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Immobilization of Cyclometalated Iridium Complex onto Multiwalled Carbon Nanotubes for Dehydrogenation of Indolines in Aqueous Solution

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S *Supporting Information*

ABSTRACT: Increasing concerns about the potentially negative impacts of chemical production on sustainable development of the overall environment have spurred numerous attempts to seek greener reaction mediums, recyclable catalysts, and high-efficiency procedures. Herein, a cyclometalated Ir complex with a pyrene tag was successfully immobilized onto multiwalled carbon nanotubes via $\pi-\pi$ stacking interactions, through which an easily reusable Ir catalyst was constructed. The immobilization process was effectively monitored by using a fluorescence spectroscopy technique, and the immobilized Ir catalyst was well characterized and evaluated. It is found that the immobilized Ir catalyst exerts activity comparable to that of the corresponding homogeneous Ir catalyst for the dehydrogenation of indolines in an aqueous solution. More importantly, the catalyst could be recycled seven times without obvious loss of the Ir-active center and noticeable decrease in the yield of the targeted product. Additionally, the observed slight deactivation of the catalyst during the recycle is also discussed.
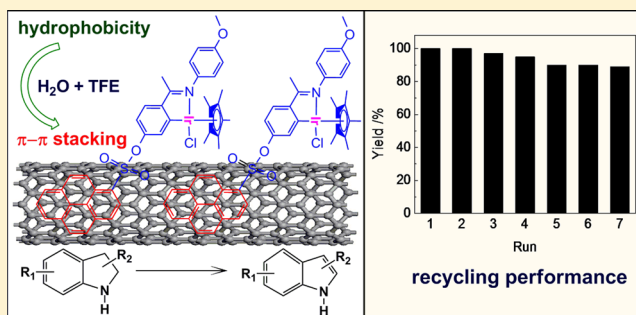
1. INTRODUCTION

Homogeneous catalysis generally has the advantages of high activity, good selectivity, and broad substrates.[1−4] However, the difficult recycling of the homogeneous catalysts hampers their applications to a large extent. It is found that immobilization may contribute greatly to the effective recycling of the homogeneous catalysts. Consequently, great efforts have been made to construct immobilized catalyst systems, in which homogeneous catalysts (mostly metal complexes) were explored to be anchored on proper supports.[5]

There are mainly three approaches to immobilize the metal complexes on the supports: (1) the formation of covalent bonds or ion pairing[6] between the support and the complex, (2) absorption or other nonbonding interaction[7] with the support, and (3) encapsulation. Various supports have been used to immobilize the metal complexes, such as polymers,[8,9] Fe₃O₄ nanoparticles,[10] alumina,[11] silicates,[12−14] zeolites,[15,16] and carbon materials.[17−21] Compared with the traditional (covalent) bonding immobilization, the noncovalent method is more facile and convenient in catalyst preparation. More importantly, the noncovalent immobilization is expected to be less likely to cause the decrease in catalyst activity as compared with that in the homogeneous system. Such immobilization

methods have been specially valued in recent years,[17−26] in which the immobilizations via $\pi-\pi$ stacking (by using graphene, carbon nanotubes (CNTs), nanoparticles, or polymers as supports) have been developed. Owing to the unique mechanical, structural, electronic, and thermal properties, CNTs have been demonstrated as a promising catalyst support. The insolubility in most solvents of CNTs ensures the facile separation of the immobilization catalyst. Moreover, it is believed that the high surface area of CNTs may provide an extended range of anchoring sites for $\pi-\pi$ stacking interactions.[27]

Cyclometalated Ir(III) complexes,[28] or iridicycles, have been widely used as versatile, efficient, and selective homogeneous catalysts in reactions such as reductive amination,[29] transfer hydrogenation of imines,[30−33] hydrogenation of N-heterocycles,[34] construction of C=C double bonds,[35] dehydrogenation of N-heterocycles,[36] and transfer hydrogenation of carbonyl groups.[37,38] Regarding the prominent blemish or

weakness in the use of the expensive iridicycles, it may be an inability of the effective recycling of such catalysts, which is similar to that in other homogeneous catalysis systems. Additionally, the typical iridicycle catalysis reported was most performed in organic solvents. Therefore, it is highly expected to find a promising way to immobilize the iridicycle, facilitating the easy recycle of the catalyst, and to seek a green medium to construct a sustainable environmentally benign catalysis system.

In the present work, a novel iridicycle was intentionally prepared (iridicycle **1**) and further modified with a pyrene end (iridicycle **2**, as shown in Scheme 1). Multiwalled carbon

Scheme 1. Synthesis of the Iridicycle 2
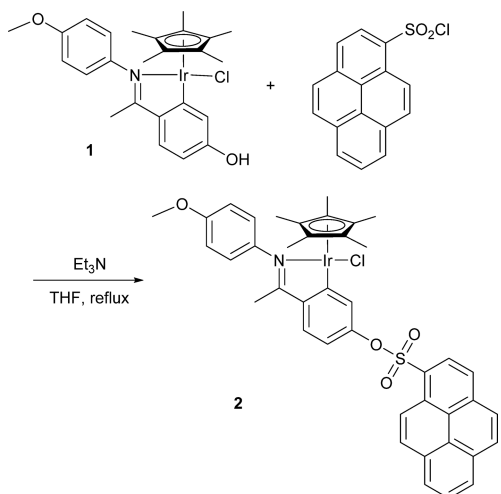
nanotubes (MWCNTs) were selected as the support. The pyrene-tagged cyclometalated iridium (Ir) complex, namely the iridicycle **2**, was immobilized onto the MWCNTs via $\pi-\pi$ stacking interactions, through which an easily reusable Ir catalyst was successfully constructed. The efficiency of the immobilized Ir catalyst was evaluated via the catalytic dehydrogenation (CDH) of indolines in an aqueous solution using H_2O/trifluoroethanol (TFE) (2:1 in volume ratio) as the reaction medium. Interestingly, the immobilization process as well as the loss of iridicycle 2 from immobilized catalyst was effectively tracked and monitored by using fluorescence spectroscopy techniques. This work is expected to distinctly promote the application of homogeneous catalysis.

2. EXPERIMENTAL SECTION

2.1. Chemical Synthesis and Catalyst Preparation. Unless otherwise specified, all reagents were obtained as analytical purity and used without further purification. Toluene was dried over sodium and distilled prior to use. MWCNTs were obtained from Time Nano (short MWCNT, OD < 8 nm, 95+% C purity).

2.1.1. Synthesis of Indolines. 1-Methylindoline, 3-methyl-indoline, 5-methylindoline, 6-methylindoline, 1-methoxy-indo-line, 5-bromo-indoline, and 6-chloro-indoline were synthesized according to literature[39] procedures: To a stirred solution of indole (5 mmol) in acetic acid (AcOH, 20 mL), NaBH₃CN (1.6 mg, 25 mmol) was added in portions at 10−15 °C. After addition, the reaction mixture was further stirred for 4 h at 20 °C. The complex was decomposed by adding water. Most of AcOH was removed via vacuum. The residue was treated with NaOH aqueous solution and then extracted with ether (Et₂O).

The organic phase was dried by Na₂SO₄. After the solvent was removed, the residual raw product was purified by chromatography to obtain the desired indolines (yield, 72−99%).

1-Benzyl-indoline was synthesized according to literature[40] procedures: Indoline (0.6 g, 5 mmol) was added to sodium bicarbonate (525.0 mg, 6.25 mmol) in 3 mL H₂O and the mixture was stirred at 90 °C. Benzyl chloride (630.0 mg, 5 mmol) was added dropwise for 1.5 h, and then the mixture was stirred for an additional 3.5 h. After the mixture was cooled, the organic phase was collected, and the aqueous layer was extracted with Et₂O (20 mL × 3). Then, the organic phase was combined, dried over calcium chloride, and evaporated to give the raw product. Finally, the raw product was purified by chromatography to obtain N-benzyl-indoline as colorless oil (812 mg, yield, 78%).

1-Ethylindoline was synthesized according to literature[40] procedures: Indoline (0.6 g, 5 mmol) was added to sodium bicarbonate (525.0 mg, 6.25 mmol) in 3 mL of H₂O. The mixture was stirred at 89.5 °C. Bromoethane (544.9 mg, 5 mmol) was added dropwise for 1.5 h, and then the mixture was stirred for an additional 3.5 h. The mixture was cooled, the layers were separated, and the aqueous layer was extracted with Et₂O (20 mL × 3). The combined organic layers were dried over calcium chloride and evaporated to give 1-ethylindoline as a white solid (727.7 mg, yield, 99%).

2.1.2. Synthesis of 4-[1-[(4-Methoxyphenyl)imino]ethyl]-phenol (Imine Ligand). In a typical experiment, NaHCO₃ (4.2 g, 50 mmol), aniline (1.2 g, 10 mmol), p-hydroxyacetophenone (1.4 g, 10 mmol), activated molecular sieves (7.0 g, 4 Å), and benzene (10 mL) were added to a Schlenk tube. The mixture was exposed to an argon atmosphere and heated to reflux overnight. After completion of the reaction, the reaction mixture was filtered through Celite, and then the filtrate was evaporated under vacuum. The product was subsequently recrystallized from MeOH and ethyl acetate. A yellowish crystal was obtained (1.95 g, yield, 81%). ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, J = 5.6 Hz, 2H), 6.90 (d, J = 5.6 Hz, 2H, 6.81 (d, J = 5.6 Hz, 2H), 6.75 (d, J = 5.2 Hz, 2H), 3.81 (s, 3H), 2.22 (s, 3H) ppm (Figure S1 in the Supporting Information). ¹³C NMR (100 MHz, CDCl₃): δ = 161.4, 158.4, 156.1, 144.3, 131.9, 130.9, 129.0, 121.2, 115.4, 115.3, 114.3, 55.5, 26.3, 17.6 ppm (Figure S2). HRMS for C₁₅H₁₅O₂N [M + H⁺], calculated: 242.1181. Found: 242.1169.

2.1.3. Synthesis of Iridicycle 1. As reported in ref 28, [Cp*IrCl₂]₂ (pentamethylcyclopentadienyl iridium(III) chloride dimer, 318.4 mg, 0.4 mmol), an imine ligand (241.0 mg, 1.0 mmol), and NaOAc (328.0 mg, 4 mmol) were placed into a Schlenk tube. The tube was then degassed and recharged with Ar three times. CH₂Cl₂ (8 mL) was then added, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was filtrated through Celite and then dried over Na₂SO₄. The resulting mixture thereafter was purified by column chromatography (5:1 hexane/ethyl acetate) to obtain iridicycle **1** as an orange solid (222.9 mg, yield, 89%). ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 2.4 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H), 2.38 (s, 3H), 1.43 (s, 15H) ppm (Figure S3). ¹³C NMR (100 MHz, CDCl₃): δ = 180.2, 170.4, 158.9, 157.6, 144.3, 141.1, 130.3, 121.3, 109.5, 89.0, 55.6, 29.7, 16.8, 8.6 ppm (Figure S4). HRMS for C₂₅H₂₉O₂NClIr [M + Na⁺], calculated: 626.1414. Found: 626.1382.

Table 1. Leaching and Desorption of Iridicycle 2 from MWCNTs after Each Run Detected via Fluorescence Spectroscopy and ICP-MS

	iridicycle 2[a]			Ir (III)[c]		
run	c ($\times 10^{-6}$ mol/L)[b]	loss ($\times 10^{-4}$ mmol)	loss (%)	c (μg/mL)	loss ($\times 10^{-4}$ mmol)	loss (%)
1	14.0	4.2	2.97	0.03	3.9	2.60
2	12.1	3.6	2.62	0.03	3.9	2.70
3	9.0	2.7	2.03	0.02	2.6	1.86
4	6.5	2.0	1.51	0.02	2.6	1.93
5	6.2	1.9	1.49	0.01	1.3	<1
6	3.2	1.0	0.65	<0.01	<1.3	<1
7	2.0	0.6	0.40	<0.01	<1.3	<1

[a]The residual iridicycle **2** in the solution after every run detected by fluorescence technique (Figure S8). [b]The volume of solution was 30.00 mL. [c]The residual Ir(III) in the solution after every run detected by ICP-MS.

2.1.4. Synthesis of Iridicycle 2. Iridicycle 1 (151.0 mg, 0.25 mmol), 1-pyrenesulfonyl chloride (90.6 mg, 0.3 mmol), triethylamine (Et$_3$N, 506.0 mg, 5 mmol), and tetrahydrofuran (THF, 15 mL dried over sodium and distilled prior to use) were placed into a flask which was then equipped with a condenser. The equipment was then degassed and recharged with Ar three times. The resulting mixture was stirred under refluxing overnight. The reaction mixture was concentrated and purified by column chromatography (10:1, 5:1 hexane/ethyl acetate) to obtain iridicycle **2** as an orange solid (214.6 mg, yield, 99%). ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.23 (d, J = 9.0 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 9.6 Hz, 1H), 8.40 (d, J = 7.2 Hz, 1H), 8.33 (d, J = 7.2 Hz, 1H), 8.23 (d, J = 9.0 Hz, 1H), 8.16−8.11 (m, 2H), 8.07 (d, J = 9.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 2.4 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 3.79 (s, 3H), 2.29 (s, 3H), 0.80 (s, 15H) ppm (Figure S5). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 167.0, 157.8, 151.7, 146.7, 143.8, 135.8, 130.8, 130.8, 130.3, 129.6, 129.1, 128.4, 127.6, 127.4, 127.3, 127.3, 127.1, 127.0, 125.2, 124.1, 123.9, 123.9, 115.9, 88.9, 55.5, 29.7, 17.0, 7.8 ppm (Figure S6). HRMS for C$_{41}$H$_{38}$O$_4$NClSIr [M$^+$], calculated: 867.1761. Found: 867.1732.

2.1.5. Immobilization of the Iridicycle 2 onto MWCNTs. The pyrene-tagged iridicycle **2** (30 mg) was dissolved in THF (30 mL) at 30 °C. Then the MWCNTs were added and stirred for 20 min. Deionized water (60 mL) thereafter was dropped within 15 min, and the mixture was stirred for 10 min. The resulting mixture was centrifuged (8000 rpm, 3 min) to separate the immobilized iridicycle **2** catalyst and then dried in vacuum.

2.2. Catalyst Characterization. ^{1}H NMR and ^{13}C NMR spectra were determined on an AVANCE 400/600 super-conducting Fourier digital NMR instrument (400/600 MHz for proton) with TMS as the internal standard at 20 °C unless otherwise stated. The X-ray photoelectron spectroscopy (XPS) analyses were performed with an Axis Ultra spectrometer (Kratos Analytical Ltd.) using Al monochromatic X-ray source (Al Kα = 1486.6 eV) at room temperature in a high-vacuum environment (approximately 5× 10^{-9} Torr). All the binding energies were calibrated by using containment carbon, the C 1s (284.0 eV). Data treatment was performed with the Casa XPS program. Fluorescence spectra were recorded by a Hitachi FL spectrophotometer (F-4600). ICP-MS (Inductively Coupled Plasma Mass Spectrometry) data was recorded on a NexIon 300x (PerkinElmer). Determination of the iridium contained in a solution (transferred to a 50 mL volumetric flask) followed these steps: 1 mL of the solution was first evaporated before destruction of the organic matrix thanks to 5 mL of

concentrated HNO$_3$ (65 wt %)/HClO$_7$. The resulting solution was transferred to a 50 mL volumetric flask by dilution with water. Then, the Ir concentration was examined by ICP-MS.

2.3. Activity of Catalyst Testing. The performances of catalysts were carried out in an eggplant flask under refluxing with an empty balloon inserted on the top of the flask. To the solution of indoline (1.5 mmol) in a mixture solvent (TFE:H$_2$O = 1:2, 9 mL) was added immobilized catalyst (functionalized MWCNTs) (1 mol %). The reaction mixture was refluxed for 12 h at 100 °C in an oil bath. The top of the condenser connected to an empty balloon in order to balance the air pressure inside and outside of the reaction system. After the completion of reaction, contents of the flask were cooled to room temperature. The mixture was centrifuged to separate the MWCNTs from the liquid. Then the MWCNTs were washed three times with solvent (3 × 5 mL). All the liquid was collected and then extracted with ethyl acetate (3 × 20 mL). The combined organic phase was dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated under reduced pressure to afford the crude product, which was finally purified by column chromatography using ethyl acetate-*n*-hexane as eluent.

2.3.1. CDH of Indolines Catalyzed by Iridicycle 2 and Immobilized Iridicycle 2 Catalysts. The indoline (0.5 mmol) and iridicycle **2** (0.005 mmol, 4 mg) were added into a mixed solvent (H$_2$O:TFE = 2:1) and then stirred at 100 °C for 3 h. Then, the reaction was stopped and the reaction mixture was cooled to room temperature. The reaction mixture was extracted with ethyl acetate and purified by column chromatography (hexane:ethyl acetate = 20:1).

Indoline (0.5 mmol) and iridicycle **2** immobilized MWCNTs catalyst (0.005 mmol, 20.0 mg, loading of 0.29 mmol/g) were added into a mixed solvent (H$_2$O:TFE = 2:1) and then stirred at 100 °C for 3 h. The mixture was submitted to centrifugation (10 000 rpm, 2 min). The remaining product on the immobilized catalyst was washed with the mixed solvent to separate the desired product. The product was extracted by ethyl acetate and analyzed by ^{1}H NMR spectroscopy to calculate the yield.

2.3.2. Recycling of Immobilized MWCNTs Catalyst in CDH of Indoline. The indoline (1.5 mmol, 178.5 mg) and **2** immobilized catalyst (0.015 mmol, 60 mg, loading of 0.29 mmol/g) was added into a mixed solvent (H$_2$O:TFE = 2:1) and then exposed to an Ar atmosphere and heated to reflux for 12 h (100 °C). The mixture was cooled to room temperature, submitted to centrifugation (10 000 rpm, 2 min) and washed with the mixed solvent to separate the desired product from the immobilized catalyst. The product was extracted by ethyl acetate and analyzed by ^{1}H NMR spectroscopy to calculate the

Scheme 2. Immobilization of Iridicycle 2 onto MWCNTs

Immobilised iridicycle **2**
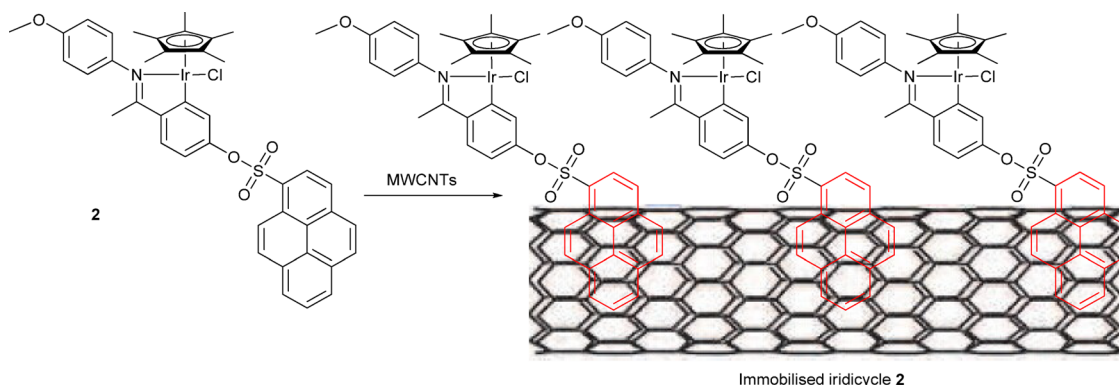
product yield. The recycled immobilized catalyst was vacuum-dried and used in the subsequent catalytic cycles followed the procedure as described.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Iridicycle 2. In our previous reports,[28,36] homogeneous Ir(III) catalysts were found to be stable and highly active and thus have been extensively used in homogeneous catalysis such as reductive amination and dehydrogenation. Hence, an Ir(III) complex, namely iridicycle **1**, was prepared and used as a model precursor to be immobilized onto the MWCNTs support.

The desired iridicycle **2** was obtained according to the synthetic route in Scheme 1. First, pyrene was sulfonated by chlorosulfonic acid and then chlorinated by thionyl chloride to form 1-pyrenesulfonyl chloride (PSC). Second, the obtained PSC was reacted with the iridicycle **1**, through which the needed iridicycle **2** was obtained in a high yield of 99%. The hydroxyl-containing iridicycle **1** was synthesized according to our previous work.[28] The iridicycle **1** and pyrene functionalized iridicycle **2** were characterized via ^{1}H and ^{13}C NMR spectroscopy (Figures S3−S6). The absorption signals at 8.06−9.24 ppm (in ^{1}H NMR) and 123.85−135.81 ppm (in ^{13}C NMR) indicate the successful tagging of pyrene in iridicycle **2**, which is also confirmed by the elemental analysis (as shown in Table 1).

3.2. Immobilization of Iridicycle 2 onto MWCNTs. We believe that the introduced pyrene group is vital for the noncovalently immobilizing of iridicycle **2** onto MWCNTs. Such an immobilizing process (Scheme 2) may be controlled by the polarity of the solvent(s) used. It was reported that for the immobilizing of pyrene-modified Rh(II) onto CNTs, dichloromethane (CH$_2$Cl$_2$) gave the lowest absorption (50%) while ethyl acetate (EtOAc) showed the highest absorption (97%).[41] Herein, mixed solvents of water and THF instead of a single solvent were used to strengthen the π−π stacking interactions between the pyrene modified Ir(III) complex (iridicycle **2**) and MWCNTs. It is believed that the immobilization efficiency may be mainly affected by three key factors, namely (1) the hydrophobic and aromatic nature of the pyrene group, (2) the difference in polarity and solvability of the solvents used (THF and water), and (3) the π−π stacking induced absorption and precipitation. The immobilization mechanism can be explained as follows.

Iridicycle **2** can be completely dissolved in THF, after which a uniform (orange) solution forms. When MWCNTs are added into the THF solution of **2**, **2** may interact with the exposed surface (both inside and outside) of MWCNTs. Because the pyrene group has a completely conjugated π-network, and each wall of MWCNTs is also fully conjugated (which may be viewed as a curved or curly graphene), we believe that such a similarity or identity in the microstructure and the resulting strong aromaticity may contribute greatly to an effective π−π stacking interaction between the pyrene group and MWCNTs. Such π−π stacking interaction may be much stronger than other noncovalent interactions (such as van der Waals forces), similar to that between pyrene and graphene reported by An et al.[42] The solvent(s) may play a significant role in the immobilization of iridicycle **2** onto the MWCNTs, whereas it seems that the well-dissolved iridicycle **2** in THF may be insufficient for the immobilization of **2** onto the MWCNTs. Water was thus introduced to adjust the solvability and polarity of the system. When water is added into the THF solution of the iridicycle **2**, the polarity or hydrophilicity of the solution increases, which should lower the solubility of **2** in the mixture while increasingly enhancing the π−π stacking interaction with MWCNTs due to the strong hydrophobicity of the pyrene group in iridicycle **2** and MWCNTs. Such an effective π−π stacking-induced absorption or precipitation may eventually contribute to the immobilization of iridicycle **2** onto MWCNTs.

Two experiments were performed to verify the proposed assumption and mechanism as follows. First, the iridicycle **2** was dissolved in THF (an orange solution as shown in Figure 1a). The solution was then mixed with MWCNTs, and the mixture was then equally divided into two portions. Thereafter, water was added into one portion (denoted as sample A;
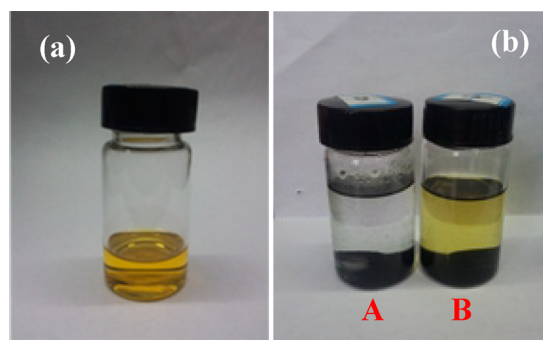
Figure 1. Absorption of iridicycle **2** onto MWCNTs in different solvents. (a) Iridicycle **2** was dissolved in THF. (b) Water was added (sample A), and THF was added (sample B).

water:THF = 2:1, volume ratio) and the same volume of THF was added into the other portion (denoted as sample B). After the two samples were stirred for approximately 20 min, the stirring was stopped and the MWCNTs precipitated. It is interesting to note that the upper phase of sample A turned colorless while that of simple B was still orange (as shown in Figure 1b). This result indicated that the existence of water may distinctly promote the immobilization of iridicycle **2** onto the MWCNTs. In this way, the impacts of the nature of the solvent(s) on the immobilization were clearly demonstrated.

Pyrene-tagged ligands have been used as fluorescence probes.[43,44] In the present work, the immobilization process of **2** onto MWCNTs was tracked and monitored by using fluorescence spectroscopy techniques. The loading of **2** was detected by comparing the amount (concentration) of iridicycle **2** before and after the immobilization. At the identical initial concentration of **2**, after the immobilization, the lower the concentration of **2** in solution, the less of **2** that remains in solution and the more of **2** that loads onto MWCNTs. To evaluate the immobilization efficiency, a series of feedings of MWCNTs was performed via which the absorption amount of **2** on MWCNTs was optimized. The loading of iridicycle **2** onto MWCNTs is shown in Table 2.

Table 2. Loading of Iridicycle 2 onto MWCNTs

entry[a]	MWCNTs feeding (mg)	fluorescence intensity[b]	loading[c] (mmol/g)	immobilization efficiency (%)[d]
1	14	425	0.40	98.09
2	12	435	0.47	97.98
3	10	436	0.56	97.97
4	8	501	0.70	97.74
5	6	567	0.93	97.39
6	4	1173	1.36	94.61

[a]The initial concentration of **2** is 1.15×10^{-3} mmol/mL (in 5 mL THF) in every entry; the volumes of THF and water are 5 and 10 mL, respectively. [b]Determined via fluorescence technique. Fluorescence intensity in the upper solution of immobilization system. [c]The amount of **2** (in mmol) per gram of MWCNTs. [d]The percentage of immobilized **2** on the initial feeding of **2**.

As shown in Table 2, with the decrease of MWCNTs feeding (from 14 to 4 mg), the loading of **2** onto MWCNTs increases (from 0.40 to 1.36 mmol/g). The immobilization efficiency of **2** on MWCNTs slightly decreases from 98.09 to 94.61%. The immobilization efficiency did not distinctly decrease until reaching the loading of 0.58 mmol/g, namely the stable maximum absorbing quality of iridicycle **2** onto MWCNTs should be 0.58 mmol/g, at which the immobilization efficiency is 97.98%. Thus, the MWCNTs-immobilized **2** with 0.58 mmol/g is selected as the catalyst for the CDH of the model substrates.

The immobilized **2** catalyst was characterized via XPS techniques. The corresponding XPS spectrum is shown in Figure 2, and the inside pattern showed that the oxidation state of iridium remains Ir(III) ($4f_{7/2}$, 62.1 eV; $4f_{5/2}$, 65.0 eV) after immobilization. Clearly, the presence of the desired Ir(III), Cl, and S indicates the successful immobilization of iridicycle **2** onto the support of MWCNTs.

3.3. Catalytic Performance of the Immobilized Iridicycle 2.
The evaluation of the targeted immobilized Ir catalyst was performed in three steps, as discussed in the following: (1)
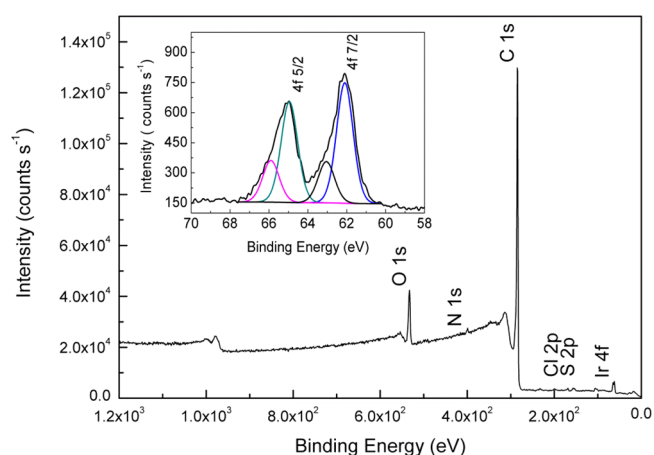
Figure 2. XPS spectra of immobilized iridicycle **2** (inset: Ir(III) narrow scan).

the optimization of the model CDH reaction conditions, (2) the activity, and (3) the recyclability.

3.3.1. Optimization of the CDH Conditions. It was reported that the homogeneous iridicycle catalysts exhibit excellent performance in the CDH of indolines.[36] In the present work, the CDH of indoline was selected as the model, through which the reaction conditions [including the solvents, reaction time, and catalyst dosage (reactant/catalyst ratio, R/C)], were investigated and optimized. The results are shown in Table 3.

Table 3. Effect of Solvents and Reaction Time on the CDH of Indoline

entry	solvent	catalyst (mol %)	time (h)	yield (%)[a]
1	EtOH	1	12	trace
2	MeOH	1	12	trace
3	THF	1	12	trace
4	DMF	1	12	N.R.
5	toluene	1	12	N.R.
6	H_2O	1	12	47
7	TFE	1	12	99
8	TFE	1	3	98
9	TFE	0.5	3	53
10	TFE	0.25	3	31
11	$V_{TFE}:V_{H_2O}$ = 1:2	1	12	99
12	$V_{TFE}:V_{H_2O}$ = 1:5	1	3	62
13	$V_{TFE}:V_{H_2O}$ = 1:4	1	3	76
14	$V_{TFE}:V_{H_2O}$ = 1:3	1	3	89
15	$V_{TFE}:V_{H_2O}$ = 1:2	1	3	97
16	$V_{TFE}:V_{H_2O}$ = 1:1	1	3	97
17	$V_{TFE}:V_{H_2O}$ = 1:2	1	2	80
18	$V_{TFE}:V_{H_2O}$ = 1:2	1	1	51

[a]Isolated yield. The reactions were carried out at 100 °C.

To our surprise, it was found that H_2O can be employed as the solvent in the CDH of indoline when iridicycle **2** was used as the catalyst. Such a greener solvent is definitely superior to trifluoroethanol (TFE) as reported in our previous work[36] because of its incomparable environmentally benign aspects, though the yield is almost half that obtained in TFE solvent (as shown in entries 6 and 7 in Table 3). We consider that TFE may promote the dissociation of chloride from the Ir(III)

complex of **2** when the CDH of indoline was performed in TFE and may thus enhance the coordination of indoline to iridicycle **2** prior to CDH taking place. Similar promotion was also demonstrated in our previous work.[36] Given that the CDH worked in water, the mixed solvent of TFE and H$_2$O may be an alternative or even a better solvent for the CDH of indoline because it is greener and more economic than TFE as well as other organic solvents.

To verify such an assumption and seek an optimized composition of the mixed solvent, the CDH of indoline in TFE−H$_2$O under a series of V_{TFE}:V_{H_2O} ratios was investigated. The results are listed in Table 3 (entries 12−16). As is clearly seen in Table 3, with the increase of H$_2$O (the V_{TFE}:V_{H_2O} ratio from 1:1 to 1:5), the yield of indole, namely the targeted product for the CDH of indoline, distinctly decreased from 97 to 62%. The highest yield of 97%, which is comparable or almost equal to that obtained in pure TFE (98% in Table 3, entry 8), is definitely achieved in 3 h when the volume ratio of TFE to H$_2$O is 1:2 (Table 3, entry 15), indicating that the aqueous surroundings may be a promising solution to the replacement of the organic one.

3.3.2. Catalytic Activity of Immobilized Iridicycle. We believe that the achieved TFE−H$_2$O solvent system and the resulting aqueous surroundings must be more significant for the immobilized iridicycle **2** catalytic system. In a more polar medium, the nonpolar pyrene-tagged **2** may prefer to attach itself onto the surface of MWCNTs via stronger π−π stacking because the hydrophobic interaction among the pyrene-tagged **2**, MWCNTs, and the medium may be enhanced as compared with that in TFE. Therefore, the stability of immobilized Ir catalyst may be effectively restrained during CDH because of the desorption of iridicycle **2** from MWCNTs. This is exactly what we valued in the present work. On the basis of such an idea, the catalytic activities of iridicycle **2** and the immobilized iridicycle **2** were compared in the CDH reaction of various indolines in H$_2$O−TFE. The results are shown in Table 4. Interestingly, it is clear that the heterogeneous catalysis systems give almost the same yield as compared with that of the

corresponding homogeneous ones (Table 4, entries 1, 2, 6, 7, 9, and 10). Moreover, although the immobilized catalyst is much less active in the CDH of 3-methylindoline (Table 4, entry 3), it is more active in that of other substrates (Table 4, entries 4 and 8). Especially when the dosage of indoline was scaled up to 1.5 mmol in TFE/H$_2$O, the heterogeneous catalysis system affords higher yield (97%) than that of the homogeneous catalysis system (64%). Additionally, it is noted that the substituted group on different positions of the aromatic ring and N-heterocycle of the indolines appears to have little impact on the yield (Table 4, entries 2, 3, 6 and 7). Both electron-donating and electron-withdrawing groups on the ring are tolerated (Table 4, entries 7−10). Nevertheless, substrates with electron-withdrawing groups are slightly less reactive with less than 90% yield observed in the CDH reactions under the optimized conditions.

3.3.3. Recyclability of the Immobilized Ir(III) Catalyst. In view of the excellent yield obtained over the immobilized Ir catalyst, its recyclability was further explored in the aqueous surroundings, in which the mixed solvent of TFE−H$_2$O (1:2 in volume ratio) was employed. The CDH of indoline was selected as the model reaction, in which the dosage of indoline was 1.5 mmol. At the end of the reaction, the catalyst was separated by centrifugation. The product was analyzed by ^{1}H NMR spectroscopy.

We attempted to adopt the optimized 0.58 mmol/g loading (detected by ICP-MS) of the immobilized iridicycle **2**. However, unexpected results emerged. First, the catalyst could hardly be centrifuged after it was recycled only three times. Moreover, the yield was found to sharply decrease from 99 to 36% in the third run of recycling. We ascribe the inability to separate the catalyst to the possible oxidation of MWCNTs when the CDH of indoline was performed in air. The sharp decrease of yield must result from the loss or desorption of iridicycle **2** from MWCNTs. Such assumptions are demonstrated as follows.

To verify and avoid the undesired oxidation of the MWCNTs support, the reaction was carried out under the identical conditions except that Ar atmosphere was used instead of air. The results are shown in Table S1. It is found that the activity of the immobilized Ir catalyst for CDH of indoline distinctly declined under Ar because the obtained indoline conversion is no more than 30% in 3 h, whereas a high conversion of approximately 97% can be successfully achieved when the reaction time is prolonged from 3 to 12 h, as shown in Table S1. Fortunately, the catalyst can be easily separated by centrifugation in every run of the recycling tests under the Ar atmosphere, even though the catalyst has been reused several times (up to ten times). It is indicated that a nonoxidative atmosphere may be a prerequisite for the separation and reuse of the MWCNTs-immobilized Ir catalyst.

The loss or desorption of iridicycle **2** from MWCNTs during the recycling is investigated. As shown in Figure 3, the yield is found to dramatically decrease from 99 to 61% after the second run, even though the reaction is carried out in Ar. Given that the iridicycle **2** on the immobilized catalyst did not decompose during the recycling, the observed decrease in yield must be derived from the desorption of iridicycle **2** from the MWCNT support.

We believe that such desorption can be restrained and that the stability of the catalyst will be improved. It is also seen that the yield does not obviously change but remains at approximately 50% from runs 2 to 7 when the iridicycle **2**

Table 4. Comparison of Iridicycle 2 and Immobilized onto MWCNTs as Catalysts in Homogeneous and Heterogeneous Catalytic Reactions

entry	R$_1$	R$_2$	Y (%) (homo)[a]	Y (%) (heter)[b]
1	H	H	99	99
2	H	1-Me	99	99
3	H	3-Me	99	56
4	H	1-Et	87	99
5	H	1-Ph	80[c]	48
6	5-Me	H	95	89
7	6-Me	H	92	84
8	5-OMe	H	75	84
9	5-Br	H	74	66
10	6-Cl	H	82	72

[a]Isolated yield. [b]Measured by ^{1}H NMR analysis of the crude reaction mixture; the loading of immobilized **2** was 0.29 mmol/g. [c]2 mol %, 24 h. Reagents and conditions: solvent (V_{TFE}:V_{H_2O} = 1:2), 1 mol %, 100 °C, 12 h.
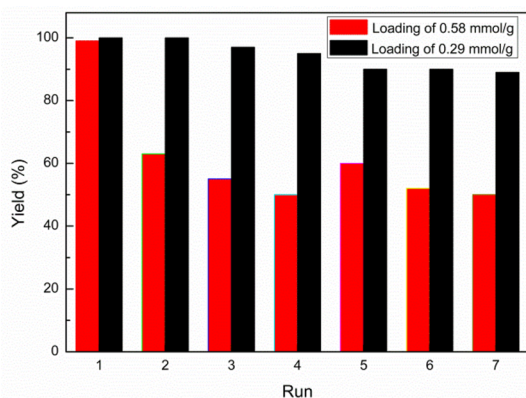
Figure 3. Recycling of different loading iridicycle **2** immobilized over MWCNTs in the CDH of indoline.

loading is 0.29 mmol/g (Figure 3). It is indicated that a lower loading of **2** onto MWCNTs may contribute to reducing or restraining the loss or leaching of **2** from MWCNTs and thus to higher stability of the catalyst.

To confirm this prediction, the recycling performance of the catalyst with lower loading of 0.29 mmol/g (detected by ICP-MS) was investigated. It is encouraging that the yield is found to fairly slightly decline from 100 to 89%, even though the catalyst has been reused in 7 runs (as shown in Figure 3). It is indicated that the catalyst in such a loading of **2** is stable during the recycling, and the leaching or the undesirable desorption of **2** from MWCNTs is effectively reduced. The leaching and desorption of iridicycle **2** from MWCNTs was investigated. The leaching and desorption results of iridicycle **2** from MWCNTs after each run detected via fluorescence spectroscopy and ICP-MS are listed in Table 1. It is clear that the iridicycle **2** leaches from the support of MWCNTs during the recycling. Such loss is found to be considerably slight [no more than 2.97% (fluorescence results) or 2.60% (ICP-MS results) in each run], and the loss degree presents a decreasing tendency (from 2.97 to 0.40% or 2.60 to less than 1%). The leaching and desorption results obtained from the two techniques are fairly close and verify each other. Such results can be well associated with the deactivation of the immobilized Ir catalyst and the resulting slight decrease in the yield of the targeted product (from 100 to 89% in Figure 3) during the recycling.

After being recycled for 7 runs, the catalyst was once more characterized via XPS, through which the used catalyst was verified to be identical to the fresh one except that a small portion of **2** is lost (Figure S7). Such loss is also verified via the XPS technique in its quantitive function (Table S2); the Ir/C atomic ratio is found to decrease by 13% [(0.0030 − 0.0026)/0.0030 × 100%] after 7 runs during the recycling.

Finally, to investigate whether the catalysis was heterogeneous or homogeneous, we followed the hot filtration test.[45] Under the above-mentioned optimized conditions (Ar atmosphere, 100 °C), the reaction mixture of the CDH of indoline was quickly filtrated after 5 h to remove the catalyst, where the conversion of indoline was 52%. Then the filtrate continued to react under the similar or identical conditions and showed 55% conversion of indoline after an additional 7 h. The results indicate that the amount of catalyst leaching into the reaction mixture was quite low and that the catalyst did act heterogeneously in the reaction. Therefore, as a novel constructed heterogeneous catalyst, the facilely immobilized

iridicycle **2** onto MWCNTs was proved to be successfully reused in the CDH of indoline for at least 7 times with slight loss and activity comparable to the CDH of indoline as compared with the iridicycle **2** without immobilizing.

4. CONCLUSIONS

Cyclometalated Ir complex with a pyrene tag was successfully synthesized and immobilized onto MWCNTs via $\pi-\pi$ stacking interactions. A facile immobilizing procedure was developed, and a novel and easily reusable Ir catalyst was constructed. The immobilization process was effectively monitored by using the fluorescence spectroscopy technique. The loading of immobilized **2** was determined and optimized, and the stability of the catalyst was evaluated. Interestingly, the immobilized catalyst showed high activity in the CDH model reaction of indolines with high yield under the green medium of aqueous conditions (H_2O-TFE). In addition to its easy separation, the immobilized Ir catalyst exerted an excellent activity (which is comparable to that of the corresponding homogeneous cyclometalated Ir catalyst) and sound stability during 7 runs of recycling in the CDH reaction. This work is eagerly expected to promote research regarding metal−organic or cyclometalated catalysts which are generally used homogeneously, effectively extending their applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b02804.

> ¹H and ¹³C NMR spectra, characterization data, XPS spectra of immobilized iridicycle **2** catalyst fresh and after seven runs, effect of atmospheres and reaction time on the CDH of indoline, and XPS analysis for fresh and used catalyst (PDF)

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