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Enediyne scaffold-based highly selective chemosensor for ratiometric sensing of $H_2PO_4^-$ ions

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ABSTRACT

Enediyne scaffold - based new chemosensor **1** has been designed and synthesized. The sensor **1** fluorometrically recognizes $H_2PO_4^-$ in CH_3CN containing 1% DMSO by exhibiting a ratiometric change in emission upon complexation. The association constant of **1** with $H_2PO_4^-$ was calculated as $(3.06 \pm 0.6) \times 10^4\ M^{-1}$.

Selective sensing of anions of biological and environmental relevance by synthetic receptors has become an important research area in supramolecular chemistry.[1] In relation to this, the binding unit, which is capable of binding anions strongly or moderately under the mastery of a synthetic spacer, has the crucial role in giving the selectivity to the designed receptor. Among the various types of binding units, amide,[2] urea/thiourea,[3] guanidinium,[4] amidinium,[5] imidazolium,[5d] benzimidazolium,[6] pyridinium,[7] polyammonium cations[8] etc., are widely used in anion binding and they were found to be creditable in functioning. Benzimidazolium like imidazolium and pyridinium motifs provides an unconventional C–H bond for bonding.[9] Further stabilization of the complex is attributed to the electrostatic interaction working in between the opposite charges of host and guest. The use of this motif in the context of anion recognition is well established.[6] It is to be noted that functioning of this motif is controlled by the organic framework that holds them in a particular array. During our work along this direction,[6c–g,10] we questioned ourselves whether we can use the enediyne motif as synthetic spacer in building up a new architecture for the recognition of anionic substrates. Enediyne is a well known moiety that undergoes Bergman cyclization under thermal condition to give benzene-1,4-diradical.[11] This reactive diradical species interacts with DNA and shows antitumor activity. Research aimed at the facile cyclization of enediyne motif present in the designed compounds in the presence of suitable cation is being pursued in different laboratories.[11,12] In this horizon, while in some cases the Bergman cyclization is assisted in the presence of metal ion, it is also disfavored or occurred at elevated temperatures in the presence of metal ions due to the modulation of the distance between two yne motifs.[11] Due to this characteristic feature, exploitation of enediyne motif in molecular recognition studies for the substrate recognition is untried. To the best of our knowledge, the use of enediyne motif in developing hosts for anions is unknown in the literature. In this Letter, we, for the first time, wish to report the design, synthesis, and the anion sensing properties of a new enediyne-based chemosensor **1**.

Compound **1** shows selective ratiometric fluorescence sensing of $H_2PO_4^-$ over the other anions such as AcO^-, malonate, succinate, HSO_4^-, F^-, Cl^-, Br^-, and I^- in CH_3CN containing 1% DMSO. The cooperativity of the two benzimidazolium motifs of **1** in anion binding was established by considering the model compound **2**, which perturbed the emission weakly in a non ratiometric fashion.

The receptor **1** was achieved in a reasonable yield according to the Scheme 1. The dibromo compound **6**, obtained based on the reported procedure,[13] was reacted with anthracene labeled benzimidazole **7**[14] in dry CH_3CN under refluxing condition to afford the dibromide salt of **1**. Anion exchange of the dibromide salt with NH_4PF_6 finally gave the desired compound **1** in an appreciable yield.[15a] Reaction of **7** with butyl bromide under refluxing condition in dry CH_3CN followed by anion exchange using NH_4PF_6 afforded the compound **2**[15b] in a good yield.

The interaction properties of **1** toward the anions of different shapes such as F^-, Cl^-, Br^-, I^-, HSO_4^-, AcO^-, malonate, succinate, and $H_2PO_4^-$ (taken as tetrabutylammonium salts) were studied by fluorescence, UV–vis, and ^1H NMR. Importantly, the receptor **1**

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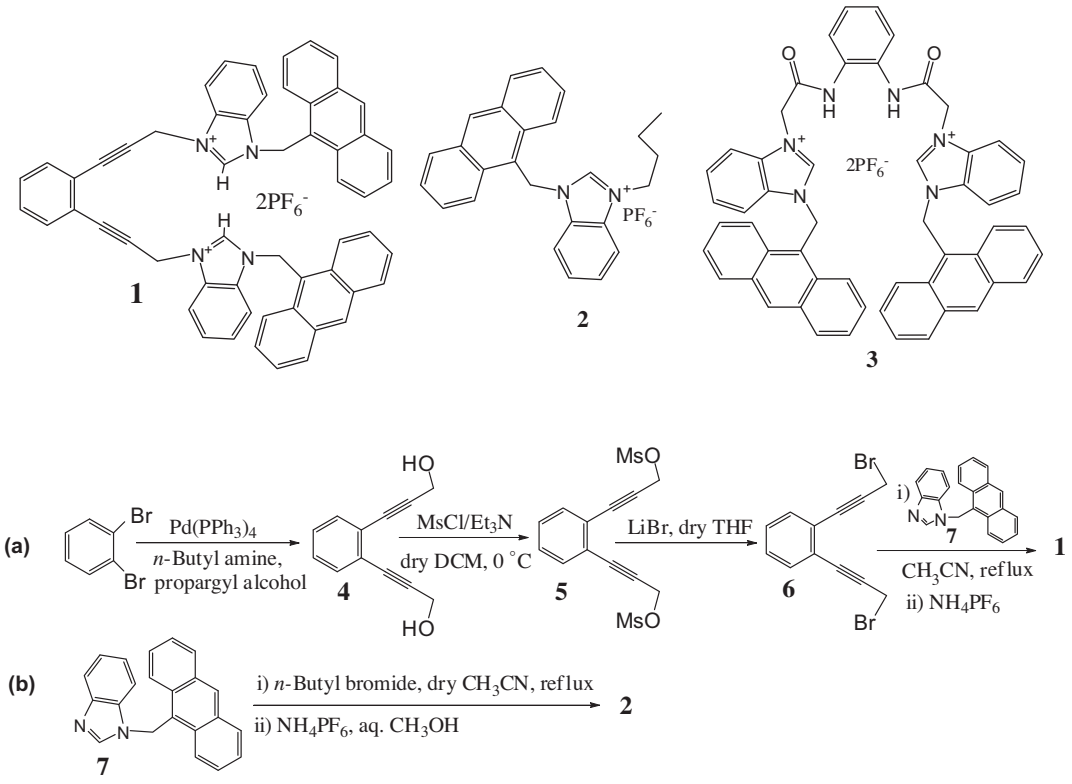

Scheme 1. Syntheses of receptors **1** and **2**.

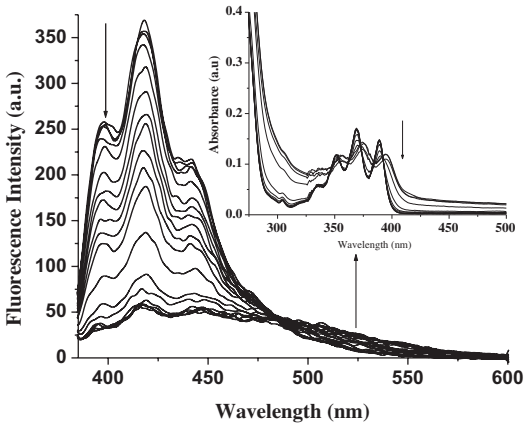

Figure 1. Fluorescence titration spectra of **1** ($c = 2.22 \times 10^{-5}$ M) upon addition of $H_2PO_4^-$ in CH_3CN containing 1% DMSO (λ_{ex} = 370 nm); Inset: UV–vis titration spectra of **1** ($c = 2.22 \times 10^{-5}$ M) with $H_2PO_4^-$ in CH_3CN containing 1% DMSO.

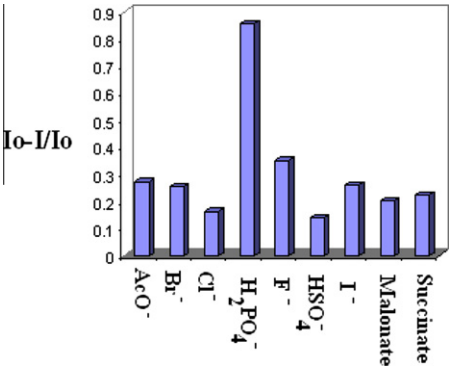

Figure 2. Change in fluorescence ratio of **1** ($c = 2.22 \times 10^{-5}$ M) at 418 nm upon addition of a particular anion in 10 equiv amounts in CH_3CN containing 1% DMSO (λ_{ex} = 370 nm).

exhibited selective sensing of $H_2PO_4^-$ in CH_3CN containing 1% DMSO. In the presence of $H_2PO_4^-$ ions, the monomer emission of **1** was greatly decreased along with the appearance of a new peak at 500 nm, ascribed to the chelation induced excimer formation between the closely spaced anthracene moieties. This characteristic emission change allowed $H_2PO_4^-$ ions to be distinguished from the other anions studied. Figure 1 demonstrates the change in emission of **1** upon successive addition of $H_2PO_4^-$ to the solution of **1** in CH_3CN containing 1% DMSO. The appearance of an isosbestic point at 486 nm in Figure 1 indicates the formation of a new species that remains in equilibrium with the free receptor in the solution. Figure 2 highlights the change in emission of **1** in the presence of 10 equiv amounts of a particular anion studied. As can be seen from Figure 2, only $H_2PO_4^-$ perturbs the emission considerably. Among the other anions F^- induces a little more change in the emission. The smaller sized dicarboxylates malonate and succinate also did not bring any measurable change in emission.

However, in the event, the anion–receptor interaction is due to hydrogen bonding and electrostatic interaction between the anion target and the benzimidazolium functions. Indeed, ^{1}H NMR spectra in DMSO-d_6 show that only the benzimidazolium protons are mainly affected by the anion addition. Due to the presence of DMSO, a competitive solvent,[16] the downfield shift of the benzimidazolium protons was found to be 0.04 ppm. A similar study in ^{1}H NMR was performed in $CDCl_3$ containing 0.8% DMSO-d_6 with the addition of $H_2PO_4^-$. Interestingly, a greater downfield movement of the benzimidazolium protons ($\Delta\delta$ = 1.19 ppm) was observed in the presence of equivalent amount of $H_2PO_4^-$. Figure 3 demonstrates this feature. Upon interaction, the anthracenyl ring protons (H_c, H_d, H_e, H_f and H_b) suffered upfield shift which anticipated the π

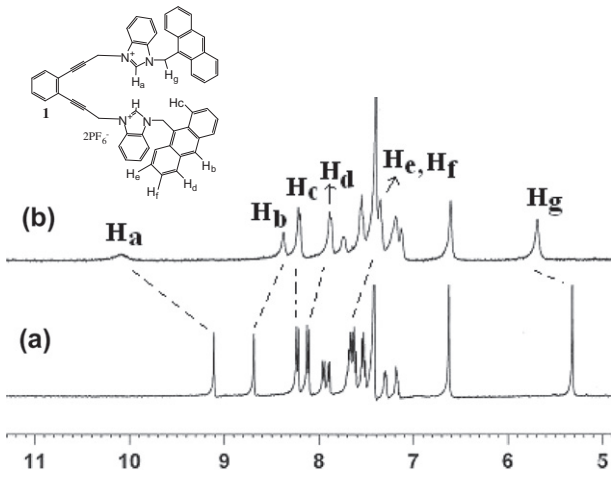

Figure 3. ^{1}H NMR (400 MHz) of (a) receptor **1** ($c = 1.45 \times 10^{-3}$ M) and (b) with equivalent amount of $H_2PO_4^-$ in $CDCl_3$ containing 0.8% DMSO-d_6.

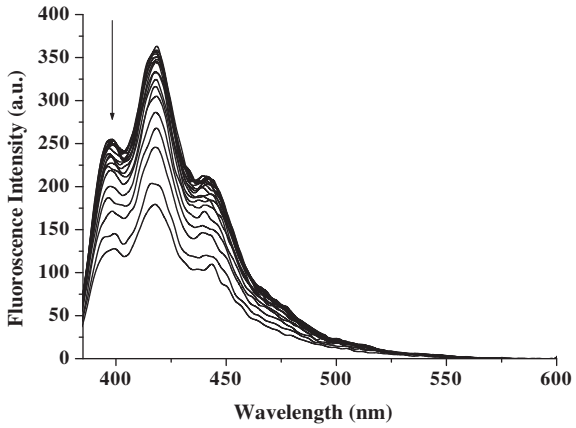

Figure 4. Fluorescence titration spectra of **1** ($c = 2.22 \times 10^{-5}$ M) upon addition of F^- in CH_3CN containing 1% DMSO ($\lambda_{ex} = 370$ nm).

stacking interaction between the pendant anthracenes. It is to be noted that F^- being smaller sized and highly basic, perturbed the emission of **1** relatively little more than the other halides and also AcO^- ions. This is attributed to the dimensional matching of F^- into the narrow cavity of **1**. Figure 4 shows the emission titration spectra for **1** with F^-. The complexation induced quenching of emission of **1** in the present case is explained due to the activation of PET process occurring in between the binding site and the excited state of anthracene. The significant PET-based quenching of monomer emission of **1** followed by the growth of an excimer peak in the presence of $H_2PO_4^-$ is worth mentioning for its selective ratiometric sensing in CH_3CN containing 1% DMSO. The ratiometric chemosensors offer advantages over the conventional monitoring of fluorescence intensity at a single wavelength. A dual emission system can minimize the measurement errors because of the factors such as phototransformation, receptor concentrations, and environmental effects.[17] A literature survey indicated that ratiometric chemosensors for $H_2PO_4^-$ are rare.[6g,18] In the interaction process, the 1:1 stoichiometry of the complex of **1** with $H_2PO_4^-$ was established from Job plot[19] (Fig. 5; also see Supplementary data) and the binding affinity was determined to be $(3.06 \pm 0.6) \times 10^4$ M^{-1}.[20] Based on these experimental observations we presume a binding structure as shown in Figure 6a. The compactness of the binding cavity, composed of benzimidazolium units only, was realized from the MM3 optimized geometry[21] (Fig. 6b).

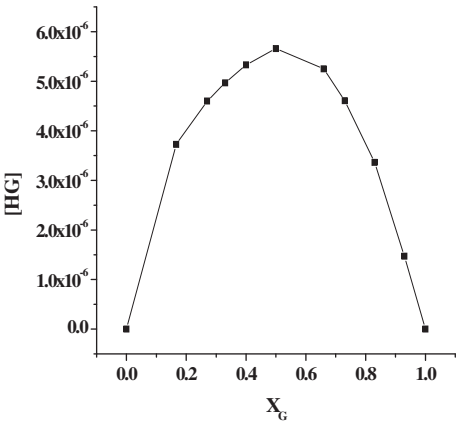

Figure 5. UV Job plot of the receptor **1** with $H_2PO_4^-$, where [G] = [H] = 2.22×10^{-5} M in CH_3CN containing 1% DMSO.

The binding selectivity of **1** toward $H_2PO_4^-$ was determined from the control experiment in fluorescence. The change in emission of **1** was noticed in CH_3CN containing 1% DMSO after the addition of 5 equiv amounts of $H_2PO_4^-$ to the receptor solution containing 5 equiv amounts of other particular anion. Figure 7, in this context, highlights the observations. It is evident from Figure 7 that interference of the other anions in the binding of $H_2PO_4^-$ is negligible.

However, in comparison to our previously reported *ortho*-phenylenediamine-based receptor **3**,[6d] the receptor **1** is much selective toward $H_2PO_4^-$ with greater binding constant value. Also the selectivity between $H_2PO_4^-$ and F^- ions is measurably high. The intramolecular hydrogen bonding between the amides in **3** which cannot be excluded presumably reduced its affinity and selectivity toward anion sensing. This is in contrast to **1**. Furthermore, the enediyne motif in **1** holds the benzimidazolium groups at a fixed distance and allows a more compact binding of $H_2PO_4^-$ ion for which the decomplexation in the presence of excess concentration of $H_2PO_4^-$ did not occur like in the case of **3**.[6d] Importantly, the cooperativity of the two benzimidazolium moieties in **1** was further understood from the weak change in emission of **2** upon titration with $H_2PO_4^-$ and F^- ions (Supplementary data).

In aqueous CH_3CN (CH_3CN: H_2O = 1:1 v/v) containing few drops of DMSO (used to make solution homogeneous) the interaction of **1** was further studied with the same anions. Almost equal change in emission of **1** established its non efficiency in discriminating the anions fluorometrically (Fig. 8) in aqueous organic solvent. Even, under identical condition, mere change in emission of **1** upon addition of the different sodium salts of phosphate derivatives as well as phosphate group containing biomolecules such as ATP, ADP and AMP, dissolved in aqueous CH_3CN (CH_3CN: H_2O = 1:1 v/v) (Supplementary data) indicated weak or no interaction.

Further to obtain insight into the ground state interaction, we recorded UV–vis spectra of **1** in CH_3CN containing 1% DMSO in the presence of the same anions. Among the anions, only $H_2PO_4^-$ brought a marked change with a red shift of ~6 nm in the UV–vis spectra of **1** and thereby indicated its significant interaction (inset of Fig. 1) in the ground state also. On the contrary, the minimal change in the absorption of **1** in the presence of other anions corroborated their weak or non involvement in the binding (Supplementary data). Thus the enediyne scaffold in **1** acts as a suitable spacer that holds the benzimidazolium groups for providing a channel like molecular cleft for the complexation of $H_2PO_4^-$ ion effectively.

As the enediyne motif is sensitive to Bergman cyclization to give benzene-1,4-diradical under thermal condition, we verified its sustainability as a spacer by recording the ^{1}H NMR at variable temper-

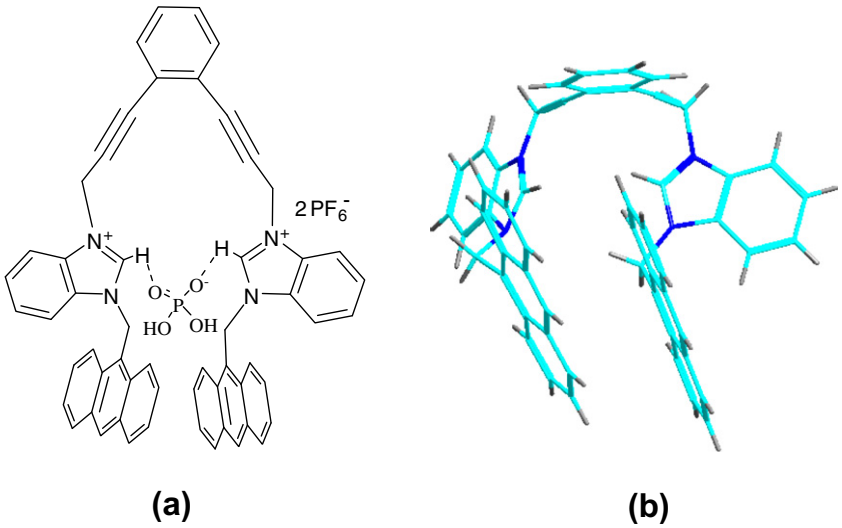

Figure 6. (a) Proposed binding structure for **1** with $H_2PO_4^-$; (b) MM3 optimized geometry of **1**.

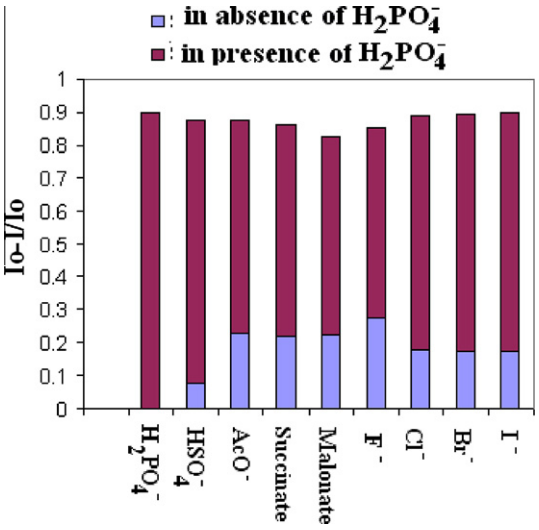

Figure 7. Change in fluorescence ratio upon addition of 5 equiv amounts of $H_2PO_4^-$ to the solutions of **1** and **1** containing other anions in 5 equiv amounts ([H] = 3.13×10^{-5} M).

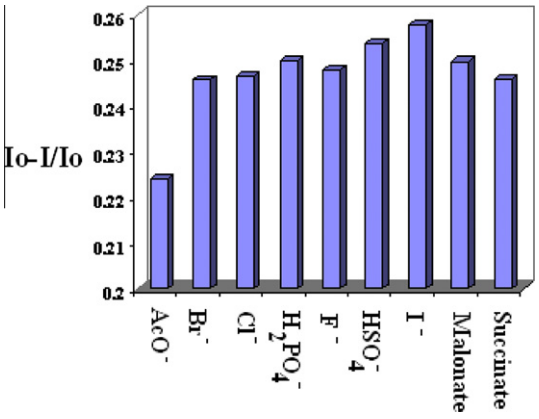

Figure 8. Change in fluorescence ratio of **1** upon addition of 13 equiv amounts of a particular guest in aqueous CH_3CN ($CH_3CN:H_2O$ = 1:1 v/v) ([H] = 3.13×10^{-5} M).

atures (Supplementary data). As can be seen from Figure 7S, no structural change was observed upto temperature 120 °C. Moreover, to be acquainted with the actual temperature range at which the enediyne scaffold in **1** is cycloaromatized to the benzene diradical, the differential scanning calorimetric (DSC)[22] experiment was carried out. In this regard, in DSC curve an inflection at 168.95 °C which presumably corresponds to the enediyne cyclization was observed (Supplementary data). Interestingly, in the presence of equivalent amount of the $H_2PO_4^-$ the inflection at 168.95 °C is shifted to 196.4 °C (Supplementary data). This is ascribed to the higher stability of the system upon complexation. Thus the experimental findings in the present communication further provide the information that the enediyne motif in **1** is sound in anion recognition without exhibiting chelation induced Bergman cyclization over a wide range of temperature.

In conclusion, we have thus designed and synthesized a new molecular architecture **1** which is found to recognize $H_2PO_4^-$ ratiometrically. In the design, enediyne motif has been exploited as synthetic spacer in building up the receptor site for anion. Although there are reports on enediyne based molecules which on complexation with cations undergo facile Bergman cyclization, there is no report on anion binding receptor built on enediyne scaffold till date. Inspite of the absence of the amide groups as extra hydrogen bond donors to anions as found in receptor **3**, the linear nature of the triple bonds in **1** makes the open cleft more compact for effective complexation of $H_2PO_4^-$. The involvement of polar C–H bonds of benzimidazolium units in hydrogen bonding and the charge–charge interaction under the guidance of the enediyne motif altogether are the essential factors that impart selectivity to the receptor **1** in the recognition of $H_2PO_4^-$ ions. To our opinion, this is a new addendum to the existing examples[6e–g,23] of receptors for $H_2PO_4^-$ in the literature. We are currently exploring this enediyne framework with a view to establishing more sophisticated systems that might perform as good hosts for other several anions of specific interest.

Acknowledgments

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Supplementary data

Supplementary data (figures showing the change in absorption and fluorescence spectra of **1** with anions, the fluorescence Job plots for $H_2PO_4^-$, change in fluorescence ratio of **1** in the presence of 13 equiv amounts of the anions in aq CH_3CN, binding constant curve, DSC curve, ^1H NMR at variable temperature) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.02.024.

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15. (a) To a solution of the compound **6** (75 mg, 0.242 mmol) in dry CH_3CN (10 mL), anthracene appended benzimidazole **7** (225 mg, 0.726 mmol) dissolved in dry mixture solvent of CH_3CN: DMF (10:1 v/v) was added at a time. The reaction mixture was refluxed for 98 h. On removal of the solvent, the dibromide salt of 1 was isolated in a 45% yield (60 mg). In the next step, the dibromide salt of **1**, dissolved in CH_3OH (15 mL), was treated with aqueous NH_4PF_6 (22 mg, 0.13 mmol) to carry out the anion exchange reaction. After heating with stirring the solution for 30 min, precipitate appeared. Filtration of the precipitate followed by thorough washing with ether afforded the receptor **1** in a 70% yield (40 mg, mp 185 °C; decomposition starts at 167 °C). ^1H NMR (400 MHz, DMSO-d_6): 8.97 (s, 2H), 8.92 (s, 2H), 8.39 (m, 6H), 8.25 (d, 4H, J = 8 Hz), 8.01 (d, 2H, J = 8 Hz), 7.81 (t, 2H, J = 8 Hz), 7.74 (t, 2H, J = 8 Hz), 7.61 (m, 8H), 7.41 (m, 2H), 7.31(m, 2H), 6.75 (s, 4H), 5.44 (s, 4H); ^{13}C (100 MH, DMSO-d_6) 162.3, 132.4, 131.7, 131.1, 130.9, 130.7, 130.5, 129.6, 129.4, 127.9, 127.1, 127.0, 125.6, 123.3, 122.9, 121.7, 114.5, 113.6, 85.1, 84.4, 43.5, 37.2; FT-IR: cm^{-1} (KBr): 2250, 1623, 1575, 1448; (ES+): m/z: 913.8 $(M-PF_6^-)^+$, 767.6 $(M-2PF_6^- -1)^+$; (b) Compound **2** (mp 195 °C): ^1H NMR (400 MHz, DMSO-d_6): 9.01 (s, 1H), 8.92 (s, 1H), 8.36–8.31 (m, 2H), 8.29–8.25 (m, 3H), 8.11 (d, 1H, J = 8 Hz), 7.81–7.73 (m, 2H), 7.65–7.63 (m, 4H), 6.71 (s, 2H), 4.31 (t, 2H, J = 7.20 Hz), 1.70–1.62 (m, 2H), 1.12–1.06 (m, 2H), 0.75 (t, 3H, J = 7.20 Hz); (ES+): m/z: 365.2 $(M-PF_6^-)^+$.
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