Carbazole-Anthryl π-Conjugates as Small and Stable Aggregation-Induced Emission-Active Fluorogens: Serving as a Reusable and Efficient Platform for Anticounterfeiting Applications with an Acid Key and Multicolor Ink for a Quill Pen

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ABSTRACT: Being a unique, simple, and inexpensive approach, continuous development on the fluorescence-based technologies remains active in fluorescent anticounterfeiting. A number of polymeric, nano-, carbon dot, and rare-earth oxide materials were preferably explored for such applications, but the complex synthesis, purity, and high cost are the major concerns to make these materials accessible for commercial applications. To address these difficulties, we herein report simple mono-carbazole-linked anthryl π-conjugates that are synthesized in a gram scale via an inexpensive and convenient route. These unsymmetrically substituted new π-conjugates are found to be promising blue-shifted aggregation-induced emission-active fluorogens (AIEgens) having a distinct color on varying substituents with electron-rich (−NEt₂) and electron-poor (−CN) functionalities. The direct link of a single carbazole unit with an anthracenyl π-conjugate possibly enforces the achievement of a highly twisted molecular structure, accountable for the AIE characteristics. The π-conjugate with −NEt₂ substituents is established to be highly sensitive under protonation−deprotonation stimuli by a sharp and rapid fluorescence color change (yellow (Φ_f = 37%) to green (Φ_f = 39.4%)) in the solid state (no fluorescence on/off). Upon the exposure of the base vapors (deprotonation), the original emission color (yellow) comes back. Such reversible and also repeatable acidchromism is demonstrated to be perfectly suitable for anticounterfeiting applications by marking the AIEgen on the paper that shows the bright image of the AIEgen under the UV torch (365 nm). Almost equal efficiencies by fabricating on different surfaces such as polyethylene paper and a fresh leaf are observed. While these spots can be duplicated with typical yellow fluorescent dyes, our AIEgen can easily be differentiated with the acid key. The emission color change of this AIEgen from yellow to green under acid stimuli is distinctly defined compared to other dyes and vividly recognized by naked eyes. Thus, one can combat the counterfeiters with the acid key. The reversible color-changing behavior on the paper remains intact even after six consecutive days of exposure to sunlight, and the AIEgen is thermally stable up to 445 °C. Further, this compound is also utilized as ink (10 μM 1,4-dioxane solution) where a pigeon feather is used as a quill pen. The mechanistic insights behind these facts have also been proposed and validated wherever possible.

INTRODUCTION

The economic growth of a society is largely hampered by the counterfeiting business on a variety of products even related to health and security.1 The overall impact brings a high risk to mankind, and a potential strategy needs to be implemented to prevent it. Development of effective and permanent anticounterfeiting methods is practically challenging. There are numerous existing methods, and nevertheless, counterfeiters keep finding the alternative path to break the tricks.1,2 The chemical method is identified as one of the developing cost-effective tools for anticounterfeiting applications that can generate easily detectable chemical tags.1 In this context, the luminescent materials are significantly explored in anticounterfeiting applications as a most convenient and low-cost approach.1 Many such fluorescent materials are available in the literature, but most of them have quite limited access and a complex nature that restrict the scope for real and commercial uses.3−5 The luminescent materials are visible under a UV torch of a specific wavelength. However, tagging a new fluorescent dye will not solve the problem because the counterfeiters can easily find similar duplicate fluorescent dyes that are available in the market. To avoid such an issue, stimuli-responsive fluorescent materials would be beneficial where stimuli will act as a key. In this context, we herein report a mono-carbazole-linked anthryl π-conjugate as a small and easily accessible stimuli-responsive AIEgen. Notably, both anthracene6,7 and carbazole8−13 were individually identified with their unique properties in the field of optoelectronics. The thorny obstacle...
with anthranyl derivatives was to experience fluorescence quenching in the aggregate state due to the flat and rigid framework. Thus, the aggregation-caused quenching (ACQ) property of anthracene was detrimental to execute real-world applications. Later, aggregation-induced emission (AIE) for anthranyl compounds was detected mainly for distyrylanthracene (DSA) derivatives. Also, much smaller anthracene-based AIEgens were reported by us. Being a hole transporter, luminescent, thermally stable, and electronically rich, single or multiple carbazole units were linked with various conjugated systems such as triarylethylene and polymers. In fact, covalently linked anthracene-carbazole fluorophores (1a and 1b, Chart 1) were reported to be efficient blue-emitting materials and used for organic light-emitting diode (OLED)-based applications.

The modified DSA (1c, Chart 1) carrying oligocarbazole units was developed as a promising AIEgen, while the compound 1d was unable to exhibit the AIE property due to the lack of molecular symmetry. However, the synthetic paths to access these directly linked anthracene-carbazole compounds including 1c are relatively expensive. The remarkable applications of such molecules and a variety of light-emitting properties with a subtle change in the molecular structure encouraged us to generate new carbazole-linked anthranyl π-conjugates in a metal-free simple synthetic route and study their AIE properties. With our current interest, we introduce the tertiary amine functionality to the fluorophore to make it useful in exhibiting a sharp reversible change in the solid-state emission behavior under protonation and deprotonation stimuli. Such luminescent materials are tagged in the paper tagged with other fluorescent materials and are found differences under the acid key. It was found to be very much unique compared to the previously existing fluorescent marks. Further, 10 μM 1,4-dioxane solution is utilized as a multicolor

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**Chart 1. Reported Anthracene-Carbazole compounds and Their Applications**

**Scheme 1. Synthesis of Carbazole-Linked Anthranyl π-Conjugates**

**Figure 1. Normalized emission spectra for (a) 3a and (b) 3b (10⁻⁵ M) in different solvents (λₑₓ = 405 nm). The images of (c) 3a and (d) 3b under a 365 nm UV lamp (10⁻⁵ M) in the following solvents: (i) cyclohexane, (ii) hexane, (iii) CCl₄, (iv) dioxane, (v) tetrahydrofuran (THF), (vi) CHCl₃, (vii) CH₂Cl₂, (viii) acetonitrile (MeCN), and (ix) MeOH.**

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ink to write with a quill pen (pigeon feather) on a piece of filter paper where there were clearly readable yellow letters under the UV torch, and the letters are reversibly changed to green under acid/base vapors. Moreover, the reversible emission color-changing behaviors under protonation–deprotonation stimuli facilitate the reusability of the fluorophore.

■ RESULTS AND DISCUSSION

As a suitable precursor for olefination reactions, carbazole-linked anthranlyphosphonate (CBZP) is easily synthesized by a methanesulfonic acid-mediated Friedel–Crafts-like reaction of α-hydroxyphosphonate (2) with only N-heptylcarbazole (without further functionalization, Scheme 1). The phosphonate was isolated with high purity and characterized by different spectroscopic methods.

Subsequently, CBZP was utilized to access the π-conjugates 3a (with an electron-withdrawing group, −CN) and 3b (with electron-donating NEt₂). In spite of being a traditional route, the access of such unsymmetrically substituted π-conjugates with high yields in a straightforward and cost-effective path is advantageous. The yield is very much comparable for both electron-withdrawing and -donating substituents. Thus, the use of expensive metals is completely avoided to make a direct link between carbazole and anthracene. Although characterized by FT-IR, NMR, and mass spectroscopy, these compounds are amorphous in nature, and therefore no single crystals could be grown in spite of several attempts.

Owing to the typical ACQ tendency of the fluorophore, generating new small AIEgens is always a challenge as shown in Chart 1 (1c: AIEgen; 1d: non-AIEgen), we focus on studying the AIE behaviors for these two π-conjugates 3a and 3b. The absorption maxima are found at ~400 nm for both 3a and 3b due to π→π* transitions (Figure S1: for all absorption and emission spectra of 3a and 3b), and emission maxima are identified around ~530 nm in tetrahydrofuran (THF) and acetonitrile (MeCN, Figure 1). However, there is not much a significant difference in the absorption spectra by changing the solvent polarity as expected, and the solvatofluorochromic behavior was observed for these compounds (a 23 nm shift for 3a and S1 nm shift for 3b in emission λmax Figure 1) by varying the solvent polarity of hexane to MeOH.

The photophysical parameters for compounds 3a and 3b are tabulated in Table S1. Both these compounds fluoresce more in a relatively nonpolar solvent such as hexane and CCl₄ (Table S1) possibly by emitting from locally excited (LE) states, while the more polar solvent facilitates decay from intramolecular charge transfer (CT) states. The twisted intramolecular charge transfer in the excited state is well recognized as a possible origin for such fluorosolvatochromism. The pronounced solvent effect with a S1 nm shift for compound 3b indicates that this compound is comparatively more suitable to emit from the CT state in a polar solvent. Thus, the compound 3b is a better donor–acceptor fluorophore than 3a, although 3a with the −CN functionality would have better CT character. The cyano group for such systems was found to be not in the plane of the aromatic ring, and eventually, the impact of the electron-withdrawing effect for the cyano group is subtle.

However, with our main focus to search new AIEgens, acetonitrile is preferred as a solvent because the fluorophores are almost nonfluorescent [quantum yield (Φ)] for 3a: 1.1% and 3b: <1%, Table S1]. Upon gradual addition of water (as a poor solvent) to the acetonitrile solution (10 μM) of 3a and 3b independently, a sudden enhancement in the relative fluorescence (FL) intensity was observed at \( f_w = 50−70\% \) (\( f_w \) = fraction of water \( (v/v\%) \), in acetonitrile; Figure 2).

Interestingly, the compound 3a exhibited a green emission maximum (\( λ_{max} = 526 \text{ nm} \)) at \( f_w = 70\% \) with 20 times fluorescence intensity enhancement compared with that in the solution state, and 3b showed a yellow emission (\( λ_{max} = 553 \text{ nm} \)) maximum at \( f_w = 50\% \) with 10 times the increment. Thus, the change of the electronic effect could display a difference in the emission wavelength for this series of compounds. (Figure S2 for UV–vis for AIE studies). Typically, the origin of the AIE properties is proved to be the restricted intramolecular motions (RIM) along with slight red shifts. Interestingly, the observed blue-shifted emission maxima (29 nm prominent in the case of 3b, while for 3a, 7 nm) on aggregation compared with the molecular state indicate the lack of conjugation in the aggregate state due to the nonplanarity of the molecular structure. When the molecules form aggregates with each other due to poor solubility in water, the polarity effect surrounding the molecules is reduced to result in a blue shift in emission. The average particle sizes at the emission maxima were measured by a dynamic light scattering (DLS) study, which exhibited the sizes of 120 nm for 3a and 111 nm for 3b (Figure S3). The formation of such nanoaggregates is also supportive of such AIE behavior. To find the role of the carbazole unit in exhibiting AIE behavior, the analogous π-conjugate 4 (without a carbazole link) is synthesized as shown in Scheme 2.

Scheme 2. Synthesis of the Carbazole Unsubstituted π-Conjugate

The compound 4 is recognized as fluorescent in the solution state and almost nonemissive in the aggregate state (Figure 3), which is established as a non-AIE-active molecule.

Hence, the presence of carbazole perhaps is a key factor to make the molecule AIE-active. Such an observation also confirms the twisted molecular conformations for 3a and 3b, which possibly originated from the linked carbazole. The twisted conformations restrict the intramolecular motion (RIM) in the solid state to facilitate the molecular relaxation from the excited state through the radiative pathways.
molecule 4 is expected to have strong intermolecular π−π stacking among anthracene rings in the aggregate state, suppressing the radiative decay. The amorphous features of these carbazole compounds are very much disadvantageous to grow a single crystal to study the molecular packing. However, with support from the literature, we speculate that the carbazole ring is considerably twisted for both the compounds. To support our speculation, the molecular structure of compound 3b is optimized using DFT (density functional theory) studies where the carbazole ring is twisted almost 80° with the anthracenyl core (Figure 4). It specifies significantly weak electronic conjugations between the anthracenyl ring and carbazole unit. The olefinic part is in a S6° torsion angle with the anthranyl core, indicating a better electronic conjugation with the arylamine part. Such a twisted conformational structure can only enhance the fluorescence property in the solid state by RIM, and thus we explain the fluorescence property in the solid state.

Both the π-conjugates 3a and 3b are thermally and photochemically stable in both solution and solid states (verified by observing the sample for four months). The thermogravimetric analysis (TGA, Figure S4) reveals the T_d (decomposition temperature) for compound 3a (350 °C) and 3b (445 °C), whereas compound 4 decomposes at only 124 °C. Thus, the attached carbazole unit not only governs the AIE properties but also contributes to achieving a high T_d. Notably, the carbazole unit is known to enhance the thermal stability of the compounds.

Being yellow in fluorescence in the solid state (Φ_f = 37%), 3° amine-containing compound 3b is utilized as a platform for reversible acidichromism. The fluorometric detection of acid vapor in the solid state would be operationally simple, cost effective, and convenient. Upon exposure to acid vapor (2.5 M aqueous solution of HCl), the yellow fluorescence of 3b peaked at 565 nm is reverted from 524 nm (Figure 5a,b). The 41 nm blue shift and the reversibility nature of such materials are thought to be utilized in anticounterfeiting applications, which can be vividly examined with the naked eye by using a simple 365 nm UV torch.

Several acids inclusive of H_2SO_4, HNO_3, CF_3SO_3H, and CF_3CO_2H are tested and a similar reversible color change is noticed by exposing to basic vapors (NH_3 or TEA). Such reversibility in color change was sustainable by protonation–deprotonation treatment for multiple times (see the inset plot, Figure 5a). Thus, the performance of this material is validated with two important parameters, that is, reversibility and repeatability. Notably, the reports on reversible acidichromism in the solid state are limited with tetraphenylethylene-spiropyran and pyridinyl fluorophores that could be accessed only by multistep Pd-catalyzed coupling reactions. In most of the cases, the fluorescence switching on–off was observed on deprotonation–protonation, while the change in the emission color reported herein is sparse in the literature.

Anticounterfeiting Applications. Based on the above discussion, this fluorescence probe looks to be appropriate for the anticounterfeiting applications in many ways. The luminescent material 3b can be tagged in different shapes to any commercial packaging or cover and can be detected under a UV torch. However, there are many such molecules that can be utilized for this purpose, and duplication might be a serious concern. In such a case, the stimuli-responsive materials are advantageous as the stimuli will act as the key that may not be available with counterfeiters. With this awareness, we have made a hexagon shape on a piece of paper (earlier tagged with triethylamine (TEA)/ammonia vapor. The emission maximum at 565 nm is reverted from 524 nm (Figure 5a,b). The 41 nm blue shift and the reversibility nature of such materials are thought to be utilized in anticounterfeiting applications, which can be vividly examined with the naked eye by using a simple 365 nm UV torch.

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The fluorescent color on the paper was intact even by exposing to strong sunlight (with an environment temperature of 42 °C) for six consecutive days. The reversible and repeatable acid-chromic nature also helps to reuse the material for multiple times.

In addition, we have also explored the possibility of fabrication on different surfaces to expand the scope of utility. As polythene is exorbitantly used for multiple purposes, we have tested the AIEgen 3b on a surface of polythene, and the molecule shows a prompt emission color change from yellow to green under acid stimuli (Figure 7). With our curiosity, compound 3b is tested on a surface of a fresh green leaf that shows yellow emission with almost equal efficiencies to other surfaces, and yellow-to-green color change upon acid exposure becomes prominent as shown in the Figure 7d–f.

**Application as a Multicolor Ink for a Quill Pen.** This fluorescent material 3b (10 μM in 1,4-dioxane) has further been used as a multicolor ink that helps to write on paper or any other surface, visible as yellow letters under a UV torch. This writing can be easily monitored or prevented from counterfeiting as the letters will be emitting green upon exposure to acid vapors (Figure 8).

To expand further, we attempt to use quills (pigeon feathers) to write the letters on a piece of Whatman filter paper using the 10 μM 1,4-dioxane solution of 3b as ink. As a primary writing instrument, quills were used to write scripts, and it was one of the most cost-effective and easily accessible natural tools in the ancient age. Hence, the solution of 3b is used as ink for a quill pen to write on a piece of Whatman filter paper as pictured in Figure 9. Nowadays, such a quill pen can be seen only in a museum or sometimes as a gift item to save the origin of writings in the Stone Age.

**Mechanism on Acidchromism.** As earlier stated, the solid-state emitting property can be ascribed by the twisted molecular structure that suppresses the ACQ behavior and activates the fluorescence enhancement in the solid state. To give mechanistic insight into the observation on reversible fluorescence color change under protonation–deprotonation stimuli, the protonation of the tertiary amine is crucial. The protonation has been confirmed by the 1H NMR studies (Figure 10) with a sharp broad peak at δ 14.0 for the protonated amine (Figure 10b), which disappeared on the treatment of triethylamine (Figure 10c). The expected proton shifts in the N−CH2CH3 group have been identified where the quartet at δ 3.47 is shifted almost ~0.3 ppm downfield with an expected splitting pattern (Figure 10b). The reversibility is demonstrated by adding TEA that brings the original spectrum back. Being conjugated with an electron donor (amine) and acceptor system (anthracene), intramolecular charge transfer upon photoexcitation (PCT) can take place for such a molecule, which can induce the decay partly in a nonradiative pathway. However, overall radiative decay governs the ΦI = 37%, and that is significant enough to visualize and utilize this material to these applications. On protonation, the electron-donating ability is reduced and leads to a blue-shifted emission. Thus, we can explain the reversible color change from yellow to green by the protonation and deprotonation method. The enhancement in the ΦI on deprotonation could be due to the blockage of PCT that is very well established in the literature.38,36

**CONCLUSIONS**

The monocarbazole-linked unsymmetrical anthranyl π-conjugates are synthesized in a simple and cost-effective route and established as promising blue-shifted AIEgens. The variation on the electronic effect for this fluorophore leads to the emission at a different wavelength (green or yellow) in the nanoaggregate state. The monocarbazole unit is found to be sufficient to make the fluorophore AIE-active by attaining a twisted molecular structure and thermally stable up to 445 °C. The designed fluorophore with a stimuli-responsive property in the solid state is judiciously placed for the development of an easily accessible, convenient, cost-effective, and reusable solution to combat counterfeiters. It has also been demonstrated on paper that is already tagged with a few other fluorescent materials. The fabrications in different surfaces such as polythene and the green leaf display the range of the scope of this material. We have also utilized the molecule as multicolor ink that can be written on a piece of filter paper using a quill pen, and the fluorescence emission is changeable reversibly under protonation–deprotonation stimuli. The protonation on amine reduces the conjugation within the molecule that results in the blue shift in emission and relatively enhanced fluorescence intensity possibly by blocking the PCT.

**EXPERIMENTAL SECTION**

**General Methods.** All experiments were carried out in hot air oven-dried glassware under a nitrogen or argon atmosphere. Diethyl (anthracen-9-yl(hydroxy)methyl)phosphonate (2) was prepared following the literature procedure.17–19 All aldehydes,
Carbazole, and alkyl bromide were purchased from Sigma-Aldrich. Potassium t-butoxide and methanesulfonic acid were purchased from Alfa Aesar. THF was redistilled from a violet solution of a sodium metal and benzophenone mixture. All other reagents were purchased from common suppliers and used without further purification. Column chromatography was performed by using silica gel of 100−200 mesh. Reactions were monitored by thin-layer chromatography on precoated silica gel 60 F254 plates (Merck & Co.) and were visualized by UV (mainly 365 nm). The 1H, 13C, and 31P NMR spectra were recorded in CDCl3 solution using Bruker Advance DRX (400 and 500 MHz). The signals were referenced to TMS, and the solvent used was deuterated chloroform (7.26 ppm in 1H NMR and 77.2 ppm in 13C NMR). Chemical shifts are reported in parts per million, and multiplicities are indicated by s (singlet), d (doublet), t (triplet), and dd (doublet of a doublet). High-performance liquid chromatography (HPLC) is performed using Agilent infinity 1260. The method used for sample monitoring is 10−100% B in 30 min with 3 min equilibration at 10% B (A = water with 0.1% TFA (triflic acid); B = acetonitrile with 0.08% TFA), and the column used for monitoring is Agilent ZORBAX SB-C3, 5 μm, 4.6 × 150 mm. The electronic absorption spectra were recorded with UV 3600 Plus (Shimadzu). The fluorescence spectra were recorded on a Hitachi spectrofluorometer (F7000) using a 1 cm path length quartz cuvette. The DLS studies for the sample were done using a Malvern particle size analyzer (Zeta sizer Nano-ZS). APCI-LCMS was done in Shimadzu LCMS-2020. TGA was carried out on a Shimadzu DTG-60 simultaneous DTA-TG apparatus with a rate of temperature rising of 10 °C/min. All data were plotted using Origin Pro 8.5 software.

**AIE Studies.** The AIE study is performed using MeCN and H2O mixture. The 10 μM concentration of the solution is kept constant throughout the studies. The samples are prepared as follows: f = 90% (MeCN 200 μL + 1800 μL H2O), f = 80% (MeCN 400 μL + 1600 μL H2O), and so on (Table 1).

**Absorption and Fluorescence Studies.** Absorption studies are performed taking the sample (2 mL, 10−5 M) in a quartz cuvette keeping the wavelength range of 550 to 250 nm. Emission spectra are simultaneously recorded with the same sample used for absorption. The excitation wavelength limit was kept from 415 to 750 nm with the excitation slit/emission slit 5.0 and a PMT voltage of 400 eV.

**Solid-State Emission Study and Absolute Quantum Yield.** The solid-state emission spectra were recorded placing the sample in between two quartz slides. The absolute

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**Figure 9.** Images of 3b (10 μM in 1,4-dioxane): (a) started writing using the quill and (b) writing completed under ambient light, (c) under a 365 nm UV lamp, (d) fumed with HCl vapor, and (e) exposed with NEt3 vapor under a 365 nm UV lamp.

**Figure 10.** The reversible protonation−deprotonation of 3b is proven by 1H NMR titration. The 1H NMR spectra in CDCl3 of (a) the compound 3b, (b) 3b + 1 equiv HCl, and (c) 3b + 1 equiv HCl + 1 equiv TEA. The 12M HCl solution is used and maintained of the equivalency. Commercially available anhydrous triethylamine (TEA) is used without further purification.
quantum yield is done for the same sample using a calibrated integrating sphere. After that, the sample was exposed to HCl vapors for 2 min and TEA vapors for another 2 min, and the absolute quantum yields were measured.

**DLS Study.** The DLS samples were prepared by taking our sample (10−5 M) in the aqueous solution in a reusable plastic cuvette filled with a cap.

**NMR Titration.** Compound 3b (0.010 g/m) was dissolved in CDCl3 (500 μL) followed by addition of 1 equiv of 12 M HCl and 1 equiv of TEA to the same NMR tube.

**Theoretical Section.** DFT calculations are performed in the gas phase using Gaussian 09 software with the CAMB3LYP exchange correlation functional. For the ground-state geometry optimization, all of the atoms were treated with the 6-31G basis set. The snapshot of the geometry is generated using Mercury CSD 2.0 software.

**Synthesis and Characterization of CBZP.** In a 25 mL round-bottom flask, diethyl (anthracen-9-yl(hydroxy)methyl)- phosphonate (2) (1,000 g, 2.940 mmol) was dissolved in 5 mL of dry dichloroethane in ice temperature followed by the addition of methanesulfonyl acid (0.398 mL, 5.808 mmol) and N-heptyl carbazole (0.863 g, 2.940 mmol). The reaction was allowed to stir for 4 h. The completion of reactions was monitored by TLC. The reaction mixture was quenched by water and extracted with dichloromethane (20 mL × 3). The organic layer was subjected to vacuum in a 50 mL round-bottom flask, washed with aqueous sodium sulfate, and evaporated under reduced pressure. The compound CBZP was purified by column chromatography using ethyl acetate and petroleum ether (5% ethyl acetate in petroleum ether). Yield: 1,460 g, 85%; mp 195 °C.

**Table 1. Change of Fluorescence Parameters against f_w.**

| fluorophores | f_w | λ_max (nm) | Φ_T (%) |
|-------------|-----|------------|--------|
| 3a          | 0%  | 533        | 1.10   |
| 70% (aggregates) | 526 | 18.20      |
| 3b          | 0%  | 582        | <1.00  |
| 50% (aggregates) | 553 | 16.35      |

“Quantum yields (Φ_T) are calculated in reference with quinine sulfate (0.1 M H2SO4). Error limit: ± 5%. λ_ex = 405 nm.

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