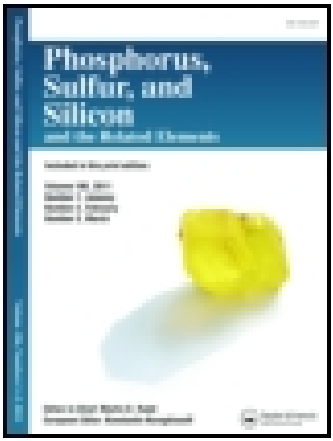

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Efficient Routes for the Synthesis of Dinaphthosulfide (BINOL Derivatives) and Dibenzosulfide Aza Podands Containing Ethanolamine

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Efficient Routes for the Synthesis of Dinaphthosulfide (BINOL Derivatives) and Dibenzosulfide Aza Podands Containing Ethanolamine

Esmael Rostami,[1] Davood Heidaryan,[2] Hanif Fattahi,[2] Abbas Shockravi,[2] Mehdi Zarei,[2] and Farokh Rakhshanderu[2]

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Four new dinaphthosulfide and dibenzosulfide aza podands were synthesized. The synthesis of these podands was performed under three different reaction conditions: 1) diester, K_2CO_3, methanol, and RT; 2) diester, ethanolamine, and microwave (MW); and 3) diacid dichloride, ethanolamine, Et_3N, CH_2Cl_2, RT. Two kinds of diester (dinaphthosulfide and dibenzosulfide) were used for the preparation of dihydroxy podands. These dihydroxy podands were reacted with thionyl chloride to afford dichloro podands. The second route gave excellent yields of dihydroxy podands. Dichloro podands are more soluble than dihydroxy podands in conventional solvents such as methanol, chloroform, and acetonitrile.

Keywords Aza podand; 2-chloro ethanolamine, dibenzosulfide; dinaphthosulfide; synthesis

INTRODUCTION

Aza crowns are an important class of host molecules.[1] After synthesis and complexation studies of crown ethers, macrocycles containing aza, thia, and other functional groups were prepared.[2] Their complexation studies were performed, and they showed strong complexation interaction between macrocycles and metal ions.[3] Aza podands are another group of receptors that can be used as important hosts in host–guest chemistry.[4] They have been used as building blocks for the construction of a large number of supramolecular systems.[5]

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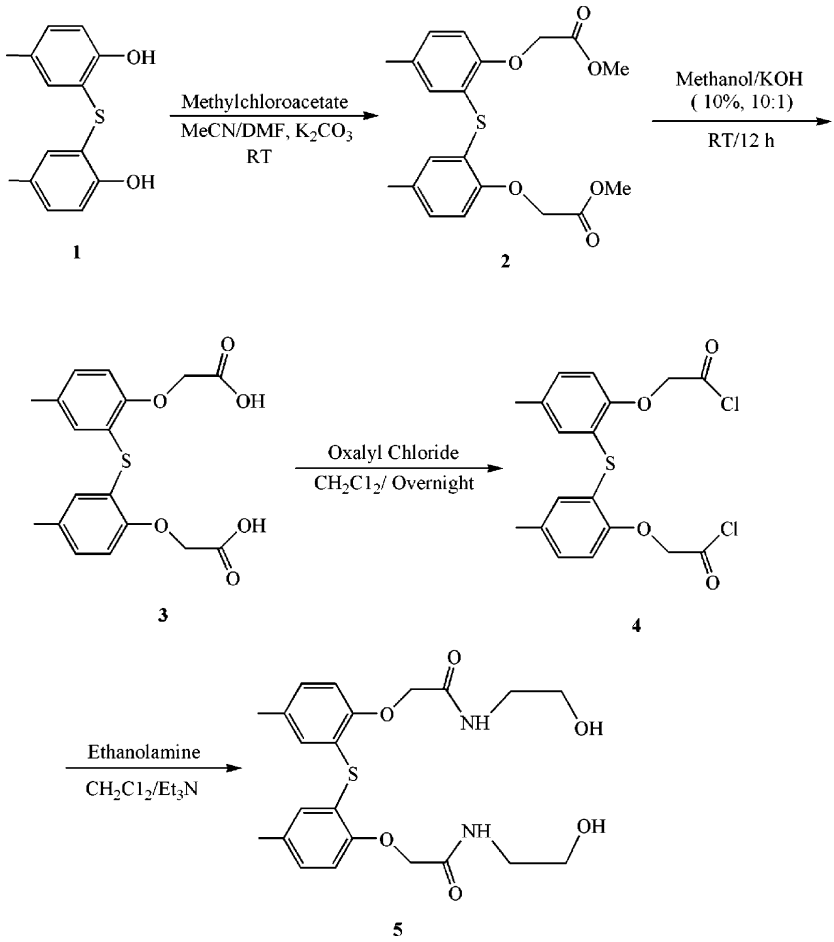
In this research work, dinaphthosulfide and dibenzosulfide aza podands (**5**, **10**, **11**, and **12**) containing ethanolamine were synthesized by three synthetic routes: 1) under microwave irradiation, 2) in room temperature via diesters (**2** and **7**), and 3) in room temperature via diacid chlorides (**4** and **9**).

RESULTS AND DISCUSSION

Here we report the synthesis of dinaphthosulfide and dibenzosulfide aza podands (**5**, **10**, **11**, and **12**). At first we synthesized **1** from the reaction of *p*-cresol and sulfur dichloride as reported previously.[6] Then this diphenol (**1**) was converted to the corresponding diester (**2**)[7] and diacid (**3**), respectively (Scheme 1).[8] The synthesis of diester (**2**) was performed efficiently in MeCN:DMF (10:1) as a binary solvent mixture; without DMF this reaction did not take place. Diacid (**3**) was prepared at room temperature from a mixture of water, methanol, and KOH. The resulting diacid (**3**) was converted to diacid dichloride (**4**) in the presence of oxalyl chloride in dichloromethane containing catalytic amounts of DMF.[9] This dichloride was reacted with ethanolamine in CH_2Cl_2 in the presence of triethylamine at 0°C (and then r.t.) to give **5** as benzo dihydroxy podand (Scheme 1).[10]

Dinaphthosulfide monomer (**6**, Figure 1) was synthesized based on the reported procedure[6] from the reaction of 2-naphthol and sulfur dichloride. This dinaphthol (**6**) was reacted with methylchloroacetate in acetonitrile in the presence of DMF (10:1) to give the corresponding diester (**7**),[7] and this diester hydrolyzed to diacid (**8**) in the presence of methanol and KOH (10%) at room temperature.[8] The resulting diacid (**8**) was converted to diacid dichloride (**9**) in the presence of oxalyl chloride and catalytic amounts of DMF in dichloromethane.[9] Diacid dichloride (**9**) was reacted with ethanolamine in CH_2Cl_2 in the presence of triethylamine to afford **10** as naphthalene dihydroxy podand (Scheme 2).[10]

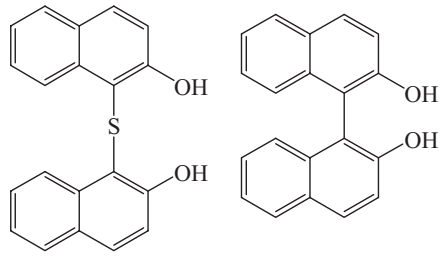
Optimization of the above procedure for the synthesis of podands (**5** and **10**) was performed as follows. First, the synthesis of diacid dichlorides (**4** and **9**) was examined in two reaction conditions: 1) in the presence of thionyl chloride, and 2) in the presence of oxalyl chloride. Then these compounds (**4** and **9**) were reacted with ethanolamine in CH_2Cl_2 in the presence of triethylamine (as a standard procedure). The better yields were obtained when oxalyl chloride was used for the synthesis of diacid dichlorides. Alternatively, the synthesis of these compounds was performed via diacides in the presence of DCC and DMAP in CH_2Cl_2 in the presence of Et_3N, but the yields were lower



SCHEME 1 Synthesis of dibenzosulfide diaza podand (**5**) via acid chloride (Route [A]).

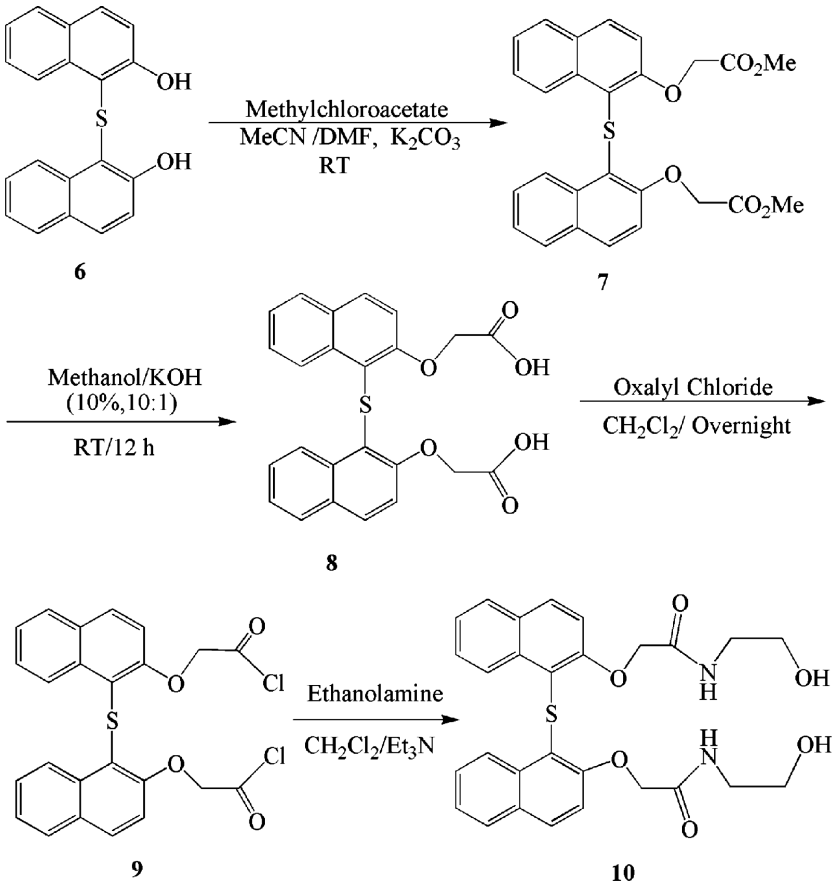
than those of the above route (because of the formation of byproducts). In conclusion, the key step for the synthesis of these podands (**5** and **10**) via the above route is the synthesis of diacid dichlorides (**4** and **9**).

The synthesis of these podands was examined in the other two reaction conditions from the corresponding diesters (**2** and **7**) (Scheme 3). The reaction of diesters and ethanolamine without solvent (ethanolamine as reagent and solvent) under microwave irradiation led to the corresponding dihydroxy podands (**5** and **10**) in lower yields.



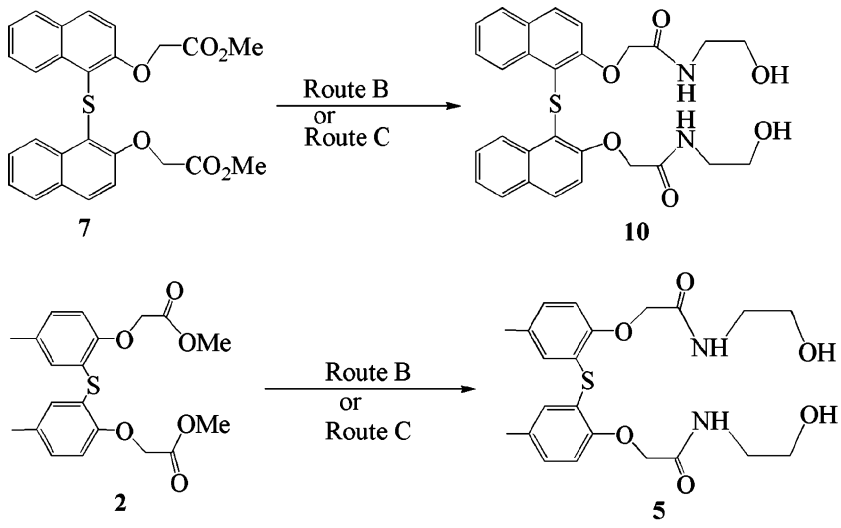
6 **BINOL**

FIGURE 1 The structures of **6** and **BINOL**.



6 **7** **8** **9** **10**

SCHEME 2 Synthesis of dinaphthosulfide diaza podand (**10**) via acid chloride (Route [A]).



Route B: Methanol/ethanolamine/ K_2CO_3/24h/RT

Route C: Ethanolamine/neat/700 W/3*30 sec

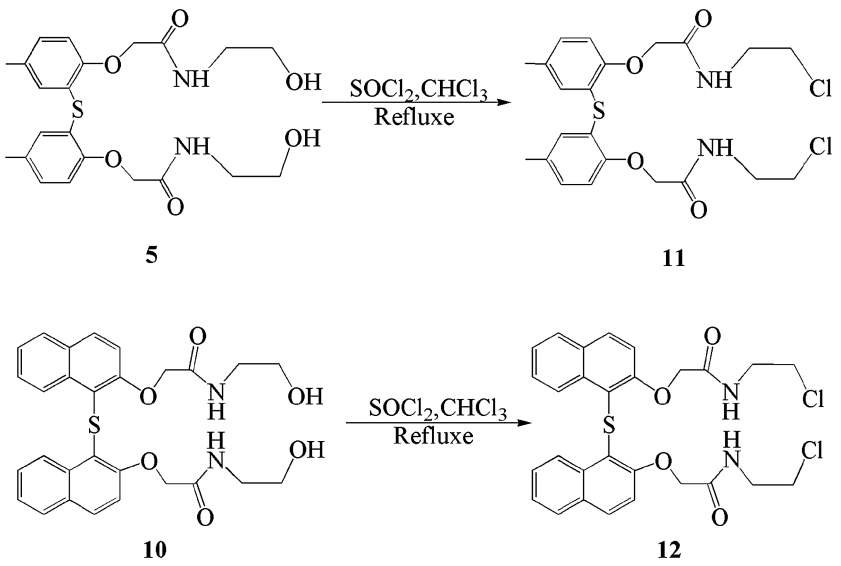
SCHEME 3 Synthesis of podands (**5** and **10**) via diesters (**2** and **7**).

This reaction was examined in methanol, ethanol, and ethylene glycol as solvent (in different equivalents of ethanolamine), and finally the use of ethanolamine as reagent and solvent, in various times and powers. The best results were obtained when ethanolamine was used as reagent and solvent in 3 × 30 sec in 700 W.

The synthesis of these podands in room temperature from diesters was an efficient route for the synthesis of these compounds. In this reaction, dihydroxy podands (**5** and **10**) were obtained from the reaction of diesters (**2** and **7**) and ethanolamine in dry methanol in the presence of potassium carbonate at room temperature in excellent yields.

This reaction was performed in the presence of catalytic or stoichiometric amounts of Et_3N, K_2CO_3, para-toluene sulfonic acid (*p*-TsOH), and $Cu(OAc)_2$ (OAc is the acetate group) in dry methanol. The best results were obtained in the presence of stoichiometric amounts of K_2CO_3 at room temperature for 24 h.

Comparison of the routes and yields reported in the synthesis of these podands (**5** and **10**) shows that the synthesis via diesters (**2** and **7**) at room temperature in the presence of K_2CO_3 ([B]) is the best procedure, because of the formation of byproducts in the other two routes ([A] and [C]). The results that were obtained via three general



5 **11**

10 **12**

SCHEME 4 Synthesis of chloropodands (**11** and **12**).

procedures for the synthesis of hydroxyl podands (**5** and **10**) show that [B] is the most efficient route, [C] is the second most efficient, and [A] is the least important route (Table I).

These two podands (**5** and **10**) were reacted with thionyl chloride in refluxing chloroform to afford dichloro derivatives (**11** and **12**) in high yields (Scheme 4).[11] The solubilities of these podands were examined in a series of solvents (Table II). According to these solubilities, the dichloro derivatives (**11** and **12**) are more soluble than their dihydroxy derivatives (**5** and **10**) in conventional solvents, and show that for application of these podands the dichloro derivatives (**11** and **12**) are more efficient than dihydroxy derivatives (**5** and **10**).

TABLE I Comparison of the Yields and Methods

Entry	Podand	Method	Yield (%)
1	**5**	[A]	36
2	**10**	[A]	45
3	**5**	[B]	91
4	**10**	[B]	94
5	**5**	[C]	71
6	**10**	[C]	67

TABLE II II Solubility[a] of Podands

Entry	$CHCl_3$	MeOH	DMF	NMP	DMAc	DMSO	MeCN	Acetone
5	–[b]	+[c]	++[d]	++	++	++	–	–
10	–	+	++	++	++	++	–	–
11	++	++	++	++	++	++	++	++
12	++	++	++	++	++	++	++	++

[a]Solubility measured at concentration of 0.05 g/mL.
[b]Insoluble.
[c]Soluble after heating.
[d]Soluble in room temperature.

EXPERIMENTAL

The reactions were carried out in an efficient hood. All the materials were purchased from Merck, Fluka, and Aldrich chemical companies. The compounds **2**, **3**, **7**, and **8** were prepared previously via different reaction conditions and routes.[12] The new experimental procedures for the synthesis of these compounds (**2**, **3**, **7**, and **8**) are reported in the References and Notes section.[13–16] Chloroform, dichloromethane, acetonitrile, and methanol were distilled and stored over a molecular sieve. DMF was distilled over a molecular sieve under reduced pressure and stored over a molecular sieve. The melting points (uncorrected) were measured with an Electrothermal engineering LTD 9100 apparatus. Elemental analyses were performed by a CHN-O- Rapid Heraeus elemental analyzer. IR spectra were measured on a Perkin-Elmer model 543. The ^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker Avance DRX 500 and Bruker Avance DPX 300 MHz apparatus. The mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Microwave apparatus was a domestic microwave oven.

General Procedure for the Synthesis of Podands (5 and 10) via Acid Chlorides (4 and 9) [A]

Diacid (**3** or **8**, 1 mmol), oxalyl chloride (2 mmol, 0.17 mL), and catalytic amounts of dimethyl formamide (DMF, 2 drops) in dichloromethane (dry, 50 mL) were stirred at 0°C for 20 min and then at room temperature overnight. After the appearance of a clear yellow solution, the reaction mixture was filtered and the solvent was evaporated to afford a yellow solid. This product was used in another step without further purification. To a reaction mixture of ethanolamine (2 mmol, 0.12 mL) and triethylamine (2 mmol, 0.28 mL) in acetonitrile (50 mL) at 0°C, the above diacid chloride in acetonitrile (20 mL) was added

dropwise. After stirring overnight under N_2, water was added, and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with HCl (10%, 2 × 50 mL) and dried (Na_2SO_4) and evaporated to afford a white solid, which was purified by recrystallization in ethanol to obtain **5** and **10** in 36% and 45% yields, respectively.

2,2′-Thio Bis(4-methyl-(1-oxa-3-oxo-4-aza-6-hydroxyhexyl)-benzene) (5)

White powder, mp = 127–128°C; IR (KBr): 3396, 3317, 2981, 2950, 2933, 2878, 1660, 1653, 1545, 1492, 1422, 1374, 1293, 1246, 1077, 1061, 814, 561 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 2.15 (3H, s), 3.15 (2H, q), 3.34–3.40 (2H, m), 4.49 (2H, s), 4.72 (1H, t, J = 6Hz), 6.87 (1H, d, J = 3Hz), 6.90 (1H, d, J = 9 Hz), 7.06 (1H, dd, J = 3, 9 Hz), 7.54 (1H, t, J = 6 Hz) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 167.4, 153.9, 131.7, 131.1, 129.1, 121.7, 113.2, 67.8, 59.6, 41.1, 20.0 ppm; Elemental analysis calculated for $C_{22}H_{30}N_2O_6S$: C, 58.65; H, 6.71; N, 6.22. Found: C, 58.56; H, 6.78; N, 6.36.

1,1′-Thio Bis(2-(1-oxa-3-oxo-4-aza-6-hydroxyhexyl)-naphthalene) (10)

White powder, mp = 192–193°C; IR (KBr): 3403, 3329, 2951, 2886, 1653, 1622, 1539, 1504, 1442, 1426, 1347, 1322, 1260, 1233, 1077, 1057, 810, 566 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 3.11 (4H, q, J = 6, 12 Hz), 3.34 (2H, broad), 4.49 (4H, s), 4.69 (2H, broad), 7.31–7.38 (4H, m), 7.42–7.46 (2H, m), 7.60 (2H, t), 7.83–7.90 (4H, two dubletes), 8.44 (2H, d) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 167.5, 156.0, 134.1, 130.1, 129.5, 128.4, 127.2, 124.6, 124.1, 117.2, 115.4, 68.4, 59.6, 41.1 ppm; MS [EI] m/z: 458 (9%), 316 (42%), 299 (100%), 244 (44%), 186 (17%), 157 (14%), 143 (15%), 115 (5%), 102 (7%); Elemental analysis calculated for $C_{28}H_{28}N_2O_6S$: C, 64.60; H, 5.42; N, 5.38. Found: C, 64.52; H, 5.45; N, 5.43.

General Procedure for the Synthesis of Podands (5 and 10) via Diesters (2 and 7) in Room Temperature [B]

Potassium carbonate (0.56 g, 4 mmol) was added to a solution of diesters (**2** or **7**, 2 mmol) and ethanolamine (4 mmol, 0.24 mL) in dry methanol (75 mL). The resulting mixture was stirred at room temperature for 24 h. After completion of the reaction (monitored by TLC), water was added and the resulting mixture was extracted with chloroform, dried (Na_2SO_4), and evaporated to give the crude product. After

recrystallization from ethanol, **5** and **10** were obtained in 91% and 94% yields, respectively.

General Procedure for the Synthesis of Podands (5 and 10) via Diesters (2 and 7) Under Microwave (MW) Irradiation [C]

To diester (**2** or **7**, 2 mmol), ethanolamine (10 mmol, excess) was added. This mixture was irradiated under microwave (3 × 30 sec) at a power of 700 W to completion (monitored by TLC). After completion, water was added (100 mL) to the mixture, and the resulting suspension was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were dried (Na_2SO_4) and evaporated to afford crude products. After recrystallization from ethanol, **5** and **10** were obtained in 71% and 67% yields, respectively.

General Procedure for the Reaction of Podands (5 and 10) with Thionyl Chloride [D]

To podands (**5** or **10**, 1 mmol) in dry chloroform (100 mL), thionyl chloride (2 mmol, 0.15 mL) was added after stirring at room temperature for 30 min. The mixture was refluxed for 4 h. After completion of the reaction (monitored by TLC), water was added, and the mixture was extracted with chloroform (3 × 50 mL). The combined chloroform layers were dried (Na_2SO_4) and evaporated to afford a crude product, which was recrystallized in ethanol to give **11** and **12** in 94% and 96% yields, respectively.

2,2′-Thio Bis(4-methyl-(1-oxa-3-oxo-4-aza-6-chlorohexyl)-benzene) (11)

White powder; mp = 98–99°C; IR (KBr): 3409, 3286, 2984, 2976, 2879, 1676, 1631, 1538, 1507, 1443, 1328, 1255, 1216, 1085, 1053, 811, 564 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 2.15 (6H, s), 3.42 (4H, q), 3.65 (4H, t), 4.53 (4H, s), 6.85- 6.90 (2H, m), 6.92–6.96 (2H, m), 7.03–7.14 (2H, m), 7.84–7.88 (2H, m) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ: 167.8, 153.8, 131.9, 131.7, 131.2, 121.8, 113.3, 67.8, 42.3, 37.9, 20.1, 20.0 ppm; Elemental analysis calculated for $C_{22}H_{26}Cl_2N_2O_4S$: C, 54.43; H, 5.40; N, 5.77. Found: C, 54.35; H, 5.49; N, 5.86.

1,1′-Thio Bis(2-(1-oxa-3-oxo-4-aza-6-chlorohexyl)-naphthalene) (12)

White powder, mp = 166–167°C; IR (KBr): 3410, 3295, 3095, 2996, 2952, 1681, 1626, 1574, 1532, 1510, 1474, 1325, 1243, 1096, 810, 755

cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.03 (4H, q), 3.22 (4H, t, J = 6.3 Hz), 4.34 (4H, s), 6.09 (2H, broad), 7.12 (2H, d, J = 9 Hz), 7.47 (2H, ddd, J = 0.9, 7.5, 7.6 Hz), 7.60 (2H, ddd, J = 1.2, 7.8, 7.9 Hz), 7.85 (4H, t), 8.70 (2H, d, J = 8.7 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.6, 154.9, 134.9, 130.1, 130.0, 129.9, 129.8, 128.6, 128.2, 119.8, 115.2, 69.9, 42.6, 41.2 ppm; MS [EI] m/z: 556 (14%), 317 (19%), 316 (38%), 298 (28%), 255 (31%), 225 (100%), 187 (12%), 186 (20%), 158 (18%), 151 (23%), 144 (17%), 115 (18%); Elemental analysis calculated for $C_{28}H_{26}Cl_2N_2O_4S$: C, 60.32; H, 4.70; N, 5.02. Found: C, 60.21; H, 4.74; N, 5.13.

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[13] Synthesis of 2,2′- thio bis (methyl-(4-methyl phenoxy acetate)) (**2**): To a mixture of **1** (4.75 g, 19 mmol), potassium carbonate (5.24 g, 38 mmol), and potassium iodide (catalytic) in acetonitrile (100 mL) and DMF (10 mL) at room temperature, methylchloroacetate (3.35 mL, 38 mmol) was added. Then the reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (monitored by TLC), water was added to the mixture and extracted with chloroform (3 × 50 mL), and the combined chloroform layers were washed with sodium hydroxid solution (10%, 50mL), dried (Na_2SO_4), and evaporated to afford a precipitate that recrystallized from ethanol to give pure **2** in 95% yield, mp = 98–100°C, IR (KBr): 2960, 2940, 1760, 1480, 1440, 1280, 1250, 1200, 1150, 1080, 990, 800 cm^{-1};^1H NMR (60 MHz, $CDCl_3$) δ: 2.2 (6H, s), 3.7 (6H, s), 4.65 (4H, s), 6.8–7.2 (6H, m) ppm; Elemental analysis calculated for $C_{20}H_{22}O_6S$: C, 61.52; H, 5.68. Found C, 61.58; H, 5.56.

[14] Synthesis of 2,2′-thio bis(4-methyl phenoxy acetic acid) (**3**): To a solution of methanol (70 mL) and potassium hydroxide (10%, 7mL), **2** was added and the resulting mixture was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC), water was added and acidified with HCl (10%, 30 mL). The resulting white precipitate was filtered and washed with water. The crude product was recrystallized in ethanol/water to obtain 3 in 92% yield, mp = 178–180°C, IR (KBr): 3400–2800, 3040, 2920, 1745, 1720, 1490, 1430, 1280, 1240, 1090, 1040, 810 cm^{-1};^{1}H NMR (90 MHz, DMSO-d_6) δ: 2.1 (6H, s), 4.7 (4H, s), 6.9–7.1 (6H, m) ppm;^{13}C NMR (62 MHz, DMSO-d_6) δ: 170.0, 154.0, 132.1, 130.5, 128.7, 121.7, 112.0, 65.0, 19.9 ppm.; MS (EI) m/z 362 M^+, 363 $(M+1)^+$, 364 $(M+2)^+$, 365 $(M+3)^+$, 317, 304, 288, 271, 257, 244, 228, 214, 201, 195, 184, 151, 121, 105, 91, 77.

[15] Synthesis of 1,1′-thio bis-(2-naphthoxy (2-methyl acetate)) (**7**): Similar to the preparation of **2**, this compound (**7**) was obtained in 91% yield. mp = 126–127°C; IR (KBr): 3040, 3000, 2970, 1750, 1595, 1500, 1450, 1300, 1250,1200, 1090, 1040, 810, 750 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ: 3.65 (6H, s), 4.65 (4H, s), 7.09 (2H, ddd, J = 8.46, J = 6.94, J = 1.32 Hz), 7.26 (2H, d, J = 9.05 Hz), 7.35 (2H, ddd, J = 7.98, J = 6.84, J = 1.11 Hz), 7.81 (2H, d, J = 7.91 Hz), 7.83 (2H, d, J = 9.02 Hz), 8.69 (2H, d, J = 8.59 Hz) ppm; Elemental analysis calculated for $C_{26}H_{22}O_6S$: C, 67.52; H, 4.79. Found: C, 67.45; H, 4.67.

[16] Synthesis of 1,1′-thio bis-(2-naphthoxy acetic acid) (**8**): Similar to the above procedure for the preparation of **3**, this diacid (**8**) was obtained in 87% yield, mp = 259–261°C, IR (KBr): 3210–2420 (broad), 1720,1710, 1620, 1580, 1500, 1460, 1430, 1350, 1290, 1275, 1250, 1215, 1150, 1100, 1020, 950, 910, 800, 775, 740 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 4.13 (4H, s), 6.77 (2H, d, J = 8.95 Hz), 6.97 (2H, dd, J = 7.41, J = 7.45 Hz), 7.09 (2H, dd, J = 8.0, J = 7.4 Hz), 7.39 (4H, d, J = 8.65 Hz), 830 (2H, d, J = 8.55 Hz) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 66.6, 115.7, 119.1, 124.3, 125.9, 127.1, 128.3, 129.6, 130.0, 135.3, 156.5, 170.8 ppm; Elemental analysis calculated for $C_{24}H_{18}O_6S$: C, 66.35; H, 4.18. Found: C, 66.29; H, 4.07.