



Synthesis and Characterization of Novel Ruthenium Diporphyrazines

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Research Article

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ABSTRACT

The synthesis and characterization of two new ruthenium diporphyrazines is reported. The ruthenium (III) chloride in cyclotetramerization reaction with 5,6-diphenylpyrazine-2,3-dicarbonitrile or 1,2-dicyanobenzene resulted the green and blue diporphyrazinato counterparts respectively. The obtained diporphyrazines will to our knowledge be useful photosensitizers.

Keywords: Diphthalocyanine; porphyrazine; photocatalyst; photosensitizer; photodynamic therapy.

1. INTRODUCTION

Solar energy applications always have attracted a lot of attention. Recently, designing the procedures to extent the absorption amounts of porphyrazine derivatives to the blue-green or visible spectral region has been one of considerable research (Wang et al., 2006; Villano et al., 2006; Zimcik et al., 2008; Keskin et al., 2008; Kemikli and Ozturk, 2008). So far, various methods such as, the organic dye photosensitization of TiO₂ (Wang et al., 2006; Zanjanchi et al., 2010), peripherally bulky annulations of porphyrazine derivatives (Keskin et al., 2008; Karadeniz et al., 2007; Kabay et al., 2009; Donzello et al., 2006), preparation of annulated binuclear phthalocyanines (Litwinski et al., 2008) have been developed. The modified porphyrazines possess an intensive absorption in the blue-green region of the solar spectrum; which can practically be applied in diverse areas as, photodynamic therapy (PDT), degradation of pollutants, photosensitizers, and anticancer therapy (Alvaro et al., 2005; Marais and Nyokong, 2008; Nensala and Nyokong, 2000; Wei et al., 2006; Atila et al.,

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2007). Diphthalocyanine complexes have also gained attention due to their rich redox chemistry and special π -electron systems. For example, lutetium diphthalocyanine complexes show photochemical behaviors six orders higher than their monomeric counterpart (Nensala and Nyokong, 2000).

2. MATERIALS AND METHODS

2.1 General

The UV-vis spectra were measured on a Shimadzu UV 160A spectrometer. The ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained with a Bruker 500 DRX-Avance NMR spectrometer. The IR spectra were taken with a Shimadzu 470 spectrometer using KBr pellets. Mass spectra were recorded on a GC-MS Agilent Technologies QP-5973N MSD instrument. Typical reaction procedures and spectroscopic data for all products are described below.

2.2 Synthesis

2.2.1 Synthesis of π -dicyano compound

A mixture of benzyl (0.036mol), DAMN (4.73g, 0.044mol) and *p*-toluenesulfonic acid (0.02g) in EtOH (50ml) was heated at reflux for 5 hours. A dark cream colored suspension was achieved in the end of reaction. The resulted mixture was filtered off, washed with MeOH and recrystallized from the solution mixture $\text{CCl}_4\text{-CHCl}_3$.

2.2.1.1 5, 6-diphenylpyrazine-2, 3-dicarbonitrile (2)

Cream needle crystals, yield 83%, 8.5g, mp 255°C; ^1H NMR (500 MHz, DMSO-d_6 /ppm) 7.48 (d, $J = 7.9$ Hz, 3H, ArH), 7.41 (t, $J = 7.3$ Hz, 2H, ArH); IR (ν_{max} KBr/cm^{-1}) 3058 (ArH), 2235 (CN), 1691 (C=N), 1512 (C=C); Exact mass (M+): calcd. for $\text{C}_{18}\text{H}_{10}\text{N}_4$, 282.0905 found 282.0912.

2.2.2 Synthesis of diporphyrzine complexes (4,5): a general procedure

A mixture of **2** (0.13g, 0.45mmol) and RuCl_3 (0.01g, 0.05mmol) in 7ml ethylene glycol were heated at 150°C for 14 hours. The solid reaction product was washed successively with acetone, dimethylformamide (DMF) and dried at 110°C. The resulting product gave three spots on a thin-layer chromatogram (silicagel/ CH_2Cl_2 -toluene). The greenish spot was scratched, solved and separated with DMF under warmth and subsequently resulted a green powder which was in agreement with ruthenium diporphyrzine **4**. The blue form of ruthenium diphthalocyanine **5** was prepared by mixing the phthalonitrile **3** (0.06g, 0.45mmol) with RuCl_3 (0.01g, 0.05mmol) in similar manner.

2.2.2.1 Ruthenium hexadecaphenylloctapirazinodiporphyrzine (4)

Green powder, yield 52%, 0.56g; ^1H NMR (400 MHz, DMSO-d_6 /ppm) 7.96-6.62 (m, ArH); IR (ν_{max} KBr/cm^{-1}) 3060-2905 (ArH), 1690 (C=N), 1610 (C=C); UV-vis (λ_{max} DMF/nm) 607; Exact mass (M+): calcd. for $\text{C}_{144}\text{H}_{80}\text{N}_{32}\text{Ru}$, 2358.6287 found 2358.6310.

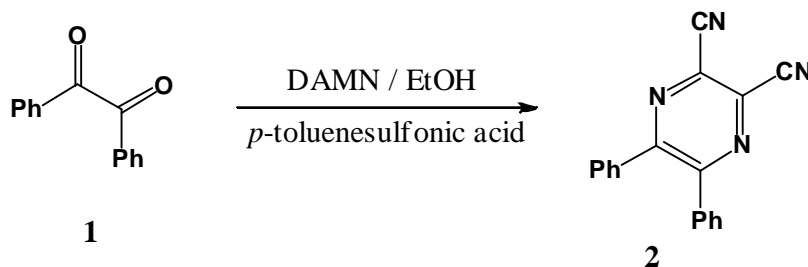
2.2.2.2 Ruthenium diphthalocyanine (5)

Blue powder, yield 84%, 0.43g; ^1H NMR (500 MHz, CDCl_3 /ppm) 7.57 (d, 1H, $J = 8.6$ Hz, ArH), 7.38 (d, 1H, $J = 2.4$ Hz, ArH), 7.16 (dd, 1H, $J = 2.4, 8.6$ Hz, ArH), 7.12 (dd, 1H, $J = 2.4, 8.4$ Hz, ArH); IR (ν_{max} KBr/cm-1) 2930 (ArH), 1715 (C=N), 1455 (C=C); Uv-vis (Amax DMF/nm) 631; Exact mass (M^+): calcd. for $\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{Ru}$, 1126.2039 found 1126.2048.

3. RESULTS AND DISCUSSION

Atypical electrochemical properties of diporphyrazines mainly influenced by the nature of the central metal ions and the substituent's presented on the periphery of porphyrazine nuclear, encouraged us to prepare the new di-counterparts. Although the electro-optic properties of some diporphyrazine derivatives are well documented, a one-pot, reliable, commercial and click preparative method leading to a single pure compound, to the best of our knowledge has not been satisfactorily reported in the literature (Nensala and Nyokong, 2000; Chang and Marchon, 1981; Nensala and Nyokong, 1997).

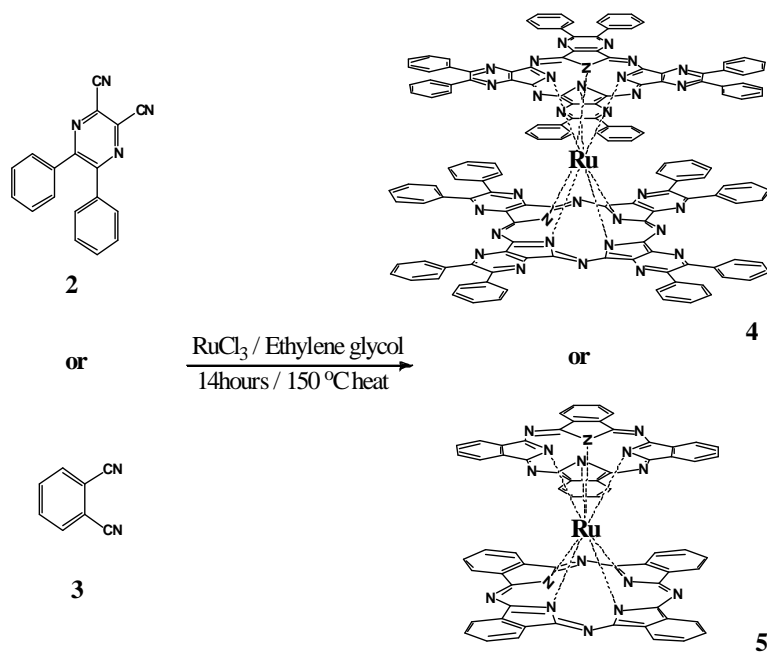
In this work, we report the design and synthesis of two ruthenium diporphyrazines as large π -conjugated systems by modification of reported procedures (Nensala and Nyokong, 2000; Nensala and Nyokong, 1997). The 5,6-diphenylpyrazine-2,3-dicarbonitrile **2** was synthesized by the condensation reaction of diaminomaleonitrile (DAMN) with benzyl **1** in ETOH (Scheme 1).



Scheme 1. Schematic route to pyrazine-2,3-dicarbonitrile derivative 2

The ruthenium hexadecaphenyl octapirazinodiporphyrazine ($\text{RuPh}_{16}\text{Pyz}_8\text{Pz}_2$) **4** and the blue form of ruthenium diphthalocyanine (RuPc_2) **5** were synthesized by mixing the RuCl_3 with π -dicarbonitrile **2** or phthalonitrile **3** in the molar ratio 1: 9 respectively (Scheme 2).

The structures of resulted compounds **2,4** and **5** were confirmed by the use of TLC, FT-IR, UV-Vis, MS and ^1H NMR techniques.



Scheme 2. Schematic route to diporphyrazine complexes 4,5

4. CONCLUSION

The two new ruthenium diporphyrazines were synthesized from cyclotetramerization of 1,2-dicyano compounds. The obtained diporphyrazines will be examined as potential photo sensitizers.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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