Supporting Information

Insight into Chalcogenolate-Bound $\{Fe(NO)_2\}^9$ Dinitrosyl Iron Complexes (DNICs): Covalent Character versus Ionic Character

By

Pai-Heng Liu,[†] Fu-Te Tsai,*[†] Bo-Hao Chen,[§] I-Jui Hsu*[‡] Hung-Hsi Hsieh,[†] and Wen-Feng Liaw*[†]

[†] Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

[‡] Research and Development Center for Smart Textile Technology, Department of Molecular Science and Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

[§] National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

E-mail: wfliaw@mx.nthu.edu.tw; ijuihsu@ntnu.edu.tw; fttsai@mx.nthu.edu.tw

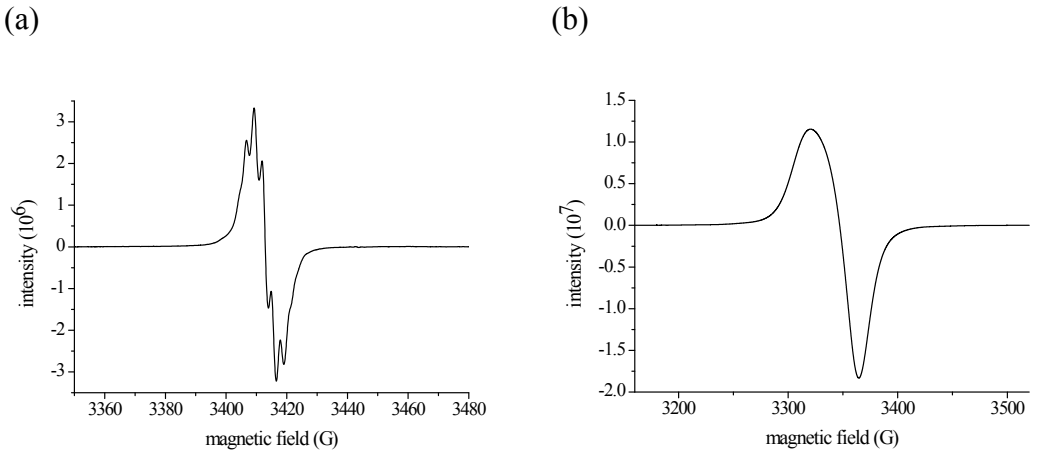


Figure S1. EPR spectra of complex **2** in THF (a) at 285 K (g_{av} = 2.022, a_N = 2.44 G), and (b) at 77 K (g_{av} = 2.023, g_1 = 2.04, g_2 = 2.02, and g_3 = 2.01).

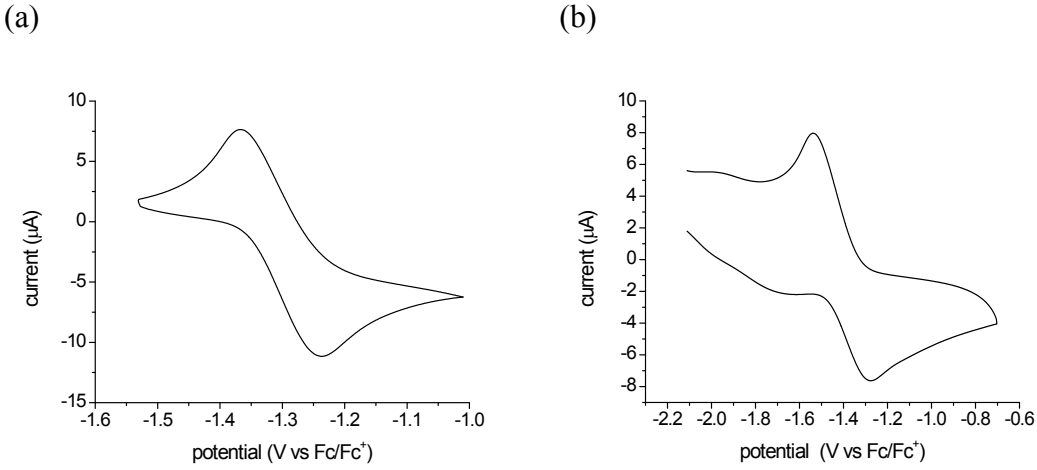


Figure S2. Cyclic voltammogram of 3 mM THF solution of (a) $[(MeO)_2Fe(NO)_2]^-$ (**2**) and (b) $[(PhO)_2Fe(NO)_2]^-$ (**6**) with 0.1 M $[^nBu_4N][PF_6]$ as the supporting electrolyte at scan rate of 0.5 V/s.

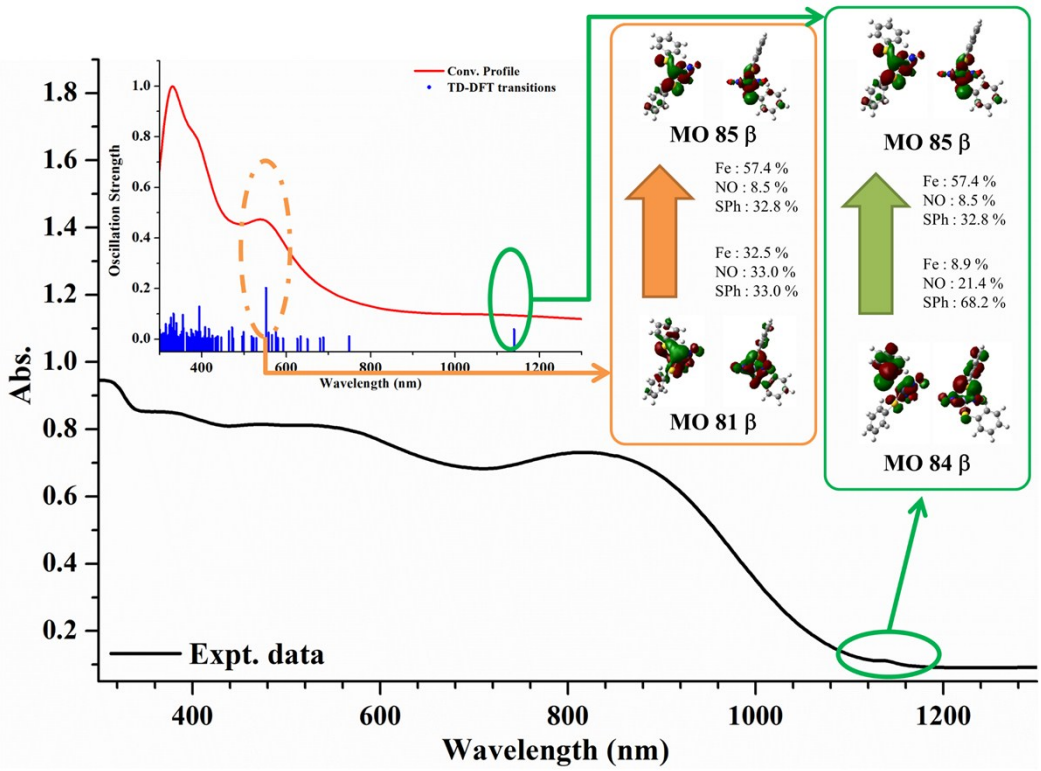


Figure S3. Experimental and simulated UV-vis spectra of complex **4**.

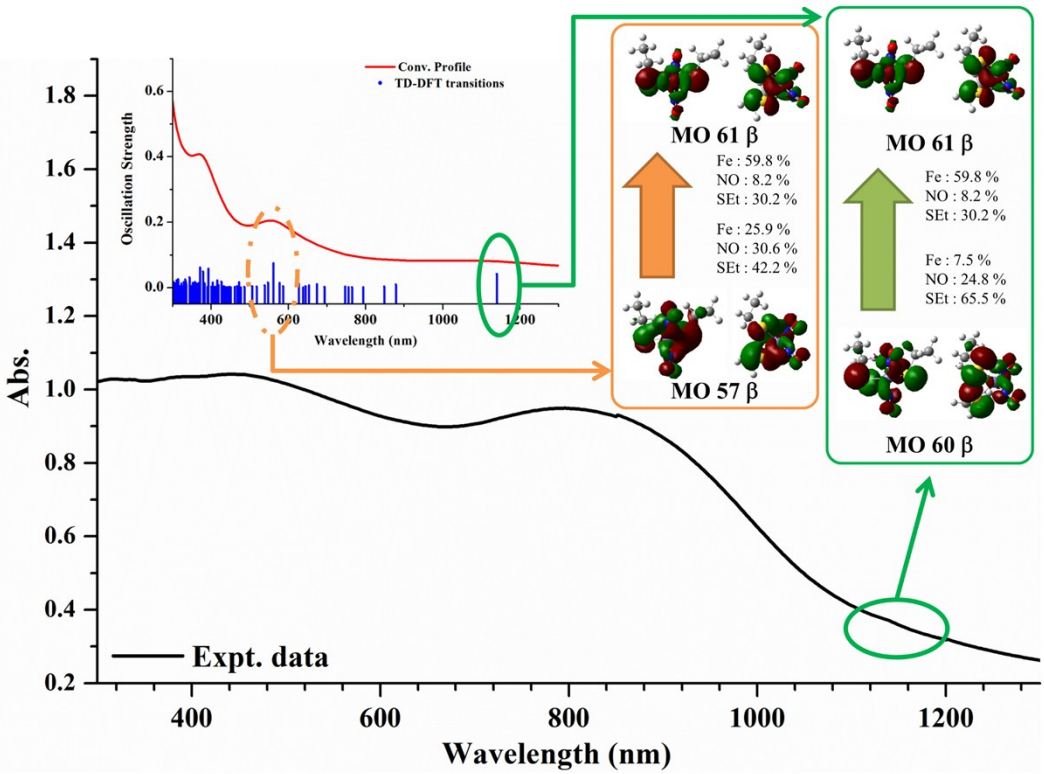


Figure S4. Experimental and simulated UV-vis spectra of complex **5**.

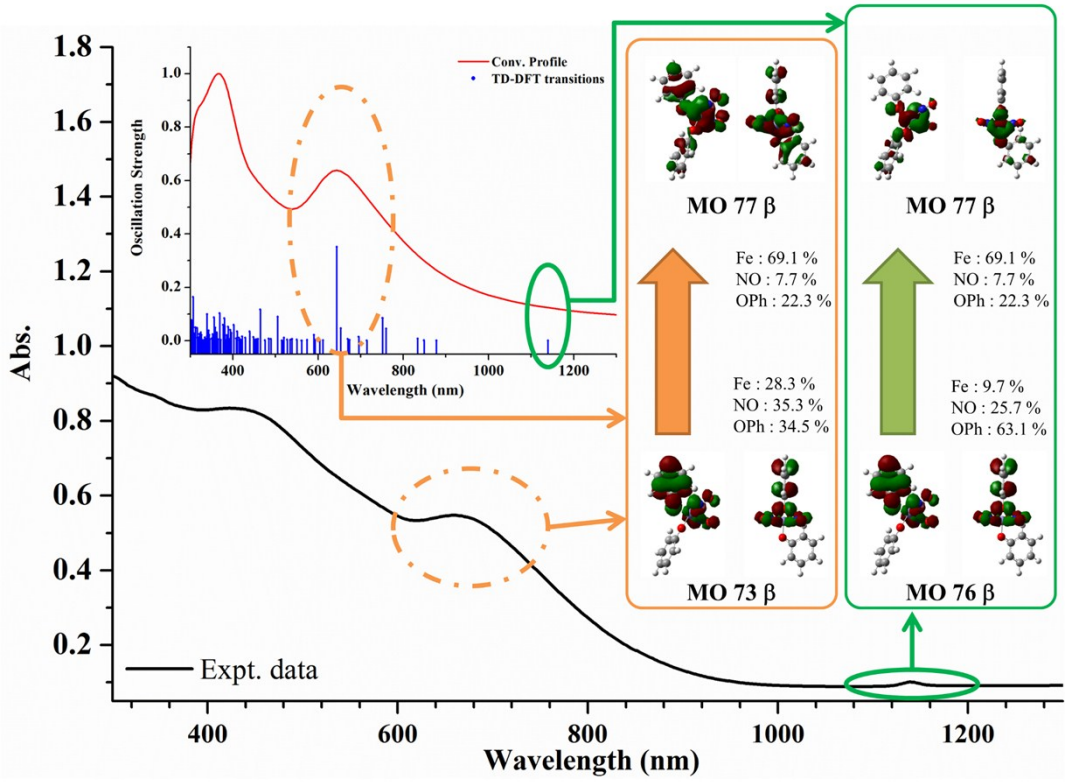
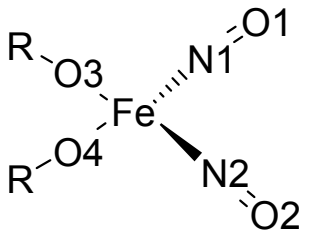


Figure S5. Experimental and simulated UV-vis spectra of complex **6**.

Table S1. The Löwdin and NBO population analysis results of **2**, **2'** and **6'**.



R is methyl group in **2** and phenyl group in **6**. In each R group, C1 is bonding to O3 and C2 is bonding to O4.

	Löwdin			NBO		
Atom	**2**	**2'**	**6'**	**2**	**2'**	**6'**
O1	-0.02195	-0.06210	-0.02230	-0.27632	-0.31004	-0.27010
O2	0.00125	-0.05604	-0.01636	-0.24822	-0.30980	-0.26515
N1	-0.05861	-0.08081	-0.05529	0.01866	0.02079	0.04407
N2	-0.05330	-0.09167	-0.06066	0.03447	0.00334	0.04403
O3	-0.14569	-0.16539	0.00275	-0.81263	-0.72964	-0.67297
O4	-0.14642	-0.16539	0.00419	-0.80968	-0.72729	-0.67803
C1	-0.34463	-0.36571	-0.22917	-0.27733	-0.27008	0.29539
C2	-0.34317	-0.36567	-0.23533	-0.27898	-0.27170	0.30131
2*NO	-0.13261	-0.290618	-0.154613	-0.47141	-0.59571	-0.44715
2*O	-0.29210	-0.330786	0.00694	-1.62231	-1.45693	-1.3510

Table S2. Summary of crystallographic data, intensity collection and structure refinement parameters for complexes **2** and **3**.

Complex number	**2**	**3**
Empirical formula	C_{14} H_{30} Fe K N_2 O_{10}	C_{13} H_{27} Fe K N_2 O_9
Formula mass	481.35	450.31
Crystal system	Orthorhombic	Monoclinic
***a*/Å**	9.9994(4)	11.8963(15)
***b*/Å**	11.3818(5)	8.4665(9)
***c*/Å**	20.3653(7)	20.035(2)
***α*/°**	90	90°
***β*/°**	90	91.071(4)
***γ*/°**	90	90°
Unit cell volume/Å^3	2317.80(16)	2017.5(4)
Temperature/K	200(2)	100(2)
Space group	P 21 21 21	P 21/c
No. of formula units per unit cell, *Z*	4	4
Radiation type	MoK_α	MoK_α
Density (calculated), Mg/m^3	1.397	1.483
Absorption coefficient, mm^{-1}	0.877	0.999
F(000)	1012	944
Reflections collected	12783	4085
Independent reflections	3602	4085
Data / restraints / parameters	3602 / 0 / 254	4085 / 0 / 237
Goodness-of-fit on F^2	1.055	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0429	R1 = 0.0436
	wR2 = 0.1027	wR2 = 0.1096
R indices (all data)	R1 = 0.0539	R1 = 0.0569
	wR2 = 0.1090	wR2 = 0.1157
Largest diff. peak and hole,e.Å^{-3}	0.396, -0.311	0.615, -0.532