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Synthesis, characterization and complexation studies of some novel cyclophane amides and sulfonamides

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ABSTRACT

A series of tricyclic tetraamides have been synthesized and were characterized from spectral and XRD studies. XRD studies revealed that the pyridine-based tricyclic cyclophane amide exists with twisted phenyl rings. All the cyclophane compounds form charge-transfer (CT) complexes with TCNQ. Metal ion complexation studies show that the cyclophane amides are more selective towards Cu(II) ions rather than Ni(II) and Cd(II) ions.

The enhanced applications of aza crown ethers in supramolecular chemistry[1–5] have influenced the synthetic chemist to modify the molecular structure. The most important aspect of supramolecular chemistry is the host–guest complexation process. Hence the basic crown ether structures were modified significantly to increase the selectivity and specificity of guest molecules for complexation. One of the key modifications is the replacement of oxygen donor atoms by sulfur and/or by nitrogen atoms.[6] The other significant modification is the insertion of functional groups, viz., amides and esters in the macrocyclic ring system.[7–10] Synthesis of amide-based supramolecular systems have been reported in the literature.[11–15] Neutral macrocyclic amides display anion-binding properties.[16] In fact peptides exhibit molecular shuttling through anion recognition.[17] Interactions between electron donors and complementary electron acceptor groups in cyclophanes can form intramolecular charge-transfer (CT) complexes and can exhibit self complementary properties in addition to π–π interactions.[18–20] Furthermore such cyclic amides can form complexes with metal ions like Cd(II),[21] Fe(III)[22] and Cu(II)[23] and hence they can be used for selective metal ion complexation. Hence it is of interest to synthesize and study the CT, metal complexation properties of novel cyclophane amides. Herein, we report the synthesis of tricyclic cyclophane amides **1** and **2,** cyclophane sulfonamide **3** and monocyclic cyclophane amides **4** and **5** along with charge transfer complex studies with TCNQ and also metal complexation studies with Cu(II), Ni(II) and Cd(II) ions.

Five different cyclophane amide derivatives **1**–**5** shown in Figure 1 were synthesized from *m*-xylylenediamine (Schemes 1 and 2). Reaction of 1 equiv of *m*-xylylenediamine **6** and 1 equiv of isophthalaldehyde **7** in ethanol under high-dilution conditions[24] at room temperature resulted in the formation of cyclophane tetraimine **8** in 95% yield. The product was slowly precipitated from the reaction mixture during the course of the reaction and used without further purification. Reduction of cyclophane imine **8** with sodium borohydride in toluene–THF–MeOH mixture at 0–5 °C afforded secondary tetraamine cyclophane **9** in about 80% yield[25] and the product was purified from cold acetonitrile (Scheme 1). The tetraamine cyclophane **9** was recrystallized from chloroform. The structure of tetraamine cyclophane **9** was confirmed from the spectroscopic and XRD data. The ^{1}H NMR spectrum of tetraamine cyclophane **9** displayed the *N*-methylene protons as a singlet at δ 3.79. The rest of the aromatic protons appeared in the region ranging from δ 7.20–7.29. In the ^{13}C NMR spectrum of **9**, the *N*-methylene carbons appeared at δ 53.8. The structure of **9** was also confirmed by XRD. The crystal parameters for cyclophane amine **9** are given in Table 1 and ORTEP diagram is shown in Figure 2.

In order to test the synthetic utility of secondary tetraamine cyclophane **9** for the synthesis of tricyclic amide, 1.0 equiv of cyclophane amine **9** was coupled with 2.0 equiv of isophthaloyl chloride **10**, pyridine-2,6-dicarboxylic acid chloride **11**, benzene-1,3-disulfonyl chloride **12** in the presence of triethylamine in dry DCM at room temperature under high dilution conditions.[26] The reaction afforded the tricyclic cyclophane amides **1**,[27] **2**[28] and **3**[29] in 65%, 70% and 75% yields, respectively, after purification by column chromatography (Scheme 1). The amide **2** was recrystallized from chloroform/acetonitrile mixture. The structure of cyclophane

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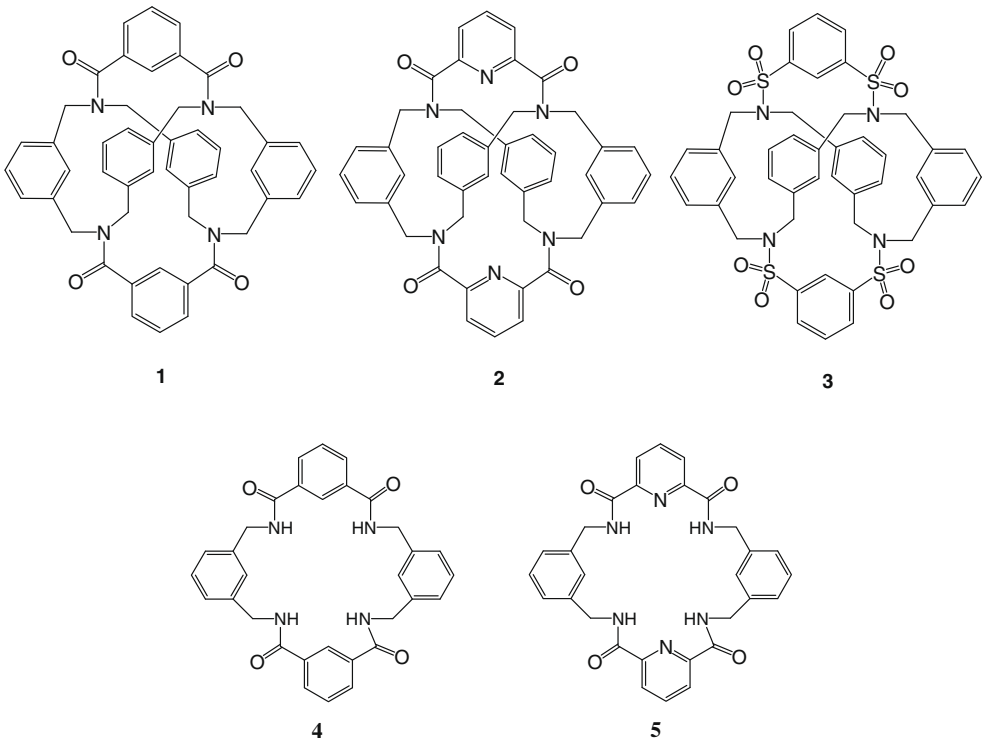


Figure 1. Structures of cyclophane amides **1**–**5**.

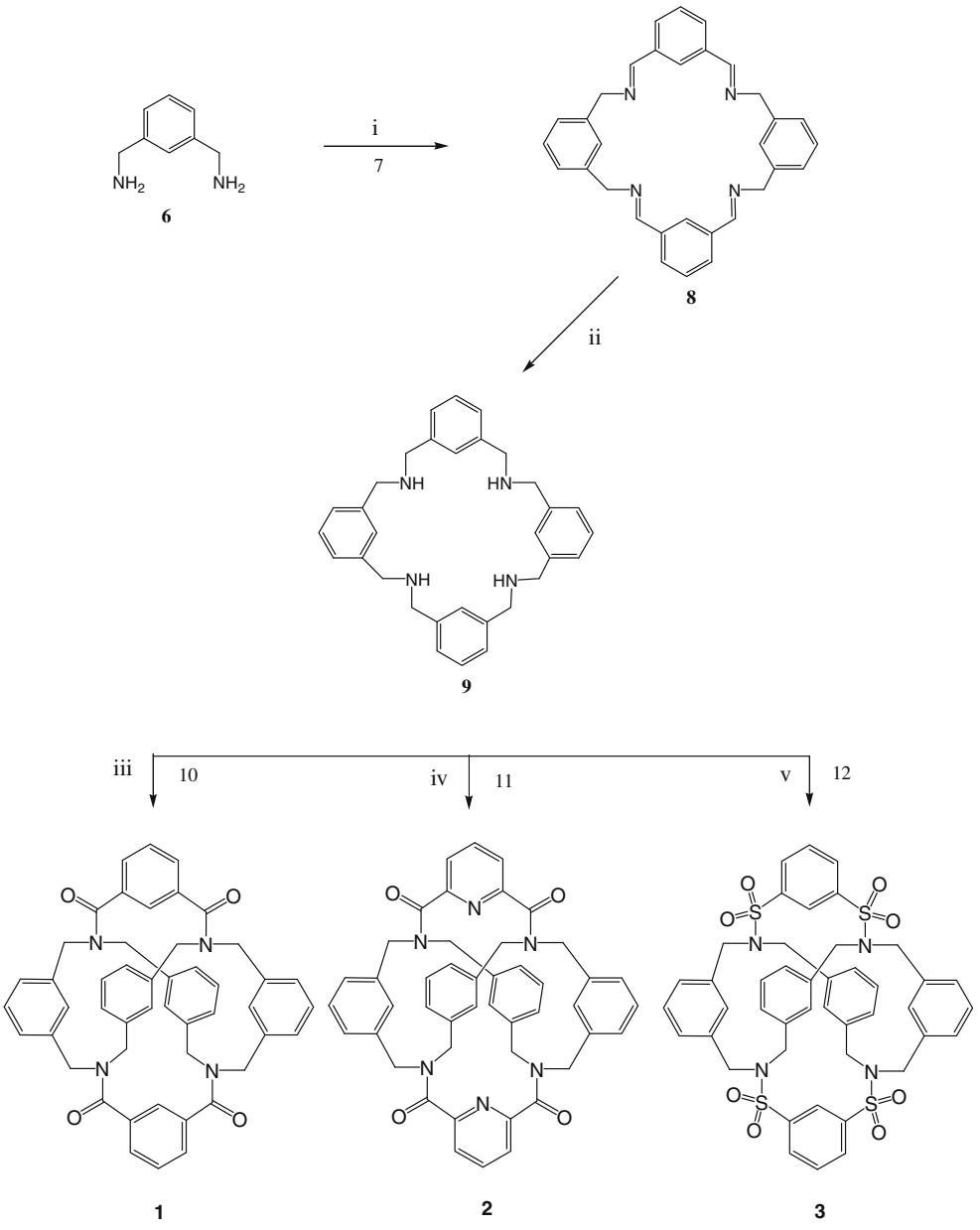
amides **1**–**3** was confirmed from the spectroscopic and XRD data. The ^{1}H NMR spectrum of cyclophane amide **2** displayed four sets of doublets for the *N*-methylene protons at δ 3.80, δ 5.00, δ 5.10 and δ 5.41. The rest of the aromatic protons appeared between δ 6.95 and 7.94. In the ^{13}C NMR spectrum of cyclophane amide **2**, the *N*-methylene carbons appeared at δ 50.8 and δ 55.0 and carbonyl carbon at δ 169.2. FT-IR spectrum shows the carbonyl stretching frequency at 1631 cm^{-1} for the cyclophane amide **2**. XRD analysis of compound **2** shows that out of four benzene rings, two of them are parallel to each other. Moreover, the pyridine moieties are parallel to each other. XRD studies indicate that intermolecular hydrogen bonding exists between cyclophane amide **2** and water. The crystal parameters for cyclophane amide **2** are given in Table 2 and ORTEP diagram is shown in Figure 3.

However, the reaction between *m*-xylylenediamine **6** and isophthaloyl chloride **10**, pyridine-2,6-dicarboxylic acid chloride **11** in the presence of triethylamine in dry DCM at room temperature under high dilution conditions[30] afforded the cyclophane amides, **4**[31] and **5**[32] each in about 80% yield (Scheme 2). The ^{1}H NMR spectrum of cyclophane amide **4** displayed the *N*-methylene protons as a doublet at δ 4.44 and NH protons as a triplet at δ 9.08. The rest of the aromatic protons appeared in the region ranging from δ 7.19–8.38. In the ^{13}C NMR spectrum of **4**, the *N*-methylene carbons appeared at δ 42.69 and the carbonyl carbon at δ 165.3 and δ 165.8. FT-IR spectrum shows the carbonyl stretching frequency at 1638 cm^{-1} for compound **4**. The structure of the cyclophane amide **4** has been confirmed from the spectral data. Similarly the structure of the cyclophane amide **5** was also confirmed from spectral and analytical data.

Cyclophane amides **1**, **2, 3, 4** and **5** exhibited charge transfer complexes with TCNQ.[33] Complexation studies of compounds **1**, **2, 3, 4** and **5** with TCNE and PQT were not successful. Cyclophanes **1**, **2, 3, 4** and **5** show UV–Vis absorption maxima at 225.5, 261.0, 262.0, 255.0 and 258.0 nm, respectively. However, the acceptor TCNQ shows an absorption maximum at 395.0 nm. Cyclophanes **1**, **2, 3, 4** and **5** form a charge transfer complex with TCNQ as evidenced by the appearance of absorption maxima at 843.5, 842.0, 842.5, 843.0 and 842.5 nm, respectively. (Table 3, Figs. 4 and 5) The plot of (concentration of cyclophane)/absorbance (Y/A) versus 1/concentration of guest (1/X) was linear. Benesi–Hildebrand equation was employed to calculate K_a values.[34] From the slope and the intercept values, K_a (K_a = intercept $\times$ slope^{-1}) and ε (ε = intercept^{-1}) were evaluated. The plot was linear suggesting that the predominate species in solution as a 1:1 complex (Fig. 6). The K_a, ε and r values of the CT complexes formed from **1**, **2**, **3**, **4** and **5** with TCNQ are shown in Tables 4 and 5.

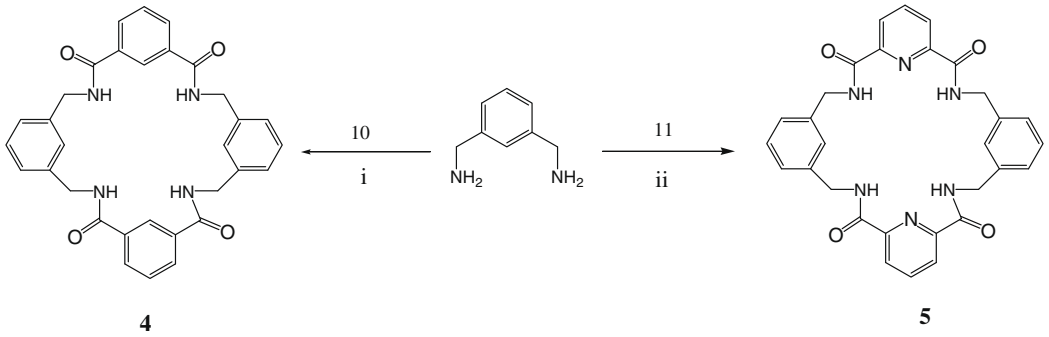
Complexation studies were carried out with cyclophane amides, **1**, **2, 3, 4** and **5** with Cu(II) acetate in a mixture of $CHCl_3$ and ethanol.[35] The complex formation was studied using an absorption spectrophotometer by following the maximum absorption of the ligands. Further studies show that the shift of the maximum absorption towards the higher wavelength was observed with Cu(II) complexes (Table 6). However, the complexation studies with Ni(II) acetate and Cd(II) acetate did not show any shift in the maximum absorption of the ligand band. Thus the cyclophane amides **1**, **2, 3, 4** and **5** are more selective towards the Cu(II) rather than Ni(II) or Cd(II) ions. This selectivity is due to the cavity size (0.73–0.85 Å) which matches with the size of Cu(II) ion (0.73 Å) rather than Ni(II) (0.69 Å) and Cd(II) (0.95 Å) ions. Thus cyclophane amides **1**, **2, 3, 4** and **5** form complexes with Cu(II) rather than Ni(II) and Cd(II) ions. Further the presence of Ni(II) ions or Cd(II) ions did not interfere with the formation of a complex by the receptor molecules with Cu(II).

In summary we have synthesized various cyclophane amides which show strong CT interactions selectively with TCNQ rather than TCNE and PQT. Complexation studies of all the five cyclophane amides show that they are more selective towards the Cu(II) rather than Ni(II) and Cd(II) ions. The biological activity and de-



6 **8** **9** **1** **2** **3**

Scheme 1. Reagents and conditions: (i) isophthalaldehyde **7**, ethanol, rt, 48 h, **8** (95%); (ii) $NaBH_4$, toluene–THF–MeOH, 0–5 °C, 1 h, **9** (80%); (iii) isophthaloyl chloride **10**, TEA, DCM, rt, 24 h, **1** (65%); (iv) pyridine-2,6-dicarboxylic acid chloride **11**, TEA, DCM, rt, 24 h, **2** (70%) and (v) benzene-1,3-disulfonylchloride **12**, TEA, DCM, rt, 24 h, **3** (75%).



4 **5**

Scheme 2. Reagents and conditions; (i) isophthaloyl chloride **10**, TEA, DCM, rt, 24 h, **4** (80%) and (ii) pyridine-2,6-dicarboxylic acid chloride **11**, TEA, DCM, rt, 24 h, **5** (80%).

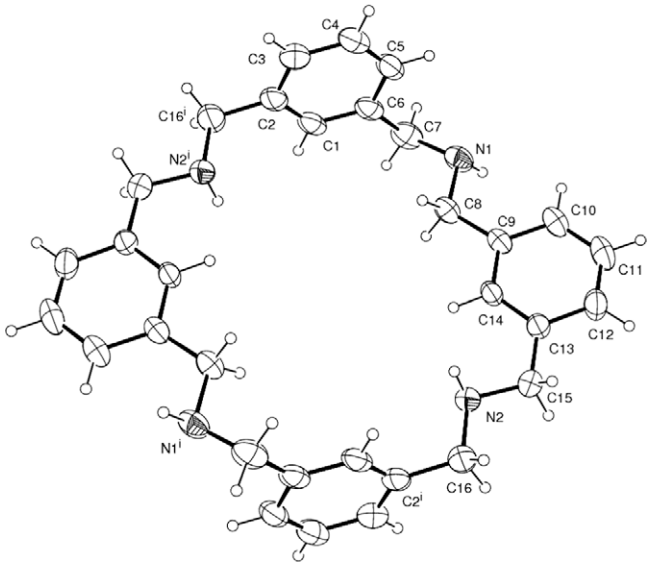


Figure 2. ORTEP diagram of cyclophane tetraamine **9**.

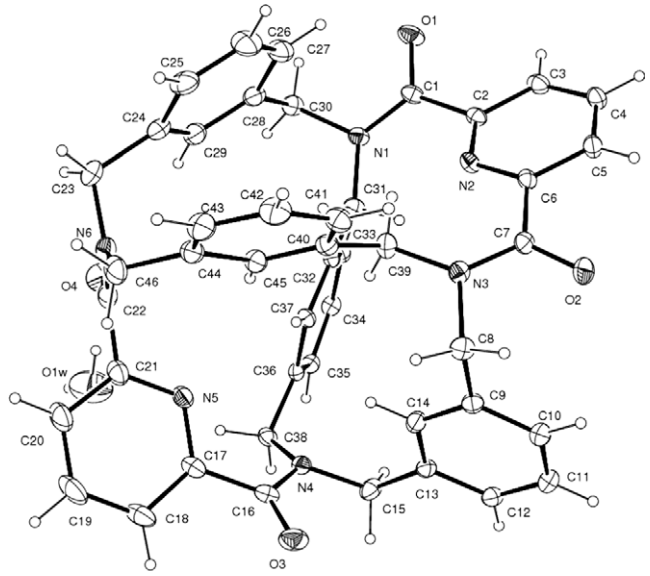


Figure 3. ORTEP diagram of cyclophane amide **2**.

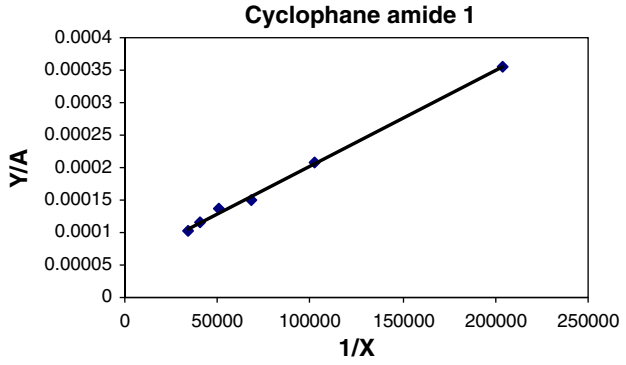


Figure 6. Plot between 1/X and Y/A for cyclophane amide **2**.

tailed charge transfer complexation studies of similar cyclophane amides with other transition metal ions are under investigation.

Table 4
Benesi–Hildebrand treatment data of the CT complex formed between the cyclophane amide, **1** and TCNQ

Concd of guest, [X] (M)	Absorbance (Å)	[Y]/A(M)	1/[X] (M^{-1})
4.9×10^{-6}	0.066	0.0003540	*204,081*
9.8×10^{-6}	0.113	0.0002080	*102,040*
14.7×10^{-6}	0.155	0.0001506	*68,027*
19.6×10^{-6}	0.171	0.0001360	*51,020*
24.5×10^{-6}	0.202	0.0001160	*40,816*
29.4×10^{-6}	0.230	0.0001018	*34,013*

λ_{max} = 843.5 nm; concentration of cyclophane amide, **1** = 2.34×10^{-5} M.
$K_a = 3.79 \times 10^4$ M^{-1}; $\varepsilon = 1.80 \times 10^4$ [M^{-1} cm^{-1}] and r = 0.9991.

Table 5
Complexation of TCNQ with cyclophane amides **1**, **2**, **3**, **4** and **5**

Cyclophane amide	K_a (mol^{-1} dm^3)	ε (M^{-1} cm^{-1})	r
1	3.79×10^4	1.80×10^4	0.9991
2	1.57×10^4	2.03×10^4	0.9996
3	1.11×10^4	2.34×10^4	0.9999
4	6.34×10^3	2.48×10^4	0.9997
5	1.22×10^4	1.68×10^4	0.9981

Table 6
Complexation of Cu (II) acetate with cyclophane amides **1**, **2**, **3**, **4** and **5**

Cyclophane amide	λ_{max} (nm) of the cyclophane amide	λ_{max} (nm) of Cu(II) complex
1	225.5	697.0
2	261.0	785.5
3	262.0	694.0
4	255.0	710.0
5	258.0	670.5

λ_{max} for Cu(II) acetate is 427.0 nm.

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Supplementary data

X-ray crystal data for cyclophane tetraamine **9** (Table 1) and cyclophane amide **2** (Table 2) are available. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 743880 and CCDC 743881. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk]. λ_{max} for cyclophane amides and TCNQ complex of cyclophane amides **1**, **2**, **3**, **4** and **5** (Table 3), CT spectra of cyclophane amides (Figs. 4 and 5) are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.077.

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25. *Procedure for the synthesis of cyclophane imine* **8**: A solution of *m*-xylylenediamine **6** (15.2 mmol) in ethanol (400 mL) and a solution of isophthalaldehyde **7** (15.2 mmol) in ethanol (400 mL) were simultaneously added dropwise to a well-stirred solution of ethanol (800 mL) for 6 h. After the addition was completed the reaction mixture was stirred for another 48 h. The precipitated solid was filtered, washed with ethanol and dried.
26. *General procedure for the synthesis of tricyclic cyclophane amides* **1**–**3**: A solution of tetraamine **9** (1.05 mmol) in dry dichloromethane (250 mL) and a solution of the corresponding diacid chloride (2.10 mmol) in dichloromethane (250 mL) were simultaneously added dropwise to a well-stirred solution of triethylamine (4.2 mmol) in dry dichloromethane (500 mL) for 6 h. After the addition was completed the reaction mixture was stirred for another 24 h. The solvent was removed at reduced pressure and the residue obtained was then dissolved in chloroform (250 mL), washed with water (2 × 200 mL) to remove triethylammonium chloride and then dried over anhydrous sodium sulfate. Removal of the chloroform under reduced pressure gave the corresponding cyclophane amide as a crude material, which was purified by column chromatography (SiO_2).
Similar procedure was adopted for the synthesis of compound, **3** by using the corresponding 1,3-benzenedisulfonylchloride.
27. *Spectral data for cyclophane amide* **1**: Yield 65%; mp 176 °C; IR (KBr, cm^{-1}): 1639, 1406; ^1H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, 8H, J = 14.7 Hz), 4.81 (d, 8H, J = 14.7 Hz), 7.15(d, 8H, J = 7.5 Hz), 7.23 (d, 4H, J = 7.5 Hz), 7.63 (ABq, 12H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.2, 49.4, 51.0, 53.6, 57.1, 124.8, 125.5, 127.1, 127.1, 127.2, 127.8, 128.0, 128.4, 128.9, 129.0, 129.2, 130.0, 130.7, 131.2, 136.3, 137.4, 137.5, 140.3, 160.7, 170.1, 172.7, 174.3; MS (ES) m/z: 737.2 (M+1), Elemental Anal. Calcd for $C_{48}H_{40}N_4O_4$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.63; H, 5.31; N, 7.92.
28. *Spectral data for cyclophane amide* **2**: Yield 70%; mp 370 °C (decomposed); IR (KBr, cm^{-1}): 1631, 1421; ^1H NMR (400 MHz, $CDCl_3$) δ 3.80 (d, 4H, J = 14.2 Hz), 5.00 (d, 4H, J = 15.7 Hz), 5.10 (d, 4H, J = 15.5 Hz), 5.41 (d, 4H, J = 14.1 Hz), 6.96 (t, 4H, J = 7.5 Hz), 7.06 (d, 4H, J = 6.8 Hz), 7.23–7.25 (m, 2H), 7.37 (s, 2H,), 7.94 (t, 8H, J = 12.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.8, 55.0, 125.7, 126.2, 127.0, 127.5, 128.1, 128.5, 129.1, 137.1, 138.3, 138.6, 152.4, 169.2; MS (ES) m/z: 739.3 (M+1), Elemental Anal. Calcd for $C_{46}H_{38}N_6O_4$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.92; H, 5.41; N, 11.87.
29. *Spectral data for cyclophane amide* **3**: Yield 75%; mp 370 °C (decomposed); IR (KBr, cm^{-1}): 1624, 1449, 1334; ^1H NMR (400 MHz, DMSO-d_6) δ 3.65 (s, 4H), 4.17 (s, 4H), 4.37 (s, 8H), 7.15–7.18 (m, 5H), 7.24–7.29 (m, 8H), 7.53 (d, 1H, J = 7.8 Hz), 7.60 (d, 2H, J = 7.5 Hz), 7.66 (t, 2H, J = 7.7 Hz), 7.83 (s, 1H), 7.94 (t, 3H, J = 8.8 Hz), 9.13 (bs, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 45.6, 48.9, 49.3, 51.8, 124.0, 127.3, 128.3, 128.7, 128.9, 129.1, 129.2, 129.3, 129.5, 129.6, 130.1, 130.4, 130.8, 131.3, 132.0, 132.3, 136.8, 138.5, 149.4; MS (ES) m/z: 881.1 (M+1), Elemental Anal. Calcd for $C_{44}H_{40}N_4O_8S_4$: C, 59.98; H, 4.58; N, 6.36. Found: C, 60.23; H, 4.65; N, 6.42.
30. *General procedure for the synthesis of cyclophane amides* **4** *and* **5**: A solution of *m*-xylylenediamine **6** (7.3 mmol) in dry dichloromethane (400 mL) and a solution of the corresponding diacidchloride (7.3 mmol) in dichloromethane (400 mL) were simultaneously added dropwise to a well-stirred solution of triethylamine (23.7 mmol) in dry dichloromethane (1000 mL) for 8 h. After the addition was completed the reaction mixture was stirred for another 24 h. The solvent was removed at reduced pressure and the solid obtained was washed with water (2 × 200 mL) to remove triethylammonium chloride and then washed with dichloromethane (25 mL), which was purified by column chromatography (SiO_2).
31. *Spectral data for cyclophane amide* **4**: Yield 80%; mp >370 °C; IR (KBr, cm^{-1}): 1638, 1542, 1303; ^1H NMR (400 MHz, DMSO-d_6) δ 4.44 (d, 8H, J = 5.9 Hz), 7.19–7.30 (m, 8H), 7.48 (t, 2H, J = 7.7 Hz), 7.95–7.99 (m, 4H), 8.28 (s, 2H), 9.08 (t, 4H, J = 5.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 42.7, 125.2, 126.1, 126.6, 128.0, 128.3, 129.8, 134.1, 134.5, 139.6, 139.8, 165.3, 165.8; MS (ES) m/z: 533 (M+1), Elemental Anal. Calcd for $C_{32}H_{28}N_4O_4$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.46; H, 5.38; N, 10.61.
32. *Spectral data for cyclophane amide* **5**: Yield 80%; mp 259 °C; IR (KBr, cm^{-1}): 1658, 1534, 1445; ^1H NMR (400 MHz, DMSO-d_6) δ: 4.48 (br s, 8H), 7.11–7.21 (m, 8H), 8.06–8.18 (m, 6H), 9.80 (br s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 42.1, 124.3, 125.5, 128.4, 139.3, 139.5, 148.5, 163.3; MS (FAB+) m/z: 534 (M), Elemental Anal. Calcd for $C_{30}H_{26}N_6O_4$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.56; H, 4.98; N, 15.93.
33. *CT complexation studies of cyclophane amides* **1**, **2**, **3**, **4** *and* **5** *with TCNQ*: A solution of TCNQ (4.9×10^{-6} M) in a 1:1 mixture of $CHCl_3/CH_3CN$ at various dilutions (1 mL, 2 mL, 3 mL, 4 mL, 5 mL and 6 mL) were prepared and added to the solution of the cyclophane amide **1, 2, 3, 4** and **5** (2.34×10^{-5} M) in a 1:1 mixture of $CHCl_3/CH_3CN$ (3 mL) in a quartz cuvette of path length 1 cm. The UV–Vis spectrum was also obtained for each of the sample separately and the changes in the absorbance of CT bands were recorded.
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35. *Complexation studies of cyclophane amides* **1**, **2**, **3**, **4** *and* **5** *with Cu(II), Ni(II) and Cd(II) acetates*: A solution of copper(II) acetate monohydrate (0.054 mmol) in ethanol (10 mL) was added to a solution of cyclophane amides **1, 2, 3, 4** and **5** (0.054 mmol) in 10 mL chloroform. The mixture was kept at room temperature for 1 h and UV–Vis spectrum was recorded. The absorbance maxima were observed at 697.0, 785.5, 694.0, 710.0 and 670.5 nm, respectively, indicate the formation of Cu(II) complex with the amides. Similarly experiments were carried out with Ni(II) and Cd(II) acetates also.