Tuning Optical Properties of Conjugated Molecules by Lewis Acids: Insights from Electronic Structure Modeling

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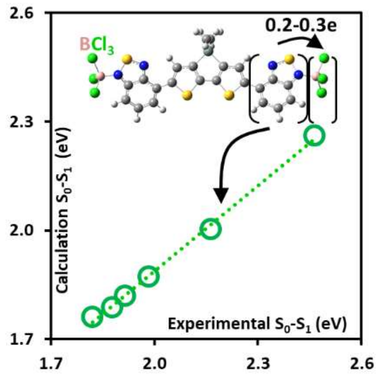
ABSTRACT Understanding and controlling the optoelectronic properties of organic semiconductors at the molecular level remains a challenge due to the complexity of chemical structures and intermolecular interactions. A common strategy to address this challenge is to utilize both experimental and computational approaches. In this contribution, we show that density functional theory (DFT) calculation is a useful tool to provide insights into the bonding, electron population distribution and optical transitions of adducts between conjugated molecules and Lewis acids (CM-LA). Adduct formation leads to relevant modifications of key properties, including a red-shift in optical transitions, and an increase in charge carrier density and charge mobility, compared to the parent conjugated molecules. We show that electron density transfer from the CM to the LA, which was hypothesized to cause the experimental redshift in absorption spectra upon LA binding, can be quantified and interpreted by population analysis. Experimental red-shifts in optical transitions for all molecular families can also be predicted by time-dependent DFT calculations with different density functionals. These detailed insights help to optimize a priori design guidelines for future applications.

TOC GRAPHICS



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Optoelectronic processes in organic semiconductors have intrigued scientists for several decades. Understanding certain phenomena at the molecular level remains a challenge due to the complexity of chemical structures and intermolecular interactions. Continued improvement and refinement of organic semiconductors relies on an immense number of chemical structures.[1–11] New families of organic and hybrid semiconductors are being continuously designed and studied. One encouraging path for methodically tuning key properties involves the adducts of conjugated molecules and Lewis acids (CM-LA).[12–21] These adducts are formed by the partial electron density transfer from a semiconducting conjugated molecule or polymer, usually containing a Lewis basic (LB) site to an external Lewis acid (LA). Boron based LAs such as BF_3, BCl_3 and $B(C_6F_5)_3$ (with the three fluorinated benzene rings abbreviated as CF) have been widely utilized. The resulting adducts have been experimentally demonstrated to have interesting optoelectronic properties, including a red-shift in optical transitions,[1-3,8,10] and an increase in charge carrier density compared to the parent conjugated molecules.[4,5,7] The underlying principles of these changes require further investigation from both experimental and computational perspectives. In this communication, we provide insights into the interaction between CM-LA, electron population distribution and optical transitions of CM-LA adducts using density functional theory (DFT) calculations. Understanding and controlling these trends via structural modifications may facilitate applications of these adducts in organic electronics and benefit the development of novel compounds incorporating coordination bonds such as B $\leftarrow$ N.[11,12]

Since the first report of CM-LA adduct in 2009,[12] there have been several investigations of CM-LA adducts, mainly employing experimental techniques.[12–16,18,20,22–26] Most of the molecules in these studies have an alternating donor-acceptor (D-A) motif, in which the acceptor unit contains atoms with a non-bonding pair of electrons capable of coordinating with LAs. In this study, we chose three donor-acceptor molecules, denoted J09G1, J11G3 and J11G8, as model compounds. Their chemical structures, presented in **Figure 1a**, contain either benzo-2,1,3-thiadiazole (BT) or pyridyl-2,1,3-thiadiazole (PT) as the electron-acceptor unit.

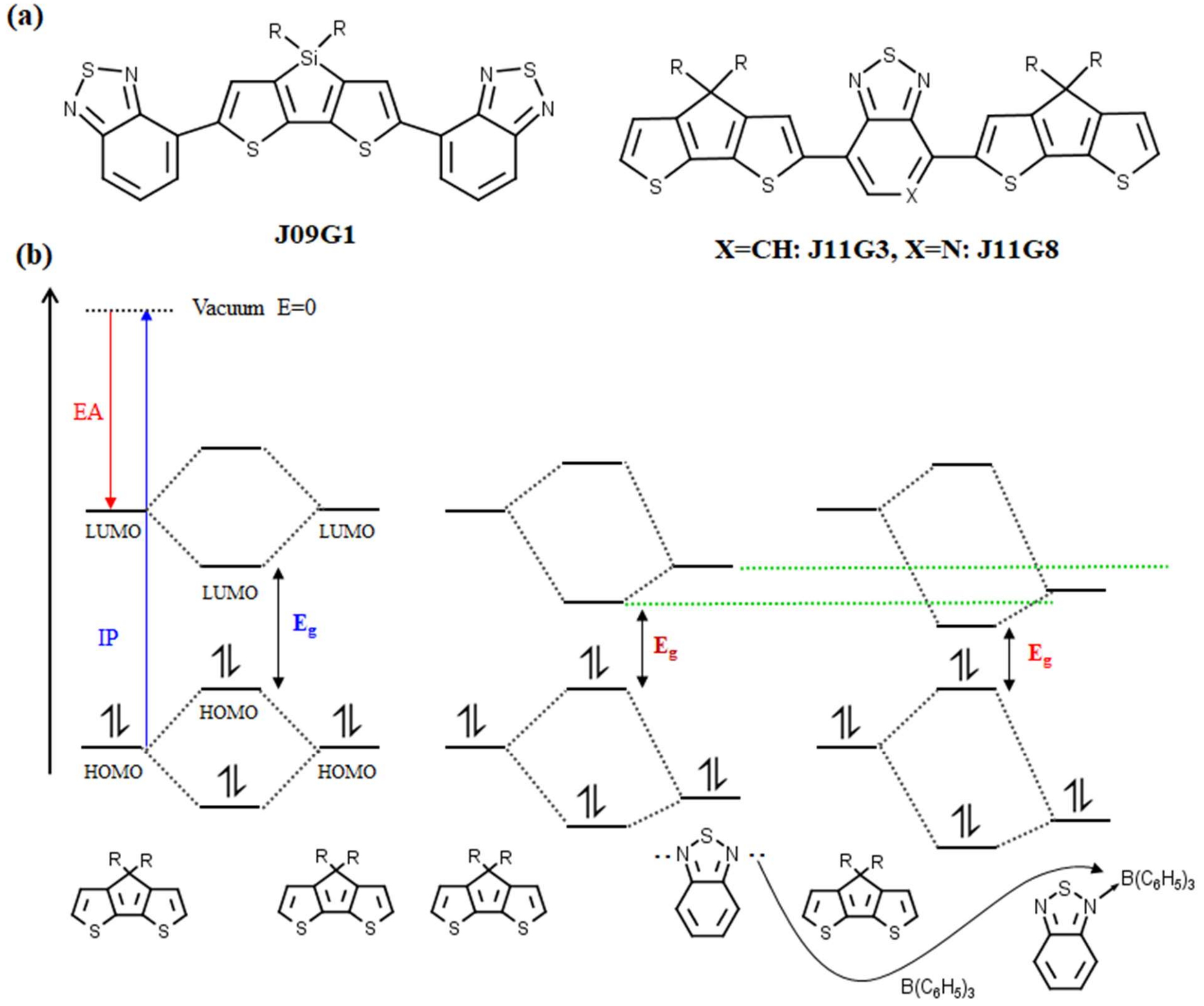

Figure 1. (a) Three model molecules mainly used in this study, J09G1, J11G3 and J11G8; and (b) schematic representation of the hypothesis of optical bandgap reduction from the original interactions of what would be D-D regions of the monomer, transitioning to the D-A hybridization with energy of the acceptor lowered in both the occupied and virtual states, and finally the D-A

bound to a Lewis acid where energy lowering of the acceptor states for hybridization is further magnified.

J09G1 is the first molecule that Welch and coworkers[12] showed to bind with a series of LAs that varied in acidity. The resulting adducts display pronounced red-shift in optical absorption, which increases with the strength of the LA. J09G1-2BCF was also isolated and studied by ^{1}H, ^{11}B and ^{19}F NMR spectroscopies. This work concluded that the two BCF are bound to the two BT units at the opposite ends of J09G1.[12] In addition, a single crystal structure of the BCF adduct with only the acceptor molecule (BT-Br),[12] verified that BCF binds to nitrogen. The reduced bandgaps of the adducts were also confirmed in DFT calculations at the B3LYP/6-31G level. J11G3 was synthesized in a subsequent study.[13] There, it was demonstrated that LA can also bind to the more sterically hindered N atom of the BT acceptor sandwiched between two donor moieties (Figure 1). J11G8, which changes BT to PT was also studied on the basis that pyridine is known to bind BCF,[2,13,14] and pyridyl N-atom is hypothesized to have higher basicity than the azole N-atom of BT.[13]

Despite studies investigating the application of CM-LA adducts, few attempts have been made to explore and quantify physical processes underlying observed trends in optoelectronic properties of those adducts. Some of the first studies hypothesized that electron donation from the electron poor fragment of the molecules to Lewis acids is the fundamental cause. When this happens, the acceptor strength increases hence reducing the bandgap of the molecule as reflected in the consequent red-shifted optical transitions.[12–14] This explanation seems particularly relevant to D-A molecules, where bandgap reduction results from the hybridization of the donor and acceptor moieties, as shown in **Figure 1b**. For example, in adducts of molecules containing either BT or PT as the electron-acceptor unit and BCF, the lone-pair orbital of nitrogen in their structure may donate an electron to boron's empty orbital in BCF. In this scenario, BCF draws electronic density from BT or PT thus enhancing its acceptor strength.

Although this electron transfer in LA-LB bonds is intuitively understood in organic chemistry, it is challenging to confirm this process experimentally, especially for an adduct with bulky conjugated molecules. For small crystalline LA-LB adducts, high-resolution X-ray diffraction at low to very low temperatures coupled with multipole refinement and population analysis can be used only to roughly estimate the charge transfer from LB to LA.[27] It has been suggested that quantitative interpretation of experimental data even for these small systems should be coupled with theoretical calculations.[27] Accordingly, in this contribution, we first aim to characterize the charge transfer from LB moiety to LA by DFT calculations and subsequently analyze the optical transitions of the adducts.

In the realm of electronic structure theory, prediction of structural motifs,[28,29] conformations,[30,31] and electronic features (particularly related to electronic transfer processes),[32–37] are subject to the choice of proper level of theory. For DFT, the presence of a fractional contribution of the orbital exchange is perhaps the most important parameter. Consequently, prior to characterizing charge transfer and optical properties, we tested several commonly used functionals and basis sets to optimize the geometry of the parent molecules and adducts. To model the electrostatic effects of a solvent in all calculations we use the conductor-like polarizable continuum model (CPCM).[38–40,32] All results presented in this communication are calculated with 6-311G(d,p) basis set.

Structural properties of the adducts including the length of coordination bonds between LA and LB, binding energy and dihedral angle changes are summarized in **Figure S1 and Table S1**, Supporting Information. The DFT-calculated N-B bond lengths (1.58 to 1.68 Å) and binding energies (~100 kJ/mol) are consistent with previous experimental and theoretical values for a wide range of small LB-LA complexes (such as NH_3:BF_3) reported in the literature.[41,42] We subsequently used time-dependent DFT (TD-DFT) to calculate the S_0-S_1 transition of the adducts. Of the popular functionals we have tried, CAM-B3LYP-D3[43,44] (thoroughly tested in our previous works)[29,32] and APFD[45] (with incorporated dispersion correction) models show stronger correlation between calculated S_0-S_1 red-shift trends and experimental red-shift. Therefore, we utilized these two methods for the calculations and analysis of other properties in all the molecules.

Population analysis provides a convenient mean to analyze molecular wavefunctions and assign net charges to each atom in a molecule. Thus, calculated charges before and after LA binding can reveal the charge transfer from LB moiety of the parent molecule to LA. Both natural atomic (NBO analysis)[46,47] and charge model 5 (CM5)[48,49] charges were used in this study and proved insensitive to basis sets among those investigated. We analyzed the change in the sum of net charges of all atoms in the LA and LB units before and after binding, as illustrated in **Figure 2**. For example, in the calculation of J09G1-2BCl_3 adduct with APFD model, where LA is BCl_3 and LB is the BT moiety, BCl_3 is initially a neutral molecule with a total net charge of zero. After binding, the total net charge of BCl_3 in the adduct becomes -0.298 e, indicating a partial electron transfer (**Figure 2**). On the other hand, the BT moiety of J09G1 has total net charge (Σ_{LB}) of -0.073 e before and 0.187 e after binding to BCl_3, respectively, corresponding to an effective donation of electronic density to BCl_3.

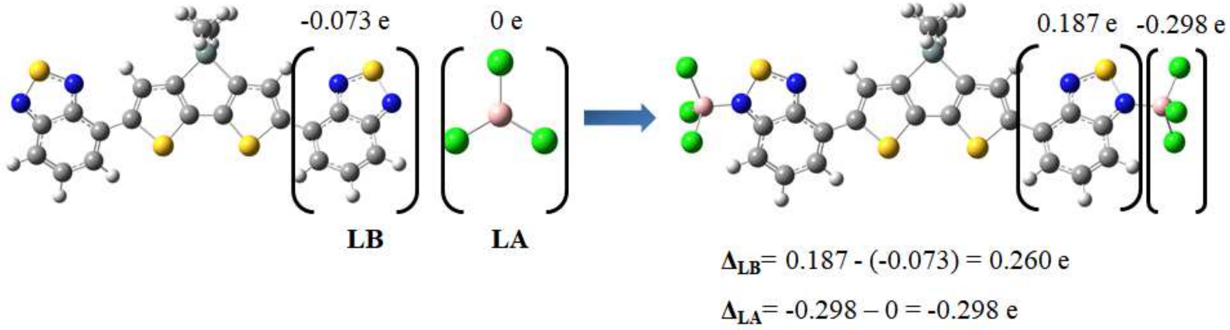

Figure 2. Illustration of charge transfer evaluated via DFT calculations and NBO analysis. Here, the CM-LA adduct (J09G1-2BCl_3) is calculated using APFD. The results of analogous calculations conducted across the adduct series are summarized in Table 1.

Table 1. Charge transfer quantification of CM-LA adducts including J09G1, J11G3 and J11G8. The values were calculated with APFD.

Molecules & Adducts	**NBO - Vacuum**				**NBO - Dichlorobenzene**			
	Σ_{LB}	Δ_{LB}	Δ_{LA}	$\Delta_{LB} + \Delta_{LA}$	Σ_{LB}	Δ_{LB}	Δ_{LA}	$\Delta_{LB} + \Delta_{LA}$
J09G1	-0.073				-0.063			
J09G1-$AlMe_3$	0.036	0.109	-0.129	-0.020	0.057	0.120	-0.146	-0.027
J09G1-$AlEtCl_2$	0.026	0.099	-0.133	-0.034	0.042	0.105	-0.159	-0.054
J09G1-AlCF	0.060	0.133	-0.171	-0.039	0.077	0.141	-0.186	-0.045
J09G1-BCF	0.261	0.334	-0.373	-0.039	0.284	0.347	-0.393	-0.046
J09G1-BCl_3	0.187	0.260	-0.298	-0.038	0.223	0.286	-0.343	-0.057
J09G1-BBr_3	0.157	0.230	-0.268	-0.038	0.196	0.259	-0.317	-0.058
J11G3	-0.162				-0.155			
J11G3-BCF	0.172	0.335	-0.372	-0.038	0.197	0.351	-0.389	-0.038
J11G8	-0.213				-0.213			
J11G8-BCF	0.031	0.244	-0.366	-0.122	0.072	0.286	-0.381	-0.096

Σ_{LB}: *The total net charge of all atoms in LB fragment of the molecule*
Δ_{LB}: *The change in total net charge of LB fragment before and after binding to LA*
Δ_{LA}: *The change in total net charge of LA fragment before and after binding to LA*

We performed population analysis of all adducts after optimizing their ground state geometry within both APFD (**Tables 1 and S2**) and CAM-B3LYP (**Table S3**), including dielectric medium effects. The results (**Tables 1, S2-S3**) uniformly reveal a significant shift in electron density from LB to LA in the adducts. We first analyze the charge transfer for the J09G1 series. With NBO, we observe that the charge transfer significantly increases from aluminum- (~0.1 – 0.15 e) to boron- (~0.27 – 0.38 e) based LAs, which is reasonable given that boron-based LAs are stronger acids. For small complexes such as NH_3:BH_3 and NH_3:BF_3, NBO calculations reveal similar ~0.35 e partial charge transfer,[27] which is larger than experimental estimates.[27] The specific values are subject to the particular charge partitioning scheme used in simulations (e.g., NBO, Hirschfield or CM5), as well as uncertainties present in the experimental measurements. Furthermore, we find that dielectric medium presence (i.e., vacuum vs dichlorobenzene) only weakly increases the amount of charge transfer.

The difference between the charge that LAs gain (Δ_{LA}) and the charge that LB fragments lose (Δ_{LB}) upon binding is characterized by the sum of the two quantities ($\Delta_{LB} + \Delta_{LA}$). In all cases, the sums of these net charges before and after LA binding are negative, meaning that the electron density gained by LAs is greater than that donated exclusively by the LB moiety that immediately binds to the LA. This indicates that LA+LB complex also withdraws electrons from other adjacent fragments of the molecule, namely the donor region. In terms of magnitude, the sum ($\Delta_{LB} + \Delta_{LA}$) is ~5 to 10 times smaller than the total charge transfer to the LA (Δ_{LA}), indicating that only a minor amount of charge is taken from other fragments of the molecule. Interestingly, the charge gained by a BCF (Δ_{LA}) is very similar among all systems considered, J09-BCF, J11G3-BCF and J11G8-BCF. The charge donated from LB (Δ_{LB}) is also similar across the series, except for J11G8-BCF when BCF binds to pyridyl nitrogen. In this J11G8-BCF case, the sum of the Δ_{LA} and Δ_{LB} is larger (~0.10 – 0.18 e), implying that other portions of the molecules contribute more charge to BCF in this adduct. This might be due to the high electron withdrawing ability of pyridyl nitrogen in the PT unit. The trends observed for charge transfer obtained with APFD calculations are consistent with the results obtained using the CAM-B3LYP functional. This lends confidence to the applicability of DFT for charge transfer analysis in CM-LA adducts, with proper choice of functionals and population analysis methods.

Our population analysis provides quantitative support of the hypothesis in **Figure 1b**. Electron withdrawing of LAs upon binding increases the acceptor strength, which results in the reduction of bandgap and consequently the red-shift in absorption. Qualitatively, this effect can be observed visually in the progression of the frontier molecular orbitals (highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO) for the parent molecule relative to those with LA additions. For example, **Figure S2** displays the LUMO evolution for J09G1, J09G1-AlCF and J09G1-BCF sequence. These images clearly illustrate that LA binding increases orbital localization to the acceptor region of the molecule compared to the original unbound molecule, where the orbital is spread over both the donor and acceptor regions. Nevertheless, such orbital visualization captures only qualitative features and trends in electronic states.[50]

To provide further quantitative support of the hypothesis in **Figure 1b**, we conducted a systematic analysis of the optical transition energies of the adducts. Specifically, using TD-DFT we computed the transition energy for the first excited state (i.e., S_0-S_1 transition) in all molecules and correlate those to experimental data (peak wavelength converted to energy, **Figure 3 and Table S4**).[12,13] First, we analyze J09G1 adducts when J09G1 binds to a series of LA with different strength, ranging from trimethylaluminum to boron tribromide, by focusing on the amount of red-shift appearing with LA binding and ordering with LA electron withdrawing capacity. An agreement with experiment is demonstrated in two respects: the difference between transition energy of the adducts and the parent molecules before binding to Lewis acids (Δ_{S1}); and the transition energy variation as a function of LA acidity. The difference between experimental and calculated Δ_{S1} is about 0.1 eV. The best agreement with experiment is observed for the J09G1 series using the APFD functional coupled with dichlorobenzene solvent model.

Figure 3 summarizes the correlation between experimental and calculated values for optical transition energies. A correlation is statistically established across all methods used in this study (i.e., for both CAM-B3LYP-D3 and APFD models, and for calculations in vacuum and solvent). Hence, these computational approaches are able to capture the effect of the relative strength of Lewis acids on the optical transitions of the adducts. The linear fit with slope close to one (0.94) and small y-intercept (0.08) is observed for the APFD calculations with implicit o-dichlorobenzene. This indicates quantitative predictive capacity of this model for direct application to novel adducts. Yet the strong R^2 for each of the four approaches shown in **Figure 3** suggests that any method could be suitable for predictive simulations with use of a linear fit employing a trial set of experimental and computational data.

For J11G3 and J11G8 adducts, the discrepancies between TDDFT and experiments are larger. In these molecules, our calculations show that the binding to LAs causes a significant deformation of the backbone, decreasing its conjugation (**Figure S1**). These deformations reduce calculated red-shift in the adducts. In experimental data, the deformation might be compensated by other intermolecular interactions, for example with the solvent environment,[23] that are not explicitly included in our current simulations. In the future work we plan to investigate these effects.

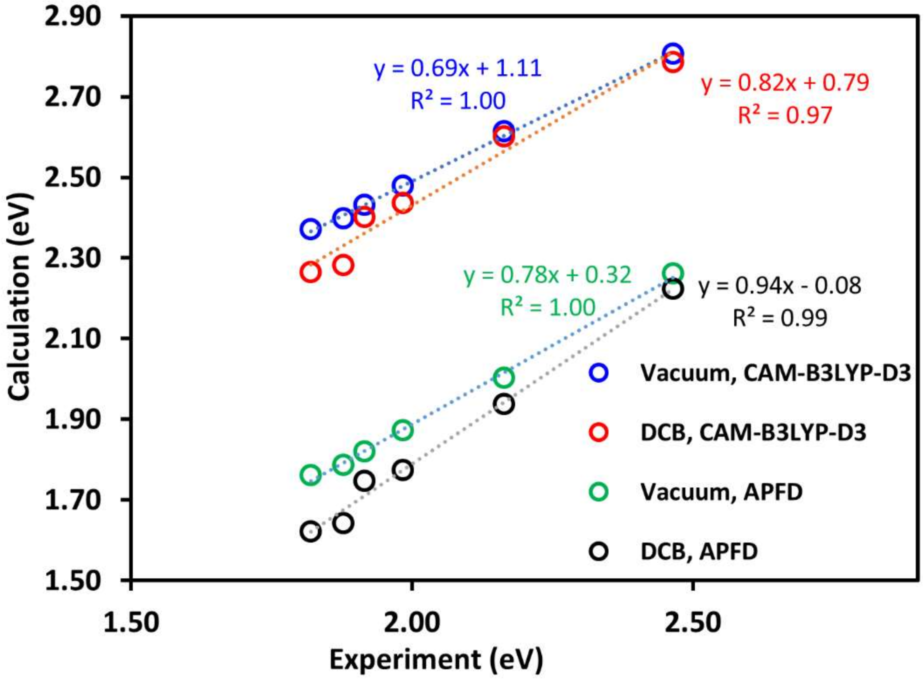

Figure 3. Correlation between calculated and experimental S_0-S_1 transition energies of J09G1 series (see Table S4). Experimental S_0-S_1 transition energies are peak wavelengths converted to

energy of UV-VIS absorption data in o-dichlorobenzene (DCB) solvent. Calculated S_0-S_1 transition energies were carried out both in vacuum and DCB medium.

Finally, we analyze the hole and electron orbitals dominating the S_0-S_1 transition using the well-established natural transition orbitals (NTO)[51] approach. **Figure 4** depicts the electron and hole NTOs for isolated J09G1 as well as with its BCF adduct. Similar to the molecular orbital picture in **Figure S2**, the electron NTO also shows that LA binding enhances localization of the excited electron onto the acceptor region of the adduct compared to that of the parent molecule where electron delocalizes across the donor and acceptor moieties. The localization of electron NTO on acceptor unit upon binding with BCF is also evident in J11G3 and less pronounced for J11G8 (**Figure S3**, SI). In contrast, the hole NTO remains essentially unchanged upon the LA binding.

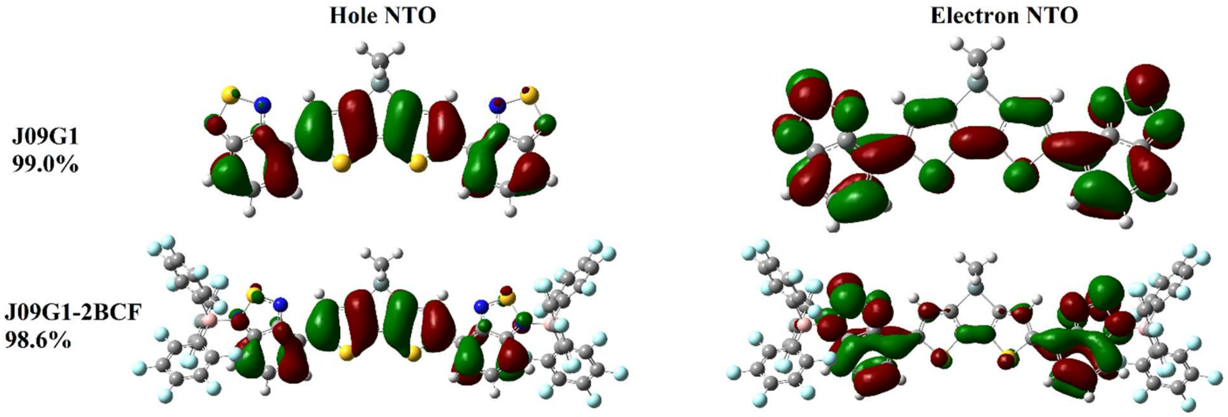

Figure 4. Hole and electron NTOs of J09G1 and J09-2BCF systems. The calculations were carried out at APFD model and o-dichlorobenzene solvent medium. Percentage indicates participation of a given NTO pair in the multiconfigurational S_0-S_1 transition to excited state.

In summary, we demonstrate that, with appropriate choice of calculation methods, DFT can provide a powerful modeling tool to analyze elemental physical processes involving the formation of CM-LA adducts and predict their optical properties. Population analysis shows a noticeable amount of charge withdrawn from the acceptor moiety of the molecules by Lewis acids, indicating a fractional electron transfer from CM to LA. This process was hypothesized to cause the experimental redshift in absorption spectra upon LA binding. This conjecture is confirmed with all our TDDFT simulations qualitatively predicting the red-shift trends for the lowest optical transition for all molecular families studied. APFD density functional coupled with implicit solvent models provides the best quantitative agreement with experimental absorption data and may be well suited for simulating other CM-LA adducts and predictive applications. Finally, it is worth noting that while the red-shifts are pronounced and are reproduced well in calculations, the underlying charge transfer is only partial and is relatively small. It seems charge transfer alone does not explain experimentally observed carrier doping effects in polymers after LA additions. Exploring other contributing phenomena will be a subject of our future studies.

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