La(OTf)₃-Catalyzed Synthesis of Nickel(II) β -Iminoporphyrins and Their Conversion to β -Substituted Porphyrin-Thiazolidinone Hybrids

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Abstract Two diverse series of nickel(II) β -iminoporphyrins were prepared in good yields by the reaction of corresponding 2-formyl- and 2-amino-5,10,15,20-tetraphenylporphyrins with primary amines and aldehydes, respectively, in toluene containing a catalytic amount of La(OTf)₃ under reflux conditions. These 2-iminoporphyrins further served as precursors to construct novel nickel(II) complexes of β -substituted porphyrinic thiazolidinones in moderate yields on reaction with mercaptoacetic acid in refluxing toluene. All the synthesized porphyrins have been characterized on the basis of spectral data analysis.

Keywords β -iminoporphyrins, lanthanum triflate, mercaptoacetic acid, synthesis, thiazolidinones

Introduction

Porphyrins are highly conjugated tetrapyrrolic macrocycles that are widely used as light absorbing dyes in photovoltaics^[1] and photosensitizers in photodynamic therapy applications for the treatment of a variety of tumors.^[2] Furthermore, the molecules of this class can be functionalized at the peripheral positions to generate numerous macrocyclic compounds with tailored properties.^[3-5] Previously, a wide range of porphyrin building blocks were synthesized by introducing diverse functionalities such as nitro, amino, formyl, hydroxy, vinyl and halides to the *meso*- and β -positions.^[6-13] However, the functionalization of porphyrin Schiff's bases in constructing π -conjugated porphyrin macrocycles have not been fully explored. So far, only few reports are available on the synthesis, functionalization and optical properties of 2-iminoporphyrins.^[14-17] Some of these reports demonstrated β -iminoporphyrins as heterodienes in Diels-Alder reaction to prepare various pyridoporphyrins and tetrahydroquinoline-substituted porphyrin analogues.^[18,17] Similarly, imines have also been employed as the key precursors for synthesis of therapeutically promising thiazolidinone-based molecules.^[18,19]

Thorough literature search revealed that 4-thiazolidinones are an important class of molecules due to their diverse biological profiles as COX-1 inhibitors,^[20,21] non-nucleoside inhibitors of HIV-RT,^[22] inhibitors of the bacterial enzyme MurB,^[23] anti-histaminic^[24] and anti-inflammatory agents.^[25] In addition, thiazolidinone embedded molecular frameworks have also been investigated for their potential applications in the field of photonics, reversible optical data storage and photo-switching of optical elements.^[26] Owing to the potential applications of porphyrins and 4-thiazolidinones, we successfully synthesized a series of *meso*-substituted porphyrinic thiazolidinones for the study of their optical characteristics. On photo-physical investigation, these compounds displayed interesting properties.^[27] Therefore, it was envisaged to synthesize β -substituted porphyrinic thiazolidinones for the study of their optical properties.

In continuation of our efforts to develop synthetic methods for various β -functionalized porphyrins,^[28-37] we present herein a La(OTf)₃-catalyzed synthetic protocol for the preparation of nickel(II) 2-imino-5,10,15,20-tetraphenylporphyrins, which have

been employed as precursors to construct a new series of β -substituted nickel(II) porphyrin-thiazolidinone hybrids. The synthetic details and spectral properties of newly prepared porphyrins are discussed in this report.

Experimental

Materials and methods

Pyrrole, aromatic aldehydes, primary amines, mercaptoacetic acid and La(OTf)₃ used in the present study were purchased from Sigma Aldrich and used without further purification. Solvents were purchased from Merck and dried according to literature procedures. Thin layer chromatography (TLC) was performed using silica gel 60 F254 (pre-coated aluminium sheets) from Merck. Reactions were monitored by TLC and products were purified by column chromatography using activated neutral aluminum oxide (Brokmann grade I–II, Merck). ¹H NMR spectra were obtained in CDCl₃, using a Bruker 300 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS, δ 0 ppm) as an internal standard. Coupling constants *J* are reported in hertz (Hz). Infrared spectra were recorded on Perkin Elmer IR spectrometer and absorption maxima ($\nu_{\max}$) are given in cm⁻¹. Mass spectra were recorded on an ESI-MS (micromass LCT, waters) mass spectrometer. Analytic jena specord 250 UV-Vis spectrophotometer was used for electronic absorption measurements. The electronic absorption spectra of prepared porphyrins were recorded in chloroform at (1.5 × 10⁻⁶ M) at room temperature.

General procedure for synthesis of nickel(II) β -imino-5,10,15,20-tetraphenylporphyrins (2a–2e)

To a solution of nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (**1a**, 0.071 mmol) in toluene (10 mL), primary amine (0.213 mmol) and La(OTf)₃ (0.014 mmol) were added. The reaction mixture was refluxed for 7 h and the progress of reaction was monitored by thin layer chromatography (TLC). After complete consumption of starting materials, the reaction mixture was allowed to cool at room temperature and filtered to remove the La(OTf)₃. The filtrate was evaporated under reduced pressure. Thus, the residue obtained was washed with

methanol and recrystallized from MeOH/CH₂Cl₂ (1 : 1) mixture.

Nickel(II) 2-[(butylimino)methyl]-5,10,15,20-tetraphenylporphyrin (**2a**). Yield: 92%; IR (KBr) ν_{max} : 3054, 2956, 1625, 1599, 1545, 1351, 1008, 795, 751 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 9.06 (s, 1H, β -pyrrolic H), 8.63–8.61 (m, 7H, β -pyrrolic H and CH), 7.90–7.85 (m, 8H, *meso*-ArH), 7.65–7.55 (m, 12H, *meso*-ArH), 3.20–3.16 (t, 2H, NCH₂), 1.56–1.51 (m, 2H, CH₂), 1.32–1.10 (m, 2H, CH₂), 0.91–0.86 (t, 3H, CH₃); UV λ_{max} : 425, 538, 572 nm; ESI MS calcd. for C₄₉H₃₈N₅Ni: 754.2; found: 754.1 [M + H]⁺.

Nickel(II) 2-[(benzylimino)methyl]-5,10,15,20-tetraphenylporphyrin (**2b**). Yield: 90%; IR (film) ν_{max} : 3055, 2921, 1622, 1599, 1557, 1351, 1008, 795, 751, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 9.20 (s, 1H, β -pyrrolic H), 8.73–8.68 (m, 7H, β -pyrrolic H and CH), 7.97–7.95 (m, 8H, *meso*-ArH), 7.79–7.61 (m, 12H, *meso*-ArH), 7.25–7.28 (m, 5H, ArH), 4.45 (s, 2H, CH₂); UV λ_{max} : 426, 538, 576 nm.

Nickel(II) 2-[(4-chlorophenylimino)methyl]-5,10,15,20-tetraphenylporphyrin (**2c**). Yield: 93%; IR (KBr) ν_{max} : 3052, 2924, 1622, 1598, 1545, 1350, 1004, 797, 750, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 9.36 (s, 1H, β -pyrrolic H), 8.73–8.67 (m, 7H, β -pyrrolic H and CH), 8.02–7.98 (m, 8H, *meso*-ArH), 7.68–7.66 (m, 12H, *meso*-ArH), 7.27 (d, *J* = 8.6 Hz, 2H, ArH), 6.87 (d, *J* = 8.4 Hz, 2H, ArH); UV λ_{max} : 431, 541, 585 nm; ESI-MS calcd. for C₅₁H₃₃ClN₅Ni: 808.1; found: 808.2 [M + H]⁺.

Nickel(II) 2-[(4-bromophenylimino)methyl]-5,10,15,20-tetraphenylporphyrin (**2d**). Yield: 91%; IR (KBr) ν_{max} : 2928, 2851, 1624, 1598, 1350, 1007, 795, 750, 701 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 9.39 (s, 1H, β -pyrrolic H), 8.75–8.69 (m, 7H, β -pyrrolic H and CH), 8.04–7.98 (m, 8H, *meso*-ArH), 7.72–7.65 (m, 12H, *meso*-ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 6.83 (d, *J* = 8.0 Hz, 2H, ArH); UV λ_{max} : 431, 541, 584 nm; ESI MS calcd. for C₅₁H₃₃BrN₅Ni: 852.1; found: 852.2 [M + H]⁺, 854.2 [(M + H) + 2]⁺.

Nickel(II) 2-[(4-methoxyphenylimino)methyl]-5,10,15,20-tetraphenylporphyrin (**2e**)

Yield: 71%; IR (KBr) ν_{max} : 3054, 3023, 1621, 1597, 1551, 1351, 1245, 1073, 1008, 796, 753, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 9.32 (s, 1H, β -pyrrolic H), 8.71–8.68 (m, 7H, β -pyrrolic H and CH), 8.03–7.99 (m, 8H, *meso*-ArH), 7.69–7.68 (m, 12H, *meso*-ArH), 6.97 (d, *J* = 8.8 Hz, 2H, ArH), 6.86 (d, *J* = 8.8 Hz, 2H, ArH); 3.85 (s, 3H, OCH₃); UV λ_{max} : 430, 543, 585 nm; ESI MS calcd. for C₅₂H₃₅N₅NiO: 804.2; found: 804.5 [M + H]⁺.

General procedure for synthesis of nickel(II) β -imino-5,10,15,20-tetraphenylporphyrins (**3a–3b**)

To a solution of nickel(II) 2-amino-5,10,15,20-tetraphenylporphyrin (**1b**, 0.072 mmol) in toluene (10 mL), aldehyde (0.213 mmol) and lanthanum triflate (0.014 mmol) were added. The reaction mixture was refluxed for 7 h and the progress of reaction was monitored by TLC. After completion of the reaction, the mixture was filtered to remove the lanthanum triflate and filtrate was evaporated to dryness. Thus, the residue obtained was washed with methanol and crude product was recrystallized in MeOH/CH₂Cl₂ (1 : 1) mixture.

Nickel(II) 2-[(4-nitro-1-benzylidene)amino]-5,10,15,20-tetraphenylporphyrin (**3a**). Yield: 95%; IR (film) ν_{max} : 3050, 2921, 1623, 1597, 1343, 1007, 796, 751, 701 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 8.74–8.64 (m, 7H, β -pyrrolic H), 8.29 (s, 1H, CH), 8.23 (d, *J* = 8.0 Hz, 2H, ArH), 8.05–7.97 (m, 6H, *meso*-ArH), 7.88–7.84 (m, 2H, ArH), 7.72–7.62 (m, 12H, *meso*-ArH), 7.54–7.50 (m, 2H, *meso*-ArH); UV λ_{max} : 417, 540, 586 nm; ESI MS calcd. for C₅₁H₃₃N₆NiO₂: 819.2; found: 819.3 [M + H]⁺.

Nickel(II) 2-[(4-trifluoromethyl-1-benzylidene)amino]-5,10,-

15,20-tetraphenylporphyrin (**3b**). Yield: 95%; IR (KBr) ν_{max} : 3062, 2918, 1621, 1596, 1442, 1351, 1322, 1009, 837, 794, 752, 701 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 8.71–8.66 (m, 6H, β -pyrrolic H), 8.60 (s, 1H, β -pyrrolic H), 8.26 (s, 1H, CH), 8.06–7.96 (m, 6H, *meso*-ArH), 7.86–7.84 (m, 2H, *meso*-ArH), 7.67–7.56 (m, 14H, *meso*-ArH and ArH), 7.52–7.50 (m, 2H, ArH); UV λ_{max} : 423, 539, 574 nm; ESI MS calcd. for C₅₂H₃₃F₃N₅Ni: 842.1; found: 842.4 [M + H]⁺.

General procedure for synthesis of β -substituted nickel(II) porphyrin-thiazolidinone hybrids (**4a–4e** and **5a–5b**)

To a solution of nickel(II) β -iminoporphyrins (**2a–2e** or **3a–3b**, 0.049 mmol) in toluene (10 mL), mercaptoacetic acid (0.30 mmol) was added. The reaction mixture was stirred at reflux for 10 h and progress of the reaction was monitored by using TLC. After completion of the reaction, the mixture was allowed to cool at room temperature and neutralized by using aqueous NaHCO₃ solution. The resulting solution was washed with water and the desired product was extracted with chloroform. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product thus obtained was washed with methanol and purified over neutral alumina column using 70% CHCl₃ in hexane as eluent.

Nickel(II) 2-[4-oxo-3-butylthiazolidin-2-yl]-5,10,15,20-tetraphenylporphyrin (**4a**). Yield: 40%; IR (KBr) ν_{max} : 2933, 2851, 1682, 1599, 1352, 1008, 754 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 8.66–8.63 (m, 6H, β -pyrrolic H), 8.41 (s, 1H, β -pyrrolic H), 7.98–7.87 (m, 8H, *meso*-ArH), 7.78–7.64 (m, 12H, *meso*-ArH), 5.51 (s, 1H, CH), 3.87–3.83 (m, 1H, NCH₂), 3.67 (d, *J* = 15.3 Hz, 1H, SCH₂CO), 3.40 (d, *J* = 15.6 Hz, 1H, SCH₂CO), 2.92 (m, 1H, NCH₂), 1.43–1.34 (m, 2H, CH₂), 1.17–1.14 (m, 2H, CH₂), 0.88 (t, 3H, CH₃); UV λ_{max} : 421, 535, 561 nm; ESI MS calcd. for C₅₁H₄₀N₅NiOS: 828.2; found: 828.1 [M + H]⁺.

Nickel(II) 2-[4-oxo-3-benzylthiazolidin-2-yl]-5,10,15,20-tetraphenylporphyrin (**4b**). Yield 50%; IR (film) ν_{max} : 3056, 3021, 2922, 2851, 1686, 1599, 1009, 753 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 8.64–8.42 (m, 7H, β -pyrrolic H), 7.88–7.87 (m, 8H, *meso*-ArH), 7.61–7.60 (m, 12H, *meso*-ArH), 7.28–7.20 (m, 2H, ArH), 6.90–6.88 (m, 2H, ArH), 5.26 (s, 1H, CH), 5.21 (d, *J* = 15.0 Hz, 1H, NCH₂), 3.76 (d, *J* = 15.1 Hz, 1H, NCH₂), 3.69 (d, *J* = 15.7 Hz, 1H, SCH₂CO), 3.43 (d, *J* = 15.5 Hz, 1H, SCH₂CO); UV λ_{max} : 421, 535, 560 nm; ESI MS calcd. for C₅₄H₃₈N₅NiOS: 862.4; found: 862.7 [M + H]⁺; Anal. calcd. for C₅₄H₃₇N₅NiOS: C, 75.18; H, 4.32, N, 8.12, S, 3.72; found: C, 75.58; H, 4.40, N, 8.20, S, 3.74.

Nickel(II) 2-[4-oxo-3-(4-chlorophenyl)thiazolidin-2-yl]-5,10,15,20-tetraphenylporphyrin (**4c**). Yield 46%; IR (KBr) ν_{max} : 2923, 2852, 1694, 1598, 1492, 1009, 753 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 8.73–8.61 (m, 6H, β -pyrrolic H), 8.51 (s, 1H, β -pyrrolic H), 7.97–7.82 (m, 8H, *meso*-ArH), 7.72–7.62 (m, 12H, *meso*-ArH), 7.38–7.21 (m, 4H, ArH), 5.91 (s, 1H, CH), 3.80 (d, *J* = 15.6 Hz, 1H, SCH₂CO), 3.52 (d, *J* = 15.9 Hz, 1H, SCH₂CO); UV λ_{max} : 421, 535, 561 nm; ESI MS calcd. for C₅₃H₃₅ClN₅NiOS: 882.1; found: 882.4 [M + H]⁺.

Nickel(II) 2-[4-oxo-3-(4-bromophenyl)thiazolidin-2-yl]-5,10,15,20-tetraphenylporphyrin (**4d**). Yield 52%; IR (film) ν_{max} : 2921, 2852, 1698, 1595, 1492, 1008, 795 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 8.73–8.66 (m, 5H, β -pyrrolic H), 8.62 (d, *J* = 4.9 Hz, 1H, β -pyrrolic H), 8.50 (s, 1H, β -pyrrolic H), 7.99–7.95 (m, 4H, *meso*-ArH), 7.83–7.80 (m, 4H, *meso*-ArH), 7.71–7.63 (m, 12H, *meso*-ArH), 7.44–7.37 (m, 3H, ArH), 7.06 (d, *J* = 8.6 Hz, 1H, ArH), 5.91 (s, 1H, CH), 3.80 (d, *J* = 16.0 Hz, 1H, SCH₂CO), 3.53 (d, *J* = 15.9 Hz, 1H, SCH₂CO); UV λ_{max} : 421, 536, 562 nm; ESI MS calcd. for C₅₃H₃₅BrN₅NiOS: 926.1 found: 926.5 [M + H]⁺.

Nickel(II) 2-[4-oxo-3-(4-methoxyphenyl)-thiazolidin-2-yl]-5,10,15,20-tetraphenylporphyrin (**4e**). Yield 60%; IR (film) $\nu_{\max}$: 3056, 3021, 2922, 2851, 1687, 1599, 1511, 1008, 753 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 8.62–8.52 (m, 6H, β -pyrrolic H), 8.20 (s, 1H, β -pyrrolic H), 7.90–7.78 (m, 8H, *meso*-ArH), 7.74–7.60 (m, 12H, *meso*-ArH), 7.16–7.13 (m, 2H, ArH), 6.76–6.73 (m, 2H, ArH), 5.84 (s, 1H, CH), 3.74 (d, $J = 15.3$ Hz, 1H, SCH_2CO), 3.62 (s, 3H, OCH_3), 3.45 (d, $J = 15.2$ Hz, 1H, SCH_2CO); UV $\lambda_{\max}$: 421, 535, 563 nm; ESI MS calcd. for $\text{C}_{54}\text{H}_{38}\text{N}_5\text{NiO}_2\text{S}$: 878.2; found: 878.5 $[\text{M} + \text{H}]^+$; Anal. calcd. for $\text{C}_{54}\text{H}_{37}\text{N}_5\text{NiO}_2\text{S}$; C, 73.81; H, 4.24; N, 7.97; S, 3.65; found: C, 73.72; H, 4.29; N, 7.82; S, 3.85.

Nickel(II) 2-[2-(4-nitrophenyl)-4-oxothiazolidin-3-yl]-5,10,15,20-tetraphenylporphyrin (**5a**). Yield: 40%; IR (film) $\nu_{\max}$: 2924, 2853, 1693, 1598, 1520, 1441, 1351, 1073, 1009, 795, 752, 701 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 8.75–8.67 (m, 7H, β -pyrrolic H), 8.02–7.91 (m, 8H, *meso*-ArH and ArH), 7.88–7.84 (m, 3H, *meso*-ArH), 7.79 (d, $J = 8.0$ Hz, 2H, ArH), 7.72–7.64 (m, 11H, *meso*-ArH and ArH), 7.20 (s, 1H, CH), 3.40 (brs, 1H, SCH_2CO), 3.30 (brs, 1H, SCH_2CO); UV $\lambda_{\max}$: 421, 537, 562 nm; ESI MS calcd. for $\text{C}_{53}\text{H}_{35}\text{N}_6\text{NiO}_3\text{S}$: 893.2; found: 893.7 $[\text{M} + \text{H}]^+$.

Nickel(II) 2-[2-(4-trifluoromethylphenyl)-4-oxo-thiazolidin-3-yl]-5,10,15,20-tetraphenylporphyrin (**5b**). Yield 50%; IR (KBr) $\nu_{\max}$: 2921, 2851, 1705, 1597, 1515, 1463, 1351, 1072, 1007, 793, 750, 700 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 8.71–8.61 (m, 7H, β -pyrrolic H), 7.99–7.97 (m, 8H, *meso*-ArH), 7.79–7.77 (m, 2H, ArH), 7.68–7.64 (m, 12H, *meso*-ArH), 7.54–7.51 (m, 2H, ArH), 7.24 (s, 1H, CH), 4.24 (d, $J = 15.3$ Hz, 1H, SCH_2CO), 4.19 (d, $J = 15.0$ Hz, 1H, SCH_2CO); ESI MS calcd. for $\text{C}_{54}\text{H}_{35}\text{F}_3\text{N}_5\text{NiO}_3\text{S}$: 916.1; found: 916.2 $[\text{M} + \text{H}]^+$.

Results and Discussion

Initially, we attempted the synthesis of key precursors, β -imino-5,10,15,20-tetraphenylporphyrins (**2a–2e** and **3a–3b**) in various solvents such as benzene, toluene, chloroform, dioxane and THF at reflux temperature using CH_3COOH , *p*-toluenesulfonic acid, MeSO_3H and ZnCl_2 as acidic catalysts. Unfortunately, all these reactions were found to be sluggish and afforded desired products in poor yields. Moreover, these porphyrin Schiff's bases were found to be unstable over column, and therefore, difficult to obtain in pure form. To this end, Cavaleiro and co-workers have been successful to synthesize porphyrin Schiff's bases in good yields using $\text{La}(\text{OTf})_3$ as a Lewis acid catalyst.^[16,17] In comparison to traditional acidic catalysts, $\text{La}(\text{OTf})_3$ is a stable and water compatible Lewis acid, which leads to the formation of products in better yields while other moisture sensitive catalysts get easily decomposed in the presence of even small amount of water.^[38] By following the strategy reported in the literature,^[16,17] a series of β -iminoporphyrins (**2a–2e** and **3a–3b**) were synthesized by the reaction of either nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (**1a**) with primary amines or nickel(II) 2-amino-5,10,15,20-tetraphenylporphyrin (**1b**) with aldehydes in toluene containing a catalytic amount of $\text{La}(\text{OTf})_3$ at reflux temperature, as shown in Scheme 1. In the next step, these nickel(II) β -iminoporphyrins (**2a–2e** and **3a–3b**) were successfully converted to the corresponding β -substituted nickel(II) porphyrin-thiazolidinone conjugates (**4a–4e** and **5a–5b**) in moderate yields on reaction with mercaptoacetic acid in toluene under reflux conditions (Scheme 1). Alternatively, the efforts have also been made to construct the desired porphyrin molecules under one-pot operation but mainly the decomposition of starting materials was observed and porphyrinic thiazolidinones were formed in trace amount.

The structures of the prepared porphyrins were assigned on

the basis of IR, ^1H NMR, mass and UV-Vis data analysis. The IR spectra of 2-iminoporphyrins (**2a–2e** and **3a–3b**) showed a characteristic peak at $\sim 1622 \text{ cm}^{-1}$ due to the C=N stretching.^[39] Similarly, IR spectra of β -substituted porphyrinic thiazolidinones (**4a–4e** and **5a–5b**) displayed a new peak at $\sim 1690 \text{ cm}^{-1}$ due to the presence of a cyclic amide group in the molecule. In the ^1H NMR spectra of (**4a–4e**), a characteristic singlet at δ 5.84 for one proton and two doublets at δ 3.74 and 3.45 for one proton each correspond to the CH and CH_2 protons of the thiazolidinone ring, respectively. Whereas in the case of porphyrin-thiazolidinone hybrids (**5a–5b**), a singlet for the CH proton of the thiazolidinone ring was found around δ 7.20 and the CH_2 protons appeared between δ 4.24 and 3.30. Furthermore, the mass spectral analysis of the synthesized molecules was also found to be in agreement with the assigned structures.

The electronic absorption spectra of all the synthesized porphyrins were measured in 1.5×10^{-6} M solution in chloroform at 298 K. The absorption spectra of nickel(II) 2-iminoporphyrins (**2a–2e**) have shown a characteristic Soret band between 425–431 nm and two Q-bands between 538–587 nm. However, the nickel(II) 2-iminoporphyrin (**3a**) displayed a broadened Soret band centered at 417 nm and two Q-bands at 540 and 586 nm. In contrast, the nickel(II) β -substituted porphyrinic thiazolidinones (**4a–4e** and **5a**) displayed a sharp Soret band at 421 nm and two Q-bands at ~ 536 and 562 nm. The preliminary results revealed a bathochromic shift of up to 15 nm in the UV-Vis spectra of nickel complexes of 2-iminoporphyrins (**2a–2e**) as compared to the simple nickel(II) *meso*-tetraphenylporphyrin (Ni-TPP; Soret band at 417 nm and Q-bands 533 and 572 nm) due to the extended π -conjugation, where the porphyrinic thiazolidinones (**4a–4e** and **5a**) have demonstrated a marginal red-shift in their electronic absorption spectra. The absorption spectra of representative nickel(II) 2-iminoporphyrins (**2d** and **3a**), porphyrin-thiazolidinone hybrids (**4d** and **5a**) and NiTPP have been illustrated in Figure 1. The characterization data of all the synthesized compounds are presented in the experimental section.

The probable mechanistic pathways for the formation of porphyrin-thiazolidinone conjugates (**4a–4e** and **5a–5b**) using either nickel(II) β -formylporphyrin (**1a**) or β -aminoporphyrin (**1b**) as the starting porphyrin substrates have been depicted in Schemes S1 and S2 (Supporting Information). The reaction in both the cases proceeds via a dehydrative condensation-cyclization mechanism. The condensation step involves the formation of 2-iminoporphyrins under the influence of $\text{La}(\text{OTf})_3$. In the next step, these 2-iminoporphyrins undergo nucleophilic attack by a thiol group of mercaptoacetic acid followed by an intramolecular cyclization to form a key geminal diol intermediate, which on dehydration provides the desired β -substituted porphyrin-thiazolidinone conjugates (**4a–4e** and **5a–5b**).

Conclusions

In summary, various nickel(II) β -iminoporphyrins and β -substituted porphyrinic thiazolidinones were successfully synthesized in good to moderate yields. On photophysical investigation, some of these porphyrin analogues have demonstrated a significant red-shift in their electronic absorption spectra as compared to the nickel(II) *meso*-tetraphenylporphyrin. Hence, these new materials may have potential applications in diverse areas. Furthermore, the results presented herein are useful to explore the β -iminoporphyrins as building blocks for synthesis of new π -extended porphyrins as photosensitizers to be used in dyes-sensitized solar cells and photodynamic therapy.

Scheme 1 Synthesis of β -substituted nickel(II) *meso*-tetraphenylporphyrin-thiazolidinone hybrids (**4a–4e** and **5a–5b**) **Figure 1** Electronic absorption spectra of porphyrins **2d**, **3a**, **4d**, **5a** and **NiTPP** in chloroform (1.5×10^{-6} M) at 298 K. Inset shows Q-bands.

Acknowledgement

Authors are thankful to the USIC and Department of Chemistry, University of Delhi, Delhi, India for providing NMR and mass spectral data. Pargat Singh is grateful to UGC, New Delhi, India for the senior research fellowship (SRF).

Supporting Information

Supporting information for this article is available on the WWW under www.genchemistry.org/EN/10.21127/yaoyigc-20200020.

Conflict of Interest

The authors declare no conflict of interest.

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Received November 10, 2020

Accepted January 15, 2021