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Supporting information for the paper

Dinuclear Rhenium pyridazine complexes containing bridging chalcogenide anions: synthesis, characterization and computational study

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Table S1. A List of Computed Molecular Orbital Energies [eV] for the Complexes [$Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-pydz})$], X = OPh (**1a**), SPh (**2a**), SePh (**3a**), TePh (**4a**), OMe (**1b**), SMe (**2b**), SeMe (**3b**), TeMe (**4b**) [a]

		1a	**2a**	**3a**	**4a**	**1b**	**2b**	**3b**	**4b**
"e_g"	LUMO + 5	–0.38	–0.55	–0.55	–0.59	–0.25	–0.31	–0.35	–0.47
	LUMO + 4	–0.75	–0.78	–0.79	–0.83	–0.60	–0.60	–0.63	–0.69
	LUMO + 3	–0.77	–1.02	–1.08	–1.09	–0.75	–1.06	–1.14	–1.13
	LUMO + 2	–0.99	–1.04	–1.22	–1.39	–0.96	–1.06	–1.20	–1.34
π* pydz	LUMO + 1	–2.52	–2.40	–2.36	–2.31	–2.44	–2.46	–2.44	–2.39
	LUMO	–3.36	–3.22	–3.18	–3.13	–3.27	–3.28	–3.25	–3.21
"t_{2g}" (+ *π Ph*)	HOMO	–6.31	–6.27	–6.23	–6.09	–6.15	–6.37	–6.29	–6.13
	HOMO – 1	*–6.42*	*–6.40*	–6.45	–6.43	–6.30	–6.42	–6.45	–6.46
	HOMO – 2	–6.44	–6.46	*–6.50*	–6.55	–6.63	–6.53	–6.65	–6.67
	HOMO – 3	*–6.48*	–6.78	–6.77	–6.76	–6.98	–6.99	–6.95	–6.89
	HOMO – 4	–6.81	–6.93	–6.98	*–7.00*	–7.01	–7.00	–6.98	–7.00
	HOMO – 5	*–7.00*	–7.05	–7.02	–7.03	–7.05	–7.07	–7.09	–7.09
	HOMO – 6	*–7.02*	–7.19	–7.15	–7.10				
	HOMO – 7	–7.11	*–7.35*	*–7.38*	*–7.37*				
	HOMO – 8	–7.16	*–7.36*	*–7.38*	*–7.38*				
	HOMO – 9	–7.20	*–7.38*	*–7.41*	*–7.41*				

[a] Data for **1a** and **1b** are taken from our previous work (ref. S1).

Table S2. Computed Excitation Energies [nm, eV] and Oscillator Strengths (*f*, in parenthesis) for the Complexes $[Re_2(\mu\text{-}X)_2(CO)_6(\mu\text{-}pydz)]$, X = OPh (**1a**), SPh (**2a**), SePh (**3a**), TePh (**4a**), OMe (**1b**), SMe (**2b**), SeMe (**3b**), TeMe (**4b**) [a]

	1a	**2a**	**3a**	**4a**	**1b**	**2b**	**3b**	**4b**
Gas-phase values								
λ_{d-d} (*f*)	256, 4.84 (0.020)	262, 4.73 (0.057)	258, 4.80 (0.028)	262, 4.73 (0.184)	257, 4.83 (0.068)	237, 5.23 (0.061)	238, 5.22 (0.049)	252, 4.91 (0.050)
						282, 4.40 (0.067)	288, 4.30 (0.028)	
λ_{MLCT} (*f*)	387, 3.20 (0.130)	368, 3.37 (0.047)	363, 3.42 (0.042)	359, 3.45 (0.033)	265, 4.68 (0.030)	359, 3.46 (0.031)	300, 4.13 (0.035)	313, 3.96 (0.046)
	409, 3.03 (0.028)	403, 3.08 (0.024)	404, 3.07 (0.028)	408, 3.04 (0.031)	401, 3.09 (0.156)	398, 3.11 (0.139)	382, 3.24 (0.031)	402, 3.09 (0.032)
	544, 2.28 (0.057)	415, 2.99 (0.059)	418, 2.97 (0.051)	413, 3.00 (0.056)	564, 2.20 (0.048)	404, 3.07 (0.029)	404, 3.07 (0.155)	408, 3.04 (0.141)
		528, 2.35 (0.029)	509, 2.44 (0.028)	499, 2.48 (0.017)		540, 2.30 (0.045)	518, 2.39 (0.037)	507, 2.45 (0.023)
Dichloromethane solution values (PCM) [b]								
λ_{MLCT} (*f*)	285, 4.35 (0.022)	328, 3.78 (0.036)	326, 3.80 (0.035)	324, 3.83 (0.021)	297, 4.17 (0.031)	318, 3.90 (0.029)	340, 3.64 (0.030)	359, 3.45 (0.032)
	327, 3.79 (0.015)	353, 3.51 (0.026)	358, 3.46 (0.029)	364, 3.40 (0.030)	361, 3.43 (0.188)	371, 3.34 (0.205)	376, 3.30 (0.200)	380, 3.26 (0.186)
	351, 3.54 (0.171)	371, 3.34 (0.072)	374, 3.31 (0.057)	372, 3.33 (0.032)	463, 2.68 (0.061)	447, 2.77 (0.066)	435, 2.85 (0.054)	429, 2.89 (0.034)
	408, 3.04 (0.010)	397, 3.12 (0.057)	397, 3.13 (0.065)	392, 3.16 (0.080)				
	441, 2.81 (0.072)	442, 2.81 (0.045)	431, 2.88 (0.042)	427, 2.90 (0.026)				

[a] λ_{d-d} and λ_{MLCT} refer to the higher and lower energy bands, respectively. Data for **1a** and **1b** in the gas phase are taken from our previous work (ref. S1). [b] The higher energy band λ_{d-d} is almost unaffected by solvation. As a consequence, only the PCM λ_{MLCT} values are reported.

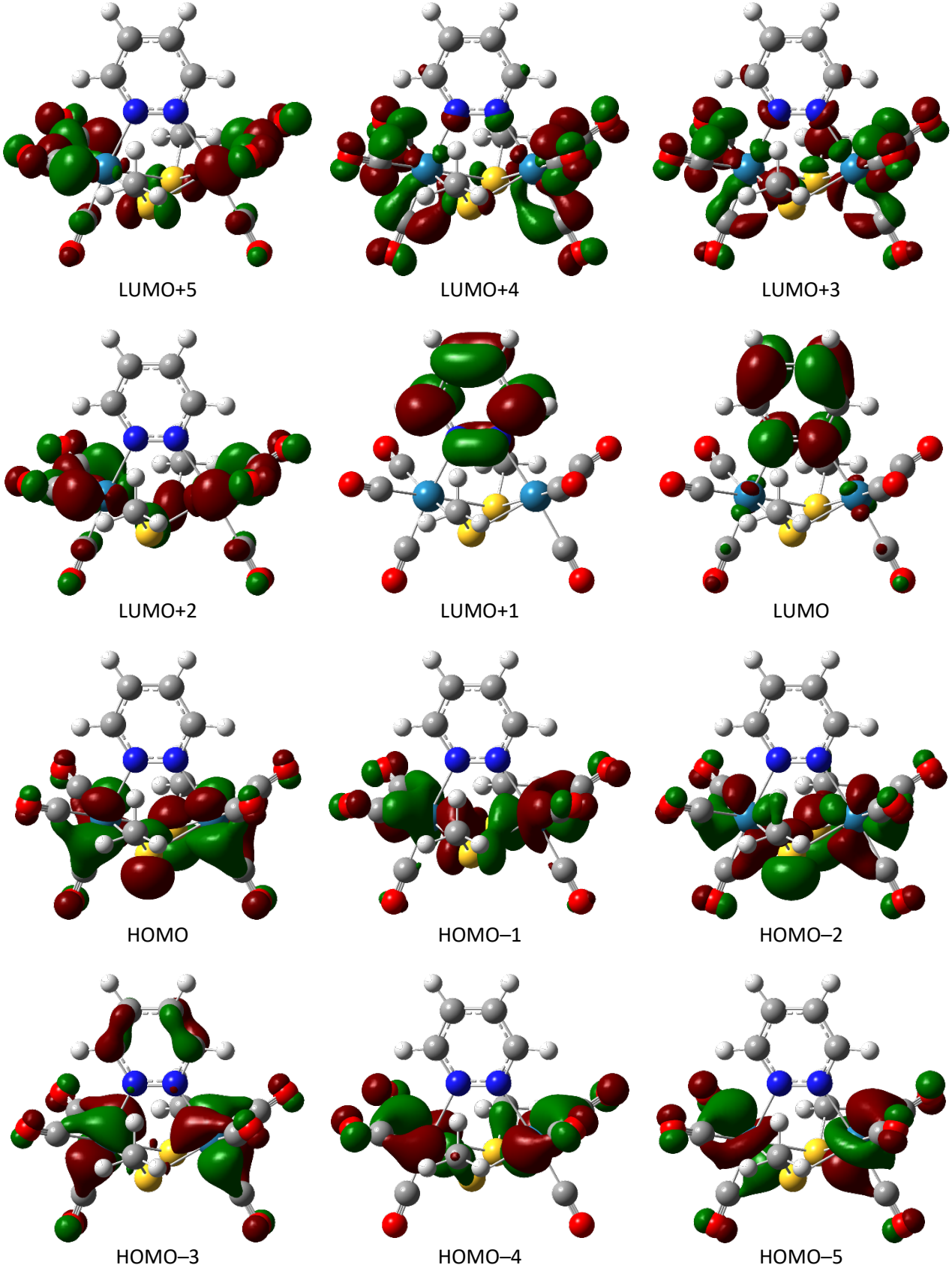

Figure S1. Isodensity surface plots of some relevant molecular orbitals of $[Re_2(\mu\text{-}SMe)_2(CO)_6(\mu\text{-}pydz)]$ **2b**.

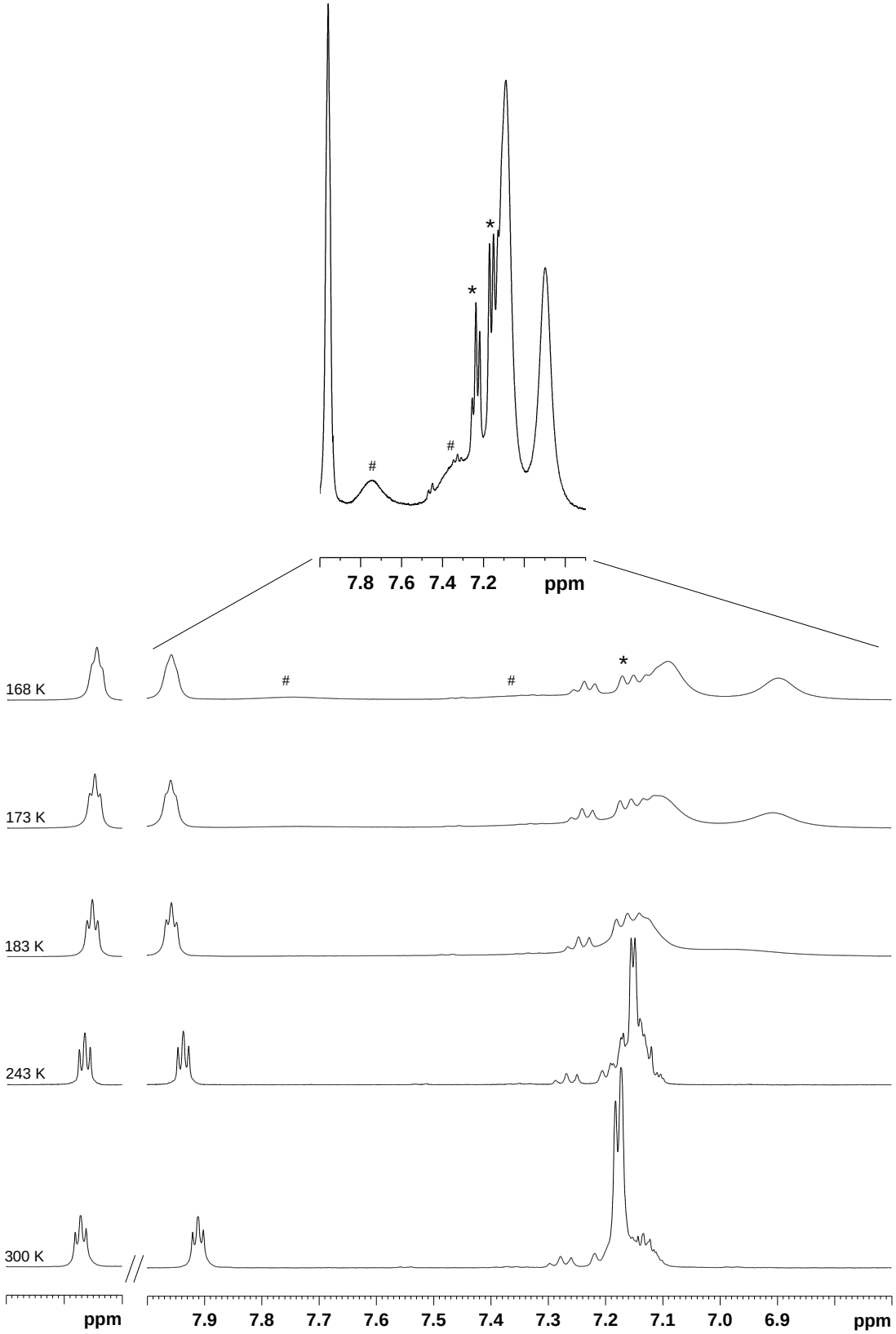

Figure S2. ^{1}H NMR at variable temperature (CD_2Cl_2, 9.4 T) for disulfide derivative **2a** (the sharp signals overlapping the phenyl signals and marked with an asterisk are due to an impurity). Inset: 10x enhancement of the 168 K trace, range 8.2-6.6 ppm.

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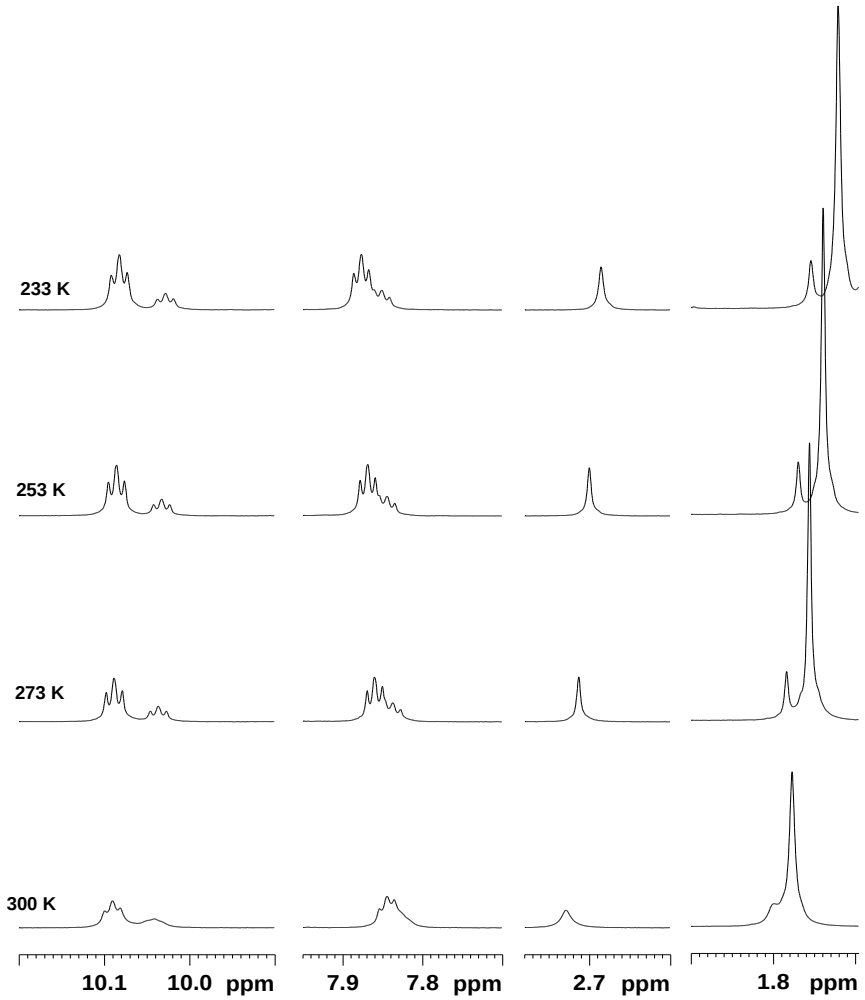

Figure S3. Selected aromatic and aliphatic regions of ^{1}H NMR variable temperature spectra of a solution of **3b** (CD_2Cl_2, 9.4 T).

References

(S1) A. Raimondi, M. Panigati, D. Maggioni, L. D'Alfonso, P. Mercandelli, P. Mussini and G. D'Alfonso, *Inorg. Chem.*, 2012, **51**, 2966–2975.