Supplementary Information

DFT Study of The Interaction between the Ni^{2+} and Zn^{2+} Metal Cations and The 1,2-Dithiolene Ligands: Electronic, Geometric and Energetic Analysis

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Table S1. Donor-acceptor energy ($E_{Donor-Accept}$) and s, p and d character of the metal-ligand bonding orbital in M-*S backdonation selected

Ligand (L)		$E_{Donor-Accept}$ / (kcal mol^{-1})	s / %	p / %	d / %	$E_{Donor-Accept}$ / (kcal mol^{-1})	s / %	p / %	d / %
		$[Ni(OH_2)_4(L)]$				$[Zn(OH_2)_4(L)]$			
Cl_2-bdt	M-*S_1	0.38	17.40	82.00	0.60	0.36	18.93	80.50	0.57
	M-*S_1, M	0.32	17.88 0.02	81.51 0.03	0.62 99.95	0.20	18.99 0.06	80.48 0.06	0.53 99.87
Cl_4-bdt	M-*S_1	0.39	16.55	82.86	0.58	0.44	1.57	98.28	0.15
	M-*S_1, M	0.40	16.50 0.03	82.92 0.02	0.58 99.94	0.07	1.89 0.06	97.93 0.12	0.18 99.83
bdt	M-*S_1	0.32	17.78	81.65	0.58	0.35	19.32	80.09	0.59
	M-*S_1, M	0.31	17.71 0.02	81.72 0.02	0.57 99.96	0.26	20.15 0.11	79.32 0.40	0.54 99.50
edt	M-*S_1	0.27	13.42	86.49	0.08	0.33	18.35	81.07	0.58
	M-*S_1, M	0.27	13.98 0.01	85.94 0.01	0.08 99.96	0.25	19.35 0.03	80.11 0.41	0.55 99.56
mdt	M-*S_1	0.33	17.44	82.01	0.55	0.32	1.48	98.42	0.10
	M-*S_1, M	0.33	17.37 0.02	82.08 0.02	0.55 99.96	0.08	20.75 0.09	78.77 0.38	0.48 99.53
mnt	M-*S_1	0.32	16.83	82.54	0.63	0.27	14.19	85.31	0.49
	M-*S_1, M	0.32	16.70 0.04	82.67 0.02	0.63 99.94	0.29	19.04 0.02	80.39 0.39	0.56 99.58
tdt	M-*S_1	0.33	17.89	81.44	0.67	0.37	19.29	80.13	0.58
	M-*S_1, M	0.32	18.980.02	80.33 0.02	0.69 99.96	0.33	21.03 0.12	78.45 0.38	0.52 99.50
tfd	M-*S_1	0.37	16.89	82.64	0.47	0.21	3.15	96.62	0.23
	M-*S_1, M	0.37	14.78 0.03	84.53 0.03	0.69 99.94	0.31	17.98 0.13	81.48 0.11	0.55 99.76
dmit	M-*S_1	0.25	17.11	82.26	0.60	0.22	18.13	81.28	0.59
	M-*S_1, M	0.25	17.17 0.02	82.22 0.03	0.61 99.95	0.31	18.32 0.01	81.07 0.38	0.62 99.61
dmio	M-*S_1	0.25	17.01	82.39	0.60	0.25	18.41	81.02	0.57
	M-*S_1, M	0.26	17.06 0.02	82.34 0.03	0.61 99.95	0.21	18.33 0.04	81.10 0.07	0.57 99.89
dmt	M-*S_1	0.25	17.99	81.38	0.63	0.28	20.24	79.18	0.58
	M-*S_1, M	0.33	16.97 0.02	82.45 0.02	0.58 99.96	0.26	20.51 0.00	78.92 0.40	0.56 99.60

Table S1. Donor-acceptor energy ($E_{Donor-Accept}$) and s, p and d character of the metal-ligand bonding orbital in M-*S backdonation selected (cont.)

Ligand (L)		$E_{Donor-Accept}$ / (kcal mol^{-1})	s / %	p / %	d / %	$E_{Donor-Accept}$ / (kcal mol^{-1})	s / %	p / %	d / %
		$[Ni(OH_2)_2(L)_2]^{2-}$				$[Zn(OH_2)_2(L)_2]^{2-}$			
Cl_2-bdt	M-*S_1	0.81	2.68	97.14	0.17	0.12	15.82	83.73	0.45
	M-*$S_{1'}$	0.84	2.51	97.32	0.17	0.10	1.79	98.11	0.10
	M-*S_2	0.75	1.32	98.55	0.13	0.07	0.01	98.11	0.08
	M-*$S_{2'}$	0.75	1.24	98.62	0.14	0.08	15.83	83.74	0.46
	M		0.00	0.00	100.00		0.00	0.28	99.72
Cl_4-bdt	M-*S_1	1.02	15.91	83.48	0.61	0.18	15.91	83.48	0.61
	M-*$S_{1'}$	1.02	15.85	83.51	0.64	0.17	15.85	83.51	0.64
	M-*S_2	1.02	16.82	82.53	0.65	0.19	16.82	82.86	0.61
	M-*$S_{2'}$	1.02	16.53	82.86	0.61	0.28	16.53	82.86	0.61
	M		0.01	0.00	99.99		0.00	0.36	99.63
bdt	M-*S_1	0.81	14.94	84.60	0.46	0.38	19.62	79.58	0.50
	M-*$S_{1'}$	0.81	14.93	84.61	0.46	0.38	19.62	79.89	0.50
	M-*S_2	0.81	14.92	84.62	0.46	0.16	21.83	77.62	0.55
	M-*$S_{2'}$	0.81	14.91	84.63	0.46	0.16	21.84	77.61	0.55
	M		0.01	0.00	99.99		0.00	0.36	99.64
edt	M-*S_1	0.38	7.83	91.92	0.25	0.10	18.19	81.32	0.48
	M-*$S_{1'}$	0.38	7.81	91.94	0.25	0.08	18.96	80.51	0.53
	M-*S_2	0.38	7.78	91.97	0.25	0.17	18.24	81.23	0.53
	M-*$S_{2'}$	0.38	7.74	92.01	0.25	0.07	18.22	81.29	0.49
	M		0.02	0.00	99.98		0.00	0.37	99.63
mdt	M-*S_1	1.07	19.96	79.68	0.36	0.08	20.79	78.67	0.54
	M-*$S_{1'}$	0.56	19.94	79.70	0.36	0.08	4.66	95.27	0.07
	M-*S_2	1.18	19.92	79.72	0.36	0.09	13.94	85.99	0.26
	M-*$S_{2'}$	1.18	19.90	79.70	0.40	0.09	4.60	95.30	0.10
	M		0.00	0.03	99.97		0.00	0.37	99.63
mnt	M-*S_1	0.21	19.97	79.53	0.50	0.18	8.94	90.78	0.28
	M-*$S_{1'}$	0.21	19.91	79.59	0.50	0.20	1.56	98.30	0.14
	M-*S_2	1.01	14.11	85.52	0.37	0.17	20.05	79.43	0.51
	M-*$S_{2'}$	1.01	14.18	85.86	0.37	0.14	20.53	79.00	0.47
	M		0.00	0.32	99.68		0.00	0.23	99.77

Table S1. Donor-acceptor energy ($E_{Donor-Accept}$) and s, p and d character of the metal-ligand bonding orbital in M-*S backdonation selected (cont.)

Ligand (L)		$E_{Donor-Accept}$ / (kcal mol^{-1})	s / %	p / %	d / %	$E_{Donor-Accept}$ / (kcal mol^{-1})	s / %	p / %	d / %
tdt	M-*S_1	0.27	20.21	79.09	0.62	0.12	14.67	85.03	0.31
	M-*$S_{1'}$	0.29	20.42	78.95	0.63	0.06	26.76	73.08	0.16
	M-*S_2	0.67	00.00	99.92	0.08	0.08	21.89	77.56	0.56
	M-*$S_{2'}$	0.60	00.00	99.93	0.08	0.10	22.65	76.92	0.43
	M		0.00	0.00	100.00		0.00	0.15	99.85
tfd	M-*S_1	0.26	2.67	97.14	0.19	0.06	13.35	86.30	0.35
	M-*$S_{1'}$	0.37	6.33	93.39	0.28	0.10	29.33	70.49	0.18
	M-*S_2	0.63	18.98	80.42	0.60	0.10	20.45	79.02	0.53
	M-*$S_{2'}$	0.38	18.13	81.27	0.60	0.08	21.66	77.81	0.53
	M		0.00	0.00	100.00		0.03	0.33	99.63
dmit	M-*S_1	0.09	19.03	80.32	0.65	0.14	0.53	99.58	0.09
	M-*$S_{1'}$	0.09	19.04	80.31	0.65	0.09	0.51	99.70	0.09
	M-*S_2	0.90	19.05	80.30	0.65	0.14	18.69	80.71	0.60
	M-*$S_{2'}$	0.90	19.06	80.29	0.65	0.19	19.05	80.33	0.62
	M		0.03	0.00	99.97		0.00	0.34	99.66
dmio	M-*S_1	1.10	18.48	80.85	0.66	0.17	17.65	81.72	0.12
	M-*$S_{1'}$	1.11	18.44	80.90	0.66	0.19	15.29	84.04	0.69
	M-*S_2	0.16	18.42	80.92	0.66	0.08	16.38	83.06	0.56
	M-*$S_{2'}$	0.14	18.49	80.91	0.66	0.06	16.56	82.74	0.70
	M		0.00	0.41	99.59		0.00	0.30	99.70
dmt	M-*S_1	0.97	18.45	81.20	0.34	0.29	18.56	80.79	0.65
	M-*$S_{1'}$	1.14	21.11	78.48	0.41	0.06	25.34	74.47	0.20
	M-*S_2	1.61	21.09	78.25	0.66	0.27	17.89	81.51	0.60
	M-*$S_{2'}$	1.35	00.00	99.92	0.03	0.05	25.78	73.94	0.28
	M		0.06	0.00	99.98		0.08	0.31	99.61

The S_1 and $S_{1'}$ parameters refer to the two S atoms of the bidentate ligand in the monosubstitution case. In the disubstitution case the S_2 and $S_{2'}$ parameters refer to the S atoms of the second bidentate ligand; the M parameter refers to the metal ion (Ni or Zn). Cl_2-bdt: 3,6-dichlorobenzene-1,2-dithiolate; Cl_4-bdt: 3,4,5,6-tetracholorobenzene-1,2-dithiolate; bdt: benzene-1,2-dithiolate; edt: 1,2-ethylenedithiolate; mdt: 1,2-dimethyl-1,2-ethylenedithiolate; mnt: maleonitrile-2,3-dithiolate; tdt: toluene-3,4-dithiolate; tfd: bis(trifluoromethyl)ethylenedithiolate; dmit: 1,3-dithiole-2-thione-4,5-dithiolate; dmio: 1,3-dithiole-2-one-4,5-dithiolate; dmt: 1,2-dithiole-3-thione-4,5-dithiolate.