



## Research paper

## Spectroscopic and theoretical studies of anionic corroles derived from phosphoryl and carbomethoxyphenyl substituted corroles



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## ARTICLE INFO

## Article history:

Received 28 November 2016

In final form 2 April 2017

Available online 5 April 2017

## Keywords:

Dianionic corroles

Anion-induced deprotonation

Spectral properties

DFT studies

## ABSTRACT

Anionic corroles were obtained by the addition of aliquots of basic anions such as  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{OAc}^-$  and  $\text{H}_2\text{PO}_4^-$  to free base corroles 5,10,15-triphenylcorrole (**1**), 5,10,15-tris(4'-diethoxyphosphorylphenyl)corrole (**2**) and 5,10,15-tris(4'-carbomethoxyphenyl)corrole (**3**) in aprotic solvents at 298 K. The 1:2 (corrole-to-anion) stoichiometry was confirmed by Hill plot and DFT studies. The dianionic corroles derived from **2** and **3** exhibited a dramatic red-shift ( $\Delta\lambda_{\text{max}} = 14\text{--}24\text{ nm}$ ) in B band as compared to that of free base corroles (**2–3**) while the opposite trend was observed in fluorescence spectral features with the enhanced fluorescence intensity. The anion-induced deprotonation constants ( $K_{\text{d}}$ ) of corroles (**1–3**) depend on the basicity of the anion used and the acidic nature of free base corrole core. The presence of excess protic solvent disfavors the formation of dianionic corroles.

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## 1. Introduction

In recent years, nonlinear optical [1–4] and sensor [5–12] applications of tetrapyrrolic macrocycles have attracted a great attention. Corroles, one of the tetrapyrrolic macrocycle which grew up tremendously after 1999 and found an independent area of research. The absence of one *meso*-methine carbon leads to decrease the core size as compared to well-known porphyrin macrocycles. These contracted macrocycles exhibit rich spectroscopic properties including high molar extinction coefficients and fluorescence quantum yields. The tribasic corrole core can stabilize a broad range of high-valent metal ions used for catalysis [13]. Since the discovery of facile synthetic methodologies of corrole and their metal derivatives, considerable research efforts have been devoted to explore their wide applications [14]. The binding specificity at inner NH core of corrole macrocycle can be facilitated by functionalization at *meso*-positions [15],  $\beta$ -pyrrole positions [6d,7,16a–c] or the aryl substituents [16d]. The corrole macrocycle shows higher acidity as compared to porphyrins and other related macrocycles [17]. Acidity of free base corrole is increased with *meso*-triphenyl substitution as compared to octa- $\beta$ -alkyl substitution [14a,16d,18c]. The deprotonation of  $\beta$ -octaalkylcorrole was reported by Johnson and Kay with 1% NaOH in DMF [14a]. Kadish et al. reported the electrochemical redox

properties and protonation/ deprotonation studies of various *meso*-substituted free base corroles and  $\beta$ -octaethylcorrole [18].

Herein, we report the UV–Vis and fluorescence spectral properties and DFT studies of anionic corroles which are generated from free base corroles (**1–3**) by the addition of aliquots of basic anions in aprotic solvents. To the best of our knowledge, this is the first report on fluorescence spectral properties of anionic corroles derived from 5,10,15-tris(4'-diethoxyphosphorylphenyl)corrole (**2**) and 5,10,15-tris(4'-carbomethoxyphenyl)corrole (**3**) in presence of  $\text{CN}^-$  ions due to anion induced deprotonation in non-aqueous media (see Chart 1).

## 2. Experimental

## 2.1. Chemicals

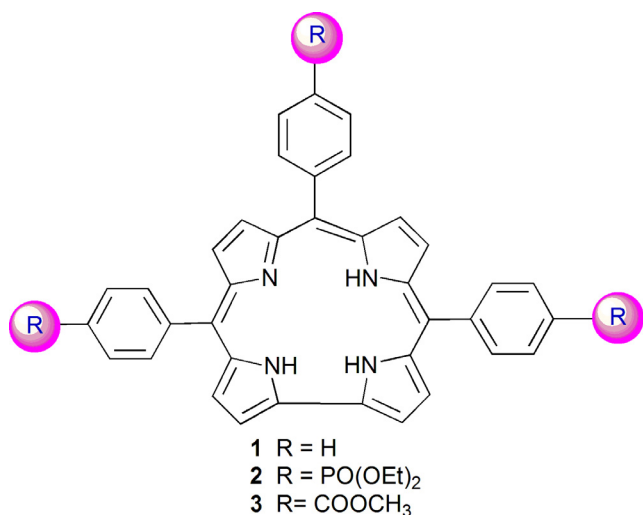
5,10,15-triphenylcorrole (**1**) [14f], 5,10,15-tris(4'-diethoxyphosphorylphenyl)corrole (**2**) [16d] and 5,10,15-tris(4'-carbo-methoxyphenyl)corrole (**3**) [14f] were synthesized according to literature methods. Spectroscopic grade  $\text{CH}_3\text{CN}$  was purchased from FINAR, India and distilled over  $\text{CaH}_2$  before use. Tetrabutylammonium salts (TBAX, X = F, Cl, Br, I, CN,  $\text{CH}_3\text{COO}$ ,  $\text{H}_2\text{PO}_4$ ,  $\text{HSO}_4$ ,  $\text{PF}_6$  and  $\text{ClO}_4$ ) were used as received from Alfa Aesar.

## 2.2. Instrumentation and methods

UV–Vis and fluorescence spectra were recorded in  $\text{CH}_3\text{CN}$  using Cary 100 and Hitachi F-4600 spectrofluorometers, respectively. The

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**Chart 1.** Molecular structure of free base corroles (**1–3**) employed in this study.

anion induced deprotonation constants,  $K_d$  were evaluated using the reported procedure [19]. The equation for the evaluation of  $K_d$  is given below

$$1/K_d = [\text{anion}]^2 \{ [\text{corrole}] L (\epsilon_c - \epsilon_{ca}) / (A_n - A_0) - 1 \}$$

Where  $\epsilon_c$  and  $\epsilon_{ca}$  are the molar extinction coefficients of the free base corrole and corrole-anion complex, respectively.  $A_0$  and  $A_n$  are the absorbance values in the absence and in the presence of added anion at a particular wavelength.  $L$  is the path length of the cell employed. A plot of  $[\text{anion}]^2$  versus  $[\text{anion}]^2 / (A_n - A_0)$  shows a straight line. Using the above equation, the  $K_d$  can be evaluated by taking the negative of  $1/\text{intercept}$  [19]. The stoichiometry of binding was analyzed by Hill method [20].

$$\log[(A_n - A_0) / (A_f - A_n)] = \log \beta_2 + n \log[\text{anion}] \quad (1)$$

A Hill plot was constructed by plotting  $\log[(A_0 - A_n) / (A_n - A_f)]$  against  $\log[\text{anion}]$  where  $A_0$  and  $A_n$  are the absorbance values of corrole employed and corrole-anion complex, respectively, at a given concentration of the anion added. Herein  $A_f$  denotes the absorbance of the completely bound corrole-anion complex at a particular wavelength. The slope of the line was found to be two, which indicates 1:2 stoichiometry between the corrole and the added anion. We have calculated the limit of detection (LOD) and the limit of quantification (LOQ) of anions with corroles (**1–3**) using the formula  $\text{LOD} = 3.3 \text{ SD}/S$  and  $\text{LOQ} = 10 \text{ SD}/S$  where  $\text{SD}$  stands for the standard deviation of a blank,  $S$  stands for slope of calibration curve [21]. For theoretical calculations, B3LYP and B3PW91, becke-style hybrid functional have proven to be superior to the traditional functionals defined so far. The ground state optimized geometries of **2**, **2+2CN<sup>-</sup>**, **2+2F<sup>-</sup>**, **2+2OAc<sup>-</sup>** and **2+2H<sub>2</sub>PO<sub>4</sub><sup>-</sup>** in CH<sub>3</sub>CN was carried out by DFT calculations using B3LYP hybrid functional with 6-31+G(d,p) diffused basis set.

### 3. Results and discussion

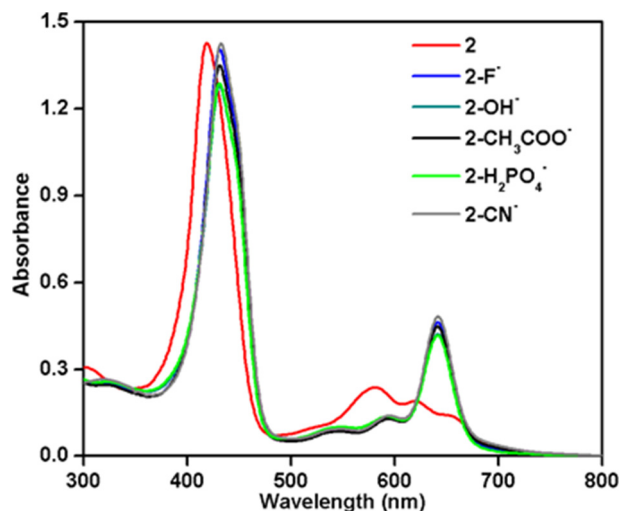
We have utilized the electron deficient *meso*-triphenyl (**1**), *meso*-phosphorylphenyl (**2**) and carbomethoxyphenyl (**3**) substituted corroles for the selective anion induced deprotonation studies. **1–3** were synthesized according to Gryko method [14f] by condensing pyrrole and appropriate aldehyde in H<sub>2</sub>O and MeOH mixture (1:1, v/v) as reported in the literature [16d]. Anion induced deprotonation properties of **1–3** were studied by UV–Vis and fluorescence spectroscopic techniques in CH<sub>3</sub>CN at 298 K.

#### 3.1. Uv–vis spectral titration of free base corroles (**1–3**) with basic anions

The deprotonation behavior of free base corroles (**1–3**) were studied in the presence of spherical (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>), linear (CN<sup>-</sup>) and bulky anions (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) as shown in Figure S1 in the supporting information (SI). Anionic corroles of **1–3** were formed only in presence of highly basic anions such as CN<sup>-</sup>, F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions and the UV–Vis spectral changes of **1–3** with these anions were similar to that of dianionic corrole species as shown in Fig. 1. Table 1 represents the UV–Vis spectral data of corroles **1–3** and with CN<sup>-</sup> ions along with their molar absorption coefficients in CH<sub>3</sub>CN at 298 K.

UV–Vis spectral titration of **3** with cyanide ions is shown in Fig. 2a. As we increase the concentration of cyanide ions, a decrement in the absorbance was observed at 421 nm as well as 579 nm and a concomitant increment in the absorbance at 445 and 646 nm, respectively with the isosbestic points at 434 and 620 nm. The anion induced deprotonation constant ( $K_d$ ) of **3** with CN<sup>-</sup> ions was calculated using a plot between  $[\text{TBACN}]^2$  versus  $[\text{TBACN}]^2 / (A_n - A_0)$  as shown in the inset of Fig. 2a.[19]

The calculated anion induced deprotonation constant ( $K_d$ ) of **3** with CN<sup>-</sup> ions was found to be 11.08 M<sup>-2</sup>. Notably, these corroles exhibited higher  $K_d$  with CN<sup>-</sup> ions in CH<sub>3</sub>CN is possibly due to high basicity of CN<sup>-</sup> ions ( $\text{p}K_a = 9.3$ ). Hill plot (Figure S2 in SI) shows a straight line between  $\log[\text{TBACN}]$  versus  $\log(A_n - A_0 / A_f - A_n)$  with a slope value of 2, which indicates 1:2 (corrole-to-CN<sup>-</sup> ion) stoichiometry as shown in Scheme 1. [19] A similar spectral features were observed for **1** and **2** using [TBACN] in CH<sub>3</sub>CN as shown in



**Fig. 1.** UV–Vis spectral changes of **2** (20 μM) in presence of basic anions (OH<sup>-</sup>, CN<sup>-</sup>, F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) in CH<sub>3</sub>CN, at 298 K.

**Table 1**

Optical absorption spectral data of corroles **1–3** and with CN<sup>-</sup> anions ( $\lambda_{\text{max}}$  (nm)  $\epsilon \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$ ) in CH<sub>3</sub>CN at 298 K.

Corrole	B band (nm)	Q bands (nm)
<b>1</b>	411(5.51)	574(0.66), 615(0.54), 648(0.44)
<b>1+CN<sup>-</sup></b>	418(5.66), 440(3.67)	588(0.70), 635(1.74)
<b>2</b>	417(6.62)	581(1.11), 621(0.88), 655(0.68)
<b>2+CN<sup>-</sup></b>	431(6.43)	592(1.12), 641(2.09)
<b>3</b>	421(4.76)	579(0.84), 625(0.67), 647(0.60)
<b>3+CN<sup>-</sup></b>	445(4.69)	593(0.67), 646(1.59)

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