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Anthracene-appended Pyridine Amide: A Simple Sensor for Monocarboxylic Acids

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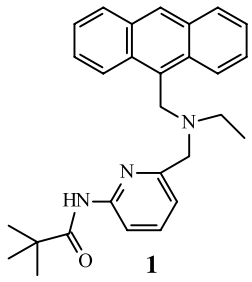
Anthracene-appended receptor 1, which can function as an "on–off" fluorescence switch for monocarboxylic acids, has been designed and synthesized. The photophysical behavior of 1 has been examined by fluorescence, UV–vis and NMR spectroscopy.

Keywords: Molecular recognition; PET sensor; Monocarboxylic acid

The design of molecular receptors capable of performing the transduction of recognition events into a fluorescence signal is an area of intense activity and potential significance for the development of chemosensors and photonic devices [1–5]. Over the past few years, considerable effort has been focused on the development of photoinduced electron transfer (PET) sensory systems for various guest species ranging in nature from charged to neutral [6–9]. In developing such systems, both specificity and sensitivity towards the guest are of importance. In addition, compounds that exhibit an increase in fluorescence intensity in the presence of the guest are of interest. The efficiency of a sensor is therefore related to the selectivity and binding efficiency of the receptor and to the ease and simplicity of detecting and measuring the displayed signal. In this regard, anthracene is an attractive fluorophore because of its strong and well-characterized emission and its chemical stability [10,11].

Pyridine amide, a simple hydrogen-bonding unit, forms a weak two-point hydrogen bond with monocarboxylic acids, which can be present in dimeric or highly associated forms (Fig. 1). The method of attachment of such a pyridine amide moiety in a PET device is so far unknown, as is the hydrogen bonding-induced photophysical behavior of the device. During the course of our ongoing program towards developing receptors for molecular recognition studies [12–14], we report here, for the first time, the design, synthesis and photophysical behavior of the PET-based anthryl fluorescent sensor **1** for a monocarboxylic acid guest. The design principle of the receptor **1** is illustrated in Fig. 2. The development of fluorescent sensors for carboxylic acids or carboxylates [3,4,15–21] is of great interest because carboxylates and carboxylic acids are involved in biological recognition processes [22].



1

The route to **1** (Scheme 1) was considered through the synthesis of functionalized anthracene derivatives by introducing the pyridine amide substituent, obtained from bromination of 2-(*N*-pivaloylamino)-6-methyl pyridine using NBS and AIBN in dry $CHCl_3$, at the 9-anthrylic position so as to generate the PET signal through the methylene ($-CH_2-$) bridge from the electron donor to the electron acceptor. The anthryl fluorescent sensor **1** was obtained in good yield as a brown gummy product.

Compound **1**: ^{1}H NMR (200 MHz, $CDCl_3$): 8.53 (d, $J = 8$ Hz, 2H), 8.37 (s, 1H), 7.99–7.92

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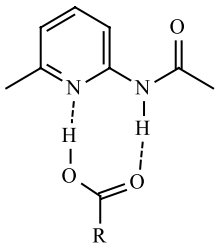


FIGURE 1 Two-point hydrogen-bonded complex.

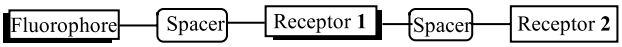
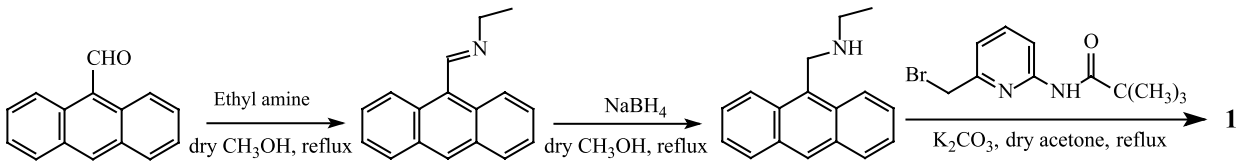


FIGURE 2 Design of a PET sensor for a carboxylic acid.

(m, 4H including NH), 7.55–7.40 (m, 5H), 6.87 (d, $J = 8$ Hz, 1H), 4.67 (s, 2H), 3.66 (s, 2H), 2.76 (q, $J = 6$ Hz, 2H), 1.35–1.20 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 176.9, 158.8, 150.32, 138.3, 134.0, 131.3, 130.0, 129.0, 127.5, 127.1, 125.5, 125.0, 124.7, 118.7, 111.5, 59.1, 50.4, 48.9, 27.4, 12.0. FTIR (KBr): 3433, 3054, 2967, 2932, 2871, 1682, 1578 cm^{-1}, MS (FAB): m/z 426 (M + 1), 396, 248, 191.

To follow the photoelectronic effect of **1** upon binding of carboxylic acids, both absorption and fluorescence spectra were measured. Receptor **1** shows strong fluorescence in $CHCl_3$ ($c = 7.058 \times 10^{-5}$ M, $\lambda_{exc} = 365$ nm), the intensity of which gradually decreases with a slight blue shift ($\Delta\lambda_{max} = 5 - 10$ nm) on successive addition of benzoic acid (up to 50.0×10^{-6} M), myristic acid (up to 57.13×10^{-6} M) and trifluoroacetic acid (TFA) (up to 80.38×10^{-6} M) as shown in Figs 3a–c, respectively, without producing any other spectral change (i.e. either exciplex or excimer formation) in the emission spectra. The observed fluorescence quenching upon addition of both aliphatic and aromatic monocarboxylic acids (Fig. 4) is associated with the formation of a receptor-carboxylic acid complex as suggested in Fig. 1. The dimeric state of the carboxylic acid (the self-association constant is of the order of 0.01–5 L M^{-1}), which is resonance stabilized, is partially converted to the monomer only at high dilution. Therefore, successful 1:1 heteroassociation of carboxylic acids with receptor **1** is only possible at the dilution of the titration experiment [12]. During complexation the more basic aliphatic nitrogen (receptor$_1$) in **1** participates in the formation of a 1:1 hydrogen-bonded complex, as evidenced by the downfield chemical shift of the adjacent methylene protons ($\Delta\delta = 0.09 - 0.12$ ppm) along with the pyridine amide (receptor$_2$) proton ($\Delta\delta = 0.10 - 0.50$ ppm) in ^{1}H NMR, and accordingly three possible forms of the hydrogen-bonded complex may exist in solution, of which form **B** is more likely than the other forms **C** and **A** due to the greater number of hydrogen bonds (Fig. 5). The small change in the amide chemical shift of **1** upon complexation with the carboxylic acids is ascribed to the steric feature of the pivaloyl group.

The diminished fluorescence emission intensity of **1** is due to thermodynamically favored primary PET between the tertiary aliphatic nitrogen (receptor$_1$) and the excited chromophore (*Anth; receptor$_2$). Complexation of this aliphatic nitrogen will stop the primary PET process, and fluorescence of **1** will, in principle, be "switched on" on the basis of normal logic of the fluorescent PET sensor. But at the same time, the opposite situation of "on–off" switching can be arranged by a secondary PET process (*Anth to pyridine amide) in **1**. The present example undoubtedly represents the union of these two opposite situations, and in the more favored hydrogen-bonded form **B** in Fig. 5, the secondary PET process (*Anth-to-pyridine amide electron transfer) comes in more action over the primary PET (aliphatic nitrogen to *Anth electron transfer), resulting in the quenching of fluorescence leading to the "off" mode. The electron deficiency of the pyridine amide, either in the free or complexed state, here presumably plays a significant role in activating the secondary PET over the primary PET process, reflecting the "on–off" switchability of **1** towards monocarboxylic acids. The same is true for the stronger acid TFA, where there is protonation of both aliphatic and pyridine ring nitrogens instead of highly hydrogen-bonding structures like those of benzoic and myristic acids. The facile protonation of both aliphatic and pyridine ring nitrogens, during complexation with TFA in $CDCl_3$, is evidenced by the appearance of peaks at 7.06 and 10.36 ppm in the ^{1}H NMR spectra of the protonated ammonium and pyridinium groups, respectively. The other carboxylic acids (benzoic and myristic) studied do not exhibit these new findings under the same



SCHEME 1

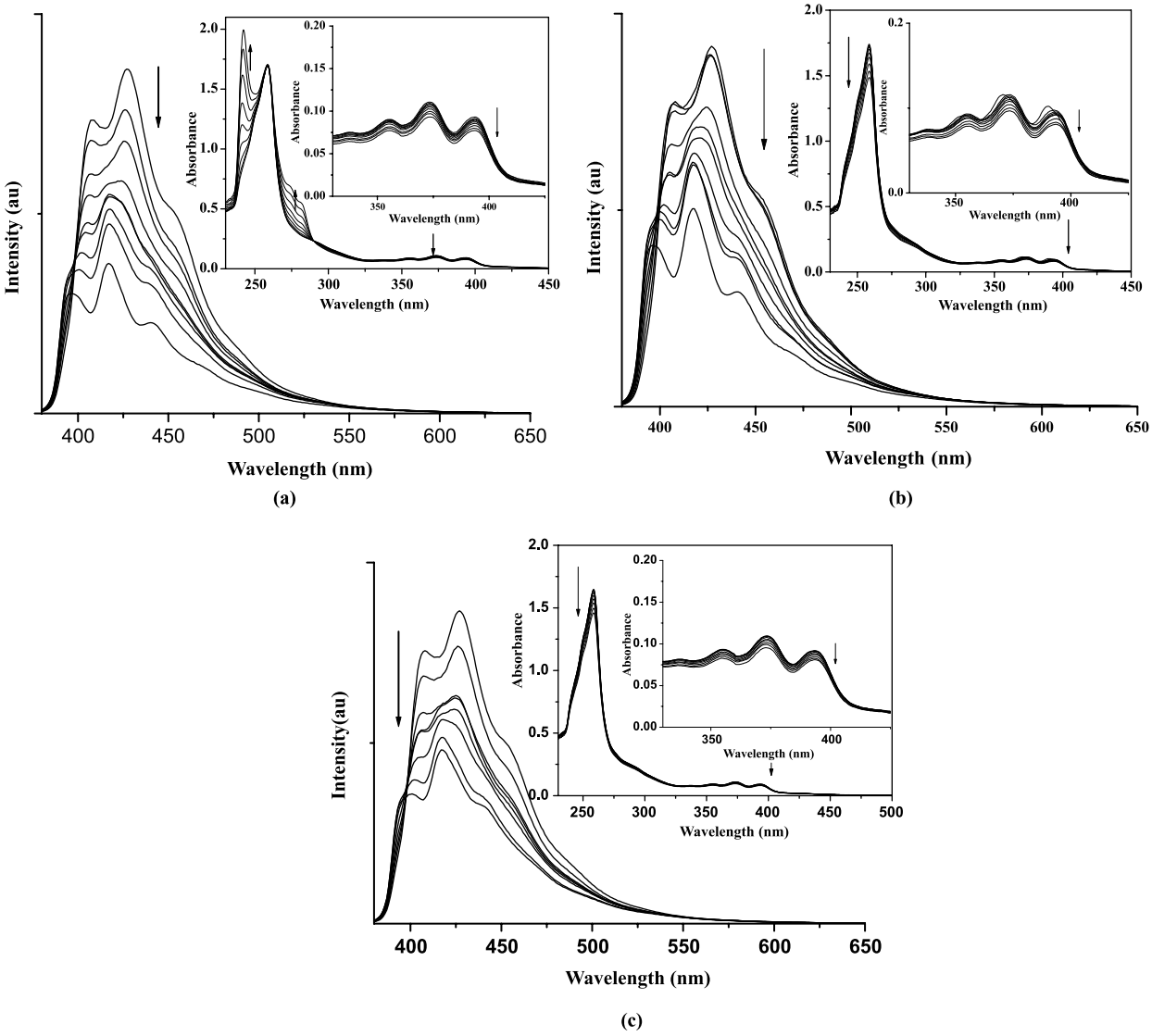


FIGURE 3 Fluorescence spectra of **1** ($c = 7.058 \times 10^{-5}$ M) in $CHCl_3$ and change in UV–vis spectra of **1** (inset) upon addition of (a) benzoic acid, (b) myristic acid and (c) TFA.

conditions. These results thus reflect clearly the existence of hydrogen-bonding structures for benzoic and myristic acids with **1** instead of protonated structures.

Upon addition of benzoic acid, myristic acid and TFA the emissions were *ca*. 60%, 41% and 46% "switched off", respectively. The Stern–Volmer plots (Fig. 4) illustrate the quenching phenomena and show greater quenching with the aromatic acid compared to the aliphatic acids ranging from moderate to stronger in nature. The sigmoidal nature of the curves clearly indicates the presence of two different binding sites in **1**.

Concurrently, the absorption spectrum of **1** in dry $CHCl_3$ ($c = 1.568 \times 10^{-5}$ M) exhibits a band at 259 nm, a characteristic feature of pyridine amide, and bands centered at 393, 373 and 355 nm,

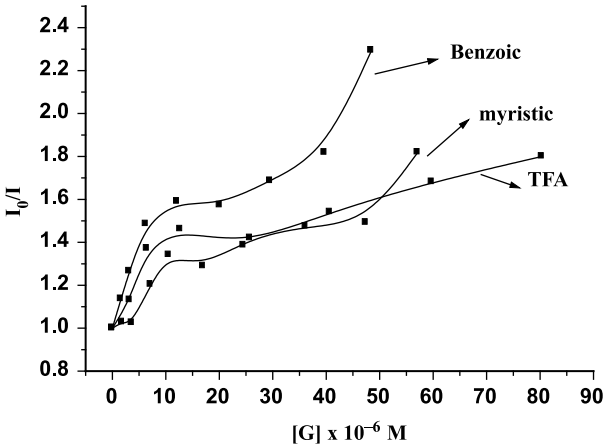


FIGURE 4 Stern–Volmer plots of I_0/I versus concentration of carboxylic acid.

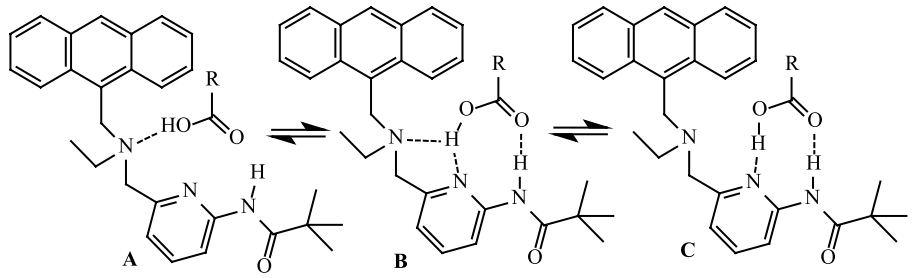


FIGURE 5 Possible forms of the hydrogen-bonded complexes.

TABLE I Association constants (K_a) of **1** with guest carboxylic acids

Carboxylic acid	K_a (M^{-1})
Benzoic acid	6.33×10^4
Myristic acid	4.96×10^3
TFA	49

Binding constants were determined by using the expression $A_0/(A - A_0) = [\varepsilon_M/(\varepsilon_M - \varepsilon_C)](K_a^{-1}C_g^{-1} + 1)$, where ε_M and ε_C are molar extinction coefficients for receptor **1** and the hydrogen-bonding complex, respectively, at a selected wavelength, A_0 denotes the absorbance of free receptor **1** at that specific wavelength and C_g is the concentration of the carboxylic acid guest. The measured absorbance $A_0/(A - A_0)$ as a function of the inverse of the carboxylic acid guest concentration fits a linear relationship, indicating 1:1 stoichiometry of the receptor-carboxylic acid complex. The ratio of the intercept to the slope was used to determine the binding constant, K_a.

attributed to the anthryl moiety of the sensor **1**. The addition of monocarboxylic acids (both in the case of myristic acid and TFA) to the solution of **1** causes a marginal decrease in the intensity of the absorption peaks for anthracene (393, 373 and 355 nm) and also a gradual decrease in the intensity of the peak centered at 258 nm (shown in insets of Figs 3b and 3c, respectively) due to weak hydrogen-bonding interactions of the pyridine amide moiety of **1** with the carboxylic acid, as indicated in Fig. 1. Similarly, as shown in Fig. 3a, on gradually increasing the concentration of benzoic acid, the intensities of the absorption bands at 393, 373 and 355 nm decrease gradually and exhibit a small change in intensity of the band centered at 258 nm, with an isobestic point at 290 nm along with an intensified band at 280 nm due to π-stacking interaction. This observation clearly shows the formation of a 1:1 hydrogen-bonding complex that exhibits a higher binding constant than the aliphatic acids (Table I) [23]. The minor change in absorbance of the anthryl moiety of **1** in the UV–vis spectrum thus demonstrates typical PET behavior.

In conclusion, we have developed a new fluorescent chemosensor **1** that is simple, easy to make and shows good photophysical behavior with regard to monocarboxylic acid recognition, allowing better "on–off" switchability towards aromatic than aliphatic carboxylic acids.

Acknowledgements

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