Metal Coordinated Urea Based Fluorescent Receptors for Anion Recognition

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Abstract: Two *bis* urea based acyclic receptors (**1** and **2**) containing two pyridyl moieties with different spacers are synthesized. These receptors are further transformed to metallo-macrocyclic receptors (**3** and **4**) by coordinating with metal center through pyridine ring 'N'. The binding-behavior as well as selectivity of the receptors towards anions upon metal coordinated cyclization is studied and the results are compared with parent acyclic receptors. Receptors **2** and **4** containing a naphthalene moiety as a spacer as well as a fluorophore behave as *'on-off'* sensors towards anions.

Keywords: Anion recognition, fluorescence sensing, urea and acyclic receptors.

1. INTRODUCTION

Anions play a vital role in different biochemical processes [1-5]. The interaction of anions with different bioactive molecules attracts the attention of scientific community towards the synthesis and study of the complexation behavior of anions by different type of artificial receptors [6]. Therefore the recognition of anions is important and it is also challenging for their wide range of sizes and shapes.

Anion binding compounds could be used to stabilize and increase the bioavailability of anionic drugs as cyclodextrin neutral drug inclusion complexes [7]. The other aspect of anion sensing is selective removal of different toxic anions to control the environmental pollution. There is also interest in producing sulfate selective hosts for removing sulfate from nitrate-rich radioactive waste [8].

Anions have larger radii and a greater variety of geometries than common cations. These characteristic properties require complexity in the three-dimensional structure of anion receptors. Recent reviews describe anion recognition [9], some with specific emphasis on the use of amine [9d], amide [9c], urea [9c], thiourea [9c], pyrrole [9e], guanidinium [9f], and metal coordination-Lewis acid groups [9g]. Also, current books on supramolecular chemistry contain summaries of research in this field [10]. Cyclic peptides are another class of anion sensors which have been studied recently [11]. On account of high sensitivity and simplicity, fluorescent chemosensor can be effectively used as a tool to analyze and measure the amount of anions as well as clarify their function in living system; therefore, the design and synthesis of fluorescent devices for the recognition of anions are currently of importance in chemical trace element detection [12,13]. Beside this tetrazole moiety containing receptors show excellent selectivity for a particular anion among the series of anions [14].

Metal coordinated synthetic receptors are widely used for the recognition of different guest substrates [15]. These types of receptors have some electrochemical properties over neutral receptors, which is better informative to study recognition pattern in different pH of the medium [16].

In the present system four N-H groups (ureido) are oriented to the same direction and available for the binding of anions. Here receptors have been synthesized having two substituted urea moieties, which are further separated by a common spacer 4-methylene phenyl group in case of receptors **1** and **3**. But in case of receptors **2** and **4**, naphthalene group is present as common spacer and fluorophore. Here receptors are designed and synthesized with pyridine moiety, which can form coordinate bond with metal center (Fig. **1**).

The receptors **1** and **2** further get macrocyclic nature by clipping two pyridine moieties with palladium metal center. This has been done to get the cavity of a fixed size, which will fit and show greater selectivity for the particular anion [17]. 3-Aminopyridine containing mixed urea based receptors have been carefully designed and synthesized for the recognition of anions to avoid intramolecular hydrogen bonding, which is observed in case of 2-aminopyridine containing urea based receptors [18].

2. SYNTHESIS

The receptors are synthesized according to the following schemes. Receptor **1** is synthesized directly from the corresponding isocyanate and 3-aminopyridine which further reacts with palladium(II) chloride in DMF and acetonitrile to afford receptor **3** (Scheme **1**).

But the receptor **2** has been synthesized from the pyridine isocyanate, which has been prepared in situ by reaction with triphosgene. Receptor **4** has been synthesized according to the receptor **3** (Scheme **2**). The structure of the receptors has been confirmed by the spectral data. The metal coordination of the receptors **3** and **4** has been confirmed by the FT-IR and mass spectra (both HRMS and FAB). However, we are unable to grow single crystals of these compounds for further structural confirmation [19].

3. BINDING STUDIES

Binding behavior of the anions with the designed receptors is studied mainly by UV-vis and fluorescence titration methods in DMSO medium. The ^{1}H NMR titration is carried out only in two cases. Among the receptors, **2** and **4** have potential fluorescence properties due to the presence of fluorophore naphthalene moiety, which is quenched during titration.

^{1}H NMR Studies

The ^{1}H NMR titrations are carried out in case of receptors **1** and **2** with F^- in the form of its tetrabutyl ammonium salt. The chemical shift of the ureido protons is quite interesting regarding the structural arrangement of the receptors. In case of the receptor **1**, the ureido protons are shifted towards downfield upon addition of the increasing amount of guests but the gap between two ureido protons remain almost unchanged during the titration process (Fig. **2**). This observation indicates that two uredo protons of one urea moiety probably bind equally with the guest F^- ion due to large cavity inside the receptor. Whereas in case of receptor **2**, two ureido protons

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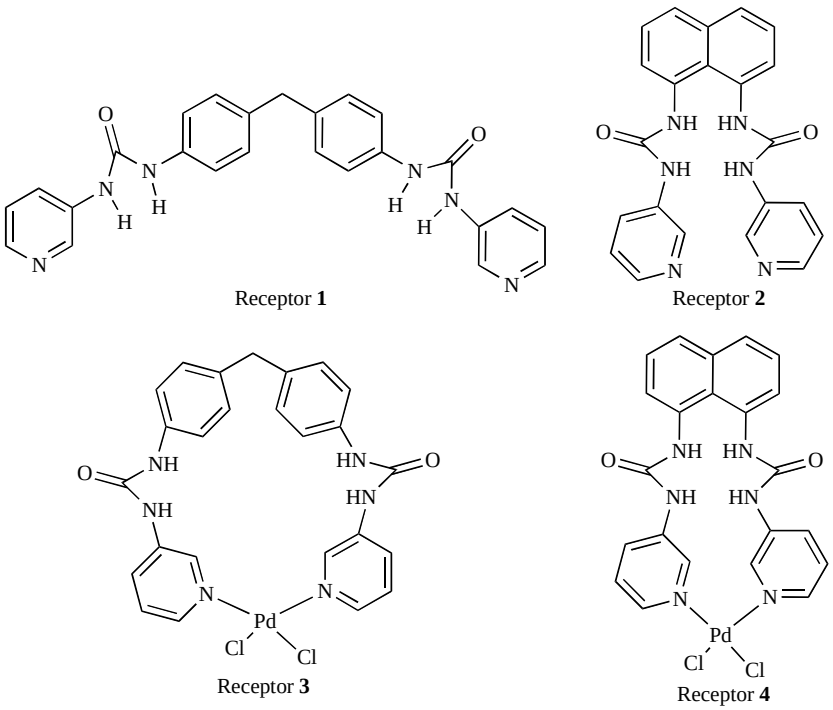
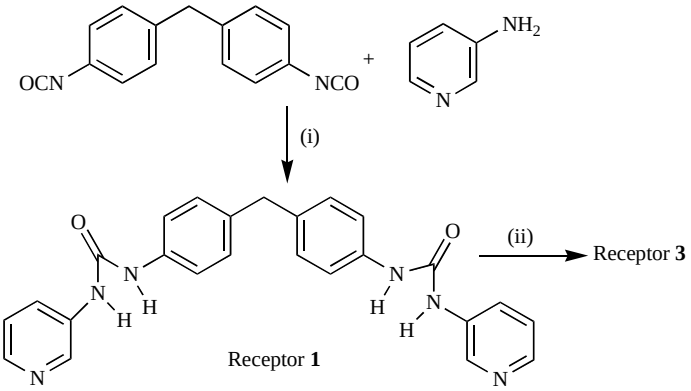
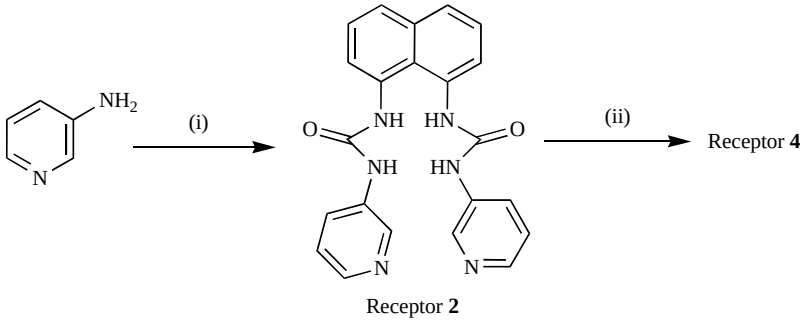


Fig. (1). Receptors for the recognition of anions.



Scheme 1. *Reagents & Conditions:* (i) Dry CH_2Cl_2, r.t., 3-5 h, 90%; (ii) $PdCl_2$, CH_3CN, r.t., 12 h, 88%.

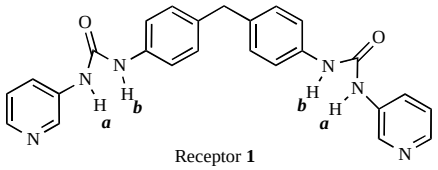


Scheme 2. *Reagents & Conditions:* (i) (a) Triphosgene, dry CH_2Cl_2, Et_3N, reflux, 30-40 min; (b) 1,8-diaminonaphthalene, dry CH_2Cl_2, Et_3N, reflux, 1 h, 72%; (ii) $PdCl_2$, CH_3CN, r.t., 12 h, 88%.

of one urea moiety are shifted towards downfield upon addition of the increasing amounts of guests but the gap between two ureido protons have been increased (Fig. **3**). So the two ureido protons possibly bind with the guest F^- ion unequally. In both cases sharp singlet of the ureido protons gradually get broadened due to strong hydrogen bonding with F^- ions.

UV-vis Studies

The binding behavior of the receptors with anions is extensively studied by means of UV-vis titration method. The titration experiments are carried out with known solution of receptors **1** (1.10×10^{-5} M), **2** (6.03×10^{-6} M), **3** (4.26×10^{-6} M) and **4** (4.48×10^{-5} M) in DMSO. The solutions of guest substrates are prepared



Receptor **1**

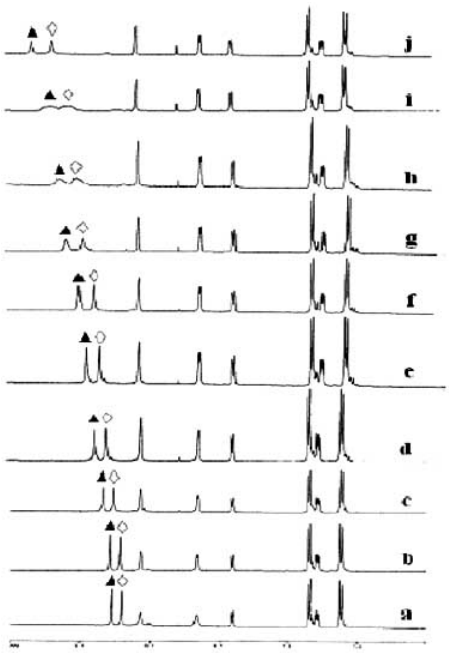
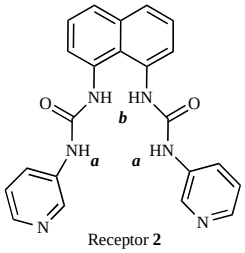


Fig. (2). Partial ^{1}H NMR titration spectra of receptor **1** *vs* TBAF (N-H$_a$= ▲; N-H$_b$= ◊) with increasing concentration (**a** to **j**).



Receptor **2**

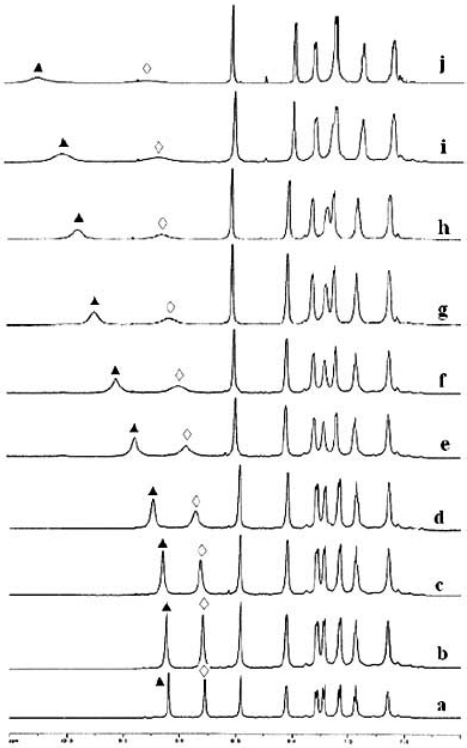


Fig. (3). Partial ^{1}H NMR titration spectra of receptor **2** *vs* TBAF (N-H$_a$= ▲; N-H$_b$= ◊) with increasing concentration (**a** to **j**).

either in 1 x 10^{-3} M or 1 x 10^{-4} M order. Each titration is performed using 2 mL stock solution of receptors and the solution of the guest with increasing amount. The binding constants for all the anions with receptors **1**-**4** are calculated by plotting 1/ΔI *vs* 1/[G] (Table **1**) [20]. The receptor **1** shows strong absorption at ~267 nm, which gradually decreases upon addition of the guest solution during titration (Fig. **4**). The nature of the absorption spectra in all the cases is almost identical. In this case highest binding constant value is observed in case of I^- whereas F^- binds most weakly. This result reflects the binding behavior of the flexible open form of the receptor.

Receptor **2** shows strong absorption at ~290 nm which gradually decreases upon addition of increasing amounts of guests (Fig. **5**). The nature of the spectral change in all the cases is almost identical except in case of AcO^- ion where a new peak is slowly generated at ~375 nm. The binding constant values were calculated from the titration data (Table **1**). From these values, it is shown that all the anions except I^-, bind comparatively better than receptor **1**.

Receptor **3** shows strong absorption at ~267 nm which gradually decreases upon addition of increasing amounts of guest to the receptor **3** during titration (Fig. **6**). The overall absorbance spectra

Table 1. Association Constants [$K_a(M^{-1})$][a] and Free Energy Changes [ΔG(Kcal/mol)] at 25 °C for Receptors 1-4, Determined by UV-vis Titration Method in DMSO

Anions	Receptor 1		Receptor 2		Receptor 3		Receptor 4	
	K_a	ΔG	K_a	ΔG	K_a	ΔG	K_a	ΔG
F^-	7.36×10^3	-5.3	1.07×10^4	-5.5	4.86×10^3	-5.0	3.71×10^4	-6.2
Cl^-	1.31×10^4	-5.6	1.29×10^4	-5.6	4.16×10^3	-4.9	1.73×10^4	-5.8
Br^-	1.17×10^4	-5.5	2.02×10^4	-5.9	8.63×10^3	-5.4	4.79×10^2	-3.7
I^-	3.12×10^4	-6.1	1.21×10^4	-5.6	1.16×10^4	-5.5	5.38×10^2	-3.7
AcO^-	1.29×10^4	-5.6	1.56×10^4	-5.7	4.62×10^4	-6.3	9.21×10^2	-4.0

[a]For receptor **1**: λ_{max}= 267 nm; receptor **2**: λ_{max}= 290 nm; receptor **3**: λ_{max}= 267 nm; receptor **4**: λ_{max}= 312 nm. All the errors are ±10%.

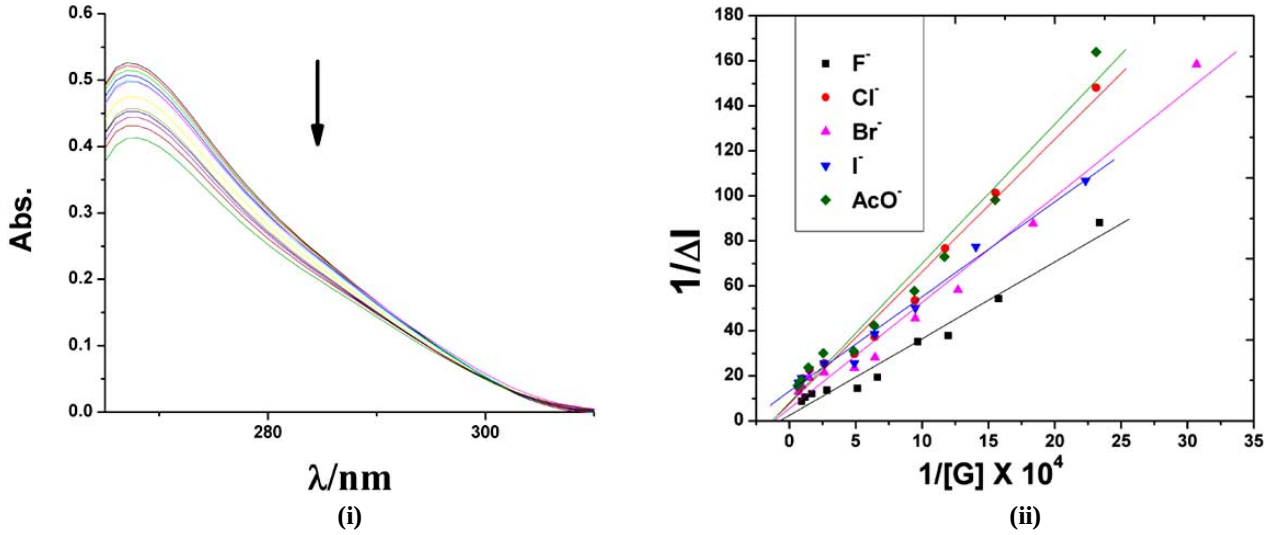


Fig. (4). (**i**) UV-vis titration spectra of receptor **1** (1.10×10^{-5} M) with F^- anions (For titration spectra of other anions see supporting information) and (**ii**) Binding constant calculation curves of receptor **1** with anions by UV-vis titration in DMSO. All the anions were used in the form of their tetrabutylammonium salts.

of the metal coordinated receptor **3** are not much different from the absorbance spectra of its parent receptor **1**. But the binding constant values are different. In this case larger anions bind better with the receptors where guests I^- and AcO^- fit better inside the close cavity compared to smaller anion. The association constant value in the case of AcO^- is thus highest among the anions for the receptor **3**.

The absorbance spectra of the receptor **4** are completely different with respect to its parent receptor **2** (Fig. **7**). In case of receptor **4**, strong absorbance is shown at ~312 nm which gradually decreases upon increasing concentration of the guest anions. In this case changing pattern of absorbance spectra is also similar with different magnitudes for all anions except AcO^- where slight increase in absorbance at ~375 nm occurs. The binding constant values also show some interesting trend in comparison with its parent molecular receptor **2**. In this case highest binding constant value is observed in case of F^- ion, which is the smallest one with respect to size. Another interesting aspect of these data is that the ions with larger size bind weakly compared to the receptor **2**.

Fluorescence Studies

The emission spectra upon complexation with the anions and the receptors **2** and **4** are recorded. The fluorescence titrations are carried out with ten times dilute solution of the receptors compared to UV-vis titration following the previously mentioned procedure. In both cases fluorescence intensity was quenched upon addition of the increasing amount of guests without producing any other observable change. The fluorescence is '*switched off*' depending upon the host-guest interactions (Table **2**). The association constants are determined by plotting I_0/I_0-I *vs* 1/[G] in case of fluorescence titration spectra (Table **3**) [21]. Separate sets of experiment have also been performed to draw the job plot, which shows the stoichiometry of the complexation.

The emission spectra show two maxima at ~364 and ~381 nm respectively (Fig. **8**). Between the two, intensity at ~381 nm is higher which is further quenched upon addition of the guest anions (Fig. **11i**). The trend of quenching in all the cases is similar but different in magnitude (Fig. **9i**). In case of receptor **2** maximum quenching is observed for Cl^- in 1:1 host-guest ratio whereas in higher guest concentration (1:15 of host-guest) maximum quenching is observed for I^-. This may be attributed from the structural flexibility of the receptor **2** which initially accommodate Cl^- (1:1) better but in higher concentration of anions, the arms of the receptors may rotate in different angles and bind anions of larger size. The stoichiometry of the complexation between receptor **2** and anions is determined by the fluorescence titration method and the corresponding job plot show 1:1 mode of interaction (Fig. **9ii**). The nature of emission spectra of receptor **4** is similar to the emission spectra of receptor **2** (Fig. **10**). But here emission at ~364 nm is of higher intensity than emission at ~381 nm. This observation is reverse in nature with respect to the receptor **2**. In this case fluorescence intensity is also quenched upon addition of the guest anions (Fig. **11i**). In this case the quenching is higher in lower concentration (1:1) of F^- ions whereas in higher concentration (1:15) quenching happens in greater extent for I^- ions (Table **2**). Receptor **4** recognizes all anions in 1:1 stoichiometry (Fig. **11ii**). Though the association constants are not much improved still it shows better selectivity towards anions with smaller size (Table **3**).

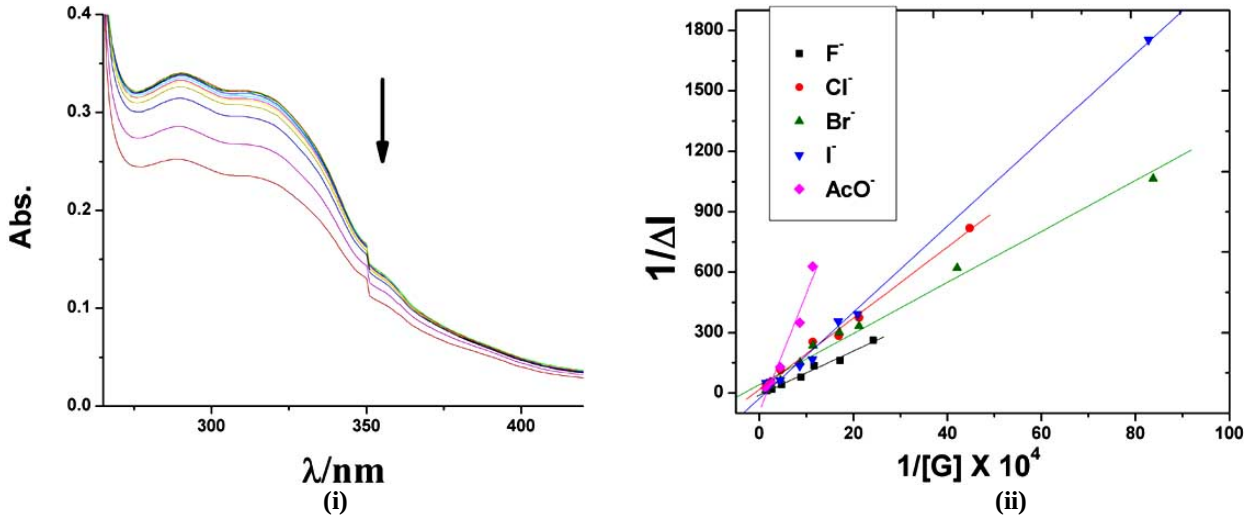


Fig. (5). (**i**) UV-vis titration spectra of receptor **2** (6.03 x 10^{-6} M) with F^- anions (For titration spectra of other anions see supporting information) and (**ii**) Binding constant calculation curve of receptor **2** with anions by UV-vis titration in DMSO. All the anions were used in the form of their tetrabutylammonium salts.

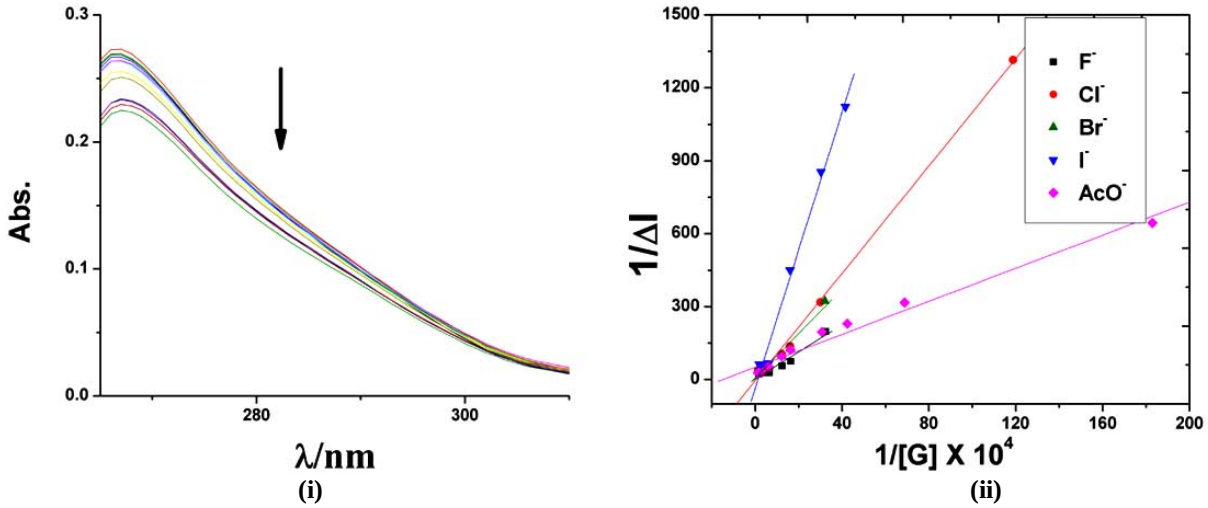


Fig. (6). (**i**) UV-vis titration spectra of receptor **3** (4.26 x 10^{-6} M) with F^- anions (For titration spectra of other anions see supporting information) and (**ii**) Binding constant calculation curve of receptor **3** with anions by UV-vis titration in DMSO. All the anions were used in the form of their tetrabutylammonium salts.

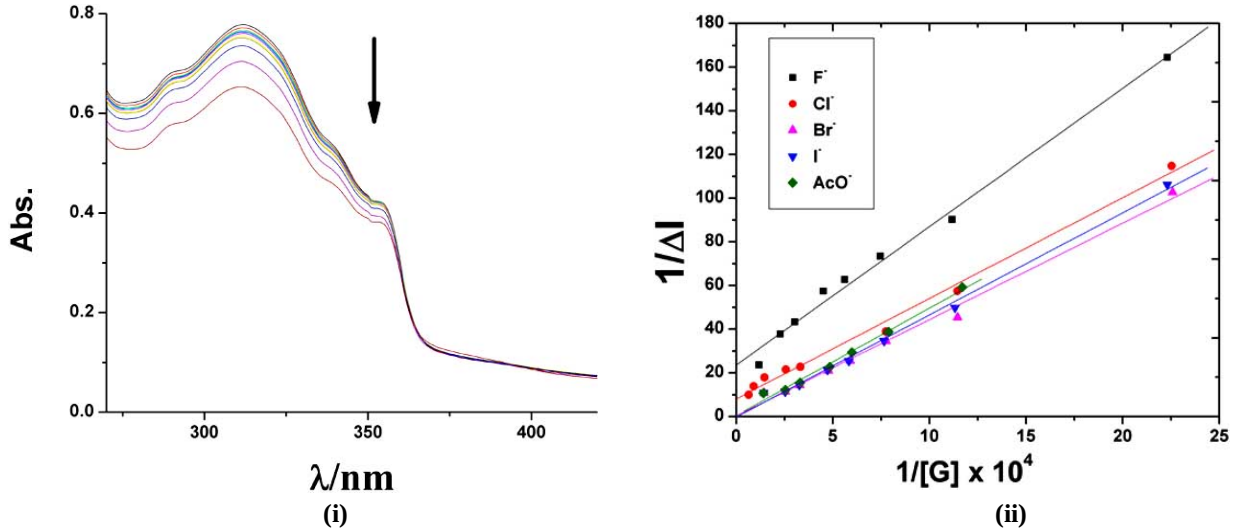


Fig. (7). (**i**) UV-vis titration spectra of receptor **4** (4.48 x 10^{-5} M) with F^- anions (For titration spectra of other anions see supporting information) and (**ii**) Binding constant calculation curves of receptor **4** with anions by UV-vis titration in DMSO. All the anions were used in the form of their tetrabutylammonium salts.

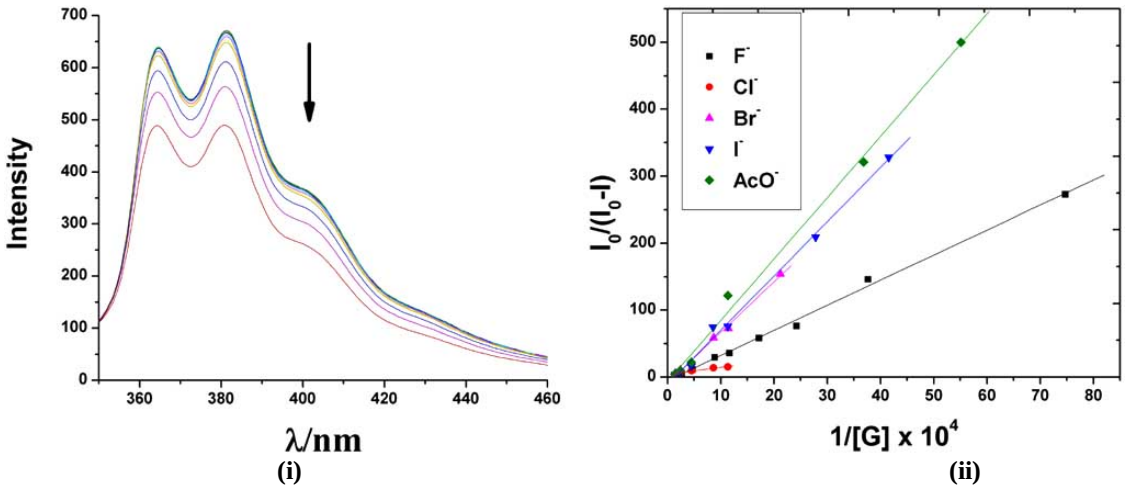


Fig. (8). (**i**) Fluorescence emission titration spectra of **2** (6.03 x 10^{-6} M) with F^- (For titration spectra of other anions see supporting information) and (**ii**) Binding constant calculation curves of receptor **2** with anions by fluorescence titration method in DMSO. All the anions were used in the form of their tetrabutylammonium salts.

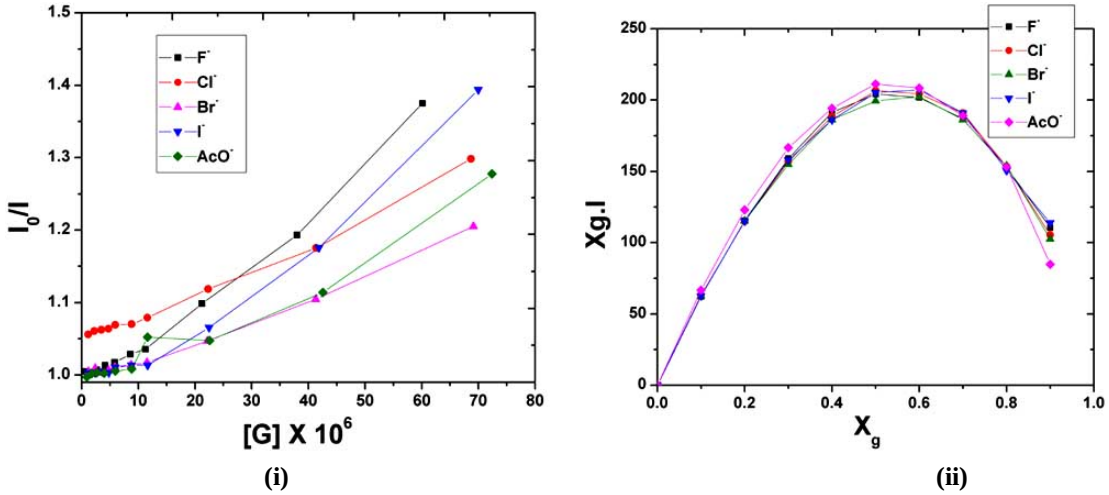


Fig. (9). (**i**) Stern-Volmer plot and (**ii**) job plot determined by fluorescence titration method between receptor **2** and anions.

Table 2. Fluorescence Quenching (%) in Different Host and Guest Ratios

Anions	Fluorescence Quenching (%)					
	1:1		1:2		1:15	
	Receptor 2	Receptor 4	Receptor 2	Receptor 4	Receptor 2	Receptor 4
F^-	1.71	2.46	1.71	4.29	27.27	27.20
Cl^-	6.47	0.91	7.32	2.37	22.99	29.47
Br^-	1.14	0.64	1.70	2.48	17.02	28.14
I^-	1.04	1.21	1.34	2.08	28.26	31.21
AcO^-	0.52	1.05	4.95	2.44	21.74	27.24

DISCUSSION

The overall binding patterns of anions with two acyclic receptors and two metal coordinated macrocyclic receptors have been studied. Attempt is also taken to study the electrochemical properties of the metallomacrocyclic receptor and its complexes with F^- but no informative observations are found. The association constants are determined both by UV-vis and fluorescence methods. The binding constant values calculated by these methods, are moderate and comparable. The observation is mainly focused on the binding behavior of the acyclic receptors and how clipping the terminal of open arm changes this behavior. Some interesting observations of this study throw light in this direction. Now if we compare the binding constant values of receptor **1** and its palladium coordinated macrocyclic receptor **3**, it is found that except F^- ion, all the ions bind moderately with receptor **1** and the binding constants are in the order of 1 x 10^4 but the receptor **3** binds well with only I^- and AcO^- ions and the order of binding constant is the same as the receptor **1**. But the order of the association constants in case of other smaller anions is weak and in 1 x 10^3 M^{-1} order. This observation indicates that in case of receptor **1** anions may bind with ureido protons in higher stoichiometry and the flexible arm of the receptor

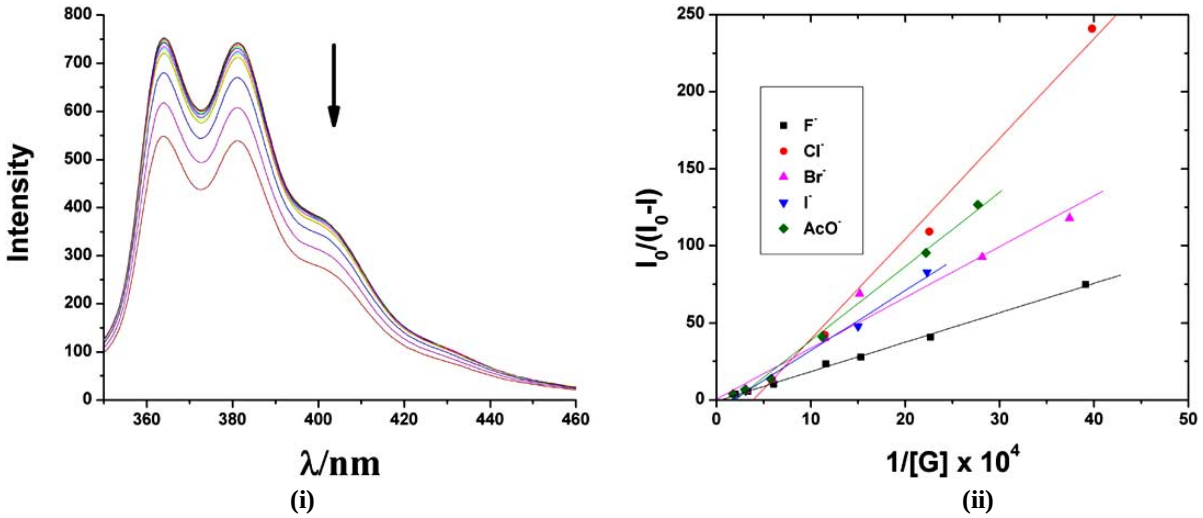


Fig. (10). (**i**) Fluorescence emission titration spectra of **4** (4.48 x 10^{-6} M) with F^- (For titration spectra of other anions see supporting information) and (**ii**) Binding constant calculation curves of receptor **2** with anions by fluorescence titration method in DMSO. All the anions were used in the form of their tetrabutylammonium salts.

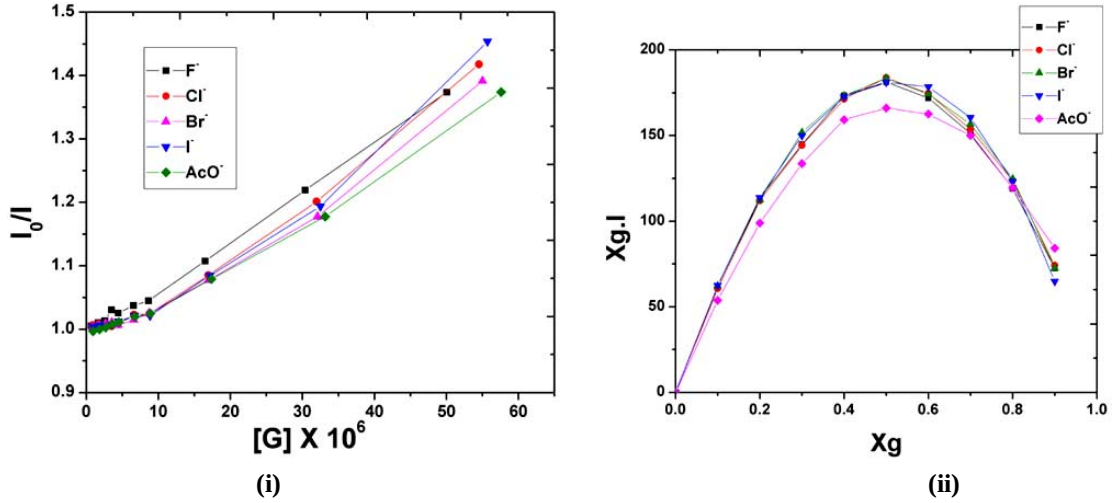


Fig. (11). (**i**) Stern-Volmer plot and (**ii**) job plot determined by fluorescence titration method between receptor **4** and anions.

Table 3. Association Constants [K_a(M^{-1})]^a and Free Energy Changes [ΔG(Kcal/mol)] at 25 °C for Receptors 2 and 4 Determined by Fluorescence Quenching in DMSO

Anions	Receptor 2		Receptor 4	
	K_a	ΔG	K_a	ΔG
F^-	1.38 x 10^4	-5.6	1.44 x 10^4	-5.7
Cl^-	3.53 x 10^4	-6.2	3.91 x 10^4	-6.3
Br^-	1.13 x 10^4	-5.5	7.43 x 10^3	-5.3
I^-	1.33 x 10^4	-5.6	2.61 x 10^3	-4.7
AcO^-	7.46 x 10^3	-5.3	1.98 x 10^4	-5.9

^{a}All the errors are ±15%. For **2**: λ_{max}(ex) = 290 nm, λ_{max}(em) = 381 nm, emission slit width = 4.5 nm, excitation slit width = 12.5 nm, Scan rate = 500 nm/min. For **4**: λ_{max}(ex) = 312 nm, λ_{max}(em) = 364 nm, emission slit width = 5.0 nm, excitation slit width = 12.5 nm, Scan rate = 500 nm/min.

may arrange each time to accommodate the guest anions with varying size which is not however possible for the receptor **3** and it binds well the larger anion for better matching the size of anion and cavity of the receptor **3**. The similar binding pattern is also observed in case of receptors **2** and **4**, where all the anions bind with receptor **2** in same order (1 x 10^4) but receptor **4** binds better only with the smaller ions ($F^-$and Cl^-). As the cavity size remains fixed upon metal co-ordination, it only binds with the smaller ions. These observations also indicate the metal coordinated macrocyclic nature of the receptors **3** and **4**.

CONCLUSION

From this study it is concluded that simple acyclic receptors (**1** and **2**) bearing pyridine moiety may be clipped with a metal center to synthesize metal coordinated macrocyclic receptors. These types of receptors show better selectivity towards different anions with

varying sizes. Here receptor **3** shows better selectivity towards larger anions whereas receptor **4** shows better selectivity towards smaller anions. Though no redox indication has been observed either in case of receptor itself or its complexes with anions still there is scope to modify the system containing another charged metal center to study the recognition behavior of these types of receptors in different electrochemical environments.

EXPERIMENTAL

General

All the melting points were determined on a hot-coil stage melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300, 400 and 500 MHz spectrometers. For NMR spectra DMSO-d_6 was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H, ^{1}H–C coupling constants in Hz. IR spectra were recorded using KBr discs.

General Procedure for ^{1}H NMR Titrations

Stock solutions of known concentration of hosts (receptors **1** and **2**) and guest (F^-) in DMSO-d_6 were prepared by accurately weighing pure substrates. Generally the guest concentration was kept much higher compared to host concentration. To a NMR tube containing host solution, a guest solution in DMSO-d_6 was added with increasing volumes by judicious choice (generally 10 μL, 20 μL, 30 μL etc. in excess). The detection of the 1:1 complex along with the change in ^{1}H NMR signal of the amide protons was followed as a function of the concentration of the variable component. The negligible change in the chemical shift value indicates the saturation point of complexation.

General Procedure for UV-vis Titration

Stock solutions of receptors **1**, **2**, **3** and **4** were prepared in the order of 1 x 10^{-5} M in DMSO. Anions were dissolved in DMSO to make concentration in order of 1 x 10^{-3} M or 1 x 10^{-4} M Then the guest solution is added to the receptor solution (taking 2 mL in the UV-cell) and continuous decrease of absorbance in UV spectra was recorded for each time. Association constants were calculated by plotting 1/[G] *vs* 1/ΔI (ΔI = change of intensity of the absorbance spectrum during titration).

General Procedure for Fluorescence Titration

Stock solutions of receptors **2** and **4** were taken and diluted in the order of 1 x 10^{-6} M in DMSO. Anions were dissolved in DMSO to make concentration in order of 1 x 10^{-4} M. Then the guest solution is added to the receptor solution (taking 2 mL in the cell) and continuous decrease of intensity of emission spectra was recorded each time. Titration and Stern-Volmer curves were determined by plotting ΔI *vs* [G]/[H] and I_0/I *vs* [G] respectively. Association constants were calculated by plotting I_0/I_0-I *vs* 1/[G] (I_0 and I are the initial and final intensities of the receptor solution after each addition during titration).

1,1'-(4,4'-methylenebis(4,1-phenylene))bis(3-(pyridin-3-yl)urea) (Receptor 1)

Methylenedi-*p*-phenyl diisocyanate (1 eqv.) was taken in 25 mL r.b and was stirred for 20 min with 5 mL dry CH_2Cl_2. The required aryl amine (2 eqv.) was dissolved in dry CH_2Cl_2 (5 mL) and added to the isocyanate solution slowly for few minutes. The reaction mixture was stirred for another 2-3 hour and the precipitate was filtered out and washed with $CHCl_3$, $CHCl_3$/MeOH (1:1) and finally MeOH. Finally the compound was obtained by drying well under reduced pressure and the yield of the compounds varies from 80-90%.

Yield: 81%; Light yellow solid.

Mp.: 235-237(decom) 328-330 °C.

^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm): 8.81 (bs, 2H), 8.74 (bs, 2H), 8.58 (d, 2H, *J* = 2.2 Hz), 8.17 (d, 2H, *J* = 4.4 Hz), 7.92 (d, 2H, *J* = 8.4 Hz), 7.36 (d, 4H, *J* = 8.4 Hz), 7.30 (dd, 2H, *J* = 8.3 Hz), 7.13 (d, 4H, *J* = 8.36 Hz), 3.82 (s, 2H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm): 152.56, 142.73, 139.96, 137.30, 136.47, 135.29, 129.65, 128.93, 125.05, 123.57, 118.59, 117.05, benzylic carbon probably merged with solvent peak.

FT-IR (KBr): 3302, 3037, 2938, 1775, 1650, 1599, 1530, 1253, 773, 702 cm^{-1}.

Mass (HRMS-ESI): Calcd for $C_{25}H_{23}N_6O_2$ (M+H) is 439.1877; found 439.1874.

Anal. Calcd for $C_{25}H_{22}N_6O_2$; C, 68.47; H, 5.05; N 19.16. Found: C, 68.35; H, 5.00; N 18.98.

1,1'-(naphthalene-1,8-diyl)bis(3-(pyridin-3-yl)urea)(Receptor 2)

To a solution of triphosgene (1.5 g. 5 mmol) in dry dichloromethane (15 mL), 3-aminopyridine (0.47 g, 5 mmol) in dry dichloromethane (15 mL) was added dropwise. After that triethyl amine (2 mL) in dry dichloromethane (10 mL) was added dropwise and stirring was continued for half an hour. The solvent was removed under reduced pressure and again dissolved in dry dichloromethane (15 mL) and 1,8-naphthalenediamine (0.4 g, 2.5 mmol) in dry dichloromethane (10 mL) was added to it. The mixture was refluxed for another half an hour. Now the solvent was evaporated out and acetone (30 mL) and water (25 mL) were added to it. The precipitate was collected and again washed with 1:1 acetone-water to afford the deep brown compound **2** (0.7 g, 70%).

Mp.: 228-231 °C.

^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm): 9.13 (s, 2H), 8.81 (s, 2H), 8.50 (s, 2H), 8.09 (d, 2H, *J* = 4.5 Hz), 7.79 (dd, 4H, *J* = 8.1, 8.1 Hz), 7.62 (d, 2H, *J* = 7.2 Hz), 7.48 (t, 2H, *J* = 7.8 Hz), 7.19 (dd, 2H, *J* = 4.5, 4.5 Hz).

^{13}C NMR (DMSO-d_6, 125 MHz): 154.33, 143.46, 140.78, 137.52, 136.53, 134.31, 126.53, 126.32, 125.88, 124.23 (d, *J* = 6.5Hz).

FT-IR (KBr): 3285, 1647, 1563, 1268, 705 cm^{-1}.

Mass (HRMS-ESI): Calcd for $C_{22}H_{18}N_6O_2$ (M+H) is 399.1564; found 399.1564.

Anal. Calcd for $C_{22}H_{18}N_6O_2$; C, 66.32; H, 4.55; N 21.09. Found: C, 66.24; H, 4.63; N 21.01.

General Procedure for the Synthesis of Palladium Coordinated Cyclic Urea Based Receptors (3 and 4)

Compounds **1** or **2** (1.0 eqv.) and $PdCl_2$(II) (1.0 eqv.) were stirred at room temperature in 1:1 DMF-CH_3CN for 10-12 hours. A precipitate was collected by filtration and washed well with acetonitrile to afford a grayish light yellow compound **3** (68%) and grayish brown compound **4** (74%).

1,1'-(4,4'-methylenebis(4,1-phenylene))bis(3-(pyridin-3-yl)urea) palladium dichloride (Receptor 3)

Mp. > 315 °C

^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm): 9.18 (s, 2H), 8.97 (s, 2H), 8.88 (s, 2H), 8.34 (d, 2H *J* = 5.1 Hz), 7.95 (d, 2H, *J* = 6.9 Hz), 7.39 (d, 4H, *J* = 8.0 Hz), 7.32 (dd, 2H, *J* = 8.6, 5.4 Hz), 7.15 (d, 4H, *J* = 7.8 Hz), 3.84 (s, 2H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm): 152.21, 146.42, 142.65, 137.48, 136.96, 135.23, 128.98, 124.99, 118.92, benzylic carbon probably merged with solvent peak.

FT-IR (KBr): 3342, 1776, 1691, 1658, 1649, 1546, 1204, 690 cm^{-1}.

Mass (ESI): m/z (%): 804.5 [$(L+PdCl_2+2DMSO+CH_3CN)^+$, 57], 798.9 (13).

Mass (FAB): m/z (%): 613.4 [$(M-2H)^+$, 100], 596.3 (20), 544.5 (28), 526 (31).

1,1'-(naphthalene-1,8-diyl)bis(3-(pyridin-3-yl)urea) palladium dichloride (Receptor 4)

Mp. > 300 °C

^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm): 9.12 (s, 2H), 8.81 (s, 2H), 8.49 (s, 2H), 8.07 (d, 2H, *J* = 4.5 Hz), 7.79 (dd, 4H, *J* = 8.1, 8.1 Hz), 7.60 (d, 2H, *J* = 7.2 Hz), 7.47 (t, 2H, *J* = 7.8 Hz), 7.18 (dd, 2H, *J* = 4.5, 4.5 Hz).

FT-IR (KBr): 3292, 1700, 1684, 1653, 1554, 1487, 1272, 691 cm^{-1}.

Mass (ESI): 1216.9 [$\{2(L+PdCl_2)+CH_3CN+Na\}^+$, 70], 821.2 [$(2L+2H+Na)^+$, 11], 820.2 [$(2L+H+Na)^+$, 35], 819.2 [$(2L+Na)^+$, 73], 797.2 [$(2L+H)^+$, 10], 421.6 [$(L+Na)^+$, 100], 399.6 [$(L+H)^+$, 20], 301[65].

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