Supporting information.

Table S1. IR spectra of the compounds **1**−**4**.

Components	MeIm	$C_6H_4Cl_2$	$[V^{II}(MeIm)_2(Pc^{2-})]\cdot MeIm$ (**1**)	$[V^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**2**)	$[Cr^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**3**)	$[Fe^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**4**)
$M^{II}Pc$			441w	441w	439w	-
			505w	506w	507w	519w
			570w	570w	568w	570w
			728s	727s	725s	734s
			751s*	751s*	752s*	754s*
			-	-	761m	-
			772w	770w	776w	780w
			799w	800w	801w	-
			946w	946w	952w	947w
			1003w	1007w	1000w	1004w
			1057m	1057m	1076m*	1070m*
			1090s	1090s	1091m	1096s
			-	1100s	-	-
			1114s*	1115s*	1117s*	1120s*
			1164m	1166m	1166m	1165s
			1322s	1322s	1322m	1327m
			1405w	1405w	-	-
			1466s	1465s	1463s	1464w
			1535w	1534w	1534w	1530w
			1572w	1572w	1565w	1596w
			3055w	3055w	3051w	3057w
MeIm	620m		615w	616w	616w	614w
	666w		660w	659w*	660w*	662w*
	741m		751s*	751s*	752s*	754s*
	820m		817w	817w	819w	-
	905m		897w	897w	900w	899w
	1026w		-	-	-	-
	1077m		-	-	1076m*	1070m*
	1109m		1114s*	1115s*	1117s*	1120s*
	1230s		1234w	1236w	1237m	1240w
	1285m		1285m	1287m	1288m	1286m
	1358w		-	-	-	-
	1420m		-	1418w	1417m	1421s
	-		-	1433w	1435m	-
	1518s		1516w	1514w	-	1509s
	2919w		2920w	2918w	2921w	2920w
	2954w		-	-	2976w	2957w
	3110w		3116w	3116w	3117w	3118w
$C_6H_4Cl_2$		658w		659w*	660w*	662w*
		743m		751s*	752s*	754s*
		1033w		1033w	1033w	1033w
		1455s		1456m	1456s	1456w

w – weak, m-middle, s – strong intensity.

* - the bands are coincided.

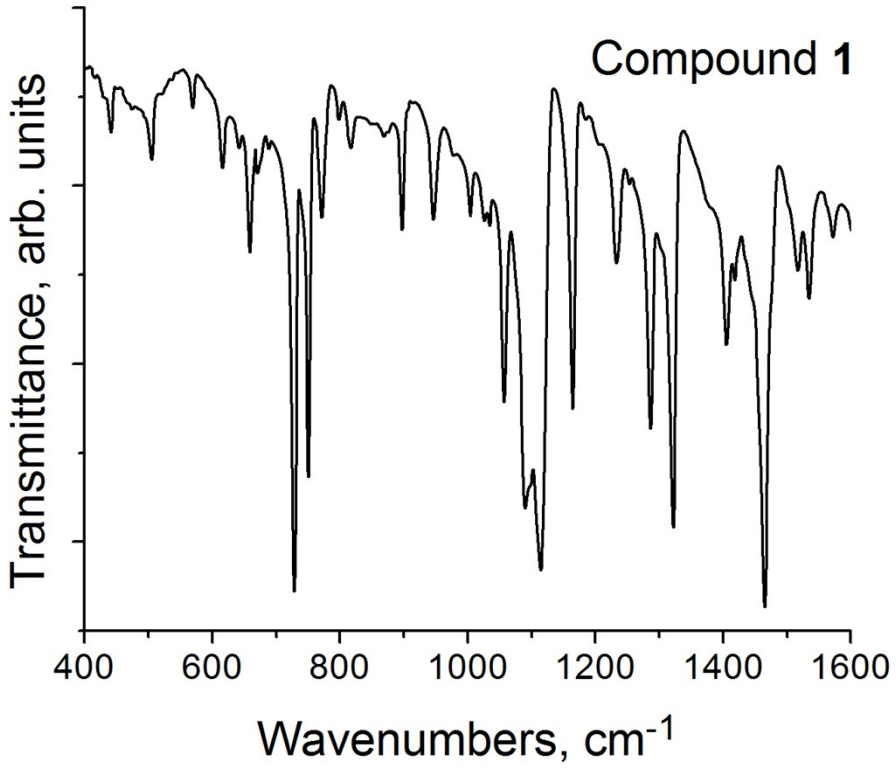

Fig. S1. IR spectrum of compound $[V^{II}(MeIm)_2(Pc^{2-})]\cdot MeIm$ (**1**) in KBr pellets. KBr pellet for **1** is prepared in anaerobic conditions.

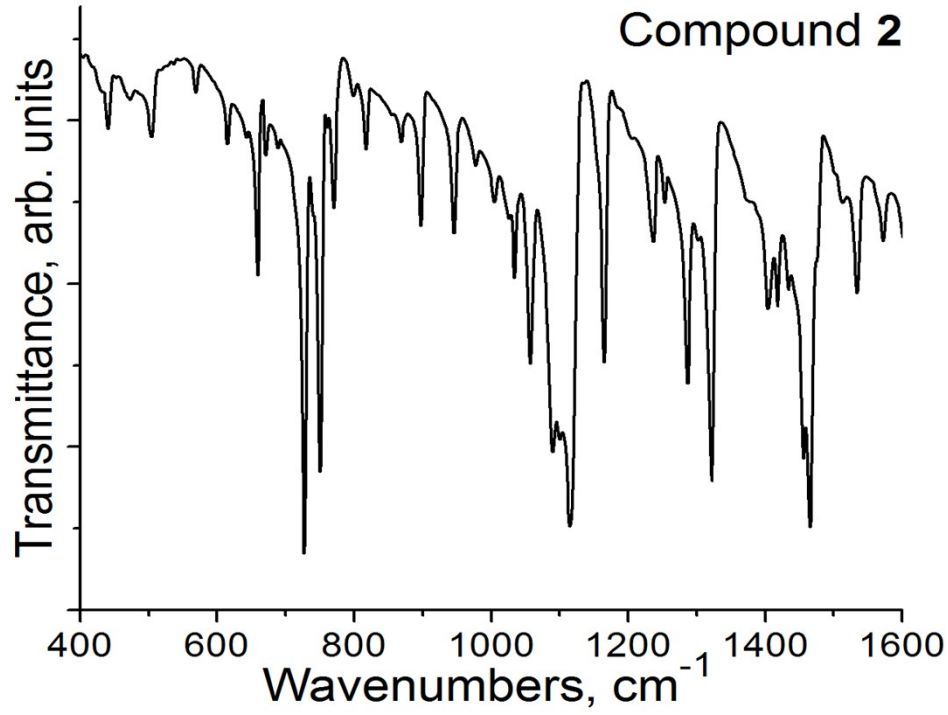

Fig. S2. IR spectrum of compound $[V^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**2**) in KBr pellets. KBr pellet for **2** was prepared in anaerobic conditions.

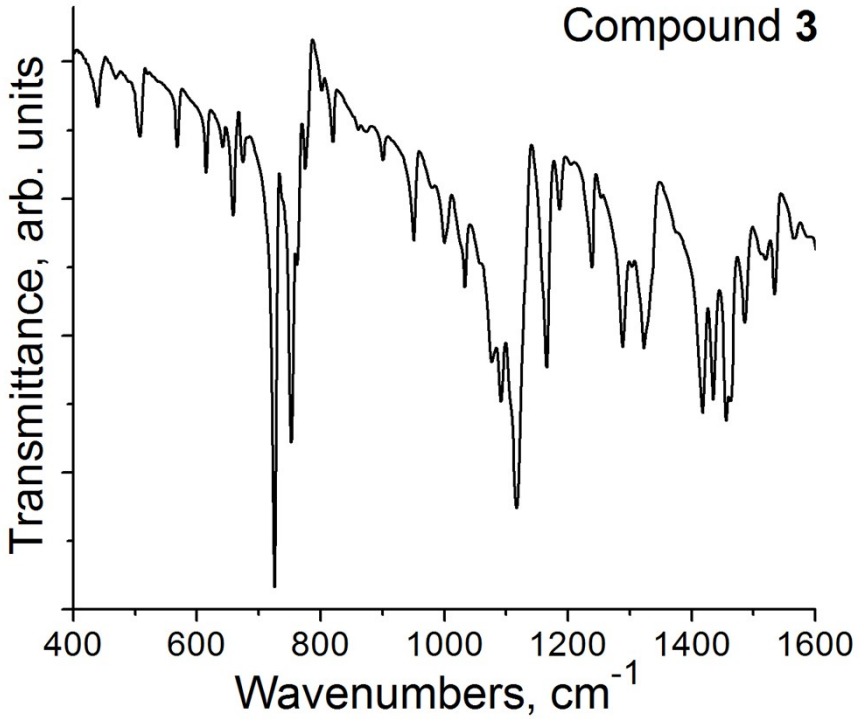

Fig. S3. IR spectrum of compound $[Cr^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**3**) in KBr pellets. KBr pellet for **3** was prepared in anaerobic conditions.

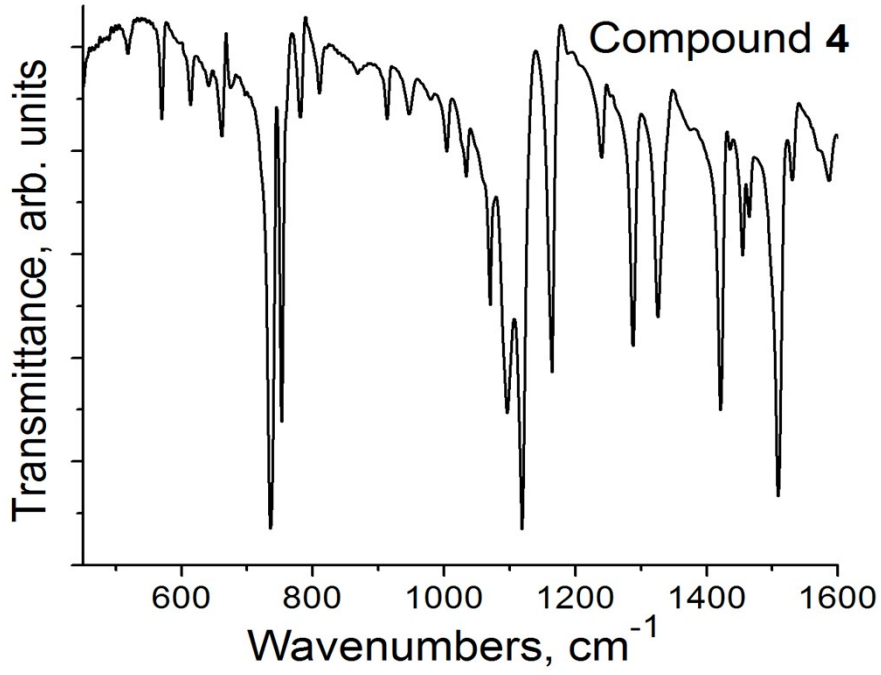

Fig. S4. IR spectrum of compound $[Fe^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**4**) in KBr pellets. KBr pellet for **4** was prepared in anaerobic conditions.

Crystal structure of complex 1.

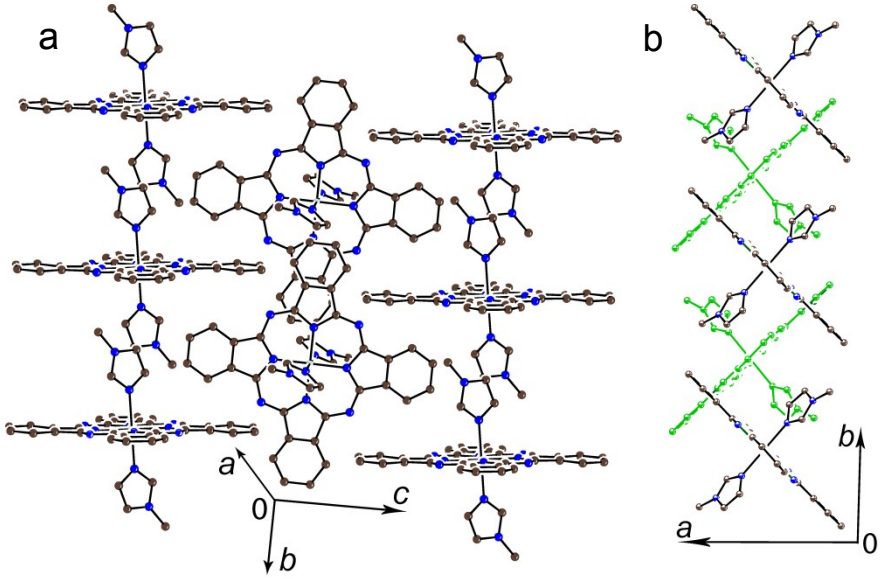

Fig. S5. Crystal structure of $[V^{II}(MeIm)_2(Pc^{2-})]\cdot MeIm$ (**1**). View on perpendicular to the Pc macrocycles of one of the chains in **1** (a) and view on two such chains along the *c* axis (b). In the latter case the $[V^{II}(MeIm)_2(Pc^{2-})]$ molecules from the behind located chain are shown by green color.

Magnetic properties of compounds 1−3.

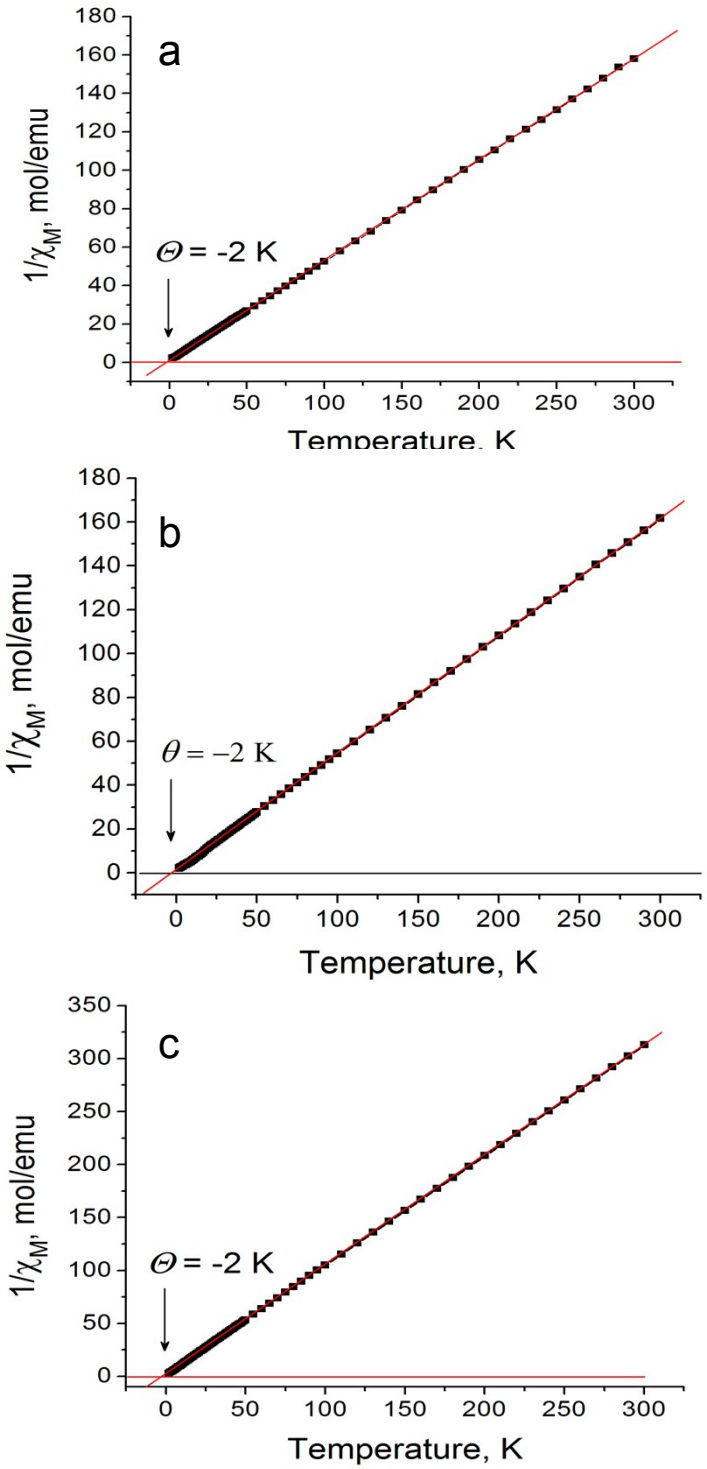

Fig. S6. Temperature dependencies of resiprocal molar magnetic sysceptibilities for the complexes: (a) $[V^{II}(MeIm)_2(Pc^{2-})]\cdot MeIm$ (**1**); (b) $[V^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**2**) and (c) $[Cr^{II}(MeIm)_2(Pc^{2-})]\cdot 2C_6H_4Cl_2$ (**3**). Fitting of the data by the Curie-Weiss law shown by red line allows to determine Weiss temperature ($\Theta = -2$ K for **1**−**3**).

Table S2. Total and relative energies (E and ΔE), and $\langle S^2 \rangle$ values of $[V(MeIm)_2Pc]^0$ and $[Cr(MeIm)_2Pc]^0$ complexes calculated at the CAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory

State	E / hartree	ΔE / K	$\langle S^2 \rangle$
$[V(MeIm)_2Pc]^0$			
^4A_g	−3141.43500	0	3.790
^2A_g	−3141.42704	2511	1.835
$[Cr(MeIm)_2Pc]^0$			
^5A_g	−3241.90947	3277	6.060
^3A_g	−3241.91984	0	2.871
^1A_g	−3241.88647	10540	1.767

Table S3. Charge and spin densities of the ^{4}Ag state in $[V(MeIm)_2Pc]^0$ and the ^{3}Ag state in $[Cr(MeIm)_2Pc]^0$ calculated at the CAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory

	MPA		NPA		
	Charge	Spin	Charge	Spin	Natural electron configuration
$[V(MeIm)_2Pc]^0$					
V	0.597	2.460	0.838	2.262	$3d^{2.74}$
Pc	−1.211	0.534	−1.358	0.675	
MeIm	0.307	0.003	0.260	0.031	
$[Cr(MeIm)_2Pc]^0$					
Cr	0.682	2.921	0.792	2.699	$3d^{4.23}$
Pc	−1.336	−0.897	−1.429	−0.739	
MeIm	0.327	−0.012	0.318	0.020	

Table S4. Occupation numbers of natural orbitals, n(HO−1), n(HO), n(SO−1), n(SO), n(SO+1), n(LU), and n(LU+1), non-spin-projected and spin-projected diradical characters, y_i and y_i^{SP} (i = 0 and 1)[a,b], of the ^4A_g state in $[V(MeIm)_2Pc]^0$, the ^3A_g state in $[Cr(MeIm)_2Pc]^0$, and open-shell singlet states in acenes at the CAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory

	$[V(MeIm)_2Pc]^0$	$[Cr(MeIm)_2Pc]^0$	Pentacene	Hexacene	Heptacene	Octacene
n(LU+1)	0.005	0.012	0.014	0.055	0.097	0.147
n(LU)	0.007	0.579	0.118	0.407	0.589	0.708
n(SO+1)	1.000	1.000	–	–	–	–
n(SO)	1.000	–	–	–	–	–
n(SO+1)	1.000	1.000	–	–	–	–
n(HO)	1.993	1.421	1.882	1.593	1.411	1.292
n(HO−1)	1.995	1.988	1.986	1.945	1.903	1.853
y_0	0.007	0.579	0.118	0.407	0.589	0.708
y_1	0.005	0.012	0.014	0.055	0.097	0.147
y_0^{SP}	0.000	0.285	0.008	0.123	0.296	0.462
y_1^{SP}	0.000	0.000	0.000	0.002	0.005	0.012

[a] $y_i = n(\text{LU}+i) = 2 - n(\text{HO}-i)$. [b] $y_i^{SP} = n^{SP}(\text{LU}+i) = 2 - n^{SP}(\text{HO}-i) = [n(\text{LU}+i)]^2/(1 + S_i^2) = 2 - [n(\text{HO}-i)]^2/(1 + S_i^2)$, $S_i = [n(\text{HO}-i) - n(\text{LU}+i)]/2$.

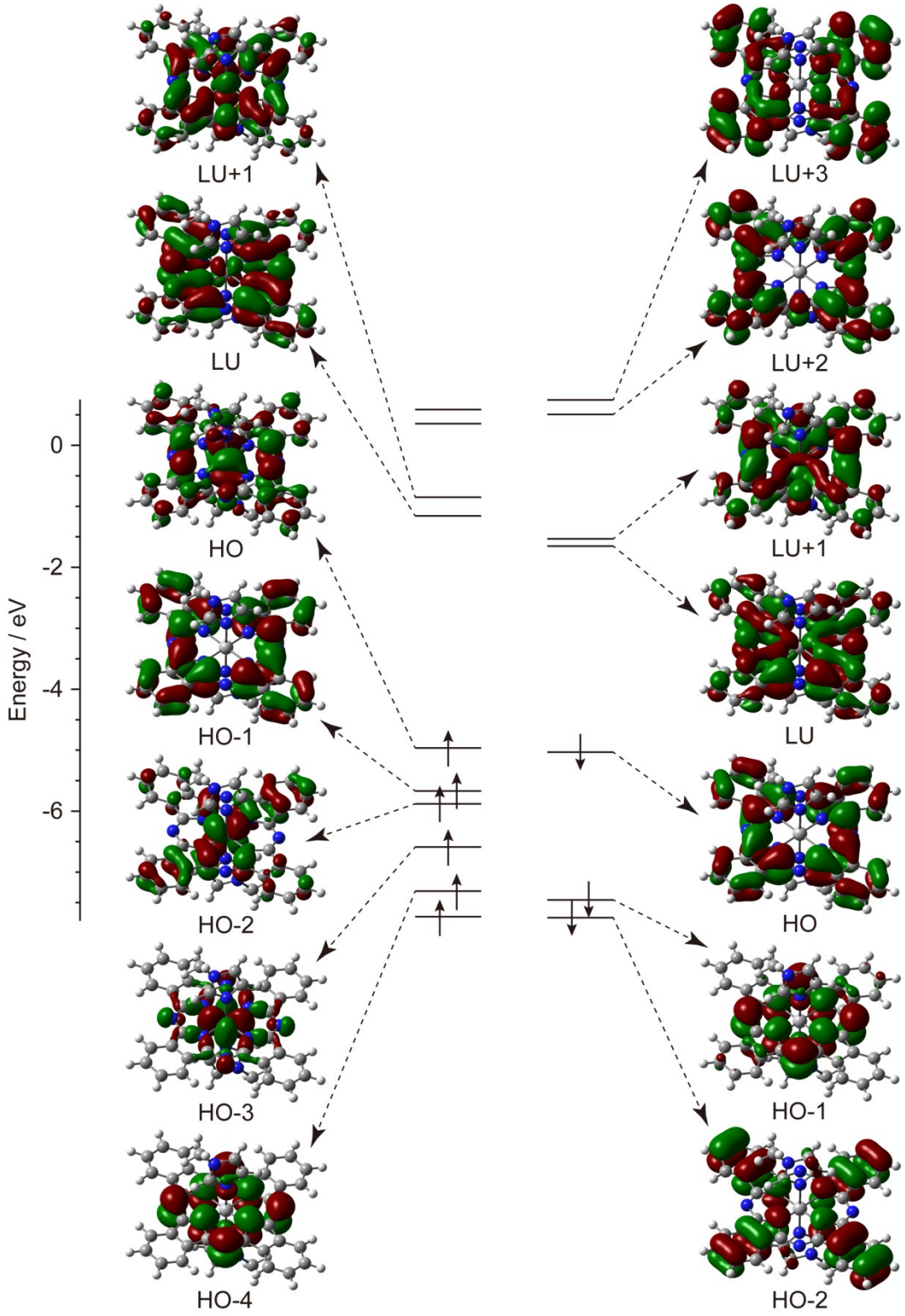

Fig. S7. Energy diagram for the frontier Kohn-Sham orbitals of the ^4A_g state in $[V(MeIm)_2Pc]^0$ calculated at the UCAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory. HO and LU denote the highest occupied and the lowest unoccupied orbitals, respectively.

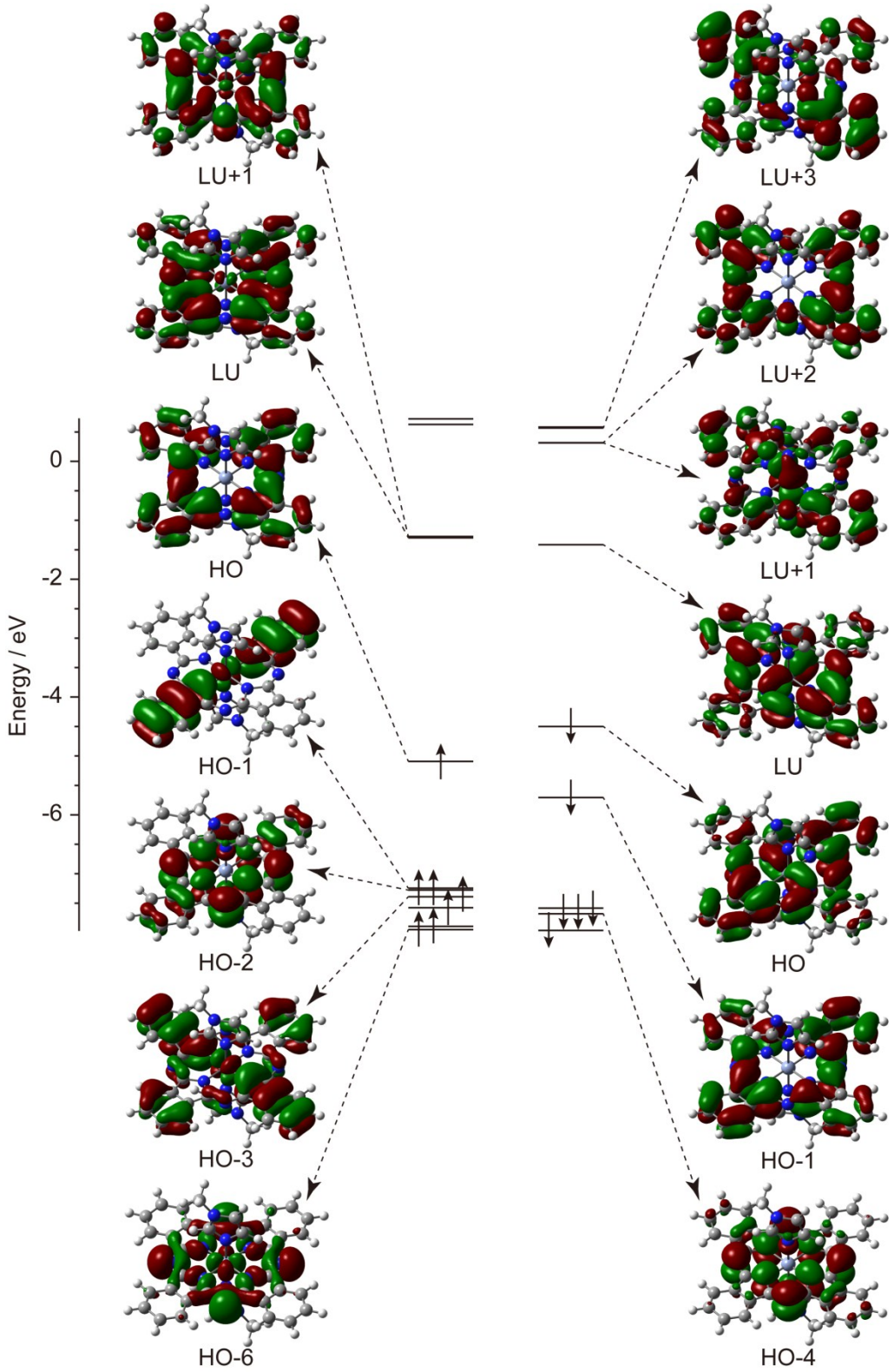

Fig. S8. Energy diagram for the frontier Kohn-Sham orbitals of the ^3A_g state in $[Cr(MeIm)_2Pc]^0$ calculated at the UCAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory. HO and LU denote the highest occupied and the lowest unoccupied orbitals, respectively.

Table S5. Excitation energies (ΔE), oscillator strengths (f), $\langle S^2 \rangle$ values and assignments on the low-lying excited states of $[V(MeIm)_2Pc]^0$ calculated at the TD-UCAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory.

	ΔE / eV	ΔE / nm	f	$\langle S^2 \rangle$	Assignment
1	0.655	1893	0.000	3.818	189α → 190α: 60% (α-HO → α-LU) 187α → 191α: 20% (α-HO-2 → α-LU+1) 189α → 191α: 9% (α-HO → α-LU+1) 187α → 190α: 4% (α-HO-2 → α-LU)
2	0.696	1782	0.031	5.150	186β → 187β: 80% (β-HO → β-LU) 188α → 190α: 14% (α-HO-1 → α-LU)
3	0.768	1616	0.000	3.818	189α → 191α: 60% (α-HO → α-LU+1) 187α → 190α: 24% (α-HO-2 → α-LU) 189α → 190α: 10% (α-HO → α-LU) 187α → 191α: 5% (α-HO-2 → α-LU+1)
4	0.842	1473	0.000	3.797	187α → 191α: 64% (α-HO-2 → α-LU+1) 189α → 190α: 27% (α-HO → α-LU) 178α → 191α: 3% (α-HO-11→ α-LU+1)
5	1.030	1204	0.068	4.485	186β → 188β: 86% (β-HO → β-LU+1) 188α → 191α: 7% (α-HO-1 → α-LU+1)
6	1.204	1030	0.000	3.788	186α → 191α: 88% (α-HO-3 → α-LU+1) 186α → 196α: 3% (α-HO-3 → α-LU+6) 175α → 191α: 3% (α-HO-14 → α-LU+1)
7	2.106	589	0.000	3.832	186α → 190α: 91% (α-HO-3 → α-LU) 187α → 190α: 3% (α-HO-2 → α-LU)
8	2.262	548	0.000	3.898	187α → 190α: 66% (α-HO-2 → α-LU) 189α → 191α: 25% (α-HO → α-LU+1) 186α → 190α: 4% (α-HO-3 → α-LU)
9	2.356	526	0.419	4.151	188α → 190α: 75% (α-HO-1 → α-LU) 186β → 187β: 15% (β-HO → β-LU) 185α → 191α: 4% (α-HO-4 → α-LU+1)
10	2.473	501	0.199	4.521	188α → 191α: 81% (α-HO-1 → α-LU+1) 186β → 188β: 7% (β-HO → β-LU+1) 185α → 190α: 6% (α-HO-4 → α-LU)
11	2.805	442	0.004	4.871	189α → 192α: 31% (α-HO → α-LU+2) 185β → 188β: 15% (β-HO-1 → β-LU+1) 185β → 187β: 10% (β-HO-1 → β-LU) 185α → 191α: 7% (α-HO-4 → α-LU+1) 185α → 190α: 6% (α-HO-4 → α-LU) 184α → 190α: 4% (α-HO-5 → α-LU) 184β → 187β: 4% (β-HO-2 → β-LU)

Table S5. (Continued)

	ΔE / eV	ΔE / nm	f	$\langle S^2 \rangle$	Assignment
12	2.835	437	0.000	3.788	187α → 209α: 55% (α-HO-2 → α-LU+19) 187α → 219α: 9% (α-HO-2 → α-LU+29) 187α → 207α: 7% (α-HO-2 → α-LU+17) 178α → 209α: 6% (α-HO-11 → α-LU+19) 187α → 221α: 4% (α-HO-2 → α-LU+31) 187α → 199α: 3% (α-HO-2 → α-LU+9) 187α → 212α: 3% (α-HO-2 → α-LU+22)
13	2.880	431	0.001	5.239	185β → 187β: 51% (β-HO-1 → β-LU) 185α → 190α: 21% (α-HO-4 → α-LU) 185β → 188β: 5% (β-HO-1 → β-LU+1) 189α → 192α: 4% (α-HO → α-LU+2) 185α → 191α: 4% (α-HO-4 → α-LU+1)
14	3.057	406	0.054	4.906	189α → 193α: 28% (α-HO → α-LU+3) 184β → 188β: 6% (β-HO-2 → β-LU+1) 186β → 191β: 6% (β-HO → β-LU+4) 182β → 187β: 6% (β-HO-4 → β-LU) 187α → 192α: 6% (α-HO-2 → α-LU+2) 188α → 196α: 5% (α-HO-1 → α-LU+6) 184α → 191α: 3% (α-HO-5 → α-LU+1) 183α → 190α: 3% (α-HO-6 → α-LU)
15	3.088	401	0.004	5.018	185β → 188β: 36% (β-HO-1 → β-LU+1) 185α → 191α: 18% (α-HO-4 → α-LU+1) 182β → 188β: 6% (β-HO-4 → β-LU+1) 189α → 192α: 5% (α-HO → α-LU+2) 186β → 192β: 4% (β-HO → β-LU+5) 184β → 187β: 3% (β-HO-2 → β-LU)
16	3.113	398	0.000	5.353	186β → 190β: 17% (β-HO → β-LU+3) 188α → 193α: 10% (α-HO-1 → α-LU+3) 189α → 195α: 6% (α-HO → α-LU+5) 181β → 187β: 5% (β-HO-5 → β-LU) 186β → 189β: 5% (β-HO → β-LU+2) 180α → 195α: 4% (α-HO-9 → α-LU+5) 183β → 188β: 3% (β-HO-3 → β-LU+1) 186α → 209α: 3% (α-HO-3 → α-LU+19) 179β → 192β: 3% (β-HO-7 → β-LU+5)

Table S5. (Continued)

	ΔE / eV	ΔE / nm	f	$\langle S^2 \rangle$	Assignment
17	3.130	396	0.000	5.352	183β → 187β: 10% (β-HO-3 → β-LU) 189α → 195α: 6% (α-HO → α-LU+5) 186β → 189β: 5% (β-HO → β-LU+2) 186β → 193β: 5% (β-HO → α-LU+3) 182α → 190α: 5% (α-HO-7 → α-LU) 186β → 190β: 5% (β-HO → β-LU+3) 188α → 194α: 5% (α-HO-1 → α-LU+4) 183β → 188β: 4% (β-HO-3 → β-LU+1) 181α → 196α: 3% (α-HO-8 → α-LU+6) 184β → 189β: 3% (β-HO-2 → β-LU+2) 186α → 209α: 3% (α-HO-3 → α-LU+19) 184α → 192α: 3% (α-HO-5 → α-LU+2)
18	3.214	386	0.000	4.010	189α → 209α: 30% (α-HO → α-LU+19) 186α → 209α: 20% (α-HO-3 → α-LU+19) 189α → 219α: 5% (α-HO → α-LU+29) 189α → 207α: 4% (α-HO → α-LU+17) 186α → 219α: 4% (α-HO-3 → α-LU+29) 189α → 199α: 3% (α-HO → α-LU+9)
19	3.221	385	0.000	4.278	186α → 209α: 28% (α-HO-3 → α-LU+19) 189α → 209α: 13% (α-HO → α-LU+19) 186β → 189β: 12% (β-HO → β-LU+2) 186α → 219α: 5% (α-HO-3 → α-LU+29) 186α → 207α: 3% (α-HO-3 → α-LU+17) 188α → 192α: 3% (α-HO-1 → α-LU+2) 186β → 190β: 3% (β-HO → β-LU+3)
20	3.233	384	0.000	5.001	186β → 189β: 39% (β-HO → β-LU+2) 189α → 209α: 14% (α-HO → α-LU+19) 188α → 192α: 10% (α-HO-1 → α-LU+2) 180β → 187β: 4% (α-HO-9 → β-LU) 186α → 209α: 3% (α-HO-3 → α-LU+19)

Table S6. Excitation energies (ΔE), oscillator strengths (f), $\langle S^2 \rangle$ values and assignments on the low-lying excited states of $[Cr(MeIm)_2Pc]^0$ calculated at the TD-UCAM-B3LYP/cc-pVTZ/cc-pVDZ level of theory.

	ΔE / eV	ΔE / nm	f	$\langle S^2 \rangle$	Assignment
1	0.407	3048	0.000	2.924	187β → 188β: 96% (β-HO → β-LU)
2	1.012	1225	0.008	4.537	189α → 191α: 34% (α-HO → α-LU+1) 189α → 190α: 33% (α-HO → α-LU) 186β → 188β: 24% (β-HO-1 → β-LU) 187β → 191β: 4% (β-HO → β-LU+3)
3	1.460	849	0.129	3.087	189α → 190α: 48% (α-HO → α-LU) 189α → 191α: 45% (α-HO → α-LU+1) 187β → 190β: 4% (β-HO → β-LU+2)
4	2.253	550	0.000	2.533	187β → 189β: 84% (β-HO → β-LU+1) 187β → 197β: 4% (β-HO → β-LU+9) 187β → 195β: 3% (β-HO → β-LU+7)
5	2.301	539	0.394	2.960	186β → 188β: 62% (β-HO-1 → β-LU) 189α → 191α: 14% (α-HO → α-LU+1) 189α → 190α: 12% (α-HO → α-LU) 187α → 190α: 3% (α-HO-2 → α-LU)
6	2.376	522	0.000	2.099	187β → 193β: 94% (β-HO → β-LU+5)
7	2.431	510	0.000	2.716	187β → 192β: 83% (β-HO → β-LU+4) 187β → 198β: 3% (β-HO → β-LU+10)
8	2.444	507	0.214	3.688	187β → 190β: 59% (β-HO → β-LU+2) 187α → 191α: 10% (α-HO-2 → α-LU+1) 183β → 188β: 7% (β-HO-4 → β-LU) 187α → 190α: 7% (α-HO-2 → α-LU) 186β → 189β: 3% (β-HO-1 → β-LU+1)
9	2.832	438	0.000	2.988	174α → 197α: 31% (α-HO-15 → α-LU+7) 186α → 197α: 17% (α-HO-3 → α-LU+7) 188α → 197α: 15% (α-HO-1 → α-LU+7) 179α → 197α: 9% (α-HO-10 → α-LU+7) 163α → 197α: 8% (α-HO-26 → α-LU+7)
10	2.841	436	0.003	3.569	187β → 191β: 44% (β-HO → β-LU+3) 187β → 194β: 18% (β-HO → β-LU+6) 186β → 188β: 10% (β-HO-1 → β-LU) 186β → 192β: 6% (β-HO-1 → β-LU+4)
11	2.894	428	0.000	2.993	173α → 197α: 30% (α-HO-16 → α-LU+7) 186α → 197α: 19% (α-HO-3 → α-LU+7) 188α → 197α: 15% (α-HO-1 → α-LU+7) 168α → 197α: 13% (α-HO-21 → α-LU+7)

Table S6. (Continued)

	ΔE / eV	ΔE / nm	f	$\langle S^2 \rangle$	Assignment
12	2.938	422	0.000	3.976	188α → 190α: 12% (α-HO-1 → α-LU) 187β → 198β: 10% (β-HO → β-LU+10) 189α → 193α: 9% (α-HO → α-LU+3) 188α → 191α: 9% (α-HO-1 → α-LU+1) 186β → 191β: 8% (β-HO-1 → β-LU+3) 186β → 194β: 5% (β-HO-1 → β-LU+6) 189α → 195α: 5% (α-HO → α-LU+5) 187β → 195β: 4% (β-HO → β-LU+7) 187β → 197β: 4% (β-HO → β-LU+9) 186α → 191α: 3% (α-HO-3 → α-LU+1) 184α → 196α: 3% (α-HO-5 → α-LU+6) 186α → 190α: 3% (α-HO-3 → α-LU)
13	3.182	390	0.000	4.249	186α → 191α: 15% (α-HO-3 → α-LU+1) 186α → 190α: 12% (α-HO-3 → α-LU) 189α → 193α: 7% (α-HO → α-LU+3) 178β → 188β: 5% (β-HO-9 → β-LU) 180α → 194α: 4% (α-HO-9 → α-LU+4) 184α → 191α: 3% (α-HO-5 → α-LU+1) 188α → 190α: 3% (α-HO-1 → α-LU) 184α → 190α: 3% (α-HO-5 → α-LU) 181β → 190β: 3% (β-HO-6 → β-LU+2)
14	3.198	388	0.025	3.621	187β → 191β: 29% (β-HO → β-LU+3) 187α → 190α: 16% (α-HO-2 → α-LU) 187β → 194β: 15% (β-HO → β-LU+6) 186β → 192β: 4% (β-HO-1 → β-LU+4) 189α → 196α: 3% (α-HO → α-LU+6) 187α → 191α: 3% (α-HO-2 → α-LU+1)
15	3.221	385	0.093	4.460	187α → 191α: 21% (α-HO-2 → α-LU+1) 183β → 188β: 21% (β-HO-4 → β-LU) 187β → 190β: 7% (β-HO → β-LU+2) 187α → 190α: 7% (α-HO-2 → α-LU) 181β → 188β: 6% (β-HO-6 → β-LU) 186β → 189β: 4% (β-HO-1 → β-LU+1) 189α → 194α: 3% (α-HO → α-LU+4)
16	3.284	378	0.000	4.087	189α → 192α: 34% (α-HO → α-LU+2) 188α → 190α: 19% (α-HO-1 → α-LU) 186β → 190β: 13% (β-HO-1 → β-LU+2) 187β → 195β: 9% (β-HO → β-LU+7)

Table S6. (Continued)

	ΔE / eV	ΔE / nm	f	$\langle S^2 \rangle$	Assignment
17	3.313	374	0.000	3.224	188α → 191α: 33% (α-HO-1 → α-LU+1) 188α → 190α: 21% (α-HO-1 → α-LU) 187β → 198β: 10% (β-HO → β-LU+10) 187β → 197β: 6% (β-HO → β-LU+9) 186β → 194β: 5% (β-HO-1 → β-LU+6) 189α → 192α: 4% (α-HO → α-LU+2) 185α → 192α: 3% (α-HO-4 → α-LU+2)
18	3.381	367	0.152	4.296	187β → 190β: 20% (β-HO → β-LU+2) 183β → 188β: 8% (β-HO-4 → β-LU) 189α → 194α: 6% (α-HO → α-LU+4) 181β → 188β: 5% (β-HO-6 → β-LU) 180α → 193α: 5% (α-HO-9 → α-LU+3) 179β → 191β: 4% (β-HO-8 → β-LU+3) 182α → 190α: 4% (α-HO-7 → α-LU) 178β → 190β: 3% (β-HO-9 → β-LU+2) 181α → 191α: 3% (α-HO-8 → α-LU+1)
19	3.437	361	0.335	3.275	187α → 190α: 35% (α-HO-2 → α-LU) 187α → 191α: 25% (α-HO-2 → α-LU+1) 187β → 191β: 12% (β-HO → β-LU+3) 185α → 190α: 6% (α-HO-4 → α-LU) 185α → 191α: 4% (α-HO-4 → α-LU+1) 189α → 191α: 3% (α-HO → α-LU+1) 187β → 194β: 3% (β-HO → β-LU+6)
20	3.522	352	0.000	3.884	184β → 188β: 18% (β-HO-3 → β-LU) 188α → 191α: 16% (α-HO-1 → α-LU+1) 186α → 190α: 14% (α-HO-3 → α-LU) 189α → 192α: 12% (α-HO → α-LU+2) 188α → 190α: 12% (α-HO-1 → α-LU) 186α → 191α: 10% (α-HO-3 → α-LU+1)