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New Building Block for C_3 Symmetry Molecules: Synthesis of *s*-Triazine-Based Redox Active Chromophores

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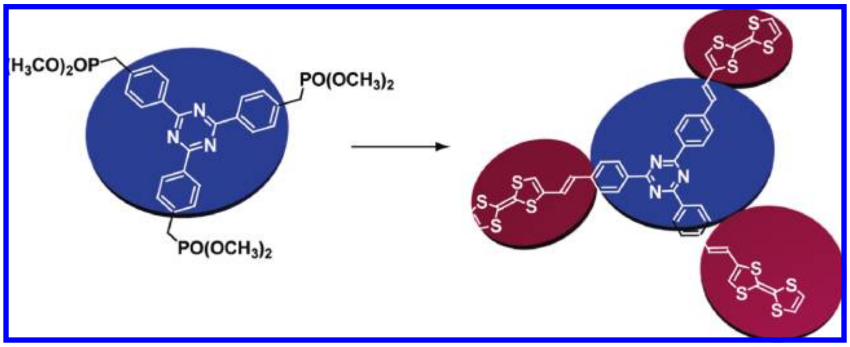
ABSTRACT



A new *s*-triazine-based C_3 building block, endowed with three phosphonate groups, has been prepared in a simple two-step synthesis starting from *p*-bromomethylbenzonitrile; the new building block easily undergoes further olefination reactions to afford in a straightforward manner tris(tetrathiafulvalene)- and tris(ferrocene)-1,3,5-triazines.

Symmetry has fascinated chemists from earlier times. In addition to the inherent beauty of symmetric molecules, symmetry plays a leading role in important chemical topics such as supramolecular self-assembly, chemical selectivity, chiral recognition, or synthesis design, including asymmetric synthesis and asymmetric catalysis, just to name a few.[1]

Among the different symmetric organic compounds, a versatile and readily available C_3 molecule is 1,3,5-triazine. This simple molecule is well-known in organic chemistry and it has been used in a variety of applications as 2,4,6-mono-, di- or trisubstituted derivatives endowed with different substituents.[2] Because of the high reactivity and easy control by temperature of chlorine atoms in cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) toward nucleophiles, this reagent has typically been used as the starting material for the preparation of *s*-triazine derivatives.[3] Actually, cyanuric chloride as building block has allowed to prepare a huge number of substituted *s*-triazines,[4] including those in which the triazine ring acts as the core for the construction of

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dendrimers.[5] Furthermore, important derivatives of cyanuric chloride such as cyanuric or isocyanuric acids and melamines acting as both hydrogen bond donors and acceptors are important types of supramolecular building blocks able to form stable aggreagates.[6]

In addition to the interest of *s*-triazines as biologically active compounds,[2,3,7] 1,3,5-triazines have also found important applications in materials science. Thus, mesoporous metal-organic frameworks have recently been prepared as truncated-octahedral crystals by solvothermal reaction between triazine-1,3,5-tribenzoic acid and $Tb(NO_3)_3.5H_2O$ forming pores of around 5 nm in diameter.[8] Furthermore, triazine-based materials for electroluminescence devices,[9] donor−acceptor redox-active materials,[10] nonlinear optics,[11] two-photon absorption materials,[12] magnetic properties,[13] as well as concave-convex supramolecular interactions between electroactive highly phenylated triamino-*s*-triazines and [60]fullerene[14] are some remarkable examples which have been reported along the last recent years.

Very recently, the synthesis and structural study of mono- and bis(tetrathiafulvalene)-1,3,5-triazines as covalently linked donor−acceptor systems has been reported.[15] Again, the synthesis of these compounds was carried out from cyanuric chloride as starting material and the resulting compounds showed a planar geometry with strong electronic interaction between the electroactive donor and acceptor moieties. Interestingly, these compounds were obtained in remarkably low yields (3%) for those compounds bearing one or two tetrathiafulvalene (TTF) units covalently linked to the *s*-triazine ring. Furthermore, no data were given for the preparation of the C_3 symmetric compound endowed with three TTF units.

TTF and its derivatives are well-known strong electron donor molecules which have been used extensively in the preparation of salts and charge transfer complexes exhibiting electrically conducting properties.[16] More recently, TTFs have found application in many other scientific areas such as chemical sensors and redox-switchable ligands, molecular shuttles, molecular switches and molecular rectifiers.[17] Furthermore, it has also been confirmed that TTF can display efficient nonlinear optic (NLO) responses in the second and third harmonic generation,[18] and as materials for photovoltaic applications.[19]

In our group we have previously reported different TTF-containing molecules built on the 1,3,5-benzene core with a C_3 symmetry.[20] In this communication we report on the preparation of a new and readily available C_3 symmetry building block (**3**) endowed with three phosphonate groups, which easily undergoes further olefination reactions to afford in a straightforward manner *s*-triazine derivatives. Since aldehydes and ketones are widely spread in the toolbox of organic chemistry, this approach represents a highly versatile procedure for the synthesis of conjugated *s*-triazine derivatives. The preparation of the intermediate building block was carried out in two steps from readily available materials as it is shown in Scheme 1. Thus, reaction of *p*-bromomethylbenzonitrile (**1**) with triflic anhydride in refluxing dichloromethane led to the new *s*-triazine **2** in 93% yield by following a similar procedure to that reported in the literature for related compounds.[21] Further Arbuzov reaction by refluxing **2** with trimethyl phosphite afforded the new building block **3** bearing three phosphonate groups in 80% yield. Compounds **2** and **3** were fully characterized by using spectroscopic techniques (UV−vis, FT-IR, ^1H and ^{13}C NMR, HR-MS). Thus, in addition to the aromatic protons, compound **2** showed a singlet at 4.58 ppm for the methylene groups whereas in **3**, these methylene protons appear as a doublet (3.31 ppm, $J = 22$ Hz) due to the coupling with the P atom of the phosphonate group. The methoxy groups of the phosphonate, again coupled with the phosphorus, appear as a doublet at 3.72 ($J = 11$ Hz). HR-MS confirmed the proposed structures, showing as the main fragmentation the retro-cyclotrimerization process which leads to the corresponding nitrile derivative (see Supporting Information).

Compound **3** is a very appealing building block for the construction of more complex *s*-triazine derivatives by Wittig−Horner olefination reactions with a variety of aldehydes. Thus, as a proof of the chemical reactivity of **3**, we have carried out the synthesis of two new 1,3,5-triazine derivatives by reaction with formylferrocene (**4**) and formyl-TTF (**6**).[22] The reactions were conducted under the same experimental conditions, *n*-butyllithium under argon atmo-

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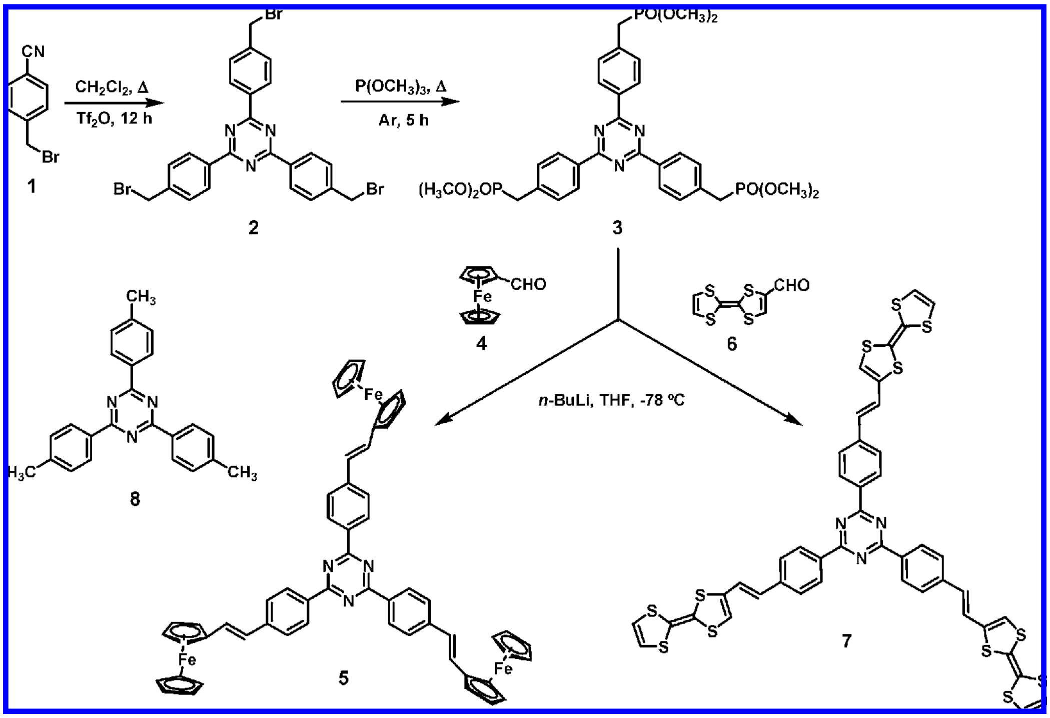
Scheme 1. Synthesis of C_3 Symmetry Building Block **3** and 1,3,5-Triazine Derivatives **5** and **7** and Molecular Structure of Compound **8**[8]



sphere at −78 °C (see Supporting Information). Compounds **5** and **7** were obtained through a 3-fold olefination reaction as stable solids after column chromatography in 45 and 23% yield, respectively. It is worth mentioning that, in contrast to the cyanuric chloride methodology, this approach allows for obtaining more soluble and readily available symmetric s-triazine derivatives in a straightforward manner. As expected, compounds **5** and **7** showed, in addition to the aromatic protons and those of the Ferrocene (Fc) and TTF units, the olefinic protons that appear as doublets at 6.83 (3H, $J = 15.9$ Hz) and 7.10 (3H, $J = 15.9$ Hz) for **5**, and 6.36 (3H, $J = 15.9$ Hz) and 6.98 (3H, $J = 15.9$ Hz) for **7**. HR-MS confirmed the proposed structures.

In the absorption spectra of both compounds the broad band in the visible region at λ_{max} ($CHCl_3$) 484 nm for **5** and 461 nm for **7** evidence the occurrence of a donor−acceptor intramolecular charge-transfer (Figure 1),[15] which was further confirmed by solvatochromic studies which reveal the larger stabilization of the LUMO with increasing the solvent polarity (inset in Figure 1, λ_{max} for **5**: 468 (hexane), 480 (toluene), 484 ($CHCl_3$), 493 (EtOH)). The difference between the λ_{max} of **5** and **7** indicates a smaller HOMO−LUMO gap for **5**, in agreement with the electrochemical measurements (see below). Despite the larger π-system connecting the TTF units to the central *s*-triazine in compound **7**, the observed λ_{max} values are hipsochromically shifted in comparison with previously reported planar *s*-triazine-TTF systems.[15] This finding can be accounted for by the loss of planarity in **7** which results in a larger HOMO−LUMO gap.

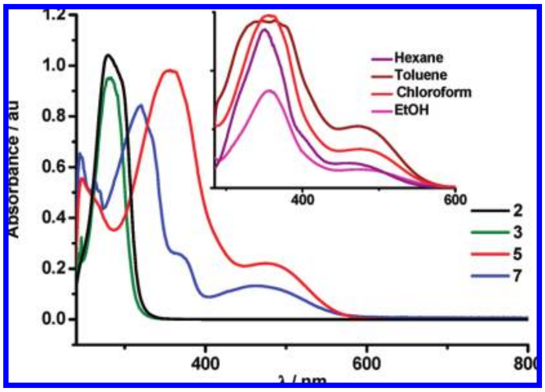


Figure 1. UV−vis spectra of **2**, **3**, **5**, and **7** recorded in $CHCl_3$ (1×10^{-5} M). (Inset) Batochromic shift of the λ_{max} of **5** when solvents of different polarity are used.

Cyclic voltammetry studies of the new electroactive compounds **5** and **7** and, tri(*p*-tolyl)-*s*-triazine (**8**),[8] Fc, and the parent unsubstituted TTF as reference compounds were measured in THF (Table 1 and Figure 2). As expected, compounds **5** and **7** showed an amphoteric redox behavior showing the oxidation features of the electron donor moiety as well as that of the triazine as the acceptor unit. Thus, compound **5** bearing three Fc units presents a reversible oxidation wave at +257 mV to form the ferrocinium species, which is in good agreement with that observed for the parent Fc which shows the first oxidation wave at +252 mV. Similarly, compound **7** endowed with three TTF moieties shows two quasi-reversible oxidation waves at +240 mV and +532 mV corresponding to the formation of the radical cation and dication species (Table 1). Interestingly, the oxidation waves for the parent TTF appear at +210 mV and +527 mV, which indicates that there is a significant electronic communication between the TTF units and the central triazine ring through the π-conjugated bridge (Figure 2). However, this interaction occurs between each TTF and the triazine ring without observing any interaction between the three TTF units, which undergo the oxidation process independently. The same trend has also been observed for the Fc derivative (**5**), although the shift observed in the oxidation wave is remarkably lower.

Table 1. Redox Potential of Derivatives **5**, **7**, **8**, and Reference Compounds (THF, in mV vs Ag/AgNO$_3$)[a]

compound	$E^1_{1/2,ox}$	$E^2_{1/2,ox}$	E^1_{red}[b]
8	–	–	−1979
Fc	+252	–	–
5	+257	–	−1793
TTF	+210	+527	–
7	+240	+532	−1853

[a] Experimental conditions: GCE as working electrode, Pt as counter, $Bu_4N^+PF_6^-$ (0.1 M) as supporting electrolyte, 100 mV/s scan rate. [b] Irreversible process, only cathodic peak potentials are reported.

On the reduction side, pristine tri(*p*-tolyl)-*s*-triazine shows only one quasi-reversible reduction wave at −1979 mV, in agreement with other *s*-triazines reported in the literature.[23] In compounds **5** and **7**, the presence of a quasi-reversible or a totally irreversible wave, respectively, is observed, which might indicate that the presence of the donor unit significantly alters the stability of the radical ion species formed in the reduction process, resulting in an irreversible redox behavior.

In summary, we have carried out the synthesis in a high yield of a new readily available (two synthetic steps) and highly versatile C_3 building block endowed with three phosphonate groups, which easily undergo further olefination reactions to afford, in a straightforward manner, a variety of *s*-triazine derivatives. As a proof-of-principle, we have carried out the synthesis of two new electroactive C_3 symmetry molecules bearing three ferrocene (**5**) or three TTF units (**7**) which have been easily obtained in moderate yields, and have been spectroscopically and electrochemically characterized. Interestingly, an electronic communication between the three electron donor units located at the periphery and the electron acceptor triazine core is observed in the cyclic voltammetry studies. However, the three donor fragments behave independently showing in the CV the signals corresponding to only one unit.

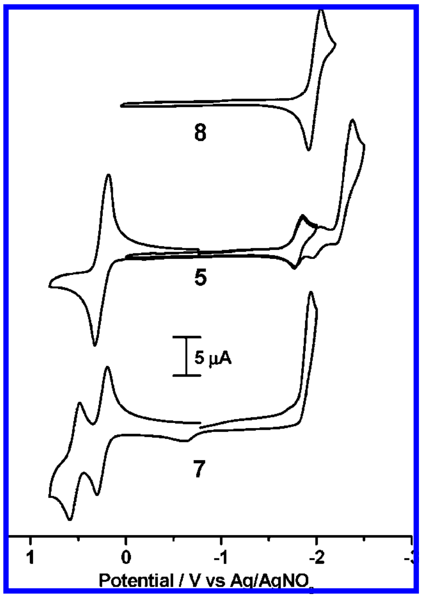


Figure 2. Cyclic voltammograms of *s*-triazines **8**, **5**, and **7**.

We feel that this work paves the way for the efficient preparation of a wide variety of C_3 symmetry molecules from this new building block (**3**) and a myriad of compounds bearing the most frequent aldehyde functionality. Investigations along this line is the focus of ongoing efforts.

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Supporting Information Available: Synthetic procedures and characterization details for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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