PAPER

Different sensing modes of fluoride and acetate based on a calix[4]arene with 25,27-bistriazolylmethylpyrenylacetamides†‡

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25,27-Bis{1′-*N*-(1-pyrenyl)-aminocarbonylmethyl-1*H*-[1′,2′,3′]tri-azolyl-4′-methoxy}-26,28-dihydroxycalix-[4]arene, **4**, is synthesized as a fluorescent chemosensor for the selective detection of both anions and ion pairs in MeCN. Sensor **4** uses bis-triazoles as ligands to bind a metal ion, bis-amides and bis-triazoles as the sites to recognize anions, and pyrenes as fluorophores. Among eight anions screened, chemosensor **4** showed a marked fluorescence change toward F$^-$, H$_2$PO$_4^-$ and AcO$^-$, but **4** responded to each anion in a distinct way. In the presence of F$^-$ at low concentrations, the dynamic excimer emission of compound **4** at λ_{max} 482 nm was quenched, but an emission at λ_{max} 472 nm appeared at large doses of F$^-$. A control compound **6** showed very similar red shifts in the UV-vis and excitation spectra as **4** did, and its 472 nm emission band grew as the fluoride doses increased. Thus, the growth of the 472 nm emission of **4** and **6** in the presence of excess F$^-$ may be because strong H-bonding interactions of amido protons with F$^-$ favoured the formation of pyrene dimers in the ground state with charge transfer characteristics. The addition of H$_2$PO$_4^-$, unlike F$^-$, to a solution of **4** showed an enhanced monomer emission but a decreased excimer emission (λ_{max} 482 nm). Adding AcO$^-$ to **4** produced a systematic change from a dynamic excimer (λ_{max} 482 nm) to λ_{max} 472 nm but with very little change in the UV-vis spectrum. Time-resolved fluorescence measurements on compound **6** with F$^-$ and AcO$^-$ confirmed that the 472 nm emission band mainly came from static excimers for the former, but was partly from a dynamic excimer for the latter because it contained a growth component in the fluorescence decay traces. Without pre-treatment with an anion, chemosensor **4** showed recognition of only metal ions Cu^{2+}, Hg^{2+} and Cr^{3+}, but it became sensitive to Ag$^+$ when it was pretreated with fluoride.

Introduction

Recognition of ions is an important research topic in supramolecular chemistry because of its prospective application in ion-selective electrodes and sensors in biological and environmental systems.[1] Calix[4]arenes have been widely used as building blocks for the synthesis of receptors because they can be readily modified at both the upper and lower rims and because their conformations are flexible for optimal recognition of guest molecules, in particular, metal ions. The structures of anion receptors typically contain one or two of the following ligands as their binding sites: pyrrolic moieties,[2] amide groups,[3] indolo-carbazoles,[4] imidazolium groups,[5] and urea or thiourea derivatives.[6] Among these ligands, those containing polarized NH groups as anion-binding motifs have attracted much attention.[2–6]

Mechanisms proposed for the signal transduction of fluorescent chemosensors include intramolecular charge transfer (ICT),[7] photoinduced electron transfer (PET),[8] metal–ligand charge transfer (MLCT),[9] and proton transfer.[10] The formation of an excimer or exciplex[3a–c,11] is another mechanism utilized in the design of fluoroionophores. For instance, Kim *et al.*[3a,b] reported a fluoride sensor based on pyrenylacetamide-modified calix[4]arene, which resulted in a red shift in the UV-vis spectrum due to a photoinduced charge transfer (PCT), and a decrease of the dynamic excimer emission and the formation of a static excimer when complexed with a fluoride anion. Fluoride, being a strong base in organic solvents, is an easy target for sensing,[12] as many different types of fluorescence

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signals can be produced by the changes in acid–base equilibria and *via* strong hydrogen bonding interactions in noncompetitive media.[13] Okamoto *et al.* reported that the trifluoroacetylaminophthalimide derivative was deprotonated to the amidate ion in the presence of an iodide anion, inducing the fluorescence bathochromic shift from λ_{max}^{em} 392 to 506 nm.[14]

The design and synthesis of heteroditopic receptors, which are able to complex cations and anions simultaneously either as ion pairs or as free ions,[15] has drawn considerable interest among supramolecular chemists. For instance, Reinhoudt and co-workers demonstrated that a calix[4]arene derivative containing ethyl ester groups on the lower rim and urea moieties on the upper rim bound Cl⁻ efficiently in the presence of Na⁺.[16] A calix[4]arene system, bearing two end pyridinyl moieties connected by amide groups, exhibited a positive allosteric effect[17] in which the host activated a lactam recognition only when it was pre-complexed with Na⁺.[18] A calix[4]arene bifunctionalized with dibenzo-crown-5 ether on the upper rim and bis-triazoles on the lower rim acted as an allosteric receptor for K⁺ and Pb²⁺;[19a] the triazole was derived from the click chemistry[20] of an azide and an alkyne.

Here we report the synthesis of a calixarene-based fluorogenic chemosensor **4** that possesses distal triazole units as the site to recognize cations and amide groups on the lower rim of the conical framework to recognize anions. Depending upon the origin of the pyrene dimer, there are two kinds of excimers: a *dynamic* excimer and a *static* excimer.[11b,20a] The former results from a pyrene dimer formed in the excited state, whereas the latter arises from a pyrene dimer formed in the ground state.[3b,11b,20a] In this work, the fluorescence sensing modes of receptor **4** towards various anions have been examined, especially those for fluoride, acetate and dihydrogenphosphate. The very similar wavelength shifts in both the fluorescence and absorption spectra of **4** and **6** upon addition of F⁻ show that, in contrast to acetate, a fluoride induced static excimer might have substantial charge transfer characteristics in the ground state. In contrast, there was little shift in either the absorption or excitation spectra of **4** and **6** when they were treated with AcO⁻. Furthermore, a positive allosteric effect of compound **4** toward cations was found when it was pretreated with F⁻.

Results and discussion

In the synthesis of target fluorescent chemosensor **4**, depicted in Scheme 1, 1-pyrenyl amine was first treated with 2-chloroacetyl chloride to afford 2-chloro-*N*-(pyren-1-yl)-acetamide **1**[22] in 93% yield. Further reaction of **1** with sodium azide gave 2-azido-*N*-(pyren-1-yl)-acetamide **2** in 92% yield. Under click chemistry conditions,[21] the pyrenyl-containing fluorogenic segment **2** was linked to 1,3-dipropargyl calix[4]arene **3**,[23] forming two triazole rings at the lower rim of calix[4]arene. The target molecule **4**, which possesses both triazolyl and amide moieties on the calix[4]arene skeleton, is expected to bind metal ions and anions cooperatively. The structure of **4** was confirmed by NMR spectra and mass spectrometry data.
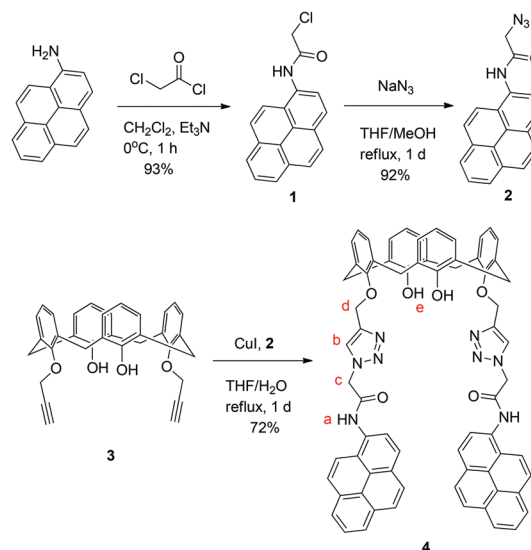
Scheme 1 Synthetic route for fluorescent chemosensor **4**.

The ¹³C NMR signal arising from the methylene bridges of **4**, near 32 ppm, indicates that **4** adapted a cone conformation.[24] Pyrene is a useful fluorogenic unit because it emits from not only the monomer but also the excimer; moreover, the ratio of its monomer to excimer emission is a sensitive probe of conformational change.[7a,11b,20,22] Excitation of compound **4** at 326 nm gave two monomer emission bands at 386 and 405 nm as well as a dynamic excimer emission band at 482 nm,[3a,b,20] which originated from the excimer formed by the interaction of a ground-state pyrene with a singlet excited pyrene.[24]

To assess the ability of compound **4** to recognize anions and metal ions, we measured ¹H NMR and UV-vis spectra, fluorescence, and time-resolved fluorescence. The fluorescence spectra of **4** (10 μM) in CH₃CN were first investigated in the absence and presence of excess (10 equiv.) tetrabutylammonium salts of F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, HSO₄⁻, NO₃⁻ and H₂PO₄⁻, in which selective sensing of F⁻, AcO⁻ and H₂PO₄⁻ ions was observed. Based on further studies (*vide infra*), we found that compound **4** showed different sensing modes toward these three anions. Titration of a solution of **4** with a fluoride anion resulted in decreased absorbances at 276 and 340 nm and the concurrent appearance of absorption bands at 296 and 392 nm in the UV-vis spectra (Fig. 1a). When the titration of **4** with F⁻ was monitored by fluorescence spectra, a monotonic decrease of both monomer and excimer emissions was observed when 0–8.0 equiv. of F⁻ was added; however, a broad emission band with λ_{max} 472 nm appeared when more than 10 equiv. of F⁻ was added (Fig. 1b). The changes in the UV-vis and fluorescence spectra of **4** upon addition of F⁻ were similar to those when tetrabutyl-ammonium hydroxide was added (see Fig. S3, ESI‡). In the presence of abundant F⁻ (or ⁻OH), the phenolic OHs of **4** were deprotonated first followed by strong H-bonding interactions of the amidopyrenes with the fluorides (see Scheme 2, pathway a) which led to new absorption bands in the ground state.
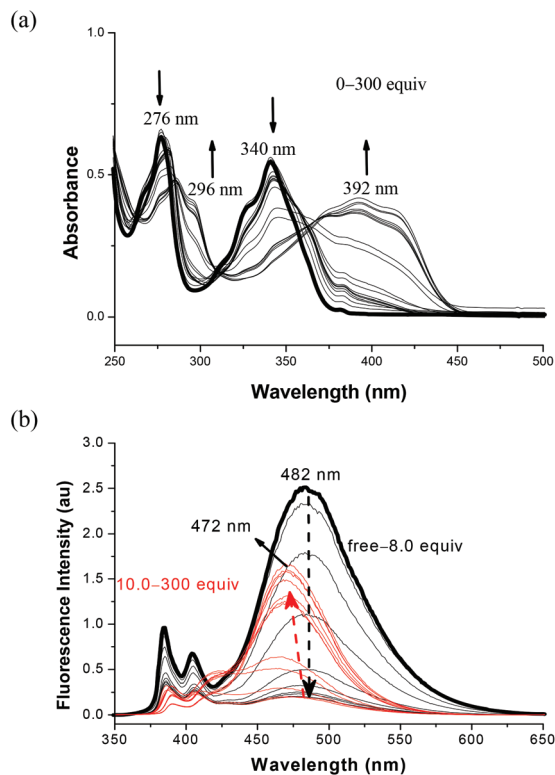
Fig. 1 Variation of the (a) UV-vis absorption and (b) fluorescent emission spectra (λ_{ex} = 326 nm) of **4** (10 μM) upon addition of various concentrations of F⁻ in CH₃CN at 25 °C.
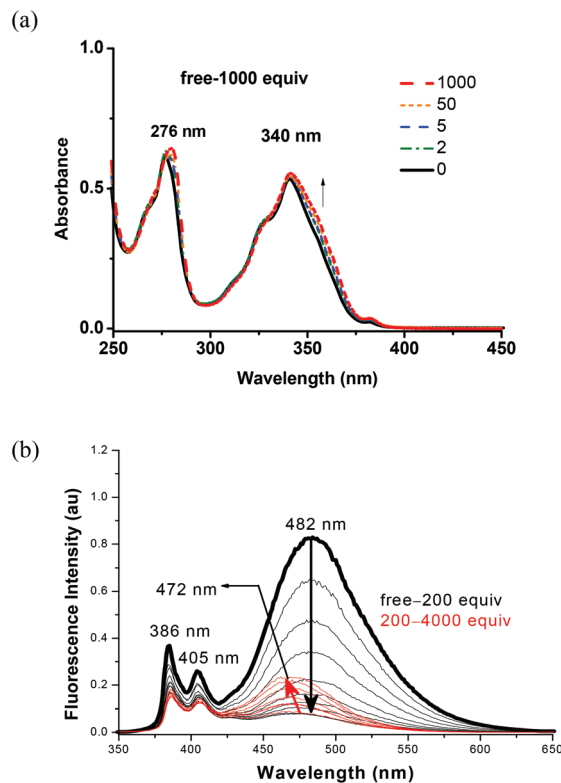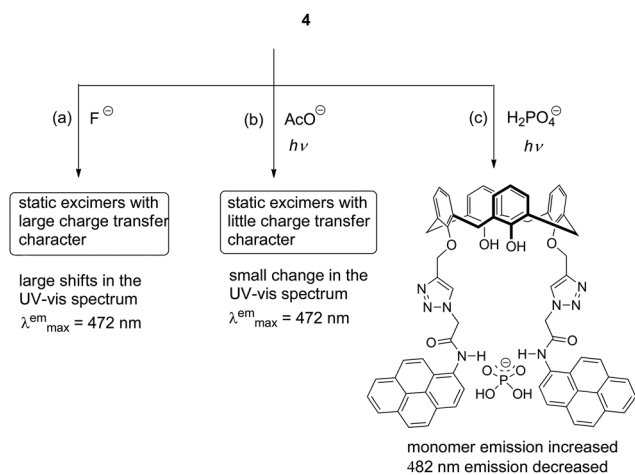

Fig. 2 Changes in the (a) UV-vis and (b) fluorescent emission spectra (λ_{ex} = 326 nm) of **4** (10 μM) upon addition of various concentrations of AcO⁻ in CH₃CN at 25 °C.

Scheme 2 Three binding modes of **4** with anions in CH₃CN.

Although the fluorescence of chemosensor **4** was also severely quenched on the addition of AcO⁻ (Fig. 2b), the UV-vis titration spectra (Fig. 2a) exhibited a very small change. Both monomer and excimer emissions were first quenched then accompanied with a blue shift of the excimer emission to 472 nm at large concentrations of AcO⁻ (Fig. 2b). When about 200 equiv. of AcO⁻ was added to the solution of **4**, both excimer and monomer emissions were significantly quenched. When more than 200 equiv. of AcO⁻ was added to the solution

of **4**, a new emission band at 472 nm appeared, while the intensity of the monomer emission at 386 and 405 nm remained nearly constant. Although the changes of fluorescence spectra of **4** upon the addition of AcO⁻ and F⁻ were similar, their corresponding UV-vis spectra changes were quite different – there was little change when AcO⁻ was added whereas two new absorption bands appeared when F⁻ was added.

To understand the details of the fluorescence spectra of **4** in the presence of F⁻ and AcO⁻, we further characterized the nature of the blue-shifted emission at 472 nm *vs.* the normal dynamic excimer emission at 482 nm. Excitation spectra have been known to be very useful in differentiating a dynamic excimer from a static one.[3a,11b,20] The excitation spectra of a free solution of **4** are the same when monitored at both the monomer (386 nm) and excimer (482 nm) emission bands (Fig. 3, traces a and b), indicating a dynamic nature of the emission at 482 nm. When monitored at 472 nm, the excitation spectrum of a solution of **4** treated with F⁻ showed a significant red shift to 398 nm (Fig. 3, trace d), compared to that of 343 nm when monitored at 386 nm of the monomer. The excitation spectrum with λ_{max} 398 nm hence does not emanate from the pyrene monomer. The results imply that in the presence of excess F⁻, the phenolic OH will be deprotonated first followed by strong H-bonding interactions of the amido protons with the excess fluoride forming a static excimer.[25] In contrast, in the presence of AcO⁻ the excitation spectrum of **4**

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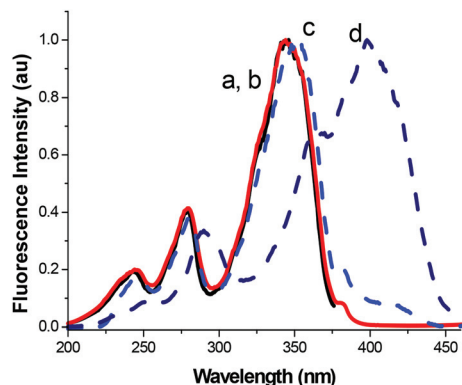This journal is © The Royal Society of Chemistry and Owner Societies 2014

Fig. 3 Normalized excitation spectra of free **4** in CH_3CN monitored at (a) 386 (black curve) and (b) 482 nm (red curve); corresponding excitation spectra monitored at 472 nm upon addition of (c) AcO^- (blue dashed curve) and (d) F^- (black dashed curve) in CH_3CN at 25 °C.
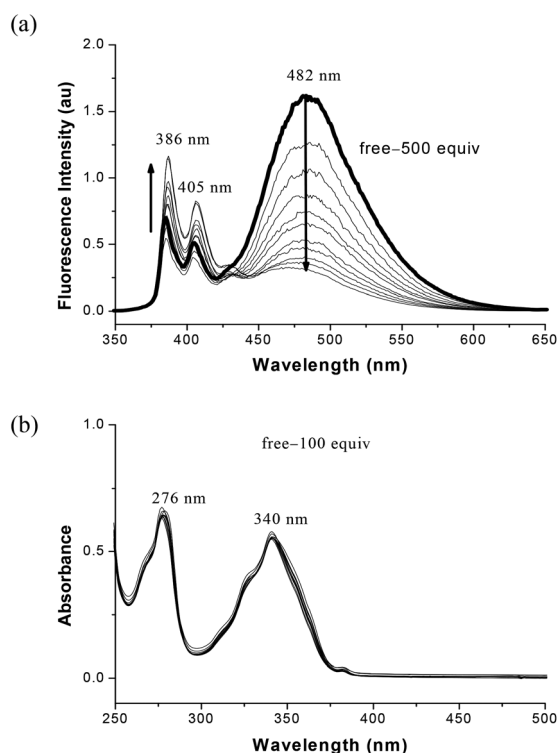

Fig. 4 Changes in (a) UV-vis and (b) fluorescence spectra (λ_{ex} = 326 nm) of **4** (10 μM) upon addition of $H_2PO_4^-$ to the solution of **4** in CH_3CN at 25 °C.
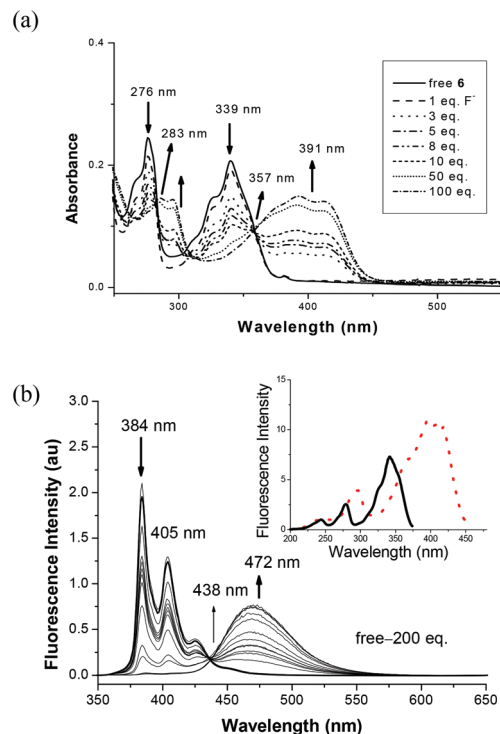

Fig. 5 Variation of (a) absorption and (b) emission spectra of **6** on addition of various concentrations of F^- in CH_3CN solution at 25 °C. The corresponding variations of the normalized excitation spectra monitored at 384 nm (solid curve) and 472 nm (dashed curve) are shown in the inset.

monitored at 472 nm was red-shifted by only 9 nm (Fig. 3, trace c). The addition of excess AcO^- to **4** led to static excimers of pyrenes with little charge transfer characteristics, whereas the static excimer of **4** in the presence of excess F^- (or hydroxide) contains substantial charge transfer characteristics (Fig. 3c,d and Scheme 2a,b).

A third type of fluorescence and UV-vis behaviour was observed during the titration of **4** with $H_2PO_4^-$, for which almost no change in the UV-vis spectrum was observed

(Fig. 4). However, the emission intensities of the pyrene monomer at 386 and 405 nm increased while those of the dynamic excimer at 482 nm decreased monotonically with increasing concentration of $H_2PO_4^-$. These results imply that $H_2PO_4^-$ might be coupled with the two amide groups of **4** through hydrogen bonding, as indicated in Scheme 2c. The insertion of $H_2PO_4^-$ at the lower rim of **4** might force the two distal pyrene groups to separate from each other, thus causing a decreased excimer emission but an increased monomer emission.

To understand the formation of static or dynamic excimers on addition of separate anions as shown in Scheme 2, we performed additional experiments on control compound **6** (Fig. 5, 6, and S14, ESI‡). When screened with various anions, the UV-vis absorption and fluorescent spectra of **6** were selectively altered only with the addition of F^- and AcO^-. In the presence of F^- (or hydroxide anion, see Fig. S6, ESI‡) at various concentrations, the UV-vis spectra of **6** showed a bathochromic shift from λ_{max} = 339 to 391 nm; two isosbestic points appeared at 283 and 357 nm (Fig. 5a). The fluorescence spectra of **6** at various concentrations (0–200 equiv.) of F^- showed a monotonic decrease of the emissions at 384, 405, and 425 nm and the appearance of a new emission band at 472 nm (Fig. 5b). Furthermore, addition of 3000 equiv. of F^- to **6** (at 1 and 10 μM, respectively), also showed a red shift of UV-vis spectra, and a decrease of the emission bands at 384, 405 and 425 nm

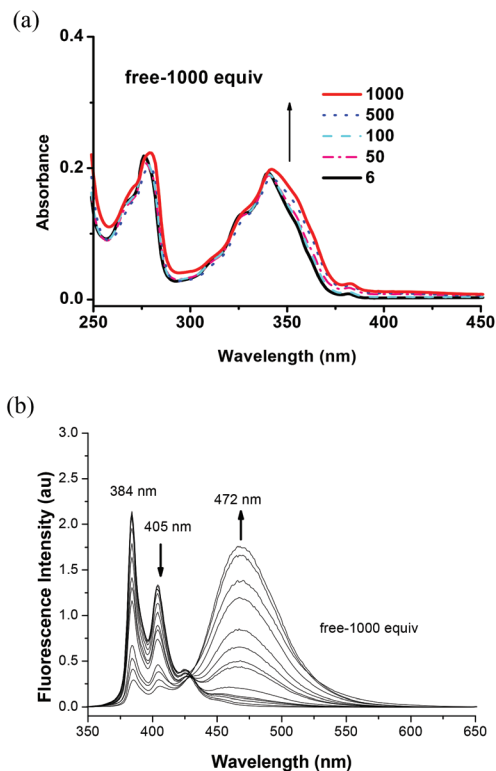This journal is © The Royal Society of Chemistry and Owner Societies 2014

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(a)

(b)

Fig. 6 Variation of (a) absorption and (b) emission spectra of **6** on addition of AcO⁻ at various concentrations in CH₃CN solution at 25 °C.

(a)

(b)

Fig. 7 Fluorescence decays of free **6**, **6**-OH⁻, **6**-F⁻ and **6**-AcO⁻ in MeCN excited at 375 nm and observed at λ_{em}/nm = (a) 385 and (b) 472. The blue traces show the IRF signals with FWHM 80 ps. The red circles are raw data; black curves are fitted results. [**6**] = 10 μM, [F⁻] = 3 mM, [AcO⁻] = 5 mM, and [OH⁻] = 3 mM.

and the appearance of an emission band at 472 nm, which indicates that the latter emission came from a static excimer of amidopyrenes with large charge transfer characteristics instead of a dynamic excimer (Fig. S7‡). To gain insight into the formation of this new emission at 472 nm, we also studied their excitation spectra monitored at 384 and 472 nm (Fig. 5b, inset). The excitation spectrum monitored at 472 nm was again red-shifted to ∼400 nm (dashed curve, Fig. 5b), which is distinct from that monitored at 384 nm (solid curve). This observation is reminiscent of what we observed when **4** was treated with F⁻, confirming that the formation of 472 nm was due to the strong H-bonding interactions of the amide group of **4** with F⁻.[25] Similarly, the addition of AcO⁻ to **6** produced little change in the UV-vis spectra (Fig. 6a), but the fluorescence spectrum altered greatly. As shown in Fig. 6b, the emission intensities of the monomer at 384 and 405 nm decreased with the concomitant increase of the emission intensity at 472 nm upon adding AcO⁻.

The results from control compound **6** on addition of AcO⁻ seem to imply little charge transfer characteristics in its absorption or excitation spectra. The assignment of the exact nature of the emission requires information from measurements of time-resolved emission of **6**. To provide additional information about the emission states of the amidopyrenes, we measured the time-resolved fluorescence of **6** in various environments at an excitation wavelength of 375 nm using a picosecond time-correlated single-photon counting (TCSPC).[26] Some TCSPC results are shown in Fig. 7. Fig. 7 displays the
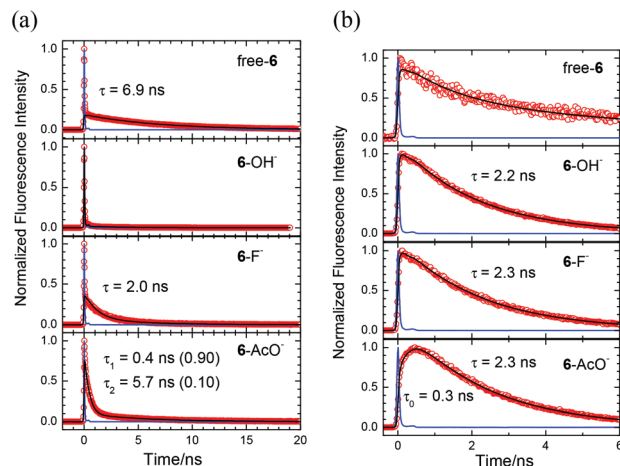
fluorescence transients for control molecule **6** in four different environments observed at (a) 385 and 472 nm. The transients observed at 385 nm suffered from the interference of the laser pulse (λ_{ex} = 375 nm) that is shown as a spike for all transients displayed in Fig. 7a. The slower fluorescence decays shown in Fig. 7a were fitted according to a parallel kinetic model with either a single exponential or a bi-exponential decay function. For free **6**, the emission exhibits a relaxation period of 6.9 ns observed at 385 nm; the detection at the λ_{em} 472 nm showed minute emission intensity because excimer formation is unfavourable under such conditions. Adding OH⁻ to the solution of **6** produced complete quenching of the monomer emission, as shown in the second panel of Fig. 7a. An intense emission of **6**-OH⁻ was observed at 472 nm, for which the transient has a decay coefficient of 2.2 ns. Similarly, the transient of **6**-F⁻ observed at 472 nm exhibited a relaxation time of 2.3 ns that differs from the emission lifetime of free **6** (τ = 6.9 ns).

When **6** was prepared in a solution with excess AcO⁻, we observed the transient at 472 nm involving both rise and decay features for which the rise coefficient obtained at 472 nm (0.3 ns) is consistent with the decay coefficient obtained at 385 nm (0.4 ns), which implies that there is a dynamic nature of the excimer formation. The transient at 472 nm decays in 2.3 ns, which is essentially the same as those obtained in the presence of OH⁻ or F⁻. Because the absorption and excitation spectra of **6** in the presence of OH⁻ or F⁻ show the same red-shifted feature, we propose that strong H-bonding interaction of the amido protons of **6** with OH⁻ or F⁻ is produced in the ground state. To verify this proposal, we performed calculations with time-dependent density-functional theory (TDDFT) at the B3LYP/6-31G(d) level. Our TDDFT results confirm that the broad red-shifted absorption near 400 nm is due to the strong H-bonding interaction and/or deprotonation of the amide group of **6** (Fig. S8, ESI‡). In the titration
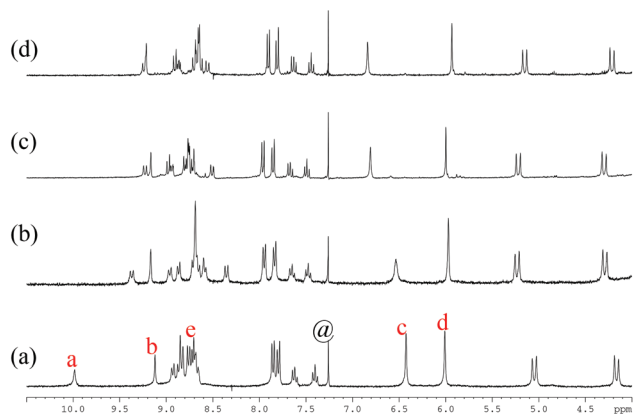
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Fig. 8 Stacked plots of ^{1}H NMR (300 MHz, 25 °C) spectra of (a) 4 (2.5 mM in CD_3CN) with the addition of tetrabutylammonium salts (5 equiv.) of (b) fluoride, (c) acetate, and (d) dihydrogenphosphate ions (CD_3CN, 300 MHz), 25 °C. The label @ denotes an external standard signal of $CHCl_3$ and the other labels (a–e) of protons are described in Scheme 1.

Fig. 9 Fluorescence emission of 4 (10 µM) in CH_3CN in the presence of various metal perchlorates (10 equiv.) at 25 °C.

experiments with high concentration of AcO^-, no such absorption was observed (Fig. 6a), indicating a dynamic nature of the 472 nm emission in the 6-AcO^- system. Under normal circumstances the distinction between static and dynamic excimers is that one can, in a time-resolved experiment, observe the growth of the excimer emission for dynamic excimers and not for static excimers.[20a] Compounds 4 and 6 seem to provide an exquisite system for the studies of static excimers with different degrees of preassociation of the amidopyrenes so that they exhibit perturbed absorption and excitation spectra.

For a free solution of 4, the signal at 10.1 ppm is assigned to the amide proton (O=C)NH$_a$– and the signal at 9.1 ppm is assigned to the 5′ triazole proton H_b. Signals around 9.0–8.7 ppm denote pyrene protons, signals around 7.9–7.3 ppm denote calixarene aromatic protons, H_c and H_d (δ 6.4 and 6.0 ppm) denote methylene protons that are connecting pyrenyl and calix[4]arene groups, and doublets at δ 5.1 and 4.2 ppm pertain to the methylene bridge protons of calix[4]arene. When F^- (1 equiv.) was added, the signal of the amide proton disappeared rapidly. With the addition of F^- (4.0 equiv.), the signals of pyrene aromatic protons (9.4–8.3 ppm) became widespread and the signal at 6.5 ppm (H_c) slightly broadened and downfield shifted (Fig. 8b). The results may be explained by the deprotonation of the phenolic OH of 4 by F^- which led to the changes in the conformation of calixarene or to hydrogen bonding between the amide residues and the HF. In the presence of excess fluoride, the amido proton of 4 is forming strong H-bonding with F^-, HF, or HO^- (in the presence of water) with some charge transfer characteristics, therefore producing significant variations of the chemical shifts of the pyrenyl protons and is consistent with the observations of UV-vis titration experiments. Addition of AcO^- and $H_2PO_4^-$ to 4 showed some effects on the chemical shifts mainly by hydrogen-bonding interactions, but the pyrenyl protons were much less affected (Fig. S11–13, ESI‡). The ^{1}H NMR spectra for the complexation of 4 with F^-, AcO^- and
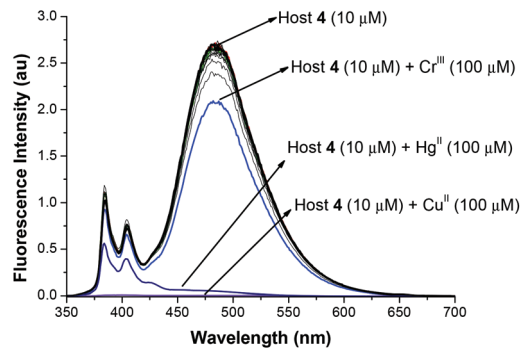
$H_2PO_4^-$ demonstrated that the variation of the fluorescence spectra originated from a strong coordination of the anion to the amide moiety. Due to the severe overlap of the phenolic OH with the pyrenyl protons, its involvement in the complexation of 4 with F^- or resulting HF cannot be ruled out.

To investigate the ditopic binding properties of receptor 4, we screened its binding properties toward metal ions with fluorescence spectroscopy. The results from the fluorescence spectral changes of 4 (10 µM) on the addition of perchlorate salts of various metal ions (Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+}, 10 equiv.) in CH_3CN are summarized in Fig. 9. The fluorescence of 4 was strongly quenched by the addition of Cu^{2+} or Hg^{2+}, whereas Cr^{3+} showed only a small quenching effect. Such a selective fluorescent quenching of triazole-containing calixarene derivatives by Cu^{2+}, Hg^{2+} and Cr^{3+} ions was previously reported by us.[19] On addition of Cu^{2+}, Hg^{2+} and Cr^{3+}, both monomer and excimer emissions were quenched, perhaps via a PET mechanism: namely, pyrene units behaved as a PET donor and the metal-bound triazole groups functioned as electron acceptors.

According to these results, the anion affinity of 4, controlled by the acidity and hydrogen-bonding ability of the amide moieties, might show a positive allosteric effect if there is a favourable electrostatic interaction between the anions and the triazole-bound cations. In the absence of anions, the fluorescence of 4 was selectively quenched by only Cu^{2+} and Hg^{2+}, and slightly by Cr^{3+} ions (Fig. 9), but when the receptor 4 was pretreated with F^-, there was moderate fluorescence quenching at 472 nm and a marked increase in the binding toward the Ag^+ ion ($K_a = 1.9 \times 10^4$ M^{-1}) besides the triad (Cu^{2+}, Hg^{2+} and Cr^{3+} ions, see Fig. 10). Selective binding toward the Ag^+ ion by the two triazole groups of 4 is expected to be favourable through the electrostatic interaction of the F^- anion (see Scheme 3). In contrast, the complexes of 4-AcO^- and 4-$H_2PO_4^-$ showed no fluorescence changes toward metal ions.

Conclusions

A triazole-modified calix[4]arene derivative (4) exhibits three different sensing modes toward various anions. In the

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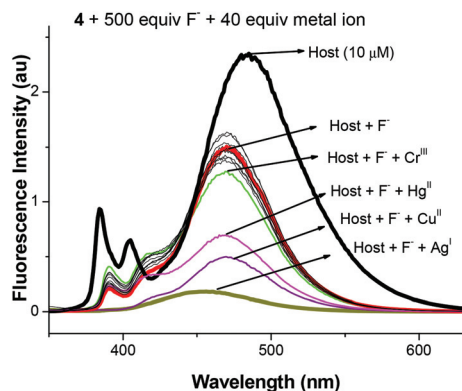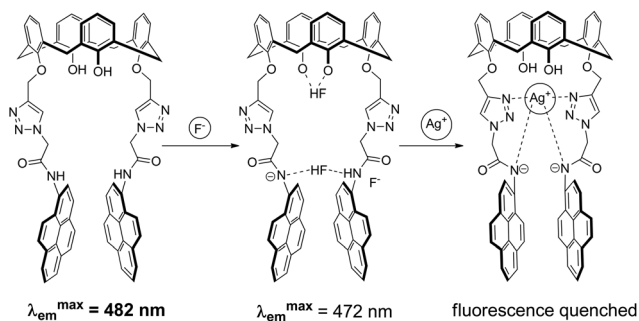Photochem. Photobiol. Sci., 2014, 13, 370–379 | 375

Fig. 10 Fluorescence spectral changes for pre-mixed **4** and fluoride anions, with subsequent addition of various metal perchlorates in CH$_3$CN at 25 °C.

Scheme 3 Possible binding modes for pre-mixed **4** and F$^-$ with silver ions.

presence of small concentrations of F$^-$, the fluorescence of compound **4** (dynamic excimer) at 482 nm was completely quenched; however, at high concentrations of F$^-$, a new emission band at 472 nm appeared with a concomitant bathochromic shift in its UV-vis absorption and excitation spectra. The addition of H$_2$PO$_4^-$ or AcO$^-$, unlike F$^-$, to the solution of **4** insignificantly altered its absorption spectrum. A novel blue shift (λ_{max} = 472 nm) of the pyrene excimer emission was observed for **4** in the presence of AcO$^-$ but not H$_2$PO$_4^-$. Because the absorption and excitation spectra of **6** in the presence of OH$^-$ or F$^-$ show the same red-shifted feature, we propose that strong H-bonding interactions of the amido proton of **6** with F$^-$ or OH$^-$ are produced in the ground state. The time resolved fluorescence of the control system **6**-AcO$^-$ at 472 nm showed a prominent rising character, indicating a dynamic nature of the 472 nm emission. Compounds **4** and **6** seem to provide an exquisite system for the studies of static excimers with different degrees of preassociation of the amidopyrenes so that they exhibit perturbed absorption and excitation spectra. Our results also showed that the bispyrenylacetamidomethyl triazolylmethylcalixarene **4** is a delicate probe which shows different sensing modes in the detection of fluoride and acetate. Furthermore, sensor **4** displayed a selective fluorescence quenching toward Ag$^+$ only after it is pretreated with fluoride.

Experimental section

As described in the literature,[18,19] compounds **1** and **3** were prepared in 93 and 75% yields. ^{1}H and ^{13}C NMR data are given in ESI.‡

2-Azido-*N*-(pyren-1-yl)acetamide 2

A solution of 2-chloro-*N*-(pyren-1-yl)acetamide **1** (0.5 g, 1.70 mmol) and sodium azide (0.22 g, 3.4 mmol) in a mixture of THF and methanol (1 : 1, 20.0 mL) was heated to reflux for 24 h. After removal of the solvent, the residue was dissolved in H$_2$O and extracted with CH$_2$Cl$_2$. The collected organic layer was dried over potassium carbonate and evaporated to give gray solid **2** (0.47 g, 92%). R_f 0.5 (EtOAc–hexane = 1 : 3). Mp 185–187 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ_H 8.80 (s, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.22–8.00 (m, 8H), 4.40 (s, 2H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz) δ_C 165.1 (Cq), 131.3 (Cq), 130.7 (Cq), 129.4 (Cq), 129.0 (Cq), 128.3 (CH), 127.3 (CH), 127.1 (CH), 126.3 (CH), 125.7 (CH), 125.3 (CH), 125.2 (CH), 125.1 (Cq), 124.7 (Cq), 123.3 (Cq), 121.7 (CH), 119.7 (CH), 53.3 (CH$_2$) ppm. FAB MS *m/z* (M$^+$) calcd for C$_{18}$H$_{12}$N$_4$O 300.1011, found 300.1014.

25,27-Bis{1′-*N*-(1-pyrenyl)-aminocarbonylmethyl-1*H*-[1′,2′,3′]-triazolyl-4′-methoxy}-26,28-dihydroxycalix[4]arene 4

The synthetic path for compound **4** is summarized in Scheme 1. To a solution of compound **3**[19] (0.5 g, 1.00 mmol) and CuI (cat.) in THF (50 mL) and H$_2$O (5 mL) was added azide **2** (0.66 g, 2.20 mmol). After heating to reflux for 1 day, the solution was cooled to 23 °C, washed three times with HCCl$_3$ (20 mL), and dried over MgSO$_4$. The solvent was evaporated under reduced pressure, and the residue was purified on a silica-gel column to give gray solid **4** (0.79 g, 72%). R_f 0.6 (EtOAc–hexane = 1/1). Mp 221–230 °C. ^{1}H NMR (CD$_3$CN, 500 MHz) δ_H 9.20 (s, 2H), 8.33 (s, 2H), 8.15–7.89 (m, 18H), 7.06 (d, *J* = 7.5 Hz, 4H), 7.00 (d, *J* = 8.0 Hz, 4H), 6.83 (t, *J* = 7.5 Hz, 2H), 6.61 (t, *J* = 8 Hz, 2H), 5.63 (s, 4H), 5.22 (s, 4H), 4.26 (d, *J* = 13.5 Hz, 4H), 3.38 (d, *J* = 13.5 Hz, 4H) ppm. ^{13}C NMR (DMSO-*d*$_6$, 125 MHz) δ_C 165.3 (Cq), 152.5 (Cq), 151.6 (Cq), 142.2 (Cq), 133.7 (Cq), 130.8 (Cq), 130.7 (Cq), 130.4 (Cq), 128.8 (CH), 128.5 (CH), 127.7 (Cq), 127.2 (CH), 127.1 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 125.3 (CH), 125.2 (CH), 125.0 (CH), 125.0 (CH), 124.3 (Cq), 123.8 (Cq), 123.0 (CH), 122.0 (CH), 119.0 (CH), 69.1 (CH$_2$), 52.3 (CH$_2$), 30.6 (CH$_2$) ppm. FAB MS *m/z* (M$^+$) calcd for C$_{70}$H$_{52}$N$_8$O$_6$ 1100.4010, found 1100.3967.

2-{4′-[(4″-*tert*-Butylphenoxy)methyl]-1*H*-[1′,2′,3′]-1-triazolyl}-*N*-(1-pyrenyl)acetamide 6

Compound **5** (0.1 g, 0.53 mmol) and CuI (cat.) were dissolved in THF (30 mL) and H$_2$O (3 mL), and azide **2** (0.18 g, 0.60 mmol) was then added. After heating at reflux for 1 day, the solution was cooled to 23 °C, washed three times with CHCl$_3$ (20 mL) and dried over MgSO$_4$. The solvent was evaporated under reduced pressure, and the residue was purified on a silica-gel column to give a white solid **6** (0.228 g, 88%). R_f 0.7 (EtOAc–hexane = 1/2). Mp 203–205 °C. ^{1}H NMR (CDCl$_3$, 500 MHz) δ_H 8.83 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.17–7.94 (m,

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8H), 7.83 (d, J = 9.0 Hz, 1H), 7.30 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 5.42 (s, 2H), 5.28 (s, 2H), 1.27 (s, 9H) ppm. ^{13}C NMR (CDCl$_3$, 125 MHz) δ_C 163.7 (Cq), 155.8 (Cq), 145.7 (Cq), 144.2 (Cq), 131.2 (Cq), 129.6 (Cq), 128.7 (Cq), 128.5 (CH), 127.2 (CH), 127.1 (CH), 126.4 (CH), 126.3 (CH), 125.7 (CH), 125.3 (CH), 125.0 (CH), 124.5 (Cq), 123.5 (Cq), 121.7 (CH), 119.7 (CH), 114.2 (CH), 71.0 (CH$_2$), 61.9 (CH$_2$), 54.0 (CH$_2$), 34.1 (Cq), 31.5 (CH$_3$) ppm. FAB MS m/z (M$^+$) calcd for C$_{31}$H$_{28}$N$_4$O$_2$ 488.2212, found 488.2219.

Acknowledgements

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25 In the presence of excess fluoride, the control compound **6**, which is lack of the phenolic OH, showed very similar changes in UV-vis and fluorescence as compared to those of **4**. The quinone, which is obtained from the deprotonation of a phenol OH of **4**, does not show such a big red shift in its UV-vis absorption spectra.

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