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Synthesis and spectral properties of aromatically π-extended coumarin-fused *meso*-tetraphenylpyridoporphyrins

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An annulative π-extension of porphyrins has been accomplished by a reaction of copper(II) 2-amino-5,10,15, 20-tetraphenylporphyrin with aromatic aldehydes and 4-hydroxycoumarin in the presence of a stoichiometric amount of trichloroacetic acid in *o*-dichlorobenzene at reflux temperature under one-pot operation. The resulting π-conjugated copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins are obtained in 56–66% isolated yields after chromatographic purification and characterized on the basis of spectral data analysis. These newly constructed copper(II) coumarin-fused pyridoporphyrins undergo demetallation in the presence of sulfuric acid in chloroform to produce free-base porphyrin analogues which on zinc insertion using $Zn(OAc)_2$ in $CHCl_3$-MeOH afford zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins in good yields. After structural identification, the photophysical characteristics of pyridoporphyrin macrocycles have been analysed by using UV-Vis spectroscopy. The preliminary results reveal a remarkable bathochromic shift in the electronic absorption spectra of coumarin-fused *meso*-tetraphenylpyridoporphyrins in contrast to the non-π-extended *meso*-tetraphenylporphyrin macrocycles.

Keywords: Absorption spectra, Bathochromic shift, π-Extension, One-pot synthesis, Pyridoporphyrins

Fused π-conjugated molecules have been extensively developed as essential components in electronic devices due to their favorable physicochemical properties and efficient charge-transport characteristics[1-3]. The incorporation of π-acceptor units into the fused π-conjugated frameworks offer significant advantages, particularly in adjusting the energies of frontier molecular orbitals[4,5]. In this context, π-extended porphyrinoids have garnered widespread interest due to their remarkable photophysical, optoelectronic, and physicochemical properties, making them promising candidates for a wide range of material applications[6-8].

In the recent years, π-extended *meso*-tetraarylporphyrins with (hetero)aromatic systems fused through the β,β'-positions have gained a considerable attention as synthetic targets due to their distinctive photophysical and optoelectronic properties[9,10]. Among the porphyrin class of compounds, the electron rich macrocycles exhibit significantly red-shifted Soret and enhanced Q bands in their electronic absorption spectra[11]. Such properties make π-extended porphyrins highly desirable for their applications in diverse areas including dye-sensitized solar cells (DSSCs)[12–14], photodynamic therapy (PDT)[15–17], and organic light-emitting diodes (OLEDs)[18–20]. Due to the improved photophysical characteristics, interest of researchers in the synthesis of π-extended porphyrins has dramatically increased over the years, surpassing that of classical porphyrin analogues. In light of this, we have previously designed and synthesized a π-extended β,β'-fused pyridoporphyrinic systems by incorporating *meso*-tetraarylporphyrin, pyridine, and a coumarin core into a single molecular framework. On photophysical evaluation, these conjugated *meso*-tetraarylpyridoporphyrins demonstrated a significant red-shifted absorption as compared to the simple non-π-extended *meso*-tetraphenylporphyrin precursors[21]. The promising photophysical results originated from the previous studies prompted us to further explore the synthesis and spectral properties of novel copper(II), free-base and zinc complexes of coumarin-fused *meso*-tetraphenylpyridoporphyrins. Therefore, in context to develop convenient methods for β-functionalized *meso*-tetraarylporphyrins[22–35], we report herein the synthesis, spectroscopic characterization and optical properties of a new series of copper(II), free-base, and zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins.

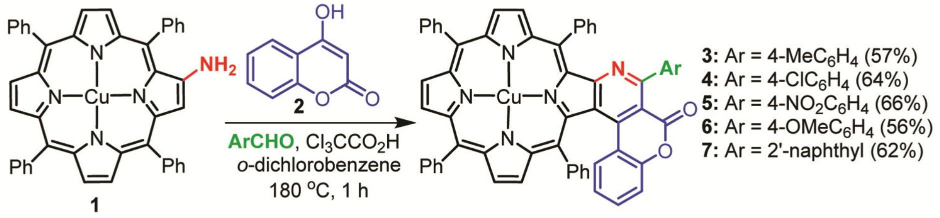
Results and Discussion

Synthesis

Initially, copper(II) 2-amino-*meso*-tetraphenylporphyrin (**1**) was prepared from copper(II) 2-nitro-

meso-tetraphenylporphyrin according to the reported procedure[36]. Later, copper(II) 2-aminoporphyrin (**1**) was employed as a key precursor for the construction of various copper(II) pyridoporphyrins (**3-7**) in good yields. Initially, a reaction of copper(II) 2-aminoporphyrin (**1**) with benzaldehyde and 4-hydroxycoumarin (**2**) was performed in the presence of a stoichiometric amount of trichloroacetic acid (TCA) in *o*-dichlorobenzene at 180 □. As indicated by the TLC, the starting materials were consumed after one hour of the reaction, and a new green spot with a lower R_f value than 2-aminoporphyrin precursor (**1**) was clearly visible on the TLC plate. After the purification by using column chromatography, a green colored material was obtained in 58% isolated yield and characterized as a copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrin (**3**) on the basis of spectral data analysis. Delightfully, the scope of methodology was further extended to synthesize copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**4**–**6**) in good yields (56–66%) by using various benzaldehydes containing electron-releasing and electron-attracting substituents (Scheme 1). Notably, the optimized procedure was successfully applied to prepare copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrin (**7**) in 62% isolated yield from a reaction of copper(II) 2-aminoporphyrin (**1**) with comparatively bulky 2-naphthaldehyde and 4-hydroxycoumarin as presented in Scheme 1. It was observed that reaction with 4-nitrobenzaldehyde afforded desired product in relatively higher yield in contrast to the less reactive *p*-tolualdehyde and *p*-anisaldehyde.

A possible mechanistic pathway for the formation of copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3-8**) from copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin (**1**) is illustrated in Fig. 1. Initially, a cascade reaction proceeds *via* a protonation of aromatic aldehydes in the presence of trichloroacetic acid. The resulting electrophilic aldehydic species reacts with copper(II) 2-amino-*meso*-tetraphenylporphyrin to afford 2-iminoporphyrin



Scheme 1 — TCA-promoted synthesis of copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3**–**8**)

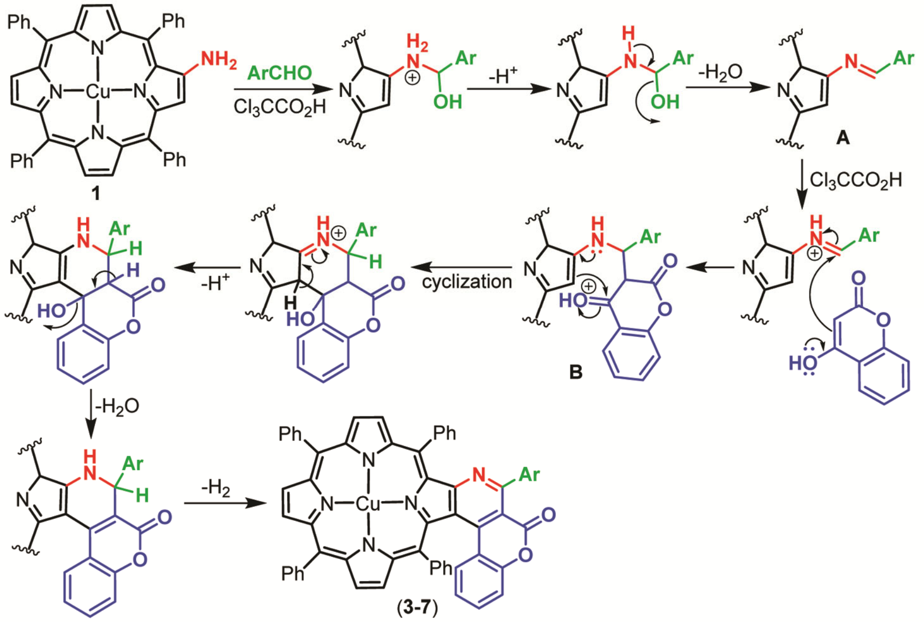
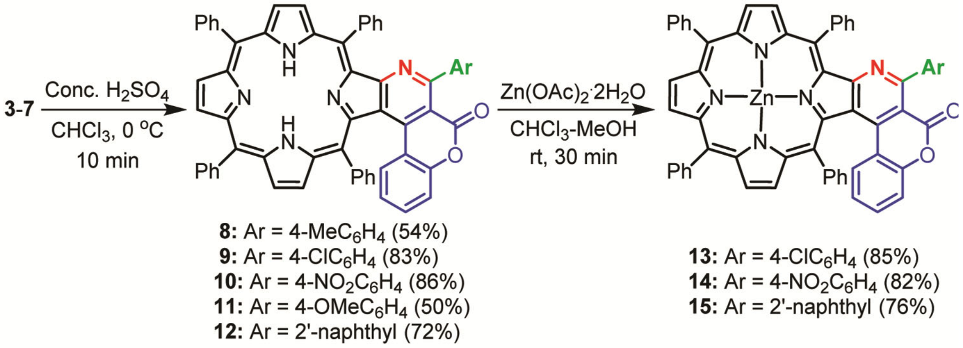


Fig. 1 — Proposed mechanism for the formation of copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3-7**)



Scheme 2 — Synthesis of free-base and zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**8–15**)

intermediate (**A**). After protonation in the presence of trichloroacetic acid, iminoporphyrin intermediate (**A**) affords corresponding iminium ion intermediate which led to the formation of intermediate (**B**) after the reaction with 4-hydroxycoumarin. Finally, intermediate (**B**) undergoes intramolecular cyclization followed by dehydration and aromatization to generate desired π-extended copper(II) coumarin-fused pyridoporphyrins in good isolated yields.

For a comparative study of electronic absorption characteristics, the copper complexes of coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3-7**) were transformed into free-base coumarin-fused *meso*-tetraphenylpyridoporphyrins (**8-12**) in 50–86% yields through a standard demetallation process using conc. H_2SO_4 in $CHCl_3$ at 0 □ as illustrated in Scheme 2. Subsequent complexation of free-base porphyrins (**9**, **10** and **12**) with zinc using $Zn(OAc)_2$ in a $CHCl_3$-MeOH mixture at ambient temperature afforded zinc(II) coumarin-fused *meso*-tetrapheny-lpyridoporphyrins (**13-15**) in good yields (76–85%). The chemical structures of newly synthesized free-base and zinc(II) coumarin-fused pyridoporphyrins (**8-15**) were assigned after analyzing their spectral data.

Photophysical characteristics

The UV-Vis spectra of newly constructed copper(II), free-base, and zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3–15**) were recorded in chloroform (1.5×10^{-6} M) at 298 K. The electronic absorption spectra of novel coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3–15**) are found to be significantly red-shifted as compared to their *meso*-tetraphenylporphyrin starting materials due to the extended π-conjugation. The copper(II) porphyrins (**3–7**) exhibited broadened and split Soret bands between 452-455 nm and two Q-bands between 575–613 nm. Both the Soret and Q-bands of these copper(II) porphyrins (**3-7**) were found to be red-shifted up to 39 nm as compared to copper(II) *meso*-tetraphenylporphyrin (**CuTPP**, Soret band at 416 nm and Q-bands at 540 and 569 nm). Further, free-base coumarin-fused pyridoporphyrins (**8–12**) displayed sharp Soret bands between 454–456 nm. Unlike the metal-porphyrins, a characteristic set of four Q-bands were observed between 543–694 nm in the case of free-base pyridoporphyrins. Both Soret and Q-bands of free-base coumarin-fused pyridoporphyrins (**8–12**) were found to be significantly red-shifted as compared to *meso*-tetraphenylporphyrin (**TPP**; Soret band at 419 nm and Q-bands at 516, 550, 594 and 646 nm). In addition, zinc(II) coumarin-fused pyridoporphyrins (**13–15**) exhibited broadened Soret bands between 458–460 nm along with two Q-bands between 579–617 nm. Similar to the copper(II) and free-base coumarin-fused pyridoporphyrins, zinc(II) coumarin-fused pyridoporphyrins also displayed considerably red-shifted (~33–35 nm) Soret and Q-bands in contrast to the zinc(II) *meso*-tetraphenylporphyrin (**ZnTPP**; Soret band at 425 nm and Q-bands at 554 and 597 nm). The electronic absorption spectra of representative copper(II), free-base and zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**4**, **9**, and **13**) have been depicted in Fig. 2.

Experimental Section

General methods

The reagents and solvents required for present study were purchased from Sigma-Aldrich (Merck) and were used as received unless otherwise stated. The progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel 60 F_{254} (pre-coated aluminium sheets) from Merck. The synthesized porphyrins were purified by column chromatography using either activated neutral aluminium oxide (Brokmann grade I-II, Merck) or

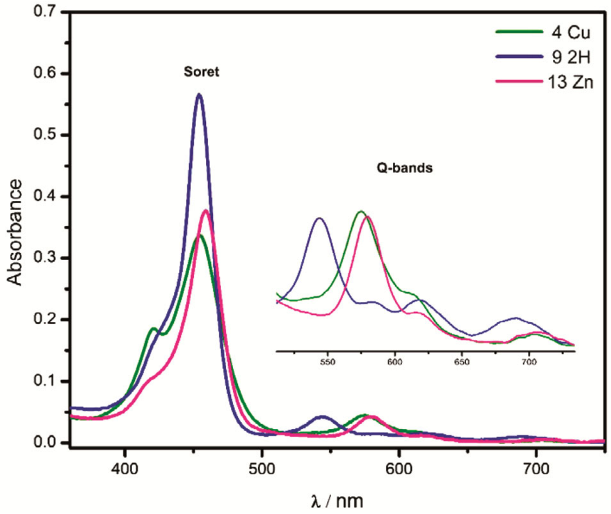


Fig. 2 — Electronic absorption spectra of copper(II), free-base, and Zn(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**4**, **9**, and **13**) in $CHCl_3$ (1.5×10^{-6} M) at 298 K. Inset shows Q-bands

silica gel (60-120 mesh). The melting points of products were determined on Buchi M-560 melting point apparatus. NMR spectra of products were recorded in $CDCl_3$ on a Jeol ECX 400P (400 MHz) NMR spectrometer by using TMS as an internal standard. The chemical shifts are expressed in parts per million (δ, ppm) relative to the residual $CHCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR). The coupling constants (*J*) are reported in Hertz (Hz). Infrared spectra of products were recorded on a Bruker ALPHA II FT-IR spectrometer and absorption maxima (υ_{max}) are given in cm^{-1}. Electronic absorption spectra were measured in $CHCl_3$ using a Lab India Analytical UV/Vis spectrophotometer. High resolution mass spectra (ESI-HRMS) were recorded on a LCMS-Waters SYNAPT G2 mass spectrometer.

General procedure for the synthesis of copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (3–7)

To an oven-dried round bottom flask charged with a solution of copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin (**1**; 50 mg, 0.072 mmol, 1.0 equiv.) in 1,2-dichlorobenzene (10 mL), 4-hydroxycoumarin (**2**; 14.0 mg, 0.086 mmol, 1.2 equiv.), aromatic aldehyde (0.086 mmol, 1.2 equiv.) and trichloroacetic acid (11.7 mg, 0.072 mmol, 1.0 equiv.) were added. The reaction mixture was refluxed in an oil bath at 180 □ for an hour and progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was allowed to cool at RT and then chromatographed over silica gel using hexane as an eluent. After the removal of 1,2-dichlorobenzene, the pure products were eluted from the column by using 60% $CHCl_3$ in hexane as an eluent.

Characterization data of coumarin-fused pyrido[2,3-*b*]porphyrin (3: Ar = 4-MeC_6H_4)

Purple solid. Yield 57%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 454 (29.4), 576 (3.5), 595 (2.5) nm; IR ($CHCl_3$): 2920, 2850, 1741 (C=O), 1597, 1539, 1440, 1338, 1259, 1222, 1170, 1064, 1006, 864, 815, 794, 750, 699, 665 cm^{-1}; ESI-HRMS: *m/z* Calcd for $C_{61}H_{37}N_5O_2Cu$: 935.2421 $[M + H]^+$. Found: 935.2401.

Copper(II) coumarin-fused pyrido[2,3-*b*]porphyrin (4: Ar = 4-ClC_6H_4)

Purple solid. Yield 64%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 455 (33.6), 575 (4.5), 610 (1.8) nm; IR ($CHCl_3$): 2959, 2924, 2854, 1746 (C=O), 1598, 1541, 1445, 1343, 1225, 1174, 1081, 1007, 852, 825, 794, 755, 698 cm^{-1}; ESI-HRMS: *m/z* Calcd for $C_{60}H_{34}ClN_5O_2Cu$: 957.1875 $[(M + H) + 2]^+$. Found: 957.5938.

Copper(II) coumarin-fused pyrido[2,3-*b*]porphyrin (5: Ar = 4-$NO_2C_6H_4$)

Purple solid. Yield 66%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 452 (24.4), 577 (4.3), 613 (1.7) nm; IR ($CHCl_3$): 2923, 2853, 1742 (C=O), 1598, 1517, 1446, 1343, 1225, 1177, 1048, 1006, 756, 701, 665 cm^{-1}; ESI-HRMS: *m/z* Calcd for $C_{60}H_{34}N_6O_4Cu$: 966.2116 $[M + H]^+$. Found: 966.6080.

Copper(II) coumarin-fused pyrido[2,3-*b*]porphyrin (6: Ar = 4-$OMeC_6H_4$)

Purple solid. Yield 56%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 455 (27.0), 576 (4.3), 595 (1.7) nm; IR ($CHCl_3$): 3054, 3017, 2851, 2836, 1738 (C=O), 1608, 1509, 1441, 1249, 1175, 1073, 1006, 966, 833, 797, 752, 701, 667 cm^{-1}; ESI-HRMS: *m/z* Calcd for $C_{61}H_{37}N_5O_3Cu$: 951.2371 $[M + H]^+$. Found 951.2396.

Copper(II) coumarin-fused pyrido[2,3-*b*]porphyrin (7: Ar = 2′-naphthyl)

Purple solid. Yield 62%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 455 (25.7), 575 (3.4), 605 (1.3) nm; IR ($CHCl_3$): 3055, 3021, 2924, 2853, 1742 (C=O), 1600, 1541, 1342, 1174, 1075, 1006, 892, 754 cm^{-1}; ESI-HRMS: *m/z* Calcd for $C_{64}H_{37}N_5O_2Cu$: 971.2421 $[M + H]^+$. Found: 971.2494.

General procedure for the synthesis of free-base coumarin-fused *meso*-tetraphenylpyrido-porphyrins (8–12)

An oven-dried round bottom flask was charged with copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (**3–7**; 0.032 mmol) and $CHCl_3$ (10 mL). The solution was stirred at 0 □ for 5 min followed by the addition of conc. H_2SO_4 (0.8 mL). The reaction mixture was stirred at 0 □ for another 5 min. After completion of the reaction, the reaction mixture was neutralized with 10% aqueous $NaHCO_3$ solution. The organic layer was washed well with water (2×30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. Thus, the residue obtained was purified on a neutral alumina column by using 50–70% chloroform in hexane as a solvent to provide pure porphyrin products.

Characterization data of free-base coumarin-fused pyrido[2,3-*b*]porphyrin (8: Ar = 4-MeC_6H_4)

Greenish-purple solid. Yield 54%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 455 (42.3), 544 (3.4), 577 (1.4), 611 (1.2), 682 (0.7) nm; IR ($CHCl_3$): 3347 (N–H), 2924, 2855, 1745 (C=O), 1601, 1543, 1504, 1461, 1374, 1349, 1263, 1226, 1159, 1070, 976, 910, 798, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.87 (d, *J* = 5.0 Hz, 1H, β-pyrrolic H), 8.77 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.63–8.59 (m, 3H, β-pyrrolic H), 8.55 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.39–8.36 (m, 1H, *meso*-ArH), 8.25–8.21 (m, 3H, *meso*-ArH), 7.98–7.93 (m, 4H, *meso*-ArH), 7.86 (d, *J* = 8.1 Hz, 1H, *meso*-ArH), 7.77–7.73 (m, 8H, *meso*-ArH), 7.56–7.50 (m, 4H, *meso*-ArH, ArH), 7.46–7.42 (m, 1H, ArH), 7.38–7.29 (m, 3H, ArH), 6.78–6.75 (m, 2H, ArH), 6.26–6.20 (m, 1H, ArH), –1.98 (s, 1H, internal NH), –2.11 (s, 1H, internal NH).

Free-base coumarin-fused pyrido[2,3-*b*]porphyrin (9: Ar = 4-ClC_6H_4)

Greenish-purple solid, Yield 83%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 454 (37.7), 543 (2.8), 574 (1.0), 615 (1.0), 689 (0.7) nm; IR ($CHCl_3$): 3349 (N–H), 3057, 3024, 2923, 2854, 1744 (C=O), 1599, 1543, 1496, 1466, 1350, 1262, 1228, 1160, 1077, 1006, 972, 799, 756, 705, 647 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.90 (d, *J* = 4.6 Hz, 1H, β-pyrrolic H), 8.79 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.65–8.62 (m, 3H, β-pyrrolic H), 8.58 (d, *J* = 4.6 Hz, 1H, β-pyrrolic H), 8.42–8.37 (m, 1H, *meso*-ArH), 8.27–8.22 (m, 3H, *meso*-ArH), 8.00–7.94 (m, 3H, *meso*-ArH), 7.87 (d, *J* = 7.3 Hz, 1H, *meso*-ArH), 7.78–7.75 (m, 8H, *meso*-ArH), 7.62–7.54 (m, 4H, *meso*-ArH), 7.49–7.47 (m, 3H, ArH), 7.37–7.28 (m, 2H, ArH), 6.95 (d, *J* = 6.3 Hz, 2H, ArH), 6.31–6.28 (m, 1H, ArH), –1.99 (s, 1H, internal NH), –2.10 (s, 1H, internal NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.88, 160.31, 155.70, 155.62, 152.34, 152.17, 150.73, 148.30, 147.20, 143.79, 142.20, 141.43, 141.36, 141.21, 139.56, 139.32, 139.13, 138.51, 136.34, 134.71, 134.11, 133.54, 131.76, 129.71, 129.04, 128.35, 128.16, 127.99, 127.91, 127.75, 127.52, 127.43, 127.23, 127.04, 126.96, 126.57, 123.95, 121.01, 120.82, 120.44, 119.03, 118.38, 116.15, 111.61.

Free-base coumarin-fused pyrido[2,3-*b*]porphyrin (10: Ar = 4-$NO_2C_6H_4$)

Greenish-purple solid. Yield 86%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 455 (38.5), 546 (3.2), 580 (1.0), 613 (1.2), 690 (0.9) nm; IR ($CHCl_3$): 3354 (N–H), 3059, 3022, 2925, 2853, 1742 (C=O), 1600, 1544, 1439, 1346, 1162, 1072, 972, 845, 797, 756, 702, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.92 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.80 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.64–8.62 (m, 3H, β-pyrrolic H), 8.51 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.39–8.33 (m, 1H, *meso*-ArH), 8.27–8.22 (m, 3H, *meso*-ArH), 8.01–7.93 (m, 4H, *meso*-ArH), 7.88–7.79 (m, 8H, *meso*-ArH), 7.59–7.53 (m, 6H, *meso*-ArH, ArH), 7.45–7.35 (m, 3H, ArH), 7.30 (d, *J* = 8.1 Hz, 1H, ArH), 6.53–6.52 (m, 2H, ArH), –2.00 (s, 1H, internal NH), –2.12 (s, 1H, internal NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.788, 160.27, 155.95, 155.79, 152.32, 150.59, 146.63, 146.23, 143.92, 143.82, 142.16, 141.48, 141.25, 141.12, 139.50, 139.24, 138.75, 136.25, 135.36, 134.78, 134.73, 134.27, 132.00, 131.72, 130.74, 129.28, 129.15, 128.91, 128.55, 128.31, 128.19, 128.08, 128.01, 127.91, 127.60, 127.47, 127.18, 127.07, 127.01, 126.61, 124.15, 123.49, 123.00, 121.20, 120.89, 120.27, 119.19, 118.13, 116.23, 111.05.

Free-base coumarin-fused pyrido[2,3-*b*]porphyrin (11: Ar = 4-$OMeC_6H_4$)

Greenish-purple solid. Yield 50%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 456 (41.6), 545 (3.0), 583 (1.2), 619 (1.5), 694 (0.9) nm; IR ($CHCl_3$): 3347 (N–H), 3049, 3019, 2921, 2842, 1739 (C=O), 1596, 1538, 1346, 1155, 1064, 998, 797, 753, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.88 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.77 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.63–8.60 (m, 3H, β-pyrrolic H), 8.57 (d, *J* = 5.0

Hz, 1H, β-pyrrolic H), 8.23–8.21 (m, 2H, *meso*-ArH), 8.13–8.05 (m, 1H, *meso*-ArH), 7.99–7.91 (m, 3H, *meso*-ArH), 7.88–7.86 (m, 1H, *meso*-ArH), 7.77–7.74 (m, 8H, *meso*-ArH, ArH), 7.59–7.49 (m, 2H, *meso*-ArH), 7.45–7.39 (m, 4H, *meso*-ArH, ArH) 7.34 (d, *J* = 7.6 Hz, 1H, ArH), 7.29 (d, *J* = 8.1 Hz, 1H, ArH), 7.01–6.96 (m, 2H, ArH), 6.86 (d, *J* = 8.9 Hz, 1H, ArH), 6.51–6.49 (m, 2H, ArH), 3.87 (s, 3H, OCH_3), –1.96 (s, 1H, internal NH), –2.09 (s, 1H, internal NH).

Free-base coumarin-fused pyrido[2,3-*b*]porphyrin (12: Ar = 2′-naphthyl)

Greenish-purple solid. Yield 72%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 455 (45.4), 544 (3.3), 586 (1.0), 619 (1.3), 690 (0.9) nm; IR ($CHCl_3$): 3346 (N–H), 3056, 3026, 2923, 2852, 1744 (C=O), 1646, 1600, 1543, 1502, 1465, 1438, 1350, 1263, 1230, 1160, 1072, 798, 755, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.90 (d, *J* = 4.7 Hz, 1H, β-pyrrolic H), 8.79 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.65 (d, *J* = 4.6 Hz, 1H, β-pyrrolic H), 8.61 (d, *J* = 4.6 Hz, 1H, β-pyrrolic H), 8.54 (d, *J* = 4.9 Hz, 1H, β-pyrrolic H), 8.41–8.36 (m, 3H, β-pyrrolic H, *meso*-ArH), 8.25–8.20 (m, 3H, *meso*-ArH), 8.00–7.95 (m, 4H, *meso*-ArH), 7.90–7.84 (m, 2H, *meso*-ArH), 7.78–7.74 (m, 11H, *meso*-ArH, ArH), 7.58–7.54 (m, 1H, ArH), 7.51–7.43 (m, 2H, ArH), 7.37-7.33 (m, 2H, ArH), 7.29 (d, *J* = 8.1 Hz, 1H, ArH), 7.20–7.17 (m, 1H, ArH), 6.81-6.78 (m, 1H, ArH), 6.57–6.52 (m, 1H, ArH), –1.92 (s, 1H, internal NH), –2.09 (s, 1H, internal NH).

General procedure for the synthesis of zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins (13–15)

An oven-dried round bottom flask was charged with free-base coumarin-fused *meso*-tetraphenylpyridoporphyrins (**9**, **10** or **12**; 0.034 mmol) and $CHCl_3$ (10 mL). Then, a solution of zinc acetate (10.9 mg, 0.051 mmol) in methanol (1 mL) was added slowly. The resulting reaction mixture was stirred at RT for 30 min. After completion of the reaction, the mixture was washed with water (2×30 mL) and the organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product obtained was purified on a neutral alumina column using chloroform as an eluent to afford pure products.

Characterization data of zinc(II) coumarin-fused pyrido[2,3-*b*]porphyrin (13: Ar = 4-ClC_6H_4)

Green solid. Yield 85%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 459 (25.1), 579 (2.9), 616 (0.8) nm; IR ($CHCl_3$): 3018, 2923, 2853, 1743 (C=O), 1598, 1539, 1216, 1176, 1079, 1004, 755, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.82-8.79 (m, 4H, β-pyrrolic H), 8.71 (d, *J* = 4.7 Hz, 1H, β-pyrrolic H), 8.58 (d, *J* = 4.5 Hz, 1H, β-pyrrolic H), 8.28–8.27 (m, 1H, *meso*-ArH), 8.22–8.18 (m, 5H, *meso*-ArH), 7.98–7.94 (m, 1H, *meso*-ArH), 7.90–7.87 (m, 3H, *meso*-ArH), 7.76-7.74 (m, 8H, *meso*-ArH) 7.57 (t, *J* = 8.0 Hz, 1H, *meso*-ArH), 7.50–7.44 (m, 2H, *meso*-ArH, ArH), 7.44–7.35 (m, 2H, ArH), 7.33–7.30 (m, 1H, ArH), 6.97 (d, *J* = 8.0 Hz, 2H, ArH), 6.43-6.40 (m, 2H, ArH).

Zinc(II) coumarin-fused pyrido[2,3-*b*]porphyrin (14: Ar = 4-$NO_2C_6H_4$)

Green solid. Yield 82%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 458 (24.0), 582 (3.4), 617 (0.9) nm; IR ($CHCl_3$): 3073, 3022, 2921, 2852, 1738 (C=O), 1598, 1538, 1443, 1340, 1266, 1174, 1074, 1001, 795, 753, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.82 (s, 2H, β-pyrrolic H), 8.76 (s, 2H, β-pyrrolic H), 8.69 (d, *J* = 4.5 Hz, 1H, β-pyrrolic H), 8.50 (d, *J* = 4.5 Hz, 1H, β-pyrrolic H), 8.28 (d, *J* = 6.0 Hz, 1H, *meso*-ArH), 8.21-8.16 (m, 4H, *meso*-ArH), 7.99–7.84 (m, 6H, *meso*-ArH), 7.79–7.73 (m, 7H, *meso*-ArH), 7.59–7.46 (m, 4H, *meso*-ArH, ArH), 7.37–7.35 (m, 3H, ArH), 7.30 (d, *J* = 8.1 Hz, 1H, ArH), 6.64 (d, *J* = 6.7 Hz, 2H, ArH).

Zinc(II) coumarin-fused pyrido[2,3-*b*]porphyrin (15: Ar = 2′-naphthyl)

Green solid. Yield 76%. m.p. >300°C. UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 460 (23.9), 580 (2.6), 617 (0.7) nm; IR ($CHCl_3$): 3057, 3022, 2922, 2853, 1738 (C=O), 1600, 1538, 1499, 1463, 1335, 1271, 1217, 1074, 1002, 797, 756, 700, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.85 (d, *J* = 4.8 Hz, 1H, β-pyrrolic H), 8.69 (d, *J* = 4.7 Hz, 1H, β-pyrrolic H), 8.56 (d, *J* = 4.8 Hz, 1H, β-pyrrolic H), 8.50–8.441 (m, 2H, β-pyrrolic H), 8.14–7.98 (m, 4H, β-pyrrolic H, meso-ArH), 7.92–7.78 (m, 5H, meso-ArH), 7.75–7.63 (m, 11H, meso-ArH), 7.62–7.54 (m, 1H, *meso*-ArH) 7.41–7.26 (m, 7H, ArH), 7.22–7.10 (m, 1H, ArH), 7.03–6.95 (m, 1H, ArH), 6.86-6.76 (m, 1H, ArH), 6.65-6.56 (m, 1H, ArH).

Conclusion

In conclusion, a new series of π-extended copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins have been synthesized through a cascade reaction of copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin with aromatic aldehydes and 4-hydroxycoumarin in presence of trichloroacetic acid in refluxing *o*-dichlorobenzene. Furthermore, free-base and zinc(II) analogues of these porphyrinoids were also prepared in good yields by using traditional demetallation and complexation protocols. On photophysical evaluation, the newly constructed π-extended pyridoporphyrins displayed remarkable bathochromic shifts in their electronic absorption spectra as compared to the non-π-extended *meso*-tetraphenylporphyrin precursors. The results originated from this investigation may be beneficial for the future designing of highly π-conjugated porphyrinic systems for diverse applications in the areas of material and medicinal chemistry.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/1234-56789/58776.

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