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Highlight Review

Tetrathiafulvalene-based Cruciform Molecules

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Abstract

Molecules with two orthogonally oriented π-systems (cruciforms) have attracted interest by virtue of the different conjugation pathways that exist between the individual parts of the molecule. In particular, the possibility for changing the conjugation pathways by an external stimulus may provide controllable molecular switches for molecular electronics. Here we highlight our design and synthesis of cruciform molecules incorporating the redox-active unit tetrathiafulvalene (TTF) placed vertically to an oligo(phenyleneethynylene) (OPE) unit. These molecules have potential as redox-controlled wires (transistors) for molecular electronics. The OPE–TTF cruciforms are prepared by a combination of stepwise metal-catalyzed cross-coupling and Wittig reactions.

◆ Introduction

Development of functional organic molecules that may serve as for example transistors, switches, or rectifiers for molecular electronics has attracted wide interest in recent years.[1] The molecular wire should have some kind of *active* moieties that can be triggered by an external stimulus, e.g., by oxidation/reduction or by light, to thereby change the orbital arrangement or conjugation pathway along the molecule. Cruciform molecules with two perpendicularly disposed π-systems could serve this purpose by having as the one π-system the redox-active unit tetrathiafulvalene (TTF, Figure 1). TTF is a good electron donor and can reversibly be oxidized in two one-electron steps. It has for this reason been widely used in materials and supramolecular chemistry and most recently as a redox-active unit in molecular electronics.[2] When it comes to molecular wires, two particular classes of molecules stand out, namely thiol-terminated oligo(phenylenevinylene)s (OPVs)[3] and oligo(phenyleneethynylene)s (OPEs).[4] With the objective to design redox-controlled molecular wires, we decided to place one or more TTFs vertically to a conjugated OPE backbone, generating a cruciform-like structure (Figure 1). Albeit the OPE and TTF units are not placed strictly vertically to each other, we shall still use the term cruciform for such molecules.

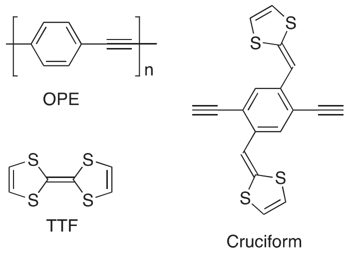


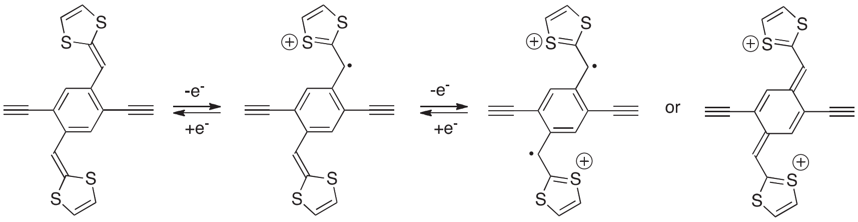
Figure 1.

The underlying idea of having an extended TTF unit placed perpendicularly to the OPE system is shown in Scheme 1. Upon oxidation of the two dithiafulvene moieties, a dication will be generated, which eventually will lead to a change in the electronic properties of the OPE backbone. Thus, a cross-conjugated pathway is possibly generated in the wire, or alternatively a diradical structure. This change is expected to be accompanied by a change in the conductance along the molecule when each end hereof is adhered to an electrode.

Before turning to the synthesis of OPE–TTF cruciforms, we shall briefly mention that several other cruciform-like, acetylenic analogs of TTF have been reported by both us and others. Examples include the tetraethynylethene-TTF **1**,[5] benzene- and anthraquinone-extended TTFs **2**[6] and **3**[7] incorporating two protected alkyne functionalities for further scaffolding, and the anthraquinone structure **4**[8] (Figure 2).

◆ Synthesis

In 2006 we developed an efficient route to the extended TTF **5**, which besides the redox-active dithiafulvene units also contained acetylenic functionalities protected by trimethylsilyl (TMS) groups (Figure 3).[9] In 2008 it was followed up by the



Scheme 1.

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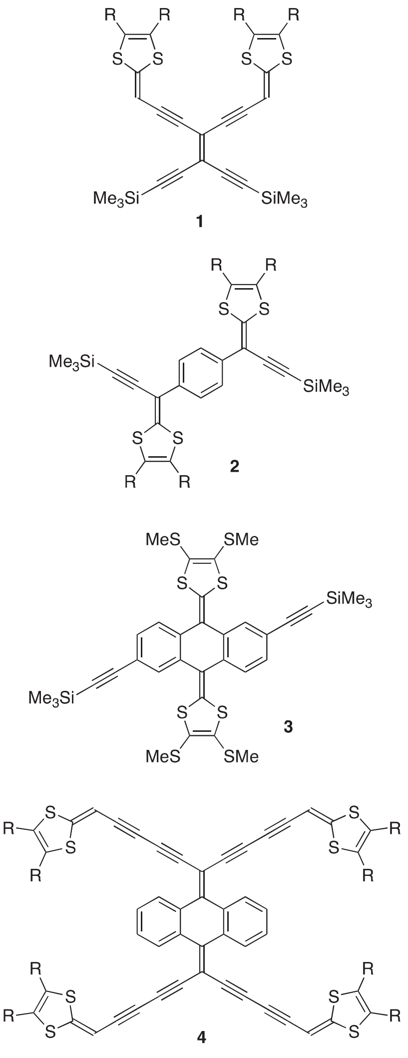
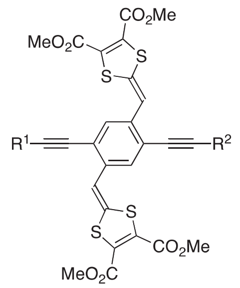


R = CO_2CH_3

Figure 2.

unsymmetrical cruciform **6** which contains a triisopropylsilyl (TIPS) group.[10]

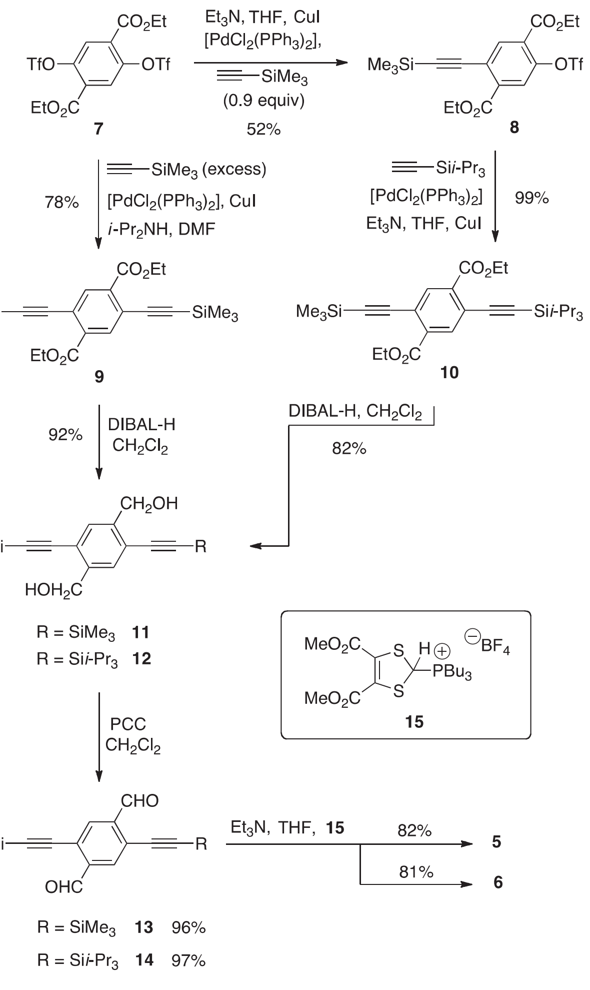
The general synthetic procedure for these parent TTF-cruciforms **5** and **6** are shown in Scheme 2. The synthesis starts with the ditriflate **7** which is easily obtained from the commercially available diethyl 2,5-dihydroxyterephthalate.[11] The triflate **7** will give either the mono- or dialkynylated product **8** and **9**, respectively, when using a specific amount of TMS-protected acetylene in the metal-catalyzed cross-coupling. Subjecting compound **8** to another cross-coupling reaction with TIPS–acetylene provided the diethynylated molecule **10** with two different protecting groups. Full reduction of the ester-groups on compounds **9** and **10** with diisobutylaluminium hydride (DIBAL-H) gave the alcohols **11** and **12** in good yields. Oxidation with pyridinium chlorochromate (PCC) gave in almost quantitative yields the aldehydes **13** and **14**. Treating these aldehydes with the phosphonium salt **15**[12] and triethylamine in a Wittig reaction furnished, after deprotonation of the phosphonium salt, the TTF-cruciforms **5** and **6**.



$R^1 = R^2 = SiMe_3$ = **5**

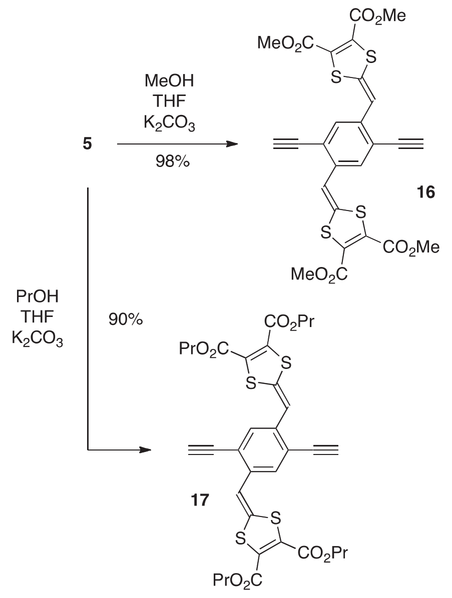
$R^1 = SiMe_3$, $R^2 = Si$*i*-Pr_3 = **6**

Figure 3.

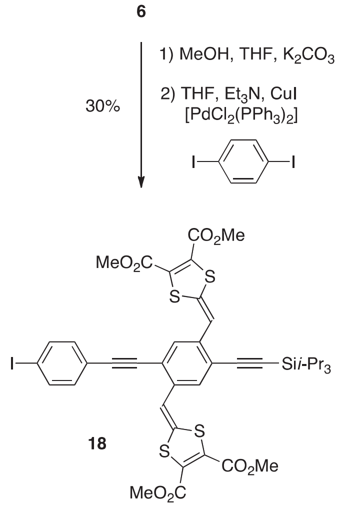


Scheme 2.

Removal of the TMS-protecting groups on TTF-cruciform **5** under mild conditions (K_2CO_3/THF/MeOH) gave the terminal alkyne compound **16** (Scheme 3). Choosing a different alcohol in the desilylation reaction will also give a fourfold trans-esterification; for example, the use of propanol furnished compound **17**. When using more bulky alcohols the desilylation reaction was strongly retarded.[13] It is worth noting that compounds **16** and **17** are stable at room temperature even though they have two terminal alkyne moieties. In our previous



Scheme 3.

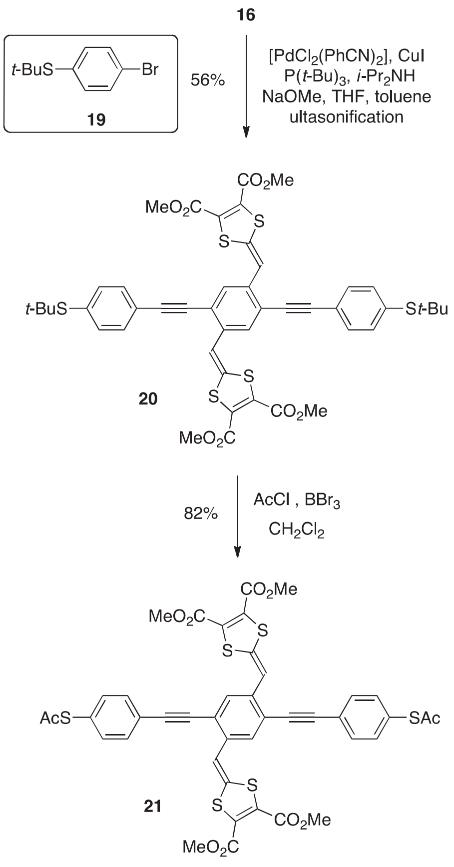


Scheme 4.

work on tetraethynylethene-extended TTFs (compound **1**), the desilylated species suffered from lack of stability, which rendered further acetylenic scaffolding difficult with this module.

Selective desilylation of differentially protected compound **6** followed by a Sonogashira cross-coupling reaction with 1,4-diiodobenzene gave rise to the OPE2 cruciform **18** shown in Scheme 4.[13] Compound **18** has an aryliodide functionality that may be used for further scaffolding, which is something to be explored in future work.

The desilylated alkyne **16** was subjected to the *tert*-butyl-protected benzenethiol **19**, which under Sonogashira cross-coupling conditions (with minor modifications) gave the OPE3 **20** presented in Scheme 5.[9] The *tert*-butyl groups were converted into acetyl groups in high yield using BBr_3/AcCl providing the OPE3–TTF **21**. Compound **21** could also be made directly from the cruciform **16** by treating it with 4-bromophenyl thioacetate under cross-coupling conditions.[13]

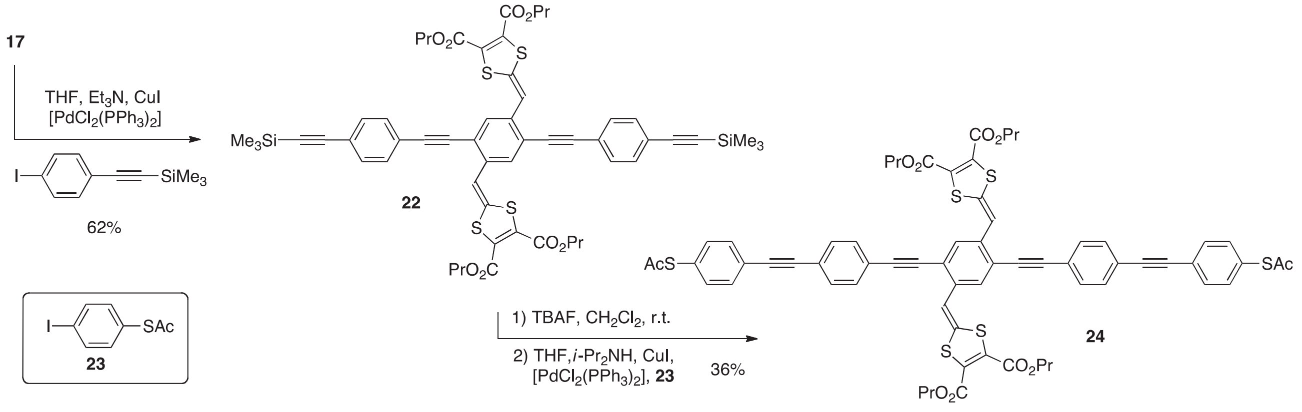


Scheme 5.

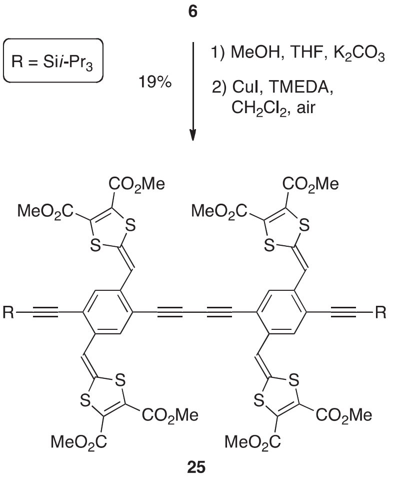
To increase solubility of larger scaffolds built from the parent TTF cruciform **5**, the desilylated alkyne **17** with four propyl esters was recently used.[13] Thus, compound **17** was expanded in a twofold cross-coupling reaction with 1-iodo-4-(trimethylsilylethynyl)benzene to the OPE3 **22** shown in Scheme 6. Desilylation of compound **22** with tetrabutylammonium fluoride (TBAF) followed by a Sonogashira cross-coupling reaction with the iodide **23** furnished the OPE5 **24** with acetyl-protected thiols.

The monosilylated compound derived from **6** can also be used in a Glaser–Hay homo-coupling reaction, generating the extended TTF dimer **25** shown in Scheme 7.[10] Compound **25** was also synthesized in a different manner, by which first the acetylenic scaffold was put together by desilylation and the Glaser–Hay homo-coupling of compound **10**. Conversion of the ester groups to aldehyde groups in two steps (via the alcohol groups) followed by a final fourfold Wittig reaction finally generated the TTF dimer **25**.[10]

Our next objective was to synthesize OPEs incorporating two extended TTFs. As described above, two strategies can be followed. The one employs acetylenic scaffolding of benzene-extended TTFs with ethynyl groups at the benzene ring; the other employs assembly of the OPE wire before functionalization with dithiafulvene groups. The second strategy is shown in Scheme 8 for preparing an OPE3 with two extended TTFs. First, compound **10** was selectively desilylated to give the free alkyne **26**, which in a high-yielding double cross-coupling reaction with 1,4-diiodobenzene furnished the OPE3 **27**. The four esters



Scheme 6.



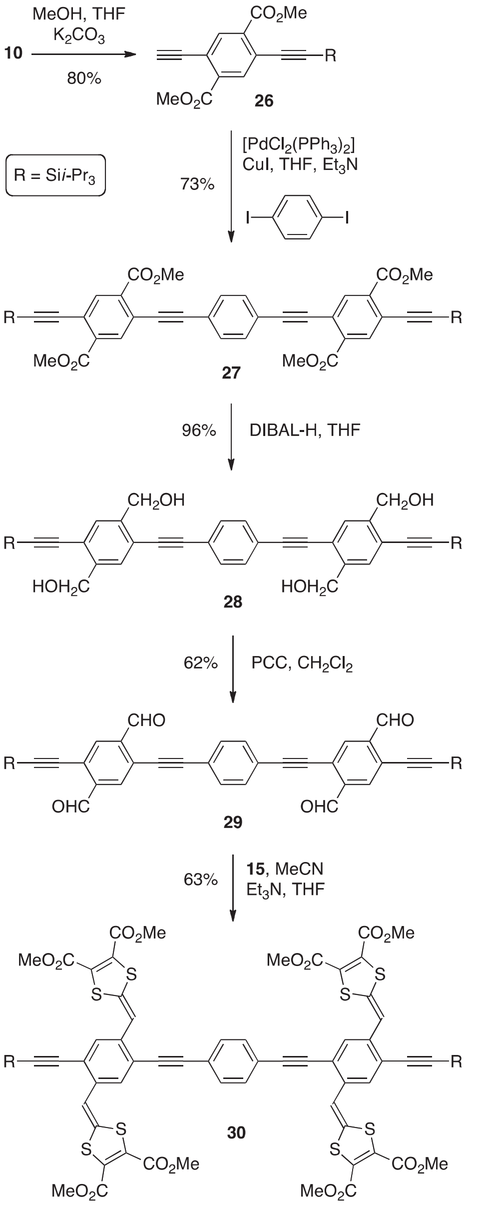
Scheme 7.

were then quantitatively converted into alcohol groups, giving compound **28**. Oxidation of the alcohols with PCC provided the cruciform-precursor **29**, which in a final fourfold Wittig reaction, by treatment with compound **15** and triethylamine, was converted to the OPE3 **30** with two perpendicularly oriented extended TTF moieties.

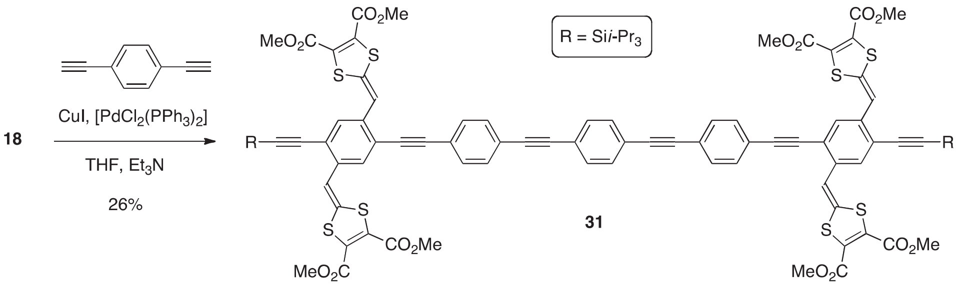
The largest yet cruciform system that we have prepared is shown in Scheme 9, here employing the first method of scaffolding as mentioned above. The OPE5 **31** was obtained from a Sonogashira cross-coupling reaction between compound **18** and 1,4-diethynylbenzene.[13] We were able to isolate this compound, but unfortunately, it exhibited limited stability, which hindered its detailed characterization.

♦ *Optical and Redox Properties*

The TTF cruciforms are strong chromophores as revealed by the UV–vis absorption spectra of selected compounds **17**, **24**, **25**, and **30** in Figure 4. The "monomer unit" **17** shows a broad absorption in the range of 400 to 440 nm ($\lambda_{\max} = 424$ nm, $\varepsilon = 67400\,\mathrm{M^{-1}\,cm^{-1}}$). Linking two of these together as in the dimer **25** results in a very broad absorption in the range from 300 to 470 nm and a red-shifted absorption onset. The OPE3 **30**, also containing two extended TTFs, exhibits similar absorption



Scheme 8.



Scheme 9.

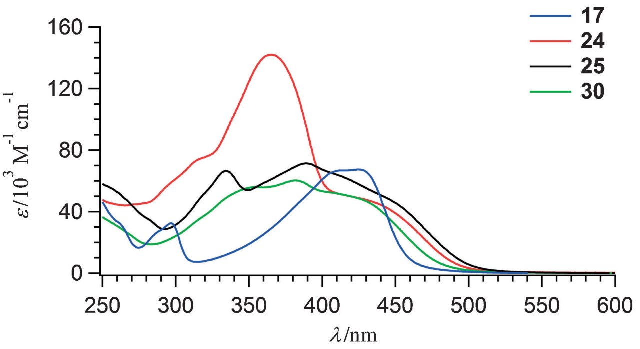


Figure 4. Absorption spectra of **17** (2.0×10^{-5} M), **24** (4.5×10^{-6} M), and **30** (2.0×10^{-5}) in CH_2Cl_2.[13] Compound **25** (1.5×10^{-5} M) was recorded in $CHCl_3$.[10]

Table 1. Potentials[a] (V) obtained from cyclic voltammetry (CV) data

Compound	6	21	25	30
$E_{ox}{}^1$	0.56	0.50	0.61	0.48
$E_{ox}{}^2$	0.67	0.85	0.96	0.86
$E_{ox}{}^3$	0.93			

[a] All the potentials were determined in CH_2Cl_2 using Ag/Ag$^+$ as reference electrode, Pt as the counter electrode, and glassy carbon as the working electrode. Potentials are referenced to Fc/Fc$^+$. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate 0.1 V s^{-1}.

properties to those of **25**. The OPE5–TTF **24** (only one TTF) stands out with a very strong absorption at λ_{max} 365 nm with a molar absorptivity of 145000 M^{-1} cm^{-1}. This absorption may originate partly from the OPE5 backbone as judged by comparison to the absorption of a related OPE5.[14] Like the other compounds, the OPE–TTF **24** also shows a broad absorption at lower energy extending to about 500 nm.

In Table 1 the redox potentials for compounds **6**, **21**, **25**, and **30** are collected based on cyclic voltammetry (CV) data.[10,13] It should be emphasized that the waves are rather broad, and the oxidations did not occur fully reversibly, which complicates a detailed interpretation of the data. Thus, oxidations of **21** and **30** resulted in formation of new species. We were for this reason not able to elucidate the optical properties of the oxidized cruciforms. It is well known that the HOMO–LUMO gap of TTF itself changes significantly upon one- and two-electron oxidations.[15] Likely the oxidized cruciform species undergo intermolecular reactions upon oxidation. This reactivity in solution should not pose a problem, however, for exploitation of these molecules in single-molecule devices, here switching between redox states as suggested in Scheme 1.

◆ Concluding Remarks

During the past five years we have prepared a variety of TTF cruciforms that vary in both the length and nature of the central wire and in the number of vertically oriented TTF units. This work has in particular benefitted from a versatile building block, namely a benzene-extended TTF with two ethynyl groups at the central benzene ring. This building block shows excellent stability and is hence well suited for acetylenic scaffolding. We have also explored an alternative route for making TTF cruciforms, in which the central wire is first constructed and in a final step the dithiafulvene groups are incorporated. The molecular electronics properties of the molecules in single-molecule devices are currently being studied by collaborators. Hopefully, the results of these studies will soon be available.

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