Supplementary information

Molecular architecture using novel types of non-covalent π-interactions involving aromatic neutrals, aromatic cations and π-anions

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Table S1 Hydrogen bond parameters of the title complex (Å, °).

D–H···A	D–H	H···A	D···A	D-H···A	Symmetry
N1–H1···O3	0.86	1.97	2.740(2)	149	---
N3–H3···O7	0.86	2.58	3.085(2)	118	---
N3–H3···O9	0.86	2.19	2.989(2)	155	---
N4–H4···O7	0.86	1.84	2.694(2)	171	1+x, 1+y, z
O1W–H1W1···O6	0.86	2.04	2.871(2)	163	-1+x, y, z
O1W–H2W1···O4	0.86	2.19	3.013(2)	160	1-x, 1-y, -z
C1–H1A···O2	0.93	2.58	3.262(2)	131	---
C1–H1A···O2	0.93	2.42	3.222(2)	145	1-x, -y, 1-z
C2–H2···O1	0.93	2.49	3.268(2)	142	1-x, -y, 1-z
C3–H3A···O5	0.93	2.53	3.344(2)	146	2-x, 1-y, 1-z
C3–H3A···O6	0.93	2.47	3.366(2)	162	2-x, 1-y, 1-z
C4–H4A···O9	0.93	2.31	3.171(2)	154	1-x, 1-y, 1-z
C13–H13···O3	0.93	2.38	3.211(2)	149	1-x, -y, -z
C15–H15···O7	0.93	2.43	3.016(2)	121	---
C15–H15···O4	0.93	2.40	3.094(2)	131	1-x, -y, -z
C19–H19···O4	0.93	2.32	3.234(2)	168	2-x, 1-y, -z

Table S2 Geometrical parameters (distance in Å) for the π–stacking moieties involved in the π^+-π and π^+-π^+ interactions for the title complex.

rings *I*-*J*	Rc[a]	R1v[b]	R2v[c]	α	β	γ	symmetry
rings 1A···2	3.6915(9)	3.4930(5)	3.3956(5)	4.27(6)	23.10	18.87	1-x, 1-y, 1-z
rings 1B···1B	3.5279(9)	3.2934(6)	3.2934(6)	0.00	21.01	21.01	1-x, -y, -z
Rings 3···1A	4.3164(9)	2.9971(6)	4.1279(5)	32.92(7)	16.99	46.02	2-x, 1-y, 1-z

[a] Centroid distance between rings *I* and *J*; [b] Vertical distance from ring centroid *I* to ring *J*; [c] Vertical distance from ring centroid *J* to ring *I*; α is the dihedral angle between planes *I* and *J*; β is the angle between Cg(*I*)-->Cg(*J*) vector and normal to plane *I*; γ is the angle between Cg(*I*)-->Cg(*J*) vector and normal to plane *J*. Ring (1A): N1/C1–C5; Ring (2): N2/C6–C10 ;Ring (1B): N3/C11–C15 and Ring (3): N4/C16–C20.

Table S3 Geometrical parameters (Å, °) for the π–anion and π^+–anion interactions for the title complex.

Y–X···Cg	X···Cg	Y···Cg	Y–X···Cg	Symmetry
N5–O1···Cg(3)	3.5994(16)	3.8503(15)	92.17(9)	x, -1+y, z
N6–O4···Cg(1B)	3.6968(16)	3.4254(15)	67.78(8)	1+x, y, z
N6–O5···Cg(2)	3.3177(15)	3.9041(14)	109.38(10)	x, y, z
N6–O5···Cg(1B)	3.4876(15)	3.4254(15)	76.90(9)	1+x, y, z
N6–O6···Cg(1B)	3.7558(17)	3.4254(15)	65.20(9)	1+x, y, z
N7–O8···Cg(1A)	3.1537(13)	4.1954(13)	141.95(11)	-1+x, y, z

Ring (1A): N1/C1–C5; Ring (2): N2/C6–C10 ;Ring (1B): N3/C11–C15 and Ring (3): N4/C16–C20.

Table S4 Crystal data and structure refinement parameters.

Structure	(**1**)
Empirical formula	$C_{20}H_{19}N_7O_{10}$
Formula Weight	517.42
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
space group	P-1
a, b, c (Å)	7.1843(7), 11.8503(12), 13.9092(14)
α, β, γ (°)	114.553(3), 95.7160(10), 91.176(2)
Volume ($Å^3$)	1069.23(18)
Z / Density (calc.) (Mg/m^3)	2 / 1.607
Absorption coefficient (mm^{-1})	0.132
F(000)	536
Crystal size (mm^3)	0.35 × 0.31 × 0.28
θ range for data collection (°)	3.82 to 25.00
Limiting indices	-8<=h<=8,-14<=k<=14,-16<=l<=16
Reflections collected / unique	10035/3757[R(int)=0.0202]
Completeness to θ (%)	99.5
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3757 / 0 / 337
Goodness-of - fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	R1=0.0330, *w*R2=0.0894
R indices (all data)	R1=0.0354, *w*R2=0.0917
Extinction Coefficient	0.052(3)
Largest diff. peak and hole ($e.Å^{-3}$)	0.361 and -0.290

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = [\sum\{(F_o^2-F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$, $w = 1/\{\sigma^2(F_o^2) + (aP)^2 + bP\}$, where a = 0.0487 and b = 0.4662 for (**1**). $P = (F_o^2 + 2F_c^2)/3$ for the title structure.

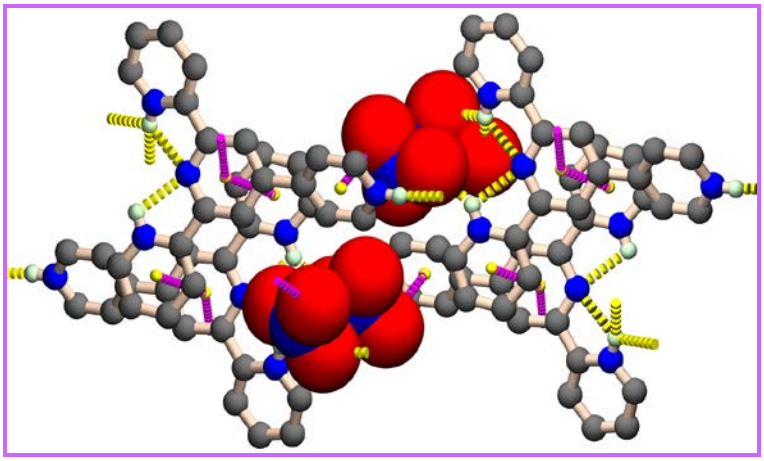

Fig. S1 $NO_3 \cdots NO_3$ interactions along with hydrogen bonding leads to positioning of nitrate ions in between successive $PTPH_3$ molecules.

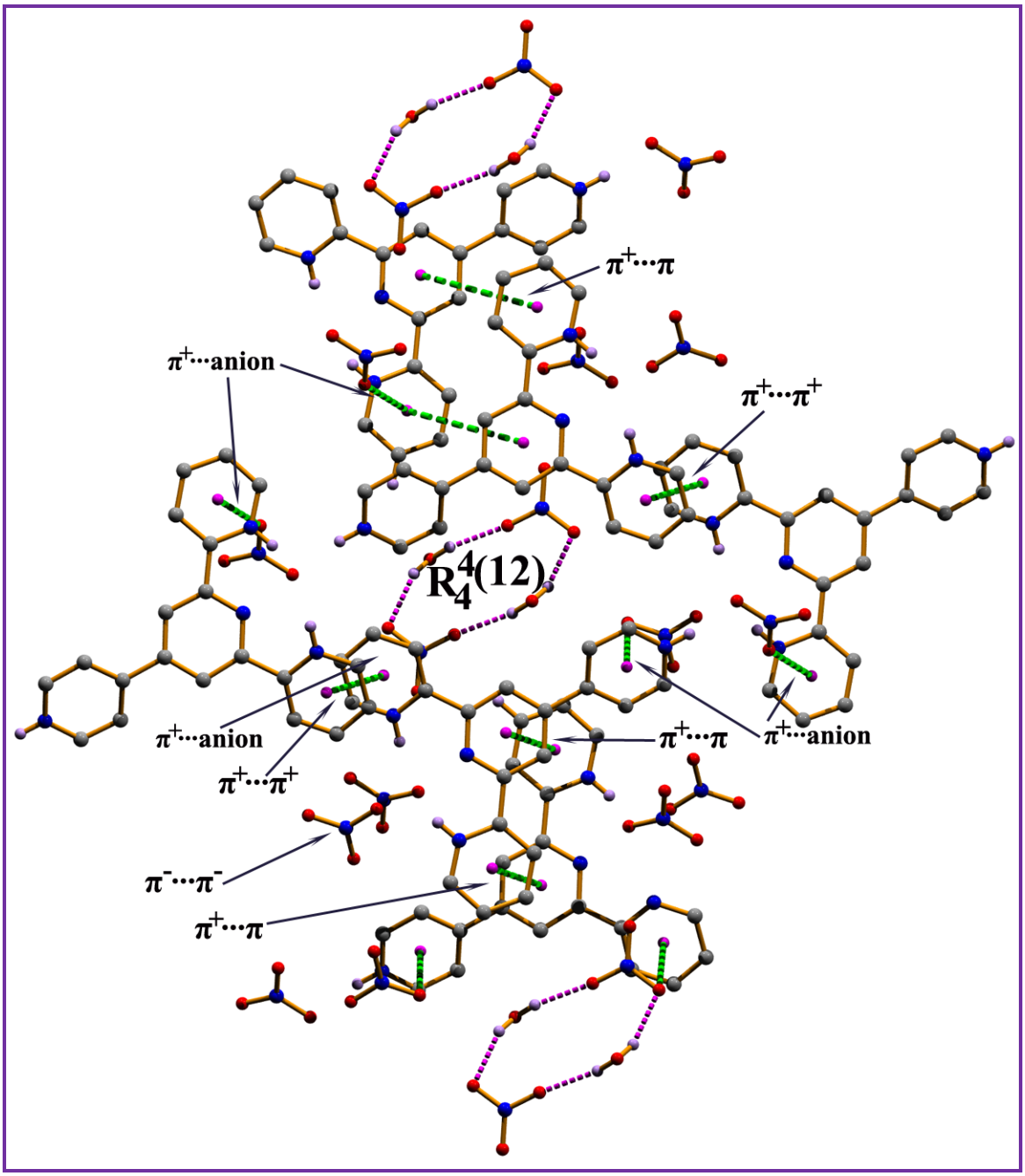

Fig. S2 Stacking arrangement of $PTPH_3$ molecules through π^+–π^+ , π^+–π, π^+–anion, π–anion and π^-–π^- interactions. The dimeric ring motif $R_4^4(12)$ has been generated through O–H···O hydrogen bonding in between water molecules and nitrate anions.

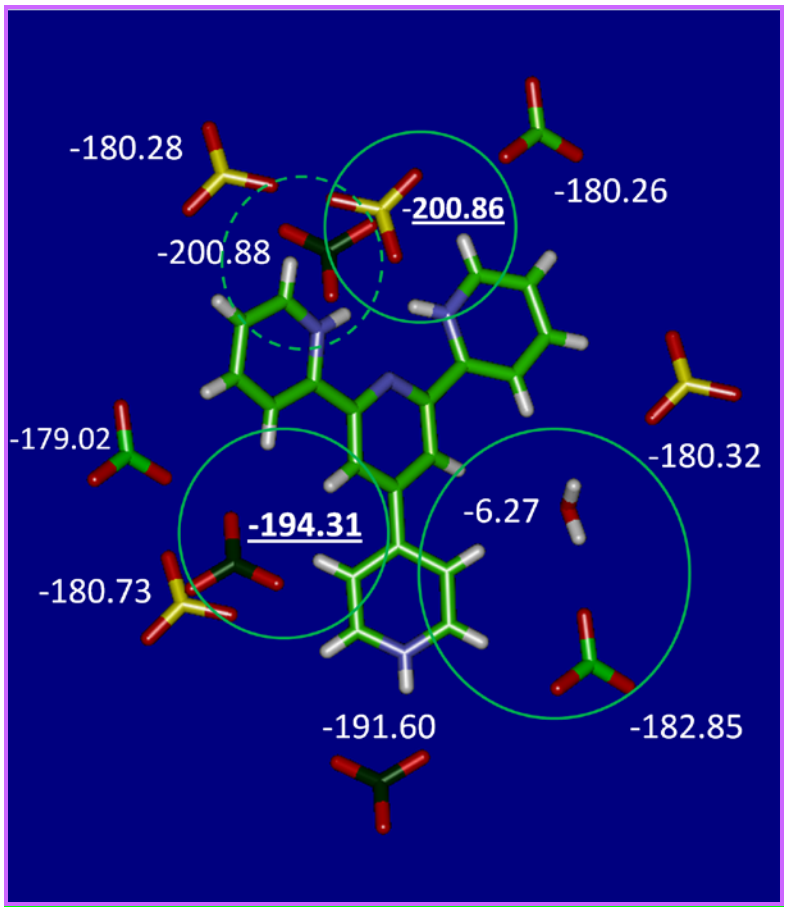

Fig. S3 Ten different non-π interactions around $PTPH_3$ in the crystal. Interactions with lowest interaction energies are circled.