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A tripodal receptor bearing catechol groups for the chromogenic sensing of F^- ions via frozen proton transfer

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ABSTRACT

A neutral tripodal Schiff base receptor (**3**) having catechol as end groups has been synthesized and characterized with the help of spectroscopic and single crystal X-ray crystallographic studies. The receptor behaves as a visually detectable optical sensor for F^- ions in DMSO, sensitive enough to recognize the ions up to a concentration 1×10^{-5} M with naked eye. The chromogenic response is based upon the deprotonation of the highly acidic catechol moieties in the presence of highly basic F^- ions in a polar solvent like DMSO.

1. Introduction

The development of anion sensing receptors[1,2] has gained impetus due to better understanding of their roles in biological, environmental, and chemical processes. Especially the sensing of F^- ions is the most important due to its function in dental care, treatment of osteoporosis,[3] and partly due to its release during hydrolysis of nerve gas Sarin.[4] Among various chemosensors, the chromogenic receptors[5] are exceptionally interesting for their recognition process is accompanied by a simple, naked eye detection, which is both quantitative and qualitative in nature. Most of the neutral chromogenic receptors for anions employ N–H··· anion H-bonding interactions for anion recognition and are based upon amides, thioureas, and amidoureas molecules.[6] These are strong, directional H-bond donors and can easily be accommodated in other preorganized scaffolds. The recognition phenomenon in these examples involves either H-bonding (incipient proton transfer) or complete deprotonation of –N–H protons (frozen proton transfer).[5h] On the other hand, in the biological context the O–H···anion H-bonding interactions[7] are almost as crucial as the ubiquitous N–H···anion interactions. Although there are a few reports known where such interactions have been seen to supplement other kinds of H-bonding interactions,[8] but there are only a few examples known[9] where the former interactions alone have been exploited for developing anion receptors. Smith and coworkers used a high throughput assay[10] to compare the anion binding ability of bisamides and phenols, and they found catechol to be a stronger H-bond donor for Cl^- ion and subsequently were successful even in developing a colorimetric response of F^- ion with catechol, which occurred via a new mechanism.[11] Working on the same lines we have incorporated catechols into the tripodal receptor (**3**) so as to study the effect of their organization on the recognition behavior, ability, and selectivity toward anions.

Here we report the synthesis, characterization, and chromogenic studies on a tripodal ditopic Schiff base receptor (**3**) with catechol moiety as the end groups so as to dispose six –OH groups capable of forming H-bonding or undergoing deprotonation in the presence of anions. There are some reports[12] for the synthesis of catechol bearing tripodal ligands but they were not used as anion sensors. Barring an off-the-shelf compound Alizarin, which is reported[8e] to sense various anions in dichloromethane, to the best of our knowledge this is the first example of a synthetic receptor, bearing catechol group being used as an anion sensor. The receptor acts as a highly selective, visually detectable optical sensor for F^- ions in DMSO working via frozen proton transfer.

2. Results and discussion

2.1. Synthesis

The receptor (**3**) was synthesized as in Scheme 1. The receptor was prepared by Schiff base condensation reaction of reactant **1** and **2** in chloroform/methanol mixture in the presence of catalytic amount of zinc perchlorate. The solution was stirred for half an

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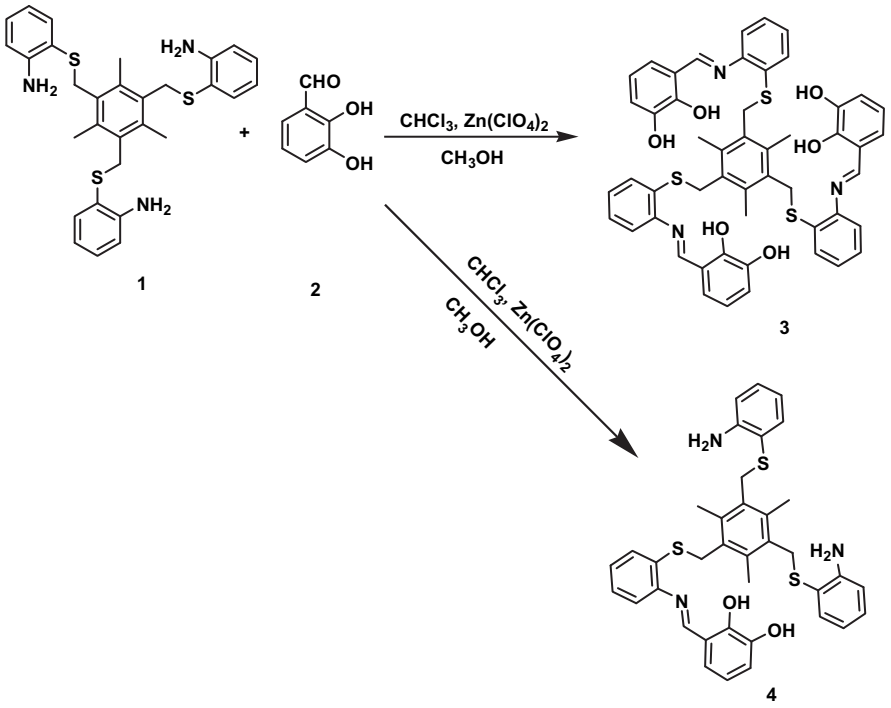

Scheme 1.

hour, orange colored solid was separated, which was filtered, washed with methanol, and dried under vacuum. It was characterized by elemental analyses, IR, ^{1}H, ^{13}C NMR, UV–vis absorption spectroscopy, and X-ray crystal structure analysis. The IR bands at 1616 and 3418 cm^{-1} show the presence of imine and H-bonded OH groups. The same are evident by the signals at δ 8.79, 9.18, and 13.08 in the ^{1}H NMR and at δ 162.88 and 182.26 in ^{13}C NMR spectra, respectively. The chemical shift of one of the hydroxyl protons is typical for the resonance-assisted hydrogen-bonded (RAHB) proton of O–H···N as found by others and us.[13] In the ^{1}H and ^{13}C NMR spectra there are single peaks corresponding to methyl, methylene, imine, and hydroxyl protons and their corresponding carbons, pointing toward a three-fold symmetry of the molecules being retained in the solution phase unlike the solid phase (cf. the X-ray structure given below). The CHN data are also in accordance with the molecular formula.

2.2. X-ray crystal structure

The X-ray crystal structure of (**3**) is shown in Figure 1. All seven aromatic rings are planar. One arm of the tripodal ligand is highly unsymmetrical with respect to the other two thus, removing any three-fold symmetry expected of the compound as found in the solution state. The rings B (C8–C13), C (C22–C27), and D (C36–C41) are making dihedral angles 78.7(2)°, 39.5(2)°, and 87.0(2)° with the central ring A (C1–C6), respectively. Thus rings B and D are almost perpendicular to the central ring A but ring C is *gauche* to it. Similarly rings E (C15–C20) and G (C43–C48) are perpendicular (dihedral angles 78.2(2)° and 80.7(2)°, respectively) but ring F (C29–C34) is parallel (dihedral angle 4.7(2)°) with respect to ring A. The torsion angles about S1–C8 and S3–C36 are *anti*, being −170.1(6)° and 171.7(7)°, respectively, but *gauche* −94.9(8)°, around S2–C22. This conformation analysis shows that the tripod is not in its fully extended form but one of its arms has folded up to make a loop having ring F parallel to ring A. This loop is stabilized by various intramolecular interactions (Table S1, Supplementary data) such as edge to edge π···π interactions between the two rings

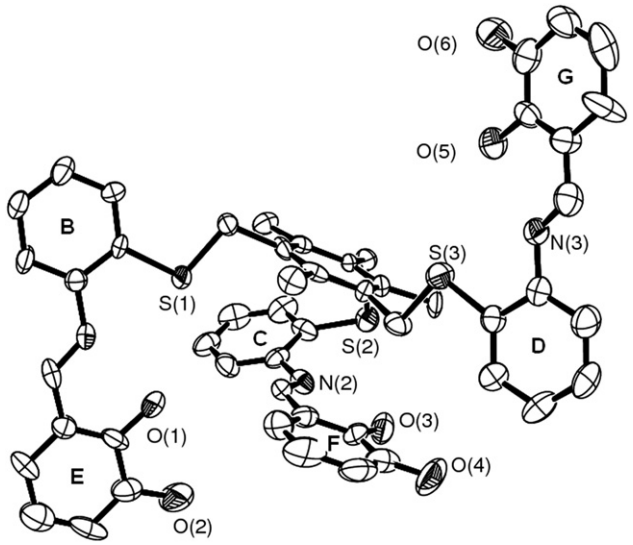

Figure 1. ORTEP diagram of the receptor (**3**) showing partial labeling scheme. The aromatic rings are labeled as in text and hydrogens have been removed for clarity.

A and F; C–H···π interaction between methylene carbon C35 and ring F and methyl carbon C51 and ring C; H-bonding between methyl carbon C50 and S2; H-bonding between phenylene carbon C41 and O4; and H-bonding between phenylene carbon C29 and O3. There are intra- and intermolecular H-bonding interactions found in the unit cell. The hydroxyl oxygens O1 and O6 are acting as double H-bond donors to imine nitrogens N1, N3 and thioether sulfurs S1 and S3, respectively, in the two extended arms. In the folded arm of the tripod however, O3 is having such intramolecular H-bonding interactions only with imine nitrogen N2 but not to S2. Intermolecular H-bonding between symmetry related O2 groups produces H-bonded dimers. The packing of the molecule in the unit cell has stacking down the *b* axis and shows weak intermolecular C–H···O and C–H···N, and C–H···S type of H-bonding interactions.

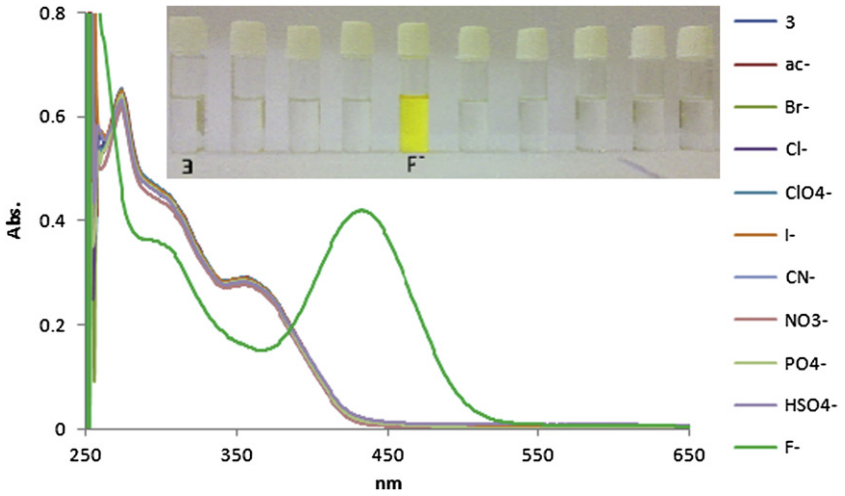

Figure 2. Showing changes in the UV–vis spectrum of (**3**) in DMSO (10 μM) on addition of (100 μM) various anions, inset shows the visual color change on addition of F^- ion.

2.3. Anion sensing

The anion binding affinity of receptor (**3**) was determined by the changes in absorption spectra of receptor (**3**) upon addition of various anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, CN^-, ClO_4^-, AcO^-, HSO_4^-, and H_2PO4^- (Fig. 2). These experiments were performed with 10 μM solution of receptor (**3**) in DMSO by 100 μM tetrabutylammonium salts of the anions. In the absence of anions, the spectrum of receptor (**3**) in DMSO showed a band at λ_{max} 274 nm (ϵ_{max} 44,600 $M^{-1}\,cm^{-1}$) and two shoulders at λ_{max} 306 nm (ϵ_{max} 30,400 $M^{-1}\,cm^{-1}$) and λ_{max} 353 nm (ϵ_{max} 19,200 $M^{-1}\,cm^{-1}$). The latter has been designated as an intraligand or internal charge transfer (ICT) band involving imine and hydroxyl group.[13e,14] Addition of F^- ion brings significant changes in the spectrum, on the other hand, no change was observed with Cl^-, Br^-, I^-, NO_3^-, CN^-, ClO_4^-, AcO^-, HSO_4^-, and H_2PO4^- ions. On addition of F^- ion in the solution of (**3**) the highest energy band shows a slight hypsochromic shift whereas the shoulder at 353 nm disappears and a new band appears at λ_{max} 433 nm. Figure 3 shows these changes with gradual increase in concentration of F^- ion.

Addition of 1.0 M equiv of F^- to a 10 μM solution of receptor **3** causes visual changes in color from very pale yellow to bright yellow, the color became more intense upon further addition of F^- to receptor (**3**) and is almost invariant after an addition of 12 equiv of F^-. The appearance of a single isobestic point indicates the presence of only two species, L and L^- in the solution, Figure 4 shows the gradual decrease and increase in the concentration of these two species with increase in equivalents of TBAF, respectively.

To investigate the binding sites of the receptor for the ions, NMR titrations were carried out in DMSO-d_6, with increasing amounts of tetrabutylammonium fluoride as shown in Figure 5. NMR spectra show that both signals for the –OH protons, which are observed at 9.18 and 13.08 ppm disappear completely much before the complete addition of 1 equiv of TBAF, indicating that the interaction with the F^- ions is not through H-bonding but through proton transfer (acid–base) process. Such a process has been found to be important in anion binding specially for basic anions such as F^- or $H_2PO_4^-$ and moderately acidic groups like N–H[15,16] and has also been seen earlier in the case of nitrocatechol for the chromogenic recognition of HSO_4^- and $H_2PO_4^-$ anions.[11] This is however, different than the two-step mechanism supposed to be working for the recognition of halide ions by neutral H-bonding receptors having urea/thiourea as binding groups.[6d,17] It has been shown there that the mechanism involves occurrence of two consecutive equilibria, i.e., formation of a genuine H-bonded complex followed by a deprotonation step. Fluoride ion sensors based upon the color change accompanied by deprotonation are well known and some of them have shown two different λ_{max} in UV–vis spectra

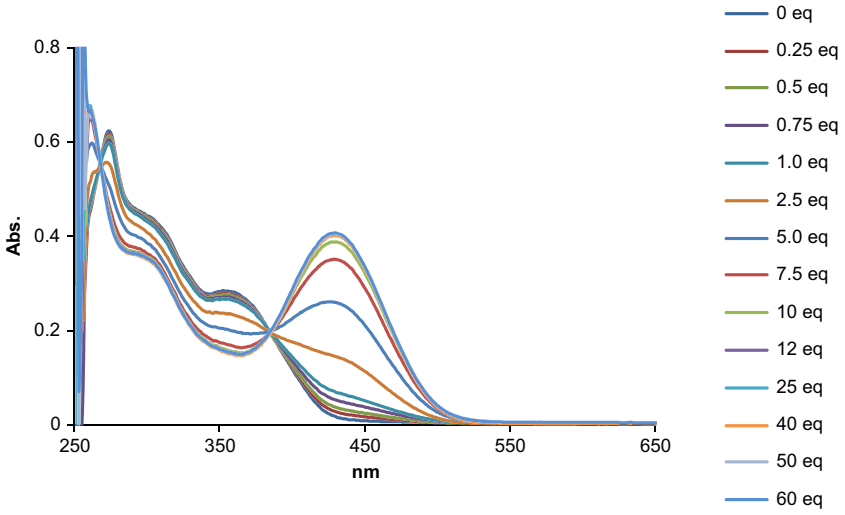

Figure 3. Changes in the absorption spectrum of (**3**) (10 μM) on adding increasing amount of F^- ion in it.

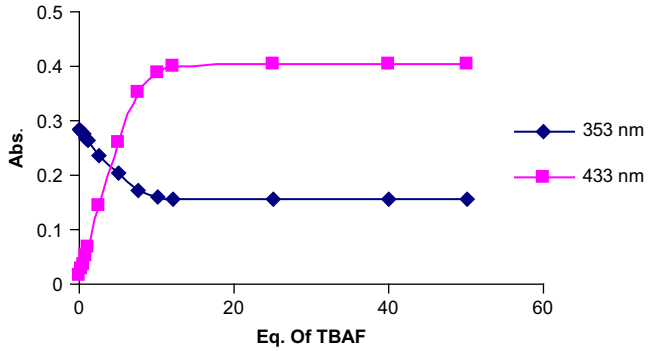

Figure 4. Showing plot of absorption versus concentration of F^- showing decrease and increase in absorption of the 353 nm and 433 nm bands, respectively.

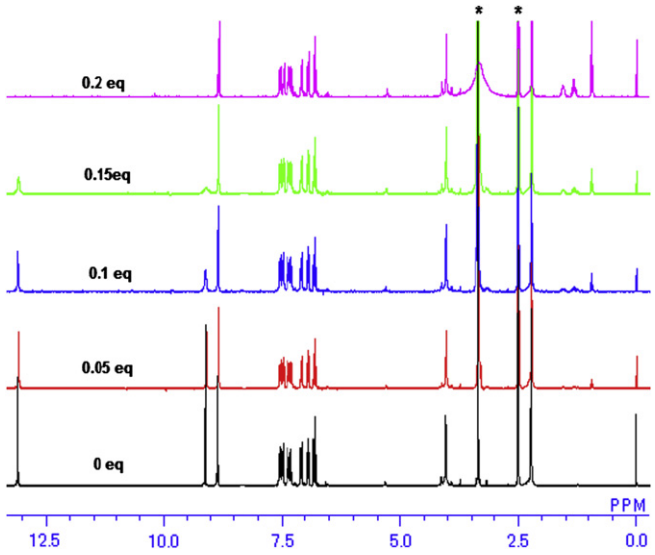

Figure 5. Showing changes in ^{1}H NMR (in DMSO) on addition of TBAF (0.0–0.2 mol equiv). *Represent the peaks due to DMSO and DMSO–water.

corresponding to the H-bonded and the deprotonated species.[5h,5m,6d,15,18]

The deprotonation of the receptor was confirmed by Bronsted acid–base reaction between (**3**) and [*n*-Bu_4]NOH (Fig. 6). A stepwise increase in the concentration of the TBAOH produces results analogous to those found in the case of F^- ion. The negative charge brought about by the anion induced deprotonation increases the dipole moment and stabilizes the excited state causing a red shift of $\Delta\lambda$=80 nm. We hypothesize that due to the strong acidity of the O–H protons in the receptor (**3**), a genuine H-bond complex, $[LH\cdots F]^-$ has not been observed during the UV–vis titration, and the anion causes deprotonation of the receptor. So the process may be described by the proton-dissociation equilibrium only. The equilibrium constant (or proton-dissociation constant) K for F^- ion has been calculated to be 2.2×10^3 M from the Benesi–Hildebrand plot.[19] The absence of H-bonding steps may further be stressed by comparison of UV–vis spectrometric results with that of nitrocatechol with $H_2PO_4^-$ anion which also gives a shift from λ 330 nm to 430 nm after deprotonation.[11]

The bright yellow color obtained on addition of TBAF to (**3**) is reverted back on addition of traces of water to it. So the receptor, unfortunately cannot be used in aqueous medium. We tried to see the effect of change of polarity on the sensing ability of (**3**) by changing the solvents from DMSO to $CHCl_3/CH_3CN$ (1:9) since (**3**) is insoluble in acetonitrile. In this solvent mixture the receptor (**3**) shows a peak at λ_{max} 316 nm and a shoulder at 366 nm (Supplementary data, Fig. S1). The latter is tentatively labeled as the one due to ICT transition as it shows a bathochromic shift of 30 nm in the presence of 10 M equiv of TBAF. This shift is much less as in comparison to what has been observed in DMSO and does not lead to any visual color change. It shows that in less polar acetonitrile the H-bonding interactions are prevalent whereas deprotonation is being favored by DMSO, which is a very good proton acceptor. It corroborates the fact that the receptor provides selectivity for F^- ion which is solely based upon its deprotonation and is related to the factors (a) intrinsic acidity of the receptor (b) basicity of the anion, and (c) polarity of the solvent. No deprotonation or colorimetric response has been seen with anions like Cl^-, Br^-, I^-, NO_3^-, CN^-, ClO_4^-, AcO^-, HSO_4^-, and H_2PO4^- ions, which are less basic than OH^- (pK_a=32 in DMSO).[20] Fluoride ion though is a weaker base (pK_a=15 in DMSO) than AcO^- (pK_a=12.3 in DMSO)[20] however the extreme stability[21] of $[HF_2]^-$ is well documented and it is known to behave as a very strong base, second to OH^- only and may induce deprotonation of even lesser acidic moieties like urea protons.[5m,6d] Here we maintain that the deprotonation forms the stable $[HF_2]^-$ anion. The existence of $[FHF]^-$ is unequivocally proved by the presence of a tell–tale,[1c,5a] well formed triplet at $\sim\delta$ 16.07 ppm in the proton NMR of (**3**) in the presence of 12 equiv F^- ion as shown in Figure 7. As the stability of $[HX_2]^-$ increases in the order[6d] $X=F^->CH_3COO^->H_2PO_4^-$ therefore the deprotonation is facilitated

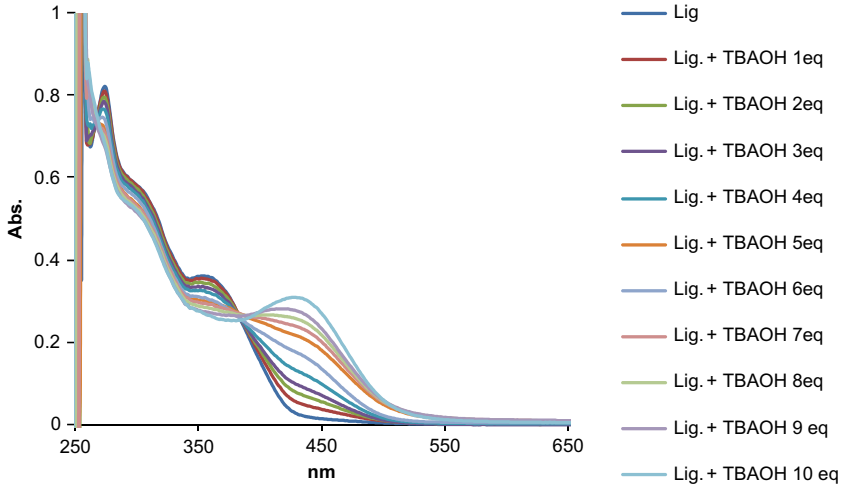

Figure 6. Showing changes in the absorption spectrum of (**3**) (10 μM) on adding increasing amount of TBAOH (10–100 μM) in DMSO.

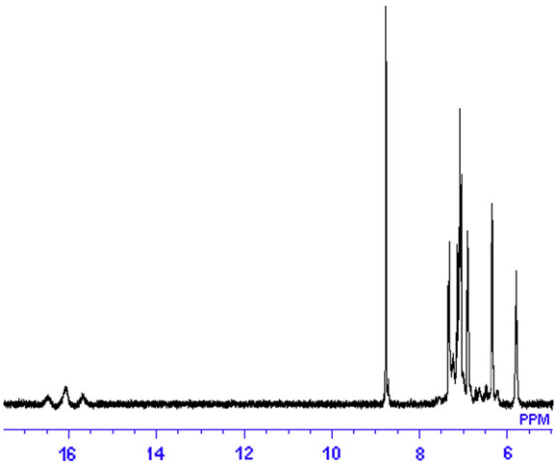

Figure 7. Partial ^{1}H NMR (DMSO) of (**3**) on addition of 12 M equiv of TBAF showing presence of triplet corresponding to $[FHF]^-$ ion.

in the same order. It is equally important that polarity of the solvent and the intrinsic acidity of the receptor itself also support the fluoride induced double deprotonation. As the catechol group is much more acidic than urea or thiourea so can be more effectively deprotonated in the presence of F^- ion. However, unlike free catechol in the presence of TBAF the deprotonation here in case of (**3**) does not lead to oxidative degradation of the catechol moiety to give muconic acid[11] because the compound remains fairly stable in the presence of higher equivalents of TBAF (cf. ^{1}H NMR) and no blue coloration is induced by the F^- ions on prolonged standing. Thus incorporation of catechol group in (**3**) has decreased its tendency of oxidative degradation and improved its prospects as a highly selective chromogenic sensor for F^- ions.

The results obtained with the tripodal receptor (**3**) were also compared with the analogous monopodal receptor (**4**) just containing one catechol moiety. For this purpose, the receptor (**4**) was prepared from the tripodal amine (**2**) by changing the amine to aldehyde ratio and was characterized by various spectroscopic methods. The anion binding affinity of receptor (**4**) for F^- was determined by tracking the changes in absorption spectra of receptor (**4**) upon addition of TBAF. This experiment was also performed with 10 μM solution of receptor (**4**) in DMSO by stepwise addition of 100 μM TBAF salt. In the absence of F^- ion, the spectrum of receptor (**4**) in DMSO showed a band at λ_{max} 310 nm (ϵ_{max} 20,600 $M^{-1}\,cm^{-1}$) and a shoulder at λ_{max} 366 nm (ϵ_{max} 9600 $M^{-1}\,cm^{-1}$). The former corresponds to presence of an intraligand CT related to amine group[22] and the latter has been designated as ICT band involving imine and hydroxyl group[13e,14] as for (**3**) above. However the intensity of the latter in (**4**) is significantly less than that in (**3**) due to only one chromophore being there. Again there are significant differences between the UV–vis spectra of (**3**) and (**4**) on addition of F^- ion. Although as similar to (**3**), on addition of TBAF to (**4**) the shoulder at 366 nm starts decreasing and a new band starts emerging at λ_{max} 433 nm. However, the intensity of the latter is significantly less on comparing with same number of equivalents of F^- anion in (**3**). In fact it never takes the shape of a well formed band unlike in (**3**) even on addition of 100 equiv of the anion in the solution of (**4**) (Fig. S2, Supplementary data). The monopodal shows some discernable optical response only at higher equivalents (~100 equiv) whereas (**3**) shows as much for quite fewer equivalents (2.5 equiv) of added TBAF. At the same time no naked eye detection of F^- ion is possible with (**4**) at these concentrations. The experiment clearly demonstrates that an enhanced colorimetric response is obtained with the tripodal system compared to the monopodal system.

3. Conclusions

In conclusion, a chromogenic tripodal receptor **3** has been synthesized that contains recognition sites for anions. The receptor had been designed to provide anion recognition through H-bonding interactions employing –OH groups of catechol only. However the results show that the deprotonation rather than the H-bonding is the key factor triggering the chromogenic effect. This deprotonation is being facilitated by the high intrinsic acidity of catechol groups, highly basic F^- and OH^- ions, and a polar solvent like DMSO. Although this frozen proton transfer[5h] from the receptor to a highly basic anion pushes the recognition event out of the realm of supramolecular chemistry but nonetheless it forms an example of a highly selective and efficient naked eye sensor for F^- ion at a concentration of 10 μM. A comparison of the sensing ability of tripodal receptor with monopodal receptor has showed that the former gives a much enhanced response towards the fluoride ion.

4. Experimental

4.1. General

All the commercially available chemicals were purchased from Aldrich and used without further purification. All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. TLC was performed on glass sheets pre-coated with silica gel. The ^{1}H and ^{13}C NMR spectra were performed in DMSO with TMS as an internal reference, on a 300 MHz NMR spectrometer. The infrared spectrum (KBr pellet) was recorded using PYE Unicam IR spectrophotometer in the range 400–4000 cm^{-1}. The electronic absorption spectra were recorded on a Shimadzu Phramaspec UV-1700 UV–vis spectrophotometer.

4.2. Synthesis of receptors

*4.2.1. Preparation of the tripodal ligand (**3**).* Ligand **3** was prepared by stirring tripodal amine[22] (**1**) (531 mg, 1.0 mmol) along with 2,3-dihydroxybenzaldehyde (**2**) (442 mg, 3.2 mmol) in the presence of 3–4 mg of zinc perchlorate taken in methanol/chloroform (8:2) solvent mixture. The color of the solution changed immediately to dark orange and precipitates separated out in quantitative yield. These precipitates were filtered and dried. Yield 74%. Mp 238–240 °C. IR (ν_{max}/cm^{-1}) 1616, 3418 (br), NMR data. δ_H (300 MHz, DMSO, TMS): 2.58 (9H, s, $-CH_3$), 3.98 (6H, s, $-CH_2$), 6.74–7.05 (9H, m, –Ar), 7.23–7.52 (12H, m, –Ar), 8.79 (3H, s, –CH═N), 9.18 (3H, s, –OH), 13.08 (3H, s, –OH). δ_C (75 MHz, DMSO, Me_4Si) 15.5 ($-CH_3$), 32.20 ($-CH_2$), 117.94 (Ar), 118.91 (Ar), 119.32 (Ar), 123.00 (Ar), 127.82 (Ar), 130.84 (Ar), 132.96 (Ar), 136.47 (Ar), 145.61 (Ar), 148.99 (Ar), 162.88 (CH═N), 186.26 (Ar). Found: C, 68.89; H, 5.09; N, 4.86; S, 10.87. Calcd for $C_{51}H_{45}N_3O_3S_3$: C, 68.66; H, 5.08; N, 4.71; S, 10.78%.

*4.2.2. Preparation of the monopodal ligand (**4**).* Ligand **4** was prepared as above but by drop wise addition of only (133.2 mg, 1.1 mmol) 2,3-dihydroxybenzaldehyde (**2**). The reaction mixture was stirred for 4 h, after the completion of reaction solvent was evaporated and product was recrystallized from methanol as reddish solid. Yield 72%. Mp 130 °C. R_f value 0.675 in 40% ethyl acetate, IR (ν_{max}/cm^{-1}) 1605, 3443 (br), 3413, NMR data. δ_H (300 MHz, DMSO, TMS): 2.30 (3H, s, $-CH_3$), 2.35 (6H, s, $-CH_3$), 3.92 (4H, s, $-CH_2$), 4.16 (2H, s, $-CH_2$), 5.32 (4H, s, $-NH_2$), 6.50 (2H, d, –Ar, J=6.9), 6.72–6.81 (3H, m, –Ar), 6.90 (1H, d, –Ar, J=6.6), 7.01–7.07 (3H, m, –Ar), 7.17–7.21 (2H, m, –Ar), 7.29–7.39 (2H, m, –Ar), 7.49 (1H, d, –Ar, J=6.6), 7.56 (1H, d, –Ar, J=7.2), 8.87(1H, s, –CH═N), 9.09 (1H, s, –OH), 13.03 (1H, s, –OH). δ_C (75 MHz, DMSO, Me_4Si) 15.79 ($-CH_3$), 34.84 ($-CH_3$), 79.34 ($-CH_2$), 84.00 ($-CH_2$), 114.78 (Ar), 116.94 (Ar),

117.03 (Ar), 117.31 (Ar), 119.37 (Ar), 123.49 (Ar), 128.34 (Ar), 129.83 (Ar), 130.67 (Ar), 132.25 (Ar), 133.81 (Ar), 134.80 (Ar), 135.10 (Ar), 135.80 (Ar), 136.14 (Ar), 145.80 (Ar), 149.30 (Ar), 149.46 (Ar), 163.26 (CH=N). Found: C, 68.26; H, 5.89; N, 6.60; S, 14.83. Calcd for $C_{37}H_{37}N_3O_2S_3$: C, 68.17; H, 5.72; N, 6.45; S, 14.76%.

4.3. Anion recognition studies

Anion binding ability of receptors (**3**) and (**4**) was determined by preparing solutions containing 10 μM of receptor and 100 μM of tetrabutylammonium salts of a particular anion in DMSO. Changes in the electronic absorption spectra of the ligands were observed. The anion binding ability of receptor (**3**) and (**4**) with tetrabutylammonium fluoride (TBAF) was investigated using UV–vis titration experiments. The titrations were carried out in DMSO with 10 μM concentration of receptor upon addition of incremental amounts of TBAF solution.

4.4. X-ray crystal structure determination

The crystals suitable for crystallographic work were grown by vapor diffusion method using $CHCl_3$ as a solvent and petroleum ether as precipitant. The intensity data were collected at 295 K with a Siemens P4 X-ray diffractometer by using θ–2θ scanning mode with graphite monochromated Mo Kα radiation. A total of 8551 reflections were measured, of which 8090 were unique and 1416 were considered observed [$I \geq 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects but not for absorption correction. The structure was solved by direct methods using *SIR-2000*[23] and refined by full-matrix least-squares refinement techniques on F^2 using SHELX-97[24] in the WINGX program.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were attached geometrically with U_{iso} values of 1.2 times (for methylene and phenylene carbon atoms) and 1.5 times (methyl carbon atoms) the U_{iso} values of their respective carrier atoms. The crystal quality was not very good and many crystals were tried before finally obtaining this data set. It has resulted in giving a low ratio of observed/unique reflections (18%). Nevertheless the anisotropic refinement of all the non-hydrogen atoms with resulting estimated standard deviations at the fourth place indicates that the overall accuracy of the structure is not compromised. The crystallographic data and other refinement parameters are given in Table 1.

Table 1
Crystal data and structure refinement for (**3**)

Empirical formula	$C_{51}H_{45}N_3O_6S_3$	
Formula weight	892.08	
Temperature	295(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	$P\,\bar{1}$	
Unit cell dimensions	a=11.466(3) Å	α=108.980(5)°
	b=12.652(5) Å	β=91.240(3)°
	c=16.172(4) Å	γ=95.450(4)°
Volume	2205.0(12) Å^3	
Z	2	
Density (calculated)	1.344 mg m^{-3}	
Absorption coefficient	0.224 mm^{-1}	
F(000)	936	
Crystal size	0.20×0.10×0.10 mm^3	
Theta range for data collection	1.33–25.50°	
Index ranges	$0\leq h\leq 13$, $-14\leq k\leq 14$, $-19\leq l\leq 19$	
Reflections collected	8551	
Independent reflections	8090 [R(int)=0.0843]	
Completeness to theta=25.50°	98.4%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8090/0/484	
Goodness-of-fit on F^2	0.703	
Final R indices [$I>2\sigma(I)$]	R_1=0.0737, wR_2=0.1631	
R indices (all data)	R_1=0.3495, wR_2=0.2798	
Largest diff. peak and hole	0.285 and −0.272 e.Å^{-3}	
CCDC number	721,608	

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.08.023.

References and notes

1. (a) Sessler, J. L.; Gale, P. A.; Cho, W. S. *Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, UK, 2006; (b) Gale, P. A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250*, 3219; (c) Gunnlaugsson, T.; Glynn, M.; Tocci (nee Hussey), G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094; (d) Steed, J. W. *Chem. Commun.* **2006**, 2637; (e) Filby, M. H.; Steed, J. W. *Coord. Chem. Rev.* **2006**, *250*, 3200; (f) Nguyen, B. T.; Anslyn, E. V. *Coord. Chem. Rev.* **2006**, *250*, 3118; (g) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989; (h) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486; (i) Schmidtchen, F. P.; Bergeer, M. *Chem. Rev.* **1997**, *97*, 1609; (j) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Hauxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515; (k) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192; (l) Sancenón, F.; Descalzo, A. B.; Martìnez- Máñez, R.; Miranda, M. A.; Soto, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2640; (m) Lee, D. H.; Lee, H. Y.; Hong, J.-J. *Tetrahedron Lett.* **2002**, *43*, 7273.
2. (a) Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S. *Chem. Soc. Rev.* **2006**, *35*, 355; (b) Amendola, V.; Vonizzoni, M.; Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M.; Sancenòn, F.; Taglietti, A. *Coord. Chem. Rev.* **2006**, *250*, 1451; (c) Martìnez-Máñez, R.; Sancenòn, F. *J. Fluoresc.* **2005**, *15*, 267; (d) Martìnez- Máñez, R.; Sancenòn, F. *Chem. Rev.* **2003**, *103*, 4419; (e) Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465; (f) Gale, P. A. *Chem. Commun.* **2005**, 376; (g) Schmidtchen, F. P. *Coord. Chem. Rev.* **2006**, *250*, 2918; (h) Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, *240*, 77; (i) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1777; (j) Starnes, S. D.; Arungundram, S.; Saunders, C. H. *Tetrahedron Lett.* **2002**, *43*, 7785; (k) Zhou, L. L.; Sun, H.; Li, H.-P.; Wang, H.; Zhang, X.-H.; Wu, S.-K.; Lee, S.-T. *Org. Lett.* **2004**, *6*, 1071.
3. (a) Krik, K. L. *Biochemistry of Halogens and Inorganic Halides*; Plenum: New York, NY, 1991; p 59l; (b) Kleerekoper, M. *Endocrinol. Metab. Clin. North Am.* **1998**, *27*, 441; (c) Matsuo, S.; Kiyomiya, K.; Kurebe, M. *Arch. Toxicol.* **1998**, *72*, 798; (d) Briancon, D. *Rev. Rhum.* **1997**, *64*, 78.
4. (a) Wallace, K. J.; Fagmemi, R. I.; Folmer-Anderson, F. J.; Morey, J.; Lynth, V. M.; Anslyn, E. V. *Chem. Commun.* **2006**, 3886; (b) Dale, T. J.; Rebek, J. *J. Am. Chem. Soc.* **2006**, *128*, 4500.
5. (a) Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Tierney, J.; Paduka Ali, H. D.; Hussey, G. M. *J. Org. Chem.* **2005**, *70*, 10875; (b) Liu, C.; Qian, X.; Sun, G.; Zhao, L.; Li, Z. *New J. Chem.* **2008**, *32*, 472; (c) Singh, N.; Jang, D. O. *Org. Lett.* **2007**, *9*, 1991; (d) Thiagarajan, V.; Ramamurthy, P.; Wel, L. H.; He, Y. B.; Wu, J. L.; Wu, X. J.; Meng, L.; Yang, X. *Supramol. Chem.* **2004**, *16*, 561; (e) Parkesh, R.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 6575; (f) Thirumalai, D.; Ramakrishnan, T. *Org. Lett.* **2005**, *7*, 657; (g) Ros-Lis, J. V.; Martìnez- Máñez, R.; Benito, A.; Soto, J. *Polyhedron* **2006**, *25*, 1585; (h) Boiocchi, M.; Boca, L. D.; Gómez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507; (i) Ghosh, K.; Adhikari, S. *Tetrahedron Lett.* **2006**, *47*, 8165; (j) Kato, R.; Cui, Y.-Y.; Nishizawa, S.; Yokobori, T.; Teramae, N. *Tetrahedron Lett.* **2004**, *45*, 4273; (k) Jun, E. J.; Swamy, K. M. K.; Bang, H.; Kim, S. J.; Yoon, J. Y. *Tetrahedron Lett.* **2006**, *47*, 3103; (l) Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P. E. *Org. Lett.* **2005**, *7*, 5357; (m) Gòmez, D. E.; Fabbrizzi, L.; Licchelli, M. *J. Org. Chem.* **2005**, *70*, 5717; (n) Linn, M. M.; Poncio, D. C.; Machado, V. G. *Tetrahedron Lett.* **2007**, *48*, 4547; (o) Gunnlaugsson, T.; Kruger, P. E.; Lee, T. C.; Jiménez, D.; Martìnez- Máñez, R.; Sancenón, F.; Soto, J. *Tetrahedron Lett.* **2002**, *43*, 2823.
6. (a) Amendola, V.; Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M. *Acc. Chem. Res.* **2006**, *39*, 343; (b) Gale, P. A. *Amide and Urea Based Anion Receptors. Encylcopedia of Supramolecular Chemistry*; Marcel Dekker: New York, NY, 2004; 31; (c) Quinlan, E.; Matthews, S. E.; Gunnlaugsson, T. *J. Org. Chem.* **2007**, *72*, 7497; (d) Gómez, D. E.; Fabbrizzi, L.; Licchell, M.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3*, 1495; (e) Kang, S. O.; Begum, R. A.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2007**, *45*, 7882; (f) Kang, S. O.; Hossain, M. A.; Bowman-James, K. *Coord. Chem. Rev.* **2006**, *250*, 3038; (g) Lin, C.; Simov, V.; Drueckhammer, D. G. *J. Org. Chem.* **2007**, *72*, 1742; (h) Pfeffer, F. M.; Seter, M.; Lewcenko, N.; Barnett, N. W. *Tetrahedron Lett.* **2006**, *47*, 5251; (i) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445; (j) Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Chem. Commun.*

2001, 2556; (k) Gunnlaugsson, T.; Davis, A. P.; Hussey, G. M.; Tierney, J.; Glynn, M. *Org. Biomol. Chem.* **2004**, *2*, 1856; (l) Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449; (m) Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Biomol. Chem.* **2005**, *3*, 48; (n) Tumcharern, G.; Tuntulani, T.; Cole, S. J.; Hursthouse, M. B.; Kilburn, J. D. *Org. Lett.* **2003**, *5*, 4971; (o) Sasaki, S.; Citterio, D.; Ozawa, S.; Suzuki, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2309; (p) Pfeffer, F. M.; Buschgens, A. M.; Barnett, N. W.; Gunnlaugsson, T.; Kruger, P. E. *Tetrahedron Lett.* **2005**, *46*, 6579; (q) dos Santos, C. M. G.; McCabe, T.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 3135; (r) Turner, D. R.; Paterson, M. J.; Steed, J. W. *J. Org. Chem.* **2006**, *71*, 1598; (s) Evans, L. S.; Gale, P. A.; Light, M. E.; Quesada, R. *Chem. Commun.* **2006**, 965; (t) Evans, L. S.; Gale, P. A.; Light, M. E.; Quesada, R. *New J. Chem.* **2006**, *30*, 1019; (u) Wu, F. Y.; Li, Z.; Guo, Z. L.; Wang, X.; Lin, M. H.; Zhao, Y. F.; Jiang, Y. B. *Org. Biomol. Chem.* **2006**, *4*, 624; (v) Russell, J. M.; Parker, A. D. M.; Evans, I. R.; Howard, J. A. K.; Steed, J. W. *Chem. Commun.* **2006**, 269; (w) Nie, L.; Li, Z.; Han, J.; Zhang, X.; Yang, R.; Liu, W. X.; Wu, F. Y.; Xie, J. W.; Zhao, Y. F.; Jiang, Y. B. *J. Org. Chem.* **2004**, *69*, 6449; (x) Quinlan, E.; Matthews, S. E.; Gunnlaugsson, T. *Tetrahedron Lett.* **2006**, *47*, 9333.

7. (a) Dutzler, R.; Campbell, E. B.; Cadene, M.; Chait, B. T.; MacKinnon, R. *Nature* **2002**, *415*, 287; (b) Lindsell, P. *J. Physiol.* **2001**, *531*, 51; (c) Wachter, R. M.; Yarbrough, D.; Kallio, K.; Remington, S. J. *J. Mol. Biol.* **2000**, *301*, 157.
8. (a) Davis, A. P.; Gilmer, J. F.; Perry, J. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 1312; (b) Kondo, S.-I.; Suzuki, T.; Yano, Y. *Tetrahedron Lett.* **2002**, *43*, 7059; (c) Arduini, A.; Giogi, G.; Pochini, A.; Secchi, A.; Ugozzoli, F. *J. Org. Chem.* **2001**, *66*, 8302; (d) Ito, K.; Miki, H.; Ohba, Y. *Yakugaku Zasshi* **2002**, *122*, 413; (e) Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154; (f) Lee, D. H.; Lee, K. H.; Hong, J.-I. *Org. Lett.* **2001**, *3*, 5; (g) Lee, D. H.; Lee, K. H.; Hong, J.-I. *Chem. Commun.* **2001**, 1188.
9. (a) Lee, K. H.; Lee, H. Y.; Lee, D. H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 5447; (b) Lee, C.; Lee, D. H.; Hong, J. I. *Tetrahedron Lett.* **2001**, *42*, 8665.
10. (a) Heath, R. E.; Dykes, G. M.; Fish, H.; Smith, D. K. *Chem.—Eur. J.* **2003**, *9*, 850; (b) Smith, D. K. *Org. Biomol. Chem.* **2003**, *1*, 3874.
11. Winstanley, K. J.; Sayer, A. M.; Smith, D. K. *Org. Biomol. Chem.* **2006**, *4*, 1760.
12. (a) Baral, M.; Sahoo, S. K.; Kanungo, B. K. *J. Inorg. Biochem.* **2008**, *102*, 1581; (b) Sahoo, S. S.; Baral, M.; Kanungo, B. K. *Polyhedron* **2006**, *25*, 722; (c) Albrecht, M.; Burk, S.; Stoffel, R.; Lüchow, A.; Fröhlich, R.; Kogej, M.; Schalley, C. A. *Eur. J. Inorg. Chem.* **2007**, 1361.
13. (a) Lo, W.-K.; Wong, W.-K.; Guo, J.-P.; Wong, W.-Y.; Li, K.-F.; Cheah, K.-W. *Inorg. Chim. Acta* **2004**, *357*, 4510; (b) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2000**, *122*, 10405; (c) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1991**, *113*, 4917; (d) Filarowski, A.; Koll, A.; Glowiak, T. *J. Chem. Soc., Perkin Trans. 2* **2002**, 835; (e) Bhardwaj, V. K.; Pannu, A. P. S.; Singh, N.; Hundal, M. S.; Hundal, G. *Tetrahedron* **2008**, *64*, 5384.
14. (a) Singh, N.; Kumar, M.; Hundal, G. *Inorg. Chim. Acta* **2004**, *14*, 4286; (b) Luneau, D.; Evans, C. *J. Chem. Soc., Dalton Trans.* **2002**, 83.
15. Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741.
16. Amendola, V.; Boiocchi, M.; Fabbrizzi, L.; Palchetti, A. *Chem.—Eur. J.* **2005**, *11*, 120.
17. Costero, A. M.; Banuls, M. J.; Aurell, M. J.; Ward, M. D.; Argent, S. *Tetrahedron* **2004**, *60*, 9471.
18. (a) Lin, Y.-S.; Tu, G.-M.; Lin, C.-Y.; Chang, Y.-T.; Yen, Y.-P. *New J. Chem.* **2009**, *33*, 860; (b) Kim, Y.-J.; Kwak, H.; Lee, S. J.; Lee, J. S.; Kwon, H. J.; Nam, S. H.; Lee, K.; Kim, C. *Tetrahedron* **2006**, *62*, 9635.
19. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
20. Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.
21. Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.
22. Singh, N.; Hundal, M. S.; Hundal, G.; Ripoll, M. M. *Tetrahedron* **2005**, *61*, 7796.
23. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.
24. Sheldrick, G. M. *SHELX-97: Programs for Crystal Structure Analysis (Release 97-2)*; Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
25. Farrugia, J. *J. Appl. Crystallogr.* **1999**, *32*, 837.