

Microscopic insights into charge formation and energetics in n-doped organic semiconductors

Chuan-Ding Dong^{*,†} and Stefan Schumacher^{†,‡}

[†]*Department of Physics and Center for Optoelectronics and Photonics Paderborn (CeOPP), Paderborn University, Warburger Strasse 100, 33098 Paderborn, Germany*

[‡]*Wyant College of Optical Sciences, University of Arizona, Tucson, AZ 85721, USA*

E-mail: cddong@mail.uni-paderborn.de

Abstract

In the molecular doping of organic semiconductors (OSC), achieving efficient charge generation and managing the energetic cost for charge release from local molecular charge transfer complexes (CTCs) to the host matrix is of central importance. Experimentally tremendous progress has been made in this direction. However, the relation between OSC film structure on a nanoscopic level including different inter-molecular geometrical arrangements and the macroscopic properties of doped OSC films is usually only established quite indirectly. Explicit microscopic insights into the underlying doping mechanisms and resulting electronic structure are still scarce and mostly limited to the study of the individual molecular constituents or isolated bi-molecular dopant:host complexes. In the present study we investigate n-type doping of the frequently investigated OSC materials ZnPC and F₈ZnPc and their mixtures which are n-doped with 2-Cyc-DMBI. We report significant electronic differences for complexes with nominally the same material composition but different geometrical structures. One specific important finding in this context is that complexes containing two adjacent dopant molecules show much reduced ionization energy values, leading to substantially reduced energy cost for charge release.

Furthermore our results demonstrate that important trends towards macroscopic system behavior can already be obtained with increasing size and varying composition of the relatively small molecular dopant-host complexes considered, including systematic shifts in the Fermi level energies in the doped OSC.

Introduction

Molecular doping is an essential process in enhancing the conductivity of organic semiconductors (OSC), and enables a wide range of organic electronic devices including light-emitting devices and transistors.¹⁻⁶ In molecularly doped OSCs, the charge transfer (CT) behaviour observed strongly depends on the specific chemical constituents' structures and conformations and on the specific types of dopant:host complexes formed. While the precise mechanisms of molecular doping and CT in OSCs are often still elusive to a certain extent,⁷ it is more and more evident that so-called integer charge transfer (ICT) resulting from the formation of bi-molecular dopant:host complexes or ion pairs plays a crucial role.⁸⁻¹⁴ In addition, electronic hybridization and partial CT were also reported for many systems or found in coexistence with ICT complex formation.¹⁵⁻¹⁹ Even though these findings are of fundamental importance, they are yet insufficient to fully support the mech-

anistic understanding of charge carrier generation and electronic transport in doped OSCs. A more comprehensive picture of CT behaviour beyond the primary bi-molecular complexes is therefore highly desirable. Recently, this was probed by a series of experimental and computational efforts through the correlation between CT and energetics, such as electron-hole Coulomb binding energy, shift of Fermi-level, energetic disorder and density of states (DOS) in macroscopic OSC films.^{20–23}

On a fully microscopic level on the other hand, valuable insights can be obtained from first principles electronic structure calculations. Given the size of realistic systems, those are typically based on density functional theory (DFT) and mostly concentrate on the principle bi-molecular CTC building blocks^{14,24–27} or just the polaron states for individual molecules.^{28–30} Attempts for larger systems are still limited and possible trends in the transition from micro to more macroscopic systems are rarely discussed.^{31–34} In the present work we particularly consider dopant:host complexes that form ICTCs with individual and stacked dopant molecules and varying number of host molecules, as illustrated in Figure ???. Based on detailed DFT calculations, we investigate the energetics and charge transfer behaviour in these systems. We demonstrate that ICTCs with adjacent dopant molecules generally possess reduced ionisation energy (IE) and therefore are favourable for charge carrier separation. We further find the CT in CTCs with stacked dopants to be partially incomplete and tuneable with the number and species of host molecules. The total CT from dopant to host shows a monotonic increase and approaches saturation with decreasing HOMO energies, which aligns well with the correlation found between these quantities in experimentally studied ternary doped systems.

Computational Details

As an efficient n-type dopant, we use the 2-Cyc-DMBI radical with an unpaired electron and spin-doublet electronic structure. In the

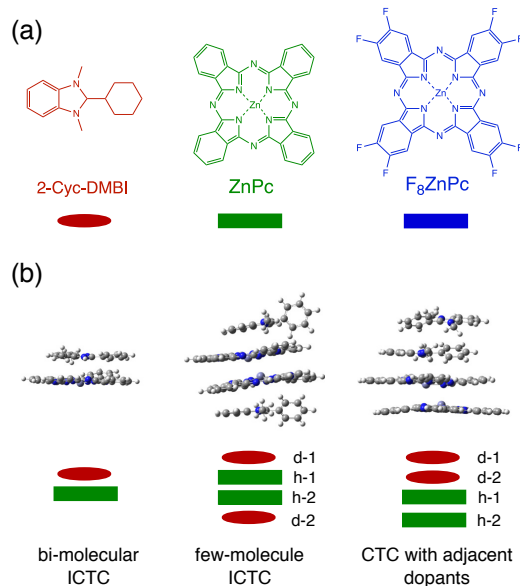


Figure 1: (a) Chemical structures of the n-type dopant 2-Cyc-DMBI and the organic semiconductors ZnPc and F₈ZnPc. The structures are schematically represented by the red ellipse (2-Cyc-DMBI), green rectangle (ZnPc), and blue rectangle (F₈ZnPc). (b) Sample molecular structures and schematic representations, respectively, of the individual bi-molecular integer charge transfer complex (ICTC), a larger few-molecule ICTC, and a CTC with two adjacent dopant molecules. d-1 and d-2 label the two dopant molecules, while h-1 and h-2 label the two host molecules. Sample structures are shown for ZnPc.

present work it is essential to capture both orbital hybridization as well as integer charge transfer between different molecular species for all complexes studied. Therefore, as the method of choice, we use spin unrestricted density functional theory (DFT), which has previously successfully been used to describe molecular doping in similar contexts. As successfully applied in our previous work,^{14,24,31} the electronic states are described with the range-separated cam-B3LYP functional and 6-31G** basis set, including van-der-Waals interaction on the level of Grimme’s D3 dispersion correction. First, the geometries of all complexes were optimized in the neutral charge state. For calculation of the ionization energy (electron affinity) values, single point calculations for the cor-

responding cations (anions) of the complexes were then performed using the geometries of the charge-neutral counterparts. All DFT calculations were done using GAUSSIAN16.³⁸ The Hirshfeld charge partitioning and the density of states calculations were performed using the Multiwfn software.³⁹

Results and Discussion

The monomer 2-Cyc-DMBI radical is known as a highly efficient n-type dopant,³⁵ while ZnPc and its fluorinated derivative F₈ZnPc are intensively studied model systems of molecular organic semiconductors and can be used as host for both n- and p-type doping.^{20–22,35,36} In particular it was demonstrated that the Fermi level of the mixture of ZnPc and its different fluorinated derivatives can be tuned via the mixing ratio.²² The planar structures of ZnPc and F₈ZnPc (Figure ??) also facilitate the structural stacking of these molecules. The formation of stacks of dopant molecules naturally relies on the dimerization of 2-Cyc-DMBI molecules in the doped thin films. This process has been shown to be highly relevant as it occurs for 2-Cyc-DMBI molecules under ambient conditions,³⁷ even though it has also been discussed that the dimer can split up upon thermal activation.²¹ In the present work we analyze the properties of dopant-semiconductor complexes in different geometrical arrangements in detail and on a microscopic level and elucidate the complexes’ respective roles to the electronic structure of corresponding disordered doped OSC thin films.

Figure 2 shows the electron affinities (EAs) for ZnPc and F₈ZnPc stacks of different sizes (**a-f**), as well as the ionization energies (IEs) for complexes containing one to three ZnPc (F₈ZnPc) and one or two 2-Cyc-DMBI molecules in different geometrical arrangements (complexes **g-r**). For both EAs and IEs we give the respective negative values to make the energy cost of charge separation, namely the difference between the IE of a given integer-charge transfer complex (ICTC) and the EA of the corresponding host molecule complex more intuitive.²¹

The significant variation of the IE and EA values with size and stacking structures reflects the energetic disorder in the corresponding doped thin systems. The variation of the EA shows a consistent increase with complex size for both ZnPc (complexes **a-c**) and F₈ZnPc (complexes **d-f**), with the onset of a saturation behavior of EA values already visible, but with an upper limit that will be reached for much larger complexes only. From single molecule to trimolecular stacks, the increase of EA is 0.30 eV for ZnPc and 0.59 eV for F₈ZnPc, which implies a larger range of EA variation for the F₈ZnPc complexes. This is consistent with the stronger coupling between F₈ZnPc, estimated from the calculated binding energy of 2.47 eV compared to 2.28 eV for ZnPc. As expected, the magnitude of EAs of F₈ZnPc complexes is larger than that for ZnPc complexes with the same size due to the fluorination.

Complexes **g-l** in Figure. 2 are ICTCs containing one 2-Cyc-DMBI molecule and a stacked arrangement of up to three ZnPc or F₈ZnPc molecules. The ICT that occurs in these complexes is for example evidenced by the partial density of states (PDOS) with broken spin symmetry as shown in Figure S1, as well as by the HOMO distribution that is localized on the ZnPc molecule as shown for the example of complex **g** in Figure S2. Interestingly, the variation of the IEs in Figure. 2 shows a weak trend of reduction with growing size of ZnPc compounds (**g-i**), and in contrast increases with the size of F₈ZnPc compounds (**j-l**). This behaviour is however consistent with the variation of calculated HOMO levels of complexes **g-l**, which shows already the same trend for the HOMO levels of the ZnPc and F₈ZnPc compounds without the presence of 2-Cyc-DMBI. As shown in Figure S3, the HOMO of the ZnPc dimer is around 0.1 eV higher than that of a single ZnPc, while the HOMO of F₈ZnPc dimer is lower than that of its single molecule counterpart. Upon closer inspection of the structures of ZnPc dimer and F₈ZnPc dimer, one finds that the F₈ZnPc dimer exhibits a larger intermolecular distance and less bending around the central Zn atoms than for ZnPc as shown in Figure S3, indicating that

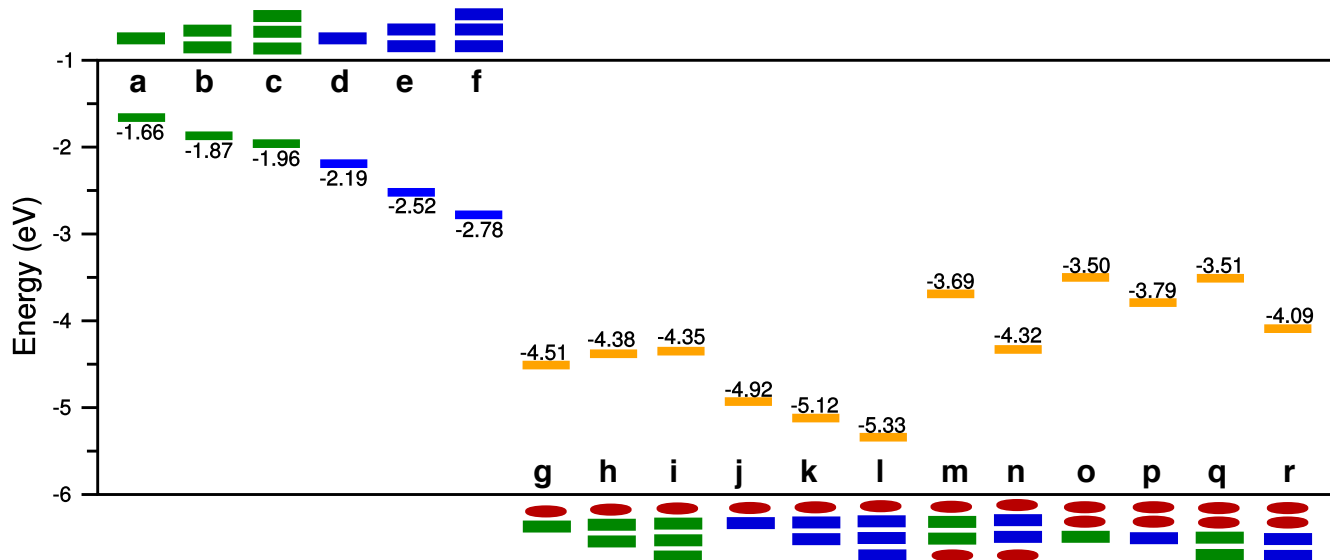


Figure 2: Calculated electron affinities (EA) of the host molecules and corresponding molecular complexes **a-f** thereof. The thin green and blue dashes mark the EA of the host compounds. The EA increases in magnitude with increasing compound size and fluorination. Negative ionization energies (-IE) of the molecular dopant:host complexes **g-r** are shown as orange dashes. For **a-r** the respective molecular complexes are schematically depicted above or below the main graph, respectively, ZnPc as green rectangle, F_8 ZnPc as blue rectangle, and 2-Cyc-DMBI as red ellipse as introduced in Fig. 1. The magnitude of IE increases with increasing fluorination. The energy cost to release a doping-induced charge from a given ICTC to a complex of host molecules can be estimated by the energy difference between the respective EA and negative IE values.

with fluorination the planar structure is better maintained in the complexes.

With complexes **m** and **n** we now move on to few-molecule ICTCs containing two 2-Cyc-DMBI molecules located on different sides of a ZnPc or F_8 ZnPc dimer, respectively. This structure can be interpreted as two interacting bi-molecular ICTCs. Complexes **m** and **n** evidently have IE values with smaller magnitude than the corresponding bi-molecular ICTCs **g** and **j**. This is expected in view of our recent work³¹ where the lower IE was attributed to the stabilization of an ionized ICTC by another adjacent ICTC. Complexes **o-r** contain two 2-Cyc-DMBI dopants located on the same side of the ZnPc or F_8 ZnPc complexes. The calculated IE values are even further reduced in magnitude compared to complexes **m** and **n**.

From the calculated EAs of host compounds and IEs of complexes shown in Figure 2, one can deduce that here the energy cost of releasing a charge carrier from the doped complexes to the host material ranges from 3.67 eV (from **l** to **a**)

to 0.72 eV (from **o** to **f**). We note that these values will depend on the computational method used and specific choice of geometrical molecular arrangement. On the other hand, however, the wide range of energies found reflects the complexity of the energetic landscape of the underlying dopant:host system. With this it also implies possible avenues for the optimization of charge-release energetics and transport properties based on specific inter-molecular geometric arrangement or (partial) inter-molecular order in doped molecular thin films. The relatively low magnitude of IEs for the bi-molecular systems of ICTCs (**g** and **j**) is also particularly noticeable, which indicates a structural advantage in the quest for easy charge release.

Interesting qualitative differences in the nature of the doping are also found in complexes with different inter-molecular arrangement of complex constituents. Although containing the same number of dopant and host molecules, the complexes **q** and **r** show quite different charge transfer character than found in the

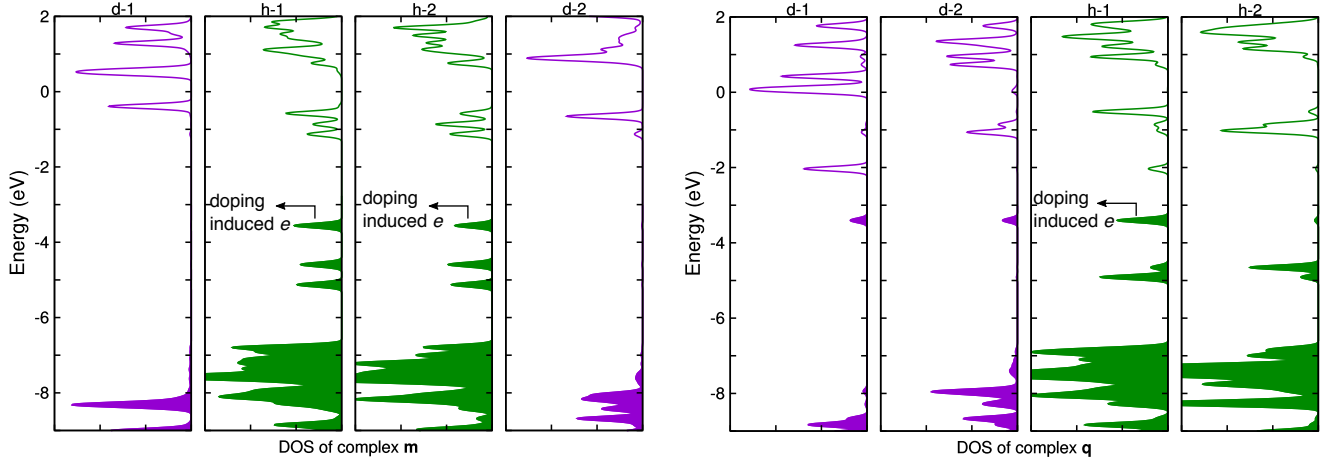


Figure 3: Projected density of states (PDOS) of complexes **m** and **q**. Only the α component of the PDOS is shown for the underlying spin symmetric electronic states. The labels d-1, d-2, h-1, and h-2 refer to the individual molecules in the complexes as introduced in Figure ???. The filled-in parts of the PDOS represent the occupied states and the doping-induced charges are marked. The DOS of isolated charge neutral ZnPc and its dimer are included as Figure S4 of the SI for comparison. The figure illustrates reveals significant differences in the nature of doping caused by geometrical rearrangements of molecular constituents as discussed in the text.

ICTCs **m** and **n**. The latter two exhibit typical integer charge transfer with both dopants possessing more than $0.7 e$ positive charge as listed in Table 1. Upon ionization of the complexes, the dopants in complexes **m** and **n** remain nearly full cations, with net charge only slightly changed, whereas the dopants in complexes **q** and **r** are significantly more positively charged after ionization (cf. Table S1). The charge transfer that occurs in complexes **q** and **r** is therefore directly correlated with the overall charge state of the complexes, leading to a significant overall reorganization of the electronic system upon ionization. To illustrate this difference in charge-transfer and electronic behaviour further, Figure 3 shows the projected density of states (PDOS) for complexes **m** and **q**. In complex **m**, the HOMO state (i.e., representing the charge induced in the OSC material by doping) is entirely localized on the two ZnPc molecules with very similar contributions on h-1 and h-2, indicating efficient integer charge transfer from the two dopants. In complex **q** the doping induced charge is not symmetrically distributed to the two OSC molecules and also partial delocalization of the HOMO orbital that is primarily localized on h-1 across the two 2-Cyc-DMBI molecules d-1 and d-2 is found. For

further illustration, a comparison of the HOMO orbitals for complexes **m** and **q** are shown in Figure S5. The observed difference in delocalization also coincides with the calculated net charge on each molecule in the complexes as listed in Table 1. Another significant difference between complexes **m** and **q** is found in the HOMO-LUMO gap, which has a value of 2.43 eV for **m** and 1.37 eV for **q**. In this context we note that the calculated absolute single-particle energies and thus also gap values depend on the DFT functional used, the reduced gap of complex **q**, however, is very evident.

In the following we extend our study also to slightly larger complexes including admixtures of both ZnPc and F_8 ZnPc molecules within the same complexes and two dopant molecules adjacent to each other. In particular we find an interesting correlation between the total amount of charge transferred in the different complexes and the energetics of the doping induced charge as shown in Figure 4. The total amount of charge transferred from the dopants to the host material shows a (nearly) monotonic increase with decreasing HOMO level energies, showing slight saturation with increasing host complex size and/or increasing number of fluorinated host molecules in the complex. This

Table 1: Hirshfeld charge partitioning results for the ICTCs **m** and **n** and ICTCs with adjacent dopants **o**, **p**, **q** and **r**. Given are the partial charges found on the complexes molecular constituents as labelled in Figure 1.

	d-1	h-1	h-2	d-2
m	0.72 <i>e</i>	-0.75 <i>e</i>	-0.69 <i>e</i>	0.72 <i>e</i>
n	0.75 <i>e</i>	-0.65 <i>e</i>	-0.87 <i>e</i>	0.77 <i>e</i>

	d-1	d-2	h-1	h-2
o	0.44 <i>e</i>	0.37 <i>e</i>	-0.81 <i>e</i>	–
p	0.72 <i>e</i>	0.41 <i>e</i>	-1.13 <i>e</i>	–
q	0.55 <i>e</i>	0.46 <i>e</i>	-0.85 <i>e</i>	-0.16 <i>e</i>
r	0.83 <i>e</i>	0.53 <i>e</i>	-1.15 <i>e</i>	-0.22 <i>e</i>

trend can be naturally interpreted as the lowering of the HOMO energies along with the increasing weight of HOMO electrons on the ZnPc and/or F₈ZnPc molecules as a result of CT. This is in turn traced back to the increasing fluorination in the host molecular stacks. The effect of increasing fluorination can be more directly demonstrated by comparing molecular complexes of equal size with ZnPc successively replaced by F₈ZnPc, mimicking different ZnPc:F₈ZnPc mixing ratios. This is presented in the inset of Figure 4 for the complexes **s**, **t**, **u**, and **v**, where the CT monotonously increases with the number of F₈ZnPc molecules, reaching the onset of saturation for large fluorination.

The variation of CT with fluorination or HOMO level shown in Figure 4 agrees well with corresponding experimental observations. In a recent combined experimental and theoretical study of ternary doped systems, where F₄TCNNQ was used as the p-type dopant and a ZnPc:F₈ZnPc mixture as the host material, the effective doping efficiency with ZnPc:F₈ZnPc mixing ratio was found to resemble the trends reported in Figure 4.²² Since the CT behaviour is closely associated with doping efficiency, the complexes **s**, **t**, **u**, **v** studied here with only five molecules, already reflect the fundamental feature of the ternary system in ref. 22. These include the tunable and partially incomplete CT. We note that in the microscopic system of the present study the latter structurally origi-

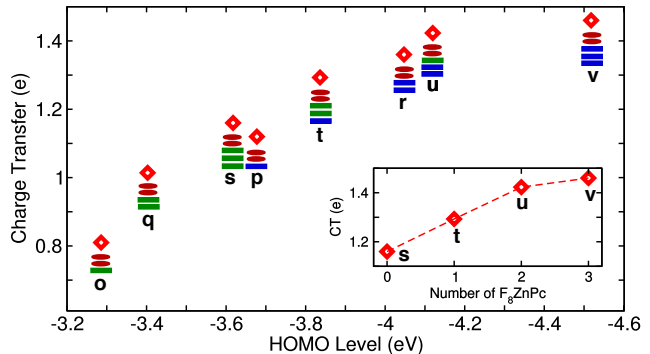


Figure 4: Amount of total charge transfer (CT) as function of HOMO energy for ICTCs with two adjacent dopant molecules for different complex sizes and host species. Respective values are marked by the red open diamonds. The inset shows the total amount of charge transferred from host to dopant molecules in complexes **s**, **t**, **u**, and **v** versus the number of F₈ZnPc host molecules present in each complex.

nates from the stacked placement of two adjacent dopant molecules, which partially screens the interaction between the topmost dopant and the host molecules. In a macroscopic OSC film, besides the specific structural arrangement studied here, dopant-host interaction strength will greatly vary due to the reduced structural order. The variation of the HOMO level found in the present study can be interpreted as microscopic counterpart to the Fermi-level shift reported for the ternary system in ref. 22.

Conclusions

In the present work we have demonstrated that valuable insights into the charge transfer behaviour and energetics in molecularly doped organic semiconductors can be gained from the explicit microscopic simulation of charge-transfer complexes of increasing size and with different geometrical structures. To this end we considered the n-type doping of the OSC materials ZnPc and F₈ZnPc with 2-Cyc-DMBI dopant molecules as well as their ternary mixtures.

One important finding is that specific geometrical arrangements between dopant and host molecules can lead to significantly reduced ion-

ization energies, reducing the energetic cost for charge release from the charge transfer complexes to the host matrix. In particular, we find that ionization energies of charge transfer complexes containing two adjacent dopant molecules are generally lower and thus favorable for efficient charge release, while the electron affinities of compounds with multiple adjacent ZnPc or F₈ZnPc molecules are increased compared to those of the individual molecules. These findings indicate possible avenues to reduce the energy cost for charge release in binary or ternary doped OSC systems through manipulating the nano-structure and relative geometrical arrangement of dopant and/or host molecules.

Another important observation is that going beyond the study of only bi-molecular complexes, important trends in the doping energetics that determines the electronic properties of doped OSC films on a macroscopic level can already be obtained from the explicit study of relatively small charge transfer complexes on a microscopic level. In the present study of molecular complexes of a few molecules we were able to reproduce important trends in the amount of charge transfer found in different CTCs in dependence of their Fermi level energy. Also the correlation between amount of charge transfer and amount of fluorination of host molecule clusters shows a very similar trend as that recently experimentally observed in the Fermi-level control of such ternary system.

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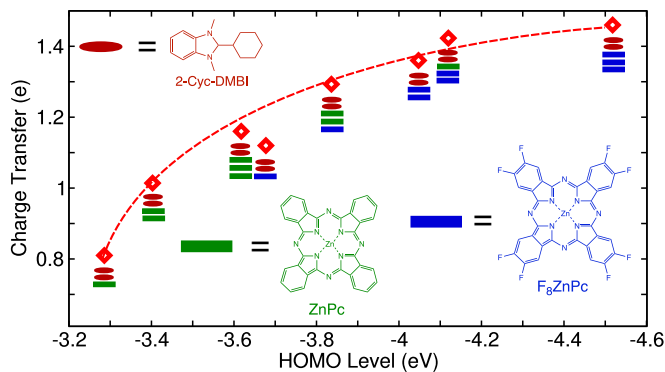
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TOC figure.