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Non-radiative recombination losses in polymer light-emitting diodes

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ABSTRACT

We present a quantitative analysis of the loss of electroluminescence in light-emitting diodes (LEDs) based on poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) due to the combination of non-radiative trap-assisted recombination and exciton quenching at the metallic cathode. It is demonstrated that for an MEH-PPV LED the biggest efficiency loss, up to 45%, arises from extrinsic non-radiative recombination via electron traps. The loss caused by exciton quenching at the cathode proves only to be significant for devices thinner than 100 nm. Removal of electron traps by purification is expected to enhance the efficiency of polymer LEDs by more than a factor of two.

1. Introduction

Polymer light-emitting diodes (PLEDs) are considered promising candidates for cheap production of flexible and large area lighting applications. The performance of PLED devices unfortunately still lags behind the performance its inorganic counterpart. In order to increase the efficiency of PLEDs, a fundamental understanding of the principle loss mechanisms is therefore essential. In general, charge transport and charge recombination are considered key ingredients in the operation of a PLED. Investigation of the charge transport in PLEDs of the model compound poly(*p*-phenylene vinylene) (PPV), and its derivatives, has led to the knowledge that the charge transport in the polymer is intrinsically dominated by holes [1]. The reduced electron transport is attributed to the presence of electrons traps [2,3], causing the electrons to drift less far into the PLED as compared to the holes. A major disadvantage of this unbalanced charge transport is that the recombination zone culminates close to the metallic cathode. The excitons formed relatively close to the cathode may transfer their energy to the metallic contact and decay non-radiatively [4,5], leading to a loss in luminous efficacy (Fig. 1A). Together with the fraction of the singlet exciton formation, photoluminescence efficiency and optical outcoupling efficiency, exciton quenching at the cathode is regarded as one of the prime limitations to the PLED performance. The second key ingredient in the PLED operation, emissive charge recombination, is generally considered to be described as the Coulombic attraction between two free charge carriers of the opposite sign as depicted in Fig. 1B [6]. However, recent work demonstrates that the trapped, immobile electrons in PPVs also actively participate in the recombination process through trap-assisted recombination with free holes [7,8]. But, the recombination is in this case shown to be non-radiative, which designates the presence of electron traps in the active layer as the origin of an additional loss mechanism (Fig. 1C). In this work, non-radiative trap-assisted recombination and exciton quenching at the cathode are quantitatively addressed. Through modeling of poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) PLED devices, we shed light on the influence- and magnitude of both these loss processes on

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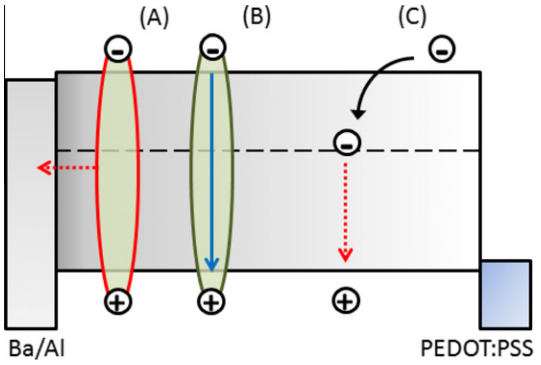

Fig. 1. Schematic illustration of (A) the quenching of the exciton by the metallic cathode, (B) bimolecular, Langevin-type, recombination, and (C) trap-assisted, SRH, recombination.

the device performance. It is worth mentioning that most conjugated polymers used in light-emitting devices today, display some form of trapping behavior, which renders the investigation described in this paper as illustrative for a vast number of materials.

2. Materials and methods

The devices were fabricated in a clean room environment and kept in a nitrogen atmosphere from the moment the polymer layer was spin-coated. Pre-patterned glass/ITO or plane glass substrates were cleaned by washing in detergent solution followed by baths in acetone and isopropyl alcohol. Subsequently, UV-ozone plasma treatment was performed. For the PLED configuration a layer of PEDOT:PSS (Bayer AG) was spin-coated on top of the ITO structure. Next, the light emitting polymer layer was spin-coated from a toluene solution under nitrogen atmosphere. Finally, the layer was topped with a thermally evaporated Ba/Al cathode under vacuum. Current density (J–V) measurements were performed using a source measure unit Keithley 2400, and the light output was recorded using a photodiode connected to a Keithley 6514 electrometer.

3. Theory

3.1. Cathode quenching

Quenching at the metallic cathode is a balance of two processes. First, the energy from the excited polymer is transferred to the metal non-radiatively via long-range dipole–dipole interaction, as depicted in Fig. 1A. The occurrence of non-radiative energy transfer to the metal will lead to a gradient in the exciton population close to the metallic contact. As a result, excitons will diffuse towards the interface, which increases the overall exciton quenching process even more. In order to quantify the exciton quenching mechanism, a one-dimensional continuity equation is used for the exciton density distribution $E(x,t)$ [9,10]

$$\frac{\partial E(x,t)}{\partial t} = D\frac{\partial^2 E(x,t)}{\partial x^2} - \frac{E(x,t)}{\tau_\infty}\left(1+\frac{x_0^3}{x^3}\right) + R_L \qquad (1)$$

The first term on the right-hand side represents the one-dimensional exciton diffusion. The second term accounts for the exciton decay in the polymer (exciton lifetime, τ_∞), further enhanced by non-radiative exciton energy transfer to the metal, described by the inverse cubic distance dependence [9,11]. The last term describes the exciton generation process which is the generation of excitons governed by the emissive Langevin recombination rate. At both polymer film interfaces the boundary condition $E(x=0, x=L)=0$ is applied, representing the negligible surface quenching on both boundaries. For MEH-PPV, the diffusion coefficient, D, and exciton decay time, τ_∞, have been measured in earlier work to be 1.1e−7 m^2/s and 455 ps which leaves the characteristic range of the energy transfer, x_0, the characteristic distance from the cathode at which most of the excitons formed at a distance larger than this range will decay radiatively and excitons formed closer than this range will transfer their energy to the metal, as a fit parameter for a steady-state exciton density profile [12].

3.2. Bimolecular and trap-assisted recombination

The bimolecular, Langevin-type, recombination rate is described by the recombination of free charge carriers according to $R_L = \frac{q}{\varepsilon}(\mu_n+\mu_p)(np-n_i^2)$ where q is the elementary charge, ε the dielectric constant of the light emitting polymer, n_i is the intrinsic carrier concentration in the sample, n and p are the electron and hole densities, and μ_n and μ_p denote the mobility of the electrons and holes, respectively (Fig. 1B) [6,13]. Recent analysis of the recombination processes in PLEDs has led to the understanding that the strength of Langevin recombination alone is not sufficient to account for the recombination and transport behavior in a PLED [14,15]. However, by inclusion of trap-assisted recombination using the Shockley–Read–Hall (SRH) formalism the experimental PLED data are excellently described (schematically depicted in Fig. 1C) [7]. It was demonstrated that trap-assisted recombination is the dominant recombination mechanism in PLEDs at low driving voltages. In line with this result, the ideality factor of the Shockley equation in the diffusion regime is measured to be exactly 2 [8], as derived by Sah et al. [16]. The difference in density dependence of Langevin and trap-assisted recombination, quadratic and linear, respectively, also explains the different voltage dependence of red and blue emission in the electroluminescence of white emissive PLEDs where both free carrier and trap-assisted recombination are emissive [8,17,18]. For the particular case of PPVs, the ideality factor in the diffusion current is measured to be 2, whereas the luminance ideality factor is found to be close to 1 [8], demonstrating that here only the Langevin-type emission is radiative. Moreover, it has been shown that for PPVs the electron traps are centered at about 0.75 eV below the lowest unoccupied molecular orbital (LUMO) [19,20], implying that eventual emission from trap-assisted recombination should be in the near infrared. This however, is not observed, confirming again that trap-assisted recombination in a PPV PLED is non-radiative. It needs to be stated that the occurrence of luminescence ideality factor of 1 and current ideality factor of 2 has been found in a variety of polymers [8,17,21]. Hence, in

most polymers the trap-assisted recombination is non-radiative, stressing once more the generality of the findings presented in this work.

The description of trap-assisted recombination rate is given by the Shockley–Read–Hall (SRH) [22,23] equation

$$R_{SRH} = C_n C_p N_t (np - n_i^2)/[C_n(n + n_1) + C_p(p + p_1)] \quad (2)$$

where C_n and C_p are the capture coefficients for electrons and holes, respectively, N_t is the density of electron traps, n and p are the electron density in the conduction band and the hole density in the valence band, respectively, and $p_1 n_1 = N_{cv}^2 \exp\left[-\frac{E_{gap}}{kT}\right] = n_i^2$, 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 capture coefficients have been shown to be governed by the diffusion of free holes towards the trapped electrons [18]. The capture coefficient for hole capture was shown to be equal to $C_p = \frac{q}{\varepsilon}\mu_p$ in the SRH expression, which leads to the simplification of the trap-assisted recombination rate in PLEDs as $R_{SRH} = \frac{q}{\varepsilon}\mu_p N_t p$, resembling the Langevin rate expression where the mobility of the trapped electron has been put to zero [18]. As a result, when assuming $C_p = C_n$ [8,24–26], the addition of trap-assisted recombination conveniently does not introduce new parameters into the model.

4. Results and discussion

Throughout this work the analysis of both loss mechanism is performed using a numerical model [27] in which drift and diffusion of charge carriers, the effect of space-charge on the electric field, density dependent mobility [28], Gaussian trap distribution for the electrons [19], quenching at the cathode [29,30], free carrier and trap-assisted recombination is included. Since MEH-PPV has been a workhorse material in the last two decades, the hole and electron transport characteristics and parameters are well known [2,31]. We have investigated MEH-PPV PLEDs with an active layer thickness of 75 nm and 165 nm, using PEDOT:PSS and Ba/Al as the anode and cathode, respectively. Temperature, field and density dependent hole mobility for both thicknesses was deduced by means of hole-only devices, resulting in the a hole mobility of 5×10^{-11} m^2/Vs for MEH-PPV at zero field and room temperature. For the full characterization of the field and density dependence of the mobility, the description and parameters derived by Tanase et al. were used [28]. The electron transport is taken as limited by the presence of electron traps, with for the free electrons $\mu_n = \mu_p$, as was shown in both field-effect transistors [32] and diodes where the effect of traps was eliminated by n-type doping [33]. These electron traps are described as a Gaussian-shaped distribution of trap states centered at 0.7 eV below the LUMO with a width σ_t of 0.10 eV and the number of traps equal to $N_t = 1.1 \times 10^{23}$ m^{-3}, as derived by Nicolai et al. [19] Fig. 2 depicts the experimental J–V data and the according perfect fits at 295 K.

In order to confirm that the calculations for the J–V fits are accurate, the current efficiency (CE; light output/current) is plotted on a sensitive linear scale in Fig. 3 for both thicknesses. In the CE calculations both free carrier and trap-assisted recombination are incorporated, though only free-carrier recombination is taken emissive and sensitive to quenching from the metallic cathode. Good CE fits are obtained for both thicknesses on a sensitive linear scale using a typical energy transfer range of 4 nm. Even on a sensitive linear scale the model evidently explains the voltage dependence of the efficiency of both the thick and thin devices well.

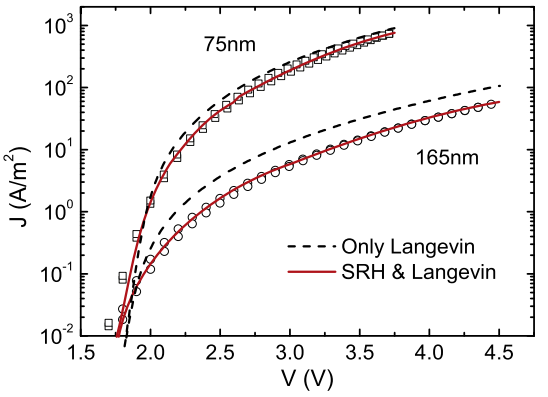

Fig. 2. Current–voltage characteristics of a 75 nm and 165 nm MEH-PPV PLED and the corresponding simulated fits. The dashed lines represent the simulations of the current when only Langevin recombination is taken into account and the contribution of SRH recombination is neglected.

Generally in a PLED, electrons flow in at the cathode and holes flow in from the anode. The number of electrons eventually flowing out at the anode and holes at the cathode define the portion of surface recombination at the contacts. In the model, we take the recombination at the surface of the contacts such that it allows for the hole current at the cathode, $J_p(0) \neq 0$, and on the other side $J_n(L) \neq 0$. Nevertheless, it follows from the calculations that even at the maximum applied voltage across the 75 nm devices, $J_p(0)$ represents only 1.7% of the total current at the cathode and $J_n(L)$ is negligible at the anode. Therefore, to a good approximation,

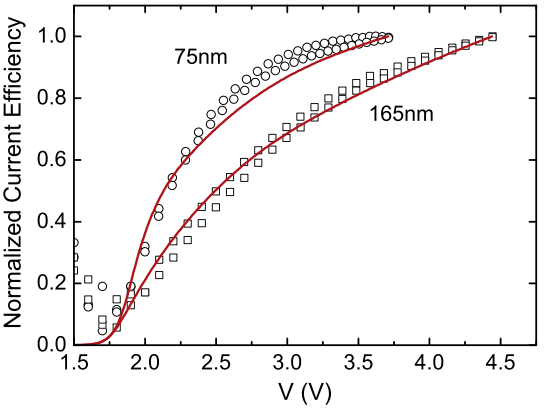

Fig. 3. Normalized current efficiency data and the corresponding fits using the drift–diffusion model, for a 75 nm and 165 nm PLED. Only Langevin recombination is considered to be emissive.

electrons do not flow out at the anode, nor do holes flow out at the cathode. Thus recombination is efficient and governs the device current according to $J = J_n(L) - J_n(0) = q \int R_L\, dx$, which leads to $J = qRL$, where R is the average recombination rate. The conversion efficiency, CE, is defined as the ratio of emitted photons per injected electrons. When assuming that Langevin recombination is the only radiative process the CE is thus represented by

$$\eta = \frac{\int R_L\, dx}{J/q} = \frac{\int R_L\, dx}{\int (R_L + R_{SRH})\, dx'} \tag{3}$$

for the case that the current is governed by both the Langevin and SRH recombination rates. It can be understood from Eq. (3) that the measured CE depicted in Fig. 3 can therefore be regarded as a fingerprint for non-radiative SRH recombination. If no traps were present in the polymer layer, SRH recombination would be absent; the CE would be independent of voltage, which is clearly not observed. It should be noted that the influence of exciton quenching at the cathode is not taken into account here yet. The effect of this loss mechanism diminishes for thicker layers, thus without SRH recombination the shape of the CE for thicker devices cannot be described. Interestingly, as a result of the trap-limited electron current, increasing the voltage does not simply shift the recombination zone towards the middle of the device layer which would eliminate the influence of quenching. Although the zone does move to the middle of the layer on average, the recombination zone also broadens considerably. Revealing that cathode quenching will never entirely disappear, not even at high electric fields, as can be observed in Fig. 4 [34].

An important question is how both individual loss mechanisms compare in magnitude. Fig. 4 represents the calculations of the relative contributions of the loss mechanisms to the CE for the operation of a 75 nm device. Despite the small difference in the J–V data and the fit comprising only Langevin recombination (dashed line) in Fig. 2, it is evident from Fig. 4 that in the operation of the device at low voltages the loss process is almost entirely dominated by trap-assisted recombination. For higher voltages both loss processes are of equal magnitude and are each responsible for an efficiency loss of about 20% with regard to the total recombination. Furthermore, with increasing voltage the emissive Langevin recombination becomes more and more important. As the traps are intrinsically present, their number, N_t, is fixed. Therefore, with increased filling of the traps at higher voltages the probability for free carrier recombination increases and becomes dominant when all the traps are filled. In thin PLEDs this process is amplified by the contribution of charge carriers that diffuse from the contacts into the active layer, thereby also enhancing the mobility and partially filling the traps [35]. Consequently, trap-assisted recombination will be less visible in the J–V characteristics of a thin PLED. This phenomenon is perhaps best illustrated in Fig. 5 showing the individual recombination rates for both the 75 nm and 165 nm device. The point at which the Langevin rate crosses the SRH rate arises at lower voltages for the thin device as compared to the thick PLED. Hence, the current of the 75 nm device is largely governed by the Langevin recombination rate, validating the rather small deviation between the fit and the dashed line in Fig. 2. It should be noted that this behavior can also be observed in systems where both Langevin and SRH recombination are emissive [8,18]. Also clearly discernible in Fig. 5 is the difference of the slopes in the diffusion regime, the ideality factor for SRH converges to 2 whereas the Langevin dominated regime converges to 1. The little difference between the data and the fit comprising only Langevin recombination in Fig. 2 (dashed line) can thus not been used as a motivation for neglecting trap-assisted recombination. As demonstrated in Fig. 4 trap-assisted recombination is significantly present at all voltages and cannot be disregarded.

In contrast, devices with a thicker active layer are less affected by effects as charge diffusion from the contacts which would expose the true impact of the presence of electron traps even more. Fig. 6 depicts the active layer thickness dependence of both loss mechanisms calculated at a current density of 100 A/m^2. Clearly, the contribution

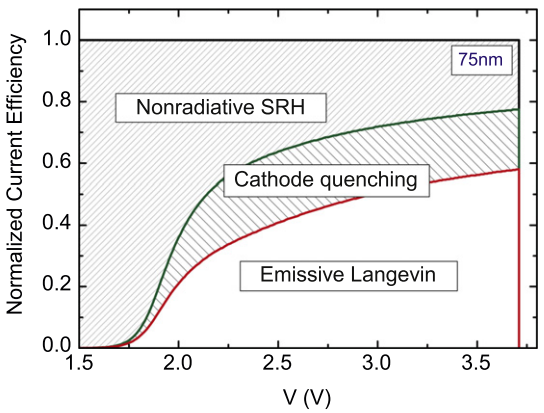

Fig. 4. Calculated contributions of the two loss processes in a 75 nm MEH-PPV PLED. At low voltages non-radiative trap-assisted recombination is the main loss mechanism while at high voltages cathode quenching and non-radiative trap-assisted recombination (SRH) nearly match in contribution to the efficiency loss.

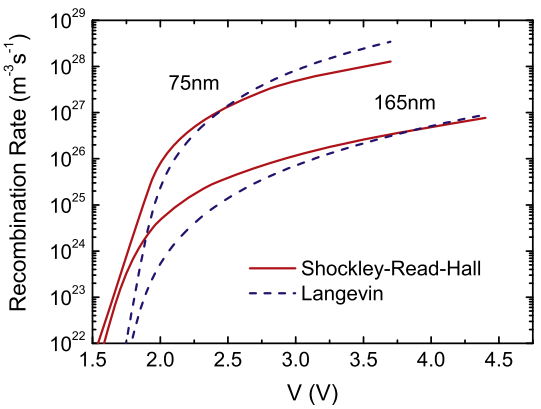

Fig. 5. Calculated individual recombination rates for the 75 nm and 165 nm device. The Langevin recombination for the 75 nm device dominates the total rate earlier then for the 165 nm device due to the different dependencies on charge densities of the Langevin and SRH recombination rates, quadratic and linear, respectively.

of the cathode quenching reduces drastically for thicker devices, starting at about 40% for a 25 nm device to less than 10% for a 1 μm device. Since the electron traps are inherently present in the active layer the non-radiative trap-assisted recombination kicks off at a significant 25% for a 25 nm device increasing to a staggering 45% for a 1 μm device. This result also shows that quenching at the cathode cannot account for the shape of the CE curves for thicker devices since its influence reduces substantially with increasing thickness. Moreover, nor quenching, nor contact effects can explain the trend of a steep curved CE for the 75 nm device and flattening of the CE for the 165 nm device in Fig. 3. It is evident that trap-assisted recombination is the only candidate to which this behavior can be ascribed. Non-radiative trap-assisted recombination dominates the recombination processes at low electric fields, increasing the layer thickness will thus increase the voltage domain at which this recombination process is dominant, thereby flattening the CE curve for thicker devices.

The presence of (filled) electron traps in the MEH-PPV layer is thus detrimental for the device performance in two ways: due to the reduced electron transport the recombination zone is mainly located close to the cathode leading to enhanced quenching of excitons, and furthermore the traps act as non-radiative recombination sites in the active layer. Therefore, the compelling question becomes what the PLED efficiency would be if the amount of electron traps could be reduced. Here we can take advantage of having a complete descriptive device model from which this effect can now be simply predicted. Fig. 7 conveys the influence on the CE by the variation of the number of traps, N_t, taking into account 25% singlet emission and 20% outcoupling efficiency [36]. Remarkably, it follows that for a reduction of a typical trap number of 1.1×10^{23} m^{-3} for MEH-PPV by one order of magnitude already results in nearly a doubling of the CE. It should be noted that reducing the amount of traps in order to improve the device performance is not an unrealistic endeavor. Craciun et al. recently reported that through proper purification of a batch of MEH-PPV hysteresis free electron currents could be obtained [37]. This result implies that whatever electron trapping species is causing the hysteresis as much as $10 \times {}^{22}$ m^{-3} of it can be removed by means of proper purification, which will ultimately lead to an improved device performance. This finding combined with the work presented in this paper emphasizes the importance of purification of the polymers used for lighting applications even more. Earlier work has already hinted towards an efficiency improvement via proper purification [38]. Equally, Campbell et al. reported in 2001 that by reducing the large imbalance between both charge carriers in poly(9,9-dioctylfluorene) (PFO) the quantum efficiency was improved [39].

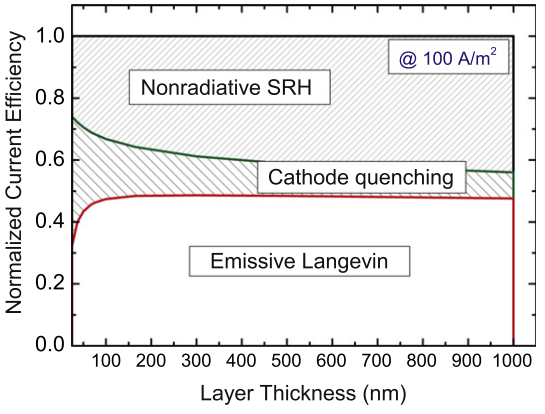

Fig. 6. Calculated thickness dependence of the two loss processes in an MEH-PPV PLED; exciton quenching at the metallic cathode and non-radiative trap-assisted recombination (SRH) calculated at 100 A/m^2.

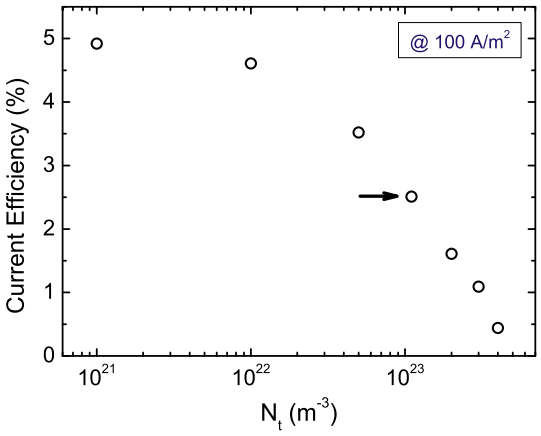

Fig. 7. The calculated current efficiency dependence on the number of electron traps per volume for the 165 nm device. The arrow indicates the number of traps for MEH-PPV as deduced by Nicolai et al. [19], and used in the modeling for the PLEDs.

5. Conclusion

In conclusion, we have quantitatively addressed the influence of electron traps on the magnitude of non-radiative trap-assisted recombination and exciton quenching from the metallic cathode in PLEDs. The results reveal that thin devices (<100 nm) suffer from severe cathode quenching, accompanied by a significant contribution of non-radiative trap-assisted recombination that increases fast with layer thickness. For devices thicker than 100 nm non-radiative trap-assisted recombination is shown to dominate the current efficiency loss by up to 45%. Evidently, future work should focus on the identification and removing of electron traps. This will not only eliminate the non-radiative trap-assisted recombination but in addition, the recombination zone will shift to the center of the device lowering the contribution of cathode quenching, leading to an efficiency improvement of more than a factor of two.

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