ORIGINAL PAPER

Fluoride-Triggered ESPT in the Binding with Sal(oph)en

Kai Liu · Jianzhong Huo · Bolin Zhu · Ran Huo

Abstract In this paper, anion binding and sensing affinity of the simple and easy-to-make salen, a typical class of ligand used comprehensively in metal coordination, was investigated. Results indicated that salophen was both a colorimetric and fluorescent selective chemosensor for fluoride ion, which operated by the anion-induced conformational changes and subsequently excited-state intramolecular proton transfer (ESPT) process. The F⁻-induced quick response, as well as noticeable optical changes, suggested that anion-sensing mechanism maybe help to design and to synthesize the new preferential selective probes for F⁻.

Keywords ESPT · Deprotonation · Anion sensors · Supramolecular chemistry · Fluorescent

Introduction

Sal(oph)ens, a well-known and oldest class of 'privileged ligands' [1] used comprehensively after the work described by Jacobsen [2] and Katsuki [3] in 1990, have constituted one of the most fundamental building blocks for the stabilization of different metals in various oxidation states, controlling the performance of the metals in a great deal of useful catalytic transformations [4, 5]. These came from the intrinsic tetradentate with N_2O_2 set of donor atoms capable of effective coordination in the planar fashion or slightly distorted geometry [4, 6]. Additionally, the metal complexes of salophens have been used comprehensively as the functional materials [7–9] and modes for superoxide dismutase [10–12]. Recently, sal(oph)en complexes of transition metal have been used as molecular sensors for anionic and neutral guests [13, 14], along with the realization of their vital importance in a wide range of biological, environmental, and chemical process.[15, 16] In fact, many sal(oph)en-metal complexes as receptors for anionic and neutral subunits were reported after the seminal work of Reinhoudt group in 1990s [17]. Uranyl-salophen complexes with a well-defined preference for pentagonal bipyramidal coordination and with the two oxygens in the apical positions [18, 19], can effectively bind the anionic guest by substituting the solvent molecules in the fifth equatorial site [20, 21]. Then, various functionalized salophen ligands and their uranyl complexes were prepared, and their anion recognition properties were investigated [13]. Additionally, zinc(II)-salophen complexes with fluorescence gained an important position in anion recognition and sensing [22, 23]. In these receptors, zinc(II) metal center with five-coordinate square pyramidal geometry, possessed remarkable Lewis acidity. The conformation allowed strong and suitable binding agents to coordinate at the axial site [24]. Whatever, to the best of our knowledge, there were few reports on the simple and easy-to-make sal(oph)en themselves, containing binding sites OH moiety and signal subunits C=N group, as receptors (sensors) for charged species by 'binding site-signaling subunit approach'[25], maybe due to the stronger metal complex of salens relative to the corresponding anion complexes. Here, the anion binding abilities of sal(oph)en were investigated.

K. Liu (✉) · J. Huo · B. Zhu · R. Huo
Tianjin Key Laboratory of Structure and Performance
for Functional Molecule, College of Chemistry,
Tianjin Normal University,
Tianjin 300387, China
e-mail: hxxylk@mail.tjnu.edu.cn

Specific anion recognition, binding and transportation by protein are carried out by H-bonds of NH and OH mainly in biological systems [26, 27], therefore, the biomimetic of N(O)-H···anion interaction is important. However, over the past 30 years, only few systematic investigations involved the O-H groups as a key component to obtain the anion binding [28–31], and anion recognition based on amide and (thio)ureas has been comprehensively studied. Furthermore, the dramatic enhancement of the phenolic OH acidity resulted from photoexcitation [32, 33], and therefore an excited-state intermolecular proton transfer (ESPT) [29, 34, 35] channel might be opened due to anion binding. In fact, the phenomenon has scarcely been exploited in anion sensing [29, 35–37]. On the basis of above-mentioned background, herein we reported the anion sensing and binding properties of sal(oph)en based on OH group as binding site by UV–VIS and fluorescence spectroscopy in dilute solution. Results indicated that sal(oph)en has a high selectivity for F⁻ by ESPT [29, 34, 35], concomitant with color changes.

Experimental
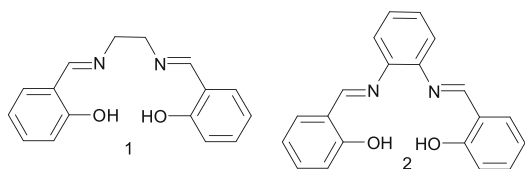
Receptor **1** and **2** were synthesized by condensation of salicyaldehyde with corresponding diamine in ethanol. Acetonitrile for spectroscopy was purchased from the J&K Scientific LTD. All tetrabutylammonium salts were purchased from Sinopharm Chemical Reagent Co., Ltd. The serial working solutions provided with incremental multiples of tetraalkylammonium salts and the definite quantity hosts (2×10^{-5} M) in the procedure were prepared using the acid-washed glass pipettes and volumetric flasks to make appropriate solutions from the stock solution and were stored in the room temperature for 0.5 h before used in the experiment. UV–VIS spectra and fluorescence were performed on Varian Cary 300 spectrophotometer and Hitachi F-4500 spectrofluorometers, respectively. For fluorescence measurements, the excitation and emission slit were 3 nm, and scan speed was 100 nm/min. All NMR spectra were measured on a buker spectrometer at 400 MHz with DMSO-d_6 as solvents.

Analysis of the solution phase anion-binding properties was made using UV–VIS and fluorescent spectroscopic titration techniques, respectively. Data analysis and stability constant determinations were then made by the satisfactory non-linear least-square analysis [38–40].

Results and Disscussion

Anion binding and sensing properties of sal(oph)en have been studied by UV–VIS spectroscopic techniques. In the absence of anions, receptor **2** (2×10^{-5} M) in CH₃CN displayed three strong absorption bands at ca. 329, 268, and 228 nm, resulting from the intramolecular charge transfer from C=N and OH group to the phenyl substituent. Upon gradually increasing the concentration of F⁻, the absorption band at 329 nm decreased slowly, and new red−shifted absorption maximum bands at 422 nm formed and developed (Fig. 1). As a result, the color of the solution turned from colorless to yellow (Supporting information Fig. S1), affording naked-eye detection of F⁻. Considering the fact that F⁻ is a strong Lewis base, and can deprotonate proton of OH [29, 35, 41], these spectral changes (bathochromic shift $\Delta\lambda \approx 93$ nm upon addition of F⁻) were presumably ascribed to the occurrence of an "incipient" and "frozen" proton-transfer process [42]. The OH proton may undergo deprotonation, due to the strong basicity of F⁻ and high stability of complex [HF₂]⁻ [15]. This would imply the occurrence of negatively charged PhO⁻ of receptor **2**, which caused a significant increase in charge density, and followed the enhancement in the push-pull effect of the intramolecular charge transfer in the groud state. Furthermore, well-defined isosbestic points (228, 288 and 339 nm) indicated a clean conversion throughout the titration process. Additionally, the interaction of **2** with other anions (Cl⁻, Br⁻, I⁻, NO₃⁻, AcO⁻, H₂PO₄⁻ and HSO₄⁻) was also investigated by UV–VIS spectroscopic titration methods (Supporting information Fig. S2). No significant spectral changes were observed specifically for Br⁻, I⁻, NO₃⁻, and HSO₄⁻, even at higher concentration, due to the weak coordination interaction. Furthermore, addition of
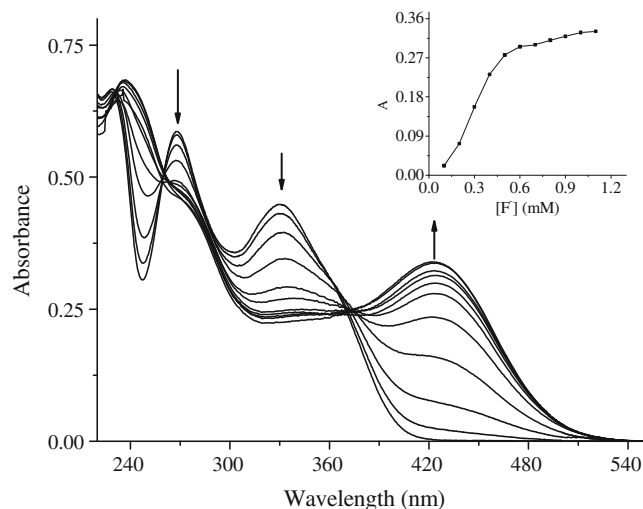
Fig. 1 UV–VIS spectral changes of receptor **2** (2×10^{-5} M) in MeCN after the addition of 0–55 equiv TBAF. The inset displayed the absorbance at 422 nm *vs* [TBAF]; the line represented the fitting of the experimental points assuming a 1:1 stoichiometry

F⁻ to those solutions of receptor **2**, containing excess Cl⁻, Br⁻, I⁻, NO_3^-, AcO⁻, $H_2PO_4^-$ and HSO_4^-, immediately produced the expected optical response. These results suggested that the simple and easy-to-make receptor **2** was preferential selective chromogenic anion sensors for F⁻ in contrast to the other anions examined.

Evidence for 1:1 complex formation was provided by non-linear least-square analysis [43] for receptor **2** with F⁻, Cl⁻, AcO⁻ and $H_2PO_4^-$. This was also proved by Job-plot analysis. The binding constants were obtained from the variation in the absorbance at the appropriate wavelength [F⁻ (422 nm), Cl⁻, AcO⁻, $H_2PO_4^-$ (329 nm)] by plotting the A as a function of the [anion] (Fig. 2). The association constants for receptor **2** with F⁻, Cl⁻, AcO⁻ and $H_2PO_4^-$ were determined to be 6.1×10^3, 91, 1.9×10^2, 1.1×10^2 M⁻¹, respectively. Moreover, few changes in UV–VIS spectra of receptor **2**, induced by Br⁻, I⁻, NO_3^- and HSO_4^-, were not enough to calculate the binding constants. Results showed that receptor **2** bond F⁻ more strongly than the other anions examined, thus, explained the phenomenon observed in anion sensing experiments.

Different from receptor **2**, receptor **1**, containing carbon-carbon bond, exhibited strong UV–VIS response on the different concentrations of F⁻ in MeCN. When increasing the concentration of F⁻, a new band centered at 393 nm gradually enhanced, and the absorption band at 315 nm significantly reduced in intensity, with concomitant formation of isosbestic point at ca. 337, 287 and 227 nm, respectively (Supporting information Fig. S3). This was presumably attributed to proton transfer from the PhOH of receptor **1** to F⁻. In the case of other anions examined (Cl⁻, AcO⁻ and $H_2PO_4^-$), few spectral changes were observed (Supporting information Fig. S4). Furthermore, UV–VIS titration showed that the selectivity trend of the binding affinity of receptor **1** was in the order of F⁻>AcO⁻>$H_2PO_4^-$>Cl⁻, and qualitatively accorded with the basicity of these anions.

To further elucidate the interaction between sal(oph)en and F⁻, ¹H NMR titrations were carried out in DMSO-d_6. Figure 3 displayed the ¹H NMR spectra of receptor **2** and its complex with different F⁻ concentration. Compared to O-H
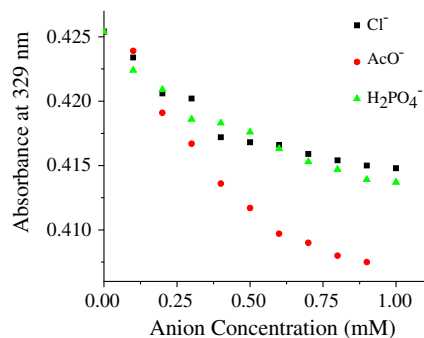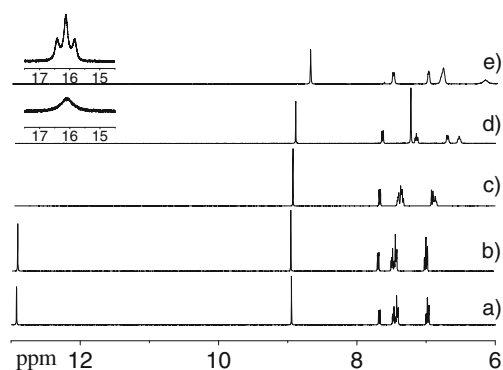
Fig. 3 Partial ¹H NMR spectra (400 MHz) of receptor **2** in DMSO−d_6 upon addition of: **a** 0, **b** 0.2, **c** 0.5, **d** 1.0, **e** 5.0 equiv. TBAF

itself, the phenolic O-H signal of receptor **2** at 12.92 ppm shifted dramatically to down field, suggesting a weak PhO-H···N=C hydrogen bond. This implied that the conformational equilibrium of receptor **2** shifted more toward closing-ring side [44–46] (Scheme 1). Furthermore, with the gradual increase of F⁻, phenolic O-H signal of receptor **2** at 12.92 ppm decreased, and, upon addition of 0.5 equiv F⁻, the phenolic O-H signal at 12.92 ppm disappeared completely, indicating the destruction of intramolecular hydrogen-bond and the formation of hydrogen bond interaction between PhO-H and F⁻. Once again, with the further gradual increase of the concentration of F⁻, the new triplet resonance at 16.1 ppm, which pertained to the bifluoride [HF₂]⁻ [47], occurred and developed. This implied the destruction of the initial O-H···F⁻ hydrogen-bonding interaction and the final proton transfer [42] from the PhOH of receptor **2** to F⁻, along with the formation of the deprotonation of receptor **2**. Results also confirmed the previous assumption. At the same time, the imine proton (CH=N) and aromatic proton signals experienced continuous upfield shifts, which resulted from the shielding effect of negative electron delocalization on the π-conjugated framework [48–50]. Similar results were also observed for receptor **1** (Supporting information Fig. S5). Such deprotonation was related to the acidity of the binding sites, the basicity of the analyte, and the corresponding stability of the conjugated base [HF₂]⁻. [15]

For further explore the anion-binding affinity of sal(oph)en, spectrofluorimetric titration experiments were performed. Figure 4 displayed the emission spectral changes of receptor **2** in presence of various concentration of TBAF in CH₃CN. Receptor **2**, with enol form of shiff base [44–46] displayed very weak fluorescence with a short-wavelength band at 431 nm, and a broad band centered at 475 nm, after the excitation at the maximum absorption band (centered at 422 nm) of composited receptor **2** with F⁻. Moreover, upon addition of F⁻, the emission peak at 475 nm increased substantially by up to 150 times, at the same time the broad

Fig.2 UV–VIS titration curves for receptor **2** with TBA salts in MeCN

Scheme 1 The proposed anion binding mode of the receptor **2** in solution
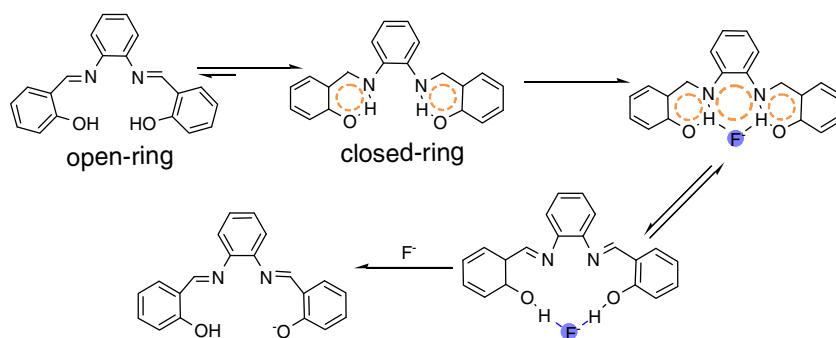
peak at 431 nm enhanced slowly. Here we attributed the fluorescence enhancement upon the anion addition to the formation of two hydrogen bonds between the OH moiety of receptor **2** and F⁻.[44–46] This implied the formation of new geometrically restricted seven-membered intramolecular hydrogen bond ring transition state, as shown in Scheme 1. Thus, the hydrogen-bond-induced π-delocalization [10] on the receptor **2** occurred and further resulted in the increase in rigidity of conformational restriction, therefore, rendering the non-radiative decay from the excited state less possible. Therefore, the increase in intensity was observed. On the other hand, the bound anions via phenolic OH, which played an important role in anion binding [23, 29, 35], led to an increase in local concentration of the anions. Subsequently, the intermolecular proton transfer in the excited state of receptor **2** to weakly basic anions occurred, due to the enhanced acidity of phenolic OH upon the photoexcitation [26, 27] and the solvation of polar CH₃CN solvents [51–53]. And the strong emission band at 475 nm was observed, due to the increase in electron density of the deprotonation phenolic O⁻, compared with phenolic OH linking F⁻, and its subsequent positive effect on the efficiency of charge transfer. Furthermore, the

F⁻-dependent fluorescent intensity at 475 nm showed a good linearity that can be expressed as $I/I_0 = 117.63 + 33550.56\,[F^-]$ ($r = 0.986$) in the F⁻ concentration range of 0.2 to 11.0 mM. The detection limit of fluoride, calculated as the concentration corresponding to triple standard deviation of the back ground, was 0.082 mM.

Additionally, no significant emission spectral changes (Supporting information Fig. S6) were found for the other anions (Cl⁻, Br⁻, I⁻, NO₃⁻, AcO⁻, H₂PO₄⁻ and HSO₄⁻), even in large excess amount. Furthermore, the association constants of receptor **2** with those anions were also determined by nonlinear regression methods [43] following the changes of fluorescent intensity. These results were in line with the equilibrium constants derived from absorption spectral titrations. The higher binding ability of F⁻, as well as the more efficient fluorescence enhancement by F⁻, compared with other anions examined, was due to its smaller size, higher electron density and the higher ratio between charge density to size, which made it stronger hydrogen bonding acceptor [54].

On the other hand, spectrofluorimetric titration technique was also used to explore the binding properties of receptor **1** for F⁻ (Fig. S7). Substitution of phenyl with carbon-carbon bond, which hindered the formation of the large conjugated system, displayed negative effect on the anion binding affinities of receptor **1**. Receptor **1** showed weak emission at 475 nm upon excitation at 393 nm. Upon continuous addition of F⁻, the broad emission band at 475 nm enhanced essentially up to 100 times. This, being similar to receptor **2** for F⁻, was ascribed to the first hydrogen-bond interaction between F⁻ and receptor **1** and the followed ESPT [29, 34–36]. Once more, addition of Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻ and NO₃⁻, even at higher concentration, induced no significant emission changes, along with the irradiation at 393 nm.

Conclusions

In summary, the simple and easy-to-make sal(oph)en, as a new kind of anion receptor, was proved to be both colorimetric and fluorescent selective chemosensor for fluoride ion in CH₃CN, by means of the anion-dependent conformational changes [32,
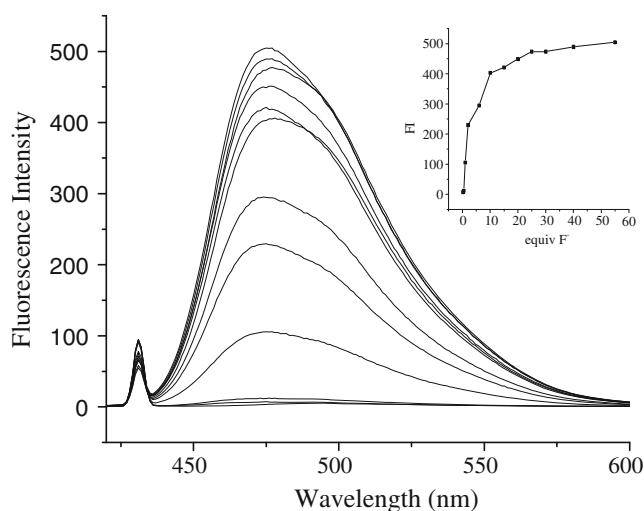

Fig. 4 Emission spectral changes of receptor **1** (2×10^{-5} M) in MeCN after the addition of 0–55 equvi. TBAF. The inset displayed the emission intensity at 475 nm *vs* [TBAF]

33] and subsequently excited-state intramolecular proton transfer process [34]. It displayed remarkable colorimetric response and naked-eye detectable color changes and fluorescent enhancement to F^- over other anions (Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and NO_3^-). The present results led us to suggest that there could be much more anion recognition work based on structure modification of salen. Investigations are continuing in order to design and synthesize new salen compounds, which operated in aqueous solution of practical use. The results of these investigations will be reported in due course.

References

1. Yoon TP, Jacobsen EN (2003) Privileged chiral catalysts. Science 299:1691–1693. doi:10.1126/science.1083622

2. Zhang W, Loebach JL, Wilson SR, Jacobsen EN (1990) Enantioselective epoxidation of unfunctionalized olefins catalyzed by salen manganese complexes. J Am Chem Soc 112:2801–2803. doi:10.1021/ja00163a052

3. Irie R, Noda K, Ito Y, Matsumoto N, Katsuki T (1990) Catalytic asymmetric epoxidation of unfunctionalized olefins. Tetrahedron Letters 31:7345–7348. doi:10.1016/s0040-4039(00)88562-7

4. Cozzi PG (2004) Metal-Salen Schiff base complexes in catalysis: practical aspects. Chem Soc Rev 33:410–421. doi:10.1039/b307853c

5. Haak RM, Wezenberg SJ, Kleij AW (2010) Cooperative multimetallic catalysis using metallosalens. Chem Commun 2713–2723. doi:10.1039/c001392g

6. Garnovskii AD, Nivorozhkin AL, Minkin VI (1993) Ligand environment and the structure of schiff base adducts and tetracoordinated metal-chelates. Coord Chem Rev 126:1–69. doi:10.1016/0010-8545(93)85032-y

7. Zhang C, Zhang X, Zhang X, Ou X, Zhang W, Jie J, Chang JC, Lee C-S, Lee S-T (2009) Facile one-step fabrication of ordered organic nanowire films. Adv Mater 21:4172–4175. doi:10.1002/adma.200802793

8. Wezenberg SJ, Kleij AW (2008) Material applications for salen frameworks. Angew Chem Int Ed 47:2354–2364. doi:10.1002/anie.200702468

9. Cho S-H, Ma B, Nguyen ST, Hupp JT, Albrecht-Schmitt TE (2006) A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation. Chem Commun 2563–2565. doi:10.1039/b600408c

10. Routier SB, Bernier JL, Catteau MP, Bailly C (1997) Highly preferential cleavage of unpaired guanines in DNA by a functionalized salen-nickel complex. Bioorg Med Chem Lett 7:63–66. doi:10.1016/S0960-894X(96)00569-0

11. Puglisi A, Tabbi G, Vecchio G (2004) Bioconjugates of cyclodextrins of manganese salen-type ligand with superoxide dismutase activity. J Inorg Biochem 98:969–976. doi:10.1016/j.jinorgbio.2004.02.012

12. Doctrow SR, Huffman K, Marcus CB, Tocco G, Malfroy E, Adinolfi CA, Kruk H, Baker K, Lazarowych N, Mascarenhas J, Malfroy B (2002) Salen-manganese complexes as catalytic scavengers of hydrogen peroxide and cytoprotective agents: structure − activity relationship studies. J Med Chem 45:4549–4558. doi:10.1021/jm020207y

13. Dalla CA, De Bernardin P, Forte G, Yafteh MF (2010) Metal-salophen-based receptors for anions. Chem Soc Rev 39:3863–3874. doi:10.1039/b926222a

14. Ganjali MR, Norouzi P, Hatambeygi N, Salavati-Niasari M (2006) Anion recognition: fabrication of a highly selective and sensitive HPO_4^{2-} PVC sensor based on a oxo-molybdenum methyl-salen. J Brazil Chem Soc 17:859–865

15. Mao S, Liu K, Lu F, Du L (2010) Colorimetric sensors based on hydrogen-bond-induced π-delocalization and/or anion-triggered deprotonation. Mini-Rev Org Chem 7:221–229

16. Amendola V, Bonizzoni M, Esteban-Gomez D, Fabbrizzi L, Licchelli M, Sancenon F, Taglietti A (2006) Some guidelines for the design of anion receptors. Coord Chem Rev 250:1451–1470. doi:10.1016/j.ccr.2006.01.006

17. Rudkevich DM, Stauthamer WPRV, Verboom W, Engbersen JFJ, Harkema S, Reinhoudt DN (1992) UO_2-salenes: neutral receptors for anions with a high selectivity for dihydrogen phosphate. J Am Chem Soc 114:9671–9673. doi:10.1021/ja00050a064

18. Vigato PA, Tamburini S (2004) The challenge of cyclic and acyclic schiff bases and related derivatives. Coord Chem Rev 248:1717–2128. doi:10.1016/j.cct.2003.09.003

19. Cametti M, Dalla Cort A, Mandolini L, Nissinen M, Rissanen K (2008) Specific recognition of fluoride anion using a metallamacrocycle incorporating a uranyl-salen unit. New J Chem 32:1113–1116. doi:10.1039/b806149a

20. Bandoli G, Clemente DA, Croatto JU, Vidali M, Vigato PA (1971) Preparation and crystal and molecular structure of [NN′-o-phenylene-bis(salicylideneiminato)UO2(EtOH)]. J Chem Soc D 1330–1331. doi:10.1039/C29710001330

21. Bandoli G, Clemente DA (1975) Preparation and crystal structure of aqua[bis(2-hydroxyphenylimino)-ethanato-OO′NN′-]dioxouranium. J Chem Soc, Dalton Trans: 612–615. doi:10.1039/DT9750000612

22. Cort AD, Mandolini L, Pasquini C, Rissanen K, Russo L, Schiaffno L (2007) Zinc-salophen complexes as selective receptors for tertiary amines. New J Chem 31:1633–1638. doi:10.1039/b700723j

23. Germain ME, Vargo TR, McClure BA, Rack JJ, Patten PGV, Odoi M, Knapp MJ (2008) Quenching mechanism of Zn(Salicylaldimine) by nitroaromatics. Inorg Chem 47:6203–6211. doi:10.1021/ic702469q

24. Kleij AW, Kuil M, Tooke DM, Lutz M, Spek AL, Reek JNH (2005) Zn-II-salphen complexes as versatile building blocks for the construction of supramolecular box assemblies. Chem-Eur J 11:4743–4750. doi:10.1002/chem.200500227

25. Martínez-Máñez R, Sancenón F (2003) Fluorogenic and chromogenic chemosensors and reagents for anions. Chem Rev 103:4419–4476. doi:10.1021/cr010421e

26. Luecke H, Quiocho FA (1990) High specificity of a phosphate transport protein determined by hydrogen bonds. Nature 347:402–406. doi:10.1038/347402a0

27. Djedovic N, Ferdani R, Harder E, Pajewska J, Pajewski R, Weber ME, Schlesinger PH, Gokel GW (2005) The C- and N-terminal residues of synthetic heptapeptide ion channels influence transport efficacy through phospholipid bilayers. New J Chem 29:291–305. doi:10.1039/b417091c

28. Sivakumar R, Reena V, Ananthi N, Babu M, Anandan S, Velmathi S (2010) Colorimetric and fluorescence sensing of fluoride anions with potential salicylaldimine based schiff base receptors. Spectrochim Acta A Mol Biomol Spectrosc 75:1146–1151. doi:10.1016/j.saa.2009.12.077

29. Xuan Zh, Lin G, Fang-Ying W, Jiang Y-B (2003) Development of fluorescent sensing of anions under excited-state intermolecular proton transfer signaling mechanism. Org Lett 5:2667–2670. doi:10.1021/ol034846u

30. Winstanley KJ, Sayer AM, Smith DK (2006) Anion binding by catechols - an NMR, optical and electrochemical study. Org Biomol Chem 4:1760–1767. doi:10.1039/B516433h

31. Winstanley KJ, Smith DK (2007) Ortho-substituted catechol derivatives: the effect of intramolecular hydrogen-bonding pathways on chloride anion recognition. J Org Chem 72:2803–2815. doi:10.1021/Jo0623989

32. Hynes JT, Tran-Thi T-H, Granucci G (2002) Intermolecular photochemical proton transfer in solution: new insights and perspectives. J Photochem Photobio A: Chem 154:3–11. doi:10.1016/s1010-6030(02)00304-0

33. Jarczewski A, Hubbard CD (2003) A review of proton transfer reactions between various carbon-acids and amine bases in aprotic solvents. J Mol Struc 649:287–307. doi:10.1016/s0022-2860(03)00086-3

34. Arnaut LG, Formosinho SJ (1993) Excited-state proton transfer reactions. I. fundamentals and intermolecular reactions. J Photochem Photobiol A: Chem 75:1–20. doi:org/10.1016/1010-6030(93)80157-5

35. Abraham Y, Salman H, Suwinska K, Eichen Y (2011) Cyclo 2 benzimidazole: luminescence turn-on sensing of anions. Chem Commun 47:6087–6089. doi:10.1039/c1cc10995b

36. Xu Y, Pang Y (2010) Zinc binding-induced near-IR emission from excited-state intramolecular proton transfer of a bis(benzoxazole) derivative. Chem Commun 46:4070–4072. doi:10.1039/c003230a

37. Gong W, Harigae J, Seo J, Lee SS, Hiratani K (2008) Controllable synthesis, structures of amidecrownophane-type macrocycles and their binding ability toward anions. Tetrahedron Lett 49:2268–2271. doi:10.1016/j.tetlet.2008.02.019

38. Dehkordi MN, Bordbar A-K, Mehrgardi MA, Mirkhani V (2011) Spectrophotometric study on the binding of two water soluble schiff base complexes of Mn (III) with ct-DNA. J Fluoresc 21:1649–1658. doi:10.1007/s10895-011-0854-y

39. Xu KX, Cheng PF, Zhao J, Wang CJ (2011) Enantioselective fluorescent sensors for amino acid derivatives based on BINOL bearing s-tryptophan unit: synthesis and chiral recognition. J Fluoresc 21:991–1000. doi:10.1007/s10895-009-0585-5

40. Huang W, Su H, Yao S, Lin H, Cai Z, Lin H (2011) A simple and neutral receptor acting as a sensitive and switch-on fluorescent chemosensor for $H_2PO_4^-$. J Fluoresc 21:1697–1702. doi:10.1007/s10895-011-0862-y

41. Saravanakumar D, Devaraj S, Iyyampillai S, Mohandoss K, Kandaswamy M (2008) Schiff's base phenol-hydrazone derivatives as colorimetric chemosensors for fluoride ions. Tetrahedron Lett 49:127–132. doi:10.1016/j.tetlet.2007.11.006

42. Steiner T (2002) The hydrogen bond in the solid state. Angew Chem Int Ed 41:48–76. doi:10.1002/1521-3773(20020104)41:1<48::AID-ANIE48>3.0.CO;2-U

43. Valeur B, Pouget J, Ernsting NP (1992) Tuning of photoinduced energy transfer in a bichromophoric coumarin supermolecule by cation binding. J Phys Chem 96:6545–6549. doi:10.1021/j100195a008

44. Cohen MD, Schmidt GM (1962) Photochromy and thermochromy of anils. J Phys Chem 66:2442–2446. doi:10.1021/j100818a030

45. Richey F, Becker RS (1968) Spectroscopy and mechanisms of the photo– and thermal reactions of photochromic Anils. J Chem Phys 49:2092–2100. doi:10.1063/1.1670370

46. Naeimi H, Moradian M (2010) Synthesis and characterization of nitro-Schiff bases derived from 5-nitro-salicylaldehyde and various diamines and their complexes of Co(II). J Coord Chem 63:156–162. doi:10.1080/00958970903225866

47. Lopez MV, Bermejo MR, Vazquez ME, Taglietti A, Zaragoza G, Pedrido R, Martinez-Calvo M (2010) Sulfonamide-imines as selective fluorescent chemosensors for the fluoride anion. Org Biomol Chem 8:357–362. doi:10.1039/B916040j

48. Gomez DE, Fabbrizzi L, Licchelli M, Monzani E (2005) Urea vs. thiourea in anion recognition. Org Biomol Chem 3:1495–1500. doi:10.1039/B500123d

49. Pfeffer FM, Lim KF, Sedgwick KJ (2007) Indole as a scaffold for anion recognition. Org Biomol Chem 5:1795–1799. doi:10.1039/B702804k

50. Duke RM, O'Brien JE, McCabe T, Gunnlaugsson T (2008) Colorimetric sensing of anions in aqueous solution using a charge neutral, cleft-like, amidothiourea receptor: tilting the balance between hydrogen bonding and deprotonation in anion recognition. Org Biomol Chem 6:4089–4092. doi:10.1039/b807579d

51. Sasaki S, Mizuno M, Naemura K, Tobe Y (2000) Synthesis and anion-selective complexation of cyclophane-based cyclic thioureas. J Org Chem 65:275–283. doi:10.1021/jo991237k

52. Chowdhury P, Panja S, Chakravorti S (2003) Excited state prototropic activities in 2-hydroxy 1-naphthaldehyde. J Phys Chem A 107:83–90. doi:10.1021/jp026404q

53. Mehata MS, Joshi HC, Tripathi HB (2002) Complexation of 6-hydroxyquinoline with trimethylamine in polar and non-polar solvents. Chem Phys Lett 366:628–635. doi:10.1016/S0009-2614(02)01579-8

54. Boiocchi M, Boca LD, Gómez DEG, Fabbrizzi L, Licchelli M, Monzani E (2004) Nature of urea-fluoride interaction: incipient and definitive proton transfer. J Am Chem Soc 126:16507–16514. doi:10.1021/ja045936c