F8−C6	2.906(9)	
F6−C3	3.167(9)	
F8−C1	3.035(8)	



A



B

Figure S1. Most occurring residue types around the interacting anion (chloride or phosphate, cut-off equal to 6 Å). These data are normalized considering the occurrence of the residue type inside the protein in which each interacting anion is found.

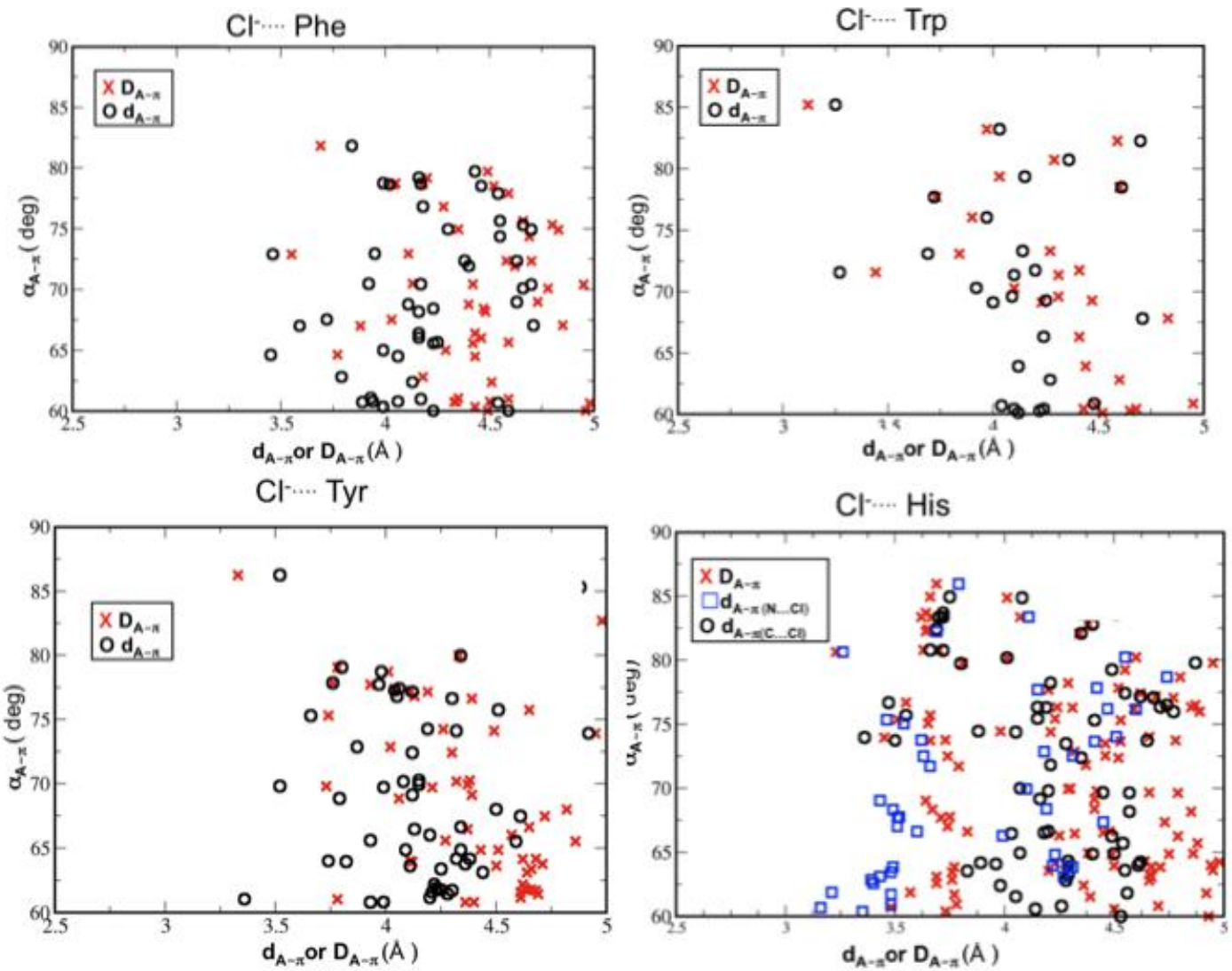


Figure S2. Scatter plot of the $d_{A-\pi}$ (and $D_{A-\pi}$) *versus* $\alpha_{A-\pi}$ for the chloride-π contacts that fulfill the search criteria. As a reference the sums of the van der Waals radii are r_{N-Cl}=3.30 Å, r_{C-Cl} =3.45 Å.

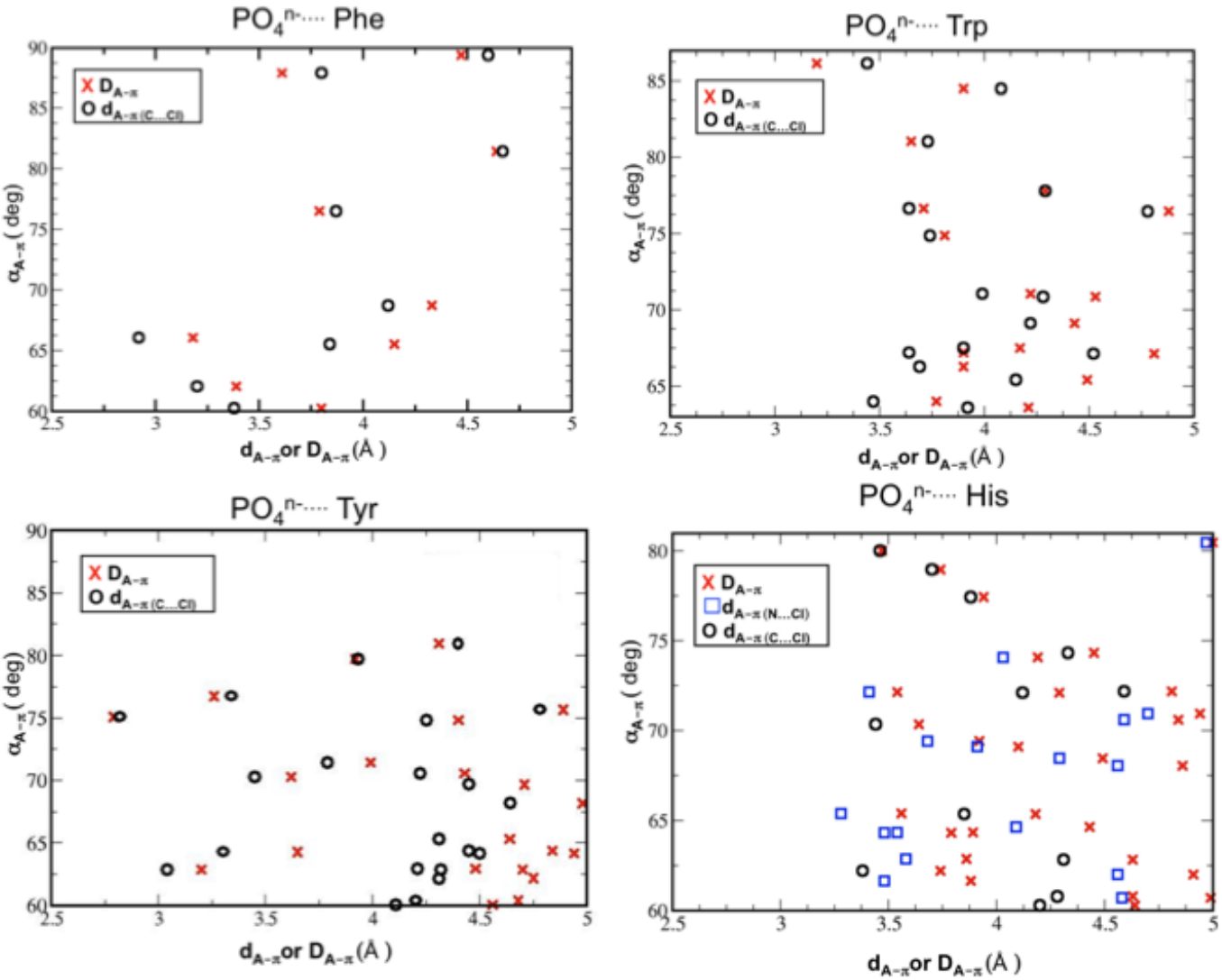
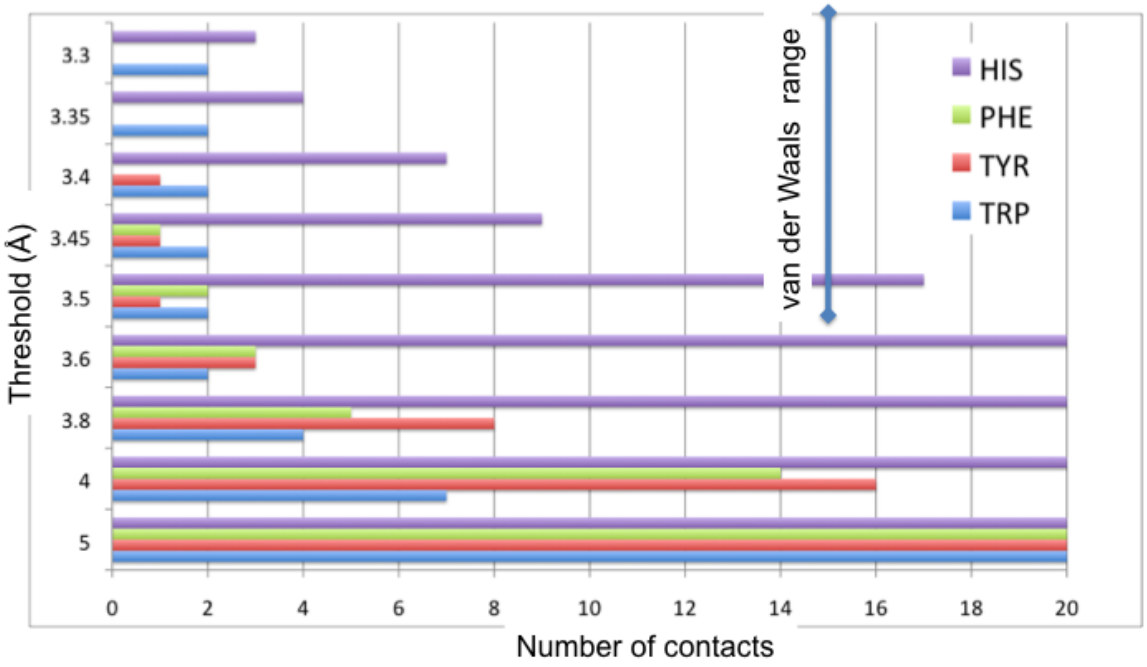
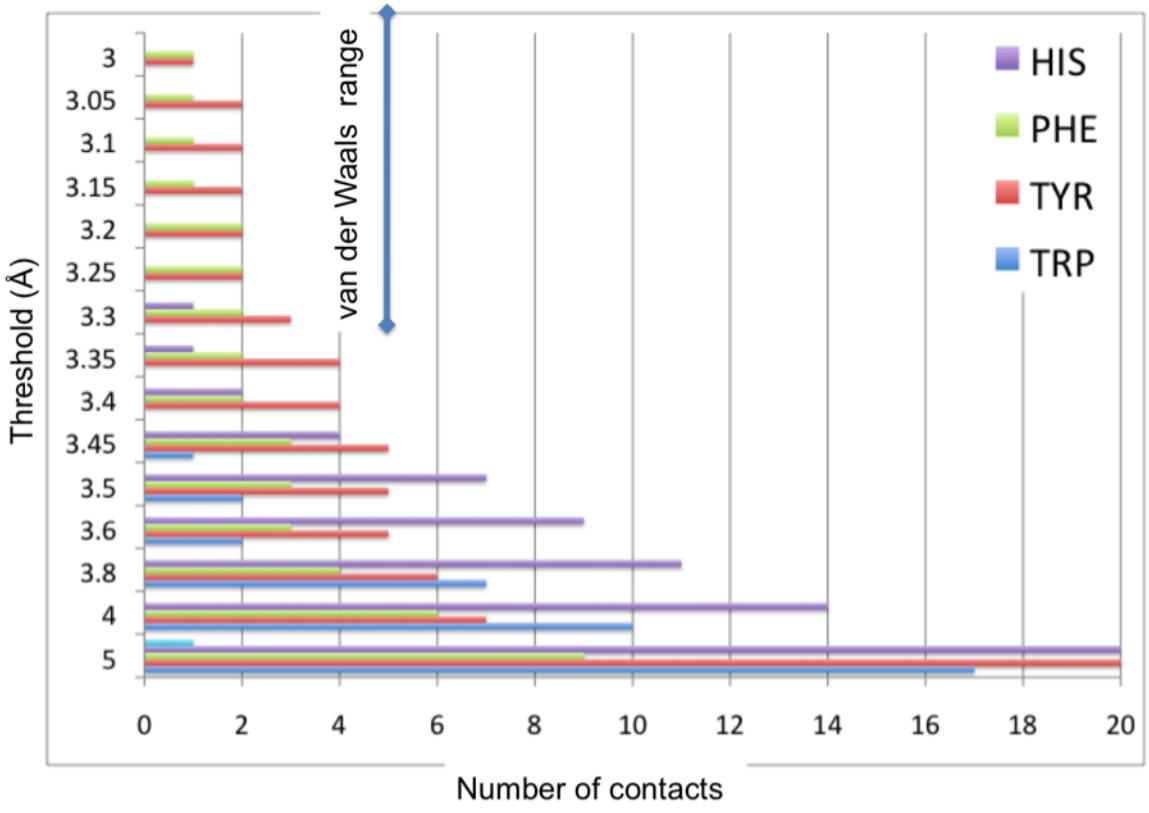


Figure S3. Scatter plot of the $d_{A-\pi}$ (and $D_{A-\pi}$) *versus* $\alpha_{A-\pi}$ for the phosphate-π contacts that fulfill the search criteria. As a reference the sums of the van der Waals radii are r_{N-O}=3.07 Å, r_{C-O}=3.22 Å.



A



B

Figure S4. Number of anion-π contacts as a function of the threshold. Around the van der Waals radius sum a total of 22 "strong interactions" are found for chloride (A) and a total of 6 strong interactions are found for phosphate (B).

References

1. R. E. Banks, M. K. Besheesh and R. G. Pritchard, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.*, 2003, **59**, M141-M143.
2. H. J. Frohn, M. Giesen, D. Welting and G. Henkel, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 841-853.