Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 202 (2018) 207–213

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

A_2B corroles: Fluorescence signaling systems for sensing fluoride ions

Omprakash Yadav [a], Atul Varshney [a], Anil Kumar [a,*], Ratneshwar Kumar Ratnesh [b], Mohan Singh Mehata [b]

[a] Department of Applied Chemistry, Delhi Technological University, Delhi 42, India
[b] Department of Applied Physics, Delhi Technological University, Delhi 42, India

ARTICLE INFO

Article history:
Received 23 September 2017
Received in revised form 10 May 2018
Accepted 14 May 2018
Available online xxxx

Keywords:
Corroles
Fluorescence
Sensor
Fluoride
Tetrapyrrole

ABSTRACT

Four free base corroles, **1**–**4**, A_2B, (where A = nitrophenyl, and B = pentafluorophenyl, 2, 6-difluoro, 3, 4, 5-trifluoro and 4-carboxymethylphenyl group) have been synthesized, characterized and demonstrated as excellent chemosensor for the detection of fluoride ions selectively in toluene solution. The reported corroles shows highest quantum yield in free base form of porphyrinoid systems so far. All these corrole, **1**–**4**, have the excellent ability to sense fluoride ion. Cumulative effect of static and dynamic factors is responsible for the quenching of fluorescence which indicates the detection of fluoride ion in solution.

1. Introduction

The established literature reveals that different fluorescence materials have been extensively explored in the domain of chemosensor. The receptor, a fluorophore and a spacer constitute the chemosensor [1]. From the porphyrinoid family, porphyrins and its analogues have been used as receptors extensively [2]. Recently, corroles have attracted scientific community attention because of the discovery of convenient protocols to synthesize corroles and their metal complexes [3]. Corroles shows unique properties and remarkable applications in catalysis, medicine, dye for solar energy conversion, optical and sensing applications due to direct pyrrole-pyrrole linkage [4,5]. The corroles are highly photostable in most of the solvents [6]. Corroles are highly fluorescent and show strong fluorescence emission with a large Stoke's shift and high radiative rate constants and absorption bands in the visible region [6]. As these chromophores are visible excitable so in vivo and environmental applications can be carried out in detail and results are quite positive. Corroles can be utilized as anion sensors due to their highly acidic nature of N—H proton [7]. It is evident from the literature that most of the research focused on the reactivity and properties of corroles. However, as compare to other porphyrinoid family, a very little development has been made for the use of corrole as anion sensors [5,8]. Because of diversification of fluoride anion in biological, chemical and environmental processes, the sensors for fluoride ion has become the domain of substantial interest for many years [9–10]. Its significant and important role in the prevention of dental caries, osteoporosis, psychiatric, hypnotic drugs and in nuclear technology to refine uranium is highly demanding [11–12]. On the other side high dose of fluoride into the living systems has resulted fluorosis, depression of thyroid activity and in disruption of immune system [13].

A large number of fluoride anion chemosensors are available in the literature due to emerging research interest in this field [14]. The molecule must be good hydrogen donor so that fluoride ion can polarize N—H bond which may result in deprotonation of an N—H bond [15–17]. This type of Bronston acid-base type mechanism will increase the fluoride concentration and will form highly stable complex $[HF_2]^-$ due to increase in basicity of fluoride [18]. But the interference from anions like benzoate, acetate and strongly basic anions such as sulphate and cyanide anion and tedious synthetic protocols are the serious drawbacks [19–20]. Mimicking of Boolean arithmetic with such type of cationic, anionic and photochemical switches are under progress to substitute silicon circuitry [21–22]. The painful fabrications and complexity to design molecule has brought success in several logic operations but advanced memory functions logic still is not so common [23–25]. It is clearly understood that anions has become the target of recent research due to their very significant and important participation into several bio-chemical processes. From our general chemistry knowledge, fluoride ion behaves like hard Lewis base, has smallest ionic radius and higher charge density. These unique properties of fluoride ions make it more interesting target for sensor design and its involvement in different technological, medical and biological processes. To overcome different technical challenges related to designing of fluoride ion sensors, herein, we present the synthesis, characterization, photophysical properties and sensing abilities of four novel free base A_2B corroles, 10-(pentaflurophenyl)-5, 15-bis(4-nitrophenyl)corrole (**1**), 10-(2, 6-Diflurophenyle)-5, 15-bis(4-nitrophenyl)corrole (**2**), 10-(3, 4, 5-triflurophenyle)-5, 15-bis(4-nitrophenyl)corrole (**3**), and

---

* Corresponding author.
E-mail address: anil_kumar@dce.ac.in (A. Kumar).

https://doi.org/10.1016/j.saa.2018.05.051
1386-1425/

10-(4-methoxycarbonylphenyl)-5, 15-bis(4-nitrophenyl)corrole (**4**) (Scheme 1). The synthesized corrole, **1**–**4**, show good sensing ability selectively towards fluoride ion in the order **1** > **2** > **3** > **4**, while compound **1** also showed significant sensing ability for bromide ion.

2. Results and Discussions

In this work, synthesis of four novel free-base corroles, **1**–**4** (Scheme 1) were carried out. The standard protocols described in the literature were used for the synthesis of these corroles, **1**–**4** [26–27]. The synthesized corroles were characterized in detail using different spectroscopic techniques and their experimental procedures for, **1**–**4**, A_2B-corroles are systematized in the experimental section. The targeted A_2B corroles, contain either electron-withdrawing or electron donating groups on the *meso* phenyl ring and thus provide us an opportunity to study the effect of substituent on their photophysical properties and sensing abilities of corroles. Also, different synthetic parameters were optimized to obtain good yields for A_2B corroles, **1**–**4**, with the negligible amount of porphyrin.

The toluene solution of corroles, **1**–**4**, was used for the measurement of photophysical properties at ambient conditions and is tabulated in Table 1. The Q-type bands appeared around 590–655 nm and the Soret type bands were observed between 420 and 450 nm in toluene solution and are shown in Fig. 1. Usually, with the increasing value of dielectric constant of solvent, bathochromic shift in absorption spectra is observed but here in the case of bis(nitro)substituted corroles, the opposite trend was observed [4,28]. Ziegler et al. also noted the same behavior in the case of 10-methoxy-5,15-bis(nitrophenyl)corrole [4b]. So, this may be assumed in terms of uniqueness of moiety, A i.e. nitro, present on *meso* position of corroles which make the difference with absence of A moiety on free base corroles. The steady state fluorescence spectra of corroles, **1**–**4**, were recorded in toluene and bands appeared in the range of 673–690 nm. The recorded fluorescence emission spectra in toluene are shown in Fig. 2. The Stokes shift of 241 cm^{-1} was measured in the recorded emission intensity of all compounds, **1**–**4**.

This large Stokes shift may be due the change in the exited state nature as compared to ground state. The quantum yield for the corroles, **1**–**4**, are tabulated in Table 1 and were calculated by using the relation shown in Eq. (1) with respect to Rhodamine 6G ($\Phi = 0.95$).

$$\Phi_S = \Phi_R(I_S/I_R)\left(1\text{–}10^{-A}{}_R/1\text{–}10^{-A}{}_s\right)\ (n^2{}_s/n^2{}_R) \tag{1}$$

where Φ_R is the absolute quantum yield of standard reference Rhodamine 6G ($\Phi = 0.95$), I_S and I_R the integrated fluorescence intensity of the corrole and standard reference Rhodamine 6G (0.95), respectively. The absorbance for reference and sample are A_R and $A_{S,}$ respectively. The term n_s and n_R represent the refractive index of solvent used. The emission intensity of corroles, **1**–**4** determined here are much higher than that of the earlier reported 5,15-bis(nitrophenyl) which indicates stronger contribution by nitrophenyl moiety via strong charge transfer [4b,28].

Table 1
The calculated photophysical data of corroles (**1**–**4**) in toluene at 298 K.

Host	λ_{max} (ε) [nm ($\times 10^4$ cm^{-1} M^{-1})]	$\lambda^a{}_{em}$ (nm)	Stoke's shift	FWHM	QY%
1	439 (2.9), 593 (7.7), 649 (3.0).	673	241	39.60	0.76
2	439 (2.4), 598 (6.9), 655 (2.4)	680	244	43.78	0.80
3	442 (6.9), 589 (1.8), 648 (1.3).	687	249	49.01	0.77
4	425 (5.6), 445 (5.6), 590 (1.6), 645 (1.3).	689	244	47.13	0.51

But opposite trend is observed in all these discussed herein novel corroles (**1**–**4**). In addition, the nanosecond range of lifetime measurements supports these trends. The highest and lowest lifetime were exhibited in the range of 4.90 (ns) to 3.61 (ns), respectively, and shown in Table 2. The observed decay curves were well fitted with multi-exponential model which is well explained by the Eq. (2) rather than mono-exponential function and shown in Fig. 3 [20].

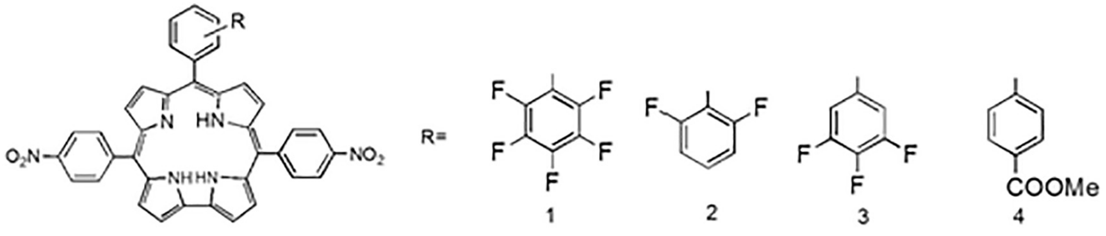
$$I(t) = \alpha_1\ \exp(-t/\tau_1) + \alpha_2\ \exp(-t/\tau_2) \tag{2}$$

where τ_1 and τ_2 represent the lifetimes and α_1 and α_2 are the corresponding pre-exponential factors, respectively. The average lifetime, τ_{av} of corrole (**1**–**4**) is calculated using the Eq. (3) and are summarized in Table 2.

$$\tau_{av} = (\alpha_1\tau^2{}_1 + \alpha_2\tau^2{}_2)/(\alpha_1\tau_1/\alpha_2\tau_2) \tag{3}$$

It is well documented in the literature that polar solvent enhances the hydrogen bonding and charge transfer as well as stabilize the excited state which results in the decrease of emission life time and fluorescence [28]. The detection ability of ions at low concentration was also studied with the use of these compounds, **1**–**4**. The major problems like photostability, solubility, and spontaneous decomposition was taken into consideration for the fluorescence study [4b]. The very important factor, photostability of these corroles, **1**–**4**, in toluene solution for fluorescence quenching study was also considered. Fluorescence quenching investigation in toluene solution has been performed using corroles as a fluorophore [27]. The toluene as a solvent was chosen because of high solubility and no photodecomposition of corroles, **1**–**4**. To be very true, corrole solution in toluene remained stable for several months. Therefore, all the fluoride ion signaling experiments were carried out in toluene.

Corroles would be sensitive to basic anions because of highly acidic nature of inner N—H and fluoride ions would be the best candidate as compared to other basic ions. This may be due to the smaller size and higher electronegativity which in turn provide stronger interactions with the N—H of corroles through hydrogen bonding. This was clearly observed between fluoride ions and compound **1**–**4** [29]. The best performance in terms of sensing ability was observed for compound **1** as compared to **2**, **3** and **4**. These results can be justified by the presence of electron withdrawing groups on the *meso* phenyl group which can increase the acidic nature of inner N—H which in turn make these compounds highly sensitive to fluoride anions [30]. The spectral change in their ground and excited state shown in Fig. 4(a–d). The change in their absorption spectrum with addition of fluoride ion to compound **1**–**4** were also observed and are shown in Fig. 5a. With the addition of



Scheme 1. Compounds used for sensing ions.