Journal of Nanosciences Research & Reports

SCIENTIFIC Research and Community

Review Article

Open d Access

Density Functional Theory Investigation on Boron-Subphthalocyanine

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ABSTRACT

In this article a Density Functional Theory (DFT) description of derivatives of boron-subphthalocyanines (**SubPc**) is investigated. Investigated structures are peripherally functionalized derivatives. It is shown that the generalized gradient functional results of the geometry dier from the geometries found with the hybrid functionals, but the deviation is only of the order of a few percent of the total bond lengths for any of the investigated functionals. A linear response investigation is also used, where experimental UV-Vis results are compared with computational results. These investigations show that none of the investigated functionals are able to compute both peak position of the Q and soret band, but that the functional CAM-B3LYP does give results that are qualitatively useful, as this is the functional that comes closest to the correct separation of the peaks. A basis set investigation shows little difference in results within the same functional. To compare results with experimental data, vibornic coupling eects are included using the Franck-Condon, Hertzberg-Teller approximation, and a close resemblance of CAM-B3LYP and experimental results are found. Linear response results found with the functionalization has inuence on the frequency and intensity of absorption. These results also show a discrepancy between hybrid functionals and BP86, where BP86 predicts transitions at much lower energies - 300 nm red-shifted compared to the linear response result found with B3LYP. This is as expected for the treatment of charge transfer states with a generalized gradient functional and illustrates why BP86, though suitable for describing the position of the Q-band for unfunctionalized **SubPc**, might not be the best density functional to utilize when investigating **SubPc** based molecular dyads and triads.

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Received: July 20, 2023; Accepted: July 25, 2023; Published: July 31, 2023

Introduction

With the increasing world population and resulting increased demand on energy, alternative energy sources need to be found in order to provide sucient and cheap energy for future generations. There are many possibilities when it comes to alternative energy, but one of the very popular concepts is to utilize the energy striking the world every day from the Sun. Dye sensitized solar cells (DSSC) are devices designed to harvest the solar energy, and have been a major research focus since the seminal paper by O'Regan and Grtzel [1]. The DSSCs are constructed from just five components, a transparent conductive oxide (TCO) substrate, a n-type semiconductor, often nanostructured TiO₂, a dye that absorbs visible light, an electrolyte for regenerating the dye and nally the counter electrode [2]. Although only a few number of components are used in the construction of the DSSCs there are still a very large number of possible combinations of materials, where especially alternative electrolytes, semi-conductors and dyes have been investigated in order to achieve high efficiency as well as low cost [3-10].

In recent years one dye that has caught the attention of the scientic community is the boron-subphthalocyanines (**SubPcs**). These are analogous of the phthalocyanines (**PCs**), but in the **SubPc** three diiminoisoindole units are fused to a central boron atom instead of four [11]. This leads to a signicantly different geometry of the

SubPcs compared to the PCs. The PCs are planar structures, but the contraction made in order to construct the **SubPcs** induces new strains in the system, and the SubPcs instead adopt a coneshaped structure [11]. This means the while planar structures easily aggregate, the **SubPcs** are more sterically hindered from doing so. This might prove an advantage when considering DSSCs, as the coordination of the n-type semi-conductor and the **SubPc** dyes can then be handled via chemical bonding with limited risk of the dye aggregating out of solution before binding to the surface of the semi-conductor. This is important, since the injection of the excited electron of the dye into the semi-conductor is the first step when generating a photo-current in the DSSC, and a low coverage of the semi-conductor will therefore result in a low photo conversion eciency (PCE).

The ambition to use SubPcs in organic photo voltaics is wellknown from the literature [12,17]. One advantage of using SubPcs is the relative ease with which the SubPc chromophore can be functionalized, both at the axial and peripheral positions. This makes it possible to fine-tune the electronic properties of the system, where for example the peripheral position might be functionalized with electron-donor (D) and electron-acceptor (A) groups to make a D-SubPc-A triad, where the electron density of the excited molecule is pushed/pulled by the functionalization towards A. This ensures both a larger charge separation between the

positive charge that will be generated on D and the negative charge on A, and a close proximity between the electron in the excited dye and the semi-conductor. This design is expected to provide longer life-times of the charge separated species, and faster injection of the electron into the semi-conductor, and thereby increasing the PCE of a **SubPc** based DSSC. Hereby, we have highlighted some of the advantages and challenges for using **SubPc** triads in DSSC. A large number of **SubPc** derivatives might be constructed using the **D-SubPc-A** scheme, and it would therefore be desirable to create a computational protocol for the investigation of envisioned **SubPcs** and **SubPc** derivatives structures before synthesis. The computational screening of potential candidates will guide the experimental work towards the most promising **SubPc** structures.

In this paper we present a Density Functional Theory (DFT) and time-dependent DFT (TD-DFT) investigation on a number of **SubPc** derivatives and by comparison to experimental results we establish a computational strategy for future investigations of **SubPc** triads.

It has previously been shown that for phthalocyanines and **SubPc** the use of generalized gradient functionals results in the best agreement between computed linear response and experimentally observed UV-Vis [18,19]. Another popular choice of functional is B3LYP [20-23].

A recent investigation the vibrationally resolved spectra of **SubPc** computed with PBE0. The computed spectra shows the same major trends as the experimental spectra, but the hybrid functional predicts a blue shifted spectrum compared to the experimental spectrum [24].

In this work we present results of geometry optimization and linear response calculations on a **SubPc** axially functionalized with p-tert-butylphenyl **SubPc**-AR treated with a number of generalized gradient and hybrid functionals. In order to compare [24]. The vibrationally resolved spectra of **SubPc**-Ar computed with the hybrid functionals B3LYP and CAM-B3LYP are also presented. Furthermore, we present 14 **SubPc** derivatives, functionalized with either electron donating or accepting groups in order to construct dyads where **SubPc** functions as either acceptor or donor to show the consequence of extending the system when choosing a computational treatment.

Computational Methodology

DFT was chosen as the method for investigating these systems since the large sizes of the chromophores limit the use of wave function based method to Hartree-Fock, and with this in mind DFT has the largest potential for accurate results compared to other methods with similar scaling like Hartree-Fock theory or semiempirical methods because of the inclusion of electron correlation in the functional. Choosing DFT as the computational methods does include some further challenges, because DFT cannot be systematically improved. Therefore it is not possible beforehand to know exactly which functional is best suited for the investigation of a specific system, though experience from literature and the test set on which the functionals were developed might guide the selection processes.

The solvent effects are modeled via the integral equation formalism polarizable continuum model (IEFPCM) [25,26]. In this model a cavity is created equal to the space that is filled up by the solute. This cavity is created via overlapping spheres centered on the atoms in the molecule, based on the atomic radii. The solvent is modeled as a continuum, where the dielectric constant is equal to that of the solvent to be modeled. This means that if for example the solvent chosen is water the continuum will be described as a continuous medium with static dielectric constant $e_{st} = 78.3553$, but no specic solvent effects are included, as for example hydrogen bonding which might be expected to influence a solute in water.

In order to compare the computations to experiment, the molecular properties of the system is also investigated. In this article the crystal structure of the model system **SubPcAr** is compared with geometries optimized with a number of DFT functionals and the basis set 6-311G(d) [27]. Furthermore, the UV-Vis absorption from experiments are compared to the result from linear response as calculated with the TD-DFT module of Gaussian16 [28,29]. In the linear response approach used for modeling the UV-Vis spectra we obtain the transition energies and transition dipole moments of the studied molecule. The latter is used to calculate the oscillator strength of the molecule.

Since the linear response TD-DFT module does not include vibrational couplings, the vibrationally resolved spectra calculated with the Franck Condon couplings are also presented for SubPc-Ar calculated with the functionals B3LYP and CAM-B3LYP.

Results

Functional Investigation

Some of the chosen functionals were hybrid functionals, some with long range correction

or dispersion eects B3LYP, CAM-B3LYP, PBE0, M06-2X, ω B97X-D, and BHandHLYP, a hybrid functional based on the half-and-half method proposed by Beck, though not completely following the formulation proposed there [30-39].

We have also included in the investigation the generalized gradient (GGA) functionals, M06-L, HCTH147, PW91, and BP86, "pure" DFT functionals, in order to illustrate the effects of omitting the Hartree-Fock exchange term [40-49].

All initial calculations were made using the basis set 6-311G(d) Bond lengths, angles and curvature

Bond Lengths, Angles and Curvature



Figure 1: Structure of **SubPc-Ar** with labels indicating the investigated atomic position. Green dots are used to dene the plane from which the bowl depth is dened. The structure is compared for all investigated functionals.

Geometries optimized with the investigated functionals were compared with the crystal structure of **SubPc-Ar** (Figure 2) The best fit of the investigated bond lengths were



Figure 2: Plot of the deviation of the bond lengths in the structure SubPc-Ar. The bonds referred to is between the atoms as labeled in Figure 1.

Table 1: Crystal Structure	Bond Lengths between Atoms	Labeled in Figure 1
	0	0

R(1,11)	R(1,6)	R(1,2)	R(2,3)	R(3,4)	R(4,5)	R(5,6)	R(6,7)	R(7,8)	R(7,9)	R(5,10)
1.435	1.487	1.500	1.366	1.341	1.344	1.362	1.365	1.344	1.455	1.453

reached when optimizing with the functional M06-L, but the lowest root mean square deviation (RMSD) was reached with the functional BHandHLYP. The computed bowl depth of **SubPc-Ar** matched well with the experimental bowl depth for with all functionals, and the closest value to the one of the crystal structure value was found with B3LYP.

The plot in Figure 2 shows the length of the bonds calculated with indicated functional relative to the bond lengths in the crystal structure and the investigated bonds are the bonds between the atoms labeled in Figure 1. The bond lengths of the crystal structure is given in Table 1.

When optimizing **SubPc-Ar** with the GGA functionals BP86, PW91 or HCTH147 almost all of the investigated bond lengths are too long when compared to the crystal structure, and especially the bonds involving the boron atom. Exceptions to this are the bonds R(3,4), R(4,5) and R(7,8), where the functional HCTH147 instead obtains an optimized structure with slightly shorter bonds.

The hybrid functional B3LYP shows a similar trend as HCTH147, though the bonds here are shorter in general. This results in a better fit for the bonds with B but worse for R(3,4), R(4,5) and R(7,8) relative to HCTH147.

For the remaining hybrid functionals, the optimized structures have in general shorter bonds than the ones in the crystal structure, except for the B-N bonds R(1,6) and R(1,2), where all functionals but BHandHLYP overestimates the bond length.

When comparing the mean absolute error of all the optimized structures compared to the crystal structure (Table 2), it is found that the Minnesota functionals M06-L and M06-2X best describe the investigated bond lengths of **SubPc-Ar**, and the functional with the largest mean absolute error is BP86. It is seen though

that even for BP86 the mean absolute error is $1.18 \cdot 10^{-2}$ Å and with the average bond length of the investigated bonds are 1.405 Å, this corresponds to an error of 0.84 %. Since the structures are all optimized in vacuum, there is a fundamental difference in the environment between the crystal structure and the DFT optimized structures, and some derivation is therefore expected.

Another geometrical parameter often referred to when discussing **SubPc** molecules is the bowl depth. In Figure 1 three green dots, mid-points of C-C bonds, are used to mark the points used to define a plane in the SubPc core. From this plane the distance to the B atom is measured, and this gives the bowl depth of the structure.

The GGA functionals HCTH147 and PW91 both have too large bowl depths, and thus a too high curvature of the system. The rest of the functionals give structures that are too planar when compared to the crystal structure. The largest deviation from the experimental bowl depth is found with the functional M06-L with an error of -0.0445 Å, and the functional with the closest resemblance to the crystal structure bowl depth is B3LYP where the error is -0.0013 Å,. Finally, to evaluate the overall resemblance of the crystal structure and DFT results, the RMSD between the structures are calculated [50] (Table 2). In these calculations the two molecules are transposed to an equal center, and rotated to get the closest fit between geometries, and this value is therefore an overall estimation of the fit of the position of all atoms in the molecule.

Table 2: The Mean Absolute Error (MAE) of the investigated bonds for the structures optimized with the indicated functional compared to the crystal structure for **SubPc-Ar**. Bowl depth is the distance from the green plane shown in Figure 1 and the boron atom. Root Mean Square Deviation (RMSD) is calculated after alignment of the crystal and DFT structure.

Structure	MAE (Å)	Bowl Depth (Å)	RMSD (Å)50	
Crystal		2.690		
BP86	1.18•10 ⁻²	2.667	0.211	
PW91	7.93•10 ⁻³	2.703	0.212	
HCTH147	4.91•10 ⁻³	2.701	0.227	
B3LYP	3.18•10 ⁻³	2.689	0.205	
CAM-B3LYP	3.07•10 ⁻³	2.673	0.198	
M06-L	4.45•10-4	2.645	0.437	
M06-2x	1.20•10 ⁻³	2.680	0.406	
BHandHLYP	8.7610-3	2.658	0.192	
PBE0	3.0910-3	2.669	0.210	
w-B97X-D	3.1910-3	2.648	0.436	

Almost all the optimized DFT structures have RMSD values close to 0.2 Å, with M06-L, M06-2x and ω -B97X-D as the exceptions. The larger RMSD values for these three functionals can from the 3D representation of **SubPc-Ar** be seen to be related to the angle between the SubPc-Core plane and the B-O bond.

Linear Absorption

First the linear absorption is calculated with the basis set 6-311G(d) for all the investigated functionals. In order to compare the linear response results with experimental results, the structure investigated initially was SubPc axially functionalized with 4- tert-Butylphenol SubPc-Ar, where experimental results are published in Ref. 28. In order to model experimental conditions closer, the solvent chloroform was modeled with PCM.

Signicant red-shifts of the allowed transitions are seen when calculating the linear absorption with the GGA functionals compared to hybrid functionals, as expected from literature [51].

As the use of HF exchange in the hybrid DFT functionals has an influence on the results of the geometry optimization, it is interesting to see the degree of difference between the hybrid DFT and GGA DFT results for linear response. In order to investigate a large range of excitation energies, 70 states were calculated with the TD module of Gaussian16.



Figure 3: The linear absorption of SubPc-Ar calculated with the investigated functionals compared to experimental results in order

to find the degree to which the computational and experimental results from ref. 28(Copyright©2017 by John Wiley Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.) agree. TD-DFT calculations were performed with solvent effects from PCM modeling chloroform which is the solvent used in experiments. The basis set is 6-311G(d).

From the linear response, the oscillator strengths and transition energies of the electronic transitions are computed. These calculations are thus vertical excitations, and cannot be directly compared to experiments, but the position of the predicted allowed transitions can give an initial estimate of whether or not a given functional is able to reproduce experimental UV-Vis. Especially the peak positions of the experimental UV-Vis and predicted vertical excitations with a large oscillator strength should be within the same range.

To guide the eye of the initial comparison between TD-DFT linear response and experimental UV-Vis, each predicted vertical transition with an oscillator strength larger than 0 is broadened with a gaussian function (Figure 3).

All of the investigated functionals reproduce the basic shape of the UV-vis spectra with one peak in the visible part of the spectrum, and two (or three) peaks in the UV region. The peaks are here defined as the areas where a signicant grouping of the predicted transition energies are seen.

For the hybrid functionals, the absorption peak in the UV region closely resembles the energy of the experimental UV-absorption, but it is blue shifted by 70 nm (0.30 eV) with the largest oscillator strength found for computed transitions in the region 496-498 nm, and the experimental λ max is 564 nm.

GGA TD-DFT results are red-shifted compared to the hybrid functionals and therefore represents the visible peak well, but here the peak belonging to the soret-band is red-shifted compared to experiments.

Another feature that separates the hybrid and GGA functional results is the spreading of the transitions. It can be seen that for the GGA functionals, a higher number of transitions are found in the region 440-570 nm, but that the intensities/magnitudes of the oscillator strengths in general are smaller for the GGA functionals. In the 300 nm region, the hybrid functionals have two distinct collections of allowed transitions, where the GGA functionals have a very broad distribution. For the GGA functionals, the right most shoulder/collection of transitions are between the soret- and Q-band compared to the experimental results.

Based on the TD-DFT linear response results for electronic transitions, a grouping of the results can be made. The GGA functionals all give comparable results, as does the hybrid functionals and finally long range corrected hybrid functionals. Based on this the vibrationally resolved spectra were computed using B3LYP and CAM-B3LYP.

Basis Set

To investigate the effects of the basis set on the reported UV-Vis spectra a basis set investigation was also performed. Based on the previous results only the functionals BP86, B3LYP and CAM-B3LYP are used in the basis set test, as the other functionals are expected to gives results either close to BP86, B3LYP or CAM-B3LYP.

In Figure S1, the result of the basis set investigation is plotted. For all functionals the change of basis set has only a very limited effect. The inclusion of diffuse and polarization functions in the triple zeta basis sets results in some degree of red-shifting (11.2-22.3 nm, 0.05-0.12 eV), but transitions in the UV region is almost unchanged.



Figure S1: Basis set investigation of the functionals B3LYP, CAM-B3LYP and BP86. It can be seen that the basis set as a limited eect on the spectroscopic features, but that diffuse functions can lead to a slightly better agreement between the computed and experimental spectra?

Comparing with the previous two results, it can be seen that if the desire is to get a good estimate of the visible peak position, these computations indicate that the best functional to use is BP86, but if the interest is more in the general trend of the entire spectrum, the CAM-B3LYP results are closer to a useful qualitative result. In either case, the inclusion of both diuse and polarization functions leads to a closer resemblance to experimental results.

Vibrationally Resolved Spectra

Based on the TD-DFT and basis set investigation, the vibrationally resolved spectra were computed for the visible region (Q-band) with functionals BP86, B3LYP and CAM-B3LYP and basis set 6-311+G(d) The vibrational resolved spectra was also computed using PCM to investigate the solvent effects from chloroform.

The vibrational coupling was included using the Franck-Condon Hertzberg-Teller approximation,

$$\langle \Psi_{ini} | \mu | \Psi_{fin} \rangle = \mu_{ij}(Q_0^{fin}) \langle \psi_{ini,\nu} | \psi_{fin,\nu} \rangle + \sum_{k=1}^N \left(\frac{\partial \mu_{ij}}{\partial Q_k^{fin}} \right)_0 \langle \psi_{ini,\nu} | Q_k^{fin} | \psi_{fin,\nu} \rangle + \cdots$$
(1)



Figure 4: The vibronically resolved spectra of SubPc-Ar calculated with CAM-B3LYP and B3LYP. Results are compared with experimental results [13].

Where the transition dipole moment is approximated as a Taylor series to first order. Including the vibrational spectra results in a close resemblance between the experimental spectra and the spectra computed with CAM-B3LYP (Figure 4, blue line). A similar trend has been observed before with the hybrid functional PBE0.

Linear Response of SubPc Derivatives

In Figure 5 we present the molecular structures investigated in this article. The structures represent pheripheral functionalizations in the system, named Cp1-7.

The electronic transitions of the **SubPc** structures were investigated in chloroform with the use of linear response / Time Dependent (TD) DFT. From the linear response the oscillator strengths and absorption energies are calculated for the 25 lowest energy transitions.



Figure 5: Schematic of the investigated structures

Peripherally Functionalized SubPcs

The SubPcs with peripheral functionalization show an inuence from the functionalization. Here the difference between B3LYP/PBE0 (Figure 5 and Figure S2(SI)), and the other hybrid functionals becomes more apparent, and BP86 can no longer be said to give results similar to any of the hybrid functionals.



Figure S2: The linear absorption of the remaining investigated structures. Each plot shows the absorption as calculated with a specic functional. Notice that the plots (a) is from 200-800nm and (b),(c) from 200-600nm.



Figure S3: The absorption of nitrobenzene, the group used to functionalize ca3. The structure was optimized with B3LYP

For B3LYP and PBE0 the addition of peripheral groups shifts the absorption peak in the visible towards longer wave lengths. In the spectrum calculated with B3LYP the spectrum is also broadened in the visible region due to additional peaks between the UV and visible peak, which with the Gaussian distribution on top of the oscillator strengths results in one broad peak.

The shift to longer wave length absorption with peripheral functionalization is even more pronounced for the results of the BP86 computations. Here the structure Cp7 has a maximum absorption at 849 nm which is in the order of 300 nm longer than the maximum absorption found with the hybrid functionals, indicating that though this functional at a first glance seems promising for the treatment

of **SubPc** structures with a reasonable peak in the visible part of the spectrum, this is not the case for all structures, and especially structures where charge transfer states are expected to play an important role. It is therefore not recommended to use BP86 to compute linear response of **SubPc** dyads and triads without experimental validation of the peak positions, and thus therefore not suitable for screening purposes.



Figure 6: The linear absorption of all the investigated structures. Each plot shows the absorption as calculated with a specic functional.

An investigation of the electron density difference between the MOs of the occupied and virtual orbitals of the lowest energy transition of Cp7 shows that BP86, B3LYP and CAMB3LYP all predict the lowest energy transition to be of charge transfer character (Figure 7). All functionals predict that the axial functionalization (phenyl-group) is unoccupied in these transitions, and rather density is moved from the N,N-Dimethylaniline group towards the SubPc core, reflecting the electron donor character of the functionalization.



Figure 7: Electron Density difference plot of the longest wavelength transition. a) BP86 b) B3LYP c) CAM-B3LYP. Blue areas are regions where electron density is gained, and red areas are regions where electron density is lost.

Among the hybrid functionals, the inuence of peripherally functionalization is largest for results of B3LYP/PBE0. For the B3LYP results, additional allowed transitions are found between the Q and soret-band. This results in large distribution of allowed transitions for the **SubPc** dyads. For the peripheral dyad structures, the transition with the largest oscillator strength is still found the UV-region of the spectrum.

For the other three functionals, M06-2x, ω -B97X-D, and CAM-B3LYP, the UV spectra are almost identical. These functionals all show two peaks in the UV region for all peripherally functionalized structures. The peak in the visible region for these functionals is not shifted signicantly when compared to **SubPc-Ar**, with a shift of 20 nm/0.1 eV, but investigation of the molecular orbitals participating in this low energy transition confirms that the functional group does indeed partake in the transition.

Conclusion

In this investigation of SubPc derivatives it becomes clear that a DFT treatment of the SubPc structures is not straightforward. The system size of the SubPc and eventually SubPc based triads system is so large, that wave function based methods beyond HF is very computationally demanding, and thus a DFT treatment seems the obvious choice. By comparing bond length in SubPc derivative SubPc-Ar it can be seen that the hybrid functionals all give comparable geometries, though the structure found with B3LYP have longer bonds. Here the first major difference between the hybrid functionals and the GGA functionals are also seen, as GGA gives bond lengths that are even longer than the B3LYP results. For the linear response results, the computed data was compared with experimental results for the structure SubPc-Ar. Here it was found that the hybrid functionals all had two absorption peaks corresponding to the expected soret- and Q-band, but that the results were blue-shifted compared to experimental ndings. For the GGA functionals, the Q-band absorption was closer to the correct wave length with an absorption maxima of 540 nm compared to the experimental 560 nm, but here the soret band was at too low an energy. Finally, a small basis set investigation is performed using the same three functionals in order to see if the soret- and Q-band separation is greatly influenced by the chosen functional and basis set. A small change is seen, where especially the inclusion of diffuse functions is important, but none of the investigated basis sets can make up for the difference seen between computed and experimental spectra. In order to compare with experimental results a vibronic treatment of the linear response is also included where the use of the FCHT shifts the CAM-B3LYP and B3LYP results, so that the hybrid functionals now predicts the O-band with close resemblance to experimental results. In order to see if this trend was specific for the axial functionalization, the linear response of 7 derivatives with peripheral functionalization was also calculated. The results for B3LYP, BP86 and CAM-B3LYP is presented here, and the results of the remaining hybrid functionals can be found in the SI. From these investigations it is clear that pheripheral functionalization can potentially shift the absorption signicantly. The change in absorption found with pheripheral functionalization is found with all the chosen functionals, but the degree to which the absorption spectra is changed differ signicantly. With the GGA functional BP86, the absorption maxima is red-shifted by more than 300 nm for some of the Cp structures when compared to SubPc-Ar, where the CAMB3LYP results on the other hand only show a shift in the order of 15-20 nm. This shows, that while the BP86 functional does seem to have close to the correct absorption maximum of the axial-functionalized structures, the pheripheral functionalization might pose a problem.

The authors thank University of Copenhagen, the Danish center for Scientic Computing, and the Center for Exploitation of Solar Energy for support.

T.H.is grateful for financial support from the Lundbeck Foundation and K.V.M. is grateful for financial support from the Danish Council for Independent Research, DFF-0136-00081B.

Supporting Information Available

The following data is available in the supplementary information

- Basis set dependence of the **SubPc-Ar** linear response
- Linear Absorption of the investigated structures calculated with the functionals PBE0, M06-2X and ω B97X-D
- Linear Absorption of nitro-benzene calculated with B3LYP

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