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REGULAR ARTICLE

Theoretical prediction of ionization/oxidation potentials in conjugated polymers

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Abstract Various density functional theory (DFT) functionals and semiempirical techniques were used to predict the ionization potentials of selected conjugated polymers. Ionization potentials at infinite chain lengths were estimated using Meier fit on oligomer data. Calculated gas-phase ionization potentials with BHandH functional showed good correlation with the experimental data. The results from the semiempirical techniques do not compare as favorably as the ones obtained from DFT methods. The data fitting allowed us to estimate the size of "*effective ionization length*", which spanned over 20–30 double bonds in the conjugated backbone of the polymer in question.

Keywords Ionization potential · Oxidation potential · Conjugated polymer

1 Introduction

Conjugated polymers are of great interest in electronic and optoelectronic devices. The rapid growth of technological applications of π-conjugated materials is expected within the next decade. In particular, the use of conjugated polymers is explored in photovoltaic cells, organic light-emitting diodes (OLEDs), and thin-film transistors. These organic semiconductors have fascinating properties due to rich variety of interplay between their electronic structure and their geometric structure. Despite the enormous interest, there still exist many theoretical challenges in predicting the electronic, optical, and electrochemical properties of these systems. One of those less addressed property of conjugated polymers is their ionization potentials (IPs) [1, 2]. The lack of such studies is not due to the absence of relevant computational methods rather than the absence of reliable theoretical protocols that can work for any conjugated polymer. It is a well-known fact that the geometrical features, structural units, and chain length as well as packing of individual chains have significant impact on the magnitude of ionization potentials in conjugated polymers [3]. Therefore, accurate predictions of ionization/oxidation potentials (IPs/OPs) of conjugated systems must also take account of the interactions in the medium.

It is crucial to know beforehand the magnitude of IP/OP of a material that will be utilized in technological applications. For instance, it is believed that the open circuit voltage of organic solar cells depends on the difference of HOMO of the donor system (usually a conjugated polymer) and LUMO of the acceptor in the active layer [4]. Therefore, the information regarding the location of frontier energy levels is vital in optimizing the photovoltaic performance of solar cells. The same argument is also true of OLED applications, where the alignment of energy levels of various chromophores is critical for efficient functioning of devices [5]. The location of HOMO energies also provides information regarding stability of the conjugated system [6]. Thus, it is clear that accessing the IPs of conjugated polymers before laborious synthetic work would be useful for speeding up the efforts to work on potentially

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interesting systems. In this context, computational chemistry-aided design of novel conjugated polymers offers vast opportunities for the scientific community.

In the present study, we carried out computational studies to reveal the predicting power of various density functional theory (DFT) methods and semiempirical techniques in estimation of ionization potentials in conjugated polymers. We have collected the IP/OP values of previously synthesized polymers and used them as reference to assess the performance of calculated IPs for each theoretical method. The polymeric IPs can be estimated based on fitting of oligomer data at infinite chain length. The prediction of IPs of thiophene-based polymers is of special interest considering the recent applications of relevant systems in photovoltaic devices.

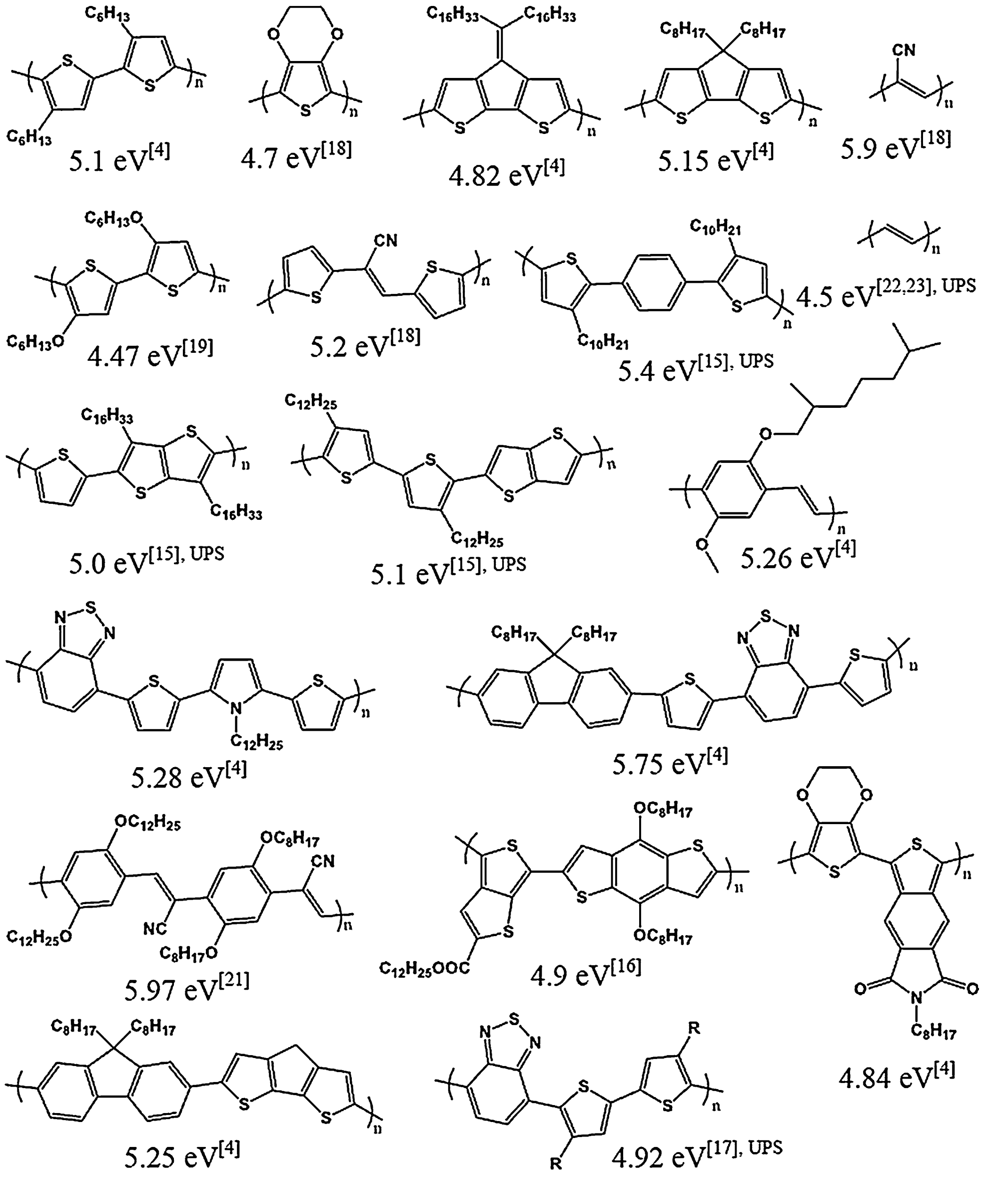
2 Theoretical methods

The gas-phase IPs were estimated by calculating the energy changes in the following reaction [7]

$$M(g) \rightarrow M^{+}(g) + e^{-} \tag{1}$$

BP86, PBE0, PW91, BHandH, B3LYP, and CAM-B3LYP DFT functionals as well as AM1, PM3, and INDO semiempirical methods were used in geometry optimizations for both neutral and cation species. The standard 6-31G(d) basis set was used throughout DFT calculations. The zero-point energy (ZPE) and enthalpy of some of the ground-state structures and cationic species were also calculated using frequency calculations. Their contribution to the estimation of IPs has been found quite small

Fig. 1 The chemical structure and experimental IPs/OPs of the conjugated polymers calculated in this study. Ionization potentials determined by ultraviolet photoelectron spectroscopy technique are noted in superscripts. *R* stands for 3,7,11-Trimethyldodecyl



(0.01–0.03 eV for ZPE and <0.05 eV for enthalpy changes); thus, frequency calculations were neglected in future calculations to save computational time. All semiempirical calculations were performed with AMPAC [8], whereas Gaussian 03 [9] and 09 packages were utilized for DFT calculations.

Depending on the size of repeat unit, oligomers in sizes up to dodecamer were considered in the theoretical calculations. Polymeric IPs were obtained by extrapolation of oligomer data for increasing chain lengths [10–13]. The oligomer IPs were plotted against the number of repeat units, and the data were fitted using Meier fit [14] to account for the saturation in the infinite chain length limit by using the following equation;

$$\mathrm{IP}_n = \mathrm{IP}_\infty + (\mathrm{IP}_1 - \mathrm{IP}_\infty)\mathrm{e}^{-a(n-1)} \tag{2}$$

Here, IP_1 is the ionization potential for the parent oligomer, IP_∞ is the ionization potential at infinite chain length, a is the fitting parameter, and n is the number of repeat units in the oligomer structure. While Meier fit is specifically designed to predict the band gaps in conjugated polymers, it has been proved to be useful for the non-linear data analyzed in the current work in characterization of lim (IP) as $n \to \infty$.

3 Results and discussion

The chemical structures of the polymers studied in this work are illustrated in Fig. 1. Our selection for this particular set of polymers is totally random. Nevertheless, we want to acknowledge the fact that most of these polymers have been utilized in organic photovoltaic devices [15–23]. Thiophene-based conjugated polymers are of particular interest for solar cells; therefore, most of the structures shown in Fig. 1 include thiophene derivatives of some sort. A considerable amount of data were taken from a few sources [4, 15] due to widespread reports of electrochemical or photoionization data even for the same conjugated polymer (see below for further discussion).

There are several ways to measure the HOMO energies of conjugated polymers. Cyclic voltammetry (CV) and ultraviolet photoelectron spectroscopy (UPS) are the most widely used experimental techniques, while other methods have also been pursued [24–26]. Although both techniques, in principle, aim to measure the HOMO level, there exists quite a spread in reported experimental ionization potentials. For instance, the oxidation potential (from CV experiments) of poly(3-hexylthiophene) (P3HT) is reported to vary between 4.75 and 5.2 eV [19, 27, 28], whereas measurements based on UPS technique resulted in numbers between 4.65 and 5.2 eV [15, 27, 29, 30]. This large discrepancy between the reported values is probably due to different experimental conditions, varying molecular weights of the polymers used in those experiments. Tada et al. [24] emphasized the importance of in situ measurements for accurate measurements of ionization potentials; otherwise, surface doping of polymers could significantly alter the results to yield erroneous data. UPS measurements are performed on solid films, and the interchain interactions in the solid state cause significant alterations in the frontier energy levels (Davydov Splitting). CV measurements are performed in solution, and the experimental oxidation potentials are a reflectance of frontier energy levels of individual polymer chains in solution. Thus, it might be reasonable to expect a few tenths of eV variation between the reported oxidation potential and ionization potential for the same polymer. IPs/OPs can also change with slight modifications in the chemical structure of the polymeric system. For instance, poly(3-methylthiophene), poly(3-butylthiophene), and poly(3-octylthiophene) have OPs as 4.6 eV [24], 5.05 eV [4], and 5.2 eV [31], respectively.

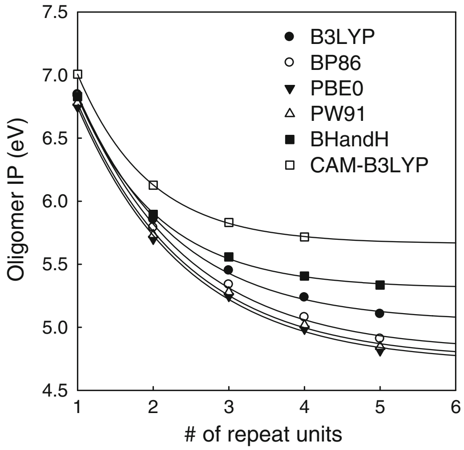


Fig. 2 Chain size evolution of the ionization potentials of P3HT oligomers as calculated using various DFT functionals along with 6-31G(d) basis set. *Solid lines* are Meier fits across the calculated values. Note that the regression coefficients for Meier fits were at least 0.998 or better for all the DFT data analyzed throughout this work

Table 1 Calculated gas-phase IPs of P3HT oligomers (in eV) with various DFT functionals along with 6-31G(d) basis set

# of Repeat units	BP86	PBE0	PW91	BHandH	B3LYP	CAM-B3LYP
1	6.84	6.75	6.78	6.83	6.85	7.01
2	5.79	5.70	5.73	5.90	5.86	6.13
3	5.34	5.25	5.28	5.56	5.45	5.83
4	5.08	4.99	5.02	5.41	5.24	5.72
5	4.91	4.82	4.85	5.34	5.11	–
∞	4.89	4.80	4.82	5.33	5.04	5.68

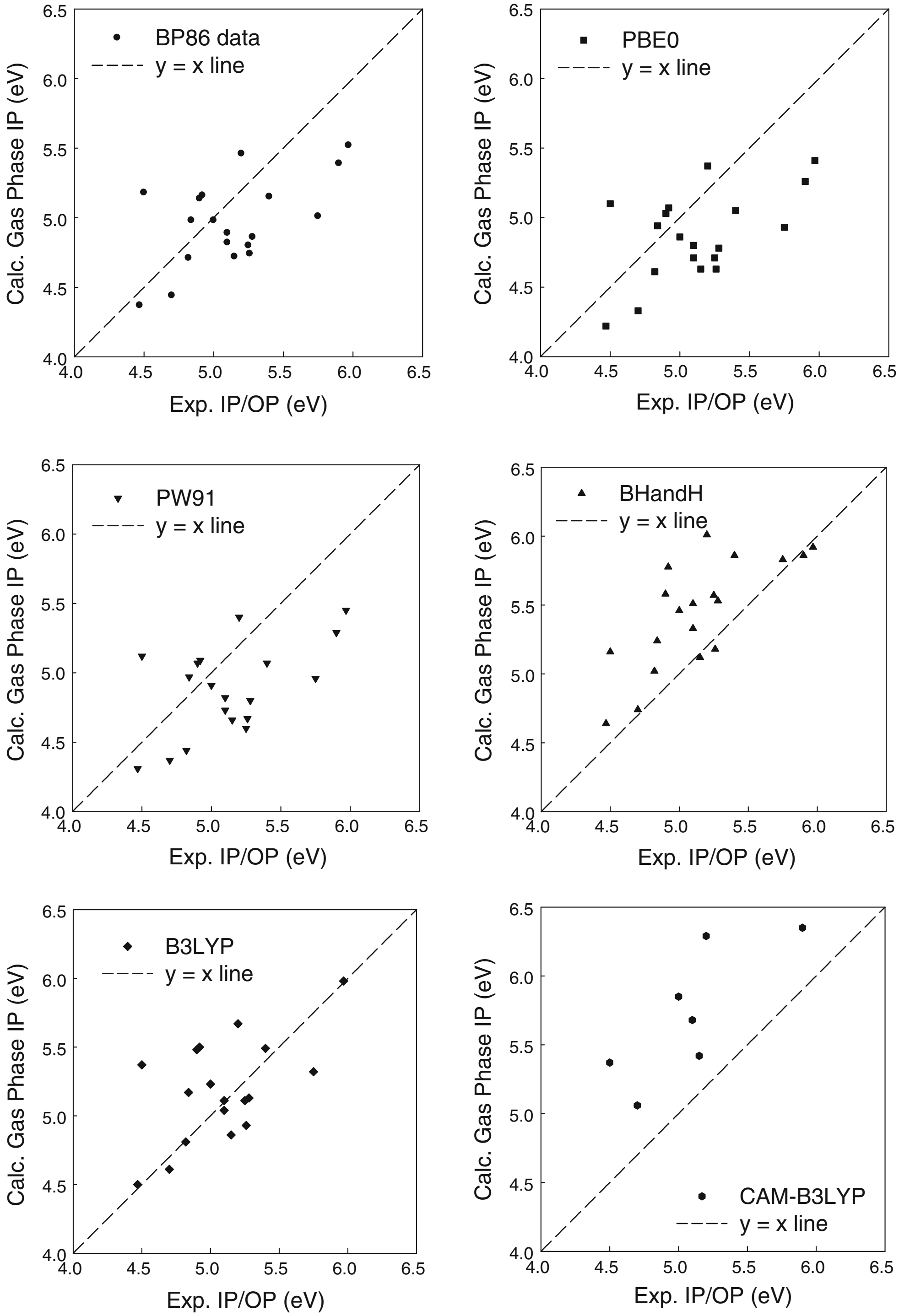


Fig. 3 Comparison of experimental ionization potential/oxidation potential of conjugated polymers with the calculated gas-phase ionization potentials using various DFT functionals

Although the electronic structure in the conjugated backbone is the same in all these systems, there is significant variation in the experimental OPs for these polymers.

Our calculations have been carried out in the gas phase, and all long alkyl chains have been truncated to methyl groups to save computational time. We have not considered the effects such as chemical disorder, structural disorder, counter-ion intercalation, and solvent effect on polymer ionization in solution. Solid state interactions were not taken into account either. Within the view of above discussion, theoretical estimation of IPs in this study could at best be a rough approximation to the experimental value. Nonetheless, it is very important to explore the IP predicting power of different theoretical approaches where a useful theoretical method can be used to guide the synthetic efforts for novel polymeric systems.

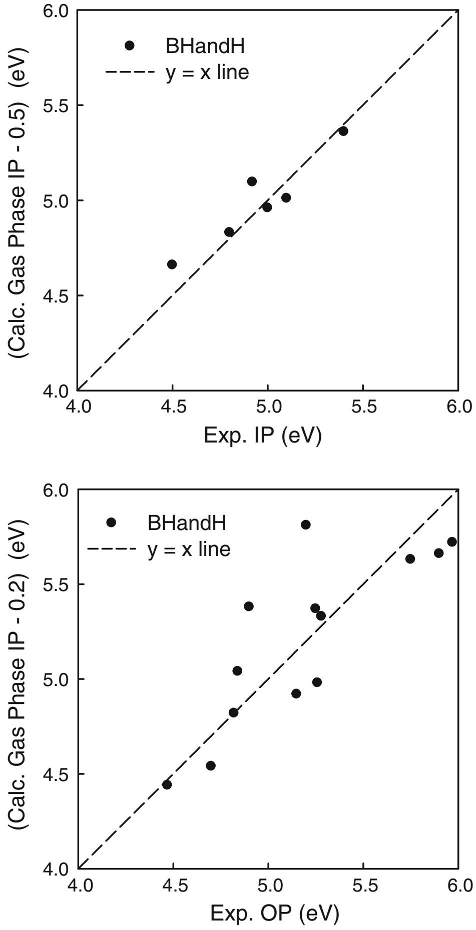


Fig. 4 Comparison of experimental ionization potential (*top*) and oxidation potential (*bottom*) of conjugated polymers with the calculated gas-phase ionization potentials using BHandH functional

There are structural differences between the ground-state and cationic-state geometries that indicate the regions where the electronic density is most distorted upon ionization (see Table S1 in supporting information). It is not possible to analyze all the geometrical variations that occur for each polymeric structure in Fig. 1. However, there are several trends evident for all systems. First, there is a tendency to adopt a quinoidal structure in cation species. However, most of the aromatic rings still maintain their aromaticity in their cationic state. Second, cationic structures possess increased planarity due to increased double-bond character between the adjacent rings. Especially, thiophene-containing cationic structures show improved planarity due to low torsional energy between the rings. Finally, although the magnitudes of IPs highly depend on the type of the structural units in the backbone of the polymer, the non-planar structures require higher energies for ionization. This is expected since delocalized systems shift the ionization energies downward as opposed to more localized systems.

Figure 2 shows the Meier fits across the P3HT oligomer data using different DFT functionals. At infinite chain length, PBE0, PW91, BP86, B3LYP, BHandH, and CAM-B3LYP functionals predict IPs of 4.80, 4.82, 4.89, 5.04, 5.33, and 5.68 eV, respectively (Table 1). Experimental IP of P3HT is taken as 4.85 eV as reported in the work by Cascio et al. [30]. This number also represents the average of IP values reported for P3HT. BHandH and CAM-B3LYP functionals significantly overestimate the experimental data, yet the results of other functionals are in relatively good agreement with the IP of P3HT. We have specifically used CAM-B3LYP hybrid functional in this study to overcome the problem regarding incorrect asymptotic decay of the exchange functional in DFT calculations. Using CAM-B3LYP as long-range corrected functional did not improve the results [32]. The fair agreement for other functionals between gas-phase and condensed-phase results is probably caused by the too fast decrease of DFT IPs with increasing chain lengths, which partially compensates the difference between gas and condensed phase. On the other hand, CAM-B3LYP functional still underestimates the experimental gas-phase IP of thiophene oligomers. Experimental gas-phase IP of thiophene dimer and tetramer has been measured as 7.87 and 7.25 eV, respectively [33]. These values are much higher than the ones estimated by CAM-B3LYP (7.01 and 6.13 eV).[1]

Figure 3 evaluates the predicted gas-phase IPs against the experimental IPs/OPs of the conjugated polymers in order to identify possible correlations. We have also plotted graphs for calculated IPs vs. experimental IPs and calculated IPs vs. experimental OPs. There were not any improvements in correlations—except for BHandH—within these plots (not shown) when compared to graphs in Fig. 3. IP predictions of BP86, PBE0, and PW91 functionals are similar, and estimated values slightly underestimate the experimental results. B3LYP calculations yield the most accurate results among the functionals used in this study in alignment with other reports in the literature [3]. Nonetheless, BHandH functional gives the best correlation in comparison of experimental results with those of theoretical calculations. However, BHandH functional slightly overestimates experimental results. In the next step, we compared experimental IPs and OPs separately with calculated gas-phase IPs obtained with BHandH functional. A downward scaling of 0.5 eV on BHandH data has given much better match to experimental IPs, whereas 0.2 eV scaling was needed for improved estimation of experimental OPs (Fig. 4). Thus, the scaled gas-phase IPs with BHandH functional not only improved the correlation but

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[1] P3HT oligomers have alkyl groups in their structure and therefore the data for thiophene oligomers has been used as reference only. Nonetheless, presence of alkyl groups are not expected to have significant effect on gas phase ionization potential.

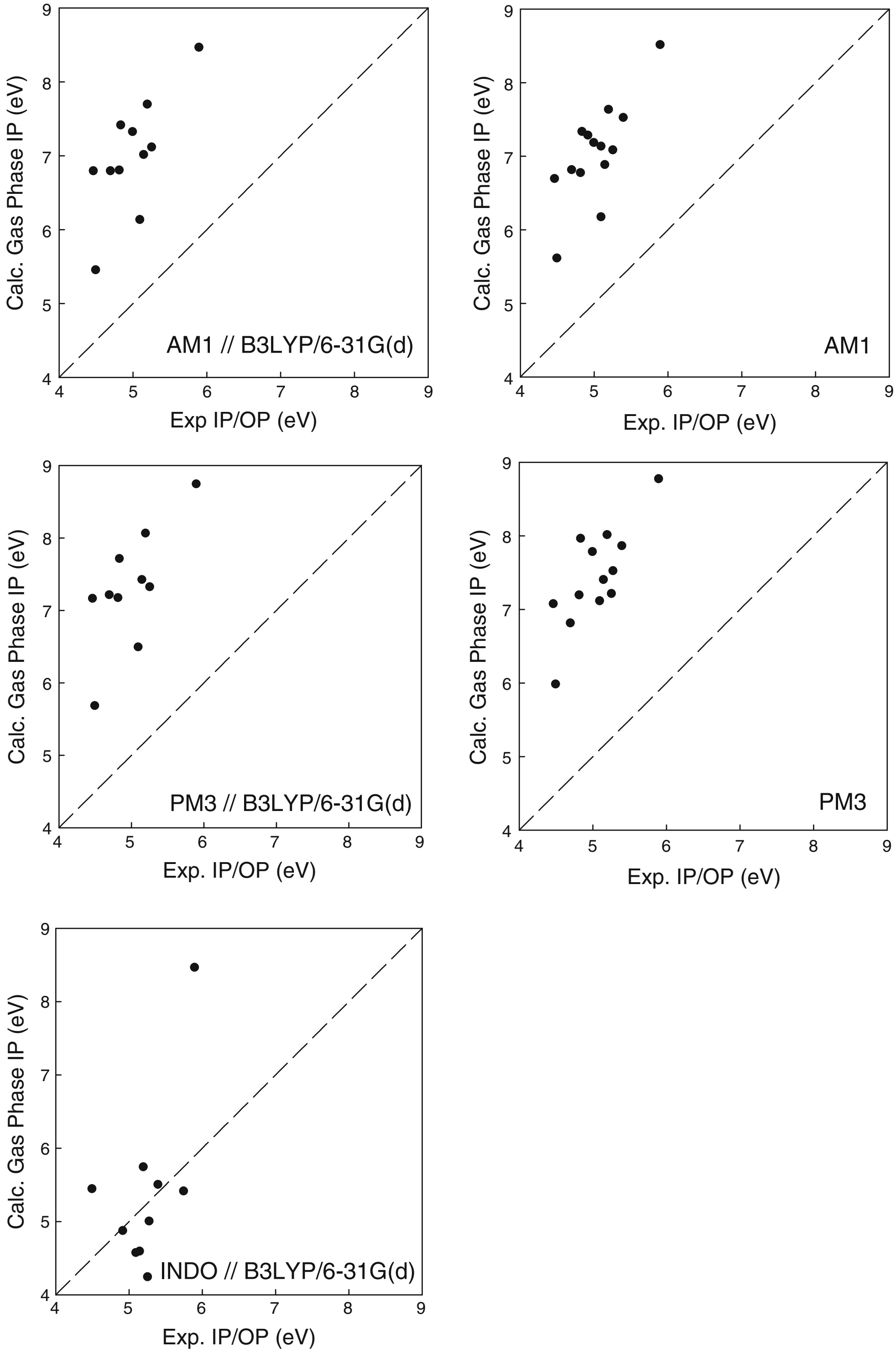

Fig. 5 Comparison of experimental ionization potential/oxidation potential of conjugated polymers with the calculated gas-phase ionization potentials calculated at AM1//B3LYP/6-31G(d), AM1//AM1, PM3//B3LYP/6-31G(d), PM3//PM3, and INDO//B3LYP/6-31G(d) levels

also resulted in better accuracy in predicting the experimental values. It is also noteworthy to emphasize that these predictions fall in 95% confidence prediction band. The results also confirm that scaling of BHandH data could lead to reasonable estimates for either IP or OP estimation of a conjugated polymer.

The amount of HF exchange increases in the order of B3LYP (20%), PBE0 (25%), and BHandH (50%). It is worth mentioning that CAM-B3LYP functional comprises of 65% HF exchange and 35% Becke 1988 exchange interaction at long-range [34]. There is no clear correlation, but it seems that theoretical IPs increase with the amount of

HF exchange employed in the functional. CAM-B3LYP largely overestimates the experimental results (see Fig. 3), yet there are not enough sufficient data to draw general conclusions in evaluation of this functional.[2]

If Eq. 2 is modified to replace the number of repeat units ($-a(n-1)$) with the number of double bonds ($-a(\mathrm{db}-1)/\mathrm{db}$, db: total number of double bonds) in the structures, then a plot of predicted IP versus the number of double bonds can show how the theoretical IPs converge to the polymeric value with increasing number of double bonds in the oligomer structure. IPs of almost all oligomers with a total number of 20–30 double bonds are 0.05 eV or less higher than the predicted IPs at infinite chain length. This means, the polaron size for P3HT is about five repeat units, two repeat units for poly[2,7-(9,9-dioctylfluorene)-alt-5,5″-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (Exp OP: 5.75 eV), and five repeat units for poly-[2,6-(4-diheadecylmethylene-cycopentadithiophene] (Exp OP: 4.82 eV). The results confirm the presence of *effective ionization length* in conjugated polymers that has also been observed in the band gap studies on conjugated oligomers for effective conjugation length [14, 35–38]. In an experimental study, Chi and Wegner concluded that the positive charge is localized over 3.5 repeat units of oligofluorenes [39]. The information regarding effective ionization length is significant, and it allowed us to estimate the nuclear relaxation energy for carrier mobility in conjugated polymers [40]. The internal reorganization energy for holes in P3HT has been found as 263 meV using B3LYP/6-31G(d) method as described in [40]. The higher the reorganization energy, the larger is the effective mass and consequently the lower the hole mobility. Unfortunately, we do not have access to the hole mobility data for the polymers shown in Fig. 1; therefore, a search for correlation between the estimated reorganization energies and hole mobilities was not carried out.

IPs were also estimated using semiempirical techniques. Calculations were carried out on both DFT-optimized (B3LYP/6-31G(d)) geometries and geometries minimized at the respective semiempirical level (Fig. 5). In both cases, the semiempirical methods do not perform as well as DFT methods. INDO calculations on DFT-optimized geometries provided the most accurate estimates to the experimental values. Nevertheless, often times it was not possible to fit the semiempirical data using Meier fit, and a linear fit is used in some cases.[3] For some polymers, it was not feasible to use any sort of fitting procedure due to inconsistent data.

4 Conclusions

The theoretical results demonstrate that one can predict the onset of redox potentials or ionization potentials of conjugated polymers to a good degree of accuracy. The theoretical gas-phase IPs obtained with BHandH functional provided the best correlation and accuracy if appropriate scaling is performed as described in the text. The polaron size can be estimated using Meier fit on the data for increasing size of oligomers. The most notable changes between ground-state and cationic-state structures are improved planarity in the conjugated backbone and increased quinoidal character of the repeat units while still maintaining their aromaticity. Finally, it is clear that an IP data set obtained under identical experimental conditions would be much more useful in the comparison of computational results with those of experiment.

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[2] CAM-B3LYP calculations had to be performed on a personal computer. Therefore, the calculations were carried out on polymers with relatively small repeat units due to limitations in computational resources.

[3] Calculated oligomer IPs sometimes increased with the increasing number of repeat units, which represented an unrealistic picture.

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