Convergent Synthesis of Alternating Fluorene-p-xylene Oligomers and Delineation of the (Silver) Cation-Induced Folding

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Abstract: Convergent synthetic routes for the preparation of hitherto unknown fluorene-p-xylene oligomers (containing up to 10 fluorene moieties) from readily available starting materials are described. The conformationally adaptable monomeric receptor (which is made of a pair of fluorene and one p-xylene ring, i.e., Z1) undergoes a simple C-C bond rotation in the presence of silver cations to produce a π-prismand-like receptor which binds a single silver cation with remarkable efficiency (i.e., K ≈ 15 000 M⁻¹). The data on ¹H NMR spectroscopic titrations with Ag⁺ together with the density functional theory and AM1 calculations allows us to establish that various oligomers of Z1 (i.e., Z2−Z9) also undergo ready folding into the structures that contain multiple π-prismand-like receptor sites in the presence of silver cations. The multiple cavities in Z3−Z9 accommodate a single silver cation per cavity with efficiency similar to that of Z1.

Introduction

There are numerous examples in nature where weak inter- and intramolecular bonding interactions (such as hydrogen bonding, π-stacking, Columbic interactions, metal-ion binding, etc.) permit structure modulation of the biopolymers (such as polypeptides, ribonucleic acid, polycarboxylates) into well-defined ‘molecular machines’ that perform complex functions from enzymatic catalysis to information storage and retrieval. Furthermore, the design and syntheses of artificial polymeric (organic) materials whose structures can be modulated by external stimuli (such as heat, light, or metal-ion binding) constitute an important area of research owing to the fact that such materials may hold potential for applications in the ever evolving areas of molecular electronics and nanotechnology. A number of such synthetic materials, generally termed “foldamers”, have been prepared and are discussed in detail in a recently published review article by Moore and co-workers.

We recently synthesized a hydrocarbon ligand 1,4-bis(9-methyl-9H-fluoren-9-yl)methylbenzene (1, see structure below) from readily available fluorene and α,α-dichloro-p-xylene that possesses an unique molecular structure where a simple C-C single bond rotation converts it from an extended (“Z”) conformer to an isoenergetic (folded) delta (“A”) conformer, as established by density functional theory (DFT) calculations at the B3LYP/6-31G* level. The cavity formed by three aromatic walls (i.e., two fluoranyl rings and one p-xyllyl ring) in the “A” conformation of 1 is remarkably similar to that found in π-prismand (2)23—a well-known and efficient receptor for the binding of a variety of metal cations22,23—as shown in Figure 1. Although, the energy difference between the two conformers of 1 is only ~0.4 kcal/mol, X-ray crystal structure analysis showed that 1 in the solid state exists exclusively as the extended...
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Figure 1. Optimized structures of the isoenergetic conformers of 1 by density functional theory (DFT) calculations at B3LYP/6-31G* level and structural similarity with tris[2.2.2]-paracyclophane or π-prismand (2).

Figure 2. X-ray structure of 1 showing the extended conformer.

“Z” conformer (Figure 2). Note that the X-ray structure of 1 was completely in accord with the calculated structure shown in Figure 1.

Moreover, variable-temperature 1H NMR analyses of 1 indicated that its two conformers (i.e., extended, Z, and folded, Δ) cannot be frozen out at lower temperatures (i.e., ca. 90 °C). However, the conformational adaptability of 1, which hereafter will be referred to as Z1, allows it to bind a single silver cation into the cavity of the Δ conformer with an excellent efficiency \( (K \approx 15 \, 000 \, M^{-1}) \), i.e., eq 1.11

\[
\text{Ag}^+ + \text{Z1} \rightleftharpoons \text{AgZ1} \tag{1}
\]

It is envisioned that the fluorene-p-xylene-based receptor Z1 (shown above in eq 1) can be easily woven into a hitherto unknown polymeric structure by linking p-xylene groups at carbon 9 of the fluorene moieties, i.e., structure A.

Structure A

Accordingly, herein we will report the first preparation of oligomers of structure A containing up to 10 fluorene moieties by a convergent synthetic approach. Furthermore, using 1H NMR spectroscopy it will be shown that these conformationally adaptable oligomers readily fold into the structures that contain multiple π-prismand-like receptor sites (which are made of a pair of fluorene and one p-xylene ring) in the presence of silver cations as follows.

Results and Discussion

Synthesis of Fluorene-p-xylene Oligomers. The initial attempt (P1) to polymerize fluorene with α,α-dichloro-p-xylene in the presence of potassium tert-butoxide as a base in tetrahydrofuran at 0 °C led to a cream-colored solid which melted at 270–274 °C, and its structure was inferred by 1H/13C NMR spectroscopy to be a mixture of cyclic oligomers (structure B), i.e., Scheme 1, reaction P1.

A similar mixture of cyclic oligomers (structure B) was obtained upon reactions of various mixtures of fluoranyl and α,α-dichloro-p-xyl derivatives (vide infra) in Scheme 1 (i.e., reactions P2–P5) in tetrahydrofuran in the presence of potassium tert-butoxide as a base, as confirmed by the observation of fairly narrow signals in the rather simple 1H/13C NMR spectra, in each case, as shown in Figure 3.14

The identity of the similar mixtures of cyclic oligomers, obtained in various reactions in Scheme 1, was further confirmed by MALDI-TOF mass spectrometry (see Figure S1 in the Supporting Information).

Thus, an unexpected formation of cyclic oligomers in Scheme 1 necessitated development of a different synthetic approach for preparation of acyclic oligomers (structure A) as follows.

The syntheses of acyclic oligomers containing up to 10 fluorene units were accomplished by a stepwise (convergent) synthetic approach. The key to the success of this (controlled) approach lies in the fact that carbon 9 of fluorene can be selectively mono- or dialkylated by a simple variation of the reaction conditions and thus allowed straightforward access to the fragments required for designing convergent routes to the various acyclic oligomers Z1–Z9 (Scheme 2).

Thus, a highly selective monolithiation of fluorene in anhydrous tetrahydrofuran using n-BuLi at −78 °C followed by reaction with an alkyl halide [such as iodomethane, ethyl-4-(bromomethyl)benzoate, or α,α-dichloro-p-xylene] led to quantitative formation of the initial building blocks as shown in Scheme 2 (bottom). [Note that the combination of notations F, H, M, E, A, C, and X with numeral subscripts for various intermediates in Scheme 2 refers to the number of fluorenes, hydrogens, methlys, ester, alcohol, chloro, and xyl groups, respectively.]

The second lithiation of the initial building blocks in Scheme 2, in the same pot or after isolation of the products, using n-BuLi at −78 °C in THF followed by reaction with ethyl-4-(bromomethyl)benzoate afforded the ester building blocks that were easily converted into their corresponding benzyl chlorides by a simple two-step procedure. For example, reduction of the esters using lithium aluminum hydride in refluxing THF followed by reaction of the resulting alcohol with thionyl chloride in chloroform at −10 °C afforded the corresponding benzyl chlorides in almost quantitative yields. Various benzyl chlorides


14 The mixture of cyclic oligomers in Scheme 1 can also bind silver cation with efficiency similar to those observed with various Za’s. We are actively pursuing the isolation of a pure oligomer to delineate its structure and usage for designing functional materials. These results will be described in a future publication.
in Scheme 2 (bottom) served as internal and capping units for the preparation of various oligomers. The capping unit FXCM can be further elongated by repeating the high-yielding reaction sequence depicted in the Scheme 2 (bottom). Thus, in a one-pot procedure reaction of FXCM with the fluoranyl anion (generated from fluorene and n-BuLi in THF at $-78^\circ$C) followed by addition of another equivalent of n-BuLi and ethyl-4-(bromomethyl)benzoate afforded $F_2X_2EM$ in excellent yield. Reduction of the resulting ester with LiAlH$_4$ followed by reaction with thionyl chloride afforded a higher homologue of the capping unit (i.e., $F_2X_2CM$). A similar reaction sequence allowed the preparation of capping units containing three and four fluorene moieties with either an electrophilic benzyl chloride group or a precursor to a nucleophilic fluoranyl anion, i.e., Scheme 2 (top).

The syntheses of linear oligomers $Z_2$–$Z_9$ were finally accomplished by piecing together various inner building blocks (i.e., fluorene, $F_2XH_2$, $FX_2C_2$, and $F_2X_3C_2$) and capping units (FXCM, $F_2XHM$, $F_3XHM$, and $F_4XHM$) in tetrahydrofuran using

\[ \text{Scheme 1. Polymerization Attempts (P1–P5) Using Various Fluoranyl and } \rho\text{-Dichloroxylyl Derivatives} \]

\[ \begin{align*}
\text{P1} & \quad + \quad \text{C} \\
\text{P2} & \quad + \quad \text{CH}_{3}\text{CH}_{2}\text{Cl} \\
\text{P3} & \quad + \quad \text{CH}_{3}\text{CH}_{2}\text{Cl} \\
\text{P4} & \quad + \quad \text{CH}_{3}\text{CH}_{2}\text{Cl} \\
\text{P5} & \quad + \quad \text{CH}_{3}\text{CH}_{2}\text{Cl}
\end{align*} \]

\[ \text{Structure B} \]

\[ \text{\textsuperscript{1}H} \]

\[ \begin{align*}
7.5 & \quad \text{PPM} \\
7.0 & \\
6.5 & \quad \text{PPM} \\
6.0 & \\
5.5 & \quad \text{PPM}
\end{align*} \]

\[ \text{\textsuperscript{13}C} \]

\[ \begin{align*}
150 & \quad \text{PPM} \\
140 & \\
130 & \quad \text{PPM} \\
120 & \\
110 & \quad \text{PPM}
\end{align*} \]

\[ \text{Figure 3.} \text{\textsuperscript{1}H/\textsuperscript{13}C NMR spectra of the mixture of cyclic oligomers obtained from Scheme 1 in CDCl}_3 \text{ at } 22^\circ\text{C.} \]

\[ \text{\textsuperscript{a}} \]

\[ \text{\textsuperscript{a}} \text{ (a) } n\text{-BuLi/THF/} -78^\circ\text{C. (b) } n\text{-BuLi/} -78^\circ\text{C/ethyl-4-(bromomethyl)benzoate. (c) LiAlH}_4/\text{THF/reflux. (d) SOCl}_2/\text{CHCl}_3/0^\circ\text{C. (e) Fluorene/} n\text{-BuLi/THF/} -78^\circ\text{C.} \]

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potassium tert-butoxide as a base at 0 °C in excellent yields as exemplified by the preparation of Z9 in Scheme 2 (top).

The acyclic oligomers Z2–Z9 were readily purified by filtration through a short pad of silica gel using mixtures of ethyl acetate–hexanes as an eluent and characterized by 1H and 13C NMR spectroscopy as well as by mass spectrometry. The 1H NMR spectra of Z1–Z9 compiled in Figure S2 in the Supporting Information confirmed that an expected ratio of the integrations of the signals due to the methyl protons with that of the methylenic or xylenic protons was observed in each case. Moreover, the 1H NMR spectra of oligomers Z2, Z3, and Z4, with an increasing number of repeating units, showed the expected number of signals for various methylene and xylenic protons. Expectedly, further increase of the repeating units in Z5–Z9 showed that the 1H NMR signals due to the additional methylenic and xylenic protons were overlapping with one of the methylenic or xylenic protons was observed in each case. Moreover, the 1H NMR spectra of oligomers Z2, Z3, and Z4, with an increasing number of repeating units, showed the expected number of signals for various methylene and xylenic protons. Expectedly, further increase of the repeating units in Z5–Z9 showed that the 1H NMR signals due to the additional methylenic and xylenic protons were overlapping with one of the methylenic (2.95 ppm) and xylenic (6.20 ppm) signals in the spectrum of Z4. The 13C NMR spectra of various acyclic oligomers Z1–Z9 are also compared in Figure S3 in the Supporting Information.

**Figure 4.** (Left) Partial 1H NMR spectra of Z1 obtained upon an incremental addition of CF3SO3Ag in CDCl3–CD3OD at 22 °C. (Right) Plot of changes in the chemical shifts of the xylenic protons (indicated by letter “a” in the structure in the Figure 4A) against the added equivalents of a solution of CF3SO3Ag in CDCl3–CD3OD at 22 °C.

Efficient binding of a single silver cation by the conformationally adaptable receptor Z1 was confirmed by a competition experiment with deltaphane 2—a well-known and efficient receptor for silver cation—as well as by a spectrophotometric determination of the binding constant $K \approx 15000$ M$^{-1}$ using the Benesi–Hildebrand procedure (see Figure 5A/B). More-over, the 1:1 complexation stoichiometry for [Z1, Ag+] was established by Job’s plot analysis (Figure 5C), i.e., eq 2.

$$\text{[Z1, Ag+] } K = 15,000 \text{ M}^{-1}$$

It is also important to note that a model compound FXM2, containing only one fluoranyl moiety, bound Ag+ with much less efficiency and required a large excess of Ag+ for complete utilization of the ligand, and a binding constant $K \approx 10$ was estimated using 1H NMR spectroscopy, i.e., eq 3.

$$\text{[FXM2, Ag+] } K = 10 \text{ M}^{-1}$$

Thus, the experiments discussed above demonstrated that Z1 binds a single silver cation with remarkable efficiency due to the fact that it readily adapts a $\pi$-prismand-like conformation by a simple C–C bond rotation (see also eq 1).

In order to determine the efficiency and binding of silver cations to the higher homologues of Z1, similar 1H NMR spectral titrations of the chloroform-d solutions of Z3, Z5, Z7, and Z9, containing even number of fluorenyl moieties, were carried out at 22 °C. For the actual 1H NMR spectra obtained upon incremental addition of Ag+ solution, see Figures 8, S10, S12, and S14 in the Supporting Information.

Figure 5. (A) Spectra obtained upon incremental addition of a 15 mM solution of Ag+ CF3SO3- in methanol (black) to a 0.8 mM solution of Z1 (red) in CH2Cl2 at 22 °C. (B) Benesi–Hildebrand plot of Z1 and Ag+CF3SO3-. (C) Job’s plot of a 1:1 complex of Z1 and Ag+ cation, where the absorption at 313 nm was plotted against the mole fraction of Z1 at an invariant total concentration of 0.02 M in a 19:1 mixture of CH2Cl2/CH3OH (v/v).

Figure 6. Plots of 1H NMR chemical shift changes (of the xylenic protons) attendant upon incremental addition of a 0.2–0.5 mM solution of Ag+ CF3SO3- in 1:1 CDCl3/CD3OD to a 0.02–0.05 mM solution of oligomers Z1, Z3, Z5, Z7, and Z9, containing even number of fluorenyl moieties, in CDCl3 at 22 °C. For the actual 1H NMR spectra obtained upon incremental addition of Ag+ solution, see Figures 8, S10, S12, and S14 in the Supporting Information.

Figure 7. Job’s plots of a 1:1 complex of Z2 and Ag+ cation (A), a 1:2 complex of Z3 and Ag+ cation (B), and a 1:3 complex of Z5 and Ag+ cation (C). The Job’s plots were obtained by plotting the growth of absorbance at 313 nm against the mole fraction of Z2, Z3, and Z5, respectively, at an invariant total concentration of 0.02 M in a 19:1 mixture of CH2Cl2/CH3OH (v/v).

In order to determine the efficiency and binding of silver cations to the higher homologues of Z1, similar 1H NMR spectral titrations of the chloroform-d solutions of Z3, Z5, Z7, and Z9, containing an even number of fluorenyl moieties, respectively, with a concentrated solution of Ag+ CF3SO3- in a 1:1 mixture of chloroform-d and methanol-d4 were carried out at 22 °C; see Figures 8, S10, S12, and

S14 in the Supporting Information. The reproducible spectral titrations thus obtained showed that Z3, Z5, Z7, and Z9 bind 2, 3, 4, and 5 equiv of Ag+, respectively, as shown in Figure 6.
The $^1$H NMR spectral titrations of homologues $Z_2$, $Z_4$, $Z_6$, and $Z_8$, containing an odd number of fluorenes (i.e., 3, 5, 7, and 9 fluoranyl moieties, respectively) with Ag$^+$ CF$_3$SO$_3^-$ showed that these oligomers bind 1, 2, 3, and 4 equiv of silver cations, respectively, as shown in Figure S4 in the Supporting Information.

Additionally, the binding of multiple silver cations to representative $Z_1$ receptors was also probed by Job’s plot analyses$^{16}$ (see Figure 7). For example, $Z_1$ (see Figure 5), $Z_3$, and $Z_5$ showed that the maximum of the binding interactions takes place at the mole fraction of 0.5 for $Z_1$, 0.33 for $Z_3$, and 0.25 for $Z_5$, which is consistent with the uptake of 1, 2, and 3 Ag$^+$ cations by $Z_1$, $Z_3$, and $Z_5$, respectively, by NMR spectroscopy titrations in Figure 6. Moreover, the maximum interaction with Ag$^+$ and $Z_2$ occurs at 0.5 mol fraction of $Z_2$, thus confirming that it binds only a single silver cation (compare Figure S4 in the Supporting Information).

As such, the number of Ag$^+$ cations captured by a given homologue of $Z_1$ (in Figures 6 and 7) is consistent with the fact that a pair of fluoranyl moieties is necessary for the effective capture of a single silver cation. As shown above in eqs 1 and 2, an efficient binding of Ag$^+$ requires formation of a $\pi$-prismand-like cavity formed by three aromatic walls (i.e., two fluoranyl moieties and one xylyl group). The oligomeric $Z_n$ exists in rapidly interconverting extended “Z” and folded “$\Delta$” conformations in the absence of silver cations at 22 °C, as can be seen with the simple $^1$H NMR spectra (Figure S1 in the Supporting Information), and the conformational mobility of various oligomers ($Z_n$) cannot be frozen at lower temperatures. However, introduction of Ag$^+$ cations induces the folding of the various oligomers, containing an even number of fluorene moieties, by simple $C=C$ bond rotations to produce 1, 2, 3, 4, and 5 deltaphane-like cavities in $Z_1$, $Z_3$, $Z_5$, $Z_7$, and $Z_9$, respectively (i.e., see Figure 8 for a representative example).

The oligomers $Z_2$, $Z_4$, $Z_6$, and $Z_8$, containing an odd number of fluorene moieties form only 1, 2, 3, and 4 deltaphane-like cavities, respectively, upon exposure to a solution of Ag$^+$ while leaving a single fluorene/xylyle pair in an extended conformation (see Figure 8 for a representative example).

Note that the receptor site with an extended conformer binds silver cation with much less efficiency, i.e., $K \approx 10^{-1}$ (see eq 3). It should be noted that the dynamic nature of silver-cation binding to various $Z_n$ would indicate that a single fluorene/xylyle pair in an extended conformation is in continuous flux over the entire chain (vide infra).

The calculated AM1 structures (using Spartan) in Figure 8 together with the $^1$H NMR spectroscopic titrations data with Ag$^+$ in Figure 6 and Job’s plots in Figure 7 clearly account for the number of Ag$^+$ cations captured by various oligomers $Z_1$–$Z_9$. Moreover, it is important to note that the simplicity of the $^1$H NMR spectra, obtained in the presence of varying equivalents of Ag$^+$ (in Figures 4 and S7–S14 in the Supporting Information), suggests the dynamic nature of the binding of Ag$^+$ to the multiple receptor sites of $Z_2$–$Z_9$.

Thus, a careful analysis of the changes in the chemical shifts of the xylene protons in the $^1$H NMR spectra of $Z_3$ obtained upon an incremental addition of Ag$^+$ solution (vide infra) provides further insight into the dynamic nature of silver cation binding. As shown in Figure 9, the oligomer $Z_3$ can exist in at least four (almost) isoenergetic conformers ($Z_3$-$A$, $Z_3$-$B$, $Z_3$-$C$, and $Z_3$-$D$), as established by density function theory (DFT) calculations at the B3LYP/6-31G* level.

On the basis of the number of observed (sharp) signals in the $^1$H NMR spectrum of $Z_3$ it can be easily concluded that the almost isoenergetic conformers of $Z_3$ in Figure 9 are rapidly interconverting on the NMR time scale. The $^1$H NMR spectrum of $Z_3$...
corresponds to a symmetrical structure in which a singlet from the inner xylenic protons (4H, indicated by ‘a’ in Figure 10) is readily distinguished from the distorted AB quartet from the outer xylenic protons (8H, indicated by ‘b’ in Figure 10). Figure 10 shows that both the xylenic signals from Z3 shift upfield upon an incremental addition of up to 1 equiv of Ag⁺ cation. Moreover, the incremental addition of Ag⁺ beyond 1 equiv shows the upfield shift of only the outer xylenic protons up to addition of 2 equiv of silver cations, while the signal due to the inner xylenic protons remains unchanged (Figure 10).

The ¹H NMR spectral change in Figure 10 can be easily reconciled with the aid of Scheme 3. Thus, exposure of Z3 to 1 equiv of Ag⁺ will afford three possible structures containing a deltaphane-like cavity (i.e., Z3-B, Z3-C, and its mirror image Z3-C’) with equal probability, thus affecting the chemical shifts of all xylenic protons equally upon binding to the silver cation (see Figure 10, right). Note that the observation of only one set of signals in the ¹H NMR spectrum indicates that all three silver-bound structures (i.e., Z3-B, Z3-C, and Z3-C’) are in dynamic equilibrium on the NMR time scale. Moreover, accommodation of a second silver cation in structures Z3-B or Z3-C or Z3-C’ requires their transformation into a structure containing two deltaphane-like cavities in such a way that they are well separated from each other to avoid Columbic repulsion between the cationic guests, i.e., structure Z3-D in Scheme 3. Such an analysis is consistent with the fact that the chemical shift of only the outer xylenic protons should be affected upon binding of the second silver cation while the protons from the central xylene ring remain unaffected (see Figure 10). Note that an alternative structure Z3-E containing two deltaphane-like cavities is much higher in energy (~5 kcal/mol) compared to the structures in Figure 9 (or Scheme 3) as established by DFT calculations.

**Summary and Conclusions**

We developed convergent syntheses of hitherto unknown fluorene-p-xylene oligomers Z1–Z9 in excellent yields with
the aid of four repetitive sequences of reactions, i.e., alkylation, lithium aluminum hydride reduction of benzoic esters, conversion of benzyl alcohols to benzyl chlorides using thionyl chloride, followed by alkylation as summarized in Scheme 2. These conformationally mobile and readily soluble oligomers, containing multiple receptor sites, were easily characterized by $^1$H and $^{13}$C NMR spectroscopy as well as mass spectrometry. The binding of multiple silver cations to $Z_3$–$Z_9$ was possible due to the folding of these oligomers, by simple C–C bond rotations, to produce structures containing multiple deltaphane-like receptor sites (see Figure 8) for efficient binding of silver cations (i.e., $K \approx 15000$ M$^{-1}$). The reproducible $^1$H NMR spectroscopic titration of the oligomers $Z_1$, $Z_3$, $Z_5$, $Z_7$, and $Z_9$ containing an even number of fluorene moieties confirmed that they bind 1, 2, 3, 4, and 5 silver cations, respectively, whereas oligomers $Z_2$, $Z_4$, $Z_6$, and $Z_8$ containing an odd number of fluorene moieties bind 1, 2, 3, and 4 silver cations, respectively (see Figure 6). The number of Ag$^+$ cations captured by various oligomers $Z_1$–$Z_9$ is readily accounted for by the fact that introduction of Ag$^+$ cations induces folding of the oligomers containing even number of fluorene moieties to produce 1, 2, 3, 4, and 5 deltaphane-like cavities in $Z_1$, $Z_3$, $Z_5$, $Z_7$, and $Z_9$, respectively, whereas oligomers ($Z_2$, $Z_4$, $Z_6$, and $Z_8$) containing odd number of fluorene moieties form 1, 2, 3, and 4 deltaphane-like cavities together with a single fluorene/xylene pair in an extended conformation. Note that the receptor site with an extended conformer binds silver cation with much less efficiency, i.e., $K \approx 10$ M$^{-1}$ (see eq 3).

We are actively exploring the syntheses of the Zn analogues containing different substituents both on xylene and fluorene moieties to further modulate the binding and selectivity of various metal cations to these conformationally adaptable nanometer-sized materials with multiple metal binding sites.

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Supporting Information Available: Synthetic details, $^1$H/$^{13}$C NMR data for various intermediates, $^1$H NMR spectral titration data with silver cation, and X-ray structural data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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