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A Comprehensive Review on the Tripodal Supramolecular Receptors and Their Application in Anion Sensing

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INTRODUCTION

Supramolecular receptors (**SR**)[1] are classes of supramolecular entity that can selectively recognize and bind various chemical species namely anions,[2] cations[3] and even neutral molecules[4] by various non-covalent interactions (hydrogen bond[5], halogen bond,[6] van der Waals interactions,[7] metal co-ordination interaction[8] etc.). Designing of versatile **SR** for anion is found to be a focus area of interest in modern synthetic supramolecular chemistry which is partly because of varied size, shape, high charge density, large salvation enthalpy etc. of the anion.[9] A closer look into the biological receptors discovered so far have boosted up scientific communities to design synthetic receptors containing amide,[10] urea,[11] pyrrole,[12] imidazole,[13] indole,[14] guanium,[15] ammonium[16] etc. backbone to facilitate anion recognition and binding. The **SR** containing various metal ions, also known as metallasupramolecular receptor[17] (**MSR**), are also known in the literature.

Tripodal[18] receptor consists of three binding sites and found widely used for anionic, cationic and neutral molecular recognition. The efficiency and selectivity of a tripodal receptor depends upon rigidity of its arm and size of the cavity it offers.[19]

Tripodal Receptor Derived from Tris(2aminoethyl)amine (Tren)

Reinhoudt *et al*. have first reported a class of amide base synthetic receptor derived from Tris-(2aminoethyl)-amine (**tren**) backbone[20] and have demonstrated anion binding events in solution (**Figure 1**). Bowman-James *et al*. have also synthesized a similar kind of sulphonamide based lipophilic receptor, single crystal structure of which revealed the encapsulation of NO_3^-.[21] In some other work they have also showed binding of halide ions by manipulating the chemical environment of the side chain of the receptors.[22] Interestingly, crystal structure suggested that none of the receptor reported by them have capsular assembly (**Figure 1**).

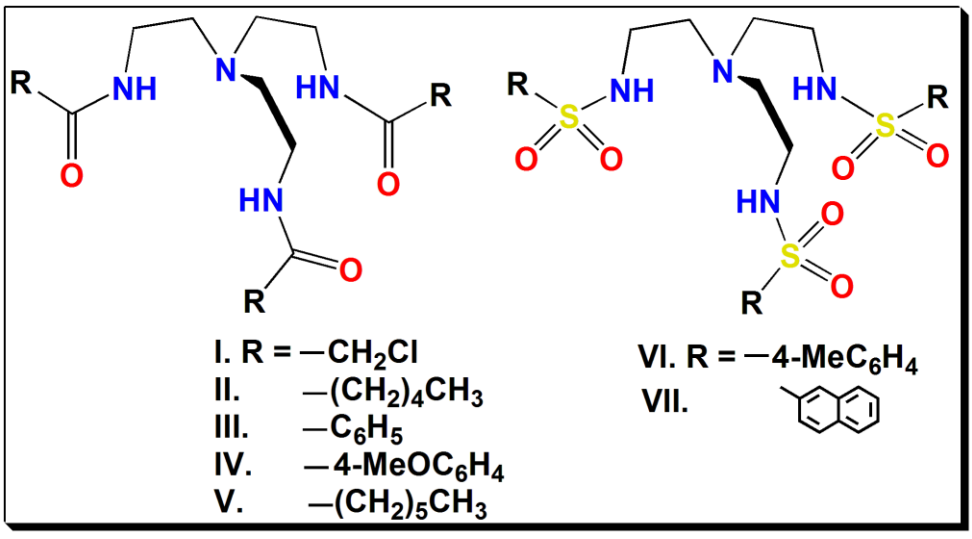

Figure 1: Tren based synthetic receptor

Binding of biologically important PO_4^{2-} ions by tripodal receptor having **tren** scaffold have been demonstrated by Morán *et. al.*[23] and their study indicated that dihydrogen phosphate bind with the C_{3v} symmetric receptors in non-capsular manner. Wu *et al.*[24] and Custelcean *et al.*[25] have studied the binding and separation of SO_4^{2-} ion by pyridyl appended urea based triodal receptor (**Figure 2**). It is important to note that the receptor designed by them have resulted into a capsular network upon anion binding and single crystal structure of the receptor-anion complex indicated that two molecule of the receptor encapsulate one SO_4^{2-}. The composition of the supramolecular complex was found to be $MSO_4.19_2(H_2O)_6$ (where M = various metal cation) and entrapped SO_4^{2-} and was held together by six O–H•••Npy and O–H•••O interactions with the six water molecules coordinated with the metal cation.

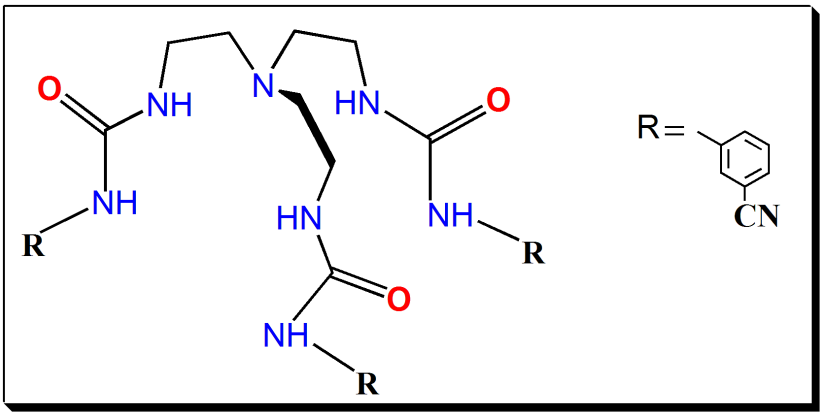

Figure 2: Tren based capsular receptor

Binding of SO_4^{2-} by a similar kind of **tren** based receptor was showed by Prof. Amitava Das and his co-workers[26]. The main advantage of their receptor is that it contained chromophoric Ph-NO_2 and the anion binding phenomena could be monitored with UV-vis spectroscopic studies.

Tripodal Receptor Derived from Sterically Biased Phenyl Scaffold

The **tren** based receptors have suffered from lack of preorganisation and thus binding constant is generally seen to be small with majority of the anions. Rigidity of receptors based on hexa-substituted benzene platform is understandably found to be more preorganised which is presumably due to steric gearing of some of the substituent by other. Thus the substituents which are positioned at 1,3,5 would occupy the same face while 2,4 and 6- substituent would be in the opposite face of the benzene ring.[27] There were many reports on designing and synthesis of receptors based on suitably decorated hexa-substituted benzene moiety. It was experienced that installation of many substituents on a ph-ring was very difficult and thus synthesis of these kinds of receptors were not easy to achieve. It was Walsdorf[28] and van der Made[29] who had devised an easy synthetic route for 1,3,5-tris(bromomethyl)-2,4,6-trialkylbenzene which could easily be transformed to 1,3,5-tris(aminomethyl)-2,4,6-trialkylbenzene and 1,3,5-tris(carboxymethyl)-2,4,6-trialkylbenzene.

Receptor Derived from Tripodal Amines

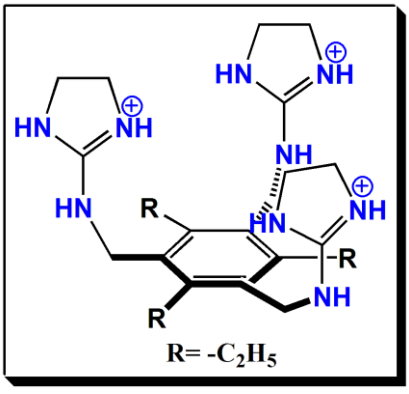

Figure 3: Citrate binding receptor

Prof. Eric V Anslyn and his school have nicely demonstrated the synthesis of anion binding receptors based on sterically geared benzene platform which had marked as one of the early reports on this idea **(Figure 3)**.

They had demonstrated the synthesis of a good number of receptors derived from C_3 symmetric tripodal amine variously substituted in 1,3 and 5-position. They had shown the binding of various biologically important poly-anions

namely citrate,[30] tartrate, malate,[31] phosphate,[32] glucose-6-phosphate,[33] inositol trisphosphate[34] etc. Schmuck and Schwegmann[35] and Steed[36] group had reported various other kind of synthetic variant of Anslyn's receptor. One of the interesting examples of receptor having hexa-substituted benzene scaffold was given by Anzenbacher[37] who had demonstrated sensing of PO_4^{2-} in blood serum. It is to be noted that anion binding did not confer any capsular network. In another report Anslyn group had also synthesized cyclophane type bicyclic receptors containing pyridyl and amide back bone **(Figure 4)** which selectively bind acetic acid over other linear mono carboxylic acids.[38]

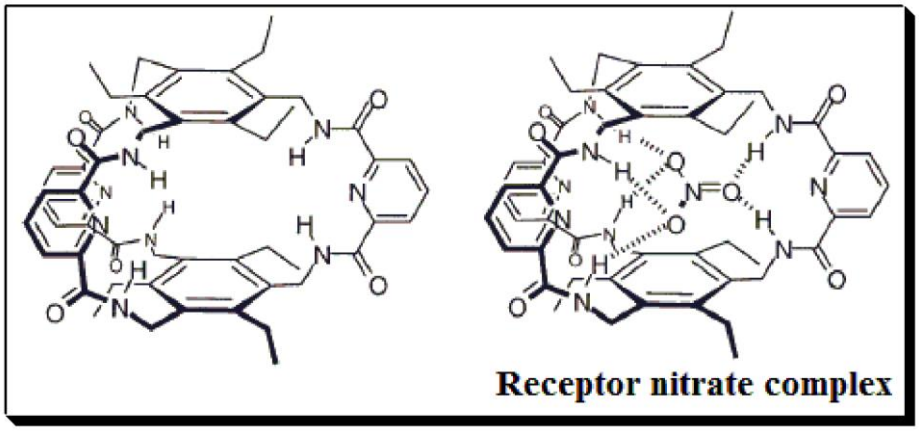

Figure 4: Bicyclic Cyclophane receptor

Designing of suitable receptor for halide was documented as very challenging task owing to its high charge density and large hydration energy. Ghosh *et al*.[39] had reported few elegant example of amide based halide binding tripodal receptors derived from 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene and nitro benzoyl chloride **(Figure 5).**

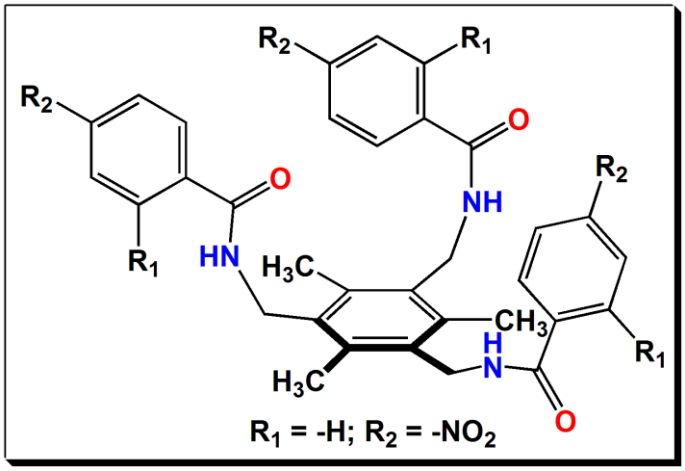

Figure 5: Tripodal receptor for halide sensing

Encapsulation of hydrated F^-, $F_2(H_2O)_6]^{2-}$ and other anions namely Cl^-, NO_3^-, AcO^- etc. by such receptors had been demonstrated by NMR titration. Single crystal structure of these supramolecular complexes revealed that the hydrated fluoride anion entrapped within the exterior of the receptor formed bowl shaped architecture. Entrapment of halide ions by supramolecular receptor from highly polar solvent like water is presumably very important for real life application to get rid of halide pollutions. Thus Steed group[40] had synthesized water soluble zwitterionic receptor **(Figure 6)** and demonstrated the binding of Br^- in capsular micro-environment.

Yield for the synthesis of 1,3,5-tris(aminomethyl)-2,4,6 trimethylbenzene and 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene are generally found to be low and the semi solid and highly polar nature of the products made it difficult to purify them. Synthesis of 1,3,5-tris(carboxymethyl)-2,4,6-trimethylbenzene and 1,3,5-tris(carboxymethyl)-2,4,6-triethylbenzene scaffold are relatively simpler with high yield from corresponding tribromide derivatives and solid products could be purified by recrystallisation. Thus there was a parallel interest among various research groups to design supramolecular receptor based on 1,3,5-tris(carboxymethyl)-2,4,6 trimethylbenzene and 1,3,5-tris(carboxymethyl)-2,4,6-triethylbenzene.

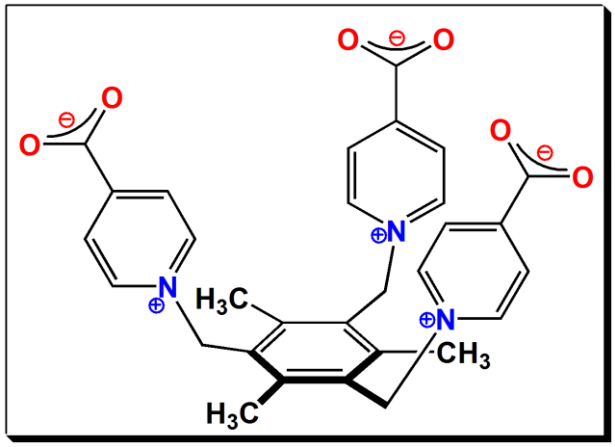

Figure 6: Zwitterionic receptor for halide sensing

CONCLUSION AND OUTLOOK

Supramolecular receptors reported herewith have found applications anion and other guest binding. All these potential guest binding phenomena are important to address issues related to health and environment. Research works have been underwent towards the construction of other tripodal molecular receptors for the recognition of other hazardous anions.

REFERENCES

[1] Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*, **2009**, Wiley; 2nd Edition New Jersey, USA. (b) Beer, P.D.; Szemes, F. *J. Chem. Soc. Chem. Commum*. **1995**, 2245.
[2] Bates, G. W.; Gale, P. A. *An introduction to anion receptors based on organic frameworks, Structure and Bonding*, **2008**, 129,1-44.
[3] Park, Y. S.; Paek, K. *Org. Lett*., **2008**, *10*, 4867-4870.
[4] Ravikumar, I.; Lakshminarayanan; P. S.; Ghosh, P. *Inorg. Chim. Acta*, **2010**, *363*, 2886-2895.
[5] Arunan, E.; Desiraju, G.R.; Klein, R.; Sadlej, R. A.; Scheiner, J.; Alkorta, S.; Clary, I.; Crabtree, D. C.; Dannenberg, R. H.; Hobza, J. J.; Kjaergaard, P.; Legon, H. G, Mennucci, A. C.; Nesbitt, B. *Definition of the hydrogen bond*, *Pure applied chemistry*, **2011**, *83*, 1637-1641. (b) Stainer, T. *Agew Chem. Int. Ed.* **2002**, *41*, 48-76.
[6] Metragolo P.; Resnati, G. *Halogen Bonding: Fundamentals and Applications*. **2008**, Springer Heidelberg, Germany. (b) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati. G. *Acc. Chem. Res*. **2005**, *38*, 386-395.
[7] Parsegian, V. A. *van der Waals Forces: A Handbook for Biologists, Chemists, Engineers, and Physicists*, **2006**, Cambridge University Press,UK.
[8] Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, **1960**, Cornell University Press, USA. (b) Cotton; F A.; Geoffrey; W.; Carlos, M. A.; Bochmann, M. *Advanced Inorganic Chemistry* **1999**, Wiley- Interscience, 6th Edition New York, USA.
[9] Bowman-James, K.; Bianchi, A.; García-Espana, *E. Anion Coordination Chemistry*, Wiley-VCH GmbH & Co. KGaA. **2012**, New jersey, USA.
[10] Kang, S.O.; Begum, R.A.; Bowman-James, K. *Angew. Chem. Int. Ed*. **2006**, *45*, 7882-7894.
[11] Amendola, V.; Fabbrizzi, L.; Lorenzo, M. *Chem. Soc. Rev*. **2010**, *39*, 3889-3915.
[12] Sessler J. L.; Barkey,N. M; Pantos;G.D.; Lynch, V. M. *New J. Chem.* **2007**, *31*, 646-654.
[13] Metzger, A.; Lynch, V. M.; Anslyn, E. V. *Angew. Chem., Int. Ed*., **1997**, *36*, 862-864.
[14] Manivannan, R.; Satheshkumar, A.; Mossalamy, E.-S.; Al-Harbi, M. L.; Kosa, S.A.; Elango, K.P. *New J. Chem.* **2015**, *39*, 3936-3947.
[15] Blondeau, P.; Sequra, M.; Pérez-Fernández, R.; de Mendoza, J. *Chem. Soc. Rev*. **2007**, *36*, 198-210.
[16] Mateus, P.; Bernier, N.; Delgado, R. *Coord. Chem. Rev*. **2010**, *254*, 1726-1747
[17] Banerjee, S.; Adrash, N. N.; Dastidar, P. *CrystEngComm*. **2013**, *15*, 245-248
[18] Gale, P.A.; Dehaen, W. *Anion Recognition in Supramolecular Chemistry*, **2010**, Springer-Verlag, Berlin Heidelberg, Germany. (b) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*, **2006**, RSC Publishing, UK.
[19] Bose, P.; Dutta, R.; Ghosh, P. *Org. Biomol. Chem*. **2013**, *11*, 4581-4584.
[20] Kuswandi, B.; Nuriman,; Verboom, W.; Reinhoudt, D. N. *Sensors*. **2006**, *6*, 978-1017.
[21] Danby, A.; Seib, L.; Alcock, N. W.; Bowman-James, K.; *Chem. Commun.* **2000**, 973-974.
[22] Md. Hossain, A.; Liljegren, J. A.; Powell, D.; Bowman-James, K.; *Inorg. Chem*. **2004**, *43*, 3751-3755.

[23] Moràn, J. R.; Raposo,C.; Almaraz, M.; Martín, M.; Weinrich, V.; Mussóns M. L., Alcàzar, V.; Caballero, M. C. *Chem. Lett*. **1995**, 759-760.
[24] Wu, B.; Liang, J.; Yang, J.; Jia, C.; Yang, X.-J.; Zhang, H.; Tang, N.; Janiak, C. *Chem. Commun*. **2008**, 1762-1764.
[25] Custelcean, R.; Remy, P.; Bonnesen, P. V.; Jiang, D.-e.; Moyer, B. A.; *Angew. Chem., Int. Ed*. **2008**, *47*, 1866-1870.
[26] Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Inorg. Chem*. **2007**, *46*, 5817–5819.
[27] Hennrich, G.; Anslyn, E. V. *Chem.-Eur. J*. **2002**, *8*, 2218-2224.
[28] Walsdorff, C.; Saak, W.; Pohl, S.; *J. Chem. Res.(M).* **1996**, 1601-1609.
[29] van der Made, A. W.; van der Made, R. H. *J. Org. Chem*. **1993**, *58*, 1262-1264.
[30] Metzger, A.; Lynch, V. M.; Anslyn, E. V. *Angew. Chem*. **1997**, *109*, 911- 914; *Angew.Chem. Int. Ed. Engl.* **1997**, *36*, 862-864.
[31] Lavigne, J. J.; Anslyn, E. V. *Angew. Chem. Int.Ed*., **1999**, *38*, 3666-3669.
[32] Niikura, K.; Anslyn, E. V. *J. Chem. Soc. Perkin Trans. 2*. **1999**, 2769- 2775.
[33] Cabell, L. A.; Monahan, M.-K.; Anslyn, E. V.; *Tetrahedron Lett.* **1999**, *40*, 7753- 7756.
[34] Niikura, K.; Metzger, A.; Anslyn, E. V.; *J. Am. Chem. Soc.* **1998**, *120*, 8533-8534.
[35] Schmuck, C.; Schwegmann, M.; *J. Am. Chem. Soc.* **2005**, *127*, 3373-3379.
[36] Belcher, W. J.; Fabre, M.; Farhan, T.; Steed, J. W. *Org. Biomol. Chem*. **2006**, *4*, 781-786.
[37] Zyryanov, G. V.; Palacios, M. A.; Anzenbacher, P.Jr. *Angew. Chem. Int. Ed*. **2007**, *46*, 7849-7852.
[38] Snowden, T.S.; Bisson, A. P.; Anslyn, E. V.; *J. Am. Chem. Soc.* **1999**, *121*, 6324-6325.
[39] Arunachalam, M.; Ghosh, P. *Chem. Commun*. **2009,** 5389-5391.
[40] Cresswell, A. L.; Piepenbrock, M. -O. M.; Steed, J. W. *Chem Commun*. **2010**, *46*, 2787-2789.