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Charge transport in a regioregular poly(3-octylthiophene) film

Yoshihito Kunugi,[a] Yutaka Harima,*[a] Kazuo Yamashita,[a] Nobuaki Ohta[b] and Sotaro Ito[b]

[a]*Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan. E-mail: harima@mls.ias.hiroshima-u.ac.jp*
[b]*Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan*

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Apparent mobilities of positive charge carriers in a regioregular poly(3-octylthiophene) (POT) film at various doping levels are evaluated by an electrochemical technique combining potential-step chronocoulometry and an *in situ* conductivity measurement. The carrier mobility decreases from 5×10^{-3} cm^2 V^{-1} s^{-1} to 5×10^{-4} cm^2 V^{-1} s^{-1} as the doping level increases from 0.014% to 1%. Further electrochemical doping results in a dramatic increase in the mobility, reaching 0.5 cm^2 V^{-1} s^{-1} at a maximum doping level of 23%. The decrease of the apparent carrier mobilities in the low doping range is ascribed to both scattering of polarons by ionized dopants and the formation of immobile π-dimers which are favored in the highly stacked POT film. The marked increase of mobilities at doping levels beyond 2% is explained by the formation of bipolarons, followed by the evolution of the metal-like conduction.

Introduction

Conducting π-conjugated polymers are receiving much attention as active components in electronic devices such as light emitting diodes,[1] photovoltaic cells,[2] field effect transistors[3] and their integrated organic devices.[4] These conducting polymers can be doped chemically and electrochemically, and their electrical conductivities vary from insulating to metallic regime accordingly. This remarkable increase in conductivity has been found to be accompanied by an increase in the mobility of charge carriers.[5–7] For example, the apparent mobility of positive charge carriers in a poly(3-methylthiophene) (PMT) film is increased monotonously from 2×10^{-5} cm^2 V^{-1} s^{-1} to 0.1 cm^2 V^{-1} s^{-1} by electrochemical ClO_4^- doping,[5] in contrast to the cases of inorganic semiconductors such as Si and GaAs, where the mobilities decrease with an increase in the doping level.[8] The dramatic increase in the apparent mobility is reasonably explained by the alternation of the main charge carrying species from polarons to bipolarons, which are much more mobile than polarons.[5]

Recently, it has been found that highly stacked π-conjugated oligomers and polymers such as sexithiophene (α-6T), pentacene, anthradithiophene and regioregular poly(3-alkylthiophene) (PAT) give high field-effect mobilities of 10^{-2}–1 cm^2 V^{-1} s^{-1} in their neutral states.[3] These values are at least two orders of magnitude greater than mobilities of 10^{-6}–10^{-4} cm^2 V^{-1} s^{-1} for amorphous π-conjugated polymers such as polyacetylene (PA) and polythiophene (PT) and PMT in their neutral or lightly doped states.[5–7] Up to the present time, however, mobilities in the highly stacked polymer films at variously doped states have not been reported yet, because the mobilities for the doped π-conjugated compounds cannot be measured by using the FET or time-of-flight technique.

In this work, mobilities of positive charge carriers in a regioregular poly(3-octylthiophene) (POT) film at various oxidation stages are evaluated by use of a recently developed electrochemical technique, combining *in situ* conductivity measurement and potential-step chronocoulometry.[5,6] POT is known to give a well-defined highly stacked film.[9] *In situ* EPR measurements are also performed in order to characterize charge carriers in the POT film.

Experimental

Chemicals used were of reagent grade or better. Tetraethylammonium perchlorate (Et_4NClO_4) was recrystallized from ethanol and dried under vacuum at 120 °C for more than 6 h. Acetonitrile (CH_3CN) was refluxed over P_2O_5 for several hours under N_2 and then distilled before use. Silver(I) perchlorate ($AgClO_4$) and regioregular POT (Aldrich) were used as received. Electrochemical measurements were carried out using a three-electrode system in CH_3CN containing 0.1 M Et_4NClO_4 under N_2 atmosphere with a Hokuto Denko Ltd. HAB-151 potentiostat/galvanostat. An Ag/0.1 M $AgClO_4$ (Ag/Ag$^+$) and a coiled Pt wire were used as the reference and counter electrodes, respectively. *In situ* conductivity (σ) measurements were performed by using a two-probe method.[5,6] A micro-array Pt electrode (100 lines, separation distance between electrodes = 20 μm, total width = 50 cm) was used for measurements of high resistance films (doped at 0–0.15 V). A conventional two-band Pt electrode (separation distance between electrodes = 20 μm, width = 5 mm) was used for measurements of low resistance films (doped at 0.1–0.8 V). The POT films were deposited on the Pt electrodes by spin-coating from the chloroform solutions. Doping and dedoping charges were measured with the potentiostat and a Hokuto Denko HF-104 bipolar coulometer, by stepping a potential from −0.1 V to a desired potential and back to −0.1 V, respectively.[5,6] Doping levels, defined as the number of charges per thiophene ring, were calculated from the dedoping charge, a weight of the dedoped film and a molecular weight of a repeated unit of the POT. Apparent carrier mobilities (μ) in the POT film at various doping levels were calculated from the relation $\mu = \sigma / ne$, where n is the density of charge carriers and e is the electronic charge. The carrier density n was estimated from the dedoping charge and film thickness of the POT film. *In situ* UV–vis–NIR spectra were measured by means of a Shimadzu UV-3101 PC spectrophotometer.[10] *In situ* EPR measurements were performed by using a JEOL FE1X EPR spectrometer as described elsewhere.[11] The intensities and the magnetic fields of the EPR spectra of the POT films were calibrated by the simultaneously measured EPR spectra of Mn^{2+} in MgO as an external standard. A relative number of

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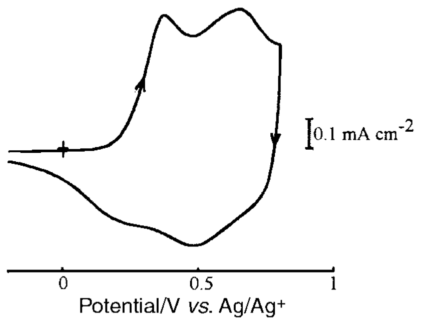

Fig. 1 Cyclic voltammogram of the POT film coated on a Pt electrode in CH_3CN–0.1 M Et_4NClO_4. Potential sweep rate is 100 mV s^{-1}.

spins (N_s) in the POT film was evaluated by double integration of an EPR spectrum. All the measurements were performed at room temperature under N_2 atmosphere.

Results

Fig. 1 shows a typical cyclic voltammogram of the POT film on a Pt electrode in CH_3CN containing 0.1 M Et_4NClO_4. Two anodic peaks are observed at 0.37 and 0.64 V with broad cathodic peaks at around 0.22 and 0.48 V, respectively. Similar two-step oxidation peaks have been observed by McCullough *et al.*[9a] and Louarn *et al.*,[9c] which are attributed to two distinct electro-oxidation processes of the POT film.

Doping levels of the POT film are plotted as a function of the electrode potential in Fig. 2(a). Doping and dedoping charges were close to each other in the whole potential range investigated and they were very reproducible with errors less than 5%. The doping level for the POT film was 0.014% at 0 V and increased with the increase in oxidation potential. At potentials between 0 V and 0.15 V, the plot yielded a straight line with a slope of 63 mV which is close to the value of 60 mV predicted from the Nernst equation for a reversible one-electron transfer reaction at room temperature. Oxidation at more positive potentials increases the doping level and it reached 23% at 0.8 V. This value is comparable with the doping levels for the fully doped PMT (23% at 0.7 V) and PT (20–26% at 0.8 V) films.[5,6]

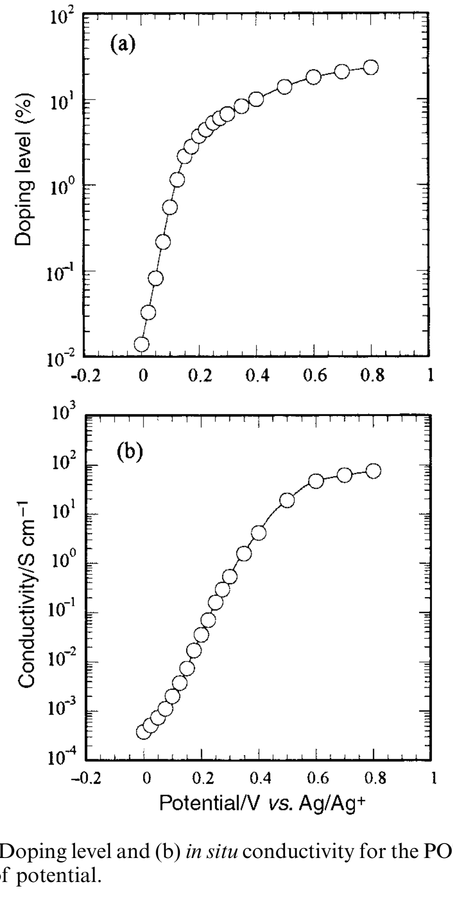

Fig. 2 (a) Doping level and (b) *in situ* conductivity for the POT film as a function of potential.

Conductivities of undoped POT films were fairly small, about 10^{-6} to 10^{-7} S cm^{-1}. However, the conductivities are increased by electrochemical doping and show an increase of *ca.* five orders of magnitude from 3.8×10^{-4} S cm^{-1} at 0 V to 74 S cm^{-1} at 0.8 V as shown in Fig. 2(b). It is noted that the conductivity of the POT film at 0.8 V is almost the same as the value reported for the POT film chemically doped with $FeCl_3$.[9a]

Fig. 3 depicts a plot of the apparent mobility *vs.* doping level for the POT film. The mobility is 4.6×10^{-3} cm^2 V^{-1} s^{-1} at the lowest doping level of 0.014% attainable in the present experiments. As is seen in the figure, the mobility tends to increase with a decrease in the doping level. In view of this, the mobility in the undoped (neutral) POT film, not measured in the present experiments, may be nearly equal to the field-effect mobilities (0.01–0.045 cm^2 V^{-1} s^{-1}) reported for undoped films of a regioregular poly(3-hexylthiophene).[3b] The carrier mobility decreases by about one order of magnitude from 4.6×10^{-3} cm^2 V^{-1} s^{-1} at 0.014% to 5.4×10^{-4} cm^2 V^{-1} s^{-1} at 1.1%. On the contrary, the mobility increases strikingly at doping levels beyond 2% and reaches 0.53 cm^2 V^{-1} s^{-1} at a maximum doping level of 23%. This V-shaped change in the mobility has not been observed with other conducting polymers such as PT, PMT and PA. In case of these ordinary conducting polymers the mobilities are increased monotonously by electrochemical or chemical doping.[5–7]

In order to characterize carrier species, *in situ* UV–vis–NIR and *in situ* EPR measurements were performed. Electrochemical oxidation of the POT film resulted in a decrease in the absorption due to π–π* transition at *ca.* 2.4 eV and, in contrast, in the increase of two absorption peaks at 1.6 eV and 0.8 eV corresponding to bipolaron bands.[9c] Such spectral changes were clearly observed with the POT films doped at levels greater than 2%, but not less than this. In other words it was very difficult to specify spectroscopically the charge carrier species in the lightly doped POT films.

Typical EPR spectra for the POT film doped at different potentials are shown in Fig. 4. An EPR signal at the lowest doping level of 0.014% at 0 V is relatively small, but it becomes larger with progress in electrochemical doping. The *g*-factors of the EPR spectra for the POT films were almost constant and close to the value for free electrons (2.0023). Fig. 5(a) shows double logarithmic plots of N_s *vs.* doping level for the POT film compared with the electrochemically synthesized PMT film.[11]

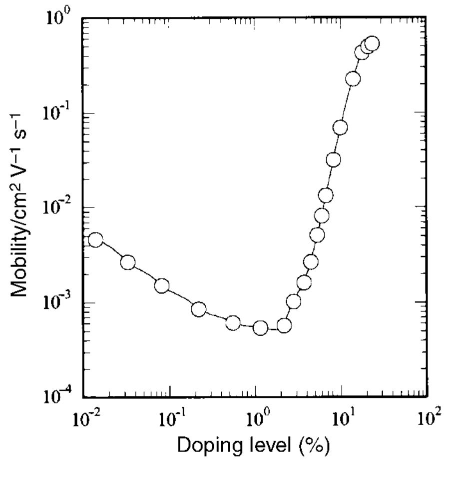

Fig. 3 Apparent mobilities of charge carriers in the POT film at different doping levels.

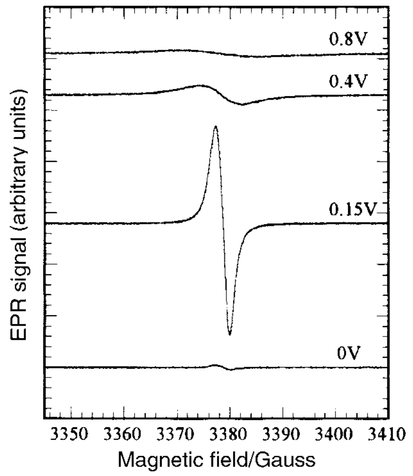

Fig. 4 Typical EPR spectra of the POT film at various doping levels.

The N_s values for the POT film increase linearly with an increase in the doping level up to about 2% and the slope of the plot is smaller than unity. This suggests that spinless species are generated as well as paramagnetic polarons. The plot levels off at doping levels beyond 2%, indicating that the spinless species are predominantly formed there. On the other hand, the N_s values for the PMT film increase in proportion to the doping level up to *ca.* 0.2%, but beyond 0.2% the plot tends to deviate downward from the straight line with a slope of unity. As shown in Fig. 5(b), peak-to-peak linewidth (ΔH_{pp}) of the EPR spectrum for the POT film is almost constant about 3 G at the doping levels below 2%, while the ΔH_{pp} for the PMT film varies from 4.7 to 1.2 G. However, the ΔH_{pp} for the POT film increases with an increase in the doping level above 2%, while the N_s levels off. It is worthy of note that the increase in the ΔH_{pp} synchronizes with that of the mobility. The ΔH_{pp} for the PMT film increases also at the doping level more than 2%. The maximum ΔH_{pp} value for the POT film (14.3 G at 23%) is much greater than those for electrochemically doped PMT[11,12] (8 G at 23%), PT[13] (3 G at 30%) and poly(3-phenylthiophene) (PPT)[14] (2 G at 22%) films.

Discussion

A salient feature to be noticed in Fig. 3 is that the apparent mobilities decrease with the increase in doping level up to *ca.* 2%. This has not been observed yet with other conducting polymers.[5–7] The following three possibilities will be discussed below to account for the anomalous change in the mobility: (i) formation of immobile carriers, (ii) stacked structure change of the film and (iii) scattering of charge carriers by anions incorporated into the POT film.

(i) The downward deviation of the N_s plot for the POT film from a straight line with unity slope in Fig. 5(a) suggests that diamagnetic species are generated as well as paramagnetic polarons in the doping range of interest. For common conducting polymers bipolarons are generally considered as the spinless species in the doped films. It should be noticed that the ΔH_{pp} values for the POT are almost constant (3 G) at doping levels less than 2%, whereas the ΔH_{pp} value for the PMT film decreases from 4.7 to 1.2 G in the doping level range of 0.1–1%. In the case of the PMT film, polarons and bipolarons are in equilibrium in the doping range and the molar fraction of bipolarons increases with the increase of the doping level. Hence, the decrease of the ΔH_{pp} value for PMT is interpreted in terms of the exchange narrowing due to interactions between the polaron and bipolaron.[11] If diamagnetic species like bipolarons are generated in the POT film and coexist with polarons in the doping range of 0.014–2%, similar exchange narrowing should be observed. However, the ΔH_{pp} values for the POT film were not decreased by increasing the doping level but remained almost constant. This indicates that the diamagnetic species in the POT film are not bipolarons. Recently, Miller *et al.* have found that oligothiophenes yield cation radical π-dimers in solutions and solids.[15] It is presumed that the cation radical π-dimer formed with two polarons on separate oligomers has a close face-to-face contact between thiophene rings. In the case of π-conjugated polymers, the cation radical π-dimer is regarded as a dimer of two polarons on neighboring polymer chains, while the bipolaron is a dimer of two polarons on the same polymer backbone. Consequently, the diamagnetic π-dimers may preferentially be formed in the POT film because of the stacked structure. So, the constant value of ΔH_{pp} for the POT film in the doping level range of 0.014–2% implies that the exchange rate of the polaron and diamagnetic π-dimer is extremely slow.

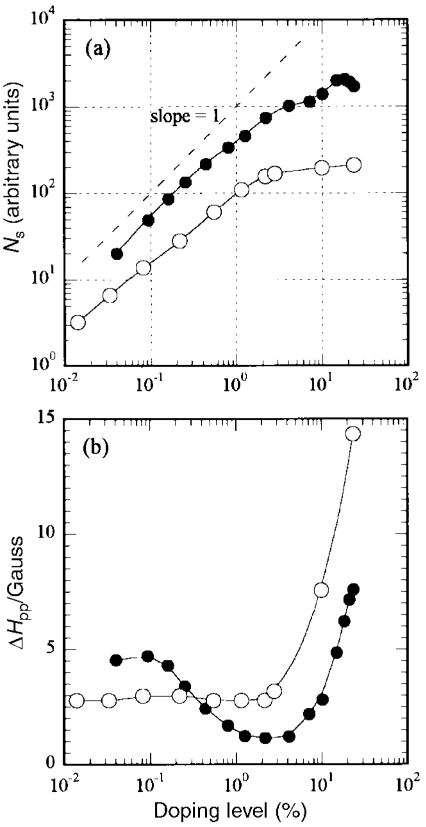

Fig. 5 (a) Double logarithmic plots of N_s *vs.* doping level for the POT (○) and PMT (●) films. (b) ΔH_{pp} of the EPR spectra for the POT (○) and PMT (●) films at different doping levels. Data of the PMT film are cited from reference 11.

In Fig. 3, the charge carrier mobility in the POT film is evaluated as an apparent mobility, which is calculated according to the equation $\mu=\sigma/ne$. However, if two kinds of charge carriers, *i.e.* polaron and π-dimer, relate to conduction in the POT film, the apparent mobility μ is given by eqn. (1),

$$\mu=\mu_p\frac{n_p}{n}+2\mu_\pi\frac{n_\pi}{n} \quad (1)$$

where μ_p (μ_π) and n_p (n_π) are mobility and density of the polaron (π-dimer), respectively and $n=n_p+2n_\pi$. The slope of the double logarithmic plot of N_s *vs.* doping level for the POT film is smaller than unity (Fig. 5(a)), suggesting that the molar fraction of paramagnetic polarons, n_p/n, decreases with increasing the doping level. If the values of μ_p and μ_π are constant and $\mu_p > \mu_\pi$, the apparent mobility decreases with the increase of the doping level. On the other hand, when μ_p is smaller than μ_π, the apparent mobility should increase with the doping level. In a previous work,[16] we have successfully evaluated mobilities of the cation radical π-dimers in poly[(-ethoxypropylsilanylene)quinque(2,5-thienylene)] (MS5T-OEt) films. In this case, the mobility of the π-dimer in the MS5T-OEt film is found to be extremely small compared with that of the polaron. Therefore, the decrease of apparent mobilities in the POT film with the increase of doping levels may be explained qualitatively by the increase of molar fractions of π-dimers. In the meanwhile, Zotti has found that for crown-5-substituted poly(cyclopentadithiophene) dimerized polarons (dimers of the polarons) are formed on neighboring polymer chains and thus behave as pinned charge species.[17]

If the π-dimer is immobile or the mobility is negligibly small compared with that of the polaron, the apparent mobility can be given by eqn. (2), derived from eqn. (1) with $\mu_\pi = 0$.

$$\mu = \mu_\mathrm{p} \frac{n_\mathrm{p}}{n} \tag{2}$$

The n_p/n values for the POT film can be estimated from the N_s-doping level plot shown in Fig. 5. The mobilities calculated by eqn. (2) are plotted against the doping level in Fig. 6, where the value of n_p/n is assumed to be unity at the lowest doping level of 0.014% and then the μ value is equal to the μ_p (4.6×10^{-3} cm^2 V^{-1} s^{-1}). It is worthy of note that the calculated mobilities tend to decrease with the increase in the doping level. However, the doping level dependence of the mobilities calculated by eqn. (2) is smaller than that experimentally observed.

(ii) It has been reported that the crystal structure of the regioregular PAT is affected by doping.[18] Namely, the distance between main chains along the side alkyl chain increases by 10–20% upon full anion doping, while the distance between neighboring conjugation planes decreases slightly. This may lead to the increase in mobility with the increase of the doping level. However, the deduction is inconsistent with the observed doping level dependence of the mobility as shown in Fig. 6. Therefore, it is unlikely that the mobilities of charge carriers are decreased by the change of the crystal structure of the POT film.

(iii) For inorganic semiconductors, it is well known that charge carriers are scattered by ionized impurities (dopants), resulting in a decrease in the mobility.[8] To the best of our knowledge, however, there is no such report concerning organic semiconductors. For inorganic semiconductors, the relation of carrier mobility (μ_I) to the number of ionized impurities per cubic metre (N_I) is given by eqn. (3),

$$\mu_\mathrm{I} \propto \frac{T^{\frac{3}{2}}}{N_\mathrm{I} \ln(1+x^2)} \tag{3}$$

where $x = 1.8 \times 10^5\ TN_\mathrm{I}^{-1/3}$ and T is the absolute temperature. Assuming that the mobility of the π-dimer is negligibly small and this equation is applicable for the organic semiconductors, *e.g.* POT, the apparent mobility μ is given by combination of eqns. (2) and (3).

$$\mu \propto \frac{T^{\frac{3}{2}}}{N_\mathrm{I} \ln(1+x^2)} \frac{n_\mathrm{p}}{n} \tag{4}$$

where N_I is regarded as the number of anions embedded by electrochemical doping. The apparent mobilities calculated by eqn. (4) at 25 °C are plotted against the doping level in Fig. 6. The calculated result agrees well with that experimentally observed at doping levels below 1%. Consequently, the doping level dependence of the apparent carrier mobility observed with the POT film is interpreted by taking account of both (i) formation of immobile π-dimers and (iii) scattering of the mobile carriers (polarons) by anion dopants.

At doping levels beyond 2%, the carrier mobilities in the POT film increase by about three orders of magnitude (Fig. 3) and ΔH_pp values also increase markedly (Fig. 5b), but the N_s values level off (Fig. 5a). These results are attributed to the formation of bipolarons,[11] which is inferred from the UV–vis–NIR spectra. Accordingly, as in ordinary conducting polymers,[5–7] bipolarons are generated predominantly as charge carriers in the POT film at doping levels beyond 2%, and then the conduction mechanism changes from the hopping transport to the metal-like conduction.

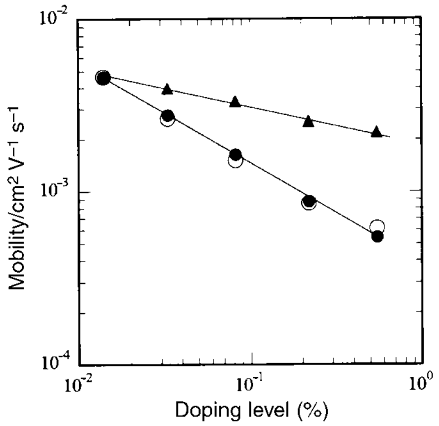

Fig. 6 Apparent carrier mobilities (○) experimentally observed and (▲ and ●) calculated from eqns. (2) and (4) at different doping levels.

Conclusions

We have successfully evaluated the apparent carrier mobilities in the POT film at various doping levels by using a novel technique combining a potential-step chronocoulometry and an *in situ* conductivity measurement. The apparent carrier mobilities decrease from 5×10^{-3} cm^2 V^{-1} s^{-1} to 5×10^{-4} cm^2 V^{-1} s^{-1} when the doping level increases from 0.014% to *ca.* 1%. This decrease is explainable in terms of the formation of immobile π-dimers and scattering of polarons by anions incorporated as dopants. Further electrochemical doping beyond 2% caused a remarkable increase of the mobility and it reached 0.5 cm^2 V^{-1} s^{-1} at the maximum doping level of 23%. Bipolarons are predominant carriers generated at doping levels greater than about 2%, and then the conduction mechanism changes from the hopping transport to the metal-like conduction.

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