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# **Graphical Abstract**

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

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# *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.

Keywords: Click chemistry, coumarin, energy-transfer, fluorescence, porphyrin, synthesis.

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### 1. Introduction

Porphyrins are a versatile class of  $\pi$ -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.

### 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 reaction involving triazole formation was carried out in dry N<sub>2</sub> atmosphere. Thin-layer chromatography (TLC) was performed on silica gel 60  $F_{254}$  (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. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> on Jeol ECX-400P (400 MHz) NMR spectrometer. Chemical shifts were quoted in  $\delta$  scale in parts per million (ppm)

relative to CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm) and DMSO-d<sub>6</sub> ( $\delta$  = 2.50 ppm) for <sup>1</sup>H NMR and CDCl<sub>3</sub> ( $\delta$  = 77.00 ppm), DMSO-d<sub>6</sub> ( $\delta$  = 39.50 ppm) for <sup>13</sup>C 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 analyzer. Infrared (IR) spectra were recorded in film or KBr on Perkin Elmer IR spectrometer and absorption maxima ( $v_{max}$ ) are given in cm<sup>-1</sup>. 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 NaNO<sub>2</sub> (0.158 mmol) and concentrated H<sub>2</sub>SO<sub>4</sub> (80 µL) were added at 0-5 °C. The reaction mixture was stirred at room temperature for 30 minutes, then a saturated aqueous solution of NaN<sub>3</sub> (0.174 mmol) in water was added dropwise and the reaction mixture was stirred for additional 20 minutes. 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 Na<sub>2</sub>SO<sub>4</sub> 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)  $\lambda_{max}$  ( $\varepsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 419 (158.17), 516 (6.43), 550 (3.00), 593 (1.14), 648 (1.48) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 651, 717 nm; IR (KBr)  $\nu_{max}/cm^{-1}$ : 3315, 3021, 2122, 2085, 1470, 1348, 1293, 1178, 1152, 965, 798, 724, 700;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>) 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 C<sub>44</sub>H<sub>30</sub>N<sub>7</sub>: 656.2557 [M+H]<sup>+</sup>; 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 minutes. After completion of the reaction, the mixture was washed with water and CHCl<sub>3</sub> layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. 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  $Et_3N$  (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) υ<sub>max</sub>/cm<sup>-1</sup>: 3053, 2930, 1730, 1630, 1423, 1209, 1134, 1036, 896, 863; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.74 (s, 1H, ArH), 7.36 (s,

1H, ArH), 6.38 (d,  ${}^{4}J$  = 1.46 Hz, 1H, CH), 2.44 (d,  ${}^{4}J$  = 1.46 Hz, 3H, CH<sub>3</sub>);  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 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 C<sub>11</sub>H<sub>7</sub>ClF<sub>3</sub>O<sub>5</sub>S: 342.9649 [M+H]<sup>+</sup>; found 342.9637; Anal. Calcd. for C<sub>11</sub>H<sub>6</sub>ClF<sub>3</sub>O<sub>5</sub>S: 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 7trifluoromethylsulfonyloxycoumarins (**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-trimethylsilanylethynylchromen-2-one (6c)

White solid; yield: 78%, mp 156-158 °C; IR (Film)  $v_{max}/cm^{-1}$ : 2960, 1734, 1386, 1246, 1157, 841, 759; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.58 (s, 1H, ArH), 7.42 (s, 1H, ArH), 6.31 (s, 1H, CH), 2.40 (d, <sup>4</sup>*J* = 1.46 Hz, 3H, CH<sub>3</sub>), 0.29 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>)  $\delta$ : 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)<sup>+</sup>; Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>ClO<sub>2</sub>Si: C, 61.95; H, 5.20. Found: C, 62.12; H, 5.41.

## 2.7. Synthesis of 7-ethynylcoumarins (7a-c)

The 7-ethynylcoumarins (**7a-c**) were prepared from 7-trimethylsilylethynylcoumarins (**6a-c**) according to the literature method [43]. The spectral data of compounds (**7a-b**) are

matched with the reported data [41, 42] and the characterization data of unknown compound (7c) are given below.

### 2.7.1. 6-Chloro-7-ethynyl-4-methyl-chromen-2-one (7c)

Brown solid; yield: 81%, mp 144-146 °C; IR (Film)  $v_{max}/cm^{-1}$ : 3235, 2960, 2110, 1718, 1382, 1197, 1154, 1081, 902, 878, 705; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.61 (d, <sup>4</sup>*J* = 1.46 Hz, 1H, ArH), 7.47 (d, <sup>4</sup>*J* = 1.46 Hz, 1H, ArH), 6.33 (s, 1H, CH), 3.54 (d, <sup>4</sup>*J* = 1.46 Hz, 1H, - C=CH), 2.41 (d, <sup>4</sup>*J* = 1.46 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 159.60, 151.31, 150.65, 131.52, 124.95, 124.81, 121.98, 121.29, 116.58, 85.49, 78.97, 18.49; ESI-MS: m/z = 219.2 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>12</sub>H<sub>7</sub>ClO<sub>2</sub>: C, 65.92; H, 3.23. Found: C, 65.87 H, 3.24.

### 2.8 Synthesis of propargyloxycoumarins (8a-e)

The propargyloxycoumarins (**8a-e**) were synthesized from 7-hydroxycoumarins (**4a-d**; 0.56 mmol) or 4-hydroxycoumarin (**4e**; 0.56 mmol) and propargylbromide (0.84 mmol) by following the literature procedure and characterized on the basis of spectral data [44, 45]. The characterization data of compounds (**8c-d**) are presented below.

### 2.8.1. 6-Chloro-4-methyl-7-prop-2-ynyloxy-chromen-2-one (8c)

White solid; yield: 84%, mp 208-210 °C; IR (Film)  $v_{max}/cm^{-1}$ : 3287, 3060, 2926, 2133, 1736, 1604, 1364, 1276, 1157, 1054, 881, 845; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.59 (s, 1H, ArH), 7.05 (s, 1H, ArH), 6.20 (s, 1H, CH), 4.85 (d, <sup>4</sup>*J* = 2.20 Hz, 2H, OCH<sub>2</sub>), 2.61 (t, <sup>4</sup>*J* = 2.20 Hz, 1H, -C=CH), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.48, 155.40, 153.21, 151.49, 125.58, 119.31, 114.52, 113.30, 102.12, 57.05, 18.61; ESI-MS: m/z = 249.1 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>13</sub>H<sub>9</sub>ClO<sub>3</sub>: C, 62.79; H, 3.65. Found: C, 62.53; H, 3.62.

2.8.2. 4-Chloromethyl-7-prop-2-ynyloxy-chromen-2-one (8d)

White solid; yield: 79%, mp 142-144 °C; IR (Film)  $v_{max}/cm^{-1}$ : 3242, 2926, 2127, 1720, 1606, 1376, 1265, 1139, 1057, 821, 739; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.59 (d, *J* = 9.52 Hz, 1H, ArH), 6.98-6.96 (m, 2H, ArH), 6.43 (s, 1H, CH), 4.77 (d, <sup>4</sup>*J* = 2.93 Hz, 2H, OCH<sub>2</sub>), 4.62 (s, 2H, CH<sub>2</sub>Cl), 2.58 (t, <sup>4</sup>*J* = 2.93 Hz, 1H, -C=CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>)  $\delta$ : 158.62, 158.15, 153.27, 148.86, 124.58, 110.98, 110.72, 109.35, 100.41, 77.51, 76.47, 54.44, 39.57; ESI-MS: m/z = 249.1 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>13</sub>H<sub>9</sub>ClO<sub>3</sub>: C, 62.79; H, 3.65. Found: C, 62.58; H, 3.53.

# 2.9. General procedure for the synthesis of zinc (II) meso-phenyl-triazole bridged porphyrincoumarin dyads (**9a,c,e, 10a,c,e,g** and **11a**)

To a well stirred solution of zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**3**; 0.139 mmol) in DMF (10 mL), CuSO<sub>4</sub>.5H<sub>2</sub>O (6.94 mg, 0.028 mmol), ascorbic acid (9.79 mg, 0.055 mmol) and the corresponding coumarinoalkynes (**7a-c** or **8a-e**; 0.166 mmol) were added and the reaction mixture was stirred at 80 °C for 2 hours under nitrogen. After completion of the reaction, the mixture was allowed to cool at room temperature and diluted with 50 mL chloroform. The resulting solution was washed thoroughly with water, the organic layer was dried over anhydrous sodium sulphate and evaporated to dryness. Thus, the crude product obtained was purified over silica gel column using 2% methanol in chloroform as eluent.

2.9.1. Zinc (II) 4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3] triazol-4-yl}-chromen-2-one (**9a**)

Purple solid; yield: 87%; mp >300 °C; UV (DMF)  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 428 (215.53), 560 (7.17), 601 (2.99) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 607, 660 nm; IR (KBr)  $\nu_{max}$ /cm<sup>-1</sup>: 2924, 2854, 1712, 1619, 1261, 1073, 1035, 796, 754, 704; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ :

9.82 (s, 1H, triazole H), 8.87 (d, J = 4.39 Hz, 2H, β-pyrrolic H), 8.82-8.78 (m, 6H, β-pyrrolic H), 8.46 (d, J = 8.05 Hz, 2H, *meso*-ArH), 8.38 (d, J = 8.05 Hz, 2H, *meso*-ArH), 8.20-8.18 (m, 6H, *meso*-ArH), 8.08-8.04 (m, 1H, ArH), 8.01 (s, 1H, ArH), 7.96-7.91 (m, 1H, ArH), 7.80-7.79 (m, 9H, *meso*-ArH), 6.44 (s, 1H, CH), 2.50 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 159.85, 153.60, 153.11, 149.48, 149.42, 149.13, 146.16, 143.45, 142.72, 135.93, 135.48, 134.24, 133.80, 131.98, 131.79, 131.74, 131.48, 127.59, 126.70, 126.43, 121.47, 121.26, 120.72, 120.58, 119.45, 118.67, 118.38, 114.33, 112.64, 18.13; HRMS (ESI, m/z) calcd for C<sub>56</sub>H<sub>36</sub>N<sub>7</sub>O<sub>2</sub>Zn: 902.2216 [M+H]<sup>+</sup>; found 902.2173. Anal. Calcd. for C<sub>56</sub>H<sub>35</sub>N<sub>7</sub>O<sub>2</sub>Zn.H<sub>2</sub>O: C, 73.00; H, 4.05; N, 10.64. Found: C, 72.92; H, 4.15; N, 10.32.

2.9.2. Zinc (II) 7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-yl}chromen-2-one (**9**c)

Purple solid; yield: 87%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 427 (151.28), 560 (4.93), 601 (1.85) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 607, 659 nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 2926, 1716, 1617, 1340, 1262, 1205, 1101, 1003, 797, 755; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), δ: 9.81 (s, 1H, triazole H), 8.87 (d, J = 5.13 Hz, 2H,  $\beta$ -pyrrolic H), 8.82-8.78 (m, 6H,  $\beta$ -pyrrolic H), 8.46 (d, J = 8.05 Hz, 2H, *meso*-ArH), 8.38 (d, J = 8.79 Hz, 2H, *meso*-ArH), 8.20-8.18 (m, 6H, *meso*-ArH), 8.12 (d, J = 9.52 Hz, 1H, CH), 8.07-8.01 (m, 2H, ArH), 7.89 (s, 1H, ArH), 7.80-7.79 (m, 9H, *meso*-ArH), 6.54 (d, J = 9.52 Hz, 1H, CH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 159.98, 154.16, 149.45, 149.38, 149.11, 146.21, 143.94, 143.43, 142.71, 135.89, 135.45, 134.21, 133.73, 131.94, 131.77, 131.72, 131.45, 129.31, 127.57, 126.66, 121.44, 121.38, 120.68, 120.55, 118.65, 118.57, 118.32, 116.11, 112.51; ESI-MS: m/z = 888.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>35</sub>H<sub>33</sub>N<sub>7</sub>O<sub>2</sub>Zn.H<sub>2</sub>O: C, 72.81; H, 3.89; N, 10.81. Found: C, 72.83; H, 3.92; N, 10.62. 2.9.3. Zinc (II) 6-chloro-4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-yl}-chromen-2-one (**9e**)

Purple solid; yield: 78%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 427 (169.39), 560 (5.57), 601 (2.21) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 607, 659 nm; IR (Film)  $\nu_{max}$ /cm<sup>-1</sup>: 2921, 1714, 1613, 1339, 1262, 1173, 1066, 1001, 798, 753; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) δ: 8.94 (s, 1H, trizole H), 8.77-8.71 (m, 8H,  $\beta$ -pyrrolic H), 8.30-8.23 (m, 3H, *meso*-ArH and ArH), 8.07-8.04 (m, 8H, *meso*-ArH), 7.61-7.58 (m, 9H, *meso*-ArH), 7.28 (s, 1H, ArH), 6.22 (s, 1H, CH), 2.33 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub> + CDCl<sub>3</sub>) δ: 159.72, 151.62, 150.61, 149.65, 149.54, 149.52, 149.07, 144.27, 143.10, 142.82, 135.54, 135.24, 134.13, 131.72, 131.50, 131.45, 130.79, 126.91, 126.19, 126.01, 125.79, 121.97, 120.63, 120.44, 120.25, 118.29, 117.85, 117.18, 115.83, 18.11; ESI-MS: m/z = 936.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>56</sub>H<sub>34</sub>ClN<sub>7</sub>O<sub>2</sub>Zn: C, 71.72; H, 3.65; N, 10.46. Found: C, 71.65; H, 3.55; N, 10.46.

2.9.4. Zinc (II) 4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3] triazol-4-ylmethoxy}-chromen-2-one (**10a**)

Purple solid; yield: 80%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 427 (195.50), 560 (6.46), 600 (2.72) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 606, 659 nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 2924, 1689, 1607, 1387, 1338, 1209, 1065, 992, 797, 758, 703; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.29 (s, 1H, triazole H), 8.85 (d, *J* = 4.39 Hz, 2H,  $\beta$ -pyrrolic H), 8.82-8.79 (m, 6H,  $\beta$ -pyrrolic H), 8.40 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.33 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.20-8.18 (m, 6H, *meso*-ArH), 7.80-7.79 (m, 9H, *meso*-ArH), 7.70 (d, *J* = 8.05 Hz, 1H, ArH), 7.26 (d, *J* = 2.20 Hz, 1H, ArH), 7.11 (dd, *J*<sub>1</sub> = 8.79, *J*<sub>2</sub> = 2.20 Hz, 1H, ArH), 6.24 (s, 1H, CH), 5.47 (s, 2H, OCH<sub>2</sub>), 2.39 (s, 3H, CH<sub>3</sub>); ESI-MS: m/z = 932.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>57</sub>H<sub>37</sub>N<sub>7</sub>O<sub>3</sub>Zn.H<sub>2</sub>O: C, 71.96; H, 4.13; N, 10.31. Found: C, 72.12; H, 4.14; N, 10.23.

2.9.5. *Zinc* (*II*) 7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-yl methoxy}-chromen-2-one (*10c*)

Purple solid; yield: 73%; mp >300 °C; UV (DMF)  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (232.06), 560 (7.42), 600 (3.02) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 607, 659 nm; IR (Film)  $\nu_{max}$ /cm<sup>-1</sup>: 2926, 1724, 1615, 1068, 992, 795, 750; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 9.27 (s, 1H, triazole H), 8.87-8.79 (m, 8H,  $\beta$ -pyrrolic H), 8.40 (d, J = 7.79 Hz, 2H, *meso*-ArH), 8.32 (d, J = 7.33 Hz, 2H, *meso*-ArH), 8.20-8.18 (m, 6H, *meso*-ArH), 8.02-7.96 (m, 1H, CH), 7.79-7.78 (m, 9H, *meso*-ArH), 7.68-7.62 (m, 1H, ArH), 7.27 (s, 1H, ArH), 7.12-7.08 (m, 1H, ArH), 6.33-6.30 (m, 1H, CH), 5.47 (s, 2H, OCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 161.13, 160.36, 155.40, 149.48, 149.41, 149.14, 144.36, 143.45, 143.30, 142.73, 135.95, 135.38, 134.24, 131.97, 131.83, 131.78, 131.52, 129.65, 127.59, 126.70, 123.53, 120.73, 120.58, 118.72, 118.42, 113.04, 112.84, 112.77, 101.74, 61.75; ESI-MS: m/z = 918.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>56</sub>H<sub>35</sub>N<sub>7</sub>O<sub>3</sub>Zn.1.5H<sub>2</sub>O: C, 71.07; H, 4.05; N, 10.36. Found: C, 71.23; H, 3.97; N, 10.42.

2.9.6. Zinc (II) 6-chloro-4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-ylmethoxy}-chromen-2-one (**10e**)

Purple solid; yield: 73%; mp >300 °C; UV-Vis (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 427 (190.64), 560 (6.10), 600 (2.36) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 606, 659 nm; IR (Film)  $v_{max}$ /cm<sup>-1</sup> <sup>1</sup>: 2922, 1727, 1605, 1495, 1339, 1276, 1158, 1068, 993, 797, 757; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) δ: 8.65-8.62 (m, 8H, β-pyrrolic H), 8.39 (s, 1H, triazole H), 8.16-8.11 (m, 2H, *meso*-ArH), 7.99-7.91 (m, 8H, *meso*-ArH), 7.54-7.47 (m, 9H, *meso*-ArH), 7.43 (s, 1H, ArH), 7.03 (s, 1H, ArH), 5.97 (s, 1H, CH), 5.30 (s, 2H, OCH<sub>2</sub>), 2.34 (s, 3H, CH<sub>3</sub>); ESI-MS: m/z = 966.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>57</sub>H<sub>36</sub>ClN<sub>7</sub>O<sub>3</sub>Zn.H<sub>2</sub>O: C, 69.45; H, 3.89; N, 9.95. Found: C, 69.65; H, 4.13; N, 10.12. 2.9.7. Zinc (II) 4-chloromethyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-ylmethoxy}-chromen-2-one (**10**g)

Purple solid; yield: 67%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 427 (190.23), 560 (6.28), 601 (2.39) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 607, 659 nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 3054, 2921, 1731, 1614, 1392, 1339, 1267, 1204, 1069, 1001, 993, 796, 754; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.31 (s, 1H, triazole H), 8.85 (d, *J* = 4.39 Hz, 2H, β-pyrrolic H), 8.81-8.78 (m, 6H, β-pyrrolic H), 8.40 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.33 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.19-8.18 (m, 6H, *meso*-ArH), 7.80-7.79 (m, 10H, *meso*-ArH and ArH), 7.32 (s, 1H, ArH), 7.19-7.17 (m, 1H, ArH), 6.54 (s, 1H, CH), 5.50 (s, 2H, OCH<sub>2</sub>), 5.00 (s, 2H, CH<sub>2</sub>Cl); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 161.29, 160.17, 155.24, 150.89, 149.55, 149.49, 149.21, 143.57, 143.49, 143.39, 142.77, 135.99, 135.45, 134.30, 132.02, 131.87, 131.83, 131.55, 127.66, 126.77, 126.54, 123.57, 120.80, 120.66, 118.77, 118.51, 113.03, 112.38, 110.91, 102.16, 61.83, 41.38; ESI-MS: m/z = 966.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>57</sub>H<sub>33</sub>ClN<sub>7</sub>O<sub>3</sub>Zn: C, 70.74; H, 3.75; N, 10.13. Found: C, 70.69; H, 3.78; N, 10.23.

2.9.8. Zinc (II) 4-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-yl methoxy}-chromen-2-one (**11a**)

Purple solid; yield: 83%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 427 (151.10), 560 (4.88), 601 (1.66) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 607, 657 nm.; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 2922, 2851, 1720, 1621, 1490, 1339, 1236, 1105, 1069, 993, 795, 750; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.98-8.95 (m, 6H, β-pyrrolic H), 8.90 (d, J = 4.39 Hz, 2H, β-pyrrolic H), 8.38-8.37 (m, 2H, *meso*-ArH), 8.28 (s, 1H, triazole H), 8.23-8.21 (m, 6H, *meso*-ArH), 8.06-8.01 (m, 2H, *meso*-ArH), 7.84-7.70 (m, 9H, *meso*-ArH), 7.57-7.51 (m, 2H, ArH), 7.33-7.30 (m, 2H, ArH), 5.83 (s, 1H, CH), 5.20 (s, 2H, OCH<sub>2</sub>); ESI-MS: m/z = 918.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>56</sub>H<sub>35</sub>N<sub>7</sub>O<sub>3</sub>Zn.H<sub>2</sub>O: C, 71.16; H, 3.98; N, 10.46. Found: C, 71.53; H, 3.83; N, 10.52.

### 2.10. General procedure for the demetallation of zinc porphyrins (9a,c, 10a,c,e,g and 11a)

To a solution of zinc porphyrins (50 mg) in CHCl<sub>3</sub> (10 mL), conc. HCl (200  $\mu$ L) was added. The reaction mixture was stirred at 25°C for 15 minutes. After completion of the reaction, the mixture was washed with water (50 mL × 3 times). The organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure. Thus, the crude products obtained after the demetallation of zinc porphyrins (**9a,c** and **10a,c,e,g**) were found to be insoluble in most of organic solvents at 25°C and therefore, used as such for the synthesis of corresponding nickel porphyrins (**9b,d** and **10b,d,f,h**). However, the free-base porphyrin (**11b**) was purified over neutral alumina column using 80% chloroform in hexane as solvent.

# 2.10.1. 4-{1-[4-(10,15,20-Triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-ylmethoxy}chromen-2-one (**11b**)

Dark purple solid; yield: 84%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 418 (132.90), 516 (4.93), 548 (2.83), 595 (0.51), 647 (1.01) nm;  $\lambda_{Em}$  (DMF;  $\lambda_{Ex}$  420 nm): 650, 718 nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 3317, 2921, 2851, 1720, 1622, 1459, 1349, 1237, 1106, 966, 800, 750; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.90-8.87 (m, 6H,  $\beta$ -pyrrolic H), 8.81 (d, J = 4.39 Hz, 2H,  $\beta$ -pyrrolic H), 8.37-8.33 (m, 3H, triazole H and *meso*-ArH), 8.23-8.21 (m, 6H, *meso*-ArH), 8.11-8.07 (m, 2H, *meso*-ArH), 7.89 (d, J = 7.32 Hz, 1H, ArH), 7.81-7.76 (m, 9H, *meso*-ArH), 7.58 (t, J = 7.32 Hz, 1H, ArH), 7.36 (d, J = 8.05 Hz, 1H, ArH), 7.29 (t, J = 7.32 Hz, 1H, ArH), 5.98 (s, 1H, CH), 5.52 (s, 2H, OCH<sub>2</sub>), -2.75 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 164.92, 162.57, 153.35, 143.33, 142.35, 141.93, 136.20, 135.49, 134.51, 132.54, 131.38, 127.82, 126.73, 126.46, 123.95, 123.14, 121.74, 120.73, 120.44, 118.73, 117.57, 116.79, 115.39, 91.29, 62.48; ESI-MS: m/z = 856.2 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>56</sub>H<sub>37</sub>N<sub>7</sub>O<sub>3</sub>: C, 78.58; H, 4.36; N, 11.45. Found: C, 78.84; H, 4.52; N, 11.24.

2.11. General procedure for the synthesis nickel (II) meso-phenyl-triazole bridged porphyrincoumarin dyads (**9b,d, 10b,d,f,h** and **11c**)

To a solution of free-base porphyrins (0.035 mmol) in CHCl<sub>3</sub> (10 mL), nickel acetate (0.053 mmol) in acetic acid (1 mL) was added. The reaction mixture was refluxed for 10 hours under stirring. After completion of the reaction, the reaction mixture was cooled to 25 °C and washed with water to remove acetic acid. The organic layer was dried over anhydrous sodium sulphate and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using chloroform as eluent.

2.11.1. Nickel (II) 4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-yl}-chromen-2-one (**9b**)

Reddish brown solid; yield: 97%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 416 (55.10), 530 (4.17) nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 3107, 1699, 1617, 1520, 1351, 1226, 1075, 1002, 801, 753, 703; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.79-8.73 (m, 8H, β-pyrrolic H), 8.49 (s, 1H, triazole H), 8.20 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.11 (d, *J* = 8.42 Hz, 2H, *meso*-ArH), 8.02-7.80 (m, 6H, *meso*-ArH), 7.97 (s, 1H, ArH), 7.85 (s, 1H, ArH), 7.73-7.66 (m, 10H, *meso*-ArH and ArH), 6.33 (s, 1H, CH), 2.48 (s, 3H, CH<sub>3</sub>); HRMS (ESI, m/z) calcd for C<sub>56</sub>H<sub>36</sub>N<sub>7</sub>NiO<sub>2</sub>: 896.2278 [M+H]<sup>+</sup>; found 896.2249; Anal. Calcd. for C<sub>56</sub>H<sub>35</sub>N<sub>7</sub>NiO<sub>2</sub>: C, 75.02; H, 3.93; N, 10.94. Found: C, 75.35; H, 3.90; N, 10.83.

2.11.2. Nickel (II) 7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-yl}chromen-2-one (9d)

Reddish brown solid; yield: 93%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 416 (72.14), 530 (5.28) nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 2923, 2851, 1710, 1617, 1353, 1235, 1075, 1004, 798, 755, 703; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.79-8.72 (m, 8H, β-pyrrolic H), 8.47 (s, 1H,

triazole H), 8.20 (d, J = 8.05 Hz, 2H, meso-ArH), 8.09 (d, J = 8.05 Hz, 2H, meso-ArH), 8.02-8.00 (m, 6H, meso-ArH), 7.93 (d, J = 7.32 Hz, 1H, CH), 7.84 (s, 1H, ArH), 7.71-7.66 (m, 10H, meso-ArH and ArH), 7.54 (d, J = 7.32 Hz, 1H, ArH), 6.43 (d, J = 8.79 Hz, 1H, CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.58, 154.43, 146.89, 142.88, 142.85, 142.80, 142.69, 142.16, 142.04, 140.69, 136.30, 134.84, 133.67, 132.58, 132.42, 132.36, 131.51, 128.41, 127.82, 126.91, 121.78, 119.39, 119.25, 118.98, 118.75, 118.62, 116.73, 116.56, 113.54; ESI-MS: m/z = 882.5 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>55</sub>H<sub>33</sub>N<sub>7</sub>NiO<sub>2</sub>: C, 74.85; H, 3.77; N, 11.11. Found: C, 74.65; H, 3.85; N, 11.22.

# 2.11.3. Nickel (II) 4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4-ylmethoxy}-chromen-2-one (**10b**)

Reddish brown solid; yield: 94%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 416 (81.93), 529 (6.15) nm; IR (Film)  $\nu_{max}$ /cm<sup>-1</sup>: 3056, 2919, 2850, 1726, 1613, 1353, 1071, 1006, 798, 753, 701; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.79-8.76 (m, 6H, β-pyrrolic H), 8.71 (d, J = 5.13 Hz, 2H, β-pyrrolic H), 8.28 (s, 1H, triazole H), 8.16 (d, J = 8.05 Hz, 2H, meso-ArH), 8.05-8.00 (m, 8H, meso-ArH), 7.73-7.66 (m, 9H, meso-ArH), 7.54 (d, J = 9.52 Hz, 1H, ArH), 7.03-7.01 (m, 2H, ArH), 6.17 (s, 1H, CH), 5.42 (s, 2H, OCH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 161.12, 160.99, 155.11, 152.38, 144.00, 142.84, 142.79, 142.69, 142.16, 141.94, 140.68, 139.27, 136.36, 134.76, 133.65, 132.56, 132.41, 132.35, 131.50, 127.81, 126.89, 125.73, 121.29, 119.38, 119.24, 119.00, 116.74, 114.14, 114.05, 112.34, 102.18, 62.22, 18.63; ESI-MS: m/z = 926.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>57</sub>H<sub>37</sub>N<sub>7</sub>NiO<sub>3</sub>: C, 73.88; H, 4.02; N, 10.58. Found: C, 74.03; H, 4.22; N, 10.32.

2.11.4. Nickel (II) 7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4ylmethoxy}-chromen-2-one (**10d**) Reddish brown solid; yield: 91%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 416 (58.26), 529 (4.34) nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 3054, 2916, 2848, 1719, 1618, 1352, 1292, 1133, 1004, 797, 749; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.77-8.53 (m, 9H, β-pyrrolic H and triazole H), 8.24 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.08 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.02-7.95 (m, 6H, *meso*-ArH), 7.90 (d, *J* = 9.52 Hz, 1H, ArH), 7.71-7.69 (m, 9H, *meso*-ArH), 7.57 (d, *J* = 8.79 Hz, 1H, CH), 7.10 (dd, *J*<sub>1</sub> = 8.79, *J*<sub>2</sub> = 2.20 Hz, 1H, ArH), 7.08 (d, *J* = 2.20 HZ, 1H, ArH), 6.50 (d, *J* = 9.52 Hz, 1H, CH), 5.55 (s, 2H, OCH<sub>2</sub>); ESI-MS: m/z = 912.1 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>56</sub>H<sub>35</sub>N<sub>7</sub>NiO<sub>3</sub>: C, 73.70; H, 3.87; N, 10.74. Found: C, 73.65; H, 4.13; N, 10.46.

# 2.11.5. Nickel (II) 6-chloro-4-methyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]-triazol-4-ylmethoxy}-chromen-2-one (**10f**)

Reddish brown solid; yield: 94%; mp >300 °C; UV (DMF)  $\lambda_{max}$  (ε×10<sup>-4</sup>, M<sup>-1</sup> cm<sup>-1</sup>): 416 (67.50), 529 (4.82) nm; IR (Film)  $\nu_{max}$ /cm<sup>-1</sup>: 2918, 2850, 1731, 1605, 1353, 1274, 1206, 1156, 1047, 1005, 799, 752; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.79-8.71 (m, 8H, β-pyrrolic H), 8.31 (s, 1H, triazole H), 8.16 (d, *J* = 8.05 Hz, 2H, *meso*-ArH), 8.04-8.00 (m, 8H, *meso*-ArH), 7.71-7.67 (m, 9H, *meso*-ArH), 7.58 (s, 1H, ArH), 7.12 (s, 1H, ArH), 6.19 (s, 1H, CH), 5.45 (s, 2H, OCH<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.44, 156.08, 153.42, 151.41, 143.56, 142.84, 142.79, 142.69, 142.18, 142.00, 140.70, 136.38, 134.77, 133.67, 132.57, 132.40, 132.35, 131.51, 127.81, 126.89, 125.55, 121.36, 119.37, 119.28, 119.24, 119.04, 116.75, 114.40, 113.26, 101.87, 63.37, 18.59; ESI-MS: m/z = 960.1 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>57</sub>H<sub>36</sub>ClN<sub>7</sub>NiO<sub>3</sub>: C, 71.23; H, 3.78; N, 10.20. Found: C, 71.43; H, 3.64; N, 10.21.

2.11.6. Nickel (II) 4-chloromethyl-7-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]-triazol-4-ylmethoxy}-chromen-2-one (**10h**)

Reddish brown solid; yield: 91%; mp >300 °C; UV (DMF)  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 416 (77.49), 529 (5.77) nm; IR (Film)  $\nu_{max}$ /cm<sup>-1</sup>: 3021, 2918, 2850, 1733, 1612, 1441, 1352, 1266,

1138, 1072, 1005, 799, 754; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.79-8.76 (m, 6H,  $\beta$ -pyrrolic H), 8.70 (d, J = 4.58 Hz, 2H,  $\beta$ -pyrrolic H), 8.27 (s, 1H, triazole H), 8.15 (d, J = 8.24 Hz, 2H, *meso*-ArH), 8.02-8.00 (m, 8H, *meso*-ArH), 7.73-7.65 (m, 9H, *meso*-ArH), 7.52 (d, J = 8.70 Hz, 1H, ArH), 7.00-6.97 (m, 2H, ArH), 6.40 (s, 1H, CH), 5.37 (s, 2H, OCH<sub>2</sub>), 4.56 (s, 2H, CH<sub>2</sub>Cl); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 161.27, 160.53, 155.52, 149.42, 142.84, 142.80, 142.68, 142.15, 141.96, 140.68, 136.44, 134.78, 133.66, 132.57, 132.41, 132.35, 131.49, 127.82, 126.90, 125.36, 119.39, 119.25, 119.03, 116.72, 113.01, 112.75, 111.36, 102.50, 62.21, 41.20; ESI-MS: m/z = 960.0 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>57</sub>H<sub>36</sub>ClN<sub>7</sub>NiO<sub>3</sub>.H<sub>2</sub>O, C, 69.92; H, 3.91; N, 10.01 Found: C, 70.13; H, 3.87; N, 9.98.

# 2.11.7. Nickel (II) 4-{1-[4-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-1H-[1,2,3]triazol-4ylmethoxy}-chromen-2-one (**11c**)

Purple solid; yield: 95%; mp >300 °C; UV (DMF)  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 416 (70.68), 530 (5.11) nm; IR (Film)  $\upsilon_{max}$ /cm<sup>-1</sup>: 2922, 2851, 1720, 1623, 1458, 1353, 1238, 1106, 1006, 798, 752; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.79-8.76 (m, 6H,  $\beta$ -pyrrolic H), 8.70 (d, J = 4.58 Hz, 2H,  $\beta$ -pyrrolic H), 8.28 (s, 1H, triazole H), 8.16 (d, J = 6.87 Hz, 2H, *meso*-ArH), 8.02-8.00 (m, 8H, *meso*-ArH), 7.86 (d, J = 7.79 Hz, 1H, ArH), 7.73-7.65 (m, 9H, *meso*-ArH), 7.56 (t, J = 7.79 Hz, 1H, ArH), 7.39-7.26 (m, 1H, ArH), 5.95 (s, 1H, CH), 5.45 (s, 2H, OCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.96, 162.59, 153.36, 142.86, 142.81, 142.68, 142.35, 142.14, 140.67, 136.24, 134.80, 133.65, 132.60, 132.44, 132.38, 131.47, 127.83, 126.90, 123.96, 123.12, 123.02, 121.75, 119.40, 119.25, 119.06, 116.80, 116.64, 115.38, 91.67, 91.30, 62.58; ESI-MS: m/z = 911.9 (M+H)<sup>+</sup>; Anal. Calcd. for C<sub>56</sub>H<sub>35</sub>N<sub>7</sub>NiO<sub>3</sub>.H<sub>2</sub>O: C, 72.27; H, 4.01; N, 10.54. Found: C, 72.27; H, 4.13; N, 10.38.

### 3. Results and Discussion

### 3.1. Synthesis and structure characterization

The synthetic protocol for the preparation of the target *meso*-phenyl-triazole bridged porphyrin-coumarin dyads is shown in scheme 3. Initially, 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (2) was synthesized in 91% yield from 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (1) according to the modified literature procedure [46] *via* the diazotization with H<sub>2</sub>SO<sub>4</sub>/NaNO<sub>2</sub> in THF, followed by *in situ* reaction with NaN<sub>3</sub>. Then, the corresponding precursor zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (2) by the insertion of zinc metal after the treatment with zinc acetate in CHCl<sub>3</sub>-MeOH mixture at room temperature (Scheme 1).

### <Insert Scheme 1>

In addition, the coumarin starting materials, 7-ethynylcoumarins (**7a-c**; Scheme 2) were synthesized according to reported methods [40, 43]. Initially, the 7-hydroxy coumarins (**4a-c**) were converted to the corresponding triflate derivatives (**5a-c**) by a reaction of trifluoromethanesulfonic anhydride and triethylamine at 0 °C in dichloromethane. Further, these molecules underwent Sonogashira coupling with trimethylsilylacetylene in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Et<sub>3</sub>N in DMF at 90 °C to afford trimethylsilyl protected coumarinoalkynes (**6a-c**) which on deprotection in the presence of K<sub>2</sub>CO<sub>3</sub> in methanol provided desired 7-ethynylcoumarins (**7a-c**) in 78-81% yields. Also, the coumarinoalkynes (**8a-e**) were prepared in good yields by the reaction of compounds (**4a-e**) with propargyl bromide in acetone containing K<sub>2</sub>CO<sub>3</sub> at 50 °C according to the literature procedure [44].

#### <Insert Scheme 2>

Then, the novel zinc (II) derivatives of *meso*-phenyl-triazole bridged porphyrin-coumarin dyads (**9a,c,e, 10a,c,e,g** and **11a**) were synthesized in 67-87% yields *via* a Cu (I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction of zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**3**) with coumarin substituted alkynes (**7a-c** or **8a-e**). Further, these zinc-triazoloporphyrin dyads (**9a,c 10a,c,e,g** and **11a**) were demetallated by conc. HCl in chloroform at room temperature. Interestingly, only free-base porphyin (**11b**) was found to be soluble in chloroform and hence it was purified by column chromatography and characterized spectroscopically, whereas the remaining free-base porphyrins were found to be insoluble in most of the organic solvents at 25 °C and therefore, used as such for the synthesis of corresponding nickel porphyrins. Finally, all the free-base porphyrins were converted to the corresponding nickel analogues (**9b,d, 10b,d,f,h** and **11c**) *via* the nickel insertion using Ni(OAc)<sub>2</sub>.4H<sub>2</sub>O in AcOH-CHCl<sub>3</sub> mixture under reflux conditions.

### <Insert Scheme 3>

All the synthesized compounds were characterized on the basis of NMR, IR, UV-Vis and mass spectral data in addition to elemental analyses. The proton NMR spectra of newly prepared porphyrin dyads (9a-e, 10a-h and 11a-c) showed a characteristic singlet of one proton in the downfield region between  $\delta$  8.27-9.82 ppm due to a triazole proton and 8  $\beta$ -pyrrolic protons for these porphyrins appeared between  $\delta$  8.62-8.98 ppm as doublets and multiplets. Two *meso*-phenyl protons linked with triazole group were found as a doublet for two protons between  $\delta$  8.15-8.46 ppm whereas 8 *meso*-phenyl protons of *ortho* position were found as doublets and multiplets in the region between  $\delta$  7.91-8.38 ppm. The remaining 9 protons of *meso*-phenyl ring were found as a multiplet between  $\delta$  7.47-7.84 ppm. The aryl protons of coumarin moieties in these compounds were found between  $\delta$  5.83-8.23 ppm. In

the porphyrins **10a-h** and **11a-c**, a characteristic singlet of two protons between  $\delta$  5.20-5.55 ppm was present due to -OCH<sub>2</sub> group. In addition, porphyrin **10g** and **10h** showed a singlet of two protons for the -CH<sub>2</sub>Cl group at  $\delta$  5.00 and 4.56 ppm, respectively. In contrast, the porphyrins (**9a,b,e** and **10a,b,e,f**) showed a singlet between  $\delta$  2.33-2.50 ppm due to three methyl protons of coumarin units. A singlet at about  $\delta$  -2.75 ppm for two protons was assigned as internal NH protons for the porphyrin **11b**. The IR spectrum of the porphyrin **11b** showed a peak at 3317 cm<sup>-1</sup> due to N-H bond stretching. In addition, a characteristic peak at 1677-1736 cm<sup>-1</sup> was found in all newly prepared coumarins as well as porphyrin-coumarin dyads due to C=O bond stretching of coumarin moiety. In addition, the structures of all the newly synthesized products were further supported by the mass spectral data, which showed the molecular ion peak as (M+H)<sup>+</sup>.

### 3.3. Photophysical properties

### 3.3.1. UV-Vis spectroscopy

The electronic absorption spectra of zinc analogues of *meso*-phenyl-triazole bridged porphyrin-coumarin dyads (**9a,c,e, 10a,c,e,g** and **11a**) displayed a strong Soret bands at ~ 427 nm and two weaker Q-bands at ~ 560 and 601 nm similar to the zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**3**). In contrast, their corresponding nickel derivatives (**9b,d**, **10b,d,f,h** and **11c**) have shown blue shifted Soret and a Q-band at 416 and 530 nm, respectively similar to the nickel (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (**Ni-N**<sub>3</sub>). In addition, the free-base porphyrin (**11b**) showed one strong Soret band at 418 nm and four Q-bands at 516, 548, 595 and 647 nm similar to the TPP (Soret band at 419 nm and Q-bands at 516, 550, 595, 647 nm). The UV-Vis absorption spectra of zinc porphyrins (**9a, 10a** and **11a**), nickel porphyrins (**9b, 10b** and **11c**) and free-base porphyrin (**11b**) in DMF are shown in figure 1. Besides the Soret and Q-bands in porphyrins **9a-b** and **10a-b**, some additional peaks were also found at ~ 320 nm due to the presence of coumarin subunits in these

molecules which suggest that there is no significant interaction between the coumarin and porphyrin subunits in the ground state.

#### <Insert Figure 1>

### 3.3.2. Fluorescence spectroscopy

The fluorescence spectra of zinc porphyrins (**9a,c,e, 10a,c,e,g** and **11a**) showed two emission bands at ~ 606 and 659 nm which are slightly intense as compared to the starting porphyrin **3**. The fluorescence bands of nickel porphyrins were found to be very weak under same experimental conditions. In contrast, the two emission bands at ~ 650 and 718 nm were observed for free-base porphyrin (**11b**). The emission spectra of zinc porphyrins (**9a, 10a** and **11a**) and free-base porphyrin (**11b**) in DMF are shown in figure 2.

### <Insert Figure 2>

Further, in order to analyze the energy transfer behaviour of porphyrin-coumarin dyads (9a,c and 10a,c), their absorption and emission spectra have been studied. Figure 3a showed the emission spectra of coumarins 7a,b and porphyrins 9a,c following 320 nm excitation. It was observed that the fluorescence intensities of coumarin moiety of porphyrins 9a and 9c at ~ 400 nm and porphyrin subunit at ~ 606 and 659 nm have been increased after the formation of 1,2,3-triazole ring as compared to Zn-TPP. Thus, it was concluded that there is an efficient and rapid intramolecular energy transfer between the porphyrin ring and coumarin subunit in the porphyrin dyads 9a and 9c. Further, a significant overlapping of the fluorescence spectrum of 7-ethynyl-4-methyl-chromen-2-one (7a) with the absorption spectrum of porphyrin 9a (Figure 3b) also support the above statement as it fulfils the first condition of energy transfer [47].

<Insert Figure 3>

Interestingly, in the case of porphyrins (**10a**) and (**10c**) as shown in figure 4a, the fluorescence at ~ 400 nm due to coumarin moiety is completely quenched on excitation of porphyrins (**10a**) and (**10c**) at 320 nm and there is an increase in the intensity of fluorescence bands of these porphyrin dyads at ~ 606 and 659 nm with respect to Zn-TPP. In addition, a significant overlapping of absorption spectrum of porphyrin (**10a**) and fluorescence spectrum of 4-methyl-7-prop-2-ynyloxy-chromen-2-one (**8a**) was occurred which also revealed an intramolecular energy transfer from coumarin subunit to the porphyrin core (Figure 4b).

<Insert Figure 4>

### 4. Conclusions

In summary, we have successfully synthesized and characterized five novel coumarin analogues as starting materials for the synthesis of target porphyrin-coumarin hybrids. Further, *meso*-phenyl-triazole bridged porphyrin-coumarin dyads were prepared in 67-95% isolated yields by combining the porphyrin, 1,2,3-triazole and coumarin moieties in a single molecular framework *via* copper (I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction. On photophysical investigation, a significant intramolecular energy transfer was observed between coumarin and porphyrin subunits in some of these hybrid molecules. The results presented in this paper are significantly encouraging and henceforth may be useful for designing of new porphyrin-coumarin hybrid materials for various applications including light harvesting and photodynamic agents for photodynamic therapy applications.

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### References

- [1] Paula RD, Simões MMQ, Neves MGPMS, Cavaleiro JAS. Homogeneous olefin epoxidation catalysed by an imidazolium-based manganese porphyrin. Catalysis Communications 2008;10:57-60.
- [2] Paula RD, Simões MMQ, Neves MGPMS, Cavaleiro JAS. Oxidation of styrene and of some derivatives with H<sub>2</sub>O<sub>2</sub> catalyzed by novel imidazolium-containing manganese porphyrins: A mechanistic and thermodynamic interpretation. Journal of Molecular Catalysis A: Chemical 2011;345:1-11.
- [3] Torre G de la, Vázquez P, Agulló-López F, Torres T. Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds. Chemical Review 2004;104:3723-3750.
- [4] Gautam P, Dhokale B, Shukla V, Singh CP, Bindra KS, Misra R. Optical limiting performance of *meso*-tetraferrocenyl porphyrin and its metal derivatives. Journal of Photochemistry and Photobiology A: Chemistry 2012;239:24-27.
- [5] Suslick KS, Watson RA. The photochemistry of chromium, manganese, and iron porphyrin complexes. New Journal of Chemistry 1992;16:633-642.
- [6] Gervaldo M, Liddell PA, Kodis G, Brennan BJ, Johnson CR, Bridgewater JW, et al.
  A photo- and electrochemically active porphyrin–fullerene dyad electropolymer.
  Photochemical and Photobiological Sciences 2010;9:890-900.
- [7] Ethirajan M, Chen Y, Joshi P, Pandey RK. The role of porphyrin chemistry in tumor imaging and photodynamic therapy. Chemical Society Review 2011;40:340-362.

- [8] Gilday LC, White NG, Beer PD. Triazole- and triazolium-containing porphyrin-cages for optical anion sensing. Dalton Transactions 2012;41:7092-7097.
- [9] Sharma R, Gautam P, Mishra R, Shukla SK.  $\beta$ -Substituted triarylborane appended porphyrins: Photophysical properties and anion sensing. RSC Advances 2015;5:27069-27074.
- [10] Liu Z-B, Xu Y-F, Zhang X-Y, Zhang X-L, Chen Y-S, Tian J-G. Porphyrin and fullerene covalently functionalized graphene hybrid materials with large nonlinear optical properties. Journal of Physical. Chemistry B 2009;113:9681-9686.
- [11] Misra R, Gautam P. Meso-tetrakis(ferrocenylethynylphenyl) porphyrins: Synthesis and Properties. Journal of Organometallic Chemistry 2015;776:83-88.
- [12] Li B, Li J, Fu Y, Bo Z. Porphyrins with four monodisperse oligofluorene arms as efficient red light-emitting materials. Journal of American Chemical Society 2004;126:3430-3431.
- [13] Sharma R, Gautam P, Mobin SM. Misra R. β-Substituted ferrocenyl porphyrins: Synthesis, structure, and properties. Dalton Transactions 2013;42:5539-5545.
- [14] Evans RA. The Rise of azide-alkyne 1,3-dipolar 'click' cycloaddition and its application to polymer science and surface modification. Australian Journal of Chemistry 2007;60:384-395.
- [15] Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. A stepwise Huisgen cycloaddition process: copper (I)-catalyzed regioselective ligation of azides and terminal alkynes. Angewandte Chemie International Edition 2002;41:2596-2599.
- [16] Fazio MA, Lee OP, Schuster DI. First triazole-linked porphyrin-fullerene dyads.Organic Letters 2008;10:4979-4982.

- [17] Flavin K, Chaur MN, Echegoyen L, Giordani S. Functionalization of multilayer fullerenes (carbon nano-onions) using diazonium compounds and "click" chemistry. Organic Letters 2010;12:840-843.
- [18] Miguel GD, Wielopolski M, Schuster DI, Fazio MA, Lee OP et al. Triazole bridges as versatile linkers in electron donor-acceptor conjugates. Journal of American Chemical Society 2011;133:13036-13054.
- [19] Shetti VS, Ravikanth M. Synthesis of triazole-bridged unsymmetrical porphyrin dyads and porphyrin-ferrocene conjugates. European Journal of Organic Chemistry 2010;494-508.
- [20] Locos OB, Heindl CC, Corral A, Senge MO, Scanlan EM. Efficient synthesis of glycoporphyrins by microwave-mediated "click" reaction. European Journal of Organic Chemistry 2010;1026-1028.
- [21] Séverac M, Pleux LL, Scarpaci A, Blart E, Odobel F. Synthesis of new azido porphyrins and their reactivity in copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction with alkynes. Tetrahedron Letters 2007; 48:6518-6522.
- [22] Palacin T, Khanh HL, Jousselme B, Jegou P, Filoramo A, Ehli C et al. Efficient functionalization of carbon nanotubes with porphyrin dendrons via click chemistry. Journal of American Chemical Society 2009;131:15394-15402.
- [23] Beamish TB, Dyllick R. Stable aqueous dispersions of fluorescent brightening agents of the coumarine type and method of preparing same. US005122304 (A), June 16, 1992.
- [24] Ren X, Kondakova ME, Giesen DJ, Rajeswaran M, Madaras M, Lenhart WC. Coumarin-based, electron-trapping iridium complexes as highly efficient and stable phosphorescent emitters for organic light-emitting diodes. Inorganic Chemistry 2010;49:1301-1303.

- [25] Kim S, Lee KJ, Kim B, Lee J, Kay K-Y, Park J. New ambipolar blue emitting materials based on amino coumarin derivatives with high efficiency for organic light emitting diodes. Journal of Nanoscience and Nanotechnology 2013;13:8020-8024.
- [26] Song Z-K, Dong B, Lei G-J, Peng M-J, Guo Y. Novel selective fluorescent probes for sensing Zn<sup>2+</sup> ions based on a coumarin Schiff-base. Tetrahedron Letters 2013;54:4945-4949.
- [27] Bazzicalupi C, Caltagirone C, Cao Z, Chen Q, Natale CD, Garau A. Multimodal use of new coumarin-based fluorescent chemosensors: Towards highly selective optical sensors for Hg<sup>2+</sup> probing. Chemistry of European Journal 2013;19:14639-14653.
- [28] Gilat SL, Adronov A, Fréchet JMJ, Ohta K, Neuwahl FVR, Fleming GR. Light harvesting and energy transfer in novel convergently constructed dendrimers. Angewandte Chemie International Edition 1999;38:1422-1427.
- [29] Trenor SR, Shultz AR, Love BJ, Long TE. Coumarins in polymers: From light harvesting to photo-cross-linkable tissue scaffolds. Chemical Review 2004;104:3059-3077.
- [30] Lindsay G, Henry RA, Hoover JM, Coumarin dyes and side-chain coumarin dyesubstituted polymers which exhibit nonlinear optical properties. US005286803(A), Feb. 15, 1994.
- [31] Rong L, Liu L-H, Chen S, Cheng H, Chen C-S, Li Z-Y, Qin S-Y, Zhang X-Z. A coumarin derivative as a fluorogenic glycoproteomic probe for biological imaging. Chemical Communication 2014;50:667-669.
- [32] Key JA, Koh S, Timerghazin QK, Brown A, Cairo CW. Photophysical characterization of triazole-substituted coumarin fluorophores. Dyes and Pigments 2009;82:196-203.

- [33] Lin W, Long L, Feng J, Wang B, Guo C. Synthesis of *meso*-Coumarin-conjugated porphyrins and investigation of their luminescence properties. European Journal of Organic Chemistry 2007;4301-4304.
- [34] Mao M, Song Q-H. Non-conjugated dendrimers with a porphyrin core and coumarin chromophores as peripheral units: Synthesis and photophysical properties. Dyes and Pigments 2012;92:975-981.
- [35] Hania PR, Heijs DJ, Bowden T, Pugžlys A, Esch JV, Knoester J, Duppen K. Ultrafast energy transport in a first-generation coumarin-tetraphenylporphyrin dendrimer. Journal of Physical Chemistry B 2004;108:71-81.
- [36] Sharma S, Nath M. Synthesis and spectroscopic properties of *meso*-substituted quinoxalinoporphyrins. New Journal of Chemistry 2011;35:1630-1639.
- [37] Sharma S, Nath M. Novel 5-benzazolyl-10,15,20-triphenylporphyrins and  $\beta$ ,*meso*-benzoxazolylbridged porphyrin dyads: Synthesis, characterization and photophysical properties. Dyes and Pigments 2012;92:1241-1249.
- [38] Bhatt RK, Singh DK, Nath M. Synthesis and characterization of *meso*-substituted triazonoporphyrins. Journal of Indian Chemical Society 2013;90:1493-1496.
- [39] Singh DK, Nath M. First synthesis of *meso*-substituted pyrrolo[1,2*a*]quinoxalinoporphyrins. Beilstein Journal of Organic Chemistry 2014;10:808-813.
- [40] Bailly C, Bal C, Barbier P, Combes S, Finet J-P, Hildebrand M-P, Peyrot V, Wattez N. Synthesis and biological evaluation of 4-arylcoumarin analogues of combretastatins. Journal of Medicinal Chemistry 2003;46:5437-5444.
- [41] Breed DR, Thibault R, Xie F, Wang Q, Hawker CJ, Pine DJ. Functionalization of polymer microspheres using click chemistry. Langmuir 2009;25:4370-4376.

- [42] Chtchigrovsky M, Primo A, Gonzalez P, Molvinger K et al. Functionalized chitosan as a green, recyclable, biopolymer-supported catalyst for the [3+2] Huisgen cycloaddition, Angewandte Chemie International Edition 2009;48:5916-5920.
- [43] Jeon M-K, Kang M-K, Park KH. 7-Triazolylcoumarin-based fluorescent tag system for stepwise, comparative assessment of small molecule microarrays. Tetrahedron 2012;68:6038-6053.
- [44] Kosiova I, Kovackova S, Kois P. Synthesis of coumarin-nucleoside conjugates via Huisgen 1,3-dipolar cycloaddition. Tetrahedron 2007;63:312-320.
- [45] Rao CP, Srimannarayana G. Claisen rearrangement of 4-propargloxycoumarins: Formation of 2*H*,5*H*-pyrano[3,2-c][1]benzopyran-5-ones. Synthetic Communications 1990;20:535-540.
- [46] Shen D-M, Liu C, Chen Q-Y. Synthesis and versatile reactions of  $\beta$ -azidotetraarylporphyrins. European Journal of Organic Chemistry 2007;1419-1422.
- [47] Leibowitz M. Remarks on forster's theory of transfer of excitation energy. Journal of Physical Cemistry 1965; 69:1061-1062.

#### **Captions for schemes and figures:**

- Scheme 1. Synthesis of zinc (II) 5-(4-azidophenyl)-10,15,20-triphenylporphyrin (3)
- Scheme 2. Synthesis of coumarinoalkynes (7a-c) and (8a-e)
- Scheme 3. Synthesis of *meso*-phenyl-triazole bridged porphyrin-coumarin dyads. Reagents and conditions (i): CuSO<sub>4</sub>.5H<sub>2</sub>O, ascorbic acid, DMF, 80 °C, (ii): Conc. HCl, CHCl<sub>3</sub>, 25 °C, (iii): Ni(OAc)<sub>2</sub>.4H<sub>2</sub>O, CHCl<sub>3</sub>-AcOH, reflux.
- Figure 1. Electronic absorption spectra of porphyrins 3 (Zn-N<sub>3</sub>), Ni-N<sub>3</sub>, 9a-b, 10a-b, and 11ac) in DMF ( $2 \times 10^{-6}$  mol L<sup>-1</sup>) at 298 K and Inset shows the Q bands.
- Figure 2. Fluorescence spectra of porphyrins 3 (Zn-N<sub>3</sub>), 9a, 10a, and 11a-b in DMF ( $2 \times 10^{-6}$  mol L<sup>-1</sup>) at 298 K,  $\lambda_{ex} = 420$  nm.
- Figure 3. (a) Fluorescence spectra of coumarins 7a,b, porphyrins 9a,c and Zn-TPP in DMF (2  $\times 10^{-6}$  mol L<sup>-1</sup>) at 298 K,  $\lambda_{ex} = 320$  nm. (b) UV-Vis spectrum of porphyrin 9a and fluorescence spectrum of 7-ethynyl-4-methyl-chromen-2-one 7a ( $\lambda_{ex} = 320$  nm) in DMF.
- Figure 4. (a) Fluorescence spectra of 8a-b, porphyrins 10a,c and Zn-TPP in DMF ( $2 \times 10^{-6}$  mol L<sup>-1</sup>) at 298 K,  $\lambda_{ex} = 320$  nm. (b) UV-Vis spectrum of porphyrin 10a and fluorescence spectrum of 4-methyl-7-prop-2-ynyloxy-chromen-2-one 8a ( $\lambda_{ex} = 320$  nm) in DMF.



Scheme 1.










## Highlights

- 1. Diverse coumarinoalkynes have been synthesized in good yields.
- 2. A modified and high yielding procedure for 5-(4-azidophenyl)-10,15,20triphenylporphyrin has been developed.
- 3. An efficient methodology for the synthesis of novel *meso*-phenyl-triazole bridged porphyrin-coumarin dyads is described by using copper (I) catalyzed Huisgen 1,3-dipolar cycloaddition reaction.
- 4. Photophysical studies revealed an efficient intramolecular energy-transfer between porphyrin and coumarin scaffolds.

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### SUPPLEMENTARY DATA

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

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Figure 1. <sup>1</sup>H NMR spectrum of compound 2 in CDCl<sub>3</sub>.



Figure 2. <sup>13</sup>C NMR spectrum of compound 2 in CDCl<sub>3</sub>.



Figure 3. <sup>1</sup>H NMR spectrum of compound 5c in CDCl<sub>3</sub>.



Figure 4. <sup>13</sup>C NMR spectrum of compound 5c in CDCl<sub>3</sub>.



**Figure 5.** <sup>1</sup>H NMR spectrum of compound **6c** in CDCl<sub>3</sub>.



Figure 6. <sup>13</sup>C NMR spectrum of compound 6c in CDCl<sub>3</sub>.



Figure 7. <sup>1</sup>H NMR spectrum of compound 7c in CDCl<sub>3</sub>.



Figure 8. <sup>13</sup>C NMR spectrum of compound 7c in CDCl<sub>3</sub>.



Figure 9. <sup>1</sup>H NMR spectrum of compound 8c in CDCl<sub>3</sub>.



Figure 10. <sup>13</sup>C NMR spectrum of compound 8c in CDCl<sub>3</sub>.



Figure 11. <sup>1</sup>H NMR spectrum of compound 8d in CDCl<sub>3</sub>.



Figure 12. <sup>13</sup>C NMR spectrum of compound 8d in CDCl<sub>3</sub> + DMSO-d<sub>6</sub>.



Figure 13. <sup>1</sup>H NMR spectrum of compound 9a in DMSO-d<sub>6</sub>.



Figure 14. <sup>13</sup>C NMR spectrum of compound 9a in DMSO-d<sub>6</sub>.



Figure 15. <sup>1</sup>H NMR spectrum of compound 9b in CDCl<sub>3</sub>.



Figure 16. <sup>1</sup>H NMR spectrum of compound 9c in DMSO-d<sub>6</sub>.



Figure 17. <sup>13</sup>C NMR spectrum of compound 9c in DMSO-d<sub>6</sub>.



Figure 18. <sup>1</sup>H NMR spectrum of compound 9d in CDCl<sub>3</sub>.



Figure 19. <sup>13</sup>C NMR spectrum of compound 9d in CDCl<sub>3</sub>.



Figure 20. <sup>1</sup>H NMR spectrum of compound 9e in CDCl<sub>3</sub> + DMSO-d<sub>6</sub>.



Figure 21. <sup>13</sup>C NMR spectrum of compound 9e in  $CDCl_3 + DMSO-d_6$ .



Figure 22. <sup>1</sup>H NMR spectrum of compound 10a in DMSO-d<sub>6</sub>.



Figure 23. <sup>1</sup>H NMR spectrum of compound 10b in CDCl<sub>3</sub>.



Figure 24. <sup>13</sup>C NMR spectrum of compound 10b in CDCl<sub>3</sub>.



Figure 25. <sup>1</sup>H NMR spectrum of compound 10c in DMSO-d<sub>6</sub>.

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Figure 26. <sup>13</sup>C NMR spectrum of compound 10c in DMSO-d<sub>6</sub>.



Figure 27. <sup>1</sup>H NMR spectrum of compound 10d in CDCl<sub>3</sub>.



Figure 28. <sup>1</sup>H NMR spectrum of compound 10e in CDCl<sub>3</sub> + DMSO-d<sub>6</sub>.



Figure 29. <sup>1</sup>H NMR spectrum of compound 10f in CDCl<sub>3</sub>.



Figure 30. <sup>13</sup>C NMR spectrum of compound 10f in CDCl<sub>3</sub>.



Figure 31. <sup>1</sup>H NMR spectrum of compound 10g in DMSO-d<sub>6</sub>.

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Figure 32. <sup>13</sup>C NMR spectrum of compound 10g in DMSO-d<sub>6</sub>.



Figure 33. <sup>1</sup>H NMR spectrum of compound 10h in CDCl<sub>3</sub>.



Figure 34. <sup>13</sup>C NMR spectrum of compound 10h in CDCl<sub>3</sub>.


Figure 35. <sup>1</sup>H NMR spectrum of compound 11a in CDCl<sub>3</sub>.



Figure 36. <sup>1</sup>H NMR spectrum of compound 11b in CDCl<sub>3</sub>.



Figure 37. <sup>13</sup>C NMR spectrum of compound 11b in CDCl<sub>3</sub>.



Figure 38. <sup>1</sup>H NMR spectrum of compound 11c in CDCl<sub>3</sub>.



Figure 39. <sup>13</sup>C NMR spectrum of compound 11c in CDCl<sub>3</sub>.