Synthesis of Novel Amide-Crownophanes and Schiff Base-Crownophanes Based on *p*-Phenylene, 2,6-Naphthalene, and 9,10-Anthracene

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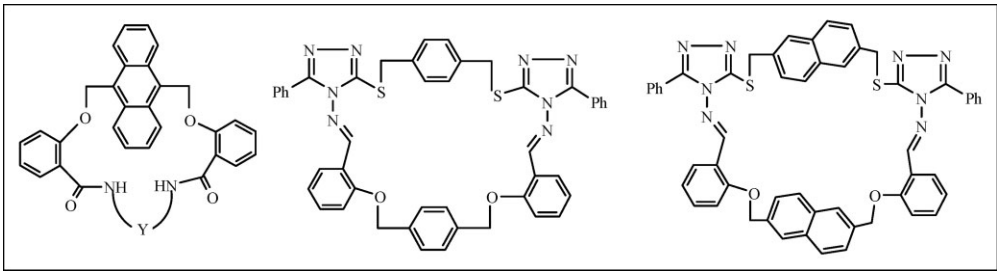

The novel macrocyclic diamides **11–13, 16–18** are obtained in 45–66% yields by the reaction of dipotassium salts **10a–c** and **15** with each of 1,4-di(bromomethyl)benzene **4**, 2,6-di(bromomethyl)naphthalene **6** and 9,10-di(bromomethyl)anthracene **8**, repectively, in boiling DMF. On the other hand, the new macrocyclic Schiff bases **28** and **29** are obtained in 44% and 42% yields by heating the appropriate bis-amines **25b**, **26b** with the corresponding bis-aldehydes **21**, **22**, respectively, in refluxing acetic acid under high-dilution conditions.

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INTRODUCTION

Over the past few decades, macrocyclic compounds have become important synthetic targets due to their wide applications in host-guest supramolecular chemistry. They have been shown to exhibit important applications, including selective ion separation and detection, molecular recognition, catalysis, biological applications as well as many other interesting applications in diverse fields of supramolecular chemistry [1–8]. In particular, macrocyclic polyethers with amide groups in the macrocyclic ring have attracted much attention. Insertion of these groups into the macrocyclic ring structure has been reported to affect the binding properties and selectivity of macrocyclic compounds with metal cation [9,10] as well as organic molecules [11–13]. Recently Kumar *et al*. [14–16] have reported that diamide-ester macrocyclic compounds showed extraordinary Ag^+ binding strength with a remarkable selectivity for Ag over other metal ions. Macrocyclic amides are also precursors in the preparation of azacrown ethers and cryptands [4,6,9,11]. Furthermore, some diamide-containing macrocycles have been utilized as new catalysts [17]. Moreover, a progressive interest was directed in the last few years to the synthesis of novel macrocyclic Schiff bases because they can be obtained by simple self-condensation of suitable formyl- or keto- and primary amine-precursors [18] and they can be functionalized by inserting appropriate groups in the aliphatic and/or aromatic chains of the precursors. They generally can contain additional donor groups (O, S, P, etc.) and this makes them good candidates for metal ion complexation and for mimicking biological systems.

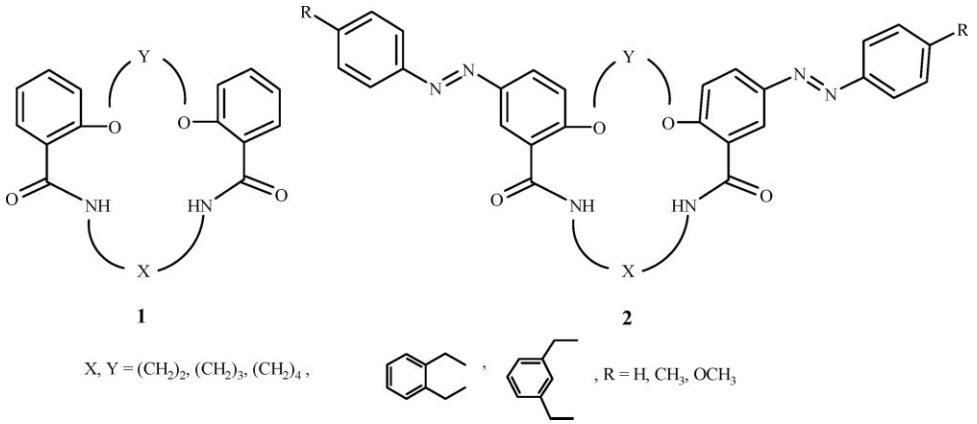
Furthermore, considerable attention has been focused on crown ethers bearing chromophores such as naphthalene and/or anthracene. They are promising analytical reagents for colorimetry and can be used for spectrophotometric determination of metal ions [19]. Anthracene is one of the most employed chromophores due to its ability to induce PET (photoinduced electron transfer) processes [20]. The naphthalene moiety is also a well-known fluorophore and its ability to block intersystem crossing in the first excited state is remarkable [21]. The detection of metal ions with a high specificity under physiologically relevant conditions is an important issue in the design of fluorescent chemosensors in biological and environmental applications [22].

We have investigated several synthetic approaches towards macrocyclic azacrown compounds where some of them showed useful application in ion selective electrodes and as spectrophotometric reagents [23].

Although up to now, many kinds of azacrownophanes were prepared, development of a mild and effective synthetic route to this type of macrocycles still remains an attractive and challenging subject for synthetic chemists. Here, we report on the synthesis of a new family of amide-crownophanes and Schiff base-crownophanes that use *p*-phenylene, 2,6-naphthalene or 9,10-anthracene as assembling units.

RESULTS AND DISCUSSION

Previously, we reported the synthesis of tribenzo- and tetra-benzosubstituted macrocyclic diamides **1** and their corresponding azo derivatives **2**, in which the arylazo groups act as chromophoric side arms, by the reaction of the potassium salts of the appropriate bis(phenols) with the corresponding dihalo compounds in refluxing DMF [23a,b,f,h].



In this study, we intended to insert the chromophoric units 2,6-naphthalene and 9,10-anthracene into the macrocyclic rings **1**. The insertion of *p*-phenylene unit into the macrocycles **1** was also investigated for a comparison study. For this purpose, the bis(bromomethyl) compounds **4**, **6**, and **8** were chosen as a key intermediate and could be readily obtained from the corresponding dimethyl derivatives **3**, **5**, and **7**, respectively, by bromination with Br_2 or *N*-bromosuccinimide (NBS) in CCl_4 according to reported methods [24] (Scheme 1).

Thus, the treatment of the bis(phenol)s **9** with ethanolic KOH afforded the corresponding dipotassium salt **10**. Alkylation of **10** with **4**, **6**, and **8** in boiling DMF led to the formation of the novel macrocyclic diamides **11–13** in 45–66% yield (Scheme 2). It is noteworthy that we were not able to isolate pure sample of **13a** by the reaction of **10a** with **8** under similar conditions.

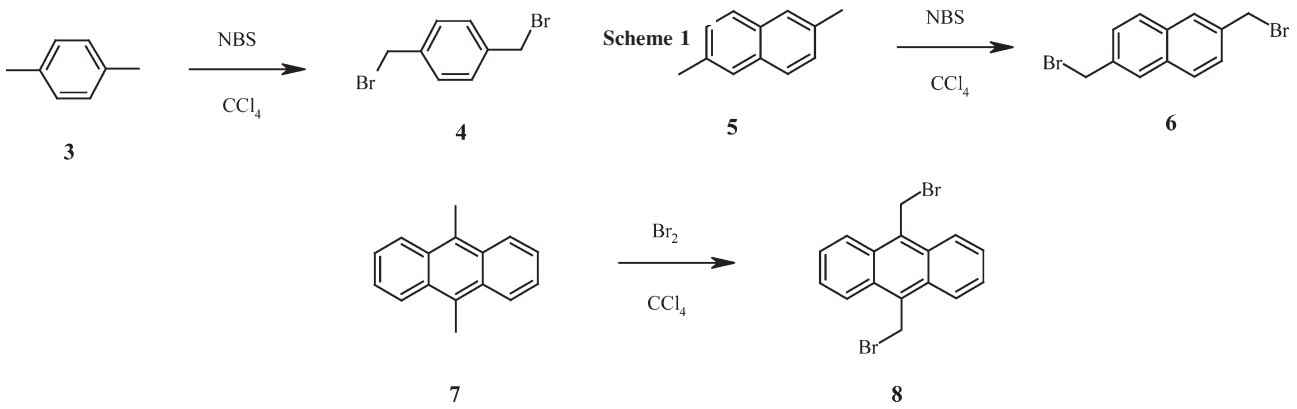
We also studied the insertion of an additional 1,3-xyly unit into the macrocyclic ring **11–13** instead of the alkylene moieties, aiming at studying the effect of rigidity provided by these groups on the ability of the ligands to form stable complexes compared with other macrocyclic analogues. Thus, reacting the dipotassium salts **15** (obtained from the corresponding bis(phenol) **14** upon treatment with ethanolic KOH) with the corresponding bis(bromomethyl)arenes **4**, **6**, and **8** under similar conditions give the corresponding macrocyclic diamides **16–18** in 49–62% yields, respectively (Scheme 3).

Our study was extended to include the insertion of chromophoric units into the macrocyclic Schiff base **19**. The latter compounds were recently obtained by cyclocondensation of the appropriate bis(carbonyl) ethers with the corresponding bis(amines) in glacial acetic acid under high-dilution conditions [23(f,l)].

To achieve this goal, the novel bis(aldehyde)s **21–23** as well as the novel bis(amine)s **25–27** were prepared as outlined in Schemes 4 and 5. Compounds **4**, **6**, and **8** serve as starting materials for the synthesis of **21–23**, **25–27**. Thus, reaction of **4**, **6**, and **8** with the potassium salt **20** (obtained upon treatment of salicylaldehyde with ethanolic potassium hydroxide) in refluxing DMF afforded the corresponding bis(aldehydes) **21–23** in 65–80% yield (Scheme 4).

On the other hand, reaction of **4**, **6** and **8** with 4-amino-1,2,4-triazol-3-thiones **24a,b** in ethanol/water mixture containing potassium hydroxide afforded the corresponding bis(4-amino-1,2,4-triazol-3-ylsulfanylmethyl)arenes **25–27** in 67–81% yield (Scheme 5).

The synthetic utility of the novel bis(aldehyde)s **21–23** and the bis(amine)s **25–27** as building blocks for novel macrocyclic Schiff bases containing *p*-phenylene, 2,6-naphthalene, or 9,10-anthracene groups incorporated into the ring system was then investigated. Thus, cyclocondensation of **21** with 1,4-bis(4-amino-5-phenyl-3-



ylsulfanylmethyl)benzene (**25b**) in glacial acetic acid under high-dilution conditions gave the corresponding macrocyclic Schiff base **28** in 44% yield. Under similar conditions **22** reacted with **26b** to give the corresponding macrocyclic Schiff base **29** in 42% yield (Scheme 6).

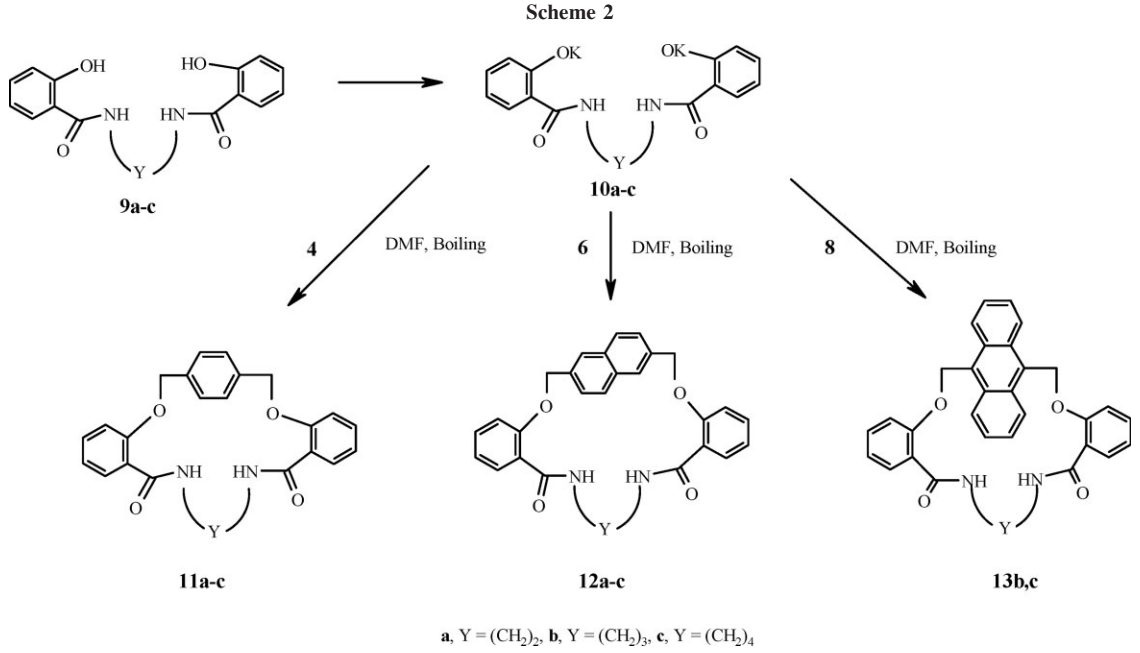
Unfortunately repeated attempts to react 9,10-bis(2-formylphenoxymethyl)anthracene **23** with with 9,10-bis(4-amino-5-phenyl-3-ylsulfanylmethyl)anthracene **27b** in refluxing acetic acid under high dilution conditions did not lead to the formation of the expected macrocyclic Schiff base **30**. Instead, the reaction gave 55% of another product which was characterized by ^{1}H NMR (DMSO), IR, and mass spectra as 9,10-bis(acetyloxymethyl)-anthracene **31**. The latter was obtained in 50% yield by heating only **23** in refluxing acetic acid (Scheme 7).

In conclusion, we prepared a new series of bis(4-amino-1,2,4-triazol-3-ylsulfanylmethyl)arenes as well as bis(2-formylphenoxymethyl)arenes and utilized them successfully as key intermediates for the synthesis of novel macrocyclic Schiff bases upon which fused triazole units and contain N, O, and S inside the macrocyclic ring as donor atoms. We also prepared a new series of amide-crownophanes by the reaction of the appropriate bis(phenol)s with the corresponding dihalo compounds. The novel macrocycles use *p*-phenylene, 2,6-naphthalene or 9,10-anthracene as assembling units. Some derivatives of the new dilactams as well as the new Schiff bases showed promising cation binding properties in a preliminary spectrophotometric study. This data will be published separately due to the large quantity of analytical data accumulated.

EXPERIMENTAL

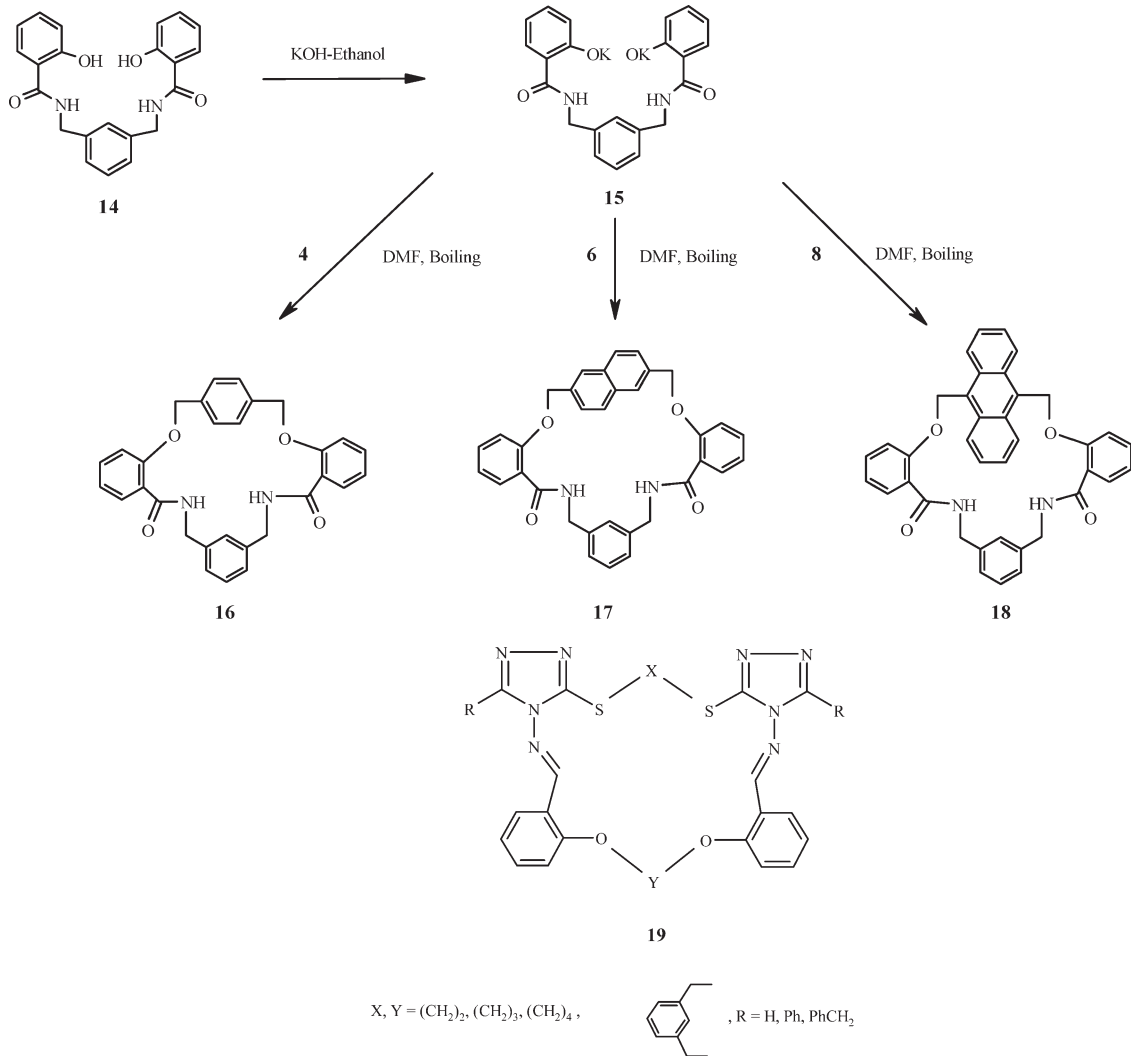
Melting points are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer 1430 spectrophotometer. NMR

Scheme 2

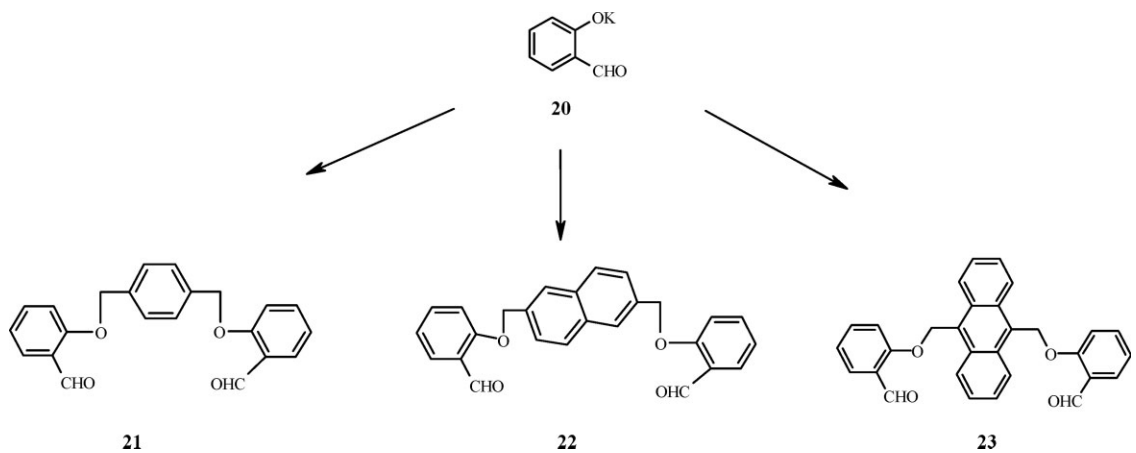


a, Y = $(CH_2)_2$, **b**, Y = $(CH_2)_3$, **c**, Y = $(CH_2)_4$

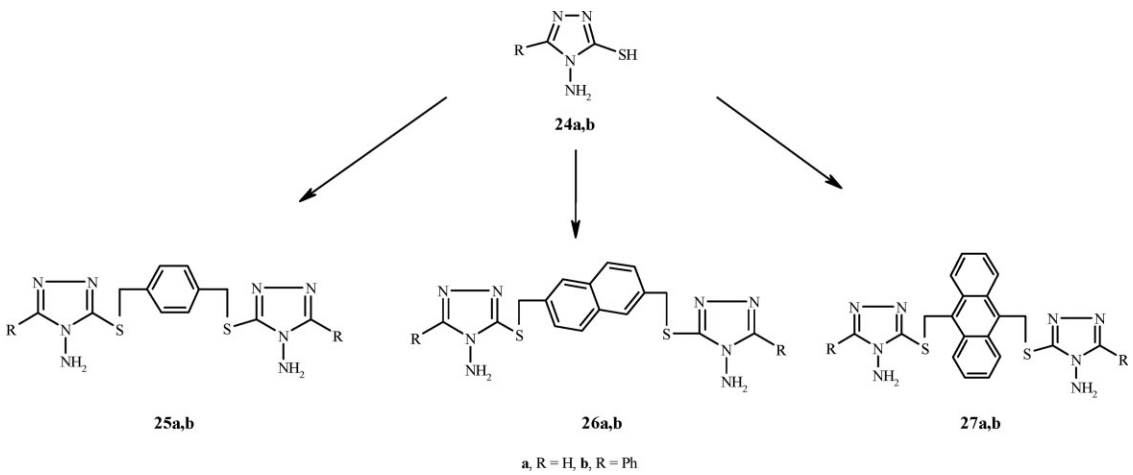
Scheme 3



Scheme 4



Scheme 5



spectra were measured with a Varian Mercury 300 (300 MHz ^{1}H NMR, 75 MHz ^{13}C NMR) spectrophotometer and chemical shifts are given in ppm from TMS. Mass spectra were recorded on GC MS-QP1000 EX (70 eV) or MS 5988 (15 eV) spectrometers. Elemental analyses were carried out at the Microanalytical Centre, Cairo University. 4-Aminotriazol-3-thione derivatives **24a**,**b** were prepared as reported [25].

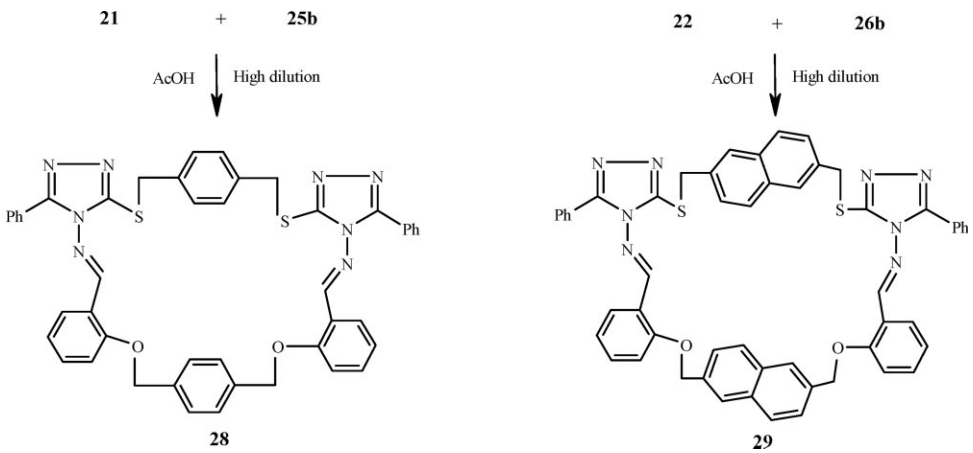
Preparation of dipotassium salts 10, 15, general procedure [28a,28s,28y]. To a solution of KOH (1.14 g, 10 mmol) in methanol (10 mL) was added the appropriate bis(phenol) **9a–c**, **14** (5 mmol). The mixture was stirred at room temperature for 10 min. The solvent was then removed *in vacuo*. The remaining solid was triturated with dry ether, collected, dried, and used in the next step without further purification.

Synthesis of macrocycles 11a–c, 12a–c, 13b,c, 16–18, general procedure. A solution of the appropriate potassium salt **10a–c**, **15** (10 mmol) and the appropriate dihalo compound **4**, **6**, **8** (10 mmol) in DMF (20 mL) was heated under reflux for 10 min. during which time KCl precipitated. The solvent was then removed *in vacuo* and the remaining material was washed with water (50 mL) and purified by crystallization from acetic acid unless otherwise noted.

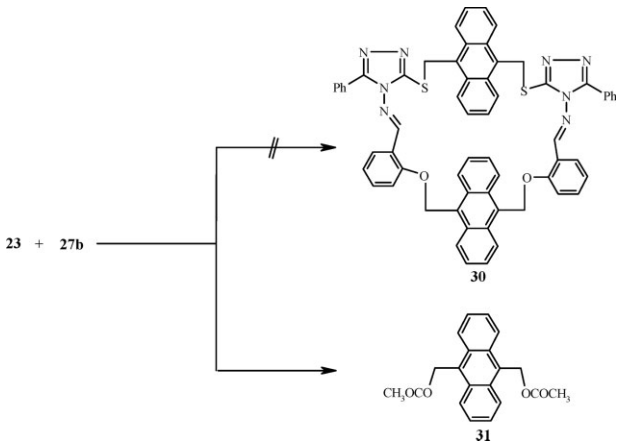
Macrocycle 11a. Reaction of **10a** with **4** produced **11a** as colorless crystals (64%), mp 253–254°C; IR: 3376 (NH), 1651 (C=O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.26 (s, 4H, CH_2NH), 5.20 (s, 4H, OCH_2), 7.02–7.57 (m, 14H, ArH's, NH); ^{13}C NMR (DMSO) δ 38.66 (CH_2N), 72.48 (OCH_2), 116.51, 121.49, 125.72, 129.35, 129.86, 131.90, 136.60, 155.77 (ArC's), 165.28 (C=O); MS (EI): *m/z* 402 (M$^+$, 2%), 282 (42.6%), 239 (15.1%), 162 (24.5%), 104 (100%). Anal. Calcd. for $C_{24}H_{22}O_4N_2$ (402.45): C, 71.63; H, 5.51; N, 6.96. Found: C, 71.80; H, 5.30; N, 7.20.

Macrocycle 11b. Reaction of **10b** with **4** produced **11b** as colorless crystals (62%), mp > 300°C; IR: 3376 (NH), 1648 (C=O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.06 (m, 2H, CH_2CH_2NH), 3.04 (m, 4H, CH_2NH), 5.17 (s, 4H, OCH_2), 7.06–7.83 (m, 14H, ArH's, NH); ^{13}C NMR (DMSO) δ 29.10 (CH_2CH_2NH), 37.20 (CH_2N), 71.20 (OCH_2), 109.26, 113.06, 120.86, 130.07, 130.32, 132.26, 136.50, 155.80 (ArC's), 164.30 (C=O); MS (EI): *m/z* 416 (M$^+$, 2.7%), 296 (47.8%),

Scheme 6



Scheme 7



178 (16.3%), 104 (100%). Anal. Calcd. for $C_{25}H_{24}O_4N_2$ (416.48): C, 72.10; H, 5.81; N, 6.73. Found: C, 72.30; H, 5.70; N, 6.70.

Macrocycle 11c. Reaction of **10c** with **4** produced **11c** as colorless crystals (61%), mp 291–292°C; IR: 3413, 3380 (NH), 1647 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.21 (s, 4H, CH_2CH_2NH), 3.19 (m, 4H, CH_2NH), 5.21 (s, 4H, OCH_2), 7.07–7.91 (m, 14H, ArH's, NH); ^{13}C NMR (DMSO) δ 26.87 (CH_2CH_2NH), 38.82 (CH_2N), 70.87 (OCH_2), 113.22, 120.93, 122.35, 130.88, 132.43, 136.39, 156.54 (ArC's), 164.21 (C=O); MS (EI): *m/z* 430 (M^+, 1.6%), 310 (49.4%), 173 (25.3%), 104 (100%). Anal. Calcd. for $C_{26}H_{26}O_4N_2$ (430.51): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.70; H, 5.90; N, 6.20.

Macrocycle 12a. Reaction of **10a** with **6** produced **12a** as colorless crystals (54%), mp 197–199°C; IR: 3390 (NH), 1636 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.47 (m, 4H, CH_2NH), 5.32 (m, 4H, OCH_2), 7.33–7.84 (m, 14H, ArH's), 8.40 (brs, 2H, NH); MS (EI): *m/z* 453 (M^++1, 2.5%), 369 (2.6%), 300 (17.5%), 247 (13.6%), 155 (4.2%). Anal. Calcd. for $C_{28}H_{24}O_4N_2$ (452.51): C, 74.32; H, 5.35; N, 6.19. Found: C, 74.50; H, 5.30; N, 6.20.

Macrocycle 12b. Reaction of **10b** with **6** produced **12b** as colorless crystals (66%), mp 287–289°C; IR: 3384 (NH), 1641 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.13 (m, 2H, CH_2CH_2NH), 2.79 (brs, 4H, CH_2NH), 5.38 (s, 4H, OCH_2), 7.03–8.16 (m, 16H, ArH's, NH); ^{13}C NMR (DMSO) δ 26.40 (CH_2CH_2NH), 37.28 (CH_2N), 73.26 (OCH_2), 114.93, 121.30, 122.32, 127.71, 128.66, 128.96, 130.82, 132.75, 133.20, 134.35, 156.96 (ArC's), 163.84 (C=O); MS (EI): *m/z* 466 (M^+, 15.6%), 346 (93.9%), 154 (100%), 121 (36.9%). Anal. Calcd. for $C_{29}H_{26}O_4N_2$ (466.54): C, 74.66; H, 5.62; N, 6.01. Found: C, 74.80; H, 5.30; N, 5.80.

Macrocycle 12c. Reaction of **10c** with **6** produced **12c** as colorless crystals (61%), mp 254–255°C; IR: 3426, 3385 (NH), 1642 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.68 (brs, 4H, CH_2CH_2NH), 2.85 (m, 4H, CH_2NH), 5.38 (s, 4H, OCH_2), 7.05–8.12 (m, 16H, ArH's, NH); ^{13}C NMR (DMSO) δ 26.76 (CH_2CH_2NH), 38.80 (CH_2N), 72.73 (OCH_2), 115.19, 121.10, 121.34, 123.76, 127.54, 128.56, 130.40, 132.27, 132.94, 134.42, 156.49 (ArC's), 164.35 (C=O); MS (EI): *m/z* 480 (M^+, 11.1%), 360 (100%), 223 (19.2%), 154 (55.7%), 121 (24.4%). Anal. Calcd. for $C_{30}H_{28}O_4N_2$ (480.57): C, 74.98; H, 5.87; N, 5.83. Found: C, 74.80; H, 5.50; N, 5.70.

Macrocycle 13b. Reaction of **10b** with **8** produced **13b** as yellow crystals (45%), mp 291–292°C; IR: 3388, 3421 (NH), 1640 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ −0.34 (brs, 2H, CH_2CH_2NH), 2.64 (m, 4H, CH_2NH), 6.37 (s, 4H, OCH_2), 7.14–8.52 (m, 18H, ArH's, NH); ^{13}C NMR (DMSO) δ 26.24 (CH_2CH_2NH), 36.41 (CH_2N), 64.23 (OCH_2), 113.74, 120.71, 121.20, 124.77, 126.65, 129.14, 130.04, 130.54, 132.54, 156.74 (ArC's), 163.56 (C=O); MS (EI): *m/z* 516 (M^+, 45.5%), 396 (100%), 314 (13.8%), 204 (81.1%), 178 (86.8%), 121 (73.5). Anal. Calcd. for $C_{33}H_{28}O_4N_2$ (516.60): C, 76.73; H, 5.46; N, 5.42. Found: C, 76.80; H, 5.30; N, 5.20.

Macrocycle 13c. Reaction of **10c** with **8** produced **13c** as yellow crystals (51%), mp 259–260°C; IR: 3402 (NH), 1650 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.28 (s, 4H, CH_2CH_2NH), 2.73 (m, 4H, CH_2NH), 6.30 (s, 4H, OCH_2), 7.14–8.50 (m, 18H, ArH's, NH). ^{13}C NMR (DMSO) δ 25.92 (CH_2CH_2NH), 37.10 (CH_2N), 63.19 (OCH_2), 113.88, 121.28, 124.68, 126.69, 128.95, 130.03, 131.13, 132.76, 156.78 (ArC's), 163.66 (C=O); MS (EI): *m/z* 530 (M^+, 14.9%), 410 (56.8%), 204 (75.6%), 121(100%). Anal. Calcd. for $C_{34}H_{30}O_4N_2$ (530.63): C, 76.96; H, 5.70; N, 5.28. Found: C, 76.80; H, 5.40; N, 5.20.

Macrocycle 16. Reaction of **15** with **4** produced **16** as colorless crystals [acetic acid-ethanol (1:1)] (62%), mp 281–282°C; IR: 3392 (NH), 1648 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.46 (m, 4H, CH_2NH), 5.15 (s, 4H, OCH_2), 7.09–7.93 (m, 16H, ArH's), 8.48 (br, 2H, NH); MS (EI): *m/z* 478 (M^+, 5.9%), 358 (25.7%), 254 (10.6%), 121 (55.9%), 104 (100%). Anal. Calcd. for $C_{30}H_{26}N_2O_4$ (478.55): C, 75.30; H, 5.48; N, 5.85. Found: C, 75.40; H, 5.70; N, 5.90.

Macrocycle 17. Reaction of **15** with **6** produced **17** as colorless crystals (ethanol) (49%), mp 258–259°C; IR: 3391 (NH), 1649 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.32 (m, 4H, CH_2NH), 5.31 (s, 4H, OCH_2), 6.50–7.97 (m, 18H, ArH's), 8.17 (br, 2H, NH); ^{13}C NMR (DMSO) δ 42.59 (CH_2N), 71.27 (OCH_2), 113.10, 120.96, 121.99, 123.36, 125.66, 126.87, 127.67, 128.19, 130.83, 132.55, 132.68, 133.33, 136.85, 156.74 (ArC's), 164.51 (C=O); MS (EI): *m/z* 528 (M^+, 9.4%), 408 (49.1%), 339 (25.7%), 288 (22%), 154 (100). Anal. Calcd. for $C_{34}H_{28}N_2O_4$ (528.61): C, 77.26; H, 5.34; N, 5.30. Found: C, 77.30; H, 5.30; N, 4.90.

Macrocycle 18. Reaction **15** with **8** produced **18** as yellow crystals [acetic acid-ethanol (1:1)] (51%), mp 245–246°C; IR: 3485, 3389 (NH), 1641 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.91 (m, 4H, CH_2NH), 6.18 (s, 4H, OCH_2), 6.50–8.39 (m, 20H, ArH's, NH); MS (EI): *m/z* 578 (M^+, 9.4%), 458 (13.7%), 338 (11.5%), 240 (17.6%), 205 (100%), 121 (51.5%). Anal. Calcd. for $C_{38}H_{30}N_2O_4$ (578.67): C, 78.87; H, 5.23; N, 4.84. Found: C, 78.80; H, 4.90; N, 4.90.

Synthesis of bis(aldehyde)s 21–23, general procedure. A solution of the potassium salt of salicylaldehyde 20 (20 mmol) and the dibromo compound **4**, **6**, **8** (10 mmol) in DMF (20 mL) was heated under reflux for 5 min. during which the potassium chloride precipitated. The solution was concentrated to small volume (ca. 2 mL) and then cold water (ca. 10 mL) was added. The solid obtained was collected and crystallized from acetic acid.

1,4-Bis(2-formylphenoxymethyl)benzene (21). Reaction of **20** with **4** produced **21** as colorless crystals (80%), mp 189–

190°C; IR: 2762, 2850 (CHO), 1686 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.30 (s, 4H, OCH_2), 7.06–7.73 (m, 12H, ArH's), 10.44 (s, 2H, CHO); ^{13}C NMR (DMSO) δ 69.77 (OCH_2), 114.15, 120.93, 124.73, 127.64, 127.86, 136.15, 136.22, 160.51 (ArC's), 189.05 (C=O); MS (EI): *m/z* 346 (M^+, 0.1%), 224 (38%), 179 (4.6%), 121.05 (11.7%), 104 (92.2%), 91 (100%). Anal. Calcd. for $C_{22}H_{18}O_4$ (346.38): C, 76.29; H, 5.24. Found: C, 76.30; H, 4.90.

2,6-Bis(2-formylphenoxymethyl)naphthalene (22). Reaction of **20** with **6** produced **22** as colorless crystals (65%), mp 191–192°C; IR: 2761, 2868 (CHO), 1674 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.45 (s, 4H, OCH_2), 7.07–8.05 (m, 14H, ArH's), 10.49 (s, 2H, CHO); ^{13}C NMR (DMSO) δ 69.98 (OCH_2), 114.13, 120.59, 120.63, 120.95, 125.84, 126.07, 127.83, 128.27, 134.33, 136.27, 160.53 (ArC's), 189.25 (C=O); MS (EI): *m/z* 396 (M^+, 0.9%), 275 (55.9%), 215 (0.9%), 169 (2.2%), 154 (100%). Anal. Calcd. for $C_{26}H_{20}O_4$ (396.45): C, 78.77; H, 5.09. Found: C, 78.70; H, 4.90.

9,10-Bis(2-formylphenoxymethyl)anthracene (23). Reaction of **20** with **8** produced **23** as yellow crystals (DMF) (70%), mp 248–249°C; IR: 2753, 2850 (CHO), 1682 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.28 (s, 4H, OCH_2), 7.14–8.51 (m, 16H, ArH's), 10.04 (s, 2H, CHO); MS (EI): *m/z* 446 (M^+, 2.5%), 325 (26%), 204 (100%), 121 (35.6%). Anal. Calcd for $C_{30}H_{22}O_4$ (446.51): C, 80.70; H, 4.97. Found: C, 80.60; H, 5.10.

Synthesis of bis(amine)s 25a,b–27a,b, general procedure. To a solution of **24a**, **b** (50 mmol) in aqueous ethanol (50 mL, 50%) containing KOH (50 mmol) was added the appropriate dibromo compound **4**, **6**, **8** (25 mmol). The reaction mixture was heated under reflux for 1 h. The solvent was then removed *in vacuo* and the remaining solid was collected and crystallized from the proper solvent.

1,4-Bis(4-amino-1,2,4-triazol-3-ylsulfanylmethyl)benzene (25a). Reaction of **24a** with **4** produced **25a** as colorless crystals (DMF/H_2O) (71%), mp 207–209°C; IR: 3333, 3092 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.35 (s, 4H, SCH_2), 6.02 (s, 4H, NH_2), 7.33 (s, 4H, ArH's), 8.44 (s, 2H, triazole H's); ^{13}C NMR (DMSO-*d*6) δ 34.73 (SCH_2), 128.95, 136.60, 146.19, 150.47 (ArC's, Triazole C's); MS (EI): *m/z* 334 (M^+, 0.4%), 218 (3.9%), 203 (8%), 183 (4%), 128 (4.9%), 116 (100%). Anal. Calcd. for $C_{12}H_{14}N_8S_2$ (334.43): C, 43.10; H, 4.22; N, 33.51. Found: C, 43.40; H, 4.30; N, 33.50.

1,4-Bis(4-amino-5-phenyl-1,2,4-triazol-3-ylsulfanylmethyl)-benzene (25b). Reaction of **24b** with **4** produced **25b** as colorless crystals (dilute acetic acid) (81%), mp 214–215°C; IR: 3309, 3181 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.42 (s, 4H, SCH_2), 6.09 (s, 4H, NH_2), 7.42–7.99 (m, 14H, ArH's); ^{13}C NMR (DMSO-d_6) δ 34.93 (SCH_2), 126.85, 127.72, 128.37, 129.03, 129.54, 136.63, 152.85, 154.02 (ArC's, Triazole C's); MS (EI): *m/z* 486 (M^+, 2.6%), 294 (11.8%), 192 (100%), 121 (20.1%). Anal. Calcd. for $C_{24}H_{22}N_8S_2$ (486.63): C, 59.24; H, 4.56; N, 23.03. Found: C, 59.30; H, 4.30; N, 22.90.

2,6-Bis(4-amino-1,2,4-triazol-3-ylsulfanylmethyl)naphthalene (26a). Reaction of **24a** with **6** produced **26a** as colorless crystals (DMF/H_2O) (69%), mp 216–217°C; IR: 3325, 3109 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.53 (s, 4H, SCH_2), 6.04 (s, 4H, NH_2), 7.53–7.86 (m, 6H, ArH's), 8.44 (s, 2H, triazole H's); ^{13}C NMR (DMSO-*d*6) δ 35.68 (SCH_2), 120.81, 127.15, 127.44, 127.80, 131.94, 135.14, 146.10 (ArC's, Triazole C's); MS (EI): *m/z* 385 (M^++1, 3.2%), 327 (2.6%), 268 (21.7%), 155 (29.2%), 116 (100%). Anal. Calcd. for $C_{16}H_{16}N_8S_2$ (384.49): C, 49.98; H, 4.19; N, 29.14. Found: C, 50.10; H, 4.30; N, 28.90.

2,6-Bis(4-amino-5-phenyl-1,2,4-triazol-3-ylsulfanylmethyl)-naphthalene (26b). Reaction of **24b** with **6** gave **26b** as colorless crystals (acetic acid) (74%), mp 240–241°C; IR: 3315, 3183 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.60 (s, 4H, SCH_2), 6.10 (s, 4H, NH_2), 7.48–7.98 (m, 16H, ArH's); ^{13}C NMR (DMSO-d_6) δ 35.33 (SCH_2), 120.71, 126.81, 127.29, 127.57, 127.86, 128.41, 129.57, 131.91, 135.17, 152.91, 154.03 (ArC's, Triazole C's). Anal. Calcd. for $C_{28}H_{24}N_8S_2$ (536.69): C, 62.66; H, 4.51; N, 20.88. Found: C, 62.40; H, 4.30; N, 21.00.

9,10-Bis(4-amino-1,2,4-triazol-3-ylsulfanylmethyl)anthracene (27a). Reaction of **24a** with **8** produced **27a** as yellow crystals (DMF/H_2O) (67%), mp 243–244°C; IR: 3332, 3281 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.46 (s, 4H, SCH_2), 6.14 (s, 4H, NH_2), 7.64–8.47 (m, 8H, ArH's), 8.55 (s, 2H, triazole H's); ^{13}C NMR (DMSO-*d*6) δ 29.40 (SCH_2), 124.79, 126.39, 128.90, 129.35, 146.39, 150.45 (ArC's, Triazole C's); MS (EI): *m/z* 434 (M^+, 2.2%), 318 (5.7%), 204 (18.2%), 116 (100%). Anal. Calcd. for $C_{20}H_{18}N_8S_2$ (434.55): C, 55.28; H, 4.18; N, 25.79. Found: C, 55.30; H, 4.30; N, 25.90.

9,10-Bis(4-amino-5-phenyl-1,2,4-triazol-3-ylsulfanylmethyl)-anthracene (27b). Reaction of **24b** with **8** produced **27b** as yellow crystals (DMF/H_2O) (75%), mp 233–235°C; IR: 3281, 3353 (NH_2) cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.52 (s, 4H, SCH_2), 6.17 (s, 4H, NH_2), 7.53–8.52 (m, 18H, ArH's); MS (EI): *m/z* 586 (M^+, 9%), 394 (46.1%), 228 (25.8%), 192 (82%), 104 (100%). Anal. Calcd. for $C_{32}H_{26}N_8S_2$ (586.75): C, 65.51; H, 4.47; N, 19.10. Found: C, 65.30; H, 4.30; N, 18.90.

Synthesis of macrocyclic bis-Schiff bases 28, 29, and 9,10-bis(acetyloxymethyl)-anthracene 31, general procedure. To a solution of the appropriate bis aldehyde **21–23** (10 mmol) in glacial acetic acid (50 mL) was added a solution of the appropriate bis amine **25b**, **26b**, **27b** (10 mmol) in glacial acetic acid (50 mL). The reaction mixture was then heated under reflux for 2 h. The solution was concentrated to small volume (ca. 2 mL) and then cold water (ca. 15 mL) was added. The precipitate obtained was collected and recrystallized from acetic acid.

Macrocycle 28. Reaction of **21** with **25b** produced **28** as colorless crystals (44%), mp 248–249°C; ^1H NMR (DMSO-d_6) δ 4.43 (s, 4H, SCH_2), 5.24 (s, 4H, OCH_2), 7.14–7.99 (m, 26H, ArH's), 9.18 (s, 2H, CH=N). MS (EI): *m/z* 796 (M^+, 0.4%), 626 (0.3%), 561 (0.8%), 558 (0.8%), 486 (1.6%), 280 (22.4%), 222 (76.5%), 177 (24.9%), 104 (100%). Anal. Calcd. for $C_{46}H_{36}N_8O_2S_2$ (796.98): C, 69.33; H, 4.55; N, 14.06. Found: C, 69.40; H, 4.30; N, 14.30.

Macrocycle 29. Reaction of **22** with **26b** gave **29** as colorless crystals (42%), mp 254–255°C; ^1H NMR (DMSO-d_6) δ 4.60 (s, 4H, SCH_2), 5.38 (s, 4H, OCH_2), 7.17–8.03 (m, 30H, ArH's), 9.21 (s, 2H, CH=N). MS (EI): *m/z* 896 (M^+, 0.5%), 522 (0.9%), 448 (1.6%), 390 (2.1%), 330 (4%), 272 (65.5%), 154 (100%). Anal. Calcd. for $C_{54}H_{40}N_8O_2S_2$ (897.10): C, 72.30; H, 4.49; N, 12.49. Found: C, 72.40; H, 4.30; N, 12.20.

9,10-Bis(acetyloxymethyl)anthracene (31). Reaction of **23** with **27b** produced **31** as yellow crystals (55%), mp 214–215°C; 178 (35.29%); IR: 1729 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.02 (s, 6H, $OCOCH_3$), 6.15 (s, 4H, OCH_2), 7.65–8.45 (m, 8H, ArH's); MS (EI): *m/z* 322 (M^+, 30.71%),

263 (10.8%), 220 (100%), 204 (18.96%), 191 (53.41%). Anal. Calcd. for $C_{20}H_{18}O_4$ (322.36): C, 74.52; H, 5.63. Found: C, 74.80; H, 5.50.

Action of acetic acid on 27b. A solution of **27b** (10 mmol) in acetic acid (20 mL) was heated under reflux for 1 h. The solid obtained upon cooling was collected and crystallized from acetic acid to give **31** as yellow crystals (50%).

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