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Periodate anion as halogen bond donor: Formation of anion···anion dimers and other adducts

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ELECTRONIC SUPPLEMENTARY INFORMATION

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S1. Materials and Methods.

S.1.1 Materials*.* All compounds were purchased from commercial suppliers (Sigma-Aldrich, TCI America) and used without further purification.

S.1.2 Characterization of the compounds.

General Remarks. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on Nuclear Magnetic Resonance Spectrometer AVANCE III, Bruker-BioSpin. All the chemical shifts are given in ppm. *DMSO-d6* was used as solvent in NMR spectra. FT-IR spectra were obtained using a Nicolet Nexus FT-IR spectrometer equipped with UATR unit.

*Synthesis of 4-Cyanopyridinium periodate (***1***).* 0.1 mmol of 4-cyanopyridine was added to an acetonitrile solution (3 mL) of H_5IO_6 (0.1 mmol) inside a clear borosilicate vial. Colourless crystals of **1** suitable for single crystal X-Ray diffraction with an elongated block shape were obtained within a week by slow evaporation of the solvent. FT-IR (selected bands, cm^{-1}) 3076, 2353, 2121, 1637, 1603, 1499, 1231, 1123, 983, 810, 734, 618. ^{1}H NMR (400.13 MHz, DMSO-d$_6$) δ 8.86 (dd), 7.89 (dd) ^{13}C NMR (100.613 MHz, DMSO-d$_6$) δ 151.2 (C$\underline{\text{C}}$N), 126.1 ($\underline{\text{C}}$CN), 119.9 ($\underline{\text{C}}$N), 117.2 ($\underline{\text{C}}$CCN).

*Synthesis of 3-Nitropyridinium periodate (***2***).* 0.1 mmol of 3-nitropyridine was added in a solution of HIO_4 (0.1 mmol in 3 mL) in acetonitrile inside a clear borosilicate vial. Colourless crystals of **2** suitable for single crystal X-Ray diffraction with an elongated block shape were obtained within a week by slow evaporation of the solvent. FT-IR (selected bands, cm^{-1}) 3110, 2365, 1637, 1608, 1543, 1525, 1365, 1346, 1102, 840, 816, 717, 663. ^{1}H NMR (400.13 MHz, DMSO-d$_6$) δ 9.38 (d), 8.98 (d), 8.62 (d), 7.75 (t) ^{13}C NMR (100.613 MHz, DMSO-d$_6$) δ 155.6 ($\underline{\text{C}}NO_2$), 145.0 (C$\underline{\text{C}}$N), 137.9 (C$\underline{\text{C}}$N), 132.0 ($\underline{\text{C}}$CN), 125.0 ($\underline{\text{C}}$CCN).

*Synthesis of 3-Carboxypyridinium periodate (***3***).* 0.1 mmol of nicotinic acid was added in a solution of HIO_4 (0.1 mmol in 3 mL) in acetonitrile inside a clear borosilicate vial. Yellow crystals of **3** suitable for single crystal X-Ray diffraction with an elongated block shape were obtained within a week by slow evaporation of the solvent. FT-IR (selected bands, cm^{-1}) 3098, 2359, 1718, 1637, 1602, 1528, 1475, 1427, 1304, 1215, 1184, 960, 831, 765, 740, 671. ^{1}H NMR (400.13 MHz, DMSO-d$_6$) δ 9.12 (brs), 8.86 (d), 8.42 (d), 7.71 (t), ^{13}C NMR (100.613 MHz, DMSO-d$_6$) δ 206.9 ($\underline{\text{C}}$O), 149.6 (C$\underline{\text{C}}$N), 147.3 (C$\underline{\text{C}}$N), 143.6 ($\underline{\text{C}}$CN), 138.8 ($\underline{\text{C}}$CN), 124.8 ($\underline{\text{C}}$CCN).

*Synthesis of 3-Fluoropyridinium periodate (***4***).* 0.1 mmol of 3-fluoropyridine was added in a solution of HIO_4 (0.1 mmol in 3 mL) in acetonitrile inside a clear borosilicate vial. White crystals of **4** suitable for single crystal X-Ray diffraction with an elongated block shape were obtained within a week by slow evaporation of the solvent. FT-IR (selected bands, cm^{-1}) 2835, 2355, 2118, 1635, 1541, 1474, 1271, 1229, 1106, 829, 768, 645. ^1H NMR (400.13 MHz, DMSO-d_6) δ 8.64 (d), 8.50 (dt), 7.81 (tdd), 7.56 (dt) ^{13}C NMR (100-613 MHz, DMSO-d_6) δ145.9 ($\underline{C}F$), 137.9 ($C\underline{C}N$), 137.7 ($C\underline{C}N$), 125.8 ($\underline{C}CF$), 124.4 ($\underline{C}CN$).

S2. Crystallographic Details.

S.2.1 General Remarks. The single crystal data of the compounds were collected at room temperature using a Bruker SMART APEX II CCD area detector diffractometer. Data collection, unit cell refinement and data reduction were performed using Bruker SAINT. Structures were solved by direct methods using SHELXT[1] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6[2]. Absorption correction was performed based on multi-scan procedure using SADABS. Structure analysis was aided by use of the programs PLATON[3]. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2\text{x}U_{eq}$ of the attached atom.

S.2.2 Crystallographic details and Figures of compounds 1-4

Table S.1. Crystal data and structure refinement for compound **1**.

Identification code	**1**
Empirical formula	$C_6H_5N_2O_4I$
Formula weight	296.02
Temperature/K	296(2)
Crystal system	monoclinic
Space group	P2(1)/c
a/Å	8.4965(7)
b/Å	20.5064(18)
c/Å	10.5561(9)
α/°	90
β/°	98.900(3)
γ/°	90
Volume/Å^3	1817.1(3)
Z	8
ρ_{calc}g/cm^3	2.164
μ/mm^{-1}	3.510
F(000)	1120.0
Crystal size/mm^3	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.852 to 65.218
Index ranges	$-12 \le h \le 11$, $-30 \le k \le 30$, $-16 \le l \le 14$
Reflections collected	22823
Independent reflections	6446 [R_{int} = 0.0272, R_{sigma} = 0.0303]
Data/restraints/parameters	6446/0/235
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0289, wR_2 = 0.0577
Final R indexes [all data]	R_1 = 0.0548, wR_2 = 0.0650
Largest diff. Peak/hole / e Å^{-3}	0.83/-0.75
CCDC Number	2168128

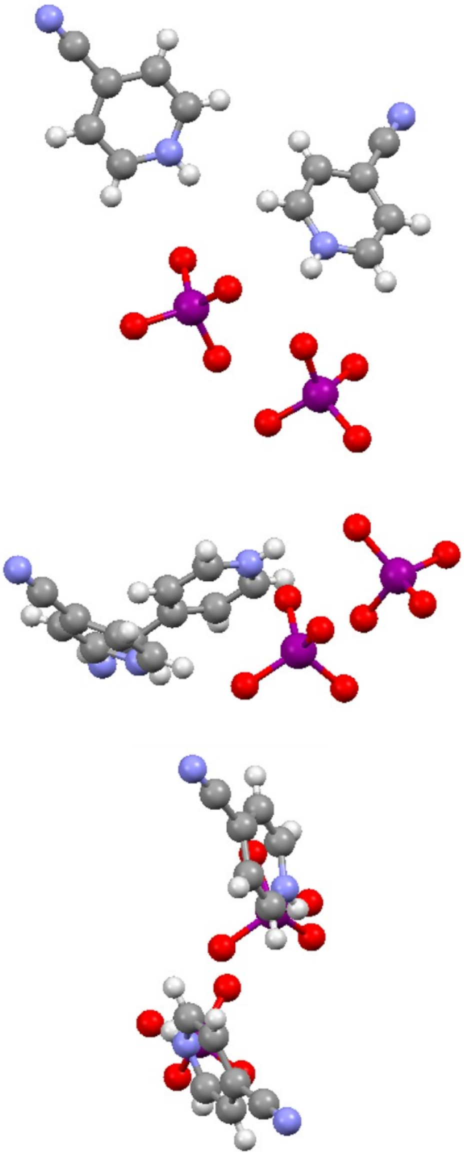

Figure S.1. Unit cell content of **1** along the three crystal axes; top *a*, middle *b*, bottom *c*. Colour code *grey* carbon, *whitish* hydrogen, *indigo* nitrogen, *red* oxygen, *purple* iodide.

Table S.2. Crystal data and structure refinement for compound **2**.

Identification code	**2**
Empirical formula	$C_5H_5N_2O_6I$
Formula weight	316.02
Temperature/K	296(2)
Crystal system	monoclinic
Space group	P2(1)/n
a/Å	5.6795(4)
b/Å	19.8304(14)
c/Å	8.0659(6)
α/°	90
β/°	99.643(2)
γ/°	90
Volume/Å^3	895.60(11)
Z	4
ρ_{calc}g/cm^3	2.344
μ/mm^{-1}	3.584
F(000)	600.0
Crystal size/mm^3	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.568 to 59.234
Index ranges	$-7 \leq h \leq 7$, $-24 \leq k \leq 27$, $-11 \leq l \leq 10$
Reflections collected	9764
Independent reflections	2519 [R_{int} = 0.0245, R_{sigma} = 0.0203]
Data/restraints/parameters	2519/0/147
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0208, wR_2 = 0.0467
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0479
Largest diff. Peak/hole / e Å^{-3}	0.43/-0.56
CCDC Number	2168129

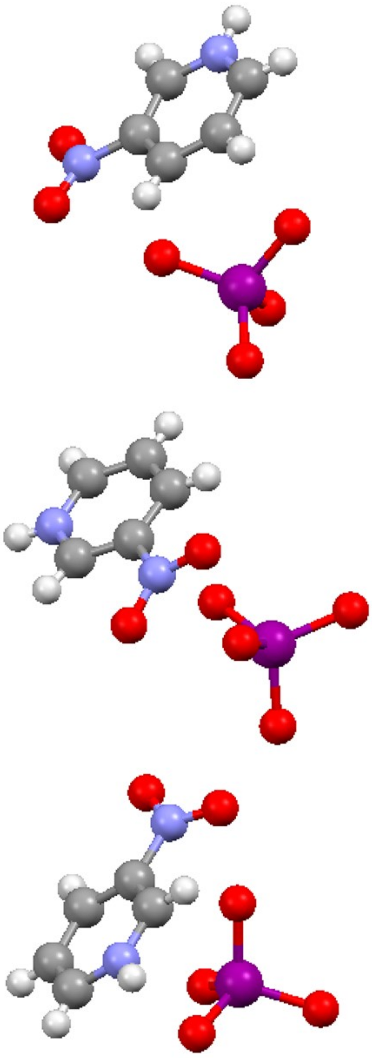

Figure S.2. Unit cell content of **2** along the three crystal axes; top *a*, middle *b*, bottom *c*. Colour code *grey* carbon, *whitish* hydrogen, *indigo* nitrogen, *red* oxygen, *purple* iodide.

Table S.3. Crystal data and structure refinement for compound **3**.

Identification code	**3**
Empirical formula	$C_6H_6NO_6I$
Formula weight	315.02
Temperature/K	296(2)
Crystal system	monoclinic
Space group	P2(1)/c
a/Å	5.5924(2)
b/Å	16.7630(6)
c/Å	10.0824(4)
α/°	90
β/°	102.879(2)
γ/°	90
Volume/Å^3	921.40(6)
Z	4
ρ_{calc}g/cm^3	2.271
μ/mm^{-1}	3.481
F(000)	600.0
Crystal size/mm^3	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.86 to 69.442
Index ranges	$-8 \le h \le 7$, $-23 \le k \le 25$, $-15 \le l \le 15$
Reflections collected	13469
Independent reflections	3476 [R_{int} = 0.0273, R_{sigma} = 0.0258]
Data/restraints/parameters	3476/0/147
Goodness-of-fit on F^2	0.867
Final R indexes [I>=2σ (I)]	R_1 = 0.0252, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1153
Largest diff. Peak/hole / e Å^{-3}	0.68/-0.79
CCDC Number	2168130

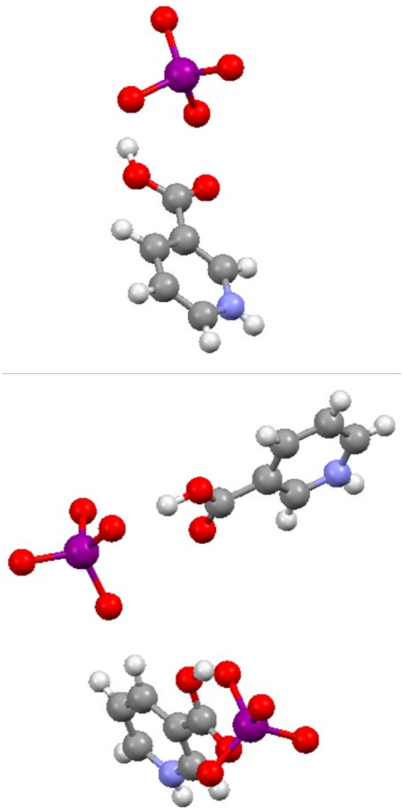

Figure S.3. Unit cell content of **3** along the three crystal axes; top *a*, middle *b*, bottom *c*. Colour code *grey* carbon, *whitish* hydrogen, *indigo* nitrogen, *red* oxygen, *purple* iodide.

Table S.4. Crystal data and structure refinement for compound **4**.

Identification code	**4**
Empirical formula	$C_5H_5NO_4FI$
Formula weight	289.00
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.5213(8)
b/Å	36.592(5)
c/Å	8.1602(11)
α/°	90
β/°	106.381(6)
γ/°	90
Volume/Å^3	1581.7(4)
Z	8
ρ_{calc}g/cm^3	2.427
μ/mm^{-1}	4.042
F(000)	1088.0
Crystal size/mm^3	0.08 x 0.07 x 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.226 to 59.442
Index ranges	$-7 \le h \le 7$, $-50 \le k \le 46$, $-11 \le l \le 10$
Reflections collected	17574
Independent reflections	4485 [R_{int} = 0.0300, R_{sigma} = 0.0267]
Data/restraints/parameters	4485/0/221
Goodness-of-fit on F^2	1.176
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0706
Final R indexes [all data]	R_1 = 0.0396, wR_2 = 0.0723
Largest diff. Peak/hole / e Å^{-3}	0.82/-1.30
CCDC Number	2168131

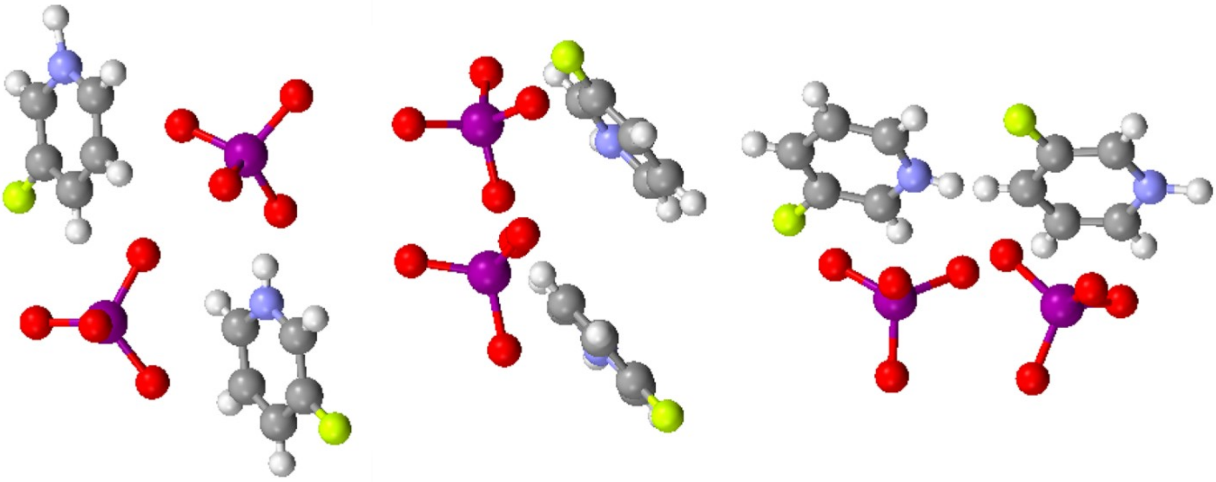

Figure S.4. Unit cell content of **4** along the three crystal axes; left *a*, middle *b*, right *c*. Colour code *gray* carbon, *whitish* hydrogen, *indigo* nitrogen, *red* oxygen, *purple* iodide, *yellow* fluoride.

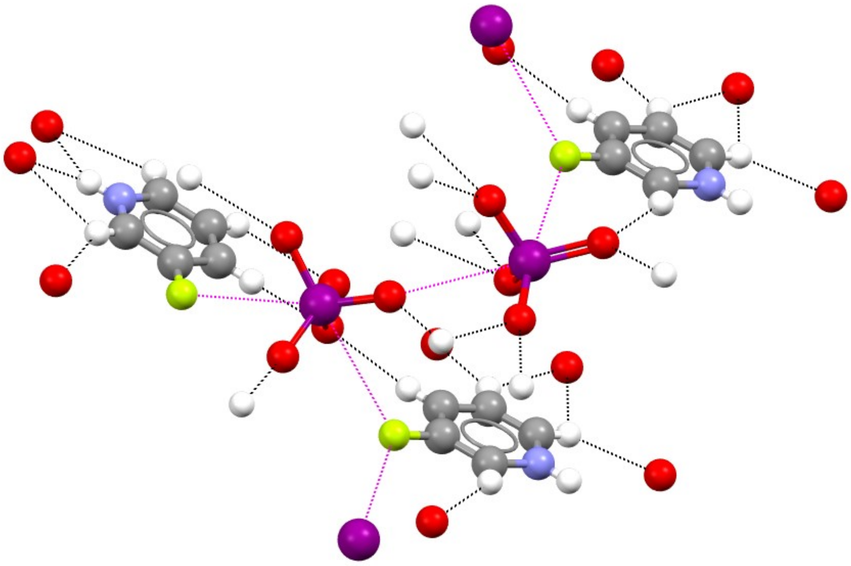

Figure S.5. Partial representation of the crystal packing of **4** evidencing the HaBs and the HBs (purple and black dotted lines, respectively) involving two halogen bonded periodate anions and halogen bonded fluoropyridines. Colour code *gray* carbon, *whitish* hydrogen, *indigo* nitrogen, *red* oxygen, *purple* iodide, *yellow* fluoride.

S3. CSD Surveys

Table S.5 Refcode of structures in the Cambridge Structural Database (CSD) containing the periodate anion; the search is set up with iodine bound to four oxygens by "any bond" and only one atom bound to each oxygen. In blue, hits displaying a contact between the iodine atom and a nucleophile (N, P, O, S, Se, F, Cl, Br, I considered) shorter than the sum of the respective van der Waals radii. According to Batsanov's[4] suggestion, the crystallographic vdW radius of iodine was set to 210 pm.

BUAMPI	**EVIHIC01**	**IHEGUZ**	**KEJTAX**	**ROSFAJ**	**VAVTAO**
CINBUW	**HAYHIY**	**IHEHAG**	**KEJTAX01**	**ROSFIR**	**WEMSUD**
CINBUW10	**HOHMOG**	**IKAMUD**	**LANNEU**	**ROSGAK**	**XOLXUU**
DEGGAX	**HOHMOG01**	**IVOMAI**	**MOHFAR**	**SOVYIL**	**YASKIP**
DOFNAN	**HOHMOG02**	**IZOHIP**	**NEGVAZ**	**UNUREB**	**YASKIP01**
DOFNAN01	**HOHMOG03**	**JOJYOY**	**NEGVAZ01**	**UYEMOB**	**ZZZUYA**
DOFNAN02	**HOHMOG04**	**JOJYOY01**	**OZEFOP**	**UYOBEQ**	**ZZZUYA01**
DOJCOU	**HOHMOG05**	**JOJYOY02**	**ROLRUI**	**UZUQUC**	**ZZZUYA02**
ECAFEW	**HOHMOG06**	**JOJZAL**	**ROQLIS**	**UZUREN**	
EVIHIC	**HOHMOG07**	**JOWRIY**	**ROSDOV**	**UZURIR**	

S4. Computational Details

The energetic features of the adducts analyzed in this work were calculated at the PBE0[5]-D3[6]/def2-TZVP[7] level of theory using either the crystallographic coordinates or fully optimized geometries. This level of theory has been used before[8,9,10] to analyze similar interactions and it has been proved to provide results similar to high level ab initio methods.[11] The GAUSSIAN-16 program has been used for the energetic calculations and NBO analysis.[12] The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method.[13] Molecular electrostatic potential (MEP) surfaces have been computed at the same level of theory and represented using several isovalues of electron density to map the electrostatic potential. The QTAIM analysis[14] has been performed using the AIMAll program at the same level of theory.[15]

In order to assess the nature of interactions in terms of being attractive or repulsive and revealed them in real space,[16] we have used NCIPLOT index, which is a method for plotting non-covalent interaction regions,[17] based on the NCI (Non-Covalent Interaction) visualization index derived from the electronic density.[18] The reduced density gradient (RDG), coming from the density and its first derivative, is plotted as a function of the density (mapped as isosurfaces) over the assembly of interest. The sign of the second Hessian eigenvalue times the electron density [i.e. sign(λ_2)ρ in atomic units] enables the identification of attractive/stabilizing (blue-green coloured isosurfaces) or repulsive (yellow-red coloured isosurfaces) interactions using 3D-Plots. For the plots shown in Figures 3 and 4 of the main text the NCIplot index parameters are: RGD = 0.45; ρ cut off = 0.04 a.u.; color range: –0.03 a.u. ≤ sign(λ_2)ρ ≤ 0.03 a.u.

Calculations of the tetrameric assemblies of 2 and 3 showing I···O HaBs

In compound **2** and **3**, tetramers held together by HBs and HaBs are observed in the solid state similar to that observed for compound **1** and analyzed in the main text (see Figure 3a). The tetramers are highlighted in Figure S5, evidencing that the formation energies (computed as dimers of the pyridinium periodate salts) are large and negative, similar to that od compound **1**. The dimerization energy of 2 is larger (in absolute value) likely due to the additional CH···O contacts.

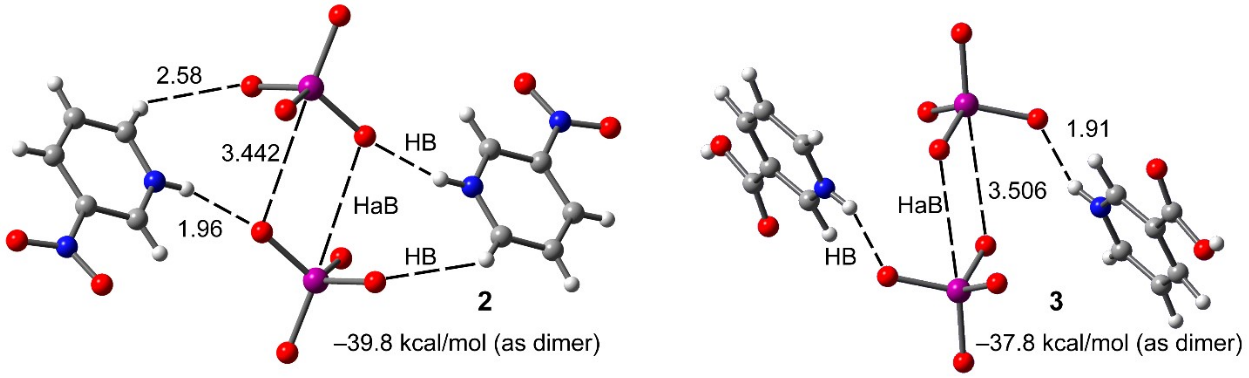

Figure S6. Tetramers of compounds **2** (left) and **3** (right) and their formation energies at the PBE0-D3/def2-TZVP level of theory. Distances in Å.

S.4.1 Cartesian Coordinates

1 (for MEP in Figure 2)

7	-1.161576	-1.035831	0.000000
1	-1.076467	0.032875	0.000000
7	-1.163859	-6.366330	0.000000
6	-1.156537	-1.703864	1.149157
1	-1.148103	-1.107086	2.054406
6	-1.156537	-1.703864	-1.149157
1	-1.148103	-1.107086	-2.054406
6	-1.159512	-5.215857	0.000000
6	-1.156537	-3.084249	1.201776
1	-1.152017	-3.602777	2.151131
6	-1.157918	-3.787455	0.000000
6	-1.156537	-3.084249	-1.201776
1	-1.152017	-3.602777	-2.151131
53	0.795049	2.044811	0.000000
8	1.685153	0.529619	0.000000
8	0.984816	2.978132	-1.468100
8	-0.973923	1.502300	0.000000
8	0.984816	2.978132	1.468100

3 (optimized Figure 4)

53	0.030373	-2.418706	0.000000
8	1.570308	-1.406872	0.000000
8	-0.847649	-2.066987	1.477834
8	0.685852	-4.042810	0.000000
8	-0.847649	-2.066987	-1.477834
6	-0.019222	2.915675	0.000000
6	0.175052	1.403809	0.000000
7	-1.524728	4.718932	0.000000
6	-1.309507	3.398152	0.000000
6	1.029551	3.822905	0.000000
6	-0.530409	5.624855	0.000000
1	-0.820745	6.666435	0.000000
6	0.771459	5.191463	0.000000
8	1.383128	1.046231	0.000000
8	-0.847649	0.733799	0.000000
1	-2.155813	2.720742	0.000000
1	1.436263	-0.338434	0.000000
1	2.039695	3.427926	0.000000
1	1.572081	5.919253	0.000000
1	-2.480447	5.050831	0.000000

S5. References

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