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Supporting Information

Application of Electron Transfer Catalyst in Light- induced Aerobic Oxidation of Alcohols

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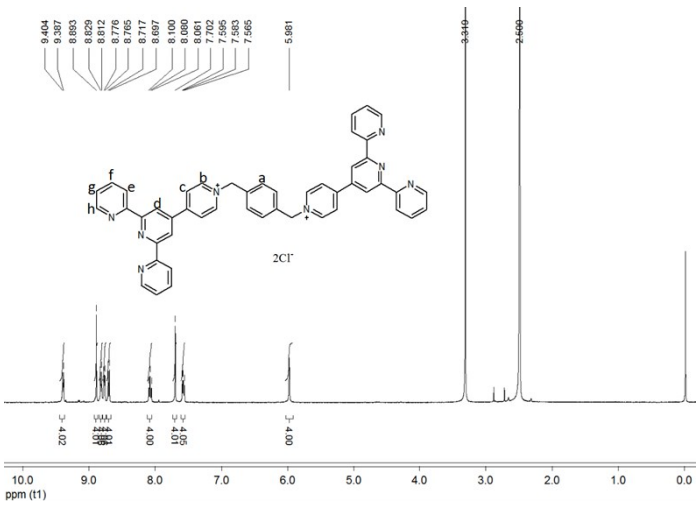
Experimental Section

Materials and Methods.

All of the chemicals were obtained from commercial sources and used without further purification. IR spectra (KBr pellets) were obtained on a Nicolet iS10 FT-IR spectrometer. Elemental analysis(C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. The UV-Vis absorption spectra were measured with a PE Lambda 900 Spectrometer. The electron spin resonance (ESR) signal was collected with a JES-FA200 ESR Spectrometer. ^{1}H NMR spectrum was carried out on a Bruker AV-400 NMR spectrometer. The powder X-ray diffraction (PXRD) pattern was recorded with a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) was performed with a ULVAC PHI Quantera SXM X-ray photoelectron spectrometer using Al Kα radiation (X-ray beam spot 200 μm). The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-5 capillary column.

Synthesis of L-Cl

To a stirred solution of 4'-(4-pyridyl)-2,2':6',2''-terpyridine (0.75g, 2.5 mmol) in dimethylformamide (10 mL), 1,4-Bis(chloromethyl)benzene (0.25 g, 1.5 mmol) was added and then the reaction temperature was increased to 110°C and maintained for 15h. The precipitate was isolated by hot filtration and washed with acetone separately, giving L-Cl as a yellow solid (yield: 60%). ^{1}H NMR(DMSO-d_6, ppm) 9.40 (4H, d, j = 6.8, H_b), 8.89 (4H, s, H_d), 8.82 (4H, d, j = 6.8, H_h), 8.70 (4H, d, j = 4.0, He), 8.70 (4H, d, j = 8.0, Hc), 8.08 (4H, t, j = 15.6, H_f), 7.70 (4H, s, Ha), 7.58 (4H, t, j = 12.0, Hg), 5.98 (4H, s, -CH_2-).



Synthesis of Zn-L-Cl

Typically, $ZnCl_2$ hydrated salt (0.15g, ~1.0 mmol) and L-Cl (0.32g, 0.4 mmol) were added to the mixed solvent of DMF (40 mL) and ethanol (40 mL) in a glass beaker. The mixed reagents were stirred for 20 min to give precipitate. The precipitate was collected by filtration and washed three times with acetone and dried at 350 K in an oven for 1h, giving Zn-L-Cl as an orange solid. Yield: 61%. Calculated for $C_{48}H_{36}N_8Zn_2Cl_6 \cdot 8H_2O$ (1212.45): C, 47.55; H, 4.32; N, 9.24; Found: C, 47.70; H, 4.05; N, 9.08.

Photocatalytic reaction

In general, a mixture of 4 μmol of Zn-L-Cl, 0.5 mmol alcohols and 2ml acetonitrile was placed in a quartz tube. The photoinduced oxidation reaction was initiated at room temperature in air atmosphere under light irradiation with different wavelengths. After the reaction, the Zn-L-Cl was separated by centrifugation, thoroughly washed with diethyl ether, and then reused in subsequent runs. The conversion of the product was calculated by GC analysis. The other control experiments were carried out under the same condition except changing the amount of Zn-L-Cl, wavelengths, or exposure to N_2/O_2 atmosphere.

The determined concentration data of reactants and products are further treated with expressions given as follows, where the conversion of substrates is expressed by Con.:

$$Con.\ (\%) = 100 \times (C_0 - C_i)/C_0 \qquad (1)$$

Where C_0 and C_i are the molar concentrations of substrates before and after the photocatalytic reaction, respectively. The selectivity to product is shown by Sel.:

$$Sel.\ (\%) = 100 \times C_j/(C_0 - C_i) \qquad (2)$$

Where C_j is the molar concentration of product. The turnover frequency (TOF) value of the reaction is calculated by an expression as follows:

$$TOF(h^{-1}) = (con. \times n_p)/(n_c \times h) \qquad (3)$$

Where n_p is the number of moles of substrates, n_c is the number of moles of catalyst, h represents the reaction time.

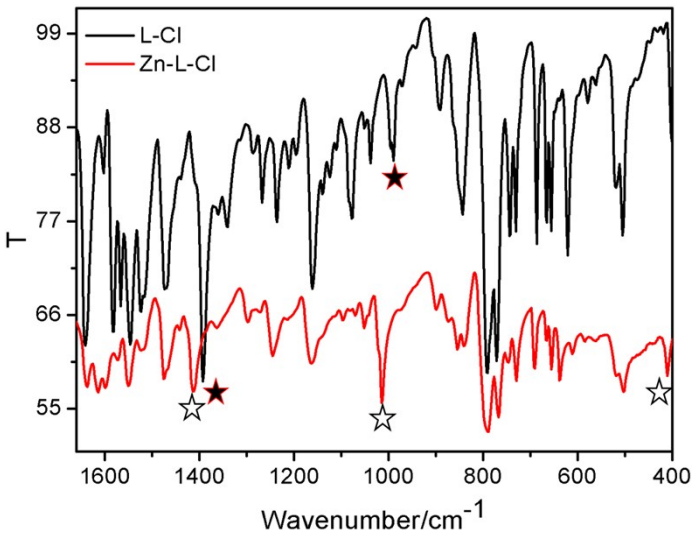


Figure S1. FT-IR spectra of L-Cl and Zn-L-Cl.

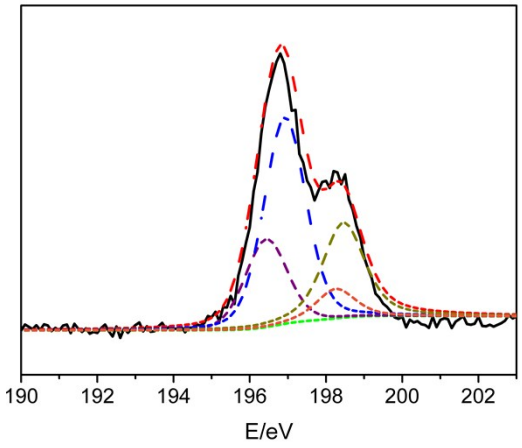


Figure S2. Cl 2p XPS core-level spectra of Zn-L-Cl. The horizontal axis represents the binding energy (dashed line: resolved and sum of peaks)

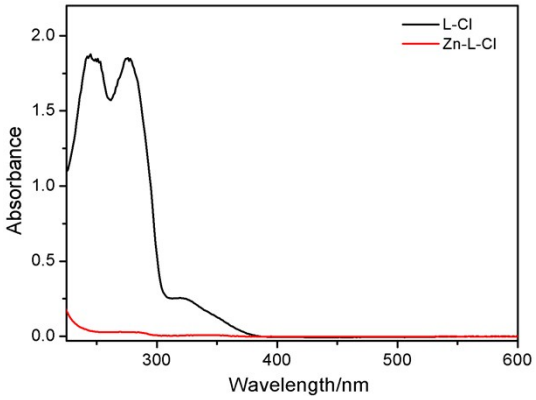


Figure S3. UV-vis absorption spectra of L-Cl and Zn-L-Cl saturated in acetonitrile solution.

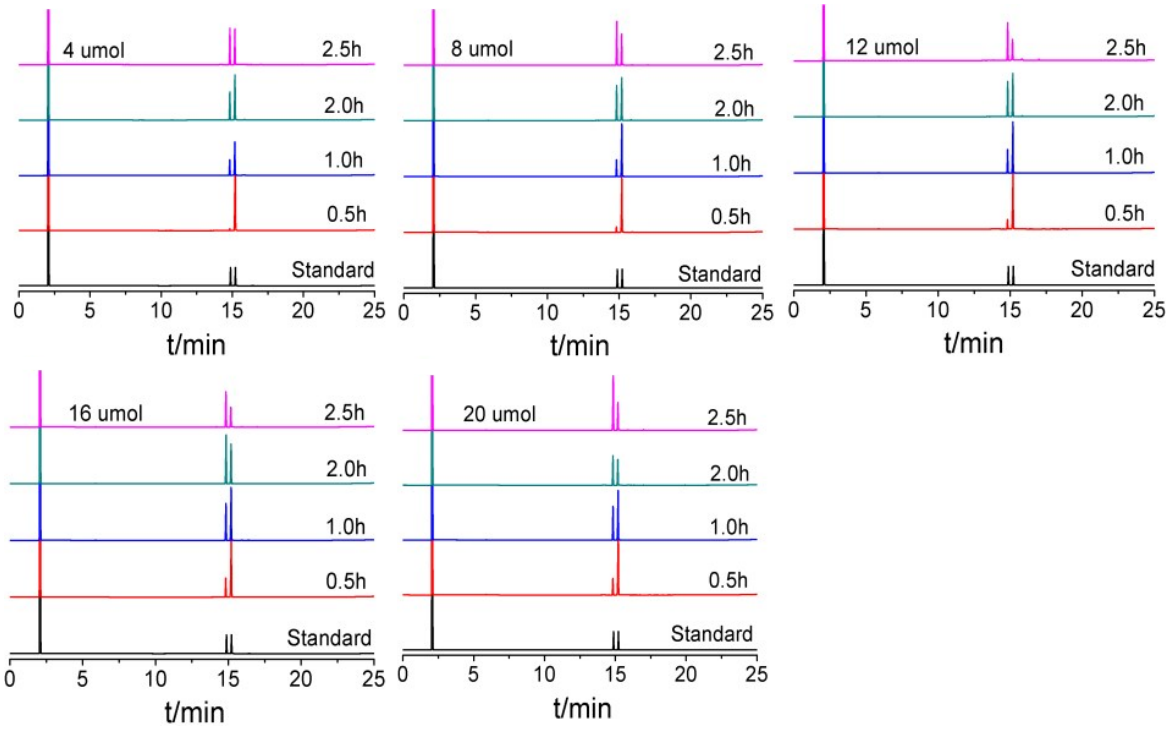


Figure S4 Gas chromatomap showing the conversion of 4-methoxy BA into corresponding aldehyde in presence of different amounts of Zn-L-Cl.

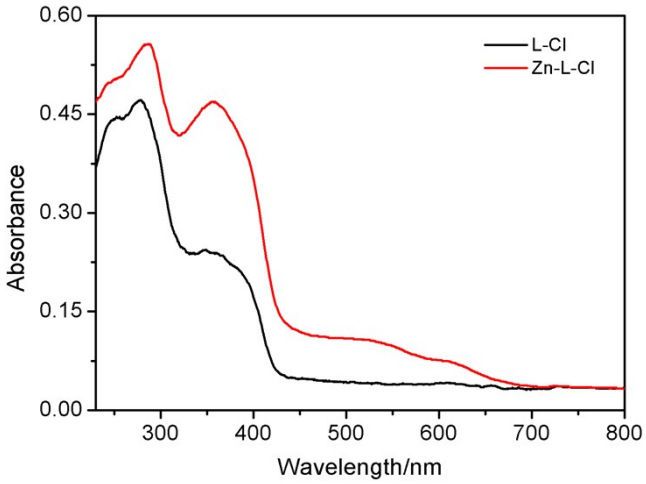


Figure S5. UV-vis diffuses-reflectance spectra of L-Cl and Zn-L-Cl.

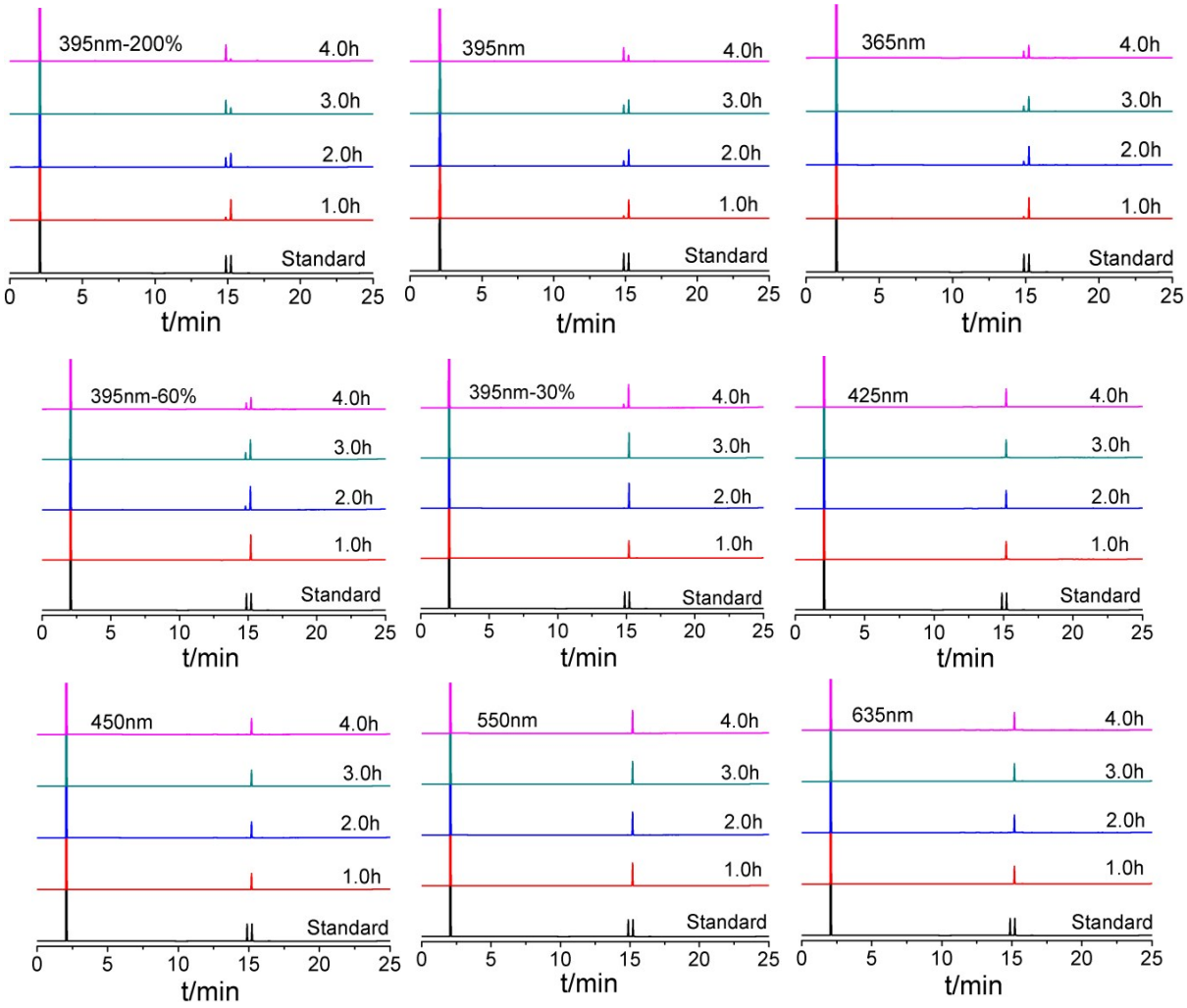


Figure S6 Gas chromatomap showing the conversion of 4-methoxy BA into corresponding aldehyde under irradiation of light sources with different intensities and wavelengths.

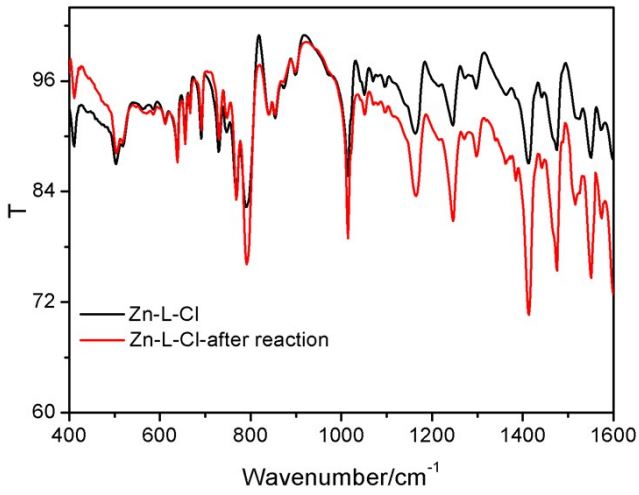


Figure S7. FT-IR spectra of Zn-L-Cl before and after five runs of reactions.

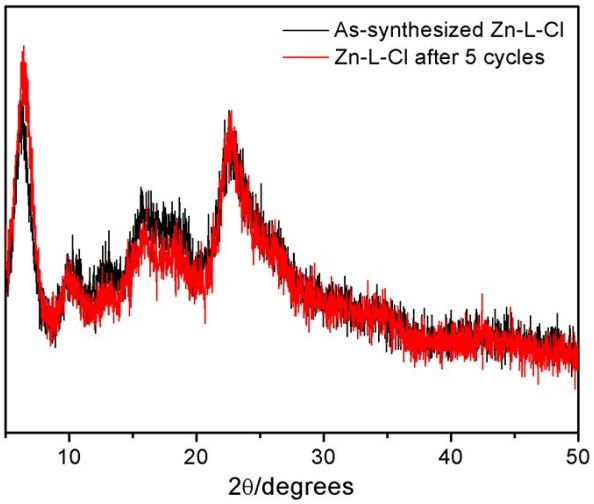


Figure S8. PXRD patterns for Zn-L-Cl before and after five runs of reactions.

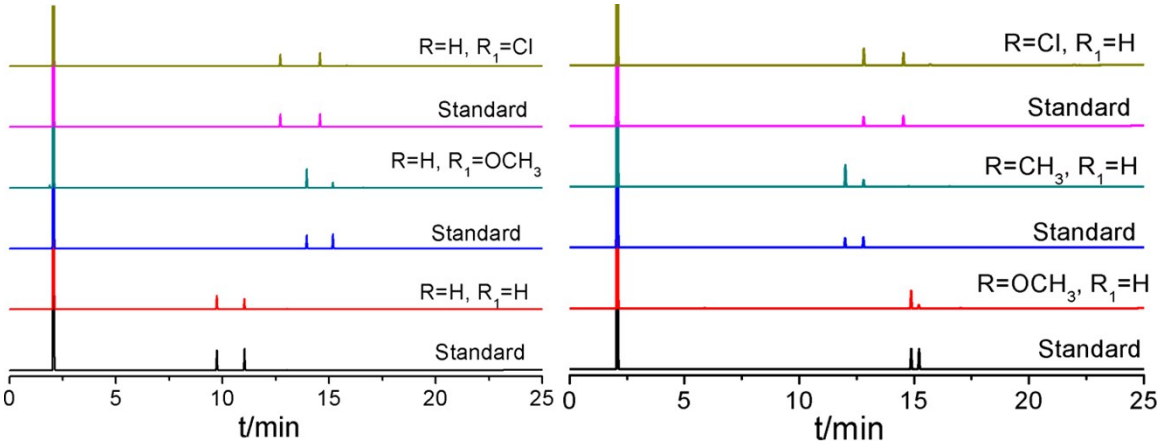


Figure S9. Gas chromatomap showing the conversion of benzyl alcohols with different substituted groups into corresponding aldehydes.

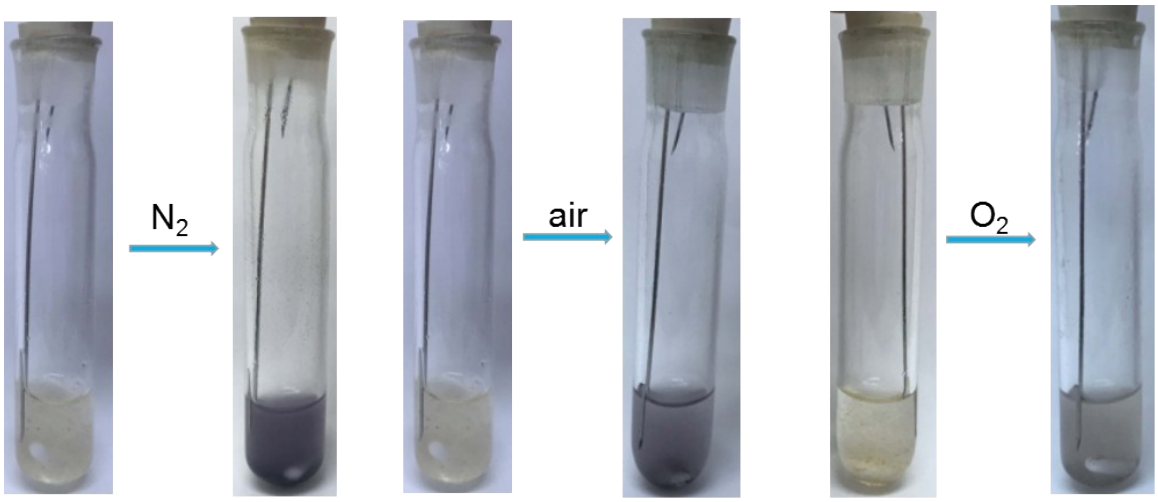


Figure S10. The color change of the reaction in three different atmospheres (N_2, air, and O_2).

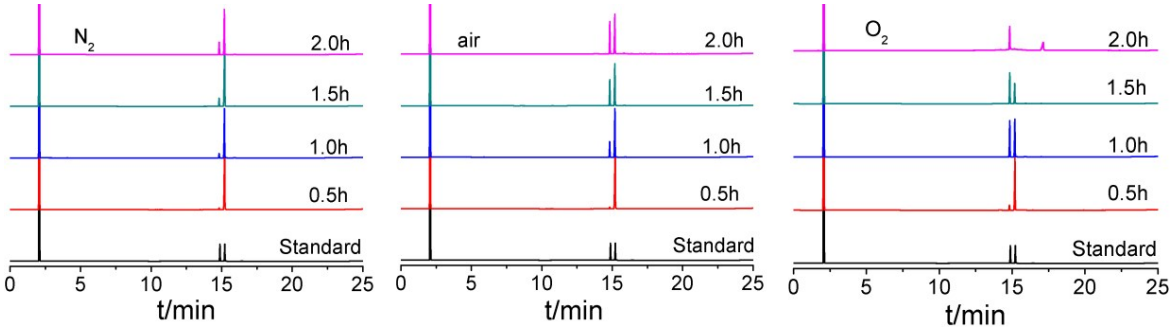


Figure S11. Gas chromatomap showing the conversion of 4-methoxy BA into corresponding aldehyde in three different atmospheres (N_2, air, and O_2).

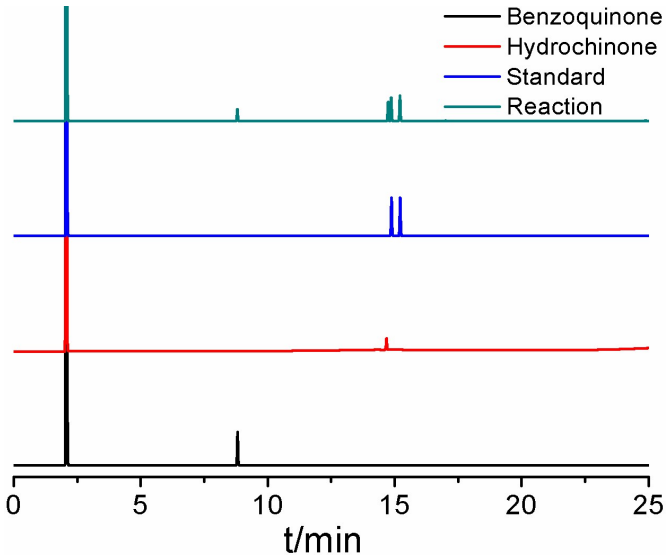


Figure S12. Gas Chromatomap of the radical scavenger benzoquinone (black line) and its reduced product hydrochinone (red line), standard 4-methoxy BA and 4-methoxybenzaldehyde (blue line), and the reaction mixture after light irradiation for 2 h (green line).

Table S1: Aerobic oxidation of 4-methoxy BA into corresponding aldehyde in different solvents.

Entry	Solvent	Conversion (%)	Selectivity (%)
1	Ethanol	3	>99
2	Methanol	2	>99
3	Water	2	>99
4	Acetonitrile	73	>99
5	Acetone	55	>99

Standard conditions: 4-methoxybenzyl alcohols (0.5 mmol), 4 umol Zn-L-Cl, 2ml solvent, rt, 4h, conversion was calculated by GC peaks.

Table S2: Comparison with different catalysts about selective oxidation of 4-methoxy BA.

Material	Entry	Substrate/mmol	Catalyst	Cocatalyst	Oxidant
Nano	1[1]	2	Au-Pd alloy NPs	-	-
	2[2]	0.05	Au-Cu alloy NPs	-	O_2
	3[3]	5ml	Pd NPs	-	O_2
	4[4]	0.5	Au@Ph-PMO NPs	-	air
	5[5]	0.1	HNb_3O_8 NS	-	O_2
	6[6]	0.5	nanoshell carbon (NSC)	-	67% HNO_3
	7[7]	1	graphene oxide	-	67% HNO_3
Complex	8[8]	1	Zinc(II) Complex	Zn	O_2, K^tBuO
	9[9]	0.3	UiO-67-TEMPO	-	t-Bu-ONO, air
	10[10]	1	$Cu_3(BTC)_2$	TEMPO	O_2
	11[11]	0.5	Ru(III) catalysts	-	H_2O_2
	12[12]	1	Cu-MOF-2	TEMPO	O_2
	13[13]	20	manganese(V) nitrido complex	$[Ru(bpy)_3]Cl_2$, $[Co(NH_3)_5Cl]Cl_2$	-
	14[14]	0.2	Cerium Complexes	-	O_2
Other	15[15]	0.2	Mixed-Valence Vanadium Oxide	-	-
	16[16]	0.8	Porous polymerized organocatalysts (PPOs)	TEMPO	hypochlorite
	17[17]	0.29	9-Fluorenone	DMSO	O_2 or air
	18[18]	0.1	Co@C−N nanoreactor	-	air
This work	19	0.5	Zn-L-Cl	-	air

Material	Entry	Catalyst amount	T/°	Time/h	Con.%	Sel.%	Yield%	TOF/h
Nano	1	50 mg	45	2	-	94	100	57.5
	2	20 mg	20	6	74	-	-	-
	3	0.1 g	130	5	60.5	99	-	-
	4	1.5 mol%	80	5	100	95	-	-
	5	8 mg	25	4	63	85	-	-
	6	10 mg	90	3	97	84	-	-
	7	5 wt%	90	2.5	-	-	94	-
Complex	8	5 mol%	60	24	-	-	71	-

	9	1 mol%	80	24	-	-	99	13.5(2.5h)
	10	150 mg	75	22	-	-	42	-
	11	1 mol%	100	6	-	-	99	-
	12	100 mg	75	16	-	99	99	-
	13	20 umol	-	0.5	-	-	-	-
	14	5 mol%	120	20	-	-	99	-
Other	15	50 mg	30	16	98	100	98	-
	16	3 mg	0	10	99	98	-	-
	17	3 mol%	rt	16-72	-	-	98	-
	18	10 mol	110	18	4	81	88	-
This work	19	4 umol	rt	4	90.7	99	90.7	29

Table3: The wavelength and out power of different light sources.

Wavelength/nm	Out Power/mw	Lop/mA
365	>420	700
395	>450	700
425	>280	700
450	>320	700
550	>220	700
635	>320	700

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