

Donor Interlocked Molecular Design for Fluorescence-like Narrow Emission in Deep Blue Thermally Activated Delayed Fluorescent Emitters

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Supporting Information

ABSTRACT: Deep blue thermally activated delayed fluorescent (TADF) emitters with a narrow emission spectrum were developed by managing the molecular structure of the TADF emitters. The deep blue TADF emitters were designed to show large steric hindrance at the central core of the molecule and small singlet—triplet energy gap. The molecular engineering of the deep blue TADF emitters enabled the fabrication of the deep blue TADF device with a full width at half-maximum of only 48 nm and a quantum efficiency of 14.0%. The full width at half-maximum of the deep blue TADF device was similar to that of conventional fluorescent devices, while the quantum efficiency was more than tripled.

INTRODUCTION

Blue thermally activated delayed fluorescent (TADF) devices have been intensively studied for the last couple of years because they have a potential as a substitute for blue phosphorescent devices.^{1–13} Since the paper reporting 20% external quantum efficiency (EQE) in the green TADF devices,¹ more interest is being focused on developing high efficiency blue TADF devices, and high EQE above 20% has been already demonstrated.^{10–13}

There have been several different design approaches for the development of the blue TADF emitters, but the main approach was to control the electron donating and accepting character of the donor and acceptor moieties comprising the TADF backbone structure. For example, a strong electron accepting dicyanobenzene moiety was combined with a weak electron donating carbazole moiety,^{1,7} while a weak electron accepting diphenylsulfone moiety was merged with a strong electron donating acridine moiety.^{2,5,6,9,11} In another approach, a diphenyltriazine or phenyltriazine acceptor was linked with multiple carbazole units.^{8,10,13} These approaches were successful to control the electron donating and accepting power and corresponding singlet and triplet energy of the TADF emitters. Therefore, several blue TADF emitters could reach high EQE close to 20% in the blue TADF devices.

Although high efficiency blue TADF devices have been reported, there are two main issues related with the emission spectrum to overcome in the development of the blue TADF devices. One issue is broad emission spectra of the current TADF emitters due to strong charge transfer (CT)



emission.^{14,15} In general, full width at half-maximum (fwhm) of common blue TADF emitters is in the range from 70 to 80 nm compared to below 50 nm of conventional blue fluorescent emitters.^{1–16} The broad emission spectrum makes it difficult to apply the blue TADF emitters in a display application because a sharp emission spectrum is essential in the display panel. The other issue is color purity of the blue TADF devices. Most TADF devices developed so far show sky blue emission rather than deep blue emission, but deep blue TADF devices are preferred in real applications in the organic light-emitting diode (OLED) panel. In fact, these two issues are related to each other, and material development to overcome the hurdles of current blue TADF emitters is necessary.

In this work, we report a new molecular design approach to improve the color purity and broad emission spectrum of common TADF emitters. We designed a target molecule with interlocked donor moieties at the central core and electron donor–acceptor moieties in the backbone structure for small singlet–triplet energy gap ($\Delta E_{\rm ST}$). Comparison of the target molecule having the interlocked donor based molecular design with a reference molecule revealed that the interlocked donor structure is crucial to reduce the fwhm and to obtain deep blue emission color as well as high EQE. A deep blue TADF device with a fwhm of 48 nm, high EQE of 14.0%, and deep blue color

Received: April 13, 2016 Revised: July 18, 2016

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 a NaH = sodium hydride, DMF = dimethylformamide, CuCN = copper(I) cyanide, Pd(dppf)Cl₂ = [1,1'-bis(diphenylphosphino)ferrocene]-dichloropalladium(II), DMSO = dimethyl sulfoxide, CsF = cesium fluoride.

coordinate of (0.14, 0.12) was demonstrated using the newly designed deep blue TADF emitter.

EXPERIMENTAL SECTION

General Information. 9H-Carbazole, [1,1'-bis-(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl₂), and copper(I) cyanide were purchased from Aldrich Chemical Co., and dimethyl sulfoxide (DMSO), magnesium sulfate and dimethylformamide (DMF) were purchased from Duksan Sci. Co. Sodium hydride, 1,5-dibromo-2,4-difluorobenzene, and 1,2-dibromo-4,5-difluorobenzene were purchased from Fluorochem Ltd. 9,9-Dimethyl-9,10-dihydroacridine was purchased from P&H tech. These chemicals were used without further purification. THF was distilled over sodium and calcium hydride. Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 400 ECX (1H NMR: 400 MHz, 13C NMR: 100 MH_z) at room temperature. Chemical shifts of the ¹H and ¹³C NMR signals were quoted relative to tetramethylsilane ($\delta = 0.00$). Ultraviolet-visible (UV-vis) absorption spectra were recorded on a PerkinElmer Lamda 950, and fluorescence spectra were recorded on Hitachi F-7000. The highest occupied molecular orbital energy level was determined using an IVIUM STAT in three electrodes with a carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The lowest unoccupied molecular orbital energy level was determined using an IVIUM STAT in three electrodes with a carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode after nitrogen bubbling to remove oxygen from the sample. Ferrocene was used as the standard material for the cyclic voltammetry measurement. The elemental analyses were carried out with a flash 2000 model. The mass spectra were collected on a Jeol JMS-AX505WA spectrometer in fast atom bombardment mode and AccuTOF-GCv 4G spectrometer in field ionization mode. Transient photoluminescence measurement was performed using a pulsed Nd:YAG laser (355 nm) as the excitation source and a photomultiplier tube as an optical detector system.

Synthesis. The synthesis of two emitters is schematically described in Scheme 1.

5-Bromo-2,4-difluorobenzonitrile. 1,5-Dibromo-2,4-difluorobenzene (10.00 g, 36.78 mmol) and copper(I) cyanide (4.94 g. 55.17 mmol) were dissolved with anhydrous DMF solvent under 100 $^{\circ}$ C. The reaction mixture was stirred with ambient atmosphere during

10 h. The solution of the reaction mixture was washed with cold distilled water in order to remove DMF solvent and then extracted by ethyl ether three times. The mixture was purified by column chromatography on silica gel with *n*-hexane and dichloromethane. The white needle shape product was obtained in 1.50 g (19%) yield. MS (FI+) m/z 216.96 [(M)].

4,4',6,6'-Tetrafluoro-[1,1'-biphenyl]-3,3'-dicarbonitrile. 5-Bromo-2,4-difluorobenzonitrile (3.00 g, 13.76 mmol), cesium fluoride (15.6 g, 103.21 mmol), and $Pd(dppf)Cl_2$ (1.12 g, 1.38 mmol) was dissolved in DMSO solvent at 100 °C. The reaction mixture was stirred during 3 h, and then distilled water was poured into the mixture flask in order to quench the reaction. The mixture was extracted with dichloromethane and then purified by column chromatography on silica gel with *n*-hexane/dichloromethane. The white powdery product was obtained in 0.30 g (16%) yield.

¹H NMR (200 MH_Z, CDCl₃): δ 8.29 (t, J = 5.2 H_Z, 2H), 7.90 (t, J = 6.6 H_Z, 2H). MS (FI+) m/z 276.13 [(M)].

4,4',6,6'-Tetra(9H-carbazol-9-yl)-[1,1'-biphenyl]-3,3'-dicarbonitrile (CzBPCN). Sodium hydride (60% in paraffin, 0.13 g, 5.43 mmol) was washed with *n*-hexane three times. A solution of 9H-carbazole (0.91 g, 5.43 mmol) in anhydrous DMF was poured into the dispersed solution of purified sodium hydride in dry DMF at room temperature. After stirring for 30 min, 4,4',6,6'-tetrafluoro-[1,1'-biphenyl]-3,3'-dicarbonitrile (0.30 g, 1.09 mmol) was dissolved in anhydrous DMF (20 mL) and then added to the stirred reaction solution under nitrogen atmosphere. The reaction solution was allowed to stir at room temperature overnight. The reaction mixture was extracted with dichloromethane and distilled water and then dried with anhydrous magnesium sulfate. The reaction product of CzBPCN was purified by silica gel chromatography with a mixture of chloroform and *n*-hexane. A light yellow powdery product was obtained in 0.60 g (64%) yield.

¹H NMR (200 MH_Z, CDCl₃): δ 8.70 (s, 4H), 8.15 (d, J = 7.8 H_Z, 8H), 7.53–7.29 (m, 24H). ¹³C NMR (50 MH_Z, CDCl₃): δ 141.85, 141.51, 140.43, 139.71, 135.11, 129.42, 126.59, 124.26, 121.45, 121.31, 120.90, 115.37, 111.99, 109. 68. MS (FAB) m/z 865 [(M + H)⁺]. Anal. Calcd for C₆₂H₃₆N₆: C, 86.09; H, 4.19; N, 9.72. Found: C, 85.90; H, 4.03; N, 9.32.

2-Bromo-4,5-difluorobenzonitrile. 2-Bromo-4,5-difluorobenzonitrile was synthesized by the same route as for 5-bromo-2,4-



Figure 1. Gaussian simulation images of CNBPCz and CzBPCN. Electron density distribution of the HOMO and LUMO was calculated by TD-DFT using Gaussian 09 software.

difluorobenzonitrile but using 1,2-dibromo-4,5-difluorobenzene instead of 1,5-dibromo-2,4-difluorobenzene.

MS (FI+) m/z 216.96 [(M)].

4,4',5,5'-Tetrafluoro-[1,1'-biphenyl]-2,2'-dicarbonitrile. 4,4',5,5'-Tetrafluoro-[1,1'-biphenyl]-2,2'-dicarbonitrile was synthesized by the same route as for 4,4',6,6'-tetrafluoro-[1,1'-biphenyl]-3,3'-dicarbonitrile but using 2-bromo-4,5-difluorobenzonitrile instead of 5-bromo-2,4-difluorobenzonitrile.

¹H NMR (200 MH₂, CDCl₃): δ 8.46 (t, *J* = 5.0 H₂, 2H), 8.03 (t, *J* = 5.2 H₂, 2H), MS (FI+) *m*/*z* 276.13 [(M)].

4,4',5,5'-Tetra(9H-carbazol-9-yl)-[1,1'-biphenyl]-2,2'-dicarbonitrile (CNBPCz). CNBPCz was synthesized by the same route as for CzBPCN but using 4,4',5,5'-tetrafluoro-[1,1'-biphenyl]-2,2'dicarbonitrile instead of 4,4',6,6'-tetrafluoro-[1,1'-biphenyl]-3,3'-dicarbonitrile.

Yield: 62%. ¹H NMR (400 MH_z, CDCl₃): δ 8.43 (s, 2H), 8.33 (s, 2H), 7.84–7.80 (m, 8H), 7.26–7.12 (m, 24H). ¹³C NMR (100 MH_z, CDCl₃): δ 139.60, 139.00, 138.75, 135.88, 135.63, 133.34, 126.14, 124.27, 124.17, 121.31, 121.20, 120.39, 120.27, 117.11, 111.84, 109.86, 109.44. MS (FAB) *m*/*z* 865 [(M + H)⁺]. Anal. Calcd for C₆₂H₃₆N₆: C, 86.09; H, 4.19; N, 9.72. Found: C, 85.94; H, 4.15; N, 9.36.

Device Fabrication and Measurements. Vacuum thermal evaporation was a basic process to grow the CNBPCz and CzBPCN devices with organic layers sandwiched between an indium tin oxide and LiF/Al double layer cathode. Spin coating of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) formed a 60 nm thick hole injection layer, and consecutive vacuum evaporation of 20 nm thick 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC) hole transport layer, 10 nm thick 1,3-bis(Ncarbazolyl)benzene (mCP) exciton blocking layer, 25 nm thick DPEPO:CNBPCz or DPEPO:CzBPCN emitting layer with 5% doping concentration, 5 nm thick diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1) exciton blocking layer, and 30 nm thick 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI) electron transport layer followed. Encapsulation of the evaporated devices was conducted after cathode deposition for device characterization in ambient conditions. Current density-voltage testing and device performances of the narrow emission blue TADF devices were measured by Keithley 2400 source measurement and CS-1000 spectroradiometer. Lambertian distribution of light emission was confirmed in all quantum efficiency measurements.

RESULTS AND DISCUSSION

The new TADF emitter, 4,4',6,6'-tetra(9H-carbazol-9-yl)-[1,1'biphenyl]-3,3'-dicarbonitrile (CzBPCN), was designed to have interlocked donor moieties at the central core to restrict molecular motion of the TADF emitters for a sharp lightemission spectrum. To prove the concept of the interlocked donor based molecular design, an isomer molecule without any interlocked donor moieties at the central core, 4.4',5.5'tetra(9H-carbazol-9-yl)-[1,1'-biphenyl]-2,2'-dicarbonitrile (CNBPCz), was also synthesized as a reference material. The CNBPCz and CzBPCN emitters were constructed based on a biphenyl core structure. Four carbazole units were attached to the biphenyl core as donor moieties and two CN units were attached as acceptor moieties. Both CNBPCz and CzBPCN have two carbazole moieties at 4- and 4'- position of the biphenyl core, but the position of the two carbazole and two CN units were different. In the case of CNBPCz, two carbazole units were substituted at 5,5'-positions and two CN units were attached at 2,2'-positions. The positions of the carbazole and CN units were reversed in the CzBPCN emitter with two carbazole units at 2,2'-positions and two CN units at 5,5'positions. The CzBPCN emitter was intended to have large steric hindrance for the rotation of the central biphenyl ring by interlocking the bulky carbazole units, while the CNBPCz emitter was designed to have little steric hindrance.

Starting materials of CNBPCz and CzBPCN were 1,2dibromo-4,5-difluorobenzene and 1,3-dibromo-4,6-difluorobenzene. Only one Br unit of each material was substituted with a CN unit using CuCN, and Pd catalyzed halogen coupling of the CN modified intermediates produced two intermediates with two CN units and four F units for carbazole modification. The carbazole modification was conducted using NaH mediated substitution of the carbazole units. The CNBPCz and CzBPCN were synthesized at synthetic yields of 60% and 85%, respectively, after vacuum train sublimation.

The sublimed CNBPCz and CzBPCN emitters with a high purity above 99% were used for identification of chemical structure and analysis of photophysical parameters. Detailed chemical analysis methods and analysis results of the CNBPCz and CzBPCN emitters were added in the Experimental Section. The analysis results include ¹H and ¹³C nuclear magnetic resonance (NMR) data, mass data, and thermal analysis data. The purity level of the sublimed compounds was confirmed by high performance liquid chromatography (HPLC). The CNBPCz and CzBPCN compounds could be differentiated by different retention times in the HPLC analysis and NMR spectra in Supporting Information (Figures S1 and S2).

The molecular design concept of interlocking two carbazole units was theoretically proven by calculating the molecular orbital and geometrical structure of the synthesized materials using the Gaussian 09 software program which employed Lee-Yang-Parr functional (B3LYP) with 6-31G* basis sets for the density functional of Becke's 3-parameters.¹⁹ The molecular orbital and geometrical structure of the two materials are shown in Figure 1. At the central biphenyl core, two carbazole units of CzBPCN are interlocked because rotation of the central biphenyl core is prohibited by large steric hindrance of the carbazole unit. In the case of CNBPCz, the steric hindarance is not significant because two CN units are substituted at the ortho-position of the biphenyl core. The small size CN unit has no effect on the rotation of two phenyl units of the biphenyl core. As a result, CzBPCN can be considered as a rigid molecule with a restricted molecular motion, and CNBPCz can be treated as a flexible molecule. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the CNBPCz and CzBPCN were also estimated by the molecular calculation, and the HOMO and LUMO were extensively isolated with weak overlap at the central biphenyl core. Both CNBPCz and CzBPCN exhibited the molecular orbital distribution required for TADF emitters. Small ΔE_{ST} for intersystem crossing from triplet excited state to singlet excited state is expected from the separated HOMO and LUMO, and high photoluminescence quantum yield is anticipated from the overlapped HOMO and LUMO. The HOMO-LUMO overlap was rather extensive in the CzBPCN emitter, which was reflected in the large oscillator strength of CzBPCN (0.230) relative to that of CNBPCz (0.193). This implies that the CzBPCN emitter may possess better light absorption and accompanying light emission characteristics than the CNBPCz emitter. Calculated physical parameters of CNBPCz and CzBPCN are presented in Table 1.

Table 1. Summary of the Photophysical Properties of CNBPCz and CzBPCN

emitter	PL peak (nm) ^a	$\Phi_{ ext{PL}}^{\ \ b}$ (prompt/ total)	$\tau (\mu s)^c$	$\frac{E_{\rm S}/E_{\rm T}}{({\rm eV})^d}$	$\frac{\Delta E_{\rm ST}}{({\rm eV})^e}$	fwhm (nm) ^f
CNBPCz	458	0.45/0.46	24.34	3.10/2.83	0.27	71
CzBPCN	453	0.20/0.76	48.22	3.14/2.87	0.27	55

^aMeasured in toluene solution. ^bAbsolute photoluminance quantum efficiency yield evaluated using an integrating sphere in toluene solution (concentrations in the 10 μ M range) without degassing (prompt) and after bubbling nitrogen gas in a few minutes (total). ^cExciton lifetime at 297 K; transient PL measured from 1 wt % doped film in polystryrene on quartz substrate. ^dSinglet energy ($E_{\rm S}$) estimated from onset of wavelength in toluene solution. Triplet energy ($E_{\rm T}$) estimated from onset of wavelength in tetrahydrofuran solution (concenctrations in the 10 μ M range) emission spectra at 77 K. ^e $\Delta E_{\rm ST} = E_{\rm S} - E_{\rm T}$. ^fCalculated by PL spectra in toluene solution.

Singlet energy and triplet energy of the two emitters were estimated by measuring fluorescence and phosphorescence emission spectra in Figure 2. Ultraviolet-visible spectra of the



Figure 2. Photoluminescence (PL) spectra of CNBPCz and CzBPCN. PL spectra were obtained from toluene solution (concentrations 1.0×10^{-5} M). All data were collected at room temperature except for the low temperature PL data at 77 K.

emitters are in the Supporting Information (Figure S3). The singlet energy and triplet energy were calculated from the onset of fluorescence and phosphorescence spectra measured in toluene solvent at a concentration of 1.0×10^{-5} M, respectively. The singlet energy/triplet energy of CNBPCz and CzBPCN were 3.10/2.83 eV and 3.14/2.87 eV, respectively. The singlet/triplet energy gap was 0.27 eV in the two emitters. The difference of geometrical structure did not affect the singlet-triplet energy gap, although increase of singlet and triplet energy was observed in the CzBPCN by the distortion of the central biphenyl ring due to interlocked carbazole units. The dihedral angles between two phenyl units of the biphenyl core were 60° and 47° in the CNBPCz and CzBPCN, while those between the phenyl unit of the biphenyl core and carbazole were 60° and 90° in the CNBPCz and CzBPCN, respectively. The large dihedral angles of the CzBPCN emitter increased the emission energy.¹⁷ The fluorescence spectra of the CNBPCz and CzBPCN also clearly showed the effect of the interlocked carbazole units. The fluorescent spectrum of CzBPCN was sharper than that of CNBPCz. The full width at half-maximum (fwhm) of CzBPCN was only 55 nm, which was much smaller than that of other TADF emitters and even smaller than that of common blue phosphorescent emitters. The large fwhm of 71 nm of CNBPCz certifies that the CzBPCN emitter shows a very narrow emission spectrum as a TADF emitter.

Delayed fluorescence behavior of CNBPCz and CzBPCN was analyzed by transient photoluminescence (PL) measurement and absolute PL measurement with and without nitrogen. In the transient PL measurement results in Figure 3, the delayed fluorescence component was very weak in the CNBPCz both at low and room temperatures, but it was gradually increased according to temperature in the CzBPCN TADF emitter. This indicates that the CzBPCN TADF emitter has large contribution of the delayed fluorescence in the light emission process, while the CNBPCz emitter has small contribution of the delayed fluorescence for light emission. This can also be confirmed by the absolute PL quantum yield of the two emitters. The PL quantum yields with/without nitrogen were 0.45/0.46 and 0.20/0.76 in the CNBPCz and CzBPCN emitters. The PL quantum yield of CNBPCz was not affected by the presence of nitrogen, but that of CzBPCN was largely increased under nitrogen, proving a large contribution of triplet excitons to the PL emission by a delayed emission



Figure 3. Transient PL decay curves of solution coated DPEPO:CNBPCz and DPEPO:CzBPCN films according to different temperatures (50 K, 100 K, 150 K, 200 K, 250 K, and 300 K) with vacuum state measured using a pulse Nd:YAG laser (340 nm) as the excitation source and a photomultiplier tube as an optical detector system.

process. The PL quantum yields of the vacuum deposited CNBPCz and CzBPCN were 0.37 and 0.94, respectively. The high PL quantum yield of the CzBPCN is in agreement with the oscillator strength of the emitters obtained by molecular calculation.

As the objective of designing the CzBPCN was to sharpen the emission spectrum of the TADF devices, electroluminescence (EL) spectra of the CzBPCN devices were investigated. Figure 4 shows EL spectra of the CNBPCz and CzBPCN



Figure 4. EL spectra of CNBPCz and CzBPCN devices. The EL spectra were measured at 1000 cd/m^2 .

devices fabricated by doping of CNBPCz and CzBPCN in a common bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) host. The CNBPCz and CzBPCN emitters showed similar deep blue emission spectra peaked at 456 and 460 nm, respectively, but the fwhm of the two emitters was quite different. The fwhm values of CNBPCz and CzBPCN were 76 and 48 nm, respectively. As expected in the molecular design, the CzBPCN emitter with the interlocked carbazole units showed a very sharp emission spectrum comparable to that of a common fluorescent emitter. The fwhm of the CzBPCN emitter was even smaller than that of common phosphorescent emitters. The narrow emission spectrum of the CzBPCN device realized a deep blue color coordinate of (0.14, 0.12) even though the peak wavelength of the CzBPCN device was in the long wavelength range compared to that of CNBPCz or other deep blue TADF emitters.¹⁸

The external quantum efficiency (EQE) of the two TADF devices is presented in Figure 5. The EQE of the CzBPCN device was much higher than that of the CNBPCz device because of triplet exciton harvesting for fluorescence emission by delayed fluorescence. As confirmed by the PL analysis data, the delayed fluorescence was activated in the CzBPCN emitter, which contributed to the high EQE of the CzBPCN device. The EQE of the CzBPCN device was 14.0%, while that of the



Figure 5. Quantum efficiency versus current density curves of CNBPCz and CzBPCN devices.

CNBPCz device was only 4.8%. This work reported high EQE in the deep blue device with a very narrow emission spectrum with a fwhm of 48 nm. The EQE was tripled while keeping the color performances of common blue fluorescent device having a common emitting layer of 2-methyl-9,10-di(2-naphthyl)anthracene:2,5,8,11-tetra-*tert*-butylperylene(MADN:TBPe).¹¹

CONCLUSIONS

In conclusion, a novel TADF emitter having a very narrow emission spectrum with a fwhm of 48 nm was developed by a new molecular design approach interlocking donor moieties for restricted molecular motion. A high efficiency of 14.0%, a deep blue color coordinate of (0.14, 0.12), and a fwhm of 48 nm were achieved in the deep blue TADF device using a new molecular design approach.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b01484.

NMR spectra and UV-vis absorption spectra of synthesized materials (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Samsung SDI and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, and future Planning (2013R1A2A2A01067447, 2016R1A2B3008845).

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