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H-bonding on spin centres enhances spin-spin coupling of organic diradicals

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Table S1. The bend angle of the acetylene bridge for **mNO-NO-HX** and **p-NN-NO-HX** as a result of the HX interactions.

Table S2. The intermolecular HB distance for HB from X of the HB donor to H atom of phenylene for **mNO-NO-HX** and **p-NN-NO-HX**.

Table S3. Summary of calculated energies for the Triplet (**T**) and Broken Symmetry (**BS**) State of **mNO-NO**, **pNN-NO**, and its HB complexes and the corresponding **$<S^2>$** values of each states.

Table S4. HOMO, LUMO and HOMO-LUMO gaps of **mNO-NO**, **pNN-NO**, and its HB complexes calculated at B3LYP/6-311++G(d,p).

Table S5. Mulliken spin density on HB donor sites for **mNO-NO-HX** and **p-NN-NO-HX**. H* refers to the hydrogen atom which is involved in HB with the NO group.

Figure S1. Spin density distribution plots of diradicals **mNO-NO** and **pNN-NO** and their HB complexes with various HX.

Figure S2. HOMO/HOMO-1 or SOMO(α)/SOMO(β) maps for the ground states (**T**) of **mNO-NO** and its H-Bonded complexes.

Figure S3. HOMO/HOMO-1 or SOMO(α)/SOMO(β) maps for the ground states (**T**) of **pNN-NO** and its H-Bonded complexes.

Figure S4. RDG isosufaces (RDG = 0.500 a.u.) for mNO-NO-HX and pNN-NO-HX (HX = NH_3, H_2O, HF, HCl and HBr). Blue-green-red color scaling range is -0.035 a.u (blue) < sign(λ_2)ρ < 0.02 a.u. (red).

Table S1. The bend angle of the acetylene bridge for **mNO-NO-HX** and **p-NN-NO-HX** as a result of the HX interactions. The change is shown in the parentheses.

HB donor	**mNO-NO-HX**	**pNN-NO-HX**
None	179.425	179.818
NH_3	177.494 (1.931)	177.470 (2.348)
H_2O	176.738 (2.687)	176.410 (3.408)
HF	176.123 (3.302)	175.483 (4.335)
HCl	178.672 (0.753)	178.085 (1.733)
HBr	179.094 (0.331)	178.650 (1.168)

Table S2. The intermolecular HB distance for HB from X of the HB donor to H atom of phenylene for **mNO-NO-HX** and **p-NN-NO-HX**.

HB donor	**mNO-NO-HX**	**pNN-NO-HX**
None	-	-
NH_3	2.380	2.440
H_2O	2.342	2.384
HF	2.564	2.544
HCl	2.952	2.959
HBr	3.039	3.059

Table S3. Summary of calculated energies for the Triplet (**T**) and Broken Symmetry (**BS**) State of **mNO-NO**, **pNN-NO**, and its HB complexes and the corresponding **$<S^2>$** values of each states.

Diradical/complex	**Energy (T), (Hartree)**	**$<S^2>_T$**	**Energy (BS), (Hartree)**	**$<S^2>_{BS}$**
mNO-NO	-959.16026580	2.039923	-959.15927920	1.021052
mNO-NO-NH_3	-1015.75380040	2.040497	-1015.75278610	1.021509
mNO-NO-H_2O	-1035.63338940	2.041375	-1035.63233350	1.021852
mNO-NO-HF	-1059.66277080	2.042534	-1059.66165110	1.022188
mNO-NO-HCl	-1420.01024280	2.042128	-1420.00914860	1.022019
mNO-NO-HBr	-3533.92783460	2.042118	-3533.92674300	1.022034
pNN-NO	-1205.30075340	2.109862	-1205.29932420	1.075631
pNN-NO-NH_3	-1261.89430120	2.110110	-1261.89283920	1.075929
pNN-NO-H_2O	-1281.77415470	2.111285	-1281.77261170	1.076052
pNN-NO-HF	-1305.80426620	2.113723	-1305.80259550	1.076987
pNN-NO-HCl	-1666.15140400	2.113535	-1666.14976430	1.076954
pNN-NO-HBr	-3780.06885600	2.113575	-3780.06721470	1.076924

Table S4. HOMO, LUMO and HOMO-LUMO gaps of **mNO-NO**, **pNN-NO**, and its HB complexes calculated at B3LYP/6-311++G(d,p).

Diradical/complex	**HOMO (eV)**	**LUMO (eV)**	**HOMO-LUMO gap (eV)**
mNO-NO	-5.5035	-2.8515	2.6520
mNO-NO-NH_3	-5.3868	-2.8452	2.5416
mNO-NO-H_2O	-5.4153	-3.0020	2.4133
mNO-NO-HF	-5.5155	-3.3301	2.1854
mNO-NO-HCl	-5.5552	-3.3013	2.2539
mNO-NO-HBr	-5.5612	-3.2934	2.2678
pNN-NO	-5.4066	-2.9987	2.4079
pNN-NO-NH_3	-5.3383	-3.0158	2.3225
pNN-NO-H_2O	-5.3642	-3.1680	2.1962
pNN-NO-HF	-5.4542	-3.4627	1.9915
pNN-NO-HCl	-5.4730	-3.4531	2.0199
pNN-NO-HBr	-5.4766	-3.4545	2.0221

Table S5. Mulliken spin density on HB donor sites for **mNO-NO-HX** and **p-NN-NO-HX**. H* refers to the hydrogen atom which is involved in HB with the NO group.

HB donor		**mNO-NO-HX**	**pNN-NO-HX**
NH_3	N	0.004680	0.004210
	H*	-0.006274	-0.006220
	H	-0.000047	-0.000022
	H	-0.000044	-0.000069
H_2O	O	0.004351	0.004188
	H*	-0.009542	-0.009594
	H	-0.000401	-0.000253
HF	F	0.003752	0.003574
	H*	-0.014272	-0.013833
HCl	Cl	0.000920	0.000607
	H*	-0.005070	-0.004931
HBr	Br	-0.001872	-0.001674
	H*	-0.001372	-0.002060

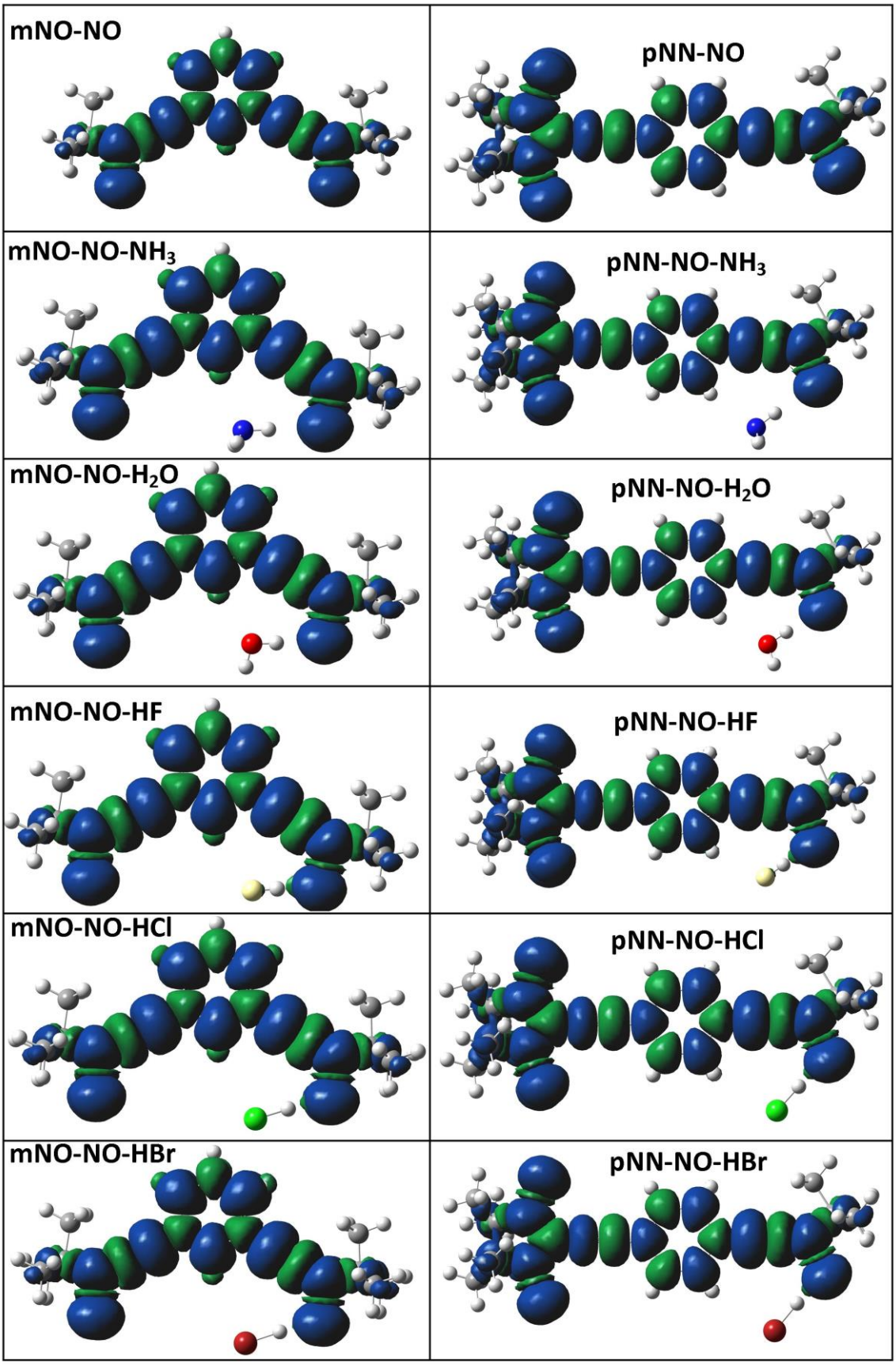

Figure S1. Spin density distribution plots of diradicals **mNO-NO** and **pNN-NO** and their HB complexes with various HX.

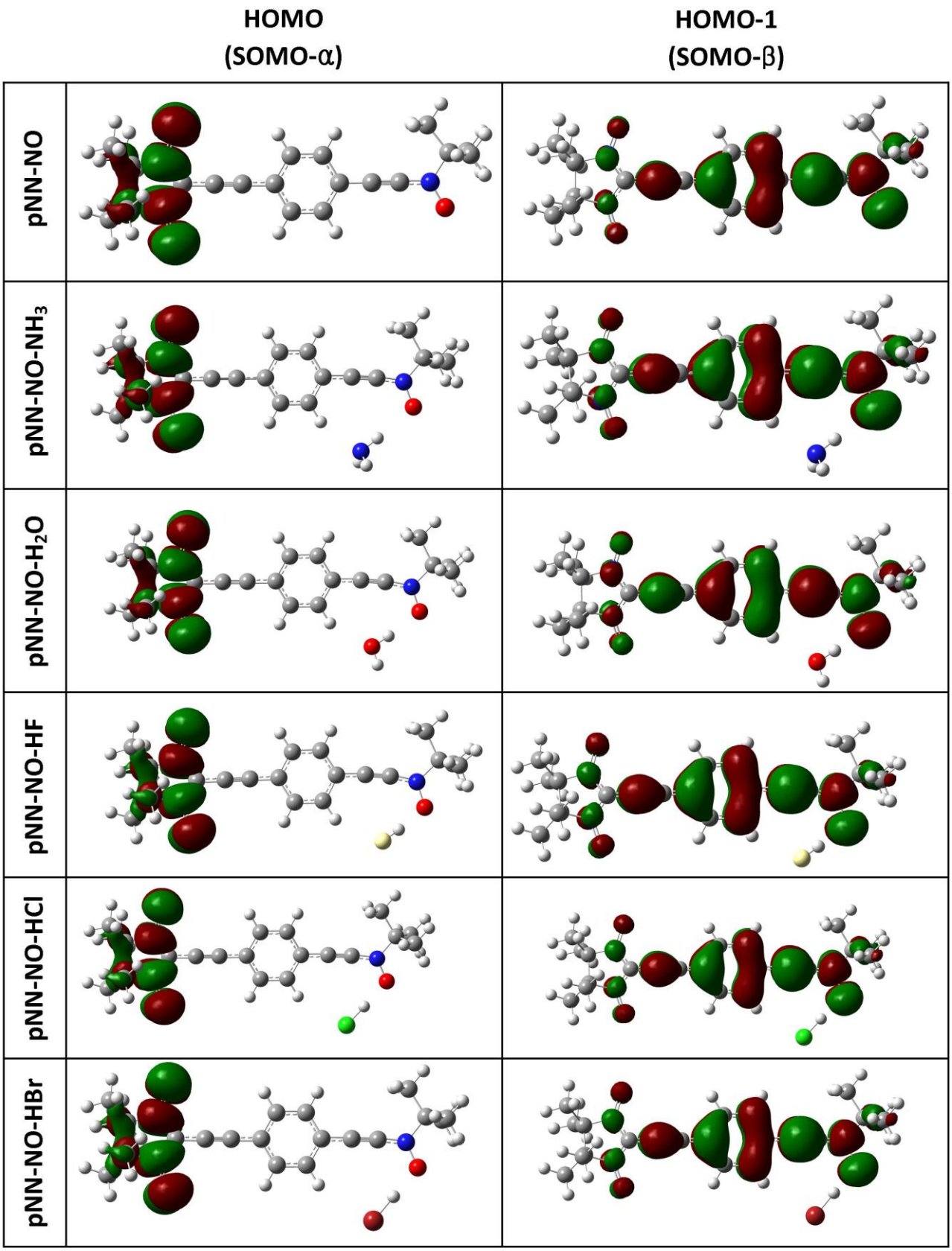

Figure S2. HOMO/HOMO-1 or SOMO(α)/SOMO(β) maps for the ground states (**T**) of **mNO-NO** and its H-Bonded complexes.

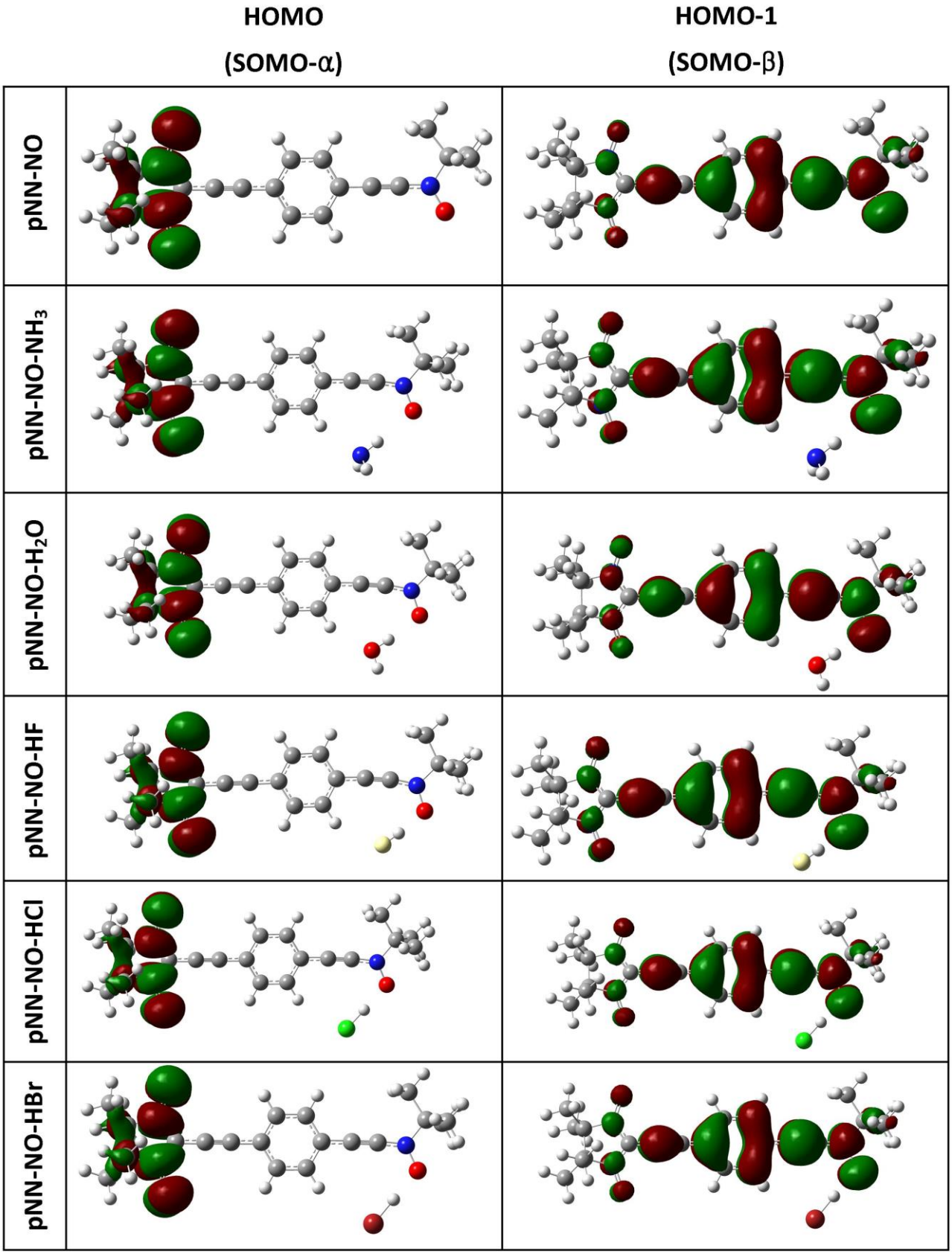

Figure S3. HOMO/HOMO-1 or SOMO(α)/SOMO(β) maps for the ground states (**T**) of **pNN-NO** and its H-Bonded complexes.

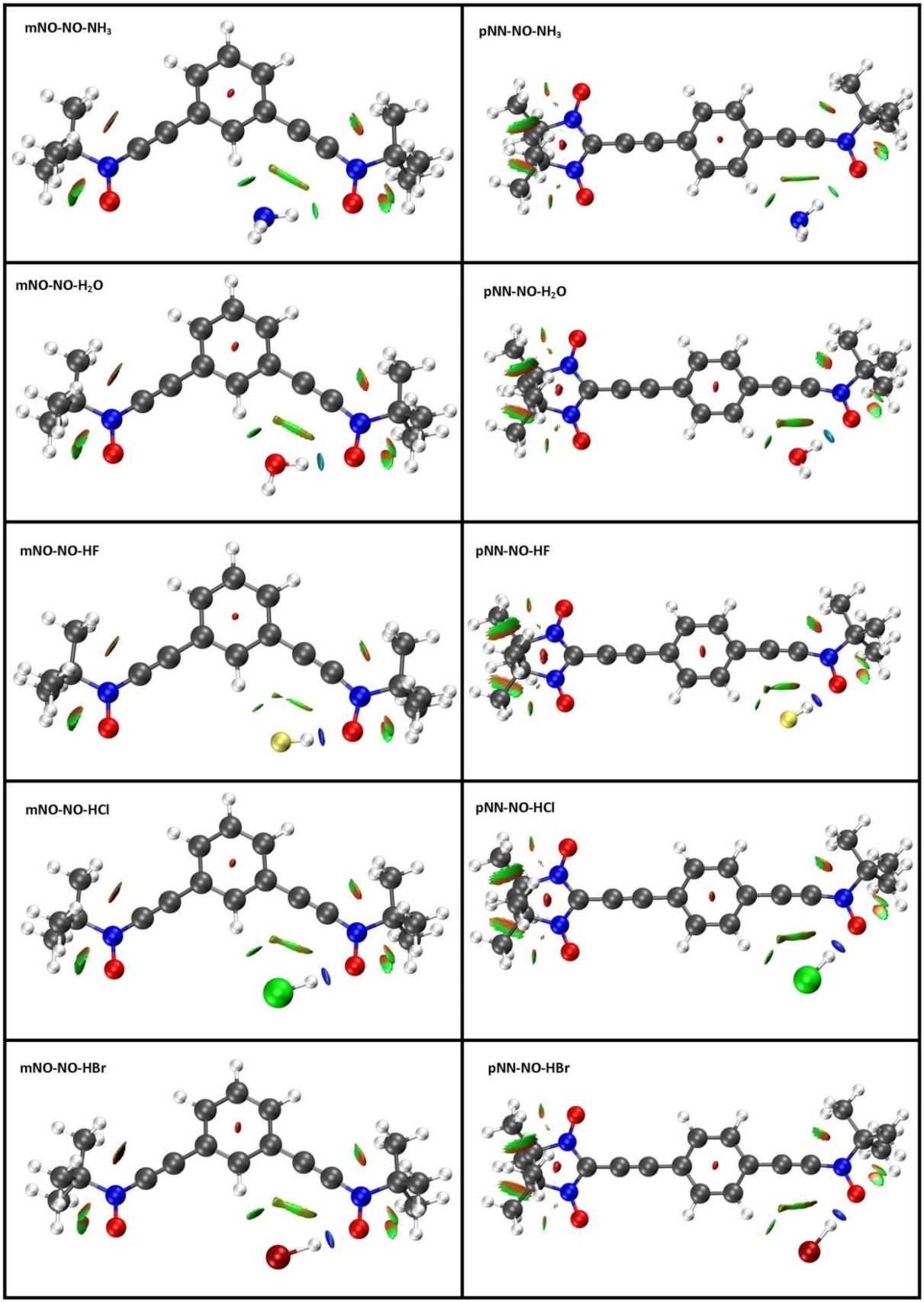

Figure S4. RDG isosufaces (RDG = 0.500 a.u.) for mNO-NO-HX and pNN-NO-HX (HX = NH_3, H_2O, HF, HCl and HBr). Blue-green-red color scaling range is -0.035 a.u (blue) < sign(λ_2)ρ < 0.02 a.u. (red).