

Role of a trap in disordered OLED host-guest systems

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Extrinsic traps created by dopants or impurities are ubiquitous in organic semiconductors and can critically influence charge transport. Here we report a comprehensive study, using low-temperature thermally stimulated luminescence measurements complemented by quantum mechanics and molecular dynamics (QM-MD) calculations, as well as kinetic Monte Carlo (KMC) simulations, to investigate trapping and energetic relaxation of charge carriers in amorphous host-guest systems containing the widely investigated thermally activated delayed fluorescence (TADF) emitter 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-9,9-dimethyl-9,10-dihydro-acridine (DMAC-TRZ) in two different hosts. DMAC-TRZ guest acts as a shallow trap in 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl (mCBP) and a deep trap in 1,3-bis(triphenylsilyl) benzene (UGH3), each forming an additional offset Gaussian density of states (DOS) distribution, as supported by the QM-MD calculations. These calculations accurately reproduce the trap depths ϵ_t and widths of the DOS distributions σ_{DOS} in the considered compositions, showing that the nominal trap depth is independent of the host-guest ratio. By experiment and KMC simulations we found that the trapping behavior differs significantly for shallow ($\epsilon_t \leq 3\sigma_{\text{DOS}}$) and deep ($\epsilon_t > 3\sigma_{\text{DOS}}$) cases. Shallow traps do not behave as distinct traps but rather broaden the host DOS and increase the density of low-energy states, causing the average activation energy to depend on guest concentration c_t , in line with the “effective disorder” concept. By contrast, when a trap is deep, the energy needed to release the trapped charges to the host is independent of the guest concentration. Furthermore, for deep traps, we observe that charge detrapping occurs simultaneously via both guest-to-host and guest-to-guest charge-transfer pathways, with the latter regime becoming dominant for concentrations exceeding $c_t = 5\%$. Remarkably, this guest-guest transfer already sets in at only 1% trap concentration. We attribute this to local guest clustering and superexchange-mediated intercluster transfer.

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I. INTRODUCTION

Host-guest systems based on organic semiconductors are widely employed in a variety of electronic devices, particularly in organic light-emitting diodes (OLEDs). In

OLEDs, guest molecules are introduced to reduce injection barriers, tune emission color via fluorescent dyes, and harvest both singlet and triplet excitations using phosphorescent (triplet) emitters [1–3]. Recent advances utilize thermally activated delayed fluorescence (TADF) emitters, which convert triplet excitations into emissive singlet excitations when doped into suitable host materials [4]. The latest OLED generation—“hyperfluorescent” OLEDs represent even more complex host-guest systems incorporating two types of guests: a terminal fluorescent emitter co-deposited with an assistant TADF emitter [5]. Beyond OLEDs, host-guest systems serve as gain media in organic solid-state lasers [6], as photoreceptors in xerography [7], and in organic long-persistent luminescence materials [8].

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Guest molecules may also appear unintentionally as impurities or degradation products [9]. In all cases, they can strongly influence charge transport by introducing traps for holes or electrons when their highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) levels lie, respectively, higher or lower than the corresponding HOMO or LUMO levels of the host matrix. Such traps can cause nonradiative recombination, unbalanced transport resulting in carrier accumulation at interfaces in OLEDs, and threshold voltage shifts along with hysteresis in organic field-effect transistors. In organic solar cells, traps hinder the extraction of carriers thus decreasing the fill factor and also lead to additional recombination losses. Therefore, a comprehensive physical understanding of the trap effect in organic functional semiconductors is of both fundamental and applied significance.

The simplest description of the trapping effects is provided by the multiple-shallow-trapping and release model suggested by Hoesterey-Letson [10]. This model is applicable to energetically ordered systems such as molecular crystals, where all traps have the same energy. The model assumes discrete trap levels and predicts that the effective mobility in the presence of traps with relative concentration $c_t = n_t/N$, where n_t is the number of traps and N is the total number of sites, is given by the trap-free mobility $\mu(c = 0)$ divided by a trapping factor h that accounts for the time a carrier spends in a trap: $\mu(c_t) = \mu(c = 0) \times h^{-1} = \mu(c = 0) \times [1 + c_t \exp(\varepsilon_t/k_B T)]^{-1}$. The trap depth is well defined by the corresponding HOMO or LUMO offset between host and guest [11,12].

In contrast, in energetically disordered neat organic systems, electronic states are distributed in space and energy forming an inhomogeneously broadened density of state (DOS) distribution centered around a mean value, ε_0 , commonly modeled by a *unimodal* Gaussian distribution, $g(\varepsilon) \propto \exp[-1/2((\varepsilon - \varepsilon_0)/\sigma_{\text{DOS}})^2]$, characterized by the width σ_{DOS} representing the energetic disorder parameter

[13]. For simplicity, the center of the intrinsic DOS, ε_0 , is set to zero hereafter. This Gaussian shape of the DOS implies that hopping from an occupied state in the tail of the distribution is difficult, since energetically similar sites may be spatially distant. As a result, tail states can act as *intrinsic* trap states, particularly at a low temperature. Thermal energy is required to promote a carrier to a site closer to the center of the DOS, where the higher density of energetically comparable sites facilitates charge transport [13]. The concept of a transport energy captures this distinction, separating the charge-transporting sites from those that localize the charge carriers. While the impact of intrinsic traps arising from the tail states of the DOS on transport is well established, the effect of the extrinsic trap states is less clear.

Extrinsic traps may, for example, be formed by the introduction of a few percent of guest molecules into a host matrix. These traps are often assumed to form an additional Gaussian distribution whose center is offset to a lower energy by ε_t with respect to the center of the intrinsic host DOS [14,15]. This energy offset between the centers of the two Gaussians defines the mean trap depth. In particular, extrinsic guest-related traps can overlap with the disorder-induced trapping associated with intrinsic tail states of the host DOS as illustrated schematically in Fig. 1. Because both intrinsic and extrinsic localized states are subject to disorder, the trap release energy becomes a variable value rather than a well-defined quantity. In particular, it can no longer be simply determined by a Boltzmann factor with the activation energy based solely on a well-defined HOMO or LUMO energy difference between pure host and guest materials.

Over the past few decades, the Gaussian disorder model (GDM) [13] has been extensively developed to describe hopping charge transport in disordered organic materials containing extrinsic traps. In their seminal work, Borsenberger and Bässler [15] introduced the concept of an “effective energetic disorder” to account for the effect

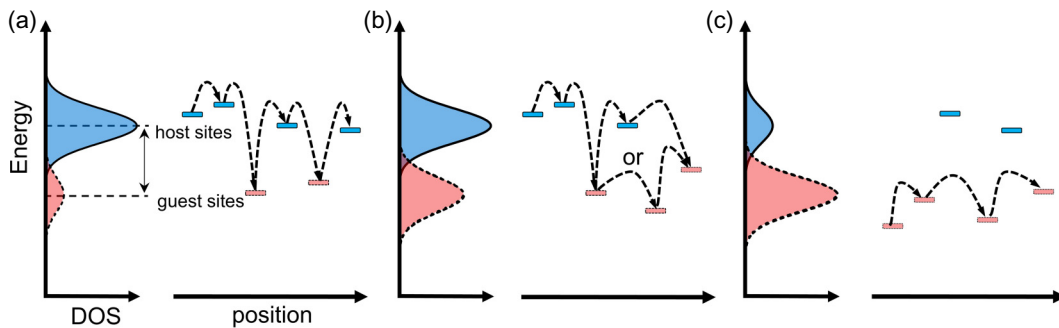


FIG. 1. Schematic illustration of different hopping regimes in a disordered host-guest system: (a) hopping via host sites at small concentration of guest sites (GH hopping, trap-limited transport); (b) intermediate regime of hopping via both host and guest sites (GH and GG hopping); (c) hopping via guest sites (GG hopping). The DOS of host (solid lines) and guest (dotted lines) with the offset ε_t in between are schematically indicated. Adapted from Ref. [16].

of shallow extrinsic traps, defined as $\varepsilon_t \leq 3\sigma_{\text{DOS}}$, where σ_{DOS} is the width of the intrinsic DOS of the host. They modeled the cumulative energy state distribution in trap-containing disordered systems using a bimodal Gaussian DOS [14,15]:

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}} \left\{ (1 - c_t) \exp \left[-\frac{1}{2} \left(\frac{\varepsilon}{\sigma_{\text{DOS}}} \right)^2 \right] + c_t \exp \left[-\frac{1}{2} \left(\frac{\varepsilon + \varepsilon_t}{\sigma_{\text{DOS}}} \right)^2 \right] \right\}, \quad (1)$$

here the width σ_{DOS} was assumed identical for intrinsic transport states and extrinsic trap states. Monte Carlo simulations revealed that shallow traps do not change the basic phenomenology of hopping transport and that their effect on transport for the conditions $c_t [\exp(\varepsilon_t/k_B T)] \gg 1$ can be captured by replacing σ_{DOS} with a broader effective width σ_{eff} [14]:

$$\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{DOS}}} \right)^2 = 1 + \left(\frac{3k_B T}{2\sigma_{\text{DOS}}} \right)^2 \left[\ln(c_t) + \frac{\varepsilon_t}{k_B T} \right]. \quad (2)$$

Phenomenologically, shallow traps increase the density of tail states, thus opening additional pathways for carrier relaxation to deeper energies. This disorder formalism was later extended to arbitrary trap concentrations, including a trap-to-trap hopping regime in an analytical treatment by Fishchuk *et al.* [17]. It was further developed via master-equation and percolation approaches by Bobbert and Coehoorn [16,18] to also include the effects of charge-carrier concentration and electric field.

Despite significant progress, the mechanisms of charge trapping and transport in host-guest organic semiconductors are not yet fully understood. A central open question is the reliable determination of the depth of guest-induced trap states. This depth is commonly approximated as the energy offset between the HOMO or LUMO DOS centers of the pure host and guest materials, under the assumption of weak intermolecular interactions that preserve molecular identity [11,14]. However, this approximation fails in cases where a difference in polarizability, induced by charging the host and guest molecules, results in a different polarization-induced stabilization in the host and guest. Consequently, host and guest energy levels can shift by a different amount, as shown by May *et al.* [19].

A second major issue is identifying hopping regimes across guest concentrations and clarifying the mechanism of charge transfer via guest states, particularly for the cases of guest concentration of only a few percent. Time-of-flight (ToF) charge-mobility measurements [20] typically reveal three hopping regimes distinguished by trap concentration [16] (see Fig. 1). (a) In the trap-limited regime (low c_t), guest sites act as spatially isolated traps, with thermally activated guest-to-host (GH) hopping dominating

the transport. The mobility strongly decreases with c_t . (b) The mixed crossover regime applies at intermediate c_t and is characterized by a minimum in the concentration dependence of the mobility. Both GH and guest-to-guest (GG) hopping contribute to transport. (c) Percolation occurs for sufficiently high c_t , which enables formation of percolation pathways. GG hopping dominates and the mobility increases with rising c_t .

Predicting the critical concentration for the mixed crossover regime [Fig. 1(b)] remains challenging but is pivotal for understanding the operating mechanism of GG transfer. Experimentally, mobility minima are typically observed near 10% guest concentration [21,22], in agreement with theoretical calculations [16,18]. However, Symalla *et al.* [23] showed that coherent “molecular superexchange,” involving the virtual occupation of host (bridge) states can shift the crossover to significantly lower concentrations by enabling long-range GG transfer without actual host occupation. While classical percolation generally requires ≥ 20 –30% guest loading, optimal concentrations of triplet emitters in OLEDs are often around 6 wt.% [24]. Similarly, high performance in low-donor-content organic solar cells (OSCs) has been observed at donor concentrations as low as 5% [25,26], where classical percolation is unlikely. Kublitski *et al.* [27] recently explained such behavior in OSCs by an acceptor-mediated superexchange mechanism. Superexchange effects are found to be particularly relevant for deep traps [23]. This was recently corroborated by Ko *et al.* [28], who analyzed current-voltage characteristics of model host-guest systems with varying trap depths. Their results revealed an efficient superexchange-mediated contribution to the GG hopping in the deepest trap case ($\varepsilon_t = 0.5$ eV) under conditions of low temperatures and low guest concentration $c_t = 3\%$.

While the effect of extrinsic guest-induced traps in disordered systems has been extensively explored through charge-transport measurements (see Refs. [9,28–30] and references therein) and theoretical modeling [17–19,23,31], systematic investigations using direct *trap detection techniques*—particularly across varying trap depths and concentrations—remain scarce. In the present study, we address this gap by combining thermally stimulated luminescence (TSL) spectroscopy with quantum mechanics and molecular dynamics (QM-MD) simulations to probe trap energetics, and kinetic Monte Carlo (KMC) simulations to study carrier energetic relaxation within bimodal DOS landscapes. TSL technique is particularly suitable for probing the DOS and extrinsic traps in luminescent organic semiconducting materials [32–38]. The aim is to clarify the conditions at which traps formed by guest molecules act as either distinct traps or rather effectively broaden the DOS in amorphous host-guest systems. We examine model amorphous systems consisting of the widely investigated TADF emitter DMAC-TRZ

embedded at varying concentrations in two different hosts, mCBP and UGH3, where DMAC-TRZ creates shallow and deep traps, respectively. We find shallow traps to broaden the intrinsic DOS without exhibiting distinct trap states, in line with the effective disorder concept, whereas deep traps yield well-defined trap states. Furthermore, we identify a concentration-dependent transition from GH to GG transfer pathways, with the latter starting to dominate charge release as observed by TSL at approximately 10% and 5% in shallow- and deep-trap containing systems, respectively. Remarkably, in deep-trap systems, the onset of GG transfer is observed at unusually low guest concentrations around 1–2.5%, which is attributed to local guest molecule clustering and superexchange-mediated intercluster transfer.

This paper is structured as follows. Section II introduces the experimental TSL method alongside the QM-D and KMC simulation techniques. Section III presents TSL measurements, first for intrinsic trapping in pure materials, and then for host-guest systems (mCBP:DMAC-TRZ and UGH3:DMAC-TRZ), where shallow and deep extrinsic traps, respectively, prevail. The section concludes with an analysis of frequency factors across temperatures, allowing us to estimate the effective carrier jump distances and thus to infer the carrier detrapping mechanisms. Section IV presents QM-D calculations of DOS distributions in the host-guest systems, quantifying guest clustering as a function of guest concentration, and evaluating electronic coupling elements. Section V describes KMC simulations of low-temperature energetic relaxation of carriers, yielding the occupied density-of-states (ODOS) as a function of guest concentration. Finally, the discussion Sec. VI integrates experimental and simulation results, offering interpretation and implications of this study.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Materials

Small-molecule host materials 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl (mCBP) and 1,3-bis (triphenylsilyl) benzene (UGH3), as well as a TADF emitter 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-9,9-dimethyl-9,10-dihydro-acridine (DMAC-TRZ), used as a guest, were purchased from Lumtec Corp. and used as received. HOMO level positions were determined by ultraviolet photoelectron spectroscopy (UPS) for DMAC-TRZ [39], mCBP [40], and UGH3 [41], while LUMO energies were calculated by corresponding HOMO and optical band gaps with accounting for singlet exciton-binding energies. The molecular structures of these materials and schematic diagram of their energy levels are depicted in Figs. 2(a) and 2(b), respectively. Thin films of host-guest compositions were prepared by dissolving the appropriate ratios of DMAC-TRZ and mCBP or UGH3 in chloroform, then the resulting solutions were spin coated onto cleaned quartz substrates that resulted in typically 50-nm-thick layers. The solids concentration of the coating solutions was 10 mg/ml. The deposited films were dried under vacuum for 2 h to remove any residual solvent.

B. Thermally stimulated luminescence technique

TSL measurements were performed in a temperature-regulated liquid-helium bath cryostat over the range 4.2–330 K. In the present study, trap population followed a two-step procedure described in Ref. [37]. First, samples were cooled to 5 K and photoexcited for 1 min with UV light from a high-pressure Hg lamp. Subsequently, UV excitation was stopped, and the samples were additionally

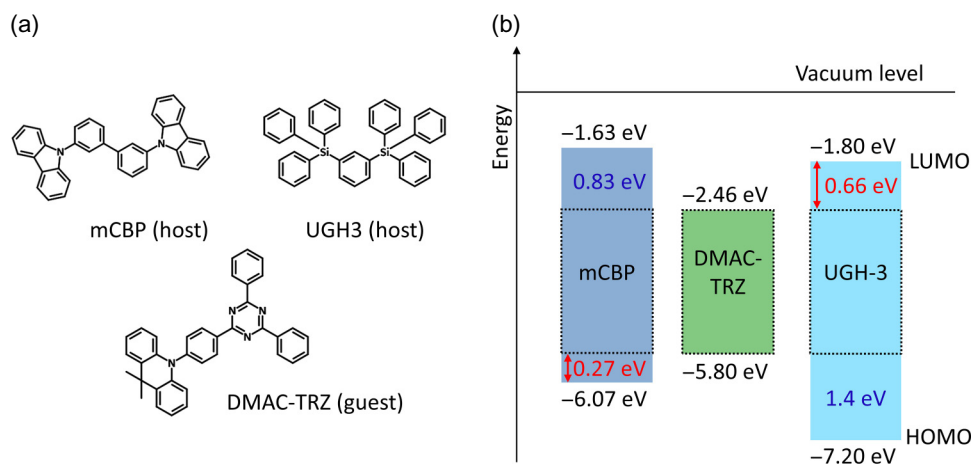


FIG. 2. (a) Molecular structures of the compounds used in this study: mCBP and UGH3 are used as host materials, while DMAC-TRZ is used as a guest. (b) Schematic representation of the average energies for the associated LUMOs and HOMOs. Expected trap depths probed by TSL are indicated by double-headed arrows between the host and guest energy levels.

irradiated for 30 min with infrared light (900–4500 nm) at 5 K. As previously shown for neat organic films [37], IR irradiation promotes energetic relaxation of charges via downward hopping within the DOS at cryogenic temperatures, forming a “relaxed” ODOS distribution.

The TSL emission was detected with a cooled photomultiplier tube operated in photon-counting mode, directly coupled to the cryostat window. Measurements were conducted under two heating protocols: uniform heating at a constant rate $\beta = 0.15$ K/s, and the so-called fractional heating method [42,43], in which small temperature oscillations are superimposed on a uniform heating ramp. The latter technique is particularly advantageous for amorphous materials with continuously distributed trap energies and does not require prior knowledge of escape frequency factors or retrapping probabilities [42,43]. Generally, the escape frequency factor represents a rate at which carriers attempt to escape, independent of temperature activation. In inorganic crystals with band transport, it is often independent of trap depth and determined by material parameters such as density of available band states and the capture cross section of the trap. However, if TSL is controlled by hopping transport, the frequency factor represents the probability of carrier hop, i.e., tunneling, when energetic resonance occurs. Fractional TSL enables determination of the charge-detrapping activation energy E_a and the escape frequency factor S (hereafter referred to simply as the “frequency factor”) for each measurement cycle with temperature change ΔT , as proposed by Tale [43]:

$$E_a(T) = -\frac{d[\ln I(T)]}{d(1/k_B T)}; \text{ at } \beta = \text{const}, \quad \Delta T \ll T, \quad (3)$$

and

$$S(T) = \frac{dT}{dt} \left(\frac{E_a}{k_B T^2} - \frac{1}{I} \frac{dI}{dT} \right) \exp \left(\frac{E_a}{k_B T} \right). \quad (4)$$

where $I(T)$ is the TSL intensity, T is the temperature of measurement cycle, k_B is the Boltzmann constant. Further experimental details are provided in Refs. [35–37].

C. Quantum mechanics and molecular dynamics (QM-MD) simulation method

Molecular dynamics (MD) simulations were performed using the GROMACS package, version 2019.3 [44,45], to generate amorphous morphologies at different host-guest ratios, as detailed in Note S3 of the Supplemental Material [46]. To parametrize the atomistic force fields the molecules were initially partitioned into rigid fragments as outlined in our previous work [38]. Bonded parameters, except for dihedrals linking two rigid fragments, were taken from OPLS-AA [58,59]. Those dihedrals, which link two rigid fragments were obtained by a restrained

dihedral-scanning procedure, as outlined in the Supplemental Material [46]. The nonbonded parameters, atomic partial charges, and Lennard-Jones parameters were all derived from density functional theory (DFT) results using the protocol proposed by Cole *et al.*, where overlapping atomic electron densities are obtained using the density-derived electrostatic and chemical (DDEC6) electron-density partitioning scheme [60–62]. By integrating these electron densities over space, one can then obtain atomic partial charges to be used in the force fields. DOS distributions were calculated using the VOTCA package, assuming one localized state per molecule, in all host-guest systems under consideration. Then molecular pairs were selected according to geometrical criteria and extracted from the MD snapshot. The selection was based on the closest atom-atom distances smaller than 0.5 nm. Transfer integrals were computed using VOTCA [63–66]. To do this we initially calculated the orbital coordinates of the single molecules of interest, in the gas phase, using the semiempirical ZINDO method in Gaussian16 [67,68] (see Note S3 of the Supplemental Material [46] for further details).

D. Kinetic Monte-Carlo simulation technique

The energetic relaxation of charges within a bimodal DOS distribution is simulated by using a grid-based kinetic Monte-Carlo (KMC) method to monitor the motion of charge carriers as hopping events. Please refer to our recent publication Ref. [37] and Note S1 of the Supplemental Material [46] for a more extensive description of our simulation approach. In brief, the KMC simulations are done by employing an isotropic three-dimensional (3D) simulation box ($100 \times 100 \times 100$ lattice sites) with a lattice constant of $a = 1.5$ nm. We have considered spatially correlated energetic disorder for the host matrix [37,69,70]. The energy correlations between the lattice sites are modeled using the approach suggested by Bobbert *et al.* [71] and further detailed in Note S1 of the Supplemental Material [46]. Trap states were introduced into the energy-correlated system by downward shifting of the energy of a randomly chosen localized host state by a trap depth energy ε_t , resulting in the cumulative bimodal DOS distribution given by Eq. (1). Hopping transitions were described using Miller-Abrahams hopping rates [72]. To consider transitions of carriers also to non-nearest hopping sites, we implemented variable range hopping (VRH) in the KMC simulations.

III. EXPERIMENTAL RESULTS

A. Intrinsic trapping in pure materials

We first consider TSL in the neat materials studied here. Figure 3 presents TSL glow curves measured in neat

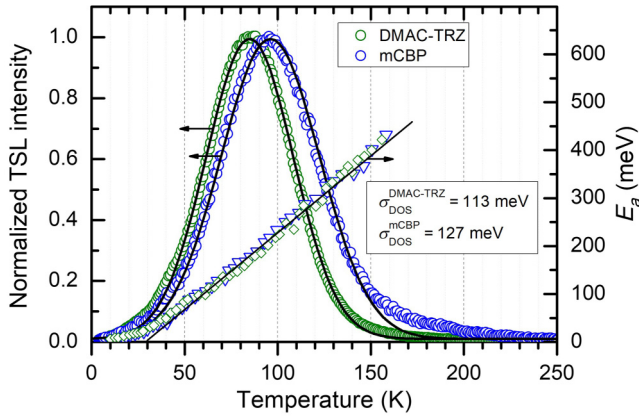


FIG. 3. Normalized TSL glow curves for neat mCBP and DMAC-TRZ films (blue and green symbols, respectively) with their Gaussian fit (solid curves). Activation energy $E_a(T)$ from fractional TSL measurements for these films (triangles and rhombi) is fitted with Eq. (5) (solid line).

films of mCBP and DMAC-TRZ, revealing broad, bell-shaped bands with maxima at 95 and 85 K, respectively, consistent with our previous reports [37]. It has already been demonstrated that the TSL in these materials originates from radiative recombination of charge carriers that are thermally released from the lower-energy part of the intrinsic DOS (i.e., disorder-induced traps) to the transport energy level near the DOS center [36]. No TSL signal is detected from wide-bandgap UGH3, which absorbs only in the deep UV ($\lambda \leq 270$ nm) [73], beyond the Hg-lamp emission range.

Fractional TSL measurements indicate quasicontinuous trap distributions in mCBP and DMAC-TRZ films, with activation energies E_a increasing linearly with temperature (Fig. 3, triangle and rhombic symbols, respectively) according to the following empirical relation [36,37] that applies to undiluted neat films as well as to trap-containing systems with very small trap concentrations where thermal detrapping via the host is realized:

$$E_a(T) = 0.0032 \times T - 0.091 (\text{in eV}). \quad (5)$$

Using this relation, the temperature scale was converted to the energy scale and the TSL curves were fitted with Gaussians (solid curves in Fig. 3), yielding the width of the TSL bands $\sigma_{\text{TSL}} = 85$ and 75 meV for neat mCBP and DMAC-TRZ films, respectively. As shown earlier [37], the TSL curve maps the ODOS distribution formed by the low-temperature energetic relaxation of photogenerated charges via their downward hopping within the available DOS, implying thus $\sigma_{\text{TSL}} = \sigma_{\text{ODOS}}$. The width of the ODOS can be used to determine the width of available DOS due to the established correlation between σ_{ODOS} and σ_{DOS} parameters [37]. Our recent KMC simulations

have revealed that under low-temperature energetic relaxation, the width of the ODOS σ_{ODOS} amounts to about 2/3 of the available DOS, which has also been confirmed experimentally for a large set of low-molecular-weight organic materials (see Ref. [37] for details). Using this approach, we obtain $\sigma_{\text{DOS}} = 127$ meV (mCBP) and 113 meV (DMAC-TRZ), in agreement with computed σ_{DOS} values for these materials, which range from 122 to 129 meV [37]. These values are characteristic of moderately polar amorphous organic materials (dipole moments of mCBP and DMAC-TRZ is 1.5–2 D). UGH3, being nonpolar, exhibits lower disorder ($\sigma_{\text{DOS}} < 100$ meV), as calculated in the present study and in agreement with previous calculations $\sigma_{\text{DOS}} \approx 80$ meV for the chemically similar UGH2 [74].

B. Effect of shallow and deep extrinsic traps

1. General observations

We next probe host-guest systems by doping mCBP and UGH3 hosts with the DMAC-TRZ guest. This introduces shallow and deep extrinsic traps, respectively. In the mCBP:DMAC-TRZ composition, the HOMO offset creates a shallow hole trap ($\varepsilon_t = 0.27$ eV), as shown in the energy diagram in Fig. 2(b). This satisfies the shallow trapping criteria of $\varepsilon_t \leq 3\sigma_{\text{DOS}}$ [14,15], given the intrinsic disorder of the mCBP host $\sigma_{\text{DOS}} = 127$ meV. Conversely, in the wide-gap UGH3 host, DMAC-TRZ forms a deep electron trap ($\varepsilon_t = 0.66$ eV), since $\varepsilon_t \gg 3\sigma_{\text{DOS}}$, where $\sigma_{\text{DOS}}(\text{UGH3}) = 97$ meV as obtained from QM-MD calculations (see Sec. IV below). At the same time, Fig. 2(b) also shows that DMAC-TRZ creates even deeper traps of the opposite polarity (0.83 eV in mCBP and 1.4 eV in UGH3), which effectively act as recombination centers and are therefore not detectable in TSL because carriers trapped at these levels recombine with those previously released from shallower traps.

a. Shallow-trapping effects. Figure 4(a) presents TSL glow curves measured in *shallow-trap containing* mCBP:DMAC-TRZ systems across a wide range of DMAC-TRZ guest concentrations. The most characteristic feature is gradual and nonmonotonic shift of the TSL band with increasing DMAC-TRZ content. At low concentrations ($c_t \leq 3\%$), the TSL band shifts towards higher temperatures by almost 100 K [Fig. 4(a)]. Beyond this point, the trend reverses, with the peak shifting to lower temperatures with further increasing c_t , eventually approaching the TSL band of neat DMAC-TRZ film. Thus, the maximum high-temperature shift occurs for an intermediate DMAC-TRZ concentration near 3%, resembling a mixed crossover between the low-concentration regime in which the guest states act as isolated trap sites and the high-concentration regime in which direct GG hopping

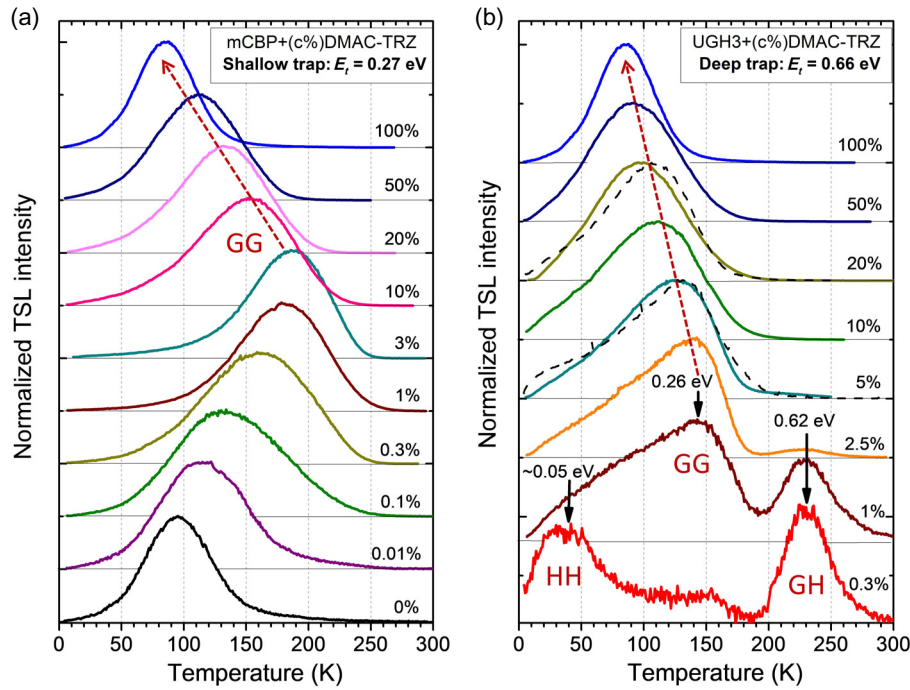


FIG. 4. Normalized TSL curves measured at different concentrations of DMAC-TRZ in (a) shallow-trap containing mCBP:DMAC-TRZ and (b) deep-trap containing UGH3:DMAC-TRZ host-guest compositions. The red dashed arrows in (a) and (b) is a visual guide to highlight the percolation regime, which is dominated by the GG-detraping pathway. Dashed curves in (b) denote the TSL curves measured in the percolation-only system based on polystyrene doped with 5% and 20% of DMAC-TRZ guest molecules. HH and GH in (b) denote TSL bands due to detrapping from very shallow tail states of intrinsic DOS of UGH3 host (HH detrapping) and from deep trap states (GH detrapping), respectively. Note that no TSL signal was detected in neat UGH3 films. TSL bands with activation energies of 0.26 and 0.62 eV in (b) are distinguished by different frequency factors of 5×10^7 s⁻¹ and 7×10^{11} s⁻¹, respectively, as will be detailed hereafter.

dominates (Fig. 1). This nonmonotonic trapping behavior in TSL is a clear indication on a transition from GH to GG detrapping pathways, where the latter governs charge release in these blends at moderately high trap concentrations $c_t \geq 10$ % [Fig. 4(a)] and will be discussed in more detail in subsequent sections.

It should be pointed out that doping mCBP with DMAC-TRZ *does not* lead to the appearance of any additional peaks in the TSL spectra [Fig. 4(a)], which may seem counterintuitive for a material with extrinsic traps. The observed shift in the TSL peak temperature [Fig. 4(a)] corresponds to changes in the activation energy measured at the TSL peak maximum, which we *denote as the mean activation energy* E_a^{mean} , as shown in Fig. 5(a). Notably, E_a^{mean} changes by more than a factor of 2 with varying DMAC-TRZ concentrations, and this variation is distinctly nonmonotonic. The concentration-dependent deviation of E_a^{mean} from the expected, concentration-independent trap energy $\varepsilon_t = 0.27$ eV contrasts sharply with crystalline materials lacking static energetic disorder, where guest-induced trap activation energies remain constant and equal to the nominal trap depth [11].

Noteworthy, the TSL bands in the mCBP:DMAC-TRZ systems [Fig. 4(a)] tend to deviate from the Gaussian

profile characteristic of the neat host (cf. Fig. 3), becoming notably asymmetric. This implies asymmetric ODOS distributions in these systems. Such behavior arises from the specific energetic relaxation of charges within a bimodal cumulative DOS distribution, and is supported by KMC simulations, as detailed in Sec. V below and Note 2 of the Supplemental Material [46], and demonstrated in Fig. S2. Additionally, the TSL peak width, as determined by the standard deviation of the measured TSL bands, varies nonmonotonically with guest concentration and exhibits a maximum width at intermediate c_t , as shown in Fig. 5(b). Previously we found that the ODOS width, σ_{ODOS} , in neat host materials under nonequilibrium conditions (as realized at 5 K) commonly amounts to $(2/3) \sigma_{\text{DOS}}$. [37]. Figure 5(c) shows that, in contrast to neat films, the ODOS width tends to increase in the host-guest systems with increasing trap depth, becoming almost equal to σ_{DOS} of the neat host for a host-guest system with $\varepsilon_t = 3\sigma$ at $c_t = 1$ –3%.

b. Deep-trapping effects. Figure 4(b) shows TSL glow curves measured in UGH3:DMAC-TRZ host-guest systems *containing deep traps* ($\varepsilon_t = 0.66$ eV) across a wide

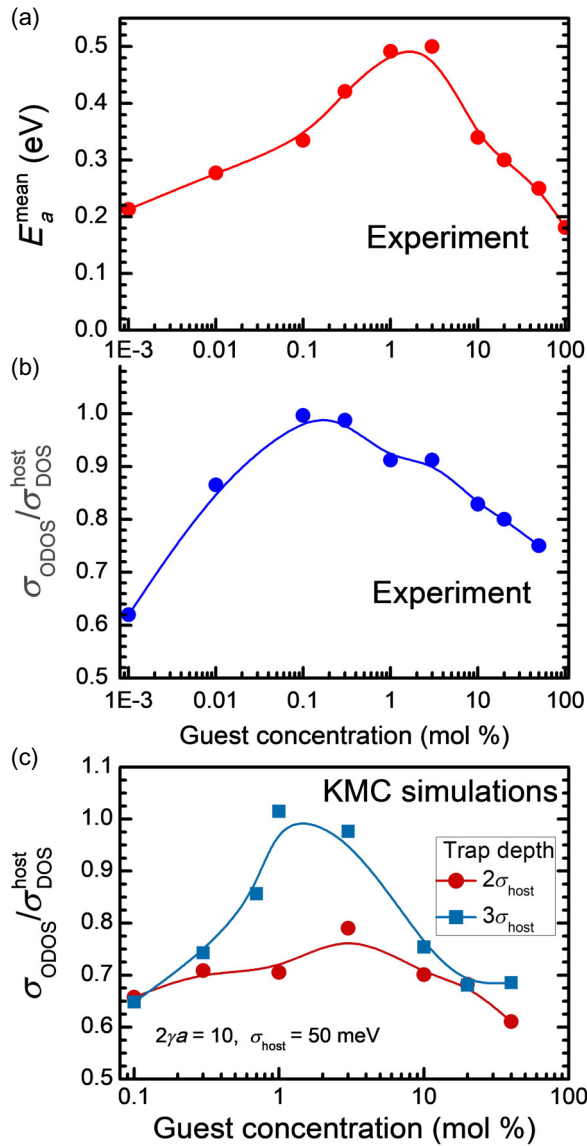


FIG. 5. (a) Mean activation energies E_a^{mean} as measured at the TSL peak maxima shown in Fig. 4(a), and (b) standard deviation of the TSL bands for mCBP:DMAC-TRZ compositions at different guest concentrations. (c) The width of the ODOS distribution (σ_{ODOS}) vs trap concentration, as derived from KMC simulations for different trap energies in host-guest systems. All lines are merely guides to the eye.

range of DMAC-TRZ concentrations. As evident from the data, the evolution of the glow curves with increasing guest concentration in this host differs drastically from the behavior observed in the shallow-trap mCBP:DMAC-TRZ systems [Fig. 4(a)]:

(1) First consider the lowest DMAC-TRZ concentration (0.3%) in the UGH3 host [see the lowest curve in Fig. 4(b)]. A distinct, deep-trap-related TSL peak emerges at 230 K at such guest concentration, characterized by

an activation energy of 0.62 eV at the peak maximum [Fig. 6(d)]. It is in good agreement with the expected electron trap depth of $\varepsilon_t = 0.66$ eV based LUMO offset between host and guest [Fig. 2(b)] and is associated with a frequency factor of $7 \times 10^{11} \text{ s}^{-1}$, which was derived from the fractional TSL using Eq. (4) as described in Sec. II B above. This is a typical value for over-barrier-activated transitions [see Fig. 6(e)]. Therefore, we attribute this 230-K TSL feature to thermally activated *charge release from DMAC-TRZ guest to UGH3 host*, representing the GH-detraping regime at low trap concentrations when traps are well spatially separated, as sketched in Fig. 1(a). Moreover, another TSL band [denoted as host-to-host (HH)] is also observed in this system at rather low temperatures around 35–40 K [see the lowest curve in Fig. 4(b)], which we ascribe to very *shallow trapping by the tail states of the intrinsic DOS* of the UGH3 host. Note that the charge-photogeneration process in UGH3:DMAC-TRZ systems occurs via photoexcitation of DMAC-TRZ molecules resulting in electron transfer to LUMO levels of UGH3 host, as will be detailed hereafter. Given the moderate DOS width of nonpolar UGH3 films, such shallow trapping by host tail states is expected. These observations suggest that in host-guest systems containing deep traps, the ODOS distribution acquires a double-peak structure directly reflecting superposition of two Gaussian DOSs, one associated with the host and one with the guest. However, this only occurs when trap concentrations are low enough (as 0.3% in our case); otherwise, all carriers would eventually be funneled to extrinsic trap states. Indeed, the low temperature band at 35–40 K is no longer distinguishable in the TSL spectra when $c_t > 0.3\%$ [Fig. 4(b)], and is not the main focus of the present study.

(2) Secondly, increasing the concentration of DMAC-TRZ in the UGH3 host causes the 230-K peak to disappear entirely from the TSL spectra once the concentration exceeds 5% [see Fig. 4(b)]. This is accompanied by the emergence of a new (third) TSL band at moderately lower temperatures, peaking at 145 K for 1% DMAC-TRZ [denoted as GG in Fig. 4(b)]. This band is characterized by the mean activation energy of 0.26 eV and reduced frequency factor of $2 \times 10^7 \text{ s}^{-1}$ [Fig. 6(e)]. The intensity of this new 145-K TSL peak increases significantly with c_t and the peak gradually shifts to lower temperatures, eventually reaching the TSL of the neat DMAC-TRZ film. We attribute this TSL feature to an alternative detrapping pathway: charge release occurring entirely within the DMAC-TRZ guest sites manifold, without involvement of the UGH3 host states [i.e., GG-detraping regime, as schematically depicted in Fig. 1(c)]. As this pathway becomes more efficient at higher guest concentrations, it increasingly dominates over the conventional GH detrapping responsible for the 230-K peak, explaining the disappearance of the latter with increasing c_t because guest sites are no longer spatially isolated. Unambiguous

evidence supporting this interpretation comes from TSL measurements of electrically inert polystyrene films doped with 5% and 20% DMAC-TRZ [dashed lines in Fig. 4(b)], where a similar TSL band is observed. In this percolation-only system, charge transfer can only occur through the guest states by definition.

(3) Thirdly, when the concentration of the guest is intermediate (1–5%), both the 230- and 145-K bands coexist in the TSL spectra of UGH3:DMAC-TRZ compositions [Fig. 4(b)]. This behavior *does NOT indicate two different ODOS distributions*; rather, it reflects the mixed regime in which charge detrapping occurs “*via both host and guest sites*”, i.e., superposition of GH and GG detrapping pathways, as depicted in Fig. 1(b). The comparable magnitudes of these TSL bands at 1% DMAC-TRZ suggest that the charge release is mediated by comparable contributions from both pathways. As the concentration increases, detrapping via guest sites becomes progressively more dominant, fully overtaking the host-mediated pathway by 10%. A remarkable finding is that the onset of GG detrapping in the UGH3:DMAC-TRZ system occurs at concentrations as low as 1%, which requires further investigation into the relevant mechanisms.

2. Analysis of TSL frequency factors

To gain a deeper insight into the kinetics of the charge-detrapping process at different guest concentrations, and thereby infer the transport mode, we analyze the temperature dependence of the frequency factor S derived from the fractional TSL using Eq. (4). In classical detrapping involving carrier release over potential barriers in solids (e.g., into the conduction band of crystals), S is typically on the order of the Debye frequency, approximately 10^{12} – 10^{13} s^{−1} [75]. In contrast, when thermally assisted tunneling dominates TSL, the frequency factor can be reduced by several orders of magnitude, sometimes below 10^3 s^{−1} [76]. This reduction, commonly observed in various disordered systems at low temperatures, is consistent with the idea of variable-range hopping [77,78]. In this regime, carriers readily hop to the nearest neighbor when the thermal energy is sufficient to overcome site-to-site energy differences. However, when thermal energy is insufficient, carriers preferentially hop to energetically similar but more distant sites, resulting in a slower detrapping process. In amorphous semiconductors with hopping charge transport, S decreases exponentially with increasing effective hopping distance, ρ as [7]

$$S = \nu_0 \exp(-2\rho/\rho_0), \quad (6)$$

where ρ_0 is a wave-function decay parameter, and the prefactor ν_0 is a characteristic phonon frequency typically taken as 10^{13} s^{−1}. This equation, being similar to the

temperature-independent “tunneling term” in the Miller-Abrahams rate model, is a key relationship that links the charge mobility to the concentration of charge transporting molecules in molecularly doped polymers [7]. In principle, with known ρ_0 , Eq. (6) allows for estimation of the effective hopping distance.

Figures 6(a) and 6(b) present the activation energies E_a and frequency factors S , respectively, as functions of temperature for shallow-trap mCBP:DMAC-TRZ compositions at guest concentrations of 1% and 10%, along with neat films. These figures reveal two key observations. First, in neat films, $S(T)$ exhibits a *substantial increase* with temperature, from approximately 10^3 s^{−1} at very low temperatures to about 6×10^{11} s^{−1} at $T \geq 150$ K, where it eventually saturates [Fig. 6(b)]. Such behavior is characteristic of TSL in disordered solids with hopping transport, including inorganic glasses [79,80] and amorphous photoconducting polymers [81]. It indicates progressively longer-range hopping as temperature decreases. Second, while the $E_a(T)$ dependence at $c_t = 1\%$ DMAC-TRZ is virtually identical to that obtained for the neat films, it turns out to be significantly lower at $c_t = 10\%$ DMAC-TRZ [solid orange symbols in Fig. 6(a)], accompanied by significantly reduced S values [solid orange symbols in Fig. 6(b)] compared to that of the neat films.

Figure 6(c) shows the effective hopping distances ρ , as calculated by Eq. (6) for different temperatures, using the $S(T)$ data from Fig. 6(b) for mCBP:DMAC-TRZ systems and assuming $\rho_0 = 0.22$ nm [36] as a representative value for organic materials. At low temperatures, ρ is relatively large (2.5–3 nm), indicating long-range hopping due to the transport energy being located well below the DOS center [32,33]. As the temperature increases, ρ expectedly decreases because the transport energy shifts closer to the DOS center, increasing the density of accessible localized states [32].

The observed trend with ρ in Fig. 6(c) reflects a gradual transition from variable-range hopping to nearest-neighbor hopping regimes as temperature increases. Notably, the obtained effective hopping distance approaches values as small as $\rho \approx 0.35$ nm at high temperatures, which is smaller than the approximately 1-nm center-of-mass distance (i.e., “average” hopping distance) in neat mCBP films. This can be explained by hopping occurring between the nearest conjugated peripheral functional groups of neighboring molecules (e.g., carbazole units) rather than entire molecules. It is worth noting that Andrienko *et al.* [82] predicted a surprisingly similar reduced lattice constant of 0.34 nm when fitting microscopic charge-transport simulations to the Gaussian disorder model and taking into account spatial site energy correlations. These results are also consistent with recent calculations showing hopping distances between peripheral groups as small as 0.4 nm for some organic semiconductors [83], and align with the

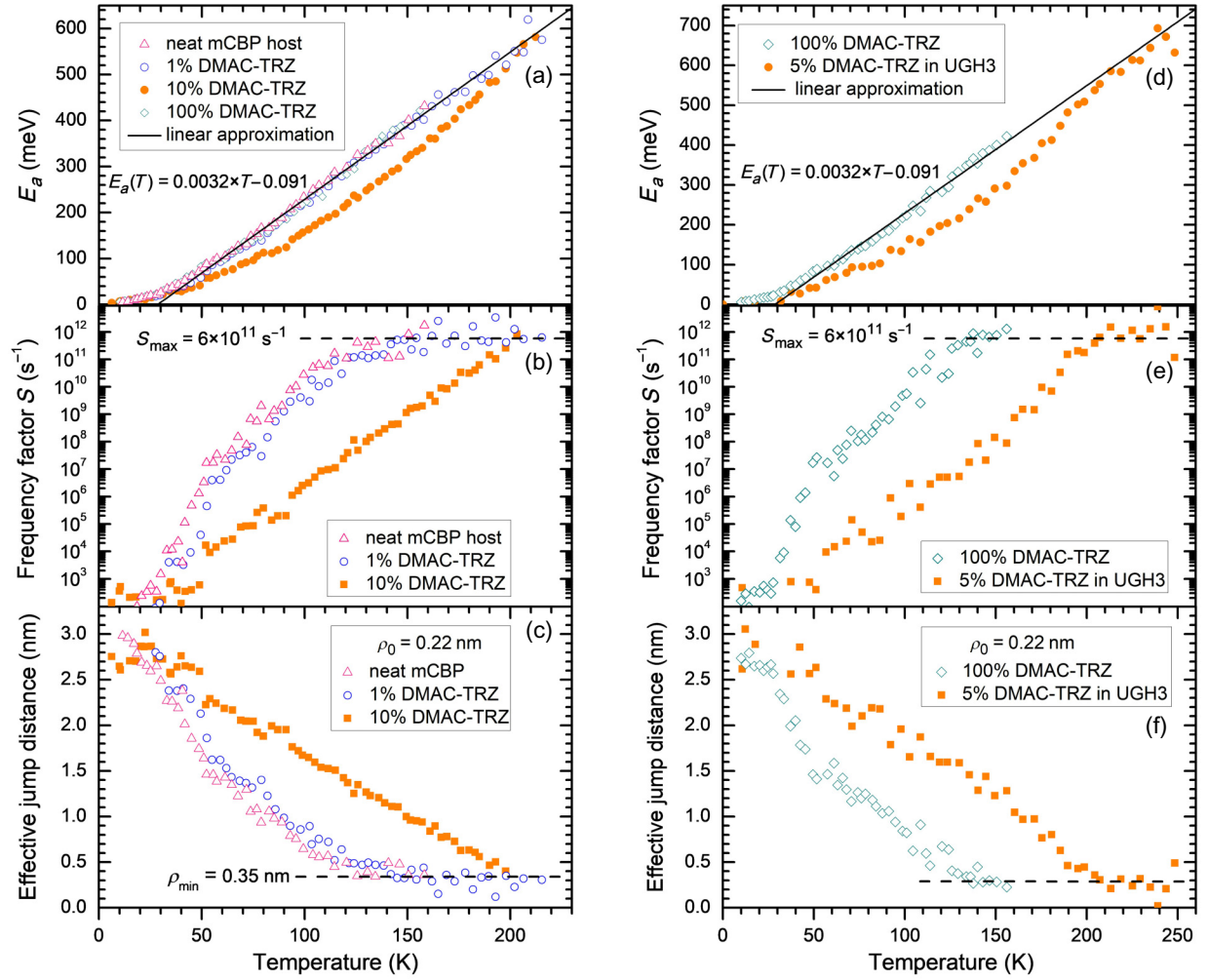


FIG. 6. Fractional TSL study of the mCBP:DMAC-TRZ composition at guest concentrations of 1% and 10%, as well as neat mCBP and DMAC-TRZ films (*left panel*) and UGH3:DMAC-TRZ composition at 5% DMAC-TRZ (*right panel*). (a),(d) Temperature dependences of the activation energy $E_a(T)$; (b),(e) the frequency factor $S(T)$, estimated by Eq. (4); and (c),(f) the effective hopping distance, estimated by Eq. (6). Note that there is significant data scattering at high temperatures, which may be because the TSL signals are much weaker at these temperatures, which makes determining E_a less reliable.

previously reported π -stacking distance of 0.42 nm for neat mCBP films [84].

Within the 80–170 K range, where TSL peaks are observed [Fig. 4(a)], the effective hopping distance ρ for the mCBP:(10%)DMAC-TRZ system is more than double that of neat films [Fig. 6(c)], in good agreement with the lattice gas model prediction of a $2.2\times$ increase at 10% guest dilution [7]. This points to direct detrapping via guest sites. No such effect is seen at 1% DMAC-TRZ, indicating charge release through host sites at this low concentration. Thus, the mCBP:(10%)DMAC-TRZ system behaves as a dilute transport network of guest molecules embedded in the mCBP host, consistent with earlier reports of strongly reduced S in percolation-only molecularly doped polymers, such as polystyrene with 10% tri-*p*-tolylamine [34].

Figures 6(d) and 6(e) show temperature dependences of E_a and S , determined by fractional TSL for deep-trap UGH3:DMAC-TRZ compositions at guest concentrations of 5% and 100%. These data are qualitatively similar to those for mCBP:DMAC-TRZ systems containing shallow traps, as discussed above. The main difference is that the reduction in frequency factors occurs at a notably lower guest concentration of 2–5%, compared to 10% in the former case.

IV. QM-MD CALCULATIONS OF HOST-GUEST SYSTEMS

In order to link experimental observations with the microscopic properties of the host-guest systems under consideration, we conducted classical molecular dynamics

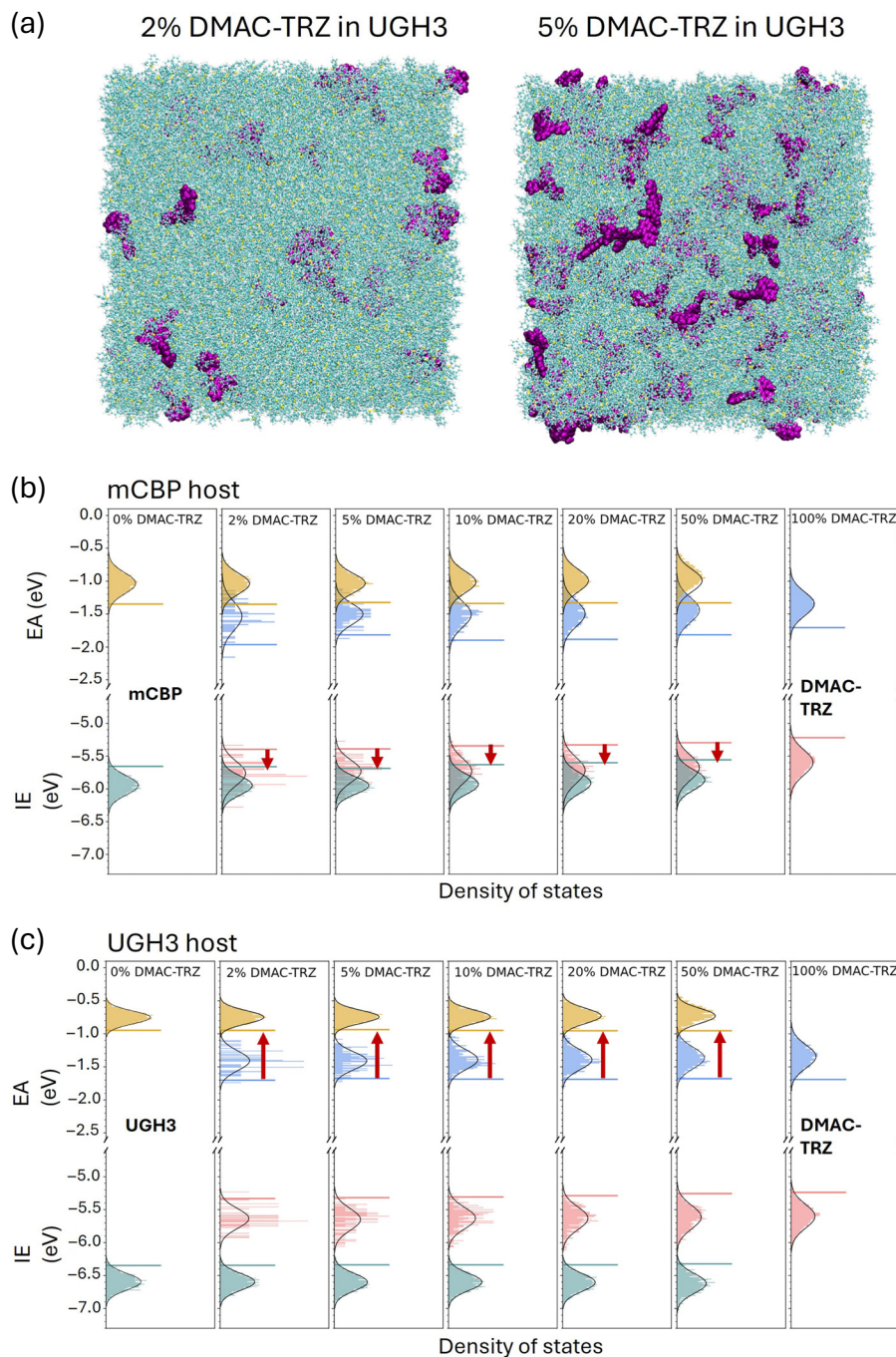


FIG. 7. (a) Simulation snapshots of molecular arrangement at 2% and 5% of DMAC-TRZ in the UGH3 host. Normalized calculated HOMO and LUMO DOS distributions for (b) mCBP:DMAC-TRZ and (c) UGH3:DMAC-TRZ compositions, at different mixing ratios. Solid-state ionization energy (IE) and electron affinity (EA) are obtained as an onset of the corresponding DOS distributions and are shown by solid lines. Red arrows indicate shallow and deep traps created by DMAC-TRZ guest, and probed by TSL measurements, in mCBP and UGH3 hosts, respectively.

(MD) simulations to generate amorphous morphologies across various host-guest ratios. Next, we performed calculations using perturbative and semiempirical methods, incorporating DFT results, to determine the electronic energy levels and intermolecular couplings (see Note S3 of the Supplemental Material [46] for detailed description).

The calculated DOS distributions in the mCBP:DMAC-TRZ and UGH3:DMAC-TRZ compositions at various guest concentrations are presented in Figs. 7(b) and 7(c), respectively, and are further detailed in Tables I and II. Notably, the calculated trap depths of 0.24 eV for holes in mCBP:DMAC-TRZ and 0.69 eV for electrons in

TABLE I. Shallow hole traps in mCBP:DMAC-TRZ: calculated ionization energy (IE) and the HOMO DOS width for host and guest components (σ_{host}^h and σ_{guest}^h) at different concentration of DMAC-TRZ guest (in %). The trap depth (ε_t^h) for holes is obtained as difference between the IE of host and guest.

		0%	2%	5%	10%	20%	50%	100%
mCBP (host)	IE (eV)	−5.946	−5.948	−5.948	−5.928	−5.911	−5.836	
mCBP (host)	σ_{host}^h (eV)	0.145	0.143	0.13	0.149	0.155	0.153	
DMAC-TRZ (guest)	IE (eV)		−5.713	−5.68	−5.688	−5.67	−5.632	−5.549
DMAC-TRZ (guest)	σ_{guest}^h (eV)		0.146	0.132	0.172	0.168	0.163	0.159
Trap depth (for h^+)	ε_t^h (eV)		0.235	0.268	0.24	0.241	0.204	

UGH3:DMAC-TRZ (based on mean energy), differ by only 0.03 eV from the experimental values presented in Fig. 2(b). The calculated DOS distributions in Fig. 7 are consistent with a bimodal Gaussian disorder model, in which the energy offset remains independent of guest concentration—indicating a nearly constant nominal trap depth across varying host-guest ratios. Interestingly, the trap-DOS distribution formed by DMAC-TRZ guest in the UGH3 host is narrower than that in the mCBP host, see Tables I and II. This behavior is expected as the nonpolar UGH3 environment creates reduced electrostatic disorder, compared to mCBP, in both host and guest site manifolds. This interpretation is consistent with the experimental observation of a similarly narrow deep trap related TSL peak at 230 K in UGH3:DMAC-TRZ blends at $c_t = 0.3\%$ [Fig. 4(b)], the width of which estimated to be $\sigma_{\text{trap}} = 113$ meV.

Representative simulated morphologies of host-guest systems for two selected low concentrations of DMAC-TRZ in the UGH3 host are shown in Fig. 7(a). Additional simulation snapshots illustrating molecular arrangements across a broader range of guest concentrations are presented in Fig. S3 of the Supplemental Material [46]. We do not observe any substantial formation of large guest molecule aggregates. To analyze the electronic connectivity within the guest-site manifold, we apply a clustering approach based on intermolecular contact distance. More specifically, two guest molecules are considered to be an electronically connected pair if the distance between any two of their nonhydrogen atoms is less than 5 Å. The results of this analysis are summarized in Table III. Two critical concentrations should be noted here. At relatively

high guest concentrations of around 20%, DMAC-TRZ molecules form a single dominant cluster that spans infinitely in one dimension in both mCBP and UGH3. However, smaller clusters already begin to dominate at concentrations slightly below 5%, where less than half of the guest molecules can be considered as “isolated.”

These critical concentrations are consistent with predictions of the random site model on the face-centered cubic lattice, where the classical percolation threshold for macroscopic transport is approximately 20%. For mCBP:(10%)DMAC-TRZ, the two largest clusters were found to be separated by only one host molecule. These clusters included 28% of all molecules and extended infinitely in one dimension, meaning that the percolation threshold is slightly above 10%. The second threshold concentration, near 5%, agrees with the random site model, which predicts that clusters begin to outnumber isolated sites at a concentration $c \approx 1/2n$, where n is the coordination number (i.e., the number of nearest neighbors). For all molecules considered here, the mean coordination number is around 15 (see Fig. S7 in the Supplemental Material). At lower concentrations, the statistical sampling becomes insufficient for definitive conclusions. Nevertheless, in the simulated UGH3:(2%)DMAC-TRZ morphology, we observe small guest clusters (consisting of two–four molecules), indicating a deviation in the clustering statistics expected from a purely random site model.

We further analyze the role of a superexchange-mediated charge transport mechanism (through-host tunneling) in the UGH3-DMAC-TRZ host-guest systems, which might be particularly relevant at low guest concentrations and low temperatures. Using first-principles

TABLE II. Deep electron traps in UGH3:DMAC-TRZ systems: calculated solid-state electron affinity (EA) and the LUMO DOS widths for host and guest components (σ_{host}^e and σ_{guest}^e) at different concentration of guest (in %). The electron trap depth (ε_t^e) is obtained as difference between the EA of host and guest.

		0%	2%	5%	10%	20%	50%	100%
UGH3 (host)	EA (eV)	−0.751	−0.749	−0.742	−0.741	−0.728	−0.705	
UGH3 (host)	σ_{host}^e (eV)	0.097	0.099	0.097	0.104	0.113	0.122	
DMAC-TRZ (guest)	EA (eV)		−1.452	−1.436	−1.43	−1.423	−1.396	−1.376
DMAC-TRZ (guest)	σ_{guest}^e (eV)		0.115	0.119	0.118	0.131	0.143	0.16
Trap depth (for e^-)	ε_t^e (eV)		0.703	0.694	0.689	0.695	0.691	

TABLE III. Statistics of DMAC-TRZ molecule clusters at the 5-Å nonhydrogen contact distance. Columns three–five give the percentage of guest molecules found in the largest cluster, dimers, and isolated sites. The next two columns show the total number of guest molecules and the sizes of the three largest clusters. “CMS” is the center-of-mass size at which half of all molecules belong to clusters that are larger than or equal to it. The last column shows the mean coordination number “CN” of the largest cluster.

Composition	Mass %	Largest %	Dimers %	Isolated %	Total	Three largest	CMS	CN
mCBP + 20% DMAC-TRZ	21.3	93	2	2	800	747,8,4	Infinite	3.5
mCBP + 10% DMAC-TRZ	10.7	17	6	14	400	69,43,22	8	2.7
mCBP + 5% DMAC-TRZ	5.3	8	24	37	100	8,4,3	2	2.3
mCBP + 2% DMAC-TRZ	2.1	10	15	68	40	4,3,2	1	1.5
UGH3 + 20% DMAC-TRZ	17.4	77	2	3	400	308,16,14	Infinite	3.5
UGH3 + 10% DMAC-TRZ	8.7	9	13	18	200	18,12,12	6	2.7
UGH3 + 5% DMAC-TRZ	4.3	8	12	43	100	8,7,5	2	2.0
UGH3 + 2% DMAC-TRZ	1.7	8	30	55	40	3,3,2	1	1.3

calculations (as detailed in Note 3 of the Supplemental Material [46]), we evaluated both direct and superexchange electronic coupling elements. We find that, in the MD-simulated microscopic morphology, the direct (through vacuum) guest-guest transfer integrals J_{ij} become negligible for nonadjacent molecules, i.e., when the two nearest atoms of the molecules are more than 0.5 nm apart. For the superexchange, we considered charge transfer from one DMAC-TRZ molecule to another via a UGH3 host molecule (see Note 3 of the Supplemental Material [46]). More specifically, we considered bridges formed between two guest molecules where no single step (guest-host, host-host, or host-guest) exceeded 0.5 nm, however, there was no explicit restriction on the guest-guest distance for pairs that were considered for pure superexchange process. In most cases, however, only single molecule-bridge paths (guest-host-guest) were found in the simulated morphologies. For pairs where the guest-guest separation was less than 0.5 nm and where there was also a possible guest-host-guest pathway for superexchange, we also considered both the hopping and superexchange contributions. However, as expected, in this case the direct hopping very much dominated due to the significantly better guest-guest orbital overlap at short distances, as seen in the transfer rates of hopping versus superexchange transfer processes. Using the Marcus relation [85], we estimated charge-transfer rates and found that superexchange rates are 5–6 orders of magnitude slower than direct hopping across all guest concentrations used (see Fig. S5 in the Supplemental Material [46]). For instance, in the 5% DMAC-TRZ:UGH3 system, the highest calculated superexchange rate is just $3 \times 10^5 \text{ s}^{-1}$. This is 5 orders of magnitude slower than the direct hopping, which occurs at a rate of $1 \times 10^{11} \text{ s}^{-1}$.

V. KMC SIMULATIONS OF ENERGETIC RELAXATION IN HOST-GUEST SYSTEMS

Having shown in Sec. IV that the cumulative DOS distribution in the considered host-guest compositions is

a superposition of Gaussian peaks due to the host and guest DOS distributions, KMC simulations were employed to investigate how traps affect the low-temperature energetic relaxation and consequently the ODOS formation in such systems. The simulation technique used in this study is similar to that we employed recently for neat host films with a single-modal Gaussian DOS [37], but with a major modification to account for a *bimodal structure of the cumulative DOS* in host-guest systems [cf. Eq. (1)]. For simplicity we assume that both intrinsic and extrinsic trap state distributions have the same Gaussian width, i.e., $\sigma_{\text{host}} = \sigma_{\text{trap}} = \sigma_{\text{DOS}}$. We employed a variable-time-step (VT) KMC approach [37] assuming $\sigma_{\text{DOS}} = 50 \text{ meV}$ and variable-range hopping for a system with spatially correlated energetic disorder. We have already demonstrated that the inclusion of correlations between the energies of adjacent sites is crucial for reproducing the experimentally determined ratio between the width of the ODOS and that of the available DOS [37]. At the beginning of the simulation, a charge carrier is generated randomly at one of the lattice sites according to the DOS distribution.

Figure 8(a) shows the evolution of the simulated ODOS distribution for different guest concentrations, assuming the trap depth $\varepsilon_t = 3\sigma_{\text{host}}$. The simulations were carried out for a temperature of 5 K to match the conditions characteristic for the trapping in the TSL experiment. Figure 8(a) demonstrates that the ODOS distribution in a shallow trap-containing host-guest system always exhibits a single-modal Gaussian shape regardless of the trap concentration, which is in agreement with the experimental observations for mCBP:DMAC-TRZ compositions [cf. Fig. 4(a)]. Moreover, the KMC simulations show a notable ODOS broadening in such compositions, which increases with increasing trap depth and exhibits a nonmonotonic dependence on the trap concentration, exhibiting a maximum width at a guest content of about 1%, as depicted in Fig. 5(c). It also shows that the ODOS width in this host-guest systems is always broader compared to neat host, and at the trap depth $\varepsilon_t = 3\sigma_{\text{host}}$ becomes equal to the width of the host DOS itself, which is in agreement with the

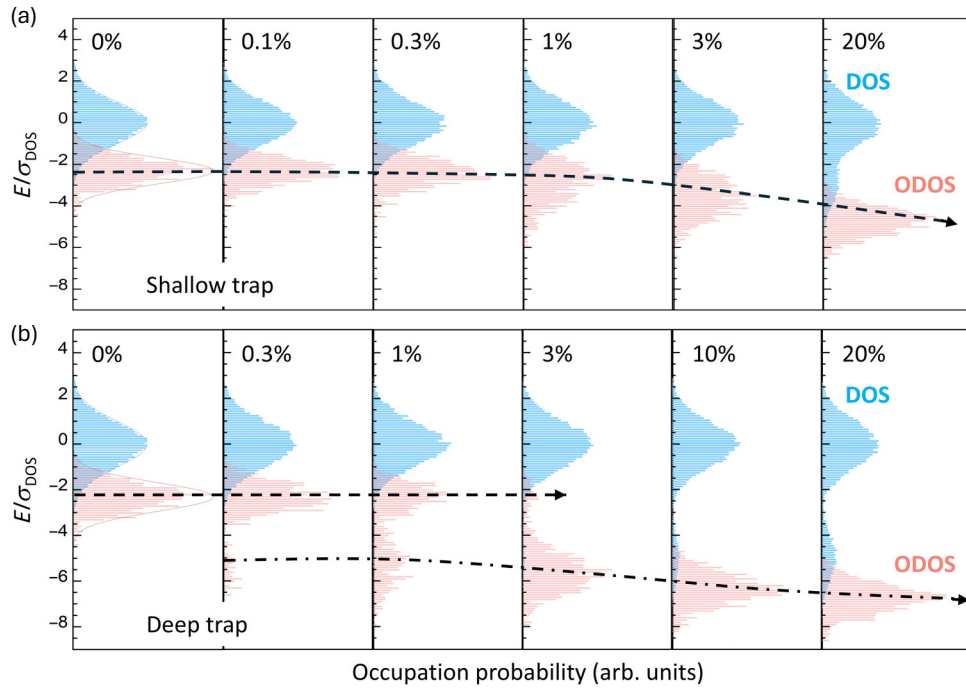


FIG. 8. KMC simulated ODOS distributions (in red) in a host-guest system with (a) shallow traps $\varepsilon_t = 3\sigma_{\text{host}}$ and (b) deep traps $\varepsilon_t = 5\sigma_{\text{host}}$, which are formed after carrier energetic relaxation within a bimodal DOS distribution (in blue) at 5 K for different guest concentrations (indicated in the insets) and considering spatial energy correlations. Note that the obtained ODOS distributions in shallow trap systems (a) are always monomodal at any trap concentration, while in systems with deep traps (b) demonstrate a double-peak structure at moderately low trap concentrations. Dashed lines are a guide to the eye to demonstrate a trend.

experimental observation for mCBP:DMAC-TRZ compositions with similar trap depth [see Fig. 5(b)]. The temporal evolution of the calculated ODOS distributions as a function of simulated time in a host-guest system with shallow traps $\varepsilon_t = 3\sigma_{\text{host}}$ at 5 K within a bimodal DOS distribution for 1% and 3% of guest concentrations is shown in Fig. S2 and its analysis is detailed in Note 2 of the Supplemental Material [46]. As can be seen in Fig. S2 in the Supplemental Material [46], the calculated ODOS distribution at 3% of the guest shows a double-peak structure at moderately short delay times, but it acquires a single-peak shape again at longer delays. Moreover, these simulations reproduce qualitatively similar asymmetric ODOS distribution profiles as observed experimentally in Fig. 4(a).

Next, we consider the case of deep traps. Figure 8(b) presents the low-temperature ODOS distributions of charge carriers derived from KMC simulations for a host-guest composition with *deep trap* ($\varepsilon_t = 5\sigma_{\text{host}}$) over a wide range of guest concentrations. In contrast to shallow trap-containing systems, the ODOS distribution in deep trap-containing systems is split into two peaks that appear at moderately low trap concentrations between 0.3% and 3% [Fig. 8(b)]. This is in line with the experimental observations for UGH3:DMAC-TRZ compositions [cf. Fig. 4(b)]. These ODOS peaks observed at lower and deeper energies are attributed to carriers trapped by the lower-energy part

of the intrinsic (host) DOS distribution and by the deep guest state distribution, respectively. It can be seen that, as the guest concentration increases, the relative intensity of the deeper guest-related ODOS peak increases due to the greater probability of trapping. When the trap concentration increases further ($\geq 10\%$), the ODOS again exhibits a single-peak distribution due to all carriers from the host DOS being retrapped by the deep guest-related traps.

Figure 9 summarizes the principal results of the above KMC simulations shown in Figs. 8(a) and 8(b). The mean energy $\langle \varepsilon \rangle_{\text{ODOS}}$ of the relaxed charge-carrier ensemble obtained for different trap depths, normalized by the DOS width σ_{DOS} , is plotted in Fig. 9 as a function of trap concentration. In the case of *shallow traps* (such as $\varepsilon_t = 2\sigma_{\text{host}}$ and $3\sigma_{\text{host}}$), the energy distribution of the relaxed charges always exhibits a single-modal ODOS. Its mean energy $\langle \varepsilon \rangle_{\text{ODOS}}$ gradually moves deeper into the band gap as trap depth and trap concentration increase [Fig. 9(a)]. This is because the presence of shallow guest sites opens additional charge-transfer pathways for downward charge hopping, thereby enhancing charge relaxation as compared to a neat system.

Unlike the shallow trapping situation, the presence of the *deep traps* (such as $\varepsilon_t = 4\sigma_{\text{host}}$ and $5\sigma_{\text{host}}$) leads to the *ODOS splitting* into two peaks (components) [labeled in Fig. 9(b) as “Intrinsic traps” and “Deep traps”,

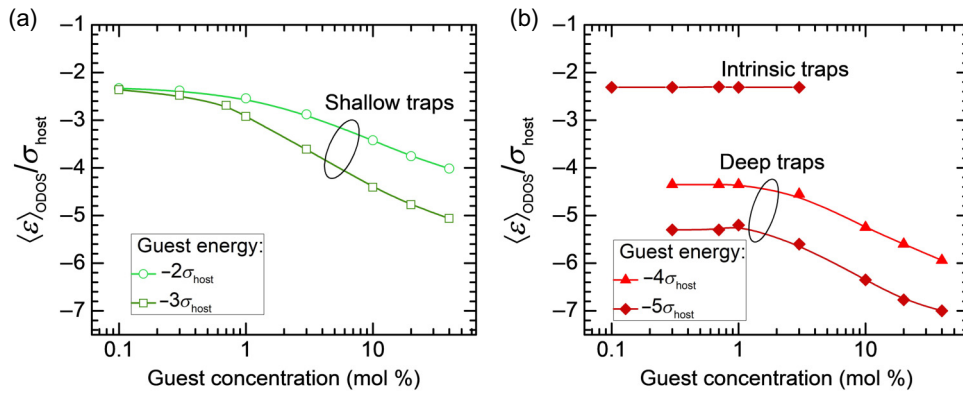


FIG. 9. The mean energy $\langle \epsilon \rangle_{\text{ODOS}}$ of the ODOS distributions as a function of trap concentration derived from KMC simulations for host-guest systems containing (a) shallow traps and (b) deep traps. Note that the ODOS distribution in systems with deep traps demonstrates splitting into two components, where the “Intrinsic trap” component is the same for both deep traps we simulated.

respectively]. Since the shallower ODOS peak corresponds to carriers that relaxed within the intrinsic host DOS, its position is invariant to trap concentrations [“Intrinsic trap” in Fig. 9(b)]. However, this peak vanishes at $c_t > 3\%$ due to charge retrapping by guest molecules, which becomes progressively more efficient with increasing guest concentration. At the same time, a deeper ODOS peak, which corresponds to carriers that are directly trapped by the guest species, is independent of c_t in the low-trap-concentration range due to the lack of the energetic relaxation within such a dilute manifold of trap sites. Thus, this ODOS peak directly represents the guest DOS distribution. Further increases in trap concentration make trap-to-trap transitions possible. As the trap concentration increases to the point where hopping transitions between trap sites become feasible, the ODOS peak begins to shift towards deeper energies at $c_t \geq 3\%$ due to the onset of energetic relaxation of carriers within the trap DOS [Fig. 9(b)]. This effect expectedly enhances with increasing guest concentration.

VI. DISCUSSION

A. Shallow traps

As demonstrated by the above TSL study of a model mCBP:DMAC-TRZ host-guest system, the main features of shallow charge-carrier trapping ($\epsilon_t < 3\sigma_{\text{DOS}}$) in organic disordered semiconductors can be summarized as follows:

(i) The shallow trap containing mCBP:DMAC-TRZ compositions consistently show a single TSL band [Fig. 4(a)], implying that the shape of *ODOS distribution remains unimodal* at any trap concentration despite the *bimodal available DOS distribution*. This means that the extrinsic trap distributions are not resolved in the ODOS distribution of such a composite system. KMC simulations [Fig. 8(a)] confirmed that the shallow traps indeed

do not act as separate charge traps; rather, they simply increase the density of deeper states within the lower-energy part of the intrinsic DOS of the host. This contrasts systems with deep traps, as will be discussed in the next subsection.

(ii) DOS calculations in Fig. 7(b) accurately quantify the energy of the shallow hole trap in mCBP:DMAC-TRZ compositions and demonstrate that the nominal trap depth remains almost unchanged across different host-to-guest ratios. The calculated hole trap depth varies (within the statistical uncertainty) from 0.204 to 0.268 eV, which is in good agreement with the experimental estimate of 0.27 eV based on UPS data (cf. Fig. 2). The constant value of the calculated trap depth proves that the nonmonotonous shift observed in the TSL spectra in Fig. 4(a) is not caused by a change in the trap energy ϵ_t when the guest concentration is varied. As expected for a molecular solid with small-to-moderate intermolecular electronic couplings, the calculated distribution of HOMO and LUMO energies for each molecular component is essentially Gaussian. This justifies the use of a *bimodal Gaussian DOS* distribution in empirical models of host-guest systems with unimodal Gaussian DOS of each component.

(iii) The measured mean activation energy E_a^{mean} in mCBP:DMAC-TRZ systems does not match the nominal trap depth ϵ_t and varies significantly with c_t [cf. Fig. 5(a)]. This suggests that shallow trapping in amorphous systems is actually the cumulative effect of intrinsic energy disorder in the host and extrinsic guest-induced traps. The increase in E_a^{mean} observed up to $c_t = 3\%$ [Fig. 5(a)] is due to enhanced energetic relaxation of carriers within the superimposed host and guest DOS distributions, which determines the mean energy of the ODOS in such systems. Additionally, the TSL peak broadens significantly and nonmonotonically as the guest concentration increases, peaking at an intermediate DMAC-TRZ concentration [see Fig. 5(b)]. This trend is reproduced well

by KMC simulations [see Fig. 5(c)] demonstrating similar nonmonotonic broadening of the ODOS distribution upon varying guest concentration.

(iv) Figure 4(a) shows that, once the guest concentration exceeds $c_t \geq 10\%$, the TSL peak in the mCBP:DMAC-TRZ system shifts gradually *towards lower temperatures* [Fig. 4(a)], implying the transition to a GG charge detrapping pathway. This is evidenced by the significant reduction in the frequency factor [Fig. 6(b)] and the average hopping distance being almost twice as large [Fig. 6(c)] in the CBP:(10%)DMAC-TRZ system. We demonstrate that such a behavior in our systems can be well explained within the concept of “transport energy” [32,33,86], which can depend on trap concentration. Coehoorn [18] used variable-range hopping calculations to show that the transport energy level in host-guest systems gradually shifts downwards towards deeper states as c_t increases. This effect is expected to affect the position of the TSL peak, because the thermal release of trapped carriers, which occurs at the transport energy level, is a rate-limiting step that governs TSL behavior [32,33] and a lower position of the transport energy level effectively reduces the depths of trapping states. To link this concept to our system under investigation, we calculated the transport energy in mCBP:DMAC-TRZ systems with $\sigma_{\text{host}} = 0.127$ eV and $\varepsilon_t = 0.27$ eV employing the effective medium approximation (EMA) approach proposed by Fishchuk in Ref. [17] (calculation details are described in Note S4 of the Supplemental Material [46]). Figure 10(a) shows significant lowering of the calculated transport energy, by approximately 0.3 eV in the GG-detrapping percolation regime as c_t increases from 3% to 100%. This agrees well with the experimentally observed decrease of the mean activation energy E_a^{mean} at $c_t > 3\%$ as shown in Fig. 5(a). Hence, the observed TSL shift towards lower temperature can be considered as well understood.

(v) Further, we discuss the nonmonotonic behavior observed in TSL upon varying guest concentrations [see Figs. 4(a) and 5(a)] in the context of the *effective energetic disorder* concept, and demonstrate that this formalism can provide a qualitative explanation for these observations. As mentioned in the Introduction section, this concept was originally introduced by Borsenberger and Bässler [14] to account for shallow trap-controlled transport within the Gaussian disorder model (GDM), which itself was developed for trap-free transport. They demonstrated that the effect of shallow traps can be quantitatively accounted for by rescaling of the width of the available intrinsic DOS of the host, σ_{host} , to an effective (broader) width σ_{eff} being a function of the σ_{host} , trap depth ε_t , and the relative concentration $c_t = n_t/N$. In other words, a disordered system containing shallow traps and exhibiting a bimodal Gaussian DOS distribution [see Eq. (1)], can effectively be replaced by a system with unimodal Gaussian DOS with an effective width σ_{eff} obtained using Eq. (2), provided that

c_t remains below the percolation threshold ($c_t < 10^{-1}$). In this case, the standard GDM can be applied to describe the charge-mobility properties in the trap-containing material as if it were in a trap-free system, just with a different DOS width. Later, Fishchuk *et al.* [17] extended this concept to the entire relative trap-concentration range ($0 < c_t < 1$) using the effective medium approximation (EMA) approach, incorporating trap-to-trap hopping to describe the nondispersive charge transport in host-guest systems. Their analytical approach yielded the following expression for the effective energetic disorder:

$$\left(\frac{\sigma_{\text{eff}}}{\sigma_{\text{host}}}\right)^2 = 1 + 2\left(\frac{k_B T}{\sigma_{\text{host}}}\right)^2 \times \ln \left\{ \frac{1 + c_t \exp \left[\frac{\varepsilon_t}{k_B T} + \frac{1}{2} \left(\frac{\sigma_{\text{host}}}{k_B T} \right)^2 (\eta^2 - 1) \right]}{1 + c_t^2 \exp \left[\frac{\varepsilon_t}{k_B T} + 2 \frac{\rho}{\rho_0} \left(1 - \frac{1}{c_t^{1/3}} \right) \right]} \right\}, \quad (7)$$

where $\eta = \sigma_{\text{host}}/\sigma_{\text{trap}}$. This theory predicts that σ_{eff} increases with c_t up to a *maximum value* at the onset of percolation, and subsequently decreases due to GG hopping, which effectively narrows the energy range of sites involved in transport. Equation (7) has previously been employed to provide a quantitative description of ToF mobility data in selected model systems containing shallow traps [17].

Figure 10(b) shows the dependence of the effective disorder calculated using Eq. (7) (red solid curve) and parameters for mCBP:DMAC-TRZ determined by TSL, along with the values calculated using Eq. (2) (black solid line). Here we assume $\eta = 1$ for simplicity. As expected, Eq. (7) reduces to Eq. (2) at low trap concentrations below the percolation threshold. Notably, the nonmonotonic variation of $\sigma_{\text{eff}}(c_t)$ obtained from Eq. (7) mirrors the trends observed in charge-transport studies [20–23], where a minimum in mobility is typically observed at an intermediate concentration and according to the calculations it corresponds to maximal σ_{eff} . This minimum has been attributed to the crossover from trap-limited transport to trap-to-trap hopping. Thus, the above effective disorder model offers a consistent qualitative explanation for the observed nonmonotonic trend of trapping behavior in TSL. It should be emphasized, however, that in Fishchuk’s model [17], σ_{eff} above the percolation threshold is no longer a measure for the standard deviation of the actual available cumulative DOS distribution of guest and host states. Rather, it is a mathematical construct that reflects the change in activation energy caused by the shift in the transport energy level induced by doping at high guest concentrations.

Finally, we discuss the situation in which the guest-induced trap is even shallower than in the mCBP:DMAC-TRZ composition. In general, the effect of shallow traps is

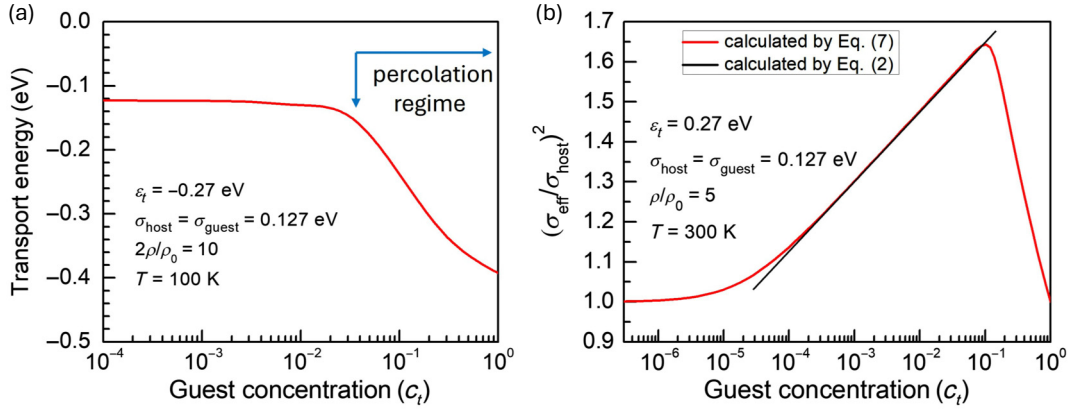


FIG. 10. (a) The transport energy vs relative guest concentration c_t calculated with respect to the host DOS center at low temperature (100 K) using the EMA approach (see Note S4 of the Supplemental Material [46]); (b) the effective disorder parameter, $\sigma_{\text{eff}}/\sigma_{\text{host}}$, calculated for mCBP:DMAC-TRZ host-guest system at 300 K using Eq. (7) for the full c_t range and Eq. (2) up to the percolation threshold. Material parameters for this system are shown in the insets.

expected to weaken significantly as the nominal trap depth decreases. We measured TSL in another shallow-trap host-guest system, mCBP:4CzIPN, over a wide range of guest concentrations (see Fig. S1 in the Supplemental Material [46]). The 4CzIPN guest represents a trap in mCBP with a nominal hole trap depth of $\varepsilon_t = 0.17$ eV, as evidenced by photoemission yield spectroscopy (PYS) measurements. PYS shows ionization energies of 5.91 eV for 4CzIPN and 6.08 eV for mCBP [40], implying that the trap depth in the mCBP:4CzIPN system is notably shallower than $\varepsilon_t = 0.27$ eV formed by DMAC-TRZ. As shown in Fig. S1 of the Supplemental Material [46], variation of 4CzIPN concentration in the mCBP host has a minimal effect on the TSL curves, except at a guest concentration of 10%, where a slight shift of the TSL peak towards a higher temperature is observed. The latter is attributed to a reduction in the frequency factor, likely due to the onset of guest-to-guest hopping transitions, which is commonly observed at such guest concentration levels in various host-guest systems [cf. Fig. 6(b)]. These TSL results are consistent with the space-charge limited current measurements, which showed no change in J - V characteristics for the mCBP:4CzIPN hole-only devices across guest concentrations of 3–15% [87]. We attribute the observed TSL invariance across 4CzIPN concentrations to the probable closeness of the nominal trap depth $\varepsilon_t = 0.17$ eV to the characteristic energy E_{onset} below the DOS center, which characterizes the onset of charge motion. This is consistent with the findings of Mandoc *et al.* [31] who proposed that shallow traps near E_{onset} no longer trap charges; rather, they participate in charge transport. This concept was recently used to explain the trap-free transport behavior observed in hyperfluorescent OLED devices, where energetic disorder in the host matrix was demonstrated to effectively disable charge trapping on the terminal emitter despite its smaller energy gap [30]. Further investigations using traps

of different depths in hosts exhibiting various energetic disorders could help establish TSL as a means of evaluating E_{onset} energy threshold in technologically important host-guest compositions.

B. Deep traps

DOS calculations for the UGH3:DMAC-TRZ host-guest composition in Fig. 7(c) indicate the formation of an electron trap with a trap energy of around 0.69–0.70 eV in such blends. This value is in good agreement with the experimental estimate of $\varepsilon_t = 0.64$ eV obtained from TSL measurements. The calculated energy of this deep electron trap remains virtually unchanged across different host-to-guest ratios, and the results presented in Fig. 7(c) corroborate the bimodal Gaussian DOS distribution for this host-guest system. As Fig. 4(b) shows, the TSL measurements reveal that deep charge trapping in amorphous host-guest semiconductors exhibits markedly different behavior compared to the shallow charge trapping discussed in the preceding section. The principal findings are as follows:

- (1) The presence of a deep trap in a host-guest system results in an explicit, well-resolved, trap-related TSL peak at 230 K (GH detrapping) appearing in addition to the shallow, disorder-related trapping caused by the tail states of the intrinsic host DOS, responsible for the low temperature peak at approximately 40 K (HH detrapping). This is seen in Fig. 4(b) at 0.3% guest concentration, where the ODOS distribution appears to be bimodal, as confirmed by KMC simulations [Fig. 9(b)]. At larger guest concentrations, the 40-K peak is no longer distinguishable most probably due to carrier retrapping by deep guest-related traps.
- (2) At sufficiently low concentrations of deep traps, carriers in such host-guest systems can energetically relax only within the host DOS distribution, as opposed to the

shallow trapping case. This is because charges generated far enough away in space from the traps can avoid this deep trapping due to their limited diffusion at 5 K, remaining confined within the host DOS. Therefore, some carriers may be stuck in the shallow tail states of the host DOS, while the rest will fill deep trap states, which leads to the bimodal ODOS observed experimentally. Because of the negligible overlap between the (main) host DOS and the deep-trap DOS distributions, deep traps have *no impact* on the intrinsic energetic disorder in such compositions, which is also supported by our KMC simulations [Figs. 8(b) and 9(b)]. This is consistent with previous ToF mobility measurements by Li *et al.* [88], who observed that deep traps act in a very different way from shallow ones. Whereas shallow traps at small concentrations greatly reduce the ToF mobility by substantially increasing the effective energetic disorder, deep traps mainly immobilize the carriers, thus reducing the amount of collected carriers in the ToF photocurrent transients without significantly affecting both the mobility and the energetic disorder. This is consistent with the fact that charge detrapping from deep traps is expected to contribute to a post-transit current rather than to a ToF signal [7]. However, charge mobility does depend on deep traps under a steady-state current when the guest concentration is large enough to enable percolation transport via guest states, as was recently demonstrated by Ko *et al.* [28].

(3) Depending on the guest concentration, charge release from deep traps occurs either through a thermally activated transition to the host DOS (GH detrapping), via the trap DOS (GG-detrapping pathway), or through combinations of both pathways. All three detrapping scenarios are clearly evident in our TSL measurements of UGH3:DMAC-TRZ host-guest systems [Fig. 4(b)], resembling the different hopping regimes [16,20] that are well established for charge transport in disordered host-guest systems (cf. Fig. 1).

(4) One of the key results of this study is the observation of the mixed-hopping regime in the UGH3:DMAC-TRZ system, which signifies the onset of a local guest-to-guest transfer at low guest concentration of about 1%, whereas established hopping transport theories conventionally predict global guest-to-guest transfer at the guest concentration level of about 10% at room temperature for a trap with $\varepsilon_t = 0.6$ eV in a host with $\sigma_{\text{DOS}} = 0.1$ eV [16]. This observation requires a detailed consideration of mechanisms responsible for such behavior.

C. On the mechanisms of guest-to-guest charge transfer

We first outline a plausible scenario for the TSL mechanism in the UGH3:DMAC-TRZ host-guest system. In general, TSL proceeds in two stages: (i) photogeneration and separation of charge carriers at a constant

low temperature, followed by (ii) thermal detrapping and recombination during the subsequent heating ramp. As discussed in Sec. III A, no TSL signal is observed from the neat UGH3 host, as it absorbs only in the deep UV ($\lambda \leq 270$ nm), beyond the irradiation range of our Hg lamp. In the host-guest system, however, the excitation occurs via the DMAC-TRZ guest, which absorbs photons in the 296–313 nm range (4–4.2 eV). This energy exceeds the LUMO offset between DMAC-TRZ and UGH3 [Fig. 2(b)], enabling autoionization of the guest and electron transfer to adjacent host molecules. The photogenerated electron then undergoes energetic relaxation within the host DOS, where it can be trapped by the tail states of this DOS, or be trapped by another DMAC-TRZ molecule. Concomitantly, the sibling hole remains deeply localized on the original DMAC-TRZ due to its HOMO lying 1.4 eV above that of UGH3 [Fig. 2(b)], enabling it to act as a recombination center during TSL. Because the electron is less deeply trapped than the hole (LUMO offset = 0.66 eV), the thermal release of trapped electrons governs the TSL kinetics in UGH3:DMAC-TRZ systems. The photogenerated carriers eventually form long-range geminate pairs, with electrons and holes localized on DMAC-TRZ molecules that are sufficiently far apart to prevent their isothermal recombination at low temperature.

The above considerations suggest that TSL involves charge transfer at both the photogeneration and detrapping stages. While the charge-transfer pathway in the photogeneration state is relatively straightforward, involving conventional *nearest-neighbor hopping* of photogenerated electrons via host states, the charge transfer during detrapping is less clear, especially in systems with deep traps and at low guest concentrations. In the UGH3:DMAC-TRZ system, an electron trapped on a DMAC-TRZ can escape via two competing pathways: (i) direct GH hopping to an adjacent UGH3 molecule, or (ii) longer-range GG hopping through the DMAC-TRZ manifold. The GH pathway requires significant thermal activation from a deep trap to the host states and is therefore only efficient at sufficiently high temperatures. This is consistent with the 230-K TSL band (with $E_a = 0.62$ eV) observed in UGH3:(0.3–2.5%)DMAC-TRZ blends [Fig. 4(b)]. In contrast, the GG transfer pathway does not require activation to host states and becomes efficient at significantly lower temperatures, provided that the concentration of traps is sufficient to enable local percolation. This mechanism is supported by the appearance of the 145-K TSL band with $E_a = 0.26$ eV for blends with $c_t \geq 1\%$ [Fig. 4(b)], demonstrating that guest-mediated hopping requires significantly less thermal energy. The GG hopping pathway is further corroborated by the observation of a similar TSL band in a percolation-only system based on polystyrene films doped with DMAC-TRZ [see Fig. 4(b)].

We now consider the possible mechanisms underlying the emergence of the *second charge-transfer pathway*

through the guest manifold, manifested as the 145-K band in the TSL spectra of the investigated host-guest systems. In the shallow-trap mCBP:DMAC-TRZ blends, clear evidence of GG detrapping is observed at a guest concentration of 10%, manifested by a strongly reduced TSL frequency factor, an increased average effective hopping distance [Figs. 6(b) and 6(c)], as well as by a low-temperature shift of the TSL peak [Fig. 4(a)] and reduced activation energy at the peak maximum [Fig. 6(a)]. This is a well-expected behavior and can be well explained by classical percolation theory [16,18,28]. In contrast, the onset of GG detrapping in the deep-trap UGH3:DMAC-TRZ blends is observed to occur at an unusually low guest concentration [Fig. 4(b)], a puzzling result that calls for closer examination.

Two prominent mechanisms are typically invoked to explain anomalous percolationlike behavior in charge-mobility measurements at low c_t and low-temperature conditions, where classical percolation is not anticipated: (i) clustering (aggregation) of guest molecules, which facilitates short-range hopping among adjacent guests [89,90], and (ii) superexchange-mediated transfer between nonadjacent guest sites via a virtual state on a bridging host molecule, a process expected to be particularly relevant when guest sites act as relatively deep traps [23,27,28,91,92]. Unlike direct incoherent hopping, which relies on real occupation and requires direct orbital overlap between guest molecules, superexchange is a coherent virtual process in which no real population of host orbitals takes place. Instead, the superexchange coupling occurs via a higher-energy host bridge state connecting two lower-energy guest states.

At first glance, the observed effect might appear attributable to guest aggregation, since cluster formation is already evident at 2–5% DMAC-TRZ concentration in simulated morphologies of both host systems (Table III), in line with the calculated radial distribution functions presented in Fig. S5 of the Supplemental Material [46]. However, this explanation conflicts with the unusually low TSL frequency factor, $S = 5 \times 10^7 \text{ s}^{-1}$, associated with the 145-K TSL band observed even at very low guest concentrations [Figs. 4(b) and 6(e)]. Such a small S value is incompatible with the notion of direct short-range hopping expected between adjacent molecules within small clusters, as such a mechanism implies a typical frequency factor on the order of 10^{11} – 10^{12} s^{-1} . Indeed, the 230-K TSL band, attributed to activated detrapping into host states (i.e., short-range GH hopping), exhibits a conventional frequency factor of $7 \times 10^{11} \text{ s}^{-1}$, consistent with direct hopping in undiluted transport systems. Moreover, simulated morphologies reveal no large-scale guest aggregates at $c_t = 2$ –5% (see Table III). Although fewer than half of the guest molecules remain isolated, the clusters that do form consist mostly of dimers or trimers, occasionally tetramers. Such small molecular ensembles cannot support the stable

accumulation of photogenerated long-range geminate pairs [32,93] (preventing their quick recombination), which typically require interchange separations of about 7 nm [94]. Finally, the sizable mean activation energy of 0.26 eV associated with the 145-K band [Fig. 4(b)] indicates the presence of substantial energetic barriers between hopping sites. Such barriers are unlikely between nearest-neighbor guests within small clusters, particularly given that spatial energy correlations [69] tend to reduce site-energy differences over nanometer-length scales. Taken together, these considerations strongly challenge the view that clustering alone accounts for the observed effect.

We propose that the pronounced reduction in the TSL frequency factor observed for the guest-to-guest transfer pathway at low DMAC-TRZ concentrations (2–5%) in a UGH3 host is consistent with the involvement of a superexchange-mediated process between nonadjacent guest molecules via a bridging host molecule [23]. Our calculations (Sec. IV) confirm the presence of such a superexchange effect in UGH3:DMAC-TRZ, although the estimated transfer rate (approximately $3 \times 10^5 \text{ s}^{-1}$) is several orders of magnitude lower than that of direct hopping (approximately 10^{11} s^{-1}) (see Sec. IV). This suggests that superexchange is unlikely to contribute significantly to *macroscopic charge transport* at high temperatures, where activated detrapping to host states enables efficient short-range hopping. Nevertheless, superexchange may play a key role in low-temperature TSL, where charge migration occurs only *over nanoscopic distances* [94]. The presence of the superexchange effect enhances the effective transfer integral $J_{ij,\text{eff}}^2$, which is a sum of the direct electronic coupling between nonadjacent guest molecules (i, j) and the superexchange coupling via bridge (host) molecule (a) [23]:

$$J_{ij,\text{eff}}^2 = J_{ij}^2 + \left[\frac{1}{2} \left[\frac{J_{ia} \times J_{aj}}{E_i - E_a} + \frac{J_{ia} \times J_{aj}}{E_j - E_a} \right] \right]^2. \quad (8)$$

Since the guest-host transfer integrals (J_{ia}) and guest-guest integrals (J_{ij}) are mostly determined by the respective intermolecular distances, and given that guest-host distances are generally shorter than guest-guest distances at low guest concentrations, it follows that $J_{ia}, J_{aj} \gg J_{ij}$ [23,28] in low c_t systems. Under these conditions, direct guest-guest coupling becomes negligible, and virtual superexchange through a bridging host provides the only viable pathway for long-range charge transfer. The latter, superexchange transfer, likely occurs between neighboring small guest clusters bridged by a single host molecule in a UGH3:DMAC-TRZ blend, as supported by our morphology simulations (Sec. IV), which frequently reveal guest clusters separated by just a single host molecule.

We therefore conclude that, at low DMAC-TRZ concentrations in UGH3, the GG charge-transfer pathway is governed by a combination of local guest clustering and

superexchange-mediated intercluster charge transfer. The photogenerated geminate electron-hole pairs responsible for the 145-K TSL peak are mostly trapped in different DMAC-TRZ clusters with different site energies, which explains the fairly large activation energy (0.26 eV) associated with this TSL band. The corresponding charge-recombination pathway involves at least one intercluster transfer step, with the slow rate-limiting process mediated by superexchange. This explains the significantly reduced TSL frequency factor of $S = 5 \times 10^7 \text{ s}^{-1}$ observed in the UGH3:DMAC-TRAZ system at a guest concentration of 5% [cf. Fig. 6(e)].

VII. CONCLUSIONS

This work addresses the question of whether a trap introduced by guest molecules in amorphous host-guest systems always acts as an active charge trap. By combining TSL measurements, QM and MD simulations, as well as KMC simulations, we elucidated how shallow and deep traps determine the actual trapping behavior. We demonstrated that DMAC-TRZ guests create an extrinsic shallow trap and a deep trap in amorphous mCBP and UGH3 hosts, respectively, resulting in an additional Gaussian distribution of sites that is offset in energy relative to the intrinsic DOS of the host by the trap depth energy ε_t . QM-MD simulations accurately reproduce both the trap depths ε_t and DOS widths, σ_{DOS} , in the considered compositions, and demonstrate negligible variations in nominal trap depths due to polarization effects with changing guest concentration.

TSL measurements reveal that shallow traps ($\varepsilon_t < 3\sigma_{\text{DOS}}$) do not behave as explicit, well-resolved traps. Instead, they broaden the DOS distribution by increasing the number of deeper states within its lower-energy part. Despite the available DOS is bimodal, the ODOS distribution remains single Gaussian, with a width that depends nonmonotonically on guest concentration and is always wider than σ_{ODOS} of the neat host. This finding was corroborated by KMC simulations of the low-temperature energetic relaxation of carriers, which showed that the ODOS distribution shifts gradually to deeper energies as the guest concentration increases, while the distribution width changes nonmonotonically with c_t . Concomitantly, the measured mean activation energy of carrier detrapping E_a^{mean} is found to be similarly concentration dependent in a nonmonotonic fashion, and does not correspond to the actual trap depth ε_t ; i.e., $E_a^{\text{mean}} \neq \varepsilon_t$. Rather, E_a^{mean} gradually increases with c_t in the regime of guest-to-host hopping, and then decreases when guest-to-guest hopping becomes dominant at higher trap densities. These results indicate that shallow trapping is actually a cumulative effect of intrinsic energetic disorder of the host and extrinsic shallow traps, in line with the previously suggested concept of “effective disorder.”

In contrast, deep traps ($\varepsilon_t > 3\sigma_{\text{DOS}}$) exhibit a qualitatively different behavior. At sufficiently low guest concentrations (approximately 0.3%), the ODOS consists of two distinct Gaussian contributions: one from the deep guest sites, producing a well-resolved TSL peak at 230 K with ($E_a^{\text{mean}} \approx \varepsilon_t$), and one from shallow UGH-3 host tail states where carriers can be trapped, observed as a peak at 40 K. Another experimental finding is that, at moderately low guest concentrations (1–5%), carriers trapped on guest sites can escape not only via host-mediated detrapping (requiring the overcoming $\varepsilon_t = 0.62 \text{ eV}$), but at the same time also through a GG pathway that gives rise to an alternative TSL band at moderate low temperature 145 K, with a substantially smaller mean activation energy (0.26 eV). The relative contributions of these detrapping pathways evolve strongly with concentration, reflecting the change from guest-to-host detrapping to guest-to-guest detrapping, with the latter setting in at the remarkably low guest concentration of 1%. We attribute this to local guest clustering and superexchange-mediated intercluster transfer as indicated by the significantly reduced frequency factor of the corresponding TSL band. This is supported by QM-MD calculations, which quantified the amount and size of guest clusters at various guest concentrations, and evaluated superexchange transfer integrals where guests are separated by a bridge (host) and the charge transfer between them involves virtual occupation of the host molecule orbital [23].

Overall, our findings challenge established beliefs by revealing distinct trapping phenomena and regimes when shallow or deep extrinsic traps are present in amorphous host-guest systems. Moreover, we highlight the dual role of guest molecules that can act either as charge traps or as transport enablers, depending on their concentration and energetic offset relative to the host.

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DATA AVAILABILITY

The data are available from the authors upon reasonable request.

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