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Synthesis, complexation studies and biological applications of some novel stilbenophanes, indolophanes and bisindolostilbenophanes via McMurry coupling

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Abstract—Various types of stilbenophanes, indolophanes and bisindolostilbenophanes were synthesized by intra-, inter- and tandem intra-, intermolecular McMurry coupling. Some of the indolophanes and bisindolostilbenophanes exhibited significant activity against the growth of various bacteria. Complexation of some of the cyclophanes with TCNQ has also been studied.

1. Introduction

The synthesis of [2,2]paracyclophane[1] by Cram and Steinberg was a revolutionary breakthrough in the field of cyclophane chemistry. In the synthesis of cyclophanes, the ring-closing step is often crucial[2] and various reagents and reaction conditions have been developed for this purpose. Many reagents containing transition metals were used for the ring-closing step in cyclophane synthesis. Samarium-catalyzed intramolecular pinacol coupling has been used in the synthesis of planar and chiral paracyclophanes.[3] Macrocyclic pyridinophanes[4] from α,ω-diynes were synthesized by cobalt-mediated [2+2+2] cycloaddition. Biaryl type cyclophanes[5] were synthesized from [2,5]metacyclophanebromides and triflates by Suzuki coupling. Electro-active tris-(tetrathiafulvaleno)dodecadehydro[18]annulenes[6] with ester substituents were synthesized by palladium-mediated cyclotrimerization of 4,5-diethynyl-tetrathiafulvalenes. Recently, ruthenium-catalyzed ring-closing metathesis proved to be a straightforward method to synthesize allenic cyclophanes.[7]

Microwave technology has been used for the synthesis of cationic cyclophanes.[8] The synthesis of thiacyclophanes by a one-pot reaction, utilizing a suitable dibromide and methanedithiolate generated from the double reduction of CS_2 with $NaBH_4$ has also been reported from this laboratory.[9] Recently, indolophanes and cylindrical indolophanes were synthesized by tandem alkylation methodology using NaH.[10] Ring-closing metathesis has been successfully used to synthesize symmetrical and unsymmetrical pyridinophanes.[11]

Use of low valent titanium for the synthesis of supramolecular structures has gained great impetus during recent times. An intramolecular McMurry coupling reaction was used as a key step in the enantiospecific synthesis of (+)-ipalbidine.[12] Molecular clocks[13] and artificial molecular devices such as light-driven molecular motors[14] were synthesized by the application of McMurry coupling. Symmetrical and unsymmetrical stilbenes[15] and highly distorted cone calyx-[4]arenes[16] and porphyrin derivatives[17] from tetrapyrroledialdehyde have also been synthesized using intramolecular McMurry coupling. Stilbenophanes are an interesting class of compounds and are synthesized by inter-[18] and intramolecular[19] McMurry coupling technique.

The synthesis of biologically active cyclophanes[20] has attracted supramolecular chemists in recent times. The indole moiety is present in a number of natural products[21] and known to be a bioactive nucleus.[22] Cyclophanes with an indole moiety, which are also called indolophanes[23] have received attention during recent times due to their applications in various fields. The synthesis of stilbene based indolophanes, bisindolostilbenophanes,[24] were reported recently from this laboratory by using McMurry coupling. We wish to report herein the synthesis and host–guest complexation studies of various types of stilbenophanes **4a–4d** and indolophanes **6a–6c**, **6d–6f**, **8a–8d** and **11a**-**11b** with TCNQ. We also wish to report the antimicrobial properties of various indolophanes towards three important types of pathogenic bacteria viz. *Salmonella typhi*, *Serratia marcensis* and *Streptococcus pneumoniae*.

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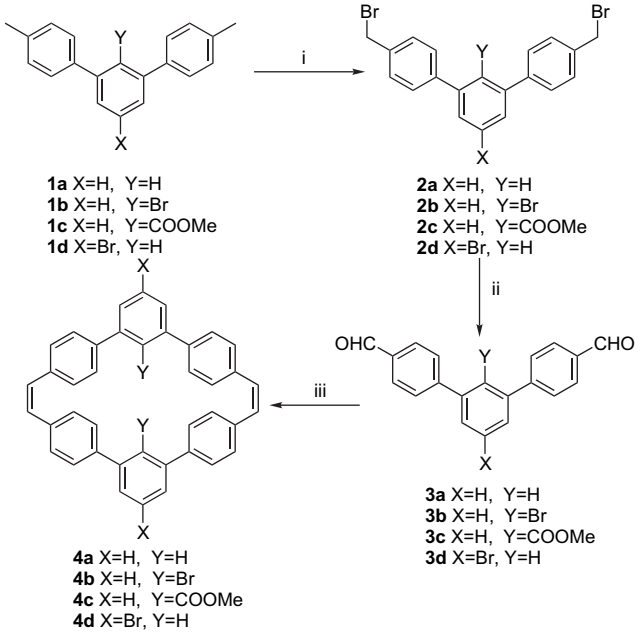
2. Results and discussion

2.1. Stilbenophanes with *m*-terphenyl moiety

m-Terphenyldibromide **2a**[25] obtained by the radical bromination of *m*-terphenyl **1a** was oxidized with tetrabutylammonium dichromate TBADC in $CHCl_3$ to give dialdehyde **3a** in 69% yield. Addition of 1 equiv of the dialdehyde to a solution of 20 equiv of $TiCl_4$ and 40 equiv of Zn in THF, followed by refluxing for 6 h resulted in the formation of stilbenophane **4a** (Scheme 1). Stilbenophanes **4b** and **4c** were synthesized by using similar methodology from the corresponding dialdehydes **3b** and **3c**. Reaction of *p*-tolylmagnesiumbromide with 2,4,6-tribromoiodobenzene in THF gave *m*-terphenyl **1d** in 78% yield. *m*-Terphenyl **1d**[25] on NBS bromination afforded the corresponding dibromide **2d**. Treatment of dibromide **2d** with TBADC in $CHCl_3$ gave dialdehyde **3d** in 69% yield. Dialdehyde **3d** underwent intermolecular McMurry coupling to give the stilbenophane **4d**.



Scheme 1. Reagents and conditions: (i) NBS (2.1 equiv), benzoyl peroxide, CCl_4, reflux, 40 h, 80% (**2a**), 80% (**2b**), 78% (**2c**), 80% (**2d**); (ii) TBADC, $CHCl_3$, reflux, 6 h, 69% (**3a**), 67% (**3b**), 60% (**3c**), 69% (**3d**); (iii) $TiCl_4$ (20 equiv), Zn (40 equiv), pyridine, THF, reflux, 6 h, 24% (**4a**), 18% (**4b**), 25% (**4c**), 24% (**4d**).

2.2. Synthesis of indolophanes with a smaller cavity

The synthetic utility of McMurry coupling has been investigated for the synthesis of indolophanes, another rare class of cyclophanes. *o*-Xylyl dibromide was reacted with indole-3-aldehyde in CH_3CN and 25% NaOH for 2 days to give preindolophane dialdehyde **5a** in 70% yield. Formation of **5a** was confirmed by ^1H NMR, ^{13}C NMR, mass spectral data and elemental analysis. When 1 equiv of dialdehyde **5a** was treated with 20 equiv of $TiCl_4$ and 40 equiv of Zn in THF under reflux, indolophane **6a** was obtained in 19% yield through intramolecular McMurry coupling. The structure of indolophane **6a** was further confirmed by ^1H NMR, ^{13}C NMR, FABMS spectral data and elemental analysis. Similarly *m*-xylyl dibromide and 2,6-bis(bromomethyl)pyridine

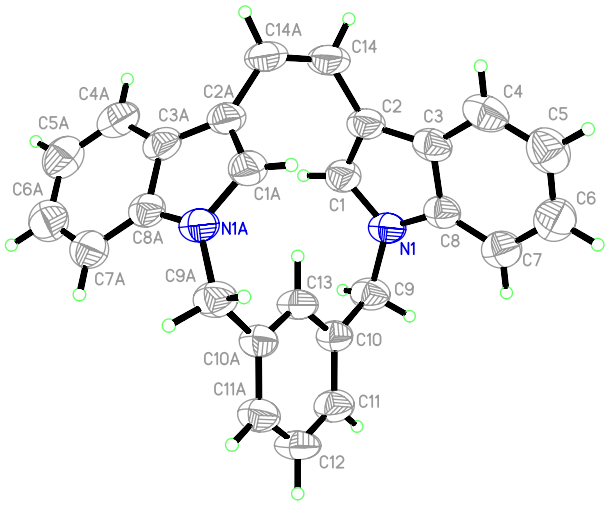


Figure 1. ORTEP diagram for the indolophane **6b**.

were treated with indole-3-aldehyde to give dialdehydes **5b** and **5c** in 72 and 74% yields, respectively. Dialdehydes **5b** and **5c** underwent intramolecular McMurry coupling to give indolophanes **6b** and **6c**. The structures of indolophanes **6b**[26] and **6c**[27] were thoroughly characterized by spectral and analytical data and further confirmed by single crystal X-ray analysis. The ORTEP diagrams of the cyclophanes **6b** and **6c** are shown in Figs. 1 and 2, respectively. However, the dialdehydes **5d–5f** with spacer units such as *p*-xylyl, 2,5-dimethoxy-*p*-xylyl and 4,4′-bis(methylene)-1,1′-biphenyl underwent intermolecular McMurry coupling to yield the indolophanes **6d–6f** (Scheme 2). From the above observation it is clear that dialdehydes **5a–5f** underwent coupling either intramolecularly or intermolecularly depending upon the spacer unit.

2.3. Synthesis of indolophanes with *m*-terphenyl spacer unit

The McMurry coupling was next used for the synthesis of indolophanes with a *m*-terphenyl spacer. Dibromide **2a** on N-alkylation with indole-3-aldehyde in 25% NaOH in CH_3CN afforded dialdehyde **7a**. The ^1H and ^{13}C NMR

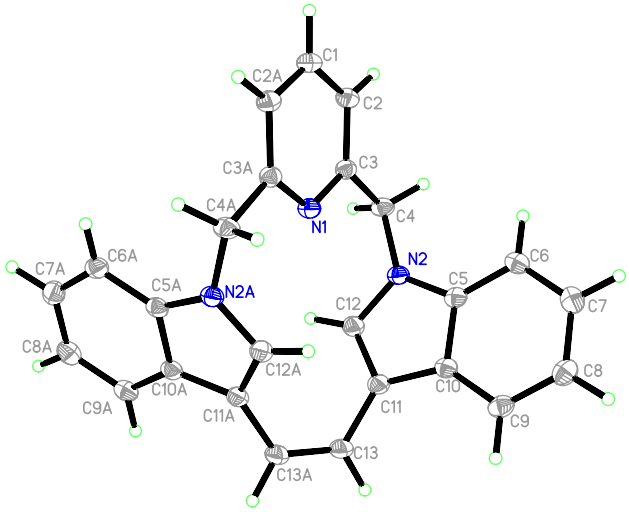
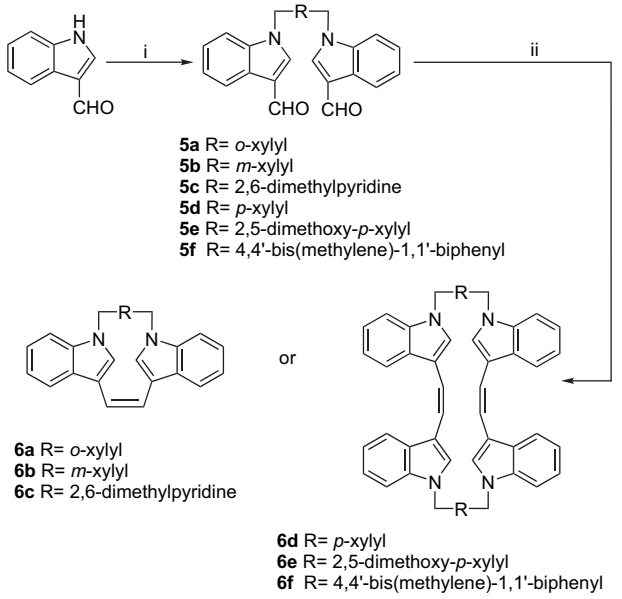
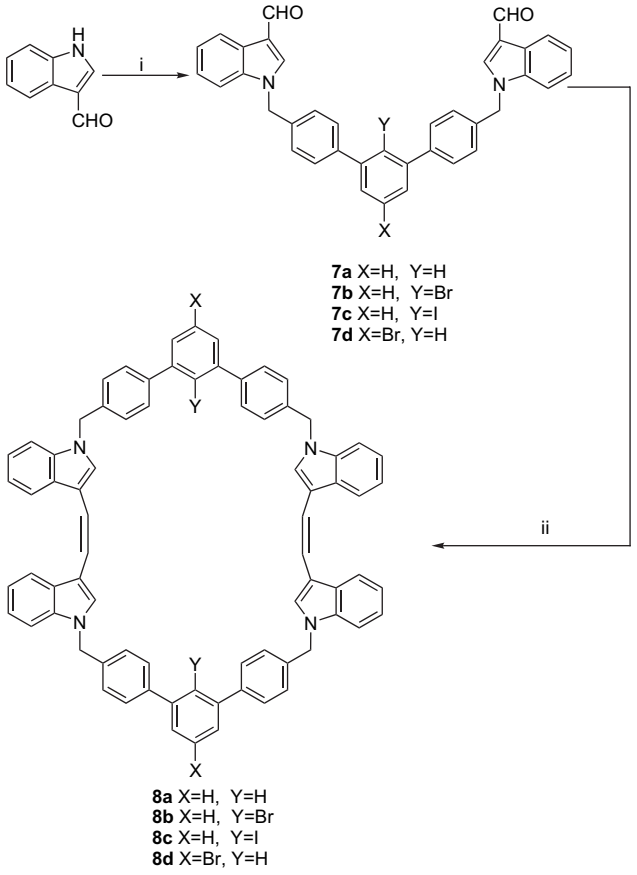


Figure 2. ORTEP diagram for the indolophane **6c**.



Scheme 2. Reagents and conditions: (i) *o*,*m*,2,6-dimethylpyridine, *p*-2,5-dimethoxy-*p*-xylyl, 4,4′-bis(bromomethyl)-1,1′-biphenyl dibromide, CH_3CN, 25% NaOH, 48 h, 70% (**5a**), 72% (**5b**), 74% (**5c**), 74% (**5d**), 66% (**5e**), 68% (**5f**); (ii)$TiCl_4$ (20 equiv), Zn (40 equiv), THF, pyridine, reflux overnight, 19% (**6a**), 24% (**6b**), 36% (**6c**), 20% (**6d**), 23% (**6e**), 18% (**6f**).

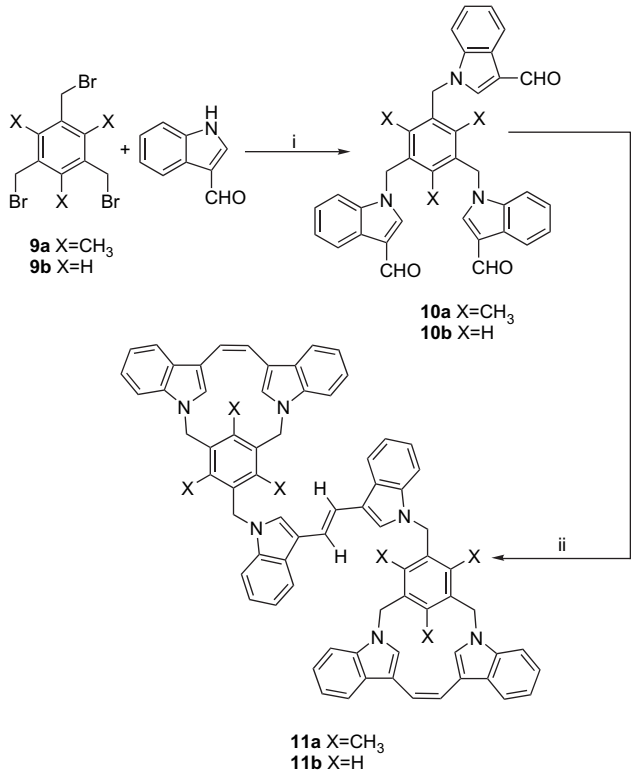
spectra are in accordance with the proposed structure. In the ^{1}H NMR spectrum, the NCH_2 and aldehydic protons appeared as a singlet at δ 5.40 and 10.01 in addition to aromatic protons. In the ^{13}C NMR spectrum, the NCH_2 carbons appeared at δ 54.8 and aldehydic carbons appeared at δ 184.8. Dialdehyde **7a** on treatment with low valent titanium under the conditions described earlier afforded indolophane **8a** in 8% yield. In the ^{1}H NMR spectrum, two singlets were observed for indolophane **8a** at δ 5.23 and 6.86 for NCH_2 and olefinic protons, in addition to aromatic protons. In the ^{13}C NMR spectrum, cyclophane **8a** showed 13 signals and the structure was further confirmed by FABMS spectrum and elemental analysis. Similar methodology was used to synthesize the indolophanes **8b**–**8d** with a *m*-terphenyl spacer unit (Scheme 3).



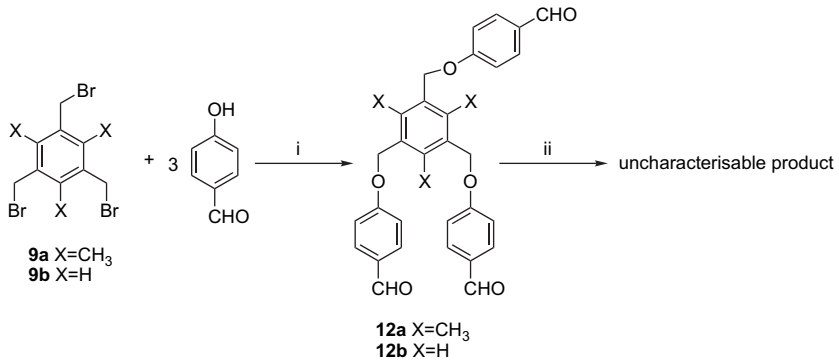
Scheme 3. Reagents and conditions: (i) **2a/2b/2c/2d**, CH_3CN, 25% NaOH, 48 h, 78% (**7a**), 76% (**7b**), 77% (**7c**), 70% (**7d**); (ii) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, pyridine, reflux overnight, 8% (**8a**), 6% (**8b**), 5% (**8c**), 8% (**8d**).

2.4. Synthesis of bisindolostilbenophanes by using tandem intra- and intermolecular McMurry coupling

Encouraged by the versatility of the McMurry coupling technique for the synthesis of stilbenophanes and indolophanes with various spacer units, the technique was further extended for the synthesis of cylindrical cyclophanes, which are a very rare class of cyclophanes. 1,3,5-Trimethyl-tris(bromomethyl)benzene[28] was N-alkylated by using indole-3-aldehyde to give the trialdehyde **10a** (Scheme 4). The trialdehyde **10a** on treatment with low valent titanium underwent both intra- and intermolecular McMurry coupling to afford only the bisindolostilbenophane **11a** in 24% yield and not the cylindrical cyclophane. The structure was further confirmed by ^{1}H NMR,[24b] ^{13}C NMR,[24b] FABMS spectra and elemental analysis. By similar methodology, 1,3,5-tris(bromomethyl)benzene was N-alkylated with indole-3-aldehyde to give trialdehyde **10b** in 78% yield. Trialdehyde **10b** also



Scheme 4. Reagents and conditions: (i) CH_3CN, 25% NaOH, rt, 48 h, 80% (**10a**), 78% (**10b**); (ii) $TiCl_4$ (30 equiv), Zn (60 equiv), THF, pyridine, reflux overnight, 24% (**11a**), 22% (**11b**).

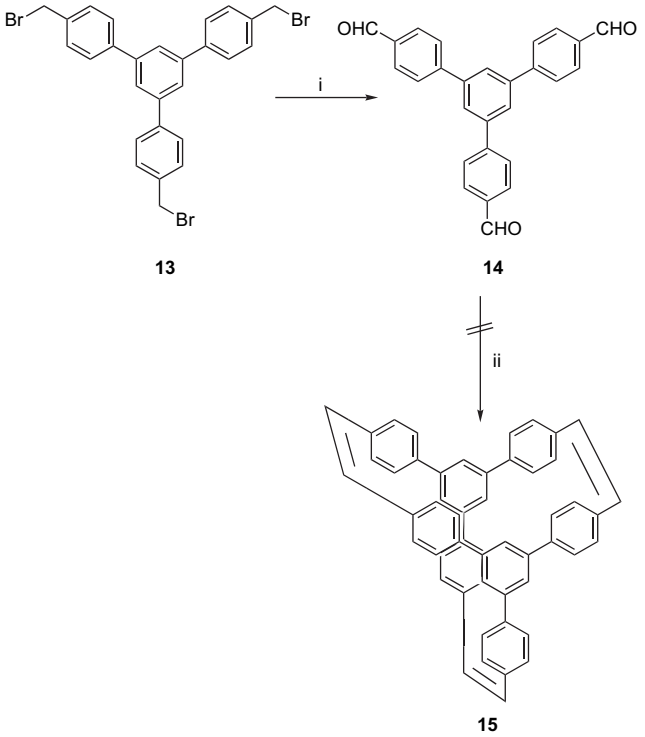


Scheme 5. Reagents and conditions: (i) DMF, K_2CO_3, 80 °C, 48 h, 65% (**12a**), 67% (**12b**); (ii) $TiCl_4$ (30 equiv), Zn (60 equiv), THF, pyridine, reflux, overnight.

underwent cyclization intra- and intermolecularly with low valent titanium in tandem nature to give bisindolostilbenophane **11b** in 22% yield. Tandem intra- and intermolecular McMurry coupling technique for the synthesis of bisindolostilbenophanes **11a** and **11b** is the first of its kind in the literature.

2.5. Synthesis of dioxastilbenophanes

McMurry coupling has been successfully used in the synthesis of dioxastilbenophanes.[29] Encouraged by such earlier reports from our laboratory, we focused our attention on the synthesis of cyclophanes from trialdehydes **12a** and **12b**. O-Alkylation of 1,3,5-trimethyl-tris(bromomethyl)benzene with *p*-hydroxybenzaldehyde afforded the trialdehyde **12a** in 65% yield. Similarly, O-alkylation of 1,3,5-tris(bromomethyl)benzene with *p*-hydroxybenzaldehyde afforded trialdehyde **12b**.[30] **12a** (1 equiv) was treated with $TiCl_4$ (30 equiv) and Zn (60 equiv) in THF under reflux gave uncharacterizable products (Scheme 5). This may be due to the non-rigidity of the trialdehyde due to the ether linkage, which can give some flexibility and hence could lead to polymerization. It is noteworthy to mention that trialdehydes **10a** and **10b** could undergo both intra- and intermolecular McMurry coupling to give cyclophanes **11a** and **11b**, whereas trialdehydes **12a** and **12b** gave only uncharacterizable products.



Scheme 6. Reagents and conditions: (i) TBADC, $CHCl_3$, reflux, 6 h, 69%; (ii) $TiCl_4$ (30 equiv), Zn (60 equiv), pyridine, THF, reflux, overnight.

2.6. Attempted synthesis of cylindrical stilbenophanes

Intermolecular McMurry coupling of dialdehydes **3a–3d** to give stilbenophanes **4a–4d** prompted us to explore this technique for the synthesis of cylindrical stilbenophane **15**. Tribromide **13**[31] on oxidation with TBADC in $CHCl_3$ afforded trialdehyde **14** in 69% yield. The structure of trialdehyde **14** was confirmed by ^1H NMR, ^{13}C NMR spectra and elemental analysis. Trialdehyde **14** on treatment with $TiCl_4$ and Zn under refluxing conditions afforded uncharacterizable products (Scheme 6).

3. Antibacterial studies of the indolophanes

S. No.	Indolophanes	Concentration (μg/mL)	Zone of inhibition[a] (mm)		
			Salmonella typhi	*Serratia marcescens*	*Streptococcus pneumoniae*
1	**6b**	25	4.4	6.0	5.0
		50	6.2	8.4	6.5
		75	9.6	10.4	9.7
2	**6c**	25	5.2	5.6	5.2
		50	8.2	8.2	6.2
		75	11.2	10.6	8.8
3	**8a**	25	4.9	5.3	4.9
		50	7.8	7.8	5.8
		75	10.9	10.3	8.5
4	**8d**	25	5.0	5.4	5.1
		50	8.0	8.0	6.0
		75	11.1	10.4	8.7
5	**11a**	25	5.0	5.4	5.8
		50	9.2	8.8	7.0
		75	12.0	10.2	10.2
6	**11b**	25	5.2	5.6	5.2
		50	8.2	8.2	6.2
		75	11.2	10.6	8.8

[a] Values of zone of inhibition are the mean of six replicates.

Bacterial cultures such as *S. typhi*, *S. marcensis* and *S. pneumoniae* were obtained from Madras Medical College, Chennai, India. All the cultures were maintained on nutrient agar medium. The activity was tested by disc diffusion method.[32]

3.1. Methodology

Each of the bacterium was inoculated in 50 mL of nutrient broth individually and was incubated in an environ shaker for 10 h at 150 rpm. About 150 μL of each of the broth culture was amended with 125 mL of molten nutrient agar medium and was plated. Indolophanes **6b**, **6c**, **8a**, **8d**, **11a** and **11b** each at 25, 50 and 75 μg/mL were prepared in $CHCl_3$ and were loaded onto filter paper disc. The discs were then dried and placed on each of the bacterium amended medium. The assay plates were incubated at 35 °C for 48 h. The zone of inhibition was measured, which was expressed in millimetre.

3.2. Results

While screening on nutrient agar medium, all the six indolophanes **6b**, **6c**, **8a**, **8d**, **11a** and **11b** at all the concentrations produced noteworthy inhibition against *S. typhi*, *S. marcensis* and *S. pneumoniae*. However, **6c**, **8a**, **8d**, **11a** and **11b** inhibited *S. typhi* significantly followed by *Serratia marcensis* when compared with *S. pneumoniae*. On the contrary, **6b** inhibited effectively *Serratia marcensis* than the others.

4. Complexation studies

Cyclophanes **6a–6c**, **11a** and **11b** exhibited charge transfer complexes with TCNQ among all the cyclophanes reported in this paper. Complexation studies of **6a–6c**, **11a** and **11b** with TCNE and PQT were not successful. Cyclophanes **6a–6c**, **11a** and **11b** show UV–vis absorption maxima at 241.3, 234, 274, 232 and 230 nm, respectively. However, the acceptor TCNQ shows absorption maxima at 274 nm. Cyclophanes **6a–6c**, **11a** and **11b** form a charge transfer complex with TCNQ as evidenced by the appearance of absorption maxima at 395, 398, 396, 398 and 397, respectively. The studies were carried out as outlined below.

In a typical experiment, 3 mL aliquot of a standard stock solution of the cyclophane in 1:1 mixture of $CHCl_3/CH_3CN$ was placed in a quartz cuvette. A known amount of the electron deficient guest molecule was added in incremental amounts and changes in absorbance of the CT bands were recorded. Table 1 shows the CT complexation studies of **6b** with various concentrations of TCNQ. A plot of [concn of cyclophane]/absorbance versus 1/concentration of guest was linear (Fig. 3). From the slope and the intercept values K_a (K_a=intercept×slope^{-1}) and ε (ε=intercept^{-1}) were evaluated. The plots were linear and suggest that the predominant species in the solution was 1:1 complex. K_a and ε values of CT complexes formed from **6a–6c**, **11a** and **11b** are shown in Table 2.

Table 1. Benesi–Hildebrand treatment data of the CT complex formed between the cyclophane **6b** and TCNQ λ_{max}=398 nm. Concentration of cyclophane **6b**=10^{-5} M

Concentration of guest, [X] (M)	Absorbance (*A*)	[Y]/*A* (M)	1/[X] (M^{-1})
4.9×10^{-6}	0.500	0.00002	204,081
9.8×10^{-6}	0.978	0.0000102	102,040
14.7×10^{-6}	1.424	0.000007	68,027
19.6×10^{-6}	1.811	0.0000055	51,020
24.5×10^{-6}	2.088	0.0000047	40,816

K_a=7.14×10^2 M^{-1}, ε=2×10^7 M^{-1} cm^{-1}, SD=99.97 (%).

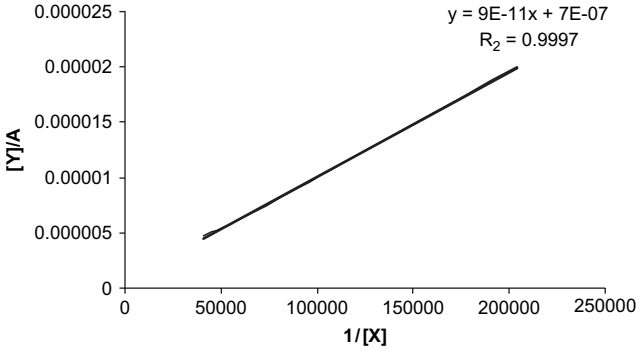


Figure 3. Plot between 1/[*X*] and [*Y*]/*A* for compound **6b**.

Table 2. Complexation of TCNQ with cyclophanes **6a–6c**, **11a** and **11b**

Cyclophane	K_a	ε
6a	1×10^3	2×10^8
6b	7.14×10^2	2×10^7
6c	7.936×10^3	1.4×10^6
11a	2.5×10^4	2×10^5
11b	2.00×10^3	1.66×10^5

Cyclophane **6c** complexes with TCNQ more strongly than **6b**, which is followed by **6a**. In the case of **11a** and **11b**, the former one complexes more effectively than the latter.

5. Conclusion

Various types of stilbenophanes, indolophanes and bisindolostilbenophanes were obtained by intra-, inter-, tandem intra- and intermolecular McMurry coupling. Some of the indolophanes exhibited noteworthy inhibition against *S. typhi*, *S. marcescens* and *S. pneumoniae.* Charge transfer studies were carried out with some indolophanes and TCNQ.

6. Experimental

6.1. General

All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL 400 and JEOL 500 spectrometers at 500, 400, 125 and 100 MHz, respectively. Mass spectra were recorded on a JEOL DX 303 HF spectrometer and FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer.

6.2. Procedure A for NBS bromination

Freshly recrystallized *N*-bromosuccinimide (NBS) (92 mmol/135 mmol) was added in 5–6 equal portions at

6 h apart to a solution of methyl aryl 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 40 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 chromatographed (SiO_2) from hexane/$CHCl_3$ and then recrystallized.

6.3. General procedure B for oxidation of dibromide to dialdehyde

Tetrabutylammonium dichromate (TBADC) was prepared by stirring a heterogeneous mixture of tetrabutylammonium hydrogen sulfate (100 mmol) in CH_2Cl_2 (100 mL) and K_2CrO_4 (250 mmol) in water (100 mL) at room temperature for 2 h. The reagent was obtained from the organic layer as orange coloured pasty mass. The dibromide was dissolved in $CHCl_3$, mixed with TBADC (1.32 equiv) and refluxed for 6 h. $CHCl_3$ was removed under reduced pressure and the resulting pasty mass was mixed with column silica gel and chromatographed. Elution with a mixture of $CHCl_3$/hexane (2:3) gave the respective dialdehyde.

6.4. General procedure C for N-alkylation

To a solution of indole-3-aldehyde (7.5 mmol) in CH_3CN (50 mL), NaOH (25%) solution was added and stirred for 10 min. The bromide (15.9 mmol/22.5 mmol) in acetonitrile (20 mL) was added at once and stirred at room temperature for 48 h. After completion of the reaction CH_3CN was removed under reduced pressure and the reaction mixture was extracted with CH_2Cl_2 (300 mL), washed with water, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed using hexane and ethyl acetate (3:2) as eluent.

6.5. General procedure D for McMurry coupling

A solution of zero valent titanium prepared from $TiCl_4$ (20 equiv/30 equiv) with zinc (40 equiv/60 equiv) in dry THF (75 mL) under a nitrogen atmosphere at 0 °C was allowed to attain room temperature after 0.5 h and then refluxed for 1 h. Aldehyde was added in one lot to the freshly prepared low valent titanium. After the addition, the reaction mixture was refluxed overnight. The reaction mixture was cooled and then quenched with saturated K_2CO_3 solution. The precipitated inorganic material was removed by filtration. The precipitate was thoroughly washed with THF for several times and the combined THF extract was removed under reduced pressure. The residue was then dissolved in water and extracted in $CHCl_3$ (200 mL), washed with water (2×200 mL), brine (100 mL) and dried over Na_2SO_4. Crude product, obtained after evaporation of $CHCl_3$, was purified by column chromatography.

6.5.1. Compound 1d. To a stirred solution of *p*-tolylmagnesiumbromide (prepared from 31.1 g, 18.1 mmol of *p*-bromotoluene and 4.41 g, 18.1 mmol of Mg in 40 mL of THF) under N_2 atmosphere was added dropwise 2,4,6-tribromobenzene in THF (150 mL) (5.6 mmol) over 1 h at reflux. Stirring was continued for 6 h, after which the reaction was quenched with cold, dilute HCl (40 mL). Then THF was removed under reduced pressure and the aqueous solution was extracted several times with CH_2Cl_2. Combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. The residue obtained after solvent removal was chromatographed in hexane to give **1d** as a white solid in 78% (15 g); mp 126–130 °C; [found: C, 71.25; H, 5.10. $C_{20}H_{17}Br$ requires C, 71.23; H, 5.08%]; δ_H (500 MHz, $CDCl_3$) 7.67–7.66 (m, 3H, Ph); 7.51–7.49 (m, 4H, Ph); 7.27–7.25 (m, 4H, Ph); 2.41 (s, 6H, C*H*$_3$); δ_C (125 MHz, $CDCl_3$) 143.6, 138.0, 137.0, 129.7, 128.5, 127.1, 124.5, 123.3, 21.3; *m*/*z* (EI) 337 (M^+), 339 (M^++2).

6.5.2. Compound 2d. Following the general procedure A, dibromide **2d** was obtained as a light yellow colour solid in 80% yield; mp 148–151 °C; [found: C, 48.51; H, 3.02. $C_{20}H_{15}Br_3$ requires C, 48.52; H, 3.05%]; δ_H (500 MHz, $CDCl_3$) 7.70–7.65 (m, 3H, Ph); 7.58–7.55 (m, 4H, Ph); 7.49–7.47 (m, 4H, Ph); 4.54 (s, 4H, C*H*$_2$); δ_C (125 MHz, $CDCl_3$) 143.0, 139.8, 137.8, 129.8, 129.2, 127.7, 127.5, 124.8, 33.1; *m*/*z* (EI) 495 (M^+), 497 (M^++2), 499 (M^++4).

6.5.3. Compound 3a. Following the general procedure B, dialdehyde **3a** was obtained as a white solid in 69% yield; mp 204–208 °C; [found: C, 83.92; H, 4.95. $C_{20}H_{14}O_2$ requires C, 83.90; H, 4.93%]; IR (KBr) ν_{max}: 1686 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.08 (s, 2H, C*H*O); 7.99 (d, 4H, *J* 8.6 Hz, Ph); 7.87 (s, 1H, Ph); 7.81 (d, 4H, *J* 8.0 Hz, Ph); 7.69–7.67 (m, 2H, Ph); 7.62–7.60 (m, 1H, Ph); δ_C (125 MHz, $CDCl_3$) 191.9, 146.7, 140.6, 135.4, 130.4, 129.7, 127.8, 127.4, 126.5; *m*/*z* (EI) 286 (M^+).

6.5.4. Compound 3b. Following the general procedure B, dialdehyde **3b** was obtained as a light yellow colour solid in 67% yield; mp 215–217 °C; [found: C, 65.75; H, 3.56. $C_{20}H_{13}BrO_2$ requires C, 65.77; H, 3.59%]; IR (KBr) ν_{max}: 1696 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.06 (s, 2H, C*H*O); 7.95–7.91 (m, 4H, Ph); 7.85–7.81 (m, 7H, Ph); δ_C (125 MHz, $CDCl_3$) 191.6, 145.0, 143.1, 137.9, 132.6, 130.2, 129.8, 127.3, 124.9; *m*/*z* (EI) 365 (M^+), 367 (M^++2).

6.5.5. Compound 3c. Following the general procedure B, dialdehyde **3c** was obtained as a light yellow colour solid in 60% yield; mp 209–211 °C; [found: C, 76.70: H, 4.73. $C_{22}H_{16}O_4$ requires C, 76.73; H, 4.68%]; IR (KBr) ν_{max}: 1699, 1720 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.06 (s, 2H, C*H*O); 7.93 (d, 4H, *J* 8.0 Hz, Ph); 7.61–7.55 (m, 3H, Ph); 7.45–7.44 (m, 4H, Ph); 3.37 (s, 3H, COOC*H*$_3$); δ_C (125 MHz, $CDCl_3$) 192.0, 169.2, 146.5, 139.6, 135.6, 132.6, 130.0, 129.9, 129.2, 52.2, 30.5; *m*/*z* (EI) 345 (M^+).

6.5.6. Compound 3d. Following the general procedure B, dialdehyde **3b** was obtained as a light yellow colour solid in 69% yield; mp 223–226 °C; [found: C, 65.79; H, 3.61. $C_{20}H_{13}BrO_2$ requires C, 65.77; H, 3.59%]; IR (KBr) ν_{max}: 1703 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.07 (s, 2H, C*H*O); 7.99 (s, 2H, Ph); 7.97 (s, 2H, Ph); 7.79–7.75 (m, 7H, Ph); δ_C (125 MHz, $CDCl_3$) 191.7, 145.2, 142.5, 135.9, 130.5, 130.2, 127.9, 125.2, 123.8; *m*/*z* (EI) 365 (M^+), 367 (M^++2).

6.5.7. Compound 4a. Following the general procedure D, stilbenophane **4a** was obtained as a light yellow colour solid in 24% yield; mp >300 °C; [found: C, 94.42; H, 5.53. $C_{40}H_{28}$ requires C, 94.45; H, 5.55%]; δ_H (400 MHz,

$CDCl_3$) 7.50–7.42 (m, 8H, Ph); 7.36 (d, 8H, *J* 8.2 Hz, Ph); 7.06 (d, 8H, *J* 8.2 Hz, Ph); 6.74 (s, 4H, C*H*=C*H*); δ_C (100.4 MHz, $CDCl_3$) 141.6, 140.2, 136.6, 131.0, 129.8, 129.2, 126.9, 125.0, 124.9; *m/z* (FABMS) 508 (M^+).

6.5.8. Compound 4b. Following the general procedure D, stilbenophane **4b** was obtained as a light yellow colour solid in 18% yield; mp >300 °C; [found: C, 72.08; H, 3.97. $C_{40}H_{26}Br_2$ requires C, 72.04; H, 3.93%]; δ_H (400 MHz, $CDCl_3$) 7.42–7.32 (m, 6H, Ph); 7.25 (d, 8H, *J* 8.3 Hz, Ph); 6.91 (d, 8H, *J* 8.3 Hz, Ph); 6.78 (s, 4H, C*H*=C*H*); δ_C (100.4 MHz, $CDCl_3$) 142.7, 139.6, 135.5, 130.7, 128.9, 128.1, 127.1, 125.2, 124.7; *m/z* (FABMS) 666 (M^+), 668 (M^++2), 670 (M^++4).

6.5.9. Compound 4c. Following the general procedure D, stilbenophane **4c** was obtained as a light yellow colour solid in 25% yield; mp >300 °C; [found: C, 84.62; H, 5.20. $C_{44}H_{32}O_4$ requires C, 84.59; H, 5.16%]; δ_H (400 MHz, $CDCl_3$) 7.48–7.41 (m, 6H, Ph); 7.36 (d, 8H, *J* 7.8 Hz, Ph); 7.22 (d, 8H, *J* 7.8 Hz, Ph); 6.86 (s, 4H, C*H*=C*H*); 3.37 (s, 6H, COOCH_3); δ_C (100.4 MHz, $CDCl_3$) 205.5, 140.5, 139.7, 138.1, 130.4, 129.4, 127.2, 127.0, 126.4, 125.7, 51.5; *m/z* (FABMS) 624 (M^+).

6.5.10. Compound 4d. Following the general procedure D, stilbenophane **4d** was obtained as a light yellow colour solid in 24% yield; mp >300 °C; [found: C, 72.02; H, 3.91. $C_{40}H_{26}Br_2$ requires C, 72.04; H, 3.93%]; δ_H (400 MHz, $CDCl_3$) 7.64–7.42 (m, 6H, Ph); 7.31 (d, 8H, *J* 8.3 Hz, Ph); 7.04 (d, 8H, *J* 7.8 Hz, Ph); 6.74 (s, 4H, C*H*=C*H*); δ_C (100.4 MHz, $CDCl_3$) 143.9, 139.0, 133.4, 128.7, 127.0, 126.6, 126.0, 123.6, 123.3; *m/z* (FABMS) 666 (M^+), 668 (M^++2), 670 (M^++4).

6.5.11. Compound 5a. Following the general procedure C, dialdehyde **5a** was obtained as a light brown colour solid in 70% yield; mp 156–158 °C; [found: C, 79.59; H, 5.11; N, 7.18. $C_{26}H_{20}N_2O_2$ requires C, 79.57; H, 5.14; N, 7.14%]; IR (KBr) ν_{max}: 1647 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.90 (s, 2H, C*H*O); 8.05 (d, 2H, *J* 8.1 Hz, Ar); 7.42 (s, 2H, Ar); 7.41–7.40 (m, 2H, Ar); 7.27–7.24 (m, 4H, Ar); 7.16–7.11 (m, 4H, Ar); 5.24 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.8, 137.5, 137.4, 133.2, 129.9, 129.8, 125.5, 124.6, 123.6, 122.4, 118.9, 110.0, 48.4; *m/z* (EI) 392 (M^+).

6.5.12. Compound 5b. Following the general procedure, C dialdehyde **5b** was obtained as a light brown colour solid in 72% yield; mp 130–132 °C; [found: C, 79.55; H, 5.12; N, 7.19. $C_{26}H_{20}N_2O_2$ requires C, 79.57; H, 5.14; N, 7.14%]; IR (KBr) ν_{max}: 1631 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.97 (s, 2H, C*H*O); 8.31 (d, 2H, *J* 7.5 Hz, Ar); 7.65 (s, 2H, Ar); 7.33–7.31 (m, 4H, Ar); 7.29–7.25 (m, 4H, Ar); 7.20–7.18 (m, 1H, Ar); 6.89 (s, 1H, Ar); 5.27 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.7, 138.3, 137.3, 136.7, 130.1, 127.1, 125.6, 124.4, 123.3, 122.3, 118.7, 110.3, 50.7; *m/z* (EI) 392 (M^+).

6.5.13. Compound 5c. Following the general procedure C, dialdehyde **5c** was obtained as a light brown colour solid in 74% yield; mp 178–182 °C; [found: C, 76.34; H, 4.89; N, 10.65. $C_{25}H_{19}N_3O_2$ requires C, 76.32; H, 4.87; N, 10.68%]; IR (KBr) ν_{max}: 1652 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.01 (s, 2H, C*H*O); 8.32 (d, 2H, *J* 7.7 Hz, Ar); 7.79 (s, 2H, Ar); 7.54 (m, 1H, Ar); 7.33–7.30 (m, 2H, Ar); 7.28–7.25 (m, 4H, Ar); 6.89 (d, 2H, *J* 7.7 Hz, Ar); 5.44 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.8, 155.8, 138.9, 138.7, 137.4, 124.4, 123.3, 122.3, 120.7, 110.4, 52.5; *m/z* (EI) 393 (M^+).

6.5.14. Compound 5d. Following the general procedure C, dialdehyde **5d** was obtained as a light brown colour solid in 74% yield; mp 187–190 °C; [found: C, 79.58; H, 5.16; N, 7.11. $C_{26}H_{20}N_2O_2$ requires C, 79.57; H, 5.14; N, 7.14%]; IR (KBr) ν_{max}: 1657 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.00 (s, 2H, C*H*O); 8.33 (m, 2H, Ar); 7.74 (s, 2H, Ar); 7.52 (d, 4H, *J* 8.4 Hz, Ar); 7.35–7.30 (m, 2H, Ar); 7.25–7.22 (m, 4H, Ar); 5.39 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.8, 140.5, 138.6, 137.5, 134.7, 127.8, 125.6, 124.3, 123.3, 122.3, 118.7, 110.5, 50.7; *m/z* (EI) 392 (M^+).

6.5.15. Compound 5e. Following the general procedure C, dialdehyde **5e** was obtained as a light brown colour solid in 66% yield; mp 196–200 °C; [found: C, 74.30; H, 5.37; N, 6.21. $C_{28}H_{24}N_2O_4$ requires C, 74.32; H, 5.35; N, 6.19%]; IR (KBr) ν_{max}: 1647 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.98 (s, 2H, C*H*O); 8.31–8.28 (m, 2H, Ar); 7.72 (s, 2H, Ar); 7.39–7.38 (m, 2H, Ar); 7.31–7.30 (m, 2H, Ar); 7.25 (s, 2H, Ar); 6.51 (s, 2H); 5.30 (s, 4H, NCH_2); 3.64 (s, 6H, OCH_3); δ_C (125 MHz, $CDCl_3$) 184.8, 151.2, 138.8, 137.6, 125.5, 124.5, 124.2, 123.1, 122.2, 118.4, 111.8, 110.4, 56.1, 46.0; *m/z* (EI) 452 (M^+).

6.5.16. Compound 5f. Following the general procedure C, dialdehyde **5f** was obtained as a light brown colour solid in 68% yield; mp 136–140 °C; [found: C, 82.05; H, 5.19; N, 5.99. $C_{32}H_{24}N_2O_2$ requires C, 82.03; H, 5.16; N, 5.98%]; IR (KBr) ν_{max}: 1651 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.01 (s, 2H, C*H*O); 8.34–8.32 (m, 2H, Ar); 7.74 (s, 4H, Ar); 7.54–7.51 (m, 2H, Ar); 7.35–7.30 (m, 4H, Ar); 7.25–7.20 (m, 6H, Ar); 5.39 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.7, 140.5, 138.5, 137.5, 134.8, 127.8, 125.6, 124.3, 123.2, 122.3, 118.7, 110.5, 50.7; *m/z* (EI) 468 (M^+).

6.5.17. Compound 6a. Following the general procedure D, indolophane **6a** was obtained as a light yellow colour solid in 19% yield; mp 126 °C; [found: C, 86.61, H, 5.63; N, 7.79. $C_{26}H_{20}N_2$ requires C, 86.64; H, 5.59; N, 7.77%]; δ_H (400 MHz, $CDCl_3$) 8.17 (d, 2H, *J* 7.4 Hz, Ar); 7.79 (d, 2H, *J* 8.6 Hz, Ar); 7.64 (t, 2H, *J* 7.5 Hz, Ar); 7.46 (d, 4H, *J* 8.6 Hz, Ar); 7.29 (t, 2H, *J* 7.5 Hz, Ar); 6.72 (s, 2H, C*H*=C*H*); 6.30 (s, 2H, Ar); 5.80 (s, 4H, NCH_2); δ_C (100.4 MHz, $CDCl_3$) 153.9, 136.4, 130.3, 129.5, 128.9, 125.1, 124.2, 120.0, 119.4, 112.0, 108.5, 46.2; *m/z* (FABMS) 360 (M^+).

6.5.18. Compound 6b. Following the general procedure D, indolophane **6b** was obtained as a light yellow colour solid in 24% yield; mp 297 °C; [found: C, 86.68; H, 5.61; N, 7.77. $C_{26}H_{20}N_2$ requires C, 86.64; H, 5.59; N, 7.77%]; δ_H (400 MHz, $CDCl_3$) 7.59 (d, 2H, *J* 7.3 Hz, Ar); 7.23 (d, 2H, *J* 7.8 Hz, Ar); 7.18–7.14 (m, 3H, Ar); 7.12 (d, 2H, *J* 7.8 Hz, Ar); 7.07 (d, 2H, *J* 7.3 Hz); 6.79 (s, 2H, C*H*=C*H*); 6.49 (s, 2H, Ar); 6.09 (s, 1H); 4.98 (s, 4H, NCH_2); δ_C (100.4 MHz, $CDCl_3$) 139.0, 138.0, 128.5, 128.1, 126.1, 125.0, 122.2, 120.1, 119.7, 114.2, 110.1, 49.6; *m/z* (FABMS) 360 (M^+).

6.5.19. Compound 6c. Following the general procedure D, indolophane **6c** was obtained as a light yellow colour solid in 36% yield; mp 228–232 °C; [found: C, 83.09; H, 5.32; N, 11.64. $C_{25}H_{19}N_3$ requires C, 83.08; H, 5.30; N, 11.63%]; δ_H (500 MHz, $CDCl_3$) 7.72 (d, 2H, *J* 7.7 Hz, Ar); 7.54 (t, 1H, *J* 7.6 Hz, Ar); 7.31–7.29 (m, 2H, Ar); 7.19 (m, 1H, Ar); 7.17–7.13 (m, 4H, Ar); 7.11 (s, 1H, Ar); 6.86 (s, 2H, Ar); 6.82 (s, 2H, C*H*=C*H*); 5.17 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 155.2, 136.9, 136.6, 131.2, 128.9, 122.9, 121.1, 120.2, 119.4, 119.0, 111.7, 108.9, 49.8; *m*/*z* (FABMS) 361 (M^+).

6.5.20. Compound 6d. Following the general procedure D, indolophane **6d** was obtained as a light yellow colour solid in 20% yield; mp 135 °C; [found: C, 86.68; H, 5.61; N, 7.76. $C_{52}H_{40}N_4$ requires C, 86.64; H, 5.59; N, 7.77%]; δ_H (400 MHz, $CDCl_3$) 7.50 (d, 8H, *J* 7.8 Hz, Ar); 7.14 (d, 8H, *J* 8.3 Hz, Ar); 7.03 (d, 4H, *J* 7.8 Hz, Ar); 7.07 (d, 4H, *J* 7.8 Hz); 6.94 (s, 4H, Ar); 6.77 (s, 4H, C*H*=C*H*); 5.13 (s, 8H, NCH_2); δ_C (125 MHz, $CDCl_3$) 140.0, 137.1, 136.7, 129.0, 127.4, 127.3, 125.9, 121.7, 119.2, 118.9, 111.1, 109.5, 49.6; *m*/*z* (FABMS) 720 (M^+).

6.5.21. Compound 6e. Following the general procedure D, indolophane **6e** was obtained as a light yellow colour solid in 23% yield; mp 134 °C; [found: C, 79.94; H, 5.77; N, 6.68. $C_{56}H_{48}N_4O_4$ requires C, 79.98; H, 5.75; N, 6.66%]; δ_H (400 MHz, $CDCl_3$) 7.48 (d, 4H, *J* 7.8 Hz, Ar); 7.21 (d, 4H, *J* 8.3 Hz, Ar); 7.09 (m, 8H, Ar); 7.02 (t, 4H, *J* 7.3 Hz, Ar); 6.80 (s, 4H, C*H*=C*H*); 6.24 (s, 4H, Ar); 5.11 (s, 8H, NCH_2); 3.49 (s, 12H, OCH_3); δ_C (100.4 MHz, $CDCl_3$) 150.8, 136.8, 128.8, 126.0, 125.9, 121.5, 118.9, 118.6, 111.1, 110.6, 109.5, 55.9, 55.8, 44.5; *m*/*z* (FABMS) 840 (M^+).

6.5.22. Compound 6f. Following the general procedure D, indolophane **6f** was obtained as a light yellow colour solid in 18% yield; mp 137 °C; [found: C, 88.06; H, 5.55; N, 6.43. $C_{64}H_{48}N_4$ requires C, 88.04; H, 5.54; N, 6.42%]; δ_H (400 MHz, $CDCl_3$) 7.52 (d, 8H, *J* 7.3 Hz, Ar); 7.38 (d, 8H, *J* 8.3 Hz, Ar); 7.18–7.07 (m, 20H, Ar); 6.84 (s, 4H, C*H*=C*H*); 5.20 (s, 8H, NCH_2); δ_C (100.4 MHz, $CDCl_3$) 137.0, 136.7, 129.0, 127.3, 127.2, 125.8, 121.7, 119.1, 118.8, 110.5, 109.4, 49.5; *m*/*z* (FABMS) 872 (M^+).

6.5.23. Compound 7a. Following the general procedure C, dialdehyde **7a** was obtained as a light brown colour solid in 78% yield; mp 218–220 °C; [found: C, 83.84; H, 5.16; N, 5.16. $C_{38}H_{28}N_2O_2$ requires C, 83.80; H, 5.18; N, 5.14%]; IR (KBr) ν_{max}: 1650 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.01 (s, 2H, C*H*O); 8.34–8.32 (m, 2H, Ar); 7.75 (s, 2H, Ar); 7.59 (d, 4H, *J* 8.6 Hz, Ar); 7.54–7.49 (m, 4H, Ar); 7.37–7.34 (m, 2H, Ar); 7.33–7.30 (m, 4H, Ar); 7.26–7.25 (m, 4H, Ar); 5.40 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.8, 141.3, 141.0, 137.5, 134.6, 128.0, 127.8, 126.5, 126.0, 125.6, 124.3, 123.3, 122.3, 118.6, 110.5, 50.8; *m*/*z* (EI) 545 (M^+).

6.5.24. Compound 7b. Following the general procedure C, dialdehyde **7b** was obtained as a light brown colour solid in 76% yield; mp 132–134 °C; [found: C, 73.24; H, 4.39; N, 4.51. $C_{38}H_{27}N_2O_2Br$ requires C, 73.20; H, 4.36; N, 4.49%]; IR (KBr) ν_{max}: 1651 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.99 (s, 2H, C*H*O); 8.35–8.33 (m, 2H, Ar); 7.76 (s, 2H, Ar); 7.39–7.37 (m, 6H, Ar); 7.33–7.31 (m, 6H, Ar); 7.25–7.21 (m, 5H, Ar); 5.54 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.9, 143.1, 138.8, 137.6, 130.5, 130.4, 130.3, 126.9, 126.8, 125.6, 118.7, 110.6, 110.5, 50.7; *m*/*z* (EI) 623 (M^+), 625 (M^++2).

6.5.25. Compound 7c. Following the general procedure C, dialdehyde **7c** was obtained as a brown colour solid in 77% yield; mp 128–132 °C; [found: C, 68.09; H, 4.09; N, 4.20. $C_{38}H_{27}N_2O_2I$ requires C, 68.07; H, 4.06; N, 4.18%]; IR (KBr) ν_{max}: 1652 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.02 (s, 2H, C*H*O); 8.34–8.33 (m, 2H, Ar); 7.77 (s, 2H, Ar); 7.41–7.36 (m, 5H, Ar); 7.35–7.30 (m, 6H, Ar); 7.25–7.20 (m, 6H, Ar); 5.36 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.8, 143.1, 142.0, 138.7, 137.6, 134.9, 130.4, 130.3, 130.8, 130.2, 126.9, 126.8, 125.6, 118.7, 97.6, 94.8, 50.7; *m*/*z* (EI) 670 (M^+).

6.5.26. Compound 7d. Following the general procedure C, dialdehyde **7d** was obtained as a brown colour solid in 70% yield; mp 218–222 °C; [found: C, 73.22; H, 4.33; N, 4.53. $C_{38}H_{27}N_2O_2Br$ requires C, 73.20; H, 4.36; N, 4.49%]; IR (KBr) ν_{max}: 1646 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.01 (s, 2H, C*H*O); 8.33–8.30 (m, 2H, Ar); 7.75 (s, 4H, Ar); 7.65 (s, 2H, Ar); 7.54 (d, 4H, *J* 8.0 Hz); 7.35–7.30 (m, 4H, Ar); 7.26–7.24 (m, 5H, Ar); 5.40 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 185.3, 142.1, 141.9, 139.6, 137.7, 135.4, 131.4, 131.1, 130.9, 130.6, 128.9, 128.6, 127.9, 125.9, 119.8, 110.9, 50.9; *m*/*z* (EI) 623 (M^+), 625 (M^++2).

6.5.27. Compound 8a. Following the general procedure D, indolophane **8a** was obtained as a light yellow colour solid in 8% yield; mp 224–229 °C; [found: C, 89.01; H, 5.53; N, 5.46. $C_{76}H_{56}N_4$ requires C, 89.03; H, 5.51; N, 5.46%]; δ_H (500 MHz, $CDCl_3$) 7.60 (s, 2H, Ar); 7.53–7.52 (m, 4H, Ar); 7.46–7.42 (m, 12H, Ar); 7.22–7.20 (m, 6H, Ar); 7.18–7.13 (m, 12H, Ar); 7.12–7.04 (m, 8H); 6.86 (s, 4H, C*H*=C*H*); 5.23 (s, 8H, NCH_2); δ_C (125 MHz, $CDCl_3$) 140.4, 129.0, 127.6, 127.4, 126.2, 126.0, 125.9, 121.8, 119.2, 118.9, 110.1, 109.5, 49.6; *m*/*z* (FABMS) 1025.

6.5.28. Compound 8b. Following the general procedure D, indolophane **8b** was obtained as a light yellow colour solid in 6% yield; mp 231–233 °C; [found: C, 77.20; H, 4.58; N, 4.78. $C_{76}H_{54}Br_2N_4$ requires C, 77.16; H, 4.60; N, 4.74%]; δ_H (500 MHz, $CDCl_3$) 7.64–7.52 (m, 6H, Ar); 7.47–7.27 (m, 8H, Ar); 7.25–7.22 (m, 12H, Ar); 7.19–7.15 (m, 8H, Ar); 7.10–7.08 (m, 8H, Ar); 6.88 (s, 4H, C*H*=C*H*); 5.25 (s, 8H, NCH_2); δ_C (125 MHz, $CDCl_3$) 131.1, 130.5, 128.8, 127.6, 126.9, 126.5, 126.2, 122.8, 121.7, 119.9, 118.9, 114.1, 110.5, 50.2; *m*/*z* (FABMS) 1180 (M^+), 1182 (M^++2), 1184 (M^++4).

6.5.29. Compound 8c. Following the general procedure D, indolophane **8c** was obtained as a light yellow colour solid in 5% yield; mp 218–220 °C; [found: C, 71.50; H, 4.28; N, 4.36. $C_{76}H_{54}I_2N_4$ requires C, 71.48; H, 4.26; N, 4.39%]; δ_H (500 MHz, $CDCl_3$) 7.53–7.48 (m, 6H, Ar); 7.35–7.27 (m, 8H, Ar); 7.22–7.18 (m, 12H, Ar); 7.16–7.14 (m, 8H, Ar); 7.12–7.11 (m, 8H, Ar); 6.94 (s, 4H, C*H*=C*H*); 5.29 (s, 8H, NCH_2); δ_C (125 MHz, $CDCl_3$) 130.3, 129.9, 127.7, 127.3, 126.9, 126.4, 126.0, 121.7, 120.9, 119.1, 118.9, 111.1, 109.5, 49.6; *m*/*z* (FABMS) 1276.

6.5.30. Compound 8d. Following the general procedure D, indolophane **8d** was obtained as a light yellow colour solid in 8% yield; mp 215–217 °C; [found: C, 77.18; H, 4.57; N, 4.76. $C_{76}H_{54}Br_2N_4$ requires C, 77.16; H, 4.60; N, 4.74%]; δ_H (500 MHz, $CDCl_3$) 7.44–7.36 (m, 6H, Ar); 7.34–7.27 (m, 8H, Ar); 7.21-7.13 (m, 12H, Ar); 7.11–7.05 (m, 8H, Ar); 7.01–6.97 (m, 8H, Ar); 6.87 (s, 4H, C*H*=C*H*); 5.24 (s, 8H, NCH_2); δ_C (125 MHz, $CDCl_3$) 131.9, 131.1, 129.3, 128.7, 127.9, 127.4, 127.1, 126.8, 123.4, 122.7, 121.2, 120.6, 119.8, 117.8, 111.2, 50.4; *m/z* (FABMS) 1180 (M^+), 1182 (M^++2), 1184 (M^++4).

6.5.31. Compound 10a. Following the general procedure C, trialdehyde **10a** was obtained as a light brown colour solid in 80% yield; mp 199–201 °C; [found: C, 79.14; H, 5.63, 6.99. $C_{39}H_{33}N_3O_3$ requires C, 79.16; H, 5.62; N, 7.10]; IR (KBr) ν_{max}: 1649 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.89 (s, 3H, C*H*O); 8.28 (d, 3H, *J* 7.5 Hz, Ar); 7.51 (d, 3H, *J* 8.0 Hz, Ar); 7.41–7.34 (m, 6H, Ar); 7.27 (s, 3H, Ar); 5.43 (s, 6H, NCH_2); 2.28 (s, 9H, CH_3); δ_C (125 MHz, $CDCl_3$) 184.6, 140.5, 137.4, 135.2, 130.9, 125.9, 124.5, 123.7, 122.1, 118.6, 109.9, 45.5, 16.6; *m/z* (EI) 591 (M^+).

6.5.32. Compound 10b. Following the general procedure C, trialdehyde **10b** was obtained as a brown colour solid in 78% yield; mp 174–178 °C; [found: C, 78.65; H, 4.96; N, 7.66. $C_{36}H_{27}N_3O_3$ requires C, 78.67; H, 4.95; N, 7.65%]; IR (KBr) ν_{max}: 1653 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.90 (s, 3H, C*H*O); 8.28 (d, 3H, *J* 8.0 Hz, Ar); 7.55 (s, 3H, Ar); 7.30–7.28 (m, 3H, Ar); 7.21–7.18 (m, 3H, Ar); 7.04 (d, 3H, *J* 8.6 Hz, Ar); 6.80 (s, 3H, Ar); 5.22 (s, 6H, NCH_2); δ_C (125 MHz, $CDCl_3$) 184.6, 138.0, 137.1, 125.5, 125.2, 124.4, 123.3, 122.4, 118.8, 110.2, 50.4; *m/z* (EI) 549 (M^+).

6.5.33. Compound 11a. Following the general procedure D, indolophane **11a** was obtained as a light yellow colour solid in 24% yield; mp 222–226 °C; [found: C, 86.11; H, 6.05; N, 7.68. $C_{78}H_{66}N_6$ requires C, 86.15; H, 6.12; N, 7.73%]; δ_H (500 MHz, $CDCl_3$) 7.62 (d, 2H, *J* 7.5 Hz, Ar); 7.53 (d, 4H, *J* 8.0 Hz, Ar); 7.47 (d, 2H, *J* 8.0 Hz, Ar); 7.38 (d, 4H, *J* 8.1 Hz, Ar); 7.29 (t, 2H, *J* 8.0 Hz, Ar); 7.25 (s, 2H, Ar); 7.20–7.17 (m, 6H, Ar); 7.08 (t, 4H, *J* 7.5 Hz, Ar); 6.87 (s, 4H, Ar); 6.42 (s, 4H, CH=CH); 6.35 (s, 2H, CH=CH); 5.50 (d, 4H, *J* 14.3 Hz, NCH_2); 5.35 (s, 4H, NCH_2); 5.23 (d, 4H, *J* 14.3 Hz, NCH_2); 2.48 (s, 12H, CH_3); 2.26 (s, 6H, CH_3); δ_C (125 MHz, $CDCl_3$) 141.2, 137.4, 137.2, 136.7, 135.1, 130.8, 129.2, 128.0, 127.5, 127.4, 123.0, 121.7, 119.8, 119.7, 119.3, 119.1, 111.9, 110.8, 109.0, 108.9, 44.7, 44.6, 16.7, 16.2; *m/z* (FABMS) 1087 (M^+).

6.5.34. Compound 11b. Following the general procedure D, indolophane **11b** was obtained as a light yellow colour solid in 22% yield; mp 282–289 °C; [found: C, 86.12; H, 5.37; N, 8.34. $C_{72}H_{54}N_6$ requires C, 86.20; H, 5.43; N, 8.38%]; δ_H (500 MHz, $CDCl_3$) 7.67 (d, 4H, *J* 7.5 Hz, Ar); 7.61 (d, 2H, *J* 7.5 Hz); 7.25–7.11 (m, 20H, Ar); 6.85 (s, 6H, Ar); 6.81 (s, 4H, Ar); 6.50 (s, 4H, C*H*=C*H*); 6.01 (s, 2H, C*H*=C*H*); 5.17 (s, 4H, NCH_2); 4.95 (s, 8H, NCH_2); δ_C (125 MHz, $CDCl_3$) 139.3, 137.8, 137.5, 136.7, 129.5, 129.0, 128.2, 128.1, 125.2, 125.1, 124.7, 124.2, 121.9, 119.8, 119.4, 119.2, 119.0, 113.8, 111.2, 109.8, 109.5, 49.5, 49.0; *m/z* (FABMS) 1002 (M^+).

6.5.35. Compound 12a. A mixture of *p*-hydroxybenzaldehyde (2 mmol) and tribromide **9a** (7.7 mmol) and K_2CO_3 (3.46 g) in anhydrous DMF (30 mL) were stirred under nitrogen for 48 h at 60 °C. The reaction mixture was poured into water (1 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 (Na_2SO_4) and evaporated to give a residue, which was chromatographed (SiO_2) using hexane/$CHCl_3$ (1:2) to give the trialdehyde **12a** in 65% yield; mp 140–142 °C [found: C, 75.81; H, 5.81. $C_{33}H_{30}O_6$ requires C, 75.84; H, 5.79%]; IR (KBr) ν_{max}: 1680 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.90 (s, 3H, C*H*O); 7.88 (d, 6H, *J* 8.4 Hz, Ph); 7.13 (d, 6H, *J* 8.4 Hz, Ph); 5.21 (s, 6H, PhCH_2); 2.45 (s, 9H, CH_3); δ_C (125 MHz, $CDCl_3$) 190.9, 164.0, 139.8, 132.2, 131.4, 130.4, 114.9, 65.3, 16.2; *m/z* (EI) 522 (M^+).

6.5.36. Compound 12b. Following the procedure as mentioned for compound **12a** trialdehyde **12b** was obtained in 67% yield; mp 141–143 °C [found: C, 75.01; H, 5.01. $C_{30}H_{24}O_6$ requires C, 74.99; H, 5.03]; IR (KBr) ν_{max}: 1682 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 9.88 (s, 3H, C*H*O); 7.83 (d, 6H, *J* 8.4 Hz, Ph); 7.49 (s, 3H, Ph); 7.06 (d, 6H, *J* 8.4 Hz, Ph); 5.18 (s, 6H, PhCH_2); δ_C (125 MHz, $CDCl_3$) 190.9, 163.5, 137.4, 132.1, 130.4, 126.3, 115.2, 69.81; *m/z* (EI) 480 (M^+).

6.5.37. Compound 14. Following the general procedure B, trialdehyde **14** was obtained as a white colour solid in 69% yield; mp 230–234 °C; [found: C, 83.04; H, 4.64. $C_{27}H_{18}O_3$ requires C, 83.06; H, 4.65%]; IR (KBr) ν_{max}: 1691 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 10.09 (s, 3H, C*H*O); 8.02 (d, 6H, *J* 8.4 Hz, Ph); 7.90 (s, 3H, *J* 8.4 Hz, Ph); 7.86 (d, 6H, *J* 7.7 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 191.9, 146.4, 141.7, 135.8, 130.5, 128.1, 126.6; *m/z* (EI) 390 (M^+).

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