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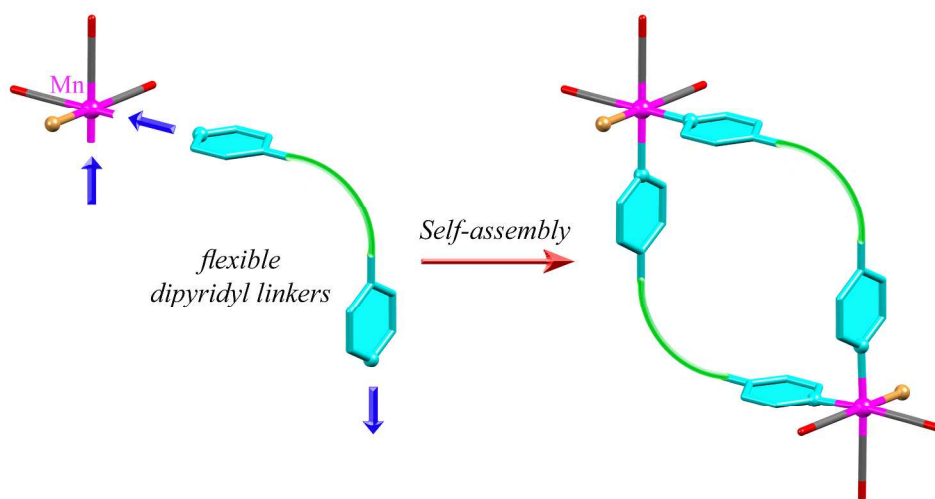
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Self-Assembly of *fac*-Mn(CO)₃-Core Containing Dinuclear Metallacycles Using Flexible Ditopic Linkers

S. Karthikeyan, R. Nagarajaprakash, Garisekurthi Satheesh, Chowan Ashok Kumar, and Bala. Manimaran*



Flexible dimanganese metallacycles have been achieved using Mn(CO)₅Br and adaptable ditopic pyridyl linkers. The host–guest chemistry of Mn(I)-dinuclear metallacycles have been explored.

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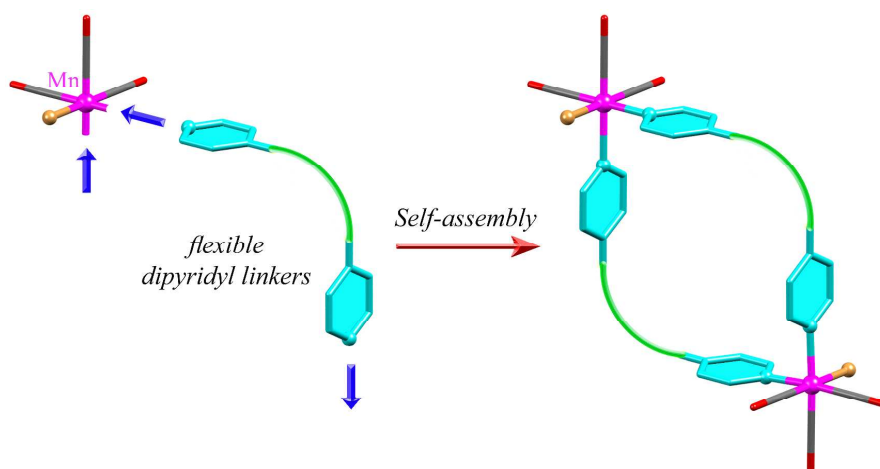
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Flexible dimanganese metallacycles have been achieved using Mn(CO)₅Br and adaptable ditopic pyridyl linkers. The host–guest chemistry of Mn(I)-dinuclear metallacycles have been explored.

Abstract

Syntheses of manganese(I)-based dinuclear metallacycles have been accomplished in facile one-pot reaction conditions at room temperature. Self-assembly of four components has resulted into the formation of M_2L_2 -type metallacycles $[Mn(CO)_3Br(\mu-NLN)]_2$ (**1–5**) using pentacarbonylbromomanganese as metal precursor and flexible ligands such as 1,2-bis(4-pyridyl)ethane (bpa), 1,2-bis(4-pyridyl)propane (bpp), 1,2-ethanediyl di-4-pyridine carboxylate (edp), 1,4-butanediyl di-4-pyridine carboxylate (budp), and 1,6-hexanediyl di-4-pyridine carboxylate (hedp) as linkers. The metallacycles have been characterized on the basis of IR, NMR, UV–vis, and ESI-Mass spectroscopic techniques and single-crystal X-ray diffraction methods. The host capability of the metallacycles has been demonstrated using single-crystal X-ray crystallography.

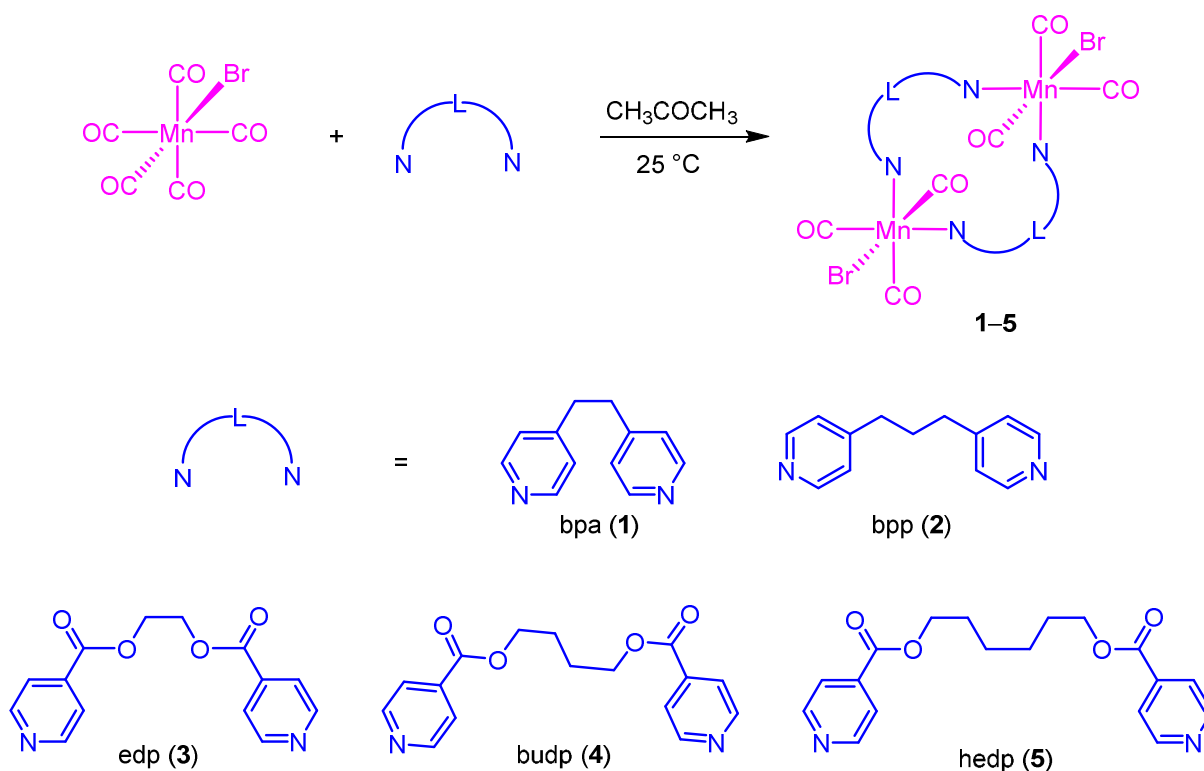
Keywords: Self-assembly; Manganese carbonyl; dinuclear metallacycles; host–guest chemistry.

Introduction

Over the past two decades, significant progress has been made towards the design and synthesis of discrete supramolecules via metal-directed self-assembly process.¹ There are numerous reports available in the literature for the construction of metallasupramolecular architectures like molecular triangles, molecular squares, molecular rectangles, prisms, cages, and other polyhedra.²⁻⁶ These architectures are important building blocks of modern supramolecular chemistry based on which, several applications such as molecular recognition, catalysis, selective guest inclusion, chemical sensors, and gas separation and storage have been demonstrated.⁷ Therefore, the synthesis of metallamacrocycles with specific topologies has received a great deal of attention. The size and shape of metallamacrocycles could be determined by the nature of bridging ligands and metal ions involved.⁸ Fujita, Stang, and Hupp reported a variety of metallacycles, whose size and topology were predetermined with the aid of directing-metallocorners and rigid organic linkers.⁹ However, in recent times, the use of flexible bridging ligands in the construction of supramolecular architectures has gained significant attention owing to their potential advantages such as adaptive recognition properties, breathing ability in solid state, and the possibility for the construction of unprecedented frameworks.^{10,11} Stang et al. established the synthesis of dinuclear metallacycles using cis-protected square-planar Pd(II) and Pt(II) metal centers and ester-containing flexible dipyridyl ligands.¹² Complex cationic structures with Pd(II)/Pt(II) metallocorners were synthesized using amide-based linkers.¹³ Self-assembly of osmium(VI)-based binuclear macrocycles from osmium tetroxide and a mixture of dipyridyl ligands and 2,3-dimethyl-2-butene were reported by Jeong and co-workers.¹⁴ Moreover, metallacycles based on various metal centers such as Re, Cu, Ag, Au etc., were also developed using flexible organic linkers.¹⁵ Some of these macrocyclic host systems were capable of changing their cavity dimensions depending upon the size and shape of the guest molecules. The ability of such host systems to change the cavity size and shape could be attributed to the flexibility

of the bridging ligands.¹⁶ Although, several examples for flexible discrete metallacycles are available, systems incorporating *fac*-Mn(CO)₃ cores are hitherto unknown and their host-guest chemistry remain unexplored.¹⁷ Despite difficulties involved in the synthesis of Mn(I)-based metallacycles, we have recently reported a series of Mn(I)-based supramolecular squares using rigid linkers.¹⁸ Herein, we describe the facile one-step self-assembly of Mn(I)-dinuclear metallacycles [Mn(CO)₃Br(μ -NLN)]₂ (**1–5**) in excellent yields, from a mixture of Mn(CO)₅Br and flexible ditopic ligands (NLN = 1,2-bis(4-pyridyl)ethane (bpa), 1,2-bis(4-pyridyl)propane (bpp), 1,2-ethanediyl di-4-pyridine carboxylate (edp), 1,4-butanediyl di-4-pyridine carboxylate (budp), and 1,6-hexanediyl di-4-pyridine carboxylate (hedp)). Metallacycles **1–5** were characterized using spectroscopic techniques. The self-assembly of dinuclear metallacycles **1** and **3** was monitored *in-situ* by ¹H NMR spectroscopy to evidence the exclusive formation of a single product. The molecular structures for compounds **2** and **3** were obtained using single-crystal X-ray diffraction methods. The host capability of Mn(I)-metallacycles has been evidenced by single-crystal X-ray structures of host-guest systems.

Results and Discussion



Scheme 1 One-Step Self-Assembly of Dinuclear Metallacycles **1–5**.

Reaction of $\text{Mn(CO)}_5\text{Br}$ with flexible dipyriddy ligands (NLN) in equimolar ratio in acetone medium at room temperature, resulted in the formation of dinuclear metallacycles of M_2L_2 -type with general formula $[\text{Mn(CO)}_3\text{Br}(\mu\text{-NLN})]_2$ (**1–5**), NLN = bpa (**1**), bpp (**2**), edp (**3**), budp (**4**), and hedp (**5**) (Scheme 1). The synthesis and purification of compounds **1–5** were performed under dark conditions owing to the light sensitive nature of Mn(I)-based compounds. The dinuclear metallacycles **1–5** were characterized using NMR, IR, UV-vis, and ESI-Mass spectroscopic techniques. The ^1H NMR spectra of compounds **1–5** displayed appropriate signals for the bidentate linkers, which were significantly shifted in comparison to the signals of free ligands, indicating coordination of ligands to Mn centers.¹⁹ The ^{13}C NMR spectra of **1–3** displayed signals relevant to various types of carbons present in the dipyriddy linkers. The IR spectra of **1–5** exhibited three

strong bands in the region $\nu_{(\text{CO})}$ 2032–1899 cm^{-1} , characteristic of *fac*- $\text{Mn}(\text{CO})_3$ moieties.²⁰ The electronic absorption spectra of **1–5** showed intense higher energy bands between λ_{max} 226–310 nm for ligand-centered transitions and weak lower energy bands in the range λ_{max} 375–385 nm due to MLCT transitions.²¹ ESI-Mass spectra of **1–5** displayed the molecular ion peaks for intact metallacycles that conclusively established their M_2L_2 composition and the details were given in Experimental Section.

Metallacycles **1–5** were obtained as a single product from the self-assembly process. To evidence this, the self-assembly of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpa})]_2$ (**1**) was monitored *in situ* by ^1H NMR spectroscopy.²² Reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with 1,2-bis(4-pyridyl)ethane (bpa) was carried out in an NMR tube in acetone- d_6 at 25 °C. The progress of this reaction was monitored by recording ^1H NMR spectra of the reaction mixture at one-hour intervals. Initially, the signals of H^2 and H^3 pyridyl, and methylene protons of the free ligand 1,2-bis(4-pyridyl)ethane appeared at δ 8.46, 7.23, and 3.00 ppm, respectively. After one hour, the proton signals corresponding to **1** appeared at δ 8.59, 7.12 and 3.13 ppm. As the reaction proceeded, the intensities of free ligand signals decreased, while the intensities of signals corresponding to **1** increased, indicating the formation of product. The self-assembly process was completed in six hours, at which time the signals of free ligands had disappeared completely and the signals corresponding to **1** alone were present. The appearance of proton signals of **1** and the absence of any additional signal, supported that the metallacycle **1** is the exclusive product formed from the self-assembly process. The stack plot of time-dependent ^1H NMR spectra is given in Fig. S1. Self-assembly of $\text{Mn}(\text{CO})_5\text{Br}$ and edp leading to the formation of metallacycle **3** was also monitored *in situ* by ^1H NMR spectroscopy. The ^1H NMR spectra recorded during the course of this reaction showed identical trend as observed for **1** that validated the formation of **3** as a single product from the self-assembly of four components (Fig. S2).

After several attempts to grow single-crystals for compounds 1–6, we first succeeded in obtaining good quality crystals for compound 3 by slow evaporation of its dichloromethane solution under dark conditions. Single-crystal X-ray analysis revealed that compound 3 had crystallized as $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**3a**) in monoclinic space group $P2_1/c$. The crystallographic data are given in Table S1 and selected bond lengths and bond angles are given in Table 1.

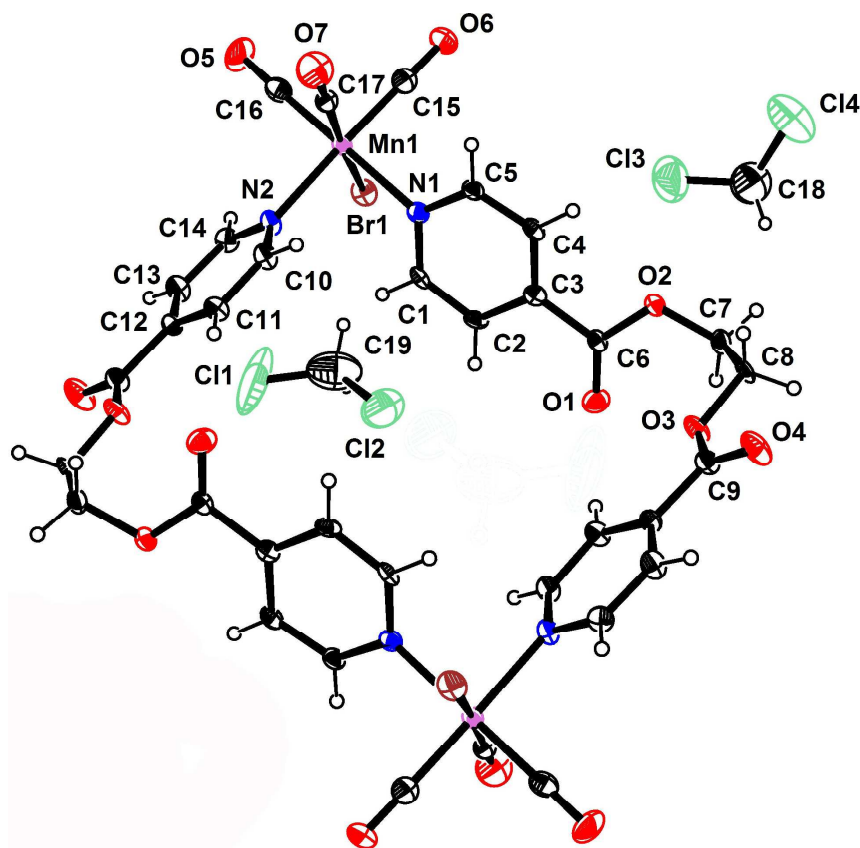


Fig. 1 ORTEP diagram of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**3a**) with thermal ellipsoids at the 50% probability level.

The ORTEP diagram of **3a** (Fig. 1) revealed a bimetallic square architecture, wherein, two manganese centers present at the two diagonal corners are linked by two 1,2-ethanediyl-di-4-pyridinecarboxylate ligand units. Selected bond lengths and bond angles are listed in Table 1. The dimensions of the bimetallic square are $\sim 8.43 \times 9.21$ Å and the distance between two diagonal manganese atoms is ~ 12.04 Å. Each manganese atom is bonded to three terminal CO groups, one

bromine atom and two nitrogen atoms from two 1,2-ethanediyl-di-4-pyridinecarboxylate linkers, giving rise to a distorted octahedral geometry around it. Atom Br(1) is substitutionally disordered with the *trans* CO group with occupancy of 90/10.²³ Promisingly, the molecular structure of **3a** exposed its host capability. Two dichloromethane guest molecules are partially encapsulated in the cavity of host that are stabilized by C...Cl interactions between C(9) of ester carbon of **3a** with Cl(3) of dichloromethane with a distance of 3.349 Å (Fig. 2).²⁴ Additionally, two molecules of dichloromethane sit above and below **3a** and C-H...Br interactions are observed between H(19A) of dichloromethane and Br(1) of **3a** at a distance of 2.962 Å.²⁵ An intermolecular C-H...Cl type hydrogen bonding interaction is existent between the dichloromethane guest molecules with a distance of 2.874 Å. The host molecule is packed with infinite channels in its solid state and the dichloromethane guest molecules are entrapped in these channels (Fig. S3).

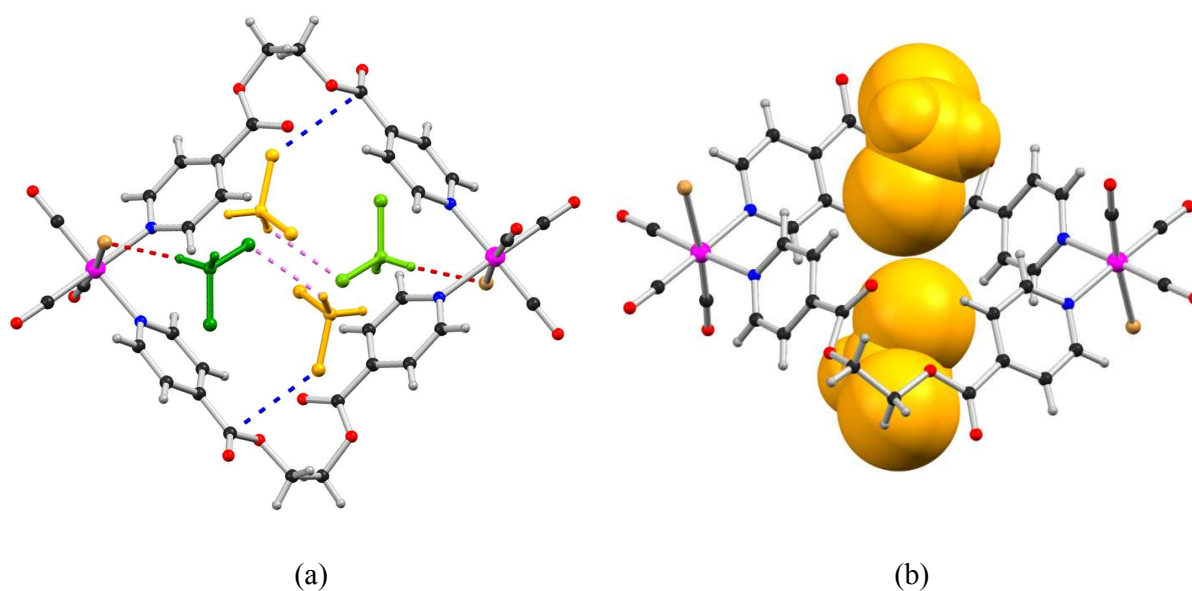


Fig. 2 (a) Top view of **3a** showing C...Cl interactions (blue dotted lines) and C-H...Br interactions (red dotted lines) between the host and dichloromethane guests. C-H...Cl hydrogen bonding interactions between the guests are shown in pale pink dotted lines. (b) Side view of **3a** showing partially entrapped dichloromethane molecules (space filling representation).

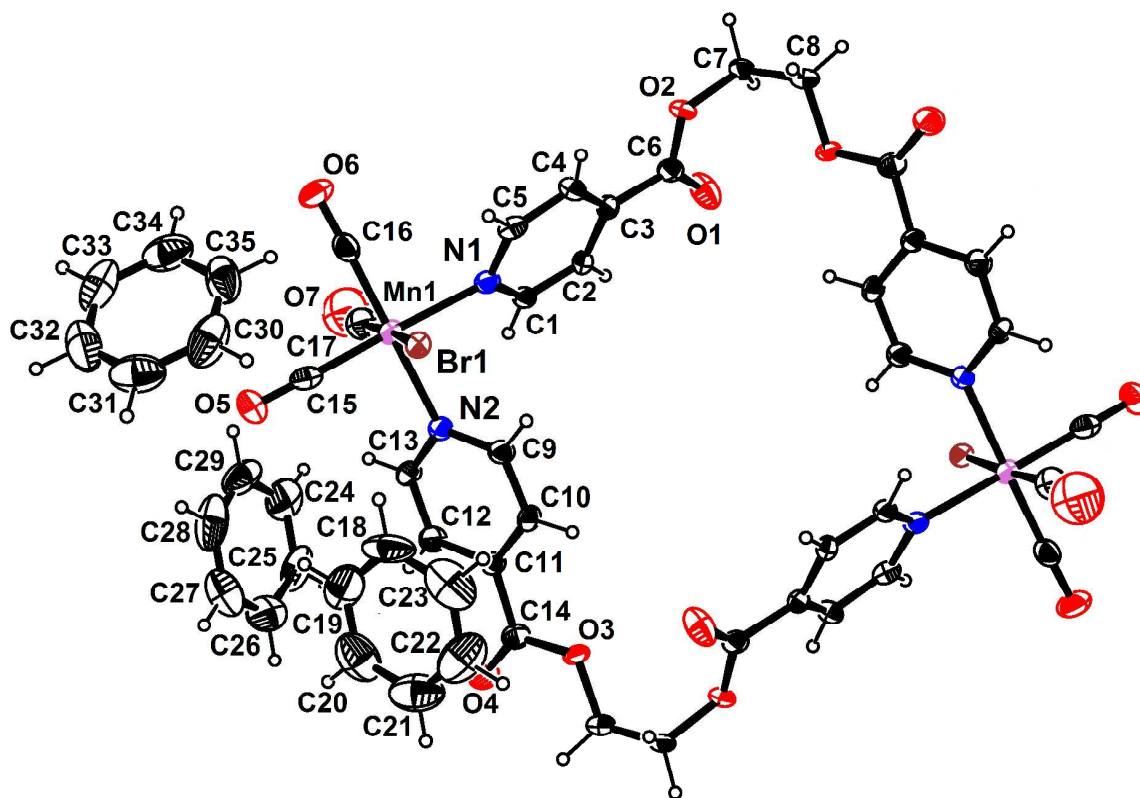
Table 1 Selected Bond Lengths (Å) and Angles (deg) for **3a**

Mn(1)–N(1)	2.095(5)	N(1)–Mn(1)–N(2)	87.72(19)
Mn(1)–N(2)	2.080(5)	N(1)–Mn(1)–Br(1)	87.16(14)
Mn(1)–Br(1)	2.5315(12)	N(2)–Mn(1)–Br(1)	90.25(14)
Mn(1)–C(15)	1.801(7)	C(15)–Mn(1)–N(1)	91.4(2)
Mn(1)–C(16)	1.806(7)	C(16)–Mn(1)–N(1)	176.1(3)
Mn(1)–C(17)	1.814(6)	C(17)–Mn(1)–N(1)	95.8(3)

Following the initial success in determining the molecular structure of dinuclear metallacycles, which also demonstrated their host potential, we endeavoured to grow their single-crystals in the presence of aromatic guests. Compound **3** was again crystallized from its dichloromethane solution in the presence of benzene. Single-crystal X-ray analysis revealed that compound **3** has crystallized as $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2 \cdot 3\text{C}_6\text{H}_6$ (**3b**) that confirmed the formation of host–guest complex. The ORTEP diagram of **3b** is shown in Fig. 3 and selected bond lengths and bond angles are listed in Table 2. Host–guest complex **3a** crystallized in triclinic space group $P\bar{1}$. Both **3a** and **3b** displayed near-identical structural arrangements. Atom Br(1) is substitutionally disordered with the *trans* CO group at 83/17 occupancy.²³ Significantly, two molecules of guest benzene are partially hosted in the cavity of **3b** as seen from its packing arrangement (Fig. 4a). It is worth recalling that dichloromethane had occupied the cavity of **3a** when crystallized in dichloromethane in the absence of benzene. However, when both dichloromethane and benzene are present in the mother liquor, it appears that benzene wins the competition, probably aided by the hydrophobic interior of the host cavity. The benzene guest molecules are stabilized by CH $\cdots\pi$ interactions between the pyridine hydrogens and π clouds of benzene guests (CH(9) $\cdots\pi$ (benzene centroid) distance = 3.005 Å). Also, the hydrogen atoms of benzene guests form CH \cdots O type hydrogen bonding with oxygen atom of ester C=O groups present in the host (CH(26) \cdots O(1) distance = 2.470 Å). Apart from the two benzene molecules present in the cavity, five more are existent in the periphery of **3b**. The host and the guest benzene molecules are found to be favoured by several CH $\cdots\pi$ interactions and a $\pi\cdots\pi$ interaction (Fig. 4b).

Table 2 Selected Bond Distances and Bond Angles for **3b**

Mn(1)–N(1)	2.081(2)	N(1)–Mn(1)–N(2)	88.11(8)
Mn(1)–N(2)	2.093(2)	N(1)–Mn(1)–Br(1)	89.16(6)
Mn(1)–Br(1)	2.5318(6)	N(2)–Mn(1)–Br(1)	90.18(6)
Mn(1)–C(15)	1.807(3)	C(15)–Mn(1)–N(1)	178.21(10)
Mn(1)–C(16)	1.798(3)	C(16)–Mn(1)–N(1)	91.66(11)
Mn(1)–C(17)	1.767(4)	C(17)–Mn(1)–N(1)	92.47(16)

**Fig. 3** ORTEP diagram of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2 \cdot 3\text{C}_6\text{H}_6$ (**3b**) with thermal ellipsoids at the 50% probability level.

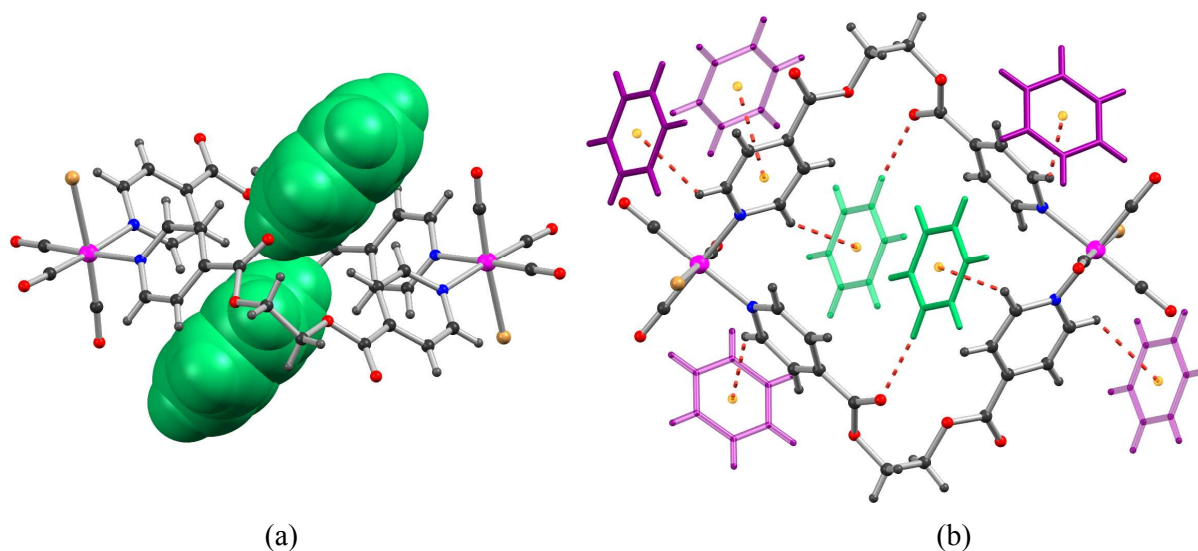


Fig. 4 (a) Side view of host **3b** showing two benzene guest molecules (green color) partially encapsulated into the host cavity (b) Top view of **3b** displaying soft interactions (red dotted lines) between the host and guest molecules (benzene molecules shown in purple color are present outside the host cavity).

Furthermore, we were also able to obtain good quality single-crystals of host-guest complex $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpp})]_2 \cdot \text{triphenylene} \cdot \text{CH}_3\text{COCH}_3$ (**2a**) from an acetone solution of **2** in presence of triphenylene. **2a** crystallized in monoclinic space group $P2_1/c$. The ORTEP drawing of **2a** is shown in Fig. 5, and selected bond lengths and bond angles are given in Table 3. Molecular structure of **2a** adopted a rectangular architecture, in which, two manganese centers are present at two diagonal corners that are linked via two units of 1,2-bis(4-pyridyl)propane. In **2a**, each manganese atom is in a distorted octahedral geometry with three terminal CO groups, one Br atom and two 1,2-bis(4-pyridyl)propane units surrounding it. The dimensions of the metallacycle **2a** are $\sim 8.62 \times 6.38 \text{ \AA}$. The distance between two diagonal manganese atoms is $\sim 11.33 \text{ \AA}$. More importantly, the X-ray structure of **2a** shows the presence of one triphenylene molecule and one acetone molecule per asymmetric unit of **2a**.

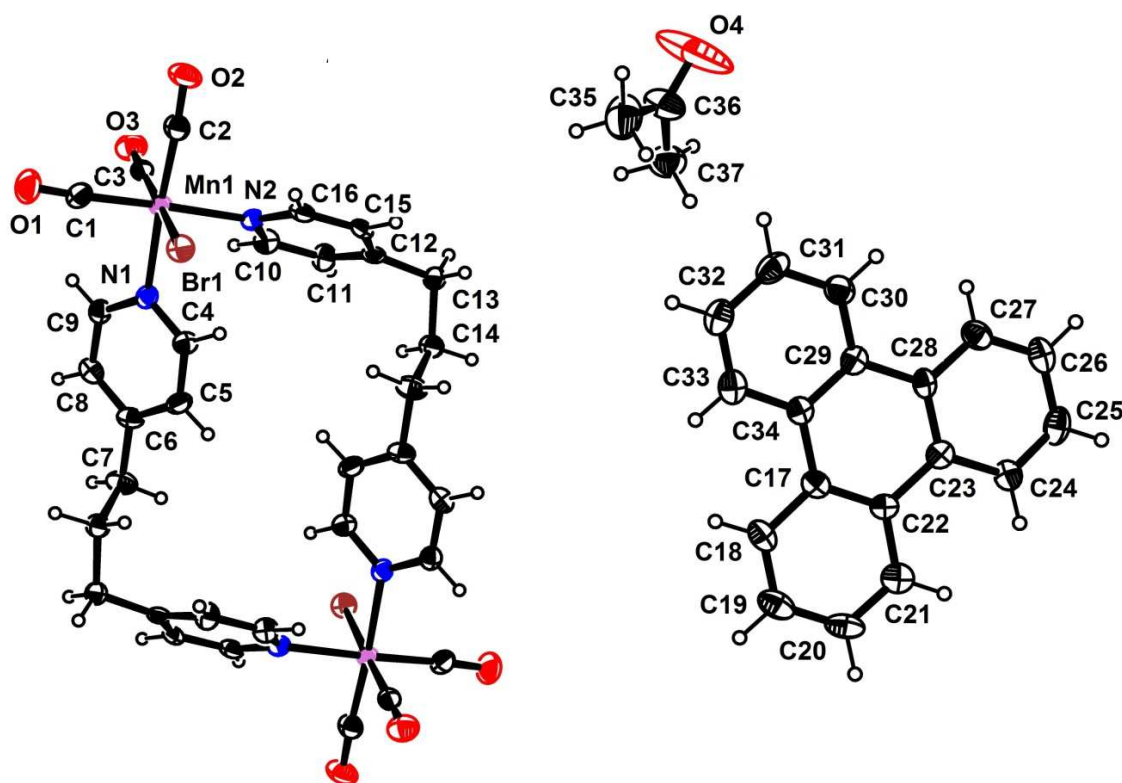


Fig. 5 ORTEP diagram of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpp})]_2 \cdot \text{triphenylene} \cdot \text{CH}_3\text{COCH}_3$ (**2a**) with thermal ellipsoids drawn at 50% probability level.

Molecular structure of **2a** shows interesting packing arrangement in the solid state. Each host molecule is surrounded by four guest triphenylene molecules in a sandwich manner and are stabilized by several reciprocal $\text{CH} \cdots \pi$ interactions (Fig. S6a).^{7a,26} Two of four triphenylene molecules sit above and below the host (parallel to the plane of host molecule) and the remaining two guests are present at the lateral positions (Fig. 6 and 7). However, the triphenylene is not encapsulated in the cavity of **2a** by virtue of its larger size in comparison with the cavity dimension of **2a**. Furthermore, it is presumed that the triphenylene guests have effectively pushed the acetone guests away from the cavity of **2a**, probably due to their strong preference for the hydrophobic environment of the host cavity. The $\text{CH} \cdots \pi$ interaction distances are in the range 2.959–3.382 Å. A $\text{CH} \cdots \text{Br}$ type hydrogen bonding is also observed between the aromatic hydrogen of triphenylene and

Br atom bonded to Mn ((triphenylene)CH(21)···Br(1) distance = 3.005 Å). In addition, two molecules of acetone linked two host molecules via CH···O hydrogen bonding interactions, which are operative at a distance of 2.692–2.719 Å (Fig. S6b).²⁷

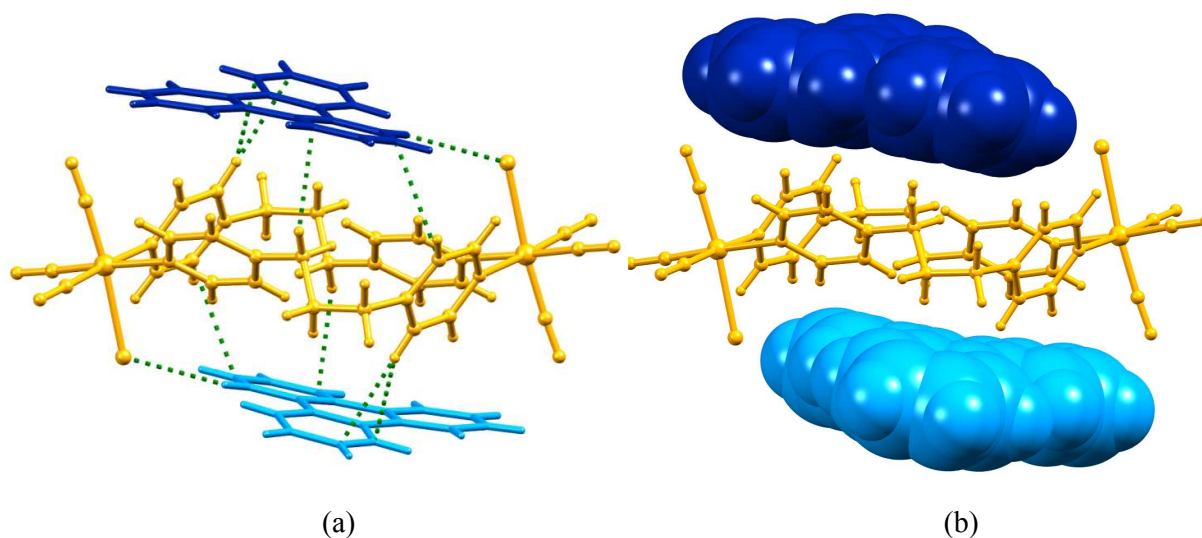


Fig. 6 (a) Side view of host (orange color) **2a** showing two triphenylene guests (blue color) sit above and below the plane host with C–H··· π interactions. (b) Side view of **2a** with triphenylene guests in space filling representation.

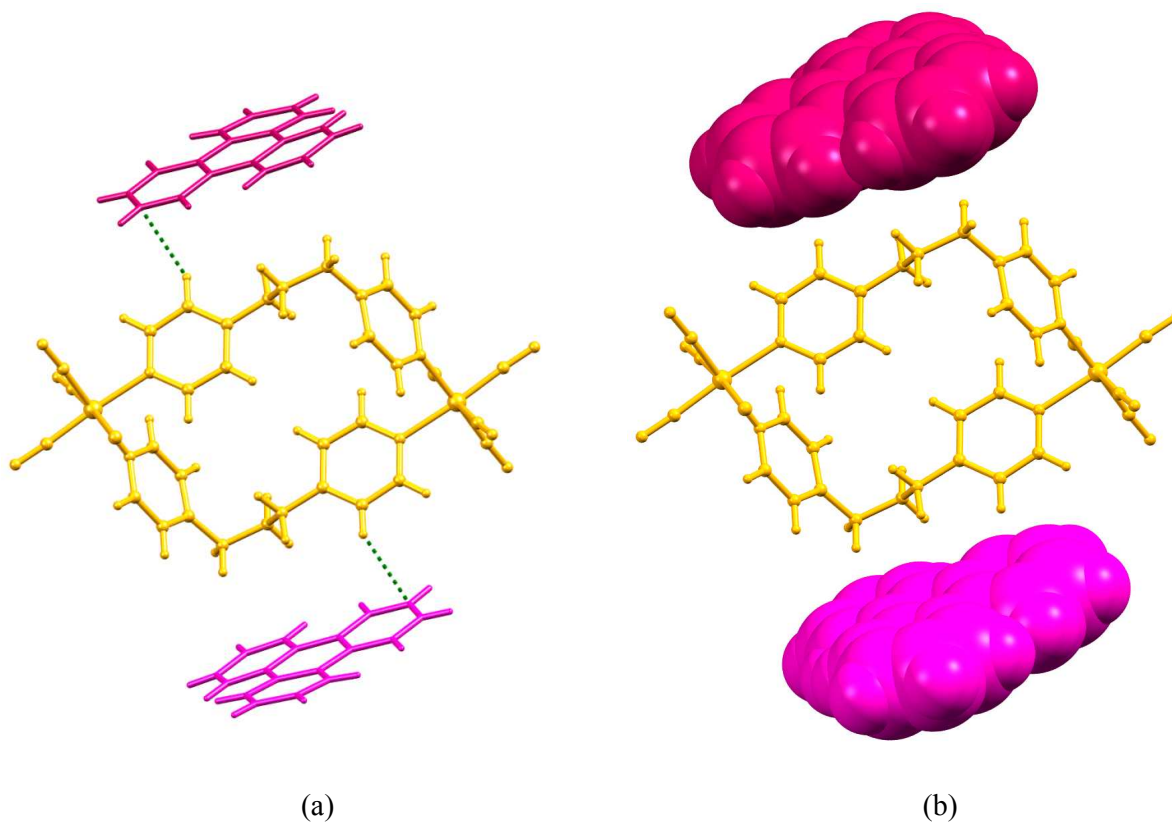


Fig. 7 (a) Top view of host **2a** (orange color) showing C–H... π interactions with two triphenylene guest molecules (pink color) located at lateral space. (b) Top view of **2a** with triphenylene guests in space filling representation.

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

Mn(1)–N(1)	2.102(5)	N(1)–Mn(1)–N(2)	85.10(17)
Mn(1)–N(2)	2.078(5)	N(1)–Mn(1)–Br(1)	88.71(13)
Mn(1)–Br(1)	2.5429(10)	N(2)–Mn(1)–Br(1)	91.45(12)
Mn(1)–C(1)	1.805(6)	C(1)–Mn(1)–N(1)	93.6(2)
Mn(1)–C(2)	1.794(6)	C(2)–Mn(1)–N(1)	176.1(2)
Mn(1)–C(3)	1.819(7)	C(3)–Mn(1)–N(1)	95.0(2)

CONCLUSIONS

In conclusion, we have synthesized a series of novel manganese(I)-based dinuclear metallacycles using flexible ditopic ligands via metal-directed self-assembly process. The dinuclear metallacycles have been characterized on the basis of IR, NMR, UV–vis, and mass spectroscopic techniques. The self-assembly process monitored *in situ* using ^1H NMR spectroscopy, supported the formation of single discrete species. Notably, the utilization of ditopic linkers of different lengths possessing

varying degree of flexibility has enabled us to tune the dimensions and modify the topologies of metallacycles. Metallacycle **2** adopted a rectangular architecture, while **3** embraced a square topology as evidenced from their single-crystal X-ray structures. Furthermore, the host capability of metallacycles demonstrated via X-ray structures has revealed the potentiality of Mn(I)-based supramolecules in molecular recognition and their guest preferences.

EXPERIMENTAL SECTION

General Details. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to standard methods and distilled prior to use.²⁸ Reaction, workup and crystallization of all manganese(I)-based compounds were carried out under dark conditions. $\text{Mn}(\text{CO})_5\text{Br}$ was prepared following literature procedure.²⁹ 1,2-bis(4-pyridyl)ethane (bpa) and 1,2-bis(4-pyridyl)propane (bpp) were used as received. 1,2-ethanediyldi-4-pyridinecarboxylate (edp) 1,4-butanediyl di-4-pyridine carboxylate (budp) and 1,6-hexanediyl di-4-pyridine carboxylate (hedp) were synthesized by literature methods.^{13,30} IR spectra were recorded on a Nicolet-6700 FT-IR spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu UV-2450 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Elemental analyses were performed in a Micro Cube CHN analyser. Compounds **1–5** were dried thoroughly under high-vacuum conditions for several hours, prior to the submission of samples for ^1H and ^{13}C NMR spectral characterization and elemental analyses.

Synthesis of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpa})]_2$ (1**).** A mixture of $\text{Mn}(\text{CO})_5\text{Br}$ (55 mg, 0.2 mmol) and 1,2-bis(4-pyridyl)ethane (bpa) (37 mg, 0.2 mmol) was placed in a 100 mL 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 acetone (40 mL), and the reaction mixture was stirred at 25 °C for 30 h

under dark conditions. The solvent was removed using vacuum and the product was washed with hexane and dried under vacuum; a yellow solid of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpa})]_2$ (**1**) was obtained. Yield: 74 mg, 92%. Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}_6\text{Br}_2\text{Mn}_2$: C, 44.69; H, 3.00; N, 6.95. Found: C, 44.16; H, 2.94; N, 6.89. IR (KBr, cm^{-1}): ν_{CO} 2024 (s), 1936 (s), 1907 (s). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$, ppm): δ 8.59 (m, 8H, H^2 , py), 7.12 (m, 8H, H^3 , py), 3.13 (m, 8H, CH_2). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$, ppm): δ 223.7 (s, CO), 155.4 (C^2 , py), 153.2 (C^4 , py), 126.6 (C^3 , py), 36.5 (CH_2). UV-vis ($\lambda_{\text{max}}^{\text{ab}}$ (CH_2Cl_2), nm): 246, 310 (LIG); 375 (MLCT). HRMS (ESI) Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}_6\text{Br}_2\text{Mn}_2\text{Na}$, $[\text{M}+\text{Na}]^+$: m/z 826.8721; found: 826.8684.

Synthesis of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpp})]_2$ (2**).** Compound **2** was synthesized by following the procedure adopted for **1**, using $\text{Mn}(\text{CO})_5\text{Br}$ (55 mg, 0.2 mmol) and 1,2-bis(4-pyridyl)propane (bpp) (40 mg, 0.2 mmol). The product obtained was washed with hexane and dried under vacuum; a yellow solid of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpp})]_2$ (**2**) was isolated. Yield: 77 mg, 92%. Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{N}_4\text{O}_6\text{Br}_2\text{Mn}_2$: C, 46.07; H, 3.38; N, 6.72. Found: C, 46.54; H, 3.34; N, 6.65. IR (KBr, cm^{-1}): ν_{CO} 2024 (s), 1933 (s), 1902 (s). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$, ppm): δ 8.59 (s, 8H, H^2 , py), 7.25 (s, 8H, H^3 , py), 2.80 (s, 8H, CH_2), 2.04 (s, 4H, CH_2). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$, ppm): δ 223.8 (s, CO), 155.3 (C^2 , py), 154.8 (C^4 , py), 126.0 (C^3 , py), 34.9 (CH_2), 33.6 (CH_2). UV-vis ($\lambda_{\text{max}}^{\text{ab}}$ (CH_2Cl_2), nm): 243, 309 (LIG); 385 (MLCT). HRMS (ESI) Calcd for $\text{C}_{32}\text{H}_{29}\text{N}_4\text{O}_6\text{Br}_2\text{Mn}_2$, $[\text{M}+\text{H}]^+$: m/z 832.9214; found: 832.9128.

Synthesis of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2$ (3**).** Compound **3** was synthesized by following the procedure adopted for **1**, using $\text{Mn}(\text{CO})_5\text{Br}$ (27 mg, 0.1 mmol) and 1,2-ethanediyldi-4-pyridinecarboxylate (edp) (27 mg, 0.1 mmol). The product obtained was washed with hexane and dried under vacuum; a yellow solid of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2$ (**3**) was isolated. Yield: 44 mg, 90%. Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_4\text{O}_{14}\text{Br}_2\text{Mn}_2$: C, 41.57; H, 2.46; N, 5.70. Found: C, 40.83; H, 2.41; N, 5.63. IR (KBr, cm^{-1}): ν_{CO} 2030 (s), 1947 (s), 1899 (s), $\nu_{\text{ester C=O}}$ 1731 (s). ^1H NMR (400 MHz, CDCl_3 , ppm): δ

8.98 (d, 8H, H², py), 7.80 (d, 8H, H³, py), 4.71 (m, 8H, OCH₂). ¹³C NMR (100 MHz, (CD₃)₂CO, ppm): δ 222.1 (s, CO), 164.6 (ester C=O), 157.0 (C², py), 139.9 (C⁴, py), 124.9 (C³, py), 64.9 (CH₂). UV-vis (λ_{max}^{ab} (CH₂Cl₂), nm): 226, 263 (LIG), and 383 (MLCT). HRMS (ESI) Calcd for C₃₄H₂₅N₄O₁₄Br₂Mn₂, [M+H]⁺: *m/z* 980.8494; found: 980.8413.

Synthesis of [Mn(CO)₃Br(μ-budp)]₂ (4). Compound **4** was synthesized by following the procedure adopted for **1**, using Mn(CO)₅Br (27 mg, 0.1 mmol) and 1,4-butanediyl di-4-pyridine carboxylate (budp) (30 mg, 0.1 mmol). The product obtained was washed with hexane and dried under vacuum; a yellow solid of [Mn(CO)₃Br(μ-budp)]₂ (**4**) was isolated. Yield: 42 mg, 82%. Anal. Calcd for C₃₈H₃₂N₄O₁₄Br₂Mn₂: C, 43.95; H, 3.11; N, 5.4. Found: C, 43.90 ; H, 3.05; N, 5.2. IR (CH₂Cl₂, cm⁻¹): ν_{CO} 2032 (s), 1953 (s), 1915 (s), ν_{ester C=O} 1733 (s). ¹H NMR (400 MHz, (CDCl₃, ppm): δ 8.94 (s, 8H, H², py), 7.82 (s, 8H, H³, py), 4.44 (s, 8H, OCH₂), 1.91 (s, 8H, CH₂). UV-vis (λ_{max}^{ab} (CH₂Cl₂), nm): 229, 265 (LIG); 380 (MLCT). HRMS (ESI) Calcd for C₃₈H₃₃N₄O₁₄Br₂Mn₂ [M+H]⁺: *m/z* 1036.9120; found: 1036.9120.

Synthesis of [Mn(CO)₃Br(μ-hedp)]₂ (5). Compound **5** was synthesized by following the procedure adopted for **1**, using Mn(CO)₅Br (27 mg, 0.1 mmol) and 1,6-hexanediyl di-4-pyridine carboxylate (hedp) (33 mg, 0.1 mmol). The product obtained was washed with hexane and dried under vacuum; a yellow solid of [Mn(CO)₃Br(μ-hedp)]₂ (**5**) was isolated. Yield: 43 mg, 79%. Anal. Calcd for C₄₂H₄₀N₄O₁₄Br₂Mn₂: C, 46.09 ; H, 3.68; N, 5.12. Found: C, 46.02 ; H, 3.61; N, 5.09. IR (CH₂Cl₂, cm⁻¹): ν_{CO} 2032 (s), 1950 (s), 1914 (s), ν_{ester C=O} 1731 (s). ¹H NMR (400 MHz, (CDCl₃, ppm): δ 8.93 (s, 8H, H², py), 7.82 (s, 8H, H³, py), 4.38 (s, 8H, OCH₂), 1.79 (s, 8H, CH₂), 1.49 (s, 8H, CH₂). UV-vis (λ_{max}^{ab} (CH₂Cl₂), nm): 230, 260 (LIG); 378 (MLCT). HRMS (ESI) Calcd for C₄₂H₄₁N₄O₁₄Br₂Mn₂ [M+H]⁺: *m/z* 1092.9746; found: 1092.9736.

In Situ ¹H NMR Spectral Study. Mn(CO)₅Br (0.0075 mmol, 2.0 mg) and 1,2-bis(4-pyridyl)ethane (bpa) (0.0075 mmol, 1.3 mg) were dissolved in acetone-*d*₆ (0.5 mL) in an NMR tube under a

nitrogen atmosphere, and the self-assembly of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-bpa})]_2$ (**1**) was monitored *in situ* by ^1H NMR spectroscopy at 25 °C. ^1H NMR spectra of the sample were recorded at one hour intervals for six hours and the stack plot of time-dependent ^1H NMR spectra were obtained. The reaction of $\text{Mn}(\text{CO})_5\text{Br}$ (0.0075 mmol, 2.0 mg) and 1,2-ethanediyldi-4-pyridinecarboxylate (edp) (0.0075 mmol, 2.0 mg) in chloroform-*d* (0.5 mL) leading to the formation of $[\text{Mn}(\text{CO})_3\text{Br}(\mu\text{-edp})]_2$ (**3**) was monitored *in situ* using ^1H NMR spectroscopy by following the procedure adopted for **1**. The self-assembly of **3** was complete at thirty six hours.

Crystallographic Structure Determination. Single-crystal X-ray structural studies of **2a**, **3a**, and **3b** were performed on an Oxford Diffraction XCALIBUR-EOS CCD equipped diffractometer equipped with an Oxford Instrument low-temperature attachment. Data were collected at 150 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda_\alpha = 0.7107 \text{ \AA}$). The strategy for data collection was evaluated using CrysAlisPro CCD software. The crystal data were collected by standard “ ψ - ω scan” techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full-matrix least-squares against F^2 using SHELXL-97 and WinGX.^{31,32} The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 times the U_{eq} value of their parent atoms. The graphics were generated using ORTEP-3.24 and Mercury 3.3.³³

ASSOCIATED CONTENT

Supporting Information

Experimental procedure, figures, and CIF files giving crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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