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Synthesis and complexation studies of intra annularly linked bicyclic cyclophanes

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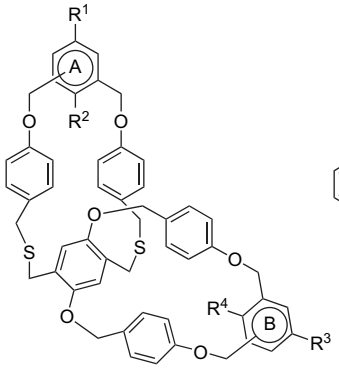
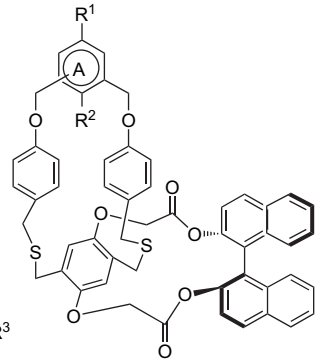
Abstract—The cyclophanes derived from 2,6-bis(chloromethyl)benzoquinone and suitable dithiols were reduced with sodium dithionate and then further coupled with various dibromides to give intra annularly linked bicyclic cyclophanes, which forms charge transfer complexes with TCNQ and TCNE.

1. Introduction

Pre-organization[1] of macrocycles plays a vital role in many biological mechanisms such as enzyme–substrate activity,[2] protein folding,[3] antisense application[4] and molecular recognition.[5] Hart and Vinod[6] have reported various novel cyclophanes with a *m*-terphenyl unit embedded within a cavity lined by three aryl rings. Stoddart and Spencer[7] have reported the synthesis of chiral macrobicyclic cyclophanes. Chiral Binol based cyclophanes[8,9] and bicompartmental bicyclic cyclophanes[10] have also been recently reported. However, to the best of our knowledge, the synthesis of self-complementary bicompartmental bicyclic cyclophanes remains to be explored. Hence, we report herein the synthesis and characterization of bicompartmental self-complementary cyclophanes **10**–**13** and **19**–**22** with electron rich and electron deficient counterparts.



10, 11, 12, 19, 20, 21



13, 22

Keywords: Cyclophanes; Bicompartmental; Self-complimentary; Electron rich; Electron deficient.
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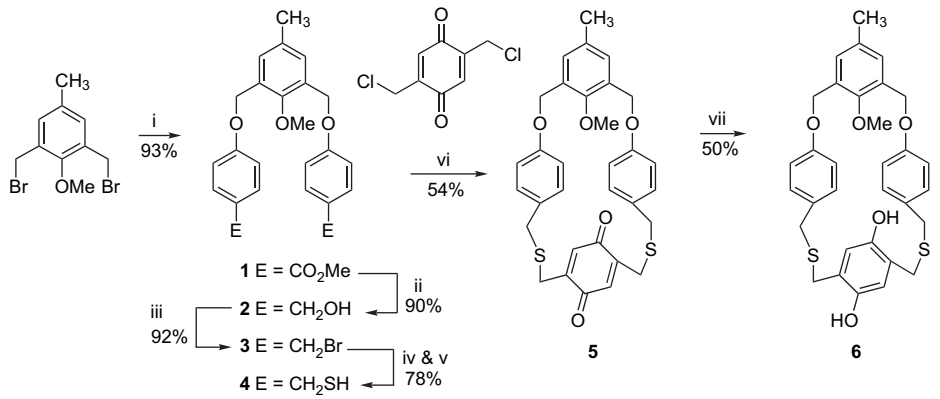
Compd	A	B	R^1	R^2	R^3	R^4
10	*m*-	*m*-	Me	OMe	Me	OMe
11	*m*-	*m*-	Me	OMe	NO_2	OAc
12	*m*-	*o*-	Me	OMe	H-	H-
13	*m*-	Binol	Me	OMe	—	—
19	*o*-	*o*-	H-	H-	H-	H-
20	*o*-	*m*-	H-	H-	Me	OMe
21	*o*-	*m*-	H-	H-	NO_2	OAc
22	*o*-	Binol	H-	H-	—	—

2. Results and discussion

In order to synthesize bicompartmental self-complementary cyclophane **10**, 2 equiv of methyl *p*-hydroxybenzoate was treated with 1 equiv of 4-methyl 2,6-bis-(bromomethyl)anisole[11] in the presence of K_2CO_3 in DMF to give diester **1** in 93% yield. Reduction of diester with $LiAlH_4$ gave diol **2**, which on further reaction with PBr_3 gave dibromide **3** in 92% yield. The thiouronium salt derived from dibromide **3** and thiourea, on hydrolysis with KOH in THF/H_2O gave dithiol **4** in 78% yield. The structure of the dithiol **4** has been confirmed from the spectral and analytical data.

Treatment of equimolar amounts of dithiol **4** and 2,6-bis-(chloromethyl)benzoquinone in EtOH/benzene under high dilution conditions[12] gave thiacyclophane **5** in 54% yield. Thiacyclophane **5** was found to be unstable and hence complete characterization could not be carried out.

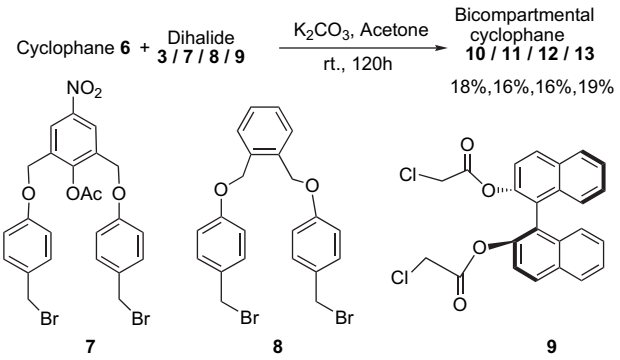
Reduction of thiacyclophane **5** with sodium dithionate in EtOAc at 0 °C afforded cyclophane **6** in 50% yield. The sulfide bonds in cyclophane **6** are not affected during the course of reaction. In the ^{1}H NMR spectrum of cyclophane **6**, the methyl and methoxy protons appeared as singlets at δ 2.06 and 3.16. Further the *S*-methylene and *O*-methylene protons



Scheme 1. Reagents and conditions: (i) methyl *p*-hydroxybenzoate, K_2CO_3, DMF, 60 °C, 48 h; (ii) $LiAlH_4$, THF, 60 °C, 12 h; (iii) PBr_3, CH_2Cl_2, 0 °C, 12 h; (iv) thiourea, THF, 60 °C, 12 h; (v) KOH, 60 °C, 12 h, THF/H_2O (1:1); (vi) EtOH/benzene, rt, 24 h; (vii) $Na_2S_2O_4$, EtOAc, 0 °C, 3 h.

appeared as two singlets at δ 3.77 and 5.22 for eight and four protons, respectively, in addition to the aromatic protons (Scheme 1).

Treatment of cyclophane **6** with dibromide **3**, in the presence of K_2CO_3 in dry acetone at room temperature for 120 h afforded the annularly linked bicyclic cyclophane **10** in 18% yield (Scheme 2). The ^{1}H NMR spectrum of electron rich bicompartmental cyclophane **10** showed two singlets for methyl and methoxy protons at δ 2.32 and 3.80 and *S*-methylene and *O*-methylene protons as singlets at δ 4.60 and δ 5.08, respectively, in addition to the aromatic protons.

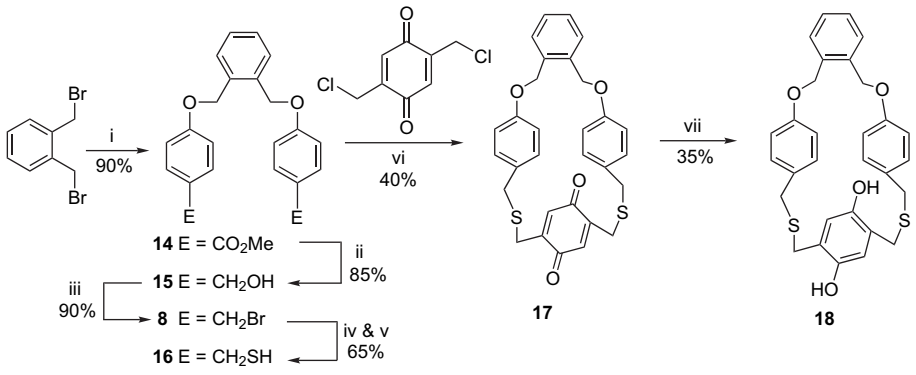


Scheme 2.

By similar methodology, electron rich cyclophane **6** was treated with various dihalides such as dibromides **7**[13] and **8**,[14] and chiral dichloride **9**[15] to give the bicompartmental cyclophanes **11** and **12** and chiral cyclophane **13** in 16, 16 and 19% yield, respectively. Bicompartmental cyclophanes **11–13** were characterized by spectroscopic and analytical data (Scheme 2).

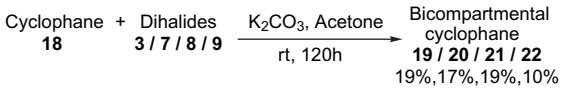
Attention was then focused on the synthesis of bicompartmental cyclophanes **19–22** by similar methodology. Dibromide **8** was obtained from *o*-xylenyl dibromide by the known procedure.[14] Treatment of dibromide **8** with thiourea in THF afforded the thiouronium salt, which on hydrolysis with KOH in THF/H_2O gave dithiol **16** in 65% yield. Treatment of equimolar amounts of dithiol **16** with 2,6-bis-(chloromethyl)benzoquinone in EtOH/benzene under high dilution conditions gave neutral thiacyclophane **17** in 40% yield. Thiacyclophane **17** could not be completely characterized due to its instability. Reduction of cyclophane **17** with sodium dithionate in EtOAc at 0 °C afforded cyclophane **18** in 35% yield (Scheme 3).

Treatment of cyclophane **18** with dibromide **8** in dry acetone and in the presence of K_2CO_3 at room temperature for 120 h afforded the bicompartmental cyclophane **19** in 19% yield. In the ^{1}H NMR spectrum, bicompartmental cyclophane **19** showed two *S*-methylene protons as two singlets at δ 4.09 and 4.55 and *O*-methylene protons as another singlet at



Scheme 3. Reagents and conditions: (i) methyl *p*-hydroxybenzoate, K_2CO_3, DMF, 60 °C, 48 h; (ii) $LiAlH_4$, THF 60 °C, 12 h; (iii) PBr_3, CH_2Cl_2, 0 °C, 12 h; (iv) thiourea, THF, 60 °C, 12 h; (v) KOH, 60 °C, 12 h, THF/H_2O (1:1); (vi) EtOH/benzene, rt, 24 h; (vii) $Na_2S_2O_4$, EtOAc, 0 °C, 3 h.

δ 5.15 in addition to aromatic protons. Using similar methodology, cyclophane **18** was treated with various dihalides such as dibromides **3** and **7**[13] and chiral dichloride **9**[15] to give bicompartmental cyclophanes **20** and **21** and bicompartmental chiral cyclophane **22** in 17, 19 and 10% yield, respectively (Scheme 4).



Scheme 4.

Bicompartmental cyclophanes **20**–**22** were characterized by spectroscopic and analytical data.

Semi empirical calculations based on MOPAC (AM_1) have been carried out for the bicompartmental cyclophane **10**–**13** and **19**–**22** and show that the two cyclophane rings are perpendicular to each other. It also reveal that the central benzene ring through which both the macrocyclic rings are connected lies in a perpendicular plane (Figs. 1 and 2).

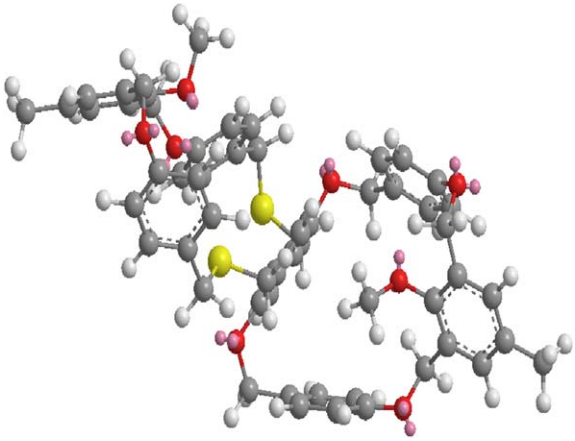


Figure 1. Energy minimization of cyclophane **10**: heat of formation of cyclophane **10** 15.0752 kcal/mol.

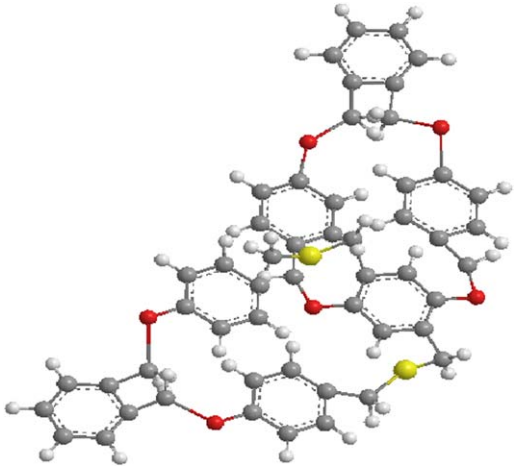


Figure 2. Energy minimization of cyclophane **19**: heat of formation of cyclophane **19** 16.7920 kcal/mol.

Cyclophanes **10**, **19**, **20** and **21** show UV–vis absorption maxima at 318, 276 and 288 nm in DMF solvent medium. However the acceptors TCNQ and TCNE show absorption maxima at 410 and 322 nm, respectively, in the same solvent. Cyclophanes **10**, **19**, **20** and **21** form charge transfer complexes with TCNQ as evident by the appearance of absorption maxima at 751, 775 and 850 nm, respectively. The equilibrium constant for the charge transfer complexation of **21** with TCNQ was observed at 850 nm (Fig. 3). Cyclophane **21** also formed a charge transfer complex with TCNE, as indicated by absorption at 825 and 849 nm, respectively. The charge transfer complexation of **21** with TCNE was observed at 848 nm (Fig. 4).

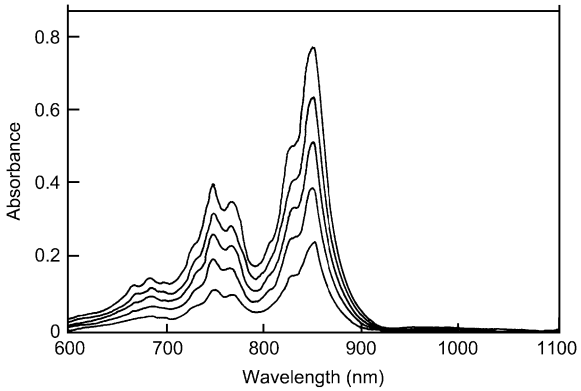


Figure 3. Charge transfer complexation behaviour of cyclophane **21** with variable concentration of TCNQ.

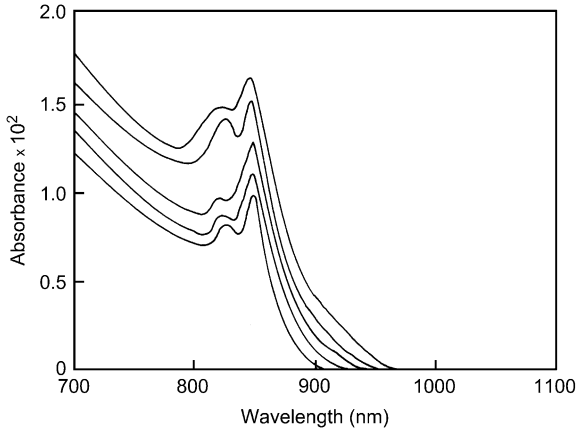


Figure 4. Charge transfer complexation behaviour of cyclophane **21** with variable concentration of TCNE.

The stability constants of the charge transfer complexes for cyclophanes **10**, **19**, **20** and **21** with acceptors TCNQ and TCNE were also determined (Table 1).

It is noteworthy to mention that cyclophane **21** forms a strong charge transfer complex with TCNQ (K_c^{AD} 1343 M^{-1} and ε^{AD} 2.19×10^5). By comparing the stability constants of the CT complexes derived from cyclophanes **10**, **19**, **20** and **21** and TCNQ and TCNE it is clear that the cavity size has no significant influence on the stability of the charge transfer complexes.

Table 1. Stability constants for the charge transfer complexes of **10**, **19**, **20** and **21** with accepters TCNQ and TCNE

Cyclophane	TCNQ		TCNE	
	K_c^{AD}	ε^{AD}	K_c^{AD}	ε^{AD}
10	183	5.9×10^5	222	5.2×10^3
19	147	2.17×10^5	189	2.0×10^6
20	128	2.0×10^5	287	2.27×10^3
21	1343	2.19×10^5	170	1.0×10^4

In conclusion, we have synthesized a new class of bicompartmental cyclophanes with electron rich, electron deficient and neutral macrocyclic units and made a preliminary study on their CT complexation ability with electron poor guest molecules TCNQ and TCNE.

3. Experimental

3.1. General

All melting points are uncorrected. The IR spectra were recorded using Shimadzu FT-IR 8000 Infrared Spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL GSX 500 NMR Spectrometer at 500 and 125 MHz, respectively, and coupling constants (*J*) are expressed in hertz, using TMS as an internal standard. The Mass spectra were recorded using a JEOL mass Spectrometer (EI, 70 eV). THF was freshly distilled from Na/benzene kettle before use. The column chromatography was performed using silica gel (Acme, 100–200 mesh). The organic layer extracts were dried using anhydrous sodium sulfate. The dibromide **7** and the dichloride **15** were prepared according to literature procedures.[13–15]

3.2. General procedure for the synthesis of diesters

Dibromide (2.0 equiv) and methyl *p*-hydroxybenzoate (2.2 equiv) were stirred with K_2CO_3 (5.0 equiv) in dry DMF (25 mL) at 60 °C for 48 h. The reaction mixture was poured into water (2 L) and stirred. The resulting precipitate was filtered, washed with water (3×150 mL) and dissolved in CH_2Cl_2 (350 mL). The organic layer was washed with NaOH solution (5% w/v, 2×100 mL), dried over Na_2SO_4 and evaporated to give a residue that was purified by column chromatography using hexane/$CHCl_3$ (4:1) as eluent.

3.2.1. Diester 1. Colourless solid; yield 93%; R_f 0.6 (hexane/$CHCl_3$ 4:1); mp 197–201 °C; IR (cm^{-1}) 1679 (C=O); ^{1}H NMR ($CDCl_3$) δ 8.01 (4H, d, *J* 8.8 Hz, Ph), 7.29 (2H, s, Ph), 7.02 (4H, d, *J* 8.8 Hz, Ph), 5.14 (4H, s, C*H*$_2$OPh), 3.89 (6H, s, COO*Me*), 2.74 (3H, s, O*Me*), 2.34 (3H, s, Me); ^{13}C NMR ($CDCl_3$) δ 180.2, 170.1, 166.7, 134.3, 133.9, 129.2, 128.9, 128.8, 114.3, 65.5, 65.1, 63.1, 20.9; *m*/*z* 450 (M^+); Anal. Calcd for $C_{26}H_{26}O_7$: C, 69.33; H, 5.78. Found: C, 69.34; H, 5.79.

3.2.2. Diester 14. Colourless solid; yield 90%; R_f 0.5 (hexane/$CHCl_3$1:1); mp 82–85 °C; IR (cm^{-1}) 1715 (C=O); ^{1}H NMR ($CDCl_3$) δ 7.19–7.65 (4H, m, Ph), 7.10 (4H, d, *J* 8.4 Hz, Ph), 6.71 (4H, d, *J* 8.4 Hz, Ph), 5.12 (4H, s, C*H*$_2$OPh), 3.82 (6H, s, COO*Me*); ^{13}C NMR ($CDCl_3$) δ 180.3, 165.0, 144.2, 140.2, 130.9, 127.9, 127.7, 122.5, 64.7, 51.5; *m*/*z* 406 (M^+); Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.94; H, 5.42. Found: C, 70.95; H, 5.43.

3.3. General procedure for the synthesis of diols

To a solution of the appropriate diester (1.0 equiv) in dry THF (300 mL) was added $LiAlH_4$ (2.2 equiv) at 0 °C in portions. The reaction mixture was stirred at room temperature for 1 h and then run into $Na_2SO_4\cdot10H_2O$ (40 g) and stirred. The reaction mixture was then digested on a water bath for 20 min and then filtered. The inorganic residue was further extracted with THF (200 mL) using a Soxhlet apparatus. The combined THF fractions were evaporated to give the diol. The crude product was purified by column chromatography using hexane/$CHCl_3$ (1:1) as eluent.

3.3.1. Diol 2. Colourless solid; yield 90%; R_f 0.3 (hexane/$CHCl_3$ 1:1); mp 183–185 °C; IR (cm^{-1}) 3340 (br, OH); ^{1}H NMR ($CDCl_3$) δ 7.29 (4H, d, *J* 8.7 Hz, Ph), 7.25 (2H, s, Ph), 6.98 (4H, d, *J* 8.7 Hz, Ph), 6.32 (2H, s, O*H*), 5.07 (4H, s, C*H*$_2$OH), 4.61 (4H, s, C*H*$_2$OPh), 3.81 (3H, s, O*Me*), 2.32 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) δ 158.3, 154.4, 134.2, 133.3, 130.7, 129.8, 128.6, 114.8, 65.1, 65.0, 63.0, 20.8; *m*/*z* 394 (M^+); Anal. Calcd for $C_{24}H_{26}O_5$: C, 73.10; H, 6.60. Found: C, 73.11; H; 6.61.

3.3.2. Diol 15. Colourless solid; yield 90%; R_f 0.4 (hexane/$CHCl_3$ 1:1); mp 194–198 °C (lit. 196 °C).[14]

3.4. General procedure for the synthesis of dibromides

To a stirred solution of diol (1.0 equiv) in dry CH_2Cl_2 (120 mL), PBr_3 (3.0 equiv) was added and the reaction mixture was stirred at 0 °C for 12 h. The reaction mixture was poured into water (500 mL) and the organic layer was extracted with water (3×150 mL) followed by brine (200 mL) and then dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo to give dibromide, which was purified by recrystallization from hexane/CH_2Cl_2 (3:1).

3.4.1. Dibromide 3. Colourless solid; yield 92%; R_f 0.7 (hexane/$CHCl_3$ 3:1); mp 160–164 °C; IR (cm^{-1}) 2924, 1610, 1218, 1009, 770; ^{1}H NMR ($CDCl_3$) δ 7.33 (4H, d, *J* 8.6 Hz, Ph), 7.25 (2H, s, Ph), 7.21 (4H, d, *J* 8.6 Hz, Ph), 4.51 (4H, s, C*H*$_2$OPh), 4.44 (4H, s, C*H*$_2$Br), 3.97 (3H, s, O*Me*), 2.28 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) δ 154.4, 132.9, 131.6, 130.7, 130.6, 121.0, 120.8, 116.2, 62.3, 39.8, 27.8, 20.7; *m*/*z* 520 (M^+); Anal. Calcd for $C_{24}H_{24}O_3Br_2$: C, 55.38; H, 4.62. Found: C, 55.39; H, 4.63.

3.4.2. Dibromide 8. Colourless solid; yield 92%; R_f 0.65 (hexane/$CHCl_3$ 3:1); mp 136–139 °C (lit. 134 °C).[14]

3.5. General procedure for the synthesis of dithiols

A stirred solution of the dibromide (1.0 equiv) and thiourea (2.2 equiv) in THF (150 mL) was refluxed for 12 h. The mixture was cooled and the thiouronium salt was filtered and dried. The salt was dissolved in H_2O/THF (1:1) under nitrogen and KOH (2.2 equiv) was added. The reaction mixture was refluxed under nitrogen for 12 h, cooled and carefully quenched with 4 M HCl (40 mL). The solvent was removed

in vacuo and the crude product was purified by column chromatography using hexane/$CHCl_3$ (4:1) to give the corresponding dithiol.

3.5.1. Dithiol 4. Colourless solid; yield 78%; R_f 0.5 (hexane/$CHCl_3$ 1:3); mp 105–110 °C; IR (cm^{-1}) 2958, 1628, 1230, 1000, 664; ^1H NMR ($CDCl_3$) δ 7.26 (4H, d, *J* 8.4 Hz, Ph), 7.19 (2H, s, Ph), 6.95 (4H, d, *J* 8.4 Hz, Ph), 5.04 (4H, s, C*H*$_2$OPh), 3.85 (3H, s, O*Me*), 3.77 (4H, d, *J* 7.6 Hz, C*H*$_2$SH), 2.23 (3H, s, *Me*), 1.92 (2H, t, *J* 7.6 Hz, S*H*); ^{13}C NMR ($CDCl_3$) δ 158.0, 154.0, 133.6, 131.0, 130.1, 130.0, 129.3, 115.0, 65.4, 63.1, 62.9, 21.0; *m*/*z* 426 (M^+); Anal. Calcd for $C_{24}H_{26}O_3S_2$: C, 67.60; H, 6.10. Found: C, 67.61; H, 6.11.

3.5.2. Dithiol 16. Colourless solid; yield 65%; R_f 0.6 (hexane/$CHCl_3$ 1:3); mp 155–158 °C; IR (cm^{-1}) 2962, 1609, 1616, 1201, 1112, 701; ^1H NMR ($CDCl_3$) δ 7.09 (4H, d, *J* 8.8 Hz, Ph), 7.21–7.35 (4H, m, Ph), 6.76 (4H, d, *J* 8.8 Hz, Ph), 4.99 (4H, s, C*H*$_2$OPh), 3.53 (4H, d, *J* 7.3 Hz, C*H*$_2$SH), 1.12 (2H, t, *J* 7.1 Hz, CH$_2$S*H*); ^{13}C NMR ($CDCl_3$) δ 130.5, 130.2, 129.6, 128.6, 151.1, 115.0, 114.8, 68.1, 59.7; *m*/*z* 382 (M^+); Anal. Calcd for $C_{22}H_{22}O_2S_2$: C, 69.11; H, 5.76. Found: C, 69.12; H, 5.77.

3.6. General procedure for the synthesis of cyclophanes

A solution containing an equimolar amount of dithiol (1.0 equiv) and dichloride (1.0 equiv) in nitrogen degassed benzene (200 mL) was added dropwise over the period of 8 h to a well stirred solution of KOH (1.2 equiv) in dry ethanol (800 mL). After the addition was complete, the reaction mixture was stirred for 12 h and then evaporated to dryness. The residue was purified by column chromatography using hexane/$CHCl_3$ (1:1) as eluent.

3.6.1. Cyclophane 5. Pale yellow solid; yield 54%; R_f 0.45 (hexane/$CHCl_3$ 1:1); mp 143–147 °C; IR (cm^{-1}) 1716 (C=O).

3.6.2. Cyclophane 17. Pale yellow solid; yield 40%; R_f 0.5 (hexane/$CHCl_3$ 1:1); mp 154–159 °C; IR (cm^{-1}) 1715 (C=O).

3.7. General procedure for dithionate reduction

To a solution of cyclophane (1.0 equiv) in ethyl acetate (25 mL) was added $Na_2S_2O_4$ (2.2 equiv) in H_2O (15 mL) at 0 °C. The reaction mixture was stirred for 3 h and then evaporated to dryness. The residue was extracted with ethyl acetate (2×100 mL), washed with water (3×150 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography using $CHCl_3$/MeOH (49:1).

3.7.1. Cyclophane 6. Colourless solid; yield 50%; R_f 0.55 ($CHCl_3$/MeOH 3:1); mp 189–192 °C; IR (cm^{-1}) 3280 (br, OH); ^1H NMR ($CDCl_3$) δ 7.15 (2H, s, Ph), 7.04 (2H, s, Ph), 6.81 (2H, s, O*H*), 6.76 (4H, d, *J* 8.4 Hz, Ph), 6.68 (4H, d, *J* 8.4 Hz, Ph), 5.22 (4H, s, C*H*$_2$OPh), 3.77 (8H, s, C*H*$_2$SPh), 3.16 (3H, s, O*Me*), 2.06 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) δ 166.9, 162.4, 154.6, 134.5, 131.9, 131.7, 131.1, 129.4, 128.9, 122.9, 114.4, 65.2, 63.2, 62.2, 52.0, 20.9; *m*/*z* 560 (M^+); Anal. Calcd for $C_{32}H_{32}S_2O_5$: C, 68.57; H, 5.71. Found: C, 68.58; H, 5.72.

3.7.2. Cyclophane 18. Colourless solid; yield 35%; R_f 0.6 ($CHCl_3$/MeOH 3:1); mp 167–170 °C; IR (cm^{-1}) 3442 (br, OH); ^1H NMR ($CDCl_3$) δ 7.33 (4H, d, *J* 8.4 Hz, Ph), 7.25 (4H, m, Ph), 7.16 (2H, s, Ph), 6.94 (4H, d, *J* 8.4 Hz, Ph), 6.37 (2H, s, O*H*), 5.04 (4H, s, CH$_2$OPh), 3.98 (4H, s, CH$_2$SPh), 2.29 (4H, s, CH$_2$SPh); ^{13}C NMR ($CDCl_3$) δ 167.6, 152.1, 145.6, 133.1, 132.2, 129.2, 126.3, 125.8, 82.7, 40.8, 29.7, 27.4, 27.2; *m*/*z* 516 (M^+); Anal. Calcd for $C_{30}H_{28}S_2O_4$: C, 69.77; H, 5.43. Found: C, 69.78; H, 5.44.

3.8. General procedure for the synthesis of bicompartmental cyclophanes

A solution of cyclophane (1.0 equiv) and dihalide (1.0 equiv) was stirred with K_2CO_3 (4.0 equiv) in dry acetone for 120 h. The reaction mixture was then acidified with 4 M HCl (10 mL) and evaporated to dryness. The residue was extracted with CH_2Cl_2 (3×100 mL) and dried over anhydrous Na_2SO_4. Evaporation of the organic layer gave a residue, which was purified by column chromatography using hexane/$CHCl_3$ (1:4) to give the corresponding bicompartmental cyclophane.

3.8.1. Bicompartmental cyclophane 10. Colourless solid; yield 18%; R_f 0.55 (hexane/$CHCl_3$ 3:1); mp 190–192 °C; IR (cm^{-1}) 2915, 1650, 1550, 1300, 1235, 1019, 665; ^1H NMR ($CDCl_3$) δ 7.30 (8H, d, *J* 8.4 Hz, Ph), 7.28 (4H, s, Ph), 7.25 (2H, s, Ph), 6.99 (8H, d, *J* 8.4 Hz, Ph), 5.80 (12H, s, CH$_2$OPh), 4.60 (8H, s, C*H*$_2$SPh), 3.80 (6H, s, O*Me*), 2.32 (6H, s, *Me*); ^{13}C NMR ($CDCl_3$) 158.4, 154.2, 134.3, 133.3, 130.8, 129.9, 128.1, 114.9, 114.7, 71.6, 65.4, 65.2, 65.1, 63.1, 59.8, 21.0; *m*/*z* 918 (M^+); Anal. Calcd for $C_{56}H_{54}O_8S_2$: C, 73.20; H, 5.88: Found: C, 73.21; H, 5.89.

3.8.2. Bicompartmental cyclophane 11. Colourless solid; yield 16%; R_f 0.5 (hexane/$CHCl_3$ 3:1); mp 182–185 °C; IR (cm^{-1}) 2980, 1728, 1609, 1520, 1308, 1212, 666; ^1H NMR ($CDCl_3$) δ 7.30 (4H, d, *J* 8.6 Hz, Ph), 7.25 (4H, m, Ph), 7.21 (4H, d, *J* 8.6 Hz, Ph), 7.15 (2H, s, Ph), 6.82 (4H, d, *J* 8.6 Hz, Ph), 6.80 (4H, d, *J* 8.6 Hz, Ph), 5.15 (4H, s, C*H*$_2$OPh), 5.13 (4H, s, C*H*$_2$OPh), 4.66 (4H, s, C*H*$_2$OPh), 4.10 (4H, s, C*H*$_2$SPh), 4.09 (4H, s, C*H*$_2$SPh), 3.97 (3H, s, COO*Me*), 3.80 (3H, s, O*Me*), 2.27 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) 168.0, 152.8, 133.6, 133.1, 132.8, 132.4, 131.3, 131.0, 130.1, 129.8, 129.4, 128.9, 128.8, 127.5, 124.3, 124.0, 117.9, 115.3, 114.1, 111.2, 68.3, 38.8, 32.0, 29.5, 23.8, 23.1, 22.8; *m*/*z* 979 (M^+); Anal. Calcd for $C_{56}H_{51}O_{11}S_2N$: C, 68.78; H, 5.22; N, 1.43. Found: C, 68.79; H, 5.21; N, 1.44.

3.8.3. Bicompartmental cyclophane 12. Colourless solid; yield 16%; R_f 0.6 (hexane/$CHCl_3$ 3:1); mp123–126 °C; IR (cm^{-1}) 2958, 1653, 1206, 658; ^1H NMR ($CDCl_3$) δ 8.80 (4H, m, Ph), 7.50 (4H, d, *J* 8.4 Hz, Ph), 7.45–7.47 (4H, m, Ph), 7.41 (4H, d, *J* 8.4 Hz, Ph), 7.32 (4H, d, *J* 8.4 Hz, Ph), 7.12 (4H, d, *J* 8.4 Hz, Ph), 5.92 (4H, s, C*H*$_2$OPh), 4.33 (4H, s, C*H*$_2$OPh), 4.00 (4H, s, C*H*$_2$OPh), 3.98 (8H, s, C*H*$_2$SPh), 3.34 (3H, s, O*Me*), 2.04 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) δ 152.7, 151.7, 130.8, 129.5, 128.3, 127.8, 127.3, 126.9, 126.3, 125.9, 124.5, 124.4, 124.1, 123.8, 121.2,

118.2, 117.9, 115.5, 46.2, 44.1, 42.8, 40.7, 40.5, 40.3, 38.2; *m/z* 874 (M^+); Anal. Calcd for $C_{54}H_{50}O_7S_2$: C, 74.14; H, 5.72. Found: C, 74.15; H, 5.73.

3.8.4. Bicompartmental cyclophane 13. Colourless solid; yield 19%; R_f 0.55 (hexane/$CHCl_3$ 3:1); $[\alpha]_D^{25}$ −108 (*c* 0.2, $CHCl_3$); mp 175–178 °C; IR (cm^{-1}) 2915, 1729, 1646, 1201, 693; ^1H NMR ($CDCl_3$) δ 8.06 (2H, s, Ph), 8.02 (2H, s, Ph), 7.90–7.95 (4H, m, Binol *H*), 7.8 (4H, d, *J* 8.4 Hz, Ph), 7.41–7.44 (4H, m, Binol *H*), 7.34–7.35 (2H, m, Binol *H*), 7.25–7.30 (2H, m, Binol *H*), 7.12 (4H, d, *J* 8.4 Hz, Ph), 5.95 (4H, s, C*H*$_2$OPh), 4.45 (4H, s, C*H*$_2$OPh), 3.79 (4H, s, C*H*$_2$SPh), 3.78 (4H, s, C*H*$_2$SPh), 3.71 (3H, s, O*Me*), 2.09 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) δ 172.1, 152.6, 133.6, 133.4, 131.8, 131.3, 130.9, 130.7, 130.2, 129.4, 128.4, 128.2, 128.1, 127.7, 127.4, 127.2, 127.1, 126.9, 126.7, 126.3, 126.1, 125.9, 46.3, 42.9, 40.7, 40.6, 40.3, 28.2; *m/z* 926 (M^+); Anal. Calcd for $C_{56}H_{46}O_9S_2$: C, 72.57; H, 4.97. Found: C, 72.58; H, 4.98.

3.8.5. Bicompartmental cyclophane 19. Colourless solid; yield 19%; R_f 0.65 (hexane/$CHCl_3$ 3:1); mp 106–108 °C; IR (cm^{-1}) 2914, 1620, 1190, 997, 670; ^1H NMR ($CDCl_3$) δ 7.51 (4H, d, *J* 5.4 Hz, Ph), 7.37 (4H, d, *J* 5.4 Hz, Ph), 7.05 (4H, d, *J* 8.4 Hz, Ph), 6.91 (4H, d, *J* 8.4 Hz, Ph), 5.15 (12H, s, C*H*$_2$OPh), 4.55 (4H, s, C*H*$_2$SPh), 4.09 (4H, s, C*H*$_2$SPh); ^{13}C NMR ($CDCl_3$) δ 166.9, 162.4, 154.6, 134.5, 131.9, 131.7, 131.1, 129.4, 128.9, 114.4, 65.6, 65.2, 52.0, 30.1; *m/z* 830 (M^+); Anal. Calcd for $C_{52}H_{46}O_6S_2$: C, 75.18; H, 5.54. Found: C, 75.19; H, 5.55.

3.8.6. Bicompartmental cyclophane 20. Colourless solid; yield 17%; R_f 0.55 (hexane/$CHCl_3$ 3:1); mp 134–136 °C; IR (cm^{-1}) 2952, 1610, 1200, 1005, 665; ^1H NMR ($CDCl_3$) δ 7.39–7.40 (2H, s, Ph), 7.33 (4H, d, *J* 8.6 Hz, Ph), 7.25 (2H, s, Ph), 7.21 (4H, d, *J* 8.6 Hz, Ph), 7.15 (4H, m, Ph), 6.82 (4H, d, *J* 8.6 Hz, Ph), 6.77 (4H, d, *J* 8.6 Hz, Ph), 4.55 (4H, s, C*H*$_2$OPh), 4.50 (8H, s, C*H*$_2$OPh), 4.43 (4H, s, C*H*$_2$SPh), 4.37 (4H, s, C*H*$_2$SPh), 3.97 (3H, s, O*Me*), 3.80 (3H, s, *Me*); ^{13}C NMR ($CDCl_3$) δ 170.4, 162.9, 162.8, 158.2, 154.6, 154.4, 142.7, 142.5, 134.7, 132.8, 132.5, 131.3, 131.2, 130.7, 130.5, 121.1, 121.0, 120.8, 62.7, 62.3, 60.5, 39.8, 32.5, 27.8, 20.7; *m/z* 874 (M^+); Anal. Calcd for $C_{54}H_{50}O_7S_2$: C, 74.14; H, 5.72. Found: C, 74.15; H, 5.73.

3.8.7. Bicompartmental cyclophane 21. Colourless solid; yield 19%; R_f 0.6 (hexane/$CHCl_3$ 3:1); mp 157–160 °C; IR (cm^{-1}) 2928, 1720, 1650, 1525, 1358, 1218, 628; ^1H NMR ($CDCl_3$) δ 7.83 (4H, m, Ph), 7.59 (4H, m, Ph), 7.57 (4H, d, *J* 6.9 Hz, Ph), 7.52 (4H, d, *J* 6.9 Hz, Ph), 6.99 (4H, d, *J* 8.4 Hz, Ph), 6.66 (4H, d, *J* 8.4 Hz, Ph), 4.29 (4H, s, C*H*$_2$OPh), 4.10 (4H, s, C*H*$_2$OPh), 3.98 (4H, s, C*H*$_2$OPh), 3.86 (8H, s, C*H*$_2$SPh), 2.47 (3H, s, COOMe); ^{13}C NMR ($CDCl_3$) 163.4, 156.2, 140.1, 134.1, 132.9, 132.6, 132.0, 131.9, 130.5, 130.3, 129.9, 129.3, 129.2, 124.0, 115.8, 114.2, 113.9, 103.7, 77.6, 68.1, 67.9, 59.7, 53.4, 49.3, 35.0; *m/z* 933 (M^+); Anal. Calcd for $C_{54}H_{47}O_{10}S_2N$: C, 69.45; H, 5.04. Found: C, 69.46; H, 5.05.

3.8.8. Bicompartmental cyclophane 22. Colourless solid; yield 10%; R_f 0.5 (hexane/$CHCl_3$ 3:1); $[\alpha]_D^{25}$ −120 (*c* 0.2, $CHCl_3$); mp 118–120 °C; IR (cm^{-1}) 2958, 1710, 1201, 998, 706; ^1H NMR ($CDCl_3$) δ 7.95 (4H, d, *J* 9.2 Hz, Ph), 7.87–7.89 (4H, m, Binol *H*), 7.38 (2H, s, Ph), 7.36 (4H, d, *J* 9.2 Hz, Ph), 7.32–7.33 (4H, m, Ph), 7.30–7.31 (2H, m, Binol *H*), 7.28–7.29 (2H, m, Binol *H*), 7.25 (4H, s, Binol *H*), 5.11 (4H, s, C*H*$_2$OPh), 3.95 (4H, s, C*H*$_2$SPh), 3.38 (4H, s, C*H*$_2$SPh); ^{13}C NMR ($CDCl_3$) δ 188.2, 155.2, 153.2, 152.8, 152.0, 149.7, 146.3, 137.6, 136.0, 136.4, 135.8, 133.5, 132.8, 129.1, 128.9, 127.6, 127.5, 127.4, 127.2, 123.1, 83.3, 80.7, 80.2, 80.1, 27.8; *m/z* 882 (M^+); Anal. Calcd for $C_{54}H_{42}O_8S_2$: C, 73.47; H, 4.76. Found: C, 73.48; H, 4.77.

3.9. Complexation studies

Charge transfer complexation studies were carried out by preparing a 1×10^{-6} M solution of cyclophanes **10**, **19**, **20** and **21** with gradual addition of acceptor (2 mg) in DMF solvent (10 mL). Gradual addition of TCNQ to cyclophanes **10**, **19**, **20** and **21** rapidly increased the intensity of charge transfer bands at 751, 775 and 850 nm. The equilibrium constant was measured at 850 nm only. The equilibrium constant for the CT complex derived from **10**, **19**, **20** and **21** with TCNE was measured at 849 nm though absorption bands were also observed at 825 and 849 nm. Absorbance was measured at a suitable wavelength while the concentration of TCNQ and TCNE was varied and the concentration of the cyclophane receptor was kept constant. Plot of D_0/A (D_0 is the concentration of cyclophane and A is the concentration of acceptor) versus $1/A_0$ (A_0 is the absorbance of the complex at charge transfer transition) gave a straight line that indicated that the stoichiometry of the complex was 1:1. Applying Benesi–Hildebrabd equation, the reciprocal of the intercept on the *Y*-axis was used to provide ε^{AD} (ε of the donor–acceptor complex) and from the slope of the line K_c^{AD} (equilibrium constant of the donor–acceptor complex) was calculated. From this data the stability constants of the charge transfer complexes of cyclophanes **10**, **19**, **20** and **21** with the acceptors TCNQ and TCNE were determined.

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