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## Immobilization of Mn(I) and Ru(II) polypyridyl complexes on TiO<sub>2</sub> nanoparticles for selective photoreduction of CO<sub>2</sub> to formic acid

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TiO<sub>2</sub> nanoparticles are successively functionalized with [Mn( $\kappa^2$ N<sup>1</sup>,N<sup>2</sup>-tppy)(CO)<sub>3</sub>Br] as catalyst and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as photosensitizer to yield Ru<sup>II</sup>/TiO<sub>2</sub>/Mn<sup>I</sup>. Under continuous irradiation at 470 nm and in the presence of a sacrificial electron donor, this triad reduces CO<sub>2</sub> to HCOOH (TON<sub>max</sub> = 27) with 100% selectivity.

Carbon dioxide (CO<sub>2</sub>) is arguably one of the most notorious greenhouse gases that contribute to global warming<sup>1</sup> and rises in sea level.<sup>2</sup> In recent years, novel molecular catalysts able to reduce CO<sub>2</sub> into more value-added products have been extensively investigated to replace the prototypical [Re(bpy)(CO)<sub>3</sub>Cl] (bpy = 2,2'-bipyridine) catalyst.<sup>3-5</sup> Those based on earth-abundant elements such as Fe, Ni, Co, Cu and Mn are of particular interest,<sup>6-8</sup> not only for academics but also industrialists for potential upscaling.<sup>9</sup> Moreover, CO<sub>2</sub> conversion to produce useful compounds must be economically viable and photochemical reduction of CO<sub>2</sub>, using renewable light energy source could be one of the solutions to solve the equation.

A general strategy to develop photoreduction system is to covalently link a photosensitizer with a molecular catalyst.<sup>1,10,11</sup> It, however, often requires challenging multi-step syntheses to obtain the desired supramolecules. An alternative approach, that combined also the advantage of heterogeneous catalysis,<sup>12</sup> consists to graft the photosensitizer and the catalyst onto the surface of nanoparticles (NPs) as they offer great surface area to accommodate the molecules.<sup>7,13,14</sup> This approach usually requires significantly less complicated syntheses than the supramolecular homogeneous approach and allows easy control of the surface occupancy and of the ratio between photosensitizer and catalyst. For instance, Neri *et al.*<sup>15</sup> grafted a [Ru(bpy)<sub>3</sub>]<sup>2+</sup> photosensitizer (Ru<sup>II</sup>) and a Ni(cyclam)<sup>2+</sup> (cyclam = 1,4,8,11-

tetraazacyclotetradecane) catalyst on ZrO<sub>2</sub> NPs for photocatalytic CO<sub>2</sub> reduction. Under visible light and in the presence of ascorbic acid as a sacrificial electron donor, Ru<sup>II</sup>/ZrO<sub>2</sub>/Ni<sup>II</sup> system reduced CO<sub>2</sub> to a mix of CO and H<sub>2</sub>. Meanwhile, the solution of homogeneous complexes Ru<sup>II</sup> and Ni(cyclam)<sup>2+</sup> only produced traces of CO. The authors concluded that the proximal immobilization of the photosensitizer and the catalyst molecules on ZrO<sub>2</sub> surface enhanced the kinetics of photo-induced electron transfer reaction between Ru<sup>II</sup>\* and Ni(cyclam)<sup>2+</sup>.

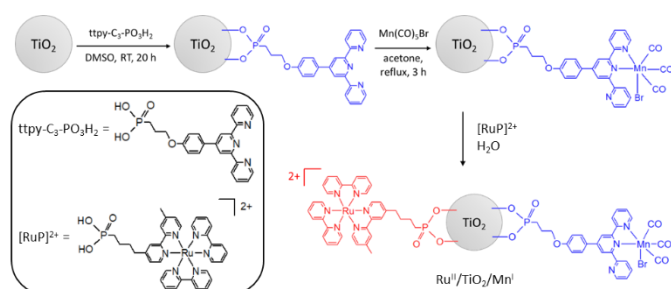
Semiconducting nanoparticles can also be used as both a substrate and an electron relay for the photo-induced electron transfer process between the photosensitizer and the catalyst. For instance, long lived charge separation state can be reach in nanostructured dye-sensitized TiO<sub>2</sub> photoelectrode thus facilitating multi-electron reduction reactions of CO<sub>2</sub>.<sup>16</sup> For instance, Kang and co-workers<sup>17,18</sup> grafted an organic dye and [Re(bpy)(CO)<sub>3</sub>Cl] catalyst on TiO<sub>2</sub> NPs. Under visible light and in the presence of a sacrificial electron donor, the Dye/TiO<sub>2</sub>/Re<sup>I</sup> system efficiently and selectively reduced CO<sub>2</sub> to CO with maximum turnover number (TON<sub>max</sub>) surpassing 570 after 30 hours. In this work TiO<sub>2</sub> worked as an electron relay between the excited dye molecules and the Re(I) catalytic center.

As an alternative for rhenium complexes, manganese complexes have been extensively investigated in recent years. The prototype [Mn(bpy)(CO)<sub>3</sub>Br] is an efficient electrocatalyst<sup>19</sup> and was shown to work in association with Ru<sup>II</sup> in a photocatalytic cycle<sup>20</sup> for the reduction of CO<sub>2</sub> to CO and HCOOH. Immobilization of this complex onto a (semi)conducting surface allowed for better product selectivity.<sup>21-24</sup> However, other Mn polypyridyl complexes than the bipyridines are still underexplored.<sup>6,8</sup> We recently reported the synthesis and characterization of a related complex [Mn( $\kappa^2$ N<sup>1</sup>,N<sup>2</sup>-tppy)(CO)<sub>3</sub>X]<sup>nt</sup> (tppy = 4-tolyl-2,2':6'-2''-terpyridine) (X = Br and n = 0 or X = MeCN and n = 1).<sup>25</sup> Herein we present (i) the homogeneous electrocatalytic and photocatalytic reduction of CO<sub>2</sub> using [Mn( $\kappa^2$ N<sup>1</sup>,N<sup>2</sup>-tppy)(CO)<sub>3</sub>Br] catalyst (Mn<sup>I</sup>), and Ru<sup>II</sup> photosensitizer and (ii) the immobilization of Mn<sup>I</sup> and Ru<sup>II</sup> on TiO<sub>2</sub> NPs (Ru<sup>II</sup>/TiO<sub>2</sub>/Mn<sup>I</sup>, Scheme 1) for heterogenous photocatalytic CO<sub>2</sub> reduction.

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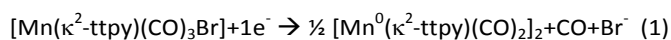
Electronic Supplementary Information (ESI) available: See



**Scheme 1** Multi-step route for Ru<sup>II</sup>/TiO<sub>2</sub>/Mn<sup>I</sup> triad

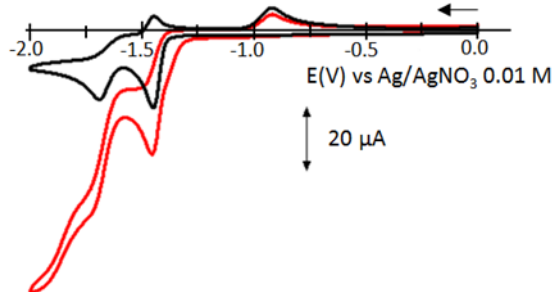
The Mn<sup>I</sup> complex was synthesized and characterized following a reported procedure<sup>25</sup> (see SI for more information).

Cyclic voltammograms (CVs) of Mn<sup>I</sup> were recorded under argon in MeCN solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (Figure 1, black line). The results are in accordance with the behavior of [Mn(terpy)(CO)<sub>3</sub>Br] (terpy = 2,2':6'-2''-terpyridine)<sup>26</sup> and the interpretation is based on relevant literature.<sup>8,26,27</sup> The CV is decoupled in figure S1. The first irreversible peak at  $E_{pc1} = -1.44$  V is assigned to the Mn<sup>+/0</sup> one electron reduction process. This process leads to the leaving of Br<sup>-</sup> and coordination of the free pyridyl of terpyridine to form a tridentate linkage between the ttpy ligand and Mn center (reaction S1-S3). This reduction event is associated to the release of a CO group and the formation of a Mn<sup>0</sup>-Mn<sup>0</sup> dimer through metal-metal bonding (equation 1).



On the reverse scan, the anodic peak at -0.89 V corresponds to the oxidation of the dimer (reaction S4). Further sweeping to more negative potentials leads to a second one-electron irreversible peak at  $E_{pc2} = -1.67$  V that is ascribed to the reduction of the Mn<sup>0</sup>-Mn<sup>0</sup> dimer to form [Mn<sup>-1</sup>(ttpy)(CO)<sub>2</sub>]<sup>-</sup> species (reaction S5-S6). The peak at -1.67 V is associated with a small oxidation peak at -1.45 V corresponding to the oxidation of the newly formed [Mn<sup>-1</sup>(ttpy)(CO)<sub>2</sub>]<sup>-</sup> to regenerate the dimer species (reaction S7-S8).

Under CO<sub>2</sub> and in the presence of water (5% v/v) as a proton source, the CV of Mn<sup>I</sup> shows significant enhancement in



**Figure 1** CVs of Mn<sup>I</sup> (1 mM) in MeCN + 0.1 M TBAPF<sub>6</sub> under Ar (black) and under CO<sub>2</sub> in the presence of 5% H<sub>2</sub>O (red).  $v = 0.1$  V s<sup>-1</sup>.

current magnitude on both reduction peaks at -1.44 V and -1.67 V (Figure 1a, red line). Without water, the CV shows negligible difference to the CV recorded under Ar. These results hence suggest that the electrocatalytic CO<sub>2</sub> reduction may occur at both potentials, as already observed for [Mn(terpy)(CO)<sub>3</sub>Br]<sup>26</sup> and [Mn(phen)(CO)<sub>3</sub>Br]<sup>27</sup> (phen = 1,10-phenanthroline).

Controlled-potential electrolysis at -1.7 V produced CO as the only product (TON<sub>max</sub> = 12, Faradaic efficiency (FE) = 100% after 4 h). This result shows remarkable improvement on catalytic activity and stability compared to [Mn(κ<sup>2</sup>-terpy)(CO)<sub>3</sub>Br] (TON<sub>max</sub>(CO) = 4.1, FE = 129%)<sup>26</sup> where such an anomalously high FE could be a consequence of the decarbonylation of the complex as side reaction.

Photocatalytic CO<sub>2</sub> reduction experiments were carried out in DMF/TEOA mixed solution (TEOA: triethanolamine, C<sub>TEOA</sub> = 1 M) in the presence of Ru<sup>II</sup> as photosensitizer, Mn<sup>I</sup> as catalyst and 1-benzyl-1,4-dihydronicotinamide (BNAH) as sacrificial electron donor. TEOA is added in the media as a base to suppress reverse reaction after oxidation of BNAH.<sup>28</sup> Excitation wavelength was chosen at 470 ± 40 nm to selectively activate the photosensitizer and not the catalyst (Figure S1), as this catalyst can undergo photo-induced decarbonylation reaction.<sup>29</sup> After 16 h, the amounts of CO and H<sub>2</sub> in the gas phase and HCOOH in the liquid phase were measured by GC and HPLC, respectively (Table 1 entries 1-5, see SI for detail on the sample treatment and product quantification). Neither CO nor HCOOH was produced in the absence of Mn<sup>I</sup> or light. We investigated various Mn<sup>I</sup>:Ru<sup>II</sup> ratios while keeping the Ru<sup>II</sup> concentration unchanged so that light absorption by the photosensitizer remained the same in all the series. All the Mn<sup>I</sup>:Ru<sup>II</sup> ratios produced both CO and HCOOH while no H<sub>2</sub> was detected. Prolonging the irradiation time did not increase the product amounts. Table 1 shows that the decrease in the Mn<sup>I</sup>:Ru<sup>II</sup> ratio leads to a higher total TON. That may be due to two combined effects: a higher possibility for each Mn<sup>I</sup> molecule being reduced by surrounding [Ru(bpy)<sub>3</sub>]<sup>+</sup> molecules,

**Table 1** Results of the photocatalytic CO<sub>2</sub> reduction process. Solution: DMF/TEOA (1 M) and BNAH (0.1 M). Irradiation was achieved by using a Xe lamp (3 × 10<sup>-4</sup> W cm<sup>-2</sup>, 5 cm apart), a UV-hot filter and a 470 ± 40 nm bandpass filter. Results were obtained after 16 h. TON uncertainties ± 2.

Entry	Ratio of Mn <sup>I</sup> :Ru <sup>IIa</sup>	HCOOH		CO		TON <sub>total</sub> <sup>c</sup>
		n	TON <sub>max</sub> <sup>b</sup>	n	TON <sub>max</sub> <sup>b</sup>	
a) For homogeneous solution of Mn <sup>I</sup> and Ru <sup>II</sup> free complexes						
1	1:1	9.8	14	5.6	8	22
2	5:10	3.9	28	1.4	10	38
3	1:10	2.2	31	1.3	19	50
4	5:1	71.4	20	18.9	5	25
5	10:1	88.9	13	35.0	5	17
b) For Ru <sup>II</sup> /TiO <sub>2</sub> /Mn <sup>I</sup>						
6	1:10	0.8	27	-	-	27

<sup>a</sup> Ru<sup>II</sup> concentration is unchanged (0.14 mM)

<sup>b</sup> Turnover number (TON) versus Mn catalyst

produced by irradiation of  $\text{Ru}^{\text{II}}$  in presence of BNAH, and a protection of the  $\text{Mn}^{\text{I}}$  catalyst against photo-induced decarbonylation by an inner filter role of  $\text{Ru}^{\text{II}}$  which absorb more strongly visible light at 470 nm ( $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ ) = 2300 for  $\text{Mn}^{\text{I}}$  and 8400 for  $\text{Ru}^{\text{II}}$ ) (Figure S2). This property has already been observed for similar molecular photocatalytic systems.<sup>11,15</sup> In the series, the best  $\text{Mn}^{\text{I}}:\text{Ru}^{\text{II}}$  ratio is determined at 1:10 where the total TON reaches the highest value of 50.

We then prepared the triad  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$  following a three-step procedure (Scheme 1, see SI for detail), in which phosphonic acid was chosen to anchor the complexes on anatase  $\text{TiO}_2$  NPs.<sup>30</sup> It is noted that  $\text{Ru}^{\text{II}}$  was functionalized with only one phosphonic acid group in order to avoid it to be grafted on different  $\text{TiO}_2$  NPs, which could lead to aggregation in colloidal solution. The ratio  $\text{Mn}^{\text{I}}:\text{Ru}^{\text{II}}$  = 1:10 was chosen following results in Table 1. After the immobilization of each complex, modified nanoparticles were separated by centrifugation and washed thoroughly with corresponding solvents. Maximum surface loading of  $\text{Mn}^{\text{I}}$  and  $\text{Ru}^{\text{II}}$  complexes was estimated at 14  $\mu\text{mol g}^{-1}$  and 140  $\mu\text{mol g}^{-1} \pm 20\%$  respectively, by measuring the UV-visible absorbance of supernatant solutions after each centrifugation step.  $\text{Mn}^{\text{I}}$  complex was anchored first so that it can presumably be well distributed on  $\text{TiO}_2$  surface and surrounded by  $\text{Ru}^{\text{II}}$  molecules. The presence of  $\text{Mn}^{\text{I}}$  on  $\text{TiO}_2$  was confirmed by IR spectroscopy (Figure S3). The merging of two antisymmetric C=O stretching bands after  $\text{Mn}^{\text{I}}$  has been grafted on  $\text{TiO}_2$  is consistent with literature for  $\text{Re}^{\text{I}}$ <sup>31</sup> and  $\text{Mn}^{\text{I}}$ <sup>21,22</sup> triscarbonyl bipyridine complexes immobilized on  $\text{TiO}_2$  NPs. The presence of  $\text{Ru}^{\text{II}}$  on  $\text{TiO}_2$  was confirmed by UV-visible absorption and emission spectroscopies (Figure S4). The absorption maximum at around 450 nm of  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$  is attributed to the singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) absorption band of  $\text{Ru}^{\text{II}}$ .<sup>32</sup> In addition, its emission spectrum shows a maximum at 618 nm, which is characteristic of the <sup>3</sup>MLCT luminescence of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  state.<sup>32</sup> Meanwhile,  $\text{TiO}_2/\text{Mn}^{\text{I}}$  does not emit light in the 500–850 nm range under excitation at 450 nm.

$\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$  NPs were then tested in a photocatalytic  $\text{CO}_2$  reduction experiment under the same conditions as described above for the mix of component complexes. The concentration of the NPs was kept at 0.4  $\text{g L}^{-1}$  as higher concentrations lead to quick precipitation and light blocking. Surprisingly this system produced only HCOOH with a quantum yield of 0.17% and  $\text{TON}_{\text{max}} = 27$  (Table 1 entry 6), while CO and  $\text{H}_2$  were not detected. Control experiments using  $\text{TiO}_2$  or  $\text{TiO}_2/\text{Ru}^{\text{II}}$  instead of  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$  (amounts of  $\text{TiO}_2$  and  $\text{Ru}^{\text{II}}$  were kept unchanged) produced no CO,  $\text{H}_2$  or HCOOH, suggesting that HCOOH was formed only in the presence of  $\text{Mn}^{\text{I}}$  catalyst. In addition, when  $\text{TiO}_2/\text{Ru}^{\text{II}}$  NPs and free  $\text{Mn}^{\text{I}}$  complex were used instead of the triad, the results were comparable to the free complexes in homogeneous solution (i.e. production of both CO and HCOOH) (Table S1). These experiments suggest that the immobilization of the  $\text{Mn}^{\text{I}}$  catalyst on  $\text{TiO}_2$  is related to the suppression of CO formation. The excellent yield and selectivity of HCOOH in this study surpass those of CO production from  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^{33}$  and HCOOH production from  $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]^{34}$  anchored on non-conducting support.

In order to elucidate the selectivity enhancement for HCOOH when  $\text{Mn}^{\text{I}}$  was anchored on  $\text{TiO}_2$ , we first used cyclic voltammetry to probe redox properties of immobilized  $\text{Mn}^{\text{I}}$ . A sample of  $\text{TiO}_2/\text{Mn}^{\text{I}}$  NPs powder was pressed inside the cavity of a platinum microelectrode and used as working electrode. Its CV recorded under Ar did not show a clear reduction signal upon cathodic scanning due to the population of electrons to the conduction band (CB) of  $\text{TiO}_2$  from around -1.4 V vs  $\text{Ag}/\text{AgNO}_3$  0.01 M (Figure S5), which occurs at similar potential than the reduction of  $\text{Mn}^{\text{I}}$  (-1.44 V for free complex in solution). Therefore, we grafted  $\text{Mn}^{\text{I}}$  on a conductive Fluorine-doped Tin Oxide (FTO) electrode to investigate the electrochemical behavior of the immobilized  $\text{Mn}^{\text{I}}$  complex. FTO was chosen as phosphonic acid is a suitable anchoring group on this surface,<sup>35</sup> and it is rather redox-inactive up to -2 V. The CV of  $\text{FTO}/\text{Mn}^{\text{I}}$  electrode (Figure S6) shows a cathodic peak at  $E_{\text{pc}} = -1.43$  V which is at the same potential as the first cathodic peak of the free complex in solution. However, on the reverse scan the associated anodic peak appears at a very different potential ( $E_{\text{pa}} = -1.16$  V) than the peak recorded for the homogeneous complex in solution (-0.89 V), which has been assigned to the oxidation of the  $\text{Mn}^0\text{-Mn}^0$  dimer formed after the first reduction step. Since  $\text{Mn}^{\text{I}}$  is immobilized, the formation of  $\text{Mn}^0\text{-Mn}^0$  dimer should be prohibited. This assumption is supported by the lack of a second reduction process which is assigned to the reduction of the  $\text{Mn}^0\text{-Mn}^0$  dimer in solution at -1.67 V. Scanning to potentials more negative than -2 V lead to the degradation of the FTO surface itself. Therefore, we conclude that the reduced form of immobilized complex is monomeric  $[\text{Mn}^0(\text{ttpy})(\text{CO})_3]$  or  $[\text{Mn}^0(\text{ttpy})(\text{CO})_2(\text{MeCN})]$  and not the dimer observed for the complex in solution. The monomeric form of a related complex,  $[\text{Mn}^0(\text{bpy})(\text{CO})_3\text{Br}]$ , anchored on a metal-organic framework<sup>36</sup> or on  $\text{TiO}_2$  particles<sup>22</sup> was proposed to be the intermediate to access 100% selectivity for HCOOH.

Previous works on the mixture of  $\text{Ru}^{\text{II}}$  and  $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$  in solution and using BNAH as sacrificial electron donor have shown that, under irradiation,  $\text{Ru}^{\text{II}}$  is first reductively quenched by BNAH to produce  $\text{Ru}^{\text{I}}$  and then  $\text{Ru}^{\text{I}}$  transfers an electron to the catalyst.<sup>20</sup> In the triad  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$ , reduction of  $\text{Mn}^{\text{I}}$  may proceed via a similar process on surface between adjacent complexes, but more probably after population of the CB of  $\text{TiO}_2$  from the  $\text{Ru}^{\text{II}*}$  excited state, since the injection of charge from  $\text{Ru}^{\text{II}*}$  is known to be very fast ( $k_{\text{inj}} > 10^{11} \text{ s}^{-1}$ ).<sup>37</sup> To understand whether the  $\text{TiO}_2$  matrix participate to the electron transfer process and if the electrons injected in the CB of  $\text{TiO}_2$  can reduced the  $\text{Mn}^{\text{I}}$  catalyst, we performed  $\text{CO}_2$  reduction experiments using a mix of free  $\text{Mn}^{\text{I}}$ , BNAH and  $\text{SiO}_2/\text{Ru}^{\text{II}}$  or  $\text{TiO}_2/\text{Ru}^{\text{II}}$  NPs in DMF/TEOA mixed solution. Both systems contained the same concentration of  $\text{Mn}^{\text{I}}$  and BNAH in solution. They give rise to different results (table S1), with an enhancement of the production of HCOOH and CO with  $\text{TiO}_2$  ( $\text{TON}_{\text{total}} = 44$ ) instead of  $\text{SiO}_2$  ( $\text{TON}_{\text{total}} = 12$ ) as support for the  $\text{Ru}^{\text{II}}$  complex. We postulate then that the electron injected in the CB of  $\text{TiO}_2$  from  $\text{Ru}^{\text{II}*}$  participate to the reduction of the  $\text{Mn}^{\text{I}}$ . The large surface of the  $\text{TiO}_2$  NPs favours the reduction of the  $\text{Mn}^{\text{I}}$  complex in solution leading to an increase in the TON

compared to the  $\text{SiO}_2/\text{Ru}^{\text{II}}$  based system where the charge injection in the NPs is not possible and the reduction of  $\text{Mn}^{\text{I}}$  only occurs from specific site of  $\text{Ru}^{\text{I}}$  transient species on surface (energy diagrams in scheme S2 and S3 summarize the photoinduced electron transfer events). EPR spectroscopy was also performed on  $\text{TiO}_2/\text{Ru}^{\text{II}}$  and  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$  under irradiation with BNAH to confirm the charge injection and the presence of  $\text{BNAH}^{\bullet}$ . For  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$ , a lower signal is obtained for  $\text{Ti}^{3+}$  sites due to the electron transfer toward from the CB to the catalyst (see figure S7 and discussion underneath).

To sum up,  $\text{Mn}^{\text{I}}$  tolylterpyridine derivative appears as promising catalyst for the reduction of  $\text{CO}_2$ . When immobilized onto  $\text{TiO}_2$  together with  $\text{Ru}^{\text{II}}$  as photosensitizer, the system efficiently and selectively reduces  $\text{CO}_2$  to  $\text{HCOOH}$  with a quantum yield of 0.17% under visible irradiation. Cyclic voltammetry suggests that monomeric  $\text{Mn}^{\text{0}}$  complexes are the catalytically active sites in the  $\text{Ru}^{\text{II}}/\text{TiO}_2/\text{Mn}^{\text{I}}$  hybrid system whereas in a mixed solution of  $\text{Ru}^{\text{II}}$  and  $\text{Mn}^{\text{I}}$ , a  $\text{Mn}^{\text{0}}\text{-Mn}^{\text{0}}$  dimer is formed as a precatalyst. Heterogenization prevents the formation of dimers and achieves 100% selectivity toward  $\text{HCOOH}$  production.

### Conflicts of interest

There are no conflicts to declare.

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