

## Electronic Structures of Reduced and Superreduced Ir<sub>2</sub>(1,8-diisocyanomenthane)<sub>4</sub><sup>n+</sup> Complexes

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### SUPPLEMENTARY INFORMATION

**Table S1.** DFT calculated vibrational wavenumbers  $\nu(\text{C}\equiv\text{N})$  in  $\text{cm}^{-1}$  (intensities in  $10^3 \text{ km/mol}$  in parenthesis) of the 3:1 orientational isomer of **2+**, **1+**, and **0** in MeCN. Calculated values are scaled by 0.956. Experimental data from ref.<sup>1</sup>

<b>2+</b>			<b>1+</b>		<b>0</b>		
long/eclp	short/twst	Exp.	Calc.	Exp.	eclipsed	twisted	Exp.
2164 (0.3)	2147(0.0)		2081(2.5)		1898(4.8)	1889(7.1)	1867-1883 <sup>a</sup>
2165 (0.0)	2147(0.1)		2088 (1.1)		1900(4.8)	1895(3.3)	
2167(6.0)	2153(5.6)	2156	2091(0.4)	2090	1924(3.5)	1919(2.8)	1915 sh
2168(5.8)	2153(5.7)		2094(6.6)		1938(0.0)	1938(0.0)	
2189(0.0)	2170(0.0)		2097(1.7)		2066(4.7)	2063(3.5)	2058
2190(0.0)	2172(0.0)		2101(4.7)		2070(4.8)	2067(6.0)	
2240(0.0)	2212(0.5)		2124(2.1)	sh	2083(1.4)	2082(0.8)	sh
2243(0.0)	2231(0.0)		2189(0.0)		1896(0.0)	2132(0.0)	

<sup>a</sup> Broad band with several apparent maxima, see Figure 3-left. sh: shoulder apparent in the experimental spectrum.

**Table S2.** DFT-calculated one-electron energies and compositions of selected frontier molecular orbitals of short/twisted deformational isomer of **2+**. (PBE0/GD3/PCM-MeCN)

MO	E (eV)	Prevailing character	Ir	(C≡N) <sub>ax</sub>	(C≡N) <sub>ax</sub>
Unoccupied					
LUMO+2	-0.57	CN( $\pi^*$ )	7	55	28
LUMO+1	-0.94	Ir (p $\sigma^*$ )+CN( $\pi^*$ )	23	46	24
LUMO	-2.74	Ir (p $\sigma$ )+CN( $\pi^*$ )	34	34	27
Occupied					
HOMO	-5.79	Ir (d $\sigma^*$ )	88	8	3
HOMO-1	-7.12	Ir (d $\pi^*$ )	75	3	16
HOMO-2	-7.13	Ir (d $\pi^*$ )	75	3	16
HOMO-3	-7.61	Ir (d $\pi$ )	69	2	21
HOMO-4	-7.62	Ir (d $\pi$ )	69	3	21
HOMO-5	-7.73	Ir (d $\sigma$ )	98	1	0
HOMO-6	-7.90	Ir (d $\pi$ )	49	3	28
HOMO-7	-7.93	Ir (d $\pi$ )	53	3	30

**Table S3.** DFT-calculated one-electron energies and compositions of selected frontier molecular orbitals of the long/eclipsed isomer of **2+**. (DFT/PBE0/GD3/PCM-MeCN)

MO	E (eV)	Prevailing character	Ir	C (C≡N)	N
Unoccupied					
LUMO+2	-0.34	CN( $\pi^*$ )	13	51	26
LUMO+1	-1.74	Ir (p $\sigma^*$ )+CN( $\pi^*$ )	24	43	26
LUMO	-2.50	Ir (p $\sigma$ )+CN( $\pi^*$ )	36	34	25
Occupied					
HOMO	-6.35	Ir (d $\sigma^*$ )	94	6	0
HOMO-1	-6.96	Ir (d $\sigma$ )	93	7	0
HOMO-2	-7.26	Ir (d $\pi^*$ )	72	2	18
HOMO-3	-7.26	Ir (d $\pi^*$ )	72	2	18
HOMO-4	-7.35	Ir (d $\pi$ )	73	2	19
HOMO-5	-7.35	Ir (d $\pi$ )	73	2	19
HOMO-6	-7.79	Ir (d $\pi$ )	52	3	28
HOMO-7	-7.81	Ir (d $\pi$ )	55	3	29

**Table S4.** DFT-calculated one-electron energies and compositions of selected frontier molecular orbitals of the short/twisted isomer of **1+**. (PBE0/GD3/PCM-MeCN; )

Prevailing character	$\alpha$ MOs				$\beta$ MOs			
	MO (eV)	Ir	C (C $\equiv$ N)	N	MO(eV)	Ir	C (C $\equiv$ N)	N
CN( $\pi^*$ )	LUMO+2 (-0.09)	12	50	26	LUMO+3 (-0.05)	12	50	26
CN( $\pi^*$ )	LUMO+1 (-0.14)	11	51	26	LUMO+2 (-0.10)	10	51	26
Ir (p $\sigma^*$ )+CN( $\pi^*$ )	LUMO (-0.35)	25	47	27	LUMO+1 (-0.10)	22	47	27
Ir (p $\sigma$ )+CN( $\pi^*$ )	HOMO (-3.54)	31	35	21	LUMO (-2.17)	28	38	23
Ir (d $\sigma^*$ )	HOMO-1 (-5.31)	83	8	28	HOMO (-5.14)	86	8	28
Ir (d $\pi^*$ )	HOMO-2 (-6.43)	74	5	7	HOMO-1 (-6.39)	74	5	5
Ir (d $\pi^*$ )	HOMO-3 (-6.45)	74	5	16	HOMO-2 (-6.41)	74	4	16
Ir (d $\pi$ )	HOMO-4 (-7.19)	67	2	16	HOMO-3 (-7.07)	68	3	16
Ir (d $\pi$ )	HOMO-5 (-7.19)	67	3	23	HOMO-4 (-7.07)	68	3	23
Ir (d $\pi$ )	HOMO-6 (-7.34)	51	3	23	HOMO-5 (-7.33)	53	3	23
Ir (d $\pi$ )	HOMO-7 (-7.36)	54	3	30	HOMO-6 (-7.34)	54	3	2
Ir (d $\sigma$ )	HOMO-8 (-7.41)	93	6	32	HOMO-7 (-7.36)	91	6	29

**Table S5.** DFT-calculated one-electron energies and compositions of selected frontier molecular orbitals of the short/twisted isomer of **0**. (PBE0/GD3/PCM-MeCN)

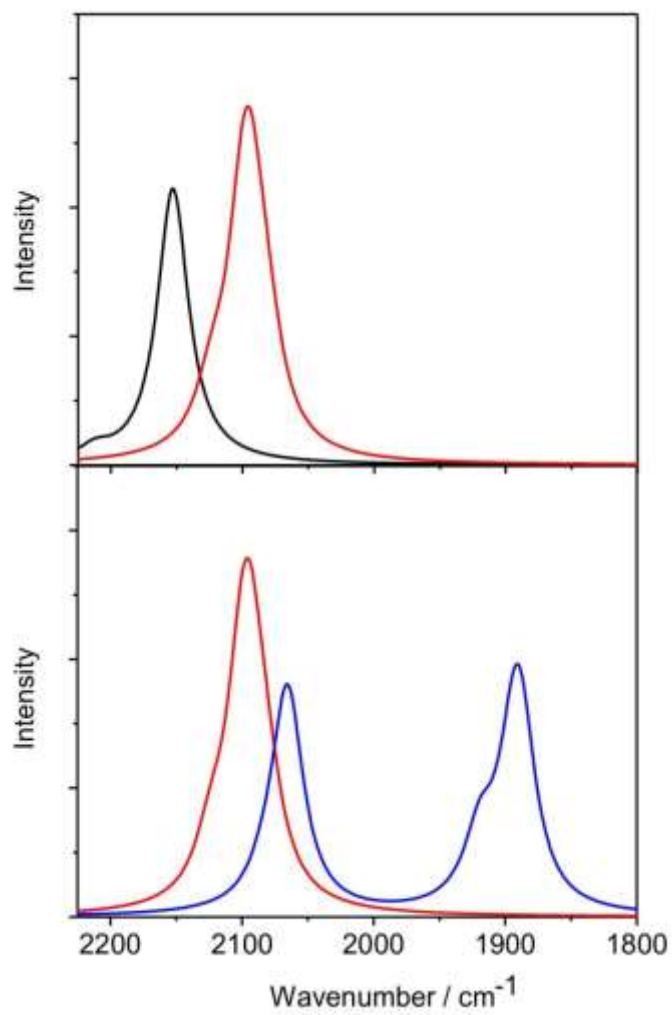
MO	E (eV)	Prevailing character	Ir	C <sub>ax</sub> (C $\equiv$ N)	C <sub>eq</sub> (C $\equiv$ N)	N <sub>ax</sub>	N <sub>eq</sub>
Unoccupied							
LUMO+2	0.21	CN( $\pi^*$ )	13	32	18	16	9
LUMO+1	0.09	CN( $\pi^*$ )	11	40	12	20	6
LUMO	0.01	Ir (p $\sigma^*$ )+CN( $\pi^*$ )	23	23	27	8	10
Occupied							
HOMO	-3.58	Ir (p $\sigma$ )+CN( $\pi^*$ )	32	14	20	13	13
HOMO-1	-5.21	Ir (d $\pi^*$ )	57	1	19	3	16
HOMO-2	-5.42	Ir (d $\sigma^*$ )	69	0	14	1	12
HOMO-3	-5.80	Ir (d $\pi^*$ )	60	2	14	4	15
HOMO-4	-6.61	Ir (d $\pi$ )	62	2	4	18	6
HOMO-5	-6.79	Ir (d $\pi$ )	62	3	1	20	5
HOMO-6	-6.93	Ir (d $\pi$ )	49	1	2	14	19
HOMO-7	-6.94	Ir (d $\pi$ )	51	5	2	15	19
HOMO-8	-7.31	Ir (d $\sigma$ )	79	4	4	2	8

**Table S6.** Calculated and experimental UV-vis spectra of the 3:1 orientational isomers of Ir(dimen)<sup>n</sup> in MeCN. Transitions with oscillator strength larger than 0.01 and spectroscopically relevant<sup>2</sup> triplet transitions (<sup>3</sup>A) are listed. The shapes of the MOs involved are shown in Figure S2.

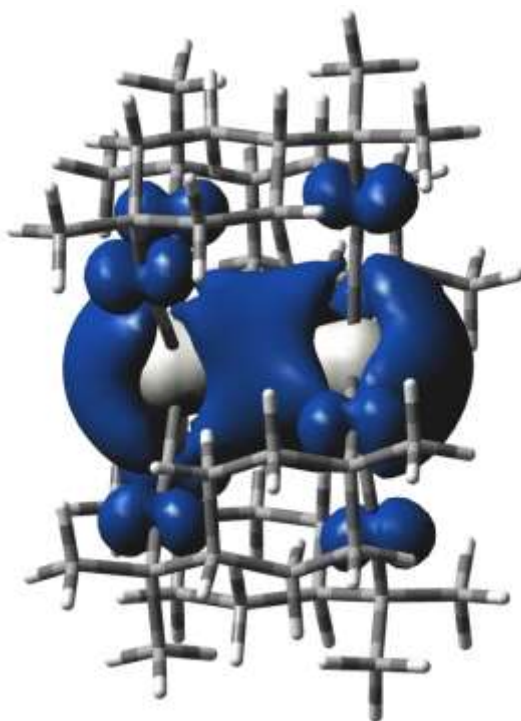
Compound	Main contributing excitations (%)	Wavelength nm	Oscillator strength	Experiment $\lambda$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
2+ long/eclipsed	HOMO→LUMO (95)	443	0.152	475 <sup>a</sup>
	HOMO-4 →LUMO (95) <sup>3</sup> A	384	-	378 <sup>a,d</sup>
	HOMO-5 →LUMO (95) <sup>3</sup> A	384	-	
	HOMO-4 →LUMO (95)	323	0.254	327 <sup>b</sup> (36600)
	HOMO-5 →LUMO (95)	323	0.254	
2+ short/twisted	HOMO→LUMO (99)	567	0.178	598 <sup>c</sup> (7300 <sup>b</sup> )
	HOMO-3 →LUMO (99) <sup>3</sup> A	367	-	377 <sup>c,d</sup> (18000 <sup>b</sup> )
	HOMO-4 →LUMO (99) <sup>3</sup> A	366	-	
	HOMO-3 →LUMO (99)	321	0.177	327 <sup>b</sup> (36600)
	HOMO-4 →LUMO (99)	320	0.201	
1+	$\beta$ HOMO→ $\beta$ LUMO (86)	711	0.018	800 <sup>b</sup> (3700)
	$\alpha$ HOMO→ $\alpha$ LUMO (81)	534	0.211	595 <sup>b</sup> (12300)
	$\alpha$ HOMO→ $\alpha$ LUMO+9 (60)	350	0.024	
	mixed	319	0.243	320 <sup>b</sup> (20900)
	mixed	319	0.228	
0 twisted	HOMO→LUMO+2 (96)	443	0.014	432 <sup>b</sup> (14400)
	HOMO→LUMO (98)	425	0.305	
	HOMO→LUMO+5 (94)	384	0.019	
	HOMO→LUMO+4 (97)	383	0.013	
	HOMO→LUMO+7 (89)	334	0.021	
	HOMO→LUMO+8 (89)	328	0.138	300 <sup>b</sup> (25100)
	HOMO→LUMO+10 (95)	317	0.037	
	HOMO-1→LUMO (90)	306	0.093	

<sup>a</sup> From ref.<sup>3</sup> at 293.5 K, <sup>b</sup> From ref.<sup>1</sup> at room temperature, <sup>c</sup> From ref.<sup>3</sup> at 150 K. <sup>d</sup> Experimentally assigned as a spin-forbidden  $d_{xz,yz} \rightarrow p\sigma$  <sup>3</sup>E<sub>u</sub> transition.<sup>2</sup>

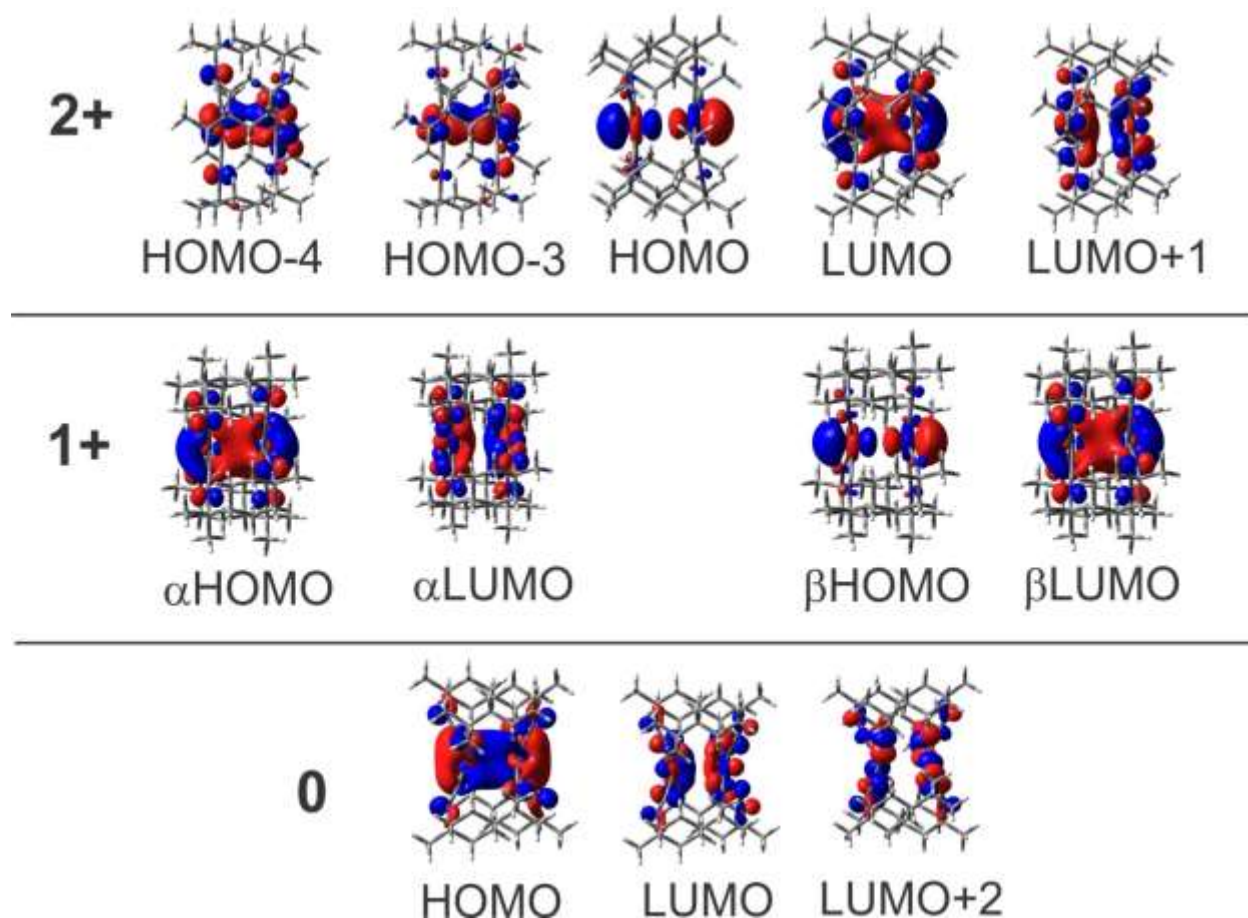
## FIGURES



**Figure S1.** Calculated  $\nu(\text{C}\equiv\text{N})$  IR spectra of the 3:1 orientational isomer of **2+** (black), **1+** (red), and **0** (blue) in MeCN. Simulated spectra assume fwhm of  $30\text{ cm}^{-1}$ .



**Figure S2.** Spin density distribution of **1+**.



**Figure S3.** Shapes of molecular orbitals involved in the lowest electronic transitions of **2+** (short/twisted), **1+**, and **0** (twisted).

#### References

- Hill, M. G.; Sykes, A. G.; Mann, K. R., Spectroelectrochemical Characterization of  $\text{Ir}_2(\text{dimen})_4^{4+}$  and  $\text{Ir}_2(\text{dimen})_4^0$  (dimen = 1,8-Diisocyanomenthane). *Inorg. Chem.* **1993**, *32*, 783–784.
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- Hunter, B. M.; Villahermosa, R. M.; Exstrom, C. L.; Hill, M. G.; Mann, K. R.; Gray, H. B., M–M Bond-Stretching Energy Landscapes for  $\text{M}_2(\text{dimen})_4^{2+}$  (M = Rh, Ir; dimen = 1,8-Diisocyanomenthane) Complexes. *Inorg. Chem.* **2012**, *51*, 6898–6905.