Substituent Effect of Fluoranthene Derivatives in Electroluminescence

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7,8,10-triphenylfluoranthene [TPF], 7,10-diphenyl-8-p-tolylfluoranthene [DPTF] and 7,10-diphenyl-8-p-cyanophenlyfluoranthene [DPCF] were synthesized by using the Knoevenagel condensation and Diels–Alder addition. TPF showed sky-blue CIE value of (0.192, 0.269) and 3.27cd/A at 10 mA/cm^2. DPTF also showed sky-blue CIE value of (0.185, 0.252) and 2.31cd/A at 10 mA/cm^2.

INTRODUCTION

Organic light-emitting diodes (OLEDs) based on organic molecules are currently the intensive subject due to their promise for full-color large display applications [1–5].

Recent studies developed materials with which both red or green have high efficiency of 10cd/A and 100,000 hours of lifetime, but blue emitting materials have not reached these with maximum capacity of 7cd/A and 12,000 hours [6]. That blue material having relatively low efficiency and short device life-time is attributed to the fact that more than 3.0 eV of band-gap is needed to have blue light. Compared to red or

green emitting materials, band-gap is relatively wide, increasing energy gap between layers, which causes charge-balance to mismatch between hole and electron. As a result, low luminance efficiency and high operating voltage are found, which leads material degradation by heating and further reduction of lifetime. Of the materials that have reported as blue materials such as Diarylanthracene [7], di(styryl) arylene [8] and pyrene [9], 4,4′-bis(2,2-diphenylvinyl)-1,1′-biphenyl (DPVBi) [8] is considered most representative. However, DPVBi has the lowest value of Tg, 64°C [10] and it is well known that low Tg has a considerable influence on life-time. Therefore, it is imperative to find new blue emitting materials with long lifetime, and it is necessary to carry out studies on various types of new blue emitting materials.

In this study, we synthesized 7,8,10-triphenylfluoranthene [TPF] [11] and TPF derivatives which are substituted by p-tolyl and p-cyanobenzene instead of phenyl at 8-position.

The materials 7,8,10-triphenylfluoranthene [TPF], 7,10-diphenyl-8-*p*-tolylfluoranthene [DPTF] and 7,10-diphenyl-8-*p*-cyanophenlyfluoranthene [DPCF] were synthesized by using the Knoevenagel condensation and Diels–Alder addition.

The thermal and electro-optical properties of these materials were characterized with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), cyclic voltammetry (CV), and UV-visible and photoluminescence (PL) spectroscopy. Moreover, multilayered EL devices were fabricated using these materials as non-doped emitting layers.

EXPERIMENTAL

Synthesis

7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one(1)

1,3-Diphenyl-2-propanone(10 g, 47 mmol) and acenaphthoquinone(8 g, 44 mmol) were added to Ethanol (300 mL), then 1 M KOH solution(47 mL, 47 mmol) was added into the reaction mixture. The mixture was heated to 50°C for 3 h under nitrogen. The reactant mixture was cooled after 1 h and then the product was filtered and washed with ethanol (yield = 14.5 g, 92.5%).

^{1}H NMR (δ, ppm): 8.07(d, 2H), 7.87(d, 2H), 7.83 (d, 4H), 7.59 (t, 2H), 7.52 (t, 4H), 7.41(t, 2H); Fab[+]-mass: 356.

7,8,10-triphenylfluoranthene [TPF]

7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one (2 g, 5.62 mmol) and ethynylbenzene (0.7 ml, 6.3 mmol) were added to xylene

(200 mL). The mixture was heated to 130°C for 10 h under nitrogen. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was dissolved in $CHCl_3$ and added to methanol. The precipitate was filtered and washed with methanol.

The yellow powder was purified by using column chromatography with $CHCl_3$: n-hexane (1:3) eluent to afford a yellowish-beige solid (TPF) (yield = 2.1 g, 86.9%).

^{1}H NMR (δ, ppm): 7.72(m, 4H), 7.55(t, 2H), 7.52 (t, 1H), 7.36 (m, 6H), 7.33 (s, 1H), 7.30(t, 2H), 7.23(d, 2H), 7.17(m, 3H), 6.68(d, 1H) ; Fab$^+$-mass: 430.

7,10-diphenyl-8-p-tolylfluoranthene [DPTF] and 7,10-diphenyl-8-p-cyanophenlyfluoranthene [DPCF]

DPTF and DPCF were synthesized as for the above series by using Diels–Alder addition.

[DPTF] (yield = 87%) ^{1}H NMR (δ, ppm): 7.71(m, 4H), 7.55(t, 2H), 7.51 (t, 1H), 7.39 (m, 6H), 7.31 (s, 1H), 7.28(m, 2H), 7.11(d, 2H), 6.99(d, 2H), 6.65(d, 1H), 3.00(s,3H); Fab$^+$-mass: 444.

[DPCF] (yield = 73%) ^{1}H NMR (δ, ppm): 7.77(d, 1H), 7.75(d, 1H), 7.69 (d, 2H), 7.55 (m, 3H), 7.46 (d, 2H), 7.40(m, 4H), 7.32(m, 5H), 7.29(d, 2H), 6.72(d, 1H), 3.00; Fab$^+$-mass: 455.

Characterization

^{1}H NMR spectra were recorded on Bruker Avance 500 spectrometers. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. The melting temperatures (T_m), glass-transition temperatures (T_g), crystallization temperatures (T_c), and degradation temperatures (T_d) of the compounds were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). A Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of 50~200 mV/s. The synthesized materials were dissolved in N,N-dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated

Ag/AgNO$_3$ reference electrode. Ferrocene was used for potential calibration and for reversibility criteria.

Density functional theoretical calculations were performed using Spartan'04 (for Windows) [12]. The structures were drawn at the entry-level of input and minimized. Equilibrium geometry was obtained at the B3LYP level of DFT for each molecule at the ground state from its initial geometry subject to symmetry with a 6–31G* basis set [13]. Orbitals and energies, atomic charges, vibrational modes, and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces were then obtained from the output.

For the EL devices, all organic layers were deposited under 10^{-6} torr, with a rate of deposition of 1 Å/s to give an emitting area of 4 mm^2. The LiF and aluminum layers were continuously deposited under the same vacuum conditions.

The current-voltage (I-V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A.

RESULTS AND DISCUSSION

Synthetic routes of three fluoranthene derivatives are described in Scheme 1. All compounds were obtained by using the Knoevenagel condensation and Diels–Alder addition.
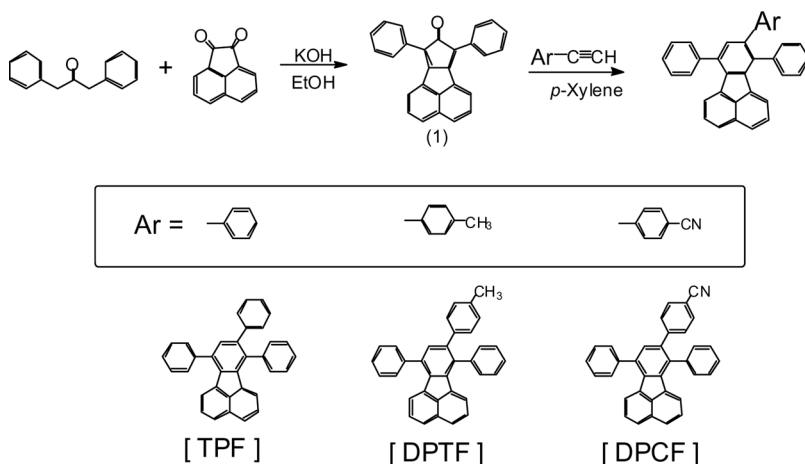
SCHEME 1 Synthetic routes of synthesized materials.

   All steps showed high yield of more than 80%. Especially it was possible to synthesize the final compound without using metal complex catalyst. This is intended to exclude a possibility that even a very small amount of metal complex could exist in the final compound. It is not easy to remove small residue portion of metal complex in synthesized compounds with various purification methods as well as sublimation. Therefore, it is possible to expect high purity of the materials and the improved life-time of device in case of this synthesis scheme.

   In the last step of purification, recrystallization and silica column were performed for all synthesized materials to increase their purity, and structures were identified with NMR, FT-IR, and Fab-Mass analysis.

   Synthesized materials are placed on glass to make a film through vacuum deposition, and UV-Visible and PL spectra are measured (Fig. 1). The data are summarized in Table 1.

   The maximum absorbance of TPF, DPTF and DPCF appeared at around 381, 380 and 384 nm, respectively. Compared to TPF or DPTF, DPCF showed UV_{onset} and UV_{max} values that are red-shifted about 4~5 nm, which is expected to be resulted from the increase of conjugation length due to triple bond of –CN.

   PL_{max} values of three compounds showed 458 nm (TPF), 461 nm (DPTF) and 453 nm (DPCF) wavelength, which are blue colors. From PL_{max} values, it was found that DPTF with electron-donating –CH_3 group was red-shifted about 3 nm more than TPF. Also, despite the increase of conjugation length by –CN group, DPCF with electrowithdrawing –CN group was blue-shifted about 5 nm. However, UV_{max} and PL_{max} values of the three materials were found to be similarly close to 381 nm and 458 nm. Based on these results, it is possible to assume that fluoranthene provides a major optical property that determines UV_{max} and PL_{max}.

   The ground-state structure and electron state of HOMO and LUMO were calculated using by B3LYP/6-31G* method of Spartan'04 program [12,13].

TABLE 1 Optical, Electrical and Thermal Properties of Synthetic Compounds

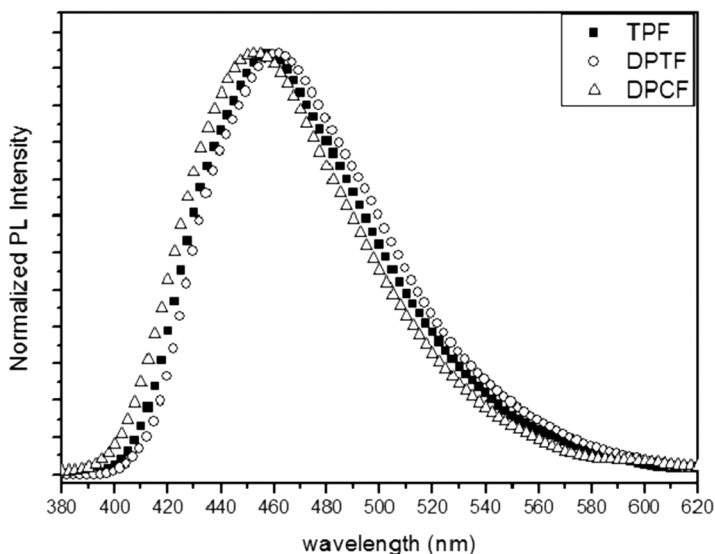|	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	HOMO (eV)	LUMO (eV)	E_g (eV)	T_g (°C)	T_m (°C)	T_d (°C)
TPF	410	381	458	5.84	2.82	3.02	–	199	323
DPTF	409	380	461	5.85	2.82	3.03	–	262	337
DPCF	415	384	453	5.89	2.90	2.99	–	236	393

FIGURE 1 Normalized PL Spectra of TPF(■), DPTF(◇) and DPCF(△) film on glass.

When the ground-state structures of three molecules were examined, it was found that the distance and the dihedral angle between fluoranthene and 7-, 8-, 10-phenyl groups were almost identical. This indicates that in TPF structure, the addition of –CH$_3$ or –CN would not have a considerable impact on the ground state structure of molecule (Table 2).

Figure 2 shows electron distribution of HOMO and LUMO in TPF, DPTF and DPCF. According to Figure 2, only DPCF shows a slight difference. Unlike TPF or DPTF, DPCF in the state of LUMO has some electron density at benzene ring of the 8-position, while the case

TABLE 2 Comparison of Distances and Dihedral Angles in Fluoranthene Derivatives at the Ground State (at Spartan'04/B3LYP/6–31G*)

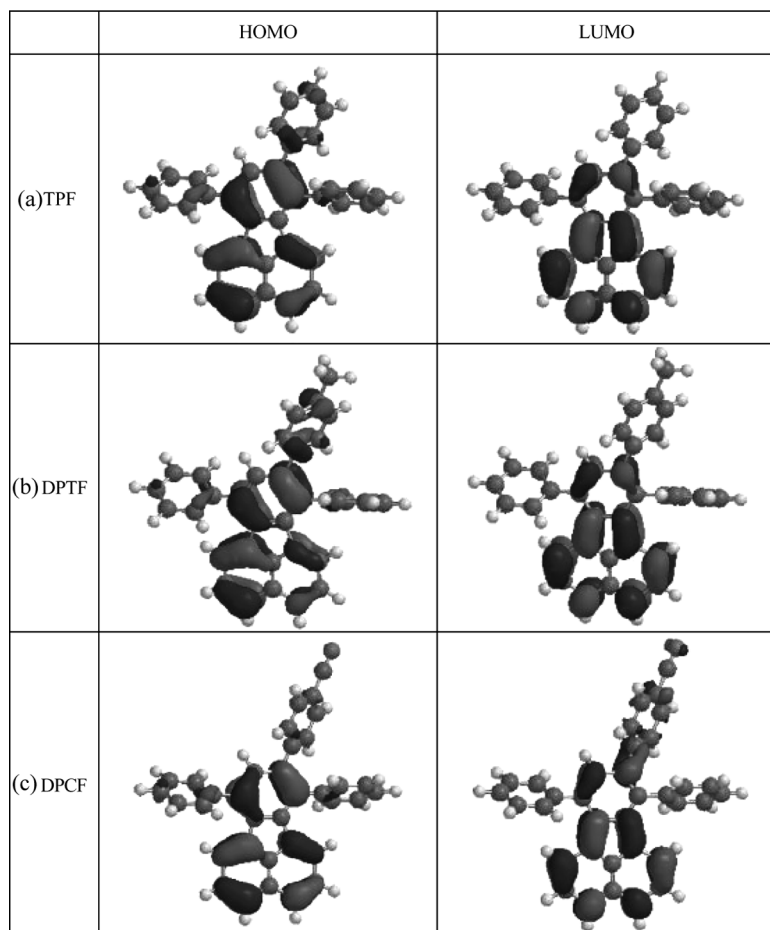| Position@fluoranthene	7		8		10	
	Distance (Å)	Dihedral (deg)	Distance (Å)	Dihedral (deg)	Distance (Å)	Dihedral (deg)
TPF	1.496	71.91	1.493	55.10	1.492	58.20
DPTF	1.496	72.25	1.493	54.27	1.491	57.44
DPCF	1.496	70.48	1.491	54.57	1.492	61.04

FIGURE 2 HOMO and LUMO levels of (a) TPF, (b) DPTF and (c) DPCF calculated at the B3LYP/6-31G* level of density functional theory with a 6-31G* basis set using Spartan'04.

of HOMO did not have electron density at benzene ring of the 8-position. On the contrary, TPF or DPTF in the state of HOMO has some electron density at benzene ring of the 8-position, but no electron density was found in the state of LUMO. This shows a possibility that when electrons come from the outside to LUMO, the withdrawing effect of –CN group may allow electron to arrive at the 8-position. However, the electron cloud of fluoranthene cannot make much change with the withdrawing effect of a single –CN group. HOMO and LUMO levels, which determine band gap in all compounds,

confirmed that electron density is concentrated on fluoranthene. HOMO and LUMO results explain why UV_{max} and PL_{max} values of three compounds are similar. CV was measured to identify HOMO values of the synthesized materials. Even when cycles are scanned for more than 50 times or so, CV result appeared stable.

By using band-gap identified with UV_{onset} and HOMO values measured through CV, LUMO was confirmed, which are summarized in Table 1. The HOMO levels of three materials showed very similar values in the range of 5.8~5.9 eV. That is, it is expected that oxidation and reduction within molecules occur in fluoranthene regardless of substituents. This result can be associated with the finding obtained through molecular simulation that the most of electrons on HOMO and LUMO exist in fluoranthene. The HOMO levels of both compounds were lower than NPB (5.4 eV) which is a hole transporting material; the LUMO levels were higher than Alq3 (3.1 eV) which is electron transporting material, showing an adequate electronic level as emitting layer.

TGA and DSC data analysis identified important thermal properties of the synthesized materials which is directly related to the lifetime property of device as mentioned above (Table 1). Through DSC, it were found that TPF, DPTF and DPCF had T_m values of 199°C, 262°C and 236°C, but a clear T_g was not observed. TGA data under the condition of nitrogen showed T_d of the materials as shown in Table 1. Temperatures at which the weight is reduced by 5% were 323°C (TPF), 337°C (DPTF) and 393°C (DPCF). Considering that T_m of DPVBi is 204°C[14], thermal properties of these materials are assumed to be excellent.

Multi-layered OLED device was fabricated in order to identify electroluminescent properties of synthesized materials. EL devices were fabricated using 4,4′,4″-tris {N,-(2-naphthyl)-N-phenylamino}-triphenylamine (2-TNATA) as a hole injection layer, 4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) as a hole transporting layer, tris(8-hydroxyquinoline) aluminum (Alq$_3$) as electron transporting layer, synthesized materials as a emitting layer, ITO as the anode and LiF/Al as the cathode; ITO/2-TNATA (60 nm)/NPB (15 nm)/TPF or DPTF or DPCF (30 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (200 nm).

Figure 3 shows the I-V curves of the devices. DPCF showed I-V property with slightly increasing turn-on voltage. This is because DPCF has a lower level of HOMO level and a little barrier energy gap with NPB than TPF or DPTF.

Figure 4 illustrates EL spectrum of the fabricated device. The device that used TPF and DPTF as emitting layers shows EL_{max} values of 471 nm and 470 nm, respectively, in the sky-blue area.
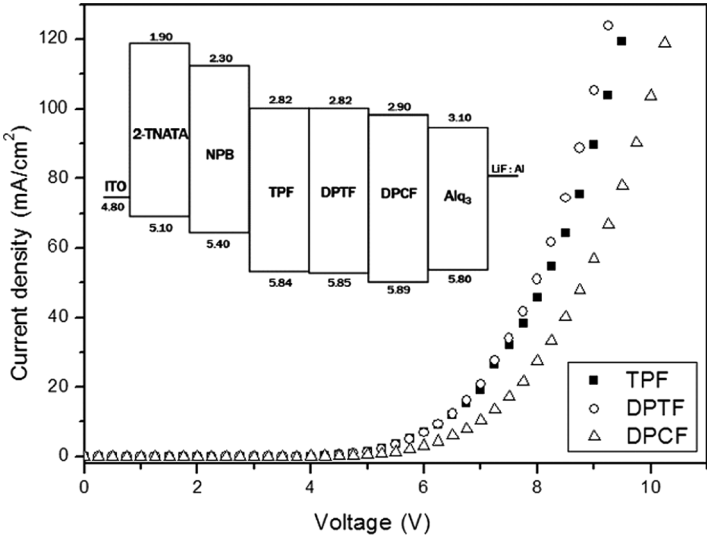
FIGURE 3 Energy diagram and current density-voltage characteristics of ITO/2-TNATA(60 nm)/NPB(15 nm)/TPF($\blacksquare$), DPTF($\circ$) and DPCF($\triangle$)(30 nm)/ Alq$_3$ (30 nm)/LiF(1 nm)/Al devices.
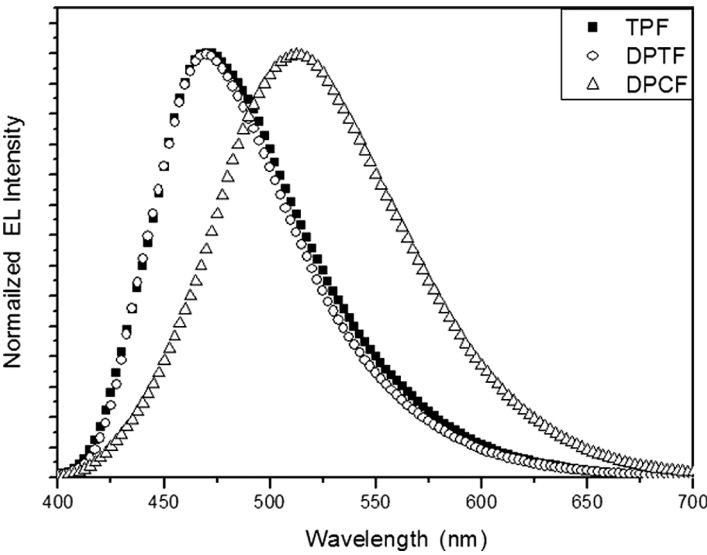
FIGURE 4 EL Spectrum of ITO/2-TNATA/NPB/TPF($\blacksquare$), DPTF($\circ$) and DPCF($\triangle$)/Alq$_3$/LiF/Al devices at 10 mA/cm^2.

TABLE 3 EL Performance of Multi-Layered Devices with the Structure: ITO/2-TNATA(60 nm)/NPB(15 nm)/Synthesized Material(30 nm)/Alq$_3$ (30 nm)/LiF(1 nm)/Al(200 nm) at 10 mA/cm^2

	EL$_{max}$ (nm)	Voltage (V)	Efficiency (cd/A)	Efficieny (1 m/W)	CIE (x,y)
TPF	471	6.3	3.27	1.63	(0.192, 0.269)
DPTF	470	6.1	3.62	1.85	(0.185, 0.252)
DPCF	513	6.9	0.28	0.13	(0.285, 0.465)

Whereas, it was identified that the device with DPCF as an emitting layer has weak emission that is expected to be Alq$_3$ wavelength (513 nm).

Table 3 shows efficiency of the fabricated device at 10 mA/cm^2 of current density. TPF showed sky-blue CIE value of (0.192, 0.269) and 3.27cd/A at 10 mA/cm^2. DPTF also showed sky-blue CIE value of (0.185, 0.252) and 2.31cd/A at 10 mA/cm^2. However, DPCF device exhibited relatively low efficiency. This result can be explained by the mismatched HOMO levels of DPCF and Alq3 that is automatically injected hole carrier from DPCF to Alq3 when hole is injected from NPB. That is why EL spectrum of DPCF device shows EL maximum value of 513 nm of Alq3 light.

In particular, DPTF device has better thermal properties, a better luminance efficiency, a lower operating voltage, and a higher power efficiency than the TPF device. As a result, we conclude that the EL efficiencies and CIE values of these synthesized compounds are affected by the presence of methyl group and their inductive effect, as was also concluded in a previous study of 9,10-di(2-napthyl)anthracene (ADN) and 2-methyl-9,10-di(2-napthyl)anthracene (MADN) [15].

CONCLUSIONS

In this study, we synthesized 7,8,10-triphenylfluoranthene [TPF] and TPF derivatives which are substituted by p-tolyl and p-cyanobenzene instead of phenyl at 8-position.

Multilayered EL devices were fabricated using these materials as non-doped blue emitting layers. DPCF device exhibited relatively low efficiency. This result can be explained by the mismatched HOMO levels of DPCF and Alq3 that is automatically injected hole carrier from DPCF to Alq3 when hole is injected from NPB. DPTF device including a methyl group has better thermal properties, a better

luminance efficiency, a lower operating voltage, and a higher power efficiency than the TPF device.

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