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Supporting Information

Anchoring Ir(III) Complex on Macroscopic Polymer Substrate as Highly Durable Photosensitizer for Photocatalytic Hydrogen Evolution†

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1. Materials

$IrCl_3 \cdot xH_2O$ (≥98.0%), 2-phenylpyridine (ppy, ≥98.0%), 2,2'-bipyridyl (bpy, ≥98.0%), 4,4'-diamino-2,2'-bipyridyl (dabpy, ≥98.0%), potassium platinochloride (K_2PtCl_4, ≥99.9%), potassium hydrogen phthalate (KHP, ≥99.8%) and phenolphthalein (A.R.) were purchased from Aladdin Industrial Corporation. Acetone (A.R.), C_2H_5OH (A.R.), petroleum ether (A.R.), ethyl acetate (A.R.), dichloromethane (A.R.), tetrahydrofuran (THF) (A.R.), dimethylformamide (DMF) (A.R.), HNO_3 (65-68%, A.R.) triethylamine (TEA) (A.R.), Acetic anhydride (A.R.), maleic anhydride (MAH) (A.R.) and NaOH (A.R.) were purchased from Beijing Chemical Works. $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene, ≥98.0%), 4-amine-2-phenylpyridine (appy, ≥98.0%) and 1,4-dioxane (99.7%, Extra Dry) was purchased from Energy Chemical Corporation. Deionized water was used throughout all experiments.

The substrates (non-woven fabric, NWF) used in this work were purchased from commercial sources, which were made of polypropylene (PP) with a thickness of 0.42 mm and a mass density of 120 g m^{-2}.

All substrates were washed with acetone and dried at 60°C for 3 h in a vacuum oven before use.

2. Experimental - general information

Structural characterization

Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. Reactions were monitored using thin layer chromatography (TLC). Commercial TLC plates were used and the spots were visualised under UV light at 254 and 365 nm. ^1H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a Varian 400 MHz spectrometer with TMS as internal standard. The chemical shifts (δ) are given in parts per million relatived to internal standard TMS (0 ppm). The molecular weight of sample was measured by matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Elemental analysis was tested by employing Flash EA1112 analyser. The fourier transformed infrared (FTIR, Bruker Vertex 70 FTIR) was employed to identify the structural information of samples. X-ray photoelectron spectroscopy (XPS) analysis used a ESCALAB 250 (Thermo Fisher Scientific) instrument. The morphology of the samples was characterized using field emission scanning electron microscopy (ESEM, XL-30) system. Energy-dispersive spectroscopy (EDS, Oxford X-MaxN 150), combining SEM with EDS capability, was used to identify the elemental composition of samples. The Ir content was measured by inductively coupled plasma massspectrometry (ICP-MS, ThermoScientific X-seriesII, USA). A Shimadzu UV-2600 spectrophotometer was employed to record the UV-visible diffuse reflectance spectra of samples. For complex **2**, $BaSO_4$ was used for a reference, and for 1@NWF-g-MAH, NWF-g-MAH was used for a reference. The emission spectra, excited-state lifetimes (τ) and photoluminescence quantum yields (φ_{PL}) were measured by Edinburgh FLS-920 spectrofluorimeter in the air at room temperature.

Visible light-driven hydrogen production

The photocatalytic hydrogen evolution tests were measured in a 250 mL quartz reaction vessel, which was connected to the closed gas circulation and evacuation system (CEL-SPH2N, CEAULIGHT). The reactor was charged with 1@NWF-g-MAH (5 pieces, d = 4 cm), complex **2** or $[Ir(appy)_2(bpy)][PF_6]$ as PS, K_2PtCl_4 as catalyst (3 μmol) and trimethylamine (TEA) as sacrificial agent (20 mL) in the mixture of DMF (60 mL) and H_2O (20 mL). The solution was degassed completely and irradiated utilizing a 300 W Xe lamp (CEL-HXF300, AULTT) with a 420 nm cut-off filter. The temperature of photocatalytic solution was maintained at 279 K by a flow of cooling water. The appreciable gases were detected by on line gas chromatography (GC-7900, CEAULIGHT) with nitrogen as the carrier gas.

3. Synthesis and characterization

Synthesis of $[Ir(ppy)_2(dabpy)][PF_6]$ (complex 1)

A suspension of cyclometalated chloride-bridged dimer $[Ir(ppy)_2Cl_2]_2$ (0.898 g, 0.838 mmol) and $AgPF_6$ (0.464 g, 1.84 mmol) in MeOH (70 mL) was stirred steadily for 2 h at room temperature. The precipitated AgCl was removed by filtration over Celite. Concentration of the yellow filtrate under reduced pressure to gain $[Ir(ppy)_2(MeOH)_2][PF_6]$ as a yellow solid. (Yield: 95%). Subsequently, a suspension of $[Ir(ppy)_2(MeOH)_2][PF_6]$ (0.124 g, 0.174 mmol) and 4,4'-diamino-2,2'-bipyridyl (dabpy, 32.7 mg, 0.176 mmol) in MeOH (15 mL) was sonicated. An excess of solid NH_4PF_6 (10 eq) was added to the solution and reacted for one hour and the mixture was filtrated. Then the solvent was removed under reduced pressure. The crude product was purified by column chromatography with petroleum ether, ethyl acetate and dichloromethane as eluent to obtain yellow solid. Yield: 75%. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 8.21 (d, J = 8.2 Hz, 1H), 7.91 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 5.3 Hz, 1H), 7.33 (s, 1H), 7.23 (t, J = 6.6 Hz, 1H), 7.18 (d, J = 6.3 Hz, 1H), 7.04 (s, 2H), 6.94 (t, J = 7.0 Hz, 1H), 6.82 (t, J = 7.9 Hz, 1H), 6.58 (dd, J = 6.4, 2.2 Hz, 1H), 6.18 (d, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.81 (s), 156.43 (s), 156.04 (s), 153.02 (s), 149.06 (s), 148.85 (s), 144.49 (s), 138.52 (s), 131.69 (s), 130.36 (s), 125.27 (s), 123.96 (s), 121.90 (s), 120.08 (s), 111.98 (s), 107.63 (s). MS: m/z = 687.2 (M^+). Anal. calcd for $C_{32}H_{26}F_6IrN_6P$: C 46.21, H 3.15, N 10.10; found: C 46.33, H 3.09, N 10.14.

Synthesis of $[Ir(appy)_2(bpy)][PF_6]$

According to the reported literature,[1] the $[Ir(appy)_2Cl]_2$ dimer was synthesized by heating $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) and 4-amine-2-phenylpyridine (appy) in 2-ethoxyethanol. The synthesis and purification of $[Ir(appy)_2(bpy)][PF_6]$ was the same as complex **1** except that $[Ir(ppy)_2Cl]_2$ was replaced with $[Ir(appy)_2Cl]_2$, and dabpy was replaced with 2,2'-bipyridyl (bpy).

A suspension of $[Ir(appy)_2Cl_2]_2$ (1.1153 g, 0.838 mmol) and $AgPF_6$ (0.464 g, 1.84 mmol) in MeOH (70 mL) was stirred steadily for 2 h at room temperature. The precipitated AgCl was removed by filtration over Celite. Concentration of the yellow filtrate under reduced pressure to gain $[Ir(appy)_2(MeOH)_2][PF_6]$ as a yellow solid. (Yield:80%). Subsequently, a suspension of $[Ir(appy)_2(MeOH)_2][PF_6]$ (0.128 g, 0.174 mmol) and bpy (27.5 mg, 0.176 mmol) in MeOH (15 mL) was sonicated. An excess of solid NH_4PF_6 (10 eq) was added to the solution and reacted for one hour and the mixture was filtrated. Then the solvent was removed under reduced pressure. The crude product was purified by column chromatography with petroleum ether, ethyl acetate and dichloromethane as eluent to obtain orange solid. Yield: 46%. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 8.82 (d, J = 8.2 Hz, 1H), 8.21 (td, J = 8.0, 1.5 Hz, 1H), 7.88 (d, J = 5.4 Hz, 1H), 7.68-7.63 (m, 1H), 7.50 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 2.4 Hz, 1H), 6.97-6.81 (m, 3H), 6.62 (s, 2H), 6.36 (d, J = 6.7 Hz, 1H), 6.25 (dd, J = 6.6, 2.5 Hz, 1H). MS: m/z = 687.2 (M^+). Anal. calcd for $C_{32}H_{26}F_6IrN_6P$: C 46.21, H 3.15, N 10.10; found: C 46.16, H 3.22, N

10.17.

Preparation of NWF-g-MAH by Co-irradiation grafting

PP NWF were washed in acetone and dried at 60 °C in a vacuum oven prior to packing them vertically into a PE bag. The saturated MAH solution (approximately 1.5 g mL^{-1} in THF, 15.3 mol L^{-1}) was added to the bag with the PP film to completely immerse it. After deaeration of the MAH solution by bubbling nitrogen gas for 4-7 min, the PE bag was sealed, thus forming a custom-made reactor accommodating any size substrate depending on the size of the bag. Subsequently, the “reactor”, i.e. PE bag with PP and MAH solution, was irradiated at room temperature with a Co-60 gamma source at a rate of 60 Gy per min to the total dose of 10 kGy. The MAH-grafted PP NWF was thus obtained. Finally, the obtained MAH-grafted PP was washed in THF by sonication to remove the residual MAH and dried at 60 °C for 12 h.

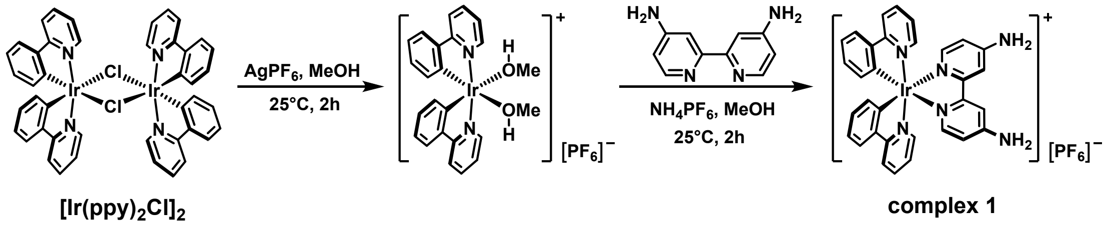
Synthesis of 1@NWF-g-MAH

The NWF-g-MAH (4 pieces, 8 × 4 cm) and acetic anhydride (1 mL) were added to dry 1,4-dioxane (200 mL). Subsequently, the reaction was refluxed and stirred for 24 h. The reaction system was connected with a drying tube (containing $CaCl_2$). After reaction, the pretreated NWF-g-MAH were taken out and dried at 60 °C for 12 h.

Subsequently, a solution of complex **1** (0.25 g) in dry 1,4-dioxane (200 mL) was stirred and refluxed with $CaCl_2$ drying tube. After 2 h, complex **1** (0.25 g) and pretreated NWF-g-MAH were added to the reaction system. Then, at 5 h, 8 h and 12 h, complex **1** (0.25g) was added to the reaction system, respectively. After reacted for 24 h, 1@NWF-g-MAH was obtained, which was subsequently rinsed by CH_2Cl_2, acetone, methanol and ethanol, and dried at 60 °C for 12 h.

Synthesis of complex 2

A solution of complex **1**(0.121 g. 0.145 mmol) and MAH (0.071 g, 0.726 mmol) in dry 1,4-dioxane (100 mL) was refluxed and stirred with $CaCl_2$ drying tube for 24 h. After reaction, the solvent was removed under reduced pressure. Then, the obtained solids were dissolved by appropriate acetone and further precipitated by the addition of water. The mixture was filtrated and the obtained orange solids were dried at 60 °C for 12 h.



Scheme S1 The synthetic routes of complex **1**.

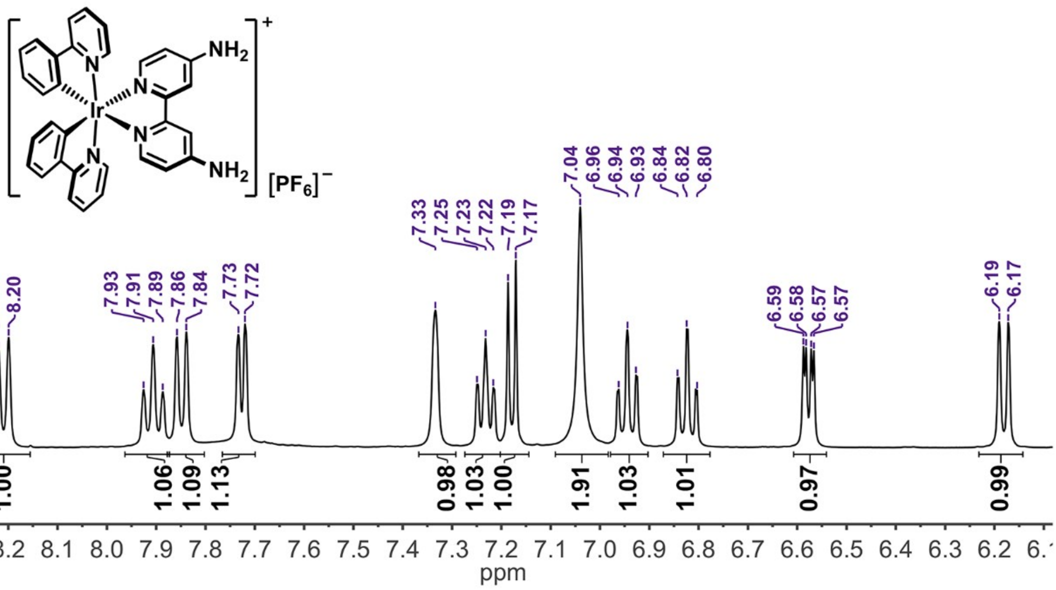


Fig. S1 ^{1}H NMR spectrum of complex **1** in in DMSO-d_6.

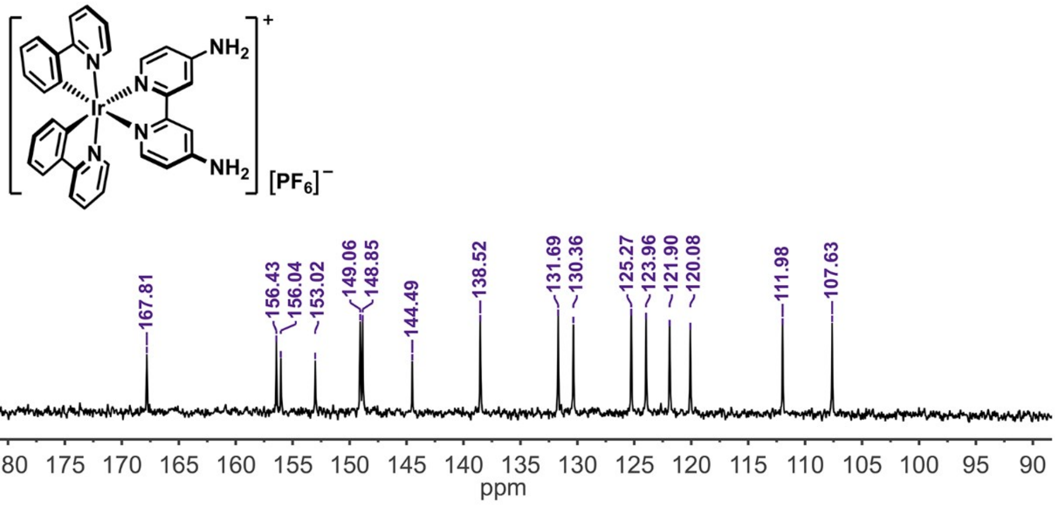


Fig. S2 ^{13}C NMR spectrum of complex **1** in DMSO-d_6.

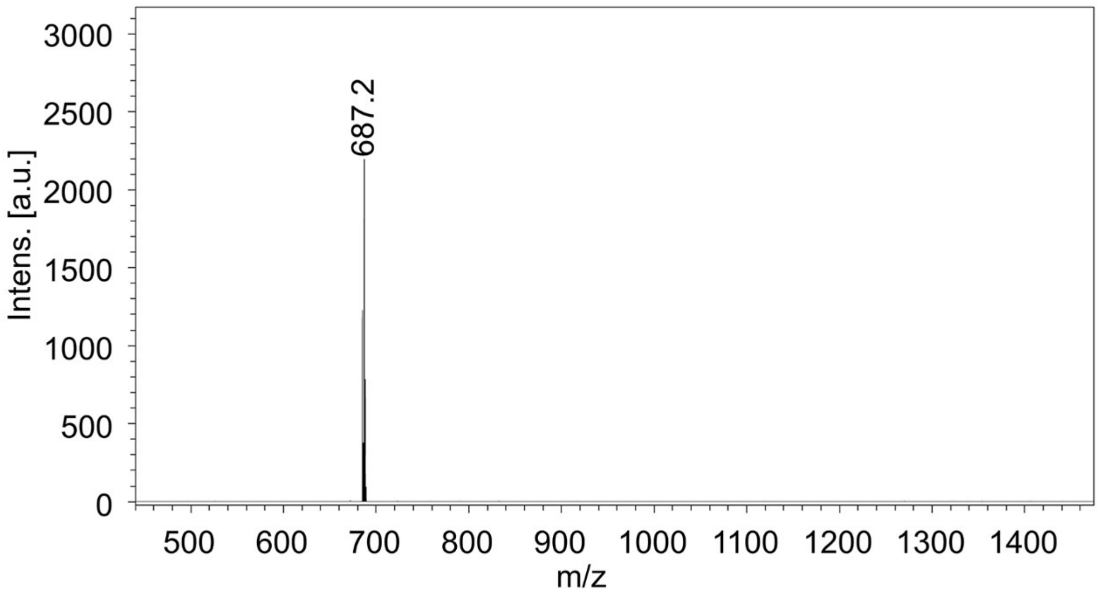


Fig. S3 MALDI-TOF-MS of complex **1**.

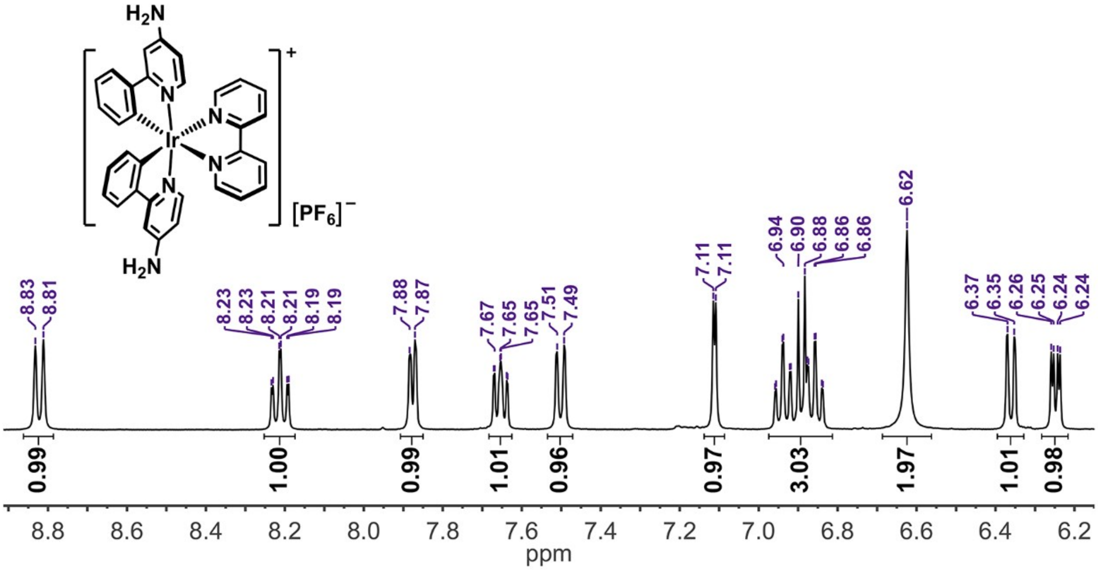


Fig. S4 ^{1}H NMR spectrum of [Ir(appy)$_2$(bpy)][PF$_6$] in DMSO-$d_{6.}$

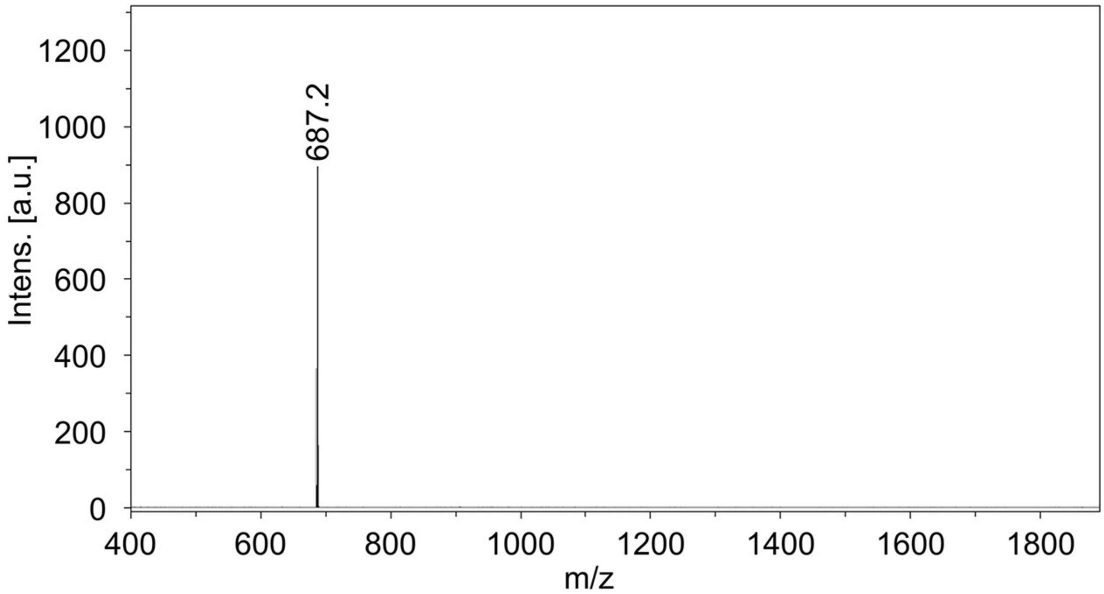


Fig. S5 MALDI-TOF-MS of [Ir(appy)$_2$(bpy)][PF$_6$].

4. Measurement of surface carboxyl density

Quantitative measurement of the amount of carboxyl groups on the irradiation-grafted surfaces was conducted using NaOH-KHP titration according to the following process:

(i) Solution preparation

Preparation of 1 mM standard KHP solution: A total of 0.2042 g KHP was weighed after heated at 110 °C for 2 h to remove water. Then, the KHP was transferred to a 1 L volumetric flask, deionized water was added, the flask was shaken, magnet was added, and the solution was stirred overnight at room temperature before use.

Preparation of *ca.* 1 mM NaOH solution: Approximately 0.040 g NaOH was weighed and transferred to a bottle, approximately 1 L deionized water was added, and the bottle was shaken. This solution was used immediately.

Preparation indicator solution: A total of 1.00 g phenolphthalein was weighed and transferred to a brown bottle, 100 mL ethanol was added, and the bottle was shaken well.

(ii) Sample processing

A total of 100 mL of NaOH solution (*ca.* 1 mM) was added to a vial containing irradiation grafted substrate (~ 50 × 150 mm). The vial was then sealed and heated at 80 °C for 2 h. A reference sample was also prepared.

(iii) Titration process

After cooling the vial, 20 mL of solution was removed from both the test sample and the reference sample, and 1 drop of indicator solution was added. The above solution was titrated using standard KHP solution (1 mM) until the pink color disappeared.

The titration of each sample was repeated 3 times, and the titration volume of standard KHP solution used for each sample was averaged from the 3 tests.

(iv) Estimation of surface density of carboxyl groups

The surface density of carboxyl groups (ρ_{-COOH}, nmol cm^{-2}) was estimated by the following equation:

$$\rho_{-COOH} = \frac{C_{KHP} \times (V_{ref} - V_t)}{S_{substrate}} \times 5 \times 1000 \qquad (1)$$

where C_{KHP} (mmol/L) is the concentration of KHP solution, as prepared; V_{ref} (mL) is the titration volume of standard KHP solution for the reference sample; V_t (mL) is the titration volume of standard KHP solution for the test sample; $S_{substrate}$ (cm^2) is the substrate surface area (double-sided for films); *5* is the ratio of the total volume of NaOH solution (100 mL) to the volume of titrated NaOH solution (20 mL); and *1000* is the conversion factor from μmol to nmol. The amount of carboxyl groups on the irradiation-grafted surfaces was 29.79 nmol cm^{-2}.

5. Measurement of Ir content on NWF-g-MAH

The Ir content on NWF-g-MAH was measured by ICP-MS through the following procedures:

(i) calibration curve preparation

Complex **2** powder (0.01 g) was mixed with HNO_3 (200 mL) and heated at 80 °C for 2.5 h for degradation completely, which was subsequently rinsed repeatedly with deionized water. All the liquid was transferred to a 1000 mL flask, and mixing well, named as mother liquor. Subsequently, 1 mL, 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, 50 mL, 75 mL mother liquor were transferred to 100 mL flask, and using deionized water to constant volume, respectively, Then, 3 mL solution was taken out for measuring the Ir ion concentration by ICP-MS. The concentration of the iridium ions increases as the weight of 2 powder is increased. The calibration curve of the 2 weight *versus* iridium concentration was thus obtained (Table S1, Figure S6, plot R-square = 0.998).

(ii) Calculation of Ir content on NWF

1@NWF-g-MAH was treated using the same process as above. 1@NWF-g-MAH (one piece, d = 4 cm) was mixed with HNO_3 (20 mL) and heated at 80 °C for 2.5 h for degradation completely. Subsequently, 1@NWF-g-MAH was rinsed repeatedly with deionized water. All the liquid was transferred to a 100 mL flask, and mixing well. The concentration of iridium was obtained after the test, and was further calculated the weight through equation (2). The Ir content on NWF-g-MAH can thus be calculated using equation (3), in which the $S_{substrate}$ is the surface area of the substrate (double sided for NWF-g-MAH).

$$C_{Ir}(\mu g/L\ ,ppb) =- 6.72438 + 0.94354 \times M_2(\mu g) \qquad (2)$$

$$Ir\ content\ (\mu g/cm^2) = M_2(\mu g)/\ S_{substrate} \qquad (3)$$

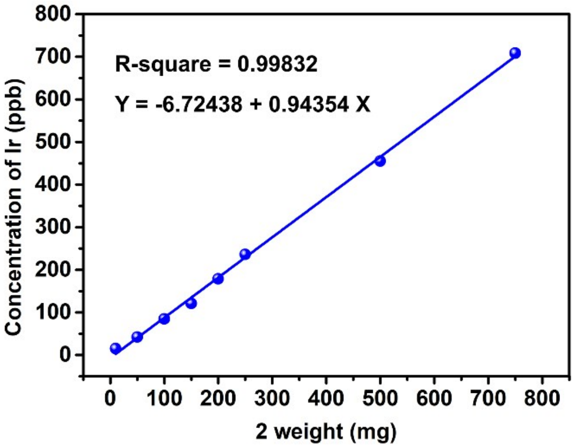


Fig. S6 Calibration curve of complex **2** weight *versus* Ir concentration.

Table S1 Complex **2** weight and the Ir concentration for the calibration curve.

Sample	2 weight (μg)	Ir concentration (μg/L, ppb)
1 mL	10	15.32
5 mL	50	42.33
10 mL	100	84.72
15 mL	150	121.16
20 mL	200	178.83
25 mL	250	236.33
50 mL	500	455.40
75 mL	750	708.64

6. Sample characterization

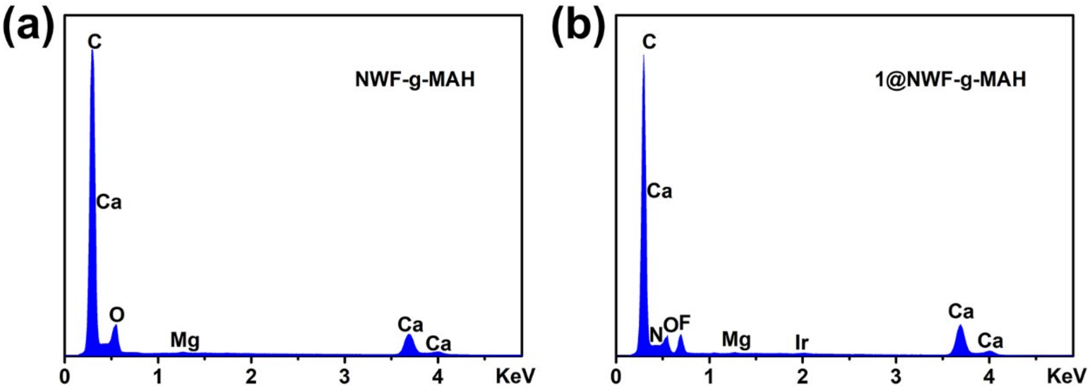


Fig. S7 EDS spectrum of NWF-g-MAH (a) and 1@NWF-g-MAH (b).

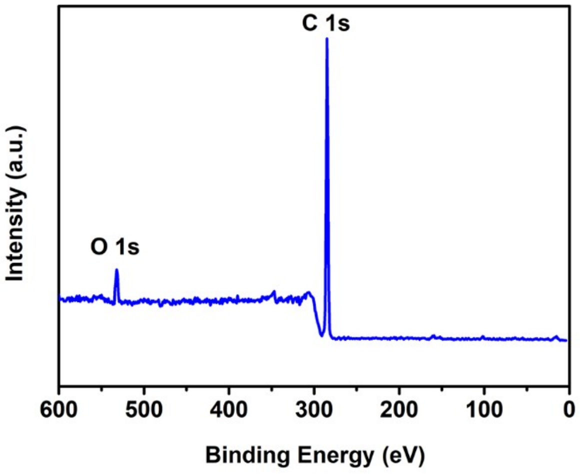


Fig. S8 XPS spectrum of NWF-g-MAH.

Table S2 Elemental composition of NWF, NWF-g-MAH and 1@NWF-g-MAH surfaces, as determined from XPS survey spectra.

	XPS Contents (at.%)			
	C 1s	N 1s	O 1s	Ir 4f7
NWF	97.16	-	2.84	-
NWF-g-MAH	93.76	-	6.24	-
1@NWF-g-MAH	96.12	0.93	2.85	0.09

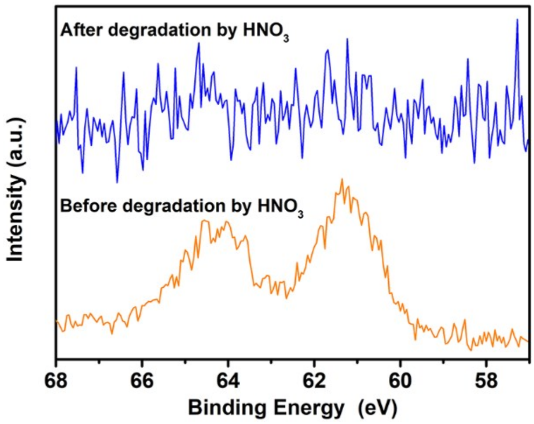


Fig. S9 The Ir 4f XPS spectra of 1@NWF-g-MAH (orange line) and 1@NWF-g-MAH after degradation by HNO_3 (blue line).

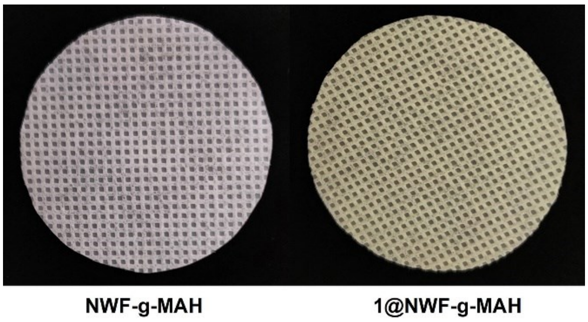


Fig. S10 Images of NWF-g-MAH and 1@NWF-g-MAH in daylight.

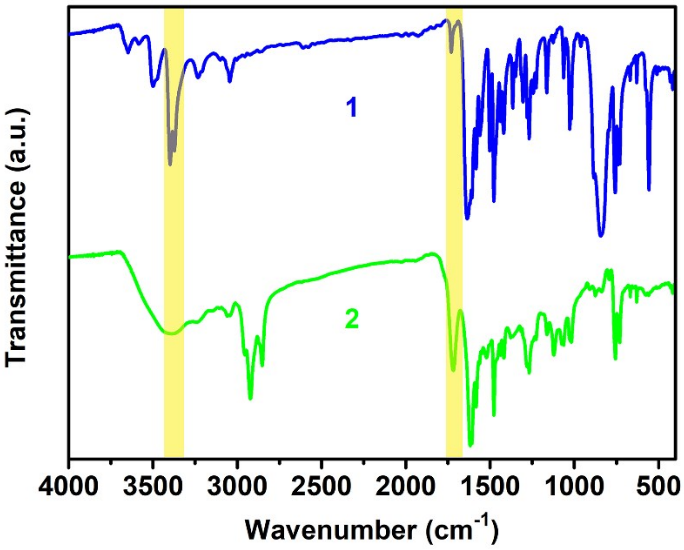


Fig. S11 IR spectrum of complex **1** and complex **2**.

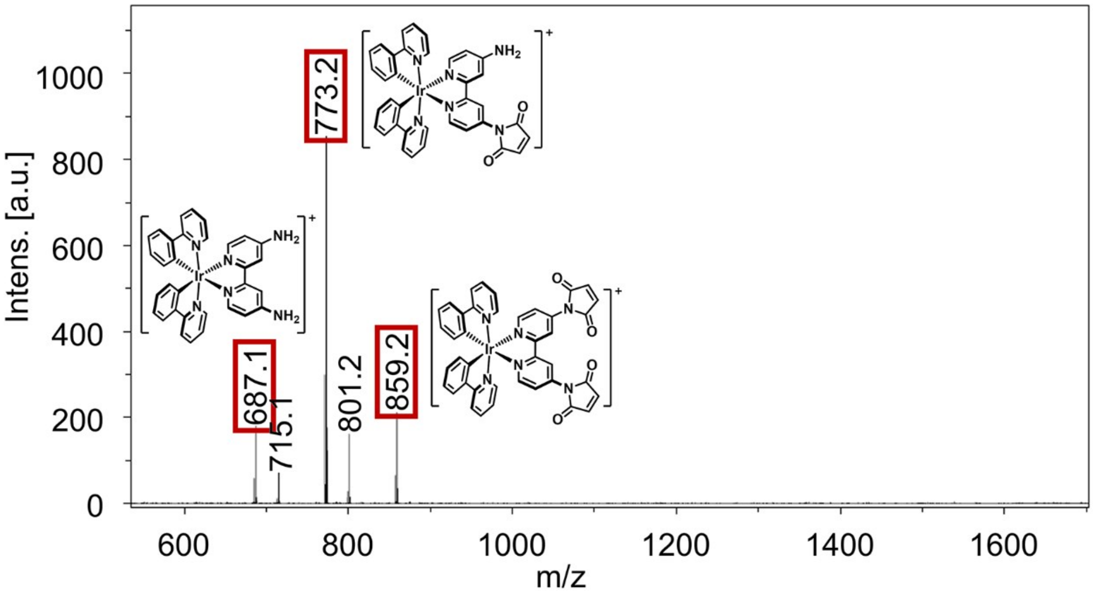


Fig. S12 MALDI-TOF-MS of complex **2**.

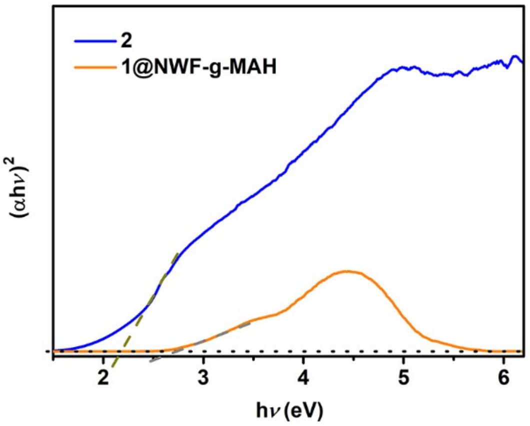


Fig. S13 Calculated energy gaps of complex **2** and 1@NWF-g-MAH by the plot of $(\alpha h\nu)^2$ *vs* $h\nu$.

The photocatalytic hydrogen evolution test was employed to confirm the position of -NH_2 on Ir(III) complex (on cyclometalated ligands or ancillary ligands). The experimental results show that under the same photocatalytic conditions, the hydrogen evolution activity of [Ir(ppy)$_2$(dabpy)][PF_6] (complex **1**) is much higher than that of [Ir(appy)$_2$(bpy)][PF_6]. Therefore, we chose to anchor complex **1** on the macroscopic polymer substrate to further explore its stability.

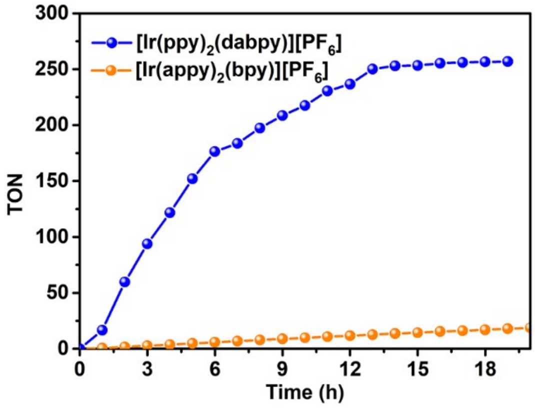


Fig. S14 Photocatalytic hydrogen evolution of [Ir(ppy)$_2$(dabpy)][PF_6] and [Ir(appy)$_2$(bpy)][PF_6]. Condition: Ir(III) photosensitizer (5 μmol), K_2PtCl_4 (3 μmol), TEA (20 mL), H_2O (20 mL) and DMF (60 mL). TON = 2n(H_2)/n(PS).

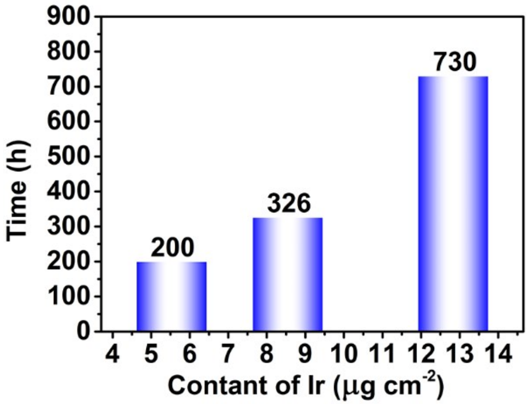


Fig. S15 The relationship between the Ir content on 1@NWF-g-MAH and the H_2 evolution duration.

Table S3. Photophysical and photocatalytic properties of 1@NWF-g-MAH, complex **2**, complex **1** and [Ir(appy)$_2$(bpy)][PF_6].

	E_g ^{a} (eV)	τ ^{b} (ns)	φ_{PL} ^{b} (%)	H_2 evolution ^{c} (μmol g^{-1})	H_2 evolution rate ^{c} (μmol g^{-1} h^{-1})
1@NWF-g-MAH	2.6	723	3.2	39129.2	53.6 (730 h)
complex **2**	2.2	232	8.2	71393.5	3966.3 (18 h)
complex **1**	2.5	225	10.4	154365.7	8124.5 (19 h)

[Ir(appy)$_2$(bpy)][PF$_6$]	2.3	166	39.6	5781.2	289.1 (20 h)

[a] Measured in solid (complex **2**, complex **1** and Ir(appy)$_2$(bpy)) or film (1@NWF-g-MAH).

[b] Calculated from the absorption edge (UV-vis diffuse reflectance spectra).

[c] Calculated from photocatalytic hydrogen evolution.

Table S4 A comparison of H_2 evolution time between the as-obtained 1@NWF-g-MAH in this study and other photocatalytic systems in literatures.

Photosensitizer	H_2 evolution (h)	Ref.
[Ir(phbpy)$_2$]PF$_6$	30	2
[Ir(F-mppy)$_2$(mVbpy)]PF$_6$	48	3
[Ir(tolpy)$_2$(dethqpy)]PF$_6$	75	4
[Ir(Fmpyb)$_2$(bpy*)]PF$_6$	15	5
IrTPS	144	6
[Ir(thpy)$_2$(bt)]	72	7
D_{Si}[Ir]	168	8
Ir(tfdpyb)Cl]$_2$(BiBzIm)	72	9
4-FlCHO-Ir	5	10
IrRu(1)	72	11
1B@Pt-TiO$_2$	8	12
Ir(B-ppy)$_2$(dppz)]PF$_6$	20	13
Ir-4	18	14
TBPyZnP-Ir	40	15
[Ir(NBI)$_2$(phen)]PF$_6$	90	16
[Ir(F$_2$ppy)$_2$(dCF$_3$bpy)]PF$_6$	96	17
1@NWF-g-MAH	**730**	**Our work**

Table S5 The Ir content of samples.

	1# [a]	2# [b]	3# [c]	4# [d]
Ir (ppb)	297.29	237.49	225.60	125.51
Ir (μg)	322.21	258.83	246.23	140.15

[a] Ir content on 1@NWF-g-MAH (one piece, d = 4 cm) before irradiation.
[b] Ir content in the solution (100 mL) after 730 h irradiation.
[c] Ir content on 1@NWF-g-MAH (one piece, d = 4 cm) after 730 h irradiation.
[d] Ir content in the solution (100 mL) after 730 h immersion in natural light.

7. References

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