Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Cooperative anion recognition by a novel heteroditopic receptor based on dibenzo[18]crown-6 fullero-bis(pyrrolidine)

Anish Kumar[a]; Shobhana K. Menon[a]
[a] Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad, Gujarat, India

First published on: 16 September 2009

To cite this Article Kumar, Anish and Menon, Shobhana K.(2010) 'Cooperative anion recognition by a novel heteroditopic receptor based on dibenzo[18]crown-6 fullero-bis(pyrrolidine)', Supramolecular Chemistry, 22: 1, 46 — 56, First published on: 16 September 2009 (iFirst)
To link to this Article: DOI: 10.1080/10610270903254183
URL: http://dx.doi.org/10.1080/10610270903254183

Supramolecular Chemistry
Vol. 22, No. 1, January 2010, 46–56

Taylor & Francis
Taylor & Francis Group

Cooperative anion recognition by a novel heteroditopic receptor based on dibenzo[18]crown-6 fullero-bis(pyrrolidine)

Anish Kumar and Shobhana K. Menon*

Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad 380009, Gujarat, India

(*Received 16 June 2009; final version received 31 July 2009*)

A novel C_2 symmetrical fullero-bis(pyrrolidine) dibenzo[18]crown-6 conjugate **3** with *trans*-1 addition pattern on the fullerene sphere has been prepared and characterised by elemental analysis, ^{1}H NMR, ^{13}C NMR and FAB-MS. NMR spectra are consistent with the isolation of a single regioisomer, assigned to the *trans*-1 bis-adduct of C_{60}. Preliminary coordination studies by fluorimetry and UV–vis spectroscopy revealed that on inclusion of K^+ in the crown ether cavity, cyclophane structured receptor **3** showed good selectivity in complexation towards $H_2PO_4^-$ as compared to other anions via favourable electrostatic effects. Cyclic voltammetric studies demonstrate that the presence of K^+ amplifies the electrochemical response of **3** towards $H_2PO_4^-$ as compared to other anions. These results were corroborated by ^{1}H NMR titration study which confirmed the binding site for both $H_2PO_4^-$ and K^+ in the receptor.

Keywords: fulleropyrrolidine; dibenzo[18]crown-6; dihydrogen phosphate; sensor; Prato reaction

Introduction

One of the emerging fields in coordination chemistry has been the design of heteroditopic receptors for anionic and cationic guest species (ion pair recognition) (*1*). A number of artificial receptors have been developed for recognition and sensing of either cations or anions; however, the recognition of ion pairs by synthetic receptors remains a less explored area. For recognition of ion pairs, heteroditopic receptors having both cation and anion binding sites have been studied. These receptors can increase the lipophilicity of ionic guests and therefore enhance ion pair solubility in non-polar media, leading to their exploitation in both extraction and membrane transport system (*2*). In addition, ion pair receptors are capable of coordinating with biological molecules such as zwitter ionic amino acids and peptides (*3*). In these systems, the cation may be bound by a number of common motifs, while the anion is coordinated using Lewis acidic, electrostatic and/or hydrogen bonding interactions. Novel cooperative and allosteric metal salt complexing behaviour in which binding of metal cationic guests can enhance, through electrostatic and conformational effects, the subsequent coordination of the pairing anion has been demonstrated by a number of ditopic crown ether functionalised receptor systems (*4*). In addition, such systems have recently been shown to solubilise and transport alkali metal salts across lipophilic membranes (*5*).

The ubiquity and importance of oxo-anions, in particular dihydrogen phosphate anion, impart an urgency to design receptors that can bind them efficiently as well as selectively. Cooperativity for binding of $H_2PO_4^-$ is greatly enhanced in the presence of bound cation, especially K^+ in the receptor (*6*). Such receptors can be easily designed by introduction of 18-crown-6 ether which is a well-known ionophore for recognition of K^+ (*7*). Moreover, the auxiliary hydrogen bonding sites can be constructed by functionalising 18-crown-6 ether with a urea group having NH as a hydrogen bond donor. The presence of an electron acceptor unit can play a crucial role in discriminating dihydrogen phosphate, which has got two OH groups, from other structurally related anions such as sulphate and acetate. In parallel, fullerenes, especially C_{60}, are particularly an attractive scaffold for a wide range of applications (*8*). Its multiple reactive sites along with a range of reported functionalisation techniques make it an ideal candidate for preparation of new chemical entities (*9*). Though generally studied for their biological application and in preparation of artificial photosynthetic systems, the development of fullerene derivatives for recognition of ions is comparatively nascent (*10*). Fulleropyrrolidines prepared by well-established Prato's 1,3-dipolar cycloaddition reaction (*11*) could be an interesting prospect in designing receptors for dihydrogen phosphate anion because (a) C_{60} with its electron-withdrawing nature can also efficiently interact with the

*Corresponding author. Email: shobhanamenon07@gmail.com

ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610270903254183
http://www.informaworld.com

hydroxyl group of dihydrogen phosphate (b). The use of C_{60} as a spectroscopic as well as electrochemical probe for monitoring the cation as well as anion binding can also be conceived.

Hence, a combination of 18-crown-6 ether, urea linkage as well as fulleropyrrolidine would be highly efficient and selective in recognising dihydrogen phosphate anion. With this perspective, we designed and synthesised a dibenzo-18-crown-6 fullero-bis(pyrrolidine) conjugate (Figure 1) with urea linkage, so that in addition to K^+, anion binding can be effected by a number of factors such as electrostatic interaction with K^+, hydrogen bonding with the urea NH group (hydrogen bond donor) and interaction of the non-bonding electrons of the OH group with the fullerene cage. There are a few reports where fullerene has been attached to crown ethers (*12*), but there are no reports where fullerene derivatised crown ether has been used as a ditopic receptor.

Taking note of the structural complications involved in the design of anion recognition motifs, an easy-to-prepare and functionalised *cis*-diamino[18]crown-6 was chosen as the molecular structure to synthesise the desired ligand. Moreover, the presence of the amino group made it possible to introduce urea linkage by means of a modified *Curtius* reaction (*13*). Fullerene C_{60} with its multiple reactive sites made it possible to obtain a cyclophane-type structure, which complements the binding of K^+ as well as $H_2PO_4^-$. Of all the regioisomers possible for the bis-adduct of fullerene (*14*) (Figure 2), the *trans*-1 isomer has the best architecture required for efficient cooperative binding of both cation and anion, since the distance between the cation binding site (crown ether cavity) and the anion binding site (urea, fullerene cage) will be less as compared to other isomers.

Herein, we report the first regioselective synthesis of a crown ether–urea–C_{60} hybrid system with a simple and modular strategy along with studies that justify its use as a heteroditopic receptor.

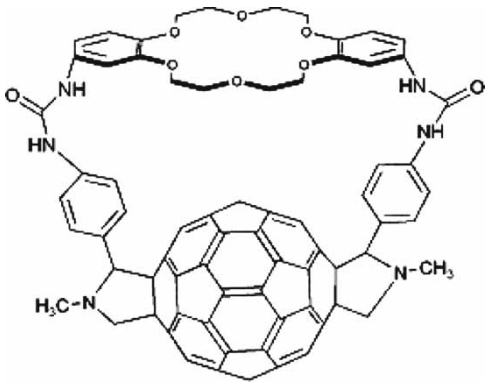


Figure 1. Structure of dibenzo-18-crown-6 fullero-bis(pyrrolidine) conjugate **3**.

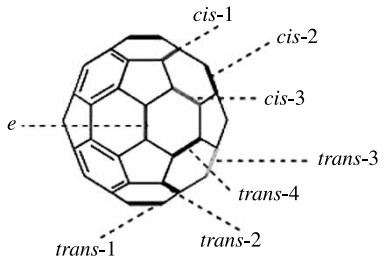


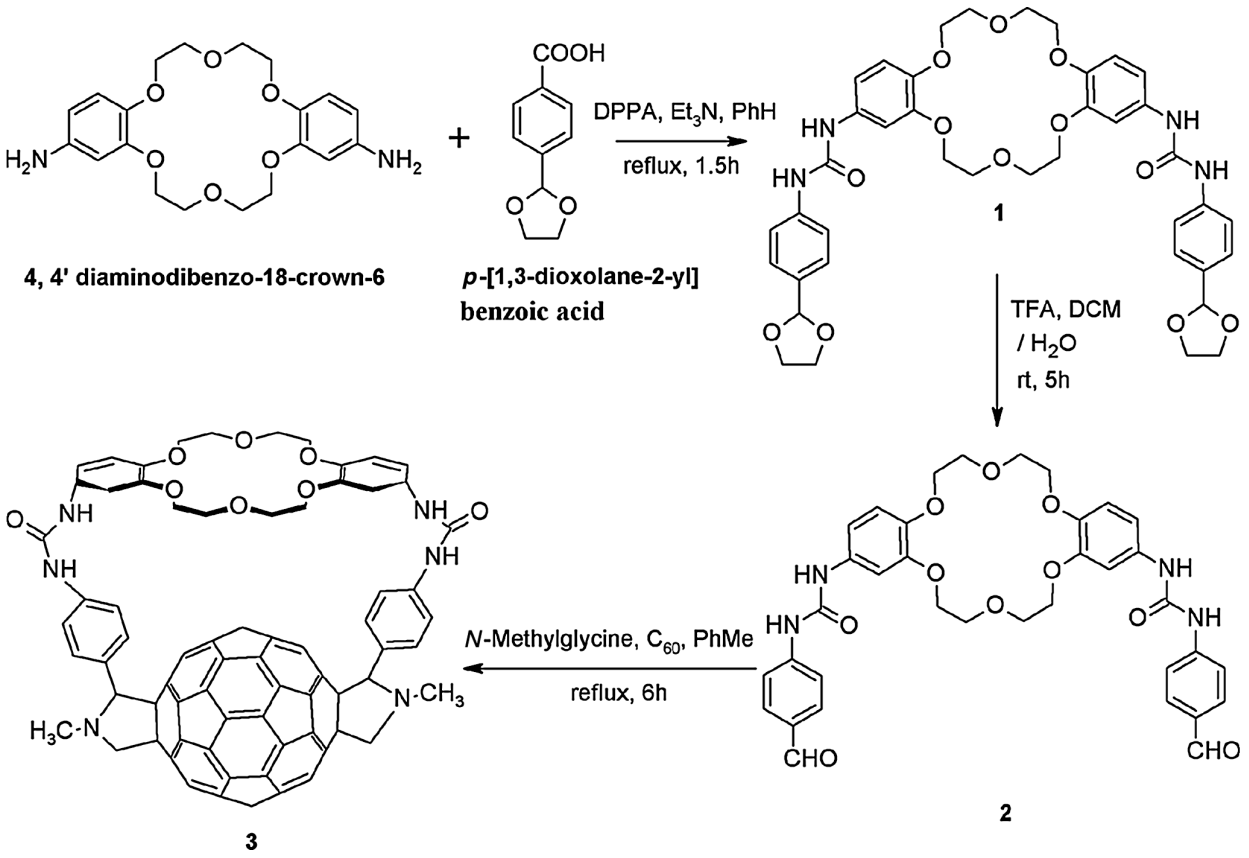
Figure 2. Regioisomers possible for bis-adducts on a fullerene sphere.

Results and discussion

Synthesis and characterisation

Prato's 1,3-dipolar cyclo-addition reaction was adopted to synthesise the desired ditopic receptor **3** (Scheme 1).

The synthesis of dibenzo[18]crown-6 (*15*), nitration to 4,4′-dinitrodibenzo[18]crown-6 (*16*) and reduction to 4,4′-diaminodibenzo[18]crown-6 (*17*) were carried out by reported procedures. *p*-[1,3-Dioxolane-2-yl] benzoic acid was prepared by a procedure similar to that reported by Imahori and co-workers (*18*) (procedure given in Supporting Information). The condensation of 4,4′-diaminodibenzo[18]crown-6 with *p*-[1,3-dioxolane-2-yl] benzoic acid in the presence of diphenyl phosphoryl azide (DPPA) and triethylamine (*Curtius* reaction) gave **1**, which on treatment with trifluoroacetic acid (TFA) in dichloromethane gave crown ether-based dialdehyde **2** in ~70% yield. Crown ether-based dialdehyde **2** was then refluxed with C_{60} and sarcosine in toluene for 6 h to give the dibenzo-18-crown-6 fullero-bis(pyrrolidine) conjugate **3** in ~33% yield. The desired *trans*-1 isomer was isolated from other regioisomers by column chromatography, since the *trans*-1 isomer was having a higher R_f value as compared to others. One possible reason for the higher R_f value of the *trans*-1 isomer could be the lower dipole moment brought about by the symmetrical structure of the molecule. All the intermediates as well as the final product were characterised by elemental analysis, ^{1}H NMR, ^{13}C NMR and FAB-MS/EI-MS. The *trans*-1 geometry of the synthesised compound was supported by the fact that only two signals were obtained in the ^{1}H NMR spectra for the urea protons, indicating a C_2 symmetry in the molecule. Moreover, the chemical shift values at δ 5.25 and 4.45 as doublets ($J = 9.3$ Hz) for CH_2 and at δ 2.85 corresponding to $-NCH_3$ protons of the pyrrolidine ring clearly support the *trans*-1 geometry of the synthesised molecule. ^{13}C NMR showed only 28 signals corresponding to sp^2 carbons of the fullerene cage, which is also an indication of the symmetrical *trans*-1 geometry. The *trans*-1 geometry of the synthesised molecule was more or less confirmed by comparing its UV–vis spectra in the 400–700 nm region with the previously reported Bingel (*19*) as well as Prato bis-adducts (*20*) (see Supporting Information).



Scheme 1. Synthesis of receptor **3**.

Moreover, its spectral properties were similar to the *trans*-1 fullerene dibenzo-18-crown-6 conjugate reported by Echegoyen and co-workers (*21*).

More insight into the ^{1}H NMR data for **3** (Figure 3) showed peaks at δ 8.65 and 8.35 as singlets corresponding to NH_1 and NH_2, respectively, integrating for two protons each. The aromatic protons appeared as multiplet between δ 7.0 and 6.6. The —OCH_2— protons of the crown ether ring appeared between δ 4.1 and 3.7 as multiplet. Other peaks like singlet at 4.89 corresponding to —CH and doublets at 5.25 and 4.45 corresponding to H_8CH and $H_{10}CH$, respectively, of the pyrrolidine ring were also observed. The peaks corresponding to aromatic protons have been resolved to observe doublets for protons H_3 ($^4J = 1.5$ Hz), H_4 ($^3J = 8.3$ Hz) and H_7 ($^3J = 8.3$ Hz), while doublet of doublets appeared for H_5 ($^3J = 8.4$ Hz, $^4J = 1.5$ Hz) and H_6 ($^3J = 8.2$ Hz, $^4J = 1.2$ Hz). ^{13}C NMR showed a peak at δ 154.7 corresponding to the C of the urea linkage. The peaks corresponding to sp^3 C of C_{60} were observed at 75.0 and 68.3, respectively. FAB-MS showed a molecular ion peak at 1458 (M^+) and a base peak at 720 for C_{60}. Mass fragmentation pattern of **3**, FAB-MS, ^{1}H NMR, ^{13}C NMR and FT-IR spectra of **3** are given in the Supporting Information.

Complexation studies of the receptor

The ability of receptor **3** to bind both cations and anions was studied. The addition of tetrabutylammonium hexafluorphosphate ($TBAPF_6$) to receptor **3** does not cause any change in either its photophysical or electrochemical properties. Hence, tetrabutylammonium cation

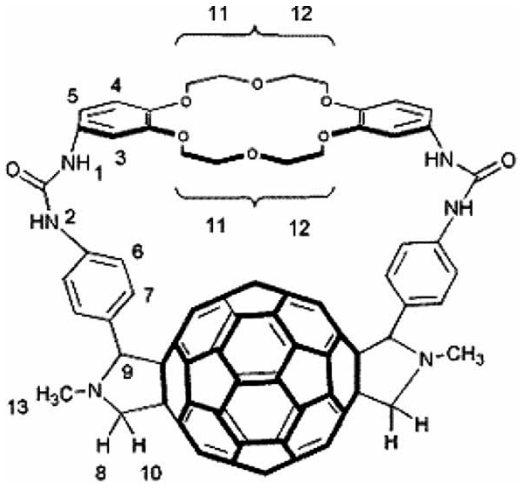


Figure 3. Numbered protons of compound **3** in the order in which they appear in the ^{1}H NMR spectra (downfield to upfield).

was chosen as the counterion for anion recognition while hexafluorphosphate anion was chosen as the counterion for cation recognition studies. The presence of the fullerene moiety in the receptor having characteristic photophysical and electrochemical properties made it possible to study the ion binding by UV–vis, fluorimetric as well as electrochemical techniques. Moreover, the presence of crown ether and urea NH protons enabled us to study ion binding by ^{1}H NMR spectral analysis.

Photophysical studies

Fluorescence studies were carried out by excitation at 450 nm (where only the fullerene cage is excited) of a solution of receptor **3** (1×10^{-5} M) in benzonitrile with emission at 708 nm corresponding to decay of the singlet excited state of the fullerene cage. The effect of cations on fluorescence was observed by adding a solution of M^+ (2×10^{-5} M) to receptor **3** (1×10^{-5} M) in benzonitrile. Metal ions M^{n+} (Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Ni^{2+}) were added as hexafluorophosphate salts. It was found that the fluorescence intensity of **3** decreased on addition of K^+ ion ($\Phi = 3.7 \times 10^{-4}$ to 2.6×10^{-4}), while other cations did not cause too much change in the spectra of **3**. This observation can be attributed to the quenching of the singlet excited state of the fullerene cage on inclusion of K^+ in the crown ether cavity (Figure 4). The stoichiometry of complexation of **3** with K^+ was found to be 1:1 while the association constant was found to be 3580 M^{-1} (see Table 1). Apart from benzonitrile, other solvent systems such as toluene, chloroform, THF and methylcyclohexane were also used for fluorimetric analysis (see Supporting Information). But since the shift in emission spectra of **3** on addition of K^+ was best observed in benzonitrile, further studies were carried out in the benzonitrile solvent system.

On the contrary, addition of 2 equiv. of anions A^- ($H_2PO_4^-$, HSO_4^-, AcO^-, ClO_4^-, Cl^- and Br^-) as tetrabutylammonium salt to solution of **3** in benzonitrile does not cause an appreciable change in the emission spectra. Only a slight increase in fluorescence intensity was observed in the case of dihydrogen phosphate, which was not enough to draw any sort of conclusion. One possible reason for such observation could be the repulsive interaction of the anion with the crown ether O atoms, thus preventing the urea group of the receptor from interacting with the anions. Hence, anion complexation studies were carried out by mixing an equimolar solution of cation (K^+) and receptor **3** with subsequent addition of anions. It was found that the fluorescence intensity at 708 nm increased remarkably on complexation with $H_2PO_4^-$, whereas other anions (AcO^-, HSO_4^-, ClO_4^-) do not cause too much perturbation in the fluorescence spectra (Figure 5). These observations indicate that there is efficient binding of $H_2PO_4^-$ by the **3**:K^+ complex. The O atoms of the crown ether ring, which were responsible for repulsive interaction with anions, were now involved in the non-covalent interaction with K^+, thus making way for better interaction of dihydrogen phosphate anion with the urea group of the receptor.

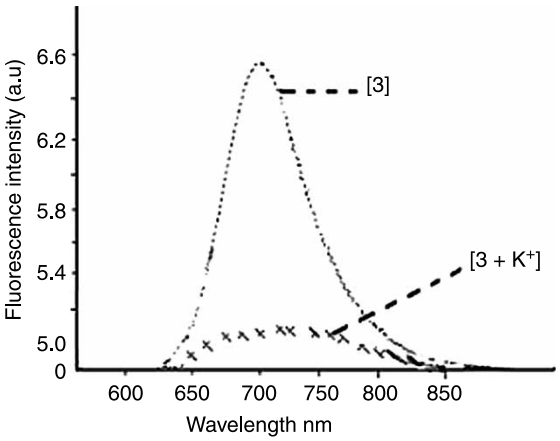


Figure 4. Fluorescence spectra of receptor **3** (1×10^{-5} M) in the absence and presence of K^+ (2×10^{-5} M) in benzonitrile at 298 K.

Table 1. Photophysical properties of uncomplexed and complexed receptor **3** along with the respective association constants.

Compound	Absorption[a] (λ_{max}) nm	Emission quantum yield[b] Φ ($\times 10^{-4}$)	Association constant[c] K (M^{-1})
3 (1×10^{-5} M)	438	3.70	
3+K^+ (1 equiv.)	433	2.60	3580
3+K^++$H_2PO_4^-$ (4 equiv.)	443	3.65	2456
3+K^++AcO^- (4 equiv.)	435	3.00	650
3+K^++HSO_4^- (4 equiv.)	434	2.80	515
3+K^++ClO_4^- (4 equiv.)	433	2.69	276
3+K^++Cl^- (4 equiv.)	433	2.67	180
3+K^++Br^- (4 equiv.)	433	2.69	276
3+$H_2PO_4^-$ (4 equiv.)	439	3.60	20
1+K^+ (1 equiv.)	329	–	–
1+K^++$H_2PO_4^-$ (4 equiv.)	331	–	–

[a] Solvent system $CHCl_3$—CH_3CN (4:1), 25°C.
[b] $\lambda_{max} = 708$ nm, solvent system benzonitrile, 25°C.
[c] Association constant calculated by the Benesi–Hildebrand plot for a 1:1 stoichiometry.

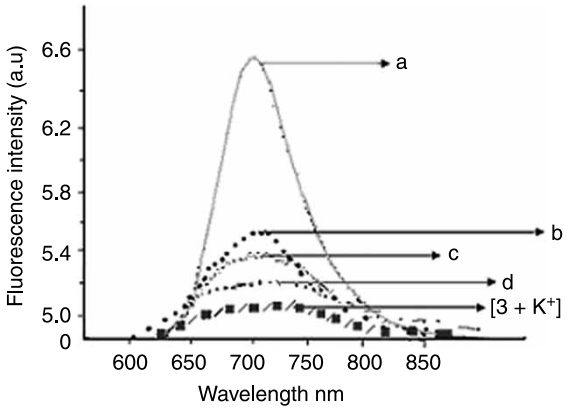


Figure 5. Fluorescence spectra of ligand **3**:K^+ complex (1×10^{-5} M) in the presence of (a) $H_2PO_4^-$, (b) AcO^-, (c) HSO_4^- and (d) ClO_4^- (5×10^{-3} M) in benzonitrile at 298 K.

Fluorimetric titrations were carried out to evaluate the binding constant and stoichiometry of anion complexation by **3**:K^+. Figure 6 shows the change in fluorescence of **3**:K^+ on increasing the concentration of $H_2PO_4^-$.

A plot of $1/(F - F_0) \rightarrow 1/[A^-]$ produced a straight line for titration with $H_2PO_4^-$, indicating the formation of a 1:1 complex (see Supporting Information). F_0 is the fluorescence intensity of **3**:K^+ and F is the fluorescence intensity after complexation with $H_2PO_4^-$. The association constant K_a can be found by the following modified Benesi–Hildebrand equation using the fluorescence data:

$$\frac{1}{F - F_0} = \frac{1}{[A^-]K_a\alpha} + \frac{1}{\alpha},$$

where $[A^-]$ is the concentration of added anion, F_0 and F are the fluorescence intensity of the **3**:K^+ complex in the absence and presence of anions and α is a constant. The K_a value was obtained from the slope and intercept of the double reciprocal plot. The plot was linear confirming 1:1

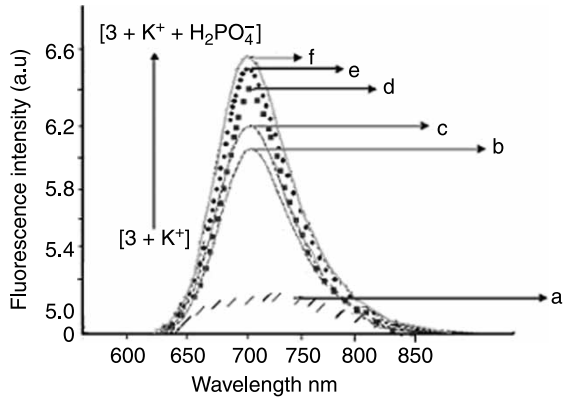


Figure 6. Fluorescence spectra of ligand **3**:K^+ complex (1×10^{-5} M) in the presence of (a) 0 mM, (b) 0.2 mM, (c) 0.4 mM, (d) 1.5 mM, (e) 2.0 mM and (f) 2.5 mM of $H_2PO_4^-$ (dihydrogen phosphate) anions in benzonitrile at 298 K.

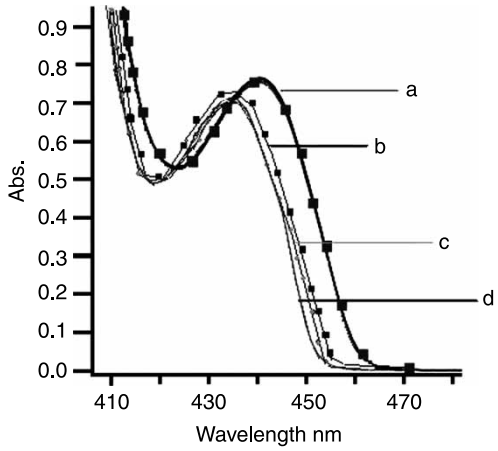


Figure 7. Absorption spectra of **3**:K^+ (1×10^{-5} M) upon addition of 4 equiv. of: (a) $H_2PO_4^-$, (b) AcO^-, (c) HSO_4^- and (d) without anions in $CHCl_3$—CH_3CN (4:1) at 298 K.

host–guest complexation in the case of $H_2PO_4^-$ with K_a evaluated as 2456 M^{-1}. The K_a for $H_2PO_4^-$ binding was much higher as compared to other anions. The binding constant values K_a calculated by fluorimetric analysis have been summarised in Table 1 (fluorimetric titration curves **3**:K^+ with AcO^- and HSO_4^- are given in the Supporting Information).

The UV–vis spectra of receptor **3** (1×10^{-5} M) in $CHCl_3$—CH_3CN (4:1) showed characteristic fullerene peaks at 202, 308, 438 and 471 nm, which extend all the way to the energetically low-lying transition at 706 nm. The addition of KPF_6 (1 equiv.) to a solution of **3** induces a moderate blue shift of 5 nm (438–433 nm) to the charge transfer band of the UV–vis spectra. Anion complexation studies were carried out on potassium cation-complexed

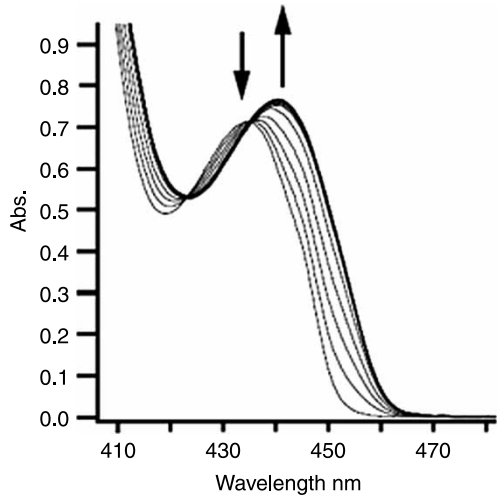


Figure 8. Change in UV–vis spectra of **3**:K^+ (1×10^{-5} M) upon increasing concentration of $H_2PO_4^-$ in $CHCl_3$—CH_3CN (4:1) at 298 K.

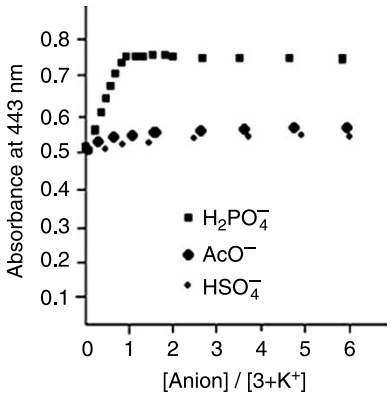


Figure 9. Change in absorbance at 443 nm for **3**:K^+ (1×10^{-5} M) with an increase in the concentration of anions in $CHCl_3$—CH_3CN (4:1) at 298 K.

receptor **3**, because addition of anions ($H_2PO_4^-$, AcO^-) to the solution of uncomplexed **3** does not cause a noticeable shift in the spectra. Figure 7 shows the absorption spectra of the **3**:K^+ complex in the absence and presence of 4 equiv. of oxo-anions ($H_2PO_4^-$, AcO^-). It was observed that the addition of HSO_4^- and AcO^- induces a small bathochromic shift of the peak at 433 nm, while the addition of $H_2PO_4^-$ causes a comparatively large bathochromic shift of 10 nm (433–443 nm). The shifts caused by the addition of chloride as well as bromide anions were also negligible. This shift can be ascribed to the occurrence of an H-bond interaction involving the two NH fragments of the urea subunit and the two oxygen atoms of the dihydrogen phosphate anion. The electron density is transferred to the urea moiety, which increases the intensity of dipole and hence shifts the charge transfer band to a longer wavelength.

On successive addition of a solution of $H_2PO_4^-$ (0, 2, 4, 6 and 10 equiv.) to the solution of **3**:K^+ in $CHCl_3$—CH_3CN (4:1), the absorbance of the peak at 433 nm decreased while the absorbance of the new peak that appeared at 443 nm was found to increase (Figure 8). The isobestic point at 436 nm indicates the absence of any long-lived intermediates. These results indicate that the **3**:K^+ complex can bind and discriminate between $H_2PO_4^-$ anion and structurally related HSO_4^- and AcO^- efficiently. UV–vis titrations of **3**:K^+ with $H_2PO_4^-$ showed the formation of a 1:1 host–guest complex from the nonlinear least-square analysis of the titration curve (Figure 9). The role of the fullerene moiety in complexation was also analysed by observing the changes in fluorescence as well as UV–vis spectra of intermediate **1** on complexation with K^+ and $H_2PO_4^-$. It was found that $H_2PO_4^-$ induced only minor perturbation in the spectra of the **1**:K^+ complex. The change in photophysical properties of compound **3** and **3**:K^+ complex on interaction with anions has been summarised in Table 1.

Electrochemical studies

In order to gain more insight into the cooperative enhancement of anion recognition by the presence of bound cation, electrochemical studies were carried out. The electrochemical response of **3** (1×10^{-4} M) as well as **3**+K^+ (1×10^{-4} M) to anion complexation was studied by cyclic voltammetry in 4:1 $CHCl_3$—CH_3CN with $TBAPF_6$ as the supporting electrolyte. Receptor **3** exhibited three quasireversible reduction peaks corresponding to the reduction of the fullerene core (Figure 10(a)). A slight anodic shift in the reduction wave was observed in **3**+K^+ (Figure 10(b)) as compared to free receptor **3**, indicating the increased tendency of the fullerene core to undergo reduction in the receptor **3**:K^+ complex. This change can be attributed to the electrostatic effect of the K^+ ion bound

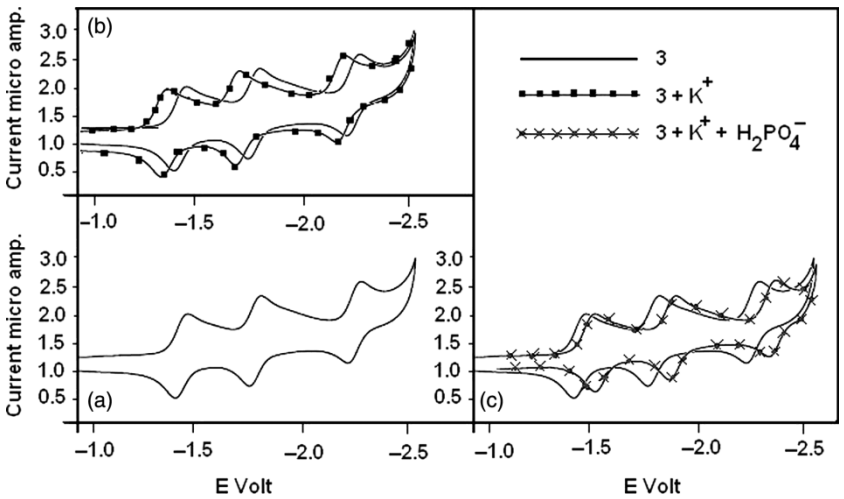


Figure 10. Cyclic voltammogram of (a) **3** (1×10^{-4} M), (b) **3**+K^+ (1 equiv.) and (c) **3**+K^++$H_2PO_4^-$ (1.5 equiv.) in $CHCl_3$—CH_3CN (4:1) at 298 K.

in close proximity to the fullerene sphere. The influence of dihydrogen phosphate as well as other anions on the reduction waves of the fullerene cage was studied by adding a solution of tetrabutylammonium salts of anions to the solution of **3**+K^+. A cathodic shift was observed in the case of dihydrogen phosphate while the other anion does not cause too much shift. This anion-induced cathodic shift (Figure 10(c)) can be attributed to the complexation of the anion near the fullerene cage, hence retarding its reduction. The change in the redox potential of compound **3** on inclusion of K^+ as well as on interaction with anions has been summarised in Table 2. Hence, it has been proved by both photophysical and electrochemical studies that the synthesised crown ether fulleropyrrolidine is an efficient heteroditopic receptor for K^+ and $H_2PO_4^-$ ions. However, the binding mode of dihydrogen phosphate by the receptor **3**:K^+ complex could not be made out from either of these studies. Hence, NMR titration was carried out to study the influence of inclusion of dihydrogen phosphate as well as potassium cation on the chemical shifts of the protons of the ligand.

NMR titrations

Receptor **3** was titrated with dihydrogen phosphate anion (added as a tetrabutylammonium salt) in the absence and presence of K^+ (added as a hexafluorophosphate salt). The choice of the solvent considering the possibility of species, such as receptor, ion-pair salt as well as cation–anion–receptor complex in the solution, was selected as 1:1 $CDCl_3$–CD_3CN. The addition of the KPF_6 salt (1.5 equiv.) to the solution of receptor **3** (1×10^{-5} M) caused a significant upfield shift ($\Delta\delta = 0.23$) in crown ether —CH_2 signals in ^{1}H NMR spectra, which is in confirmation with the inclusion of K^+ with the crown ether cavity. On titration with dihydrogen phosphate anions, it was found that the presence of K^+ significantly increases the magnitude of the anion-induced perturbation of urea protons (which were shifted downfield). Moreover, the addition of dihydrogen phosphate alone does not cause too much shift in the urea NH signals, which is in good agreement with the results obtained from photophysical measurement and electrochemical methods. These results indicate that dihydrogen phosphate anion is bound to the urea linkage in the **3**:K^+ complex, with the urea group acting as a H-bond donor. On increasing the concentration of the dihydrogen phosphate added, the urea signals were shifted more downfield and were broadened (Figure 11). A signal at δ 2.38 was observed for the proton of dihydrogen phosphate anion, which is at the upfield position as compared to dihydrogen phosphate alone, clearly indicating some kind of interaction of the OH group of $H_2PO_4^-$ with the fullerene cage. The ^{1}H NMR titration data of **3**:K^+ with AcO^- and HSO_4^- are given in the Supporting Information. It was found that the peaks corresponding to protons of the urea linkage did undergo a downfield shift but the shift was much less when compared with $H_2PO_4^-$. The change in the chemical shift for protons of ligand **3**, after complexation with potassium cation and subsequently with dihydrogen phosphate anion, has been described in Table 3. A 1:1 binding stoichiometry with $H_2PO_4^-$ and other oxo-anions by **3**:K^+ was confirmed by Job plots (*22*).

Conclusion

Hence, from photophysical, electrochemical and ^{1}H NMR titration experiments, it has been ascertained that the synthesised dibenzo[18]crown-6 fullero-bis(pyrrolidine) conjugate **3** on complexation with potassium cation can efficiently recognise and discriminate dihydrogen phosphate from other structurally similar anions. Moreover, ^{1}H NMR titration studies have revealed that NH groups of urea linkage in the ligand act as H-bond donors. Additional factors such as the electrostatic effect from the bound cation (K^+) and electron-accepting nature of C_{60} made the receptor **3**:K^+ complex highly efficient in recognising $H_2PO_4^-$. Based on these results, the structure of the complex will be K^+ in the crown ether cavity and $H_2PO_4^-$ in the space between crown ether ring and fullerene with H-bonding between O and H of the urea group in the receptor and OH groups of $H_2PO_4^-$ pointed towards the fullerene cage. Furthermore, the linker between the crown ether and the fullerene moiety could be further modified to incorporate

Table 2. Voltammetric data of **3** (1×10^{-4} M) upon complexation with K^+ and anions, obtained in $CHCl_3$—CH_3CN (4:1) at 298 K.

Compound	$\Delta E^1_{1/2}$ [a] (mV)	$\Delta E^2_{1/2}$ [a] (mV)	$\Delta E^3_{1/2}$ [a] (mV)	Min. equiv.[b]	Max. equiv.[c]
3+K^+[d]	60	56	58	0.1	1
3+K^++$H_2PO_4^-$[e]	−59	−57	−55	0.1	1.5
3+K^++AcO^-[e]	−28	−27	−27	0.25	1.0
3+K^++HSO_4^-[e]	−24	−22	−23	0.5	1.0

[a] Difference calculated with reference to $E_{1/2}$ values of compound **3** ($E^1_{1/2} = -1.46$ V, $E^2_{1/2} = -1.81$ V, $E^3_{1/2} = -2.28$ V).
[b] Minimum equivalents of salt required to give detectable electrochemical response.
[c] Maximum equivalents required to saturate voltammetric response.
[d] Added as the hexafluorophosphate salt.
[e] Added as the tetrabutylammonium salt.

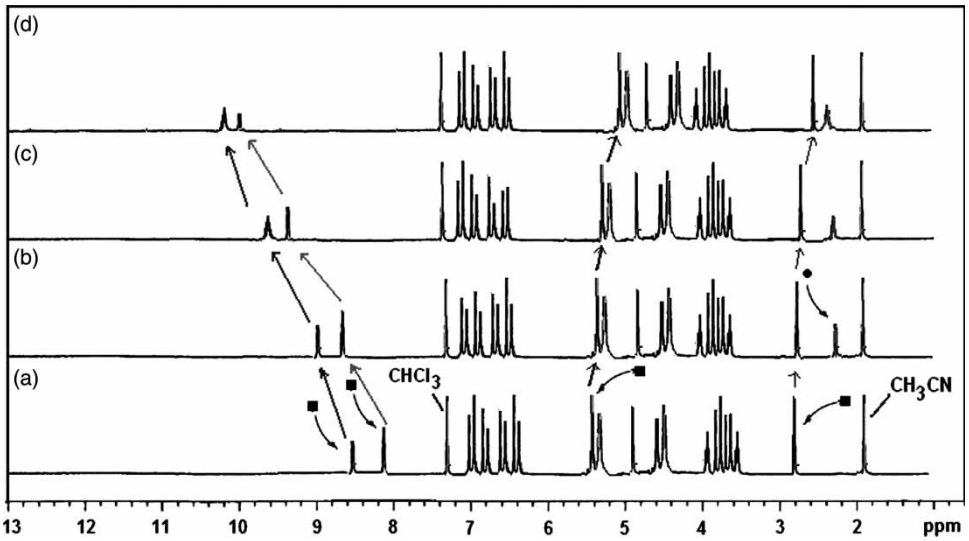


Figure 11. ^{1}H NMR spectral changes observed for the protons of **3**+K^+ (1×10^{-5} M), in $CDCl_3$–CD_3CN (1:1), after the addition of (a) 0, (b) 0.5, (c) 1.0 and (d) 1.6 equiv. of $H_2PO_4^-$. ■ represents the protons under consideration. • represents the protons of dihydrogen phosphate.

other anion recognition elements (e.g. thiourea, amides, sulfanamides, etc.) as such, additional fine tuning of anion binding properties may be envisioned. This work opens interesting perspectives for the design of efficient C_{60}-based sensors for ion-pair recognition.

Experimental

Materials and methods

All the chemicals including C_{60} were purchased from Sigma Aldrich and E. Merck and were of analytical grade. The cycloaddition reaction was performed under argon. The cycloaddition reactions as well as other preceding steps were monitored by TLC using Merck silica gel 60-F254. Melting point was taken on Veego (VMP-DS) using a Mel-Temp apparatus. Silica gel (Merck, 0.040–0.063 mm) was used for column chromatography. FAB-MS was recorded on a Jeol SX-102/DA 600 mass spectrometer using argon/xenon as the accelerating gas and nitrobenzylalcohol as the matrix. EI-MS were recorded on a SHIMADZU QP-5050A. ^{1}H and ^{13}C NMR spectra were recorded on a DRX 400 spectrophotometer operating at 400 and 125 MHz, respectively, with TMS as the internal standard. The following abbreviations for stating the multiplicity of the signals in the NMR spectra were used: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet), Cq (quaternary carbon). ^{1}H and ^{13}C NMR spectra were referenced to the residual

Table 3. ^{1}H NMR chemical shifts and chemical shift changes of ligand **3** (1×10^{-5} M) protons on complexations with K^+ and on subsequent complexation with $H_2PO_4^-$ (1.6 equiv.).

Protons	**3** (δ ppm), δ_1	**3**+K^{+a} (δ ppm), δ_2	$\Delta\delta$ ppm, $\delta_2-\delta_1$	**3**+K^{+a}+$H_2PO_4^{-b}$ (δ ppm), δ_3	$\Delta\delta$ ppm, $\delta_3-\delta_2$
1	8.65	8.48	−0.17	10.17	1.69
2	8.35	8.20	−0.15	9.97	1.77
3	6.99	7.01	0.02	7.04	0.03
4	6.88	6.90	0.02	6.92	0.02
5	6.75	6.77	0.02	6.78	0.01
6	6.66	6.67	0.01	6.69	0.03
7	6.59	6.60	0.01	6.61	0.02
8	5.25	5.26	0.01	5.08	−0.18
9	4.90	4.91	0.01	4.75	−0.16
10	4.45	4.47	0.02	4.29	−0.18
11, 12	4.12–3.70	3.89–3.48	0.23[c]	3.97–3.56	0.08[c]
13	2.85	2.84	−0.01	2.58	−0.26

[a] Added as KPF_6 (1.5 equiv.).
[b] Added as $TBAH_2PO_4$ (1.5 equiv.).
[c] Calculated as the average change for all the crown ether protons.

solvent peak (^{1}H δ($CHCl_3$)) at 7.27 ppm and to the solvent peak (^{13}C δ($CDCl_3$)) at 77.23 ppm. The absorption spectra were recorded on a Hitachi U-3210 UV–visible spectrophotometer using a 10-mm quartz cell. Elemental analysis was done on a Carlo Erba 1108 analyser. FT-IR spectra were recorded on a BRUKER-TENSOR 27 FT-IR spectrophotometer as KBr pellets. Cyclic voltammograms were recorded on a CH Instruments 620A electrochemical analyser using a three-electrode system. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas. For all electrochemical studies, the voltammetric cell was maintained at 25.0 ± 0.2°C. Nitrogen was passed through all the solutions for 20 min to remove oxygen. A platinum electrode was used in all experiments as the working electrode. A silver–silver chloride reference electrode and a platinum wire counter electrode were used in all experiments. The scan rate for cyclic voltammetry was 100 mV/s and the supporting electrolyte was $TBAPF_6$ (0.1 M). The square wave pulse was 25 mV, the step height was 4 mV and the square wave period was varied randomly over a range of values. All of the potential values reported are relative to the Fc^+/Fc couple at room temperature. In ^{1}H NMR titrations, aliquots of anions (tetrabutylammonium salts, 0.5 M, 2.5×10^{-4} M in 0.5 ml of the deuterated solvent) were added to a solution of receptor **3** (0.01 M, 5×10^{-6} in 0.5 ml of the deuterated solvent). Thirteen aliquots were added (0, 2, 4, 5, 6, 8, 10, 12, 14, 16, 18, 20, 30 μl) corresponding to 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0 equiv. of anion. For titration in the presence of potassium cation, the above procedure was repeated for addition of anions to a mixture of receptor **3** (5×10^{-6} in 0.4 ml of the deuterated solvent) and KPF_6 (5×10^{-6} in 0.4 ml of the deuterated solvent).

*Procedure for preparation of dibenzo[18]crown-6 fullero-bis(pyrrolidine) conjugate **3** and intermediates **1** and **2***

Synthesis of 1,1′-(6,7,9,10,17,18,20,21-octahydrodibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecine-2,14-diyl) bis(3-(4-(1,3-dioxolan-2-yl)phenyl)urea) **1**. A solution of 4,4′-diaminodibenzo-18-crown-6 (390 mg, 1 mmol), *p*-[1,3-dioxolane-2-yl] benzoic acid (388 mg, 2 mmol), DPPA (800 mg, 3 mmol) and Et_3N (700 mg, 7 mmol) in benzene (150 ml) was heated under reflux for 1.5 h. After adding methanol (30 ml), the reaction mixture was further heated for 2 h and then cooled, concentrated *in vacuo* to get a white solid product. The product was then dissolved in chloroform, washed with dilute HCl, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc–hexane = 1/25 to afford compound **1** as a white solid product (430 mg; 55%); mp 189°C (dec); IR (KBr; cm^{-1}) 1130, 1262, 1638, 3257; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, 298 K) δ (ppm) 8.70 (s, 2H, —CONH-Ar), 8.35 (s, 2H, —CONH-Ar), 7.0 (d, ^4J(H,H) = 1.7 Hz, 2H, ArH), 6.88 (d, ^3J(H,H) = 8.1 Hz, 2H, ArH), 6.77 (dd, ^3J(H,H) = 8.2 Hz, 2H, ^4J(H,H) = 1.3 Hz, ArH), 6.68 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.2 Hz, 4H, ArH), 6.58 (d, ^3J(H,H) = 8.5 Hz, 4H, ArH), 5.90 (s, 2H, O—CH—O), 4.3 (s, 8H, —OCH_2—CH_2O—), 4.25–4.18 (m, 8H, —OCH_2 crown ether), 4.06–4.00 (m, 8H, —OCH_2 crown ether); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, 298 K) δ (ppm) 152.2 (2C, CONH), 144.7 (2C, Ar-Cq), 140.1 (2C, Ar-Cq), 137.3 (2C, Ar-Cq), 132.8 (2C, Ar-Cq), 130.4 (2C, Ar-Cq), 127.1 (2C, Ar-CH), 120.3 (2C, Ar-CH), 115.0 (2C, Ar-CH), 114.1 (2C, CH of dioxolane), 112.6 (2C, Ar-CH), 106.0 (2C, Ar-CH), 73.3 (4C, CH_2 of dioxolane), 72.7–70.5 (8C, crown ether); EI-MS *m/z* (relative intensity) 772 (M+ , 100), 320 (60); Anal. calcd for $C_{40}O_{12}H_{44}N_4$: C, 61.38; H, 5.62; N, 6.90. Found: C, 61.50; H, 5.71; N, 6.50.

1,1′-(6,7,9,10,17,18,20,21-Octahydrodibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecine-2,14-diyl) bis(3-(4-formylphenyl)urea) **2**. Compound **1** (350 mg, 0.01 mol) was mixed with 2.5 ml TFA in 75 ml of dichloromethane and 10 ml of water. The biphasic mixture was stirred at room temperature for 12 h. The solution was diluted with dichloromethane and washed with saturated sodium bicarbonate until the organic phase became light brown. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the light yellow solid residue was purified by column chromatography on silica gel with toluene–methanol = 50/1 to get compound **2** as a pure white product (230 mg; 70%); mp 158°C (dec); IR (KBr; cm^{-1}) 1130, 1262, 1638, 1710, 3320; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, 298 K) δ (ppm) 9.91 (2H, s, —CHO), 8.60 (s, 2H, —CONH-Ar), 8.40 (s, 2H, —CONH-Ar), 6.95 (d, ^4J(H,H) = 1.6 Hz, 2H, ArH), 6.89 (d, ^3J(H,H) = 8.1 Hz, 2H, ArH), 6.74 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.6 Hz, 2H, ArH), 6.64 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.3 Hz, 4H, ArH), 6.58 (d, ^3J(H,H) = 8.4 Hz, 4H, ArH), 4.30–4.20 (m, 8H, —OCH_2 crown ether), 4.00–3.91 (m, 8H, —OCH_2 crown ether); ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si, 298 K) δ 190.0 (2C, CHO), 152.2 (2C, CONH), 144.7 (2C, Ar-Cq), 140.1 (2C, Ar-Cq), 137.3 (2C, Ar-Cq), 132.8 (2C, Ar-Cq), 130.4 (2C, Ar-Cq), 127.8 (2C, Ar-CH), 120.3 (2C, Ar-CH), 115.0 (2C, Ar-CH), 112.6 (2C, Ar-CH), 106.0 (2C, Ar-CH), 73.3–70.7 (8C, crown ether); EI-MS *m/z* (relative intensity) 685 (M+1, 100), 320 (57); Anal. calcd for $C_{36}O_{10}H_{36}N_4$: C, 63.15; H, 5.26; N, 8.18. Found: C, 63.50; H, 5.41; N, 8.10.

Dibenzo[18]crown-6 fullero-bis(pyrrolidine) conjugate **3**. A mixture of dialdehyde **2** (151 mg, 0.22 mmol), *N*-methylglycine (40.2 mg, 0.44 mmol) and C_{60} (120 mg, 0.17 mmol) was refluxed in dry toluene in inert atmosphere for 6 h. After cooling to room temperature, the brown mixture was purified by column chromatography (silica gel) set-up with a gradient of toluene to toluene–ethyl acetate (20:1) as the eluant. Adduct **3**, a brown solid, was dried under vacuum and characterised by elemental

analysis and spectroscopic methods (114 mg; 33%); mp 228°C (dec); IR (KBr; cm^{-1}) 526 (C_{60}), 1429 (C_{60}) 1634 (urea CO stretching), 1134 (crown C—O—C stretching), 1268 (crown Ar-O—C stretching), 3250 (urea NH stretching); UV–vis ($CHCl_3$—CH_3CN) λ_{max} ($\log \varepsilon$) 202 (4.88), 308 (4.52), 405 (sh, 3.74), 438 (3.61), 471(3.64), 540 (sh, 2.89), 706 (2.00) nm; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, 298 K) δ (ppm) 8.65 (s, 2H, NH of urea on crown ether side), 8.35 (s, 2H, NH of urea on fullerene side), 6.97 (d, ^4J(H,H) = 1.5 Hz, 2H, Ar-H), 6.88 (d, ^3J(H,H) = 8.3 Hz, 2H, ArH), 6.75 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.5 Hz, 2H, ArH), 6.66 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.2 Hz, 4H, ArH), 6.59 (d, ^3J(H,H) = 8.3 Hz, 4H, ArH), 5.25 (d, ^2J(H,H) = 9.3 Hz, 2H, *H*HC—*N*—), 4.90 (s, 2H, HC—N—), 4.45 (d, ^2J(H,H) = 9.3 Hz, 2H, H*H*C—N—), 4.12–3.70 (m, 16H, OCH_2 of crown ether), 2.85 (6H, s, N—CH_3) ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si) (unassigned values refers to sp^2 C of C_{60}) 154.7 (2C of urea group), 154.1 (2C), 153.5 (2C), 151.4 (2C), 150.8 (2C), 150.5 (2C), 149.5 (2C), 149.1 (2C), 148.9 (2C), 148.2 (2C), 147.5 (2C), 147.3 (2C), 146.2 (2C), 145.9 (4C), 145.7 (2C), 145.6 (2C), 145.3 (2C), 144.6 (2C), 144.0 (2C, Ar-Cq), 142.9 (2C), 142.1 (2C), 141.8 (2C), 141.7 (2C), 141.3 (2C), 140.6 (2C), 140.1 (2C, Ar-Cq), 139.4 (2C), 138.9 (2C), 138.7 (2C, Ar-Cq), 136.4 (2C), 135.8 (2C), 135.7 (2C), 132.8 (2C, Ar-Cq), 130.5 (2C, Ar-Cq), 127.8 (2C, Ar-CH), 120.3 (2C, Ar-CH), 114.5 (2C, Ar-CH), 112 (2C, Ar-CH), 106 (2C, Ar-CH), 83.3 (2C, NCH of the pyrrolidine ring), 77.0 (solvent), 75.0 (2C, sp^3 C— of C_{60}), 73.0 (2C, crown ether), 72.4 (2C, crown ether), 71.0 (2C, crown ether), 70.5 (2C, crown ether), 69.2 (2C, NCH_2 of pyrrolidine ring), 68.3 (2C, sp^3 C of C_{60}), 40.3 (2C, CH_3 linked to N of the pyrrolidine ring); FAB-MS *m*/*z* (relative intensity) 1458 (M + , 59), 1459 (M+1, 8), 1016 (20), 834 (27), 806 (23), 720 (C_{60}, 100), 320 (44), *m*/2*z* 222 (10); Anal. calcd for $C_{100}H_{46}O_8N_6$: C, 82.30; H, 3.15; N, 5.76. Found: C, 82.40; H, 3.19; N, 5.21.

Acknowledgements

We are thankful to the UGC for the financial assistance and CDRI, Lucknow for the spectral analysis. A. Kumar would like to thank the Council of Scientific and Industrial Research (CSIR), New Delhi for the Senior Research Fellowship.

Supporting Information

Synthesis of *p*-[1,3-dioxolane-2-yl] benzoic acid; a copy of FAB-MS, ^{1}H NMR, ^{13}C NMR and FT-IR spectra of **3**; mass fragmentation pattern of **3**; UV–vis spectra of bingel bis-adduct *trans*-1 C_{62} $(CO_2Et)_4$ and synthesised compound **3** in $CHCl_3$; change in fluorescence spectra of **3** upon addition of K^+ in different solvents; stoichiometry of the complex between $H_2PO_4^-$ and **3**:K^+; change in fluorescence of **3**+K^+ on addition of HSO_4^- and AcO^-; change in cyclic voltammogram of **3**+K^+ on addition of other anions (HSO_4^-, AcO^-, ClO_4^-); ^{1}H NMR titration plots of **3**+K^+ with HSO_4^-, AcO^-; Benesi–Hildebrand plot for a 1:1 stoichiometry of $H_2PO_4^-$ complexation by **3**:K^+.

References

(1) For recent contributions and reviews see, for example: (a) Hamon, M.; Menand, M.; Le Gac, S.; Luhmer, M.; Dalla, V.; Jabin, I. *J. Org. Chem*. **2008**, *73*, 7067–7071. (b) Lankshear, M.D.; Dudley, I.M.; Chan, K.M.; Cowley, A.R.; Santos, S.M.; Felix, V.; Beer, P.D. *Chem.-Eur. J*. **2008**, *14*, 2248–2263. (d) Miyaji, H.; Kim, D.S.; Chang, B.-Y.; Park, E.; Park, S.M.; Ahn, K.H. *Chem. Commun.* **2008**, 753–755. (e) Le Gac, S.; Jabin, I. *Chem.-Eur. J.* **2008**, *14*, 548–557. (f) Gale, P.A.; García-Garrido, S.E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151–190. (g) Lankshear, M.D.; Dudley, I.M.; Chan, K.M.; Beer, P.D. *New J. Chem.* **2007**, *31*, 684–690. (h) Cametti, M.; Nissinen, M.; Dalla Cort, A.; Mandolini, L.; Rissane, K. *J. Am. Chem. Soc*. **2007**, *129*, 3641–3648. (i) Mahoney, J.M.; Stucker, K.A.; Jiang, H.; Carmichael, I.; Brinkmann, N.R.; Beatty, A.M.; Noll, B.C.; Smith, B.D.; Rissane, K. *J. Am. Chem. Soc.* **2005**, *127*, 2922–2928. (j) Oton, F.; Tarraga, A.; Espinosa, A.; Velasco, M.D.; Molina, P. *Dalton Trans*. **2006**, 3685–3692. (k) Sessler, J.L.; Gale, P.A.; Cho, W.S. *Synthetic Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, 2006, Chapter 6, pp 259–293. (l) Smith, B.D. In *Macrocyclic Chemistry: Current Trends and Future Perspectives*; Gloe, K.; Springer: Dordrecht, 2005; pp 137–151. (m) Kirkovits, G.J.; Shriver, J.A.; Gale, P.A.; Sessler, J.L. *J. Inclusion Phenom. Macrocyclic Chem*. **2001**, *41*, 69–75. (n) Caltagirone, C.; Gale, P.A. *Chem. Soc. Rev.* **2009**, DOI: 10.1039/b806422a.

(2) (a) Tong, C.C.; Quesada, R.; Sessler, J.L.; Gale, P.A. *Chem. Commun*. **2008**, 6321–6323. (b) Koulov, A.V.; Mahoney, J.M.; Smith, B.D. *Org. Biomol. Chem*. **2003**, *1*, 27–29. (c) Pelizzi, N.; Casnati, A.; Friggeri, A.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1307–1312. (d) Reetz, M.T.; Niemeyer, C.M.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1472–1474. (e) Reetz, M.T.; Johnson, B.M.; Harms, K. *Tetrahedron Lett.* **1994**, *35*, 2525–2528. (f) Rudkevich, D.M.; Brzozka, Z.; Palys, M.; Visser, H.C.; Verboom, W.; Reinhoudt, D.N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 467–468. (g) Rudkevich, D.M.; Mercer-Chalmers, J.D.; Verboom, W.; Ungaro, R.; de Jong, F.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1995**, *117*, 6124–6125. (h) Beer, P.D.; Hopkins, P.K.; McKinney, J.D. *Chem. Commun.* **1999**, 1253–1254. (i) White, D.J.; Laing, N.; Miller, H.; Parsons, S.; Coles, S.; Tasker, P.A. *Chem. Commun.* **1999**, 2077–2078.

(3) (a) Breccia, P.; Gool, M.V.; Perez-Fernandez, R.; Martin-Santamaria, S.; Gago, F.; Prados, P.; de Mendoza, J. *J. Am. Chem. Soc.* **2003**, *125*, 8270–8284. (b) Tsukube, H.; Wada, M.; Shinoda, S.; Tamiaki, H. *Chem. Commun.* **1999**, 1007–1008. (c) Hossain, M.A.; Schneider, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 11208–11209. (d) Kinnear, K.I.; Mousley, D.P.; Arafa, E.; Lockhart, J.C. *J. Chem. Soc., Dalton Trans.* **1994**, 3637–3643.

(4) (a) Evans, A.J.; Beer, P.D. *Dalton Trans*. **2003**, 4451–4456. (b) Cooper, J.B.; Drew, M.G.B.; Beer, P.D. *J. Chem. Soc., Dalton Trans*. **2001**, 392–401. (c) Cooper, J.B.; Drew, M.G.B.; Beer, P.D. *J. Chem. Soc., Dalton Trans.* **2000**, 2721–2728. (d) Deetz, M.J.; Shang, M.; Smith, B.D. *J. Am. Chem. Soc*. **2000**, *122*, 6201–6207. (e) Teramae, N.; Shigemon, K.; Nishizawa, S. *Chem. Lett.* **1999**, *28*, 1185–1186.

(f) Chrisstoffels, A.J.; de Jong, F.; Reinhoudt, D.N.; Sivelli, S.; Gazzola, L.; Casnati, A.; Ungaro, R. *J. Am. Chem. Soc.* **1999**, *121*, 10142–10151. (g) White, D.J.; Lang, N.; Miller, H.; Parsons, S.; Coles, S.; Tasker, P. *Chem. Commun*. **1999**, 2077–2078. (h) Reetz, M.T.; Niemeyer, C.M.; Harris, K. *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 1472–1474. (i) Rudkevich, D.M.; Brzozka, Z.; Palys, M.; Visser, H.C.; Verboom, W.; Reinhoudt, D.N. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 467–468.

(5) Chrisstoffels, A.J.; de Jong, F.; Reinhoudt, D.N.; Sivelli, S.; Gazzola, L.; Casnati, A.; Ungaro, R. *J. Am. Chem. Soc.* **1999**, *121*, 10142–10151.

(6) Gunning, P.T. *Org. Biomol. Chem.* **2005**, *3*, 3877–3879.

(7) Cooper, S.R., Ed.; *Crown Compounds: Toward Future Applications*; VCH: Weinheim, 1992.

(8) (a) Langa, F.; Nierengarten, J.F. *Fullerenes: Principle and Applications*; Royal Society of Chemistry: Cambridge, 2007. (b) Bonifazi, D.; Enger, O.; Diederich, F. *Chem. Soc. Rev.* **2007**, *36*, 390–414. (c) Martin, N.; Nierengarten, J.F. *Tetrahedron* **2006**, *62*, 1917–1917. (d) Martin, N. *Chem. Commun*. **2006**, 2093–2104. (e) Bosi, S.; Da Ros, T.; Spalluto, G.; Prato, M. *Eur. J. Med. Chem*. **2003**, *38*, 913–923. (f) Dunsch, L. *Angew. Chem., Int. Ed. Engl*. **2003**, *5*, 529–530.

(9) Troshin, P.A.; Lyubovskaya, R.N. *Russ. Chem. Rev.* **2008**, *77*, 305–349.

(10) Hirsch, A.; Soi, A.; New *J. Chem.* **1998**, *12*, 1337–1339.

(11) Maggini, M.; Scorrano, G. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

(12) (a) Guo, Z.; Li, Y; Yan, J.; Bai, F.; Li, F; Zhu, D.; Si, J.; Ye, P. *Appl. Phys. B* **2000**, *70*, 257–260. (b) Díaz, M.C.; Illescas, B.M.; Martín, N.; Stoddart, J.F.; Canales, M.A.; Barbero, J.J.; Sarova, G.; Guldi, D.M. *Tetrahedron* **2006**, *62*, 1998–2002. (c) Illescas, B.M.; Santos, J.; Díaz, M.C.; Martín, N.; Atienza, C.M.; Guldi, D.M. *Eur. J. Org. Chem.* **2007**, *2007*, 5027–5037. (d) Harikrishnan, U.; Menon, S.K. *Fuller. Nanotub. Carb. Nanostruct.* **2008**, *16*, 165–177. (e) Santos, J.; Grimm, B.; Illescas, B.M.; Guldi, D.M.; Martín, N. *Chem. Commun.* **2008**, 5993–5995.

(13) Shiori, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203–6205.

(14) (a) Iglesias, R.S.; Claessens, C.G.; Rahman, G.M.A.; Herranz, M.A.; Guldi, D.M.; Torres, T. *Tetrahedron* **2007**, 63, 12396–12404. (b) Sergeyev, S.; Schär, M.; Seiler, P.; Lukoyanova, O.; Echegoyen, L.; Diederich, F. *Chem. Eur. J.* **2005**, *11*, 2284–2294.

(15) Pederson, C.J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.

(16) Feigenbaum, W.M.; Michel, R.H. *J. Polym. Sci. A-1* **1971**, *9*, 817–820.

(17) Harikrishnan, U.; Menon, S.K. *Dyes Pigments* **2008**, *77*, 462–468.

(18) Imahori, H.; Tamaki, K.; Yamada, H.; Yamada, K.; Sakata, Y.; Nishimura, Y.; Yamazaki, I.; Fujitsuka, M.; Ito, O. *Carbon* **2000**, *38*, 1599–1605.

(19) Hirsch, A.; Lamparth, I.; Karfunkel, H.R. *Proc.-Electrochem. Soc.* **1994**, *94*, 734–746.

(20) Lu, Q.; Schuster, D.I.; Wilson, S.R. *J. Org. Chem.* **1996**, *61*, 4764–4768.

(21) Bourgeois, J.-P.; Seiler, P.; Fibbioli, M.; Pretsch, E.; Diederich, F.; Echegoyen, L. *Helv. Chim. Acta* **1991**, *82*, 1572–1595.

(22) Connors, K.A. *Binding Constants, The Measurement of Molecular Complex Stability*; Wiley: New York, NY, 1987; p 24.