Tetrahedron Letters 51 (2010) 2865–2867

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

One-pot synthesis of β-carboxy tetra aryl porphyrins: potential applications to dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 16 February 2010
Revised 17 March 2010
Accepted 19 March 2010
Available online 27 March 2010

ABSTRACT

A facile one-pot conversion of 2-formyl-5,10,15,20-tetra aryl-substituted porphyrins and their zinc derivatives to the corresponding 2-carboxy-5,10,15,20-tetra aryl-substituted porphyrins was achieved for the first time by using hydroxylamine hydrochloride and phthalic anhydride. All these substituted carboxy porphyrins were completely characterized by using mass, CHN analysis, ^{1}H NMR, UV–vis, Fluorescence spectroscopies, and cyclic voltammetry. Both the absorption maxima and emission maxima were red shifted by 5–7 nm. The LUMO of these porphyrins are above the TiO_2 conduction band and HOMO was below the redox electrolytes. These carboxy porphyrins are potential applications as sensitizers to dye-sensitized solar cell.

Porphyrins and their metal complexes are involved in widespread applications that include self-assembly, sensors, liquid crystalline materials, non-linear optical studies, light emitting diodes, and as sensitizers in dye-sensitized solar cells (DSCs) for the conversion of sunlight into electricity.[1] Of these, conversion of sunlight into electricity using photovoltaic devices is particularly interesting. In this regard, DSC is currently attracting paramount importance because of their low cost, easy processing, and high conversion efficiency than the conventional solid-state photovoltaic devices.[2] In these cells, dye sensitizer is one of the key components for high power conversion efficiencies. The most successful charge-transfer sensitizers employed so far in such cells are *bis*(tetrabutylammonium)-*cis*-di(thiocyanato)-*N*,*N*′-*bis*(4-carboxylato-4′-carboxylic acid-2,2′-bipyridine)ruthenium(II) (the N719 dye) and trithiocyanato 4,4′4″-tricaboxy-2,2′:6′,2″-terpyridine ruthenium(II) (the black dye) with an efficiency of >12%.[3] In spite of this, the main drawbacks of these sensitizers are the lack of absorption in the red region of the visible spectrum as well as rarity of the metal in the earth crust. As Ru dyes are exclusive, metal-free organic molecules, tetrapyrrolic compounds such as porphyrins and phthalocyanines are potential alternative sensitizers for DSC applications based on their thermal as well as electronic properties.[4]

Plants and bacteria capture solar energy using porphyrin-based chromophores for converting it into chemical energy. Some metalloporphyrins have been tested for the photosensitization of wideband-gap semiconductors, the most common being either free-base or its zinc derivative of the *meso*-benzoic acid substituted porphyrins.[5] However, the efficiency of *meso*-substituted porphyrins remained around 3%. The ability to modify and tune the photophysical properties of synthetic porphyrins via the introduction of specific substituents either at *meso*- or at pyrrole-β position/s in order to further improve the efficiency of porphyrin-based DSC devices is being explored. Imahori and co-workers have used quinoxaline-fused porphyrins at pyrrole-β position containing either one or two carboxylic-anchoring groups and achieved the efficiency of 5.2%.[6] Officer and co-workers have reported a combination of conjugated ethenyl or diethenyl linker in the pyrrole-β position and a carboxylate-binding group gives the device efficiencies up to 7.1%.[7] All these porphyrins have carboxylic anchoring groups present on the linker (either on extended-π conjugation or extended aromatic ring) and are not directly connected to pyrrole-β position. If the anchoring carboxylic group is directly connected to pyrrole-β position, then the porphyrin in excited state can efficiently inject electron into TiO_2 conduction band and it will improve the efficiency as well as durability of device. To the best of our knowledge such type of molecules have not been reported in the literature so far. Here in, we report the synthesis and characterization of free-base and zinc tetraaryl substituted porphyrins having carboxylic acid group directly connected to pyrrole-β position.

The 2-formyl-5,10,15,20-tetra aryl-substituted porphyrins and their zinc derivatives were synthesized as per the literature procedure.[8] The oxidation of 2-formyl tetra unsubstituted porphyrins to the corresponding carboxylic acid has been achieved by the use of a mixture of chromium trioxide and sulfuric acid.[9] Officer and co-workers have applied the same reaction conditions to the 2-formyl-5,10,15,20-tetra aryl-substituted porphyrins and failed to convert into corresponding carboxylic group even after prolonged heating.[8] Other strong oxidizing agents $KMnO_4$, *m*-chloroperbenzoic acid, and Corey's cyanohydrins oxidation conditions have also failed and led to a very complex mixture of products.[10]

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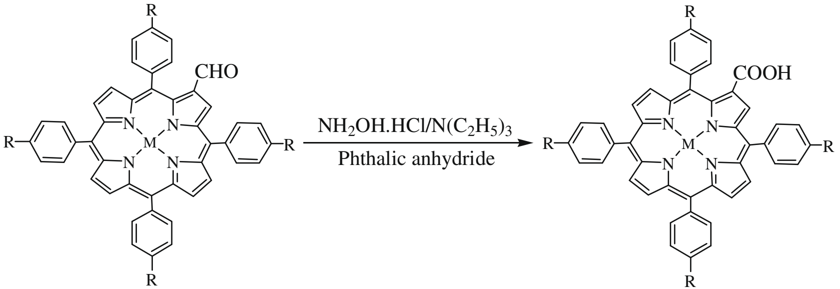
0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.03.088



R = H and M = 2H, **1**; R = H and M = Zn(II), **Zn1**
R = -CH_3 and M = 2H, **2**; R = -CH_3 and M = Zn(II), **Zn2**
R = -OCH_3 and M = 2H, **3**; R = -OCH_3 and M = Zn(II), **Zn3**
R = -*tert*-butyl and M = 2H, **4**; R = -*tert*-butyl and M = Zn(II), **Zn4**

Scheme 1. Synthesis of β-carboxy tetra aryl porphyrins.

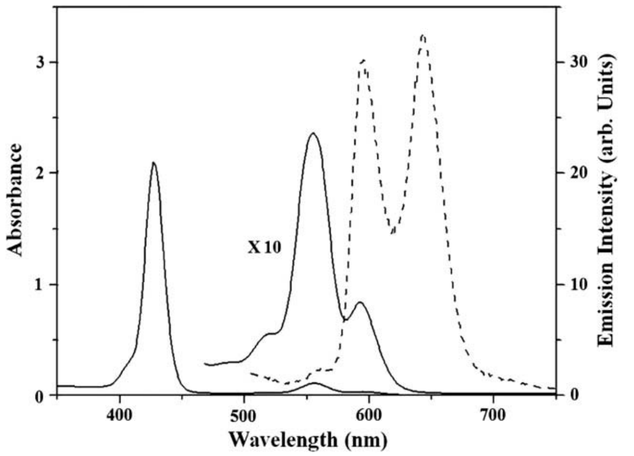


Figure 1. Absorption (—) and emission (——) spectra of **Zn1** in CH_2Cl_2.

The exact reason is not clear and this might be due to the steric hindrance of aryl groups.[8]

We have adopted an one-pot, mild reaction condition using hydroxylamine hydrochloride and phthalic anhydride for the conversion of 2-formyl-5,10,15,20-tetra aryl-substituted porphyrins to the corresponding carboxylic acid porphyrins (Scheme 1). By using this method, Wang and Lin have converted simple alky or aryl aldehydes to the corresponding nitriles in good yields.[11] Aq Ammonia has been used to quench the reaction at nitrile stage. Whereas in Mathew's dry hydrolysis reaction, the nitriles were converted into their corresponding carboxylic acids by using phthalic acid under solvent-free condition.[12] We have not used aq ammonia in this reaction and by refluxing the reaction mixture for a prolonged time, the formyl porphyrin converted to corresponding carboxylic porphyrin. Initially, we have used this one-pot method for the conversion of 2-formyl-5,10,15,20-tetra phenyl porphyrin (**1**) to 2-carboxy-5,10,15,20-tertra phenyl porphyrin (80%).[13] We have extended this methodology to other tetra aryl-substituted porphyrins having electron-releasing groups on phenyl ring, viz. –CH_3, –OCH_3, –*tert*-butyl groups, and their zinc derivatives. Both free-base and their zinc tetra aryl-substituted carboxy porphyrins were obtained in >80% yield. All these 2-carboxy tetra aryl-substituted porphyrins were completely characterized by mass, CHN analysis, IR, ^{1}H NMR, UV–vis, Fluorescence spectroscopy, and cyclic voltammetry (see Fig. 1).

The absorption spectra of free-base and zinc carboxy porphyrin were measured in CH_2Cl_2 solvent. The absorption spectra of all free-base carboxy porphyrins have an intense Soret band and four less intense Q-bands whereas its zinc derivatives have only two less intense Q-bands and an intense Soret band like its parent tetraaryl porphyrin. However, the absorption maxima of both Soret and Q-bands red shifted by 5–7 nm, probably due to the presence of electron-withdrawing carboxyl group. The emission spectra of both free-base and its zinc derivatives of carboxy porphyrins were measured in CH_2Cl_2 solvent. The emission maxima of all 2-carboxy porphyrins are red shifted by 5–7 nm when compared to those of its corresponding parent tetraaryl porphyrins. The singlet excited state ($E_{0\text{-}0}$) of free-base carboxy porphyrins is ranging from 1.85 to 1.90 ± 0.5 eV and that of its zinc derivatives is from 2.03 to 2.09 ± 0.05 eV. The redox potentials of carboxy porphyrins were

Table 1
UV–vis, emission and electronchemical data[a]

Compound	λ_{max}[b], nm (log ε, M^{-1} cm^{-1})	$\lambda_{em,\ max}$[c], nm (φ)	$E_{1/2}$[d]		$E_{0\text{-}0}$[e] (eV)
			Ox	Red	
1	424 (5.77), 520 (4.28), 557 (3.90), 598 (3.78), 654 (3.65)	663, 725 (0.09)	0.92	−1.24	1.90
2	426 (5.64), 523 (4.51), 559 (4.18), 600 (4.04), 661 (3.90)	669, 728 (0.10)	0.94	−1.27	1.86
3	427 (5.53), 524 (4.51), 561 (4.17), 600 (4.00), 659 (3.91)	675 (0.07)	0.90	−1.28	1.87
4	431 (5.10), 526 (4.32), 563 (4.11), 602 (3.97), 662 (.3.89)	668, 727 (0.09)	0.88	−1.30	1.85
Zn1	420 (5.88), 554 (4.38), 593 (3.95)	595, 644 (0.041)	0.79	−1.36	2.09
Zn2	428 (5.79), 556 (4.45), 594 (4.20)	606, 658 (0.043)	0.77	−1.40	2.06
Zn3	431 (5.42), 559 (4.38), 600 (3.97)	610, 660 (0.038)	0.75	−1.39	2.06
Zn4	429 (5.67), 557 (4.42), 594 (4.20)	619, 662 (0.047)	0.74	−1.41	2.03

[a] Solvent: CH_2Cl_2.
[b] Error limits, λ_{max} ± 1 nm, log ε, ±10%.
[c] φ, ±10%.
[d] 0.1 M TBAP, reference electrode: standard calomel electrode, working: glassy carbon, auxiliary electrode: Pt wire, error limits: $E_{1/2}$, ±0.03 V.
[e] Error limits, ±0.05 eV.

measured using cyclic voltammetry technique. It has two reversible or quasireversible reductions and oxidations. From Table 1, it is clear that the reduction potential of all new carboxy porphyrins are below the reduction of potentials of redox electrolyte (I^-/I_3^-).[14] The dye easily regenerates by taking electron from redox electrolyte. The excited state oxidation potentials (E^*_{ox}) of these sensitizers which corresponds to the LUMO were found to be above the TiO_2 conduction band and the electron in the excited state can efficiently inject into the conduction band (−0.8 V vs SCE).[15] The photovoltaic device studies by using these sensitizers are currently under progress.

In conclusion, we have used one-pot mild reaction conditions for the oxidation of 2-formyl-5,10,15,20-tetra aryl-substituted porphyrin to the corresponding 2-carboxy-5,10,15,20-tetra aryl-substituted porphyrin. From the singlet excited state and reduction potential, it is clear that the excited electron can be easily injected into the TiO_2 conduction and the oxidized state of dye can easily get reduced by taking electron from redox electrolyte. These sensitizers are potential applications to dye-sensitized solar cells.

Acknowledgments

We are thankful to the projects GAP-0220 and SR/S1/IC21/2008 for financial support of this work.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.03.088.

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13. Hydroxylamine hydrochloride (0.38 g, 5.5 mmol), triethyl amine (0.55 g, 5.5 mmol), and the corresponding 2-formyl-5,10,15,20-tetra aryl substituted porphyrin (5 mmol) were added in 50 ml of dry acetonitrile under nitrogen atmosphere. The resulting reaction mixture was stirred for 30 min. To this phthalic anhydride (0.063 g, 0.5 mmol) was added and the reaction mixture was refluxed for 7 h. The solvent was removed under reduced pressure and the solid material was obtained. The obtained solid material was subjected to silica gel column chromatography and eluted with $CHCl_3/CH_3OH$ (95:5) mixture and the purple color band was collected and recrystallized from CH_2Cl_2/hexane mixture. Analytical data: Compound **1**: Yield: 80% (2.63 g). Anal. Calcd for $C_{45}H_{30}N_4O_2$: C, 82.05; H, 4.59; N, 8.51%. Found: C, 82.00; H, 4.55; N, 8.53%. MS: *m*/*z* 658, requires 658.75. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 9.00 (s, 1H), 8.85 (m, 6H), 8.15 (m, 8H), 7.70 (m, 12H) −2.71 (b, 2H). Compound **2**: Yield: 84% (2.99 g). Anal. Calcd for $C_{49}H_{38}N_4O_2$: C, 82.33; H, 5.36; N, 7.84%. Found: C, 82.60; H, 5.05; N, 7.90%. MS: *m*/*z* 714, requires 712.85. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 9.02 (s, 1H), 8.85 (m, 6H), 8.15 (m, 8H), 7.75 (m, 8H), 2.60 (s, 12H), −2.71 (b, 2H). Compound **3**: Yield: 85% (3.31 g). Anal. Calcd for $C_{49}H_{38}N_4O_6$: C, 75.56; H, 4.92; N, 7.19%. Found: C, 75.60; H, 4.95; N, 7.15%. MS: *m*/*z* 778, requires 778.85. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 9.00 (s, 1H), 8.85 (m, 6H), 8.15 (m, 8H), 7.70 (m, 12H), 3.73 (s, 12H) −2.71 (b, 2H). Compound **4**: Yield: 87% (3.75 g). Anal. Calcd for $C_{61}H_{62}N_4O_2$: C, 82.96; H, 7.08; N, 6.34%. Found: C, 83.00; H, 7.10; N, 6.30%. MS: *m*/*z* 882, requires 883.12. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 9.05 (s, 1H), 8.80 (m, 6H), 8.18 (m, 8H), 7.75 (m, 8H), 1.62 (s, 36H), −2.65 (b, 2H). Compound **Zn1**: Yield: 91% (3.28 g). Anal. Calcd for $C_{45}H_{28}N_4O_2Zn$: C, 74.85; H, 3.91; N, 7.76%. Found: C, 74.81; H, 3.89; N, 7.75%. MS: *m*/*z* 720, requires 720.15. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 8.95 (m, 7H), 8.18 (m, 6H), 7.95 (d, 2H), 7.75 (m, 12H). Compound **Zn2**: Yield: 89% (3.45 g). Anal. Calcd for $C_{49}H_{36}N_4O_2Zn$: C, 75.62; H, 4.66; N, 7.20%. Found: C, 75.60; H, 4.70; N, 7.15%. MS: *m*/*z* 776, requires 776.21. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 8.95 (m, 7H), 8.15 (m, 6H), 7.95 (d, 2H), 7.60 (m, 12H), 2.72 (s, 12H). Compound **Zn3**: Yield: 91% (3.82 g). Anal. Calcd for $C_{49}H_{36}N_4O_6Zn$: C, 69.88; H, 4.31; N, 6.65%. Found: C, 69.90; H, 4.30; N, 6.65%. MS: *m*/*z* 840, requires 840.19. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 8.95 (m, 7H), 8.18 (m, 6H), 7.95 (d, 2H), 7.70 (m, 12H), 3.76 (s, 12H). Compound **Zn4**: Yield: 90% (4.25 g). Anal. Calcd for $C_{61}H_{60}N_4O_2Zn$: C, 77.40; H, 6.39; N, 5.92%. Found: C, 77.35; H, 6.40; N, 5.90%. MS: *m*/*z* 945, requires 945.19. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 8.95 (m, 7H), 8.18 (m, 6H), 7.95 (d, 2H), 7.75 (m, 12H), 1.80 (s, 36H).
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