Electronic Supplementary Information

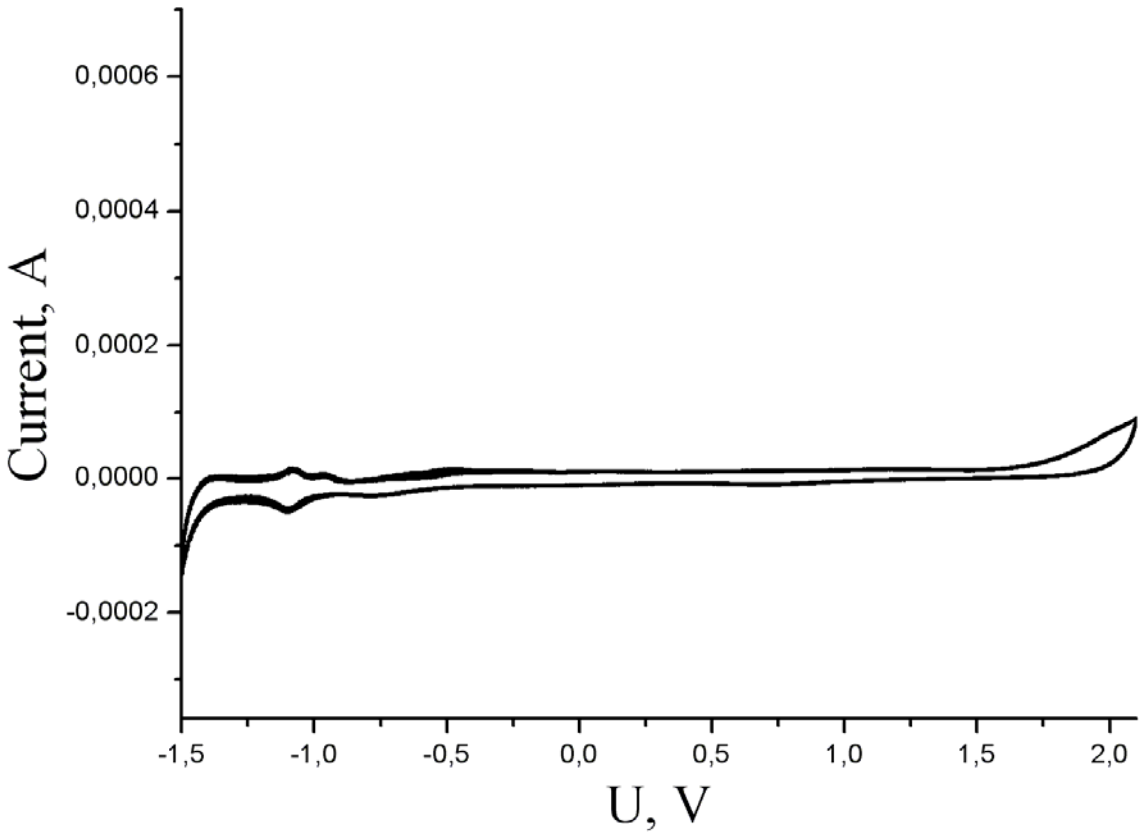

Fig.S1. Cyclic voltammogram of supporting electrolyte (0.5 M $NaClO_4$ in CH_3CN). Scan rate 100 mV/s.

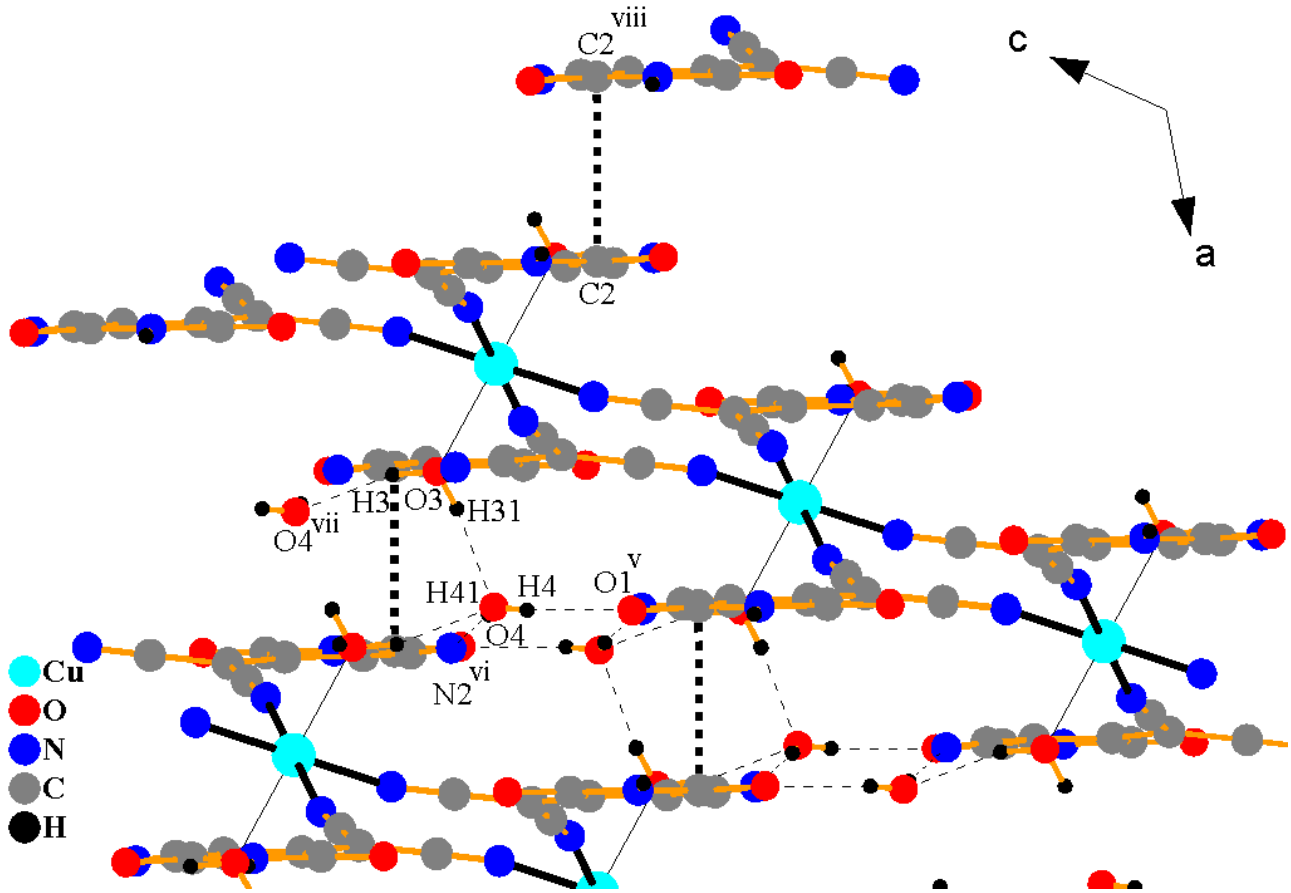

Fig.S2. 3D structure of **1** constructed of 2D layers, which are connected by hydrogen bonds and π-π stacking interactions. Hydrogen bonds are depicted as dashed lines. Stacking interactions are depicted as dotted lines. [Symmetry codes: (v) 0.5-x;0.5+y;-0.5-z; (vi) 0.5+x,1.5-y,0.5+z; (vii) 1-x, y,0.5-z; (viii) -x,y,-0.5-z].

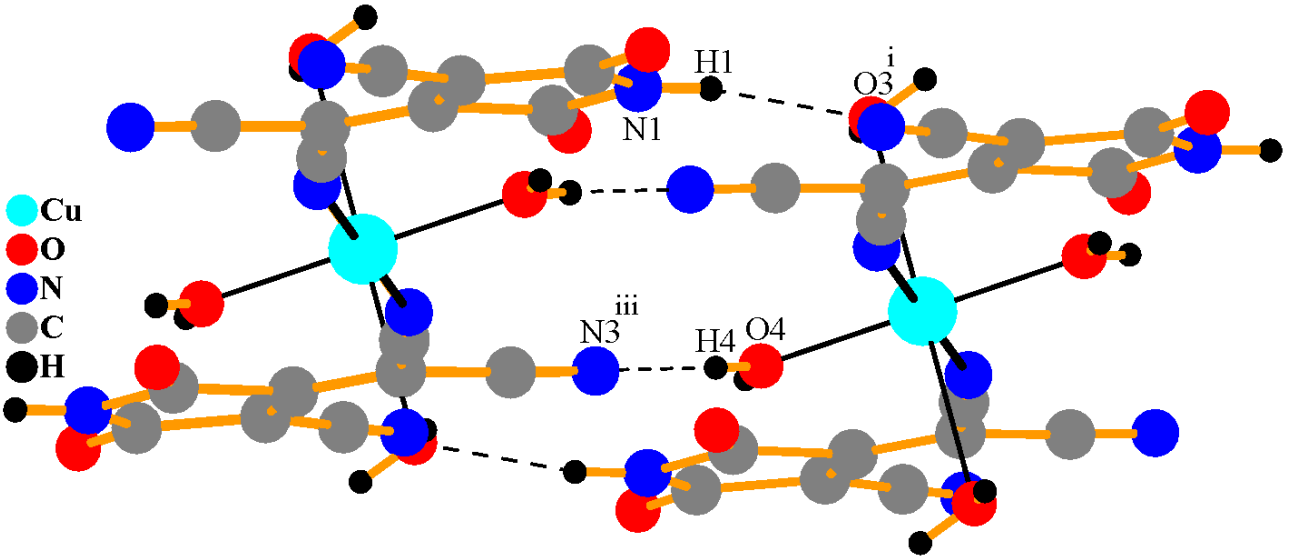

Fig.S3. Adjacent rods, connected by hydrogen bonds in crystal structure of **2**. Hydrogen bonds are depicted as dashed lines. [Symmetry codes: (i) 1-x,-y,-z; (iii) -x,-y,1-z].

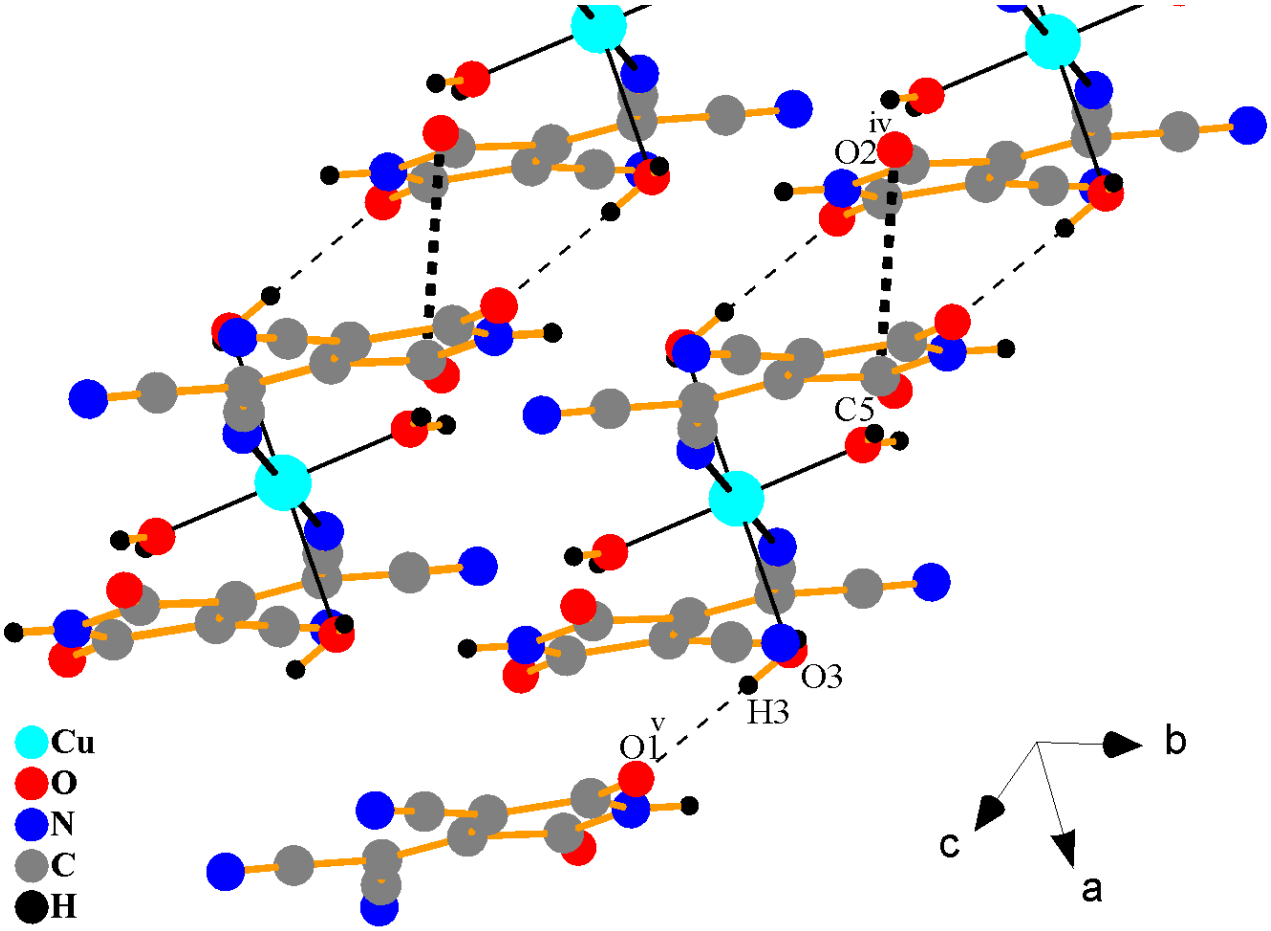

Fig.S4. A view of **2**, showing how stacking interactions and hydrogen bonds link adjacent layers. Hydrogen bonds are depicted as dashed lines. π-π Stacking interactions are depicted as dotted lines. [Symmetry codes: (iv) -x,1-y,-z; (v) 1+x,-1+y,z].

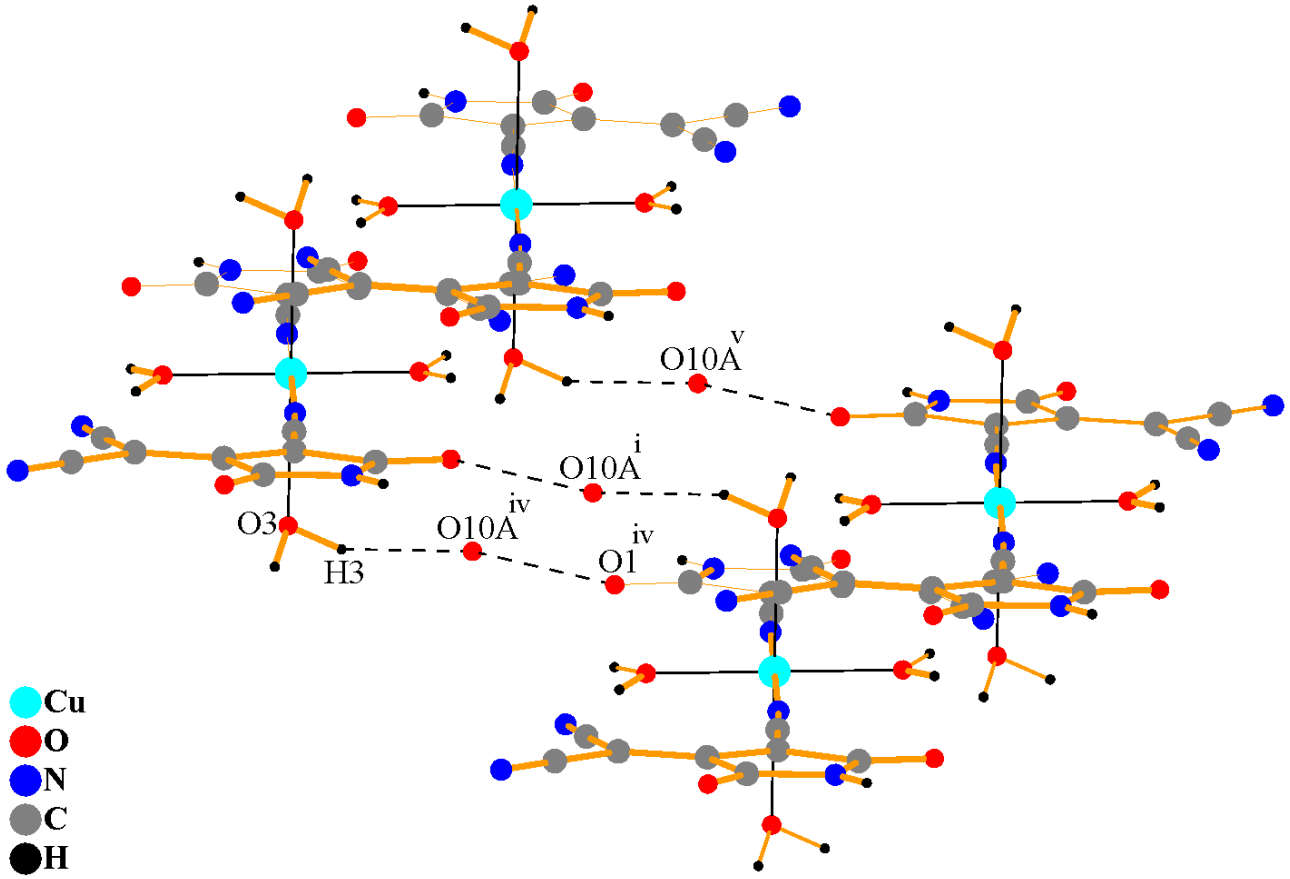

Fig.S5. Adjacent walls, connected by hydrogen bonds in crystal structure of **3**. O10A^{i}, O10A^{iv}, O10A^{v} atoms belong to solvated water molecules. Hydrogen bonds are depicted as dashed lines. [Symmetry codes: (i) -x,-y,-z; (iv) -1+x, -1+y, z; (v)-2+x,-1+y,z].

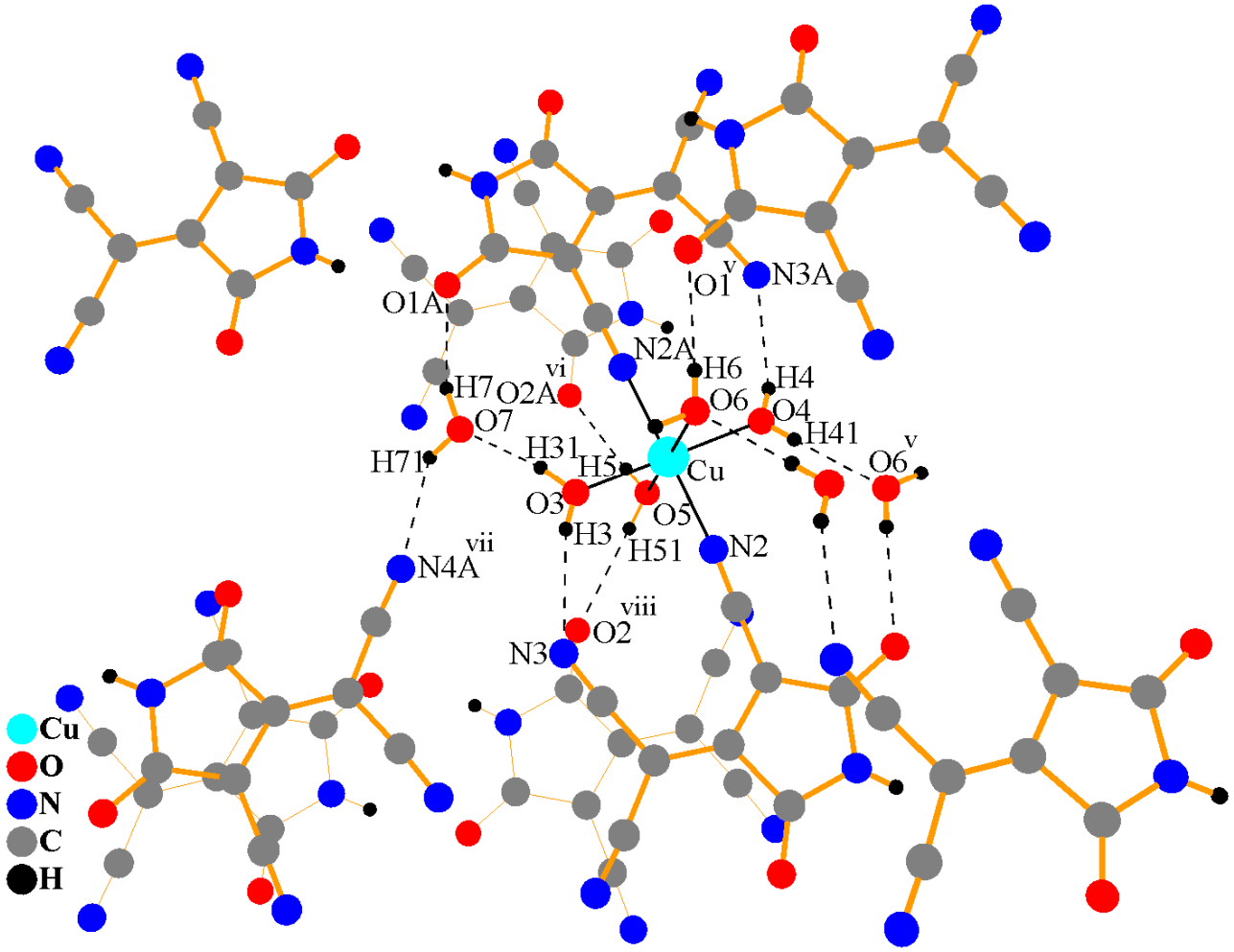

Fig.S6. Part of the crystal structure of **4**, showing adjacent anionic walls, connected by Cu–N coordination bonds and by hydrogen bonds. Hydrogen bonds are depicted as dashed lines. Hydrogen bonds geometry and symmetry codes are listed in Table 2.

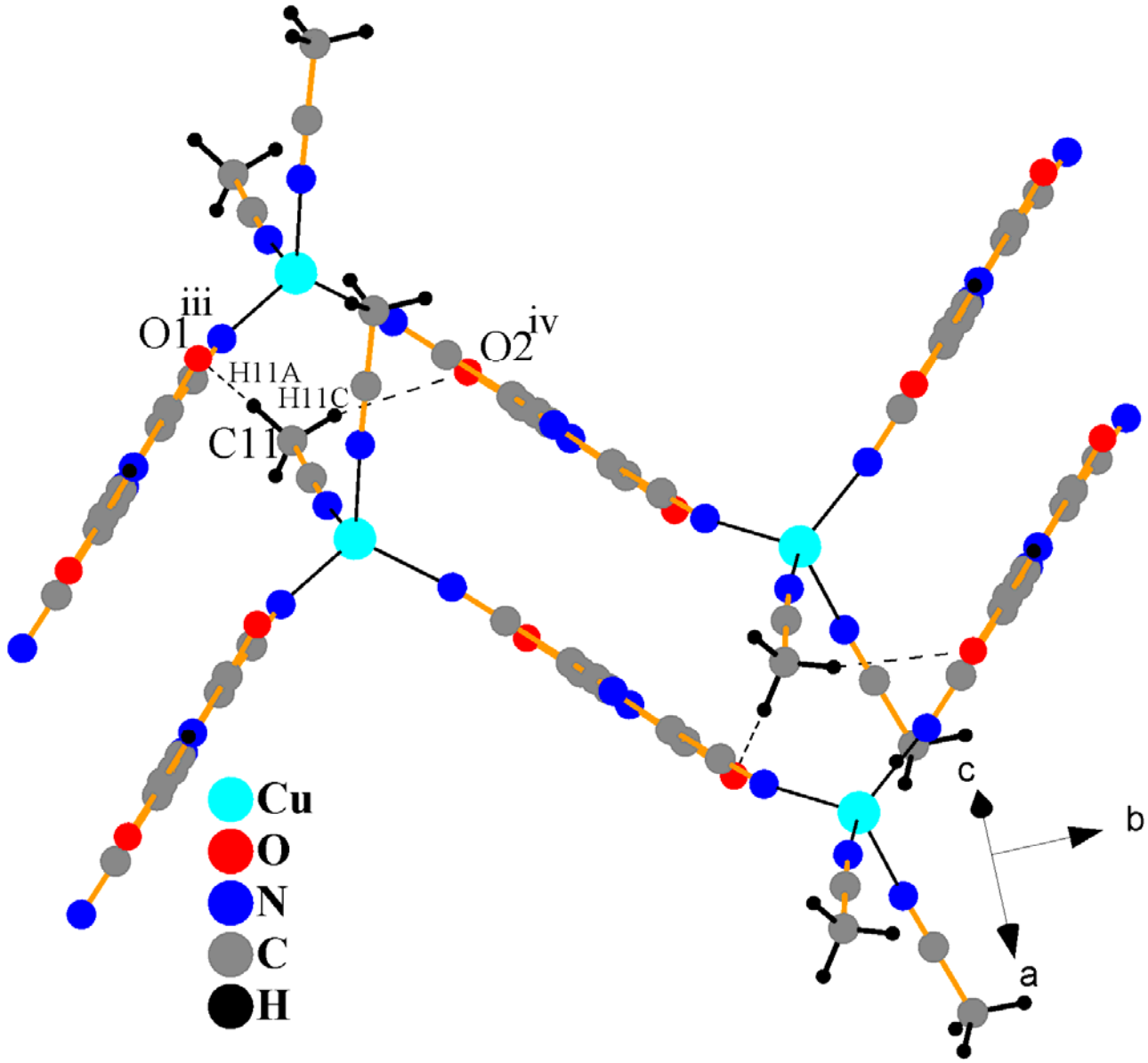

Fig.S7. 3D structure of **5** constructed of 2D layers, which are connected by C–H···O hydrogen bonds. Hydrogen bonds are depicted as dashed lines. [Symmetry codes: (iii) -x,-0.5+y,-1-z; (iv) -1+x,y,z].

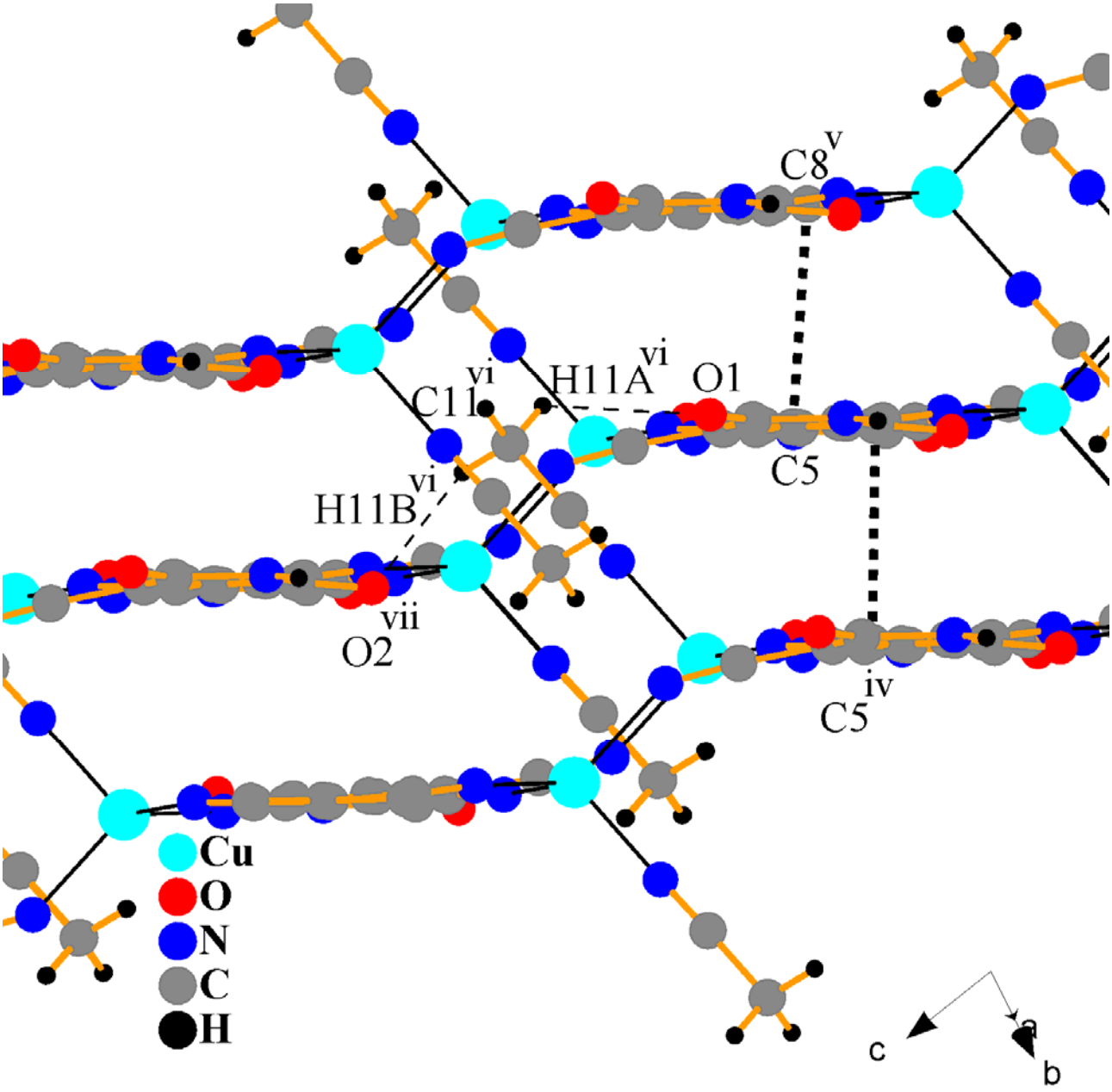

Fig.S8. 3D structure of **6** constructed of 2D layers, which are connected by C–H···O hydrogen bonds and π-π stacking ineractions. Hydrogen bonds are depicted as dashed lines. π-π Stacking interactions are depicted as dotted lines. [Symmetry codes: (iv) 1-x,2-y,-z; (v) 1-x,1-y,-z; (vi) -x,2-y,1-z; (vii) -1+x,y,1+z].

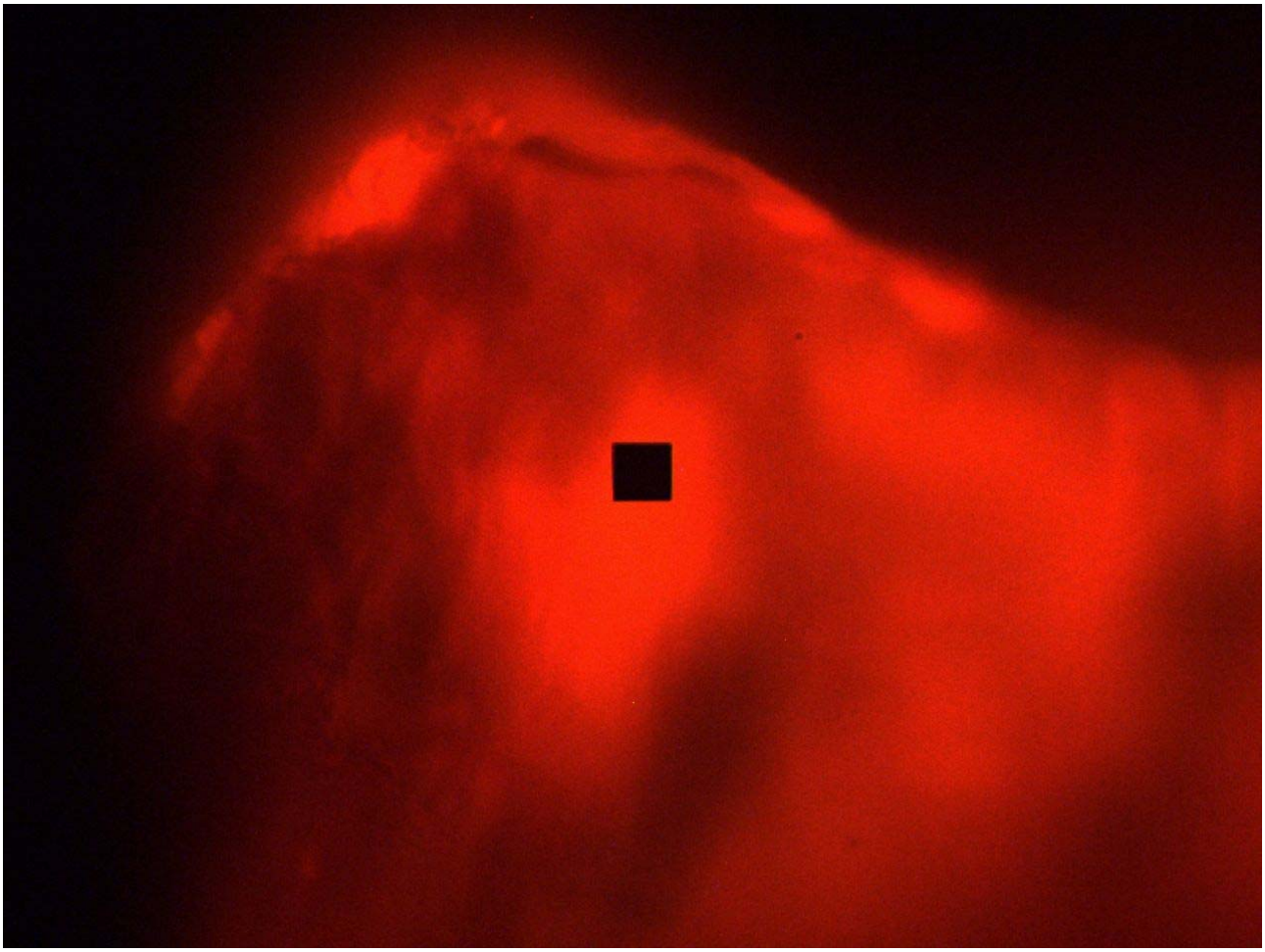

Fig.S9. Photoluminescence microscopy image of crystal of $\{[Cu^{I}(HA)(CH_3CN)_2]\}_n$ (**5**) under green light (wavelength 515-560 nm) excitation.

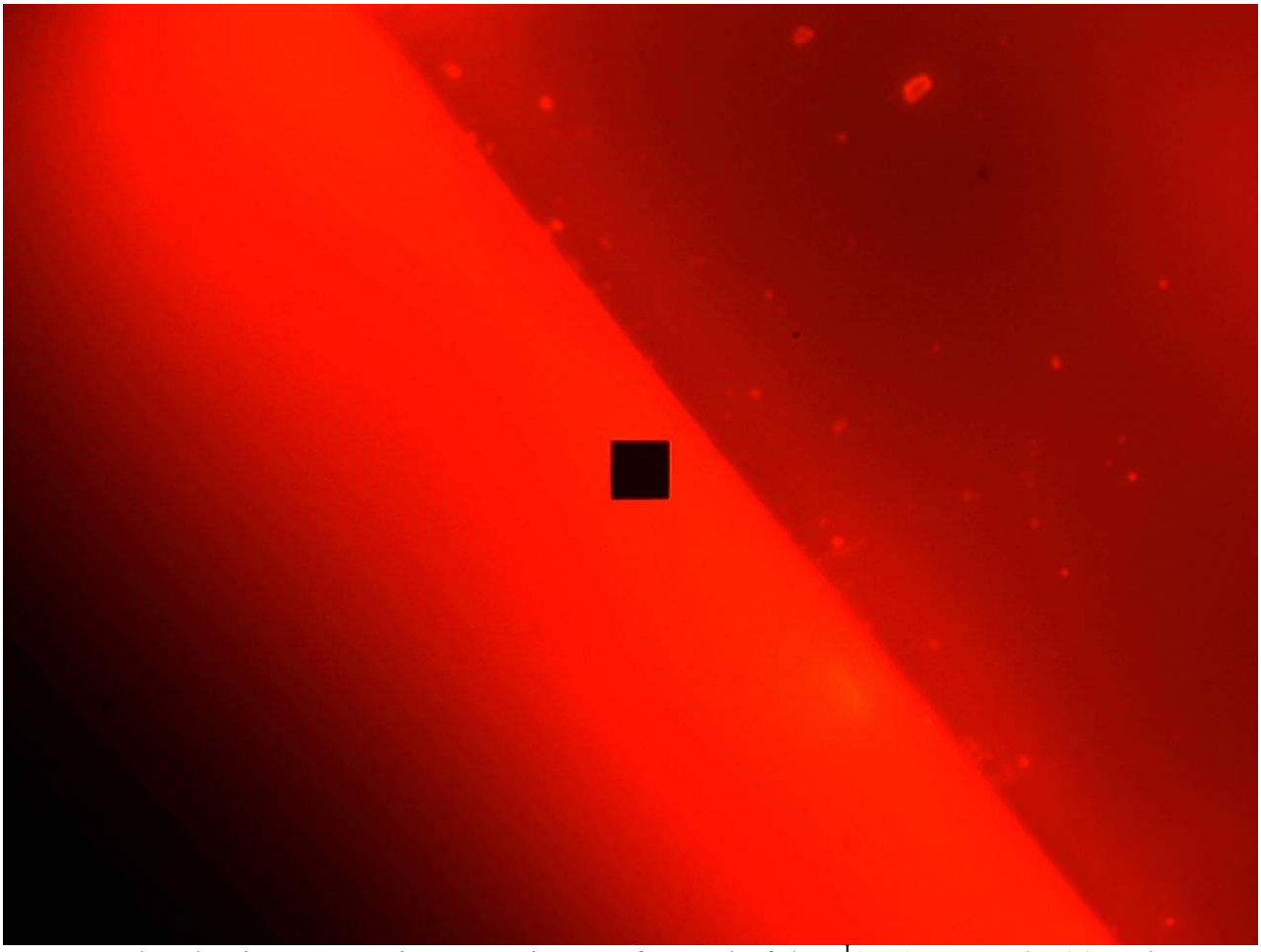

Fig.S10. Photoluminescence microscopy image of crystal of $\{[Cu^{I}(HA)CH_3CN]\}_n$ (**6**) under green light (wavelength 515-560 nm) excitation.

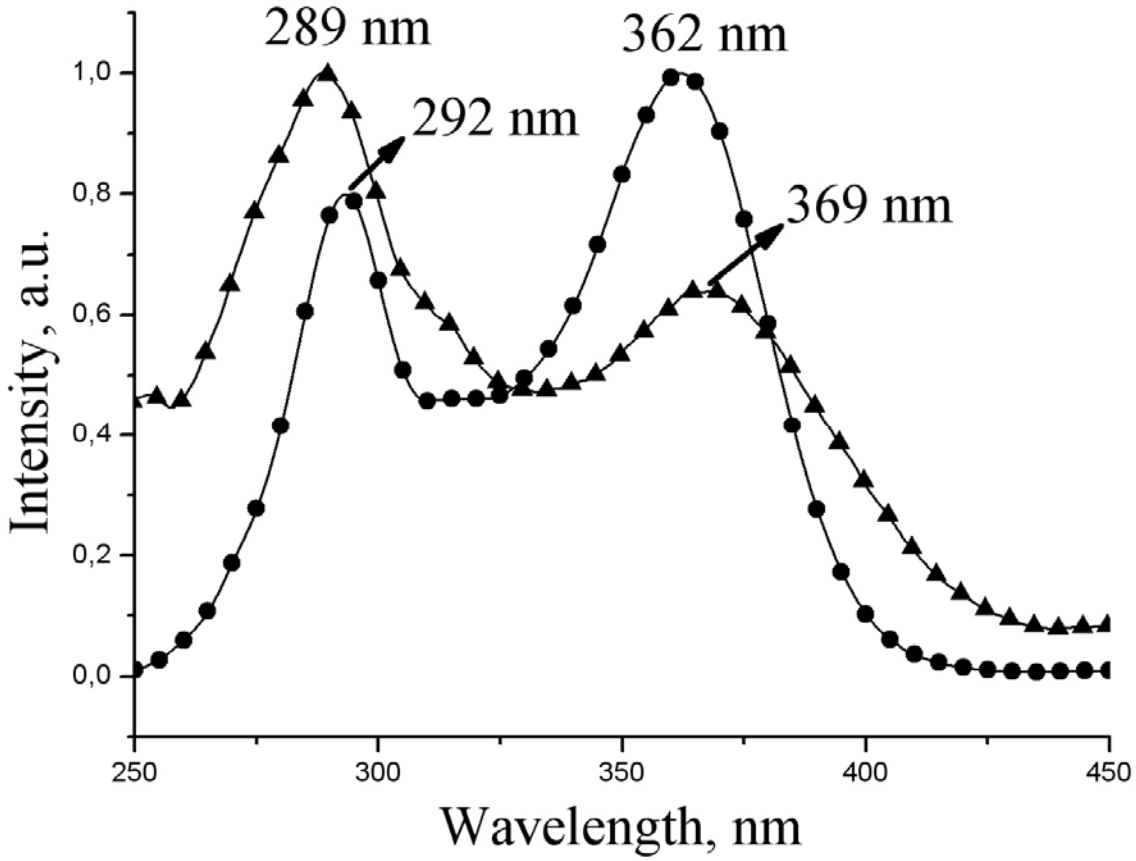

Fig.S11. Normalized excitation spectra of K(HA) ($2.7 \cdot 10^{-4}$ M) (line with triangles; 494 nm emission band), K(HA) ($2.7 \cdot 10^{-4}$ M) + $Cu(H_2O)_6(ClO_4)_2$ ($4.2 \cdot 10^{-4}$ M) (line with circles; 502 nm emission band) solutions in acetonitrile.

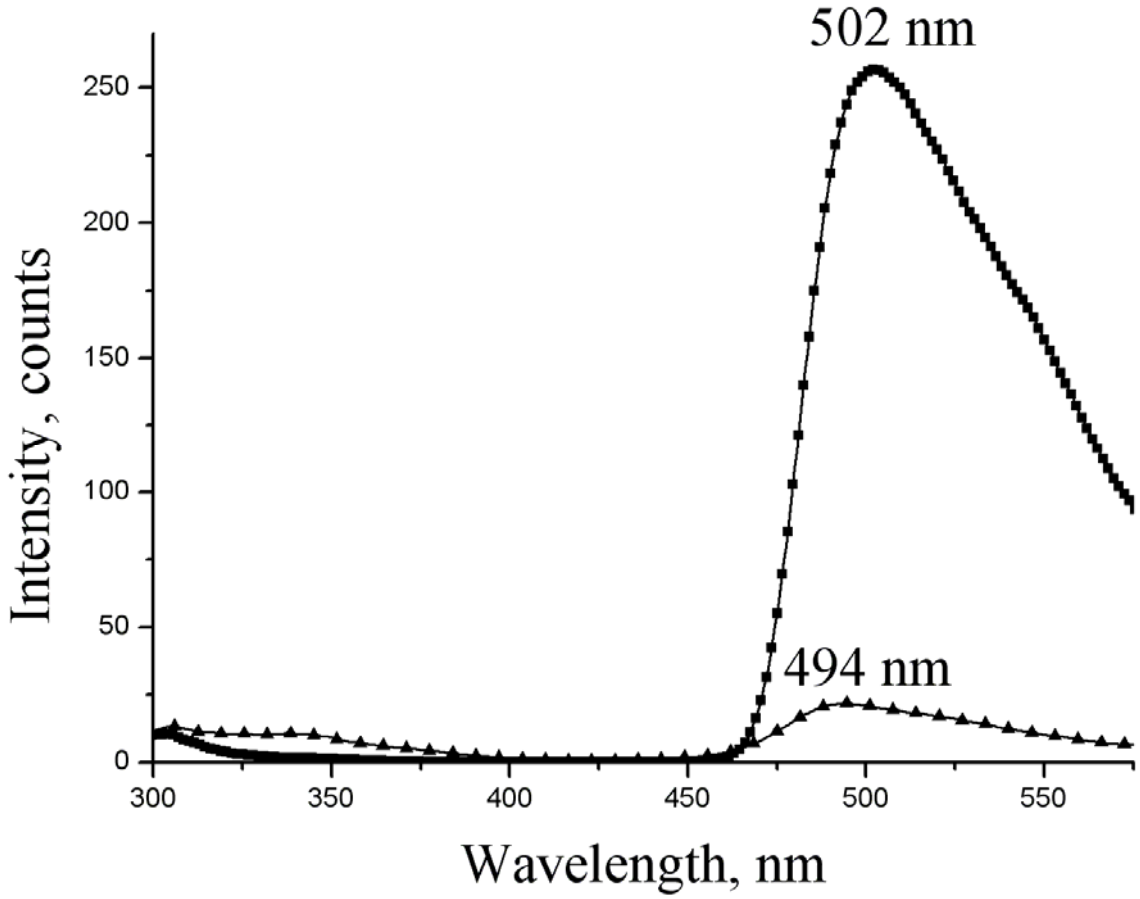

Fig.S12. Photoluminescence spectra of K(HA) ($2.7\cdot10^{-4}$ M) (line with triangles), $\{[Cu^{II}(HA)_2(H_2O)_2]\}_n\cdot 2nH_2O$ (**1**) ($0.8*10^{-4}$ M) (line with squares) solutions in acetonitrile (excitation wavelength 275 nm). For excitation spectra of $\{[Cu^{II}(HA)_2(H_2O)_2]\}_n\cdot 2nH_2O$ (502 nm emission band) solution in acetonitrile see Fig.S14.

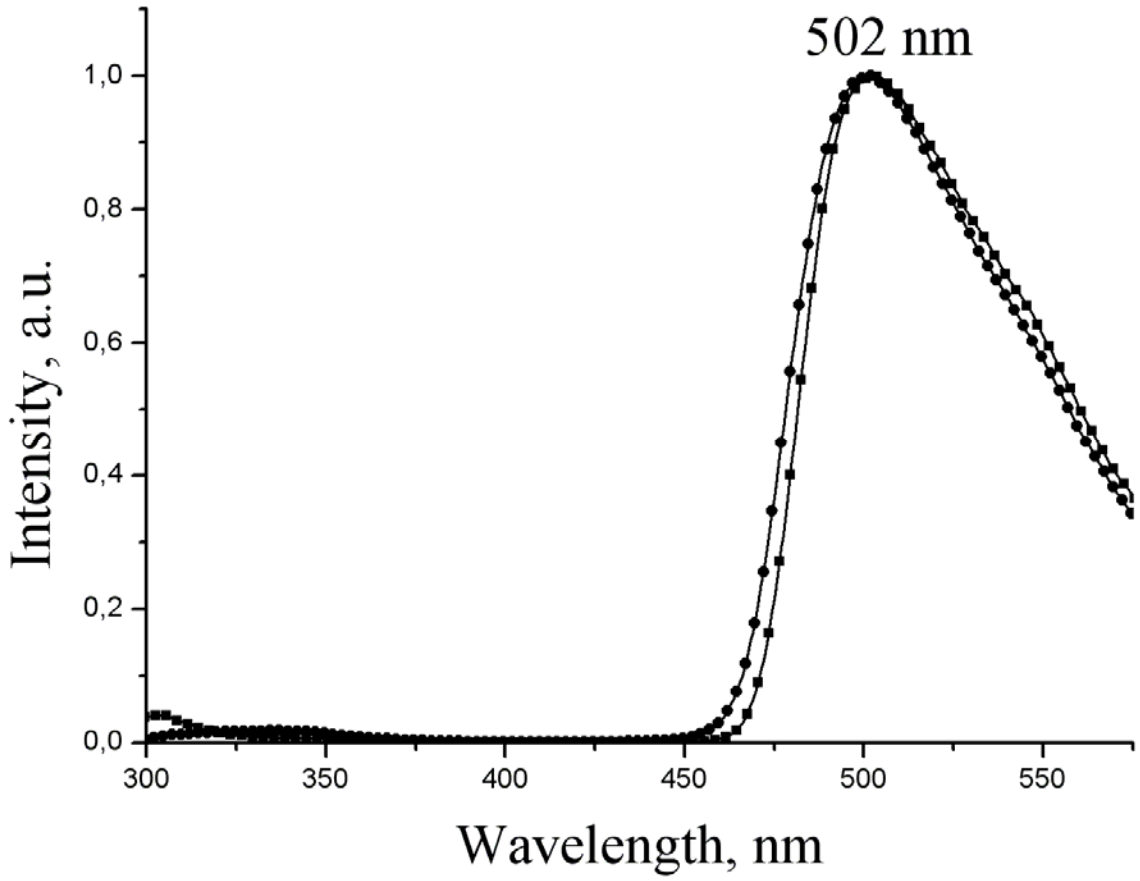

Fig.S13. Normalized photoluminescence spectra of K(HA) ($2.7\cdot10^{-4}$ M) + $Cu(H_2O)_6(ClO_4)_2$ ($4.2\cdot10^{-4}$ M) (line with circles), $\{[Cu^{II}(HA)_2(H_2O)_2]\}_n\cdot2nH_2O$ (**1**) ($0.8*10^{-4}$ M) (line with squares) solutions in acetonitrile (excitation wavelength 275 nm).

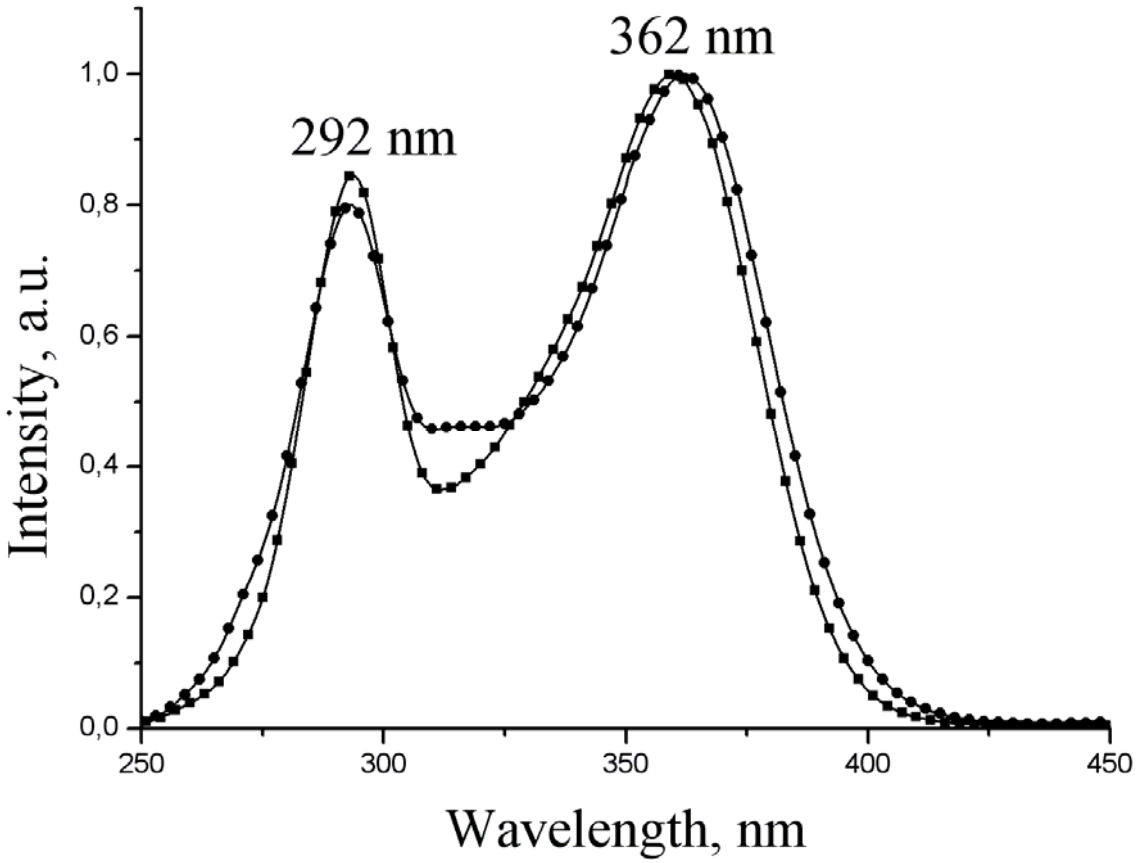

Fig.S14. Normalized excitation spectra of K(HA) ($2.7\cdot10^{-4}$ M) + $Cu(H_2O)_6(ClO_4)_2$ ($4.2\cdot10^{-4}$ M) (line with circles; 502 nm emission band), $\{[Cu(HA)_2(H_2O)_2]\}_n\cdot2nH_2O$ (**1**) ($0.8*10^{-4}$ M) (line with squares; 502 nm emission band) solutions in acetonitrile.

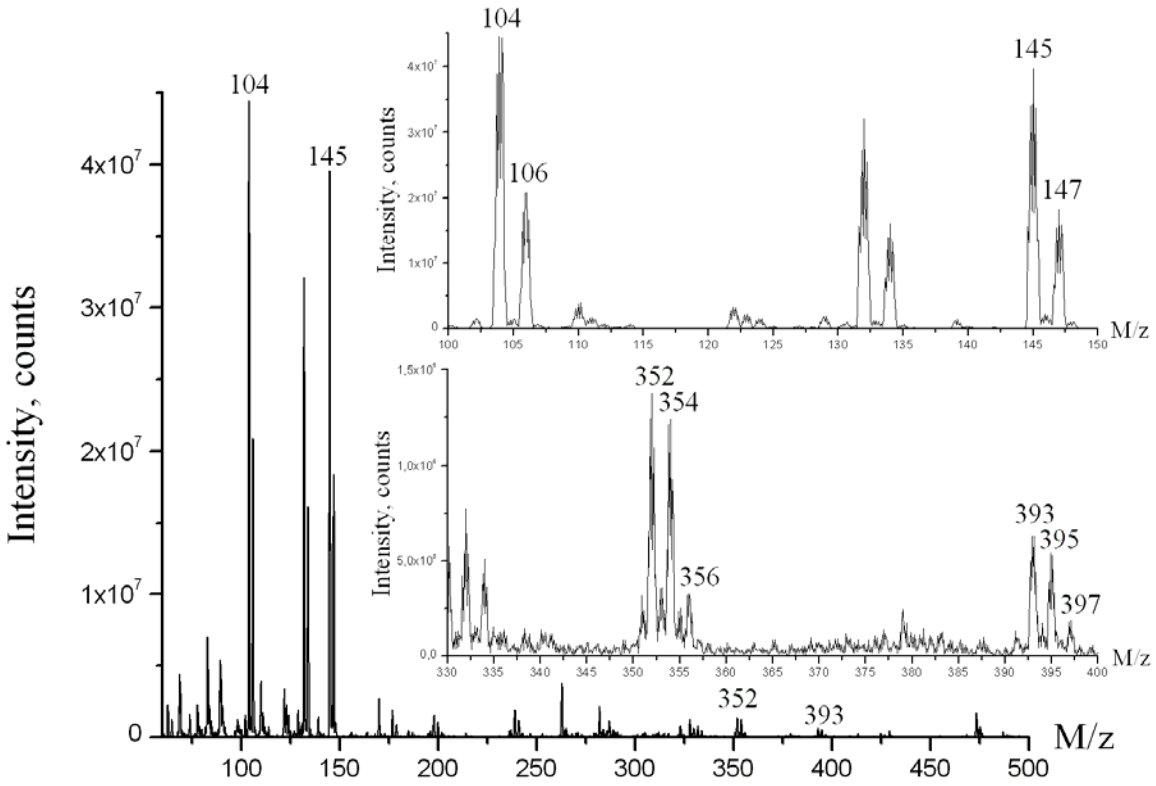

Fig.S15. Electrospray mass spectrum (positive ions) of K(HA) ($1.4 \cdot 10^{-4}$ M) + $Cu(H_2O)_6(ClO_4)_2$ ($2.1 \cdot 10^{-4}$ M) solution in acetonitrile.

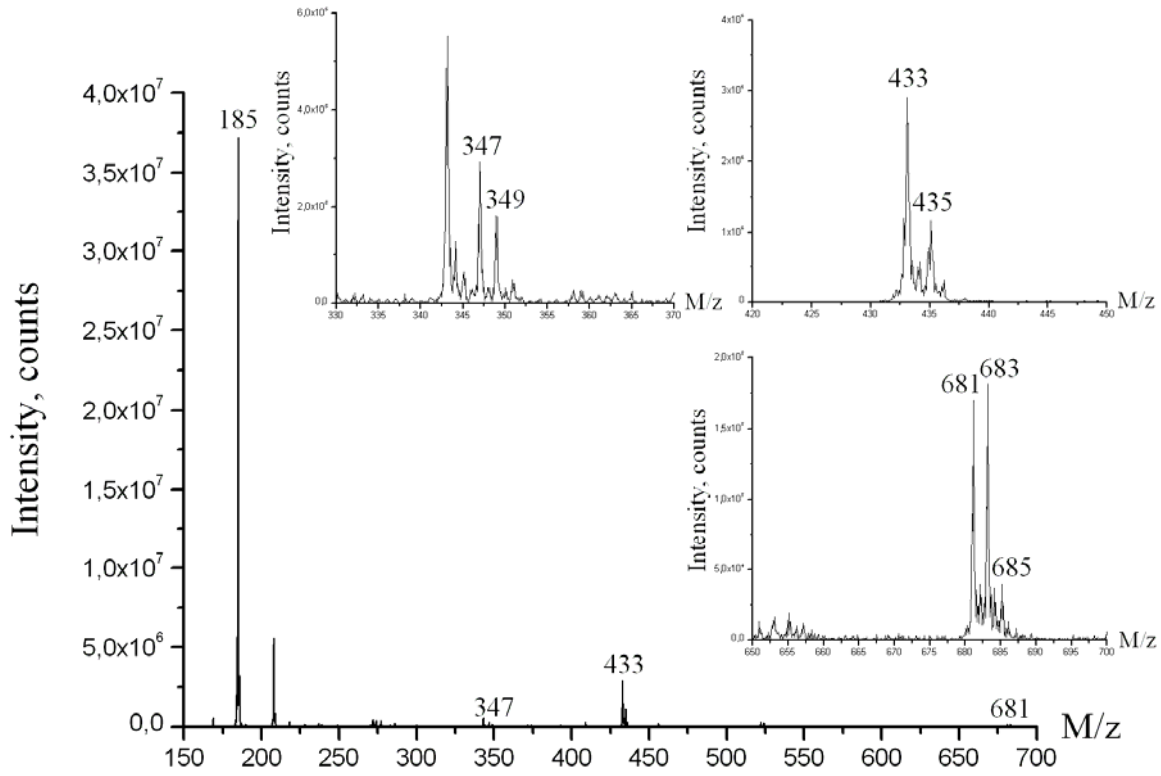

Fig.S16 Electrospray mass spectrum (negative ions) of K(HA) ($1.4 \cdot 10^{-4}$ M) + $Cu(H_2O)_6(ClO_4)_2$ ($2.1 \cdot 10^{-4}$ M) solution in acetonitrile.

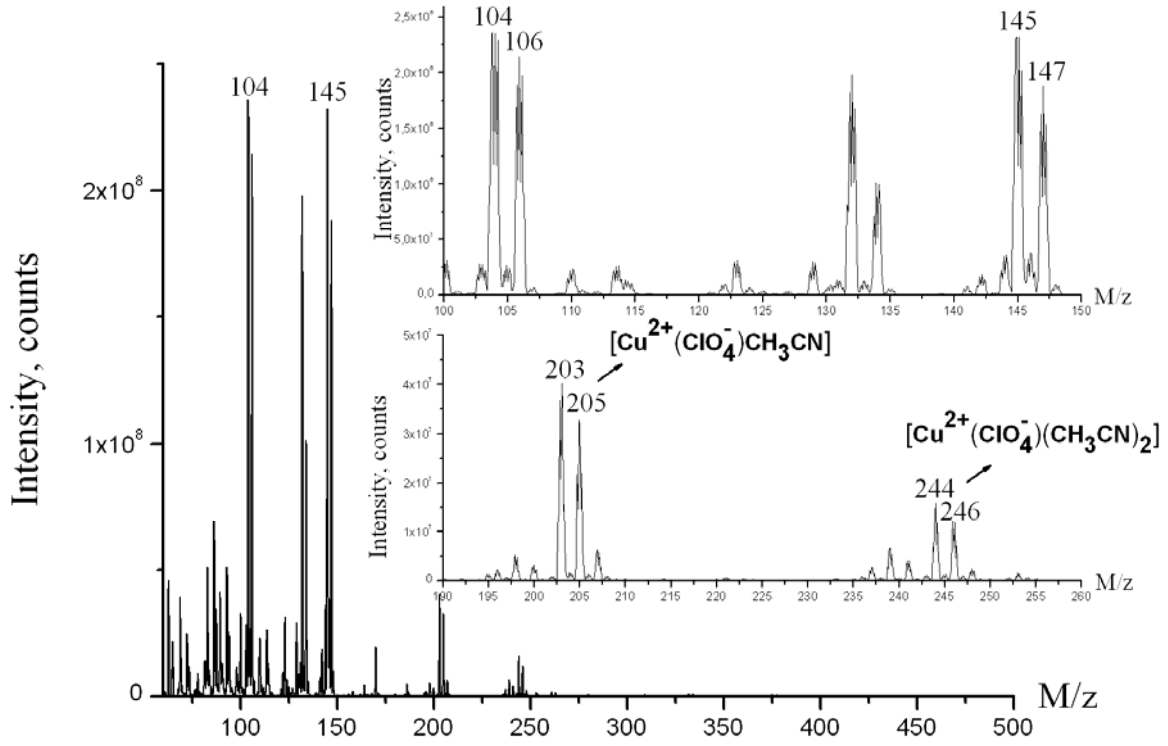

Fig.S17. Electrospray mass spectrum (positive ions) of $Cu(H_2O)_6(ClO_4)_2$ ($4.3 \cdot 10^{-4}$ M) solution in acetonitrile.

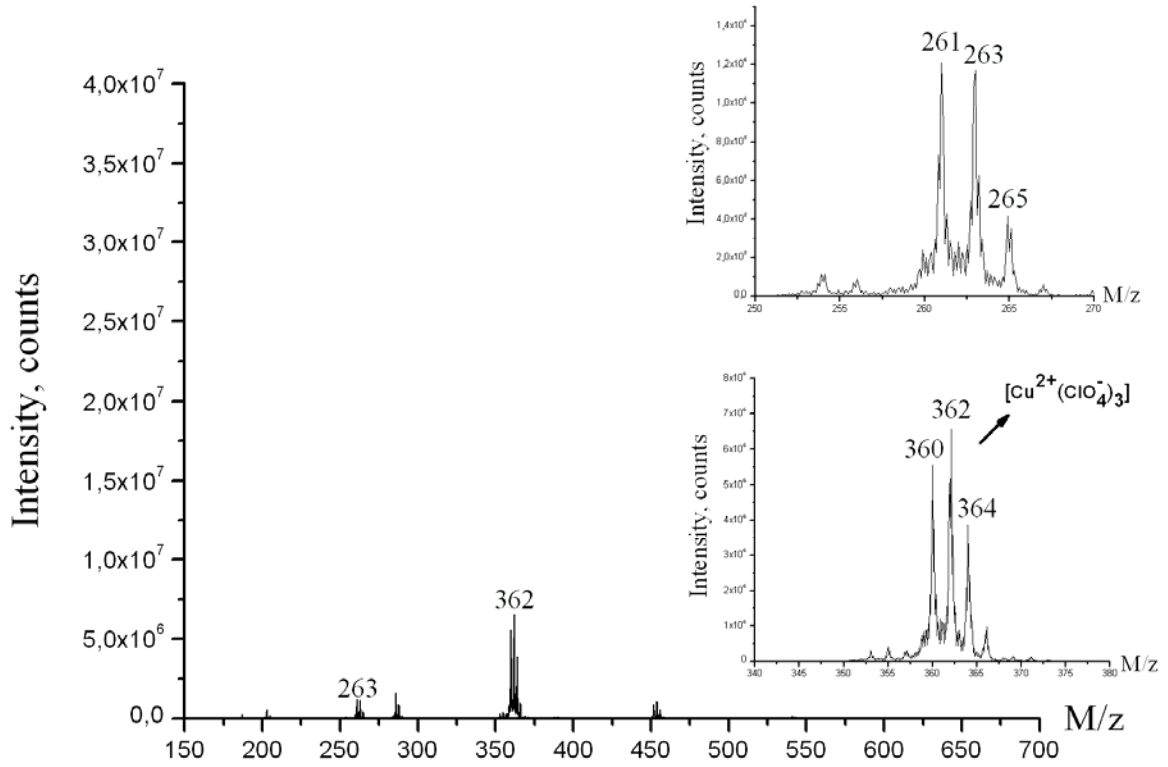

Fig.S18. Electrospray mass spectrum (negative ions) of $Cu(H_2O)_6(ClO_4)_2$ ($4.3 \cdot 10^{-4}$ M) solution in acetonitrile.

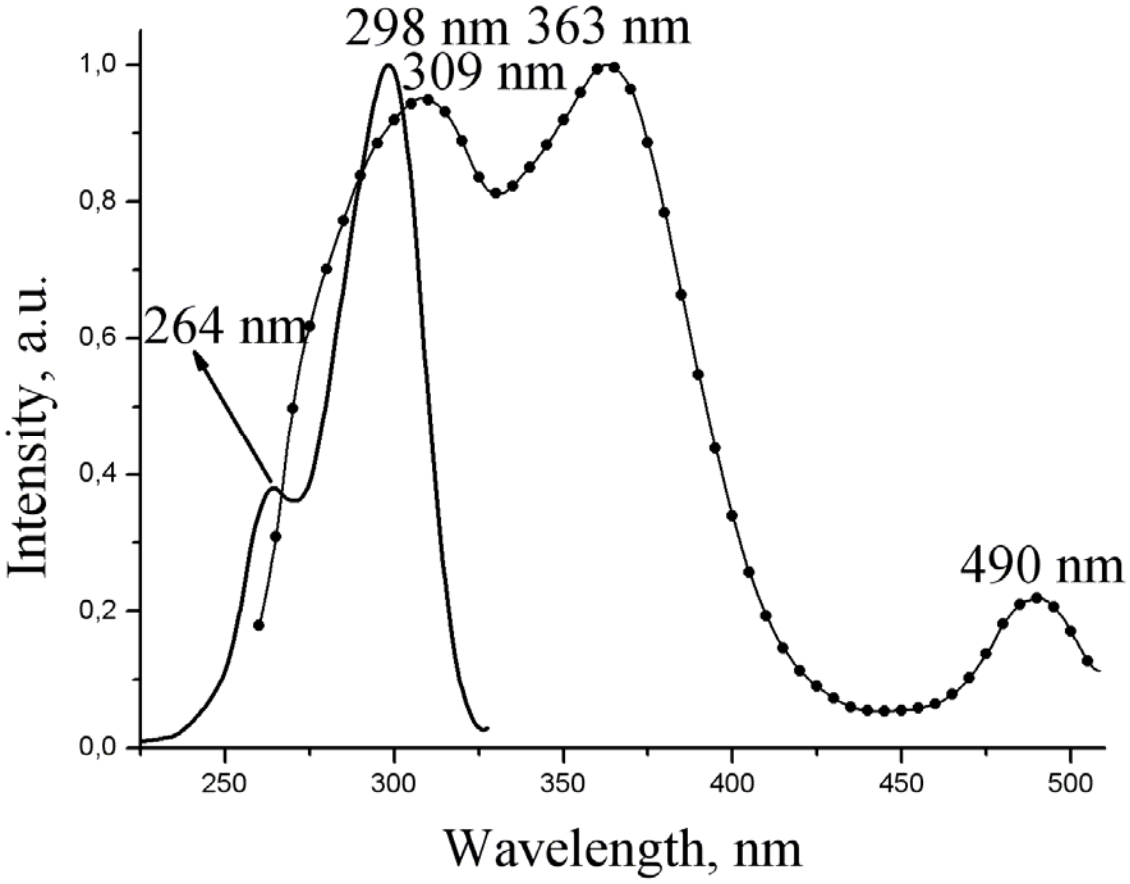

Fig.S19. Normalized excitation spectra of K(HA) ($2.7 \cdot 10^{-4}$ M) + $Cu(H_2O)_6(ClO_4)_2$ ($4.2 \cdot 10^{-4}$ M) acetonitrile solution diluted twice with water: 342 nm emission band (solid line), 520 nm emission band (line with circles).

Table S1. The distances Cu–O(N) in complexes **1-6**

Complex №	Copper coordination number	Wyckoff copper position	Distance, Å (Cu–O)	Distance, Å (Cu–N)
1	6 (2 O[1], 4N_{HA}[2]);	*d*	2.319(2)	1.975(2), 2.020(2)
2	6 (4 O, 2 N_{HA})	*d*	1.943(3), 2.435(3)	1.982(2)
3	6 (4 O, 2 N_{HA})	*a*	1.960(3), 2.486(3)	1.944(3)
4	6 (4 O, 2 N_{HA})	*i*	1.930(4), 1.948(4), 2.486(4), 2.513(4)	1.956(5), 1.976(3)
5	4 (2 N_{HA}, 2 N_{acn})	*a*		1.975(2), 1.978(3), 1.980(2), 2.018(2)
6	4 (3 N_{HA}, 1 N_{acn})	*i*		1.992(2), 2.000(2), 2.011(2), 2.032(2)

[1]O is oxygen atom from water molecule; [2]N_{HA} is nitrogen atom from cyano-group of HA^- anion; [3]N_{acn} is nitrogen atom from cyano-group of acetonitrile.