Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# SUPPLEMENTARY INFORMATION

# Aerogen Bonds Formed between $AeOF_2$ (Ae = Kr, Xe) and Diazines: Comparisons between σ-Hole and π-Hole Complexes

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Table S1. vdW and covalent radii of the N, Kr and Xe atoms, in Å

| | vdW[a] | vdW[b] | Covalent radii[c] |
|---|---|---|---|
| N | 1.55 | 1.66 | 0.71 |
| Kr | 2.02 | 2.25 | 1.16 |
| Xe | 2.16 | 2.06 | 1.40 |
| F | 1.47 | 1.46 | |
| H | 1.20 | 1.20 | |
| O | 1.52 | 1.50 | |
| Sum N…Kr | 3.57 | 3.91 | 1.87 |
| Sum N…Xe | 3.71 | 3.72 | 2.11 |
| Sum F…H | 2.67 | 2.66 | |
| Sum O…H | 2.72 | 2.70 | |

[a] from ref. [83]
[b] from ref. [84]
[c] from ref. [85]

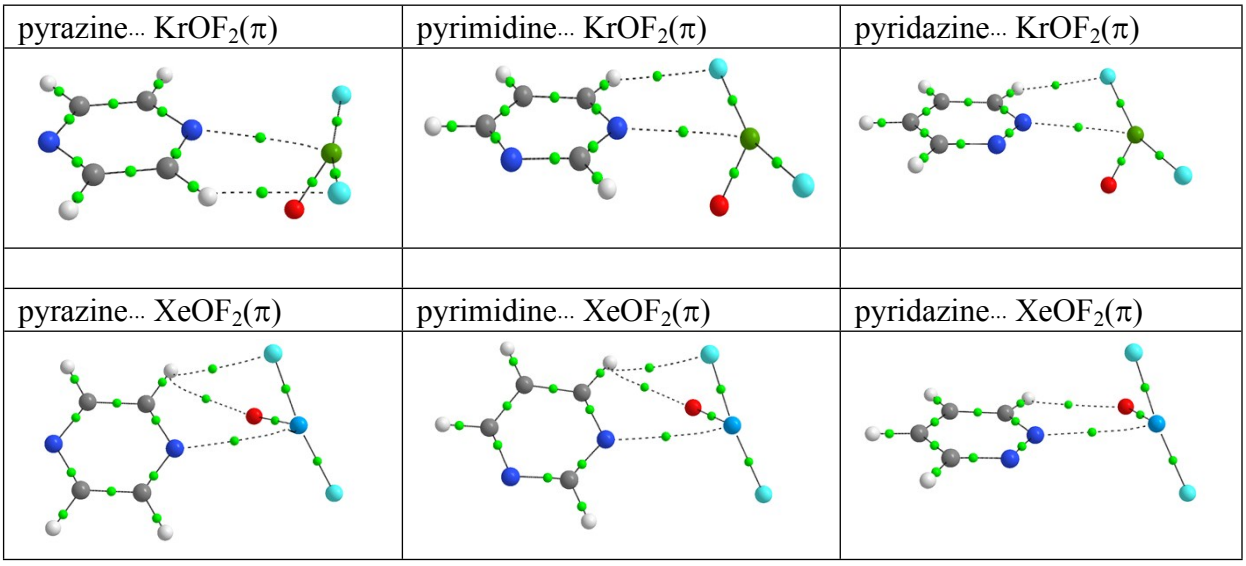


Fig. S1 AIM molecular graphs of π-hole bonded $AeOF_2$ (Ae = Kr, Xe) complexes with diazines. Small green dots represent critical points. Results obtained at the MP2/aug-cc-pVDZ level.

TABLE S2. Second-order NBO perturbation energies ($E^2$) for charge transfer between indicated orbitals in π-hole bonded $AeOF_2$ (Ae = Kr, Xe) complexes with diazines (kcal $mol^{-1}$). Results obtained at DFT level.

| System | LP(N1)→σ*AeF2 | LP(F1)→σ*C2H2 | LP(O)→RyN1 |
|---|---|---|---|
| pyrazine···$KrOF_2$(π) | 2.28 | 0.58 | - |
| pyrimidine···$KrOF_2$(π) | 2.48 | 0.61 | - |
| pyridazine···$KrOF_2$(π)[a] | 2.00 | 0.72 | - |
| pyrazine···$XeOF_2$(π) | 2.04[a] | 0.33 | 0.15 |
| pyrimidine···$XeOF_2$(π) | 1.69[a] | 0.35 | 0.20 |
| pyridazine···$XeOF_2$(π) | 0.41 | - | 0.26 |

[a] transfer into unfilled valence nonbonding orbital.

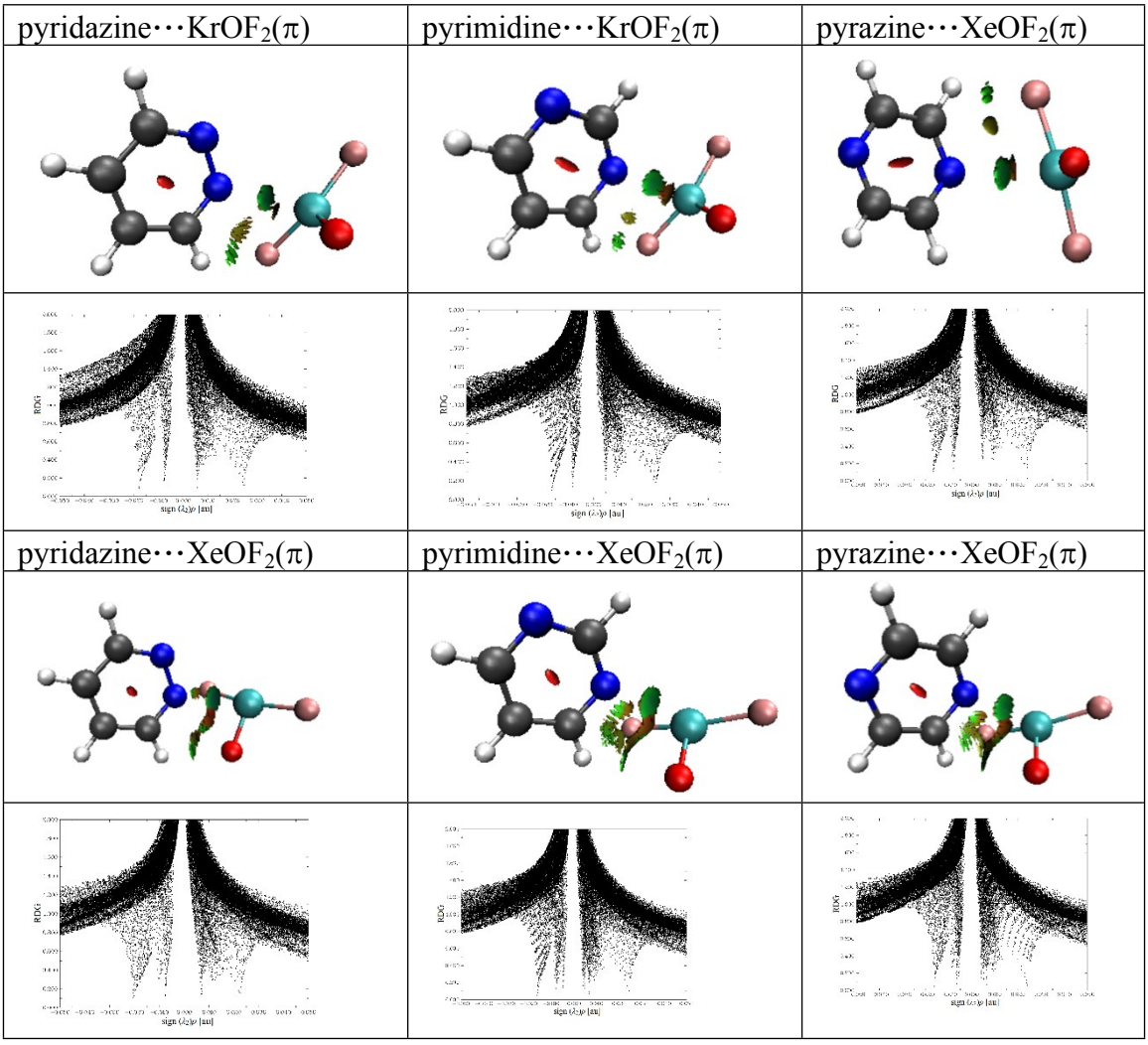


Fig. S2 Plots of the RDG versus sign ($\lambda_2$)$\rho$ and noncovalent interaction regions (bonding isosurfaces are illustrated as green and blue disks while red parts represent repulsive forces) for the π-hole bonded $AeOF_2$ (Ae=Kr, Xe) complexes with diazines.

TABLE S3. EDA/BLYP/ZORA/TZ2P decomposition of the total DFT-D interaction energy (ΔE) of σ-complexes into Pauli repulsion ($E_{Pauli}$), electrostatic ($E_{elstat}$) orbital interaction ($E_{oi}$) and dispersion ($E_{disp}$) terms. All energies in kcal $mol^{-1}$. The values in percent express the contribution to the sum of all attractive energy terms.

| | ΔE | $E_{Pauli}$ | $E_{elec}$ | % | $E_{oi}$ | % | $E_{disp}$ | % |
|---|---|---|---|---|---|---|---|---|
| pyrazine··· $KrOF_2$ | -6.60 | 9.54 | -9.75 | 60 | -3.09 | 19 | -3.30 | 20 |
| pyrimidine··· $KrOF_2$ | -6.75 | 9.57 | -9.91 | 61 | -3.14 | 19 | -3.28 | 20 |
| pyridazine··· $KrOF_2$ | -8.27 | 10.77 | -11.21 | 59 | -4.56 | 24 | -3.27 | 17 |
| pyrazine··· $XeOF_2$ | -6.87 | 11.25 | -10.37 | 57 | -3.68 | 20 | -4.07 | 22 |
| pyrimidine··· $XeOF_2$ | -7.01 | 11.13 | -10.31 | 57 | -3.66 | 20 | -4.16 | 23 |
| pyridazine··· $XeOF_2$ | -8.82 | 13.24 | -13.36 | 61 | -4.88 | 22 | -3.82 | 17 |

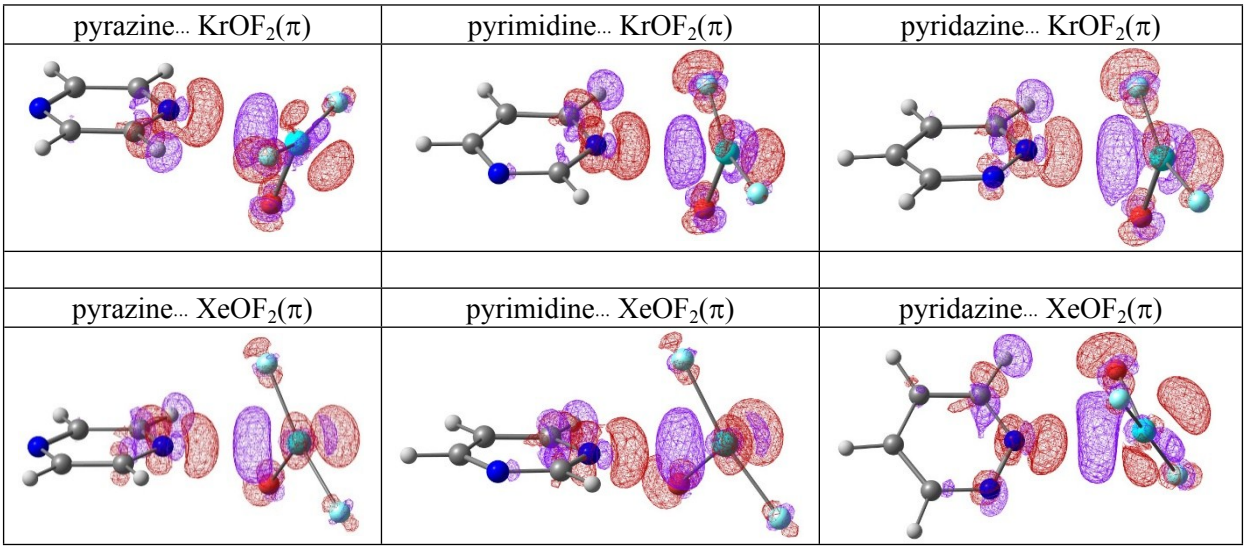


Fig. S3 Electron density shift in π-hole bonded $AeOF_2$ (Ae = Kr, Xe) complexes with diazines. The brown isosurface represents the regions in which electron density is increased as a result of complex formation (+0.001 a.u.), while the purple contour denotes decrease (-0.001 a.u.). Results obtained at the MP2/aug-cc-pVDZ level.