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Trap-assisted and Langevin-type recombination in organic light-emitting diodes

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Trapping of charges is known to play an important role in the charge transport of organic semiconductors, but the role of traps in the recombination process has not been addressed. Here we show that the ideality factor of the current of organic light-emitting diodes (OLEDs) in the diffusion-dominated regime has a temperature-independent value of 2, which reveals that nonradiative trap-assisted recombination dominates the current. In contrast, the ideality factor of the light output approaches unity, demonstrating that luminance is governed by recombination of the bimolecular Langevin type. This apparent contradiction can be resolved by measuring the current and luminance ideality factor for a white-emitting polymer, where both free and trapped charge carriers recombine radiatively. With increasing bias voltage, Langevin recombination becomes dominant over trap-assisted recombination due to its stronger dependence on carrier density, leading to an enhancement in OLED efficiency.

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I. INTRODUCTION

In the past decades, organic semiconductors received wide interest due to their potential for novel applications as organic light-emitting diodes (OLEDs) and organic solar cells.[1–3] Understanding the physical processes governing the operation of these devices is essential for improving their performance. Previous research has revealed the presence of trap states in a variety of organic semiconductors, strongly hindering electron transport.[4,5] However, the possible role of these traps in the recombination mechanism in OLEDs, next to the well-known[6,7] bimolecular recombination of the Langevin type,[8] has not been addressed. Since trap-assisted recombination is usually nonradiative, proving its existence is not straightforward, nor is estimation of its relevance for the efficiency of OLEDs.

The simplest form of an OLED comprises a thin layer of organic semiconductor sandwiched between two metallic electrodes, which form an Ohmic hole and electron contact, respectively. Due to the difference in work function of the electrodes, a built-in voltage (V_{bi}) across the OLED exists. The current density-voltage (J-V) characteristics of an OLED (Fig. 1) therefore show three discernable regimes: At low voltages, the current is dominated by parasitical currents between the electrodes, referred to as leakage current, which depends linearly on voltage. The second regime, with V lower than V_{bi}, is diffusion dominated and shows an exponential dependence on voltage according to the Shockley diode equation, given by[9]

$$J = J_0 \left[\exp\left(\frac{qV}{\eta k T} \right) - 1 \right], \tag{1}$$

where J_0 denotes the saturation current density, η the ideality factor, k the Boltzmann constant, and T the temperature. Hence, the ideality factor is a measure of the slope of the J-V characteristics on a semilogarithmic plot. In the absence of recombination, the ideal diode equation should apply, where η equals unity. At the built-in voltage, a transition from the exponential regime to the drift-dominated, space-charge-limited regime occurs,[4] which is characterized by a quadratic dependence of the current on the voltage in the case of trap-free transport, according to the Mott-Gurney square law.[10]

As first described by Sah *et al.*, the ideality factor of a classical *p*-*n* junction is affected by trap-assisted recombination in the space-charge region.[11] Here, electrons immobilized in trapping sites recombine with free holes as described by the Shockley-Read-Hall (SRH) formalism.[12,13] When SRH recombination is the dominant loss mechanism, the ideality factor is expected to be exactly 2.[11] As a result, the ideality factor can be used as a fingerprint for trap-assisted recombination. In this paper, we demonstrate that the diode characteristics and ideality factor for a variety of conjugated polymers are dominated by trap-assisted recombination, whereas the luminance is governed by Langevin recombination. In addition, we show that the guest emission in a host-guest system can be accurately described by an SRH process.

II. IDEALITY FACTOR OF AN OLED

In the present study, the OLEDs were prepared on top of a glass substrate, patterned with a transparent indium-tin oxide electrode. For organic semiconductors, a variety of conjugated polymers have been used. For anode and cathode, spin-casted poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS; Clevios CH8000) and thermally evaporated Ba(5 nm)/Al(100 nm) were used, respectively. The electrical measurements were conducted under controlled N_2 atmosphere with a Keithley 2400 source meter. A voltage sweep of a typical OLED is depicted in Fig. 1, where the poly(*p*-phenylene vinylene) (PPV) derivative Super Yellow (SY) was used as emitter. As the present study focuses on the ideality factor, the slope of the diffusion regime below V_{bi} is of predominant interest. Conventionally, the ideality factor is determined by fitting the experimental data with Eq. (1)

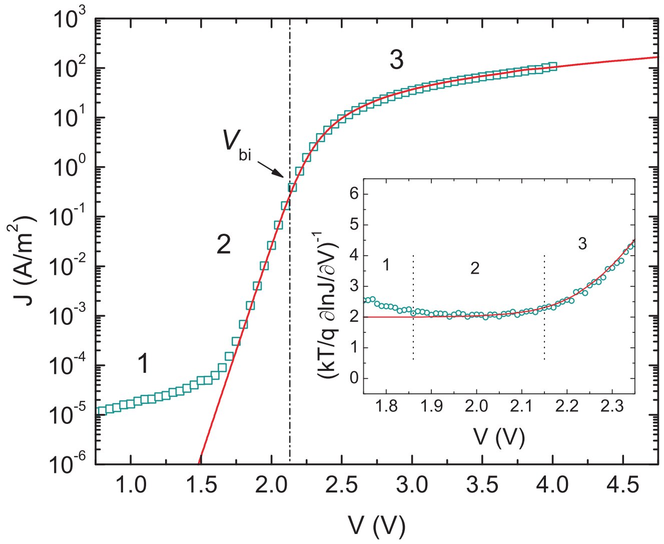

FIG. 1. (Color online) Experimental *J*-*V* characteristics (symbols) of a 43 nm SY OLED and the corresponding calculations (solid line) from a drift-diffusion model, using $C_n = C_p = 2 \times 10^{-18}$ m^3/s and $N_t = 5 \times 10^{-22}$ m^{-3}, with a trap depth of 0.5 eV. The inset shows the differential plot of the data and simulation according to Eq. (2). The leakage (1), diffusion (2), and drift (3) regimes are indicated.

However, in order to prevent erroneous fitting, we determine the ideality factor by numerical differentiation according to

$$\eta = \left(\frac{kT}{q} \frac{\partial \ln J}{\partial V} \right)^{-1}. \tag{2}$$

By plotting this quantity against voltage, as shown in the inset of Fig. 1, the three regimes in the *J*-*V* characteristics can be distinguished again, where the ideality factor is obtained from the plateau value. The plateau value can be regarded as the steepest exponential incline of the *J*-*V* characteristics. For a correct determination of the ideality factor, it is of paramount importance that the exponential part is clearly discernable, requiring low leakage currents and high current densities in the space-charge limit. The latter can be achieved for materials with a high charge carrier mobility or by decreasing the layer thickness.

As can be seen from Fig. 1, an ideality factor of 2 was determined for the SY device, in exact correspondence to the value that is predicted from the Sah-Noyce-Shockley theory[11] in the case of trap-assisted recombination. In addition, both the drift and diffusion regimes can be accurately described by using a numerical drift-diffusion model[14] that, along with Langevin recombination, includes an additional SRH recombination mechanism, for which the recombination rate is given by

$$R_{\mathrm{SRH}} = \frac{C_n C_p N_t (np - n_1 p_1)}{C_n (n + n_1) + C_p (p + p_1)}, \tag{3}$$

with C_n and C_p the capture coefficients for electrons and holes, respectively, N_t the density of electron traps, n and p the electron and hole densities, and $n_1 p_1 = n_i^2$ their product under equilibrium conditions in the case that the Fermi level coincides with the position of the recombination centers, where n_i denotes the intrinsic carrier concentration in the sample. The expression for the Langevin recombination rate reads

$$R_{\mathrm{L}} = \frac{q}{\varepsilon} (\mu_n + \mu_p) (np - n_i^2), \tag{4}$$

with ε the dielectric constant and μ_n and μ_p the electron and hole mobilities, respectively. The sum of both recombination rates enters the continuity equations according to

$$\frac{1}{q} \frac{\partial}{\partial x} J_n = -\frac{1}{q} \frac{\partial}{\partial x} J_p = R_{\mathrm{L}} + R_{\mathrm{SRH}}, \tag{5}$$

where J_n and J_p denote the electron and hole current densities, respectively.

As a first step to verify whether the observed ideality factor of 2 is general and due to recombination, a variety of conjugated polymers were tested in double- and single-carrier devices. In the latter, a cathode blocking the electron injection was used, yielding so-called hole-only diodes. Due to the absence of an electron current, electron-hole recombination is not present. If recombination were the cause of the ideality factor amounting to 2, a single carrier device would exhibit a substantially smaller ideality factor, approaching unity in the ideal case. In Fig. 2, the differentiated *J*-*V* characteristics for double- and single-carrier diodes of another PPV derivative poly[2,5-bis(2′-ethylhexyloxy)-*co*-2,5-bis(butoxy)-1,4-phenylenevinylene] (BEH/BB-PPV) are plotted. The ideality factor of the double-carrier devices yields 2, in accordance with the value obtained for the SY device. For single-carrier diodes, the obtained ideality factors are indeed substantially lower than 2; however, they do not fully approach unity. In previous reports,[15–17] this deviation from unity has mostly been ascribed to a violation of the classical Einstein relation,[18] arising from a charge-density dependence of the ratio between diffusivity and mobility, which is related to the shape of the density-of-states (DOS) distribution.[19,20] Here, the observed difference between double- and single-carrier diodes clearly

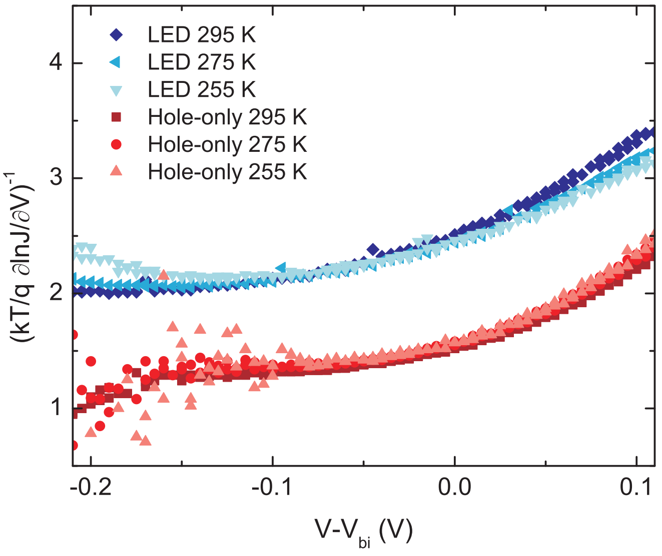

FIG. 2. (Color online) Temperature-dependent η-*V* characteristics of single- and double-carrier diodes of a PPV derivative. The difference between single- and double-carrier diodes shows that recombination plays an essential role.

indicates the essential influence of charge-carrier recombination on the ideality factor. Another important feature appears when looking at the temperature dependence. In contrast to earlier reports,[15–17] the ideality factor was observed to be temperature independent for both single- and double-carrier diodes. From our study on a large number of organic diodes, we found that a temperature-dependent ideality factor is an experimental artifact caused by a too large leakage current (regime 1). In that case, the leakage current masks the diffusion regime as the drift current reduces upon cooling, due to the temperature dependence of the mobility,[21] and the plateau cannot be discerned anymore. The apparent ideality factor will then be too high and temperature dependent. For materials with a high charge-carrier mobility, and hence exhibiting a weakly temperature-activated transport,[21] we observed a temperature-independent ideality factor at temperatures down to 215 K, with a variance less than 0.05. The temperature independence of the ideality factor corresponds with the conventional Shockley diode equation and contradicts the proposed invalidity of the classical Einstein relation.[15,20] This observation further supports the dominance of trap-assisted recombination on the ideality factor in OLEDs. In our study, temperature independence as well as similar magnitudes for η was also obtained for other classes of conjugated polymers, including polyfluorenes, polythiophenes, polyspirobifluorenes, and polytriarylamines, as well as fullerene derivatives.

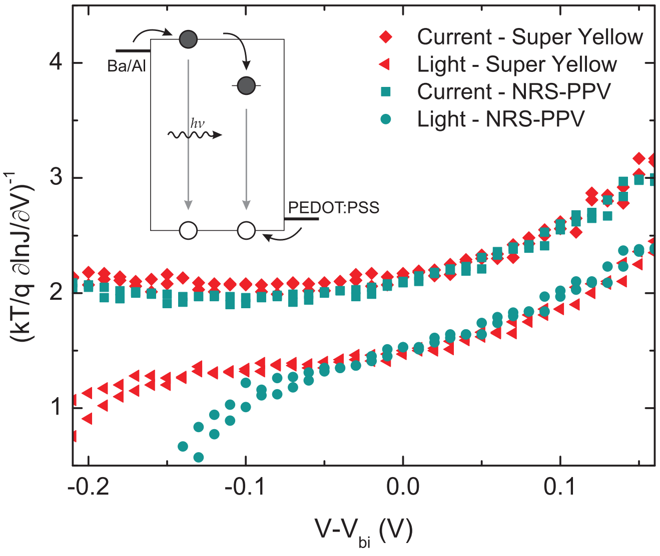

FIG. 3. (Color online) η-V characteristics of SY and poly[{2-(4-(3′,7′-dimethyloctyloxyphenyl))}-*co*-{2-methoxy-5-(3′,7′-dimethyloctyloxy)}-1,4-phenylenevinylene] (NRS-PPV) OLEDs derived from the current and the luminance. The luminance ideality factor approaching unity indicates that light emission is governed by a Langevin process. The inset shows a schematic representation of the recombination mechanisms.

III. LUMINANCE IDEALITY FACTOR

As stated above, an ideality factor of 2 in the current of an OLED can be explained by the fact that the dominant recombination mechanism is trap assisted. However, previous studies[6,7] concluded that charge recombination in organic semiconductors is a bimolecular process of the Langevin type,[8] controlled by the diffusion of oppositely charged free carriers toward each other in their mutual Coulomb field. This apparent discrepancy can be resolved by also studying the ideality factor of the luminance (L) vs voltage (V) characteristics, analogous to the case for the current density. An important requirement for reliable extraction of such a luminance ideality factor is a sufficient luminous efficiency, as the length of the exponential regime is limited by the sensitivity of the photodiode used to record light output. When plotting the ideality factors of the current and the luminance (Fig. 3), it appears that a distinct dissimilarity in the slope of the exponential part of the characteristics is present. In contrast to case for the current density ($\eta = 2$), the ideality factor determined from the L-V characteristics approaches unity, consistent with Langevin recombination. This is a strong indication that in these diodes nonradiative trap-assisted recombination is the most dominant type and controls the current, whereas light emission is a result of a competing bimolecular recombination process.

In order to experimentally verify this hypothesis, we studied the L-V characteristics of a diode in which emissive recombination from *trapped* charge carriers is present, as is the case in host-guest systems, frequently applied in highly efficient OLEDs. An ideal compound for this test is a state-of-the-art white-emitting polymer (Merck),[22] where green- and red-emitting chromophores are incorporated in the blue-emitting backbone. In this polymer the highest occupied molecular orbital (HOMO) levels of the chromophores align with the HOMO of the blue host, whereas the lowest unoccupied molecular orbital (LUMO) levels of the chromophores are substantially below the LUMO of the blue host due to the smaller band gap.[23] The chromophores are therefore expected to trap electrons. Hence, the blue part of the emission spectrum is assumed to arise from Langevin recombination, whereas the red emission can be ascribed to recombination of holes with electrons that are trapped on the chromophore. By measuring the L-V characteristics through selective optical filters, the different recombination mechanisms may be disentangled. Therefore, a blue dichroic filter (serving as a bandpass filter) and a 550 nm longpass filter were used, splitting the electroluminescence (EL) spectrum into a blue and a red component. As can be observed from Fig. 4(a), the ideality factor for the current density again amounts to 2, consistent with materials that lack chromophores. Remarkably, Fig. 4(b) shows a clear difference in the slope of the L-V characteristics when either the red or the blue part of the spectrum is measured. The ideality factor for the red light also amounts to 2, confirming that it originates from SRH recombination of an electron that is trapped on the chromophore with a free hole. For the blue emission, a substantially lower ideality factor approaching unity, was observed, in line with the bimolecular Langevin recombination. The unfiltered L-V characteristics are governed by the trap-assisted recombination from the red chromophores, since this mechanism prevails in the low-voltage regime. The observation of a luminance ideality factor shifting to 2 when emissive traps are introduced strongly substantiates that the ideality factor of 2 in OLEDs originates from trap-assisted recombination.

It is evident that the efficiency of a conventional OLED is directly related to the competition between nonradiative

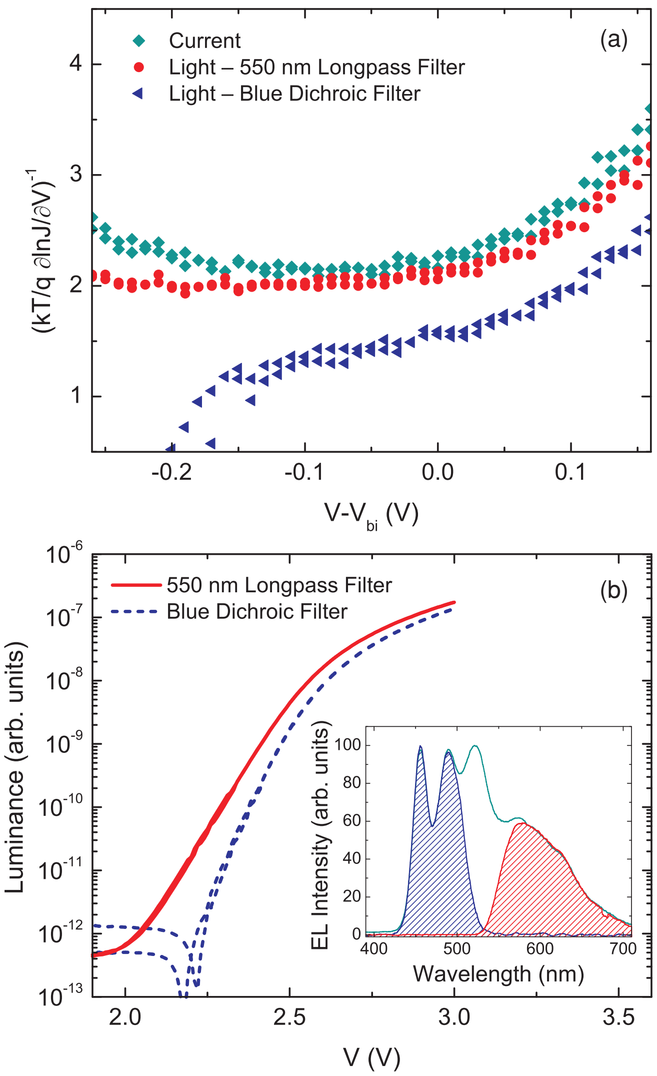

FIG. 4. (Color online) (a) η-V and (b) L-V characteristics of a 30 nm white OLED using selective optical filters, indicating the difference in ideality factor for the red and blue light components. The inset shows the corresponding EL spectrum, where the filled areas represent the spectra of the filtered light.

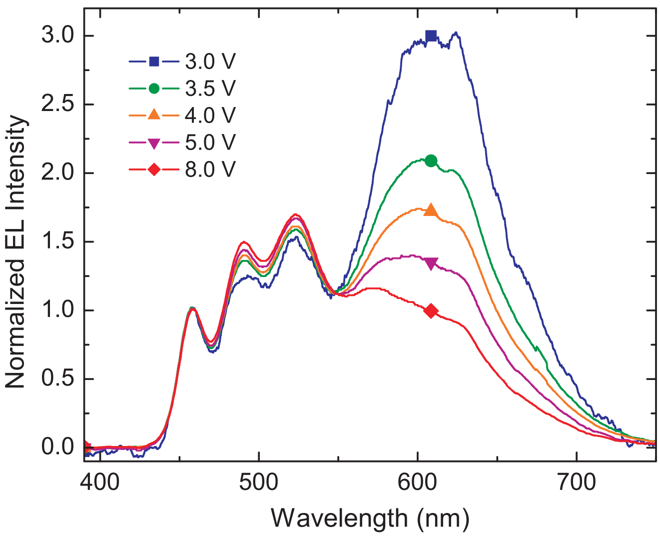

FIG. 5. (Color online) Voltage-dependent EL spectrum of an 80 nm white OLED, normalized at the first blue peak. The red component of the spectrum decreases relative to the blue peak with increasing bias, due to a difference in carrier density dependence of the competing recombination mechanisms.

trap-assisted recombination and the radiative bimolecular recombination process. The voltage dependence of this competition can be visualized in the (normalized) EL spectrum of the white OLED (Fig. 5). We observe that the blue Langevin recombination exhibits a stronger dependence on voltage than the red SRH process, as shown by the relative decrease of red emission compared to the blue peak with increasing voltage. The stronger voltage dependence of the bimolecular Langevin recombination arises from the fact that it is quadratically dependent on the carrier density, whereas SRH recombination only exhibits a linear dependence. In order to quantitatively estimate the relevance of nonradiative trap-assisted recombination, the SRH and Langevin recombination rates are simulated for a typical 100 nm thick OLED, as shown in Fig. 6, using the same capture coefficient and trapping parameters as determined for the SY device (Fig. 1). The difference in the slope of the exponential part of the recombination rates is immediately visible, yielding ideality factors of 2 and 1 for SRH and Langevin recombination, respectively, as expected. At low bias voltage, SRH recombination clearly dominates, explaining the observation of a simple ideality factor of 2 for the device current. As voltage increases, the Langevin recombination gradually approaches the SRH characteristics and becomes dominant above a certain voltage. This competition therefore leads to an intrinsic voltage dependence of the OLED efficiency. Until now, the occurrence of SRH recombination has been disregarded in the device modeling of OLEDs. Our study shows that, especially at low bias voltage, SRH is an important loss process. In general, the relevance of SRH recombination in OLEDs will depend on the amount of traps, the trap depth, as well as the SRH capture

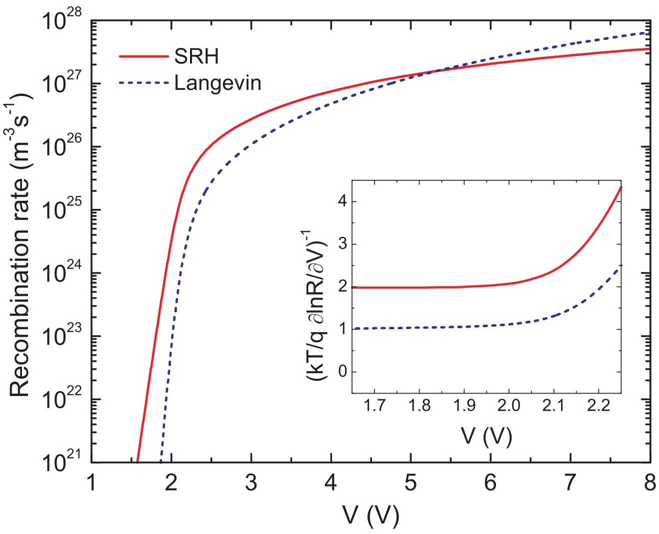

FIG. 6. (Color online) Simulated R-V characteristics of a typical 100 nm OLED for SRH (solid line) and Langevin (dashed line) recombination. The inset shows the differential plot of the simulations according to Eq. (2).

coefficients, and it is expected to vary for the various organic materials, which is a subject of further study.

IV. CONCLUSIONS

In conclusion, we demonstrate that at low bias the dominant recombination mechanism in OLEDs is trap assisted. For a variety of OLEDs, a temperature-independent ideality factor of 2 in the current was determined, which evidences the presence of SRH recombination from trapping sites. In line with this finding, the ideality factor shifts toward unity in the absence of recombination. Furthermore, an ideality factor approaching unity was also determined for the luminance, showing that the emissive recombination is determined by a bimolecular Langevin process, and that recombination from trapping sites is nonradiative. This was further confirmed by selective filtering of the blue and red parts of the EL spectrum of a white OLED, where red chromophores incorporated in the blue backbone function as emissive traps, allowing disentanglement of both competing recombination mechanisms by measurement of the luminance ideality factor. Drift-diffusion simulations show that with increasing bias Langevin recombination becomes more dominant, which is also reflected in the voltage-dependent emission spectrum of a white OLED.

Our study shows that the ideality factor can be regarded as an effective tool for studying the recombination mechanisms in OLEDs for both single-color and white-emitting devices. Accurate determination and understanding of the recombination processes is essential for identification of nonradiative loss mechanisms, thereby providing insights on improving the efficiency of OLEDs.

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