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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND OPTOELECTRONIC INVESTIGATIONS OF THIOPHENE SUBSTITUTED 1,3,4-OXADIAZOLE DERIVATIVES AS FLUORESCENT MATERIALS

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ABSTRACT

We have designed and synthesized a novel series of unsymmetrical small bipolar organic molecules **5(a-h)** via the palladium catalyzed Suzuki coupling reaction. The structural identities and purities were confirmed by ^{1}H NMR, ^{13}C NMR, IR and MS and were found to be in good agreement with the proposed structures. We have studied the photophysical and thermal properties of the synthesised compounds with UV-Vis/fluorescence spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The systematic investigations of photophysical and thermal properties of newly synthesised compounds were performed with a view to under their suitability in optoelectronics.

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INTRODUCTION

Optoelectronic properties of thiophene related compounds have gained a significant research interest due to their wide application as organic semiconductors in light emitting diodes (OLED's), field effect transistors (FETs), electrochemical and chemical sensors and other optoelectronic devices (Mishra *et al*., 2009; Pron *et al*., 2010; Hains *et al*., 2010; Bujak *et al*., 2013). Organic compounds have been studied extensively to develop thin, efficient and stable devices with wide viewing angles and fast response. In recent years, Photoluminescence (PL) of organic materials with excellent characteristics has been exploited for the development and commercialization display materials. Materials composed of an organic donor-acceptor groups exhibit an interesting property of electric conductivity in optoelectronic devices (Special issue on Molecular Conductors, 2004; Pfeiffer *et al*., 2003; Wang *et al*., 2013). The HOMO and LUMO levels of thiophene derivatives governess the electron affinity (EA) and ionization potential (IP) (Pron *et al*., 2010). Since these two parameters determine the redox, spectroscopic, electronic and optoelectronic properties of molecule and their tuning is of crucial importance in design of new organic semiconductors. One of the possible ways of the preparation of low molecular mass semiconductors, showing higher than oligothiophene IP values, is to synthesize molecules in which a central electron accepting group attached to the electron donor groups on either side. Such compounds containing thiadiazole (Kurach *et al*., 2013; Kotwica *et al*., 2013; McCairn *et al*., 2006; Zapala *et al*., 2013; Mitschke *et al*., 1998; Mitschke, 2000), oxadiazole (Fisyuk *et al*., 2005; Lee *et al*., 2009) or tetrazine units (Clavier and Audebert, 2010; Gong *et al*., 2009; Audebert *et al*., 2004) as electron acceptor. By employing donor/acceptor strategy one can improve the device efficiency and operational lifetime along with fluorescence properties (Clavier and Audebert, 2010). In order to achieve high fluorescence, small bipolar molecules can be designed by incorporating electron-withdrawing groups like 1,3,4-oxadiazole, phosphineoxide, triazine and electron-donating groups like carbazole, diphenylamine etc (Okumoto and Shirota, 2003; Cheng *et al*., 2013; Guan *et al*., 2011; Chou *et al*., 2012; Inomata *et al*., 2009; Ge *et al*., 2008).

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Moreover, luminescence properties of these derivatives are superior to those of the corresponding penta-ring oligothiophenes. For example, the central heterocycle ring replacement in substituted quinquethiophene by 1,3,4-oxadiazole leads to a substantial increase of the fluorescence quantum yield. Among all fluorescent heterocyclic ring systems, the molecules containing 1,3,4-oxadiazole, play a crucial roles like excellent electron-acceptor, high thermal stability, high quantum yields. They are also used as electron-transporting/hole-blocking materials in OLEDs (Ma *et al.*, 2013; Liu *et al.*, 2009). Indeed, oxadiazole units advantageously restrict π-conjugation to afford materials with deeply lying highest occupied molecular orbital's (HOMOs) such that the triplet energies (ETs) are high (Ge *et al.*, 2008; Ma *et al.*, 2013)

In the present investigation, we have designed 1,3,4-oxadiazole derivatives as donor-acceptor (D/A) systems which can be tuned either by altering the strength of D/A units or by extending π conjugation. The incorporation of electron deficient 1,3,4- oxadiazole ring with electron rich aryl substituted thiophenes acts as a donor results in strong intramolecular charge transfer (ICT) chromophores (Curtis *et al.*, 2008; Wang *et al.*, 2007). In view of this, we have designed and synthesized a novel series of unsymmetrical small bipolar organic molecules 5(a-h) (Fig. 1) with thiophene substitution as an electron donor.

RESULTS AND DISCUSSION

Synthesis and Characterization

Designed title compounds 5(a-h) are illustrated in Fig 1. A relatively simple and efficient synthetic protocol was employed for the synthesis of compounds 5(a-h) as depicted in scheme 1. The required precursor 4-bromobenzohydrazide was obtained by the esterification of 4-bromobenzoic acid followed by treating with hydrazine hydrate. The key intermediate 2-(4-bromophenyl)-5-(5-chlorothiophen-2-yl)-1,3,4-oxadiazole (4) was synthesized by treatment of 4-bromobenzohydrazide with 5-chlorothiophene-2-carboxylic acid in refluxing $POCl_3$. Subsequent Pd-catalyzed Suzuki cross-coupling reaction between 4 and aryl/heteroarylboronic acids afforded the target compounds in 80-85% yield.

We successfully replace both bromo at the para position of the phenyl group and chloro at the fifth position of the thiophene with different aryl/heteroarylboronic acids. The resulting bipolar molecules were purified by column chromatography on silica gel followed by recrystallization in ethanol before spectral characterization. All these compounds **5(a-h)** are amorphous in nature and can be stored under ambient conditions for longer time without any detectable decomposition. All these compounds are readily soluble in common organic solvents like EtOH, $CHCl_3$, DCM and THF etc.

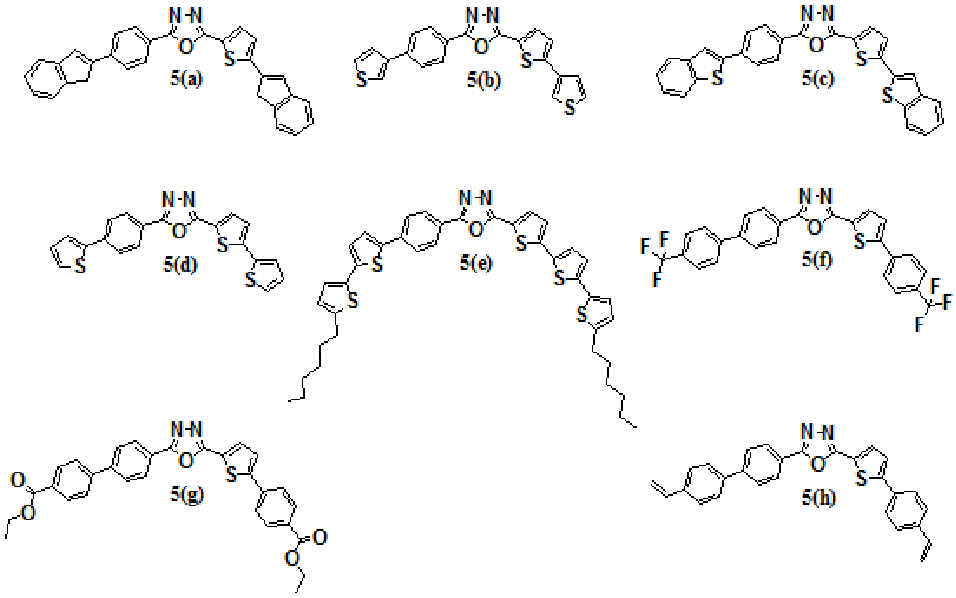


Fig. 1. Chemical structures of target compounds 5(a-h)

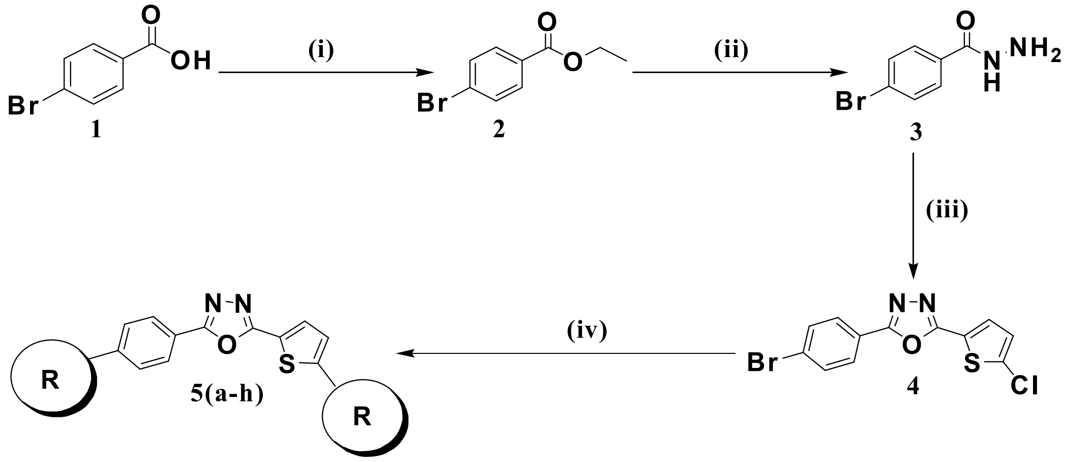
We have studied the optoelectronic properties such as UV-Vis/fluorescence spectra of newly synthesised compounds. Additionally, we have investigated thermal properties of compounds by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The systematic investigation of photophysical and thermal properties of newly synthesised compounds reveals that, desired compounds could be used as active component of donor/acceptor in optoelectronic devices.

Their structural identities and purities were confirmed by ^{1}H NMR, ^{13}C NMR, IR and MS and were found to be in good agreement with the proposed structures.

Photophysical Properties

UV-Vis Absorption and Photoluminescence (PL) spectra

The target compounds 5(a-h) soluble in all common organic solvents and they produce faint blue to green coloured solution exhibiting clear fluorescence property.



Reagents and conditions: (i) $SOCl_2$, Ethanol, reflux, 5-6 h.
(ii) $NH_2NH_2.H_2O$, reflux, 3-4 h.
(iii) 5-chlorothiophene-2-carboxylic acid, $POCl_3$, Reflux, 12 h.
(iv) Aryl/Heteroarylboronic acid, $Pd(dppf)_2Cl_2$, K_2CO_3, dioxane 80°C, 6 h.

Scheme 1. Synthetic route for the target compounds 5(a-h)

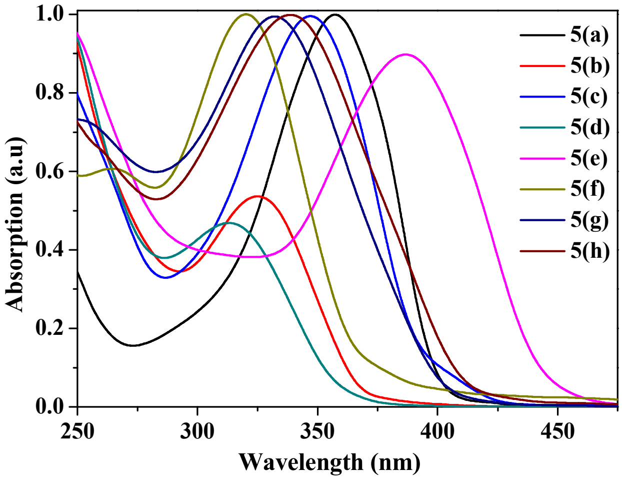


Fig. 2. UV-Vis absorption spectra of compounds 5(a-h) in ethanol at RT

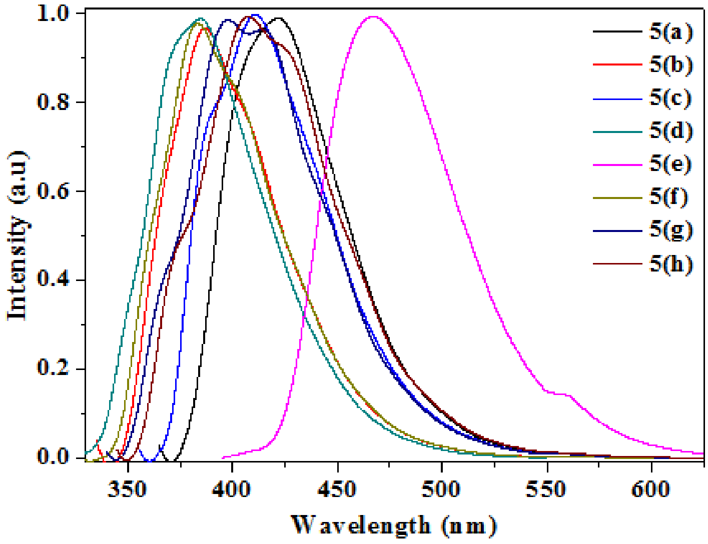


Fig. 3. Emission spectra of compounds 7(a-h) in ethanol at RT

Table 1. Summary of Optical and thermal properties of π-conjugated molecules 5(a-h)

Compounds	Absorption λ_{max}^{abs} (nm)[a]	Emission λ_{max}^{emi} (nm)[b]	Stoke shift Δλ (nm)	$E_g^{opt}(eV)$ [c]	$T_g/T_m/T_c/T_{5d}$ [°C][d]
5a	358	421	63	3.08	-/215/-/291
5b	325	386	61	3.35	-/164/-/232
5c	347	411	64	3.04	157.61/220/-/267
5d	313	384	71	3.41	-/141/-/240
5e	387	466	79	3.29	-/142/-/335
5f	319	382	63	2.77	97.22/134/-/312
5g	333	414	81	3.06	96.45/173/-/306
5h	338	407	69	3.10	96.73/-/176/292

[a] The absorption spectra were measured in ethanol at 10 µM concentration.
[b] The emission spectra were measured in ethanol at 10 µM concentration.
[c] Optical band gap energies were calculated from the equation $E_{opt} = hc/\lambda = 1240/\lambda$ (eV), where λ is the edge wavelength (in nm) of the UV-Vis absorption spectrum.
[d] Obtained from DSC and TGA measurements; T_g-glass transition temperature, T_m-melting temperature and T_c-crystallization temperature.

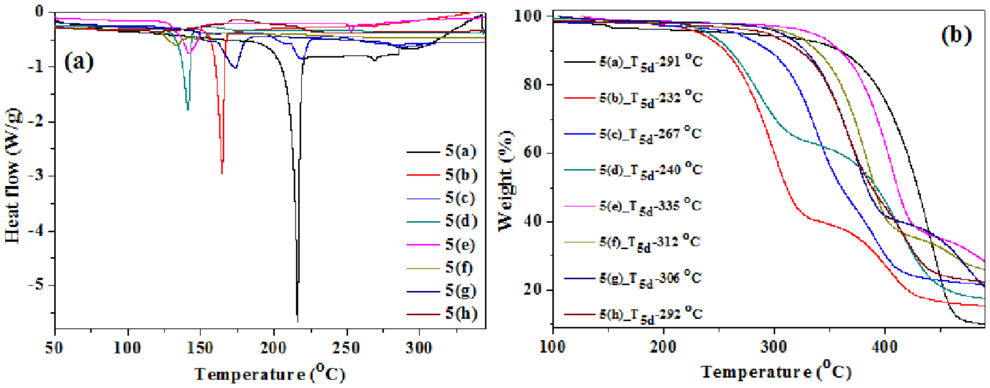


Fig. 4. (a) DSC and (b) TG Curve of the compounds 7(a-h) measured at a heating rate of 10 °C min^{-1} under N$_2$

The absorption and emission maximum of their solutions in ethanol were recorded in Fig. 2 and their spectral parameters were tabulated in Table 1. All eight derivatives display a broad absorption band at the visible range edge, ascribable, on account of its energy, to a π-π* transition. The maximum absorption wavelengths (λ_{max}^{abs}) of 5a, 5b, 5c, 5d, 5e, 5f, 5g and 5h are 358, 325, 347, 313, 387, 319, 333 and 338 nm, respectively. Among the eight derivatives, compound 5e consisting of an electron withdrawing 1,3,4-oxadiazole uint with asymmetrically end-capped alkyl bithiophene shows high solubility with smallest absorption band energy of 387 nm compared to other derivatives, this may leads to narrowing of the frontier molecular orbital gap and increase in the molecular HOMO level. In the series 5(a-h), the derivative 5e shown highest λ_{max}^{abs} of 387 nm and 5d exhibited least λ_{max}^{abs} of 313 nm. The chemical nature of the central oxadiazole ring with neighboring aromatic substitutions plays an important role in the absorption maxima of the compounds and it also depends on the bonding position of the substituents. In this context compound 5b and 5d shows absorption maxima of 325 and 313 nm respectively, these compounds differ by the passion of C-C bond formation with terminal thiophene unit on either side of the central oxadiazole core. Upon excitation with the UV light, all investigated compounds feature strong photoluminescence (PL) shown in Fig. 3. Compared to the featureless absorption spectra, the broad structured fluorescence spectra's were observed in the low energy side. Photoluminescence provides good deal of information on the electronic structure of the synthesised molecules. Their emission maxima arrange themselves in the order i.e.: 466 > 421 > 414 > 411 > 407 > 386 > 384 > 382. We notice that, both the number of donor groups and the chemical nature of the central electron accepting ring exert strong influence on fluorescence performance of the compounds. As accepted, an increasing in the number of thiophene units shifts the emission maxima to longer wavelength side, clearly observed in 5e.

Optical Band Gap

In organic molecules, the energy levels of the electronic states correspond to the energy carried by UV or visible radiation. At resonance, the molecules can absorb quantified energy transported by the electromagnetic radiation, and promote an electron from the low-energy molecular orbital to higher energy molecular orbital. These transitions can be measured using a UV-Vis spectrophotometer. The optical band (E_g^{opt}) corresponds to the energy of the long wavelength edge of the exciton absorption band. The optical band gap values (E_g^{opt}) were approximated from the onset of the low energy side of the absorption spectra (λ_{onset}, solution) to the baseline according to the equation (2) and are presented in Table. 1.

$$E_g^{opt} = \frac{1240}{\lambda onset} \qquad (2)$$

Thermal Properties

The good thermal stability of the compounds is indicated by their high decomposition temperatures (T_d, corresponding to 5% weight loss) in the range of 335-232 ^oC in the thermogravimetric analysis (Fig. 4). The glass transition temperatures (T_g) determined through differential scanning calorimetry (DSC). The phase transition properties of these compounds 5c, 5f, 5g and 5h were analyzed by an endothermic baseline shift related to the glass transition temperature (T_g) at 157.61, 97.22, 96.45 and 96.73 respectively. Compounds 5(a-h) shows an endothermic melting peak in the temperature range of 220-134 ^oC, it indicates compounds exhibiting good amorphous glass state stability. Compound 7h shows broad exothermic peak at 176 ^oC. The good thermal and morphological stability of these materials helps in the preparation of homogeneous and stable amorphous thin films through solution processing, which is crucial for the operation of OLEDs.

Conclusion

We have successfully designed and synthesized a novel series of highly conjugated 1, 3, 4-oxadiazole containing donor-acceptor (D/A) chromophores by employing a relatively simple synthetic protocol (Suzuki reaction). Structures of these newly synthesized compounds were confirmed by their analytical and spectral data. We have studied the optoelectronic properties like UV-Vis spectra, PL spectra and thermal properties. These studies have clearly revealed that, there is a pronounced effect of chemical structure on the optical properties of the compounds. Compound **5e** has shown highest λ_{max}^{abs} and λ_{max}^{emi} of around 387 nm, 466 nm respectively, which might be due to the presence of bithiophene unit on either side of the molecule. The thermal and morphological stabilities of compounds were confirmed by DSC and TGA analysis and they are found to be stable at higher temperatures. The optoelectronic and thermal studies suggest that, these compounds may be used as potential candidates for optoelectronics.

Experimental Section

Physical Measurements

All chemicals are reagent/analytical grade and used without further purification. All boronic acids were purchased from Sigma-Aldrich. Melting points were determined by open capillary method and are uncorrected. The IR spectra were recorded on Nicolet Impact 410 FT IR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR were recorded on Bruker 400-MHz FT NMR spectrometer in $CDCl_3$ or DMSO-d*6* by using TMS as internal standard. Chemical shifts are reported in ppm downfield (δ) from TMS. Mass spectra were recorded using Quadrupole LC/MS system with ESI resource. Elemental analyses were performed on a Vario III elemental analyzer. The UV-is absorption spectra were recorded using JASCO UV-Vis NIR Spectrophotometer (Model V-670). Photoluminescence spectra were measured using Spectro-fluorometer (JY Horiba, Floromax-4. DSC and TGA were performed with a TA Instruments DSC Q20 V24.10 Build 122 and TA Instruments SDT Q600 V20.9 Build 20, respectively, under nitrogen with heating rates of 10 ^oC min^{-1}.

Materials and Synthesis

All solvents were freshly distilled over appropriate drying reagents prior to use. All starting materials were purchased from Sigma Aldrich and were used without further purification. The required intermediate 4-bromobenzhydrazide and compound 6 was synthesized according to the procedure. The catalyst Pd(dppf)2Cl2 and aryl/heteroarylboronic acids were purchased from Sigma-Aldrich.

Procedure for the synthesis of intermediate 2-(4-bromophenyl)-5-(5-chlorothiophen-2-yl)-1,3,4-oxadiazole (4)

4-bromobenzohydrazide (5.0 g, 0.023 mol) and 5-chlorothiophene-2-carboxylic acid (4.1 g, 0.025 mol) were dissolved in $POCl_3$ (50 ml). The mixture was refluxed for 12 h at 100 ^oC. Completion of the reaction was monitored by TLC. After completion of the reaction, allowed the reaction mixture to reach room temperature, the quenching of reaction mixture in ice water bath was carefully carried out under efficient fume hood. The solid that separated was collected by filtration and then washed with saturated $NaHCO_3$ solution to remove excess of un-reacted carboxylic acid, the crude product was subjected to re-crystallization from ethanol, followed by column chromatography on silica gel using plane chloroform as an eluting solvent to obtain desired compound in 85-90% yield. White colour. Isolated yield: 85%. Mp: 158-160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.62 (s, 1H), 7.04 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.39, 159.92, 135.76, 132.49, 129.24, 128.32, 127.49, 126.66, 123.43, 122.38. MS m/z calculated for $C_{12}H_6BrClN_2OS$ 341.61, found 342 (M^{+1}). Anal. Calcd (%) for $C_{12}H_6BrClN_2OS$: C 42.19, H 1.77, N 8.20. Found: C 42.21, H 1.75, N 8.22.

General procedure for the synthesis of final compounds 5(a-h)

To a mixture of 6 (0.5 g, 0.0014 mol), Aryl/Heteroarylboronic acid, (0.389 g, 0.0032 mol), $Pd(dppf)_2Cl_2$ (0.102 g, 0.00014 mol), as a catalyst were added to a mixure of 1,4 dioxane (10 mL) and aqueous 2M K_2CO_3 (5 mL). The reaction mixture was heated for 6-8 h at 85-90 ^oC under nitrogen. The progress of the reaction was frequently monitored by TLC, the solution was extracted with CH_2Cl_2 and the organic layer was washed with water (25 mL) and brine solution (25 mL), and then dried over anhydrous Na_2SO_4. Organic solvent was removed completely under reduced pressure, the crude residue was purified by flash column chromatography on silica gel using plane chloroform as an eluting solvent to obtain desired compound in 80-85% yield.

2-(4-(1H-inden-2-yl) phenyl)-5-(5-(1H-inden-2-yl)thiophen-2-yl)-1,3,4-oxa diazole (5a)

Light green colour. Isolated yield: 85%, Mp: 160-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11-8.09 (m, 2H), 7.81-7.75 (m, 3H), 7.62 (d, *J* = 4.0 Hz, 1H), 7.51 (d, *J* = 6.7 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.40 (s, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 4.0 Hz, 2H), 3.85 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ:

164.01, 159.81, 144.92, 144.88, 143.34, 139.41, 135.44, 132.47, 129.07, 129.01, 128.34, 127.44, 127.40, 127.37, 127.34, 127.30, 126.88, 126.11, 125.58, 123.83, 122.01, 121.55, 39.11; MS m/z calculated for $C_{30}H_{20}N_2OS$ 456.56, found 456 (M^+). Anal. Calcd (%) for $C_{30}H_{20}N_2OS$: C 78.92, H 4.42, N 6.14, Found: C 78.85, H 4.38, N 6.10.

2-(4-(thiophen-3-yl) phenyl)-5-(5-(thiophen-3-yl)thiophen-2-yl)-1,3,4-oxa diazole (5b)

Green colour. Isolated yield: 85%. Mp: 170-173 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 8.08 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 2H), 8.01 (d, *J* = 2.0 Hz, 2H), 7.88-7.84 (m, 5H), 7.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.40, 162.56, 142.15, 139.30, 138.98, 136.12, 128.94, 128.69, 127.87, 126.84, 122.58. MS m/z calculated for $C_{20}H_{12}N_2OS_3$ 392.52, found 392 (M^+). Anal. Calcd (%) for $C_{20}H_{12}N_2OS_3$: C 61.20, H 3.08, N 7.14 Found: C 61.16, H 3.10, N 7.09.

2-(4-(benzo[b] thiophen-2-yl) phenyl)-5-(5-(benzo [b] thiophen-2-yl)thioph en-2-yl)-1,3,4-oxadiazole (5c)

Green colour. Isolated yield: 85%. Mp: 179-182 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 8.05 (d, *J* = 4.7 Hz, 1H), 8.04 (d, *J* = 1.9 Hz, 2H), 8.02 (d, *J* = 2.0 Hz, 2H), 8.21-8.14 (m, 8H), 8.01 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.15, 162.31, 143.49, 142.48, 140.07, 136.12, 132.37, 131.04, 128.94, 128.69, 125.77, 124.17, 123.91, 122.58, 119.91. MS m/z calculated for $C_{28}H_{16}N_2OS_3$ 492.63, found 492 (M^+). Anal. Calcd (%) for $C_{28}H_{16}N_2OS_3$: C 68.27, H 3.27, N 5.69 Found: C 68.23, H 3.20, N 5.65.

2-(4-(thiophen-2-yl)phenyl)-5-(5-(thiophen-2-yl)thiophen-2-yl)-1,3,4-oxa diazole (5d)

Green colour. Isolated yield: 85%. Mp: 180-183 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 8.07 (d, *J* = 4.8 Hz, 1H), 8.02 (d, *J* = 1.9 Hz, 2H), 8.00 (d, *J* = 2.0 Hz, 2H), 7.86-7.82 (m, 5H), 7.39 (d, *J* = 4.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.02, 162.74, 138.28, 136.09, 135.80, 133.53, 131.35, 129.16, 128.58, 128.26, 126.98, 126.38, 125.39, 124.80, 123.52, 122.25. MS m/z calculated for $C_{20}H_{12}N_2OS_3$ 392.52, found 392 (M^+). Anal. Calcd (%) for $C_{20}H_{12}N_2OS_3$: C 61.20, H 3.08, N 7.14 Found: C 61.22, H 3.10, N 7.13.

2-(4-(5-(5-hexylthiophen-2-yl) thiophen-2-yl)phenyl)-5-(5-(5-(5-hexylthiophen-2-yl) thiophen-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (5e)

Intence green colour. Isolated yield: 85%. Mp: 230-235 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 8.10 (d, *J* = 8.6 Hz, 2H), 7.92-7.86 (m, 4H), 7.68 (d, *J* = 3.8 Hz, 2H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.30 (d, *J* = 3.8 Hz, 1H), 7.24 (d, *J* = 3.9 Hz, 2H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.15 (dd, *J* = 14.4, 3.7 Hz, 1H), 6.84 (d, *J* = 3.7 Hz, 1H), 2.79 (t, *J* = 7.4 Hz, 4H), 2.69-2.64 (m, 2H), 2.35-2.29 (m, 2H), 1.67-1.58 (m, 4H), 1.33-1.27 (m, 8H), 0.86 (dd, *J* = 8.0, 6.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.76, 162.65, 143.09, 138.01, 135.88, 134.05, 132.98, 132.46, 129.28, 129.03, 127.19, 126.61, 126.37, 126.11, 125.85, 125.60, 124.79, 124.01, 43.21, 33.13, 31.27, 29.96, 21.76, 15.14. MS m/z calculated for $C_{40}H_{40}N_2OS_5$ 725.08, found 726 (M^+). Anal. Calcd (%) for $C_{40}H_{40}N_2OS_5$: C 66.26, H 5.56, N 3.86 Found: C 66.22, H 5.58, N 3.80.

2-(4-(4-(trifluoromethyl) phenyl) phenyl) -5-(5-(4-(trifluoromethyl) phenyl) thiophen-2-yl)-1,3,4-oxadiazole (5f)

Green colour. Isolated yield: 85%. Mp: 192-197 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ: 8.26 (d, *J* = 1.6 Hz, 1H), 8.21-8.18 (m, 2H), 8.02-7.97 (m, 6H), 7.86 (m, *J* = 5.6, 3.3 Hz, 4H), 7.39 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.49, 162.65, 140.92, 138.82, 138.01, 136.40, 132.46, 131.64, 131.13, 130.36, 127.70, 127.45, 126.87, 126.61, 126.37, 124.79, 124.27. MS m/z calculated for $C_{26}H_{14}F_6N_2OS$ 516.46, found 517 $(M+H)^+$. Anal. Calcd (%) for $C_{26}H_{14}F_6N_2OS$: C, 60.47, H, 2.73, N 5.42 Found: C 60.45, H 2.75, N 5.46.

Ethyl4-(5-(5-(4-(4-ethoxycarbonyl (phenyl))phenyl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl) benzoate (5g)

Green colour. Isolated yield: 80% Mp: 185-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25-8.09 (m, 5H), 7.83-7.77 (m, 4H), 7.76-7.71 (m, 3H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 4.0 Hz, 1H), 7.04 (d, *J* = 4.0 Hz, 1H), 4.46-4.37 (m, 4H), 1.47-1.38 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.59, 164.23, 162.40, 139.58, 138.82, 138.57, 136.40, 132.72, 130.62, 130.36, 129.79, 129.28, 128.78, 128.45, 127.70, 127.45, 124.79, 59.37, 14.61. MS m/z calculated for $C_{30}H_{24}N_2O_5S$ 524.59, found 525 $(M+H)^+$. Anal. Calcd (%) for $C_{30}H_{24}N_2O_5S$: C 68.69, H 4.61, N 5.34 Found: C 68.65, H 4.66, N 5.37.

2-(4-(4-vinylphenyl) phenyl)-5-(5-(4-vinylphenyl)thiophen-2-yl)-1,3,4-oxadiazole (5h)

Green colour. Isolated yield: 82%. Mp: 178-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25-8.13 (m, 3H), 7.83-7.74 (m, 4H), 7.66-7.63 (m, 4H), 7.55-7.52 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 1H), 6.76 (ddd, *J* = 17.6, 13.2, 11.4 Hz, 2H), 5.83 (dd, *J* = 17.7, 4.4 Hz, 2H), 5.32 (d, *J* = 10.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.77, 159.81, 148.96, 144.19, 143.95, 139.09, 138.94, 138.14, 137.66, 137.61, 136.25, 136.04, 135.46, 132.49, 130.71, 129.04, 127.52, 127.44, 127.40, 127.28, 126.99, 126.88, 126.23, 123.90, 123.83, 122.53, 122.28, 114.80, 114.60, 114.55. MS m/z calculated for $C_{28}H_{20}N_2OS$ 432.54, found 433 $(M+H)^+$. Anal. Calcd (%) for $C_{28}H_{20}N_2OS$: C 77.75, H 4.66, N 6.48 Found: C 77.73, H 4.68, N 6.44.

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