



Synthesis and characterization of molecular and supramolecular compounds based on 11th group metals for optoelectronics and/or biological applications

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Synthesis and characterization

IUPAC Periodic Table of the Elements																																																																	
1 1 H hydrogen 1.001 [1.0078; 1.0082]	2 3 Li lithium 6.94 [6.938; 6.997]	4 Be beryllium 9.0122	5 11 Na sodium 22.990 [24.304; 24.307]	6 12 Mg magnesium 24.305 [24.304; 24.307]	7 23 V vanadium 50.942	24 25 Cr chromium 51.996 54.938	26 27 Fe iron 55.845(2) 56.933	28 29 Ni nickel 58.693 63.546(3)	10 11 Cu copper 63.546(3)	13 14 B boron 10.805 [10.805; 10.821]	16 17 O oxygen 16.998 [16.998; 17.001]	18 2 He helium 4.0026 [4.0026; 4.0028]	5 6 C carbon 12.008; 12 [12.008; 12.009]	7 N nitrogen 14.007 [14.007; 14.010]	8 S sulfur 32.065 [32.059; 32.076]	9 F fluorine 18.998 [18.998; 19.001]	10 Ne neon 20.180 [20.180; 20.182]	11 12 Zn zinc 65.38(2) 65.38(2)	15 16 Si silicon 28.085 [28.084; 28.085]	17 18 Cl chlorine 35.45 [35.446; 35.457]	19 20 Ca calcium 40.078(4) 40.078(4)	21 22 Sc scandium 44.956 47.867	23 24 Ti titanium 50.942 51.996	25 26 Mn manganese 54.938 55.845(2)	27 28 Co cobalt 58.933 58.693	29 30 Cu copper 63.546(3) 65.38(2)	31 32 Zn zinc 66.723 72.630(8)	33 34 As arsenic 74.922 78.971(8)	35 36 Br bromine 79.901 [79.901; 79.907]	37 38 Rb rubidium 85.468 87.62	39 40 Sr strontium 88.906 89.906	41 42 Zr zirconium 91.224(2) 92.905	43 44 Nb niobium 95.95 95.95	45 46 Tc technetium 101.07(2) 102.91	47 48 Pd palladium 106.42 107.87	49 50 Cd cadmium 112.41 114.82	51 52 In indium 116.71 118.71	53 54 Sn tin 121.76 127.60(3)	55 56 Ba barium 132.91 137.33	57-71 72 Hf hafnium 178.49(2) 180.95	73 74 Ta tantalum 183.84 186.21	75 76 Re rhenium 186.21 186.21	77 78 Os osmium 190.23(3) 192.22	79 80 Pt platinum 195.08 196.97	81 82 Hg mercury 200.59 [204.38; 204.39]	83 84 Tl thallium 207.2 208.98	85 86 Pb lead 207.2 208.98	87 88 Ra radium actinoids 232.04 231.04	89 90 Ac actinium 238.03 231.04	91 92 Pa protactinium 238.03 231.04	93 94 U uranium 238.03 231.04	95 96 Np neptunium 238.03 231.04	97 98 Pu plutonium 238.03 231.04	99 100 Am americium 238.03 231.04	101 102 Cm curium 247.03 247.03	103 104 Bk berkelium 247.03 247.03	105 106 Ds darmstadtium 247.03 247.03	107 108 Mt meitnerium 247.03 247.03	109 110 Rg roentgenium 247.03 247.03	111 112 Cn copernicium 251.03 251.03	113 114 Nh nihonium 251.03 251.03	115 116 Fl flerovium 251.03 251.03	117 118 Lv moscovium 251.03 251.03	119 120 Ts tennessine 251.03 251.03	121 122 Og oganesson 251.03 251.03

For notes and updates to this table, see www.iupac.org. This version is dated 1 December 2018.
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Prof.s

Synthesis and characterization of molecular and supramolecular compounds based on 11th group metals for optoelectronics and/or biological applications

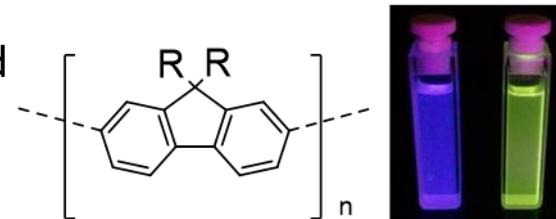


- Optoelectronics is the study and application of electronic devices that detect control and emit the light
- Some important technological applications:
 - Solar cells
 - Lasers
 - Sensors
 - OLEDs



Most important classes of emitters:

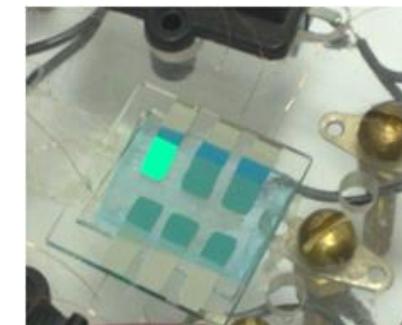
- Organic Polymers or small organic molecules with extended π - π^* framework



Polyfluorene based emitters

- Rare earth metal coordination complexes

(mostly Eu(III), Tb(III) and Tm(III))



Tb(III) based OLED

- Transition metal coordination complexes

(mostly Re(I), Ir(III), Pt(II), Ru(II), Cu(I))



Φ_{PL} (RT) up to 100%
 $k_f = 10^5 - 10^6 \text{ s}^{-1}$
EQE = 19.4%



Copper(I) based emitter



Biological applications

What are biological properties of 11° group coordination compounds?



GOLD

Antiarthritic

Antiinfective (antiparasitic, antibacterial, antiviral)

Anticancer several cancers or leukemia (e.g., lung cancer, recurrent ovarian epithelial cancer, chronic lymphocytic leukemia)



COPPER

Anticancer Exhibit a potent *in vitro* **cytotoxicity** in H460 human lung carcinoma cells, comparable to that displayed by Adriamycin



SILVER

Antifungal properties

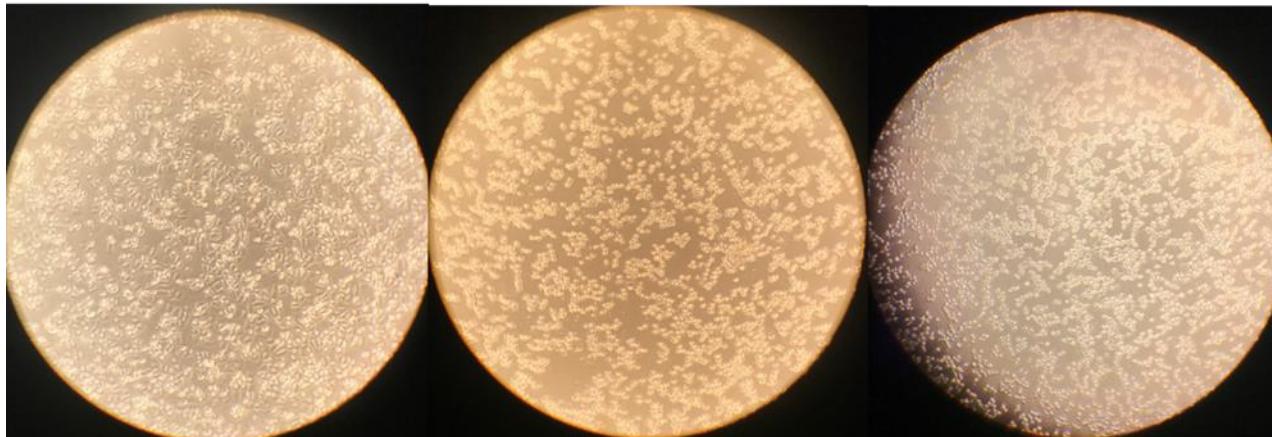
Antimicrobial properties

Ag(I) carbene and phosphane complexes is an emerging class of **anticancer agents**

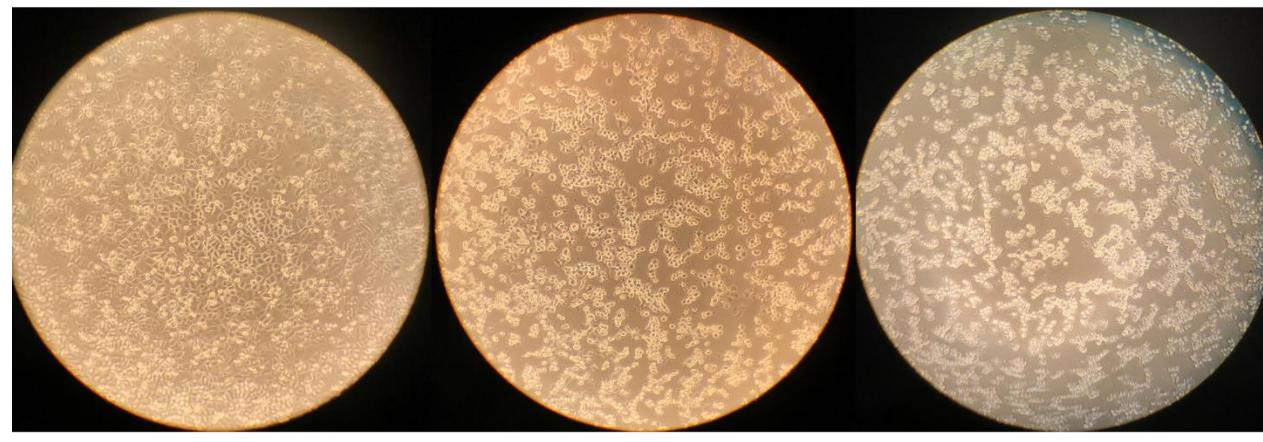
biological applications

Anticancer activity

SKBR3 cells treated with 6 μ M compound 5 and compound 6 for 4 hours

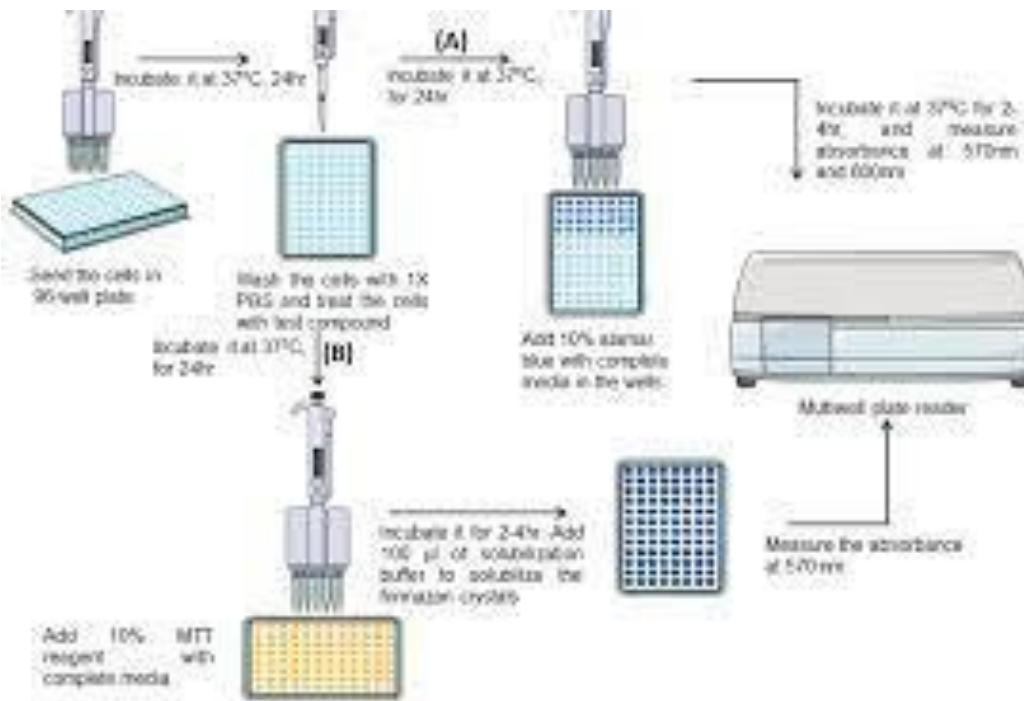


SKBR3 cells treated with 0, 3, 6 μ M compound 6 for 12 hours



biological applications

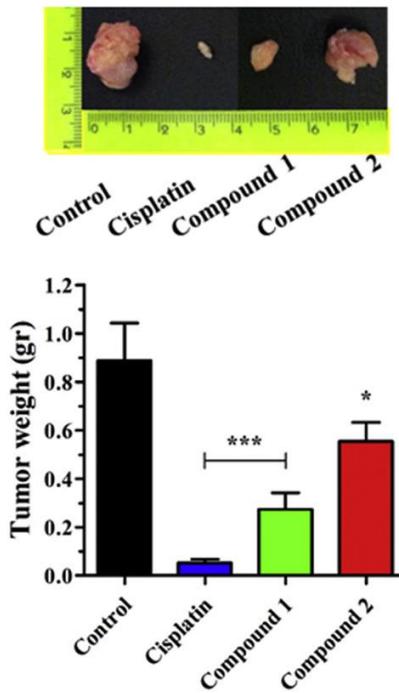
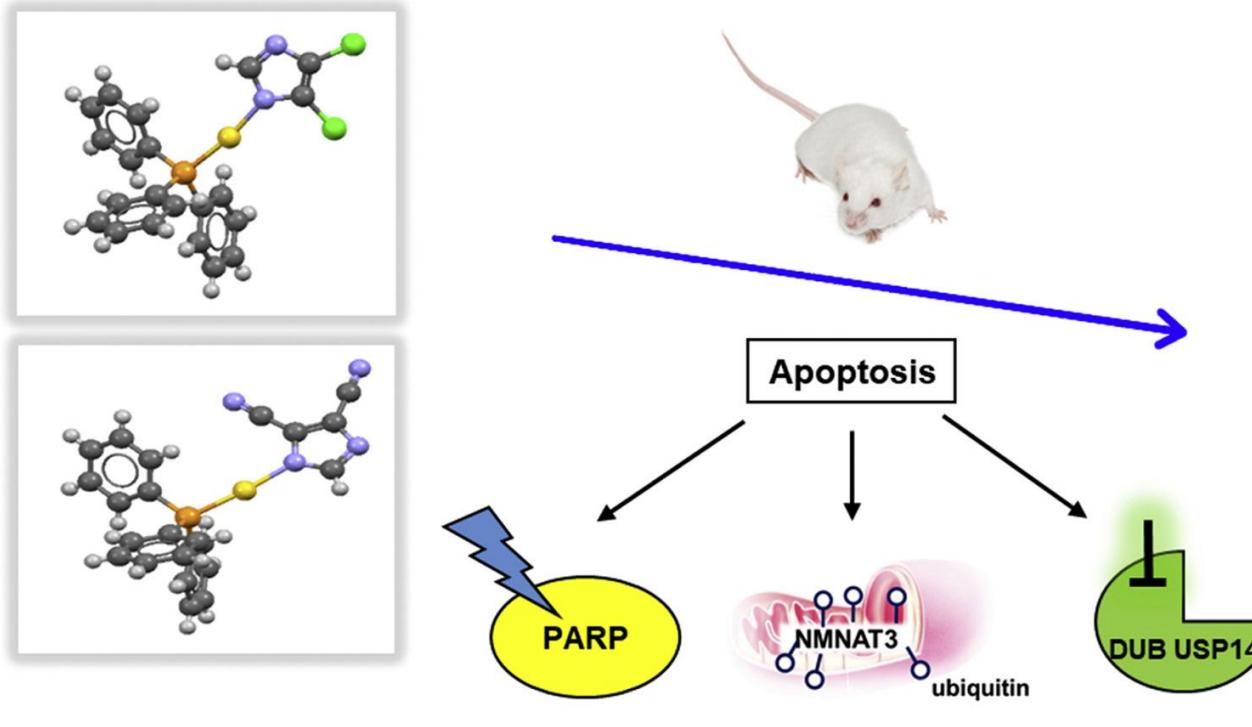
Anticancer activity: In vitro tests



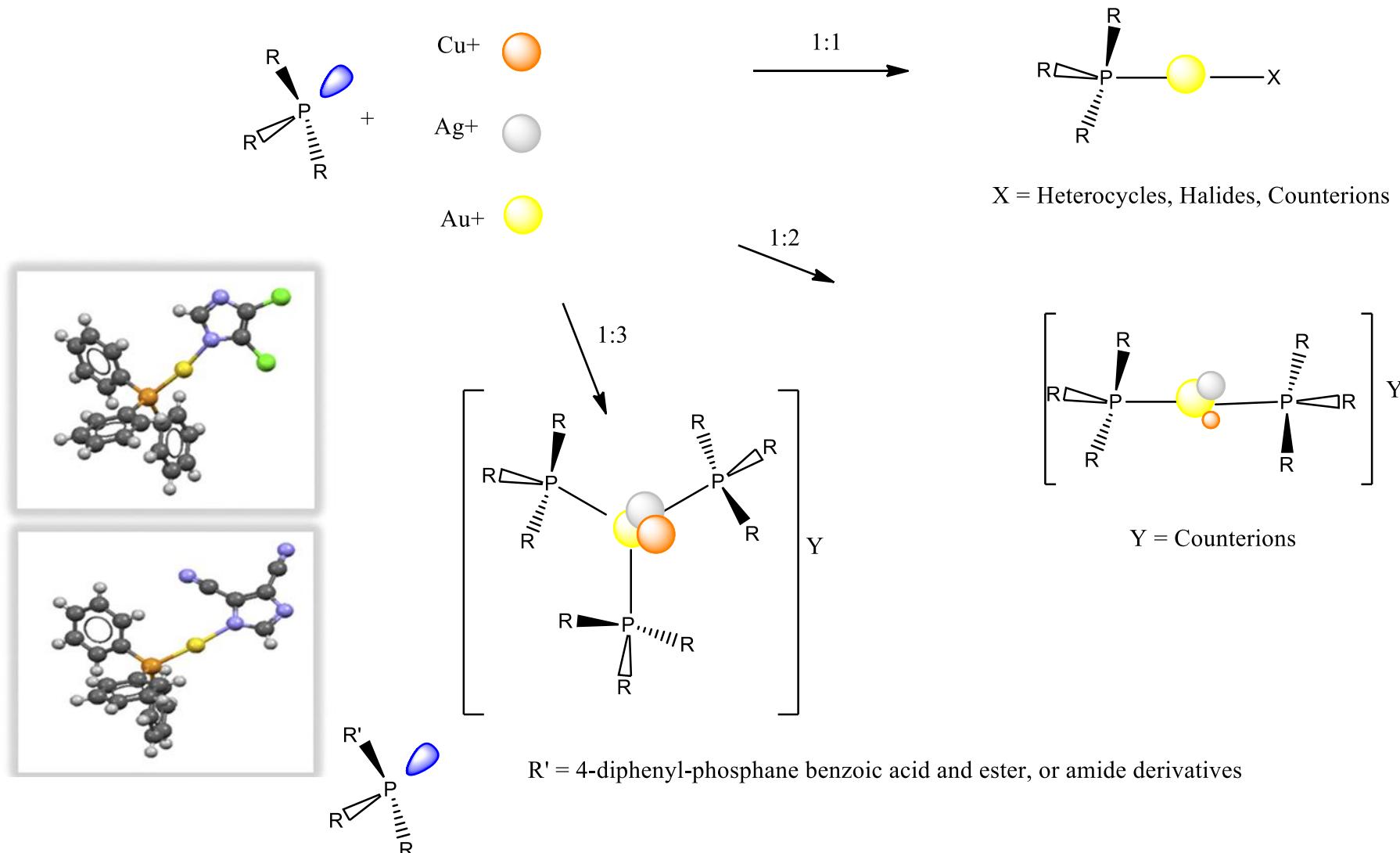
Compound	Cell Line	Time	IC ₅₀ Mean ± SD ^a [µM]
Compound 1	A17	24 h	11.38 ± 1.05
	MDA-MB-231	24 h	19.28 ± 1.06
	MDA-MB-468	24 h	13.62 ± 1.05
Compound 2	HMLE/FoxQ1	24 h	7.41 ± 1.06
	A17	24 h	11.95 ± 1.04
	MDA-MB-231	24 h	14.83 ± 1.05
Cisplatin	MDA-MB-468	24 h	11.25 ± 1.14
	HMLE/FoxQ1	24 h	9.27 ± 1.06
	A17	24 h	15.86 ± 1.17
Cisplatin	MDA-MB-231	48 h	50.49 ± 2
	MDA-MB-468	24 h	32.50 ± 1.12
	HMLE/FoxQ1	48 h	34.12 ± 2.17

biological applications

Anticancer activity: In vivo tests

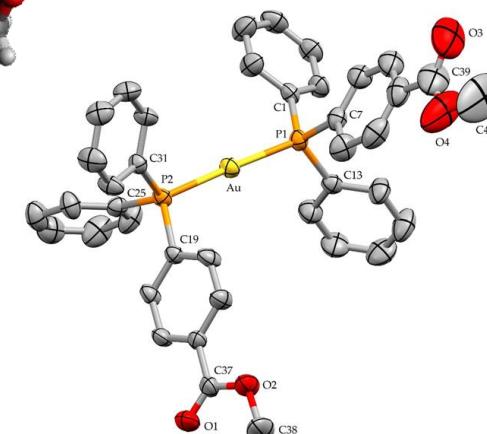
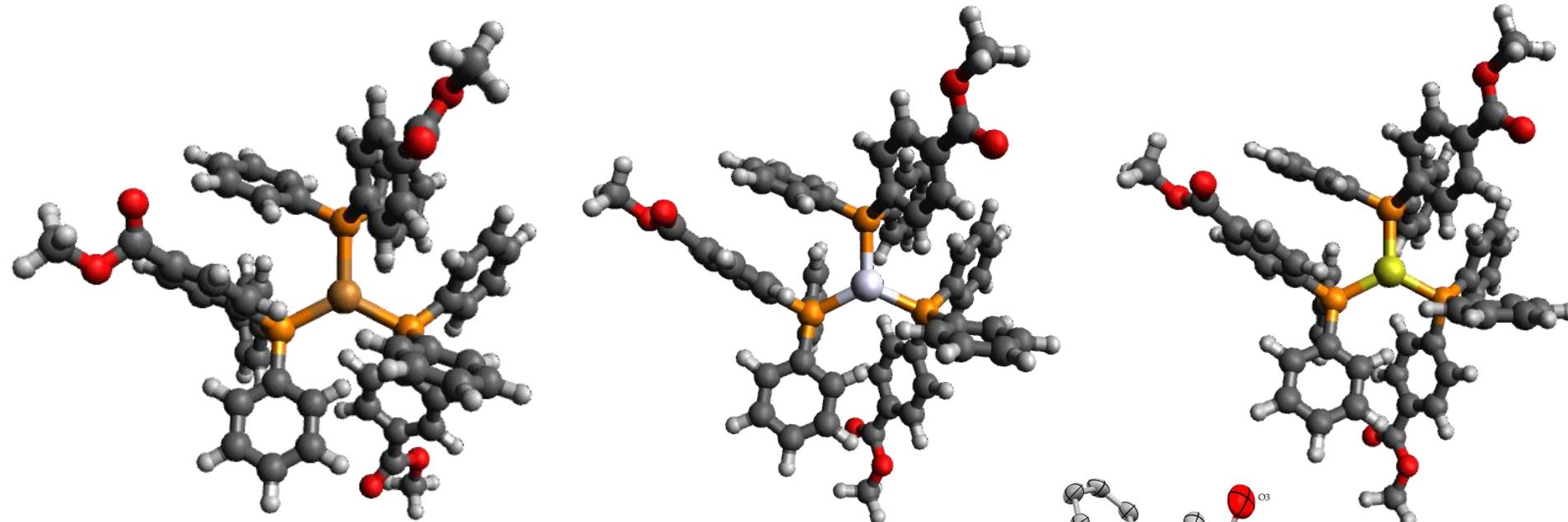


Synthesis and characterization: classic methods



Characterization of molecular compounds

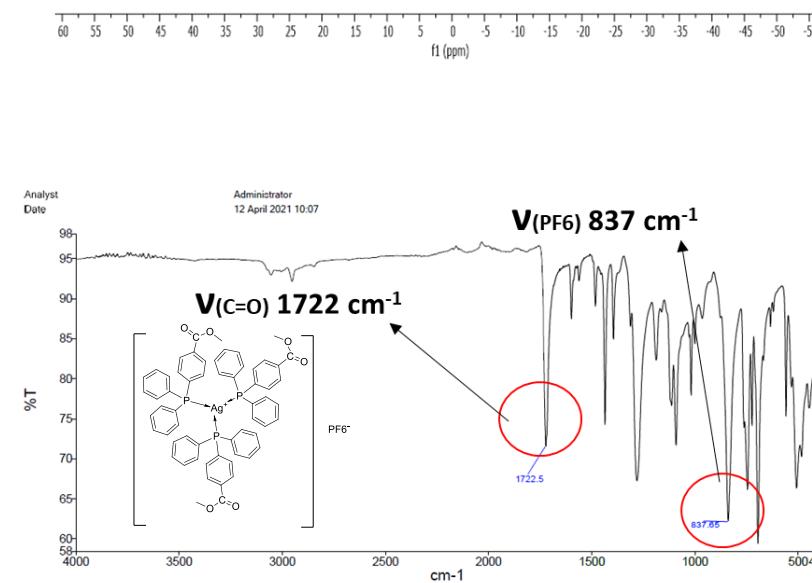
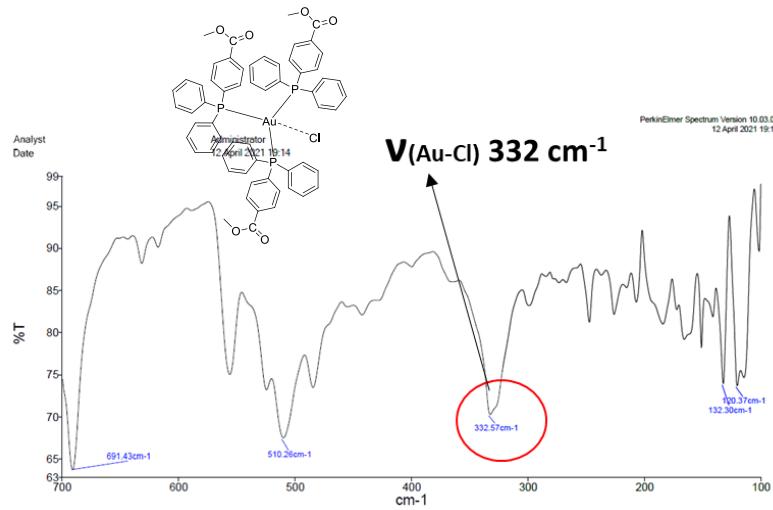
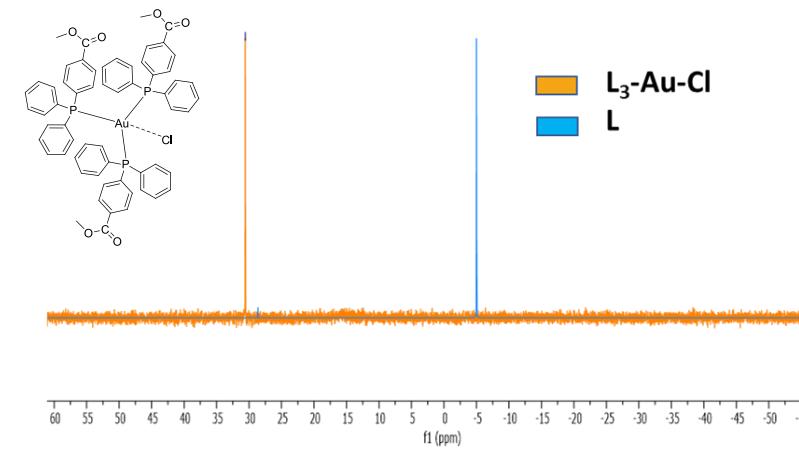
DFT OPTIMIZATION OF COMPLEXES $[M(PR_3)_3]^+$ ($M = Cu, Ag, Au$)



X-ray crystal structure determination

Characterization of molecular compounds

L ₃ -Au(I)-Cl\	L3-Cu(I)-BF ₄	L3-Ag(I)-PF ₆			
Calculated (%)	Found (%)	Calculated (%)	Found (%)	Calculated (%)	Found (%)
C 60,39	C 60,16	C 64,85	C 65,03	C 59,37	C 59,09
H 4,31	H 4,47	H 4,63	H 4,68	H 4,24	H 4,24



Characterization: in vitro acitivity

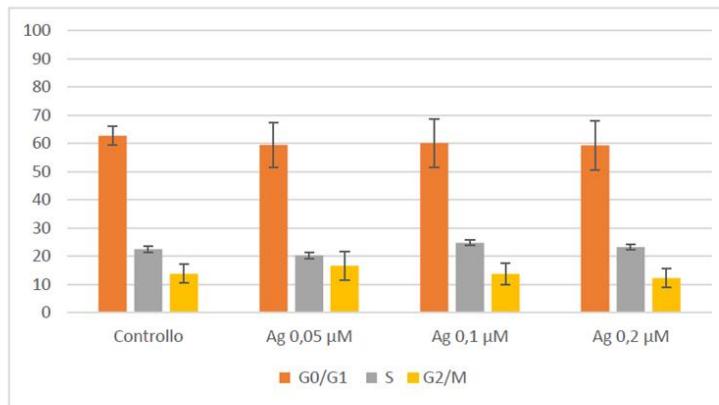
Compounds	A2780 (GI ₅₀ μM)	A2780 <i>cis</i> (GI ₅₀ μM)	HT-29 (GI ₅₀ μM)	MDA-MB- 231 (GI ₅₀ μM)
Ligand (L)	>20	>20	> 20	> 20
L₃-Ag-PF₆	0, 17 ± 0,07	0,94 ± 0,10	2,98 ± 0,40	4,33 ± 0,45
L₃-Au-Cl	0,17 ± 0,03	4,68 ± 0,86	8,17 ± 0,61	12,64 ± 0,93
L₃-Cu-BF₄	1,78 ± 0,15	4,40 ± 0,18	4,80 ± 0,50	10,78 ± 0,88
Cisplatin (reference)	1,08 ± 0,35	4,50 ± 0,88	3,02 ± 0,47	23 ± 0,53

- The ligand (**L**), is **not active** in all the studied cell lines
- The most active complex is the **L₃-Ag-PF₆**
- GI₅₀ of the **L₃-Ag-PF₆** on the A2780*cis* is almost 5 times smaller with respect to the cisplatin
- The GI₅₀ of the **L₃-Au-Cl** and the **L₃-Cu-BF₄** are comparable in almost all studied cell lines
- The GI₅₀ of the **L₃-Au-Cl** is the same of the **L₃-Ag-PF₆** for the A2780 cell line.

Characterization: in vitro acitivity

5.1 Cellular cycle alterations

Figure 1 and 2: A2780 percentages in the different cellular phases



	Controllo	Ag 0,05 μM	Ag 0,1 μM	Ag 0,2 μM
G ₀ /G ₁	62.7 ± 3.3	59.5 ± 7.9	60.1 ± 8.4	59.3 ± 8.7
S	22.5 ± 1.0	20.3 ± 2.1	24.8 ± 5.9	23.2 ± 3.8
G ₂ /M	13.8 ± 3.3	16.6 ± 5.1	13.7 ± 3.8	12.3 ± 3.3

Treatment: 48 ore Fluorophore: Propidium iodide

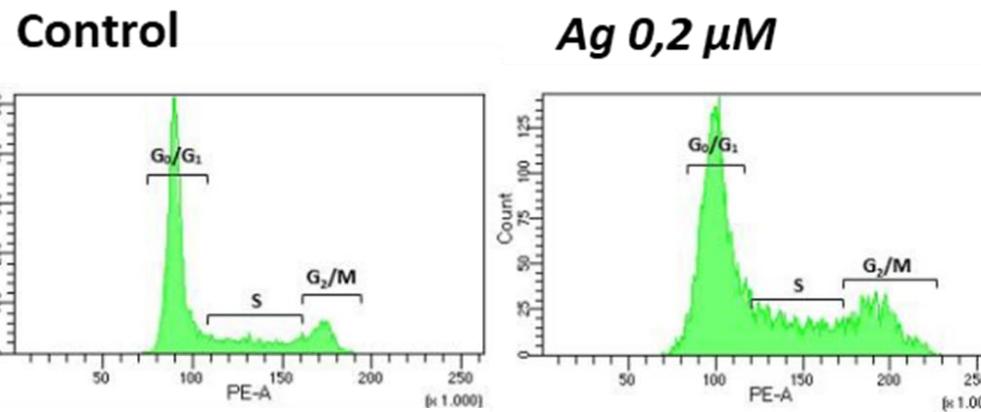


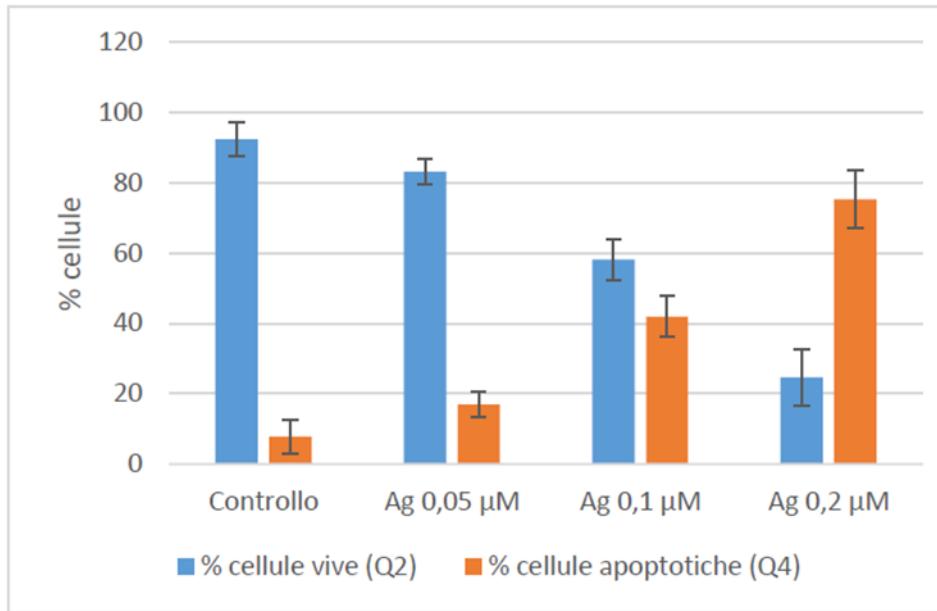
Figure 3: Cytofluorimetric analysis of the A2780 cellular cycle of untrated (control) and Silver treated (Ag 0,2 μM) cells.

- Cytofluorimetric analysis highlights that the **L₃-Ag-PF₆** complex does not modify the cellular cycle

Characterization: in vitro acitivity

5.3 Mitochondrial Membrane Depolarization

Figure 6: histogram (up) and table (down) of A2780 cells percentage.



Treatment: 48 hours

Fluorophore: JC1

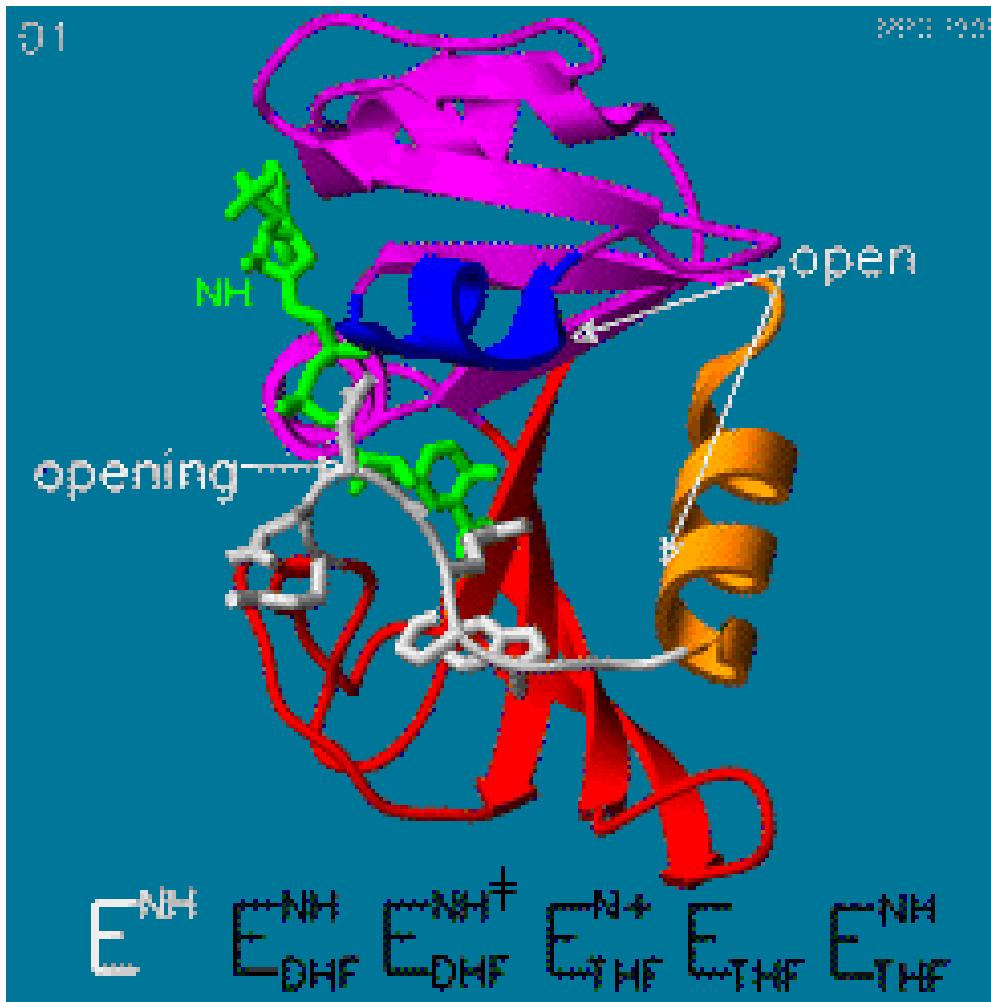
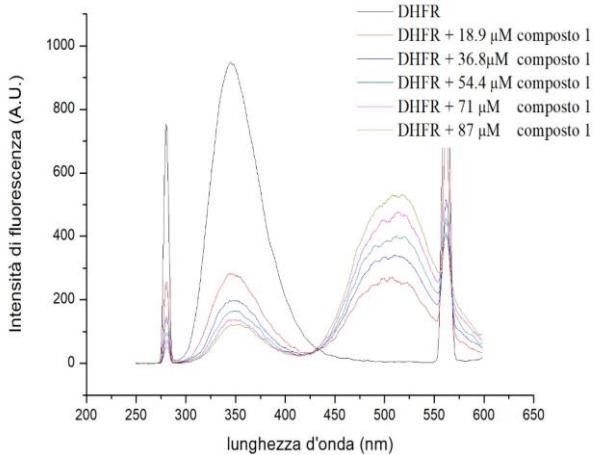
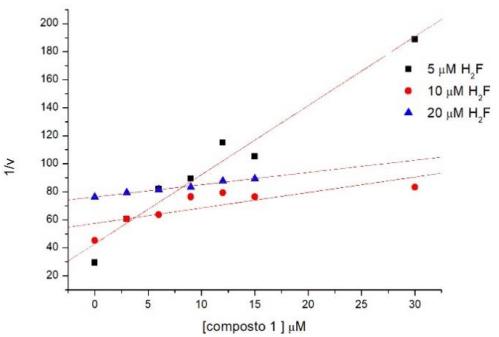
Q2: healthy cells with high mitochondrial membrane potential.
Fluorescence in **red** region

Q4: Apoptotic cells with collapsed mitochondrial potential.
Fluorescence in the **green** region

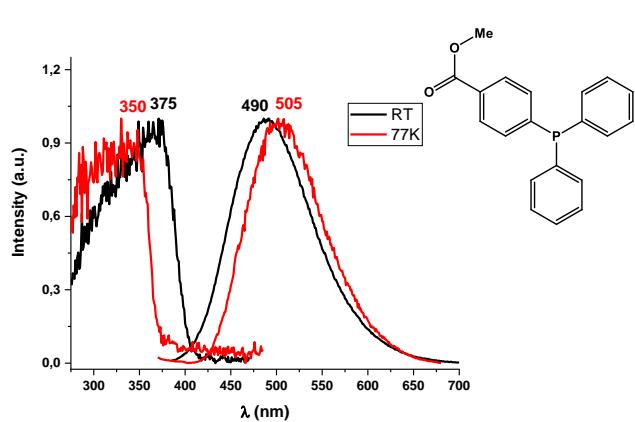
- The treatment of **A2780** cells with growing concentrations of **Silver** complex increases the percentage of cells with collapsed **mitochondrial** transmembrane potential

Characterization: in vitro activity

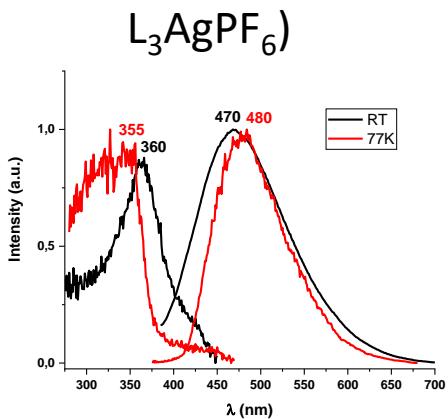
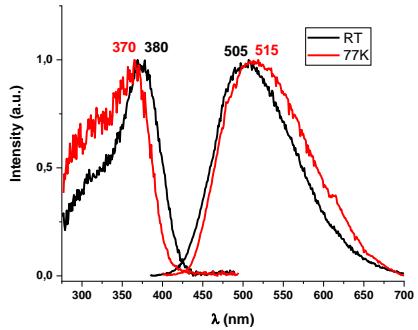
5.4 Enzyme inhibition



Characterization: emissive properties



(L_3CuBF_4)



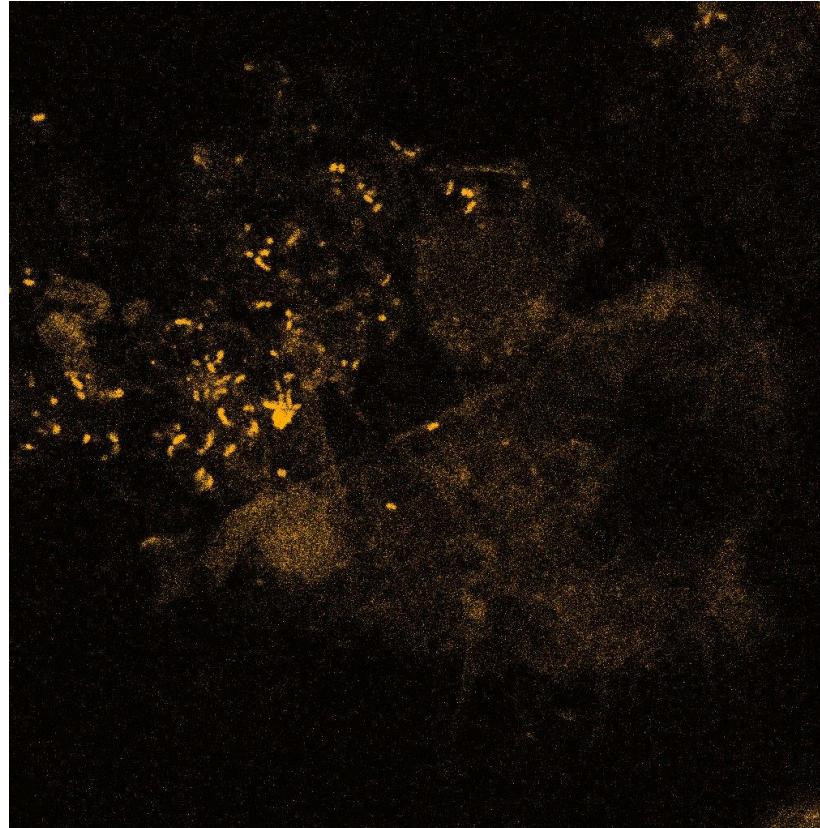
(L_3AuCl)

L Cu Ag Au



Future remarks

5.5 Theranostics



Composto di oro luminescente
all'interno di una cellula
tumorale A2780 visto con il
microscopio confocale



Biological applications: collaborations

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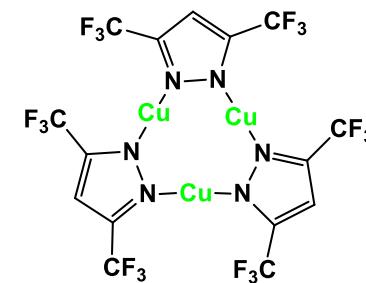
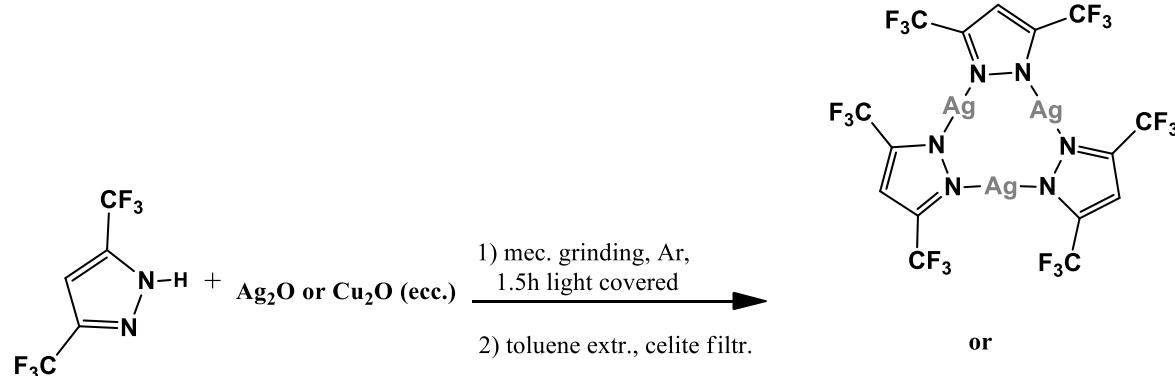


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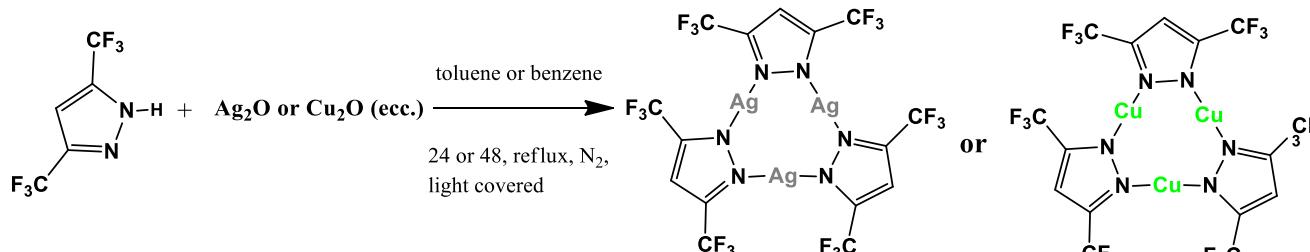


- School of Biosciences and Veterinary Medicine
- School of Drugs and Health Products Sciences,

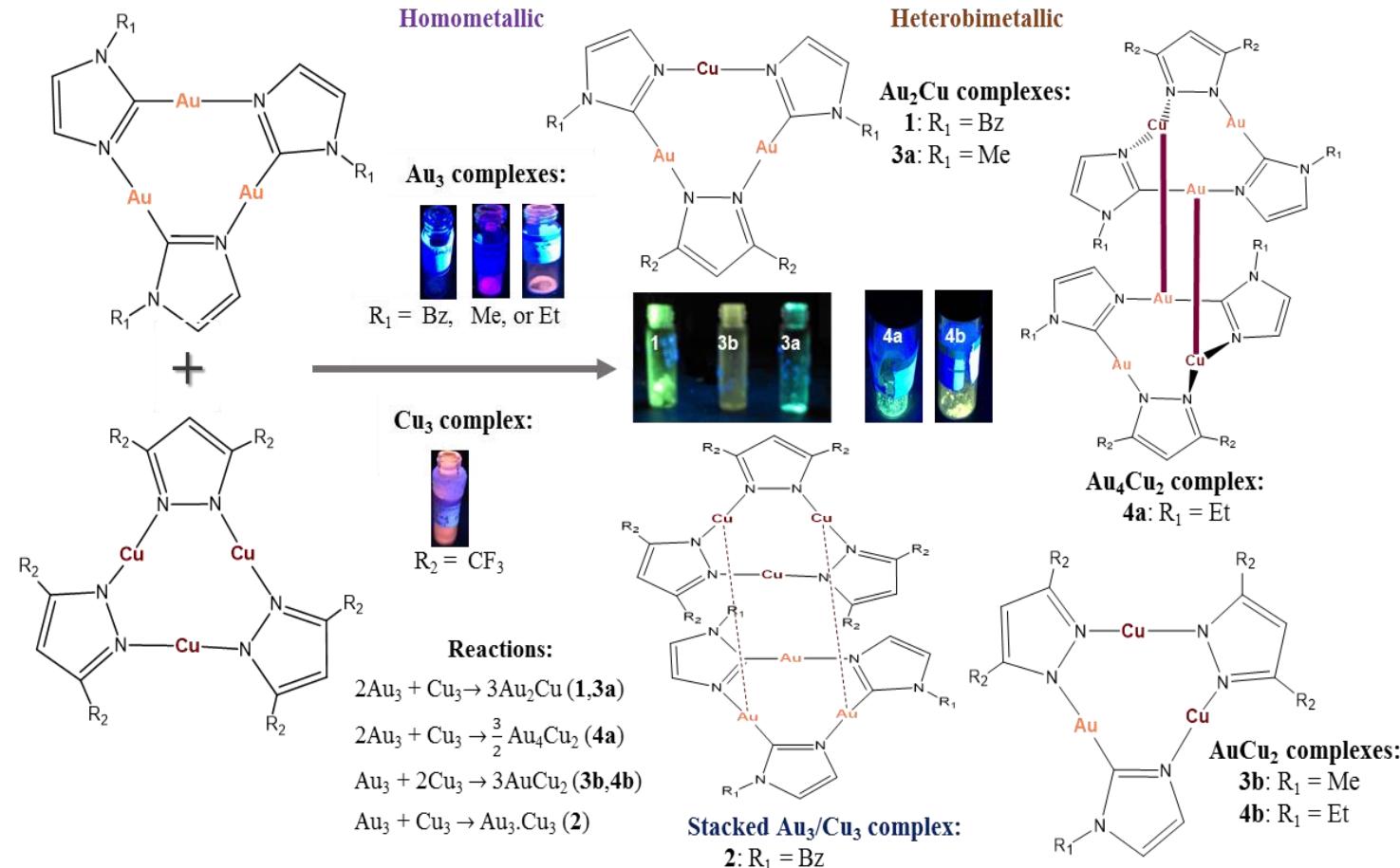
Molecular and supramolecular ... means what?



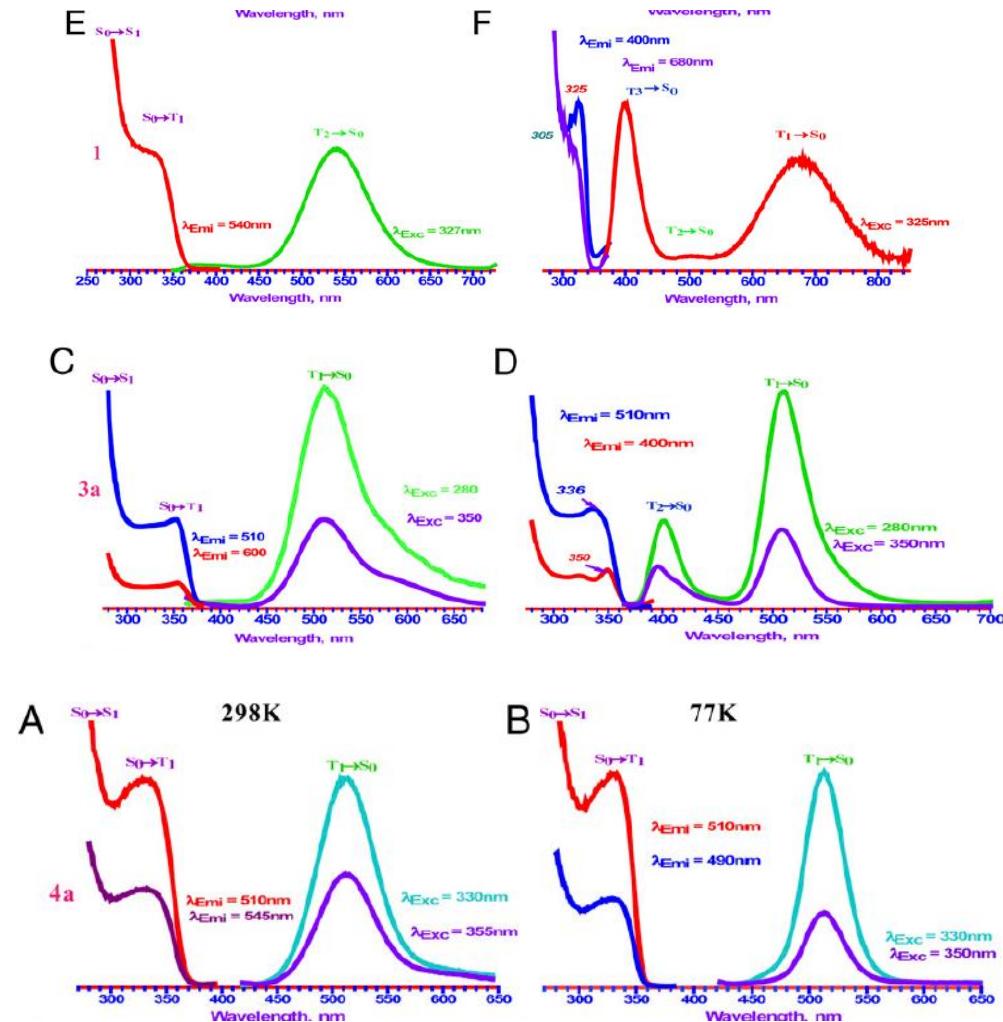
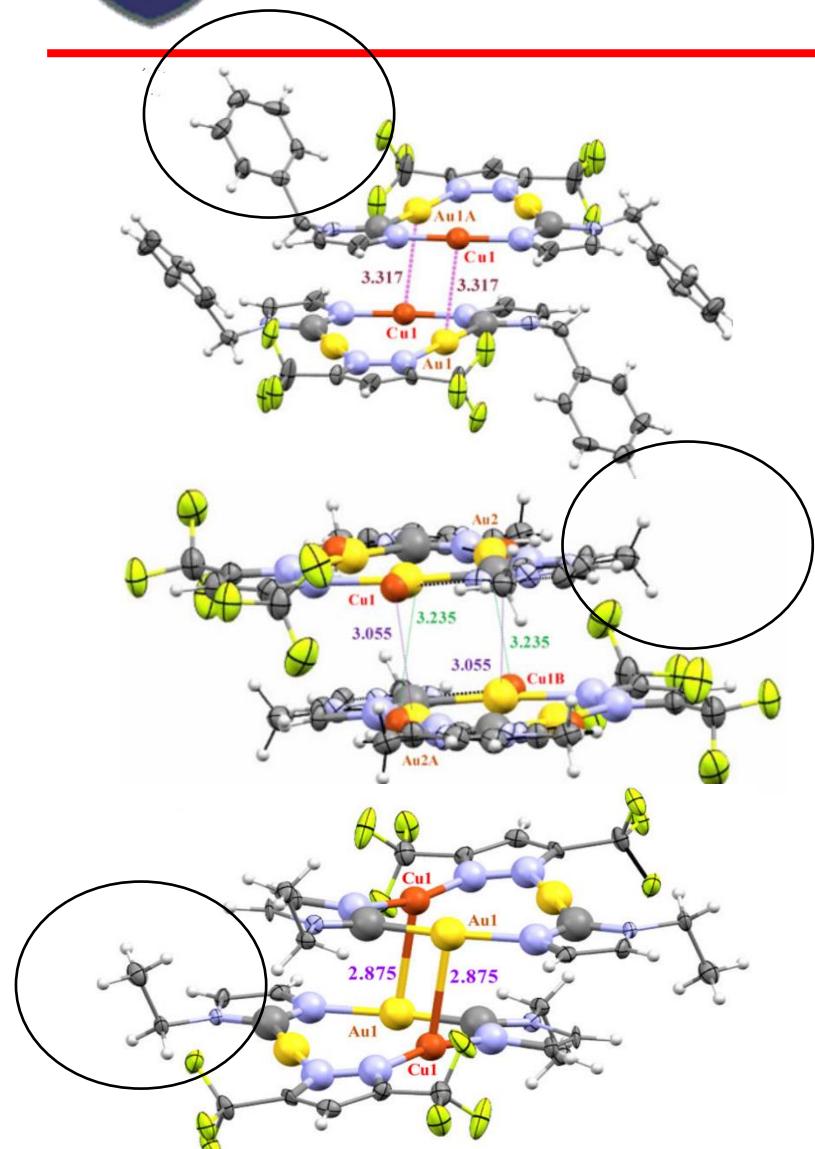
Conventional syntheses



Molecular → supramolecular



→ Proprietà emissive

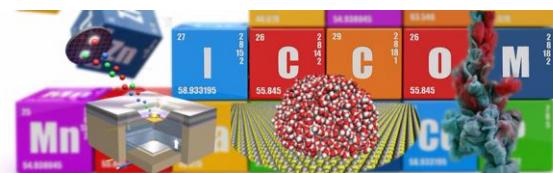




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Prof.ssa Rossana Galassi



Grazie!

