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Graphical Abstract

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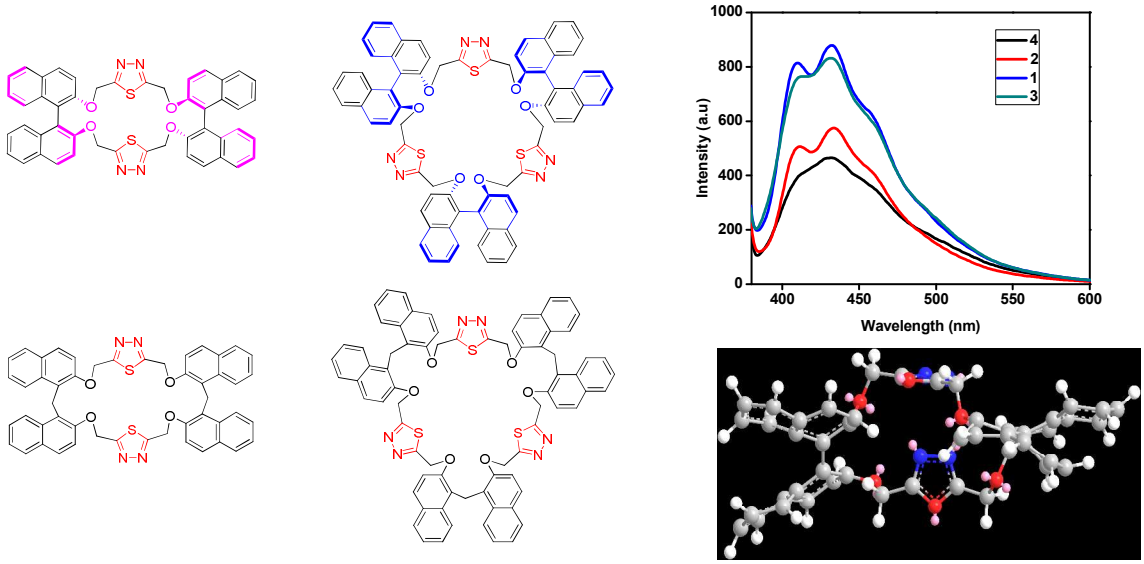
Ayyavu Thirunarayanan and Perumal Rajakumar*



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Synthesis, photophysical and electrochemical properties of chiral and achiral thiadiazolophanes

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Introduction:

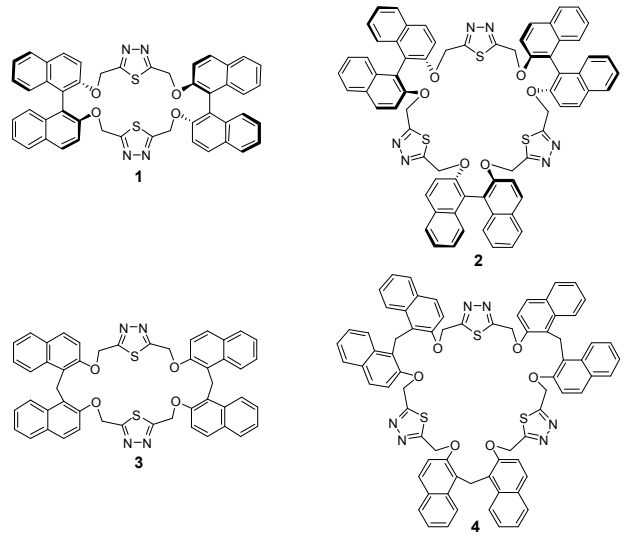
The capability of cyclic polyethers to solubilise organic and inorganic cations in non-polar organic media has made such polyethers available for organic syntheses and has provided a useful probe for reaction mechanism.[1] During the last few decades, a remarkable development has been brought about in this area of organic chemistry by the design and synthesis of macrocyclic molecules to mimic certain biological host-guest interactions.[2] Cram and others have exploited the synthesis of stereospecifically functioning hosts with chiral barriers, by which "chiral recognition" between enantiomeric guest molecules has been realized.[3]

Synthetic methods so far known for chiral crown ethers are based on the incorporation of (R)- and (S)-binaphthol, D-mannitol, L-tartaric acid as the starting chiral source, thereby the resulting macrocycles being chiral as a whole.[4] It is of interest to undertake the design and synthesis of chiral as well as achiral crown ethers[5] with chirality either on the ring or at the side chain. The molecules so designed should impose a stereo chemically specific environment in the neighbourhood of the ring, so that they might duly be expected to make feasible an efficient chiral recognition and an asymmetric induction.

Five membered aromatic systems containing three heteroatoms at the symmetrical positions have interesting physiological properties.[6] In the recent decades, the syntheses of substituted thiadiazoles[7] and related compounds have attracted considerable attentions because such substrates constitute the structural frameworks of several naturally occurring alkaloids that show a wide range of pharmaceutical and industrial importances.[8a] The technological uses of these compounds include dyes, optically active liquid crystals and photographic materials.[8-9] Thiadiazolines, thiadiazoles and oxadiazolines possess a wide range of biological properties such as antitumor,[10] antibacterial[11] and tyrosinase inhibitory activities.[12] And also the synthesis of crown-ether type macrocycles and their ability of complexation with electron deficient guest molecule are great interest during recent times.

Crown-ethers like macrocyles[13] with heteroatoms deliver a favorable binding site for complexation with metal ions and their complexation with electron deficient guest molecule is great interest.[14]

Only very few 1,3,4-thiadiazole cyclophanes have been synthesised and their properties were studied.[15] Inspired by the wide applications of thiadiazole and their derivatives, we report herein the one pot synthesis and characterization of novel 1,3,4-thiadiazole-based crown ether type chiral and achiral cyclophanes **1**, **2**, **3** and **4** (**Figure 1**).



(Figure 1): Molecular structure of chiral and achiral Thiadiazolophane **1, 2, 3** and **4**.

Chiral 2,2-binaphthol (BINOL) is one of the most important C-2 symmetry compound with the unique structure and has been used to construct enantioselective fluorescence sensors and asymmetric catalyst.[16] Design and synthesis of chiral receptor molecules are of challenge in cyclophane chemistry. Recently, synthesis of some chiral crown type receptor molecules using

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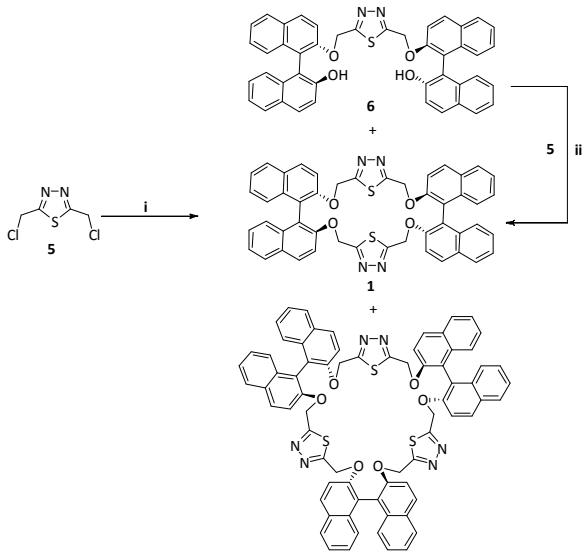
various spacers like pyridine, m -terphenyl, and chiral binaphthol has been reported from our laboratory.[17] Hence, the synthesis of cyclophanes with optically active (*S*)-BINOL unit would be more promising for complexation with chiral guest molecules in terms of their chiral recognition. The synthesis of chiral thiadiazolophanes as molecular hosts continues to be of interest due to size, shape, rigidity and non-covalent interactions at the cavity. Hence, the supramolecular hosts of chiral and achiral crown ether functionality **1** and **2** were synthesized by simple one pot *O*-alkylation procedure as shown in scheme 1.

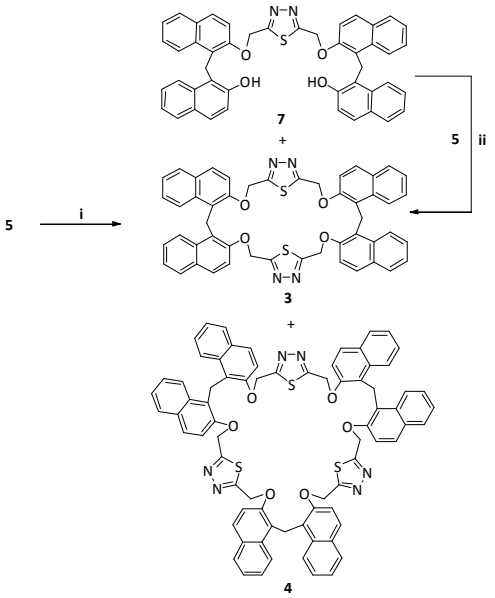


Reagents and conditions: i) (*S*)-BINOL, K_2CO_3, acetone, rt, 48 h, **6** (38%), **1** (in one pot condition 28%, in over all 31%), **2** (19%). ii) K_2CO_3, acetone, rt, 48 h.

Scheme 1

Treatment of 1.0 equiv. of 2,5-bis(chloromethyl)1,3,4-thiadiazole **5**[18] with 2.1 equiv. of *(S)*-BINOL in the presence of K_2CO_3 in dry acetone at room temperature for 48 h afforded chiral prethiadiazolophane **6**[19] in 38% yield along with chiral thiadiazolophanes **1** and **2** in 28% and 19% yields, respectively (Scheme 1). Further of reaction of prethiadiazolophane **6** with one more equivalent of **5** in acetone at room temperature in presence of K_2CO_3 afforded again chiral thiadiazolophane **1** in 80% yield. Thus thiadiazolophane **1** was prepared in overall yield of 31% by stepwise process.

^{1}H NMR spectrum of thiadiazolophane **1** displayed two doublets at δ 5.35 and 5.46 for *O*-CH_2 protons and the aromatic protons appeared at δ 7.02-8.07. The ^{13}C NMR spectrum of **1** displayed the *O*-methylene carbon at δ 66.5 in addition to the signals for the thiadiazole and (*S*)-Binol unit carbons. The mass spectrum of chiral thiadiazolophane **1** showed the molecular ion peak at m/z 794 $[M+H]^+$. The structure of thiadiazolophane **1** was also confirmed from the spectral and analytical data. Similarly, in the ^{1}H NMR spectrum, chiral 2:2 oligomeric thiadiazolophane **2** displayed as a set of doublet at δ 5.05 and 5.13 for *O*-methylene protons and the aromatic protons appeared in the region at δ 6.82-7.83. The ^{13}C NMR spectrum of **2** displayed the *O*-methylene carbon at δ 66.3 in addition to the signal for the aromatic carbons. The mass spectrum of **2** showed the molecular ion peak at m/z 1189 $[M+H]^+$. The structure of thiadiazolophane **2** was also confirmed from the spectral and analytical data. Thus, the structure of thiadiazolophane **1** and **2** is thoroughly characterized from spectral and analytical data.[20-21] Synthesis of achiral thiadiazolophanes using methylene bis-naphthyl as a spacer unit would be important from structural point of view.[22] Further, such molecules are very useful for host-guest chemistry. Methylene bis-naphthyl and their derivatives are well documented during recent times due to their broad applications in the field of biological and material sciences.[23-24] In order to test the utility of bis-naphthol for the synthesis of thiadiazolophanes **3** and **4**, 1.0 equiv. of dichloride **5** was reacted with 2.1 equiv. of 2,2'-dihydroxy-1,10-dinaphthylmethane in dry acetone in the presence of K_2CO_3 at room temperature for two days. The reaction after usual workup afforded the prethiadiazolophane **7**[25] in 32% yield along with thiadiazolophanes **3** and **4** in 27% and 13% yields, respectively (Scheme 2). Further reaction of **5** with one more equivalent of **7** in acetone at room temperature and in the presence of K_2CO_3 afforded again thiadiazolophanes **3** in 78% yield. Thus, thiadiazolophane **3** was synthesized in overall yield of 25% by stepwise process.



Reagents and conditions: i) 2,2'-dihydroxy-1,10-dinaphthylmethane, K_2CO_3, acetone, rt, 2 days, **7** (32%), **3** (in one pot condition 27%, in over all 25%), **4** (13%). ii) K_2CO_3, acetone, rt, 48 h.

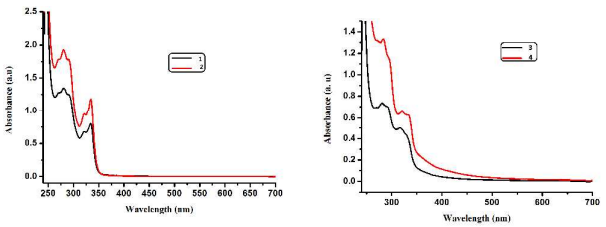
Scheme 2

The ^{1}H NMR spectrum of thiadiazolophane **3** displayed two sharp singlets at δ 4.84, δ 5.53 for the Ar-CH_2-Ar of bis-naphthyl methylene unit and *O*-methylene protons in addition to the aromatic protons at δ 7.05-8.17. In ^{13}C NMR spectrum, thiadiazolophane **3** showed two peaks at δ 22.4 and δ 66.1 for Ar-CH_2-Ar of bis-naphthyl methylene and *O*-methylene carbons in addition to the signals for thiadiazole and bis-naphthyl carbons.

The mass spectrum (ESI-MS) of thiadiazolophane **3** showed the molecular ion peak at m/z 822 $[M+H]^+$. Further, the structure of the thiadiazolophane **3** was confirmed from elemental analysis. Similarly, the structure of 3:3 oligomeric thiadiazolophane **4** was also confirmed from the spectral and analytical data.[26-27] The structure of the prethiadiazolophanes **6** and **7** and thiadiazolophanes **1**, **2**, **3** and **4** was thoroughly characterized from spectral and analytical data.

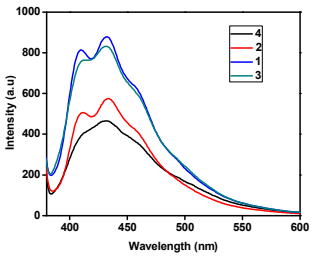
Optical and fluorescence studies of the chiral and achiral macrocycles 1-2 and 3-4:

The UV-Vis absorption spectrum of the chiral thiadiazolophanes **1**, **2** and achiral thiadiazolophanes **3**, **4** was recorded at a concentration of 10^{-5} mol/L. A main band at 334 nm and a weak band at 280 nm are observed (**Figure 2**). The intensity of the bands at 334, nm and 281 nm decreases as from chiral thiadiazolophane **1** to chiral thiadiazolophanes **2** at the given concentration**.** No red shift or blue shift for the thiadiazolophanes **1** and **2** were observed. Similarly, the electronic absorption spectrum of achiral thiadiazolophanes **3** and **4** are almost identical to chiral thiadiazolophanes **1** and **2** an intense absorption band at 333 nm and a weak band at 283 nm are observed (**Table 1)**. The decreases in intensity of the band at 334-331 nm and 281-280 nm at the given concentration for cyclophanes from **1** to **2** and for the cyclophanes from **3** to **4** probably indicate the presence of large degree of aggregation in cyclophane **2** and **4** when compared to cyclophane **1** and **3**.



(Fig. 2): UV-vis absorption spectra of thiadiazolophanes **1-2** and **3-4** (1.0 x 10 $^{-5}$ M) in $CHCl_3$.

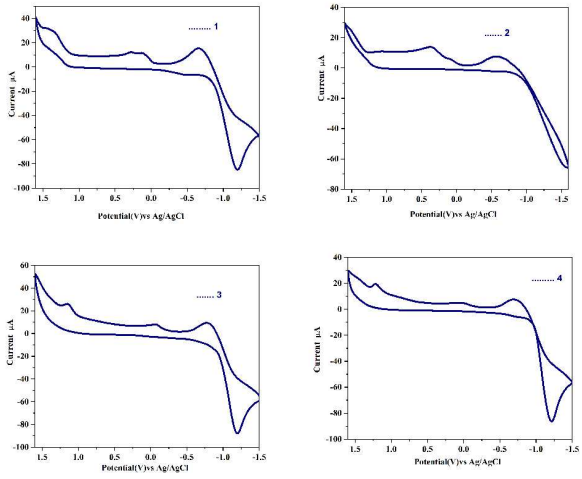
The chiral and achiral oligomeric thiadiazolophanes exhibited three fluorescence emission bands. Thiadiazolophanes **1** showed three fluorescence bands at 410, 433 and 458 nm. Similarly, thiadiazolophanes **2, 3** and **4** showed fluorescence emission at 433, 432 and 432 nm (**Figure 3**). The fluorescence intensity of the chiral and achiral thiadiazolophanes **1, 2, 3** and **4** decreases with increasing cavity size among the thiadiazolophanes **1** and **2** as well as among the cyclophanes **3** and **4** (**Table 1)**. The thiadiazolophanes **1** and **3** has the highest rigidity between two binaphthyl ring system than the thiadiazolophanes **2** and **4**.



(Fig. 3): Fluorescence emission spectra of thiadiazolophanes **1-2** and **3-4** (1.0 x 10 $^{-5}$ M) in $CHCl_3$.

Electrochemical studies of the chiral and achiral macrocycles 1-2 and 3-4:

The redox behavior of chiral and achiral 2:2 oligomeric and 3:3 oligomeric thiadiazolophanes **1, 2, 3** and **4** were studied using cyclic voltammetry at the scan rate of 50 mVs^{-1} (CV) in CH_3CN (1×10^{-5} M) solution at room temperature. All the cyclophanes have an electrochemical response, and the cyclic voltammogram of all the cyclophanes are shown in **Figures 4**, with redox potentials listed in **Table 1**. The redox behavior of cyclophane **1** exhibited three oxidation peaks between -0.66 to 0.27 V with two reduction peaks (-0.48 to -1.19 V) where as thiadiazolopahne **2** shows three oxidation peaks in the potential window of -0.58 to 0.36 V. Hence, thiadiazolopahne **2** is very difficult to reduce than the thiadiazolopahne **1**. Further, thiadiazolophane **3** and **4** show three oxidation peaks with one reduction peak. This result suggests that the reduction process was significantly affected by chirality of the thiadiazolophanes. It has been reported that the perpendicular arrangement of trpy and $DMcT^{2-}$ in Pt–trpy complex could be the reason for the absence of redox peaks.[9b]



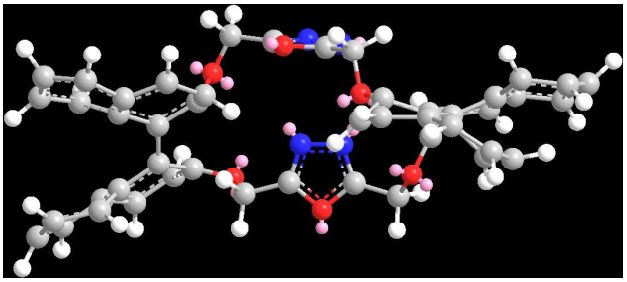
(Fig. 4.): Cyclic voltammograms of thiadiazolophanes **1 2**, **3** and **4** in (1×10^{-3} M) CH_3CN, scanned at 50 mVs^{-1}

In the present investigation we have studied the electrochemical behavior of all the synthesized thiadiazolophanes **1, 2, 3** and **4** in the potential range of -0.48 to -1.21 V against Ag/AgCl. A three step redox reaction has been observed from the CV curves (**Figure 4**).

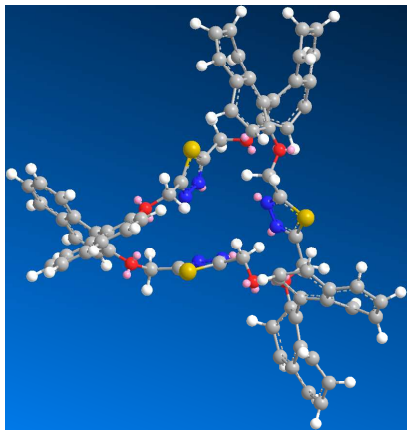
Conformation studies of the chiral and achiral macrocycle 1-2 and 3-4:

In order to examine the stability of 2:2 oligomeric and 3:3 oligomeric forms of thiadiazolophanes, theoretical calculations based on Molecular mechanics (MM2) on chiral thidiazolophane **1** and of that on the 3:3 oligomeric chiral thiadiazolophanes **2** has been carried out. Thiadiazolophane **2** has a smaller heat of formation (-58.9006 kcal/mol) than the corresponding 2:2 oligomeric thidiazolophane **1** (-

64.1049kcal/mol), which is in accordance with our experimental observation the chiral thidiazolophane. The 1,3,4 thiadiazole unit lye in a vertical position to the binaphthyl ring to avoid the steric repulsion and which may leads to form the coordination sites for the guest molecules (**Figure 5**).



2:2 oligomeric chiral thidiazolophane **1** (Heat of formation = -64.1049kcal/mol)



3:3 oligomeric chiral thidiazolophane **2** (Heat of formation = -58.9006 kcal/mol)

(Fig. 5) Energy minimized (MM2 structures) and Heats of formation of chiral thidiazolophane **1** and **2.**

(Table 1). Summary of the optical and electrochemical measurements of chiral and chiral 2:2 oligomeric and 3:3 oligomeric thiadiazolophanes **1**, **2** and **3**, **4**.

Cyclophane	λ_{max} [a] (nm)	Emiss (a.u)	E_{pc1} [a] (V)	E_{pc2} [a] (V)	E_{pc3} [a] (V)	E_{pa1} (V)	E_{pa2} (V)	ΔE_{pa3} (V)	ΔEp_2 (V)	ΔEp_3 (V)
1	280.39 334.13	410 433	-	-0.48	-1.19	0.27	0.12	-0.66	0.36	0.53
2	280.89 334.53	410 433	-	-	-	0.36	0.08	-0.58	-	-
3	283.08 333.33	412 432	-	-	-1.20	1.55	0.07	-0.78	-	0.42
4	280.39 331.54	411 432	-	-	-1.21	1.22	0.05	-0.70	0.72	0.51

*Cyclic voltammograms of thiadiazolophanes **1, 2** and **3**, **4** in (1×10^{-3} M) CH_3CN

Conclusions

In conclusion, we have synthesized some novel chiral and achiral 2:2 oligomeric and 3:3 oligomeric thiadiazolophane using chiral binaphthyl and achiral methylene bis- naphthyl as building blocks through simple *O*-alkylation methodology in one pot reaction and studied their photophysical, electrochemical behavior and energy minimization calculation reveal that cyclophane **2** has less heat of formation than cyclophane **1**. Synthesis of other thiadiazolophanes with various spacer units and their host-guest study with various metal ion and OLED application are underway.

GENERAL CONSIDERATIONS

All the melting points were determined by using a Toshniwal melting point apparatus by open capillary tube method and were uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 MHz spectrometers. The chemical shifts are reported in ppm (δ) with TMS as internal standard and coupling constant (*J*) are expressed in Hz. EI-MS spectra on JEOL DX-303 and Waters -Q-Tof HAB213 mass spectrometer mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240B elemental analyzer. The UV-Vis spectra were recorded on a Shimadzu 260 spectrophotometer. The emission spectra were recorded on Perkin-Elmer LS-5B spectrophotometer. The optical rotations were recorded on Autopol-II automatic spectropolarimeter with cell length of 50 mm D-line of sodium at 25 ^{o}C. (S)-1,1'-Bi-2-naphthol (BINOL) (99%; $[\alpha]_D^{25}$: -34.0; *c*1, THF), purchased from Gerchem Labs (India) Pvt. Ltd., Hyderabad was used in all experiments without any further purification. Glass plates coated with silica gel-G (ACME) of about 0.25 mm thickness were used for TLC and visualized with iodine. Column chromatography was carried out with silica gel (ACME, 100-200 mesh). The organic extracts of crude products were dried over anhydrous magnesium sulphate or sodium sulphate. Electrochemical studies were carried out on a CH Instruments electrochemical analyzer.

EXPERIMENTAL SECTION

General procedure for the synthesis of chiral and achiral thiadiazolophanes by *O*-alkylation

A mixture of bischloride (2 g, 10.92 mmol) dihydroxy compound (7.2 g, 22.95 mmol) and K_2CO_3 (54.6 g, 59.85 mmol) in dry acetone (250 mL) was stirred at room temperature for 48 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$ (300 mL), washed with water (3 x 100 mL), brine (150 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and residue was column chromatographed using hexane/ethyl acetate (4:1) as eluent.

Electrochemical measurements:

Cyclicvoltammetric measurements were performed in a conventional three electrode system on CHI modal 1100A series electro chemical analyzer (CH Instrument, USA). Glassy carbon electrode (GCE) was used as working electrode with Pt foil (large surface area) and a silver-silver chloride (Ag/AgCl) as counter and reference electrodes, respectively. Prior to each electrochemical experiment, this GCE was mechanically polished with 0.05 micron alumina powder and cleaned in 1:1 acetone/ethanol mixture in an ultrasonic bath to remove impurities, rinsed with water and then dried in air. Then the electrode was cleaned by cycling between the potentials of -0.3 to -3.0 V and 0.4 to -1.8 versus AgCl in 1×10^{-6} M of tetrabutylammonium perchlorate ($TBAClO_4$) in CH_3CN at a scan rate of 50 mV s^{-1} for approximately 30 min until reproducible scans were recorded. All the electrochemical experiments were performed in a quiescent solution at room temperature (25 ± 1 ºC).

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19. **Chiral Prethiadiazolophane 6**: Yield 38%; mp 138 ^{o}C; IR (KBr):ύ = 3472, 3066, 2929, 2846, 1637, 1587, 1520, 1467, 1281, 1221, 1048, 822, 809, 756. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.91-5.01 (m, 4H); 6.71 (s, 2H); 6.93 (d, 2H, *J* = 9.3 Hz); 6.99-7.43 (m, 15H); 7.76-7.81 (m, 3H); 7.91 (d, 2H, *J* = 8.4 Hz); 8.00 (d, 2H, *J* = 8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 65.9, 114.7, 115.5, 116.2, 118.0, 122.3, 123.4, 124.6, 125.3, 126.6, 128.1, 128.9, 130.1, 130.9, 131.2, 133.9, 136.6, 139.3, 151.6, 153.8, 163.9. (ESI-MS) *m/z* 683 $[M+H]^+$. Elemental Anal. Calcd for $C_{44}H_{30}N_2O_4S$: C, 77.40; H, 4.43; N, 4.10%. Found: C, 77.31; H, 4.47; N, 4.17%.

20. **Chiral Thiadiazolophane 1**: Yield 28%; mp 155 ^{o} C; IR (KBr):ύ = 3049, 2923, 2845, 1639, 1581, 1508, 1474, 1281, 1221, 1148, 1088, 1048, 802, 755. $[\alpha]^{25}$ D -91.6 (*c* 0.01, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 5.21 (d, 4H, *J* = 13.2 Hz); 5.46 (d, 4H, *J* = 13.5 Hz); 7.04 (d, 2H, *J* = 8.4 Hz); 7.18 (d, 2H, *J* = 8.4 Hz); 7.22 (d, 2H, *J* = 6.3 Hz); 7.35 (t, 6H, *J* = 7.5 Hz); 7.43 (d, 2H, *J* = 7.8 Hz); 7.49 (d, 4H, *J* = 9.3 Hz); 7.87 (d, 2H, *J* = 7.8 Hz); 7.93 (d, 2H, *J* = 8.4 Hz); 8.05 (d, 2H, J = 8.7 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 66.5, 117.8, 124.5, 125.0, 125.2, 127.6, 128.2, 130.1, 131.2, 133.8, 153.8, 163.4. (ESI-MS) *m/z* 794 $[M+H]^+$. Elemental Anal. Calcd for $C_{48}H_{32}N_4O_4S_2$: C, 72.71; H, 4.07; N, 7.07%. Found: C, 72.84; H, 4.01; N, 7.19%.

21. **Chiral Thiadiazolophane 2**: Yield 19%; mp 240 ^{o}C; IR (KBr):ύ = 3066, 2938, 2855, 2376, 1632, 1588, 1510, 1467, 1278, 1223, 1151, 1087, 1049, 815, 752. $[\alpha]^{25}$ D -78.6 (*c* 0.01, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 5.05 (d, 6H, *J* = 15.3 Hz); 5.13 (d, 6H, *J* = 15.6 Hz); 6.82 (d, 4H, *J* = 9.0 Hz); 7.04 (d, 4H, *J* = 8.7 Hz); 7.13 (d, 4H, *J* = 7.2 Hz); 7.17-(m, 6H); 7.34-7.39 (m, 3H); 7.66 (d, 3H, *J* = 8.4 Hz); 7.78 (d, 6H, *J* = 8.1 Hz); 7.82 (d, 6H, *J* = 7.8 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 66.3, 118.8, 124.9, 125.4, 126.5, 126.9, 128.8, 130.1, 130.7, 133.8, 151.7, 163.9. (ESI-MS) *m/z* 1189 $[M+H]^+$. Elemental Anal. Calcd for $C_{72}H_{48}N_6O_6S_3$: C, 72.71; H, 4.07; N, 7.07%. Found: C, 72.66; H, 4.12; N, 7.17%.

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25. **Prethiadiazolophane 7**: Yield 32%; mp 142 ^{o}C; IR (KBr):ύ = 3467, 3064, 2934, 2852, 2378, 1631, 1584, 1513, 1468, 1273, 1221, 1152, 1089, 1046, 816, 752. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.13 (s, 4H); 4.83 (s, 4H); 5.53 (s, 2H); 7.03 (d, 4H, *J* = 8.1 Hz); 7.25-7.41 (m, 4H); 7.60 (d, 4H, *J* = 8.1 Hz); 7.74 (d, 8H, *J* = 8.4 Hz); 8.16 (d, 4H, *J* = 8.1 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 29.7, 65.4, 114.3, 117.8, 118.7, 119.2, 122.7, 122.9, 123.0, 123.9, 126.5, 128.4, 128.7, 128.8, 129.3, 129.4, 130.1, 130.5, 133.4, 133.5, 152.3, 164.0. (ESI-MS) *m/z* 712 $[M+H]^+$. Elemental Anal. Calcd for $C_{46}H_{34}N_2O_4S$: C, 77.72; H, 4.82; N, 3.94%. Found: C, 77.61; H, 4.89; N, 3.83%.

26. **Thiadiazolophane 3**: Yield 27%; mp 198 ^{o}C; IR (KBr):ύ = 3080, 2942, 2861, 2377, 1666, 1634, 1596, 1512, 1468, 1238, 1097, 815, 745. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.83 (s, 4H); 5.53 (S, 8H); 7.05 (d, 4H, *J* =8.1 Hz); (d, 2H); 7.25-7.40 (m, 6H); 7.59 (d, 4H, *J* =8.1 Hz); 7.74 (d, 6H, *J* =8.4 Hz); 8.15 (d, 4H, *J* =8.1 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 22.4, 66.1, 117.8, 123.9, 124.4, 126.5, 127.1, 129.2, 129.5, 130.3, 133.4, 152.3, 161.6. (ESI-MS) *m/z* 822 $[M+H]^+$. Elemental Anal. Calcd for $C_{50}H_{36}N_4O_4S_2$: C, 73.15; H, 4.42; N, 6.82%. Found: C, 73.23; H, 4.31; N, 6.91%.

27. **Thiadiazolophane 4**: Yield 13%; mp 280 ^{o}C; IR (KBr):ύ = 3064, 2928, 2856, 2367, 1666, 1632, 1593, 1515, 1462, 1380, 1233, 1083, 810, 752. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.81 (s, 6H); 5.46 (S, 12H); 6.90 (d, 6H, *J* = 8.4 Hz); 7.31- 7.53 (m, 6H); 7.70 (d, 6H, *J* =7.8 Hz); 7.77 (d, 12H, *J* = 8.7 Hz); 8.14 (d, 6H, *J* = 8.4 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 22.7, 66.6, 117.9, 123.8, 124.8, 126.3, 127.5, 129.1, 129.6, 130.4, 133.9, 152.7, 162.8. (ESI-MS) *m/z* 1232 $[M+H]^+$. Elemental Anal. Calcd for $C_{75}H_{54}N_6O_6S_3$: C, 73.15; H, 4.42; N, 6.82%. Found: C, 73.19; H, 4.30; N, 6.91%.