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Electronic Supplementary Information (ESI)

Pentavalent Phosphorus as a Unique Phosphorus Donor in $POCl_3$ Homodimer and $POCl_3$-H_2O Heterodimer: Matrix Isolation Infrared Spectroscopic and Computational Studies

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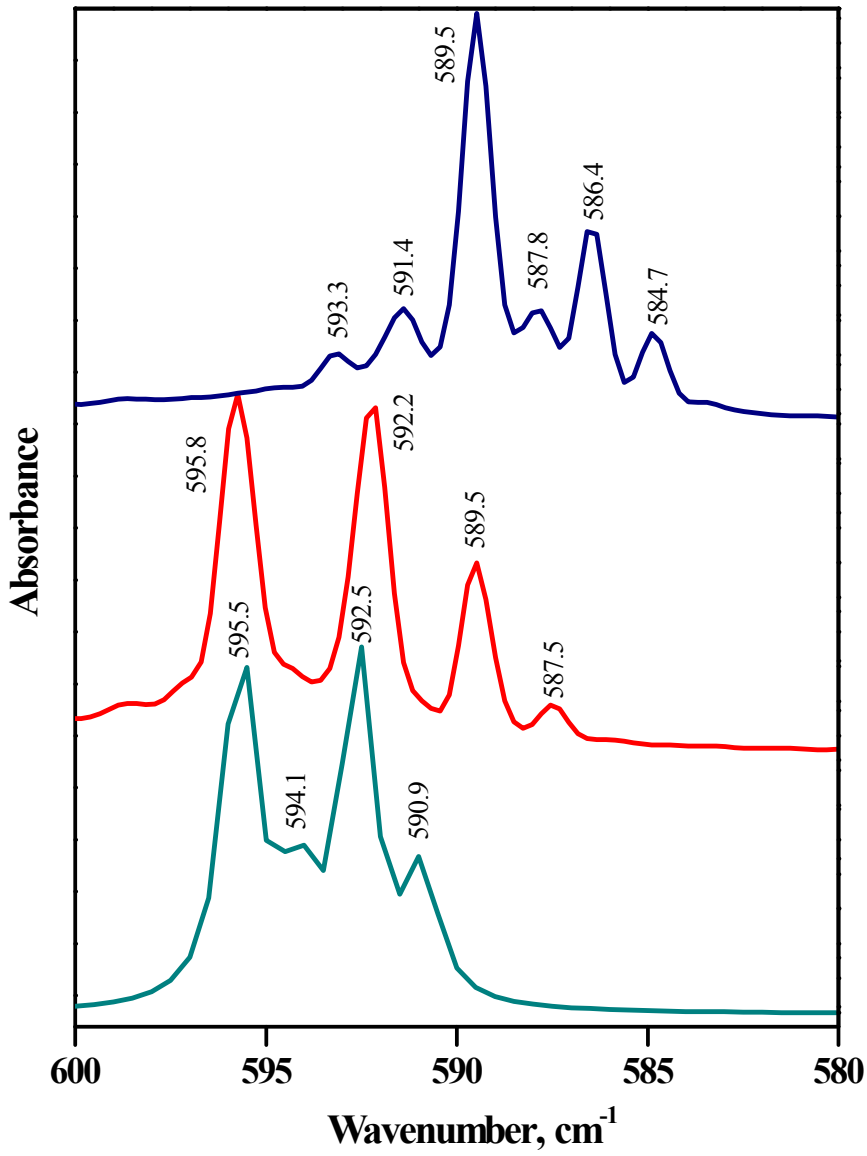


Figure S1. Infrared spectrum of antisymmetric P-Cl stretching region of $POCl_3$. a) simulated spectrum including Cl^{35}/Cl^{37} population; b) Ar matrix; c) N_2 matrix.

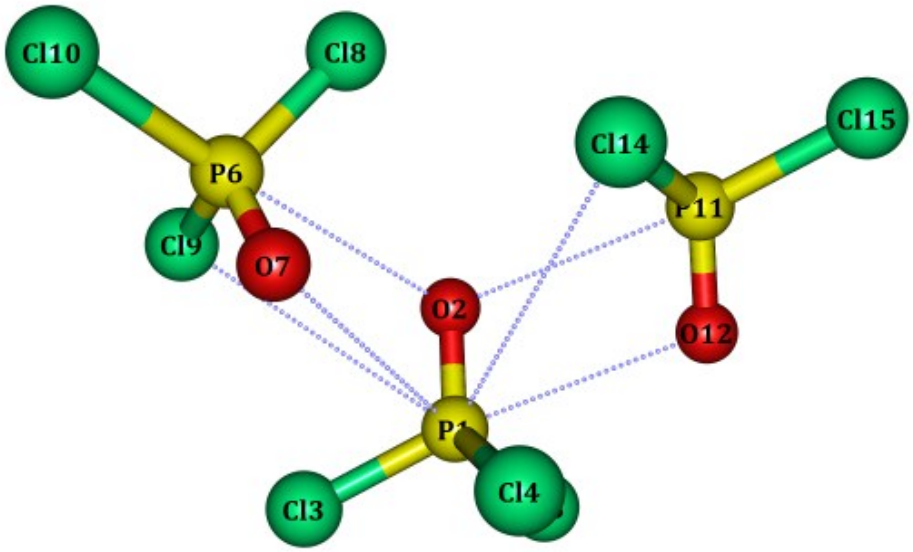
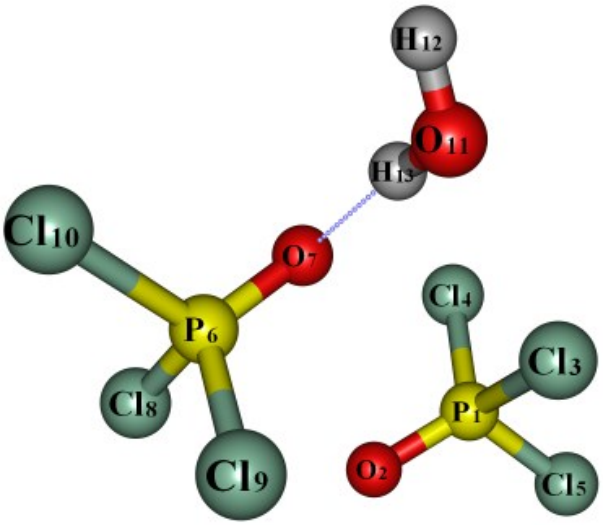
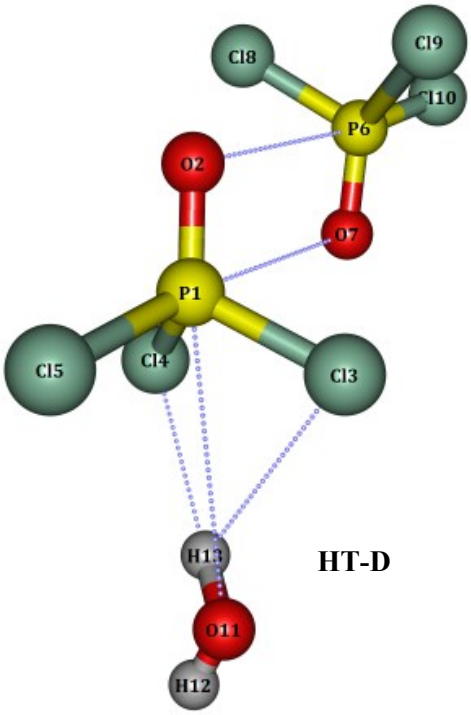


Figure S2. The structure of $POCl_3$ trimer optimized at MP2 level of theory with aug-cc-pVDZ basis set.



HT-C



HT-D

Figure S3. Computed structures of $(POCl_3)_2$ -H_2O heterotrimer optimized at MP2/aug-cc pVDZ level of theory.

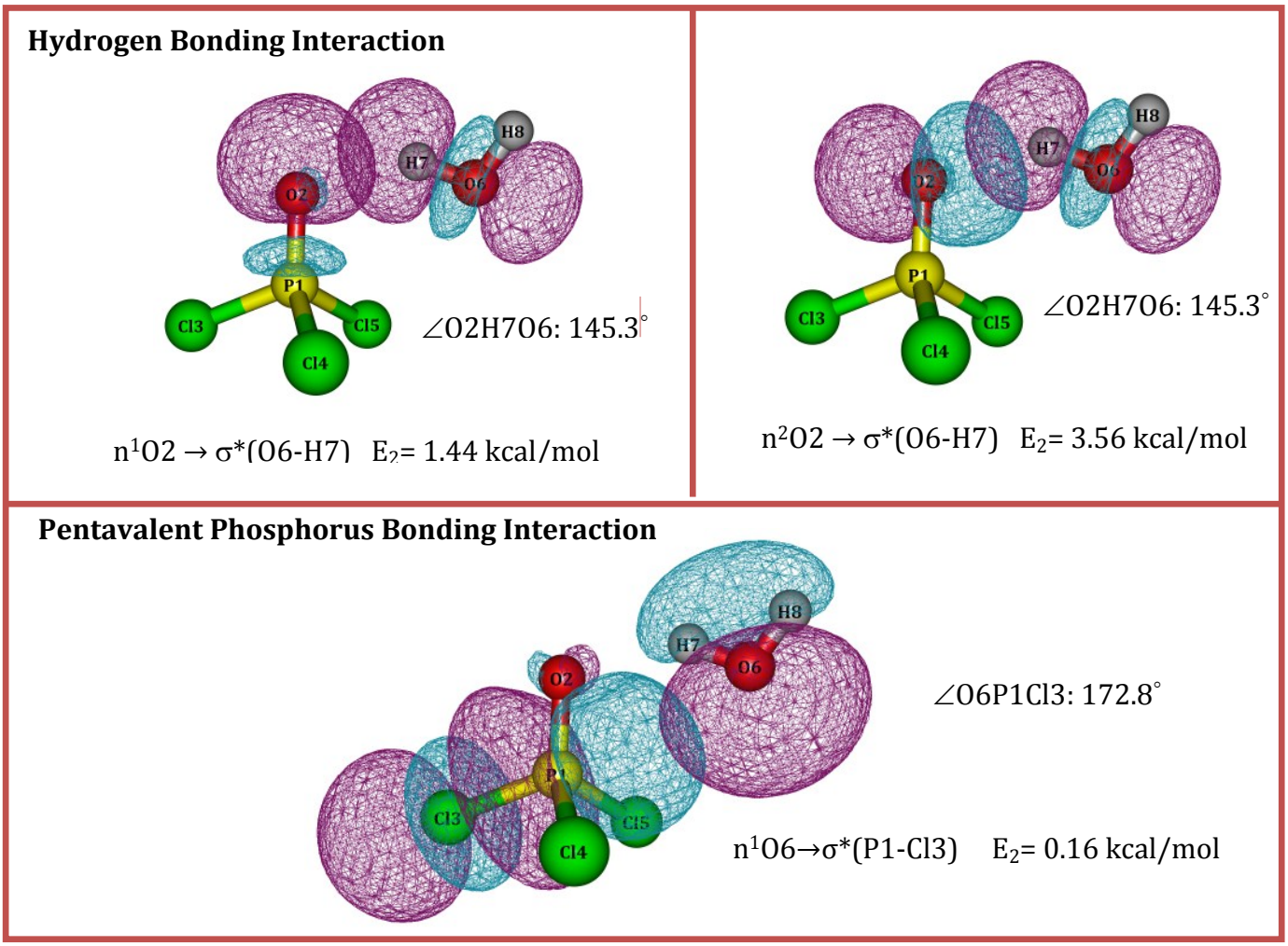


Figure S4. Orbital overlap view of different delocalization interaction of $POCl_3$–H_2O heterodimer A. The angle between the donor and acceptor orbitals along with E_2 energy is also shown.

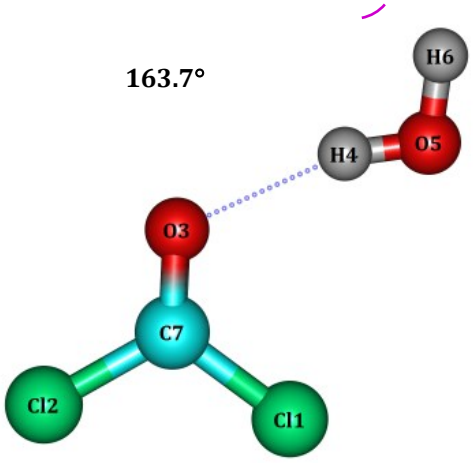
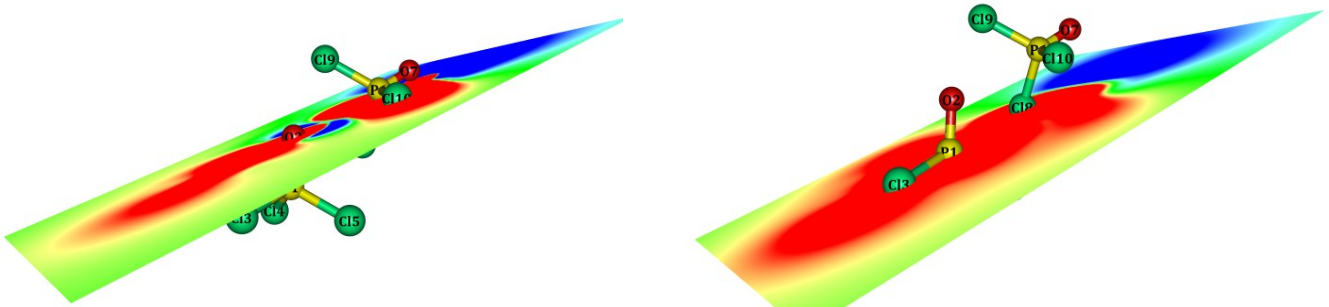
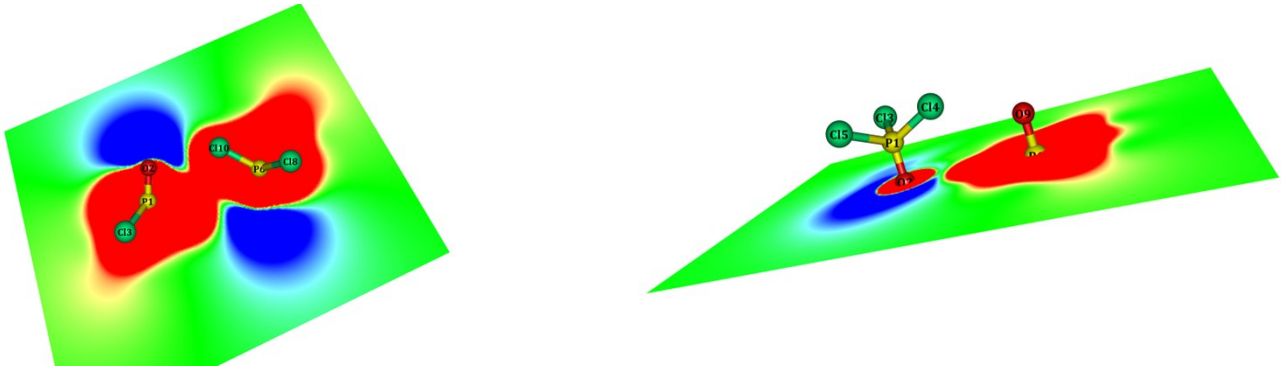


Figure S5. Computed structure of ($COCl_2$)-H_2O heterodimer optimized at MP2/aug-cc pVDZ level of theory.

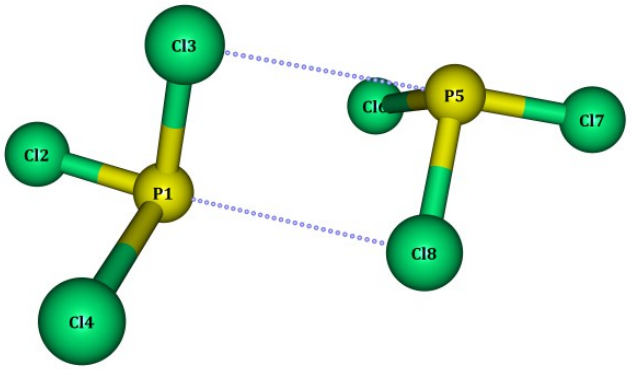


Dimer B



Dimer C

Figure S6. Molecular electrostatic potential $POCl_3$ dimer B and C, computed on the 0.001 au contour of the electronic density. Computations were performed at MP2 level of theory with aug-cc-pVDZ basis set.



Electrostatic: -5.03 kcal/mol (39 %)

Charge-Transfer: -3.04 kcal/mol (24 %)

Dispersion: -4.73 kcal/mol (37 %)

Pauli Repulsion: +10.23 kcal/mol

Figure S7. Global minimum structure of PCl_3 dimer optimized at MP2 level of theory with aug-cc-pVDZ basis set. The results of energy decomposition analysis of PCl_3 dimer at B3LYP-D3/TZ2P level of theory with ADF package.

Table S1. Computed and experimental vibrational wavenumbers, shifts in the wavenumbers and mode assignments for $POCl_3$-$(H_2O)_2$ heterotrimer B calculated at the MP2 level of theory using aug-cc-pVDZ basis set.

Computed Wavenumber[a] (cm^{-1})		Experimental Wavenumber (cm^{-1})				Mode Assignment
		N_2		**Ar**		
ν	**Δ ν**	**ν**	**Δ ν**	**ν**	**Δ ν**	
H_2O						
3803.3(4)	-	3635.3	-	3638.3	-	O-H symmetric stretch mode (ν_1) of H_2O
3937.5(67)	-	3727.6	-		-	O-H asymmetric stretch mode (ν_3) of H_2O
$POCl_3$						
1251.3(127)	-	1313.5/1310.8/ 1316.1	-	1315.6/1314.3/ 1312.8	-	P=O stretching mode (ν_1) in $POCl_3$
Heterotrimer B						
3785.3(15) 3684.2(216)	-18.3/- 119.1	-[b]	-	-[b]	-	O-H symmetric stretch mode (ν_1) of H_2O sub-molecule in trimer B
3915.4(125) 3892.5(94)	-22.1/-45	-[b]	-	-[b]	-	O-H asymmetric stretch mode (ν_3) of H_2O sub-molecule in trimer B
1247.8(138)	-3.6	-[b]	-	-[b]	-	P=O stretching mode (ν_1) in $POCl_3$ sub-molecule in trimer B

[a] Intensities, in km/mol given in parenthesis.

[b] Features not observed experimentally

Table S2. Electron occupancies of various NBOs of $POCl_3$ homodimers computed at MP2/aug-cc-pVDZ basis set. The donor–acceptor delocalization interaction and delocalization energies (E_2) are also shown.

Dimer	NBO	Occupancy	Donor-Acceptor delocalization interaction	E_2 (Kcal/mol)
Dimer A	n^1O2	1.97230(1.97348)[a]	$n^1O2 \rightarrow \sigma^*$(P6-Cl10)	0.42
	σ^*(P6-Cl10)	0.17015(0.17462)[b]		
	n^2O2	1.83192(1.97348)[a]	$n^2O2 \rightarrow \sigma^*$(P6-Cl10)	1.02
	σ^*(P6-Cl10)	0.17015(0.17462)[b]		
	n^2O2	1.83192(1.97348)[a]	$n^2O2 \rightarrow \sigma^*$(P6-O7)	0.30
	σ^*(P6-O7)	0.10198(0.09868)[b]		
	n^2O2	1.83192(1.97348)[a]	$n^2O2 \rightarrow \sigma^*$(P6-Cl8)	0.11
	σ^*(P6-Cl8)	0.16865(0.17462)[b]		
	n^2O2	1.83192(1.97348)[a]	$n^2O2 \rightarrow \sigma^*$(P6-Cl9)	0.11
	σ^*(P6-Cl9)	0.16865(0.17462)[b]		
	σ^*(P1-Cl5)	0.17018(0.17462)[a]	σ^*(P1-Cl5) $\rightarrow \sigma^*$(P6-O7)	0.07
	σ^*(P6-O7)	0.10198(0.09868)[b]		
	n^1O7	1.97229(1.97348)[b]	$n^1O7 \rightarrow \sigma^*$(P6-Cl5)	0.43
	σ^*(P1-Cl5)	0.17018(0.17462)[a]		
	n^2O7	1.83192(1.97348)[b]	$n^2O7 \rightarrow \sigma^*$(P6-Cl5)	1.03
	σ^*(P1-Cl5)	0.17018(0.17462)[a]		
	n^2O7	1.83192(1.97348)[b]	$n^2O7 \rightarrow \sigma^*$(P1-O2)	0.30
	σ^*(P1-O2)	0.10198(0.09868)[a]		
	n^2O7	1.83192(1.97348)[b]	$n^2O7 \rightarrow \sigma^*$(P1-Cl4)	0.12
	σ^*(P1-Cl4)	0.16865(0.17462)[b]		
	n^2O7	1.83192(1.97348)[b]	$n^2O7 \rightarrow \sigma^*$(P1-Cl3)	0.12
	σ^*(P1-Cl3)	0.16865(0.17462)[a]		
	σ^*(P6-Cl10)	0.17015(0.17462)[b]	σ^*(P6-Cl10) $\rightarrow \sigma^*$(P1-O2)	0.07

	σ*(P1-O2)	0.10198(0.09868) [a]		
Dimer B	n^1O2	1.97293(1.97348) [a]	n^1O2→ σ*(P6-O7)	0.06
	σ*(P6-O7)	0.10083(0.09868)[b]		
	n^2O2	1.82457(1.81998)[a]	n^2O2→σ*(P6-O7)	0.19
	σ*(P6-O7)	0.10083(0.09868)[b]		
	σ*(P1-O2)	0.10083(0.09868)[a]	σ*(P1-O2) →σ*(P6-O7)	0.19
	σ*(P6-O7)	0.10083(0.09868)[b]		
	n^2Cl8	1.95450(1.95547)[b]	n^2Cl8→σ*(P1-O2)	0.18
	σ*(P1-O2)	0.10083(0.09868)[a]		
	n^2Cl8	1.95450(1.95547)[b]	n^2Cl8→σ*(P1-Cl3)	0.49
	σ*(P1-Cl3)	0.17151(0.17462)[a]		
	n^2Cl9	1.95499(1.95547)[b]	n^2Cl9→σ*(P1-O2)	0.13
	σ*(P1-O2)	0.10083(0.09868)[a]		
	n^2Cl10	1.95460(1.95547)[b]	n^2Cl10→σ*(P1-O2)	0.08
	σ*(P1-O2)	0.10083(0.09868)[a]		
	n^3Cl8	1.95558(1.95547)[b]	n^3Cl8→σ*(P1-Cl3)	0.05
	σ*(P1-Cl3)	0.17151(0.17462)[a]		
Dimer C	n^2O2	1.82694(1.81998)[a]	n^2O2→σ*(P6-Cl10)	0.16
	σ*(P6-Cl10)	0.16631(0.17462)[b]		
	n^2Cl4	1.95104(1.95547)[a]	n^2Cl4→ σ*(P6-O9)	0.06
	σ*(P6-O9)	0.10047(0.09868)[b]		
	n^2O9	1.82698(1.81998)[a]	n^2O9→ σ*(P1-Cl4)	0.15
	σ*(P1-Cl4)	0.16638(0.17462)[b]		
	n^2Cl10	1.95102(1.95547)[a]	n^2Cl10→ σ*(P1-O2)	0.06
	σ*(P1-O2)	0.10049(0.09868)[b]		

[a] Occupancy of monomeric $POCl_3$ I is given in parentheses.
[b] Occupancy of monomeric $POCl_3$ II is given in parentheses.

Table S3. Second order perturbation energies (E_2) of $POCl_3$ homodimers classified into phosphorus and halogen bonding interactions.

Dimer	Phosphorus bonding		Halogen bonding	
	Interaction between donor and acceptor orbitals	**Interaction (E_2) energy (kcal/mol)**	**Interaction between donor and acceptor orbitals**	**Interaction (E_2) energy (kcal/mol)**
Dimer A	$n^1O2 \rightarrow \sigma^*$(P6-Cl10)	0.42	---	
	$n^2O2 \rightarrow \sigma^*$(P6-Cl10)	1.02		
	$n^2O2 \rightarrow \sigma^*$(P6-O7)	0.30		
	$n^1O7 \rightarrow \sigma^*$(P6-Cl5)	0.43		
	$n^2O7 \rightarrow \sigma^*$(P6-Cl5)	1.03		
	$n^2O7 \rightarrow \sigma^*$(P1-O2)	0.30		
	$n^2O2 \rightarrow \sigma^*$(P6-Cl8)	0.11		
	$n^2O2 \rightarrow \sigma^*$(P6-Cl9)	0.11		
	$n^2O7 \rightarrow \sigma^*$(P1-Cl4)	0.12		
	$n^2O7 \rightarrow \sigma^*$(P1-Cl3)	0.12		
Total		***3.53***		***0.46***
Dimer B	$n^1O2 \rightarrow \sigma^*$(P6-O7)	0.06	$n^2Cl9 \rightarrow \sigma^*$(P1-O2)	0.13
	$n^2O2 \rightarrow \sigma^*$(P6-O7)	0.19	$n^2Cl10 \rightarrow \sigma^*$(P1-O2)	0.08
	$n^2Cl8 \rightarrow \sigma^*$(P1-O2)	0.18		
	$n^2Cl8 \rightarrow \sigma^*$(P1-Cl3)	0.49		
	$n^3Cl8 \rightarrow \sigma^*$(P1-Cl3)	0.05		
Total		***0.97***		***0.21***
Dimer C	$n^2O2 \rightarrow \sigma^*$(P6-Cl10)	0.16	$n^2Cl4 \rightarrow \sigma^*$(P6-O9)	0.06
	$n^2O9 \rightarrow \sigma^*$(P1-Cl4)	0.15	$n^2Cl10 \rightarrow \sigma^*$(P1-O2)	0.06
Total		***0.31***		***0.12***

Table S4. Electron occupancies of various NBOs of $POCl_3$-H_2O heterodimers computed at MP2/aug-cc-pVDZ basis set. The donor-acceptor delocalization interaction and delocalization energies (E_2) are also shown.

Heterodimer	NBO	Occupancy	Donor-Acceptor delocalization interaction	E_2 (Kcal/mol)
Heterodimer A	n^1O2	1.82411(1.97598)[a]	$n^1O2 \rightarrow \sigma^*$(O6-H7)	1.44
	σ^*(O6-H7)	0.00609(0.00001)[b]		
	n^2O2	1.83187(1.81998) [a]	$n^2O2 \rightarrow \sigma^*$(O6-H7)	3.56
	σ^*(O6-H7)	0.00609(0.00001)[b]		
	n^1Cl4	1.98780(1.98853) [a]	$n^1Cl4 \rightarrow \sigma^*$(O6-H7)	0.05
	σ^*(O6-H7)	0.00609(0.00001)[b]		
	n^1Cl5	1.98779(1.98853) [a]	$n^1Cl5 \rightarrow \sigma^*$(O6-H7)	0.05
	σ^*(O6-H7)	0.00609(0.00001)[b]		
	σ^*(P1-O2)	0.10263(0.08571)[a]	σ^*(P1-O2)$\rightarrow\sigma^*$(O6-H7)	0.21
	σ^*(O6-H7)	0.00609(0.00001)[b]		
	σ (O6-H7)	1.99803(1.99918)[b]	σ (O6-H7) $\rightarrow \sigma^*$(P1-O2)	0.10
	σ^*(P1-O2)	0.10263(0.08571)[a]		
	σ (O6-H7)	1.99803(1.99918)[b]	σ (O6-H7)$\rightarrow\sigma^*$(P1-Cl3)	0.11
	σ^*(P1-Cl3)	0.16773(0.17462) [a]		
	σ (O6-H8)	1.99858(1.99918) [b]	σ (O6-H8)$\rightarrow\sigma^*$(P1-O2)	0.09
	σ^*(P1-O2)	0.10263(0.08571)[a]		
	n^1O6	1.99739(1.99747)[b]	$n^1O6 \rightarrow \sigma^*$(P1-Cl3)	0.16
	σ^*(P1-Cl3)	0.16773(0.17462) [a]		
Heterodimer B	n^3Cl3	1.95756(1.95358)[a]	$n^3Cl3 \rightarrow$ σ * (O6-H8)	1.92
	σ * (O6-H8)	0.00279(0.00002)[b]		
	n^2Cl5	1.95206(1.95547)[a]	$n^2Cl5 \rightarrow$ σ * (O6-H7)	0.08
	σ * (O6-H7)	0.00035(0.00002)[b]		

Table S5. Energy decomposition analysis (EDA) of $POCl_3$ homodimers and $POCl_3$-H_2O heterodimers using B3LYP-GD3/TZ2P level of theory using ADF package. Percentage contribution to total attractive interactions is shown in parenthesis.

Dimers	Electrostatic	Orbital	Dispersion	Pauli Repulsion	Total Binding Energy
$POCl_3$ Dimer					
Dimer A	-9.54 (54%)	-2.51 (14%)	-5.64 (32%)	+12.04	-5.65
Dimer B	-4.28 (39%)	-1.29 (12%)	-5.44 (49%)	+7.68	-3.33
Dimer C	-3.62 (47%)	-0.96 (12%)	-3.16 (41%)	+4.46	-3.28
$POCl_3$-H_2O heterodimer					
HD-A	-6.98 (60%)	-2.80 (24%)	-1.83 (16%)	+6.43	-5.18
HD-B	-1.47 (31%)	-1.28 (27%)	-2.03 (42%)	+2.97	-1.81