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Concurrent anion···π interactions between a perchlorate ion and two π-acidic aromatic rings, namely pentafluorophenol and 1,3,5-triazine†

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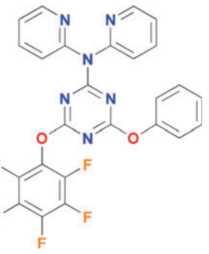
The rational design of a ligand containing two electron-poor π-rings, *i.e.* a triazine and a pentafluorophenoxy groups, has allowed the preparation of a copper complex where both the anticipated anion···π interactions are present.

Noncovalent contacts such as hydrogen bonds,[1] C–H···π,[2] π···π,[3] and cation···π[4] interactions are widely regarded as stabilizing interactions for a number of bio(macro)molecules, molecular recognition, and supramolecular assemblies. Since the past 5 years, a new type of supramolecular bonding force is being considered by the scientific community, namely the anion···π interaction with electron-deficient aromatic rings.[5,6] After having being clearly evidenced by theoretical studies,[7–9] the first crystallographic examples of anion···π interactions recognized as such were reported in 2004.[10,11] This field of supramolecular chemistry has subsequently developed and exciting new examples of anion···π binding associations are now increasingly described in the literature.[12–14]

Both 1,3,5-triazine and perfluoro aromatic rings are electron-poor rings whose anion binding properties have been comprehensively, independently investigated, both theoretically and experimentally.[7,15,16] These two categories of aromatic groups appear to represent prime electron-deficient hosts for anion guests,[17,18] and more generally for electron-rich molecules.[19]

In the present study, these two types of π-acidic moieties have been *combined* within a single molecule to examine its potential joint anion binding properties. The ligand 2-(*N*,*N*-di(pyridin-2-yl))-4-(perfluorophenoxy)-6-phenoxy{1,3,5}triazine (**dppftz**; Scheme 1) was prepared from 2,4,6-trichloro-{1,3,5}triazine, applying an experimental procedure described earlier (see ESI†).[20] Ligand **dppftz** possesses a 1,3,5-triazine core bearing three different functional groups as substituents. Thus, **dppftz** holds both an electron-rich and an electron-poor aromatic ring, respectively a phenoxy and a pentafluorophenoxy unit. The presence of these electronically opposite π-substituents is aimed at verifying the sole involvement of the π-acidic one in the expected anion···π interactions. The third substituent, *i.e.* the dipyridylamine group, would coordinate to a metal cation to ensure charge neutrality of the host–guest system.

Single crystals of the ligand **dppftz** were obtained which were analysed by X-ray diffraction (see Fig. S1 and ESI† for X-ray data). Remarkably, the solid-state structure of the free ligand **dppftz** already reveals the exceptional π-acidic characters of the 1,3,5-triazine and the pentafluorophenol rings. The crystal packing of **dppftz** is shown in Fig. S2 (ESI†). The crystal structure of the compound is composed of two slightly distinct **dppftz** molecules (indicated by the triazine rings ***A*** and ***A′*** in Fig. S2, ESI†). This differentiation most likely arises from the packing of the **dppftz** molecules which involves lone pair···π interactions.[19] As is evidenced in Fig. S2, the fluoride atom F138 is strongly interacting with the triazine ring of a neighbouring molecule of **dppftz** (see Table S2, ESI,†for all distances between F138 and each atom of the triazine ring ***A***). The F138···centroid ***A*** distance is 2.941(8) Å and the angle F138–ring centroid–aromatic plane amounts to 78.7(3)°. Both the distance (which is below the sum of the F and C, and of the F and N van der Waals radii,[21] respectively 3.17 and 3.02 Å) and the angle close to 90° are indicative of a significant bonding association. This value is just above the calculated distance (2.6 Å) for the anion···π interaction between a fluoride ion and a simple triazine ring.[7] Lone pair (l.p.)···π interactions between acetonitrile and a triazine ring have been previously observed with experimental and calculated lone pair(acetonitrile)···π(triazine) contact distances of 3.087 and 3.116 Å, respectively.[22] Interestingly, this electron-poor pentafluorophenol π-ring (ring ***B*** in Fig. S2) is acting as a lone pair host as well, through its interaction with the nitrogen atom N217 of a second neighbouring **dppftz** molecule (Fig. S2). The N217···centroid ***B*** separation distance is 3.122(9) Å and the



Scheme 1 Representation of the ligand **dppftz**.

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† Electronic supplementary information (ESI) available: Experimental procedures for the preparation of **dppftz** and complex **1**, illustrative schematic representations of **dppftz** and complex **1**, selected bond lengths and angles for **1**, contact distances reflecting the lone pair···π (**dppftz**) and anion···π (complex **1**) interactions, computational details, X-ray crystal data. CCDC 679994 (**dppftz**) and 679693 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b803817a

angle N217–ring centroid–aromatic plane is 79.5(4)° (see Table S2 for all distances between N217 and each atom of the pentafluorophenol ring ***B***). In comparison, the theoretical distance for an anion$\cdots\pi$ interaction between a cyanide ion and hexafluorobenzene is 2.80 Å (for an ideal anion–centroid–ring plane angle of 90°).[16] In the same way, the triazine ring ***A*** undergoes lone pair$\cdots\pi$ interactions through its nitrogen atom N117 with the pentafluorophenol unit ***B′*** (distance N117$\cdots$***B′*** = 3.202(3) Å and angle N117–centroid ***B′***–ring plane = 75.9(3)°), and the pentafluorophenol group ***B′*** is associated, through its fluoride atom F234, to the triazine ring ***A′*** (distance F234$\cdots$***A′*** = 3.093(9) Å and angle F234–centroid ***A′***–ring plane = 83.1(4)°). These four lone pair$\cdots\pi$ orbitals give rise to the formation of an infinite one-dimensional supramolecular chain.

The reaction of one equivalent of $Cu(ClO_4)_2\cdot 6H_2O$ with two equivalents of **dppftz** in methanol produces the coordination compound [Cu(**dppftz**)$_2$(ClO_4)$_2$](H_2O)$_5$ (**1**), whose X-ray crystal structure is depicted in Fig. S3 (see Table S3, ESI,† for X-ray data).[1,2] Our selection for the perchlorate ion is based on a search at the Cambridge Structural Database (CSD) which reveals 1933 examples of anion–π close contacts between this anion and nitrogen-containing six-membered aromatic rings.[23] Thus, this ion is the most commonly observed for anion–π interactions in the CSD, and is therefore a candidate of choice for anion binding studies.

Complex **1** is constituted of two **dppftz** ligands coordinated at the equatorial plane of an octahedral copper atom which lies on an inversion center (Fig. S3, ESI†). The axial positions of the octahedron around Cu are occupied by two perchlorate ions, at normal distances for an elongated octahedral geometry. The Cu–N bond lengths (Table S4, ESI†) are in the usual range for such CuN_4O_2 chromophore. The in-plane angles are very close to the ideal value of 90° for a perfect octahedron (Table S4).

The fascinating crystal packing of the solid-state structure of **1** is shown in Fig. 1. As anticipated, the two π-acidic rings are involved in anion–π interactions, while the phenoxy group is not. Indeed, each perchlorate ion exhibits intramolecular close contacts with a triazine ring (ring ***A*** in Fig. 1) and intermolecular anion–π interactions with a pentafluorophenol group from an adjacent **dppftz** molecule (ring ***B*** in Fig. 1). Interestingly, the perchlorates adopt two crystallographic orientations in the crystal lattice with occupancy factors of 0.5. The two crystallographically independent ClO_4^- ions are labelled {Cl1O11–O14} and {Cl2O21–O24}. As is evidenced in Fig. 1, the oxygen atom O11 is strongly interacting with an intramolecular triazine ring (see Table S5, ESI,† for all separation distances between O11 and each atom of the triazine ring ***A***). The O11$\cdots$centroid ***A*** distance is 3.203(8) Å and the angle O11–ring centroid–aromatic plane amounts to 61.4(3)°. The perchlorate oxygen atom O12 is also in contact with the triazine ring ***A*** (O12$\cdots$centroid ***A*** = 3.356(11) Å; O12–ring centroid–aromatic plane = 73.8(4)°). Finally, the oxygen atom O14 is weakly interacting with an intermolecular pentafluorophenol ring (ring ***B*** in Fig. 1 and Table S5, ESI†). The O14$\cdots$centroid ***B*** distance is 3.651(6) Å and the angle O14–ring centroid–aromatic plane amounts to 53.6(4)°. The second perchlorate orientation experiences anion$\cdots\pi$ contacts as well. The oxygen atom O21 shows significant interactions with the intramolecular triazine unit ***A*** (Fig. 1; O21$\cdots$centroid ***A*** = 3.188(7) Å and O21–ring centroid–aromatic plane = 60.1(4)°). O22 exhibits a very strong bonding association with the triazine ring ***A*** (see Table S5) with a short distance O22$\cdots$centroid ***A*** of 2.939(10) Å and an angle O22–ring centroid–aromatic plane of 75.1(3)°. In addition, O22 is in contact with the intermolecular ring ***B*** (Fig. 1; O22$\cdots$centroid ***B*** = 3.601(8) Å and O22–ring centroid–aromatic plane = 63.4(3)°). The two spatial orientations of the ClO_4^- ions in the lattice are most likely induced by competitive interactions between the two different electron-poor rings. This experimental observation has been investigated by theoretical calculations to confirm the energetical equivalence of these two anion positions.

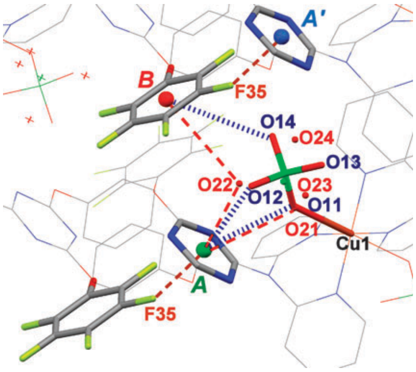

Fig. 1 Crystal packing of complex **1** illustrating the anion$\cdots\pi$ contacts shown by the two crystallographically independent perchlorate ions.

While most popular DFT functionals are not suitable for systems governed by dispersive forces,[24–28] high-level *ab initio* methods such as MP2 and CCSD,[28–30] which correctly describe these forces, require a computational cost that is only affordable for relatively small molecules. For complexes such as those studied here, a valuable alternative is represented by the use of the hybrid BHandH functional, which has recently been shown to describe surprisingly well geometries and energies of a variety of systems for which dispersive forces are crucial.[24,31–35]

The BHandH/6-31 + G(d) level of theory has therefore been employed in order to estimate the interaction energies of "model A" and "model B" corresponding to the two crystallographic positions of the ClO_4^- ions in the crystal lattice of complex **1** (see Fig. 2 and ESI†). In addition, by means of the Bader's Atom-in-Molecule theory (AIM),[36] intra- and intermolecular interactions were characterized involving the perchlorate group. It is worth mentioning that the electron density at the so-called bond critical points (blue and red balls for inter- and intramolecular interactions, respectively; Fig. 2; for further details see the ESI†) roughly correlates with the strength of hydrogen bonds,[37,38] covalent bonds[39] and $\pi\cdots\pi$ interactions.[24] As a reference, BHandH calculated values for bond critical points in the water, argon and benzene dimers are 0.0343, 0.0059 and 0.0141 au, respectively.

First, single-point calculations with BHanH/6-31 + G(d) confirmed that both configurations have a similar interaction energy, differing by < 3 kJ mol^{-1} (Table S6, ESI†). Second, the

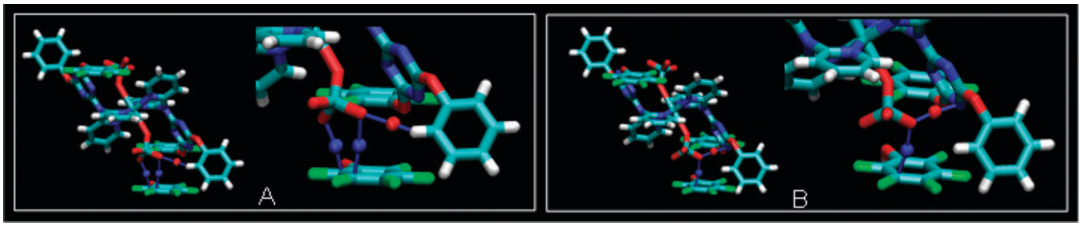

Fig. 2 Schematic views of Atoms in Molecules topology of (A) "model A" and (B) "model B". The blue lines represent the bond paths. The red and blue balls are the bond critical points of the intra- and intermolecular interactions, respectively. For the sake of clarity, only the electron density relative to the interactions involving the perchlorate group is displayed. Further details on AIM theory and topology are reported in the ESI.†

AIM analysis revealed that different interactions contribute to these values (Fig. 2). In particular two O···C lone pair···π-interactions were found between the perchlorate group and the pentafluorophenol ring in model A, with an overall electron density at the bond critical point of 0.00660 au. In addition, an O···H–C hydrogen bond was also found between the perchlorate and the phenoxy ring as displayed in Fig. 2. By contrast, model B shows one O···C and one strong O···N lone pair···π interactions with the pentafluorophenol and triazine rings, respectively, the overall electron density being equal to 0.0165 au (Table S6). Notably, the electron density of the inter-molecular interactions between the perchlorate and the pentafluorophenol rings in models A and B are virtually equivalent (0.00660 *vs.* 0.00571 au), giving a rationale for the similar binding energies and therefore the equal probability of the two perchlorate orientations in the crystal structure.

Supramolecular assemblies are generally stabilized by a range of weak dispersive interactions. The comprehension of these various interactions is crucial for the rational design of supramolecular structures. The present experimental and theoretical study has clearly shown that l.p.···π and anion···π interactions should be considered by the supramolecular chemist to build intricate molecular architectures.

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Notes and references

1. G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond In Structural Chemistry and Biology*, Oxford University Press, New York, 1999.
2. M. Nishio, M. Hirota and Y. Umezawa, *The C–H/π Interaction: Evidence, Nature and Consequences*, Wiley-VCH, New York, 1998.
3. S. K. Burley and G. A. Petsko, *Science*, 1985, **229**, 23–28.
4. J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303–1324.
5. B. L. Schottel, H. T. Chifotides and K. R. Dunbar, *Chem. Soc. Rev.*, 2008, **37**, 68–83.
6. P. Gamez, T. J. Mooibroek, S. J. Teat and J. Reedijk, *Acc. Chem. Res.*, 2007, **40**, 435–444.
7. M. Mascal, A. Armstrong and M. D. Bartberger, *J. Am. Chem. Soc.*, 2002, **124**, 6274–6276.
8. D. Quinonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deya, *Angew. Chem., Int. Ed.*, 2002, **41**, 3389–3392.
9. D. Kim, P. Tarakeshwar and K. S. Kim, *J. Phys. Chem. A*, 2004, **108**, 1250–1258.
10. S. Demeshko, S. Dechert and F. Meyer, *J. Am. Chem. Soc.*, 2004, **126**, 4508–4509.
11. P. de Hoog, P. Gamez, H. Mutikainen, U. Turpeinen and J. Reedijk, *Angew. Chem., Int. Ed.*, 2004, **43**, 5815–5817.
12. M. Mascal, I. Yakovlev, E. B. Nikitin and J. C. Fettinger, *Angew. Chem., Int. Ed.*, 2007, **46**, 8782–8784.
13. A. Garcia-Raso, F. M. Alberti, J. J. Fiol, A. Tasada, M. Barcelo-Oliver, E. Molins, D. Escudero, A. Frontera, D. Quinonero and P. M. Deya, *Inorg. Chem.*, 2007, **46**, 10724–10735.
14. K. V. Domasevitch, P. V. Solntsev, I. A. Gural'skiy, H. Krautscheid, E. B. Rusanov, A. N. Chernega and J. A. K. Howard, *Dalton Trans.*, 2007, 3893–3905.
15. T. J. Mooibroek and P. Gamez, *Inorg. Chim. Acta*, 2007, **360**, 381–404.
16. I. Alkorta, I. Rozas and J. Elguero, *J. Am. Chem. Soc.*, 2002, **124**, 8593–8598.
17. P. U. Maheswari, B. Modec, A. Pevec, B. Kozlevcar, C. Massera, P. Gamez and J. Reedijk, *Inorg. Chem.*, 2006, **45**, 6637–6645.
18. O. B. Berryman, F. Hof, M. J. Hynes and D. W. Johnson, *Chem. Commun.*, 2006, 506–508.
19. M. Egli and S. Sarkhel, *Acc. Chem. Res.*, 2007, **40**, 197–205.
20. P. de Hoog, P. Gamez, W. L. Driessen and J. Reedijk, *Tetrahedron Lett.*, 2002, **43**, 6783–6786.
21. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
22. T. J. Mooibroek, S. J. Teat, C. Massera, P. Gamez and J. Reedijk, *Cryst. Growth Des.*, 2006, **6**, 1569–1574.
23. T. J. Mooibroek, C. A. Black, P. Gamez and J. Reedijk, *Cryst. Growth Des.*, 2008, **8**, 1082–1093.
24. M. P. Waller, A. Robertazzi, J. A. Platts, D. E. Hibbs and P. A. Williams, *J. Comput. Chem.*, 2006, **27**, 491–504.
25. J. van deVondele, R. Lynden-Bell, E. J. Meijer and M. Sprik, *J. Phys. Chem. B*, 2006, **110**, 3614–3623.
26. J. Cerny and P. Hobza, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1624–1626.
27. M. Swart, T. van der Wijst, C. F. Guerra and F. M. Bickelhaupt, *J. Mol. Model.*, 2007, **13**, 1245–1257.
28. P. Hobza and J. Sponer, *Chem. Rev.*, 1999, **99**, 3247–3276.
29. P. Hobza and J. Sponer, *J. Am. Chem. Soc.*, 2002, **124**, 11802–11808.
30. P. Jurecka and P. Hobza, *J. Am. Chem. Soc.*, 2003, **125**, 15608–15613.
31. W. Z. Wang, M. Pitonak and P. Hobza, *ChemPhysChem*, 2007, **8**, 2107–2111.
32. A. Magistrato, A. Robertazzi and P. Carloni, *J. Chem. Theory Comput.*, 2007, **3**, 1708–1720.
33. J. Overgaard, M. P. Waller, R. Piltz, J. A. Platts, P. Emseis, P. Leverett, P. A. Williams and D. E. Hibbs, *J. Phys. Chem. A*, 2007, **111**, 10123–10133.
34. X. L. Dong, Z. Y. Zhou, L. J. Tian and G. Zhao, *Int. J. Quantum Chem.*, 2005, **102**, 461–469.
35. M. Meyer, T. Steinke and J. Suhnel, *J. Mol. Model.*, 2007, **13**, 335–345.
36. R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.
37. R. J. Boyd and S. C. Choi, *Chem. Phys. Lett.*, 1986, **129**, 62–65.
38. S. J. Grabowski, *Chem. Phys. Lett.*, 2001, **338**, 361–366.
39. S. T. Howard and O. Lamarche, *J. Phys. Org. Chem.*, 2003, **16**, 133–141.