

## Samarium(III) nitrate-catalyzed one-pot synthesis of 42-membered *N,S,O*-containing cyclophanes

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### Abstract

An effective one-pot method for the synthesis of *N*-aryl-substituted 1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]paracyclophanes by  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ -catalyzed heterocyclization of *N,N*-bis(methoxymethyl)-*N*-arylamines with 4,4'-dimercaptodiphenyl oxide has been developed. The structural features of the obtained *N,S,O*-containing cyclophanes have been studied.

**Keywords:** Samarium(III) catalysis, cycloaminomethylation, 4,4'-dimercaptodiphenyl oxide, *N,N*-bis(methoxymethyl)-*N*-arylamines, cyclophanes, macrocycles

### Introduction

Intermolecular condensation of aryl-containing  $\alpha,\omega$ -bifunctional compounds is a well-known method for cyclophane synthesis.<sup>1-7</sup> A considerable drawback of this method is the formation of by-products arising from linear polycondensation or simultaneous [n+n]-cyclocondensation of the initial  $\alpha,\omega$ -bifunctional compounds.<sup>8-14</sup> The formation of by-products is minimised, as a rule, by using high dilution,<sup>11,15,16</sup> templates,<sup>17-22</sup> and catalytic reactions.<sup>23-27</sup>

Cyclophanes containing benzene rings in the molecule have rigid cyclic skeletons, which is important for their complexation of metal ions<sup>5</sup> and organic molecules.<sup>1</sup> Heterocyclophanes and their derivatives show a broad spectrum of biological activity<sup>28-30</sup> and find use as phase transfer catalysts,<sup>31,32</sup> extractants,<sup>33-35</sup> and analytical reagents.<sup>32</sup>

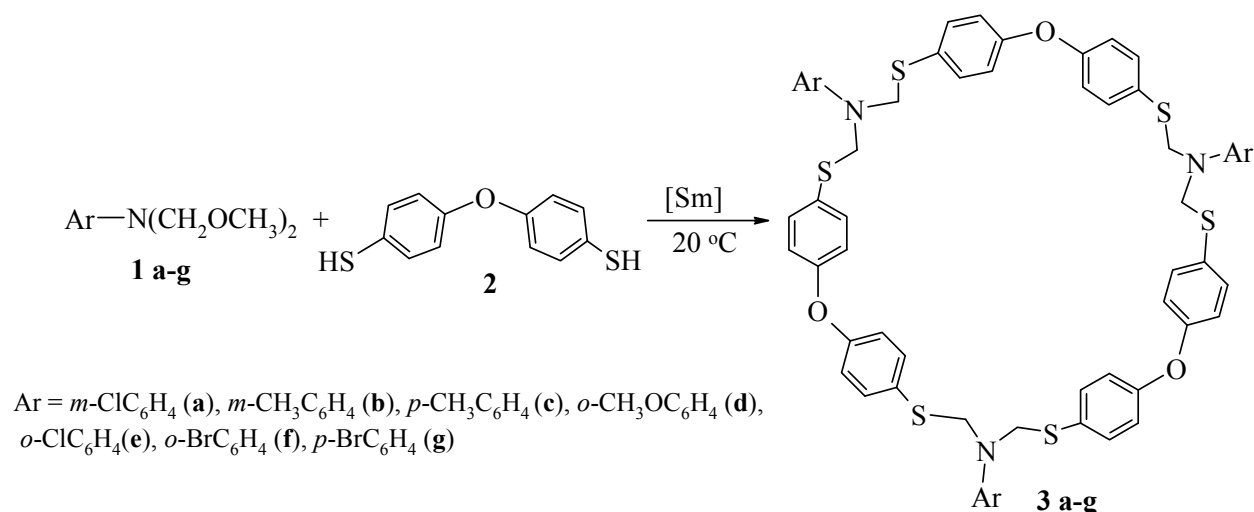
### Results and Discussion

As a continuation of the research into catalytic synthesis of heterocyclic compounds<sup>36-44</sup> and to develop a selective route to 42-membered *N,S,O*-containing cyclophanes, we studied the

heterocyclization of *N,N*-bis(methoxymethyl)-*N*-arylamines with  $\alpha,\omega$ -dithiols catalyzed by samarium(III).

In previous studies of non-catalyzed heterocyclization of aminophenols,<sup>45</sup> and primary hydroxylamines<sup>14</sup> with CH<sub>2</sub>O and SH-acids, we found that multicomponent cyclocondensation affords cyclophanes as mixtures with by-products. For the more selective synthesis of heteroatom cyclophanes, we performed catalytic heterocyclization of *N,N*-bis(methoxymethyl)-*N*-arylamines with 4,4'-dimercaptodiphenyl oxides.<sup>47</sup> *N,N*-Bis(methoxymethyl)-*N*-arylamines were chosen as the starting compounds because, when introduced into catalytic heterocyclization with  $\alpha,\omega$ -alkanethiols, they afford 1,5,3-dithiazacycloalkanes according to a [1+1]-cyclocondensation route with high selectivity<sup>40,46</sup> while conformationally rigid 4,4'-dimercaptodiphenyl oxide favours the formation of macroheterocycles upon [3+3]-cyclocondensation, for example, with CH<sub>2</sub>O and primary hydroxylamines.<sup>14</sup>

In relation to the reaction of *N,N*-bis(methoxymethyl)-*N*-(*m*-chlorophenyl)amine **1a** with 4,4'-dimercaptodiphenyl oxide **2**, we found that in the presence of 5 mol% Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (20 °C, 7 h), macroheterocycle **3a** is formed in 70% yield according to Scheme 1. This catalyst was chosen for its high activity and selectivity of action in the previously studied heterocyclizations.<sup>46</sup> Without a catalyst, macroheterocycle **3a** is not formed.



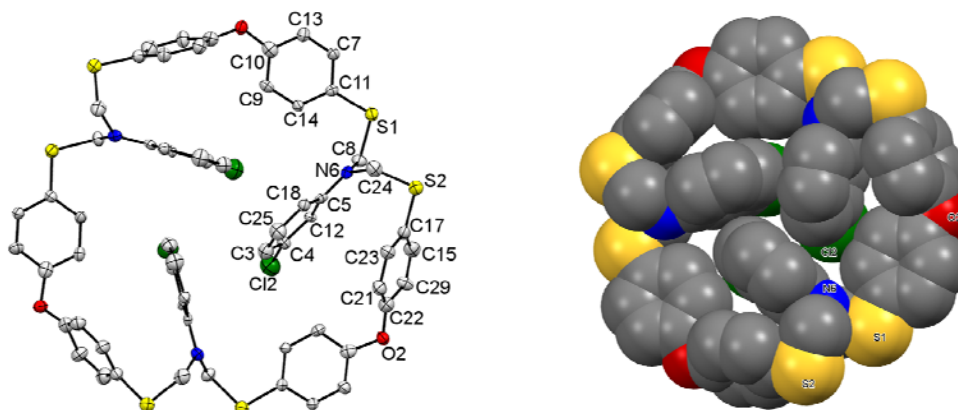
**Scheme 1.** Synthesis of macrocyclophanes **3a-g** ([Sm] = Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O).

The structure of *N*-(*m*-chlorophenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia[1.5.1.5.1.5]-paracyclophane **3a** was established by 1D and 2D NMR spectroscopy. The singlet signal of the hydrogen atom at  $\delta$  4.65 ppm correlates in HSQC experiment with the signal of the carbon atom at  $\delta$  51.58 ppm that corresponds to bridged methylene group between the tertiary nitrogen atom and the sulfur atom. In <sup>1</sup>H NMR spectrum, two doublets at  $\delta$  6.97 ppm (*J* 8.6 Hz) and  $\delta$  7.42 ppm (*J* 8.6 Hz) belong to bis-para-dithia-phenoxy groups of heterocyclophane. The hydrogen atoms of *m*-Cl-aryl substituent at the nitrogen atom resonate in <sup>1</sup>H NMR spectrum as two triplets ( $\delta$

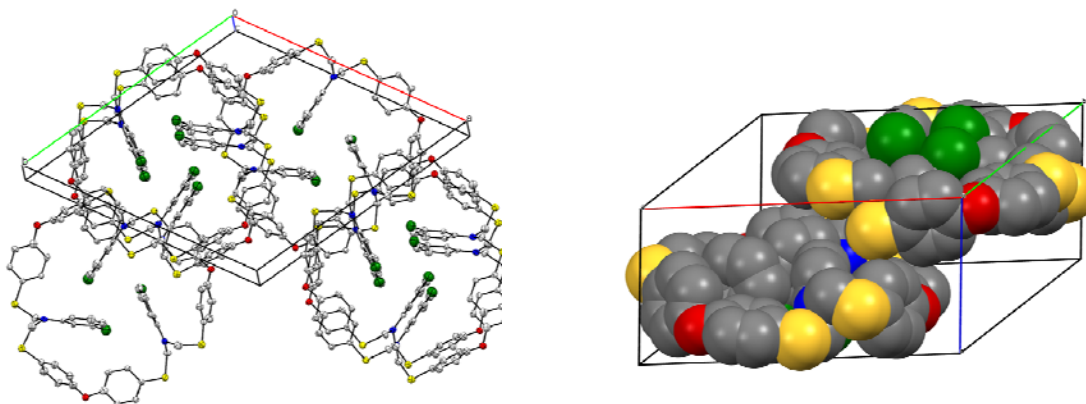
6.67 ppm ( $J$  8.0 Hz),  $\delta$  7.14 ppm,  $J$  8.8 Hz) and two doublet of doublets ( $\delta$  6.57 ppm ( $J$  8.0, 2.0 Hz),  $\delta$  6.79 ppm ( $J$  8.0, 2.0 Hz)).

The IR spectrum of **3a** shows the characteristic absorption band of the CS group ( $680\text{ cm}^{-1}$ ), ether group COC ( $1237\text{ cm}^{-1}$ ) and CN group ( $1383\text{ cm}^{-1}$ ). The molecular ion  $[M-H]^+$  with  $m/z$  1156.225 was observed in the MALDI-TOF mass spectrum (HCCA matrix), confirming the structure of paracyclophane **3a**.

For compound **3a** (Figure 1), crystals were obtained from a  $C_6H_{12} : EtOAc = 5 : 1$  solvent mixture by slow evaporation at room temperature. A crystal was studied by X-ray diffraction.



**Figure 1.** Geometry of the structure of **3a** with atoms represented by the thermal vibration ellipsoids ( $p=50\%$ ) (left) and by the van der Waals radii (right).



**Figure 2.** The packing arrangement of **3a** with atoms represented by the thermal vibration ellipsoids ( $p=50\%$ ) (left) and by the van der Waals radii (right).

According to the X-ray diffraction data, the paracyclophane **3a** has a threefold symmetry axis. The highly symmetric structure of **3a** consists of three repeating phenylsulfanyl-methylaminomethylsulfanylphenol moieties, which form the cyclophane cavity. In the crystalline state, an endocyclic arrangement of the *N*-aryl substituents with *syn*-oriented chlorine atoms is observed. The oxodibenzene moiety has pseudo-perpendicular phenyl groups, the angle between the planes being 107.46°.

The molecules of compound **3a** form crystals with a trigonal crystal lattice. In the crystal, these molecules form stacks along the *c* axis corresponding to a crystallographic direction. It is noteworthy that adjacent stacks overlap near the phenylsulfanylmethylaminomethylsulfanylphenol moieties (Figure 2).

Under the developed conditions (5 mol% Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 20 °C, 7 h), heterocyclization of *N,N*-bis(methoxymethyl)-*N*-aryl(*m*-methylphenyl, *o*-methoxyphenyl, *p*-methylphenyl, *o*-chlorophenyl, *m*-chlorophenyl, *m*-bromophenyl, *p*-bromophenyl, *m*-fluorophenyl)amines **1 a-g** with 4,4'-dimercaptodiphenyl oxide **2** resulted in highly selective syntheses of new 42-membered *N*-aryl-substituted N,S,O-containing cyclophanes **3 a-g** in 65-81% yields.

## Conclusion

An effective one-pot method for the selective synthesis of *N*-aryl-substituted 1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]paracyclophanes in 65–81% yields by the Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O-catalyzed reaction of *N,N*-bis(methoxymethyl)-*N*-arylamines with 4,4'-dimercaptodiphenyl oxide has been developed.

## Experimental Section

**General.** All reactions were performed at room temperature under an air atmosphere in a round bottom flask equipped with a magnetic stir bar. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 and 100 MHz, respectively) in CDCl<sub>3</sub>, internal standard was TMS. Two-dimensional homonuclear (COSY, NOESY) and heteronuclear (HSQC, HMBC) experiments were carried out under Bruker standard procedures at the same operating frequencies. The mixing time for the NOESY experiments was 0.3 s. Mass spectra were recorded on a Bruker Autoflex III MALDI TOF/TOF instrument with  $\alpha$ -cyano-4-hydroxycinnamic acid as a matrix. Samples of the compounds were prepared by the "dried droplet method". Elemental analysis was carried out on a Carlo Erba 1106 analyzer. The content of S, Cl and Br was determined by the Shenigers method.<sup>48</sup> Melting points were determined on a PHMK 80/2617 apparatus. The progress of reactions was monitored by TLC on Sorbfil (PTSKh-AF-V) plates, eluent was C<sub>6</sub>H<sub>12</sub> : EtOAc, 5:1 (compounds **3 a-g**), visualization with I<sub>2</sub> vapour. For column chromatography, silica gel KSK (100-200  $\mu$ m) was used.

Single crystals of **3a** was grown from C<sub>6</sub>H<sub>12</sub> : EtOAc, 5:1 solution at room temperature. Data were recorded on a XCalibur Eos diffractometer (graphite monochromated Mo K $\alpha$  radiation,  $\lambda$  =

0.71073 Å,  $\omega$ -scan technique). Crystallographic details of cell data, data collection and refinement are summarized in Table. Collection and processing of data performed with using the program CrysAlisPro Oxford Diffraction Ltd., Version 1.171.36.20. Structure solution and refinement were performed with SHELX.<sup>49</sup> The structure was refined by a full-matrix least-square technique using anisotropic thermal parameters for non-hydrogen atoms. Crystallographic data for the structures of **3a** have been deposited in the Cambridge Crystallographic Data Centre as a CIF deposition with file number CCDC- 1430901. Copies of these data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk) or from [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table.** Crystal data and structure refinement for **3a**

Empirical formula	C <sub>60</sub> H <sub>48</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>3</sub> S <sub>6</sub>
Formula weight	1156
Temperature/K	293(2)
Crystal system	trigonal
Space group	P-3
a/Å	18.7453(9)
b/Å	18.7453(9)
c/Å	9.4988(6)
$\alpha$ /°	90.00
$\beta$ /°	90.00
$\gamma$ /°	120.00
Volume/Å <sup>3</sup>	2890.6(3)
Z	2
$\rho_{\text{calc}}$ /mg/mm <sup>3</sup>	1.330
m/mm <sup>-1</sup>	0.422
F(000)	1200.0
2 $\Theta$ range for data collection	9.06 to 62.3°
Index ranges	-23 ≤ h ≤ 23, -5 ≤ k ≤ 25, -8 ≤ l ≤ 13
Reflections collected	5170
Independent reflections	3229[R(int) = 0.1328]
Data/restraints/parameters	3229/0/226
Goodness-of-fit on F <sup>2</sup>	0.973
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.1009, wR <sub>2</sub> = 0.1657
Final R indexes [all data]	R <sub>1</sub> = 0.2563, wR <sub>2</sub> = 0.2145
Largest diff. peak/hole / e Å <sup>-3</sup>	0.62/-0.27

**Heterocyclization of 4,4'-dimercaptodiphenyl oxide with *N,N*-bis(methoxymethyl)-*N*-arylamines**

**General procedure.** *N,N*-Bis(methoxymethyl)-*N*-arylamine (1.00 mmol) obtained in situ by a reported procedure,<sup>50</sup> the solvent (10 mL), and Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.05 mmol) were stirred under argon for 30 min at room temperature, then solution of 4,4'-dimercaptodiphenyl oxide (1.00 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The choice of solvent was determined by the solubility of *N,N*-bis(methoxymethyl)-*N*-arylamines **1a-g** (CH<sub>2</sub>Cl<sub>2</sub> for **1 a,f,g**; EtOAc + CH<sub>2</sub>Cl<sub>2</sub> for **1 b,c**; EtOAc + EtOH for **1 d**; EtOAc for **1 e**).<sup>46</sup> The reaction mixture was stirred ~ 20 °C for 7 h and concentrated, and the residue was purified by column chromatography on SiO<sub>2</sub> to isolate pure heterocyclic product.

***N*-(*m*-Chlorophenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (**3a**).** Pale yellow crystals (0.81 g, 70%), mp 134 °C; IR (cm<sup>-1</sup>): 3063, 1805, 1681, 1482, 1383, 1237, 1162, 1090, 827, 743, 650. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 4.65 (s, 12H, NCH<sub>2</sub>S), 6.57 (dd, 3 H, *J* 8.0 Hz, *J* 2.0 Hz), 6.67 (t, 3H, *J* 8.0 Hz), 6.79 (dd, 3 H, *J* 8.0 Hz, *J* 2.0 Hz), 7.14 (t, 3H, *J* 8.8 Hz), 6.97 (d, 12H, *J* 8.6 Hz), 7.42 (d, 12H, *J* 8.6 Hz) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 51.58 (NCH<sub>2</sub>S), 112.54, 114.12, 118.92, 119.60, 130.26, 130.31, 131.09, 135.84, 146.29, 156.99 (Ar) ppm. MALDI TOF, *m/z*: 1156.225 [M-H]<sup>+</sup>. Anal. Calcd. for C<sub>60</sub>H<sub>48</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub>: C, 62.24; H, 4.18; Cl 9.19; N, 3.63; O 4.15; S, 16.62. Found: C, 62.10; H, 4.02; Cl 9.06; N, 3.54; S, 16.55%.

***N*-(*m*-Methylphenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (**3b**).** Colorless oil (0.75 g, 68%), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 2.32 (9H, s, CH<sub>3</sub>), 4.69 (s, 12H, NCH<sub>2</sub>S), 6.96 (d, 12H, *J* 8.5 Hz), 7.43 (12H, d, *J* 8.5 Hz), 6.51-6.52 (m, 3H), 6.66 (d, 3H, *J* 7.5 Hz), 6.92-6.94 (m, 3H), 7.39-7.40 (m, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 21.27 (CH<sub>3</sub>), 60.47 (NCH<sub>2</sub>S), 111.24, 114.73, 119.40, 120.57, 131.82, 135.27, 136.14, 139.32, 145.58, 156.54 (Ar) ppm. MALDI TOF, *m/z*: 1095.220 [M-H]<sup>+</sup>. Anal. Calcd. for C<sub>63</sub>H<sub>57</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub>: C, 69.01; H, 5.24; N, 3.83; O, 4.38; S, 17.55. Found: C, 68.97; H, 5.12; N, 3.69; S, 17.41%.

***N*-(*p*-Methylphenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (**3c**).** Colorless oil (0.71 g, 65%), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 2.34 (s, 9H), 4.71 (s, 12H, NCH<sub>2</sub>S), 6.91 (d, 12H, *J* 8.5 Hz), 7.35 (d, 12H, *J* 8.5 Hz), 6.87-6.90 (m, 6H), 7.34-7.39 (m, 6H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 20.40 (CH<sub>3</sub>), 60.68 (NCH<sub>2</sub>S), 119.38, 119.66, 134.41, 135.25, 135.39, 136.15, 143.20, 156.64 ppm. MALDI TOF, *m/z*: 1095.133 [M-H]<sup>+</sup>. Anal. Calcd. for C<sub>63</sub>H<sub>57</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub>: C, 69.01; H, 5.24; N, 3.83; O, 4.38; S, 17.55. Found: C, 68.92; H, 5.14; N, 3.80; S, 17.43%.

***N*-(*o*-Methoxyphenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (**3d**).** Colorless oil (0.80 g, 70%), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.83 (s, 9H), 4.74 (s, 12H, NCH<sub>2</sub>S), 6.96 (d, 12H, *J* 8.5 Hz), 7.40 (d, 12H, *J* 8.5 Hz), 6.80 (t, 3H, *J* 8.5 Hz), 6.82 (t, 3H, *J* 8.5 Hz), 6.83 (t, 3H, *J* 8.5 Hz), 6.94 (d, 3H, *J* 8.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 51.85 (NCH<sub>2</sub>S), 55.55 (OCH<sub>3</sub>), 109.95, 112.11, 118.34, 119.42, 121.23, 128.72, 134.78, 135.78, 147.46, 156.86 (Ar) ppm. MALDI TOF, *m/z*: 1143.345 [M-H]<sup>+</sup>. Anal. Calcd. for

C<sub>63</sub>H<sub>57</sub>N<sub>3</sub>O<sub>6</sub>S<sub>6</sub>: C, 66.11; H, 5.02; N, 3.67; O, 8.39; S, 16.81. Found: C, 66.05; H, 4.97; N, 3.45; S, 16.55%.

***N*-(*o*-Chlorophenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (3e).** Pale yellow oil (0.87 g, 76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 4.72 (s, 12H, NCH<sub>2</sub>S), 6.97 (d, 12H, *J* 10 Hz), 7.39 (d, 12H, *J* 10 Hz), 6.77 (d, 3H, *J* 8.0 Hz), 6.85 (d, 3H, *J* 8.0 Hz), 7.23 (d, 3H, *J* 8.0 Hz), 7.30 (d, 3H, *J* 8.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 51.34 (NCH<sub>2</sub>S), 113.35, 119.03, 119.61, 120.29, 127.69, 129.34, 136.21, 136.18, 141.02, 157.14 (Ar) ppm. MALDI TOF, *m/z*: 1156.435 [M-H]<sup>+</sup>. Anal. Calcd. for C<sub>60</sub>H<sub>48</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub>: C, 62.24; H, 4.18; Cl 9.19; N, 3.63; O 4.15; S, 16.62. Found: C, 62.11; H, 4.10; Cl 9.16; N, 3.59; S, 16.55%.

***N*-(*o*-Bromophenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (3f).** Pale yellow oil (0.94 g, 76%), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 4.71 (s, 12H, NCH<sub>2</sub>S), 6.98 (d, 12H, *J* 8.5 Hz), 7.39 (d, 12H, *J* 8.5 Hz), 6.70 (t, 3H, *J* 8.0 Hz), 6.84 (d, 3H, *J* 8.0 Hz), 7.26 (t, 3H, *J* 8.0 Hz), 7.46 (t, 3H, *J* 8.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 51.45 (NCH<sub>2</sub>S), 113.47, 119.55, 119.64, 127.72, 128.37, 131.11, 132.61, 136.28, 141.99, 157.16 (Ar) ppm. MALDI TOF, *m/z*: 1248.274 [M-H]<sup>+</sup>. Anal. Calcd. for C<sub>60</sub>H<sub>48</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub>: C, 55.81; H, 3.75; Br 18.57; N, 3.25; O 3.72; S, 14.90. Found: C, 55.75; H, 3.51; Br 18.52; N, 3.14; S, 14.79%.

***N*-(*p*-Bromophenyl)-1,15,29-trioxa-6,10,20,24,34,38-hexathia-8,22,36-triaza[1.5.1.5.1.5]-paracyclophane (3g).** Pale yellow oil (1.49 g, 81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 4.62 (s, 12H, NCH<sub>2</sub>S), 6.93 (d, 12H, *J* 8.5 Hz), 7.36 (d, 12H, *J* 8.5 Hz), 6.87-6.91 (m, 6H), 7.39-7.41 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 60.08 (NCH<sub>2</sub>S), 119.52, 119.63, 129.14, 135.25, 135.41, 135.86, 146.63, 156.81 ppm. MALDI TOF, *m/z*: 1248.554 [M-H]<sup>+</sup>. Anal. Calcd. for C<sub>60</sub>H<sub>48</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S<sub>6</sub>: C, 55.81; H, 3.75; Br 18.57; N, 3.25; O 3.72; S, 14.90. Found: C, 55.72; H, 3.63; Br 18.49; N, 3.16; S, 14.81%.

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