Supporting Information

to the paper

Recent advances in anion $-\pi$ interactions

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Table S1. Contact distances characterizing the anion- π interaction between a SbF₆⁻ 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 F5-C2 F4-C1	2.831(5) 2.886(5) 2.858(6)	F2 F4 F2 F4

Table S2. Contact distances characterizing the anion- π interaction between an AsF₆⁻ 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)	$\begin{array}{c} F7 \\ F6 \\$
F6-C3	3.167(9)	Fod
F8-C1	3.035(8)	

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CI – occurrence of neighboring amino acids (normalized)



B

Figure S1. Most occurring residue types around the interacting anion (chloride or phosphate, cutoff 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.

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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.



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

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- 2. H. J. Frohn, M. Giesen, D. Welting and G. Henkel, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 841-853.