

Low Current Density Driving Leads to Efficient, Bright and Stable Green Electroluminescence

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Electroluminescent devices have the potential to reshape lighting and display technologies by providing low-energy consuming solutions with great aesthetic features, such as flexibility and transparency. In particular, light-emitting electrochemical cells (LECs) are among the simplest electroluminescent devices. The device operates with air-stable materials and the active layer can be resumed to an ionic phosphorescent emitter. As a consequence, LECs can be assembled using solution-process technologies, which could allow for low-cost and large-area lighting applications in the future. High efficiencies have been reported at rather low luminances ($<50 \text{ cd m}^{-2}$) and at very low current densities. Moreover, these efficiencies could be sustained for a brief moment only during operation time. Here, we demonstrate that a pulsed driving mode at low current densities leads to unequalled overall performances with excellent efficiencies throughout the lifetime of the device. The lifetime of the LECs is defined as the time it takes to reach 50% of the peak luminance. Upon optimization of various parameters (frequency, duty cycle and average current density), the green LEC reaches efficacies and power efficiencies of 28.2 cd A^{-1} and 17.1 lm W^{-1} , respectively, at a luminance above 750 cd m^{-2} and 98 hours lifetime. The present work also rationalizes why high efficiencies have been obtained only at low current densities so far.

1. Introduction

Lighting accounts for about 10% of the world global energy consumption. There is therefore a strong incentive for new, low consumption lighting solutions to reduce global energy demand. In this context, organic light-emitting diodes (OLEDs) have considerable advantages compared to other solid-state lighting technologies, which are based on inorganic semiconductors. The benefits of using OLED technology are twofold. Firstly, they use less toxic materials that are obtained in an unsustainable manner, as this lowers environmental impact and favours a more amenable end-of-life cycle of the finished product. Secondly, it is expected that the processing costs of OLED technology will be reduced in comparison to inorganic LEDs, which is essential for large-scale production.

In recent years OLEDs have become a serious alternative to conventional inorganic technology due to improved efficiency and stability.^[1] The most effi-

cient and stable OLEDs are based on a multi-stack of small molecular-weight components. The multi-layer architecture is obtained by sequential evaporation of the active species under high-vacuum conditions. Alternatively, OLEDs using polymeric emitters usually employ only few layers and are processed from solution.^[2–5] These have somewhat lower performances, which is most likely due to the lack of a multi-layer structure.^[6] Another type of electroluminescent device, referred to as light-emitting electrochemical cell (LEC), has a much simpler architecture with great promise towards the making of low-cost lighting and display applications. Contrary to OLEDs,^[7] LECs do not rely on air-sensitive injection layers and metals used for electron injection.^[8–14] Therefore, encapsulation does not have to be as rigorous, which allows for preparing devices by solution process instead of vacuum deposition.^[15] Additionally, the LEC architecture can be reduced to a single active layer composed of an ionic transition-metal complex (iTMC).^[16–20] The presence of mobile ions facilitates the formation of ionic junctions, which lowers the barrier for electron and hole injection. As a result, LEC devices are independent of the work function of the electrode material.^[21–28]

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High efficiencies, high luminances and high stabilities have been obtained for iTMCs-based LECs. In particular high efficiencies have been obtained at very low luminance levels. However, a single device excelling in these three figures of merit remains elusive. Record green-emitting LECs have efficiencies as high as 39.8,^[29] 26.2^[30] and 28.7^[31] lm W⁻¹ at a very low luminance (below 52 cd m⁻²). Similarly, high efficiencies of 36.8 lm W⁻¹ at a luminance below 50 cd m⁻² were obtained for orange LECs that were prepared by dispersing an orange iTMC in a matrix of green iTMC.^[32] In both cases, the peak efficiency was briefly observed, after which it rapidly dropped to much lower values.

The efficiency and lifetime of the device are linked to the intrinsic properties of the emitter used. However, one should not overlook the driving method applied to the device. Record LECs have been obtained at constant voltage and low current densities, which favours efficiency at the expense of the device luminance, turn-on time and lifetime (a few hours only for the devices outlined above). In a recent report, LECs were operated with a pulsed current (PC) driving mode instead of a constant voltage,^[33] which lead to exceptionally stable luminances, efficiencies and long lifetimes (over 4000 hours).

Herein, we report on highly efficient stable green LECs whose overall performances are unmatched. Under optimized PC-conditions, the devices reach efficacies and power efficiencies of 28.2 cd A⁻² and 17.1 lm W⁻¹, respectively, at a luminance above 750 cd m⁻². Importantly, the efficiency decreases slowly during operation such that lifetimes of almost 100 hours are observed. These excellent performances are obtained by optimizing pulsed currents in terms of duty cycles and current densities. In particular, we show that low current densities are a prerequisite to obtain high efficiencies.

2. Results

2.1. Design and Properties of the Emitter

In order to obtain high efficiency LECs, iridium emitters with high photoluminescent quantum yields (PLQY) are required. The PLQY of iTMCs generally improves with increasing bandgap and with decreasing vibrational modes.^[28,34] For this reason, complexes with fluoro-substituted cyclometalating ligands often exhibit higher PLQY than their non-fluorinated equivalents.^[35,36] Unfortunately, these favorable emission properties can come at the expense of the stability of the LECs. As the emission is shifted towards lower wavelength, the stability of the corresponding complex tends to decrease. For example, a link has been identified between the number of fluorine atoms and the stability of the LEC employing this iTMC.^[37]

We selected therefore [Ir(4-Fppy)₂(dtb-ppy)][PF₆] (**1**) as the emitter (**Figure 1**). The complex was synthesized following a three-steps standard procedure.^[37,38] Synthetic details can be found in the Supporting Information. Complex **1** exhibits high PLQY values of 69 and 82% in dilute solution and when dispersed (5% wt.) in a polymethylmethacrylate (PMMA) film, respectively. The PLQY of the complex in the device configuration is measured to be 48%. This value is

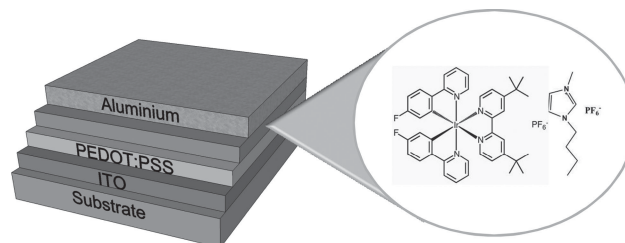


Figure 1. Schematic representation of the device layout and chemical structures of the iTMC and ionic liquid employed.

remarkable considering that the iTMC concentration in those films is around 93 wt.%. Photophysical and electrochemical data are similar to previously published emitters and can be found in Figure S1, S2 and S3 and Table S1 of the Supporting Information.^[39,40]

2.2. Light-Emitting Electrochemical Cells

Simple two-layer LECs were prepared by spin coating a thin layer (90 nm) of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on top of a patterned indium tin oxide (ITO)-coated glass substrate, followed by the active layer (80 nm). The emitting layer consists of a 4:1 molar ratio mixture of complex **1** and 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM⁺:PF₆⁻] as ionic liquid. The latter was added to reduce the turn-on time. A 70-nm aluminium layer was used as the top electrode contact. The architecture of the LECs is depicted in Figure 1. The LECs emit green light with a maximum at 554 nm and CIE coordinates of $x = 0.375$ and $y = 0.566$. More details concerning the device preparation can be found in the Experimental section.

2.3. Pulsed Current Driving Mode Optimization

To evaluate the effect of the duty cycle on the device performances, the LECs were operated using a PC-driving mode at an average current density of 50 A m⁻². The pulsed currents consist of block waves at a frequency of 1000 Hz with duty cycle of 25, 50 and 75%. Direct current (DC), which is obtained at a duty cycle of 100%, was also applied. Prior to this study, the effect of the frequencies was evaluated for a duty cycle of 50% and an average current density of 50 A m⁻² (Figure S4). Regardless of the frequency, no significant differences were observed. Due to this observation and one previous report that used a frequency of 1000 Hz for a pulsed voltage operation, we have in the remainder of this manuscript used a frequency of 1000 Hz.^[41] The main figures of merit for all devices can be found in Table 1.

All LECs turned-on in less than 5 seconds and showed no dependence from the type of bias applied, as expected with current driving mode (**Figure 2a**). The average voltage required to sustain the set current density of 50 A m⁻² drops rapidly over the first minutes, after which it remains almost constant with only a very small decrease over the next 50 hours (**Figure 2a**).

Table 1. Performance of LEC devices biased with a block-wave pulsed current at a frequency of 1000 Hz and an average current of 50 A m^{-2} at different duty cycles

Duty Cycle [%]	t_{on} [s]	Lum_{max} [cd m^{-2}]	$t_{1/2}$ [h]	Efficacy [cd A^{-1}]	Power Efficiency [lm W^{-1}]	EQE [%]
25	<5	747	174.2	14.9	6.0	4.3
50	<5	924	99.3	18.6	10.1	5.4
75	<5	1240	57.1	25.4	13.6	7.4
100	<5	1107	0.25	22.6	15.7	6.6

This can be understood in view of the operational mechanism of LECs, which requires ionic motion to reduce the electronic injection barriers. Upon biasing the device, the initial barriers for electrons and holes are high due to the difference in energy levels of the HOMO and LUMO of the iTMC and the work-function of the electrodes. Therefore, initially a relatively high voltage is required to maintain the current density at 50 A m^{-2} . This high voltage leads to rapid ion movement and, subsequently, to the reduction of the electronic injection barriers. As this effect takes place, the voltage needed to sustain the current density drops gradually to reach the value that is related to the bulk transport through the iTMC layer. Upon decreasing the duty cycle the on-time of the pulse decreases, which implies that the peak current-density increases to maintain the desired average current density. Due to the increased peak current-densities the voltage in the peak also increases. As the current-density versus voltage curve is not a linear line, the increase in peak voltage is not proportional to the increase in current density, which is why a lower average voltage is observed for decreasing duty cycles.

Best luminances of 1107 and 1240 cd m^{-2} are measured for LECs that operate at 100% and 75% duty cycle, respectively. Note that the first point is measured after 5 seconds of operation. The luminance decay over time strongly depends on the driving mode. For DC-driven LECs, a very fast drop is observed, which gives a lifetime of 15 min only. This is in sharp contrast to PC-driven LECs for which lifetimes of 57, 99 and 174 hours are obtained at 75, 50 and 25% duty cycle, respectively.

Similarly, best current efficiencies are observed for devices that are driven at high duty cycles. For example, LECs driven at a 75% duty cycle reach efficacies of 25 cd A^{-1} at a luminance of 1000 cd m^{-2} , which are excellent values (Figure 2b). Interestingly, the efficacy decreases much slower for devices operated with pulsed currents. This observation compares favourably with previously reported green LECs that operated under constant voltage.^[29–31] For those, maximum efficacies were sustained for a short interval, typically a few hours only, which further demonstrates the advantage of the PC-driving method.

On the other hand, PC-driven devices give lower power efficiency than their DC-driven equivalents. This is caused by the higher power consumption of pulsed operation. At 100% duty cycle, the LECs display efficiencies up to 15.7 lm W^{-1} . A good trade-off between efficiency and stability is obtained at 75% duty cycle. In these conditions, our best LECs operate with a power efficiency of 13.6 lm W^{-1} with 57 hours lifetime instead of 15 min as was obtained for the DC-operated ones.

2.4. Current Density Optimization

As mentioned in the introduction, record efficiencies were obtained until now by operating the device at low luminance levels and subsequently at low current densities.^[29–31] These LECs were driven using a constant voltage such that the current densities varied over time as a consequence of the operation mechanism of the device. Using a PC-driving method, one can also control the average current density, which provides the

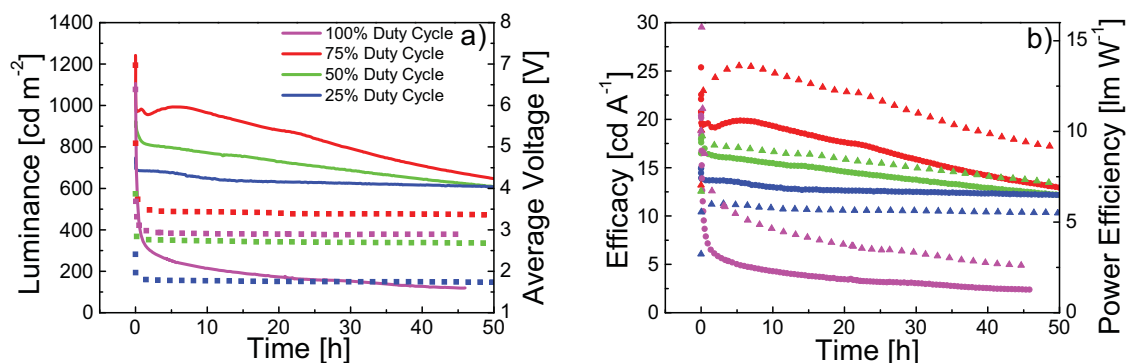
**Figure 2.** a) Luminance (line) and average voltage (squares) vs. time and b) efficacy (circles) and power efficiency (triangles) vs. time for LECs biased with a block-wave pulsed current at a frequency of 1000 Hz and an average current density of 50 A m^{-2} for different duty cycles.

Table 2. Performance of LEC devices biased with a block-wave pulsed current at a frequency of 1000 Hz and a duty cycle of 75% at different current densities

Average J [A m ⁻²]	t _{on} [s]	Lum _{max} [cd m ⁻²]	t _{1/2} [h]	Efficacy [cd A ⁻¹]	Power Efficiency [lm W ⁻¹]	EQE [%]
150	< 5	1535	36.5	9.8	6.2	2.8
100	< 5	1536	42.2	14.4	9.1	4.2
75	< 5	1444	43.2	19.1	11.9	5.5
50	< 5	1240	57.1	25.4	13.6	7.4
25	0.2	757	98.0	28.2	17.1	8.2
18.75	< 5	421	160.9	22.5	15.9	6.5

means to further test and improve the device performances. This optimization is implemented here with current densities ranging from 18.75 to 150 A m⁻² at 75% duty cycle. Data are summarized in Table 2.

As expected, the maximum luminance follows the average current density (Figure 3a). Yet, very interestingly, the decrease in luminance is not proportional such that the device efficiency increases with decreasing current density (Figure 3b). Figure 4 gives better insights into the effect of the average current density on the efficacy and the power efficiency. An almost threefold efficiency improvement, from 6.2 to 17.1 lm W⁻¹, is

obtained by solely decreasing the current density from 150 to 25 A m⁻². At lower current density, the efficiency no longer increases; instead, a slightly lower value is obtained. At such low current density, only a low voltage is needed to drive the device. Likely, injection barriers are still present in this case, which may result in unbalanced carrier density.

The best LECs are obtained at a current density of 25 A m⁻², that leads to an efficacy of 28.2 cd A⁻¹ and a power efficiency of 17.1 lm W⁻¹. In these conditions, the turn-on time was determined with higher precision and, after 0.2 seconds, the device showed a luminance of 746 cd m⁻² with a lifetime of 98 hours.

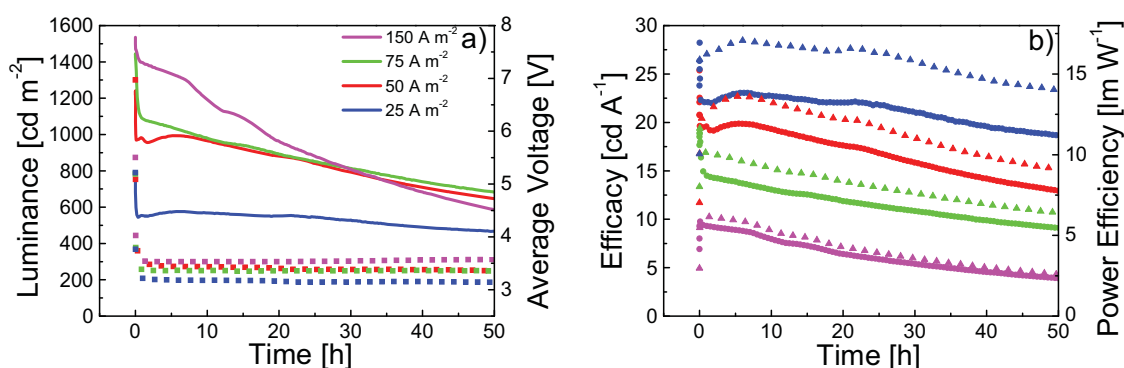


Figure 3. a) Luminance (line) and average voltage (squares) vs. time and b) efficacy (circles) and power efficiency (triangles) vs. time for LECs biased with a block-wave pulsed current at a frequency of 1000 Hz and at 75% duty cycle for different current densities.

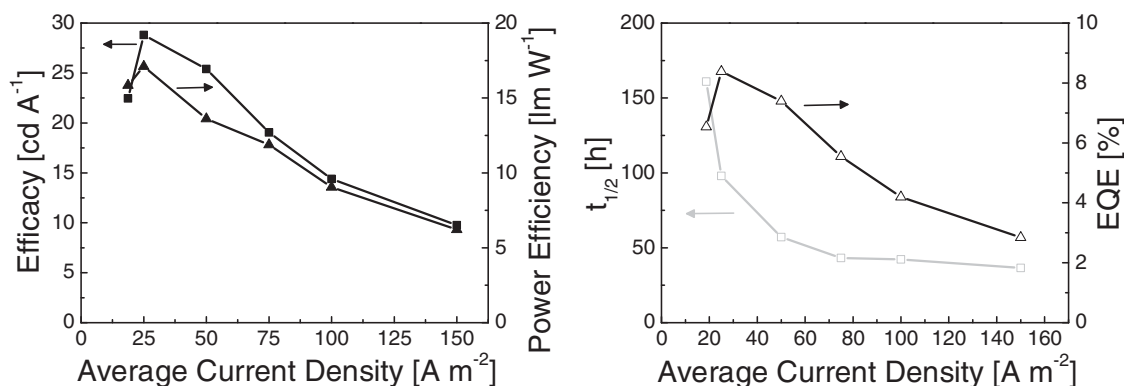


Figure 4. Left) Efficacy (squares) and power efficiency (triangles) vs. average current density and Right) life-time (open squares) and external quantum efficiency (open triangles) vs. average current density for LECs biased with a block-wave pulsed current at a frequency of 1000 Hz and a duty cycle of 75%.

2.5. Efficiency and Stability of LECs

In a first approximation, the external quantum efficiency (EQE) is defined by Equation (1), where b is the recombination efficiency (equal to 1 for two ohmic contacts),^[42] ϕ is the fraction of excitons that decay radiatively and n is the refractive index of the glass substrate and is equal to 1.5 (the factor $1/2n^2$ accounts for the coupling of light out of the device).

$$\text{EQE} = b\phi/2n^2 \quad (1)$$

As iridium(III) complexes can harvest both singlet and triplet excitons, ϕ should be in the same order of magnitude than the value measured for the PLQY. Assuming $\phi = 0.48$, which is the PLQY measured for **1** in the device configuration, a theoretical maximum efficiency EQE_{th} of 9.5% is expected. With an experimental EQE of 8.2%, the maximum efficiency of the device is approaching the theoretical limit. Considering the degree of uncertainty regarding the outcoupling efficiency, these results are particularly impressive.

Finally, the stability of the LECs increases super-linearly with decreasing current density (Figures 3a and 4b), such that the lifetime is strongly improved below current densities of 50 A m^{-2} . The lifetime of LECs is described by the decay in luminance over time and depends strongly on the maximum luminance. Decay reactions that are responsible for a decrease in luminance are proportional to the current density applied. Hence, if the same luminance levels can be obtained at a lower current density (due to the improved efficiency) the degradation reactions are reduced and the luminance decays more slowly. Decay reactions increase with increasing current density, due to either an increase in the hole and electron density or by the increase in exciton density. In a previous work we studied the lifetime of LECs with and without illumination. No decrease in lifetime was observed for the illuminated devices, indicating that the exciton density is not the main cause of device degradation. Therefore, we attribute the increase in lifetime primarily due to a decrease in charge carriers. Additionally, as low current densities give rise to more confined doped zones, exciton quenching is also reduced, which lowers the non-permanent component of the luminance decrease with time.^[27] Beyond the scope of this work, our results also explain why high efficiencies could only be obtained at low current densities so far and why efficiencies of LECs decrease so rapidly under constant voltage.

3. Conclusion

Solid state films containing high concentrations of the ionic iridium complex $[\text{Ir}(\text{4-Fppy})_2(\text{dtb-ppy})][\text{PF}_6]$ exhibit high photoluminescence quantum yields. When used as the active material in light-emitting electrochemical cells (LECs), very efficient green light-emission is obtained. We demonstrated that the LECs efficiency depends strongly on the current density applied, such that a threefold increase in efficiency is obtained by lowering the current density from 150 to 25 A m^{-2} . Optimization of the various driving parameters (frequency, duty cycle and average current density) results in

an “all-in-one” device with fast turn-on, high luminance, high power efficiencies and good lifetimes. Importantly, the high efficiencies decrease only slowly with operation time, which is a key requirement for lighting applications where sustained excellent performances throughout the lifetime of the device are needed. This work also illustrates that simple, although carefully, designed molecules can lead to outstanding performances in LECs.

4. Experimental Section

Complex synthesis and purification: The green emitting complex $[\text{Ir}(\text{4-Fppy})_2(\text{dtb-ppy})][\text{PF}_6]$, where 4-Fppy is 2-(4-fluorophenyl)pyridine and dtb-ppy is 4,4'-di-*tert*-butyl-2,2'-bipyridine, complex **1**, was synthesized following three standard steps. First, the cyclometalating ligand 4-Fppy was synthesized in 72% yield by Suzuki coupling between 4-fluorophenylboronic acid and 2-bromopyridine. Two purifications by column chromatography are necessary to obtain 4-Fppy as a white solid instead of a yellowish oil. Reaction of 4-Fppy with IrCl_3 in a 2:1 2-ethoxyethanol/water mixture afforded $[\text{Ir}(\text{4-Fppy})_2(\mu\text{-Cl})_2]$ in 81% yield. Finally, complex **1** was obtained in 85% yield by reacting the chloro-bridged iridium dimer with 4,4'-di-*tert*-butyl-2,2'-bipyridine in a 7:1 dichloromethane/methanol mixture. Further details can be found in the Supporting Information.

Device preparation: The solvents were supplied by Aldrich. The thickness of films was determined with an Ambios XP-1 profilometer. Indium tin oxide ITO-coated glass plates ($15 \Omega \square^{-1}$) were patterned by conventional photolithography (www.naranjosubstrates.com). The substrates were cleaned by sonication in water-soap, water, and 2-propanol baths, in that order. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42–220) for 20 min.

The electroluminescence devices were made as follows. First, a 90-nm layer of PEDOT:PSS (CLEVIOS P VP Al 4083, aqueous dispersion, 1.3–1.7% solid content, Heraeus) was spin-coated on the ITO glass substrate to improve the reproducibility of the devices and to prevent the formation of pinholes. Then, 80-nm transparent films of complex $[\text{Ir}(\text{4-Fppy})_2(\text{dtb-bpy})][\text{PF}_6]$ and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (>98.5%, Sigma-Aldrich) in a 4 to 1 molar ratio were spin-coated from 20 mg mL^{-1} acetonitrile solution at 1000 rpm for 20 s. The devices were transferred to an inert atmosphere glovebox (<0.1 ppm O_2 and H_2O , MBraun). The Al electrode (70 nm) was thermally vapor deposited using a shadow mask under a vacuum (< 1×10^{-6} mbar) using an Edwards Auto500 evaporator integrated in the glovebox. The area of the device was 6.5 mm^2 . The devices were not encapsulated and were characterized inside the glovebox at room temperature.

LEC Characterization: An Avantes luminance spectrometer was used to measure the EL spectrum. Device lifetime was measured by applying pulsed currents and monitoring the voltage and luminance by a True Colour Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System. The average current density is determined by multiplying the peak current density by the time-on and dividing by the total cycle time. The average luminance is directly obtained by taking the average of the obtained photodiode results and correlate it to the value of a luminance meter. The current efficiency is obtained by dividing the average luminance by the average current density.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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