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Synthesis, electrochemical and photophysical properties of β-carboxy triaryl corroles

Kolanu Sudhakar, Veerapandian Velkannan, Lingamallu Giribabu *

Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

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ABSTRACT

An unswerving one-pot conversion of 3-formyl-5,10,15-triaryl substituted corroles and their copper(III) derivatives to the corresponding 3-carboxy-5,10,15-triaryl substituted corroles was achieved by adopting mild reaction conditions by using hydroxylamine hydrochloride and phthalic anhydride. All these substituted carboxy corroles were completely characterized by using Mass, CHN analysis, IR, ^{1}H NMR, UV–vis., Fluorescence spectroscopies and cyclic voltammetry. Both the absorption maxima and emission maxima of carboxy corroles were red shifted by 5–13 nm. The LUMO level of these corroles is above the TiO_2 conduction band and HOMO level was below the redox electrolytes. These β-carboxy corroles confined with may find applications as sensitizers in dye-sensitized solar cells.

Corrole macrocyle is a contracted analogue of a porphyrin in which one -*meso* position has been eliminated, yet possessing the 18-π electron aromaticity of porphyrins.[1] The structure of corrole represents an intermediate between porphyrin and the corrin ring in the *B12* cofactor. The first investigation on corrole was carried out by Johnson and Kay in the late 1960s when the macrocycle was produced as a by-product during the synthesis of *B12*.[2] Thus, while corroles have been known for more than 40 years, research in the field was slow to progress. However, investigations of corroles have recently increased with the synthetic work of the groups of Paolesse and Gross, with each of the respective groups reporting a one-pot synthesis of triaryl corroles.[3]

Unlike porphyrins, corroles are *tri*-anionic ligands that stabilize unusual high oxidation states of transition metal centers like Fe(IV), Cu(III), Co(IV), Ge(IV), Sn(IV), P(V) etc.[4] Corrole and its metallo derivatives are involved in many applications that include a catalyst in oxidation, reduction and group transfer reactions of many organic transformations, sensors, in photodynamic therapy, metastasis and as sensitizers in dye-sensitized solar cells (DSSC) for the generation of electricity from sunlight.[5] Of these, we are particularly interested in corroles as sensitizers for DSSC applications. DSSC is a low-cost and environmentally benign technology, an envisaged alternative to solid-state *p*–*n* photovoltaic devices. In these devices the sensitizer is one of the key component for achieving high efficiency and durability. The widely used sensitizers in DSSC devices are ruthenium(II) polypyridyl complexes with an efficiency of >11%.[6] However, ruthenium(II) polypyridyl complexes present two primary drawbacks: (1) rarity of the Ru metal in the earth's crust making it very expensive and (2) lack of absorption in red region of the visible spectrum. As an alternative, tetrapyrrolic compounds, which includes porphyrins and phthalocyanine are particularly of interest based on their absorption, thermal, photo- and electrochemical properties.[7] Even though, the efficiency of DSSC devices based on porphyrin sensitizers have shown around 10%, but their durability is low.[8] In contrast, phthalocyanine based sensitizers showed efficiency up to 4.6% but, is not ready for commercialization of technology.[9] For this reason, we found corroles are potential alternative sensitizers for DSSC applications.

Zeev Gross and co-workers have used sulfonated corroles having either Ga(III) or Sn(IV) in their central cavity for DSSC applications.[10] Ga(III) complex of corrole has shown an overall conversion efficiency of up to 1.6%. This is the only example reported in the literature of corroles as sensitizers for DSSC applications to the best of our knowledge. However, the sulfonic acid anchoring group does not strongly bind on to the nanocrystalline TiO_2 surface. It is known from the literature that the carboxylic acid groups bind more strongly on to the TiO_2 surface than sulfonic acid and phosphonic acid groups.[11] Here in the present manuscript we report the synthesis and characterization of β-carboxy triaryl corroles having electron releasing groups on its peripheral positions.

5,10,15-Triaryl substituted corroles and 3-formyl-5,10,15-triaryl substituted corroles were synthesized as per the methods reported in the literature.[3,12] The Cu(III) metal insertion of 3-formyl-5,10,15-triaryl substituted corroles was synthesized by a modified procedure reported in the literature.[13] We have initiated the oxida-

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* Corresponding author. Tel.: +91 40 27191724; fax: +91 40 27160921.
E-mail address: giribabu@iict.res.in (L. Giribabu).

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tion of 3-formyl corroles to 3-carboxy corroles using strong oxidizing agents like $KMnO_4$ and $K_2Cr_2O_7$, which fails to convert and lead to a very complex mixture of products. This is true even for the oxidation of 2-formyl tetraarylporphyrins to corresponding 2-carboxy tetraaryl porphyrins.[14] We have adopted a one-pot, mild reaction condition for the conversion of 3-formyl-5,10,15-triaryl substituted corroles to the corresponding carboxylic acid corroles using hydroxylamine hydrochloride and phthalic anhydride (Scheme 1). By implementing this method recently, we have successfully converted 2-formyl-5,10,15,20-tetraaryl-substituted porphyrins to corresponding carboxy substituted porphyrins in quantitative yield.[15] We have adopted similar reaction conditions for the oxidation of 3-formyl triaryl substituted corroles to the corresponding carboxy triaryl substituted corroles. Initially, we have applied this one-pot oxidation reaction to the conversion of 3-formyl-5,10,15-triaryl corrole to the corresponding 3-carboxy corrole in 70–80% yield.[16] We have extended this methodology to other triaryl substituted corroles having electron releasing groups on phenyl ring viz. 4-methyl phenyl, 4-methoxy phenyl and 3,5-dimethyl phenyl groups and their copper derivatives. All these carboxy corroles were completely characterized by CHN, Mass, IR, UV–vis., ^{1}H NMR and Fluorescence spectroscopies as well as cyclic voltammetry (see Fig. 1).

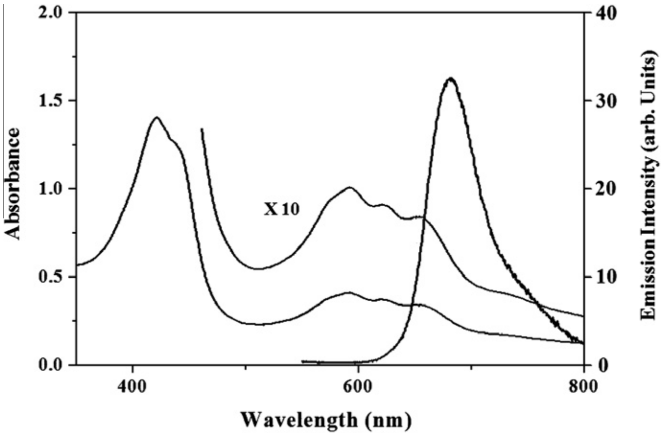
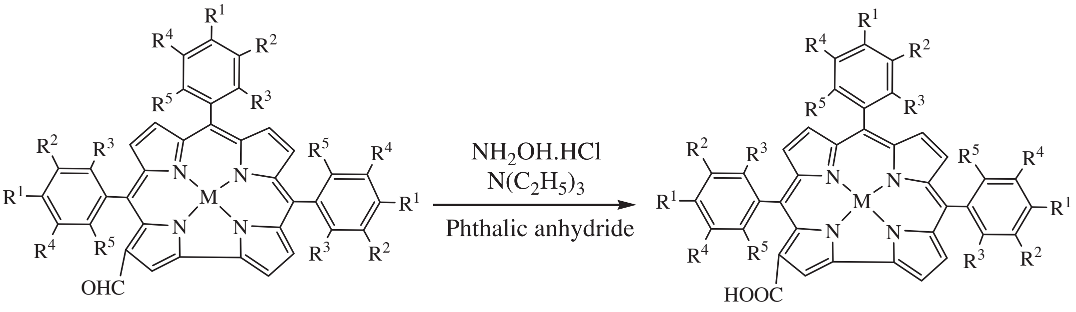


Figure 1. Absorption and emission spectra of **1** in CH_2Cl_2.

The electronic absorption spectra of all free-base and copper(III) carboxy corroles were measured in dichloromethane solvent. The absorption spectrum of corrole **1** is presented in Figure 1 and the corresponding absorption data are presented in Table 1. The absorption spectrum of corroles are dominated by π–π* transitions analogous to those of normal porphyrins, with an intense Soret band around 420 nm and lower intensity either three (free-base) or two (copper(III)) Q-bands higher than 500 nm. Both Soret and Q-bands of free-base and copper(III) carboxy corroles are red shifted by 5–12 nm, when compared to the corresponding 5,10,15-triaryl corroles. This may be due to the presence of electron-withdrawing carboxyl group at pyrrole-β position. The Soret band of copper(III) corroles are red shifted, when compared to the corresponding free-base corroles expect **Cu1**, which is blue



$R^1 = R^2 = R^3 = R^4 = R^5 = H$; M = 3H; **1**; M = Cu(III), **1Cu**
R^1 = -CH_3, $R^2 = R^3 = R^4 = R^5 = H$; M = 3H; **2**; M = Cu(III), **2Cu**
R^1 = -OCH_3, $R^2 = R^3 = R^4 = R^5 = H$; M = 3H; **3**; M = Cu(III), **3Cu**
$R^1 = R^3 = R^5 = H$, $R^2 = R^4$ = -CH_3; M = 3H; **4**; M = Cu(III), **4Cu**

Scheme 1. Synthesis of β-carboxy triaryl corroles.

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

Compound	λ_{max}, nm (log ε, M^{-1} cm^{-1})[b]	$\lambda_{em,max}$, nm (Φ)[c]	$E_{1/2}$ (V)[d]			E_{0-0} (eV)[e]
			$Cor^{0/+}$	$Cu^{(III)/(II)}$	$Cor^{0/-}$	
1	421 (4.45), 593 (3.91), 621 (3.87), 653 (3.83)	682 (0.015)	0.58	–	−1.67	1.88
2	421 (4.66), 593 (4.04), 627 (4.02), 654 (4.01)	684 (0.269)	0.57	–	−1.65	1.85
3	423 (5.04), 590 (4.35), 631 (4.36), 657 (4.34)	694 (0.397)	0.48	–	−1.65	1.83
4	421 (4.72), 593 (4.08), 626 (4.05), 653 (4.05)	681 (0.439)	0.57	–	−1.63	1.86
Cu1	414 (4.65), 554 (3.83), 639 (3.69)	654 (0.012)	0.80	−0.10	−1.65	1.92
Cu2	424 (4.76), 554 (3.97), 643 (3.87)	647 (0.001)	0.73	−0.13	−1.50	1.92
Cu3	438 (4.56), 549 (3.89), 638 (3.73)	645 (0.004)	0.65	−0.20	−1.63	1.93
Cu4	423 (4.83), 554 (4.01), 642 (3.84)	645 (0.104)	0.72	−0.15	−1.70	1.93

[a] Solvent: CH_2Cl_2.
[b] Error limits, λ_{max} ±1 nm, log ε, ±10%.
[c] Φ, ±10%.
[d] 0.1 M TBAP, Solvent: CH_2Cl_2, 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.

shifted.[17] The emission spectra of both free-base and its copper(III) derivatives of carboxy corroles were measured in CH_2Cl_2 solvent at room temperature. The emission maxima of all 3-carboxy corroles are red shifted by 5–13 nm, when compared to those of its corresponding parent triaryl corroles. The singlet state (E_{0-0}) energies of free-base carboxy corroles are in the range of 1.85 ± 0.05 eV and that of its copper derivatives are 1.92 ± 0.05 eV. The redox potentials of both free-base and Cu(III) carboxy corroles were measured using cyclic and differential pulse voltammetric techniques. All new compounds have either reversible or quasireversible three oxidations. The excited state oxidation potentials (E^*) of all new compounds, which correspond to 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.[18] Both free-base and Cu(III) carboxy derivatives are having either one or two reduction potentials. The reduction of Cu(III) carboxy corroles at around -0.20 V corresponds to the Cu(III)/(II) redox couple, whereas the reduction at -1.65 V corresponds to the generation of corrole π-anion, which is below the reduction potential of redox electrolyte (I^-/I_3^-).[19] The photovoltaic device studies by using these corrole sensitizers are currently under progress.

In conclusion, we have used one-pot mild reaction conditions for the oxidation of 3-formyl-5,10,15-triaryl substituted corroles to the corresponding 3-carboxy-5,10,15-triaryl substituted corroles. The singlet state and electrochemical properties of these 3-carboxy corroles suggested that the LUMO of these compounds above the TiO_2 conduction band making an efficient electron injection from excited state of dye to TiO_2 conduction band and HOMO is more positive than the redox couples, which can reoxidize the sensitizer easily by taking an electron from redox electrolyte. These sensitizers have potential for applications in dye-sensitized solar cells.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.12.068.

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16. Hydroxylamine hydrochloride (0.076 g, 1.1 mmol), triethyl amine (0.15 g, 1.1 mmol) and the corresponding free-base 3-formyl-5,10,15-triaryl substituted corroles (1 mmol) were added in 60 mL of dry acetonitrile under nitrogen atmosphere. The resulting reaction mixture was stirred for 30 min. To this phthalic anhydride (0.015 g, 0.1 mmol) was added and the reaction mixture was refluxed for 4–5 h. The reaction mixture was filtered under suction and the solvent was removed under reduced pressure. The obtained solid material was subjected to silica gel column chromatography and eluted with $CHCl_3$:CH_3OH (92:8) mixture and the green color band was collected and recrystallized from CH_2Cl_2:hexane mixture.
    In the case of 3-carboxy-5,10,15-triaryl substituted copper(III) corroles derivative, we have taken 3-formyl-5,10,15-triaryl copper(III) corroles instead of corresponding free-base triaryl corroles.
    Analytical data: **1**: Yield: 70% (0.400 g). Anal. Calcd for $C_{38}H_{26}N_4O_2$: C, 79.98; H, 4.59; N, 9.82%. Found: C, 80.00; H, 4.55; N, 9.83%. MS: *m*/*z* 570, requires 570.6386. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 10.70 (br, 1H), 9.00 (s, 1H), 8.90 (s, 1H), 8.75 (m, 5H), 8.20 (m, 6H), 7.75 (m, 9H). IR (KBr) cm^{-1}: 3413, 1699, 1549, 1441, 1240, 1054, 970, 701, 572. **2**: Yield: 78% (0.478 g). Anal. Calcd for $C_{41}H_{32}N_4O_2$: C, 80.37; H, 5.26; N, 9.14%. Found: C, 80.40; H, 5.25; N, 9.170%. MS: *m*/*z* 612, requires 612.7184. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 10.70 (br, 1H), 8.80 (m, 3H), 8.55 (m, 4H), 8.00 (d, 6H), 7.30 (d, 6H), 2.70 (m, 9H). IR (KBr) cm^{-1}: 3378, 1716, 1411, 1247, 960, 701, 495. **3**: Yield: 75% (0.495 g). Anal. Calcd for $C_{41}H_{32}N_4O_5$: C, 74.53; H, 4.88; N, 8.48%. Found: C, 74.50; H, 4.90; N, 8.50%. MS: *m*/*z* 660, requires 660.7166. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 10.70 (br, 1H), 8.80 (m, 3H), 8.55 (m, 4H), 8.05 (d, 6H), 7.30 (d, 6H), 4.05 (m, 9H). IR (KBr) cm^{-1}: 3398, 1719, 1600, 1245, 1171, 790, 597. **4**: Yield: 79% (0.517 g). Anal. Calcd for $C_{44}H_{38}N_4O_2$: C, 80.71; H, 5.85; N, 8.56%. Found: C, 80.75; H, 5.85; N, 8.50%. MS: *m*/*z* 654, requires 654.7981. ^1H NMR ($CDCl_3$) (300 MHz) δ ppm: 10.70 (br, 1H), 8.80 (m, 3H), 8.55 (m, 4H), 8.00 (s, 3H), 7.30 (d, 6H), 2.40 (m, 18H). IR (KBr) cm^{-1}: 3153, 1720, 1464, 1279, 1065, 791, 515 **Cu1**: Yield: 72% (0.454 g). Anal. Calcd for $C_{38}H_{23}N_4O_2Cu$: C, 72.31; H, 3.67; N, 8.88%. Found: C, 72.35; H, 3.69; N, 8.90%. MS: *m*/*z* 630, requires 631.1608. ^1H NMR (DMSO-d_6) (300 MHz) δ ppm: 10.65 (br, H), 8.25 (s, 1H), 7.80 (m, 9H), 7.70–7.20 (m, 6H). IR (KBr) cm^{-1}: 3215, 1697, 1427, 1311, 1068, 792, 578 **Cu2**: Yield: 80% (0.538 g). Anal. Calcd for $C_{41}H_{29}N_4O_2Cu$: C, 73.14; H, 4.34; N, 8.32%. Found: C, 73.20; H, 4.40; N, 8.35%. MS: *m*/*z* 672, requires 673.2406. ^1H NMR (DMSO-d_6) (300 MHz) δ ppm: 10.60 (br, 1H), 8.15 (s, 1H), 7.85 (m, 1H), 7.60 (m, 6H), 7.50 (m, 6H), 7.30 (m, 6H), 2.50 (m, 9H). IR (KBr) cm^{-1}: 3285, 1640, 1457, 1312, 1183, 901, 790, 577 **Cu3**: Yield: 76% (0.548 g). Anal. Calcd for $C_{41}H_{29}N_4O_5Cu$: C, 68.28; H, 4.05; N, 7.77%. Found: C, 68.30; H, 4.10; N, 7.80%. MS: *m*/*z* 720, requires 721.2388. ^1H NMR (DMSO-d_6) (300 MHz) δ ppm: 12.20 (m, 1H), 8.25 (s, 1H), 7.60 (m, 6H), 7.35–6.85 (m, 9H), 3.98 (m, 9 H). IR (KBr) cm^{-1}: 3426, 1640, 1471, 1390, 1031, 795. **Cu4**: Yield: 80% (0.572 g). Anal. Calcd for $C_{44}H_{35}N_4O_2Cu$: C, 73.88; H, 4.93; N, 7.83%. Found: C, 73.85; H, 4.90; N, 7.85%. MS: *m*/*z* 715, requires 715.3203. ^1H NMR (DMSO-d_6) (300 MHz) δ ppm: 12.26 (br, 1H), 8.18 (s, 1H), 7.60 (m, 6H), 7.15 (m, 9H), 2.50 (m, 18H). IR (KBr) cm^{-1}: 3423, 1656, 1425, 1262, 788, 550.
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