Tetrahedron Letters 50 (2009) 223–227

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Investigation of the role of 1,3,4-oxadiazole on the spectroscopic, optical, and electrochemical properties of benzimidazolophanes

Perumal Rajakumar *, Sebastian Raja

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

ARTICLE INFO

Article history:
Received 20 August 2008
Revised 22 October 2008
Accepted 28 October 2008
Available online 3 November 2008

Keywords:
Macrocycle
Cyclophane
Dicationic
1,3,4-Oxadiazole
Receptor
Electron deficient

ABSTRACT

The synthesis of 1,3,4-oxadiazole (OXD)-based dicationic cyclophanes has been achieved via an N-alkylation route, and UV–vis spectra proved the absence of charge transfer interactions. Electrochemical studies showed interference of the OXD unit on the characteristic redox properties of dicationic benzimidazolophanes.

Macrocycles with cationic systems are an attractive area in the field of supramolecular chemistry, and the presence of a heteroatom delivers a favorable binding site for metal ions.[1] Due to their structural versatility and potential for synthetic modifications, macrocycles play a prominent role in host–guest interactions, molecular self-assembly, and specific receptor activity.[2–4] In this context, 1,3,4-oxadiazoles are important heterocycles which demonstrate a wide range of pharmaceutical and biological applications.[5,6] As a result of the electron deficiency, high thermal, and oxidative stability, OXD derivatives are used widely as electron transporting and hole blocking materials in organic light emitting devices (OLEDs).[7,8] They find applications in electroluminescence,[9] liquid crystals,[10] molecular wires,[11] and dendrimers.[12] To the best of our knowledge, the 1,3,4-oxadiazole ring system has been rarely used[13,14] for the synthesis of cyclophanes. The 1,3,4-oxadiazole ring system can function as a potential receptor for anionic guests. We report herein the synthesis, spectroscopic, optical, and electrochemical properties of 1,3,4-oxadiazole-based dicationic cyclophanes **1a–c**, **2**, **3**, **4**, **5**, and **6**.

The synthesis of dicationic receptors **1a–c** can be achieved starting from either 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole and capping with *o*-, *m*-, or *p*-xylenyl dibromide or from *o*-, *m*-, or *p*-xylenyl dibromide and capping with 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole. Both routes have been used for the synthesis of all the dicationic receptors shown in Figure 1 depicted above. Reaction of 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole **7**[15] with 2.1 equiv of benzimidazole in DMF in the presence of NaH at 80 °C for 12 h gave the precyclophane **8** in 77% yield, which was characterized from spectral and analytical data.[16] Coupling of precyclophane **8** with *o*-, *m*- or *p*-xylenyl dibromide in CH_3CN under reflux for 5 days afforded the dicationic receptors **1a–c** in 69%, 71%, and 70% yields, respectively. Using the second route, *o*-, *m*-, or *p*-xylenyl dibromides **9a–c** were reacted with 2.1 equiv of benzimidazole in CH_3CN in the presence of 25% aq NaOH at room temperature for 2 days to give the bridged xylenyl derivatives **10a–c**, which were treated with **7** in CH_3CN at reflux to give macrocyclic receptors **1a–c** in 70%, 71%, and 73% yields, respectively (Scheme 1). The ^1H NMR spectrum of **1a**[17] displayed the *N*-methylene protons as singlets at δ 5.84 and δ 5.90 and the methine protons of the benzimidazole at δ 10.00. The rest of the aromatic protons appeared in the usual region. In the ^{13}C NMR spectrum of **1a**, the *N*-methylene carbons appeared at δ 47.9 and δ 49.7. The structures of **1b**[18] and **1c**[19] were also confirmed by spectroscopic methods.

Benzimidazolophanes **2** and **3** can function as self-complementary cyclophanes as they possess both electron-rich and electron-deficient units. Such cyclophanes can show intense charge transitions and can bind both electron-rich and electron-deficient guest molecules in their cavity. Moreover, such molecules can show self-assembling properties via stacking of electron-rich and electron-deficient units one over the other. Thus 1,4-dimethoxy-2,5-xylenyl and pyridyl dibromides were used as spacer units.[20] Benzimidazolophanes **2** and **3** can be synthesized by two approaches. In the first

* Corresponding author. Tel: +91 044 22351269x213, fax: +91 44 22300488.
E-mail address: perumalrajakumar@hotmail.com (P. Rajakumar).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.10.142

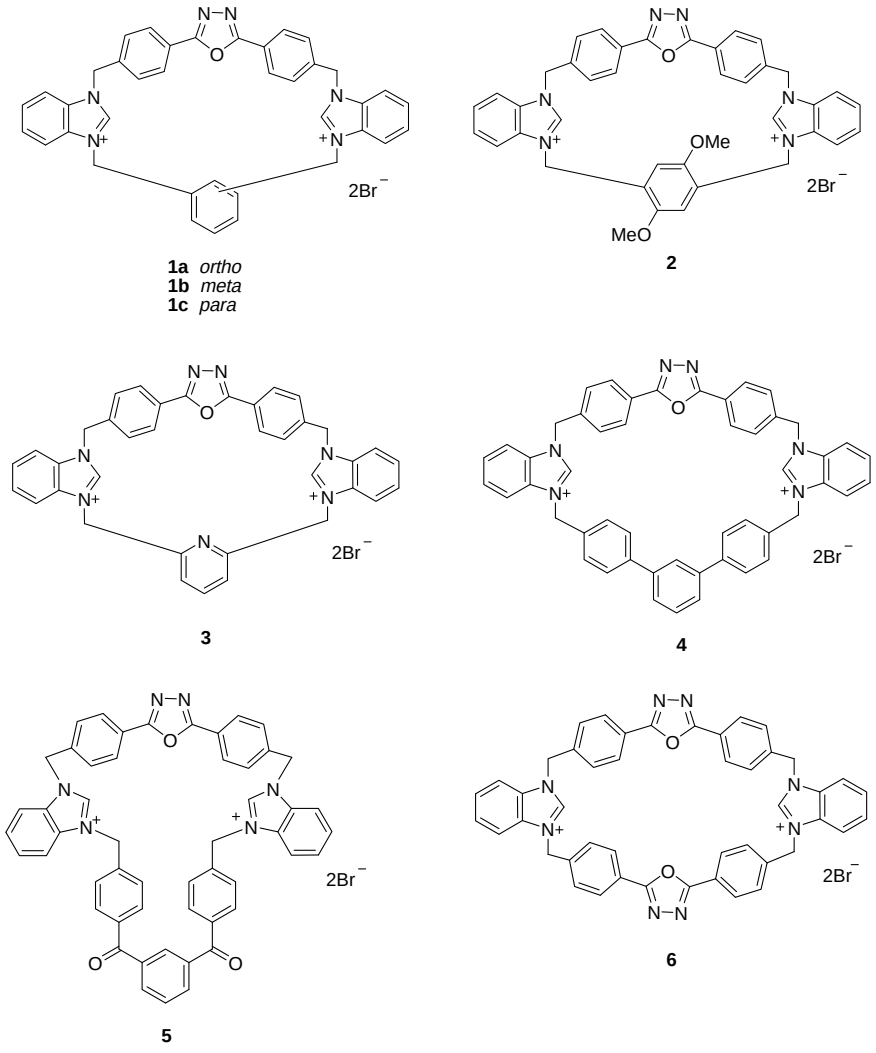
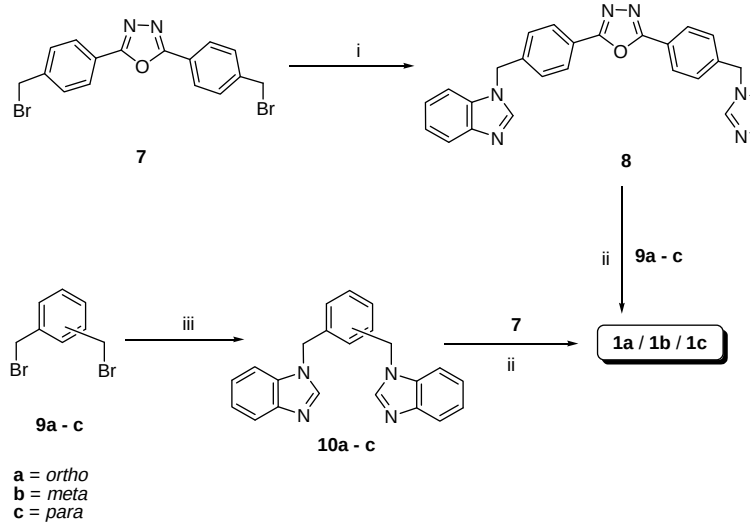
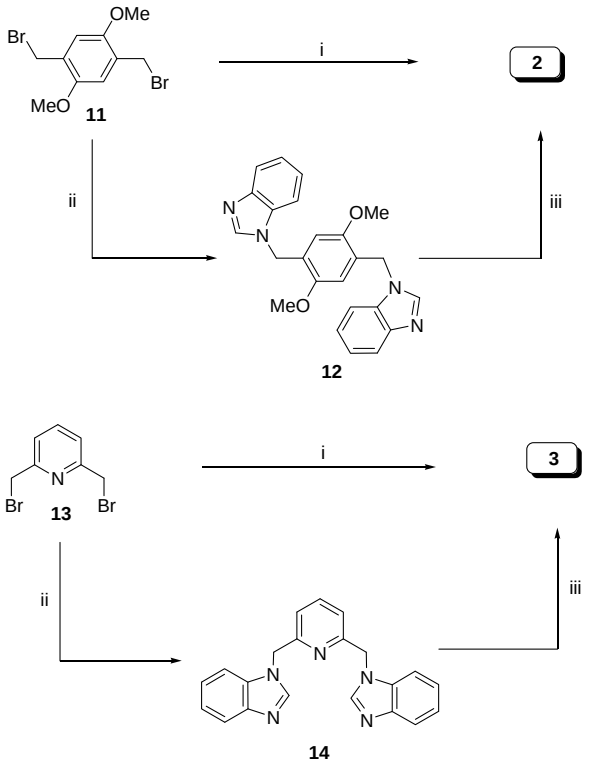


Figure 1. Structures of cyclophanes **1**–**6**.



Scheme 1. Reagents and conditions: (i) 2.1 equiv benzimidazole, NaH, DMF, 0–80 °C, 12 h, **8**, 77%, (ii) CH_3CN, reflux, 120 h, **1a** (69%, 70%), **1b** (71%, 71%), **1c** (70%, 73%), (iii) 2.1 equiv benzimidazole, CH_3CN, aq NaOH (25%), rt, 48 h, **10a**, 72%; **10b**, 68%; **10c**, 70%.

approach, reaction of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene **11** with 1 equiv of precyclophane **8** in CH_3CN at reflux for 5 days afforded the dicationic cyclophane **2** in 74% yield. In another approach, dibromide **11** was treated with 2.1 equiv of benzimid-

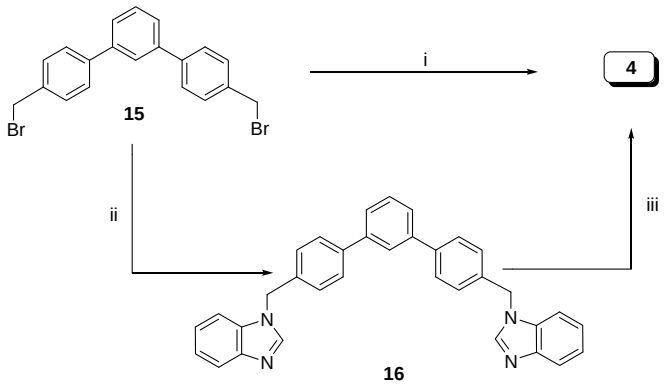


Scheme 2. Reagents and conditions: (i) **8**, CH_3CN, reflux, 120 h, **2**, 74%; **3**, 65%, (ii) 2.1 equiv benzimidazole, aq NaOH (25%), CH_3CN, rt, 48 h, **12**, 70%; **14**, 62%, (iii) **7**, CH_3CN, reflux, 120 h, **2**, 72%; **3**, 64%.

azole in CH_3CN in the presence of 25% aq NaOH to give the bisbenzimidazole **12** in 70% yield as reported previously by our group,[21] which on further reaction with dibromide **7** in CH_3CN afforded the dicationic cyclophane **2** in 72% yield (Scheme 2). The ^{1}H NMR spectrum of **2**[22] shows the two methoxy groups as a singlet at δ 3.85, which proves that they are equivalent and hence free rotation of the 1,4-dimethoxy-xylenyl unit occurs. The *N*-methylene protons appeared as singlets at δ 5.71 and δ 5.96 in addition to the aromatic protons. It is noteworthy to mention that the methine protons of the benzimidazole ring system appeared as a singlet at δ 10.22. In the ^{13}C NMR spectrum of **2**, the *N*-methylene and methoxy carbons appeared at δ 46.3, δ 49.2, and δ 56.2 in addition to the aromatic carbons. A similar sequence starting from pyridyl dibromide gave the cationic cyclophane **3**[23] in nearly 65% yield via both routes. Cyclophane **3** was also characterized completely from spectral and analytical data.

Incorporation of an *m*-terphenyl building block in such supramolecular systems would provide receptor systems with a large non-collapsible rigid cavity with intra-annular functionality.[24] Dicationic cyclophanes **4** and **5** were thus synthesized by two similar approaches as mentioned earlier. In the first approach, 4,4″-bis(bromomethyl)-1,1′:3′1′-terphenyl **15** was coupled with 1 equiv of precyclophane **8** to give the benzimidazolophane **4** in 70% yield. In another approach, precyclophane **16**[25] was treated with 1 equiv of 2,5-bis[4-(bromomethyl)phenyl]-1,3,4-oxadiazole **7** to give the dicationic cyclophane **4**[26] in 67% yield (Scheme 3).

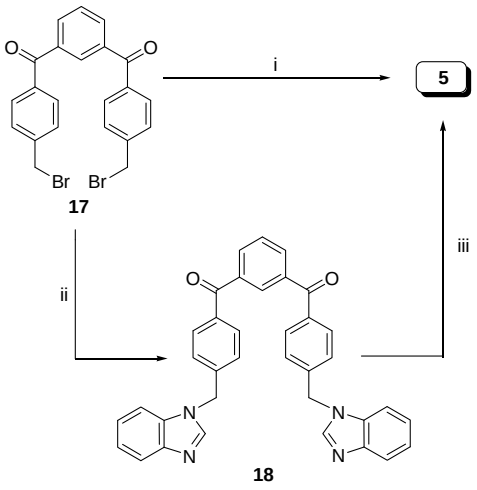
The synthesis of dicationic cyclophane **5** is of interest due to the presence of carbonyl functionalities in the annular cavity. Hence, its electron-deficient nature would alter the position of the charge transfer complexation band. Also functional group transformations can be carried out on the carbonyl group. In the first approach, reaction of dibromide **17** with 1 equiv of precyclophane **8** in CH_3CN under refluxing condition for 5 days afforded the cationic cyclophane **5** in 66% yield. In the second method, precyclophane **18**[27] was obtained by reaction of dibromide **17** and 2.1 equiv of benzimidazole in CH_3CN in the presence of 25% aq NaOH for 2 days. Coupling of precyclophane **18** with dibromide **7** in CH_3CN gave the dicarbonyl benzimidazolophane **5**[28] in 65% yield (Scheme 4). The structures of **4** and **5** were confirmed spectroscopically.



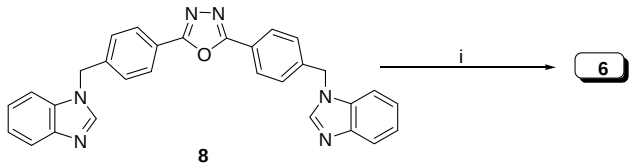
Scheme 3. Reagents and conditions: (i) **8**, CH_3CN, reflux, 120 h, 70%, (ii) 2.1 equiv benzimidazole, aq NaOH (25%), CH_3CN, rt, 48 h, 75%, (iii) **7**, CH_3CN, reflux, 120 h, 67%.

The dicationic cyclophane **6** was synthesized by reaction of precyclophane **8** with the dibromide **7** (1:1 ratio) in CH_3CN at reflux for 5 days to give cyclophane **6** in 69% yield (Scheme 5). The ^{1}H NMR spectrum of cyclophane **6**[29] displayed eight *N*-methylene protons as a singlet at δ 5.94, and the methine protons of benzimidazoles appeared as singlet at δ 10.10 in addition to the aromatic protons. The structure of cyclophane **6** was fully characterized from spectral and analytical data.

The UV–vis absorption spectra of compounds **1a–c**, **2**, **3**, **4**, **5**, and **6** were recorded in DMSO (1×10^{-3} M) and the values are summarized in Table 1. All the compounds showed strong absorption bands between 264 and 291 nm assigned to π–π^* transitions of oxadiazole (OXD) group.[30] Absorption bands at longer wavelengths (400–600 nm) were not observed for all the compounds which implies that intramolecular charge transition is absent in all the cyclophanes, and even the presence of 1,4-dimethoxy xylenyl and pyridyl units did not significantly alter the optical properties of the cyclophanes.[31]



Scheme 4. Reagents and conditions: (i) **8**, CH_3CN, reflux, 120 h, 66%, (ii) 2.1 equiv benzimidazole, aq NaOH (25%), CH_3CN, rt, 48 h, 68%, (iii) **7**, CH_3CN, reflux, 120 h, 65%.



Scheme 5. Reagents and conditions: (i) **7**, CH_3CN, reflux, 120 h, **6**, 69%.

Table 1
Summary of the optical and electrochemical parameters of compounds **1a–c**, **2**, **3**, **4**, **5**, and **6** in DMSO

Compound	λ_{max}[a] (nm)	E_{pc1}[a] (V)	E_{pc2}[a] (V)	E_{pc3}[a] (V)	E_{pa2} (V)	E_{pa3} (V)	ΔE_{p1} (V)	ΔE_{p2} (V)
1a	278	−0.80	−2.11	−2.57	−1.87	−2.27	0.24	0.30
1b	278	−0.80	−2.11	−2.55	−1.99	−2.28	0.12	0.27
1c	278	−0.67	−2.11	−2.61	−1.93	−2.29	0.18	0.32
2	291	−0.74	−2.12	−2.60	−2.00	−2.28	0.12	0.32
3	278	−0.66	−2.11	−2.59	−1.99	−2.29	0.12	0.30
4	265	−0.66	−2.09	−2.55	−1.95	−2.27	0.14	0.28
5	264	−0.84	−2.10	−2.50	−1.91	−2.28	0.19	0.22
6	278	−0.84	−2.08	−2.58	−2.00	−2.28	0.08	0.30

[a] Measured in DMSO (1×10^{-3} M) solution.

Electrochemical studies of cyclophanes with oxadiazole units are of interest due to the electron-deficient nature of the oxadiazole unit.[32] It is of interest to examine the effect of the oxadiazole unit on the benzimidazolium ion during the electrochemical process. Hence, the electrochemical properties of compounds **1a–c**, **2**, **3**, **4**, **5**, and **6** were determined by cyclic voltammetry in DMSO (1×10^{-3} M) solutions, using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. A glassy carbon rod was used as the working electrode, $Ag/AgNO_3$ (0.1 M) as the reference electrode, and Pt as the counter electrode. The redox behaviors of all the cyclophanes are summarized in Table 1. All the compounds exhibited one irreversible reduction and two quasi-reversible redox processes. For example, compound **1c** showed one irreversible reduction at −0.84 V and two quasi-reversible redox processes with reduction peaks at −2.08 V and −2.58 V, and the corresponding oxidation peaks at −1.93 V and −2.29 V, respectively. Similarly, compound **3** showed one irreversible reduction peak at −0.66 V and two quasi-reversible redox processes with reduction peaks at −2.11 V and −2.59 V and the corresponding oxidation peaks at −1.99 V and −2.29 V, respectively (Fig. 2). We assume that the curve at lower reduction potential may be due to the more electron-deficient dications in the ring system, and the curve at higher reduction potential can be attributed to the redox behavior of the oxadiazole unit.[33]

In summary, we have synthesized benzimidazolophanes containing an oxadiazole unit and studied their spectroscopic, optical, and electrochemical properties. The spectroscopic and optical properties revealed the absence of self-complementary properties in all the cyclophanes, which show that the oxadiazole ring system is electron deficient by nature. The synthesis of dicationic 1,3,4-oxadiazolophanes possessing imidazole and benzotriazole units and studies on their complexation with anionic guests are underway.

Acknowledgments

The authors thank UGC, New Delhi, India, for financial assistance and DST-FIST for providing NMR facilities to the department. S.R. thanks UGC, New Delhi, for a fellowship.

References and notes

1. Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.
2. Alcade, E.; Ramos, S.; Garcia, L. P. *Org. Lett.* **1999**, *1*, 1035.
3. Yuan, Y.; Gao, G.; Jiang, Z.; You, J.; Zhou, Z.; Yuan, D.; Xie, R. *Tetrahedron* **2002**, *58*, 8993.
4. Qin, D.; Xu, F.; Wan, X.; Zhao, Y.; Zhang, Z. *Tetrahedron Lett.* **2006**, *47*, 5641.
5. Tully, W. R.; Gardner, C. R.; Gillespie, R. J.; Westwood, R. *J. Med. Chem.* **1991**, *34*, 2060.
6. Holla, B. S.; Gonsalves, R.; Shenoy, S. *Eur. J. Med. Chem.* **2000**, *35*, 267.
7. Yu, W. L.; Meng, H.; Pei, J.; Huang, W.; Li, Y.; Heeger, A. J. *Macromolecules* **1998**, *31*, 4838.
8. Chen, C.; Xu, X.; Liu, Y.; Qiu, W.; Yu, G.; Sun, X.; Zhang, H.; Qi, T.; Lu, K.; Gao, X.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2007**, *17*, 3788.
9. Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077.
10. Apreutesei, D.; Mehl, G. H. *J. Mater. Chem.* **2007**, *17*, 4711.
11. Wang, C.; Palsson, L.-O.; Batsanov, A. S.; Bryce, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 3789.
12. Verheyde, B.; Dehaen, W. *J. Org. Chem.* **2001**, *66*, 4062.
13. Pérez, M. A.; Bermejo, J. M. *J. Org. Chem.* **1993**, *58*, 2628.
14. Wang, S.; Zheng, S. P.; Meng, H.; Hua, W. T. *Synth. Met.* **1998**, *93*, 181.
15. Zhang, Y.; Hu, Y.; Li, H.; Wang, L.; Jing, X.; Wang, F.; Ma, D. *J. Mater. Chem.* **2003**, *13*, 773.
16. Precyclophane **8**: Yield 77%; mp 185 °C (dec); ^1H NMR (300 MHz, $CDCl_3$): δ 5.33 (s, 4H); 7.16–7.21 (m, 10H); 7.75 (d, 2H, J = 6.3 Hz); 7.90–7.97 (m, 6H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.4, 109.9, 120.6, 122.6, 123.4, 123.7, 127.6, 127.6, 133.7, 139.5, 143.2, 143.9, 164.1; (GC–MS) m/z 482 (M^+). Elemental Anal. Calcd for $C_{30}H_{22}N_6O$: C, 74.67; H, 4.60; N, 17.42. Found: C, 74.55; H, 4.73; N, 17.56.
17. Cyclophane **1a**: Yield 69%; mp 275 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.84 (s, 4H); 5.90 (s, 4H); 7.32 (m, 4H); 7.47–7.49 (m, 8H); 7.61–7.68 (m, 4H); 8.06–8.13 (m, 4H); 10.00 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 47.9, 49.7, 114.0, 123.4, 126.9, 127.1, 127.3, 129.2, 129.5, 131.0, 131.1, 131.4, 131.9, 137.7, 143.2, 163.7; (GC–MS) m/z 746 (M^+). Elemental Anal. Calcd for $C_{38}H_{30}Br_2N_6O$: C, 61.14; H, 4.05; N, 11.26. Found: C, 61.23; H, 4.19; N, 11.15.
18. Cyclophane **1b**: Yield 71%; mp 270 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.82 (s, 4H); 5.92 (s, 4H); 7.49–7.68 (m, 12H); 7.75 (s, 4H); 8.14–8.16 (m, 4H); 10.02 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.7, 49.9, 113.9, 123.5, 126.8, 126.9, 127.3, 128.3, 128.7, 129.2, 129.8, 130.9, 131.0, 134.6, 137.8, 143.0, 163.7; (GC–MS) m/z 746 (M^+). Elemental Anal. Calcd for $C_{38}H_{30}Br_2N_6O$: C, 61.14; H, 4.05; N, 11.26. Found: C, 61.21; H, 4.15; N, 11.17.
19. Cyclophane **1c**: Yield 70%; mp 280 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.85 (s, 4H); 5.93 (s, 4H); 7.63 (m, 8H); 7.77 (m, 4H); 7.95 (m, 4H); 8.17 (m, 4H); 10.21 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.6, 49.7, 114.0, 123.5,

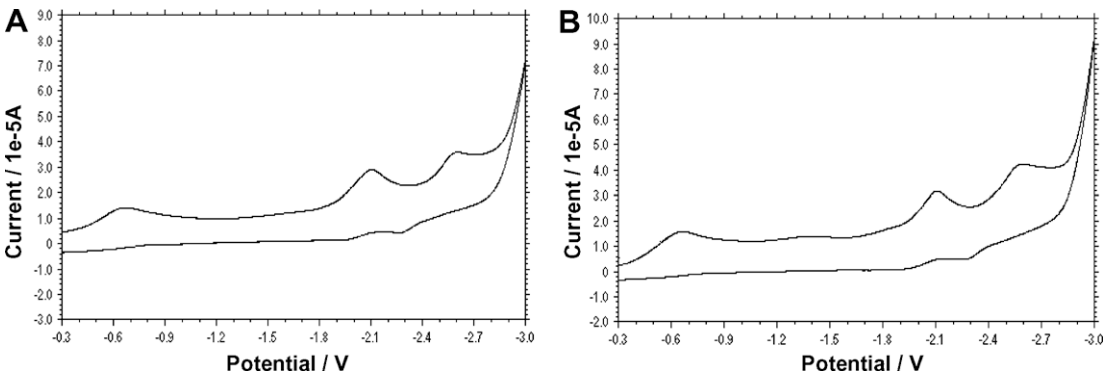


Figure 2. Cyclic voltammograms of compounds **1c** (A) and **3** (B) in (1×10^{-3} M) DMSO, scanned at 100 mV s^{-1}.

126.9, 127.3, 128.1, 128.3, 128.9, 129.3, 131.0, 134.4, 137.8, 143.1, 163.7; *m/z* (GC–MS) *m/z* 746 (M^+). Elemental Anal. Calcd for $C_{38}H_{30}Br_2N_6O$: C, 61.14; H, 4.05; N, 11.26. Found: C, 61.02; H, 4.11; N, 11.14.

20. Srinivasan, K.; Rajakumar, P. *Supramol. Chem.* **2005**, *17*, 215.
21. Rajakumar, P.; Selvam, S.; Dhanasekaran, M. *Tetrahedron Lett.* **2005**, *46*, 6127.
22. Cyclophane **2**: Yield 74%; mp >300 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 3.85 (s, 6H); 5.71 (s, 4H); 5.96 (s, 4H); 7.60–7.75 (m, 10H); 7.94–8.11 (m, 8H); 10.22 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 46.3, 49.2, 56.2, 113.8, 114.9, 122.8, 123.4, 126.7, 126.9, 127.3, 128.9, 130.7, 131.0, 138.1, 143.3, 151.5, 163.7; (GC–MS) *m/z* 806 (M^+). Elemental Anal. Calcd for $C_{40}H_{34}Br_2N_6O_3$: C, 59.57; H, 4.25; N, 10.42. Found: C, 59.71; H, 4.36; N, 10.59.
23. Cyclophane **3**: Yield 65%; mp 290 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.92 (s, 8H); 7.02 (t, 1H, J = 6.3 Hz); 7.27 (d, 2H, J = 8.4 Hz); 7.53–7.60 (m, 4H); 7.70–7.79 (m, 6H); 7.90–7.92 (m, 4H); 8.11–8.12 (m, 2H); 10.16 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.3, 50.8, 113.4, 123.2, 126.3, 126.7, 126.9, 127.2, 129.3, 129.7, 131.0, 137.2, 137.7, 142.6, 152.3, 162.9; (GC–MS) *m/z* 747 (M^+). Elemental Anal. Calcd for $C_{37}H_{29}Br_2N_7O$: C, 59.45; H, 3.91; N, 13.12. Found: C, 59.57; H, 3.79; N, 13.21.
24. Kannan, A.; Rajakumar, P.; Kabaleeswaran, V.; Rajan, S. *J. Org. Chem.* **1996**, *61*, 5090.
25. Rajakumar, P.; Srisailas, M. *Tetrahedron Lett.* **1997**, *38*, 5323.
26. Cyclophane **4**: Yield 70%; mp 300 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.92 (s, 4H); 6.03 (s, 4H); 7.55–7.63 (m, 12H); 7.73 (d, 4H, J = 7.2 Hz); 7.87 (d, 4H, J = 7.2 Hz); 8.00 (s, 4H); 8.18 (d, 4H, J = 7.2 Hz); 10.41 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 48.3, 48.5, 112.8, 113.0, 117.0, 122.2, 125.2, 126.0, 126.3, 126.4, 126.5, 127.2, 127.3, 129.7, 129.8, 130.0, 132.3, 137.2, 138.5, 138.8, 142.0, 162.3; (GC–MS) *m/z* 896 (M^+). Elemental Anal. Calcd for $C_{50}H_{38}Br_2N_6O$: C, 66.82; H, 4.26; N, 9.35. Found: C, 66.70; H, 4.12; N, 9.49.
27. Rajakumar, P.; Murali, V.; Kalaivasan, N. *Synth. Commun.* **2002**, *32*, 1685.
28. Cyclophane **5**: Yield 66%; mp 275 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.95 (s, 4H); 6.00 (s, 4H); 7.55–7.64 (m, 12H); 7.80–7.84 (m, 8H); 7.90–7.94 (m, 4H); 8.05–8.11 (m, 4H); 10.19 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.5, 49.6, 113.9, 123.2, 127.2, 127.3, 127.4, 127.6, 128.5, 128.6, 129.2, 130.5, 130.8, 131.00, 133.6, 136.5, 137.3, 137.8, 139.0, 143.0, 163.6, 194.7; (GC–MS) *m/z* 954 (M^+). Elemental Anal. Calcd for $C_{52}H_{38}Br_2N_6O_3$: C, 65.42; H, 4.01; N, 8.80. Found: C, 65.53; H, 4.14; N, 8.91.
29. Cyclophane **6**: Yield 69%; mp >300 °C (dec); ^1H NMR (300 MHz, DMSO-d_6): δ 5.94 (s, 8H); 7.59–7.77 (m, 12H); 7.95 (s, 4H); 8.18–8.27 (m, 8H); 10.10 (s, 2H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.3, 114.0, 127.3, 127.5, 128.0, 129.3, 130.7, 138.4, 150.6, 163.4; (GC–MS) *m/z* 890 (M^+). Elemental Anal. Calcd for $C_{46}H_{34}Br_2N_8O_2$: C, 62.03; H, 3.85; N, 12.58. Found: C, 62.15; H, 3.97; N, 12.73.
30. Ichikawa, M.; Kawaguchi, T.; Kobayashi, K.; Miki, T.; Furukawa, K.; Koyama, T.; Taniguchi, Y. *J. Mater. Chem.* **2006**, *16*, 221.
31. Mashraqui, S. H.; Sundaram, S.; Bhasikuttan, A. C. *Tetrahedron* **2007**, *63*, 1680.
32. Wan, J. H.; Feng, J. C.; Wen, G. A.; Wei, W.; Fan, Q. L.; Wang, C. M.; Wang, H. Y.; Zhu, R.; Yuan, X. D.; Huang, C. H.; Huang, W. *J. Org. Chem.* **2006**, *71*, 2565.
33. Hughes, G.; Kreher, D.; Wang, C.; Batsanov, A. S.; Bryce, M. R. *Org. Biomol. Chem.* **2004**, *2*, 3363.