Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Exploring the Nature of Excitation Energies in $[Re_6(\mu_3\text{-}Q_8)X_6]^{4-}$ Clusters: A Relativistic Approach

Walter A. Rabanal-León,[†] Juliana A. Murillo-López,[‡] Dayán Páez-Hernández,[†] and Ramiro Arratia-Pérez[*,†]

[‡] *Universidad Andrés Bello, Facultad de Ciencias Exactas, Ph.D. Program in Molecular Physical Chemistry, Relativistic Molecular Physics (ReMoPh) Group, Santiago, Chile, and*

[¶] *Universidad de Talca, Facultad de Ingeniería, Centro de Bioinformática y Simulación Molecular (CBSM), 2 Norte 685, Casilla 721, Talca, Chile*

E-mail: rarratia@unab.cl

Phone: +56-2-2770-3352. Fax: +56-2-2770-3352

[*]To whom correspondence should be addressed

[†]Universidad Andrés Bello, Relativistic Molecular Physics (ReMoPh) Group

[‡]Universidad de Talca, Centro de Bioinformática y Simulación Molecular (CBSM)

Figure S1: Excitation energies for the $[Re_6(\mu_3\text{-}Se_8)X_6]^{4-}$ (X = F^-, Cl^-, Br^- and I^-) clusters at spin-orbit relativistic level with the SAOP functional in acetonitrile solvent.

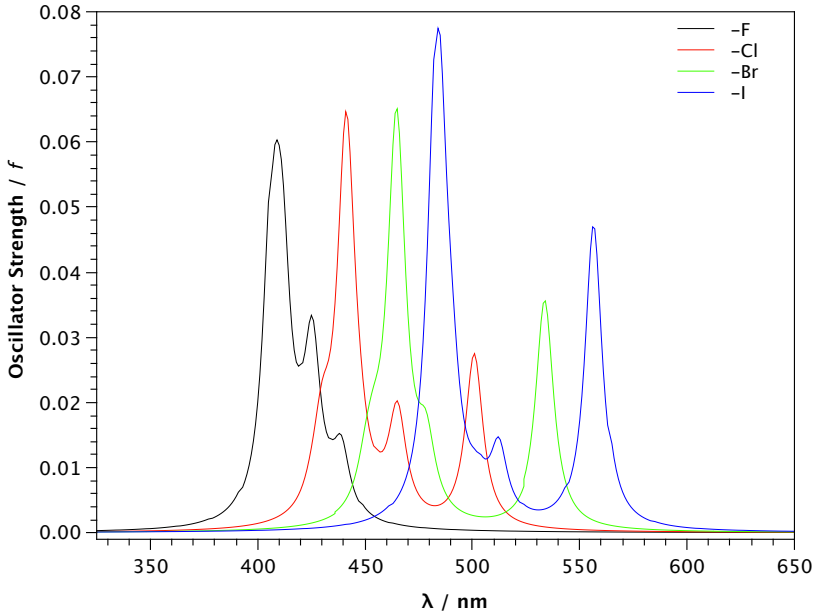


Figure S2: Excitation energies for the $[Re_6(\mu_3\text{-}Te_8)X_6]^{4-}$ (X = F^-, Cl^-, Br^- and I^-) clusters at spin-orbit relativistic level with the SAOP functional in acetonitrile solvent.

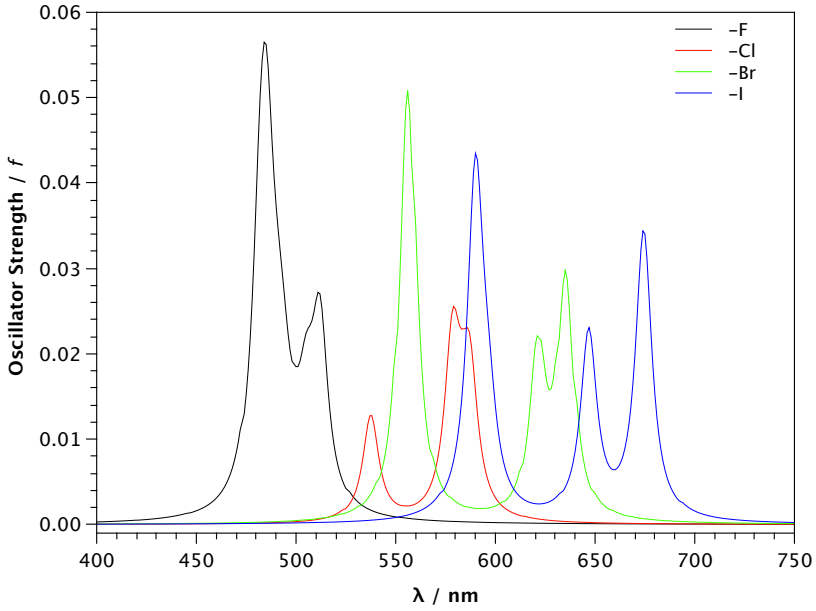


Figure S3: Excitation energies for the $[Re_6(\mu_3\text{-}Se_8)X_6]^{4-}$ (X = CN^-, NC^-, SCN^-, NCS^-, OCN^-, NCO^-) clusters at spin-orbit relativistic level with the SAOP functional in acetonitrile solvent.

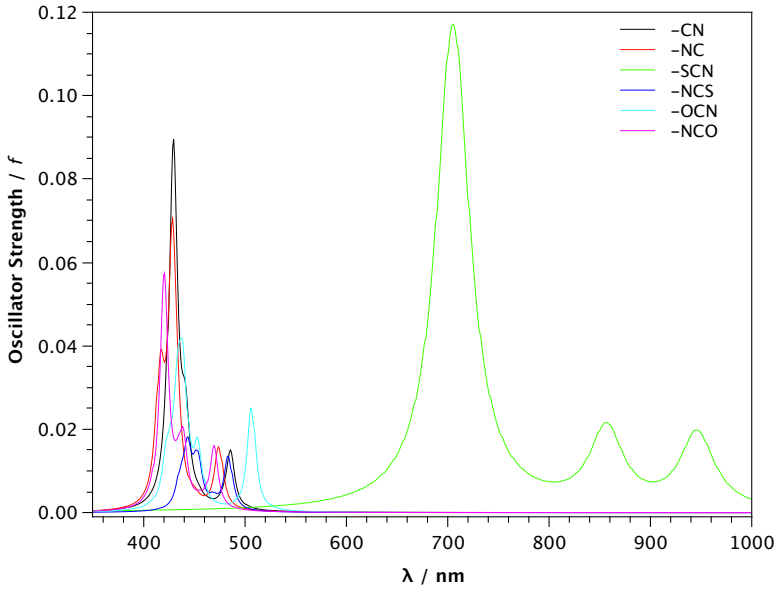


Figure S4: Excitation energies for the $[Re_6(\mu_3\text{-}Te_8)X_6]^{4-}$ (X = CN^-, NC^-, SCN^-, NCS^-, OCN^-, NCO^-) clusters at spin-orbit relativistic level with the SAOP functional in acetonitrile solvent.

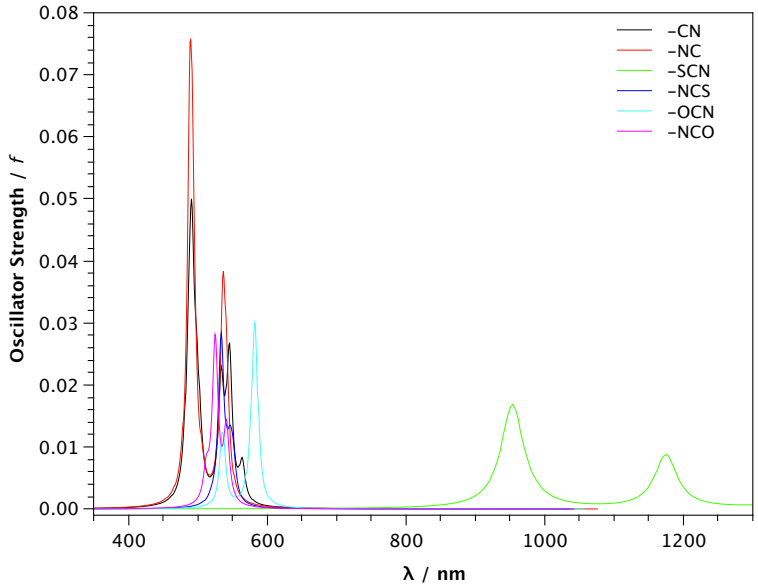
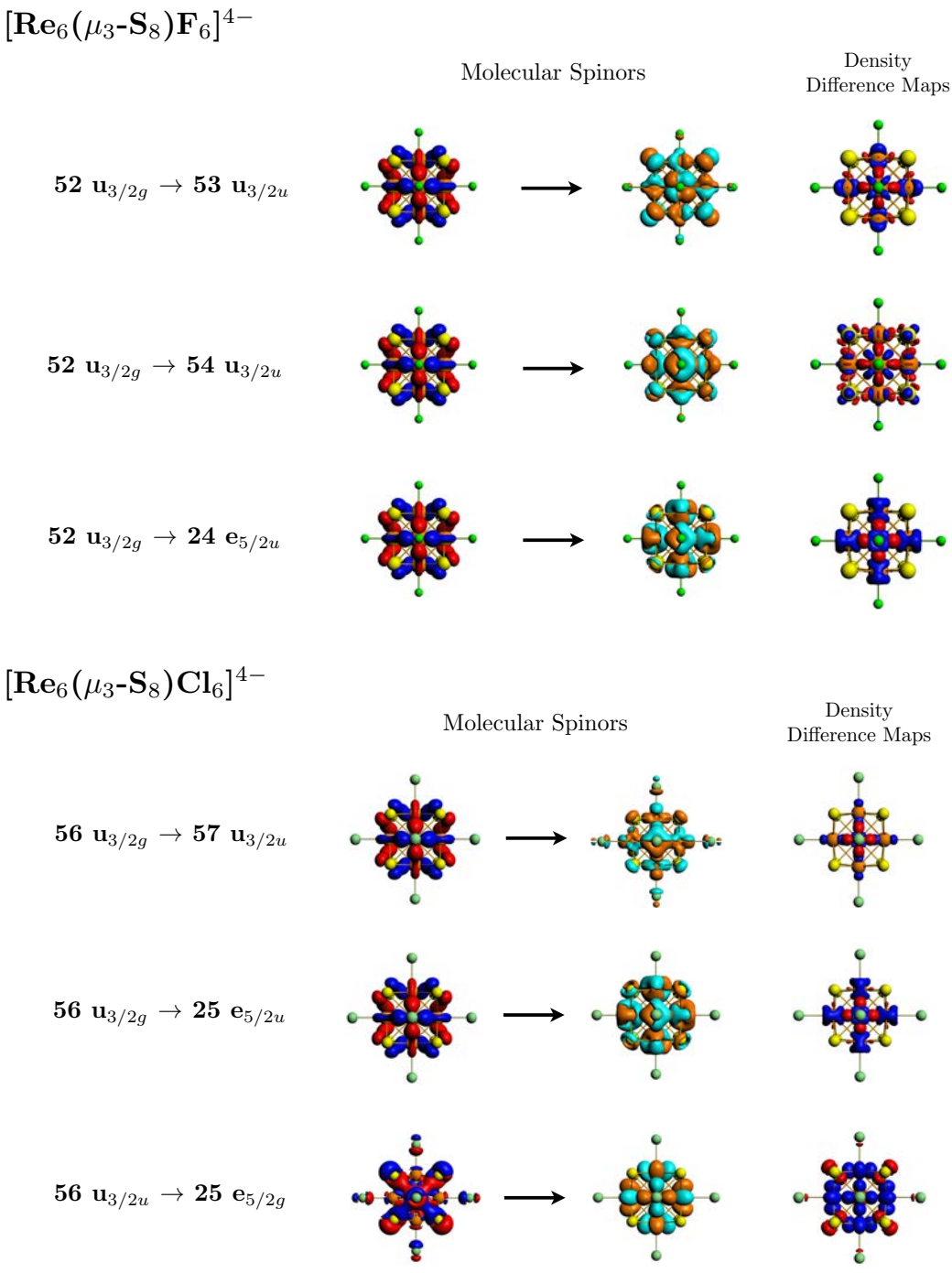
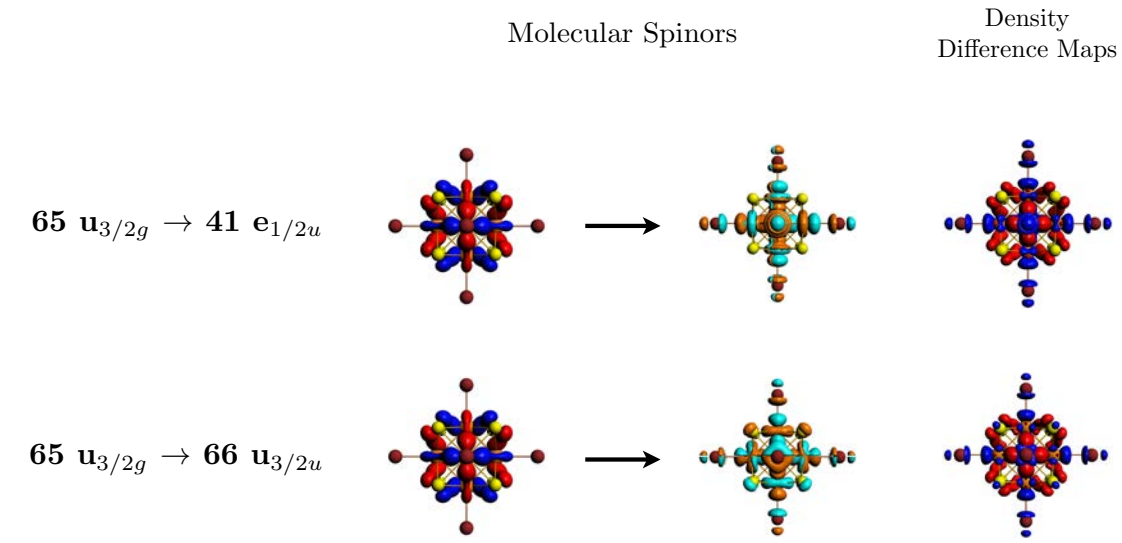


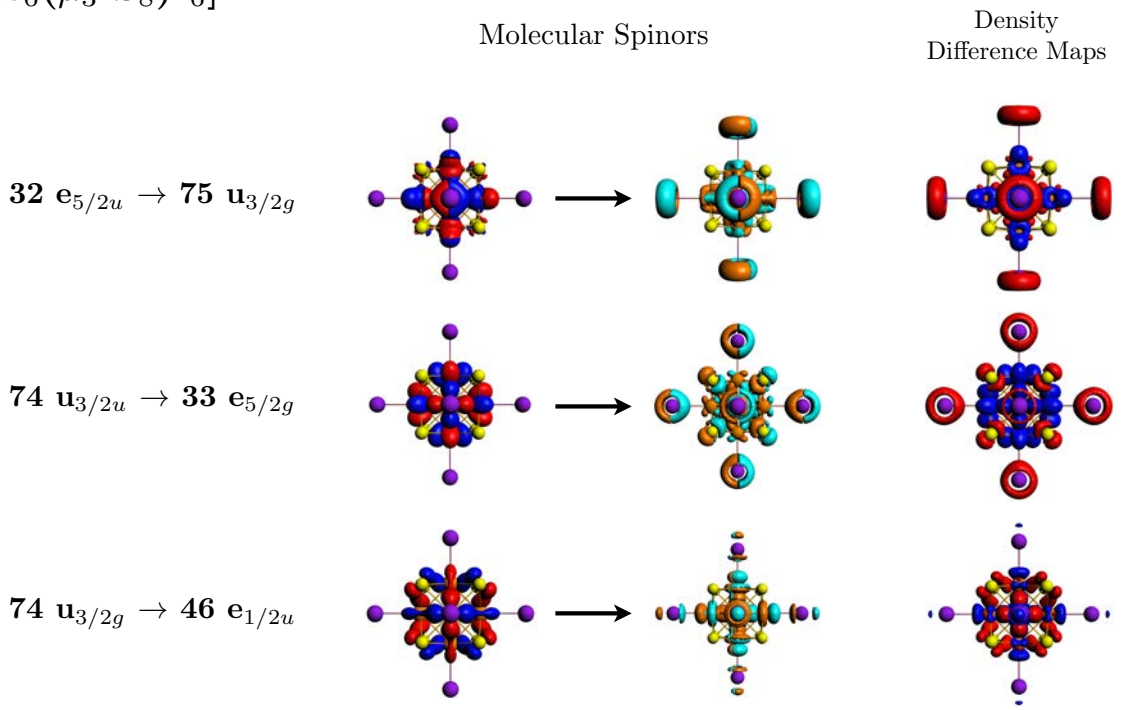
Figure S5: Molecular spinor plots and density difference maps for all the $[Re_6(\mu_3\text{-}Te_8)X_6]^{4-}$ (X = CN^-, NC^-, SCN^-, NCS^-, OCN^-, NCO^-) clusters at spin-orbit relativistic level of theory.



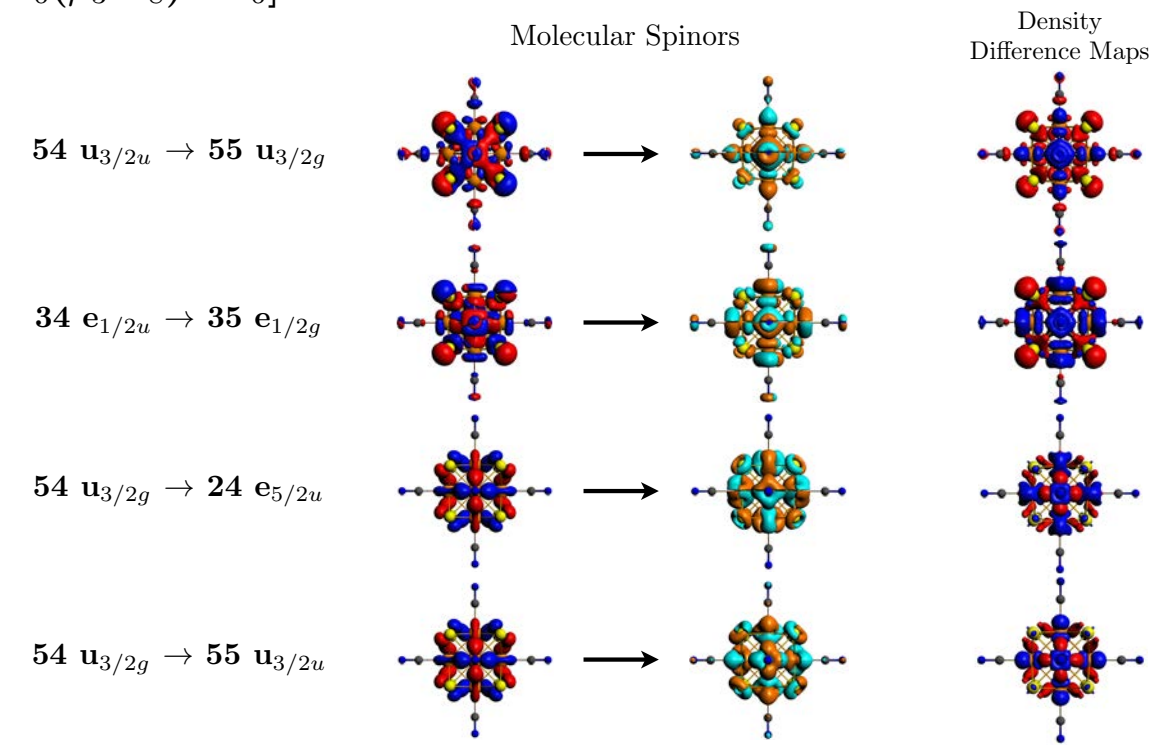
$[\mathbf{Re_6(\mu_3\text{-}S_8)Br_6}]^{4-}$



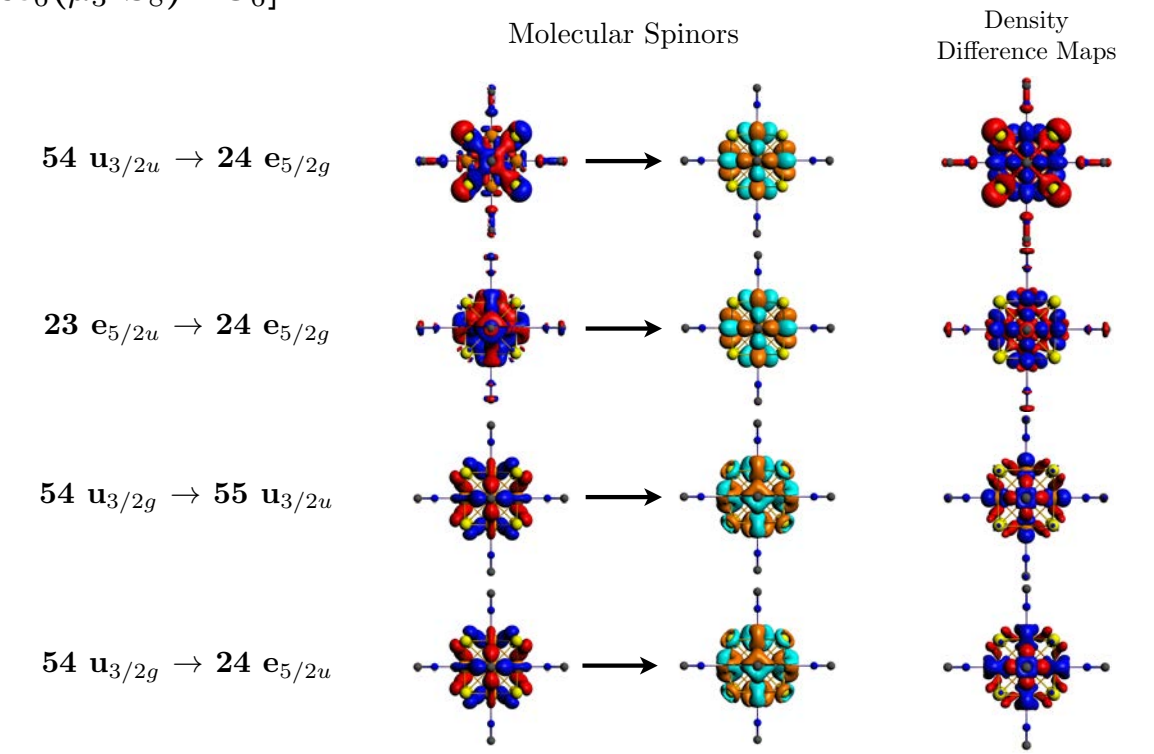
$[\mathbf{Re_6(\mu_3\text{-}S_8)I_6}]^{4-}$



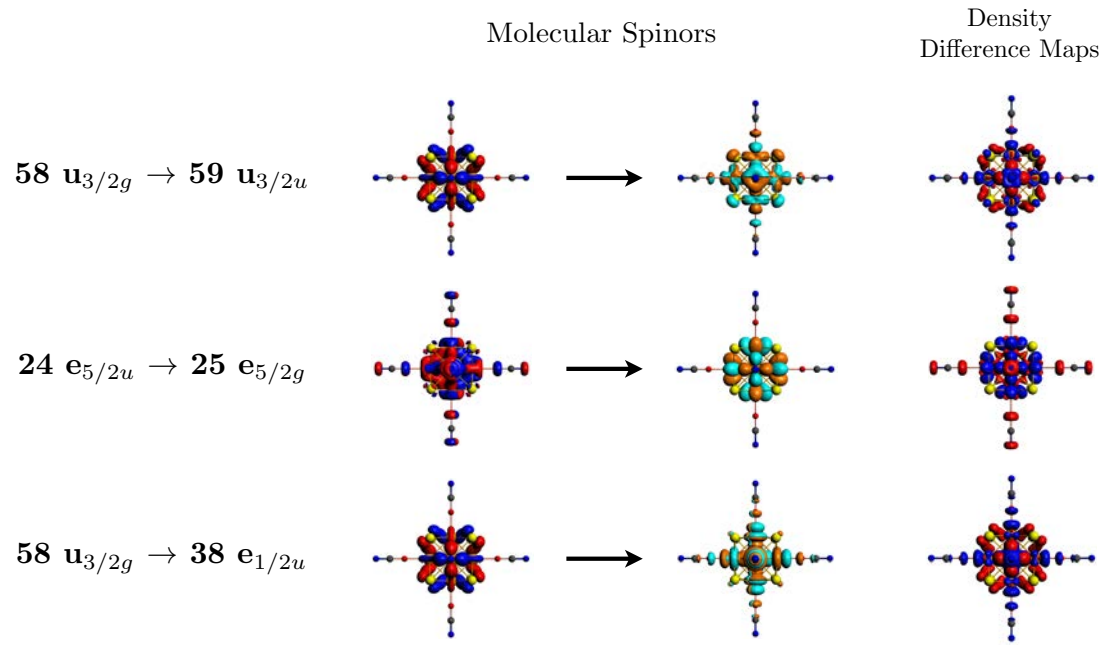
$[\mathbf{Re_6(\mu_3\text{-}S_8)CN_6}]^{4-}$



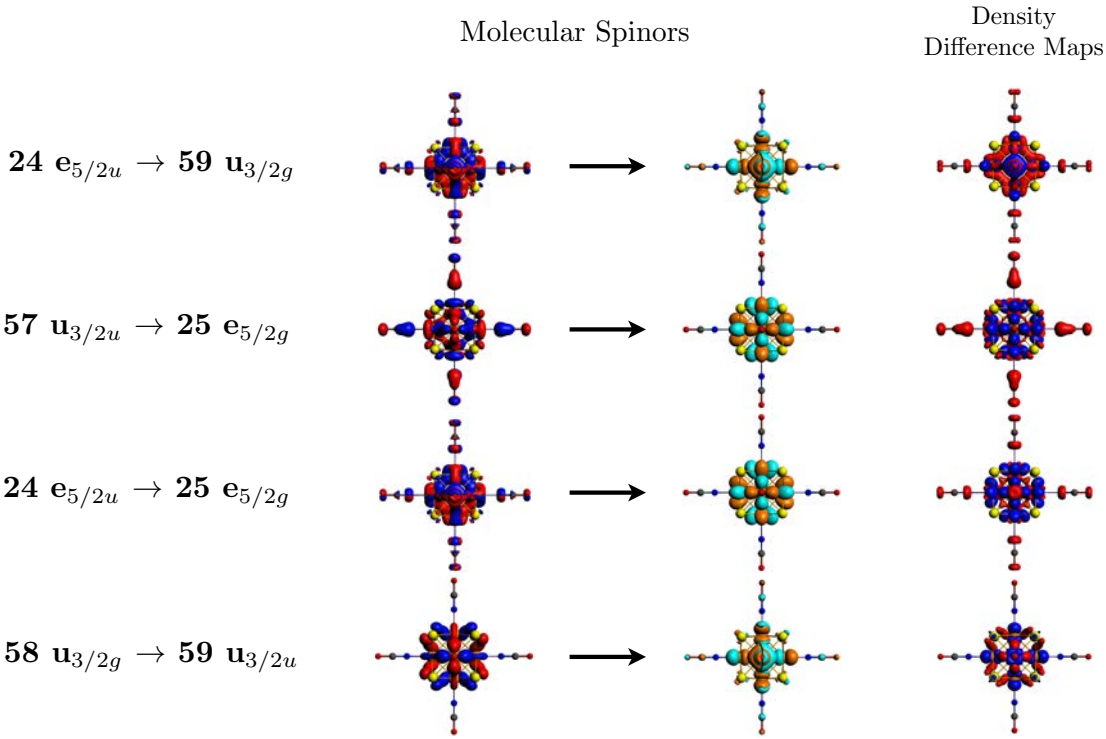
$[\mathbf{Re_6(\mu_3\text{-}S_8)NC_6}]^{4-}$



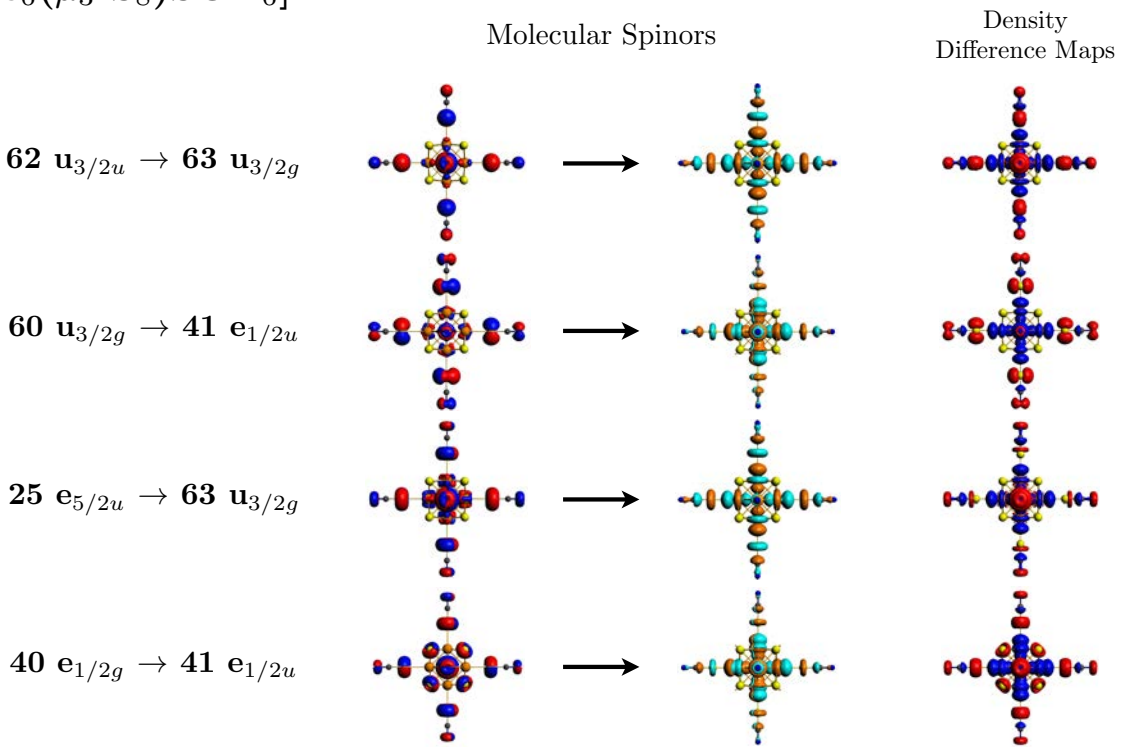
$[\mathbf{Re_6(\mu_3\text{-}S_8)OCN_6}]^{4-}$



$[\mathbf{Re_6(\mu_3\text{-}S_8)NCO_6}]^{4-}$



$[\mathbf{Re_6(\mu_3\text{-}S_8)SCN_6}]^{4-}$



$[\mathbf{Re_6(\mu_3\text{-}S_8)NCS_6}]^{4-}$

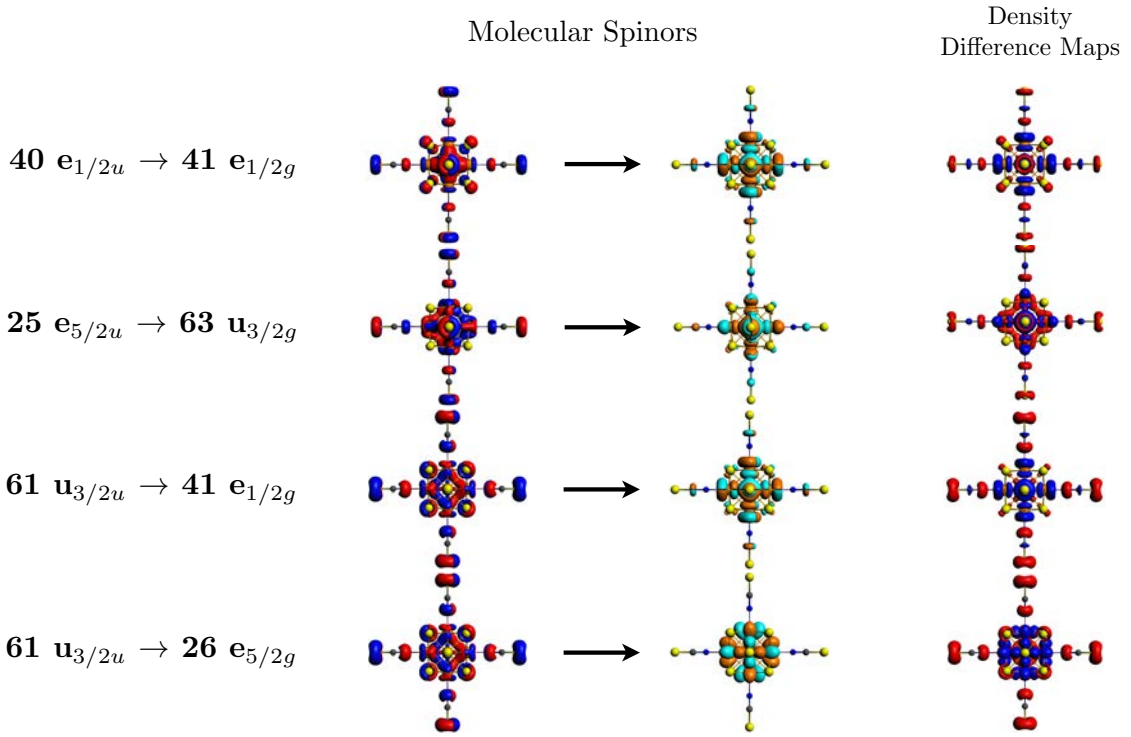


Table S1 : Excitation energies (eV), wavelengths (nm), oscillator strengths (f) and orbital assignation for the $[Re_6(\mu_3\text{-}Se)_8X_6]^{4-}$ complexes (X = F^-, Cl^-, Br^-, I^-).

Band	Energy	λ	f(x100)	Active MOs	%	Assignation
$[Re_6(\mu_3\text{-}Se)_8F_6]^{4-}$						
a	3.04	406	1.2812	64 $u_{3/2g}$ → 65 $u_{3/2u}$	57	$Core_{Re}$ - $Core_{Se}$
				64 $u_{3/2g}$ → 66 $u_{3/2u}$	19	$Core_{Re}$ - $Core_{Re}$
				64 $u_{3/2u}$ → 30 $e_{5/2g}$	16	$Core_{Re}$ - $Core_{Re}$
b	2.91	425	0.8608	64 $u_{3/2g}$ → 39 $e_{1/2u}$	86	$Core_{Re}$ - $Core_{Re}$
c	2.83	438	0.3324	29 $e_{5/2u}$ → 30 $e_{5/2g}$	58	$Core_{Re}$ - $Core_{Re}$
				64 $u_{3/2g}$ → 65 $u_{3/2u}$	18	$Core_{Re}$ - $Core_{Se}$
$[Re_6(\mu_3\text{-}Se)_8Cl_6]^{4-}$						
a	2.80 (2.84†)	442	1.9980	68 $u_{3/2g}$ → 69 $u_{3/2u}$	69	$Core_{Re}$ - $Core_{Re}$
				30 $e_{5/2u}$ → 31 $e_{5/2g}$	15	$Core_{Re}$ + Lig - $Core_{Re}$
				64 $u_{3/2u}$ → 31 $e_{5/2g}$	12	Lig - $Core_{Re}$
b	2.66	465	0.5482	68 $u_{3/2g}$ → 69 $u_{3/2u}$	36	$Core_{Re}$ - $Core_{Re}$
				30 $e_{5/2u}$ → 31 $e_{5/2g}$	28	$Core_{Re}$ + Lig - $Core_{Re}$
				68 $u_{3/2g}$ → 31 $e_{5/2u}$	25	$Core_{Re}$ - $Core_{Re}$
c	2.47	501	0.88999	68 $u_{3/2g}$ → 42 $e_{1/2u}$	98	$Core_{Re}$ - $Core_{Re}$
$[Re_6(\mu_3\text{-}Se)_8Br_6]^{4-}$						
a	2.66	465	2.0655	77 $u_{3/2g}$ → 78 $u_{3/2u}$	93	$Core_{Re}$ - $Core_{Re}$ + Lig
b	2.59	468	0.35515	77 $u_{3/2g}$ → 78 $u_{3/2u}$	54	$Core_{Re}$ - $Core_{Re}$ + Lig
				34 $e_{5/2u}$ → 35 $e_{5/2g}$	27	$Core_{Re}$ + Lig - $Core_{Re}$
				77 $u_{3/2g}$ → 35 $e_{5/2u}$	10	$Core_{Re}$ - $Core_{Re}$
c	2.32	534	1.1779	77 $u_{3/2g}$ → 47 $e_{1/2u}$	98	$Core_{Re}$ - $Core_{Re}$ + Lig
$[Re_6(\mu_3\text{-}Se)_8I_6]^{4-}$						
a	2.56 (2.58†)	484	2.4050	86 $u_{3/2g}$ → 87 $u_{3/2u}$	90	$Core_{Re}$ - $Core_{Re}$ + Lig
b	2.42	512	0.3568	38 $e_{5/2u}$ → 39 $e_{5/2g}$	77	Lig - $Core_{Re}$
				86 $u_{3/2g}$ → 87 $u_{3/2u}$	15	$Core_{Re}$ - $Core_{Re}$ + Lig
c	2.22	556	1.5591	86 $u_{3/2g}$ → 52 $e_{1/2u}$	97	$Core_{Re}$ - $Core_{Re}$ + Lig

†J. Chem. Phys., Vol. 115 N° 2 (2001), pp. 726.

Table S2 : Excitation energies (eV), wavelengths (nm), oscillator strengths (f) and orbital assignation for the $[Re_6(\mu_3\text{-}Te)_8X_6]^{4-}$ complexes (X = F^-, Cl^-, Br^-, I^-).

Band	Energy	λ	f(x100)	Active MOs	%	Assignation
$[Re_6(\mu_3\text{-}Te)_8F_6]^{4-}$						
a	2.55	485	1.0673	76 $u_{3/2g}$ → 36 $e_{5/2u}$	48	$Core_{Re}$ + Lig - Core
				75 $u_{3/2g}$ → 77 $u_{3/2u}$	37	$Core_{Re}$ - Core
b	2.45	505	0.3414	76 $u_{3/2g}$ → 77 $u_{3/2u}$	86	$Core_{Re}$ + Lig - Core
c	2.42	511	0.6993	76 $u_{3/2u}$ → 36 $e_{5/2g}$	96	$Core_{Te}$ - Core
$[Re_6(\mu_3\text{-}Te)_8Cl_6]^{4-}$						
a	2.30	537	0.4141	80 $u_{3/2u}$ → 37 $e_{5/2g}$	99	$Core_{Re}$ + Lig - $Core_{Re}$
b	2.14	579	0.6772	79 $u_{3/2g}$ → 48 $e_{1/2u}$	96	$Core_{Re}$ - $Core_{Re}$ + Lig
c	2.11	586	0.5436	80 $u_{3/2g}$ → 48 $e_{1/2u}$	97	$Core_{Re}$ + Lig - $Core_{Re}$
$[Re_6(\mu_3\text{-}Te)_8Br_6]^{4-}$						
a	2.22	556	1.6695	89 $u_{3/2g}$ → 90 $u_{3/2u}$	88	$Core_{Te}$ + Lig - Core + Lig
				88 $u_{3/2g}$ → 90 $u_{3/2u}$	11	Core - Core + Lig
b	1.99	621	0.6209	88 $u_{3/2g}$ → 53 $e_{1/2u}$	98	Core - Core + Lig
c	1.95	635	0.9143	89 $u_{3/2g}$ → 53 $e_{1/2u}$	99	$Core_{Te}$ + Lig - Core + Lig
$[Re_6(\mu_3\text{-}Te)_8I_6]^{4-}$						
a	2.10	590	1.3382	98 $u_{3/2g}$ → 99 $u_{3/2u}$	91	Core + Lig - Core + Lig
b	1.91	647	0.7220	97 $u_{3/2g}$ → 58 $e_{1/2u}$	98	Core + Lig - Core + Lig
c	1.83	675	1.1250	98 $u_{3/2g}$ → 58 $e_{1/2u}$	99	Core + Lig - Core + Lig