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Visible light assisted reduction of CO_2 into formaldehyde by heteroleptic ruthenium metal complex-TiO_2 hybrid in aqueous medium

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Experimental section

Materials: The entire chemical were taken by the commercial sources and used without further purification. 2,2-bypyridine, 1, 10-Phenanthroline (phen), and $RuCl_3.xH_2O$ were purchased form Merck India. Ammonium acetate, KBr, 4-formylbenzoic acid, and 4-nitro benzaldehyde were taken from Spectrochem. All the solvents were GR grade .

Synthesis of 1

The ligands were synthesized from previously adapted method.[1] For the typical synthesis, 1, 10-Phenanthroline (5.0g), was dissolved in concentrated sulphuric acid (30 ml) in 100 ml round bottom flask. Than 2.5 g KBr was added followed by 15 ml HNO_3 at 4-5 ^oC. The mixtures were allowed for reflux for 2h. After cooling down at room temperature 500 ml ice cold deionised water was added. The mixture was carefully neutralized by using the sodium hydroxide. Than the solvents extraction were done in dichloromethane (DCM) and water to afford the yield 95% for compound **1**. ^{1}HMNR (400 MHz, DMSO-d_6, δ ppm): 9.08 (2H, m), 8.48 (2H, m), 7.58 (2H, m).

Synthesis of L1OH

0.42 g (2 mmol) of 1 and 0.34g (2.2 mmol) of 4-formylbenzoic acid were taken in round bottom flask. 30 ml glacial acetic acid was added followed by addition of 2.31 g (30 mmol) ammonium acetate. The mixture was allowed to reflux for 3.5 h. At room temperature deionised water wad added and yellow colour precipitate was obtained (yield, 86%). The compound was characterised by ^{1}H NMR before further used. ^{1}HMNR (400 MHz, DMSO-d_6, δ ppm): 12.67 (1H, s), 7.76 (2H, d), 7.64 (2H, d), 7.11 (2H, d), 6.91 (2H, d), 6.57 (2H, m). ^{13}C-NMR (400 MHz, DMSO-d_6, δ ppm) δ 167.71 (COOH), 150.15-124.12 (ArC). Calculated mass for $C_{20}H_{12}N_4O_2$ (M = 340.33) and found (MALDI Tof MS): m/z = 341.5 $[M + H]^+$.

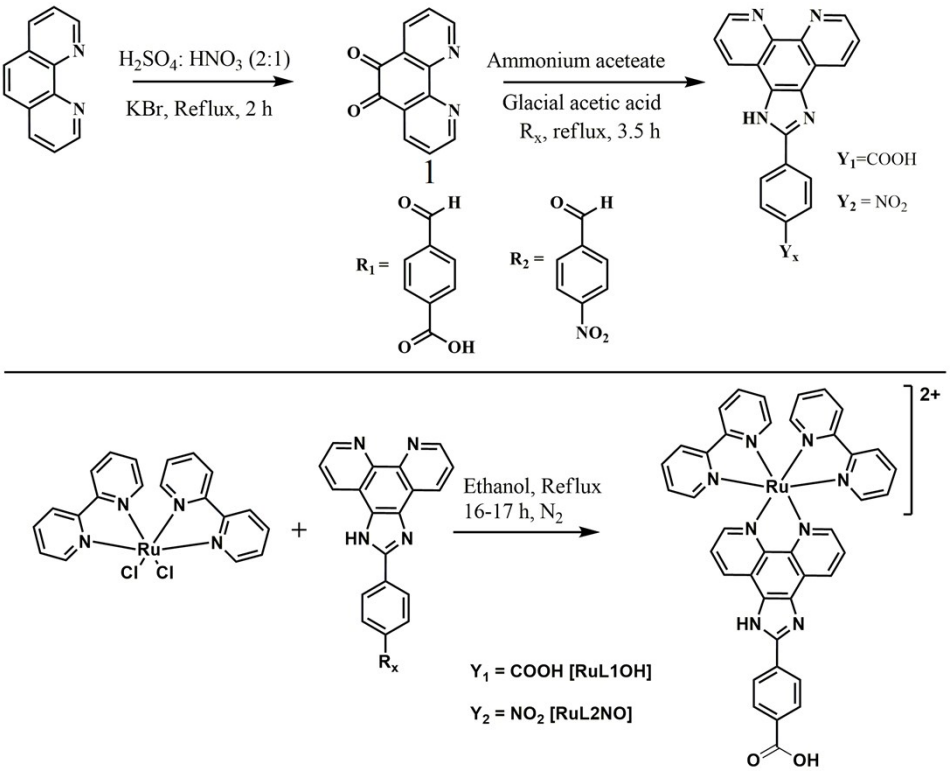
Synthesis of L2NO

All the procedure was followed as for L1OH synthesis, however, 4- nitrobenzaldehyde was used instead of 4-formylbenzic acid. ^{1}HMNR (400 MHz, DMSO-d_6, δ ppm): 7.84 (2H, d),

7.71 (2H, d), 7.29 (4H, m), 6.66 (2H, m). Calculated mass for $C_{19}H_{11}N_5O_2$ (M = 341.32) and found (MALDI Tof MS): m/z = 342.5 $[M + H]^+$. Isolated yield was obtained 93% after purification.

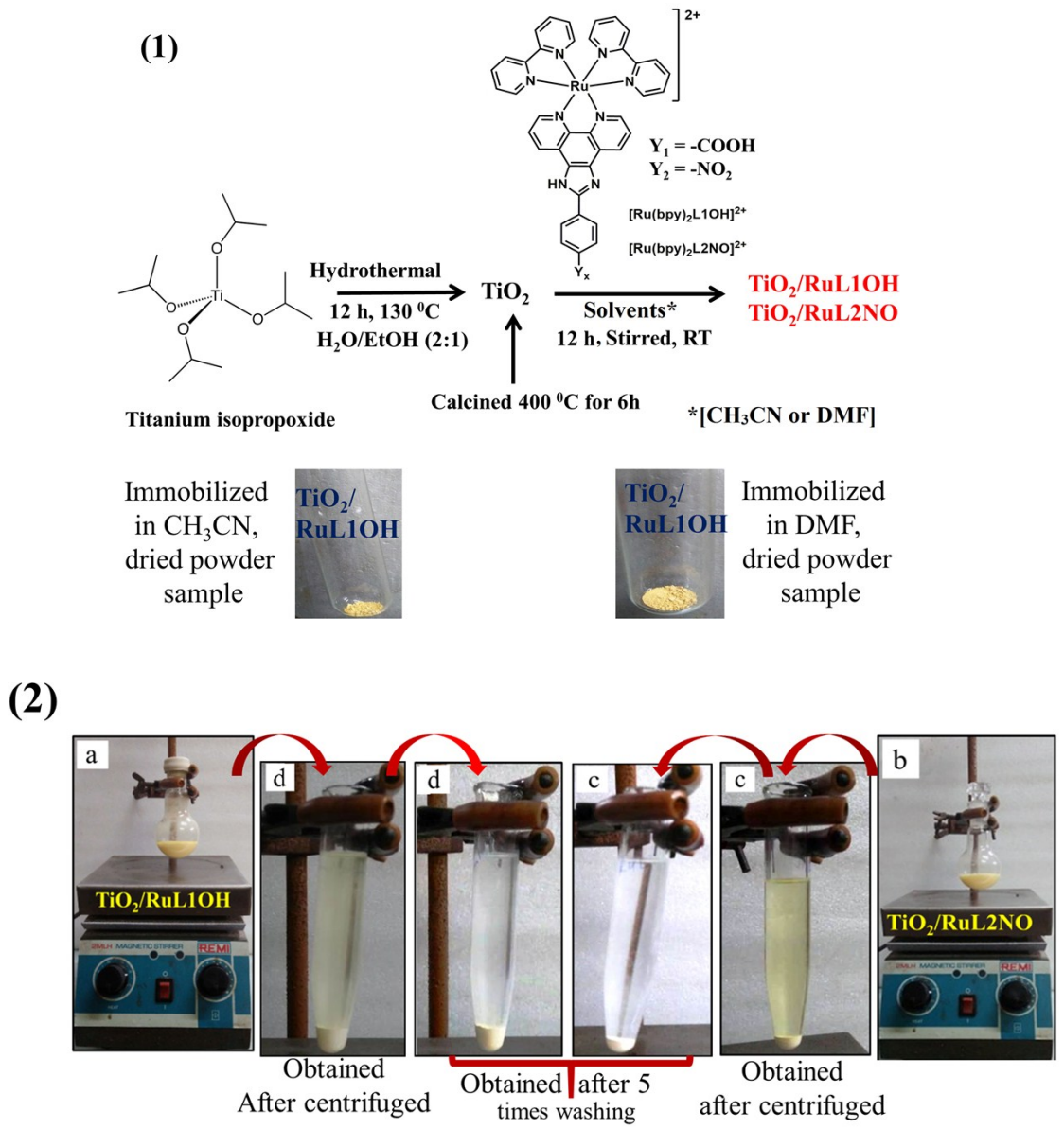
Synthesis of metal complexes

Firstly, $[Ru(bpy)_2Cl_2]$ metal precursor was prepared form previous report.[2] 0.3 g (0.619 mmol) of metal precursor and 0.21 g (0.619) of L1OH was refluxed in ethanol under nitrogen atmosphere. The crude product was collected using rotary evaporator and minimum amount of cold methanol was added. The unreacted ligand was obtained as precipitate and a red orange color solution was evaporated to afford crystalline metal complex product. ^{1}HMNR (400 MHz, DMSO-d_6, δ ppm): ^{1}H NMR (DMSO-d_6): d 7.31 (t, J = 6.6, 2H, bpy), 7.56–7.63 (m, 4H, bpy), 7.83 (d, J =5.2, 2H, bpy), 7.98 (m, 2H, phen), 8.02–8.15 (m, 4H, bpy), 8.18–8.21 (m, 4H, bpy, C_6H_4), 8.45 (d, J =8.2, 2H, C_6H_4), 8.82–8.88 (m, 4H, phen, bpy), 9.1–9.2 (m, 2H, phen), 13.8 (s, 1H, COOH). Calculated mass for $C_{40}H_{28}N_8O_2Ru$ (M = 754) and found (MALDI Tof MS): m/z = 755.07 $[M + H]^+$.



Scheme S1. Synthetic route of ligands and metal complexes

Synthesis of TiO_2 nano particles and catalyst



Scheme S2 (1) Repretative sythesis Scheme of TiO_2 nano particles. (2) immobilization process, for example, 1000 mg of TiO_2 powder and 2.5 µM of metal complexes (RuL1OH, RuL2NO) were stirred in CH_3CN solvent for 12 h (a). The solution was centrifuged to separate TiO_2 powder (b, d). TiO_2 was washed 5 times using mother solvents and water (c,d). the dried pawder is shown above in both the solvents (CH_3CN and DMF).

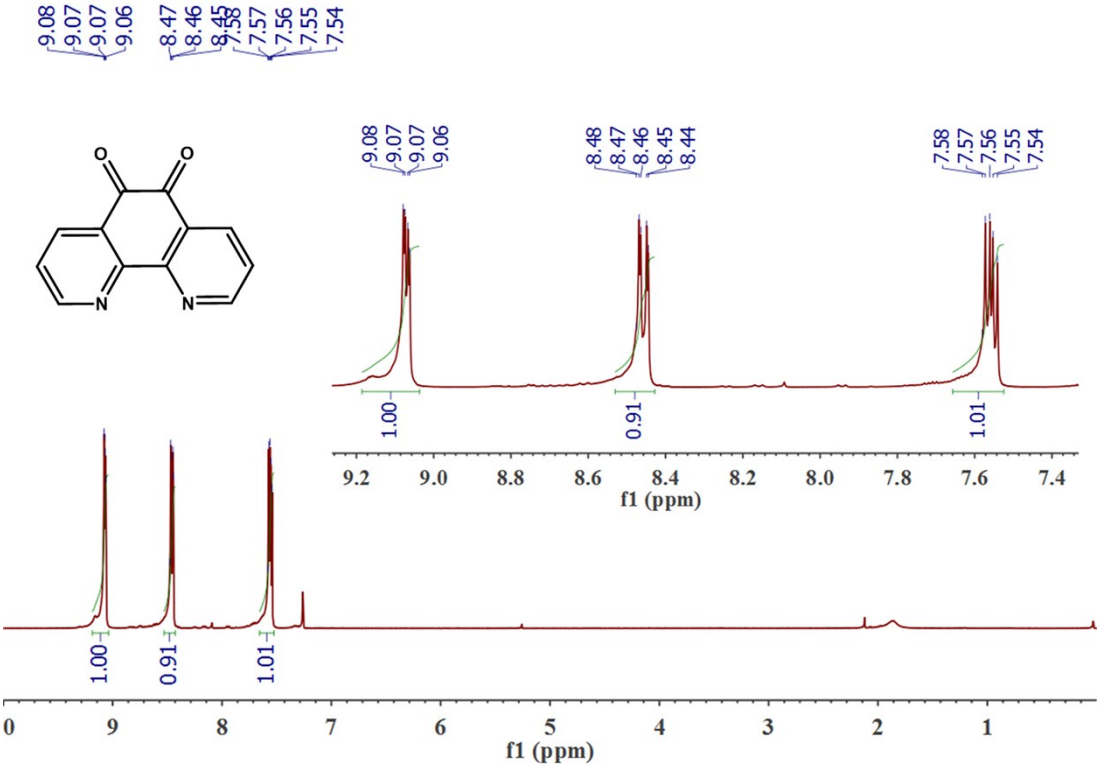


Fig. S1. ^{1}H NMR spectra of ligand recorded at room temperature in DMSO-d$_{6}$

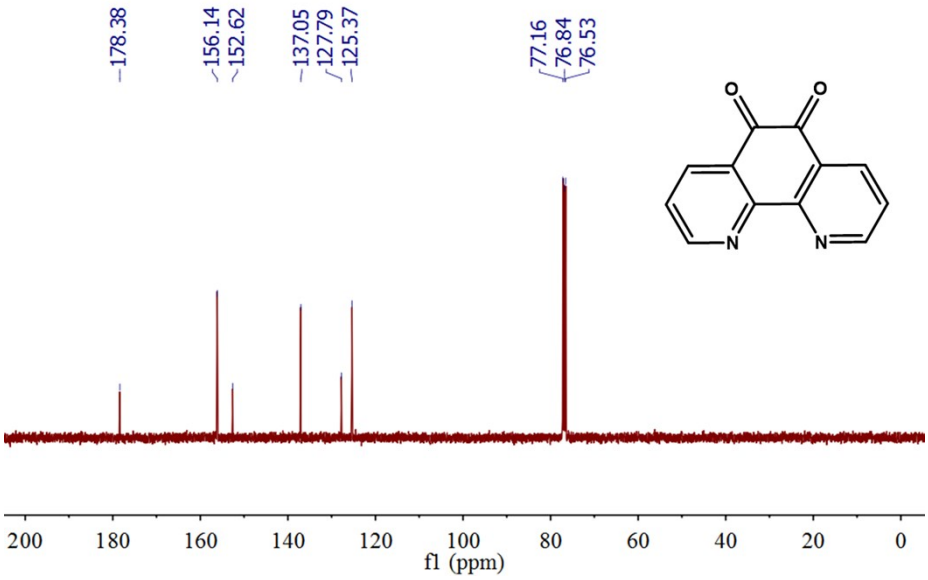


Fig. S2. ^{13}C NMR spectra of ligand recorded at room temperature in DMSO-d$_{6}$

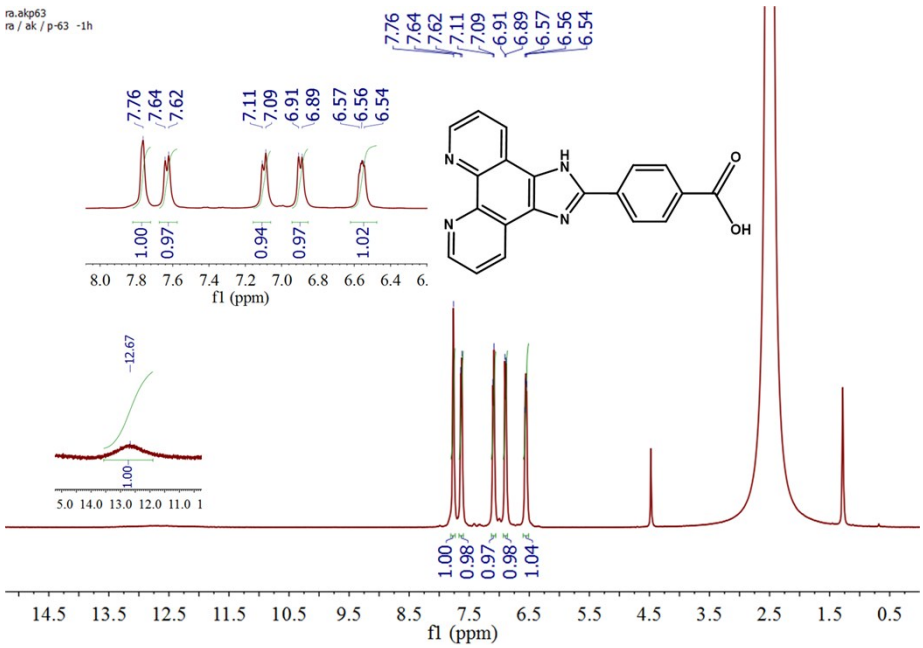


Fig. S3. ^{1}H NMR spectra of ligand (L1) recorded at room temperature in DMSO-d$_{6}$

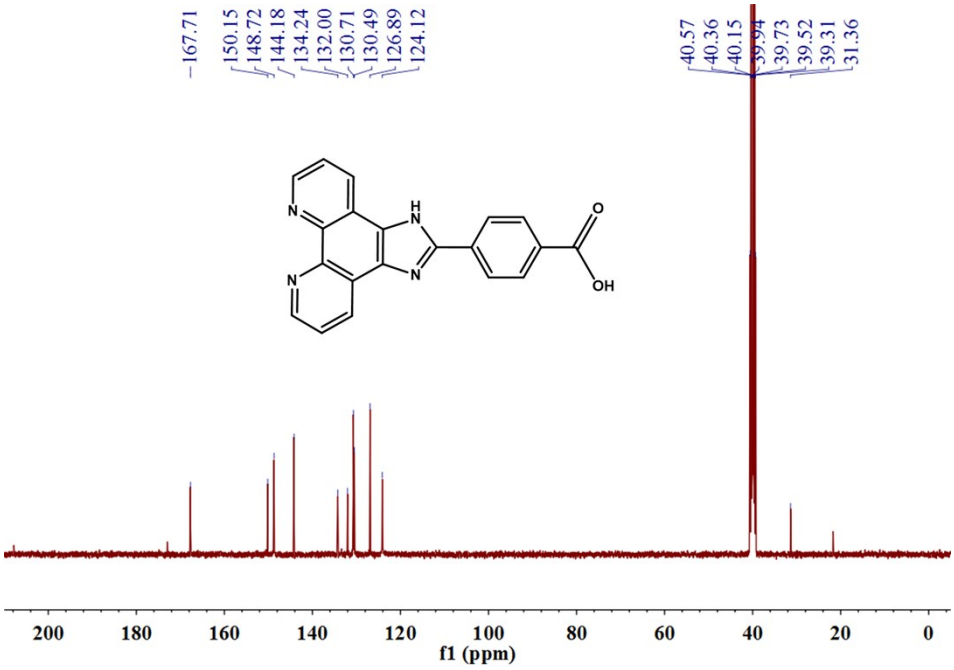


Fig. S4. ^{13}C NMR spectra of Ligand (L1) recorded at room temperature in DMSO-d$_{6}$

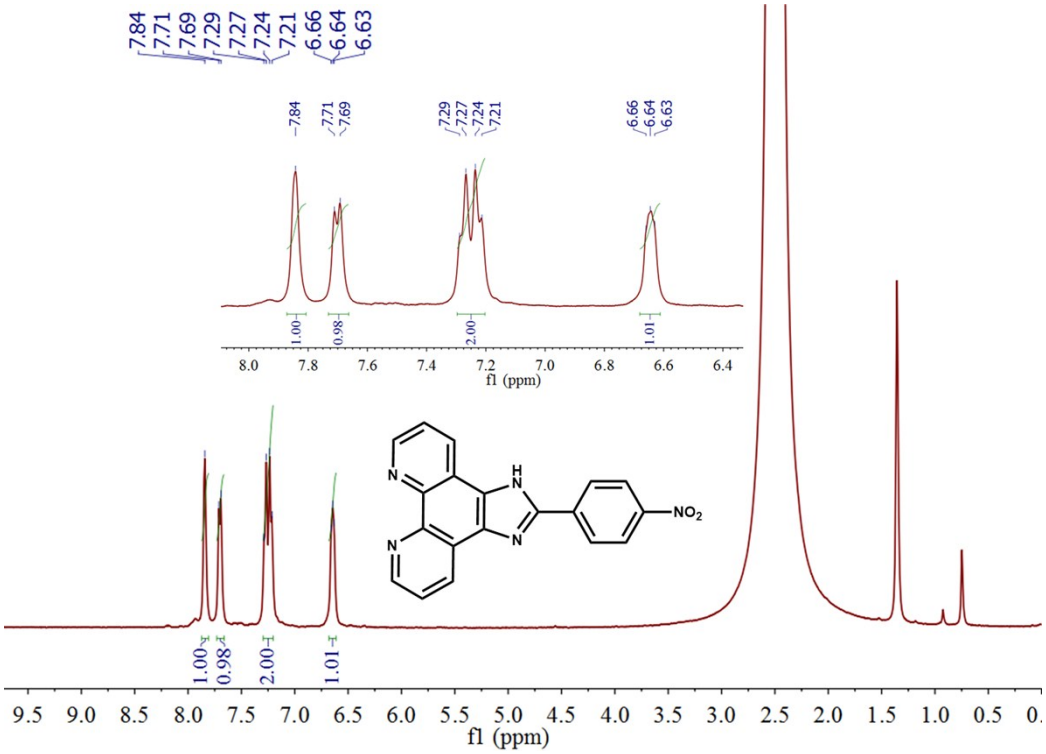


Fig. S5. ^{1}H NMR spectra of ligand (L2) recorded at room temperature in DMSO-d$_{6}$

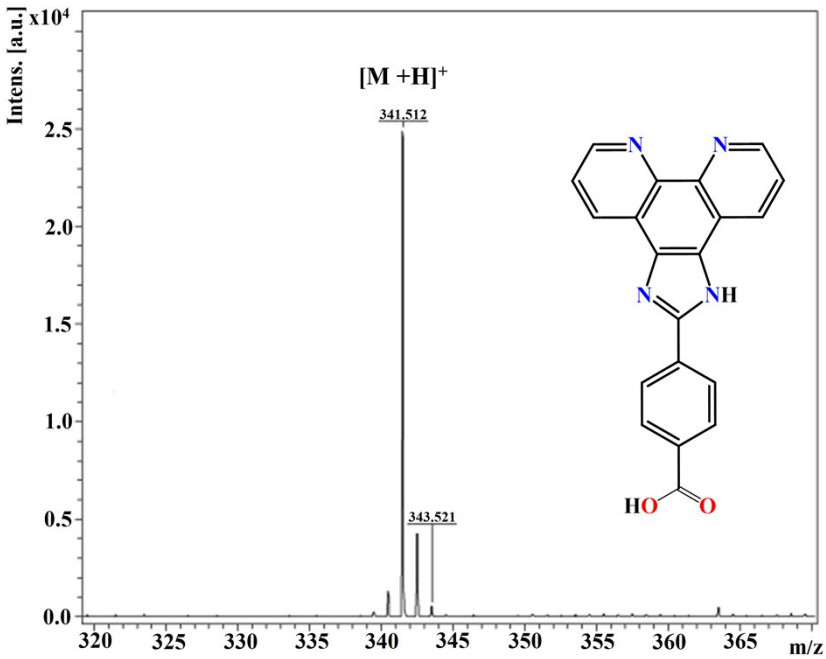


Fig. S6. MALDI Tof MS of ligand L1 (2,4 DHB used as matrix).

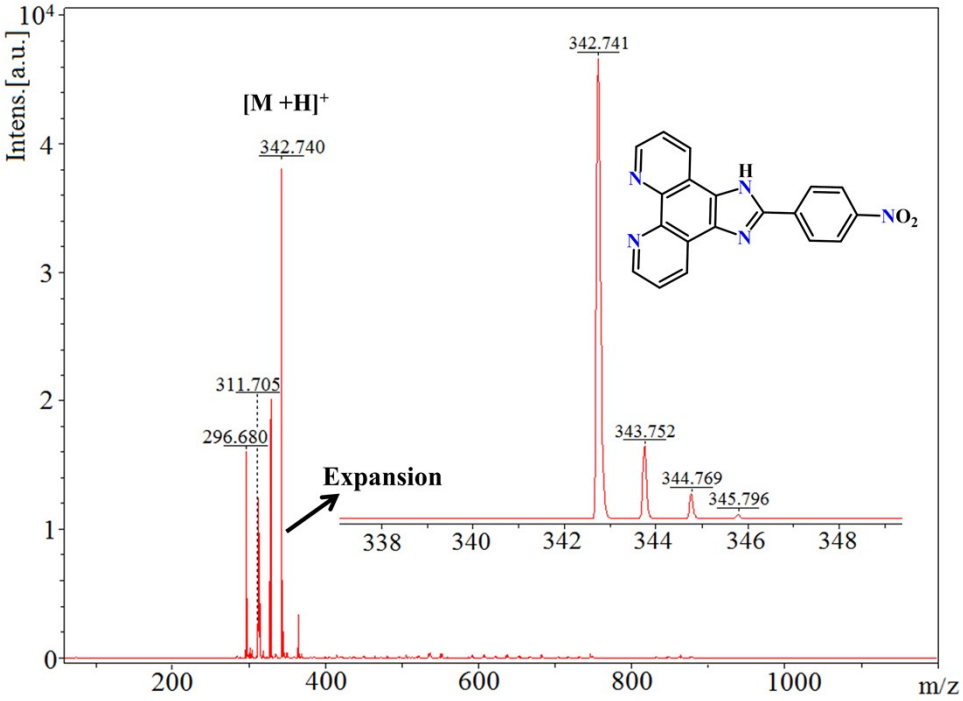


Fig. S7. MALDI Tof MS of ligand L2 (2,4 DHB used as matrix).

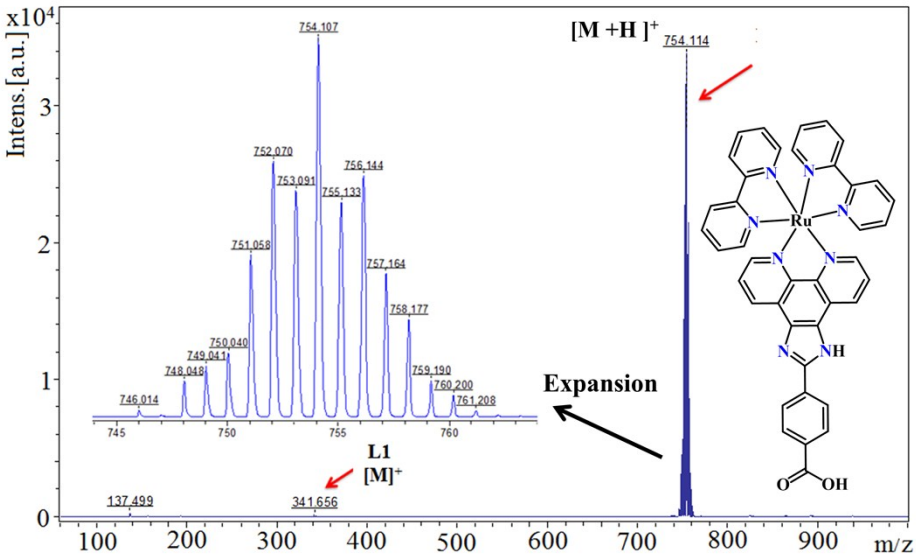


Fig. S8. MALDI Tof MS of ligand $[RuL1(bpy)2]^{2+}$ (2,4 DHB used as matrix).

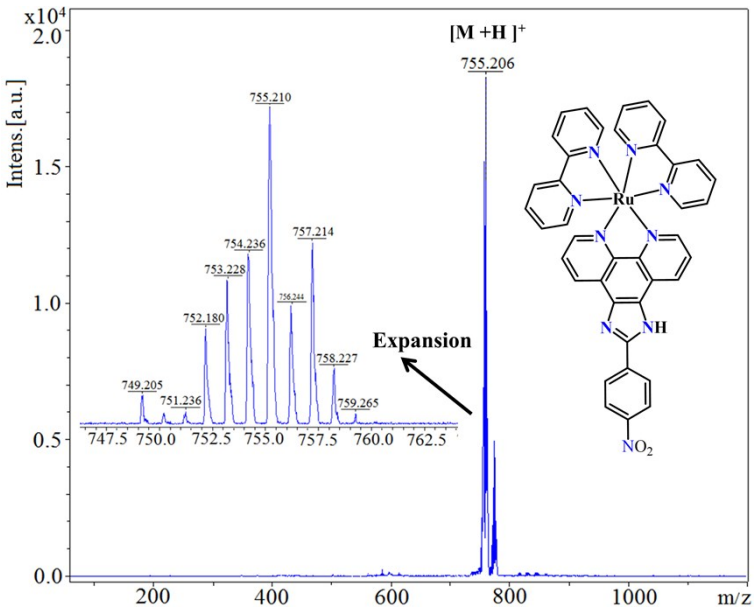


Fig. S9. MALDI Tof MS of ligand $[RuL2(bpy)2]^{2+}$ (2,4 DHB used as matrix).

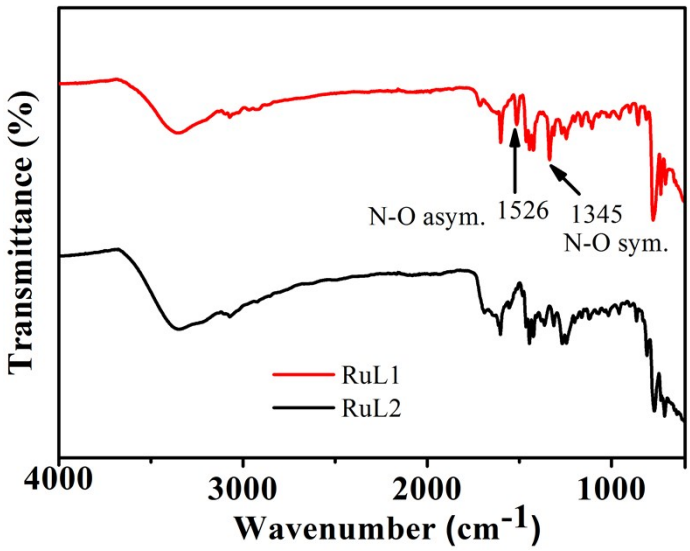


Fig. S10 (a) ART-FTIR spectra of metal complex $[RuL1(bpy)_2]^{2+}$ and $[RuL2(bpy)_2]^{2}$

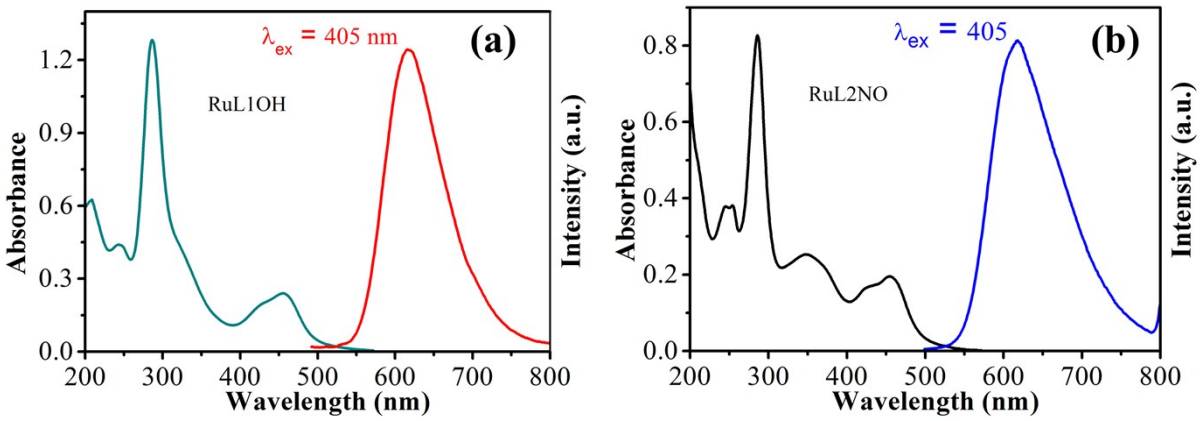


Fig. S11 (a) UV-Vis and fluorescence spectra of metal complexes $[RuL1(bpy)_2]^{2+}$, and (b) $[RuL2(bpy)_2]^{2+}$ measured in MeCN at pH 7

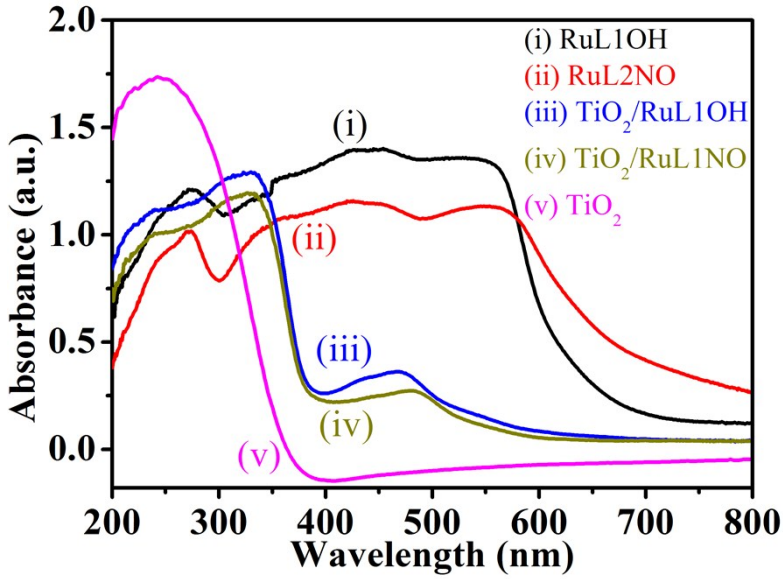


Fig. S12 UV-Vis diffuse reflectance spectra (DRS) of pure metal complexes, TiO_2 and TiO_2 hybrids. (i) RuL1OH. (ii) RuL2NO. (iii) TiO_2/RuL1OH. (iv) TiO_2/RuL2NO. (v) TiO_2.

Table S1. Photophysical properties of synthesied metal complex.

Samples	**λ_{abs} [a](nm) (ε (1x 10^3 M^{-1} cm^{-1}))**	**[b]λ_{em} (nm)**	***<τ> (μs)*[c]**
RuL1OH	246 (28), 286 (78), 457 (15)	618	0.165
RuL2NO	244 (29), 287 (89), 353 (21), 460 (18)	636	0.064
$[Ru(bpy)_3]^{2+}$	244(25), 287(84), 451(14)	621	0.855

[a]Absorption maxima (molar extinction coefficient). [b]Emision maxima. [c]avefarge life time

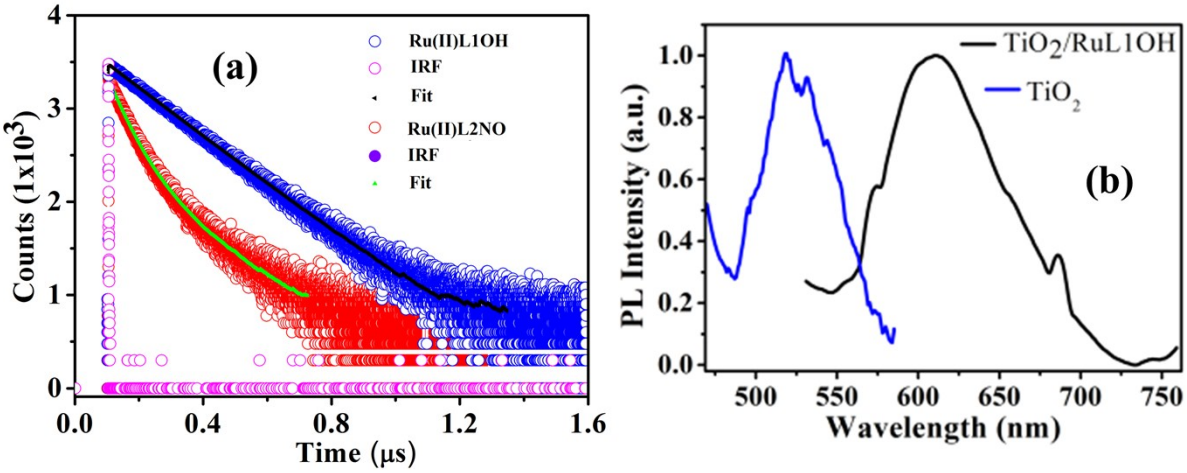


Fig. S13 (a) Fluorescence life time of metal complexes $[RuL1(bpy)_2](PF6)_2$ and $[RuL2(bpy)_2]^{2+}$. (b) Solid state fluorescence of hybrid photo catalyst along with TiO_2

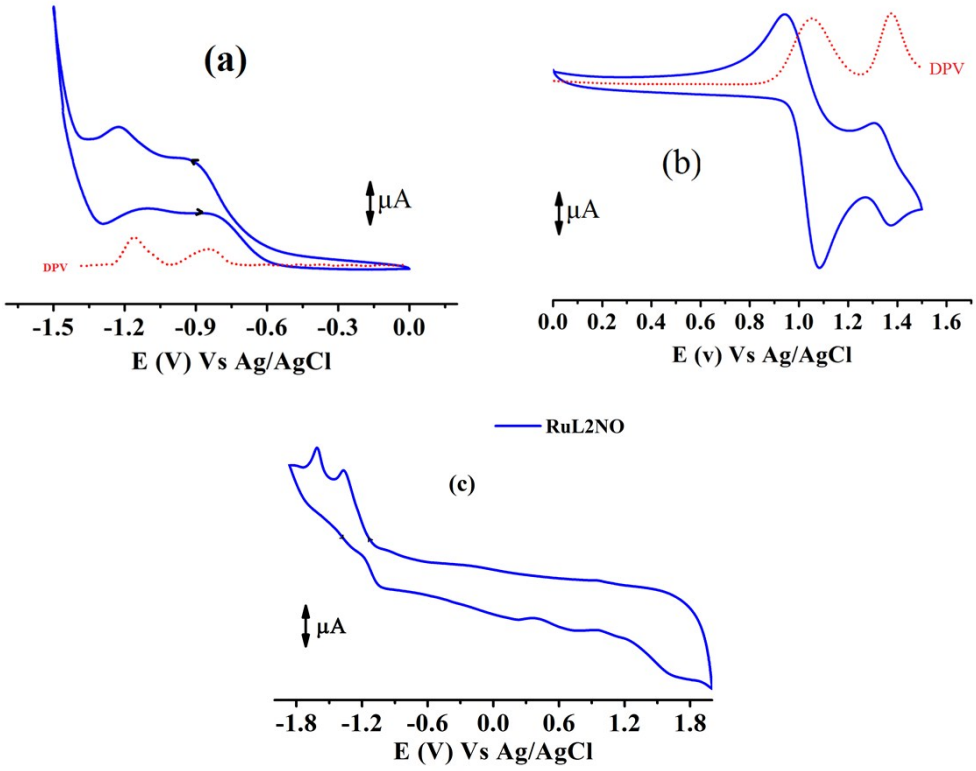


Fig. S14 Cyclic voltammogram of $[RuL1(bpy)_2](PF6)_2$ in MeCN with AgCl as reference electrode. (a) Scan at negative direction. (b) Scan 0 to 1.6 V. (c) Full scan of $[RuL2(bpy)_2](PF6)_2$.

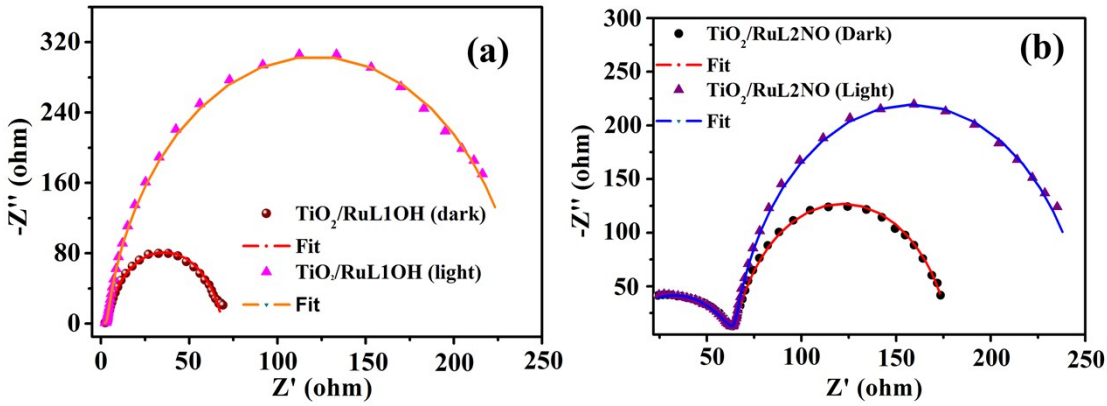


Fig. S15 Nyquist plots of TiO_2/RuL1OH and TiO_2/RuL2NO measured at 0.70 V bias under dark and light.

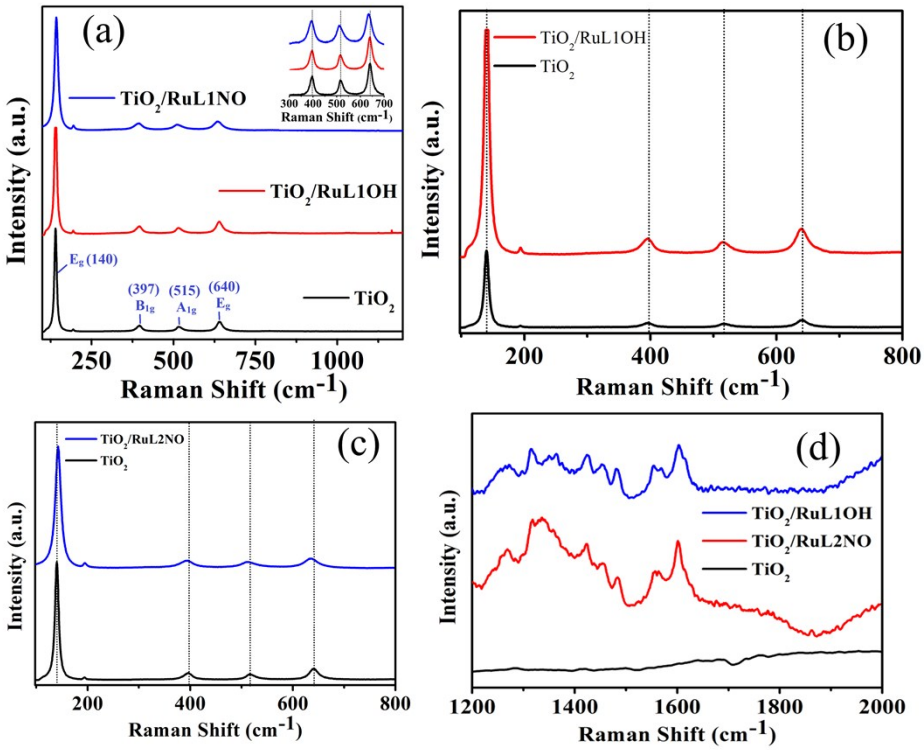


Fig. S16 Raman spectra of TiO_2 and hybrid photocatalyst (TiO_2/RuL1OH, TiO_2/RuL2NO) with excitation wavelength at 514 nm.

Table S2 Gaussian Fit of the wavenumber and the corresponding FMWH of E_g (140) phonon (cm^{-1})

Samples	Wavenumber (cm^{-1})	FWHM (cm^{-1})
TiO_2	140.0	8.7
TiO_2/RuL1OH	140.5	10.2
TiO_2/RuL2NO	142.5	13.6

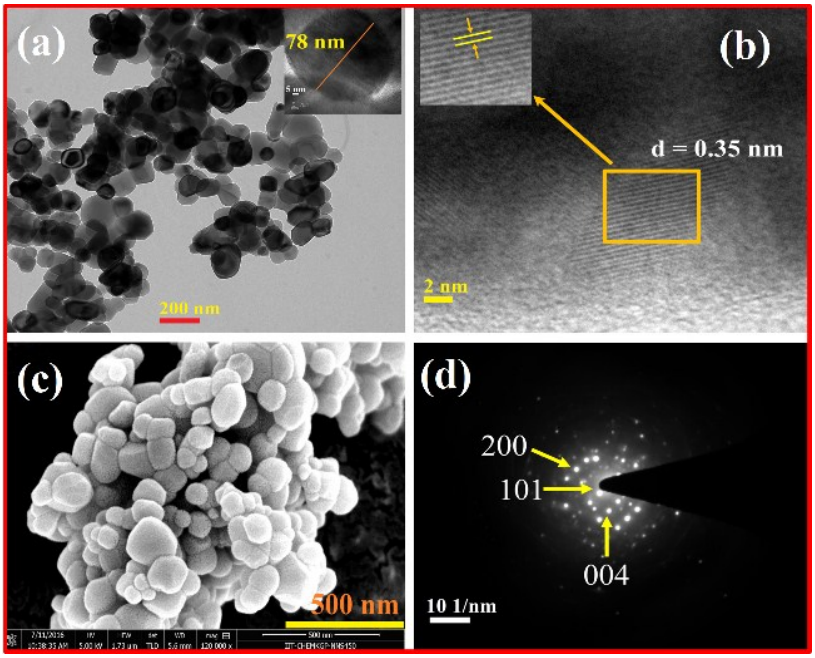


Fig. 17 (a) TEM images of as prepare hybrid catalyst TiO_2/RuL1OH. (b) HRTEM lattice fringes pattern. (c) FESEM images. SEAD images of hybrid .

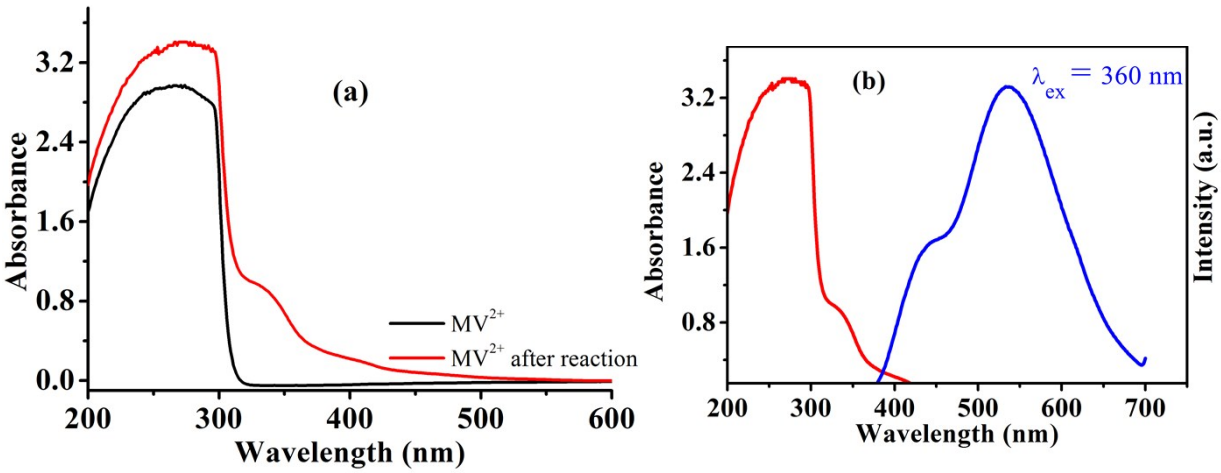


Fig. S18 (a) UV-Vis spectra of freshly prepared MV^{2+} and after light reaction in H_2O. (b) Corresponding fluorescence spectra was measured at excited wavelength 360 nm in H_2O.

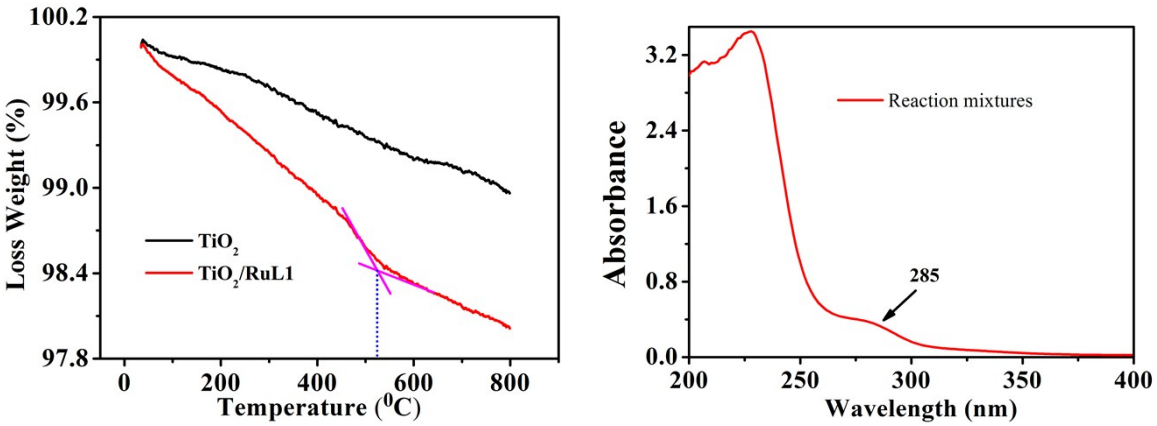


Fig. S19 (a) TGA of hybrid photocatalyst and TiO_2. The weight loss of metal complex is indicated by slope. (b) UV-Vis spectra of reaction mixture in water.

Immobilization of metal complexes over the TiO_2

$$\frac{A(intial) - A(final)\ X\ C\left(\frac{mol}{L}\right) X\ 0.025\ L}{A(initail)\ X\ 0.05g}$$

The amounts of meal complexes adsorbed over the TiO_2 surface were determined by UV-Vis spectroscopy. 50 mg of TiO_2 nanoparticle dried in vacuum at 50 ^{0}C for 6 h and the same was dispersed in DMF (25 ml) solution. The amount of metal complex was added to achieve the concentration 8.0 µM. The mixtures were stirred at room temperature in dark for 12 h. the solid particles were isolated and absorbance of the solutions were recorded. The adsorbed amount of the complexes was estimated by using the following equation.

For a typical example, Initial and final absorption of metal complex (RuL1OH) were obtained as 0.45 and 0.062 respectively. The initianl stock solution was 10 μM. Therefore the adsorbed metal complex over the TiO_2 surface was 4.3 nM/g of the TiO_2.

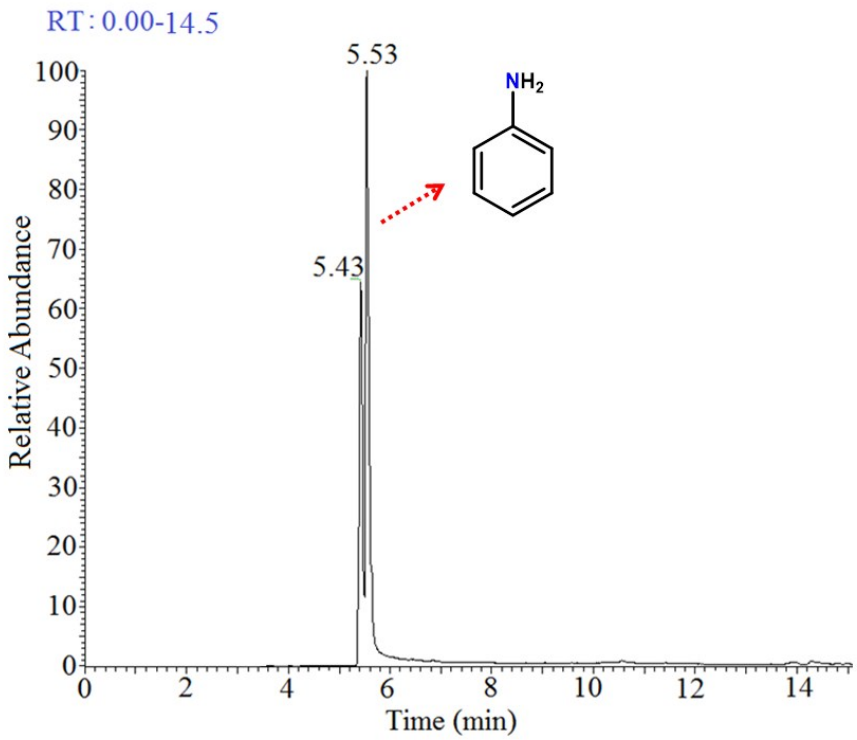


Fig.20 Represnetative GC chromatogram of pure aniline.

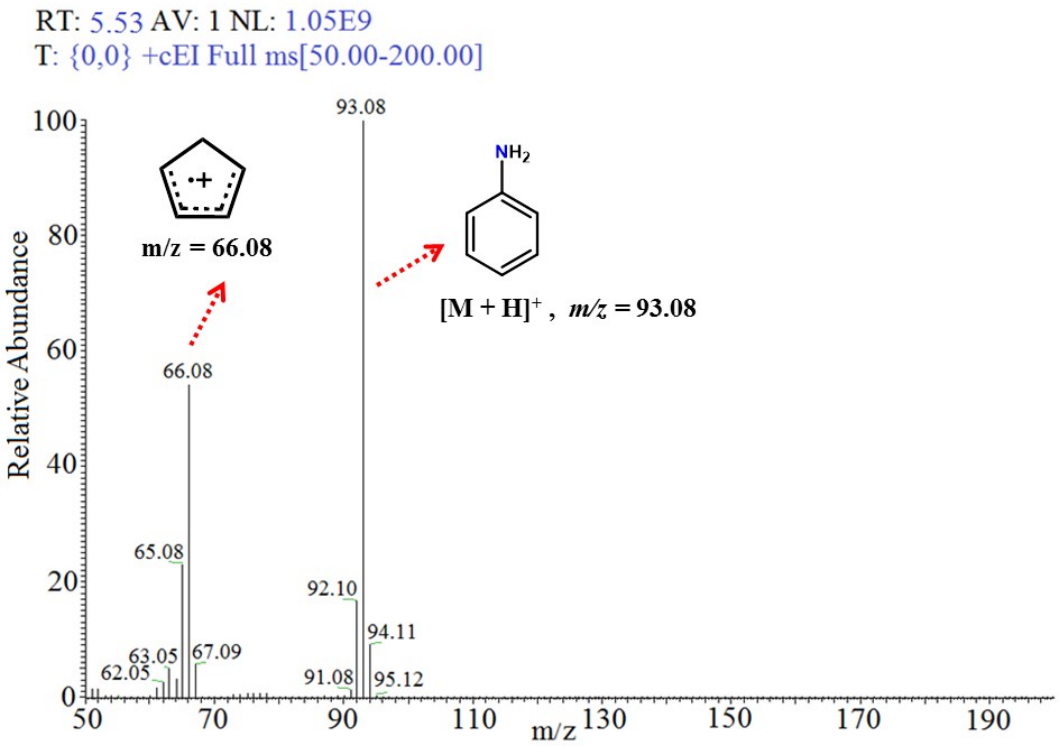


Fig.21 Mass spectrum of pure aniline at corresponding retention time 5.43-5.53 min.

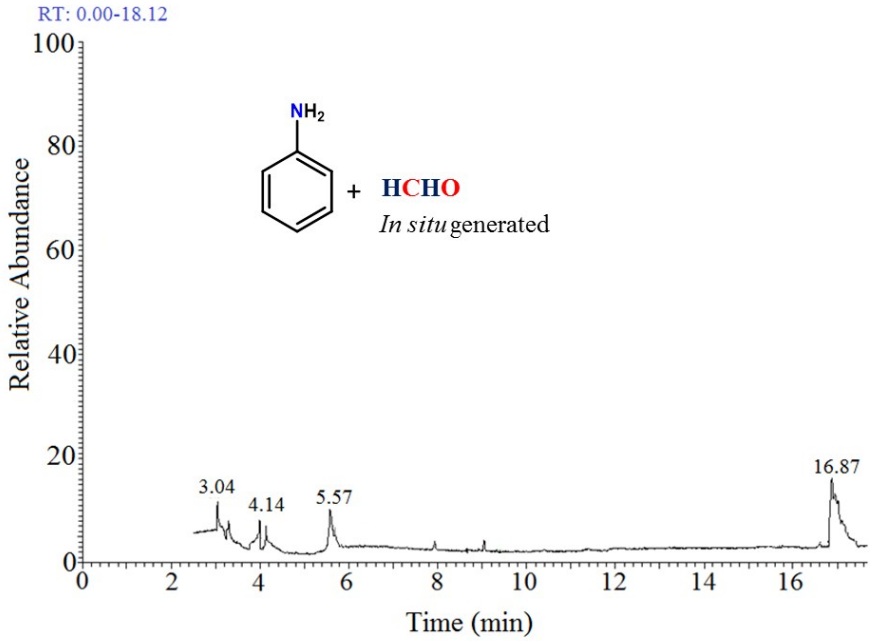


Fig.22 GC-MS chromatogram of aniline after *in situ* reaction with formaldehyde).

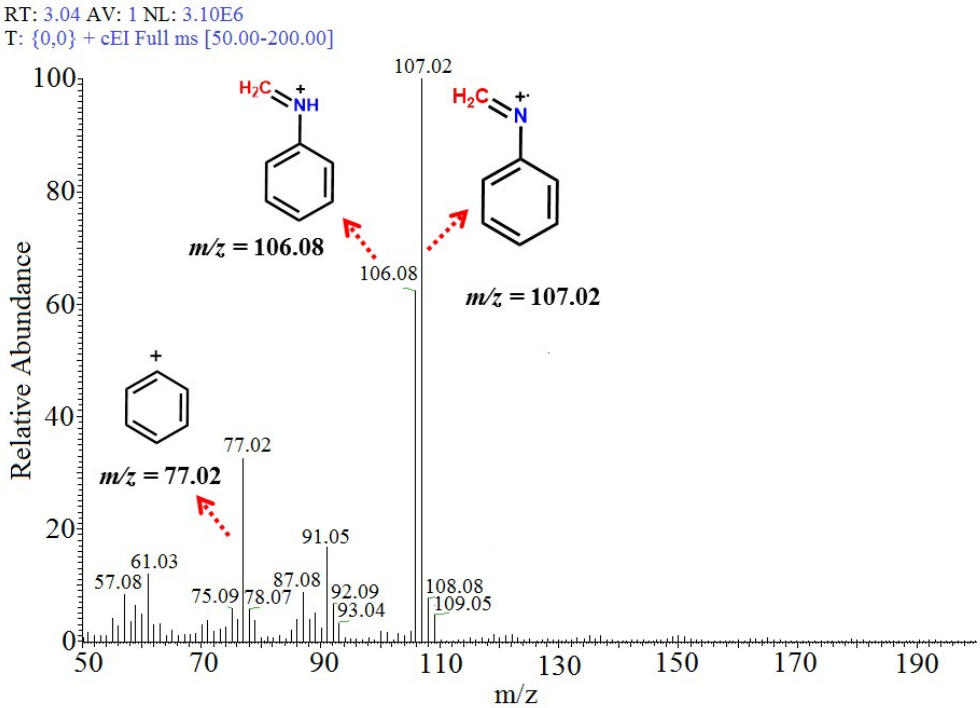


Fig. S23 Mass spectrum of aniline after *in situ* reaction with formaldehyde. The corresponding m/z value at retention time 3.04 min.

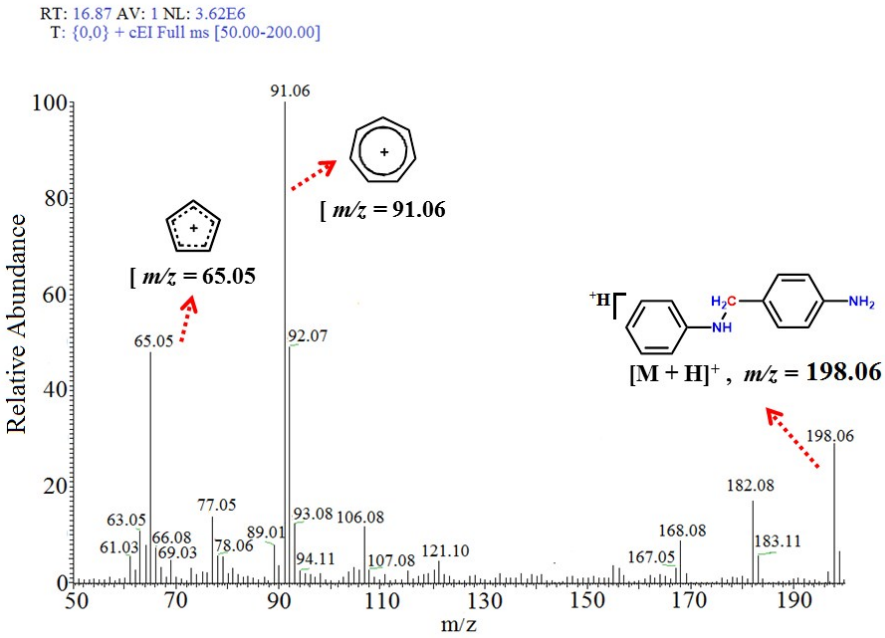


Fig. S24 Mass spectrum of aniline after *in situ* reaction with formaldehyde. The corresponding m/z value at retention time 16.87 min

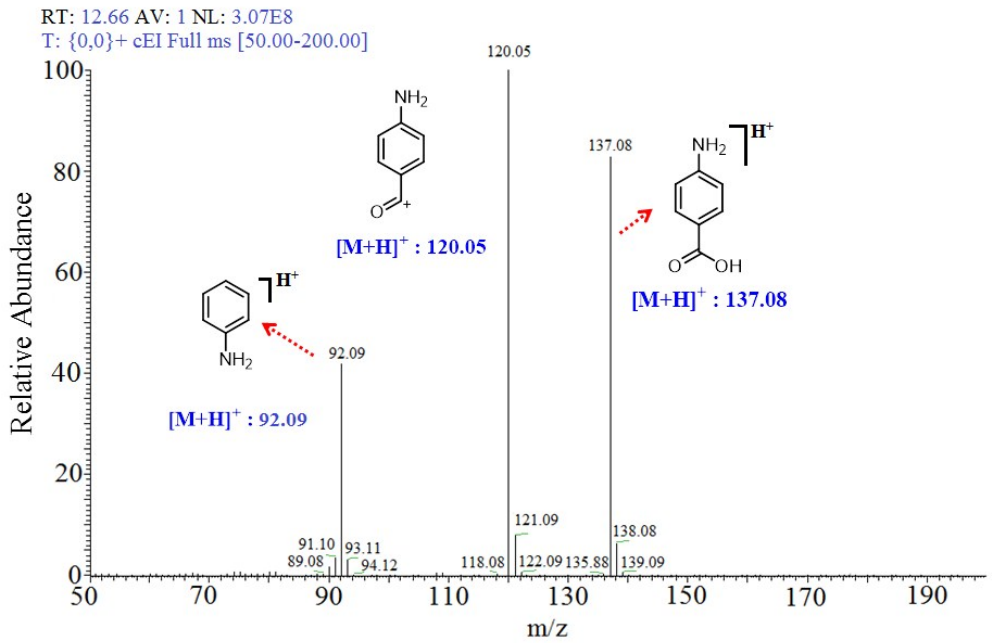


Fig. S25. GC-MS spectra of standard 4-aminobenzoic acid recorded in H_2O.

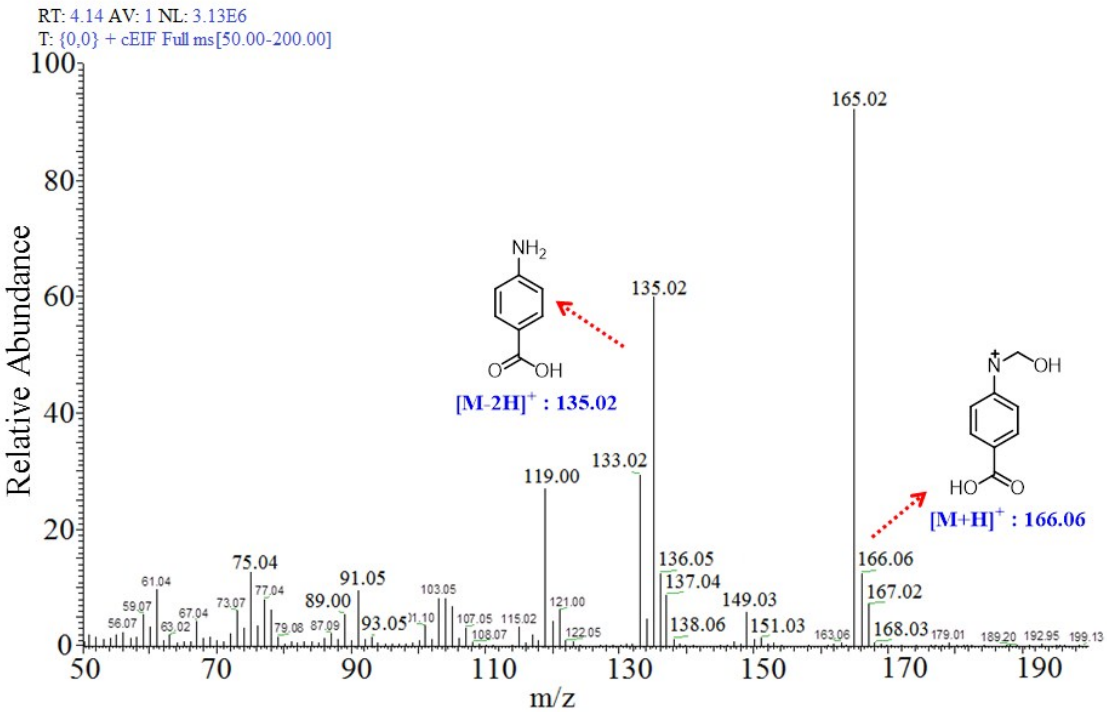


Fig. S26. GC-MS spectra of 4-aminobenzoic acid after reaction recorded in H_2O.

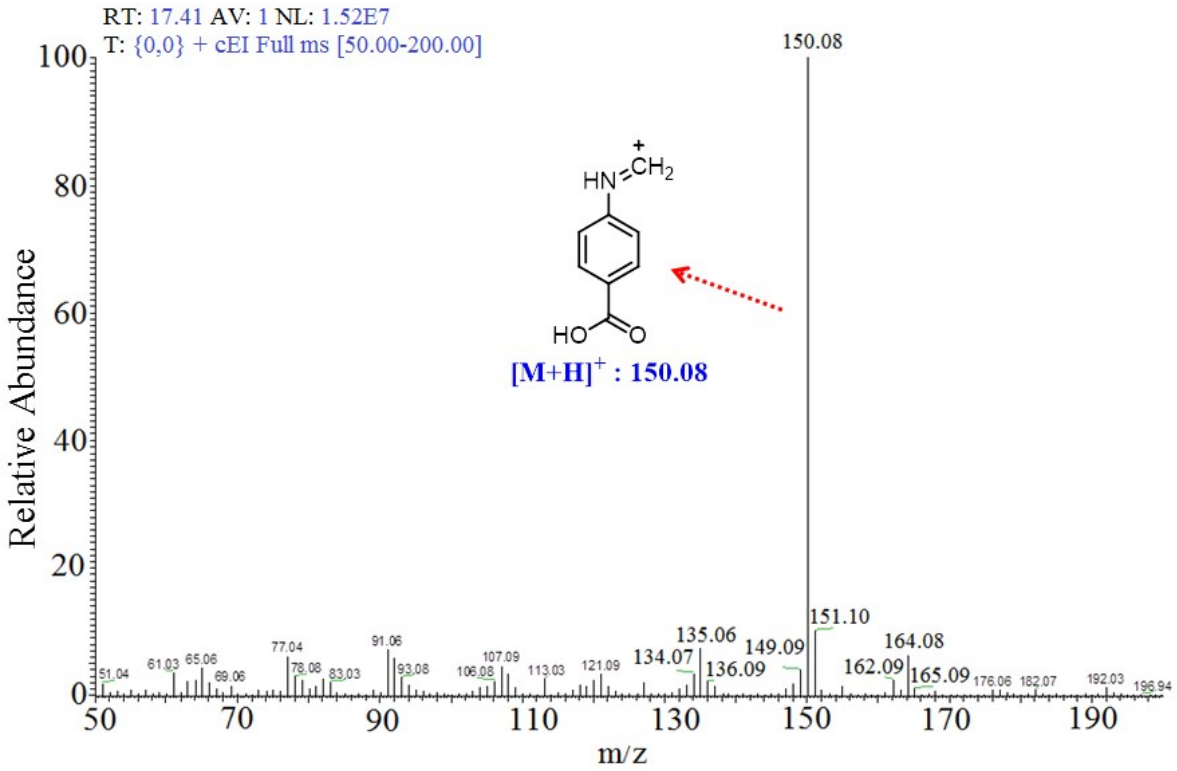


Fig. S27. GC-MS spectra of 4-aminobenzoic acid after reaction recorded in H_2O

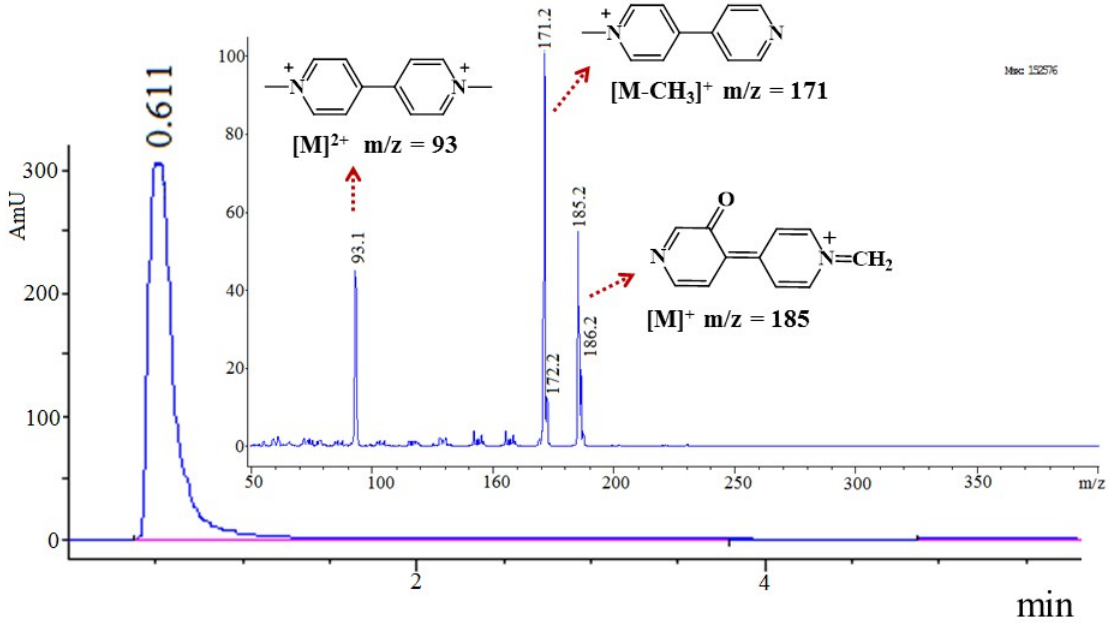


Fig. S28. LC-MS chromatogram and corresponding ESI-MS of standard paraquat (MV^{2+}) recorded in H_2O

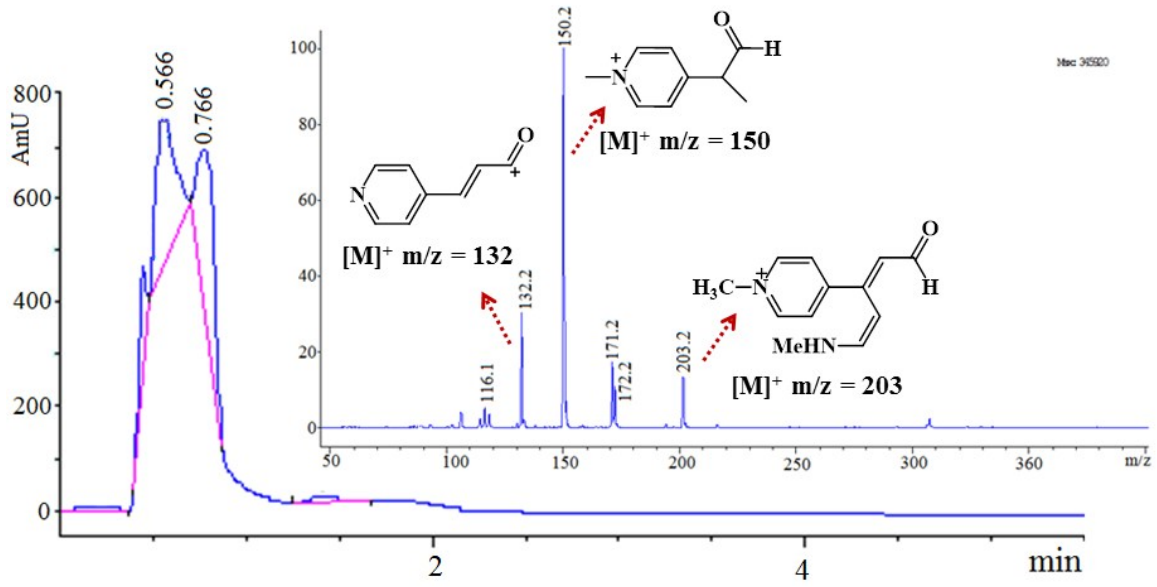


Fig. S29. LC-MS chromatogram and corresponding ESI-MS of paraquat (MV^{2+}) after 2.5 h irradiation in presence of catalyst (TiO_2/RuL1OH, $\lambda > 400$ nm) recorded in H_2O

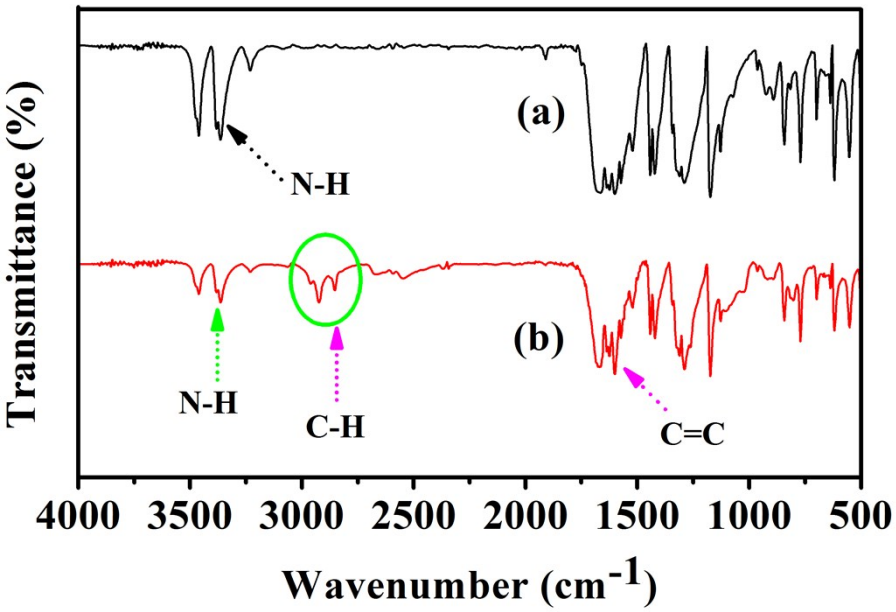


Fig. S30 FTIR spectra of pure 4-aminobenzoic acid (a) and after reaction in homogeneous medium under CO_2 pressure (b).

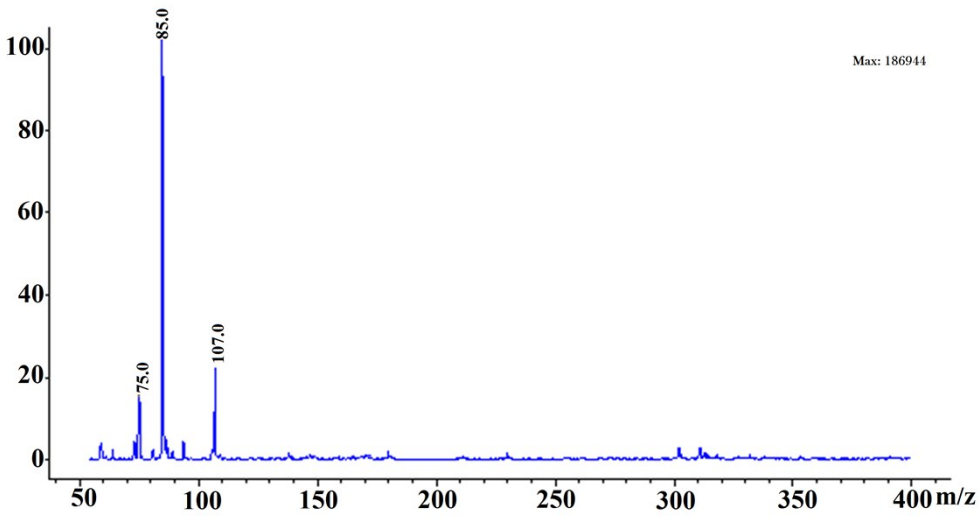


Fig S31 LCMS of aniline after reaction in homogenous medium

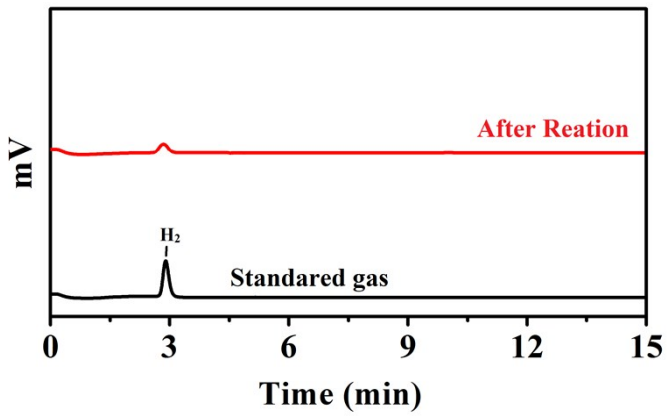


Fig. S32. GC-Trace chromatogram of TCD3 and the peak at retention time 2.93 is corresponding to hydrogen as per the standard.

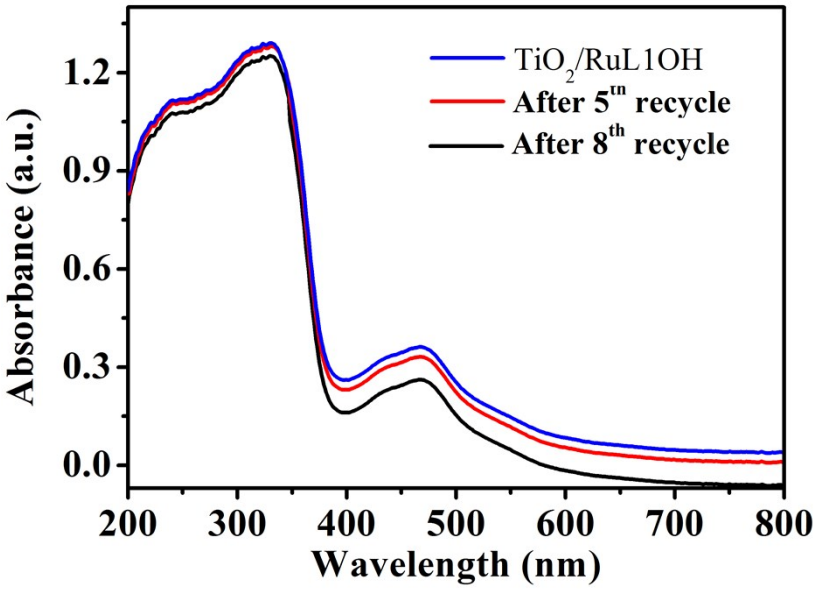


Fig. S33. DRS spectra of hybrid catalyst (TiO_2/RuL1OH) after catalysis. The sample was first dried after catalysis (5th and 8th recycle) then DRS specra were recorded.

XPS spectra of befor and after catalysis

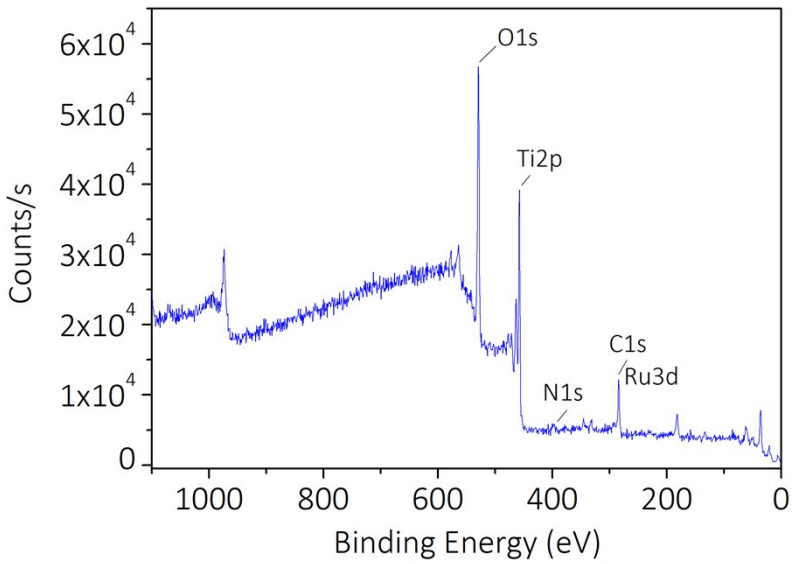


Fig. S34. XPS survey of hybrid photocatalyst (TiO_2/RuL1OH).

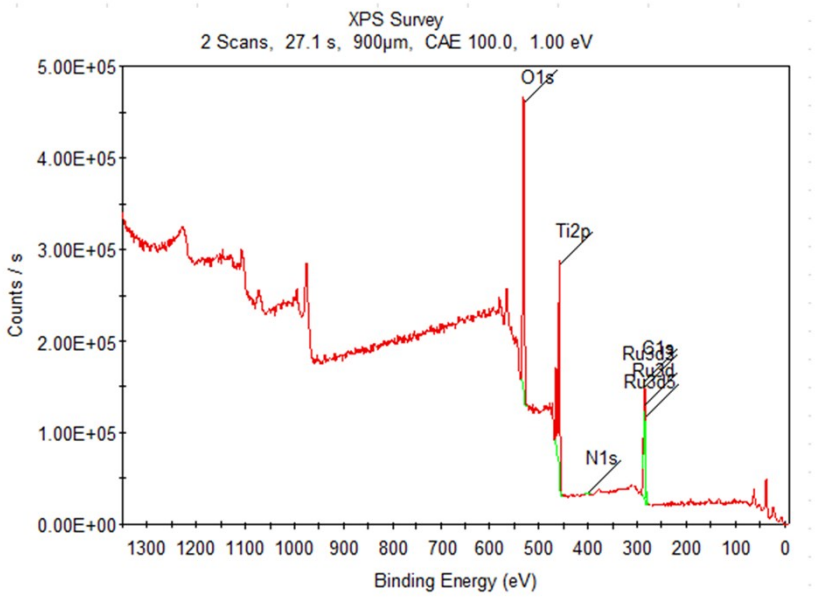


Fig. S35. XPS survey of hybrid photocatalyst (TiO_2/RuL1OH) after 3 time catalytic reaction in water.

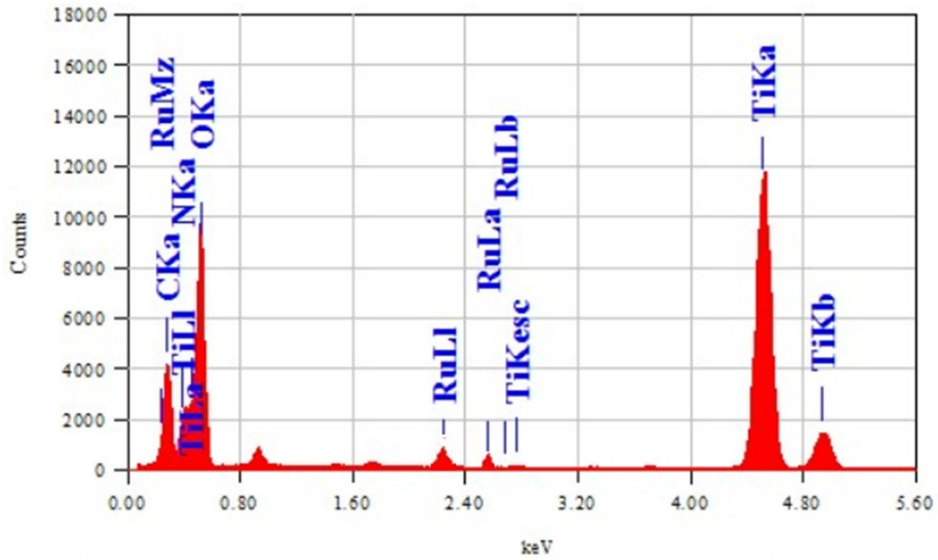


Fig. S36 EDX profle of hybrid photocatalyst

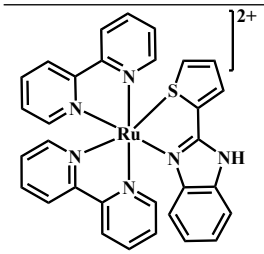
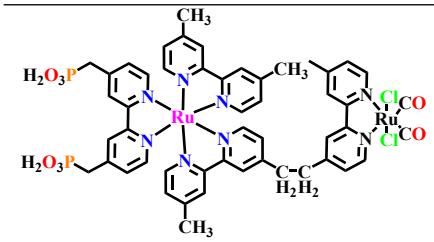
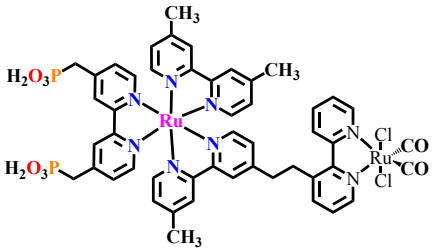
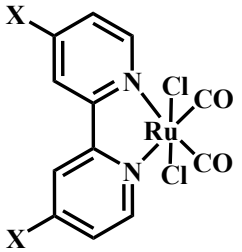
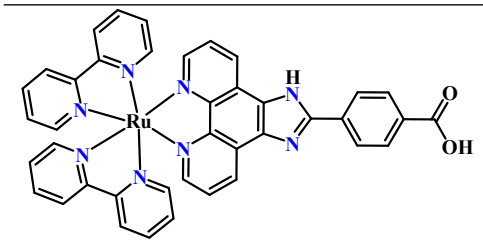
Materials	Reaction conditions	Products [μmol] (TON)	Selectivity (%)	Ref.
	Water and a DMF system, Only visible light mentined	CH_3OH [2050 g^{-1} cat.]	Not defined Single product reported	3
Ru-loaded TiO_2–SiO_2	1000 W Hg-lamp (365 nm), CO_2 saturated aqueous solution containing 1 M 2-propanol	CH_3OH [210 mmol g^{-1}] for 6 h; CH_4 [40 mmol g^{-1}] for 6 h over 0.5% Ru–TiO_2/SiO_2	Not defined Depende on Ru doped TiO_2 loading	4
Pd-loaded TiO_2	500 W Hg-lamp (λ > 350 mg catalyst in 1.5 mL CO_2 saturated solution	CO and CH_4 [1.1]	Not defined CO is major products	5
Ru/TiO_2 hybrid nanocomposite	20 W white cold LED, water and a DMF system	CH_3OH [1876 g^{-1}]	Not defined Single product reported	6
TiO_2 film sensitised by ruthenium N719.	A 300 W Xe lamp (L25, λ_{max} = 500 nm)	HCOOH [8.35], HCHO [120] and CH_3OH [17] cm^{-2}	Not defined Three products reported	7
Mononuclear C_5H_5-RuH complex oxo-bridged TiO_2 hybrid	visible light (λ > 420 nm) irradiation 300w Xe lamp	CH_4 (44.0 μL g^{-1} h^{-1}] at 0.6 wt% Ru content in water medium	Almost 100 % reported	8

Table S3: Summary of Ruthenium metal complex based photcatalytic CO_2 redution.

 Adsorbed onto Ag-loaded TaON (Ag/TaON)	500 W Hg lamp Methanol	HCOOH [0.956] (41) H_2 [0.678] CO [0.068] (2.8)	Formic acid as a reduction product and formaldehyde as the Oxidized product of methanol.	9
	λ > 400 nm with a high-pressure Hg lamp. Aqueous solutions	HCOOH [7.0] (600) CO[0.3] (28) H_2[11.4] (978)	37 %	10
 X = COOH, PO3H2, CH2PO3H2	Visible light (l > 420 nm) irradiation MECN DMA	CO [2050] g^{-1} cat.	50% selectivity for CO the loading amount of 7.8 μmol g^{-1}.	11
Fluorinated Anatase TiO_2 Nanosheets, Exposed {001} Facets	UV illumination	CH_4 [1.23] CH_3OH [1.09] HCHO [0.38]	Not defined Mixture of products	12
TiO_2 sensitization	250-watt tungsten lamp (λ > 420 nm) combined with $NaNO_2$ aqueous solution filter	HCHO [90] (720) CO [17] 136 CH_4 [8] 64	65 % selective for HCHO	This work



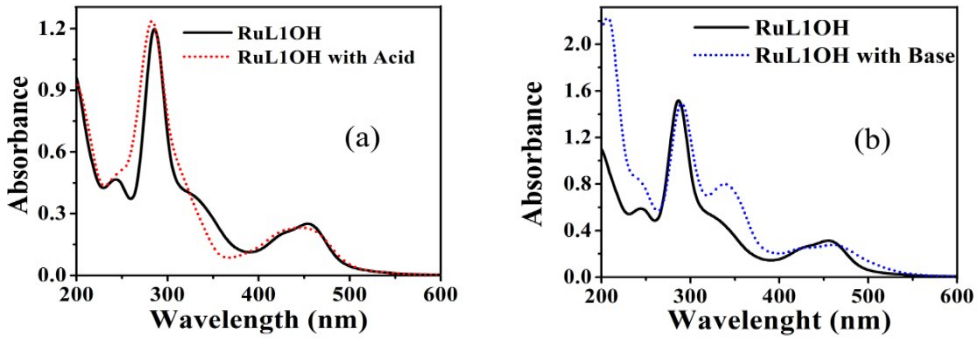


Fig. S37 (a) UV-visible spectra of complex (RuL1OH) in acidic (Perchloric acid) medium (pH 5) recorded in MeCN. (b) UV-visible spectra in basic medium (pH 8). Tetrabutylammonium hydroxide was used as the base.

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