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Synthesis, optical and electrochemical properties of new receptors and sensors containing anthraquinone and benzimidazole units

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ABSTRACT

Novel anion receptors and sensors, **HBIMANQ** and **BIMANQ** fabricated from the imidazolole unit and anthraquinone moieties were synthesized. ^{1}H NMR spectroscopy and UV–vis titrations in DMSO-d_6 and DMSO, respectively, showed that both receptors underwent deprotonation at the N*H*– moiety of the amide–anthraquinone unit in the presence of basic anions such as F^- and AcO^-. These phenomena gave a dramatic color change due to charge transfer transition corresponding to the shift of λ_{max} from 371 nm to 489 nm. Redox chemistry of **HBIMANQ** and **BIMANQ** in the presence of anions (F^-, Cl^-, AcO^-, BzO^-, and $H_2PO_4^-$) using cyclic voltammetry showed the different CV responses upon addition of various anions. In the case of **HBIMANQ** with various anions, the CV changes are dependent on the basic strength of anions in order of $F^->AcO^-$, $BzO^->H_2PO_4^->Cl^-$, Br^-. Interestingly, the CV responses of **BIMANQ** with $H_2PO_4^-$ exhibited the most significant changes. **BIMANQ**, thus, has an excellent electrochemical selectivity toward $H_2PO_4^-$.

1. Introduction

In recent years, a number of research groups have used anthraquinone derivatives to function as potential naked-eye anion sensors.[1] Das and co-workers[2] reported a novel colorimetric receptor based on disubstituted-1,2-diaminoanthraquinone as a chromogenic signaling unit for detecting fluoride ion. Miyaji and Sessler[3] evaluated the visual properties of the complexes of anthraquinone derivatives with various anions, and found that the significant color change depends on the basicity and the appropriate orientation of anions to undergo hydrogen bonding interactions with the N*H*$_2$-site of anthraquinone. Brooks and co-workers[4] investigated an anthraquinone-based anion receptor to study hydrogen bonding through intra- or intermolecular interactions using the cyclic voltammetry, in the presence of F^-. Two one-electron quasi-reversible electrochemical properties were observed. Carneiro and coworkers[5] used anthraquinone-based chlorotriazine reactive dyes as dyeing agents removed from aqueous solution using electrochemical reduction.

Imidazolium cations have been widely used in ionic liquids[6–11] and for generation of carbenes in organometallic processes and catalysts.[12–16] Moreover, imidazolium derivatives are employed as a complementary binding enhancement for anions. Particularly, (C–*H*)$^+\cdots$X$^-$ interaction at the C(2)*H* position is a powerful tool to encourage strong hydrogen bonding interaction with concomitant electrostatic forces toward anions.[17] Beer and co-workers synthesized and studied interlock molecules, known as pseudorotaxanes and rotaxanes employing the (C–*H*)$^+\cdots$X$^-$ hydrogen bonding interaction.[18–22] Such fascinating behaviors prompted to synthesize novel molecular sensors, **HBIMANQ** and **BIMANQ**, based on imidazolium as a binding site, and anthraquinone as a visual and electrochemical sensory unit. Herein, we studied the binding and sensing behaviors of **HBIMANQ** and **BIMANQ** toward F^-, Cl^-, Br^-, $H_2PO_4^-$, AcO^-, and BzO^-. We would like to compare binding properties between receptors with and without the positive charge on the benzimidazole unit, which was expected to enhance the binding affinity toward anions. Binding and sensing properties of **HBIMANQ** and **BIMANQ** were studied by ^{1}H NMR spectroscopy, UV–vis spectrophotometry, and cyclic voltammetry.

2. Results and discussion

2.1. Synthesis

Compounds **HBIMANQ** and **BIMANQ** were synthesized as outlined in Scheme 1. The synthesis of **HBIMANQ** was started by a reaction between benzimidazole and 1-bromohexane using NaOH as base in dimethylformamide at reflux to give compound **2** in 80% yield. A coupling reaction of **2** with compound **3** in a mixture of acetone and chloroform in the presence of NaI followed by conversion of counter anions using KPF_6 in THF yielded **HBIMANQ** in 85% yield. **BIMANQ** was synthesized in 80% yield by coupling benzimidazole with compound **3** using NaH as base in THF. The

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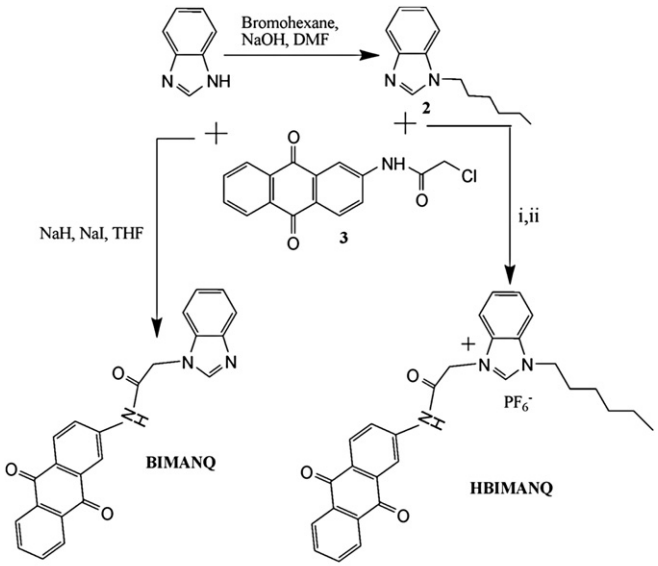
structures of **HBIMANQ** and **BIMANQ** were characterized by NMR spectroscopy, ESI MS spectroscopy, and elemental analysis. However, the elemental analysis result of **HBIMANQ** obtained from the experiment is not in good agreement with those from calculation since this ligand is very hygroscopic.



i: NaI, acetone, CH_3Cl, RT, ii KPF_6, THF, RT

Scheme 1. Synthesis of **HBIMANQ** and **BIMANQ**.

2.2. Binding studies using ^{1}H NMR spectroscopy and UV–vis spectrophotometry

From the ^{1}H NMR spectra, the characteristic peaks namely, the N*H*$_{amide}$ on anthraquinone, C(2)*H*, and –N$_{imid}$C*H*$_2$N$_{amide}$– of **HBIMANQ** and **BIMANQ** displayed at 11.30 and 11.13 ppm, 9.78 and 8.45 ppm as well as 5.60 and 5.28 ppm, respectively. Binding studies of **HBIMANQ** toward F^-, Cl^-, Br^-, $H_2PO_4^-$, AcO^-, and BzO^- were carried out by NMR spectroscopy in DMSO-d_6. Figure 1 shows the ^{1}H NMR spectra of the complexation of **HBIMANQ** and all guests at 4 equiv.

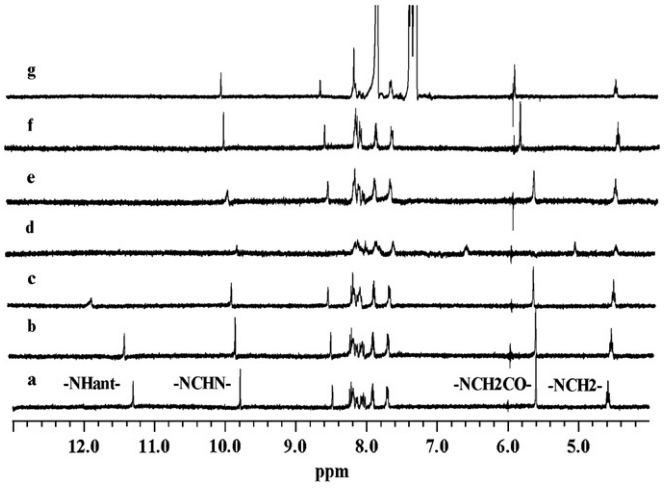


Figure 1. ^{1}H NMR spectrum in DMSO-d_6 at 298 K of (a) **HBIMANQ** (5×10^{-3} M), (b) **HBIMANQ**+4 equiv Bu_4NBr, (c) **HBIMANQ**+4 equiv Bu_4NCl, (d) **HBIMANQ**+4 equiv Bu_4NF, (e) **HBIMANQ**+4 equiv $Bu_4NH_2PO_4$, (f) **HBIMANQ**+4 equiv Bu_4NAcO, and (g) **HBIMANQ**+4 equiv Bu_4NBzO.

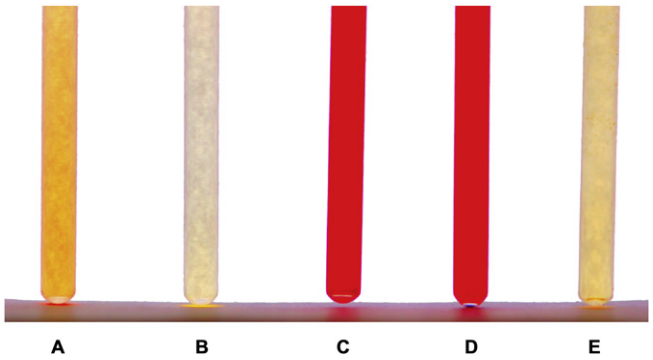


Figure 2. The color change of (A) **HBIMANQ**+4 equiv CH_3COO^-, (B) **HBIMANQ**, (C) **HBIMANQ**+4 equiv F^-, (D) **HBIMANQ**+10 equiv F^-, and (E) **HBIMANQ**+4 equiv F^-+H_2O under each condition in DMSO.

The N*H*$_{ant}$ signals of **HBIMANQ** vanished upon addition of 0.1, 0.1, 0.1, and 2.5 equiv of F^-, AcO^-, BzO^-, and $H_2PO_4^-$, respectively. The features of the spectra for the bound ligand differ from the spectral pattern for the unbound ligand indicating that **HBIMANQ** can bind with all guests with the different binding abilities independent of size or geometry of the anions, only on the basicity. From ^{1}H NMR titrations for ligand and F^-, it should be noted that N*H*$_{ant}$ resonances shifted downfield and were then followed by the disappearance of a proton and the upfield-shift of aromatic protons on further addition of F^-. Moreover, an appearance of new triplet signals of bifluoride (HF_2^-) protons was found ca. 16.05 ppm (Supplementary data). These evidences showed that H-bond interactions occurred between N*H*$_{ant}$ with F^- prior to deprotonation.

Upon addition of 5 equiv of $H_2PO_4^-$, AcO^-, BzO^-, and F^- into **BIMANQ** solutions, it was found that the N*H*$_{ant}$ signal disappeared signifying deprotonation. However, the –C(2)*H*– signal of **BIMANQ** slightly shifted downfield due to hydrogen bonding interactions. We attempted to find the association constants of **BIMANQ** toward anions, but they could not be obtained due to the deprotonation process.

Concomitant with deprotonation, dramatically color changes were observed upon addition of F^- and AcO^- to **HBIMANQ** and **BIMANQ**. In the presence of 4 equiv F^-, the color of the solution was changed from yellow to orange, and further addition of F^- shifted the color to deep red (Fig. 2). However, the color change is less intense in the case of AcO^-. This is probably due to the stronger basic character of F^-. Upon addition of H_2O, the red color of **HBIMANQ**·F^- turned to the initial color (Fig. 2). This signified that the deprotonation of **HBIMANQ** is reversible. In the case of BzO^- and $H_2PO_4^-$, the color of the solutions of **HBIMANQ** changed slightly upon addition of such anions. For Br^- and Cl^-, there was no color change at all. This agrees with the ^{1}H NMR spectra, which showed that the N*H*$_{ant}$ was still present. The behavior of **BIMANQ** has a similar fashion to **HBIMANQ**. The UV–vis spectra of **HBIMANQ** and **BIMANQ** with 4 equiv F^- are illustrated in Figure 3. The new peak at 489 nm developed in the spectrum (as shown in Fig. 3d) is concomitant with color changes from colorless to yellow. Presumably, F^- is able to deprotonate N*H*$_{ant}$ and to induce charge transfer from the negative charge of N*H*$_{ant}$ to anthraquinone.[3] Upon addition of NH_4OH to the solution of **HBIMANQ**, a new absorption band displayed at 489 nm (green line in Fig. 3c) and the color of the solution turned deep red similar to the case of F^-. This band was undoubtedly corresponding to the deprotonated **HBIMANQ** species. This result agrees with Gunnlaugsson's report on the deprotonation process of a urea-based anion receptor.[23–25] For other anions, UV–vis spectra of **HBIMANQ** exhibit a gradual decrease of the initial absorption band without the appearance of a new peak. Interestingly, the color change and a new absorption band were not

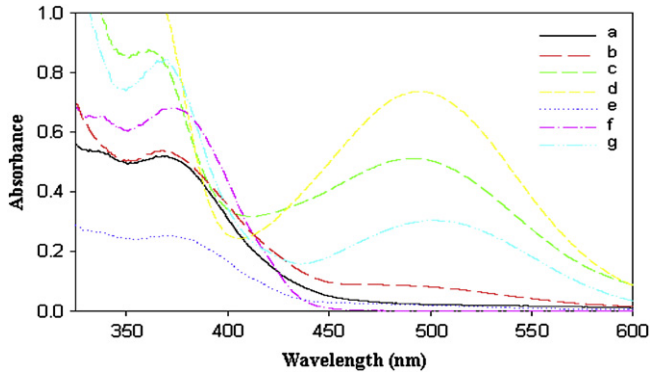


Figure 3. UV spectrum of (a) **HBIMANQ** (7.5×10^{-4} M), (b) **HBIMANQ**+4 equiv Bu_4NF, (c) **HBIMANQ**+4 equiv Bu_4NOH, (d) **HBIMANQ**+4 equiv Bu_4CH_3COO, (e) **HBIMANQ**+4 equiv Bu_4NF+ex. H_2O, (f) **BIMANQ**, and (g) **BIMANQ**+4 equiv Bu_4NF in DMSO at 298 K.

observed upon the addition of AcO^- to **HBIMANQ**, possibly caused by the low concentration of **HBIMANQ**. The naked-eye detectability of **HBIMANQ** and **BIMANQ** with F^- is independent of its concentration. Deprotonation was found to be completely reversible because **HBIMANQ**·F^- showed the original color and spectrum of **HBIMANQ** in the presence of H_2O (blue line in Fig. 3e).

Anion binding constants of receptors **HBIMANQ** and **BIMANQ** were measured by UV–vis titrations in DMSO. The titration graph of **HBIMANQ** with F^- is shown in Figure 4. Job's plot measured by UV spectrophotometry indicated that ligands bind anions in a 1:1 fashion. Results of titrations of **BIMANQ** toward anion guests are similar to those of **HBIMANQ**. All log *K* values were calculated by Spectfit 32 program in the model of 1:1 complexation. The log *K* values of **HBIMANQ** with various anions are of 3.71 for Cl^-, 3.63 for Br^-, 4.22 for $H_2PO_4^-$, and 5.63 for BzO^-. Unfortunately, we could not obtain the binding constants between **HBIMANQ** with F^- and AcO^- because of the occurrence of two processes toward ligands including binding and deprotonation. The log *K* values of **HBIMANQ** with anions are in order of $Br^-<Cl^-<H_2PO_4^-<C_6H_5COO^-$. The results showed that **HBIMANQ** appreciated Y-shape anions over spherical anions. In the case of **BIMANQ**, its binding constants could not be refined because this receptor contained one N*H* amide and no positive charge on benzimidazole. Therefore, the binding site may not have enough binding affinity.

2.3. Electrochemical properties of HBIMANQ and BIMANQ

HBIMANQ and **BIMANQ** have anthraquinone moiety, which typically exhibits two redox couples. The reversible first wave represents an electron transfer of the quinone moiety (AQ) to form

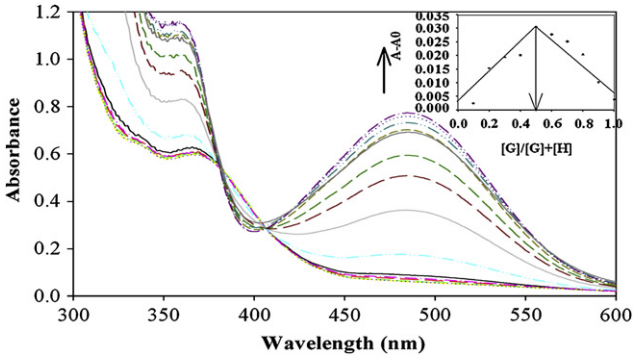


Figure 4. UV–vis titrations of **HBIMANQ** with Bu_4NF in DMSO. [**HBIMANQ**]=7.5×10^{-4} mol L^{-1} and [Bu_4NF]=0–0.004 mol L^{-1}.

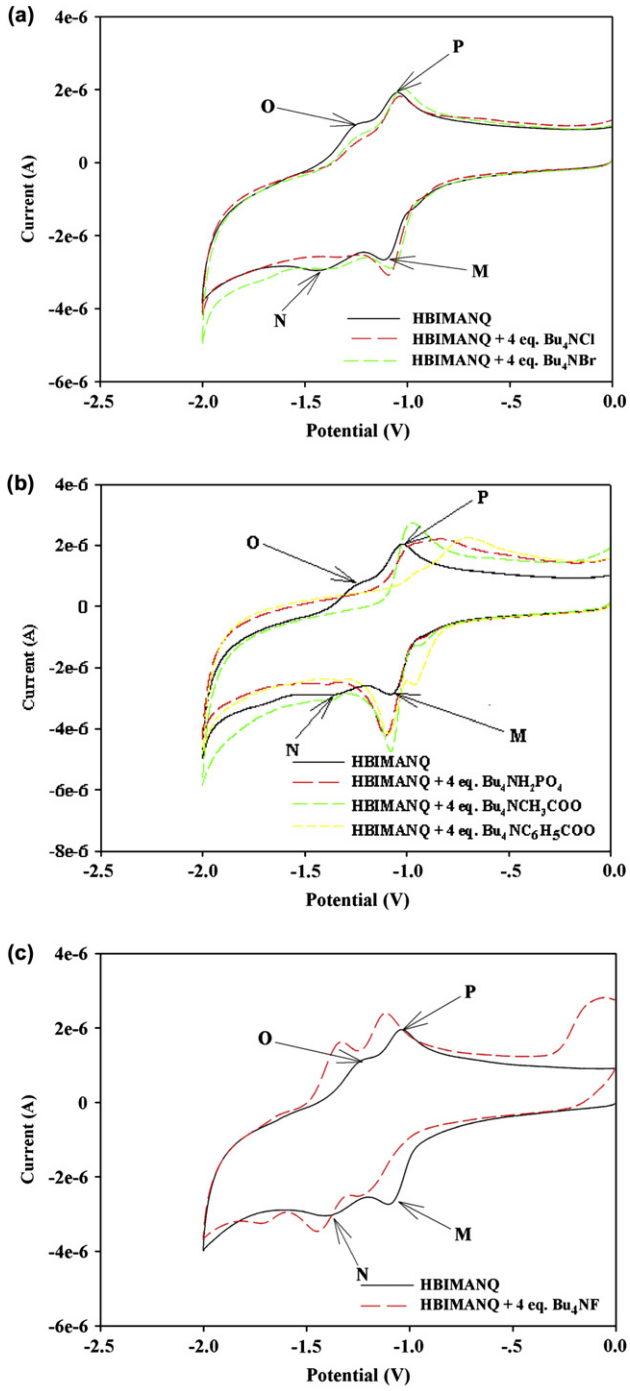


Figure 5. Cyclic voltammograms of ligand **HBIMANQ** upon addition of 4 equiv of (a) Bu_4NBr and Bu_4NCl, (b) $Bu_4NH_2PO_4$, Bu_4NCH_3COO, and $Bu_4NC_6H_5COO$, and (c) Bu_4NF.

a semiquinone anion radical ($AQ^{\bullet-}$). The second irreversible reduction wave corresponds to the subsequent addition of a second electron to the semiquinone anion radical, producing a hydroquinone dianion (AQ^{2-}).[26,27] To explore the electrochemical behaviors of **HBIMANQ** and **BIMANQ** with anions, both ligands were examined by cyclic voltammetry.

The electrochemical studies of **HBIMANQ** upon adding 4 equiv of various anions. The cyclic voltammograms are shown in Figure 5 and the potential values are collected in Table 1. In the case of Br^- and Cl^-, the CVs showed slight shifts from the initial electrochemical potential because both anions can bind to the ligand with a weak interaction.

Table 1
The potential values of compound **HBIMANQ** with 4 equiv of various anions

	E_{pc} (V)	E_{pc} (V)	E_{pa} (V)	E_{pa2} (V)	ΔE_{pc} (V)	ΔE_{pc} (V)	ΔE_{pa} (V)	ΔE_{pa} (V)
	M	N	O	P	M	N	O	P
HBIMANQ	−1.083	−1.392	−1.257	−1.041	—	—	—	—
$+Cl^-$	−1.083	—	−1.038	−1.251	0	—	−0.219	0.200
$+F^-$	−1.193	−1.443	−1.352	−1.120	0.110	0.051	0.095	0.079
$+H_2PO_4^-$	−1.099	—	−0.967	—	0.0160	—	−0.290	—
$+CH_3COO^-$	−1.077	—	−0.983	—	−0.006	—	−0.274	—
$+C_6H_5COO^-$	−0.970	−1.047	−0.784	—	−0.113	−0.345	−0.473	—

In the presence of Cl^-, Br^-, CH_3COO^-, $C_6H_5COO^-$, and $H_2PO_4^-$, CVs of these anions with **HBIMANQ** showed a similar shape but gave different shifts of reduction and oxidation waves, which depend on the basicity of the anions. As with NMR and UV–vis results mentioned above CH_3COO^-, $C_6H_5COO^-$, and $H_2PO_4^-$ could bind to **HBIMANQ** by electrostatic forces and hydrogen bonding interaction, which occurred from the intermolecular proton transfer of the N*H*$_{ant}$ amide and anions. These complexes might inhibit further reduction process of the semiquinone species to dianion species resulting in the high current intensity of semiquinone peak with concomitant low current intensity or disappearance of dianion peak.

In the case of F^-, both redox couples of **HBIMANQ** show the cathodic shifts because of the enhancement of negative charge by the deprotonation of the N*H* amide moiety.[4,28,29] Therefore, it is difficult to reduce the anthraquinone of **HBIMANQ**. Since the F^- anion is a strong base, it prefers to deprotonate the N*H* amide without the hydrogen bonding formation. Possibly, this anion could not obstruct the further reduction process to the dianion species. Therefore, this receptor has the ability to detect the F^- anion selectively, correlating to the significant change of CV response.

The complexation behaviors of **BIMANQ** with anions were investigated by cyclic voltammetry. Unlike the typical cyclic voltammogram of anthraquinone, **BIMANQ** showed two redox couples, which were not the reversible processes. The first redox couple was a one-electron irreversible process, corresponding to the semiquinone species and the second one was attributed to the dianionic species as shown in Figure 6. The CV responses of **BIMANQ** with 4 equiv of Cl^-, CH_3COO^-, $C_6H_5COO^-$, and F^- changed slightly with the intensities of the oxidation peaks but **BIMANQ** with F^- and AcO^- displayed the largest changes of intensities of the semiquinone species (see in Supplementary data).

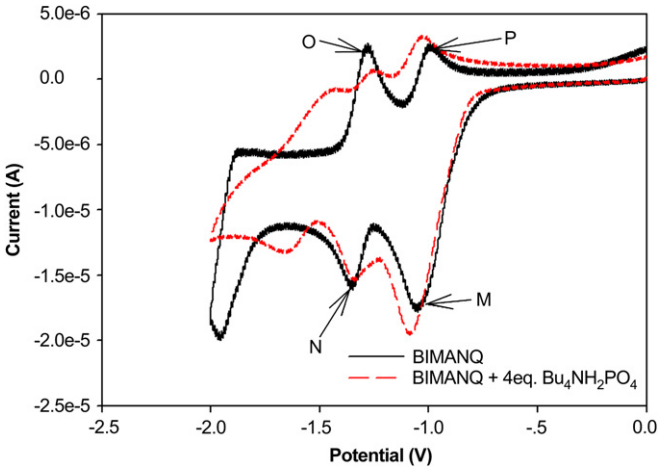


Figure 6. Cyclic voltammograms of ligand **BIMANQ** upon the addition of 4 equiv of $Bu_4NH_2PO_4^-$.

Interestingly, $H_2PO_4^-$ induced the significant change in cyclic voltammogram most depicted in Figure 6. CV response exhibits three reduction and oxidation peaks. The appearances of the new reduction and oxidation peaks were observed at −1.624 V and −1.470 V, respectively. The semiquinone peak of **BIMANQ** and $H_2PO_4^-$ showed the shift to a more negative potential and the enhancement of the current.

In addition, **BIMANQ** has no charge on benzimidazole to encourage the electrostatic interactions toward anions. The significant changes of CV responses possibly stemmed from multiple hydrogen bonding interactions between the reduced form of **BIMANQ** and $H_2PO_4^-$ leading to the strong binding affinity compared to other anions.

3. Conclusions

We have developed novel colorimetric anion sensors for F^- and AcO^-. Interestingly, **HBIMANQ** in the presence of F^-, AcO^-, BzO^-, and $H_2PO_4^-$ underwent deprotonation on N*H*$_{ant}$. From complexation studied by UV–vis and NMR techniques, **HBIMANQ** prefers Y-shape anions over spherical anions due to the complementary π–π stacking interactions. Meanwhile, **BIMANQ** could bind with anions with a weak interaction. Cyclic voltammograms of **HBIMANQ** in the presence of various anions showed changes of redox signals. It means that this receptor has responded to all anions electrochemically. However, it was found that CVs showed the most significant changes by shifting to more negative potentials in the presence of F^-. Interestingly, CVs of **BIMANQ** with all anions except $H_2PO_4^-$ exhibited only small changes. The electrochemical study of **BIMANQ** with $H_2PO_4^-$ showed a larger change than other anions probably due to multiple hydrogen bonding interactions between two hydrogens of $H_2PO_4^-$ and the oxygen of anthraquinone. Therefore, **BIMANQ** was a powerful electrochemical sensor for $H_2PO_4^-$.

4. Experimental

4.1. Materials and methods

Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6, $CDCl_3$, and CD_3CN on a Varian 400 MHz spectrometer. Electrospray mass spectra were determined on a Micromass Platform quadrupole mass analyser with an electrospray ion source using acetonitrile as solvent. All melting points were obtained on an Electrothermal 9100 apparatus. Infrared spectra were carried out on a Nicolet Impact 410 FTIR spectrometer at room temperature with potassium bromide (KBr) disks. Elemental analyses were carried out on a Perkin–Elmer CHON/S analyzer (PE 2400 series II). Absorption spectra were measured by a Varian Cary 50 UV–vis spectrophotometer. Cyclic voltammetry was performed using a μAutolab Type III potentiostat. Unless otherwise specified, the solvents and all materials were reagent grade without further purification prior to use. Commercial grade solvents such as acetone, dichloromethane, hexane, methanol, and ethylacetate were purified by distillation before use. Acetonitrile, dimethylformamide, and dichloromethane were dried over calcium hydride and THF was dried over benzoquinone and sodium and freshly distilled under nitrogen atmosphere prior to use. All anion salts and ligands were dried in vacuo prior to use.

4.2. Synthesis

*4.2.1. 1-n-Hexylbenzimidazole (**2**)*

To a stirred solution of benzimidazole (0.50 g, 4.2 mmol) and sodium hydroxide (0.17 g, 4.2 mmol), a solution of hexylbromide (0.60 mL, 2.3 mmol) in 65 mL dimethylformamide was slowly

added and heated at reflux for 24 h under nitrogen atmosphere. The mixture was evaporated in vacuo. The residue was purified by column chromatography (SiO_2) using 50% ethylacetate/dichloromethane as eluent to afford compound **2** as colorless liquid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H, –NC*H*N–), 7.58 (m, 2H, –Ar*H*–), 7.22 (m, 2H, –Ar*H*–), 4.21 (m, 2H, –NCH_2–), 1.75 (m, 2H, –CH_2–), 1.22 (m, 6H, –CH_2–), 0.80 (m, 3H, –CH_3); FTIR (KBr disk) ν [cm^{-1}] 2928 (m), 1496 (s), 1457 (s), 1368 (s), 743 (s).

4.2.2. Chloroethyleneamidoanthraquinone (**3**)[30]

A solution of aminoanthraquinone (1.00 g, 4.5 mmol) and pyridine (0.86 mL, 5.4 mmol) was stirred in 50 mL dichloromethane and cooled to 0 °C. After slowly adding a solution of chloroacetylchloride (0.61 g, 5.4 mmol) in (15 mL) dichloromethane, a brown precipitate appeared. HCl (3 M) was added to the mixture and the organic layer was extracted with water (3×50 mL). The organic layer was dried with anhydrous sodium sulfate and evaporated in vacuo to obtain a brown solid and further crystallized with dichloromethane/hexane. The purified compound **3** yielded as the brown crystalline solid in 70%. Mp 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H, –N*H*–), 8.36 (m, 4H, –Ar*H*–), 8.26 (s, 1H, –Ar*H*–), 7.85 (m, 2H, –Ar*H*–), 4.30 (s, 2H, –CH_2–); FTIR (KBr disk) ν [cm^{-1}] 3344 (m), 1720 (s), 1669 (s), 1420 (m); ESI MS: m/z=299.03.

4.2.3. 2-(1H-Benzo[d]imidazol-1-yl)-N-(9,10-dioxo-9,10-dihydroanthracen-2-yl) hexyl actamide, ***HBIMANQ***

To a solution of **2** (0.20 g, 1.0 mmol) and a catalytic amount of sodium iodide in (15 mL) acetone/chloroform, **3** (0.29 g, 1.00×10^{-3} mol) was added and the mixture was stirred. The precipitate was separated and recrystallized in a mixture of dichloromethane/hexane to obtain the product **HBIMANQCl** (10% yield). Anion exchange of **HBIMANQCl** was carried out using KPF_6 in THF for 24 h to afford **HBIMANQ** (85%yield); mp 355–357 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.30 (s, 1H, –N*H*–), 9.78 (s, 1H, –NC*H*N–), 8.48 (s, 1H, –Ar*H*–), 8.22 (m, 2H, –Ar*H*–), 8.15 (m, 2H, –Ar*H*–), 8.08 (m, 2H, –Ar*H*–), 7.90 (m, 2H, –Ar*H*–), 7.70 (m, 2H, –Ar*H*–), 5.60 (s, 2H, –CH_2CON–), 4.58 (m, 2H, –NCH_2–), 1.91 (m, 2H, –CH_2–), 1.30 (m, 6H, –CH_2–), 0.83 (m, 3H, –CH_3). ^{13}C NMR (400 MHz, DMSO-d_6) δ 183.4, 182.6, 165.2, 144.5, 143.8, 135.3, 135.3, 134.9, 134.1, 134.1, 132.8, 131.7, 129.7, 129.4, 127.8, 127.6, 127.5, 127.5, 125.0, 117.1, 114.5, 114.3, 50.1, 48.0, 31.4, 29.3, 26.2, 22.8, 14.2; FTIR (KBr disk) ν [cm^{-1}] 3384 (m), 2925 (s), 1724 (s), 1672 (s), 841 (s); HRMS (positive ESI) m/z calcd for $C_{29}H_{28}N_3O_3$ (M^+) 466.213, found 466.223; UV–vis (DMSO) λ_{max}=368 nm.

4.2.4. 2-(1H-Benzo[d]imidazol-1-yl)-N-(9,10-dioxo-9,10-dihydroanthracen-2-yl) actamide, ***BIMANQ***

To a solution of benzimidazole (0.123 g, 0.5 mmol) and a catalytic amount of sodium iodide in (60 mL) DMF, **3** (0.179 g, 0.6 mmol) and NaH (0.012 g., 0.5 mmol) were added and the reaction mixture was stirred for 24 h under nitrogen atmosphere. Then, the mixture was evaporated in vacuo. The residue was purified by column chromatography (SiO_2) using ethylacetate as eluent to afford compound **BIMANQ** as brown solid (80% yield). Mp 300–301 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H, –CON*H*–), 8.45 (s, 1H, –NC*H*=N), 8.27 (s, 1H, –Ar*H*–), 8.20 (m, 3H, –Ar*H*–), 8.07 (d, 1H, –Ar*H*–), 7.89 (m, 2H, –Ar*H*–), 7.59 (d, 1H, –Ar*H*–(benzimidazole)), 7.56 (d, 1H, –Ar*H*–(benzimidazole)), 7.23 (m, 2H, –Ar*H*–(benzimidazole)), 5.28 (s, 2H, –COCH_2–); ^{13}C NMR (400 MHz, DMSO-d_6) δ 31.2, 36.2, 47.9, 110.9, 116.4, 119.7, 122.2, 123.0, 124.4, 127.1, 127.2, 128.7, 129.0, 133.5, 134.7, 135.1, 144.4, 145.4, 162.7, 181.8, 182.8; FTIR (KBr disk) ν [cm^{-1}] 3366 (w), 3058 (m), 1712 (s), 1663 (s), 1423 (s); ESI MS (ES^+): m/z(%)=381.764 (100) [M+H$^+$]. Anal. Calcd for $C_{23}H_{15}N_3O_3$: C, 72.43; H, 3.96; N, 11.02. Found: C, 72.15; H, 3.97; N, 11.02.

4.3. NMR studied on host and guests

The NMR experiments were measured in DMSO-d_6. The solution of ligand in DMSO, which was added with 4 equiv of solid tetrabutylammonium salts (F^-, Cl^-, Br^-, AcO^-, BzO^-, and $H_2PO_4^-$) was recorded.

4.4. UV–vis titrations for binding constants of host–guests

All UV–vis experiments were carried out in DMSO with tetrabutylammoniumhexafluorophosphate as supporting electrolyte. The solutions of **HBIMANQ** (7.5×10^{-4} M) and **BIMANQ** (1.5×10^{-4} M) were prepared and gradually added with the solution of guests (0.02 M) until the system reached the equilibrium point observed by a small change in UV–vis spectrum. Each addition was recorded and all data were used for the calculation of the stability constants with Spectfit 32 program.

4.5. CV studies on host and guests

Typically, a 0.001 mol dm^{-3} solution of a ligand (5×10^{-6} mol) in 0.1 mol dm^{-3} supporting electrolyte (5 mL of NBu_4PF_6 in freshly distilled DMSO) was prepared. A stock solution of an anionic 0.5 mmol in supporting electrolyte (0.1 mol dm^3) was prepared. All electrochemical experiments were carried out in a three-electrode cell designed in-house comprising of a working electrode, a counter electrode, and a reference electrode. The working electrode was a glassy carbon disk with a diameter of 3 mm embedded in Teflon and the counter electrode was a platinum coil. $Ag/AgNO_3$ electrode was used as a reference electrode in DMSO solution.

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Supplementary data

The analysis of the synthesized compounds including NMR spectra, mass spectrometry, and cyclic voltammograms are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.073.

References and notes

1. (a) Gale, P. A.; Quesada, R. *Coordin. Chem. Rev.* **2006**, *250*, 3219–3244; (b) Gunnlaugsson, T.; Glynn, M.; Tocci, M. G.; Kruger, P. E.; Pfeffer, F. M. *Coordin. Chem. Rev.* **2006**, *250*, 3094–3117; (c) Sukai, C.; Tuntulani, T. *Top. Curr. Chem.* **2005**, *255*, 163–198.
2. Jose, A. A.; Kumar, K. D.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445–3448.
3. Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed* **2001**, *40*, 154–157.
4. Brooks, S. J.; Birkin, P. R.; Gale, P. A. *Electrochem. Commun.* **2005**, *7*, 1351–1356.
5. Carneiro, P. A.; Boralle, N.; Stradiotto, N. R.; Furlan, M.; Zanoni, M. V. B. *J. Braz. Chem. Soc.* **2004**, *15*, 587–594.
6. Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
7. Liu, Z.; Chen, Z.-C.; Zheng, Q.-G. *Org. Lett.* **2003**, *5*, 3321–3323.
8. Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228–4229.
9. Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3026–3027.
10. Forbes, D. C.; Patrawala, S. A.; Tran, K. L. T. *Organometallics* **2006**, *25*, 2693–2695.
11. Fei, Z.; Kuang, D.; Zhao, D.; Klein, C.; Ang, W. H.; Zakeeruddin, S. M.; Gratzel, M.; Dyson, P. *J. Inorg. Chem.* **2006**, *45*, 10407–10409.
12. Voutchkova, A. M.; Appelhans, L. N.; Chianese, A. R.; Crabtree, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17624–17625.
13. Fei, Z.; Zhao, D.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2004**, *23*, 1622–1628.
14. Boydston, A. J.; Rice, J. D.; Sanderson, M. D.; Dykhno, O. L.; Bielawski, C. W. *Organometallics* **2006**, *25*, 6087–6098.

15. Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692.
16. Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Texeira, S. R. *Inorg. Chem.* **2003**, *42*, 4738–4742.
17. Kim, H.; Kang, J. *Tetrahedron Lett.* **2005**, *46*, 5443–5445.
18. (a) Wisner, J. A.; Beer, P. D.; Drew, M. G. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3606–3609; (b) Wisner, J. A.; Beer, P. D.; Berry, N. G.; Tomapatanaget, B. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4983–4986.
19. (a) Tomapatanaget, B.; Tuntulani, T.; Wisner, J. A.; Beer, P. D. *Tetrahedron Lett.* **2004**, *45*, 663–666; (b) Wong, W. W. H.; Vickers, M. S.; Cowley, A. R.; Paul, R. L.; Beer, P. D. *Org. Biomol. Chem.* **2005**, *3*, 4201–4208.
20. Kim, S. K.; Kang, B.-G.; Koh, H. S.; Yoon, Y. J.; Jung, S. J.; Jeong, B.; Lee, K.-D.; Yoon, J. *Org. Lett.* **2004**, *6*, 4655–4658.
21. Ihm, H.; Yun, S.; Kim, H. G.; Kim, J. K.; Kim, K. S. *Org. Lett.* **2002**, *4*, 2897–2900.
22. Yun, S.; Ihm, H.; Kim, H. G.; Lee, C.-W.; Indrajit, B.; Oh, K. S.; Gong, Y. J.; Lee, J. W.; Yoon, J.; Lee, H. C.; Kim, K. S. *J. Org. Chem.* **2003**, *68*, 2467–2470.
23. (a) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741–744; (b) Gunnlaugsson, T.; Kruger, P. E.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 8909–8913; (c) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162–2187; (d) Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P. E. *Org. Lett.* **2005**, *7*, 5357–5360.
24. Vázquez, M.; Fabbrizzi, L.; Taglietti, A.; Pedrido, R. M.; González-Noya, A. M.; Bermejo, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1962–1965.
25. Boiocchi, M.; Boca, L. D.; Gómez, D. E.; Fabbrizz, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507–16514.
26. Gupta, N.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6384–6391.
27. Pletcher, D.; Thompson, H. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3445–3450.
28. Gomez, M.; Gonzalez, F. J.; Gonealez, I. *J. Electroanal. Chem.* **2005**, *578*, 193–202.
29. Gomez, M.; Gomez-Castro, C. Z.; Padilla-Martínez, I. I.; Martínez-Martínez, F. J.; González, F. J. *J. Electroanal. Chem.* **2004**, *567*, 269–276.
30. Ngeontae, W.; Aeungmaitrepirom, W.; Tuntulani, T. *Talanta* **2007**, *71*, 1075–1082.