A Water-stable Zinc(II)-organic Framework as an "on-off-on" Fluorescent Sensor for Detection of Fe^{3+} and Reduced Glutathione

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1. Photoluminescent sensing experiments.

The fluorescence performance of complex **1** in the phosphate buffered saline (PBS) of pH = 7.0 (0.1 M) was studied at room temperature. Firstly, 0.01 M various cations (including Na^{+}, Ag^{+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Ba^{2+}, Mn^{2+}, Cd^{2+}, Fe^{2+}, Pb^{2+}, Hg^{2+}, Cr^{3+}, Al^{3+}, Fe^{3+}) and reduced glutathione (GSH), ascorbic acid (AA), amino acid (including glutamine (Glu), aspartic (Asp), cysteine (Cys), methionine (Met), proline (Pro), glycine (Gly), valine (Val), threonine (Thr), asparagine (Asn), phenylalanine (Phe), histidine (His), leucine (Leu) and $_{L}$-isoleucine (Lie)) PBS solutions were prepared at room temperature. Secondly, 2.0 mg of a powder sample of complex **1** was soaked in PBS solution of different analytes (2 mL) and the fluorescence intensity of complex **1** in analytes was recorded. For Fe^{3+}@**1** sensing reduced GSH, firstly, 45 μL (0.01 M) of Fe^{3+} ions were added to the suspension of complex **1** (2 mL) and record the fluorescence intensity of complex **1**. Based on the first step, 100 μL (0.01 M) of GSH were added and the fluorescence intensity of Fe^{3+}@**1**-GSH was collected.

2. Fluorescence Titration experiments.

The process of fluorescence titration experiments were achieved by gradually adding various target analytes solution (0.01 M) to the suspensions of complex **1**.

3. Time-dependent fluorescence sensing experiments.

The fluorescence intensities of complex **1** within the Fe^{3+} solution (0.225 mM), Pb^{2+} solution (0.48 mM), were recorded at 30 s, 1 min, 2 min, 3 min, 4 min, 6 min 8 min and 10 min. For Fe^{3+}@**1** sensing reduced GSH, firstly, 45 μL of Fe^{3+} ions solution were added to the suspension of complex **1** (2 mL), secondly, based on the first step, 100 μL of reduced GSH solution were added, the fluorescence intensity of complex **1** was collected at next 30 s, 1 min, 2 min, 3 min, 4 min, 6 min, 8 min and 10 min.

4. Recyclable Luminescence Experiments.

After the first fluorescence detection of various analytes, the powder sample of complex 1 was recovered by centrifugation and washed by water and EtOH. After drying, the samples collected were used again for the detection of various analytes.

5. Sensing of reduced GSH in practical samples.

10 μL of diluted serum and 100 μL of real samples were added into the solution of complex **1** (2 $mg{\cdot}mL^{-1}$), respectively. A stable suspension was obtained after 30 min of ultrasound. Then, PBS solution of Fe^{3+} (0.01 M, 45 μL) was added into the suspension. With gradually adding reduced GSH solution, the fluorescence emission spectrum of Fe^{3+}@**1** was recorded.

Table S1 Selected bond lengths (Å) and angles (°) of complex **1**.

$Zn2^{i}$—O2	2.092(8)	Zn2—O5	2.341(8)
$Zn2^{i}$—O1	2.242(9)	$Zn1^{ii}$—O5	1.993(9)
$Zn2^{i}$—C1	2.498(10)	Zn2—O6	2.184(9)
Zn2—$O4^{ii}$	2.003(6)	Zn2—N2	2.055(7)
O3—Zn1	1.911(6)	C1—O2—$Zn2^{i}$	94.6(7)
C1—O1—$Zn2^{i}$	86.1(7)	O2—C1—$Zn2^{i}$	56.6(5)
O1—C1—$Zn2^{i}$	63.6(6)	C2—C1—$Zn2^{i}$	175.1(7)
C21—O5—Zn2	87.3(7)	C21—O5—$Zn1^{ii}$	126.9(7)
$Zn1^{ii}$—O5—Zn2	118.6(3)	C21—O6—Zn2	96.5(8)
$O2^{iii}$—Zn2—$O1^{iii}$	59.1(3)	$O2^{iii}$—Zn2—$C1^{ii}$	28.8(3)
$O2^{iii}$—Zn2—O5	94.6(3)	$O2^{iii}$—Zn2—O6	92.0(4)
$O1^{iii}$—Zn2—$C1^{iii}$	30.3(3)	$O1^{iii}$—Zn2—O5	118.4(3)
O5—Zn2—$C1^{iii}$	107.9(3)	O6—Zn2—$O1^{iii}$	151.0(4)
O6—Zn2—C13	120.7(4)	O6—Zn2—O5	57.3(3)
$O4^{ii}$—Zn2—$O2^{iii}$	138.3(4)	$O4^{ii}$—Zn2—$O1^{iii}$	83.1(3)
$O4^{ii}$—Zn2—$C1^{iii}$	111.7(4)	$O4^{ii}$—Zn2—O5	88.1(3)
$O4^{ii}$—Zn2—O6	123.3(4)	$O4^{ii}$—Zn2—N2	95.9(3)
N2—Zn2—$O2^{iii}$	105.4(3)	N2—Zn2—$O1^{iii}$	97.6(3)
N2—Zn2—O6	103.8(3)	N2—Zn2—O5	144.0(3)
N2—Zn2—$O2^{iii}$	91.7(3)	C8—O3—Zn1	131.5(6)
$O5^{iv}$—Zn1—$O5^{v}$	94.7(5)	O3—Zn1—$O5^{v}$	107.6(3)
O3—Zn1—$O5^{iv}$	117.1(3)	$O3^{vi}$—Zn1—$O5^{v}$	117.1(3)
$O3^{vi}$—Zn1—$O5^{iv}$	107.6(3)	$O3^{vi}$—Zn1—O3	112.1(4)

Symmetry codes: (i) 1+x,+y,+z; (ii) -1+x,-1+y,+z; (iii) -1+x,+y,+z; (iv) 1-x,-x+y,-2/3-z; (v) 1+x,1+y,+z; (vi) x,-x+y,-2/3-z.

Table S2. Comparison of reported MOF-based sensors for Fe^{3+} and Pb^{2+} detection.

	MOF	Metal ions	Detection Limit	Medium Used	Ref.
1	$[Zn_3(TNB)(DPE)_2]\bullet 2H_2O\bullet DMF$	Fe^{3+}	3.4×10^{-7} M	PBS solution	This work
2	$[Cd_2(HDDB)(bimpy)(NMP)(H_2O)]\bullet 3H_2O$	Fe^{3+}	5.9×10^{-7} M	H_2O	30
3	$[Zn(bimpy)(1,4\text{-ndc})]\bullet H_2O$	Fe^{3+}	8.82×10^{-7} M	H_2O	22
4	$\{[Cd(L)(H_2O)_2]\bullet 4H_2O\}_n$	Fe^{3+}	0.78 μM	H_2O	49
5	$[TbL\bullet 2H_2O)]_n$	Fe^{3+}	8.32×10^{-6} M	H_2O	50
6	$\{[Eu_2(L)_2(H_2O)_2]\bullet 5H_2O\bullet 6DMAC\}_n$	Fe^{3+}	10^{-5} M	H_2O	51
7	$\{Zn_2(tpt)_2(tad)_2\bullet H_2O\}$	Fe^{3+}	4.72×10^{-6} M	H_2O	52
8	$Ti_2(HDOBDC)_2(H_2DOBDC)$	Fe^{3+}	0.45 μM	H_2O	53
9	$\{[Cd_2(L)(DMA)]\bullet H_2N(Me)_2\}_n$	Fe^{3+}	1.2×10^{-3} M	H_2O	54
10	$\{Zn_2(NO_3)_2(4,4'\text{-bpy})_2(TBA)\}$	Fe^{3+}	1.2×10^{-6} M	H_2O	55
11	$[CH_3\text{-dpb}]_2[Mg_3(1,4\text{-NDC})_4(\mu\text{-}H_2O)_2(CH_3OH)(H_2O)]\bullet 1.5H_2O$	Fe^{3+}	4.7×10^{-4} M	H_2O	56
12	$\{[Mg_2(\mu_6\text{-L})(\mu_2\text{-}OH_2)(H_2O)_4]\cdot DMF\}_n$	Fe^{3+}	1.68×10^{-3} M	H_2O	57
13	$[Ca_2(\mu_{10}\text{-L})(EtOH)]_n$	Fe^{3+}	1.70×10^{-3} M	H_2O	57
14	$\{[Zn\text{-}(ATA)(L)]\bullet H_2O\}_n$	Fe^{3+}	3.76 μM	H_2O	58
15	$\{[Cd(ATA)(L)]\bullet 2H_2O\}_n$	Fe^{3+}	1.77 μM	H_2O	58
16	$[Zn_3(TNB)(DPE)_2]\bullet 2H_2O\bullet DMF$	Pb^{2+}	4.59×10^{-7} M	PBS solution	This work
17	$\{[Mg_2(\mu_6\text{-L})(\mu_2\text{-}OH_2)(H_2O)_4]\bullet DMF\}_n$	Pb^{2+}	1.32×10^{-3} M	H_2O	57
18	$[Ca_2(\mu_{10}\text{-L})(EtOH)]_n$	Pb^{2+}	6.94×10^{-4} M	H_2O	57
19	$[Zn(HL)(bipy)_{0.5}(H_2O)]\bullet 2H_2O$	Pb^{2+}	0.8 μM	H_2O	59
20	$\{[Eu_2(PBA)_3(H_2O)_3]\bullet DMF\bullet 3H_2O\}_n$	Pb^{2+}	68.13 μM	DMF	60
21	$\{[Cd(BIPA)(HIPA)]\bullet DMF\}_n$	Pb^{2+}	5.0×10^{-7} M	H_2O	61
22	$\{[Cd(BIPA)(IPA)]\bullet DMF\}_n$	Pb^{2+}	7.5×10^{-7} M	H_2O	61
23	$(Eu_2(FDC)_3DMA(H_2O)_3]\bullet DMA\bullet 4.5H_2O$	Pb^{2+}	8.22 μM	H_2O	62

Table S3. Comparison of reported substances for reduced GSH detection.

	MOF		Detection Limit	Medium Used	Ref.
1	$[Zn_3(TNB)(DPE)_2]•2H_2O•DMF$	FL (turn-on)	2.48×10^{-8} M	PBS solution	This work
2	Cu-MOF	Colorimetric	0.97 μM	MOPS buffer	66
3	g-CNQD-Hg^{2+}	FL (turn-on)	37 nM	PBS solution	4
4	GQDs-MnO_2	FL (turn-on)	150 nM	PBS solution	67
5	GQDs-Au@MnO_2	FL (turn-on)	0.11 μM	PBS solution	35
6	B-CQDs	FL (turn-on)	0.5 nM	PBS solution	68
7	N-CDs	FL (turn-on)	0.226 μM		36

Table S4 Determination of reduced GSH in fruits and vegetables by the proposed fluorescence sensing method.

Sample	Added (μM)	Detected (μM)	Recovery (%)	RSD (%, n=3)
Tomato	0.300	0.321	86.3	3.03
	0.450	0.462	88.8	2.17
Cherry tomato	0.300	0.315	85.5	2.28
	0.450	0.473	103.7	2.13
Cucumber	0.300	0.305	92.2	3.33
	0.450	0.465	97.2	5.79
White grape	0.300	0.298	95.8	6.25
	0.450	0.469	101	1.73
Purple grape	0.300	0.301	82.1	3.20
	0.450	0.473	92.9	1.24

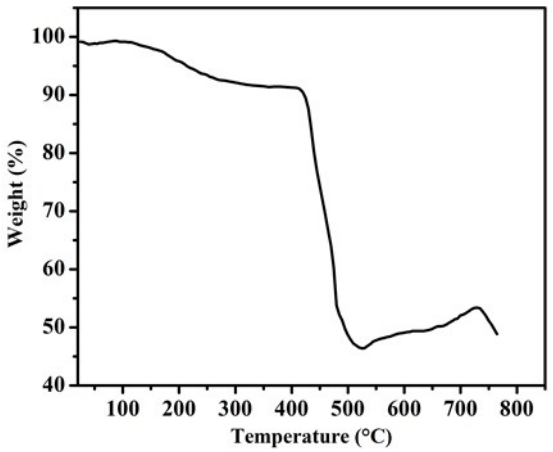

Fig. S1 TGA pattern of complex **1**.

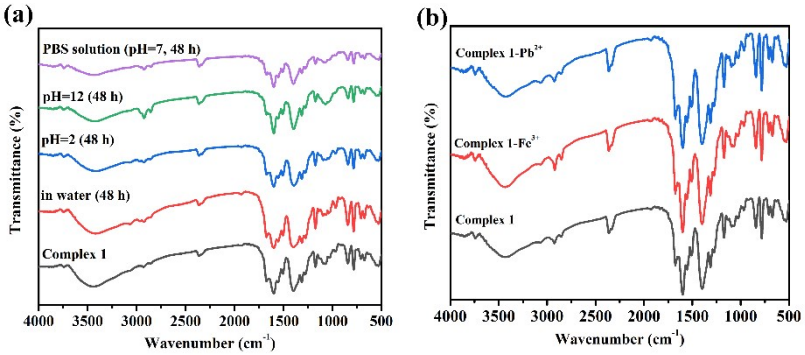

Fig. S2 FTIR spectra of complex **1** recorded in aqueous solution and different pH value of 2, 12 and PBS solution for 48 h (a); and after immersing in Fe^{3+} and Pb^{2+} for 48 h (b).

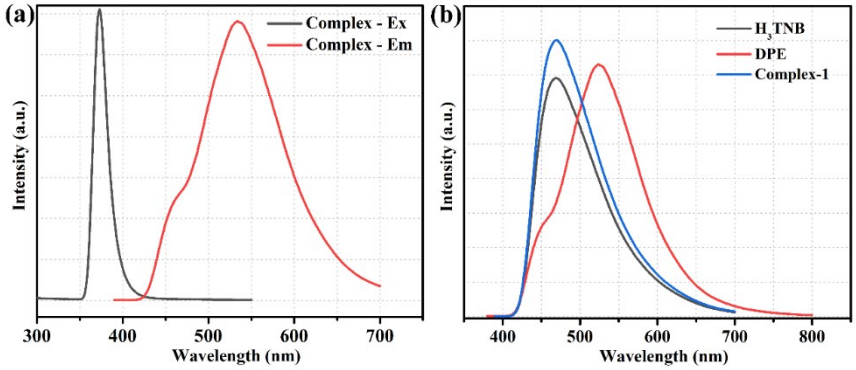

Fig. S3 (a) Solid state fluorescence excitation and emission spectra of complex **1**; (b) The fluorescence emission spectra of H_3TNB ligand, DPE ligand and complex **1**.

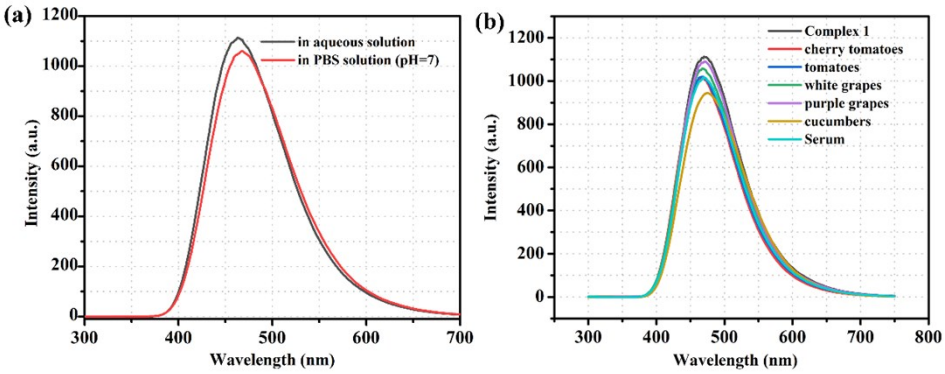

Fig. S4 (a) The fluorescence intensity of complex **1** in aqueous solution (Black) and PBS solution (Red); (b) The fluorescence intensity of complex **1** in serum, cherry tomatoes, tomatoes, white grapes, purple grapes and cucumbers solution.

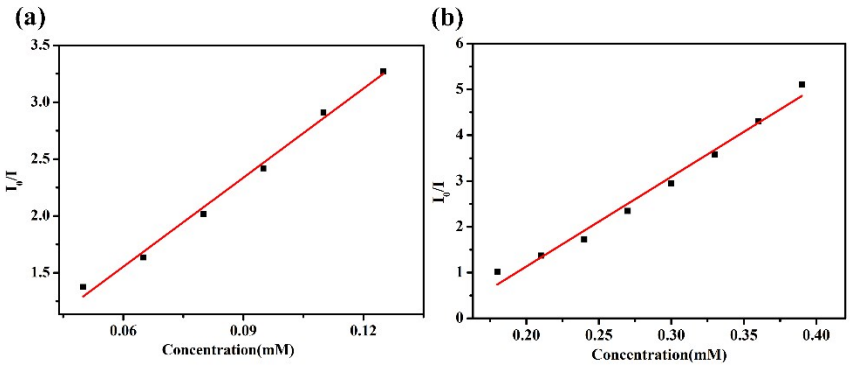

Fig. S5 The *SV* plot for the fluorescence titration experiments of Fe^{3+} and Pb^{2+}.

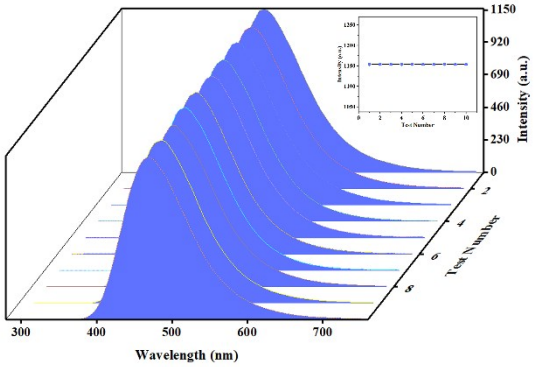

Fig. S6 The fluorescence intensity of complex **1** was measured 10 times in water.

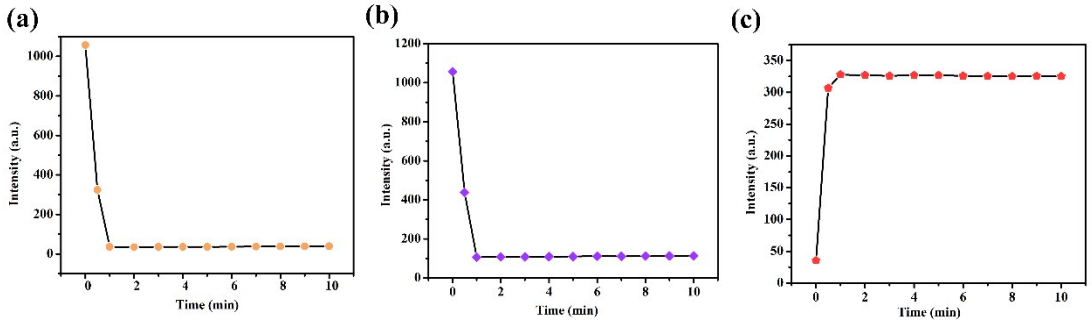

Fig. S7 Time-dependent fluorescence intensity of complex **1** with the addition of Fe^{3+} (a), Pb^{2+} (b), Fe^{3+}@**1**-GSH (c).

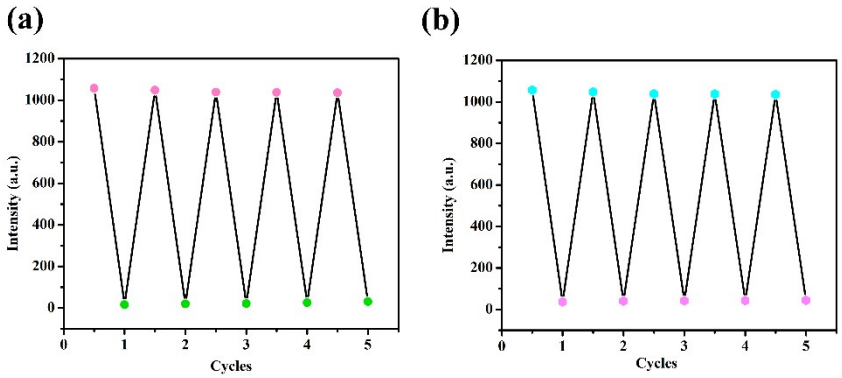

Fig. S8 The recyclable fluorescence experiments of Fe^{3+} (a), Pb^{2+} (b).

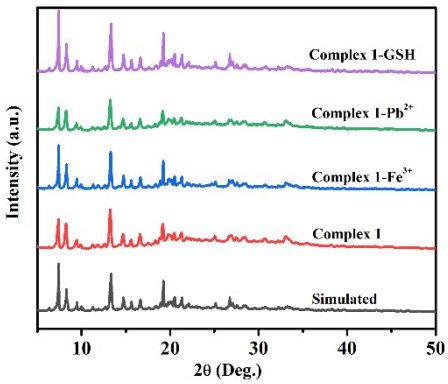

Fig. S9 PXRD patterns of complex **1** after soaked in Fe^{3+}, Pb^{2+} and reduced GSH.

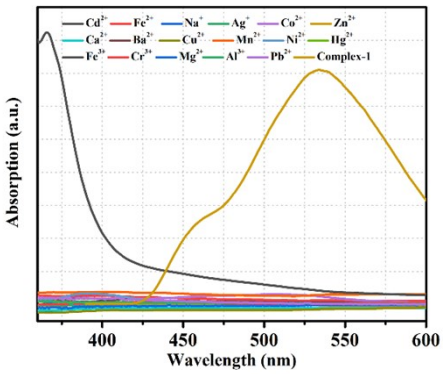

Fig. S10 The UV-vis absorption spectra of different cations and the emission spectrum of complex **1**.

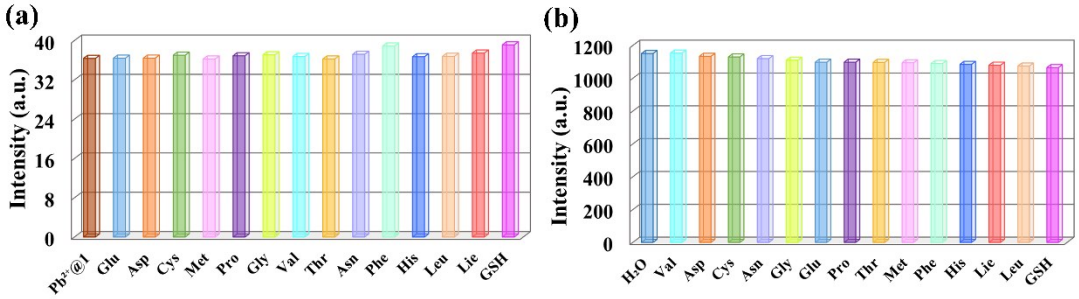

Fig. S11 (a) The fluorescence intensity of Pb^{2+}**@1** after adding different amino acids and reduced GSH; (b) The fluorescence intensity after adding different amino acids and reduced GSH to the suspension of complex **1.**

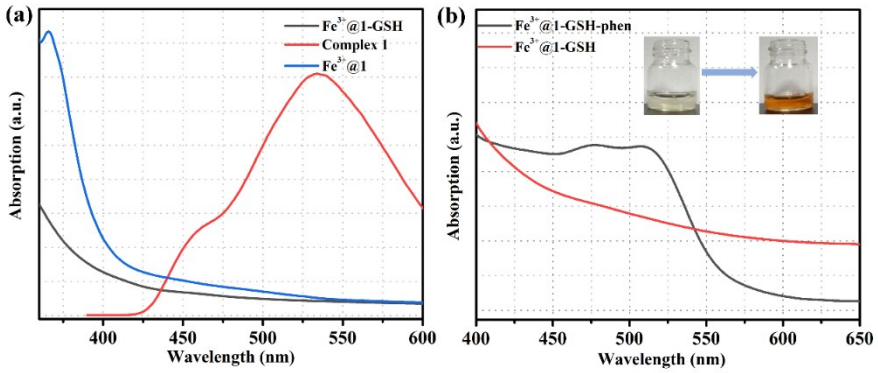

Fig. S12 (a) Fluorescence emission spectrum of **1** (red) and the UV-vis absorption spectra of Fe^{3+}@**1** (blue) and Fe^{3+}@**1**-GSH (black); (b) UV-vis absorption spectrum of Fe^{3+}@**1**-GSH (red) and Fe^{3+}@**1**-GSH-phen (black). Inset: The photograph of the solutions of Fe^{3+}@**1**-GSH before (left) and after (right) addition of 1,10-phen under visual light.