Three Synthetic Routes to a Commercial N3 Dye

R. Jitchati, Y. Thathong, and K. Wongkhan

Abstract—**We present the synthesis and characterization of a commercial standard ruthenium dye namely, N3, by cheap and easily prepared starting materials from three synthetic routes: the Grätzel's protocol and the other two new methods designed in our laboratory, *i.e.*, the one-pot reaction and *via* the reaction of cymeme complex.**

Index Terms—**Dye-sensitized solar cells (DSCs), N3, ruthenium complexes dye.**

I. INTRODUCTION

In the next few year, we will run out the fossil fuel enegy so the sciencentists have tried to find the replace of energy source. Solar energy is one of the most promising future energy which referred as "photovoltaic cells" (PV) [1]. However, the first generation of PV is an inorganic thin-film photovoltaic devices, *i.e.*, CdTe [2] and CuIn(As)Se [3], which contain highly toxic and expensive materials. For that reason, the second generation of solar converters called "dye-sensitized solar cells **(**DSCs**)**" has been developed [4], [5]. This solar cell architecture has emerged as a promising candidate for practical photovoltaic applications by virtue of their low manufacturing costs and good conversion efficiencies [1], [2]. Numerous sensitizers have been prepared and their performance has been tested. DSSCs with power conversion efficiencies over 10% under AM 1.5 irradiation were initially demonstrated using prototype *cis*-di(thiocyanato)-*bis*[2,2′-bipyridyl-4,4′-dicarboxylic acid] ruthenium(II) (**N3**), its *bis*-tetrabutylammonium (TBA) salt counterpart (**N719**), or the black dye [tri(thiocyanato)-(4,4′,4″-[2,2′:6′,2″-terpyridine] tricarboxylic acid]ruthenium(II) as a sensitizers in combination with thicker titania films (>12–15 μm) and volatile electrolytes [2]. In DSSCs, the sensitizer is one of the critical components because it absorbs sunlight and induces intramolecular charge transfer from the ancillary to the anchoring ligand with subsequent electron injection to the TiO$_2$ *via* the carboxylic acid groups. Then, the electron is transported to and collected at an electrode. Subsequent hole transfer from the oxidized dye to I$^-$/I$_3^-$ takes place, where the hole is transported to and collected at the counter electrode [1].

Grätzel's group reported the synthetic route to **N3** dye from isolated expensive starting material; *cis*-di(chloro)-N,N′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)-ruthenium(II) dihydrate (**3**.2H$_2$O).
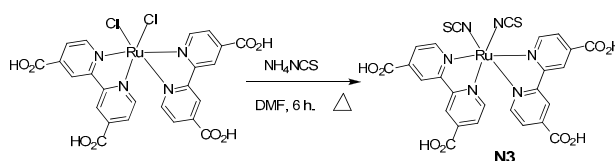

Fig. 1. The **N3** synthetic route by Grätzel's group.

The **N3** derivative called **N719** has also been delveloped and has shown more promising efficiency of about 11% [6]. Until now, these two materials have been used as the standard complexes to benchmark other new synthetic dyes in the dye-sensitized solar cell system [7], [8].

Herein, we report three synthetic routes of **N3**: the Grätzel's protocol and two new methods designed from our laboratory, *i.e.*, the one-pot reaction and *via* the reaction of cymeme complex where **N3** can be synthesized from cheap starting material and easily producible methods.

II. MATERIALS AND METHODS

2-Chloroisonicotinic acid, α-phellandrene and Pd(OAc)$_2$, were purchased from Acros organic and used without further purification. Anhydrous dimethyl formamide (DMF) was distilled using calcium hydride. RuCl$_3$.3H$_2$O were purchased from Precious Metals Online PMO Pty Ltd. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts are quoted downfield from internal standard TMS. IR spectra were measured on a Perkin–Elmer FT-IR spectroscopy spectrum RXI spectrometer as KBr disc. Melting points were measured in open-end capillaries using a Bŭchi 530 melting point apparatus. The temperatures at the melting points were ramped at 2.5 ^{o}C/min and were uncorrected.

A. Methyl-2-Chloroisonicotinate (2)

2-Chloroisonicotinic acid (2.5 g, 0.02 mol), methanol (50 mL) and H$_2$SO$_4$ (2.5 ml) were placed in 100 mL round bottom flask. The reaction mixture was refluxed for 24 hours. The cooled reaction was extracted with dichloromethane (3-4 times), followed by the removed of organic solvent to afford the target product (2.1632 g , 81%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.96 (s, 3H), 7.75 (d, *J* = 6 Hz, 1H), 7.77 (d, *J* = 6 Hz, 1H), 7.87 (s, 1H), 8.52 (d, *J* = 6 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 53.0, 121.6, 124.1, 140.2, 150.5, 163.3.

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B. Methyl 2-(4-(Methoxy Carbonyl)Pyridine-2-yl) Isonicotinate (3)

The mixture of methyl-2-chloroisonicotinate (**2**) (0.5076 g, 3 mmol), K_2CO_3 (3.04 g, 20 mmol) and $Pd(OAc)_2$ (0.07 g, 0.3 mmol) was introduced in 15 mL of anhydrous DMF in a two necked round bottom flask. Then, 0.47 mL portion of anhydrous isopropanol was syringed at once to the reaction flask. The reaction mixture was then heated to reflux under nitrogen atmosphere at 150 °C for 2 days. After the reaction mixture was cooled to room temperature, the content was extracted into dichloromethane (DCM). The crude reaction was evaporated to dryness and finally passed through silica column chromatography using 5% (v/v) methanol/DCM to get the target product as a white solid (0.037 g, 9%). m.p. 130-135°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.00 (s, 3H) 7.91 (dd, $J = 5.0$, 1.6 Hz, 1H), 8.87 (dd, $J = 5.0$, 0.9 Hz, 1H), 8.97 (dd, $J = 1.6$, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 68.2, 120.6, 128.8, 130.8, 138.7, 150.1, 165.6

C. 2,2'-Bipyridine-4,4'-Dicarboxylic Acid (4)

The 0.3 M sodium hydroxide (10 mL, 2.55 mmol) was added into methyl 2-(4-(methoxy carbonyl) pyridine-2-yl)isonicotinate (**3**) (0.28 g, 1.02 mmol) and methanol 25 mL with stirring. After the reaction was refluxed for 3 hours, the reaction mixture was poured into 50 mL of cooled water and slowly acidified to pH 2 with 10% aqueous hydrochloric acid. After filtration, the crude product was dried under vacuum to afford a white solid (0.25 g, 100%). ^{1}H NMR (DMSO−d_6, 300 MHz): δ 7.89 (d, $J = 6$ Hz, 1H), 8.80 (s, 1H), 8.90 (d, $J = 6$ Hz, 1H)

D. The Synthesis of Ruthenium Cymene Complex (6)

$RuCl_3.3H_2O$ (0.12 g, 0.45 mmol) was added to 50 mL two necked round bottom flask with stirring in ethanol (10 mL) under nitrogen balloon. After α-phellandrene (0.70 mL, 4.30 mmol) was introduced, the reaction mixture was refluxed for 4 hours. The red precipitate in red solution was observed. The solvent was then removed under vacuum followed by filtration to obtain the red product (0.07 g, 25%). mp: 190 °C (decomposed); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.29 (d, $J = 6$ Hz, 6H), 2.71 (s, 3H), 2.93 (q, $J = 6$ Hz, 1H), 5.35 (d, $J = 6$ Hz, 2H), 5.49 (d, $J = 6$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.9, 22.1, 30.6, 80.5, 81.3, 96.7, 101.2; IR (KBr) 878, 1387, 1471, 2364, 2873, 2957, 3053 cm^{-1}

E. The Synthesis Method of N3

1) The First Method (Grätzel's Model)

$RuCl_3.3H_2O$ (63 mg, 0.24 mmol) and 2,2'-bipyridine-4,4'-dicarboxylic acid (**4**) (120 mg, 0.48 mmol) were dissolved in 20 mL anhydrous DMF. The reaction mixture was then heated to reflux under nitrogen gas at 150 °C for 8 hours under reduced light. The reaction mixture was cooled to room temperature. The solid was filtered to afford a red-black solid and then washed with the mixture solvent (1:4 acetone:ether). After that, the residual solid was further refluxed with 0.10 M aqueous sodium hydroxide (7.50 mL) and ammonium thiocyanate (120 mg, 1.56 mmol) in 20 mL of DMF for 6 hours. The solvent of the

cooled reaction mixture was removed by reduced pressure distillation. Then, the residual solid was disollved with water and some of the impurity was filtered off. The filtrate was slowly added by 0.10 M aqueous nitric acid to pH 2 to give the red-dark solid. The solid was filtered again to obtain a red-dark solid (**N3**) as the pure product (24 mg, 25%). ^{1}H NMR (CD_3OD, 300 MHz): δ 7.68 (dd, $J = 5.9$, 1.7 Hz, 1H), 7.84 (d, $J = 5.9$ Hz, 1H), 7.98 (s, 1H), 8.35 (dd, $J = 5.8$, 1.7 Hz, 1H), 8.94 (d, $J = 1.2$ Hz, 1H), 9.10 (d, $J = 1.2$ Hz, 1H), 9.62 (d, $J = 5.8$ Hz, 1H). This ^{1}H NMR spectrum is identical with the commercial standard complex.

2) The Second Method (the One-Pot Reaction)

$RuCl_3.3H_2O$ (100 mg, 0.38 mmol) and 2,2'-bipyridine-4,4'-dicarboxylic acid (**4**) (190 mg, 0.77 mmol) were dissolved in 20 mL anhydrous DMF. The reaction mixture was then heated to reflux under nitrogen atmosphere at 150 °C under reduced light for 8 hours. The reaction was cooled to room temperature. The 0.10 M aqueous sodium hydroxide (8.3 mL, 0.82 mmol) and ammonium thiocyanate (0.13 g, 1.73 mmol) were added directly to the crude reaction mixture, which was then heated to reflux again for 6 hours as previously described. Then, DMF was removed by reduced pressure distillation to afford a red-dark residue solution, from which the red solid was disolved with water and acidified by 0.10 M aqueous nitric acid to pH 2. The precipitate was filtered again to obtain a red-dark solid product (**N3**) (0.14 g, 58%). The ^{1}H NMR spectra is identical with the product obtained by Grätzel's method.

3) The Third Method (via the Cymene Complex Reaction)

Diruthenium(III) (**6**) (200 mg, 0.34 mmol), 2,2'-Bipyridine-4,4'-dicarboxylic acid (**4**) (165 mg, 0.68 mmol) was dissolved by 30 mL to 100 mL of DMF in two necked round bottom flask. The reaction mixture was stirred for 4 hours in the dark and heated to 160 °C under nitrogen balloon. Finally, an excess of NH_4SCN (206 mg) was added at 130 °C for 5 hour. The solvent was evaporated in a vacuum then water was added to get the insoluble dark red solid which was collected on the sintered glass crucible by suction filtration. The dark red solid product was obtained after purified by column chromatography (sephadex, MeOH) (40 mg, 17%). The ^{1}H NMR spectra is identical with the product obtained by Grätzel's method.

III. RESULTS AND DISCUSIONS

A. The Synthesis of 4,4′-Dicarboxylic-2,2′-Bipyridine (4)

4,4′-Dicarboxylic-2,2′-bipyridine (**4**) can be synthesized from commercially available compound **1**. With esterification reaction of compound **1**, the compound **2** was obtained in high yield. Then the Pd-catalyzed homo-coupling reaction of compound **2** was applied to yield compound **3**. Finally, compound **3** was then hydrolyzed in base to the target ligand **4** in quantitative yield, as shown in Fig 1.

B. The Synthesis of N3 Ruthenium Complex

N3 dye can be synthesized from the cheap ruthenium source, *i.e.*, ruthenium(III) chloride trihydrate and 2

equivalents of 4,4′-dicarboxylic-2,2′-bipyridine (**4**). The synthesis of **N3** dye can be established *via* 3 pathways. The first method called Grätzel's model; the second, one-pot reaction and the final reaction was called "by cymene complex".
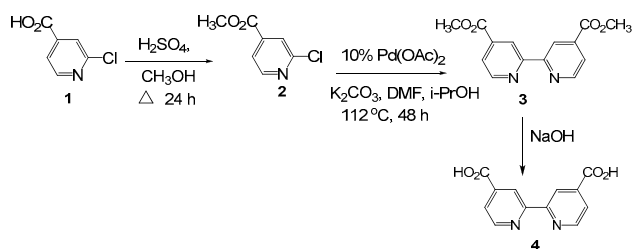

Fig. 1. The synthetic route of 4,4′-dicarboxylic-2,2′- bipyridine (**4**).

The synthesis of **N3** *via* the Grätzel's model was the reaction between ruthenium(III)chloride trihydrate and compound **4** in the refluxing DMF for 8 hours. By using this method, the intermediate content was isolated and followed by the ligand NH₄SCN exchange as shown in Fig 2. After the reaction was finished, 25 % of **N3** final product was obtained. The product was fully characterized by NMR spectroscopy. .
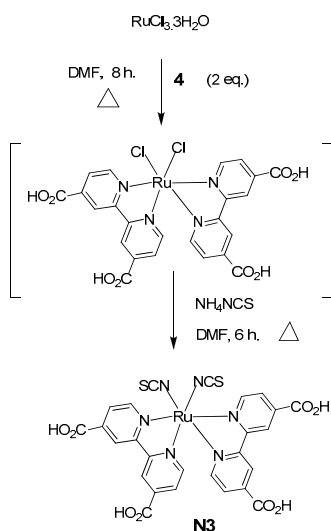

Fig. 2. The synthetic route of **N3** *via* Grätzel's method.

The second protocol, the new one-pot reaction designed by our group was applied for the synthesis of **N3**. The protocal started with the reaction between ruthenium(III)chloride trihydrate and compound **4** under DMF refluxing shown in Fig 3. This reaction step was the same as that in the Grätzel's model. However, after the content was refluxed, the reaction mixture was follwed by the addition of NH₄SCN for ligand exchange without any isolation. Then the intermediate reaction was continully refluxed in DMF for 6 hours. After the reaction was completed, the final pure product **N3**, confirmed by ^{1}H and ^{13}C NMR, was isolated in 58% yield *via* the simple filtration. As described, this one-pot reaction procedure not only short and easily for **N3** preparation but also give a better yield (58%).

The last **N3** synthetic route was created *via* ruthenium cymene precursor **6** synthesized by refluxing ruthenium chloride and α-phellandrene (**5**). The synthesis of cymene **6** is

shown in Fig 4. After the intermediate cymene **6** was separated, 2 equivalents of dicarboxylic pyridine ligand **4** was added and refluxed in DMF for 4 hours. Then, without any isolation, the excess of NH₄NCS was added for ligand exchange. The reaction was continully refluxed for 5 hours. The final product **N3** dye was obtained in 17 % yield from column chromatography.
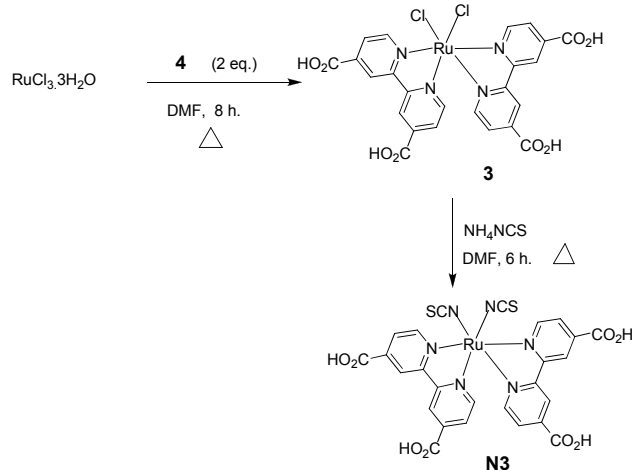

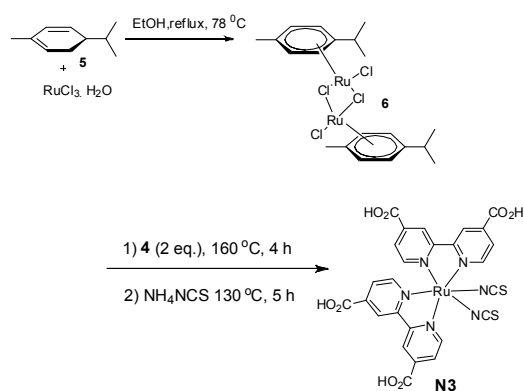Fig. 3. The synthetic route of **N3** *via* the one-pot reaction.

Fig. 4. The synthetic route of **N3** *via* ruthenium cymene.

IV. Conclusion

The **N3** dye was successfully synthesized *via* three different pathways, *i.e*, the Grätzel's protocol, the one-pot reaction and *via* the reaction of cymeme complex. Both one-pot reaction and the reaction *via* the cymeme complex were developed in our laboratory. The highest yield **N3** final product was obtained from the one-pot reaction.

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