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New panchromatic dyes comprising benzothiadiazole units within a donor-acceptor π -conjugated spacer. Synthesis and photophysical properties

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ABSTRACT

Four new organic dyes (**D1**–**D4**) having donor–(π -conjugated spacer(donor–acceptor))–acceptor (D– π (D–A)–A) type conjugated systems were synthesized. The dyes were studied for their photophysical and electrochemical properties. The dyes comprised electron donor bis(4-hexyloxy)triphenylamine (D), and electron acceptor cyanoacrylic acid (A) ends connected through a donor–acceptor conjugated spacer group. The conjugated spacer was designed as donor–acceptor system having thiophene to terthiophene and selenophene as donors and benzothiadiazole as acceptor. Thus, optical absorption strengths of the dyes successfully tuned by using the electron accepting property of benzothiadiazole and varying numbers of thiophenes and selenophene. Panchromatic absorption with high extinction coefficient was observed for all four dyes **D1–D4**.

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1. Introduction

Conversion of solar energy to electrical energy by using dyesensitized solar cells (DSSCs) represents one of the most promising methods.¹ Although silicon based semiconductors dominated solar cell² applications for decades, but Grätzel's idea of DSSCs based on nanocrystalline TiO₂ opened up the opportunity to use organic dyes in DSSC. Some metal based (Ru) dyes, such as N3,³ N719,⁴ and black dye,⁵ have achieved remarkable power conversion efficiency upto 10–11%. Recently, porphyrin based dye has been reported with remarkable 12% efficiency.⁶ Due to the cost factor of Ru-metal, use of metal-free dyes as photo sensitizer for DSSC is more desirable. Organic dyes as photo sensitizer have many advantages; such as: (i) they have high molar absorption coefficients (higher than Ru-dyes) because metal-free dipolar organic compounds possessing charge-transfer character. (ii) Wide variety of structures can be designed more easily and the synthesis routes are also easy. (iii) The most important factor is the low cost of the organic dyes compared to the Ru-based complexes. Variety of organic dyes, such as perylene,⁷ cyanine,⁸ xanthene,⁹ merocyanine,¹⁰ coumarin,^{11,8a} hemicyaine,^{10a,12} indoline¹³ have been reported with remarkable efficiency in the DSSCs devices.

The organic dyes commonly consist of conjugated systems comprising donor, linker, and acceptor groups (i.e., a $D-\pi-A$

molecular structure). Their various properties could be finely tuned by altering independently or matching the different groups of $D-\pi-A$ dyes. Triarylamine and cyanoacrylic acid were often used as donor and acceptor, respectively, in the conventional dyes for DSSC. Bezothiadiazole has been extensively studied as acceptor in donor–acceptor (D–A) polymers.¹⁴ Recently, the application to donor–acceptor type small molecules containing benzothiadiazole (BDT) structural motifs has been exploited for DSSCs.¹⁵



Panchromatic optical absorption is a highly desirable property of the dyes for enhancing the efficiency of DSSCs. Here, we have designed and synthesized new dyes having donor– π (donor– acceptor)–acceptor (D– π (D–A)–A) arrangement.¹⁶ Triphenylamine moiety was chosen as donor with bis-*p*-hexyloxy substituents. The triphenylamine moiety is known to greatly locate the cationic charge and efficiently restrict charge recombination between the photoelectron and the oxidized sensitizer. The two





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hexyloxy segments in the *para*-position of the two phenyl groups will prevent unfavourable dye aggregation also enhance the molecular rigidity and reduce the vibration induced non-radiative decays and simultaneously increase solubility in common organic solvents. The *p*-hexyloxy substituents additionally enhance the donor property by mesomeric effect (+M). BDT unit was attached to the cvanoacrylic acid functionality to improve the electron acceptance property. Stronger donor-acceptor combination in the dyes enhances the charge separation ability as well as reduces the band gap. To study the affect of π -conjugated spacer on the photophysical properties of the dyes, we have incorporated thiophene, bithiophene, terthiophene and selenophene as a part of π -conjugated spacers, respectively. Selenium is more polarizable and less electronegative than sulfur; as a result photophysical properties of the dye upon changing thiophene to more conjugated selenophene will change significantly. Thus, all four dyes absorb in the whole visible region, which is one of the most important criteria of good dye for DSSC.

2. Result and discussion

2.1. Synthesis of dyes

The organic sensitizers **D1**, **D2** and **D4** were synthesized by the protocol shown in Scheme 1 and dye **D3** was synthesized as shown in Scheme 2. 1-(Hexyloxy)-4-iodobenzene was synthesized from 4-iodophenol by following the reported literature.¹⁷ Compound **1** was synthesized according to the literature method.¹⁸ 2-Tributylstannylthiophene,¹⁹ 2-tributylstannylselenophene,²⁰ 7-bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde,²¹ and 2-trimethylstannyl-5-thinylthiophne²² were synthesized by reported procedure. Compounds **3a–c** were synthesized by Stille coupling of **1** and monostannyl thiophene and selenophene

analogues 2a-c. Compounds 4a-c were prepared from 3a-c in THF by lithiation and treatment with corresponding stannyl reagents. Further Stille coupling of compounds **4a**–**c** and 7-bromobenzo[1,2,5]thiadiazole-4-carbaldehyde in toluene in presence of Pd(0) catalyst led to the compounds **5a-c**. Knoevenagel addition between **5a**–**c** and cvanoacetic acid afforded the final dves **D1**. **D2** and **D4**. For addition reaction between cvanoacetic acid and **5a**–**c**. chloroform turned out to be better solvent than acetonitrile. To synthesize D3, we have modified the route used for D1, D2 and D4. Compound 6 was synthesized by Stille coupling of 4b and 2bromothiophene. Stannylation of **6** and further Stille coupling with 7-Bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde led to the formation of compound 5d. Condensation reaction of 5d with cyanoacetic acid gave the dye D3. All the new compounds were characterized by ¹H NMR, ¹³C NMR, HRMS and other characterization methods.

2.2. Photophysical properties

The UV–vis absorption spectra of **D1–D4** were recorded in chloroform (Fig. 1a) and THF (Fig. 1b). Absorption maxima and molar absorption coefficients of **D1–D4** were listed in Table 1. All four dyes **D1–D4** showed three bands structure in UV–vis spectrum. Out of these two absorption bands are prominent. A higher energy band (λ_{max} in the region 368–412 nm) can be attributed to π – π * transition and a lower energy band (λ_{max} in the region 562–595 nm) can be assigned to the intramolecular charge transfer (ICT). The higher energy absorption band was red-shifted in the order **D1**<**D2**<**D3** due to increase of the conjugation by incorporation of the additional thiophene ring sequentially (~20–25 nm for each additional thiophene ring). The λ_{max} of lower energy ICT bands remained nearly same for all three thiophene-based dyes **D1–D3**, however, the intensity was decreased with



Scheme 1. Synthetic route for D1, D2 and D4.



Scheme 2. Synthetic route of D3.

increasing the number of thiophene rings. This can be explained on the basis of change in the spacer's conjugation length.²³ In order to produce the low-energy absorption band, formation of charge-separated states is important. As the spacer length increased upon moving from **D1** to **D3**, the ability of the dye to separate charge

decreased due to decrease in the efficiency to transfer the charge from donor to acceptor. This reduction in ability to separate intramolecular charge led to a decrease in the absorption coefficient of the low-energy band when moving from **D1** to **D3**. Both the absorption bands of **D4** were red-shifted compared to that of **D1**. It can



Fig. 1. Normalized absorption spectra of the dyes D1-D4 in (a) chloroform, (b) THF, (c) THF+triethylamine.

 Table 1

 Absorption maxima and molar absorption coefficients of dyes D1–D4^a

Dye	Absorbance					
	CHCl ₃		THF		THF+triethylamine	
	$\lambda_{\max}^1(\varepsilon_{\max})$	$\lambda_{\max}^2 \left(\varepsilon_{\max} \right)$	$\lambda_{\max}^1(\varepsilon_{\max})$	$\lambda_{\max}^2 (\varepsilon_{\max})$	λ_{max}^1	λ_{max}^2
D1	368 (2.8)	570 (2.5)	362 (3.0)	546 (3.0)	362	526
D2	393 (4.4)	562 (4.0)	390 (6.0)	538 (5.0)	389	527
D3	412 (2.8)	562 (2.0)	412 (4.2)	520 (3.8)	412	517
D4	375 (3.5)	595 (3.8)	372 (3.0)	575 (3.2)	369	538

^a λ_{max} and ε_{max} reported in nm and M⁻¹ cm⁻¹×10⁴, respectively.

be attributed to the better conjugation of selenophene than that of thiophene spacer as a result of more polarizability and less electronegativity of selenium atom.²⁴

When the absorption spectra of dyes **D1–D4** were recorded in solvent of higher dielectric constant (THF (7.5)), lower energy bands showed solvatochromic changes, while the higher energy bands remained at the same λ_{max} values (Fig. 1b). Lower energy bands of **D1**, **D2** and **D3** showed blue shift of \sim 15–20 nm by changing solvent chloroform to THF, however, for D3 it was 42 nm. This phenomenon may be attributed to the interaction of polar solvent molecules with the carboxylic acid, which decreases the electronwithdrawing strength of the acceptor by coordinating with COOH group. Further blue shift was observed by the addition of triethylamine to the THF solution of dyes **D1–D4**. It can be attributed to the lower strength of acceptor by deprotonation of carboxylic acid group (Fig. 1c).²⁵ Extinction coefficients increased with increasing spacer length from **D1** to **D2**, however, it again decreased for **D3**. Molar extinction coefficient of **D4** was higher than that of **D1**. Thus replacement of thiophene by selenophene is beneficial for both absorption wavelength and molar extinction coefficient.

Due to the incorporation of BDT, the absorption regions of the dyes penetrated through the whole visible light spectrum. The λ_{max}

values of the dyes **D1**, **D2** and **D4** were red-shifted by 55, 40 and 70 nm compared to that of related dyes without BDT unit **C213**, **C214** (**D21L6**²⁶) and **C215**, repsetively.²⁷ Due to enhanced D–A property, the absorption band-width of the dyes **D1**, **D2** and **D4** was also increased compared to that of **C213–C215**. The UV–vis absorption spectra of **D1–D4** are comparable with that of **BzTCA** and **BzTMCA** dyes.^{15b}

The emission spectra of all dyes were recorded in THF solution (10^{-5} M) (Fig. S21 in Supplementary data). Emission intensities of all dyes were negligible indicating highly efficient charge-transfer process from the donor to the acceptors.²⁸

2.3. Electrochemical properties

The cyclic voltammetry of dilute solution (10^{-5} M) of **D1–D4** was measured in dichloromethane containing 0.1 M tetrabutylammonium tetrafluoroborate (TBAF) with 100 mV/s scan rate with Ag/AgCl as reference and platinum wire as counter electrode (Fig. 2). The dyes D1, D2 and D4 exhibited two reversible oxidation peaks, however, for D3 the second oxidation peak showed quasireversible nature. The first oxidation potential was nearly same (0.67–0.7 V) for all the dyes, which correspond to the removal of electron from the triphenylamine segment.²⁹ The second oxidation occurred at higher potentials, which can be assigned to the removal of an electron from the conjugated backbone of the dyes. The second oxidation potential followed the order D1=D4>D2>D3. As conjugation length increased from **D1** to **D3**, the second oxidation potential decreased. The first and second oxidation potentials for **D1** and **D4** were nearly same. Thus replacement of thiophene by selenophene did not produce the significant changes in the oxidation potentials. The first oxidation potentials were more positive than I_3^-/I^- redox couple, which is an important factor for the efficient dye regeneration in DSSC devices. HOMO energy levels of the dyes were calculated by following Eq. 1.



Fig. 2. CV of 10⁻⁵ M solution of (a) D1, (b) D2, (c) D3 and (d) D3 was measured in DCM containing 0.1 M TBAF with 100 mV/s scan rate with Ag/AgCl as reference and platinum wire as counter electrode.

HOMO =
$$-[E_{OX} - E_{1/2} + 4.81]$$
 eV (1)

where E_{ox} is the onset oxidation potential and $E_{1/2}$ is 0.21 for the ferrocene couple in the above experimental condition.

Optical HOMO–LUMO gaps (E_g) of the dyes were measured from the onset value of absorption spectra (Eq. 2) and thus LUMO energy levels were calculated by Eq. 3 (Table 2). $E_g = 1240/\lambda_{onset}$ (2)

$$LUMO = HOMO + E_{\sigma}$$
(3)

Table 2			
Electrochemical	data	of dy	es

Dye	$E_{\mathrm{ox}}^{1}\left(V\right)$	$E_{\rm ox}^2 \left({\sf V} \right)$	$\lambda_{onset} (nm)$	HOMO ^a (eV	') LUMO (eV)	Optical band gap (eV)
D1	0.70	1.31	713	-5.17	-3.43	1.74
D2	0.67	1.10	730	-5.10	-3.40	1.70
D3	0.67	0.98	743	-5.03	-3.36	1.67
D4	0.67	1.29	743	-5.16	-3.49	1.67

^a HOMO energy levels were calculated from the onset oxidation potential.

The HOMO energies of all dyes are in the region of -5.0 to -5.2 eV below the vacuum level, which are comparable with that of **BzTCA** and **BzTMCA** (Fig. 3). The HOMO energy levels of the dyes must be more positive than the I_3^-/I^- redox couple (4.75 eV) to ensure a fast and efficient regeneration of the dyes from cation radical. The HOMO energy levels of **D1–D4** are higher (by ~0.3 eV) than iodide/triiodide redox potential. Similarly, the LUMOs of all dyes **D1–D4** are higher by at least 0.5 eV than the energy level of TiO₂ conduction band edge. These observations indicate that the redox potentials of the dyes in the ground and excited states are favourable for efficient electron injection to TiO₂ conduction band and the dye regeneration by iodine/iodide redox system.



Fig. 3. Energy diagram of the HOMO and LUMO energies of dyes D1, D2, D3 and D4, conduction band edge of TiO_2 and standard potential of the iodide/triiodide redox couple.

2.4. Theoretical approach

In order to visualize the geometry, electronic structure, and estimate the HOMO–LUMO gaps of the dyes, density functional theory (DFT) calculation at B3LYP/6-31G(d) level was carried out using Gaussian 09 program.³⁰ For geometry optimization, hexyloxy substituent of triphenylamine segment was replaced with methoxy groups. Fig. 4 shows the electron distribution of the HOMO and LUMO of **D1** and **D2**. The HOMO–LUMO gaps are in good

agreement with the experimental values (Table 3). As expected, the electron density of HOMOs of the dyes is delocalized on the triphenylamine and thiophene conjugated segment, while the LUMOs are located on acceptor region (BDT-cyanoacrylic acid). The HOMOs and LUMOs are also found to partly overlap at the spacer (thiophenes and selenophene unit), which indicates appreciable donor-acceptor interaction between the donors and acceptors. It could facilitate intramolecular electron transfer from the donor to the acceptor moiety of the dyes. Trends in the calculated energy values of HOMO and LUMO of D1-D4 are in good agreement with the experimentally obtained values from CV (Table 3). TD-DFT calculations at B3LYP/6-31G(d) on D1 and D2 reproduced the three-band structure, however, the energy values were underestimated (Table 4). Trends in the oscillator strengths from D1 to D2 are in the increasing order, which match well with the trend of increasing molar extinction coefficients from D1 to D2. Three transitions correspond to the excitation from HOMO→LUMO, HOMO $-1 \rightarrow$ LUMO, HOMO \rightarrow LUMO+1, respectively, with increasing order of energy.

3. Conclusions

In summary, a series of new dyes were designed and synthesized. Benzothiadiazole was incorporated as acceptor within the donor-acceptor π -conjugated spacer to increase the overall D-A strength of the dyes. We have shown that by using D–A type π conjugated spacer optical properties of the dyes can be tuned and broaden the absorption range. Although with increasing number of thiophenes within the donor-acceptor π -conjugated spacer the lower energy absorption peak is red-shifted, the absorption coefficient is decreased. It indicates that with the increase in the length of π -conjugated spacer the rate of charge-transfer from donor to acceptor is decreased. As selenophene enhances the conjugation and facilitates charge-transfer process due to more polarizable and less electronegative selenium than sulfur in thiophene, dye **D4** showed better photophysical properties than that of **D1**. As a result **D4** exhibited the broader absorption band with higher molar extinction coefficient than that of **D1**. On the basis of photophysical and electrochemical studies, it can be concluded that (i) the absorption spectra of dyes cover the whole visible region and (ii) HOMO and LUMO levels are ideal to be promising material for DSSC devices.

4. Experimental

4.1. General methods

All reactions were performed under nitrogen atmosphere. Dry toluene and THF was distilled from sodium/benzophenone prior to use. Anhydrous dichloromethane, thiophene, selenophene, 1.0 M trimethyltin chloride in hexane, Pd(PPh₃)₄ and tetrabutylammonium tetrafluoroborate (TBABF₄) were purchased from Aldrich and used without further purification. n-BuLi (1.6 M solution in hexane) was purchased from Neo-Synth. All the new compounds are characterized by ¹H NMR, ¹³C NMR and HRMS. ¹H NMR and ¹³C NMR spectra of the compounds were taken on Bruker Advance 500 MHz and Jeol ECS 400 MHz spectrometers in CDCl₃, acetone d_6 and DMSO- d_6 and chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as the internal standard. Electrochemical studies were carried out with a Princeton Applied Research 263A potentiostat using platinum (Pt) disk electrode as the working electrode, a platinum wire as counter electrode, and a AgCl coated Ag wire, which was directly dipped in the electrolyte solution, as the reference electrode. Non-aqueous Ag/AgCl wire was prepared by dipping silver wire in a solution of FeCl₃ and HCl. UV-vis spectra were recorded on



Fig. 4. Orbital picture generated by DFT at B3LYP/6-31G(d) level.

Table 3	
Calculated values of HOMO	and LUMO of D1 and D2

Dye	HOMO (eV)	LUMO (eV)	Band gap (eV)
D1	-4.88	-3.12	1.76
D2	-4.80	-3.19	1.62
D3	-4.74	-3.23	1.51
D4	-4.87	-3.13	1.74

Table 4	
Calculated low-lying transitions for the dyes D1 and D2	

Dye	State	Excitation	$\lambda_{cal} [eV]$	F
D1	S1	H to L (85.4%)	1.6014	0.6200
	S2	H-1 to L (78.4%)	2.4065	0.3655
	S3	H to L+1 (90.5%)	2.7313	0.3752
D2	S1	H to L (88.7%)	1.4622	0.5962
	S2	H-1 to L (80.9%)	2.1219	0.6533
	S3	H to L+1 (90.7%)	2.6183	0.4496

a HITACHI U-4100 UV–vis–NIR spectrophotometer. All electrochemical potentials were reported against Ag/AgCl taking ferrocene as external standard, the $E_{1/2}^{\text{terrocene}}$ is +0.21 V.

4.2. Synthesis of compound 3

A solution of compound **1** (4.30 g, 8.2 mmol), 2-tributylstannylthiophene (or 2-tributylstannylselenophene or 5-trimethylstannylbithiophene) (8.2 mmol) in dry toluene (150 ml) was purged in N₂ for 10 min. Then Pd(PPh₃)₄ (460 mg, 0.41 mmol) was added and refluxed for 24 h. After removal of solvent under reduced pressure, the residue was directly loaded onto a silica gel column for purification with ethylacetate/hexane (1:5, v/v) as eluent. 4.2.1. Compound **3a**. Yield: 66%; ¹H NMR (500 MHz, acetone- d_6 , ppm) δ : 0.89 (6H, t, *J* 6.8 Hz), 1.36 (8H, m), 1.41 (4H, m), 1.75 (4H, m), 3.99 (4H, t, *J* 6.4 Hz), 6.85 (2H, d, *J* 8.8 Hz), 6.91 (4H, d, *J* 8.8 Hz), 7.05 (4H, d, *J* 8.8 Hz), 7.05 (1H, d), 7.28 (1H, d, *J* 4.4 Hz), 7.33 (1H, d, *J* 6.0 Hz), 7.46 (2H, d, *J* 8.8 Hz).

4.2.2. Compound **3b**. Yield: 60%; ¹H NMR (500 MHz, acetone- d_6 , ppm) δ : 0.89 (6H, t, *J* 6.8 Hz), 1.35 (8H, m), 1.41 (4H, m), 1.75 (4H, m), 3.99 (4H, t, *J* 6.4 Hz), 6.85 (2H, d, *J* 8.8 Hz), 6.92 (4H, d, *J* 8.8 Hz), 7.06 (4H, d, *J* 8.8 Hz), 7.05 (1H, d, *J* 8.8 Hz), 7.21 (1H, d, *J* 4.0 Hz), 7.24 (1H, d, *J* 4.0 Hz), 7.26 (1H, d, *J* 4.0 Hz), 7.38 (1H, d, *J* 4.0 Hz), 7.47 (2H, d, *J* 8.8 Hz); ¹³C NMR (125 MHz, C₆D₆, ppm) δ : 14.2, 23.0, 26.1, 29.6, 31.9, 68.2, 115.8, 121.2, 122.8, 124.1, 125.1, 125.9, 126.8, 127.1, 127.1, 128.3, 129.2, 135.8, 138.1, 141.1, 148.9, 156.3; HRMS (ESI): M⁺, found 609.2743, C₃₈H₄₃NO₂S₂ requires 609.2735.

4.2.3. Compound **3c**. Yield: 70%; ¹H NMR (400 MHz, acetone- d_6 , ppm) δ : 0.90 (6H, t, *J* 6.4 Hz), 1.34 (8H, m), 1.41 (4H, m), 1.75 (4H, m), 3.98 (4H, t, *J* 4.4 Hz), 6.84 (2H, d, *J* 5.6 Hz), 6.91 (4H, d, *J* 6.0 Hz), 7.06 (4H, d, *J* 6.0 Hz), 7.27 (1H, m), 7.41 (2H, d, *J* 5.6 Hz), 7.42 (1H, d, *J* 2.4 Hz), 7.95 (1H, d, *J* 3.6 Hz).

4.3. Synthesis of compound 4

n-BuLi (1.6 M in hexane, 0.34 ml, 0.55 mmol) was added dropwise to a stirred THF solution of compound **2** (0.5 mmol) and cooled at -78 °C. Then the reaction mixture was stirred for 15 min at -78 °C, allowed to come at -50 °C, stirred for 1 h and again cooled to -78 °C. Trimethylstannyl chloride (1.0 M in hexane, 0.55 ml, 0.55 mmol) was added slowly at -78 °C then the mixture allowed to warm at rt and stirred for overnight. The reaction was quenched by adding water. Water layer was extracted by diethyl ether. The organic layer was dried over sodium sulfate; solvent was removed and the residue was used for the next step without further purification. Conversion yields were ~50%–60%. Characteristic peak at δ 0.28–0.38 ppm (s) was observed in ¹H NMR for methyl proton of trimethylstannyl group.

4.4. Synthesis of compound 5

7-Bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (243 mg, 1 mmol) was taken in a dry three-necked round bottom flask and compound **4** in toluene (25 ml) was added. The solution mixture was purged with nitrogen for 10 min; then $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) was added to the reaction mixture. The reaction mixture was heated at 110 °C under nitrogen for 24 h. It was cooled to rt; toluene was evaporated by rotary evaporator. The crude mixture was directly loaded to the column. Product was separated by flash column chromatography using ethylacetate/hexane mixture as eluent.

4.4.1. Compound **5a**. Yield: 64%; ¹H NMR (500 MHz, CDCl₃, ppm) δ : 0.86 (6H, t, *J* 7 Hz), 1.36 (8H, m), 1.45 (4H, m), 1.75 (4H, m), 3.99 (4H, t, *J* 6.5 Hz, 4H), 6.86 (4H, d, *J* 8.5 Hz), 6.93 (2H, d, *J* 8.5 Hz), 7.08 (4H, d, *J* 8.5 Hz), 7.32 (1H, d, *J* 4.4 Hz), 7.50 (2H, d, *J* 6.0 Hz), 7.95 (1H, d, *J* 7.5 Hz), 8.20 (1H, d, *J* 7.5 Hz), 8.30 (1H, d, *J* 4 Hz), 10.71 (1H, s); ¹³C NMR (125 MHz, CDCl₃, ppm) δ : 14.0, 22.6, 25.7, 29.3, 31.6, 68.3, 115.3, 119.7, 123.0, 123.1, 125.0, 125.1, 126.6, 126.9, 131.7, 132.8, 133.3, 136.0, 140.0, 149.2, 149.3, 152.3, 153.8, 155.9, 188.4; HRMS (ESI): M⁺, found 689.2732, C₄₁H₄₃N₃O₃S₂ requires 689.2746.

4.4.2. Compound **5b**. Yield: 71%; ¹H NMR (500 MHz, CDCl₃, ppm) δ : 0.92 (6H, t, *J* 7 Hz), 1.36 (8H, m), 1.46 (4H, m), 1.78 (4H, m), 3.94 (4H, t, *J* 6.5 Hz), 6.87 (4H, d, *J* 8.5 Hz), 6.91 (2H, d, *J* 8.5 Hz), 7.08 (4H, d, *J* 8.5 Hz), 7.12 (1H, d, *J* 4 Hz), 7.28 (2H, d, *J* 4.0 Hz), 7.40 (2H, d, *J* 6.0 Hz), 7.94 (1H, d, *J* 7.5 Hz), 8.19 (1H, d, *J* 7.5 Hz), 8.22 (1H, d, *J* 4 Hz), 10.69 (1H, s); ¹³C NMR (125 MHz, CDCl₃, ppm) δ : 14.0, 22.6, 25.7, 29.3, 31.5, 68.2, 115.3, 120.0, 122.4, 123.2, 124.3, 125.2, 126.3, 126.8, 131.2, 132.6, 132.8, 134.2, 136.4, 140.2, 142.2, 145.1, 148.7, 152.2, 153.8, 155.7, 188.3; HRMS (ESI): M⁺, found 771.2615, C₄₅H₄₅N₃O₃S₃ requires 771.2623.

4.4.3. *Compound* **5***c*. Yield: 62%; ¹H NMR (500 MHz, CDCl₃, ppm) δ : 0.92 (6H, t, *J* 7 Hz), 1.36 (8H, m), 1.46 (4H, m), 1.78 (4H, m), 4.00 (4H, t, *J* 6.5 Hz), 6.86 (2H, d, *J* 8.5 Hz), 6.95 (4H, d, *J* 8.5 Hz), 7.11 (4H, d, *J* 8.5 Hz), 7.57 (2H, d, *J* 4 Hz), 7.65 (1H, d, *J* 4 Hz), 8.28 (2H, d, *J* 4 Hz), 8.46 (1H, d, *J* 4 Hz), 10.69 (1H, s); ¹³C NMR (100 MHz, CDCl₃, ppm): 14.0, 22.5, 25.7, 29.2, 31.5, 68.2, 115.3, 119.6, 122.2, 124.4, 124.6, 126.8, 126.9, 127.3, 132.6, 132.7, 134.9, 139.8, 149.1, 152.3, 153.5, 155.9, 157.4, 188.2; HRMS (ESI): M⁺, found 737.2186, C₄₁H₄₃N₃O₃SSe requires 737.2190.

4.5. Synthesis of compound 6

A mixture of compound 4b (1.2 mmol) and 2-bromothiophene (250 mg, 1.2 mmol) was taken in dry toluene (20 ml) and the mixture was purged with nitrogen for 10 min. Then Pd(PPh₃)₄ (70 mg, 0.06 mmol) was added and reaction mixture refluxed for 24 h. After removal of solvent under reduced pressure, the residue was directly loaded onto a silica gel column for purification with ethylacetate/hexane (1:5, v/v) as eluent. Yield: 80%; ¹H NMR (400 MHz, CDCl₃, ppm) δ: 0.90 (6H, t, J 7 Hz), 1.36 (8H, m), 1.46 (4H, m), 1.78 (4H, m), 3.98 (4H, t, J 6.5 Hz), 6.86 (2H, d, J 8.5 Hz), 6.95 (4H, d, J 8.5 Hz), 7.07 (5H, m), 7.26 (2H, d, J 4 Hz), 7.21 (2H, d, J 4 Hz), 7.30 (1H, d, J 4 Hz), 7.44 (1H, d, J 4 Hz), 7.48 (2H, d, J 4 Hz); 13 C NMR (125 MHz, C₆D₆, ppm) δ : 14.2, 23.0, 26.1, 29.6, 31.9, 68.2, 115.8, 121.1, 122.9, 124.0, 124.3, 124.5, 124.8, 125.1, 125.9, 126.8, 127.1, 127.9, 128.2, 128.5, 135.4, 137.6, 141.0, 144.2, 149.0, 156.3; HRMS (ESI): M⁺, found 691.2603, C₄₂H₄₅NO₂S₃ requires 691.2612.

4.6. Synthesis of compound 7

Compound **6** (345 mg, 0.5 mmol) was dissolved in dry THF (20 ml), cooled to -78 °C and *n*-BuLi (1.6 M in hexane, 0.35 ml, 0.55 mmol) was added dropwise and stirred for 15 min then the reaction mixture was allowed to come at -50 °C, stirred for 1 h at this temperature and then again cooled to -78 °C. Trimethylstannyl chloride (0.55 ml, 0.55 mmol) was added slowly and allowed the mixture to warm at rt. The reaction was quenched by adding water. Water layer was extracted with diethyl ether. The organic layer was dried over sodium sulfate; solvent was removed under reduced pressure and residue was used for next step without further purification. Conversion yield was calculated from the singlet proton for trimethylstannyl group at δ : 0.38 ppm.

4.7. Synthesis of compound 5d

7-Bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (243 mg, 1 mmol) was taken in a dry three-necked round bottom flask and compound 7 (1.2 mmol) in dry toluene (25 ml) was added. The solution mixture was purged with nitrogen for 10 min. Pd(PPh₃)₄ (110 mg, 0.1 mmol) was added to reaction mixture and refluxed at 110 °C for 24 h. The reaction mixture was cooled at rt; toluene was evaporated by rotary evaporator. The crude mixture was directly loaded to column. The product was purified silica gel column chromatography using ethylacetate/hexane as eluent. Yield: 65%; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.92 (6H, t, J 7 Hz), 1.36 (8H, m), 1.46 (4H, m), 1.78 (4H, m), 4.00 (4H, t, J 6.5 Hz), 6.86 (2H, d, / 8.5 Hz), 6.95 (4H, d, / 8.5Hz), 7.11 (4H, d, / 8.5 Hz), 7.57 (2H, d, / 4 Hz), 7.65 (1H, d, / 4 Hz), 8.28(2H, d, / 4 Hz), 8.46 (4H, d, / 4 Hz), 10.69 (1H, s); ¹³C NMR (125 MHz, CDCl₃, ppm): 14.0, 22.6, 25.5, 29.3, 31.5, 68.2, 115.2, 120.0, 122.1, 124.8, 124.4, 123.8, 123.2, 125.1, 125.3, 125.4, 126.1, 126.7, 131.0, 132.4, 132.4, 134.3, 136.7, 137.8, 140.1, 141.5, 144.1, 148.4, 152.0, 153.6, 155.7, 188.2; HRMS (ESI): M⁺, found 853.2512, C₄₉H₄₇N₃O₃S₄ requires 853.2500.

4.8. Synthesis of compound D1–D4

Compound **5** was dissolved in dry chloroform in dry threenecked round bottom flask fitted with condenser. Cyanoacetic acid and piperidine were added and reaction mixture was refluxed for 12 h, then water added to the reaction mixture and organic layer was separated by dichloromethane and dried over Na_2SO_4 . The product was purified by column chromatography dichloromethane/methanol (9:1, v/v) as elutant.

4.8.1. Compound **D1**. Yield: 80%; ¹H NMR (500 MHz, DMSO- d_6 , ppm) δ : 0.86 (6H, t, *J* 7 Hz), 1.29–1.34 (8H, m), 1.4–1.5 (4H, m), 1.6–1.7 (4H, m), 3.94 (4H, t, *J* 6.5 Hz), 6.79 (2H, d, *J* 8.5 Hz), 6.93 (4H, d, *J* 8.5 Hz), 7.07 (4H, d, *J* 8.5 Hz), 7.55 (1H, d, *J* 8.5 Hz), 7.59 (2H, d, *J* 4.0 Hz), 8.27 (1H, d, *J* 5.0 Hz), 8.30 (1H, d, *J* 5.0 Hz), 8.65 (1H, d, *J* 5.0 Hz), 8.81 (1H, s); ¹³C NMR (125 MHz, DMSO- d_6 , ppm) δ : 13.8, 22.0, 25.1, 28.6, 30.9, 67.6, 113.6, 115.5, 118.7, 122.4, 122.4, 123.2, 123.4, 123.4, 124.2, 124.4, 126.4, 127.1, 129.2, 130.8, 135.4, 139.3, 148.1, 148.7, 150.6, 154.2, 155.6; HRMS (ESI): M⁺, found 756.2798, C₄₄H₄₄N₄O₄S₂ requires 756.2804.

4.8.2. Compound **D2**. Yield:75%; ¹H NMR (400 MHz, DMSO- d_6 , ppm) δ : 0.86 (6H, t, *J* 7 Hz), 1.29–1.34 (8H, m), 1.4–1.5 (4H, m), 1.6–1.7 (4H, m), 3.94 (4H, t, *J* 6.5 Hz), 6.76 (2H, d, *J* 8 Hz), 6.91 (4H, d, *J* 8 Hz), 7.04 (4H, d, *J* 8 Hz), 7.35 (1H, d, *J* 4 Hz), 7.4–7.5 (4H, m), 8.21 (1H, d, *J* 4.0 Hz), 8.30 (1H, d, *J* 8.0 Hz), 8.56 (1H, d, *J* 8.0 Hz), 8.76 (1H, d, *J* 4.0 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 12.0, 20.2, 23.3, 27.1, 29.1, 65.7, 101.9, 113.4, 114.2, 117.0, 119.8, 121.1, 122.2, 122.4, 122.6, 124.1, 124.9, 128.0, 128.3, 128.8, 131.6, 134.0, 136.8, 137.5, 139.6,

142.1, 144.2, 146.4, 152.3, 153.6, 161.2; HRMS (ESI): M^+ , found 838.2684, $C_{48}H_{46}N_4O_4S_3$ requires 838.2681.

4.8.3. *Compound* **D3**. Yield: 70%; ¹H NMR (400 MHz, DMSO- d_6 , ppm) δ : 0.86 (6H, t, *J* 7 Hz), 1.29–1.34 (8H, m), 1.4–1.5 (4H, m), 1.6–1.7 (4H, m), 3.94 (4H, t, *J* 6.5 Hz), 6.76 (2H, d, *J* 8.5 Hz), 6.91 (4H, d, *J* 8.5 Hz), 7.03 (4H, d, *J* 8.5 Hz), 7.31–7.34 (3H, m), 7.4–7.5 (3H, m), 7.53 (1H, d, *J* 4.4 Hz), 8.20 (1H, d, *J* 6.0 Hz), 8.30 (1H, d, *J* 7.5 Hz), 8.54 (1H, d, *J* 7.5 Hz), 8.69 (1H, d, *J* 4 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 13.8, 22.0, 25.1, 28.6, 30.9, 67.6, 116.0, 115.5, 118.9, 119.3, 123.1, 124.6, 124.7, 124.9, 125.6, 125.7, 126.1, 126.9, 124.9, 127.3, 127.6, 129.3, 134.3, 134.4, 136.2, 136.8, 139.2, 139.4, 139.6, 143.1, 148.2, 150.7, 154.0, 155.4, 162.1; HRMS (ESI): M⁺, found 920.2559, C₅₂H₄₈N₄O₄S₄ requires 920.2558.

4.8.4. Compound **D4**. Yield: 80%; ¹H NMR (500 MHz, DMSO- d_6 , ppm) δ : 0.92 (6H, t, *J* 7.0 Hz), 1.36 (8H, m), 1.46 (4H, m), 1.78 (4H, m), 4.00 (4H, t), 6.86 (2H, d, *J* 8.5 Hz), 6.95 (4H, d, *J* 8.5 Hz), 7.57 (2H, d, *J* 4.0 Hz), 7.65 (1H, d, *J* 4.0 Hz), 8.28 (2H, d, *J* 4.0 Hz), 8.46 (1H, d, *J* 4.0 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm) δ : 14.0, 22.5, 25.7, 29.2, 31.5, 68.2, 101.4, 115.3, 115.9, 119.3, 121.1, 122.8, 124.5, 126.8, 127.0, 127.1, 130.8, 132.8, 133.9, 139.8, 147.8, 149.2, 151.2, 154.8, 155.9, 157.9, 166.2; HRMS (ESI): M⁺, found 804.2240, C₄₄H₄₄N₄O₄SSe requires 804.2248.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.071.

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