Supplementary information for

Separating σ-Inductive and π-Resonance Effects of Substituent on Modulating Resonance-Assisted Hydrogen Bonds

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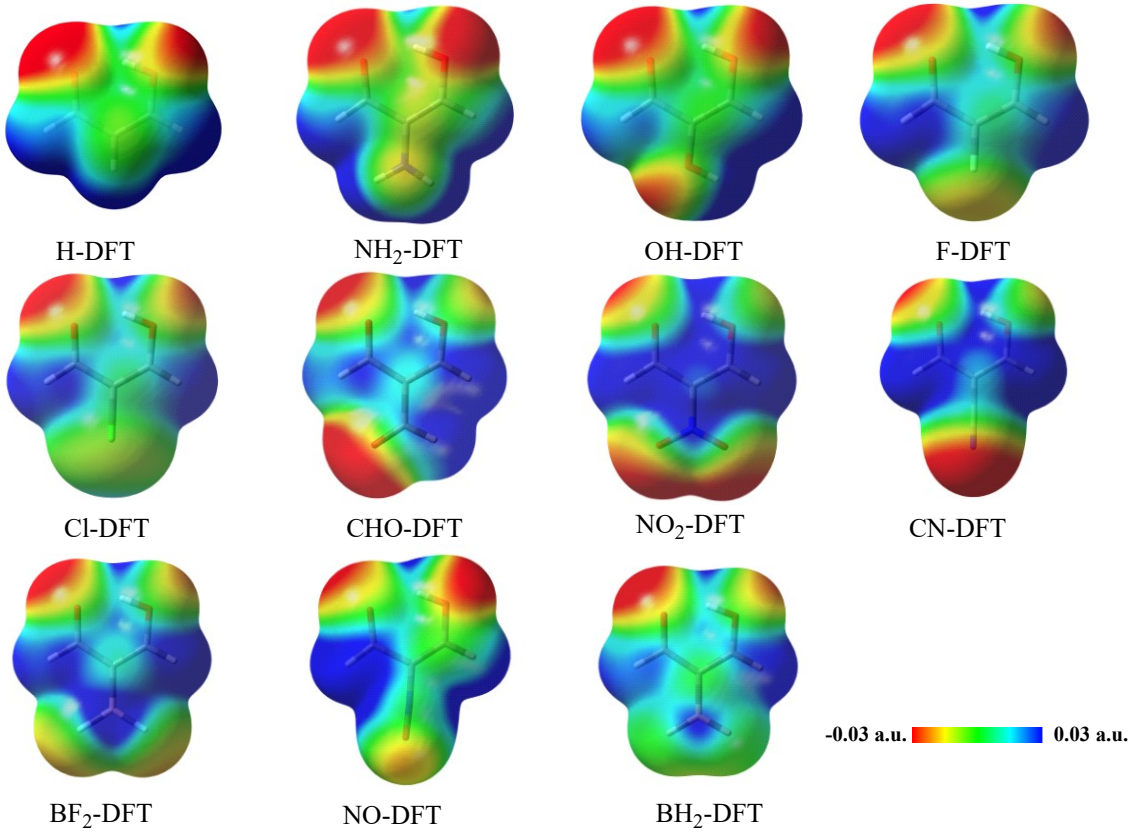

Figure S1. Electrostatic potential maps by DFT methods.

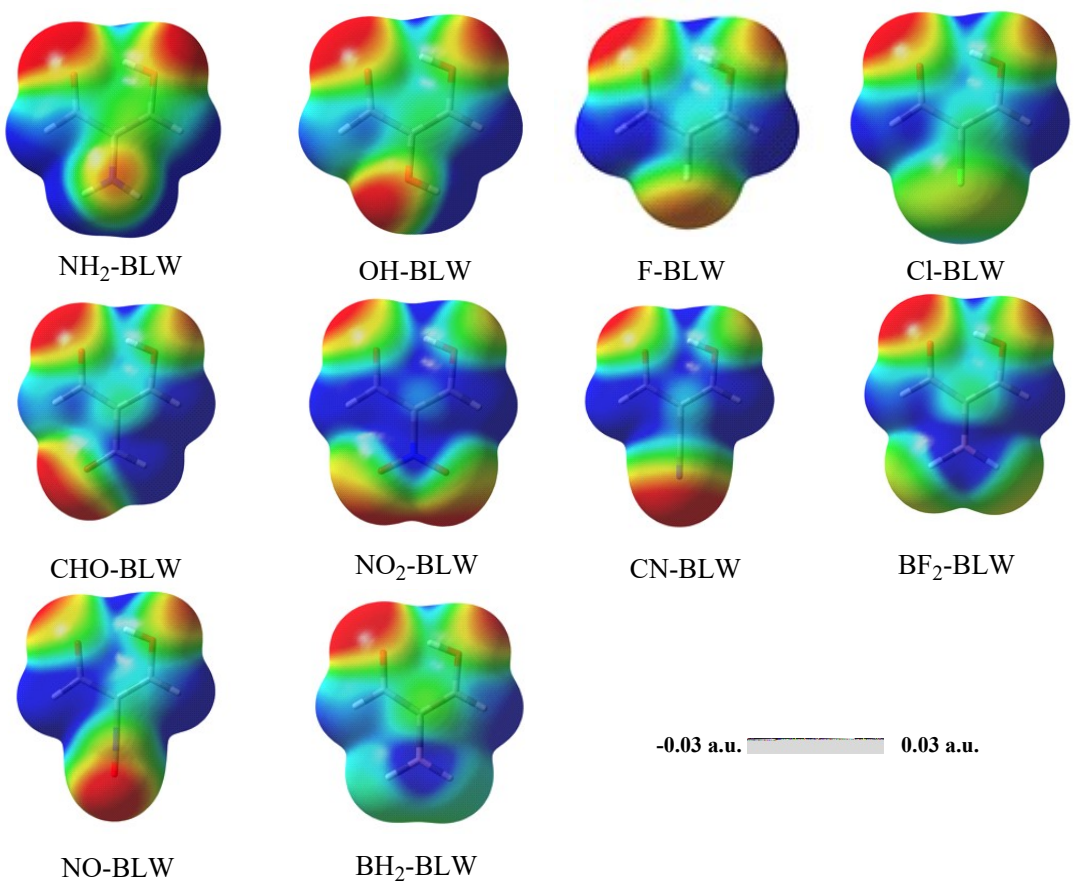

Figure S2. Electrostatic potential maps by BLW methods.

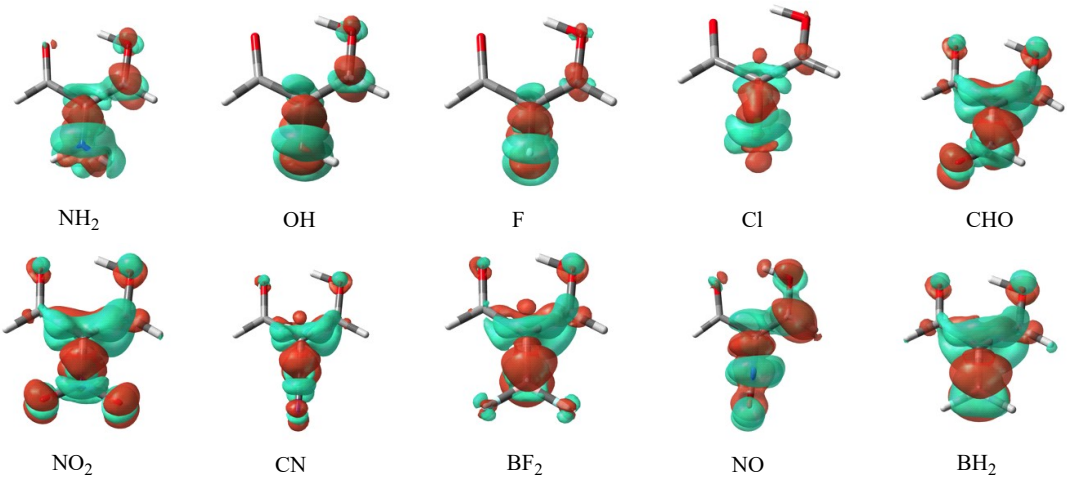

Figure **S3**. Electron density difference (EDD) maps with the isovalue of 0.001 a.u. showing the movement of electron density due to π conjugation. The orange/cyan color indicates increasing/decreasing of the electron density.

Table S1. σ-inductive effect by means of the variation of the H-bond distance ($d_{A...H}$), stretching vibrational frequencies (ν_{DH}), interaction energies (ΔE_{int}), Mulliken and NPA charge difference (Δq) for acceptor CHO from DFT datafor unsubstituted system to BLW-DFT data for substituted systems.

R	$\Delta d_{A...H}$	$\Delta \nu_{DH}$	$\Delta\Delta E_{int}$	Δq_{CHO} (M)	Δq_{CHO} (NPA)
NH_2	0.042	138	1.05	0.0049	0.0099
OH	0.065	153	1.06	0.0096	0.0209
F	0.096	177	2.16	0.0572	0.0639
Cl	0.04	93	1.24	0.0136	0.0348
CHO	-0.001	-13	-0.09	-0.0002	0.0658
NO_2	0.018	22	1.14	0.0335	0.0026
CN	-0.007	-12	0.86	-0.0060	-0.0708
BF_2	-0.055	-153	-0.63	-0.0475	-0.0356
NO	0.074	201	2.51	0.0184	0.0831
BH_2	-0.065	-179	-1.13	-0.0572	-0.0443

Table S2. π-resonance by means of the variation of the H-bond distance ($d_{A...H}$), stretching vibrational frequencies (ν_{DH}), interaction energies (ΔE_{int}), Mulliken and NPA charge difference (Δq) for acceptor OH from BLW-DFT to DFT date for for substituted systems.

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R	$\Delta d_{A...H}$	$\Delta \nu_{DH}$	$\Delta\Delta E_{int}$	Δq_{OH} (M)	Δq_{OH} (NPA)
NH_2	0.024	89	0.84	-0.0187	-0.0076
OH	0.01	50	0.4	-0.0142	-0.0049
F	-0.003	16	0.03	-0.0094	-0.0029
Cl	-0.005	4	-0.03	-0.0037	-0.0008
CHO	-0.024	-111	-0.21	0.0220	0.0116
NO_2	-0.052	-155	-0.59	0.0194	0.0132
CN	-0.018	-31	-0.2	0.0124	0.0078
BF_2	-0.017	-78	-0.19	0.0190	0.0092
NO	0.056	193	2.28	-0.0447	-0.0195
BH_2	-0.025	-109	-0.27	0.0265	0.0136