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Donor–acceptor ferrocenyl triazines: synthesis and properties

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A series of star shaped donor–π–acceptor type symmetrical triazine was designed and synthesized by the Pd-catalysed Sonogshira cross coupling reaction. The ferrocenyl moiety with different spacer groups acts as donor and 1,3,5-triazine as acceptor. The photophysical results show intramolecular charge transfer from ferrocene to the 1,3,5-triazine unit. The cyclic voltammetric analysis reveals substantial donor–acceptor interaction. The triazines exhibit good thermal stability with high decomposition temperature.

Donor–acceptor (D–A) organic materials have attracted substantial interest in opto-electronic applications such as organic photovoltaics (OPV), organic light emitting diodes (OLED) and thin film transistors (TFT).[1–3] The 1,3,5-triazine derivatives show excellent photonic, and electronic properties due to the high electron affinity, and symmetrical structure.[4] The literature reveals that integrating the donor groups into the triazine moiety results in donor–acceptor system, which exhibits high two-photon absorbing (2PA) cross-section.[5]

Recently we have reported the donor–acceptor triazine, where the donor group is connected via phenyl spacers to the triazine.[6] Our group is interested in molecular systems with strong electronic communication.[7–11] The literature reveals that thiophene spacers exhibit better communication compared to phenyl spacers in donor–acceptor system.[12]

In order to enhance the electronic communication between the donor and acceptor group, we have introduced the thiophene bridge. Ferrocene is a widely studied strong donor. In this Letter we have incorporated ferrocenyl moiety into the 1,3,5-triazine core with different spacers and explored its photophysical and electrochemical properties.

The donor substituted triazines **6**–**10** were synthesized by the Pd-catalysed Suzuki and Sonogshira cross-coupling reaction of triazine **3** and triazine **5** with the corresponding ferrocenyl derivatives. Triazine **2** was synthesized by the trimerization reaction of thiophene-2-carbonitrile in the presence of trifluoromethanesulfonic acid in chloroform.[13] The treatment of triazine **2** with threefold excess of N-bromosuccinimide (NBS) resulted in triazine **3** in 87% yield.[14] The Sonogshira cross-coupling reaction of triazine **3** with trimethylsilylacetylene resulted in triazine **4** in 80% yield. The deprotection of the trimethylsilylacetylene group by a mixture of NaOH and methanol resulted in triazine **5** in 68% yield (Scheme 1).

The Sonogashira coupling reaction of triazine **3** with ethynyl ferrocene in the presence of $Pd(dba)_3$ and $AsPh_3$ as a catalyst resulted in triazine **6** in 52% yield.[15] The Suzuki coupling of triazine **3** with ferrocene boronic acid in the presence of $Pd(PPh_3)_4$ as a catalyst resulted in triazine **7** in 57% yield (Scheme 2). In order to synthesize the tri substituted ferrocenyl triazine, the Suzuki coupling reaction was repeated by conventional as well as the microwave method in the presence of $Pd(PPh_3)_4$, Ag_2O and CsF with excess boronic acid. However the isolation of 2,4,6-tris(-5-ferrocene-thiophene-2-yl)-1,3,5-triazine (tri ferrocenyl substituted triazine) resulted in failure.

The Sonogashira coupling reaction of triazine **5** with 1-ferrocene-4-iodo-phenyl, 1-ferrocene-3-iodo-phenyl and 1-ethynyl ferrocene-4-iodo-phenyl in the presence of $Pd(PPh_3)_4$ catalyst resulted in triazines **8**, **9** and **10** in 39%, 40% and 32% yields, respectively, (Scheme 3).[16]

Triazines **5**–**10** were well characterized by ^{1}H NMR, ^{13}C NMR and HRMS techniques (see Supplementary data). The ^{1}H NMR spectra of triazines **6**–**10** exhibit following types of signals; (a) two characteristic doublets between 8.12–8.02 ppm and 7.43–7.02 ppm, corresponding to the thiophene unit; (b) the ferrocenyl group exhibits three different types of peaks, the unsubstituted cyclopentadienyl moiety of ferrocene shows a sharp singlet around 4.21–3.98 ppm the mono substituted cyclopentadienyl ring exhibits two broad singlets around 4.66–4.48 ppm and 4.33–4.20 ppm.

The thermal properties of the ferrocenyl substituted triazines **6**, **8**, **9** and **10** were evaluated using thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} up to 800 °C under a nitrogen

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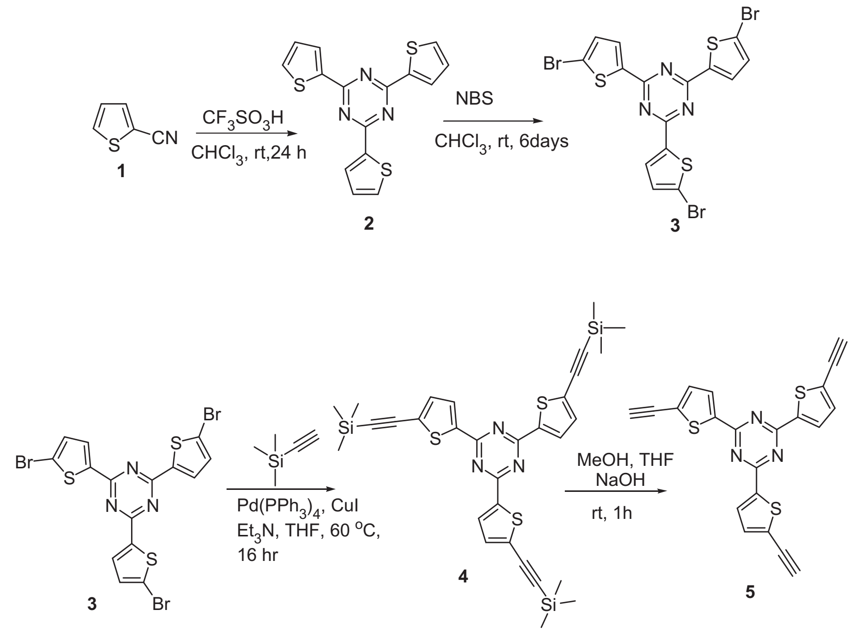
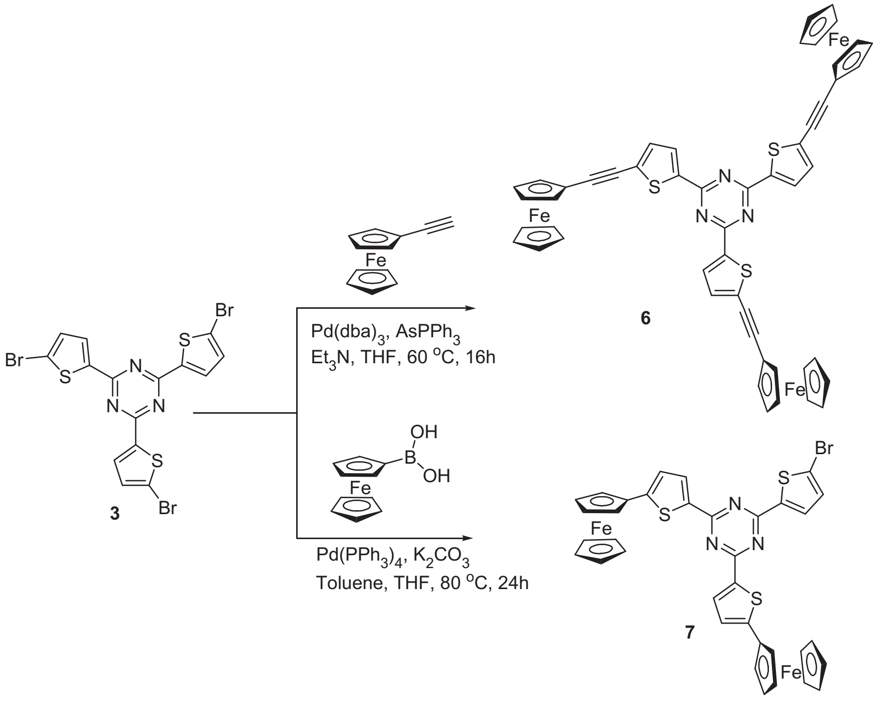


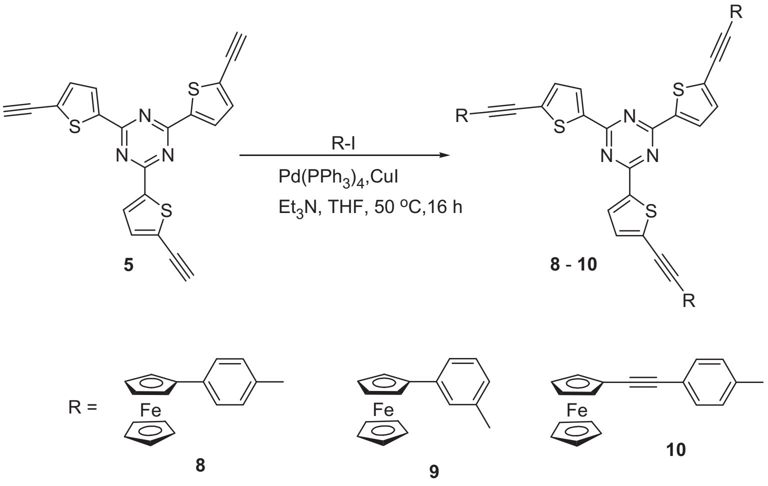
Scheme 1. Synthesis of triazines**2**–**5**.



Scheme 2. Synthesis of triazines **6**–**7**.

atmosphere as shown in Figure 1. The ferrocenyl substituted triazines **6**, **8**, **9** and **10** exhibits good thermal stability with high decomposition temperature. Triazines **6** and **10** exhibit 10% decomposition temperature above 650 °C, whereas triazines **8** and **9** exhibit 10% decomposition temperature below 650 °C, which shows that triazines **6** and **10** are robust compared to the triazines **8** and **9**. The trend in thermal stability follows the order **10** > **6** > **8** > **9**.

The electronic absorption spectra of the ferrocenyl substituted triazines **5**–**10** were recorded in dichloromethane at room temperature (Fig. 2) and the data are listed in Table 1. The ferrocenyl substituted triazines **6**–**10** exhibit strong absorption band between 349 and 382 nm, corresponding to $\pi \rightarrow \pi^*$ transition.[17–19] The $\pi \rightarrow \pi^*$ transition of the ferrocenyl substituted triazines **6**–**10** shows red shift and enhanced molar extinction coefficient (ε) as compared to triazine **5**, which reflects strong electronic communication between the donor and the acceptor moiety. The absorption spectra of triazine **6** and **7** exhibit band at 488 and 504 nm due to the charge-transfer from ferrocene to the triazine unit.[20,21] The presence of separate charge-transfer band was not observed for



Scheme 3. Synthesis of triazines **8–10**.

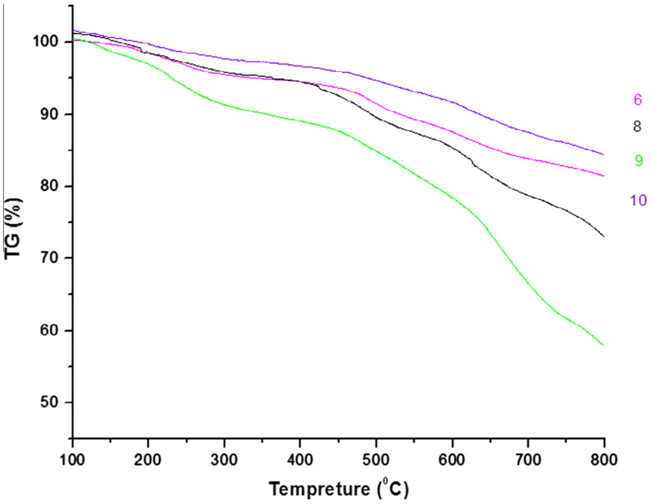


Figure 1. TGA plots of triazines.

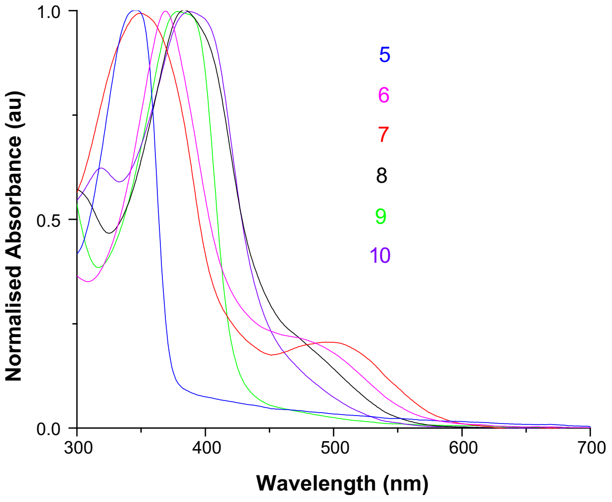


Figure 2. Normalized electronic absorption spectra of triazines **5–10** in CH_2Cl_2 (1.0×10^{-4} M).

Table 1
The photophysical and electrochemical data for triazines **5–10**

Compound	λ_{max} (nm)	ε^a (M^{-1} cm^{-1})	E_{oxid} (V)	E_{red}(V)
5	348 –	5400	–	−1.01 −1.41
6	369 488	7250	0.61	−0.93 −1.49
7	349 504	6450	0.57	−0.92 −1.51
8	382 –	16,400	0.52	−0.93 −1.48
9	378 –	10,440	0.50	−0.93 −1.45
10	387 –	18,680	0.57	−0.92 −1.60
Ferrocene	–	–	0.46	–

[a] The absorption coefficient (ε) values belong to absorption maxima (λ_{max} (nm) of triazines **5–10**)

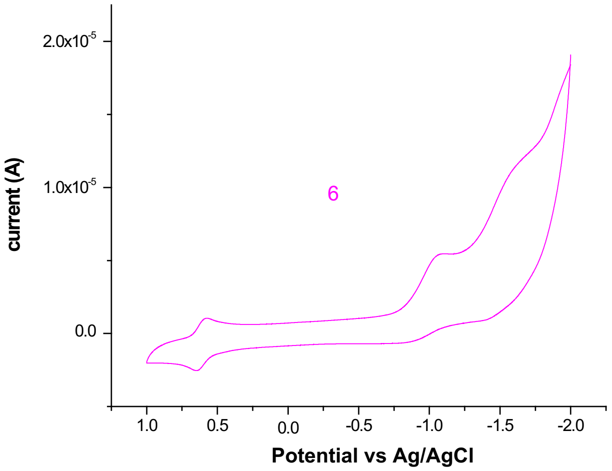


Figure 3. Cyclic voltammogram of triazine **6** in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 (1.0×10^{-4} M) at 100 mV S^{-1} scan rate.

triazines **8**, **9** and **10**, this may be due to the overlap of the charge-transfer absorption with the $\pi \rightarrow \pi^*$ transition.[22] Triazines **6–10** are non-emissive in nature.[23]

The electrochemical behaviour of the ferrocenyl substituted triazines **5–10** were explored by the cyclic voltammetric analysis in dichloromethane solution using tetrabutylammonium-hexafluorophosphate as supporting electrolyte. A representative cyclic voltammogram of ferrocenyl substituted triazine **6** is shown in Figure 3 and the electrochemical data are listed in Table 1. Triazines **6**–**10** exhibit one reversible oxidation wave corresponding to the ferrocene moiety and two quasi reversible reduction waves corresponding to 1,3,5-triazine unit.[24] The oxidation potential of the ferrocenyl moiety in triazine **6**–**10** follows the order **6** > **10** > **8** > **9**. The ferrocene oxidation potential shows harder oxidation compared to free ferrocene, confirming the strong electronic communication between the ferrocenyl unit and the triazine core in triazines **6**–**10**. The trend observed in the oxidation potential depends upon the nature of the spacer group. The compound **6** linked by acetylenic spacer shows harder oxidation potential compared to compounds **8**–**10** due to maximum electronic communication. The *meta* branching in compound **9** disrupts the extended π-conjugation compared to the other phenyl acetylene spacers and thus exhibits lower oxidation potential than triazines **6**, **8** and **10**.

In conclusion, we have synthesized a new set of donor–π–acceptor type ferrocenyl substituted 1,3,5-triazine via Sonogshira coupling reaction. The photophysical and electrochemical behaviour of the triazines shows substantial electronic communication. The study of optical limiting behaviour of these trazines is currently underway in our group.

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Supplementary data

Supplementary data (general experimental methods and copies of ^{1}H NMR, ^{13}C NMR and HRMS spectra and cyclic voltammograms of all new compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.07.119.

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