Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information to the paper:

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

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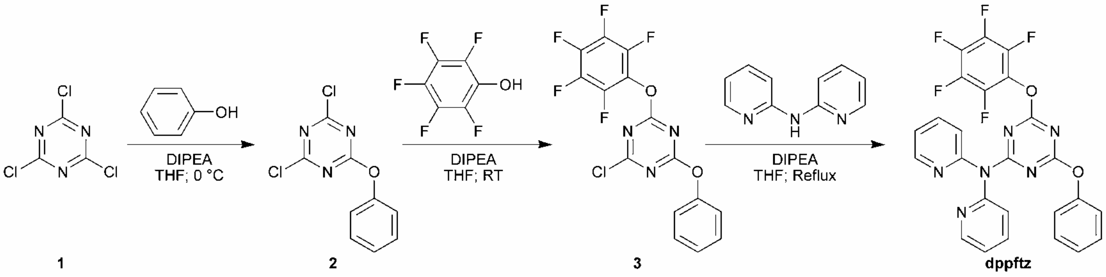
Experimental procedure for the preparation of dppftz

The synthesis of **dppftz** was performed in three steps according to the following scheme:



Synthesis of 2-phenoxy-4,6-dichloro-{1,3,5}triazine (**2**): 10.0 g (54.22 mmol) of 2,4,6-trichloro-{1,3,5}triazine (**1**) were dissolved in 100 mL of THF. One equivalent (7.01 g; 54.22 mmol) of *N*-ethyldiisopropylamine (DIPEA) was added under stirring. The resulting solution was cooled to 0 °C and one equivalent (5.103 g; 54.22 mmol) of phenol was subsequently added. After 30 minutes, the color of the solution changed from yellow to colorless and a yellow precipitate (identified *N*-ethyldiisopropylamine hydrochloride salt) appeared which was separated from the reaction mixture by filtration. The filtrate was evaporated under reduced pressure using a Rotavap. After removal of the solvent and drying, 12.04 g (49.8 mmol) of pure 2-phenoxy-4,6-dichloro-{1,3,5}triazine (**2**) were obtained.

Data for 2-phenoxy-4,6-dichloro-{1,3,5}triazine (2) (Mw: 242.06): The product was obtained as a white powder with a yield of 92%. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.47 (t, 2H, H2-phe), 7.35 (t, 1H, H3-phe), 7.18 (d, 2H, H1-phe) ppm. IR (neat): 1591, 1533, 1505, 1483, 1417, 1294, 1254, 1175, 1069, 1022, 1011, 997, 914, 865, 798, 770, 692, 667 cm^{-1}.

Synthesis of 2-chloro-4-pentafluorophenoxy-6-phenoxy-{1,3,5}triazine (**3**): one equivalent (5.875 g; 45.44 mmol) of DIPEA was added to a solution of 11.00 g (45.44 mmol) of **2** in 100 mL of THF. Next, one equivalent (8.361 g; 45.44 mmol) of pentafluorophenol was added. The reaction was performed at room temperature in a round-bottomed flask equipped with a reflux condenser. The yellow precipitate of *N*-ethyldiisopropylamine hydrochloride salt was separated by filtration. The filtrate was then evaporated under reduced pressure. The resulting solid, crude compound was purified by chromatography on silica using ethyl acetate:n-hexane (1:9) as eluent. Yield: 3.5 g (9 mmol) of 2-chloro-4-pentafluorophenoxy-6-phenoxy-{1,3,5}triazine (**3**).

Data for chloro-pentafluorophenoxy-phenoxy-triazine (3) (Mw: 389.66): The product was obtained as a white powder with a yield of 20%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34 (t, 2H, H2-phe), 7.23 (t, 1H, H3-phe), 7.07 (d, 2H, H1-phe) ppm. IR (neat): 1558, 1515, 1506, 1486, 1451, 1435, 1362, 1296, 1229, 1192, 1163, 1070, 990, 942, 839, 804, 773, 705, 690, 638 cm^{-1}. Elemental analyses, found (calcd): C 46.66 (46.23), H 1.54 (1.29), N 10.78 (10.78)

Synthesis of 2-(*N*,*N*-di(pyridin-2-yl))-4-(perfluorophenoxy)-6-phenoxy {1,3,5}triazine (**dppftz**): 3 g (7.7 mmol) of **3** were dissolved in 18 mL of THF. Next, one equivalent of DIPEA (1.00 g; 7.7 mmol), followed by 1.318 g (7.7 mmol) of 2,2'-dipyridylamine were added to the solution. The reaction mixture was refluxed at 67 °C for a three days. After cooling down to room temperature, a yellow precipitate (*N*-ethyldiisopropylamine hydrochloride salt) formed which was separated by filtration. The resulting filtrate was evaporated under reduced pressure using a Rotavap. The crude compound was purified by column chromatography on silica with ethyl acetate:n-hexane (1:9) as eluent, yielding 2.46 g of pure **dppftz**.

Single crystals of the free ligand were obtained by slow evaporation of a methanolic solution of **dppftz**.

Data for dppftz (Mw: 525.50): The product was obtained as a white powder with a yield of 61%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (t, 2H, H2-phe), 7.30 (t, 1H, H3-phe), 7.14 (d, 2H, H1-phe) ppm. IR (neat): 1546, 1517, 1465, 1367, 1299, 1196, 1075, 987, 809, 773, 748, 688, 653 cm^{-1}. Elemental analyses, found (calcd): C 57.18 (57.26), H 2.60 (2.50), N 16.02 (16.03)

Figure S1. PLUTON view of the molecular structure of **dppftz**.

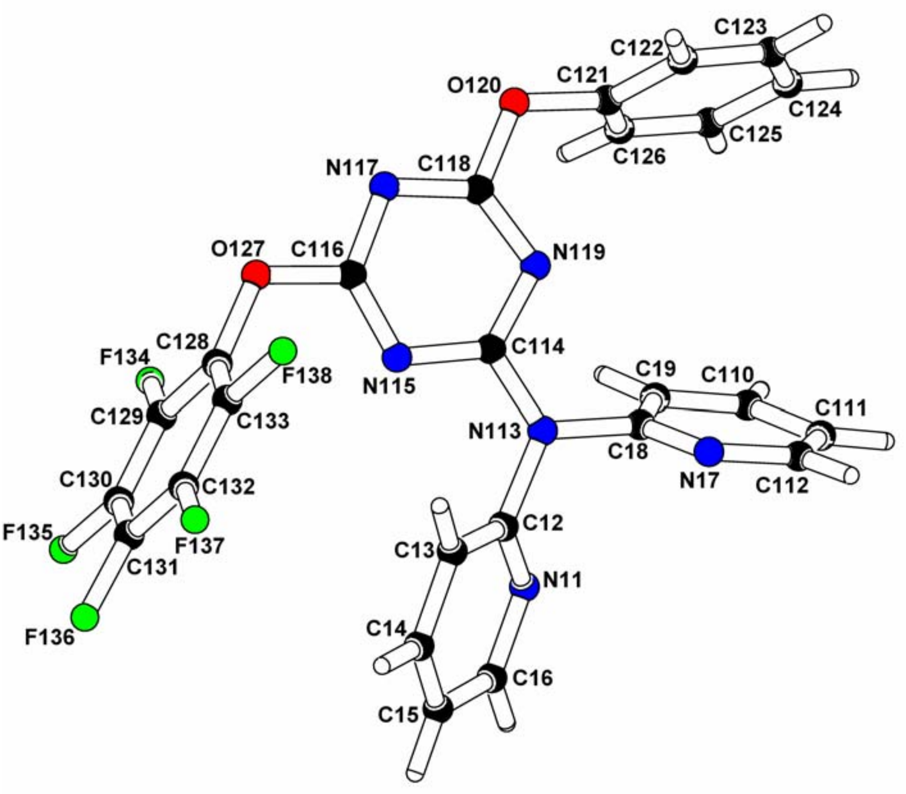
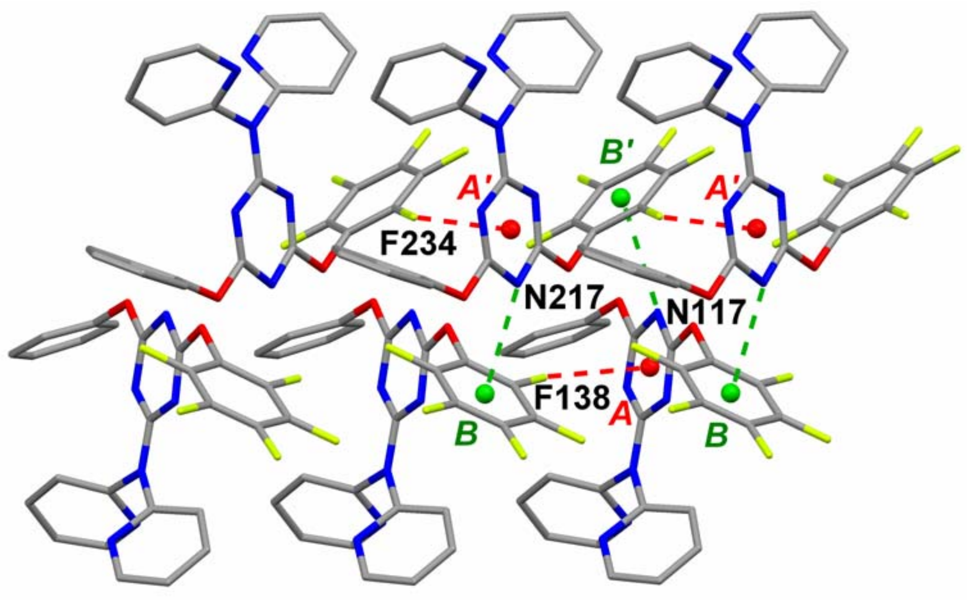


Figure S2. Crystal packing of **dppftz** showing the different types of lone pair···π interactions which generate an infinite 1D supramolecular chain.



Experimental procedure for the preparation of complex 1

100 mg (0.190 mmol) of **dppftz** were dissolved in 10 mL of MeOH. This solution was added dropwise to a solution of 0.5 equivalent of $Cu(ClO_4)_2·6H_2O$ (35 mg; 0.095 mmol) in 10 mL of MeOH. The reaction mixture was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After a few days, blue, block-shaped single crystals of **1** were obtained. Yield = 81 mg (63% based on Cu) after drying under reduced pressure at 50 ºC. Elemental analyses: calcd. for [Cu(**dppftz**)$_2$(ClO_4)$_2$](H_2O)$_2$ ($C_{50}H_{30}Cl_2CuF_{10}N_{12}O_{14}$; Mw = 1347.28 g mol^{-1}) C 44.57, H 2.24, N 12.48; found C, 44.84, H 1.81, N 12.57. Characteristic IR bands υ/cm^{-1} (neat) 3430, 1603, 1558, 1520, 1367, 1309, 1186, 1119, 1030, 994, 810, 690, 621.

Table S1. Crystal data and structure refinement for **dppftz**.

Identification code	**dppftz**	
Empirical formula	$C_{25}H_{13}F_5N_6O_2$	
Formula weight	524.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 16.139(3) Å	α = 90°
	b = 6.2526(13) Å	β = 98.20(3)°
	c = 44.715(8) Å	γ = 90°
Volume	4466.1(15) $Å^3$	
Z	4	
Density (calculated)	1.560 Mg/m^3	
Absorption coefficient	0.132 mm^{-1}	
$F(000)$	2128	
Crystal size	0.20 × 0.08 × 0.06 mm^3	
Theta range for data collection	2.55 to 25.10°	
Index ranges	−19<=h<=19, −6<=k<=7, −53<=l<=53	
Reflections collected	45709 [R(int) = 0.1536]	
Refinement method	Full-matrix least-squares on F^2	
Data / parameters	4215 / 685	
Goodness-of-fit on F^2	1.113	
R1 (wR2) [$F_o>4\sigma(F_o)$]	R1 = 0.1260, wR2 = 0.2388	
Largest diff. peak and hole	0.465 and −0.402 e.$Å^{-3}$	

Table S2. Contact distances for the lone pair···π interactions observed in the crystal structure of **dppftz** (see Figure S2).

Contact distances between F138 and the triazine ring ***A*** (ligand **dppftz**)

F138···C114_e	**2.973(8) Å**
F138···N115_e	**3.162(8) Å**
F138···C116_e	**3.325(9) Å**
F138···N117_e	3.473(8) Å
F138···C118_e	**3.288(8) Å**
F138···N119_e	**3.121(7) Å**

Contact distances between F234 and the triazine ring ***A’*** (ligand **dppftz**)

F234···C214	**3.206(8) Å**
F234···N215	**3.192(8) Å**
F234···C216	**3.151(9) Å**
F234···N217	3.548(8) Å
F234···C218	3.421(8) Å
F234···N219	3.353(9) Å

Contact distances between N217 and the pentafluorophenol ring ***B*** (ligand **dppftz**)

N217···C128	**3.227(9) Å**
N217···C129	**3.174(10) Å**
N217···C130	3.374(9) Å
N217···C131	3.581(10) Å
N217···C132	3.635(9) Å
N217···C133	3. 441(8) Å

Contact distances between N117 and the pentafluorophenol ring ***B’*** (ligand **dppftz**)

N117···C228_b	**3.195(9) Å**
N117···C229_b	3.504(9) Å
N117···C230_b	3.799(10) Å
N117···C231_b	3.737(9) Å
N117···C232_b	3.453(9) Å
N117···C233_b	**3.163(10) Å**

In **green**: strong interaction; in **red**: moderate interaction; in black: very weak interaction. Symmetry operations: b = x, 1+y, z; e = x, –1+y, z

Figure S3. PLUTON view of the molecular structure of [Cu(**dppftz**)$_2$(ClO$_4$)$_2$]. H atoms and lattice water molecules are not shown for clarity. Symmetry operation: a = –x, 2–y, –z.

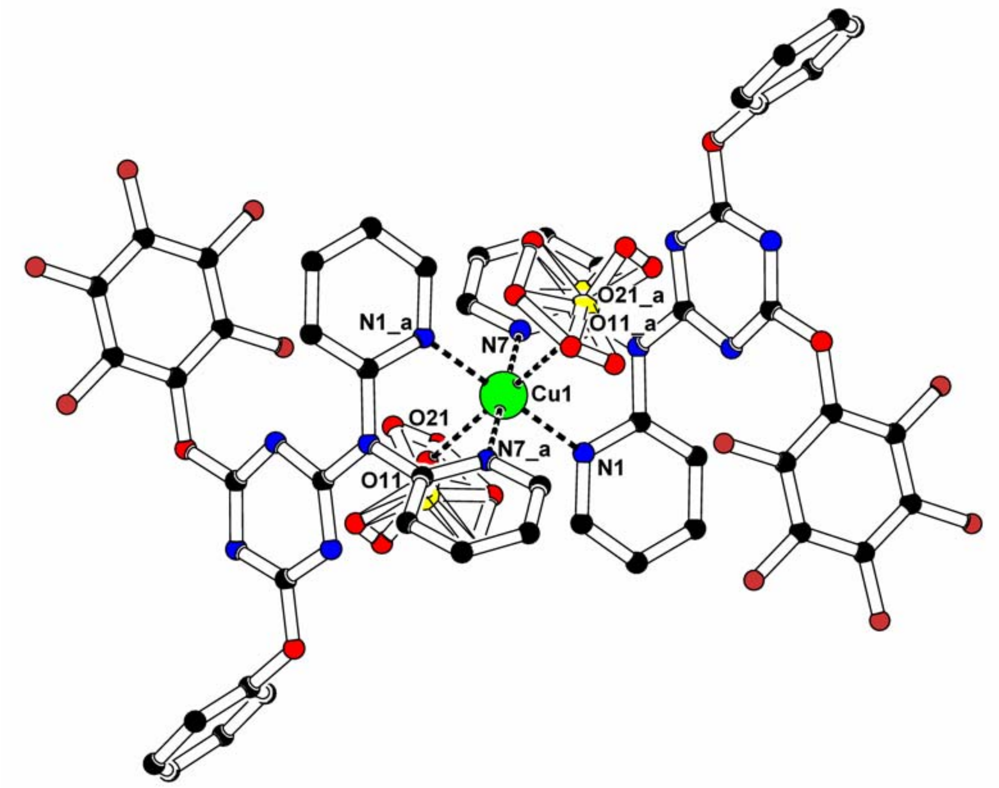


Table S3. Crystal data and structure refinement for complex **1**.

Identification code	**1**	
Empirical formula	$C_{50}H_{33}Cl_2CuF_{10}N_{12}O_{17}$	
Formula weight	1398.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*−1 (No. 2)	
Unit cell dimensions	a = 9.042(2) Å	α = 93.50(2)°
	b = 12.299(2) Å	β = 97.41(2)°
	c = 13.776(2) Å	γ = 105.67(2)°
Volume	1455.3(5) $Å^3$	
Z	1	
Density (calculated)	1.595 Mg/m^3	
Absorption coefficient	0.580 mm^{-1}	
F(000)	706	
Crystal size	0.06 × 0.08 × 0.10 mm^3	
Theta range for data collection	3.3 to 25.99°	
Index ranges	−11<=h<=11, −15<=k<=15, −16<=l<=16	
Reflections collected	22067 [*R*(int) = 0.0400]	
Refinement method	Full-matrix least-squares on F^2	
Data / parameters	4305 / 469	
Goodness-of-fit on F^2	1.04	
R1 (wR2) [$F_o > 4\sigma(F_o)$]	R1 = 0.0550, wR2 = 0.1357	
Largest diff. peak and hole	0.700 and −0.381 e.$Å^{-3}$	

Table S4. Selected bond lengths [Å] and angles [°] for **1**

distances			
Cu1–N1	2.016(3)	Cu1–N7	1.996(3)
Cu1–O11	2.537(9)	Cu1–O21	2.478(8)
angles			
N1–Cu1–N7	88.06(13)	N7–Cu1–N1_a	91.94(13)
O11–Cu1–O11_a	180.00		

Symmetry transformation used to generate equivalent atoms:
a: −x, 2−y, −z

Table S5. Contact distances for the lone pair···π interactions observed in the crystal structure of complex **1** (see Figure 1).

Contact distances between O11 and the triazine ring ***A***	
O11···C14_c	**2.824(8) Å**
O11···N15_c	**3.214(8) Å**
O11···C16_c	3.730(9) Å
O11···N17_c	4.048(8) Å
O11···C18_c	3.693(8) Å
O11···N19_c	**3.139(9) Å**
Contact distances between O12 and the triazine ring ***A***	
O12···C14_c	3.832(11) Å
O12···N15_c	3.970(10) Å
O12···C16_c	3.657(10) Å
O12···N17_c	**3.350(12) Å**
O12···C18_c	**3.241(12) Å**
O12···N19_c	3.542(10) Å
Contact distances between O14 and the triazine ring ***B***	
O14···C28_h	3.844(8) Å
O14···C29_h	**3.048(6) Å**
O14···C30_h	**3.123(7) Å**
O14···C31_h	3.956(7) Å
O14···C32_h	4.603(6) Å
O14···C33_h	4.540(7) Å
Contact distances between O21 and the triazine ring ***A***	
O21···C14_c	**2.781(7) Å**
O21···N15_c	**3.198(8) Å**
O21···C16_c	3.736(8) Å
O21···N17_c	4.056(7) Å
O21···C18_c	3.681(8) Å
O21···N19_c	**3.100(7) Å**
Contact distances between O22 and the triazine ring ***A***	
O22···C14_c	3.493(10) Å
O22···N15_c	3.460(10) Å
O22···C16_c	**3.094(10) Å**
O22···N17_c	**2.909(10) Å**
O22···C18_c	**2.991(10) Å**
O22···N19_c	**3.348(11) Å**

Contact distances between O22 and the triazine ring ***B***	
O22···C28_h	4.339(8) Å
O22···C29_h	3.784(8) Å
O22···C30_h	**3.229(9) Å**
O22···C31_h	**3.300(9) Å**
O22···C32_h	3.929(9) Å
O22···C33_h	4.382(8) Å

In **green**: strong interaction; in **red**: moderate interaction; in black: very weak interaction. Symmetry operations: c = –1–x, 2–y, –1–z; h = x, y, 1+z

Table S6. Binding energies, electron density and distance of inter-molecular interactions in Models A and B.

	ΔE_r[a] (kJ/mol)	interaction	d[b] (Å)	ρ[c] (au)
		O···C	3.05	0.00729
Model A	+2.9	O···C	3.45	0.00331
		O···H	2.85	0.00329
Model B	0.0	O···C	3.23	0.00571
		O···N	2.91	0.0108

a: relative energy of Model A compared to Model B; b: distance between the atoms involved in the interaction taken from the X-ray structure; c: electron density at the bond critical points.

X-ray Structural determination details

The molecular structure of compounds **dppftz** and complex **1** were determined by single-crystal X-ray diffraction methods. Crystallographic data and refinement details are given in Tables S1 and S3 above.

X-ray crystallographic data for **dppftz** and complex **1** were collected on Nonius KappaCCD diffractometer and the crystal was mounted to the glass fiber using the oil drop method (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615-619) and data were collected at 173 K. The intensity data were corrected for Lorentz and polarization effects and for absorption. The nonhydrogen atoms were refined anisotropically. The H atoms were situated in calculated positions and refined using riding model.

Crystallographic data for **dppftz** and complex **1** have been deposited in the Cambridge Structural Database. CCDC 679994 and 679693 contain the supplementary crystallographic data for **dppftz** and complex **1**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Computational Details

All calculations were carried out using the Gaussian03 suite of programs.[1] Extensive use of Becke's "half-and-half" functional, BHandH, was made.[2] This is an *ad hoc* mixture of exact (HF) and local density approximation exchange, coupled with Lee, Yang, and Parr's expression[3] for the correlation energy. Recently, this functional combined with medium-sized basis sets has been shown to reproduce high level calculations for a variety of systems governed by dispersive forces.[4-9] In this study, BHandH was used in combination with Pople's[10] basis sets, varying levels of polarisation and diffuse functions as in 6-31G, 6-31G(d) and 6-31+G(d).

To analyze the intra- and inter-molecular interactions, the Atoms-In-Molecules (AIM) theory was employed.[11, 12] AIM is based upon those critical points where the gradient of the density, $\nabla\rho$, vanishes. Such points are classified by the curvature of the electron density, for example bond critical points (extensively employed in this study, represented as red and blue balls in Figure 2) have one positive curvature (in the internuclear direction) and two negative ones (perpendicular to the bond). Two bonded atoms are then connected with a bond path (blue line in Figure 2) through the bond critical point. The properties evaluated at such bond critical points characterise the bonding interactions present, and have been previously used to study molecular interactions.[4, 11-15]

Since the interactions between the perchlorate group of a crystallographic unit and a triazine ring of another crystallographic unit are believed to play a crucial role, Models A and B have been built from the crystal structure determined by X-ray techniques (Figure 2). Both models contain one entire unit as well as the phenolic ring of the second unit cut along the O–C bond. The oxygen atom was then saturated with a hydrogen atom. The total number of atoms in Models A and B is 126.

In vacuo single point calculations with different basis sets (6-31G, 6-31G(d) and 6-31+G(d)) were then performed on these structures to test the convergence of the internal energy. The interaction energies in Models A and B, calculated with these basis sets, differ by 10.2, 4.9 and 2.9 kJ/mol, confirming that convergence was virtually achieved with the largest basis set.

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