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

SUPPORTING INFORMATION

Study of the interaction among cisplatin and the $Au_{18}(SR)_{14}$ cluster: In search of an appropriated cisplatin carrier

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Part I. **Figure S1**. Comparison of calculated optical absorption spectra of thiolated Au_{18} cluster using ORCA with previous Gaussian calculations.

Part II. **Figure S2.** Principal contribution from frontier orbitals (HOMO, LUMO) to the $Au_{18}(SR)_{14}$ absorption spectra.

Part III**. Figure S3-S6.** Calculated bond lengths of studied structures.

Part IV**. Table S1-S3.** Table reporting Boltzmann's weight of a set of isomers. Images of the isomers are included.

Part V**. Table S4-S9.** Electronic transition**,** UV and CD spectra.

Part VI. **Figure S7.** Comparison of spectra in an aqueous and gaseous medium.

PART I

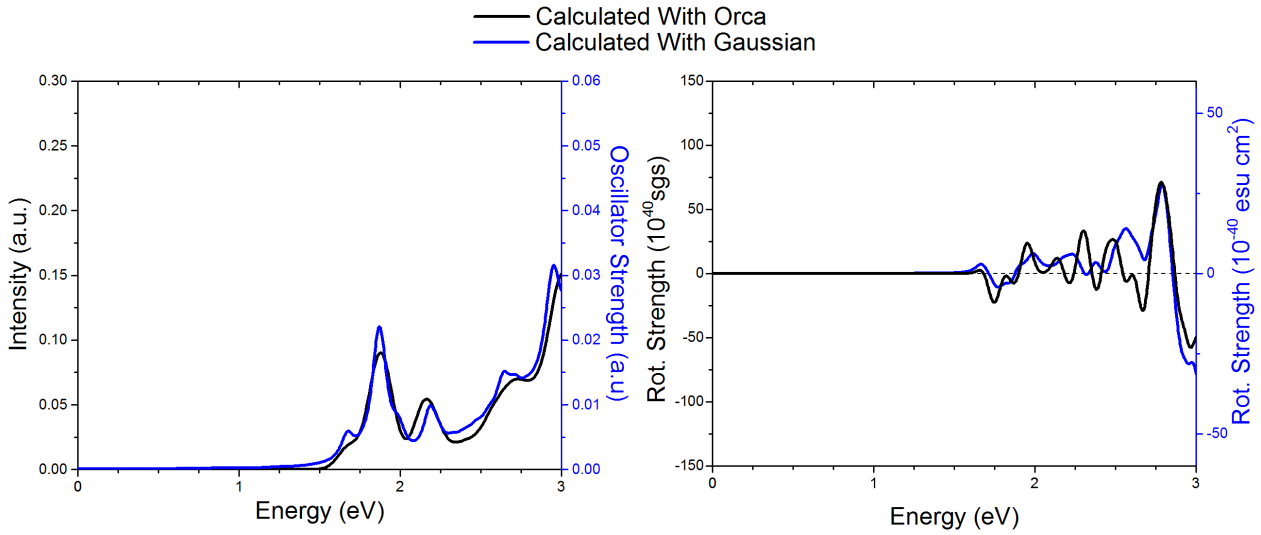


Figure S1. Calculated optical absorption and circular dichroism spectra for [Au18(SCH_3)14] cluster using Orca package and their comparison with the previously calculated one by using Gaussian: A. Tlahuice-Flores, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27738- 27744. It was used a 0.16 eV Gaussian broadening for the UV spectra. Worthy of note is the great coincidence of UV spectra. CD spectra compared at right panel feature coincidences in their peaks and mainly in the strong positive peak located at 2.787 eV.

PART II

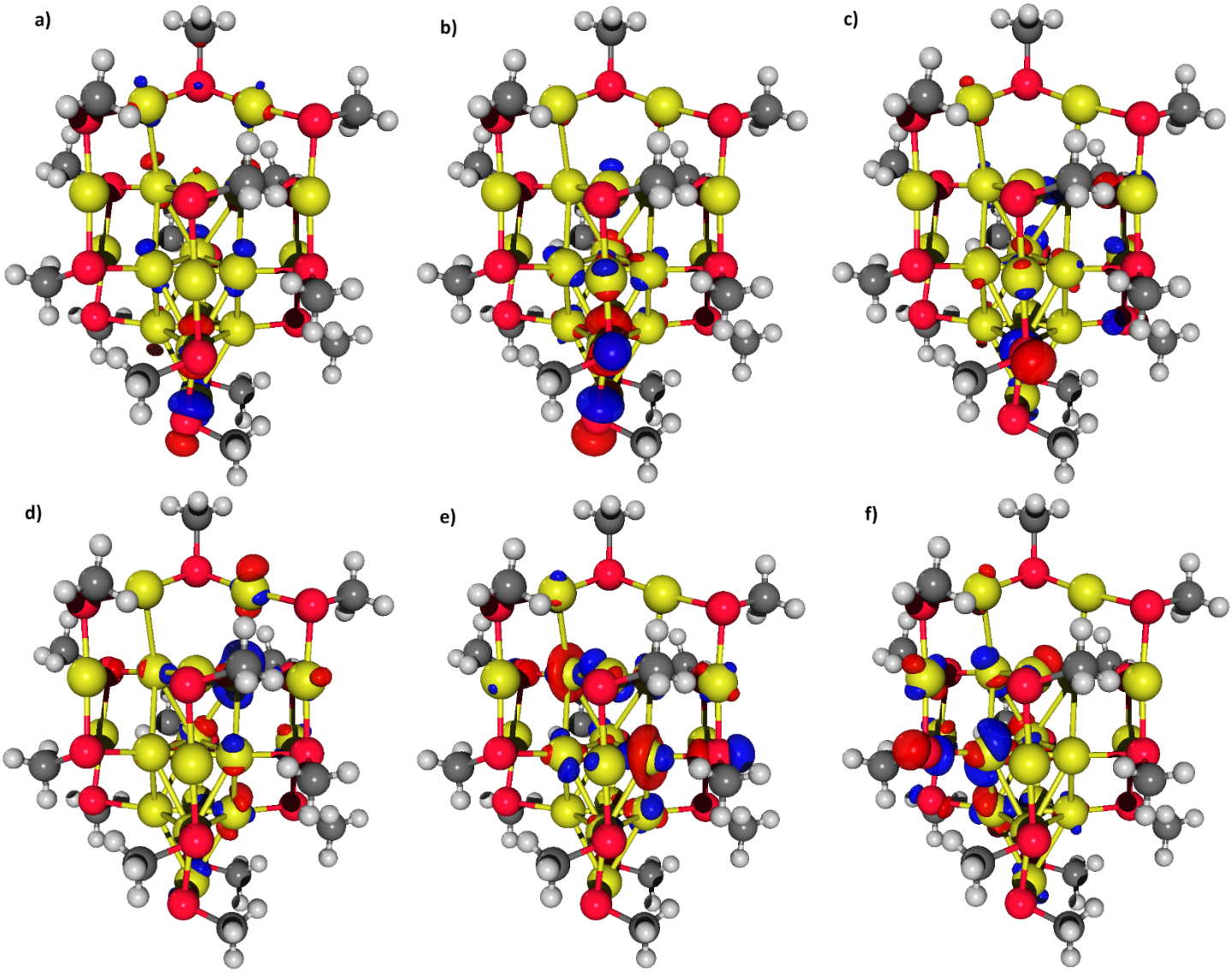


Figure S2 – Molecular orbitals for $Au_{18}(SR)_{14,}$ **a)** LUMO, **b)** HOMO, **c)** HOMO-1, **d)** HOMO-2, **e)** HOMO-3, **f)** HOMO-4. It is evident that monomer staple linked to the special Au atom (linked to two S atoms) has a large contribution to HOMO and LUMO while Au located in the inner core are contributing to other frontier orbitals

PART III

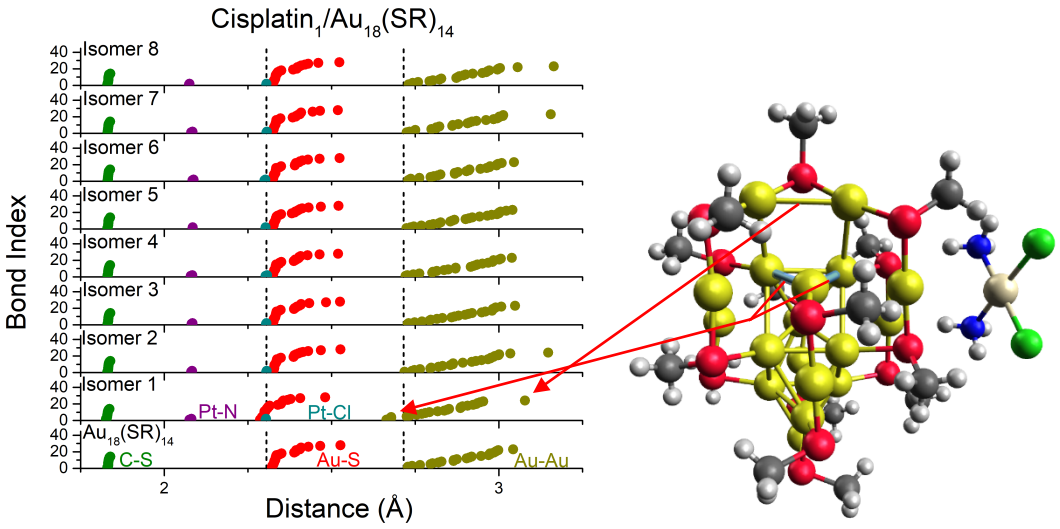


Figure S3 - Calculated bond lengths of studied structures including one cisplatin molecule. Each type of bonds is indicated by labels. C-H and N-H bonds are not displayed since they do not show any appreciable variation. Vertical lines indicate changes in bond lengths. Au-S bonds (in red color) seem to decrease slightly with respect to the parent Au_{18} cluster (first vertical line). Isomer 1 (the lowest energy one) displays similar Au-Au bonds except by two near the 2.66 Å bond length located in the inner Au(core) and a larger bond of 3.077 Å bond length corresponding to the Au-Au of the dimer in the upper part. Right panel shows the Au(core) bonds previously mentioned. We can conclude that the adsorption of one cisplatin molecule induces distortion of Au-Au bonds mainly.

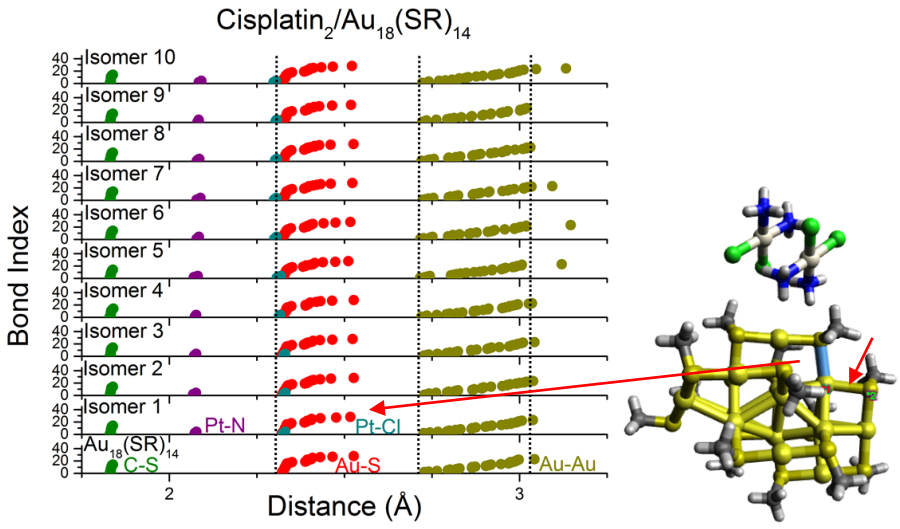


Figure S4 - Calculated bond lengths of studied structures including two cisplatin molecules. Each type of bonds is indicated by labels as in figure S3. Isomer 1 shows slightly contracted Au-S bonds ($Au_{special}$ - S(dimer) and $Au_{special}$-S(monomer) bonds) (red color) and the same behavior is found in Au-Au bonds (to compare the bottom panel with Isomer 1). Right panel shows in blue $Au_{special}$ and S(monomer) and with numbers the $Au_{special}$-S(dimer) bonds; those bonds are more distorted after cisplatin dimer adsorption. $Au_{special}$ is indicated by one number.

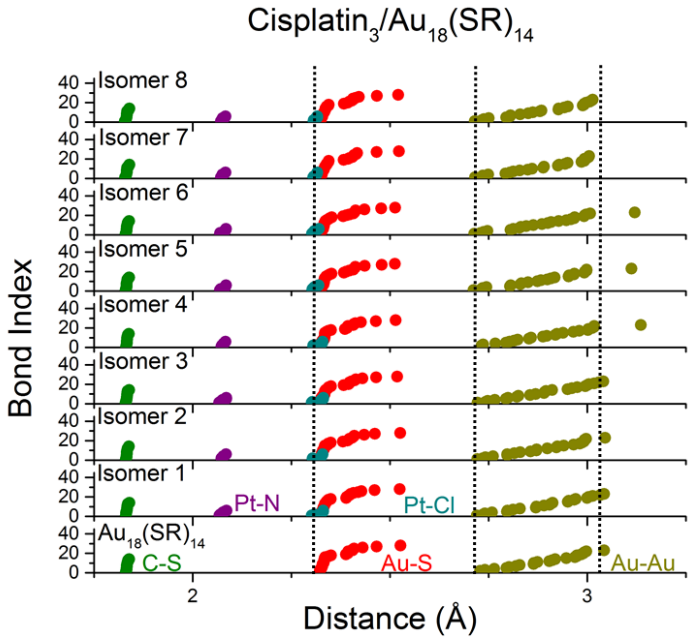


Figure S5 - Calculated bond lengths of studied structures including three cisplatin molecules. Labels are similar to figure S3. Displayed Au-S bonds are remarkable similar among isomer 1 and parent Au_{18} cluster and a slight expansion is indicated by first vertical line. It is evident that one Au(core)-Au(staple) bond is slightly short with respect to the parent Au_{18} cluster (third vertical line). The distribution of the Au-Au bonds might indicate that the gold core is slightly more symmetric given that points are forming groups.

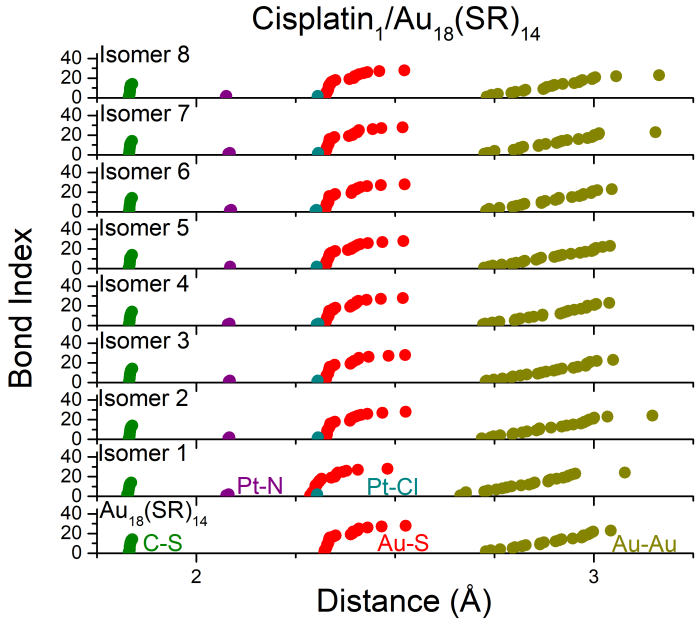
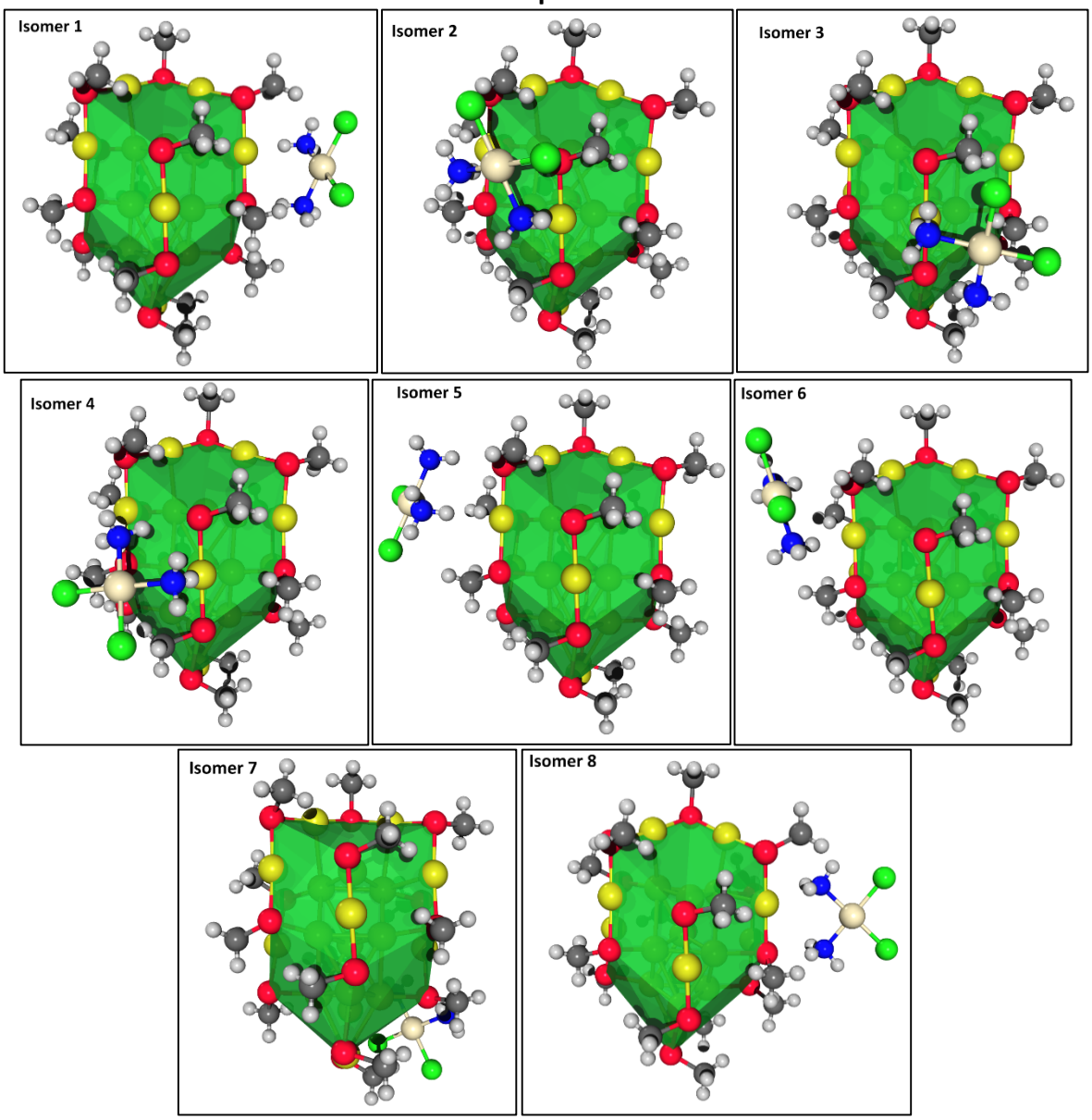


Figure S6 - Calculated bond lengths of studied structures including four cisplatin molecules. Again, the Au(core)-Au(staple) bonds are slightly compacted and Au-S bonds are similar to the parent Au_{18} cluster. The distribution of the Au-Au bonds seems to indicate that the core is more distorted with respect to the parent Au_{18} cluster, given the fact that the bonds are more dispersed.

PART IV

1 Cisplatin



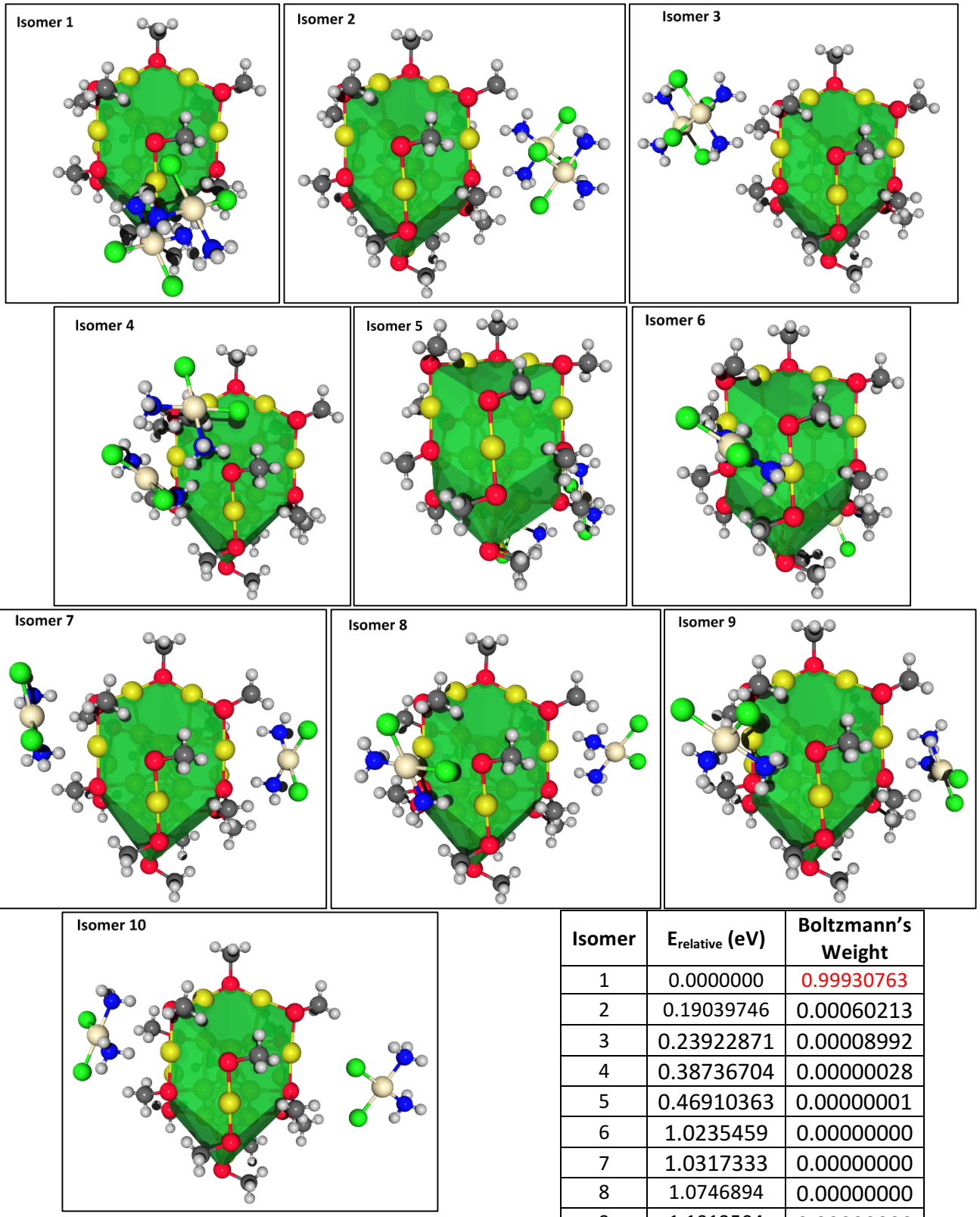
Isomer	$E_{relative}$ (eV)	Boltzmann's Weight
1	0.0000000	0.41926631
2	0.0132247	0.25051484
3	0.0148276	0.23535575
4	0.0483979	0.06367708
5	0.0773893	0.02059111
6	0.1033877	0.00748162
7	0.1261969	0.00307784
8	0.2407943	0.00003549

Sum of the denominator: 2.385119

$$BW(i) = \frac{e^{-\frac{E_i}{K_B T}}}{\sum_j e^{-\frac{E_j}{K_B T}}}$$

Table S1 - Table reporting Boltzmann weights of an extended set of isomers for various locations for one cisplatin.

2 Cisplatin

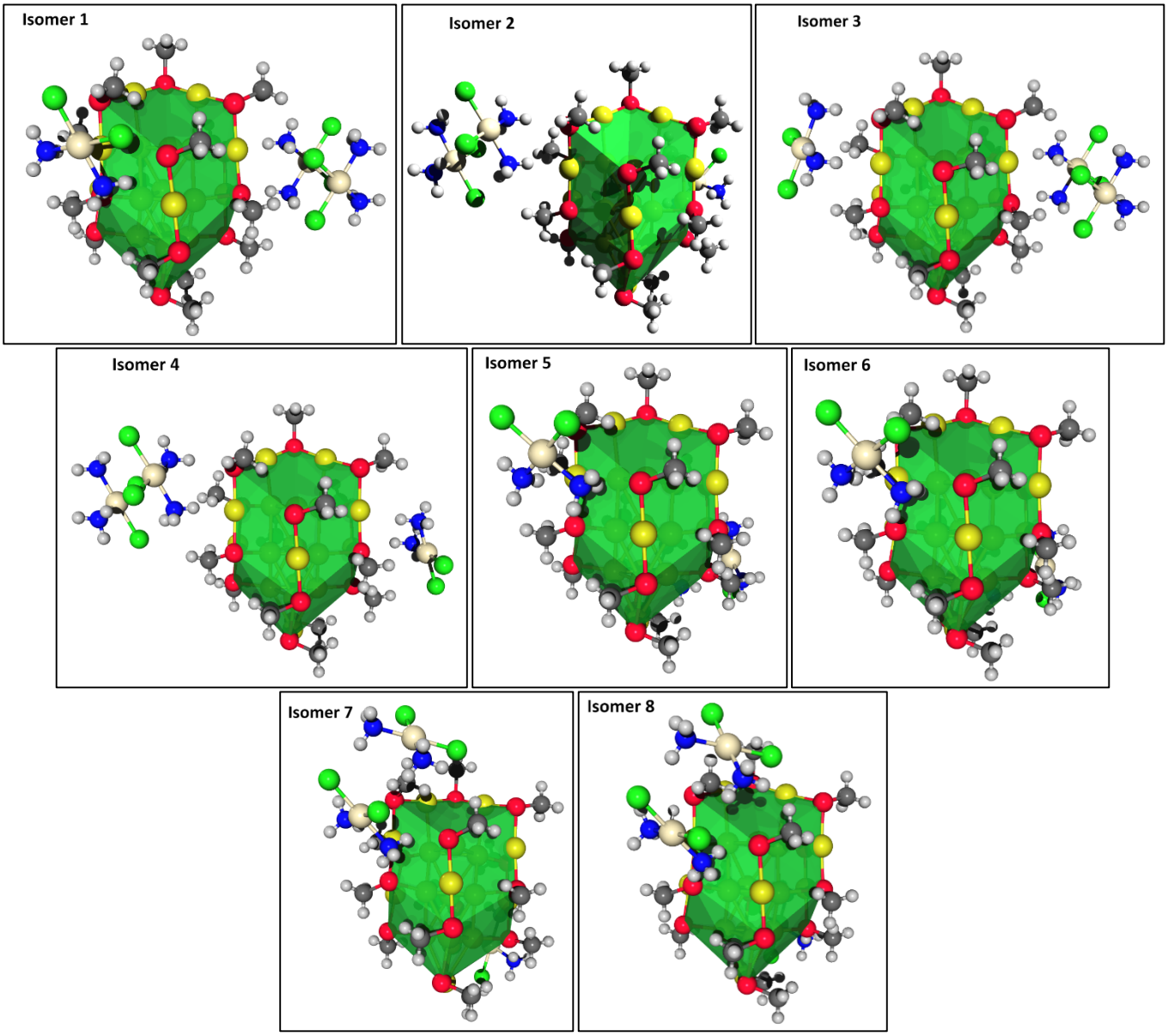


Isomer	$E_{relative}$ (eV)	Boltzmann's Weight
1	0.0000000	0.99930763
2	0.19039746	0.00060213
3	0.23922871	0.00008992
4	0.38736704	0.00000028
5	0.46910363	0.00000001
6	1.0235459	0.00000000
7	1.0317333	0.00000000
8	1.0746894	0.00000000
9	1.1013504	0.00000000
10	1.3647741	0.00000000

Sum of the denominator: 1.0006928

Table S2 - Table reporting Boltzmann weights of an extended set of isomers for various locations for two cisplatin.

3 Cisplatin

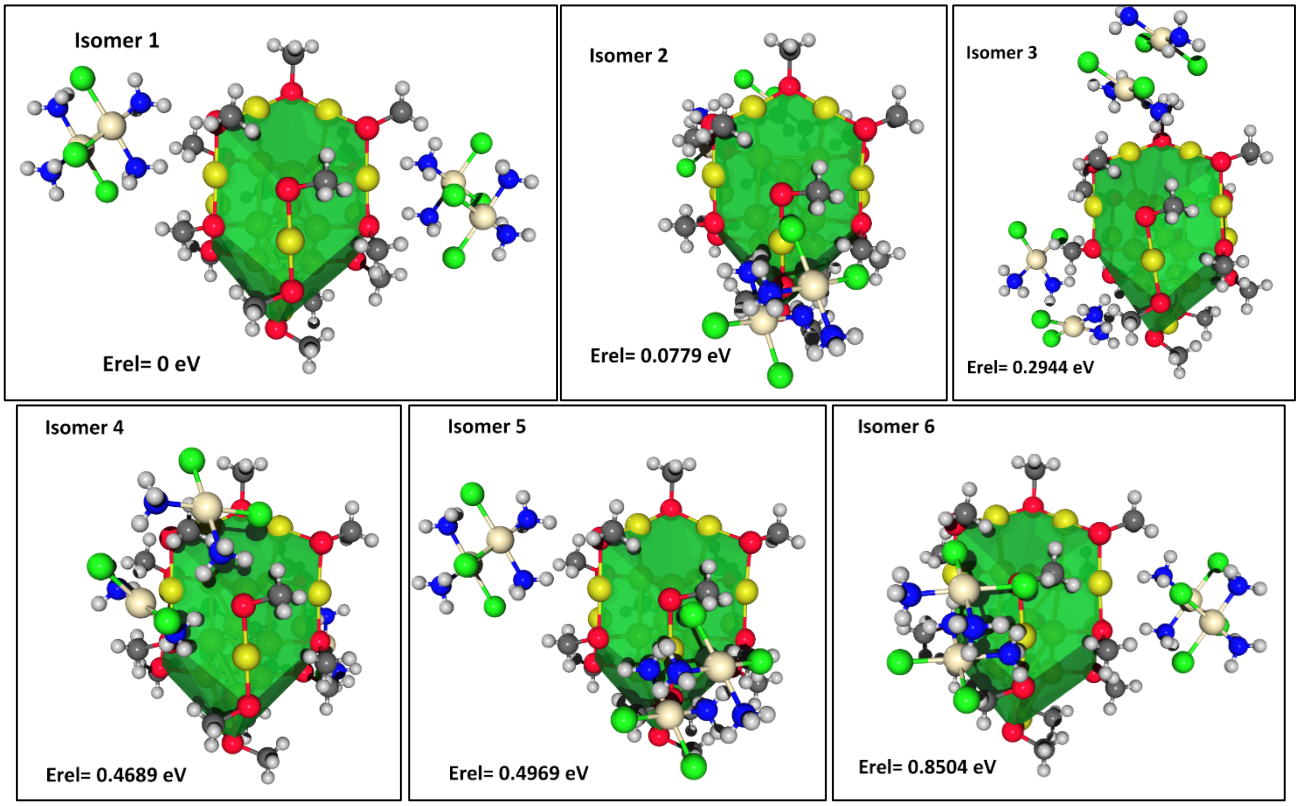


Isomer	$E_{relative}$ (eV)	Boltzmann's Weight
1	0.0000000	0.77540439
2	0.0546547	0.09230099
3	0.0602249	0.07430241
4	0.0665893	0.05799210
5	0.4503989	0.00000001
6	0.4582525	0.00000001
7	0.4858979	0.00000000
8	0.4870186	0.00000000

Sum of the denominator: 1.2896496

Table S3 - Table reporting Boltzmann weights of an extended set of isomers for various locations for three cisplatin.

4 Cisplatin


Isomer 1
Erel= 0 eV
Isomer 2
Erel= 0.0779 eV
Isomer 3
Erel= 0.2944 eV
Isomer 4
Erel= 0.4689 eV
Isomer 5
Erel= 0.4969 eV
Isomer 6
Erel= 0.8504 eV

Part V

Peak	E_{peak} (eV)	Transition from occupied → unoccupied orbital	Weight (%)
a	1.678	HOMO → LUMO	77.8
		HOMO-2 → LUMO	16.3
	1.747	HOMO-1 → LUMO	94.1
b	1.836	HOMO-3 → LUMO	90.0
	1.87	HOMO-2 → LUMO	61.0
		HOMO → LUMO	10.5
	1.951	HOMO-4 → LUMO	88.7
c	2.14	HOMO-5 → LUMO	43.9
		HOMO-4 → LUMO	43.9
	2.215	HOMO-6 → LUMO	89.9
d	2.701	HOMO-15 → LUMO	74.3
	2.71	HOMO-14 → LUMO	53.3
		HOMO-1 → LUMO+3	20.0
	2.753	HOMO-2 → LUMO+4	38.8
		HOMO-1 → LUMO+4	21.7
		HOMO → LUMO+5	10.6

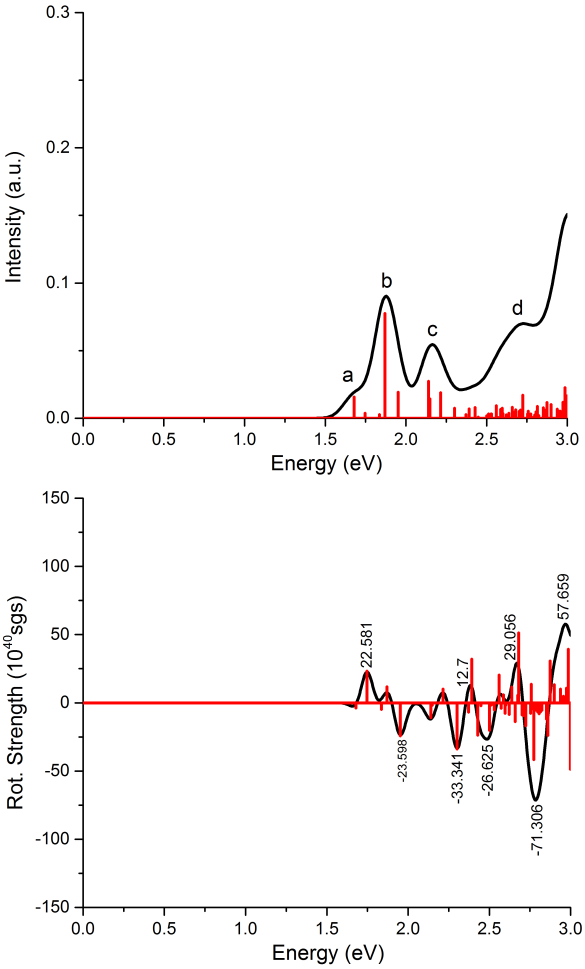


Table S4 – Left side shows all the electronic transitions on the $Au_{18}(SR)_{14}$ cluster, which correspond to the peaks obtained on the UV spectra (Upper right side image). The lower right one corresponds to the circular dichroism.

Peak	E_{peak} (eV)	Transition from occupied → unoccupied orbital	Weight (%)
a	3.143	HOMO → LUMO	99.2
	3.349	HOMO-1 → LUMO	98.6
	3.386	HOMO-2 → LUMO	86.3
		HOMO-3 → LUMO	13.4
b	3.616	HOMO-3 → LUMO	85.9
		HOMO-2 → LUMO	13.4
	3.622	HOMO → LUMO	99.5
	3.8	HOMO-1 → LUMO+1	99.8
c	4.058	HOMO-2 → LUMO+1	95.2

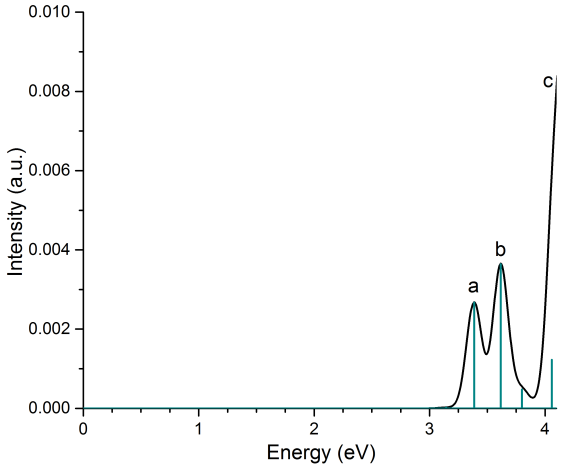


Table S5 – Left side shows all the electronic transitions for the cisplatin, which correspond to the peaks obtained on the UV spectra (Right side image).

Peak	E_{peak} (eV)	Transition from occupied → unoccupied orbital	Weight (%)
a	1.612	HOMO-2 → LUMO	52.07
		HOMO → LUMO	22.17
		HOMO-1 → LUMO	16.4
	1.702	HOMO-2 → LUMO	41.43
		HOMO → LUMO	24.47
		HOMO-1 → LUMO	17.3
	1.737	HOMO-4 → LUMO	86.29
	1.792	HOMO-3 → LUMO	60.35
		HOMO-2 → LUMO	17.92
b	1.983	HOMO-7 → LUMO	33.71
		HOMO-6 → LUMO	18.5
		HOMO-4 → LUMO	15.39
	1.991	HOMO-8 → LUMO	92.0
c	2.173	HOMO → LUMO+1	52.04
		HOMO-1 → LUMO+1	46.37
	2.185	HOMO-9 → LUMO	71.82
		HOMO-10 → LUMO	15.81
	2.206	HOMO-10 → LUMO	66.11
d	2.768	HOMO-20 → LUMO	27.61
		HOMO-5 → LUMO+3	18.74
		HOMO-1 → LUMO+5	13.88
	2.772	HOMO-20 → LUMO	21.98
		HOMO-3 → LUMO+4	17.96
		HOMO-5 → LUMO+3	17.04
	2.782	HOMO-7 → LUMO+2	57.95
		HOMO-8 → LUMO+2	15.29
	2.802	HOMO-21 → LUMO	61.18
e	2.975	HOMO → LUMO+7	47.69
		HOMO-2 → LUMO+6	19.28
		HOMO-27 → LUMO	14.78
	2.991	HOMO-28 → LUMO	36.89
		HOMO-3 → LUMO+5	32.95
	2.994	HOMO-2 → LUMO+6	32.19
		HOMO-1 → LUMO+7	21.74
		HOMO-28 → LUMO	13.46
		HOMO → LUMO+7	11.17
	3.001	HOMO-2 → LUMO+5	78.27

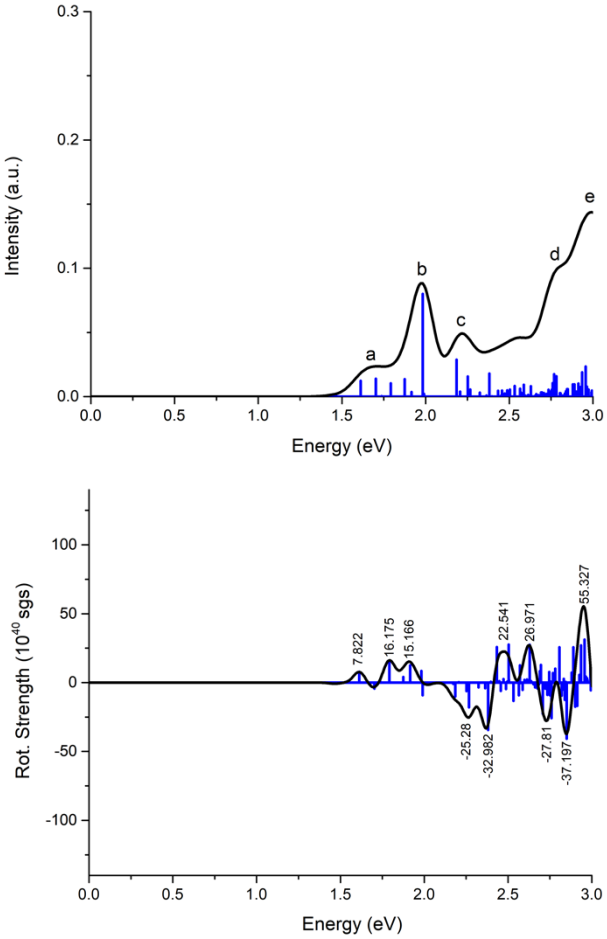


Table S6 – Left side shows all the electronic transitions for the cisplatin$_1$/$Au_{18}(SR)_{14}$, which correspond to the peaks obtained on the UV spectra (Upper right side image). The lower right one corresponds to the circular dichroism.

Peak	E_{peak} (eV)	Transition from occupied → unoccupied orbital	Weight (%)
a	1.736	HOMO-3 → LUMO	73.1
		HOMO-1 → LUMO	17.1
	1.747	HOMO-1 → LUMO	51.0
		HOMO-3 → LUMO	21.1
		HOMO-4 → LUMO	17.0
b	1.847	HOMO-6 → LUMO	70.6
		HOMO-5 → LUMO	24.0
	1.894	HOMO-5 → LUMO	44.1
		HOMO-6 → LUMO	20.3
		HOMO-7 → LUMO	13.1
	1.931	HOMO → LUMO+1	99.9
c	2.121	HOMO → LUMO+2	99.9
	2.127	HOMO-12 → LUMO	92.9
	2.142	HOMO-10 → LUMO	65.8
		HOMO-13 → LUMO	12.8
	2.16	HOMO → LUMO+3	99.9
d	2.561	HOMO-5 → LUMO+1	39.0
		HOMO-4 → LUMO+2	23.0
		HOMO-7 → LUMO+1	11.8
	2.571	HOMO-4 → LUMO+2	31.9
		HOMO-19 → LUMO	20.2
		HOMO-3 → LUMO+2	19.9
	2.582	HOMO-3 → LUMO+3	29.2
		HOMO-3 → LUMO+2	23.3
		HOMO-19 → LUMO	16.6
	2.608	HOMO-7 → LUMO+1	81.9
e	2.915	HOMO-2 → LUMO+6	42.4
		HOMO-2 → LUMO+5	38.3
	2.924	HOMO-9 → LUMO+2	94.0
	2.945	HOMO → LUMO+9	46.2
		HOMO-4 → LUMO+6	24.5
	2.96	HOMO-3 → LUMO+6	41.1
		HOMO-3 → LUMO+7	11.7
	2.973	HOMO-4 → LUMO+6	28.4
		HOMO-33 → LUMO	14.2
		HOMO-5 → LUMO+5	12.3
	2.989	HOMO-35 → LUMO	66.8
		HOMO-34 → LUMO+	19.7
	3.0	HOMO → LUMO+12	98.8

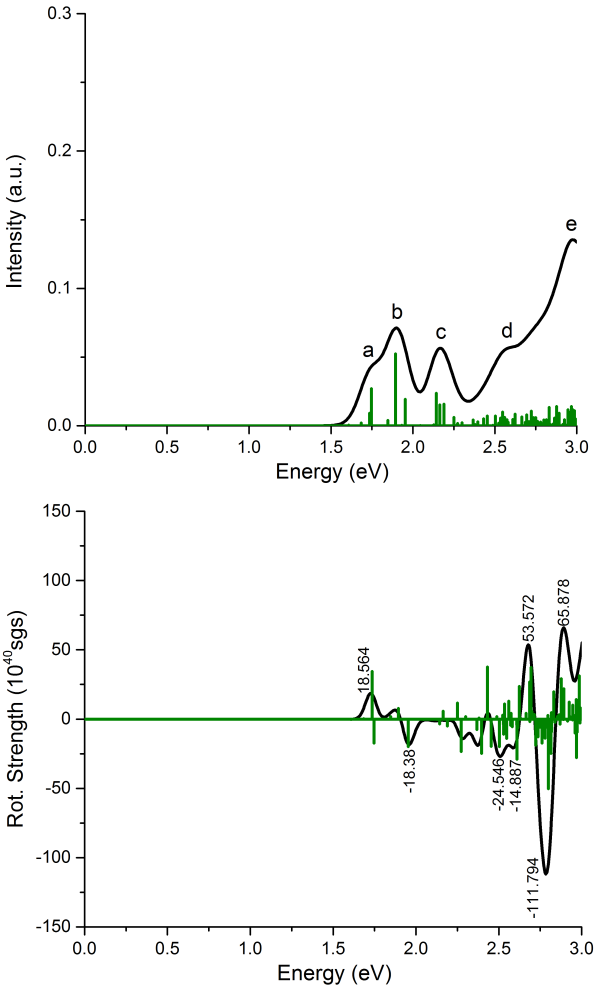


Table S7 – Left side shows all the electronic transitions for the cisplatin$_2$/$Au_{18}(SR)_{14}$, which correspond to the peaks obtained on the UV spectra (Upper right side image). The lower right one corresponds to the circular dichroism.

Peak	E_{peak} (eV)	Transition from occupied → unoccupied orbital	Weight (%)
a	1.857	HOMO → LUMO+1	99.9
	1.894	HOMO-10 → LUMO	35.9
		HOMO-11 → LUMO	24.8
		HOMO-9 → LUMO	14.2
	1.925	HOMO-12 → LUMO	93.1
	1.931	HOMO-1 → LUMO+1	99.9
	1.949	HOMO → LUMO+2	99.7
b	2.139	HOMO-15 → LUMO	66.6
		HOMO-17 → LUMO	13.1
	2.141	HOMO-1 → LUMO+3	99.8
	2.142	HOMO → LUMO+4	95.1
	2.181	HOMO-17 → LUMO	67.5
	2.191	HOMO-2 → LUMO+2	94.1
	2.216	HOMO-1 → LUMO+4	95.0
c	2.43	HOMO-20 → LUMO	35.2
		HOMO-3 → LUMO+3	34.4
		HOMO-4 → LUMO+3	11.0
	2.444	HOMO-5 → LUMO+3	83.0
	2.453	HOMO-1 → LUMO+5	94.4
	4.466	HOMO-8 → LUMO+1	34.8
		HOMO-7 → LUMO+2	20.6
		HOMO-10 → LUMO+1	15.1
		HOMO-9 → LUMO+1	10.3
	2.487	HOMO-3 → LUMO+4	87.5
d	2.674	HOMO-2 → LUMO+6	78.3
	2.681	HOMO-3 → LUMO+1	46.3
		HOMO-11 → LUMO+1	16.9
	2.699	HOMO → LUMO+9	85.8
		HOMO → LUMO+8	11.8
	2.701	HOMO-9 → LUMO+3	35.5
		HOMO-8 → LUMO+3	24.6
	2.707	HOMO-28 → LUMO	61.3
		HOMO-3 → LUMO+5	14.7
	2.709	HOMO-3 → LUMO+5	42.2
		HOMO-29 → LUMO	13.8
e	2.904	HOMO-4 → LUMO+7	37.6
		HOMO-16 → LUMO+2	17.9
	2.911	HOMO-15 → LUMO+2	44.4
		HOMO-4 → LUMO+7	13.0
	2.92	HOMO-12 → LUMO+4	94.6
	2.927	HOMO-17 → LUMO+2	38.1
		HOMO-15 → LUMO+2	15.0
		HOMO-6 → LUMO+6	11.5
	2.931	HOMO-6 → LUMO+6	28.5
		HOMO-17 → LUMO+2	14.8
		HOMO-7 → LUMO+6	13.0
	2.944	HOMO-13 → LUMO+4	50.5
		HOMO-37 → LUMO	16.0

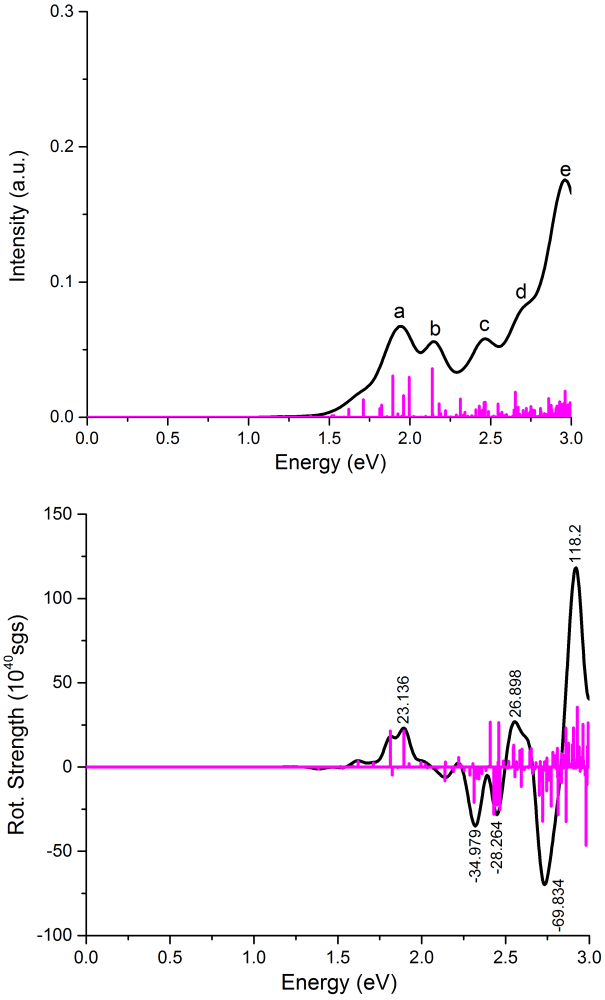


Table S8 – Left side shows all the electronic transitions for the cisplatin$_3$/Au$_{18}$(SR)$_{14}$, which correspond to the peaks obtained on the UV spectra (Upper right side image). The lower right one corresponds to the circular dichroism.

Peak	E_{peak} (eV)	Transition from occupied → unoccupied orbital	Weight (%)
a	1.787	HOMO-8 → LUMO	90.5
	1.809	HOMO-7 → LUMO	62.09
		HOMO-9 → LUMO	26.3
	1.878	HOMO-9 → LUMO	50.8
		HOMO-10 → LUMO	26.9
	1.921	HOMO → LUMO+1	99.9
	1.941	HOMO-1 → LUMO+1	99.9
	1.948	HOMO-11 → LUMO	90.0
b	2.111	HOMO-19 → LUMO	26.6
		HOMO-18 → LUMO	25.3
		HOMO-16 → LUMO	21.4
		HOMO-20 → LUMO	14.5
	2.125	HOMO-1 → LUMO+3	99.9
	2.149	HOMO-18 → LUMO	32.1
		HOMO-15 → LUMO	21.8
		HOMO-17 → LUMO	14.3
		HOMO-19 → LUMO	12.7
	2.2	HOMO-21 → LUMO	80.0
	2.231	HOMO- → LUMO+4	99.9
c	2.9	HOMO- → LUMO+14	66.5
		HOMO-7 → LUMO+5	14.3
	2.911	HOMO-12 → LUMO+3	88.6
	2.934	HOMO-41 → LUMO	78.6
	2.947	HOMO-43 → LUMO	78.5
	2.961	HOMO-44 → LUMO	63.0
		HOMO-8 → LUMO+5	10.6
	2.977	HOMO-8 → LUMO+6	71.2
		HOMO-6 → LUMO+6	17.7

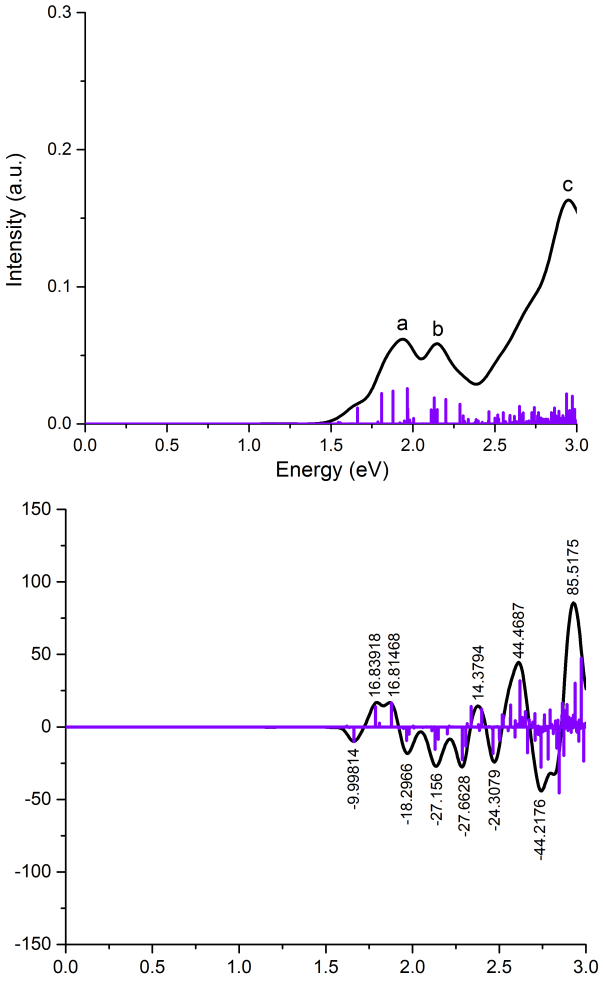


Table S9 – Left side shows all the electronic transitions for the cisplatin$_4$/$Au_{18}(SR)_{14}$, which correspond to the peaks obtained on the UV spectra (Right side image).

Part VI

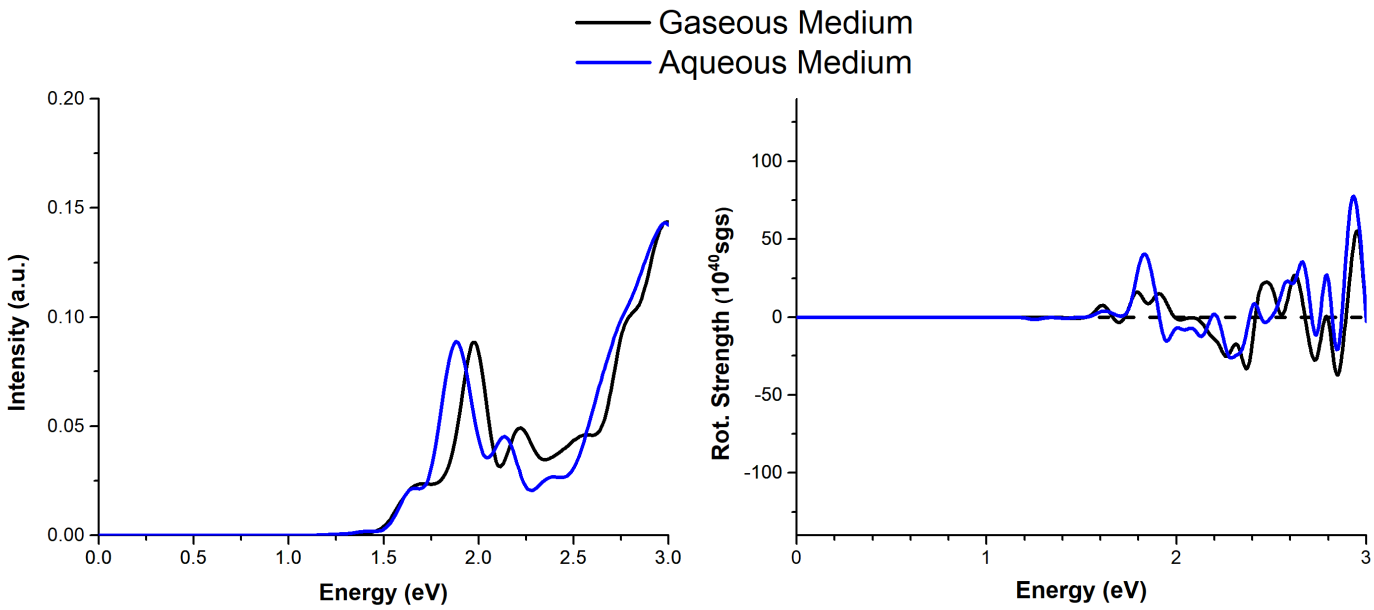


Figure S7 – Comparison between the lowest energy spectra for the cisplatin$_1$/$Au_{18}(SR)_{14}$ complex. Both spectra are alike with a translation of respective peaks by 0.0924 eV.