Tetrahedron Letters 52 (2011) 6465–6469

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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

Differentiation of *cis*- and *trans*-isomers of the novel napthalene-aza receptor by naked-eye colorimetric anion sensing

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ARTICLE INFO

Article history:
Received 1 September 2011
Revised 15 September 2011
Accepted 22 September 2011
Available online 29 September 2011

Keywords:
Isomers
Urea
Anions
Colorimetric sensors
Fluorescence
Photoinduced electron transfer

ABSTRACT

Novel chromofluorogenic receptors **1** (*cis*-isomer) and **2** (*trans*-isomer) were developed using an aza-nitro-phenyl group as a chromophore, urea moiety as a binding unit, and naphthalene as a fluorophore. The position of nitro-phenyl moiety in the chromophores influences the naked-eye colorimetric anion sensing which differentiates the geometrical isomers. Receptor **2** showed sensitivity toward F^- than $HP_2O_7^{3-}$ and its fluorescence emission (λ_{max} = 370 nm) was significantly 'switched-off' at an excitation wavelength of 260 nm in CH_3CN:DMSO (90:10, v/v) solution at 25 °C. The fluorescence titration experimental results revealed that the receptor **2** binds strongly with F^- than $HP_2O_7^{3-}$ ions in 1:1 stoichiometry. The quantum mechanical calculations through time dependant density functional theory (TD-DFT) using basis set B3LYP/6-31G(d) supported our experimental findings agreeably.

Introduction

Anion recognition and sensing have received considerable attention in recent years.[1,2] The limited reports on colorimetric anion sensing and selective affinity describe the complexity of the design and synthesis required to increase the intrinsic association and ion specificity of a receptor.[3] Targets such as pyrophosphate and fluoride are of particular interest, as they possess important biological and medicinal properties, and there are many reports of their detection using fluorescent and colorimetric techniques.[2] As they offer suitable binding sites for guests and stabilize complexes by non-covalent interactions such as hydrogen and ionic bonding, urea-based anion sensors are of utmost importance.[4] Deprotonation of the more acidic urea proton and the subsequent charge-transfer phenomenon were previously reported to occur with the addition of $[(n\text{-}Bu)_4N^+]OH^-$, which produces a color change similar to that of urea derivatives upon addition of F^-/$HP_2O_7^{3-}$.[2d,3c,4e]

Due to its simplicity and high sensitivity, fluorescence has become increasingly important for chemical trace detection. Receptors based on anion-induced changes in fluorescence are particularly attractive, because they offer the potential for high sensitivity at low analyte concentrations.[5] Fluorosensors for a large number of biotic and abiotic analytes have been designed in the past decade by appending a fluorescent fragment to the envisaged receptor framework: in all cases, an efficient mechanism has to be provided for either quenching or reviving fluorescence, following substrate recognition.[5–10]

Isomers play a fundamental role in science and are widely studied because of their significance in living systems.[11] A number of approaches have been used for quantitative and qualitative detection of isomers; the methods are based on either detection or spectroscopy characterization.[12] The development of fluorescent receptors with the properties of isomer recognition and optical change, has attracted increasing attention because such receptors have increased sensitivity and potential application in pharmaceuticals, biology, and as catalysts.[13] For these reasons, the design, synthesis and structural activity relationships of enantioselective receptors are still vital areas of research.[14] Much attention has been paid recently to the synthesis of molecular receptors with the ability to recognize chiral molecules.[13b,c] Fluorescent sensors are preferred because they are well-suited to meet the need for *in vivo* probes, such as mapping the spatial and temporal distribution of the biological analyses.[15]

Herein, we report synthesis, characterization, binding studies, theoretical calculations, and differentiation of new fluorescent receptor isomers with dual purposes: (1) normal colorimetric

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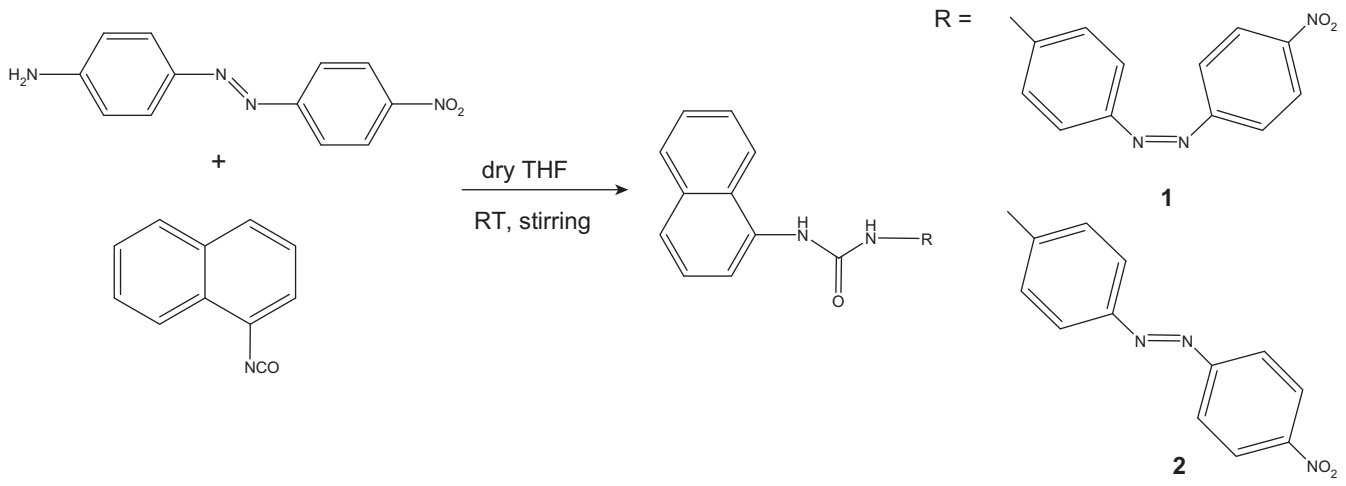
doi:10.1016/j.tetlet.2011.09.103



Scheme 1. Syntheses of receptor **1** and **2**.

naked-eye anion detection; (2) differentiation of isomers through anion detection. To the best of our knowledge, we provide the first example of differentiation of geometric isomers through anion recognition of new fluorescent receptors **1** (*cis*-isomer) and **2** (*trans*-isomer) in less than a minute time.

Results and discussion

The reaction of a 1:1 molar ratio of 4-(4-nitrophenylazoenyl)aniline and 1-naphthyl isocyanate in dry THF followed by filtration afforded **1** (*cis*-isomer, 40%) as pale yellow and filtrate afforded **2** (*trans*-isomer, 50%) as orange microcrystals (Scheme 1). The structures of **1** and **2** were elucidated by elemental, spectral (UV–vis, ^{1}H, and ^{13}C NMR), and mass analyses (Supplementary data, Figs. S1–S6).

The colorimetric selective sensing abilities of receptors **1** and **2** with anions in CH_3CN:DMSO (90:10, v/v) were monitored by UV–vis absorption and by 'naked eye' observation. In the absence of anions, the UV–vis spectrum of **1** and **2** were characterized by two peaks (316 and 409 nm for **1**; 260 and 401 nm for **2**). The anions were added as tetrabutylammonium salts to the solutions of **1** and **2** (host:anion; 1:100 equiv). Upon the addition of anions, receptor **1** solution did not show any significant color/absorption spectral change, but the color of the receptor **2** solution changed from yellow (λ_{max} = 401 nm) to blue (599 nm) and green (617 nm) upon addition of F^- and $HP_2O_7^{3-}$ ions, respectively, which could be easily observed by the naked eye (Fig. 1; for corresponding UV–vis spectrum, Supplementary data, Fig. S7). This is associated with deprotonation of more acidic urea proton and the subsequent charge-transfer phenomenon.[3b,c,16] As the receptor

Figure 1. Color changes of 0.075 mM hosts (A – *cis* isomer; B – *trans* isomer) upon the addition of tetrabutylammonium salts of anions (7.5 mM) at a 1:100 equivalent ratio in CH_3CN:DMSO (90:10, v/v) mixture. (a) Host only; (b) H + F^-; (c) H + Cl^-; (d) H + Br^-; (e) H + I^-; (f) H + HSO_4^-; (g) H + $H_2PO_4^-$; (h) H + CH_3COO^-; (i) H + $HP_2O_7^{3-}$; (j) H + NO_3^-. Color pictures of *trans*-isomer H + F^- and H + $HP_2O_7^{3-}$ were taken after diluting twice with solvent in order to improve the clarity of the color.

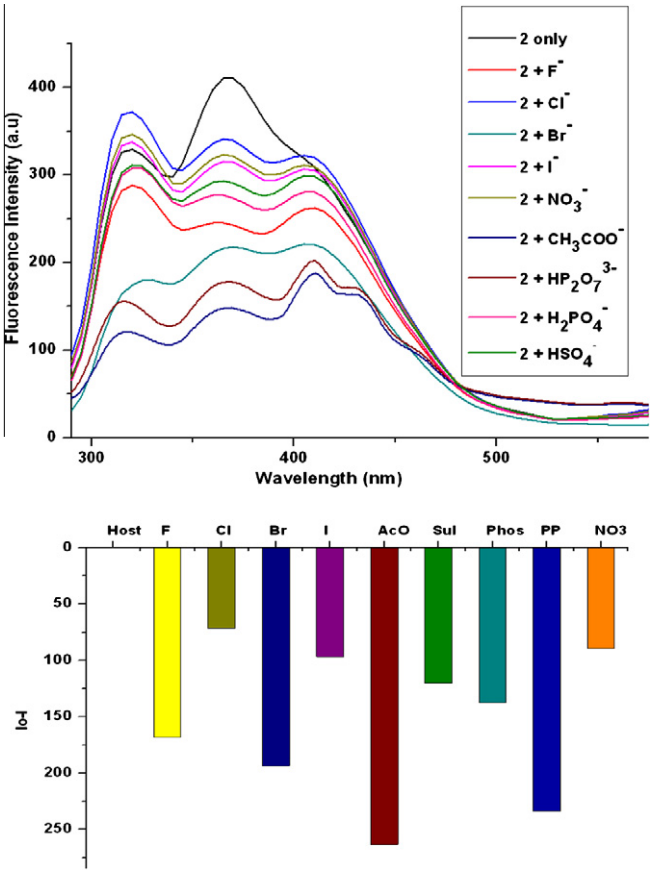


Figure 2. Fluorescence emission spectral changes of receptor **2** (5 μM) upon the addition of tetrabutylammonium salts of anions (500 μM) at 1:100 equivalent ratio in CH_3CN:DMSO (90:10, v/v) mixture (slit width = 3 nm; excitation = 260 nm).

bound to the anions, hydrogen bonds were constructed to form stable complexes, and the electron density in the supramolecular system was increased. It promotes the charge-transfer phenomenon between the electron-deficient urea-bound anion and the electron-rich aza-nitro-phenyl center of **2** in neutral/deprotonated form, thus causing a color change in the host solution.[17,4a] On the other hand, exposure of receptor **2** to solutions of Cl^-, Br^-, I^-, CH_3COO^-, HSO_4^-, $H_2PO_4^-$, and NO_3^-, did not lead to any conspicuous change in color, and no significant change in absorption spectra was observed (Fig. S7), suggesting no/very very weak binding for those anions to the receptor **2**. This dramatic combination of anion-specific response/non-response makes this system an effective naked-eye-detectable anion sensor under solution-phase conditions. Interestingly, addition of F^- and $HP_2O_7^{3-}$ ions to **1** and **2** solutions resulted in differentiation of *cis*- and *trans*-isomers.

The fluorescence emission changes of **2** upon the addition of anions in the form of tetrabutylammonium salts at a 1:100 equiv ratio in the CH_3CN:DMSO (90:10, v/v) mixture is illustrated in Figure 2 (for **1**, Supplementary data, Fig. S9). Both **1** and **2** display fluorescent quenching effects with all the anions via a photo-induced electron transfer (PET) mechanism.[18]

We were unable to perform ^1H NMR and UV–vis titrations of **2** with anions due to the disappearance of the urea –NH proton signals after the addition of small equivalents of anion and the lack of a uniform decrease or increase in absorbance intensity (Supplementary data, Figs. S13 and S8). Both shifts and substantial line broadening were observed during the ^1H NMR titration. Upon addition of 0.5 equiv. F^- and $HP_2O_7^{3-}$ ions, the urea moiety –NH signals (9.68 and 9.00 ppm) disappeared and the aromatic region signals broadened, which implied deprotonation of one –NH fragment and interaction of the anions with the other –NH fragment of compound **2** through intermolecular hydrogen bonding.[19] The signals of the urea group disappeared completely with the further addition of anions (e.g., 1.0 equiv of F^- and $HP_2O_7^{3-}$), and additionally, the signals of the aromatic protons exhibited slight upfield shifts from 8.44 and 8.15 ppm, indicating an increase in the electron density on the phenyl ring owing to through-bond effects.[20] The disappearance of –NH signals may be understood in terms of the following equilibria:

$$LH + X^- \leftrightarrow [L \cdot H \cdot X]^- \quad (1)$$

$$[L \cdot H \cdot X]^- \leftrightarrow L^- + HX \quad (2)$$

$$[L \cdot H \cdot X]^- + X^- \leftrightarrow L^- + [HX_2]^- \quad (3)$$

However, it should be noted that we observed no signal for $[HX_2]^-$ in its ^1H NMR spectral titrations even up to δ 20 ppm, probably as the result of its instability in highly polar solvents such as DMSO.[21]

To investigate the sensitivity of **2** toward biologically important anions, we carried out fluorescence titrations using tetrabutyl ammonium salts of F^- and $HP_2O_7^{3-}$ ions in a degassed dry CH_3CN:DMSO (90:10, v/v) mixture (Fig. 3). We found that fluorescence intensity was gradually decreased as the concentration of

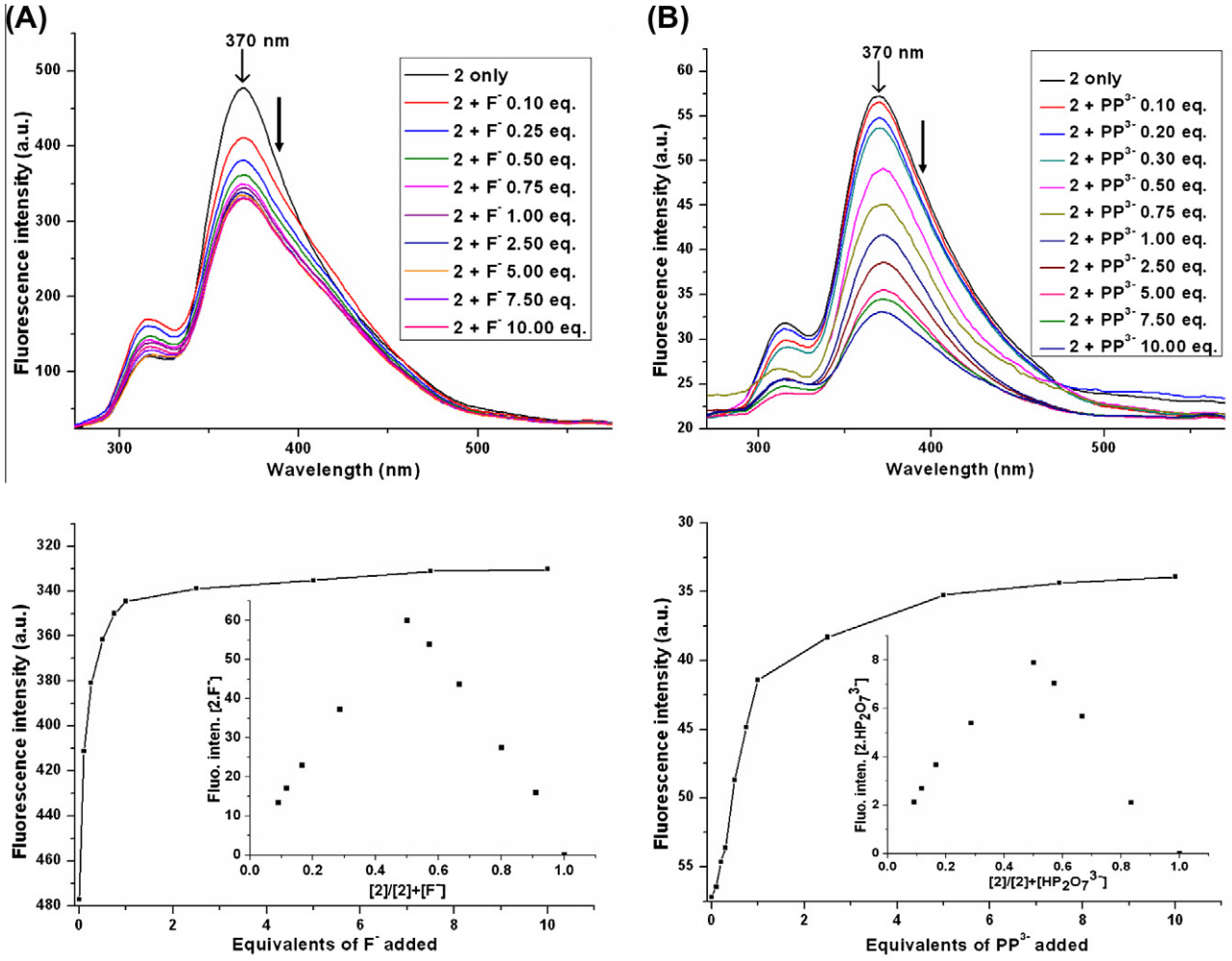
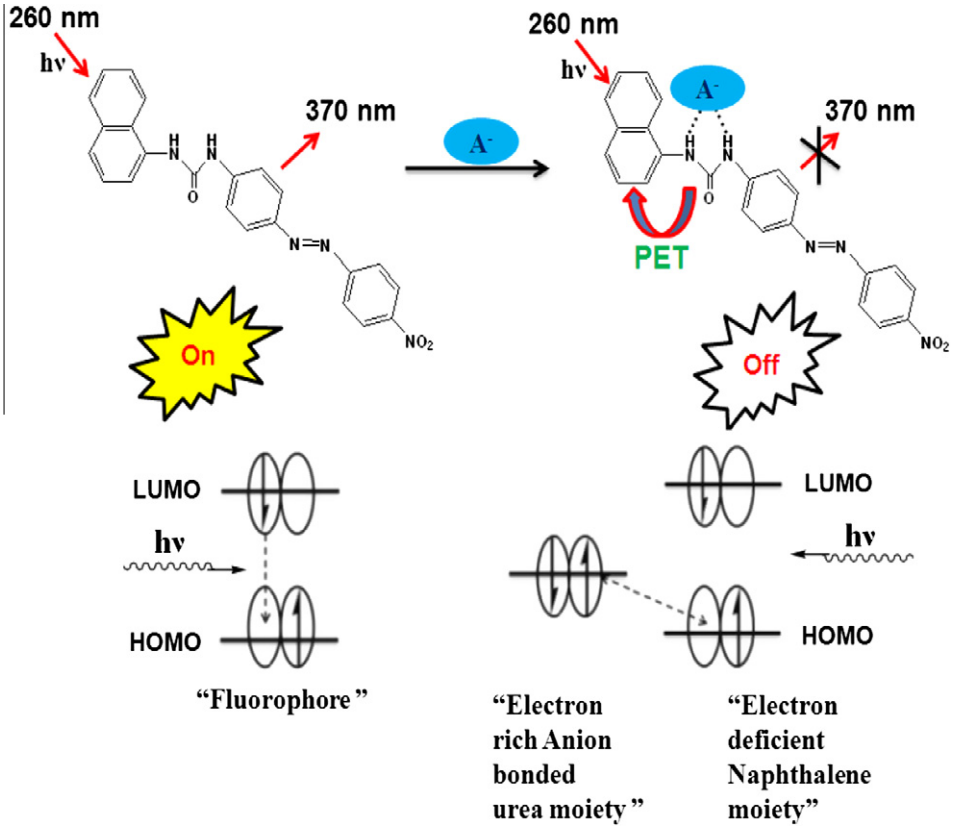


Figure 3. Fluorescence emission spectral changes of receptor **2** with increasing concentrations of TBAF (A) and TBAPPi (B) in CH_3CN:DMSO (90:10, v/v) mixture. For F^-, **2** (2 μM) (slit width = 5 nm; excitation = 260 nm); for $HP_2O_7^{3-}$, **2** (1 μM) (slit width = 3 nm; excitation = 260 nm); (inset) Job plot analysis for **2**·F^- and **2**·$HP_2O_7^{3-}$ complexes in CH_3CN:DMSO (90:10, v/v).



Scheme 2. Proposed PET mechanism of fluorescence 'on–off' behavior of compound **2** upon the addition of anion.

the anions increased, due to PET behavior upon anion sensing.[18] The excited state of the fluorophore was not quenched, or was quenched only to a minimal extent, by electron transfer (ET) from the receptor to the fluorophore prior to the sensor-anion interactions. However, upon interaction with anions, the reduction potential of sensor **2** was increased; in other words, electron transfer from the electron-rich amide moiety bonded with the anion to the electron-deficient naphthalene moiety became more feasible. Upon further addition of F^- and $HP_2O_7^{3-}$, it appeared that the deprotonated species, which was more electron-rich than the hydrogen-bonded complex with anion, activated the PET process more efficiently and evidenced more profound quenching (Scheme 2).[22] The titration data were fitted to the 1:1 binding profile with F^- and $HP_2O_7^{3-}$ ($\log K_a = 6.50$ for F^- and 5.30 for $HP_2O_7^{3-}$) according to the standard equation.[23] Based on the fluorescence titration experimental result, the detection limit (LOD) of the sensor **2** is calculated to be ca. 20 and 80 nM for F^- and $HP_2O_7^{3-}$, respectively (for receptor **1** fluorescence titrations, Supplementary data, Figs. S10 and S11).

Optimized geometries and vibrational frequencies for possible *cis*- and *trans*-isomers of hosts and anions were obtained at the B3LYP level[24] with the 6-31G(d) basis set. At the respective optimized geometries, time-dependent DFT (TD-DFT) calculations,[25] using the B3LYP/6-31G(d) level were carried out in order to obtain the vertical excitation energies of singlet states, and UV-visible spectra of anions were simulated. The simulated UV-visible spectra of host molecules are well matched with the experimental ones. TD-DFT calculations revealed that the origin of the newly developed spectral band upon complexation of **2** with F^- and $HP_2O_7^{3-}$ ions around 600 nm is due to the contributions from intramolecular transitions (Supplementary data Fig. S14). The B3LYP optimized structures of both *cis*- and *trans*-isomers of hosts show large deviation from planar geometry. When F^- anion is added to the *trans*-isomer, the geometry changes drastically from a distorted structure to a planar one, whereas the nonplanar *cis*-isomers are scarcely affected by the addition of F^- anion. This shows that the *trans*-isomers have much larger π-conjugation length than the *cis*-isomers, which may lead to a favorable intramolecular charge transfer in the *trans*-isomer upon addition of anions.

Conclusion

In summary, we developed novel colorimetric receptors **1** and **2** containing both chromogenic and fluorogenic signaling subunits and urea as the binding site for anion sensing. Anion recognition via hydrogen-bonding interactions can be easily monitored by anion-complexation-induced changes in UV–vis absorption spectra and with the naked eye. Theoretically calculated results support our experimental findings that the receptor **2** binds with F^- and $HP_2O_7^{3-}$ ions in 1:1 stoichiometry. Furthermore, the observed chemical shifts upon complexation of these anions were also rationalized by the calculated results. Fluorescence studies showed that the complexation of **2** with F^- and $HP_2O_7^{3-}$ could quench the emission intensity via PET mechanism. From the binding study experiments, we concluded that the receptor **2** is flexible enough to orient itself according to the size of the binding anion. In this Letter, we have successfully demonstrated the differentiation of geometrical isomers by naked-eye anion detection technique. Molecular sensors of this kind are likely to be particularly useful in field tests and other situations, where sophisticated instrumentation might be lacking.

Acknowledgments

This work was supported by the Priority Research Centers Program (NRF 2010-0029634) and the International Joint Research Program (F01-2009-000-10082-0) through the National Research Foundation of Korea.

Supplementary data

Supplementary data (product characterization of **1** and **2** (copies of ^{1}H and ^{13}C NMR), experimental details, and theoretical calculations) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.09.103.

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$$\log[(I_{max} - I_F)/(I_F - I_{min})] = \log[\text{anion}] - \log K_a$$

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