Supporting Information

π Back-Bonding of Iron(II) Complexes Supported by Tris(pyrid-2-ylmethyl)amine and its Nitro-Substituted Derivatives

Shinya Furukawa,[†] Yutaka Hitomi,*[,‡] Tetsuya Shishido,[†] Kentaro Teramura,[†] and Tsunehiro Tanaka[†]

[†]*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto 606-8501, Japan.*
Tel:+81- 075- 383- 2562, Fax: +08- 075 -383 -2561
E-mail: syinya-furukawa@t14.mbox.media.kyoto-u.ac.jp

[‡]*Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan.*
Tel: +81-077-465-7437, Fax: +81-077-465-6848
E-mail: yhitomi@mail.doshisha.ac.jp

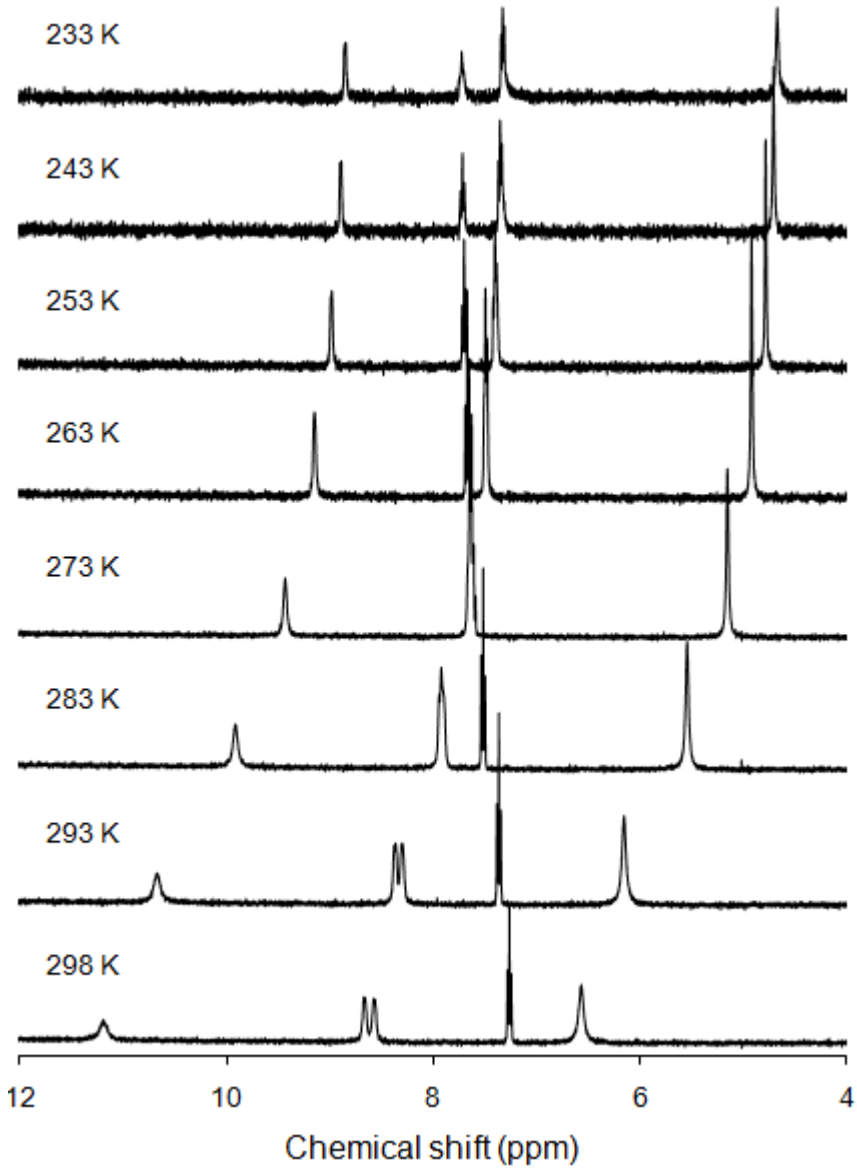

Figure S1. ^{1}H NMR spectra of **1** in MeCN-d_3 at various temperatures (298 K to 233 K)

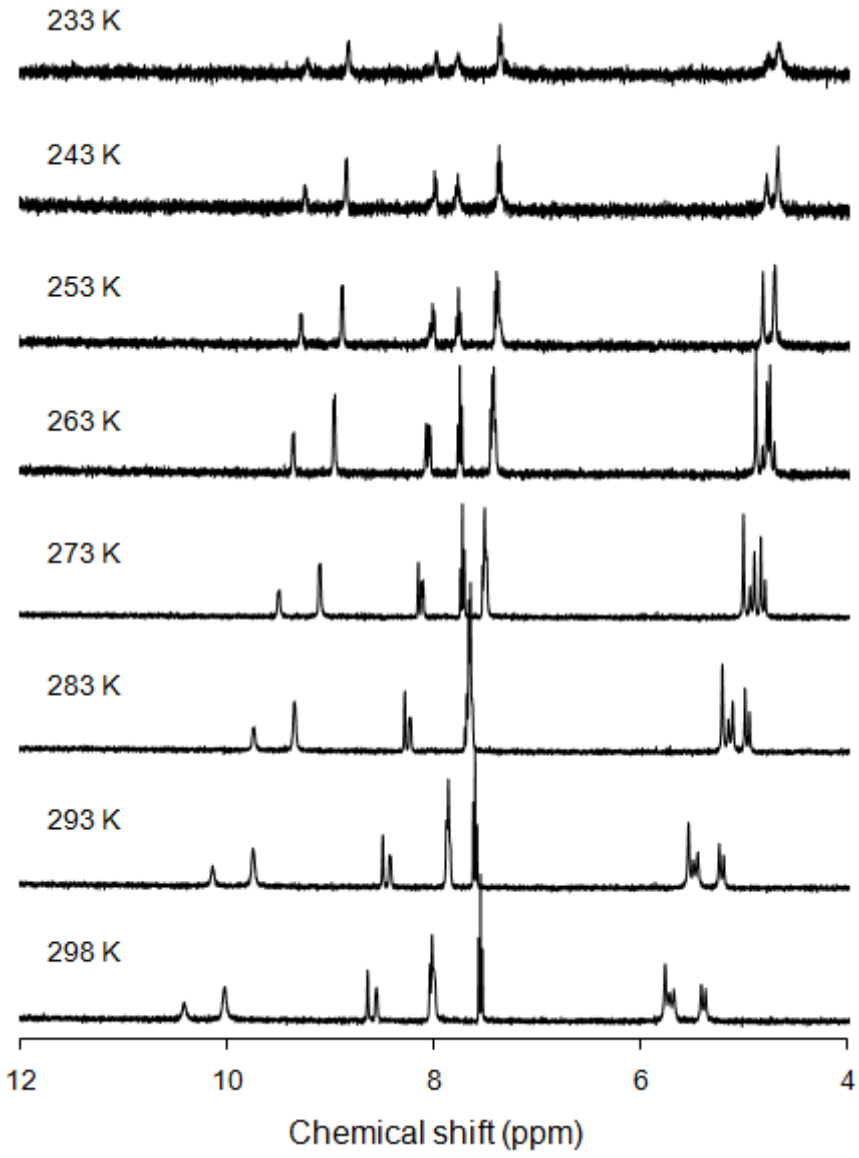

Figure S2. ^{1}H NMR spectra of **2** in MeCN-d_3 at various temperatures (298 K to 233 K)

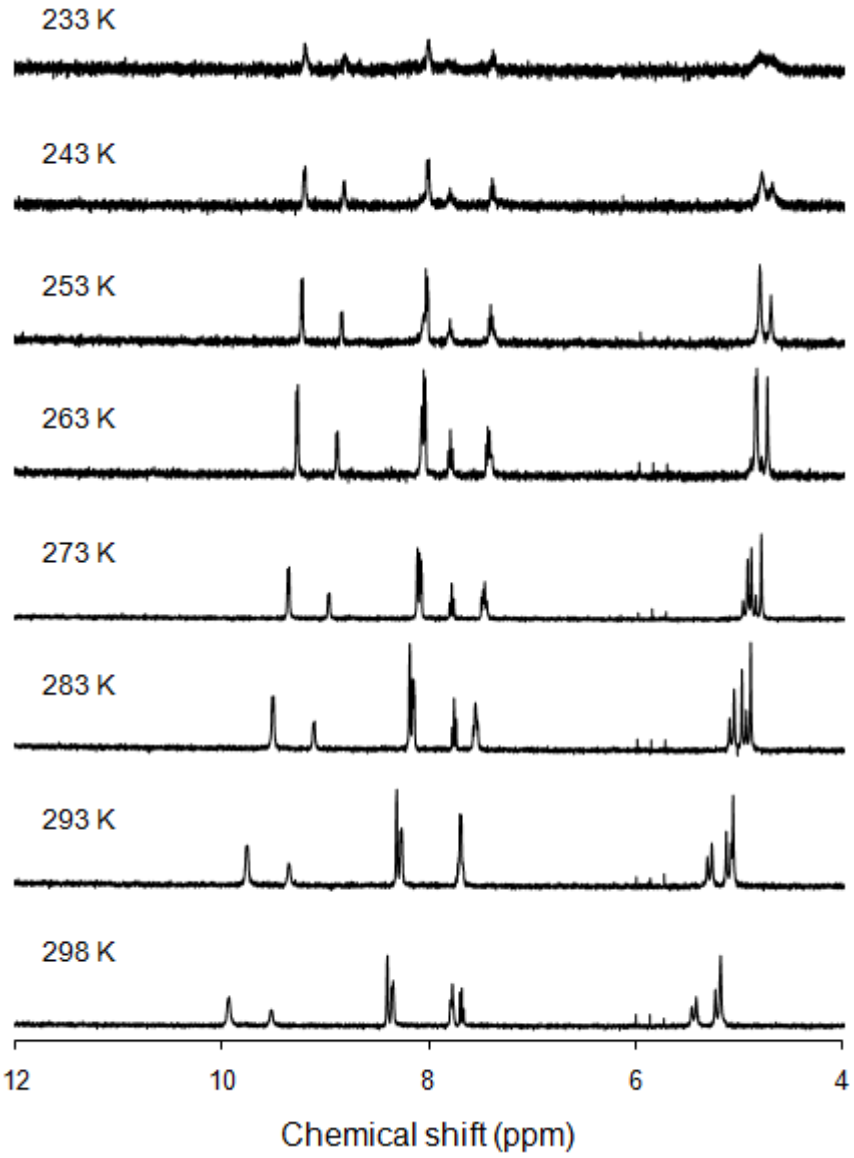

Figure S3. ^{1}H NMR spectra of **3** in MeCN-d_3 at various temperatures (298 K to 233 K)

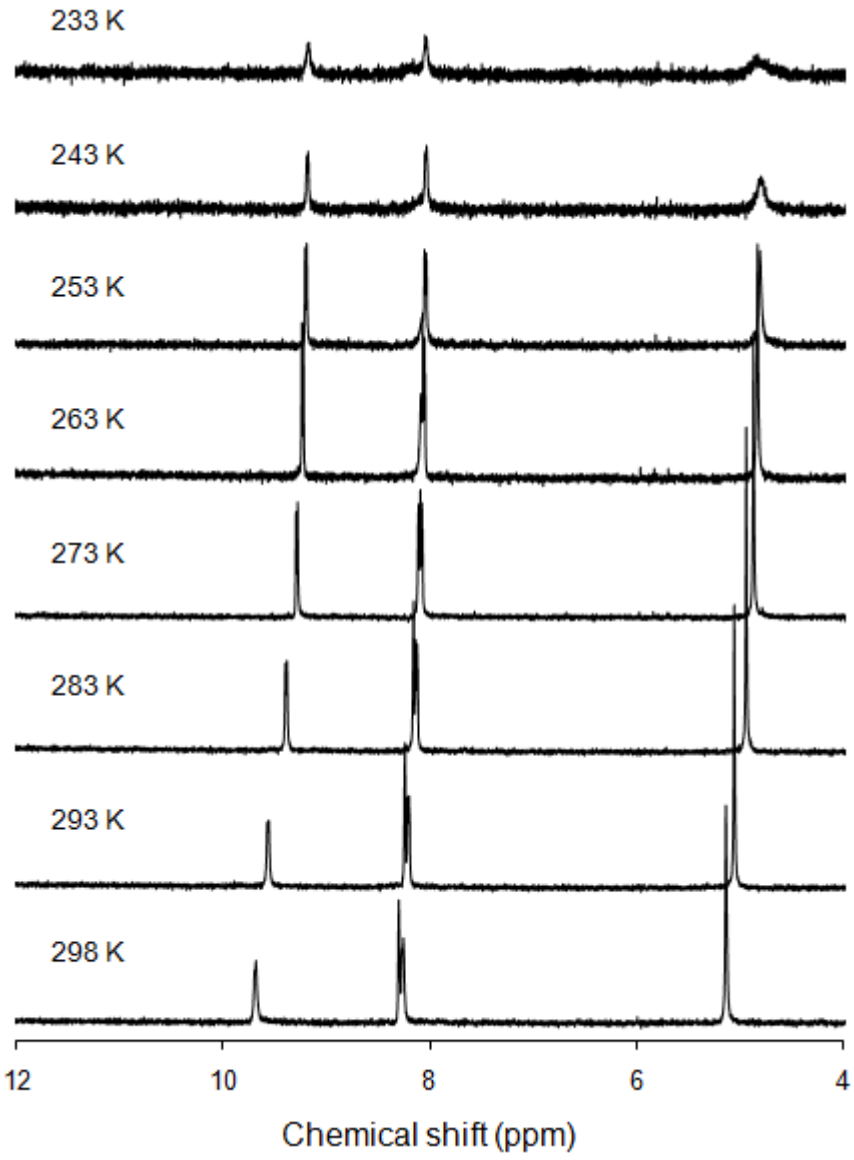

Figure S4. ^{1}H NMR spectra of **4** in MeCN-d_3 at various temperatures (298 K to 233 K)

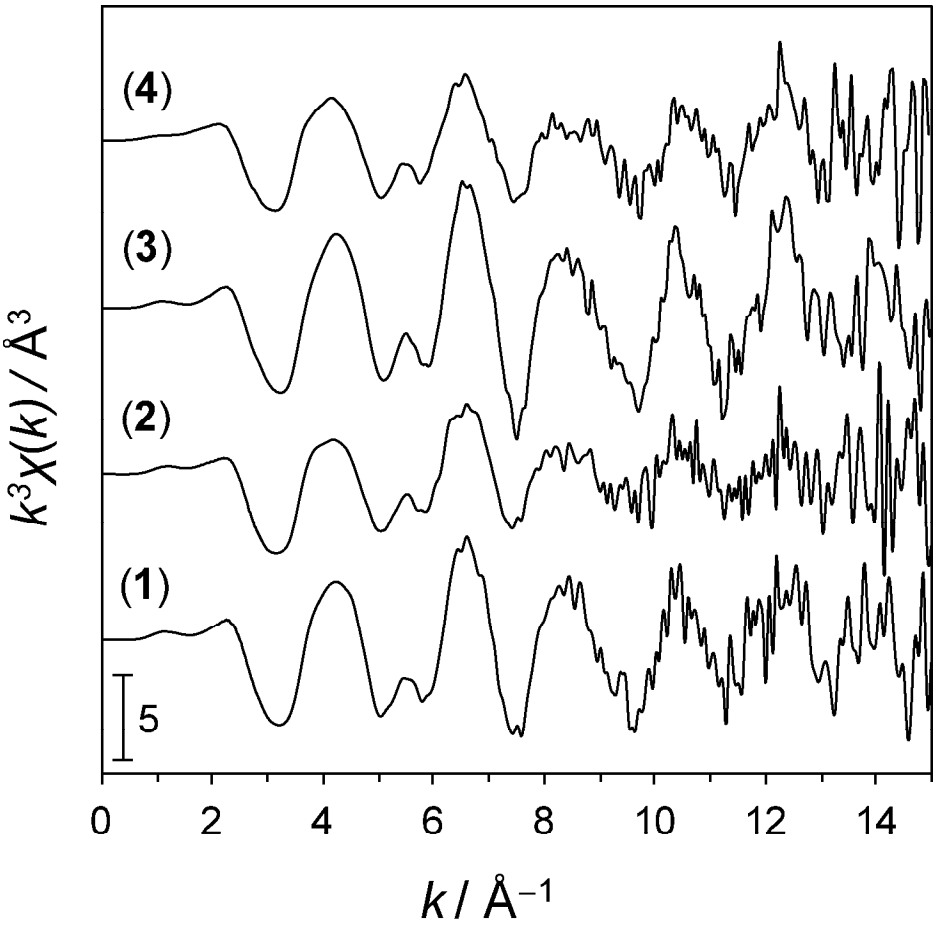

Figure S5. k^3-Weighted EXAFS spectra of **1**–**4**.

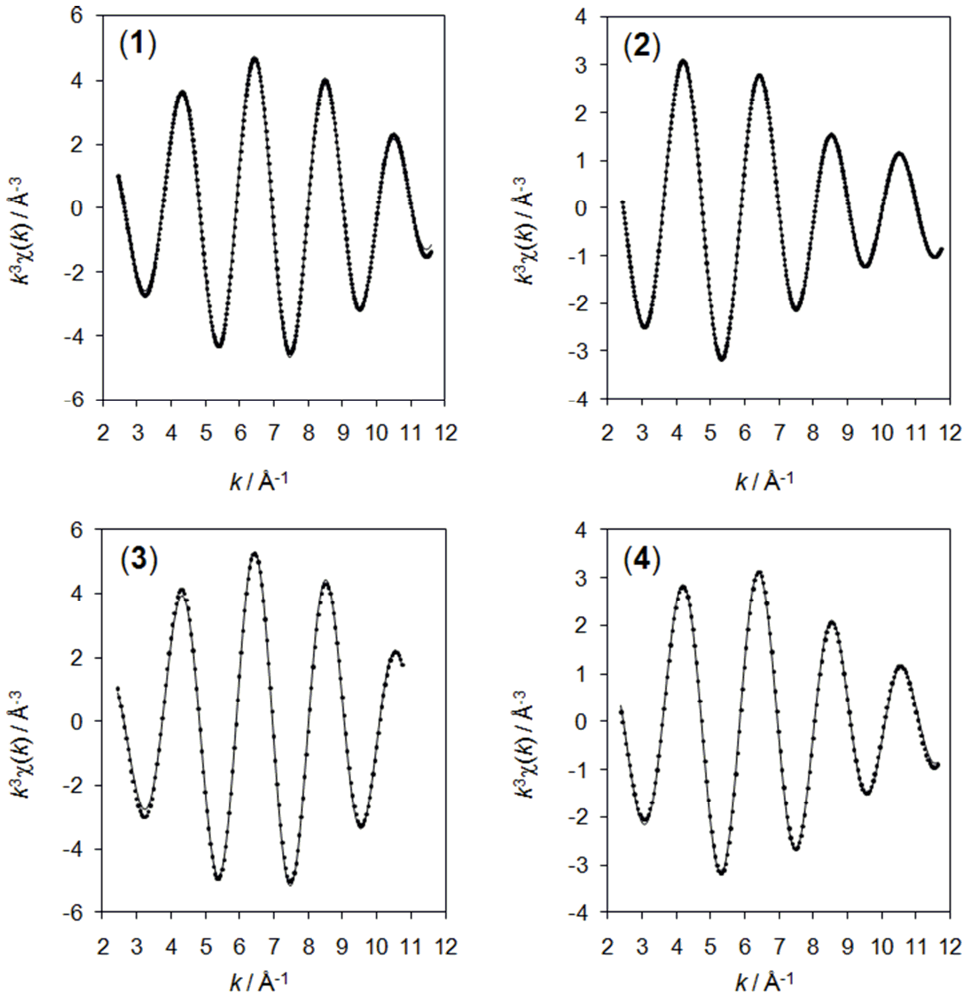

Figure S6. Fourier filtered EXAFS oscillations (solid curve) and the curve fit (circle) for complexes **1**–**4**.

Table S1. Energy levels of d orbitals of **1–4**.

complex	orbital energy / eV [a]		
	dσ	dπ	dσ – dπ
1	-0.577	-6.414	5.836
2a	-0.740	-6.611	5.871
2b	-0.737	-6.597	5.860
3a	-0.879	-6.772	5.893
3b	-0.879	-6.781	5.902
4	-1.021	-6.952	5.931

[a] Energies of the highest dπ orbitals and the lowest dσ ones are listed.

Table S2. Orbital energies and atomic orbital contributions for frontier KSOs of the complexes **1–4**.

KSO	**1**					
	E (eV)	%Fe	%Py	%NO_2-Py	%MeCN	symmetry [a]
LUKS+8	–0.340	44.0	12.9	–	42.1	π^*(MeCN) – d_{x2-y2}
LUKS+7	–0.477	33.3	7.3	–	57.5	d_{x2-y2} – π^*(MeCN)
LUKS+6	–0.577	63.9	9.5	–	17.9	d_{z2} – π^*(MeCN)
LUKS+5	–1.045	0.2	96.1	–	0.5	π^*(Py)
LUKS+4	–1.360	1.0	93.4	–	0.2	π^*(Py)
LUKS+3	–1.399	0.1	95.8	–	0.1	π^*(Py)
LUKS+2	–1.711	1.0	95.0	–	0.9	π^*(Py) – d_{xy}
LUKS+1	–1.828	4.9	94.0	–	0.1	π^*(Py) – d_{xy}
LUKS	–1.987	0.9	93.5	–	0.3	π^*(Py)
HOKS	–6.414	79.1	15.8	–	4.7	d_{xy} – π(Py)
HOKS-1	–6.647	87.4	4.3	–	7.2	d_{yz} – π(MeCN)
HOKS-2	–6.680	85.0	1.8	–	11.4	d_{zx} – π(MeCN)
KSO	**2a**					
	E (eV)	%Fe	%Py	%NO_2-Py	%MeCN	symmetry
LUKS+9	–0.464	20.9	4.9	0.9	72.2	π^*(MeCN) – d_{x2-y2}
LUKS+8	–0.615	56.3	10.9	2.8	27.8	d_{x2-y2} – π^*(MeCN)
LUKS+7	–0.740	66.2	9.9	1.3	14.0	d_{z2} – π^*(MeCN)
LUKS+6	–1.194	0.2	86.7	9.7	0.3	π^*(Py)
LUKS+5	–1.394	1.1	87.1	5.6	0.5	π^*(Py)
LUKS+4	–1.440	1.3	22.5	73.9	0.9	π^*(NO_2-Py) – d_{xy}
LUKS+3	–1.727	2.1	58.0	37.5	0.2	π^*(Py) – d_{xy}
LUKS+2	–1.892	2.5	54.9	39.0	0.2	π^*(Py) – d_{xy}
LUKS+1	–2.068	0.8	84.9	7.8	0.3	π^*(Py)
LUKS	–3.657	2.3	10.6	86.5	0.2	π^*(NO_2-Py) – d_{xy}
HOKS	–6.611	78.1	11.2	6.0	4.3	d_{xy} – π(Py) – π(NO_2-Py)
HOKS-1	–6.830	87.2	3.5	0.6	7.4	d_{yz} – π(MeCN)
HOKS-2	–6.883	85.2	1.2	1.0	11.0	d_{zx} – π(MeCN)
KSO	**2b**					
	E (eV)	%Fe	%Py	%NO_2-Py	%MeCN	symmetry
LUKS+9	–0.467	20.1	4.1	1.8	73.0	π^*(MeCN) – d_{x2-y2}
LUKS+8	–0.594	58.1	10.4	4.7	25.1	d_{x2-y2} – π^*(MeCN)
LUKS+7	–0.737	65.7	6.3	2.7	16.3	d_{z2} – π^*(MeCN)
LUKS+6	–1.171	0.3	88.1	7.2	0.5	π^*(Py)
LUKS+5	–1.357	0.9	45.4	51.5	0.2	π^*(NO_2-Py)
LUKS+4	–1.535	1.5	54.2	38.0	0.4	π^*(NO_2-Py) – d_{xy}
LUKS+3	–1.736	0.3	36.0	61.4	0.2	π^*(NO_2-Py)
LUKS+2	–1.856	2.0	80.7	14.5	0.6	π^*(Py) – d_{xy}
LUKS+1	–1.972	2.0	73.5	18.4	0.2	π^*(Py) – d_{xy}
LUKS	–3.658	2.3	0.4	96.7	0.1	π^*(NO_2-Py) – d_{xy}
HOKS	–6.597	78.1	10.5	6.2	4.7	d_{xy} – π(Py) – π(NO_2-Py)
HOKS-1	–6.841	87.4	2.6	1.7	7.1	d_{yz} – π(MeCN)
HOKS-2	–6.857	85.2	1.5	0.3	11.3	d_{zx} – π(MeCN)

KSO	**3a**					
	E (eV)	%Fe	%Py	%NO_2-Py	%MeCN	symmetry
LUKS+10	–0.540	15.2	1.7	2.2	80.0	π*(MeCN) – d_{x2-y2}
LUKS+9	–0.767	63.5	5.6	11.0	18.2	d_{x2-y2} – π*(MeCN)
LUKS+8	–0.879	67.9	3.2	5.9	13.6	d_{z2} – π*(MeCN)
LUKS+7	–1.286	0.5	68.0	27.9	0.6	π*(Py) – d_{xy}
LUKS+6	–1.433	1.7	10.9	83.3	0.4	π*(NO_2-Py) – d_{xy}
LUKS+5	–1.573	0.4	0.2	97.6	0.2	π*(NO_2-Py)
LUKS+4	–1.794	0.5	23.0	73.8	0.0	π*(NO_2-Py) – d_{xy}
LUKS+3	–1.905	1.7	87.2	8.5	0.7	π*(Py) – d_{xy}
LUKS+2	–1.925	1.0	0.0	90.3	0.2	π*(NO_2-Py)
LUKS+1	–3.605	3.6	0.0	96.0	0.0	π*(NO_2-Py) – d_{xy}
LUKS	–3.725	0.2	0.2	98.8	0.1	π*(NO_2-Py)
HOKS	–6.772	78.0	5.8	11.1	4.8	d_{xy} – π(NO_2-Py) – π(Py)
HOKS-1	–7.008	85.5	1.2	0.9	10.9	d_{yz} – π(MeCN)
HOKS-2	–7.008	87.1	0.8	3.2	7.6	d_{zx} – π(MeCN)
KSO	**3b**					
	E (eV)	%Fe	%Py	%NO_2-Py	%MeCN	symmetry
LUKS+10	–0.541	12.5	1.1	2.1	83.4	π*(MeCN) – d_{x2-y2}
LUKS+9	–0.762	65.3	5.4	11.7	15.9	d_{x2-y2} – π*(MeCN)
LUKS+8	–0.879	67.6	3.9	6.8	12.6	d_{z2} – π*(MeCN)
LUKS+7	–1.285	0.6	78.9	16.3	0.3	π*(Py)
LUKS+6	–1.477	1.9	3.6	92.6	0.4	π*(NO_2-Py) – d_{xy}
LUKS+5	–1.479	1.5	4.8	91.5	1.0	π*(NO_2-Py) – d_{xy}
LUKS+4	–1.796	0.8	17.8	77.6	0.2	π*(NO_2-Py)
LUKS+3	–1.910	0.4	10.8	83.4	0.2	π*(NO_2-Py)
LUKS+2	–2.025	1.9	73.1	19.0	0.3	π*(Py) – d_{xy}
LUKS+1	–3.651	3.6	0.1	95.8	0.1	π*(NO_2-Py) – d_{xy}
LUKS	–3.693	0.3	0.4	98.6	0.1	π*(NO_2-Py)
HOKS	–6.781	77.9	5.4	11.8	4.5	d_{xy} – π(NO_2-Py) – π(Py)
HOKS-1	–6.997	87.1	1.6	2.4	7.6	d_{yz}
HOKS-2	–7.033	85.5	0.6	1.6	10.7	d_{zx}
KSO	**4**					
	E (eV)	%Fe	%Py	%NO_2-Py	%MeCN	symmetry
LUKS+11	–0.621	10.4	–	2.3	86.2	π*(MeCN) – d_{x2-y2}
LUKS+10	–0.914	67.7	–	17.9	12.7	d_{x2-y2} – π*(MeCN)
LUKS+9	–1.021	68.7	–	10.8	11.3	d_{z2} – π*(MeCN)
LUKS+8	–1.446	1.6	–	95.6	1.2	π*(NO_2-Py) – d_{xy}
LUKS+7	–1.519	2.5	–	95.5	0.3	π*(NO_2-Py) – d_{xy}
LUKS+6	–1.648	1.0	–	97.1	0.2	π*(NO_2-Py) – d_{xy}
LUKS+5	–1.657	0.3	–	96.2	0.2	π*(NO_2-Py)
LUKS+4	–1.915	0.6	–	93.2	0.3	π*(NO_2-Py)
LUKS+3	–2.088	0.5	–	92.8	0.1	π*(NO_2-Py)
LUKS+2	–3.636	3.0	–	96.5	0.0	π*(NO_2-Py) – d_{xy}
LUKS+1	–3.685	1.7	–	97.9	0.2	π*(NO_2-Py) – d_{xy}
LUKS	–3.761	0.6	–	98.4	0.1	π*(NO_2-Py)
HOKS	–6.952	78.0	–	16.9	4.6	d_{xy} – π(NO_2-Py)
HOKS-1	–7.158	86.8	–	3.6	8.4	d_{yz}
HOKS-2	–7.181	85.9	–	2.4	10.2	d_{zx}

Table S3. Fe–N distances in the optimized structures of **1'–4'**. [a)]

N atom		**1'**	**2a'**	**2b'**	**3a'**	**3b'**	**4'**
N^1	$R^1 = H$	2.179	2.179				
	$R^1 = NO_2$			2.154	2.185	2.156	2.183
N^2	$R^2 = H$	2.175		2.176	2.174		
	$R^2 = NO_2$		2.177			2.189	2.172
N^3	$R^3 = H$	2.180	2.163	2.171		2.178	
	$R^3 = NO_2$				2.143		2.155
	N^4	2.269	2.247	2.250	2.240	2.253	2.237
	N^5	2.090	2.102	2.108	2.105	2.104	2.106
	N^6	2.167	2.158	2.159	2.155	2.143	2.145