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ARTICLE

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De Yuan,^a Lianbin Niu,^b Qiusong Chen,^a Weiyao Jia,^a Ping Chen,^{*a} and Zuhong Xiong^{*a}

In organic semiconductors, the triplet-charge annihilation (TCA) is one of the most common excitonic interactions influencing the opto-electronic power conversion efficiency of the devices. However, it is still unclear whether the TCA reaction goes through the "Scattering Channel" or the "Dissociation Channel". In this work, by measuring the organic magneto-current (OMC) of the conjugated co-polymer poly[{9,9-dioctyl-2,7-divinylene-fluorenylene}-alt-co-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenyene}] (PFOPV)-based organic light-emitting diodes (OLEDs) containing both localized exciton (LE) and charge-transfer-complex (CT), it is found that ³LE and ³CT are playing a crucial role in "Scattering Channel" and "Dissociation Channel" of TCA, respectively. This argument was supported by the simulations of Lorentzian and non-Lorentzian functions used respectively for intersystem crossing (or reverse intersystem crossing, RISC) and TCA effects. Moreover, by inserting a Tris(2,4,6-triMethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) layer between PFOPV and cathode, we improved the electroluminescence efficiency of PFOPV-based OLEDs by suppressing the TCA when ³CT involve in RISC. Our results give insights into the spin-dependent TCA limiting the efficiency of hotly discussed CT-based OLEDs.

Introduction

In organic molecular solids, excited states (i.e., bound electron-hole pairs) are responsible for optical transitions. Since excited states are typically two-electron system, they can be divided into singlets and triplets according to their different quantum spin number S. For triplets (S=1), the number is three times as that of singlets (S=0) and their direct transition to ground state (S=0) is forbidden.¹ These allow triplets to involve in many kinds of excitonic interactions influencing the device efficiency such as triplet-singlet reverse intersystem crossing (RISC),²⁻⁷ singlet-triplet annihilation (STA),⁸ triplet-triplet annihilation (TTA),⁹⁻¹¹ and triplet-charge annihilation (TCA)¹¹⁻¹⁴. Among these excitonic interactions, TCA is the most common process to influence the efficiency of the devices by changing singlet/triplet ratio and charge densities in organic semiconducting materials.¹¹ Therefore, elucidating the mechanism and evolution of TCA is a critical issue to understand its useful or non-useful outcomes in organic lightemitting and photovoltaic devices.

In general, the TCA occurs via two possible channels: (i) the triplets can collide with free carriers, resulting in non-radiative decay of triplet and decrease of charge mobility;¹³ (ii) the triplets can also react with free or trapped charge carriers, dissociating themselves into free electrons and holes.^{11,12} The former is known as "Scattering Channel", while the latter is socalled "Dissociation Channel". However, due to the diversity of triplets (e.g., triplet localized exciton (³LE) and triplet chargetransfer-complex (³CT)) and difficulties in measuring TCA directly, there are few reports discussing these two reaction channels. In 2013, Shao et.al., compared TCA and TTA by using magnetic field effects of electroluminescence (EL), and concluded that TCA is more important than TTA in organic semiconductors.¹¹ Although "Scattering Channel" and "Dissociation Channel" are both considered in this study, it did not tell which channel is more important for TCA under specific conditions. We note that, TCA is a highly spindependent process that can also generate sizeable organic magneto-current (OMC) responses in organic semiconductor devices.¹¹⁻¹⁴ Moreover, the OMC of two TCA channels are completely different, i.e., positive OMC for the "Scattering Channel"13 but negative OMC for the "Dissociation Channel" ^{11,12}. Therefore, the OMC should be a feasible tool to investigate the "Scattering Channel" and "Dissociation Channel" of TCA process in organic semiconductors and thus provides theoretical basis for improving the efficiency of organic optoelectronic devices.

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^a School of Physical Science and Technology, MOE Key Laboratory on Luminescence and Real-Time Analysis, Southwest University, Chongqing 400715, P. R. China E-mails: chenping206@126.com, zhxiong@swu.edu.cn.

^{b.} College of Physics and Electronic Engineering, Chongqing Normal University, Chongqing 400047, P. R. China

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ARTICLE

In this paper, we clarify the two channels of TCA through OMC technique in the conjugated polymer-based organic lightemitting diodes (OLEDs) with an active emission layer of poly[{9,9-dioctyl-2,7-divinylene-fluorenylene}-alt-co-{2-

methoxy-5-(2-ethylhexyloxy)-1,4-phenylene}] (PFOPV). PFOPV is a co-polymer consisting of poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4phenylenevinylene] (MEH-PPV) groups, which simultaneously contains ³LE and ³CT states under electrical excitation. By measuring the OMC of PFOPV-based OLEDs under different currents and temperatures, the sign changes of high-fieldcomponent (HFC, > 40 mT) were observed, and they are strongly correlated with the LE/CT ratio in the device. Specifically, when ³LE is dominant over ³CT, the OMC exhibits a positive HFC. Otherwise, the HFC is negative if ³CT are more important. These results indicate that ³LE and ³CT are playing a crucial role in "Scattering Channel" and "Dissociation Channel" of TCA, respectively. Based on these findings, finally we proposed a strategy to enhance the EL efficiency of PFOPVbased OLEDs through suppressing the TCA when ³CT involve in reverse intersystem crossing (RISC).

Experimental section

OLEDs fabrication

Patterned indium-tin oxide (ITO, 15 Ω /square)-coated glass substrates were cleaned successively using ethanol, acetone, and detergent water in an ultrasonic bath. After treatment with oxygen plasma, PEDOT:PSS was spin-coated onto the ITO substrate (3000 rpm/min, 45 nm) and dried at 120°C for 30 min. Subsequently, ~80 nm PFOPV emission layer was spincoated from a 8 mg/mL chlorobenzene solution at a speed of 2000 rpm/min, and dried at 80 °C for 30 min. All spin-coating processes were carried out in a glove box with H_2O and $O_2 \le 0.1$ ppm. Then, the organic electron-transport layer of Tris(2,4,6triMethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) with thinness of 0~50 nm, and the cesium fluoride (CsF)/Al cathode were continuously deposited on PFOPV layer by thermal evaporation under high vacuum of $< 5 \times 10^{-5}$ Pa. The device active area was $2 \times 2 \text{ mm}^2$.

The EL and OMC measurements

After device preparation, the EL and OMC measurements were carried out immediately. The EL spectra were measured by SpectraPro-2300i spectrometer. For OMC measurement, the samples were mounted on a cold finger of close-cycle cryostat (CCS-350S, 20-300 K) located between two poles of an electromagnet (Lakeshore EM647) with a maximum magnetic field strength of 500 mT. The magnetic field was applied parallel to the device surface and perpendicular to the current direction. When sweeping the magnetic field, the Keithley 2400 was used to provide constant voltage bias for the sample and simultaneously recorded the current. The OMC is generally defined as OMC= $\Delta I/I=[I(B)-I(0)]/I(0)$, where I(B) and I(0) are the current flowing through the sample with and without external magnetic fields, respectively.¹¹⁻¹⁴

Results and discussion

A. The LE and CT properties of PFOPV

The chemical structure of PFOPV, PFO and MEH-PPV are shown in Figure 1 (a). As can be seen, PFOPV is a co-polymer with sequential PFO and MEH-PPV groups. In addition to the LE feature originally from PFO and MEH-PPV groups, this type of co-polymer structure may enable "inter-molecular" electron transition between PFO and MEH-PPV molecules, resulting in CT feature of PFOPV.



Figure 1. (a) The chemical structure of PFOPV, PFO and MEH-PPV molecules; (b) The absorption spectra of PFOPV, PFO and MEH-PPV thin films, and the inset shows the HOMO and LUMO of PFO and MEH-PPV, indicating the CT of PFOPV forms between the LUMO of PFO and the HOMO of MEH-PPV molecules; (c) EL spectra of PFOPV-based OLEDs, and the inset shows the device structure and its energy diagram.

In order to identify the LE and CT properties of PFOPV, the absorption spectra of PFOPV, PFO and MEH-PPV thin films were measured, as shown in Figure 1 (b). As can be seen, the PFOPV shows three absorption peaks locating at ~365 nm, ~445 nm and ~490 nm. Accordingly, the excited states of PFOPV can be divided into two categories. First, the ~365 nm and ~490 nm peaks of PFOPV are in good agreements with PFO and MEH-PPV film absorptions maximized at ~370 nm and ~495 nm, respectively,¹⁵ indicating LE residing on PFO and MEH-PPV molecules in PFOPV. Second, the additional ~445 nm peak of PFOPV is quite different from LE absorptions of PFO and MEH-PPV, indicating another excited state generated in PFOPV. To investigate this type of excited state, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PFO and MEH-PPV were examined. The energy gap between HOMO of MEH-PPV and LUMO of PFO is ~2.70 eV, which is very close to the absorption energy at ~445 nm (i.e., ~2.78 eV). This means CT formations between the LUMO of PFO and the HOMO of MEH-PPV molecules in PFOPV. Moreover, the CT property can be also

Journal Name

evidenced by solvatochromic effect^{5,6,16,17} of PFOPV solution (see Figure S1 in Supplementary). By increasing the solvent polarity from hexamethylene, tetrahydrofuran to dimethylformamide, a large red-shift of PL and enhanced CT emission were observed. This solvatochromic shift, which is commonly consistent with the large dipole moment of a CT state, further confirms that PFOPV possesses a certain CT character.

The EL spectra of PFOPV-based OLEDs (device structure: ITO/PEDOT:PSS/PFOPV/CsF/AI) is shown in Figure 1 (c). As compared with absorption spectra, the EL spectra exhibit an overall red-shift. Nevertheless, we can still observe distinct emission peaks from LE (c.a., 520 nm and 600 nm) and CT (c.a., 558 nm) states, respectively. Therefore, we conclude that LE and CT states coexist in PFOPV under electrical excitation. Due to its efficient multi-emission character, PFOPV was employed as a fluorescent quantum-dot to fabricate white OLEDs.¹⁵ There are several advantages to clarify TCA through OMC in such PFOPV device. First, PFOPV contains both LE and CT in a single device, thus we can study ³LE and ³CT mediated TCA simultaneously. Second, the measurements of OMC in one device eliminates the errors arising from the different materials^{18,19} and different processes of fabricating the LE and CT devices separately^{18,20}. Therefore, OMC of such copolymerbased OLED will be more accurate to reflect the TCA process. Third, the LE/CT ratio can be easily controlled by external conditions such current and working temperature. Thus, the corresponding change of OMC, especially the sign change of HFC, can indicate the transition of TCA between "Scattering Channel" and "Dissociation Channel" and successfully identify the roles of ³LE and ³CT in these two channels (please see Section B).

B. OMC results of PFOPV-based OLEDs

The current and temperature dependence of EL spectra of PFOPV-based OLEDs are shown in Figure 2 (a) and (b), respectively. To keep the charge density the same under different temperatures, the bias voltage were carefully chosen for fixing currents through the device. As can be seen, with deceasing the current and temperature, the emission from CT becomes prominent over that of LE, indicating LE/CT ratio reduces at lower current and temperature level. This is because the charge mobility is reduced under lower electric field and temperature, which is in favor of forming CT between PFO and MEH-PPV groups.²¹ Meanwhile, great changes of OMC with LE/CT ratio under different currents and temperatures were observed, as summarized in Figure S2 in Supplementary. Figure 2 (c) and (d) are selected from these data. When temperature is fixed at 100 K, as shown in Figure 2 (c), lowering the current causes the sign changes both in LFC and HFC of OMC. Specifically, by decreasing the current from 150 μ A to 5 μ A, the rapid low-field-increasing (*i.e.*, positive LFC) gradually changes into rapid low-field-decreasing (i.e., negative LFC). Meanwhile, the slow high-field-increasing (i.e., positive HFC) gradually turns into slow high-field-decreasing (i.e., negative HFC). Very similar changes of OMC at LFC and HFC are also observed during lowering the temperature from

300 K to 20 K at a fixed current of 20 μ A, as shown in Figure 2 (d). From these observations, it seems that LE and CT are strongly correlated with positive and negative OMC, respectively. To find out the role of ³LE and ³CT in "Scattering Channel" and "Dissociation Channel" of TCA, ³LE and ³CT mediated OMC needs to be carefully discussed.



Figure 2. (a) EL spectra of PFOPV-based OLEDs at fixed temperature of 100 K under different currents of 150 μ A, 100 μ A, 20 μ A, and 5 μ A; (b) EL spectra of PFOPV-based OLEDs at fixed current of ~20 μ A under different temperatures of 300 K, 200 K, 100 K, and 20 K; (c) The OMC responses at fixed temperature of 100 K under different currents of 150 μ A, 100 μ A, 20 μ A, and 5 μ A; (d) The OMC responses at fixed current of ~20 μ A under different temperatures of 300 K, 200 K, 100 K, and 20 K.

The LFC and HFC of OMC are governed by different mechanisms. For the LFC of OMC, it is generally explained by hyperfine-field assisted singlets-triplets (S-T) inter-conversion under the magnetic field.^{12,16,19,21-23} And the HFC of OMC can be ascribed to magnetic field dependent TCA process.^{11-13,24} If triplets are involved in "Scattering Channel", they collide with free carriers, resulting in decrease of charge mobility and reduced the current. Once "Scattering Channel" is suppressed by external magnetic field, the charge mobility will be increased and then the current increases, generating the positive OMC.^{13,24} But if triplets are involved in "Dissociation Channel", they will be dissociated into free electrons and holes after reaction with free or trapped charge carriers. Once triplets dissociation is suppressed by external magnetic field, the charge current density will be reduced and the current decreases, resulting in the negative OMC.^{11,12} Therefore, the sign of OMC in HFC, can be a feasible tool to identify the "Scattering Channel" and "Dissociation Channel". Moreover, it should be noted that ³LE and ³CT would play different role in "Scattering Channel" and "Dissociation Channel" due to different binding energy of LE and CT states. In principle, ³LE and ³CT have larger and smaller binding energy arising from long and short electron-hole pair distance in LE and CT states, respectively.¹² Thus, when collided with charge carriers, ³CT

ARTICLE

are dominant in "Dissociation Channel" because of their relative weak electrostatic attraction between the electron and the hole, while ³LE are more likely to involve in "Scattering Channel" because of its relative strong electrostatic attraction between the electron and the hole. Therefore, it is expected that when ³CT are dominant over ³LE in the device, the OMC exhibits a negative HFC. Otherwise, the HFC is positive if ³LE are more important. This explanation is quite consistent with the evolutions of OMC with changing the current and temperature of the device.

To support above arguments, we fitted the experimental OMC results using an equation containing two Lorentzian functions and one non-Lorentzian function with different saturation fields for LFC and HFC, respectively. The equation is as follows:

$$OMC(B) = a_1 \frac{B^2}{|B|^2 + B_1^2} + a_2 \frac{B^2}{|B|^2 + B_2^2} + a_3 \frac{B^2}{(|B| + B_3)^2}$$
(1)

where the first two terms are Lorentzian functions describing the magnetic field mediated ISC and RISC respectively, resulting in positive and negative LFC;^{12,16,22,25} and the third term is non-Lorentzian function for HFC denoting the magnetic field dependent TCA process,²⁶ and its sign could clearly represent the outcome of TCA (*i.e.*, "Scattering Channel" or "Dissociation Channel"). During the fitting, *B* is the applied magnetic field. a₁, a₂ and a₃ are pre-factors for the three functions, denoting the strength of ISC, RISC and TCA respectively. B₁, B₂ and B₃ are the saturation fields, similar to Ref. [16,19,25,26], with ~2.1 mT, ~4.9 mT and ~127 mT respectively.



Figure 3. Fitting results of OMC at current of 20 μ A under (a) 200 K and (b) 100 K. The fitting (red line) contains two Lorentzian functions and one non-Lorentzian function. The two Lorentzian terms describing the magnetic field tuned ISC (blue line) and RISC (green line) respectively, resulting in positive and negative LFC; and the non-Lorentzian term is for HFC denoting the magnetic field dependent TCA process (magenta line). Positive and negative HFC show the outcome of TCA with "Scattering Channel" or "Dissociation Channel", respectively.

By using equation (1), the experimental OMC at different currents and temperatures were fitted. The fitting results of OMC at current of 20 μ A under 200 K and 100 K are shown in Figure 3 (a) and (b), respectively. Equation (1) should be reasonable because all the experimental OMC curves can be perfectly fitted, consisting of three effects of magnetic field tuned ISC, RISC and TCA processes. As can be seen, by lowering the temperature from 200 K to 100 K, obvious sign change of

TCA-related HFC was observed, although ISC-related LFC and RISC-related LFC always persist. Specifically, when LE emission is dominant over CT emission at 200 K (*i.e.*, LE/CT ratio > 1, please see Figure 2 (a) or (b)), the fitted TCA-related HFC is positive exhibiting slow increase of current with increasing the magnetic field. But when CT emission is more important than LE emission at lower temperature of 100 K (*i.e.*, LE/CT ratio < 1), the fitted TCA-related HFC becomes negative exhibiting slow decrease of current with increasing the magnetic field. The fitted results of HFC provide strong evidence that ³LE and ³CT are playing a crucial role in "Scattering Channel" and "Dissociation Channel" of TCA, respectively.

	a ₁	a ₂	a3		
300 K	0.579	-0.016	0.638		
200 K	0.274	-0.257	0.341		
100 K	0.0197	-0.879	-0.083		
20 K	0.0062	-1.863	-0.496		

Table1 The fitting narameters for OMC

a1, a2 and a3 are from equation (1) at fixed current of ~20 μA under different temperatures of 300 K, 200 K, 100 K, and 20 K.

Table2 The fitting parameters for OMC				
	aı	a ₂	a ₃	
150 μA	0.432	-0.234	0.353	
100 µA	0.393	-0.441	0.321	
20 μΑ	0.0197	-0.879	-0.083	
5 μΑ	0.0084	-1.440	-0.251	

a1, a2 and a3 are from equation (1) at fixed temperature of 100 K under different currents of 150 μ A, 100 μ A, 20 μ A, and 5 μ A.

The fitting parameters of a_1 , a_2 and a_3 summarized in Table 1 and Table 2 give more insights into magnetic field tuned ISC, RISC and TCA when LE/CT ratio changes. When CT is dominant under lower currents and temperatures, the magnitude of a_1 is smaller than that of a_2 , meanwhile the sign of a_3 is negative. This means CT are more likely to involve in RISC and "Dissociation Channel" of TCA. In contrast, under high currents and temperatures where LE is more important, the magnitude of a_1 is larger than that of a_2 , and the sign of a_3 is positive, suggesting LE have dominant contribution to ISC and "Scattering Channel" of TCA.

C. Improving the EL efficiency of PFOPV-based OLEDs

Highly efficient fluorescent materials with CT character have recently attracted much attention because of their excellent performance in OLEDs.²⁻⁷ The CT materials, characterized by extremely small singlet–triplet energy splitting (ΔE_{S-T}), allow highly efficient up-conversion from non-radiative triplet states to radiative singlet states (*i.e.*, RISC) and thereby harvest both singlet and triplet excitons for light emission.²⁻⁴ However, before their applications, CT materials still face great challenge of exciton quenching, such as TTA²⁷, STA⁸ and TCA²⁸, reducing the device EL efficiency. For CT material of PFOPV, TCA might be the most important issue limiting the EL efficiency in our device because of the inefficient charge injection at

Journal Name

Journal Name

PFOPV/cathode interface. Specifically, the LUMO of PFOPV is $\sim -2.10 \text{ eV}^{15}$ and the work function of CsF/Al is $\sim -2.80 \text{ eV}^{17}$. This energy barrier of $\sim 0.7 \text{ eV}$ prohibits efficient electron injection into PFOPV emission layer from CsF/Al cathode, resulting in exciton formation zone close to the PFOPV/cathode. Thus, the ³CT are likely to be annihilated by extra electrons accumulated at PFOPV/cathode interface through "Dissociation Channel", reducing their RISC efficiency and finally the EL efficiency of the device. Therefore, it is critical to optimize the PFOPV device by suppressing the TCA at PFOPV/cathode interface.

One promising strategy of suppressing TCA is to insert an electron transporting layer between the emission layer and the cathode.¹² For our studies, 3TPYMB was selected as the electron transporting layer, for three purposes. First, 3TPYMB is an excellent electron transporting material with LUMO of ~-3.30 eV,³ which is slightly lower than the work function of CsF/Al. Thus, the energy barrier for electron injection is removed, avoiding the accumulation of extra electrons at PFOPV/cathode interface. Second, 3TPYMB is also an excellent hole-blocking material because of its high HOMO of ~6.80 eV.³ Thus, the ³CT can be formed in PFOPV separating from extra electrons at 3TPYMB/cathode interface, reducing the possibility of TCA. Third, the triplet energy level of 3TPYMB is very high of ~2.98 eV,²⁹ which can prevent ³CT from energy transferring back to cathode. Thus, the efficiency of RISC is enhanced.



Figure 4. (a) The optimized device structure of PFOPV-based OLEDs and energy diagram; (b) The *I-B* characteristics of optimized PFOPV-based OLEDs with different 3TPYMB thicknesses of 0, 10 nm, 30 nm and 50 nm; (c) EL spectra of optimized PFOPV-based OLEDs with different 3TPYMB thicknesses; (d) The OMC responses of optimized PFOPV-based OLEDs with different 3TPYMB thicknesses at 20 μA, 300 K.

The optimized device structure and energy diagram are displayed in Figure 4 (a). By increasing the thickness of 3TPYMB from 0 to 30 nm, the EL efficiency of device increases to its maximum, and then decreases when the 3TPYMB is further increased to 50 nm, as shown in Figure 4 (b). As mentioned above, the increase of the EL efficiency with

ARTICLE

3TPYMB could be ascribed to the enhanced RISC of ${}^{3}CT$ in PFOPV by suppressing the TCA at PFOPV/cathode interface, evidenced by the EL spectra in Figure 4 (c) and OMC in Figure 4 (d). By increasing the 3TPYMB from 0 to 30 nm, the CT emission becomes more prominent in EL spectra, indicating ³CT involve in RISC without being annihilated by extra electrons. Meanwhile, the OMC shows a sign change from positive to negative after inserting the 3TPYMB layer. Specifically, when the device is without 3TPYMB layer, the OMC shows a positive HFC with a slow increase with magnetic field, indicating ³LE dominated TCA through "Scattering Channel". After inserting thin 3TPYMB layer, the HFC turns into negative with a slow decrease with magnetic field (please see Figure 4 (d)), indicating ³CT dominate in PFOPV and take part in the "Dissociation Channel" of TCA. This result indicates that ³CT generated in PFOPV are nearly involved in RISC without being annihilated by TCA. At the condition of 30 nm 3TPYMB, the EL efficiency of device increases to its maximum. For 3TPYMB with higher thickness, such as 50 nm, the EL efficiency of device starts to decrease although the TCA is also successfully suppressed (because the line-shape of OMC keeps almost unchanged). Therefore, the device with 30 nm 3TPYMB should be optimal in design based on these considerations.

Conclusions

In summary, we investigated the OMC of co-polymer PFOPV-based OLED, and clarified the two manners of TCA (i.e., "Scattering Channel" and "Dissociation Channel") in organic semiconductors. By measuring the OMC and EL spectra at different temperatures and voltage bias, the sign changes of HFC with LE/CT ratio were observed. Specifically, when LE dominates over CT, the OMC exhibits a positive HFC with a slow increase with magnetic field. Otherwise, the HFC is negative showing a slow decrease with magnetic field. These results indicate that ³LE and ³CT are playing a crucial role in "Scattering Channel" and "Dissociation Channel" of TCA respectively, confirmed by the simulations of Lorentzian and non-Lorentzian functions combing ISC (or RISC) and two TCA effects. To improve the EL efficiency of PFOPV device, we suppressed the TCA effect by inserting a 3TPYMB layer between PFOPV/cathode and enhanced the RISC of ³CT in PFOPV. The OMC results reported here, in particular with a deeper understanding of the TCA, shall cast a renewed sight in the spin-dependent processes influencing the device EL efficiency.

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