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Synthesis and characterization of benzo[*c*]thiophene analogs incorporating benzo[*b*]thiophene/1-hexylindole/benzo[*b*]furan

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ABSTRACT

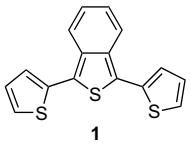
Synthesis of 1,3-disubstituted benzo[*c*]thiophene analogs incorporating heterocycles such as benzo[*b*]thiophene/1-hexylindole/benzo[*b*]furan and thiophene units is described. Optical and electrochemical studies of the benzo[*c*]thiophene analogs are also reported.

1. Introduction

Synthesis and application of thienyl oligomers have been of great interest for chemists and material scientists due to their intrinsic photo physical and redox properties.[1] Indeed, the thienyl oligomers have been widely used as components in Organic Light-Emitting Diodes (OLEDs),[2] Organic Solar Cells (OSC),[3] Organic Field-Effect Transistors (OFETs),[4] and photo refractive holography.[5] On the other hand, polythiophene is superior to polyphenylene as a semiconductor. In general, arylenevinylenes as well as hetero-arylenevinylenes have also attracted attention in the fabrication of electroluminescent devices.[6] Specifically, poly(thienylenevinylene) has attracted considerable interest as a material with enhanced third-order nonlinear susceptibilities. The synthesis and investigation of well-defined model oligomers have recently become useful in gaining insight into the structural and electronic peculiarities of the corresponding polymers. Indeed, the extent of conjugation does not make major difference between thienyl oligomers and polymers, since electronic properties are saturated after a particular chain length.[7]

The synthesis and characterization of 1,3-dithienylbenzo[*c*]-thiophene **1** have been reported independently by four different groups.[8] During the last 15 years, synthesis and characterization of wide variety of 1,3-disubstituted benzo[*c*]thiophene analogs have been realized.[9] The synthesis of a novel nucleoside analog replacing a DNA base with 1,3-dithienylbenzo[*c*]thiophene has been explored as fluorescent labels.[10] The benzo[*c*]thiophene analogs are also explored as components in OLEDs[11] as well as photovoltaics.[12] Very recently, Swager and co-workers reported push–pull type benzo-[*c*]thiophenes as near-IR fluorophores.[13]

In continuation of our interest on synthesis and characterization of 1,3-diarylbenzo[*c*]thiophenes,[14] we have recently reported synthesis of benzo[*c*]thiophenes containing other heterocycles such as benzo[*b*]thiophene and 1-hexylindole.[15] We report herein our detailed study on synthesis and characterization of benzo[*c*]thiophenes incorporating benzo[*b*]heterocycles, which can be used as potential electro-optical materials.



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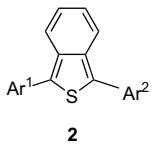

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2. Results and discussion

Benzo[*b*]heterocycles **3a–c** on Friedel–Crafts phthaloylation in the presence of anhydrous $AlCl_3$ in dry DCM at room temperature for 4 h followed by routine workup furnished keto-acids **5a–c** in

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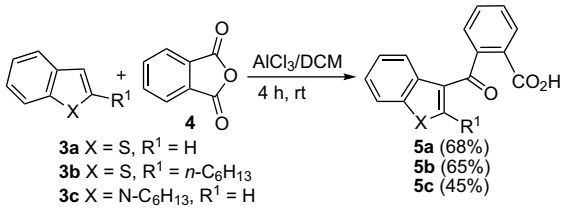
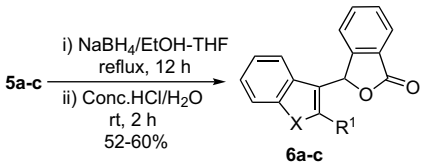
45–68% yields. Selective reduction of the ketone-carbonyl function of **5a–c** using $NaBH_4$ in THF/EtOH (2:5) at reflux for 12 h followed by acid catalyzed cyclization and subsequent column chromatographic purification led to the isolation of the respective hetero-aryl phthalides **6a–c** as colorless solid in 52–60% yields, Scheme 1.

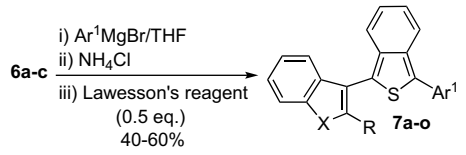




Compound	X	R^1	Yield (%)
5a/6a	S	H	54
5b/6b	S	n-C_6H_{13}	60
5c/6c	N-C_6H_{13}	H	52

Scheme 1.

Ring opening of the phthalides **6a–c** using freshly prepared aryl/hetero-aryl Grignards followed by aq NH_4Cl quenching and DCM extraction gave the corresponding keto-alcohol. The DCM solution of the resulting keto-alcohol on interaction with 0.5 equiv of Lawesson's reagent at room temperature led to the thionation of ketone-carbonyl function followed by intramolecular cyclization and subsequent aromatization to yield crude benzo[*c*]thiophenes. Column chromatographic purification of the crude products furnished benzo[*c*]thiophene analogs **7a–o** in 40–60% yields, Scheme 2.



Scheme 2.

The nature of the phthalide as well as Grignards employed and the resulting benzo[*c*]thiophenes obtained along with their yields and physical characteristics are outlined in Table 1.

As expected, reaction of hetero-aryl phthalides **6a–c** with aryl as well as hetero-aryl Grignards followed by thionation furnished expected benzo[*c*]thiophenes **7a–o** in moderate yields. The ring opening of benzo[*b*]thienyl phthalide **6a** using thienyl-2-magnesium bromide followed by thionation and column chromatographic purification gave benzo[*c*]thiophene **7a** as an orange solid in 54% yield (entry 1). Similarly, the reaction of **6a** with hexyl-substituted-2-thienylmagnesium bromides followed by interaction with Lawesson's reagent led to the isolation of corresponding benzo[*c*]thiophenes **7b** and **7c** as thick yellow liquids in 60 and 56% yields, respectively (entry 1). As expected, the interaction of **6a** with aryl Grignards followed by subsequent thionation also yielded benzo[*c*]thiophenes **7d–f** in 48–55% yields (entry 2). Under identical conditions, 1-naphthyl-benzo[*c*]thiophene **7g** could also be prepared (entry 3). The ring opening of the 2-hexyl-substituted benzo[*b*]thiophenyl phthalide **6b** with thienyl Grignards followed by thionation led to the isolation of benzo[*c*]thiophenes **7h–j** as thick orange liquids in 45–56% yields (entry 4). Reaction of 1-hexylindolyl lactone **6c** with heteroaryl/aryl Grignards followed by thionation afforded the corresponding benzo[*c*]thiophenes **7k–o** as thick orange liquids in 40–48% yields (entries 6 and 7).

Conventional Friedel–Crafts phthaloylation of 3-methylbenzo[*b*]furan **8**[16] in the presence of anhydrous $AlCl_3$ in DCM at room temperature for 4 h furnished keto-acid **9** in 45% yield. As mentioned earlier, the selective reduction of the ketone-carbonyl function of **9** using $NaBH_4$ in THF/EtOH (2:5) at reflux followed by acid catalyzed cyclization furnished 3-methylbenzo[*b*]furanyl phthalide **10** as colorless solid in 72% yield, Scheme 3. It should be noted that an attempted preparation of 3-(benzofuran-3-yl)isobenzofuran-1(3*H*)-one via Friedel–Crafts phthaloylation of parent benzo[*b*]furan followed by reductive cyclization was unsuccessful due to the highly insoluble nature of the corresponding keto-acid.

Treatment of phthalide **10** with thienyl Grignards followed by thionation using 0.5 equiv of Lawesson's reagent and subsequent column chromatographic purification led to the isolation of 1-(benzo[*b*]furan-3-yl)-3-(2-thienyl)benzo[*c*]thiophenes **11a**/**11b** as red solid/thick orange liquid in 58 and 55% yields, respectively. Similarly, the ring opening of the lactone **10** with aryl Grignards followed by thionation furnished the corresponding benzo[*c*]thiophenes **12a–d** as an orange solid in 52–62% yields, Scheme 4.

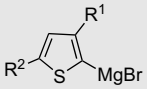
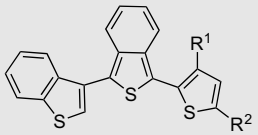
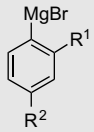
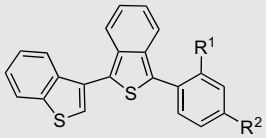
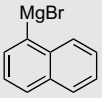
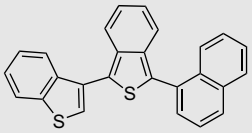
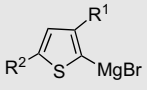
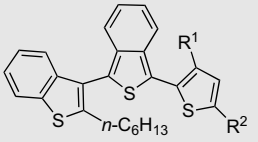
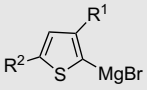
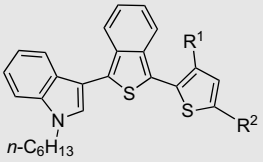
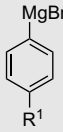
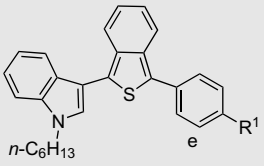
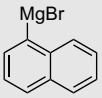
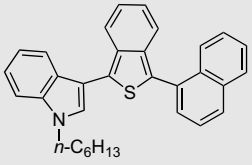
Having synthesized the benzo[*b*]heterocycle incorporated benzo[*c*]thiophenes, the next plan was to dimerize some of these compounds in a controlled manner to afford the respective dimerization products in acceptable yields. Survey of literature revealed that regio-selective oligomerization of thienyl monomers using $FeCl_3$ has been reported.[9a,17]

Recently Kita and co-workers[18] reported a synthesis of 2,2′-bithiophene derivatives involving an oxidative coupling of the corresponding alkylthiophenes using a combination of phenyliodide bis(trifluoroacetate) and $BF_3{\cdot}OEt_2$. As expected the dimerization of benzo[*c*]thiophenes **7a**,**b** and **7h**,**i** could be successfully carried out using either anhydrous $FeCl_3$ in DCM at room temperature or PIFA/$BF_3{\cdot}OEt_2$ at −78 °C to yield the respective dimers **13a**,**b** and **13c**,**d** as a dark solids in 40–60% yields, Scheme 5. To our delight, the dimerization of benzo[*c*]thiophens **7a**/**7b** proceeded selectively at the thiophene-2-position rather than the 2-position of benzo[*b*]thiophene. Interaction of indolyl benzo[*c*]thiophene **7k** as well as benzofuranyl benzo[*c*]thiophene **11b** with anhydrous $FeCl_3$ led to the formation of expected dimers **14** and **15** in 40 and 45% yields, respectively. Even with the benzo[*c*]thiophenes **7k**/**11b**, gratifyingly the expected dimerization proceeded preferentially at the thiophene-2-position rather than the 2-position of indole or benzo[*b*]furan.

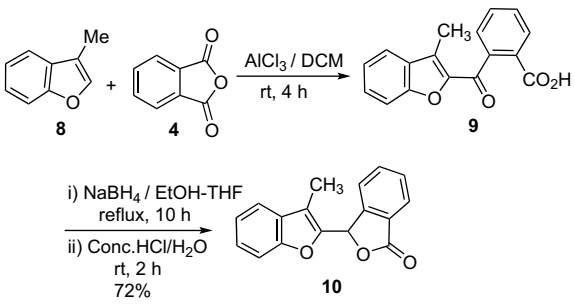
Next, the synthesis of push–pull type benzo[*c*]thiophene analog is planned. Accordingly, Vilsmeier–Haack formylation of **7a**/**7k** using DMF/$POCl_3$ in dry DCM at room temperature followed by basic workup and column chromatographic purification led to the isolation of respective monoaldehyde **16a**/**16b** as red solid/thick red liquid in 70 and 49% yields. Under similar conditions, the formylation of benzofuranyl benzo[*c*]thiophene **11a** afforded corresponding monoaldehyde **17** as brown solid in 62% yield, Scheme 6.

Having prepared the required aldehydes **16a**,**b** and **17**, preparation of benzo[*c*]thiophene based cyanovinylene is planned. As expected, condensation of the aldehyde **16a** with malononitrile/thiophene-2-acetonitrile using piperidine/*t*-BuOK as a base led to the isolation of cyanovinylenes **18a** and **18b** in 55 and 60% yields, respectively. Under identical conditions, the aldehyde **17** could also be converted into the corresponding cyanovinylenes **19a** and **19b**. As a representative case, Wittig reaction of the aldehyde **16a** with 4-*N*,*N*-dibutylaminobenzylphosphonium iodide[19] using *n*-BuLi in THF/MeOH followed by workup and column chromatographic purification gave compound **21** as a thick red liquid. The trans-

Table 1
Synthesis of benzo[*c*]thiophene analogs containing benzo[*b*]thiophene/benzo[*b*]pyrrole

Entry	Lactone	ArMgBr	Product		Yield[a] (%) mp
1	**6a**			**7a** R^1=H, R^2=H **7b** R^1=*n*-C_6H_{13}, R^2=H **7c** R^1=H, R^2=*n*-C_6H_{13}	54 (118 °C) 60 (thick liquid) 56 (thick liquid)
2	**6a**			**7d** R^1=Me, R^2=H **7e** R^1=H, R^2=Me **7f** R^1=H, R^2=OMe	50 (62 °C) 48 (thick liquid) 55 (105 °C)
3	**6a**			**7g**	40 (78 °C)
4	**6b**			**7h** R^1=H, R^2=H **7i** R^1=*n*-C_6H_{13}, R^2=H **7j** R^1=H, R^2=*n*-C_6H_{13}	45 (thick liquid) 56 (thick liquid) 50 (thick liquid)
5	**6c**			**7k** R^1=H, R^2=H **7l** R^1=H, R^2=*n*-C_6H_{13}	45 (thick liquid) 48 (thick liquid)
6	**6c**			**7m** R^1=Me **7n** R^1=OMe	42 (thick liquid) 45 (thick liquid)
7	**6c**			**7o**	40 (thick liquid)

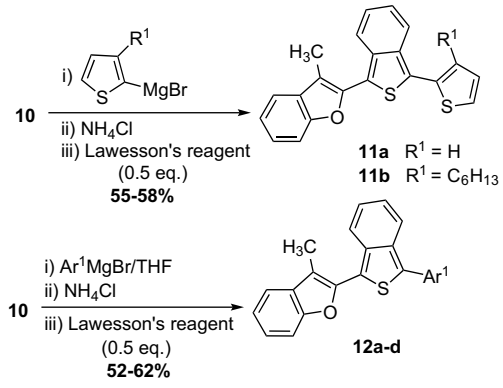
[a] Isolated yield after column chromatography.



Scheme 3.

stereochemistry of **21** was assigned on the basis ^{1}H NMR coupling constant value of the vinylic proton (Scheme 7).

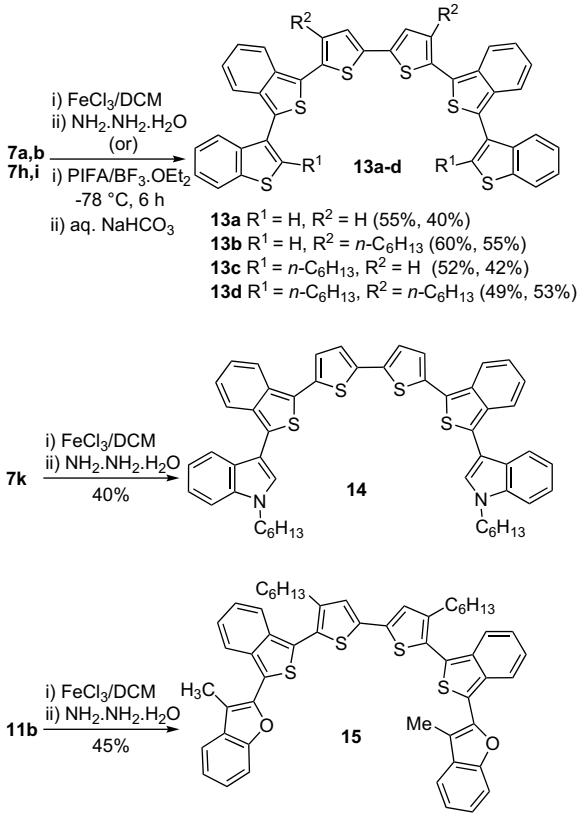
The UV–vis spectra of monomeric benzo[*c*]thiophenes exhibited a strong absorption in the region of 435–464 nm due to the π–π* electronic transition of the conjugated backbone system. Compared to parent 1,3-dithienylbenzo[*c*]thiophene **1**, replacement of thiophene ring by benzo[*b*]thiophene has increased the λ_{max} value around 12 nm (**1** to **7a**). On contrary to the 1,3-dithienylbenzo[*c*]thiophene **1**,[9a] the introduction of hexyl substituent in the case of **7a** enhanced the λ_{max} value. Replacement of benzo[*b*]thiophene unit of **7a** with 1-hexylindole has led to the enhancement of π-conjugation. However, exchange of benzo[*b*]-thiophene unit with 3-methylbenzo[*b*]furan has only slightly increased (~5 nm) the λ_{max} value (**7a** to **7k**). The presence of electron-withdrawing groups such as aldehyde/cyanovinylenes



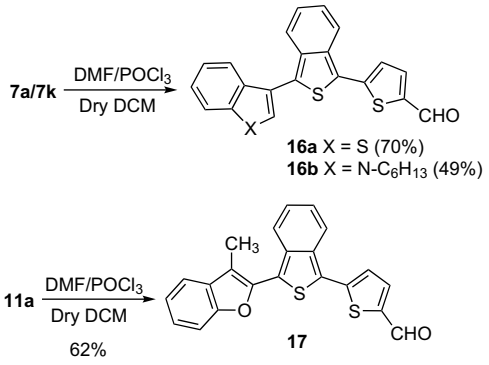
Compound	Ar^1	Yield(%)
12a	Phenyl	62
12b	*p*-Tolyl	53
12c	*p*-Anisyl	56
12d	1-Naphthyl	52

Scheme 4.

at one end of benzo[*c*]thiophenes (**16a**,**b**, **17**, **18b**, and **19**) resulted in red shift of absorption value in the range of 60–81/153–161 nm, which confirms the significant enhancement of π-electron delocalization. The dimerization of monomeric benzo[*c*]thiophenes red shifted the λ_{max} values in the range of 162–171 nm, which is more than twice as observed in the case of dimerization of parent benzo[*c*]thiophene **1**.[9a] Of course compared to dibenzoheterocycles containing benzo[*c*]thiophenes,[14e] the enhancement of λ_{max} value for the dimerization of **7a** is almost tripled. The exact absorption λ_{max} values of representative benzo[*c*]thiophenes are presented in Table 2.



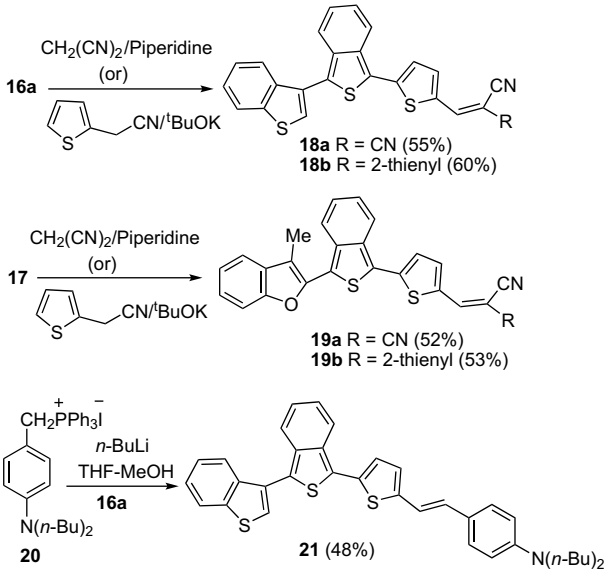
Scheme 5.



Scheme 6.

The qualitative emission data of selected benzo[*b*]heterocycles incorporated benzo[*c*]thiophenes were recorded in DCM solution and the emission values are also presented in Table 2. The monomeric benzo[*c*]thiophenes showed emission in the range of 510–567 nm. As observed in the case of absorption spectra, the emission values of these benzo[*c*]thiophenes are also red shifted with increasing π-conjugation. The presence of electron-withdrawing groups such as aldehyde/cyanovinylenes at one end of benzo[*c*]-thiophenes (**16a**,**b**, **17**, **18b**, and **19**) exhibited emission values in the range of 584–720 nm. The dimeric benzo[*c*]thiophenes (**13a**,**d**, **14**, and **15**) displayed emission values in the range of 690–730 nm. The HOMO and LUMO energy levels of benzo[*c*]thiophenes were calculated from the absorption and the onset oxidation potential. The Eg, HOMO, and LUMO values obtained for representative benzo[*c*]thiophenes are presented in Table 2. The monomeric benzo[*c*]thiophene analogs showed Eg values in the range of 2.7–2.8 eV. Introduction of electron-withdrawing aldehyde/cyanovinylene function at one end of the benzo[*c*]thiophenes has reduced band gap value ~0.4 eV/0.7 eV. The dimerization of benzo[*c*]thiophenes also reduced the Eg values around ~0.7 eV. Indeed, the dimerization has significantly enhanced the LUMO energy levels (~2.4 eV to ~3.0 eV). However, relatively HOMO energy levels were only slightly (~5.2 eV to ~5.1 eV) reduced.

The electrochemical properties of representative benzo[*c*]thiophenes are summarized in Table 3. The anodic peak potential of benzo[*c*]thiophene **7a** was observed at +0.60 V at scan rate of 100 mV S^{-1}. The anodic peak potential of **7a** was less compared to



Scheme 7.

Table 2
Summary of the physical measurements for some selected benzo[*c*]thiophenes

Comp.	λ_{max}[a] (nm)	λ_{emiss}[b] (nm)	E_g[c] (eV)	E_{ox}^{onset} (eV)	HOMO[d] (eV)	LUMO[e] (eV)
1	433	532	2.66	0.64	5.08	2.42
7a	445	515	2.78	0.54	4.98	2.20
7b	455	533	2.72	0.84	5.28	2.56
7h	455	521	2.72	0.63	5.07	2.35
7i	464	539	2.67	0.55	4.99	2.32
7k	458	549	2.70	0.72	5.16	2.46
11a	449	542	2.76	0.60	5.04	2.28
11b	459	567	2.70	0.71	5.15	2.45
13a	615	691	2.01	0.54	4.98	2.97
13d	635	730	1.95	0.64	5.08	3.13
14	620	725	2.00	0.71	5.15	3.15
15	625	720	1.98	0.58	5.02	3.04
16a	505	584	2.45	0.79	5.23	2.78
16b	525	620	2.36	0.65	5.09	2.73
17	530	615	2.34	0.69	5.13	2.79
18b	598	720	2.07	1.00	5.44	3.37
19a	610	705	2.03	0.95	5.39	3.36

[a] Measured in dilute dichloromethane solution.
[b] Excited at absorption maxima.
[c] Estimated from the absorption (E_g=1240/λ_{max}).
[d] Calculated using the empirical equation: HOMO=(4.44+E_{ox}^{onset}).
[e] Calculated from: LUMO=HOMO-Eg.

Table 3
Redox behavior of some selected benzo[*c*]thiophenes

Compound	$^1E_{pa}$[a] (V)	$^1E_{pc}$[b] (V)	$^1\Delta E_p$[c] (mV)	$^2E_{pa}$[a] (V)
7a	+0.60	+0.47	130[d]	
7b	+0.89			+1.21
7c	+0.80			+0.94
7h	+0.66			+0.93
7i	+0.59			
7k	+0.79	+0.42	370[e]	
7l	+0.53			
11a	+0.65	+0.39	260[e]	
11b	+0.76			

[a] $^1E_{pa}$ and $^2E_{pa}$ are the anodic peak potentials of the first and second redox process, respectively.
[b] $^1E_{pc}$ is the cathodic peak potentials of the first redox process.
[c] $^1\Delta E_p$ is the differences between the cathodic and anodic peak potentials of the first redox process.
[d] Quasireversible.
[e] Irreversible.

parent 1,3-dithienylbenzo[*c*]thiophene (+0.71).[8] The introduction of hexyl substituents at the α/β-position of benzo[*c*]thiophene **7a** significantly diminished its electro-oxidation behavior, which is in agreement with our earlier observation.[9a] Surprisingly, the simultaneous introduction of two hexyl units on benzo[*c*]thiophene **7a** has only a minimum influence on its electro-oxidation potential. Replacement of benzo[*b*]thineyl unit of **7a** with 1-hexylindole/3-methylfuran increased its anodic peak potential value and consequently the electro-oxidation behavior has been slightly reduced.

3. Conclusions

In summary, the synthesis of a variety of benzo[*c*]thiophene analogs possessing heterocycles such as benzo[*b*]thiophene/1-hexylindole/benzo[*b*]furan has been achieved in reasonable yields. The highly soluble nature of these benzo[*c*]thiophenes may make them suitable for transistor applications through spin-coating techniques. Since, the emission values of dimeric benzo[*c*]thiophenes as well as benzo[*c*]thiophenes possessing electron-withdrawing groups are in the range of 700–730 nm, they may be regarded as potential NIR contrast agents for biomedical applications.[13] Additionally, the higher-lying HOMO energy levels of these benzo[*c*]thiophenes (~5.0 to 5.3 eV) may find them as suitable candidates for application as hole-transporting materials in double-layer OLEDs.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Bruker-300 spectrometer. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. Elemental analyses were carried out on a Perkin–Elmer series II 2400 (IIT Madras) instrument. All UV–vis spectra were recorded in CH_2Cl_2 solution. The emission spectra were recorded on Perkin–Elmer LS-45 spectrophotometer. The cyclic-voltammogram of 10^{-3} M solution of benzo[*c*]thiophenes was carried out on a CHI 600C electrochemical analyzer. All the measurements were carried out under oxygen free condition using three electrode cells in which glassy carbon electrode was working electrode, saturated Ag/AgCl electrode was reference electrode, and platinum wire was used as an auxiliary electrode. Tetrabutylammonium hexafluoro phosphate ($TBAPF_6$) was used as supporting electrolyte and its concentration was 10^{-1} M.

4.2. A representative procedure for the preparation of lactone from heterocycle 3a (procedure A)

*4.2.1. 3-(Benzo[b]thiophen-3-yl)isobenzofuran-1(3H)-one (**6a**)*

To a stirred suspension of phthalic anhydride (6.07 g, 41.01 mmol) in dry DCM (150 mL), powdered anhydrous $AlCl_3$ (6.47 g, 48.50 mmol) was added in two portions, resulted in yellow solution which was then cooled to 0 °C. The benzo[*b*]thiophene **3a** (5 g, 37.31 mmol) in DCM (20 mL) was added dropwise to the above solution at 0 °C and stirred for 4 h at room temperature. The reaction mixture was quenched with ice water containing HCl and extracted with DCM (2×30 mL). Evaporation of the solvent gave crude keto-acid, which was dissolved in THF/EtOH (2:5). To this, $NaBH_4$ (7.08 g, 186.56 mmol) was added in small portions and refluxed for 10 h. The reaction mixture was poured into water and concd HCl was added dropwise under stirring (pH=1–2). It was then extracted with EtOAc and dried (Na_2SO_4). Solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (10% EA/Hexane) to give the title compound **6a** [5.35 g, 54% (two steps)].

*4.2.2. 3-(Benzo[b]thiophen-3-yl)isobenzofuran-1(3H)-one (**6a**)*

Colorless solid; mp 114 °C [Found: C, 72.3; H, 3.8; S, 12.2. $C_{16}H_{10}O_2S$ requires: C, 72.16; H, 3.78; S, 12.04%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 1759, 1595, 1500, 745 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.03 (1H, d, *J* 7.5 Hz, ArH), 7.88 (1H, t, *J* 4.5 Hz, ArH), 7.74–7.68 (2H, m, ArH), 7.63 (1H, t, *J* 7.5 Hz, ArH), 7.52 (1H, t, *J* 7.5 Hz, ArH), 7.41–7.38 (2H, m, ArH), 7.35 (1H, s, ArH), 6.82 (1H, s, ArH); δ_C (75.6 MHz, $CDCl_3$) 170.2, 148.1, 140.8, 137.2, 134.4, 131.1, 128.7, 126.7, 126.3, 125.9, 125.1, 124.7, 123.1, 122.1, 77.7; MS (EI): *m*/*z* (%)=266 [M]$^+$.

*4.2.3. 3-(2-Hexylbenzo[b]thiophen-3-yl)isobenzofuran-1(3H)-one (**6b**)*

Following the above-mentioned procedure (**A**), lactone **6b** (4.81 g, 60%) was obtained using 2-hexyl benzo[*b*]thiophene **3b** (5 g, 22.93 mmol), phthalic anhydride (3.73 g, 25.22 mmol), $AlCl_3$ (3.98 g, 29.81 mmol), and $NaBH_4$ (4.35 g, 114.67 mmol) as a colorless solid. Mp 115 °C; [Found: C, 75.5; H, 6.2; S, 8.9. $C_{22}H_{22}O_2S$ requires: C, 75.39; H, 6.33; S, 9.15%.] ν_{max} (KBr) 2867, 1755, 1585, 1500, 741 cm^{-1}; R_f (10% EA/Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.04 (1H, d, *J* 6.3 Hz, ArH), 7.71 (1H, d, *J* 7.8 Hz, ArH), 7.62–7.57 (2H, m, ArH), 7.25–7.16 (2H, m, ArH), 7.06 (1H, t, *J* 7.5 Hz, ArH), 6.80–6.78 (2H, m, ArH), 2.94 (2H, t, *J* 7.5 Hz, CH_2), 1.74 (2H, t, *J* 7.05 Hz, CH_2), 1.38–1.29 (6H, m, CH_2), 0.91 (3H, t, *J* 7.8 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$); 170.6, 149.0, 148.6, 138.2, 137.8, 134.6, 129.6, 126.5, 125.7, 124.4, 123.9,

123.7, 122.6, 122.3, 121.4, 76.9, 32.1, 31.5, 28.9, 28.8, 22.5, 14.1; MS (EI): m/z (%)=350 $[M]^+$.

*4.2.4. 3-(1-Hexyl-1H-indol-3-yl)isobenzofuran-1(3H)-one (**6c**)*

Following the above-mentioned procedure (**A**), lactone **6c** (4.30 g, 52%) was obtained using 1-hexyl-1*H*-indole **3c** (5 g, 24.87 mmol), phthalic anhydride (4.04 g, 27.36 mmol), $AlCl_3$ (4.31 g, 32.33 mmol), and $NaBH_4$ (4.72 g, 124.37 mmol) as a thick yellow liquid. [Found: C, 79.4; H, 7.1; N, 4.0. $C_{22}H_{23}NO_2$ requires: C, 79.25; H, 6.95; N, 4.20%.] R_f (10% EA/Hexane) 0.58; ν_{max} (KBr) 2811, 1759, 1605, 1500, 755, 685 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.91 (1H, d, *J* 7.5 Hz, ArH), 7.67–7.46 (2H, m, ArH), 7.42 (1H, d, *J* 7.5 Hz, ArH), 7.32 (1H, d, *J* 8.4 Hz, ArH), 7.17 (1H, t, *J* 8.7 Hz, ArH), 7.13–6.99 (2H, m, ArH), 7.02 (1H, d, *J* 6.9 Hz, ArH), 6.76 (1H, s, ArH), 4.05 (2H, t, *J* 7.05 Hz, CH_2), 1.81–1.78 (2H, m, CH_2), 1.35–1.25 (6H, m, CH_2), 0.86 (3H, t, *J* 6.1 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 170.6, 149.4, 136.8, 134.1, 129.3, 128.2, 126.8, 126.4, 125.5, 123.1, 122.3, 120.0, 119.2, 109.9, 109.5, 77.7, 46.6, 31.3, 30.1, 26.6, 22.5, 13.9; MS (EI): m/z (%)=333 $[M]^+$.

4.3. A representative procedure for the preparation of benzo[c]thiophene (7a) from lactone (6a) (procedure B)

To a solution of lactone **6a** (0.75 g, 2.81 mmol) in anhydrous THF (25 mL) was added 2-thienylmagnesium bromide [prepared from 2-bromothiophene (0.68 g, 4.22 mmol) and magnesium turnings (0.12 g, 5.0 mmol)] at 0 °C under N_2. The reaction mixture was slowly raised to room temperature and stirred for 4 h. It was then quenched with aq NH_4Cl solution (30 mL), extracted with DCM (2×20 mL), and dried (Na_2SO_4). The DCM solution was then stirred with Lawesson's reagent (0.56 g, 1.40 mmol) at room temperature for 4 h. Solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (100% Hexane) to give the title compound **7a** (0.52 g, 54%) as an orange solid.

*4.3.1. 3-(1-(Thiophen-2-yl)benzo[c]thiophen-3-yl)-benzo[b]thiophene (**7a**)*

Mp 118 °C; [Found: C, 69.1; H, 3.5; S, 27.8. $C_{20}H_{12}S_3$ requires: C, 68.93; H, 3.47; S, 27.60%.] R_f (100% Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 8.73 (1H, d, *J* 7.8 Hz, ArH), 7.95 (1H, d, *J* 7.8 Hz, ArH), 7.80–7.76 (2H, m, ArH), 7.71 (1H, d, *J* 4.2 Hz, ArH), 7.58–7.53 (2H, m, ArH), 7.47 (1H, t, *J* 7.8 Hz, ArH), 7.35 (1H, d, *J* 4.8 Hz, ArH), 7.31–7.18 (1H, m, ArH), 7.10–7.04 (2H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 140.8, 140.2, 139.8, 136.8, 133.9, 127.9, 127.1, 125.4, 125.3, 125.0, 124.9, 124.3, 123.8, 122.9, 122.7, 122.3, 122.0, 120.9, 119.8, 119.8; MS (EI): m/z (%)=348 $[M]^+$.

*4.3.2. 1-(Benzo[b]thiophen-3-yl)-3-(3-hexylthiophen-2-yl)-benzo[c]thiophene (**7b**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7b** (0.72 g, 60%) was obtained using the lactone **6a** (0.75 g, 2.81 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.04 g, 4.22 mmol) and Mg (0.12 g, 5.0 mmol)], and Lawesson's reagent (0.56 g, 1.40 mmol) as a thick yellow liquid. [Found: C, 72.3; H, 5.7; S, 22.1. $C_{26}H_{24}S_3$ requires: C, 72.18; H, 5.59; S, 22.23%.] R_f (100% Hexane) 0.92; δ_H (300 MHz, $CDCl_3$) 7.97–7.92 (2H, m, ArH), 7.64–7.56 (3H, m, ArH), 7.43–7.37 (3H, m, ArH), 7.11–7.01 (3H, m, ArH), 2.68 (2H, t, *J* 7.8 Hz, CH_2), 1.62–1.55 (2H, m, CH_2), 1.28–1.17 (6H, m, CH_2), 0.81 (3H, t, *J* 6.9 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 142.4, 140.3, 138.3, 137.3, 136.2, 129.3, 129.2, 128.0, 127.6, 126.2, 125.9, 125.3, 124.9, 124.6, 124.2, 123.9, 123.4, 122.9, 121.6, 121.5, 31.6, 30.9, 29.2, 29.1, 22.6, 14.1; MS (EI): m/z (%)=432 $[M]^+$.

*4.3.3. 1-(Benzo[b]thiophen-3-yl)-3-(5-hexylthiophen-2-yl)-benzo[c]thiophene (**7c**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7c** (0.67 g, 56%) was obtained using the lactone **6a** (0.75 g, 2.81 mmol), 5-hexyl-2-thienyl magnesium bromide [prepared from 2-bromo-5-hexylthiophene (1.04 g, 4.22 mmol) and Mg (0.12 g, 5.00 mmol)], and Lawesson's reagent (0.56 g, 1.40 mmol) as a thick yellow liquid. [Found: C, 72.3; H, 5.7; S, 22.1. $C_{26}H_{24}S_3$ requires: C, 72.18; H, 5.59; S, 22.23%.] R_f (100% Hexane) 0.92; δ_H (300 MHz, $CDCl_3$) 8.0–7.91 (3H, m, ArH), 7.59 (1H, s, ArH), 7.54 (1H, d, *J* 9.0 Hz, ArH), 7.42–7.38 (2H, m, ArH), 7.18 (1H, d, *J* 3.6 Hz, ArH), 7.11 (1H, t, *J* 6.2 Hz, ArH), 7.02 (1H, t, *J* 6.4 Hz, ArH), 6.81 (1H, d, *J* 3.6 Hz, ArH), 2.86 (2H, t, *J* 7.6 Hz, CH_2), 1.79–7.72 (2H, m, CH_2), 1.44–1.30 (6H, m, CH_2), 0.9 (3H, t, *J* 7.1 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 146.6, 140.3, 138.3, 137.0, 134.5, 133.2, 129.1, 127.9, 126.1, 125.4, 125.3, 124.8, 124.6, 124.4, 124.1, 123.4, 122.9, 121.7, 121.6, 31.6, 30.9, 28.8, 22.6, 14.1; MS (EI): m/z (%)=432 $[M]^+$.

*4.3.4. 3-(1-o-Tolylbenzo[c]thiophen-3-yl)benzo[b]thiophene (**7d**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7d** (0.50 g, 50%) was obtained using the lactone **6a** (0.75 g, 2.81 mmol), *o*-tolylmagnesium bromide [prepared from *o*-bromotoluene (0.71 g, 4.23 mmol) and Mg (0.12 g, 5.01 mmol)], and Lawesson's reagent (0.56 g, 1.40 mmol) as a yellow solid. Mp 62 °C; [Found: C, 77.6; H, 4.7; S, 18.1. $C_{23}H_{16}S_2$ requires: C, 77.49; H, 4.52; S, 17.99%.] R_f (100% Hexane) 0.85; δ_H (300 MHz, $CDCl_3$) 7.99–7.91 (2H, m, ArH), 7.60 (1H, s, ArH), 7.58 (1H, d, *J* 3.7 Hz, ArH), 7.46 (1H, d, *J* 6.9 Hz, ArH), 7.42–7.28 (6H, m, ArH), 7.03–7.0 (2H, m, ArH), 2.33 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 140.4, 138.4, 138.1, 136.2, 136.0, 133.1, 132.7, 132.2, 130.6, 129.4, 128.5, 126.3, 125.9, 125.8, 124.8, 124.5, 123.7, 123.4, 122.9, 121.6, 121.5, 20.7; MS (EI): m/z (%)=356 $[M]^+$.

*4.3.5. 3-(1-p-Tolylbenzo[c]thiophen-3-yl)benzo[b]thiophene (**7e**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7e** (0.48 g, 48%) was obtained using the lactone **6a** (0.75 g, 2.81 mmol), *p*-tolylmagnesium bromide [prepared from *p*-bromotoluene (0.71 g, 4.23 mmol) and Mg (0.12 g, 5.01 mmol)], and Lawesson's reagent (0.56 g, 1.40 mmol) as a thick orange liquid. [Found: C, 77.3; H, 4.6; S, 18.2. $C_{23}H_{16}S_3$ requires: C, 77.49; H, 4.52; S, 17.99%.] R_f (100% Hexane) 0.85; δ_H (300 MHz, $CDCl_3$) 7.98–7.86 (2H, m, ArH), 7.62–7.56 (2H, m, ArH), 7.47 (2H, d, *J* 7.8 Hz, ArH), 7.41 (1H, t, *J* 3.6 Hz, ArH), 7.32–7.21 (4H, m, ArH), 7.11–7.01 (2H, m, ArH), 2.37 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 140.3, 137.5, 137.0, 136.7, 133.1, 132.7, 131.3, 129.8, 129.4, 129.1, 126.8, 125.9, 124.8, 124.6, 124.1, 123.8, 123.4, 122.9, 121.7, 121.2, 21.1; MS (EI): m/z (%)=356 $[M]^+$.

*4.3.6. 1-(Benzo[b]thiophen-3-yl)-3-(4-methoxylphenyl)-benzo[c]thiophene (**7f**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7f** (0.57 g, 55%) was obtained using the lactone **6a** (0.75 g, 2.81 mmol), *p*-anisylmagnesium bromide [prepared from *p*-bromoanisole (0.78 g, 4.23 mmol) and Mg (0.12 g, 5.03 mmol)], and Lawesson's reagent (0.56 g, 1.40 mmol) as a yellow solid. Mp 105 °C; [Found: C, 74.4; H, 4.4; S, 17.1. $C_{23}H_{16}OS_2$ requires: C, 74.16; H, 4.33; S, 17.22%.] R_f (100% Hexane) 0.80; δ_H (300 MHz, $CDCl_3$) 7.87–7.81 (2H, m, ArH), 7.70 (1H, d, *J* 8.4 Hz, ArH), 7.53–7.45 (3H, m, ArH), 7.35 (2H, d, *J* 8.7 Hz, ArH), 7.37–7.30 (1H, m, ArH), 6.99–6.91 (3H, m, ArH), 6.83 (1H, d, *J* 8.7 Hz, ArH), 3.75 (3H, s, OCH_3); δ_C (75.6 MHz, $CDCl_3$) 159.4, 158.7, 140.3, 138.4, 137.0, 134.4, 133.5, 130.5, 129.4, 127.7, 126.7, 125.8, 124.8, 124.5, 124.1, 123.8, 123.4, 122.9, 121.7, 121.2, 114.6, 114.2, 55.4; MS (EI): m/z (%)=372 $[M]^+$.

*4.3.7. 3-(1-(Naphthalen-1-yl)benzo[c]thiophen-3-yl)-benzo[b]thiophene (**7g**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7g** (0.44 g, 40%) was obtained using the lactone **6a** (0.75 g, 2.81 mmol), 1-napthylmagnesium bromide [prepared from 1-bromnapthalene (0.87 g, 4.23 mmol) and Mg (0.12 g, 5.03 mmol)], and Lawesson's reagent (0.56 g, 1.40 mmol) as a yellow solid. Mp

78 °C; [Found: C, 79.7; H, 4.2; S, 16.1. $C_{26}H_{16}S_2$ requires: C, 79.55; H, 4.11; S, 16.34%.] R_f (100% Hexane) 0.85; δ_H (300 MHz, $CDCl_3$) 8.37 (1H, d, *J* 6.9 Hz, ArH), 8.02–7.77 (5H, m, ArH), 7.66–7.41 (7H, m, ArH), 7.22–7.05 (3H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 140.4, 138.4, 136.9, 136.2, 134.3, 133.9, 132.8, 131.6, 130.9, 129.3, 128.7, 128.4, 126.5, 126.3, 126.2, 126.1, 126.0, 125.4, 124.9, 124.6, 123.9, 123.8, 123.5, 122.9, 121.8, 121.6; MS (EI): *m*/*z* (%)=392 $[M]^+$.

4.3.8. 1-(2-Hexylbenzo[b]thiophen-3-yl)-3-(thiophen-3-yl)-benzo[c]thiophene (**7h**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7h** (0.41 g, 45%) was obtained using the lactone **6b** (0.75 g, 2.14 mmol), 2-thienylmagnesium bromide [prepared from 2-bromothiophene (0.52 g, 3.21 mmol) and Mg (0.09 g, 3.82 mmol)], and Lawesson's reagent (0.43 g, 1.07 mmol) as a thick orange liquid; [Found: C, 72.0; H, 5.6; S, 22.4. $C_{26}H_{24}S_3$ requires: C, 72.18; H, 5.59; S, 22.23%.] R_f (100% Hexane) 0.92; δ_H (300 MHz, $CDCl_3$) 7.72–7.60 (3H, m, ArH), 7.36 (1H, d, *J* 3.8 Hz, ArH), 7.32–7.15 (3H, m, ArH), 7.09–6.99 (2H, m, ArH), 6.93–6.87 (1H, m, ArH), 6.83–6.78 (1H, m, ArH), 2.89 (2H, t, *J* 7.8 Hz, CH_2), 1.69–1.60 (2H, m, CH_2), 1.31–1.08 (6H, m, CH_2) 0.71 (3H, t, *J* 5.5 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 146.9, 139.3, 138.2, 134.0, 127.8, 125.4, 125.2, 124.6, 124.6, 124.2, 123.8, 123.5, 122.9, 122.5, 122.2, 122.2, 121.9, 120.6, 120.2, 119.7, 31.9, 31.6, 29.8, 29.0, 22.6, 14.1; MS (EI): *m*/*z* (%)=432 $[M]^+$.

4.3.9. 2-Hexyl-3-(1-(3-hexylthiophen-2-yl)benzo[c]-thiophen-3-yl)benzo[b]thiophene (**7i**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7i** (0.61 g, 56%) was obtained using the lactone **6b** (0.75 g, 2.14 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (0.79 g, 3.21 mmol) and Mg (0.09 g, 3.85 mmol)], and Lawesson's reagent (0.43 g, 1.07 mmol) as a thick orange liquid. [Found: C, 74.5; H, 7.1; S, 18.4. $C_{32}H_{36}S_3$ requires: C, 74.37; H, 7.02; S, 18.61%.] R_f (100% Hexane) 0.92; δ_H (300 MHz, $CDCl_3$) 7.75–7.69 (2H, m, ArH), 7.38 (1H, d, *J* 7.2 Hz, ArH), 7.30–7.20 (4H, m, ArH), 7.05–7.0 (2H, m, ArH), 6.72 (1H, d, *J* 6.8 Hz, ArH), 2.91–2.84 (4H, m, CH_2), 1.80–1.71 (4H, m, CH_2), 1.47–1.26 (12H, m, CH_2), 0.82–0.73 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 146.6, 139.7, 138.3, 134.2, 128.0, 125.5, 125.3, 124.8, 124.6, 124.2, 123.7, 123.4, 122.9, 122.6, 122.5, 122.3, 122.0, 120.7, 119.6, 31.9, 31.5, 31.4, 30.8, 29.4, 29.1, 28.9, 22.5, 22.4, 14.2; MS (EI): *m*/*z* (%)=516 $[M]^+$.

4.3.10. 2-Hexyl-3-(1-(5-hexylthiophen-2-yl)benzo[c]-thiophen-3-yl)benzo[b]thiophene (**7j**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7j** (0.55 g, 50%) was obtained using the lactone **6b** (0.75 g, 2.14 mmol), 5-hexyl-2-thienyl magnesium bromide [prepared from 2-bromo-5-hexylthiophene (0.79 g, 3.21 mmol) and Mg (0.09 g, 3.85 mmol)], and Lawesson's reagent (0.43 g, 1.07 mmol) as a thick orange liquid. [Found: C, 74.6; H, 7.1; S, 18.5. $C_{32}H_{36}S_3$ requires: C, 74.37; H, 7.02; S, 18.61%.] R_f (100% Hexane) 0.92; δ_H (300 MHz, $CDCl_3$) 7.74–7.65 (2H, m, ArH), 7.41 (1H, d, *J* 7.4 Hz, ArH), 7.30–7.18 (4H, m, ArH), 7.06–6.99 (2H, m, ArH), 6.84 (1H, d, *J* 6.5 Hz, ArH), 2.90–2.86 (4H, m, CH_2), 1.82–1.66 (4H, m, CH_2), 1.44–1.26 (12H, m, CH_2), 0.84–0.70 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 146.6, 139.5, 138.3, 134.1, 127.9, 125.5, 125.3, 124.7, 124.6, 124.2, 123.7, 123.4, 122.9, 122.7, 122.4, 122.3, 122.1, 120.6, 120.3, 119.6, 31.9, 31.6, 31.4, 30.8, 29.4, 29.2, 28.9, 22.5, 22.4, 14.3; MS (EI): *m*/*z* (%)=516 $[M]^+$.

4.3.11. 1-Hexyl-3-(1-thiophen-2-yl)benzo[c]thiophen-3-yl-1H-indole (**7k**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7k** (0.42 g, 45%) was obtained using the lactone **6c** (0.75 g, 2.25 mmol), 2-thienylmagnesium bromide [prepared from 2-bromothiophene (0.55 g, 3.37 mmol) and Mg (0.10 g, 4.04 mmol)], and Lawesson's reagent (0.45 g, 1.12 mmol) as a thick orange liquid. [Found: C, 75.3; H, 5.9; N, 3.5; S, 15.6. $C_{26}H_{25}NS_2$ requires: C, 75.14; H, 6.06; N, 3.37; S, 15.43%.] R_f (100% Hexane) 0.85; δ_H (300 MHz, $CDCl_3$) 7.89–7.81 (2H, m, ArH), 7.62 (1H, d, *J* 8.7 Hz, ArH), 7.30–7.09 (6H, m, ArH), 7.03–6.99 (2H, m, ArH), 6. 91 (1H, t, *J* 7.5 Hz, ArH), 4.02 (2H, t, *J* 7.2 Hz, NCH_2), 1.79–1.74 (2H, m, CH_2), 1.35–1.15 (6H, m, CH_2), 0.77 (3H, t, *J* 6.2 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 135.5, 134.4, 133.9, 126.9, 126.6, 126.1, 125.9, 125.5, 124.7, 123.6, 123.6, 123.2, 122.1, 121.3, 121.1, 120.2, 119.3, 119.1, 108.7, 107.3, 45.6, 30.3, 29.1, 25.6, 21.5, 12.9; MS (EI): *m*/*z* (%)=415 $[M]^+$.

4.3.12. 1-Hexyl-3-(1-(5-hexylthiophen-2-yl)benzo[c]-thiophen-3-yl)-1H-indole (**7l**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7l** (0.53 g, 48%) was obtained using the lactone **6c** (0.75 g, 2.25 mmol), 5-hexyl-2-thienyl magnesium bromide [prepared from 2-bromo-5-hexylthiophene (0.83 g, 3.37 mmol) and Mg (0.10 g, 4.04 mmol)], and Lawesson's reagent (0.45 g, 1.12 mmol) as a thick orange liquid. [Found: C, 77.1; H, 7.3; N, 2.9; S, 13.1. $C_{32}H_{37}NS_2$ requires: C, 76.90; H, 7.46; N, 2.80; S, 12.83%.] R_f (100% Hexane) 0.85; δ_H (300 MHz, $CDCl_3$) 7.94 (1H, d, *J* 9.0 Hz, ArH), 7.91 (1H, d, *J* 7.8 Hz, ArH), 7.70 (1H, d, *J* 8.7 Hz, ArH), 7.41–7.38 (2H, m, ArH), 7.31–7.21 (1H, m, ArH), 7.19–7.17 (1H, m, ArH), 7.14 (1H, d, *J* 3.3 Hz, ArH), 7.12–7.07 (1H, m, ArH), 7.02–6.98 (1H, m, ArH), 6.79 (1H, d, *J* 3.6 Hz, ArH), 4.16 (2H, t, *J* 7.2 Hz, NCH_2), 2.84 (2H, t, *J* 7.6 Hz, CH_2), 1.93–1.84 (2H, m, CH_2), 1.78–1.68 (2H, m, CH_2), 1.42–1.29 (12H, m, CH_2), 0.85–0.92 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 145.7, 136.5, 135.4, 134.6, 133.9, 127.2, 127.1, 125.2, 124.7, 124.5, 124.3, 123.1, 122.4, 122.2, 121.5, 120.4, 120.1, 109.7, 108.5, 46.6, 31.6, 31.4, 30.3, 30.2, 28.9, 26.7, 22.6, 22.5, 14.1, 14.0; MS (EI): *m*/*z* (%)=499 $[M]^+$.

4.3.13. 1-Hexyl-3-(1-p-tolylbenzo[c]thiophen-3-yl)-1H-indole (**7m**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7m** (0.40 g, 42%) was obtained using the lactone **6c** (0.75 g, 2.25 mmol), *p*-tolylmagnesium bromide [prepared from *p*-bromotoluene (0.57 g, 3.37 mmol) and Mg (0.10 g, 4.02 mmol)], and Lawesson's reagent (0.45 g, 1.12 mmol) as a thick orange liquid. [Found: C, 82.5; H, 6.7; N, 3.4; S, 7.7. $C_{29}H_{29}NS$ requires: C, 82.22; H, 6.90; N, 3.31; S, 7.57%.] R_f (100% Hexane) 0.65; δ_H (300 MHz, $CDCl_3$) 7.92 (1H, d, *J* 7.8 Hz, ArH), 7.83 (1H, d, *J* 8.1 Hz, ArH), 7.72 (1H, d, *J* 8.4 Hz, ArH), 7.61 (2H, t, *J* 7.5 Hz, ArH), 7.42–7.28 (4H, m, ArH), 7.24–7.19 (1H, m, ArH), 7.11–7.03 (3H, m, ArH), 4.20 (2H, t, *J* 6.7 Hz, NCH_2), 2.42 (3H, s, CH_3), 1.91–1.82 (2H, m, CH_2), 1.55–1.25 (6H, m, CH_2), 0.87 (3H, t, *J* 7.51 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 136.9, 136.5, 135.5, 131.8, 129.7, 129.0, 127.8, 127.0, 122.9, 122.3, 122.1, 121.2, 121.05, 120.92, 120.45, 120.0, 119.1, 109.3, 100.8, 46.6, 31.4, 30.2, 26.7, 22.5, 21.2, 14.0; MS (EI): *m*/*z* (%)=423 $[M]^+$.

4.3.14. 1-Hexyl-3-(1-(4-methoxyphenyl)benzo[c]-thiophen-3-yl)-1H-indole (**7n**)

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7n** (0.44 g, 45%) was obtained using the lactone **6c** (0.75 g, 2.25 mmol), *p*-anisylmagnesium bromide [prepared from *p*-bromoanisole (0.62 g, 3.37 mmol) and Mg (0.10 g, 4.04 mmol)], and Lawesson's reagent (0.45 g, 1.12 mmol) as a thick orange liquid. [Found: C, 79.5; H, 6.7; N, 3.0; S, 7.4. $C_{29}H_{29}NOS$ requires: C, 79.23; H, 6.65; N, 3.19; S, 7.29%.] R_f (100% Hexane) 0.75; δ_H (300 MHz, $CDCl_3$) 7.92 (1H, d, *J* 7.8 Hz, ArH), 7.80–7.72 (2H, m, ArH), 7.63 (2H, d, *J* 8.7 Hz, ArH), 7.48–7.39 (3H, m, ArH), 7.29–7.26 (1H, m, ArH), 7.19–7.00 (3H, m, ArH), 6.94 (1H, d, *J* 9.0 Hz, ArH), 4.17 (2H, t, *J* 7.1 Hz, NCH_2), 3.86 (3H, s, OCH_3), 1.92–1.88 (2H, m, CH_2), 1.38–1.30 (6H, m, CH_2), 0.88 (3H, t, *J* 6.9 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 159.0, 136.6, 135.5, 134.6, 133.5, 130.4, 127.7, 127.3, 126.6, 123.9, 122.4, 122.1, 121.0, 120.4, 120.0, 114.5, 114.2, 113.5, 109.7, 108.8, 55.4, 46.6, 31.5, 30.2, 26.7, 22.6, 14.0; MS (EI): *m*/*z* (%)=439 $[M]^+$.

*4.3.15. 1-Hexyl-3-(1-(napthalen-1-yl)benzo[c]-thiophen-3-yl)-1H-indole (**7o**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **7o** (0.41 g, 40%) was obtained using the lactone **6c** (0.75 g, 2.25 mmol), 1-napthylmagnesium bromide [prepared from 1-bromonapthalene (0.69 g, 3.37 mmol) and Mg (0.10 g, 4.01 mmol)], and Lawesson's reagent (0.45 g, 1.12 mmol) as a thick orange liquid. [Found: C, 83.8; H, 6.5; N, 3.0; S, 7.1. $C_{32}H_{29}NS$ requires: C, 83.62; H, 6.36; N, 3.05; S, 6.98%.] R_f (100% Hexane) 0.75; δ_H (300 MHz, $CDCl_3$) 7.93–7.88 (2H, m, ArH), 7.83–7.80 (2H, m, ArH), 7.71 (1H, d, *J* 8.7 Hz, ArH), 7.59 (1H, d, *J* 6.6 Hz, ArH), 7.48–7.40 (2H, m, ArH), 7.37–7.31 (3H, m, ArH), 7.23–7.15 (2H, m, ArH), 7.11 (1H, s, ArH), 6.92–6.83 (2H, m, ArH), 4.08 (2H, t, *J* 7.5 Hz, NCH_2), 1.81 (2H, t, *J* 6.7 Hz, CH_2), 1.29–1.16 (6H, m, CH_2), 0.82 (3H, t, *J* 7.5 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 134.7, 134.2, 132.3, 131.6, 130.5, 129.2, 127.4, 126.5, 126.4, 126.1, 125.9, 124.8, 124.7, 124.1, 123.9, 123.7, 123.1, 121.3, 120.5, 120.0, 119.6, 119.3, 118.1, 117.7, 107.4, 106.3, 44.3, 29.1, 27.8, 24.4, 20.2, 11.6; MS (EI): *m*/*z* (%)=459 $[M]^+$.

4.4. 3-(3-Methylbenzofuran-2-yl)isobenzofuran-1-(3*H*)-one (10)

Following the above-mentioned procedure (**A**), lactone **10** (7.2 g, 72%) was obtained using 3-methylbenzofuran **8** (5 g, 37.87 mmol), phthalic anhydride (6.16 g, 41.66 mmol), $AlCl_3$ (6.57 g, 49.24 mmol), and $NaBH_4$ (7.19 g, 189.39 mmol) as a colorless solid. Mp 146 °C; [Found: C, 77.4; H, 4.7. $C_{17}H_{12}O_3$ requires: C, 77.26; H, 4.58%.] R_f (10% EA/Hexane) 0.70; ν_{max} (KBr) 1759, 1600, 1379, 1174, cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.99 (1H, d, *J* 7.5 Hz, ArH), 7.67 (1H, t, *J* 7.5 Hz, ArH), 7.60 (1H, d, *J* 7.5 Hz, ArH), 7.52 (1H, d, *J* 7.5 Hz, ArH), 7.37 (1H, d, *J* 7.5 Hz, ArH), 7.29–7.28 (2H, m, ArH), 7.26–7.23 (1H, m, ArH), 6.64 (1H, s, ArH), 2.30 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 170.1, 154.5, 146.7, 145.1, 134.4, 129.8, 129.3, 126.2, 125.8, 125.5, 122.9, 122.7, 119.8, 116.9, 111.4, 74.6, 7.9; MS (EI): *m*/*z* (%)=264 $[M]^+$.

*4.4.1. 3-Methyl-2-(1-(thiophen-2-yl)benzo[c]-thiophen-3-yl)benzofuran (**11a**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **11a** (0.56 g, 58%) was obtained using the lactone **10** (0.75 g, 2.84 mmol), 2-thienylmagnesium bromide [prepared from 2-bromothiophene (0.69 g, 4.26 mmol) and Mg (0.12 g, 5.07 mmol)], and Lawesson's reagent (0.57 g, 1.42 mmol) as a red solid. Mp 86 °C [Found: C, 73.0; H, 3.9; S, 18.3. $C_{21}H_{14}OS_2$ requires: C, 72.80; H, 4.07; S, 18.51%.] R_f (100% Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 8.09–8.11 (1H, m, ArH), 7.86 (1H, m, ArH), 7.42–7.38 (2H, m, ArH), 7.25–7.06 (4H, m, ArH), 6.92–6.83 (3H, m, ArH), 2.38 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 154.3, 146.9, 136.8, 135.6, 134.7, 130.6, 127.9, 125.7, 125.1, 124.8, 124.5, 123.1, 122.7, 121.2, 121.1, 119.2, 112.6, 110.8, 9.7; MS (EI): *m*/*z* (%)=346 $[M]^+$.

*4.4.2. 2-(1-(3-Hexylthiophen-2-yl)benzo[c]thiophen-3-yl)-3-methylbenzofuran (**11b**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **11b** (0.67 g, 55%) was obtained using the lactone **10** (0.75 g, 2.84 mmol), 3-hexyl-2-thienylmagnesium bromide [prepared from 2-bromo-3-hexylthiophene (1.04 g, 4.26 mmol) and Mg (0.12 g, 5.07 mmol)], and Lawesson's reagent (0.57 g, 1.42 mmol) as a thick orange liquid. [Found: C, 75.1; H, 6.3; S, 14.7. $C_{27}H_{26}OS_2$ requires: C, 75.31; H, 6.09; S, 14.89%.] R_f (100% Hexane) 0.92; δ_H (300 MHz, $CDCl_3$) 8.09–8.06 (1H, m, ArH), 7.44–7.41 (1H, m, ArH), 7.25–7.15 (2H, m, ArH), 7.12–7.05 (2H, m, ArH), 6.82–6.77 (4H, m, ArH), 2.52–2.47 (2H, m, ArH), 2.37 (3H, s, CH_3), 1.52–1.46 (2H, m, CH_2), 1.24–1.14 (6H, m, CH_2), 0.76 (3H, t, *J* 6.8 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 154.8, 145.1, 137.1, 135.9, 131.2, 129.5, 129.4, 128.4, 126.3, 125.1, 124.8, 124.6, 124.5, 122.8, 121.5, 120.7, 119.9, 119.3, 113.9, 110.9, 31.8, 30.6, 30.4, 29.2, 22.7, 14.2, 9.1; MS (EI): *m*/*z* (%)=430 $[M]^+$.

*4.4.3. 3-Methyl-2-(1-phenylbenzo[c]thiophen-3-yl)-benzofuran (**12a**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **12a** (0.60 g, 62%) was obtained using the lactone **10** (0.75 g, 2.84 mmol), phenylmagnesium chloride (0.93 g, 6.85 mmol), and Lawesson's reagent (0.57 g, 1.42 mmol) as an orange solid. Mp 114 °C; [Found: C, 81.3; H, 4.9; S, 9.5. $C_{23}H_{16}OS$ requires: C, 81.14; H, 4.74; S, 9.42%.] R_f (100% Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 8.20 (1H, d, *J* 7.5 Hz, ArH), 7.82 (1H, d, *J* 7.8 Hz, ArH), 7.68 (2H, d, *J* 7.8 Hz, ArH), 7.55–7.45 (4H, m, ArH), 7.38 (1H, d, *J* 7.5 Hz, ArH), 7.33–7.26 (2H, m, ArH), 7.20–7.09 (2H, m, ArH), 2.48 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 154.3, 147.2, 137.0, 135.9, 134.7, 133.9, 130.7, 129.3, 129.1, 127.8, 124.7, 124.4, 123.1, 122.6, 122.0, 120.9, 119.2, 112.3, 110.9, 9.7; MS (EI): *m*/*z* (%)=340 $[M]^+$.

*4.4.4. 3-Methyl-2-(1-p-tolylbenzo[c]hiophen-3-yl)-benzofuran (**12b**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **12b** (0.53 g, 53%) was obtained using the lactone **10** (0.75 g, 2.84 mmol), *p*-tolylmagnesium bromide [prepared from *p*-bromotoluene (0.72 g, 4.26 mmol) and Mg (0.12 g, 5.07 mmol)], and Lawesson's reagent (0.57 g, 1.42 mmol) as a orange solid. Mp 90 °C; [Found: C, 81.5; H, 5.3; S, 9.3. $C_{24}H_{18}OS$ requires: C, 81.32; H, 5.12; S, 9.05%.] R_f (100% Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 8.10 (1H, d, *J* 7.8 Hz, ArH), 7.71 (1H, d, *J* 7.5 Hz, ArH), 7.50–7.42 (4H, m, ArH), 7.36 (2H, d, *J* 7.8 Hz, ArH), 7.21–7.18 (2H, m, ArH), 7.13–7.08 (2H, m, ArH), 2.39 (3H, s, CH_3), 2.32 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 154.3, 138.3, 137.8, 137.0, 136.7, 136.3, 134.5, 131.1, 129.8, 129.4, 129.2, 126.8, 124.7, 124.5, 124.4, 123.0, 122.6, 121.0, 119.1, 112.2, 110.9, 21.3, 9.7; MS (EI): *m*/*z* (%)=354 $[M]^+$.

*4.4.5. 2-(1-(4-Methoxyphenyl)benzo[c]thiophen-3-yl)-3-methylbenzofuran (**12c**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **12c** (0.59 g, 56%) was obtained using the lactone **10** (0.75 g, 2.84 mmol), *p*-anisylmagnesium bromide [prepared from *p*-bromoanisole (0.79 g, 4.26 mmol) and Mg (0.12 g, 5.07 mmol)], and Lawesson's reagent (0.57 g, 1.42 mmol) as an orange solid. Mp 88 °C; [Found: C, 77.9; H, 4.7; S, 8.9. $C_{24}H_{18}O_2S$ requires: C, 77.81; H, 4.90; S, 8.66%.] R_f (100% Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 7.99 (1H, d, *J* 7.5 Hz, ArH), 7.72 (1H, d, *J* 7.8 Hz, ArH), 7.62 (1H, d, *J* 7.5 Hz, ArH), 7.42–7.36 (2H, m, ArH), 7.26 (1H, d, *J* 7.2 Hz, ArH), 7.16–7.14 (2H, m, ArH), 6.92–6.89 (3H, m, ArH), 6.66 (1H, d, *J* 7.8 Hz, ArH), 3.75 (3H, s, OCH_3), 2.54 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 158.8, 158.7, 154.3, 132.2, 130.7, 130.5, 126.1, 125.4, 125.1, 124.6, 124.1, 123.8, 122.6, 121.2, 120.2, 119.6, 118.9, 115.7, 114.6, 110.7, 55.4, 8.8; MS (EI): *m*/*z* (%)=370 $[M]^+$.

*4.4.6. 3-Methyl-2-(1-(naphthalen-1-yl)benzo[c]-thiophene-3-yl)benzofuran (**12d**)*

Following the above-mentioned procedure (**B**), benzo[*c*]thiophene **12d** (0.57 g, 52%) was obtained using the lactone **10** (0.75 g, 2.84 mmol), 1-napthyllmagnesium bromide [prepared from 1-bromonaphthalene (0.87 g, 4.26 mmol) and Mg (0.12 g, 5.06 mmol)], and Lawesson's reagent (0.57 g, 1.42 mmol) as an orange solid. Mp 128 °C; [Found: C, 83.3; H, 4.5; S, 8.1. $C_{27}H_{18}OS$ requires: C, 83.05; H, 4.65; S, 8.21%.] R_f (100% Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 8.36–8.32 (1H, m, ArH), 8.19 (1H, d, *J* 7.8 Hz, ArH), 7.92–7.80 (4H, m, ArH), 7.55–7.45 (5H, m, ArH), 7.27–7.22 (2H, m, ArH), 7.09–6.99 (2H, m, ArH), 2.59 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 154.4, 145.1, 138.8, 134.3, 130.8, 130.7, 129.9, 128.8, 128.6, 127.9, 127.2, 126.6, 126.3, 126.2, 125.8, 125.6, 125.5, 125.3, 124.3, 123.3, 123.2, 122.8, 121.2, 119.7, 119.1, 110.9, 8.8; MS (EI): *m*/*z* (%)=390 $[M]^+$.

4.5. A representative procedure for the preparation of compound 13a (procedure C)

To a stirred solution of **7a** (0.3 g, 0.86 mmol) in dry DCM (20 mL) was added $FeCl_3$ (0.27 g, 1.72 mmol) under N_2 atmosphere. The reaction mixture was stirred for 12 h at room temperature and quenched with dilute solution of $N_2H_4 \cdot H_2O$. Then, it was filtered through Celite, extracted with DCM and dried (Na_2SO_4). Evaporation of solvent followed by column chromatographic purification (Silica gel, hexane) afforded **13a** as black solid (0.17 g, 55%).

Using PIFA/$BF_3 \cdot OEt_2$. $BF_3 \cdot Et_2O$ (0.12 g, 0.86 mmol) and PIFA (0.37 g, 0.86 mmol) were added sequentially to a stirred solution of **7a** (0.3 g, 0.86 mmol) in CH_2Cl_2 (10 ml) at −78 °C under nitrogen atmosphere. The reaction mixture was stirred at the same temperature for 6 h. Aqueous workup with saturated $NaHCO_3$ (10 mL) at 0 °C followed by column chromatographic purification gave the dimer **13a** (0.13 g, 40%).

*4.5.1. 3-(1-(5-(5-(1-(Benzo[b]thiophen-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)benzo[b]thiophene (**13a**)*

Mp 130 °C; [Found: C, 69.4; H, 3. 3; S, 27.5. $C_{40}H_{22}S_6$ requires: C, 69.13; H, 3.19; S, 27.68%.] R_f (5% EA/Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.07 (2H, d, *J* 8.4 Hz, ArH), 7.98–7.94 (4H, m, ArH), 7.64 (2H, s, ArH), 7.59 (2H, d, *J* 8.7 Hz, ArH), 7.44–7.39 (4H, m, ArH), 7.33–7.32 (2H, m, ArH), 7.28–7.17 (4H, m, ArH), 7.10–7.05 (2H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 140.3, 138.2, 137.2, 136.7, 135.0, 134.8, 126.8, 126.4, 125.9, 125.4, 124.9, 124.6, 124.4, 124.3, 123.5, 123.3, 122.9, 121.9, 121.7, 121.4; MS (EI): *m*/*z* (%)=694 $[M]^+$.

*4.5.2. 3-(1-(5-(5-(1-(Benzo[b]thiophen-3-yl)benzo[c]thiophen-3-yl)-4-hexylthiophen-2-yl)-3-hexylthiophen-2-yl)benzo[c]-thiophen-3-yl)benzo[b]thiophene (**13b**)*

Following the above-mentioned procedure (**C**), dimer **13b** was obtained using the monomer **7b** (0.3 g, 0.69 mmol) and $FeCl_3$ (0.22 g, 1.36 mmol) as a dark solid (0.17 g, 60%). Mp 180 °C; [Found: C, 72.6; H, 5.5; S, 22.0. $C_{52}H_{46}S_6$ requires: C, 72.34; H, 5.37; S, 22.29%.] R_f (5% EA/Hexane) 0.80; δ_H (300 MHz, $CDCl_3$) 7.98–7.90 (3H, m, ArH), 7.77–7.74 (3H, m, ArH), 7.62–7.57 (3H, m, ArH), 7.41–7.34 (4H, m, ArH), 7.20–7.05 (7H, m, ArH), 2.69 (4H, t, *J* 7.5 Hz, CH_2), 1.65–1.54 (4H, m, CH_2), 1.24–1.17 (12H, m, CH_2), 0.82 (6H, t, *J* 6.5 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 143.1, 140.3, 138.3, 137.3, 137.2, 136.3, 129.1, 127.8, 127.3, 126.3, 126.0, 124.9, 124.8, 124.6, 124.4, 124.1, 123.8, 122.9, 121.6, 121.5, 31.6, 30.8, 29.4, 29.1, 22.6, 14.1; MS (EI): *m*/*z* (%)=862 $[M]^+$.

Using PIFA/$BF_3 \cdot OEt_2$. Following the above-mentioned procedure (**C**), dimer **13b** was obtained using the monomer **7b** (0.3 g, 0.69 mmol), $BF_3 \cdot Et_2O$ (0.10 g, 0.69 mmol) and PIFA (0.29 g, 0.69 mmol) as a dark solid (0.16 g, 55%).

*4.5.3. 2-Hexyl-3-(1-(5-(5-(1-(2-hexylbenzo[b]thiophen-3-yl)-benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)-benzo[c]thiophen-3-yl)benzo[b]thiophene (**13c**)*

Following the above-mentioned procedure (**C**), compound **13c** was obtained using the compound **7h** (0.3 g, 0.86 mmol) and $FeCl_3$ (0.22 g, 1.36 mmol) as black solid (0.15 g, 52%). Mp 192 °C; [Found: C, 72.7; H, 5. 5; S, 22.0. $C_{52}H_{46}S_6$ requires: C, 74.51; H, 5.37; S, 22.29%.] R_f (5% EA/Hexane) 0.90; δ_H (300 MHz, $CDCl_3$) 7.78–7.70 (4H, m, ArH), 7.42 (2H, d, *J* 6.9 Hz, ArH), 7.35–7.25 (6H, m, ArH), 7.95–7.05 (4H, m, ArH), 6.87 (2H, t, *J* 7.5 Hz, ArH), 6.80–6.75 (2H, m, ArH), 2.72–2.68 (4H, m, CH_2), 1.52–1.48 (4H, m, CH_2), 1.27–1.21 (12H, m, CH_2), 0.79 (6H, t, *J* 6.9 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 143.1, 140.4, 138.3, 137.3, 137.2, 136.3, 129.0, 127.9, 127.4, 126.1, 126.0, 125.1, 124.9, 124.7, 124.5, 124.1, 123.4, 123.0, 121.6, 121.5, 31.6, 30.8, 29.4, 29.1, 22.6, 14.1. MS (EI): *m*/*z* (%)=862 $[M]^+$.

Using PIFA/$BF_3 \cdot OEt_2$. Following the above-mentioned procedure (**C**), compound **13c** was obtained using the compound **7h** (0.3 g, 0.86 mmol), $BF_3 \cdot Et_2O$ (0.10 g, 0.86 mmol) and PIFA (0.27 g, 0.86 mmol) as a dark solid (0.12 g, 42%).

*4.5.4. Hexyl-3-(1-(3-hexyl-5-(4-hexyl-5-(1-(2-hexylbenzo[b]-thiophen-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]thiophen-3-yl)benzo[b]thiophene (**13d**)*

Following the above-mentioned procedure (**C**), dimer **13d** was obtained using the monomer **7i** (0.3 g, 0.58 mmol) and $FeCl_3$ (0.18 g, 1.11 mmol) as a thick red liquid (0.14 g, 49%). [Found: C, 74.8; H, 7.0; S, 18.4. $C_{64}H_{70}S_6$ requires: C, 74.51; H, 6.84; S, 18.65%.] R_f (Hexane) 0.40; δ_H (300 MHz, $CDCl_3$) 7.70 (2H, d, *J* 7.8 Hz, ArH), 7.42–7.37 (2H, m, ArH), 7.28–7.10 (8H, m, ArH), 7.06–6.88 (6H, m, ArH), 2.89 (4H, t, *J* 7.0 Hz, ArH), 2.72 (4H, t, *J* 7.8 Hz, CH_2), 1.72–1.68 (8H, m, CH_2), 1.29–1.20 (24H, m, CH_2), 0.89–0.80 (12H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 159.6, 147.0, 142.9, 140.7, 137.9, 137.2, 137.1, 136.8, 129.4, 126.8, 125.9, 125.7, 124.4, 124.1, 123.7, 122.8, 122.1, 121.6, 120.6, 119.8, 31.9, 31.6, 31.5, 30.9, 29.4, 29.1, 28.8, 22.6, 22.5, 14.1; MS (EI): *m*/*z* (%)=1030 $[M]^+$.

Using PIFA/$BF_3 \cdot OEt_2$. Following the above-mentioned procedure (**C**), dimer **13d** was obtained using the monomer **7e** (0.3 g, 0.58 mmol), $BF_3 \cdot Et_2O$ (0.08 g, 0.58 mmol) and PIFA (0.25 g, 0.58 mmol) as a thick red liquid (0.13 g, 45%).

*4.5.5. 1-Hexyl-3-(1-(5-(5-(1-(1-hexyl-1H-indol-3-yl)benzo[c]-thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]-thiophen-3-yl)-1H-indole (**14**)*

Following the above-mentioned procedure (**C**), dimer **14** was obtained using the monomer **7k** (0.3 g, 0.72 mmol) and $FeCl_3$ (0.23 g, 1.41 mmol) as thick red liquid (0.11 g, 40%). [Found: C, 75.1; H, 6.0; N, 3.5; S, 15.3. $C_{52}H_{48}N_2S_4$ requires: C, 75.32; H, 5.83; N, 3.38; S, 15.47%.] R_f (5% EA/Hexane) 0.50; δ_H (300 MHz, $CDCl_3$) 7.97–7.94 (2H, m, ArH), 7.88–7.85 (2H, m, ArH), 7.67 (2H, d, *J* 7.5 Hz, ArH), 7.36–7.30 (4H, m, ArH), 7.24–7.11 (6H, m, ArH), 6.98–6.93 (2H, m, ArH), 6.89–6.81 (4H, m, ArH), 4.04 (4H, t, *J* 7.6 Hz, NCH_2), 1.78–1.72 (4H, m, CH_2), 1.26–1.15 (12H, m, CH_2), 0.80–0.70 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 136.1, 135.6, 134.8, 134.1, 133.6, 130.9, 126.7, 126.2, 125.7, 125.2, 124.9, 123.8, 123.6, 122.4, 121.6, 121.3, 120.4, 119.4, 111.6, 107.6, 44.8, 31.1, 29.2, 26.1, 21.8, 13.4; MS (EI): *m*/*z* (%)=828 $[M]^+$.

*4.5.6. 3-Methyl-2-(1-(5-(5-(1-(3-methylbenzofuran-3-yl)benzo[c]-thiophen-3-yl)thiophen-2-yl)thiophen-2-yl)benzo[c]-thiophen-3-yl)benzofuran (**15**)*

Following the above-mentioned procedure (**C**), dimer **15** was obtained using the monomer **11b** (0.3 g, 0.69 mmol) and $FeCl_3$ (0.22 g, 1.39 mmol) as thick red liquid (0.13 g, 45%). [Found: C, 75.1; H, 6.0; S, 15.2. $C_{54}H_{50}O_2S_4$ requires: C, 75.48; H, 5.87; S, 14.93%.] R_f (10% EA/Hexane) 0.70; δ_H (300 MHz, $CDCl_3$) 8.10–7.95 (4H, m, ArH), 7.41–7.32 (4H, m, ArH), 7.18–7.08 (4H, m, ArH), 6.92–6.81 (6H, m, ArH), 2.62–2.51 (4H, m, CH_2), 2.39 (6H, s, CH_3), 1.56–1.48 (4H, m, CH_2), 1.26–1.12 (12H, m, CH_2), 0.81–0.73 (6H, m, CH_3); δ_C (75.6 MHz, $CDCl_3$) 155.1, 146.2, 138.2, 136.2, 130.3, 128.9, 128.5, 126.5, 126.1, 125.4, 125.2, 124.6, 124.1, 123.1, 122.4, 121.8, 121.2, 120.1, 114.4, 111.2, 31.9, 30.6, 30.5, 29.3, 22.9, 14.4, 9.2; MS (EI): *m*/*z* (%)=858 $[M]^+$.

4.6. A representative procedure for the preparation of compound 16a (procedure D)

$POCl_3$ (0.66 g, 4.31 mmol) was slowly added to a mixture of dry DCM (30 mL) and DMF (0.31 g, 4.31 mmol) at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature until a pale yellow color (Vilsmeier reagent) formed. Then it was added to a solution benzo[*c*]thiophene **7a** (1.0 g, 2.87 mmol) in dry DCM (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for additional 10 h. Then the solvent was completely removed and treated with aqueous NaOH (5 g in

100 mL water) at room temperature for 15 min. The crude product was then extracted into DCM (50 mL) dried (Na_2SO_4) and solvent was removed. The column chromatographic purification of the crude product on neutral alumina (eluent: 10% EA in hexane) afforded product **16a** (0.75 g, 70%) as a red solid.

4.6.1. 5-(1-(Benzo[b]thiophen-3-yl)benzo[c]thiophen-3-yl)thiophene-2-carbaldehyde (**16a**)

Mp 148 °C; [Found: C, 67.2; H, 3.4; S, 25.2. $C_{21}H_{12}OS_3$ requires: C, 66.99; H, 3.21; S, 25.55%.] R_f (10% EA/Hexane) 0.70; ν_{max} (KBr) 1660, 1510, 1500, 730 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.92 (1H, s, CHO), 8.11 (1H, d, *J* 9.0 Hz, ArH), 7.98–7.91 (2H, m, ArH), 7.78 (1H, d, *J* 3.9 Hz, ArH), 7.68 (1H, s, ArH), 7.62 (1H, d, *J* 9.0 Hz, ArH), 7.48–7.42 (3H, m, ArH), 7.31–7.28 (1H, m, ArH), 7.15–7.10 (1H m, ArH); δ_C (75.6 MHz, $CDCl_3$) 182.3, 146.1, 141.8, 140.3, 137.9, 137.5, 135.9, 130.0, 128.3, 127.2, 126.4, 125.2, 125.1, 124.8, 124.5, 123.1, 123.0, 122.3, 121.1; MS (EI): *m*/*z* (%)=376 $[M]^+$.

4.6.2. 5-(1-(1-Hexyl-1H-indol-3-yl)benzo[c]thiophen-3-yl)thiophene-2-carbaldehyde (**16b**)

Yield: 0.26 g (49%); thick red liquid; [Found: C, 73.4; H, 5.8; N, 3.3; S, 14.2. $C_{27}H_{25}NOS_2$ requires: C, 73.10; H, 5.68; N, 3.16; S, 14.46%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2890, 1680, 1530, 770 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.86 (1H, s, CHO), 8.07 (1H, d, *J* 9.0 Hz, ArH), 7.93 (1H, d, *J* 7.8 Hz, ArH), 7.80 (1H, d, *J* 8.7 Hz, ArH), 7.71 (1H, d, *J* 6.9 Hz, ArH), 7.47 (1H, s, ArH), 7.42–7.39 (2H, m, ArH), 7.33 (1H, d, *J* 8.1 Hz, ArH), 7.29 (1H, d, *J* 6.1 Hz, ArH), 7.26–7.21 (1H, m, ArH), 7.10–7.07 (1H, m, ArH), 4.19 (2H, t, *J* 7.2 Hz, NCH_2), 1.96–1.86 (2H, m, CH_2), 1.36–1.25 (6H, m, CH_2), 0.88 (3H, t, *J* 6.8 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 182.1, 147.2, 140.7, 137.3, 136.6, 136.2, 135.8, 127.7, 126.7, 126.5, 124.2, 123.7, 122.8, 122.6, 121.2, 120.6, 120.2, 110.0, 108.1, 46.8, 31.4, 30.2, 26.7, 22.5, 14.0; MS (EI): *m*/*z* (%)=443 $[M]^+$.

4.6.3. 5-(1-(3-Methylbenzofuran-2-yl)benzo[c]thiophen-3-yl)thiophene-2-carbaldehyde (**17**)

Yield: 0.67 g (62%); brown solid; mp 190 °C; [Found: C, 70.8; H, 3.9; S, 16.9. $C_{22}H_{14}O_2S_2$ requires: C, 70.56; H, 3.77; S, 17.13%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2851, 1672, 1490, 745 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.91 (1H, s, CHO), 8.32–8.30 (1H, m, ArH), 8.08–8.06 (1H, m, ArH), 7.74–7.76 (1H, m, ArH), 7.56–7.46 (3H, m, ArH), 7.34–7.28 (4H, m, ArH), 2.52 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 182.3, 154.4, 146.4, 145.7, 141.9, 136.9, 135.7, 130.3, 126.6, 126.4, 125.3, 125.2, 123.7, 122.9, 120.8, 119.5, 114.2, 110.9, 9.9; MS (EI): *m*/*z* (%)=374 $[M]^+$.

4.6.4. 2-((5-(1-(Benzo[b]thiophen-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)methylene)malononitrile (**18a**)

To a solution of aldehyde **16a** (0.1 g, 0.26 mmol) and malononitrile (0.02 g, 0.30 mmol) in dry ethanol (10 mL), piperidine (one drop) was added. The above reaction mixture was stirred at room temperature for 6 h. The solid obtained was filtered, washed with ethanol, and dried to give **18a** (0.06 g, 55%). Black solid; mp 230 °C; [Found: C, 67.6; H, 2.9; N, 6.7; S, 22.8. $C_{24}H_{12}N_2S_3$ requires: C, 67.90; H, 2.85; N, 6.60; S, 22.66%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2210, 1500, 730 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.12 (1H, d, *J* 9.0 Hz, ArH), 8.0–7.93 (2H, m, ArH), 7.79 (1H, s, ArH), 7.74 (1H, d, *J* 4.2 Hz, ArH), 7.72 (1H, s, ArH), 7.67 (1H, d, *J* 7.8 Hz, ArH), 7.52 (1H, d, *J* 4.2 Hz, ArH), 7.48–7.45 (2H, m, ArH), 7.21–7.16 (2H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 153.3, 149.6, 148.6, 145.4, 142.3, 140.4, 139.7, 137.7, 136.5, 133.5, 130.2, 127.6, 127.5, 125.3, 125.2, 124.9, 123.0, 122.6, 121.2, 117.5, 117.1; MS (EI): *m*/*z* (%)=424 (67).

4.6.5. 3-(5-(1-(Benzo[b]thiophen-3-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)-2-(thiophen-2-yl)acrylonitrile (**18b**)

To a solution of **16a** (0.1 g, 0.26 mmol) in dry ethanol (10 mL), thiophene-2-acetonitrile (0.04 g, 0.34 mmol), and *t*-BuOK (0.03 g, 0.31 mmol) was added. The reaction mixture was then stirred at room temperature for 6 h. The solid obtained was filtered and washed with ethanol and dried to give **18b** (0.07 g, 60%). Black solid; mp 177 °C; [Found: C, 67.1; H, 3.4; N, 3.1; S, 26.3. $C_{27}H_{15}NS_4$ requires: C, 67.33; H, 3.14; N, 2.91; S, 22.63%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2215, 1490, 730 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.09 (1H, d, *J* 8.4 Hz, ArH), 7.98–7.91 (2H, m, ArH), 7.65–7.58 (3H, m, ArH), 7.50–7.41 (4H, m, ArH), 7.34 (1H, s, ArH), 7.26 (2H, d, *J* 6.6 Hz, ArH), 7.18–7.07 (2H, m, ArH); δ_C (75.6 MHz, $CDCl_3$) 140.9, 140.3, 139.1, 138.0, 137.3, 136.6, 135.3, 133.4, 131.6, 128.5, 128.2, 126.8, 126.7, 126.1, 125.9, 125.8, 125.2, 125.1, 124.7, 124.5, 123.2, 122.9, 122.1, 121.4, 117.2, 102.0; MS (EI): *m*/*z* (%)=481 $[M]^+$.

4.6.6. 2-((5-(1-(3-Methylbenzofuran-2-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)methylene)malononitrile (**19a**)

To a solution of **17** (0.1 g, 0.26 mmol) and malononitrile (0.02 g, 0.34 mmol) in dry ethanol piperidine (one drop) was added. The reaction mixture was then stirred at room temperature for 6 h. The solid obtained was filtered, washed with ethanol, and dried to give **19a** (0.06 g, 52%). Black solid; mp 226 °C; [Found: C, 71.3; H, 3.4; N, 6.5; S, 15.0. $C_{25}H_{14}ON_2S_2$ requires: C, 71.07; H, 3.34; N, 6.63; S, 15.18%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2910, 2230, 1520, 720 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.41 (1H, d, *J* 8.7 Hz, ArH), 8.07 (1H, d, *J* 8.1 Hz, ArH), 7.77 (1H, s, ArH), 7.74–7.73 (1H, m, ArH), 7.61–7.53 (3H, m, ArH), 7.39–7.27 (4H, m, ArH), 2.58 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 152.3, 149.1, 147.6, 144.1, 142.3, 140.1, 138.7, 137.7, 136.5, 134.5, 131.2, 127.6, 126.5, 125.3, 125.2, 123.9, 123.0, 122.1, 120.4, 117.5, 117.1, 10.1; MS (EI): *m*/*z* (%)=422 $[M]^+$.

4.6.7. 3-(5-(1-(3-Methylbenzofuran-2-yl)benzo[c]thiophen-3-yl)thiophen-2-yl)-2-(thiophen-2-yl)acrylonitrile (**19b**)

To a solution of **17** (0.1 g, 0.26 mmol) and thiophene-2-acetonitrile (0.04 g, 0.34 mmol) in dry ethanol (10 mL), *t*-BuOK (0.03 g, 0.34 mmol) was added. The reaction mixture was then stirred at room temperature for 6 h. The solid obtained was filtered washed with ethanol and dried to give black solid **19b** (0.07 g, 53%). Mp 165 °C; [Found: C, 70.4; H, 3.4; N, 2.7; S, 20.2. $C_{28}H_{17}NOS_3$ requires C, 70.12; H, 3.57; N, 2.92; S, 20.06%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2900, 2220, 1495, 745 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.27 (1H, d, *J* 7.8 Hz, ArH), 8.01 (1H, d, *J* 7.8 Hz, ArH), 7.53–7.45 (3H, m, ArH), 7.38–7.24 (8H, m, ArH), 7.04 (1H, d, *J* 3.9 Hz ArH), 2.49 (3H, s, CH_3); δ_C (75.6 MHz, $CDCl_3$) 154.3, 146.7, 140.6, 139.1, 136.9, 136.7, 135.2, 133.4, 131.5, 130.5, 128.2, 127.3, 126.7, 126.2, 125.8, 125.4, 125.2, 124.9, 123.8, 123.6, 122.8, 121.1, 119.3, 117.2, 113.6, 110.9, 102.1, 9.9; MS (EI): *m*/*z* (%)=479 $[M]^+$.

4.6.8. 4-((E)-2-(5-(1-(Benzo[b]thiophen-3-yl)benzo-[c]thiophen-3-yl)thiophen-2-yl)vinyl)-N,N-dibutylbenzeneamine (**21**)

The monoaldehyde **16a** (0.2 g, 0.47 mmol) was reacted with 4-*N*,*N*-dibutylaminobenzylphosphonium iodide **20** (0.064 g, 0.52 mmol) in the presence of BuLi (0.064 g, 0.57 mmol) in dry THF/MeOH (20 mL; 3:1). The reaction mixture was then stirred at room temperature for 6 h, extracted into DCM (50 mL), and dried (Na_2SO_4). Solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography to give compound **21** (0.06 g, 48%) as thick red liquid. [Found: C, 74.6; H, 6.0; N, 2.3; S, 16.9. $C_{36}H_{35}NS_3$ requires C, 74.82; H, 6.10; N, 2.42; S, 16.65%.] R_f (10% EA/Hexane) 0.62; ν_{max} (KBr) 2851, 1610, 1330, 1210 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.07 (1H, d, *J* 9.0 Hz, ArH), 7.97–7.92 (2H, m, ArH), 7.61 (1H, s, ArH), 7.56 (1H, d, *J* 8.7 Hz, ArH), 7.54–7.40 (2H, m, ArH), 7.34 (2H, d, *J* 8.4 Hz, ArH), 7.25 (1H, d, *J* 5.1 Hz, ArH), 7.15 (1H, t, *J* 8.7 Hz, ArH), 7.07–6.98 (3H, m, ArH), 6.98 (1H, d, *J* 15.9 Hz, ArH), 6.46 (2H, d, *J* 8.4 Hz, ArH), 3.28 (4H, t, *J* 7.5 Hz, NCH_2), 1.63–1.53 (4H, m, CH_2), 1.42–1.32 (4H, m, CH_2), 0.96 (6H, t, *J* 7.3 Hz, CH_3); δ_C (75.6 MHz, $CDCl_3$) 147.9, 144.3, 140.3, 138.3, 137.2, 134.5, 133.1, 129.1, 129.0, 127.9,

127.7, 126.2, 125.7, 125.4, 124.9, 124.6, 124.1, 123.4, 122.9, 121.8, 121.6, 116.6, 111.7, 50.80, 29.52, 20.37, 14.0; MS (EI): m/z (%)=577 $[M]^+$

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