

Self-assembly of rectangles via building units bearing salen and oxazoline ligands

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Abstract

Rigid spacer-chelator with the framework of **3** has been prepared. Building units with two parallel coordination sites such as salen and oxazoline units have also been synthesized. The spacer-chelators, **11** and **15**, readily self-assembled with metal complexes such as Zn^{++} and Co^{++} to form molecular rectangles. The overall dimensions of the rectangles, **13** and **17**, are $6.2 \text{ \AA} \times 23.5 \text{ \AA}$. The characterization of the supramolecules by NMR, mass spectroscopy, and X-ray crystal structures is also reported.

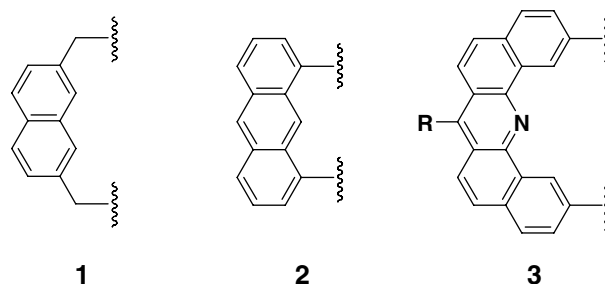
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Keywords: Self-assembly; Rectangle; Salen; Oxazoline; Molecular clip; Rigid spacer-chelator

1. Introduction

The metal-directed self-assembly of supramolecular entities from discrete molecular ensembles has received considerable attention [1]. The interest in these macrocycles arises from their size- and shape-selective properties with potential applications in catalysis and sensing devices [2]. The directed assembly of supramolecules has proven to be very effective for construction of well-defined supramolecular entities such as squares [1,3], triangles [4], hexagons [5], and cubes [6]. As lower symmetry hosts can be expected to show enhanced guest selectivity [7], rectangles represent a crucial geometrical model in the development of this area. Despite their relative simplicity, molecular rectangles are much less common [8]. The difficulty in the construction of rectangles lies in the necessity of designing a building unit with two parallel coordination sites facing in the same direction [9]. Although the molecular rectangles were formed

by several flexible binucleating ligands [10], the rigid building units such as **1**, **2**, and **3** provides a cavity of well-defined size and shape.

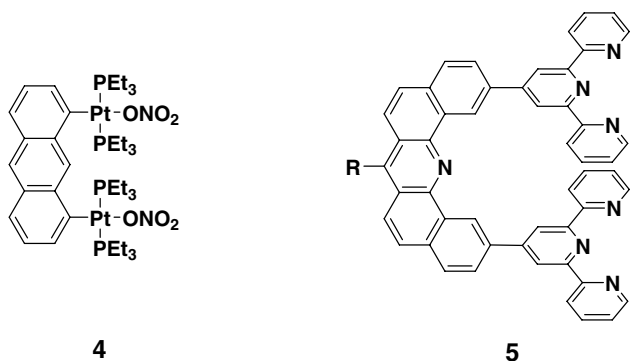


The spacer, **1**, incorporating two acetylacetonate or dithiocarbamate chelators was found by Maverick [11] and Beer [12] groups to give the Cu^{++} cofacial complexes. Stang and co-workers [13] have described the self-assembly reactions of a molecular 'clip', **4**, as an efficient entry into the rectangular shape with the anthracene framework (**2**). Bosnich and co-workers [14] have reported the molecular recognition and self-assembly using rigid spacer-che-

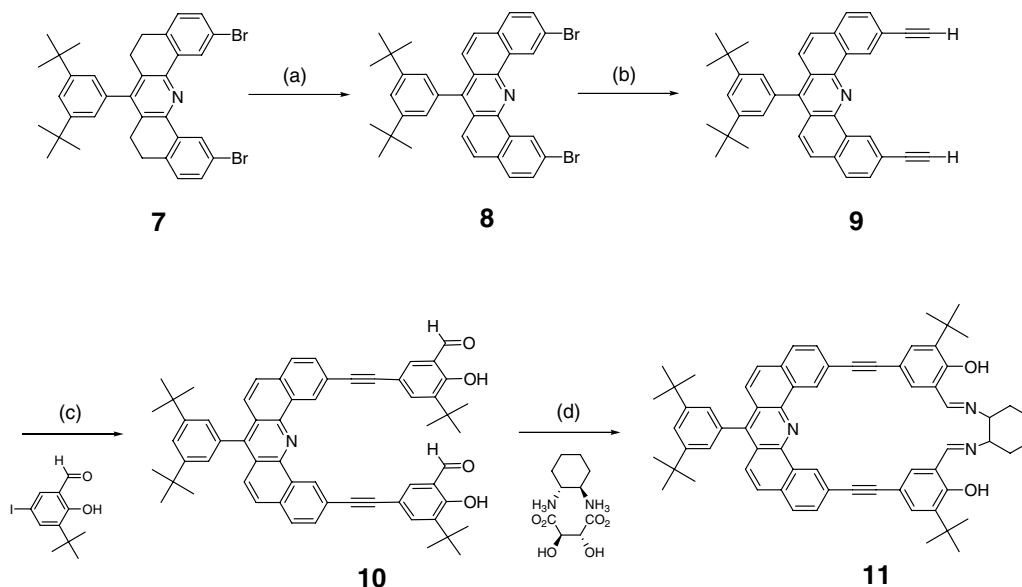
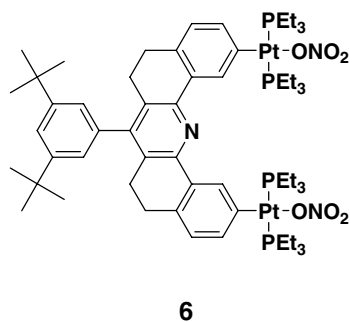
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lator, **5**, bearing cofacial terpyridyl palladium(II) complexes.



Recently, we [15] have reported the self-assembly of rectangles via a molecular “clip”, **6**, as shown. Accordingly, we envisioned that if we could incorporate coordinating groups such as salen and oxazoline units into the rigid framework, **3**, such a subunit would offer another entry into new rectangles for catalysis and guest substrate.



Scheme 1. ^aKey: (a) DDQ, 1,4-dioxane; (b) (i) trimethylsilylacetylene, Pd(PPh₃)₄, CuI, NEt₃, (ii) MeOH, NaOH, THF; (c) Pd(PPh₃)₄, CuI, NEt₃; (d) K₂CO₃, H₂O, THF.

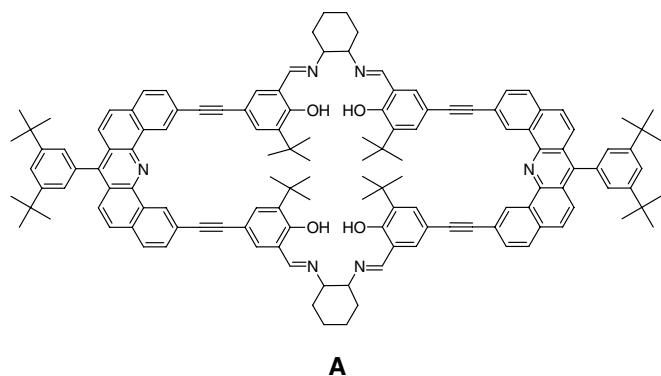
Herein, we describe the metal-directed self-assembly reactions and characterization of the members of a family of molecular rectangles via a new type of subunit.

2. Results and discussion

2.1. Synthesis of spacer-chelator (**11**)

Our strategy for the synthesis of self-assembled supramolecules of molecular rectangles utilizes the building unit with two parallel coordination sites facing in the same direction. The synthesis of spacer-chelator, **11**, followed many of the procedures described previously for analogous compounds [15,16]. The synthetic steps are outlined in Scheme 1.

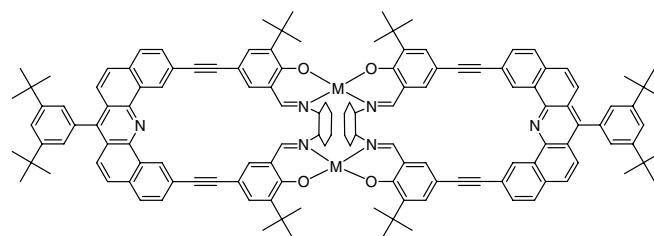
The synthesis of **11** is conveniently prepared in four steps from the 2,12-dibromo-[7-(3,5-di-*tert*-butylphenyl)-5,6,8,9-tetrahydrodibenzo[*c, h*]acridine] (**7**). The spacer, **7**, is efficiently oxidized to the all-aromatic compound, **8**, with DDQ in dioxane in 67% yield. The Sonogashira coupling of **8** with 3 equiv. of trimethylsilylacetylene followed by basic hydrolysis yielded **9** in 84% yield. The palladium catalyzed cross-coupling of 3 equiv. of 3-*tert*-butyl-2-hydroxy-5-iodobenzaldehyde [17] with **9** afforded **10** in 87% yield. The mass spectrum of **10** showed a molecular ion at *m/z* 868. A low-field resonance due to the aldehyde proton and alcohol were detected at 9.61 and 11.88 ppm in the ¹H NMR spectrum, respectively. The spacer-chelator, **11**, was readily synthesized by the reaction of **10** with (R,R)-diaminocyclohexane tartrate salt and potassium carbonate.



Initially we expected the bis(salen) ligand, **A**, as a product with two parallel sites facing in the same direction through the reaction of **11** and (*R,R*)-aminocyclohexane. The initial indication of an unexpected formulation for **11** stemmed from the observation of a parent ion in the mass spectrum at m/z 946. ^1H NMR signals ascribable to the alcohol and imine protons were observed at 14.17 and 8.41 ppm, respectively. The alcohol signal in **11** had clearly shifted from 11.88 ppm in **10** to 14.17 ppm due to the hydrogen bonding between the imine and alcohol. The value is comparable to that observed for the salen chelator ligand [18]. Judged from above spectroscopic data and elemental analysis, the structure of **11** can be reasonably assigned.

2.2. Synthesis of complexes (**12** and **13**)

The synthetic methodology using the metal directional approach for molecular self-assembly has been well documented [19]. We had already demonstrated the formation of molecular rectangles using a molecular clip in combination with 4,4'-bipyridyl and isocyanide donor ligands [15]. To diversify the synthetic approach to the previous strategy, we have selected the ligand (**11**) as a rigid organic clip in combination with the 3d-metal acetate as linear linker. Recently, many research groups [20] have reported a family of metal complexes having two phenoxy-imine chelate ligands for olefin polymerization. However, coordination-driven self-assembly of discrete molecular entities using phenoxy-imine chelate ligand has never been explored. Zn(II) and Co(II) acetates were successfully reacted with ligand **11** in an 1:1 ratio, resulting in the formation of dimetallic rectangular products as shown.



M = Co (**12**), Zn (**13**)

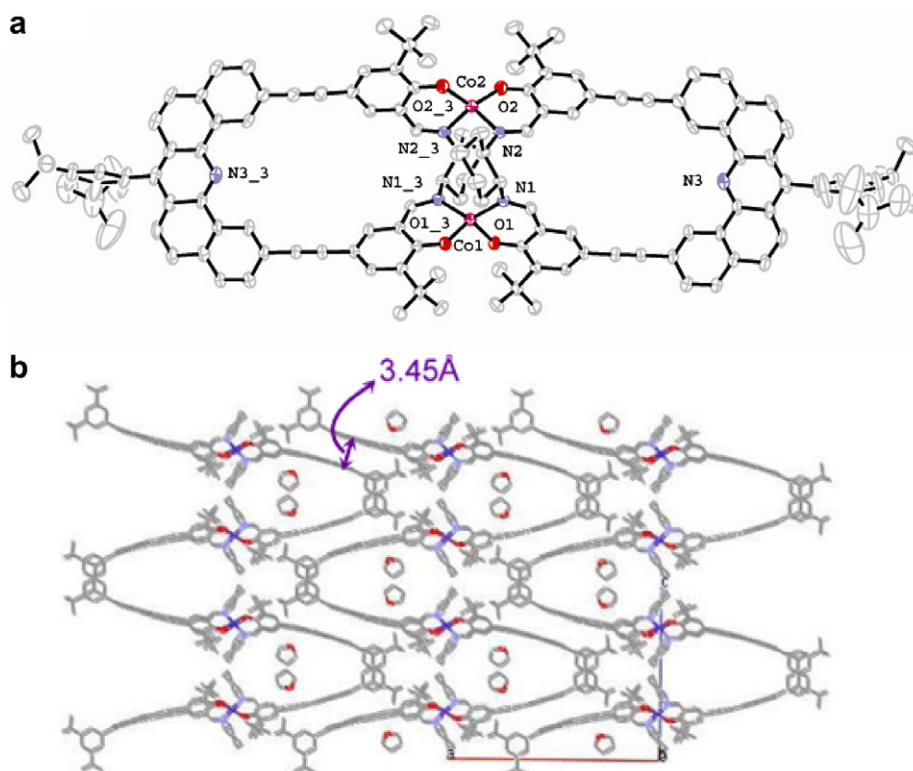


Fig. 1. (a) ORTEP drawing [28] of rectangle **12** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Packing diagram of **12** in the molecular layer.

To provide structural information for one of the new compounds prepared, a single-crystal X-ray diffraction study of the cobalt product **12** was undertaken. The molecular structure and packing diagram of **12** are shown in Fig. 1. A summary of cell constants and data collection parameters is appeared in the reference [21].

The X-ray crystal structure of **12** confirmed the presence of a discrete neutral rectangular molecule. The structure consists of a dicobalt motif and two organic connectors per formula unit. Two cobalt atoms, Co(1) and Co(2), have the usual four-coordinate tetrahedral cobalt coordination. The Co(1) atom is coordinated by two phenoxy-imine chelated atoms. The dinuclear cobalt compound in **12** may be attributed to the strong tendency to form a stable four-coordinate configuration. The environment of two cobalts, Co(1) and Co(2), is slightly different due to the presence of diaminocyclohexyl group exhibiting the chiral characteristics. Therefore, the bond distances of O1–O1_3 (3.111 Å), N1–N1_3 (3.581 Å) in Co(1) and O2–O2_3 (3.349 Å), N2–N2_3 (3.149 Å) in Co(2) are different. The packing diagram of **12** exhibits a characteristic π – π stacking between two dibenzoacridine units of different molecules. The intermolecular distance is 3.45 Å. The rectangular molecule is found to be bented upward about 7° due to the face–face intermolecular interaction. Spectroscopic data for **13** are consistent with its proposed structure. The MALDI-mass spectrum of **13** showed a molecular ion at m/z 2018 [MH]⁺ (see Fig. 2). The ¹H NMR spectrum of **13** exhibits two singlets at 8.46 and 8.44 ppm assigned to the imine

proton. The two resonances can be attributed to the environmental difference of two imines.

2.3. Synthesis of spacer-chelator (**15**)

The synthesis of **15** is given in Scheme 2. The 2-(4,4-dimethyloxazolin-2-yl)-4-iodophenol (**14**) was obtained by the condensation reaction of 5-iodosalicylic acid with 2-amino-2-methyl-1-propanol in 90% yield. 2,12-Bis[3-(4,4-dimethyloxazolin-2-yl)-4-hydroxyphenylethynyl]-[7-(3,5-di-*tert*-butyl)phenyl]dibenzo[*c,h*]acridine (**15**) was synthesized by the cross-coupling of **14** and **9**. All of the new compounds were fully characterized with spectroscopic techniques, including ¹H and ¹³C NMR spectroscopy and high-resolution mass spectroscopy. The ¹³C NMR spectrum of **15** reveals the expected 21 lines in the aromatic region. ¹H NMR signal assigned as the alcohol was observed at 12.53 ppm. The mass spectrum of **15** showed a molecular ion at m/z 894.

2.4. Synthesis of complexes (**16** and **17**)

As a variety of metal complexes containing oxazoline ligand have been well-established [22], we attempted the self-assembly of rectangles using a molecular clip **15**. The molecular rectangles of **16** and **17** were obtained by the reaction of metal acetates with ligand **15** in a mixture of ethanol and toluene as shown below.

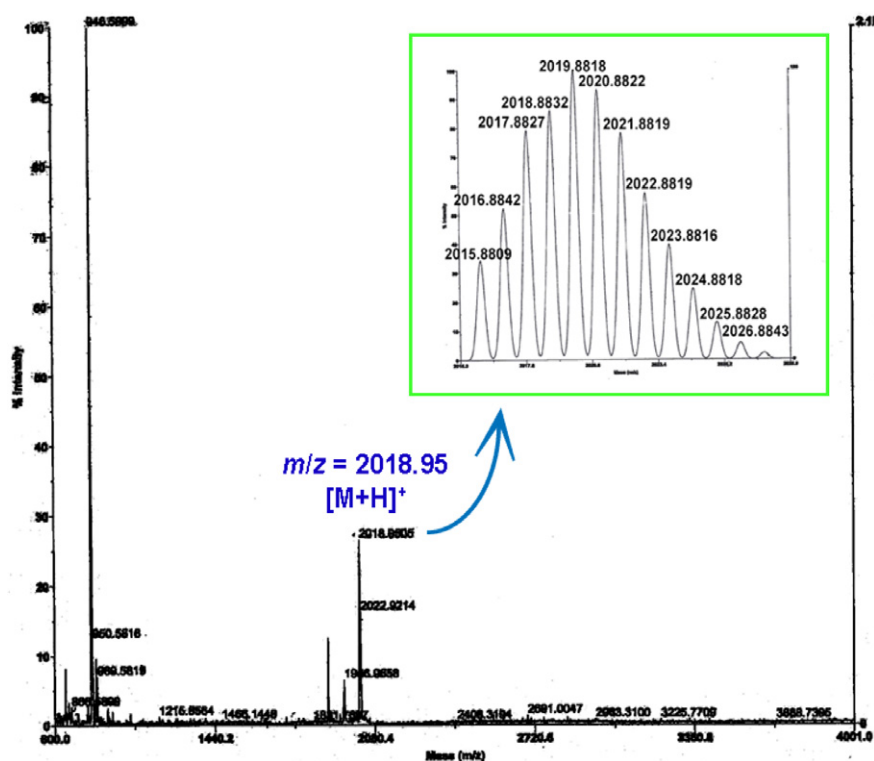
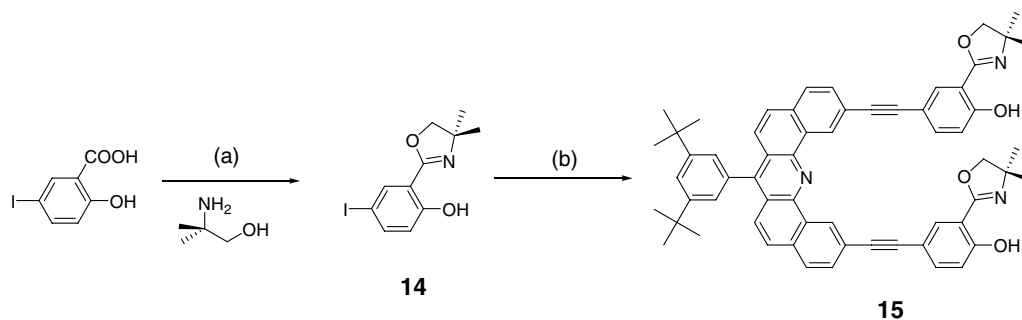
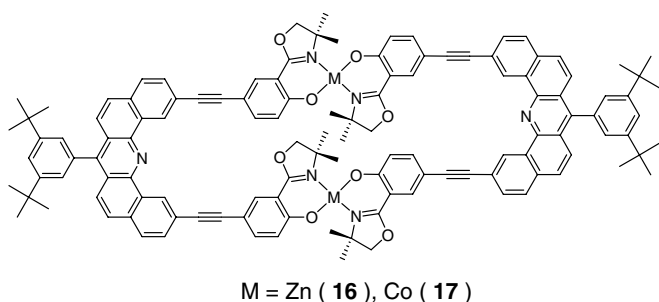


Fig. 2. MALDI-mass spectrum of compound **13**.



Scheme 2. ^aKey: (a) PPh₃, NEt₃, CH₂Cl₂, CHCl₃; (b) **9**, Pd(PPh₃)₄, CuI, NEt₃.



The complexes of **16** and **17** are highly soluble in common organic solvents such as dichloromethane and chloroform. Both complexes are stable enough to handle in air and can be stored for a long time. Complexes **16** was structurally characterized by ¹H and ¹³C NMR spectroscopy and mass spectroscopy. ¹H NMR of complex **16** showed the disappearance of the phenoxo-OH proton. However, other protons exhibited only slight changes in the chemical shifts compared with those of the corresponding unbound

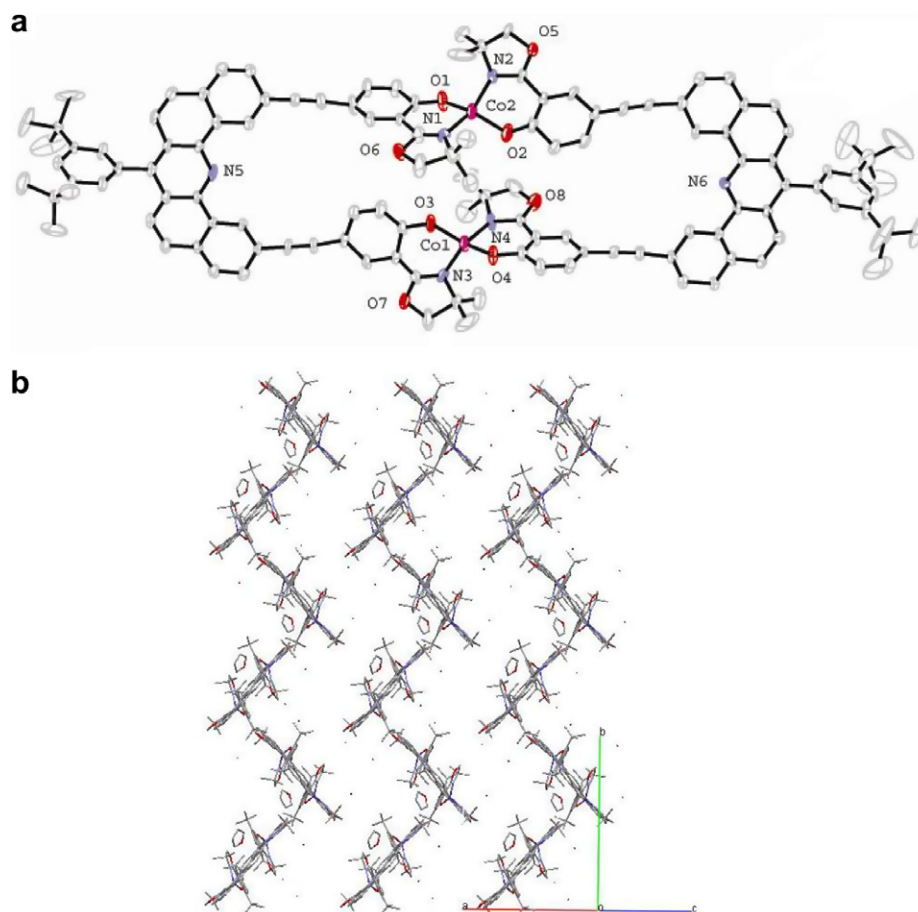


Fig. 3. (a) ORTEP drawing of rectangle **17** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Packing diagram of **17** in the molecular layer.

ligand **15**. The ^{13}C NMR of **16** reveals the expected 21 lines in the aromatic region. The $\nu\text{C}=\text{N}$ vibration for **16** is found at 1602 cm^{-1} , and is shifted by $20\text{--}25\text{ cm}^{-1}$ to a lower frequency compared to the free ligand **15**, indicating that the imine nitrogen of the oxazoline ring is strongly coordinated to the metal center. The mass spectrum of **16** showed a molecular ion at m/z 1916.

The structure of **17** was established by single-crystal X-ray analysis and is shown in Fig. 3. The crystallographic data and processing parameters are given in the reference [23]. The geometry around the cobalt center is common tetrahedral configuration with two units of bidentate (N, O) oxazoline ligands. The bond lengths and angles of primary coordination sphere are comparable to the other reported cobalt complexes [24]. The average Co(1)–O bond length 1.873 \AA and Co(2)–O bond length 1.925 \AA are significantly shorter than those reported for Co(OAc)2(imid)2 [$1.984(1)\text{ \AA}$] [24] and Co(OAc)2(2-Me-imid)2 [$2.098(1)\text{ \AA}$] [24] and are comparable to those of [Co{O(Ox)}₂] (1.9052 \AA). The average Co(1)–N bond length 1.919 \AA and Co(2)–N bond length 1.998 \AA are also shorter than those observed for Co(OAc)2(imid)2 [$2.0135(1)\text{ \AA}$] and Co(OAc)2(2-Me-imid)2 [$2.062(3)\text{ \AA}$]. The overall dimension of the rectangle, as defined by the front dibenzoacridine corners, is $23.5 \times 6.2\text{ \AA}$. No solvent molecules were not located in the cavity. Cobalt oxazoline complex **17** shows a molecular order dominated by edge-to-face interactions, leading to a heringbone arrangement with no π -stacking (Fig. 3b).

3. Conclusion

Two rigid spacer-chelators bearing salen and oxazoline unit were prepared. The molecular clips were found to be effective ones to assemble metal acetates such as cobalt and zinc. Supramolecular rectangles (**12–13** and **16–17**) were readily prepared via self-assembly. X-ray crystallography, NMR, and mass spectral data unambiguously established the proposed structure. Work will involve the binding of guest molecules and the study of catalysis with use of the cofacial binuclear Zn and Co complexes.

4. Experimental section

4.1. General procedures

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. 1,4-Dioxane, THF, toluene, ether, and hexane were distilled from sodium and benzophenone. Dichloromethane, MeOH, and EtOH were distilled under nitrogen from P₂O₅. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00 and 75.44 MHz, respectively. IR spectra were recorded on a Biorad FTS-165 spectrometer. MALDI-MS spectra were recorded on a Voyager-DE STR MALDI TOF mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108

analyzer. 5-Iodosalicylic acid, 2-amino-2-methyl-1-propanol were purchased from Aldrich Chemical Co. 2,12-Dibromo-[7-(3,5-di-*tert*-butylphenyl)-5,6,8,9-tetrahydro-dibenzo[*c, h*]acridine] were prepared according to the literature methods [15].

4.2. Synthesis of 2,12-dibromo-[7-(3,5-di-*tert*-butylphenyl)dibenzo[*c, h*]acridine] (**8**)

A 100 ml flask equipped with a condenser was flame dried under a continuous stream of argon. The flask was charged with **7** (1.01 g, 2.04 mmol) dissolved in hot, anhydrous 1,4-dioxane (70 ml). To the hot solution was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (3.65 g, 2.14 mmol). Upon addition, the color of the reaction immediately became brown-red. The reaction was refluxed for a period of 24 h. The reaction was poured into 100 mL of a saturated Na₂CO₃ solution. This was warmed to 65 °C. The mixture was extracted with CH₂Cl₂ (100 mL \times 3) and was washed with saturated NaHCO₃ (100 mL), distilled water (100 mL), and brine (100 mL). The organic layer was collected and was dried over Na₂SO₄. Filtration, followed by removal of the solvent afforded the crude product as a tan-colored solid. This was dissolved in dichloromethane and was chromatographed using silica gel with CH₂Cl₂/hexane (1/3, v/v) as an eluent. The appropriate fractions were combined, and the solvent was removed under reduced pressure. The gray solid was then dissolved in methylene chloride and was crystallized by the addition of hexane to afford colorless crystals. Yield: 67%. m.p. = 347 °C. ^1H NMR (300 MHz, CDCl₃): δ 9.88 (s, 2H), 7.84 (d, 2H, $J = 8.7\text{ Hz}$), 7.75 (d, 2H, $J = 8.7\text{ Hz}$), 7.66 (d, 2H, $J = 9.3\text{ Hz}$), 7.63 (s, 1H), 7.61 (d, 2H, $J = 9.3\text{ Hz}$), 7.30 (s, 2H), 1.42 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl₃): δ 151.19, 147.78, 144.66, 135.22, 133.43, 132.33, 129.57, 128.84, 128.16, 127.05, 126.16, 125.46, 124.76, 124.44, 121.72, 35.21, 31.73. Anal. Calc. for C₃₅H₃₁NBr₂: C, 67.21; H, 5.00. Found: C, 66.84; H, 4.92%.

4.3. Synthesis of 2,12-bis(trimethylsilylethynyl)-[7-(3,5-di-*tert*-butylphenyl)dibenzo[*c, h*]acridine]

To a mixture of **8** (0.63 g, 1.01 mmol) and tetrakis(triphenylphosphine)palladium (0.12 g, 0.10 mmol) and copper(I) iodide (0.008 g, 0.04 mmol) in triethylamine (40 mL) are added trimethylsilylacetylene (0.43 mL, 3.03 mmol). The reaction mixture is stirred at 80 °C for 36 h under nitrogen. Then the solvent is removed under reduced pressure. The residue is extracted with diethyl ether and purified by chromatography on silica gel using dichloromethane/hexane (1:3, v/v) as an eluent to afford 0.46 g of product. Yield: 88%. m.p. = 61 °C. ^1H NMR (300 MHz, CDCl₃): δ 10.01 (s, 2H), 7.85 (m, 4H), 7.69 (d, 2H, $J = 9.3\text{ Hz}$), 7.65 (s, 1H), 7.63 (d, 2H, $J = 9.3\text{ Hz}$), 7.32 (s, 2H), 1.43 (s, 18H), 0.41 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl₃): δ 151.13, 147.58,

145.25, 135.37, 133.42, 131.84, 129.89, 127.78, 127.02, 125.42, 124.69, 124.31, 124.13, 122.17, 121.71, 106.04, 95.28, 35.21, 31.71, 0.32. Anal. Calc. for $C_{45}H_{49}NSi_2$: C, 81.89; H, 7.48. Found: C, 80.11; H, 7.40%.

4.4. Synthesis of 2,12-diethynyl-[7-(3,5-di-tert-butylphenyl)dibenzo[*c,h*]acridine] (9)

A catalytic amount of 1 M NaOH solution was added to a stirred solution of 2,12-bis(trimethylsilylethynyl)-[7-(3,5-di-tert-butylphenyl)dibenzo[*c,h*]acridine] (0.44 g, 0.86 mmol) in a mixture of THF (20 mL) and methanol (20 mL). After complete consumption of the starting material, the reaction mixture was dried and extracted with dichloromethane and washed with H_2O . The organic phase was dried over $MgSO_4$, and the crude product was purified by chromatography on silica gel using dichloromethane/hexane (1:3, v/v) as an eluent to afford 0.54 g of product. Yield: 96%. m.p. = 195 °C. 1H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 2H), 7.85 (m, 4H), 7.68 (d, 2H, $J=9.3$ Hz), 7.63 (s, 1H), 7.62 (d, 2H, $J=9.3$ Hz), 7.30 (s, 2H), 3.34 (s, 2H), 1.41 (s, 18H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 151.12, 147.64, 145.16, 135.30, 133.57, 132.13, 131.81, 129.85, 127.86, 126.99, 125.41, 124.70, 124.30, 122.13, 120.73, 84.91, 84.43, 35.18, 31.61. Anal. Calc. for $C_{39}H_{33}N$: C, 90.83; H, 6.45. Found: C, 90.22; H, 6.38%.

4.5. Synthesis of 2,12-bis(3-tert-butyl-4-hydroxy-5-formylphenylethynyl)-[7-(3,5-di-tert-butylphenyl)dibenzo[*c,h*]acridine] (10)

This compound was prepared with 3-tert-butyl-2-hydroxy-5-iodobenzaldehyde using the same procedure as that described for 2,12-bis(trimethylsilylethynyl)-[7-(3,5-di-tert-butylphenyl)dibenzo[*c,h*]acridine] (reaction condition: 60 °C, 36 h). Yield: 87%. m.p. = 287 °C. 1H NMR (300 MHz, $CDCl_3$): δ 11.88 (s, 2H), 10.06 (s, 2H), 9.61 (s, 2H), 7.89 (m, 4H), 7.75 (s, 4H), 7.69 (d, 2H, $J=9.3$ Hz), 7.67 (s, 1H), 7.63 (d, 2H, $J=9.3$ Hz), 7.32 (s, 2H), 1.43 (s, 18H), 1.37 (s, 18H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 196.59, 161.36, 151.16, 147.76, 145.25, 138.96, 137.91, 136.78, 135.65, 135.34, 134.31, 133.32, 132.02, 129.92, 128.31, 127.97, 125.46, 124.67, 124.40, 121.77, 120.56, 118.98, 114.50, 89.49, 35.21, 35.06, 30.34, 29.25. MALDI-TOF-MS: $m/z = 868.40$ (M+H) $^+$ calcd 868.43. Anal. Calc. for $C_{61}H_{57}NO_4$: C, 84.40; H, 6.62. Found: C, 83.99; H, 6.54%.

4.6. Preparation of 11

To a solution of K_2CO_3 (0.61 g, 4.41 mmol) and (R,R)-diaminocyclohexane tartrate salt (0.06 g, 0.23 mmol) in H_2O (30 mL) was added THF (12 mL), and the solution was heated to reflux. A solution of **10** in THF (7 mL) was added dropwise over 30 min. The addition funnel was washed with THF (3 mL) and the reaction was stirred at reflux for 8 h. After the solution was cooled to room temperature, the solution was poured into Et_2O

(30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2×20 mL). The combined organic layers were washed with brine, and dried over Na_2SO_4 . The product was recrystallized by hexane to afford a white solid. Yield: 97%. m.p. = 164 °C. 1H NMR (300 MHz, $CDCl_3$): δ 14.17 (s, 2H), 10.01 (s, 2H), 8.41 (s, 2H), 7.89 (m, 4H), 7.70 (d, 2H, $J=9.3$ Hz), 7.64 (s, 1H), 7.62 (d, 2H, $J=9.3$ Hz), 7.58 (s, 2H), 7.47 (s, 2H), 7.32 (s, 2H), 3.93 (m, 2H, cyclohexyl), 2.32 (m, 2H, cyclohexyl), 1.91 (m, 2H, cyclohexyl), 1.45 (s, 18H), 1.42 (s, 18H), 1.64–1.25 (m, 4H, cyclohexyl). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 161.25, 151.09, 147.73, 14.29, 138.25, 135.49, 133.98, 133.12, 132.55, 132.03, 131.78, 129.86, 128.01, 127.21, 125.69, 124.83, 124.36, 122.92, 122.28, 120.87, 118.55, 112.74, 90.38, 88.40, 35.14, 31.68, 29.89, 29.55, 22.87, 14.22, 1.12. IR (KBr pellet: cm^{-1}): 1630 ($\nu(C=N)$). MALDI-TOF-MS: $m/z = 946.36$ (M+H) $^+$ calcd 946.52. Anal. Calc. for $C_{67}H_{67}N_3O_2$: C, 85.04; H, 7.14. Found: C, 85.64; H, 7.02%.

4.7. Preparation of 12

A degassed solution of $Co(OAc)_2 \cdot 4H_2O$ (0.11 g, 0.436 mmol) in MeOH (20 mL) was added to a degassed solution of ligand **11** (0.34 g, 0.18 mmol) in toluene (8 mL) via cannula under N_2 . The resulting mixture was stirred under N_2 for 8 h. The mixture was concentrated under reduced pressure and extracted with CH_2Cl_2 and washed with H_2O . The organic phase was dried over $MgSO_4$. The crude product was purified by chromatography on silica gel using dichloromethane/hexane (1:3, v/v) as an eluent to afford 0.34 g of product. Yield: 97%. m.p. > 400 °C. IR (KBr pellet: cm^{-1}): 1601 ($\nu(C=N)$). MALDI-TOF-MS: $m/z = 2007.07$ (M+H) $^+$ calcd 2006.89. Anal. Calc. for $C_{134}H_{130}N_6O_4Co_2$: C, 80.22; H, 6.53. Found: C, 78.76; H, 6.41%.

4.8. Preparation of 13

This compound was prepared with $Zn(OAc)_2 \cdot 2H_2O$ and EtOH using the same procedure as that described for **12**. Yield: 92%. m.p. > 400 °C. 1H NMR (300 MHz, $CDCl_3$): δ 10.07 (s, 2H), 10.05 (s, 2H), 8.46 (s, 2H), 8.44 (s, 2H), 7.97 ~ 7.89 (m, 8H), 7.74 ~ 7.50 (m, 14H), 7.35 ~ 7.17 (m, 8H), 3.99 (m, 2H, cyclohexyl), 3.46 (m, 2H, cyclohexyl), 2.40 (m, 2H, cyclohexyl), 2.15 ~ 1.97 (m, 6H, cyclohexyl), 1.67 ~ 1.19 (m, 8H, cyclohexyl), 1.46 (s, 18H), 1.44 (s, 36H), 1.42 (s, 18H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 172.81, 171.00, 168.39, 151.13, 147.53, 143.30, 142.83, 139.50, 137.90, 135.49, 133.07, 132.82, 132.07, 131.70, 131.17, 129.18, 128.72, 128.37, 127.92, 127.08, 125.44, 125.13, 124.37, 122.72, 122.56, 118.32, 118.06, 108.89, 108.74, 90.99, 90.74, 88.20, 87.72, 72.29, 35.64, 35.42, 35.22, 31.72, 29.45, 29.35, 21.59, 1.17. IR (KBr pellet: cm^{-1}): 1598 ($\nu(C=N)$). MALDI-TOF-MS: $m/z = 2018.95$ (M+H) $^+$ calcd 2018.87. Anal. Calc.

for $C_{134}H_{130}N_6O_4Zn_2$: C, 79.70; H, 6.49. Found: C, 79.13; H, 6.30%.

4.9. Synthesis of 2-(4,4-dimethyloxazolin-2-yl)-4-iodophenol (**14**)

To a stirred solution of 5-iodosalicylic acid (5.28 g, 20.0 mmol), 2-amino-2-methyl-1-propanol (1.91 mL, 20.0 mmol), PPh_3 (15.74 g, 60.0 mmol), NEt_3 (8.32 mL, 60.0 mmol) in CH_2Cl_2 (100 mL) was added CCl_4 (19.30 mL, 200 mmol) via cannula for 8 h at 0 °C. The resulting solution was stirred at 50 °C for an additional 12 h. The reaction mixture was allowed to cool to room temperature and was dried *in vacuo*. The crude product was purified by chromatography on silica gel using benzene/hexane (1:1, v/v) as an eluent to give pale yellow oil. Yield: 90%. 1H NMR (300 MHz, $CDCl_3$): δ 12.20 (s, 1H), 7.90 (s, 1H), 7.57 (d, 1H, $J = 9.0$ Hz), 6.76 (d, 1H, $J = 9.0$ Hz), 4.06 (s, 2H), 1.36 (s, 6H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 162.34, 159.50, 141.52, 136.20, 119.06, 113.13, 79.38, 67.24, 28.45. Anal. Calc. for $C_{11}H_{12}NO_2I$: C, 41.66; H, 3.81. Found: C, 41.08; H, 3.62%.

4.10. Synthesis of 2,12-bis[3-(4,4-dimethyloxazolin-2-yl)-4-hydroxyphenylethynyl]-[7-(3,5-di-tert-butylphenyl)dibenzo[*c,h*]acridine] (**15**)

This compound was prepared using the same procedure as that described for **10**. Yield: 86%. m.p. = 246 °C. 1H NMR (300 MHz, $CDCl_3$): δ 12.53 (s, 2H), 10.04 (s, 2H), 8.04 (s, 2H), 7.88 (m, 4H), 7.71 (d, 2H, $J = 8.4$ Hz), 7.68 (d, 2H, $J = 9.3$ Hz), 7.66 (s, 1H), 7.64 (d, 2H, $J = 9.3$ Hz), 7.33 (s, 2H), 7.03 (d, 2H, $J = 8.4$ Hz), 3.97 (s, 4H), 1.43 (s, 18H), 1.40 (s, 12H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 163.14, 160.06, 151.05, 147.45, 145.20, 136.57, 135.39, 133.02, 131.98, 131.80, 131.42, 128.94, 127.87, 126.96, 125.04, 124.28, 122.11, 121.99, 117.11, 113.84, 111.24, 90.21, 89.27, 78.45, 67.27, 65.33, 35.14, 31.66, 28.55. IR (KBr pellet: cm^{-1}): 1624 ($\nu(C=N)$). MALDI-TOF-MS: $m/z = 894.37$ ($M+H$)⁺ calcd 894.42. Anal. Calc. for $C_{61}H_{55}N_3O_4$: C, 81.94; H, 6.20. Found: C, 81.62; H, 6.07%.

4.11. Preparation of **16**

This compound was prepared using the same procedure as that described for **13**. Yield: 81%. m.p. > 400 °C. 1H NMR (300 MHz, $CDCl_3$): δ 10.06 (s, 4H), 8.17 (s, 4H), m 7.89 (m, 8H), 7.72–7.62 (m, 14H), 7.35 (s, 4H), 6.88 (d, 4H, $J = 8.4$ Hz), 4.09 (s, 8H), 1.45 (s, 36H), 1.44 (s, 24H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 170.71, 167.79, 151.04, 147.40, 145.24, 138.52, 135.85, 134.37, 132.78, 132.05, 131.23, 128.98, 128.36, 127.83, 127.02, 125.08, 124.31, 123.83, 122.69, 109.23, 108.62, 91.13, 88.21, 77.98, 68.09, 66.82, 35.19, 31.70, 28.62. IR (KBr pellet: cm^{-1}): 1602 ($\nu(C=N)$). MALDI-TOF-MS: $m/z = 1916.59$ ($M+H$)⁺ calcd 1916.66. Anal. Calc. for

$C_{122}H_{106}N_6O_8Zn_2$: C, 76.52; H, 5.58. Found: C, 76.22; H, 5.41%.

4.12. Preparation of **17**

This compound was prepared using the same procedure as that described for **12**. Yield: 84%. m.p. > 400 °C. Anal. Calc. for $C_{122}H_{106}N_6O_8Co_2$: C, 77.04; H, 5.62. Found: C, 75.68; H, 5.55%.

4.13. X-ray crystallography

Suitable crystals of **12** and **17** were grown by THF/hexane. All X-ray intensity data of compounds **12** and **17** were collected on a Bruker SMART 1000 CCD diffractometer [25] with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The collected data were processed for integration; an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities (SADABS) [26]. Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using SHELXL97 [27]. All non-hydrogen atoms in compounds **12** and **17** were refined anisotropically. All hydrogen atoms were included in the calculated positions.

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Appendix A. Supplementary data

CCDC 617645 and 617646 contains the supplementary crystallographic data **12** and **17**. These data can be obtained free of charge via <http://www.ccdc.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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