PCCP

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Xu, W. Wang, S. Yin and Y. Wang, *Phys. Chem. Chem. Phys.*, 2017, DOI: 10.1039/C7CP01534H.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

Evaluation of Electronic Polarization energy in Oligoacene Molecular Crystals Using solvated supermolecular approach

Tao Xu^a, Wenliang Wang^a, Shiwei Yin^{a*} and Yun Wang^bReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The solvated supermolecular approach, i.e., block-localized wavefunction coupled with polarizable continuum model (BLW/PCM), is proposed to calculate molecular ionization potential (IP), electron affinity (EA) in solid phase and their related electronic polarization. By the calculations of solvated supermolecule (5M) including four closest molecules, BLW/PCM overcomes the shortage of the monomer PCM calculation, that is, the nearly same electronic polarization for cation (P₊) and anion (P₋). The solvated supermolecular approach successfully describes asymmetric behaviors of P₊ and P₋ for oligoacene crystals. In addition, we also compared two charge-localized methods, i.e., BLW and constrained density functional theory (CDFT) to calculate molecular IP and EA in supermolecule with/without PCM. Our results demonstrate that both BLW and CDFT correctly estimate EA and IP values in gas phase cluster while CDFT/PCM fails to evaluate the P₋ value of bulk system.

Introduction

The organic semiconductors based on π -conjugated molecules are widely used in various applications such as organic thin-film transistors (OTFTs), organic photovoltaics (OPV), and organic light-emitting diodes (OLEDs).¹⁻⁶ The design of novel materials requires a fundamental understanding of whole key processes such as exciton energy transfer, exciton dissociation, charge transfer, charge injection. Among them, the site energies of exciton and charge carriers in the bulk or interface region play a key role in controlling the efficiency of those processes. Due to the low dielectric constant ($\epsilon \sim 3$) of most organic solids, the site energies of excitons and charge carriers strongly are depended both on the intrinsic electronic properties of molecules and their packing behaviors. In particular, for the charged systems, the molecular packing effects can greatly influence site energies of charge carriers.^{7,8} Energy shifts of IP or EA in the gas phase and condensed phase, which are called as electronic polarization, represent the electrostatic interactions between charge carriers and its surrounding neutral molecules. Thus, the electronic polarization can be a very importance factor to understand the functions of materials from a molecular view.

According to the Lyons relationship, the electronic polarization energy of the hole carrier (P₊) and electron carrier

(P₋) are defined as follows,^{9,10}

$$P_+ = IP_{solid} - IP_{gas} \quad (1a)$$

$$P_- = EA_{gas} - EA_{solid} \quad (1b)$$

the subscript gas/solid means single molecular IP or EA values in the gas or solid phase, respectively. The energy necessary to create a well-separated electron-hole pair, i.e., the transport gap (E_t) is defined as¹¹

$$E_t = IP_{solid} - EA_{solid} \quad (2)$$

Experimentally, these quantities can be determined using the ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES), respectively.^{12,13} The energy levels of charge carriers can be calculated either by the full QM^{14,15}, QM/PCM¹⁶⁻²⁰, QM/MM¹⁶, or MM^{8,21-23} method. Very recently, D'Avino et al. review a broad spectrum of theoretical methods to evaluate the electronic polarization in organic solids.²⁴ According to the Lyons definition eq.1, P₊/P₋ can be theoretically estimated by calculating the IP and EA values of molecules in the gas and solid phase. The gas-phase IP and EA values are readily obtained by the energy difference between the total molecular energies of neutral and charged molecules. Under Koopmans approximation, IP and EA values can also be treated as the energies of the HOMO and LUMO of the neutral molecule. In particular, when the self-interaction error are well overcome by optimally tuned range-separated functional such as LC- ω PBE, the IP and EA of the neutral molecule can be directly obtained by solving the Kohn-Sham equation.¹⁷

Moreover, the solid-phase IP and EA values can be calculated using the QM method coupled with the solvent model, such as PCM^{25, 26}. Norton and Brédas have used the DFT coupled with Conductor-like PCM (CPCM) to calculate the energies of a charged/neutral molecule in the solvent cavity. Interactions between surrounding neutral molecules and target molecule are

^a Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an city, China, 710062

^b Centre for Clean Environment and Energy, Griffith School of Environment, Gold Coast Campus, Griffith University, QLD 4222, Australia

^c Correspondent email address: yin_sw@snnu.edu.cn (S.W. Yin)

Electronic Supplementary Information (ESI) available: Electronic Energies (E_0), Ionization Potential (IP), Electron Affinity (EA), transport gap (E_t) and Polarization Energies (P_±) of oligoacene with BLW/PCM method. See DOI: 10.1039/x0xx00000x

ARTICLE

Journal Name

simulated by a dielectric constant (4.0) of typical nonpolar organic semiconductors.¹⁶ Nayak and Periasamy also used DFT/PCM methods to calculate IP and EA of organic molecules in solids, and the dielectric constant was obtained from Clausius-Mossotti equation and QM calculation.^{19,20} In this method, no experimental data is required other than the molecular structure. These totally implicitly PCM-based approaches can quantitatively evaluate the IP and EA values in the solid phase. The P_+/P_- of oligoacenes crystals are summarized in Table 1. However, as Brédas mentioned before¹⁷, the method by putting single molecule in the solvent cavity cannot capture the molecular packings effects in crystals or thin films, which determine the exact nature of the intermolecular interactions⁸. Thus, these calculations using the PCM solvent model give identical or near identical values for P_+ and P_- , which could not reveal the asymmetric nature of polarization energies between P_+ and P_- , as demonstrated in experiments. To solve this problem, a supermolecular model coupled with PCM is employed to calculate the molecular IP and EA values in the solid phase. The solvated supermolecular method explicitly includes some neighboring molecules with the consideration of long-range interactions. The coupling of surrounding molecule can, therefore, more accurately describe the molecular packing character in the solid phase. This method has been successfully used to simulate the electronic spectra of solvents. Herein, in order to simulate the localized charge within a molecule, a specific method is required to build the charged localized diabatic state. To this end, we compare the two fragment-based methods including (BLW)²⁷ and constrained DFT (CDFT)²⁸ methods to simulate the changed localized state in the oligoacene supermolecular models. Our results demonstrate that the utilization of the solvated supermolecule methods can greatly enhance the accuracy of calculated polarization energies and the asymmetric P_+ and P_- in comparison with the experimental data.

Theoretical Methods

BLW method

The BLW method involves a combination of valence bond (VB) and molecular orbital (MO) theory. For a supermolecular system, the electrons and primitive basis orbitals are naturally divided into subgroups belonging to individual monomer molecules. Each localized molecular orbital is expanded in terms of primitive orbitals which belong only to one subgroup. The molecular orbitals belonging to the same molecule are constrained to be orthogonal, while the orbitals belonging to different molecules are free to overlap. The final block-localized wave function is expressed by a Slater determinant:

$$\Psi^{\text{BLW}} = \hat{A}\{\Phi_1\Phi_2\cdots\Phi_n\} \quad (3)$$

where $\hat{A}$ is the antisymmetry operator and Φ_i is the successive product of all occupied molecular orbitals in an isolated i^{th} molecule. If all Φ_i are set to their isolated molecular ground-state occupancies, the BLW wavefunction forms an approximation to the standard wavefunction generated by the ground-state MO theory. However, if the i^{th} molecule is assigned an ionized occupancy, the corresponding wavefunction is defined as the diabatic-state one where the charge is localized on the i^{th} molecule. We label this ion as a target system whilst the remaining molecules are labeled as its explicit surrounding molecules. In this representation, Ψ^{BLW} for the

Table 1 Recent results^{16,17,20} from earlier PCM method to evaluate the polarization energies (P , eV) of oligoacene molecular crystals

		P_+	P_-	ΔP
Naphta	B3LYP/CPCM ^b (4.0)	-1.48	-1.48	0
	B3LYP/PCM ^c (2.43)	-1.11	-1.15	0.04
	exp.	-1.72	-1.10	-0.62
Antcen	B3LYP/CPCM ^b (4.0)	-1.32	-1.34	0.02
	B3LYP/PCM ^c (2.95)	-1.11	-1.17	0.07
	exp.	-1.65	-1.09	-0.56
Tetcen	B3LYP/CPCM ^b (4.0)	-1.19	-1.24	0.05
	B3LYP/PCM ^c (3.69)	-1.11	-1.20	0.09
	exp.	-1.63 ^e	-0.92 ^f	-0.71
Pencen	B3LYP/CPCM ^b (4.0)	-1.10	-1.15	0.05
	B3LYP/PCM ^c (4.82)	-1.10	-1.22	0.11
	LC- ω PBE*/PCM ^d (4.0)	-1.21	-1.17	-0.04
	exp.	-1.63	-1.17	-0.46

^a $\Delta P = P_+ - P_-$. Experimental values are taken from reference 29. The values in parentheses are the dielectric constant.

^bReference 16. ^cReferences 19 and 20. ^dReference 17.

^eReferences 30 and 31. ^fReference 32.

ground-state can be calculated iteratively using the Jacobi-rotation method³³, which prevents electrons on one subgroup from borrowing the atomic orbitals of the other subgroups. When the restriction on the length of expansion of the molecular orbitals in eq.3 is removed, the BLW method returns to the traditional MO theory.

After the BLW electron wavefunctions for charged and neutral molecules are optimized, the IP and EA values for the i^{th} molecule in the supermolecule can be calculated as follows

$$IP_{\text{sup}}^{\text{BLW}} = E_{i,\text{cation}}^{\text{BLW}} - E_{\text{neutral}}^{\text{BLW}} \quad (4a)$$

$$EA_{\text{sup}}^{\text{BLW}} = E_{\text{neutral}}^{\text{BLW}} - E_{i,\text{anion}}^{\text{BLW}} \quad (4b)$$

In eq.4a, the energy $E_{i,\text{cation}}^{\text{BLW}}$ of i^{th} cation is solved by $\langle E_{i,\text{cation}}^{\text{BLW}} | \hat{H} | E_{i,\text{cation}}^{\text{BLW}} \rangle$. The wavefunction of localized charged state is expressed as

$$\Psi_{i,\text{cation}}^{\text{BLW}} = \hat{A}\{\Phi_1 \cdots \Phi_i^+ \cdots \Phi_n\} \quad (4c)$$

Here, Φ_i^+ means the wavefunction of the i^{th} cation. The neutral ground state energy ($E_{\text{neutral}}^{\text{BLW}}$) of molecule is calculated by using $\Psi_{i,\text{neutral}}^{\text{BLW}} = \hat{A}\{\Phi_1 \cdots \Phi_i \cdots \Phi_n\}$ with all molecules in their ground states. An analogous definition for $E_{i,\text{anion}}^{\text{BLW}}$ is obtained by using Φ_i^- instead of Φ_i^+ in eq.4c.

Constrained-DFT

Constrained DFT method can also be used to describe the localized charged state by adding a Lagrange multiplier term (V_c) to Kohn-Sham energy functional.

$$W[\rho, V_c] = E_{\text{KS}}[\rho] + V_c \left(\int w_c(r) \rho(r) d^3r - N_c \right) \quad (5)$$

where $E_{\text{KS}}[\rho]$ is Kohn-Sham energy functional, $w_c(r)$ is weight function which enforces N_c electrons within the specified molecule. Through this Lagrange multiplier term V_c , CDFT can solve the minimized energy of charged localized state which putting an excess charge on a target molecule. Then the IP/EA for the supermolecule are solved:

$$IP_{\text{sup}}^{\text{CDFT}} = E_{i,\text{cation}}^{\text{CDFT}} - E_{\text{neutral}}^{\text{SCF}} \quad (6a)$$

$$E_{\text{sup}}^{\text{CDFT}} = E_{\text{neutral}}^{\text{SCF}} - E_{i,\text{anion}}^{\text{CDFT}} \quad (6b)$$

$E_{i,\text{charged}}^{\text{CDFT}}$ means the minimum charge state energy of supermolecule where the target molecule i are enforced as charged occupation by Lagrange multiplier in eq.5. $E_{\text{neutral}}^{\text{SCF}}$ is the supermolecular neutral energy which is obtained from traditional MO theory. The main difference between $E_{\text{neutral}}^{\text{SCF}}$ and $E_{\text{neutral}}^{\text{BLW}}$ in eq.4 is that BLW strictly limits intermolecular charge transfer (CT). This difference can be successfully used to analyze the CT contributions to total intermolecular interaction.³³

Through this supermolecule approach, both BLW and CDFT methods can more accurately describe the short-range molecular interaction which includes the molecular packing information. Additionally, the long-range interactions also can be considered as the reaction field approaches, i.e., PCM solvent model. Then the IP and EA values in the solid phase can be calculated. For more "first-principles" to evaluate the long-range interaction by solvent reaction field, we also use the Clausius-Mossotti equation to calculate the solid dielectric constant on the basis of the QM calculated molecular volume. In this paper, our studies aim at the electronic polarization energy. Thus, both EA and IP values are calculated on the basis of the fixed molecular geometry. The adiabatic EA and IP in solid phase can also be solved during the geometric structure optimization processes using the solvated supermolecular BLW/DFT method.

Computational details

In this study, the most neighboring four molecules of the studied molecule are considered to form supermolecules in oligoacene crystals of naphthalene (NAPHTA06)³⁴, anthracene (ANTCEN09)³⁵, tetracene (TETCEN01)³⁶, and pentacene (PENCEN04)³⁷. These pentamer supermolecules (they are defined as 5M) are shown in Figure 1. To testify the size effects of supermolecules on the electronic polarization, we also enlarge the pentamer to the nonamer (9M) by adding four extra neighboring molecules in the ab-plane of naphthalene crystal.

Here, the charge is restricted in the central molecule using the BLW and CDFT methods, respectively. The BLW-based DFT calculations are conducted using a special GAMESS-US package^{38,39}

including the BLW module developed by Mo and his coworkers^{27,40,41}. The CDFT calculations are performed by using the NWChem package⁴². All the computations are at the B3LYP/6-311G(d,p) level.⁴³⁻⁴⁵

To simulate the long-range environment, we employ the PCM solvent model with a molecular cavity built up from the united atom model, and the solvent is defined by the dielectric constant. The dielectric constant (ϵ) is calculated based on the Clausius-Mossotti equation^{19,20}

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\rho}{M} N_A \alpha \quad (7)$$

where ρ , M , N_A and α are the density of material, molecular mass, Avogadro number and the electronic polarizability, respectively. $\rho N_A / M$ is reciprocal of the molecular volume. Molecular volume is obtained at the 6-311G(d,p) level (IOp(6/45=512000) is used in the volume calculation for better accuracy). The isotropic static molecular polarizability is calculated on the optimized geometry at the 6-311G(d,p) level. The molecule is defined as a sphere which has an equivalent volume of the concerned molecule. The dielectric constant calculations are carried out using the Gaussian 09 code.⁴⁶

Results and Discussion

Comparison of BLW and CDFT method for naphthalene trimer model

We first take a face-to-face naphthalene trimer model with different separation distances as an example to compare the performances of the BLW and CDFT methods on the estimation of electronic polarizations under the gas-phase and solid-phase environment. In order to verify whether the BLW and CDFT methods can really localize an excess charge on the central molecule, the spin densities are plotted, which are shown in Figure 2. We can clearly see that the unpaired electron densities are localized in the center of trimer, which demonstrates that the BLW and CDFT methods can effectively deal with electron localization. Furthermore, a naphthalene trimer model with radical cation center is similar to only one electron in HOMO and radical anion center is similar to only one electron in LUMO for the isolated naphthalene molecule, which have the similar orbital character.

Fig. 1 Naphthalene various models (a) monomer(1M), (b) 5M and (c) 9M. Brown molecule is the charged molecule and other closest surrounding molecules are from crystal structure. These molecules are embedding in gray solvent cavity.

Fig. 2 Spin density surface (iso-surface value = 0.005 a.u.) of the naphthalene trimer model using BLW method (a,b) and CDFT method (c, d). Among of them, a and c mean cationic state localized on the center molecule while b and d mean with anionic state. Alpha density is indicated in red, and beta density is indicated in blue. HOMO (e) and LUMO (f) (iso-surface value = 0.05 a.u.) are the monomer of naphthalene, respectively.

Fig. 3 Effective polarization energy from BLW method and CDFT method for naphthalene trimer models with a face-to-face distance range from 3.0 Å to 6.0 Å. (a) The optimized geometry of neutral naphthalene at B3LYP/6-311G(d,p) level. In this trimer, the middle molecule is the system molecule and the other two molecules are set as explicit solvation molecules. The center molecules showed with the ball-and-stick model represents the system molecule, the tube model represents the neighboring molecules treated with explicit solvation model. Calculated polarization energy (b) P_+ and (c) P_- of the naphthalene trimer, as a function of distance.

Gas-phase environment The electron polarization energy obtained from the BLW and CDFT methods as a function of the distances between naphthalenes are reported in Figure 3. It suggests that the results based on the BLW and CDFT methods are similar to each other, in particular, when the distance is larger than 3.4 Å. The small difference of electron polarization at the short distance can be explained according to eqs.4-6 where the contributions of charge transfer are included in the CDFT method but excluded in the BLW calculations for the neutral trimer. In addition, the electronic polarization of cation (P_+) has more negative values than that of anion (P_-). It indicates that calculations using the BLW and CDFT methods can successfully capture the electrostatic polarization feature. On the other hand, P_+ and P_- have been demonstrated to possess the asymmetric nature due to opposite sign of charge-quadrupole interaction.

Figure 3 also show that the P_+ values decrease with the increase of the distance. However, the P_- values firstly decrease and then gradually increases with the increase of the distance. This phenomenon can be attributed to the balance of polarization and electrostatic interactions since the polarization energy is related with the molecular polarizability and its applied field from the environment. But the P_+ values are always negative and decrease with the increase of separation distance. For electrostatic interactions, the quadrupole moments play a dominant role in electrostatic interactions because of the lack of dipole for neutral acenes. Among all the components of molecular quadrupole, there are negative values along molecular normal direction and positive ones around the molecular plane.²¹ It leads to the charge-quadrupole values for a positive charge in the center of trimer are always negative while the charge-quadrupole values of negatively charged systems are positive.

Solid-phase environment The molecule in solid is considered as a solvated system with its own type of molecules as solvent. The solvent in the PCM model is defined by the dielectric constant. To further explore whether the BLW and CDFT methods in combination with the PCM model indeed capture the polarization effect, we consider a classic electrostatic model of polarization associated with a charge in a dielectric.^{13,17,47,48} In Born expression⁴⁹, the polarization energy from induced dipole (P^{id}), i.e., "real" polarization excluding electrostatic interaction is described as

$$P_{+/-}^{id} = -\frac{e^2}{8\pi\epsilon_0 R} \left(1 - \frac{1}{\epsilon}\right) \quad (8)$$

where e is the elemental electron charge and R is an effective molecular radius. Because of only two electrons difference, we can image that sizes of cationic and anionic molecule are very similar. If the polarization effects can be properly described, the calculated

value of P_+/P_- should be linear in $1 - (1/\epsilon)$ for any ϵ , and the slopes of P_+ and P_- are very close to each other. Using our BLW/PCM and CDFT/PCM results of the face-to-face naphthalene trimers, Figure 4 shows the relationship between the calculated P_+/P_- values and $1 - (1/\epsilon)$. The slope of a straight line is related to the reciprocal of $2R$. From the slope of P_+/P_- with the BLW method, we can get the effective radii for cationic and anionic molecules are 4.316 Å and 4.478 Å, respectively, which are larger than that of neutral molecules listed in Table 2. In Figure 4, P_+ and P_- using the CDFT/PCM method have a good linear relationship with $1 - (1/\epsilon)$. Yet the slopes of P_+ and P_- are quite different. The effective radii for cation and anion are 4.337 Å and 2.692 Å, respectively. Compared with those from the BLW/PCM calculations, the CDFT/PCM calculations give a similar cationic size while much underestimated anionic radii in solvated trimer model. Those means that PCM reaction field coupled with CDFT calculations would notably change the size of localized anions, which is in contrast to Born expression eq.8. In a short summary, the BLW/PCM method can successfully capture electrostatic polarization effect while the CDFT/PCM method cannot correctly describe anion polarization effects.

Fig. 4 Calculated polarization energy P (eV) of the face-to-face orientation of trimer model of naphthalene using BLW method and CDFT method in combination with PCM model, as a function of $1 - (1/\epsilon)$. Straight dashed lines are a linear fit.

Effect of charge delocalization on the electronic polarization

When the electronic coupling between the neighboring molecules are not much smaller than the charge reorganization energy, the charge carriers may delocalize on several neighboring molecules. At this situation, the excess charge can not be constrained on the single molecule as we proposed before. Herein, we separately restrain the excess charge on 1-4 face-to-face naphthalene

Table 2 Calculated values for electronic polarizability, molecular volume, radius of the molecule and dielectric constant (ϵ). Experimental ϵ values are given for the comparison purpose.

Compound	$\alpha/\text{\AA}^3$	Volume/ $\text{\AA}^3$	$R/\text{\AA}$	ϵ^a	$\epsilon(\text{exp.})$
Naphta	15.70	178.74	3.495	2.75 (2.43)	2.82 ^{b51}
Antcen	24.32	238.82	3.849	3.23 (2.95)	3.20 ^{b52,53}
Tetcen	34.63	298.84	4.148	3.83 (3.69)	3.2 ^{c54}
Pencen	46.54	358.96	4.410	4.56 (4.82)	4.0 ^{c55}

^aThe value in parentheses had been determined at the B3LYP/6-31G(d) level of theory and reported in ref²⁰. ^bCapacitive measurement (± 0.1). ^cOptical measurement.

Fig. 5 The face-to-face naphthalene multimers (a) 3M-paral, (b) 4M-paral, (c) 5M-paral and (d) 6M-paral whose neighbors separated distance is 4 Å. These multimers are embedding in the polarizable continuum environment with dielectric constant 2.75. All the multimers keep two outermost molecules act as explicit solvent molecules (light blue), and the remaining molecules as a whole charge local (deep blue).

multimer models. The distance of neighboring molecules is fixed at 4 Å. These models are showed in Figure 5. In practical BLW/DFT calculations, we make the one or several center molecules as a whole subgroup which has an excess charge to investigate the charge delocalization effect on the electronic polarization. When the charge is delocalized on several molecules, the gas-phase IP and EA in eq.1 are for models with several molecules instead of the single molecule in gas phase.

As is evident from Table 3, the larger charge delocalization leads to the smaller $P_{+/-}$, which is very similar to results from COHSEX/MM method⁵⁰. In addition, the charge delocalization notably decrease the transport gap E_t , which does not agree with GW/CR results reported by Li et al., i.e. E_t is independent with charge delocalization.⁵⁰ This difference may be due to the delocalization error of hybrid B3LYP functional. To this end, we compare the effect of range-separated functional (CAM-B3LYP⁵¹) and B3LYP functionals on the electronic polarization and transport energy. We can note that the utilization of the range-separated functional can remarkably weaken the charge delocalization effect on the E_t . However, the electronic polarization($P_{+/-}$) show little dependent on the choice of functionals.

Table 3 Calculated electronic polarization energy and transport gap for face-to-face parallel multimers. xM-paral models mean an excess charge is located on x-2 center molecules combined with two explicitly neutral molecules.

Method	Model	E_t	P_+	P_-
B3LYP	3M-paral	6.09	-1.51	-0.84
	4M-paral	5.32	-1.18	-0.77
	5M-paral	5.00	-0.98	-0.71
	6M-paral	4.83	-0.85	-0.66
CAM-B3LYP	3M-paral	6.25	-1.51	-0.83
	4M-paral	5.92	-1.18	-0.77
	5M-paral	5.79	-1.00	-0.76
	6M-paral	5.75	-0.89	-0.74

Electron polarization for naphthalene supermolecules

Table 2 shows our calculated molecular electronic polarizability, volume, radius. Based on these parameters, the dielectric constant is solved using the Clausius-Mossotti eq.6. Briefly speaking, the calculated dielectric constant increases with the increasing conjugated lengths of oligoacenes. Compared with experimental data, we find that the calculated ϵ values agree well with the experimental data of naphthalene and anthracene, but and slightly larger than that of tetracene and pentacene. After carefully checking the measurement method, we find that the experimental ϵ values of naphthalene and anthracene were derived from the capacitive measurement, while the ϵ values of tetracene and pentacene were derived from optical measurement. Generally, the ϵ values from the optical measurement are smaller than the that from the capacitive estimation.²² For example, the ϵ values of C_{60} have been inferred from optical measurements and capacitive estimate is 4.08 and 4.4, respectively.^{52, 53} In this regard, our calculations can well reproduce the dielectric constant from the optical measurement.

However, our calculated ϵ values are 0.2 ~ 0.3 away from other theoretical values²⁰, which can be ascribed to the different number of points per Bohr³ for Monte-Carlo calculation of molecular volume. We already testified that 512000 points per Bohr³ would produce very accuracy isodensity molecular volume.⁵⁴

Based on those data, we calculate P_+ , P_- for the naphthalene's monomer (1M), 5M, and 9M supermolecules in the gas/solid phases. The molecular structures are showed in Figure 1. The experimental data are also listed in Table 4.

In the gas phase, the BLW and CDFT calculations can give very similar P_+ and P_- values for supermolecular 5M and 9M models, which is in accordance with the trimer's polarizations shown in Figure 3. Both P_+ and P_- increase with the increase of the size of clusters from 5M to 9M. And the short-range intermolecular interactions cause the improved asymmetric feature for P_+ and P_- . Yet, P_+ and P_- for the 5M and 9M in the gas phase are much smaller than their experimental data, which is due to the neglect of the long-range interaction in the gas phase. When the supermolecules

Table 4 Calculated polarization energies (P , eV) of naphthalene various model and compare with experimental values.^a

Method	Model	Gas-phase			Solid-phase		
		P_+	P_-	ΔP	P_+	P_-	ΔP
BLW	1M				-1.198	-1.319	0.121
	5M	-0.496	-0.095	-0.401	-1.347	-1.067	-0.280
	9M	-0.586	-0.233	-0.353	-1.359	-0.992	-0.367
CDFT	1M				-1.424	-1.470	0.046
	5M	-0.451	-0.079	-0.371	-1.557	-1.414	-0.143
	9M	-0.533	-0.212	-0.320	-1.582	-1.433	-0.149
	exp.				-1.72	-1.10	-0.62

^a $\Delta P = P_+ - P_-$. Gas-phase and solid-phase denote the polarization energy without and with PCM model, respectively.

Table 5 Polarization energies (P , eV) of oligoacenes obtained from the solvated 5M model and compare with experimental values.

	Solvated 5M			exp.		
	P_+	P_-	ΔP	P_+	P_-	ΔP
Naphta	-1.347	-1.067	-0.280	-1.72	-1.10	-0.62
Antcen	-1.253	-1.053	-0.201	-1.65	-1.09	-0.56
Tetcen	-1.242	-0.972	-0.270	-1.63	-0.92	-0.71
Pencen	-1.134	-0.995	-0.139	-1.63	-1.17	-0.46

are embedding in the solvent, the calculated P_+ and P_- values are, then, closer to the experimental data. This illustrates the long-range interaction described by the PCM reaction field is essential in the calculations of the bulk polarization for oligoacenes.

Moreover, how the short-range interactions from neighboring molecules affect the polarization energies of oligoacene molecular crystals is discussed based on our results. Without neighboring molecules, i.e., 1M, P_- is slightly larger than P_+ , which is opposite to experimental data. The PCM calculations of 1M completely ignore the molecular packing effect. The anionic and cationic molecules have a same solute reaction cavities on the basis of UFF radii. Thus, anionic system has a stronger solute-solvent interaction which results in a slightly larger P_- value than P_+ . After adding four neighboring molecules, the BLW/PCM calculations can give a better P_+ and P_- behaviors i.e. larger P_+ due to more stabilized electrostatic interactions between cations. With the increase of the number of neighboring molecules from 5M to 9M, the calculated P_+ values just increase by 0.013 eV and P_- decrease by 0.074 eV, respectively. The summation of explicit short-range electrostatic interaction and implicit long-range interaction is almost independent of the size of QM region, which is very agreement with the recent QM/MM embedding results.⁵⁰ Model 5M already captures both short-range and long-range interaction by BLW/PCM method to estimate electronic polarization of electron and hole carriers.

As we mentioned on trimer model in Fig.3, the CDFT/PCM results show the different slopes of P_- and P_+ with the increase of the dielectric constant ϵ . This difference of P_- and P_+ is much smaller in the solvated 5M and 9M models.

Polarization energies for the oligoacenes using the solvated supermolecular approach

The BLW method combined with the solvated 5M supermolecular models are employed to study electronic polarization of oligoacene crystal since they can give the optimal calculation results based on aforementioned discussion. The calculated P_+ and P_- values are listed in Table 5. Our calculated P_- values can well match the

experimental data. Yet, the P_+ values are 0.4 ~ 0.5 eV lower than the experimental values. However, in contrast to PCM calculation results of 1M listed in Table 1 or in literature^{16,17,20}, the solvated supermolecular approach will remarkably improve difference between the P_+ and P_- values because of the explicit consideration of neighboring molecules. Specifically, this solvated supermolecular method can consider the molecular packing effect and include the short-range charge-quadrupole interaction.⁶⁰ The different signs of charge-quadrupole interactions for anions and cations successfully represent the asymmetric nature of P_- and P_+ . Although our calculated ΔP values are 0.3~0.4 eV smaller than the experimental data, the results with the solvated 5M demonstrate the qualitative asymmetric ΔP character. From the calculations with the 9M models listed in Table 4, it suggests that the more accurate electronic polarization may be achieved when more neighboring molecules are included in the solvated supermolecule model.

Given the effect of the conjugated length on the electronic polarization, our results demonstrate that the larger extended π -conjugated molecules are related to the smaller electronic polarization. This trend is similar to other group's numerical

Table 6. Calculated transport gap and polarization Energies ($P_{\pm}$) obtained from solvated 5M supermolecular models coupled with different DFT functionals.

Properties	Functional	Naphta	Antcen	Tetcen	Pencen
E_t	CAM-B3LYP	6.31	4.79	3.77	2.89
	BLYP	6.01	4.46	3.46	-
	B3LYP	6.14	4.61	3.59	2.74
P_+	CAM-B3LYP	-1.34	-1.25	-1.24	-1.13
	BLYP	-1.35	-1.25	-1.24	-
	B3LYP	-1.35	-1.25	-1.24	-1.13
P_-	CAM-B3LYP	-1.07	-1.06	-0.98	-1.01
	BLYP	-1.07	-1.05	-0.97	-
	B3LYP	-1.07	-1.05	-0.97	-1.00

ARTICLE

Journal Name

results.^{16,22}**Effect of exchange-correlation functionals on the electronic polarization**

From Table 3, we also investigated the effect of the exchange-correlation functionals of DFT on the electronic polarization and E_t for 5M supermolecule on the basis of crystal structure. Here we respectively chose range-separated functional CAM-B3LYP, hybrid B3LYP and pure GGA functional BLYP^{61,62} to calculate the molecular IP and EA in gas and solid phase which is listed in Table S6 (Supporting Information). The transport gap and electronic polarization are listed in Table 6. The exchange-correlation functionals can significantly influence the transport gap in the solid phase. The calculations with the pure GGA BLYP produce the smaller E_t values, followed by those with the B3LYP. And the calculations with the range-separated functional CAM-B3LYP generate the largest energy transport gap. Interestingly, the electronic polarizations are independent with the choice of the exchange-correlation functionals, which may be due to the delocalization errors of DFT functionals to the IP/EA values in gas and solid phase can be canceled in eq.4a-b. Thereby, the BLW coupled with PCM model can be accurately estimated the electronic polarization.

Conclusion

By supermolecule approach, BLW method can partially include molecular packing effect on localized charged state and PCM model can effectively simulate the long-range interaction in solid phase. Thus the solvated supermolecule approach, i.e., BLW/PCM combine explicit and implicit advantages to estimate solid-phase IP and EA value. The electronic polarization obtained from 5M behaves very nice asymmetric feature of P_+ and P_- , which will more accurately estimate the absolute values of IP and EA in solid phase. The limits of BLW/PCM is the short-range interaction is related to how many neighbor molecules are included in supermolecular model. Basically the more neighbor molecules result in more accurate solid-phase IP and EA. However, large supermolecule also cost large computation time for BLW calculations. Thus, the multi-core parallel computation needs to develop to testify larger sized BLW/PCM calculations.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (21173138), Fundamental Research Funds of Central Universities (GK201303004). Author SW Yin thanks for helpful and insightful discussions with Dr. David Beljonne and acknowledges Prof. Yirong Mo to provide the BLW program.

References

- S. R. Forrest, *Nature*, 2004, **428**, 911-918.
- A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269-277.
- S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, **459**, 234-238.
- H. Ma, H.-L. Yip, F. Huang and A. K. Y. Jen, *Adv. Funct. Mater.*, 2010, **20**, 1371-1388.
- V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Brédas, *Chem. Rev.*, 2007, **107**, 926-952.
- S. R. Forrest and M. E. Thompson, *Chem. Rev.*, 2007, **107**, 923-925.
- O. L. Griffith, J. E. Anthony, A. G. Jones and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 2010, **132**, 580-586.
- S. M. Ryno, C. Risko and J.-L. Brédas, *J. Am. Chem. Soc.*, 2014, **136**, 6421-6427.
- L. E. Lyons, *J. Chem. Soc.(Resumed)*, 1957, 5001-5007.
- E. A. Silinsh, *Organic Molecular Crystals: Their Electronic States*, Springer: New York, 1978.
- J.-L. Brédas, *Materials Horizons*, 2014, **1**, 17-19.
- I. G. Hill, D. Milliron, J. Schwartz and A. Kahn, *Appl. Surf. Sci.*, 2000, **166**, 354-362.
- I. G. Hill, A. Kahn, Z. G. Soos and J. R. A. Pascal, *Chem. Phys. Lett.*, 2000, **327**, 181-188.
- F. Castet, P. Aurel, A. Fritsch, L. Ducasse, D. Liotard, M. Linares, J. Cornil and D. Beljonne, *Phys. Rev. B*, 2008, **77**, 115210.
- L. E. Ratcliff, L. Grisanti, L. Genovese, T. Deutsch, T. Neumann, D. Danilov, W. Wenzel, D. Beljonne and J. Cornil, *J. Chem. Theory Comput.*, 2015, **11**, 2077-2086.
- J. E. Norton and J.-L. Brédas, *J. Am. Chem. Soc.*, 2008, **130**, 12377-12384.
- H. Sun, S. Ryno, C. Zhong, M. K. Ravva, Z. Sun, T. Körzdörfer and J.-L. Brédas, *J. Chem. Theory Comput.*, 2016, **12**, 2906-2916.
- P. E. Schwenn, P. L. Burn and B. J. Powell, *Org. Electron.*, 2011, **12**, 394-403.
- P. K. Nayak and N. Periasamy, *Org. Electron.*, 2009, **10**, 532-535.
- P. K. Nayak and N. Periasamy, *Org. Electron.*, 2009, **10**, 1396-1400.
- S. M. Ryno, S. R. Lee, J. S. Sears, C. Risko and J.-L. Brédas, *J. Phys. Chem. C*, 2013, **117**, 13853-13860.
- G. D'Avino, L. Muccioli, C. Zannoni, D. Beljonne and Z. G. Soos, *J. Chem. Theory Comput.*, 2014, **10**, 4959-4971.
- G. D'Avino, S. Mothy, L. Muccioli, C. Zannoni, L. Wang, J. Cornil, D. Beljonne and F. Castet, *J. Phys. Chem. C*, 2013, **117**, 12981-12990.
- D. A. Gabriele, M. Luca, C. Frédéric, P. Carl, A. Denis, G. S. Zoltán, C. Jérôme and B. David, *J. Phys.: Condens. Matter*, 2016, **28**, 433002.
- R. Improtà, V. Barone, G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2006, **125**, 054103.
- R. Improtà, G. Scalmani, M. J. Frisch and V. Barone, *J. Chem. Phys.*, 2007, **127**, 074504.
- Y. Mo, L. Song and Y. Lin, *J. Phys. Chem. A*, 2007, **111**, 8291-8301.
- Q. Wu and T. Van Voorhis, *Phys. Rev. A*, 2005, **72**, 024502.
- N. Sato, H. Inokuchi and E. A. Silinsh, *Chem. Phys.*, 1987, **115**, 269-277.
- M. Pope, J. Burgos and J. Giachino, *J. Chem. Phys.*, 1965, **43**, 3367-3371.
- R. S. Berry, J. Jortner, J. C. Mackie, E. S. Pysh and S. A. Rice, *J. Chem. Phys.*, 1965, **42**, 1535-1540.
- N. Ando, M. Mitsui and A. Nakajima, *J. Chem. Phys.*, 2008, **128**, 154318.
- Y. Mo and S. D. Peyerimhoff, *J. Chem. Phys.*, 1998, **109**, 1687-1697.
- C. P. Brock and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1982, **38**, 2218-2228.
- C. P. Brock and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1990, **46**, 795-806.
- D. Holmes, S. Kumaraswamy, A. J. Matzger and K. P. C. Vollhardt, *Chem. - Eur. J.*, 1999, **5**, 3399-3412.
- C. C. Mattheus, A. B. Dros, J. Baas, A. Meetsma, J. L. d. Boer and T. T. M. Palstra, *Acta Crystallogr., Sect. C*, 2001, **57**, 939-941.

38. M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347-1363.
39. M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry*, eds. G. Frenking, K. S. Kim and G. E. Scuseria, Elsevier, Amsterdam, 2005, pp. 1167-1189.
40. Y. Mo, J. Gao and S. D. Peyerimhoff, *J. Chem. Phys.*, 2000, **112**, 5530-5538.
41. Y. Mo, L. Song, Y. Lin, M. Liu, Z. Cao and W. Wu, *J. Chem. Theory Comput.*, 2012, **8**, 800-805.
42. M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus and W. A. de Jong, *Comput. Phys. Commun.*, 2010, **181**, 1477-1489.
43. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
44. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
45. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
46. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. o. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, d. n. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09; Gaussian, Inc.: Wallingford, CT, USA, 2009.
47. S. Refaely-Abramson, S. Sharifzadeh, M. Jain, R. Baer, J. B. Neaton and L. Kronik, *Phys. Rev. B*, 2013, **88**, 081204.
48. S. Sharifzadeh, A. Biller, L. Kronik and J. B. Neaton, *Phys. Rev. B*, 2012, **85**, 125307.
49. I. N. Levine, *Quantum chemistry*, Upper Saddle River, NJ: Pearson Prentice Hall, 2009.
50. J. Li, G. D'Avino, I. Duchemin, D. Beljonne and X. Blase, *J. Phys. Chem. Lett.*, 2016, **7**, 2814-2820.
51. T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51-57.
52. P. C. Eklund, A. M. Rao, Y. Wang, P. Zhou, K.-A. Wang, J. M. Holden, M. S. Dresselhaus and G. Dresselhaus, *Thin Solid Films*, 1995, **257**, 211-232.
53. A. F. Hebard, R. C. Haddon, R. M. Fleming and A. R. Kortan, *Appl. Phys. Lett.*, 1991, **59**, 2109-2111.
54. S. Y. Zhou, S. W. Yin, W. P. Lai, Y. Z. Liu and Y. Wang, *Comput. Mater. Sci.*, 2016, **112**, Part A, 67-74.
55. R. W. Munn and D. F. Williams, *J. Chem. Phys.*, 1973, **59**, 1742-1746.
56. N. Karl, H. Rohrbacher and D. Siebert, *phys. stat. sol. (a)*, 1971, **4**, 105-109.
57. R. W. Munn, J. R. Nicholson, H. P. Schwob and D. F. Williams, *J. Chem. Phys.*, 1973, **58**, 3828-3832.
58. S. Tavazzi, L. Raimondo, L. Silvestri, P. Spearman, A. Camposeo, M. Polo and D. Pisignano, *J. Chem. Phys.*, 2008, **128**, 154709.
59. T. Li, J. W. Balk, P. P. Ruden, I. H. Campbell and D. L. Smith, *J. Appl. Phys.*, 2002, **91**, 4312-4318.
60. P. J. Bounds and R. W. Munn, *Chem. Phys.*, 1981, **59**, 41-45.
61. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
62. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.