

Letter

Charge transport and density of trap states in balanced high mobility ambipolar organic thin-film transistors

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ABSTRACT

We report on charge transport and density of trap states (trap DOS) in ambipolar diketopyrrolopyrrole–benzothiadiazole copolymer thin-film transistors. This semiconductor possesses high electron and hole field-effect mobilities of up to 0.6 cm²/V-s. Temperature and gate-bias dependent field-effect mobility measurements are employed to extract the activation energies and trap DOS to understand its unique high mobility balanced ambipolar charge transport properties. The symmetry between the electron and hole transport characteristics, parameters and activation energies is remarkable. We believe that our work is the first charge transport study of an ambipolar organic/polymer based field-effect transistor with room temperature mobility higher than 0.1 cm²/V-s in both electrons and holes.

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1. Introduction

Ambipolar organic semiconductors, which transport both electron and hole carriers with similar mobilities in the conducting channel, are useful for applications ranging from light-emitting devices to logic circuits [1–6]. There have been very few such semiconductors reported to date with balanced electron and hole mobilities that both are more than 0.1 cm²/V-s. One such ambipolar organic semiconductor is diketopyrrolopyrrole–benzothiadiazole copolymer (PDPP–TBT) [7]. Significantly, there have been no prior studies on charge transport and the density of trap states (trap DOS) for both electrons and holes in such high mobility ambipolar organic semiconductors [8–13]. In this letter we are reporting on the results of such a study on PDPP–TBT. This semiconductor possesses high field-effect mobility and balanced transport of electron and hole with mobilities more than 0.5 cm²/V-s at room temperature. Such high mobilities are a result of the low band-gap due to the donor–acceptor building blocks, their intramolecular interactions and suitable energy levels of the π^* and π

bands (which correspond to the conduction and valence bands).

In order to understand the charge transport behavior of this unique material (PDPP–TBT) which has high mobilities and balanced ambipolar charge transport in organic thin-film transistor (OTFT) devices, the activation energy has been measured as a function of gate bias (or induced carrier concentration) at various temperatures in the range 120–300 K. We have also calculated the trap DOS in ambipolar PDPP–TBT TFTs based on activation energy as a function of gate voltages using two analytical methods following the approach by Lang et al. [14] and Kalb and Batlogg [15].

2. Experimental

Device fabrication started with an n-type silicon substrate with a resistivity of 1–10 Ω cm. This substrate was also used as the bottom-gate electrode. This silicon substrate was thermally oxidized resulting in a 200 nm thick silicon dioxide bottom-gate insulator. All samples were sonicated in acetone, methanol and isopropyl alcohol for 5 min each, dried with nitrogen gas, baked in a 120 °C oven for 10 min to remove remaining water, and then exposed

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to UV ozone treatment for 5 min. A 47.5 nm thick chrome/gold (2.5/45 nm) bi-layer was deposited by thermal evaporation for source and drain electrodes. In order to reduce the contact resistance between the source/drain metal and the PDPP-TBT semiconductor, samples were treated with pentafluorobenzenethiol (PFBT) to form a self-assembled mono-layer (SAM) [16]. These samples were immersed in a dilute PFBT solution with isopropyl alcohol (10 mM) for 1 h, then rinsed with pure isopropyl alcohol to remove residual PFBT, and annealed at 120 °C for 30 min. The samples were exposed to the octyltrichlorosilane (OTS-8) vapor at 110 °C for 6 h and then treated with isopropyl alcohol to improve the interface between the silicon dioxide gate dielectric and the polymer semiconductor [17,18]. Both PFBT and OTS-8 treatment were performed under an inert atmosphere.

The PDPP-TBT solution was formed using chloroform as the solvent (7 mg/mL concentration) and was stirred at 53 °C for 6 h in an inert environment. The synthesis and purification of the PDPP-TBT have been described in detail by Sonar et al. [7]. A 33 nm thick semiconductor film was formed by spin-coating and then pre-annealed at 200 °C

for 30 min. Next, the as-supplied polymeric D139 dielectric as a top-gate insulator was spin-coated onto the PDPP-TBT layer and cured gradually from 25 to 130 °C over 1 h of which capacitance value is ~ 4 nF/cm². Finally, a 45 nm thick gold as a top-gate electrode was deposited by thermal evaporation. The annealing was performed on a hot plate in a nitrogen glove box. The conditions are at 140 °C for 10 h. The spin-coating and thermal annealing of the PDPP-TBT and D139 were performed under a nitrogen atmosphere. The dimension of OTFT devices are a channel width of 1000 μ m and a channel length of 50 μ m. The temperature-dependent measurements were performed in a Desert Cryogenics vacuum probe station with a chamber pressure lower than 10^{-3} Torr. DC measurements for the device characteristics were carried out using Agilent 4155C semiconductor parameter analyzer.

3. Results and discussion

Fig. 1a and b shows the chemical structure of diketopyrrolopyrrole–benzothiadiazole copolymer and schematic

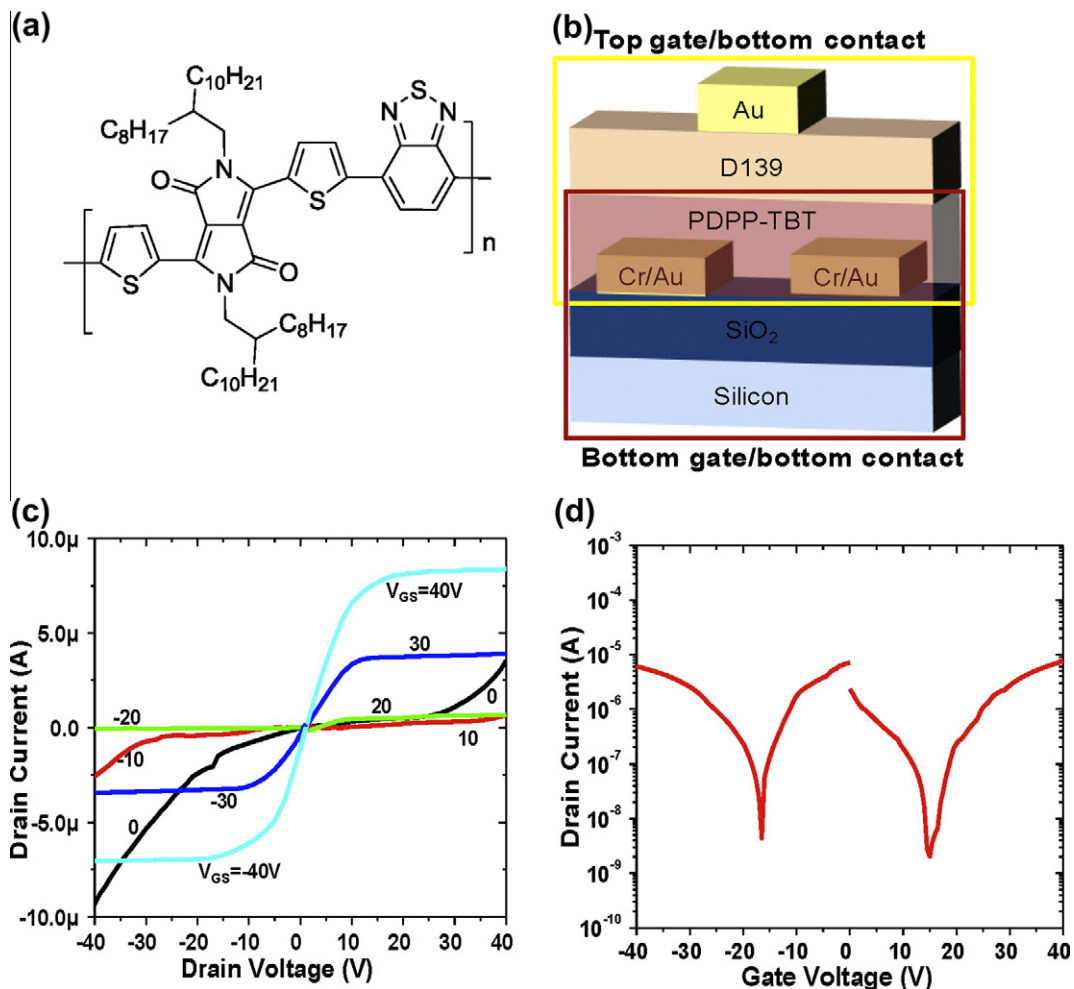


Fig. 1. (a) The chemical structure of diketopyrrolopyrrole–benzothiadiazole copolymer (PDPP-TBT), (b) the schematic cross-section of TFT geometry, (c) the output, and (d) the transfer characteristics of top-gate bottom-contact PDPP-TBT TFTs.

cross-section of a TFT structure used in this study. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in PDPP-TBT semiconductor are located at 5.2 and 4.0 eV, respectively. These energy level values were calculated from a combination of cyclic voltammetry and optical absorption measurements. The HOMO value was calculated from the oxidation onset of CV curve whereas LUMO value was calculated from the difference between optical band gap and HOMO value. The value of the HOMO and LUMO energies are very suitable for inducing both electron and hole transport without substantial trapping in immobile interface states. It is widely believed that the LUMO value must be equal to or greater than 4.0 to get n-channel performance without too many deep traps. Similarly, a HOMO value of 5.2 is considered as optimal for p-channel operation. Our material has a LUMO value of 4.0 eV and a HOMO value of 5.2 eV [7,19].

Fig. 1c and d shows the output and the transfer characteristics of a top-gate bottom-contact TFT based on PDPP-TBT operating in both electron- and hole-enhancement modes, indicating typical ambipolar characteristics. Optimized top-gate PDPP-TBT TFTs possess a hole field-effect mobility of $0.53 \text{ cm}^2/\text{V}\cdot\text{s}$ and an electron field-effect mobility of $0.58 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature. These mobility

values are high and most balanced among the reported ambipolar organic semiconductors. The results are the highest minimum electron and hole field-effect mobility values with balanced transport characteristics attained in a single organic semiconductor so far, which is greater than $0.4 \text{ cm}^2/\text{V}\cdot\text{s}$ reported by Sonar et al. [7]. The work function of the electrode affects injection of carriers. This has been well documented by Singh and co-workers in a prototypical system [19]. Other researchers have also noted this. In the case of the present material, Au coated with PFBT serves as a suitable electron injecting and hole injecting contact.

In order to analyze charge transport, temperature-dependent field-effect mobility measurements were performed from 120 to 300 K with bottom-gate bottom-contact PDPP-TBT TFTs. There was a stability problem at low temperatures in the top-gate configuration. For this reason, temperature dependent measurements are reported only for bottom gate devices. The device characteristics of bottom-gate bottom-contact PDPP-TBT TFTs were re-measured at room temperature after temperature cycling and were almost unchanged compared to initial characteristics. It means that the physical and material properties of PDPP-TBT were not substantially altered by the temperature cycling. The contact resistance is not expected to be

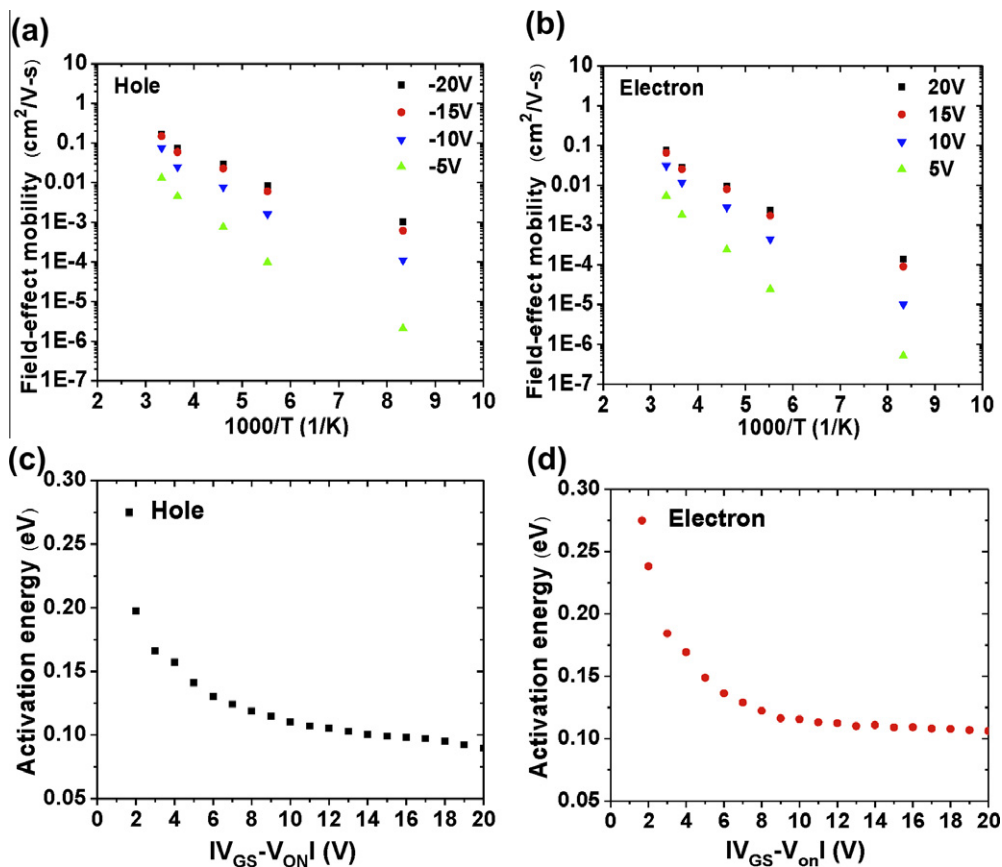


Fig. 2. The plots of field-effect mobility vs. reciprocal temperature in both (a) hole- and (b) electron-enhancement modes in PDPP-TBT TFTs with $V_{GS}-V_{ON}$ ranging from ± 5 to ± 20 V and the activation energy as a function of $V_{GS}-V_{ON}$ in (c) holes and (d) electrons.

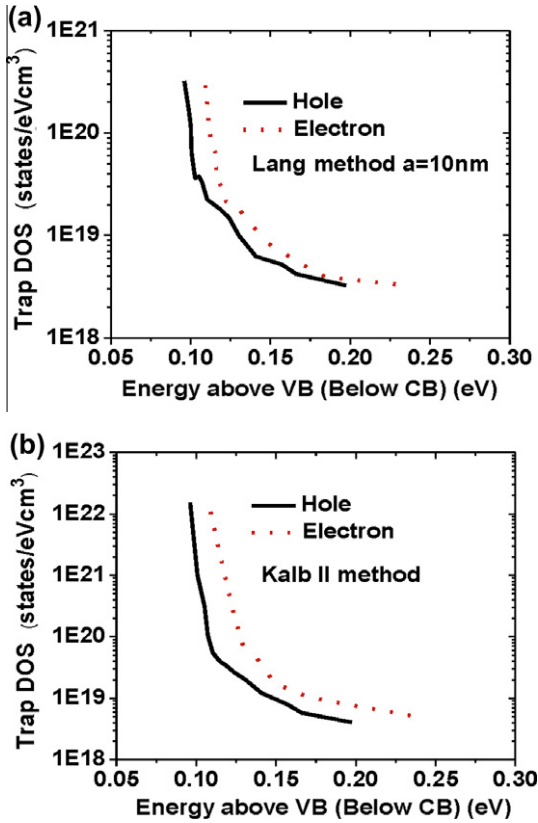


Fig. 3. The density of trap states in the band gap as calculated with two different methods of (a) Lang et al., and (b) Kalb and Batlogg in PDPP-TBT TFTs.

dominant in these experiments because the channel length was very long and a SAM treatment improved the electrical contact between the electrodes and the semiconductor. Fig. 2a and b shows the plot of field-effect mobility vs. reciprocal temperature in both hole- and electron-enhancement modes with applied gate voltages (depending on polarity). The field-effect mobilities of both electrons and holes decrease with temperature, as it expected for thermally activated transport [20,21]. The activation energy is extracted from Arrhenius plots by fitting to the following equations:

$$\mu = \mu_0 e^{-\frac{E_A}{kT}} \quad (1)$$

where k is the Boltzmann constant, T is a temperature, E_A is activation energy and μ is field-effect mobility. Activation energies are extracted from the slope by fitting the above equation with logarithm for thermally activated mobilities. Fig. 2c and d shows the activation energy as a function of $V_{GS}-V_{ON}$ for holes and electrons. V_{ON} is the turn-on voltage of the device at which significant carrier accumulation is observed. To determine V_{ON} , we first calculate dI_D/dV_G . The gate voltage at which it becomes positive is V_{ON} . The activation energy decreases with increasing $V_{GS}-V_{ON}$ for both holes and electrons. This decrease in activation energy fits the multiple trap and thermal release (MTR) model of charge transport [20,21]. The measured activation

energy roughly corresponds to the energy distance from occupied trap states to the delocalized band edge [22]. As the applied gate voltage increases, the Fermi level moves toward the band-edge, decreasing the measured activation energy. This behavior has been observed in several high mobilities organic field-effect transistors with active semiconductor layers such as pentacene or liquid crystalline polymers [23–26]. The rate at which the activation energy falls in dependent on the trap DOS. The value of μ_0 is about $5 \text{ cm}^2/\text{V}\cdot\text{s}$. The combination of a fairly high mobility and the activation energy of $\sim 100 \text{ meV}$ strongly suggest the charge transport is by multiple trap and release. The data appear to be consistent with the MTR model [8]. The Visenberg–Matters VRH model is suitable for lower mobility doped systems. Fig. 3a and b shows the density of trap states in the band gap of PDPP-TBT TFTs as calculated with two different methods as following.

$$N(E) = \frac{C_i}{qA} \left[\frac{\partial E_A}{\partial V_G} \right]^{-1}, \quad (2)$$

$$N(E) = \frac{\partial}{\partial E_A} \left[\frac{\varepsilon_0 \varepsilon_i^2}{\varepsilon_s L} V_G \left(\frac{\partial E_A}{\partial V_G} \right)^{-1} \right] \quad (3)$$

where C_i is capacitance of gate dielectric, A is gate-voltage-independent effective accumulation-layer thickness, V_G is applied gate voltage and L is the thickness of gate dielectric. Eqs. (2) and (3) are derived by Lang et al. and Kalb and Batlogg, respectively [14,15]. Using $C-V$ measurements, a value of 2.4 for the relative dielectric constant is obtained. The trap DOS depends critically on the rate of change of activation energy with gate voltage. In particular, at high gate biases, the values of the trap DOS calculated by Eq. (3) are quite different from those by Eq. (2). This is a difference of two orders of magnitude between two methods, in which Eq. (3) is more sensitive to variations in activation energy in the high gate bias regime. Similar observations have been also reported by Kalb and Batlogg [15].

Experiments were performed with different device sets of bottom-gate bottom-contact PDPP-TBT TFTs to evaluate the effects of run-to-run variation. In a lower mobility set of samples compared to that reported above, the field-effect mobility is $0.13 \text{ cm}^2/\text{V}\cdot\text{s}$ in hole-enhancement mode and $0.07 \text{ cm}^2/\text{V}\cdot\text{s}$ in electron-enhancement mode. Fig. 4a shows the comparison of activation energy as a function of $V_{GS}-V_{ON}$ between the high mobility sample and the low mobility sample for both holes and electrons. The low mobility sample possesses higher activation energy over the high mobility sample. The difference between high and low mobility samples is less than a factor of two. Hence, the difference of the activation energy is not large. It is expected that the lower mobility PDPP-TNT TFTs possess a different density-of-trap states distribution. This is consistent with increased activation energy related with density of localized states. As shown in Fig. 4a, the increase in activation energy for the electrons is more than that of the holes. It is very likely that these variations in mobility are due to different degrees of exposure to air which affects electron transport more than hole transport [27,28]. Upon long exposure to air, the electron mobility falls. This is fairly a common observation in n-channel FETs. The μ_0 val-

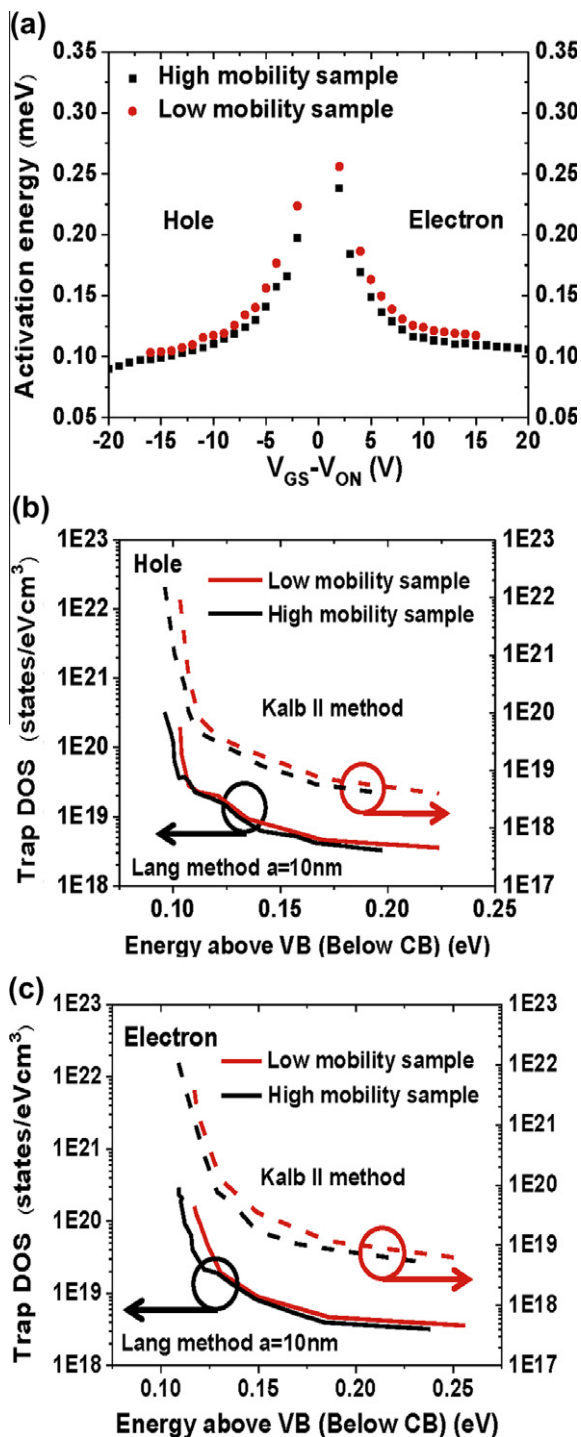


Fig. 4. (a) The comparison of activation energy as a function of $V_{GS} - V_{ON}$ and the density of trap states in the band gap as calculated with two different methods of (b) Lang et al., and (c) Kalb and Batlogg in PDPP-TBT TFTs between high mobility sample and low mobility sample in both holes and electrons.

ues of low mobility samples are also more than $4 \text{ cm}^2/\text{V}\cdot\text{s}$ at most temperatures. As shown in Fig. 4b and c, the calculated trap DOS in the high mobility sample is less than that

in the low mobility sample for a given energy, which is expected. This is confirmed by the trap DOS of holes and electrons calculated by Eq. (3) which well reflects the difference of activation energy between the high and low mobility samples as compared to Eq. (2).

The symmetry between the electron and hole transport characteristics, parameters and activation energies is remarkable. This is evident in the figures. We believe that our work is the first charge transport study of an ambipolar organic/polymer based field-effect transistor with room temperature mobility higher than $0.1 \text{ cm}^2/\text{V}\cdot\text{s}$ in both electrons and holes [28–30]. Polymers that have exhibited ambipolar behavior through the use of suitable dielectrics have hitherto generally exhibited low mobilities [31].

4. Conclusion

In summary, we have reported charge transport studies on high mobility and balanced transport ambipolar PDPP-TBT TFTs. Through temperature and gate-bias dependent field-effect mobility measurements, the activation energies and trap DOS were calculated for electron and hole charge carriers. The decrease in activation energy with increasing $V_{GS} - V_{ON}$ in both holes and electrons indicate that the main charge transport mechanism in this organic semiconductor is multiple trap and thermal release. The trap density of states in ambipolar PDPP-TBT TFTs has also been calculated using two analytical methods developed by Lang et al. and Kalb and Batlogg. The trap DOS depends on sample processing conditions, device geometry and history of the samples exposure to ambient conditions. This materials is unique in that there is appears to be delocalization of both holes and electrons as well as relatively low and symmetric trap distributions for both electrons and holes. This leads to the observed high electron and hole mobilities.

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