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# A bifunctional small molecular photocatalyst with a redox center and a Lewis acid site for one-pot tandem oxidation-

# acetalization

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#### **Section 1. Experimental details**

#### **1.1 General information**

All chemicals were obtained from commercial sources and were of GR/AR grade unless otherwise noted. IR spectra (KBr pellets) were obtained on a Nicolet IS10 FT-IR spectrometer. The UV-Vis absorption spectra were measured with a Shimadzu UV3600 Spectrometer. The electron spin resonance (ESR) signal was recorded with a JES-FA200 ESR Spectrometer. NMR measurements were carried out on a Bruker Bio Spin AVANCE III spectrometer. The GC analysis was performed on Shimadzu GC-2014C with an FID detector equipped with an Rtx-5 capillary column. HRMS was were performed on Q Exactive HF-X LC-MS, Chromatograph: U3000nano UPLC, Vanquish UPLC; Ion Spray: ESI, nanoESI, APCI, APPI. The light-induced catalysis reactions were tested on a multi-channel photochemical reaction system SSSTECH-LAL1CV1.0 from Shanghai 3S Technology Co., Ltd.

#### 1.2 Synthesis

**PTP-dq·Cl**: 4'-(4-pyridyl)-2,2':6',2"-terpyridine (PTP: 1.00 g, 3.2 mmol) and 3,6dichloropyridazine (dq: 4.00 g, 26.8 mmol) was added into in a 50 mL flask and stirred in the molten state at 110°C for 15 h. After that, 30 mL acetonitrile was added into the reaction and ultrasonic cleaning for 10 min. The precipitate was collected by filtration and washed with acetonitrile for three times. The crude product was recrystallized with distilled water to give a yellow power (1.12 g, yield: 75.7%). IR (KBr pellet, cm<sup>-1</sup>): 3394(s), 3116(w), 3039(m), 1635(m), 1585(w), 1527(s), 1456(w), 1371 (s), 1323(w), 1176(w), 823(m), 748(w), 530(w). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  = 9.22 (d, J=6.8, 2H), 8.34 (m, J=6.9, 2H), 8.04(d, J=7.4, 2H), 8.00 (d, J=7.4, 2H), 7.04 (m, 3H), 7.43 (t, J=7.4, 2H), 6.99 (t, J=5.8, 2H). <sup>13</sup>C NMR (176 MHz, DMSO-d<sub>6</sub>)  $\delta$  159.0, 157.0, 156.7, 156.6, 154.6, 149.9, 144.5, 143.8, 138.2, 133.0, 127.5, 126.3, 125.5, 121.7, 119.5. HRMS (ESI<sup>+</sup>) m/z: [PTP-dq]<sup>+</sup> calcd for C<sub>24</sub>H<sub>16</sub>ClN<sub>6</sub>: 423.11195; found: 423.11198.



Scheme S1. Synthetic route of catalyst PTP-dq·Cl.

**PTP-dq·PF**<sub>6</sub> crystal: **PTP-dq·Cl** (15 mg) was added into a solution of KPF<sub>6</sub> (30 mg) in water (3 mL). After filtration, the filtrate stands for 7 days to afford yellowish block crystals with the yield of ~50%.

#### 1.3 X-ray crystallographic analysis

The X-ray diffraction data of **PTP-dq·PF**<sub>6</sub> was collected on a Gemini A Ultra diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The absorption correction was performed by using the multi-scan program, and the structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using the SHELXL-2016 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were calculated in ideal positions and refined by riding on their respective carbon atoms. CCDC 2152910

# Section 2. Data of Tables and Schemes

PTP-dq·PF <sub>6</sub>
$C_{72}H_{48}C_{13}F_{18}N_{18}P_3$
1706.54
293
monoclinic
P2 <sub>1</sub> /n
15.627(3)
21.005(8)
21.972(6)
78.05(3)
7056(4)
4
1.606
0.306
3456.0
$51953/17539 \ [R_{int} = 0.0792]$
1.017
$R_1 = 0.0957, wR_2 = 0.2478$
$R_1 = 0.2577, wR_2 = 0.3531$

Table S1. Crystal data and structural refinement parameters of PTP-dq·PF<sub>6</sub>

Table S2. The tandem oxidation-acetalization reaction under different light irradiation.

R	он 1а		<mark>PTP-dq•Cl</mark> , 5 mol% MeCN, air, rt, h <i>v</i>		2a $+$ $3a$
Entry	Light sources	Conv. (%)	Sel./% 3a	Sel./% 2a	Light intensity (mW/cm <sup>2</sup> )
1	365 nm	73	13	60	373
2	395 nm	76	25	52	370
3	410 nm	78	38	40	336
4	White light	13	6	7	222

Reaction conditions: Benzyl alcohol (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL acetonitrile/1,2-propanediol (3.5:1.5, v/v) mixture at room temperature under air atmosphere, irradiation for 3h.

	н + но он	PTP-dq•Cl, MeCN, air,	$\frac{5 \text{ mol}\%}{\text{rt, hv}}$		+ R 3
Entry	Substrates	Time/h	Conv.%	Sel.% 3	Sel.% 2
1	4-OCH <sub>3</sub>	2.0	100	7	88
2	4-CH <sub>3</sub>	4.0	87	3	80
3	4-C1	4.5	78	9	91
4	4-F	4.5	79	3	97
5	4-H	4.5	75	1	99

**Table S3.** Tandem oxidation-acetalization reaction of substituted benzyl alcohols with 1,2-propanediol.

Benzyl alcohol (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL acetonitrile/1,2-propanediol (3.5:1.5, v/v) mixture at room temperature under air atmosphere, irradiation with 365 nm light source.

 $R \xrightarrow{II} O \xrightarrow{\text{PTP-dq} \cdot \text{Cl}, 5 \text{ mol}\%}_{\text{MoOH air st by}} R \xrightarrow{II} O$ 

Table S4. Acetalization reaction of substituted-benzaldehydes with methanol.

		MeOH, air, rt, h <i>v</i>	→ R	0
Entry	Substrates	Time/min	Conv. (%)	Sel. (%) of 4
1	4-H	120	96	99
2	4-CH <sub>3</sub>	90	99	99
3	4-F	110	99	92
4	4-Br	110	99	99
5	3-OCH <sub>3</sub>	80	99	90
6	3-CH <sub>3</sub>	90	99	99
7	3-C1	110	99	97
8	3,4-OCH <sub>3</sub>	120	99	40
9	2-furfural	120	80	

Reaction conditions: Substrates (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol at room temperature under air atmosphere, irradiation with 365 nm light source.

	Ć	3	<mark>PTP-dq-Cl,</mark> 5 mol% MeOH, N <sub>2</sub> , rt, hv	°→ (	4
Entry	Quencher	Equivalent	Conv. (%)	Sel. (%)	Notes
1			99	99	No scavenger
2	TEMPO	0.3	6	99	Radical scavenger
3	CuCl <sub>2</sub>	0.3	96	99	Electron scavenger
4	tert-Butanol	0.3	99	99	Hydroxide radical scavenger

**Table S5.** Inhibition impact of different scavengers on acetalization reaction of benzaldehyde and methanol.

Reaction conditions: Benzaldehyde (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) and scavenger (0.06 mmol) in 5 mL methanol at room temperature under  $N_2$  atmosphere, irradiation with 365 nm light source for 1h.

## Section 3. Additional figures



Figure S1. <sup>1</sup>H NMR (400 MHz) spectrum of PTP-dq·Cl in D<sub>2</sub>O.



Figure S2. <sup>13</sup>C NMR (176 MHz) spectrum of PTP-dq·Cl in DMSO-d<sub>6</sub>.



Figure S3. IR spectrum of PTP-dq·Cl.

A #11-22 RT: 0.06-0.11 AV: 12 SB: 9 0.01-0.05 NL: 2.48E9 T: FTMS + p ESI Full ms [100.0000-1000.0000]



**Figure S4.** HRMS spectra for catalyst PTP-dq·Cl, HRMS (ESI<sup>+</sup>) m/z:  $[PTP-dq]^+$  calcd for  $C_{24}H_{16}CIN_6$ : 423.11195; found: 423.11198 (up); HRMS (ESI<sup>+</sup>) m/z: [PTP-dq + H] found: 212.05962 (down).



Figure S5. The molecular structure of  $PTP-dq \cdot PF_6$  obtained by X-ray single crystal diffraction analysis.



**Figure S6.** UV-visible spectra of **PTP-dq·Cl**, **PTP-dq·PF**<sub>6</sub> and **PTP** (20  $\mu$ M) in methanol at room temperature.



**Figure S7.** Time-dependent conversion of benzyl alcohol. Reaction conditions: Benzyl alcohol (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%), and 1,2-propanediol (100  $\mu$ L) in 5 mL acetonitrile solution at room temperature under an air atmosphere, irradiation with 365 nm light source.



**Figure S8.** Hammett plot for tandem reaction of various substituted benzyl alcohol (BA) with 1,2propanediol over 5 mol% **PTP-dq·Cl**. Reaction rates were calculated from initial Kinetic studies of the reaction. Reaction rate constant- $k_x$  was calculated from the slope of the ln([BA]<sub>0</sub>/[BA]) vs. time plots according to ln([BA]<sub>0</sub>/[BA])= $k_x$ t. Hammett's equation log( $k_x/k_H$ ) =  $\sigma p \ge \rho$  is considered. Experimental results using  $\rho$  for para-substituted benzyl alcohol was fitted with the Hammet's equation with  $\rho$  = -0.84. The negative value of  $\rho$  indicates that the tandem reaction is promoted by the electron-donating substituents.



**Figure S9.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of the acetalization product of benzaldehyde with methanol after photocatalysis reaction. Reaction conditions: Benzaldehyde (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol at room temperature under a N<sub>2</sub> atmosphere, irradiation with 365 nm light source for 1.5 h. The product was obtained through the following steps: removing the reaction solution by rotary evaporator at 35 °C, then hexane (2.5 mL) was added, the catalyst settled down and removed by centrifugal separation, finally the filtrate was removed by rotary evaporator at 35 °C to give the product. The product was tested without further purification.



**Figure S10**. UV-Vis spectral changes of the reaction solution under different irradiation time. Reaction condition: Benzyl alcohol (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol at room temperature under an air atmosphere, irradiation with 365 nm light source. The inset shows color changes of the reaction solution when irradiated for 5 min.



**Figure S11.** ESR signals of the pyridinium radical obtained after mixing benzyl alcohol and **PTPdq·Cl** in acetonitrile-methanol (3.5/1.5, v/v) mixture and exposing it to 365 nm light for different time under air atmosphere. The internal standard signals for Mn(II) ions are shown on the two sides for comparison.



**Figure S12.** ESR spectra for TEMP-<sup>1</sup>O<sub>2</sub> for the mixture of **PTP-dq**·**Cl** (1 mg) and TEMP (6  $\mu$ L) in 1 mL acetonitrile-methanol (3.5:1.5, v/v) solution, irradiation with 365 nm light source under air. The signal for singlet oxygen was quenched after NaN<sub>3</sub> (1 mg) was added (brown line). The internal standard signals for Mn(II) ions are shown on the two sides for comparison.



**Figure S13.** ESR spectra for TEMP-<sup>1</sup>O<sub>2</sub> in the mixture of **PTP-dq·Cl** (1 mg), benzyl alcohol (6  $\mu$ L), and TEMP (6  $\mu$ L) in 1 mL acetonitrile-methanol (3.5:1.5, v/v) solution under air, irradiation with 365 nm light source in air. The internal standard signals for Mn(II) ions are shown on the two sides for comparison.



**Figure S14.** ESR spectra for the mixture of **PTP-dq·Cl** (1 mg), benzyl alcohol (6  $\mu$ L) and DMPO (4  $\mu$ L) in 1 mL acetonitrile-methanol (3.5:1.5, v/v) solution under air, irradiation with 365 nm light source in air. Only signal for DMPO-'O<sub>2</sub><sup>-</sup> was detected out when the reaction was operated in pure acetonitrile solution (purple line). The internal standard signals for Mn(II) ions are shown on the two sides for comparison.



**Figure S15.** ESR spectra for mixture of **PTP-dq·Cl** (1 mg), benzyl alcohol (BA: 6  $\mu$ L), and DMPO (4  $\mu$ L) in acetonitrile (1 mL), irradiation with 365 nm light. (b) ESR spectra for mixture of catalyst (1 mg), methanol (6  $\mu$ L), benzyl alcohol (BA, 6  $\mu$ L), p-benzoquinone (BQ: 1 mg), and DMPO (4  $\mu$ L) in acetonitrile (1 mL) under air, irradiation with 365 nm light.



**Figure S16.** (a) <sup>1</sup>H NMR (CD<sub>3</sub>OD) spectrum of the product in acetalization reaction of 4-methoxy benzaldehyde with CD<sub>3</sub>OD, the product was tested without further purification. (b) <sup>1</sup>H NMR (CD<sub>3</sub>OD) spectrum of standard acetal product. Note: The signal of Ha was disappeared, but the  $\alpha$ -H (H<sub>b</sub>) remained, indicating that H<sub>b</sub> is from the aldehyde group.



Figure S17. The GC-analysis for the inhibition impact of TEMPO on acetalization reaction of benzaldehyde and methanol under different reaction time. Reaction condition: Benzaldehyde (0.2 mmol), **PTP-dq·Cl** (0.01 mmol, 5 mol%), TEMPO (0.06 mmol) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source.



**Figure S18.** The GC-MS analysis for the inhibition impact of TEMPO on acetalization reaction of benzaldehyde and methanol. Reaction condition: Benzaldehyde (0.2 mmol), **PTP-dq·Cl** (0.01 mmol, 5 mol%), TEMPO (0.06 mmol) in 5 mL methanol in  $N_2$  at room temperature, irradiation with 365 nm light source for 90 min.

## Section 4. Product analysis



**Figure S19**. The GC-analysis of benzyl alcohol to benzaldehyde dimethyl acetal at different reaction time. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S20.** The GC-analysis of 4-methoxybenzyl alcohol conversion at different reaction time. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S21.** The GC-analysis of 3-methylbenzyl alcohol to acetal after reaction for 110 min. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S22.** The GC-analysis of 3-chlorobenzyl alcohol to acetal after reaction for 130 min. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S23.** The GC-analysis of 4-methyl benzyl alcohol to acetal after reaction for 90 min. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S24.** The GC-analysis of 4-chlorobenzyl alcohol to acetal after reaction for 120 min. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S25.** The GC-analysis of 3-methoxybenzyl alcohol to acetal after reaction for 4 h. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S26.** The GC-analysis of 4-fluorobenzyl alcohol to acetal after reaction for 110 min. Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source.



**Figure S27.** The GC-analysis of 3,4-dimethoxybenzyl alcohol and 3,4-dimethoxybenzaldehyde to acetal. (a) Reaction conditions: 3,4-dimethoxybenzyl alcohol (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source for 130 min. (b) Reaction conditions: 3,4-dimethoxybenzaldehyde (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 110 min.



Figure S28. The GC-analysis of 4-bromobenzyl alcohol and 4-bromobenzaldehyde to acetal. (a) Reaction conditions: 4-bromobenzyl alcohol (0.2 mmol), catalyst PTP-dq·Cl (0.01 mmol, 5 mol%) in 5 mL methanol at room temperature under an air atmosphere, irradiation with 365 nm light source for 130 min. (b) Reaction conditions: 4-bromobenzaldehyde (0.2 mmol), catalyst PTP-dq·Cl (0.01 mmol, 5 mol%) in 5 mL methanol at room temperature under N<sub>2</sub> atmosphere, irradiation with 365 nm light source for 110 min.



**Figure S29**. The GC-analysis of 4-methoxybenzyl alcohol and 4-methoxybenzaldehyde to acetal. (a) Reaction conditions: 4-methoxybenzyl alcohol (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source for 70 min. (b) Reaction conditions: 4-methoxybenzaldehyde (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 70 min.



**Figure S30.** The GC-analysis of 2-furaldehyde to acetal. Reaction conditions: 2-furaldehyde (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol at room temperature under a  $N_2$  atmosphere, irradiation with 365 nm light source for 120 min.



**Figure S31.** <sup>1</sup>H NMR spectrum of acetal. Reaction conditions: Benzaldehyde (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL acetonitrile/1,2-propanediol (3.5:1.5, v/v) mixture in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 5 h. The product was purified by column chromatography to give benzaldehyde propylene glycol acetal (isomer mixture).



**Figure S32.** <sup>1</sup>H NMR spectrum of acetal product in the acetalization of 4-methylbenzaldehyde and methanol after reaction for 2 h. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h. NMR measurements were carried out in DMSO-d<sub>6</sub>. Product was obtained through the method in Figure S9.



**Figure S33.** <sup>1</sup>H NMR spectrum of acetal product in the acetalization of 4-fluorobenzaldehyde and methanol after reaction for 2 h. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h. NMR measurements were carried out in DMSO-d<sub>6</sub>. Product was obtained through the method in Figure S9.



**Figure S34.** <sup>1</sup>H NMR spectrum of acetal product in the acetalization of 3-methoxybenzaldehyde and methanol after reaction for 2 h. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h. NMR measurements were carried out in DMSO-d<sub>6</sub>. Product was obtained through the method in Figure S9.



**Figure S35.** <sup>1</sup>H NMR spectrum of acetal product in the acetalization of 4-bromobenzaldehyde and methanol after reaction for 2 h. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq**·**Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h. NMR measurements were carried out in DMSO-d<sub>6</sub>. Product was obtained through the method in Figure S9.



**Figure S36.** <sup>1</sup>H NMR spectrum of acetal product in the acetalization of 3-methylbenzaldehyde and methanol after reaction for 2 h. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq**·**Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h. NMR measurements were carried out in DMSO-d<sub>6</sub>. Product was obtained through the method in Figure S9.



**Figure S37.** <sup>1</sup>H NMR spectrum of acetal product in the acetalization of 3-chlorobenzaldehyde and methanol after reaction for 2 h. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h. NMR measurements were carried out in DMSO-d<sub>6</sub>. Product was obtained through the method in Figure S9.



**Figure S38.** GC-MS of the acetalization reaction of benzaldehyde with 1,2-propanediol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL acetonitrile/1,2-propanediol (3.5:1.5, v/v) mixture in N<sub>2</sub> at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S39.** HRMS spectrum for product benzaldehyde propylene glycol acetal, HRMS (ESI<sup>+</sup>) m/z: [M + H] calcd for  $C_{10}H_{13}O_2$ : 165.09155; found: 165.09041.



**Figure S40.** GC-MS of the acetalization reaction of 4-methoxybenzyl alcohol with 1,2-propanediol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL acetonitrile/1,2-propanediol (3.5:1.5, v/v) mixture in air at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S41.** GC-MS of the acetalization reaction of 3-chlorobenzyl alcohol of methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source for 2 h.



Figure S42. GC-MS of the acetalization reaction of 4-methylbenzyl alcohol with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in air at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S43.** GC-MS of the acetalization reaction of 2-furfural with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S44.** GC-MS of the acetalization reaction of 4-bromobenzaldehyde with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S45.** GC-MS of the acetalization reaction of 4-fluoroformaldehyde with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S46.** GC-MS of the acetalization reaction of 4-methoxybenzaldehyde with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S47.** GC-MS of the acetalization reaction of 3-methylbenzaldehyde with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S48.** GC-MS of the acetalization reaction of 3-chlorobenzaldehyde with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.



**Figure S49.** GC-MS of the acetalization reaction of 3,4-dimethoxybenzaldehyde with methanol. Reaction condition: Substrate (0.2 mmol), catalyst **PTP-dq·Cl** (0.01 mmol, 5 mol%) in 5 mL methanol in  $N_2$  at room temperature under irradiation with 365 nm light source for 2 h.

Section 5. Light source parameters



Figure S50. The spectra of 365-370 nm light source.



Figure S51. The spectra of 395-400 nm light source.



Figure S52. The spectra of 410-415 nm light source.



Figure S53. The spectra of white light source (6500K).

Entry	Electric Power	365-370 nm mW/cm <sup>3</sup>	395-400 nm mW/cm <sup>3</sup>	410-415 nm mW/cm <sup>3</sup>	6500 K mW/cm <sup>3</sup>
1	1W	136.02	138.66	127.38	98.85
2	2W	185.10	185.76	168.51	125.40
3	3W	236.85	234.21	214.29	151.26
4	4W	281.97	279.99	258.09	177.15
5	5W	329.10	323.70	285.92	201.03
6	6W	373.53	370.23	336.39	222.27
7	7W	409.38	413.34	372.87	242.16
8	8W	424.62	457.14	410.70	260.76
9	9W	421.32	498.27	443.22	275.34
10	10W	417.99	538.08	476.37	289.29
11	11W	432.60	575.25	508.23	301.89
12	12W	429.93	607.74	537.42	307.86

**Figure S54.** Corresponding relationship between light intensity and electric power of light source. Measuring instrument: THORLABS, 8-color brightness test, single lamp epoxy board; electric power: 1-12w, test environment: 26 °C, fan cooling.



Figure S55. The images of photo-reactor. Instrument model: SSSTECH-LAL1CV1.0.