



meso-Phenyl-triazole bridged porphyrin-coumarin dyads: Synthesis, characterization and photophysical properties



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ABSTRACT

Novel zinc (II) *meso*-phenyl-triazole bridged porphyrin-coumarin dyads have been synthesized in good to excellent yields through copper (I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction of zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin with diverse coumarinoalkynes in dimethylformamide containing ascorbic acid at 80 °C. These compounds successfully underwent demetallation in the presence of concentrated hydrochloric acid to afford the corresponding free-base porphyrins which on treatment with nickel acetate in chloroform-acetic acid mixture produced various nickel (II) *meso*-triazole bridged porphyrin-coumarin dyads in good yields. All the newly synthesized products were characterized on the basis of spectral data and elemental analyses. The preliminary photophysical results revealed a significant intramolecular energy transfer between porphyrin core and coumarin moiety in the case of zinc porphyrin analogues.

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1. Introduction

Porphyrins are a versatile class of π -conjugated macrocycles which display high absorbance in visible region and possess interesting biological, photophysical and electrochemical properties. They are highly desirable for numerous applications in diverse fields including catalysis [1,2], Optical limiters [3,4], photochemistry [5,6], medicinal chemistry [7], anion recognition [8,9] and material science [10–13]. In the last several decades, the porphyrin chemistry has been explored to develop a series of novel macrocyclic compounds through peripheral functionalization of *meso*-tetraarylporphyrins. Recently, the copper (I)-catalyzed Huisgen 1,3-dipolar cycloaddition [14,15] of an azide with terminal alkyne has become a straightforward route to afford 1,2,3-triazole as a chemical linker to connect porphyrins with various scaffolds such as fullerene [16–18], ferrocene [19] and carbohydrate [20] in a single molecular framework for the study of their photophysical and therapeutic properties. In addition, 1,2,3-triazole subunit is also found useful in the synthesis of *meso-meso*-linked porphyrin dimers [21] and carbon nanotube functionalized porphyrin analogues [22].

Among the biologically active chromophores, the coumarins are an important class of heterocyclic compounds with diverse pharmacological and optical properties. These molecules have been widely used as fluorescent brightening agents [23], organic light emitting diodes [24,25], optical sensors [26,27], light harvesting materials [28,29], non linear optical materials [30] and fluorogenic probe in biological imaging [31,32]. In the past, various *meso*-substituted porphyrin-coumarin dyads [33] and different porphyrin-cored dendrimers linked with non-conjugated coumarins as dendrons [34] have been synthesized and investigated for their photophysical properties. The photophysical investigations revealed that the intramolecular energy transfer occurs from coumarin moiety to the porphyrin core. Hania et al. have synthesized coumarin-porphyrin donor-acceptor systems [35] and studied their optical properties using time- and frequency-resolved fluorescence spectroscopy. These molecules have shown interesting photophysical characteristics and considered as a first generation dendrimers with four donor groups for every acceptor unit. By considering the biological significance of porphyrin, 1,2,3-triazole and coumarin scaffolds and in continuation of our work on *meso*-substituted porphyrins [36–39], we report herein the synthesis, spectroscopic characterization and photophysical properties of a novel series of *meso*-phenyl-triazole bridged porphyrin-coumarin dyads.

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2. Experimental section

2.1. Reagents and solvents

All the reagents and solvents used in the present work were purchased from Sigma–Aldrich Chemical Pvt. Ltd., Bangalore, India and Merck Specialities Pvt. Ltd., Mumbai, India and used as received unless otherwise stated. Spectroscopic grade DMF was used to measure UV–Vis absorption and emission spectra of the samples. All the reactions involving triazole formation were carried out in dry N₂ atmosphere. Thin-layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ (pre-coated aluminium sheets) from Merck. The column chromatographic purification of all the products were carried out using either activated neutral aluminium oxide (Brokmann grade I-II, Merck) or silica gel (60–120 mesh).

2.2. Instruments

The melting points of all newly prepared products were determined in open capillary tubes on Buchi M-560 melting point apparatus and are uncorrected. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ or DMSO-d₆ on Jeol ECX-400P (400 MHz) NMR spectrometer. Chemical shifts were quoted in δ scale in parts per million (ppm) relative to CDCl₃ (δ = 7.26 ppm) and DMSO-d₆ (δ = 2.50 ppm) for ¹H NMR and CDCl₃ (δ = 77.00 ppm), DMSO-d₆ (δ = 39.50 ppm) for ¹³C NMR. The coupling constants were expressed as (J) and reported in Hertz (Hz). Elemental analyses for all the compounds were performed on Elementar Analysensysteme GmbH VarioEL elemental analyser. Infrared (IR) spectra were recorded in film or KBr on Perkin Elmer IR spectrometer and absorption maxima (ν_{max}) are given in cm⁻¹. UV–Vis absorption and fluorescence spectra were measured by using an Analytik Jena's Specord 250 UV–Vis spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively. The mass spectra were recorded on THERMO Finnigan LCQ Advantage max ion trap mass spectrometer and Agilent G6530 AA LC-HRMS Q-TOF system in positive mode.

2.3. Synthesis of 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**2**)

To a stirred solution of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**1**; 100 mg, 0.158 mmol) in THF (20 mL), a saturated aqueous solution of NaNO₂ (0.158 mmol) and concentrated H₂SO₄ (80 μL) were added at 0–5 °C. The reaction mixture was stirred at room temperature for 30 min, then a saturated aqueous solution of NaN₃ (0.174 mmol) in water was added dropwise and the reaction mixture was stirred for additional 20 min. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, 20 mL chloroform was added to the reaction mixture. The resulting solution was washed with water (30 mL × 3 times), the organic layer was dried over anhydrous Na₂SO₄ and solvent was evaporated under reduced pressure. Thus, the crude product obtained was purified over activated neutral alumina column using 20% chloroform in hexane as eluent. Purple solid; yield: 91%; mp > 300 °C; UV (DMF) λ_{max} (ε × 10⁻⁴, M⁻¹ cm⁻¹): 419 (158.17), 516 (6.43), 550 (3.00), 593 (1.14), 648 (1.48) nm; λ_{Em} (DMF; λ_{Ex} 420 nm): 651, 717 nm; IR (KBr) ν_{max}/cm⁻¹: 3315, 3021, 2122, 2085, 1470, 1348, 1293, 1178, 1152, 965, 798, 724, 700; ¹H NMR (400 MHz, CDCl₃) δ: 8.87–8.83 (m, 8H, β-pyrrolic H), 8.23–8.19 (m, 8H, meso-ArH), 7.80–7.73 (m, 9H, meso-ArH), 7.43 (d, J = 8.79 Hz, 2H, meso-ArH), –2.78 (s, 2H, internal NH); ¹³C NMR (100 MHz CDCl₃) δ: 142.14, 142.07, 139.82, 138.91, 135.70, 134.54, 131.17, 127.74, 126.69, 120.32, 120.25, 120.12,

118.81, 117.42; HRMS (ESI, m/z) calcd for C₄₄H₃₀N₇: 656.2557 [M + H]⁺; found 656.2558.

2.4. Synthesis of zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**3**)

To a solution of 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**2**; 50 mg, 0.076 mmol) in chloroform (10 mL), a solution of zinc acetate (20 mg, 0.091 mmol) in methanol (1 mL) was added. The reaction mixture was stirred at 25 °C for 30 min. After completion of the reaction, the mixture was washed with water and CHCl₃ layer was dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to afford the crude product, which was purified by silica gel column using 30% chloroform in hexane as eluent. The pure product was obtained as a purple solid in 93% yield. The spectroscopic data of the porphyrin (**3**) were matched with the reported data [17].

2.5. Synthesis of 7-trifluoromethylsulfonyloxycoumarins (**5a-c**)

The coumarins (**5a-c**) were synthesized by the reaction of 7-hydroxycoumarins (**4a-c**) (0.56 mmol) and trifluoromethanesulfonic anhydride (0.72 mmol) in the presence of Et₃N (0.74 mmol) as reported in the literature [40]. The spectral data of known compounds (**5a-b**) are found to be in good agreement with the reported data [41,42] whereas the characterization data of unknown compound **5c** are given below.

2.5.1. (6-Chloro-4-methyl-2-oxo-2H-chromen-7-yl) trifluoromethanesulfonate (**5c**)

White solid; yield: 93%; mp 142–144 °C; IR (film) ν_{max}/cm⁻¹: 3053, 2930, 1730, 1630, 1423, 1209, 1134, 1036, 896, 863; ¹H NMR (400 MHz, CDCl₃) δ: 7.74 (s, 1H, ArH), 7.36 (s, 1H, ArH), 6.38 (d, ⁴J = 1.46 Hz, 1H, CH), 2.44 (d, ⁴J = 1.46 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 158.85, 152.20, 150.26, 146.64, 126.57, 122.92, 120.82, 116.94, 116.84, 112.09, 18.63; HRMS (ESI, m/z) calcd for C₁₁H₇ClF₃O₅S: 342.9649 [M + H]⁺; found 342.9637; Anal. Calcd. for C₁₁H₆ClF₃O₅S: C, 38.55; H, 1.76; S, 9.36. Found: C, 38.57; H, 1.75; S, 9.32.

2.6. Synthesis of 7-trimethylsilylethynylchromen-2-ones (**6a-c**)

The title compounds were prepared by the Sonogashira reaction of 7-trifluoromethylsulfonyloxycoumarins (**5a-c**; 0.32 mmol) with trimethylsilylacetylene (0.4 mmol) in DMF (2 mL) in the presence of bis(triphenylphosphine)palladium(II) dichloride (0.007 mmol) and triethylamine (2.5 mmol) as reported in the literature procedure [43]. The spectral and analytical data of known compounds (**6a-b**) were found in good agreement with the reported data [41,42]. The characterization data of compound (**6c**) are given below.

2.6.1. 6-Chloro-4-methyl-7-trimethylsilylethynylchromen-2-one (**6c**)

White solid; yield: 78%; mp 156–158 °C; IR (Film) ν_{max}/cm⁻¹: 2960, 1734, 1386, 1246, 1157, 841, 759; ¹H NMR (400 MHz, CDCl₃) δ: 7.58 (s, 1H, ArH), 7.42 (s, 1H, ArH), 6.31 (s, 1H, CH), 2.40 (d, ⁴J = 1.46 Hz, 3H, CH₃), 0.29 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz CDCl₃) δ: 159.79, 151.32, 150.73, 131.50, 125.98, 124.64, 121.42, 120.86, 116.32, 104.32, 99.76, 18.49, –0.33; ESI-MS: m/z = 291.2 (M + H)⁺; Anal. Calcd. for C₁₅H₁₅ClO₂Si: C, 61.95; H, 5.20. Found: C, 62.12; H, 5.41.

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