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COMMUNICATION

C₃ Symmetric Ferrocenyl Triazines: Synthesis, Structure, and Properties

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A series of C₃ symmetric ferrocenyl substituted 1,3,5-triazine have been designed, and synthesized by Sonogshira crosscoupling reaction. The Photophysical, and electrochemical properties of these triazines show substantial donor-acceptor 10 interaction. The single crystal X-ray structure of triazine 3 is reported, which show planar structure. The supramolecular structure of 3 exhibits intermolecular π --- π interaction, which leads to formation of 2D layer structures.

Donor - acceptor molecular system are of great interest, because 15 of their wide variety of applications in the molecular electronics, and photonics.^{1,2} There has been substantial interest in the design, and synthesis of 1,3,5-benzene, and 1,3,5-triazine core. However the 1,3,5-triazine core surpasses, the 1,3,5-benzene core due to its superior electron withdrawing property. The compounds 20 containing 1,3,5-triazine core exhibits good optical, and electrical properties.³ Therefore 1,3,5-triazine compounds has been explored for myriad of applications, such as two-photon absorbing materials, liquid crystalline materials, supra molecular chemistry, electron transporting materials in the light emitting 25 diode, and photovoltaic devices.⁴⁻⁷ There are few reports, where the donor group is attached to the 1,3,5-triazine moiety.^{8,9} our group is interested in the design, and synthesis of donor-acceptor molecular system for NLO applications.¹⁰⁻¹⁵ Ferrocene is a strong donor, thermally, and photochemically stable.¹⁶

In this communication, we have incorporated ferrocenyl moiety into the 1,3,5-triazine core with different spacers, and explored its structural, Photophysical, and electrochemical properties.

The D-A molecular system (3-6) was designed in such a manner, 35 so that the donor moiety ferrocene is attached with the acceptor 1,3,5-triazine via different spacers. The key intermediate 2a, and 2b were synthesized by the cyclization reaction of the corresponding 1a, 1b under strong acid condition (triflouromethanesulfonic acid) in chloroform.¹⁷ The ferrocenvl 40 substituted triazine 3-6 were synthesized by the Pd-catalyzed Sonogshira cross-coupling reaction of the 2a, and 2b with the corresponding ferrocenvl derivatives. The triazine 3, and 4 were synthesized by the conventional method (Scheme 1), whereas the triazine 5, and 6, by the microwave method (Scheme 2). The 45 Sonogshira coupling reaction of the triazine with the corresponding alkynyl ferrocene in the presence of CuI as a cocatalyst, and tetrahydrofuran (THF) as a solvent, and degased with argon gas resulted in Glaser-type homo-coupling of the corresponding alkyne, instead of Sonogshira cross-coupling 50 reaction. The analysis of the reaction condition reveals that the starting material was not completely soluble in THF, and the presence of CuI intiates the homo coupling of the corresponding alkyne. Therefore modifying the solvent system to toluene, and THF (3:1) in which the starting material was soluble, and the 55 removal of the CuI (co-catalyst) which initates homo coupling, resulted in the successfull Sonogshira coupling reaction.



Scheme 1. Synthesis of triazine 3-4

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In a standard procedure the triazine was dissolved in the mixture of solvents toluene, and THF in (3:1) ratio, and the base at 80 °C. The resultant mixture was allowed to attain room temperature, then the catalyst Pd(PPh₃)₂Cl₂, and ethynyl-ferrocene was added, 5 and the reaction mixture was allowed to be stirred at 60 °C for 16 h, using this procedure we succesfully synthesized the triazine 3, and 4 (scheme 1). On the other hand using the same reaction condition for the synthesis of triazine 5, and 6 resulted in failure. Using the microwave under the same solvent condition, and ¹⁰ Pd(PPh₃)₄ as a catalyst at 85 °C for 8 h, we were able to

synthesize triazine 5, and 6 (scheme 2).



Scheme 2.Synthesis of triazine 5-6

The triazines (3-6) are readily soluble in common organic such as dichloromethane, chloroform, solvents and tetrahydrofuran. The triazines (3-6) were well characterized by ¹H-NMR, ¹³C-NMR, and HRMS techniques. The thermal 20 stability of the ferrocenyl substituted triazine 3-6 were carried out

by thermo gravimetric analysis (TGA) under nitrogen atmosphere. The triazines 3-6 shows 10 % wt. loss from 260 °C to 500 °C (Supporting information). The triazine 5 was found to be thermally more stable compared to rest of the triazines. The 10 25 % wt. loss of triazine 5 was around 500 °C. The thermal stability of the triazines follows the order 5 > 3 > 6 > 4.

The single crystal of 3 was grown by the slow evaporation of tetrahydrofuran. The triazine 3 crystallizes in the triclinic $P \bar{1}$ space group, with one molecule of triazine, and three THF 30 solvent molecules in the asymmetric unit. The crystal structure of the triazine 3 is shown in Figure 1. The crystal structure of triazine 3 shows that the phenyl rings are deviated from planarity with respect to the triazine core. The triazine core $\{N(1), C(1), C(1)$ N(2), C(2), N(3), C(3)} shows 1.40° (1) tilt from plane, and the 35 phenyl rings are oriented in different manner around the triazine core. The phenyl ring {C12, C13, C14, C15, C16, C17} is slightly deviated from the planarity with respect to the triazine core {N(1), C(1), N(2), C(2), N(3), C(3)} by 4.94° (3). The second phenyl ring {C4, C5, C6, C7, C8, C9} shows moderate deviation from planarity by the angle of 8.63° (3) due to the direct interaction with solvent (THF) molecule, and the indirect interaction with the solvent (THF) molecule via the ferrocene unit. The third phenyl ring $\{C20, C21, C22, C23, C24, C25\}$ shows greater deviation from planarity by the angle of 13.90° (8) 45 due to the formation of H-bond (O--H) directly with solvent (THF) molecule.



Fig. 1 Single crystal X-ray structure of triazine 3. (i) Front view, and (ii) Side View (THF molecules are deleted)

The crystal structure of the triazine **3** shows stacking between two adjacent molecules. The packing diagram reveals that the triazine core participates in intermolecular π --- π interaction with two adjacent molecules. The triazine core stacked with phenyl {C20, C21, C22, C23, C24, C25} ring of one molecule, and with mono substituted cyclopentadiene ring of the ferrocene belonging to other molecule forms a ⁵ 2D layer structures as shown in Figure 2.



Fig. 2 Supramolecular interaction in compound 3, the interactions are shown by dashed lines through a-axis.

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The UV-vis absorption spectra of the ferrocenyl substituted triazine **3-6** is shown in Figure 3, and the data is summarized in Table 1. The triazine **3-6** shows three types of bands. (a) The ¹⁵ absorption band between 257-286 nm, which can be attributed to d-d transition of the ferrocene moiety. (b) The absorption band between 279 - 349 nm shows high intensity band due to $\pi \rightarrow \pi^*$

- transition of the triazine core. (c) The absorption band between 439-479 nm is due to the charge transfer band. The $\pi \rightarrow \pi^*$ ²⁰ transition of the triazine **3,5**, and **6**, shows red shifted by 31nm, 47nm, 38 nm as compared to the the absorption band of reference compound of 2,4,6-tris-(4-ethynyl-phenyl)-1,3,5-triazine (λ_{max} at 302 nm),¹⁸ whereas triazine **4** shows blue shifted by 23 nm. The absorption coefficient (ε) values for this ²⁵ absorption band were increased in comparison to the reference compound of 2,4,6-tris-(4-ethynyl-phenyl)-1,3,5-triazine, which supports strong electronic communication between the donor, and acceptor moiety. The triazine **3-6** are non-fluorescent in nature. The presence of Charge transfer (CT) band^{19,20} in case of triazine
- 30 3, and 5 shows better donor-acceptor interaction, and the presence of distinct CT band was not observed for

triazine **4** and **6**. This may be due to the overlap of the charge-transfer absorption with the $\pi \rightarrow \pi^*$ absorption.²¹



Fig. 3 Normalized electronic absorption spectra of triazine 3-6 in CH₂Cl₂.

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The electrochemical behaviors of the triazine **3-6** were studied by the cyclic voltammetric analysis in THF as a solvent (Figure. 4). The triazine 3-6 exhibits one reversible reduction wave, and one oxidation wave corresponding to 1,3,5-triazine, and ferrocene 5 moiety respectively. The cyclic voltammograms of triazines 3-6 are shown in supporting information. The oxidation potential of

- triazine lie in the range of 0.60 to 0.69 V (Table 1). The oxidation potential data of triazine 3-6 reveals that the oxidation of the ferrocene unit in the triazines becomes difficult compared to free
- 10 ferrocene, which indicates that the electron density of the ferrocenyl moiety is delocalized into the triazine unit. The compound 3 show hardest oxidation compare to rest of the indicates maximum strong electronic triazines. which communication in triazine 3. The oxidation potential of the 15 triazines following the order 3 > 4 > 5 > 6. The reduction potential of the triazines are not much affected by the donor group as the reduction potential data show small difference.



Fig. 4 Cyclic voltammogram of compound 3 in 0.1 M solution of Bu4NPF6 in THF ($1.0 \times 10-4$ M) at 100 mV S-1 scan rate

Table 1. Photophysical and electrochemical data for triazine 3-6

Compound	λ _{max} (nm)	$b\varepsilon (\mathbf{M}^{-1} \mathbf{cm}^{-1})$	E _{oxid} (V)	E _{red} (V)
3	267 333 479	6916	0.69	- 0.91
4	257 279 -	11416	0.67	- 0.95
5	283 349 468	18083	0.67	-0.95
6	286 340 -	15500	0.60	-0.93
Ferrocene	_	_	0.58	-

³⁰ ^bThe absorption cofficient (ε) values belongs to absorption maxima

 $(\lambda_{\max} (nm) \text{ of triazine } 3-6)$

In summary we report the synthesis of donor-acceptor type ferrocenyl substituted 1,3,5-triazine by Sonogshira coupling 35 reaction via conventional and microwave method. The

- photophysical, and electrochemical studies show strong electronic communication between the donor, and acceptor units. The triazine 3-6 are thermally and photophysically stable. The crystal structure of 3 exhibits interesting layer pattern structures.
- 40 The studies towards the use of these triazines multi-photon absorbing materials are presently being carried out in our laboratory.

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Notes and References

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The three ferrocenyl groups in triazine show different conformations; staggered, eclipsed skew, and eclipsed.