

Jeff Morton: MS 2010

Thesis “Further Investigations of Silver(IV) Cyanoximates”

Jeff Morton joined my research group in the Fall of 2008, and continued work in the field of visible light insensitive Silver(I) cyanoximates with several ligands shown below. Out of 42 known cyanoximes only those shown below in Figure 1 showed light stability of the Ag-complexes formed. He considerably further developed the project that has been successfully initiated and significantly moved forward by two other undergraduate students in the past: David Lewis in the summer of 2007, and Garrett Glover in 2007-2008. Their ground-braking work allowed identification of a series of visible light insensitive Ag(I) complexes that possess interesting properties such as: 1) antimicrobial agents, 2) nonelectric sensors for several gases of industrial importance – CO, H₂, C₂H₂, C₂H₄, NO, 3) thermally stable up to 150°C coordination polymers, 4) practically insoluble in water at room temperature.

During his work in my group Jeff demonstrated outstanding motivation and work ethic, generated numerous complexes and performed their comprehensive studies including X-ray crystallographic characterization.

Thus, at first Jeff made large quantities (3-5 grams) of these 11 ligands depicted in Figure 1 with applied synthetic routes shown in Figure 2. Then he performed synthesis of AgL complexes (Figure 3) followed by their detailed spectroscopic, structural and photophysical characterization. The rest of presented here figures were extracted from Jeff's MS thesis and keep their number scheme. His thesis is available from the MSU library upon request.

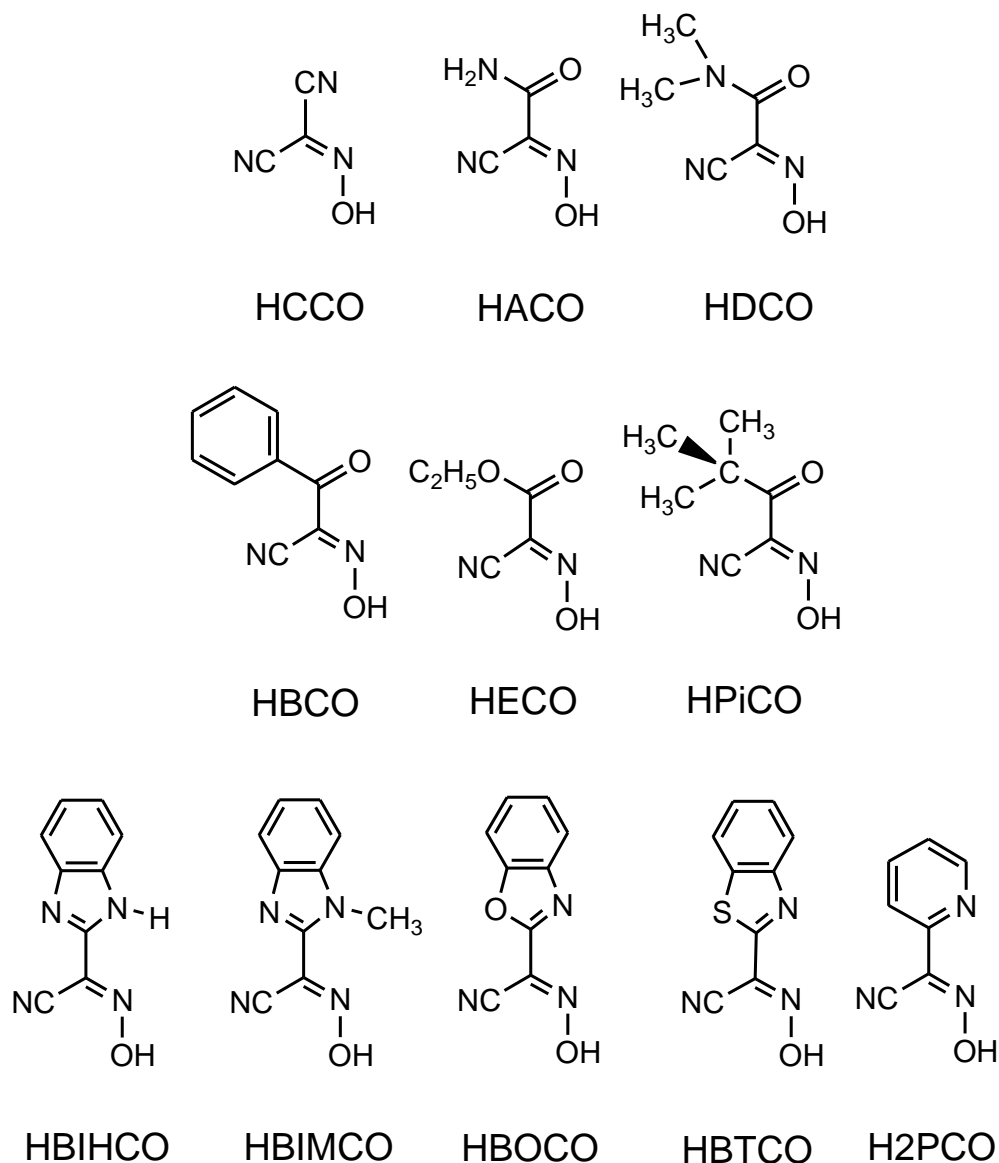


Figure 1. Structure and short-hand naming representation of 11 cyanoximes that form visible-light stable silver(I) cyanoximates of AgL composition. First row cyano-, and amido-cyanoximates; second row keto, and ester-cyanoximates; third row 2-heteroaryl-cyanoximates

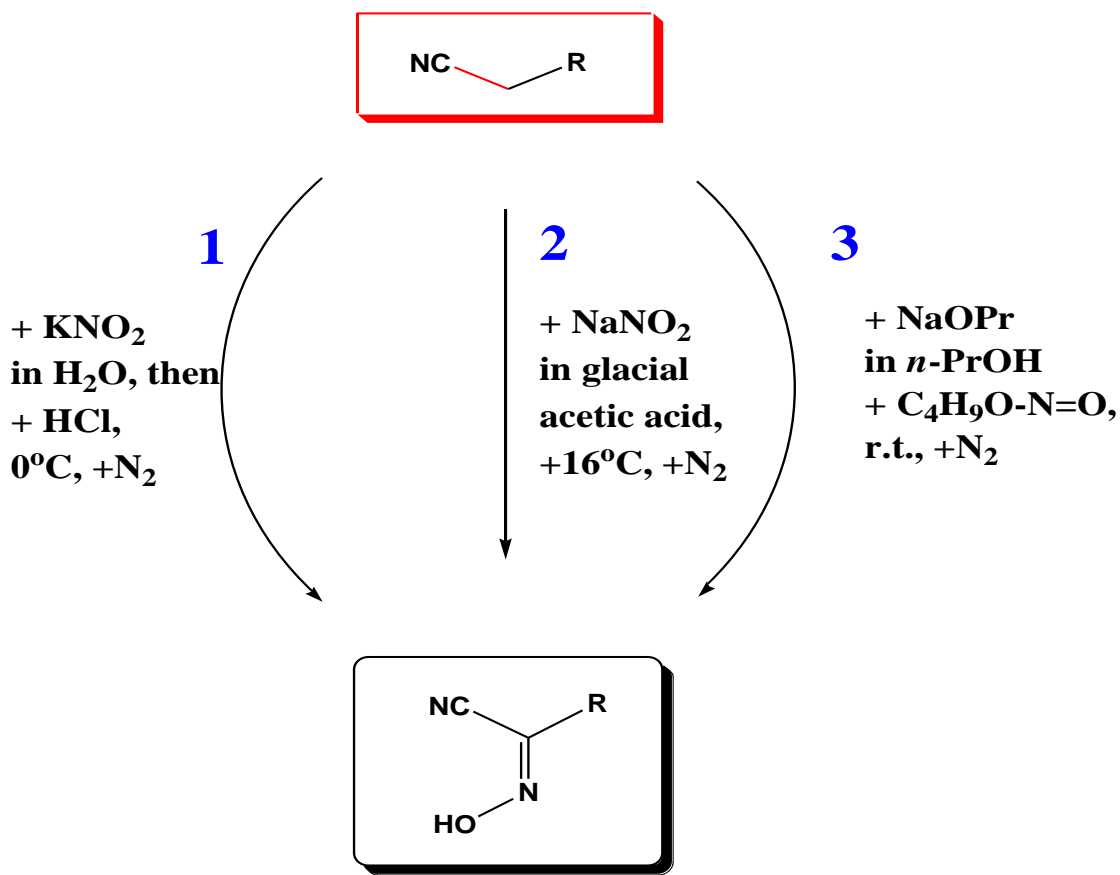


Figure 2. Three modifications of the Meyer reaction to synthesize cyanoximes from precursor acetonitriles.

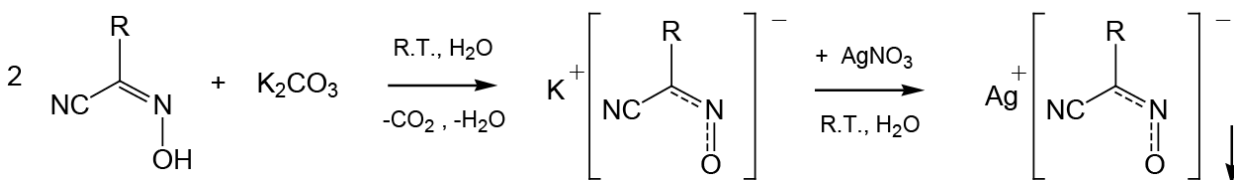


Figure 3. Simple two-step route to poorly water soluble silver(I) cyanoximates.

Crystal structures of compounds that were prepared by Jeff Morton are presented below in several figures.

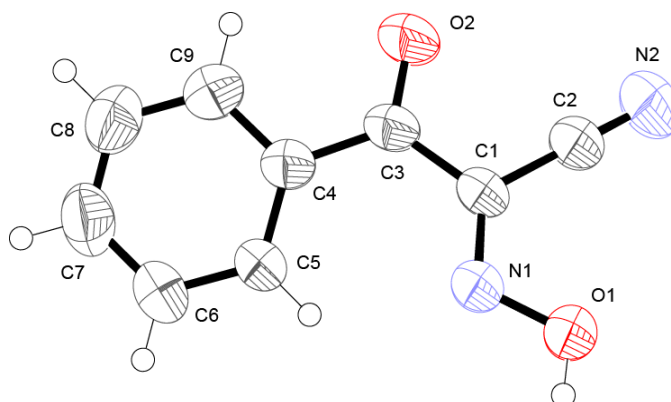


Figure 4. Molecular structure and numbering scheme for H(BCO). An ORTEP drawing at 50% thermal ellipsoids probability level.

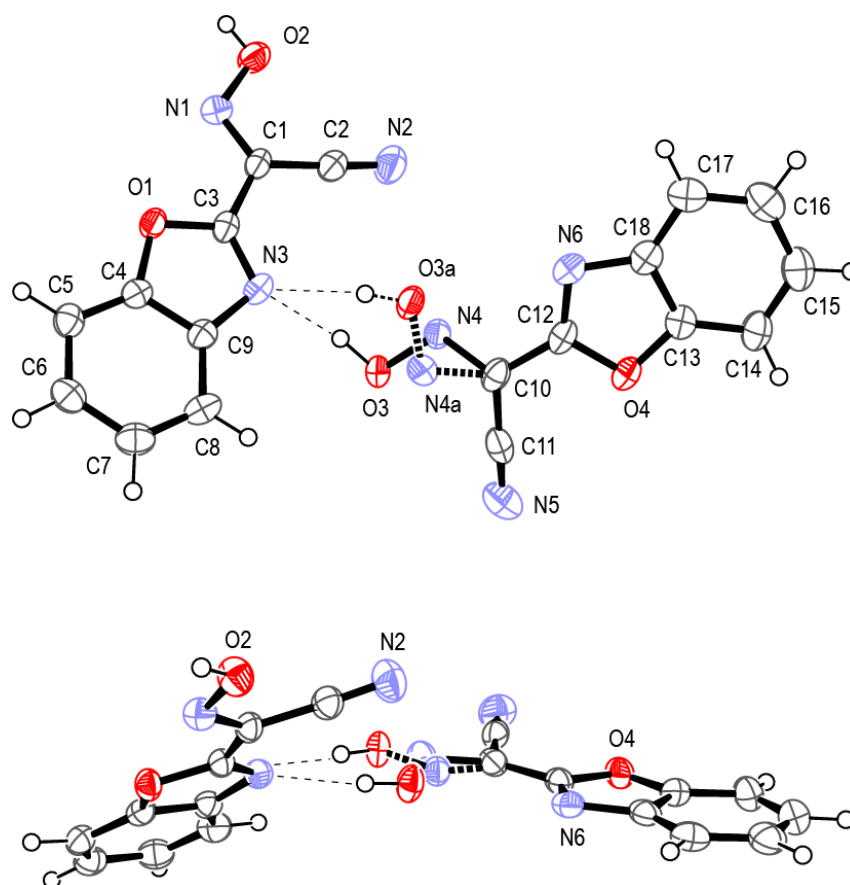


Figure 5. Molecular structure and numbering scheme for H(BOCO). Shown two orthogonal projections; the H-bonding is indicated as dotted lines, while *syn*- isomer is depicted as thick dashed line.

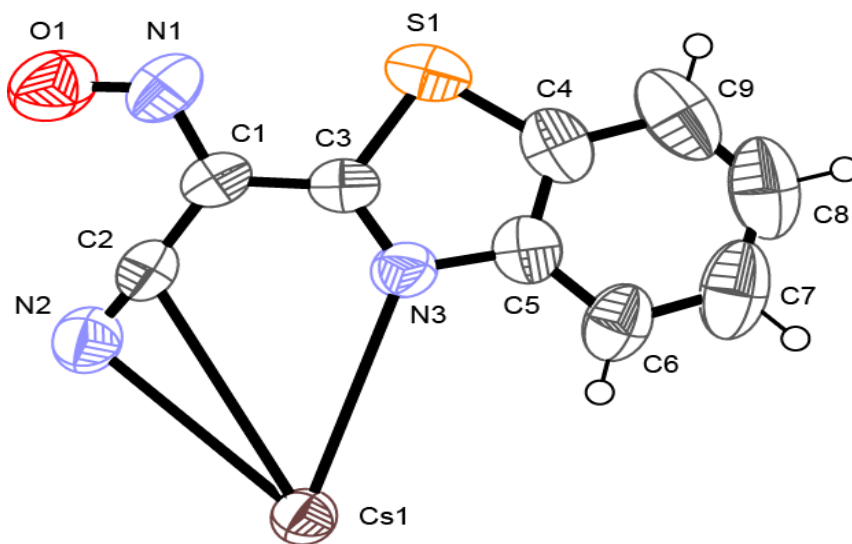


Figure 6. The ASU and numbering scheme in the structure of Cs(BTCO). An ORTEP drawing at 50% thermal ellipsoids probability.

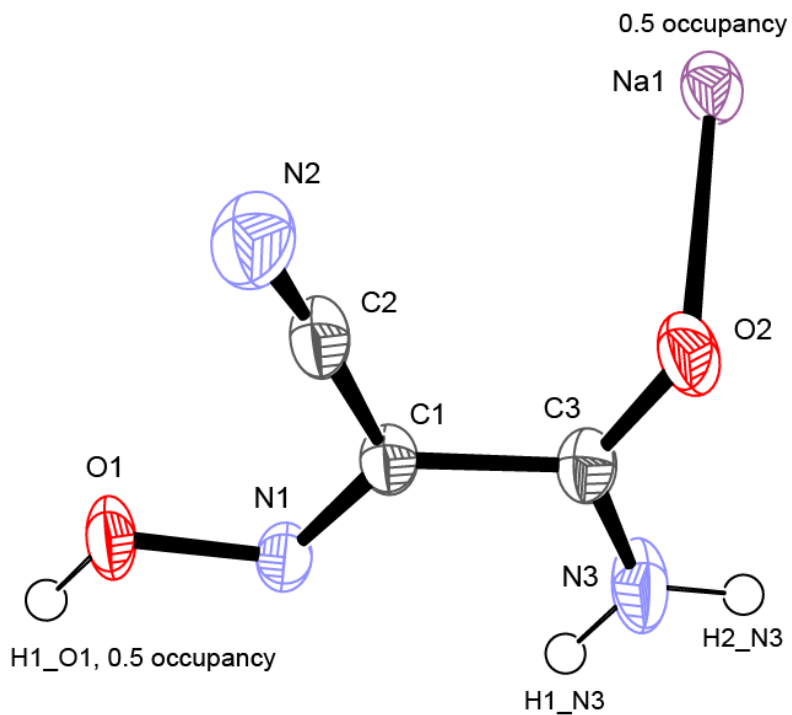


Figure 7. The ASU (asymmetric unit) in the structure of NaH(ACO)₂.

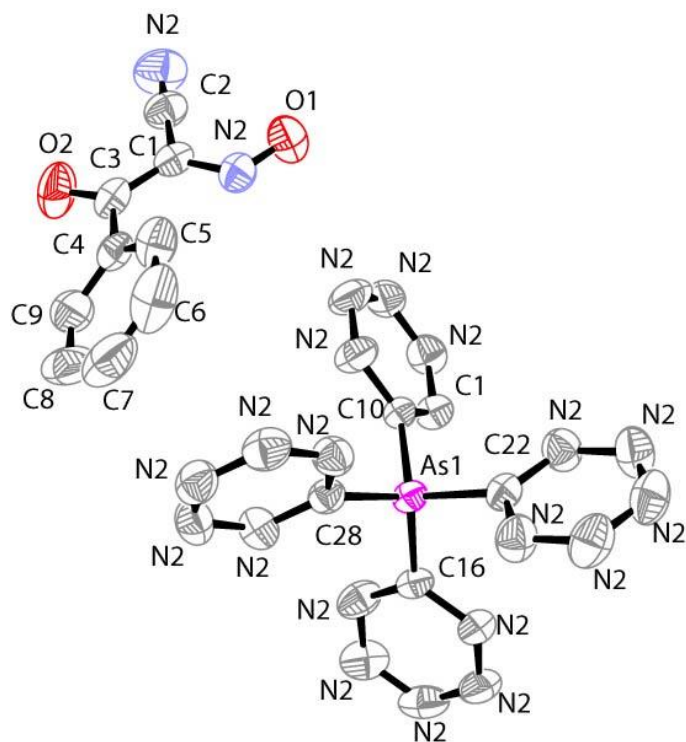


Figure 8. Molecular structure and numbering scheme for AsPh₄(BCO).

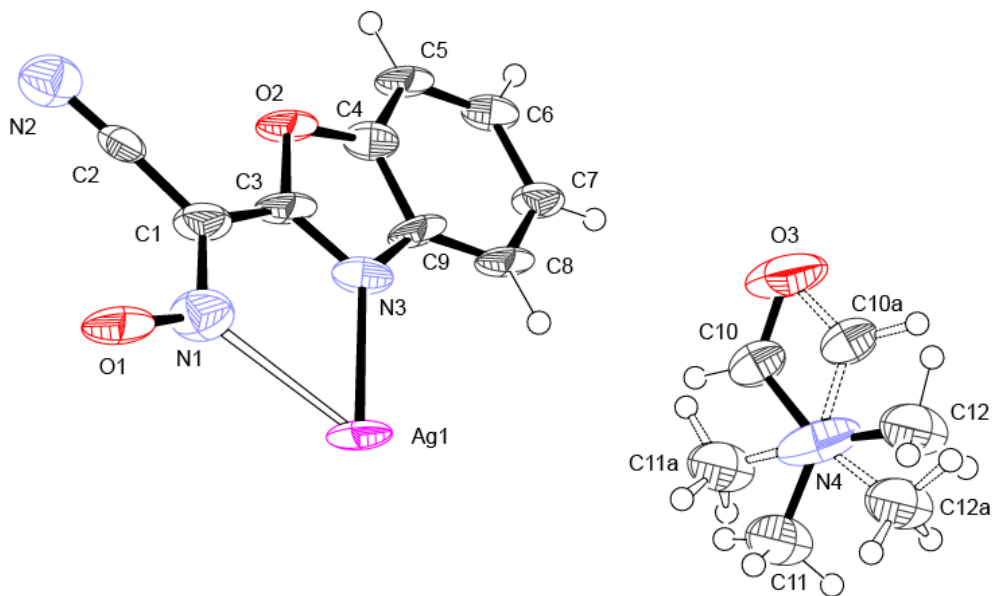


Figure 9. The ASU and its numbering scheme in the structure of Ag(BOCO)_x(DMF). The disordered solvent molecule is shown with dashed bonds. Unexpectedly long N1-Ag1 contact in a chelate ring is shown as an open bond.

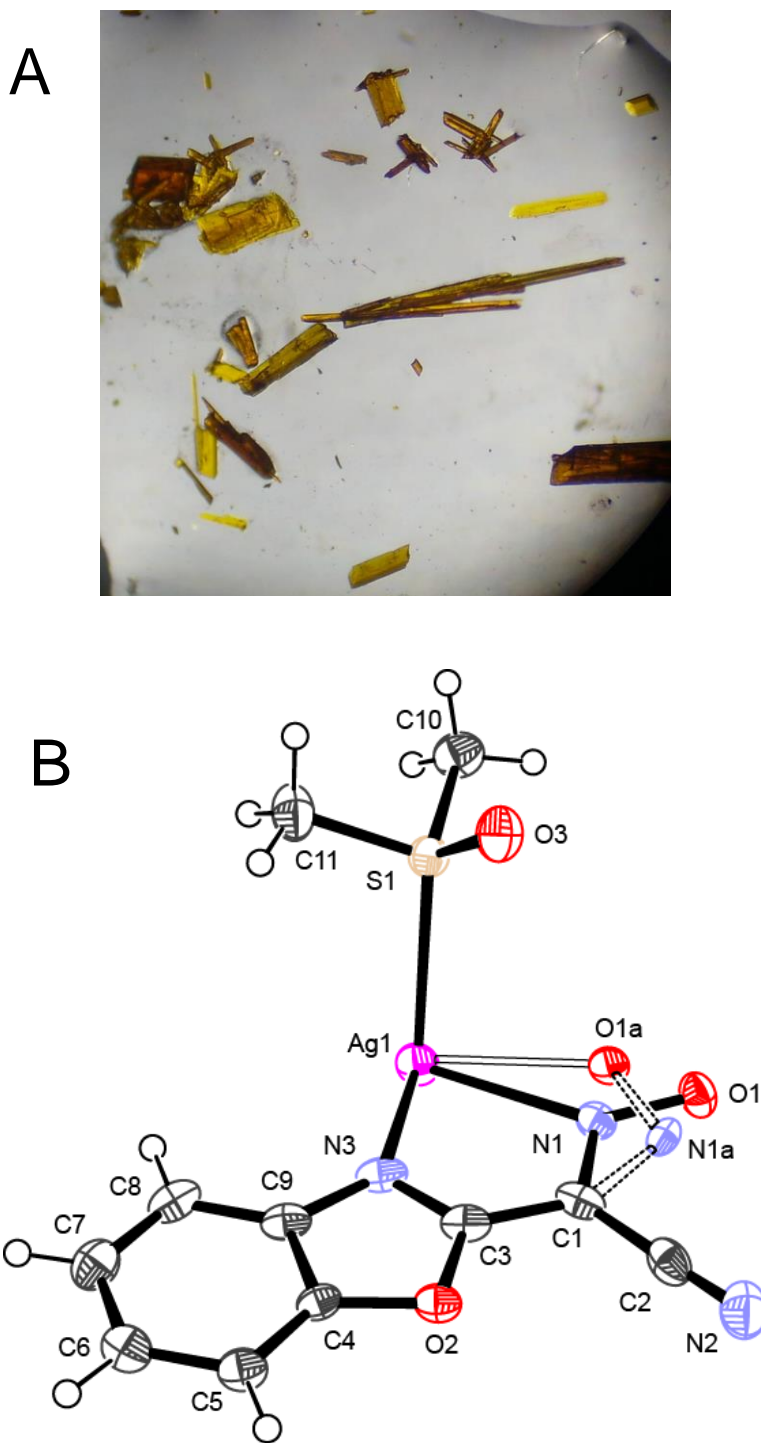


Figure 10. Actual crystal specimen used for X-ray studies (A), and the ASU in the structure of $\text{Ag}(\text{BOCO})_x(\text{DMSO})$ (B). Shown nitroso-group that adopts *anti*- and *syn*- configuration (83% and 17% respectively).

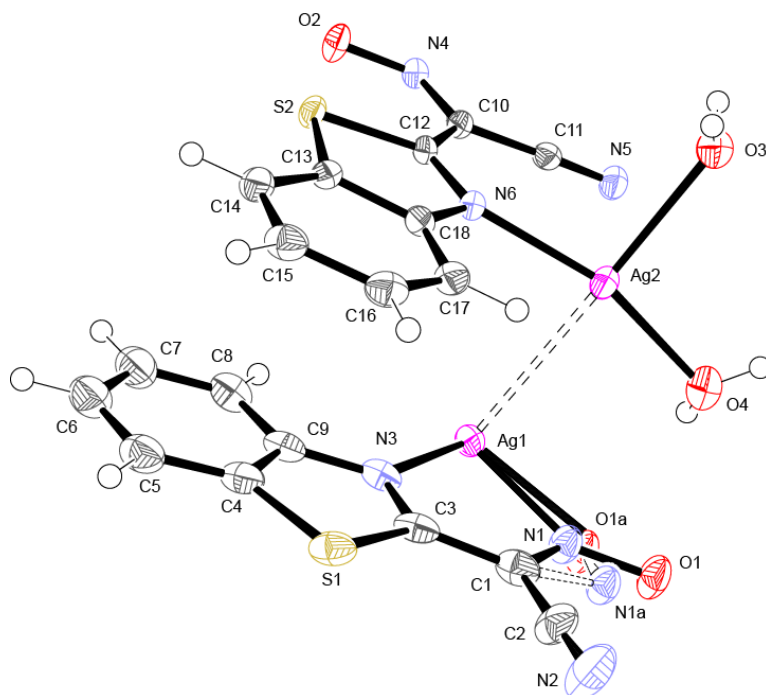


Figure 11. The ASU in the structure of $\text{Ag}(\text{BTCO})_x(\text{H}_2\text{O})$ showing atomic numbering scheme. Disordered nitroso-group of one of the anions is displayed in dashed lines. The disorder is related to coexistence of *anti*- and *syn*-isomers of one of the anions. The second anion is ordered and adopts exclusively *syn*- geometry. There is also a short intermetallic Ag...Ag distance of 3.055 Å.

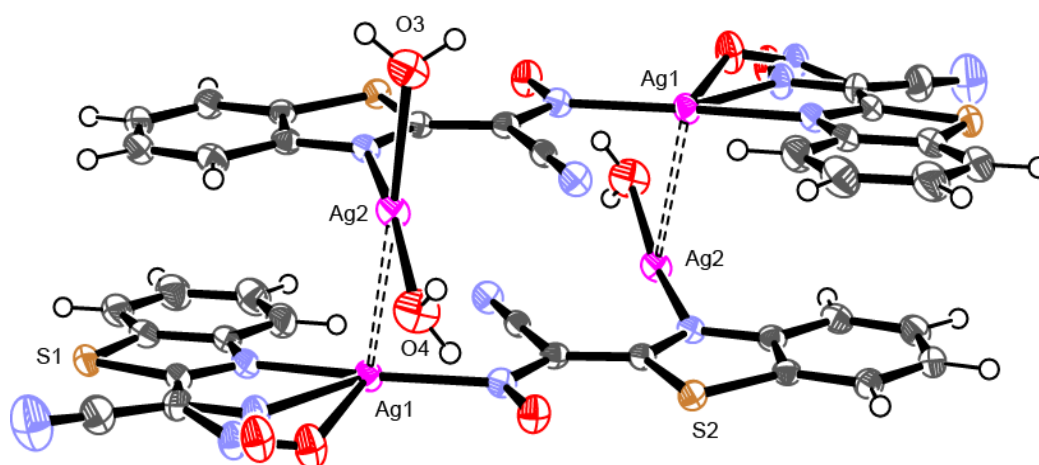


Figure 12. The “building block” of the crystal structure of $[\text{Ag}(\text{BTCO}) \cdot \text{Ag}(\text{BTCO}) 2\text{H}_2\text{O}]$: tetrameric unit.

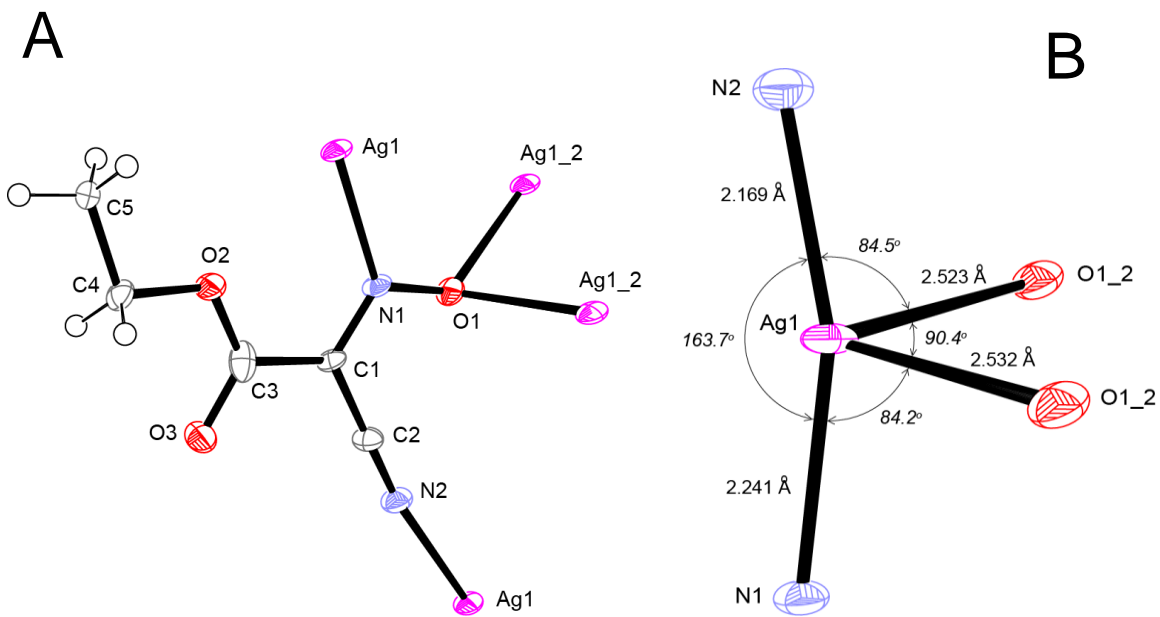


Figure 13. A- Molecular structure and numbering scheme for Ag(ICO) showing one cyanoxime anion and its Ag(I) environment [the mirror image of the disordered ethoxy-group is not shown for clarity]; B - Geometry of coordination polyhedron of Ag(I) in the structure of Ag(ICO). An ORTEP representation at 50% thermal ellipsoids probability.

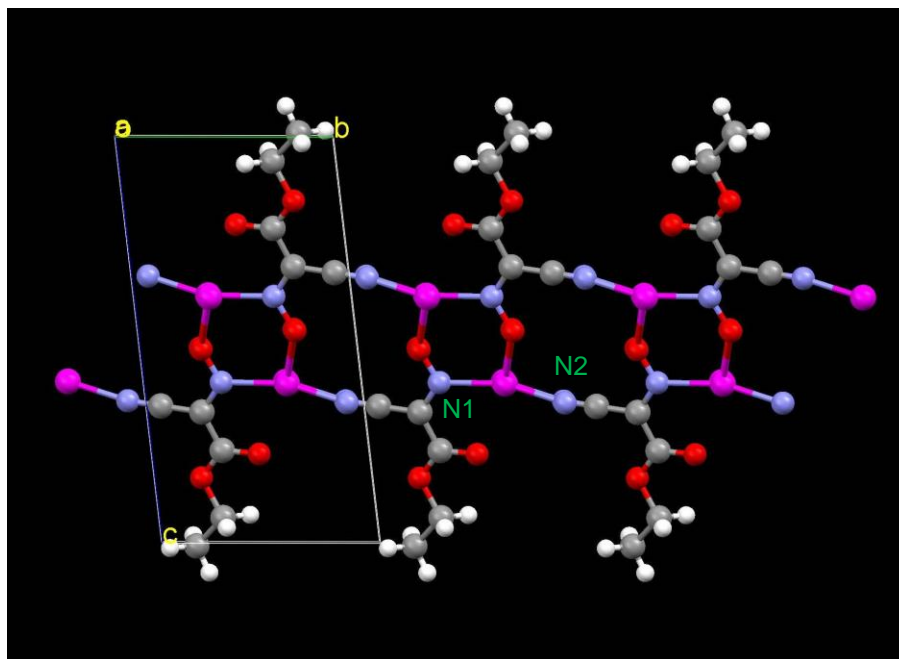


Figure 14. View of one sheet as seen down the *a*-axis. It can be seen that the nitrogen atoms N1, and N2 serve to bridge units along the *b*-axis.

Obtained by Jeff Morton compounds are completely stable on a day light – visible light stable. However, it was interesting to see whether they are responding to higher energy photons such as UV-light. Therefore, Jeff meticulously studied dry AgL on stability towards short-wavelength UV-light. Samples were prepared as smeared pure, solid AgL complexes that were subjected to intense UV-radiation as explained in Figure 15. The exposure time was strictly monitored using a timer.

At 30 minutes intervals samples status was carefully measured using the Diffuse Reflectance Spectroscopy (SDR) using the integrating sphere shown in Figure 16. Thus, at objectively selected wavelength in the SDR he monitored change in sample's reflectivity with time. That time was experimentally selected based on a sample's condition: quickly darkened samples were monitored for lesser time period, while slowly changing color samples were controlled longer time. For instance, it varied from 180 to 650 minutes.

Photodegradation studies

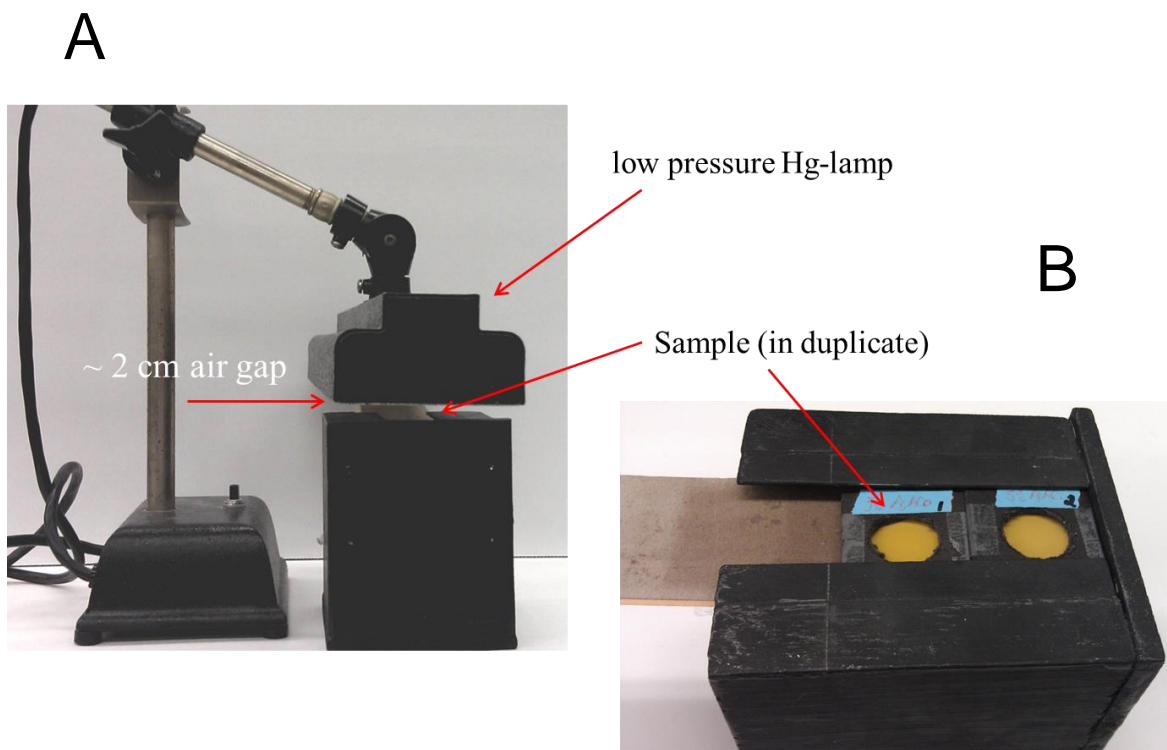


Figure 15. High-output short-wavelength mercury vapors UV-lamp (A) and blackened wooden rack with two independently prepared samples for studies of their photo-response (B).

Hardware: integrating sphere.

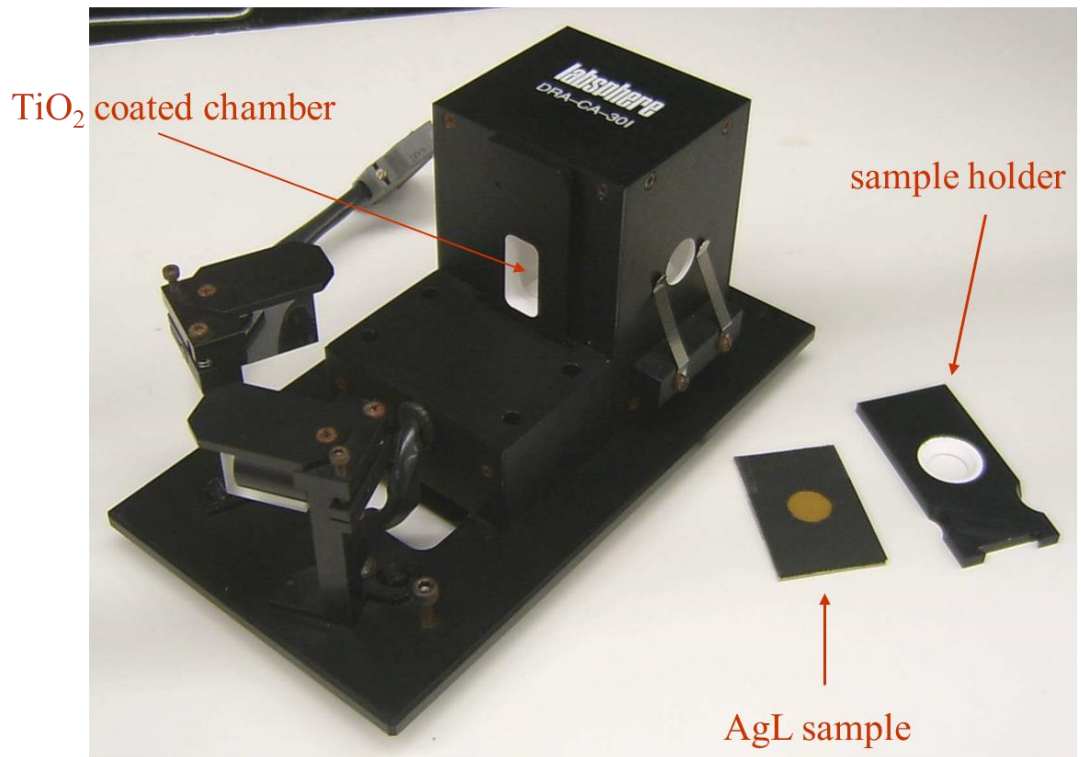
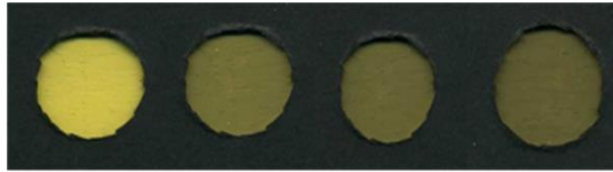


Figure 16. Integrating sphere for the SDR recording and quantitative monitoring of samples' photo-response.

Results of Jeff's investigations are presented in a series of figures below.

Ag(2PCO)



0 min 60 min 120 min 180 min

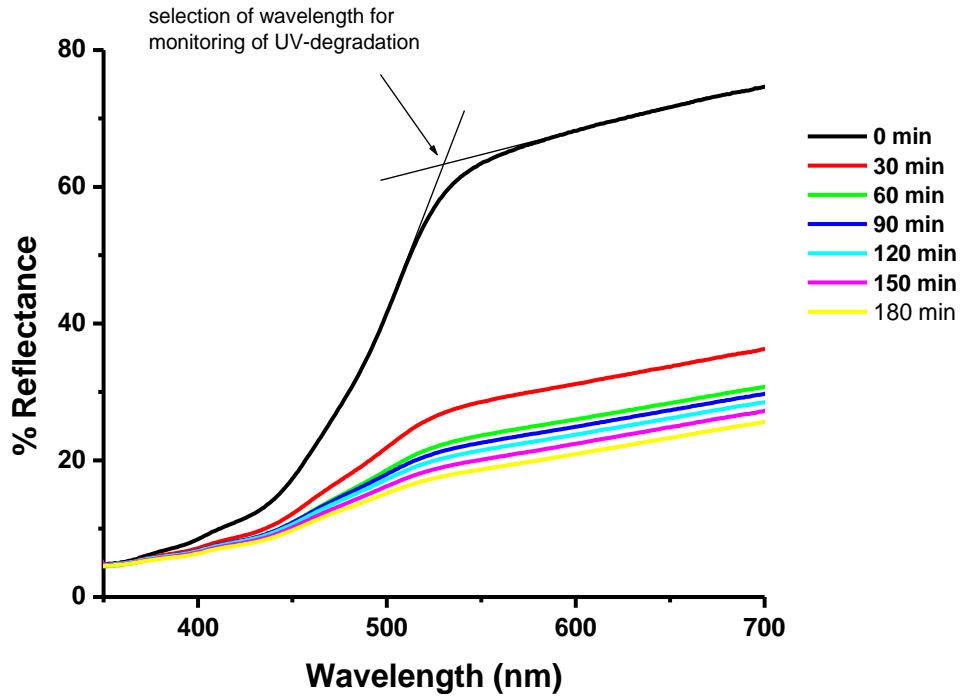


Figure 17. Actual Ag(2PCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(ACO)

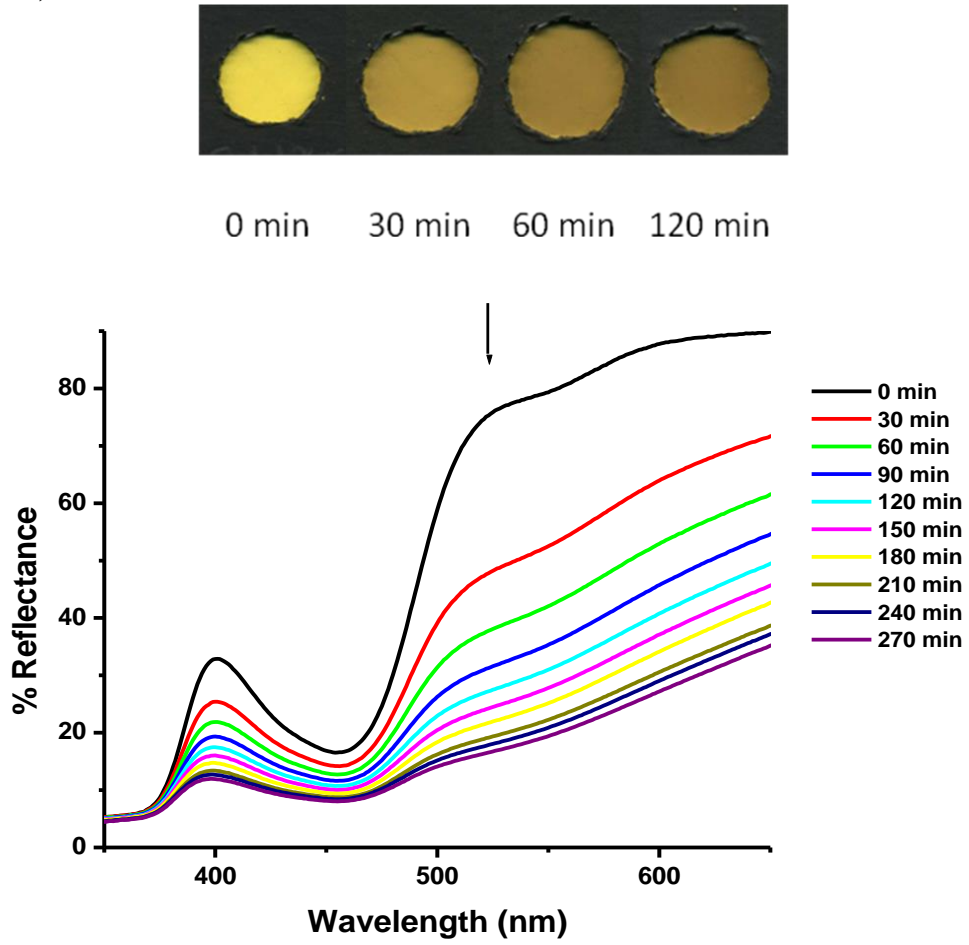


Figure 18. Actual Ag(ACO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(BCO)

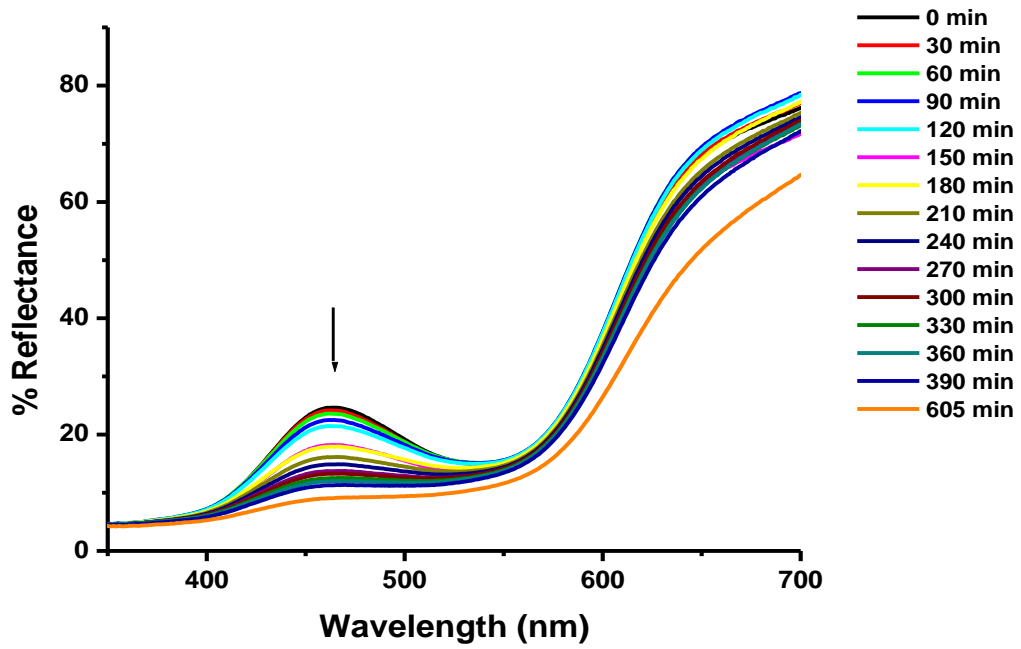
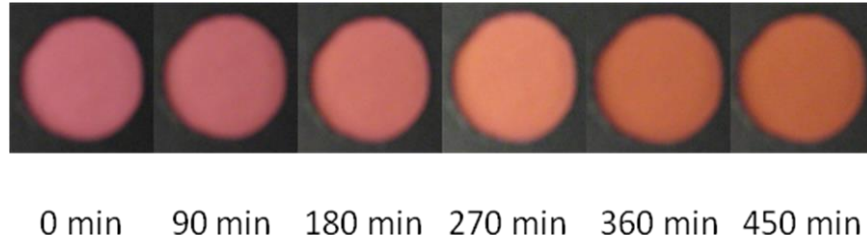


Figure 19. Actual Ag(BCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(BIHCO)

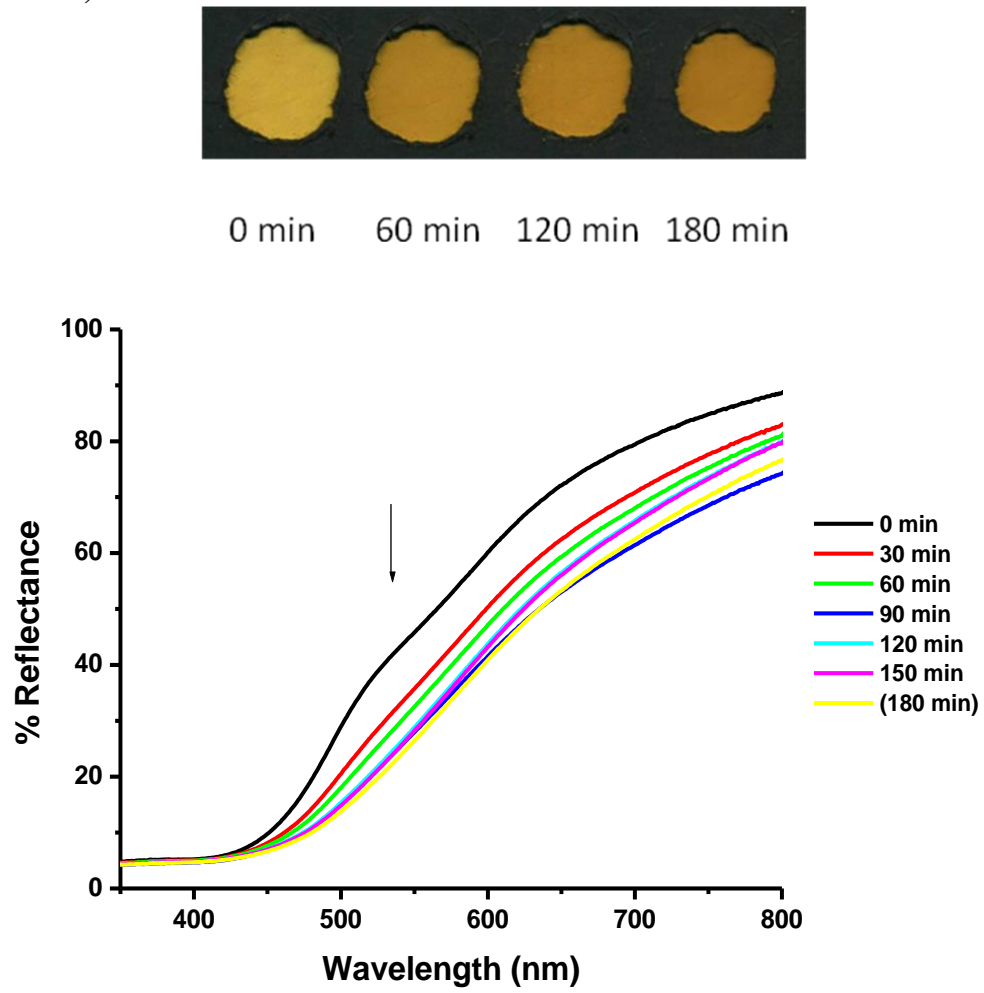
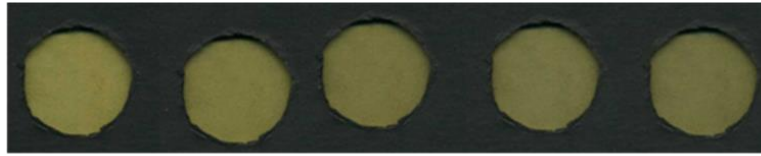


Figure 20. Actual Ag(BIHCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(BIMCO)



0 min 90 min 180 min 270 min 360 min

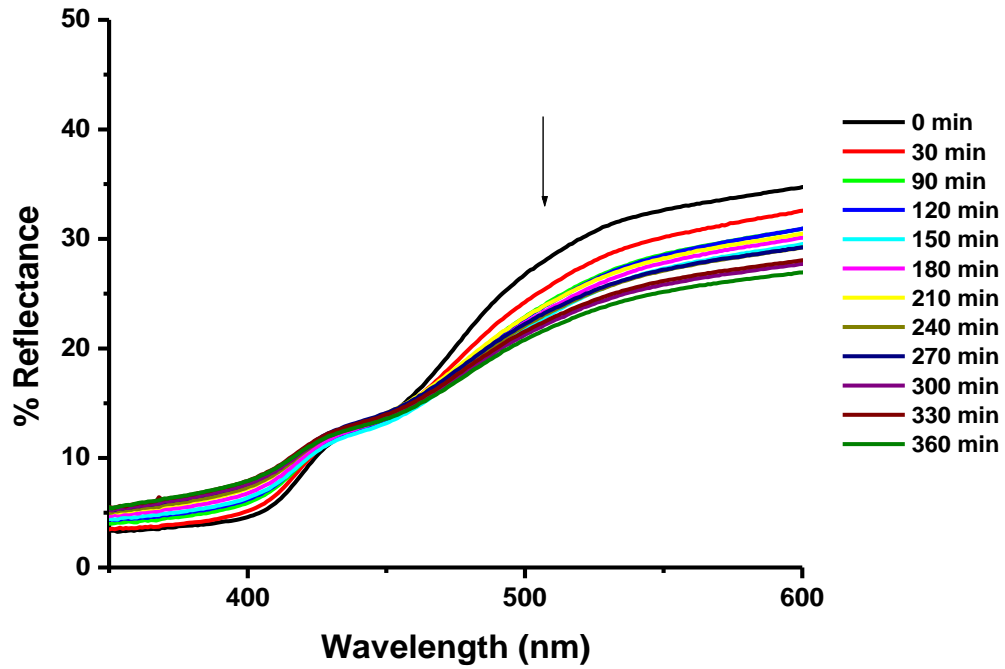
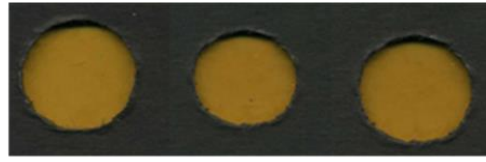


Figure 21. Actual Ag(BIMCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(BOCO)



0 min 60 min 120 min

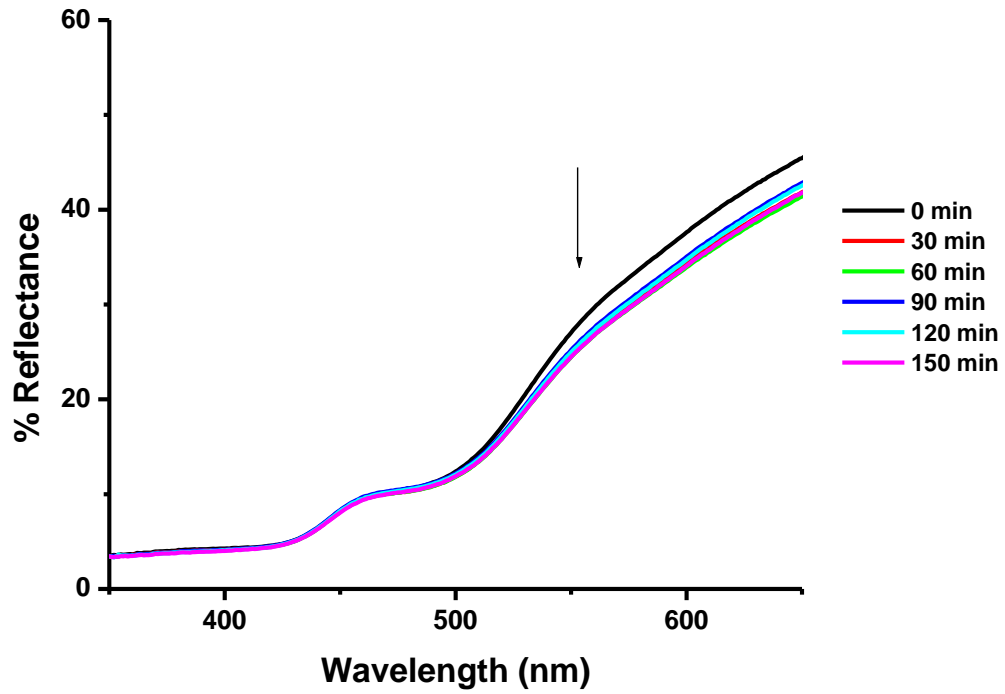
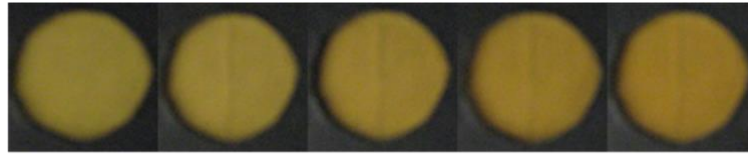


Figure 22. Actual Ag(BOCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(BTCO)



0 min 120 min 240 min 360 min 480 min

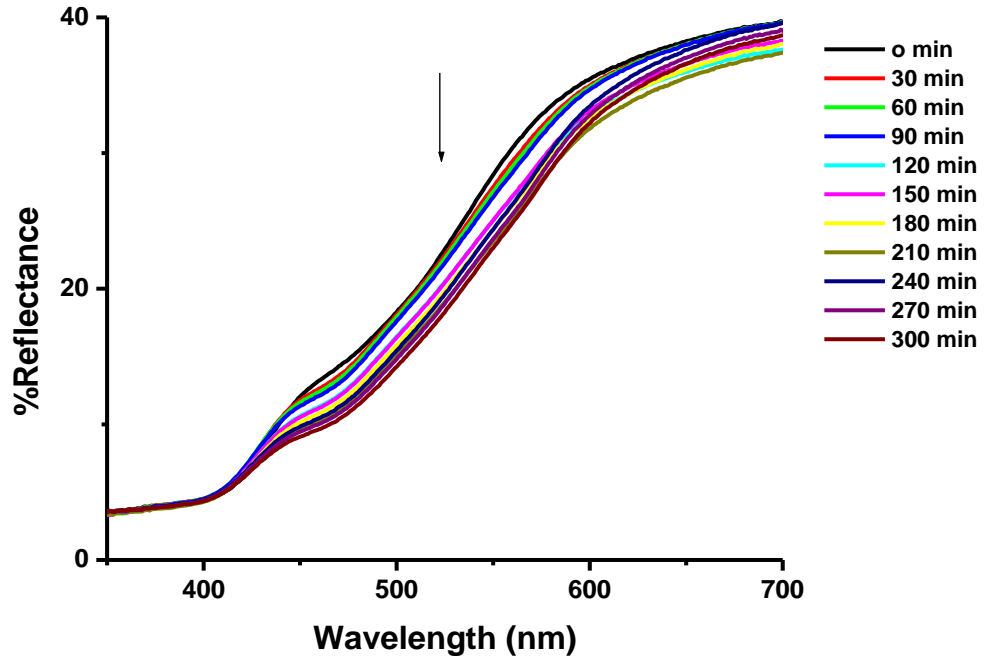


Figure 23. Actual Ag(BTCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(CCO)

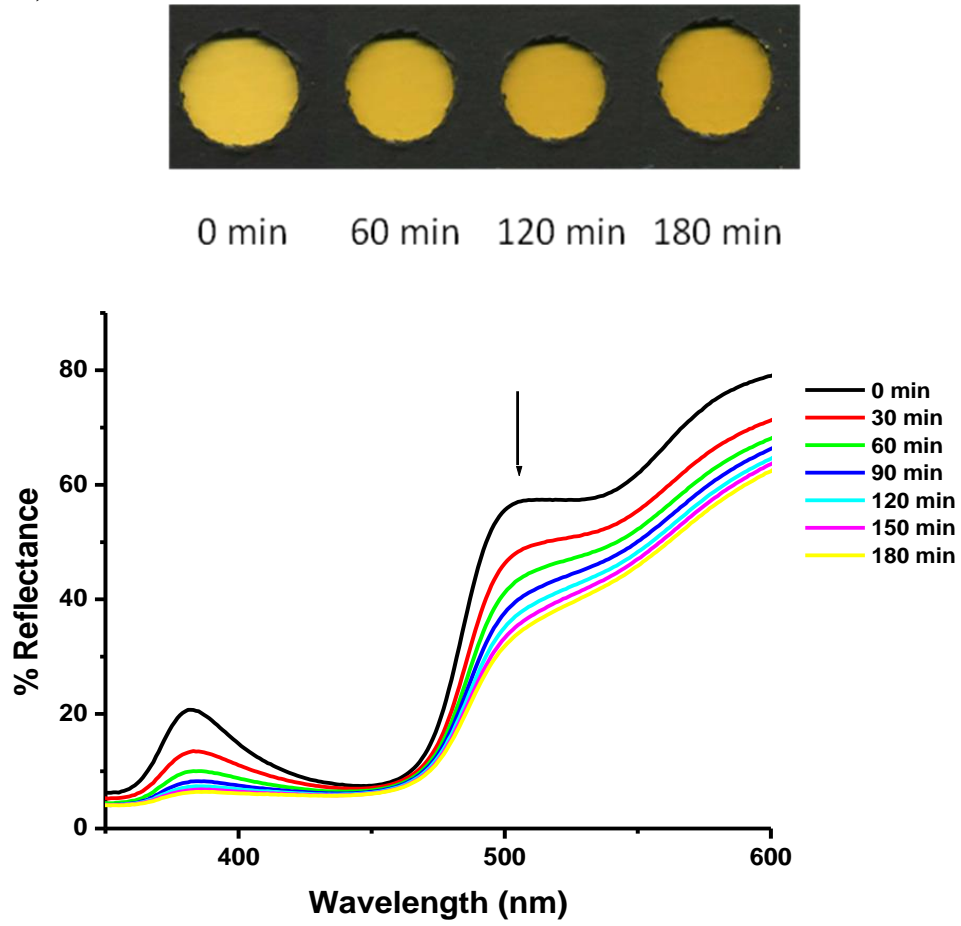


Figure 24. Actual Ag(CCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(DCO)

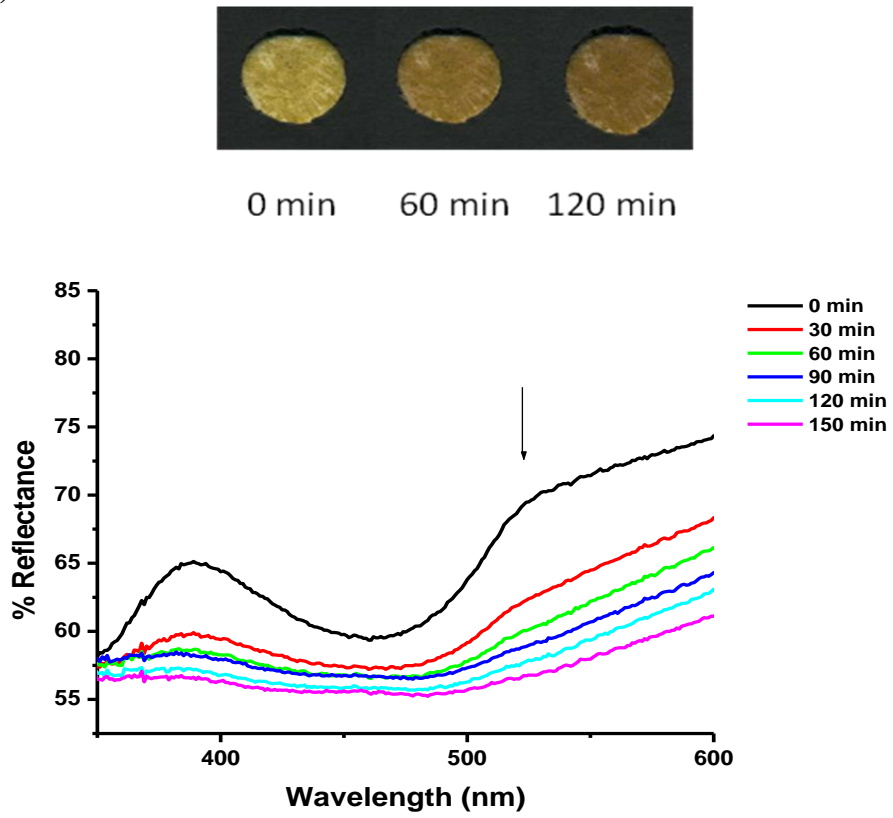


Figure 25. Actual Ag(DCO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

Ag(ECO)

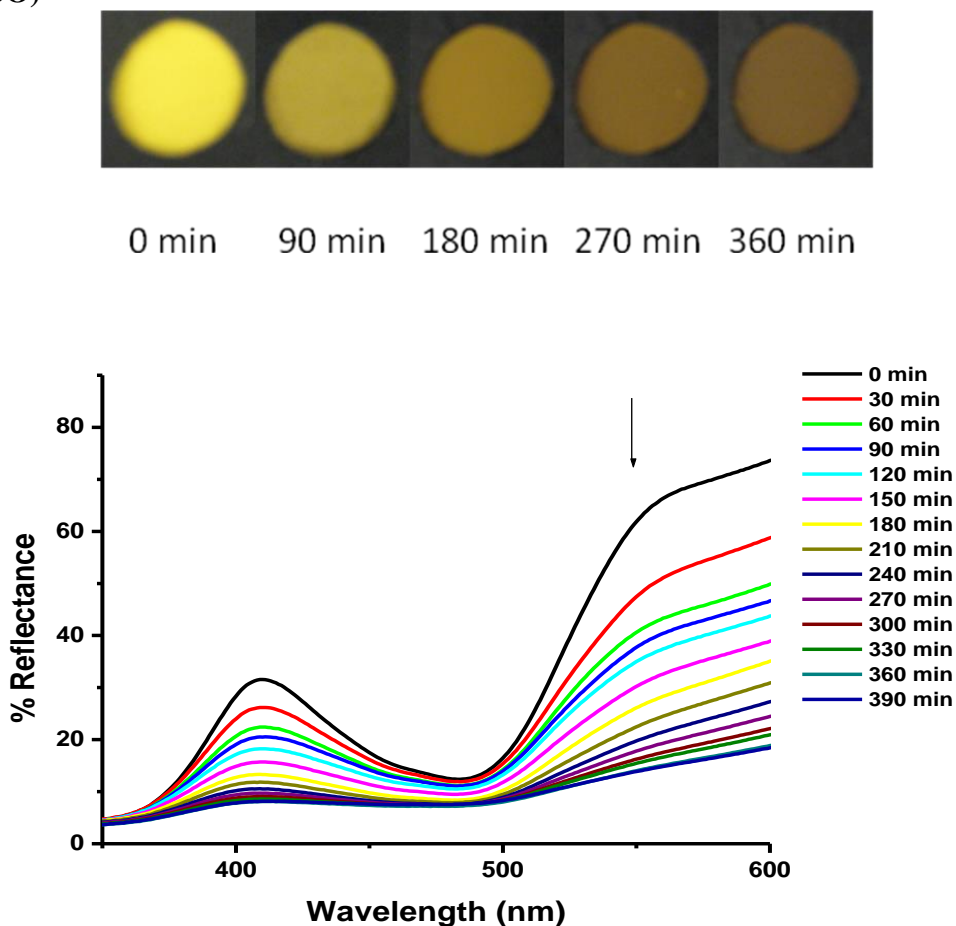


Figure 26. Actual Ag(ECO) sample's photographs during the duration of the photo-degradation experiment (A) and corresponding SDR traces (B).

The observed change in samples' reflectivity was plotted against time of the UV-radiation and showed an exponential decay profile (Figure 27). This fact allowed quantification of samples' sensitivity/stability towards UV-light by using the initial rate of the photo-degradation.

Values of measured initial rate were surprisingly in correlation with the sum of bond length Ag-N and Ag-O in structures of complexes that were determined by the X-ray analysis (Table 1). The graph of correlation between these parameters is presented on Figure 28. It clearly demonstrates non-linear behavior of the initial rate change from the sum of distances! This is due (quite possible to tunneling effect) electron transfer from one silver atom to another via the nitroso-group bridge in these coordination polymers as depicted in Figure 29.

Typical samples's reflectance change with time of irradiation

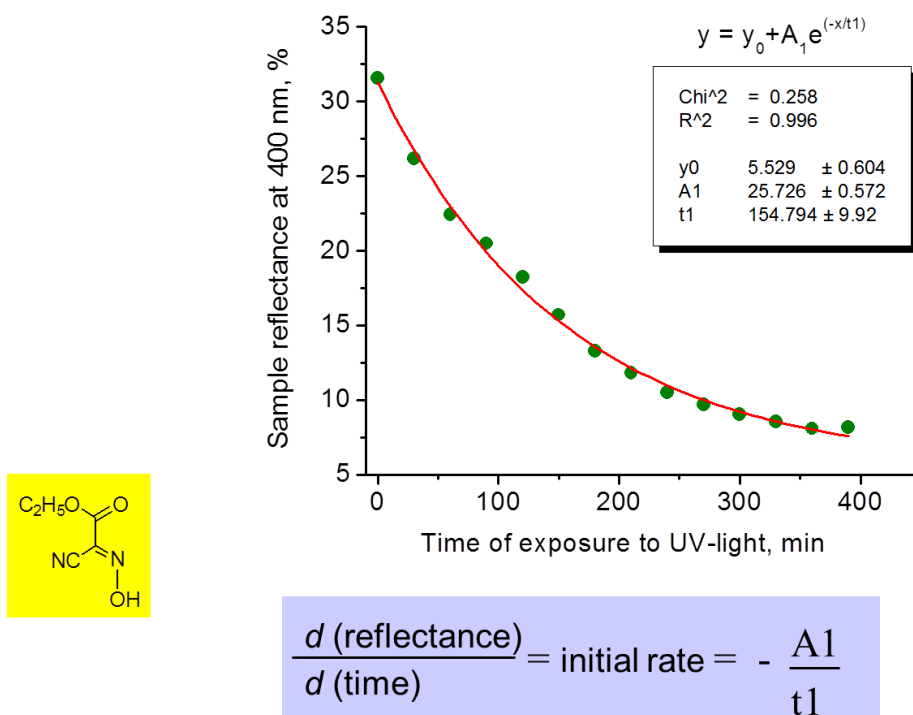


Figure 27. Change in sample's reflectance vs time for Ag(ECO) chosen as example.

Table 1.

Geometrical parameters of AgL and rate of photodegradation: search for correlation.

A Complex	B Ag-CN	C Ag-N	D Ag-O	E <i>Init. Rate</i>	sum C+D	sum B+C+D
Ag(BCO)	2,182	2,254	2,567	-0,061	4,821	7,003
Ag(ACO)		2,352	2,414	-0,233	4,766	
Ag(DCO)	2,128	2,217	2,5817	-0,231	4,799	6,9267
Ag(CCO)	2,232	2,318	2,363	-0,328	4,681	6,913
	2,327			-0,328		
Ag(ECO)	2,169	2,241	2,525	-0,166	4,766	6,935
Ag(BTCO)		2,559	2,332	-0,028	4,891	
		2,157		-0,028		
Ag(PiCO) red	2,204	2,213	2,374	-0,697	4,587	6,791
Ag(PiCO) yellow	2,684	2,323	2,358	-0,281	4,681	7,365
	2,634	2,323	2,465	-0,281		7,422

Slowest/fastest: ~ 25 times difference!

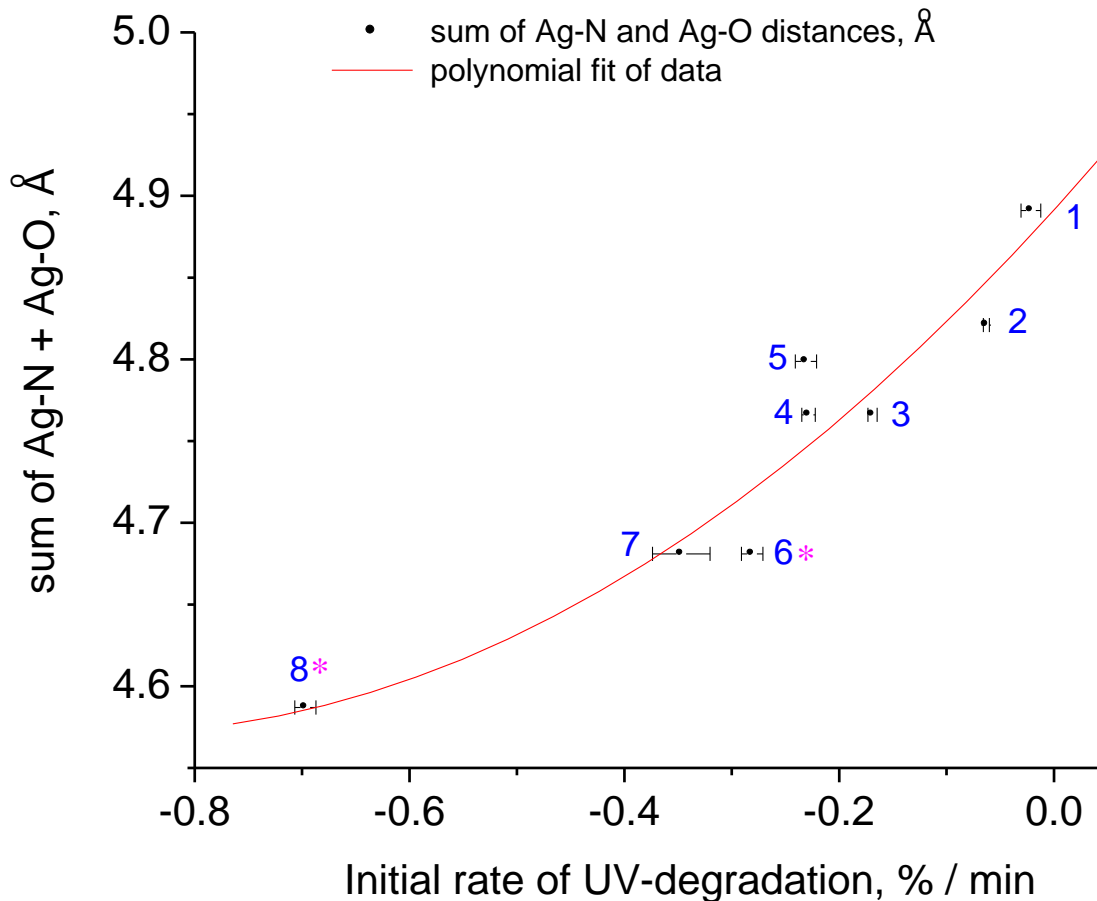
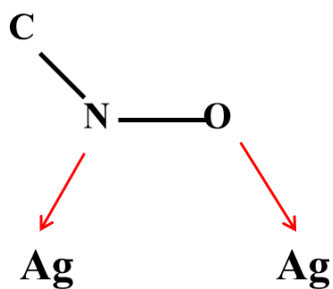


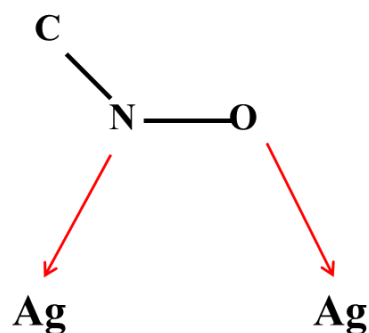
Figure 28. A correlation between average initial rate of AgL UV-degradation and the sum of Ag-N and Ag-O distances in the bridging nitroso- group. Second order polynomial fit $y = A + B_1x + B_2x^2$, where $A = 4.891$, $B_1 = 0.7251$, $B_2 = 0.4103$ and $R = 0.908$.

Data of the X-ray single crystal only; error bars from two independent measurements. Studied complexes were: 1 – Ag(BTCO); 2 – Ag(BCO); 3 – Ag(ECO); 4 – Ag(ACO); 5 – Ag(DCO); 6 – Ag (PiCO), yellow; 7 – Ag(CCO); 8 – Ag(PiCO), red. Both Ag(PiCO) polymorphic compounds – marked with magenta asterisks – were obtained from Garrett Glover, former group student.

The sum of Ag-N and Ag-O distances:



$$\Sigma = 4.681 \text{ \AA}, \text{ rate} = -0.328$$



$$\Sigma = 4.821 \text{ \AA}, \text{ rate} = -0.029$$

The smaller the distance – the greater rate of photodegradation!

The ligand's role as a bridge for the electron transfer is clear.

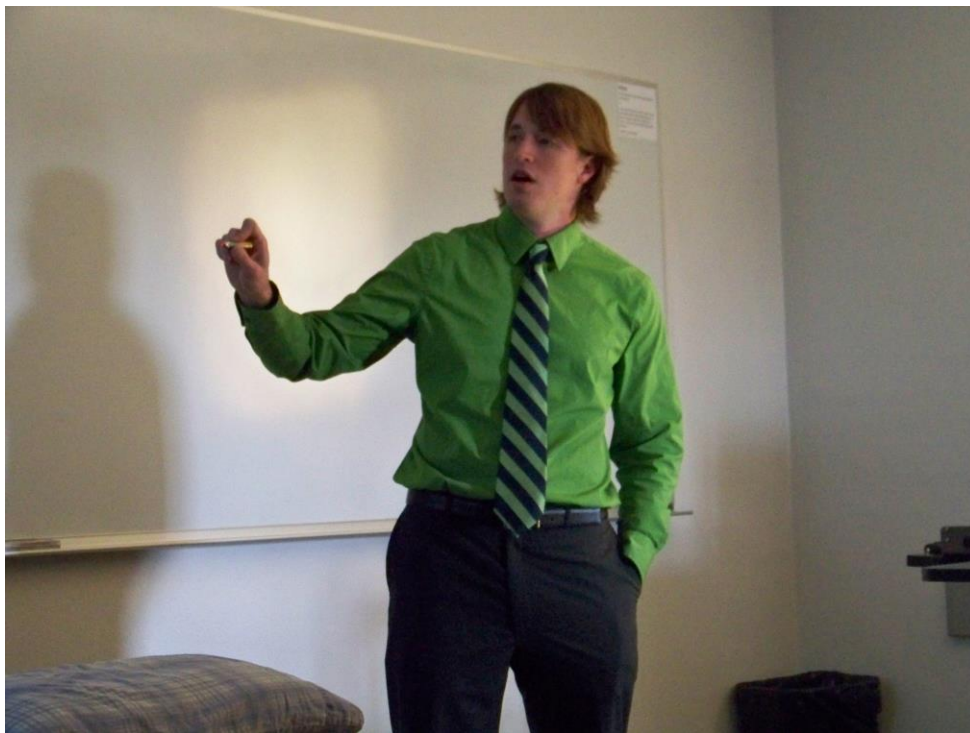
Figure 29. The role of bridging of the nitroso-anion between two silver centers in polymeric complexes: the shorter the distance – the faster electron transfer and complex's photo-degradation.

CONCLUSIONS from Jeff Morton's work:

1. Eleven Ag(I) cyanoximates were obtained and characterized by C,H,N elemental analysis and thermal decomposition studies.
2. Synthesized silver(I) compounds were analyzed by means of IR- and UV-visible absorbance spectroscopy (as suspensions in mineral oil).
3. Crystal structures were determined for two protonated cyanoximes. The HBCO adopts trans-anti configuration in solid state. The HBOCO exist in crystal as two independent molecules: one – in *trans-anti* configuration, while the second one – as *cis-syn* and *cis-anti* isomer.
4. Crystal structures of two alkaline (Na, Cs) and one onium (AsPh_4^+) salts. All salts are ionic compounds and contain cyanoxime anion in the nitroso- form.
5. Similarly, crystal structures were determined for five Ag(I)L and revealed formation of 2D coordination polymers of different complexity. In all studied silver(I) cyanoximates the anion act as a bridging ligand via the nitroso-group.
6. Photodecomposition studies between 0-8 hrs were performed for all Ag(I) cyanoximates and values of initial rates of photo-degradation were measured. A correlation between Ag-N and Ag-O bond lengths in crystal structures and values of rates of photo-decomposition for studied Ag(I) cyanoximates was established.
7. Products of photo-degradation were indentified to be fine particles of elemental silver in colloidal state. This conclusion was reached by investigation of the XRD powder patterns of decomposed AgL compounds coupled with UV-vis spectroscopic data and light-scattering in solutions of complexes in DMSO and Py.



Jeff is presenting his MS work at public defense.





After defense with his father, who was in attendance.



Graduation!