Adıyaman University Journal of Science
https://dergipark.org.tr/en/pub/adyujsci
DergiPark AKADEMİK
ISSN 2147-1630
e-ISSN 2146-586X

Theoretical Study of Substitution Effects on Reorganization Energy in Indeno[1,2-b]fluorene-6,12-dione-Based Molecular Semiconductors

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Received: 09.10.2024 **Accepted:** 28.11.2024 **Published:** 31.12.2024

Abstract

The reorganization energy of an organic semiconductor can be modulated through molecular design. Density functional theory (DFT) calculations enable researchers to strategically design organic molecular semiconductors with low reorganization energy through chemical substitution. Herein, hole and electron reorganization energies of unsubstituted indeno[1,2-b]fluorene-6,12-dione (IFDK), and its 5,11- and 2,8-disubstituted derivatives were computed. Substituents positioned along the molecular long axes and short axes were employed to enhance understanding of how substitution position influences the molecular reorganization energy. Additionally, substituents with varying electron-withdrawing and electron-donating properties were also investigated to reveal the structure-property relationship in IFDKs. Based on DFT calculations, triphenylamine (TPA) substitution at the 5,11 and 2,8 positions exhibited the largest decreases in hole reorganization energy compared to the parent IFDK, reducing it from 240 meV to 80 meV and 110 meV, respectively. This suggests that more effective charge transfer is expected with TPA substitution in IFDKs due to lower reorganization energy. This work reveals the significant substitution effect on reorganization energy through the specific position and

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DOI: 10.37094/adyujsci.1564147

electronic characters (EWG vs EDG), providing a foundation for the future design of IFDK-based molecules with high charge transfer efficiency.

Keywords: Organic semiconductors; Small molecules; Reorganization energy.

İndeno[1,2-b]fluoren-6,12-dion Bazlı Moleküler Yarı İletkenlerde Sübstitüsyonun Yeniden Düzenlenme Enerjisi Üzerindeki Etkilerinin Teorik Olarak İncelenmesi

Öz

Organik bir yarı iletkenin yeniden düzenleme enerjisi moleküler tasarım yoluyla modüle edilebilir. Yoğunluk fonksiyonel teorisi (DFT) hesaplamaları araştırmacıların kimyasal sübstitüsyon yoluyla düşük yeniden düzenleme enerjisine sahip organik moleküler yarı iletkenleri stratejik olarak tasarlamalarına olanak tanır. Burada, sübstitüye olmamış indeno[1,2-b]fluoren-6,12-dion (IFDK) ve onun 5,11- ve 2,8-disübstitüe türevlerinin boşluk ve elektron yeniden düzenleme enerjileri hesaplandı. Moleküler uzun eksen ve kısa eksen boyunca konumlandırılan sübstitüye gruplar, sübstitüsyon konumunun moleküler yeniden düzenleme enerjisini nasıl etkilediğinin anlaşılmasını için kullanıldı. Ek olarak, değişen elektron çekme ve elektron itme özelliklerine sahip sübstitüentler IFDK'lardaki yapı-özellik ilişkisini ortaya çıkarmak için kullanıldı. DFT hesaplamalarına göre, 5,11 ve 2,8 pozisyonlarındaki trifenilamin (TPA) sübstitüsyonu, ana IFDK molekülü ile karşılaştırıldığında boşluk yeniden düzenleme enerjisinde en büyük azalmayı gösterdi ve bunu sırasıyla 240 meV'den 80 meV'ye ve 110 meV'ye düşürdü. Bu, daha düşük yeniden düzenleme enerjisi nedeniyle IFDK'lerde TPA sübstitüsyonu daha etkili yük transferinin beklendiğini göstermektedir. Bu çalışma, belirli pozisyon ve elektronik karakterler (EWG ve EDG) aracılığıyla yeniden düzenleme enerjisi üzerindeki önemli sübstitüsyon etkisini ortaya koyarak, yüksek yük transfer verimliliğine sahip IFDK tabanlı moleküllerin gelecekteki tasarımı için bir temel sağlamaktadır.

Anahtar Kelimeler: Organik yarıiletkenler; Küçük moleküller; Yeniden düzenlenme enerjisi.

1. Introduction

Organic semiconductors have garnered considerable attention from both industry and academia due to their superior properties, including lightweight, low cost, large area coverage, and compatibility with plastic substrates compared to inorganic counterparts. In addition to traditional applications such as Organic Field-Effect Transistors (OFETs) [1,2], Organic Light-

Emitting Diodes [3,4] (OLEDs), and Organic Photovoltaics (OPVs) [5] organic semiconductors are also utilized in Electrochemical Transistors (OECTs) [6], bio(chemical) sensors [7], thermoelectrics (OTEs) [8] and photodetectors [9]. Compared to polymeric semiconductors, small molecules offer advantages such as facile synthesis with good reproducibility, well-defined chemical structure and molecular weight, good solubility in common organic solvents and high purity due to their suitability for chromatographic purification. Over the past few decades, there has been significant interest in developing novel molecular semiconductors to enhance the efficiency of organic semiconductors in above-mentioned applications. However, the advancement of *n*-type molecular organic semiconductors has lagged behind that of their p-type analogues in terms of material diversity and device performance [10].

Among the electron deficient π-conjugated building blocks developed to date, indeno[1,2-b]fluorene-6,12-dione (IFDK) stands out due to its highly coplanar π-backbone, excellent physicochemical and thermal stability, and structural versatility resulting from various functionalization and substitution positions [11]. In recent years, numerous reports have emerged on the experimental studies of IFDK-based OFET applications, including our previous work on TIPS-IFDK [12] and 2OD-TTIFDK [13] molecules. However, the literature reveals a limited number of theoretical studies examining the structure-property relationships of IFDKs. For instance, Martinez *et al.* investigated the effects of electron-donating and electron-withdrawing groups on the electronic structure of 6,12-disubstituted IFDK derivatives. Their findings indicated that NH_2, NO_2, and CN functional groups could serve as effective light harvesters and sensitizers in solar cells [14]. Additionally, Ma *et al.* explored the influence of 2,8-butyl, 2,8-butylthio and 2,8-dibutylamino substitution on the electronic and optical properties of IFDK-based molecules [15]. They examined the reorganization energies, intermolecular electronic couplings and charge-injection barriers, concluding that the incorporation of sulfur atom into the side chains decreased the hole reorganization energies. In contrast, the dibutylamino functional group reduced the electronic coupling between π-cores due to increased steric interactions among the side chains. Thus, a comprehensive theoretical investigation is necessary to deepen our understanding of the structure-property relationships in IFDKs and to guide the future design of new organic semiconductors aimed at achieving high device performance with this material class. A detailed theoretical study is needed that explores a greater variety of substituents with different electronic characteristics, as well as the effects of substitution positions by using the same substituents in different locations on the IFDK molecule.

Charge transport ability plays a crucial role in the device performance of organic semiconductors. It is well known that organic materials exhibit two charge transport patterns at the molecular scale: the band regime for delocalized electrons and the hopping regime for localized electrons. The majority of organic molecules typically transport charge via a thermally activated hopping process [16]. The charge hopping rate in organic molecules is typically described accurately by Marcus–Hush theory. As shown in Eq. 1, this theory quantifies the hopping rate for holes (or electrons) in the absence of an external electric field and assumes that the trap states are degenerate.

$$W = \frac{V^2}{\hbar} \left(\frac{\pi}{\lambda k_B T}\right)^{\frac{1}{2}} \exp\left(- \frac{\lambda}{4k_B T}\right) \tag{1}$$

Here, V represents the coupling matrix element, λ denotes the reorganization energy, k_B is the Boltzmann constant, $\hbar$ is the Planck constant, and T is the temperature in Kelvin. As shown, the electronic coupling matrix element and reorganization energy are the two critical parameters that influence the charge hopping rate which determines the charge mobility. Electronic coupling matrix elements (or transfer integrals), which is largely dictated by orbital overlap, heavily depends on the relative position and orientation of adjacent molecules. Therefore, optimizing V requires molecular reorientation in the solid state, which can be achieved through various techniques, including annealing, adjusting thin-film fabrication parameters, and employing solvent vapor annealing processes to enhance charge mobility. Without single crystal structures, it is not possible to calculate the transfer integrals*(V)*. On the other hand, reorganization energy (λ) is a geometric relaxation in a molecule upon charge transfer, can be calculated with Density Functional Theory (DFT) [17,18] prior to synthesis.

The reorganization energy of an organic semiconductor can be modulated through molecular design. Molecular engineering via chemical substitution, employed in the early stages of molecular design, is an effective method for achieving low reorganization energy. This approach typically enhances intermolecular interactions, increases solubility, and improves the quality of thin films, leading to lower synthesis costs and time savings. In addition to revealing the consistency between experimental results and theoretical calculations [19-22], DFT enables researchers to strategically design organic molecular semiconductors with low reorganization energy through chemical substitution.

In this study, the hole and electron reorganization energies of unsubstituted IFDK, as well as its 5,11- and 2,8-disubstituted derivatives, were computed using quantum mechanical calculations. Substituents positioned along the molecular long axes and short axes were employed to enhance understanding of how substitution position influences the molecular reorganization energy. Additionally, substituents with varying electron-withdrawing and electron-donating properties were also investigated to reveal the structure-property relationship in IFDKs. The chemical structures of parent IFDK and its derivatives obtained through substitution at molecular short (5,11-position) and long axis (2,8-position) are depicted in Fig. 1.

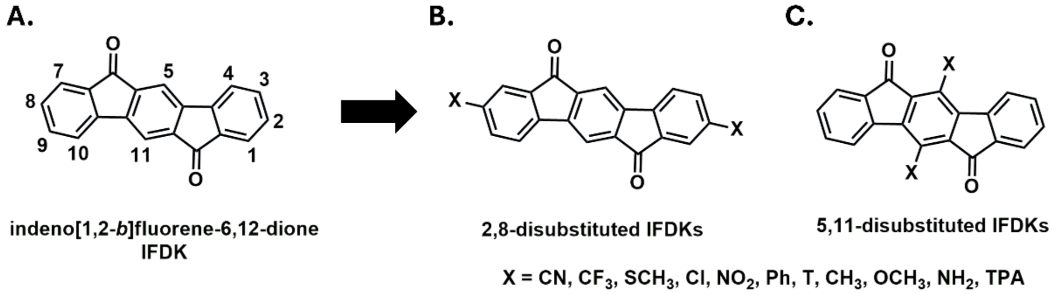

Figure 1: Chemical structures of indeno[1,2-b]fluorene-6,12-dione (IFDK) are shown, highlighting the number of carbon atoms (A), and its derivatives with substitution at the long molecular axis (2,8-positions) (B) and the short molecular axes (5,11-positions) (C), which are used for intramolecular hole and electron reorganization energy calculations in this study.

2. Computational Methodology

In this work, the total reorganization energy was calculated using potential energy surface method. The molecular geometry optimizations and single point energy calculations for the neutral and charged states were carried out in Gaussian 03W using density functional theory (DFT) at the B3LYP/6-31G** level.[23] The hole and electron reorganization energies in the 5,11- and 2,8-substituted IFDK derivatives were determined using a standard procedure outlined in the literature.[24]

A total of 23 molecules were studied for hole reorganization energy calculations in both neutral and cationic states, including 11 2,8-disubstituted derivatives, 11 5,11-disubstituted derivatives, and a parent IFDK molecule. Similarly, a total of 23 molecules were analyzed for electron reorganization energy calculations in both their neutral and anionic forms. This included 11 derivatives with substitutions at the 2,8 positions, 11 derivatives with substitutions at the 5,11 positions, and one parent IFDK molecule.

As illustrated in Figure 2, M, M^- and M^+ denote the neutral, anionic and cationic states. E_1, E_3, and E_6 represent the energy of neutral, anionic and cationic states in their lowest energy geometries, respectively. E_4 and E_7 represent the energy of neutral state at the geometry of the anion and cation, respectively. E_2 and E_5 represent the anionic and cationic states at the geometry of neutral molecule, respectively.

Here, $\lambda^{(3)}$ and $\lambda^{(4)}$ stand for the energies of geometric relaxation for the neutral and cationic states, respectively. The hole reorganization energy ($\lambda_h^{(+)}$) is the sum of the geometric relaxation energies involved in transitioning from the neutral state geometry to the cationic state geometry, and vice versa. It is defined as:

$$\lambda_h^{(+)} = \lambda^{(3)} + \lambda^{(4)} \tag{2}$$

where $\lambda^{(3)} = E_7 - E_1$ and $\lambda^{(4)} = E_5 - E_6$

In Figure 2, $\lambda^{(1)}$ and $\lambda^{(2)}$ represent the energies of geometric relaxation for the neutral and anionic states, respectively. The reorganization energy for electron transfer ($\lambda_e^{(-)}$) consists of $\lambda^{(1)}$ and $\lambda^{(2)}$, which correspond to the energies of geometric relaxation for the neutral and anionic states, respectively. It is evaluated as follows:

$$\lambda_e^{(-)} = \lambda^{(1)} + \lambda^{(2)} \tag{3}$$

where $\lambda^{(1)} = E_4 - E_1$ and $\lambda^{(2)} = E_2 - E_3$

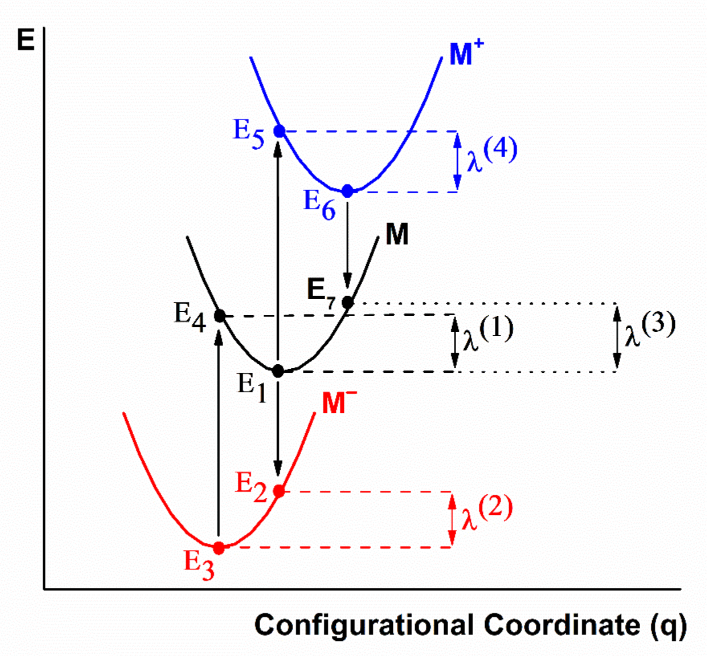

Figure 2: Sketch of Potential Energy Surfaces (PES) for anionic (M^-), neutral (M) and cationic (M^+) states.

3. Results and Discussion

First, the hole and electron reorganization energies, along with frontier molecular orbital energies and topographies of the parent molecule were calculated. Next, the effects of chemical substitution on the parent IFDK were examined to determine how these alterations impacted the initial results.

Figure 3 displays the results for the hole and electron reorganization energies of the parent IFDK and its derivatives, with substitutions along the short molecular axes (5,11-positions) and long molecular axes (2,8-positions), using the equations 2 and 3.

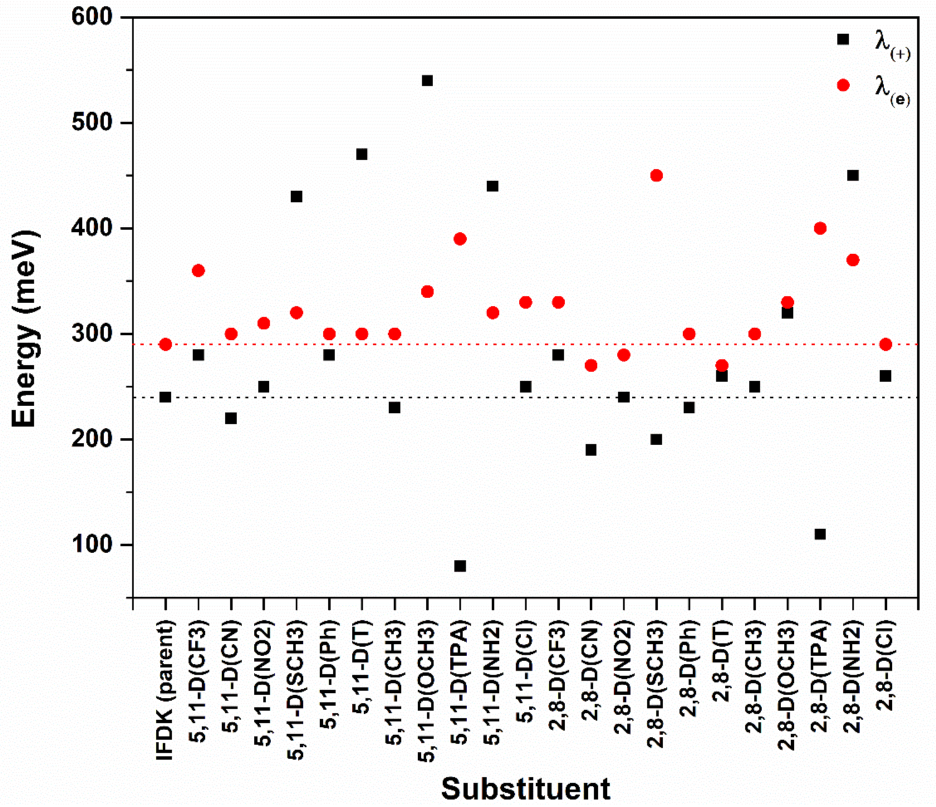

Figure 3: Results for the hole ($\lambda_h^{(+)}$) and electron ($\lambda_e^{(-)}$) reorganization energy of the parent IFDK molecule and its derivatives along the short molecular axes (5,11-positions) and long molecular axis (2,8-positions).

The numerical results have been displayed in Table 1. Notably, some of the substituents reduce the reorganization energy to some extent while some enhance it. Among all the substituents the methoxy (-OCH_3) group in 5,11-position leads to the highest increase in the hole reorganization energy, while the methylthio (-SCH_3) group at the 2,8-position results in the greatest increase in the electron reorganization energy. Other substituents at 5,11-position including -CF_3, -NO_2, -SCH_3, -Ph, -T, -NH_2 and -Cl also increased the hole reorganization energy. Additionally, all substituents at this position increased the electron reorganization energy. These results showed that most of the substituents used here increased the reorganization energy compared to parent molecule regardless of the position of the substituents.

The HOMO/LUMO topographies and energy levels of all substituents are shown in Fig. 4. Parent IFDK molecule, without any substitution, has HOMO energy level of -6.06 eV and a

LUMO energy level of -2.89 eV (Fig. 4), with reorganization energies of 240 meV for holes and 290 meV for electrons (Table 1).

The largest decrease in the hole reorganization energy, about threefold (80 meV), was observed with triphenylamine (TPA) substitution at the 5,11 positions, attributed to the localization of HOMO electrons on the TPA units. This behavior may stem from the strong electron-donating nature of TPAs. Additionally, cyano (-CN) and methyl (-CH_3) substitutions at the this position resulted in decreases of 20 meV and 10 meV in the hole reorganization energy, respectively. This cannot be explained solely by the nature of the substituents, as cyano is a strong electron-withdrawing group (EWG) while alkyl group is a weak electron-donating group (EDG).

The HOMO energy levels in TPA and CH_3-substituted IFDKs were upshifted by 1.08 eV and 0.11 eV, respectively, while CN-substitution resulted in a decrease of 0.66 eV. Thus, there is no clear relationship between the HOMO energy level and the hole reorganization energy.

Based on the frontier orbital topographies, the localization of HOMO electrons on substituents favors a reduction in the hole reorganization energy, whereas the delocalization of HOMO electrons throughout the entire molecule increases it. Therefore, substitution along the short molecular axes appears promising for designing *p*-type IFDK-based molecular semiconductors.

On the other hand, no decrease in the electron reorganization energy was observed in 5,11-substituted IFDKs compared to the parent molecule. There was also no significant change in wavefunction distribution of LUMO electrons upon substitution at 5,11-position. As shown in Figure 4, regardless of the electronic character of substituents, there is no relationship between the LUMO energy level and the electron reorganization energy. Additionally, correlation between the LUMO coefficients on the 5 and 11 carbons, and the reorganization energy could not be established.

Table 1: The hole and electron reorganization energies of 5,11- and 2,8-disubstituted IFDKs calculated at B3LYP/6-31G** theory level.

Molecule		**E_1 (eV)**	**E_2 (eV)**	**E_3 (eV)**	**E_4 (eV)**	**E_5 (eV)**	**E_6 (eV)**	**E_7 (eV)**	**$\lambda^{(4)}$ (eV)**	**$\lambda^{(3)}$ (eV)**	**$\lambda_h^{(+)}$ (meV)**	**$\lambda^{(1)}$ (eV)**	**$\lambda^{(2)}$ (eV)**	**$\lambda_e^{(-)}$ (meV)**
IFDK (parent)		-24997.49	-24998.93	-24999.07	-24997.34	-24990.00	-24990.12	-24997.37	0.12	0.12	240	0.15	0.14	290
5,11-IFDK	CF_3	-43339.01	-43340.83	-43341.01	-43338.83	-43331.15	-43331.29	-43338.87	0.14	0.14	280	0.18	0.18	360
	CN	-30017.14	-30019.31	-30019.46	-30016.99	-30009.06	-30009.17	-30017.03	0.11	0.11	220	0.15	0.15	300
	NO_2	-36125.89	-36128.09	-36128.24	-36125.73	-36117.72	-36117.84	-36125.76	0.12	0.13	250	0.16	0.15	310
	SCH_3	-48807.29	-48808.91	-48809.07	-48807.13	-48800.04	-48800.26	-48807.08	0.22	0.21	430	0.16	0.16	320
	Ph	-37572.17	-37573.60	-37573.75	-37572.02	-37564.94	-37565.08	-37572.03	0.14	0.14	280	0.15	0.15	300
	T	-55028.34	-55029.86	-55030.01	-55028.19	-55021.04	-55021.24	-55028.07	0.20	0.27	470	0.15	0.15	300
	CH_3	-27137.37	-27138.77	-27138.92	-27137.22	-27130.03	-27130.14	-27137.25	0.11	0.12	230	0.15	0.15	300

	OCH_3	-31230.00	-31231.51	-31231.68	-31229.83	-31222.78	-31223.10	-31229.78	0.32	0.22	540	0.17	0.17	340
	TPA	-65733.99	-65735.50	-65735.69	-65733.79	-65728.10	-65728.14	-65733.95	0.04	0.04	80	0.2	0.19	390
	NH_2	-28010.63	-28012.04	-28012.20	-28010.47	-28003.90	-28004.16	-28010.45	0.26	0.18	440	0.16	0.16	320
	Cl	-50009.49	-50011.24	-50011.40	-50009.32	-50001.77	-50001.89	-50009.36	0.12	0.13	250	0.17	0.16	330
2,8-IFDK	CF_3	-43339.84	-43341.78	-43341.94	-43339.67	-43331.85	-43331.99	-43339.70	0.14	0.14	280	0.17	0.16	330
	CN	-30017.39	-30019.65	-30019.79	-30017.26	-30009.29	-30009.39	-30017.30	0.10	0.09	190	0.13	0.14	270
	NO_2	-36126.78	-36129.21	-36129.35	-36126.64	-36118.41	-36118.53	-36126.66	0.12	0.12	240	0.14	0.14	280
	SCH_3	-48807.66	-48809.20	-48809.41	-48807.42	-48800.93	-48801.03	-48807.56	0.10	0.1	200	0.24	0.21	450
	Ph	-37572.63	-37574.20	-37574.35	-37572.48	-37565.73	-37565.85	-37572.52	0.12	0.11	230	0.15	0.15	300
	T	-55028.88	-55030.54	-55030.67	-55028.74	-55022.18	-55022.32	-55028.76	0.14	0.12	260	0.14	0.13	270
	CH_3	-27137.44	-27138.81	-27138.96	-27137.29	-27130.23	-27130.36	-27137.32	0.13	0.12	250	0.15	0.15	300
	OCH_3	-31230.29	-31231.65	-31231.81	-31230.12	-31223.47	-31223.62	-31230.12	0.15	0.17	320	0.17	0.16	330
	TPA	-65734.46	-65736.01	-65736.21	-65734.26	-65728.67	-65728.72	-65734.40	0.05	0.06	110	0.2	0.2	400
	NH_2	-28010.30	-28011.46	-28011.65	-28010.12	-28003.85	-28004.11	-28010.11	0.26	0.19	450	0.18	0.19	370
	Cl	-50009.81	-50011.63	-50011.77	-50009.66	-50002.22	-50002.35	-50009.68	0.13	0.13	260	0.15	0.14	290

Among the 11 substituents, cyano (-CN), methylthio (-SCH_3), phenyl (-Ph) and TPA at the 2,8- position showed reductions in the hole reorganization energy of 50 meV, 40 meV, 10 meV and 130 meV, respectively, compared to the parent IFDK. Similar to the 5,11-substitution, the 2,8- substitution with TPA results in the largest decrease in the hole reorganization energy, with a downshift of 2.2 times. In this case, the 2,8-substitution with TPA leads to full localization of HOMO electrons on the substituent groups, which exhibit a strong electron-donating character. However, the relationship between the HOMO energy level and the hole reorganization energy at this position remains unclear. Additionally, cyano (-CN), nitro (-NO_2) and thiophene (-T) substitutions at this position resulted in smaller decrease in the electron reorganization energy of 20 meV, 10 meV, and 20 meV, respectively. While the strong EWG character of the -CN and -NO_2 groups appears to play a role in reducing the electron reorganization energy, thiophene, which is weak EDG, has a similar impact. This suggests that there is no clear relationship between the electronic character of substituents and the reduction in the electron reorganization energy. Compared to parent IFDK LUMO energy level, all these substituents have lower (stabilized) LUMO energy levels, Similar to the 5,11-substitution, the relationship between the wavefunction distribution of LUMO electrons and the LUMO coefficients at the 2,8 carbons, and electron reorganization energy has not been clearly established in this position.

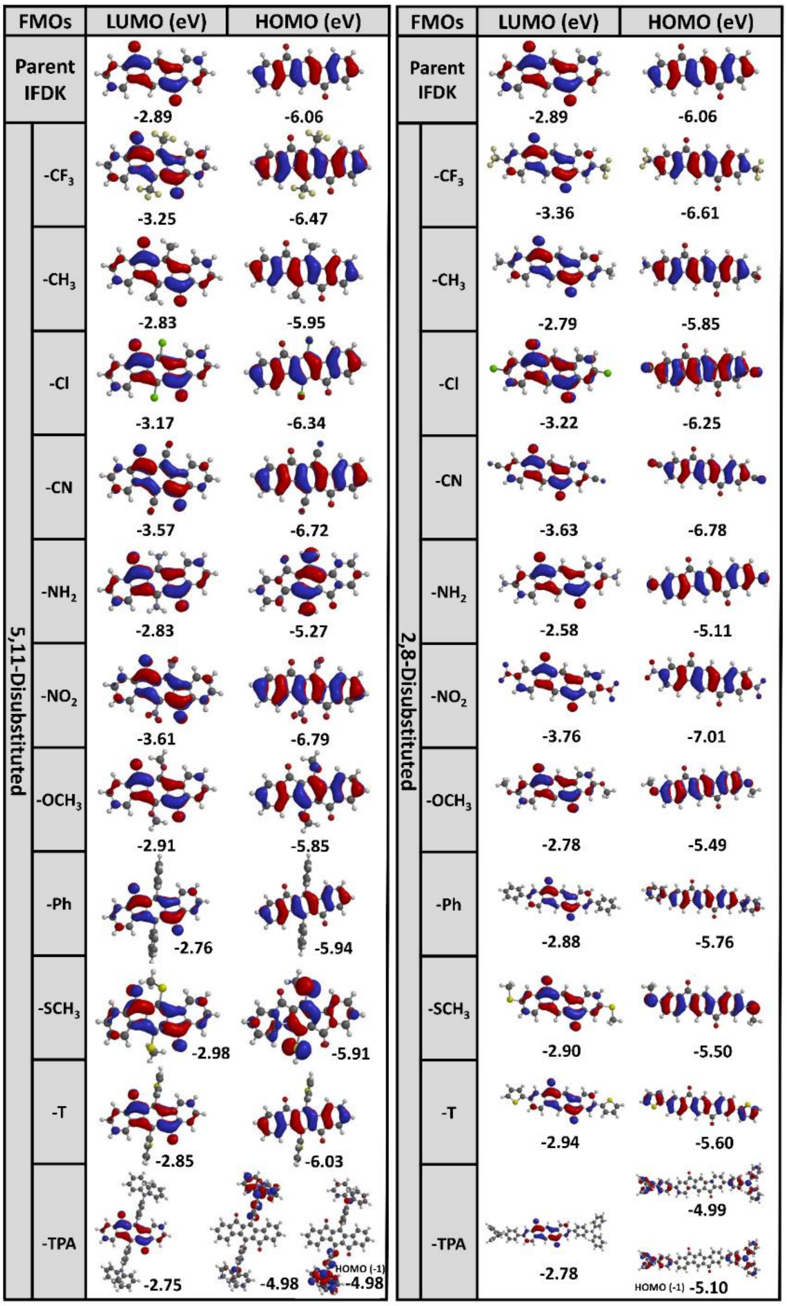

Figure 4: Computed HOMO and LUMO energy levels, and topographical representations of IFDK derivatives with DFT and B3LYP/6-31G** basis set.

4. Conclusion

In conclusion, the hole and electron reorganization energies of 23 IFDK-based small molecules were calculated using DFT for the first time, systematically investigating the impact of substituent nature and position on the reorganization energy. Owing to its strong electron-donating ability, 5,11-ditriphenylamine substituted IFDK molecule exhibited a much lower hole reorganization energy than its unsubstituted counterpart, with a significant difference of 160 meV observed, alongside the localization of HOMO electrons on the TPA groups. This behavior became less pronounced when moving from the 5,11-position to the 2,8-position with the same substituent, where a downshift of 130 meV was noted in the hole reorganization energy. The same substituent group showed varying reorganization energy based on the specific substitution position, highlighting the significant impact of substitution on the reorganization energy. More effective charge transfer is expected upon TPA substitution in IFDKs, due to lower reorganization energy.

In contrast to general observation for other substituent that typically resulted in an absolute increase, -CN and -CH_3 substitutions at 5,11-position, as well as -CN, -SCH_3, and -Ph substitutions at 2,8-position, displayed similar downshift in the hole reorganization energy, albeit to a lesser extent compared to TPA substitution. The same substituent groups including -TPA and -CN resulted in different hole reorganization energies based on the precise position of the substitution. To the best of my knowledge, this is the first study in literature comparing the reorganization energy of the same substituent at different positions around the IFDK π-core.

It was found that introducing any of the substituents used in study into the IFDK molecule at the 5,11-position increased the electron reorganization energy. Meanwhile, substitutions at the 2,8-position with -CN, -NO_2, and -T groups resulted in a slight decrease in the electron reorganization energy. These results clearly indicate the importance of substitution position around the IFDK molecule. Substitution at the 2,8-position appears to be more favorable for designing n-type molecular semiconductors within this family. Additionally, the downshift in the hole reorganization energies upon substitution at the same position suggests that achieving ambipolar semiconductivity with 2,8-substituted IFDKs is highly feasible. Moreover, 5,11-substitution of IFDK appears promising for designing *p*-type semiconductors, as the electron reorganization energy increased for all substituents, while the hole reorganization energy decreased upon -CN and -CH_3 substitution.

With these new results, the crucial structure–property relationships for IFDKs are better established now/have been better established, paving the way for future material designs in this family by identifying the optimal positions and substituents for improving charge transport properties through the reduction of the reorganization energy. The findings here demonstrate that 5,11- and 2,8-disubstituted IFDKs with lower hole and electron reorganization energies are promising candidates for *p*-type and *n*-type semiconducting materials.

Acknowledgements

I would like to thank Prof. Hakan Usta for his helpful discussions.

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