New diformyldihydroxyaromatic precursors for luminescent Schiff base macrocycles: Synthesis, characterization, and condensation studies

Britta N. Boden, Amir Abdolmaleki, Cecily T.-Z. Ma, and Mark J. MacLachlan

Abstract: With the goal of preparing luminescent, fully conjugated Schiff base macrocycles, a series of precursors based on benzene, phenanthrene, and triphenylene with formylhydroxy functionalization have been prepared and characterized. The condensation of these compounds with substituted phenylenediamines to afford conjugated [2+2] or [3+3] Schiff base macrocycle has been investigated. Although the [3+3] Schiff base macrocycles could not be isolated, two new soluble and luminescent [2+2] Schiff base macrocycles with N_2O_2 binding pockets have been prepared and characterized.

Key words: Schiff base, macrocycle, condensation, salicylaldehyde, conjugated.

Résumé : Afin de pouvoir obtenir des bases de Schiff macrocycliques complètement conjuguées et luminescentes, on a préparé et caractérisé une série de précurseurs à base de benzène, de phénanthrène et de triphénylène portant des groupes hydroxyle et formyle. On a ensuite étudié la condensation de ces composés avec des phénylènediamines substituées qui peuvent conduire à des bases de Schiff macrocycliques avec conjugaison [2+2] ou [3+3]. Même si on n'a pas pu isoler les bases de Schiff macrocycliques [3+3], on a pu préparer et caractériser deux nouvelles bases de Schiff macrocycliques [2+2], solubles et luminescentes, comportant des poches de fixation du N_2O_2.

Mots-clés : base de Schiff, macrocycle, condensation, salicylaldéhyde, conjugué.

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Introduction

Schiff base macrocycles formed from the condensation of diamines and dialdehydes are attractive ligands for multimetallic complexes (1–20). 2,6-Diformylphenol **1** and its analogues condense with diamine compounds in a 2:2 ratio to form compartmental ligands (Robson macrocycles **2**) (21–25) (Chart 1). Bimetallic complexes formed in the interior of this macrocycle are of interest for studying magnetic and electronic interactions between metal centres, and may serve as models for the active sites of enzymes (26, 27).

The hydroxyl group adjacent to the formyl moiety in the precursor is important for producing an N_2O_2 chelate and for stabilizing the imine in the metal-free macrocycle. While a vast assortment of diamines is available for incorporation into Schiff base macrocycles, much less attention has been placed on the bis(formylhydroxy) precursor development. By varying the geometry and structure of this component, one may access novel macrocycles with different sizes, shapes, and number of metal-binding sites (28–30). For example, condensation of compounds **3** (31–33) and **4** (34) with *o*-phenylenediamines gives triangular [3+3] and hexagonal [6+6] Schiff base macrocycles, respectively, and **5** (35) is expected to form [2+2] Schiff base macrocycles. Only a few other bis(formylhydroxy) compounds have been explored as precursors for Schiff base macrocycles (36–40). Expanding the number of bis(formylhydroxy) compounds available will open up avenues to explore macrocycles with new electronic, optical, and coordinating properties.

In this paper, we significantly expand the library of dihydroxydiformyl compounds predisposed for [2+2] and [3+3] Schiff base macrocycles. In an effort to obtain fully conjugated, luminescent macrocycles, we have prepared the first phenanthrene and triphenylene precursors with bis(formylhydroxy) functionality. Phenanthrene and triphenylene have received very little attention for incorporation into macrocycles (41, 42), yet they may have a large effect on the ring size and electronic or optical properties of the products. In addition, we have prepared new conjugated *m*-diethynylbenzene precursors for the preparation of [2+2] Schiff base macrocycles. We report on the optical properties of the novel diamond-shaped macrocycles.

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B.N. Boden, A. Abdolmaleki, C.T.L. Ma, and M.J. MacLachlan.[1] Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada.

[1]Corresponding author (email: mmaclach@chem.ubc.ca).

Experimental

General

Tetrahydrofuran (THF) was distilled over Na and benzophenone under N_2. Triethylamine was distilled over NaOH under N_2. Stilbene **6** (43), 3,6-dimethoxyphenanthrene **7** (44), 3,6-dimethoxyphenanthrene-9,10-quinone **10** (45), 1,2-dibromo-4,5-dihexylbenzene **15** (46), 4-methoxyphenylboronic acid **16** (47), 1,3-diethynylbenzene **24** (48), 2,6-diethynylpyridine **25** (49), 1,2-diamino-4,5-dialkoxy-

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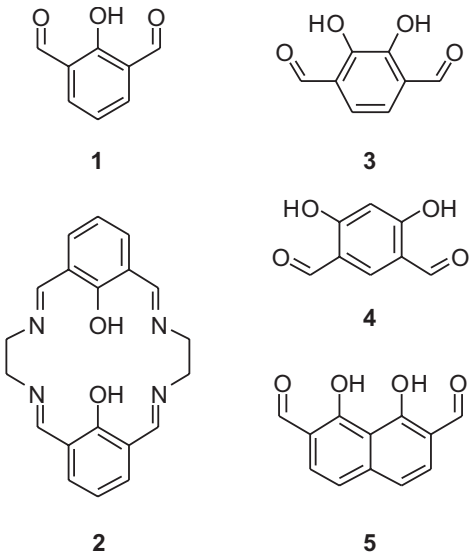
Chart 1.



benzenes **28** (50), and BOC-protected phenylenediamine **32** (51) were prepared according to literature procedures. $Pd(PPh_3)_4$ was obtained from Strem Chemicals, Inc. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. All other chemicals were purchased from Aldrich, TCI, or Fisher and used as received. All reactions were carried out under nitrogen unless otherwise noted. ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75.5 or 100.7 MHz) spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers and were referenced internally to residual protonated solvent. Infrared spectra were obtained as KBr discs or on NaCl plates with a Bomem MB-100 spectrometer or a Nicolet 4700 FTIR spectrometer. UV–vis spectra were obtained on a Varian Cary 5000 UV–vis/near IR spectrometer using a 1 cm cuvette. Fluorescence spectra were obtained on a Photon Technology Intl. QuantaMaster fluorimeter. Matrix assisted laser desorption/ionization(MALDI) mass spectra were obtained on a Bruker Biflex IV time-of-flight (TOF) mass spectrometer equipped with a MALDI ion source. Electrospray ionization (ESI) mass spectra were obtained on a Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. Samples were analyzed in methanol:dichloromethane at 1 μmol/L. EI spectra were obtained with a double focusing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of: source temperatures 120–220 °C and ionization energy 70 eV. Elemental analyses were obtained at the UBC Microanalytical facility. Melting points were recorded on a Fisher John's melting point apparatus.

Synthesis of 2,7-diformyl-3,6-dimethoxyphenanthrene (8)

3,6-Dimethoxyphenanthrene **7** (0.718 g, 3.01 mmol) was dissolved in 20 mL THF. BuLi (6.1 mL, 1.6 mol/L) was added, and the solution was stirred for 30 min, after which anhyd. DMF (0.77 mL, 9.98 mmol) was added. The reaction solution was poured into aq. HCl and extracted with dichloromethane (DCM). After drying over $MgSO_4$, the solvent was removed by rotary evaporation to reveal an orange solid. The product was chromatographed over silica with DCM and recrystallized from DCM to obtain 0.150 g of yellow solid (17% yield).

Data for 8

Mp 280 °C dec. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 281 (5.6×10^4), 338 (2.5×10^4), 440 (2.2×10^3) nm (L mol^{-1}cm^{-1}). IR (KBr): ν = 2947, 2862, 1681, 1615, 1502, 1457, 1406, 1369, 1265, 1220, 1181, 1136, 1109, 1017, 970, 842, 655 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 10.63 (s, 2H, C*H*O), 8.36 (s, 2H, aromatic C*H*), 7.92 (s, 2H, aromatic C*H*), 7.65 (s, 2H, aromatic C*H*), 4.17 (s, 6H, OCH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ: 189.7, 159.0, 134.3, 130.6, 127.3, 126.1, 126.0, 103.8, 55.9 ppm. ESI-MS: *m*/*z* = 295 ([M + H]$^+$). Anal. calcd. for $C_{18}H_{14}O_4 \cdot 0.5\ H_2O$: C, 71.28; H, 4.98. Found: C, 71.35; H, 4.80.

Synthesis of 2,7-diformyl-3,6-dihydroxyphenanthrene (9)

To an ice-cooled solution of compound **8** (0.413 g, 1.40 mmol) in DCM was added BBr_3 (1 mL, 10.6 mmol). After stirring overnight, the solution was poured into 200 mL of ice water to obtain an orange solid. The solid was filtered, and the remaining aq. solution was extracted with DCM. The organic layer was dried and combined with the solid. After flashing the product through silica with DCM, 0.268 g (1.01 mmol) of orange crystals were obtained (72% yield).

Data for 9

Mp > 300 °C. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 284, 304, 326, 465 nm. IR (KBr): ν = 3449, 3253, 3017, 2884, 1652, 1530, 1338, 1205, 1157, 1106, 899 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ: 10.96 (s, 2H, O*H*), 10.46 (s, 2H, C*H*O), 8.29 (s, 2H, aromatic C*H*), 7.99 (s, 2H, aromatic C*H*), 7.67 (s, 2H, aromatic C*H*) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6, 25 °C) δ: 191.3, 157.6, 134.0, 133.0, 130.6, 128.2, 125.9, 125.1, 124.2, 109.2 ppm. EI-MS: *m*/*z* = 266 (M$^+$). Anal. calcd. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.05; H, 4.00.

Synthesis of 2,7-dibromo-3,6-dimethoxyphenanthrene-9,10-quinone (11)

To a solution of 3,6-dimethoxy-9,10-phenanthrenequinone **10** (1.090 g, 4.06 mmol) in 25 mL each DCM and MeCN was added Br_2 (1 mL, 19.5 mmol) and $FeCl_3$ (1.317 g, 8.12 mmol). The solution was heated to reflux until an orange solid precipitated. After filtration of the solid, the filtrate was poured in H_2O and extracted with DCM. The solvent was removed under vacuum until further precipitation. Both solids were combined and recrystallized from DCM to yield 1.298 g (3.05 mmol, 75%). The product was sometimes chromatographed on silica with DCM.

Data for 11

Mp > 300 °C. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 247 (1.6×10^4), 297 (5.8×10^4), 344 (1.3×10^4) nm (L mol^{-1}cm^{-1}). IR (KBr): ν = 3448, 2946, 1670, 1578, 1545, 1436, 1333, 1312, 1274, 1262, 1203, 1040, 854, 696, 678 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.33 (s, 2H, aromatic C*H*), 7.22 (s, 2H, aromatic C*H*), 4.11 (s, 6H, OCH_3) ppm; ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 177.7, 162.0, 136.5, 136.1, 125.9, 114.7, 105.9, 57.0 ppm. EI-MS: *m*/*z* = 426

(M^+). Anal. calcd. for $C_{16}H_{10}O_4Br_2$: C, 45.10; H, 2.37. Found: C, 44.95; H, 2.66.

Synthesis of 2,7-dibromo-3,6,9,10-tetramethoxyphenanthrene (12)

Compound **11** (0.567 g, 1.33 mmol), Bu_4NBr (0.113 g, 0.351 mmol), $Na_2S_2O_4$ (0.610 g, 3.50 mmol), THF (50 mL) and H_2O (50 mL) were combined in a round-bottomed flask and stirred for 10 min, after which dimethyl sulfate (3 mL, 31.7 mmol) was added, followed by aq. sodium hydroxide (2 mL, 14 mol/L). After stirring 1 h, the aq. layer was separated and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL), NH_4OH solution (2 × 50 mL), and brine (1 × 50 mL). The organic layer was dried with $MgSO_4$, filtered, and the solvents were removed under vacuum, resulting in a brown solid. Washing the product with MeOH gave an orange solid. Additional impurities were removed by flashing the product through silica with a 1:1 mixture of hexanes and DCM, followed by recrystallization from DCM. Yield: 0.473 g, 1.0 mmol, 78%.

Data for 12

Mp 217–218 °C. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 264 (5.3 × 10^4), 225 (3.8 × 10^4), 384 (1.0 × 10^3) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3448, 2933, 1597, 1491, 1451, 1432, 1364, 1245, 1074, 1056, 993, 676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 8.38 (s, 2H, aromatic C*H*), 7.77 (s, 2H, aromatic C*H*), 4.09 (s, 6H, OCH_3), 4.02 (s, 6H, OCH_3) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 154.2, 142.1, 128.0, 127.5, 125.2, 114.1, 103.9, 61.3, 56.8 ppm. EI-MS: *m*/*z* = 456 (M^+). Anal. calcd. for $C_{18}H_{16}O_4Br_2$: C, 47.40; H, 3.54. Found: C, 47.2; H, 3.66.

Synthesis of 2,7-diformyl-3,6,9,10-tetramethoxyphenanthrene (13)

Compound **12** (0.373 g, 0.818 mmol) was dissolved in 18 mL THF and cooled to 0 °C. To the solution was added BuLi (1.2 mL, 1.6 mol/L). After 10 min stirring, DMF (0.3 mL, 3.87 mmol) was added. The solution was poured into acidified H_2O and extracted with DCM. Evaporation of the solvent gave a yellow solid (0.188 g, 0.531 mmol, 65% yield).

Data for 13

Mp 294 °C dec. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 287 (5.2 × 10^4), 342 (2.0 × 10^4), 448 (2.0 × 10^3) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3448, 2935, 2858, 1686, 1610, 1491, 1452, 1429, 1358, 1278, 1249, 1205, 1145, 1128, 1014, 976, 570 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 10.62 (s, 2H, C*H*O), 8.68 (s, 2H, aromatic C*H*), 7.68 (s, 2H, aromatic C*H*), 4.15 (s, 6H, OCH_3), 4.05 (s, 6H, OCH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ: 190.0, 158.8, 143.3, 132.6, 126.3, 125.3, 104.3, 61.4, 56.2 ppm. EI-MS: *m*/*z* = 354 (M^+). HR-MS calcd. for $C_{20}H1_8O_6$: 354.11034. Found: 354.11005.

Synthesis of 2,7-diformyl-3,6-dihydroxyphenanthrene-9,10-quinone (14)

Compound **13** was dissolved in 10 mL dry DCM and cooled to 0 °C. To the solution was added BBr_3. After stirring overnight, the dark solution was poured into H_2O to precipitate a purple solid. After filtration, some of the solid was dissolved in THF to make an initially purple solution, which slowly became yellow upon standing. The solvent was removed to give a brown solid (**14**). We believe the initially obtained solid is a tautomer or partially reduced form of **14**, but it was not possible to obtain a pure sample of the purple intermediate.

Data for 14

Mp > 300 °C. UV–vis (DMSO): λ_{max} (ϵ) = 314 nm. IR (KBr): ν = 3422, 2925, 2856, 1692, 1665, 1613, 1551, 1361, 1320, 1252, 1197, 1154, 947, 789, 652 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6, 25 °C) δ: 12.12 (s, 2H, O*H*), 10.33 (s, 2H C*H*O), 8.34 (s, 2H, aromatic C*H*), 7.59 (s, 2H, aromatic C*H*) ppm. EI-MS: *m*/*z* = 296 (M^+). HR-MS calcd. for $C_{16}H_8O_6$: 296.03209. Found: 296.03142.

Synthesis of 4′,5′-dihexyl-4,4″-dimethoxy-1,1′:2′,1″-terphenyl (17)

A mixture of 1,2-dibromo-4,5-dihexylbenzene **15** (1.049 g, 2.59 mmol), 4-methoxyphenylboronic acid **16** (0.971 g, 6.39 mmol), sodium carbonate (0.971 g, 9.16 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.050 g, 0.043 mmol) was stirred under reflux in a mixture of toluene (18 mL), EtOH (18 mL), and water (6 mL) for 4 h. The solution was poured into water and extracted with DCM (3 × 100 mL). After drying with $MgSO_4$ and evaporating the solvent, a brown oil was obtained and purified by chromatography in 3:1 hexanes/DCM. Additional impurities were crystallized out from EtOH. The product was a colorless oil. Yield: 0.732 g, 1.60 mmol, 62%.

Data for 17

UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 251 (4.7 × 10^4) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 2955, 2928, 2855, 1608, 1512, 1490, 1467, 1290, 1245, 1107, 1033, 831 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 7.14 (s, 2H, aromatic C*H*), 7.06 (d, 4H, aromatic C*H*), 7.74 (d, 4H, aromatic C*H*), 3.76 (s, 6H, OCH_3), 2.64 (m, 4H, CH_2), 1.62 (m, 4H, hexyl chain), 1.41 (m, 4H, hexyl chain), 1.33 (m, 8H, hexyl chain), 0.89 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 158.3, 139.8, 137.5, 134.5, 131.5, 131.1, 113.5, 55.4, 32.7, 32.0, 31.6, 29.8, 22.9, 14.3 ppm. EI-MS: *m*/*z* = 458 (M^+). HR-MS calcd. for $C_{32}H_{42}O_2$: 458.31848. Found: 458.31810.

Synthesis of 2,3-dihexyl-7,10-dimethoxytriphenylene (18)

Compound **17** (0.778 g, 1.69 mmol) and iodine (0.667 g, 2.6 mmol) were dissolved in 250 mL dry toluene. The solution was exposed to UV light for 72 h. Excess iodine was removed by washing the solution with aq. $NaSO_3$, and the resulting organic layer was dried with $MgSO_4$, and the solvent was removed under vacuum. Recrystallization of the product from EtOH afforded off-white crystals of **18**, while 0.629 g of terphenyl **17** was recovered and reused in subsequent reactions. Yield: 0.098 g (0.215 mmol, 66% yield based on recovered **17**).

Data for 18

Mp 73–75 °C. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 262 (9.3 × 10^4), 271 (1.2 × 10^5) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 2953, 2926, 2852, 1619, 1508, 1464, 1416, 1367, 1231, 1203,

1178, 1050, 1027, 835, 812 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 8.52 (d, 2H, aromatic C*H*), 8.24 (s, 2H, aromatic C*H*), 7.92 (d, 2H, aromatic C*H*), 7.23 (dd, 2H, aromatic C*H*), 4.00 (s, 6H, OCH_3), 2.80 (m, 4H, CH_2), 1.71 (m, 4H, hexyl chain), 1.50 (m, 4H, hexyl chain), 1.24 (m, 8H, hexyl chain), 0.92 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 158.6, 139.6, 130.8, 127.1, 125.0, 124.5, 123.1, 115.6, 106.3, 55.7, 33.4, 32.1, 31.8, 29.8, 22.9, 14.4 ppm. EI-MS: *m*/*z* = 456 (M^+). Anal. calcd. for $C_{32}H_{40}O_2$: C, 84.16; H, 8.83. Found: C, 84.32; H, 8.61.

Synthesis of 6,11-dibromo-2,3-dihexyl-7,10-dimethoxytriphenylene (19)

To an ice-cooled solution of **18** (0.532 g, 1.16 mmol) in DCM (20 mL), bromine (0.1 mL, 1.9 mmol) was added dropwise. The solution was allowed to stir for 2 h. After washing with aq. $Na_2S_2O_4$, the organic layer was dried with $MgSO_4$, and the solvent was removed under vacuum. Recrystallization from EtOH and DCM afforded white fibrous crystals. Yield: 0.563 g, 0.916 mmol, 79%.

Data for 19

Mp 166–168 °C. UV–vis (CH_2Cl_2): λ_{max} (ε) = 274 (1.6×10^5) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 2956, 2926, 2853, 1600, 1494, 1464, 1401, 1252, 1201, 1059, 866, 830, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 8.71 (s, 2H, aromatic C*H*), 8.13 (s, 2H, aromatic C*H*), 7.76 (s, 2H, aromatic C*H*), 4.11 (s, 6H, OCH_3), 2.81 (m, 4H, CH_2), 1.70 (m, 4H, hexyl chain), 1.47 (m, 4H, hexyl chain), 1.34 (m, 8H, hexyl chain), 0.91 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 154.7, 140.7, 129.4, 128.6, 126.2, 125.7, 123.2, 114.0, 104.9, 56.7, 33.4, 32.0, 31.9, 29.8, 22.9, 14.4 ppm. EI-MS: *m*/*z* = 614 (M^+). Anal. calcd. for $C_{32}H_{38}O_2Br_2$: C, 62.55; H 6.23. Found: C, 62.70; H, 6.54.

Synthesis of 6,11-diformyl-2,3-dihexyl-7,10-dimethoxytriphenylene (20)

To a solution of **19** (0.795 g, 1.29 mmol) in dry THF (40 mL) cooled to –78 °C, 1.6 mol/L *n*-BuLi (4 mL, 6.4 mmol) was added to produce a milky white solution. After 10 min, anhyd. DMF (0.8 mL, 10.3 mmol) was added to form a pale yellow solution. The solution was warmed to room temperature, then poured into aq. HCl (1 mol/L). Extraction with DCM, drying with $MgSO_4$, and evaporation of the solvent afforded a brown oil. Yellow solid precipitated out upon addition of EtOH. Yield: 0.534 g, 1.04 mmol, 81%.

Data for 20

Mp 165–167 °C. UV–vis (CH_2Cl_2): λ_{max} (ε) = 264 (7.0×10^4), 279 (6.2×10^4), 384 (1.2×10^4) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 2960, 2927, 2860, 1687, 1614, 1472, 1421, 1412, 1255, 1207, 1165, 1047, 869, 830 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 10.60 (s, 2H, C*H*=O), 8.94 (s, 2H, aromatic C*H*), 8.22 (s, 2H, aromatic C*H*), 7.67 (s, 2H, aromatic C*H*), 4.07 (s, 6H, OCH_3), 2.79 (m, 4H, CH_2), 1.68 (m, 4H, hexyl chain), 1.48 (m, 4H, hexyl chain), 1.36 (m, 8H, hexyl chain), 0.92 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 190.0, 159.4, 141.2, 134.3, 126.9, 125.4, 125.2, 124.8, 123.5, 105.0, 55.9, 33.5, 32.1, 32.0, 29.9, 22.9, 14.4 ppm. EI-MS: *m*/*z* = 512 (M^+). Anal. calcd. for $C_{34}H_{40}O_4$: C, 79.65; H, 7.86. Found: C, 79.52; H, 7.93.

Synthesis of 6,11-diformyl-2,3-dihexyl-7,10-dihydroxytriphenylene (21)

To an ice-cooled solution of **20** (0.495 g, 0.965 mmol) in dry DCM (50 mL), boron tribromide (2.2 mL, 23.3 mmol) was added to produce a dark brown solution, which subsequently faded to orange. The solution was allowed to warm to room temperature overnight, then was poured into ice water (200 mL). After the mixture had warmed, it was filtered, and the filtrate was extracted with $CHCl_3$ (3 × 50 mL). The filtered solid and organic layer from extraction were combined, and the solvent was removed under vacuum. The residue was passed through a plug of silica in $CHCl_3$. After removal of the solvent, the product was recrystallized from $CHCl_3$ to obtain 0.357 g (0.736 mmol, 76% yield) of a yellow solid.

Data for 21

Mp 260–262 °C. UV–vis (CH_2Cl_2): λ_{max} (ε) = 248 (3.5×10^4), 274 (6.1×10^4), 393 (8.0×10^3) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3444, 2952, 2926, 2855, 1659, 1584, 1543, 1467, 1341, 1230, 1184, 880, 826, 790, 725, 600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 10.68 (s, 2H, O*H*), 10.19 (s, 2H, C*H*=O), 8.71 (s, 2H, aromatic C*H*), 8.18 (s, 2H, aromatic C*H*), 7.96 (s, 2H, aromatic C*H*), 2.82 (m, 4H, CH_2), 1.72 (m, 4H, hexyl chain), 1.49 (m, 4H, hexyl chain), 1.36 (m, 8H, hexyl chain), 0.91 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ: 196.8, 158.7, 141.1, 135.4, 130.4, 126.4, 124.8, 123.1, 121.9, 112.1, 33.4, 33.0, 31.9, 29.8, 22.9, 14.4 ppm. EI-MS: *m*/*z* = 484 (M^+). Anal. calcd. for $C_{32}H_{36}O_4$: C, 79.31; H, 7.49. Found: C, 79.06; H, 7.52.

Synthesis of 4-Iodosalicylaldehyde (23)

Under a nitrogen atmosphere, dry paraformaldehyde (4.05 g, 135 mmol) was added to a mixture of the 3-iodophenol **22** (4.40 g, 20 mmol), anhyd. $MgCl_2$ (2.86 g, 30 mmol), and anhyd. Et_3N (10.5 mL) in dry MeCN (100 mL). After heating the mixture to reflux for 2 h, the mixture was cooled to RT, and 100 mL of 2 mol/L aq. HCl was added. The product was extracted with 3 × 100 mL of Et_2O, dried over $MgSO_4$, filtered, and dried by rotary evaporation. The residue was dissolved in a mixture of 1:1 CH_2Cl_2/hexanes and was filtered through a short pad (~5 cm) of SiO_2 using the same solvent mixture as eluent. Rotary evaporation of the filtered solution gave an off-white solid. Recrystallization from hexanes gave white crystals of **23** (2.22 g, 9.0 mmol, 45%).

Data for 23

Mp 91–92 °C (lit. 87 °C) (52). UV–vis (CH_2Cl_2): λ_{max} (ε) = 327 (5.32×10^3) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3431, 2927, 2856, 1665, 1609, 1458, 1260, 1169, 891, 796, 752, 704 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 11.00 (s, 1H, O*H*), 9.83 (s, 1H, C*H*=O), 7.41 (s, 1H, C*H*), 7.37 (dd, $^3J_{HH}$ = 9.48 Hz, 1H, C*H*), 7.23 (d, $^3J_{HH}$ = 8.07 Hz, 1H, C*H*) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 221.0, 196.0, 134.2, 129.4, 127.2, 105.1, 97.7 ppm. EI-MS: *m*/*z* = 247 (M^+, 100%).

Anal. calcd. for $C_7H_5IO_2$: C, 33.90; H, 2.03. Found: C, 34.11; H, 2.10.

Synthesis of Compound 26

Under a nitrogen atmosphere, 1,3-diethynylbenzene **24** (0.254 g, 2.0 mmol), 4-iodosalicylaldehyde **23** (0.992 g, 4.0 mmol), Ph_3P (0.015 g, 0.06 mmol), and *trans*-$[PdCl_2(Ph_3P)_2]$ (0.06 g, 0.08 mmol) were dissolved in 25 mL of anhyd. THF. Dry Et_3N (2.3 mL) was added, turning the solution from yellow to orange. After stirring for 20 min, CuI (0.02 g, 0.10 mmol) was added, and the solution then turned to dark brown. The solution was stirred overnight at RT, then the yellow precipitate was isolated on a Büchner funnel and washed with CH_2Cl_2/hexane (1:2). Yield: 0.549 g (1.5 mmol, 75%) of yellow powder.

Data for 26

Mp > 250 °C dec. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 297 (3.24×10^4), 331 (3.29×10^4) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3430, 2958, 2926, 2855, 1664, 1609, 1224, 1168, 799, 704 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 10.98 (s, 2H, O*H*), 10.28 (s, 2H, C*H*=O), 7.82 (s, 1H, *C*H), 7.68 (m, 4H, C*H*), 7.53 (t, $^3J_{HH}$ = 10.6 Hz, 1H, C*H*) 7.12–7.15 (m, 4H, *C*H) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 190.3, 160.4, 134.4, 132.3, 129.5, 129.1, 122.5, 122.3, 119.6, 91.3, 89.3 ppm. EI-MS: *m*/*z* = 366 (M^+, 100%), 338 (85%). Anal. calcd. for $C_{24}H_{14}O_4 \cdot H_2O$: C, 74.99; H, 4.20. Found: C, 75.28; H, 4.20.

Synthesis of compound 27

Compound **27** was prepared using the same procedure as for **26**. Light yellow powder; yield: 0.514 g (1.4 mmol, 70%).

Data for 27

Mp > 250 °C dec. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 310 (3.52×10^4) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3430, 2926, 2855, 1660, 1609, 1553, 1434, 1260, 1180, 795, 752, 704 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ: 11.00 (s, 2H, O*H*), 10.29 (s, 2H, C*H*=O), 7.96 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *C*H), 7.74 (d, $^3J_{HH}$ = 7.7 Hz, 2H, C*H*), 7.70 (d, $^3J_{HH}$ = 7.8 Hz, 2H, C*H*) 7.18 (m, 4H, *C*H) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6): δ: 190.2, 160.5, 142.3, 137.9, 129.1, 128.1, 127.7, 123.1, 122.7, 120.1, 90.7, 87.9 ppm. EI-MS: *m*/*z* = 367 (M^+, 100%), 339 (80%). Anal. calcd. for $C_{23}H_{13}O_4N \cdot 0.5H_2O$: C, 73.40; H, 3.75; N, 3.72. Found: C, 73.51; H, 3.75; N, 4.36.

Attempted synthesis of macrocycle 29

Equimolar amounts of compound **9** and 1,2-diamino-4,5-dialkoxybenzenes **28** were combined in a Schlenk flask. Degassed $CHCl_3$ was added, and the resulting solution was heated to reflux for 24 h. After cooling, any precipitate was filtered, or MeCN was added until precipitate formed. The products are unstable to chromatographic separation on silica or alumina.

Data for the insoluble product obtained when R = $^nC_6H_{13}$ (29b)

IR (KBr): ν = 3051, 2952, 2928, 2857, 1636, 1611, 1506, 1465, 1370, 1256, 1190, 1165, 1120, 1017, 959 cm^{-1}.

Data obtained for filtrate when R = $^nC_8H_{17}$ (29c)

^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 12.97, 10.61, 10.07, 10.05, 8.66, 8.01, 7.99, 7.82, 7.49, 6.80, 6.34, 3.95, 1.82–0.86 (hexyloxy chain) ppm. ESI-MS: *m*/*z* = 614 (M^+, 1+1 fragment).

Data for solid obtained from reaction with R = $^nC_8H_{17}$ (29c)

^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 13.00, 12.93, 10.63, 10.11, 10.09, 8.72, 8.52, 8.06, 8.03, 7.87, 7.51, 7.49, 6.83, 6.36, 3.95, 1.83–0.86 (hexyloxy chain) ppm. MALDI-TOF: *m*/*z* = 1785 ([**29c** + H]$^+$).

Attempted synthesis of macrocycle 30

Equimolar amounts of compound **21** and 1,2-diamino-4,5-dialkoxybenzenes were combined in a Schlenk flask. Solvent was added, and the resulting solution was heated to reflux. For specific conditions, see later. In each case, nearly the same inseparable mixture was obtained as indicated by ^1H NMR spectroscopy.

Data for 30

^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 14.84, 13.66, 13.21, 13.02, 12.35, 12.28, 12.06, 11.65, 9.2–6.3, 4.2–3.8, 2.9–2.7, 2.0–0.8 ppm. MALDI-TOF-MS: *m*/*z* = 1935 ([M + H]$^+$).

Synthesis of compound 33

Compound **21** (0.058 g, 0.120 mmol) and *p*-anisidine **31** (0.46 g, 0.373 mmol) were combined in a flask and dissolved in dry THF to form a yellow solution. After refluxing for 4 h, the solution was cooled, and the volume of solvent was reduced. Upon addition of MeOH, an orange solid precipitated, was filtered, and was washed with MeOH and petroleum ether to yield 0.071 g (0.102 mmol, 86%) of product.

Data for 33

Mp 212–213 °C. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 287 (5.8×10^4), 340 (2.8×10^4), 359 (3.2×10^4), 401 (5.2×10^4) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3424, 3029, 2952, 2926, 2861, 1616, 1507, 1457, 1366, 1297, 1250, 1183, 1032, 832, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 13.21 (s, 2H, O*H*), 8.86 (s, 2H, C*H*=N), 8.50 (s, 2H, aromatic C*H*), 8.16 (s, 2H, aromatic C*H*), 8.01 (s, 2H, aromatic C*H*), 7.36 (d, 4H, aromatic C*H*), 6.96 (d, 4H, aromatic C*H*), 3.85 (s, 6H, OCH_3), 2.81 (m, 4H, CH_2), 1.73 (m, 4H, hexyl chain), 1.48 (m, 4H, hexyl chain), 1.36 (m, 8H, hexyl chain), 0.92 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ: 160.1, 159.3, 158.9, 141.5, 140.0, 132.9, 127.8, 126.8, 123.7, 122.9, 122.7, 120.9, 114.9, 110.9, 55.8, 33.5, 32.1, 31.9, 29.9, 23.0, 14.4 ppm. EI-MS: *m*/*z* = 694 (M^+). Anal. calcd. for $C_{46}H_{50}N_2O_4$: C, 79.51; H, 7.25; N, 4.03. Found: C, 79.74; H, 7.41; N, 4.19.

Synthesis of compound 34

Compound **21** (0.062 g, 0.128 mmol) and *N*-(*tert*-butyloxycarbonyl)-1,2-diaminobenzene **32** (0.087 g, 0.418 mmol) were combined in a flask and dissolved in 10 mL of THF. After refluxing the solution overnight, the solvent was reduced and precipitated by MeOH. The product

was recrystallized in DCM and hexanes. Filtration of the yellow solid yielded 0.091 g (0.105 mmol, 83%) of product.

Data for 34

Mp 223–226 °C. UV–vis (CH_2Cl_2): λ_{max} (ϵ) = 263 (5.2×10^4), 289 (5.5×10^4), 410 (3.8×10^4) nm (L $mol^{-1}cm^{-1}$). IR (KBr): ν = 3436, 2955, 2925, 1736, 1639, 1609, 1595, 1510, 1447, 1366, 1216, 1159, 1048, 898, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 12.22 (s, 2H, O*H*), 8.90 (s, 2H, N=C*H*), 8.63 (s, 2H, aromatic C*H*), 8.21 (s, 2H, aromatic C*H*), 8.20 (d, 2H, N*H*), 8.12 (s, 2H, aromatic C*H*), 7.31 (m, 2H, aromatic C*H*), 7.17–7.07 (m, 6H, aromatic C*H*), 2.82 (m, 4H, CH_2), 1.73 (m, 4H, hexyl chain), 1.53 (s, 18H, *t*-butyl *H*), 1.48 (m, 4H, hexyl chain), 1.36 (m, 8H, hexyl chain), 0.90 (t, 6H, hexyl CH_3) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$, 25 °C) δ: 164.2, 158.5, 152.8, 140.4, 138.1, 133.4, 132.9, 128.8, 128.5, 126.7, 124.2, 123.5, 123.0, 120.9, 119.6, 118.6, 111.2, 81.2, 33.4, 32.0, 31.9, 29.8, 28.6, 22.9, 14.4 ppm. ESI-MS: *m*/*z* = 865 (M^+). Anal. calcd. for $C_{54}H_{64}N_4O_6 \cdot 2\ H_2O$: C, 71.97; H, 7.61; N, 6.22. Found: C, 71.88; H, 7.29; N, 6.40.

Synthesis of macrocycle 35

Under a nitrogen atmosphere, compound **26** (0.366 g, 1.0 mmol) and 1,2-diethylhexyloxy-4,5-diaminobenzene **28d** (0.364 g, 1.0 mmol) were dissolved in 20 mL of degassed $CHCl_3$ and 10 mL of degassed MeCN. The solution was heated to reflux (90 °C) for 24 h, giving a clear, red solution. Upon cooling and adding MeCN, a red powder precipitated, which was isolated on a Büchner funnel and washed with MeCN. Yield: 1.22 g (0.88 mmol, 88%).

Data for 35

Mp > 300 °C. UV–vis (THF): λ_{max} (ϵ) = 325 (2.53×10^4), 362 (2.23×10^4) nm (L $mol^{-1}cm^{-1}$). Fluorescence: λ_{ex} = 370 nm, Φ = 3.0%. IR (KBr): ν = 3430, 2926, 2855, 2130, 1609, 1506, 1260, 1188, 752, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.34 (s, 4H, O*H*), 8.62 (s, 4H, C*H*=N), 7.75 (s, 2H, C*H*), 7.48 (d, $^3J_{HH}$ = 7.8 Hz, 4H, C*H*), 7.38–7.30 (m, 4H, C*H*), 7.26 (s, 4H, C*H*), 7.07 (d, $^3J_{HH}$ = 7.9 Hz, 4H, C*H*), 6.82 (s, 4H, C*H*), 3.94 (d, $^3J_{HH}$ = 5.3 Hz, 8H, OCH_2), 1.85–0.90 (m, 60H, $OCH_2C_7H_{15}$) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 160.9, 160.5, 149.7, 135.7, 135.0, 131.9, 131.4, 128.5, 127.2, 123.4, 122.1, 120.7, 119.5, 104.2, 90.7, 89.9, 72.0, 39.6, 30.6, 29.1, 23.9, 23.1, 14.1, 11.2 ppm. MALDI-TOF-MS: *m*/*z* = 1390 ([M + H]$^+$, 100%), 1445 ([M + K + H_2O]$^+$, 10%). Anal. calcd. for $C_{92}H_{100}N_4O_8 \cdot 0.5H_2O$: C, 78.99; H, 7.28; N, 4.01. Found: C, 78.95; H, 7.22; N, 4.09.

Synthesis of macrocycle 36

Macrocycle **36** was prepared using the same procedure as for **35**, starting from compound **27**. Red solid; yield: 1.11 g (0.80 mmol, 80%).

Data for 36

Mp > 300 °C. UV–vis (THF): λ_{max} = 352 nm. Fluorescence (THF): λ_{ex} = 370 nm, Φ = 4.9%. IR (KBr): ν = 3430, 2926, 2855, 2130, 1609, 1506, 1446, 1260, 1180, 799, 752, 704 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.31 (s, 4H, O*H*), 8.62 (s, 4H, C*H*=N), 7.65 (t, $^3J_{HH}$ = 8.3 Hz, 2H, C*H*), 7.47 (d, $^3J_{HH}$ = 7.83 Hz, 4H, C*H*), 7.0 – 7.4 (m, 12H, C*H*), 6.81 (s, 4H, C*H*), 3.93 (d, $^3J_{HH}$ = 5.0 Hz, 8H, OCH_2), 1.98–0.90 (m, 60H, $OCH_2C_7H_{15}$) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 160.9, 160.7, 149.7, 143.7, 136.4, 135.0, 131.8, 126.3, 123.0, 122.5, 121.3, 120.0, 104.5, 90.1, 89.3, 72.0, 39.6, 30.6, 29.2, 23.9, 23.1, 14.1, 11.2 ppm. MALDI-TOF-MS: *m*/*z* = 1392 ([M + H]$^+$, 100%), 1453 (35%), 1495 (15%). Anal. calcd. for $C_{90}H_{98}N_6O_8 \cdot 5H_2O$: C, 72.95; H, 7.35; N, 5.67. Found: C, 72.22; H, 7.32; N, 6.00.

X-ray crystallography[2]

A crystal of **14**·2DMSO was mounted on a glass fiber, and data were collected on a Bruker X8 APEX II diffractometer with graphite monochromated Mo Kα radiation. The data were collected to a maximum 2θ value of 55° in a series of ϕ and ω scans in 0.5° oscillations with 20 s exposures. The crystal-to-detector distance was 36 mm. Compound **14** crystallizes as a two-component twin with the two components related by a 180° rotation about the (010) reciprocal axis. Data were integrated for both twin components, including both overlapped and non-overlapped reflections. In total, 25882 reflections were integrated (10175 from component one only, 9903 from component two only, 5804 overlapped). Data were collected and integrated using the Bruker SAINT software packages (53). Data were corrected for absorption effects using the multi-scan technique (54), and were corrected for Lorentz and polarization effects.

The structure was solved by direct methods using non-overlapped data from the major twin component (55). Subsequent refinements were carried out using an HKLF 5 format data set containing complete data from both twin components. The material crystallizes with two molecules of DMSO in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in calculated positions but were not refined. The batch scale refinement showed a roughly 3:1 ratio between the major and minor twin components. The final cycle of full-matrix least-squares refinement (56) on F^2 was based on 5845 reflections from component one (including overlaps with component two) and 278 variable parameters. The data converged (largest parameter shift was 0.0 times its esd) with unweighted and weighted agreement factors of R_1 = 0.111 and wR_2 = 0.191. The standard deviation of an observation of unit weight (57) was 0.96. The weighting scheme was based on counting statistics. Neutral atom scattering factors were taken from Cromer and Waber (58). Anomalous dispersion effects were included in F_{calcd} (59); the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley (60). The values for the mass attenuation coefficients are those of Creagh and Hubbell (61). All refinements were performed

[2] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5249. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 639250 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Data for **14**·2DMSO.

Crystal	**14**·2DMSO
Empirical formula	$C_{20}H_{20}O_8S_2$
Formula Mass	452.48
Color, habit	Yellow, tablet
Crystal dimensions (mm)	0.05 × 0.12 × 0.35
Crystal system	Triclinic
Space group	*P-1* (no. 2)
Z	2
a (Å)	6.5283(14)
b (Å)	12.203(3)
c (Å)	13.460(3)
α (°)	106.691(12)
β (°)	99.401(12)
γ (°)	95.689(12)
Collection ranges	$-8 \le h \le 8$; $-15 \le k \le 15$; $0 \le l \le 17$
Temperature	173(2)
Volume (Å^3)	1001.1(4)
D_{calcd} (Mg m^{-3})	1.501
Radiation	Mo Kα (λ = 0.71073 Å)
Absorption coeff. (μ) (mm^{-1})	0.313
Absorption correction	Multi-scan
F(000)	472
θ range for data collection (°)	1.6–27.5
Observed reflections	25882
Independent reflections	5845 (R_{int} = 0.060)
Data/restraints/parameters	5845/0/278
Maximum shift/error	0.00
Goodness-of-fit on F^2	0.96
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.069, wR_2 = 0.171
R indices (all data)	R_1 = 0.111, wR_2 = 0.191
Largest diff. peak and hole (e Å^{-3})	0.80 and –0.60

using the SHELXTL crystallographic software package of Bruker-AXS (62). Additional details of the data collection and refinement are in Table 1.

Results and discussion

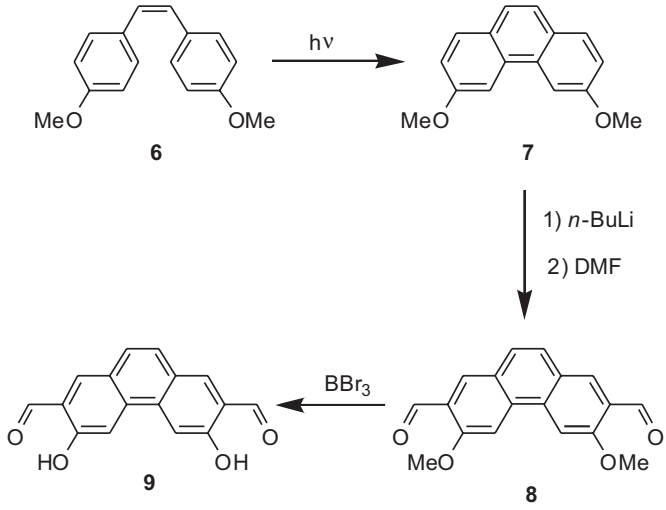
Diformyldihydroxy precursors

Phenanthrene derivatives

Scheme 1 shows the sequence of reactions used to obtain the parent diformyldihydroxyphenanthrene **9**. Photocyclization of 4,4′-dimethoxystilbene **6** gave 3,6-dimethoxyphenanthrene **7**. Dilithiation of **7** followed by quenching with DMF gave (after work-up) compound **8** with formyl groups in the 2,7 positions. Deprotection of the phenol groups with BBr_3 afforded target compound **9** in moderate yield. ^{1}H NMR spectroscopy of **9** confirms the structure of the diol, with a single hydroxyl resonance observed at 10.96 ppm (DMSO-d_6), shifted downfield due to hydrogen-bonding with the formyl groups.

The low solubility of compound **9** is a potential limitation to its further utility. To make soluble diformyldihydroxyphenanthrenes, we attempted to incorporate alkoxy groups

Scheme 1. Synthesis of diformyldihydroxyphenanthrene **9**.



on the ring as shown in Scheme 2. We have previously reported the preparation of 3,6-dimethoxyphenanthrene-9,10-quinone **10** (45). Bromination of this compound gave **11**, along with some other by-products, which can easily be separated by chromatography. Reduction and methylation of the quinone yielded **12**, which was subsequently lithiated and quenched with dimethylformamide to give compound **13**. Reaction of **13** with BBr_3 gave, after work-up, compound **14**. This compound showed the expected ^{1}H NMR resonances, but we undertook a single crystal X-ray diffraction study to verify the correct tautomer was present. The solid-state structure of crystals of **14** grown from DMSO is depicted in Fig. 1, with relevant crystallographic details summarized in Table 1. The compound exhibits a nearly planar structure, with the formyl groups directed slightly out of the plane. In structures of salicylates, the formyl groups are typically hydrogen-bonded to the hydroxyl groups. The structure for **14** shows the oxygen of the aldehydes pointing away from the alcohol and the hydroxyl moieties instead hydrogen-bonding with the oxygen in co-crystallized DMSO. The extended structure shows phenanthrene molecules stacked in a staggered arrangement, with intermolecular separations of 3.1–3.3 Å, characteristic of π–π interactions.

To incorporate alkoxy groups on phenanthrene **14**, it was necessary to protect the hydroxyl groups. Having confirmed that the 3,6-dihydroxy tautomer was in solution, we anticipated that these could be readily protected. Unfortunately, attempts to selectively protect the 3,6-dihydroxy groups of **14** failed. Upon adding base to **14**, the compound undergoes a dramatic color change to purple, and reaction with protecting groups (e.g., Me_2SO_4) gave mixtures of products. It seems that with deprotonation compound **14** tautomerizes changing the reactivity of the hydroxyl groups, though we cannot isolate this intermediate in pure form. This approach was abandoned.

Triphenylene derivatives

We prepared diformyldihydroxytriphenylene **21** with peripheral hexyl groups by the route shown in Scheme 3. The synthesis of triphenylene **18** was based on previous research into unsymmetrically hexasubstituted triphenylenes (63, 64).

Scheme 2. Synthesis of diformyldihydroxyphenanthrenequinone **14**.

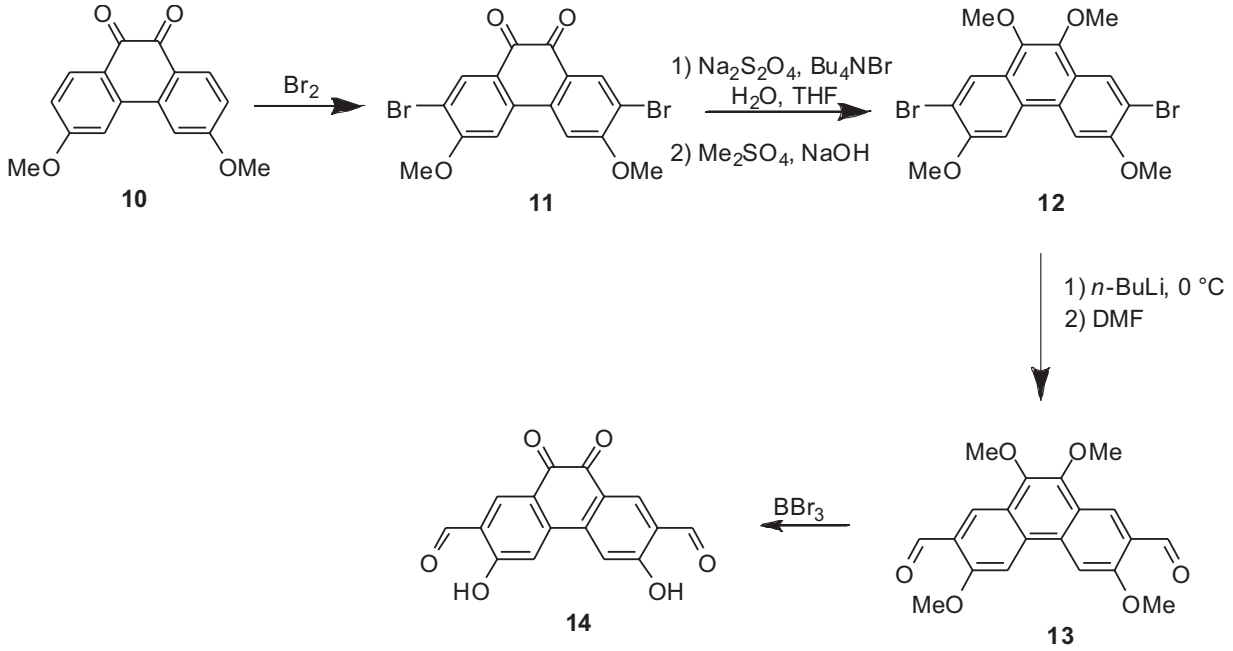
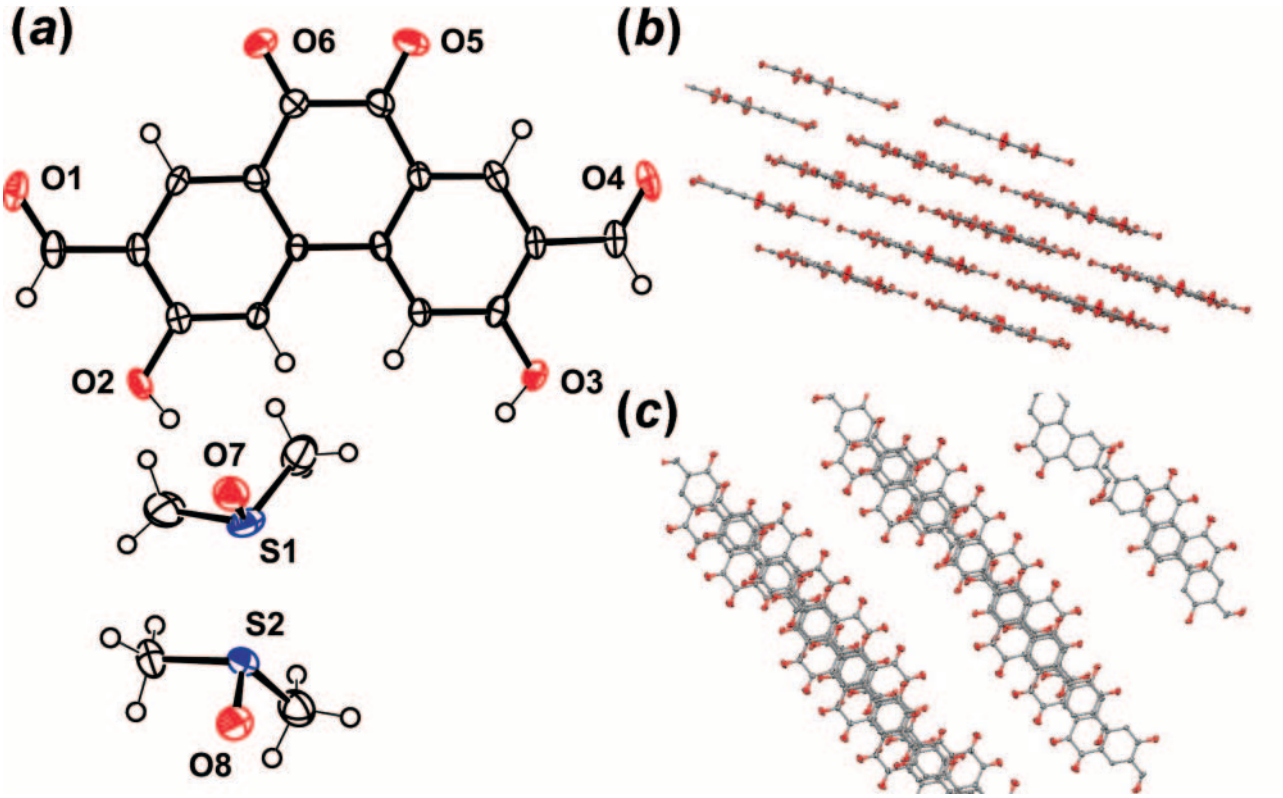
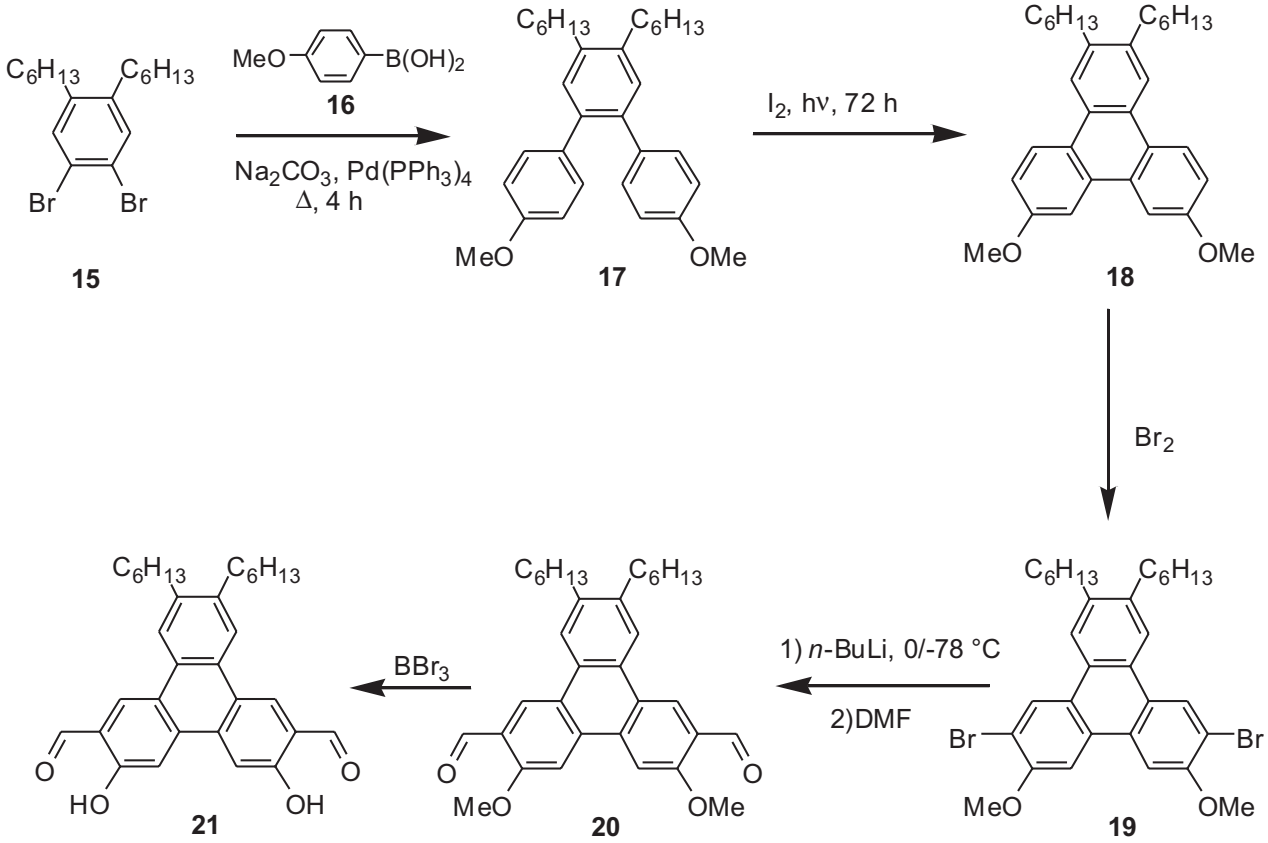


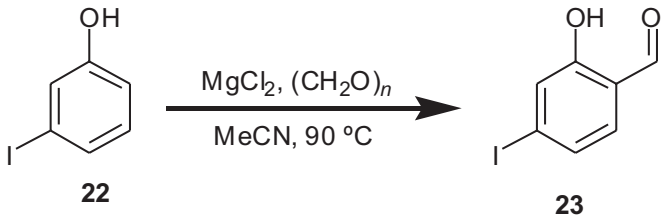
Fig. 1. Solid-state structure of **14**·2DMSO as determined by SCXRD. (*a*) The molecular structure, including two co-crystallized DMSO molecules, shows the planar structure with no intramolecular hydrogen-bonding. (*b*, *c*) The extended structure of **14**·2DMSO in the solid-state reveals strong intermolecular π–π interactions. Hydrogen atoms and DMSO molecules are omitted in the extended structure for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths: Aldehyde C=O: 1.202(4), 1.204(4) Å; hydroxyl C—O: 1.325(3), 1.334(4) Å; ketone C=O: 1.193(4), 1.201(4) Å.



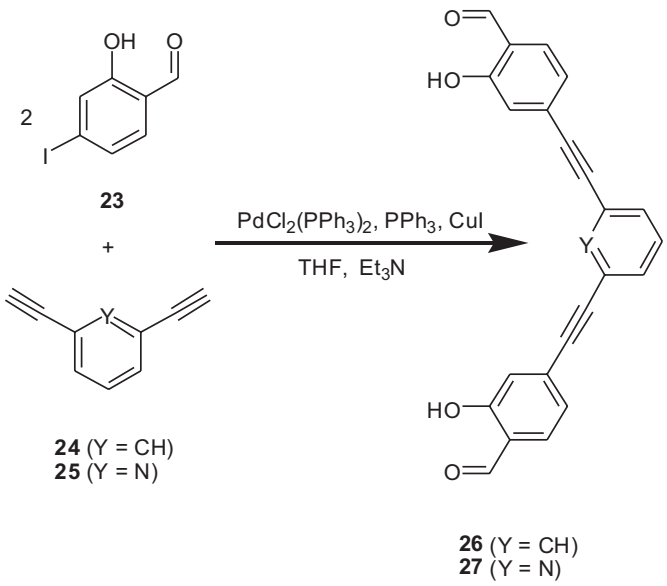
Scheme 3. Synthesis of diformyldihydroxytriphenylene **21**.



Scheme 4. Synthesis of 4-iodophenol **23**.



Scheme 5. Synthesis of bis(salicylaldehyde)s **26** and **27**.

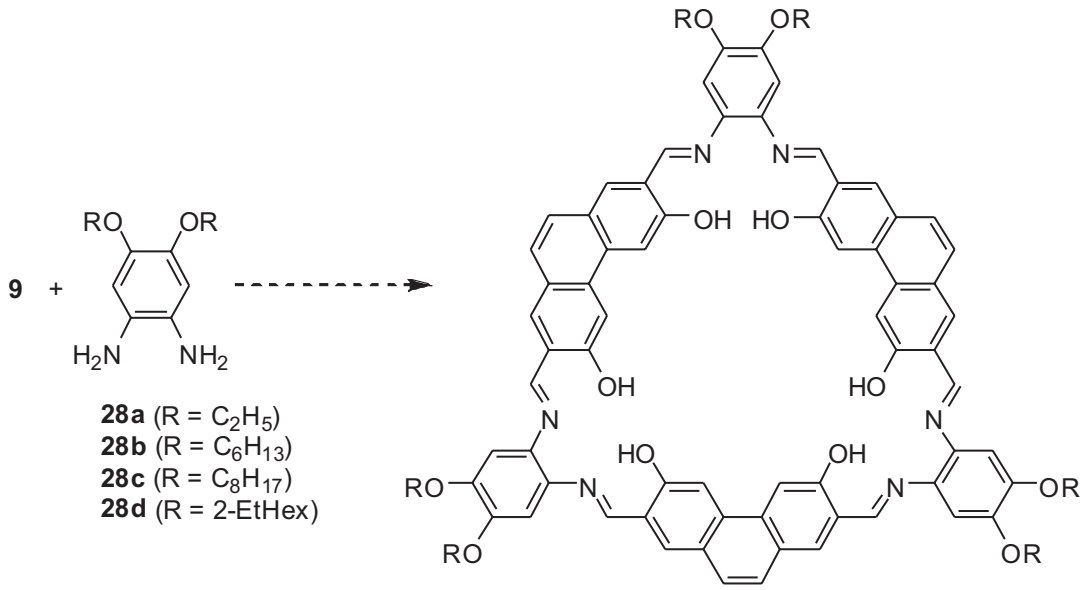


In the first step, terphenyl **17** was formed by Suzuki coupling of 1,2-dibromo-4,5-dihexylbenzene **15** and 4-methoxyphenylboronic acid **16**. Photocyclization in the presence of iodine gave triphenylene **18**. Selective double bromination of triphenylene **18** occurred at the 6,11 positions, yielding compound **19**. Subsequent metal–halogen exchange with ^{n}BuLi, and reaction with DMF gave the diformyldimethoxytriphenylene **20** after work-up. In the last step, the phenol was deprotected with BBr_3 to afford the diformyldihydroxytriphenylene **21** in 20% overall yield. All of the steps, with the exception of the photocyclization, are fast and high-yielding. Compounds **18**–**21** are easily purified through recrystallization, making **21** a convenient precursor for macrocycle studies.

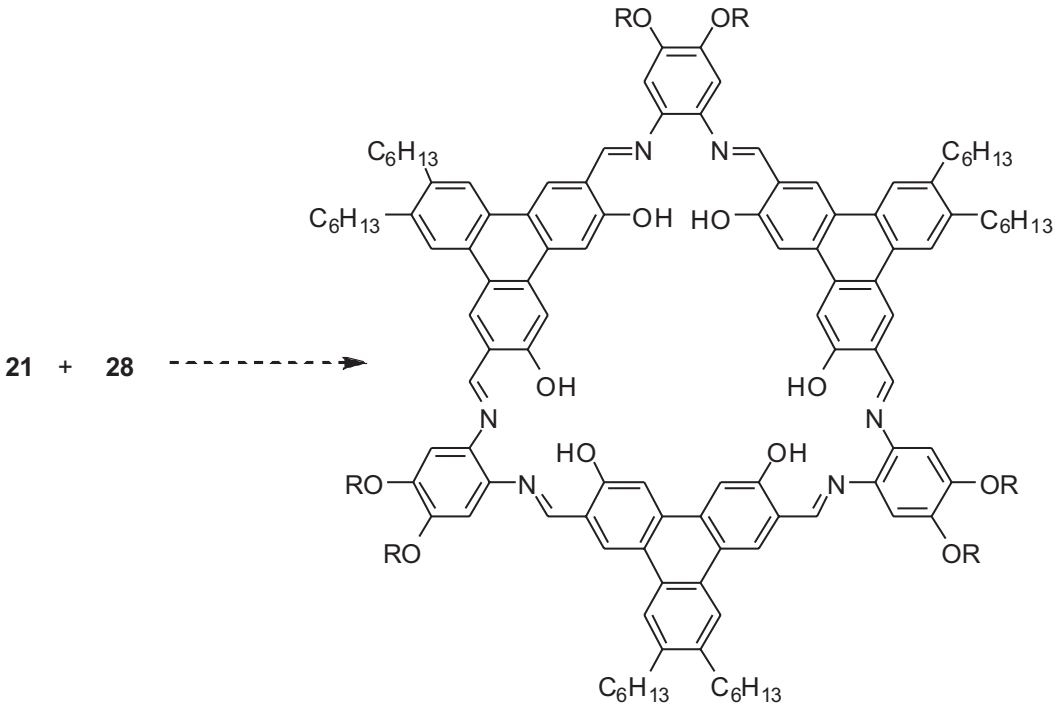
m-*Bis(4-ethynylsalicylaldehyde)benzene and* m-*Bis(4-ethynylsalicylaldehyde)pyridine*

To synthesize conjugated bent bis(4-ethynylsalicylaldehyde) compounds, we required 4-iodosalicylaldehyde **23**. This compound has been made previously by the Reimer–Tiemann reaction starting with 3-iodophenol **22**, but this reaction generally proceeds in low yield and gives a mixture of products; the major products are 3-iodosalicylaldehyde and 2-iodo-4-hydroxybenzaldehyde (65–67). We found that using $MgCl_2$ and paraformaldehyde (68,69) reliably gave compound **23** in better (45%) yield, Scheme 4. This compound will likely prove useful for synthesizing other functionalized precursors to large macrocycles, such as [3+3] macrocycles we have previously studied (37).

Scheme 6. Proposed syntheses of target macrocycles **29** and **30**.



29



30

Pd(0)-catalyzed Sonogashira–Hagihara coupling of **24** with two equiv. of **23** yielded the bis(salicylaldehyde) **26** in 75% yield, Scheme 5. Pyridine analogue **27** was prepared by a similar procedure in 70% yield from **25**. The elbow-shaped bis(ethynylsalicylaldehyde) compounds were characterized by NMR spectroscopy and mass spectrometry.

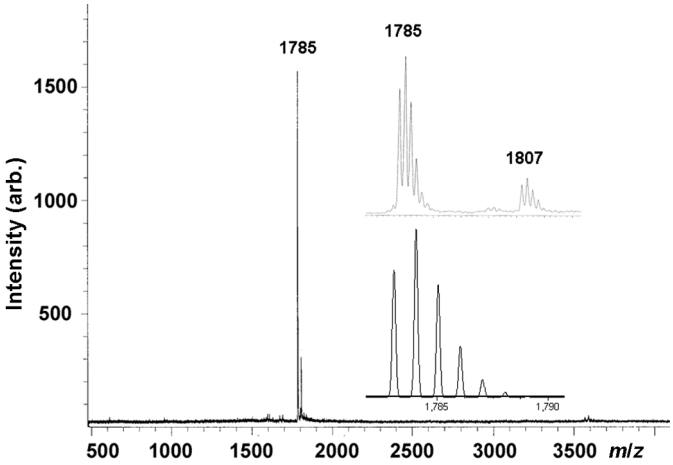
Condensation studies

We investigated the condensation of the new diformyldihydroxy precursors with 4,5-diamino-1,2-dialkoxybenzenes in an effort to obtain conjugated Schiff base macrocycles. Reactions to form macrocycles are typically performed in mixtures of organic solvents selected to precipitate the macrocycle as it forms.

Phenanthrene derivatives

We expected that the reaction of **9** with diaminobenzene derivatives would afford [3+3] Schiff base macrocycle **29**, Scheme 6. Reaction of **9** was undertaken with several different *o*-phenylenediamines to control solubility. With 1,2-

Fig. 2. MALDI-TOF mass spectral evidence for the formation of macrocycle **29** (R = n-C_8H_{17}). The insets show a simulation of the isotope distribution for the [**29** + H]$^+$ ion (bottom) and the expanded experimental data for this peak (top). The peak at m/z = 1807 is the [**29** + Na]$^+$ ion.



dioctyloxy-4,5-diaminobenzene **28c**, a solid was obtained. The ^{1}H NMR spectra of the product showed that multiple species were formed, and it appears that the major product is the 1:1 diol:diamine condensation species. Electrospray ionization mass spectrometry (ESI-MS) showed this fragment as the dominant species and also showed larger fragments of the expected macrocycle. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Fig. 2) of the solid showed the presence of macrocycle **29** as the dominant high molecular mass component, along with traces of a larger [4+4] macrocycle. While there was evidence for the formation of the desired macrocycle in this reaction, we were unable to find conditions where the macrocycle selectively formed in the reaction mixture, an essential feature since the Schiff base macrocycles cannot be separated by column chromatography.

Triphenylene derivatives

Condensation of **21** with *o*-phenylenediamines was anticipated to form macrocycle **30**, Scheme 6. Unfortunately, the reaction of **21** with 4,5-dialkoxy-1,2-phenylenediamines **28** in an appropriate solvent, conditions that have worked well for other [3+3] Schiff base macrocycle reactions, afforded only inseparable mixtures of products. The ^{1}H NMR spectrum of the orange solid collected from the reaction showed several hydroxyl protons between 11.6 and 14.8 ppm. While the largest resonance at 13.2 ppm is characteristic of a hydroxyl group hydrogen-bonded to an imine, as in the intended Schiff base macrocycle, the positions of the other peaks are reminiscent of those observed for partially reduced Schiff base macrocycles, where imines are reduced in situ (this is a common problem in the formation of Schiff base macrocycles) (70–75). MALDI-TOF mass spectrometry of the orange product confirmed that the macrocycle was indeed present in the mixture. In fact, only the ring-closed [3+3] macrocycle **30** is observed in the MALDI-TOF mass spectrum. Further evidence for the formation of the [3+3] Schiff base macrocycle came from a metallation experiment, wherein the product was heated in THF in the presence of a metal salt. A color change indicated that reaction occurred, and, with vanadyl acetylacetonate, the MALDI-TOF mass spectrum clearly shows the incorporation of three metal centers into the macrocycle. The incorporation of three metals into the macrocycle supports the formation of macrocycle **30** in the reaction mixture.

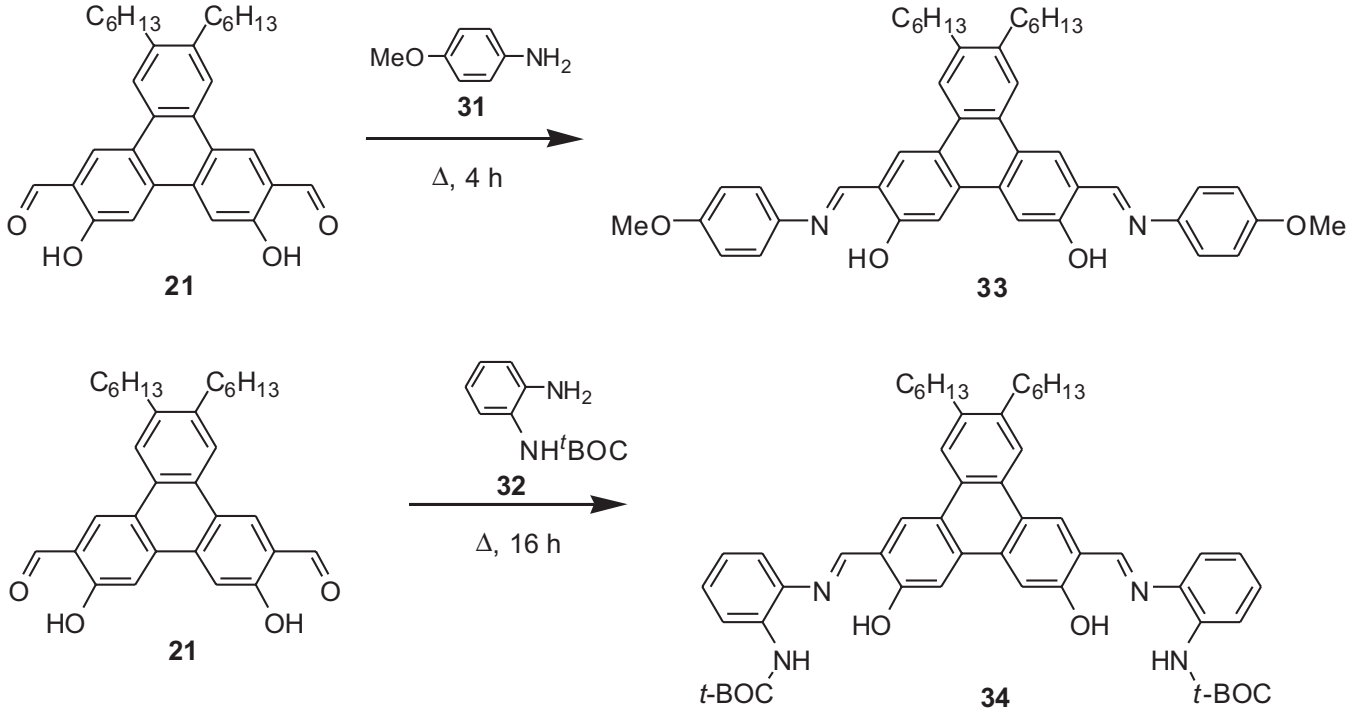
Table 2. Conditions attempted for macrocycle **30** synthesis.

Solvent	R	Metal
$CHCl_3$/MeCN	C_6H_{13}	N/A
CH_2Cl_2/MeCN	C_2H_5	N/A
THF	C_2H_5	N/A
Toluene	C_2H_5	N/A
EtOH	C_2H_5	$Ni(OAc)_2$
EtOH	C_2H_5	$Zn(OAc)_2$

In an effort to selectively form macrocycle **30**, and to prevent possible side reactions (e.g., partial reduction of the macrocycle), a variety of conditions was used (Table 2). In all cases, the exact same series of resonances was reproduced in the ^{1}H NMR spectrum of the isolated solid, sometimes combined with fragments of the macrocycle. ESI-MS confirmed that fragments of the macrocycle were also present. Metal templation, which has proved to be critical in the synthesis of many Schiff base macrocycles, was also unsuccessful to obtain the fully conjugated macrocycle. Reaction of the diol and diamine in the presence of Ni^{2+} gave a black solid, which was revealed to be a 2:1 diol to diamine fragment coordinated to the metal through MALDI-TOF mass spectrometry. The same reaction in the presence of Zn^{2+} gave a mixture that included the starting material.

We were frustrated and surprised that compounds **9** and **21**, which appear ideal for forming [3+3] Schiff base macrocycles, were only yielding inseparable mixtures. In our experience, most diformyldihydroxyaromatics, such as **3**, yield the macrocycle in high yield. To understand whether or not the reactivity of the aldehydes on **9** and **21** were unusual, we made two model compounds by reaction of **21** with aniline derivatives **31** and **32**, Scheme 7. Compounds **33** and **34** were obtained as microcrystalline solids in high yield. The ^{1}H NMR spectra of these compounds show imine resonances

Scheme 7. Synthesis of model compounds **33** and **34**.



at 8.86 and 8.90 ppm, respectively. There is no indication of either reduction of the imine bond or isomerization to the keto–enamine tautomer, which was observed previously in a macrocycle prepared with a naphthalene diol (40). Isolation of these model compounds supports the use of **9** and **21** to build new multidentate Schiff base ligands.

m-*Bis(4-ethynylsalicylaldehyde)benzene and* m-*Bis(4-ethynylsalicylaldehyde)pyridine*

The geometry of compounds **26** and **27** are likely to favor [2+2] Schiff base macrocycles. Condensation of precursor **26** with 4,5-bis(2-ethylhexyloxy)-1,2-phenylenediamine **28d** gave the diamond-shaped macrocycle **35** in 88% yield, Scheme 8. Ethylhexyloxy substituents were required to render the macrocyclic product soluble. In this case, the branched substituents and the presence of a chiral center impart disorder to the macrocycles and ensure solubility. Macrocycles were initially prepared using phenylenediamines substituted with *n*-alkoxy chains (**28a**, **28b**), but these macrocycles were found to be insufficiently soluble in organic solvents to easily characterize or purify, though MALDI-TOF mass spectra indicated that the [2+2] macrocycles were the major, if not exclusive, products in each case.

The structure of red macrocycle **35** was verified by ^{1}H and ^{13}C NMR spectroscopies. Notably, the OH and imine groups are evident as singlets at 13.34 and 8.61 ppm, respectively, in $CDCl_3$, consistent with average D_{2h} symmetry for the macrocycle. The large downfield shift of the phenol resonance is characteristic of strong hydrogen-bonding to the imine group in the macrocycle. MALDI-TOF MS of **35** (Fig. 3) showed the molecular ion expected for the macrocycle ([**35** + H]$^+$) at m/z = 1390. The aldehyde C=O stretch observed at 1664 cm^{-1} in the IR spectrum of **26** was replaced by an intense C=N stretching mode at 1609 cm^{-1}.

With the goal of incorporating coordinating pyridine moieties into the macrocycles, we reacted **27** with diamine **28d** to yield macrocycle **36** in 80% yield, Scheme 8. The ^{1}H and ^{13}C NMR data were consistent with the proposed ring structure. MALDI-TOF MS showed the expected protonated molecular ion as the major peak for macrocycle **36**.

During the synthesis of macrocycles **35** and **36**, we found no evidence for formation of polymeric by-products. ^{1}H NMR analysis of the supernatant solution from the reaction showed mostly more macrocycle as well as putative oligomers that could not be separated. As with [3+3] Schiff base macrocycles we have previously investigated, these conjugated [2+2] macrocycles can be cleanly prepared in high yield. It was not necessary to use high dilution methods to favor macrocycle formation, or to remove water during the reaction to promote the condensation reaction. The macrocycles are stabilized from hydrolysis by the formation of strong hydrogen bonds between the imine and the phenol.

Optical properties

Our stated goal in expanding the conjugation of the dialdehyde precursors was to develop luminescent Schiff base macrocycles. These may be useful for chemical sensing applications or electronic devices. Figure 4 illustrates the absorption and emission spectra of macrocycle **35** in solution, which are similar to those of macrocycle **36**. An intense π–π* transition at 345 nm is accompanied by weaker transitions that extend the absorption edge to ~500 nm. Both macrocycles are weakly luminescent in solution, with maxima observed at 564 nm for both compounds, and quantum yields of 3%–5% in THF. This is almost identical to the fluorescence spectrum for **37**, a previously reported macrocycle (37) (Fig. 5), indicating that conjugation is essentially localized to the *N*,*N*′-bis(salicylidene)-1,2-phenylenediimine moi-

Scheme 8. Synthesis of conjugated diamond-shaped Schiff base macrocycles **35** and **36**.

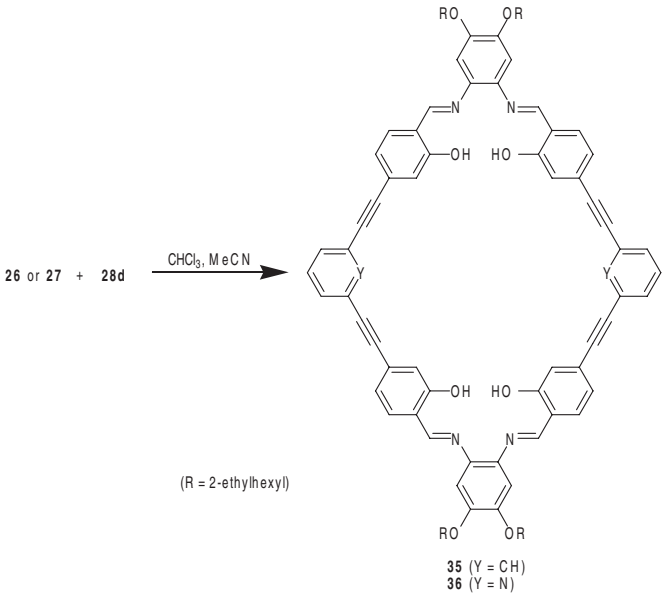
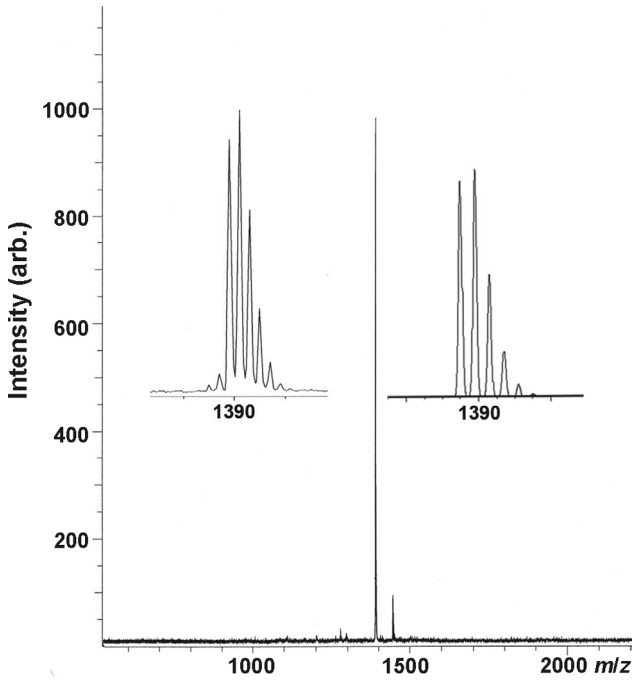


Fig. 3. MALDI-TOF MS of macrocycle **35**. Inset: Experimental (left) and simulated (right) isotope distribution patterns for the molecular ion.



ety and is unaffected by the spacer. The meta linkage of the phenyl and pyridyl groups in **35** and **36**, respectively, should limit conjugation between the salicylaldehyde groups, and this is observed.

Conclusions

We have developed convenient routes to the first examples of diformyldihydroxy-functionalized phenanthrene (**9**, **14**) and triphenylene (**21**), as well as two new *m*-bis(4-ethynylsalicylaldehyde)aromatic compounds (**26**, **27**). Studies showed that **9** and **21** do not undergo clean cyclization reactions with *o*-phenylendiamines to selectively afford [3+3] Schiff base macrocycles, but these compounds are useful precursors for other Schiff base ligands, and perhaps even macrocycles with the appropriate choice of diamine. On the other hand, **26** and **27** underwent selective condensation to form fully conjugated [2+2] Schiff base macrocycles **35** and **36**. These luminescent macrocycles with two N_2O_2 binding pockets are anticipated to have interesting coordination chemistry and aggregation behavior, which we are studying.

Fig. 4. UV–vis (—) and fluorescence (---) spectra of macrocycle **35** (THF). Both spectra are normalized to unity intensity.

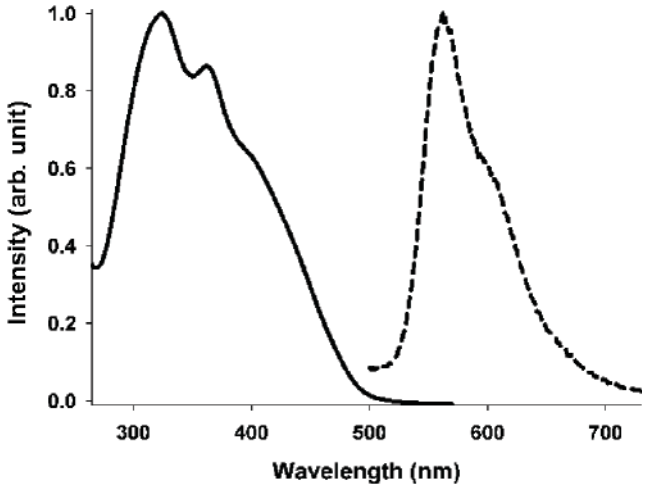
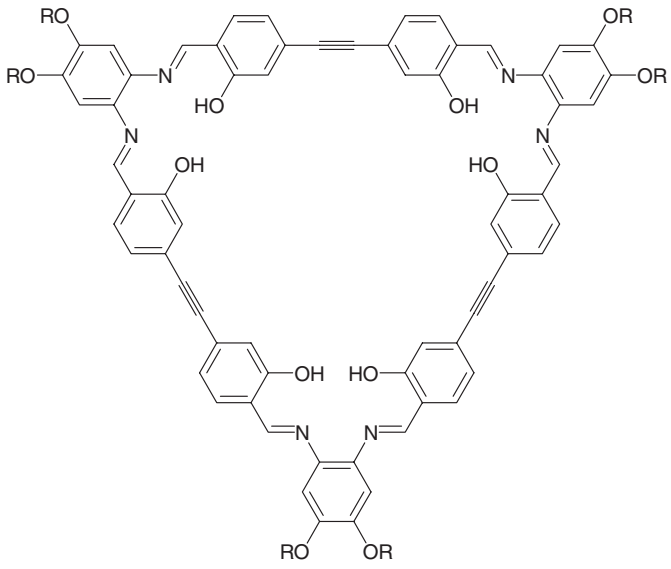


Fig. 5. Structure of macrocycle **37**.



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57. Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2 - F_c^2)/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables.
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