New Journal of Chemistry

Supplementary Information for

Effects of transition metal cations and temperature on luminescence of 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrole-2-olate anion

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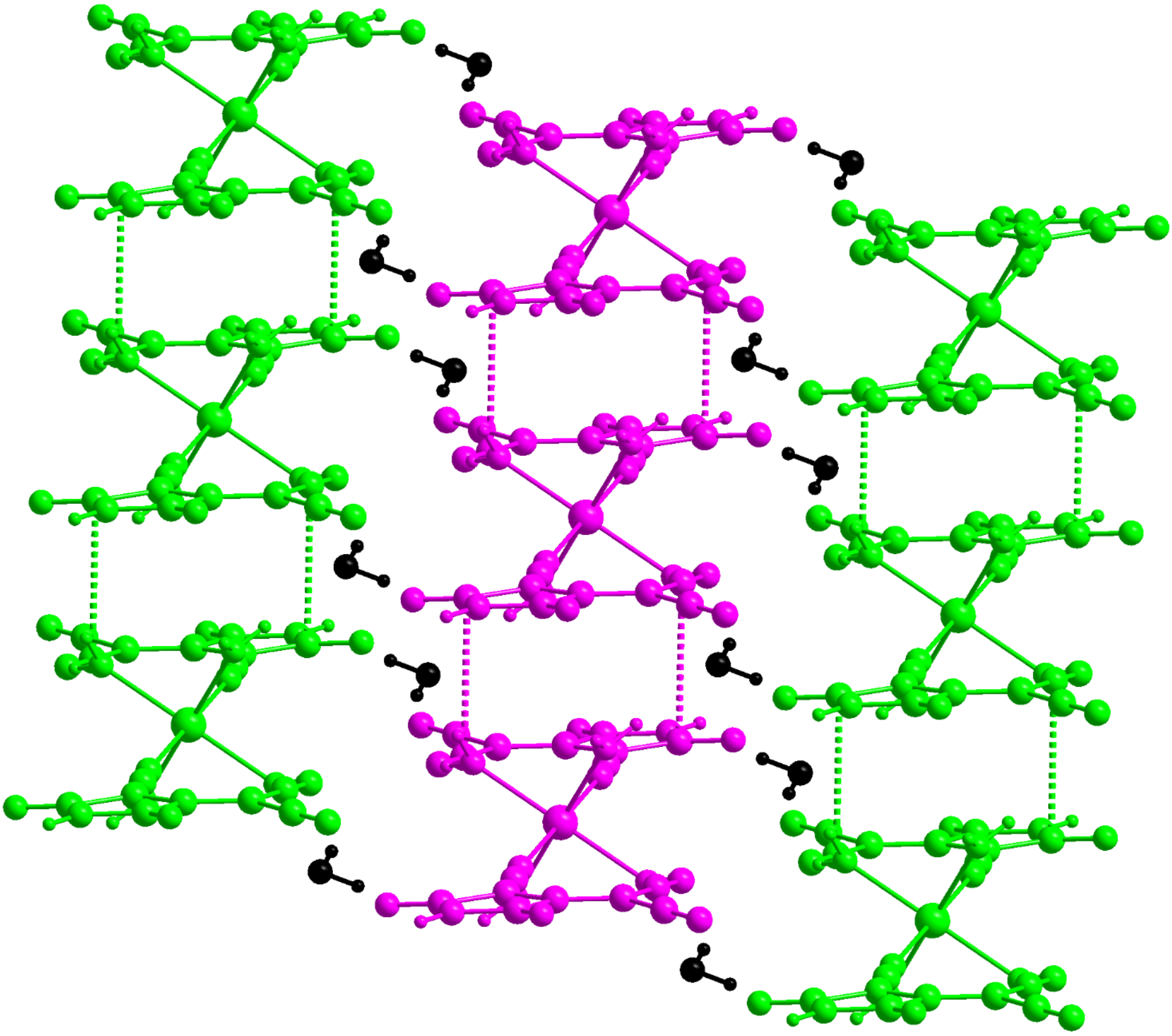


Fig. S1 Walls (marked with green and pink), which are built of $[Mn(HA)_2(H_2O)_4]_n$ infinite rods, in the crystal structure of complex $[Mn(HA)_2(H_2O)_4]\cdot 2H_2O$ (**1**). Water solvent molecules (marked with black) are located between the walls. π-π-Stacking interactions are depicted as dotted lines.

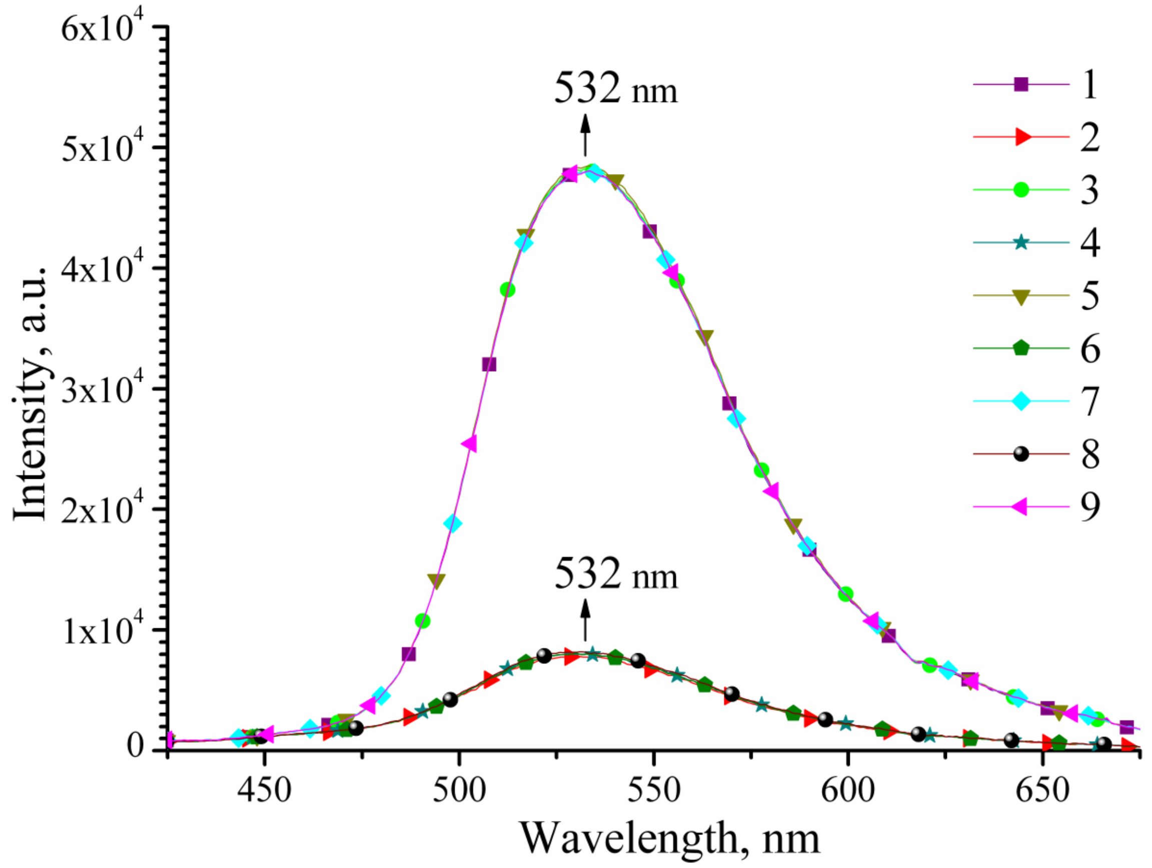


Fig. S2 Photoluminescence spectra recorded during repeated heating (up to 122-125 °C) and cooling (down to 27 °C) cycles of ashless cellulose filter paper saturated with $Mn(HA)_2$ ($2.9 \cdot 10^{-3}$ mol/L) water solution. Excitation wavelength is 365 nm. Paper temperatures are: (1) 27 °C, (2) 125 °C, (3) 27 °C, (4) 123 °C, (5) 27 °C, (6) 123 °C, (7) 27 °C, (8) 122 °C, (9) 27 °C.

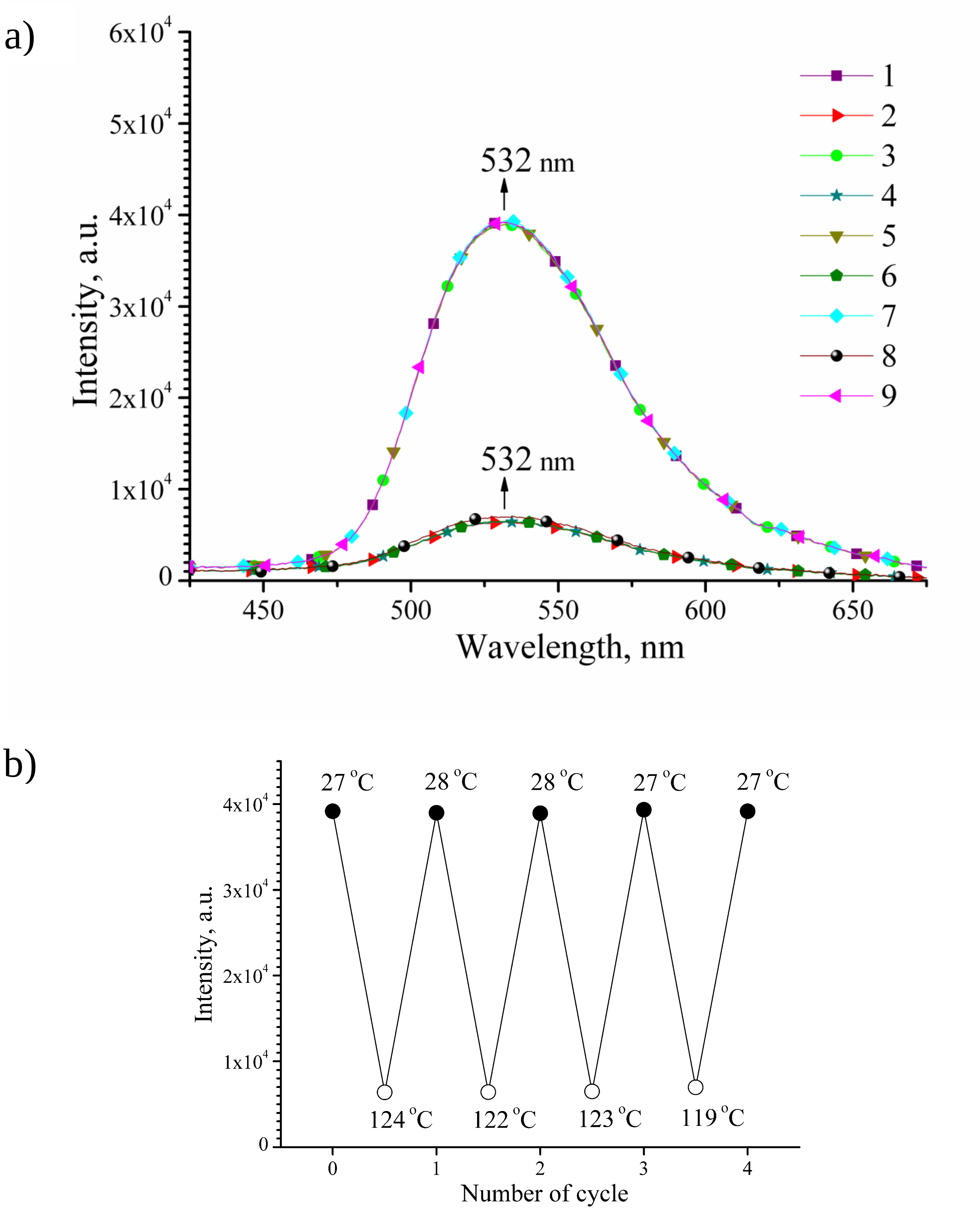


Fig. S3 Photoluminescence of ashless cellulose filter paper saturated with $Zn(HA)_2$ ($1.1\cdot10^{-3}$ mol/L) water solution (excitation wavelength is 365 nm):
(a) Spectra recorded during repeated heating (up to 122-124 °C) and cooling (down to 27-28 °C) cycles. Paper temperatures are: (1) 27 °C, (2) 124 °C, (3) 28 °C, (4) 122 °C, (5) 28 °C, (6) 123 °C, (7) 27 °C, (8) 119 °C, (9) 27 °C;
(b) Reversible switching of photoluminescence intensity at 532 nm by repeated heating (up to 119-124 °C) and cooling (down to 27-28 °C) cycles.

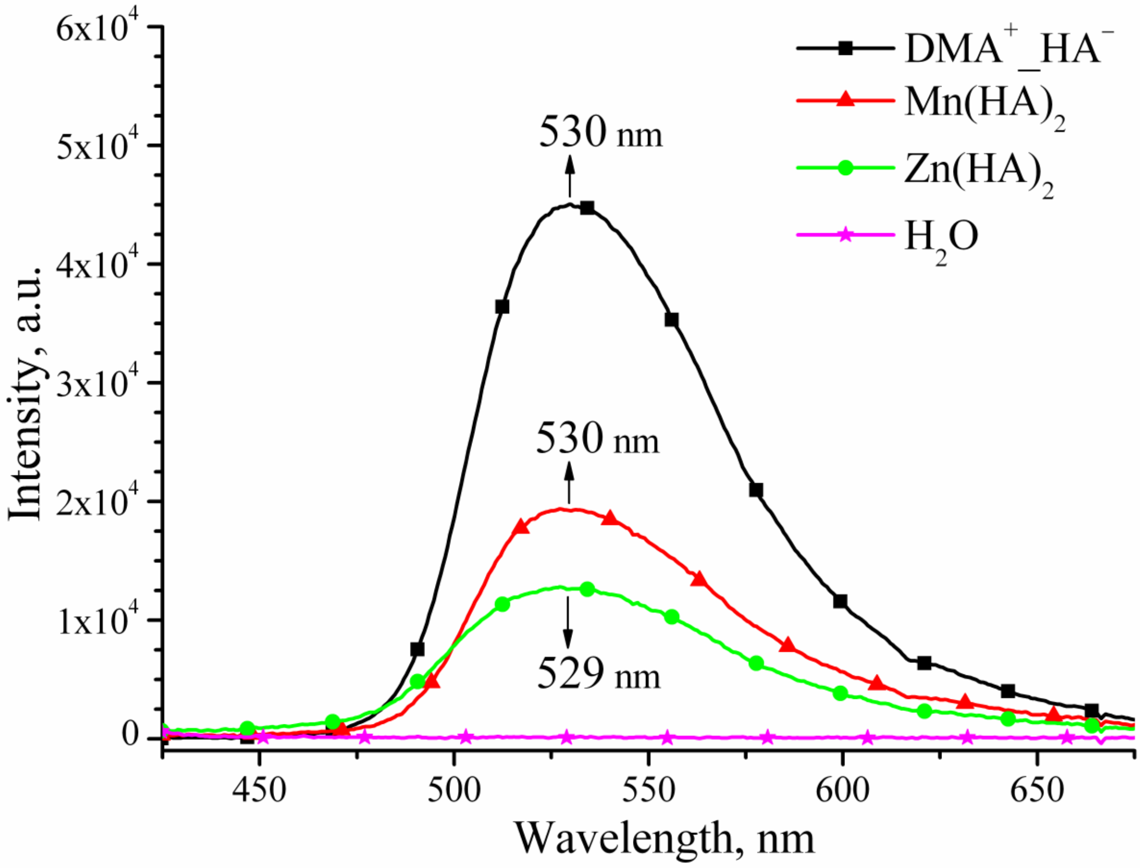
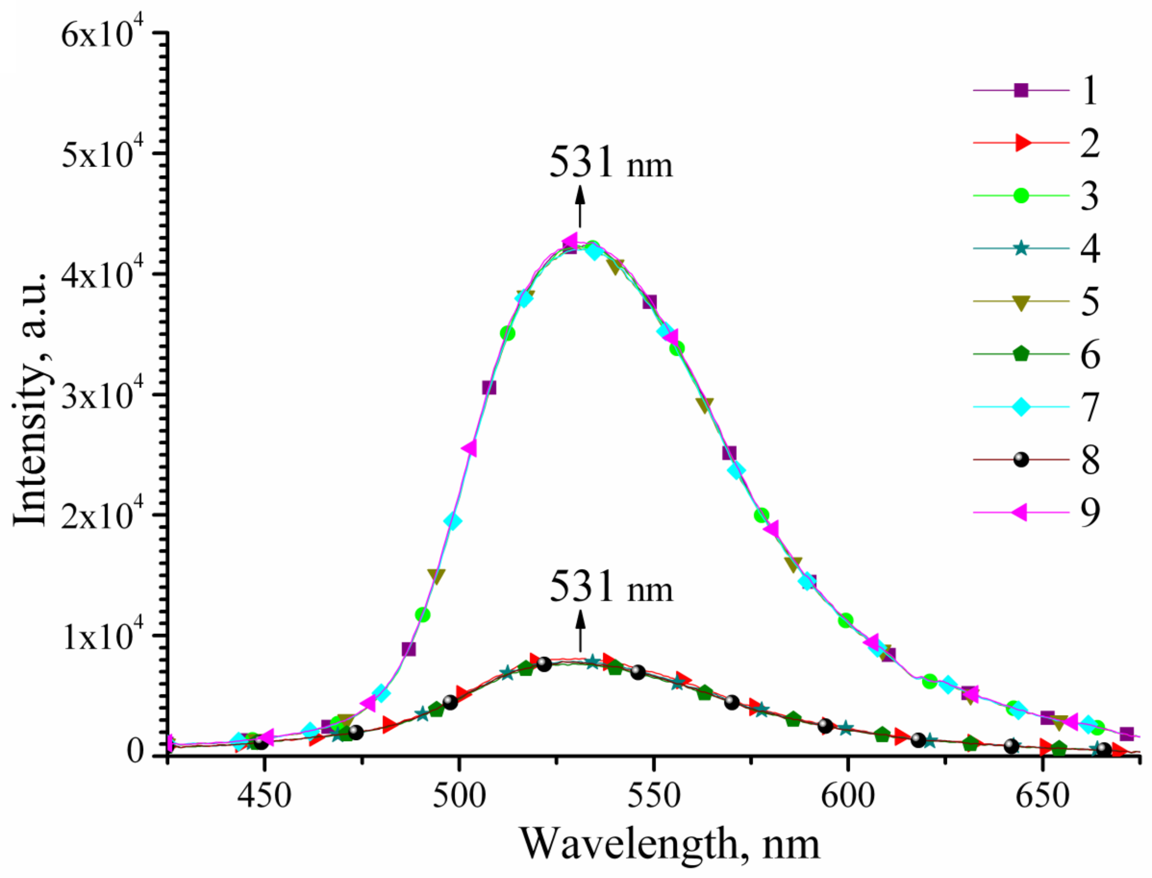


Fig. S4 Photoluminescence spectra of salts $M(HA)_2$ (M = Mn, Zn), DMA^+_HA^- (DMA^+ = *N*,*N*-dimethylanilinium cation) dissolved in water. Excitation wavelength is 365 nm. Concentration of $M(HA)_2$ in solution is $2.9 \cdot 10^{-4}$ mol/L (M = Mn), $1.1 \cdot 10^{-4}$ mol/L (M = Zn). Concentration of DMA^+_HA^- in solution is $2.9 \cdot 10^{-4}$ mol/L.

a)



b)

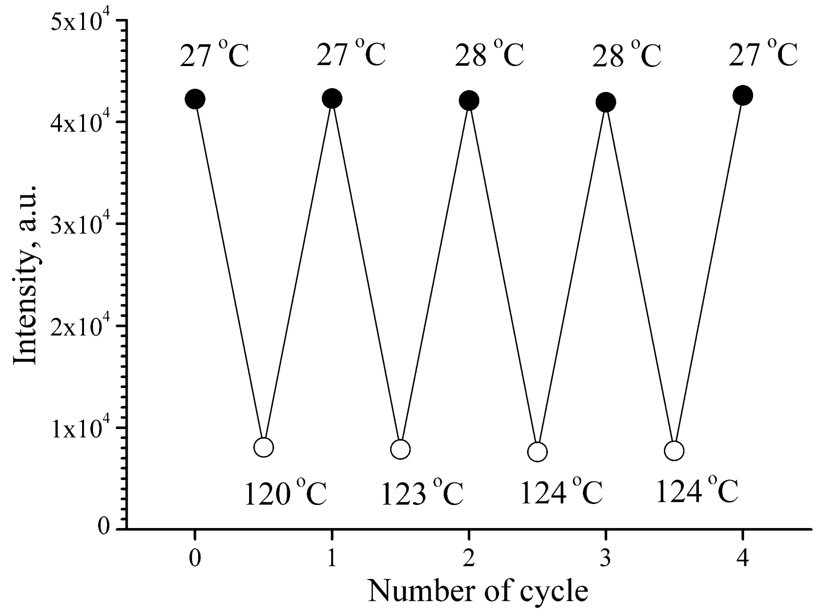
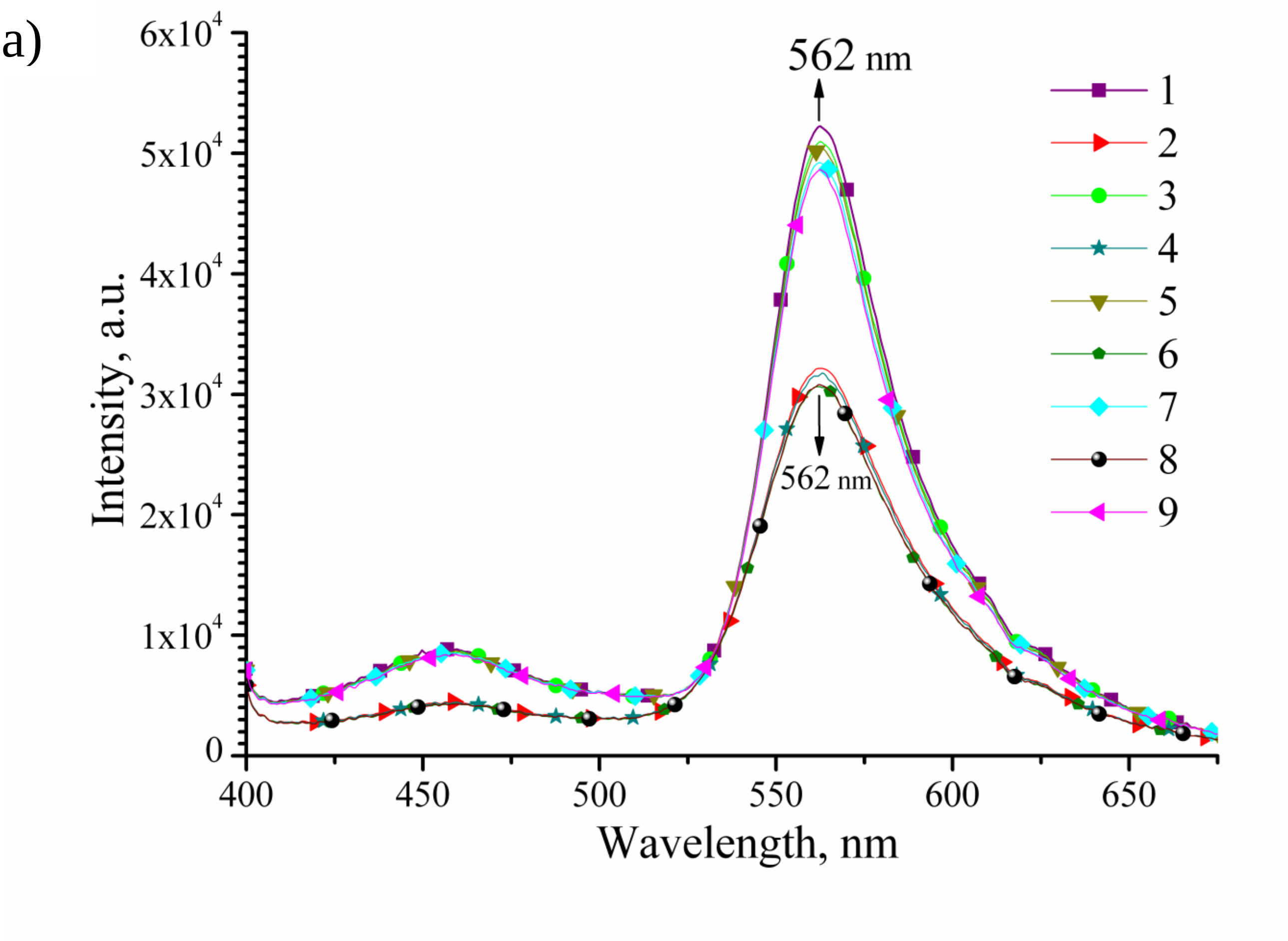


Fig. S5 Photoluminescence of ashless cellulose filter paper saturated with $DMA^+\_HA^-$ ($2.9{\cdot}10^{-3}$ mol/L) water solution (excitation wavelength is 365 nm):
(a) Spectra recorded during repeated heating (up to 120-124 °C) and cooling (down to 27-28 °C) cycles. Paper temperatures are: (1) 27 °C, (2) 120 °C, (3) 27 °C, (4) 123 °C, (5) 28 °C, (6) 124 °C, (7) 28 °C, (8) 124 °C, (9) 27 °C;
(b) Reversible switching of the emission intensity at 531 nm by repeated heating (up to 120-124 °C) and cooling (down to 27-28 °C) cycles.



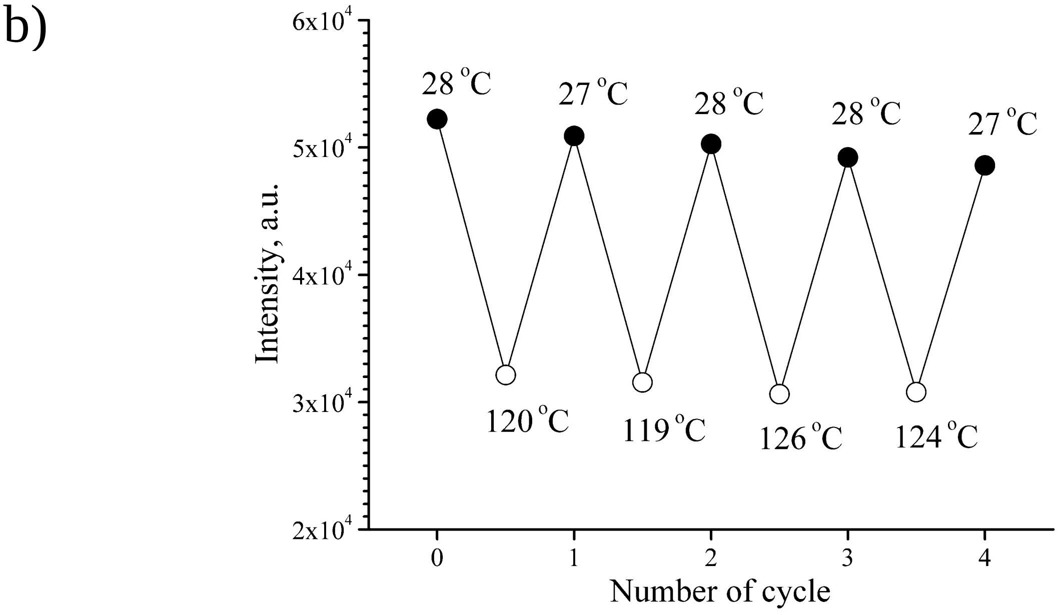
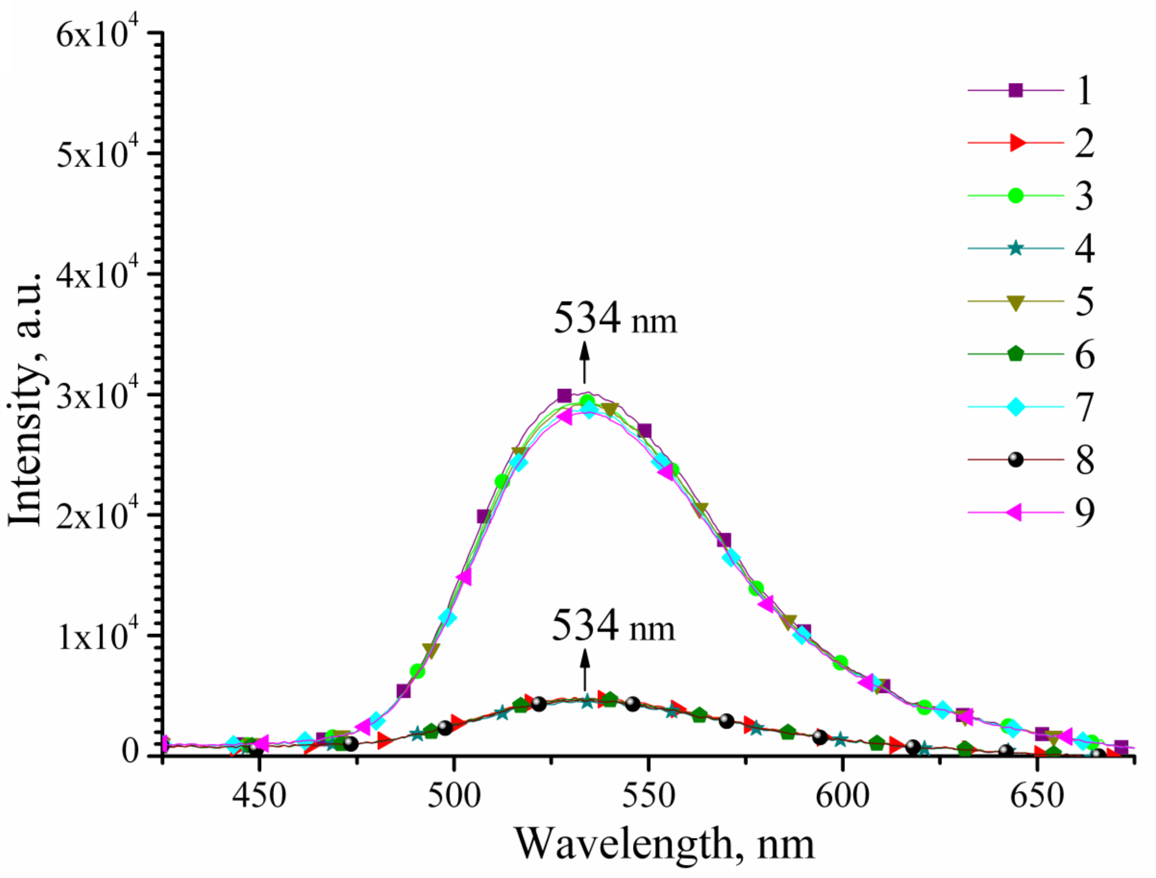


Fig. S6 Photoluminescence of ashless cellulose filter paper saturated with Rhodamine 6G ($6.1\cdot10^{-5}$ mol/L) water solution (excitation wavelength is 365 nm):

(a) Spectra recorded during repeated heating (up to 119-126 °C) and cooling (down to 27-28 °C) cycles. Paper temperatures are: (1) 28 °C, (2) 120 °C, (3) 27 °C, (4) 119 °C, (5) 28 °C, (6) 126 °C, (7) 28 °C, (8) 124 °C, (9) 27 °C;

(b) Reversible switching of the emission intensity at 562 nm by repeated heating (up to 119-126 °C) and cooling (down to 27-28 °C) cycles.

a)



b)

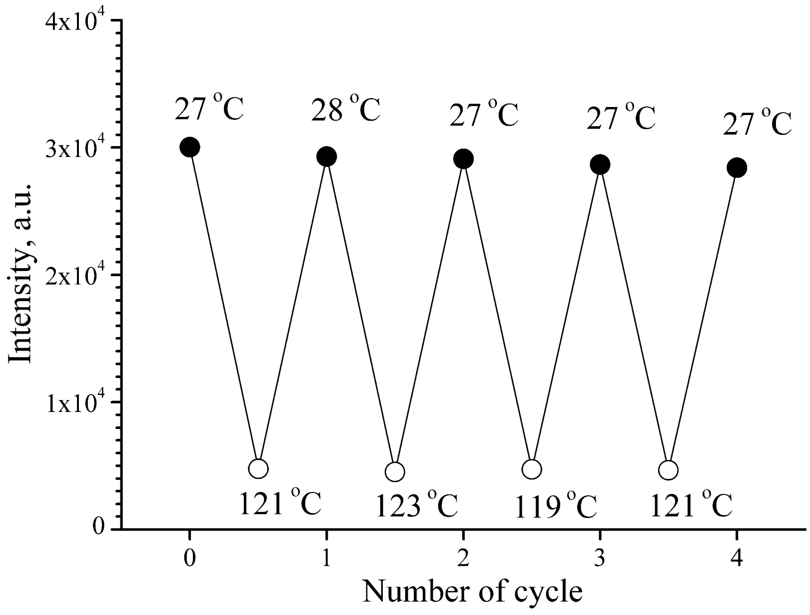
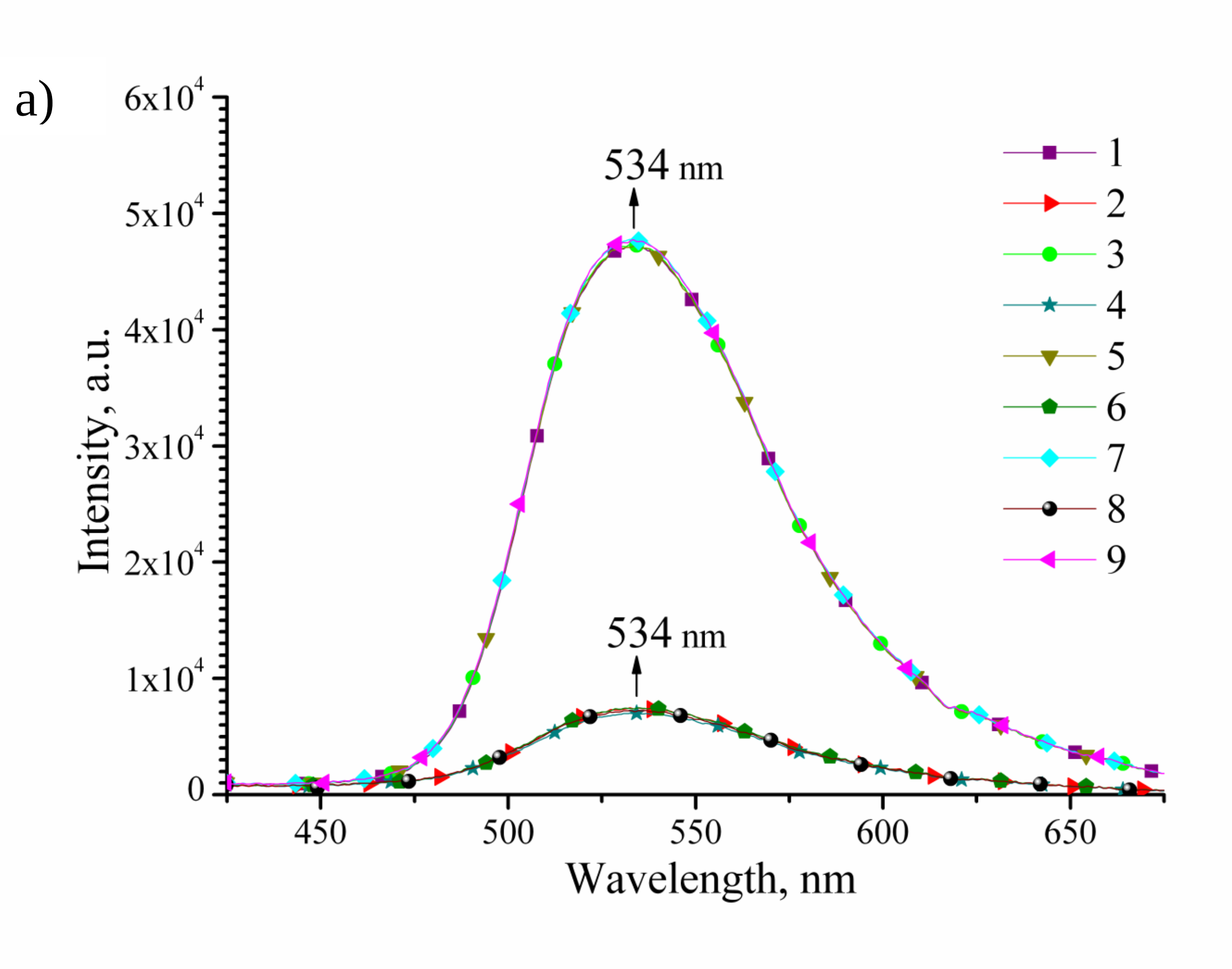


Fig. S7 Photoluminescence of ashless cellulose filter paper saturated with $Cu(HA)_2$ ($1.5\cdot10^{-3}$ mol/L) water solution (excitation wavelength is 365 nm):
(a) Spectra recorded during repeated heating (up to 119-123 °C) and cooling (down to 27-28 °C) cycles. Paper temperatures are: (1) 27 °C, (2) 121 °C, (3) 28 °C, (4) 123 °C, (5) 27 °C, (6) 119 °C, (7) 27 °C, (8) 121 °C, (9) 27 °C;
(b) Reversible switching of the emission intensity at 534 nm by repeated heating (up to 119-123 °C) and cooling (down to 27-28 °C) cycles.



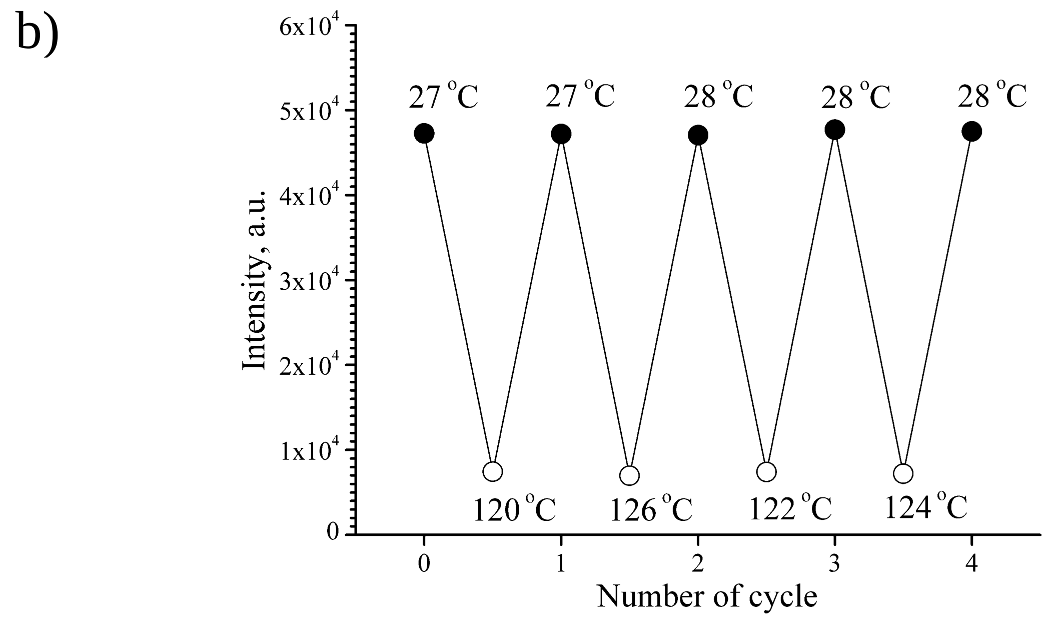


Fig. S8 Photoluminescence of ashless cellulose filter paper saturated with $Cd(HA)_2$ ($3.0 \cdot 10^{-3}$ mol/L) water solution (excitation wavelength is 365 nm):
(a) Spectra recorded during repeated heating (up to 122-124 °C) and cooling (down to 27-28 °C) cycles. Paper temperatures are: (1) 27 °C, (2) 121 °C, (3) 28 °C, (4) 123 °C, (5) 27 °C, (6) 119 °C, (7) 27 °C, (8) 121 °C, (9) 27 °C.
(b) Reversible switching of the emission intensity at 534 nm by repeated heating (up to 119-123 °C) and cooling (down to 27-28 °C) cycles.

a)

b)

c)

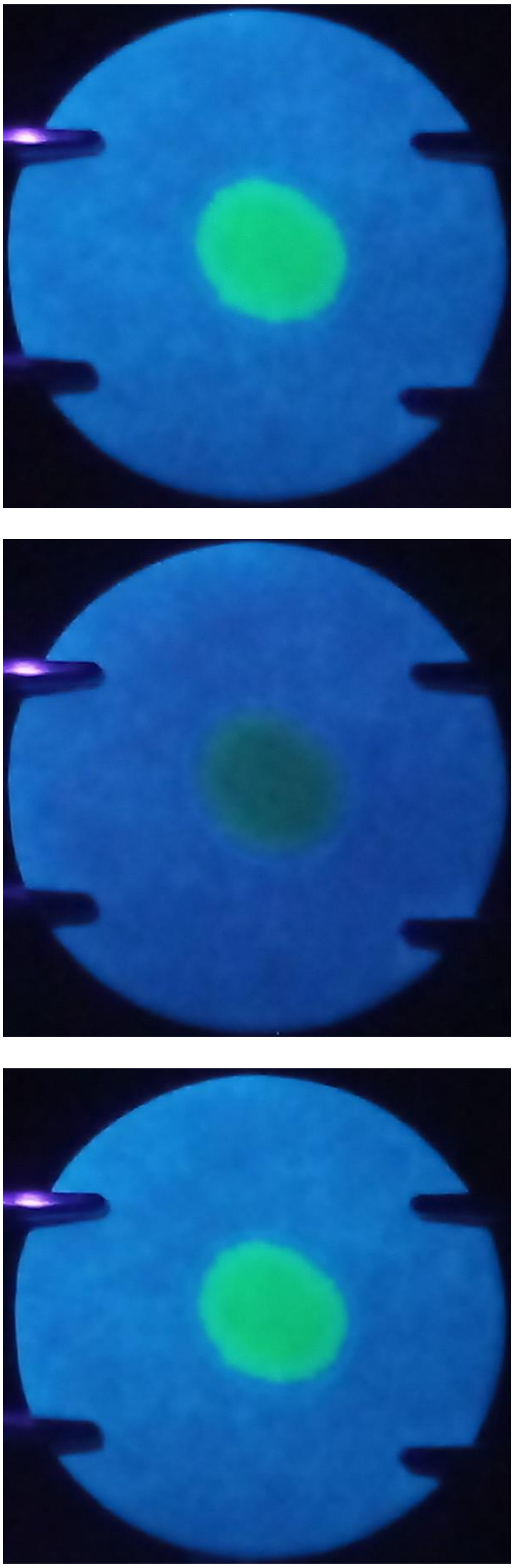


Fig. S9 Photoluminescence of salt $Cu(HA)_2$ adsorbed on ashless cellulose filter paper from water solution (excitation wavelength is 365 nm). Concentration of $Cu(HA)_2$ in water solution was $1.5 \cdot 10^{-3}$ mol/L. Paper temperatures are:
(a) 27 °C (before heating);
(b) 123 °C (during heating);
(c) 27 °C (after cooling).

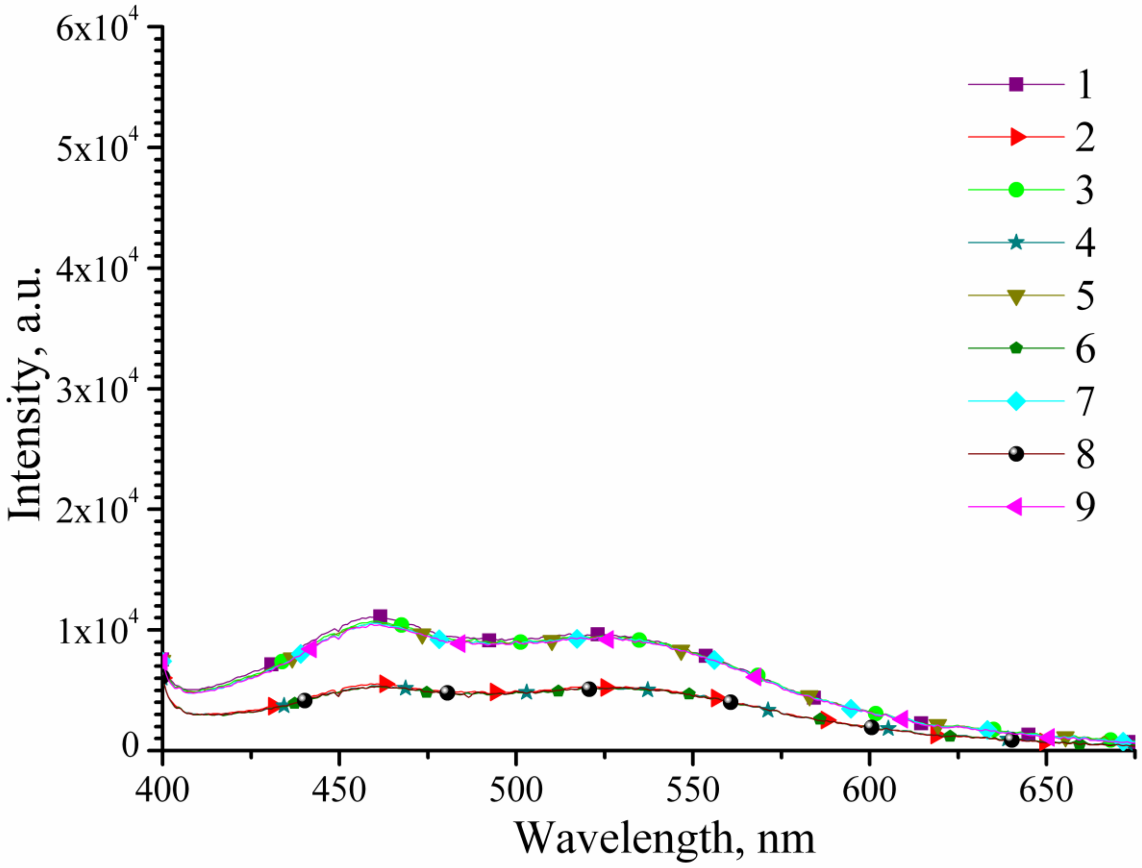


Fig. S10 Photoluminescence spectra recorded during repeated heating (up to 119-126 °C) and cooling (down to 27-28 °C) cycles of ashless cellulose filter paper. Excitation wavelength is 365 nm. Paper temperatures are: (1) 27 °C, (2) 120 °C, (3) 27 °C, (4) 120 °C, (5) 27 °C, (6) 122 °C, (7) 27 °C, (8) 120 °C, (9) 27 °C.

Table S1 Crystallographic data and structure refinement results for complexes $[Mn(HA)_2(H_2O)_4]\cdot 2H_2O$ (**1**) and $[Zn(HA)_2(H_2O)_4]$ (**2**).

Complex №	**1**	**2**
Chemical formula	$[Mn(C_8HN_4O_2)_2(H_2O)_4]\cdot 2H_2O$	$[Zn(C_8HN_4O_2)_2(H_2O)_4]$
Formula weight	533.29	507.69
Temperature/K	295(2)	295(2)
Wavelength/Å	1.54184	0.71054
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	6.963(2)	7.0540(6)
b/Å	8.5910(10)	7.9485(6)
c/Å	10.532(2)	9.4149(7)
α/°	105.20(2)	90.829(6)
β/°	97.89(2)	110.004(6)
γ/°	109.80(2)	93.622(6)
V/Å^3	554.0(2)	494.68(7)
Z	1	1
Calculated density/mg·m^{-3}	1.598	1.704
Absorption coefficient/mm^{-1}	5.500	1.307
F(000)	271	256
Reflections measured	2257	5028
Independent reflections	2130	2120
R_{int}	0.0356	0.0933
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2130/0/189	2120/0/167
Goodness-of-fit on F^2	1.076	0.973
R [a] $[I > 2\sigma(I)]$	0.0389	0.0616
w$R(F^2)$ [b] (all reflections)	0.1053	0.1685
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e·Å^{-3}	0.324, -0.667	1.116, -0.502

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths [Å] and angles [°] for complexes [Mn(HA)$_2$(H$_2$O)$_4$]·2H$_2$O (**1**) and [Zn(HA)$_2$(H$_2$O)$_4$] (**2**).

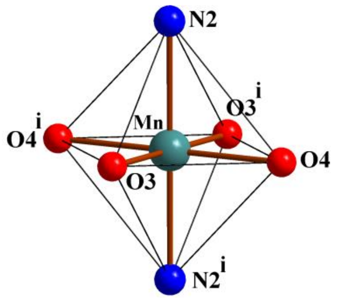
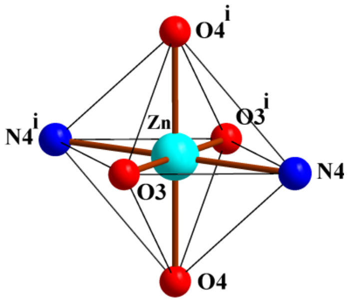
Coordination polyhedron	Bond length	Bond angles
1		
	Mn-O3 2.161(2) Mn-O4 2.135(2) Mn-N2 2.253(2)	O3-Mn-N2 86.41(9) O4-Mn-O3 90.16(10) O4-Mn-N2 90.08(10)
Symmetry transformations used to generate equivalent atoms: (i) –x+1, –y+1, –z		
2		
	Zn-O3 2.170(4) Zn-O4 2.046(4) Zn-N4 2.117(4)	O3-Zn-N4 88.27(17) O4-Zn-N4 86.07(17) O4-Zn-O3 90.84(18)
Symmetry transformations used to generate equivalent atoms: (i) –x+1, –y, –z		

Table S3 Hydrogen bond geometries for complexes $[Mn(HA)_2(H_2O)_4]\cdot 2H_2O$ (**1**) and $[Zn(HA)_2(H_2O)_4]$ (**2**).

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
1				
N1-H1···O1^{vi}	0.80(3)	2.08(4)	2.876(3)	176(3)
O3-H3···O5^{v}	0.80(4)	2.07(4)	2.833(4)	159(4)
O3-H31···O2^{ii}	0.83(5)	2.01(6)	2.835(3)	176(5)
O4-H4···O5	0.85(4)	1.94(5)	2.787(4)	176(4)
O4-H41···N3	0.79(5)	2.33(5)	2.976(3)	141(5)
O4-H41···N4^{viii}	0.79(5)	2.65(5)	3.221(4)	131(5)
O5-H5···N4^{iii}	0.95(6)	1.94(6)	2.861(4)	162(5)
O5-H51···O1^{vii}	0.89(7)	2.25(8)	2.917(3)	132(6)
Symmetry transformations used to generate equivalent atoms: (ii) –x+2, –y+1, –z+1; (iii) x–1, y, z–1; (v) x+1, y, z; (vi) –x+1, –y, –z+1; (vii) x, y+1, z; (viii) –x+2, –y+2, –z+1				
2				
N1-H1···O3^{v}	0.86	2.20	3.000(6)	155.2
O3-H3···O1^{vii}	0.69(7)	2.06(8)	2.748(6)	173(8)
O3-H31···N2^{ii}	0.78(8)	2.14(8)	2.871(6)	155(7)
O4-H4···N3^{vi}	0.71(8)	2.03(8)	2.732(6)	169(8)
O4-H41···O2	0.81(7)	2.07(7)	2.810(5)	151(6)
Symmetry transformations used to generate equivalent atoms: (ii) x–1, y–1, z–1; (v) x, y+1, z; (vi) x–1, y, z–1; (vii) –x+2, –y+1, –z				

Table S4 Effect of temperature on luminescence intensity of ashless cellulose filter paper saturated with salt ($Mn(HA)_2$, $Zn(HA)_2$, $DMA^+\_HA^-$, $Cu(HA)_2$, $Cd(HA)_2$, Rhodamine 6G) water solution [a].

$Mn(HA)_2$	Luminescence peak intensity at 27 °C (I_{Peak_27}), a.u.	Luminescence intensity of background at 532 nm at 27 °C (I_{0_27}), a.u.	Luminescence peak intensity at 123 °C (I_{Peak_123}), a.u.	Luminescence intensity of background at 532 nm at 123 °C (I_{0_123}), a.u.	$\frac{I_{Peak\_27} - I_{0\_27}}{I_{Peak\_123} - I_{0\_123}}$
	48413	568	8097	568	**6.4**
$Zn(HA)_2$	Luminescence peak intensity at 28 °C (I_{Peak_28}), a.u.	Luminescence intensity of background at 532 nm at 28 °C (I_{0_28}), a.u.	Luminescence peak intensity at 123 °C (I_{Peak_123}), a.u.	Luminescence intensity of background at 532 nm at 123 °C (I_{0_123}), a.u.	$\frac{I_{Peak\_28} - I_{0\_28}}{I_{Peak\_123} - I_{0\_123}}$
	38979	1061	6513	749	**6.6**
$DMA^+\_HA^-$	Luminescence peak intensity at 27 °C (I_{Peak_27}), a.u.	Luminescence intensity of background at 531 nm at 27 °C (I_{0_27}), a.u.	Luminescence peak intensity at 123 °C (I_{Peak_123}), a.u.	Luminescence intensity of background at 531 nm at 123 °C (I_{0_123}), a.u.	$\frac{I_{Peak\_27} - I_{0\_27}}{I_{Peak\_123} - I_{0\_123}}$
	42287	789	7826	624	**5.8**
$Cu(HA)_2$	Luminescence peak intensity at 28 °C (I_{Peak_28}), a.u.	Luminescence intensity of background at 534 nm at 28 °C (I_{0_28}), a.u.	Luminescence peak intensity at 123 °C (I_{Peak_123}), a.u.	Luminescence intensity of background at 534 nm at 123 °C (I_{0_123}), a.u.	$\frac{I_{Peak\_28} - I_{0\_28}}{I_{Peak\_123} - I_{0\_123}}$
	29267	620	4536	402	**6.9**
$Cd(HA)_2$	Luminescence peak intensity at 28 °C (I_{Peak_28}), a.u.	Luminescence intensity of background at 534 nm at 28 °C (I_{0_28}), a.u.	Luminescence peak intensity at 124 °C (I_{Peak_124}), a.u.	Luminescence intensity of background at 534 nm at 124 °C (I_{0_124}), a.u.	$\frac{I_{Peak\_28} - I_{0\_28}}{I_{Peak\_124} - I_{0\_124}}$
	47825	673	7254	547	**7.0**
Rhodamine 6G	Luminescence peak intensity at 28 °C (I_{Peak_28}), a.u.	Luminescence intensity of background at 562 nm at 28 °C (I_{0_28}), a.u.	Luminescence peak intensity at 124 °C (I_{Peak_124}), a.u.	Luminescence intensity of background at 562 nm at 124 °C (I_{0_124}), a.u.	$\frac{I_{Peak\_28} - I_{0\_28}}{I_{Peak\_124} - I_{0\_124}}$
	49246	3856	30795	2489	**1.6**

[a] Concentration of $M(HA)_2$ in water solution is $2.9 \cdot 10^{-3}$ mol/L (M = Mn), $3.0 \cdot 10^{-3}$ mol/L (M = Cd), $1.5 \cdot 10^{-3}$ mol/L (M = Cu), $1.1 \cdot 10^{-3}$ mol/L (M = Zn). Concentration of $DMA^+\_HA^-$ in water solution is $2.9 \cdot 10^{-3}$ mol/L. Concentration of Rhodamine 6G in water solution is $6.1 \cdot 10^{-5}$ mol/L.
Excitation wavelength is 365 nm.