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Benzoquinone-imidazole hybrids as selective colorimetric sensors for cyanide in aqueous, solid and gas phases

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Abstract

Five new chemosensors (**R1-R5**), possessing benzoquinone as signaling unit and imidazole as H-bond donor unit, for cyanide sensing have been rationally designed, synthesized and characterized by NMR and mass spectroscopy. The structure of **R5** was confirmed by single crystal XRD studies. These receptors exhibited prominent visual colour change toward cyanide ion over other common anions in aqueous HEPES buffer-DMF (9:1 v/v) medium. The complexation of receptor-CN^- has been addressed by UV-Vis, fluorescence and ^{1}H NMR spectra and was supported by electrochemical and DFT studies. The mechanism of sensing involves formation of H-bond between imidazole N-H and CN^- ion. The stoichiometry of the receptor- CN^- complexes was found to be 1:2 (receptor- CN^-) and the detection limit was observed to be in the range of 1.1-3 nM. The test strips based on **R5** were fabricated, which could act as convenient and efficient CN^- test kits. Notably, the novelty of the present investigation is that the receptor **R5** selectively senses CN^- ion in solid, aqueous and gas phases i.e. *'a complete receptor'*.

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Introduction

The development of molecular sensors for anions such as cyanide ion has been a subject of intense research interest because cyanide ion is a well-known hazardous chemical both in biology and the environment due to its extreme toxicity to physiological system.[1,2] It is known that 0.5-3.5 mg of cyanide per kilogram of body weight is fatal for human.[3] According to the World Health Organization (WHO) maximum permissible level of cyanide in drinking water is 1.9 μg.[4] Review of literature revealed that a number of analytical techniques such as colorimetry, and fluorescent method,[5-10] ion chromatography,[11] voltammetry,[12] flow injection analysis[13] and electrochemical analysis[14] have been developed for the detection of cyanide ion. The molecular probes reported for sensing cyanide ions are mainly based on H-bonding interaction,[15-18] nucleophilic addition,[19-22] complex formation,[23,24] coordination with Cu(II) ion,[25-27] supra-molecular self-assembly[28-30] and rearrangement reaction.[31] Although, so far a wide variety of sensors has been reported for the detection of cyanide ion, improving the detection selectivity and sensitivity in the context of interference from coexisting anions such as fluoride, acetate and dihyrogen phosphate and compatibility within an aqueous environment have been still challenging.[32-34] Therefore, the search for receptors which can sense cyanide ion sensitively and selectively in aqueous solution is still on. It is well known that the main disadvantage, with most of the traditional chemosensors which depend on the H-bonding moieties, is the lack of selectivity. Other anions such as fluoride, acetate and phosphate ions often interfere with such assays.[32-34]

Recently we have reported few anion receptors based on quinone as signaling unit in which the H-bond donor moiety is directly attached to the quinone moiety so as to have enhanced intramolecular charge transfer (ICT) transition.[35-37] Such an assembly will exhibit striking colour changes as and when form H-bond with the anions. One such report involves

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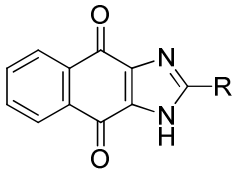
naphthoquinone-imidazole hybrid structures of the type **I**.[35] It was found that the H-bond donor property of the imidazole N-H moiety can be tuned by varying the substituent (R). However, the receptors are not selective towards a particular anion and impart colour changes with cyanide and fluoride ions in DMSO.



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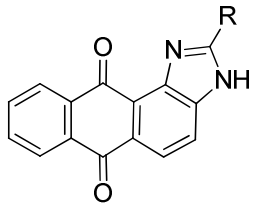
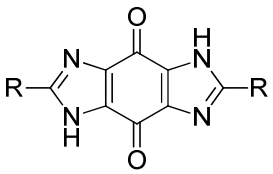


II

Similarly, Batista *et al.*[38,39] have reported anthraquinone-imidazole based colorimetric and fluorimetric receptors of the type **II**. These receptors are also not selective and showed colour change from yellow to pink with cyanide, fluoride and hydroxide ions in acetonitrile medium. Hence, it is presumed that the following quinone-imidazole type receptors with a relatively weaker quinone i.e. benzoquinone in them may exhibit different selectivity and sensitivity behaviour towards anions.



Where R= alkyl, aryl or heterocyclic substituent

Also, in the case of receptors that works via the formation of H-bond with the anions, compared to the single H-bond donor moiety (like N-H), the receptors with multiple H-bond donor moieties can both significantly increase the anion affinity and allow the receptors to tolerate a substantial amount of water from the solvent.[40] Here again, in the case of receptors having urea (**III**), thiourea (**IV**) and guanidine (**V**) as H-bond donor moieties, as the two N-H groups are close to each other, they can make H-bonds with anions like acetate and phosphate in a bidentate manner leading to lack of selectivity.

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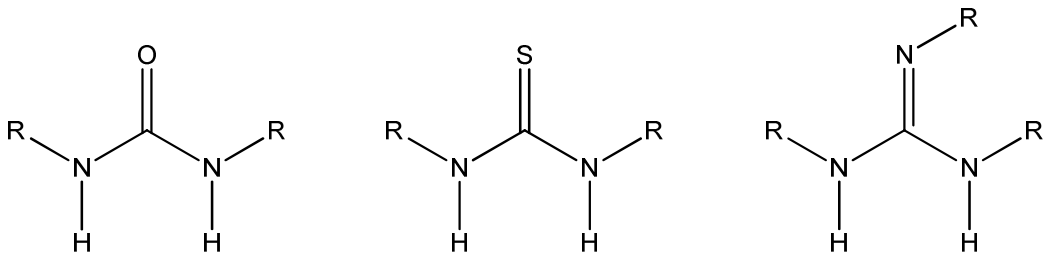
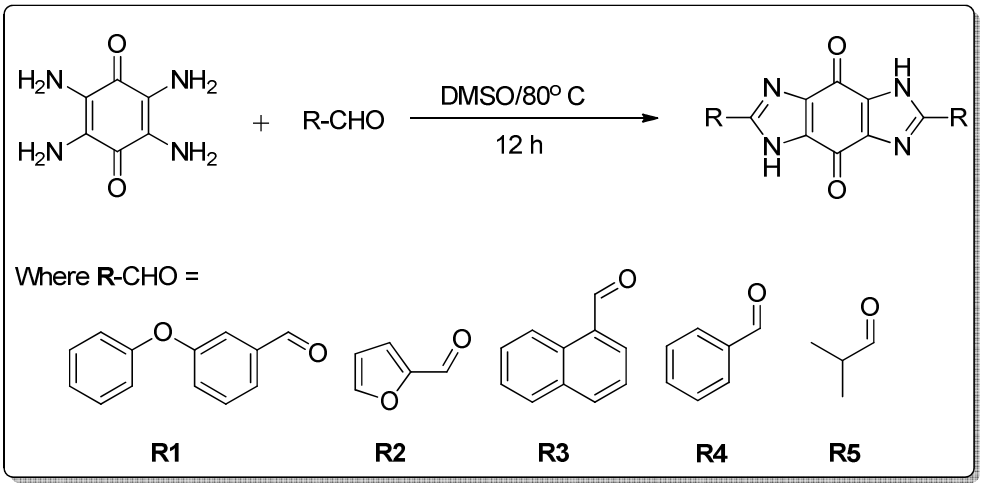


III **IV** **V**

Under these circumstances, the proposed benzoquinone-imidazole hybrids are expected to exhibit higher affinity towards anions, higher selectivity and can accommodate higher amount of water in the medium, as they possess two N-H moieties that are away from one another. The main objective, therefore, of the present endeavour is to synthesize benzoquinone-imidazole hybrids with different substituents and to investigate their cyanide ion sensing properties using spectral (UV-Vis, fluorescence, NMR), electrochemical and theoretical studies in aqueous solution.

Results and discussion

The following five new benzoquinone-imidazole hybrids possessing different substituents (**R1-R5**) were synthesized via the condensation of 2,3,5,6-tetramine-1,4-benzoquinone with corresponding aldehydes (Scheme 1).



Scheme 1. Synthesis of **R1-R5.**

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The receptors were characterized using ^{1}H NMR, LC-MS and UV-Vis spectral techniques (See Experimental section). Owing to limited solubility of the receptors, we are not able to record the ^{13}C NMR spectra of the compounds. The structure of **R5** was confirmed using single crystal X-ray diffraction study. X-ray quality crystals of **R5** were developed by diffusing chloroform and acetone to a methanolic solution of **R5**. The ORTEP diagram of **R5** is shown in Figure 1 and the crystal data are collected in Table 1. The packing diagram of **R5** is shown in Figure S1. As seen from the Figure 1 that in **R5** the two imidazole N-H groups that are *trans* to each other. The N-H bond length was observed to be 1.02 Å, which longer than that in similar benzimidazole compound (0.86 Å).[41]

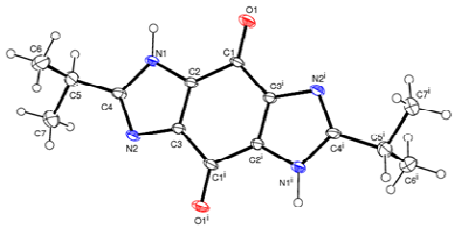

Figure 1. Crystal structures of **R5**.

This observation suggested that the N-H proton in **R5** is relatively more acidic than simple benzimidazole N-H proton and thus can acts as a better H-bond donor towards anions. The anion sensing property of the receptors **R1-R5** was investigated by spectral (UV-Vis, fluorescence and ^{1}H NMR), electrochemical and theoretical studies in aqueous solution.

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Table 1. Crystal data and structure refinement for **R5** and **R5-CN$^-$**

Molecule	**R5**	**R5+CN$^-$**
Empirical formula	C_{14} H_{16} N_4 O_2	$(C_{14}H_{14}N_4O_2)1$, $(C_{16}H_{36}N_1)1$, $(H_2O_1)2$
Formula weight	272.31	548.78
Temperature	293(2) K	100(2) K
Wavelength	0.71073 A	1.54184 A
Crystal system, space group	monoclinic, P21/c	Monoclinic, P21/n
Unit cell dimensions	a = 14.7426(13) Åa= 90°. b = 9.9228(7) Åb= 92.030(7)° c = 9.8994(7) Åg = 90°.	a = 7.8417(2) Åa= 90°. b = 24.0400(8) Åb= 98.963(3)° c = 17.3481(5) Åg = 90°.
Volume	1447.25(19) Å^3	3230.43(17) Å^3
Z, Calculated density	4, 1.250 Mg/m^3	4, 1.128 Mg/m^3
Absorption coefficient	0.087 mm^{-1}	0.596 mm^{-1}
F(000)	576	1204
Crystal size	0.350 x 0.300 x 0.300 mm^3	0.5 x 0.4 x 0.35 mm^3
Theta range for data collection	2.475 to 25.253°	4.475 to 72.145°
Index ranges	-17<=h<=17, -11<=k<=11, -11<=l<=11	-9<=h<=9, -28<=k<=29, -19<=l<=21
Reflections collected	16234	17250
Independent reflections	16234 [R(int) = ?]	0.06
Completeness to theta = 25.242°	99.1 %	99.9
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9799 and 0.9710	0.812 and 0.751
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	16234 / 108 / 210	6373 / 0 / 350
Goodness-of-fit on F^2	1.020	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0694, wR2 = 0.1537	R1 = 0.0769
R indices (all data)	R1 = 0.1291, wR2 = 0.1837	R1 = 0.0899, wR2 = 0.242
Extinction coefficient	n/a	0.0005(3)
Largest diff. peak and hole	0.247 and -0.423 e.Å^{-3}	1.248 and -0.626 e.Å^{-3}
CCDC No.	**1039004**	**1423570**

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Visual detection

To investigate the anion sensing abilities of the receptors, visual inspection of **R1-R5** ($6.25x10^{-4}$ M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26) before and after the addition of one equivalent of tetrabutylammonium salts of various anions such as F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^- , $H_2PO_4^-$ and CN^- were carried out. As a representative case the colour change observed for **R5** is shown in Figure 2 and that for **R1-R4** is given in Figure S2. As shown in the Figure 2, the receptor **R5** immediately responded with obvious colour change from yellow to pink when CN^- ion was added to the aqueous solution of **R5** at room temperature. However, the colour remained unchanged after the addition of the other chosen common anions. All the other receptors **R1-R4** also exhibited similar colour changes only with CN^- ions and not with other anions. This observation indicated that the receptors **R1-R5** can serve as selective 'naked-eye' colorimetric sensors for CN^- ion in aqueous solution. The effect of pH on the sensing behaviour of **R5**, as a representative case, has also been investigated and the colour change observed is shown in Figure S3. The results indicated that the receptor exhibited a clear colour change with cyanide ions only around pH 7. However, at other pH values (both acidic and basic) similar colour change has been observed by bringing the pH of the solution to nearly neutral before adding cyanide ions.

Figure 2. Colour changes observed in aq. HEPES buffer/DMF (9:1 v/v) solution of **R5** ($6.25x10^{-4}$ M) upon addition of various anions.

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UV-Vis spectral studies

After establishing the selectivity of the receptors **R1-R5** towards CN^- ion, to further investigate the sensing properties of the receptors, UV-Vis spectral studies were performed. All the receptors **R1-R5** ($6.25x10^{-4}$ M) exhibited an intense absorption in the 433-500 nm range (log ε 2.99-3.32) in aq. HEPES buffer-DMF (9:1 v/v) medium (Table 2). This intense absorption peak in the visible region corresponds to the intramolecular charge transfer (ICT) transition from imidazole N-atoms (donor) to the electron deficient quinone moiety (acceptor).[42,43] The existence of the ICT transition is supported by the fact that the N-H bond length in **R5** is relatively longer in length than that in benzimidazole (by 0.16 Å). That is charge transfer from donor N-H group to acceptor quinone render the N-atom relatively electron deficient, thus makes the N-H bond longer and consequently can allow the N-H group to act as a relatively better H-bond donor towards CN^- ions.

Table 2. Data obtained from the UV-Vis spectra upon titration of **R1-R5** with CN^- in aq. HEPES buffer-DMF (9:1 v/v) medium.

Receptor	In Receptor λ_{ICT} (nm)	log ε	In complex λ_{ICT} (nm)	Red shift $\Delta\lambda_{ICT}$ (nm)	Isosbestic point (nm)	K_A (M^{-1})
R1	495	3.28	601	106	530	$5.4x10^6$
R2	500	3.30	570	70	445	$3.4x10^6$
R3	470	3.26	532	62	517	$2.7x10^6$
R4	460	3.32	540	80	523	$2.3x10^6$
R5	433	2.99	525	92	481	$4.3x10^5$

On gradual addition of CN^- ion to the solution of the receptors **R1-R5**, the absorbance of the ICT transition band decreased and a new band at higher wavelength emerged and the

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absorbance of which increased gradually with a distinct isosbestic point (Table 2). As a representative case, the UV-Vis spectral changes of **R5** is given in Figure 3. The electronic spectral titration studies of **R1-R4** are collected in Figures S4-S7. The appearance of an isosbestic point indicated the formation of only one species between the receptors and CN^- ion. The bathochromic shift ($\Delta\lambda_{ICT}$ = 62-106 nm) observed in the ICT transition band after the addition of CN^- ion is due to the fact that the formation of H-bond between N-H group and CN^- ions (N-H**…**CN^-) render the N-atom relatively electron rich and thus makes the ICT transition relatively energetically easier.[35]

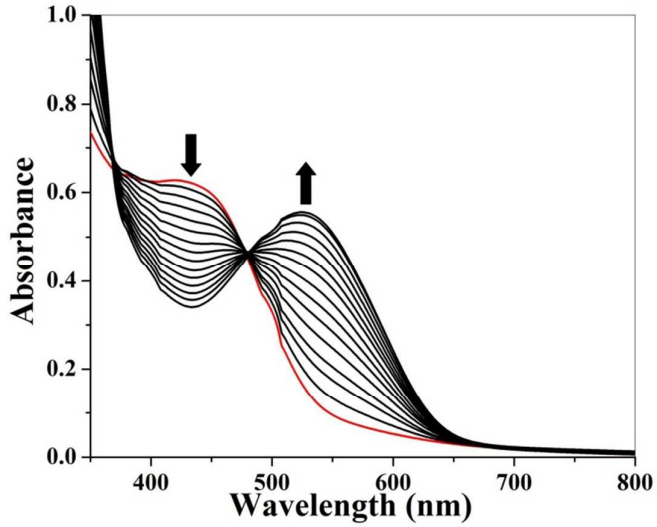

Figure 3. UV-Vis spectra of **R5** ($6.25x10^{-4}$ M) with the incremental addition of TBACN (0 - $6.25x10^{-6}$ M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

As a representative case, the UV-Vis spectra of **R5** in the presence of one equivalent of tetrabutylammonium salts of the chosen anions were also recorded in aq. HEPES buffer-DMF (9:1 v/v) solution. The results are shown in Figure 4. The results indicated that only addition of CN^- ion caused a bathochromic shift in the λ_{ICT} and all other chosen anions showed no significant influence on the UV-Vis spectra of **R5**. The absorbance of **R5**-CN^- ion solution in the presence of other anions is collected in Figure S8. Likewise, the absorbance of

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the **R5**-CN^- ion solution in the presence of cations is also recorded (Fig. S9) and the results indicated that the chosen cations exhibited no appreciable influence on the electronic spectra of the receptor. The results of the effect of other anions and cations on the UV-Vis spectra of **R5** indicated that the receptor exhibited high selectivity towards CN^- ion. The Job's plots indicated that a 1:2 (receptor-CN^-) H-bonded complex was formed between the receptors **R1-R5** and CN^- ions (Figure S10).[44] The association constants K_A for the **R**-CN^- complexes, calculated using Scott plot,[45,46] are also collected in Table 2. The observed magnitude (10^6 M^{-1}) of the K_A values indicated the formation of strong complexes between the receptors and CN^- ions.[36] The high selectivity and the striking colour changes observed in these receptors on adding CN^- ion observed in the visual detection experiments is well supported by the results of UV-Vis spectral studies.

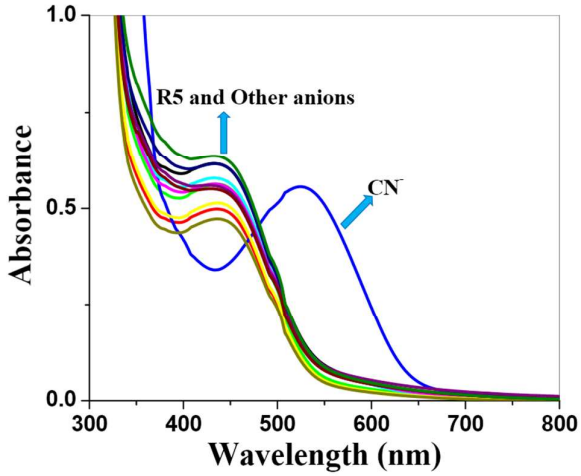

Figure 4. UV-Vis absorption changes of **R5** ($6.25x10^{-4}$ M) upon addition of 1 eqv. of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, AcO^-, S^{2-}, N^{3-}, SCN^- and CN^-.

Fluorescence spectral studies

The cyanide ion binding properties of the receptors **R1-R5** were also investigated using fluorescence spectral studies. Figure 5 shows a group of fluorescence emission spectra

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relating to the titration of **R5** with CN^- ions (as a representative case). It can be observed that with the addition of incremental amounts of CN^- ions, the fluorescence emission of the receptor **R5** is quenched indicating the formation of a complex between **R5** and CN^- ions. Also, there observed no shift in the emission wavelength, on adding CN^- ion, suggesting the receptor-CN^- complex quenching its intrinsic fluorescence.[36] All the other receptors **R1-R4** exhibited similar fluorescence emission spectral changes on adding CN^- ions (Fig. S11-S14). From the decrease in the emission intensity, the binding constant of the receptor-CN^- complexes was calculated as reported earlier.[47] The binding constants thus determined are collected in Table 3. The results indicated that the magnitude of the binding constants is in the order of 10^6 M^{-1} suggesting strong binding between the receptors and CN^- ions. The detection limit of the receptors was determined at S/N=3 (Table 3).[48] The detection limit was much lower than the maximum permissible level for cyanide ion in drinking water (1.9 μM) set by the World Health Organization (WHO).[4]

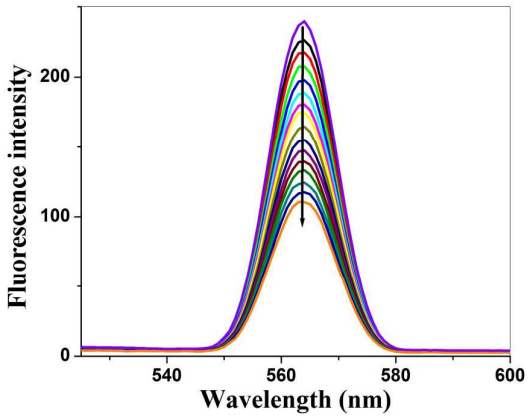

Figure 5. Fluorescence emission spectra of **R5** ($6.25x10^{-4}$ M) with incremental addition of TBACN (0 - $6.25x10^{-6}$ M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

Table 3. Fluorescence spectral data for the interaction of the receptors with CN^- in aq. HEPES buffer-DMF (9:1 v/v) medium.

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Receptor	λ_{ex}(nm)	λ_{em}(nm)	Stokes shift (nm)	Binding constant (M^{-1})	Detection limit (nM)
R1	495	629	134	$1.5x10^7$	1.1
R2	500	576	76	$5.6x10^6$	1.5
R3	470	626	156	$3.6x10^6$	2.2
R4	460	610	150	$1.3x10^6$	2.6
R5	433	564	131	$1x10^6$	3

^{1}H NMR spectral studies

The mechanism of the intermolecular interaction of the receptors with CN^- ions was studied using ^{1}H NMR spectroscopy in DMSO-d_6. The imidazole N-H protons of **R1-R5** initially appeared at 13.400-14.324 ppm (Table S1). In all the receptors the two N-H protons appeared as a singlet indicating that these two protons are in chemically same environment. The ^{1}H NMR spectral changes caused by the addition of CN^- ion as tetrabutylammonium salt in DMSO-d_6 containing **R1-R5** were studied. As a representative case, the ^{1}H NMR spectra of **R5** before and after addition of CN^- ion is shown in Figure 6. Upon the addition of CN^- (0.5 equiv.) the singlet due to N-H protons was downshifted from 13.400 ppm to 13.534 ppm ($\Delta\delta$ = 0.134 ppm) due to H-bonding with CN^- ion.[49] After the further addition of CN^- ion (2 equiv.), the N-H protons disappeared immediately. These results clearly showed that the mechanism of the sensing involves the formation of H-bond between the imidazole N-H protons and CN^- ions. All other receptors exhibited similar ^{1}H NMR spectral changes upon addition of two equivalents of CN^- ions (Fig. S15-S22).

The downfield shift observed in the signal of the N-H protons ($\Delta\delta$) after the addition of 0.5 equivalent of CN^- ion to the receptors is in the range of 0.103-0.142 ppm (Table S1). The high $\Delta\delta$ values observed in the present study indicated stronger interaction between the

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receptors and CN^- ions. Also, there exists a good correlation (r = 0.99) between log K_A and Δδ values with unit slope (Fig. S23). Thus, stronger is the interaction between the receptor and CN^- ions, higher is the association constant of the receptor- CN^- complex and higher is the downfield shift experienced by the N-H protons.

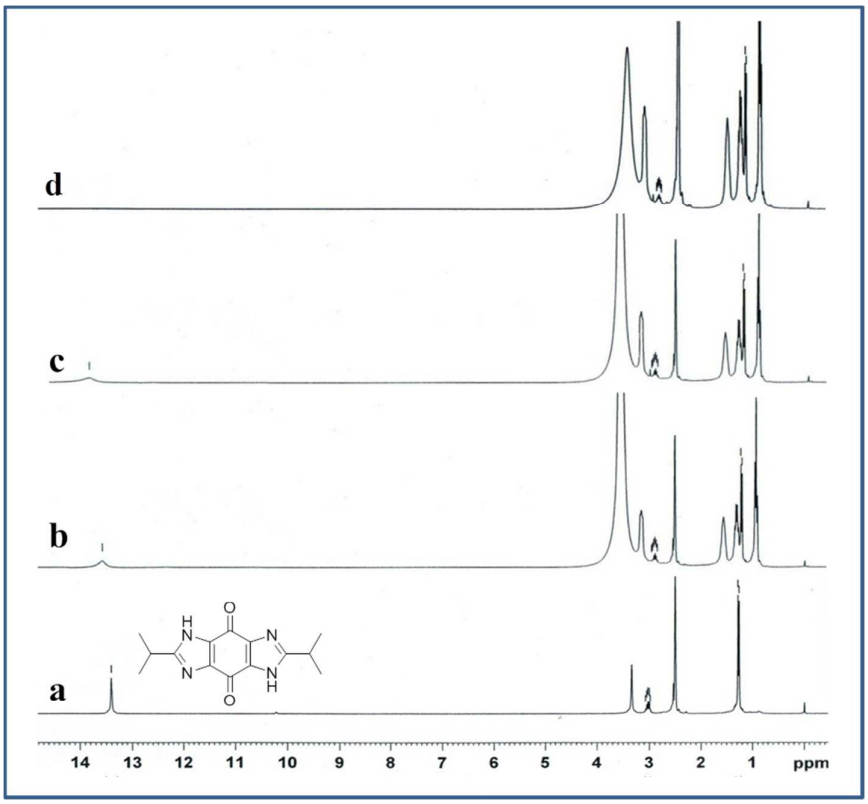

Figure 6. ^{1}H NMR spectrum of **R5** with (a) 0, (b) 0.5 (c) 1.0 and (d) 2.0 eqv. of CN^- ion in DMSO-d_6.

The results of the spectral studies indicated that the mechanism of sensing of cyanide ion by the receptors is via H-bond formation between the imidazole N-H and the cyanide ion followed by deprotonation. This proposed mechanism is further confirmed by the single crystal XRD study of the **R5**-CN^- complex. The ORTEP diagram of **R5**-CN^- complex is shown in Figure 7 and the crystal data are also collected in Table 1. The packing diagram of

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R5 CN^- complex is shown in Figure S1. The crystal structure clearly indicated that the imidazole N-H exists as tetrabutylammonium salt after deprotonation. It is to note that the results of the NMR spectral and Job's method studies indicated that the receptor-cyanide complex possesses 1:2 (receptor:CN^-) stoichiometry. However, the single crystal structure given in Figure 7 showed that while crystallization only deprotonation of one N-H group has occurred.

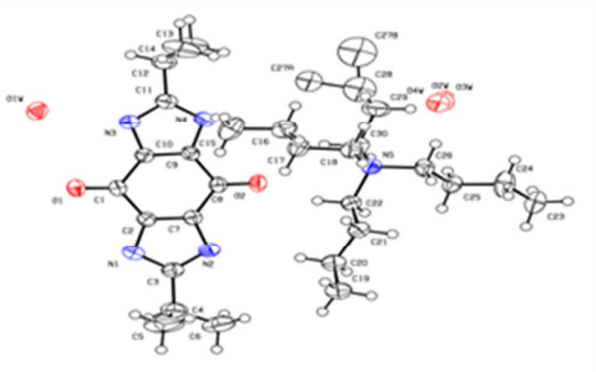

Figure 7. Crystal structure of R5-CN^- complex.

Electrochemical studies

Since the receptors (**R1-R5**) under investigation contain redox active quinone moiety, it would of interest to study the electrochemical behaviour of the receptors before and after the addition of cyanide ions. Such a study would substantiate the proposed mechanism of sensing based on spectral investigations. The cyclic voltammograms of the free receptors and that upon addition of incremental amounts of CN^- ions are shown in Figures 8 and S24-S27. The electrochemical data obtained are collected in Table 4. It is evident from the voltammograms that all the free receptors exhibit reversible redox peaks in the potential ($E_{1/2}$) range -0.360 to -0.480 V, characteristic of the quinone redox couple.[50] Also, with the addition of incremental amounts of CN^- ions, an anodic shift towards more negative potential with a concomitant lowering in current density was observed suggesting that the electro reduction of the quinone becomes relatively difficult. This is due to the fact that the added CN^- ion to the

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receptor solution forms H-bond with the imidazole N-H proton (which leads to deprotonation) increases the electron density on the N-atom and consequently render the ICT transition relatively easier, as explained in the spectral studies. Such an enhanced ICT transition makes to quinone relatively electron rich and thus its electro reduction becomes difficult.[51,52]

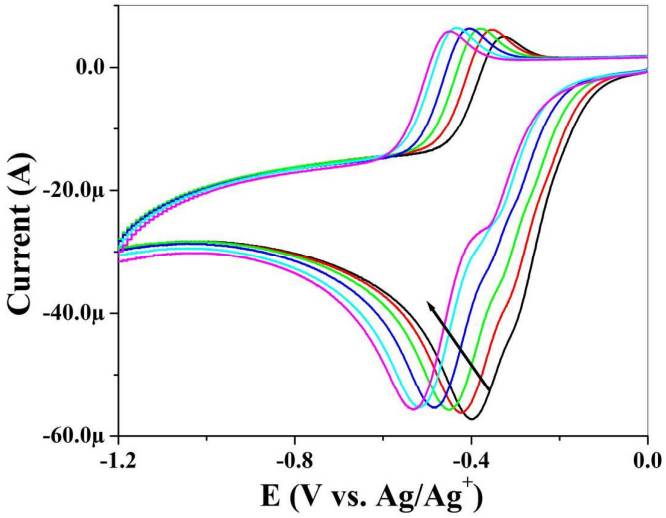

Figure 8. CV response of receptor **R5** with CN^- ion.

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Table 4. Electrochemical data of the receptors with the addition of CN^- ion.

Receptor	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	$\Delta E_{1/2}$(V)
R1	-0.430	-0.530	-0.480	
R1+CN^-	-0.538	-0.646	-0.592	0.112
R2	-0.423	-0.518	-0.470	
R2+CN^-	-0.538	-0.650	-0.594	0.124
R3	-0.408	-0.514	-0.461	
R3+CN^-	-0.496	-0.602	-0.549	0.088
R4	-0.336	-0.412	-0.374	
R4+CN^-	-0.443	-0.521	-0.482	0.108
R5	-0.326	-0.395	-0.360	
R5+CN^-	-0.433	-0.517	-0.490	0.130

Theoretical studies

With an aim to shed more light on the CN^- ion sensing behaviour of the receptors **R1-R5**, the structural and electronic properties of the free receptors and their cyanide complexes were studied using Density Functional Theory. The geometry optimization was carried out using B3LYP exchange function with 6311G basic sets using Gaussian 03 package.[53] The optimized geometries of the receptors and receptor-CN^- complexes are shown in Figure S28. The relevant frontier molecular orbitals (HOMO and LUMO) of the receptors and their cyanide complexes are depicted in Figures S29 and S30, respectively. As seen from the

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optimized geometry of **R5**, the lengths of imidazole N-H and quinone C=O bonds were found to be 1.007 and 1.24 Å, respectively. These bond lengths are in good agreement with those obtained from single crystal XRD study (1.02 and 1.21 Å, respectively).

It is evident from Figure S29 that the HOMO orbital of the free receptors is delocalized on the entire molecule symmetrically on both sides of the quinone ring, indicating the existence of conjugation between the imidazole ring and the substituent attached to it. The LUMO orbital is mainly localized on the quinone moiety. This is consistent with a strong stabilization of this LUMO due to the presence of electron withdrawing quinone moiety.[54,55] Such a distribution of the MOs resulted in a charge transfer from imidazole moiety to quinone moiety (i.e. ICT transition). The energies of the molecular orbitals and the energy correspond to the ICT transition (ΔE) in the free receptors and their cyanide complexes are given in Table S2. The results indicated that the energy required for ICT transition (ΔE) is relatively low in the receptor-CN^- complexes, indicating that the occurrence of ICT transition is relatively easier in the complex when compared to the free receptor. And thus the λ_{ICT} experienced a bathochromic shift upon addition of CN^- ions to the receptor solutions as shown in UV-Vis spectral studies. The calculated electronic nature (and structural features of **R5**) of the receptors complies nicely with the experimental observations.

The foregoing results and discussion indicated that the receptors, under investigation, have sense cyanide ion colorimetrically with high selectivity and sensitivity. The overall experimental observations and their corresponding scientific inferences derived are collected in Scheme 2.

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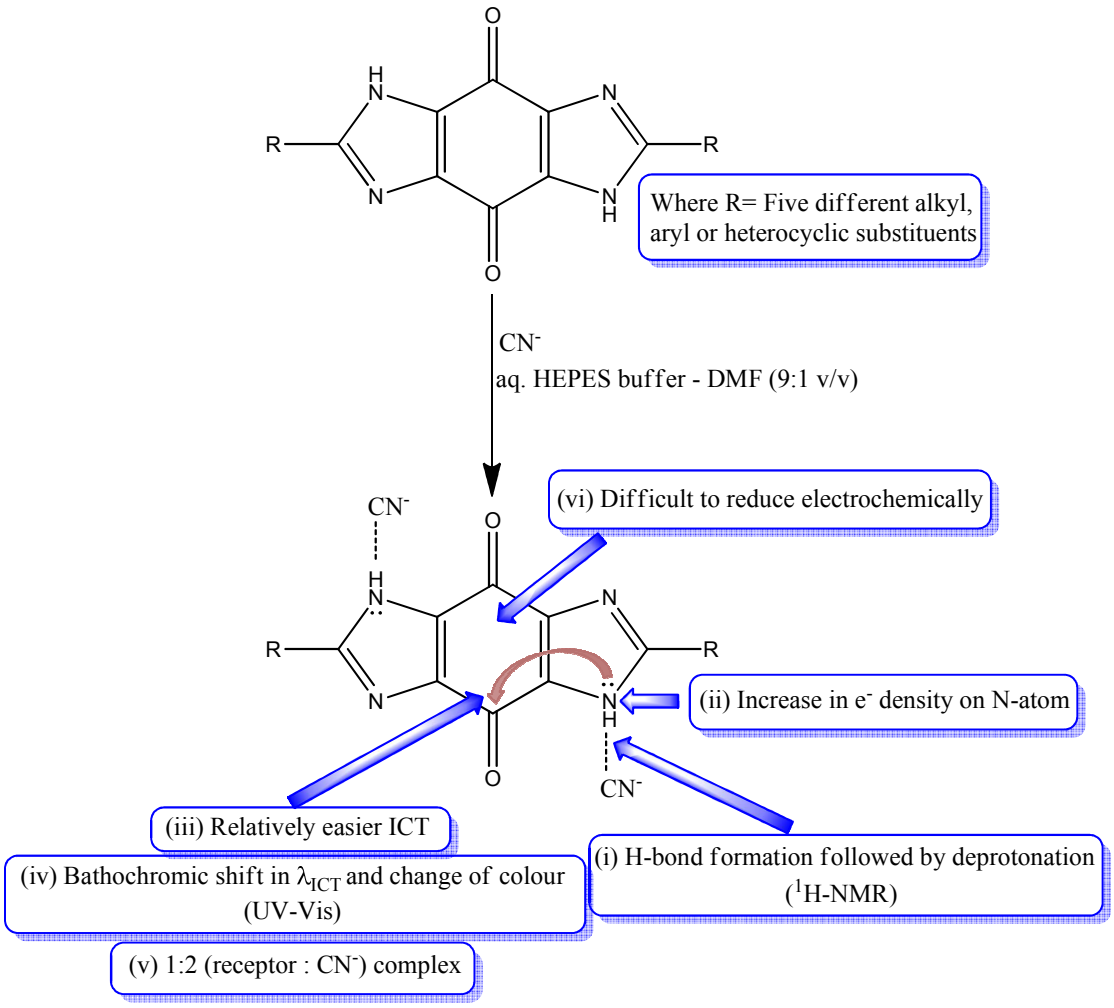

Scheme 2. Overall experimental observations and inferences upon addition of CN^- ion to the receptors.

Practical application

To investigate the practical application of the receptors, test strips were prepared by immersing filter papers into a DMF solution of **R5** (as a representative case) and then drying them in air. The test strips were utilized to sense CN^- ions of different concentrations in water. As shown in Figure 9, when the test strips were immersed in aqueous solution of CN^- ions, clear colour changes from yellow to pink was observed instantaneously. Development

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of such test strips approach is extremely attractive for 'in-the field' qualitative identification of toxic CN^- ions as it doesn't require any additional equipment.

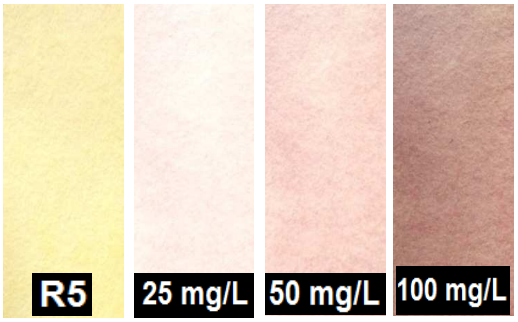

Figure 9. Colour changes of the test papers (coated with **R5**) for detecting CN^- of different concentrations in water.

Encouraged by the selective response observed with the receptors for the sensing of CN^- ions in aqueous solution, we have tested the applicability of the receptors for the chromogenic detection of CN^- in solid state also. To our delight, the receptor **R5** exhibited an excellent colour change from yellow to pink (Fig. 10) on simple grinding with solid tetrabutylammonium cyanide in a mortar for few minutes (< 5 min). In the solid phase also the receptor **R5** showed the same selectivity. However, other receptors **R1-R4** exhibited only a feeble colour change in the solid phase. To the best of our knowledge **R5** is the first receptor which selectively senses CN^- ion colorimetrically in solid phase. Such a receptor will no doubt be useful in the detection of cyanide in many solid materials.

Figure 10. Colour change of the receptor **R5** with CN^- in solid state.

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Obviously, it is quite natural (when the receptor **R5** can act as selective chemosensor for the detection of CN^- ion solid and aqueous phases) to test the applicability of the receptor **R5** to sense cyanide in gas phase also. As a preliminary attempt one of the test strip (mentioned above) was kept on the top of a reaction vial containing tetrabutylammonium cyanide (150 mg) and Con. HCl was added to it. Here again, the test strip showed noticeable colour change upon exposure to HCN gas for 2 min (Fig. 11). [CAUTION: HCN gas is extremely toxic and the experiment should be carried out in a well-ventilated fume hood].

Figure 11. Colour change of the receptor **R5** with CN^- in gaseous state.

Conclusion

Five new receptors were designed, synthesized and tested for their utility as chemosensors for CN^- ions. The receptors exhibited selective, sensitive and rapid colorimetric response toward CN^- ion in aqueous solution. As spelt in the introduction section, selection of benzoquinone as the signalling unit along with good HBD unit (imidazole) improved the selectivity of sensing when compared to similar naphthoquinone and anthraquinone based receptors. Also, the receptors with multiple H-bond donor moieties have accommodated substantial amount of water in the medium. Though the hydration energy of CN^- (ΔH_{hyd} = -67 kJ mol^{-1}) is relatively lower than that of other common anions,[56] the cyanide sensor which work via H-bond formation are less in number than chemodosimeters. Here again majority of the receptors can tolerate only <75% of water in the

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medium.[35,39,40,57,58] But in the present case the receptors developed sense CN^- ion in a medium containing 90% water. The most interesting result of the present investigation is that one of the receptor **R5** selectively senses CN^- ions colorimetrically in solid, aqueous and gas phases i.e. *'a complete receptor'*.

Experimental section

Chemical and apparatus

All the reagents for synthesis of the receptors **R1**-**R5** were obtained commercially and were used without further purification. Spectroscopic grade solvents were used as received. UV-Vis spectral studies were carried out in a double beam spectrophotometer. Steady state fluorescence spectra were obtained on a spectrofluorimeter. The excitation and emission slit width (5 nm) and the scan rate (250 nm) was kept constant for all of the experiments. Nuclear magnetic resonance spectra were recorded in DMSO-d_6 (^{1}H NMR 300 MHz). The ^{1}H-NMR spectral data is expressed in the form: Chemical shift in units of ppm (normalized integration, multiplicity, and the value of J in Hz). The ^{13}C NMR spectra of the compounds were not recorded due to their low solubility. The cyclic voltammetric (CV) experiments, of 1 mmol solutions of the compounds, were carried out using GC as working, Pt wire as reference and Ag wire as auxiliary electrodes in DMF containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte at a scan rate of 100 mVs^{-1}.

Synthesis and characterization of 2,3,5,6-tetraaminocyclohexa-2,5-diene-1,4-dione.(1)

One of the starting compounds (for the synthesis of **R1-R5**) was prepared as reported earlier[59] (Scheme 3).

Step1: To a stirred solution of tetrachloro-p-benzoquinone (50 g, 0.20 mol) in ACN (500 mL), potassium phthalimide (150 g, 0.80 mol) was added. The reaction mixture was refluxed for 12 h under nitrogen atmosphere. Afterwards the reaction mixture was cooled to room

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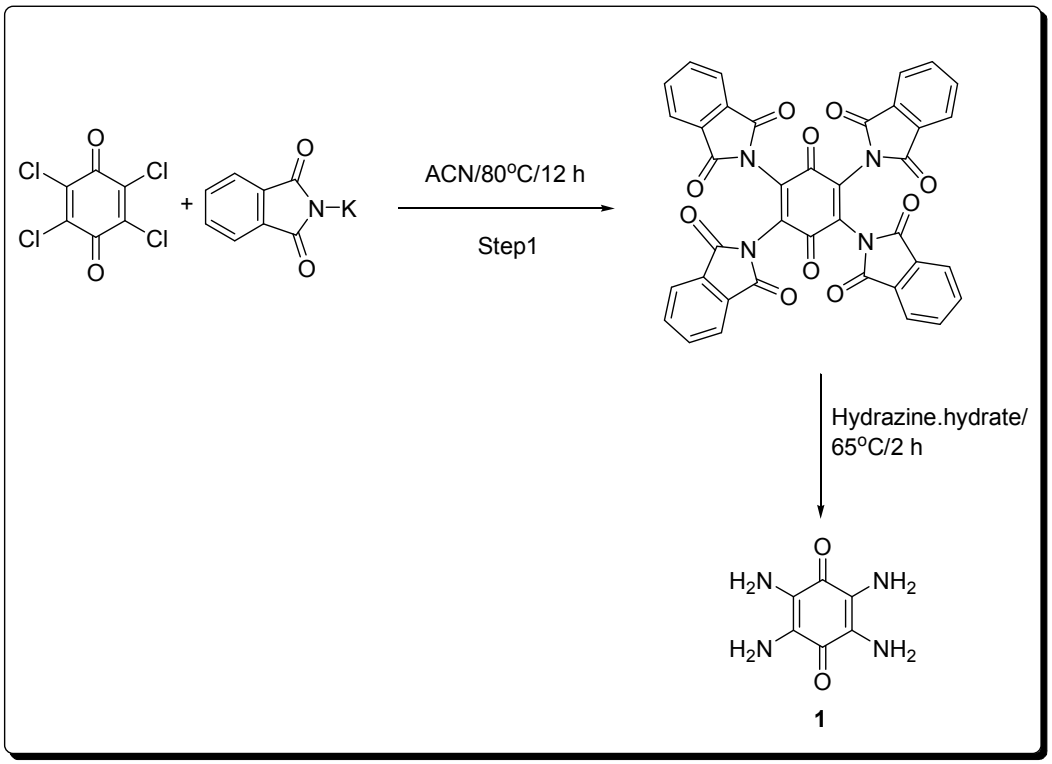
temperature and filtered through a filter paper and the filtered solid was redissolved in DMF (200 mL) and stirred at 100 °C for 10 min and the hot solution was filtered to get white solid.

Step2: The white solid thus obtained was transferred to a 1L round bottom flask and then 500 mL of hydrazine hydrate was added. The reaction mixture was heated to 65ºC for 2 h. Finally the reaction mixture was cooled to roomtemperature and the crystal formed in the reaction mixture was filtered to get the pure product as a purple crystalline solid (10 g, Yield= 29%). δ_H (300 MHz; DMSO-d6; Me_4Si): 4.55 (s, 8H) (Fig. S31). δ_C (75 MHz; DMSO-d6; Me_4Si): 121.36, 178.81 (Fig. S32). LCMS (ESI-APCI) m/z: Calcd for $C_5H_4ClN_3O_2$ $[M-H]^+$: 168.0; Found: 167.0 (Fig. S33).



Scheme 3. Synthesis of 2, 3, 5, 6-tetraaminocyclohexa-2, 5-diene-1, 4 – dione.

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General procedure for the synthesis of receptors (R1-R5)

A mixture of compound **1** (1 mmol) and corresponding aldehyde (2 mmol) in DMSO (5 mL) was heated at 90º C with stirring for 12 h. After cooling to room temperature, the precipitate obtained from the reaction mixture was filtered through a filter paper and washed with cold ethanol to obtain the pure product. The receptors **R1-R5** were characterized using ^{1}H NMR and LCMS spectral techniques. The results obtained are:

Receptor **R1**: Brown solid (0.4 g, yield =42.8%). δ_H (300 MHz; DMSO-d_6; Me_4Si): 7.09-7.23 (m, 8H), 7.42-7.56 (m, 6H), 7.78 (s, 2H), 7.93-7.95 (d, 2H, J=7.5Hz), 14.32 (s, 2H) (Fig.S34). LCMS (ESI-APCI) m/z: Calcd for $C_{32}H_{20}N_4O_4$ $[M-H]^+$: 524.15; Found: 523.20 (Fig. S35).

Receptor **R2**: Reddish brown solid (0.3 g, yield =52.5%). δ_H (300 MHz; DMSO-d_6; Me_4Si): 6.71-6.72 (t, 2H, J=1.5Hz, J=1.8Hz), 7.23-7.24 (d, 2H, J=3Hz), 7.93 (s, 2H), 14.28 (s, 2H) (Fig. S36). LCMS (ESI-APCI) m/z: Calcd for $C_{16}H_8N_4O_4$ $[M-H]^+$: 320.05; Found: 319.0 (Fig. S37).

Receptor **R3**: Yellowish orange solid (0.35 g, yield = 44.5%). δ_H (300 MHz; DMSO-d_6; Me_4Si): 7.62-7.70 (m, 6H), 8.02-8.14 (m, 6H), 8.89-8.92 (d, 2H, J=7.5Hz), 14.21 (s, 2H) (Fig. S38). LCMS (ESI-APCI) m/z: Calcd for $C_{28}H_{16}N_4O_2$ $[M-H]^+$: 440.13; Found: 439.10 (Fig.S39).

Receptor **R4**: Yellowish orange solid (0.35 g, yield =57.6%). δ_H (300 MHz; DMSO-d_6; Me_4Si): 7.52-7.68 (m, 6H), 8.17-8.19 (m, 4H), 14.13 (s, 2H) (Fig. S40). LCMS (ESI-APCI) m/z: Calcd for $C_{20}H_{12}N_4O_2$ $[M-H]^+$: 340.10; Found: 339.10 (Fig. S41).

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Receptor **R5**: Yellow solid (0.35 g, yield =72%). δ_H (300 MHz; DMSO-d_6; Me_4Si): 1.26-1.28 (d,12H, J=6.9Hz), 2.98-3.08 (m,2H), 13.40 (s, 2H) (Fig. S42).LCMS (ESI-APCI) m/z: Calcd for $C_{14}H_{16}N_4O_2$ $[M-H]^+$: 272.13; Found: 271.10 (Fig.S43).

Appendix A

CCDC numbers 1039004 and 1423570 contain the supplementary crystallographic data for the receptor R5 and R5-CN^- complex, respectively given as CIF file. Crystallographic data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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