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Improving Coloration time and Moisture Stability of Photochromic Viologen–Carboxylate Zwitterion†

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Content

Table S1 Crystal and structure data for **L**·6H_2O.

	L·6H_2O (as-synthesized)
Chemical formula	$C_{16}H_{16}N_2O_4$ 6H_2O
M_r	408.40
Crystal system	Monoclinic
space group	*C*2/*c*
Temperature (K)	293
a, *b*, *c* (Å)	15.239(16), 7.250(7), 18.806(19)
β (°)	96.75(11)
V (Å^3)	2063(4)
Z	4
Radiation type	Mo-K_α
μ (mm^{-1})	0.11
Crystal size (mm)	0.15 × 0.02 × 0.02
Data collection Diffractometer	Rigaku Pilatus 200K
Absorption correction	Multi-scan
T_{min}, T_{max}	0.583, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10523, 2379, 1121
R_{int}	0.098
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.066, 0.183, 0.85
No. of reflections	2379
No. of parameters	145
No. of restraints	9
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^{-3})	0.31, −0.42

Table S2 Selected bond length [Å] and angles [°] of **L**·6H_2O.

Bond	**Length / Å**	**Bond**	**Length / Å**
O1—C8	1.241(3)	C5—H5	0.9300
O2—C8	1.253(3)	C6—C7	1.506(4)
N1—C1	1.342(3)	C6—H6A	0.9700
N1—C5	1.350(3)	C6—H6B	0.9700
N1—C6	1.496(3)	C7—C8	1.548(4)
C1—C2	1.383(3)	C7—H7A	0.9700
C1—H1	0.9300	C7—H7B	0.9700
C2—C3	1.388(3)	O1W—H1WA	0.844(10)
C2—H2	0.9300	O1W—H1WB	0.862(10)
C3—C4	1.394(3)	O3W—H3WA	0.857(10)
C3—C3^{i}	1.498(4)	O3W—H3WB	0.853(10)
C4—C5	1.371(3)	O2W—H2WA	0.833(10)
C4—H4	0.9300	O2W—H2WB	0.836(10)
Bond	**Angle / °**	**Bond**	**Length / °**
C1—N1—C5	120.2(2)	C7—C6—H6A	109.1
C1—N1—C6	119.7(2)	N1—C6—H6B	109.1
C5—N1—C6	120.1(2)	C7—C6—H6B	109.1
N1—C1—C2	121.0(2)	H6A—C6—H6B	107.8
N1—C1—H1	119.5	C6—C7—H7A	109.3
C2—C1—H1	119.5	C8—C7—H7A	109.3
C1—C2—H2	119.9	C6—C7—H7B	109.3
C3—C2—H2	119.9	C8—C7—H7B	109.3
C5—C4—H4	119.6	H7A—C7—H7B	108.0
C3—C4—H4	119.6	O1—C8—O2	124.9(2)
N1—C5—C4	120.6(2)	O1—C8—C7	118.1(2)
N1—C5—H5	119.7	O2—C8—C7	117.0(2)
C4—C5—H5	119.7	H1WA—O1W—H1WB	103(2)
N1—C6—C7	112.5(2)	H3WA—O3W—H3WB	107(2)
N1—C6—H6A	109.1	H2WA—O2W—H2WB	108(2)

Symmetry code: (i) −x+1/2, y, −z+1.

Table S3 Crystal and structure data for **ZnLCl**.

	ZnLCl (as-synthesized)
Chemical formula	$C_{16}H_{16}Cl_4N_2O_4Zn_2$
M_r	572.88
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature (K)	293
a, b, c (Å)	6.7262(19), 12.841(4), 12.304(4)
β (°)	94.395(5)
V (Å^3)	1059.6(6)
Z	2
Radiation type	Mo-K_α
Crystal size (mm)	0.35 × 0.28 × 0.21
Diffractometer	Rigaku Pilatus 200K
Absorption correction	Multi-scan Sphere (Rigaku CrystalClear)
R_{int}	0.029
T_{min}, T_{max}	0.854, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10982, 2433, 1883
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.071, 1.03
No. of reflections	2433
No. of parameters	127
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^{-3})	0.34, −0.29

Table S4 Selected bond lengths [Å] and angles [°] for **ZnLCl**.

Bond	**Length / Å**	**Bond**	**Length / Å**
Zn1—O2^{i}	1.9791(18)	O2—Zn1^{i}	1.9791(18)
Zn1—O1	1.9803(19)	N1—C15	1.330(3)
Zn1—Cl1	2.2168(9)	N1—C11	1.333(3)
Zn1—Cl2	2.2346(8)	N1—C16	1.496(3)
O2—C18	1.250(3)	O1—C18	1.255(3)
Bond	**Angle / °**	**Bond**	**Length / °**
O2^{i}—Zn1—O1	112.14(9)	C15—N1—C16	119.6(2)
O2i—Zn1—Cl1	113.26(7)	C11—N1—C16	120.1(2)
O1—Zn1—Cl1	106.01(6)	C18—O1—Zn1	130.90(18)
O2^{i}—Zn1—Cl2	99.44(6)	O2—C18—O1	125.3(2)
O1—Zn1—Cl2	105.94(6)	O2—C18—C17	116.3(2)
Cl1—Zn1—Cl2	119.94(4)	O1—C18—C17	118.4(2)
C18—O2—Zn1^{i}	125.66(17)	N1—C15—C14	121.2(2)
C15—N1—C11	120.3(2)	N1—C16—C17	110.6(2)

Symmetry codes: (i) −x, −y+1, −z+1.

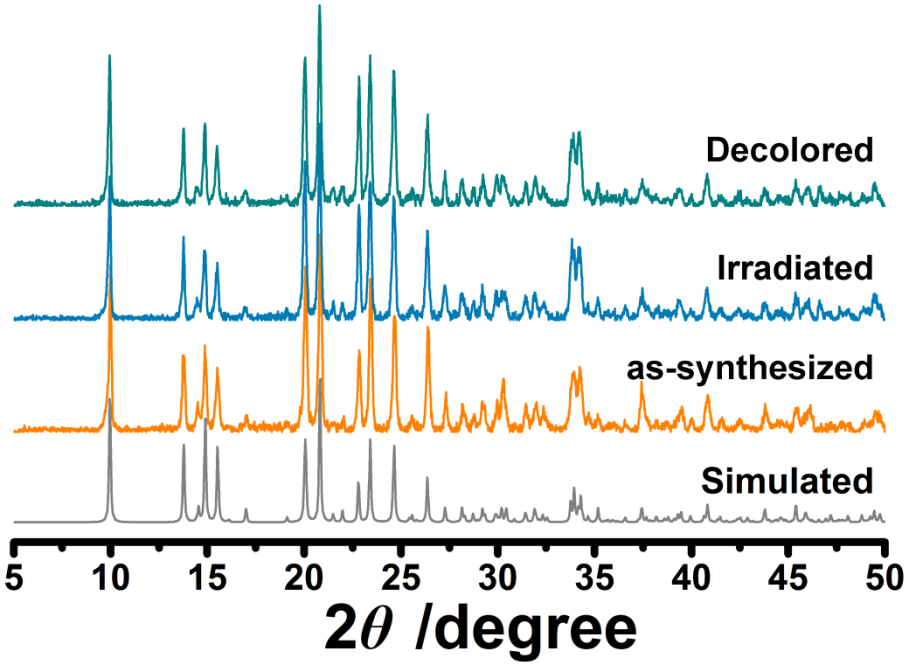

Fig. S1 PXRD patterns of **ZnLCl** in the photochromic process. For comparison, the simulated result from the single-crystal diffraction data is also shown.

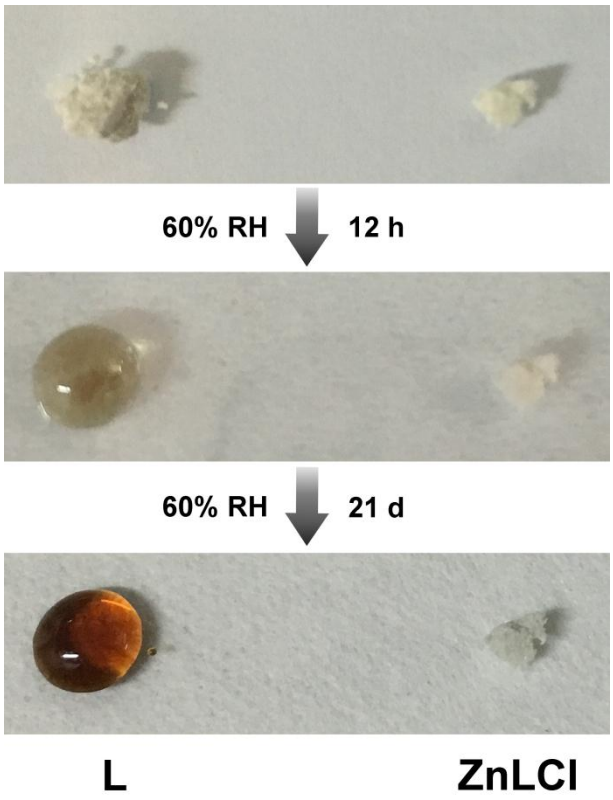

Fig. S2 Time-dependent humidity test of free ligand **L** and **ZnLCl**. RH: relative humidity**.**

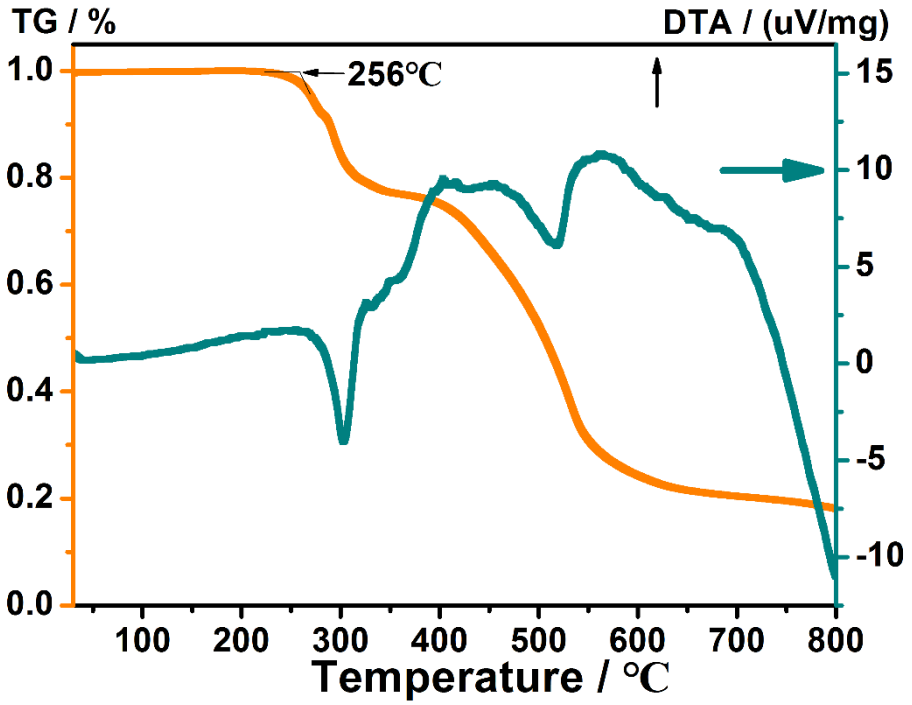

Fig. S3 Thermogravimetric analysis (TGA) of **ZnLCl** in the N_2 atmosphere.

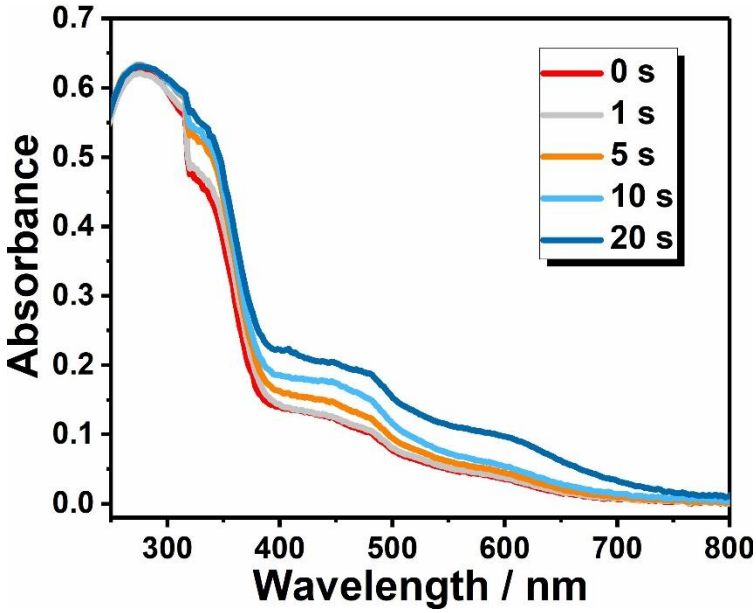

Fig. S4 Time-dependent UV–vis spectra of **L**.

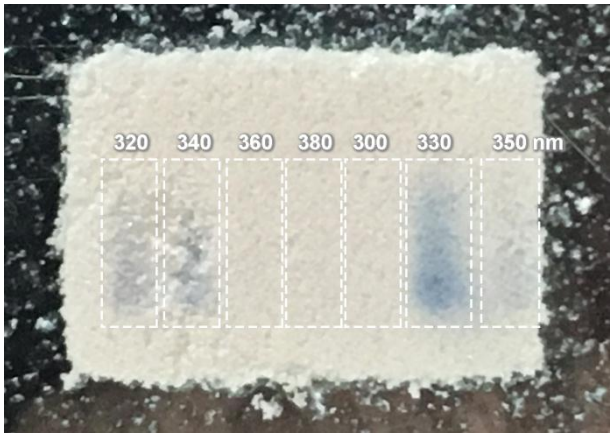

Fig. S5 Photoresponse range of **ZnLCl** upon irradiation of UV light at characteristic wavelength (nm). Every spot was irradiated for 1 min.

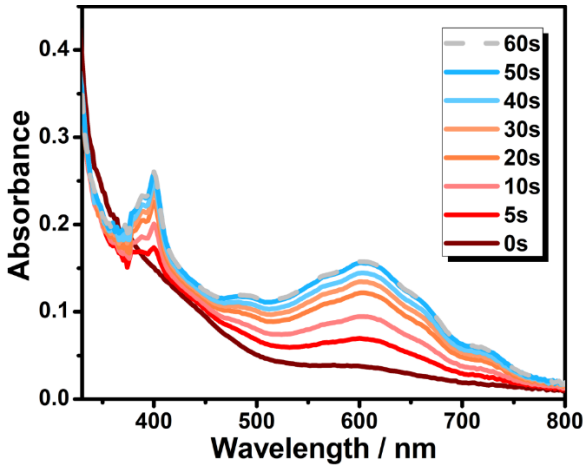

Fig. S6 Time-dependent UV–vis spectra of **ZnLCl**.

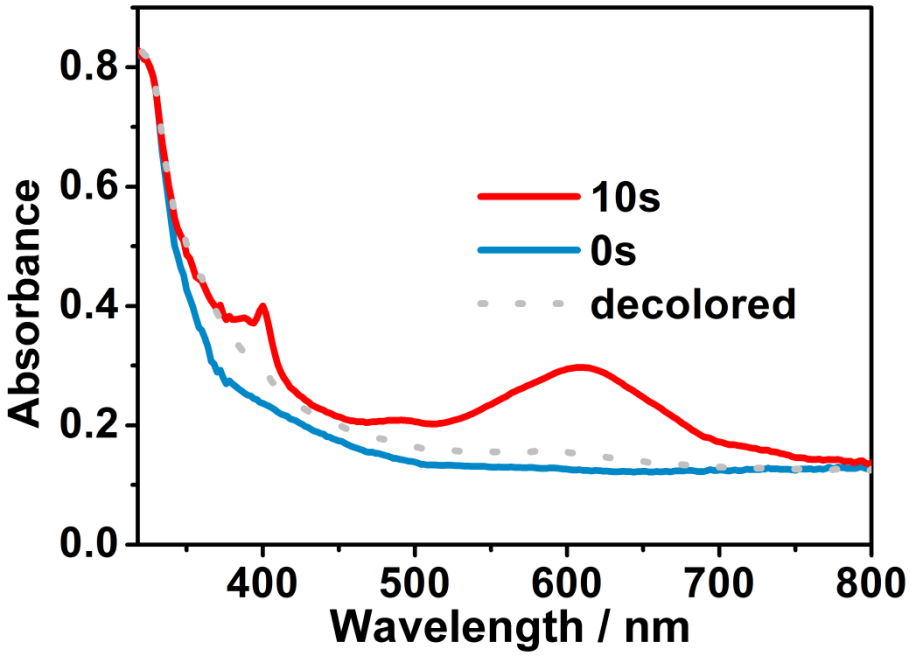

Fig. S7 UV–vis absorbance spectra of **ZnLCl** in one photochromic process. The decolored sample was obtained by leaving the irradiated sample in dark in air at ambient temperature for 12 h.

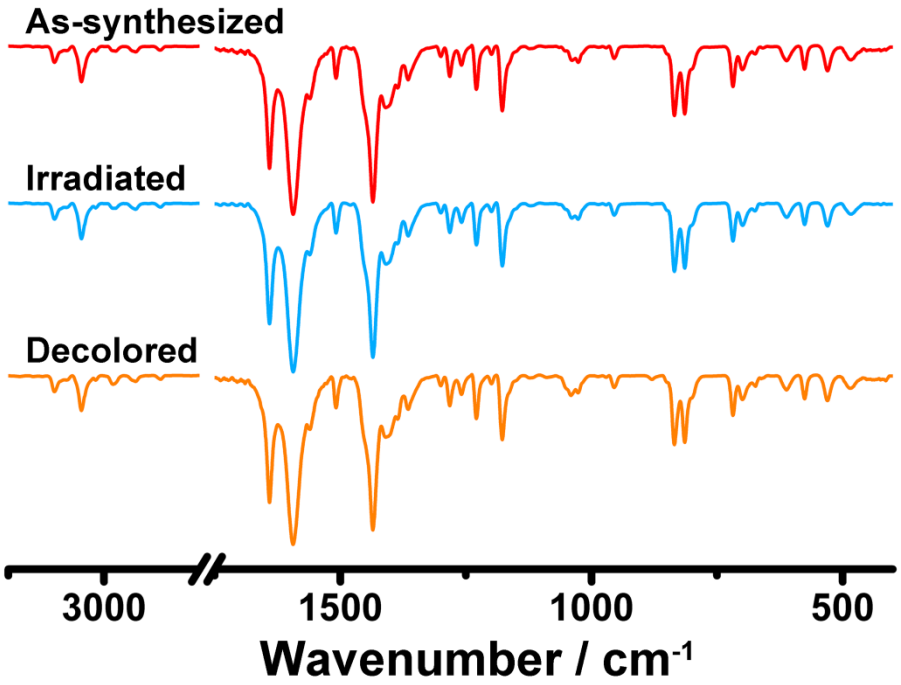

Fig. S8 IR spectra of **ZnLCl** in one photochromic process.

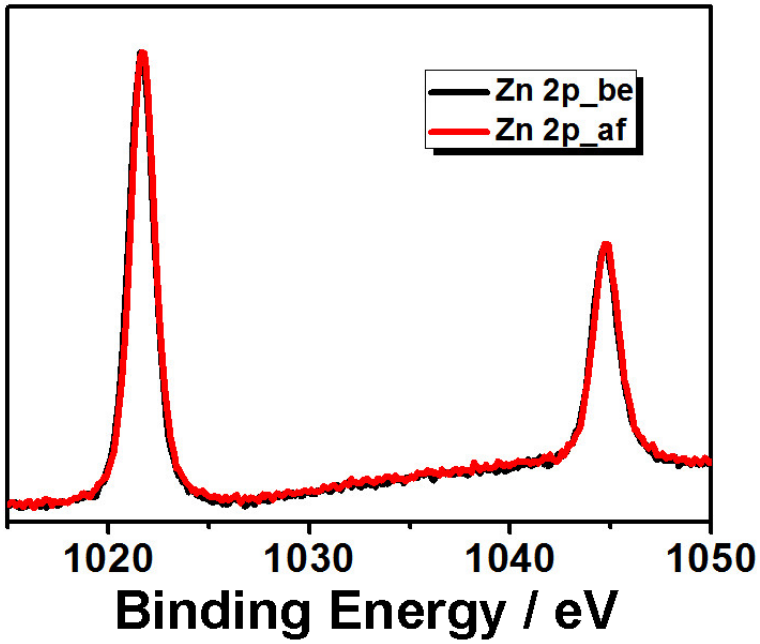

Fig. S9 Normalized XPS core-level spectra of **ZnLCl** before and after irradiation under Xe lamp for 30 min. **be**: before irradiation; **af**: after irradiation.