Accepted Manuscript

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PII: DOI: Reference:	S1010-6030(18)30186-2 https://doi.org/10.1016/j.jphotochem.2018.04.016 JPC 11231				
To appear in:	Journal of Photochemistry and Photobiology A: Chemistry				
Received date:	9-2-2018				
Revised date:	7-4-2018				
Accepted date:	8-4-2018				

Please cite this article as: Kumaraguru Duraimurugan, Vaithialingam Dhanamoorthy, Jagannathan Madhavan, Ayyanar Siva, Synthesis and Photophysical Investigations of C3-Triazine Based Star-like Conjugated Molecules, Journal of Photochemistry and Photobiology A: Chemistry https://doi.org/10.1016/j.jphotochem.2018.04.016

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Synthesis and Photophysical Investigations of C₃-Triazine Based Star-like Conjugated Molecules

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Graphical abstract:



Highlights

C₃-triazine based star-like D-π-A compounds (C8TR and C8PVT) with a very good yield were synthesized.

- Photophysical, aggregation enhanced emission and electrochemical behaviour was studied.
- These two compounds showed a large halochromic effects upon addition of acid and base.

Abstract: Here, we reported two different C_3 -triazine based star-like D- π -A compounds with a very good yield by Wittig-Horner reaction. Photophysical, aggregation enhanced emission and electrochemical properties were systematically studied. These compounds showed a large halochromic effect on its emission color that changes from greenish-yellow to wine red upon addition of trifluoroacetic acid. Further, the spectral changes are confirmed by ¹H-NMR studies.

Keywords: *C*₃-triazine derivatives, Wittig-Horner, Photophysical properties, Aggregation enhanced emission and Halochromic.

1. Introduction

Organic smart molecules with donor- π -acceptor (D- π -A) system have attracted much attention because of their potential applications in photonic and optoelectronics [1]. Generally, a fully conjugated architecture with an alternate double and triple bonds along a chain have these kinds of properties. Many devices have been developed based on these type of compounds. In particular, poly (*p*-phenylenevinylenes) linker is most widely used in lightemitting/light-sensitive devices to increase their electro-optical properties depending on its chain length and substituents [2]. D- π -A or D- π -A- π -D molecules exhibit fluorescence properties with an intramolecular charge transfer (ICT) and act as chromophores [3]. The

electron-rich nature of the donor moiety increases the energy of the highest occupied molecular orbital (HOMO), while the electron-poor nature of the acceptor concurrently lowers the lowest unoccupied molecular orbital (LUMO). This leads to a very narrow energy gap for small chromophores [4]. Therefore, the *N*-containing aromatic ring is an excellent candidate to be incorporated in such constructions. In addition, this heterocycle is reported to have a high electron-withdrawing character, significant aromaticity that leads to highly conjugated molecules with basic and potential luminescent properties. These properties help in modulating the optoelectronic properties of molecules as reported in earlier studies [5].

During the past, an intensive research has been contributed towards the synthesis of N-based heterocycles such as pyrimidine, pyridazine and pyrazine heterocycles with π conjugated materials [6]. In specific, various shape based structures with electronwithdrawing group display intense emission, halochromic behavior and optical properties [7]. Among these, triazine has a highly π -deficient character and an easy functionalizing 1,3,5positions, which makes it an appropriate electron withdrawing heteroaromatic for the construction of D- π -A architectures [8]. In this context, a variety of donor-substituted triazine derivatives, in which the electron-donating unit is linked either directly or via a π -spacer, have been synthesized by several research groups [9]. Likewise, another study on triarylamine and 1,3,5-triazine-based TPA materials synthesized along with their electrical and optical properties were also reported [10]. Raquel et al., have reported on the synthesis of C_3 -symmetrical system 2,4,6-tris (triazolyl)-1,3,5- triazine for n-type organic semiconductors [8]. Several reports on 1,3,5-triazine based conjugated molecules exhibits increased nonlinear optical and two-photon absorption properties depending on the intramolecular charge transfer properties [11]. Very recently, s-triazine-based conjugated molecules showed excellent columnar mesomorphism and n-type semiconductor applications were reported.[12].

Inspired by the available literature, we have attempted the following objectives in the present study. (i) to synthesize two different C_3 -triazine based D- π -A compounds with conjugation and an extended π -conjugation along with tris-alkoxy at the end of periphery, (ii) to test the two compounds for photophysical, aggregation enhanced emission, halochromic and electrochemical behaviors, and finally; (iii) to characterize all the final and intermediate compounds by ¹H-NMR, ¹³C-NMR, MALDI-TOF mass and FT-IR spectroscopy.

2. Experimental section

2.1. Materials and methods

Methyl gallate, lithium aluminium hydride (LAH), methyltriphenylphosphonium bromide, pyridinium chlorochromate (PCC), tetrabutylammonium bromide (TBAB), *N*-bromosuccinimide (NBS), 4-bromobenzaldehyde, *p*-tolunitrile, triethylphosphite, potassium *tert*-butoxide (K'OBu) and palladium(II) acetate were acquired from Sigma-Aldrich. 1-bromooctane, trifluoromethanesulfonic acid, trifluroacetic acid and triethylamine were purchased from Avra. Solvents used for chromatography were distilled before use.

2.2. Characterization

Bruker Avance (300 MHz) was used to record ¹H-NMR and ¹³C-NMR spectra. Deuterated solvent was obtained from Aldrich chemicals. Chemical shifts (δ) is indicated in ppm relative to residual solvent peaks or TMS, and the coupling constants are reported in Hz. For TLC analysis, silica gel-G plates (Merck) were used with a mixture of n-hexane and ethyl acetate as an eluent. Silica gel (60-120 mesh) was used for column chromatography using hexane and ethyl acetate acting as an eluent. JASCO V-630 spectroscopy was used to measure absorbance, Agilent 8000 was employed to measure emission spectra and JASCO FT/IR-410 spectrometer was used to record IR stretchings. The quantum yield (Φ_F) of C8TR

and **C8PVT** were calculated using quinine sulfate as standard ($\Phi_F = 0.54$) in 0.1 M H₂SO₄. The different water fractions of THF/water mixtures were prepared by slowly adding distilled water into THF solution of different aliquot and ultra-sonicated at room temperature. CHI 680 electrochemical workstation was used to measure CV at room temperature with a scan rate of 100 mV/s. Scanning electron microscopy image of **C8TR** and **C8PVT** were studied by VEGA 3 TESCAN instrument at 15 Kv.

2.3. Preparation of (*E*)-4-(tris(octyloxy)styryl)benzaldehyde (6)

4-Bromo benzaldehyde (0.68 g, 3.6 mmol) and styrene **5** [13] (1.5 g, 3.06 mmol) was taken in mixture of toluene/DMF (1:1) (20 mL) and nitrogen gas was purged for 15 mins, to this TBAB (0.98 g, 3.06 mmol) and triethylamine (1.23 mL) were added one by one. Finally, 10 mol % of palladium acetate was added. The reaction mass was agitated at 80 - 90 °C and maintained for 12 hrs. Then the reaction was monitored by TLC. The completed reaction mixture was poured into methanol and the solid was separated. The separated compound was washed with methanol and then dried. The crude product was purified by column chromatography. The yield is 1.7 g (93 %). ¹H-NMR (300 MHz, CDCl₃): δ = 9.98 (s, 1H), 7.88-7.85 (d, *J*=9Hz, 2H), 7.65-7.62 (d, *J*=9Hz, 2H), 7.19-7.14 (d, *J*=15Hz, 1H), 7.03-6.95 (d, *J*=24Hz, 1H), 6.74 (s, 2H), 4.05-3.96 (m, 6H), 1.8-1.78 (m, 6H), 1.49-1.47 (m, 6H), 1.29(m, 30H), 0.90-0.86 (t, *J*=12Hz, 9H); ¹³C NMR (75 MHz, CDCl₃) δ = 191.8, 153.9, 143.9, 133.1, 131.9, 130.5, 127.0, 126.6, 106.0, 74.0, 69.9, 32.2, 29.7, 29.6, 26.5, 23.0, 14.4.

2.4. Preparation of C8TR (11)

Phosphonate salt (0.25 g, 0.32 mmol) and compound **4** (0.52 g, 1.05 mmol) were taken in dry THF under a nitrogen atmosphere; K'OBu (0.23 g, 1.92 mmol) was added all at once. Then the reaction mixture was stirred at room temperature. After the completion of the reaction, the mass was quenched by 1.5 N HCl solution. The mass was extracted with DCM

and washed with NaCl solution and concentrated it. The crude product was purified by column chromatography using 10% ethyl acetate in hexane. The yield is 0.59 g (96%). Yellow sticky solid was obtained. ¹H-NMR (300 MHz, CDCl₃); $\delta = 8.78-8.75$ (d, *J*=9Hz, 6H), 7.71-7.68 (d, *J*=9Hz, 6H), 7.22-7.17 (d, *J*=15Hz, 3H), 7.11-7.06 (d, *J*=15Hz, 3H), 6.78 (s, 6H), 4.08-3.98 (m, 18H), 1.90-1.73 (m, 18H), 1.51-1.49 (m, 18H), 1.33-1.25 (m, 90H), 0.90-0.88 (t, *J*=6Hz, 27H);¹³C NMR (75 MHz, CDCl₃) $\delta = 171.5$, 153.7, 142.0, 139.1, 135.5, 132.6, 131.4, 129.7, 127.3, 126.9, 124.8, 124.2, 116.4, 116.2, 74.2, 69.6, 32.3, 32.2, 31.8, 30.7, 30.5, 29.9, 29.8, 29.7, 26.5, 23.1, 14.5; MALDI-TOF mass for C₁₁₇H₁₇₇N₃O₉ (m/z) is 1769.3518, found: 1769.4460.

2.5. Preparation of C8PVT (12)

The procedure was followed same as above, yield is 0.87 g (94%). Yellow fluffy solid was obtained. ¹H-NMR (300 MHz, CDCl₃): $\delta = 8.80-8.78$ (d, *J*=6Hz, 6H), 7.75-7.72 (d, *J*=9Hz, 6H), 7.60-7.52(d, *J*=24Hz, 12H), 7.38-7.36 (d, *J*=6Hz, 3H), 7.27-7.23 (d, *J*=12Hz, 3H), 7.18-7.14 (d, *J*=12Hz, 3H), 7.12-7.04 (d, *J*=24Hz, 6H), 7.02 (s, 6H), 4.06-3.96 (m, 18H), 2.08-1.81 (m, 18H), 1.50-1.48 (m, 18H), 1.33-1.30 (m, 90H), 0.90-0.86 (t, *J*=12Hz, 27H). ¹³C-NMR (75 MHz, CDCl₃) $\delta = 171.2$, 153.7, 153.6, 141.8, 138.7, 137.6, 136.4, 135.8, 133.0, 127.5, 127.1, 118.3, 115.2, 105.5, 74.4, 69.5, 32.3, 32.2, 30.7, 30.0, 29.8, 29.7, 26.5, 23.1, 14.5; MALDI-TOF mass for C₁₄₁H₁₉₅N₃O₉ (m/z) is 2076.1230, found: 2077.6255.

3. Results and discussion

3.1. Synthesis

The synthetic way to the preparation of aldehydes (4 and 6) is shown in scheme 1. Methyl gallate reacts with 1-bromooctane to give the product 2 with a very good yield. Further, the ester gets reduced with LAH to give compound 3. The compound 3 was oxidized by PCC under the inert atmosphere to give aldehyde 4. The compound 4 is confirmed by the

appearance of the carbonyl stretching frequency at 1695 cm⁻¹ in FT-IR. Further, the aldehyde is treated with Wittig salt to give the styrene **5**. In the ¹H-NMR spectrum, alkene proton shows doublet of doublet at 5.58 and 5.18 ppm. On further treatment of compound **5** [13] with 4-bromo benzaldehyde in the presence of palladium acetate (Heck reaction) give rises to product **6**. The formation of compound **6** was confirmed by the appearance of $v_{C=O}$ stretching frequency at 1731 cm⁻¹. Further, triazine precursor was synthesized, according to previously reported earlier [14]. This intermediate was heated with triethyl phosphite at 130 °C for 12 hrs to give phosphonate salt as a colorless solid with a good yield (Scheme. 2).



Reagent and conditions: (a). 1-bromo octane, K_2CO_3 , DMF, rt, (b). LAH, THF, 0 °C, rt, (c). PCC, DCM, 0 °C, rt, (d). Wittig salt, K'OBu, DCM, 0 °C, rt, (e). Pd(OAc)₂, TBAB, triethylamine, toluene/DMF, 90 °C, 12 hrs.

Scheme 1. Synthetic way of intermediates 4 and 6.



Reagent and conditions: (a) Tf₂O, CHCl₃, 0 $^{\circ}$ C, rt, (b) NBS, BPO, benzene, reflux, (c) triethyl phosphite, 120 $^{\circ}$ C, 12 hrs, (d) **4** or **6**, K^tOBu, DCM, 0 $^{\circ}$ C, rt.

Scheme 2. Synthesis of intermediate 10 and target molecules 11 and 12.

3.2. Photophysical properties



Fig. 1. Absorption (a) and emission spectra (b) of **C8TR** and **C8PVT** in solution (THF) and thin film.

Compounds	Solution		Thin film		Stoke's	$\Phi_{\rm F}$
	$\lambda_{abs}(nm)$	$\lambda_{emi}(nm)$	$\lambda_{abs}(nm)$	$\lambda_{emi}(nm)$	- shift (cm ⁻¹) (solution)	(solution)
C8TR	376	532	380	537	7799	0.37
C8PVT	396	563	400	568	7490	0.43

Table 1. Absorption, emission and quantum yield values of C8TR and C8PVT in solution(THF) and thin film.

The absorption and emission spectra of **C8TR** and **C8PVT** were measured in solution (THF) and thin film. The absorption spectra show a major absorption band near 375-400 nm, which corresponds to intramolecular charge transfer transition between donor and acceptor moiety (Fig. 1a). The emission spectra were also obtained by exciting **C8TR** and **C8PVT** compounds at its absorption maximum and their corresponding emission values are tabulated as 532, 563 nm in solution and 537, 568 nm in thin film respectively (Table 1). The absorption and emission value of both the compounds in the solid state are red shifted in comparison with that in solution due to π - π stacking interaction [15,16]. The solvent effect investigation on the photophysical behavior of these compounds was measured to their absorption and emission spectra in different solvents varying from non-polar to polar aprotic solvents such as hexane, benzene, chloroform and ethyl acetate in a sequence of their dielectric constant (Figure. 1-2, ESI).

The absorption spectra of **C8TR** and **C8PVT** show negligible solvatochromic changes. (Table. 1, ESI) Whereas, the wavelength in the emission spectra of **C8TR** seems to be increased showing large Stokes shifts with increasing the solvent polarity. This behavior indicates that the intramolecular charge transfer (ICT) is greater in the excited state than the ground state. Meanwhile, the emission value of **C8PVT** shows a bathochromic shift

compared to **C8TR** in the same solvent (around 510 to 530 nm) which indicates the extended conjugation of a donor-acceptor moiety. Further, the increased emission wavelength was observed from non-polar to polar aprotic solvents, This might be due to charge separation upon excitation, which is confirmed by Dimroth-Reichardt solvent polarity correlations [17] (Figure 3, ESI). The quantum yield value of **C8TR** and **C8PVT** are measured in THF solution with respect to quinine sulfate as standard, which has quantum values of 0.54 in 0.1M sulfuric acid solution (Table 1).

3.3. Aggregation enhanced emission



Fig. 2. (a) Absorption (Insect picture shows the differential spectra of **C8TR** in THF and increasing water fraction) and emission spectra (b) of **C8TR** in THF: H₂O mixtures. (Insect picture shows **C8TR** in THF and at 70 % water fraction).

To study the Aggregation properties of the compounds, the spectral behavior of the diluted THF-water mixtures with different water fractions were examined. Both the molecules were found to be soluble in THF and insoluble in H₂O. On increasing the percentage of H₂O, the existing form of **C8TR** in pure THF has changed to aggregated form. This aggregated form is believed to enhance the emission behavior due to the restriction of intramolecular rotation. The absorption result shows a gradual rise in the intensity and moved

to longer wavelength region. A level of a tail in the visible region was observed, which may due to the formation of nanoparticle suspensions in the aggregated state. The change in absorbance with increasing water fraction as shown in Fig.2a (insect spectra). The redshift in the absorption is due to the weak π - π stacking interaction of the solute molecule in its aggregated state and attributed to the J-aggregation formation [18-19].

The emission spectra of **C8TR** are found to exhibit very weak emission in pure THF solution, whereas on increasing water fraction from 0 to 50 %, the emission intensity is gradually increased. On further increase of water fraction to 60 %, an enhanced twofold intensity is achieved. The plot of [(I/Io)-1] Vs f_w , (where I and Io are the emission intensities with and without water in the THF-water mixtures) displayed the emitting change process of **C8TR** in the THF- H₂O mixed solvent (Figure 5, ESI). This enhanced emission intensity could be due to the AEE effect caused by the formation of molecular aggregates in the presence of a large amount of non-solvent. This concept is explained by the enhanced radiative transition led by the limitation of the rotation of the molecules at the aggregation state (Fig.2b). The formation of nano-aggregates was confirmed by Scanning Electron Microscopy (Figure 6, ESI).

On the other hand, the emission spectra of **C8PVT** differ slightly from **C8TR**. On increasing the water content from 0 to 20 %, there is a slight increase in the emission intensity. On further increase up to 40-60 %, the emission gets red shifted by 25 nm with two-fold enhancements. Upon increasing the water fraction, the emission wavelength showed a remarkable blue shift to 575 nm [20] (Figure 4, ESI), a further increase of the water fraction resulted in a decreased emission intensity. Two reasons are commonly cited for this kind of spectral behavior. Firstly, a restricted the rotation of intramolecular aromatic rings at the aggregation state which could have to enhance the light emission. Second, the aggregation of the solute molecule as nanoparticle suspensions might have led to a reduced intensity [21].

This behavior indicates that AEE properties are mainly based on intramolecular rotation in solution can minimize the emission efficiency. But in the aggregated state, such rotations effectively can be restricted that would lead to blue shifted emission with distorted conformation [11c-d, 13].



3.4. Trifluoroacetic acid titration

Fig. 3. Absorption (a) and emission spectra (b) of **C8TR** in DCM upon addition of TFA at rt. (c) Normalised emission spectra of **C8TR** with and without TFA addition in DCM at excitation wavelength of 385 nm (Insect picture shows reversible color change of **C8TR** towards addition of TFA and TEA).

The nitrogen atoms present in **C8TR** and **C8PVT** are basic in nature that can be easily protonated. Thus, the effect of protonation on **C8TR** and **C8PVT** in DCM solutions was studied [7, 15a]. The DCM solution of these compounds underwent a significant color

change in the presence of trifluoroacetic acid (TFA) (10^{-1} M). This color change was fully reversible by neutralization with a base like triethylamine (TEA) or potassium *tert*-butoxide (K^tOBu).

The spectral change in the absorption and emission of **C8TR** upon addition of TFA acid is illustrated in Fig. 3. The absorption spectra were recorded with increasing amount of trifluoroacetic acid with **C8TR** in DCM solution. On observation, new and more intense red-shifted bands are observed at around 485 nm. This may be due to the presence of protonated species. The bathochromic shifts of the absorption can be explained by an increased charge transfer from the donor to the triazine moiety. For increasing additions of TFA up to 10⁻¹M, we observed an increase in the absorbance band at 485 nm with a concomitant decrease in the absorbance band at 376 nm. The spectral shift between the absorbance maximum of **C8TR** before and after addition of TFA is 110 nm. Such a remarkable shift could be readily visible by naked-eye (wine red) at ambient temperature (Fig. 3a) [15a,22]. The observation of isosbestic points (325 and 420 nm) reveals that the presence of the neutral and protonated forms are in equilibrium and is more predominant at higher concentrations of TFA. Based on the above results, it is inferred that the compound exhibits acid-base equilibria [23].

In the emission spectra, the fluorescence spectral changes of **C8TR** upon the addition of TFA are shown in Fig. 3b. It was clearly indicated that the maximum emission band at 558 nm in DCM solution. The fluorescence intensity was gradually decreased and quenched by various additions of TFA with a slight red shift. A further increase in TFA, the solution emits a wine red fluorescence with new red-shifted peak appeared at ca. 590 nm [Table 2]. The yellow emission of **C8TR** could be quenched significantly by TFA. Therefore, **C8TR** could be used as a probe to detect TFA by the naked eye. The spectral change in optical properties induced by TFA could be recovered by the addition of triethylamine (TEA) (Fig. 4). A similar spectral change also observed for **C8PVT** too (Figure 7, ESI).

We infer that the spectral behavior exhibited in **C8TR** and **C8PVT** aroused from predominant stepwise protonation of the molecules, because of the π -electron donation from the tris-alkoxy peripheral groups. It is possible that the triazine nitrogen is protonated first, causing the red shifts in the absorption and emission. Protonation of the acceptor triazine will greatly enhance its electron withdrawing ability and forming a strong charge-transfer system which leads to red-shifted emission. The possible explanation behind the decreased emission might be due to the twisting of the aromatic system that would lead to non-emissive TICT state which is confirmed by the formation of locally excited state (LE) at 444 nm in **C8TR** and 470 nm in **C8PVT** indicating twisted conformation that would interrupt charge transfer process [6-7, 22-25] (Fig. 3c.).

Table 2. Summary of absorption and emission value changes after addition of TFA (10⁻¹M).

Compd	Abs λ_{max}	$\Delta \lambda_{abs}$	Emi λ_{max}	$\Delta \lambda_{emi}$
C8TR	376 (485 ^a)	109	558 (589 ^b)	31
C8PVT	396 (520ª)	124	590 (620 ^b)	30

^aAbsorption value changes after addition of TFA

^b Emission value changes after addition of TFA



Fig. 4. Protonation and deprotonation of C8TR in the addition of TFA and triethylamine.

3.5. NMR studies

To validate the above hypothesis, we also carried out ¹H-NMR titration of **C8TR** with TFA. ¹H-NMR spectral changes of **C8TR** with the various addition of TFA was monitored in CDCl₃ at room temperature. **C8TR** shows a sharp doublet peak at 8.781 and 7.711 ppm corresponding to aromatic proton adjacent to triazine as indicated (a and b) in Fig. 5 respectively. After 20 µL addition of TFA (10⁻¹M), there is a slight upfield shift from 8.781 to 8.689 ppm and 7.711 ppm that has slightly moved to 7.740 ppm downfield shift is observed [15a]. On further addition of TFA, we observed upfield shift from 8.689 to 8.596 and downfield from 7.740 to 7.765 ppm and a doublet of doublet peak at 7.112 ppm which corresponds to -CH=CH- moving towards the downfield at 7.251 ppm and multiplets peak at 4.080 ppm become well resolved and simplified with addition of TFA which indicates that the aromatic system gets twisted. A similar result also was observed for **C8PVT** too (Figure 8, ESI).



Fig. 5. ¹H-NMR spectra of **C8TR** in CDCl₃ (blue) and 20 μ L (black) and 40 μ L (red) addition of TFA (10⁻¹M).

3.6. Electrochemical studies

Cyclic voltammetry was used to investigate the electrochemical properties of the **C8TR** and **C8PVT** and to estimate their HOMO and LUMO energy levels in 0.1 M solution of (Bu_4N)PF₆ in DCM using Ag/AgCl as a reference electrode (Figure 8, ESI). Both the molecules showed a similar trend of the irreversible oxidation process. Electrochemical band gap (Eg) of the compounds was calculated from the difference between E_{HOMO} and E_{LUMO} . The HOMO levels of molecules are calculated as - 4.99 and - 5.18 eV with the onset oxidation potential starting at 0.232 V for **C8TR** and 0.424 V for **C8PVT**. Likewise, the band gap of the compounds is estimated as 2.64 and 2.78 eV respectively. We have observed the increased LUMO energy values from 2.34 to 2.39 eV of **C8TR** to **C8PVT** [12]. This might be due to the existence of extended conjugation present in **C8PVT**. From the band gap and HOMO-LUMO values, it can be inferred that the synthesized **C8TR** and **C8PVT** could be effectively used as green emitters in fluorescent OLED applications.

4. Conclusion

We have synthesized C_3 -triazine based donor-acceptor functionalized π -conjugated fluorescent molecules with extended conjugation by Wittig-Horner reaction. These two molecules showed a significant photophysical and aggregation enhanced emission properties and also compounds show an intense and reversible color change upon addition of TFA as a result of the protonation of the nitrogen in the triazine ring. These finding reveals that a design of the molecules with the heteroaromatic ring as an acceptor in D- π -A system and understanding their optical properties could aid in the development of promising colorimetric and pH sensor applications.

Acknowledgments

The authors acknowledge the financial support of the Department of Science and Technology, SERB, Extramural Major Research Project (Grant No. EMR/2015/000969), Council of Scientific and Industrial Research (CSIR), HRDG, No. 01(2901)/17/EMR-II, and 01(2540)/11/EMR-II), New Delhi, Department of Science and Technology DST/TM/CERI/C130(G), New Delhi, India.

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