SUPPLEMENTARY MATERIAL FOR:

Metallophilic Interactions in Stacked Dinuclear Rhodium 2,2'-biimidazole Carbonyl Complexes

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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A., Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X., Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K., Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I., Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople J. A. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

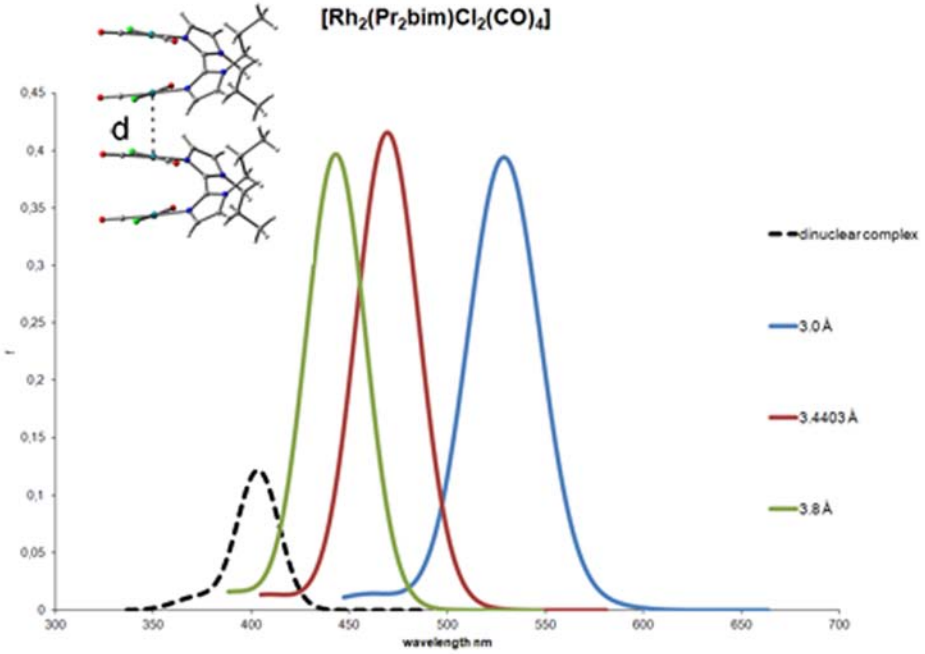


Figure S1. The peak shift of the absorption signal corresponding to the different intermolecular Rh···Rh distance (d) in the $[Rh_2(Pr_2bim)Cl_2(CO)_4]_2$ system. The Rh···Rh distance of 3.4403(3) Å is the experimental value.

Table S1. The contribution of the dominating charge transfer and the details of the lowest energy transition for compound **2** at different intermolecular Rh···Rh distances.

Rh···Rh (Å)	HOMO-LUMO+n %	λ (nm)	f	HOMO-LUMO+n gap (eV)	HOMO (eV)	LUMO (eV)
Isolated complex*	80	409	0.1062	4.23	-5.43	-1.20
3.0 Å	85	543	0.3688	3.21	-4.56	-1.34
3.4345. exp[a]	84	479	0.4026	3.58	-4.86	-1.28
3.4990. exp[b]	83	464	0.4129	3.67	-4,84	-1,17
3.8 Å	80	451	0.3835	3.79	-5.03	-1.24

[a] experimental intranuclear distance of Rh···Rh of structure at 100K.
[b] experimental intranuclear distance of Rh···Rh of structure at 260K.
In the chain structures the dominating charge transfer is from HOMO to LUMO+2 at all analysed intermolecular Rh···Rh distances.
*In the case of isolated dinuclear complex the dominating transition is from HOMO to LUMO+1.
λ is the absorption wavelength.
f is the oscillator strength of the transition.

Table S2. The contribution of the dominating charge transfer and the details of the lowest energy transition for compound **3** at different intermolecular Rh···Rh distances.

Rh···Rh (Å)	HOMO-LUMO+n %	l (nm)	f	HOMO-LUMO+n gap (eV)	HOMO (eV)	LUMO (eV)
Isolated complex*	84	403	0.1212	4.26	-5.36	-1.10
3.0 Å	85	529	0.394	3.27	-4.48	-1.21
3.4403. exp.[a]	84	470	0.4156	3.63	-4.79	-1.16
3.4944. exp.[b]	84	459	0.4137	3.71	-4.86	-1.15
3.8 Å	80	443	0.3968	3.83	-4.95	-1.12

[a] experimental intranuclear distance of Rh···Rh of structure at 100K.
[b] experimental intranuclear distance of Rh···Rh of structure at 260K.
In the chain structures the dominating charge transfer is from HOMO to LUMO+2 at all analysed intermolecular Rh···Rh distances.
*In the case of isolated dinuclear complex the dominating transition is from HOMO to LUMO+1.
λ is the absorption wavelength.
f is the oscillator strength of the transition.

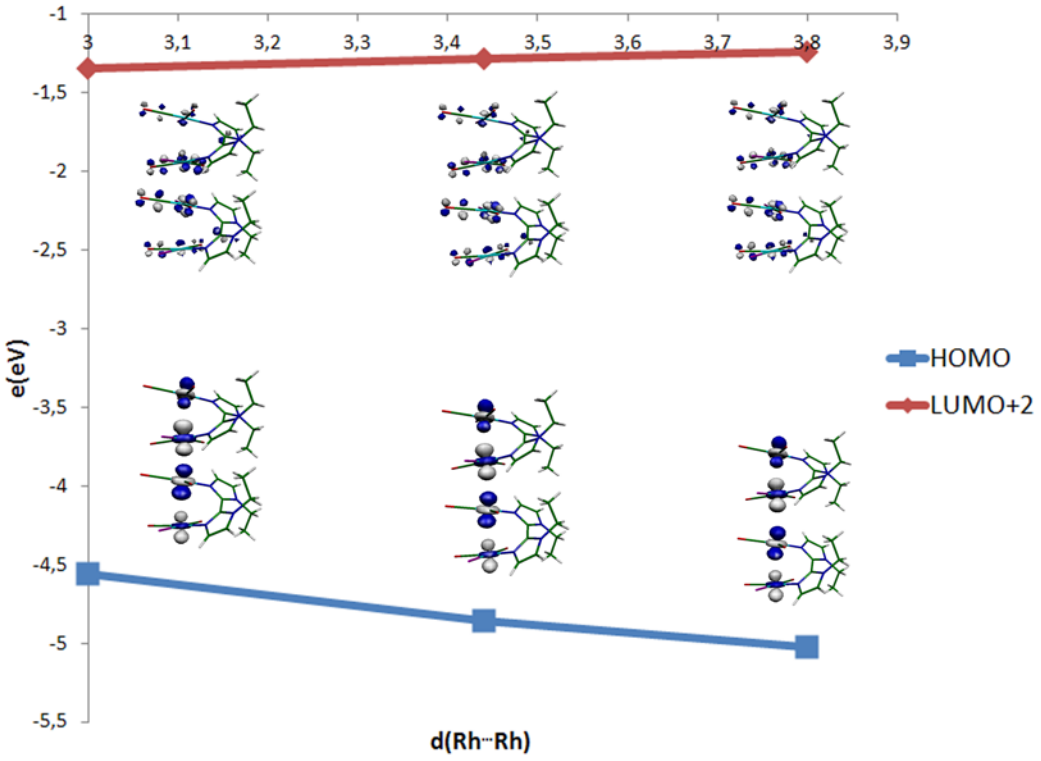
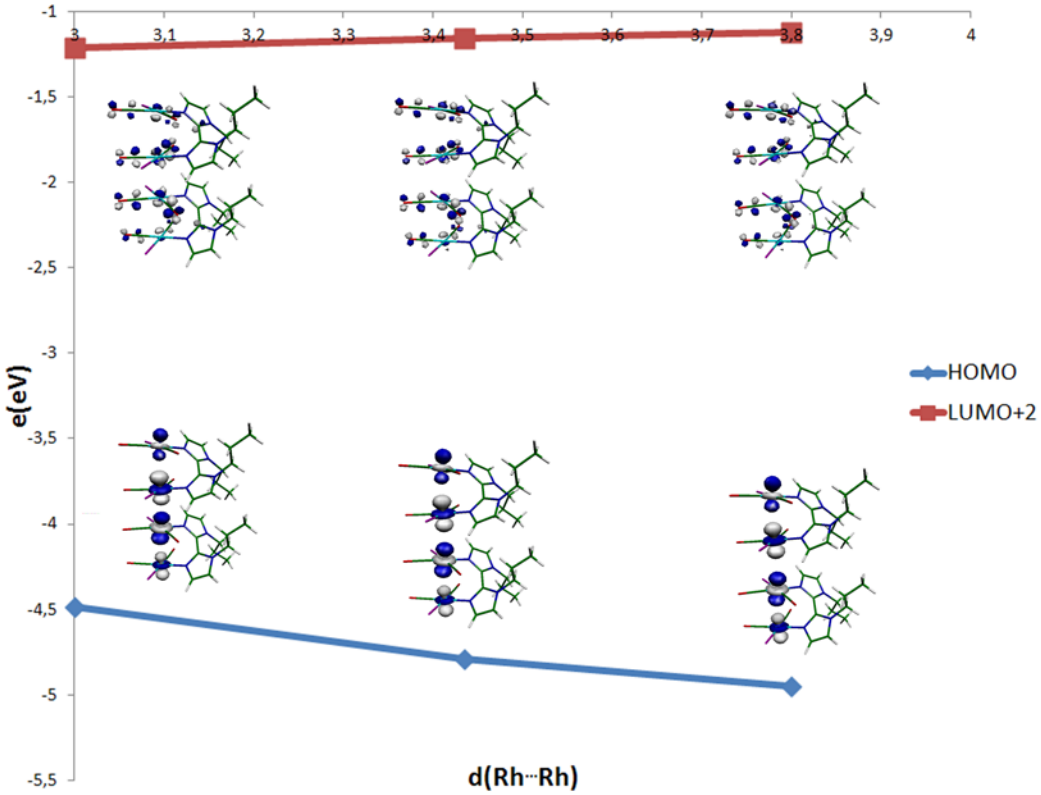


Figure S2. Dependence of the HOMO and LUMO orbital energies on the Rh···Rh distance (Å) in the $[Rh_2(Et_2bim)Cl_2(CO)_4]_2$ system.



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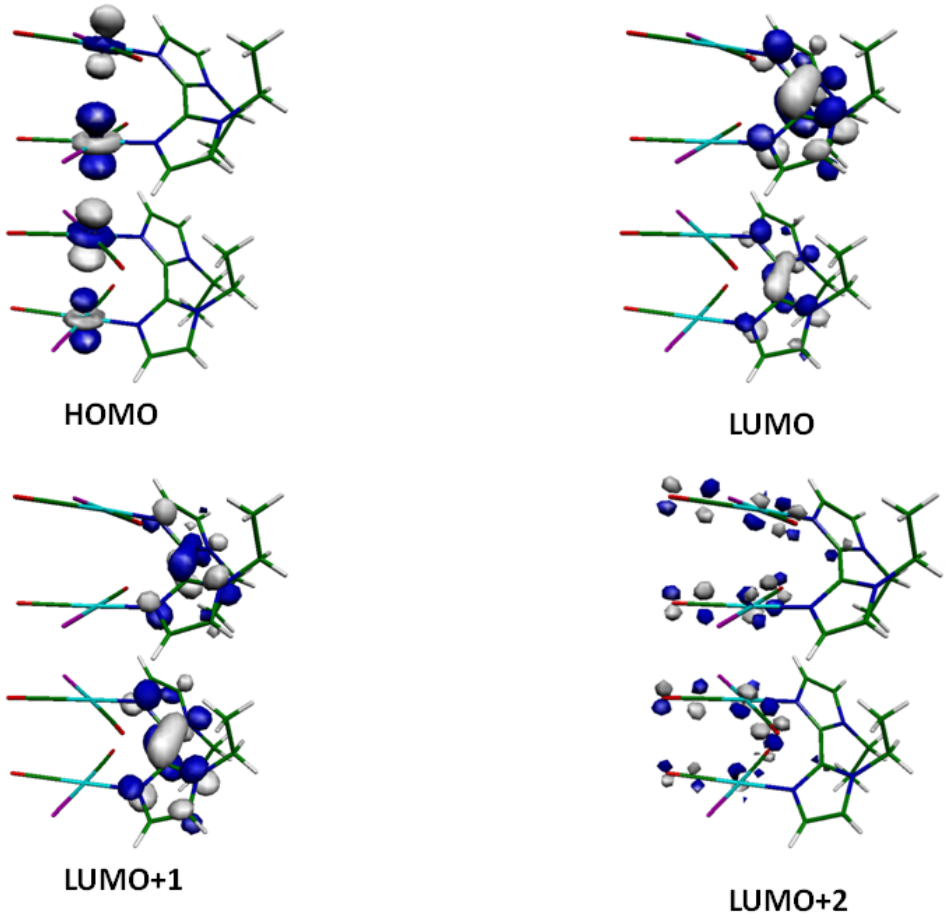
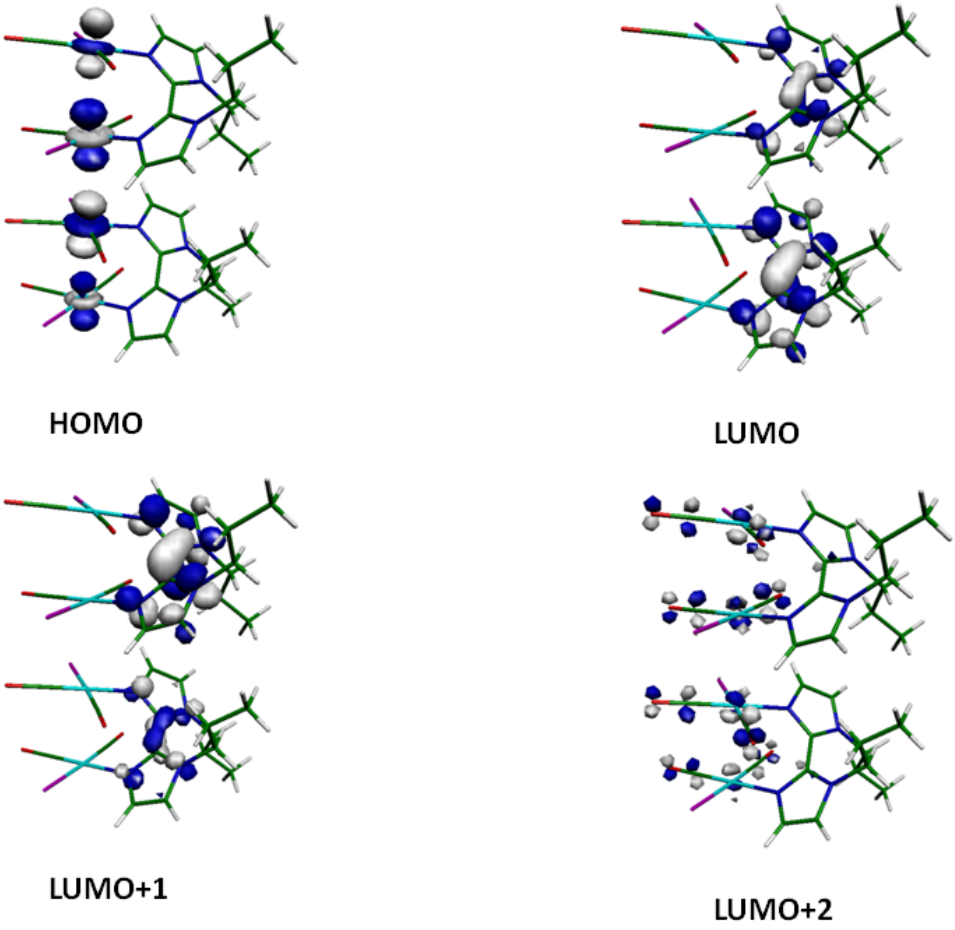


Figure S4. The HOMO. LUMO. LUMO+1 and LUMO+2 orbitals of the $[Rh_2(Et_2bim)Cl_2(CO)_4]_2$ system at experimental intermolecular rhodium···rhodium distance of 3.4345(6) Å.



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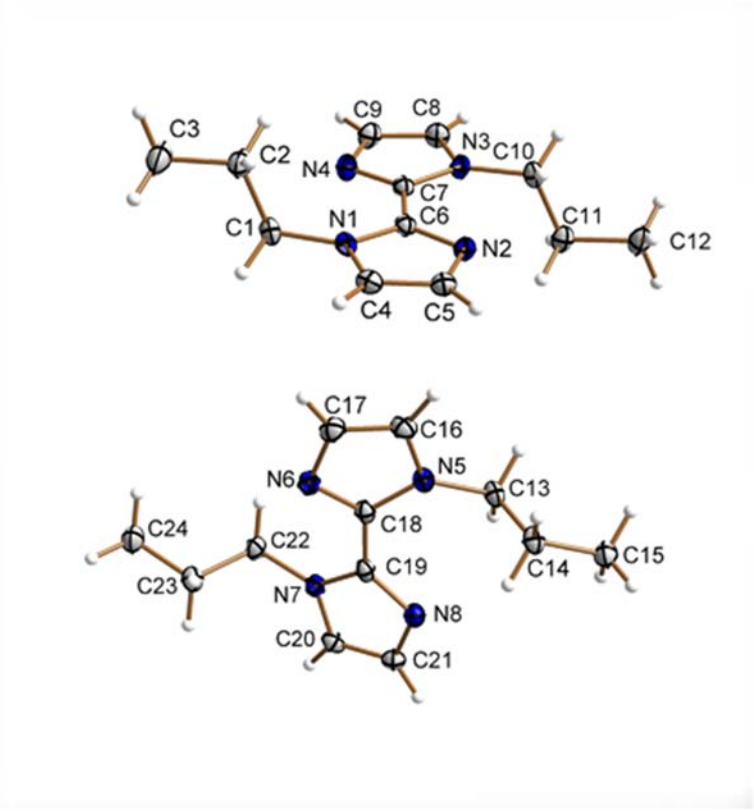

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