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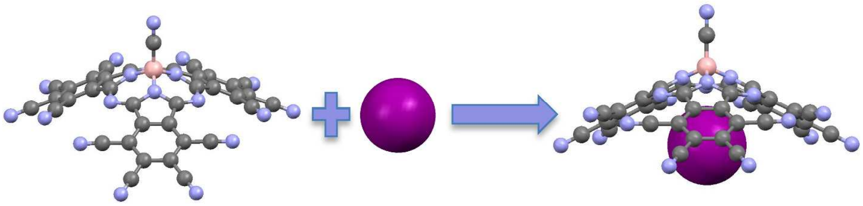

Subphthalocyanines are used as the framework to built chromogenic grippers for anion capture, even in solvents like water.

Theoretical Design of Molecular Grippers for Anion Recognition Based in Subporphyrazines and Subthalocyanines.

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Abstract

Subphthalocyanines (SubPcs) are 14 π-electron aromatic macrocycles containing three 1,3-diiminoisoindol units N-fused around a central boron atom. Their particular concave π-extended structure sets them potentially useful in fields related to optoelectronics and molecular electronics. Also, their structure sets them as potential receptors of complementary convex-shaped molecules. Inspired by the Subphthalocyanine properties and previous works about the possibility of obtaining neutral receptors composed of aromatic rings that can bind anions, we have performed a theoretical study to analyze the ability of subphthalocyanines and some SubPcs analogues to catch anions by non-covalent interactions. This may be relevant, since it can produce a kind of chromogenic reagents for anion detection that are not destroyed on the detection process, since the non-covalent interactions are weak enough to reverse the procedure. We characterized complexes formed between several SubPc derivatives and different anions, and have also studied the influence of this process on the optical properties of these molecules. The stabilization trend reflected by the energetic results and the changes shown in the absorption wavelengths of the host molecule under complexation confirm our hypothesis about the possibility of this kind of molecules being used as chromogenic reagents for anion capture, even in solvents with a large dielectric constant like water.

Introduction

Molecular recognition is an essential part in the different processes to build supramolecular systems acting as nanodevices in areas like materials science or biochemistry.[1-5] Hence, it is very important to design molecular receptors that possess selective interactions with the different components making part of these devices. This selective bonding depends essentially on noncovalent intermolecular interactions like hydrogen bonds, aryl-aryl interactions, ionic interactions, etc.[2,6] Therefore, in order to build a specific receptor its topology and electronic characteristics should be controlled to fit to some particular requirements.[7]

Since anion receptors are very important for different chemical and biological applications,[8-10] the possibility of stabilizing interactions between anions and electron-deficient aromatic systems in the so-called anion-π interaction has aroused interest.[8,11,12] Moreover, the design of neutral receptors that are capable of binding anions is of particular importance, because it avoids the presence of counter-ions complexes and improves selectivity, owing to the relevance of directional interactions.[13] Several studies[11,13-21] describe the interactions of electron deficient π-systems with different anions. The most important attractive contributions to the total interaction energies are from the electrostatic and induction terms; however, unlike the case of cation-π complexes the dispersion energies have a non-negligible contribution.[13]

The Klämer´s molecular tweezers are among the different receptors designed in the last few years.[22,23] These molecules are characterized by a concave-convex topology and a negative molecular electrostatic potential in the concave region. Recently, using theoretical models, we have shown the feasibility of this family of molecular tweezers to bind anions, [24,25] provided that the aromatic rings have enough fluorine or cyanide substitution. Another family of molecules with a concave-convex typology that has aroused interest in the last few years is the so-called buckybowls. These molecular bowls are aromatic systems formed by joining six- and five-carbon rings in a similar way as in fullerenes, the five-carbon rings introducing curvature on the delocalized system.[26,27] They exhibit differences in the electrostatic potential depending on whether the concave or convex face is considered.[28] In a recent study, Cabaleiro-Lago et al.[29] have shown that buckybowls constructed from corannulene by substituting several hydrogen atoms by electron-withdrawing groups produce an inversion of the molecular electrostatic potential, allowing a stabilizing interaction with anions. By following the same rationale we have used Subphthalocyanines (SubPcs) as molecular bowls into the design of molecular grippers.

Subphthalocyanines (SubPcs) are 14 π-electron aromatic macrocycles containing three 1,3-diiminoisoindol units N-fused around a central boron atom. Their particular concave π-extended structure sets them potentially useful in fields related to optoelectronics[30] and molecular electronics[31] due to the unique optical and electrochemical properties arising from its 14 π-electron conjugated system. [32-34] Also, their concave structure sets them as potential receptors of complementary convex-shaped molecules, such as fullerenes[35], widely used in the field of molecular materials. Moreover, its structure made them especially interesting for the construction of supramolecular architectures.[36,37] In their work, Ros-Lis et al.[38] have used subphthalocyanines as chromogenic sensing molecules for the detection of several anions. This application is based in a selective reaction of these anions with the subphthalocyanine that produces observable color modulations in the system. This process is relevant since there are not many chromogenic reagents for anion detection and even less are effective in water or water-organic solvent mixtures. We have found in the literature theoretical studies about the stability of different subphthalocyanines with several central atoms,[39] also studies analyzing the spectroscopic properties[40] of SubPcs but, to the best of our knowledge, there is not any experimental or theoretical study analyzing the ability of subphthalocyanines to catch anions by noncovalent interactions. This may be a relevant issue, since it can produce a kind of chromogenic reagents for anion detection that can be used in water or water mixtures and that are not destroyed on the detection process, since the noncovalent interactions are weak enough to reverse the procedure.

In the current work it is presented a computational study of complexes formed by several anions and substituted SubPcs or SubPc analogues. The original SubPc backbone has been subjected to structural modifications in order to obtain subporphyrazines (SubPzs) and annulated SubPcs. We termed these last structures "molecular grippers" which have three arms to distinguish them from molecular tweezers and clips, which only have two arms. For all analyzed molecules electron-withdrawing fluorine or cyanide groups substitute several hydrogen atoms in order to increase a stabilizing interaction with anions. The bromide anion was employed extensively in this work as the main test anion, but chloride, iodide and tetrafluoroborate were also used. Chloride being the smaller anion was used to check the effect of shorter distances between the anion and the molecular gripper where presumably the electrostatic component of the interaction would have a large importance. Iodide and BF_4^- were used to estimate the effect of larger anions on the dispersive component of the interaction. By studying these systems, information can be obtained regarding the characteristics of the anion interaction with this kind of molecules. By comparing the different molecules it will be possible to assess the effect produced by changing the structure of the SubPc and adding up new arms to the original SubPc backbone. Also, insight can be gained about the influence of complexation on the optical properties of these molecules by performing an analysis of the spectroscopic properties.

In their different papers, Ros-Lis et al.[38] and Xu et al[41] show that subthalocyanines may change color because they react with anions. So, the question rises if the same will happen to the systems in this work and therefore the host-guest complex will not appear. Regarding to the work of Xu et al., the reaction is an axial substitution of a 4-hydroxybenzaldehyde moiety for a fluorine group, this kind of reaction is unlikely in our systems since the axial position is occupied by strongly nucleophilic groups. With respect to the results of Ros-Lis et al., the authors do not specify what kind of reaction produces the change of color but they claim that the change is due to a strong modification on the 14 π-electron conjugated system. We cannot say for certain that this will not happen in our systems, however we think that some considerations are worth to be done. First, the reaction only occurs with some anions and it does not happen when anions as Cl^-, Br^- and I^- are used; and second, the effect of water as solvent prevents the reaction with most anions in such a way that it occurs only with cyanide. Taking this into account it can be said that, even if in some situations the subthalocyanines will react with some anions there will be many cases where the reaction will not occur and so the possibility of a host-guess complex will be present. Also, the reactivity of the subthalocyanines can change due to the modifications performed to obtain their derivatives. Finally, we should say that the anions employed in this work are used as a model to describe and predict the characteristics and the size of the intermolecular interactions between this kind of molecules and anions. We think that the insight obtained from studying these systems can be useful to extrapolate the characteristics of the interaction between subthalocyanine derivatives and bigger anions, like for example large organic carbanions.

Computational details

In this work complexes between different SubPcs or SubPc analogues, shown in Figure 1, and anions were computationally studied by using density functional theory (DFT). Calculations were performed starting from structures where the anion is located within the concave cavity of the molecules. These initial structures were fully optimized employing the BLYP functional corrected by an empirical dispersion term as designed by Grimme (BLYP-D2).[42] This method was chosen since, according to the literature,[29,43] it gives a good estimation of the intermolecular and dispersion interactions in curved systems together with anions. Atoms in neutral molecules were described by the cc-pVTZ basis set, atoms in Cl^-, Br^- and BF_4^- anions by the aug-cc-pVTZ basis set, and the iodine atom by the def2-TZVPP[44] basis set for the valence electrons and the Stuttgart-Dresden[45,46] effective core potential for the core electrons. The resolution of identity (RI) approach was used in order to save computational cost; the def2-TZVPP[44] was used for all atoms as auxiliary basis set. The BSSE corrected interaction energy of the optimized geometries was obtained together with the deformation energy. The binding energy is the result of adding up these two terms.

We have not performed frequency calculations to check the minimum nature of the stationary points. Based in our experience with analogous systems[24,25] and the results of Cabaleiro et al.,[29] stationary points where the anion in placed in the center of the cavity are mostly minima. Also, we think that the electron withdrawing nature of the substituents prevent the existence of minima where the anion is placed in the edges or in the convex side of the gripper. Therefore, any possible minima will be inside the gripper cavity and the energy differences with the obtained stationary points will not be large enough to change substantially the obtained results.

Single point calculations have been carried out in the optimized gas phase geometries using the COSMO model.[47] The result of these calculations together with the BSSE and the deformation energies in gas phase has been used to estimate the binding energy with water as solvent.

Time dependent DFT calculations have been done to analyze the modifications of the absorption spectrum of some of the studied molecules when complexation occurs. To perform these calculations Martin's[48] B2GP-PLYP perturbatively corrected double hybrid functional with RI approach has been used together with the Ahlrichs-VDZ basis set[49] and the auxiliary basis set for correlation fitting.[50]

To shed more light on the nature of the binding energy between the anions and the molecular grippers, we used the symmetry-adapted perturbation theory combined with density functional theory, DFT-SAPT,[51] to obtain a physical interpretation of the interaction energy of some complexes. In this method the interaction energy is expressed as a sum of perturbative corrections, each of these corrections results from a different physical effect. The several intermolecular terms obtained from this method can be summarized in electrostatic, exchange-repulsion, induction and dispersion contributions.[6] This method was used employing the BLYP functional together with the aug-cc-pVDZ basis set and density fitting to save computation time. Grüning asymptotic correction was applied,[52] ionization potentials being obtained at the BLYP/aug-cc-pVDZ level.

All calculations but DFT-SAPT were performed with the Orca[50] set of programs. DFT-SAPT calculations were done with Molpro2009.1.[53]

Results and discussion

As we said before, in this study we have been working with the molecules shown in Figure 1. From now on we are going to name each molecule by using a notation obtained from this Figure. Thus, we will name a molecule with a character string with the following structure "Roman Number-Y-X-Z(-W)". The name will start with the roman number assigned to the structure of the molecule in Figure 1, then it will follow "-Cl or –CN" depending on Y equal to -Cl or Y equal to -CN, then it will be -B or -P depending on the X value, next it will be –F or –CN according to the Z value, finally –O or –S may be written if W has some value.

There are two types of arms in the annulated SubPcs, one is the same as the Klämer´s tweezers[23] and in the other the –CH-O-CH- moiety is substituted by two ether or two tioether groups. Also, the studied systems include molecules where a phosphorous atom substitutes the boron atom of the SubPcs backbone. This kind of systems where a phosphorous atom stands as central atom of a SubPcs backbone has not been obtained experimentally. However, there are in the literature similar frameworks with phosphorous as central atom,[54,55] taking this into account we have considered this kind of systems to analyze the influence of a bigger central atom in the interactions.

Some examples of the obtained complexes with the proposed structures are presented in Figure 2. As can be seen, in all examples the anion stays more or less in the center of the cavity of the host molecule and does not show any preference to locate itself close to only a single arm of the molecule. The same happens with all studied complexes. Several geometric parameters together with the cartesian coordinates for all obtained structures are provided in the supplementary information of this paper. In general, the geometrical changes in the gripper structure are small for all studied complexes and there are not big differences when the anion changes. For most cases the change is lower than 10 % of the parameter value. However there are some exceptions, the most noticeable is the changes in the **IV-CN-B-CN-S···Br$^-$** complex, where the radius of the circumference created by the carbons at the tip of the pincers (see supplementary information) decreases from 4.920 Å to 4.087 Å.

Table 1 shows the binding and deformation energies of structure **I** in gas phase. It can be seen that all complexes have large or very large binding energies and rather small deformation energies. A perusal of the energies gathered in Table 1 allow us to see that, independently of the considered system, the energy difference is from 2 to 3 kcal/mol whether a chlorine atom or a cyanide group is bonded to the central atom. On the other hand, the stability of the complexes increases between 3 and 4 kcal/mol when the central atom changes from phosphorous to boron. Also, systems with fluorine as substituent are about 23 kcal/mol less stable than complexes substituted with the cyanide group. As it has already been shown in a previous work,[25] the lower stability in gas phase of systems with fluorine is a consequence of the dominant inductive effects of these groups, which are smaller than the dominant resonance effects of cyanide groups. The energies collected in Table 1 also show that as the size of the anion increases the binding energy in gas phase decreases. Most likely it is a consequence of the enlargement of the distances between the anion and the backbone of the molecular receptor, which have influence in the attractive interactions.

A deeper description of the characteristics of the interaction of the studied systems can be obtained by means of DFT-SAPT[51] calculations, which provide a partition of the interaction energy in several contributions. The results of these calculations are shown in Figures 3 and 4 for complexes of structure **I** with different anions. It should be noted that E_{sapt} is not equal to the interaction energy obtained by the supermolecule method since the last one contains high order terms not included in the

DFT-SAPT method. From Figure 3 it can be seen that when halides are considered the importance of the electrostatic and induction terms decreases when the anion size increases. A good representation of the induction term comes from classical expressions depending on localized properties[56] (polarizabilities). Bearing this in mind we can infer that when the anion gets bigger the increase in size of the electronic cloud (and of the polarizabilities) is not enough to compensate the effect of the distances enlargement. Unlike the previous terms, the repulsion and dispersion contributions increase with the anion size. These two terms strongly depend on the size of the electronic clouds; the repulsion term is determined by the overlap between the electronic clouds and the dispersion term by the quantum-mechanical fluctuations of the electron density. Even though the intermolecular distances get larger with the size of the anion, the electronic overlap and the deformation capacity of the electron densities also increase. They not only compensate the effects of the larger intermolecular distances but also increase the magnitude of the repulsion and dispersion terms. Since the electrostatic energy decreases and the repulsion contribution increases, the total energy decreases with the size of the anion. Also, the nature of the interaction changes, going from an electrostatic nature with small anions to a more dispersive kind of complexes with the largest anions. The DFT-SAPT partition of the interaction between **I-CN-B-CN** and BF_4^- has also been obtained. In this complex the weight of the dispersion contribution is the largest of all studied systems. This result, together with the size of the dispersion term for the iodine complex, points out the importance of this contribution on anion-π systems when medium size or large anions are considered.

The partition displayed in Figure 4 shows that when the cyanide group is used as substituent the complexes are more electrostatic than when the host molecule is substituted with fluorine atoms. It also shows that when the substituents are fluorine atoms the weight of the dispersion contribution increases. As it has been said, complexes where fluorine is used as substituent are less stable than those substituted with cyano groups. It is because all energy contributions get smaller but also because there is a larger reduction in the electrostatic contribution than in the repulsive term, which increases the weight of the repulsive interactions. It does not seem to be much difference in the nature of the interaction between complexes with boron or with phosphorous as central atom of the host molecule. It should be mentioned that the repulsion term is much larger with phosphorous, most likely because the size of the electronic cloud is bigger and so the overlap with the anion.

Binding energies of structure **I** with different anions in water are collected in Table 2. In order to obtain the binding energies it has been assumed that the BSSE and the deformation energies in gas phase and in water are the same. We do not think that this approximation will change the observations that can be extracted from the results, since by far the largest variation between gas phase and water solution is reflected in the interaction energies. As can be seen the most noticeable change is the drastic reduction of the binding energies in all studied complexes. It agrees with previous results found in the literature.[25,29] Also, the gas phase energy differences due to the composition of molecule **I** get much smaller in water solution. Thus, the energy difference is lower than 1 kcal/mol whether a chlorine atom or a cyanide group is bonded to the central atom. The same happens if the central atom of the backbone changes. The large differences in gas phase due to the change of the substituents decrease to less than 4.5 kcal/mol in water solution (around 2.5 kcal/mol in molecules with boron as central atom and around 4.2 kcal/mol when the central atom is phosphorous). The behavior of the binding energy in water solution when the anion varies is the opposite of gas phase results. In water the stability of the complexes increases with the size of the anion, contrary to what happens in the gas phase. All binding energies are negative, which means that according to our results all complexes are stable in water solution. However, some of the energies are small and very likely entropic effects will turn these energies positive, so the complexes will not be stable in water solution. Despite of that, several of the binding energies are not so small (some complexes with bromide, complexes with iodine and above all complexes with BF_4^-) and the value of these energies is big enough to think that after including entropic effects the free energies would still be negative. Consequently, some of the studied complexes may be stable in water solution. If a comparison is performed between our results in water solution and the energies obtained by Cabaleiro-Lago et al.[29] for complexes of corannulene, it can be seen that the aggregates studied in this work are most stable (for example the binding energy of **I-CN-P-CN** with BF_4^- is almost twice as big as the binding energy of BF_4^- with corannulene substituted with five cyanide groups and it is still 1.6 kcal/mol larger than the binding energy of the complex formed by corannulene with ten cyanide substituents). The adequacy of a compound for anion recognition is defined by several criteria, like the stability of the compound in solution, its solubility, the stability of the complexes with anions, etc. However, regarding the stability of the complexes, our calculations indicate that SubPcs and SubPzs are a better choice than corannulenes to be used as backbone of a molecular device to catch anions.

Bearing in mind the results from the DFT-SAPT method illustrated in Figures 3 and 4, a perusal of the binding energies in water gives some insight about the characteristics and behavior of complexes in solution. From the binding energies in gas phase and from DFT-SAPT results it can be said that a larger contribution of the electrostatic term produces a more stable complex. However, the opposite occurs in solvated complexes. Anions that have large electrostatic terms in gas phase will also have a strong electrostatic interaction with water. This will increase the desolvation cost and so the destabilizing effect of the solvent will be larger. Complexes where the electrostatic contribution is not so strong and where the dispersion term increases its importance will not suffer such big penalty when they are solvated, not only because anion interactions have not such large electrostatic term with water but also because the dispersive term with the solvent is not as important as with the host molecule. In keeping with this explanation, complexes where the substituents are fluorine instead of cyanide groups undergo a lower destabilizing effect when solvated. DFT-SAPT results have shown that the relative contribution of the dispersion term is larger in complexes where the host molecule is substituted with fluorine atoms than in complexes where the host molecule was substituted with cyanide groups, and that the opposite happens regarding to the electrostatic term. It should be noted that even though the destabilizing effect of solvation is lower for complexes with fluorine as substituent, the difference between these effects is not big enough to compensate the energy difference in gas phase and so complexes substituted with fluorine are less stable than complexes substituted with cyanide groups.

Figure 5 shows the UV-VIS spectra of the isolated **I-CN-B-CN** molecule and of complexes of **I-CN-B-CN** with some anions (coefficients of the transitions for all obtained spectra are given in the supplementary information). All spectra have two bands, one in the ultraviolet region and the other in the visible region. Both bands undergo a shift towards red frequencies due to the complexation of **I-CN-B-CN** with anions. The band in the ultraviolet region suffers a shift between 20 and 25 nm, and the change in the visible region is between 15 and 20 nm, which is enough to modify the observed color of the substance. Considering only the values of the wavelengths, the observed color of the isolated molecule will be yellow and the complexes will be yellow-orange. This change of color prompts to use these structures as possible chromogenic reagents for anion detection and thus allow monitoring the process to capture anions. There are not mayor intensity changes under complexation apart from the ultraviolet band of the **I-CN-B-CN** complex with bromide. Yet, the low intensity of this band does not affect the color of the complex with bromide. Orbital transitions of the isolated **I-CN-B-CN** and of the complexes with bromide and with BF_4^- are represented in Figure 6. Except the transition of the **I-CN-B-CN**···Br- complex, which is from HOMO-1 to LUMO, all transitions are from HOMO to LUMO. The initial orbital of the three transitions has similar characteristics with most of the electron density localized in the five-membered rings and with a C_3 symmetry or very close to it. The final orbital of the electronic transition for the isolated molecule also keeps this symmetry. However, it is broken in the final orbital of the electronic transitions for both complexes. The anions presence breaks the C_3 symmetry of the electron density and only a plane of symmetry remains. This variation in the final orbital for the complexes is likely to be the reason of the bands shifting. Finally, it should be noted that charge transfer transitions between the molecule and the anion do not contribute to the band in the visible region.

Energies of complexes formed by structure **II** with bromide, iodine or BF_4^- are collected in Tables 3 and 4. The binding energies in gas phase of complexes between bromide and structure **II** substituted with cyanide are between 10 to 14 kcal/mol more stable than complexes with structure **I**, but when the substituents are fluorides the stability increases in only 2 to 5 kcal/mol. It suggests that adding up a six-membered aromatic ring to each arm of the central core of the molecule enhances the resonant effects more than the inductive effects. This increases the stability difference due to the substituent in complexes of structure **II** to around 30 kcal/mol. Also, it should be noted that there is not much difference in the deformation energy of complexes with structure **II** and those with structure **I**, therefore the interactions between SubPcs and the anions are not strong enough to produce an extra deformation energy due to the distortion of the six-membered rings. This is also reflected in the geometries since for all complexes these rings keep their planarity under complexation and there are not large geometry differences when the anion changes (see supplementary information). The binding energies in water of SubPcs complexes substituted with cyanide groups are more or less the same as those for complexes with SubPzs, but if the substituents are fluoride atoms the binding energies are smaller. The energy difference between aggregates with different substituents is between 3 to 5 kcal/mol. These results show that even though introducing the six-membered rings raises the dispersive effects of fluoride groups (see gas phase results) it also increases the stability of the host molecule alone in water, and therefore, the stability of SubPcs complexes substituted with fluorine decreases regarding to those of SubPzs.

In Figure 7 are represented the UV-VIS spectra of the isolated **II-CN-B-CN** molecule and of the **II-CN-B-CN**···Br- complex. In both spectra there is a band of low intensity. This band is in the ultraviolet region for the isolated molecule but it is shifted around 40 nm for the complex, so it is located at violet wavelengths in the visible region for the complex. There is also a high intensity band for both cases in the visible region. The shifting is around 23 nm, a little larger than in complexes with structure **I**. Considering only the wavelengths of each band the color change under complexation would be from the yellow-orange of the isolated molecule to the red-orange (almost red) of the complex. As it happens before, this change of color may be enough to follow the capture of the bromide anion by the SubPc molecule. Figure 8 shows the main orbital transition that contributes to each band in the visible region. For the isolated molecule this is a HOMO-LUMO transition but for the complex it is a transition between the HOMO-3 and the LUMO orbitals. Occupied orbitals with higher energy than HOMO-3 correspond to “p” orbitals of bromide. Unlike in the SubPzs spectra, it seems that the symmetry of the initial and final orbitals of the complex transition is the same. However, the interactions with bromide are enough to decrease the difference between energy levels of the host molecule and then shift the absorption band. In the spectrum of the complex there is a band placed very close to the infrared region that has low intensity. This is a charge transfer band between the HOMO orbital and the LUMO+2 orbital. There are also transitions between HOMO and LUMO orbitals but at larger wavelengths and with negligible probabilities.

The energies of complexes formed by bromide and structures **III** or **IV** are collected in Table 5. For complexes with the structure **III**, changes in the central atom of the backbone or in the substituent of this atom produce small differences in the gas phase binding energy (these differences are more or less of the same size as for SubPzs complexes). Aggregates where the host molecule is substituted with cyanide groups have a stabilizing binding energy of the same size as complexes with structure **II**, but if the substituent is fluoride the binding energy is around 10 kcal/mol more stable than previous aggregates. As a consequence, the energy difference within the complexes with structure **III** due to the change of substituent is around 22 to 24 kcal/mol. This variation is smaller than the difference within the complexes with SubPcs and more or less the same as complexes with SubPzs as host molecule. Considering all together, complexes formed with structure **III** have the largest stability. Structure **IV** follows the same model as the previous structure but groups that extend the electron delocalization of the backbone and at the same time allow certain flexibility are used as hinge. The increase of the electron delocalization by these groups does not seem to enhance the interaction between the molecule and the bromide and the binding energies are a little smaller than in complexes with structures **II** and **III**. BSSE and deformation energies for complexes with **III** or **IV** are more or less of the same size as with structure **I** or **II** with one exception, the deformation energy of **IV-CN-B-CN-S**···Br- complex. The large deformation energy of this complex cancels any extra stabilization due to the effect of an extended electron delocalization.

Table 6 gathers the energies of complexes between structure **III** and iodine or BF_4^-. The gas phase binding energies are larger than with bromide, especially with BF_4^- where there is a noticeable increase of stability. This is most likely because the size of iodine and BF_4^- is more suitable to fit better in the cavity of the host molecule. The BSSE and deformation energies of these complexes are a little larger than those with bromide. The large BSSE for the **III-CN-B-F···BF_4^-** complex is a consequence of the anion basis set being used to describe the host molecule. Thus, if we split the BSSE of this complex in the contributions due to each molecule, the contribution due to the anion is 0.52 kcal/mol and the rest, 4.97 kcal/mol, bellows to the gripper

In water solution the binding energies of complexes between bromide and structure **III** substituted with cyanide groups are similar to those with structures **I** and **II**. However, if fluorine is used as substituent the binding energies are positive and therefore, according to our results, the bromide complexes substituted with fluorine are not stable in water. It seems that the influence of dispersive effects due to fluorine substituents in structure **III** is not enough to obtain negative binding energies for bromide complexes in water. If structure **IV** is considered in water, it gives complexes with lower stability than complexes with structure **III**. Therefore, using as hinge in our systems ether or thioether groups that keep the electron delocalization does not enhance the ability of the host molecule to capture anions in water but the opposite. Finally,

Table 6 shows the largest stabilities in water found for any complex in this work. The larger stabilities in gas phase of complexes between structure **III** and iodine or BF_4^- are also reflected in water, especially with BF_4^-. For this last anion, the binding energies of complexes with the cyanide group as substituent are big enough to consider that these aggregates will be stable in water when entropic effects are introduced.[57,58]

Figure 9 presents the UV-VIS spectra of the isolated **III-CN-B-CN** molecule and of the **III-CN-B-CN**···Br- complex. The intensity of these spectra is lower than that of previous spectra analyzed in this work and so the intensity of the observed color is going to be lower as well. The monomer spectrum has two bands, one in the ultraviolet region and the other in the violet region of the visible wavelengths. In contrast, the complex spectrum has only one band in the violet region. There is a small shift of 7 nm between the visible bands of both spectra. This shift is not enough to change the observed color between the **III-CN-B-CN** monomer and the complex with bromide but it will likely modulate the color hue. The small size of the shift due to complexation makes structure **III** a less suitable option to track the process of capturing anions. However, considering the binding energies obtained with this structure we think it is a possibility worth exploring. The main orbital transition that gives rise to each band in the visible region is reflected in Figure 10. For the isolated monomer this is the transition HOMO to LUMO and for the complex it is the transition HOMO-3 to LUMO. As it happens with the **II-CN-B-CN**···Br- complex, the highest occupied orbitals belong to the bromide anion. The two transitions have a similar initial orbital with C_3 symmetry but they differ in the final orbital, although only a plane of symmetry remains in the final orbital of both transitions.

Conclusions

Different complexes of anions with anion receptors constructed from SubPcs and SubPzs have been optimized and analyzed by using DFT, TD-DFT and DFT-SAPT techniques. In all optimized geometries the anion stays in the center of the cavity of the host molecule. All aggregates have a large stabilizing binding energy in gas phase, with values similar or even larger than those found in the literature for other systems.[13,25,29] Also, when the host molecule is substituted with cyanide groups the stabilizing binding energy is 20 to 30 kcal/mol more stable than when the substituent is fluorine.

The energy decomposition shows that the electrostatic and induction terms decrease when the anion size increases, and unlike the previous terms, the repulsion and dispersion contributions increase with the size of the anion. Since the electrostatic energy (the largest of all contributions) decreases and the repulsion contribution increases, the total (and binding) energy decreases with the anion size. Also, the nature of the interaction changes in going from an electrostatic nature with small anions to a more dispersive kind of complexes with the largest anions.

In contrast to gas phase, in water the binding energy increases with the size of the anion. This is because in complexes where the electrostatic contribution is not so strong and where the dispersion term increases its importance the desolvation cost will not be so large, not only because anions have not such large electrostatic term with water but also because the dispersive term with the solvent is not as important as with the host molecule. The binding energies in water of some complexes are big enough to consider that even when entropic effects are considered the resulting free energies will be negative and so these aggregates will be likely stable in water.

TD-DFT calculations show changes in the absorption wavelengths of the host molecule under complexation big enough to produce a change in the color of the substance. This characteristic points out that these molecules can be used as possible chromogenic reagents for anion detection that allow monitoring the process of anion capture.

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Table 1: Binding and deformation (in parenthesis) energies in gas phase (kcal/mol) for structure **I** with several anions.

Anion	**I-CN-B-CN**	**I-CN-P-CN**	**I-Cl-B-CN**	**I-Cl-P-CN**
Cl^-	-57.10 (1.39)	----	----	----
Br^-	-52.65 (1.43)	-50.83 (2.01)	-50.32 (1.57)	-47.48 (2.08)
I^-	-51.51 (1.44)	-48.89 (2.19)	-49.24 (1.36)	-45.63 (2.38)
BF_4^-	-49.30 (1.33)	-46.34 (2.27)	----	----
	I-CN-B-F	**I-CN-P-F**	**I-Cl-B-F**	**I-Cl-P-F**
Br^-	-29.99 (0.96)	-26.82 (1.70)	-27.84 (1.13)	-23.54 (1.75)

Table 2: Binding energies in water and BSSE (in parenthesis) in gas phase (kcal/mol) for structure **I** with several anions.

Anion	**I-CN-B-CN**	**I-CN-P-CN**	**I-Cl-B-CN**	**I-Cl-P-CN**
Cl^-	-0.63 (5.64)	----	----	----
Br^-	-5.21 (0.43)	-5.23 (0.52)	-4.88 (0.43)	-4.67 (0.52)
I^-	-6.19 (0.90)	-6.01 (0.89)	-5.97 (0.90)	-5.35 (0.88)
BF_4^-	-8.03 (1.21)	-8.94 (1.46)	----	----
	I-CN-B-F	**I-CN-P-F**	**I-Cl-B-F**	**I-Cl-P-F**
Br^-	-2.55 (0.97)	-1.49 (1.31)	-2.36 (0.96)	-1.15 (1.26)

Table 3: Deformation and BSSE energies in gas phase, and binding energies in gas phase and water for structure **II** with Br^-. All energies are given in kcal/mol.

	$E_{binding}$	**$E_{deformation}$**	**BSSE**	**$E_{binding}$ in water**
II-CN-B-CN	-63.17	1.81	0.40	-4.77
II-CN-P-CN	-65.30	1.70	0.50	-5.86
II-CN-B-F	-32.74	1.19	0.48	-1.33
II-CN-P-F	-31.75	1.32	0.62	-0.82

Table 4 Deformation and BSSE energies in gas phase, and binding energies in gas phase and water for structure **II** with I^- and BF_4^-. All energies are given in kcal/mol.

	$E_{binding}$		**$E_{deformation}$**		**BSSE**		**$E_{binding}$ in water**	
	I^-	**BF_4^-**	**I^-**	**BF_4^-**	**I^-**	**BF_4^-**	**I^-**	**BF_4^-**
II-CN-B-CN	-61.79	-61.60	1.48	1.52	0.90	1.01	-6.24	-8.32
II-CN-B-F	-31.60	-33.82	1.01	1.14	0.86	1.75	-3.08	-5.22

Table 5: Deformation and BSSE energies in gas phase, and binding energies in gas phase and water for structures **III** and **IV** with Br^-. All energies are given in kcal/mol.

	$E_{binding}$	$E_{deformation}$	**BSSE**	$E_{binding}$ **in water**
III-CN-B-CN	-66.29	1.40	0.68	-5.33
III-Cl-B-CN	-62.25	1.98	0.65	-3.25
III-CN-P-CN	-64.45	2.14	0.86	-7.79
IV-CN-B-CN-O	-61.18	1.92	0.86	-3.49
IV-CN-B-CN-S	-60.17	6.24	0.66	1.69
III-CN-B-F	-42.31	0.74	1.90	2.19
III-Cl-B-F	-40.62	0.89	1.89	2.36
III-CN-P-F	-40.39	1.47	1.78	4.16

Table 6: Deformation and BSSE energies in gas phase, and binding energies in gas phase and water for structure **III** with I^- and BF_4^-. All energies are given in kcal/mol.

	$E_{binding}$		**$E_{deformation}$**		**BSSE**		**$E_{binding}$ in water**	
	I^-	**BF_4^-**	**I^-**	**BF_4^-**	**I^-**	**BF_4^-**	**I^-**	**BF_4^-**
III-CN-B-CN	-66.61	-72.97	2.25	2.95	1.53	2.49	-12.72	-22.55
III-CN-P-CN	-63.76	-67.94	1.62	2.72	1.56	2.48	-11.83	-19.48
III-CN-B-F	-40.63	-47.69	0.97	1.02	1.46	6.01	-0.63	-9.49

Figure captions

Figure 1. Chemical structure of SubPc and SubPc analogues.X=B, P; Y=Cl, CN; Z=F, CN, W=O, S.

Figure 2. Some examples of clusters found in this work.

Figure 3. DFT-SAPT results for complexes formed between **I-CN-B-CN** and different anions. E_{sapt}=E_{elec}+E_{rep}+E_{ind}+E_{disp}.

Figure 4. DFT-SAPT results for complexes formed between bromide and different SubPzs. E_{sapt}=E_{elec}+E_{rep}+E_{ind}+E_{disp}.

Figure 5. Obtained UV-VIS spectra of isolated **I-CN-B-CN** and its complexes with Br^- and with BF_4^-.

Figure 6. Main orbital transition producing the band in the visible region a) for the isolated **I-CN-B-CN**, b) for the complex with Br^- and c) for the complex with BF_4^-.

Figure 7. Obtained UV-VIS spectra of isolated **II-CN-B-CN** and its complex with Br^-.

Figure 8. Main orbital transition producing the band in the visible region a) for the isolated **II-CN-B-CN** and b) for the complex with Br^-.

Figure 9. Obtained UV-VIS spectra of isolated **III-CN-B-CN** and its complex with Br^-.

Figure 10. Main orbital transition producing the band in the visible region a) for the isolated **III-CN-B-CN** and b) for the complex with Br^-.

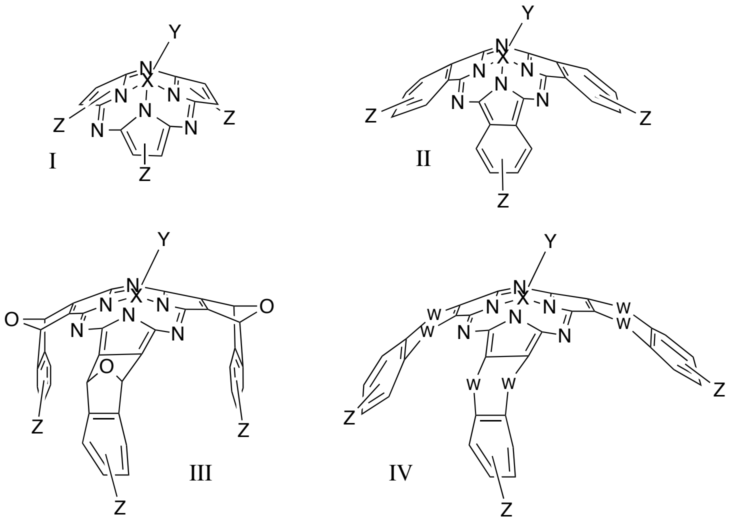

Fig. 1

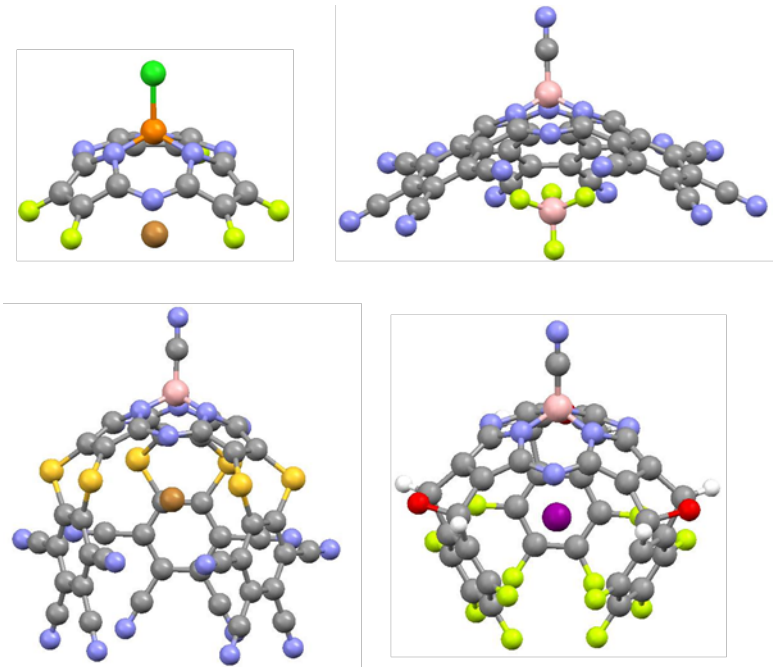

Fig. 2

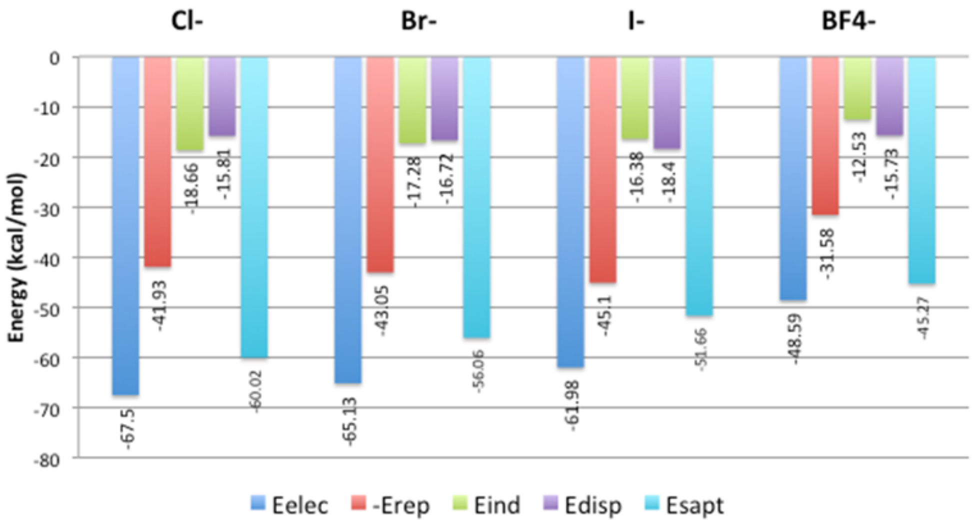
Cl-
Br-
I-
BF4-
Energy (kcal/mol)
0
-10
-20
-30
-40
-50
-60
-70
-80
-67.5
-41.93
-18.66
-15.81
-60.02
-65.13
-43.05
-17.28
-16.72
-56.06
-61.98
-45.1
-16.38
-18.4
-51.66
-48.59
-31.58
-12.53
-15.73
-45.27
Eelec
-Erep
Eind
Edisp
Esapt

Fig. 3

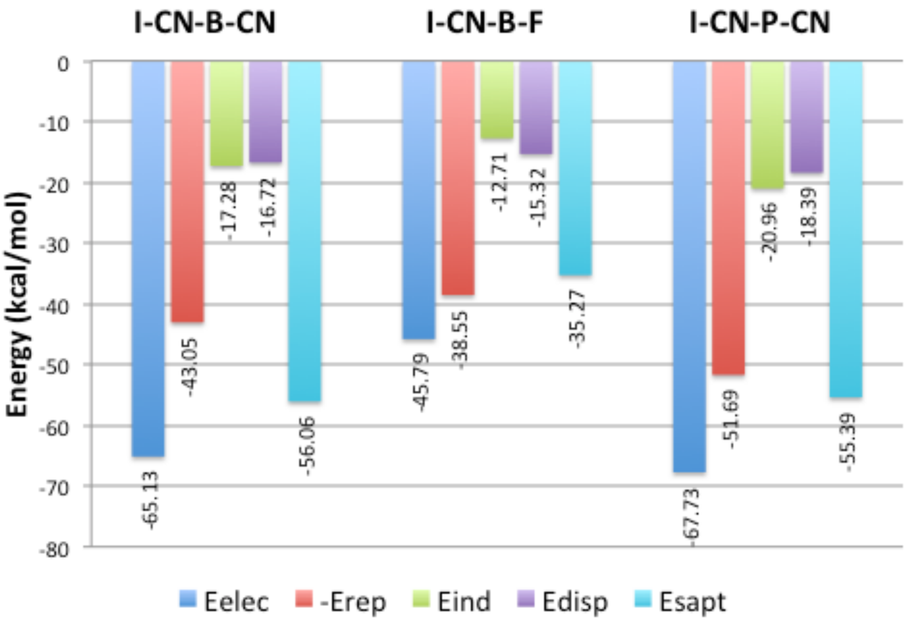
I-CN-B-CN
I-CN-B-F
I-CN-P-CN
Energy (kcal/mol)
0
-10
-20
-30
-40
-50
-60
-70
-80
-65.13
-43.05
-17.28
-16.72
-56.06
-45.79
-38.55
-12.71
-15.32
-35.27
-67.73
-51.69
-20.96
-18.39
-55.39
Eelec
-Erep
Eind
Edisp
Esapt

Fig. 4

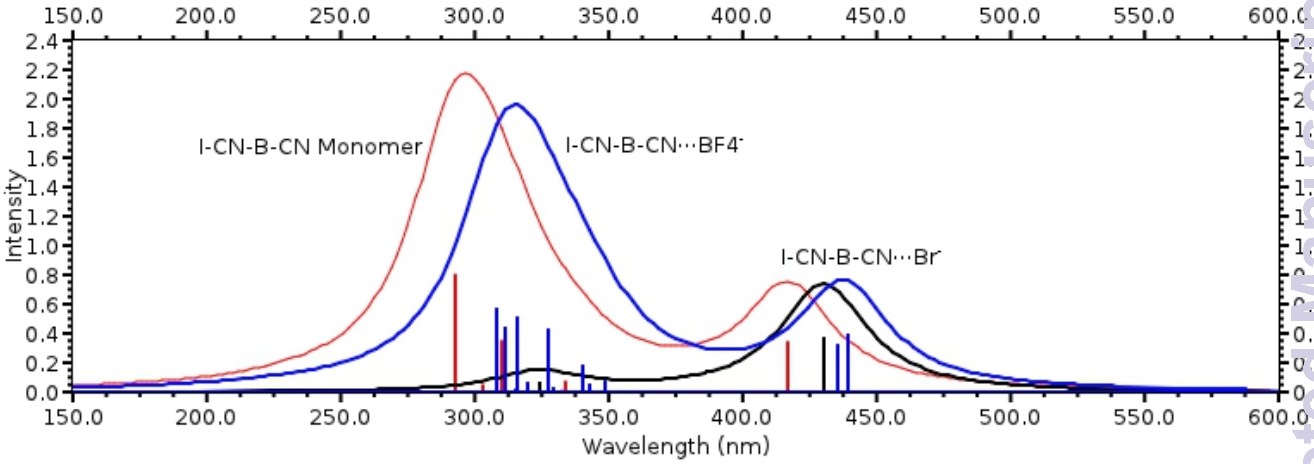
I-CN-B-CN Monomer
I-CN-B-CN···BF4-
I-CN-B-CN···Br-
Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
150.0
200.0
250.0
300.0
350.0
400.0
450.0
500.0
550.0
600.0

Fig. 5

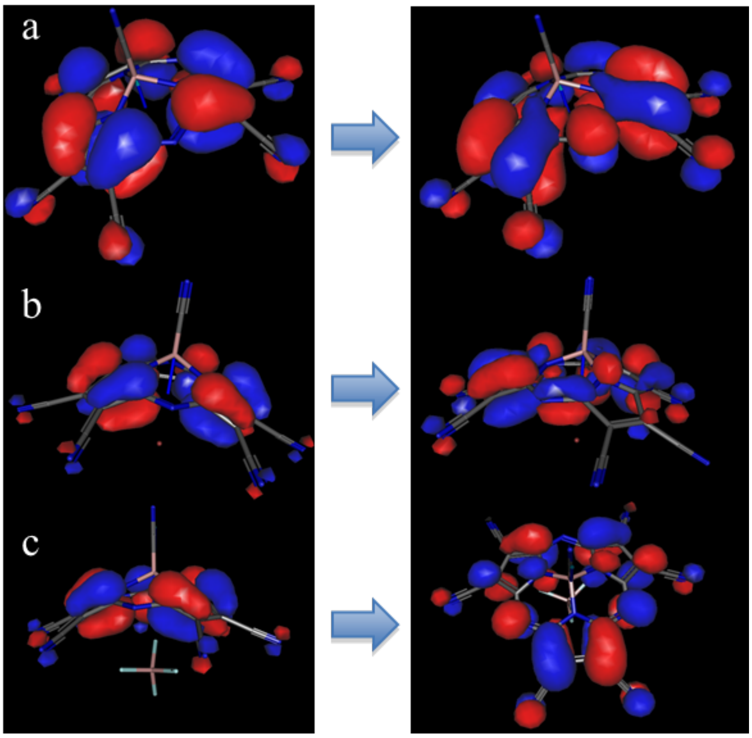

Fig. 6

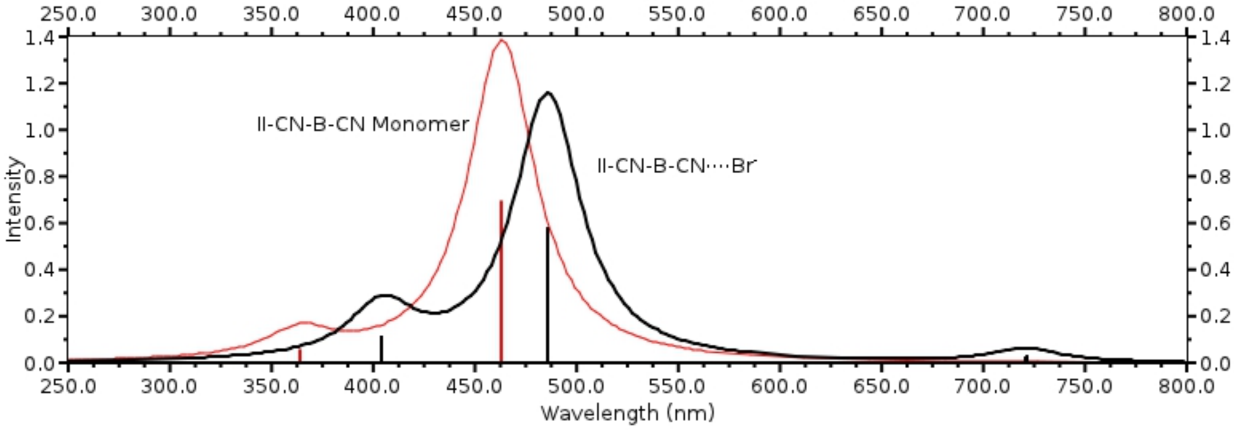
II-CN-B-CN Monomer
II-CN-B-CN····Br⁻
Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
250.0
300.0
350.0
400.0
450.0
500.0
550.0
600.0
650.0
700.0
750.0
800.0

Fig. 7

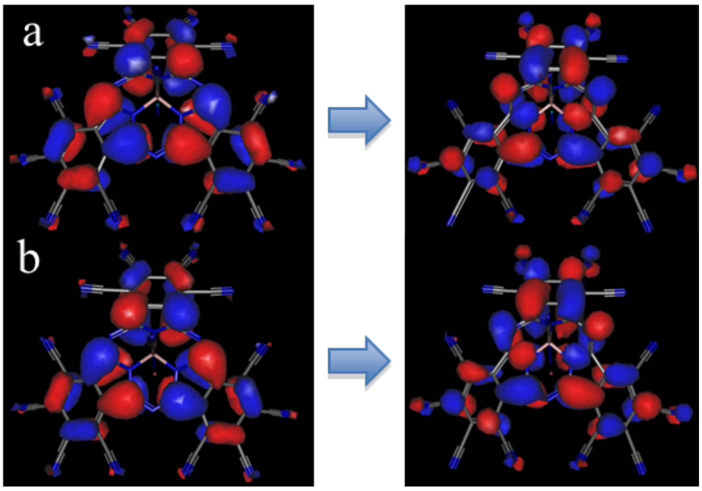

Fig. 8

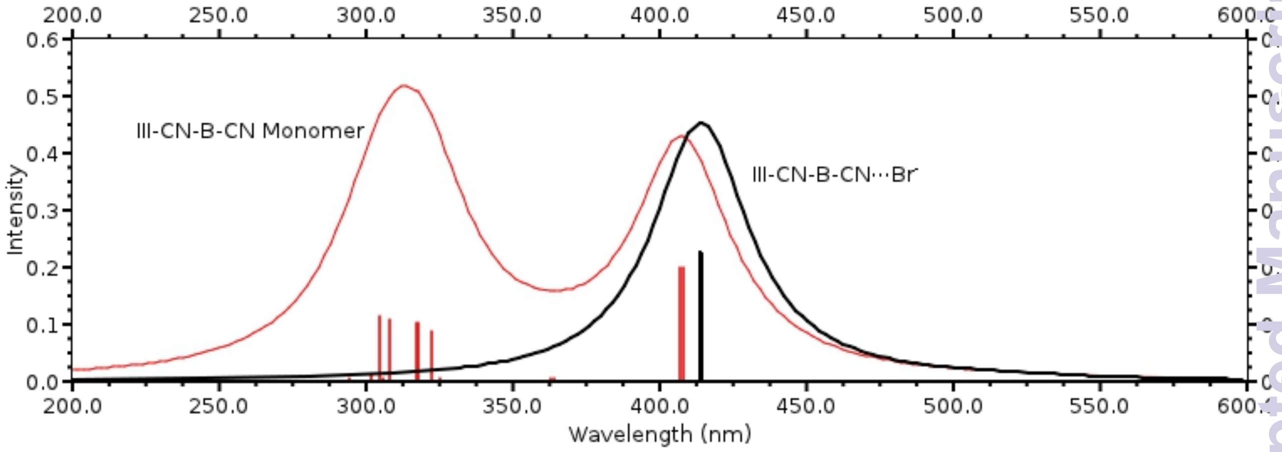
200.0
250.0
300.0
350.0
400.0
450.0
500.0
550.0
600.0
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Intensity
III-CN-B-CN Monomer
III-CN-B-CN···Br$^-$
Wavelength (nm)

Fig. 9

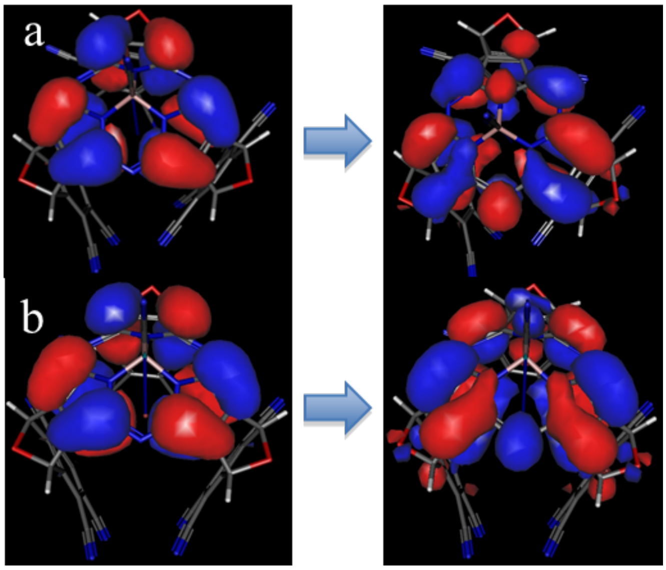

Fig. 10