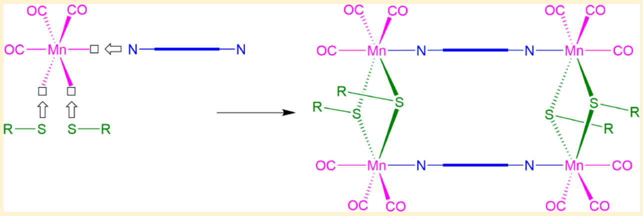
Inorganic Chemistry
Article
pubs.acs.org/IC

Self-assembly of Thiolato-Bridged Manganese(I)-Based Metallarectangles: One-pot Synthesis and Structural Characterization

Chowan Ashok Kumar, R. Nagarajaprakash, Buthanapalli Ramakrishna, and Bala. Manimaran*

Department of Chemistry, Pondicherry University, Puducherry, 605014, India

Supporting Information



ABSTRACT: A new series of thiolato-bridged manganese(I)-based supramolecular rectangles have been achieved by three-precursor self-assembly of $Mn_2(CO)_{10}$, diaryl disulfides (RSSR), and linear ditopic azine ligands (L) [L = pyrazine (pz), 4,4′-bipyridine (bpy), and *trans*-1,2-bis(4-pyridyl)-ethylene (bpe)] using a one-pot synthetic strategy. Oxidative addition of RSSR (diphenyl disulfide and *p*-tolyl disulfide) to manganese decacarbonyl in the presence of rigid bidentate ligands (L) afforded metallarectangles of the general formula $[\{(CO)_3Mn(\mu\text{-SR})_2Mn(CO)_3\}_2(\mu\text{-L})_2]$ (**1**−**6**). Compounds **1**−**6** were characterized using elemental analyses and NMR, IR, and UV−vis absorption spectroscopic techniques. The molecular structures of metallarectangles **1**, **3**, and **5** were elucidated by single-crystal X-ray diffraction methods. The guest binding ability of **3** and **5** has been investigated with two aromatic guests using electronic absorption and fluorescence emission spectroscopy, and the results revealed a strong binding interaction between host−guest species.

INTRODUCTION

The construction of transition-metal containing supramolecules has garnered great deal of attention owing to their prominent applications in different fields like molecular recognition, host−guest chemistry, crystal engineering, and molecular devices.[1] Numerous varieties of nanoscale architectures such as triangles, squares, rectangles, pentagons, hexagons, boxes, cages, and more complex structures have been fabricated to date.[2−8] Molecular rectangles, specifically, comprise an interesting class of metallasupramolecules that are accomplished using diverse synthetic strategies based on the nature of the metal ion used in self-assembly. In the beginning, a predesigned Pt-based dinuclear molecular clip and linear ditopic bridging ligands were employed for the construction of molecular rectangles.[9] Similarly, dinuclear arene ruthenium complexes of various bis-chelating organic bridges were treated with linear bidentate ligands to render a wide range of rectangular frameworks.[10] However, *fac*-$Re(CO)_3$-core based metallarectangles with a variety of chelating ligands have been explored for their interesting photophysical, sensing, and cytotoxic properties.[11] Re(I)-rectangles of type $[\{(CO)_3Re(\mu\text{-ER})_2Re(CO)_3\}_2(\mu\text{-L})_2]$ (E = O; R = H, $-CH_3$, $-CH_2CH_3$, and $-CH_2CH_2OH$; L = bpy; E = S; R = $-CH_2CH_2CH_3$ and Ph; L = bpy and pz; E = Se; R = Ph; and L = bpy) were at first developed via a stepwise synthesis.[12] Alternately, Re(I)-rectangles were also achieved under one-pot reaction conditions by treating $Re_2(CO)_{10}$ with linear ditopic pyridyl ligands in the presence of corresponding higher alcohols or dialkyl/diaryl diselenide.[13] Hupp et al. developed bis-benzimidazolato bridged Mn(I)- and Re(I)-based molecular rectangles $[\{(CO)_3M(\mu\text{-BiBzIm})_2M(CO)_3\}_2(\mu\text{-bpy})_2]$ (M = Mn, Re) in a two-step synthetic route using a preformed $[\{(CO)_4M\}_2BiBzIm]$ bimetallic edge and linear dipyridyl ligands. The resultant Mn(I)-based molecular rectangle was found to be a sensor for various volatile organic compounds.[14] Furthermore, $Mn(CO)_3$-core based complexes are known for their promising CO releasing properties and for their applications in radiopharmaceuticals and copolymerization.[16] Although, the supramolecular chemistry of rhenium has been extensively studied, the comparable manganese chemistry is still at a nascent stage.[15] This is in part due to the difficulty in synthesis involving Mn(I) and the stability of formed assemblies. In this scenario, developing Mn(I)-based metallacycles is not only challenging but also may offer interesting prospects owing to its natural abundance. Herein, we report on the one-step self-assembly of thiolato-bridged manganese-rectangles $[\{(CO)_3Mn(\mu\text{-SR})_2Mn(CO)_3\}_2(\mu\text{-L})_2]$ (**1**−**6**) from $Mn_2(CO)_{10}$, diaryl disulfides, and linear dipyridyl ligands (L) in the presence of Me_3NO at ambient temperature in the absence of light. Supramolecular rectangles **1**−**6** were characterized using elemental analyses and NMR, IR, and UV−vis absorption spectroscopic techniques. The molecular structures for compounds **1**, **3**, and **5** were determined by single-crystal X-ray diffraction methods. The guest binding capabilities of thiolato-bridged host rectangles **3** and **5** with pyrene and triphenylene were investigated by UV−visible absorption and emission spectral studies.

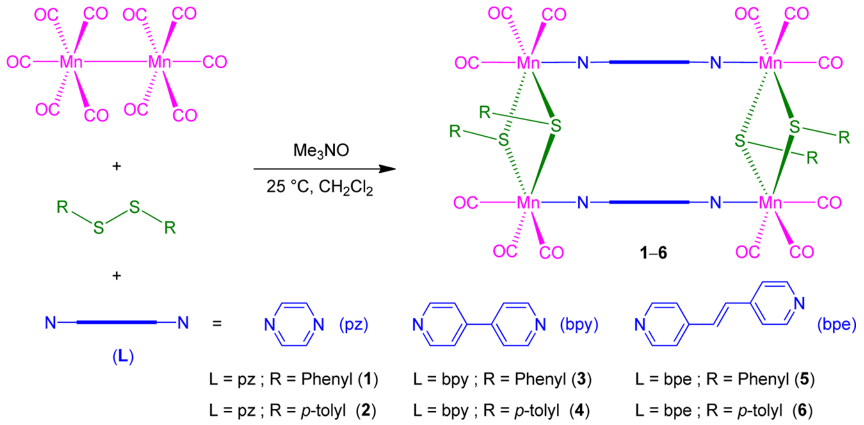
RESULTS AND DISCUSSION

Self-assembly of $M_4S_4L_2$-type thiolato-bridged Mn(I)-based supramolecular rectangles was accomplished via an orthogonal-bonding approach, wherein two phenyl/*p*-tolyl thiolato linkers

Received: May 18, 2015
Published: August 19, 2015

DOI: 10.1021/acs.inorgchem.5b01118
Inorg. Chem. 2015, 54, 8406−8414

Scheme 1. Preparation of Mn(I)-Based Metallarectangles 1−6



and a linear ditopic N-donor ligand were simultaneously introduced at the equatorial sites and the axial site of *fac*-Mn(CO)$_3$ core, respectively.[12,13] Reaction of Mn$_2$(CO)$_{10}$ and diaryl disulfides (RSSR = diphenyl disulfide and *p*-tolyl disulfide) with linear ditopic pyridyl linkers (L = pyrazine (pz), 4,4′- bipyridine (bpy), and *trans*-1,2-bis(4-pyridyl)-ethylene (bpe)) in the presence of Me$_3$NO in dichloromethane medium at 25 °C under dark conditions afforded tetranuclear rectangles of the general formula [{(CO)$_3$Mn(μ-SR)$_2$Mn-(CO)$_3$}$_2$(μ-L)$_2$] (**1−6**) (Scheme 1). Metallarectangles **1−6** were soluble in polar organic solvents and were characterized using spectroscopic techniques, and single-crystal X-ray structures were obtained for **1**, **3**, and **5**.

IR spectra of compounds **1−6** in CH$_2$Cl$_2$ exhibited four bands with similar patterns in the region ν 2025−1917 cm^{-1} characteristic of *fac*-Mn(CO)$_3$ core.[13] UV−vis spectra of **1−6** in CH$_2$Cl$_2$ displayed ligand centered transitions in the higher energy region λ_{max} 228−378 nm as intense bands and MLCT transitions in the lower energy region λ_{max} 436−511 nm as less intense bands.[13] ^{1}H NMR spectrum of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_3$(μ-pz)$_2$] (**1**) displayed a singlet at δ 9.29 ppm due to pyrazine protons. The signals corresponding to phenyl thiolato group protons (H$^2_{Ph}$, H$^3_{Ph}$, and H$^4_{Ph}$) appeared at δ 7.92, 7.41, and 7.31 ppm, respectively. A downfield shift observed for the proton signals of **1** in comparison to the free ligand signals indicated the complexation of ligands with Mn metal centers. ^{1}H NMR spectra of rectangles **2−6** showed appropriate signals for various protons corresponding to ditopic pyridyl ligands and phenyl/*p*-tolyl thiolato groups bonded to Mn centers, and the spectral data are given in Experimental Section.

Good quality single-crystals of **1**, **3**, and **5** grown from a near-saturated acetone solution of the corresponding compounds by slow evaporation were subjected to single-crystal X-ray diffraction analysis. The ORTEP diagrams of rectangles **1**, **3**, and **5** are shown in Figures 1a−3a and their selected bond lengths and angles are listed in Tables 1−3, respectively. The crystallographic data and structural refinement details are summarized in Table S1 (Supporting Information). Compound **1** crystallized in triclinic space group $P\bar{1}$, while **3** and **5** crystallized in monoclinic space groups $P2_1/n$ and $P2_1/a$, respectively. The molecular structure of [{(CO)$_3$Mn(μ-SPh)$_2$-Mn(CO)$_3$}$_2$(μ-pz)$_2$] (**1**), [{(CO)$_3$Mn(μ-SPh)$_2$Mn(CO)$_3$}$_2$(μ-bpy)$_2$] (**3**), and [{(CO)$_3$Mn(μ-SPh)$_2$Mn(CO)$_3$}$_2$(μ-bpe)$_2$] (**5**) revealed a rectangular architecture, wherein the four vertices occupied by *fac*-Mn(CO)$_3$ cores are bridged by two phenyl thiolato groups along the shorter edges and by two linear ditopic pyridyl ligands (L) along the longer edges. Each manganese center in four *fac*-Mn(CO)$_3$ corners of the rectangles is surrounded by a nitrogen atom of the pyridyl ring and two sulfur atoms of phenyl thiolato groups to afford a slightly distorted octahedral geometry around the metal center. On the basis of Mn···Mn distances, the dimensions of rectangles **1**, **3**, and **5** are found to be ∼3.63 × 7.02, ∼3.64 × 11.36, and ∼3.64 × 13.57 Å, respectively. The Mn···Mn distances along the shorter edges are lesser than those observed for analogous Re(I)-rectangles due to the shorter Mn−S bond distance in comparison with the Re−S bond distance.[12,13] The Mn$_2$S$_2$ rings are found to be noncoplanar with a torsional angle of 12.59° and 14.82° between the S(1)−Mn(1)−S(2) and S(1)−Mn(2)−S(2) planes for compounds **1** and **3**, respectively. In the case of rectangle **5**, two crystallographically independent molecules are present in an asymmetric unit, and the torsion angle between S(1)−Mn(1)−S(2) and S(1)−Mn(2)−S(2) planes for one of the molecules was 11.19°, whereas for the second molecule the corresponding angle is

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Mn(1)−N(1)	2.104(3)	N(1)−Mn(1)−S(1)	84.81(9)
Mn(1)−S(1)	2.3790(13)	N(1)−Mn(1)−S(2)	84.25(10)
Mn(1)−S(2)	2.3771(13)	S(2)−Mn(1)−S(1)	79.11(4)
Mn(1)−C(1)	1.807(6)	Mn(1)−S(2)−Mn(2)	99.41(4)
Mn(1)−C(2)	1.806(6)	C(1)−Mn(1)−N(1)	91.11(18)
Mn(1)−C(3)	1.806(5)	C(3)−Mn(1)−N(1)	175.4(2)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Mn(1)−N(1)	2.119(2)	N(1)−Mn(1)−S(1)	84.30(6)
Mn(1)−S(1)	2.3948(8)	N(1)−Mn(1)−S(2)	85.91(6)
Mn(1)−S(2)	2.3851(8)	S(2)−Mn(1)−S(1)	78.85(3)
Mn(1)−C(1)	1.812(3)	Mn(1)−S(2)−Mn(2)	99.42(3)
Mn(1)−C(2)	1.818(3)	C(1)−Mn(1)−N(1)	93.69(11)
Mn(1)−C(3)	1.801(3)	C(3)−Mn(1)−N(1)	176.16(11)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

Mn(1)−N(1)	2.097(4)	N(1)−Mn(1)−S(1)	84.42(11)
Mn(1)−S(1)	2.3765(14)	N(1)−Mn(1)−S(2)	84.66(11)
Mn(1)−S(2)	2.3943(13)	S(1)−Mn(1)−S(2)	79.67(4)
Mn(1)−C(1)	1.806(6)	Mn(1)−S(1)−Mn(2)	99.64(5)
Mn(1)−C(2)	1.799(5)	C(1)−Mn(1)−N(1)	91.83(18)
Mn(1)−C(3)	1.805(6)	C(3)−Mn(1)−N(1)	91.50(19)

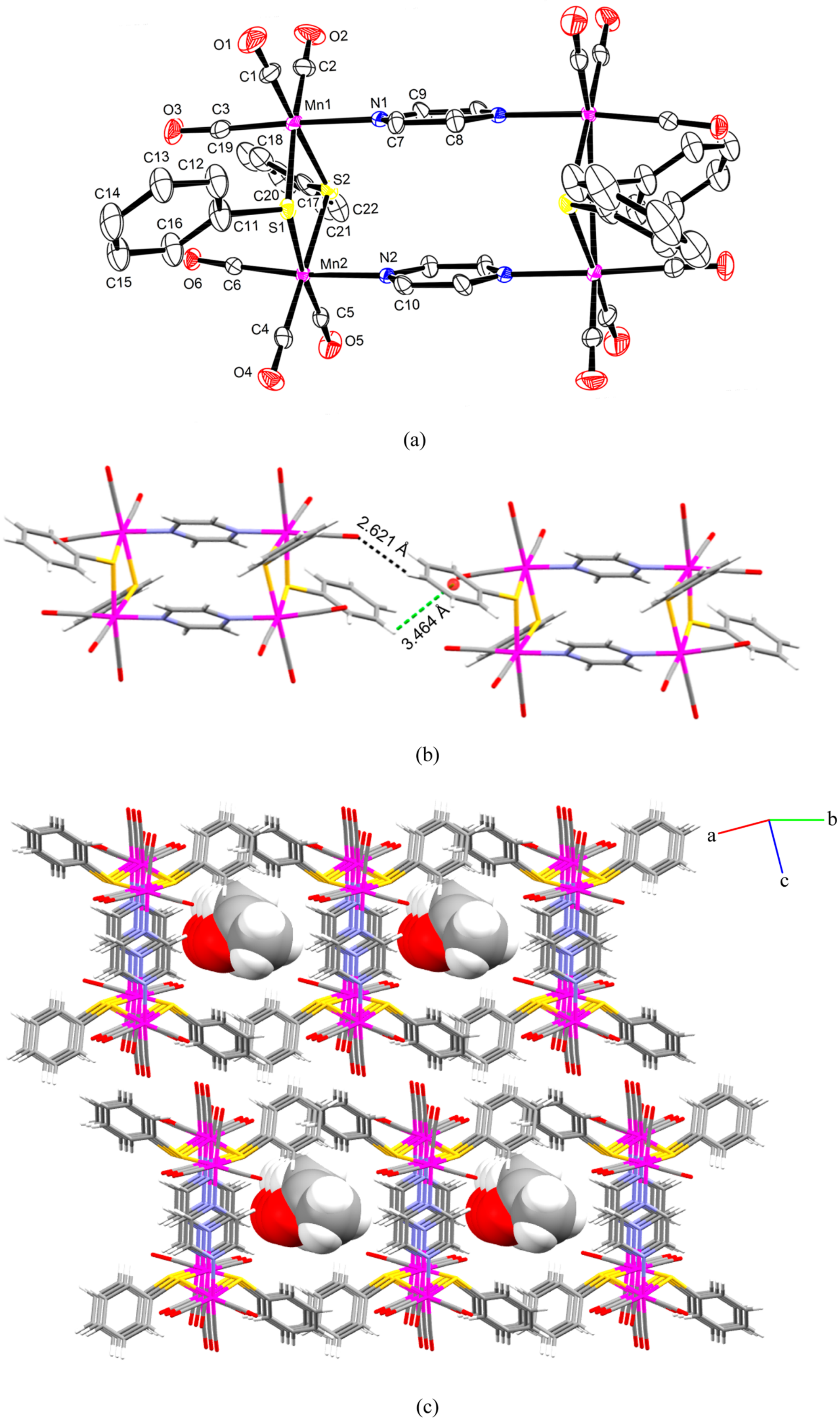


Figure 1. (a) ORTEP diagram of metallarectangle **1** with thermal ellipsoids drawn at the 40% probability level. Solvent molecules are omitted for clarity. (b) Intermolecular CH···O hydrogen bonding (black dotted line), and CH···π (green dotted lines) interactions shown in stick representation. (c) Packing diagram of **1**, viewed along the *a* axis, showing the presence of acetone molecules in the crystal lattice.

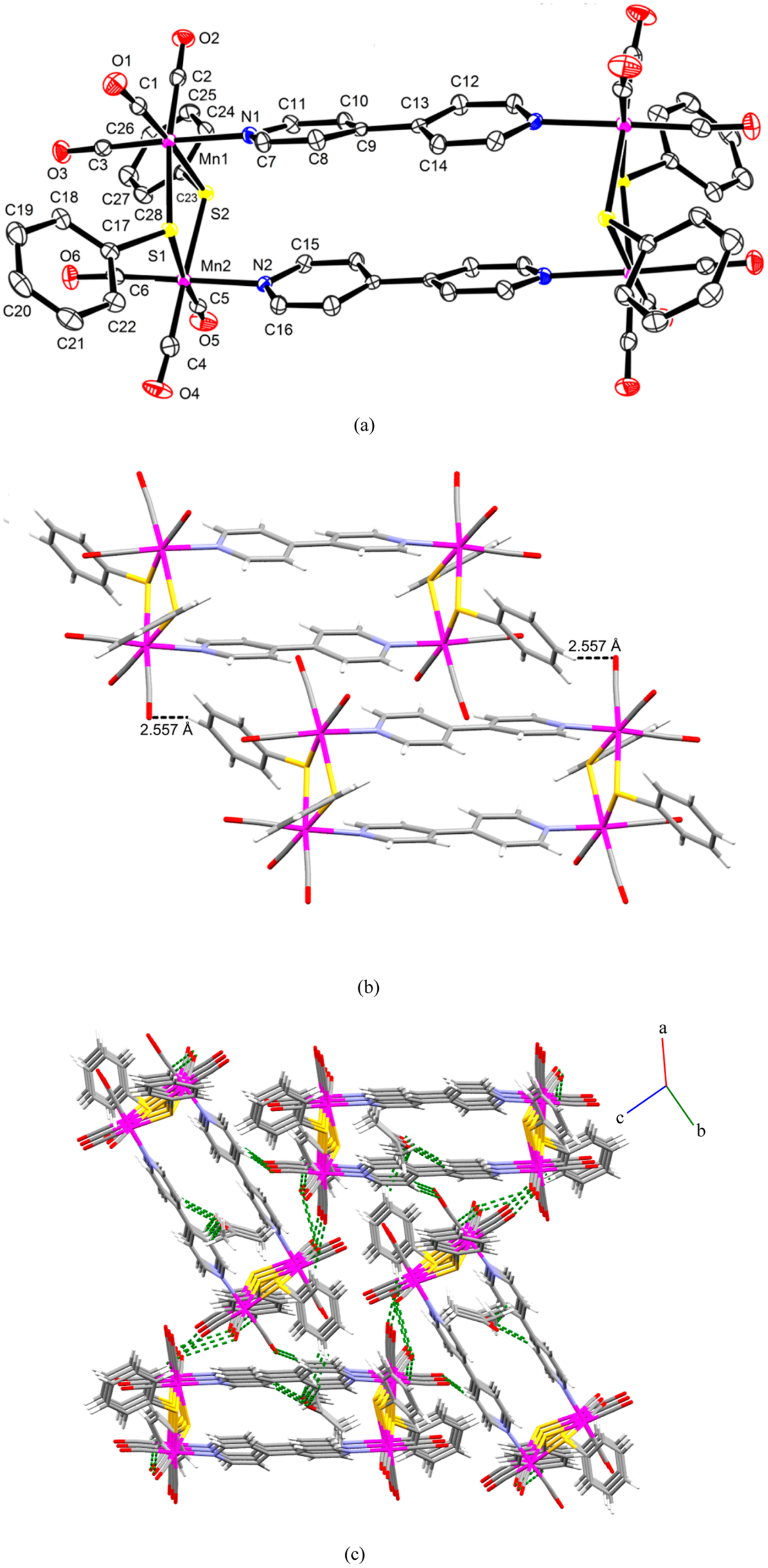
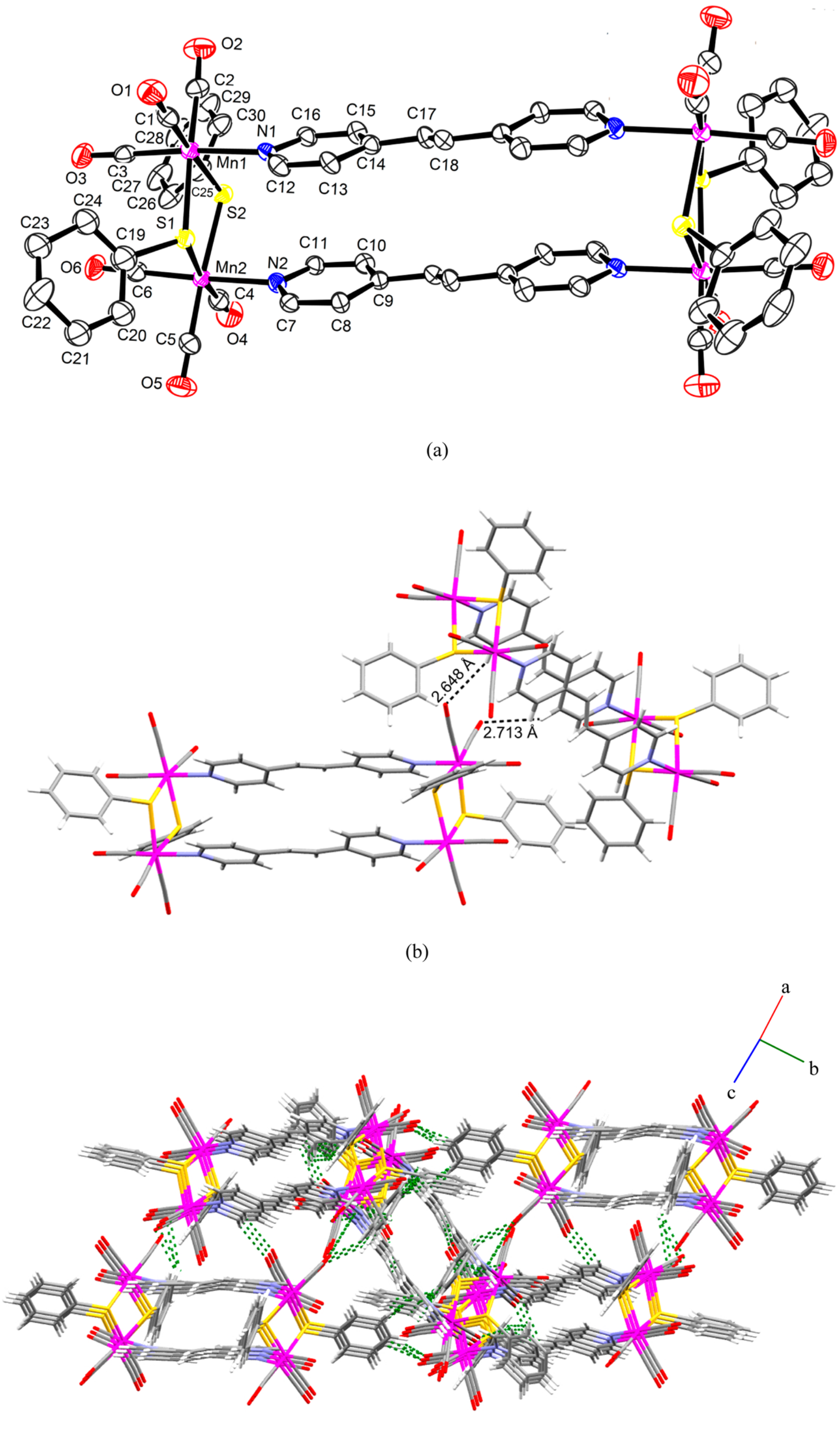


Figure 2. (a) ORTEP diagram of metallarectangle **3** with thermal ellipsoids drawn at the 50% probability level. Solvent molecules are omitted for clarity. (b) Intermolecular CH···O hydrogen bonding (black dotted line) interactions. (c) Packing diagram of **3** showing the formation of a 2-D network when viewed along the *a*-axis.



(a)

(b)

(c)

Figure 3. (a) ORTEP diagram of metallarectangle **5** with thermal ellipsoids drawn at the 40% probability level. (b) Intermolecular C≡O···H hydrogen bonding (black dotted line) interactions. (c) Packing diagram of **5** viewed along the *c*-axis showing C≡O···H type soft interactions.

found to be 8.60° (between S(3)−Mn(3)−S(4) and S(3)−Mn(4)−S(4) planes).

The crystal packing of pyrazine bridged rectangle **1** revealed the presence of intra- and intermolecular soft interactions. An intermolecular C≡O···H hydrogen bonding interaction is observed between O(3) of the terminal CO group of one rectangular molecule and H(14) of the phenyl group present in the adjacent molecule with a distance of 2.621 Å (Figure 1b).[17] Apart from this, a CH···π interaction is also present between H(15) of the phenyl group with the π cloud of the aryl moiety of the adjacent rectangle with a distance of 3.464 Å (Figure 1b).[18] Interestingly, acetone solvent molecules are found to

Table 4. Binding Constants (K_b) and Stern–Volmer Quenching Constants (K_{sv}) for the Host–Guest Systems of Molecular Rectangles 3 and 5 with Pyrene and Triphenylene

with pyrene	K_b (M^{-1})	K_{sv} (M^{-1})	with triphenylene	K_b (M^{-1})	K_{sv} (M^{-1})
3	2.7×10^4	2.0×10^5	3	4.9×10^4	4.7×10^4
5	6.7×10^4	1.2×10^5	5	7.1×10^4	7.6×10^4

occupy the infinite channels observed between the rectangles in the packing diagram of compound **1** (Figure 1c).

In rectangle **3**, an intermolecular hydrogen bonding interaction is observed between the oxygen atom of the terminal CO group and a phenyl hydrogen from an adjacent molecule (O(5)···H(20)–C(20)) with a distance of 2.557 Å (Figure 2b). The packing diagram of **3** shows the formation of two-dimensional network via C≡O···H and C=O···H type hydrogen bonding (Figure 2c).

In rectangle **5**, two intermolecular C≡O···H type hydrogen bonding interactions are observed among the oxygen atom of carbonyl group and pyridyl hydrogen atom present in the neighboring rectangle **5** with a distance of 2.648 Å (O(13)···H(10)–C(10)) and 2.713 Å (O(19)···H(16)–C(16)), respectively (Figure 3b). The packing diagram of **5** realized a three-dimensional network with the aid of C≡O···H type hydrogen bonding interactions (Figure 3c).

To the best of our knowledge, although molecular recognition capabilities of various rhenium based supramolecular systems have been thoroughly explored, parallel studies pertaining to manganese systems are not available. Therefore, we intended to study the guest binding ability of the thiolato-bridged molecular rectangles. However, the single-crystal X-ray structure of **1** showed that even an acetone molecule could not be encapsulated inside its small cavity (Figure 1c) owing to the very short Mn···Mn transannular distances. We then envisioned that it could still be possible to exploit "out of cavity" interactions between electron rich planar aromatic guests such as pyrene/triphenylene and electron deficient bpy and bpe linkers bonded to electrophilic Mn(I) metal corners of the hosts. Hence, we monitored the changes in UV–visible absorption and emission spectral patterns of solutions of polycyclic aromatic guests (pyrene and triphenylene) with increasing concentrations of hosts **3** and **5**. The absorbance of guest species was enhanced with the incremental addition of hosts during UV–vis absorption titration experiments. Nevertheless, the fluorescence intensities of guests were quenched with increasing concentrations of host rectangles (Figure S1–S4). These spectral observations were indicative of the formation of ground state charge-transfer complexes between the host rectangles and guests. The details pertaining to UV–vis and emission titration experiments, data analysis, and Benesi–Hildebrand and Stern–Volmer equations are provided in Supporting Information. The binding constants (K_b) were estimated from the slope and intercept of a Benesi–Hildebrand linear regression plot,[11j,13b,c,20] while the Stern–Volmer constants (K_{SV}) were calculated from the slope of a linear Stern–Volmer plot (Table 4).[11j,21] The binding constants of manganese rectangles were found to be larger than analogous thiolato-bridged rhenium counter parts, probably due to the more electron-withdrawing nature of Mn than Re that facilitated efficient charge-transfer from the aromatic guests to host rectangles.[13b] The large binding constant values revealed effective binding of planar guests by the rectangular hosts, and it is presumed that the planar guest molecules might locate on the exterior of bpy or bpe linkers of the host rectangle via CH···π/π···π interactions.[13b]

Furthermore, in order to understand the mode of binding interactions of the guest with the rectangular host, single-crystals of **3**·pyrene host–guest system suitable for X-ray diffraction analysis were grown in DMF at 25 °C. The structural analysis of the **3**·pyrene system substantiated the ability of host rectangles to bind with planar guest species. The details about data collection and refinement are summarized in Table S2. Although crystals of **3**·(pyrene)$_3$ provided weak diffractions, the data were nearly sufficient to resolve their overall molecular structures and ascertain that the pyrene guests have out of cavity interactions with bpy spacers coordinated to Mn centers. The packing arrangement showed that rectangle **3** is surrounded by four pyrene guest molecules on all four sides. Two of the pyrene guests are present above and below the rectangle and are aligned parallel to the surface of bpy ligands. Several π···π interactions are observed between the pyrene guests and bpy linkers in the range of 3.664–4.129 Å (Figure S5).[12] Two more pyrene guests, existent at the lateral positions in the opposite ends of the rectangles and oriented orthogonal to the plane of bpy ligands, are found to be stabilized by CH···π interactions in the range of 3.130–3.490 Å (Figure S6).[18] In addition, CH···O interaction is observed between a CH of the pyrene guest and an O atom of a carbonyl group of the host rectangle with a distance of 2.596 Å.[17] Overall, these observations strongly corroborate the formation of a host–guest complex between metallarectangles and π-rich aromatic guests.

■ CONCLUSIONS

We have demonstrated a successful one-step methodology to synthesize thiolato-bridged manganese(I)-based metallarectangles (**1**–**6**) using manganese carbonyl, diaryl disulfides and linear dinucleating pyridyl ligands of varying lengths. The Mn(I)-metallacycles were spectroscopically characterized, and single-crystal X-ray analysis confirmed their rectangular architecture as evidenced in the molecular structures of compounds **1**, **3**, and **5**. Guest binding ability of metallarectangles **3** and **5** was quantitatively studied by absorption and emission spectrophotometric titrations, and the host–guest complex formation was further supported by single-crystal X-ray analysis. The current account of research comprises the first set of *fac*-Mn(CO)$_3$ core based thiolato-bridged molecular rectangles accomplished in a single step and the prime report on Mn(I)-based host–guest system. The study on the host–guest system sheds some light to rationally design in the future diverse shaped supramolecular ensembles susceptible to various guest encapsulation by tuning Mn···Mn nonbonding distances. The synthetic methodology demonstrated here for developing Mn(I)-based supramolecular rectangles utilizing two different ligand systems provides a more convenient and economical route in comparison to its Re(I) congener. Current efforts are directed toward creating diverse supramolecular architectures with the *fac*-Mn(CO)$_3$ core by exploiting various bis-chelating and multidentate ligands.

■ EXPERIMENTAL SECTION

Materials and Methods. All reactions and manipulations were performed under inert, dry, and dark conditions using standard Schlenk techniques. All of the starting materials were used as received from Strem Chemicals Inc. and Sigma-Aldrich Chemicals. Dichloromethane and other solvents were purified and dried using standard methods and freshly distilled prior to use.[19] IR spectra were taken on a Thermo Nicolet 6700 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV-2450 UV−vis spectrophotometer. Elemental analyses were performed using a Thermo Scientific Flash 2000 CHNS analyzer.

Synthesis of [{(CO)$_3$Mn(μ-SPh)$_2$Mn(CO)$_3$}$_2$(μ-L)$_2$]: General Procedure. A mixture of $Mn_2(CO)_{10}$ (0.2 mmol), diphenyl disulfide (0.2 mmol), pyridine ligand (L) (0.2 mmol), and trimethylamine *N*-oxide (0.4 mmol) was taken in a Schlenk flask equipped with a magnetic stirring bar. The system was evacuated and purged with nitrogen using a vacuum Schlenk line. To this was added freshly distilled dichloromethane (20 mL), and the reaction mixture was stirred at room temperature (25 °C) for 50−54 h. The solution was filtered through a short silica gel column (3 cm) to remove unreacted trimethylamine *N*-oxide. The solvent was removed by vacuum, and the product was washed with hexane to give a red solid of [{(CO)$_3$Mn(μ-SR)$_2$Mn(CO)$_3$}$_2$(μ-L)$_2$].

*Synthesis of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_2$(μ-pz)$_2$] (**1**).* $Mn_2(CO)_{10}$ (78 mg, 0.2 mmol), diphenyl disulfide (43 mg, 0.2 mmol), pyrazine (16 mg, 0.2 mmol), and trimethylamine *N*-oxide (32 mg, 0.4 mmol) were taken up in dichloromethane medium (20 mL), and the reaction mixture was stirred at room temperature (25 °C) for 51 h. The color of the reaction mixture changed from pale red to dark red during the course of the reaction. The dark red solution was passed through a short silica gel column to remove unreacted trimethylamine *N*-oxide. The solvent was removed using vacuum, and the product was further washed with hexane to furnish a red solid of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_2$(μ-pz)$_2$] (**1**). Yield: 66 mg, 57% (based on $Mn_2(CO)_{10}$). Anal. Calc. for $C_{44}H_{28}N_4O_{12}S_4Mn_4$: C, 45.85; H, 2.45; N, 4.86; S, 11.13. Found: C, 45.90; H, 2.35; N, 4.80, S, 11.13. ^{1}H NMR (400 MHz, CDCl$_3$ ppm): δ 9.29 (s, 8H, H, pyrazine), 7.92 (d, 8H, H^2, Ph), 7.41 (s, 8H, H^3, Ph), 7.31 (m, 4H, H^4, Ph). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 226.8, 217.9 (1:2, CO), 150.7 (pyrazine), 136.2 (C^1, Ph), 132.5 (C^2, Ph), 129.1 (C^3, Ph), 132.1 (C^4, Ph). UV−vis. {λ_{max}^{ab} (CH$_2$Cl$_2$)/(nm) (ε) dm^3 mol^{-1} cm^{-1}}: 228 (56,350) (LIG), 266 (25,218) (LIG), 331 (9,732) (LIG), 506 (6,772) (MLCT). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2025 (s), 2016 (vs), 1950 (sh), 1930 (vs) cm^{-1}.

*Synthesis of [{(CO)$_3$Mn(μ-SC$_6$H$_4$CH$_3$)$_2$Mn(CO)$_3$}$_2$(μ-pz)$_2$] (**2**).* Compound **2** was prepared using $Mn_2(CO)_{10}$ (78 mg, 0.2 mmol), *p*-tolyl disulfide (49 mg, 0.2 mmol), pyrazine (16 mg, 0.2 mmol), and trimethylamine *N*-oxide (32 mg 0.4 mmol) by following the procedure adopted for **1**. The reaction mixture was stirred at room temperature for 50 h. The product was isolated as a red solid of [{(CO)$_3$Mn(μ-SC$_6$H$_4$CH$_3$)$_2$Mn(CO)$_3$}$_2$(μ-pz)$_2$] (**2**). Yield: 80 mg, 66% (based on $Mn_2(CO)_{10}$). Anal. Calc. for $C_{48}H_{36}N_4O_{12}S_4Mn_4$: C, 47.68; H, 3.00; N, 4.63; S, 10.61. Found: C, 47.72; H, 2.95; N, 4.59; S, 10.58. ^{1}H NMR (400 MHz, CDCl$_3$ ppm): δ 9.26 (s, 8H, H, pyrazine), 7.80 (d, 8H, H^2, *p*-tolyl), 7.21 (d, 8H, H^3, *p*-tolyl), 2.39 (s, 12H, CH$_3$, *p*-tolyl). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 227.0, 218.0 (1:2, CO), 150.6 (pyrazine), 136.6 (C^1, *p*-tolyl), 132.0 (C^2, *p*-tolyl), 129.9 (C^3, *p*-tolyl), 134.3 (C^4, *p*-tolyl), 21.2 (CH$_3$, *p*-tolyl). UV−vis. {λ_{max}^{ab} (CH$_2$Cl$_2$)/(nm) (ε) dm^3 mol^{-1} cm^{-1}}: 228 (33,996) (LIG), 356 (4,422) (LIG), 511 (3,742) (MLCT). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2024 (s), 2013 (vs), 1948 (sh), 1929 (vs) cm^{-1}.

*Synthesis of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_2$(μ-bpy)$_2$] (**3**).* Compound **3** was prepared using $Mn_2(CO)_{10}$ (78 mg, 0.2 mmol), diphenyl disulfide (43 mg, 0.2 mmol), 4,4′-bipyridine (31 mg, 0.2 mmol), and trimethylamine *N*-oxide (32 mg 0.4 mmol) by following the procedure adopted for **1**. The reaction mixture was stirred at room temperature for 52 h. The product was isolated as a red solid of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_2$(μ-bpy)$_2$] (**3**). Yield: 85 mg, 65% (based on $Mn_2(CO)_{10}$). Anal. Calc. for $C_{56}H_{36}N_4O_{12}Mn_4S_4$: C, 51.54; H, 2.78; N, 4.29; S, 9.83. Found: C, 52.36; H, 2.64; N, 4.14; S, 9.70. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 9.33 (d, 8H, H^2, py), 7.98 (d, 8H, H^3, py), 7.40 (t, 8H, H^3, Ph), 7.33 (s, 8H, H^2, Ph), 7.29 (m, 4H, H^4, Ph). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 226.6, 218.8 (1:2, CO), 157.6 (C^2, py), 144.1 (C^1, Ph), 139.5 (C^4, py), 132.3 (C^2, Ph), 128.9 (C^3, Ph), 126.0 (C^4, Ph), 120.2 (C^3, py). UV−vis. {λ_{max}^{ab} (CH$_2$Cl$_2$)/(nm) (ε) dm^3 mol^{-1} cm^{-1}}: 234 (34,440) (LIG), 269 (17,828) (LIG), 372 (6,638) (LIG), 436 (4,656) (MLCT). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2024 (m), 2005 (s), 1936 (sh), 1919 (vs) cm^{-1}.

*Synthesis of [{(CO)$_3$Mn(μ-SC$_6$H$_4$CH$_3$)$_2$Mn(CO)$_3$}$_2$(μ-bpy)$_2$] (**4**).* Compound **4** was prepared using $Mn_2(CO)_{10}$ (78 mg, 0.2 mmol), *p*-tolyl disulfide (49 mg, 0.2 mmol), 4,4′-bipyridine (31 mg, 0.2 mmol), and trimethylamine *N*-oxide (32 mg 0.4 mmol) by following the procedure adopted for **1**. The reaction mixture was stirred at room temperature for 51 h. The product was isolated as a red solid of [{(CO)$_3$Mn(μ-SC$_6$H$_4$CH$_3$)$_2$Mn(CO)$_3$}$_2$(μ-bpy)$_2$] (**4**). Yield: 90 mg, 66% (based on $Mn_2(CO)_{10}$). Anal. Calc. for $C_{60}H_{44}N_4O_{12}Mn_4S_4$: C, 52.94; H, 3.26; N, 4.12; S, 9.42. Found: C, 52.96; H, 3.21; N, 4.09; S, 9.38. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 9.31 (d, 8H, H^2, py), 7.86 (d, 8H, H^3, py), 7.31 (d, 8H, H^2, *p*-tolyl), 7.21 (d, 8H, H^3, (*p*-tolyl), 2.39 (s, 12H, CH$_3$, *p*-tolyl). UV−vis. {λ_{max}^{ab} (CH$_2$Cl$_2$)/(nm) (ε) dm^3 mol^{-1} cm^{-1}}: 229 (1,20,950) (LIG), 330 (23,526) (LIG), 375 (21,838) (LIG), 452 (13,874) (MLCT). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2022 (m), 2006 (s), 1936 (sh), 1918 (vs) cm^{-1}.

*Synthesis of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_2$(μ-bpe)$_2$] (**5**).* Compound **5** was prepared using $Mn_2(CO)_{10}$ (78 mg, 0.2 mmol), diphenyl disulfide (43 mg, 0.2 mmol), *trans*-1,2-bis(4-pyridyl)ethylene (36 mg, 0.2 mmol), and trimethylamine *N*-oxide (32 mg 0.4 mmol) by following the procedure adopted for **1**. The reaction mixture was stirred at room temperature for 53 h. The product was isolated as a red solid of [{(CO)$_3$Mn(μ-SC$_6$H$_5$)$_2$Mn(CO)$_3$}$_2$(μ-bpe)$_2$] (**5**). Yield: 93 mg, 68% (based on $Mn_2(CO)_{10}$). Anal. Calc. for $C_{60}H_{40}N_4O_{12}Mn_4S_4$: C, 54.11; H, 2.97; N, 4.13; S, 9.45. Found: C, 54.45; H, 3.01; N, 4.04; S, 8.98. ^{1}H NMR (400 MHz, (CD$_3$)$_2$SO, ppm): δ 8.99 (d, 8H, H^2, py), 8.26 (s, 4H (ethylenic)), 7.93 (d, 8H, H^3, py), 7.55 (m, 8H, H^2, Ph), 7.39 (t, 8H, H^3, Ph), 7.26 (m, 4H, H^4, Ph). ^{13}C NMR (100 MHz, (CD$_3$)$_2$SO, ppm): δ 227.1, 218.4 (1:2, CO), 155.8 (C^2, py), 144.6 (C^1, Ph), 140.0 (C^4, py), 133.0 (ethylenic), 131.8 (C^2, Ph), 128.5 (C^3, Ph), 125.5 (C^4, Ph), 121.8 (C^3, py). UV−vis. {λ_{max}^{ab} (CH$_2$Cl$_2$)/(nm) (ε) dm^3 mol^{-1} cm^{-1}}: 230 (63,400) (LIG), 288 (60,314) (LIG), 376 (15,200) (LIG), 449 (9,656) (MLCT). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2023 (m), 2007 (s), 1938 (sh), 1918 (m) cm^{-1}.

*Synthesis of [{(CO)$_3$Mn(μ-SC$_6$H$_4$CH$_3$)$_2$Mn(CO)$_3$}$_2$(μ-bpe)$_2$] (**6**).* Compound **6** was prepared using $Mn_2(CO)_{10}$ (78 mg, 0.2 mmol), *p*-tolyl disulfide (49 mg, 0.2 mmol), *trans*-1,2-bis(4-pyridyl)ethylene (bpe) (36 mg, 0.2 mmol), and trimethylamine *N*-oxide (32 mg 0.4 mmol) by following the procedure adopted for **1**. The reaction mixture was stirred at room temperature for 54 h. The product was isolated as a red solid of [{(CO)$_3$Mn(μ-SC$_6$H$_4$CH$_3$)$_2$Mn(CO)$_3$}$_2$(μ-bpe)$_2$] (**6**). Yield: 95 mg, 67% (based on $Mn_2(CO)_{10}$). Anal. Calc. for $C_{64}H_{48}N_4O_{12}Mn_4S_4$: C, 54.39; H, 3.42; N, 3.96; S, 9.08. Found: C, 54.45; H, 3.39; N, 3.88; S, 9.01. ^{1}H NMR (400 MHz, (CDCl$_3$, ppm): δ 9.15 (s, 8H, H^2, py), 8.95 (s, 4H (ethylenic)), 7.85 (d, 8H, H^3, py), 7.18 (s, 8H, H^2, *p*-tolyl), 7.11 (s, 8H, H^3, *p*-tolyl), 2.37 (s, 12H, CH$_3$, *p*-tolyl). UV−vis. {λ_{max}^{ab} (CH$_2$Cl$_2$)/(nm) (ε) dm^3 mol^{-1} cm^{-1}}: 228 (95,272) (LIG), 288 (82,526) (LIG), 378 (24,720) (LIG), 452 (16,102) (MLCT). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2021 (m), 2006 (s), 1933 (sh), 1917 (m) cm^{-1}.

Crystallographic Structure Determination. Single crystal X-ray structural studies of **1**, **3**, and **5** were performed on an Oxford Diffraction XCALIBUR-EOS CCD equipped diffractometer, with an Oxford Instrument low-temperature attachment. Crystal data were collected at 150 K using graphite-monochromated Mo Kα radiation (λ_α = 0.7107 Å). CrysAlisPro CCD software was used to evaluate the data collection. The data were collected by a standard ψ−ω scan method and were scaled and reduced using CrysAlisPro, version 1.171.36.21 software. The structures were solved by direct methods using SHELXS and refined by full matrix least-squares with SHELXL[22] refining on F^2. The positions on all the atoms were obtained by direct methods. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 × U_{eq} of their parent atoms. In compound **5**, atoms C26, C27, C28, C29, and C30 of the phenyl group are positionally disordered with an occupancy ratio of 54/46, and atom C49 is positionally disordered with 74/26 occupancy. Furthermore, atoms C50, C51, C52, C53, and C54 of the phenyl group exhibit positional disorder with an occupancy ratio of 63/37, while atom C55 of the phenyl group has two disordered positions with 53/47 occupancy. Atoms C56, C57, C58, C59, and C60 of the phenyl group are positionally disordered with an occupancy ratio of 73/27 and atoms C35, C36, O11, and O12 of the carbonyl group show positional disorder with an occupancy ratio of 56/44.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01118.

Crystallographic data and structure refinement details of **1** (CCDC No. 1401269), **3** (CCDC No. 1401270), **3**.pyrene (CCDC No. 1401271), **5** (CCDC No. 1401272) (PDF)

X-ray data (CIF)

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: manimaran.che@pondiuni.edu.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Department of Science and Technology, Government of India for financial support. C.A.K. acknowledges University Grants Commission, Government of India for a research fellowship. We are grateful to the Central Instrumentation Facility, Pondicherry University for providing spectral data. We are thankful for the DST-FIST program sponsored Single-crystal X-ray Diffraction Facility of the Department of Chemistry, Pondicherry University.

■ DEDICATION

Dedicated to Professor Pradeep Mathur on the occasion of his 60th birthday.

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