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Cyclooctapyrroles, novel macrocycles containing biladiene-a,c units

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Abstract—Cyclooctapyrroles, novel macrocycles containing two biladiene-a,c units, were synthesized in high yield from the condensation of 3,3′-dipyrromethanes with 5,5′-diformyl-2,2′-dipyrromethane under acidic conditions. These macrocycles form dinuclear complexes with zinc(II).

1. Introduction

Macrocycles containing polypyrrolic units have been attracting considerable interest[1–7] due to their applications in theory,[1,2] photodynamic therapy (PDT),[1,2,8] neutral substance binding, anion recognition[9,10] and complexation with metallic ions.[10,11] Among these polypyrrolic macrocycles, cyclooctapyrroles are of particular interest because of their figure-eight conformations,[6,10,12] their ability to form dinuclear complexes with metal ions such as Cu(II), and Pd(II),[10] and their anion binding properties.[13]

[32]Octaphyrin(1.0.1.0.1.0.1.0) **1a** was synthesized by Vogel's group[4] using an acid-catalyzed MacDonald[14] type [2+2+2+2] condensation of 5,5′-diformyl-2,2′-bipyrrole with a 5,5′-biscarboxy-2,2′-bipyrrole or by a [4+4] condensation of a tetrapyrrolic derivative in yields of 7–11%. *meso*-Tetraphenyl [32]octaphyrin[1.0.1.0.1.0.1.0] was prepared via a Rothemund type[15] synthesis from the condensation of a 2,2′-bipyrrole with benzaldehyde with a yield of 7%.[12] More recently [30]heptaphyrin (1.1.1.1.1.0.0),[16a] cyclo[8]pyrrole,[16b] dioxa-[40]decaphyrin (1.0.1.0.0.1.0.1.0.0),[16c] [64]hexadecaphyrin (1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0),[17a] calix[*n*]furano[*m*]pyrroles (*n*=3,4,6,8) and (*m*=2,4),[17b] and calix[*m*]pyrrole,[17c] have been reported.

Recently, we found that the condensation of a 5,5′-biscarboxy-3,3′-dipyrroyl sulfide with a 5,5′-diformyl-3,3′-dipyrrolyl sulfide or a 5,5′-diformyl-2,2′-dipyrromethane under acidic conditions resulted in a [2+2+2+2] cyclization to give the dicationic octacyclopyrrole **1b** or **1c** in 80–90% yields.[18] This high yield condensation using simple materials is attractive as a synthetic method for macrocycles containing pyrrolic units. To extend our work, we were interested in preparing octacyclopyrroles **7**–**9**, whose structures are similar to that of compound **1c**, but where the sulfur bridge is replaced by one, two or three carbon bridges. We describe here our findings and show that novel macrocycles, **7**–**9**, are formed in high yield by acidic condensation of 5,5′-diformyl-4,4′-dimethyl-3,3′-diethyl-2,2-dipyrromethane (**6**) with 5,5′-biscarboxy-2,2′,4,4′-tetramethyl-3,3′-dipyrrolyl-methane (**2**), 1,2-bis(5-carboxy-2,4-dimethylpyrrole-3-yl)ethane (**3**), and 1,3-bis(5-carboxy-2,4-dimethyl-pyrrole-3-yl)propane (**4**).

2. Results

The starting material (**2**, or **3**, or **4** (0.95 mmol)) was stirred in trifluoroacetic acid (TFA, 10 mL) at 40°C until all solid had dissolved, the mixture was then cooled down to room temperature. 5,5′-Diformyl-4,4′-dimethyl-3,3′-diethyl-2,2′-dipyrromethane (**6**) (0.95 mmol) was added at once, followed by a mixture of hydrobromic acid (48% in glacial acetic acid, 2 mL), methanol (20 mL) and dichloromethane (20 mL). The mixture was left to stir for another 3 h at room temperature. The product was precipitated by adding anhydrous ether and collected by filtration. The yields of **7**, **8**, and **9** were 95, 90, and 90%, respectively. It is worth noting that the condensation of compounds **5** and **6** under similar acidic conditions resulted only in a [2+2] product **10**, in a yield of 72%. Compounds **7**–**10** were all isolated as HBr salts.

The ^{1}H NMR, ^{13}C NMR, FAB-MS spectra of **7**–**9** are consistent with the proposed structures, in which there are two biladiene-a,c units, linked by one, two or three carbon bridges at their β,β′-positions. All these macrocycles have limited solubility in dichloromethane, chloroform, acetone, methanol, acetonitrile, acetic acid, pyridine, dimethyl

Keywords: cyclooctapyrrole; cyclopolypyrroles; biladiene-ac; dipyrromethene; macrocycle.

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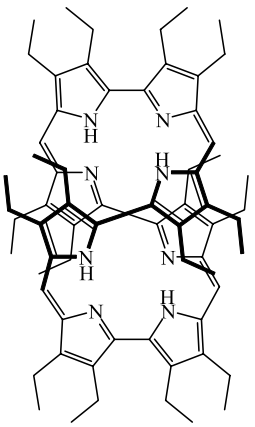
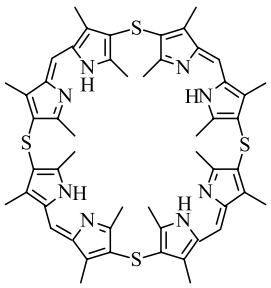


1a



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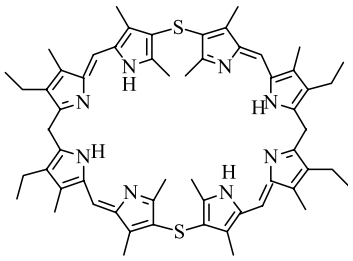

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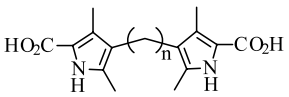

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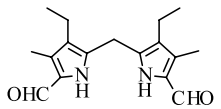

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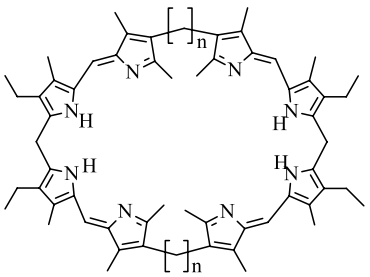

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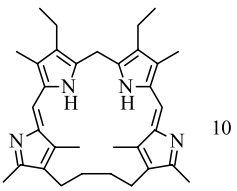

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formamide or dimethyl sulfoxide. They are, however, soluble in TFA. Combustion analysis confirms that they are tetracationic hydrobromide salts. Based on the ^{1}H NMR and UV–Vis spectra, macrocycles **7**–**9** showed, as expected, no macrocyclic aromaticity. Attempts to oxidize these macrocycles (**7**–**9**) to their fully conjugated systems using common oxidizing agents such as DDQ, Br_2, $Pb(OAc)_4$, etc have so far failed in our hands.

Compounds **7**–**9** form binuclear complexes with Zn(II) in high yield from the reaction with $Zn(OAc)_2$.

3. Discussion

Although X-ray structures of **7**–**9** are not available, results from molecular modeling[19] showed that, unlike octapyrrin **1a**, which adopted a 'figure-eight' conformation, they tend to adopt a chair conformation (Fig. 1), while the zinc(II) complexes adopt square-shaped conformations (Fig. 2). These conformations presumably result from the greater flexibility of **7**–**9** compared to **1a**. Like biladienes the dipyrrin units in our cyclooctapyrroles are flat and fully conjugated and the optical spectra of compounds **7**–**10** are very similar to those of biladienes-a,c. However, unlike biladienes, where the pyrrolic rings in the dipyrromethene units adopt a Z-conformation, an *E*-conformation is seen in the cyclooctapyrroles. Modeling also suggests that the flat

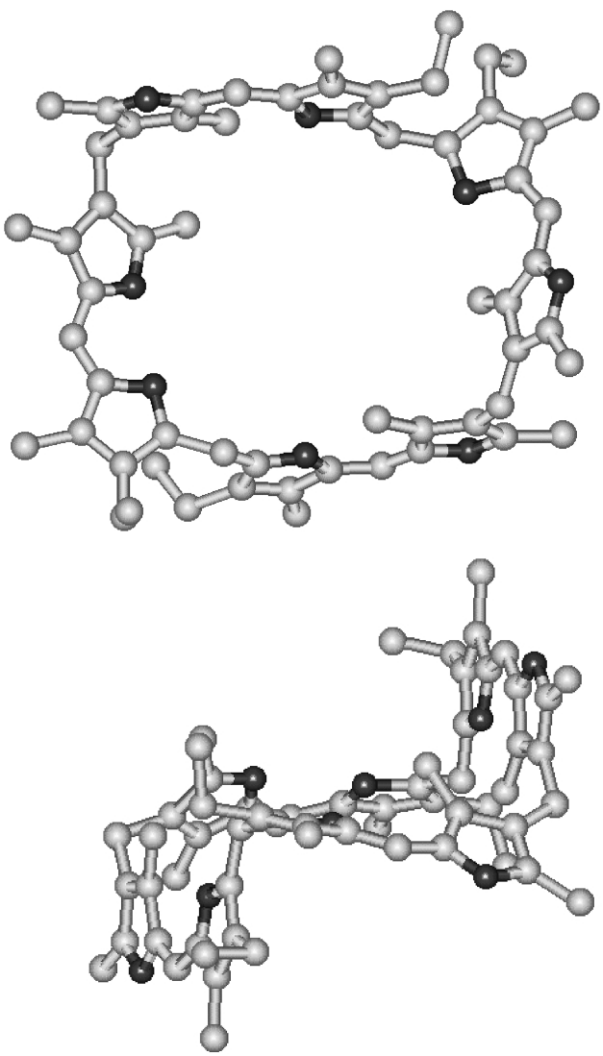

Figure 1. Lowest energy conformation of **7**, obtained using Hyperchem (Release 5.01).[17] For clarity, all H atoms have been omitted, top view (upper), and edge view (lower).

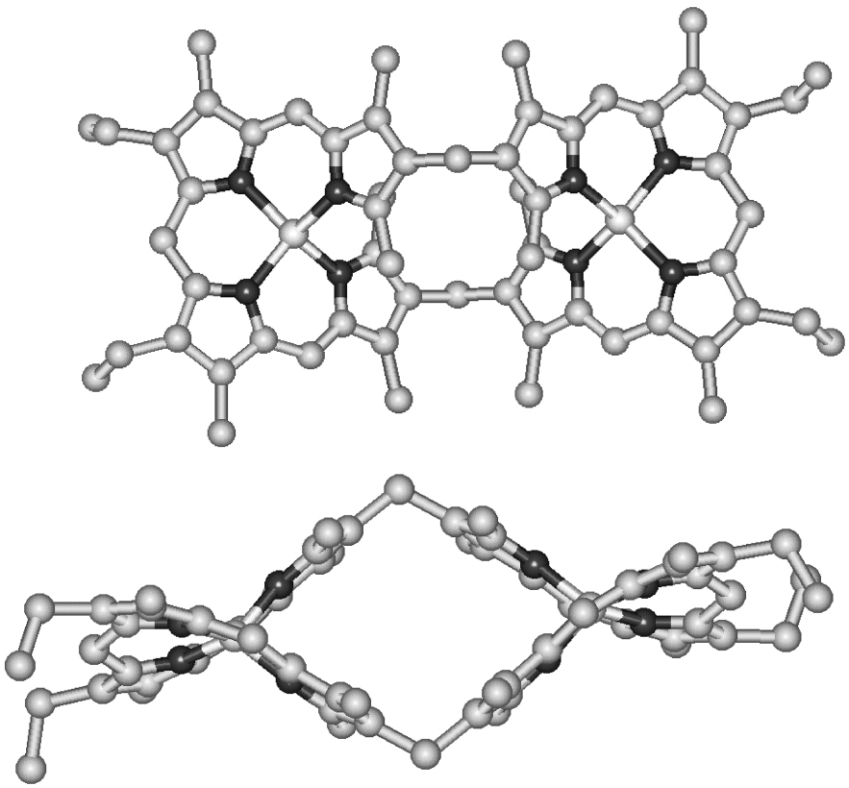

Figure 2. Lowest energy conformation of **7** complexed with Zn (II) obtained using Hyperchem (Release 5.01).[17] For clarity, all H atoms have been omitted, top view (upper), and edge view (lower).

'aromatic' systems are conformationally unstable and that the peripheral alkyl groups play an important role in forming the twisted conformations. Upon metal [Zn^{2+}] binding the binuclear complexes exhibit dramatic conformational changes where the biladiene units adopt a 'porphyrin-like' geometry. However, the two sets of four pyrrolic rings are not coplanar, rather they adopt a helical conformation.

4. Conclusion

It is clear from recent studies[4,18] that [2+2+2+2] MacDonald type condensations can occur, under appropriate conditions, in preference to the more common [2+2] reactions. Unlike the fully conjugated octaphyrin (**1a**) the macrocycles described here cannot be fully oxidized and show no macrocyclic aromaticity. To a large extent this reflects the inherent stability of the dipyrromethene units themselves.

5. Experimental

5.1. General

All reagents and solvents were purchased and used as received. Melting points were determined on a Thomas hot stage or Buchi apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 or AMX-300 instrument. The high and low-resolution mass spectra were obtained by the departmental mass spectrometry service laboratory. Combustion analyses were performed by the departmental microanalytical laboratory. UV–Vis spectra were recorded on an HP8452A photo diode array spectrophotometer (instrumental precision ±2 nm).

The carboxylic acids **2–5** readily decarboxylate and satisfactory combustion analyses were not obtained. The macrocyclic zinc complex all showed very low solubility and gave NMR spectra that were too broad to be of use.

Starting materials, 1,2-bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)ethane, 1,3-bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)propane and 1,4-bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)butane were prepared according to literature procedures.[20]

5.1.1. 5,5′-Bisbenzoxycarbonyl-2,2′,4,4′-tetramethyl-3,3′-dipyrromethane. Paraformaldehyde (2.6 g, 86.7 mmol, 2.0 mol equiv.) was suspended in glacial acetic acid (100 mL) containing conc. hydrochloric acid (33%, 5 mL). The mixture was stirred with heating until the solid had dissolved. After cooling to room temperature, 2-benzoxycarbonyl-3,5-dimethylpyrrole (9.9 g, 43.3 mmol) was added. The mixture was allowed to stir at 40°C for 3 h. After removal of solvent, the residue was crystallized from methanol. The product was obtained as white crystals (9.10 g, 90%). Mp 282–284°C. ^1H NMR (200 MHz, DMSO-d_6) δ: 1.95 (s, 6H, 2 CH_3), 2.05 (s, 6H, 2CH_3), 3.25 (s, 2H, CH_2), 5.25 (s, 4H, 2CH_2), 7.25 (m, 10H, 2 Ph), 11.05 (s, 2H, 2NH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ: 10.7 (CH_3), 12.0 (CH_3), 19.5 (CH_2), 64.3 (OCH_2) 115.4, 119.4, 126.7, 127.8, 128.5, 131.0, 137.1, 160.6 (COO) ppm. Anal. calcd for $C_{19}H_{26}N_2O_4$: C 65.87; H 7.56; N 8.09; found: C 65.45; H 7.51; N 7.58.

5.1.2. 1,1-Bis(5-carboxy-2,4-dimethylpyrrole-3-yl)methane (2). 1,2-Bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)methane (9.0 g, 19 mmol) was dissolved in tetrahydofuran (150 mL). Palladium on carbon (10%, 0.1 g) and a drop of triethylamine was then added. The mixture was stirred for 20 h under a hydrogen atmosphere at room temperature. The catalyst was removed by suction filtration. After removal of solvent, the residue was dried under vacuum. The product was obtained as a white powder (5.40 g, 99%), which was used directly for the next step synthesis without further purification. Mp 220°C (dec.). IR (KBr), ν=3309, 3072, 2920, 1678, 1579, 1466, 1375, 1251, 1199, 1153, 1124, 1085, 982, 900, 767, 727, 642, 561 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6) δ: 1.90 (s, 6H, $2CH_3$), 2.10 (s, 6H, $2CH_3$), 3.20 (s, 2H, CH_2), 10.95 (s, 2H, 2NH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ: 11.2 (CH_3), 11.3 (CH_3), 19.5 (CH_2), 121.3, 127.7, 130.3, 136.4, 161.5 (COOH) ppm.

5.1.3. 1,2-Bis(5-carboxy-2,4-dimethylpyrrole-3-yl)-ethane (3). Prepared following the procedure for compound **2** using 1,2-bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)ethane as starting material. Yield 99%. Mp 233°C (dec.). IR (KBr), ν=3408, 2924, 2862, 1655, 1579, 1498, 1466, 1375, 1259, 1186, 1095, 1002, 903, 775, 752, 561 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6) δ: 1.90 (s, 6H, 2 CH_3), 2.10 (s, 6H, $2CH_3$), 2.30 (s, 4H, $2CH_2$), 10.90 (s, 2H, 2NH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ: 10.2 (CH_3), 10.6 (CH_3), 24.0 (CH_2), 116.2, 120.3, 125.6, 130.0, 162.5 (COO) ppm.

5.1.4. 1,3-Bis(5-carboxy-2,4-dimethylpyrrole-3-yl)propane (4). Prepared following the procedure for compound **2** using 1,3-bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)propane[20] as starting material. Yield 98%. Mp 230°C (dec.). IR (KBr), ν=3257, 2928, 2856, 1655, 1500, 1466, 1375, 1263, 1170, 1109, 1065, 962, 779, 729, 540 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6) δ: 1.45 (t, J=7.3 Hz, 2H, CH_2), 2.05 (s, 6H, 2 CH_3), 2.10 (s, 6H, $2CH_3$), 2.30 (t, J=7.3 Hz, 4H, $2CH_2$), 10.90 (s, 2H, 2NH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ: 10.1 (CH_3), 10.4 (CH_3), 22.1 (CH_2), 24.1 (CH_2), 117.2, 122.3, 130.6, 137.0, 161.3 (COO) ppm.

5.1.5. 1,3-Bis(5-carboxy-2,4-dimethylpyrrole-3-yl)butane (5). Prepared following the procedure for compound **2** using 1,4-bis(5-benzoxycarbonyl-2,4-dimethylpyrrole-3-yl)butane[20] as starting material. Yield 98%. Mp 245°C (dec.). IR (KBr), ν=3275, 2926, 2856, 1657, 1500, 1460, 1375, 1261, 1159, 1094, 1008, 893, 773 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6) δ: 1.20 (t, J=7.3 Hz, 4H, $2CH_2$), 2.05 (s, 6H, $2CH_3$), 2.10 (s, 6H, $2CH_3$), 2.30 (t, J=7.3 Hz, 4H, $2CH_2$), 10.90 (s, 2H, 2NH, 2COOH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ: 10.1 (CH_3), 10.4 (CH_3), 22.1 (CH_2), 24.1 (CH_2), 117.2, 122.3, 130.6, 137.0, 161.3 (COO) ppm.

5.1.6. Macrocycle 7·4HBr. 1,2-Bis(5-carboxy-2,4-dimethylpyrrole-3-yl)methane (**2**, 400 mg, 1.38 mmol) was suspended in trifluoroacetic acid (10 mL), and stirred at 40°C until all the solid had dissolved. The mixture was cooled to room temperature and 5,5′-diformyl-4,4′-dimethyl-3,3′-diethyl-dipyrromethane (**6**, 394 mg, 1.38 mmol, 1.0 mol equiv.) and a mixture of dichloromethane (20 mL), methanol (20 mL) and hydrogen bromide (48% in acetic acid, 2 mL) were added. The red mixture was left to stir overnight at room temperature. Anhydrous ether (100 mL) was added. The suspension was allowed to stir for another 30 min. The red solid was collected by suction filtration and washed with anhydrous ether containing a few drops of HBr (48% in glacial acetic acid). The crude product was suspended in methanol (50 mL) containing a few drops of HBr (48% in glacial acetic acid) and stirred at room temperature for a period of 30 min. The solid was collected by filtration to afford the product (800 mg, 95%). An analytic sample was obtained by repeating the following procedure three times: the crude product was dissolved in a minimum amount of trifluoroacetic acid, then dichloromethane (1 mL), methanol (1 mL) and a few drops of HBr (48% in glacial acetic acid) were added, followed by anhydrous ether to precipitate the product. The red solid was collected by centrifugation and dried in vacuo. Mp 295°C (dec.). IR (KBr), ν=3460, 2933, 2854, 1610, 1512, 1452, 1377, 1236, 1168, 1097, 1051, 964, 914, 846, 681 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$+10% TFA-D, v/v), δ: 0.75 (t, J=7.3 Hz, 6H, $2CH_3$), 1.10 (s, 6H, $2CH_3$), 2.20 (s, 24H, $8CH_3$), 2.30 (m, 8H, $4CH_2$), 2.55 (s, 12H, $4CH_3$), 3.75 (s, 4H, $2CH_2$ at β,β-position), 4.40 (s, 4H, $2CH_2$ at α,α-position), 7.20 (s, 4H, 4-CH═), 9.25 (s, 1H, NH), 10.60 (brs, 1H, NH), 12.80–13.30 (m, 6H, 6 NH) ppm. ^{13}C NMR ($CDCl_3$+10% TFA-D, v/v, 75 MHz), δ: 10.0, 13.8, 14.3, 14.5, 17.3, 19.4, 23.1, 120.9, 121.4, 126.9, 127.4, 131.1, 145.5, 147.2, 155.0, 156.3 ppm. UV–Vis ($CHCl_3$+1% of TFA), $\lambda_{max}(\varepsilon)$=370 (29800), 455 (111600), 490 (105900), 538 (79300) nm. MS: LRP+LSIMS (matrix: thioglycerol): m/e=905 (M^++1). HRMS (LSIMS, matrix: thioglycerol+$CHCl_3$), found: 904.58818, [$C_{60}H_{72}N_8$] requires: 904.58799. Anal. calcd for $C_{60}H_{72}N_8$·4HBr: C 58.63; H 6.18; N 9.12; found: C 59.09; H 6.38; N 8.97.

5.1.7. Preparation of 7·Zn_2. The ligand (~100 mg) was dissolved in trifluoroacetic acid (5 mL) and dichloromethane (50 mL) was then added. To this mixture, a solution of zinc acetate (~20 mg) in methanol (20 mL) was added at once, followed by triethylamine (5 mL). The red mixture was allowed to stir for 2 h at room temperature. The solvent was removed under vacuum and the residue was stirred with methanol (20 mL) for 2 h. The red dark solid was collected and further purified by repeating this procedure three times. IR (KBr), ν=3441, 2960, 2925, 2868, 1597, 1438, 1396, 1225, 1167, 1107, 972, 922, 856, 783, 733, 663 cm^{-1}. UV–Vis ($CHCl_3$), $\lambda_{max}(\varepsilon)$=360 (16800), 485 (68600), 545 (42600) nm. MS: LRP+LSIMS (thioglycerol): m/e=1033 (M^++1), $C_{60}H_{68}N_8Zn_2$ requires 1032. HRMS. (ESI) found: 1031.4163, [$C_{60}H_{68}N_8Zn_2$] requires 1031.4197. Anal. calcd for $C_{60}H_{68}N_8Zn_2$: C 69.83; H 6.64; N 10.86; found: C 69.50; H 6.85; N 10.44.

5.1.8. Macrocycle 8·4HBr. Prepared according to the procedure for compound **7**. Yield 90%. Mp 300°C (dec.). IR (KBr), ν=3441, 2921, 2853, 1612, 1512, 1453, 1378, 1261, 1168, 1050, 960, 915, 825, 678, 508 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$+10%TFA-d, v/v), δ: 1.05 (t, J=7.3 Hz, 12H, $4CH_3$), 2.00–2.80 (m, 52H, $12CH_3$, $8CH_2$), 4.40 (s, 4H, $2CH_2$), 7.20 (m, obscured by $CHCl_3$ signal, 4-CH═), 11.60 (brs, obscured by TFA signal, NH) ppm. ^{13}C NMR ($CDCl_3$+10% TFA-d, v/v, 50 MHz), δ: 9.8, 12.5, 14.4, 17.2, 17.3, 23.3, 23.7, 120.8, 121.3, 126.8, 127.7, 130.9, 144.0,

145.2, 155.6, 159.6 ppm. UV–Vis ($CHCl_3$), $\lambda_{max}(\varepsilon)$=372 (27500), 456 (171000), 494 (82600), 525 (68800) nm. MS: LRP+LSIMS (thioglycerol): *m/e*=933 (M^++1). HRMS (LSIMS, matrix: thioglycerol+$CHCl_3$), found: 933.62752, [$C_{62}H_{77}N_8$] requires 933.62712. Anal. calcd for $C_{62}H_{77}N_8$·4HBr: C 59.24; H 6.41; N 8.91; found: C 59.74; H 6.57, N 8.67.

5.1.9. Compound 8·Zn_2. Prepared following the procedure for compound **7**·Zn_2. IR (KBr), ν=3440, 2958, 2930, 2871, 1561, 1439, 1396, 1224, 1677, 1108, 972, 923, 865, 783, 732, 662 cm^{-1}. UV–Vis ($CHCl_3$), $\lambda_{max}(\varepsilon)$=365 (17900), 488 (78600), 546 (39800) nm. MS (FAB): *m/e*=1061 (M^++1), $C_{62}H_{72}N_8Zn_2$ requires 1060. HRMS (ESI) found: 1059.4501, [$C_{60}H_{68}N_8Zn_2$] requires 1059.4510. Anal. calcd for C: C 70.25; H 6.85; N 10.57: found: C 69.92; H 6.51; N 10.43.

5.1.10. Macrocycle 9·4HBr. Prepared following the procedure for compound **7**. Yield 90%. Mp 285°C (dec.). IR (KBr), ν=3400, 2930, 2872, 1610, 1566, 1510, 1444, 1390, 1238, 1163, 1097, 1061, 953, 922, 899, 685 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$+10%TFA-d, v/v), δ: 1.05 (t, *J*=7.3 Hz, 12H, $4CH_3$), 2.65 (brs, 4H, $2CH_2$), 2.20–2.80 (m, 52H, $12CH_3$, $8CH_2$), 4.40 (s, 4H, $2CH_2$), 7.20 (s, obscured by $CHCl_3$ signal, 4-CH═), 11.00 (brs, obscured by TFA signal, NH) ppm. ^{13}C NMR ($CDCl_3$+10% TFA, 75 MHz), δ: 10.0, 13.1, 14.6, 17.4, 22.8, 23.8, 24.4, 30.3, 120.4, 126.6, 127.8, 130.2, 130.2, 143.0, 145.2, 145.3, 157.2 ppm. UV–Vis ($CHCl_3$), $\lambda_{max}(\varepsilon)$=375 (29000), 454 (186000), 525 (88600) nm. MS: LRP+LSIMS (matrix: thioglycerol): *m/e*=961 (M^++1). HRMS (LSIMS, matrix: thioglycerol+$CHCl_3$); found: 961.65689, [$C_{64}H_{81}N_8$] requires 961.65842. Anal. calcd for $C_{64}H_{80}N_8$·4HBr·4H_2O: C 56.64; H 6.78 N 8.25; found: C 56.89; H 6.67; N 8.37.

5.1.11. Compound 9·Zn_2. Prepared following the procedure for compound **7**·Zn_2. IR (KBr), ν=3440, 2926, 2864, 1597, 1439, 1396, 1230, 1164, 1107, 956, 931, 887, 781, 733, 669 cm^{-1}. UV–Vis ($CHCl_3$), $\lambda_{max}(\varepsilon)$=370 (18900), 475 (81200), 539 (40200) nm. MS (ESI) *m/e*=1089 (M^++1), [$C_{64}H_{76}N_8Zn_2$] requires 1088. HRMS (ESI) found: 1085.4841, [$C_{64}H_{76}N_8Zn_2$] requires: 1085.4854. Anal. calcd for $C_{64}H_{76}N_8Zn_2$: C 70.64; H 7.04; N 10.30, found: C 70.20; H 6.85; N 9.90.

5.1.12. Macrocycle 10·2HBr. Prepared following the procedure for compound **7**. Yield 72%. Mp 246°C (dec.). IR (KBr), ν=3440, 2930, 2869, 1610, 1568, 1510, 1443, 1389, 1238, 1164, 1097, 1074, 960, 922, 685, 663 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$+10% TFA-d), δ: 1.05 (t, *J*=7.3 Hz, 6H, $2CH_3$), 1.54 (brs, 4H, $2CH_2$), 2.25 (s, 12H, $4CH_3$), 2.40–2.80 (m, 14H, $4CH_2$, $2CH_3$), 4.20 (s, 2H, CH_2), 7.24 (s, obscured by $CHCl_3$ signal, –CH═), 11.05 (brs, obscured by TFA signal, NH) ppm. UV–Vis ($CDCl_3$), $\lambda_{max}(\varepsilon)$=375 (12500), 455 (58600), 535 (82000) nm. MS: LRP+LSIMS (matrix: thioglycerol): *m/e*=495 (M^++1). HRMS (ESI) found: 495.3483, [$C_{33}H_{42}N_4$] requires: 495.3488. Anal. calcd for $C_{33}H_{42}N_4$·2HBr·H_2O: C 58.76; H 6.87; N 8.31%; found: C 58.54; H 6.39, N 7.90.

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