

Electronic Supplementary Information

Figure 1S Comparison of IR spectra computed for HS (red lines) and LS (blue lines) states of complex 1 with the use of a) 6-31G*, b) 6-31+G*, c) 6-311++G** basis sets.

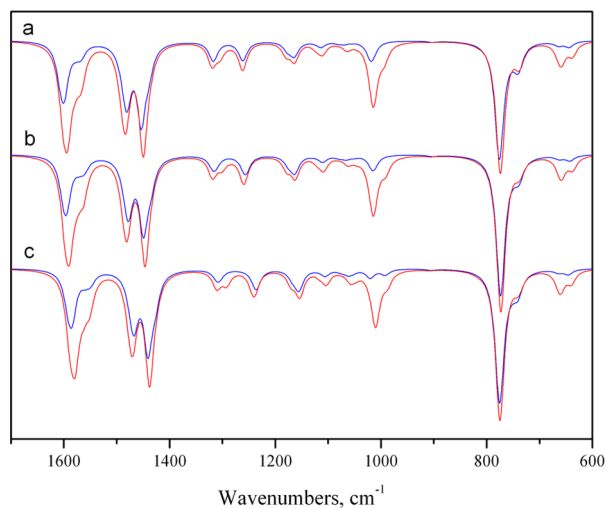


Table 1S. Scaling factors for the force fields of the compounds studied.

scaling factor		value
stretch	CC, CN	0.9207 ^a
stretch	CH (arom.)	0.915 ^b
stretch	CH (aliph.)	0.889 ^b
bend	NCN, CNN, CCC	1.0144 ^a
bend	CCH, NCH	0.950 ^a
bend	HCH	0.9016 ^a
torsion	all	0.9523 ^a

^a J. Baker, A. Jarzecki and P. Pulay, *J. Phys. Chem. A* 1998, **102**, 1412 – 1424.

^b S. Katsyuba, R. Schmutzler and J. Grunenberg, *Dalton Trans.* 2005, **9**, 1701 – 1706.

Table 2S. Experimental and calculated at B3LYP/Type-I level of theory IR spectra of **6** in the range 600-1610 cm⁻¹.

S=0		S=2	
Assignments ^a	Experiment ^b (solid) v, cm ⁻¹ , I ^c	Computations v, cm ⁻¹ (I, km·mole ⁻¹)	Experiment ^b (solid) v, cm ⁻¹ , I ^v
vCC	1630 (m),	1628 (1), 1628 (6)	1626 (m)
			1624 (6), 1623 (18)
vCC, vCN	1600	(vw), 1607 (2), 1607 (0),	1609 (1), 1609 (1),
	1578	(s), 1588 (3), 1588 (14),	1592 (m), 1592 (15), 1592 (2),
		1582 (1), 1580 (2),	1577 (s), 1577 (10), 1576 (20),
	1511 (w), 1494 (w)	1512 (1), 1512 (3),	1512 (10), 1511 (37)
in-plane bendings, vCC, vCN	1490 (w), 1488 (w),	1504 (4), 1502 (7),	1505 (6), 1504 (9),
	1455	(m), 1459 (14), 1458 (6),	1458 (1), 1458 (10),
	1431	(vs), 1437 (32), 1436 (12),	1437 (w), 1437 (30), 1436 (61),
	1424	(vs), 1422 (9), 1421 (1),	1425 (vs), 1425 (1), 1424 (8),
	1412 (vs), 1408 (w),	1420 (4), 1420 (21),	1402 (vs), 1402 (0), 1402 (2),
	1385 (w), 1342 (m),	1346 (2), 1346 (15),	1349 (m), 1349 (2), 1347 (8),
	1339 (m), 1320 (w),	1327 (1), 1327 (4),	1324 (w), 1324 (1), 1324 (4),
	1307 (w), 1300 (w)	1307 (2), 1307 (7)	1306 (1), 1306 (8)
in-plane CH and phenantroline ring bendings, vCC, vCN	1226	1262 (4), 1262 (2),	1269 (1), 1269 (0),
	1209	(s), 1224 (3), 1224 (0),	1224 (3), 1224 (1),
		(w), 1211 (0), 1208 (0),	1211 (0), 1209 (2),
		1204 (0), 1203 (0)	1200 (0), 1200 (1)
in-plane bendings	1144 (w)	1147 (1), 1147 (1),	1147 (0), 1147 (1),
		1145 (4), 1145 (9)	1143 (6), 1143 (13)
in-plane CH vibrations and ring		1113 (1), 1110 (4)	1109 (4), 1108 (23)
			in-plane CH and phenantroline ring

bendings		bendings,	
in-plane bendings	ring	1095	1094 (6), 1093 (2),
		1058	1046 (3), 1046 (0),
γ CH			1033 (0), 1032 (1)
		975 (w)	996 (0), 996 (0),
		947 (w)	981 (1), 981 (0),
in-plane bendings	ring	913 (w)	973 (0), 973 (2),
			961 (0), 961 (1),
γ CH			950 (1), 950 (2)
γ CH			899 (1), 898 (0),
			894 (13), 868 (2)
ϕ (CC), ϕ (CN)			867 (53), 862 (37)
ν CS, ν NiN			852 (1), 851 (6)
			832 (0), 831 (0)
γ CH		809 (vs), 807 (vs),	807 (0), 806 (0),
		760 (m)	773 (6), 773 (2)
in-plane bendings	ring	735 (m)	732 (28), 732 (33)
ϕ (CC), ϕ (CN)		725 (vs), 722 (vs)	731 (4), 730 (11)
			721 (2), 719 (11),
in-plane bendings	ring		646 (4), 645 (13)

$\varphi(\text{CC})$, $\varphi(\text{CN})$	620 (0), 616 (0)	608 (0), 605 (0)	$\varphi(\text{CC})$, $\varphi(\text{CN})$
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^a ν , stretch; γ , out of plane; φ , torsion; ^bRef³¹, ^cw, weak; m, medium; s, strong; v, very; sh, shoulder.