Tetrahedron Letters 51 (2010) 3320–3323

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Selenodiazole-fused diacetamidopyrimidine, a selective fluorescence sensor for aliphatic monocarboxylates

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ARTICLE INFO

Article history:
Received 8 March 2010
Revised 13 April 2010
Accepted 20 April 2010
Available online 24 April 2010

ABSTRACT

A designed sensor, selenodiazole-fused pyrimidine ring having two acetylamino groups at 2,4-positions has been synthesized for selective recognition of aliphatic monocarboxylate anions over a wide range of other anions. The recognition study has been carried out by UV–vis and fluorescence methods. A significant bathochromic shift of the fluorescence intensity of the receptor in the presence of carboxylate makes the receptor a discriminating sensor for aliphatic monocarboxylates.

The design and synthesis of artificial colorimetric and fluorescence receptors for sensing a particular anion over a wide range of anions are an interesting field in molecular recognition and supramolecular chemistry.[1–3] In recent years the following techniques such as change in fluorescence, color change, or chemical shift of protons in NMR of the sensor are utilized for detecting anions.[4] Anions such as carboxylates play an important role in chemical and biological processes.[5] To date various receptors have been designed for the detection of carboxylates.[6]

Selenium-containing heterocyclic compounds have been well recognized because of their remarkable reactivities, chemical phenomena, and their potential pharmaceutical applications.[7,8] Previously, metal complexes of various 2,1,3-benzoselenodiazole derivatives (selenodiazole-fused benzene ring) have been documented.[9] However only a few reports have been found for the synthesis and application of selenodiazole-fused heterocyclic rings such as pyridine or pyrimidine.[10] Recently we have reported a new selenium-based fluorescent sensor for selective sensing of hindered carboxylate more than acetate by changing its mode of binding site.[11] Here in this Letter, we explore another new selenodiazole-fused pyrimidine-based chromogenic fluorescent sensor (5,7-diacetylamino-1,2,5-selenodiazolo-[3,4-*d*]-pyrimidine) for the recognition of both small and hindered carboxylates (acetate and pivalate).

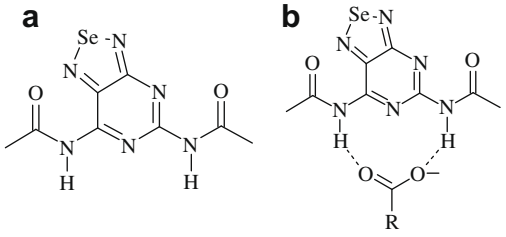
In receptor **1**, the selenodiazole-fused pyrimidine ring has two pyrimidine acetamide protons in same direction which are used as hydrogen bond donors for recognition of anions (Scheme 1).

The receptor **1** was synthesized by straightforward reactions summarized in Scheme 2. Initially compound **3** has been prepared by the condensation of 2,4,5,6-tetraamino-pyrimidine dihydrochloride (**2**) and selenium dioxide in solid phase by eco-friendly microwave technique.[12] Receptor **1** is isolated on acetylation of compound **3** by acetic anhydride.

The binding properties of receptor **1** have been studied by UV–vis and fluorescence methods in acetonitrile.[13] The absorption spectrum of receptor **1** (1.03×10^{-4} M) shows a maximum (λ_{max}) at 351 nm (Fig. 1). Upon addition of monocarboxylate anions such as acetate, pivalate, and phenyl acetate, the absorption maxima gradually decrease with simultaneous formation of another two maxima at 303 nm and 385 nm, respectively. Two prominent isosbestic points at 317 and 373 nm indicate the formation of a new complex between receptor and carboxylate anions.

Here a bathochromic shift by 34 nm is observed for the addition of carboxylate anions in favor of a strong complex between receptor and carboxylate anions. The UV–vis titration of receptor **1** is also carried out in the presence of other anions such as F^-, Cl^-, Br^-, and I^-. Except fluoride, the absorption intensity does not change in the presence of other halide anions. In the case of F^-, the absorption intensity slowly decreases initially and the rate of decrease of absorption maxima increases on addition of higher concentration of F^- (Fig. 2).

The 1:1 stoichiometry of receptor **1** with the anions in the complexes has been determined by Job's plot (Fig. 3).[14]



Scheme 1. (a) Receptor **1**; (b) possible binding mode with carboxylate anions.

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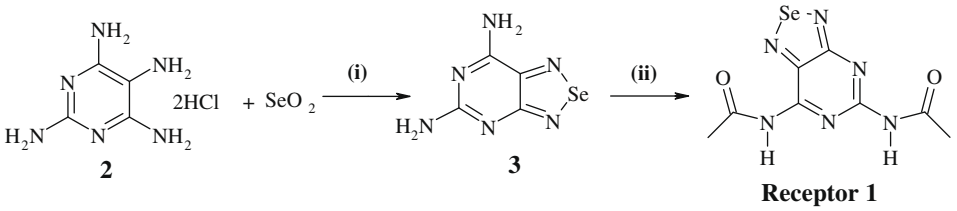
doi:10.1016/j.tetlet.2010.04.085



Scheme 2. Reagents and conditions: (i) MW, 400 W, 20 min; (ii) acetic anhydride, 80–90 °C, 10 h.

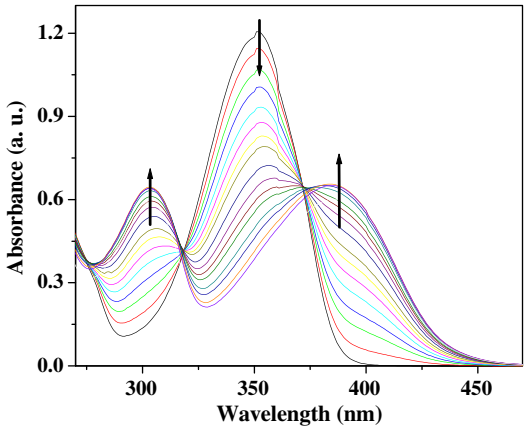


Figure 1. Change of absorption spectra of receptor **1** upon addition of tetrabutylammonium acetate in acetonitrile.

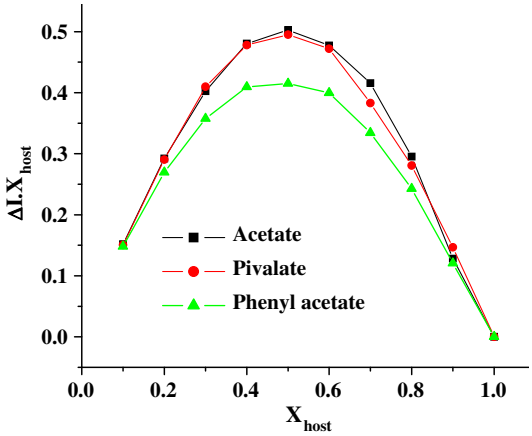


Figure 3. Job plots of receptor **1** with different carboxylates determined by UV–Vis method in acetonitrile.

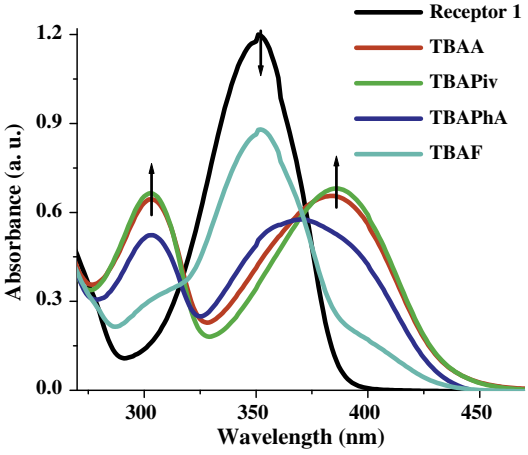


Figure 2. Change of absorption spectra of receptor **1** upon addition of different tetrabutylammonium carboxylate and fluoride salts (4 equiv) in acetonitrile.

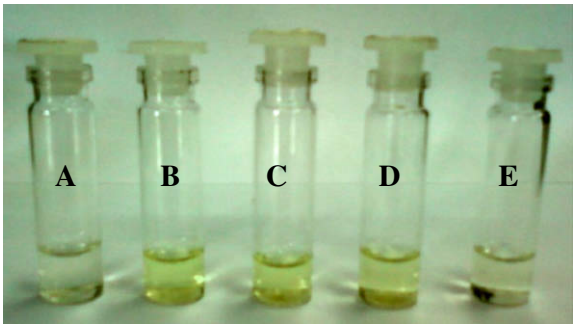


Figure 4. Color change of receptor **1** (A) upon addition of 1 equiv of different tetrabutylammonium salts of (B) acetate, (C) pivalate, (D) phenyl acetate, and (E) fluoride in acetonitrile.

The evidence of bathochromic shift is also confirmed by observing color change with the naked eye. The colorless solution of receptor (1.0×10^{-4} M) turns pale yellow after the addition of 1 equiv carboxylates (tetrabutylammonium salt of acetate, pivalate, and phenylacetate) (Fig. 4). In the case of tetrabutylammonium fluoride, the color of the receptor **1** remains unchanged by the addition of 1 equiv of this salt but a pale yellow color is observed by the addition of high concentration (4 equiv) of F^- ion in acetonitrile solution of receptor **1**. Color change is not observed on addition of benzoate and other anions.

Fluorescence study has been carried out for sensing the selectivity of receptor **1** toward different anions. Receptor **1** shows a broad peak at 412 nm when it is excited at 351 nm (excitation slit width 14 nm, emission slit width 10 nm). The emission spectrum of receptor **1** has shifted toward higher wavelength (at 459 nm)

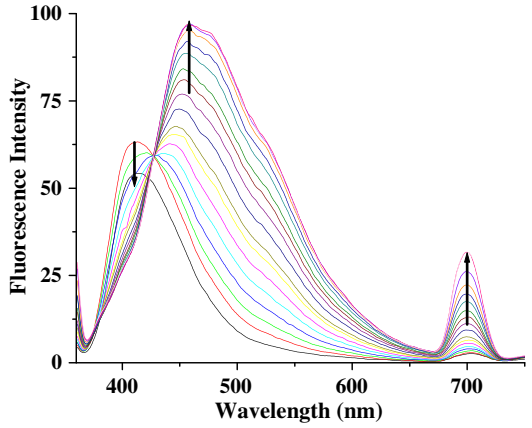


Figure 5. Change of fluorescence intensity of receptor **1** upon gradual addition of tetrabutylammonium acetate in acetonitrile.

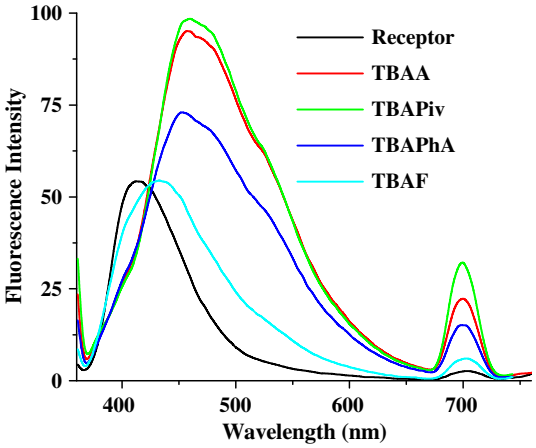


Figure 6. Enhancement of fluorescence intensity of receptor **1** upon addition of different tetrabutylammonium carboxylate and fluoride salts (4 equiv) in acetonitrile on excitation at 351 nm.

Table 1
Binding constant values of receptor **1** with different carboxylates (tetrabutylammonium salts)

Guests	K_a (M^{-1}) in UV–Vis method	K_a (M^{-1}) in fluorescence method
Acetate	3.77×10^3	3.87×10^3
Pivalate	1.10×10^3	2.56×10^3
Phenyl acetate	2.65×10^3	3.85×10^3
Adamantane-1-carboxylate	1.15×10^3	3.04×10^3

All errors are ±10%.

with significant enhancement of emission maxima upon gradual addition of monocarboxylates (Fig. 5).

A significant red shift, about 47 nm of the receptor **1** is observed on addition of carboxylate anions. The fluorescence intensity of receptor **1** is not affected in the presence of aromatic carboxylate such as benzoate and other halide ions apart from F^-. In the case of benzoate we observed very small decrease of the absorption maxima with negligible blue or red shift and small quenching of the emission maxima without red shift in comparison with the other carboxylates. This is probably due to the presence of benzene ring which decreases the hydrogen bond accepting tendency of carboxylate anion. Therefore receptor **1** is less selective toward aromatic carboxylate. The fluorescence spectra of receptor **1** with fluoride ion behave like carboxylate ions but the enhancement of emission intensity is comparatively much lower than carboxylates. Initially on addition of F^-, a minor and irregular change of fluorescence intensity occurs but the intensity increases and shifted slightly toward higher wavelength on addition of high concentration of F^- (after 4 equiv) (Fig. 6). Interestingly after the addition of 4 equiv of carboxylates, the enhancement of fluorescence intensity becomes close and further enhancement does not occur on addition of higher equivalents of carboxylates.

Table 2
Binding constant values of receptor **1** with sodium and potassium acetates

Guests	K_a (M^{-1}) in UV–Vis method	K_a (M^{-1}) in fluorescence method
Sodium acetate	3.48×10^3	3.29×10^3
Potassium acetate	3.51×10^3	3.08×10^3

All errors are ±10%.

Earlier we reported a selenium-based receptor which was highly selective for sensing hindered carboxylates such as pivalate and adamantane-1-carboxylate and less selective toward acetate.[11] But in this case the enhancement of fluorescence intensity of acetate is however close to pivalate and the binding constant for acetate is slightly higher than other aliphatic carboxylate anions (Table 1).

Now the UV–vis and fluorescence studies of the receptor **1** have been carried out with acetate anion by changing the counter cation part such as sodium (Na^+) or potassium (K^+) ions instead of tetrabutylammonium (Bu_4N^+) ion to observe the change of spectra and binding affinity. The solutions of sodium acetate and potassium acetate were prepared in acetonitrile and water (95:5 v/v). Here decrease of the absorption maxima with blue and red shifts and the enhancement of fluorescence intensity with red shift of receptor **1** are also observed upon addition of sodium acetate or potassium acetate solutions (Fig. 7).

The nature of both UV–vis and fluorescence spectra of receptor **1** with sodium acetate and potassium acetate is similar to the spectra of receptor **1** with tetrabutylammonium acetate. The binding constants are close to each other (Table 2). Therefore the receptor

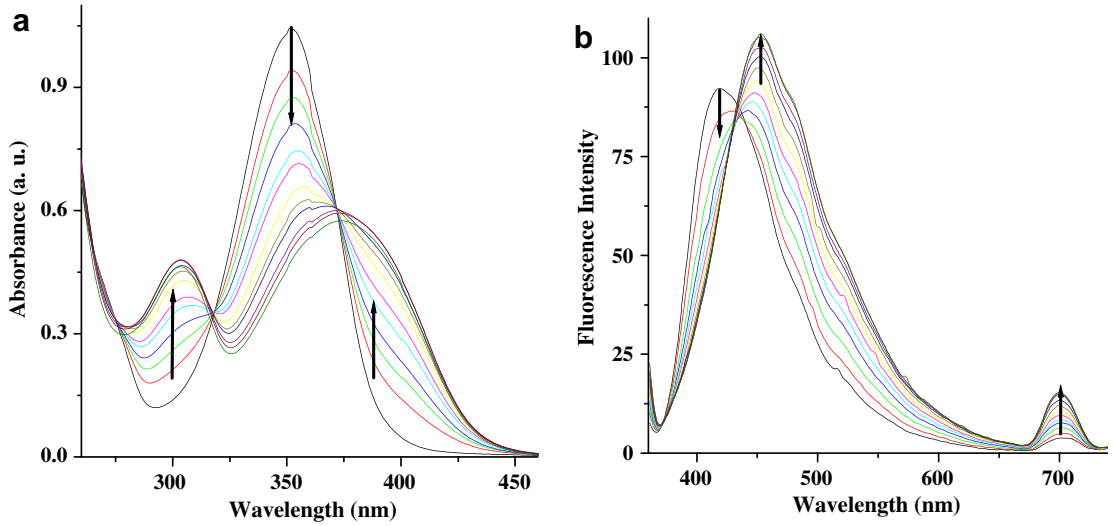


Figure 7. (a) Change of absorption spectra of receptor **1** upon addition of potassium acetate and (b) enhancement of fluorescence intensity of receptor **1** upon addition of sodium acetate on excitation at 351 nm in acetonitrile/water (95:5 v/v).

1 selectively binds the acetate anion and the complex formation is not affected by these counter cations (Na^+, K^+, or Bu_4N^+).

The UV–vis and fluorescence studies of intermediate compound **3** have also been tested in 5% DMSO in acetonitrile solution with tetrabutylammonium acetate. In the case of UV–vis study, the absorption maximum (358 nm) gradually decreases with red shift and in the fluorescence method, initially very minor and irregular change occurs after which the emission maximum (434 nm) gradually quenches. Here the enhancement of fluorescence intensity with remarkable red shift is not observed like receptor **1**. As a result receptor **1** is a better selective probe for detecting aliphatic monocarboxylate rather than its intermediate compound **3**.

In conclusion, a selenodiazole-fused pyrimidine-based receptor has been synthesized for the recognition of anions. From the above-described fluorescence and UV–vis studies, it is observed that this receptor selectively recognizes both small and hindered aliphatic monocarboxylates specially acetate among all the other anions. Hence receptor **1** can be used as a colorimetric fluorescence sensor for aliphatic monocarboxylates.

Acknowledgments

We thank the CSIR [No. 01(2292)/09/EMR-II], Government of India for financial support. A.H. and M.D. acknowledge the CSIR, Government of India for research fellowships. We appreciate Professor T. Schrader of Duisburg-Essen University, Essen, Germany for mass spectral help.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.085.

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