Supplementary material

Influence of proline and hydroxyproline as antimicrobial and anticancer peptide components on the silver(I) ion activity: structural and biological evaluation with a new theoretical and experimental SAR approach

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Table S1 Crystal data and structure refinement for silver(I) complexes.

	AgPro	**AgHyp**
Empirical formula	$C_{10}H_{18}Ag_2N_4O_{10}$	$C_{10}H_{18}Ag_2N_4O_{12}$
Formula weight	570.02	602.02
Temperature [K]	120(2)	120(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions	a = 5.4739(1)	a = 5.5261(4)
[Å, °]	b = 11.0228(3)	b = 11.2082(8)
	c = 13.9383(4)	c = 14.0565(12)
	α = 90	α = 90
	β = 98.0410(10)	β = 97.992(3)
	γ = 90	γ = 90
Volume [Å^3]	832.74(4)	862.17(11)
Z	2	2
Calculated density [g.cm^{-3}]	2.273	2.319
Absorption coefficient [mm^{-1}]	2.414	2.346
F(000)	560	592
Crystal size [mm^3]	0.437 x 0.070 x 0.066	0.171 x 0.162 x 0.058
θ range for data collection [°]	2.365 – 29.980	2.333 – 26.489
Index ranges	$-6\leq h\leq 7$, $-15\leq k\leq 15$, $-19\leq l\leq 18$	$-6\leq h\leq 6$, $-14\leq k\leq 14$, $-17\leq l\leq 17$
Reflections collected/unique	21750 / 4834	31594 / 3526
Data / restraints / parameters	4834 / 0 / 251	3526 / 17 / 267
Completeness to theta = 25.242° [%]	99.9	99.6
Max. and min. transmission	0,86 and 0.66	0.88 and 0.72
Goodness-of-fit on F^2	1.036	1.108

Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0152$; $wR2 = 0.0329$	$R1 = 0.0351$; $wR2 = 0.1062$
R indices (all data)	$R1 = 0.0156$; $wR2 = 0.0331$	$R1 = 0.0358$; $wR2 = 0.1071$
Largest diff. peak and hole [e.Å^{-3}]	0.544, -0.426	2.396, -1.008

Table S2 Bond distances (Å) and angles (°) for **AgPro**

Bond distances			
Ag(1)—O(2)	2.2210(18)	C(5)—H(5B)	0.9900
Ag(1)—O(3)	2.2334(18)	O(3)—C(6)	1.262(3)
Ag(1)—O(1)^{i}	2.4230(15)	O(4)—C(6)	1.249(3)
Ag(1)—O(8)	2.592(2)	C(6)—C(7)	1.523(3)
Ag(1)—Ag(2)	2.8375(3)	C(7)—N(2)	1.504(3)
Ag(2)—O(4)	2.2748(18)	C(7)—C(8)	1.535(4)
Ag(2)—O(1)	2.3605(17)	C(7)—H(7)	1.0000
Ag(2)—O(3)^{ii}	2.3887(17)	N(2)—C(10)	1.506(4)
O(1)—C(1)	1.251(3)	N(2)—H(2NA)	0.85(4)
O(2)—C(1)	1.256(3)	N(2)—H(2NB)	0.83(3)
C(1)—C(2)	1.522(3)	C(8)—C(9)	1.522(4)
C(2)—N(1)	1.508(3)	C(8)—H(8A)	0.9900
C(2)—C(3)	1.547(4)	C(8)—H(8B)	0.9900
C(2)—H(2)	1.0000	C(9)—C(10)	1.507(4)
N(1)—C(5)	1.494(4)	C(9)—H(9A)	0.9900
N(1)—H(1NA)	0.97(4)	C(9)—H(9B)	0.9900
N(1)—H(1NB)	0.77(4)	C(10)—H(10A)	0.9900
C(3)—C(4)	1.526(4)	C(10)—H(10B)	0.9900
C(3)—H(3A)	0.9900	N(3)—O(5)	1.241(3)
C(3)—H(3B)	0.9900	N(3)—O(7)	1.256(3)
C(4)—C(5)	1.529(4)	N(3)—O(6)	1.259(3)
C(4)—H(4A)	0.9900	N(4)—O(9)	1.234(3)
C(4)—H(4B)	0.9900	N(4)—O(10)	1.255(3)
C(5)—H(5A)	0.9900	N(4)—O(8)	1.272(3)
Bond angles			
O(2)—Ag(1)—O(3)	165.63(7)	C(4)—C(5)—H(5A)	111.3
O(2)—Ag(1)—O(1)^{i}	112.77(6)	N(1)—C(5)—H(5B)	111.3
O(3)—Ag(1)—O(1)^{i}	81.20(6)	C(4)—C(5)—H(5B)	111.3
O(2)—Ag(1)—O(8)	91.55(7)	H(5A)—C(5)—H(5B)	109.2
O(3)—Ag(1)—O(8)	82.06(7)	C(6)—O(3)—Ag(1)	124.81(16)
O(1)^{i}—Ag(1)—O(8)	101.08(7)	C(6)—O(3)—Ag(2)^{i}	130.33(15)
O(2)—Ag(1)—Ag(2)	90.03(5)	Ag(1)—O(3)—Ag(2)^{i}	101.98(7)
O(3)—Ag(1)—Ag(2)	77.04(5)	C(6)—O(4)—Ag(2)	116.45(16)
O(1)^{i}—Ag(1)—Ag(2)	154.63(5)	O(4)—C(6)—O(3)	126.8(2)
O(8)—Ag(1)—Ag(2)	88.75(5)	O(4)—C(6)—C(7)	118.6(2)
O(4)—Ag(2)—O(1)	152.80(8)	O(3)—C(6)—C(7)	114.6(2)
O(4)—Ag(2)—O(3)^{ii}	113.16(6)	N(2)—C(7)—C(6)	110.30(19)
O(1)—Ag(2)—O(3)^{ii}	79.40(6)	N(2)—C(7)—C(8)	104.7(2)
O(4)—Ag(2)—Ag(1)	85.08(5)	C(6)—C(7)—C(8)	111.5(2)
O(1)—Ag(2)—Ag(1)	75.21(4)	N(2)—C(7)—H(7)	110.1
O(3)^{ii}—Ag(2)—Ag(1)	150.92(5)	C(6)—C(7)—H(7)	110.1
C(1)—O(1)—Ag(2)	128.04(15)	C(8)—C(7)—H(7)	110.1
C(1)—O(1)—Ag(1)^{ii}	128.13(16)	C(7)—N(2)—C(10)	108.4(2)
Ag(2)—O(1)—Ag(1)^{ii}	97.36(6)	C(7)—N(2)—H(2NA)	107(2)
C(1)—O(2)—Ag(1)	117.15(16)	C(10)—N(2)—H(2NA)	109(2)
O(1)—C(1)—O(2)	127.1(2)	C(7)—N(2)—H(2NB)	114(2)
O(1)—C(1)—C(2)	115.8(2)	C(10)—N(2)—H(2NB)	111(2)
O(2)—C(1)—C(2)	117.0(2)	H(2NA)—N(2)—H(2NB)	108(3)
N(1)—C(2)—C(1)	111.2(2)	C(9)—C(8)—C(7)	103.6(2)

N(1)—C(2)—C(3)	105.0(2)	C(9)—C(8)—H(8A)	111.0
C(1)—C(2)—C(3)	111.1(2)	C(7)—C(8)—H(8A)	111.0
N(1)—C(2)—H(2)	109.8	C(9)—C(8)—H(8B)	111.0
C(1)—C(2)—H(2)	109.8	C(7)—C(8)—H(8B)	111.0
C(3)—C(2)—H(2)	109.8	H(8A)—C(8)—H(8B)	109.0
C(5)—N(1)—C(2)	107.4(2)	C(10)—C(9)—C(8)	102.9(2)
C(5)—N(1)—H(1NA)	110(2)	C(10)—C(9)—H(9A)	111.2
C(2)—N(1)—H(1NA)	107(2)	C(8)—C(9)—H(9A)	111.2
C(5)—N(1)—H(1NB)	113(3)	C(10)—C(9)—H(9B)	111.2
C(2)—N(1)—H(1NB)	112(3)	C(8)—C(9)—H(9B)	111.2
H(1NA)—N(1)—H(1NB)	108(4)	H(9A)—C(9)—H(9B)	109.1
C(4)—C(3)—C(2)	105.0(2)	N(2)—C(10)—C(9)	103.2(2)
C(4)—C(3)—H(3A)	110.7	N(2)—C(10)—H(10A)	111.1
C(2)—C(3)—H(3A)	110.7	C(9)—C(10)—H(10A)	111.1
C(4)—C(3)—H(3B)	110.7	N(2)—C(10)—H(10B)	111.1
C(2)—C(3)—H(3B)	110.7	C(9)—C(10)—H(10B)	111.1
H(3A)—C(3)—H(3B)	108.8	H(10A)—C(10)—H(10B)	109.1
C(3)—C(4)—C(5)	102.4(2)	O(5)—N(3)—O(7)	120.6(2)
C(3)—C(4)—H(4A)	111.3	O(5)—N(3)—O(6)	120.5(3)
C(5)—C(4)—H(4A)	111.3	O(7)—N(3)—O(6)	118.9(2)
C(3)—C(4)—H(4B)	111.3	O(9)—N(4)—O(10)	120.9(2)
C(5)—C(4)—H(4B)	111.3	O(9)—N(4)—O(8)	120.6(2)
H(4A)—C(4)—H(4B)	109.2	O(10)—N(4)—O(8)	118.5(2)
N(1)—C(5)—C(4)	102.4(2)	N(4)—O(8)—Ag(1)	109.77(15)
N(1)—C(5)—H(5A)	111.3		

Symmetry codes: (i) x+1,y,z; (ii) x-1,y,z

Table S3 Possible hydrogen bonds (Å, °) for **AgPro**

D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
N(1)—H(1NA)...N(3)^{iii}	0.97(4)	2.55(4)	3.462(3)	156(3)
N(1)—H(1NA)...O(6)^{iii}	0.97(4)	1.94(4)	2.903(3)	170(3)
N(1)—H(1NA)...O(7)^{iii}	0.97(4)	2.54(4)	3.265(3)	131(3)
N(1)—H(1NB)...O(7)^{iv}	0.77(4)	2.11(4)	2.845(3)	160(4)
N(2)—H(2NA)...O(4)	0.85(4)	2.16(4)	2.674(3)	119(3)
N(2)—H(2NA)...O(10)^{v}	0.85(4)	2.24(4)	2.905(3)	135(3)
N(2)—H(2NB)...O(8)^{vi}	0.83(3)	2.03(3)	2.815(3)	156(3)
N(2)—H(2NB)...O(10)^{vi}	0.83(3)	2.52(3)	2.979(3)	116(3)

Symmetry codes: (iii) -x,y-1/2,-z; (iv) -x+1,y-1/2,-z; (v) -x+1,y+1/2,-z+1; (vi) -x+2,y+1/2,-z+1

Table S4 Bond distances (Å) and angles (°) for **AgHyp**

Bond distances			
Ag(1)—O(4)	2.184(6)	N(1)—H(1B)	0.86(4)
Ag(1)—O(1)	2.215(6)	O(4)—C(6)	1.259(12)
Ag(1)—O(5)^{ii}	2.522(8)	C(6)—O(5)	1.224(11)
Ag(1)—Ag(2)	2.8756(9)	C(6)—C(7)	1.518(12)
Ag(2)—O(5)	2.309(7)	C(7)—N(2)	1.514(11)
Ag(2)—O(2)	2.318(6)	C(7)—C(8)	1.530(11)
Ag(2)—O(1)^{i}	2.381(6)	C(7)—H(7)	1.0000
Ag(2)—O(7)	2.595(8)	C(8)—C(9)	1.525(12)
O(1)—C(1)	1.262(10)	C(8)—H(8A)	0.9900
C(1)—O(2)	1.242(11)	C(8)—H(8B)	0.9900
C(1)—C(2)	1.533(11)	C(9)—O(6)	1.423(10)
C(2)—N(1)	1.498(11)	C(9—C(10)	1.520(12)
C(2)—C(3)	1.518(12)	C(9)—H(9)	1.0000
C(2)—H(2)	1.0000	O(6)—H(6)	0.83(4)

C(3)—C(4)	1.529(12)	C(10)—N(2)	1.519(11)
C(3)—H(3A)	0.9900	C(10)—H(10A)	0.9900
C(3)—H(3B)	0.9900	C(10)—H(10B)	0.9900
C(4)—O(3)	1.431(13)	N(2)—H(2A)	0.9100
C(4)—C(5)	1.533(13)	N(2)—H(2B)	0.9100
C(4)—H(4)	1.0000	N(3)—O(8)	1.232(11)
O(3)—H(3)	0.81(4)	N(3)—O(7)	1.255(11)
C(5)—N(1)	1.506(12)	N(3)—O(9)	1.260(11)
C(5)—H(5A)	0.9900	N(4)—O(10)	1.248(11)
C(5)—H(5B)	0.9900	N(4)—O(11)	1.257(11)
N(1)—H(1A)	0.87(4)	N(4)—O(12)	1.259(11)
Bond angles			
O(4)—Ag(1)—O(1)	165.6(2)	C(5)—N(1)—H(1A)	102(8)
O(4)—Ag(1) —O(5)[ii]	111.9(2)	C(2) —N(1) —H(1B)	119(8)
O(1)—Ag(1)—O(5) [ii]	79.1(2)	C(5) —N(1)—H(1B)	101(8)
O(4)—Ag(1)—Ag(2)	86.76(18)	H(1A)—N(1)—H(1B)	107(10)
O(1) —Ag(1) —Ag(2)	79.32(17)	C(6) —O(4) —Ag(1)	120.8(6)
O(5) [ii]—Ag(1) —Ag(2)	147.64(16)	O(5) —C(6) —O(4)	127.1(8)
O(5) —Ag(2) —O(2)	150.6(2)	O(5) —C(6) —C(7)	116.2(8)
O(5) —Ag(2) —O(1) [i]	80.3(2)	O(4) —C(6) —C(7)	116.6(7)
O(2) —Ag(2) —O(1) [i]	112.1(2)	C(6)—O(5)—Ag(2)	128.1(7)
O(5) —Ag(2) —O(7)	96.0(2)	C(6)—O(5) —Ag(1) [i]	126.9(6)
O(2) —Ag(2) —O(7)	92.1(2)	Ag(2) —O(5) —Ag(1) [i]	96.8(2)
O(1) [i]—Ag(2) —O(7)	136.9(2)	N(2) —C(7) —C(6)	111.9(7)
O(5) —Ag(2) —Ag(1)	76.73(19)	N(2) —C(7) —C(8)	104.0(7)
O(2) —Ag(2) —Ag(1)	80.03(16)	C(6) —C(7) —C(8)	117.5(7)
O(1) [i]—Ag(2) —Ag(1)	147.65(16)	N(2) —C(7) —H(7)	107.6
O(7) —Ag(2) —Ag(1)	68.66(17)	C(6) —C(7) —H(7)	107.6
C(1) —O(1)—Ag(1)	124.1(5)	C(8) —C(7) —H(7)	107.6
C(1) —O(1) —Ag(2) [ii]	132.2(5)	C(9) —C(8) —C(7)	102.5(7)
Ag(1) —O(1) —Ag(2) [ii]	103.7(2)	C(9) —C(8) —H(8A)	111.3
O(2) —C(1) —O(1)	127.1(8)	C(7) —C(8) —H(8A)	111.3
O(2) —C(1) —C(2)	117.7(7)	C(9) —C(8) —H(8B)	111.3
O(1) —C(1) —C(2)	115.0(7)	C(7) —C(8) —H(8B)	111.3
C(1)—O(2) —Ag(2)	113.6(5)	H(8A) —C(8) —H(8B)	109.2
N(1) —C(2) —C(3)	102.8(7)	O(6) —C(9) —C(10)	111.4(7)
N(1) —C(2) —C(1)	110.7(7)	O(6) —C(9) —C(8)	107.6(7)
C(3) —C(2) —C(1)	110.0(7)	C(10) —C(9) —C(8)	102.3(7)
N(1) —C(2) —H(2)	111.0	O(6) —C(9) —H(9)	111.7
C(3) —C(2) —H(2)	111.0	C(10) —C(9) —H(9)	111.7
C(1) —C(2) —H(2)	111.0	C(8) —C(9) —H(9)	111.7
C(2) —C(3) —C(4)	103.7(7)	C(9) —O(6) —H(6)	109(7)
C(2) —C(3) —H(3A)	111.0	N(2) —C(10) —C(9)	104.2(7)
C(4) —C(3) —H(3A)	111.0	N(2) —C(10) —H(10A)	110.9
C(2) —C(3) —H(3B)	111.0	C(9) —C(10) —H(10A)	110.9
C(4) —C(3) —H(3B)	111.0	N(2) —C(10) —H(10B)	110.9
H(3A) —C(3) —H(3B)	109.0	C(9)—C(10)—H(10B)	110.9
O(3) —C(4) —C(3)	107.2(8)	H(10A) —C(10) —H(10B)	108.9
O(3) —C(4) —C(5)	111.9(8)	C(7) —N(2) —C(10)	107.7(7)
C(3) —C(4) —C(5)	103.1(7)	C(7) —N(2) —H(2A)	110.2
O(3) —C(4) —H(4)	111.4	C(10) —N(2) —H(2A)	110.2
C(3) —C(4) —H(4)	111.4	C(7) —N(2) —H(2B)	110.2
C(5) —C(4) —H(4)	111.4	C(10) —N(2) —H(2B)	110.2
C(4) —O(3) —H(3)	110(10)	H(2A) —N(2) —H(2B)	108.5
N(1) —C(5) —C(4)	105.4(7)	O(8) —N(3) —O(7)	120.6(9)
N(1) —C(5) —H(5A)	110.7	O(8) —N(3) —O(9)	121.2(9)
C(4) —C(5) —H(5A)	110.7	O(7) —N(3) —O(9)	118.2(8)
N(1) —C(5) —H(5B)	110.7	N(3) —O(7) —Ag(2)	98.9(6)
C(4) —C(5) —H(5B)	110.7	O(10) —N(4) —O(11)	120.4(8)
H(5A) —C(5) —H(5B)	108.8	O(10) —N(4) —O(12)	119.1(8)
C(2) —N(1) —C(5)	108.8(7)	O(11) —N(4) —O(12)	120.5(8)

C(2) —N(1) —H(1A)	117(8)	

Symmetry codes: (i) x+1, y, z; (ii) x-1, y,z

Table S5 Possible hydrogen bonds (Å, °) for **AgHyp**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(12)^{iii}	0.81(4)	2.08(9)	2.792(10)	146(13)
N(1)-H(1A)...N(4)^{iv}	0.87(4)	2.51(6)	3.340(11)	159(10)
N(1)-H(1A)...O(10)^{iv}	0.87(4)	2.21(7)	3.029(12)	155(11)
N(1)-H(1A)...O(11)^{iv}	0.87(4)	2.38(9)	3.016(10)	130(9)
N(1)-H(1B)...N(4)^{v}	0.86(4)	2.61(8)	3.347(11)	145(10)
N(1)-H(1B)...O(10)^{v}	0.86(4)	2.30(9)	2.939(12)	132(10)
N(1)-H(1B)...O(12)^{v}	0.86(4)	2.20(8)	2.914(11)	141(10)
O(6)-H(6)...O(9)^{viii}	0.83(4)	1.96(5)	2.773(9)	168(10)
N(2)-H(2A)...O(6)^{ii}	0.91	1.99	2.773(10)	144
N(2)-H(2B)...O(3)^{viii}	0.91	1.98	2.823(10)	154

Symmetry codes: (ii) x-1,y,z; (iii) x,y+1,z; (iv) -x+1,y+1/2,-z+1; (v) -x,y+1/2,-z+1; (viii) x+1,y-1,z

Table S6 IR spectral data assignments (cm^{-1}) for complexes AgPro and AgHyp and their appropriate ligands Pro and Hyp.

	Pro	**AgPro**	**Hyp**	**AgHyp**
ν(OH)	-	-	3270	3261
$\nu(NH_2^+) + \nu(CH_2)$	3330–2875	3300–2872	3200–2820	3200–2850
$\delta(NH_2^+)$	1605	1595	1635	1632
$\nu_{as}(COO^-)$	1552	1561	1574	1569
$\nu_s(COO^-)$	1447	1418	1392	1413
$\Delta(\nu_{as} - \nu_s)$	-	143	-	156
$\delta(CH_2)_{sciss.}$	1472	1471	-	-
ν_3	-	1450, 1360	-	1444, 1365
ν_4	-	767, 754	-	753, 720
$\Delta\nu_3$	-	90	-	79
$\Delta\nu_4$	-	13	-	33
$\omega(CH_2)$	1375	1335	1358	1361
$\nu(NO_3^-)$	-	1288	-	1318
ν_{ring}	1032, 913	1033, 925	1029, 919	1025, 920
ν(CCN)	847	853, 821	882, 843	821
δ_{ring}	639	671	613	694
$\rho(COO^-)$	447	467	460	483

Table S7 Concentrations, absorbance at 600 nm and standard deviations for complexes AgPro and AgHyp

AgPro	*Bacillus cereus*		*Pseudomonas aeruginosa*		*Staphylococcus aureus*	
c[mM]	**A_{600} ± SD**	**mean of diff. ± SE**	**A_{600} ± SD**	**mean of diff. ± SE**	**A_{600} ± SD**	**mean of diff. ± SE**
0.5	0.273 ± 0.030	0.280±0.03	0.064 ± 0.009	0.949±0.021	0.103 ± 0.019	0.963±0.027
0.25	0.323 ± 0.032	0.230±0.03	0.049 ± 0.004	0.963±0.021	0.099 ± 0.020	0.967±0.027
0.125	0.383 ± 0.026	0.170±0.03	0.055 ± 0.018	0.957±0.021	0.085 ± 0.023	0.982±0.027
0.063	0.412 ± 0.019	0.141±0.03	0.069 ± 0.002	0.944±0.021	0.845 ± 0.025	0.221±0.027
0.031	0.410 ± 0.021	0.143±0.03	0.977 ± 0.026	0.036±0.021	0.985 ± 0.029	0.081±0.027
0.016	0.419 ± 0.027	0.134±0.03	0.987 ± 0.047	0.026±0.021	1.012 ± 0.037	0.055±0.027
0.008	0.437 ± 0.041	0.117±0.03	1.013 ± 0.076	0.026±0.021	1.028 ± 0.035	0.038±0.027

AgHyp	*Bacillus cereus*		*Pseudomonas aeruginosa*		*Staphylococcus aureus*	
c[mM]	**A_{600} ± SD**	**mean of diff. ± SE**	**A_{600} ± SD**	**mean of diff. ± SE**	**A_{600} ± SD**	**mean of diff. ± SE**
0.5	0.043 ± 0.002	0.510±0.028	0.05 ± 0.001	0.963±0.022	0.075 ± 0.003	0.991±0.04
0.25	0.053 ± 0.006	0.501±0.028	0.089 ± 0.013	0.923±0.022	0.101 ± 0.036	0.966±0.04
0.125	0.047 ± 0.001	0.507±0.028	0.075 ± 0.006	0.937±0.022	0.137 ± 0.055	0.929±0.04
0.063	0.048 ± 0.002	0.506±0.028	0.083 ± 0.009	0.929±0.022	0.614 ± 0.041	0.453±0.04
0.031	0.356 ± 0.031	0.031±0.028	0.863 ± 0.049	0.150±0.022	0.795 ± 0.075	0.272±0.04
0.016	0.503 ± 0.033	0.050±0.028	0.953 ± 0.053	0.059±0.022	0.812 ± 0.074	0.255±0.04
0.008	0.512 ± 0.003	0.041±0.028	1.027 ± 0.045	0.014±0.022	0.906 ± 0.085	0.160±0.04

Table S8 Effect of the level of theory used on the predicted difference $\Delta_{21}(\log P)$ in the $\mathbf{2}^{N}$ and $\mathbf{1}^{N}$ $\log P$ values. Except from XTB, PM7 (see the footnote), 3-21G was chosen as the basis set, CPCM as the solvation model. The calculated equilibrium constants for the mutual isomeric interconversion $\mathbf{1}^{O}\rightarrow\mathbf{1}^{N}$, $\mathbf{2}^{O}\rightarrow\mathbf{2}^{N}$ are provided as well.

Level of theory	**Complex AgPro**			**Complex AgHyp**			diff. Δ_{21} ($\log P$)
	$\log K^{w}$ ($1^{O}\rightarrow1^{N}$)	$\log K^{oc}$ ($1^{O}\rightarrow1^{N}$)	$\log P$	$\log K^{w}$ ($2^{O}\rightarrow2^{N}$)	$\log K^{oc}$ ($2^{O}\rightarrow2^{N}$)	$\log P$	
experiment			−1.46			−1.16	0.30
XTB [a)]	4.49	3.63	−0.41	2.33	1.68	−0.98	−0.57
PM7 [b)]	6.32	5.43	−2.42	4.75	3.85	−2.92	−0.50
HF	1.41	1.03	−2.46	−0.52	−0.93	−2.80	−0.34
X3LYP	2.96	2.70	−1.87	1.59	1.23	−2.21	−0.35
O3LYP	1.38	1.09	−1.96	0.19	−0.20	−2.37	−0.41
BLYP	2.66	2.32	−1.79	1.69	1.51	−1.88	−0.09
LC-BLYP	3.41	4.09	−0.91	2.46	2.09	−2.28	−1.37
B3LYP	3.44	2.62	−2.42	1.41	1.05	−2.22	0.20
CAM-B3LYP	3.69	3.17	−2.14	1.92	1.48	−2.30	−0.16
B3LYP+GD3	3.94	3.83	−1.72	2.79	2.44	−2.21	−0.48
M06	3.91	3.15	−2.69	2.32	1.87	−2.36	0.33
M06HF	6.07	5.36	−2.47	5.09	4.84	−2.34	0.13
M06-2X	4.49	4.23	−2.06	2.65	2.28	−2.46	−0.40
wB97	3.47	3.28	−1.95	2.02	1.49	−2.54	−0.59
wB97X	3.42	3.09	−2.01	2.06	1.51	−2.56	−0.55
wB97XD	4.40	4.11	−2.04	2.94	2.42	−2.52	−0.48
MP2	1.90	1.71	−2.03	0.79	0.53	−2.35	−0.32

[a)] XTB/GFN2 with the ALPB solvation model

[b)] PM7 with the CPCM solvation model

Table S9 Effect of the basis set used on the predicted difference $\Delta_{21}(\log P)$ in the $\mathbf{2}^{N}$ and $\mathbf{1}^{N}$ log *P* values. In all cases, B3LYP functional together with CPCM as the solvation model was utilized. The calculated equilibrium constants for the mutual isomeric interconversion $\mathbf{1}^{O}\rightarrow\mathbf{1}^{N}$, $\mathbf{2}^{O}\rightarrow\mathbf{2}^{N}$ are provided as well.

Basis set	**Complex AgPro**			**Complex AgHyp**			diff. Δ_{21} (log *P*)
	log K^{w} ($1^{O}\rightarrow1^{N}$)	log K^{oc} ($1^{O}\rightarrow1^{N}$)	log *P*	log K^{w} ($2^{O}\rightarrow2^{N}$)	log K^{oc} ($2^{O}\rightarrow2^{N}$)	log *P*	
experiment			−1.46			−1.16	0.30
STO-3G	7.04	6.78	−0.85	6.22	6.05	−0.88	−0.03
CEP-4G	6.70	6.64	−1.68	6.75	6.30	−2.03	−0.36
3-21G	3.44	2.62	−2.42	1.41	1.05	−2.22	0.20
6-31G* [a)]	2.85	2.13	−2.57	1.21	0.48	−2.81	−0.24
6-311+G* [a)]	6.34	6.05	−2.84	4.30	3.60	−3.12	−0.29

[a)] 3-21G basis set was set for the silver(I) atom.

Table S10 Effect of the chosen implicit solvation model on the predicted difference $\Delta_{21}(\log P)$ in the $\mathbf{2}^{N}$ and $\mathbf{1}^{N}$ log *P* values. In all cases, B3LYP functional together with 3-21G basis set was used. The calculated equilibrium constants for the mutual isomeric interconversion $\mathbf{1}^{O}\rightarrow\mathbf{1}^{N}$, $\mathbf{2}^{O}\rightarrow\mathbf{2}^{N}$ are provided as well.

Solvation model	Complex AgPro			Complex AgHyp			diff. Δ_{21} (log *P*)
	log K^{w} ($1^{O}\rightarrow1^{N}$)	log K^{oc} ($1^{O}\rightarrow1^{N}$)	log *P*	log K^{w} ($2^{O}\rightarrow2^{N}$)	log K^{oc} ($2^{O}\rightarrow2^{N}$)	log *P*	
experiment			−1.46			−1.16	0.30
CPCM	3.44	2.62	−2.42	1.41	1.05	−2.22	0.20
IEFPCM	3.32	2.47	−2.86	1.35	0.74	−2.98	−0.12
SMD	2.40	2.91	−3.41	1.26	1.45	−4.80	−1.38

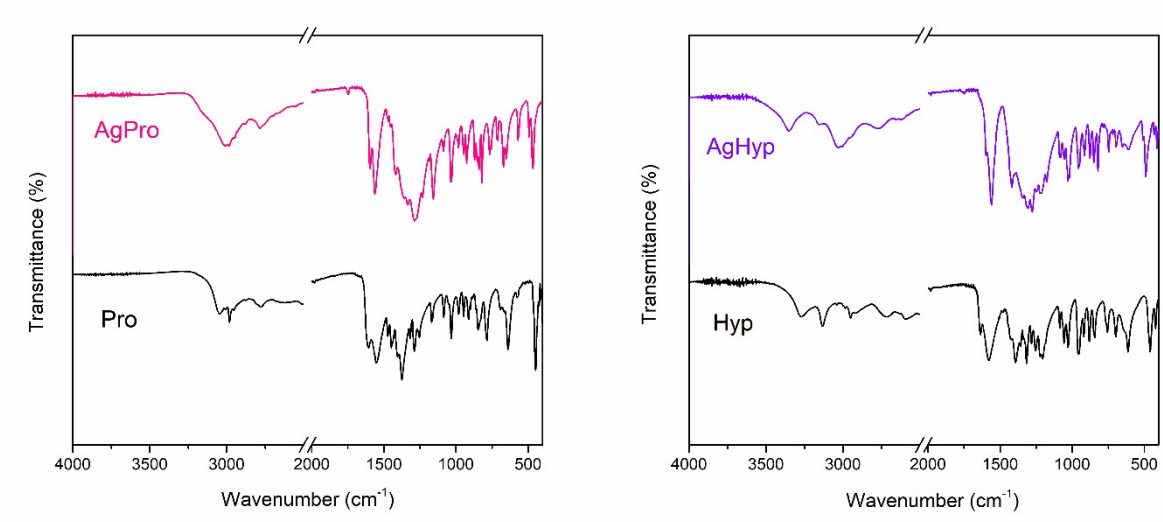


Figure S1 IR spectra of free ligands (black lines) and silver(I) complexes AgPro (pink line) and AgHyp (violet line)

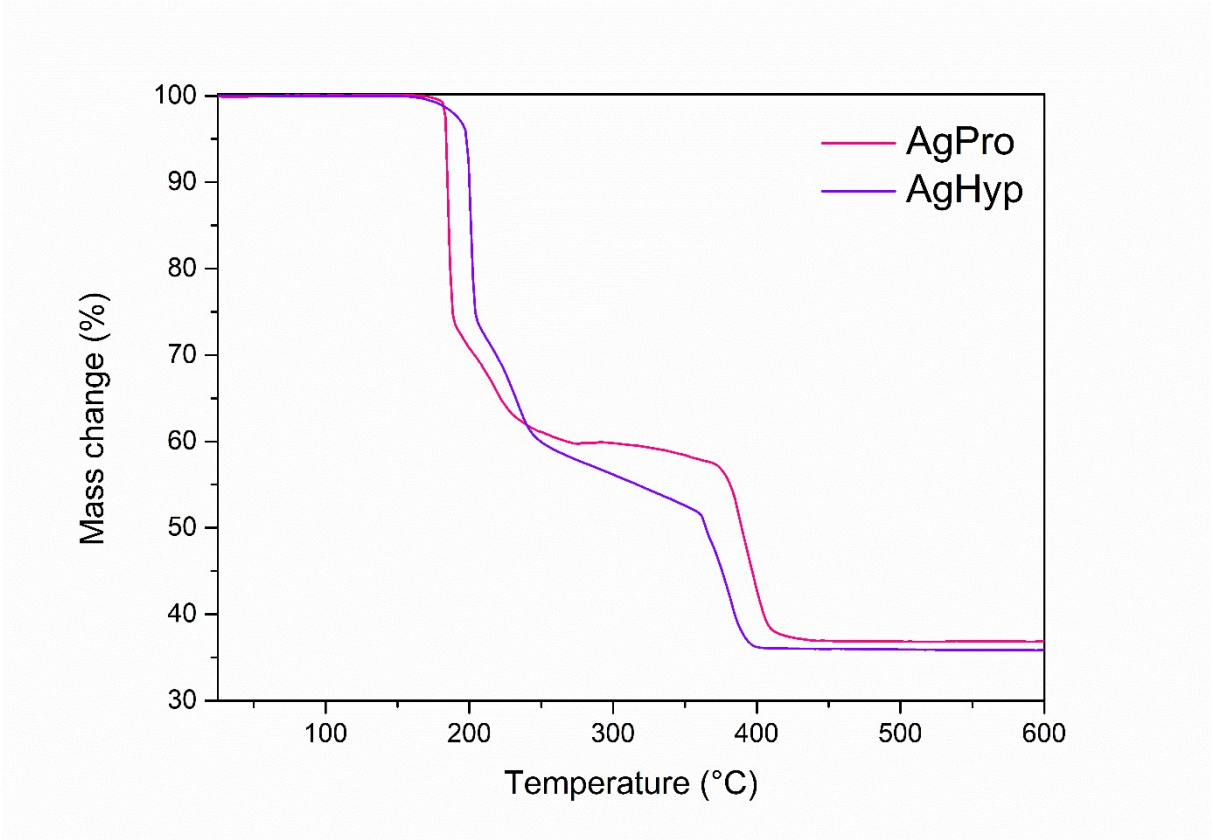


Figure S2 Thermogravimetric curves for studied silver(I) complexes measured in the air atmosphere in the temperature range of 25–600 °C.

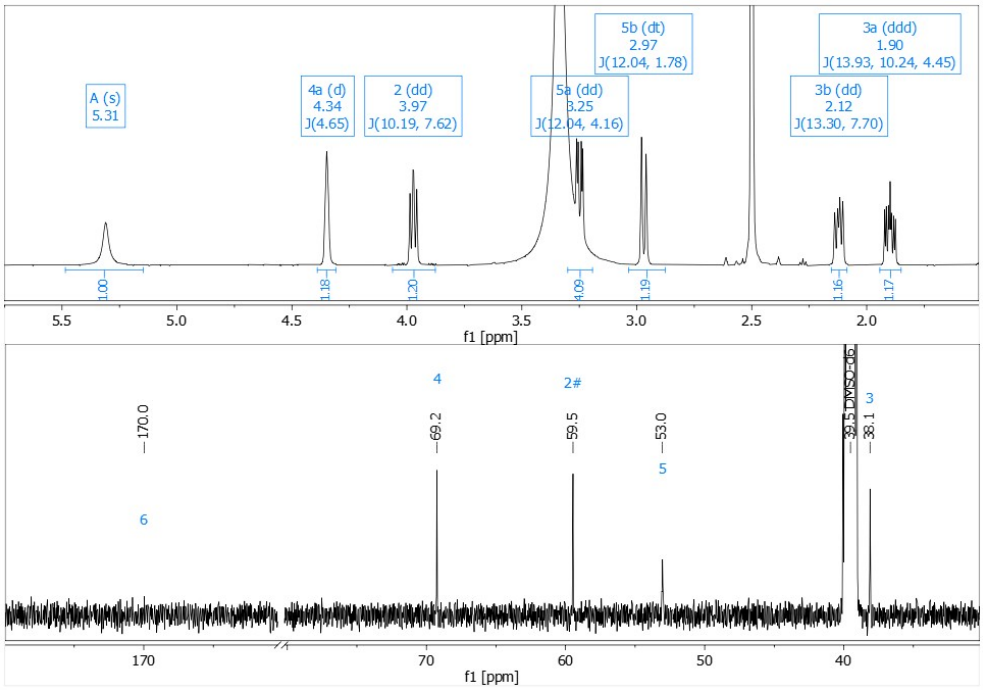


Figure S3 ^{1}H NMR (600 MHz, DMSO-d_6) and ^{13}C NMR (150 MHz, DMSO-d_6) spectra of complex AgHyp.

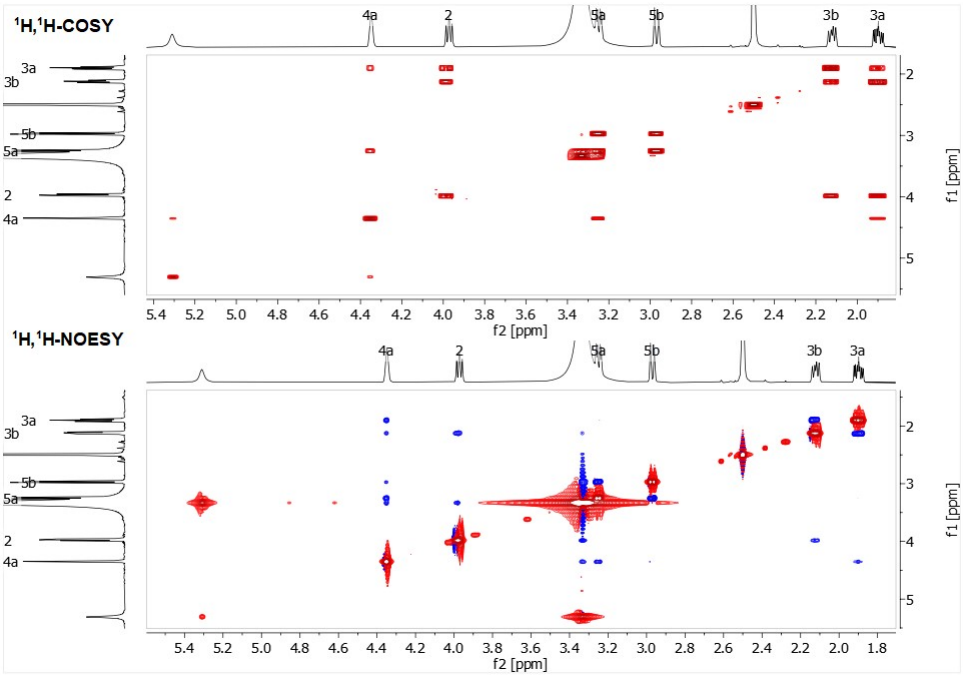


Figure S4 ^{1}H,^{1}H-COSY and ^{1}H,^{1}H-NOESY (DMSO-d_6) spectra of complex AgHyp.

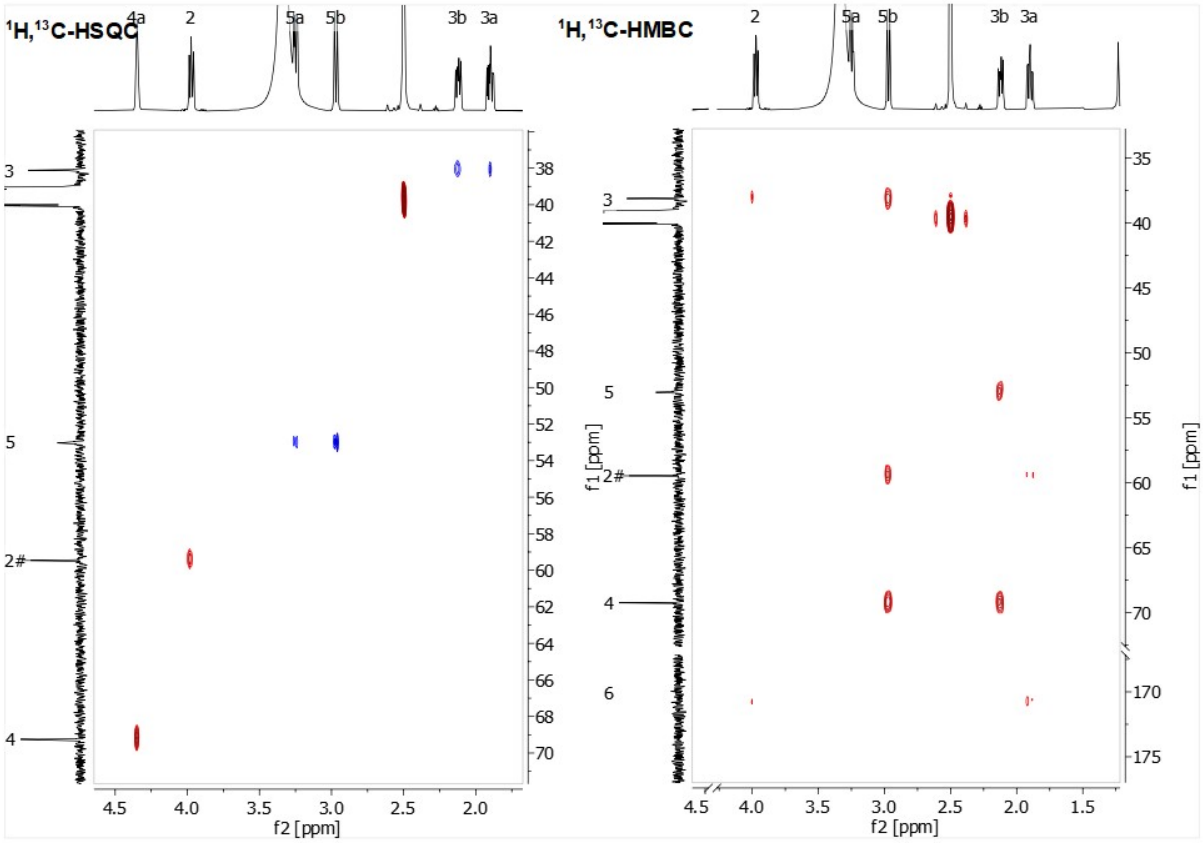


Figure S5 ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC (DMSO-d_6) spectra of complex AgHyp.

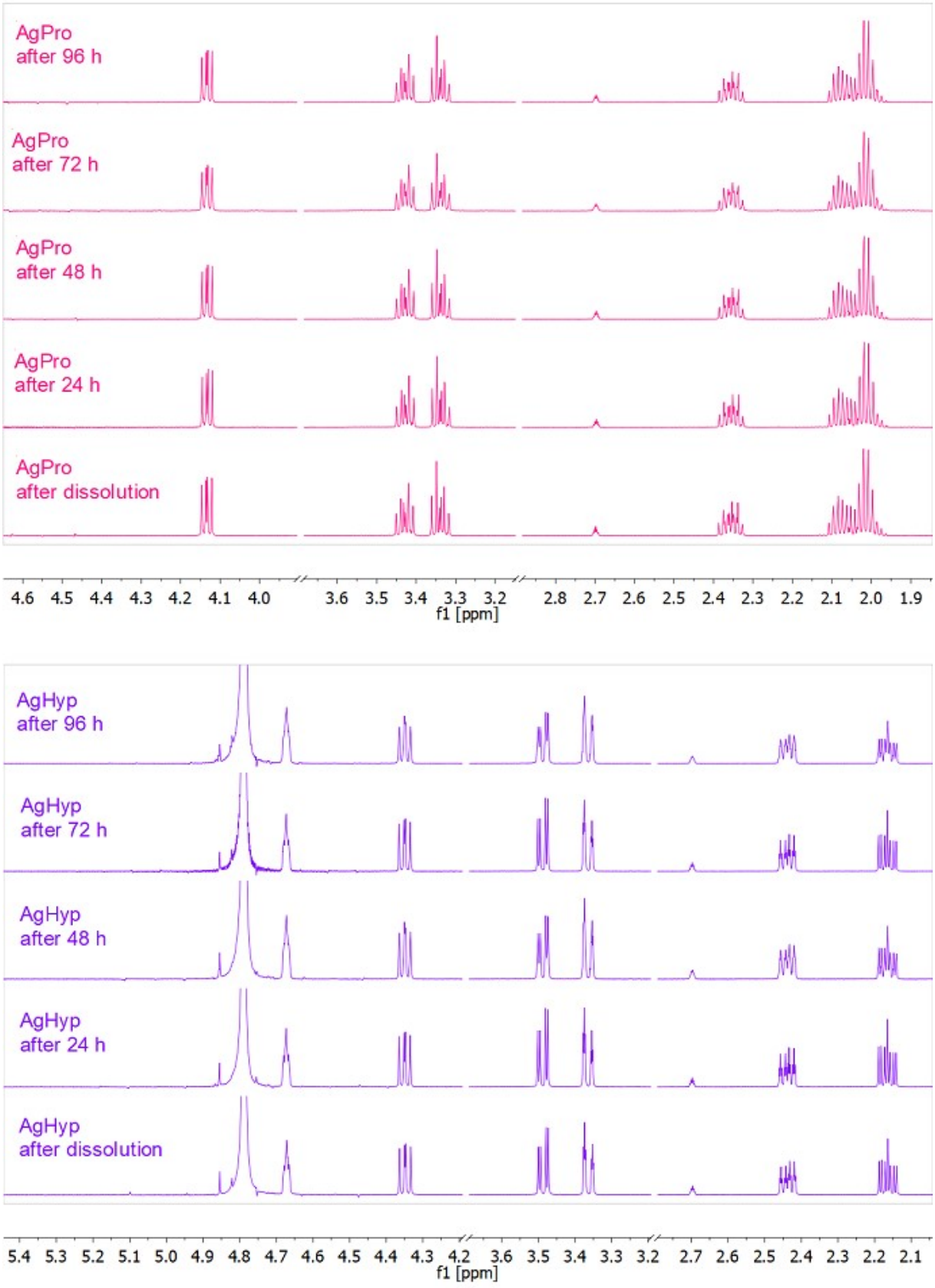


Figure S6 Time-dependent ^{1}H NMR spectra of AgPro (pink lines) and AgHyp (violet lines) complexes recorded in 1% DMSO-d_6/D_2O.

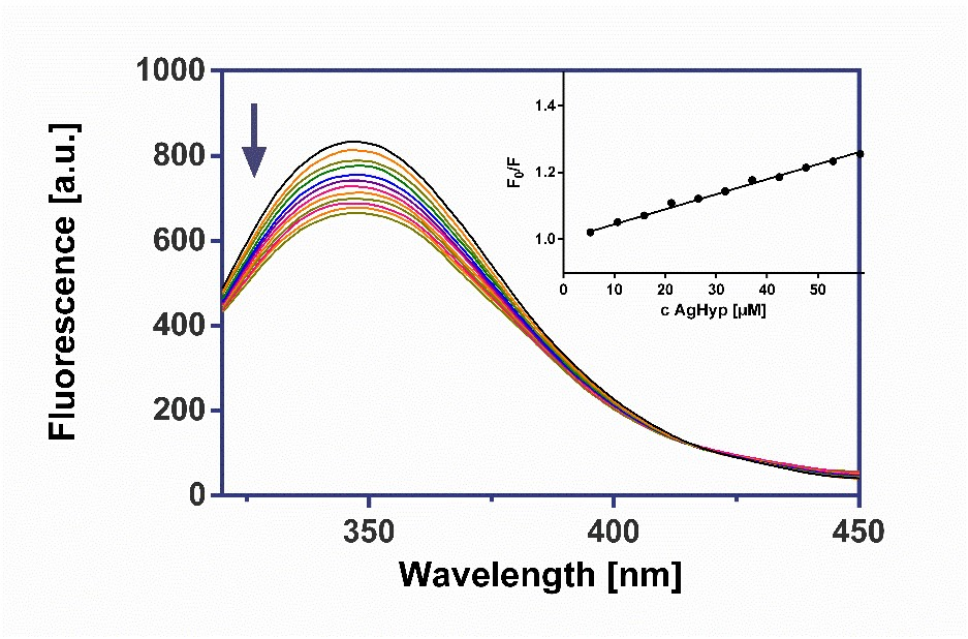


Figure S7 Fluorescence quenching spectra of BSA in presence of AgHyp. Inset: The corresponding Stern–Volmer plot for AgHyp and BSA at 293.15 K.

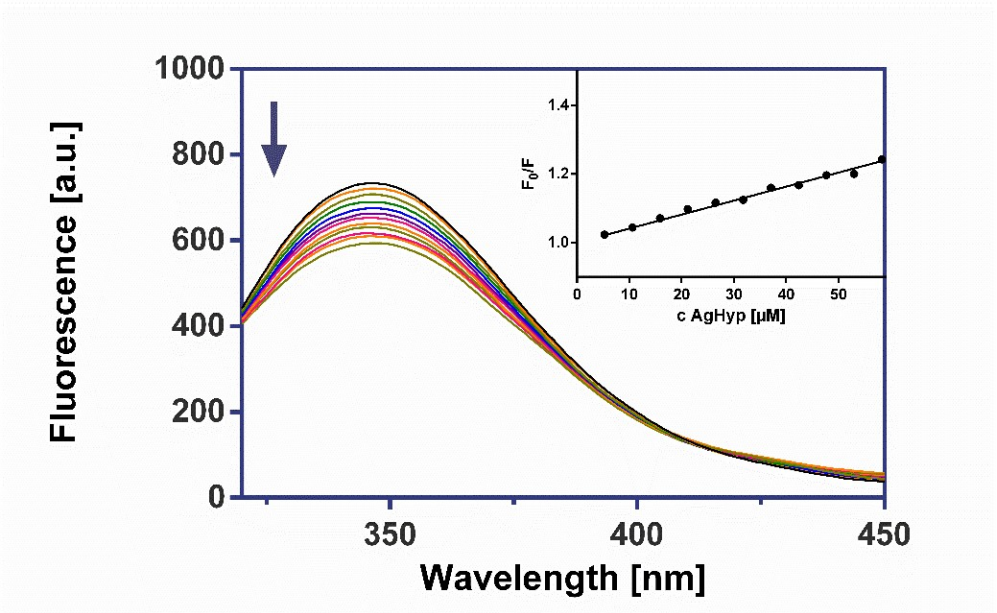
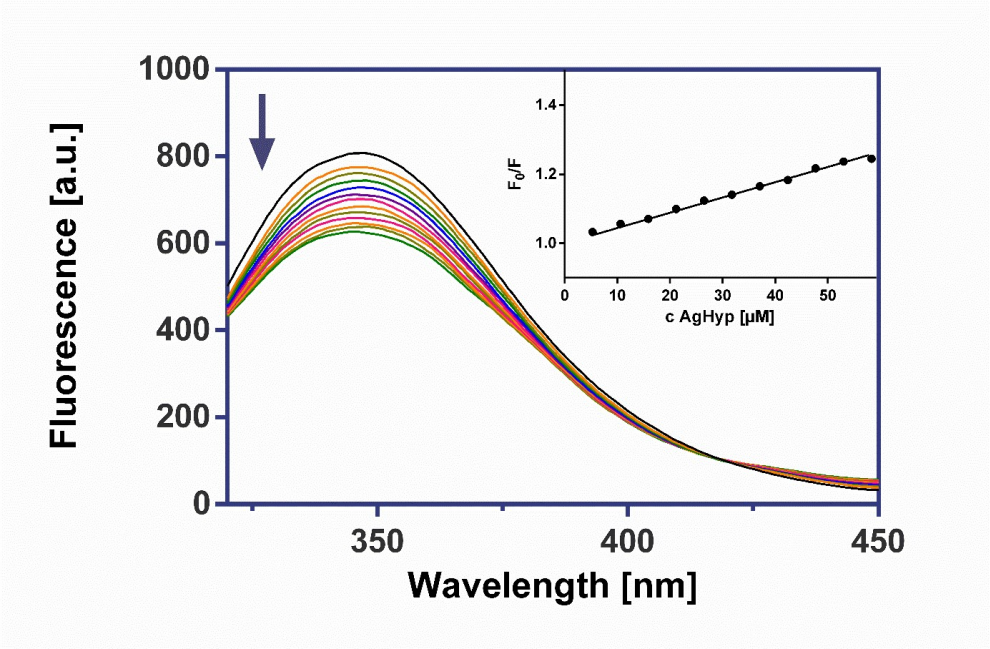


Figure S8 Fluorescence quenching spectra of BSA in presence of AgHyp. Inset: The corresponding Stern–Volmer plot for AgHyp and BSA at 303.15 K.



Figure

Figure S9 Fluorescence quenching spectra of BSA in presence of AgHyp. Inset: The corresponding Stern–Volmer plot for AgHyp and BSA at 308.15 K.

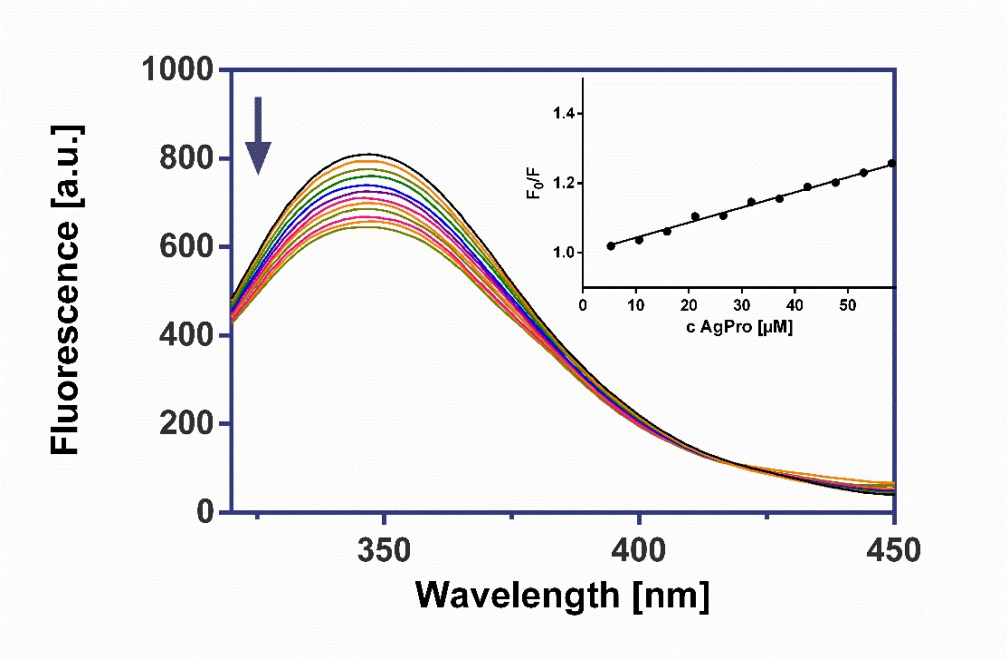


Figure S10 Fluorescence quenching spectra of BSA in presence of AgPro. Inset: The corresponding Stern–Volmer plot for AgPro and BSA at 293.15 K.

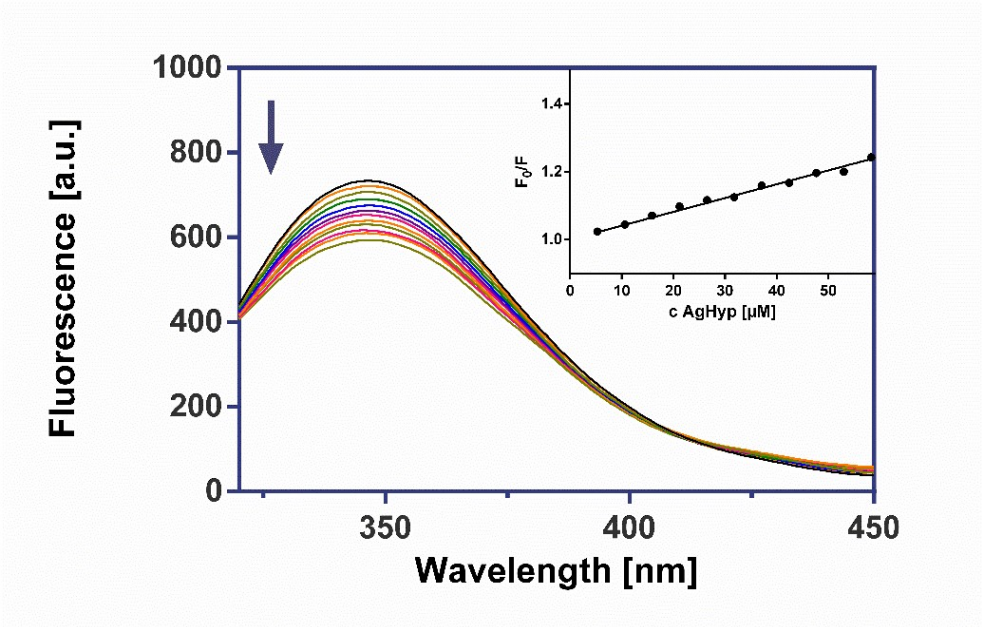


Figure S11 Fluorescence quenching spectra of BSA in presence of AgPro. Inset: The corresponding Stern–Volmer plot for AgPro and BSA at 303.15 K.

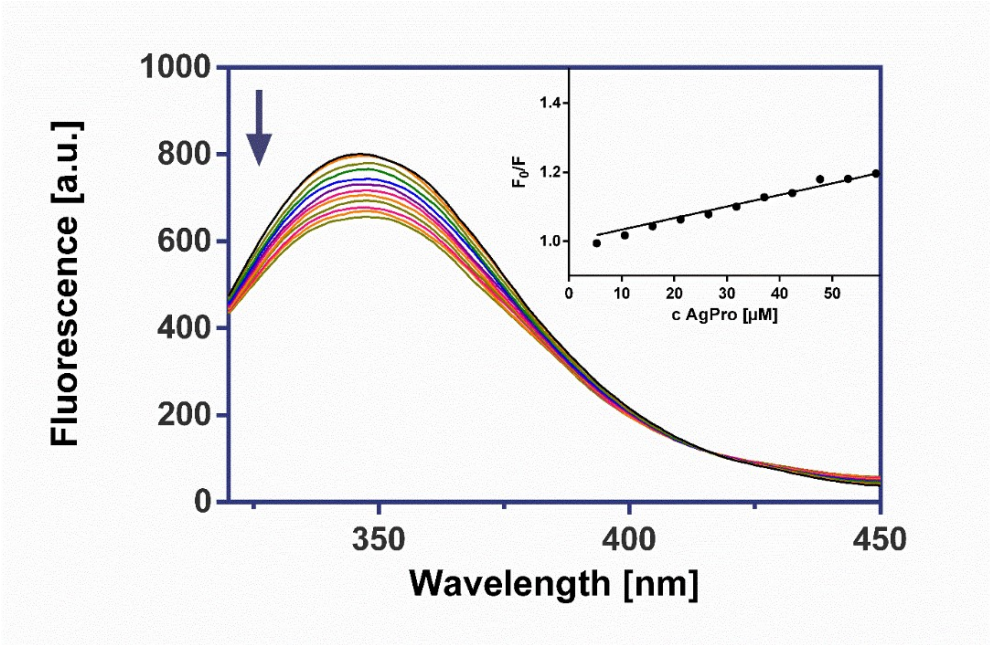


Figure S12 Fluorescence quenching spectra of BSA in presence of AgPro. Inset: The corresponding Stern–Volmer plot for AgPro and BSA at 308.15 K.

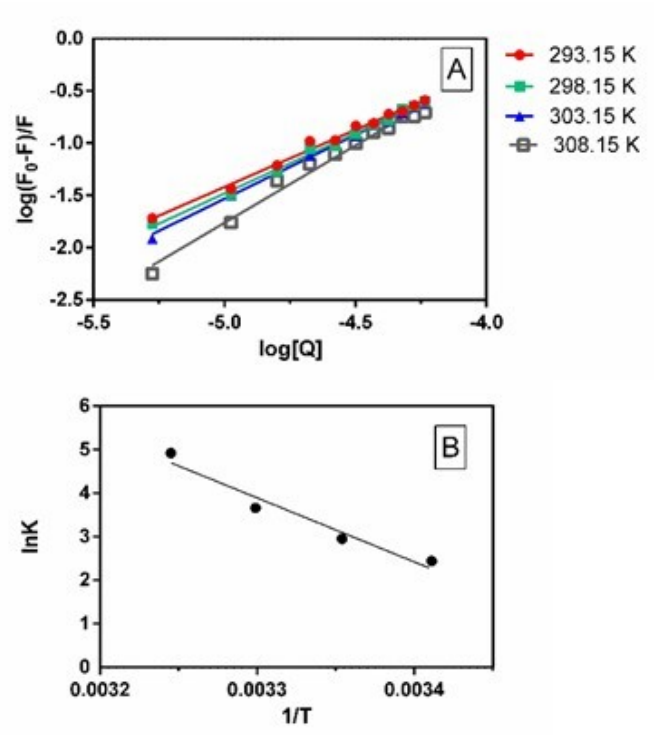


Figure S13 (A) Plot of log[(F_0 - F) / F] vs. log[AgPro] at different temperatures. (B) Van't Hoff diagram of the AgPro complex interaction with BSA**.**

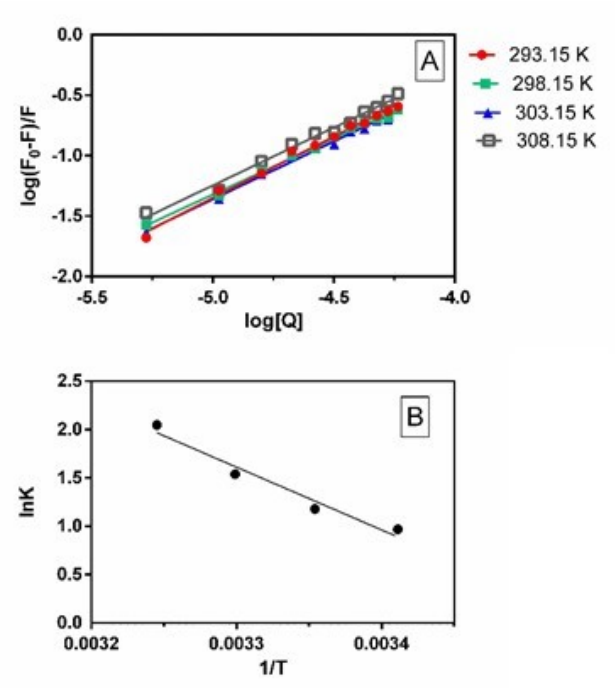


Figure 14 (A) Plot of log [(F_0 - F) / F] vs. log[AgHyp] at different temperatures. (B) Van't Hoff diagram of the AgHyp complex interaction with BSA.