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Light-active dinuclear iridium pentahydride complexes catalyze the decomposition of formic acid to generate H_2 by irradiation (λ =395 nm) under ambient temperature and base-free conditions. The catalyst activity is sensitive to light producing H_2 under light irradiation, but with no reaction being observed in the absence of light or when the light is switched off, thereby demonstrating the clear ON/OFF switching ability of this system. Importantly, the dinuclear structure of the catalyst is sufficiently stable to be maintained under the catalytic conditions employed herein.

As a result of the continuous rise in the global energy demand, in addition to the negative impact of fossil fuel consumption on climate change, the discovery and development of alternative energy resources and more sustainable technologies has received growing attention.¹⁻³ More specifically, the efficient utilization of renewable resources such as biomass, wind, and sunlight has received considerable attention in recent years, and as a result, new technologies for energy storage are in strong demand. For example, fuel cells have shown promise for the generation of electricity from hydrogen for powering vehicles and/or power units.⁴ In terms of the safety concerns associated with the use of compressed hydrogen gas, which is highly flammable and difficult to store, formic acid (FA) has been accepted as a suitable liquid hydrogen carrier.5,6 FA has a high hydrogen content (4.4 wt% hydrogen; 5.22 MJ kg⁻¹), and it presents many advantageous physical and chemical properties, such as being a low toxic liquid (bp = 101 °C), which allows its facile transportation, and a feasible hydrogenation/dehydrogenation cycle that can be achieved in the presence of suitable catalysts.

To date, a wide variety of homogeneous and heterogeneous catalysts for the selective generation of hydrogen (with low CO contents) through the catalytic decomposition of FA have been reported.⁷⁻¹² In terms of the efficient utilization of the

On-demand hydrogen production from formic acid by light-active dinuclear iridium catalysts[†]

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generated hydrogen, the production of an on-demand hydrogen supply through appropriate catalysis control is a matter of special importance. However, control of the catalyst reactivity by external stimuli is difficult, and understandably, switching of the reaction remains an unexplored area.^{11,12} Previously, we have reported the syntheses and photocatalytic activities of multinuclear metal catalysts composed of visible-light absorbing units.^{13–18} Building on this previous work, we herein report our study into on-demand hydrogen production through the catalytic decomposition of FA by light-active catalysts using light as an external stimulus.

HCOOH
$$\xrightarrow{\text{cat. 1 (3.3 mol%)}}$$
 H2 + CO₂
irr. (395 nm) or dark, 6 h (1)
MeOH- d_4
NMR tube

Following our report into the syntheses of novel light-active dinuclear iridium pentahydride complexes,¹⁹ we additionally synthesized catalysts **1d** and **1e** bearing 3,5-dimethylphenyl and 4-dimethylamino-3,5-dimethylpheny substituents, respectively, on the phosphorous atom of the BINAP ligand (ESI,† Fig. S1–S7). Both complexes showed similar spectroscopic features to the previously described catalysts in the ¹H NMR and ³¹P NMR spectra, in addition to their UV-vis absorption spectra (Fig. S8, ESI†).

The catalytic FA decomposition reaction was conducted in a Pyrex 5 ϕ NMR tube containing a MeOH solution of the dinuclear iridium catalyst (**1a–1e**, 3 mol%, Fig. 1) at ambient temperature under light irradiation (3 W LED lamp, λ = 395 nm) (eqn (1)). All catalysts were active in the catalytic reaction, and the obtained results are summarized in Table 1, whereby each value is an average of 3 experiments. The reaction was found to proceed under light irradiation, but was sluggish under the corresponding dark conditions, thereby confirming a sharp ON/OFF switching behavior (entries 1 and 2). Catalyst **1d**, bearing the 3,5-dimethylphenyl substituent, was most active in this reaction presenting a contrasting trend to the activity of alkene hydrogenation¹⁹ (entries 1, 3–6). In order to check the wavelength dependence,

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Table 1 Catalytic FA decomposition activities of 1a-1e (X = BF₄)^a

Entry	Catalyst	${\rm H_2}^b/{\rm mL}$	FA conversion ^{<i>c</i>} /%	TON
1	1a	0.23	27	9.3
2	1a , dark	0.01	0	0
3	1b	0.27	32	10.1
4	1c	0.17	21	6.4
5	1d	0.39	47	16.2
6	1e	0.23	33	11.3
7	1d , 365 nm	0.24	29	9.1
8	1d, 425 nm	0.18	22	7.1

^{*a*} Catalytic FA decomposition conducted in MeOH- d_4 in 5 ϕ NMR tubes under a N₂ atmosphere with 395 nm irradiation (3 W LED lamp) unless otherwise noted. ^{*b*} H₂ volume was quantified by TCD-GC. Each value is an average of 3 experiments. ^{*c*} Calcd based on the % of (mol H₂ production)/ (mol starting FA).

the reaction was conducted under different wavelength irradiation (entries 7 and 8, 3 W LED lamp, λ = 365 nm and 425 nm, respectively). Irradiation under 365 nm resulted in the lower activity (entries 7 *vs.* 5) than that obtained under 395 nm due to the decomposition of the catalyst although ε at 365 nm is much higher than that of 395 nm (ε_{365} = 12621 *vs.* ε_{395} = 4803 for 1d).²⁰ Irradiation under 425 nm also gave lower activity (entries 8 *vs.* 5) according to the less absorption coefficient of 1d at 425 nm (ε_{425} = 2702, ε_{395} = 4803).

These reactions were also scaled up in a glass tube (Table 2, 7.8- or 14.2 mL volume) with stirring to give higher turnover numbers (TONs). Although these TONs are lower than those of the reported catalysts taking part in thermal reactions,^{7,21} catalysts **1a–1e** are sufficiently stable to continue generating H_2 even after 24 h. The reaction by **1a** in MeOH over 24 h, the reaction mixture was collected, dried, and the residual solid was analyzed by ¹H NMR spectroscopy to give signals originating from the corresponding monoformate complex (intermediate **A**, *vide infra*). This result confirmed that the stability of the catalyst

Table 2 Solvent effect in the catalytic decomposition of FA by **1d** and **1e** $(X = BF_4)$ in a 7.8 mL Pyrex glass tube^a

Entry	Time/h	Cat.	Solvent	${\rm H_2}^b/{\rm mL}$	FA conv. ^c /%	TON
1	24	1d	MeOH	3.06	12	125
2	24	1d	H_2O	0.89	3	37
3	24	1d	HCOOH	0.72	3	28
4^d	24	1d	CH_3NO_2	6.44	28	280
5^{de}	8	1d	CH_3NO_2	3.75	96	102
6	24	1e	H_2O	3.57	19	184

^{*a*} Catalytic FA (1000 eq. *vs.* catalyst) decomposition conducted in a 7.8 mL Pyrex screw glass tubes under a N_2 atmosphere with 395 nm irradiation and with stirring unless otherwise noted. ^{*b*} H₂ volume was quantified by TCD-GC. Each value is an average of 3 experiments. ^{*c*} Calcd based on the % of (mol H₂ production)/(mol starting FA). ^{*d*} A 14.2 mL Pyrex screw glass tube was used. ^{*e*}100 eq. *vs.* catalyst was used.

is sufficiently high to conduct the reaction iteratively. Upon investigation of the solvent effect, nitromethane exhibited a higher reactivity compared to other solvents such as methanol, H_2O , and neat FA (Table 2). It was also found that the catalysts can promote FA decomposition under the base-free conditions in water or neat FA. Catalyst **1e** can present a higher activity in H_2O than **1d**, likely due to the greater solubility of **1e**.

As mentioned above, it is notable that the sharp ON/OFF switching behavior was observed by simply turning on and off the LED lamp. To confirm the switching behavior of the system, a solution of **1d** in MeOH (0.1 mol% *vs.* FA) was exposed to light, and dark conditions of 12 and 6 h intervals, respectively (Fig. 2). After each interval, the volume of H₂ gas produced was quantified, and the solution was degassed using the freezethaw-pump method to initialize the system. In addition to the ON/OFF switching behavior, it was obvious that the catalyst maintained its activity after each dark period, and with similar reaction rates being observed upon commencing irradiation once again. These results imply that on-demand H₂ gas production could be possible using this system, thereby indicating its potential to contribute to an efficient and energy-saving supply of H₂ for fuel cells.

When the reaction of 1a was followed by ¹H NMR spectroscopy, two intermediate species A^a and B^a (intermediates A and B formed from 1a, respectively, Fig. 3) were observed in the



Fig. 2 Total amount of H_2 gas formed through ON/OFF switching of the light source by a MeOH solution of **1d** containing FA (1000 eq.).



Fig. 3 Time course of the NMR spectral progression in the reaction of ${\rm 1a}$ with FA (30 eq.) in THF- d_8 under irr. at 395 nm.

reaction mixture under irradiation at 395 nm (A:B = 0.17:0.83after 7.0 h). In the reactions catalyzed by the other catalysts, *i.e.*, 1b-1e, only the corresponding intermediate A, but not B, was observed. It should be noted that the relationship between the A to B ratio and the catalytic activity is not clear at this moment. Furthermore, examination of the ESI-MS spectrum of the reaction mixture after the photocatalysis showed signals corresponding to the monoformate $(m/z \ 1791)$ and bisformate $(m/z \ 1835)$ complexes together with the corresponding mono-oxidized species (Fig. S9, ESI[†]). Intermediate species A^a and B^a were independently synthesized in a quantitative reaction between FA and 1a (eqn (2) and (3)).²² Indeed, the isolated species presented identical spectroscopic features to those observed in the NMR spectra during the reaction. However, the ¹³C NMR spectrum of A^a displayed broad signals even at -30 °C, and so the corresponding formate complex with ligand c (A^c) was measured (Fig. S10–S13, ESI^{\dagger}), and this presented a characteristic carbon signal corresponding to the μ-κ,κ'-OCHO formate ligand at 175 ppm. The NMR data of A^{c} are presented in the ESI,† (Fig. S10-S13).

A single crystal of **B**^b suitable for analysis by X-ray diffraction study was then obtained from toluene at -30 °C, and its molecular structure was determined. The ORTEP diagram of the cationic unit of **B**^b is shown in Fig. S14 (ESI†), where a single BF₄ anion and two toluene molecules per Ir₂ unit were present. This complex possessed μ - κ , κ' -OCHO formate ligands between the two iridium centers, and the Ir–Ir bond distance was lengthened from 2.5174(7) Å in **1b** to 3.0733(7) Å in **B**^b. This lengthening of the Ir–Ir bond may affect the photophysical properties of the complex as a photocatalyst.

The independently synthesized A^a (eqn (2) and (3)) was then employed as a catalyst under the conditions outlined in Table 1, and the reaction proceeded similarly under irradiated conditions, although the reactivity was about 1/3 (0.07 mL (A^a) vs. 0.23 mL (1a)) of that of the parent complex **1a**. Although the reason for this difference is currently unclear, it is possible that the lower absorption coefficient of $\mathbf{A}^{\mathbf{a}}$ to **1a** at 395 nm may affect the catalyst reactivity (Fig. S15, ESI[†]). More specifically, when comparing the UV-vis absorption spectra of **1a**, $\mathbf{A}^{\mathbf{a}}$, and $\mathbf{B}^{\mathbf{a}}$, the absorption coefficients of the intermediates at 395 nm were found to be less than 1/2 of that of the parent complex (*i.e.*, ε_{395} M⁻¹ cm⁻¹ = 1884 ($\mathbf{A}^{\mathbf{a}}$), 1845 ($\mathbf{B}^{\mathbf{a}}$), 4328 (**1a**)).



When the isolated intermediate B^a was independently exposed to irradiation, slight conversion to A^a was observed under irradiation (18% conversion after 6 h of irradiation). These results indicate the presence of an equilibrium between A and B, which slightly shifts toward A upon irradiation. Based on the above observations, a plausible reaction mechanism was proposed, as depicted in Scheme 1. Starting from complex 1, reaction with 1 eq. of FA gives the monoformate complex A with H_2 gas discharge (steps (i) and (ii)).^{23–25} A second reaction with FA gives the bisformate complex B as the resting state. CO2 elimination from monoformate complex A via C regenerates the starting catalyst to complete the catalytic cycle (steps (iii) and (iv)). However, whether the CO₂ elimination process takes place via a dinuclear process or through β-H elimination on the single Ir center, remains unclear at this moment.^{26–28} Since complex 1 and intermediate A did not react with FA without irradiation, it is apparent that direct protonation



Scheme 1 Plausible reaction mechanism for the catalytic decomposition of FA. Steps requiring light irradiation are indicated in red.

of the hydride ligand to generate H2 does not occur in this system.^{29,30} Most importantly, light is required to drive the processes of (i) and (iii), (iv).

In summary, we herein demonstrated the ON/OFF switching behavior of light-active dinuclear iridium hydride complexes in the catalytic decomposition of formic acid (FA), resulting in on-demand H₂ production using light as an external stimulus. Among the various catalysts examined, 1d bearing a 3,5-dimethylphenyl substituent on the phosphorous atom of the BINAP ligand exhibited the highest catalytic activity under the base-free conditions employed herein. In addition, the catalysts were stable enough to conduct the reaction without deterioration even after continuous switching cycles for 54 h. The highest activity was observed in nitromethane solution, and the catalytic process also proceeded in water or a neat FA solution. Furthermore, careful analysis allowed observation of the mono- and bisformate intermediates, and these were independently synthesized from the quantitative reactions. The isolated intermediates exhibited catalytic activity under irradiated conditions, thereby confirming their contribution to the catalytic cycle. These results are expected to contribute to the use of FA as a liquid hydrogen carrier for energy storage applications.

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Conflicts of interest

There are no conflicts to declare.

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