Abstract:

Terphenyl diamines namely 4,4''-diamino-4',5'-bis(tert-butyldimethylsilyloxy)-1',1',2',1''-terphenyl 3, 4,5-bis(4',4''-diaminophenyl)benzo[15]crown-5 7, 4,4''-diamino-4',5'-dimethoxy 1,1',2',1''-terphenyl 13 and 4,4''-diamino-1,1',2',1''-terphenyl 17 were synthesized by Suzuki-Miyaura cross coupling. Using these diamines, various imino linked terphenyl derivatives 5, 8, 10, 11, 15, 18, 20a-c, 21 appended with fluorophores viz. pyrene, quinoline and phenanthroline have been designed and synthesized. The binding behaviour of these chemosensors toward different metal ions was investigated by UV-Vis, fluorescence and NMR spectroscopy. Based on the results of fluorescence and NMR studies, the switching behaviour of these chemosensors has been evaluated. The pyrene and quinoline based receptors 5, 8, 10, 11 showed ‘turn-on’ fluorescent enhancement in the presence of Hg$^{2+}$ ions whereas receptors having phenanthroline units 15 and 18 showed fluorescence enhancement in the presence of Zn$^{2+}$ ions. Terphenyl based receptor 20a obtained by reaction of diamine 3 with 5-nitro salicylaldehyde, showed selectivity toward copper as well as fluoride ions owning to the simultaneous presence of imine units and hydroxyl groups.
2.1 Introduction

Cations play an important role in a wide range of chemical reactions including biological metabolism as well as many other processes. Much attention has been focused on the development of chemosensors for the selective and efficient detection of these biologically and chemically important species. Chemosensors based on the metal ion induced changes in fluorescence appear to be particularly attractive and one of the first choices due to the simplicity and high detection limit of fluorescence. So, designing fluorescent sensors for metal ions has drawn worldwide attention. Basically, a fluorescent chemosensor consists of an ion recognition unit (ionophore) for binding of an ion and a fluorogenic unit (fluorophore) where the role of a fluorophore is to signal the binding event through changes in the fluorescence emission. In fact a number of chemosensors for hard metal ions have already been reported. On the other hand, the development of chemosensors for soft metal ions like mercury, zinc and copper particularly needs attention because of the important role played by these metal ions in day to day life. In particular, mercury is considered highly toxic as both elemental and ionic mercury can be converted into methyl mercury by bacteria in the environment which enters the food chain and accumulates in the higher organisms. Mercury contamination also occurs through a variety of natural and soft metal anthropogenic sources including oceanic and volcanic emission, gold mining, solid waste incineration and combustion of fossil fuels.

On the other hand, zinc is a second most abundant transition metal ion \textit{in vivo} and major regulatory ion in many channels and receptors, in the metabolism of cells, and in metalloenzyme regulation. Several organs \textit{e.g.}, brain, pancreas, spermatozoa, vesicles of presynaptic neurons, contain zinc either in the free-state or sequestered form. The cellular zinc ion concentration varies from the nanomolar range to about 0.3 mM.

Similarly, the selective sensing of copper, which is third in abundance among the essential transition metal ions in human body has gained attention due to its significance in biological systems. Copper kills a variety of potentially harmful pathogens and hence have antimicrobial effect against MRSA, Escherichia coli and other pathogens. But the over-accumulations of copper produce severe or lethal intoxications. Thus, the diversity of their functions, both beneficial and otherwise, makes the monitoring and detection of mercury, zinc and copper ions important.
For the selective binding of such soft metal ions, the incorporation of soft binding sites like Schiff bases (imines), nitrogen and sulphur are desirable. Schiff base (imine) moiety is one of the important tools for soft metal ion sensing. Reversibility associated with an imine bond formation makes Schiff’s discovery especially significant particularly since relatively few covalent bonds are capable of being formed, broken and reformed under equilibrium control. Schiff bases also possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties. The availability of directed lone pair of electrons for soft metal ion coordination, the stabilization of metal ions in variable oxidation states and structural rigidity in Schiff bases led to the enhanced research activity in the field of templated synthesis, catalysis and self-assembly.

Since the origin of host-guest chemistry, a wide range of synthetic organic receptors like crown ethers, cryptands, spherands, porphyrins, calixarenes, thiacalixarenes, and cyclodextrins have been utilized as scaffolds for ion sensing. For a molecular receptor to be an effective host, its basic molecular scaffold should be easy to synthesize and should undergo chemical modification without much difficulty. Recently, terphenyls have attracted attention due to a wide range of significant biological activities e.g. potent immunosuppressant, neuroprotective, antithrombotic, anticoagulant, specific 5- lipoxygenase inhibitory and cytotoxic activities. These are also being used as key intermediates for the synthesis of symmetrically and unsymmetrically substituted triphenylenes which have great potential for supramolecular and material chemistry as their liquid crystalline behaviour can be modified by changing electronic properties of their substituents. To the best of our knowledge there was no report where terphenyl scaffold had been decorated with different ligating sites to prepare chemosensors for different types of analytes. Thus, there is much more potential in using terphenyl scaffold for preparing different types of artificial receptors. We envisaged that derivatizing terphenyl scaffold in particular \( o \)-terphenyl framework with soft binding sites particularly imine units possessing suitable signaling units should give a host capable of interacting with soft metal ions. So, in the present investigation, we have designed and synthesized a variety of fluorogenic receptors based on \( o \)-terphenyl scaffold bearing pyrene, quinoline and phenanthroline moieties. For the sake of convenience we have used the word...
‘terphenyl’ instead of ‘o-terphenyl’ throughout this thesis. The results of our findings in this chapter have been divided in four sections and are discussed as follows:

Section 2.2.1 Terphenyl based receptors having pyrene as a fluorophore

Section 2.2.2 Terphenyl based receptors having quinoline as a fluorophore

Section 2.2.3 Terphenyl based macrocycles having phenanthroline as a fluorophore

Section 2.2.4 Terphenyl based fluorescent chemosensors for Cu$^{2+}$ and F$^{-}$ employing excited state intramolecular proton transfer

2.2 Results and Discussion

2.2.1 Terphenyl based receptors having pyrene as a fluorophore

Of the different fluorogenic units, pyrene is most useful because of its efficient and sensitive monomer emission in the range of 370–430 nm and its excimer emission at around 480 nm.$^{25}$ The intensity ratio of the excimer to monomer emission ($I_E/I_M$) is very sensitive to conformational change and the guest ion (cation and anion) concentration,$^{26}$ and hence it is a very informative tool in sensing systems. Thus, in the present investigation, we have designed and synthesized terphenyl based pyrene appended fluorogenic receptors 5 and 8 having imine units. The receptors behave as ‘turn-on’ fluorescent sensors for Hg$^{2+}$ ions.

Suzuki-Miyaura cross coupling of compound 1 with compound 2 catalyzed by Pd (II) furnished diamine 3 in 55% yields (Scheme 2.1). The $^1$H NMR spectrum of compound 3 showed two singlets (18H, 12H) for tert-butyldimethylsilyl (TBS) group, one broad signal for amino (NH$_2$) group, one singlet, and two doublets (2H, 4H, 4H) for aromatic protons of terphenyl moiety. The FAB mass spectrum showed a parent ion peak at 520 (M$^+$) corresponding to the coupled product 3. Using the same procedure, Suzuki-Miyaura coupling of boronic ester 2 with compound 6 catalyzed by Pd (II) furnished compound 7 in 50% yields (Scheme 2.2). The $^1$H NMR spectrum of compound 7 showed one singlet and two triplets (8H, 4H, 4H) for crown protons, one broad signal for amino (NH$_2$) protons, and two multiplets and one singlet (4H, 4H, 2H) for aromatic protons of terphenyl moiety. The FAB mass spectrum showed a parent ion peak at 450 (M$^+$) corresponding to the coupled product 7.

Condensation of diamine 3/7 with 2-pyrene carboxaldehyde 4 in ethanol at room temperature for 2h gave compounds 5 and 8 in 75% and 74% yields, respectively (Schemes 2.1 and 2.2). The structures of compounds 5 and 8 were confirmed from
their spectroscopic and analytical data. The \(^1\)H NMR spectrum of compound 5 showed two singlets (18H, 12H) for TBS group, two singlets and one doublet (2H, 4H, 2H) for aromatic protons of terphenyl moiety, one multiplet (18H) for pyrene ring, and one singlet (2H) for imino protons (N=CH). \(^1\)H NMR spectrum of receptor 8 showed one singlet and two triplets (8H, 4H, 4H) for crown protons, one singlet and one multiplet (2H, 8H) for aromatic protons of terphenyl moiety, one singlet (2H) for the imino protons (N=CH), one multiplet and two doublets (14H, 2H, 2H) for the pyrene ring. The IR spectra of compounds 5 and 8 showed C=N stretching band at 1632 cm\(^{-1}\). FAB mass spectra showed the parent ion peaks at 945 (M+1\(^+\)) and 875 (M\(^+\)) corresponding to the condensation products 5 and 8, respectively. These spectroscopic data corroborate the structures 5 and 8 for these compounds.

The binding behaviour of receptor 5 toward various metal ions was evaluated by UV-Vis, fluorescence and NMR experiments. The absorption spectrum of compound 5 (10.0 µM) in THF exhibited bands at 264, 282, 325 and 345 nm. Upon addition of Hg\(^{2+}\) ions (10.0 µM), an increase in absorption bands at 264 and 284 nm occurs (figure 2.1).

In the fluorescence spectrum, compound 5 exhibited a weak monomer emission at 389 nm when excited at \(\lambda = 345\) nm. This weak emission from compound 5 was due to
photo-induced electron transfer (PET)\textsuperscript{27} from the imino nitrogen to the photoexcited pyrene which leads to poor emission. Upon addition of increasing amounts of Hg\textsuperscript{2+} ions from 0.1 to 30.0 µM to the solution of compound 5 in THF–H\textsubscript{2}O (9.5:0.5), a significant increase (375\%) in the emission band attributed to the [5–Hg\textsuperscript{2+}] complex was observed (\textbf{figure 2.2}).

Such fluorescence enhancement observed for compound 5 in the presence of Hg\textsuperscript{2+} ions was attributed to the co-ordination of imino nitrogens of compound 5 with Hg\textsuperscript{2+} ions as a result of which the PET from imino nitrogen to pyrene moiety is suppressed which results in fluorescence enhancement. Under the same conditions as used above for Hg\textsuperscript{2+} ions, we also tested the fluorescence response of 5 to other metal ions such as Pb\textsuperscript{2+}, Ag\textsuperscript{+}, Cd\textsuperscript{2+}, Zn\textsuperscript{2+}, Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, K\textsuperscript{+}, and Li\textsuperscript{+} besides Hg\textsuperscript{2+}, and as shown in \textbf{figure 2.3}, no significant fluorescence change of compound 5 occurred in the presence of these metal ions which indicates that all these metal ions are not coordinating with the imino nitrogen atoms of the compound 5. The reversibility of binding of mercury ions with compound 5 was observed by addition of potassium iodide to the [5-Hg\textsuperscript{2+}] complex. On addition of potassium iodide to the solution of [5-Hg\textsuperscript{2+}], the fluorescence got quenched owning to the strong affinity of I\textsuperscript{−} ions for Hg\textsuperscript{2+} ions which leads to the decomplexation of the [5-Hg\textsuperscript{2+}] complex. As a result, Hg\textsuperscript{2+} ions are not available to bind with the imino nitrogen atoms of receptor due to which the PET phenomena from imino nitrogens will be operative which will quench the fluorescence. On further addition of Hg\textsuperscript{2+} ions to above solution, the fluorescence intensity was revived again.
indicating that the change in fluorescence on addition of mercury is reversible (figure 2.4).

The stoichiometry of the complex formed between compound 5 and Hg$^{2+}$ ion was evaluated by the method of continuous variation (Job’s plot). The total concentration of the compound 5 and Hg$^{2+}$ ions was constant (2.5 X 10$^{-5}$ M) with a concomitant variable molar fraction of guest ([Hg$^{2+}$] / [5 + Hg$^{2+}$]). The Job’s plot of compound 5 with Hg$^{2+}$ ions at 389 nm showed that the complex concentration approached maxima when the molar concentration of Hg$^{2+}$ ion is 0.5 which means compound 5 and Hg$^{2+}$ formed a 1:1 complex (figure 2.5). The association constant (log β) of compound 5
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with Hg\(^{2+}\) ions was calculated from fluorescence titration experiments by means of SPECFIT program (global analysis system V3.0 for 32-bit Window system), which uses singular value decomposition and non-linear regression modeling by the Levenberg–Marquardt method\(^{29}\) and was found to be 5.12. The global analysis showed that the titration curves were consistent with the formation of 1:1 (H:G) complex.

The practical applicability of compound 5 as a Hg\(^{2+}\) selective fluorescence sensor was tested by carrying out competitive experiments in the presence of Hg\(^{2+}\) at 30.0 \(\mu\)M mixed with Li\(^+\), K\(^+\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Ag\(^+\) and Pb\(^{2+}\) at 300.0 \(\mu\)M. As shown in figure 2.6, no significant variation in fluorescence intensity change (I-I\(_o\)/I\(_o\) \(\times\) 100) was found by comparison with or without the other metal ions besides Hg\(^{2+}\) ions, except for Cu\(^{2+}\) ions which interfere with the detection of Hg\(^{2+}\) ions. The fluorescence quantum yield\(^{30}\) of compound 5 in free and Hg bound state was found to be 0.04 and 0.49 respectively.

To elucidate the binding mode of receptor 5 with Hg\(^{2+}\) ions, the \(^1\)H NMR spectrum of its complex with mercury perchlorate was also recorded. A significant downfield shift of 1.26 ppm is observed for the imino protons, which indicates that the imino nitrogens are coordinating with Hg\(^{2+}\) ions through their lone pairs of electrons (figure 2.7). Thus, from this NMR study, it can be concluded that mercury is interacting with receptor 5 as supported by fluorescence studies.

To determine the detection limit, the fluorescence titration of compound 5 with Hg\(^{2+}\) ions was carried out by adding aliquots of mercury solution of micromolar concentration and the fluorescence intensity as a function of Hg\(^{2+}\) ions added was then

![Figure 2.7 Partial \(^1\)H NMR spectrum (CDCl\(_3\)--CD\(_3\)CN, 8:2) of receptor 5 before (a) and after (b) addition of Hg\(^{2+}\) ions]
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plotted (figure 2.8). From this graph the concentration at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor 5 gave the detection limit. The detection limit of 5 as a fluorescent sensor for the analysis of Hg$^{2+}$ was found to be 2.1 μM which is sufficiently low for the detection of submillimolar concentrations of Hg$^{2+}$ ions as found in many chemical systems.

In a similar manner, we studied the binding behaviour of compound 8 having crown ring along with the imine units as binding sites. The idea behind synthesis of receptor 8 was that the introduction of crown-5 ring in addition of imine moieties may lead to an ‘on-off’ switchable binuclear chemosensor. Moreover, the electrons on the crown ring were expected to enhance the photo-induced electron transfer (PET) to the fluorophore moiety which may make the receptor very weakly fluorescent, and the percentage enhancement of fluorescence will be more on coordination with the specific metal ion.

The absorption spectrum of compound 8 (10.0 μM) in THF exhibited bands at 288, 368 and 394 nm. Upon addition of Hg$^{2+}$ ions (8.0 equiv), an increase in absorption bands at 368 and 394 nm occur along with the formation of new weak band at 500 nm (figure 2.9). The fluorescence spectrum of compound 8 exhibited a weak monomer emission at 388 nm in THF/H$_2$O (9.5:0.5) as the solvent mixture. Upon addition of Hg$^{2+}$ ions (15.0 μM), a significant increase of 1900% in the emission band attributed to [8-Hg$^{2+}$] complex was observed (figure 2.10).
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The chemosensor was found to be highly selective over various metal ions (Sm$^{3+}$, Nd$^{3+}$, Pb$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^{+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, K$^{+}$, Mg$^{2+}$, Na$^{+}$, and Li$^{+}$) tested (figure 2.11).

The practical applicability of chemosensor as a Hg$^{2+}$ selective sensor was checked by carrying out the competitive experiments in the presence of Hg$^{2+}$ ions mixed with (Sm$^{3+}$, Nd$^{3+}$, Pb$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^{+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, K$^{+}$, Mg$^{2+}$, Na$^{+}$, and Li$^{+}$) and as shown in figure 2.12, no significant variation in fluorescence intensity change was found by comparison with or without the other metal ions besides Hg$^{2+}$ ions.

The method of continuous variation (Job’s plot) was used to prove the 1:1 stoichiometry (host: guest) (figure 2.13). The binding constant (log $\beta$) of receptor 8

Figure 2.9 UV-Vis spectra of receptor 8 (10.0 µM) in the presence of Hg$^{2+}$ ions (80.0 µM) in THF.

Figure 2.10 Fluorescence response of receptor 8 (1.0 µM) on addition of Hg$^{2+}$ (15.0 µM) in THF/H$_2$O (9.5:0.5), $\lambda_{ex}$ = 345 nm.

Figure 2.11 Fluorescence enhancement of receptor 8 (1.0 µM) at 345 nm upon addition of different metal ions (15.0 µM) in THF/H$_2$O (9.5:0.5).

Figure 2.12 Competitive selectivity of receptor 8 (1.0 µM) towards Hg$^{2+}$ ions (15.0 µM) in the presence of other metal ions (150.0 µM)
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with Hg$^{2+}$ ions was found to be 5.98 inferred from Hg$^{2+}$ titration curves, using the nonlinear regression analysis program SPECFIT. The fluorescence quantum yield (Φ) of compound 8 in the free and Hg$^{2+}$-bound state was found to be 0.03 and 0.58, respectively. The substantial increase in the quantum yield of compound 8 in the presence of 10.0 μM of Hg$^{2+}$ ions and its high Hg$^{2+}$ selectivity showed its credibility as a good Hg$^{2+}$ sensor.

To test if the proposed complex could be reversed, KI solution was added. The addition of 50.0 μM of KI could restore the fluorescent signal of compound 8 to its original level and that could be revived again on addition of Hg$^{2+}$ ions (figure 2.14). The detection limit of 8 as fluorescent sensors for the analysis of Hg$^{2+}$ was found to be 40 nM, which is sufficiently low for the detection of submillimolar concentrations of Hg$^{2+}$ ions as found in many chemical systems. The binding mode of receptor 8 with Hg$^{2+}$ ions was confirmed by recording the $^1$H NMR spectrum of its complex with mercury perchlorate. A significant downfield shift of 1.2 ppm in case of 8 was observed for the imino protons, which indicated that the imino nitrogens were coordinating with Hg$^{2+}$ ions through their lone pairs of electrons (figure 2.15).

![Figure 2.13](image)  
**Figure 2.13** Job’s plot for determining the stoichiometry of 8 and Hg$^{2+}$ ion in THF/H$_2$O (9.5:0.5)

![Figure 2.14](image)  
**Figure 2.14** Reversibility of Hg$^{2+}$ coordination to receptor 8 by KI. Blue line, free 8 (1.0 μM), pink line, 8 + 15 equiv Hg$^{2+}$; red line, 8 + 15 equiv Hg$^{2+}$ + 100 equiv KI, green line, 8 + 15 equiv Hg$^{2+}$ + 100 equiv KI + 30 equiv Hg$^{2+}$.
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Thus, from the UV-Vis, fluorescence and NMR studies, it may be concluded that compounds 5 and 8 selectively complex with mercury ions in comparison to other cations. Based on the results of these binding studies we envisaged that it should be possible to construct mercury ion selective PVC membranes using these pyrene based chemosensors 5 and 8. Thus, a sensor membrane for one of the pyrene appended terphenyl derivative 5 was prepared and assembled as previously reported from our laboratory for mercury ions.\(^{31}\) The composition of this membrane is listed in Table 2.1. The PVC membrane of the cation receptor generated a stable potential when placed in contact with mercury nitrate solution. The EMF response of the membrane in the presence of a wide range of mercury ion solutions is shown in figure 2.16. The electrodes demonstrate a linear response for Hg\(^{2+}\) ions in the concentration range from 1.0 \(\times\) 10\(^{-1}\) to 5.0 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\). The slope of the plot was 28.86 mV (approx.) per decade of concentration which indicates the near Nernstian nature of the electrode. The response time of the membrane was measured at different concentrations and was found to be less than 10s and no change was observed up to 5 min. Potentials were measured periodically at a fixed concentration and the standard deviation of ten

![Figure 2.15](image) Partial \(^1\)H NMR spectrum (CDCl\(_3\)–CD\(_3\)CN, 8: 2) of receptor 8 before (a) and after (b) addition of Hg\(^{2+}\) ions

**Application of receptor 5 as mercury ion selective electrode**

<table>
<thead>
<tr>
<th>PVC (mg)</th>
<th>DOS (mg)</th>
<th>NaTPB (mg)</th>
<th>Ionophore (mg)</th>
<th>Linear Range(M)</th>
<th>Slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101.2</td>
<td>201.1</td>
<td>1.3</td>
<td>5.4</td>
<td>1.0x10(^{-1})–5.0x10(^{-5})</td>
<td>28.86</td>
</tr>
</tbody>
</table>

NaTPB: Sodium tetraphenylborate; DOS = Dioctyl sebacate as plasticizer
identical measurements was ±1 mV. The dependence of the membrane potentials on pH was studied at 1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Hg}^{2+} \text{ ion concentration. The potential remained constant from pH 1.3 to 4.3 which may be taken as the operational pH range of the sensor. The most important feature of an ion selective electrode is its response to its primary ion in the presence of various other cations. This is measured in terms of the potentiometric selectivity coefficient (K_{pot}^{A,B}) which was evaluated by the fixed interference method at 1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ concentrations of various interfering ions. Table 2.2 shows the potentiometric selectivity coefficient data of the imine derivatized terphenyl-based PVC membrane electrode for the interfering cations relative to Hg}^{2+} \text{ ions. K}_{pot}^{A,B} \text{ was fairly low for all the cations tested which indicates that there is no interference present with the determinant ion (Hg}^{2+}).

<table>
<thead>
<tr>
<th>Secondary ions</th>
<th>Na^{+}</th>
<th>K^{+}</th>
<th>NH_{4}^{+}</th>
<th>Ag^{+}</th>
<th>Co^{2+}</th>
<th>Ca^{2+}</th>
<th>Mg^{2+}</th>
<th>Cd^{2+}</th>
<th>Cu^{2+}</th>
<th>Pb^{2+}</th>
<th>Ni^{2+}</th>
<th>Zn^{2+}</th>
<th>Fe^{3+}</th>
</tr>
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<tbody>
<tr>
<td>\text{Log } K_{Hg}^{pot}_{A,B}</td>
<td>-1.05</td>
<td>-1.08</td>
<td>-0.95</td>
<td>-0.15</td>
<td>-2.85</td>
<td>-3.10</td>
<td>-2.80</td>
<td>-3.02</td>
<td>-2.75</td>
<td>-2.78</td>
<td>-2.75</td>
<td>-2.95</td>
<td>-4.34</td>
</tr>
</tbody>
</table>

The electrode assembly was tested as an indicator electrode to determine the end point in the potentiometric titration of Hg^{2+} with a standard solution of sodium iodide. A 20 ml solution of 1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ mercury nitrate was titrated against 1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ sodium iodide solution. The sharp rise in the potential indicates the end point (figure 2.17).}
In conclusion, highly selective fluorescent chemosensors 5 and 8 based on terphenyl appended with pyrene as a fluorophore were synthesized and evaluated as ‘turn-on’ sensors for Hg$^{2+}$ ions. Receptor 8 showed much better sensitivity and detection tendency for Hg$^{2+}$ ions in comparison to receptor 5 which indicate that crown-5 ring is playing role in the signalling phenomenon.

### 2.2.2 Terphenyl based receptors having quinoline as a fluorophore

In continuation of this investigation on terphenyl based receptors for soft metal ions, in the next part of investigation, we were interested in increasing the number of soft binding sites in the receptor for efficient binding of soft metal ions. Thus, we envisaged that attachment of quinoline moiety to terphenyl scaffold will not only increase the number of nitrogen atoms in comparison to the number of nitrogen atoms in case of receptors 5 and 8 but will also exhibit high detection sensitivity. Thus, compounds 10 and 11 having quinoline moieties were designed for this purpose.

Compounds 10 and 11 were synthesized from previously synthesized diamines 3 and 7, respectively. Condensation of diamine 3/7 with quinoline carboxaldehyde 9 gave compounds 10 and 11, respectively, in 85% and 77% yields, respectively (Scheme 2.3 & 2.4). The structures of compounds 10 and 11 were confirmed from their spectroscopic and analytical data. In the $^1$H NMR spectrum, compound 10 showed two singlets (18H, 12H) for the tert-butylidimethylsilyl (TBS) group, one singlet and two doublets (2H, 4H, 4H) for aromatic protons of terphenyl moiety, four doublets (2H, 2H, 2H, 2H) and two triplets (2H, 2H) for quinoline protons, and one singlet (2H) for imine protons (N=CH). In the IR spectrum of compound 10, an absorption band
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appeared at 1632 cm\(^{-1}\) due to the C=N group, and there was no band corresponding to the free aldehyde and amino group, which indicated that condensation has taken place. The \(^1\)H NMR spectrum of receptor 11 showed one singlet and two triplets (8H, 4H, 4H) for crown protons, one singlet and one multiplet (2H, 8H) for aromatic protons of terphenyl moiety, four doublets (2H, 2H, 2H, 2H) and two triplets (2H, 2H) for quinoline protons and one singlet (2H) for the imine protons (N=CH). In the FAB mass spectra, the parent ion peaks were observed at 799 (M\(^+\)) and 729 (M\(^+\)) corresponding to the condensation products 10 and 11, respectively. These spectroscopic data corroborate structures 10 and 11 for these compounds.

![Scheme 2.3](image1)

![Scheme 2.4](image2)

The binding behaviour of receptors 10 and 11 toward various metal ions was evaluated by UV-Vis, fluorescence and NMR experiments. The absorption spectrum of compound 10 (10.0 μM) in THF exhibited a strong band at 354 nm. Upon addition of Hg\(^{2+}\) ions (30.0 μM), a new red-shifted band was formed at 417 nm. The formation of new band at 417 nm was attributed to the interaction of mercury ions with imino nitrogens leading to intramolecular charge transfer (ICT)\(^{32}\) from the quinoline moiety to imino group (figure 2.18). An obvious colour change from colourless to pale yellow was observed by the naked eye (inset figure 2.18). A clear isosbestic point at 393 nm was observed in absorption spectra, indicating the formation of a well-defined [10-Hg\(^{2+}\)] complex (figure 2.18). Similarly, UV-Vis experiments were carried out for compound 11 which contained a crown-5 ring in addition to a quinoline unit with
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different metal ions (Sm$^{3+}$, Nd$^{3+}$, Pb$^{2+}$, Hg$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^+$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, and Li$^+$). A more pronounced red shift of 80 nm was observed on addition of Hg$^{2+}$ ions (30.0 $\mu$M) to a solution of compound 11 (figure 2.19).

![Figure 2.18 UV-Vis spectra of receptor 10 (10.0 $\mu$M) in the presence of Hg$^{2+}$ ions (30.0 $\mu$M) in THF; Inset: Showing the change in the color of receptor 10 (1x10$^{-5}$ M) upon addition of Hg$^{2+}$ ions (30.0 $\mu$M).]

![Figure 2.19 UV-Vis spectra of receptor 11 (10.0 $\mu$M) in the presence of Hg$^{2+}$ ions (30.0 $\mu$M) in THF]

In the fluorescence spectrum, compound 10 exhibited very weak fluorescence emission at 415 nm in THF when excited at 310 nm (figure 2.20). The weak fluorescence emission was due to photo-induced electron transfer (PET) from imino nitrogen atoms to the photoexcited quinoline moiety (nonradiative channel from the nπ* state of emission of the quinoline groups by lone pair of electrons of the imine nitrogen atoms). Upon addition of increasing amounts of Hg$^{2+}$ ions (10.0 $\mu$M) to the solution of compound 10 in THF, a remarkable 5000% enhancement with a red shift (38 nm) in the emission maximum from 415 to 453 nm was observed (figure 2.20) while in the case of compound 5, 375% fluorescence enhancement was observed upon adding Hg$^{2+}$ ions to the solution of compound 5. Fluorescence enhancement observed for compound 10 was attributed to the formation of the [10-Hg$^{2+}$] complex as a result of which the PET from imino nitrogen to the photoexcited quinoline moiety was suppressed (the energy of the nπ* state of emission is increased and that of ππ* state of the emission of the quinoline group become the lowest excited state), resulting in the fluorescent enhancement. Under the same conditions as used above for Hg$^{2+}$, we also tested the fluorescence response of compound 10 to other metal ions (Sm$^{3+}$, Nd$^{3+}$, Pb$^{2+}$, Hg$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^+$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$,
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and Li\(^+\)) and as shown in figure 2.21, a negligible change in fluorescence occurred in the presence of these metal ions. Further, to check the practical applicability of compound 10 as a Hg\(^{2+}\) selective fluorescent sensor, the competitive experiments in the presence of Hg\(^{2+}\) at 10.0 \(\mu\)M mixed with Sm\(^3+\), Nd\(^3+\), Pb\(^{2+}\), Ba\(^{2+}\), Cd\(^{2+}\), Ag\(^+\), Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\), Fe\(^{3+}\), K\(^+\), Mg\(^{2+}\), Na\(^+\), and Li\(^+\), at 100.0 \(\mu\)M were carried out. As shown in figure 2.22, no significant variation in the fluorescence intensity change was found by comparison with or without the other metal ions.

The detection limit of compound 10 as a fluorescent sensor for the analysis of Hg\(^{2+}\) ions was found to be 1 x \(10^{-7}\) M which was sufficiently low for the detection of submillimolar concentrations of Hg\(^{2+}\) ions as found in many chemical systems.

Figure 2.20 Fluorescence response of receptor 10 (1.0 \(\mu\)M) on addition of Hg\(^{2+}\) (10.0 \(\mu\)M) in THF, \(\lambda_{ex}=310\) nm. Inset: Showing the emission intensity of 10 (1x10^{-5} M) at 365 nm as a function of Hg\(^{2+}\) ions.

Figure 2.21 Fluorescence enhancement ratio (I-\(I_o/I_o\)*100 of receptor 10 (1.0 \(\mu\)M) at 310 nm upon addition of different metal ions (10.0 equiv, 10.0 \(\mu\)M) in THF.

Figure 2.22 Competitive selectivity of receptor 10 (1.0 \(\mu\)M) towards Hg\(^{2+}\) ions (10.0 \(\mu\)M) in the presence of other metal ions (100.0 \(\mu\)M).
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Fitting the changes in fluorescence spectra of compound 10 with Hg$^{2+}$ ions, using the nonlinear regression analysis program SPECFIT$^{29}$ gave a good fit and demonstrated that 1:1 stoichiometry (host: guest) was the most stable species in the solution with the binding constant ($\log \beta$) = 4.71. The method of continuous variation (Job’s plot)$^{28}$ was also used to prove the 1:1 stoichiometry (host: guest) (figure 2.23).

![Job's plot](image1)

**Figure 2.23** Job’s plot for determining the stoichiometry of receptor 10 and Hg$^{2+}$ ion in THF

![Fluorescence spectra](image2)

**Figure 2.24** Reversibility of Hg$^{2+}$ coordination to 10 by KI. Yellow line, free 10 (1.0 µM), pink line, 10 + 5 equiv Hg$^{2+}$, Blue line, 10 + 5 equiv Hg$^{2+}$ + 100 equiv KI, sky blue line, 10 + 5 equiv Hg$^{2+}$ + 100 equiv KI + 20 equiv Hg$^{2+}$.

![NMR spectrum](image3)

**Figure 2.25** Partial $^1$H NMR spectrum (CDCl$_3$–CD$_3$CN, 8:2) of receptor 10 before (a) and after (b) addition of Hg$^{2+}$ ions.

The fluorescence quantum yield$^{30}$ ($\Phi_F$) of compound 10 in the free and Hg$^{2+}$- bound state was found to be 0.001 and 0.45 respectively. The substantial increase in the quantum yield of compound 10 in the presence of 10.0 µM of Hg$^{2+}$ ions and its high
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Hg$^{2+}$ selectivity showed its credibility as a good Hg$^{2+}$ sensor. The reversibility experiment was also carried out which proved that Hg$^{2+}$ binding to compound 10 is reversible (figure 2.24). The binding of Hg$^{2+}$ ions with compound 10 has also been confirmed by NMR spectroscopy as there was a considerable downfield shift of imino protons by $\delta$ 1.8 ppm (figure 2.25). The corroborative evidence for the [10-Hg$^{2+}$] complex was observed in the mass spectrum of its solid complex which showed parent ion peak at 998 (M$^+$) corresponding to [10-Hg$^{2+}$].

The compound 11 consisting of both crown-5 and quinoline also showed high binding affinity for mercury. On adding 8.0 µM of Hg$^{2+}$ ions to the solution of compound 11 in THF, 5700% increase in the emission band was observed. Besides, a considerable red shift of 26 nm in the emission band was observed (figure 2.26). The fluorescence quantum yield$^{30}$ ($\Phi_F$) of compound 11 in the free and Hg$^{2+}$-bound state was found to be 0.001 and 0.58 respectively. Under the same conditions as used above for Hg$^{2+}$, the fluorescence enhancement effects of various metal ions (Sm$^{3+}$, Nd$^{3+}$, Pb$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^+$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, K$^+$, Mg$^{2+}$, Na$^+$ and Li$^+$) on compound 11 in THF were also investigated.

As shown in figure 2.27, no significant spectral changes of compound 11 occurred in the presence of these metal ions. The competition experiments revealed that Hg$^{2+}$ induced fluorescence response was unaffected in the background of 100.0 µM of other metal ions (figure 2.28). The possible interferences by other metal ions were assessed by measuring Hg$^{2+}$ induced fluorescence changes of compound 11 in the presence of background metal ions (Sm$^{3+}$, Nd$^{3+}$, Pb$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^+$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Co$^{2+}$,
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$Fe^{2+}$, $Fe^{3+}$, $K^+$, $Mg^{2+}$, $Na^+$ and $Li^+$ (figure 2.28). The compound 11 was found to have a detection limit of $1 \times 10^{-7}$ M for $Hg^{2+}$ ions, which was sufficiently low for the detection of $Hg^{2+}$ ions in many chemical and biological systems.

**Figure 2.28** Competitive selectivity of receptor 11 (1.0 µM) towards $Hg^{2+}$ ions (8.0 µM) in the presence of other metal ions (100.0 µM)

We also carried out a reversibility experiment that proved that $Hg^{2+}$ binding to compound 11 is reversible. In the presence of 100 equiv of KI, the iodide ion because of its strong affinity for the $Hg^{2+}$ ion, forms a complex with it, which results in decomplexation of the receptor $Hg^{2+}$ complex (figure 2.29). The method of continuous

![Reversibility of Hg²⁺ coordination to receptor 11 by KI. Yellow line, free 11 (1.0 µM), pink line, 11 + 10.0 equiv Hg²⁺, black line, 11 + 15.0 equiv Hg²⁺ + 50.0 equiv KI, blue line, 11 + 10.0 equiv Hg²⁺ + 50.0 equiv KI + 30.0 equiv Hg²⁺ ions](image)

![Job’s plot for determining the stoichiometry of receptor 11 and Hg²⁺ ions in THF](image)
variation (Job’s plot) was also used to prove the 1:1 stoichiometry (host: guest) (figure 2.30). The value of binding constant (log $\beta$) was found to be 4.57.

In conclusion, we designed, synthesized and evaluated new Hg$^{2+}$ selective fluorescent sensors 10 and 11 based on terphenyl appended with quinoline moieties which showed remarkable fluorescence enhancement in the presence of Hg$^{2+}$ ions.

To sum up the results of sections 2.2.1 and 2.2.2, we designed, synthesized and evaluated four new easily available ‘turn-on’ fluorescent sensors 5, 8, 10 and 11 based on terphenyl, which showed remarkable fluorescence enhancement in the presence of Hg$^{2+}$ ions and a high selectivity towards Hg$^{2+}$ ions over a wide range of metal ions in THF and mixed aqueous media (THF:H$_2$O, 9.5:0.5). The receptors 8 and 11 with crown moieties further increase the fluorescence enhancement by involvement of crown oxygens in PET phenomenon whereas in receptors 5 and 10, only imine units are involved in PET phenomenon. Also the receptors appended with quinoline as the fluorophore increase the fluorescence enhancement by increasing the soft metal binding sites in comparison to the receptors containing pyrene as the fluorophore. Moreover, the background metal ions showed small or no interference with the detection of Hg$^{2+}$ ions, indicating that the receptors could be used as an efficient Hg$^{2+}$ ion selective ‘turn-on’ fluorescent sensors, and subsequently found practical applications in chemical and biological systems.

### 2.2.3 Terphenyl based macrocycles having phenanthroline as a fluorophore

In sections 2.2.1 and 2.2.2, mercury selective terphenyl based podands appended with pyrene/quinoline fluorophores were discussed. In continuation of this work on terphenyl based receptors, in this part of investigation, we were interested to observe the binding behavior of macrocyclic systems based on terphenyl scaffold toward various cations and for this purpose we designed receptors 15 and 18 having phenanthroline moieties. Phenanthroline owning to its structural features such as planarity, rigidity, as well as intense fluorescence is an ideal candidate for applications in complexation studies with cations. Phenanthroline derivatives are among the most widely studied chemical systems owing to their applications in the synthesis of herbicides, pharmaceuticals, and analytical probes as well as their relevance in optoelectronic devices.

The receptors 15 and 18 were synthesized from diamines 13 and 17, respectively (Schemes 2.5 and 2.6). Suzuki-Miyaura cross coupling of compound 12 with
compound 2 catalyzed by Pd (II) furnished diamine 13 in 55% yields (Scheme 2.5). The $^1$H NMR spectrum of compound 13 showed one singlet (6H) for methoxy (OCH$_3$) group, one singlet, one doublet and one multiplet (2H, 4H, 4H) for aromatic protons of terphenyl moiety. The FAB mass spectrum showed a parent ion peak at 321(M+1$^+$)

Scheme 2.5

Using the same procedure as used for 13, we prepared compound 17 by Pd (II) catalyzed Suzuki-Miyaura coupling of 16 with boronic ester 2 in 60% yields (Scheme 2.6). The $^1$H NMR spectrum of compound 17

Scheme 2.6
showed two doublets and one multiplet (4H, 4H, 4H) for aromatic protons of terphenyl moiety. The FAB mass spectrum showed a parent ion peak at 260 (M⁺) corresponding to coupled product 17. Condensation of diamines 13 and 17 with 1.0 mol equiv. of phenanthroline dialdehyde in ethanol (100 ml) gave compounds 15 and 18 in 75% and 68% yields, respectively (Scheme 2.5 and 2.6). The products were separated as pure solids which gave a satisfactory elemental analysis.

The structures of compounds 15 and 18 were confirmed from their spectroscopic and analytical data. The ¹H NMR spectrum of compound 15 showed one singlet (12H) for methoxy protons, one singlet (4H) and two doublets (4H, 4H) for phenanthroline protons, one singlet (4H) and two doublets (8H, 8H) for terphenyl protons and one singlet (4H) for imino (N=CH) protons. The ¹H NMR spectrum of compound 18 showed one singlet (4H), three doublets (12H, 4H, 4H) and one multiplet (12H) for aromatic protons and one singlet (4H) for imino (N=CH) protons. In the FAB mass spectra, parent ion peaks were observed at 1041 (M⁺) and 921 (M⁺) corresponding to the condensation products 15 and 18, respectively. These spectroscopic data corroborate structures 15 and 18 for these compounds.

The binding behavior of compound 15 toward different cations (Pb²⁺, Hg²⁺, Ba²⁺, Cd²⁺, Ag⁺, Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺, K⁺, Mg²⁺, Na⁺ and Li⁺) was investigated by UV-Vis and fluorescence spectroscopy. The UV-Vis spectrum of compound 15 exhibited absorption bands at 217, 284 and 374 nm in THF. Among the various metal ions tested, the addition of Zn²⁺ and Cd²⁺ ions only, resulted in the formation of a red-shifted (Δλ = 56 nm) weak band at 430 nm with a clear isosbestic point at 398 nm (figures 2.31 & 2.32). This is attributed to the interactions of Zn²⁺/Cd²⁺ ions with
nitrogen atoms of imino and phenanthroline moieties leading to the intramolecular charge transfer (ICT) from the phenanthroline moiety to imino units.

In the fluorescence spectrum, the compound 15 (2.0 μM) exhibited a weak emission band centered at 438 nm when excited at $\lambda_{ex} = 280$ nm (figure 2.33). This weak emission from compound 15 is due to photo-induced electron transfer (PET) from the imino nitrogens to the photo excited phenanthroline units which leads to poor emission. On addition of zinc ions (5 equiv.), a significant fluorescence enhancement along with red shift of 22 nm occurred leading to the formation of an emission band at 457 nm. This is attributed to the modulation of the photo-induced charge (PCT) process induced by binding of Zn$^{2+}$ ions with nitrogen atoms of imino and phenanthroline moieties.

Under the same conditions as used for Zn$^{2+}$ ions, we also tested the fluorescence response of compound 15 to other metal ions (Pb$^{2+}$, Hg$^{2+}$, Ba$^{2+}$, Ag$^{+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$ and Li$^+$) and as shown in figure 2.34 (series 1), no significant change in fluorescence occurred in the presence of these metal ions. To test the practical applicability of compound 15 as a Zn$^{2+}$ selective sensor, competitive experiments were carried out in the presence of Zn$^{2+}$ ions at 25 μM mixed with the other metal ions at 100 μM and as shown in figure 2.34 (series 2), no significant variation in the fluorescence intensity was found by comparison with and without other metal ions.

Having done this we were interested to gain insight into the binding behavior of [15-Zn$^{2+}$] complex toward various anions (F$,\ CI$, Br$,\ I$, HSO$_4^-$, NO$_3^-$, H$_2$PO$_4^-$), as chemosensing ensemble approach is a kind of competitive approach for the design of
Fluorescent chemosensors for anions. We carried out the fluorescence titration experiments toward different anions with tetrabutylammonium as counter cation. Among all the anions tested, the change in the fluorescence intensity of $[15-\text{Zn}^{2+}]$ complex was observed on addition of $\text{F}^-$, $\text{CH}_3\text{COO}^-$, and $\text{HPO}_4^{2-}$ ions. The addition of all three anions $\text{F}^-$ (10.0 equiv), $\text{CH}_3\text{COO}^-$ (10.0 equiv) and $\text{H}_2\text{PO}_4$ (10.0 equiv) to the solution of $[15-\text{Zn}^{2+}]$ complex led to fluorescence quenching and finally reaching emission corresponding to that of compound 15 (figure 2.35).

Further, to observe, whether the binding of three anions is reversible in nature we again added $\text{Zn}^{2+}$ ions (100.0 equiv) to the solution containing $15-\text{Zn}^{2+}.\text{CH}_3\text{COO}^-$.
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$\text{Zn}^{2+} \cdot \text{F}^-/\text{H}_2\text{PO}_4^-$ species. The fluorescence emission was enhanced at 438 nm in case of $\text{F}^-$ and $\text{CH}_3\text{COO}^-$ ions while a blue shifted broad band appeared at 418 nm in case of $\text{H}_2\text{PO}_4^-$ ions (figure 2.36).

The above fluorescence behaviour of $\text{F}^-$/$\text{AcO}^-$ and $\text{H}_2\text{PO}_4^-$ ions is attributed to the binding of these anions with $\text{Zn}^{2+}$ ions of $[\text{15-Zn}]$ complex resulting in the decomplexation of $\text{Zn}^{2+}$ ions, due to which the fluorescence emission of the receptor 15 gets quenched. The revival of fluorescence intensity on further addition of $\text{Zn}^{2+}$ ions in case of $\text{F}^-$/$\text{AcO}^-$ is ascribed to the binding of $\text{Zn}^{2+}$ with nitrogen atoms of imine and phenanthroline moieties. However, in case of $\text{H}_2\text{PO}_4^-$, we observed contrasting

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**Figure 2.36** Fluorescence spectra of receptor 15 (2.0 $\mu$M) on addition of $\text{Zn}^{2+}$ ions (100.0 equiv) in presence of $\text{H}_2\text{PO}_4^-$ ions (10.0 equiv) in THF as solvent; $\lambda_{ex} = 300$ nm

**Figure 2.37** Fluorescence spectra of receptor 15 (2.0 $\mu$M) on addition of $\text{H}_2\text{PO}_4^-$ ions (100.0 equiv) in THF as solvent
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behaviour due to binding of protons of \(H_2PO_4^-\) to the imino nitrogen atoms and nitrogen of phenanthroline moiety. This was confirmed from the fluorescence titration experiment of \(H_2PO_4^-\) with free ligand 15 where in enhancement of fluorescence emission was observed (figure 2.37). This enhancement in the fluorescence emission could be ascribed to the binding of \(H_2PO_4^-\) to the imino nitrogen atoms and nitrogen atoms of phenanthroline moiety resulting in inhibition of PET.

To further strengthen this mechanism, we also synthesized a model compound 17 in which methoxy groups were not present and studied its fluorescence behavior in the presence of \(Zn^{2+}\) and \(H_2PO_4^-\) ions. On addition of \(Zn^{2+}\) ions to compound 17, a fluorescence of receptor 17 gets enhanced at \(\lambda_{em} = 414\) nm (figure 2.38) which got quenched with a red shift in the emission in the presence of \(H_2PO_4^-\) ions. This behavior was similar to the fluorescence response of compound 15. But on addition of \(Zn^{2+}\) ions again, no blue shifted band was obtained (figure 2.39). These results support our proposed mechanism.

**Figure 2.38** Fluorescence spectra of receptor 17 (2.0 \(\mu\)M) on addition of \(Zn^{2+}\) ions (20.0 equiv) in THF as solvent; \(\lambda_{ex} = 300\) nm

**Figure 2.39** Fluorescence spectra of 17-\(Zn\) ensemble (2.0 \(\mu\)M) on addition of \(H_2PO_4^-\) (50.0 equiv) in THF as solvent; \(\lambda_{ex} = 300\) nm

We propose that \(Zn^{2+}\) ions interact with \(H_2PO_4^-\) and hence interaction between \(Zn^{2+}\) and receptor 15 gets weakened (Scheme 2.7). As a result, PET gets operational and fluorescence gets quenched. On further addition of \(Zn^{2+}\) ions, \(Zn^{2+}\) ions will also bind to methoxy groups, as a result of which fluorescence revives again with a blue shift.
Thus, terphenyl–phenanthroline based macrocycle has been synthesized as a selective ‘turn-on’ sensor for Zn$^{2+}$ ions. In the presence of H$_2$PO$_4^-$ in Zn complex, binding preference for Zn$^{2+}$ get shifted to methoxy groups leading to blue shifted band.

2.2.4 Terphenyl based fluorescent chemosensors for Cu$^{2+}$ and F$^-$ employing excited state intramolecular proton transfer

In the sections 2.2.1, 2.2.2 and 2.2.3, we reported synthesis and binding behavior of terphenyl based chemosensors appended with different fluorophores for sensing of mercury and zinc ions. However, the design and synthesis of chemosensors for both anions as well as cations is an important area of research within the field of supramolecular chemistry. So, in this part of investigation, we synthesized bifunctional receptors based on terphenyls which can recognize cations as well as anions.

The different kinds of signalling mechanisms including internal charge transfer (ICT), photo-induced electron transfer (PET), metal-to-ligand charge transfer (MLCT), excimer/exciplex formation, and tuning proton transfer have been
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utilized for designing fluorescent chemosensors. Recently, fluorescent chemosensors based on excited state intramolecular proton transfer (ESIPT) has achieved a significant interest in the fundamental investigation and the applications of organic molecules because of their four level photophysical scheme involving ground and excited state of two tautomers, spectral sensitivity to the surrounding medium and a large Stokes’ shifted fluorescence.\(^4\) The ESIPT chromophores exist in the cis-enol form at the ground state, in which the intramolecular hydrogen bond is formed. Upon photoexcitation, the singlet excited state of the enol form is populated. Then an ultrafast ESIPT process occurs and the cis-keto form at the singlet excited state is produced, which is stabilized by the intramolecular hydrogen bond (figure 2.40). Thus, ESIPT process involves a phototautomerization reaction to yield an excited keto form in the subpicosecond time region, with the molecule changing from the original enol form to the keto form on photoirradiation.\(^2\) The intramolecularly hydrogen bonded chromophores generally exhibit this process. Utilizing this concept, we designed receptor \(20a\) for this purpose. In addition, we also designed and synthesized model compounds \(20b, 20c\) and \(21\). All these receptors have imine moieties for binding of soft metal ions while the binding with anions is dependent upon the phenolic moieties in the receptors. The presence of electron withdrawing nitro group is expected to increase the acidity of phenols and hence the hydrogen bond donor properties of the receptors can be fine tuned for sensing of anions.

Condensation of diamine 3 with 2.2 mol equiv. of aldehydes \(19a-c\) in ethanol furnished target compounds \(20a-c\) (Scheme 2.8). The structures of compounds \(20a-c\) were confirmed from their spectroscopic and analytical data. The \(^1\)H NMR spectrum of compound \(20a\) showed two singlets (18H, 12H) for tert-butyldimethylsilyl (TBS) group, one singlet (2H) and one doublet (8H) for aromatic protons of terphenyl moiety, two doublets (2H, 2H) and one singlet (2H) for
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nitrosalicylaldehyde protons, one singlet (2H) for imino (N=CH) protons and one singlet (2H) for hydroxyl protons. The \(^1\)H NMR spectrum of compound 20b showed two singlets (18H, 12H) for tert-butylidemethylsilyl (TBS) group, one singlet (6H) for methoxy protons, three singlets (2H, 8H, 2H) and two doublets (2H, 2H) for aromatic protons and one singlet (2H) for imino protons. The \(^1\)H NMR spectrum of compound 20c showed two singlets (18H, 12H) for tert-butylidemethylsilyl (TBS) group, two singlets (2H, 10H), one doublet (2H) and one multiplet (4H) for aromatic protons, one singlet (2H) for imino (N=CH) protons and one singlet (2H) for hydroxyl protons. Similarly, the condensation of diamine 7 with 2.2 mol equiv. of 19a in ethanol furnished compound 21 (Scheme 2.10).
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The $^1$H NMR spectrum of compound 21 showed one singlet and two triplets (8H, 4H, 4H) for crown protons, two singlets (2H, 2H) and three doublets (2H, 8H, 2H) for aromatic protons, one singlet (2H) for imino (N=CH) protons and one singlet (2H) for hydroxyl protons. The IR spectra of compound 20a-c and 21 showed C=N stretching bands at 1630, 1632, 1633 and 1632 cm$^{-1}$, respectively. In the FAB mass spectra, the molecular ion peaks were observed at 819 (M$^+$) for 20a, 847 (M$^+$) for 20b, 730 (M$^+$) for 20c and 748 for 21, which correspond to 1:2 condensation products. These spectroscopic data corroborate the structures 20a-c and 21 for these compounds.

The binding behaviour of compound 20a toward different cations (Pb$^{2+}$, Hg$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Ag$^+$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$ and Li$^+$) was investigated by UV-Vis and fluorescence spectroscopy. The titration experiments were carried out in mixed aqueous media (THF: H$_2$O; 9:1). The UV–Vis spectrum of the compound 20a exhibited absorption bands at 210 nm, 265 nm and 342 nm in THF/H$_2$O (9:1) (figure 2.41). The band at 210 nm was ascribed to the excitation of $\pi$-electrons of the aromatic system. The band at 265 nm was due to the transition between the $\pi$ orbitals localized on the imine (C=N) linkage. The third band at 342 nm may occur due to the intramolecular charge transfer (ICT) transitions within the whole structure of the Schiff’s base.$^{43}$

Among the various metal ions tested, the addition of Cu$^{2+}$ (10.0 equiv) ions only, resulted in a slight red shift (9 nm) of absorption band at 342 nm to 351 nm (figure 2.41). This is presumably because of intramolecular charge transfer interactions between phenolic OH and Cu$^{2+}$ bound imino nitrogen (figure 2.43).
In the fluorescence spectrum, the compound 20a (2.0 µM) exhibited an emission band centered at 517 nm when excited at 360 nm which can be attributed to a very fast enol-imine 20a to keto-amine 20aa tautomerism involving the phenomenon of excited state intramolecular proton transfer (ESIPT) (Scheme 2.9). To confirm the keto-enol tautomerism, a reference compound 20b was synthesized in which the phenolic hydroxyl groups of compound 20a were protected by methyl groups. On excitation at 360 nm, the compound 20b did not exhibit any band at 517 nm. This experiment confirms the presence of ESIPT phenomenon in compound 20a. Upon addition of increasing amounts of Cu$^{2+}$ ions (5.0 µM) to the solution of compound 20a in mixed aqueous media (THF: H$_2$O; 9: 1), the fluorescence intensity was found to be completely quenched (figure 2.42) indicating the formation of [20a-Cu$^{2+}$] complex (figure 2.43). This may be due to the coordination of Cu$^{2+}$ ions to imino nitrogens leading to the prohibition of ESIPT phenomenon and hence fluorescence quenching.

**Figure 2.43.** Schematic representation of the complexation process for 20a with Cu$^{2+}$ ions

![Figure 2.43](image)

**Figure 2.44** Fluorescence quenching ratio (Io-I/Io) x 100 of receptor 20a (2.0 µM) at 517 nm upon addition of different metal ions (10.0 µM)

**Figure 2.45** Competitive selectivity of receptor 20a (2.0 µM) towards Cu$^{2+}$ (5.0 µM) in the presence of other metal ions (150.0 µM)
Under the same conditions as used for Cu\(^{2+}\) ions, we also tested the fluorescence response of compound 20a to other metal ions (Pb\(^{2+}\), Hg\(^{2+}\), Ba\(^{2+}\), Cd\(^{2+}\), Ag\(^{+}\), Zn\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), K\(^{+}\), Mg\(^{2+}\), Na\(^{+}\) and Li\(^{+}\)) and as shown in figure 2.44, no significant change in fluorescence occurred in the presence of these metal ions. To test the practical applicability of compound 22a as a Cu\(^{2+}\) selective sensor, competitive experiments were carried out in the presence of Cu\(^{2+}\) ions at 5.0 µM mixed with the other metal ions at 150.0 µM as shown in figure 2.45, no significant variation in fluorescence intensity was found by comparison with or without other metal ions.

We also carried out a reversibility experiment which proved that Cu\(^{2+}\) binding to compound 20a is reversible. In the presence of 20.0 equiv of EDTA, Cu\(^{2+}\) ions formed complex with EDTA, resulting in the decomplexation of receptor-Cu\(^{2+}\) complex, as a result of which the fluorescence emission of the receptor was revived again. On adding Cu\(^{2+}\) ions again to the above solution, the fluorescence of receptor 20a was quenched indicating the reversible complexation of Cu\(^{2+}\) with the receptor 20a (figure 2.46). The detection limit of 20a as a fluorescent sensor for the analysis of Cu\(^{2+}\) ions was determined from a plot of fluorescence intensity as a function of the concentration of added metal ions and was found to be 100 nM which is sufficiently low for the detection of nanomolar concentration range of Cu\(^{2+}\) ions found in many chemical systems.

Fitting the changes in fluorescence spectra of compound 20a with Cu\(^{2+}\) ions, using the nonlinear regression analysis program SPECFIT gave a good fit and demonstrated
that 1:1 stoichiometry (host: guest) was the most stable species in the solution with the binding constant \((\log \beta) = 5.40\). The method of continuous variation (Job’s plot)\(^{28}\) was also used to prove the 1:1 stoichiometry (host: guest) (figure 2.47).

Recently, it has been reported that hydroxyl groups of serine and tyrosine play an important role in anion binding pockets of biological systems like ClC chloride channels\(^{28}\) and halorhodopsin.\(^{29}\) Keeping in view the important role played by hydroxyl groups in the binding pockets of the biological systems, the development of receptors having hydroxyl groups for recognition of anions is very important in supramolecular chemistry.\(^{30}\) Since our receptor 20a has reasonably acidic phenolic moieties, we also investigated the sensing properties of compound 20a toward different anions (\(\text{F}^-, \text{Cl}^-, \text{Br}^-, \Gamma, \text{HSO}_4^-, \text{NO}_3^-, \text{and} \text{H}_2\text{PO}_4^-\)) with tetrabutylammonium as counter cation using UV-Vis, fluorescence and NMR experiments.

In the UV-Vis spectrum of the compound 20a, the addition of increasing amounts of \(\text{F}^-\) ions (3.0 \(\mu\)M) resulted in a decrease in absorption at 265 nm and 342 nm along with the formation of new red-shifted band at 447 nm with a clear isosbestic point at 379 nm (figure 2.48). Besides, a colorimetric change from colorless to yellow was also observed by the naked eye (inset figure 2.48). When the \(\text{F}^-\) ions come in contact with compound 20a, the intermolecular proton transfer takes place between phenolic oxygens and fluoride ions. The modulation in the electron donating abilities of phenolic oxygen in the presence and absence of fluoride ions directly influences the intramolecular charge transfer (ICT) from the phenolic oxygen to the electron deficient

![Image](image1.png)

**Figure 2.48** UV-Vis spectra of compound 20a (10.0 \(\mu\)M) on addition of \(\text{F}^-\) ions (3.0 equiv) in THF; Inset showing the change in the color of receptor 20a (1x10\(^{-5}\) M) upon addition of \(\text{F}^-\) ions (3.0 \(\mu\)M)

![Image](image2.png)

**Figure 2.49** Changes in fluorescence emission spectra of 20a (2.0 \(\mu\)M) upon addition of \(\text{F}^-\) ions (350.0 \(\mu\)M) in THF; \(\lambda_{ex} = 360\) nm
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$p$-nitrophenyl moiety. In the absence of fluoride ions, ICT is inefficient while in the presence of fluoride ions, ICT is facilitated by proton transfer from phenolic oxygen to fluoride ions. Thus, we propose that the spectral changes in figure 2.48 are due to the deprotonation of the phenolic protons, which results in enhanced charge transfer interactions between electron rich and electron deficient moieties resulting in visible color change. Similar results were obtained when tetrabutylammonium hydroxide was specifically employed. This further confirms our doubt that the proton transfer between phenolic oxygen and the fluoride ions is responsible for the observed change. Similarly, UV-Vis experiments were carried out in the presence of the other anions (Cl\(^-\), Br\(^-\), I\(^-\), HSO\(_4\)^-, NO\(_3\)^-, and H\(_2\)PO\(_4\)^-), besides F\(^-\) ion but no significant change in UV-Vis spectra of 20a was observed.

In the fluorescence spectrum, addition of F\(^-\) ions (5.0 \(\mu\)M) in compound 20a leads to a significant decrease in the emission band at 517 nm in THF. On further addition of F\(^-\) ions (350.0 \(\mu\)M), a new blue shifted band centered at 478 nm appeared (figure 2.49). We propose that this fluorescence response of compound 20a is due to the modulation of the existing ESIPT state by the interaction of F\(^-\) ions along with the simultaneous desilylation reaction of compound 20a in the presence of F\(^-\) ions in THF. The quenching of emission band of 20a at 517 nm on addition of F\(^-\) ions indicates that the presence of F\(^-\) ions completely inhibits ESIPT phenomenon. This inhibition of ESIPT phenomenon is ascribed to the intermolecular proton transfer from phenolic oxygen to the F\(^-\) ions. The formation of new band at 478 nm is due to the cleavage of Si-O bond which results in increased negative charge on oxygen atoms leading to the charge delocalization of the system. To confirm this assumption and evaluate the intermolecular interactions between the compound 20a and F\(^-\) ions, we carried out NMR studies in CDCl\(_3\). It was found that on addition of tetrabutylammonium fluoride to the solution of compound 20a in CDCl\(_3\), signal of phenolic hydroxyl groups at \(\delta\) 14.4 disappeared which indicates that the deprotonation occurred on addition of F\(^-\) ions. The signals due to OTBS group also disappeared in the presence of F\(^-\) ions indicating that desilylation has taken place on addition of F\(^-\) ions.

To further investigate the binding mechanism of receptor 20a towards Cu\(^{2+}\) and F\(^-\) ions, we also synthesized model compounds 20c and 21. The compound 20c contains relatively weak acidic phenolic protons whereas in compound 21, OTBS groups were replaced by crown-5 ring.
Compound 21 showed similar fluorescence quenching on addition of Cu$^{2+}$ ions as was found in compound 20a in the presence of Cu$^{2+}$ ions (figure 2.50) whereas, on addition of F$^-$ ions, the fluorescence intensity of receptor 21 got quenched, however, no new band was formed at 478 nm (figure 2.51). This indicates that OTBS groups in compound 20a are involved in the formation of new band at 478 nm in the presence of F$^-$ ions (figure 2.52).

On the other hand, in compound 20c which lacks crown-5 ring and nitro groups (NO$_2$) but have OTBS groups showed very weak emission indicating that PET from imino nitrogen to phenol predominates. The addition of F$^-$ ions (400.0 µM) to the solution of 20c (2.0 µM) in THF resulted in the formation of a new band at 478 nm as was observed in 20a which confirms that the desilylation is responsible for fluorescence enhancement (figure 2.52).
Thus from above two control experiments we conclude that the presence of nitro groups in receptor 20a makes the phenolic protons relatively more acidic which is responsible for emission at 517 nm. The behavior of model compounds 21 and 20c illustrate the importance of OTBS groups in compound 20a responsible for blue shifted band.

Under the same conditions as used for F$^-$ ions, we also tested the fluorescence response of compound 20a to other anions (Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, NO$_3^-$, and H$_2$PO$_4^-$) and as shown in figure 2.53, no significant fluorescence change was observed in the presence of these anions. The practical applicability of compound 20a as a F$^-$ selective fluorescence sensor was tested by carrying out competitive experiments in the presence of F$^-$ ions mixed with Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, NO$_3^-$, and H$_2$PO$_4^-$ ions. No significant variation in fluorescence intensity change was found by comparison with or without other anions besides, F$^-$ ions (figure 2.54). The detection limit of compound 20a as a fluorescence sensor for the analysis of F$^-$ ions was found to be 10 nM which is sufficiently low for the detection of nanomolar concentration range of F$^-$ ions found in many chemical systems.

In conclusion, we have synthesized a highly selective fluorescent chemosensor for Cu$^{2+}$ and F$^-$ ions based on terphenyl as a scaffold employing ESIPT. The recognition of Cu$^{2+}$ ions give rise to the quenched fluorescence of receptor 20a whereas F$^-$ ions recognition leads to the appearance of a blue shifted band at 478 nm. The detection limits for Cu$^{2+}$ and F$^-$ ions were found to be 100 nM and 10 nM, respectively. Thus
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receptor 20a may be considered as a potential bifunctional fluorescent chemosensor for Cu$^{2+}$ and F$^-$ ions.

To sum up, in chapter 2 we designed and synthesized a number of chemosensors based on terphenyl scaffold having imine units and possessing different types of fluorophores viz. pyrene, quinoline, phenanthroline, salicylaldehyde, nitrosalicylaldehyde and 5-nitro-2-methoxybenzaldehyde. The various chemosensors behaved as molecular switches on addition of various metal ions. The pyrene and quinoline appended terphenyl derivatives were highly selective for Hg$^{2+}$ ions. Moreover, these receptors showed selective ‘turn-on’ response to Hg$^{2+}$ ions which could be utilized to detect trace amounts of Hg$^{2+}$ ions in biological systems. Terphenyl based macrocycle formed by appending phenanthroline showed ‘turn-on’ fluorescence enhancement in the presence of Zn$^{2+}$ ions. In the presence of H$_2$PO$_4^-$ the binding preference of Zn$^{2+}$ for receptor 15 gets modulated and hence shows a blue shifted band on addition of Zn$^{2+}$ ions. Besides, a bifunctional receptor based on terphenyl was also synthesized using ESIPT phenomenon which selectively detected Cu$^{2+}$ ions and F$^-$ ions in contrasting modes. The receptor showed fluorescence quenching in the presence of Cu$^{2+}$ ions. Similarly, on addition of F$^-$ ions (5 µM), the fluorescence of receptor got quenched but addition of higher equivalents of F$^-$ ions (350 µM) leads to a blue shifted band owning to desilylation mechanism.

2.3 Experimental

2.3.1 General methods and instrumentations

Physical measurements: Most of the chemicals and reagents were obtained from Sigma-Aldrich and were used as such without further purification. Solvents for carrying out reactions and studies were dried prior to use. Tetrahydrofuran was dried by refluxing it over sodium metal and benzophenone for 5h and then fractionally distilled. Dichloromethane was shaken with portions of conc. H$_2$SO$_4$ until the acid layer remained colourless, washed with water, aqueous 5% Na$_2$CO$_3$ and then with water again. Pre-dried with CaCl$_2$, and then distilled from CaSO$_4$ to get dry dichloromethane. Melting points were determined in capillaries and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using CDCl$_3$/C$_2$D$_2$Cl$_4$/CD$_3$CN as solvent and TMS as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constants (Hz),
integration, and interpretation. Elemental analysis was done using Flash EA 1112 CHNS-O analyzer of Thermo Electron Corporation. IR spectra were recorded with Shimadzu FTIR 8400S IR spectrophotometer by using KBr as medium. UV-Vis spectra were recorded on SHIMADZU UV-2450 PC spectrophotometer with a quartz cuvette (path length: 1 cm). The cell holder was thermostatted at 25°C. All the fluorescence spectra were recorded on SHIMADZU RF-5301 PC spectrofluorometer.

UV-Vis and fluorescence titrations

UV-Vis titrations were performed on 1x10^{-5} M solution of ligands 5, 8, 10, 11, 15, 18, 20a-c and 21 in THF. Fluorescence titrations were performed using 10^{-6} M solutions of ligands 5 and 8 in THF: H_{2}O (9.5:0.5) and 10, 11, 15, 18, 20a-c, 21 in THF. Typically, aliquots of freshly prepared M(ClO_{4})_{2} (M= Sm^{3+}, Nd^{3+}, Pb^{2+}, Hg^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Fe^{2+}, K^{+}, Mg^{2+}, Na^{+}, and Li^{+}) standard solutions (10^{-1} to 10^{-4} M) in THF were added and the fluorescence spectra of the samples were recorded. THF was dried over sodium and benzophenone for the studies.

\[ ^1H \text{ NMR experiments} \]

Stock solutions (10 mM) of receptors were prepared in CDCl_{3}/CD_{3}CN (8:2). Similarly, stock solutions (20 mM) of cations (Hg^{2+}, Zn^{2+}) perchlorate salts were prepared in CDCl_{3}/CD_{3}CN (8:2) for \[^1H\] NMR experiments. The stock solutions (20 mM) of anions (H_{2}PO_{4}^{-}, F^{-}) were prepared in CDCl_{3}.

2.3.2 Stoichiometry of terphenyl based complexes

The stoichiometry of various complexes of terphenyl derivatives designated as ‘molecular hosts’ (chapter 2: 5, 8, 10, 11, 15, 18, 20a-c and 21; chapter 3: 23, 24, 28 and 31) with cations and anions as ‘guests’ were determined by using method of continuous variation (Job’s Plot). The total concentration of molecular host ‘H’ and guest ‘G’ was constant (2.5 x 10^{-5} M), with a continuous variable molar fraction of guest ([G]/[H] + [G]). For 1:1 stoichiometry, molar fraction of guest should be 0.5 while for 1:2 stoichiometry molar fraction of guest should be 0.7.

2.3.3 Binding constants of terphenyl based complexes

The binding constants (log \( \beta \)) of different terphenyl derivatives (chapter 2: 5, 8, 10, 11, 15, 18, 20a-c and 21; chapter 3: 23, 24, 28 and 31) with cations and anions were calculated from fluorescence titration experiments by means of SPECFIT programme (global analysis system V3.0 for 32-bit Window system), which uses singular value
decomposition and non-linear regression modelling by the Leverberg-Marquardt method.

2.3.4 Fluorescence quantum yield

Fluorescence quantum yield $\phi_f$ was determined in analytical grade THF using optically matching solutions of resublimed pyrene ($\phi_{fr} = 0.65$ in ethanol as the standard at an excitation wavelength ($\lambda_{ex}$) of 343 nm for compounds 5 and 8, quinine sulphate ($\phi_{fr} = 0.546$ in 0.5 M H$_2$SO$_4$ as the standard at $\lambda_{ex} = 310$ nm for compounds 10 and 11, anthracene ($\phi_{fr} = 0.27$ in ethanol at $\lambda_{ex} = 300$ nm for compounds 15 and 18, naphthalene ($\phi_{fr} = 0.21$ in ethanol at 345 nm and rhodamine B ($\Phi_{fr} = 0.49$ in ethanol at 550 nm. The quantum yield was calculated using following equation 1.

$$\phi_s = \phi_{fr} \times \frac{1-10^{-\alpha_d}}{1-10^{-\alpha_d}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Equation 1

The quantum yields are measured at room temperature at their respective excitation wavelength coming from Xenon lamp of the spectrofluorophotometer and calculated according to the above equation. $\phi_{fr}$ is the radiative quantum yield of the sample, $\phi_{fr}$ radiative quantum yield of reference, $A_s$ and $A_r$ are the absorbance of the sample and the reference respectively, $D_s$ and $D_r$ the respective areas of emission for sample and reference. $L_s$ and $L_r$ are the lengths of the absorption cells respectively. $N_s$ and $N_r$ are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively.

2.3.5 ISE membrane preparation and potential measurement

Membranes were prepared using DOS (plasticizer), PVC, ionophore (5) and N-butyl-3-methylimidazolium hexafluorophosphate (additive) dissolved in dry THF and evaporated slowly. The potentiometric cell used was Ag|AgCl| 1.031022 M NaCl| PVC membrane| test solution| Ag| AgCl.

Membranes were conditioned in 0.01 M NaCl for 12h and deionised water for half an hour prior to ISE titrations, unless stated otherwise. The pH of the solution was varied using HNO$_3$/hexamine solutions.
2.3.6 Synthesis of various terphenyl derivatives

Synthesis of 4,5-dibromo-1,2-bis(tert-butyldimethylsilyloxy)benzene (1): To the solution of dibromocatechol (2.0 g, 7.46 mmol) and imidazole (2.08 g, 2.98 mmol) in DMF (dry) was added tert-butyldimethylsilyloxychloride (3.38 g, 22.38 mmol) in small proportions and the reaction mixture was stirred for 12h at room temperature. The resulting mixture was then treated with water, extracted with ethyl acetate, and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound was purified by column chromatography using hexane as an eluent to give 2.0 g of compound 1 as pure liquid.

Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2dioxaborolane-2-yl)aniline (2): To a suspension of [PdCl₂(PPh₃)₂] (5.08 g, 39.73 mmol) in dioxane (15 ml) were added 4-bromoaniline (2.5 g, 14.45 mmol), 4,4,5,5- tetramethyl-1,3,2-dioxaborolane (5.087 g, 39.74 mmol), and triethylamine (5.83 g, 57.8 mmol) under argon. After stirring for 5 h at 80 ºC, dioxane was removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound was purified by column chromatography using dichloromethane as an eluent to give 2.3 g (75%) of compound 2 as brown solid. mp: 160 ºC; ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.32 (s, 12H, C(CH₃)₂), 3.83 (s, 2H, NH₂), 6.61 (d, J = 6 Hz, 2H, ArH), 7.62 (d, J = 6 Hz, 2H, ArH); ¹³C NMR (300 MHz, CDCl₃): d 24.82, 83.28, 114.06, 136.39, 149.26; MS (FAB): 219 (M⁺).

Synthesis of 4, 4"-diamino-4’,5’-Bis (tert-butyldimethylsilyloxy) 1,1’,2’,1"-terphenyl (3): To a solution of compound 2 (1.1 g, 5.03 mmol) and compound 1 (1.0 g, 2.20 mmol) in dioxane were added K₂CO₃ (1.10 g, 8.02 mmol), distilled H₂O (10 ml), and [Pd(Cl)₂(PPh₃)₂] (0.21 g, 0.302 mmol) under argon and the reaction mixture was then refluxed overnight. The dioxane was then removed under vacuum and the residue so obtained was treated with
water, extracted with dichloromethane, and dried over anhydrous Na$_2$SO$_4$. The organic layer was evaporated and the compound was purified by column chromatography using dichloromethane–ethyl acetate mixture (10:1, v/v) as eluent to give 0.627 g (60%) of compound 3 as light yellow solid. **mp**: 150 °C; **$^1$H NMR** (300 MHz, CDCl$_3$, ppm): δ 0.23 (s, 12H, Si(CH$_3$)$_2$), 1.00 (s, 18H, C(CH$_3$)$_3$), 3.57 (br, 4H, NH$_2$), 6.53 (d, J = 9 Hz, 4H, ArH), 6.80 (s, 2H, ArH), 6.87 (d, J = 9 Hz, 4H, ArH); **$^{13}$C NMR** (75 MHz, CDCl$_3$): δ -4.02, 18.42, 25.96, 114.66, 122.84, 130.69, 132.20, 133.41, 144.30, 145.37; **MS** (FAB): 520 (M$^+$), 522 (M+2$^+$); **Anal. Calcd** for C$_{30}$H$_{44}$N$_2$O$_2$Si$_2$: C, 69.18; H, 8.51; N, 5.38. Found: C, 68.98; H, 8.23; N, 5.09.

**Synthesis of ((4',5'-bis(tert-butyldimethylsilyloxy)4''-bis(2-(pyreneimino)-1,1',2',1"-terphenyl) {5}:** 1-Pyrenecarbaldehyde (4) (0.046 mg, 0.201 mmol) was added portion wise to a stirred solution of diamine 3 (0.050 mg, 0.096 mmol) in ethanol (15 ml). The resulting reaction mixture was refluxed for 1h during which a yellow solid was obtained. The solid compound was filtered and washed with ethanol (10 ml) to give 0.068 mg (75%) of 5 as yellow solid. **mp**: > 280 °C; **IR** $v_{max}$ (KBr, cm$^{-1}$): 1632 (C = N); **$^1$H NMR** (300 MHz, CDCl$_3$, ppm): δ 0.31 (12H, s, Si(CH$_3$)$_2$), 1.06 (18H, s, C(CH$_3$)$_3$), 6.99 (2H, s, ArH), 7.27 (4H, s, ArH), 7.60–8.36 (18H, m, ArH), 8.91 (2H, d, ArH), 9.05 (2H, s, N=CH); **$^{13}$C NMR** (75 MHz, CDCl$_3$, cm$^{-1}$): δ -3.93, -3.97, 18.52, 26.01, 114.80, 120.69, 120.87, 122.49, 123.03, 123.20, 124.62, 124.90, 125.05, 125.86, 126.09, 126.18, 126.68, 127.05, 127.47, 127.58, 128.97, 130.58, 130.83, 131.25, 132.29, 133.37, 139.45, 150.66, 158.32; **MS** (FAB): 945 (M$^{+}$); **Anal. Calcd** for C$_{64}$H$_{60}$N$_2$O$_2$Si$_2$: C, 81.31; H, 6.40; N, 2.96. Found: C, 81.03; H, 6.06; N, 2.7.

**Synthesis of 4,5-dibromo benzo[15]crown 5 {6}:** A mixture of 3,4 dibromocatechol (2.0 g, 7.46 mmol), K$_2$CO$_3$ (2.0 g, 14.92 mmol), tetraethyleneglycol ditosylate (5.31 g, 11.19 mmol) and catalytic amount of 18-crown-6 in 25 ml of dry THF was refluxed for 24h. After the completion of reaction, the solvent was removed and the residue
so obtained was treated with water, extracted with dichloromethane and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound was purified by column chromatography using ethyl acetate and hexane mixture (3:7, v/v) as an eluent to give 1.81 g (57%) of compound 6 as white solid. **mp**: 85-90 °C. **¹H NMR** (300 MHz, CDCl₃, ppm): δ 3.74 (s, 8H, crownH), 3.89 (t, 4H, crownH), 4.09 (t, 4H, crownH), 7.07 (s, 2H, ArH); **¹³C NMR** (75 MHz, CDCl₃, ppm): 69.2, 69.3, 70.3, 71.0, 115.1, 118.4, 149.0; **Anal. Calcd** for C₁₄H₁₈Br₂O₅: C, 39.46; H, 4.26. Found: C, 39.01; H, 4.12

**Synthesis of 4,5-bis (4’,4”-diaminophenyl)benzo[15]crown 5 {7}:** To a solution of 6 (1.00 g, 2.34 mmol) and 2 (1.29 g, 5.86 mmol) in dioxane were added K₂CO₃ (0.85 g, 9.36 mmol), distilled H₂O (8mL), and [Pd (Cl)₂(PPh₃)₂] (0.36 g, 0.51 mmol) under argon and the reaction mixture was refluxed overnight. The dioxane was then removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound was purified by column chromatography using ethyl acetate as an eluent to give 0.58 g (55%) of compound 7 as white solid. **mp**: 220°C. **¹H NMR** (300 MHz, CDCl₃, ppm): δ 3.52 (br, 2H, NH₂), 3.78 (s, 8H, crownH), 3.92 (t, 4H, J = 4.5 Hz, crownH), 4.18 (t, 4H, J = 4.5 Hz, crownH), 6.54 (m, 4H, ArH), 6.86 (s, 2H, ArH), 6.90 (m, 4H, ArH). **¹³C NMR** (75 MHz, CDCl₃, ppm): 68.63, 68.91, 69.76, 70.25, 113.68, 115.89, 129.61, 129.88, 129.88, 133.03, 145.69, 146.99. **MS** (FAB): 450 (M⁺). **Anal. Calcd** for C₂₆H₃₀N₂O₅: C, 69.31; H, 6.71; N, 6.22. Found: C, 68.95; H, 7.06; N, 5.90.

**Synthesis of 4,5-bis(4’,4”-bis[2-(pyrene)iminophenyl]benzo[15]crown-5 {8}:** Compound 8 was synthesized by portion wise addition of 1-pyrenecarbaldehyde 4 (0.064 g, 0.28 mmol) to the stirred solution of diamine 7 (0.06 g, 0.13 mmol) in ethanol (10 mL). The resulting reaction mixture was stirred at room temperature for 1h during which a yellow solid was obtained. The solid compound was filtered and washed with ethanol to give 0.085 g (74%) of compound 8. **mp**: 190 °C. **¹H NMR** (300 MHz, CDCl₃, ppm): δ 3.82 (s, 8H, crownH), 3.98 (t, 4H, J = 4.5 Hz, crownH), 4.27 (t, 4H, J = 4.5 Hz, crownH), 7.05 (s, 2H, ArH), 7.26 (m, 8H, ArH), 8.01 - 8.25 (m,
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14H, pyreneH), 8.75 (d, 2H, \( J = 7.8 \) Hz, pyreneH), 9.03 (d, 2H, \( J = 9.3 \) Hz, pyreneH), 9.53 (s, 2H, imineH). 13C NMR (300 MHz, CDCl3, ppm): 69.29, 69.60, 70.51, 71.10, 116.41, 120.92, 122.38, 124.53, 124.82, 124.99, 125.85, 126.08, 126.15, 126.61, 127.42, 128.44, 128.95, 130.50, 130.88, 131.18, 133.22, 133.34, 139.36, 148.42, 150.79, 158.39. IR \( \nu_{\text{max}} \) (CHCl3, cm\(^{-1}\)): 1632 (C=N). MS (FAB): 875 (M\(^+\)). Anal. Calcd for C\(_{60}\)H\(_{50}\)N\(_2\)O\(_7\): C, 79.03; H, 5.48; N, 3.07. Found: C, 79.34; H, 5.38; N, 2.97.

Synthesis of `(4',5'-bis(tert-butyldimethylsilyloxy)4,4'-bis(2-(quinolineimino)1,1',2',1''-terphenyl) \{10\}: To synthesize compound \textbf{10}, 2-quinoline carboxaldehyde \textbf{9} (0.063 g, 0.40 mmol) was added portion wise to a stirred solution of diamine \textbf{3} (0.10 g, 0.19 mmol) in ethanol (15 mL). The resulting reaction mixture was stirred at room temperature for 2h during which an off-white solid was obtained. The solid compound was filtered and then washed with ethanol (10 mL) to give 0.13 g (85 %) of compound \textbf{10} \( \text{mp: } 380 \) °C. \( ^{1}H \) NMR (300 MHz, CDCl3, ppm): \( \delta \) 0.27 (s,12H, Si(CH\(_3\))\(_2\)), 1.14 (s, 18H, C(CH\(_3\))\(_3\)), 6.96 (s, 2H, ArH), 7.06 (d, 4H, \( J = 1.95 \) Hz, ArH), 7.22 (d, 4H, \( J = 1.95 \) Hz, ArH), 7.27 (t, 2H, \( J = 1.95 \) Hz, QuinH\(_b\)), 7.79 (t, 2H, \( J = 1.95 \) Hz, QuinH\(_b\)), 7.88 (d, 2H, \( J = 8.1 \) Hz, QuinH\(_a\)), 8.16 (d, 2H, \( J = 8.1 \) Hz, QuinH\(_b\)), 8.25 (d, 2H, \( J = 8.1 \) Hz, QuinH\(_b\)), 8.37 (d, 2H, \( J = 8.4 \) Hz, QuinH\(_a\)), 8.81 (s, 2H, N=CH). 13C NMR (75 MHz, CDCl3, ppm): 3.94, 18.48, 25.98, 118.69, 121.04, 123.07, 127.62, 127.74, 128.87, 129.73, 129.85, 130.78, 133.13, 136.55, 140.29, 140.29, 146.29, 148.00, 148.72, 154.98, 160.31. IR \( \nu_{\text{max}} \) (KBr, cm\(^{-1}\)): 1632 (C=N). MS (FAB): 799 (M\(^+\)), 800 (M\(^+\)+1). Anal. Calcd for C\(_{50}\)H\(_{54}\)N\(_4\)O\(_2\)Si\(_2\): C, 75.15; H, 6.81; N, 7.01. Found: C, 74.91; H, 6.49; N, 6.91.

Compound 11 was synthesized by portion wise addition of 2-quinoline carbaldehyde 9 (0.073 g, 0.47 mmol) to the stirred solution of diamine 7 (0.1 g, 0.22 mmol) in ethanol (10 mL). The resulting reaction mixture was stirred at room temperature for 1h during which an off-white solid was obtained. The solid compound was filtered and washed with ethanol to give 0.125 g (77%) of compound 11 mp: 250 °C. \textbf{IR} ν\textsubscript{max} (CHCl\textsubscript{3}, cm\textsuperscript{-1}): 1632 (C=N). \textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}, ppm): δ 3.81 (s, 8H, crownH), 3.91 (t, 4H, J = 4.2 Hz, crownH), 4.25 (t, 4H, J = 4.3 Hz, crownH), 6.87 (s, 2H, ArH), 7.23-7.57 (m, 8H, ArH), 7.69 (t, 2H, J = 8.7 Hz, QuinH), 7.78 (t, 2H, J = 8.7 Hz, QuinH), 7.87 (d, 2H, J = 7.2 Hz, QuinH), 8.15 (d, 2H, J = 8.1 Hz, QuinH), 8.25 (d, 2H, J = 8.7 Hz, QuinH), 8.36 (d, 2H, J = 8.4 Hz, QuinH), 8.80 (s, 2H, imineH). \textbf{\textsuperscript{13}C NMR} (75 MHz, CDCl\textsubscript{3}, ppm): 69.27, 69.61, 70.55, 71.12, 116.23, 118.63, 121.04, 127.61, 127.69, 128.82, 129.66, 129.83, 130.83, 133.01, 134.54, 140.24, 147.94, 148.51, 148.86, 154.87, 160.42. \textbf{MS} (FAB): 729 (M\textsuperscript{+}), 730 (M\textsuperscript{+}+1). \textbf{Anal. Calcd} for C\textsubscript{26}H\textsubscript{30}N\textsubscript{2}O\textsubscript{5}: C, 69.31; H, 6.71; N, 6.22. Found: C, 68.85; H, 7.06; N, 5.90.

Synthesis of 4,4"-diamino-4',5'-dimethoxy 1,1',2',1"-terphenyl {13}:

To a solution of 12 (1.00 g, 2.34 mmol) and 2 (1.29 g, 5.86 mmol) in dioxane were added K\textsubscript{2}CO\textsubscript{3} (0.85 g, 9.36 mmol), distilled H\textsubscript{2}O (8mL), and [Pd (Cl)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (0.36 g, 0.51 mmol) under argon and the reaction mixture was refluxed overnight. The dioxane was then removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. The organic layer was evaporated and the compound was purified by column chromatography using ethyl acetate as an eluent to give 0.58 g (55%) of compound 13 as white solid. mp: 230°C. \textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}): δ 3.92 (s, 6H, OCH\textsubscript{3}), 6.57 (d, 4H, J = 9Hz, ArH), 6.95 (s, 2H, ArH), 6.90 (m, 4H, ArH). \textbf{\textsuperscript{13}C NMR} (75 MHz, CDCl\textsubscript{3}): 55.9, 113.5, 114.7,
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127.2, 130.7, 132.0, 132.7, 144.5, 147.6. **MS** (FAB): 321 (M+1⁻). **Anal. Calcd.** for C₂₀H₂₀N₂O₂: C, 74.98; H, 6.29; N, 8.74. **Found:** C, 74.78; H, 6.15; N, 8.52.

**Synthesis of compound 15:** Compound 15 was synthesized by portionwise addition of phenanthroline 2,9 dialdehyde (14) (0.08 g, 0.31 mmol) to the stirred solution of diamine 13 (0.1 g, 0.31 mmol) in ethanol (100 ml). The resulting reaction mixture was stirred at room temperature for overnight, during which a yellow colored solid was obtained. The solid compound was filtered and washed with ethanol to give 0.25 g (77%) of compound 15. **mp:** >260 °C; **¹H NMR** (300 MHz, C₂D₂Cl₄, ppm): δ 3.64 (s, 12H, OCH₃), 6.69 (s, 4H, ArH), 6.96 (d, 8H, J = 8 Hz, ArH), 7.03 (d, 8H, J = 6 Hz), 7.55 (s, 4H, ArH), 8.02 (d, 4H, J = 8.4 Hz), 8.20 (d, 4H, J = 8.4 Hz), 8.78 (s, 4H, HC=N); **¹³C NMR** (75 MHz, C₂D₂Cl₄, ppm): δ 57.7, 115.1, 123.0, 129.2, 131.3, 132.6, 134.0, 142.1, 147.2, 149.8, 149.9, 155.9 **MS:** 1041 (M⁺); **Anal. Calcd** for C₆₈H₄₈N₈O₄: C, 78.44; H, 4.65; N, 10.76; **Found:** C, 78.23; H, 4.71; N, 10.59.

**Synthesis of compound 4,4"-diamino-1,1',2',1"-terphenyl {17}:** To a solution of dibromobenzene 16 (1.00 g, 2.34 mmol) and 2 (1.29 g, 5.86 mmol) in dioxane were added K₂CO₃ (0.85 g, 9.36 mmol), distilled H₂O (8mL), and [Pd (Cl)₂(PPh₃)₂] (0.36 g, 0.51 mmol) under argon and the reaction mixture was refluxed overnight. The dioxane was then removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound was purified by column chromatography using ethyl acetate as an eluent to give 0.58 g (55%) of compound 17 as white solid. **mp:** 230°C. **¹H NMR** (300 MHz, CDCl₃, ppm): δ 6.55 (d, 4H, J = 8.4 Hz, ArH), 6.95 (d, 4H, J = 8.4 Hz, ArH), 7.30-7.37 (m, 4H, ArH); **¹³C NMR** (75 MHz, CDCl₃, ppm): δ 114.7,
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126.7, 128.4, 128.6, 130.4, 130.7, 131.9, 132.1, 140.2, 144.6. **MS:** 260 (m/e); **Anal. Calcd for C\textsubscript{64}H\textsubscript{40}N\textsubscript{8}:** C, 83.04; H, 6.19; N, 10.76; Found: C, 83.21; H, 5.98; N, 11.01.

**Synthesis of compound 18:** Compound 18 was synthesized by portionwise addition of phenanthroline 2,9 dialdehyde 14 (0.04 g, 0.15 mmol) to the stirred solution of diamine 17 (0.04 g, 0.15 mmol) in ethanol (50 ml). The resulting reaction mixture was stirred at room temperature for overnight, during which a brown colored solid was obtained. The solid compound was filtered and washed with ethanol to give 0.1 g (68%) of 18. **mp >260 °C;** **\textsuperscript{1}H NMR** (300 MHz, CDCl\textsubscript{3}, ppm): δ 7.34 (d, 12H, J = 9 Hz, ArH), 7.47-7.50 (m, 12H, ArH), 7.87 (s, 4H, ArH), 8.33 (d, 4H, J = 8.4 Hz, ArH), 8.56 (d, 4H, J = 8.4 Hz), 9.14 (s, 4H, HC=N); **\textsuperscript{13}C NMR** (75 MHz, CDCl\textsubscript{3}, ppm): δ 115.1, 123.0, 129.2, 131.3, 132.6, 134.0, 142.1, 147.2, 149.8, 149.9, 155.9. **MS:** 921 (M\textsuperscript{+}); **Anal. Calcd** for C\textsubscript{64}H\textsubscript{40}N\textsubscript{8}: C, 83.46; H, 4.38; N, 12.17; Found: C, 83.05; H, 4.42; N, 11.89.

**General procedure for synthesis of compounds 20a-c and 21:** A solution of aldehyde 19a/b/c (2.2 mmol) in ethanol (2 ml) was added to the solution of diamine 3/7 (1 mmol) in minimum amount of ethanol. The resulting reaction mixture was stirred at room temperature for 2h during which solid was obtained. The solid compound was filtered, washed with ethanol (10 mL) and dried to give compounds 20a/b/c and 21.

**Synthesis of (4',5'-bis(tert-butyldimethylsilyloxy)4,4''-bis(5-nitro-2-hydroxyphenylimino)-1,1',2',1''-terphenyl)**

\[ \text{20a} \] Yield: 85 %; **mp: >280 °C;** **\textsuperscript{1}H NMR** (300 MHz, CDCl\textsubscript{3}, ppm): δ 0.28 (s, 12H, Si(CH\textsubscript{3})\textsubscript{2}), 1.04 (s, 18H, C(CH\textsubscript{3})\textsubscript{3}), 6.92 (s, 2H, ArH), 7.08 (d, J = 9.3 Hz, 2H, ArH), 7.24 (d, 8H, ArH), 8.27 (d, 2H, ArH), 8.37 (s, 2H, ArH), 8.72 (s, 2H, N=CH), 14.48 (s, 2H, OH). **\textsuperscript{13}C NMR** (75 MHz, CDCl\textsubscript{3},

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ppm): 3.9, 18.5, 25.9, 118.7, 121.0, 123.1, 127.6, 127.7, 128.9, 129.7, 129.9, 130.8, 133.1, 136.6, 140.2, 140.3, 146.3, 148.0, 148.7, 154.9, and 160.3. IR $v_{\text{max}}$(KBr, cm$^{-1}$): 1630 (C=N). MS (FAB): 819 ($M^+$); Anal. Calcd for $C_{44}H_{50}N_4O_8Si_2$: C, 64.52; H, 6.15; N, 6.84, Found: C, 64.65; H, 6.05; N, 6.91.

Synthesis of $((4',5'-\text{bis(tert-butyldimethylsilyloxy)}4,4''-\text{bis(5-nitro-2-methoxyphenylimino)-1,1',2',1''-terphenyl)})$

{20b}: Yield: 80 %; mp: >280°C; IR $v_{\text{max}}$(KBr, cm$^{-1}$): 1632 (C=N). $^1H$ NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 0.28 (s, 12H, Si(CH$_3$)$_2$), 1.04 (s, 18H, C(CH$_3$)$_3$), 4.05 (s, 6H, OCH$_3$), 6.92 (s, 2H, ArH), 7.04 (d, J = 9.3 Hz, 2H, ArH), 7.14 (s, 8H, ArH), 8.32 (d, 2H, ArH), 8.88 (s, 2H, ArH), 9.04 (s, 2H, N=CH). $^{13}C$ NMR (75 MHz, CDCl$_3$, ppm): 4.0, 18.6, 25.9, 118.6, 121.1, 123.2, 127.7, 128.9, 129.7, 129.9, 130.8, 133.1, 136.6, 140.2, 140.3, 146.3, 148.0, 148.7, 154.9, 156.9 and 160.3. MS: 847 ($M^+$) Anal. Calcd for $C_{46}H_{54}N_4O_8Si_2$: C, 65.22; H, 6.43; N, 6.61, Found: C, 64.96; H, 6.62; N, 6.49.

Synthesis of $((4',5'-\text{bis(tert-butyldimethylsilyloxy)}4,4''-\text{bis(5-nitro-2-methoxyphenylimino)-1,1',2',1''-terphenyl)})$

{20c}: Yield: 86 %; mp: 370°C; $^1H$ NMR (300 MHz, CDCl$_3$, ppm): $\delta$ 0.11 (s, 12H, Si(CH$_3$)$_2$), 1.04 (s, 18H, C(CH$_3$)$_3$), 6.92 (s, 2H, ArH), 7.01 (d, J = 8.1 Hz, 2H, ArH), 7.16 (s, 10H, ArH), 7.34-7.39 (m, 4H, ArH), 8.64 (s, 2H, N=CH), 13.31 (s, 2H, OH). $^{13}C$ NMR (75 MHz, CDCl$_3$, ppm): 4.0, 18.5, 26.0, 117.2, 119.0, 119.3, 120.9, 123.1, 130.8, 132.9, 133.0, 140.1, 146.4. IR $v_{\text{max}}$(KBr, cm$^{-1}$): 1630 (C=N). MS (FAB): 730 ($M^+$). Anal. Calcd for $C_{46}H_{52}N_2O_4Si_2$: C, 72.49; H, 7.19; N, 3.84, Found: C, 72.8; H, 7.30; N, 3.67.
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Synthesis of 4,5-bis(4',4''-bis(5-nitro-2-hydroxyphenylimino)phenyl)benzo[15]crown-5 \(\{21\}\): Yield: 81 %; mp: 280°C; \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm): \(\delta\) 3.80 (s, 8H, crown H), 3.96 (t, J = 4.2 Hz, 4H, crown H), 4.25 (t, 4H, J = 4.2 Hz, crown H), 6.97 (s, 2H, ArH), 7.08 (d, J = 9.0 Hz, 2H, ArH), 7.24 (d, J = 9.0 Hz, 8H, ArH), 8.26 (d, J = 6.3 Hz, 2H, ArH), 8.37 (s, 2H, N=CH), 14.44 (s, 2H, OH). \(^13\)C NMR (75 MHz, CDCl\(_3\), ppm): 3.9, 18.5, 25.9, 118.7, 121.0, 123.1, 127.6, 127.7, 128.9, 129.7, 129.9, 130.8, 133.1, 136.6, 140.3, 146.3, 148.0, 148.7, 154.9, and 160.3. IR \(\nu_{\text{max}}\) (KBr, \(\text{cm}^{-1}\)): 1632 (C=N).

MS (FAB): 748 (M\(^+\)). Anal. Caled for \(\text{C}_{40}\text{H}_{36}\text{N}_4\text{O}_{11}\): C, 64.17; H, 4.85; N, 7.48; Found: C, 64.56; H, 5.06; N, 7.09.

References


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