

# Synthesis, characterization and photophysical studies of $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads

DILEEP KUMAR SINGH and MAHENDRA NATH\*

Department of Chemistry, University of Delhi, Delhi 110 007, India  
e-mail: mnath@chemistry.du.ac.in

MS received 18 December 2015; revised 9 February 2016; accepted 11 February 2016

**Abstract.** A new series of zinc(II)  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads have been synthesized in appreciable yields through a copper(I)-catalyzed “click” reaction of zinc(II) 2-azidomethyl-5,10,15,20-tetraphenylporphyrin with various benzo- $\alpha$ -pyronoalkynes. These novel zinc(II) porphyrin-benzo- $\alpha$ -pyrone dyads successfully underwent demetallation in the presence of concentrated hydrochloric acid in chloroform at 25°C to form the corresponding free-base porphyrin analogues in good yields. The newly synthesized products were characterized on the basis of spectral data and evaluated for their electronic absorption and fluorescence properties. Some of these molecules have shown a significant intramolecular energy transfer between the benzo- $\alpha$ -pyrone and porphyrin subunits.

**Keywords.** Benzo- $\alpha$ -pyronoalkynes; click reaction; photophysical properties; synthesis; porphyrin-benzo- $\alpha$ -pyrone dyads.

## 1. Introduction

Porphyrins are an important class of  $\pi$ -conjugated heteroaromatic compounds which exhibit promising applications in diverse fields such as supramolecular chemistry,<sup>1</sup> catalysis,<sup>2</sup> biomimetic models for photosynthesis<sup>3</sup> and medicine.<sup>4</sup> Additionally, these molecules have been widely used in the study of various charge-transfer<sup>5</sup> and energy-transfer<sup>6</sup> processes. In the past decades, a large number of porphyrinoids linked with various  $\pi$ -electron rich and biologically relevant chromophores including anthracene,<sup>7</sup> anthraquinone,<sup>8</sup> fluorescein,<sup>9</sup> perylene,<sup>10</sup> fluorene,<sup>11</sup> pyrrolo [1,2-a]quinoxaline,<sup>12</sup> coumarin,<sup>13</sup> quinoline,<sup>14</sup> imidazole,<sup>15</sup> thiazole,<sup>16</sup> and pyrazole<sup>17</sup> have been synthesized through peripheral functionalization involving *meso*- and  $\beta$ -positions of *meso*-tetraarylporphyrins. Among these, the  $\beta$ -substituted porphyrins often demonstrate interesting electronic properties because of direct conjugation of attached scaffold with the 18 $\pi$ -macrocylic system. Similarly, benzo- $\alpha$ -pyrones are known to display unique optical and biological properties<sup>18</sup> and therefore, widely used as fluorescent probes,<sup>19</sup> signaling units in sensors,<sup>20</sup> laser dyes<sup>21</sup> and therapeutic agents.<sup>22</sup>

By considering the photophysical and biological significance of these two classes of heterocycles, our aim was to connect benzo- $\alpha$ -pyrone units to the  $\beta$ -position of *meso*-tetraphenylporphyrins through a 1,2,3-triazole bridge which can be easily constructed by using click reaction<sup>23</sup> and often affords the hybrid molecules with a wide range of applications in medicinal and material chemistry.<sup>24</sup>

Previously, we have synthesized a series of 1,2,3-triazole linked porphyrin-coumarin dyads in good yields<sup>25</sup> by using click chemistry. In these molecules, the triazole-linked coumarin subunits were directly attached to the porphyrin periphery. On photophysical investigation, these molecules have demonstrated a significant bathochromic shift in their electronic absorption spectra and an efficient intramolecular energy transfer between the porphyrin and benzo- $\alpha$ -pyrone chromophores. These results prompted us to investigate the photophysical characteristics of various  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads where the porphyrin and triazole-linked benzo- $\alpha$ -pyrone chromophores are connected by a methylene spacer. Therefore, in continuation of our efforts to develop efficient synthetic strategies for  $\beta$ -functionalized *meso*-tetraphenylporphyrins,<sup>26</sup> we report herein the synthesis, spectroscopic characterization and optical properties of a new series of  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads.

\*For correspondence

## 2. Experimental

### 2.1 Materials and Procedures

The reagents and solvents used in this work were purchased from Sigma-Aldrich Chemical Pvt. Ltd., Bangalore, India and Merck Specialities Pvt. Ltd., Mumbai, India and used without further purification. Thin layer chromatography (TLC) was performed on silica gel 60 F<sub>254</sub> (pre-coated aluminium sheets) from Merck. The synthesized products were purified by column chromatography using either activated neutral aluminium oxide (Brokmann grade I-II, Merck) or silica gel (60-120 mesh). <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 obtained in  $\delta$  scale in parts per million (ppm) relative to CDCl<sub>3</sub> ( $\delta = 7.26$  ppm for <sup>1</sup>H NMR and  $\delta = 77.00$  ppm for <sup>13</sup>C NMR) and DMSO-d<sub>6</sub> ( $\delta = 2.50$  ppm for <sup>1</sup>H NMR and  $\delta = 39.50$  ppm for <sup>13</sup>C NMR). The coupling constants were expressed as (J) and reported in Hertz (Hz). The infrared (IR) spectra of all the synthesized compounds were recorded in film or KBr on Perkin Elmer IR spectrometer and absorption maxima ( $\nu_{\max}$ ) are presented in cm<sup>-1</sup>. The mass spectra (ESI-MS) were recorded on a THERMO Finnigan LCQ Advantage max ion trap mass spectrometer and Agilent G6530 AA LC-HRMS Q-TOF system in positive mode. UV-Vis absorption and fluorescence spectra were measured in spectroscopic grade chloroform by using an Analytik Jena's Specord 250 UV-Vis spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively. Elemental analyses of all compounds were performed on Elementar Analysensysteme GmbH VarioEL elemental analyzer. The melting points of all the newly prepared products were determined by using Buchi M-560 melting point apparatus in open capillary tubes and are uncorrected.

### 2.2 General procedure for the synthesis of zinc(II) $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (**8a,c**, **9a,c,e,g** and **10a**)

To a solution of zinc(II) 2-azidomethyl-5,10,15,20-tetraphenylporphyrin (**4**; 50 mg, 0.068 mmol) in DMF (10 mL), CuSO<sub>4</sub>·5H<sub>2</sub>O (3.5 mg, 0.014 mmol), ascorbic acid (5.0 mg, 0.028 mmol) and benzo- $\alpha$ -pyronoalkynes (0.081 mmol) were added and the reaction mixture was stirred at 80°C for 2 h. The progress of the reaction was monitored by thin layer chromatography. 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 sulfate and evaporated under reduced pressure. The crude product obtained was purified over a neutral alumina column by using 2% methanol in chloroform as eluent.

**2.2a Zinc(II) 4-methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]-triazol-4-yl]-chromen-2-one (8a):** Purple solid; yield: 82%; M.p. >300°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (97.98), 555 (4.02), 601 (1.37) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 609, 651 nm; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 3057, 1683, 1617, 1596, 1440, 1337, 1174, 1068, 1003, 992, 795, 753, 700; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.83 (s, 1H, triazole H), 8.76-8.71 (m, 5H,  $\beta$ -pyrrolic H), 8.60 (d,  $J = 3.66$  Hz, 1H,  $\beta$ -pyrrolic H), 8.18-8.14 (m, 6H, *meso*-ArH), 8.11 (s, 1H,  $\beta$ -pyrrolic H), 8.06-8.04 (m, 2H, *meso*-ArH), 7.87-7.85 (m, 3H, ArH), 7.82-7.77 (m, 9H, *meso*-ArH), 7.61-7.60 (m, 3H, *meso*-ArH), 6.40 (s, 1H, CH), 5.74 (s, 2H, CH<sub>2</sub>), 2.46 (s, 3H, CH<sub>3</sub>); ESI-HRMS (m/z) Calcd. for C<sub>57</sub>H<sub>38</sub>N<sub>7</sub>O<sub>2</sub>Zn: 916.2372 (M+H)<sup>+</sup>; found 916.2361; Anal. Calcd. (%) for C<sub>57</sub>H<sub>37</sub>N<sub>7</sub>O<sub>2</sub>Zn·2H<sub>2</sub>O: C, 71.81; H, 4.33; N, 10.28; found (%): C, 71.78; H, 4.35; N, 10.32.

**2.2b Zinc(II) 7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl]-chromen-2-one (8c):** Purple solid; yield: 83%; M.p. >300°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (87.17), 555 (3.11), 602 (0.67) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 609, 651 nm; IR (film)  $\nu_{\max}$ /cm<sup>-1</sup>: 2919, 1688, 1617, 1384, 1337, 1225, 1068, 1003, 795, 753, 700; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.80 (s, 1H, triazole H), 8.77-8.74 (m, 4H,  $\beta$ -pyrrolic H), 8.73-8.71 (d,  $J = 5.13$  Hz, 1H,  $\beta$ -pyrrolic H), 8.61 (d,  $J = 5.13$  Hz, 1H,  $\beta$ -pyrrolic H), 8.31 (s, 2H, ArH), 8.18-8.14 (m, 6H, *meso*-ArH), 8.13 (s, 1H,  $\beta$ -pyrrolic H), 8.09-8.05 (m, 3H, *meso*-ArH and ArH), 7.87-7.85 (m, 1H, ArH), 7.82-7.79 (m, 9H, *meso*-ArH), 7.62-7.60 (m, 3H, *meso*-ArH), 6.49 (d,  $J = 9.52$  Hz, 1H, CH), 5.75 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 160.02, 154.10, 150.09, 149.66, 149.53, 149.48, 149.36, 146.78, 145.17, 144.88, 143.98, 142.58, 142.46, 142.37, 139.50, 134.22, 134.18, 132.90, 132.46, 132.08, 131.99, 131.91, 131.87, 131.77, 131.36, 129.19, 128.60, 127.58, 127.38, 126.67, 126.37, 123.59, 121.37, 120.95, 120.55, 119.96, 119.80, 118.29, 115.90, 112.35, 79.17; ESI-MS: m/z = 902.2 (M+H)<sup>+</sup>; 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, 72.98; H, 4.15; N, 10.67.

**2.2c Zinc(II) 4-methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]-triazol-4-ylmethoxy]-chromen-2-one (9a):** Purple solid; yield: 88%; M.p.

>300°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (89.67), 555 (3.67), 602 (1.24) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 607, 653 nm; IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3057, 3018, 2919, 2850; 1723, 1612, 1490, 1387, 1343, 1278, 1156, 1071, 1004, 800, 754, 702; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.77-8.72 (m, 5H,  $\beta$ -pyrrolic H), 8.60-8.58 (m, 1H,  $\beta$ -pyrrolic H), 8.28 (s, 1H,  $\beta$ -pyrrolic H), 8.18-8.17 (m, 4H, *meso*-ArH), 8.10 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 8.05-8.03 (m, 3H, *meso*-ArH and ArH), 7.85-7.74 (m, 9H, *meso*-ArH), 7.72-7.64 (m, 4H, *meso*-ArH and triazole H), 7.14 (d,  $J = 2.20$  Hz, 1H, ArH), 7.01 (d,  $J = 8.79$  Hz, 1H, ArH), 6.21 (s, 1H, CH), 5.69 (s, 2H, CH<sub>2</sub>), 5.26 (s, 2H, OCH<sub>2</sub>), 2.37 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 161.04, 160.14, 154.66, 153.40, 150.06, 149.65, 149.50, 149.43, 149.32, 146.77, 144.86, 142.57, 142.44, 142.33, 142.07, 139.86, 134.17, 132.85, 132.23, 132.91, 131.87, 131.77, 131.33, 128.51, 127.57, 127.40, 127.28, 126.66, 126.49, 126.39, 125.54, 120.92, 120.52, 119.89, 119.75, 113.34, 112.70, 111.27, 101.56, 61.53, 49.30, 18.14; ESI-MS:  $m/z = 946.1$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>58</sub>H<sub>39</sub>N<sub>7</sub>O<sub>3</sub>Zn: C, 73.53; H, 4.15; N, 10.35; found (%): C, 73.59; H, 3.98; N, 10.32.

2.2d *Zinc(II) 7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl-methoxy]-chromen-2-one (9c)*: Purple solid; yield: 90%; M.p. >300°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (90.00), 556 (3.76), 601 (1.38) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 608, 650 nm; IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3052, 2921, 1732, 1612, 1440, 1384, 1278, 1119, 1003, 795, 757, 702; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.78-8.73 (m, 5H,  $\beta$ -pyrrolic H), 8.61 (d,  $J = 4.12$  Hz, 1H,  $\beta$ -pyrrolic H), 8.28 (s, 1H,  $\beta$ -pyrrolic H), 8.18-8.17 (m, 4H, *meso*-ArH), 8.12-7.95 (m, 6H, *meso*-ArH and ArH), 7.84-7.74 (m, 9H, *meso*-ArH), 7.70-7.61 (m, 4H, *meso*-ArH and triazole H), 7.16 (s, 1H, ArH), 7.00 (d,  $J = 8.70$  Hz, 1H, ArH), 6.29 (d,  $J = 9.16$  Hz, 1H, CH), 5.70 (s, 2H, CH<sub>2</sub>), 5.26 (s, 2H, OCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 161.14, 160.29, 155.32, 150.07, 149.64, 149.50, 149.44, 149.33, 146.77, 144.88, 144.31, 142.59, 142.44, 142.32, 142.04, 139.84, 134.16, 132.90, 132.26, 132.04, 131.90, 131.80, 131.33, 129.53, 128.53, 127.57, 127.39, 127.31, 126.66, 126.41, 125.54, 120.93, 120.54, 119.90, 119.77, 112.99, 112.65, 112.57, 101.56, 61.55; ESI-MS:  $m/z = 932.2$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>57</sub>H<sub>37</sub>N<sub>7</sub>O<sub>3</sub>Zn.2H<sub>2</sub>O: C, 70.62; H, 4.26; N, 10.11; found (%): C, 70.61; H, 4.32; N, 10.27.

2.2e *Zinc(II) 6-chloro-4-methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one (9e)*: Purple solid; yield: 89%;

M.p. >300°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (88.44), 555 (3.59), 602 (1.22) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 605, 651 nm; IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 2922, 1731, 1607, 1384, 1275, 1156, 1056, 1004, 795, 753, 702; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.77-8.70 (m, 5H,  $\beta$ -pyrrolic H), 8.59-8.57 (m, 1H,  $\beta$ -pyrrolic H), 8.27 (s, 1H,  $\beta$ -pyrrolic H), 8.18-8.16 (m, 4H, *meso*-ArH), 8.10-8.07 (m, 3H, *meso*-ArH and ArH), 8.04-8.02 (m, 2H, *meso*-ArH), 7.85-7.73 (m, 10H, *meso*-ArH and triazole H), 7.65-7.63 (m, 3H, *meso*-ArH), 7.47 (s, 1H, ArH), 6.27 (s, 1H, CH), 5.71 (s, 2H, CH<sub>2</sub>), 5.35 (s, 2H, OCH<sub>2</sub>), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 159.75, 155.88, 153.17, 150.08, 149.62, 149.50, 149.42, 149.33, 147.36, 147.26, 146.76, 144.91, 144.56, 143.59, 142.58, 142.43, 141.51, 139.61, 134.16, 132.87, 132.05, 131.78, 131.34, 127.56, 127.23, 126.66, 126.38, 125.97, 120.90, 120.52, 119.79, 117.80, 115.51, 112.23, 111.10, 102.14, 100.59, 62.54, 18.16; ESI-MS:  $m/z = 980.0$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>58</sub>H<sub>38</sub>ClN<sub>7</sub>O<sub>3</sub>Zn.H<sub>2</sub>O: C, 69.67; H, 4.03; N, 9.81; found (%): C, 69.63; H, 3.97; N, 9.88.

2.2f *Zinc(II) 4-chloromethyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one (9g)*: Purple solid; yield: 87%; M.p. >300°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (65.51), 553 (2.46), 602 (0.76) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 607, 651 nm; IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 2919, 1627, 1263, 1069, 1003, 795, 753; ESI-MS:  $m/z = 980.0$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>58</sub>H<sub>38</sub>ClN<sub>7</sub>O<sub>3</sub>Zn.2H<sub>2</sub>O: C, 68.44; H, 4.16; N, 9.63; found (%): C, 68.34; H, 4.21; N, 9.60.

2.2g *Zinc(II) 4-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl-methoxy]-chromen-2-one (10a)*: Purple solid; yield: 90%; M.p. 234-236°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 427 (92.91), 556 (3.45), 602 (1.04) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 609, 653 nm; IR (film)  $\nu_{\max}/\text{cm}^{-1}$ : 3055, 2925, 1718, 1618, 1339, 1237, 1106, 1070, 1003, 795, 751, 701; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.92-8.90 (m, 3H,  $\beta$ -pyrrolic H), 8.87 (d,  $J = 5.13$  Hz, 1H,  $\beta$ -pyrrolic H), 8.84 (d,  $J = 4.39$  Hz, 1H,  $\beta$ -pyrrolic H), 8.61 (d,  $J = 4.39$  Hz, 1H,  $\beta$ -pyrrolic H), 8.20 (s, 1H,  $\beta$ -pyrrolic H), 8.19-8.16 (m, 4H, *meso*-ArH), 7.99 (d,  $J = 6.59$  Hz, 2H, *meso*-ArH), 7.82 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 7.76 (s, 1H, triazole H), 7.75-7.68 (m, 6H, *meso*-ArH), 7.59 (d,  $J = 7.32$  Hz, 1H, ArH), 7.54-7.47 (m, 4H, *meso*-ArH), 7.42-7.37 (m, 2H, *meso*-ArH), 7.16 (d,  $J = 7.69$  Hz, 1H, ArH), 7.06-7.04 (m, 2H, ArH), 5.50 (s, 1H, CH), 5.29 (s, 2H, CH<sub>2</sub>), 4.29 (s, 2H, OCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 164.35,

161.58, 152.84, 150.08, 149.63, 149.50, 149.43, 149.33, 146.78, 144.86, 142.57, 142.44, 142.34, 140.97, 139.95, 134.16, 134.09, 132.91, 132.04, 131.98, 131.90, 131.80, 131.75, 131.25, 128.54, 127.57, 127.33, 126.65, 126.29, 126.04, 124.22, 122.85, 120.94, 120.55, 119.90, 119.71, 116.53, 115.17, 91.33, 62.65; 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: C, 73.35; H, 4.00; N, 10.50; found (%): C, 73.62; H, 3.86; N, 10.31.

### 2.3 General procedure for the synthesis of free-base $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (**8b,d**, **9b,d,f,h** and **10b**)

To a solution of zinc(II)  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (50 mg) in CHCl<sub>3</sub> (10 mL), conc. HCl (200  $\mu$ L) was added and the reaction mixture was stirred at room temperature for 15 min. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the mixture was washed thoroughly with water (50 mL  $\times$  3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified over neutral alumina column by using chloroform as eluent.

**2.3a 4-Methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl]-chromen-2-one (8b):** Purple solid; yield: 72%; M.p. 258-260°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 422 (90.39), 518 (5.04), 542 (1.76), 599 (1.16), 648 (1.41) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 656, 720 nm; IR (film)  $\nu_{\max}$ /cm<sup>-1</sup>: 3317, 2920, 1725, 1612, 1351, 1222, 965, 800, 752, 702; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.88-8.80 (m, 5H,  $\beta$ -pyrrolic H), 8.67 (s, 1H,  $\beta$ -pyrrolic H), 8.45 (s, 1H,  $\beta$ -pyrrolic H), 8.22-8.19 (m, 4H, *meso*-ArH), 8.13 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 8.06 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 7.85-7.70 (m, 9H, *meso*-ArH), 7.68-7.65 (m, 3H, *meso*-ArH), 7.63 (s, 1H, ArH), 7.53 (s, 1H, triazole H), 7.50-7.48 (m, 2H, ArH), 6.19 (s, 1H, CH), 5.80 (s, 2H, CH<sub>2</sub>), 2.35 (s, 3H, CH<sub>3</sub>), -2.73 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.59, 153.71, 151.88, 145.60, 141.91, 141.79, 141.62, 141.17, 134.57, 134.52, 134.17, 133.15, 128.93, 127.94, 127.83, 127.60, 126.80, 126.71, 126.64, 124.86, 121.35, 121.11, 120.74, 120.56, 120.17, 119.24, 114.24, 114.68, 113.42, 18.42; ESI-MS:  $m/z = 854.2$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>57</sub>H<sub>39</sub>N<sub>7</sub>O<sub>2</sub>.H<sub>2</sub>O: C, 78.51; H, 4.74; N, 11.24; found (%): C, 78.56; H, 4.48; N, 11.36.

**2.3b 7-[1-(5,10,15,20-Tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl]-chromen-2-one (8d):** Purple solid; yield: 75%; M.p. 255-257°C; UV-Vis (CHCl<sub>3</sub>)

$\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 422 (95.38), 518 (5.22), 545 (1.70), 600 (1.11), 648 (1.37) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 658, 719 nm; IR (film)  $\nu_{\max}$ /cm<sup>-1</sup>: 3328, 3057, 3018, 2919, 2850, 1734, 1618, 1458, 1350, 1218, 1072, 965, 800, 754, 702; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.88-8.80 (m, 5H,  $\beta$ -pyrrolic H), 8.67 (d,  $J = 4.39$  Hz, 1H,  $\beta$ -pyrrolic H), 8.45 (s, 1H,  $\beta$ -pyrrolic H), 8.22-8.19 (m, 4H, *meso*-ArH), 8.13 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 8.05 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 7.83-7.70 (m, 9H, *meso*-ArH), 7.68-7.63 (m, 3H, *meso*-ArH), 7.60-7.56 (m, 2H, ArH and triazole H), 7.52-7.50 (m, 2H, ArH), 7.36 (d,  $J = 8.05$  Hz, 2H, ArH), 6.32 (d,  $J = 9.52$  Hz, 1H, CH), 5.80 (s, 2H, CH<sub>2</sub>), -2.73 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.58, 154.31, 145.60, 142.87, 141.90, 141.78, 141.60, 141.15, 134.56, 134.51, 134.30, 133.14, 128.93, 128.14, 127.94, 127.84, 127.59, 126.80, 126.71, 126.64, 121.65, 121.12, 120.74, 120.56, 120.17, 119.23, 118.16, 116.22, 113.32; ESI-MS:  $m/z = 840.1$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>56</sub>H<sub>37</sub>N<sub>7</sub>O<sub>2</sub>: C, 80.08; H, 4.44; N, 11.67; found (%): C, 80.16; H, 4.42; N, 11.58.

**2.3c 4-Methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-yl-methoxy]-chromen-2-one (9b):** Purple solid; yield: 73%; M.p. 265-267°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 421 (83.55), 517 (4.58), 542 (1.49), 598 (0.82), 648 (1.16) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 656, 721 nm; IR (film)  $\nu_{\max}$ /cm<sup>-1</sup>: 3328, 1718, 1611, 1387, 1277, 1198, 1145, 1071, 1001, 965, 800, 752, 702; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.88-8.82 (m, 5H,  $\beta$ -pyrrolic H), 8.66 (d,  $J = 5.13$  Hz, 1H,  $\beta$ -pyrrolic H), 8.36 (s, 1H,  $\beta$ -pyrrolic H), 8.22-8.19 (m, 4H, *meso*-ArH), 8.12 (d,  $J = 6.22$  Hz, 2H, *meso*-ArH), 8.02 (d,  $J = 6.59$  Hz, 2H, *meso*-ArH), 7.83-7.66 (m, 12H, *meso*-ArH), 7.39-7.38 (m, 1H, ArH), 7.36 (s, 1H, triazole H), 6.82-6.80 (m, 2H, ArH), 6.07 (s, 1H, CH), 5.75 (s, 2H, CH<sub>2</sub>), 5.12 (s, 2H, OCH<sub>2</sub>), 2.30 (s, 3H, CH<sub>3</sub>), -2.75 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 161.05, 161.02, 154.96, 152.26, 142.47, 141.91, 141.80, 141.62, 141.14, 134.56, 134.53, 134.49, 133.07, 128.93, 127.91, 127.84, 127.57, 126.79, 126.71, 126.63, 125.46, 123.41, 120.72, 120.54, 120.09, 119.21, 113.83, 112.20, 112.11, 101.97, 18.51; ESI-MS:  $m/z = 884.3$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>58</sub>H<sub>41</sub>N<sub>7</sub>O<sub>3</sub>.H<sub>2</sub>O: C, 77.23; H, 4.81; N, 10.87; found (%): C, 77.36; H, 4.72; N, 10.63.

**2.3d 7-[1-(5,10,15,20-Tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one (9d):** Purple solid; yield: 74%; M.p. 262-264°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 421 (74.97), 517 (4.24), 540 (2.07), 600 (0.95), 648 (1.27) nm;  $\lambda_{\text{Em}}$

(CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 656, 720 nm; IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3327, 1734, 1611, 1349, 1276, 1228, 1121, 1002, 832, 800, 752, 702; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.87-8.81 (m, 5H,  $\beta$ -pyrrolic H), 8.65 (d,  $J = 4.58$  Hz, 1H,  $\beta$ -pyrrolic H), 8.36 (s, 1H,  $\beta$ -pyrrolic H), 8.21-8.18 (m, 4H, *meso*-ArH), 8.12 (d,  $J = 7.34$  Hz, 2H, *meso*-ArH), 8.01 (d,  $J = 7.34$  Hz, 2H, *meso*-ArH), 7.82-7.66 (m, 12H, *meso*-ArH), 7.52 (d,  $J = 9.17$  Hz, 1H, ArH), 7.35 (s, 1H, triazole H), 7.24-7.23 (m, 1H, ArH), 6.81-6.78 (m, 2H, ArH), 6.19 (d,  $J = 6.19$  Hz, 1H, CH), 5.75 (s, 2H, CH<sub>2</sub>), 5.12 (s, 2H, OCH<sub>2</sub>), -2.76 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 161.21, 160.95, 155.57, 143.11, 142.42, 141.92, 141.81, 141.63, 141.13, 134.56, 134.54, 134.50, 133.09, 132.47, 130.71, 130.45, 130.28, 128.94, 128.65, 127.92, 127.84, 127.59, 126.80, 126.73, 126.64, 123.41, 120.73, 120.56, 120.10, 119.22, 113.31, 112.53, 101.98, 62.18; ESI-MS:  $m/z = 870.2$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>57</sub>H<sub>39</sub>N<sub>7</sub>O<sub>3</sub>: C, 78.69; H, 4.52; N, 11.27; found (%): C, 78.67; H, 4.43; N, 10.98.

**2.3e 6-Chloro-4-methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one (9f):** Purple solid; yield: 76%; M.p. 210-212°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 421 (71.71), 517 (3.78), 540 (1.84), 602 (0.60), 648 (0.95) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 657, 720 nm; IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3327, 3058, 2922, 2851, 1729, 1607, 1492, 1382, 1274, 1158, 1081, 1003, 965, 800, 753, 703; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.82-8.79 (m, 6H,  $\beta$ -pyrrolic H), 8.63 (s, 1H,  $\beta$ -pyrrolic H), 8.20-8.17 (m, 4H, *meso*-ArH), 8.08-8.07 (m, 5H, *meso*-ArH and ArH), 7.82-7.68 (m, 13H, *meso*-ArH and triazole H), 7.38 (s, 1H, ArH), 6.20 (s, 1H, CH), 5.72 (s, 2H, CH<sub>2</sub>), 5.29 (s, 2H, OCH<sub>2</sub>), 2.32 (s, 3H, CH<sub>3</sub>), -2.93 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.28, 156.01, 153.12, 151.12, 141.93, 141.79, 141.63, 141.11, 134.56, 134.53, 133.13, 132.31, 130.70, 130.29, 128.93, 127.92, 127.81, 127.59, 127.22, 126.79, 126.71, 126.65, 123.68, 120.68, 120.52, 120.12, 119.27, 118.95, 113.79, 112.84, 101.41, 63.15, 49.84, 18.28; ESI-HRMS ( $m/z$ ) Calcd. for C<sub>58</sub>H<sub>41</sub>ClN<sub>7</sub>O<sub>3</sub>: 918.2953 (M+H)<sup>+</sup>; found 918.2961; Anal. Calcd. (%) for C<sub>58</sub>H<sub>40</sub>ClN<sub>7</sub>O<sub>3</sub>: C, 75.85; H, 4.39; N, 10.68; found (%): C, 75.89; H, 4.28; N, 10.72.

**2.3f 4-Chloromethyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one (9h):** Purple solid; yield: 69%; M.p. 246-248°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 421 (73.26), 517 (3.87), 541 (1.63), 602 (0.63), 647 (0.96) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 656, 720 nm; IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3326, 2920, 2850, 1718, 1604,

1376, 1263, 1136, 1072, 799, 701; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.87-8.81 (m, 5H,  $\beta$ -pyrrolic H), 8.65 (d,  $J = 5.50$  Hz, 1H,  $\beta$ -pyrrolic H), 8.37 (s, 1H,  $\beta$ -pyrrolic H), 8.22-8.18 (m, 4H, *meso*-ArH), 8.12 (d,  $J = 7.34$  Hz, 2H, *meso*-ArH), 8.01 (d,  $J = 7.34$  Hz, 2H, *meso*-ArH), 7.80-7.66 (m, 12H, *meso*-ArH), 7.44-7.35 (m, 2H, ArH and triazole H), 6.84-6.81 (m, 2H, ArH), 6.32 (s, 1H, CH), 5.75 (s, 2H, CH<sub>2</sub>), 5.13 (s, 2H, OCH<sub>2</sub>), 4.48 (s, 2H, CH<sub>2</sub>Cl), -2.76 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 161.33, 160.46, 155.37, 149.28, 142.30, 141.91, 141.81, 141.62, 141.13, 134.56, 134.54, 134.50, 133.08, 130.79, 130.61, 130.37, 128.94, 127.91, 127.85, 127.58, 127.25, 126.80, 126.73, 126.64, 125.01, 123.46, 120.74, 120.57, 120.10, 119.22, 112.74, 112.58, 110.96, 102.32, 101.99, 62.19, 62.12; ESI-MS:  $m/z = 918.2$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>58</sub>H<sub>40</sub>ClN<sub>7</sub>O<sub>3</sub>.H<sub>2</sub>O: C, 74.39; H, 4.52; N, 10.47; found (%): C, 74.28; H, 4.47; N, 10.51.

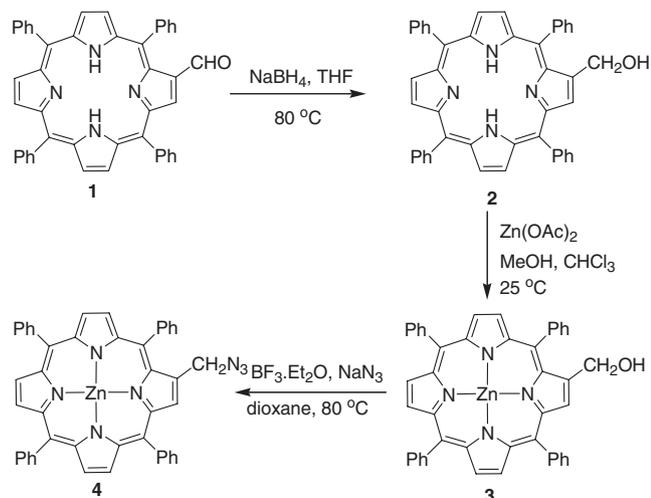
**2.3g 4-[1-(5,10,15,20-Tetraphenylporphyrin-2-ylmethyl)-1H-[1,2,3]triazol-4-ylmethoxy]-chromen-2-one (10b):** Purple solid; yield: 79%; M.p. 262-264°C; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ , M<sup>-1</sup> cm<sup>-1</sup>): 421 (88.36), 517 (4.85), 542 (1.46), 600 (0.94), 648 (1.23) nm;  $\lambda_{\text{Em}}$  (CHCl<sub>3</sub>;  $\lambda_{\text{Ex}}$  420 nm): 657, 721 nm; IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3327, 2920, 2850, 1718, 1622, 1369, 1235, 1106, 965, 800, 751, 702; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.87 (d,  $J = 4.39$  Hz, 1H,  $\beta$ -pyrrolic H), 8.83 (d,  $J = 5.13$  Hz, 2H,  $\beta$ -pyrrolic H), 8.81 (m, 2H,  $\beta$ -pyrrolic H), 8.67 (d,  $J = 5.13$  Hz, 1H,  $\beta$ -pyrrolic H), 8.34 (s, 1H,  $\beta$ -pyrrolic H), 8.20-8.18 (m, 4H, *meso*-ArH), 8.11 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 8.05 (d,  $J = 7.32$  Hz, 2H, *meso*-ArH), 7.83-7.65 (m, 12H, *meso*-ArH), 7.60 (dd,  $J_1 = 8.05$ ,  $J_2 = 1.46$  Hz, 1H, ArH), 7.48 (m, 1H, ArH), 7.41 (s, 1H, triazole H), 7.27 (m, 1H, ArH), 7.12 (t,  $J = 7.32$  Hz, 1H, ArH), 5.78 (m, 3H, CH and CH<sub>2</sub>), 5.19 (s, 2H, OCH<sub>2</sub>), -2.75 (s, 2H, internal NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 164.80, 162.46, 153.18, 141.88, 141.79, 141.58, 141.16, 140.88, 134.55, 134.48, 133.11, 132.36, 128.98, 127.85, 127.62, 126.79, 126.72, 126.59, 123.84, 123.68, 122.92, 120.74, 120.58, 120.09, 119.19, 116.61, 115.28, 90.96, 62.54; ESI-MS:  $m/z = 870.4$  (M+H)<sup>+</sup>; Anal. Calcd. (%) for C<sub>57</sub>H<sub>39</sub>N<sub>7</sub>O<sub>3</sub>.H<sub>2</sub>O: C, 77.10; H, 4.65; N, 11.04; found (%): C, 77.12; H, 4.54; N, 10.98.

### 3. Results and Discussion

#### 3.1 Synthesis

For the synthesis of novel  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (**8a-d**, **9a-h** and **10a-b**),

zinc(II) 2-azidomethyl-5,10,15,20-tetraphenylporphyrin (**4**) was synthesized in 85% yield from 2-formyl-5,10,15,20-tetraphenylporphyrin (**1**) in three steps by following literature procedure<sup>27</sup> (scheme 1).

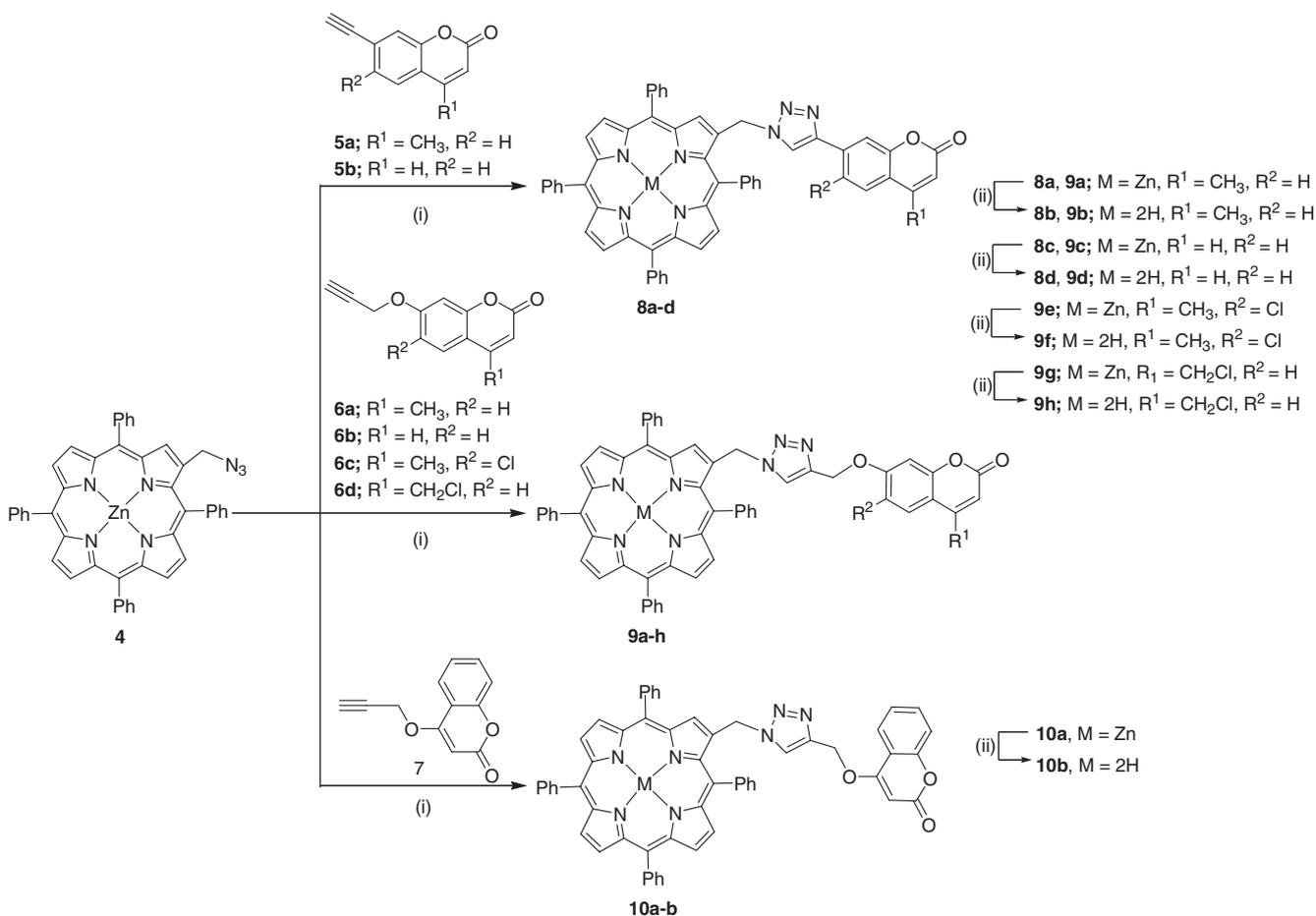


**Scheme 1.** Synthesis of zinc(II) 2-azidomethyl-5,10,15,20-tetraphenylporphyrin (**4**).

Further, the zinc(II) complexes of  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (**8a,c**, **9a,c**, **e,g** and **10a**) were prepared in 82-90% yields *via* a click reaction between zinc(II) 2-azidomethyl-5,10,15,20-tetraphenylporphyrin (**4**) and benzo- $\alpha$ -pyronoalkynes<sup>25a</sup> (**5a-b** or **6a-d** or **7**) in the presence of CuSO<sub>4</sub>·5H<sub>2</sub>O and ascorbic acid in DMF at 80 °C. These novel zinc(II) porphyrins (**8a,c**, **9a,c,e,g** or **10a**) underwent demetallation after the treatment with conc. HCl in CHCl<sub>3</sub> at room temperature to afford corresponding free-base  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (**8b**, **d**, **9b,d,f,h** and **10b**) in 69-79% yields (scheme 2).

### 3.2 Structure characterization

All the newly prepared porphyrins were purified by using column chromatography and characterized on the basis of spectral and analytical data. In the <sup>1</sup>H NMR spectrum of zinc(II) 4-methyl-7-[1-(5,10,15,20-tetraphenylporphyrin-2-ylmethyl)-1*H*-[1,2,3]triazol-4-yl]-chromen-2-one (**8a**), the triazole proton appeared as a singlet in the downfield region at  $\delta$  8.83 ppm. The characteristic  $\beta$ -pyrrolic protons were found as a



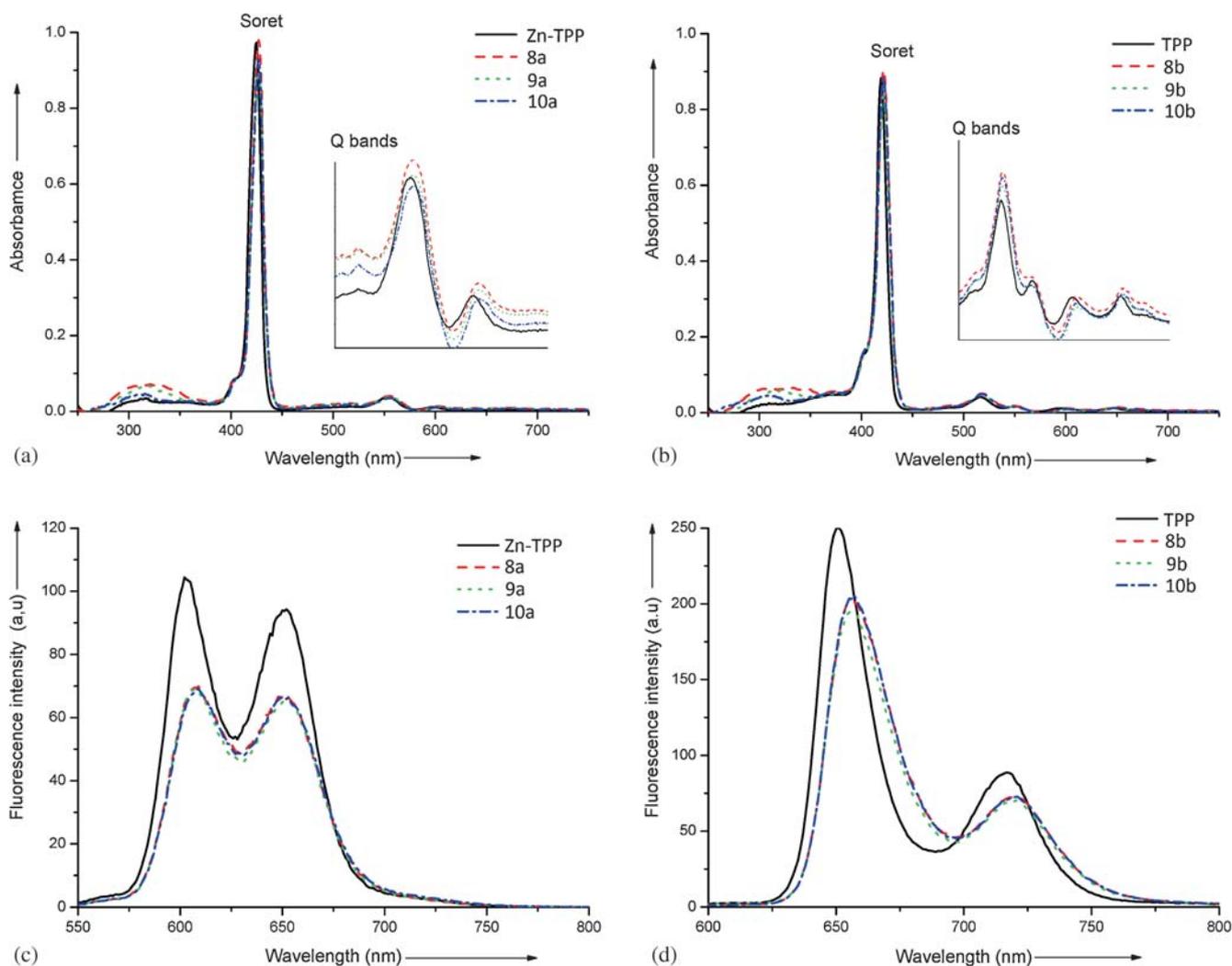
**Scheme 2.** Synthesis of  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads (**8a-d**, **9a-h** and **10a-b**).

multiplet between  $\delta$  8.71 and 8.76 ppm for five protons, a doublet ( $J = 3.66$  Hz) at  $\delta$  8.60 ppm for one proton and a singlet for one proton at  $\delta$  8.16 ppm. Two multiplets between  $\delta$  8.14–8.18 ppm and  $\delta$  8.04–8.06 ppm were attributed for eight protons of *meso*-phenyl rings. Remaining twelve *meso*-phenyl protons appeared as multiplets between  $\delta$  7.77–7.82 ppm and  $\delta$  7.60–7.61 ppm. The three aromatic protons corresponding to the benzo- $\alpha$ -pyrone moiety were assigned as a multiplet between  $\delta$  7.85–7.87 ppm. In addition, the two singlets at  $\delta$  6.40 ppm and at  $\delta$  2.46 ppm were assigned to the methine and methyl protons of the pyrone ring, respectively. A characteristic singlet at  $\delta$  5.74 ppm appeared due to the presence of two methylene protons in the molecule (**8a**). In the IR spectrum, the disappearance of an azide peak at around  $2200\text{ cm}^{-1}$  and the presence of an absorption peak at  $1683\text{ cm}^{-1}$  due to the carbonyl functionality of benzo- $\alpha$ -pyrone scaffold further

confirmed the formation of desired product (**8a**). Additionally, the mass spectral analysis supported the assigned structure of compound (**8a**) by showing the  $(M+H)^+$  ion peak at  $m/z$  916.2361. Similarly, other newly synthesized zinc(II) porphyrins (**8c**, **9a,c,e,g** and **10a**) and free-base porphyrins (**8b,d**, **9b,d,f,h** and **10b**) were characterized and their spectral and analytical data are presented in the experimental section.

### 3.3 Photophysical properties

The UV-Vis absorption and fluorescence spectra of zinc porphyrins (**8a**, **9a** and **10a**) and free-base porphyrins (**8b**, **9b** and **10b**) in chloroform are shown in figures 1a-d. The electronic absorption spectra of zinc porphyrins **8a**, **9a** and **10a** showed a strong Soret band at  $\sim 427$  nm and two weaker Q bands at  $\sim 555$  and 601 nm (figure 1a). In contrast, the free-base porphyrins **8b**,



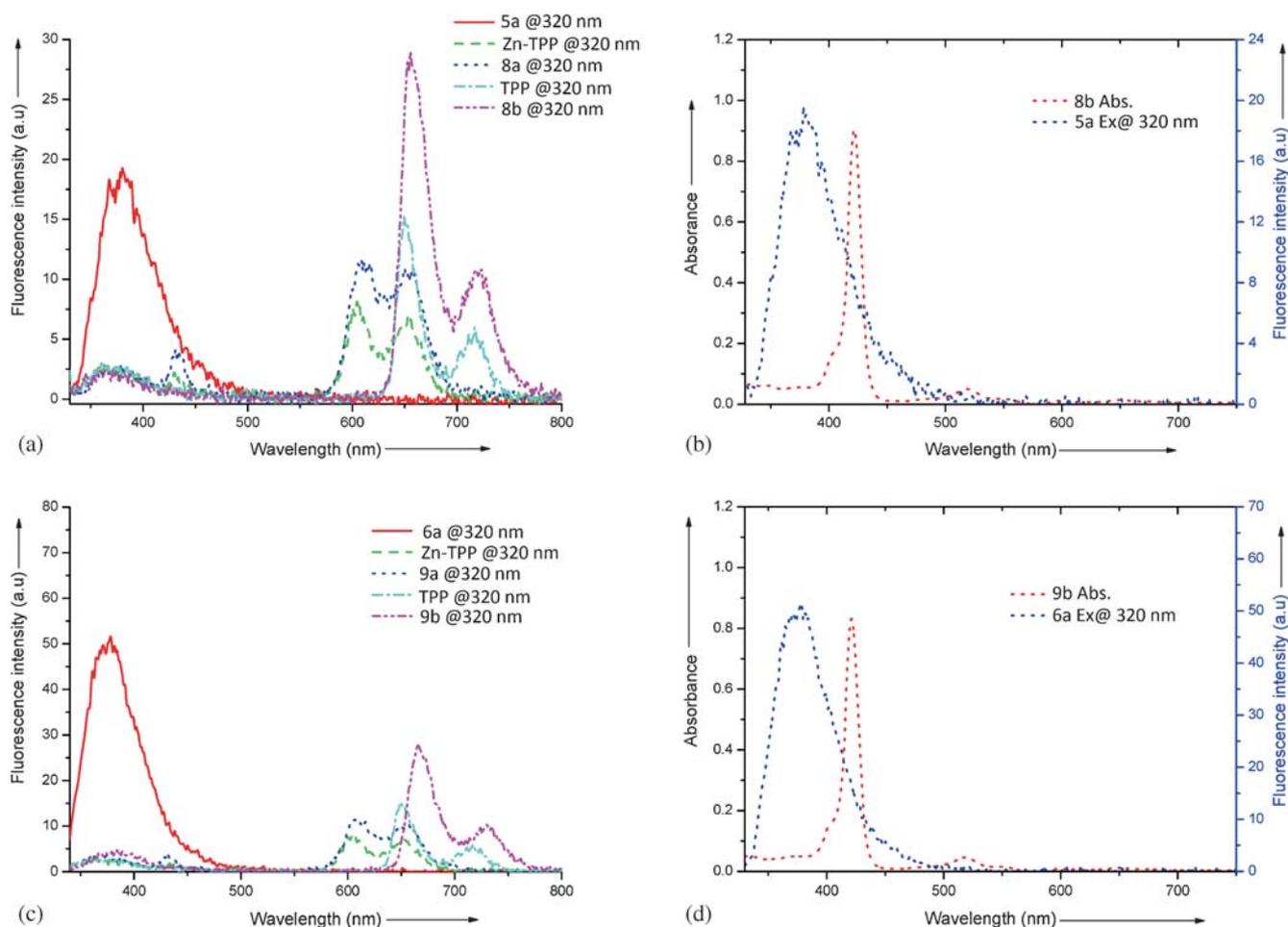
**Figure 1.** (a) Electronic absorption spectra of **Zn-TPP**, **8a**, **9a** and **10a**; (b) Electronic absorption spectra of **TPP**, **8b**, **9b** and **10b**; (c) Fluorescence spectra of **Zn-TPP**, **8a**, **9a** and **10a**; (d) Fluorescence spectra of **TPP**, **8b**, **9b** and **10b**, in  $\text{CHCl}_3$  ( $1.5 \times 10^{-6}$  mol  $\text{L}^{-1}$ ) at 298 K,  $\lambda_{\text{ex}} = 420$  nm.

**Table 1.** Electronic absorption and emission data of porphyrins (**8a-d**, **9a-h** and **10a-b**).

Compound	Absorption <sup>a</sup> $\lambda_{\max}/\text{nm}$ ( $\epsilon \times 10^{-4}$ , $\text{M}^{-1} \text{cm}^{-1}$ )	Fluorescence <sup>a,b</sup> $\lambda_{\text{em}}/\text{nm}$
<b>8a</b>	427 (97.98), 555 (4.02), 601 (1.37)	609, 651
<b>8b</b>	422 (90.39), 518 (5.04), 542 (1.76), 599 (1.16), 648 (1.41)	656, 720
<b>8c</b>	427 (87.17), 555 (3.11), 602 (0.67)	609, 651
<b>8d</b>	422 (95.38), 518 (5.22), 545 (1.70), 600 (1.11), 648 (1.37)	658, 719
<b>9a</b>	427 (89.67), 555 (3.67), 602 (1.24)	607, 653
<b>9b</b>	421 (83.55), 517 (4.58), 542 (1.49), 598 (0.82), 648 (1.16)	656, 721
<b>9c</b>	427 (90.00), 556 (3.76), 601 (1.38)	608, 650
<b>9d</b>	421 (74.97), 517 (4.24), 540 (2.07), 600 (0.95), 648 (1.27)	656, 720
<b>9e</b>	427 (88.44), 555 (3.59), 602 (1.22)	605, 651
<b>9f</b>	421 (71.71), 517 (3.78), 540 (1.84), 602 (0.60), 648 (0.95)	657, 720
<b>9g</b>	427 (65.51), 553 (2.46), 602 (0.76)	607, 651
<b>9h</b>	421 (73.26), 517 (3.87), 541 (1.63), 602 (0.63), 647 (0.96)	656, 720
<b>10a</b>	427 (92.91), 556 (3.45), 602 (1.04)	609, 653
<b>10b</b>	421 (88.36), 517 (4.85), 542 (1.46), 600 (0.94), 648 (1.23)	657, 721

<sup>a</sup>Absorption and emission data were taken in  $\text{CHCl}_3$  solution of porphyrins at 298 K.

<sup>b</sup>The excitation wavelength for emission data is 420 nm.



**Figure 2.** (a) Fluorescence spectra of 7-ethynyl-4-methyl-chromen-2-one **5a** and porphyrins **8a**, **8b** with **TPP** and **Zn-TPP** in  $\text{CHCl}_3$  ( $1.5 \times 10^{-6} \text{ mol L}^{-1}$ ) at 298 K,  $\lambda_{\text{ex}} = 320 \text{ nm}$ . (b) UV-Vis spectrum of **8b** and fluorescence spectrum of **5a** ( $\lambda_{\text{ex}} = 320 \text{ nm}$ ) in  $\text{CHCl}_3$ . (c) Fluorescence spectra of 4-methyl-7-prop-2-ynyloxy-chromen-2-one (**6a**) and porphyrins **9a**, **9b** with **TPP** and **Zn-TPP** in  $\text{CHCl}_3$  ( $1.5 \times 10^{-6} \text{ mol L}^{-1}$ ) at 298 K,  $\lambda_{\text{ex}} = 320 \text{ nm}$ . (d) UV-Vis spectrum of **9b** and fluorescence spectrum of **6a** ( $\lambda_{\text{ex}} = 320 \text{ nm}$ ) in  $\text{CHCl}_3$ .

**9b** and **10b** exhibited their Soret bands at  $\sim 421$  nm and four weaker Q bands at  $\sim 517$ , 540, 600 and 648 nm (figure 1b). The Soret and Q-bands of these newly prepared zinc(II) and free-base porphyrins were found to be red shifted by about 2 nm as compared to the Zn-TPP (Soret band at 425 nm and Q bands at 555, 597 nm) and TPP (Soret band at 419 nm and Q bands at 516, 551, 590 and 646 nm), respectively. Besides the Soret and Q bands, some additional peaks were also found at  $\sim 320$  nm in the UV-Vis spectra of these porphyrins (figure 1a-b) due to the presence of benzo- $\alpha$ -pyrone moiety which suggest that there is no substantial interaction between the benzo- $\alpha$ -pyrone and porphyrin subunits in the ground state.<sup>28</sup>

The fluorescence spectra of zinc porphyrins (**8a**, **9a** and **10a**) have shown two characteristic emission bands at  $\sim 607$  and 651 nm (figure 1c) whereas in the case of free-base porphyrins (**8b**, **9b** and **10b**), the emission bands were found at  $\sim 656$  and 720 nm (figure 1d). The emission spectra of these porphyrins further revealed a significant quenching and red shift in their fluorescence bands as compared to the Zn-TPP (emission bands at 602 and 651 nm) and TPP (emission bands at 650 and 715 nm), respectively. Though, these porphyrin dyads have exhibited a bathochromic shift in their electronic absorption and emission spectra as compared to the *meso*-tetraphenylporphyrins but it was found to be less as compared to the red shift observed in the absorption and emission bands of directly linked  $\beta$ -triazole bridged porphyrin-benzo- $\alpha$ -pyrone dyads.<sup>25b</sup> Therefore, it can be concluded that the direct conjugation of triazole bridged benzo- $\alpha$ -pyrone moiety with the porphyrin ring is necessary to obtain better photophysical characteristics. The UV-Vis and fluorescence data of the new porphyrin analogues (**8a-d**, **9a-h** and **10a-b**) are presented in table 1.

The absorption and emission spectra of zinc(II) porphyrin-benzo- $\alpha$ -pyrone dyads (**8a** and **9a**) and free-base porphyrin-benzo- $\alpha$ -pyrone dyads (**8b** and **9b**) were further analyzed to study the occurrence of intramolecular energy transfer between the two chromophores. Figures 2a and 2c show the emission spectra of 7-ethynyl-4-methyl-chromen-2-one (**5a**), porphyrins (**8a**, **8b**) and 4-methyl-7-prop-2-ynyloxy-chromen-2-one (**6a**), porphyrins (**9a**, **9b**) with TPP and Zn-TPP at 320 nm excitation. It was observed that in the fluorescence spectra of zinc(II) porphyrins (**8a** and **9a**) and free-base porphyrins (**8b** and **9b**), emission at  $\sim 400$  nm due to the benzo- $\alpha$ -pyrone moiety is completely quenched after the formation of a triazole ring and there is an increase in the intensity of the emission bands of zinc-porphyrins (**8a** and **9a**) at  $\sim 607$  and 651 nm with respect to the Zn-TPP and free-base porphyrins (**8b** and **9b**) at  $\sim 656$

and 720 nm with respect to the TPP. Thus, in these porphyrins the energy was transferred from benzo- $\alpha$ -pyrone moiety to the porphyrin core. Further, the significant overlapping of the fluorescence spectra of benzo- $\alpha$ -pyrones **5a** and **6a** with the absorption spectra of free-base porphyrins **8b** and **9b** (figures 2b and 2d) also supports the above statement as it fulfills the first condition of energy transfer.<sup>29</sup>

#### 4. Conclusions

In summary, we have successfully synthesized  $\beta$ -triazolomethyl-bridged porphyrin-benzo- $\alpha$ -pyrone dyads using a copper(I)-catalyzed Huisgen 1,3-dipolar cyclo addition reaction in 69-90% yields. All the synthesized molecules were successfully characterized on the basis of spectral data. On photophysical investigation, these porphyrin dyads have demonstrated a bathochromic shift in their electronic absorption and emission spectra in comparison to the *meso*-tetraphenylporphyrins. In addition, some of these newly synthesized porphyrin dyads have shown efficient intramolecular energy transfer from benzo- $\alpha$ -pyrone subunit to the porphyrin core. Hence, these results may be useful for the future development of novel porphyrin-benzo- $\alpha$ -pyrone based systems for various material and medicinal applications.

#### Supplementary Information (SI)

Supplementary file contains <sup>1</sup>H and <sup>13</sup>C NMR spectra (figures S1-S25) of all the newly synthesized products. Supplementary Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

#### Acknowledgements

We thank University of Delhi, India for providing necessary financial support for this work. DKS is grateful to Council of Scientific and Industrial Research, New Delhi, India for Senior Research Fellowship. The JEOL ECX 400P (400 MHz) NMR and DU-DST mass facility at USIC, University of Delhi and SAIF, CDRI, Lucknow are acknowledged for the NMR and mass spectra, respectively.

#### References

- (a) Boyd P D W, Hosseini A, van Paauwe J D and Reed C A 2011 In *Handbook of Carbon Nano Materials* Francis D'Souza and Karl M Kadish (Eds.) Vol. 1 p. 375 (World Scientific: Singapore); (b) Kondratuk D V, Sprafke J K, O'Sullivan M C, Perdigao L M A, Saywell A, Malfois M, O'Shea J N, Beton P H, Thompson A L and Anderson H L 2014 *Chem. Eur. J.* **20** 12826

2. (a) Srour H, Le Maux P and Simonneaux G 2012 *Inorg. Chem.* **51** 5850; (b) Hopmann K H and Ghosh A 2011 *ACS Catal.* **1** 597
3. (a) Kaplan A, Korin E and Bettelheim A 2014 *Eur. J. Inorg. Chem.* 2288; (b) Lahtinen R, Fermín D J, Kontturi K and Girault H H 2000 *J. Electroanal. Chem.* **483** 81
4. (a) Hanakova A, Bogdanova K, Tomankova K, Pizova K, Malohlava J, Binder S, Bajgar R, Langova K, Kolar M, Mosinger J and Kolarova H 2014 *Microbiol. Res.* **169** 163; (b) Thomas A P, Babu P S S, Nair S A, Ramakrishnan S, Ramaiah D, Chandrashekar T K, Srinivasan A and Pillai M R 2012 *J. Med. Chem.* **55** 5110
5. (a) Krokos E, Spaänig F, Ruppert M, Hirsch A and Guldi D M 2012 *Chem. Eur. J.* **18** 1328; (b) Hosseini A, Taylor S, Accorsi G, Armaroli N, Reed C A and Boyd P D W 2006 *J. Am. Chem. Soc.* **128** 15903
6. (a) Williams D E, Rietman J A, Maier J M, Tan R, Greytak A B, Smith M D, Krause J A and Shustova N B 2014 *J. Am. Chem. Soc.* **136** 11886; (b) Lazarides T, Charalambidis G, Vuillamy A, Réglie M, Klontzas E, Froudakis G, Kuhri S, Guldi D M and Coutsolelos A G 2011 *Inorg. Chem.* **50** 8926
7. (a) Davis N K S, Pawlicki M and Anderson H L 2008 *Org. Lett.* **10** 3945; (b) Davis N K S, Thompson A L and Anderson H L 2011 *J. Am. Chem. Soc.* **133** 30
8. Giribabu L, Reeta P S, Kanaparthi R K, Srikanth M and Soujanya Y 2013 *J. Phys. Chem. A* **117** 2944
9. Lu J-Z, Du Y-fan, Wu B, Huang J-W and Jiang J 2010 *Transition Met. Chem.* **35** 451
10. Zhou X, Liu D, Wang T, Hu X, Guo J, Weerasinghe K C, Wang L and Li W 2014 *J. Photochem. Photobiol. A* **274** 57
11. Xiang H, Zhou L, Feng Y, Cheng J, Wu D and Zhou X 2012 *Inorg. Chem.* **51** 5208
12. Singh D K and Nath M 2014 *Beilstein J. Org. Chem.* **10** 808
13. Santos C I M, Oliveira E, Santos H M, Menezes J C J M D S, Faustino M A F, Cavaleiro J A S, Capelo J L, Neves M da G P M S and Lodeiro C 2015 *Photochem. Photobiol. Sci.* **14** 757
14. Akhigbe J, Luciano M, Zeller M and Brückner C 2015 *J. Org. Chem.* **80** 499
15. Ogawa K, Hasegawa H, Inaba Y, Kobuke Y, Inouye H, Kanemitsu Y, Kohno E, Hirano T, Ogura S-I and Okura I 2006 *J. Med. Chem.* **49** 2276
16. Ormond A B and Freeman H S 2013 *Dyes Pigm.* **96** 440
17. Moura N M M, Núñez C, Santos S M, Faustino M A F, Cavaleiro J A S, Neves M G P M S, Capelo J L and Lodeiro C 2014 *Inorg. Chem.* **53** 6149
18. (a) Karapire C, Kolancilar H, Oyman Ü and Icli S 2002 *J. Photochem. Photobiol. A* **153** 173; (b) Bell W, Block M H, Cook C, Grant J A and Timms D 1997 *J. Chem. Soc. Perkin Trans.* **1** 2789; (c) Shakeri A, Iranshahy M and Iranshahi M 2014 *J. Asian Nat. Prod. Res.* **16** 884; (d) Ruan B, Cheng H, Ren J, Li H, Guo L, Zhang X and Lio C 2015 *Eur. J. Med. Chem.* **103** 185
19. Zhang Y-G, Shi Z-H, Yang L-Z, Tang X-L, An Y-Q, Ju Z-H and Liu W-S 2014 *Inorg. Chem. Commun.* **39** 86
20. Shao J 2010 *Dyes Pigm.* **87** 272
21. Esnal I, Duran-Sampedro G, Agarrabeitia A R, Bañuelos J, García-Moreno I, Macías M A, Peña-Cabrera E, López-Arbeloa I, de la Moya S and Ortiz M J 2015 *Phys. Chem. Chem. Phys.* **17** 8239
22. (a) Jayashree B S, Nigam S, Pai A and Chowdary P V R 2014 *Arab. J. Chem.* **7** 885; (b) Torres F C, Brucker N, Andrade S F, Kawano D F, Garcia S C, Poser G L V and Eifler-Lima V L 2014 *Curr. Top. Med. Chem.* **14** 2600; (c) Peng X, Damu G L V and Zhou C *Curr. Pharm. Des.* **19** 3884
23. (a) Kolb H C, Finn M G and Sharpless K B 2001 *Angew. Chem. Int. Ed.* **40** 2004; (b) Totobenazara J and Burke A J 2015 *Tetrahedron Lett.* **56** 2853; (c) Haldon E, Nicasio M C and Perez P J 2015 *Org. Biomol. Chem.* **13** 9528
24. (a) Velázquez H D, García Y R, Vandichel M and Verpoort A M F 2014 *Org. Biomol. Chem.* **12** 9350; (b) Hou J, Liu X, Shen J, Zhao G and Wang P G 2012 *Expert Opin. Drug Dis.* **7** 489; (c) Xi W, Scott T F, Kloxin C J and Bowman C N 2014 *Adv. Funct. Mater.* **24** 2572; (d) Wu W, Ye C, Qin J and Li Z 2013 *ACS Mater. Interfaces* **5** 7033; (e) Musumeci F, Schenone S, Desogus A, Nieddu E, Deodato D and Botta L 2015 *Curr. Med. Chem.* **22** 2022
25. (a) Singh D K and Nath M 2015 *Dyes Pigm.* **121** 256; (b) Singh D K and Nath M 2015 *RSC Adv.* **5** 68209
26. (a) Singh D K and Nath M 2015 *Beilstein J. Org. Chem.* **11** 1434; (b) Sharma S and Nath M 2012 *J. Heterocycl. Chem.* **49** 88; (c) Tiwari R and Nath M 2015 *New J. Chem.* **39** 5500; (d) Singh D K and Nath M 2015 *Org. Biomol. Chem.* **13** 1836
27. (a) Ponomarev G V 1994 *Chem. Heterocycl. Compd.* **30** 1444; (b) Garg A 2012 *Synthesis and spectroscopic properties of novel  $\beta$ -functionalized 5,10,15,20-tetraarylporphyrins and diporphyrin analogues*, Ph.D Thesis (University of Delhi, Delhi, India) p. 147
28. (a) Tao M, Liu L, Liu D and Zhou X 2010 *Dyes Pigments* **85** 21; (b) Zhou X, Liu D, Wang T, Hu X, Guo J, Weerasinghe K C, Wang L and Li W 2014 *J. Photochem. Photobiol. A: Chem.* **274** 57
29. Gai F, Zhou T, Zhang L, Li X, Hou W, Yang X, Li Y, Zhao X, Xu D, Liu Y and Huo Q 2012 *Nanoscale* **4** 6041