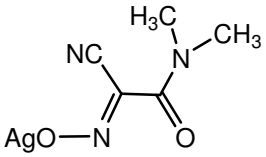
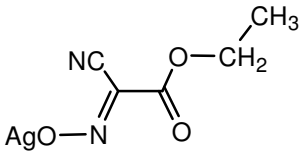
S1 Supplementary Information

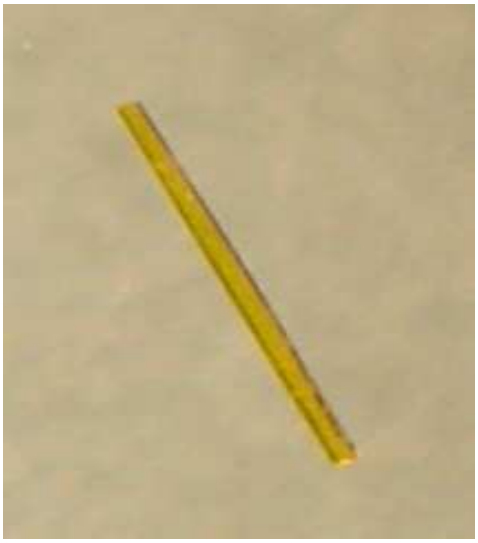
Photographs of crystals of studied silver(I) cyanoximates.

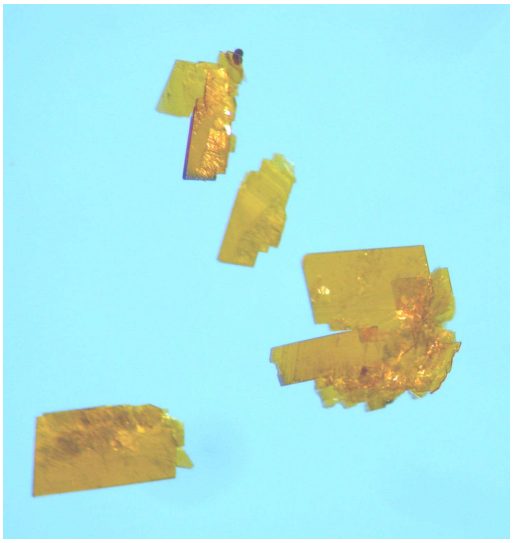
Ag(DCO),



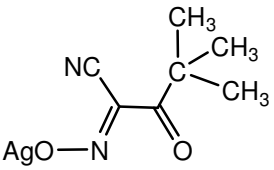
Ag(ECO),







Ag(PiCO),



S2 Details of structures solutions for two complexes: Ag(ACO) and Ag(DCO)

Crystals of Ag(ACO) turned out to be multidomain species but one suitable for analysis twin specimen (a non-merohedral twin) was found and collected data set allowed the structure solution. The crystal was indexed by harvesting reflections over the entire data collection, and with the use of the CELL_NOW program it was possible to determine the twin law: -0.9998 0.00030 0.00010 -0.00033 -1.0000 0.00007 0.36296 0.00014 0.99998. The data was integrated using both unit cells, and the TWINABS program was applied for absorption correction and refinement of reflections data. A total of 996 reflections (BASF = 0.374) were used for the successful structure solution of Ag(ACO).

Crystal sample of Ag(DCO) contained disordered solvent molecule trapped inside channels in the structure. The best fit for the ASU was obtained modeling the solvent with 1 oxygen atom and 1 carbon atom leading to a conclusion about methanol inclusion into the lattice. Unfortunately, hydrogen atoms were not reliably identified, and thus the disorder was only partially resolved. Moreover, the solvent had partial occupancy approaching, but below 0.5, which made the resolution of disorder even more difficult. Therefore, a PLATON SQUEEZ was used to remove electron density for the disordered solvent. Total solvent access void in the structure was determined to be 390 A^3, which could be accounted for 139 electrons per unit cell. Solvent accessible volume corresponds to ~11 methanol molecules, which in comparison with Z=16 gives less than one molecule of disordered solvent per Ag(DCO) formula. All respective comments about this procedure are incorporated into the CIF file.

S3

Complete set of bonds and angles around silver(I) center in the structure of Ag(ACO).

Bonds:	
Ag(1)-N(1)	2.352(5)
Ag(1)-O(1)#1	2.414(4)
Ag(1)-O(2)	2.455(4)
Ag(1)-O(1)#2	2.532(4)
Ag(1)-O(2)#3	2.547(4)
Ag(1)-O(2)#4	2.579(4)
Ag(1)-Ag(1)#5	3.1934(8)
Ag(1)-Ag(1)#6	3.1934(7)
O(1)-Ag(1)#1	2.414(4)
O(1)-Ag(1)#3	2.532(4)
O(2)-Ag(1)#2	2.547(4)
O(2)-Ag(1)#4	2.579(4)

Angles:	
N(1)-Ag(1)-O(1)#1	118.45(14)
N(1)-Ag(1)-O(2)	68.11(14)
O(1)#1-Ag(1)-O(2)	142.29(12)
N(1)-Ag(1)-O(1)#2	133.03(15)
O(1)#1-Ag(1)-O(1)#2	102.98(15)
O(2)-Ag(1)-O(1)#2	92.86(12)
N(1)-Ag(1)-O(2)#3	90.26(14)
O(1)#1-Ag(1)-O(2)#3	85.54(12)
O(2)-Ag(1)-O(2)#3	132.15(5)
O(1)#2-Ag(1)-O(2)#3	70.93(12)
N(1)-Ag(1)-O(2)#4	131.82(14)
O(1)#1-Ag(1)-O(2)#4	72.27(12)
O(2)-Ag(1)-O(2)#4	77.43(13)
O(1)#2-Ag(1)-O(2)#4	79.50(13)
O(2)#3-Ag(1)-O(2)#4	137.77(16)

S4

Complete set of bonds and angles around silver(I) center in the structure of Ag(ACO) (continued).

	Angles:
N(1)-Ag(1)-Ag(1)#5	96.62(11)
O(1)#1-Ag(1)-Ag(1)#5	51.43(9)
O(2)-Ag(1)-Ag(1)#5	91.89(9)
O(1)#2-Ag(1)-Ag(1)#5	127.67(9)
O(2)#3-Ag(1)-Ag(1)#5	134.04(8)
O(2)#4-Ag(1)-Ag(1)#5	51.02(8)
N(1)-Ag(1)-Ag(1)#6	86.08(11)
O(1)#1-Ag(1)-Ag(1)#6	132.27(9)
O(2)-Ag(1)-Ag(1)#6	83.33(9)
O(1)#2-Ag(1)-Ag(1)#6	48.18(9)
O(2)#3-Ag(1)-Ag(1)#6	51.92(8)
O(2)#4-Ag(1)-Ag(1)#6	122.89(8)
Ag(1)#5-Ag(1)-Ag(1)#6	173.22(2)
N(1)-O(1)-Ag(1)#1	107.4(3)
N(1)-O(1)-Ag(1)#3	112.1(3)
Ag(1)#1-O(1)-Ag(1)#3	80.39(11)
C(2)-O(2)-Ag(1)	116.4(3)
C(2)-O(2)-Ag(1)#2	121.8(3)
Ag(1)-O(2)-Ag(1)#2	105.16(13)
C(2)-O(2)-Ag(1)#4	126.4(3)
Ag(1)-O(2)-Ag(1)#4	102.57(13)
Ag(1)#2-O(2)-Ag(1)#4	77.06(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z #2 -x,y-1/2,-z+1/2 #3 -x,y+1/2,-z+1/2

#4 -x,-y+1,-z #5 x,-y+3/2,z-1/2 #6 x,-y+3/2,z+1/2

S5

Complete set of bonds and angles around silver(I) center in the structure of Ag(DCO).

Bonds:	
Ag(1) - N(2)#1	2.128(2)
Ag(1) - N(1)	2.217(2)
Ag(1) - O(1)	2.5817(16)
N(2) - Ag(1)#2	2.128(2)

Angles:	
N(2)#1 - Ag(1) - N(1)	166.11(7)
N(2)#1 - Ag(1) - O(1)	123.22(6)
N(1) - Ag(1) - O(1)	69.14(6)
O(2) - N(1) - Ag(1)	122.54(14)
C(1) - N(1) - Ag(1)	119.00(14)
C(2) - N(2) - Ag(1)#2	172.79(18)
C(3) - O(1) - Ag(1)	104.63(13)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/4,-y+3/4,z+3/4 #2 x-1/4,-y+3/4,z-3/4

S6

Complete set of bonds and angles around silver(I) center in the structure of Ag(PiCO).

Bonds:

Ag(1)-N(1)#1	2.3230(15)
Ag(1)-O(1)#2	2.3584(13)
Ag(1)-O(1)#3	2.4652(13)
Ag(1)-N(2)	2.6340(17)
N(1)-Ag(1)#1	2.3230(15)
O(1)-Ag(1)#4	2.3585(13)
O(1)-Ag(1)#5	2.4653(13)

Angles:

N(1)#1-Ag(1)-O(1)#2	109.28(5)
N(1)#1-Ag(1)-O(1)#3	126.00(5)
O(1)#2-Ag(1)-O(1)#3	121.49(4)
N(1)#1-Ag(1)-N(2)	89.17(5)
O(1)#2-Ag(1)-N(2)	91.39(5)
O(1)#3-Ag(1)-N(2)	73.34(5)
O(1)-N(1)-Ag(1)#1	118.97(11)
C(1)-N(1)-Ag(1)#1	119.56(11)
C(2)-N(2)-Ag(1)	118.38(14)
N(1)-O(1)-Ag(1)#4	114.62(10)
N(1)-O(1)-Ag(1)#5	127.89(10)
Ag(1)#4-O(1)-Ag(1)#5	96.20(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 x,y-1,z #3 -x+1,y-1/2,-z+1/2
#4 x,y+1,z #5 -x+1,y+1/2,-z+1/2

S7

Complete set of bonds and angles around silver(I) center in Ag(ECO).

Bonds:	
Ag(1)-N(2)#1	2.169(4)
Ag(1)-N(1)	2.241(3)
Ag(1)-O(1)#2	2.523(3)
Ag(1)-O(1)#3	2.532(3)
N(2)-Ag(1)#4	2.169(4)
O(1)-Ag(1)#2	2.524(3)
O(1)-Ag(1)#3	2.532(3)

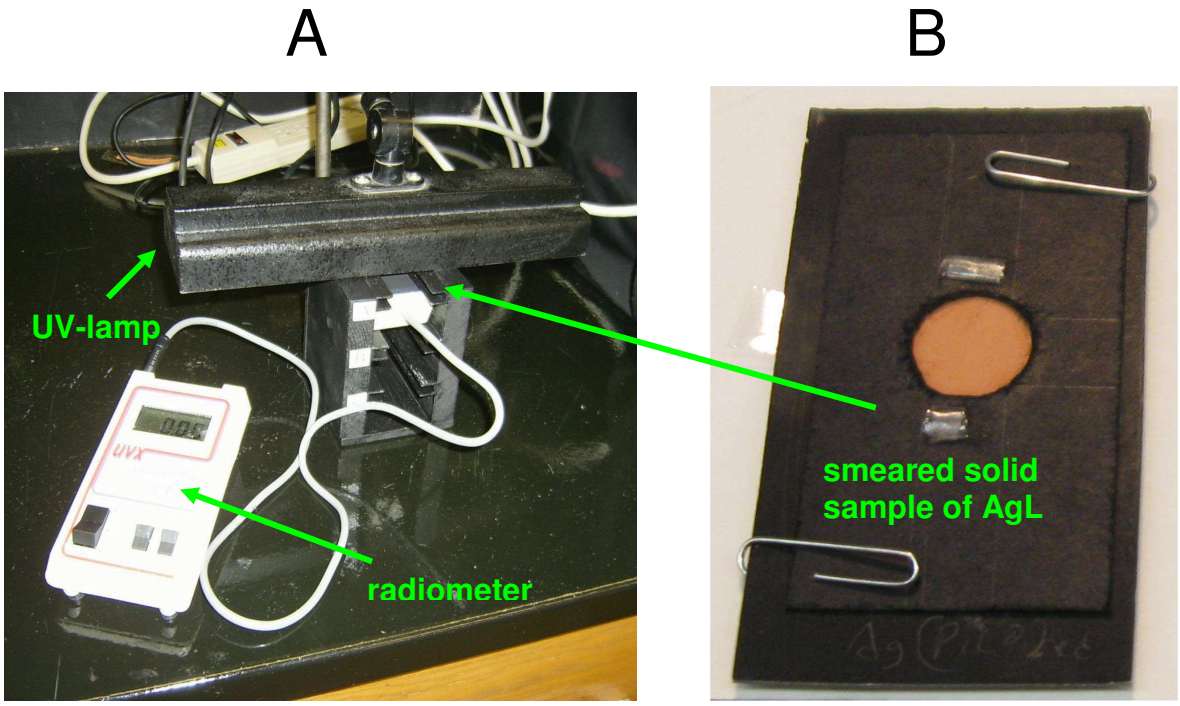
Angles:

N(2)#1-Ag(1)-N(1)	163.66(13)
N(2)#1-Ag(1)-O(1)#2	84.54(11)
N(1)-Ag(1)-O(1)#2	105.33(11)
N(2)#1-Ag(1)-O(1)#3	109.10(12)
N(1)-Ag(1)-O(1)#3	84.21(11)
O(1)#2-Ag(1)-O(1)#3	90.41(9)
O(1)-N(1)-Ag(1)	118.1(2)
C(1)-N(1)-Ag(1)	124.9(3)
C(2)-N(2)-Ag(1)#4	171.2(4)
N(1)-O(1)-Ag(1)#2	130.3(2)
N(1)-O(1)-Ag(1)#3	115.7(2)
Ag(1)#2-O(1)-Ag(1)#3	90.41(9)

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y+1,z #2 -x,-y+2,-z+1 #3 -x+1,-y+2,-z+1
#4 x+1,y-1,z

S8 Supplementary Information

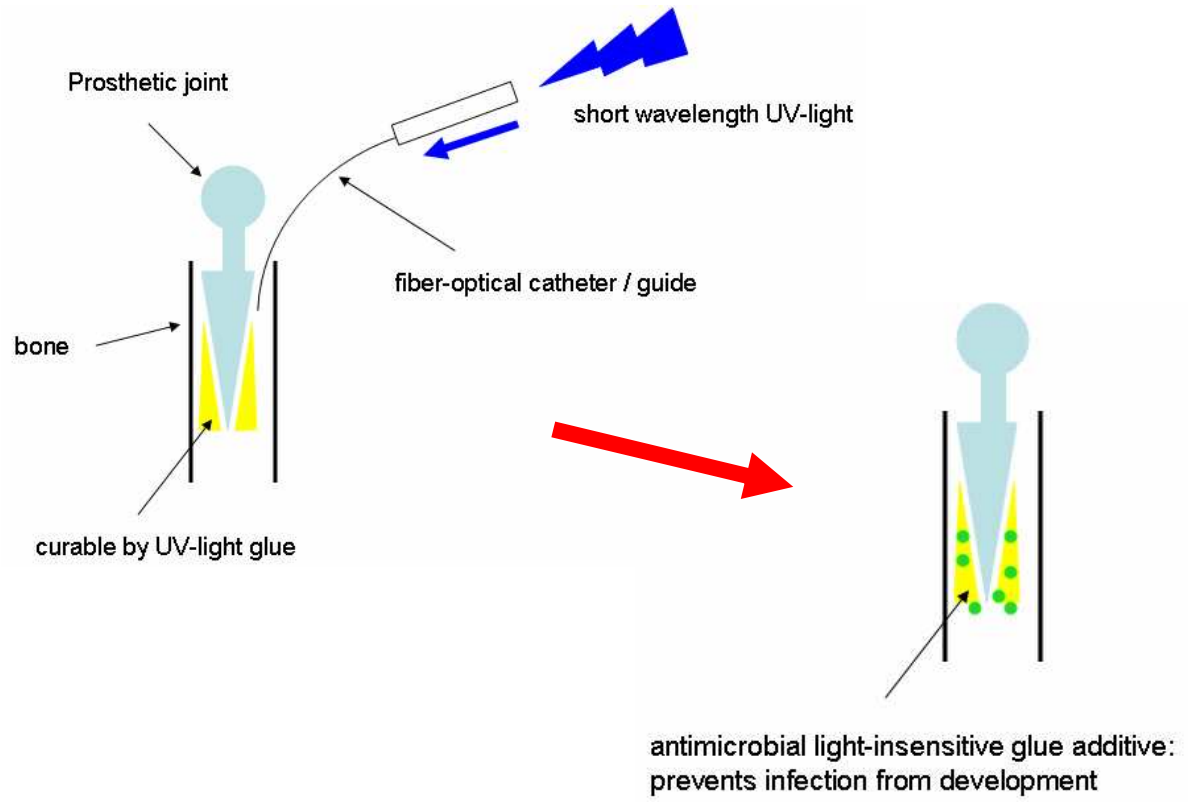
Experimental setup for the UV irradiation and photo-degradation studies of silver(I) cyanoximates.



A - Low-pressure Hg lamp that provides ~90% intensity of UV radiation at 254 nm, rack for a sample and UV sensor holding; **B** - powdery sample spread on a black cardboard tray with a round mask of 2 cm diameter. Temperature in all tests was 296 K.

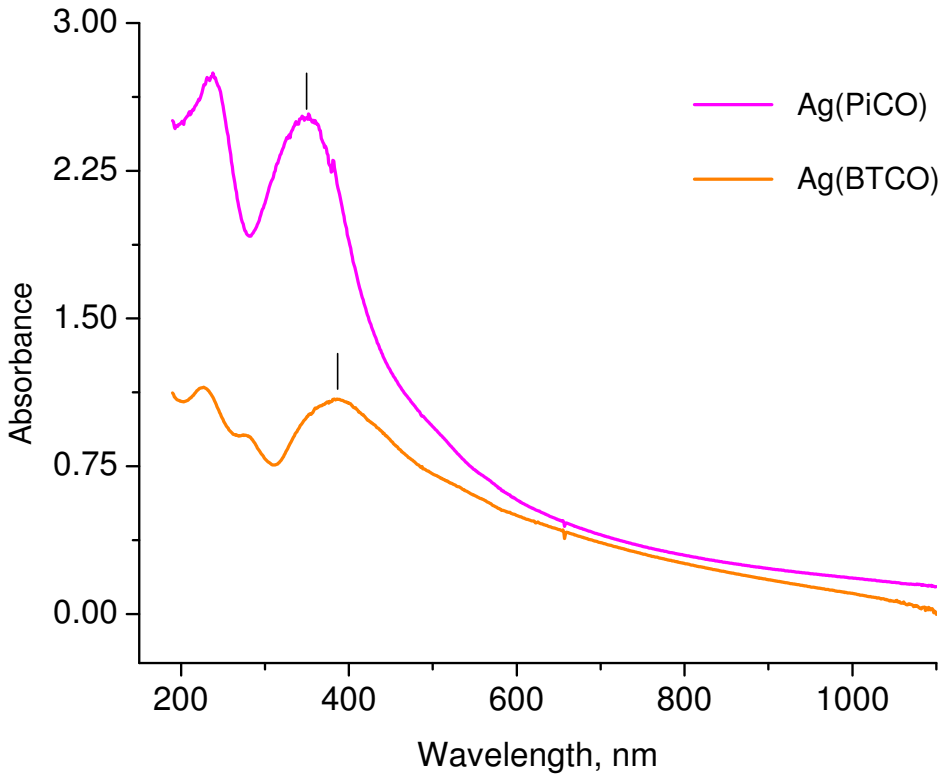
S9 Supplementary Information

A schematic representation of the conventional artificial joint insertion procedure and proposed addition of UV light resistant antimicrobial silver(I) cyanoximate component.



S10 Supplementary Information

Visible spectra of two silver(I) cyanoximates (suspensions in mineral oil). Values of the band gap were determined to be 3.52 eV for Ag(PiCO) and 3.20 eV for Ag(BTCO).



S11 Supplementary Information

The observed growth inhibition zone (in mm) from samples deposited on paper disks of PCM strains (**A**) and strains from nosocomial infections (**B**). The most significant zones are shown in bold.

A

AgL	*E. coli*	*P. aeruginosa*	*E. hirae*	*S. aureus*	*C. albicans*
Ag(BCO)	1	1	<1	1	**4**
Ag(BiMCO)	1	**2**	<1	1	**4**
Ag(BOCO)	1	**2**	1	1	**4**
Ag(CCO)	1	1	<1	1	**4**
Ag(DCO)	1	**3**	<1	1.5	**6**
Ag(ECO)	<1	1	<1	1.5	**4**
Ag(PiCO)	**2**	**2**	1	1	**4**

B

AgL	*Klebsiella pneumoniae* 244	*Pseudomonas aeruginosa*	*AMA*	*Enterococcus faecium* VRE	*Stapyloccocus aureus methicillin-resistant MRSA*	*S. aureus methicillin-resistent coagulaso-negative MRSC*	*Streprococcus pneumoniae* PCI
Ag(ACO)	0	2,5	3	0	0,5	0	2,5
Ag(BCO)	4	5	7	3	2	1	7
Ag(BIHCO)	0,5	2	3	0	0	0	3
Ag(BIMCO)	2,5	2,5	0	5	6	4	0
Ag(BOCO)	3	2,5	0	6	8	2	0
Ag(BTCO)	0,5	1	0	0	6	0,5	0
Ag(CCO)	3	3	0,5	7,5	5	2	0
Ag(DCO)	6	1	0	2,5	0	4	2
Ag(PiCO)	0	4	0	4	0,5	7	2

S12 Supplementary Information

Inhibition (in mm) of microbial growth by solid pellets of Ag(I) cyanoximates.

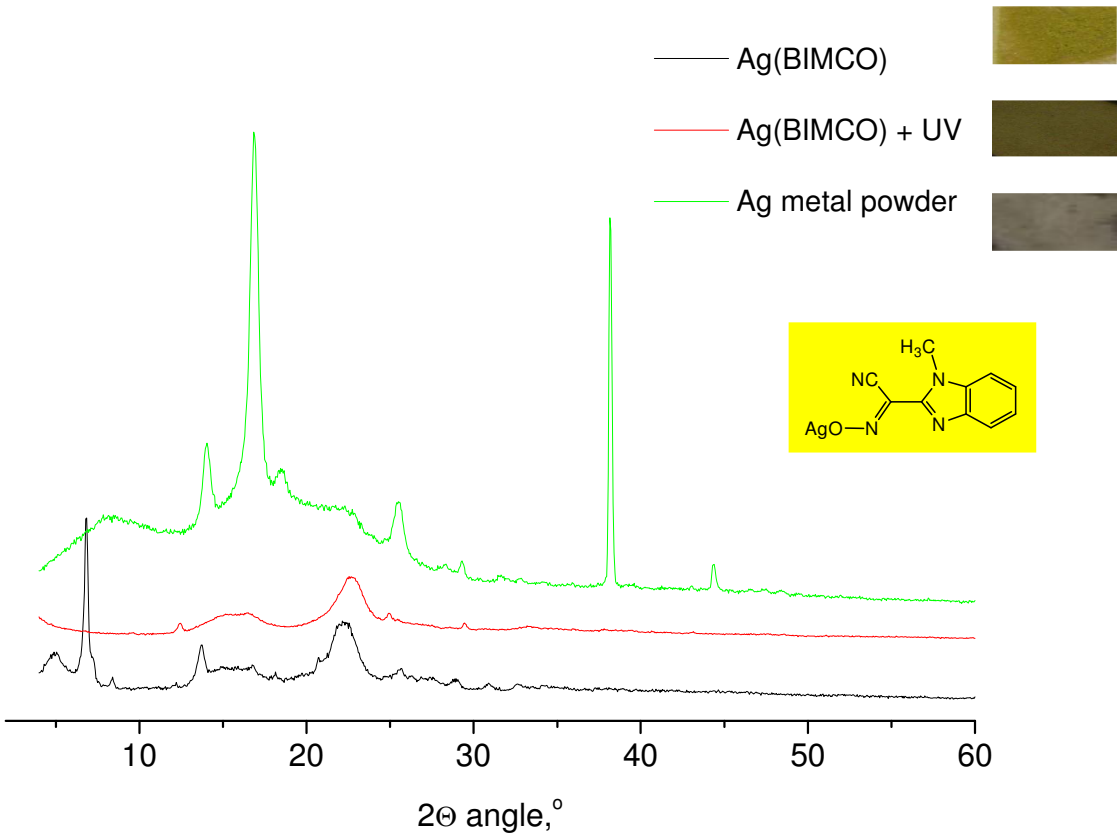
AgL	***E. coli***	***P. aeruginosa***	***S. aureus***	***M. fortuitum***	***C. albicans***
Ag(BCO)	-	4	-	18	10
Ag(BIMCO)	-	5	-	14	-
Ag(BOCO)	-	4	-	15	-
Ag(CCO)	-	2	6	-	-
Ag(DCO)	3	2	-	10	12
Ag(ECO)	-	-	8	5	13
Ag(PICO)	3	2	7	13	-

– no inhibition effect was detected.

S13 Supplementary Information

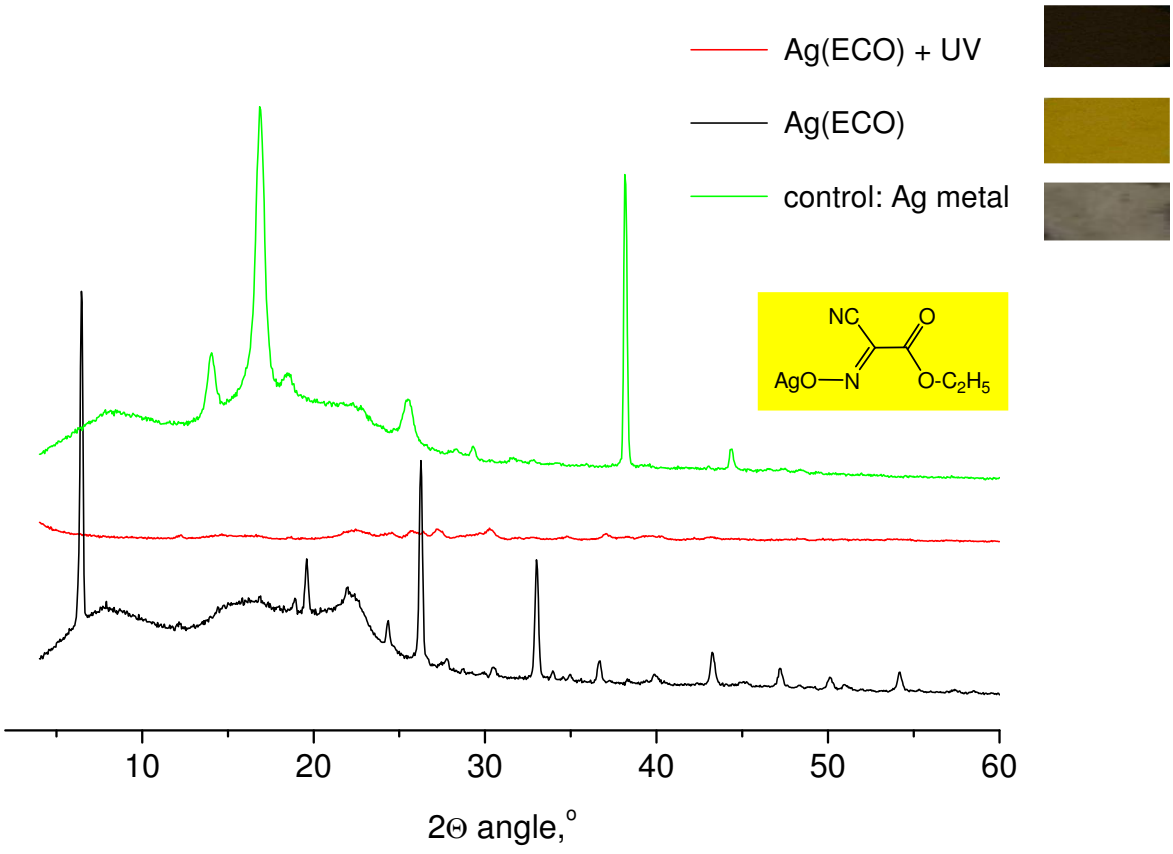
XRD powder Θ–2Θ scans of some Ag-cyanoximates in comparison with that for control sample – microcrystalline powder of metallic silver. Data were obtained at 296 K using Bruker Discover X-ray powder diffractometer equipped with Cu-source (40 kV, 30 mA; filtered, monochromated radiation; λ = 1.5406 Å)

Shown XRD patterns for fine powders of metallic silver, initial Ag(BIMCO), and exposed to intense UV-light Ag(BIMCO). Showed cropped actual photographs of samples used for the XRD studies.



S14 Supplementary Information

XRD patterns for powders of metallic silver, initial yellow-orange Ag(ECO) and its darkened product after an intense UV-radiation.

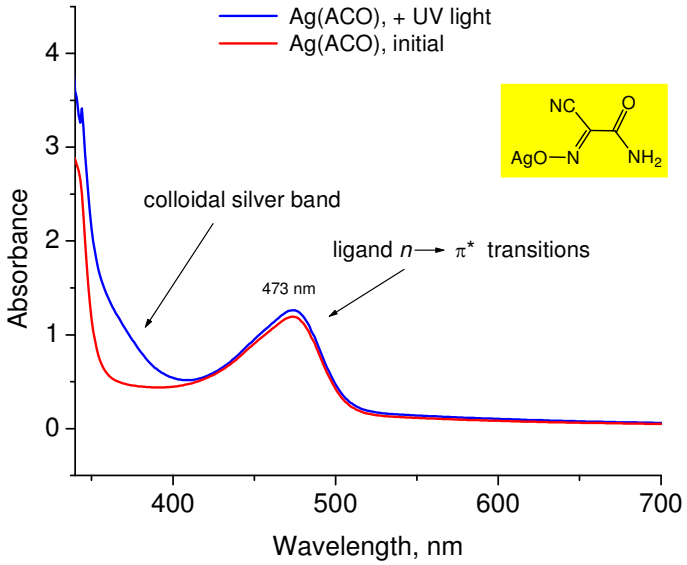


XRD patterns of both Ag(BIMCO) (**S12**) and Ag(ECO) samples exposed to prolonged, many hours of intense UV-radiation showed a very significant amorphization. This we attribute to their partial photodecomposition which leads to the brake-down of microcrystals of studied Ag-cyanoximates into an amorphous powder and formation of silver nano-particles.

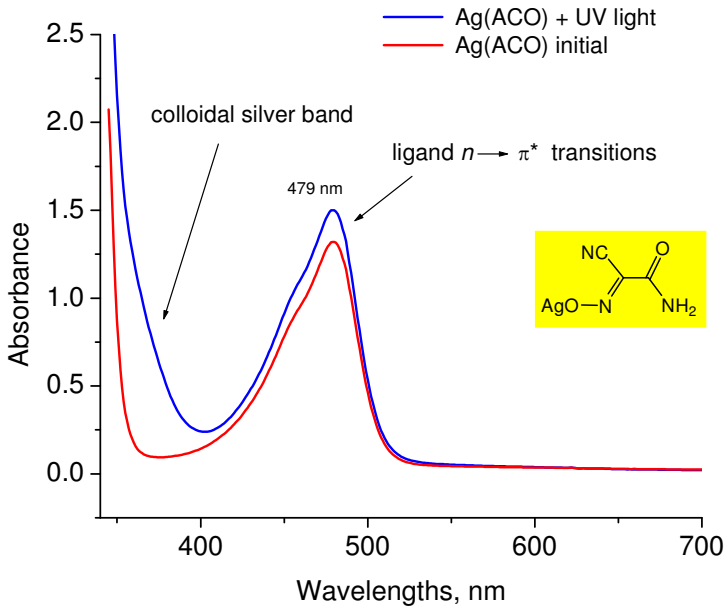
S15 Supplementary Information

UV-visible spectra of samples of solutions of Ag(ACO) before and after UV-radiation; samples were 5 – 6 mg / 2 mL of solvent, 1 cm cuvette, T = 296 K.

DMSO



Py



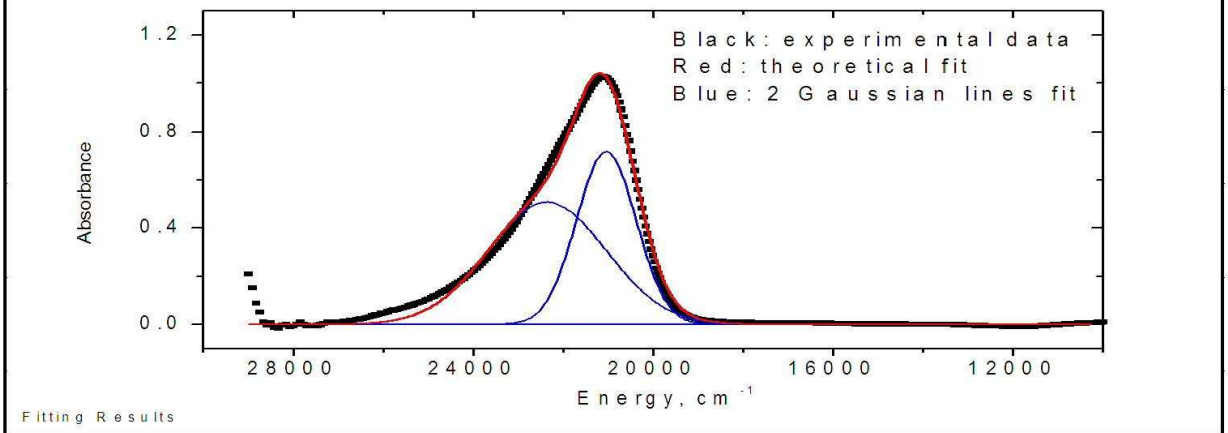
Position of the “plazmon” band of Ag-colloidal particles depends on their size: larger particles absorb in the “red” region of spectrum. Therefore, the band’s bathochromic shift is used to confirm increasing size of colloidal particles and even estimate their size.

S16 Supplementary Information

Full line shape analysis of visible region of spectra of Ag(ACO) samples in solutions prior and after UV-light exposure.

Ag(ACO) initial, solution in DMSO

Source File: Data2 | Data Set: Data2_B | Date:10
Chi^2=2.959254452E-4 | COD=0.99394 | # of Data Points=756
SS=0.2219440839 | Corr Coef=0.99696 | Degree of Freedom=750

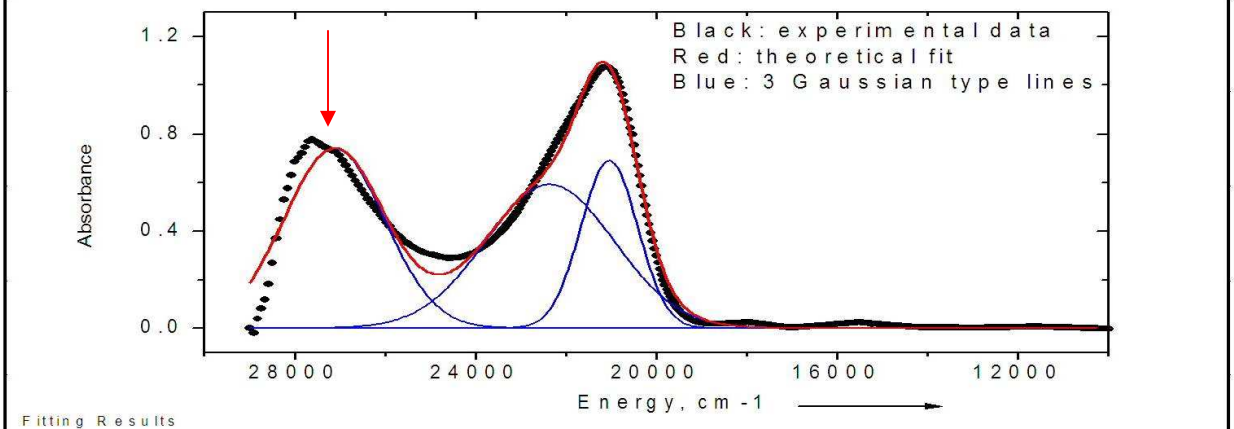


Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	1193.81206	1564.22276	0.71698	21043.17919	41.66827
2	Gaussian	1671.22682	3095.35671	0.50722	22360.88261	58.33173
		2865.03888				

Ag(ACO) after UV-radiation, DMSO solution

Source File: Data2 | Data Set: Data2_B | Date:10
Chi^2=8.607398525E-4 | COD=0.98765 | # of Data Points=756
SS=0.6446941495 | Corr Coef=0.9938 | Degree of Freedom=749



Fitting Results

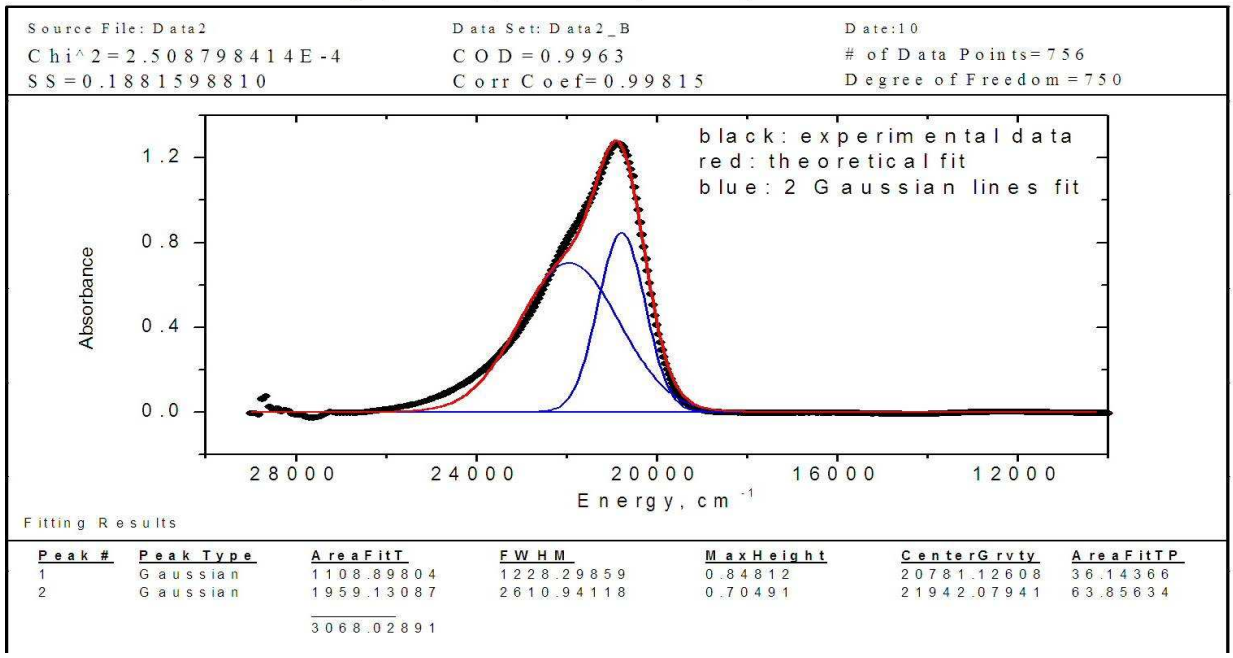
Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	1092.55877	1487.60368	0.68996	21043.24414	21.05407
2	Gaussian	2124.52694	3372.76069	0.59176	22360.57813	40.94053
3	Gaussian	1972.21419	2633.58936	0.73972	27134.42544	38.0054
		5189.29991				

Clearly seen an intense “plazmon” band of colloidal silver at ~27,000 cm^{-1} (370 nm).

S17 Supplementary Information

Full line shape analysis of visible region of spectra of Ag(ACO) samples in solutions prior and after UV-light exposure.

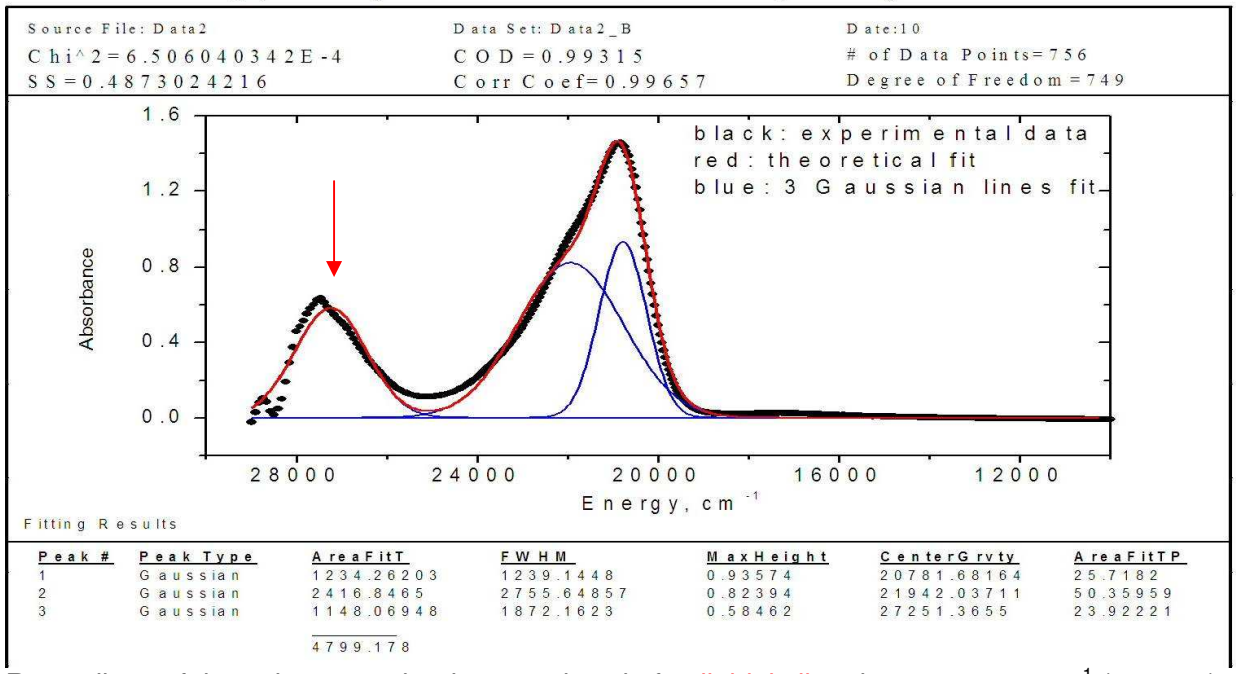
Ag(ACO) initial, in Py solution.



Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	1108.89804	1228.29859	0.84812	20781.12608	36.14366
2	Gaussian	1959.13087	2610.94118	0.70491	21942.07941	63.85634
		3068.02891				

Ag(ACO) after UV-radiation, in Py solution



Fitting Results

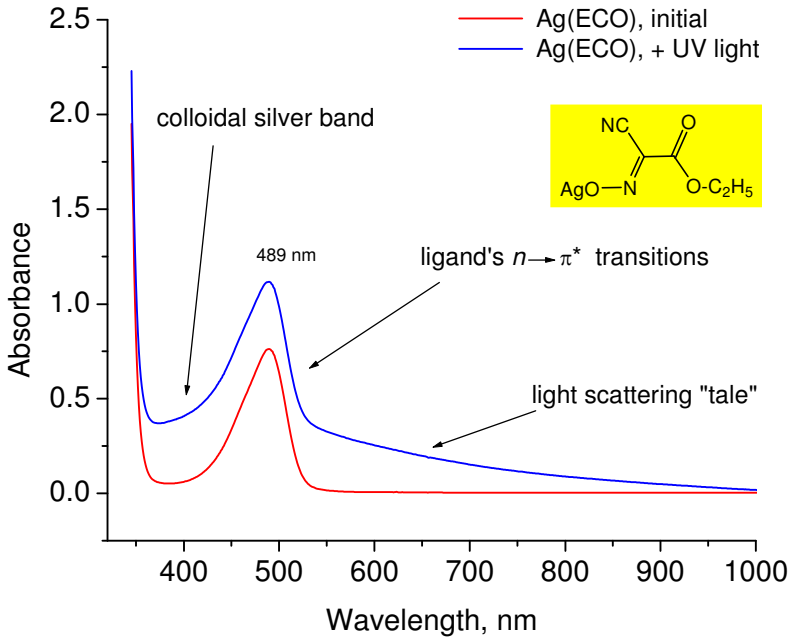
Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	1234.26203	1239.1448	0.93574	20781.68164	25.7182
2	Gaussian	2416.8465	2755.64857	0.82394	21942.03711	50.35959
3	Gaussian	1148.06948	1872.1623	0.58462	27251.3655	23.92221
		4799.178				

Regardless of the solvent used, “plazmon” band of colloidal silver is at ~27,000 cm^{-1} (370 nm).

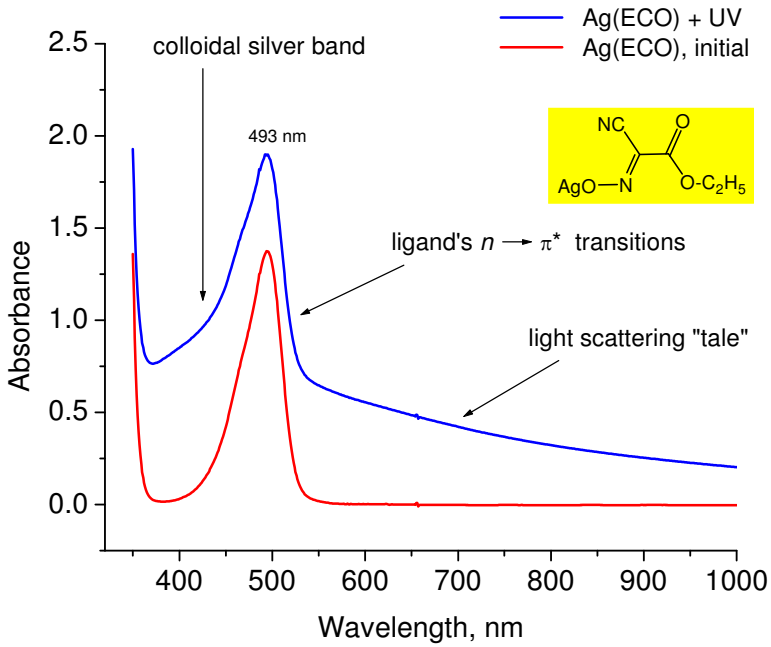
S18 Supplementary Information

UV-visible spectra of samples of solutions of Ag(ECO) before and after UV-radiation; samples were 4 – 5 mg / 2 mL of solvent, 1 cm cuvette, T = 296 K.

DMSO



Py

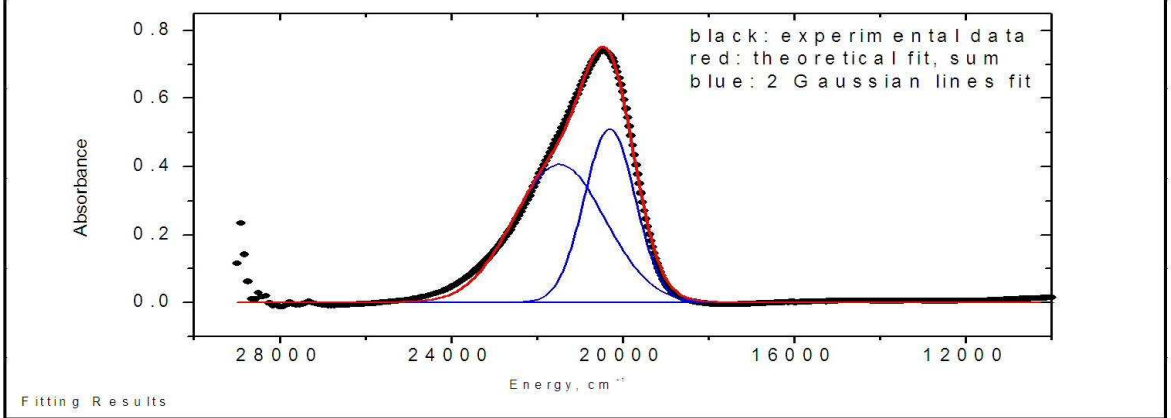


S19 Supplementary Information

Full line shape analysis of visible region of spectra of Ag(ECO) samples in DMSO solutions prior and after UV-light exposure.

Ag(ECO) initial sample, in DMSO

Source File: Data2 | Data Set: Data2_B | Date:10
Chi^2=2.095419175E-4 | COD=0.99168 | # of Data Points=756
SS=0.1571564381 | Corr Coef=0.99583 | Degree of Freedom=750

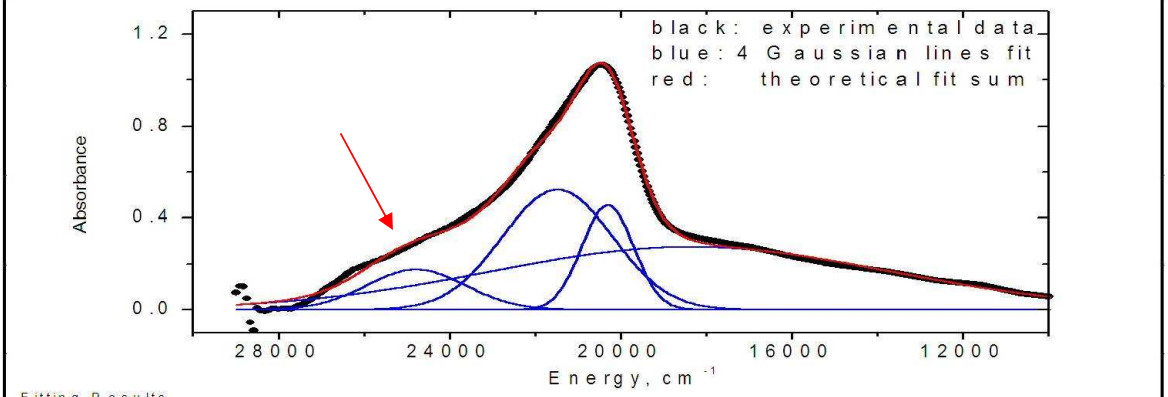


Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	761.35202	1398.52789	0.51143	20304.47505	41.08811
2	Gaussian	1091.62199	2524.45967	0.40623	21481.20908	58.91189
		1852.97401				

Ag(ECO) after UV-radiation, DMSO solution

Source File: Data3 | Data Set: Data3_B | Date:10
Chi^2=1.566623601E-4 | COD=0.99716 | # of Data Points=756
SS=0.1168701206 | Corr Coef=0.99858 | Degree of Freedom=746



Fitting Results

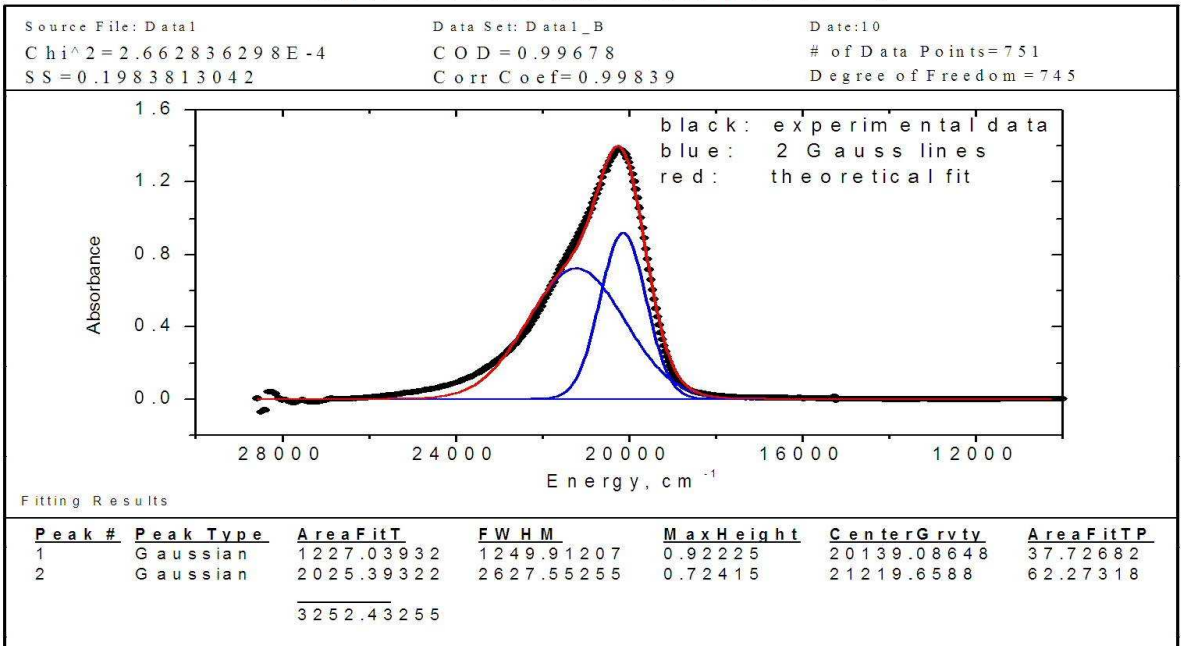
Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	3116.83535	11079.0998	0.27425	18368.22869	51.71816
2	Gaussian	692.50178	1427.76887	0.45565	20304.5918	11.4908
3	Gaussian	1704.00624	3060.46166	0.52306	21481.8418	28.27485
4	Gaussian	513.23506	2746.96424	0.17555	24792.55119	8.51619
		6026.57843				

A broad band of colloidal silver in this sample is observed at ~403 nm; a very broad light scattering band for apparently bigger Ag-particles is centered at ~544 nm.

S20 Supplementary Information

Full line shape analysis of visible region of spectra of Ag(ECO) samples in Py solutions prior and after UV-light exposure.

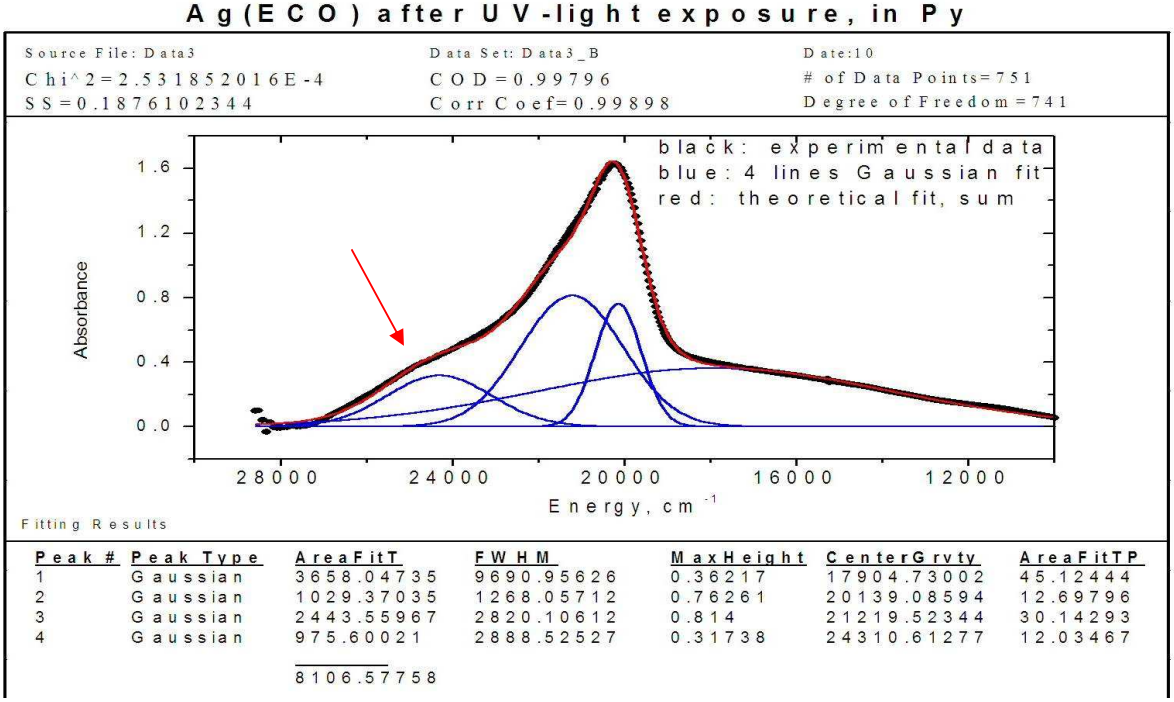
Ag(ECO), initial sample in Py



Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	1227.03932	1249.91207	0.92225	20139.08648	37.72682
2	Gaussian	2025.39322	2627.55255	0.72415	21219.6588	62.27318
		3252.43255				

Ag(ECO) after UV-light exposure, in Py



Fitting Results

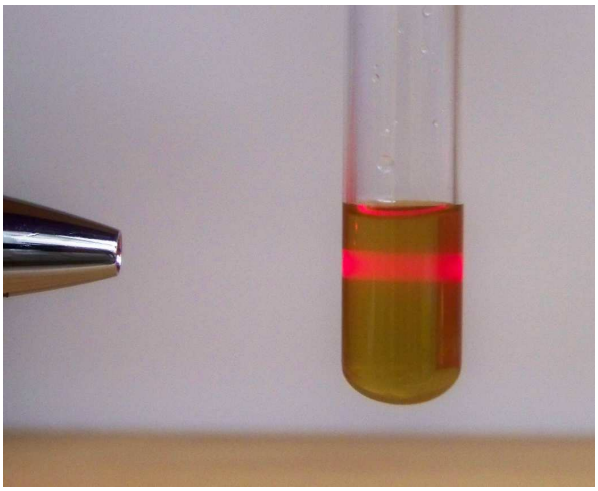
Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
1	Gaussian	3658.04735	9690.95626	0.36217	17904.73002	45.12444
2	Gaussian	1029.37035	1268.05712	0.76261	20139.08594	12.69796
3	Gaussian	2443.55967	2820.10612	0.814	21219.52344	30.14293
4	Gaussian	975.60021	2888.52527	0.31738	24310.61277	12.03467
		8106.57758				

A broad band of colloidal silver in this sample is observed at ~411 nm; a very broad light scattering band for apparently bigger Ag-particles is centered at ~555 nm.

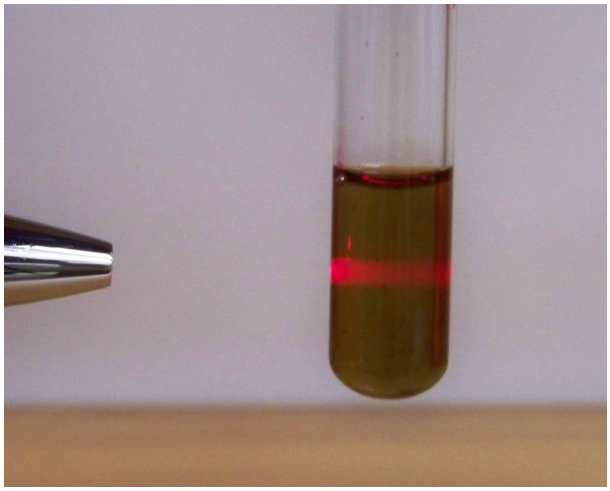
S21 Supplementary Information

The Tyndall effect in colloid solutions of some Ag-cyanoximates exposed to an intense UV-light. A small intensity He-Ne red gas laser is shown on the left; pictures taken at 296 K.

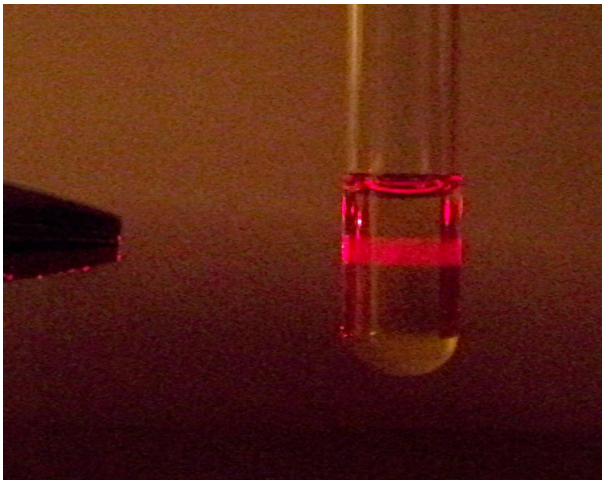
Ag(ECO) after exposure to UV-light in DMSO; sample of 5.4 mg in 2 mL.



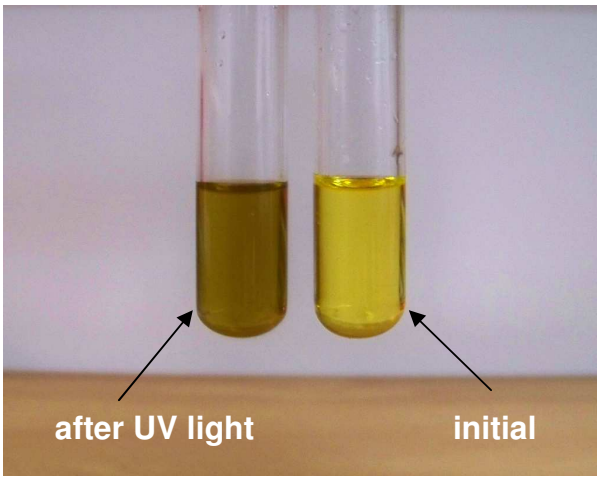
Ag(ACO) after UV-irradiation in DMSO; sample of 5.2 mg in 2 mL.



Sample of Ag(ACO) after UV-light exposure in Py; 4.6 mg / 2 mL. Picture taken at deemed light for clarity of demonstration of the Tyndall effect.

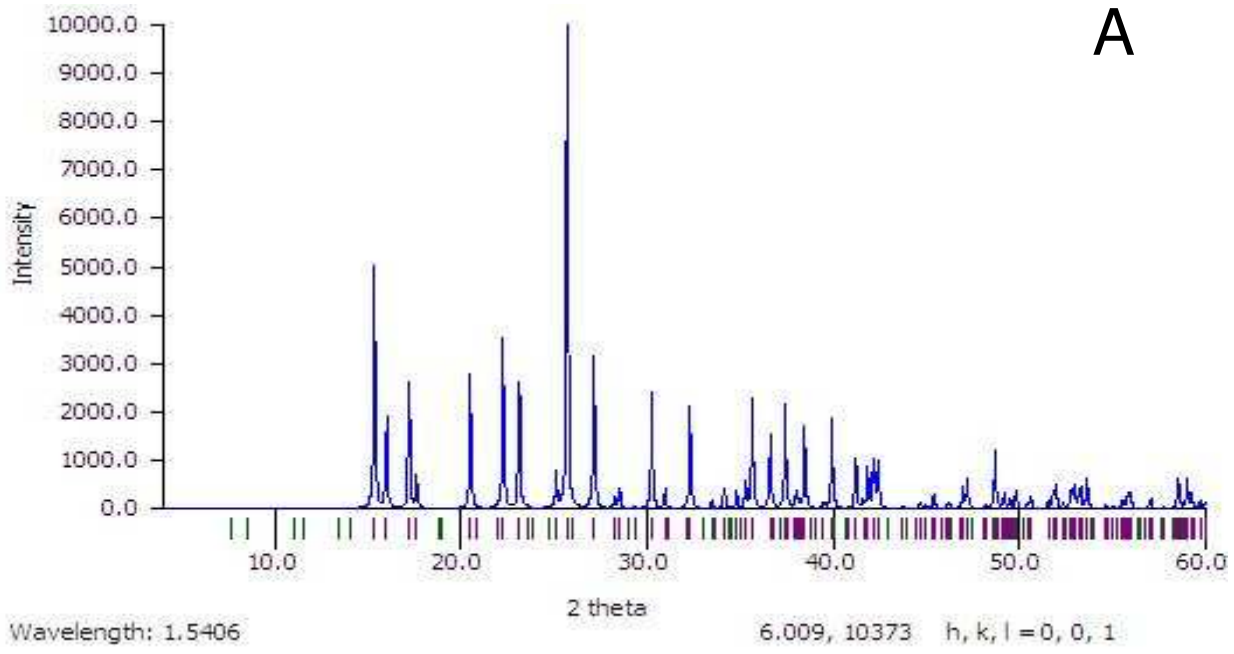


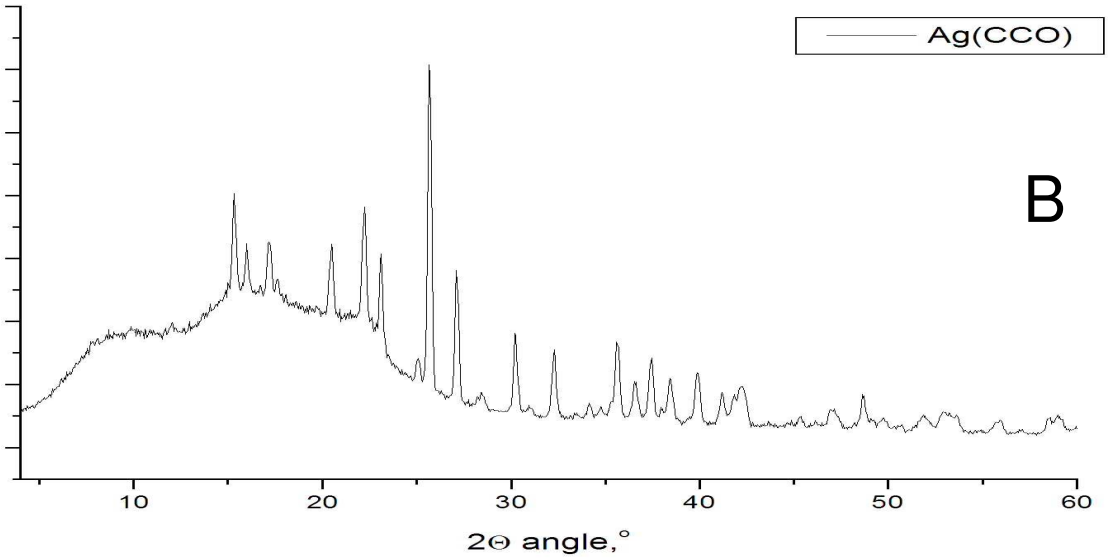
Comparative view of two test-tubes with solutions of Ag(ECO) in DMSO. Solutions with colloidal silver appear to be clear, but much darker.



S22 Supplementary Information

Comparison of calculated (**A**, from single crystal data) and experimental (**B**, from bulk powdery material) XRD patterns for Ag(CCO) coordination polymer. The experimental data were obtained on a Bruker Discover instrument at 296 K using Cu-radiation source. The crystal structure of this compound we published last year in *Inorganic Chemistry*, **2009**, *48* (6), p.2371-2382 – reference 41 of this paper.





S23 Supplementary Information

Comparison of calculated (**A**, from single crystal data) and experimental (**B**, from bulk powdery material) XRD patterns for Ag(ACO) coordination polymer. The experimental data were obtained on a Bruker Discover instrument at 296 K using Cu-radiation source.