

Quenching of Pyrene Fluorescence by Calix[4]arene and Calix[4]resorcinarenes

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Abstract Interactions involving calixarene and its derivatives are of major importance due to their widespread applications as unique hosts. Fluorescence from a common probe pyrene is used to study interactions involving calix[4]resorcinarene [**1a**] and its tetra-morpholine derivative [**1b**] in 1 M aqueous NaOH. These compounds efficiently quench the pyrene fluorescence. A comparison with the fluorescence quenching behavior of *N*-methylmorpholine clearly indicates the presence of long-range interactions involving **1a** and **1b**; the interactions are specific to the calixarene molecular framework. This is not the case for a tetra-nitro-substituted calix[4]arene [**2b**], an electron/charge acceptor quencher, as *p*-nitrophenol also shows similar interactions with pyrene. Effectiveness of cesium as the quencher of pyrene fluorescence is reduced in the presence of electron/charge donating **1b**; fluorescence enhancement is observed upon addition of cesium as the concentration of **1b** is increased in the solution. The role of calixarene framework in interactions involving such compounds is established.

Keywords Pyrene · Calix[4]arene · Calix[4]resorcinarene · Fluorescence · Quenching

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Introduction

Calixarenes and related compounds have been of continuous interest to the scientific community due to their widespread applications as unique hosts [1]. Molecular architecture of calixarenes and resorcinarenes are similar in the fact that both classes of compounds possess a cavity with distinct hydrophobic and hydrophilic sites represented by upper and lower rims of these molecular baskets [1, 2]. By suitable modification of these sites one may obtain several different calixarenes/resorcinarenes for a wide variety of applications in ionic and molecular recognition and for designing separation and detection devices for analytes of major biological and environmental interests [3–5]. It has been demonstrated that calixarenes/resorcinarenes and related compounds can interact with a variety of organic and inorganic species; many smaller molecules/ions are shown to be incorporated in their cavity. Such interactions have established these hosts as potential chemosensing agents [6–12].

Almost all analytical techniques have been utilized to investigate interactions and sensing processes involving calixarenes and related compounds. Among the analytical techniques employed to study interactions involving calixarenes, optical spectroscopic methods especially uv-vis absorbance and molecular fluorescence, are perhaps the most used. Molecular fluorescence is better suited to furnish information regarding such a system due to the high sensitivity usually inherent to the fluorescence-based techniques [13–18]. Consequently, fluorescence-based investigations of complexation and sensing involving calixarenes and related compounds are routine [19–21]. In general, one of the two approaches is used in such investigations. Either the calixarene-based host is suitably modified by covalent attachment(s) of fluorophoric moiety

(moieties), or the fluorescence from the guest and/or external analyte forms the basis of analysis. Although appending and modifying calixarene framework by covalent attachment has been a more widespread strategy, fluorescence from guest has not been used as much, and very few recent studies may be cited as examples of such cases [22–26]. For instance, considerable fluorescence enhancement has been demonstrated following supramolecular complex formation between berberine and *p*-sulfonated calixarenes [22]. Likewise fluorescence probe, 2, 3-diazabicyclo[2.2.2]oct-2-ene (DBO), has been shown to form inclusion complexes with *p*-sulfonatocalix[4]arene (CX4), addition of CX4 to DBO solutions resulted in an efficient fluorescence quenching (up to 90%). Further addition of choline and carnitine derivatives and tetraalkylammonium ions helped to regenerate this fluorescence [23]. Fluorescence spectroscopic study on complexation of oxazine 1 (OX) by calix[8]arenesulfonate (SCA8) is reported by Kubinyi et. al. [24]. The fluorescence of OX undergoes a strong static quenching upon complexation. These results indicate that the complexes are held together by strong electrostatic forces. The addition of non-fluorescent tetramethylammonium chloride to OX-SCA8 mixtures resulted in a dramatic enhancement of fluorescence signal demonstrating the potential applicability of this supramolecular system in fluorescence assays. Luminescence behavior of Tb^{3+} due to energy transfer after complexation with calix[4]arenetetrasulfonate is also reported [25]. In an interesting earlier study, fluorescence enhancement of guests upon formation of inclusion complexes with *p*-*tert*-butylcalix[8]arene bearing polyoxyethylene chains (C3) in aqueous solution is reported by Shi et. al. [26]. A pronounced fluorescence enhancement of the guests on inclusion revealed that C3 can shield the guests from quenchers or the bulk solvent and can protect against the quenching of their excited states [26].

Fluorescence from a guest or an analyte may be used effectively to gather fundamental information on interac-

tions present in the solutions containing calixarenes and related compounds. As discussed earlier, changes in fluorescence response of the probes, e.g., any shift in the wavelength maxima, enhancement or quenching of fluorescence signal, changes in fluorescence anisotropy or lifetime, etc., may form the basis of such investigations. In this manuscript, we report our findings on fluorescence behavior of a common and popular fluorophore pyrene in the presence of different derivatives of calix[4]resorcinarene and calix[4]arene in basic media. Effect of the presence of cesium ion on pyrene fluorescence in the presence of a calix[4]resorcinarene derivative is also investigated.

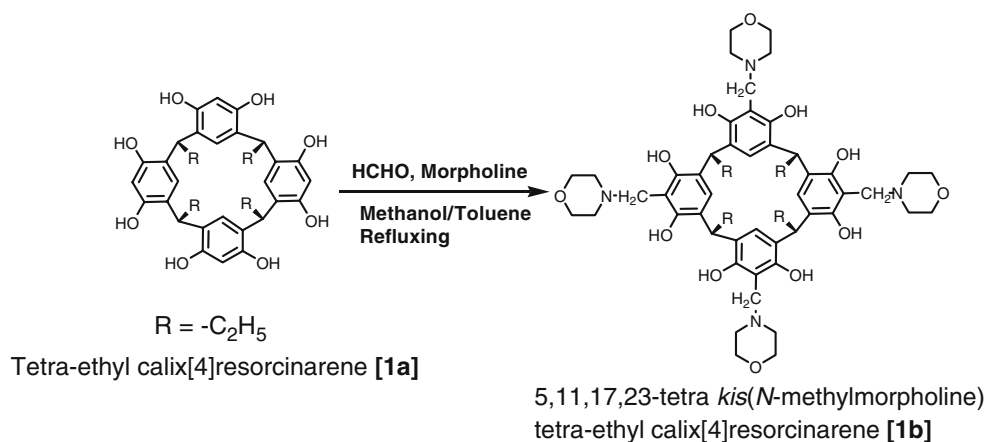
Experimental

Materials Doubly-distilled deionized water was obtained from a Millipore, Milli-Q Academic water purification system having ≥ 18 M Ω cm resistivity. Following materials were used as received: pyrene from Sigma-Aldrich, Cs_2CO_3 , *N*-methylmorpholine, *p*-nitrophenol and NaOH from Acros Organics. Ethanol (99.9%) was obtained from sd fine-chem Ltd.

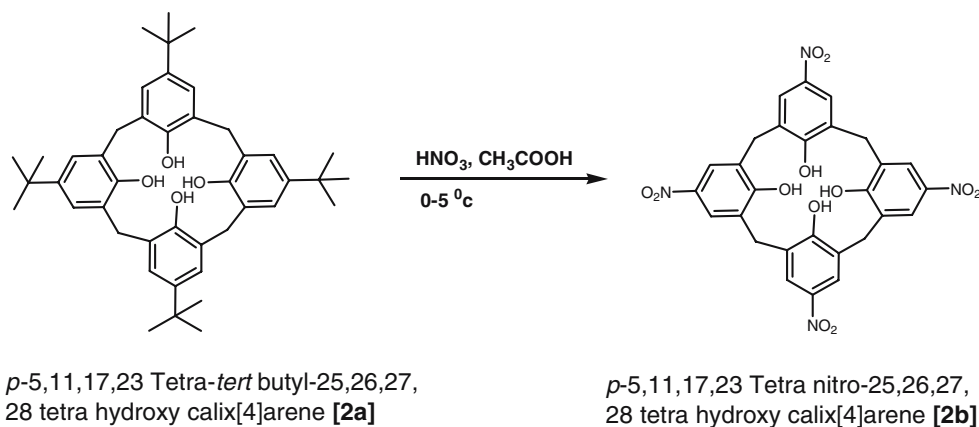
Synthesis of 1b and 2b Starting compounds **1a** and **2a** were synthesized as described in the literature [1, 2]. 5,11,17,23-tetra-*kis*(*N*-methylmorpholine)tetra-ethyl calix[4]resorcinarene [**1b**] and *p*-5,11,17,23-tetra-nitro-25,26,27,28 tetra hydroxy calix[4]arene [**2b**] were prepared by adapting procedure described by Matsushita [27] and Chawla [28, 29]. After synthesis, and repeated recrystallization pure compounds were characterized by NMR, IR and uv-vis spectrometry; analytical data for **1b** and **2b** were found to be the same as reported in the literature [27–29] (Schemes 1 and 2).

Methods Required amounts of materials were weighed on a Mettler-Toledo AB104-S balance with a precision of

Scheme 1 Tetra-ethyl calix[4]resorcinarene [**1a**], 5,11,17,23-tetra *kis*(*N*-methylmorpholine) tetra-ethyl calix[4]resorcinarene [**1b**]



Scheme 2 *p*-5,11,17,23
Tetra-*tert* butyl-25,26,27,28 tetra
hydroxy calix[4]arene [**2a**],
p-5,11,17,23 Tetra nitro-
25,26,27,28 tetra hydroxy calix
[4]arene [**2b**]



± 0.1 mg. Stock solution of the fluorescence probe pyrene was prepared in ethanol and stored in pre-cleaned amber glass vials at -4°C . $0.5\ \mu\text{M}$ pyrene solution in 1 M aqueous NaOH was prepared taking appropriate aliquots of the probe from the stock and evaporating ethanol using a gentle stream of high purity nitrogen gas before adding 1 M NaOH. The solution is thoroughly mixed using vortex and magnetic stirring with gentle heating. Complete solubilization of pyrene was confirmed *via* uv-vis molecular absorbance and/or fluorescence intensity measurements. Solutions of compounds **1a**, **1b**, **2b**, *N*-methyl morpholine, and *p*-nitrophenol were prepared in 1 M NaOH. These solutions contained $0.5\ \mu\text{M}$ pyrene such that the pyrene concentration remained constant during the titrations. 1 M aqueous NaOH solution of the aforementioned compounds of desirable concentration was added to achieve required final concentration. Solutions thus prepared were subjected to uv-vis absorbance and fluorescence spectroscopic acquisitions.

Fluorescence spectra were acquired on model FL 3–11, Fluorolog-3 modular spectrofluorometer with single Czerny-Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector purchased from Horiba-Jobin Yvon, Inc. A Perkin-Elmer Lambda bio-20 double beam spectrophotometer with variable bandwidth was used for acquisition of the uv-vis molecular absorbance. All the data were acquired using 1-cm^2 path length quartz cuvettes. Spectral response from appropriate blanks was subtracted before data analysis. All the measurements were taken in triplicate and averaged. All data analysis was performed using Microsoft Excel and SigmaPlot 8.0 softwares.

Inner-filtering corrections In order to acquire its fluorescence, probe pyrene is generally excited at or around 337 nm [30]. Since **1a**, **1b**, **2b**, and *p*-nitrophenol have appreciable absorbance at the excitation wavelength of pyrene (337 nm), molar absorptivity of each of the compounds, **1a**, **1b**, **2b**, *N*-methylmorpholine and *p*-

nitrophenol, in 1 M aqueous NaOH at 337 nm was calculated by electronic absorbance measurements and subsequent utilization of Beer–Lambert law (a linear relationship was observed between absorbance of the species at 337 nm and its concentration in the solution). Pyrene emission intensities associated with the quenching measurements were corrected for primary inner-filtering artifacts (f_{prim}) arising from the absorption of excitation radiation by the aforementioned quenching species according to the following expression [30]

$$f_{\text{prim}} = \frac{F^{\text{corr}}}{F^{\text{obs}}} = 10^{\frac{A@_{\lambda_{\text{excitation}}}}{2}} \quad (1)$$

where, F^{corr} and F^{obs} refer to the corrected and observed fluorescence emission signals, respectively, and $A@_{\lambda_{\text{excitation}}}$ is the absorbance per centimeter of the pathlength at the excitation wavelength.

Results and discussion

Solubility of pyrene in water is reported to be $\sim 0.7\ \mu\text{M}$ at ambient conditions [30]. As a result, pyrene concentration was kept constant at $0.5\ \mu\text{M}$ in all our measurements. Complete solubilization of pyrene was confirmed spectroscopically before acquiring fluorescence data.

First, we investigated the effect of 5,11,17,23-tetra-*kis*-(*N*-methylmorpholine)tetra-propyl calix[4]resorcinarene (**1b**) addition on pyrene fluorescence when dissolved in 1 M aqueous NaOH. Figure 1 presents fluorescence spectra of pyrene in the presence of increasing concentration of **1b** at ambient conditions. It is clear that pyrene fluorescence is significantly decreased in the presence of increasing amount of **1b**; **1b** strongly quenches pyrene fluorescence. Quenching of pyrene fluorescence and the fluorescence of other similar polycyclic aromatic hydrocarbons by aliphatic and aromatic amines is well-documented [30–34]. The quenching in this case could be due, in part, to electron/

charge transfer from amino nitrogen of the quencher **1b** to the excited fluorophore pyrene, which acts as an electron/charge acceptor in this case. A plot of F_0/F versus $[1b]$ where F_0 is the fluorescence intensity of band I of pyrene (372–373 nm) in the absence of **1b** and F is the corresponding fluorescence intensity in the presence of **1b** corrected for primary inner-filtering (*vide supra*) is provided in Fig. 2. A careful inspection reveals that upon addition of 3×10^{-4} M **1b**, nearly 26-times decrease in initial pyrene fluorescence intensity results. It is important to mention the control experiment in which we have used *N*-methylmorpholine as the quencher in similar conditions. The F_0/F versus $[N\text{-methylmorpholine}]$ is also presented in Fig. 2. It is interesting to note that quenching efficiency is much lower with *N*-methylmorpholine as the quencher ($F_0/F \sim 2.0$ with 3×10^{-4} M *N*-methylmorpholine addition). Although each molecule of **1b** contains four *N*-methylmorpholine functionalities, the quenching of pyrene fluorescence is still significantly less efficient by *N*-methylmorpholine in comparison to that by **1b**. Trends in F_0/F versus $[Q]$, where Q is the quencher, for both **1b** and *N*-methylmorpholine highlight another interesting contrast in the quenching behavior of the two species. While F_0/F varies linearly with $[Q]$ for *N*-methylmorpholine, an upward curvature is clearly observed in case of **1b** suggesting the possibility of a rather complex quenching behavior for the later.

It is well-established that collisional quenching of fluorescence may be described by a simple Stern–Volmer equation [30]

$$\frac{F_0}{F} = 1 + K_D[Q] \quad (2)$$

where $[Q]$ is the quencher concentration and K_D is the dynamic quenching constant. According to Eq. 2, in the event of dynamic quenching, F_0/F is expected to vary

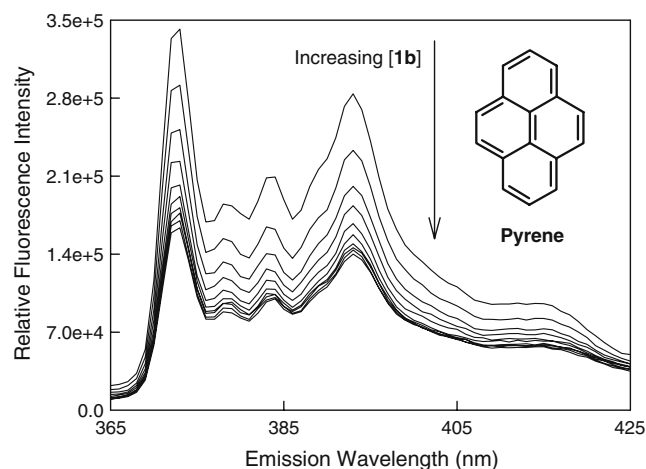


Fig. 1 Fluorescence spectra of 0.5 μM pyrene in 1 M aqueous NaOH in the presence of increasing **1b** at ambient conditions ($\lambda_{\text{excitation}} = 337$ nm, excitation and emission slits are 2 and 2 nms, respectively)

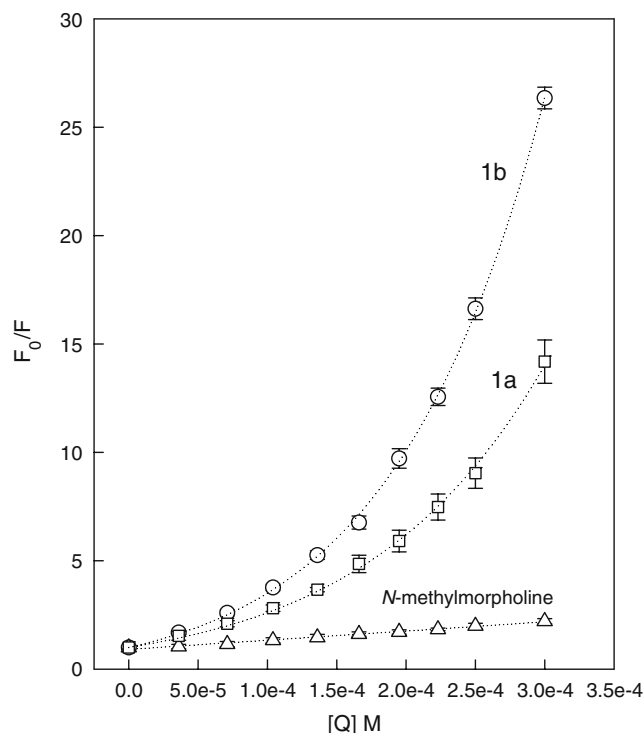


Fig. 2 F_0/F versus $[Q]$ for 0.5 μM pyrene in the presence of **1b** (circles), **1a** (squares), and *N*-methylmorpholine (triangles) in 1 M aqueous NaOH at ambient conditions ($\lambda_{\text{excitation}} = 337$ nm, excitation and emission slits are 2 and 2 nms, respectively). Dotted curves represent fit of the data according to the quenching ‘sphere-of-action’ model (Eq. 6) for **1a** and **1b**, and to a simple dynamic quenching model (Eq. 2) for *N*-methylmorpholine, respectively

linearly with the quencher concentration where all fluorophores are proposed to be equally accessible to the quencher. However, it is clear from the data in Fig. 2 that all population of pyrene may not have identical accessibility to **1b** and that the quenching process is not purely dynamic in nature. If quenching is a result of the formation of a nonfluorescent ground state complex between pyrene and **1b** with an association constant K_S , a similar equation represents pyrene quenching [30]

$$\frac{F_0}{F} = 1 + K_S[Q] \quad (3)$$

Obviously, quenching of pyrene fluorescence in the presence of **1b** is not due to ground-state complex formation between the two. In the event where combined dynamic and static quenching may be the cause of the reduction in fluorescence intensity, a relationship of the form [30],

$$\begin{aligned} \frac{F_0}{F} &= (1 + K_D[Q])(1 + K_S[Q]) \\ &= 1 + K_D K_S [Q]^2 + (K_D + K_S)[Q] \end{aligned} \quad (4)$$

which rearranges into a convenient expression,

$$\frac{F_0 - 1}{[Q]} = K_D K_S [Q] + (K_D + K_S) \quad (5)$$

should explain the quenching data. However, a plot of $(F_0/F - 1)/[Q]$ versus $[Q]$ for pyrene quenching by **1b** shows a poor linear correlation ($r^2=0.9224$) with unacceptable fit, excluding the possibility of a combined dynamic and static quenching mechanism to be operative in this case. Obviously the quenching of pyrene fluorescence by **1b** in 1 M aqueous NaOH is more complicated than that suggested by the aforementioned simple models. It is important to mention that quenching of pyrene fluorescence by *N*-methylmorpholine, on the other hand, may be considered to be purely dynamic in nature with a quenching constant $K_D=4,225\pm 238 \text{ M}^{-1}$ (linear regression analysis between F_0/F and [*N*-methylmorpholine] provides an $r^2=0.9901$ with an acceptable linear fit).

In the event of weak complexation/association, it is proposed that the quenching of fluorescence may be due to the quencher being adjacent to the fluorophore at the moment of excitation [30]. This type of quenching is usually interpreted in terms of ‘sphere-of-action’ within which the probability of quenching is unity, and F_0/F versus $[Q]$ invariably represents an upward curvature. The modified form of the Stern–Volmer equation describing such quenching behavior is given by the following equation [30]

$$\frac{F_0}{F} = (1 + K_D [Q]) \exp(V [Q]) \quad (6)$$

where V is the volume of the quenching ‘sphere-of-action.’ Dashed curve in Fig. 2 shows F_0/F as a function of [**1b**] according to the ‘sphere-of-action’ model (Eq. 6). It is clear that the experimental quenching behavior of pyrene fluorescence by **1b** is most adequately described by this model ($r^2=0.9996$). The recovered dynamic quenching constant $K_D=7,376\pm 490 \text{ M}^{-1}$, while the volume of the quenching sphere of action $V=7,020\pm 163 \text{ M}^{-1}$ which corresponds to a radius of $65\pm 4 \text{ \AA}$. While the recovered K_D represents a significantly efficient quenching process, the radius of the quenching ‘sphere-of-action’ is appreciably high suggesting that even when excited pyrene and quencher **1b** are $\sim 65 \text{ \AA}$ apart from each other there exists unit probability that quenching will take place before pyrene and **1b** diffuse away. With increasing [**1b**] the probability of fluorophore being within this radius increases thus increasing quenching efficiency dramatically. Presence of long-range interactions between pyrene and **1b** is established nonetheless.

Quenching mechanism of pyrene fluorescence is significantly different in the presence of calixarene architecture (*N*-methylmorpholine shows a purely dynamic quenching behavior while quenching ‘sphere-of-action’ is operable for

1b, *vide supra*). A comparison of K_D recovered for *N*-methylmorpholine (i.e., $4,225\pm 238 \text{ M}^{-1}$) with that for **1b** (i.e., $7,376\pm 490 \text{ M}^{-1}$) suggests more efficient dynamic quenching of pyrene fluorescence by **1b**. To further explore the possible reasons for this, we investigated the quenching of pyrene fluorescence by **1a** (i.e., a species similar to **1b** except for morpholine functionalities). Figure 2 also presents F_0/F versus [**1a**] under identical conditions. Again to our surprise, an upward curvature is observed and, an adequate data fit is obtained only when ‘sphere-of-action’ model is evoked (fit shown with dashed curve; $r^2=0.9985$; recovered $K_D=4,105\pm 734 \text{ M}^{-1}$ and $V=6,128\pm 351 \text{ M}^{-1}$). The radius of the quenching ‘sphere-of-action’ is calculated to be $62\pm 5 \text{ \AA}$, which is similar to the radius of the quenching ‘sphere-of-action’ calculated in case of **1b**. The most important outcome here is that the quenching of pyrene fluorescence is not solely by the morpholine moiety; the **1a** reduces the fluorescence of pyrene as well. It appears that K_D for **1b** (i.e., $7,376\pm 490 \text{ M}^{-1}$) may be a manifestation of the combined dynamic quenching efficiencies of **1a** ($K_D=4,105\pm 734 \text{ M}^{-1}$) and *N*-methylmorpholine ($K_D=4,225\pm 238 \text{ M}^{-1}$). It may be inferred that calix[4]resorcinarene framework *in concert with* morpholine functionalities is responsible for the quenching of pyrene fluorescence in 1 M aqueous NaOH. Electron/charge transfer from phenolic $-\text{OH}$ and/or $-\text{O}^-$ to excited pyrene may be proposed to be the primary reason for the fluorescence quenching here.

Next, we investigated the interaction of pyrene with a calixarene system [**2b**] appended by nitro groups. Nitro compounds are established quenchers of pyrene fluorescence where quenching originates due to the electron/charge acceptor properties of the nitro group; excited-state pyrene acts as a charge donor [30–34]. We would like to reinstate that amines and phenols/phenolates as quenchers, in contrast, act as electron/charge donors while excited-state pyrene is the charge acceptor during fluorescence quenching. Figure 3 presents F_0/F versus [**2b**] in 1 M aqueous NaOH at ambient conditions. It is clear that quenching of pyrene fluorescence by **2b** is extremely efficient ($F_0/F\sim 600$ with $3\times 10^{-4} \text{ M } \mathbf{2b}$). The fact that nitro compounds are one of the most efficient quenchers of pyrene fluorescence is clearly evident from our data. It is also clear from the data that, similar to **1b**, a linear behavior is not observed between F_0/F and [**2b**]. In a control experiment quenching of pyrene fluorescence by *p*-nitrophenol in 1 M NaOH solution is investigated and the results are also included in Fig. 3. A careful examination of the data reveals an interesting outcome. The quenching efficiency of **2b** is observed to be fairly high with a nonlinear quenching behavior between F_0/F and $[Q]$ (one molecule of **2b** contains four units of *p*-nitrophenol). The F_0/F versus $[Q]$ for both **2b** and *p*-nitrophenol again best fit to the quenching ‘sphere-of-action’ model. For quenching of

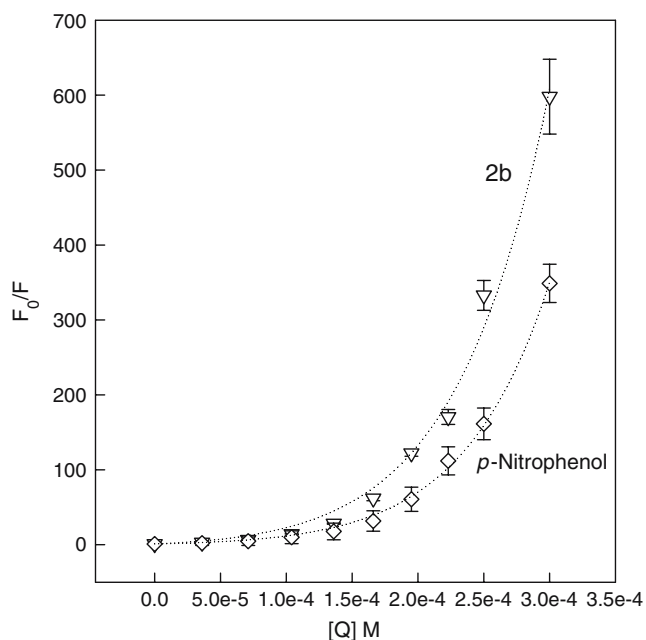


Fig. 3 F_0/F versus $[Q]$ for $0.5 \mu\text{M}$ pyrene in the presence of **2b** and *p*-nitrophenol in 1 M aqueous NaOH at ambient conditions ($\lambda_{\text{excitation}} = 337 \text{ nm}$, excitation and emission slits are 2 and 2 nms, respectively). Dotted curves represent fit of the data according to the quenching 'sphere-of-action' model (Eq. 6)

pyrene fluorescence by **2b**, the recovered parameters are as follows: $K_D = 62,715 \pm 16,209 \text{ M}^{-1}$ and $V = 11,415 \pm 863 \text{ M}^{-1}$ with $r^2 = 0.9910$, and for *p*-nitrophenol: $K_D = 23,065 \pm 3,521 \text{ M}^{-1}$ and $V = 12,633 \pm 463 \text{ M}^{-1}$ with $r^2 = 0.9981$. While the radii of quenching sphere of action are fairly similar ($76 \pm 6 \text{ \AA}$ for **2b** and $79 \pm 4 \text{ \AA}$ for *p*-nitrophenol), the dynamic quenching constant K_D for **2b** is ~ 3 times that of K_D for *p*-nitrophenol. This is conceivable due to the presence of four nitrophenol-like moieties within one molecule of **2b**.

We investigated behavior of cesium, an environmentally important metal cation, toward quenching of pyrene fluorescence in the presence of **1b** dissolved in 1 M aqueous NaOH. We envisaged that the cation might tie up the lone pair of nitrogen on the morpholine moiety thus reducing the quenching efficiency. Figure 4 presents the effect of cesium addition on pyrene fluorescence in the presence of varying amount of **1b**. It is clear that fluorescence intensity of pyrene decreases with addition of cesium in the absence and presence of 10 and $100 \mu\text{M}$ **1b**, respectively (inset of Fig. 4). It is observed that quenching efficiency decreases as the concentration of **1b** in the solution is increased. The most interesting pyrene fluorescence behavior is observed in the presence of $300 \mu\text{M}$ **1b**. Apparently, a slight decrease in pyrene fluorescence intensity is observed till the addition of 0.5 M cesium. Fluorescence enhancement is clearly observed with further addition of Cs^+ (inset Fig. 4). Plots of F_0/F versus $[\text{Cs}^+]$ in the presence of 0, 10, 100, and $300 \mu\text{M}$ **1b** in 1 M aqueous

NaOH is also presented in Fig. 4. Clearly a linear behavior between F_0/F and $[\text{Cs}^+]$ is observed ($r^2 = 0.9999$) when no **1b** is present in the solution. A dynamic quenching constant $K_D = 12.8 \pm 1.1 \text{ M}^{-1}$ is recovered. It is interesting to note that F_0/F versus $[\text{Cs}^+]$ shows acceptable linear behavior in the presence of 10 and $100 \mu\text{M}$ **1b** ($r^2 = 0.9841$ and 0.9945 , respectively). A clear decrease in quenching efficiency upon addition of **1b** is further manifested by the recovered K_D values of $8.7 \pm 0.9 \text{ M}^{-1}$ in the presence of $10 \mu\text{M}$ and $6.8 \pm 0.7 \text{ M}^{-1}$ in the presence of $100 \mu\text{M}$ **1b**. In the presence of $300 \mu\text{M}$ **1b**, as mentioned earlier, no quenching of pyrene fluorescence is observed; rather an increase in fluorescence intensity results as Cs^+ is added to the solution. While Cs^+ is able to efficiently quench the fluorescence of pyrene in 1 M NaOH solution, its quenching efficiency decreases significantly in the presence of **1b**. It may be proposed that the nitrogen lone pair and/or OH/O^- interact electrostatically with Cs^+ , thus decreasing the overall quenching efficiency in the process.

Conclusions

Fluorescence of probe pyrene is observed to be quenched efficiently by calix[4]resorcinarene [**1a**] and its morpholine-derivative [**1b**] when dissolved in 1 M aqueous NaOH. While the reduction in pyrene fluorescence in the presence of *N*-methylmorpholine can be explained on the basis of a simple dynamic quenching mechanism, calix[4]resorcinarene and its morpholine derivative clearly indicate the presence of long range interactions with pyrene that results

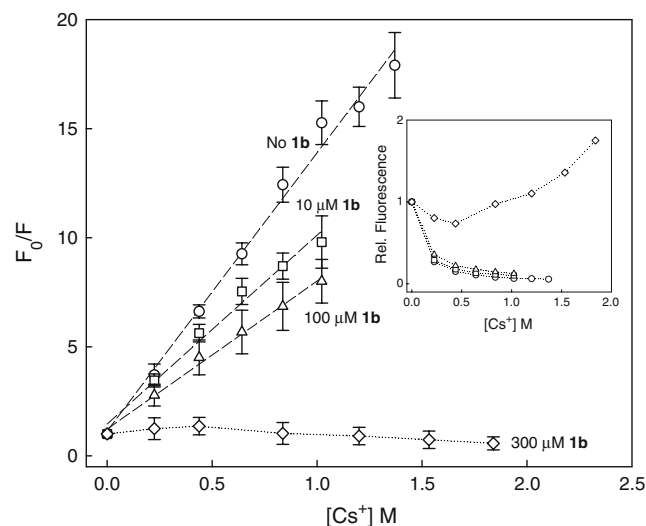


Fig. 4 F_0/F versus $[\text{Cs}^+]$ for $0.5 \mu\text{M}$ pyrene in the presence of 0, 10, 100, and $300 \mu\text{M}$ **1b** in 1 M aqueous NaOH at ambient conditions ($\lambda_{\text{excitation}} = 337 \text{ nm}$, excitation and emission slits are 2 and 2 nms, respectively). Dashed lines represent results of the linear regression analysis. Inset shows changes in the relative fluorescence of pyrene upon Cs^+ addition in the presence of 0, 10, 100, and $300 \mu\text{M}$ **1b**

in quenching data to follow ‘sphere of action’ model. Whereas quenching of pyrene fluorescence by an electron/charge acceptor tetra-nitro-calix[4]arene is also shown to follow the ‘sphere of action’ quenching model; the long range interactions are not specific to the tetra-nitro-calix[4]arene as *p*-nitrophenol also demonstrates similar quenching behavior. Apparently, electron/charge transfer abilities of calixarene derivatives play a key role in deciding the interactions involving such molecules. This is further demonstrated by the enhancement in pyrene fluorescence on cesium ion addition in the presence of electron/charge donating tetra-morpholine-appended calix[4]resorcinarene. Insight into the interactions involving calixarene and resorcinarene-based compounds will help increase the potential application of such compounds in host–guest chemistry.

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