Continuum time-delayed electron hopping in the extended dynamical molecules and entropy-ruled Einstein relation for organic semiconductors

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Keywords: hopping transport, diffusion coefficient, mobility, site-energy fluctuation, entropy, dynamic disorder, organic semiconductors

Abstract
Charge transport (CT) in dynamically disordered molecular systems is still unclear; though it is fundamentally important to understand the semiconducting properties of molecular devices. In this regard, we explore vibronically coupled polaron hopping transport in the extended hopping systems (N + 1 sites) of thiazolothiazole (TZTZ) based molecules. The molecular vibrations correlated charge transfer integral and site energy fluctuation effects on polaron transport are analyzed by kinetic Monte-Carlo simulations. In order to quantify the CT properties more precisely, we have proposed the continuum time delayed CT mechanism, which takes account of typical disordered (static or dynamic) effect via dispersion on each CT quantity (like charge transfer rate, diffusion coefficient, mobility, current density and etc) at each hopping. The charge compressibility analysis further addresses the electronic level understanding of all CT quantities, which originally relates the thermodynamic density of states with CT. Using differential entropy-dependent charge density and diffusion expressions, the drift-diffusion transport has been elucidated for different extended systems of TZTZ derivatives. Besides, we have mainly developed entropy-ruled diffusion-mobility relation for both degenerate and nondegenerate materials to study the validity and limitations of original Einstein relation, which directly pertain to the device performance. Here, the traversing chemical potential along the hopping sites is the deterministic parameter of diffusion-mobility ratio. Using our continuum time delayed model, we can categorize the typical disordered transport in the molecular semiconductors; whether is dynamic or static or intermediate disordered transport.

1. Introduction
Effect of dynamic and static disorder on charge transport in organic semiconductors is of much practical importance for device level understanding [1–5]. Looking at the time scale between electronic and nuclear dynamics reveals the typical disordered charge transport and the localization property in most of the organic molecular systems [5, 6]. The temperature dependent structural dynamic correlations on both charge transfer integrals and site-energy fluctuations have been elucidated by many authors. Especially, Berlin and Böhlin’s coworkers demonstrated the variation of charge transfer integral and its consequences on charge transfer kinetics at different time scales of dynamic disorder domain [5, 7]. On the other hand, the site energy difference associated with forward and backward hopping rates and the effective transport in different organic molecules have explicitly been analyzed by Andrienko et al [8–10]. Interestingly, this site energy disorder importantly maps the charge transfer route in any organic and bio complex systems, which strongly depends on structural disorder and applied electric field [10–12]. Moreover, various studies on site energy fluctuations in charge carrier dynamics for different organic and hybrid systems motivate further to understand the interface physics in...
semiconducting devices [13–15]. The site energy difference between the adjacent energy levels can be modified via external interactions like, electric field, doping, etc. The interfacial effect, bias voltage and contact phenomena on charge transport can generally be incorporated in to the site energy difference, which has been shown to be the main controlling parameter for device performance [13, 16]. Thus, the fundamental understanding between structural dynamics associated with site energy fluctuations leading to fluctuations in transport property is crucial to design better organic semiconducting devices.

Interestingly, flickering resonance method and Troisi’s studies emphasize the dynamic disorder assisted delocalization transport in organic molecular systems [1–3, 11, 17]. These models clearly show that the limitation of localization transport in dynamic disordered molecular systems lead towards the band-like transport. Also, our recent studies strongly suggest the possibility of transformation from dynamic to static disordered charge transport, in which dispersion appears at each hopping step in the extended dynamical molecular units [16, 18]. Here, the existence of dispersion in charge transport and its corresponding time delayed CT mechanism is directly dependent on the amplitude of site energy fluctuations and structural fluctuation time (or oscillation time). This is in direct compliance with the flickering resonance and Troisi’s models [1–3, 11, 16]. Moreover, various experimental and spectroscopic studies also confirm the intermediate mechanism between localized (hopping) and delocalized (band) charge transport in different molecular systems, which show the importance of dynamic to static disorder conversion study on charge transport mechanisms [17, 19]. This typical disorder conversion can usually be modified by electric field and hence the drift coupled diffusion transport is expected to play major roles in such dynamical molecular systems. In this scenario, revising the Einstein relation of diffusion-mobility is necessarily important to understand the physics of molecular devices. Hitherto, microscopic understanding on the nature of intermediate charge transport from dynamic to static disorder conversion in device physics is still not completely clear [16]. Moreover, the study of typical disorder mediated dispersion effect and its relevant time delayed character on charge transport in organic semiconductors is quite important to further explore the quantum devices.

Based on the above analysis, here, we demonstrate the time delayed mechanism via dispersion effect on each charge transport parameters (such as, the charge transfer rate, diffusion, drift force, mobility, current density etc) for different site energy disorder values, with the aid of kinetic Monte-Carlo simulations. The dispersion is actually the factor that causes the time delay for charge transfer (CT) process at each hopping steps, which is termed as CT delay factor. In the present study, the dispersion correction is carried out in each of these charge transport parameters to calculate the exact CT properties for different number of stacked/conjugated units. Importantly, we have introduced the charge compressibility parameter which is originally associated with the thermodynamic density of states (TDOS). Here, the charge compressibility analysis is fundamentally to grasp the quantum picture of molecular electronics. The dispersion correction in TDOS (or electronic compressibility) is of great significance to explore the energy disorder-electron dynamics correlations in the molecular devices, which originally quantifies the continuum time-delayed CT in extended systems. The dispersion corrected diffusion and its consequences on mobility are main parameters to characterize the diode performance via the ideality factor (or enhancement factor). To study the effect of dispersion in molecular semiconductors, revisiting the Einstein relation is fundamentally required to explain the polaron dynamics in molecular level devices.

In this regard, to carry out the dispersion implemented-charge transport calculation, here we have considered three different thiazolo-thiazole based oligomers as the model systems. To understand the structure-property relationship, the structural information with chemical structure of these thiazolo-thiazole-based molecular systems (TZTZ1, TZTZ2 and TZTZ3) is given in the supplementary material. The chemical structures of these molecules are given in the Supplementary Material. In this work, we have proposed a new version of entropy-ruled Einstein diffusion-mobility equation which is more suitable for both degenerate and nondegenerate molecular systems. In fact, the diffusion-mobility equation, which is developed here is originally derived from generalized Einstein relation, incorporating the entropy effect with it. The electric field coupled site energy dynamics on carrier transport has been quantified by the differential entropy, which gives rise to degeneracy strength on diffusion and carrier density. In this work, we have considered the differential entropy derived from Gaussian function, as more appropriate for charge transport in disordered molecular solids.

The paper is organized as follows. In section 2, we have presented the equations of continuum time delayed (or dispersion corrected) charge transport parameters like, CT rate, diffusion coefficient, charge-energy flux, current density etc. Also, the chemical potential is calculated to explore the charge compressibility (or TDOS) based charge transport analysis in these molecular solids. Besides, the momentum-energy distribution functions and kinetic Monte-Carlo simulations are explained in this section. Based on our formalism, we have numerically calculated these charge transport parameters under dispersion condition for three different thiazolo-thiazole molecular solids at various site energy disorder values for different extended oligomers (N + 1 sites), and the results are discussed in section 3. The CT delay factor (due to dispersion effect) is monitored in each time steps of the simulations, and thus the continuum time delayed charge transport properties are analyzed with respect to that. For each hopping steps, we have verified the validity and limitations of Einstein relation using the charge
compressibility parameter at each hopping site of the dynamical system of extended units for the given set of site-energy disorder values. Interesting point is that using our model, one can easily classify whether the studied molecular solids follow Langevin or Shockley-Read-Hall (SRH) mechanism. Finally, some important corollaries and concluding remarks are presented in section 4.

2. Model

2.1. Charge transfer rate

The charge transfer rate \( k \) is calculated using semi-classical Marcus theory, and is described as [8, 10, 20],

\[
  k = \frac{I_{\text{eff}}^2}{\hbar} \frac{\pi}{\lambda k_B T} \exp \left[ -\frac{(\Delta E_{ji} - \lambda)^2}{4 \lambda k_B T} \right] 
\]

where, \( I_{\text{eff}} \), \( h \), \( k_B \), \( \lambda \), \( T \) and \( \Delta E_{ji} \) are effective charge transfer integral, reduced Planck constant, Boltzmann constant, reorganization energy, temperature and site energy difference between adjacent electronic states of neighboring molecular units, respectively. In the present study, site energy difference can be tuned by external electric field, and it can be explicitly expressed as \( \Delta E_{ji} = E_i - E_j - qE_j \hat{R}_{ji} = -\left( E_j - E_i + qE_j \hat{R}_{ji} \right) \) [13, 14, 21], where, \( E_i \) and \( E_j \) are site energies of electron (hole) in the \( i \)th and \( j \)th molecular orbitals, and \( qE_j \hat{R}_{ji} \) is electric charge (1.6 \( \times \) 10\(^{-19} \) C), external electric field and intermolecular distance, respectively. Here, the electric field induced site energy difference is \( \Delta E(\hat{E}) = qE \hat{R}_{ji} \). The charge transport parameters, like, CT rate, diffusion, mobility and total current density are calculated for different \( \Delta E(\hat{E}) \) values of 0, 25, 50 and 75 meV. Note that, the CT rate is directly associated with the other CT parameters such as, diffusion, mobility, current density etc. The electric field coupled drift-diffusion mechanism in charge transport is analyzed by site energy disorder (or site energy difference) for three different thiazolothiazole based oligomeric derivatives. Using kinetic Monte-Carlo (KMC) simulations, the structural dynamics correlated CT rate at each hopping step is calculated for different values of the site energy differences. The numerically calculated CT rate for different \( \Delta E(\hat{E}) \) of 0, 25, 50 and 75 meV is termed as \( k_0 \), \( k_1 \), \( k_2 \) and \( k_3 \), respectively. With respect to CT rate variation, other CT parameters might vary for each hopping steps of simulation with different set of \( \Delta E(\hat{E}) \) values. As described in earlier studies, the continuum time delayed charge transport mechanism can be investigated through dispersive parameters, which can vary with the hopping number along the consequential sites and applied electric field [16, 18, 22]. To validate our continuum time delayed CT (due to dispersion weightage) mechanism in organic semiconductors, we have used the values of effective charge transfer integral, reorganization energy and structural disorder information for three different oligomeric thiazolothiazole molecular systems that are reported in our earlier study [23].

2.2. Kinetic Monte-Carlo simulations

The earlier studies suggested that the structural fluctuations in the form of periodic fluctuation in \( \pi \)-stacking angle strongly influence the CT rate, mobility and current density etc. [23–25]. Thus, to explore the charge transfer kinetics in the dynamic disordered molecular systems, the information about stacking angle and its fluctuation around the equilibrium is required. The molecular conformation-dependent site energy distribution (disordered energy landscape at each position) and charge transfer integral distributions and time scale of structural fluctuation are essential to study the charge transport in dynamic medium. In this regard, the computed equilibrium stacking angle and fluctuation ranges from molecular dynamics (MD) simulations for three different thiazolothiazole dimer systems are used in KMC simulation to study the structural dynamics effect on the charge transport phenomena. Along with the reorganization energy, the stacking angle dependent effective charge transfer integral \( (I_{\text{eff}}(\theta)) \), and the site energy difference \( \Delta E_{ji}(\theta) \) are interpolated for 300 values that are taken as input to the KMC simulation to analyze the carrier dynamics. Here, the KMC simulations are performed up to the time scale of 1 ps with a time step of 1 fs. For each 10 steps, the mean values of CT quantities (e.g., survival probability, charge transfer rate) are sampled, and hence 100 sampled dynamical points are saved in the output file. In this study, the chosen structural oscillation (or fluctuation) time is 0.1 ps, which is taken from MD simulation. Moreover, the time step of MD simulations (0.1 ps) and temperature (300K) are provided in the numerical simulation. During simulation, the charge propagates on the basis of rate of charge transfer, which is calculated from equation (1). For disordered \( \pi \)-stacks of thiazolothiazole based molecules, the effective charge transfer integral and site energy difference vary with respect to the stacking angle [23]. Due to the disordered nature in energy landscape (e.g., site energy disorder), we perform the simulation using the random walk procedure over the space of configurations, which suits well for the charge transport in disordered (random site) systems. Hence, the expected localization transport through charge hopping process is studied with the aid of Marcus theory and KMC simulations. In each step of KMC simulation, the most probable hopping pathway is found from the simulated trajectories based on the charge transfer rate at a particular conformation. For our KMC simulation, we have implemented the Metropolis algorithm to sample the configuration with respect to
the probability distribution, which is non-other than Boltzmann probability. In this study, the charge hopping probability is estimated from Franck-Condon density of states, which gives the thermally populated states. In this method, the charge transport parameters like, CT rate and diffusion are numerically calculated by kinetic Monte-Carlo simulations. The π-stack is denoted by a consecutive localized site, which is sufficiently long so that the charge does not reach the ends of molecular chain within the time scale of simulations. Besides that, to achieve the thermal equilibrium in the diffusion process, more number of sites (number of sites considered are 10000) are chosen in the KMC simulations. Here, the charge is allowed to move from site to site by incoherent charge transport with a hopping rate which is equal to the Marcus charge transfer rate. The stacking angle is 10000° for TZTZ1, θequ=21° for TZTZ2 and θequ=26° for TZTZ3 dimers.[23] The time dependent characteristics of effective charge transfer integral (J(0),t) and site energy difference (ΔEj(t)) is purely dependent on conformation dynamics in the form of stacking angle fluctuations. These structural dynamics significantly modifies the magnitudes of charge transfer rate, mobility and current density etc. In each step of KMC simulation, the most probable hopping pathway is found out from the simulated trajectories based on the charge transfer rate and mean squared displacement at a particular conformation. Also, the loss of CT kinetics is calculated in each time step of simulation at different external field (Δ) values, which is actually incorporated with the site energy difference. The declining nature of charge transport for every sequence in the hopping sites is numerically characterized by the dispersive parameter, which is incorporated in each CT parameters.

2.3. Dispersion corrected charge transport parameters

The effect of structural dynamics on CT rate (or rate coefficient) with time, k(t), can be numerically estimated for each time step of simulation by the following relation as [5, 23],

\[ k(t) = -\frac{d \ln P(t)}{dt} \]  (2)

where, P(t) is the survival probability of charge carrier at a particular site. In this study, the time dependency of CT rate (or hopping rate) is analyzed by KMC simulation for different ΔE(Δ) values of 0, 25, 50 and 75 meV. Based on time varying CT rate, the loss of CT kinetics can be monitored at each hopping process. According to Maclaurin series, the CT rate can be expanded as,

\[ k(t) = k_0 \pm \frac{\partial k}{\partial t} t \pm \frac{1}{2} \frac{\partial^2 k}{\partial t^2} t^2 \pm ... \]  (3)

where, k0 is the initial CT rate, which is termed as CT rate in the first hopping step in the extended molecular units (i.e., i → j ≡ 1st site → 2nd site; thus, k0 = k12), and i is the time. In the extended hopping systems, the CT rate for each hopping satisfies the following relation, k12 ≥ k23 ≥ k34 ≥ ... ≥ k(N-1)N. Based on the nature of slope in CT rate trajectory at each time step of KMC simulations, + or -ve sign will appear in higher order terms in the above equation (3). Thus, decrease in CT rate is hypothetically related with the dispersive parameter a, which makes sure the time delay in each hopping, and its time dependence can be defined as,

\[ a(t) = \frac{a(t)}{k_0} = 1 \pm \frac{1}{k_0} \frac{\partial k}{\partial t} t \]

\[ \pm \frac{1}{2k_0} \frac{\partial^2 k}{\partial t^2} t^2 \pm ... \geq 1 - \Delta a(t) \]  (4)

Here, \( \Delta a(t) = \frac{1}{2k_0} \frac{\partial k}{\partial t} t \pm \frac{1}{2k_0} \frac{\partial^2 k}{\partial t^2} t^2. \) In our model, we assume the dispersive parameter for the initial hopping to be 1, i.e., a(t = 0) = 1, for the initial time step of simulation. It has been well-known that the dispersion-free hopping transport is expected for a → 1, and a strong incoherent transport is anticipated (or charge trapping) at a → 0 [16]. In equation (4), \( \Delta a(t) \) represents the dispersion weightage on CT kinetics at each hopping step in the extended system of N + 1 sites. Here, the CT delay for each hopping is directly proportional to \( \Delta a(t) \), which naturally lie between 0 and 1. In fact, the dispersion strongly affects the CT rate, diffusion-mobility, current density and other CT parameters. Thus, the effect of dispersion correction in these parameters is necessarily important to understand the device functionality in a precise manner.

Now, the continuum time delayed CT rate (via the dispersion correction) for (N + 1) extended sites can be defined as (for detailed analysis, see Supplemental Material),

\[ k_d(N) = k_0 \sqrt{\prod_{j=1}^{N} a_j} \]  (5)

where, N, k12 and ai are the total number of hopping, CT rate of first hopping (i.e., jumping from 1st site to 2nd site) and dispersive parameter of jth hopping in the (N + 1) extended sites, respectively. Here, \( \prod_{j=1}^{N} a_j \) is the...
geometric mean of the dispersive parameter up to N hopping steps in the dynamical system of N + 1 sites. Note that, the mean CT rate and other relevant mean CT quantities of an extended system depend on the time delay factor of polaron hopping at each site. That means, the magnitude of hopping rate $k_{mn}$ strongly depends on magnitudes of earlier rates like, $k_{ij}, k_{dk}, k_{dj}$ and so on. For each hopping step, there is a loss in CT rate which can be characterized by the parameter, $\alpha$. In this context, the dispersion corrected total diffusion coefficient for the extended one-dimensional chain (or molecular system) can be expressed as,

$$D_d(N) = \frac{R_j^2 k_{ij}^{-2}}{2} \sqrt{\prod_{j=1}^{N} a_j}$$

(6)

where, $R_j$ is the intermolecular distance. Using the above diffusion relation, we propose the modified version of empirical form of Einstein equation for N + 1 sites as \[16, 26,\]

$$\mu_d(N) = \left(\frac{q}{\eta_N k_B T}\right) D_d(N)$$

(7)

where, $q$ is the electric charge, $\eta_N$ is the effective diode ideality factor for N hopping CT process (i.e., for the system with N + 1 sites), $k_B$ is the Boltzmann constant and $T$ is the temperature. In this study, the ideality factor ($\eta_N$) is calculated from the generalized Einstein relation \[27, 28,\]

$$\eta_N = \frac{1}{k_B T} \frac{\partial_n d}{\partial \Phi_{CP,d}} = \frac{1}{k_B T} \left(\frac{d \ln n_d}{d \Phi_{CP,d}}\right)^{-1}$$

(8)

where, $n_d$ and $\Phi_{CP,d}(N)$ are the dispersion corrected carrier density and chemical potential in the extended dynamical system of N + 1 sites (or N hopping), respectively. In this regard, we can incorporate the dispersion relation (or continuum time delayed mechanism) in diffusion-mobility and ideality factor as,

$$\mu_d(N) = \frac{q D_d(N)}{n_d} \frac{\partial n_d}{\partial \Phi_{CP,d}(N)} = \frac{1}{\eta_N} \frac{q D_d(N)}{k_B T}$$

(9)

The term, $\frac{\partial n_d}{\partial \Phi_{CP,d}(N)}$ is actually the charge compressibility in the concerned electronic states, which provides the information about thermodynamic density of states \[29, 30,\]. In this study, the carrier density is calculated from the relationship \[16, 18,\]

$$n_d = \frac{\varepsilon}{q^2 D_d(N)} \left(\frac{\partial E_d(N)}{\partial n}\right),$$

(10)

where, $\varepsilon$ is the electric permittivity of the medium ($=\varepsilon_0 \varepsilon_r$), and $\frac{\partial E_d(N)}{\partial n}$ is the dispersion corrected rate of carrier energy, which is the energy flux during the charge transport process. As described in our model, the dispersion corrected drift force ($F_{d}^0(N)$), and total current density relation for the extended system of N + 1 sites can be expressed as \[16, 18,\]

$$J_d(N) = \frac{3q}{h} \left(\frac{1}{3n_{\text{av}}^2/3F_{d}^0(N)R_j^2}\right)^{1/3}$$

(11)

In the above equation 11, $F_{d}^0(N)$ is the minimized drift force due to dispersion effect (or time delayed CT mechanism) that continuously modifies the charge carrier current, depending on the temperature, disorder weight and applied electric field. That is, the charge carrier motion is controlled by the factor, $F_{d}^0(N)$, which arise from the carrier momentum redistribution due to dynamic disorder and electric field (see Refs. \[16 and 18,\]).

As described in our earlier studies, the parameters, such as, drift force and rate of traversing energy are calculated using momentum and energy redistribution functions \[16, 18,\]

$$P_{\text{mom}}(t) = P_{\text{mom},0} \left[\exp\left(\frac{8(1 - P(t))}{15}\right)\right]$$

(12)

$$\Delta E(t) = E_{K,0} \left[1 - \exp\left(\frac{16(1 - P(t))}{15}\right)\right]$$

(13)

where, $P(t), P_{\text{mom},0}$ and $E_{K,0}$ are the survival probability, the initial momentum and the initial kinetic energy of the charge carrier, respectively, and $\Delta E(t)$ is the change of potential energy with respect to traversing carrier energy during the transport. Through KMC simulations, the numerically calculated survival probability of charge carrier is directly used in equations (12) and (13) to analyze the momentum and energy redistribution during the charge transport in the extended dynamical system of N + 1 sites. In this analysis, the initial kinetic energy is equivalent to that of thermal energy, $E_{K,0} = k_B T$, since our study is based on thermally activated hopping mechanism. By taking the numerical differentiation of momentum and energy redistribution plots, we can obtain the drift force on the charge carrier and rate of traversing energy along the consequential hopping
sites, respectively. In this context, under the dispersion condition, the expected drift force and rate of traversing energy can be estimated by the following expressions,

\[
F_D^d(N) = \frac{dP_{\text{mon}}(t)}{dt} = \frac{8}{15} \alpha_1 P_{\text{mon},0} k_1^2 \sqrt{N} \prod_{j=1}^{N} a_j
\]  
(14)

\[
\frac{\partial E_d(N)}{\partial t} = \frac{16}{15} \alpha_2 k_2 T k_{12} \gamma \sqrt{N} \prod_{j=1}^{N} a_j
\]  
(15)

Here, \( \alpha_1 \) and \( \alpha_2 \) are the obtained from fitting the momentum and the energy redistribution plots, respectively. The rate of traversing energy (or energy flux) obtained from equation (15) is used in equation (10) to evaluate the dispersion corrected carrier density. On the other hand, along with the carrier density, the governed dispersion corrected-drift force from equation (14) is substituted in equation (11) to obtain the dispersion corrected current density. In the present model, we have included the dispersion correction in the all the charge transport parameters (e.g. CT rate, diffusion, mobility, charge compressibility, drift force, rate of traversing energy and current density), which are numerically estimated with the aid of KMC simulation in the dynamical system of \( N + 1 \) sites for the different site energy disorder values (0, 25, 50 and 75 meV). This is the continuum time delayed CT in the extended dynamical hopping systems.

2.4. Differential entropy and dispersion effects on carrier density, diffusion and mobility

In general, the charge transport in organic semiconductors follows Gaussian disorder model. The existence of degenerate states due to applied electric field (via site-energy difference) is normally analyzed by Gaussian disorder width (\( \sigma \)), which is directly connected with the differential entropy. Here, the differential entropy (\( h_S \)) is derived from Gaussian distribution function (\( \Phi \)) as,

\[
h_S(x) = -\int \Phi(x) \ln \Phi(x) dx = \ln (\sigma \sqrt{2\pi})
\]  
(16)

As like in our earlier model studies, the electric field dependent entropy can be derived from the traversing energy rate expression [16, 18],

\[
h_S(E) = \ln \left( \frac{dE(\tilde{E})/dt}{dE(\tilde{E} = 0)/dt} \right)
\]  
(17)

where, \( dE(\tilde{E})/dt \) and \( dE(\tilde{E} = 0)/dt \) are the rate of traversing energy (or rate of energy flux) along the CT hopping path with and without electric field. For different electric field strengths, the rate of traversing energy along the consecutive sites has been calculated using equation (15). In this study, the Gaussian disorder width is considered as, \( \sigma (\tilde{E}) = \frac{1}{\sqrt{2\pi}} \exp (h_S(\tilde{E})) \), which gives the effect of field dependent degeneracy on drift-diffusion and activated-carrier density for charge transport. To find out the electric field (via site energy difference) modulated dispersion effect on continuum time delayed charge transport in the extended system, we have derived the dispersion corrected-differential entropy, which can explicitly be written as,

\[
h_S^d(N, \tilde{E}) = \ln (dE(\tilde{E})/dt) + \frac{1}{N} \ln \left( \prod_{j=1}^{N} a_j(\tilde{E}) \right) - \ln (dE(\tilde{E} = 0)/dt)
\]  
(18)

However, on the basis of equation (15), the dispersion-differential entropy relation can be rewritten as,

\[
h_S^d(N, \tilde{E}) = \ln \left( \frac{\alpha_2(\tilde{E}) k_2(\tilde{E}) \sqrt{N} \prod_{j=1}^{N} a_j(\tilde{E})}{\alpha_2(\tilde{E} = 0) k_2(\tilde{E} = 0)} \right)
\]  
(19)

Now, the electric field coupled time delayed effect by dispersion on charge density and diffusion coefficient in the extended hopping systems can be studied by the following equations (16).

\[
n_d(N, \tilde{E}) = n(\tilde{E} = 0) \exp \left( \frac{3h_S^d(N, \tilde{E})}{5} \right),
\]  
(20)
where, \( n(\vec{E} = 0) \) and \( D(\vec{E} = 0) \) are the charge carrier density and diffusion coefficient at zero electric field conditions, which are calculated by \( n(\vec{E} = 0) = \frac{\varepsilon}{e^2 D(\vec{E} = 0) \left( \frac{\partial n(\vec{E} = 0)}{\partial \vec{E}} \right)} \) and \( D(\vec{E} = 0) = \frac{1}{2} R_0^2 k(\vec{E} = 0) \), respectively. In this procedure, the calculated quantities \( D_d(\vec{N}, \vec{E}) \) and \( n_d(\vec{N}, \vec{E}) \) are inserted in equations (9) and (11) to evaluate the effective mobility and the total current density under the dispersion condition at different electric field values for thiazolothiazole based extended molecular systems. The zero field charge diffusion (self-diffusion transport, \( D(\vec{E} = 0) \)) and its appropriate dispersion effect is generally estimated from equation (6). Here, the expected dispersion effect on charge transport parameters varies with the applied electric field or site energy disorder, \( \Delta E_{ij} = E_i - E_j - q\vec{E}.\vec{R}_{ij} \). Using equations (20) and (21) in equation (9), the entropy-ruled Einstein mobility relation is expressed as,

\[
\frac{D_d(\vec{N}, \vec{E})}{\mu_d(\vec{N}, \vec{E})} = \frac{5}{3q} \left[ \frac{\partial h_s}{\partial \Phi_{CP,d}(\vec{N}, \vec{E})} \right]_D \times (\vec{E} = 0) \exp \left( \frac{2h_s}{5} \right) 
\]

(22)

Here, the calculated differential entropy is associated with the external electric field. For different sets of electric field induced site energy differences, one can plot the changes of chemical potential with respect to the differential entropy. In this regard, the governing dispersion corrected-mobility equation for the extended system of \( N + 1 \) site can be written as

\[
\mu_d(\vec{N}, \vec{E}) = \frac{3q}{5} \left( \frac{\Delta h_s}{\Delta \Phi_{CP,d}(\vec{N}, \vec{E})} \right)_D \times (\vec{E} = 0) \exp \left( \frac{2h_s}{5} \right) 
\]

(23)

Here, the parameter \( n_d(\vec{N}, \vec{E}) \) is calculated using equation (20). In this work, the calculated dispersive parameter is mainly responsible for continuum time delayed CT at every consequent hopping steps. According to the entropy-ruled Einstein relation, the Shockley diode equation is modified here as,

\[
J = J_0 \exp \left( \frac{3q}{5} \left( V - \frac{\Delta h_s}{\Delta \Phi_{CP}} \right) - 1 \right) 
\]

(25)

where, \( J, J_0, V \) and \( \Delta h_s/\Delta \Phi_{CP} \) are the current density, saturation current density, applied voltage and the variation of differential entropy with respect to the chemical potential, respectively. This modified version of Shockley diode equation is named as Navamani-Shockley (NS) diode equation.

### 3. Results and discussion

#### 3.1. Charge transport in an extended dynamical system

In order to explore the effect of structural dynamics on charge transport properties for an extended system of \( N + 1 \) sites, the computed CT basic parameters (effective charge transfer integral, site energy difference, reorganization energy) of various thiazolothiazole oligomers and their conformational disorder in the form of stacking angle distributions are used as inputs for the KMC simulations. Here, the site energy difference in Marcus theory of charge transfer rate (see equation (1)) can be tuned by applied electric fields, which in turn would change the drift coupled diffusion transport in the disordered molecular solids. In the present study, the electron transport parameters like, CT rate (or rate coefficient), mobility and current density are calculated in the extended dynamical system of TTTZ1, TTTZ2 and TTTZ3 oligomers for different values of electric field-assisted site energy difference, \( \Delta E(\vec{E}) = q\vec{E}.\vec{R}_{ij} \). Here, different \( \Delta E(\vec{E}) \) values (0, 25, 50 and 75 meV) have been fixed in our KMC simulations to study the charge transport along with the effects of both the applied electric field and structural fluctuations. The applied electric field generally reduces the site energy barrier in the disordered systems. In principle, the site energy difference is equivalent to that of site energy disorder.
To analyze the drift-diffusion transport in these three test molecular oligomeric systems, we have numerically studied the thermally activated hopping mechanism for different $\Delta E(\vec{E})$ values. In this context, the survival probability $(P(t))$ of charge carrier and the variation in CT rate, $(k(t))$, has numerically been characterized using KMC simulations with the conjunction of equations (1) and (2) for different site energy disorder values of 0, 25, 50 and 75 meV, respectively. From KMC simulations, the survival probability has been noted at each time steps in the three $\pi$-stacked dynamical systems, which are shown in figures 1 and S2 (available online at stacks.iop.org/JPCO/5/075012/mmedia). The survival probability plot shows that the applied electric field (via site energy difference) enhances the charge migration process from the initial site to next to next site in the extended molecular hopping systems (see figure 1). By applying exponential relation of $P(t) = P_0 \exp(-kt)$, we have estimated the CT rate (or the rate coefficient of charge, $k$) for different site energy disorder values, which are summarized in tables 1, 2 and S1–S3. The calculated electron rate coefficients for the first hop (jumping from

![Figure 1. Survival probability of electron in the $\pi$-stacked (a) TZTZ1 and (b) TZTZ2 molecules with respect to time, at different set of electric field induced site energy differences of 0, 25, 50 and 75 meV. From this survival probability plot, we have calculated the electron transfer rate coefficients ($k_1$, $k_2$, $k_3$ and $k_4$) for these molecules at different site energy difference values (0, 25, 50 and 75 meV).](image-url)

### Table 1. Applied electric field ($\vec{E}$), inter-molecular distance ($R$), electric field assisted site-energy difference ($\Delta E(\vec{E})$), rate coefficient ($k$), drift force ($F_d$), rate of energy flux ($\frac{\partial n}{\partial t}$), carrier density $n(\vec{E})$ and current density ($I$) for electron transport in TZTZ1, TZTZ2 and TZTZ3 molecules at different set of $\Delta E(\vec{E})$ values of 0, 25, 50 and 75 meV for dimer system of 2-site model.

| Molecule | $\vec{E}$ ($\times 10^5$ V cm$^{-1}$) | $R_0$ (Å) | $\Delta E(\vec{E})$ (meV) | $k$ (s$^{-1}$) | $F_d$ (N) | $\frac{\partial n}{\partial t}$ (eV s$^{-1}$) | $n(\vec{E})$ (cm$^{-3}$) | $I$ (mA cm$^{-2}$) |
|----------|---------------------------------|-----------|--------------------------|--------------|----------|-----------------------------|-----------------|-----------|
| TZTZ1    | 0.0                             | 3.53      | 0                        | $1.48 \times 10^{13}$ | 1.19       | $3.07 \times 10^{12}$       | 1.84            | 1.52      |
|          | 7.082                           | 3.53      | 25                       | $2.62 \times 10^{13}$ | 3.07       | $6.98 \times 10^{11}$       | 3.01            | 5.44      |
|          | 14.164                          | 3.53      | 50                       | $4.26 \times 10^{13}$ | 4.70       | $9.97 \times 10^{11}$       | 3.72            | 9.62      |
|          | 21.246                          | 3.53      | 75                       | $6.93 \times 10^{13}$ | 7.43       | $14.79 \times 10^{11}$      | 4.72            | 17.80     |
| TZTZ2    | 0.0                             | 3.53      | 0                        | $3.34 \times 10^{15}$ | 2.55       | $6.36 \times 10^{11}$       | 1.69            | 3.08      |
|          | 7.082                           | 3.53      | 25                       | $5.27 \times 10^{15}$ | 3.17       | $7.79 \times 10^{11}$       | 1.91            | 4.15      |
|          | 14.164                          | 3.53      | 50                       | $8.57 \times 10^{15}$ | 5.98       | $13.58 \times 10^{11}$      | 2.66            | 9.78      |
|          | 21.246                          | 3.53      | 75                       | $13.95 \times 10^{15}$ | 10.7       | $22.67 \times 10^{11}$      | 3.62            | 21.50     |
| TZTZ3    | 0.0                             | 3.59      | 0                        | $6.21 \times 10^{13}$ | 8.17       | $1.91 \times 10^{12}$       | 2.65            | 13.77     |
|          | 9.646                           | 3.59      | 25                       | $8.17 \times 10^{13}$ | 8.63       | $2.20 \times 10^{12}$       | 3.12            | 16.24     |
|          | 13.928                          | 3.59      | 50                       | $13.30 \times 10^{13}$ | 12.78      | $2.80 \times 10^{12}$       | 3.34            | 25.15     |
|          | 20.891                          | 3.59      | 75                       | $21.64 \times 10^{13}$ | 22.05      | $4.40 \times 10^{12}$       | 4.36            | 51.86     |
1st site to 2nd site) of the extended dynamical TZTZ1 oligomeric units are $1.48 \times 10^{13}$ and $4.26 \times 10^{13}$ s$^{-1}$ with the site energy disorder values ($\Delta E(\vec{E})$) of 0 and 50 meV, respectively.

Among the three thiazolothiazole oligomeric systems considered, TZTZ3 has relatively large electron transfer rate values for all $\Delta E(\vec{E})$ (see tables 1, 2 and S1–S3). The results show that TZTZ3 has three times larger CT rate than the TZTZ1.

The numerical analysis clearly shows that there is a significant loss in CT rate at each hopping in the extended dynamical systems of $(N + 1)$ molecular units. As described in section 2.3., the loss in CT rate is calculated by CT delay factor (or dispersion parameter, $\alpha$) at each hopping for different site energy disorder values in these molecular solids. The time delay factor normally underlies in the range from 0 to 1. In the case of $\alpha \rightarrow 1$, the charge transport becomes non-dispersive kind of carrier motion along the consequential hopping sites, which facilitates the unrestricted polaron transport. That is, the electron hops continuously without time delay along the consequential sites of extended systems. On the other hand (\(\alpha \rightarrow 0\)), the charge transport follows highly dispersive transport which leads to charge trapping due to strong localizations. Based on the dispersion value ($\alpha$), the charge transfer delay is expected in each hopping steps (for detailed descriptions, see Supplemental Material). With our proposed equations of dispersion corrected-CT quantities, such as, the CT rate, diffusion coefficient, mobility, current density and ideality factor, etc. (see section 2.3.), we have studied the charge transport properties for the extended TZTZ1, TZTZ2 and TZTZ3 systems of $(N + 1)$ molecular sites with the different values of site energy disorder. The dispersion corrected CT quantities are summarized in tables 1–4 and S1–S6, which explicitly provides the restricted CT. In the dynamical system of $(N + 1)$ hopping sites, the applied
Table 4. Applied electric field (\(\vec{E}\)), electric field assisted site-energy gap (\(\Delta E(\vec{E})\)), relative differential entropy (\(b(E)\)), diffusion coefficient (\(D(E)\)), dynamically coupled chemical potential (\(\dot{\chi}(E)\)), charge compressibility (\(\frac{d\chi(E)}{dE}\)), mobility (\(\mu\)) and ideality factor (\(\eta\)) for electron transport in trimer (3-site) system of TZTZ1, TZTZ2 and TZTZ3 molecules at different set of \(\Delta E(\vec{E})\) values of 0, 25, 50 and 75 meV.

| Molecule | \(\vec{E}\) (\(10^3 V\) cm\(^{-1}\)) | \(\Delta E(\vec{E})\) (meV) | \(b(E)\) (\(10^{-2} cm^2s^{-1}\)) | \(D(E)\) (\(10^{-2} cm^2s^{-1}\)) | \(\dot{\chi}(E)\) (meV) | \(\frac{d\chi(E)}{dE}\) (cm\(^3\) eV\(^{-1}\)) | \(\mu\) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) | \(\eta\) |
|----------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------|
| TZTZ1    | 0.0             | 0              | -0.050         | 0.90           | 24.98          | 0.762 \(\times 10^{18}\) | 0.350          | 1.00      |
|          | 7.082           | 25             | 0.689          | 1.21           | 36.27          | 1.063 \(\times 10^{18}\) | 0.471          | 1.00      |
|          | 14.164          | 50             | 0.941          | 1.35           | 40.15          | 1.240 \(\times 10^{18}\) | 0.525          | 1.00      |
|          | 21.246          | 75             | 1.097          | 1.43           | 42.55          | 1.370 \(\times 10^{18}\) | 0.556          | 1.00      |
| TZTZ2    | 0.0             | 0              | -0.076         | 2.02           | 24.53          | 0.641 \(\times 10^{18}\) | 0.786          | 1.01      |
|          | 7.082           | 25             | 0.043          | 2.12           | 26.35          | 0.678 \(\times 10^{18}\) | 0.825          | 1.01      |
|          | 14.164          | 50             | 0.463          | 2.31           | 32.84          | 0.860 \(\times 10^{18}\) | 0.977          | 1.01      |
|          | 21.246          | 75             | 0.622          | 2.67           | 35.28          | 0.945 \(\times 10^{18}\) | 1.039          | 1.01      |
| TZTZ3    | 0.0             | 0              | 0              | 4.00           | 25.70          | 0.998 \(\times 10^{18}\) | 1.556          | 1.00      |
|          | 6.964           | 25             | 0.238          | 4.40           | 29.38          | 1.190 \(\times 10^{18}\) | 1.712          | 1.00      |
|          | 13.928          | 50             | 0.325          | 4.56           | 30.72          | 1.260 \(\times 10^{18}\) | 1.774          | 1.00      |
|          | 20.891          | 75             | 0.728          | 5.35           | 36.92          | 1.584 \(\times 10^{18}\) | 2.082          | 1.00      |

Electric field (via site energy difference) maximizes the dispersion effect in each hopping which significantly reduces the charge transfer process along the consecutive sites, which is the continuum time delayed electron/hole hopping transport. That is, the magnitude of CT quantities (CT rate, diffusion, current density and etc) significantly decreases at each step of hopping (along the consequential sites) with the site energy disorder. Thus, the CT rate (or rate coefficient) for each hopping can be written as, \(k_{12} \geq k_{33} \geq k_{34} \geq ... \geq k_{N-1N} \geq k_{N(N+1)}\). In this study, the consequential CT rate in the extended TZTZ1 molecule are as follows, \(k_{12} = 1.48 \times 10^{13}\), \(k_{33} = 1.41 \times 10^{13}\), \(k_{34} = 1.38 \times 10^{13}\) and \(k_{45} = 1.36 \times 10^{13} s^{-1}\) for zero value of \(\Delta E(\vec{E})\). In similar way, at \(\Delta E(\vec{E}) = 50 meV\), the calculated CT rate values along the every hopping steps are \(k_{12} = 4.26 \times 10^{13}\), \(k_{33} = 3.36 \times 10^{13}\), \(k_{34} = 3.04 \times 10^{13}\), \(k_{45} = 2.83 \times 10^{13} s^{-1}\) and etc. Here, it has been pointed out that the CT rate is rapidly decreasing with site energy disorder, \(\Delta E(\vec{E})\), in the extended dynamical systems (see figures 2, S3 and tables 1, 2 and S1–S3). In other words, for larger value of \(\Delta E(\vec{E})\), the expected dispersion effect on charge transport is more in the dynamical system of extended hopping sites. The same trend is noted in TZTZ3 molecule with different \(\Delta E(\vec{E})\) values. It is observed from our analysis, the large site energy fluctuation causes more loss in charge transfer kinetics (i.e., dispersion initiated CT delay) in the extended dynamical hopping system of TZTZ1, TZTZ2 and TZTZ3, which can be controlled by applied bias or electric field. In other words, the value of parameter ‘\(a\)’ will be decreasing (or increasing the CT delay due to dispersion) while increasing the site energy disorder which is noted in figure 2 and S3, and tables 1, 2 and S1–S3. The results clearly emphasize that for any dynamical system of extended \(N + 1\) hopping sites (\(\pi\)-stacked/conjugated molecules), the applied electric field via site energy difference (\(\Delta E(\vec{E})\)) subsequently increases the dispersion effect on carrier motion for each hopping process which in turn gives rise to static disorder rather than a dynamic disorder. Here, the existence of transition from dynamic to static disordered transport in the extended dynamical system can be controlled by either electric filed/bias voltage or frequency of molecular oscillation about its equilibrium. It is concluded that...
the applied electric field or voltage does not favor the charge transport in an extended dynamically disordered systems, but it favors only for the dynamical system of limited hopping sites (i.e., few stacked units). From our study it has been observed that the charge transport goes from dynamic to static disordered regime, while we increase the number of molecular units in the extended systems (i.e., conjugation length). Our theoretical results are in compliance with earlier studies proposed by Troisi et al \[2, 17\], and Beratan et al \[3\]. Importantly, one can directly show the validity of our present continuum time delayed (or dispersion corrected) CT through the flickering resonance method \[3, 11\]. Our theoretical analysis confirms that for large site energy fluctuation, the transformation from dynamic to static disordered transport occur in the extended systems of TZTZ1, TZTZ2 and TZTZ3 molecules, which essentially leads to dispersion initiated time delayed-hopping transport. In this context, the existence of static disorder emprises the large dispersion effect for all charge transport quantities in every hopping steps of simulations, which is extensively analyzed in the Supplemental Material.

### 3.2. Electric field-driven differential entropy on carrier density and diffusion

The effect of electric field coupled site energy difference ($\Delta E(\vec{E})$) on carrier density and diffusion is an important study to understand the device physics in molecular electronics. On the basis of electric field (or bias) response-transport behavior, we can classify the system to be degenerate or nondegenerate. In general, the degenerate materials are quite good for potential applications due to the presence of more delocalized electron density. The existence of degeneracy levels due to applied electric field (stark effect) further improves device performance via the electronic transport. In our study, the degeneracy effect on disordered molecular systems can be numerically quantified by the differential entropy ($h_S$) parameter. Using our earlier model \[16\], the parameter $h_S$ can be quantified from the ratio between rate of carrier energy flux, with and without electric field under dispersion conditions for different extended molecules (see section 2.4). Accordingly, the calculated $h_S$ values for different stacked thiazolothiazole molecules with the different $\Delta E(\vec{E})$ are summarized in tables 3 and 4, and S4–S6. It is observed that the differential entropy increases with $\Delta E(\vec{E})$ for limited hopping sites (few stacked/conjugated molecular units). On the other hand, the $h_S$ value decreases for large extended molecules under strong site energy fluctuation of $\Delta E(\vec{E})$. In this work, the dispersion correction is included in the parameter $h_S$ for different extended (or stacked) dynamical TZTZ1, TZTZ2 and TZTZ3 molecules at different set of $\Delta E(\vec{E})$ values of 0, 25, 50 and 75 meV. Here, the parameter $h_S$ is related to the field-response degeneracy.
Figure 4. The $\pi$-electron density with respect to the chemical potential in different number of stacked units of (a) TZTZ1 and (b) TZTZ2 molecules for different set of $\Delta \mathcal{E}(\hat{E})$ values. The dispersion correction is included in this calculation. The closed circles represent the calculated carrier density (by our model) at different electric field assisted $\Delta \mathcal{E}(\hat{E})$ values, and the solid line is a fitted plot.

Figure 5. The thermodynamic density of states (or electronic compressibility) under the dispersion correction for different extended dynamical molecules of (a) TZTZ1 and (b) TZTZ2 at different values of $\Delta \mathcal{E}(\hat{E})$. 

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**Figure 4.** The $\pi$-electron density with respect to the chemical potential in different number of stacked units of (a) TZTZ1 and (b) TZTZ2 molecules for different set of $\Delta \mathcal{E}(\hat{E})$ values. The dispersion correction is included in this calculation. The closed circles represent the calculated carrier density (by our model) at different electric field assisted $\Delta \mathcal{E}(\hat{E})$ values, and the solid line is a fitted plot.

**Figure 5.** The thermodynamic density of states (or electronic compressibility) under the dispersion correction for different extended dynamical molecules of (a) TZTZ1 and (b) TZTZ2 at different values of $\Delta \mathcal{E}(\hat{E})$. 

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under the dispersion condition in the studied molecules. This entropy quantifies the variation in Gaussian disorder width at different $\Delta E(\bar{E})$ in different stacked systems. Due to degeneracy weighed-$h_S$, the changes in localized $\pi$-electron density provoke the diffusion, which are directly computed from equations (20) and (21).

Here, degeneracy formation makes sure the chemical potential enhancement which in turn improves the carrier transport. In principle, the chemical potential is a direct evidence of field-response transport in any semiconducting materials. This connects the degenerate states and its consequences on electronic transport [27, 30, 33, 34]. The chemical potential due to $\Delta E(\bar{E})$-response differential entropy can be computed for different extended molecular units of TZTZ1, TZTZ2 and TZTZ3, which is shown in figures 3 and S4.

Interestingly, we observe that the raising chemical potential due to stark effect-based orbital splitting (or degeneracy) has linear relationship with the differential entropy, $h_S$. That is, the charge delocalization nature is purely depending up on the chemical potential, which is strongly influenced by carrier doping, electric field, gate voltage and temperature. In this connection, the linear dependent nature of chemical potential - differential entropy relation (see figures 3 and S4) suggests that there is no possibility for deviation in Einstein $D/\mu$-ratio for these thiazolothiazole based molecular solids (TZTZ1, TZTZ2 and TZTZ3), which is in compliances with the earlier experimental observations [26, 35]. According to the typical disorder (static or dynamic) magnitude, the chemical potential is reformed mandatorily with respect to the dispersion effect (see equation (24)). For large dispersions, the calculated chemical potential will be decreasing; accordingly, the other charge transport quantities will be declining which is shown in tables 3, 4 and S4–S6. Within a small energy window of chemical potential, the populated degenerate states have been quantified by electronic compressibility which is the thermodynamic density of states (TDOS). In this context, the variation in $\pi$-electron density with respect to the chemical potential is an important study to analyze the bias or electric field-response electronic transport in the different stacked TZTZ1, TZTZ2 and TZTZ3 molecules with the effect of dispersion. The variation of charge density with respect to chemical potential explicitly provides the TDOS (or electronic compressibility). This clearly describes the microscopic level understanding of charge transport in the studied molecular solids (see Supplemental Material for detailed analysis). Through our method, one can easily trace out the field-response transport characteristics behavior in molecular semiconducting devices, which is essential for material scientists to design ideal devices. Using equations (20) and (24), the carrier density and chemical potential are calculated.

Figure 6. The diffusion coefficient with respect to the thermodynamic density of states for the different stacked molecular system of (a) TZTZ1 and (b) TZTZ2 under the different site energy difference values of 0, 25, 50 and 75 meV. The dispersion correction (CT delay factor) is included in both the diffusion coefficient and the density of states. The closed circles are theoretically computed diffusion coefficient with respect to the populated electronic states (or TDOS) at different site energy dynamics of $\Delta E(\bar{E})$ values, and solid line represents the curve fitting.
with dispersion corrections at different set of $\Delta E(\bar{E})$ which are given in tables 1–2, and S1–S6. The chemical potential associated electron density is calculated for different stacked units of TZTZ1 and TZTZ2 molecules, which is shown in figure 4.

As described in section 2.4, the carrier density and diffusion coefficient has been quantified with the aid of differential entropy in different stacked (i.e., N + 1 sites) thiazoletetrazole molecules for the given $\Delta E(\bar{E})$ values, which are summarized in tables 1–4 and S1–S6. For instance, the calculated carrier density and diffusion coefficient at zero $\Delta E(\bar{E})$ value in the dimer system (2-site) of TZTZ1 are $1.84 \times 10^{19}$ cm$^{-3}$ and $0.92 \times 10^{-2}$ cm$^2$ s$^{-1}$, respectively. At $\Delta E(\bar{E})$=75 meV, the carrier density and diffusion coefficient are $4.72 \times 10^{19}$ cm$^{-3}$ and $1.73 \times 10^{-2}$ cm$^2$ s$^{-1}$. On the other hand of an extended system of pentamer (5-site) TZTZ1, the calculated carrier density and diffusion are $1.75 \times 10^{19}$ cm$^{-3}$ and $0.89 \times 10^{-2}$ cm$^2$ s$^{-1}$, respectively, for zero value of $\Delta E(\bar{E})$. At the same time of $\Delta E(\bar{E}) = 75$ meV, the computed carrier density and diffusion coefficient in the pentamer system are $2.8 \times 10^{19}$ cm$^{-3}$ and $1.22 \times 10^{-2}$ cm$^2$ s$^{-1}$. It has been observed that for TZTZ1 dimer at $\Delta E(\bar{E}) = 75$ meV conditions, the quantities (carrier density and diffusion) are increased by more than four times with reference to the zero field situations. In the case of extended TZTZ1 pentamer system, the above quantities increase only by more or less 1.5 times. The analysis clearly emphasis that for large extended system, the electric field (or bias voltage)-assisted site energy fluctuation, does not significantly improves the charge transport efficiency. Here, the large value of $\Delta E(\bar{E})$ transits from dynamic to static disordered transport which introduce the dispersion effect on each CT quantities, which leads to restricted CT via the continuum time delayed mechanism. The time delayed CT (due to dispersion) in the extended molecules completely restricts the CT at particular site of polymers, leads to charge trapping, which is in agreement with the recent observation by Abbazadeh et al [36] Generally, the carrier density has mutual relationship with the chemical potential. With the inclusion of dispersion effect at different $\Delta E(\bar{E})$, the total chemical potential is calculated for different stacked system using equation (24). To further understanding the effect of electric field coupled (via site energy difference, $\Delta E(\bar{E})$) dispersion and its corresponding CT delay property in molecular semiconductors, we have plotted the carrier density with respect to chemical potential, which assists us to quantify the electronic compressibility (or TDOS) for different extended molecules of TZTZ1, TZTZ2 and TZTZ3 at different $\Delta E(\bar{E})$ conditions. In this work, the computed TDOS is mainly associated with the Franck-Condon weighed factor on molecular orbitals in high temperature regime (T > 200K). Due to the fluctuation of $\Delta E_{ij}(=E_i - E_j - \Delta E(\bar{E}))$, the TDOS underlies in the category of non-steady states. With respect to the dynamical nature of $\Delta E(\bar{E})$ in
different extended system, the dispersion effect is ruled in the parameter of electronic compressibility (or TDOS), see figures 5 and S6. This compressibility intriguingly describes the charge density within small energy (or chemical potential, $\Phi_{\text{CP}}$) window, $\frac{\partial \rho}{\partial \Phi_{\text{CP}}}$. In this study, the dispersion correction in TDOS has been carried out for different extended molecules with different values of $\Delta E(\bar{E})$, see tables 3, 4 and S4–S6 (also see figures 5 and S6).

Our present analysis clearly emphasizes that for limited hopping systems (few stacked units, e.g. dimer), the TDOS increases with the applied field via site energy difference. Here, the bias dependent degenerate levels are mainly responsible for enhancement of TDOS. On the other hand of extended molecular units, the TDOS diminishes for large $\Delta E(\bar{E})$ values, which is noted in figure 5. The large site energy fluctuation resists the formation of degenerate states due to more dispersion in the extended TZTZ1, TZTZ2 and TZTZ3 molecules. This is mainly responsible for restricted CT in the extended typical polymer systems, which is experimentally proved by Abbaszadeh et al[36]. For instance, the TDOS of TZTZ1 dimer sub-linearly increases with the $\Delta E(\bar{E})$, which is shown in figure 5. Whereas, TDOS of pentamer and hexamer of TZTZ1 decreasing when increasing the $\Delta E(\bar{E})$ values from 0 to 75 meV. In the case of large $\Delta E(\bar{E})$ fluctuation, the dispersion effect limits the formation of degenerate states in these molecular solids. In principle, the TDOS (or compressibility) is the direct consequence of charge distribution (either localization or delocalization) in the $\pi$-orbitals of molecular systems. In such that the existence of charge density difference reveals the charge flux, under certain chemical potential, makes sure the diffusion process along the disordered hopping sites. In this regard, the relationship between the TDOS and diffusion coefficient is a quite important to study both the quantum and classical nature of charge transport in molecular semiconducting devices.

From our model, it is noted that the TDOS is an influencing parameter for the diffusion transport (see figure 6 and S7). For large DOS, there is a possibility for more delocalized $\pi$-electron density (in molecular orbitals) which pertains to the diffusion enhancement. Interestingly, we find that the diffusion coefficient is semi-linearly dependent on TDOS (or electronic compressibility), which can be tuned by suitable doping, applied gate voltage (or electric field) and etc. The main point here is that the TDOS diminishes while the disorder goes from dynamic to static disorder, which strongly depends on amplitude of site energy fluctuation. In this scenario, we conclude that diffusion-based mobility in any molecular systems strongly depends on TDOS, which is quite important to understand the fundamental electronic transport (see figures 6 and 7).

### 3.3. Dispersion corrected current density and ideality factor for molecular devices

Using carrier drift energy–total current density relation (see section 2.3., and equation (11)), we have calculated the current density for different sets of site energy difference values in different number of $\pi$-stacked molecules of TZTZ1, TZTZ2 and TZTZ3. Here, the drift energy is directly related to the carrier drift force, $E_D = F_D R_p$. In the present study, the dispersion correction has been included in the current density values via the parameters of drift force and carrier density for different stacked molecular units with the different set of $\Delta E(\bar{E})$, see tables 1, 2 and S1–S3. As described in our previous studies[16, 18], the average drift force acting on a carrier can be calculated by momentum redistribution analysis. Note that the magnitude of drift force depends on the applied electric field, kind of disorder (either static or dynamic) and its weightage. In addition to that the rate of carrier energy flux (or shuttling energy rate, $\frac{\partial E}{\partial t}$) along the consequential hopping sites is an important factor to understand the charge-energy correlation in the molecular devices. This shuttling energy rate at different set of $\Delta E(\bar{E})$ can be calculated from energy redistribution analysis (see Supplemental Material, Figure S11). Here, the momentum and energy redistributions are nonlinear relation with the survival probability of charge carrier (see equations (12)–(15)). In this investigation, the dispersion effect on momentum–energy redistribution in the molecular systems can be counted at each step of simulations for different values of $\Delta E(\bar{E})$. In such a way, the dispersion corrected drift force and rate of energy flux (or shuttling energy rate) is calculated with the aid of equations (14) and (15), which are summarized in tables 1, 2 and S1–S3. It has been observed that the applied electric field via site energy difference enhances the drift force and rate of energy flux for first few steps of hopping, after that these values subsequently decreases by dispersion, in the dynamical system of extended $N + 1$ sites. That is, the restricted carrier’ momentum–energy redistributions limits the charge transfer kinetics and make sure the charge trapping at particular site in the extended systems. Using rate of carrier energy flux, one can calculate the carrier density as described in section 2.4. In this consequence, the electric field induced differential entropy is obtained for all studied thiazolothiazole based molecular system by equation (19), which is presented in tables 3, 4 and S4–S6. The dispersion effect on differential entropy has been computed with the aid of equations (18) and (19). As we discussed in previous section 3.2, the differential entropy explicitly provides the degeneracy strength on charge transport. According to entropy dependent charge density and diffusion expressions (see equations (20) and (21)), the carrier density and diffusion coefficient are calculated at different electric field assisted site energy difference, which are summarized in tables 1–4 and S1–S6. Here, zero field carrier density is estimated from equation (10). Now, the computed drift force and carrier density are used to calculate current density for different $\Delta E(\bar{E})$ values (see equation (11)). In the case of large $\Delta E(\bar{E})$ fluctuation,
the strong localization due to large dispersion has been observed in extended dynamical hopping systems of TZTZ1, TZTZ2 and TZTZ3 pentamer or hexamer (see Tables S2 and S3), and hence the expected total current density is almost zero, which is termed as restricted CT. For example, at zero $\Delta E(\bar{E})$, the computed current density for the dimer (2-site), trimer (3-site) and tetramer (4-site) system of TZTZ2 has 3.08, 2.72 and 2.57 mA cm$^{-2}$, respectively. On the other hand for $\Delta E(\bar{E}) = 50$ meV, the current density values are 9.78 (for dimer), 6.1 (for trimer) and 4.84 mA cm$^{-2}$ (for tetramer) in the TZTZ2 molecule. The results show that the current density can be tuned only in the limited hopping systems with the help of applied electric field, which is the non-restricted transport. The significant reduction of current density values in the extended systems further confirms the restricted CT. The non-restricted to restricted-CT conversion mechanism is direct relation with the transformation from dynamic to static disordered transport, can be analyzed by dispersive parameter ($a$).

According to our model, the calculated current density is exponentially increasing with the TDOS. In principle, the charge distribution and charge dynamics is closely associated with the TDOS of the studied molecular solids, which is highly solicited to achieve high performance. We intriguingly noted that the enhancement of current density with TDOS follows the trend of Shockley diode equation while forward bias condition. Thus, the TDOS is a tunable parameter by chemical potential via gate voltage, doping or electric field. Here, the charge compressible nature in electronic states of semiconducting materials can be modified by electric field assisted site energy fluctuation of $\Delta E(\bar{E})$. Notably, the dynamics of energy disorder miserably connects the dispersion-controlled charge transport (or CT delay) for different number of stacked molecules, which can be traced out from the current density (see tables 1, 2 and S1–S3). According to the amplitude of $\Delta E(\bar{E})$ fluctuation, the time delay occurred by dispersion effect at each hopping of extended molecules. This dispersion directly reduces the electron current in the typical molecular device, which is known as restricted CT. Here, the dispersion assisted localization is mainly responsible for charge trapping. This gives rise to the trap assisted recombination in these typical systems (e.g., polymer), which is in agreement with the recent study carried by Blom and his collaborators [36]. In other words, the significant loss of charge transfer kinetics occurs at each hopping along the consequential sites, and is termed as dispersion-initiated charge trapping in the conjugated systems. Now one can expect zero diffusion transport (i.e., zero diffusion-mobility which means that restricted-CT) in these typical dynamically disordered extended systems. In such situation, the recombination process is significantly slow.
process has been apparently anticipated in an extended system (stacked or conjugated) of TZTZ1, TZTZ2 and TZTZ3 molecules.

Due to the effect of site energy fluctuation on charge transport, there is a drift coupled diffusion transport in molecular solids of TZTZ1, TZTZ2 and TZTZ3, which varies with the number of stackings \((N + 1\) sites). According to the amplitude of site energy fluctuation, the carrier drift is imposed in carrier diffusion which possibly makes the deviation in Einstein diffusion-mobility relation, \(\eta = \eta_{EE}\). With respect to the Shockley diode mechanism, the value of diffusion-mobility ratio can be quantified as the ideality factor \((\eta)\) times the thermal energy \((k_B T)\) \([16, 35]\). Here, the factor \(\eta\) is known as enhancement factor of semiconducting devices. Based on the value of \(\eta\), we can classify the typical materials either it follows the Langevin \((\eta \rightarrow 1)\) or Shockley-Read-Hall (SRH) mechanism \((\eta \rightarrow 2)\). The Langevin mechanism pertains to the trap-free diffusion transport which normally occurs in charge transporting devices \(e.g.,\) photo voltaic cells. The SRH mechanism belongs to trap-assisted recombination process which apparently involves in light emitting devices, such as OLEDs. In the present study, the amplitude of site energy fluctuation is mainly responsible for the transition from dynamic to static disordered transport. The charge transport is limited by static disorder and is assisted by dynamic disorder. From our analysis, we observed more time-delayed CT (restricted-CT) due to dispersion in static disorder regime of molecular systems which gives rise to the charge trapping; and hence it favors the light emission process. On the other regime of dynamic disorder, we logically expect the charge transport mechanism in the studied molecular solids of TZTZ1, TZTZ2 and TZTZ3, which mandatorily varies with the number of stacked units. As described in section 2, we have investigated the dispersion corrected CT quantities like rate coefficient, carrier density, diffusion constant, chemical potential, TDOS, mobility, current density and other CT quantities, for different stacked molecules of TZTZ1, TZTZ2 and TZTZ3 under various set of \(\Delta E(\bar{E})\) values \((0, 25, 50 \) and \(75 \) meV). In such that we have plotted the logarithm of carrier density for different electric field situations in dimer system. For TZTZ3, the calculated current density linearly increases with the chemical potential for different extended dynamical units of TZTZ1, TZTZ2 and TZTZ3. This observation is strongly suggesting the similarity variation in the quantities of diffusion coefficient and mobility.

Importantly, we noted that the calculated ideality factor \((\eta)\) of these molecules is 1, does not vary with the number of stacking. Moreover, our model presumably confesses that the factor \(\eta\) does not belong on dispersion effect. In other words, the dispersion equally affects both the parameters of diffusion and mobility, and therefore it preserves the Einstein’s diffusion-mobility ratio. With our model, the calculated ideality factor \((\eta = 1)\) of these molecular solids clearly emphasize that the charge current in these molecules follows the Langevin mechanism and hence these are suitable to make the charge transporting devices. The earlier experimental observation suggested that the thiazolothiazole based oligomers have quite good mobility, which strongly supports our present study \([37]\). For instance, the field effect characteristic study shows that at 25 and 50 K, the TZTZ2 molecule has mobility values are 0.12 and 0.3 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\), respectively. \([37]\). Through our model, computed mobility values of TZTZ2 are in the same order \(\text{see tables 3, 4 and S4–S6}\), and it strongly depends on the number of stackings. Among the thiazolothiazole molecules, TZTZ3 molecule has good mobility \((-1.6 \text{cm}^2\text{V}^{-1}\text{s}^{-1})\) even at zero electric field situations in dimer system. For TZTZ3, the calculated current density is also relatively high due to large value of contributed carrier density. Interesting part is that there is no significant dispersion effect on the CT parameters in different extended units of TZTZ3, even at different electric field assisted site energy fluctuation \(\text{see tables 1–4 and S1–S6}\) and hence there is no significant CT delay along the consequential sites. From our extensive analysis, we suggest that the TZTZ3 molecule is more appropriate for molecular semiconducting devices in the range from few layers to multilayers, which usually determines the film thickness. Moreover, the TZTZ1 based molecular solids are also recommendable to the molecular electronics. On the other hand, due to more dispersion in the extended system of TZTZ2, one can use it for few layered devices only, but not suitable to make the multilayered devices.

### 3.4. Validation of Einstein relation via entropy-ruled diffusion-mobility method

Numerous reports clearly manifests that the presence of disorder drives the charge separation efficiency in molecular devices which directly gives rise to diffusion \([38–42]\). In principle, the disorder can be quantified by the parameter entropy \([38–42]\). In the present study, the diffusion enhancement at different \(\Delta E(\bar{E})\) values \(0, 25, 50 \) and \(75 \) meV are computed by differential entropy dependent diffusion equation \(\text{see equation (21)}\), and results are summarized in tables 3, 4 and S4–S6. According to number of stacking \(\text{i.e.,} N + 1\) sites\), the dispersion correction is accounted in CT rate, differential entropy, diffusion coefficient and other quantities.

The dispersion reveals the continuum time delayed CT properties of studied molecular solids. Here, the electric field assisted drift effect on diffusion has been explored by the entropy parameter, \(h_0\). In this scenario, we can expect the deviation in Einstein diffusion-mobility ratio from original value of \(k_B T/q\). The physics of deviation in Einstein relation for real devices is quite important to categorize the materials; whether it is suitable
for charge transporting devices or light emitting devices. The physics of deviation can be analyzed by the ideality factor ($\eta$). In this paper, we proposed the alternate version of diffusion-mobility ratio, $\frac{D}{\mu} = \frac{5}{3} \frac{\Delta \Phi_{CP}}{k} \frac{\Delta h_{S}}{\Delta N}$, which directly relates to the variation of chemical potential with respect to the entropy. This is named as entropy-ruled diffusion-mobility relation. The chemical potential and charge density are one to one correspondent, and hence the variation in chemical potential facilitates the diffusion-based mobility. In this study, the differential entropy ($h_{S}$) is derived from Gaussian function, which is more appropriate for molecular transport. Here, the physics of deviation of diffusion-mobility ratio depends only on slope of the chemical potential with respect to the entropy parameter, $h_{S}$ (see figures 3 and S4). Noteworthy, the traversing nature of chemical potential in the molecular solids decides whether $D/\mu$ will be a linear or nonlinear transport. For nondegenerate cases of high temperature and disordered systems, the changes of chemical potential is in the order of thermal energy $k_{B}T$. In this limit, the $D/\mu$ factor is only dependent on temperature. In this connection (for pure classical domain), the transport is termed as the thermally activated hopping and now we preserve the original Einstein relation, $\Delta \Phi_{CP} \rightarrow k_{B}T$. That is, the computed energy flux and its corresponding drift force acting on a carrier (along the hopping path) for different values of $\Delta E(\bar{E})$ underlies in the order of thermal energy ($k_{B}T$). The main observation is that the existence of driving force on $D/\mu$ relation falls under classical domain. Thus, our predicted $D/\mu$ values (or $D/\mu$ enhancement) for all studied molecular systems (TZTZ1, TZTZ2 and TZTZ3) follows $k_{B}T/q$ order, which is the classical Einstein relation. This result is consistent with the earlier report by Mendels and Tessler [43].

As we proposed equation (22), the differential entropy ($h_{S}$) is directly proportional to the logarithmic carrier density (see figures 3 and 8). The shift of chemical potential with respect to $h_{S}$ parameter is a direct evidence for the drift-diffusion transport (see figures 3 and S4); accordingly, the calculated slope confirms the validation of Einstein relation. For example, the slope $\left(-\frac{\Delta \Phi_{CP}(N)}{\Delta h_{S}(N)}\right)$ value of TZTZ2 molecular solids is 15.42 meV for different extended systems at different $\Delta E(\bar{E})$ values of 0, 25, 50 and 75 meV.

According to equation (22), the calculated slope value (15.42 meV) times of 5/3 directly gives the thermal energy of 25.7 meV, which conserves the original Einstein relation. The same trend has been noted in other studied molecular solids of TZTZ1 and TZTZ3. In this scenario, the $h_{S}$-dependent chemical potential shifting is mainly responsible for device ideality factor ($\eta$). It is to be noted that without inclusion of dispersion effect on charge transport in these molecular solids, there is a large deviation of Einstein relation in nonlinear manner, which is shown in figure S12. In this case, the dispersion based charge trapping causes more impact on diffusion coefficient rather than mobility, which reveals the large value of ideality factor. In our study of dispersion corrected charge transport, we preserve the original Einstein relation, and it is in good corroboration with the experimental observation.[26] Here, the important point is that using our entropy-ruled method, the computed diffusion-mobility ratio is equal to the Einstein’s diffusion-mobility ratio (see figures 9 and S10). From our extensive analysis under room temperature, we conclude that the site energy fluctuation based energy disorder and the number of molecular stacking (or conjugation length) does not make any deviation in Einstein relation for TZTZ1, TZTZ2 and TZTZ3 molecules. The results further emphasize that the electric field coupled energy disorder and dispersion effects equally affects both the diffusion coefficient and mobility for different extended molecules.
4. Summary and conclusions

The effects of vibronic coupled charge transfer integral and site energy fluctuations on electron transport in the extended thiazolothiazole derivatives (TZTZ1, TZTZ2 and TZTZ3 molecules) have been investigated. With respect to the dynamics of site energy disorder, the loss in each CT parameters (or CT delay) at every hopping step is observed, which sequentially controls the polaron dynamics in the extended systems of N + 1 sites. In order to quantify the exact charge transport in any molecular devices, we have included the dispersion correction in all CT parameters like, hopping rate, diffusion coefficient, mobility, current density and etc. It has been observed that the charge transport goes from dynamic to static disordered regime, while we increase the number of molecular units in the extended systems (i.e., conjugation length). Herein, the dispersion limited CT (or restricted-CT due to dispersion) is strongly influenced by the amplitude of site energy fluctuation, which can be modified by adjusting the applied electric field or bias voltage. Fast fluctuations with low amplitude of energetic disorder (or site energy difference) reveal dynamic disordered transport and the expected dispersion is minimal. Thus, the loss in charge transfer kinetics at each hopping is less in the extended dynamical molecules. Slow fluctuations with large amplitude of site energy disorder leads to static disorder which facilitates the large dispersion in the charge transport. Transformation from dynamic to static disordered transport is noted for large amplitude of site energy fluctuation, leads to diffusion limited transport. It is inferred that the crossover from non-restricted to restricted CT is a direct consequence of dynamic to static disordered transport. The field response degeneracy strength and its consequences on polaron transport have been studied by the differential entropy-dependent carrier density and diffusion coefficient equations, with dispersion correction (i.e., time delay effect by dispersion). The main point here is that the effect of degeneracy formation (due to electric field assisted site energy difference) on CT is quantified by differential entropy. To elucidate the polaron dynamics in the molecular orbitals (LUMOs for electron/HOMOs for hole) of different number of stacked or extended TZTZ1, TZTZ2 and TZTZ3 molecules, the charge compressibility analysis has been studied. This study relates the localization to delocalization behavior through the thermodynamic density of states. Our proposed entropy-ruled Einstein diffusion-mobility ratio purely depends on the variation of chemical potential with respect to the differential entropy, and it can explain the physics of deviation in original Einstein relation. Through our entropy-ruled diffusion-mobility relation, we have shown the validity of Einstein relation in these molecules of TZTZ1, TZTZ2 and TZTZ3. Noteworthy, the amplitude of site energy fluctuation and molecular vibrations are equally affected in both the diffusion coefficient and mobility for these molecules, which preserves the Einstein relation \( \frac{D}{\mu} = \frac{k_B T}{q} \). According to the entropy-ruled Einstein relation, we have modified the Shockley diode equation and it is named as Navamani-Shockley diode equation for molecular devices.

From our theoretical analysis, we have summarized four important corollaries as follows, 1) The calculated diode ideality factor for the studied molecules of TZTZ1, TZTZ2 and TZTZ3 is one, which suggests the Langevin transport (trap-free diffusion) mechanism; and hence these molecules are suitable for charge transporting devices like, photovoltaics. 2) There is no significant loss in CT parameters due to negligible dispersion effect at each hopping in the extended TZTZ3 molecular units, which suggests that TZTZ3 is more appropriate for molecular semiconducting devices in the range from few layers to multilayers. The TZTZ3 molecule has good mobility (∼1.6 cm²V⁻¹s⁻¹) and current density (∼13.8 mA cm⁻²) even at zero electric field situations in the dimer system. 3) Due to the large dispersion in the extended system of TZTZ2, one can use it for few layered semiconducting devices only, but not suitable for multilayered devices, which alternatively suggest the application in light emitting devices (e.g., OLED). 4) By our continuum time delayed CT (or dispersion corrected CT) model, we can easily switch over the dynamic to static disordered transport or vice-versa or intermediate transport in molecular semiconductors with the help of two descriptors, bias voltage (or electric field) and molecular vibrational frequency. Here, the main implication for the device performance is that the cooperative behavior between the molecular vibration and applied electric field (or bias voltage) is important factor to functionalize the appropriate properties (either CT or light emission) in any molecular devices; and thus these two descriptors (vibrational frequency and applied voltage) are indeed ideal for better device performance.

Acknowledgments

The author thanks to Prof. Swapan K. Pati, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, INDIA for his valuable scientific suggestions on this work.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Supplemental material

Calculation methods of dispersion corrected charge transfer rate for different extended (N + 1 sites) molecular systems of TZTZ1, TZTZ2 and TZTZ3 at $\Delta E(\bar{E})$ value of 0, 25, 50 and 75 meV are presented in S1 (A, B, C and D)–S3 (A, B, C and D). Procedures of dispersion corrected-charge compressibility (or TDOS) calculation for different extended (N + 1 sites) molecular systems of TZTZ1, TZTZ2 and TZTZ3 at different $\Delta E(\bar{E})$ values (0, 25, 50 and 75 meV) have been given in S4(A)–S4(C), respectively. The chemical structures of TZTZ1, TZTZ2 and TZTZ3 molecules are given in figure S1. The plot of survival probability of electron in the $\pi$-stacked TZTZ3 molecule with respect to time, at different sets of electric field induced site energy differences ($\Delta E(\bar{E})$) of 0, 25, 50 and 75 meV has been provided in figure S2. The decreasing nature of charge transfer rate at each hopping step in the extended TZTZ3 molecular system at different values of $\Delta E(\bar{E})$ (0, 25, 50 and 75 meV) has been plotted in figure S3. The plot of the chemical potential enhancement with respect to the electric field–driven differential entropy in different extended TZTZ3 molecular units at different site energy fluctuation, ($\Delta E(\bar{E})$), of 0, 25, 50 and 75 meV is given in figure S4. The graph of $\pi$-electron density with respect to the chemical potential in different extended (number of stacked units) system of TZTZ3 molecule for different $\Delta E(\bar{E})$ values of 0, 25, 50 and 75 meV is presented in figure S5. The thermodynamic density of states (or electronic compressibility) under the dispersion correction for different extended dynamical molecules of TZTZ3 at different values of $\Delta E(\bar{E})$, (0, 25, 50 and 75 meV) has been plotted in figure S6. The diffusion coefficient with respect to the thermodynamic density of states for the different stacked molecular system of TZTZ3 at different values of $\Delta E(\bar{E})$ 0, 25, 50 and 75 meV is given in figure S7. The enhancement of current density with respect to the thermodynamic density of states in different extended units of TZTZ3 molecules under the dispersion correction for different set of site energy fluctuation of 0, 25, 50 and 75 meV has been plotted in figure S8. The plot between logarithmic carrier density and chemical potential for different $\Delta E(\bar{E})$ values of 0, 25, 50 and 75 meV in different stacked units of TZTZ3 molecule is presented in figure S9. The differentiation of logarithmic carrier density plot, figures 9(b) and S9, (with respect to the chemical potential) of TZTZ2 and TZTZ3 molecules is given in figures S10(a) and S10(b), respectively. The redistributions of carrier momentum–energy with respect to the time during the charge transport at different site energy fluctuation in (a) TZTZ1, (b) TZTZ2 and (c) TZTZ3 molecules has been plotted in S10(a)–S10(c), respectively. The plot of logarithmic current density (with inclusion of dispersion effect) with respect to the electric field coupled site energy difference values (without dispersion effect in $\Delta E(\bar{E})$) of 0, 25, 50 and 75 meV for electron transport in the different stacked molecular units of (a) TZTZ1, (b) TZTZ2 and (c) TZTZ3 molecules are given in figures S12(a)–S12(c), respectively. The computed CT quantities such as transfer rate, dispersion parameter, drift force, rate of energy flux, carrier density, and current density of TZTZ1, TZTZ2 and TZTZ3 molecules at different set of $\Delta E(\bar{E})$ values of 0, 25, 50 and 75 meV for different stacked/extended systems of tetramer (4-site), pentamer (5-site) and hexamer (6-site) are summarized in Tables S1–S3, respectively. The estimated relative differential entropy, diffusion coefficient, dynamically coupled chemical potential, charge compressibility, mobility and ideality factor for electron transport in tetramer (4-site), pentamer (5-site) and hexamer (6-site) systems of TZTZ1, TZTZ2 and TZTZ3 molecules at different set of $\Delta E(\bar{E})$ values of 0, 25, 50 and 75 meV have been summarized in Tables S4–S6, respectively.

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