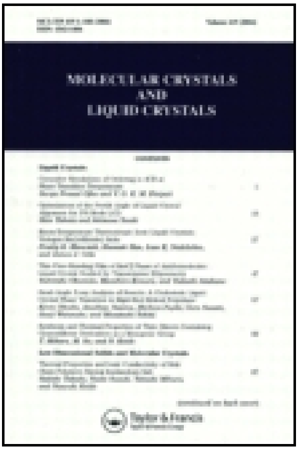

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Effect of Liquid Crystal Classes on the Improvement of Dynamic Scattering by Electron Donor-Acceptor Dopants†

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Effect of chemically different nematic liquid crystal (LC) classes are described with the improvement of their dynamic scattering (DS) cut-off frequency f_c by electron donor and acceptor dopants. The f_c improvement was found to be typically classified into the following categories, according to the LC classes:

1) The simultaneous doping of a donor and an acceptor is the most effective or needed for increase in f_c.

2) The single doping of only an acceptor realizes such an f_c improvement as equivalent to or more effective than the simultaneous one.

3) Even the doping of a donor-acceptor pair is not useful for increase in f_c.

4) Any dopant of a donor type presents no noticeable f_c improvement.

Based on these results, the new schemes for electrochemical behavior of donor and acceptor dopants in LCs under dc electric fields are proposed, in which a cation and an anion are assumed to be generated by the ionic dissociation of charge transfer complexes.

1 INTRODUCTION

Liquid crystal (LC) display devices are operated mostly with ac excitation, but not with dc excitation, mainly because of drastic electrochemical degradation of LCs under dc electric fields. DC excitation is, however, very desirable from

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†This work was presented at The Eighth International Liquid Crystal Conference, Kyoto, June 30-July 4, 1980.

a viewpoint of simplifying the electronic circuit for driving the display devices, and in some cases, typically, such as a video display device of the dynamic scattering mode employing an integrated FET switching array,[1,2] dc operation seems to be inescapable. This research deals with conductivity dopants for use in dc dynamic scattering display devices.

Pure nematic LCs with high electrical resistivities do not show the dynamic scattering phenomenon. Therefore, conductivity dopants are essentially prerequisite for dynamic scattering.[3,4] A variety of organic electrolytes (salts) has been used effectively as such dopants. However, the electrolytes are not suitable for dc dynamic scattering, because of an electrochemical degradation in LCs.[5] Hence, a usage of some electron donor and acceptor types of dopants has been tried in the dc case.[6–12]

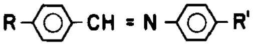
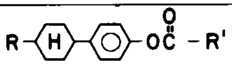
In this paper, we concentrate on describing the effect of chemically different nematic LC classes on the improvement of the dynamic scattering cut-off frequency f_c by electron donor and acceptor dopants and comment on the electrochemical behavior of the dopants in the LCs.

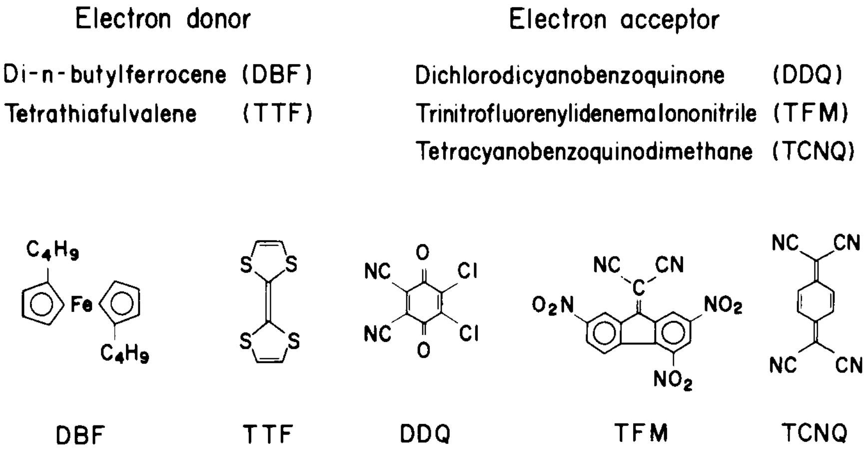
2 EXPERIMENTAL

The nematic LCs used were negative dielectric multicomponent mixtures summarized in Table I, where the parenthesized numbers indicate the number of mixed components in each mixture and the symbol NI denotes the nematic-isotropic transition temperature. They belong to Schiff base, phenyl cyclohexanoate, phenylcyclohexane and phenyl benzoate classes, respectively, and

TABLE I

Multicomponent nematic mixtures of different liquid crystal (LC) classes used in the experiments.

Mixture	Chemical class	Chemical structure	NI (°C)
SB	Schiff base	 (2)	63
ECH	Phenyl cyclohexanoate	 (7)	69
PC	Phenylcyclohexane	 (3)	80
PB	Phenyl benzoate	 (3)	60
ECH/PB	Phenyl cyclohexanoate + Phenyl benzoate (9)		67
PC/ECH	Phenylcyclohexane + Phenyl cyclohexanoate (3)		51



Electron donor		Electron acceptor	
Di-n-butylferrocene	(DBF)	Dichlorodicyanobenzoquinone	(DDQ)
Tetrathiafulvalene	(TTF)	Trinitrofluorenylidenemalononitrile	(TFM)
		Tetracyanobenzoquinodimethane	(TCNQ)

FIGURE 1 Electron donor and acceptor types of conductivity dopants added to the LC mixtures.

their mixed-class mixtures. The abbreviations for the mixtures shown in the first column of the Table are used in the following.

The conductivity dopants added to the LC mixtures included typical electron donors such as DBF and TTF, and strong electron acceptors such as DDQ, TFM and TCNQ, which are shown in Figure 1.

Samples for f_c measurements were prepared by doping LC mixtures with donors and acceptors separately, as well as simultaneously. The doping concentration was typically 0.5% wt. in separate doping and about 1.0% wt. totally in simultaneous doping.

Here we must explain why we use the dynamic scattering f_c instead of the electrical resistivity itself in this work. The reason is that the parameter f_c has more practical meaning, that is, the upper excitation frequency limit for dynamic scattering induction. For convenience, we adopt f_c at ac sine-wave 25 Vrms through this work. The f_c value was measured by observing the disappearance of the dynamic scattering phenomena in LC samples in course of increasing the excitation frequency.

3 RESULTS AND DISCUSSION

Figure 2 represents the typical f_c dependence of optical transmission in a dynamic scattering cell under dc electric fields. The transmission decreases with increasing f_c and then reaches a constant value. These results show that an increase in f_c to a certain level is basically needed to obtain a sufficient dynamic scattering intensity, even under dc excitation.

The needed f_c level was found at around 400 to 500 Hz for the LC mixtures

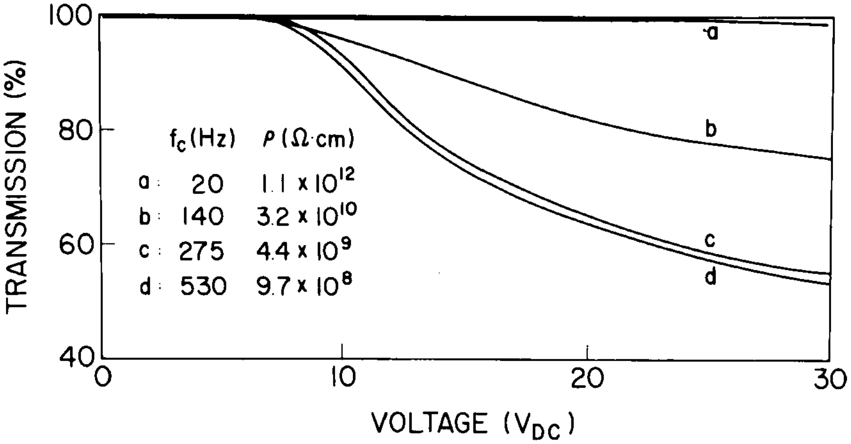


FIGURE 2 Transmission vs applied dc voltage curves for a dynamic scattering (DS) cell of ECH/PB LC mixture with various values of f_c, doped with a DBF·TCNQ pair.

used in this work. Tables II shows the f_c improvement by various electron donors and acceptors and by their pairs for different LC classes, where all values except the lower ones in the second column indicate the f_c (Hz) at ac-sw 25 Vrms and the lower ones, the specific resistivities measured at 25 Vdc.

TABLE II

Effect of donor and acceptor dopants on the DS cut-off frequency f_c (Hz) for various LC classes.

Dopant / LC class	non	DBF	DDQ	DBF DDQ	TCNQ	DBF TCNQ	TFM	DBF TFM
SB	29 (8.3×10^{11})	55	9K	4.6K	10K	10K	3K	2.3K
ECH	<10 (2.2×10^{13})	40	150	2K	100	300	25	40
PC	<10 (2.8×10^{11})	20	—	—	50	40	—	—
PB	40 (2.8×10^{10})	120	150	5.5K	800	3K	23	2.5K
ECH/PB	20 (1.1×10^{12})	40	30	1.2K	100	400	—	—
PC/ECH	<10 (1.3×10^{12})	25	30	800	—	—	—	—

From these experimental results, we can see that the improving effect depends largely on LC classes, as well as dopants. From a f_c improvement LC class-dependence viewpoint, we can classify the dopant effects into the following four categories:

(1) For the LC classes of ECH, PB, mixed ECH and PB and mixed PC and ECH, the simultaneous addition of a donor and an acceptor is the most effective or needed for increase in f_c.

(2) The single doping of only an acceptor realizes f_c improvement, which is equivalent to or more effective than the usage of a donor-acceptor pair. Only the SB LC class belongs to this case.

(3) For the PC and ECH LC classes, even the addition of a donor-acceptor pair is completely not effective for f_c increase.

(4) The last case is where no donor-type dopant shows noticeable f_c improvement for all LC classes.

Here we will propose possible schemes for electrochemical behavior of donor and acceptor dopants in LCs, which are consistent with the preceding experimental facts described in the cases (1), (2) and (4). Figures 3 (a), (b) and (c) show our new schemes. Figures 3 (a'), (b') and (c'), on the other hand, represent the schemes proposed recently by the Hughes' research group, which correspond to the cases of our schemes (a), (b) and (c), respectively.

It should be noted that there is a large fundamental difference between our schemes and theirs. In our schemes, a pair of ions are assumed to be generated

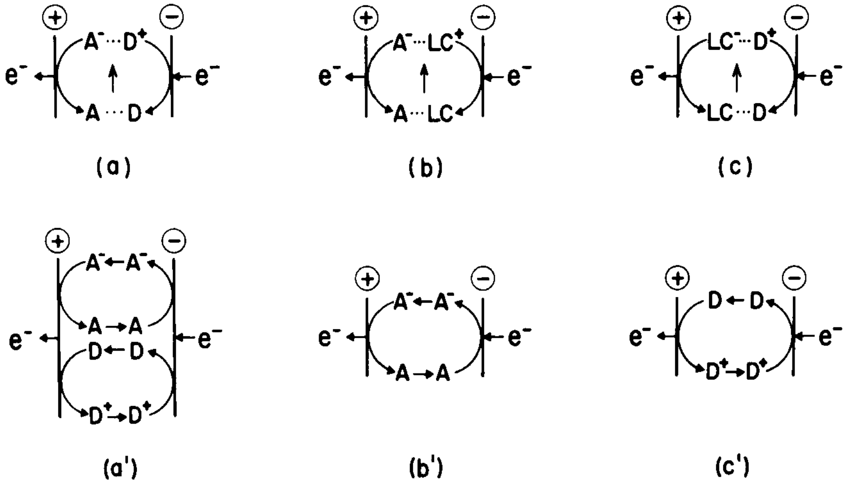


FIGURE 3 Schemes for electrochemical behavior of the electron donor (D) and acceptor (A) dopants in LCs: (a), (b), (c) are our new ones; (a'), (b'), (c') are the ones proposed by Lim, *et al.*

chemically, but not electrochemically, by the ionic dissociation of charge transfer complexes according to the following equations:

$$D + A \rightleftharpoons D \cdot A \rightleftharpoons D^{+} + A^{-} \qquad (1)$$

$$LC + A \rightleftharpoons LC \cdot A \rightleftharpoons LC^{+} + A^{-} \qquad (2)$$

$$D + LC \rightleftharpoons D \cdot LC \rightleftharpoons D^{+} + LC^{-} \qquad (3)$$

The complexes (D · A, LC · A, D · LC) are obviously formed by the association between an electron donor (D) and an acceptor (A) or one of them and a LC, as shown in the above equations.

Therefore, in our schemes, the chemically generated cation and anion migrate to the cathode and anode, respectively, under a dc electric field, discharge at the electrodes and give back the initial neutral dopants and LCs. Then, they diffuse to the center of the cell, where they recombine into a donor-acceptor complex and regenerate a pair of ions chemically, as shown in Figures 3 (a), (b) and (c).

On the other hand, according to the Hughes' schemes, ions are generated only electrochemically by a charge injection at the electrodes, as shown in Figures 3 (a′), (b′) and (c′). In these schemes, no charge transfer interaction between a donor and an acceptor and no LC participation in the generation of ions are taken into consideration. Hence, even for the LCs doped with a donor-acceptor pair, the scheme (a′) of Figure 3 was suggested by the Hughes group, in which the scheme (b′) of Figure 3 for an acceptor and the scheme (c′) of Figure 3 for a donor coexist independently. So, it seems that the scheme (a′) of Figure 3 can hardly explain the experimental fact of case (1).

In our scheme (a) of Figure 3, the increase in f_c realized by a simultaneous doping but not by a separate doping of donor and acceptor dopants is attributable to the ions generated through the dissociation of ionizable charge transfer complexes, comprizing strong donors and acceptors. Our schemes (b) and (c) of Figure 3, suggested for the electrochemical behavior of singly doped acceptors and donors, assume LC participation in the f_c improvement and need the electron donating and accepting abilities of LCs, respectively.

The experimental facts concerning case (2), that the f_c improving action of a given acceptor depends highly on LC classes and that the improvement is the most conspicuous in the SB LC class having the strongest electron-donating ability, which ability is obvious from comparison of the cyclic voltammograms of LCs shown in Figure 4, may support the presence of the charge transfer interaction between acceptors and LCs depicted in the scheme (b) of Figure 3. The electronic apparatus employed for the cyclic voltammetry of LCs and dopants is schematically shown in Figure 5. Potentials were measured against a Ag/AgCl reference electrode, using acetonitrile as a solvent and tetrabutylammonium perchlorate as the supporting electrolyte.

In our scheme (c) of Figure 3, LCs are assumed to function as electron

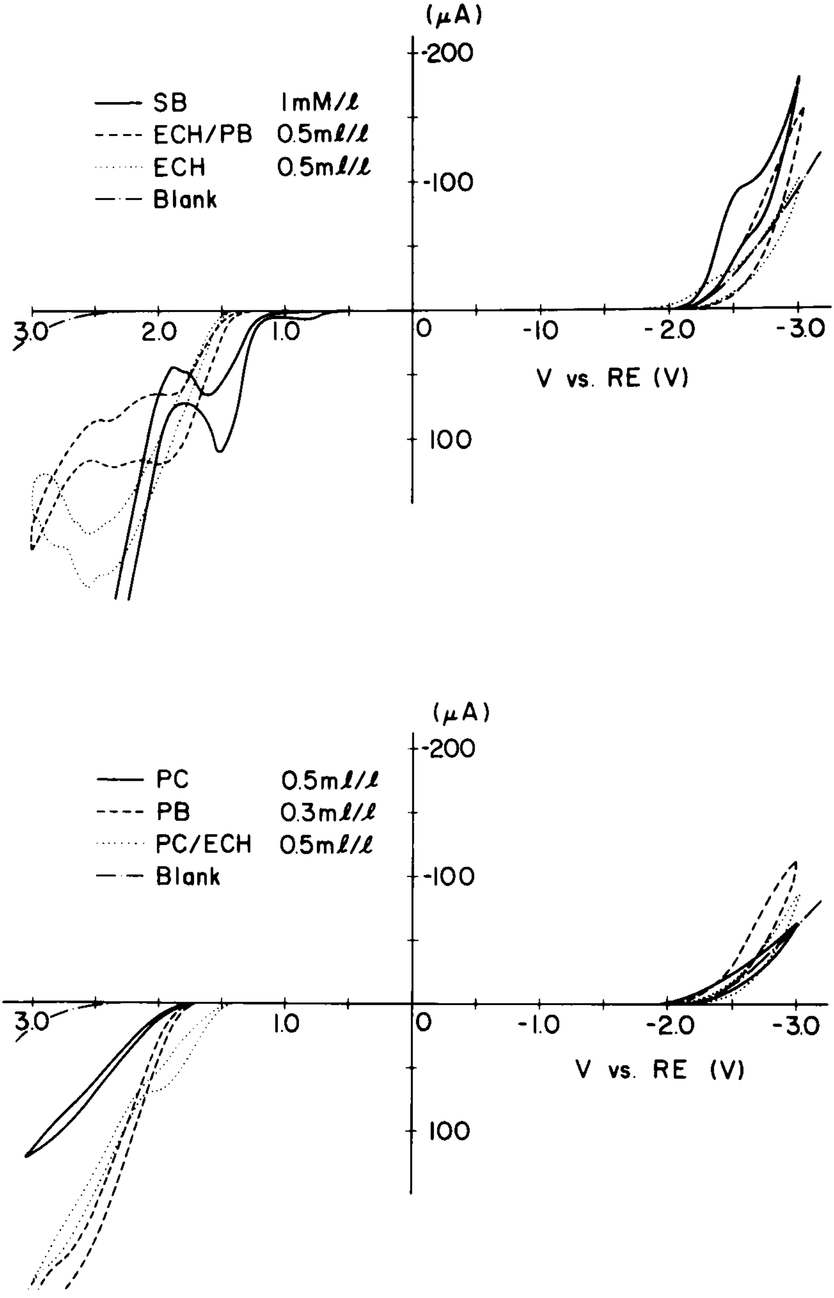


FIGURE 4 Cyclic voltammograms of different LC classes in 0.01 M TBAP solution of acetonitrile.

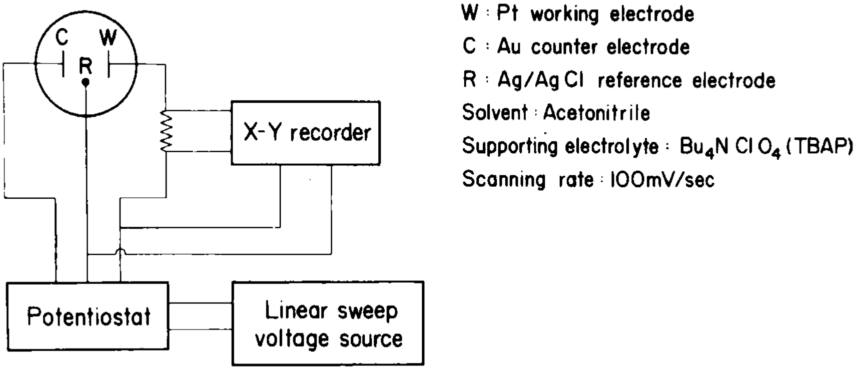


FIGURE 5 Schematic drawing of a cyclic voltammetric apparatus.

acceptors. Nevertheless, such a function can be hardly expected, because of their relatively high reduction potential shown in the voltammograms of Figure 4. This is consistent with the fact that even such a strong donor as DBF presented no noticeable f_c improvement for all LCs.

If the Hughes' schemes (b') and (c') are adopted instead of our schemes (b) and (c) (Figure 3), then the conspicuous LC class-dependence of the f_c improvement by acceptors and the ineffectiveness of donors for the improvement described before, have to be explained mainly in terms of physical parameters such as the solubility of dopants in LCs and the dielectric constant of LCs as a solvent.

However, there is not such a sufficiently large difference in dielectric constants as explains the large LC class-dependence. For solubility, for example, DBF donor which is not effective for the f_c increase is easily soluble in all LCs. This means that the solubility of dopants, as well as the dielectric constant of LCs, does not play an important role in determining the f_c improvement in this work. So, the schemes (b') and (c') of Figure 3 do not seem applicable to the explanation of our experimental results.

Here we must briefly mention the accelerated degradation life test for LCs doped with dopants under dc excitation. The dc operational lifetimes of LCs doped with a donor-acceptor pair were longer by more than one order of magnitude, as compared to those of LCs doped with a single dopant. This observation is also consistent with our schemes (a), (b) and (c) of Figure 3.

According to the scheme (a), in the LCs with a donor-acceptor pair, the electrochemical behavior should be dominated by the reversible redox reaction of both dopants, preventing LCs themselves from electrochemical reaction, since the redox potentials of the dopants used are quite low (see Figure 6), compared to those of LCs (Figure 4). This may explain the long dc operational lifetime of LCs doped with a donor-acceptor pair.

In case of LCs with a single dopant, LCs themselves must participate in

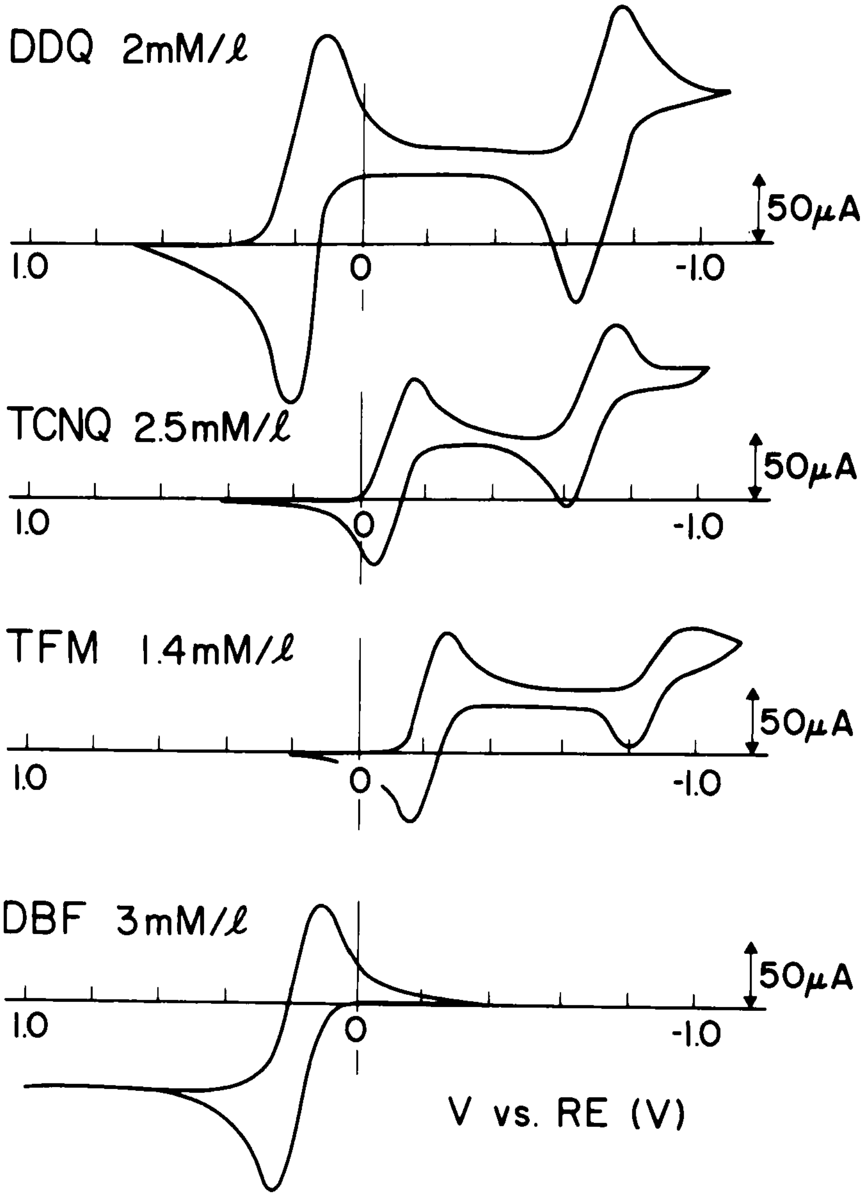


FIGURE 6 Cyclic voltammograms of electron donor and acceptors in 0.1 M TBAP solution of acetonitrile.

electrode reaction, as shown in the schemes (b) and (c) of Figure 3. This may cause a drastic degradation in LCs and remarkably shorten the dc operational lifetime, because the redox potentials of the LCs are extremely high, compared to those of the dopants, and their electrochemical redox reaction is not reversible, as shown in their voltammograms of Figure 4.

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