CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Accepted Article

Title: NIR Absorbing Donor-Acceptor Based 1,1,2,2-Tetracyanobutadiene (TCBD) and Cyclohexa-2,5-Diene-1,4-Ylidene-Expanded TCBD Substituted Ferrocenyl-Phenothiazines

Authors: Rajneesh Misra and Madhurima Poddar

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Chem. Asian J.* 10.1002/asia.201700879

Link to VoR: http://dx.doi.org/10.1002/asia.201700879

A Journal of
ACES Asian Chemical Editorial Society

A sister journal of Angewandte Chemie and Chemistry – A European Journal

WILEY-VCH

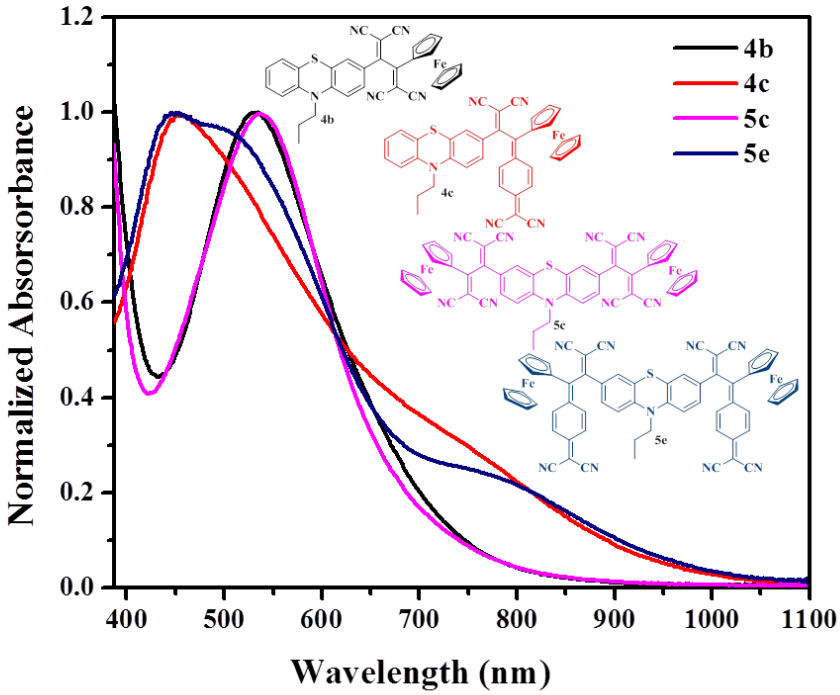
10.1002/asia.201700879

NIR Absorbing Donor–Acceptor Based 1,1,4,4–Tetracyanobuta–1,3–Diene (TCBD) and Cyclohexa–2,5–Diene–1,4–Ylidene–Expanded TCBD Substituted Ferrocenyl Phenothiazines

Madhurima Poddar and Rajneesh Misra*

Department of Chemistry, Indian Institute of Technology Indore, Indore 453552, India

TOC:



This article is protected by copyright. All rights reserved.

Accepted Manuscript

Abstract

A series of unsymmetrical (D–A–D_1, D_1–π–D–A–D_1 and D_1–A_1–D–A_2–D_1) and symmetrical (D_1–A–D–A–D_1) type of phenothiazines **4b**, **4c**, **4c′**, **5b**, **5c**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′**were designed and synthesized by [2 + 2] cycloaddition–electrocyclic ring-opening reaction of ferrocenyl substituted phenothiazines with tetracyanoethylene (TCNE) and 7,7,8,8–tetracyanoquinodimethane (TCNQ). The photophysical, electrochemical and computational studies show strong charge-transfer (CT) interaction in the phenothiazine derivatives which can be tuned by the variation of number of TCNE/TCNQ acceptors. The phenothiazines **4b**, **4c**, **4c′**, **5b**, **5c**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′** show red shifted absorption in 400–900 nm region, resulting in low HOMO–LUMO gap which is supported by TD-DFT calculations. The electrochemical study exhibits reduction waves at low potential due to strong 1,1,4,4–tetracyanobuta–1,3–diene (TCBD) and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptors. The incorporation of cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD stabilizes the LUMO energy level to greater extent as compared to TCBD.

Introduction

π-Conjugated molecular systems containing sulfur (S) and nitrogen (N) atoms are of significant interest for various optoelectronic applications.[1] A wide variety of S and N based heterocyclic units such as thiazoles, benzothiazoles, benzothiadiazole, phenothiazines and many more have been explored for non-linear optics (NLO), organic light emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field-effect transistors (OFETs).[2] The tuning of the photonic properties of these systems can be achieved by altering the strength of donor or

This article is protected by copyright. All rights reserved.

Accepted Manuscript

acceptor units, and the connecting π-linker.[3] Our group is interested in the design and synthesis of small molecule based heterocyclic π-conjugated molecular systems for organic photovoltaics.[4]

The incorporation of heterocyclic moiety into the chromophore backbone leads to higher chemical and thermal robustness.[5] Phenothiazines are interesting mainly because of their inherent folded conformation (folding angle of 158.58°). It can be transformed into a planar conformation by the substitution of different functionalities in the N position of the phenothiazine moiety.[6] Phenothiazine allows variety of reactions including electrophilic substitution at the aromatic position, nucleophilic reaction at the N position, oxidation at the sulfur, *etc*.[6c] In addition, phenothiazines possess low reversible oxidation potential which makes them suitable as electrophores in organic materials.[7] The ferrocene is a strong electron donor and its derivatives play an important role in NLO, superconductor, magnetic, semiconductor, and redox catalyst materials.[8] We were interested to incorporate cyano based 1,1,4,4–tetracyanobuta–1,3–diene (TCBD) and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptors on the ferrocenyl phenothiazine derivatives to study the effect of the acceptors on photonic and electrochemical properties of ferrocenyl phenothiazine. Cyano-based acceptors are one of the most powerful unit for the application in organic electronic devices.[9] The [2+2] cycloadditions of tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with the electron rich alkynes followed by the electrocyclic ring-opening results in donor–acceptor type molecular systems.[10,11,12] They have been used to form charge transfer (CT) complexes with a variety of electron-rich organic and organometallic compounds which exhibit a number of interesting properties such as electric conductivity.[10] Diederich *et al.* are pioneer in the field of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD chemistry and have studied a large variety of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD derivatives.[11,12]

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Michinobu *et al.* have extensively explored the TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD substituted polymers which are supposed to be promising materials for photovoltaic applications.[13] Shoji *et al.* have reported donor–acceptor based TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD molecules as redox active ICT chromophores.[14] Butenschoen *et al.* have reported a variety of 1,1´ -disubstituted ferrocenyl TCBD derivatives.[15] Nakamura and coworkers have studied carbazole and its TCBD derivatives.[16] Our group has reported a vast variety of TCBD functionalized chromophores for organic electronics.[4f, 17]

In continuation of our work on cyano based (TCNE/TCNQ) donor–acceptor materials, herein we report the design and synthesis of unsymmetrical and symmetrical TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD chromophores where phenothiazine and ferrocene are acting as strong donors. In this manuscript our objective was to improve the photonic and electronic properties of ferrocene substituted phenothiazines by incorporating TCNE and TCNQ in between phenothiazine and ferrocene building blocks. We have further explored a comparative photophysical and electrochemical studies by varying the number of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptor as well as ferrocene donor on the phenothiazine moiety. Additionally, theoretical calculations were performed in order to study the conformation and the photonic properties of phenothiazines.

Results and Discussion

The TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD substituted ferrocenyl phenothiazines **4b**, **4c**, **4c′**, **5b**, **5c**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′** were designed and synthesized by the [2 + 2] cycloaddition–electrocyclic ring-opening reaction of ferrocenyl

This article is protected by copyright. All rights reserved.

Accepted Manuscript

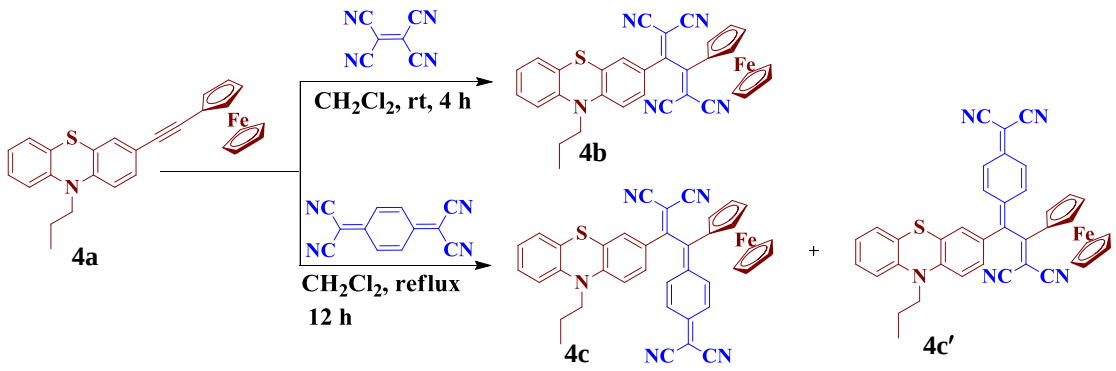
phenothiazines **4a** and **5a** with TCNE and TCNQ (Scheme 1, Scheme 2 and Scheme 3). The ferrocenyl phenothiazines **4a** and **5a** were synthesized by the Sonogashira cross-coupling reaction of 3-bromo-10-propylphenothiazine and 3,7-dibromo-10-propylphenothiazines with the ethynyl ferrocene. The Pd-catalyzed Sonogashira cross-coupling reaction of phenothiazines **3a** and **3b** with ethynyl ferrocene at 60 °C resulted ferrocenyl phenothiazines **4a** and **5a** in 50% and 51% yields respectively (Scheme S1).

In order to explore the effect of number of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptors on the ferrocenyl phenothiazines the mono-(**4b**, **4c**, **4c′, 5b** and **5d, 5d′**) and di-(**5c**, **5e, 5e′, 5f** and **5f′**) substituted ferrocenyl phenothiazines were synthesized. The precursors **4a** and **5a** undergo the [2 + 2] cycloaddition–electrocyclic ring-opening reaction with TCNE at room temperature within 4 hours in CH_2Cl_2 solvent, resulted TCBD functionalized phenothiazines **4b** and **5b** in 83% and 85% yield, respectively (Scheme 1 and Scheme 2). The ferrocenyl phenothiazine **5a** undergoes a similar transformation by using excess amount of TCNE which resulted phenothiazine **5c** in 90% yield at 40 °C, for 12 hours in CH_2Cl_2 solvent. The derivatives of cyclohexa–2,5–diene–1,4–ylidene–expanded TCBDs were obtained as non-separable regioisomeric mixtures. The reaction of ferrocenyl phenothiazine **4a** with 1 equivalent of TCNQ at 40 °C, for 12 hours in CH_2Cl_2 solvent results in 40.5:59.5 regioisomeric phenothiazines **4c** and **4c′** in 85% yield. The reaction of ferrocenyl phenothiazine **5a** with 1 equivalent of TCNQ at 40 °C, for 12 hours in CH_2Cl_2 solvent results in 37.5:62.5 regioisomeric phenothiazines **5d** and **5d′** in 80% yield. The phenothiazines **5e** and **5e′** was obtained in 45.1:54.9 regioisomeric mixtures by the similar reaction of excess amount of TCNQ with phenothiazine **5a** at 40 °C, for 4 days in CH_2Cl_2 solvent and resulted in 70% yield (Scheme 2).

This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/asia.201700879



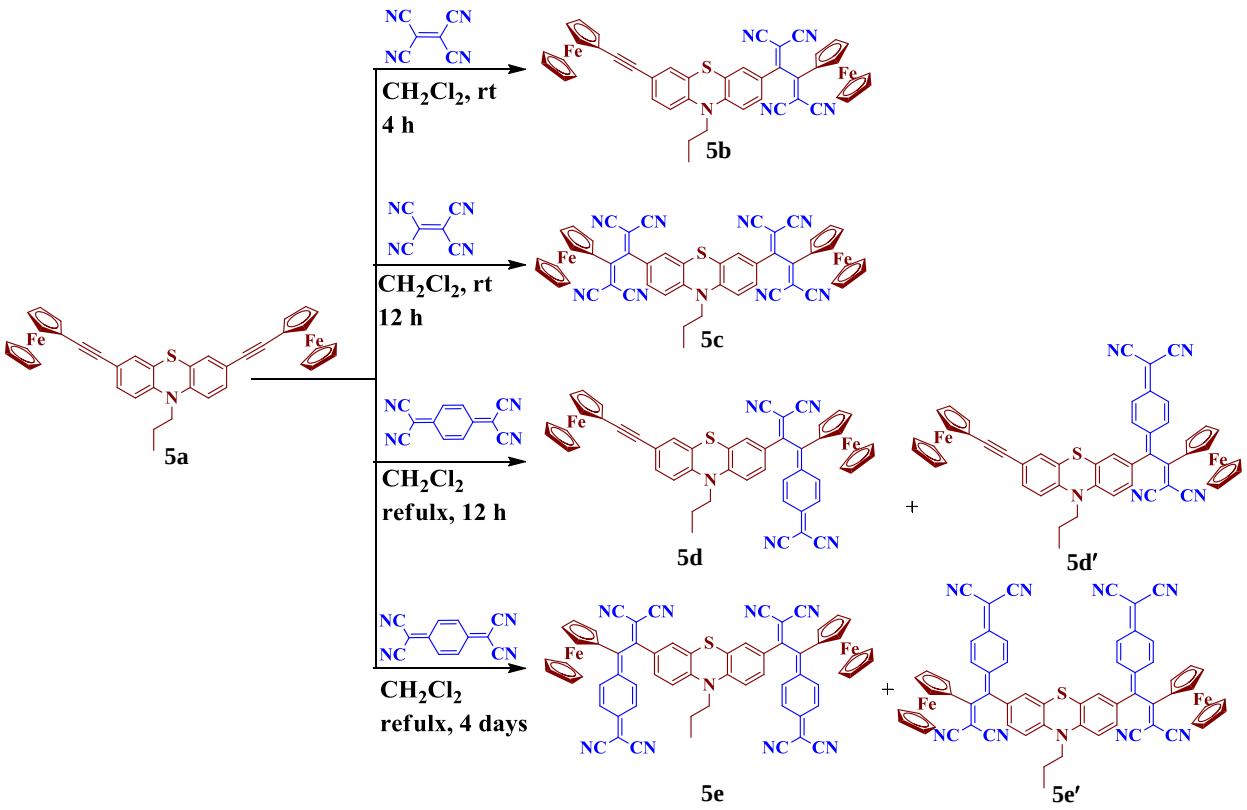
Scheme 1. Synthetic route for ferrocenyl phenothiazines **4b**, **4c** and **4c′**.

The reaction of isomeric cyclohexa–2,5–diene–1,4–ylidene–expanded TCBDs functionalized phenothiazine **5d** and **5d′** with TCNE at 40 °C, for 12 hours in CH_2Cl_2 solvent results in 33.1:66.9 regioisomeric phenothiazine **5f** and **5f′** in 80% yield. The phenothiazines **5f** and **5f′** was also synthesized from TCBD functionalized phenothiazine **5b** with TCNQ at 40 °C, for 12 hours in CH_2Cl_2 solvent which resulted in 33.1:66.9 regioisomeric mixtures with 81% yield, (Scheme 3). The ferrocenyl phenothiazines as well as TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD functionalized ferrocenyl phenothiazines **4b**, **4c**, **4c′**, **5b**, **5c**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′** are soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, toluene and were well characterized by ^{1}H NMR, ^{13}C NMR and HRMS techniques.

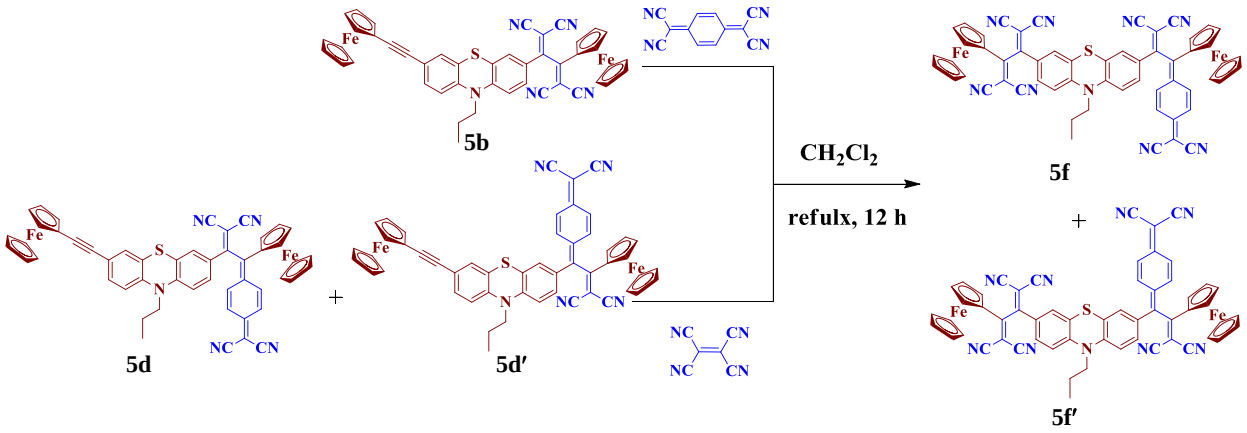
This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/asia.201700879



Scheme 2. Synthetic route for ferrocenyl phenothiazines **5b, 5c, 5d, 5d′, 5e** and **5e′**.



Scheme 3. Synthetic route for ferrocenyl phenothiazines **5f** and **5f′**.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/asia.201700879

Photophysical Properties

The electronic absorption spectra of the ferrocenyl phenothiazines and their TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD conjugates **4b**, **4c** and **5b**–**5f** were recorded in dichloromethane at room temperature (Figure 1), and the data are compiled in Table 1.

The TCBD functionalized phenothiazines **4b**, **5b** and **5c** exhibit ICT transition at 531 nm, 547 nm and 537 nm respectively which indicates that the incorporation of TCBD unit results in strong donor–acceptor interaction. On the other hand, the cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD substituted phenothiazines **4c**, **5d** and **5e** exhibit two strong absorption bands due to the strong electron accepting capability of cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD.

The absorption band between 454–468 nm and 737–794 nm can be attributed to the π–π* transition band and CT band, respectively. The TCBD/cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD substituted phenothiazine **5f** exhibit π–π* transition band and CT band at 524 nm and 800 nm respectively. It also shows a shoulder band at 439 nm which may be due to the presence of two different acceptors in phenothiazine **5f**. The incorporation of the TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptor units resulted in strong donor–acceptor interaction which was further explained by TD-DFT calculation in dichloromethane phase.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

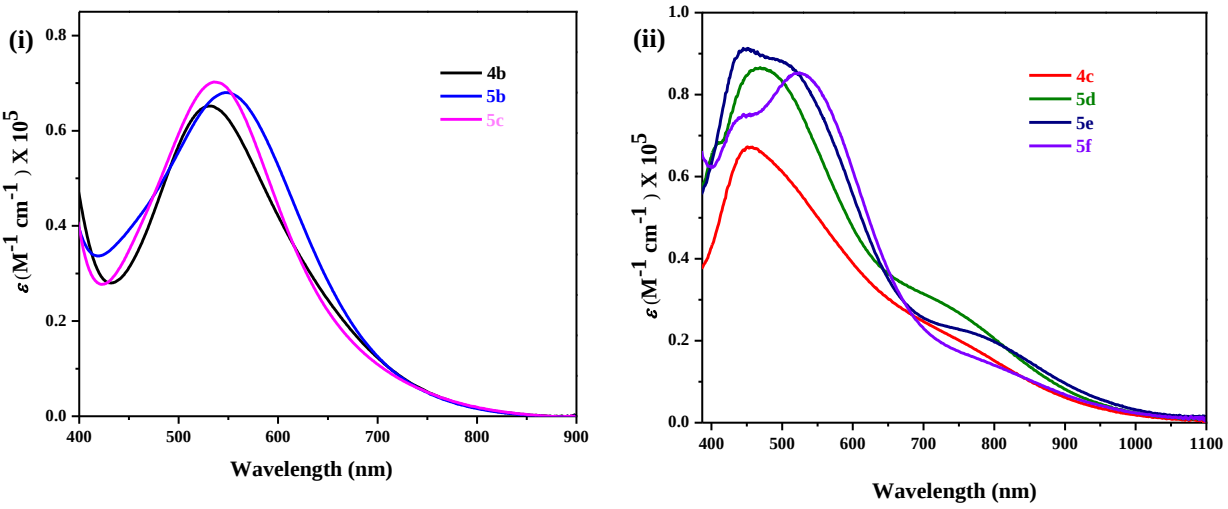


Figure 1. The electronic absorption spectra of phenothiazines **(i) 4b**, **5b** and **5c**, and **(ii) 4c**, **5d**, **5e** and **5f** in dichloromethane (1 $\times 10^{-5}$ M).

The optical band gap of phenothiazines **4b**, **4c** and **5b–5f** follow the order **4b>5c>5b>5f>4c>5e>5d**. The trend clearly indicates the influence of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD on ferrocenyl phenothiazines leading to the red shifted electronic absorption and low optical band gap which is further explained by TDDFT calculations where the effect of regioisomeric mixture on the electronic spectra is also discussed.

Electrochemical Properties

The electrochemical properties of ferrocenyl phenothiazines **4b**, **4c** and **5b**–**5f** were explored by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dry dichloromethane (DCM) solution at room temperature using tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. The electrochemical data are compiled in Table 1, and the representative CV and DPV plots are shown in Figure 2, and Figure S22–S27.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/asia.201700879

In general, phenothiazine shows one reversible oxidation wave.[18] The TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD substituted ferrocenyl phenothiazines show an additional reversible oxidation wave which corresponds to the oxidation of ferrocenyl ring.

Table 1. Photophysical and electrochemical properties of phenothiazines **4b**, **4c**, **4c′**, **5b**, **5c**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′**.

Phenothiazines	Photophysical data[a]			Theoretical data[c]	Electrochemical data[d]	
	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	Optical Band Gap (eV)[b]	HOMO-LUMO energy gap (eV)	E_{ox}(V)	E_{red}(V)
4b	531	65323	1.59	2.64	0.71	–0.75 –1.04
4c, **4c′**	454	60222	1.23	2.22, 2.04	0.55 0.65	–0.56
5b	547	68007	1.54	2.49	0.33 0.68 0.81	–0.76 –1.06
5c	537	70166	1.57	2.63	0.68 0.95	–0.72 –1.07
5d, **5d′**	468	77333	1.19	2.03, 1.87	0.32 0.55 0.68	–0.55
5e, **5e′**	448	80368	1.21	2.24, 2.00	0.54 0.79	–0.56
5f, **5f′**	524	77158	1.24	2.28, 2.11	0.56 0.67 0.85	–0.54 –0.83 –1.11

[a] Absorbance measured in dichloromethane at 1×10^{-5} M concentration; λ_{abs}: absorption wavelength; ε: extinction coefficient. [b] determined from onset wavelength of the UV/Vis absorption; [c]obtained from density functional theory calculations at B3LYP/6-31+G** level; [d] recorded by cyclic voltammetry, in 0.1 M solution of $TBAPF_6$ in DCM at 100 mV s^{-1} scan rate versus SCE electrode.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/asia.201700879

The phenothiazines **4c**, **5c** and **5e** show two oxidation potentials at (+0.68 V, +0.95 V), (+0.55 V, +0.66 V) and (+0.54 V, +0.79 V) respectively, where the first oxidation potentials are attributed to the ferrocenyl moiety and the second oxidation potentials are due to the phenothiazinyl moiety. The phenothiazine **4b** exhibits only one oxidation wave at +0.71 V due to the simultaneous reversible oxidation of ferrocene and phenothiazine units.[17a–c] The phenothiazines **5b**, **5d** and **5f** show three oxidation peaks at (+0.33 V, +0.68 V and +0.81 V), (+0.32V, +0.55V, +0.68 V) and (+0.56 V, +0.67V and +0.85 V), respectively where the first two oxidation potentials correspond to the ferrocene moiety and the third oxidation potential can be attributed to the phenothiazine moiety. The trend in the first oxidation potential of the phenothiazines **4b**, **4c** and **5b–5f** follows the order **4b>5c>5f>4c>5e>5b>5d**.

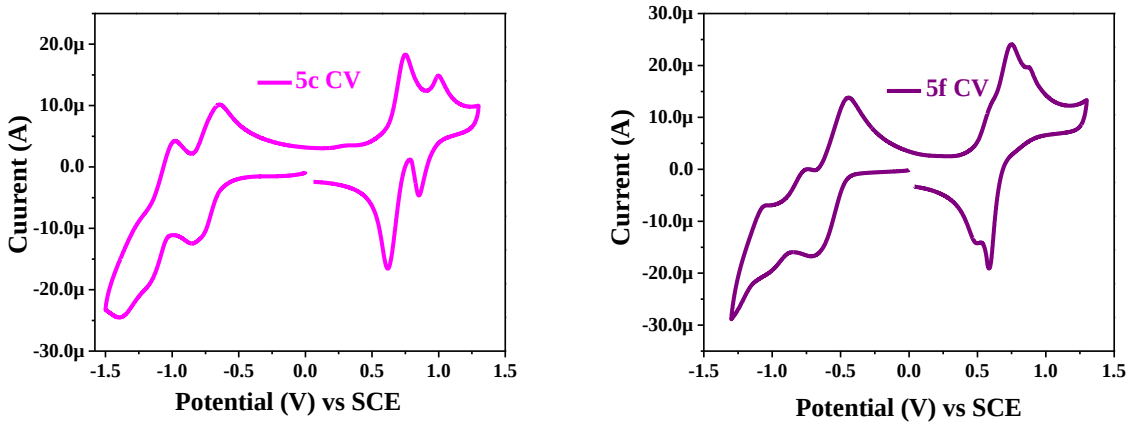


Figure 2. Cyclic voltammograms of phenothiazines **5c** and **5f** 0.01 M in 0.1 M $TBAPF_6$ in dichloromethane at a scan rate of 100 mV s^{-1} standard calomel electrode (SCE) at 25° C.

The TCBD functionalized phenothiazines **4b**, **5b** and **5c** exhibit a reversible two–step reduction wave attributed to one–electron transfer in each step and show the reduction potential value at (–0.75 V, –1.04 V), (–0.76 V, –1.06 V) and (–0.72 V, –1.07 V), respectively due to the TCBD units. The two reduction waves correspond to the formation of radical anions and dianions. A

This article is protected by copyright. All rights reserved.

Accepted Manuscript

positive shift in the first reduction potential was observed in phenothiazine **5c** because of the presence of two electron withdrawing TCBD units. This indicates that increasing the number of TCBD unit enhances the π-accepting properties. The cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD adduct of phenothiazines **4c**, **5d** and **5e** show only one reduction wave, whose potentials were identified at –0.56 V, –0.55 V and –0.56 V, respectively which is due to the simultaneous electrochemical reduction of cyclohexa–2,5diene–1,4ylidene–expanded TCBD units.[17a–c] The phenothiazine **5f** shows three reduction wave at –0.54 V, –0.83 V, –1.11 V where the first reduction potential value corresponds to the cyclohexa–2,5diene–1,4ylidene–expanded TCBD moiety and potential at –0.83 V and –1.11 V could be attributed to the TCBD moiety. Therefore the introduction of cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD adduct shows lower reduction potential as compared to TCBDs. The result reveals that the cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD unit stabilizes the LUMO energy level to greater extent than that of TCBD. The HOMO and LUMO energy levels are calculated from the onset oxidation and reduction potentials. The corresponding HOMO and LUMO energy levels of phenothiazines **4b**, **4c**, **5b**, **5c**, **5d**, **5e** and **5f** are –4.98 eV, –4.83 eV, –4.53 eV, –4.91 eV, –4.62 eV, –4.84 eV, –4.86 eV and –3.82 eV, –3.94 eV, –3.79 eV, –3.81 eV, –3.96 eV, –4.00 eV, –3.88 eV, respectively.

Theoretical Calculations

The density functional theory calculation was performed on phenothiazines **4b**, **4c**, **5b**, **5c**, **5d**, **5e** and **5f** to explore the structure and electronic properties at B3LYP/6-31+G** level for B, C, F, H, N and S.[19] The optimized structures of phenothiazines are nonplanar with twisted geometry (Table S1–S3). The incorporation of strong cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptor unit lower the LUMO energy level to greater extent as compared to TCBD, which results in low HOMO–LUMO gap and red shifted electronic absorption. The theoretically

This article is protected by copyright. All rights reserved.

Accepted Manuscript

10.1002/asia.201700879

determined HOMO levels of phenothiazines **4b**, **4c**, **5b**, **5c**, **5d**, **5e and 5f** are –5.53 eV, –5.62 eV, –5.41 eV, –5.95 eV, –5.39 eV, –6.03 eV and –6.0 eV whereas LUMO levels are –2.89 eV, –3.40 eV, –2.92 eV, –3.31 eV, –3.36 eV, –3.79 eV and –3.72 eV (Figure 3). The comparison between FMOs of the isomeric phenothiazines (**4c** and **4c′**), (**5d** and **5d′**), (**5e** and **5e′**) and (**5f** and **5f′**) are shown in the Supporting Information (Table S4–S7), where the calculated HOMO levels of **4c′**, **5d′**, **5e′**and **5f′** are –5.45 eV, –5.29 eV, –5.87 eV and –5.93 eV, and the LUMO levels are –3.41 eV, –3.42 eV, –3.87 eV and –3.82 eV respectively. The data reveals that the LUMO energy levels of the isomeric phenothiazines **4c′**, **5d′**, **5e′**and **5f′** are more stabilized as compared to the **4c**, **5d**, **5e** and **5f**, respectively.

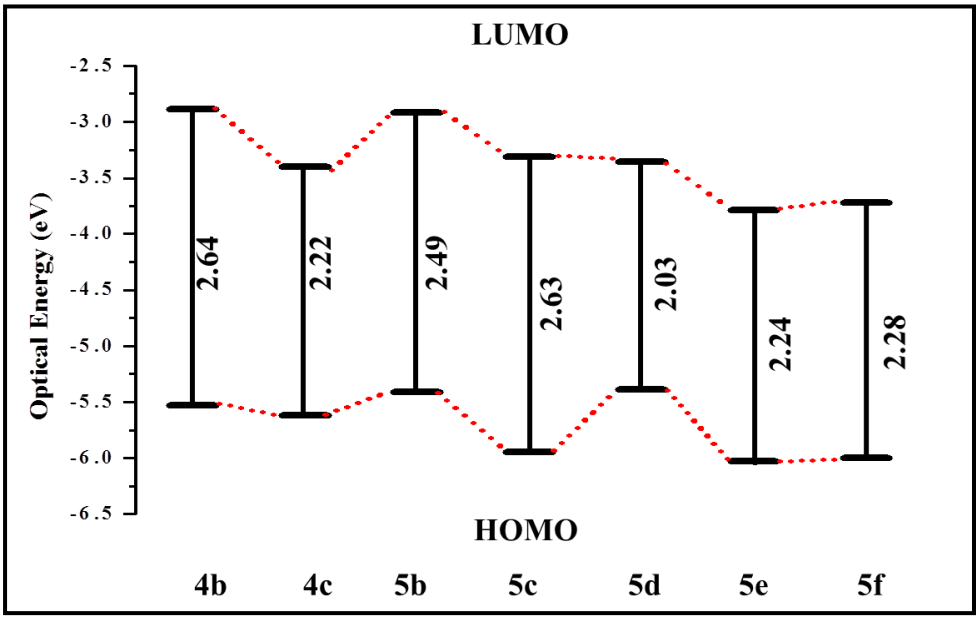


Figure 3. Energy diagram of phenothiazines **4b**, **4c** and **5b–5f** estimated by DFT calculations.

The time-dependent DFT calculation was performed at the B3LYP/6-31G (d, p) level on optimized phenothiazines in dichloromethane to evaluate the absorption properties. The

This article is protected by copyright. All rights reserved.

Accepted Manuscript

transitions with composition, oscillator strengths, and assignments are as shown in Table S8. The molecular orbital diagrams are shown in Table S1–S3.

The TD-DFT calculation shows absorption band at 578, 625 and 602 nm respectively for phenothiazines **4b**, **5b** and **5c** due to the ICT, whereas the phenothiazines **4c**, **4c′**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′**exhibit two absorption bands in the visible region which can be attributed to the π–π* transition at shorter wavelength and ICT at longer wavelength (Table S8). The main ICT transition for phenothiazine **4b** occurs from HOMO→LUMO+1, and HOMO→LUMO for phenothiazines **5b** and **5c**. The charge-transfer occurs from HOMO→LUMO+2, HOMO–3→LUMO, HOMO–2→LUMO and HOMO–1→LUMO in phenothiazines **4c**, **5d**, **5e** and **5f**, respectively whereas for **4c′**, **5d′**, **5e′**and **5f′** the charge-transfer occurs from HOMO→LUMO. The data shows that the isomeric phenothiazines **4c′**, **5d′**, **5e′** and **5f′** are red shifted as compared to **4c**, **5d**, **5e** and **5f**, respectively. The theoretical electronic absorption wavelengths were found to be higher than those of experimental values which might be due to various factors, e.g. solvent effect, dipole moment and temperature.

Conclusion

In summary, a series of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD substituted phenothiazines **4b**, **4c**, **4c′**, **5b**, **5c**, **5d**, **5d′**, **5e**, **5e′**, **5f** and **5f′** were synthesized by [2+2] cycloaddition–electrocyclic ring-opening reactions. Their electrochemical properties reveals that the incorporation of strong acceptors TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD facilitates the reduction process of the ferrocenyl-phenothiazines which leads to low HOMO–LUMO gap . The electronic absorption spectra exhibit strong ICT at longer wavelength and strong donor–acceptor interactions. In particular, DFT and TDDFT calculations

This article is protected by copyright. All rights reserved.

Accepted Manuscript

reveal a broad understanding of the electronic structure and absorption spectra of the phenothiazine chromophores which reveal that the incorporation of TCBD and cyclohexa–2,5–diene–1,4–ylidene–expanded TCBD acceptor group perturbs HOMO–LUMO gap of the phenothiazines to a greater extent which is in a good agreement with the experimental values. The results provide an important procedure of designing new donor–acceptor chromophores with low band gaps. The photovoltaic applications of these phenothiazines are currently ongoing in our laboratory.

Experimental Section

General Methods. Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere. ^{1}H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {$CDCl_3$, 7.26 ppm}. ^{13}C NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard {$CDCl_3$, 77.0 ppm}. The ^{1}H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". UV/Vis spectrums of all compounds were recorded in dichloromethane solution. Cyclic voltammograms were recorded on electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. The scan rate was 100mVs^{-1} for Cyclic Voltammetry. A solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2 (0.1M) was used as supporting electrolyte.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Synthesis of 4b. Tetracyanoethylene (TCNE) (28.2 mg, 0.22 mmol) was added to a solution of compound **4a** (98.8 mg, 0.22 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at room temperature for 4 h. After the completion of the reaction the solvent was removed in vacuum, and the product was purified by column chromatography with CH_2Cl_2 as the eluent which yield **4b** as a dark violet colored solid. Yield: 106.9 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 7.28 Hz, 1H), 7.30 (s, 1H), 7.16 (t, J = 7.56 Hz, 1H), 7.06-6.95 (m, 2H), 6.87-6.81 (m, 2H), 5.18 (s, 1H), 4.95 (s, 1H), 4.84 (s, 1H), 4.70 (s, 1H), 4.45-4.37 (m, 5H), 3.82 (t, J=7.04 Hz, 2H), 1.85-1.79 (m, 2H), 1.01 (t, J = 7.28 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 163.5, 150.8, 142.2, 129.7, 128.6, 127.9, 127.6, 127.5, 125.3, 124.3, 124.2, 122.6, 116.1, 114.9, 113.7, 112.8, 112.5, 80.3, 79.1, 75.5, 75.4, 74.9, 72.7, 72.5, 72.0, 71.9, 71.5, 49.9, 19.9, 11.1; HRMS (ESI-TOF): m/z calculated for $C_{33}H_{23}FeN_5S$= 578.1097 $[M+H]^+$, measured 578.1082 $[M+H]^+$

Synthesis of 4c and 4c′. Tetracyanoquinodimethane (TCNQ) (44.9 mg, 0.22 mmol) was added to a solution of compound **4a** (98.8 mg, 0.22 mmol) in CH_2Cl_2 (50 mL). The mixture was refluxed at 40 °C for 12 h. After the completion of the reaction the solvent was removed in vacuum and the product was purified by column chromatography with CH_2Cl_2 as the eluent which yield **4c** and **4c′** in 40.5:59.5 calculated regioisomeric mixtures as a dark brown colored solid. Overall Yield: 122.0 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 9.28 Hz, 1H), 7.55 (d, J = 7.52 Hz, 1H), 7.45 (d, J = 9.52 Hz, 1H), 7.38 (d, J = 9.52 Hz, 1H), 7.23–7.10 (m, 9H), 7.02–6.95 (m, 4H), 6.89–6.77 (m, 5H), 4.97–4.76 (m, 7H), 4.42–4.26 (m, 11H), 3.85 (t, J = 7.04 Hz, 2H), 3.80 (t, J = 7.04 Hz, 2H), 1.87–1.77 (m, 4H), 1.04–0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 167.4, 157.1, 154.6, 154.2, 150.4, 149.6, 148.5, 142.9, 142.3, 134.7, 135.2, 134.1, 131.6, 131.4, 130.6, 130.5, 129.9, 129.0, 128.9, 128.2, 127.9, 127.6, 126.7, 126.0,

This article is protected by copyright. All rights reserved.

Accepted Manuscript

125.6, 125.4, 125.1, 124.8, 124.2, 124.0, 123.8, 115.0, 114.9, 114.3, 113.8, 113.7, 113.5, 113.3, 80.0, 79.6, 79.5, 79.4, 77.8, 76.2, 76.1, 75.5, 75.0, 74.9, 74.8, 74.7, 73.9, 72.8, 72.6, 72.5, 72.4, 71.8, 71.1, 49.8, 49.4, 20.1, 20.0, 11.2, 11.1; HRMS (ESI-TOF): m/z calculated for $C_{39}H_{27}FeN_5S$= 676.1229 $[M+Na]^+$, measured 676.1210 $[M+Na]^+$

Synthesis of 5b. Tetracyanoethylene (TCNE) (19.2 mg, 0.15 mmol) was added to a solution of compound **5a** (98.6 mg, 0.15 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at room temperature for 4 h. After the completion of the reaction the solvent was removed in vacuum, and the product was purified by column chromatography with CH_2Cl_2 as the eluent to yield **5b** as a dark violet colored solid. Yield: 100.10 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 8 Hz, 1H), 7.28 (s, 2H), 7.16 (s, 1H), 6.83–6.76 (m, 2H), 5.29 (s, 3H), 5.18 (s, 1H), 4.95 (s, 1H), 4.85 (s, 1H), 4.71 (s, 1H), 4.45 (s, 6H), 6.94 (s, 6H), 3.81 (t, J = 6.04 Hz, 2H), 1.83–1.79 (m, 2H), 1.02 (t, J = 6.76 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 163.4, 150.2, 141.4, 130.9, 130.0, 129.7, 127.5, 124.8, 124.5, 122.6, 120.1, 115.8, 115.1, 113.7, 112.8, 112.7, 112.4, 89.5, 84.2, 80.6, 79.1, 75.5, 75.0, 72.5, 72.0, 71.4, 70.0, 68.9, 64.9, 49.9, 19.9, 11.1; HRMS (ESI-TOF): m/z calculated for $C_{45}H_{31}Fe_2N_5S$= 824.0633 $[M+K]^+$, measured 824.0630 $[M+K]^+$

Synthesis of 5c. Tetracyanoethylene (TCNE) (38.4 mg, 0.3 mmol) was added to a solution of compound **5a** (98.6 mg, 0.15 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at room temperature for 12 h. After the completion of the reaction the solvent was removed in vacuum, and the product was purified by column chromatography with CH_2Cl_2 as the eluent which yield **5c** as a dark violet colored solid. Yield: 123.4 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (t, J = 8.28 Hz, 2H), 7.22 (d, J = 6.04 Hz, 2H), 6.89–6.86 (m, 2H), 5.30 (d, J = 7.76 Hz, 2H), 5.01 (s, 2H), 4.88 (s, 2H), 4.59 (d, J = 5.28 Hz, 2H), 4.46 (s, 8H), 3.82 (t, J = 7.04 Hz, 2H), 1.84–1.79 (m, 2H), 1.03 (t, J = 7.28 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 163.5, 147.9, 147.8,

This article is protected by copyright. All rights reserved.

Accepted Manuscript

129.8, 127.5, 127.4, 126.2, 124.3, 116.1, 113.6, 112.8, 112.2, 111.9, 82.9, 78.8, 74.5, 72.7, 72.2, 71.8, 50.3, 19.9, 11.1; HRMS (ESI-TOF): m/z calculated for $C_{51}H_{31}Fe_2N_9S$= 952.0756 $[M+K]^+$, measured 952.1018 $[M+K]^+$

Synthesis of 5d and 5d′. Tetracyanoquinodimethane (TCNQ) (30.6 mg, 0.15 mmol) was added to a solution of compound **5a** (98.6 mg, 0.15 mmol) in CH_2Cl_2 (50 mL). The mixture was refluxed at 40 °C for 12 h. After the completion of the reaction the solvent was removed in vacuum and the product was purified by column chromatography with CH_2Cl_2 as the eluent which yield **5d** and **5d′** in 37.5:62.5 calculated regioisomeric mixtures as a dark brown colored solid. Overall Yield: 103.4 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 9.8 Hz, 1H), 7.56 (d, *J* = 8.28 Hz, 1H), 7.46 (d, *J* = 9.52 Hz, 2H), 7.38 (d, *J* = 9.52 Hz, 1H), 7.20 (t, *J* = 8.76 Hz, 5H), 7.13 (s, 1H), 7.03 (d, *J* = 9.28 Hz, 1H), 6.88 (d, *J* = 8.52 Hz, 1H), 6.80–6.74 (m, 5H), 5.28 (s, 2H), 4.93 (s, 1H), 4.83 (s, 3H), 4.76 (s, 1H), 4.45–4.20 (m, 31H), 3.84 (t, *J* = 7.0 Hz, 2H), 3.79 (t, *J* = 7.04 Hz, 2H), 1.87–1.77 (m, 4H), 1.05–0.98 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 156.9, 154.6, 154.2, 149.8, 149.4, 147.9, 142.2, 141.5, 134.6, 134.1, 134.0, 131.5, 130.9, 130.5, 130.1, 130.0, 129.8, 129.2, 129.0, 128.2, 127.0, 126.1, 125.5, 125.1, 124.9, 124.6, 124.1, 122.9, 122.7, 119.9, 119.5, 115.7, 115.6, 115.3, 115.0, 114.3,113.8, 113.6, 113.4, 113.2, 89.5, 89.4, 89.2, 84.2, 80.3,79.5, 79.4, 77.9, 77.8, 76.1, 75.7, 74.9, 74.8, 73.8, 72.7, 72.6, 72.5, 72.4, 71.8, 71.3, 69.9, 49.8, 20.1, 19.9, 11.2, 11.1; HRMS (ESI-TOF): m/z calculated for $C_{51}H_{35}Fe_2N_5S$= 861.1309 $[M]^+$, measured 861.1283 $[M]^+$.

Synthesis of 5e and 5e′. Tetracyanoquinodimethane (TCNQ) (61.2 mg, 0.3 mmol) was added to a solution of compound **5a** (98.6 mg, 0.15 mmol) in CH_2Cl_2 (50 mL). The mixture was refluxed at 40 °C for 4 days. After the completion of the reaction the solvent was removed in vacuum and the product was purified by column chromatography with CH_2Cl_2 as the eluent which yield **5e**

This article is protected by copyright. All rights reserved.

Accepted Manuscript

and **5e′** in 45.1:54.9 calculated regioisomeric mixtures as a dark brown colored solid. Overall Yield: 111.9 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30–8.26 (m, 3H), 7.55–7.42 (m, 7H), 7.31–7.28 (m, 4H), 7.22–7.18 (m, 6H), 7.13 (s, 1H), 7.02 (s, 2H), 6.91–6.73 (m, 8H), 5.28 (s, 1H), 4.95–4.80 (m, 13H), 4.36–4.29 (m, 21H), 3.82 (t, *J* = 8.0 Hz, 2H), 3.75 (t, *J* = 9.52 Hz, 2H), 1.87–1.74 (m, 4H), 1.05–0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 156.3, 156.0, 154.4, 153.9, 148.3, 148.1, 147.5, 147.4, 145.4, 134.0, 133.8, 132.1, 131.5, 130.6, 130.5, 130.1, 129.9, 128.9, 128.6, 127.8, 125.0, 124.2, 123.9, 115.9, 115.8, 115.6, 115.0, 114.9, 113.4, 113.1, 112.9, 112.8, 112.7, 82.1, 81.7, 79.3, 79.1; HRMS (ESI-TOF): m/z calculated for $C_{63}H_{39}Fe_2N_9S$= 1088.1644 $[M+Na]^+$, measured 1088.1651 $[M+Na]^+$.

Synthesis of 5f and 5f′. Tetracyanoethylene (TCNE) (15.4 mg, 0.12 mmol) was added to a solution of compound **5d** and **5d′** (103.4 mg, 0.12 mmol) in CH_2Cl_2 (50 mL). The mixture was refluxed at 40 °C for 12 h. After the completion of the reaction the solvent was removed in vacuum, and the product was purified by column chromatography with CH_2Cl_2 as the eluent which yield **5f** and **5f′** in 33.1:66.9 calculated regioisomeric mixtures as a dark colored solid. Overall Yield: 95 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 9.6 Hz, 1H), 7.58–7.45 (m, 5H), 7.34–7.28 (m, 2H), 7.21–7.07 (m, 6H), 6.93–6.75 (m, 5H), 5.28–5.23 (m, 3H), 4.99–4.81 (m, 11H), 4.65 (d, *J*=7.28 Hz, 1H), 4.57 (s, 2H), 4.44–4.30 (m, 20H), 3.85 (t, *J* = 6.52 Hz, 2H), 3.78 (t, *J* = 6.52 Hz, 2H), 1.84–1.75 (m, 4H), 1.05–0.99 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 172.5, 167.2, 163.5, 163.4, 158.2, 154.5, 153.9, 148.7, 148.3, 147.9, 147.4, 145.3, 134.2, 134.0, 133.9, 133.8, 132.1, 131.4, 130.7, 130.5, 129.9, 129.8, 129.7, 129.0, 128.7, 128.1, 128.0, 127.8, 127.5, 126.0, 125.8, 125.0, 124.2, 124.1, 123.9, 116.0, 115.9, 115.8, 115.0, 114.2, 113.7, 113.5, 113.4, 112.9, 112.8, 112.7, 112.4, 112.2, 111.9, 82.7, 82.6, 82.2, 82.1, 79.1, 78.9, 78.8, 75.8, 75.3, 75.1, 74.9, 73.9, 73.0, 72.7, 72.6, 72.1, 71.8, 71.7, 53.4, 50.2, 19.9, 19.8,

This article is protected by copyright. All rights reserved.

Accepted Manuscript

11.1, 11.0; HRMS (ESI-TOF): m/z calculated for $C_{58}H_{39}Fe_2N_9S$= 1012.1330 $[M+Na]^+$, measured 1012.1462 $[M+Na]^+$.

Supporting Information

General experimental methods and ^1H and ^{13}C NMR and HRMS spectra of all the new compounds, cyclic voltammograms, computational results.

Acknowledgements

The work was supported by DST, INSA and CSIR Govt. of India, New Delhi. We are grateful to the Sophisticated Instrumentation Centre (SIC), IIT Indore.

Keywords: Cross-coupling, Cycloaddition–Electrocyclic ring-opening, UV/Vis spectroscopy, Cyclic Voltammetry, Density functional calculations, TD-DFT calculations.

Notes and References

Department of Chemistry, Indian Institute of Technology Indore, MP 453552, India. Fax: +91 7312361482; Tel: +91 7312438710; E-mail: rajneeshmisra@iiti.ac.in

[1] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402. (b) C. H. Chen, J. Shi, C. W. Tang, K. P. Klubek, *Thin Solid Films* **2000**, *363*, 327. (c) S. Ellinger, K. R. Graham, P. Shi, R. T. Farley, T. T. Steckler, R. N. Brookins, P. Taranekar, J. Mei, L. A. Padilha, T. R. Ensley, H. Hu, S. Webster, D. J. Hagan, E. W. V. Stryland, K. S. Schanze, Reynolds, *J. R. Chem. Mater.* **2011**, *23*, 3805– 3817. (d) J. Roncali, *Acc. Chem. Res.* **2009**, *42*, 1719–1730. (e) Y. Li, T. Liu, H. Liu, M.-Z. Tian, Y. Li, *Acc. Chem. Res.* **2014**, *47*, 1186–1198.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

[2] (a) P. Sonar, S. P. Singh, Y. Li, M. S. Soh, A. Dodabalapur, *Adv. Mater.* **2010**, *22*, 5409−5413. (b) K. M. Omer, S. Y. Ku, K. T. Wong, A. Bard, *J. J. Am. Chem. Soc.* **2009**, *131*, 10733−10741. (c) S. Kato, T. Furuya, A. Kobayashi, M. Nitani, Y. Ie, Y. Aso, T. Yoshihara, S. Tobita, Y. Nakamura, *J. Org. Chem.* **2012**, *77*, 7595−7606. (d) Y. Lin, H. Fan, Y. Li, X. Zhan, *Adv. Mater.* **2012**, *24*, 3087–3106. (e) S. Chen, Y. Li, W. Yang, N. Chen, H. Liu, Y. Li, *J. Phys. Chem. C* **2010**, *114*, 15109–15115. (f) T. Meyer, D. Ogermann, A. Pankrath, K. Kleinermanns, Thomas J. J. Müller, *J. Org. Chem.* **2012**, *77*, 3704−3715. (g) H. Tian, X. Yang, R. Chen, Y. Pan, L. Li, A. Hagfeldt, L. Sun, *Chem. Commun*. **2007**, 3741–3743.

[3] (a) F. Bures, W. B. Schweizer, J. C. May, C. Boudon, J.-P. Gisselbrecht, M. Gross, I. Biaggio, F. Diederich, *Chem. Eur. J.* **2007**, *13*, 5378−5387. (b) J.-L. Wang, Q. Xiao, J. Pei, *Org. Lett.* **2010**, *12*, 4164−4167. (c) W.-W. Zhang, W.-L. Mao, Y.-X. Hu, Z.-Q. Tian, Z.-L. Wang, Q.-J. Meng, *J. Phys. Chem. A* 2009, **113**, 9997–10004

[4] (a) R. Misra, P. Gautam, T. Jadhav, S. M. Mobin, *J. Org. Chem.* **2013**, *78*, 4940−4948, (b) R. Misra, P. Gautam, S. M. Mobin, *J. Org. Chem.* **2013**, *78*, 12440−12452. (c) R. Misra, B. Dhokale, T. Jadhav, and S. M. Mobin, *Organometallics* **2014**, *33*, 1867−1877. (d) Y. Patil, T. Jadhav, B. Dhokale, R. Misra, *Eur. J. Org. Chem.* **2016**, 733–738. (e) B. Dhokale, P. Gautam, R. Misra, *Tetrahedron Lett.* **2012**, *53*, 2352–2354. (f) T. Jadhav, R. Maragani, R. Misra, V. Sreeramulu, D. N. Rao, S. M. Mobin, *Dalton Trans.* **2013**, *42*, 4340–4342.

[5] F. Bureš, *RSC Adv.* **2014**, *4*, 58826–58851.

[6] (a) S. Massie, *Chem. Rev.* **1954**, *54*, 797. (b) M. Hauck, J. Schonhaber, A. J. Zucchero, K. I. Hardcastle, T. J. J. Müller, U. H. F. Bunz, *J. Org. Chem.* **2007**, **72**, 6714−6725. (c)

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Gupta, R. R.; Ojha, K .G. *In Phenothiazines and 1,4-Benzothiazines: Chemical and Biochemical Aspects*; Gupta, R. R., ed.; Elsevier: Amsterdam, 1988, p. 163-269.

[7] (a) M. Hauck, M. Stolte, J. Schçnhaber, H.-G. Kuball, T. J. J. Muller, *Chem. Eur. J.* **2011**, *17*, 9984–9998. (b) M. Sailer, R.-A. Gropeanu, T. J. J. Müller, *J. Org. Chem.* **2003**, *68*, 7509–7512. (c) T. J. J. Müller, *Tetrahedron Lett.* **1999**, *40*, 6563-6566. (d) C. S. Krämer, T. J. J. Müller, *Eur. J. Org. Chem*. **2003**, 3534–3548. (e) C. S. Krämer, K. Zeitler, T. J. J. Müller, *Org. Lett.* **2000**, *2*, 3723–3726.

[8] (a) M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky, R. J. Jones, *Nature* **1987**, *330*, 360. (b) P. Gautam, B. Dhokale, V. Shukla, C. P. Singh, K. S. Bindra, R. Misra, *J. Photochem. Photobiol., A. Chem.* **2012**, *239*, 24–27. (c) M. Sailer, F. Rominger, T. J. J. Müller, *J. Organomet. Chem.* **2006**, *691*, 299–308.

[9] (a) T. L. Cairns, B. C. McKusick, *Angew. Chem.* **1961**, *73*, 520–525. (b) O. W. Webster, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 210–221. (c) T. Mochida, S. Yamazaki, *J. Chem. Soc., Dalton Trans*. **2002**, 3559–3564. (d) X. Wu, J. Wu, Y. Liu, A. K-Y. Jen, *J. Am. Chem. Soc.* **1999**, *121*, 472–473. (c) Y. Morioka, N. Yoshizawa, J.-i. Nishida, Y. Yamashita, *Chem. Lett.* **2004**, *33*, 1190 -1191 *Chem. Lett.* **2004**, *33*, 1190–1191. (d) D. Koszelewski, A. Nowak-Krol, D. T. Gryko, *Chem. Asian J.* **2012**, *7*, 1887–1894. (e) R. García, M[a] Á. Herranz, M[a] R. Torres, P.-A. Bouit, J. L. Delgado, J. Calbo, P. M. Viruela, E. Ortí, N. Martín, *J. Org. Chem.* **2012**, *77*, 10707−10717. (f) S.-i. Sasaki, K. Mizutani, M. Kunieda, H. Tamiaki, *Tetrahedron* **2013**, *69*, 9772–9778. (g) M. Betou, N. Kerisit, E. Meledje, Y. R. Leroux, C. Katan, J.- F. Halet, J.-C. Guillemin, Yann Trolez, *Chem. Eur. J.* **2014**, *20*, 9553–9557. (h) F. G. Perrin, G. Kiefer, L. Jeanbourquin, S. Racine, D.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Perrotta, J. Waser, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2015**, *54*, 13393–13396.

[10] (a) E. B. Vickers, T. D. Selby, M. S. Thorum, M. L. Taliaferro, J. S. Miller, *Inorg. Chem.* **2004**, *43*, 6414–6420. (b) S. Hünig, E. Herberth, *Chem. Rev.* **2004**, *104*, 5535–5563; (c) E. B. Vickers, I. D. Giles, J. S. Miller, *Chem. Mater.* **2005**, *17*. (d) M. Pfeiffer, K. Leo, X. Zhou, J. S. Huang, M. Hofmann, A. Werner, J. Blochwitz-Nimoth, *Org. Electron.* **2003**, *4*, 89–103. (e) J. Ferraris, D. O. Cowan, V. Walatka Jr, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948–949. (f) K. Walzer, B. Maennig, M. Pfeiffer, K. Leo, *Chem. Rev.* **2007**, *107*, 1233–1271.

[11] (a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, 737–739. (b) T. Michinobu, I. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem.–Eur. J.* **2006**, *12*, 1889–1905. (c) M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Angew. Chem.* **2007**, *119*, 6473–6477.

[12] (a) M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4731–4733. (b) P. Reutenauer, M. Kivala, P. D. Jarowski, C. Boudon, J. Gisselbrecht, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4898–4900. (c) S. Kato, M. Kivala, W. B. Schweizer, C. Boudon, J.- P. Gisselbrecht, F. Diederich, *Chem.–Eur. J.* **2009**, *15*, 8687–8691.

[13] (a) T. Michinobu, *J. Am. Chem. Soc.* **2008**, *130*, 14074–14075. (b) Y. Li, T. Kazuma, T. Michinobu, *Macromolecules* **2010**, *43*, 5277–5286 (c) T. Michinobu, *Chem. Soc. Rev.* **2011**, *40*, 2306–2316. (d) T. Fujita, K. Tsuboi, T. Michinobu, *Macromol. Chem. Phys.* **2011**, *212*, 1758–1766.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

[14] (a) T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Chem.–Eur. J.* **2008**, *14*, 8398–8408. (b) T. Shoji, S. Ito, K. Toyota, T. Iwamoto, M. Yasunami, N. Morita, *Eur. J. Org. Chem.* **2009**, 4316–4324. (c) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunami, N. Morita, *Org. Biomol. Chem.* **2012**, *10*, 2431–2438.

[15] N. Kraußе, M. Kielmann, J. Ma, H. Butenschön, *Eur. J. Org. Chem.* **2015**, 2622–2631.

[16] S.-i. Kato, H. Noguchi, S. Jin, Y. Nakamura, *Asian J. Org. Chem.* **2016**, *5*, 246–256.

[17] (a) R. Misra, P. Gautam, *Org. Biomol. Chem.* **2014**, *12*, 5448–5457. (b) P. Gautam, R. Maragani, R. Misra, *Tetrahedron Letters* **2014**, *55*, 6827–6830. (c) B. Dhokale, T. Jadhav, S. M. Mobin, R. Misra, *Dalton Trans*., **2016**, *45*, 1476 (d) Y. Rout, P. Gautam, R. Misra, *J. Org. Chem.*, **DOI:** 10.1021/acs.joc.7b00991, (e) P. Gautam, R. Sharma, R. Misra, M. L. Keshtov, S. A. Kuklin, G. D. Sharma, *Chem. Sci*. **2017**, *8*, 2017. (f) Y. Patil , R. Misra, R. Singhal, G. D. Sharma, *J. Mater. Chem. A.* DOI: 10.1039/C7TA03322B

[18] (a) R. Y. Lai, E. F. Fabrizio, L. Lu, S. A. Jenekhe, A. J. Bard, *J. Am. Chem. Soc.* **2001**, *123*, 9112. (b) A. P. Kulkarni, P.-T. Wu, T. W. Kwon, S. A. Jenekhe, *J. Phys. Chem. B* **2005**, *109*, 19584.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. ; Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, Revision C.01, Gaussian, Inc., Wallingford, CT, USA, **2009**.

Accepted Manuscript

This article is protected by copyright. All rights reserved.