

Two-walled phthalimide extended calix[4]pyrrole: Experimental and computational anion binding investigations

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ARTICLE INFO

Keywords:

Calix[4]pyrrole
Phthalimide
Anion binding
Anion receptor complex
Anion- π interaction
CH-anion interaction
Halides
Oxoanions

ABSTRACT

In this study, a two-walled phthalimide extended C4P (**11**) was probed as an anion receptor for tetrabutylammonium (TBA) salts of spherical halides, trigonal/tetrahedral oxoanions and linear anions with the aid of DFT/TD-DFT calculations and UV-vis spectroscopy. Optimized geometries indicate the non-covalent interaction present between the guest and host. Interestingly, anion receptor complex (**11**@F⁻) has been found more reactive among various studied anion receptor complexes. Furthermore, TD-DFT analyses provided insights into electronic transitions within the studied species and found the absorption spectra in the range of 180 nm to 400 nm. UV-vis absorbance titrations of receptor **11** with various anions in CH₃CN have revealed 1:1 binding stoichiometry and considerably higher binding affinities with F⁻, Cl⁻, CH₃COO⁻, and SCN⁻ as compared to the one-walled phthalimide C4P (**13**) and simple C4P (**1**) existing in the literature. Notably, higher anion binding affinities of the receptor **11** as compared to the C4Ps **1** and **13** certifies the contribution of weaker anion- π interactions from phthalimide subunits as well as the CH-anion interactions from the aliphatic methylene (CH₂) protons besides primary hydrogen bonding of the pyrrolic NHs-anions as observed from ¹H NMR studies.

1. Introduction

Remarkably, it always remain a great challenge for the supramolecular chemists to design and develop synthetic receptors, having the ability of anion complexation/recognition *via* the exploitation of various non-covalent (supramolecular) interactions [1,2]. Infact, anion recognition by means of artificial receptors has evolved as a keynote subject in the realm of supramolecular chemistry in the past few decades [3,4]. This is owing to the fact that anions offer significant roles in the chemical, biological and industrial world. Interestingly, anions govern most of the enzymatic reactions and in particular, anions like ATP, DNA, RNA, GMP, PPi, *etc.*, play a crucial role in physiological processes comprising cell signaling, gene expression, and metabolism [5]. It has been revealed that Dent's disease, cystic fibrosis, Pendred's syndrome are associated with defective anion-transport channels [6,7]. On the other hand, excess levels of anions like phosphate and nitrate lead to eutrophication of water bodies and thus pose a serious environmental threat. The proper fluoride ion concentration in beverages helps us to combat with dental carries, whereas high fluoride ion concentration provokes bone density loss and teeth mottling [8]. As a consequence, significant efforts are being devoted for the generation of novel synthetic

receptors, having enhanced anion binding affinities as well as selectivity for a target anion.

In the arena of anion complexation and recognition, octamethylporphyrinogen—well-known as the *meso*-octamethyl calix[4]pyrrole (C4P), has made its advent way back in the year 1996, when Sessler and coworkers have carried out extensive binding studies of parent C4P with diverse anions like F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, and H₂PO₄⁻ in dichloromethane-*d*² [9]. Remarkably, it was found that comparatively non-polar 1,3-alternate conformation of C4P gets reorganized into the cone conformation, upon the addition of anionic guests. The cone conformation in turn directs all the four pyrrolic NH-hydrogen bond donors towards anionic guests—acting as hydrogen bond acceptors [10]. Since the participation of simple C4P in anion recognition ceremony, researchers worldwide have exploited its *meso*-/ β -positions for the modulation of binding affinities towards anions, cations, ion-pairs, and even neutral molecules too [11–13]. The modulated anion binding affinities of functionalized C4Ps in turn makes them ideal candidates for receptors [14–18], sensors [19–22], ligands [23], polymers [24,25], molecular switches [26,27], catalysis [28,29], adsorption [30,31], transmembrane ion transport [32,33], drug delivery [34], and therapeutic agents [35–37].

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<https://doi.org/10.1016/j.molstruc.2025.144990>

Received 29 November 2024; Received in revised form 28 November 2025; Accepted 4 December 2025

Available online 5 December 2025

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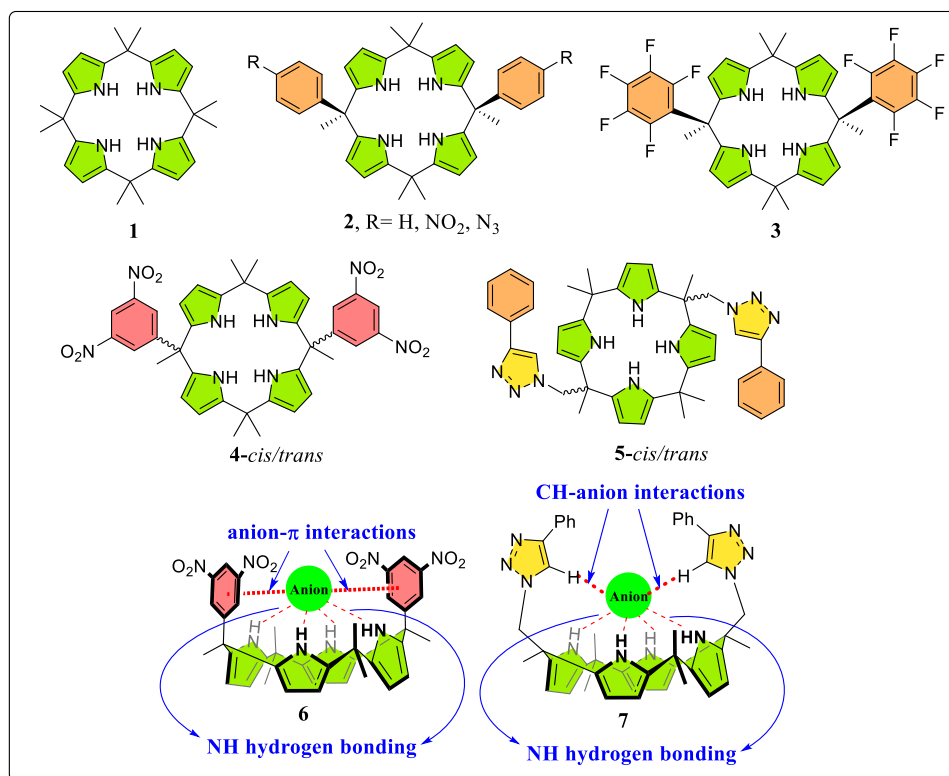
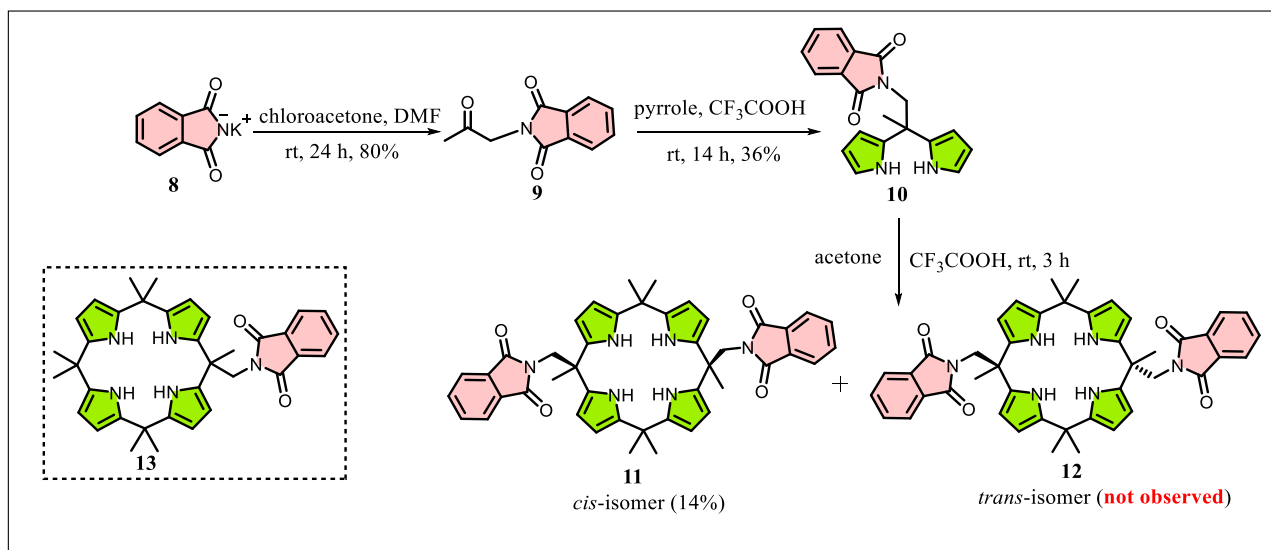


Fig. 1. Simple and two-walled C₄P_s (1–5) acting as efficient anion receptors via exploitation of various non-covalent interactions (depicted in 6 and 7).

In particular, the *meso*-substituted two-walled *cis*/ α,α -C₄P isomers have been recognized as promising anion receptors, as they capture anions in a sandwich manner between the two electron deficient aromatic walls (Fig. 1), thereby rendering them as perfect tools for the exploration of thermodynamic stabilities of the anion receptor complexes and interaction energies between the aromatic π -system and the anions. This scenario has become possible by means of backbone NH-hydrogen bonding interactions offered by four NH-hydrogen bond donors of cone-shaped C₄P network, in addition to the anion- π /CH-anion interactions offered by two π -acidic appended aromatic walls (Fig. 1) [38,39]. In this direction, Ballester and teammates have quantified

nitrate- π interactions between various α,α -C₄P isomers (2–4) and nitrate ion [40], whereas, Park and coworkers have probed and evaluated anion- π interactions between dinitrophenyl based two-walled C₄P isomers (*cis*-/*trans*-4, Fig. 1) [41]. On the other hand, strong binding affinity of two walled triazole based C₄P isomers (*cis*-/*trans*-5) towards spherical halide ions—investigated by Kim et al., has supplied adequate evidence of CH-anion interactions in the anion recognition event (Fig. 1) [42]. Noticeably, in two-wall aryl-extended calix[4]pyrroles, the two aromatic panels in *cis*-isomers assists the anion binding through secondary anion- π /CH-anion interactions by sandwiching the anionic guests between the panels, while keeping the C₄P framework in cone



Scheme 1. Synthesis of phthalimide functionalized DPM (10) and two-walled phthalimide extended C₄P (11). Moreover, the structure of two-walled *trans*-isomer (12) along with one-walled phthalimide extended C₄P (13) is also displayed.

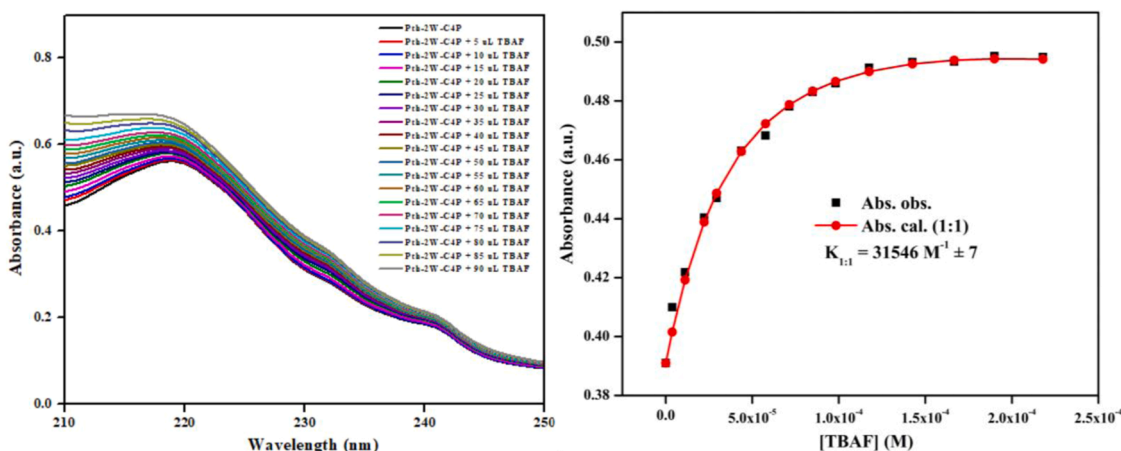


Fig. 2. UV–vis spectrum of receptor **11** (15 μM in CH_3CN) observed upon the incremental addition of TBAF (1500 μM in CH_3CN) (Left). Plot of absorbance vs concentration of TBAF added, fitted to 1:1 binding model of BindFit v0.5 at 227 nm (Right). The calculated binding constant (K_a) is the mean of the three independent experiments.

conformation, thereby offering higher binding affinity. Whereas in the case of *trans*-isomers only one aromatic panel originates the secondary interactions, resulting lower binding ability and usually C4P core exists in 1,3/1,2-alternate conformation [40]. Moreover, *trans*-isomers by virtue of their structural and conformational flexibility usually offer higher ordered self-assembled supramolecular functional constructs and have also proven useful in building supramolecular polymers and self-assemblies [42].

Taking all these observations in consideration, anion-binding affinities of the previously reported *meso*-phthalimide substituted two-walled C4P **11** has been investigated towards various spherical halides, trigonal/tetrahedral oxoanions, and linear anions by virtue of UV–vis spectrophotometric titrations, DFT/TD-DFT studies and NMR spectral data (Scheme 1) [43]. Literature reveal that phthalimide moiety is electron deficient in nature—rendering the synthetic receptors as π -acidic by dint of supramolecular non-covalent interactions [38, 44–47]. Therefore, it is anticipated that the incorporation of phthalimide subunit(s) at the *meso*-position(s) of the C4P-framework will serve as a superior anion binding agent than the simple C4P (**1**). This in turn will add new value to the anion– π /CH–anion interactions, if any—in the designing and fabrication of novel anion receptors of particular interest. Moreover, knowing the fact that phthalimide unit(s) in the synthetic receptors are capable of acting as molecular sensory probes (colorimetric/fluorescence/electrochemical) for various analytes [48–52], the

newly developed *meso*-phthalimide two-walled C4P (**11**), may prove an effective molecular sensor for specific analytes in future studies.

2. Results and discussion

2.1. Synthesis and characterization

The synthesis of two-walled phthalimide extended C4P-based anion receptor (**11**) is delineated in the Scheme 1. Briefly, the synthesis begins with already reported *N*-acetyl phthalimide (**9**) by means of nucleophilic substitution reaction between chloroacetone and potassium phthalimide [53]. The *N*-acetyl phthalimide (**9**) was later utilized for the construction of phthalimide functionalized dipyrromethane (DPM, **10**) upon treatment with freshly distilled pyrrole in the presence of trifluoroacetic acid (TFA), as reported in the literature [53]. Subsequently, the DPM (**10**) with an excess of acetone in the presence of TFA leads to the formation of the *cis*-two walled phthalimide extended C4P (**11**) in acceptable yield (14 %). Based on spectral evidences from NOESY and COSY spectra along with chemical shift values and higher anion binding constants, the authors concluded that compound **11** exists as *cis*-isomer. Surprisingly, the formation of *trans*-two walled phthalimide extended C4P (**12**) has not been observed. The C4P (**11**) was characterized through ^1H NMR, ^{13}C NMR, COSY, NOESY, and HRMS spectral data (see SI). The same synthetic scheme along with full

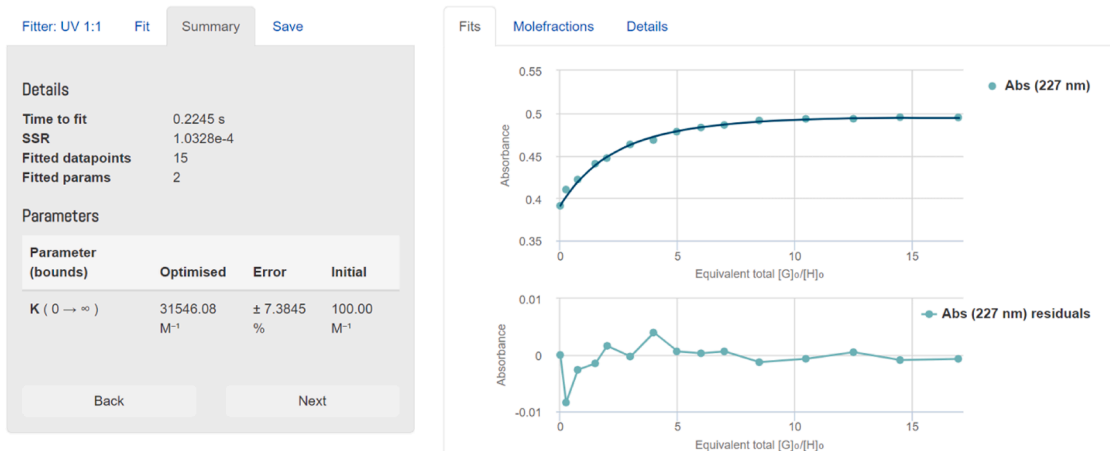


Fig. 3. UV–vis absorbance titration data (at 227 nm) of receptor **11** (15 μM) observed upon the addition of TBAF (1500 μM in CH_3CN) and fitted to 1:1 binding model of BindFit v0.5.

Table 1

Binding constants (K_a , M^{-1}) of anion receptors (**11** and **13**) with varied anions (used as TBA salts), determined through UV–vis titrations in CH_3CN at ambient temperature.

Anion added (as TBA salt)	11 (K_a , M^{-1})	13 (K_a , M^{-1})
F^-	$31,546 \pm 7$	$22,427 \pm 5$
Cl^-	$26,293 \pm 4$	$17,270 \pm 6$
Br^-	1958 ± 1	847 ± 2
I^-	223 ± 2	<10
CH_3COO^-	$20,706 \pm 4$	NA
NO_3^-	2521 ± 1	73 ± 2
HSO_4^-	ND	NA
$H_2PO_4^-$	ND	NA
SCN^-	4678 ± 2	NA

Table 2

TD-DFT calculated electronic transitions assignment, excitation energy (cm^{-1}) and oscillator strengths of species (C4P (**1**), C4P (**11**), C4P (**12**), **11@F⁻**, **11@NO₃⁻**, and **11@SCN⁻**).

Wavelength (λ in nm)	Excitation Energy (cm^{-1})	Oscillation Strength (f)	Transitions assignment	Percentage contribution
C4P (1)				
182	55,064.8	0.05	HOMO (α) $\rightarrow$ LUMO+17 (α)	12.4 %
185	54,110.3	0.04	HOMO -1 (α) $\rightarrow$ LUMO+13 (α)	20.3 %
193	51,877.7	0.32	HOMO -2 (α) $\rightarrow$ LUMO+7 (α)	18.8 %
199	50,198.4	0.16	HOMO -1 (α) $\rightarrow$ LUMO+7 (α)	16.3 %
211	47,333.8	0.14	HOMO -2 (α) $\rightarrow$ LUMO+2 (α)	12.3 %
228	43,794.3	0.02	HOMO (α) $\rightarrow$ LUMO+3 (α)	31.2 %
C4P (11)				
252	39,717.3	0.03	HOMO-11 (α) $\rightarrow$ LUMO (α)	33.4 %
265	37,707.1	0.03	HOMO-1 (α) $\rightarrow$ LUMO+1 (α)	26.9 %
333	30,079.5	0.01	HOMO (α) $\rightarrow$ LUMO+1 (α)	30.8 %
370	27,176.9	0.01	HOMO-2 (α) $\rightarrow$ LUMO+1 (α)	15.6 %
C4P (12)				
252	39,635.8	0.04	HOMO-11 (α) $\rightarrow$ LUMO (α)	33.7 %
269	37,135.2	0.03	HOMO-8 (α) $\rightarrow$ LUMO+1 (α)	32.4 %
11@F⁻				
290	34,463.1	0.02	HOMO (β) $\rightarrow$ LUMO+2 (β)	33.0 %
405	24,686.7	0.01	HOMO (β) $\rightarrow$ LUMO (β)	37.3 %
11@NO₃⁻				
286	34,795.1	0.01	HOMO-15 (β) $\rightarrow$ LUMO+1 (β)	10.2 %
388	25,781.8	0.01	HOMO (α) $\rightarrow$ LUMO (α)	40.4 %
11@SCN⁻				
291	34,210.5	0.02	HOMO (α) $\rightarrow$ LUMO+2 (α)	41.1 %
400	24,956.1	0.01	HOMO (α) $\rightarrow$ LUMO (α)	39.8 %

characterization of receptor **11** has already been reported in a separate paper, whereby the ion-transport studies of **11** has been compared with that of the two-walled *meso*-trifluorophenyl C4P system [43].

2.2. Experimental anion binding investigation

Anion binding studies of the two-walled phthalimide extended C4P (**11**) were probed through UV–vis spectroscopy in HPLC grade acetonitrile. After proper optimization, 5 μM solution of **11** in CH_3CN was chosen as the best concentration, depicting a λ_{max} at 219 nm. The 15 μM solution of C4P **11** in CH_3CN was titrated with different solutions of anions used as their tetrabutyl ammonium (TBA) salts. Upon the incremental addition of TBAF (1500 μM in CH_3CN) to 2 ml of **11** (15 μM in CH_3CN) taken in a cuvette, the absorbance continuously increases till a saturation point is reached along with a slight bathochromic shift in λ_{max} from 219 to 220 nm (Fig. 2). Both increase in absorbance and slight bathochromic shift not only signifies the binding of TBAF with **11** through four NH-hydrogen bonding interactions, but also offer clues of the participation of two phthalimide units in TBAF binding via weaker CH-anion interactions and anion- π interactions (Fig. 3). The presence of these three cooperative non-covalent interactions are held responsible for the strong binding of TBAF with **11**, as revealed through binding constant (K_a) value of $31,546 \pm 7 M^{-1}$ (Table 1 and Fig. 3), calculated after fitting the absorbance titration data at 227 nm to a 1:1 binding model of BindFit v0.5 software [54,55]. As expected, the binding ability of **11** with other TBA halide salts like TBACl, TBABr, and TBAI decreases with an increase in the size of halide ions from F^- to I^- (Table 2). After fitting the absorbance titration data of all the tested halides with **11** in different binding models (1:1, 1:2, and 2:1) of BindFit v0.5, 1:1, binding model was found to be most suitable one with minimum error for 1:1 stoichiometries (Fig. S7-S9 and Fig. S14-S16). As expected and shown in the Table 1, the newly constructed two-walled phthalimide extended C4P (**11**) offer superior anion binding affinity with halide ions as compare to the one-walled phthalimide extended C4P (**13**) and/or C4P (**1**) [9,56]. Thus, higher K_a values of receptor **11** compared to the parent C4P (**1**) as well as one-walled phthalimide C4P (**13**) offers strong evidence that **11** exists as *cis*-isomer, where both the phthalimide moieties are facing towards the same direction, thereby paving the way to bind various anions through cooperative effect of diverse non-covalent interactions, depicted in Fig. 3.

After successful binding assessment of **11** with different halides, and in order to extend the scope of **11** as an anion receptor, attention has been shifted towards the binding ability of **11** with trigonal oxoanions (CH_3COO^- and NO_3^-), tetrahedral oxoanions (HSO_4^- and $H_2PO_4^-$), and linear anion (SCN^-). It has been observed that all these anions bind with **11** in 1:1 binding stoichiometry, as minimum error was found in 1:1 binding model after fitting of absorbance titration data at different wavelengths in various binding models (1:1, 1:2, and 2:1) of BindFit v0.5 online software (Fig. S10-S13 and Fig. S17-S19). Noticeably, the anion receptor **11** offers appreciated anion binding affinity towards CH_3COO^- ($K_a = 20,035 \pm 4 M^{-1}$), HSO_4^- ($K_a = 6570 \pm 6 M^{-1}$). Moreover, substantial anion binding affinity were also observed with NO_3^- and SCN^- anions (Table 1). Thus, the two phthalimide units in receptor **11** not only assist in the modulation of anion binding affinity towards spherical halides, but also towards trigonal oxoanions and linear anions. It was anticipated that availability of additional cooperative anion binding forces (anion- π and CH-anion interactions) besides preliminary NH-hydrogen bonding contacts makes newly synthesized two-walled phthalimide extended C4P (**11**) as an efficient anion receptor in comparison to the pristine C4P (**1**) and one-walled phthalimide extended C4P (**13**). It is to be pointed out that in the presence of anionic species, the cone shaped C4P (**1**) binds only through NH-hydrogen bonding interactions (Fig. 4 & Table 1), hence comparatively lower stability constants were recorded [9]. While, in case of receptor **13** also, CH-anion interaction along with the primary NH-hydrogen bonding interactions has been observed without any practical evidence of anion- π interaction

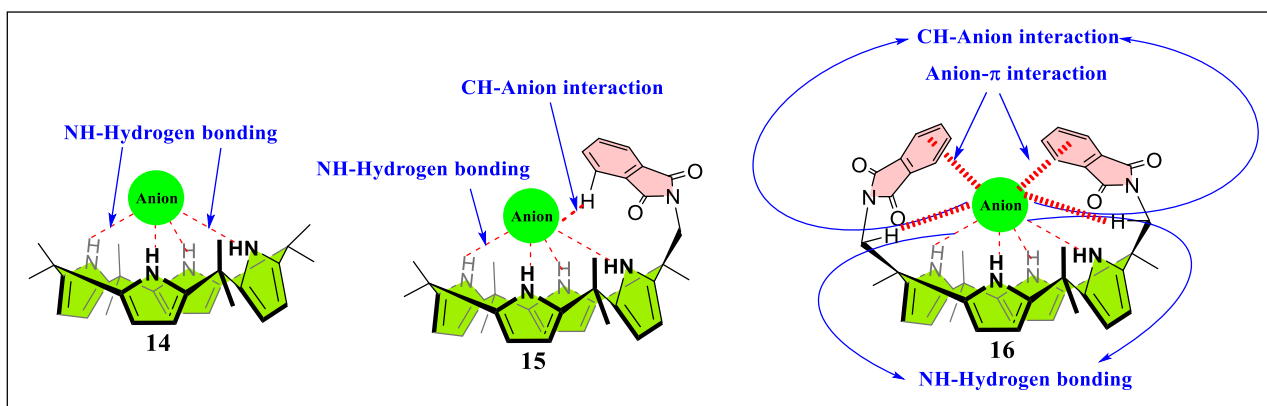


Fig. 4. Illustration of various cooperative non-covalent interactions in anion receptor complexes (14, 15 and 16).

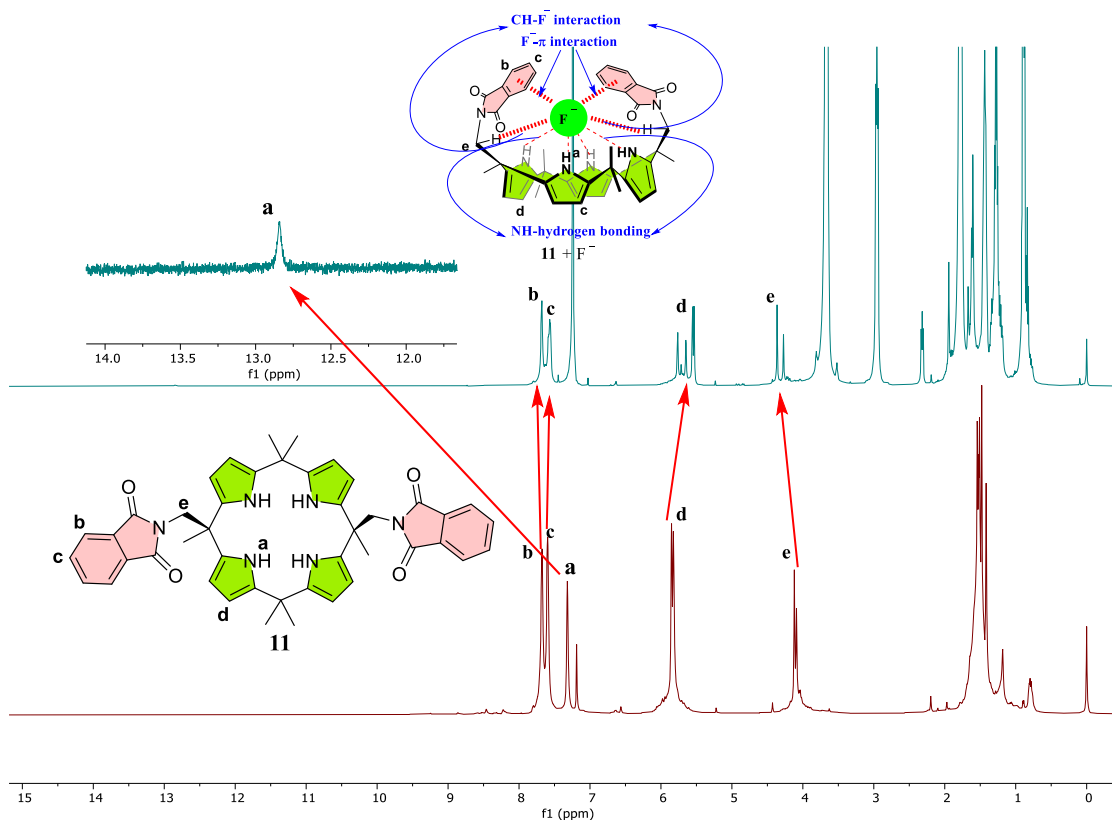


Fig. 5. ^1H NMR of **11** (bottom) and $[\mathbf{11}\text{-F}^-]$ (top) recorded in CDCl_3 at room temperature. TBA cation has been omitted for clarity.

(Fig. 4) [56].

2.3. ^1H NMR and ESI-MS investigation of fluoride and chloride ion binding

It is a well-known fact that whenever an anion (hydrogen bond acceptor) interacts with pyrrolic NH protons (hydrogen bond donors), these protons get deshielded in the ^1H NMR spectrum due to decrease in the electron density around them [40]. Similarly, if there is a presence of aliphatic methylene (CH_2) protons, they can interact with an anticipated anion via CH-anion interactions causing the downfield shift in ^1H NMR [17,40]. In contrast, when aromatic protons interact with the desired anion via anion- π interactions, the electron density around them increases, hence shielded is being observed in the ^1H NMR. Keeping these literature studies in consideration, ^1H NMR spectra of **11**@TBAF (1:1

equiv., Fig. 5) was recorded in CDCl_3 for the investigation of fluoride ion binding with receptor **11**. Interestingly, quite large downfield shifts ($\Delta\delta = 5.47$ ppm) of pyrrolic NH-protons (a) along with a substantial downfield shift ($\Delta\delta = 0.176$ and 0.126 ppm) of methylene ($-\text{CH}_2$) protons (e) upon F^- ion binding have been noticed. The downfield shifts of pyrrolic NH-protons (a) and $-\text{CH}_2$ protons (b) depicts that F^- ion binds with the receptor **11** by means of NH-hydrogen bonding and $\text{CH}\cdots\text{F}^-$ interactions. On the other hand, phenyl CH-protons (b and c) were found to be slight shielded ($\Delta\delta = 0.051$ and 0.085 ppm) upon F^- ion binding, which hints towards the existence of weaker F^- - π interactions. Moreover, pyrrolic CH-protons (d) have also been shifted upfield ($\Delta\delta = 0.342$ ppm) due to increase in electron density upon F^- binding. This in turn gives a clear indication of conversion of 1,3-alternate conformation of receptor **11** into the cone conformation upon binding with F^- ion.

As far as binding of receptor **11** with chloride ion (used as TMACl) is

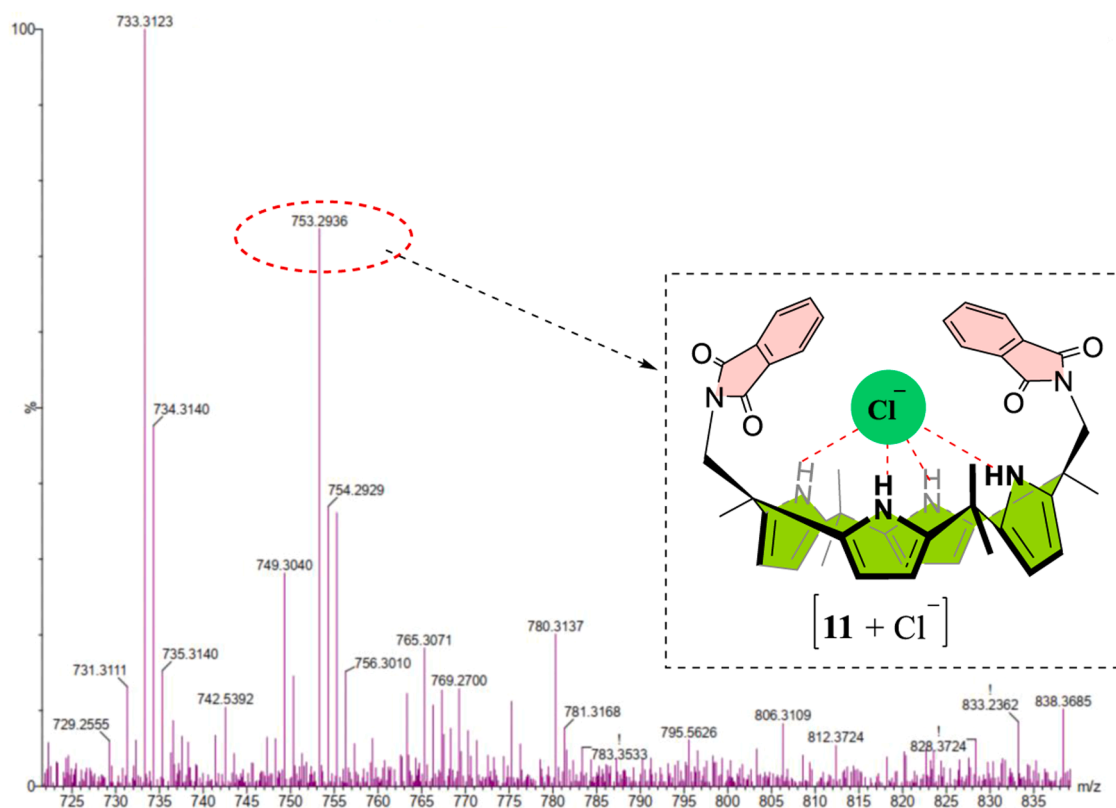


Fig. 6. ESI-MS spectrum of 1:1 mixture of receptor **11** and TMAcI recorded in CH_3CN . (m/z calculated for $[\mathbf{11} + \text{Cl}^-] = 753.2961$).

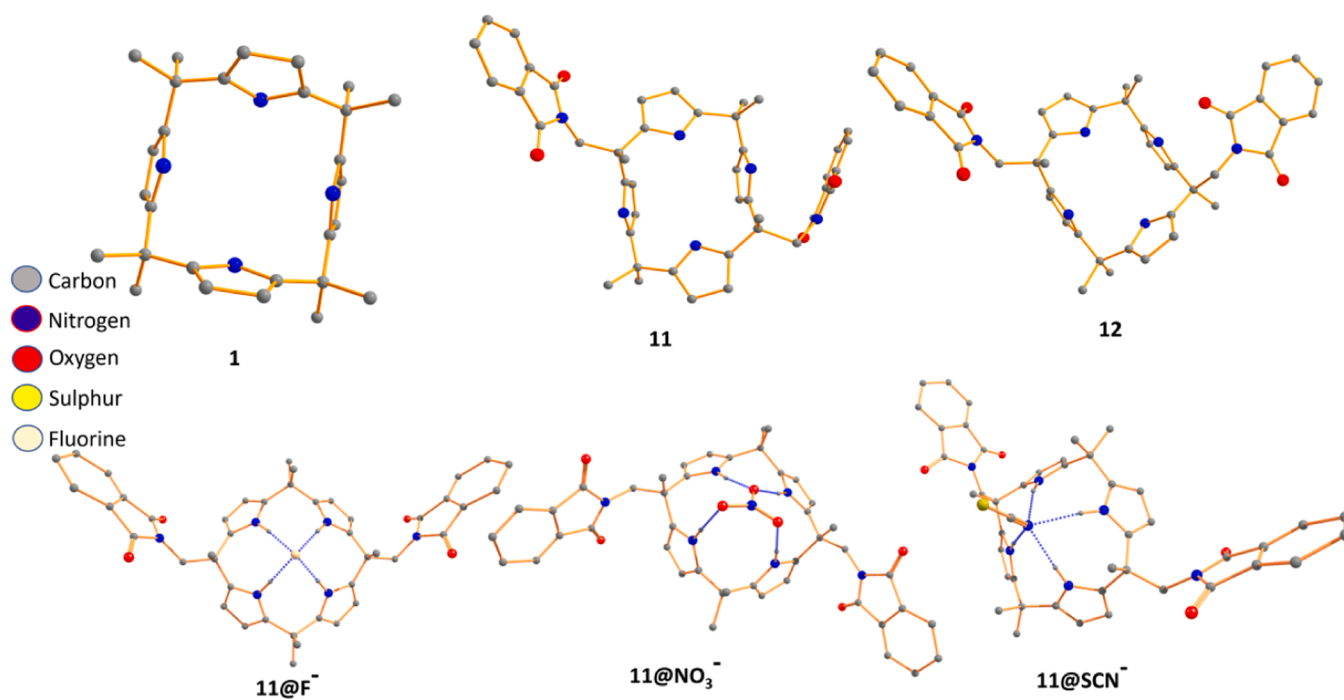


Fig. 7. M06-2X optimized structures of simple C4P (**1**), C4P (**11**), C4P (**12**), and anion receptor complexes (**11@F⁻**, **11@NO₃⁻**, and **11@SCN⁻**).

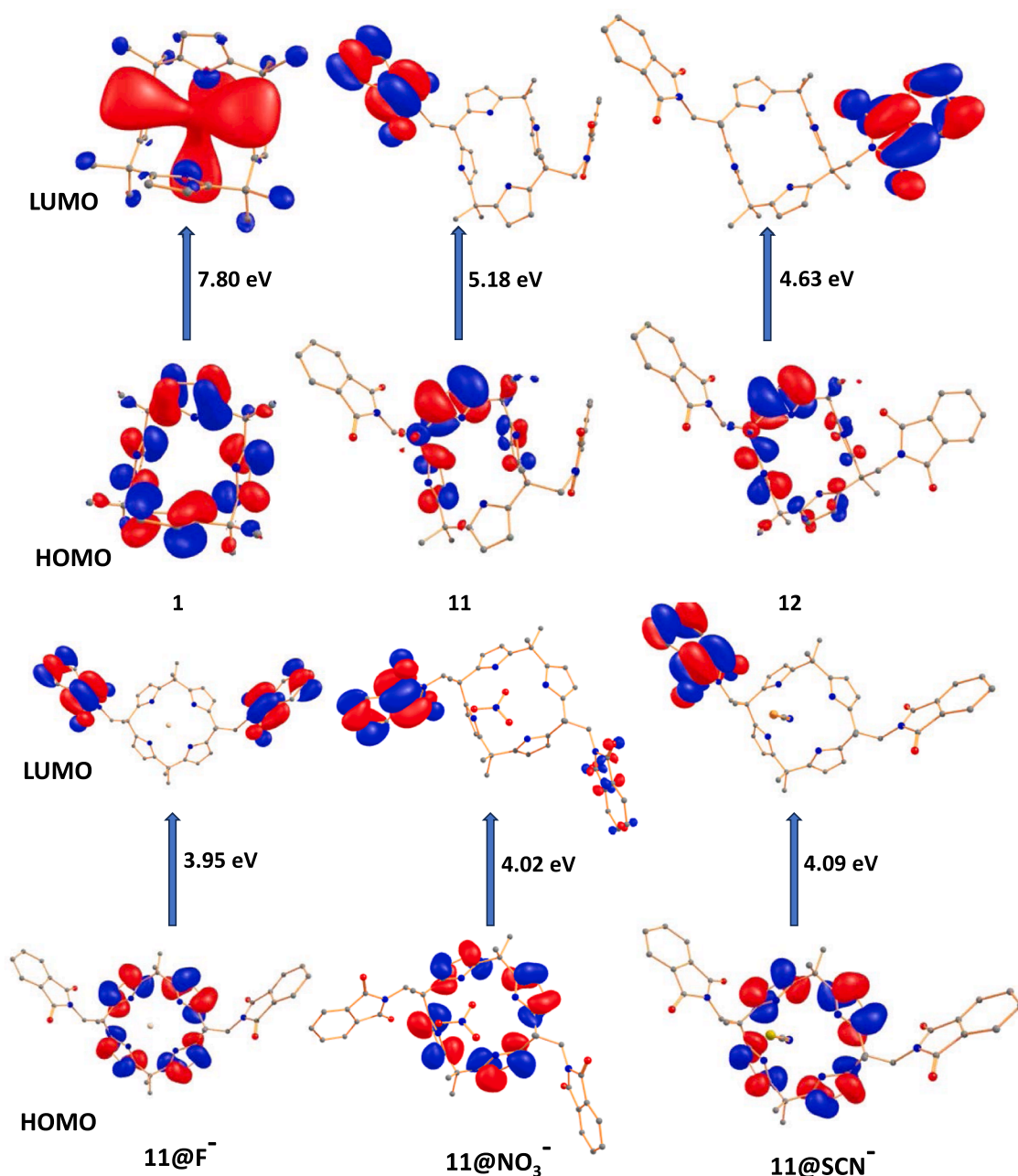


Fig. 8. Computed HOMO-LUMO gaps of simple C4P (1), C4P (11), C4P (12), and anion receptor complexes (11@F⁻, 11@NO₃⁻, and 11@SCN⁻).

concerned, ESI-MS investigation revealed a 1:1 binding geometry with a peak at $m/z = 753.2936$ tallies to [11+Cl⁻] complex (Fig. 6). Thus, it supports the 1:1 binding geometry observed between receptor 11 and diverse halide anions through UV-absorbance titration studies.

2.4. DFT and TD-DFT studies

DFT calculations have been carried out in acetonitrile solvent in order to gain further insight into the electronic structure and reactivity of simple C4P (1), C4P (11), C4P (12), and anion receptor complexes (11@F⁻, 11@NO₃⁻, and 11@SCN⁻). At first, *cis*- and *trans*-isomers of 11@NO₃ have been optimized and the computed results reveal that *cis*-isomer is more stable than its corresponding *trans*-isomer by 5.76 kJ/mol. Similarly, *cis*-isomers of other two species i.e., 11@F⁻ and 11@SCN⁻ have also been optimized. The optimized structures of all the species are shown in Fig. 7. The computed electronic structures show that the both simple C4P (1) and two-walled phthalimide extended C4Ps (11 and 12)

acts as anion receptors. The optimized structures clearly show the non-covalent interactions between the anionic guest and host (see 11@F⁻, 11@NO₃⁻, and 11@SCN⁻ of Fig. 7). The interactions shown by the anion and the hydrogen atoms of the pyrrole ring of receptor are shown in the Fig. 7. In this figure, the phthalimide moiety becomes far away from the anion in the optimized structure may be due to the steric hindrance. Moreover, the frontier molecular orbital (FMO) of all the above mentioned C4P receptors and anion-receptor complexes have also been analyzed. The FMO analysis provides the data on chemical reactivity of the species [57–59]. FMOs are the related energies of E_{LUMO} and E_{HOMO} of the compounds. A HOMO reflects the ability to donate electrons, whereas a LUMO reflects the ability to accept electrons. The computed E_{LUMO} values of C4P (1), C4P (11), C4P (12), 11@F⁻, 11@NO₃⁻, and 11@SCN⁻ are found to be 1.35, -1.45, -1.63, 0.54, 0.54 and 0.44 eV, respectively, whereas the E_{HOMO} values of these species are -6.56, -6.62, -6.29, -3.41, -3.46 and -3.68 eV, respectively. The chemical stability of a molecule can be described by ΔE_{gap} [60]. The computed ΔE_{gap} values of

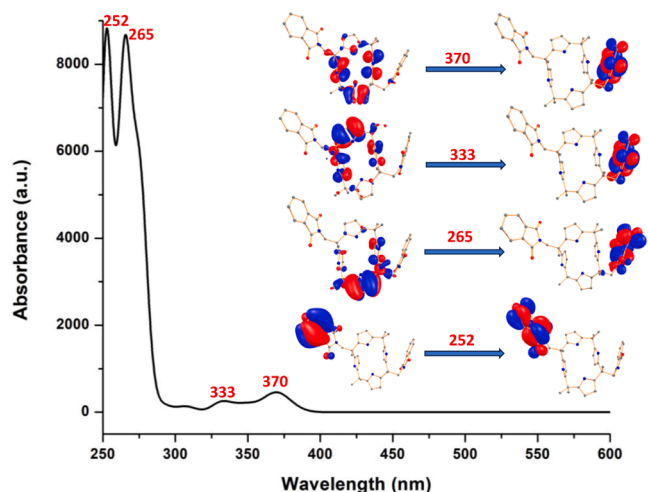


Fig. 9. M06-2X TD-DFT simulated electronic absorption spectra of C4P (11) along with its corresponding orbitals involved in electronic transitions.

these C4P (1), C4P (11), C4P (12), 11@F⁻, 11@NO₃⁻, and 11@SCN⁻ are found to be 7.80, 5.18, 4.63, 3.95, 4.02 and 4.09 eV, respectively. The structural reactivity of any receptor is demonstrated by a low ΔE_{gap} [61]. Molecular softness is also indicated by a small ΔE_{gap} , which in turn reflects that the molecule is highly polarizable with a low kinetic stability and high chemical reactivity. The HOMO and LUMO maps incorporated into the structures of aforesaid species are depicted in Fig. 8. The distribution of molecular orbital wave functions in the negative and positive phases is shown in green and red, respectively. The C4P (1) has the highest energy gap while the anion receptor complex (11@F⁻) has the lowest energy gap which demonstrate the high reactivity of 11@F⁻ and high stability of C4P (1).

To support the experimental anion binding studies (in acetonitrile as a solvent), we also estimate the Gibbs free energies of binding (ΔG_{bind}) for selected anions (e.g., F⁻, NO₃⁻ and SCN⁻) with the two-walled phthalimide extended calix[4]pyrrole receptor 11. The computed ΔG_{bind} values were -203.2, -46.1 and -20.0 kJmol⁻¹ for 11@F⁻, 11@NO₃⁻ and 11@SCN⁻, respectively. These values clearly support the formation of two-walled phthalimide with the selected anions.

To further explore the electronic structure and active sites of C4P (1), C4P (11), C4P (12), 11@F⁻, 11@NO₃⁻, and 11@SCN⁻, the TD-DFT calculations have also been performed in acetonitrile solvent [62–66]. Here, the TD-DFT calculation of aforesaid species have been employed to investigate the absorption properties and computed the vertical TD-DFT transition energies of the 150 lowest excited states. The computed absorption peaks, significant oscillator strengths (*f*), and their characters are listed in Table 2. The computed absorption peaks of these species are in good agreement with the reported experimental UV-visible of similar architectures [67–72]. Absorption spectrum of C4P (1) exhibits six peaks at 182, 185, 193, 199, 211 and 228 nm (Fig. S20). The first four computed absorption peaks of C4P (1) at 182, 185, 193 and 199 nm correspond to HOMO (α) to LUMO+17 (α), HOMO-1 (α) to LUMO+13 (α), HOMO-2 (α) to LUMO+7 (α) and HOMO-1 (α) to LUMO+7 (α), respectively (Fig. S20 and Table 2). The peak at 193 nm with the significant oscillator strength of 0.03 shows the contribution of 18.8 % from HOMO-2 (α) to LUMO+7 (α). The next two peaks at 211 and 228 nm shows 12.3 % and 31.2 % contributions from HOMO-2 (α) to LUMO+2 (α) and HOMO (α) to LUMO+3 (α), respectively. All of these peaks show intra-ligand charge transfer.

The computed TD-DFT absorption spectrum of C4P (11) shows four peaks at 252 (experimental peak at 245 nm), 265 (experimental peak at 273 nm), 333 and 370 nm (Fig. 9). The first three peaks having contribution of 33.4 %, 26.9 % and 30.8 % from HOMO-11 (α) to LUMO (α), HOMO-1 (α) to LUMO+1 (α) and HOMO (α) to LUMO+1 (α),

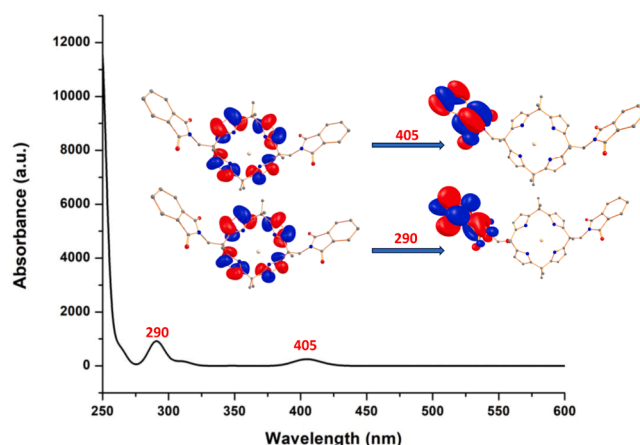


Fig. 10. M06-2X TD-DFT simulated electronic absorption spectra of anion receptor complex (11@F⁻) along with its corresponding orbitals involved in electronic transitions.

respectively (Fig. 9 and Table 2). The peak at 370 nm with the oscillator strength of 0.01 shows the contribution of 15.6 % correspond to HOMO-2 (α) to LUMO+1 (α). Similarly, the absorption spectra for the species C4P (12) are computed and found peaks in the range of 250–270 nm which are generally corresponds to the intra-ligand charge transfer transitions. The C4P (12) exhibits two peaks at 252 and 269 nm (Fig. S21 and Table 2). The peak at 252 nm having contribution of 33.7 % shows transition from HOMO-11 (α) to LUMO (α) transition. The next peak at 269 nm which corresponds to the HOMO-8 (α) to LUMO+1 (α), show intra-ligand charge transfer. The anion receptor complex (11@F⁻) also displays intra-ligand charge transfer at the peaks 290 and 405 nm (Fig. 10) which correspond to HOMO (β) to LUMO+2 (β) and HOMO (β) to LUMO (β) transitions, respectively (Fig. 10 and Table 2). At 290 nm, it shows 33.0 % contribution with a significant oscillator strength of 0.02.

Two separate spectral peaks for the anion receptor complex (11@NO₃⁻) can be seen at wavelengths of 286 and 388 nm, respectively (Fig. S22 and Table 2). These peaks have significant oscillator strength of 0.02 and 0.01 having a 10.2 % and 40.4 % contribution from HOMO-15 (α) to LUMO+1 (α) and HOMO (α) to LUMO (α) transition anticipates intra-ligand charge transfer. The anion receptor complex (11@SCN⁻) also shows two peaks at 291 and 400 nm (Fig. S23 and Table 2). The two peaks at 291 and 400 nm with significant oscillator strength of 0.02 and 0.01 which involves 41.1 % contribution of HOMO (α) to LUMO+2 (α) and 39.8 % contribution of HOMO (α) to LUMO (α) shows intra-ligand charge transfer. The TD-DFT studies of these molecules plays an essential role in advancing the understanding of such type of molecules, especially their excited-state properties, optical spectra, and charge-transfer dynamics. The insights provided by TD-DFT enable the rational design of new C4P-based complexes with optimized properties for these diverse applications.

3. Conclusions

In summary, two-walled phthalimide extended C4P (11) has been probed as an anion receptor with the aid of experimental (e.g., UV-vis spectroscopy, ¹H NMR and mass spectrometry) as well as computational studies (DFT/TD-DFT calculations). The computed electronic structures indicate that the C4Ps (1, 11 and 12) acts as worthy anion receptors. The computed HOMO-LUMO gap shows that the anion receptor complex (11@F⁻) is more reactive as compared to the other species. On the basis of the results obtained from the TD-DFT calculations, it is found that all the anion receptor complexes are stabilized by intra-ligand charge transfer. The 1:1 binding stoichiometry observed through UV-spectroscopy was further supported by ESI-MS studies. Anion binding affinity of two-walled phthalimide extended C4P (11) towards diverse

anions were found to be considerably higher in comparison to one-walled phthalimide extended C4P (**13**), owing to complementary anion- π and CH-anion interactions assisting preliminary NH-hydrogen bonding interactions of C4P framework. Notably, due to small size and acting as best hydrogen bond acceptor, F⁻ ion displayed highest binding affinity with receptor **11**. From the authors perspective, these preliminary anion binding studies of anion receptor (**11**) through cooperative effect of NH-hydrogen bonding, anion- π , and CH-anion interactions will strengthen anion-receptor chemistry, and may prove fruitful to evaluate the role of receptor (**11**) in transmembrane anion transport. On the other hand, C4P receptors (**11** and **13**) are also expected to unveil therapeutic potential, as phthalimide derivatives have high medicinal value and simple/functionalized C4Ps have also proven effective against various tumours of breasts, ovary, brain, and prostate.

Acknowledgements

The authors are obliged for the financial support from DST-SERB, New-Delhi (Project File no. ECR/2017/000821) and are also grateful to Jamia Millia Islamia for providing the wonderful infrastructure. I. A. R. thanks CSIR, New-Delhi for the SRF fellowship.

CRediT authorship contribution statement

Ishfaq Ahmad Rather: Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation. **Mukhtar Ahmed:** Writing – review & editing, Visualization, Validation, Software, Formal analysis, Data curation. **Azaj Ansari:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation. **Rashid Ali:** Writing – review & editing, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare no competing interests.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2025.144990](https://doi.org/10.1016/j.molstruc.2025.144990).

Data availability

No data was used for the research described in the article.

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