Supplementary Information for Chemical Communications

Immobilized Mn(I) and Ru(II) complexes on TiO$_2$ nanoparticles as a highly selective catalyst for CO$_2$ photoreduction to formic acid

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I- Materials and Instrumentation  
II- Synthesis  
III- Characterization  
  Electrochemistry, UV-visible and IR spectroscopy  
  Results of catalysis experiments  
  Energy diagram  
  EPR spectroscopy  
IV- Bibliography
I. Materials and instrumentation

I.1. Materials

**Solvents**: Acetonitrile (CH$_3$CN), dichloromethane (CH$_2$Cl$_2$) and ethanol (C$_2$H$_5$OH, all purchased from Fisher, HPLC grade), dimethyl sulfoxide (DMSO, Acros, anhydrous 99.7%), N,N-dimethylformamide (DMF, Acros, anhydrous 99.8%), diethyl ether (Aldrich, 99.8%), hexane (95%), pentane (Carlo Erba), methanol (SDS anhydrous, analytical grade) and acetone (Aldrich, 99.5%) were used as purchased without any further purifications. Dry solvents were obtained by distillation under argon. Distilled water was prepared with a Milli-Q system.

**Reagents**: all reagents have been used without further purifications, unless otherwise stated.

**Nanoparticles (NPs)**: commercially available TiO$_2$ (anatase, d < 25 nm, Aldrich), specific surface area of 50 ± 5 m$^2$/g and SiO$_2$ (d < 20 nm, Aldrich ), specific surface area of 640 ± 50 m$^2$/g were used as received.

**Others**: Column chromatography was carried out on silica gel 60 (Merck, 70-230 mesh). Thin layer chromatography (TLC) was performed on plates coated with silica gel 60 F$_{254}$.

I.2. Instrumentation

**Nuclear magnetic resonance (NMR)**: $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR spectra were recorded with a 400 or 300 MHz Bruker spectrometer at room temperature (RT). Chemical shifts in the $^1$H NMR spectra were referenced to residual solvent peaks. Coupling constants ($J$) and the chemical shifts ($\delta$) were shown in Hz and ppm, respectively. The abbreviation for the characterization of the peaks are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet.

**Infra-red spectroscopy**: The NPs or complexes were well mixed with KBr and pressed into a pellet for measurement. Experiments were carried out at room conditions after subtracting the KBr signal with a Perkin Elmer Spectrum GX instrument.

**Electrochemistry**: All electrochemical measurements were performed in a standard three-electrode cell at RT under a continuous Ar flow or in a glovebox. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Aldrich) was used as electrolyte without further purifications. Ag/AgNO$_3$ 0.01 M (in CH$_3$CN + 0.1 M TBAPF$_6$ ) and Pt were used as reference electrode and counter electrode, respectively. A carbon disk electrode (diam. = 3 mm) or a Pt cavity microelectrode (CME)$^3$ (diam. = 50 $\mu$m, d = 25 $\mu$m, V = 1x10$^{-8}$ cm$^3$) was used as working electrode. Before experiment, the carbon disk electrode was polished using diamond paste (PRESI PM 2 $\mu$m) and cleaned with ethanol. Cyclic voltammograms (CV) were recorded with a
CHI 630 potentiostat (CH Instrument), or a Biologic SP300 potentiostat (Science Instruments). All reported potentials are versus the Ag/AgNO$_3$ reference electrode. One should subtract 0.070 V to convert them against Fc$^+$/Fc reference. Half-wave potential ($E_{1/2}$) and peak-to-peak splitting ($\Delta E_p$) are calculated as follows:

\[
\frac{E_{1/2}}{2} = \frac{E_{pa} + E_{pc}}{2}, \quad \Delta E_p = E_{pa} - E_{pc}
\]

where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials respectively.

**Electrocatalytic CO$_2$ reduction:** Experiments were carried out at RT under CO$_2$/CH$_4$ (95/5 v/v) mixture in a conventional, gas-tight three-electrode cell. The solvent was MeCN + TBAPF$_6$ (0.1 M) + H$_2$O (5% v/v) . Reference and counter electrodes were Ag/AgNO$_3$ 0.01 M and Pt plate, respectively. Working electrode was a carbon plate (8 cm$^2$) which had been cleaned by diamond paste (PRESI PM 2 $\mu$m) and washed with ethanol prior to experiment. In a normal setting with 3 electrodes and 10 mL solution, the headspace volume was measured at 170 mL. During the experiments, at each time interval a 100 µL sample was taken from the headspace gas using a gas tight injection syringe. Gas products were analyzed with the gas chromatograph described below. At the end of the experiments, a liquid sample was taken for HCOOH analysis.

**Photocatalytic CO$_2$ reduction:** A glass tube (12.5 mL) was charged with [Ru(bpy)$_3$]$^{2+}$ photosensitizer and [Mn(ttpy)(CO)$_3$Br] catalyst in DMF/TEOA mixture (5 mL, $C_{TEOA} = 1$ M). The photosensitizer and the catalyst can be homogeneous or anchored on TiO$_2$ NPs. The mixture was sonicated for a few minutes prior to be purged with Ar (20 min) and then CO$_2$/CH$_4$ (95/5 v/v) mixture (20 min) in dark. The dead volume was 7.5 mL. Afterwards, the tube was irradiated with a Xenon lamp (4 cm apart) in the presence of a UV filter and a 470 ± 40 nm band pass filter in order to selectively excite the PS and prevent the complex from degradation. The light power is estimated to be $3 \times 10^{-4}$ W cm$^{-2}$. The flux of photon has been estimated to $8.3 \times 10^{-9}$ einst. s$^{-1}$ by actinometry using the ferrioxalate reference system. During the experiment, at each time interval a 100 µL sample was taken from the headspace gas using a gas tight injection syringe. Gas contents were analyzed by GC. At the end of the experiment, a liquid sample was taken to analyze HCOOH content by HPLC.

**Gas chromatography (GC):** Gas samples (100 µL) were taken from the headspace of the tube containing the reaction mixture. The analysis was conducted with a Perkin Elmer Clarus 500 gas chromatograph equipped with a TCD detector and a 5 Å molecular sieve column (Restek). The gas contents were calculated against 5 % CH$_4$ as internal reference in the gas phase. The results were compared to a standard gas mixture of CO, H$_2$, CH$_4$ and CO$_2$ (Air Liquid). Helium was used as the carrier gas.

**High performance liquid chromatography (HPLC):** Content of HCOOH produced by electrocatalysis was determined using a Perkin Elmer liquid chromatograph equipped with a
Series 200 pump, 785 A UV-vis detector, Series 200 vacuum degasser and a SiELC primesep SB packed column (100 mm, 5 µm pore size, 20 µL injection volume), with the column eluent containing 46 mM methane sulphonic acid in H₂O. The HCOOH content produced by photocatalysis was analyzed using a Shimadzu liquid chromatograph LC-10AS equipped with an Alltech Select degassing system, a Perkin Elmer Series 200 UV-vis detector and a Perkin Elmer polypore H column (220 mm, 10 µm pore size, 20 µL injection volume), with the column eluent containing 10 mM H₂SO₄ in H₂O. Both chromatographs were checked by injecting an aqueous solution of HCOONa (0.01 M) prior to the experiments.

EPR Spectroscopy: Continuous wave EPR experiments were performed using a Bruker EMX spectrometer operating at X-band frequency with an ER-4116 dual mode cavity and an Oxford Instruments ESR-900 flow cryostat. EPR Experimental settings for analysis: microwave frequency = 9.654 GHz, modulation amplitude = 5G, temperature = 10 K. The spectrum of the TiO₂/RuⅡ dyad was recorded for 56 minutes, the spectrum of the RuⅡ/TiO₂/MnⅠ for 14 minutes. The simulated EPR spectra were computed by using the EasySpin suite. Irradiations were performed in the EPR spectrometer using a 455 nm LED.

II. Synthesis

fac-[Mn(ttpy)(CO)₃Br]. The synthesis procedure was already reported.³ In a typical experiment, [Mn(CO)₅Br] (200 mg, 0.73 mmol) and 4’-(4-methylphenyl)terpyridine (ttpy, 120 mg, 0.37 mmol) were dissolved in 30 mL diethyl ether. The resulting solution was refluxed for 3 h, and allowed to cool down to room temperature before the orange solid was filtered. Excess [Mn(CO)₅Br] precursor was eliminated by stirring the solid in 50 mL diethyl ether for 30 min, then the remaining solid was filtered and washed with diethyl ether. The solid product was dried under vacuum for 2 h, yielding a pale-yellow powder (170 mg, 85%). ¹H NMR (400 MHz, [D₆]DMSO): δ (ppm) = 9.25 (d, J = 5.1 Hz, 1H), 9.00 (m, 2H), 8.80 (d, J = 4.8 Hz, 1H), 8.29 (m, 1H), 8.09 (m, 4H), 7.96 (m, 1H), 7.75 (m, 1H), 7.65 (m, 1H), 7.42 (d, J = 8.4 Hz, 2H), 2.50 (s, 3H). FT-IR (KBr pellet, C=O stretching): ν (cm⁻¹) = 2022, 1948, 1916.

bpy-PO₂Et₂.
The synthesis of this ligand requires two steps. In the first step, lithium diisopropylamine (LDA) was prepared by dissolving diisopropylamine (DIPA, 630 µL, 1.29 mmol) in 3 mL THF under Ar in an oven-dried flask. The solution was cooled to -40 °C, stirred for 30 minutes before slowly adding n-butyllithium solution (2.5 M in hexane, 0.58 mL, 1.29 mmol). The LDA solution was kept stirring for one hour while the temperature was raised to 0 °C, forming a pale green solution. In another oven-dried flask, a solution of 4,4'-dimethyl-2,2'-dipyridine (dmbpy, 227.5 mg, 1.235 mmol) in 8 mL dried THF was prepared under Ar and cooled to -40 °C. The LDA solution was added dropwise to the dmbpy solution at -40 °C, and the mixture was stirred for 1.5 hour.

In the second step, diethyl(3-bromopropyl)phosphonate (0.3 mL, 1.56 mmol) was added to the mixture, and the temperature was slowly raised to room temperature overnight. The reaction was stopped by adding 10 mL saturated NH₄Cl aqueous solution, then extracted with CHCl₃ (x2) and washed with ethanol + H₂O. The product was subsequently separated by chromatography. First, SiO₂ column was washed with pentane + 10 % trimethylamine (2 times) before the separation step. A mix of CH₂Cl₂/MeOH was used as eluent. The amount of MeOH was gradually increased from 1 to 3 %. The solution was evaporated and the product was dried under vacuum to yield a white powder (397.6 mg, yield: 90%).

[Ru(bpy)₂(bpy-PO₃Et₂)]Cl₂ (denoted as [Ru-PO₃Et₂]²⁺).

Precursors cis-bis(2,2′-bipyridine)-dichlororuthenium(II) dihydrate ([Ru(bpy)₂Cl₂].2H₂O, 167 mg, 0.345 mmol) and the bpy-PO₃Et₂ ligand (150 mg, 0.414 mmol, 1.2 equiv) were solubilized in EtOH/H₂O (8/2 v/v) mixed solvent under Ar for 30 minutes. Afterwards, the mixture was refluxed at 85 °C overnight. The solution color changed to bright red. Addition of an excess of acetone lead to formation of red precipitates. The solvent mixture was evaporated under vacuum. The solid part was solubilized again in ethanol and acetone then evaporated several times to remove water. The crude product was purified with flash chromatography using MeCN/H₂O/saturated aqueous KNO₃ solution (100/5/0.5) as mobile phase and silica to yield a bright red powder (230 mg, 76%).

[¹H NMR (400 MHz, CD₃CN): δ (ppm) = 8.49 (d, J = 7.7 Hz, 4H), 8.41 (s, 1H), 8.37 (s, 1H), 8.06 – 8.02 (m, 4H), 7.74 – 7.70 (m, 4H), 7.55 – 7.52 (m, 2H), 7.42 – 7.36 (m, 4H), 7.23 – 7.22 (m, 2H),
4.04 – 3.93 (m, 4H), 2.83 (t, J = 7.5 Hz, 2H), 2.53 (s, 3H), 1.82 – 1.72 (m, 4H), 1.64 – 1.55 (m, 2H), 1.24 (t, J = 7.0 Hz, 6H). **Electrochemistry** (WE = C disk, RE = Ag/AgNO₃ 0.01 M, electrolyte = MeCN + 0.1 M TBAPF₆, v = 100 mV.s⁻¹): $E_{1/2} (V) = 0.92, -1.67, -1.86, -2.12.$

$[\text{Ru(bpy)}_2(\text{bpy-PO}_3\text{H}_2)]\text{Cl}_2$ (denoted as $[\text{RuP}]^{2+}$).

![Image of Ru(bpy)$_2$(bpy-PO$_3$H$_2$)Cl$_2$]

The complex was synthesized by hydrolysis of $[\text{Ru-PO}_3\text{Et}_2]^{2+}$ (180 mg, 0.213 mmol) in acidic solution containing 10 mL H$_2$O and 10 mL saturated HCl solution. The mixture was refluxed at 100 °C for 48 hours. The color changed to slightly dark red during the reaction. After the reaction, the solvent was evaporated under vacuum. The solid part was solubilized in ethanol/acetone mixture then evaporated several times to eliminate the water content. Finally, the solid product was dried under vacuum to give a dark red powder (110 mg). Reaction yield cannot be determined due to the presence of remaining HCl.

$^1$H NMR (400 MHz, CD$_3$CN): $\delta$ (ppm) = 8.50 (d, $J = 7.9$ Hz, 4H), 8.39 (s, 1H), 8.36 (s, 1H), 8.06 – 8.02 (m, 4H), 7.77 – 7.72 (m, 4H), 7.56 – 7.52 (m, 2H), 7.40 – 7.36 (m, 4H), 7.23 (m, 2H), 2.83 (t, $J = 7.4$ Hz, 2H), 2.52 (s, 3H), 1.81 – 1.73 (m, 4H), 1.68 – 1.63 (m, 2H). **Electrochemistry** (WE = C disk, RE = Ag/AgNO₃ 0.01 M, electrolyte = MeCN/H$_2$O (95/5 v/v) + 0.1 M TBAPF₆, v = 100 mV.s⁻¹): $E_{1/2} (V) = 0.92, -1.20$ (irreversible), -1.89 (irreversible).

**tppy-(CH$_2$)$_3$-PO$_3$H$_2$.**

![Image of tppy-(CH$_2$)$_3$-PO$_3$H$_2$]

The synthesis requires three consecutive steps as follows:

(i) **Step 1: Synthesis of [3-(4-formyl-phenoxy)-propyl]-phosphonic acid diethyl ester:**
4-hydroxybenzaldehyde (200 mg, 1.637 mmol) was dissolved in 5 mL of MeCN before addition of K$_2$CO$_3$ (340 mg, 2.457 mmol, 1.5 equiv) and diethyl(3-bromopropyl)phosphonate (0.35 mL, 1.802 mmol, 1.1 equiv). The reaction was heated at 50°C overnight. After cooling to RT, 50 mL of water was added and the solution was extracted with 50 mL of CH$_2$Cl$_2$ (3 times). The organic layer was washed with brine before being dried with MgSO$_4$. After filtration and evaporation, the crude was purified by chromatography on silica gel with ethyl acetate as eluent to give 389 mg (1.295 mmol) of the pure compound as a white solid with 79 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 9.85 (s, 1H), 7.80 (d, $J$ = 8.7 Hz, 2H), 6.96 (d, $J$ = 8.7 Hz, 2H), 4.10 (m, 6H), 2.18-1.86 (m, 4H), 1.30 (t, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 190.8, 163.9, 132.1, 130.1, 114.8, 67.9, 67.7, 61.8, 61.7, 23.3, 22.6, 21.4, 16.6, 16.5. $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ (ppm) = 31.2. MS-APCI: $m/z = 301$ [M+H]$^+$

(i) Step 2: Synthesis of [3-(4-[2,2';6',2'']-terpyridin-4'-yl-phenoxy)-propyl]-phosphonic acid diethyl ester

The aldehyde (558 mg, 1.858 mmol) was dissolved in 12 mL of methanol before addition of 2-acetylpyridine (0.42 mL, 3.1716 mmol, 2 equiv), KOH (208 mg, 3.1716 mmol, 2 equiv) and 12 mL of NH$_4$OH (30%). The reaction was heated at 50 °C for 3 days. After cooling to RT, the solvent was evaporated and the crude was purified by chromatography on silica gel. The elution started with AcOEt and went on with MeOH 2%, 5% before finishing with a mixture of AcOEt/MeOH/ Et$_3$N (94/5/1). The crude compound was dissolved in EtOH and precipitated with addition of water. After filtration, the compound was recrystallized twice with a mixture of AcOEt/Cyclohexane to give 209 mg (0.415 mmol) of a white powder with a 22% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.75-8.73 (m, 4H), 8.68 (d, $J$ = 8.0 Hz, 2H), 7.92-7.88 (m, 4H), 7.38-7.35 (m, 2H), 7.02 (d, $J$ = 8.5 Hz, 2H), 4.17-4.09 (m, 6H), 2.19-2.09 (m, 2H), 2.02-1.94
(m, 2H), 1.34 (t, J = 7.0 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) = 159.9, 156.3, 155.7, 150.0, 149.0, 137.4, 130.9, 128.8, 124.0, 121.7, 118.7, 115.1, 67.7, 67.6, 61.8, 61.7, 23.2, 22.9, 21.8, 16.7, 16.6. $^{31}$P NMR (162 MHz, CDCl$_3$): δ (ppm) = 31.6. MS-APCI: m/z = 504 [M+H]$^+$

(iii) Step 3: Synthesis of [3-(4-[2,2';6',2'']-terpyridin-4'-yl-phenoxy)-propyl]-phosphonic acid

![Chemical structure diagram]

To a solution of bromotrimethylsilane (TMSBr, 0.315 mL, 2.383 mmol, 10 equiv) in 5 mL of anhydrous CH$_2$Cl$_2$ under inert atmosphere, 120 mg of the phosphonic ester dissolved in 5 mL of CH$_2$Cl$_2$ was added dropwise in 5 minutes at RT. After two hours of reaction, 1 mL of a mixture acetone/water (1/1) was added. After one more hour, the solvent was evaporated and the crude was triturated in 20 mL of hot ethanol. After cooling to RT, the compound was filtrated and dried. A yellow powder was obtained (126 mg). The yield cannot be determined because of the unknown amount of HBr in the molecule.

$^1$H NMR (400 MHz, [D$_6$]DMSO): δ (ppm) = 9.02 (d, J = 8.0 Hz, 2H), 8.94 (d, J = 4.8 Hz, 2H), 8.86 (s, 2H), 8.44-8.40 (m, 2H), 8.05 (d, J = 8.7 Hz, 2H), 7.87-7.84 (m, 2H), 7.19 (d, J = 8.8 Hz, 2H), 4.16 (t, J = 6.3 Hz, 2H), 2.02-1.92 (m, 2H), 1.76-1.68 (m, 2H). $^{13}$C NMR (100 MHz, [D$_6$]DMSO): δ (ppm) = 160.2, 152.1, 151.2, 150.1, 146.7, 141.6, 128.6, 128.2, 126.0, 123.0, 119.2, 115.2, 67.8, 67.6, 24.6, 23.2, 22.8. $^{31}$P NMR (162 MHz, [D$_6$]DMSO): δ (ppm) = 25.9. MS-MALDITOF: m/z = 448 [M+H]$^+$

**TiO$_2$/Mn$^1$ NPs:** It was synthesized following a two-step procedure. First, the ttpy-(CH$_2$)$_3$PO$_3$H$_2$ ligand (4.5 mg, 10 µmol) and TiO$_2$ anatase NPs (50 mg) were mixed in 25 mL DMSO. The mixture was stirred at RT for 20 h in dark. Afterwards, the modified NPs were separated by centrifugation and washed multiple times with DMSO and acetone to remove unadsorbed ligands. In the second step, the NPs were mixed with Mn(CO)$_5$Br (2.8 mg, 10 µmol) in 25 mL acetone and refluxed at 45 °C for 3 h in dark. Finally, the TiO$_2$/Mn$^1$ NPs were centrifuged and washed thoroughly with acetone prior to be dried under vacuum to yield a pale yellow powder (40.7 mg). Loading of Mn$^1$ on TiO$_2$ is estimated to be 0.20 mmol g$^{-1}$ (about 3800 Mn$^1$ molecules per particle or 2 Mn$^1$ molecules per nm$^2$). **FT-IR** (KBr pellet, C=O stretching): ν (cm$^{-1}$) = 2022, 1900-1950 (broad).
**TiO<sub>2</sub>/Ru<sup>II</sup> and SiO<sub>2</sub>/Ru<sup>II</sup> NPs.** In a typical experiment, a suspension of the TiO<sub>2</sub> NPs (anatase, 50 mg) or SiO<sub>2</sub> (d < 20 nm, 50 mg) in ethanol/acetone (8/2, v/v) was sonicated for 20 minutes. Subsequently, [RuP]<sup>2+</sup> complex (14.2 mg, 14 µmol) was added to the suspension, and the mixed solvent was also added to a total volume of 25 mL. The mixture was vigorously stirred in 60 hours. The dye-sensitized NPs were excessively washed and separated by centrifugation (4000 rpm, 45 minutes), then dried in an oven overnight to yield an orange fine powder (46 mg). The maximum Ru loading is estimated to be 0.21 mmol g<sup>-1</sup> for TiO<sub>2</sub>/Ru<sup>II</sup> and 0.076 mmol g<sup>-1</sup> for SiO<sub>2</sub>/Ru<sup>II</sup>. For the commercially available anatase TiO<sub>2</sub> NPs, assuming they are all spherical with diameter of 25 nm and bulk density of 3.9 g cm<sup>-3</sup>, one can roughly estimate the Ru<sup>II</sup> loading to be 4000 Ru<sup>II</sup> molecules per particle or 2 Ru<sup>II</sup> molecules per nm<sup>2</sup>. Similarly, Ru loading on commercially available SiO<sub>2</sub> NPs is estimated at 460 Ru<sup>II</sup> molecules per particle or 0.5 Ru<sup>II</sup> molecules per nm<sup>2</sup>, taken into account the diameter of 20 nm and density of 2.4 g cm<sup>-3</sup>.

**Electrochemistry** (in MeCN + 0.1 M TBAPF<sub>6</sub>, WE = Pt CME, v = 100 mV.s<sup>-1</sup>): \(E_{1/2} = 0.92\) V (SiO<sub>2</sub>/Ru<sup>II</sup>) or 0.98 V (TiO<sub>2</sub>/Ru<sup>II</sup>).

**Ru<sup>II</sup>/TiO<sub>2</sub>/Mn<sup>I</sup> (Mn:Ru = 1:10) NPs.** It was synthesized by stepwise grafting the Mn<sup>I</sup> and Ru<sup>II</sup> complexes on TiO<sub>2</sub> anatase NPs (50 mg), respectively. The grafting procedure for Mn<sup>I</sup> is similar to that described for TiO<sub>2</sub>/Mn<sup>I</sup> NPs in the above paragraph, except that the contents of ttpy-(CH<sub>2</sub>)<sub>3</sub>-PO<sub>3</sub>H<sub>2</sub> and Mn(CO)<sub>5</sub>Br were reduced to 0.7 µmol (ie. 0.31 mg for ttpy-(CH<sub>2</sub>)<sub>3</sub>-PO<sub>3</sub>H<sub>2</sub> and 0.19 mg for Mn(CO)<sub>5</sub>Br). After being washed thoroughly with acetone and dried under vacuum, the TiO<sub>2</sub>/Mn<sup>I</sup> NPs were mixed with [RuP]<sup>2+</sup> (7.1 mg, 7 µmol) in 25 mL H<sub>2</sub>O. The mixture was stirred at RT for 20 h in dark. Afterwards, the modified NPs were separated by centrifugation and washed thoroughly with water, then acetone to remove water from the particles. Finally, the acetone solvent was evaporated to yield a pale orange powder (23.6 mg).
III. Characterization

III.1. Electrochemistry, UV-visible and IR spectroscopy:

Figure S1. Cyclic voltamogram of [Mn(ttpy)(CO)3Br] in CH3CN + 0.1M TBAPF6 under argon, v= 100 mV.s⁻¹ The redox reaction are summarized in the following equations.

**Reaction S1:** $\text{[Mn}^{\text{I}}(\kappa^2\text{-ttppy})(\text{CO})_3\text{Br}] + \text{e}^- \rightarrow [\text{Mn}^{\text{I}}(\kappa^2\text{-ttppy}^*)(\text{CO})_3] + \text{Br}^- \quad E_{pc1} = -1.44 \text{ V}$

**Reaction S2:** $[\text{Mn}^{\text{I}}(\kappa^2\text{-ttppy}^*)(\text{CO})_3] \rightarrow [\text{Mn}^{0}\text{(ttppy})(\text{CO})_3]$  

**Reaction S3:** $[\text{Mn}^{0}\text{(ttppy})(\text{CO})_3] \rightarrow 1/2 [\text{Mn}^{0}\text{(ttppy})(\text{CO})_2]_2 + \text{CO}$

**Reaction S4:** $1/2 [\text{Mn}^{0}\text{(ttppy})(\text{CO})_2]_2 + \text{MeCN} \rightarrow [\text{Mn}^{1}((\text{ttppy})(\text{CO})_2(\text{MeCN}))^+ + \text{e}^- \quad E_{pa1} = -0.89 \text{ V}$

**Reaction S5:** $1/2 [\text{Mn}^{0}\text{(ttppy})(\text{CO})_2]_2 + \text{e}^- \rightarrow [\text{Mn}^{1}(\text{ttppy})(\text{CO})_2]^-$  

**Reaction S6:** $[\text{Mn}^{1}(\text{ttppy})(\text{CO})_2]^+ + \text{MeCN} \rightarrow [\text{Mn}^{1}(\text{ttppy})(\text{CO})_2(\text{MeCN})]^-$

**Reaction S7:** $[\text{Mn}^{1}(\text{ttppy})(\text{CO})_2]^+ \rightarrow [\text{Mn}^{0}(\text{ttppy})(\text{CO})_2] + \text{e}^- \quad E_{pa2} = -1.45 \text{ V}$

**Reaction S8:** $[\text{Mn}^{0}(\text{ttppy})(\text{CO})_2] \rightarrow 1/2 [\text{Mn}^{0}(\text{ttppy})(\text{CO})_2]_2$
Scheme S1. Chemical structures of the intermediate complexes mentioned in reaction S1-S8

Figure S2. UV-vis absorption spectra of [Ru(bpy)$_3$]$^{2+}$ (red) and [Mn(tppy)(CO)$_3$]Br (blue) in MeCN under Ar
Figure S3. IR spectra of [Mn(ttpy)(CO)₃Br] (black), anatase TiO₂ (blue) and TiO₂/MnI (red) in solid state.
Figure S4. (a) Solid-state UV-vis absorption spectra of TiO$_2$ (dotted line), TiO$_2$/Mn$^{1}$ (black) and Ru$^{II}$/TiO$_2$/Mn$^{1}$ (red) nanoparticles. (b) Emission spectra of Ru$^{II}$/TiO$_2$/Mn$^{1}$ colloidal solution in MeCN after excitation at 450 nm.

Figure S5: Cyclic voltamogramm of TiO$_2$ NPs recorded in solid state using a Pt cavity microelectrode (φ = 50 μm, d= 25 μm) in MeCN +0.1 M TBAPF$_6$ under Ar (v= 100 mV s$^{-1}$)
Figure S6: a) Cyclic voltamogramm of FTO/[Mn(PO$_3$H$_2$-ttppy(CO)$_3$Br)] electrode in MeCN + TBAPF$_6$ (0.1 M) solution under Ar, $v = 100$ mV s$^{-1}$; b) $I_{pc}$- scan rate plot based on the first reduction peak of the CV of FTO/[Mn(PO$_3$H$_2$-ttppy(CO)$_3$Br]) and a linear fitting ($R^2 = 0.996$).

III.3. Results of catalysis experiments

Table S1. Results of photocatalytic CO$_2$ reduction using TiO$_2$/Ru$^{II}$ NPs + free Mn$^I$ in solution, and SiO$_2$/Ru$^{II}$ NPs + free Mn$^I$ complex in solution. The DMF solution contained TEOA (1 M) and BNAH (0.1 M). Irradiation was achieved by using a Xe lamp (3×10$^{-4}$ W cm$^{-2}$, 5 cm apart), a UV-hot filter and a 470 ± 40 nm bandpass filter. The results were obtained after 16 hours of irradiation.

<table>
<thead>
<tr>
<th>System</th>
<th>$n_{\text{Ru}}$ (µmol)</th>
<th>$n_{\text{Mn}}$ (µmol)</th>
<th>HCOOH</th>
<th>CO</th>
<th>Total TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Ru$^{II}$ + free Mn$^I$</td>
<td>0.3</td>
<td>0.03</td>
<td>1.1</td>
<td>0.2</td>
<td>44</td>
</tr>
<tr>
<td>SiO$_2$/Ru$^{II}$ + free Mn$^I$</td>
<td>0.3</td>
<td>0.06</td>
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<td>0.2</td>
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</table>
III.4. Energy diagram

Summary of the photoinduced reduction process of Mn$^I$ catalyst after irradiation of Ru$^{II}$/SiO$_2$ NPs (scheme S2) and Ru$^{II}$/TiO$_2$ NPs (scheme S3).

$$\text{Ru}^{II}/\text{SiO}_2 + \text{Mn}^I$$

**Scheme S2.** Energy diagram of Ru$^{II}$/SiO$_2$ + Mn$^I$ and photo-induced electron transfer events: (1) Ru$^{II}$ is excited to Ru$^{II*}$, (2) Ru$^{II*}$ is reductively quenched by BNAH to form [Ru(bpy)$_3$]$^+$, (3) electron transfer between neighboring [Ru(bpy)$_3$]$^+$ and Mn$^I$ moieties to form Ru$^{II}$ and Mn$^0$. Redox potentials of Ru$^{2+/+}$ and Mn$^{+/0}$ couples are based on the electrochemical behaviors described in the main text. Potential of BNAH$^+/\text{BNAH}$ has been reported by Y. Yamazaki et al.$^4$ Potential of the excited state Ru$^{2+/+}$ is estimated by the simplified Rehm-Weller equation:

$$E(\text{Ru}^{2+/+}) \approx E^0(\text{Ru}^{2+/+}) + \frac{1240}{\lambda_{\text{emission}} \text{ (nm)}}$$
**Scheme S3.** Energy diagram of \( \text{Ru}^{\text{II}}/\text{TiO}_2 + \text{Mn}^{\text{I}} \) and photo-induced electron transfer events: (1) \( \text{Ru}^{\text{II}} \) is excited to \( \text{Ru}^{\text{II}^*} \), (2) \( \text{Ru}^{\text{II}^*} \) is quenched by \( \text{TiO}_2 \) to form \( [\text{Ru(bpy)}_3]^{3+} \) (the charge injection is known to be fast and may proceed either from the \( ^1\text{MLCT} \), or hot \( ^3\text{MLCT} \) states),\(^5\) (3) electron transfer between sacrificial BNAH and the transient \( [\text{Ru(bpy)}_3]^{3+} \) species to regenerate the \( \text{Ru}^{\text{II}} \) starting complex, (4) reduction of \( \text{Mn}^{\text{I}} \) by the electron injected in the CB of \( \text{TiO}_2 \). Redox potentials of \( \text{TiO}_2, \text{Ru}^{2+/3+}, \text{Mn}^{+/0} \) couples are based on the electrochemical behaviors described in the main text. Potential of BNAH\(^+\)/BNAH has been reported by Y. Yamazaki et al.\(^4\) Potential of the excited state \( \text{Ru}^{2+^*/3+^*} \) is estimated by the simplified Rehm-Weller equation:

\[
E(\text{Ru}^{2+^*} (^1\text{MLCT})) \approx E^0(\text{Ru}^{3+/2+}) + \frac{1240}{\lambda_{\text{absorption}} (\text{nm})}
\]

\[
E(\text{Ru}^{2+^*} (^3\text{MLCT})) \approx E^0(\text{Ru}^{3+/2+}) + \frac{1240}{\lambda_{\text{emission}} (\text{nm})}
\]
EPR spectroscopy and computation

EPR spectra of the Ru/TiO\textsubscript{2} dyad and Ru\textsuperscript{II}/TiO\textsubscript{2}/Mn\textsuperscript{I} triad were recorded in the presence of BNAH and with visible light irradiation.

![EPR spectra](image)

**Figure S7.** EPR spectra (and corresponding numerical simulations) of TiO\textsubscript{2}/Ru\textsuperscript{II} dyad and Ru\textsuperscript{II}/TiO\textsubscript{2}/Mn\textsuperscript{I} triad 455 nm irradiated colloidal samples containing BNAH as an electron donor. The concentrations of TiO\textsubscript{2} NP (6g.L\textsuperscript{-1} in acetonitrile) and BNAH (0.1M) are the same in both samples and the irradiations were performed in the EPR spectrometer using the same fibered 455nm LED setup.

The EPR spectrum observed for the TiO\textsubscript{2}/Ru\textsuperscript{II} dyad sample irradiated in the presence of BNAH (see the blue curve) contains two remarkable features at 3464.6 G ($g_{\perp} = 1.990$) and 3517.7 G ($g_{//}=1.959$) which are typical of Ti\textsuperscript{3+} sites in anatase TiO\textsubscript{2}.\textsuperscript{6} It also contains a broader feature centered at 3440.5 G, which can be assigned to the neutral BNA° free radical obtained by removing an electron and a proton from the BNAH electron donor (the proton is removed from the position C4) (figure S8). The BNAH° radical cation would have a much wider EPR spectrum due the stronger ~150 MHz (~50 G) hyperfine coupling of the 2 protons in C4 position.\textsuperscript{7} In order to support this assignment, the g and hyperfine tensors of BNA° were computed by DFT (see next paragraph). The experimental EPR spectra of the irradiated dyad and triad (blue and pink curves, resp.) are well reproduced by numerical simulations (red and
green curves, resp.) using a g tensor (2.0013, 2.0027, 2.0033) shifted by 0.0007 compared with the tensor computed by DFT (2.0020, 2.0034, 2.0040) and by correcting the hyperfine tensors of $^{14}$N and $^1$H computed by DFT by a 0.9 multiplicative factor.

![Chemical structure of BNAH and BNA°](image)

**Figure S8.** Chemical structure of BNAH and BNA°

Remarkably, the EPR spectrum obtained by irradiating the TiO$_2$/Ru$^{II}$ dyad in the presence of BNAH (blue curve), is very well reproduced by a simulation made using 50% of BNA° radical and 50 % of Ti$^{3+}$ sites in anatase (red curve). This indicates that the Ru$^{II}$ photosensitizers grafted on the TiO$_2$ nanoparticles transfer electrons efficiently to TiO$_2$ and that, in the absence of an electron acceptor, these electrons are stored in TiO$_2$ as Ti$^{3+}$ paramagnetic sites.

On the opposite the EPR spectrum obtained by irradiating the Ru$^{II}$/TiO$_2$/Mn$^{II}$ triad in the presence of BNAH (pink curve), is reproduced by a simulation (green curve) made assuming a strong excess of BNA° radical (86%) compared with Ti$^{3+}$ sites in anatase (14%). This suggests that in the triad, most of the electrons transferred from the Ru$^{II}$*photosensitizers do not remain on TiO$_2$, but are further transferred to the grafted Mn$^{II}$ catalysts.

At last the intensity of the signal from BNA° free radical is much higher (~5 times) with for the Ru$^{II}$/TiO$_2$/Mn$^{II}$ triad than with the TiO$_2$/Ru$^{II}$ dyad (remark: the experimental spectra were normalized in the figure S7 for the comparison with simulated spectra). This suggests that the electron transfer from BNAH to transient Ru$^{III}$ species is more efficient in the triad than in the dyad. This may be because the presence of Mn$^{II}$ in the triad prevents the charge recombination by removing faster electrons from TiO$_2$.

**Computation of the g-tensor and ($^{14}$N, $^1$H) hyperfine coupling tensors of BNAH (1-benzyl-1,4-dihydronicotinamide)**

DFT calculations have been performed with the ADF (Amsterdam Density Functional) code developed by E. J. Baerends and co-workers using triple-zeta basis sets (no frozen core) in two steps. First, we geometry optimized both radical variants derived from BNAH resulting either from oxidation (BNAH°+ or H° abstraction (BNA°), in the gas phase at the Generalized Gradient Approximation (GGA) VBP exchange-correlation (XC) potential (VWN + BP: Vosko, Wilk & Nusair + corrective terms by Becke for the exchange, and Perdew for the correlation) with ADF grid precision 6. We then computed g-tensors (for both variants) and ($^{14}$N, $^1$H) hyperfine coupling tensors (for the neutral BNA° variant) using the (Statistical Average of Orbital
Potentials) SAOP exchange-correlation potential coupled with the relativistic (full spin-orbit) ZORA (two-component Zeroth-Order Regular Approximation) option.

As for g-tensors, the cationic BNA\textsuperscript{**} radical has been used as a test of the DFT methodology. An experimental average value of 2.0031 was already proposed.\textsuperscript{7} We computed an average value of 2.0038 (eigenvalues: 2.0031, 2.0042, 2.0052) deviating from the experimental value by only 0.0007. For the BNA\textsuperscript{+} radical variant, then, we predict an average value of 2.0031 (eigenvalues: 2.0020, 2.0034, 2.0040) which may therefore have to be slightly lowered.

As for hyperfine coupling tensors computed for the neutral BNA\textsuperscript{+} variant, we found one non-negligible \textsuperscript{14}N tensor:

\begin{table}[h]
\begin{tabular}{ccc}
\textsuperscript{14}N hcc's (MHz) \\
0.2 & 7.0 & -8.1 \\
7.0 & 6.4 & -12.7 \\
-8.1 & -12.7 & 10.9 \\
\end{tabular}
\end{table}

and five non-negligible \textsuperscript{1}H tensors, among which three major ones:

\begin{table}[h]
\begin{tabular}{ccc}
\textsuperscript{1}H hcc's (MHz) & \textsuperscript{1}H hcc's (MHz) & \textsuperscript{1}H hcc's (MHz) \\
-21.9 & -11.0 & -6.0 \\
-11.0 & -27.1 & -7.0 \\
-6.0 & -7.0 & -33.8 \\
-22.9 & 9.3 & 10.0 \\
9.3 & -42.2 & -6.7 \\
10.0 & -6.7 & -28.6 \\
-18.9 & 16.1 & -0.1 \\
-16.1 & -42.2 & -6.7 \\
18.9 & 16.1 & -0.1 \\
\end{tabular}
\end{table}

and two minor ones:

\begin{table}[h]
\begin{tabular}{ccc}
\textsuperscript{1}H hcc's (MHz) & \textsuperscript{1}H hcc's (MHz) & \textsuperscript{1}H hcc's (MHz) \\
7.5 & -1.5 & 1.9 \\
-1.5 & 4.4 & 1.8 \\
1.9 & 1.8 & 4.0 \\
-6.3 & 0.2 & 0.5 \\
0.2 & -3.1 & 3.1 \\
0.5 & 3.1 & -3.6 \\
\end{tabular}
\end{table}

These full tensors have been used to provide initial values for the simulation of the EPR experimental spectrum containing the BNA\textsuperscript{+} component.
IV- Bibliography