Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Synthesis and host-guest complexation, photophysical and electrochemical studies on novel thiophenophanes

Perumal Rajakumar[a]; Kathiresan Visalakshi[a]
[a] Department of Organic Chemistry, University of Madras, Chennai, India

To cite this Article Rajakumar, Perumal and Visalakshi, Kathiresan(2009) 'Synthesis and host-guest complexation, photophysical and electrochemical studies on novel thiophenophanes', Supramolecular Chemistry, 21: 8, 674 — 680
To link to this Article: DOI: 10.1080/10610270802709535
URL: http://dx.doi.org/10.1080/10610270802709535

Supramolecular Chemistry
Vol. 21, No. 8, December 2009, 674–680

Taylor & Francis
Taylor & Francis Group

Synthesis and host–guest complexation, photophysical and electrochemical studies on novel thiophenophanes

Perumal Rajakumar* and Kathiresan Visalakshi

Department of Organic Chemistry, University of Madras, Chennai, India

(*Received 2 November 2008; final version received 8 December 2008*)

Synthesis of thiophene-based cyclophanes called thiophenophanes is described. The photophysical and electrochemical properties of thiophenophanes synthesised reveal that they show permanent fluorescence-sensing property, and the cyclic voltammogram reflects the ease with which the electron on the sulphur atom can be removed. Complexation studies of the thiophenophanes with TCNQ reveal the formation of 1:1 complex.

Keywords: chiral thiophenophanes; Suzuki coupling; supramolecules; host–guest complexation

Introduction

Cyclophanes bearing five-membered hetero-aromatic ring(s) are well documented (*1*) and have attracted greater attention. They exhibit unique structural features and hence their photophysical and electrochemical properties are quite different from that of the substituted benzene derivatives (*1–3*). 2,5-Diaryl hetero-aromatic compounds show novel liquid crystalline (*4*) and tuneable light-emitting characteristics (*5*). The thiophenic sulphur is considered to coordinate poorly with the transition metals (*6*). However, if incorporated into a macrocycle, the rigid thiophene unit may impose limitations on the size and shape of the macrocyclic cavity and on the coordination (*7*, *8*) as well as host–guest complexation properties. Synthesis of thiophene-based supramolecules has been well investigated due to their chemical and environmental stability and their potential applications in many fields such as field-effect transistors (*9*), photoswitches (*10*), light-emitting diodes (*11*), photovoltaic cells (*12*), light modulators (*13*), electroactive surfactants (*14*) and thin film transistors (*15*). Although thiophene-based cyclophanes known as thiophenophanes have been reported (*16*), chiral thiophenophanes are not known in the literature to the best of our knowledge. We wish to report herein the synthesis of chiral thiophenophanes **1**–**4** and their complexation, photophysical and electrochemical studies.

Results and discussion

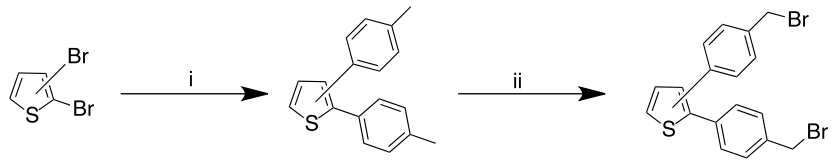
The synthetic pathway leading to 2,5-bis(4-bromomethylphenyl)thiophene **8** and 2,3-bis(4-(bromomethyl)phenyl)thiophene **11** is outlined in Scheme 1. Synthesis of 2,5-di-*p*-tolylthiophene **7** has been reported in the literature (*17*) from 1,4-alkane dione and Lawesson's reagent. However, in the present investigation, a common procedure was developed for the synthesis of ditolylthiophenes **7** and **10**. In fact, the literature procedure cannot be adopted for the synthesis of ditolylthiophene **10**, and hence the present method is better than the existing one. Ditolylthiophenes **7** and **10** were obtained in good yield by the application of Suzuki coupling. Suzuki coupling (*18*) of the dibromide **5** (*19*) with 2.1 equiv. of *p*-tolylboronic acid **6** (*20*) using $Pd(PPh_3)_4$ in dry toluene and in the presence of Na_2CO_3 resulted in the formation of 2,5-di-*p*-tolylthiophene **7** in 69% yield. By a similar sequence, 2,3-di-*p*-tolylthiophene **10** was obtained in 73% yield from 2,3-dibromothiophene **9** and *p*-tolylboronic acid **6**. Two-fold radical bromination of **7** and **10** with 2.2 equiv. of *N*-bromosuccinimide (NBS) in CCl_4 in the presence of Bz_2O_2 gave the dibromides **8** and **11** in 79 and 81% yields, respectively, and characterised from spectral and analytical data (Scheme 1).

The symmetrical thiophenophane **1** was obtained in 28% yield by the treatment of 1 equiv. of the dibromide **8** with 1 equiv. of (*S*)-BINOL in acetone and in the presence of K_2CO_3 at room temperature for 120 h. The ^{1}H NMR of the thiophenophane **1** showed a set of four-proton doublet at δ 5.02 and 5.19 ($J = 13.1$ Hz) due to the *O*-methylene protons, two doublets at δ 6.92–6.94 ($J = 8$ Hz) and at δ 7.06–7.08 ($J = 8$ Hz) integrating for eight protons each and a singlet at δ 6.91 integrating for four protons present in the thiophene unit in addition to a multiplet at δ 7.20–7.93 for the BINOL protons. In the ^{13}C NMR spectra, thiophenophane **1** displayed the *O*-methylene carbons at δ 69.8 in addition to the aromatic carbons in the region of δ 115.2–153.7. The structure of thiophenophane **1** was

*Corresponding author. Email: perumalrajakumar@hotmail.com

ISSN 1061-0278 print/ISSN 1029-0478 online

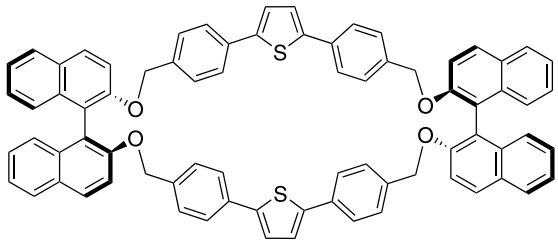
DOI: 10.1080/10610270802709535
http://www.informaworld.com



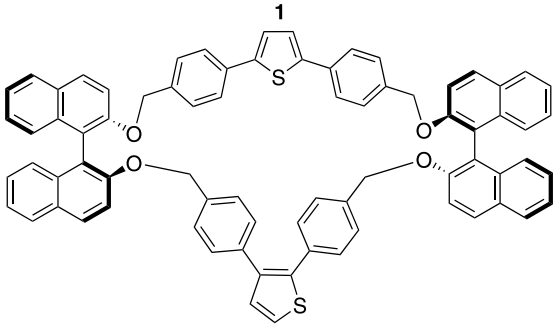
5; 2,5-dibromo **7;** 2,5-di-*p*-tolyl **8;** 2,5-bis(4-bromomethylphenyl)
9; 2,3-dibromo **10;** 2,3-di-*p*-tolyl **11;** 2,3-bis(4-bromomethylphenyl)

Scheme 1. Reagents and conditions: (i) 2.1 equiv. of *p*-tolyboronic acid **6**, Pd $(PPh_3)_4$, Na_2CO_3, EtOH, dry toluene, 12 h, **7** (69%), **10** (73%) and (ii) NBS (2.2 equiv.), CCl_4, Bz_2O_2, **8** (79%), **11** (81%).

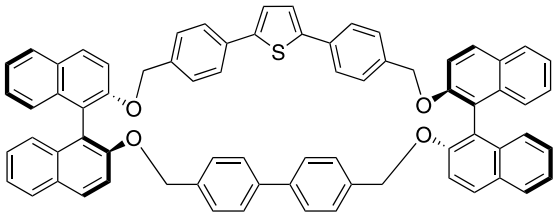
further confirmed by FAB mass spectra and from satisfactory elemental analysis.



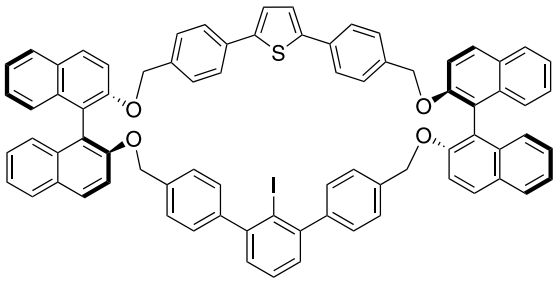
1



2



3



4

The bis-alkylated product **12** was obtained in 52% yield by treating 1 equiv. of dibromide **8** with 2.1 equiv. of (*S*)-BINOL in acetone in the presence of K_2CO_3 at room temperature for 48 h. The ^{1}H NMR of precyclophane **12** displayed AB quartet at δ 4.96–5.02 ($J = 12.6$ Hz) due to the *O*-methylene protons in addition to the aromatic protons and the IR spectrum showed the OH stretching at 3325 cm^{-1}. In the ^{13}C NMR, precyclophane **12** showed the *O*-methylene carbon at δ 70.9 along with 25 carbon signals in the aromatic region. Precyclophane **12** could be smoothly converted into thiophenophane **1** in 30% yield by reacting it with one more equivalent of the dibromide **7** in the presence of K_2CO_3 in acetone. Thus, thiophenophane **1** obtained by the one-pot procedure as well as by the two-step procedure did not show significant changes in the percentage yields.

However, the advantage of the two-step procedure is that it allows synthesising unsymmetrically substituted thiophenophanes **2**, **3** and **4**. Coupling of precyclophane **12** with one more equivalent of the dibromides **11**, **13** and **14** afforded the unsymmetrical thiophenophanes **2**, **3** and **4** in 22, 19 and 32% yields, respectively (Scheme 2). Thiophenophanes **2**, **3** and **4** were completely characterised based on the spectral and analytical data.

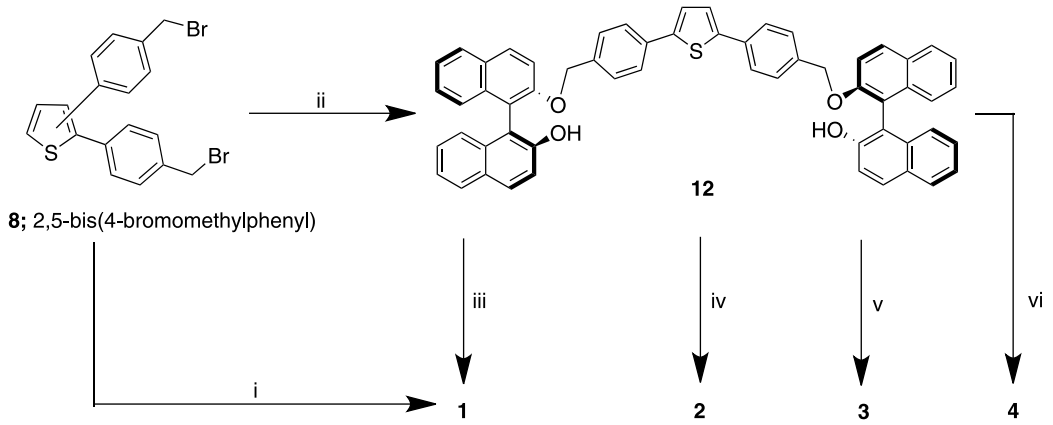
Experimental

General

Melting points were determined by using a Toshniwal melting point apparatus by the open capillary tube method and are uncorrected. The UV–vis spectra were recorded on a Hitachi U-3210 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-3010 spectrophotometer. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 MHz and Jeol 400 MHz spectrometers. Elemental analyses were performed on a Perkin-Elmer 240B instrument. Electrochemical studies were carried out on a CH Instrument electrochemical analyser.

General procedure for Suzuki coupling

A stirred mixture of dibromothiophene (0.016 mol) and $Pd(PPh_3)_4$ (0.5 mmol) in dry toluene (200 ml) under nitrogen was successively treated with *p*-tolylboronic acid



Scheme 2. Reagents and conditions: (i) 1 equiv. (*S*)-BINOL, K_2CO_3, dry acetone, rt, 120 h, **1** (28%); (ii) 2.1 equiv. (*S*)-BINOL, K_2CO_3, dry acetone, rt, 48 h, **12** (52%); (iii) 1 equiv. **8**, K_2CO_3, dry acetone, rt 120 h, **1** (30%); (iv) **1** equiv. **11**, K_2CO_3 dry acetone, rt, 120 h, **2**(22%); (v) 1 equiv. 4,4′-bis(bromomethyl)biphenyl **13**, K_2CO_3, dry acetone, rt, 120 h, **3** (19%); (vi) 1 equiv. 2′-lodo-4,4″-bis (bromomethyl)-1,1′:3′,1″-terphenyl **14**, K_2CO_3, dry acetone, rt, 120 h, **4** (32%).

(0.037 mol), dissolved in a minimum amount of ethanol (15 ml) and aqueous sodium carbonate solution (25 ml, 2 M). The resulting mixture was heated at reflux for 8 h, cooled and subjected to filtration. The filtrate was evaporated to dryness *in vacuo*. The residue was extracted with CH_2Cl_2 (3×100 ml), washed with water (3×100 ml) and dried over anhydrous Na_2SO_4. Evaporation of the organic layer gave a residue, which was purified by column chromatography over SiO_2 using hexane as an eluent to give the corresponding di-*p*-tolyl thiophene.

General procedure for NBS bromination

Freshly recrystallised NBS (92 mmol) was added in five to six equal portions 6 h apart to a solution of the compound (44 mmol) in CCl_4 (350 ml) heated at reflux; each addition was immediately followed by adding a few milligrams of benzoyl peroxide. After 24 h of total reaction time at reflux, the mixture was cooled and the precipitated succinimide was removed by filtration. The solvent was removed and the residue was recrystallised from CH_2Cl_2–hexane mixture.

Synthesis of 2,5-bis(4-(bromomethyl)phenyl)thiophene 8

Following the general procedure for NBS bromination, two-fold radical bromination of 2,5-di-*p*-tolylthiophene **7** gave dibromide **8**. Yield 79%; mp 195°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.52 (s, 4H), 7.30 (s, 2H), 7.40–7.42 (d, 4H, $J = 8$ Hz) and 7.59–7.60 (d, 4H, $J = 8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 33.4, 124.6, 126.0, 129.8, 134.0, 137.8 and 141.4; *m/z* (EI-MS, 70 eV): 422 (M, 14.8%), 424 (M + 2, 24.7%) and 426 (M+4, 14.3%). Elemental anal. calcd for $C_{18}H_{14}Br_2S$: C, 51.21; H, 3.34. Found: C, 51.30; H, 3.46.

*Synthesis of 2,3-di-*p*-tolylthiophene 10*

Reaction of 2,3-dibromothiophene **9** (0.016 mol) with *p*-tolylboronic acid (0.037 mol) under Suzuki coupling conditions using $Pd(PPh_3)_4$ (0.5 mmol) in dry toluene (200 ml) gave 2,3-di-*p*-tolylthiophene **10** as yellow solid. Yield 73%; mp 81–83°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.38 (s, 3H), 6.99 (s, 2H), 7.15–7.18 (d, 2H, $J = 7.8$ Hz), 7.21–7.24 (d, 2H, $J = 8.4$ Hz), 7.38–7.41 (d, 2H, $J = 8.4$ Hz) and 7.46–7.49 (d, 2H, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 21.0, 21.1, 110.7, 122.7, 125.5, 126.8, 129.4, 129.6, 130.8, 130.9,136.7, 137.9, 138.3 and 146.1; *m/z* (EI-MS, 70 eV): 264 (M^+, 100%). Elemental anal. calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10. Found: C, 81.69; H, 6.20.

Synthesis of 2,3-bis(4-(bromomethyl)phenyl)thiophene 11

Following the general procedure for NBS bromination, two-fold radical bromination of 2,3-di-*p*-tolylthiophene **10** gave dibromide **11**. Yield 81%; mp 103–105°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.42 (s, 4H), 6.94–6.96 (d, 1H, $J = 3.6$ Hz), 6.97–6.99 (d, 1H, $J = 3.9$ Hz) and 7.30–7.42 (AB q, 8H, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 33.0, 111.9, 123.6, 125.9, 129.7, 130.9, 133.7, 137.3 and 145.0; *m/z* (EI-MS, 70 eV): 422 (M, 9.8%), 424 (M+2, 18.3%) and 426 (M+4, 9.7%). Elemental anal. calcd for $C_{18}H_{14}Br_2S$: C, 51.21; H, 3.34. Found: C, 51.08; H, 3.22.

Synthesis of thiophenophane 1 by one-pot method

A solution of dibromide **8** (1.0 mmol) and (*S*)-BINOL (1.0 mmol) was stirred with K_2CO_3 (20 mmol) in dry acetone (200 ml) at room temperature for 120 h, after which the reaction mixture was acidified and evaporated

to dryness. The residue obtained was extracted with CH_2Cl_2 (3×100 ml), washed with water (3×100 ml) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography over SiO_2 using hexane–$CHCl_3$ (1:1) as an eluent to give thiophenophane **1** as a colourless solid. Yield 28%; mp 199–202°C; $[\alpha]_D^{25}$ −170.37 ($c = 1$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.00–5.02 (d, 4H, $J = 13.1$ Hz), 5.16–5.19 (d, 4H, $J = 13.1$ Hz), 6.91 (s, 4H), 6.92–6.94 (d, 8H, $J = 8.0$ Hz), 7.06–7.08 (d, 8H, $J = 8.0$ Hz), 7.20–7.39 (m, 16H) and 7.87–7.93 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 69.8, 115.2, 120.3, 123.6, 123.8, 125.1, 125.2, 126.4, 127.2, 128.0, 129.2, 129.3, 133.1, 134.3, 136.4, 142.8 and 153.7; *m/z* (FAB-MS): 1092 (M^+). Elemental anal. calcd for $C_{76}H_{52}O_4S_2$: C, 83.49; H, 4.79. Found: C, 83.64; H, 4.87.

Synthesis of precyclophane 12

A solution of dibromide **8** (1.0 mmol) and (*S*)-BINOL (2.0 mmol) was stirred with K_2CO_3 (20 mmol) in dry acetone (200 ml) at room temperature for 48 h, after which the reaction mixture was acidified and evaporated to dryness. The residue obtained was extracted with CH_2Cl_2 (3×100 ml), washed with water (3×100 ml) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography over SiO_2 using hexane–$CHCl_3$ (1:1) as an eluent to give the corresponding precyclophane **12** as a yellow solid. Yield 52%; mp 135–138°C; $[\alpha]_D^{25}$ −24.08 ($c = 1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.92–5.02 (AB q, 4H, $J = 12.6$ Hz), 7.05 (s, 2H) and 6.89–7.88 (m, 32H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 70.89, 115.1, 115.9, 117.0, 117.6, 123.3, 124.0, 124.5, 125.0, 125.1, 125.5, 126.5, 127.4, 127.5, 128.2, 129.2, 129.8, 129.9, 130.9, 133.6, 133.9, 134.1, 136.2, 143.1, 151.4 and 154.9; *m/z* (FAB-MS): 832 (M^+). Elemental anal. calcd for $C_{58}H_{40}O_4S_2$: C, 83.63; H, 4.84. Found: C, 83.53; H, 4.90.

General procedure for the synthesis of thiophenophanes from precyclophane 12 by **O***-alkylation*

A solution containing an equimolar amount of precyclophane **12** (1.0 mmol) and dibromide (1.0 mmol) was stirred with K_2CO_3 (20 mmol) in dry acetone (200 ml) at room temperature for 120 h, after which the reaction mixture was acidified and evaporated to dryness. The residue obtained was extracted with CH_2Cl_2 (3 × 100 ml), washed with 10% NaOH (2 × 50 ml) and water (3 × 100 ml) and then dried over anhydrous Na_2SO_4. Evaporation of the organic layer gave a residue, which was purified by column chromatography over SiO_2 using hexane–$CHCl_3$ (1:1) as an eluent to give the corresponding thiophenophane.

Synthesis of thiophenophane 1 from precyclophane 12

Following the general procedure for *O*-alkylation, thiophenophane **1** was obtained as a colourless solid from precyclophane **12** and dibromide **8** (yield 30%).

Synthesis of thiophenophane 2 from precyclophane 12

Following the general procedure for *O*-alkylation, thiophenophane **2** was obtained as a yellow solid from precyclophane **12** and dibromide **11**. Yield 22%; mp 252–254°C; $[\alpha]_D^{25}$ −131.04 ($c = 1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.93–5.02 (AB q, 8H, $J = 12.6$ Hz), 6.9–7.16 (m, 16H), 6.78–6.86 (m, 10H), 7.20–7.30 (m, 10H) and 7.79–7.89 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 70.7, 111.2, 115.9, 120.8, 123.1, 123.8, 125.3, 125.4, 125.5, 125.6, 126.4, 127.4, 127.9, 129.4, 129.5, 130.7, 132.6, 133.3, 134.2, 136.7, 137.2, 143.0, 145.5, 153.9 and 154.0; *m/z* (FAB-MS): 1092 (M^+). Elemental anal. calcd for $C_{76}H_{52}O_4S_2$: C, 83.49; H, 4.79. Found: C, 83.25; H, 4.95.

Synthesis of thiophenophane 3 from precyclophane 12

Following the general procedure for *O*-alkylation, thiophenophane **2** was obtained as a yellow solid from precyclophane **12** and dibromide **13**. Yield 19%; mp 141–143°C; $[\alpha]_D^{25}$ −168.28 ($c = 1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.95–5.04 (AB q, 8H, $J = 12.0$ Hz), 6.72–7.32 (m, 26H), 7.45–7.48 (d, 4H, $J = 9.0$ Hz), 7.93–7.96 (d, 4H, $J = 9.0$ Hz) and 7.77–7.86 (m, 8H); *m/z* (FAB-MS): 1092 (M^+). Elemental anal. calcd for $C_{72}H_{50}O_4S$: C, 85.52; H, 4.98. Found: C, 85.65; H, 4.87.

Synthesis of thiophenophane 4 from precyclophane 12

Following the general procedure for *O*-alkylation, thiophenophane **2** was obtained as a yellow solid from precyclophane **12** and dibromide **14**. Yield 32%; mp 188–189°C; $[\alpha]_D^{25}$ −125.36 ($c = 1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.92–5.12 (AB q, 4H, $J = 12.9$ Hz) and 6.78–7.87 (m, 45H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 70.4, 115.6, 116.2, 120.5, 120.7, 123.7, 123.8, 125.3, 125.4, 125.6, 125.9, 126.4, 127.4, 127.9, 128.6, 129.3, 129.4, 133.4, 134.3, 136.6, 136.8, 143.1, 144.3, 147.5, 153.8 and 154.0; *m/z* (FAB-MS): 1213 (M^+). Elemental anal. calcd for $C_{78}H_{53}IO_4S$: C, 77.22; H, 4.30. Found: C, 77.16; H, 4.36.

Photophysical properties of thiophenophanes

The UV absorption spectra were recorded in $CHCl_3$ and the λ_{max} values are shown in Table 1. Thiophenophanes **1**–**4** and precyclophane **12** exhibit an intense absorption band between 240 and 391 nm, indicating that the electronic

Table 1. Photophysical data for precyclophane **12** and thiophenophanes **1**–**4** in $CHCl_3$.

Thiophenophanes	UV λ_{max} (nm)	Emission λ_{max} (nm)
12	334, 391	452
1	241, 336	446
2	296, 335	451
3	240, 338	434
4	285, 338	438

transitions are mostly $\pi \rightarrow \pi^*$, originating from the conjugated substituents on di-*p*-tolylthiophene, and absorption bands at <325 nm are assigned as $n \rightarrow \pi^*$ transitions. Precyclophane **12** and thiophenophanes **1**–**4** exhibit intense fluorescence emission in the region 433–452 nm. Furthermore, the same emission spectra were obtained irrespective of the excited wavelengths, indicating that the downhill relaxation to the lowest excited state is efficient (*21*).

In general, 2,5-disubstituted thiophenes are unstable towards H_2SO_4 and decompose slowly owing to protonation (*22*). Moreover, they undergo isomerisation in the presence of acid to give the 2,4-disubstituted products. In order to test the stability of thiophenophanes **1**–**4** and also to check their fluorescence activity, thiophenophanes **1**–**4** were independently treated with TFA until pH 1 for 1×10^{-5} M of the cyclophane. Fluorescence quenching did not occur even after adding TFA to precyclophane **12** and thiophenophanes **1**–**4**, which shows that precyclophane **12** and thiophenophanes **1**–**4** do not undergo such rearrangements and hence can function as permanent fluorescence-sensing material even under highly acidic conditions.

Electrochemical behaviour of thiophenophanes

The electrochemical behaviour of thiophenophanes **1**, **2**, **3** (Figure 1) and **4** were then investigated. CV studies were carried out on a Pt electrode from the solutions of the substrates (1 mM) in $CHCl_3$ using tetrabutylammonium perchlorate (TBAP) (0.1 M) as supporting electrolyte in the potential range of -0.8 to 1.2 V against Ag/AgCl. Table 2 summarises the electrochemical parameters obtained from the thiophenophanes.

Thiophenophanes **1**–**4** and precyclophane **12** exhibited reduction potential in $CHCl_3$ with ΔE_p value of -0.828 to -1.013 V. The reduction results in the loss of one electron from sulphur atom of thiophene nucleus generating cationic species. From Table 2, it can be seen that thiophenophane **4** has the highest value of ΔE_p (-1.013 V) and precyclophane **12** has the lowest value of ΔE_p (-0.828 V). It is noteworthy to mention that the parent unsubstituted thiophene has the ΔE_p of -0.350 V. By converting it to the cyclophane, an increase in the negative value of ΔE_p is observed.

Based on the ΔE_p values, we can say that the reduction process is quasi-reversible.

$$\text{Thiophenophane} \xrightarrow{-e^-} \text{Thiophenophane}^{+} \xrightarrow{+e^-} \text{Thiophenophane}$$

On substituting the parent compound with ditolyl group at 2 and 5 positions, the ΔE_p value changes to -0.666 V. The higher negative value of ΔE_p for thiophenophanes when compared with either parent thiophene or 2,5-ditolylthiophene could be due to the inaccessibility of electrons on sulphur atom, which may be bound in the cavity of the cyclophane. The higher negative

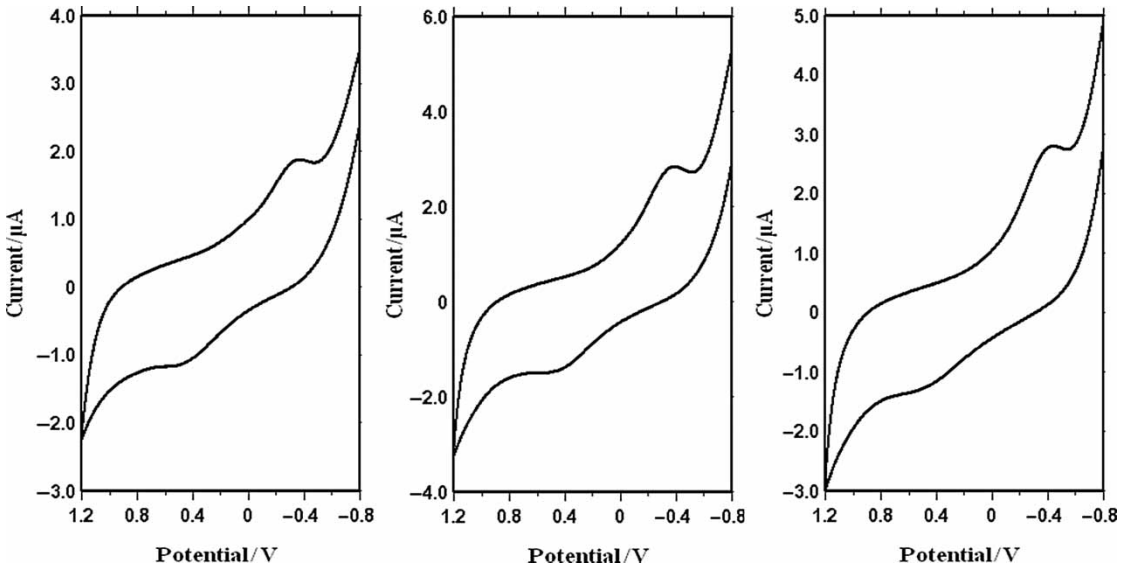


Figure 1. Cyclic voltammograms of 1 mM **1**, **2** and **3** on Pt electrode in $CHCl_3$ containing 0.1 M TBAP; scan rate, 0.05 V s^{-1}; temperature, 25°C.

Table 2. The electrochemical parameters obtained for thiophenophanes **1**–**4**, precyclophane **12**, 2,5-di-tolylthiophene **7** and thiophene in $CHCl_3$ at 25°C.

Compounds	E_{pa} (V)	E_{pc} (V)	ΔE_p (V)
1	0.490	−0.345	−0.835
2	0.457	−0.376	−0.833
3	0.498	−0.418	−0.916
4	0.776	−0.237	−1.013
12	0.635	−0.193	−0.828
7	0.608	−0.058	−0.666
Thiophene	0.220	−0.130	−0.350

E_{pa} and E_{pc} are the anodic and the cathodic peak potentials, respectively and ΔE_p is the difference between the cathodic and anodic peak potentials.

Table 3. Specific rotation values for precyclophane **12** and thiophenophanes **1**–**4**.

Thiophenophanes	Specific rotation
12	−24.08
1	−170.37
2	−131.04
3	−168.28
4	−125.36

value of ΔE_p observed for thiophenophane **4** among thiophenophanes **1**–**4** could be due to the bulky iodine atom that could hinder the removal of electron from sulphur atom. The ΔE_p value of thiophenophane **3** is slightly less when compared with thiophenophane **4**. This could be due to the orthogonal geometry of biphenyl unit, which also could relatively prevent the removal of electron from the sulphur atom.

Chiro-optical properties

Due to the presence of (*S*)-BINOL unit, all the thiophenophanes and precyclophane **12** exhibited chiro-optical properties. CD spectrum of precyclophane **12** and thiophenophane **1** is shown in Figure 2. Maxima for precyclophane **12** and thiophenophane **1** were observed at 349 and 361, and 343 and 364 nm for the negative and positive Cotton effects, respectively. Precyclophane **12** exhibited the specific rotation value of −24.08, which indicates that there exists free rotation and hence the dihedral angle is not affected to a greater extent. However, in thiophenophane **1**, the molecule is rigid with probably maximum dihedral angle at the (*S*)-BINOL unit and hence exhibited a higher specific rotation value. Similarly, thiophenophane **3** also exhibited higher specific rotation value probably due to the presence of biphenyl unit, which might increase the dihedral angle. However, thiophenophanes **2** and **4** exhibited lower value of specific rotation values probably due to slight reduction in the dihedral angle at the (*S*)-BINOL unit. The variation in specific rotation values for precyclophane **12** and thiophenophanes **1**–**4** are shown in Table 3. The value of dihedral angle has significant effect on the specific rotation values and a similar observation has also been reported from our laboratory (*23*).

Table 4. Stability constant for the charge-transfer complexation of the thiophenophanes **1**–**4** with the acceptor TCNQ using Benesi–Hildebrand method.

	TCNQ	
Thiophenophanes	K_c^{AD}	ε^{AD}
1	600	2.50×10^5
2	300	1.25×10^5
3	500	1.00×10^5
4	500	1.00×10^5

Complexation studies of thiophenophanes

The charge-transfer complexation behaviour of the thiophenophanes **1**–**4** with electron-deficient guest molecules like TCNE and TCNQ were investigated using the Benesi–Hildebrand method (*24*). An aliquot (3 ml) of a standard stock solution of thiophenophanes (0.00001 M) in DMF was placed in a quartz cuvette. The thiophenophanes **1**–**4** show UV–vis absorption maxima at 394, 370, 338 and 378 nm, respectively, in DMF. However, the acceptors

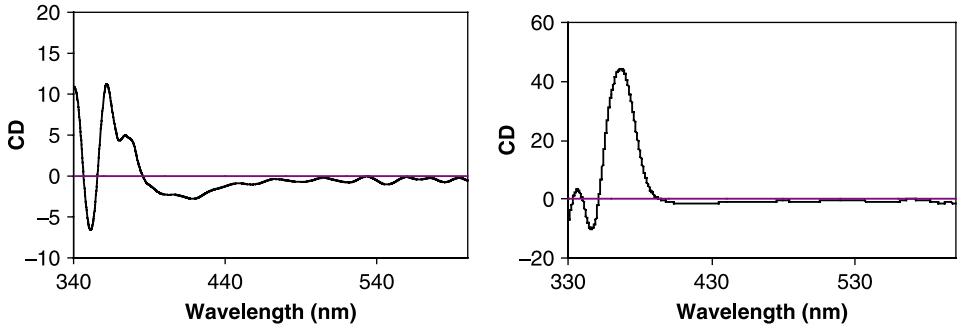


Figure 2. CD spectrum of precyclophane **12** and thiophenophane **1**.

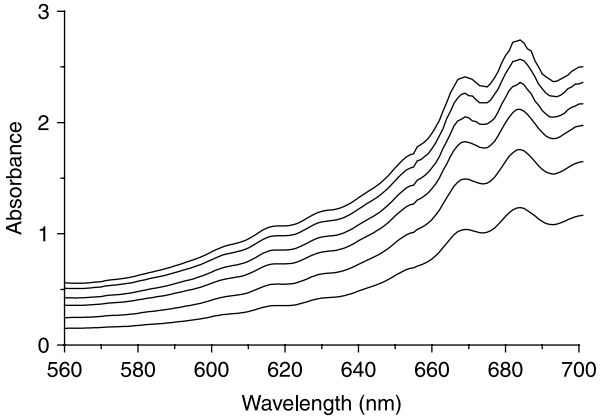


Figure 3. Charge-transfer complexation of thiophenophane **1** with varying concentration of TCNQ.

TCNE and TCNQ show absorption maxima at 410 and 322 nm, respectively, in the same solvent medium. A known amount of TCNQ was added by incremental amounts (2 mg) and changes in the absorbance (*A*) at 668 nm were recorded. A plot of [concentration of thiophenophane/*A* vs. 1/concentration of TCNQ] was linear, which suggests that the predominant species in solution is a 1:1 complex. Complexation studies of thiophenophanes with TCNE were not successful. The equilibrium constant for the CT complex derived from thiophenophanes **1**–**4** with TCNQ was measured at 668 nm, though absorption bands were observed both at 668 and 684 nm. The equilibrium constant values (K_c^{AD}) and ε^{AD} values are shown in Table 4, from which it is evident that thiophenophane **1** forms strong CT complexes with TCNQ ($K_c^{AD} = 600\,M^{-1}$ and $\varepsilon^{AD} = 2.5 \times 10^5$) (Figure 3).

Synthesis of other BINOL-based chiral thiophenophanes and their photophysical, optochiral and electrochemical studies as well as their biological activity are under investigation.

Acknowledgements

The authors thank DST-FIST, New Delhi, for NMR spectral facility. KTV thanks UGC for the award of JRF.

References

(1) (a) Tseng, J.C.; Huang, S.-L.; Lin, C.-L.; Lin, H.-C.; Jin, B.-Y.; Chen, C.-Y.; Yu, J.-K.; Chou, P.-T.; Luh, T.-Y. *Org. Lett.* **2003**, *5*, 4381–4384. (b) Kaikawa, T.; Takimiya, K.; Aso,Y.; Otsubo, T. *Org. Lett*. **2000**, *2*, 4197–4199. (c) Vinod, T.K.; Rajakumar, P.; Hart, H. *Tetrahedron* **1995**, *51*, 2267–2272. (d) Vögtle, F. *Cyclophane Chemistry*; Wiley: New York, NY, 1993.

(2) (a) Pahor, N.B.; Calligaris, M.; Randaccio, L. *J. Chem. Soc., Perkin Trans. 2* **1978**, 42–45. (b) Haley, J.F.; Rosenfeld, S.M.; Keehn, P.M. *J. Org. Chem.* **1977**, *42*, 1379–1386. (c) Cooke, M.P. *J. Org. Chem.* **1981**, *46*, 1747–1750.

(3) Vogel, E.; Jux, N.; Dorr, J.; Pelster, T.; Berg, T.; Bohm, H.-S.; Behrens, F.; Lex, J.; Bremm, D.; Hohlneicher, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1101–1105.

(4) Mochizuki, H.; Hasui, T.; Kawamoto, M.; Shiono, T.; Ikeda, T.; Adachi, C.; Taniguchi, Y.; Shiroto, T. *Chem. Commun.* **2000**, 1923–1924.

(5) Mori, A.; Sekiguchi, A.; Masui, K.; Shimada, T.; Horie, M.; Osakada, K.; Kawamoto, M.; Ikeda, T. *J. Am. Chem. Soc.* **2003**, *125*, 1700–1701.

(6) Angelici, R.J. *Coord. Chem. Rev.* **1990**, *105*, 61–76.

(7) (a) Liu, S.C.; Lucas, R.; Newlands, M.J.; Charland, J.-P. *Inorg. Chem.* **1990**, *29*, 4380–4385. (b) Lucas, C.R.; Liu, S.; Newlands, M.J.; Charland, J.-P.; Gabe, E.J. *Can. J. Chem.* **1988**, *66,* 1506–1512.

(8) (a) Latos-Grazynski, L.; Lisowski, J.; Olmstead, M.M.; Balch, A.L. *J. Am. Chem. Soc.* **1987**, *109*, 4428–4429. (b) Latos-Grazynski, L.; Olmstead, M.M.; Balch, A.L. *Inorg. Chem*. **1989**, *28*, 4065–4066.

(9) Torsi, L.; Dodabalapur, A.; Rothberg, L.J.; Fung, A.W.P.; Katz, H.E. *Science* **1996**, *272*, 1462–1464.

(10) Tsivgoulis, G.M.; Lehn, J.-M. *Adv. Mater.* **1997**, *9*, 39–42.

(11) (a) Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2574–2580. (b) MacDiarmid, A.G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581–2590. (c) Heeger, A.J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591–2611. (d) Kraft, A.; Grimsdale, A.C.; Holmes, A.B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428.

(12) Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater.* **1995**, *7*, 647–648.

(13) Fichou, D.; Nunzi, J.-M.; Charra, F.; Pfeffer, N. *Adv. Mater.* **1994**, *6*, 64–67.

(14) Edder, C.; Frechet, J.M.J. *Org. Lett.* **2003**, *5*, 1879–1882.

(15) Pappenfus, T.M.; Chesterfield, R.J.; Frisbie, C.D.; Mann, K.R.; Casado, J.; Raff, J.D.; Miller, L.L. *J. Am. Chem. Soc.* **2002**, *124*, 4184–4185.

(16) (a) Miyahara, Y. *J. Org. Chem.* **2006**, *71*, 6516–6521. (b) Mashraqui, S.H.; Sangvikar, Y.S.; Meetsma, A. *Tetrahedron Lett*. **2006**, *47*, 5599–5602. (c) Baxter, P.N.W. *J. Org. Chem.* **2004**, *69*, 1813–1821. (d) Sprutta, N.; Swiderska, M.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **2005**, *127*, 13108–13109. (e) Taleshita, M.; Nagai, M.; Yamato, T. *Chem. Commun*. **2003**, 1496–1497. (f) Chaffin, J.D.E.; Barker, J.M.; Huddleston, P.R. *J. Chem. Soc.*, *Perkin Trans. 1* **2001**, 1398–1405. (g) Hanton, L.R.; Richardson, C.; Robinson, W.T.; Turnbull, J.M. *Chem. Commun*. **2000**, 2465–2466. (h) Kaikawa, T.; Takimiya, K.; Aso, Y.; Otsubo, T. *Org. Lett*. **2000**, *2*, 4197–4199.

(17) Sridhar, D.R.; Jogibhuktha, M.; Shanthan Rao, P.; Handa, V.K. *Synthesis* **1982**, *12*, 1061–1062.

(18) Sharp, M.J.; Cheng, W.; Snieckus, V. *Tetrahedron Lett.* **1987**, *28*, 5093–5096.

(19) Norrild, C.J.; Eggert, H. *J. Am. Chem. Soc.* **1995**, *117*, 1479–1484.

(20) Keegstra, M.A.; Brandsma, L. *Synthesis* **1988**, *11*, 890–891.

(21) Sappan, P. *Chemistry and Light*; The Royal Society of Chemistry: Cambridge, 1994.

(22) Carmody, M.P.; Cook, J.M.; Dassanayake, N.L.; Katritzky, A.R.; Lina, P.; Tack, R.D. *Tetrahedron Lett.* **1976**, *32*, 1767–1771.

(23) Rajakumar, P.; Ganesan, K. *Tetrahedron Asymm.* **2005**, *16*, 2295–2298.

(24) Benesi, H.A.; Hildebrand, J.H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.