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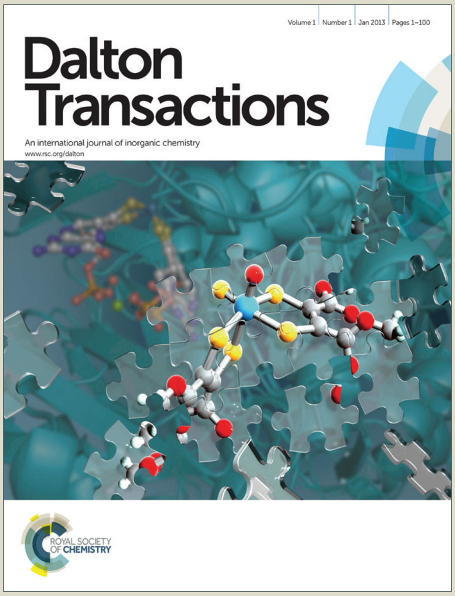

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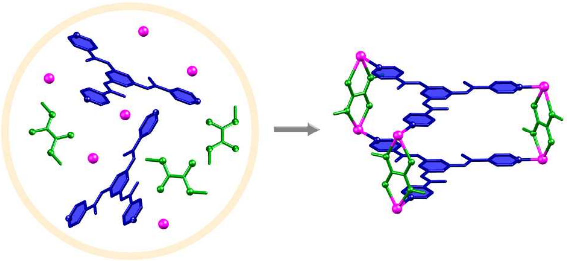


Self-assembly of hexarhenium trigonal prisms using *fac*-$Re(CO)_3$ cores (pink), bischelating oxamide ligands (green) and ester-containing tritopic linkers (blue) has been accomplished via orthogonal bonding approach.

Abstract

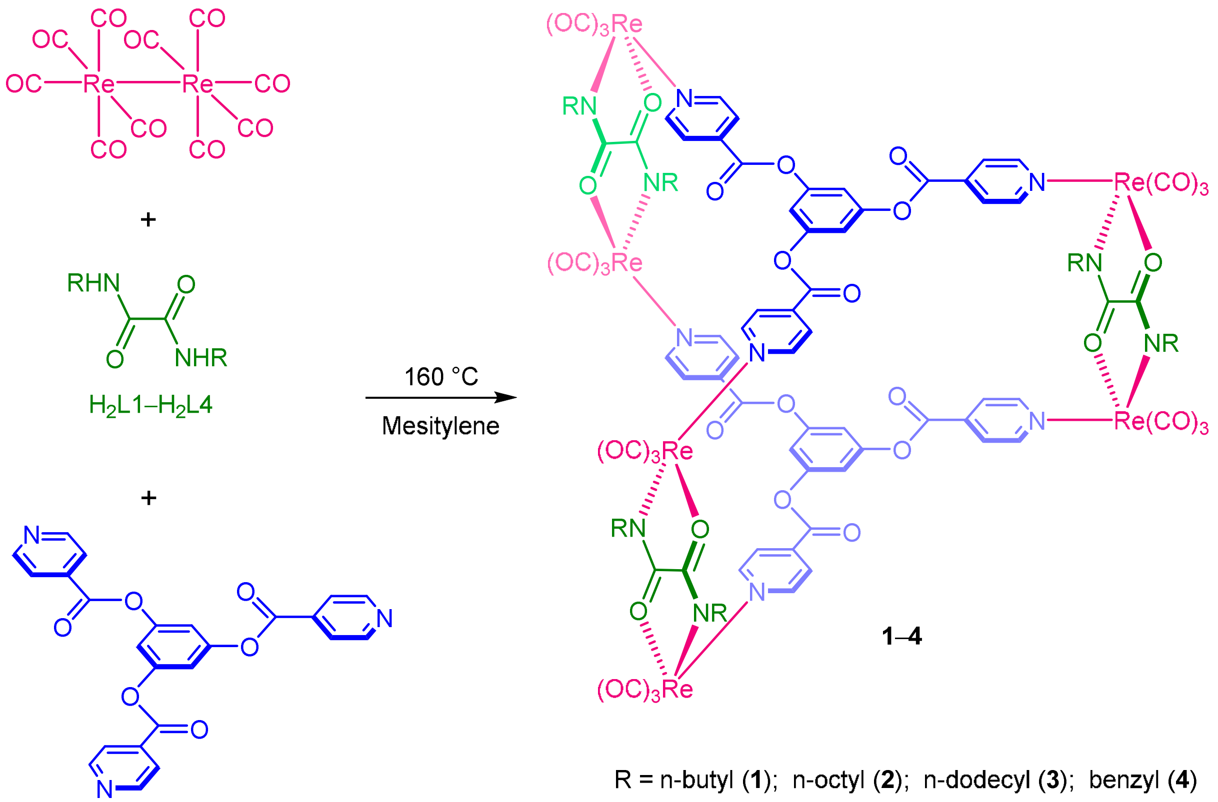
Oxamidato-bridged Re(I)-based hexanuclear trigonal prisms with ester functionality have been synthesised via a multicomponent self-assembly process under solvothermal conditions. Self-assembly of $Re_2(CO)_{10}$, oxamide ligands (H_2L1 = N,N′-dibutyloxamide, H_2L2 = N,N′-dioctyloxamide, H_2L3 = N,N′-didodecyloxamide and H_2L4 = N,N′-dibenzyloxamide) and phenyl-1,3,5-tris(isonicotinate) (ptin) has resulted in the formation of metallaprisms of general formula $[\{(CO)_3Re(\mu\text{-}\eta^4\text{-}L)Re(CO)_3\}_3(\mu_3\text{-ptin})_2]$ (**1**–**4**). Metallaprisms **1**–**4** have been characterised using spectroscopic techniques and the molecular structure of **4** has been elucidated by single-crystal X-ray diffraction methods. Investigations on guest binding ability of **2** with few aromatic alcohols and L-tryptophan using UV–vis and fluorescence spectroscopic titration experiments revealed strong host–guest interactions. Luminescence enhancement studies of **2** and **3** have been carried out using organic-aqueous solvent mixtures.

Keywords: Self-assembly; hexarhenium prisms; molecular recognition; luminescence tuning.

Introduction

Rational design and self-assembly of discrete metallasupramolecular architectures based on metal-ligand coordination motifs have witnessed an exponential growth over the past two decades.[1–9] A multitude of high-symmetry architectures of varied shapes and geometry have been realised by judicious choice of complementary building blocks that are encoded with specific information such as coordination geometry, number of available coordination sites, turning angles, symmetry of bridging units, etc.[10–14] Several of these metallasupramolecules find applications in various fields like host−guest chemistry, chemosensors, molecular devices, separations and catalysis.[15–21] In general, generation of highly symmetrical metallacycles and cages are comparatively straightforward, since they mostly require a simple two-component self-assembly process.[1a,22,23] On the other hand, as the structural complexity of the desired shape increases, precise positioning of molecular components in three-dimensional space becomes increasingly challenging and hence, more sophisticated approaches were required. For example, construction of three-dimensional trigonal prismatic architectures, which is of our current interest, generally involves either a templated synthetic approach or a stepwise process that entail usage of predesigned metal fragments.[24,25] That, the lower symmetry of trigonal prisms endows better selectivity in guest binding is well-known and inspires further development of different metallaprisms.[26,27] Fujita *et al.* have reported on the multicomponent self-assembly of Pd(II)-based trigonal prisms of $M_6L_2L'_3$ type that self-assembled in the presence of aromatic templates.[28] Stang and co-workers have used a Pt(II)-based predesigned bimetallic clip with parallel labile coordination sites disposed in the same direction and a rigid tridentate ligand in 3:2 ratio that led to the formation of prismatic cages.[29] A fair number of Ir(I), Rh(I), Ru(II) and Os(II) based hexanuclear trigonal prisms were obtained via a two-step synthetic methodology.[30–32] Recently, Ir(I) based hexanuclear prisms were obtained via C−H activation-directed multicomponent assembly.[33] In case of Re(I), few trigonal prisms of $M_6L_2L'_6$ and $M_6L_2L'_3$ types were obtained via multicomponent self-assembly process in a single step.[34–37] A survey on the shapes of these $M_6L_2L'_6$ and $M_6L_2L'_3$ type prisms revealed that in most of the cases, triangular faces of the prisms are occupied by rigid tridentate ligands. Although, M_3L_2 type prismatic cages with flexible angular linkers are known, they often require the usage of templates to accomplish the assembly process.[38–40] In contrast, metallaprisms of $M_6L_2L'_6$ or $M_6L_2L'_3$ types, wherein the triangular faces are occupied by flexible tritopic ligands are much less studied. This scarcity is probably due to the less predictable self-assembly process and possibility for the formation of mixture of discrete and polymeric structures when flexible angular units are employed.[41–43] Recently, we have developed few different classes of Re(I)-based discrete metallasupramolecules and explored their potentialities.[44] Herein, we present a new series of hexarhenium trigonal prisms $[\{(CO)_3Re(\mu\text{-}\eta^4\text{-}L)Re(CO)_3\}_3(\mu_3\text{-ptin})_2]$ (**1**–**4**), self-assembled from $Re_2(CO)_{10}$, oxamide ligands (H_2L1–H_2L4) and a semi-rigid tritopic linker, phenyl-1,3,5-tris(isonicotinate) (ptin). Prisms **1**–**4** were engineered via an orthogonal bonding approach and to the best of our knowledge, these are the first examples of $M_6L_2L'_3$ metallaprisms with flexible angular units and oxamidato bridges. Molecular structure for **4** has been determined using single-crystal X-ray diffraction methods. We have intentionally incorporated ester functionality in the prismatic architecture, anticipating guest binding interactions with hydrogen bond donors such as aromatic alcohols. UV–vis and fluorescence spectral titration studies pertinent to guest binding ability of prism **2** with few aromatic alcohols and an amino acid have been carried out. We have also endeavoured to manipulate the luminescence properties of **2** and **3** in organic-aqueous solvent mixtures.

Results and discussion



Scheme 1 Self-Assembly of Re(I)-metallaprisms **1**–**4**

Multicomponent self-assembly of $Re_2(CO)_{10}$, oxamide ligands (H_2L1 = N,N′-dibutyloxamide, H_2L2 = N,N′-dioctyloxamide, H_2L3 = N,N′-didodecyloxamide and H_2L4 = N,N′-dibenzyloxamide) and phenyl-1,3,5-tris(isonicotinate) (ptin) in mesitylene, under solvothermal conditions has resulted in the formation of supramolecular hexarhenium prisms $[\{(CO)_3Re(\mu\text{-}\eta^4\text{-L})Re(CO)_3\}_3(\mu_3\text{-ptin})_2]$ (**1**–**4**) (Scheme 1). The prisms were quite stable and soluble in common organic solvents. IR spectra of **1**–**4** displayed characteristic bands for *fac*-$Re(CO)_3$ core in the range 1892–2027 cm^{-1}.[36] A medium band at 1755 cm^{-1} was due to ester C=O groups. The oxamidato C=O stretching frequency of the complexes appeared as a strong band at around 1597–1602 cm^{-1}, whereas the C=O stretching frequency of the free ligands (H_2L1–H_2L4) appeared at 1650 cm^{-1}. The NH stretching bands of oxamide group were not present in **1**–**4**. These observations indicated the coordination of oxamide ligands with rhenium centers. The electronic absorption spectra of **1**–**4** displayed two intense bands in the region λ_{max}^{ab} 220–280 nm and two weak bands in the region λ_{max}^{ab} 310–400 nm (Fig. S1). The higher energy bands were assigned to intra ligand transitions as evidenced by similar absorption pattern in free ligands and the broad, lower energy bands that were observed solely for complexes were assigned to MLCT transitions by analogy with similar *fac*-$Re(CO)_3$ containing complexes reported in the literature.[36] Photoexcitation of **1**–**4** at λ_{max}^{ab} 388–391 nm resulted in a broad emission centered at λ_{max}^{em} 610–612 nm. The emission quantum yields (Φ_{em}) calculated with reference to $[Ru(bpy)_3]Cl_2$ (bpy = 2,2′-bipyridine) were found to be in the range 3.12×10^{-4}–2.66×10^{-4}. ^{1}H NMR spectra of **1**–**4** displayed relevant signals corresponding to the protons of ptin and oxamidato ligands. Compared to free ligands, the oxamidato proton signals were shifted downfield, whereas the signals due to tritopic pyridyl ligand were shifted upfield in **1**–**4**.[37] ^{13}C NMR spectra of **2**–**4** displayed signals pertaining to different types of carbons present in the prismatic framework.

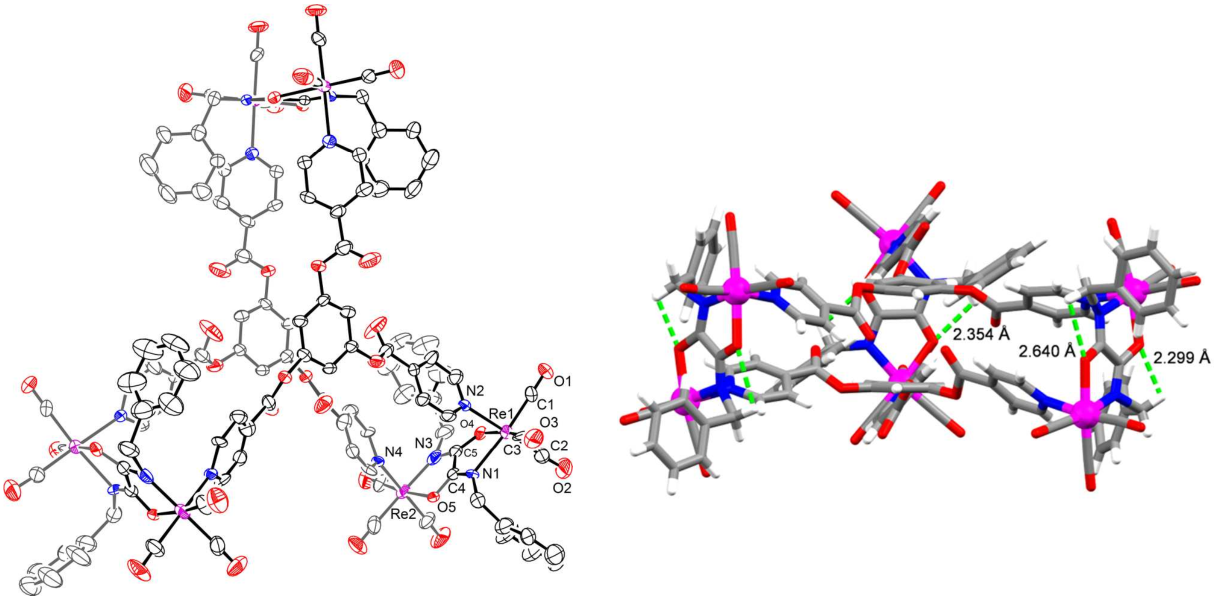


Fig. 1 ORTEP diagram of [{(CO)$_3$Re(μ-η^4-dibenzyloxamidato)Re(CO)$_3$}$_3$(μ_3-ptin)$_2$] (**4**) with thermal ellipsoids drawn at 30% probability level and stick representation of **4** (side view- intramolecular hydrogen bonds are shown in green dotted lines).

The molecular structure of **4** has been determined by single-crystal X-ray diffraction methods. Compound **4** crystallised in monoclinic crystal system in *C2/n* space group and the ORTEP diagram of **4** is shown in Fig. 1. Selected bond lengths and bond angles of **4** are listed in Table 1 and the crystallographic data and structure refinement details are given in Table S1. The ORTEP diagram of **4** revealed a distorted trigonal prismatic architecture of $M_6L_2L'_3$ type, wherein two ptin ligands occupying the opposite trigonal faces are coordinated to three {(CO)$_3$Re(μ-η^4-dibenzyloxamidato)Re(CO)$_3$} pillars. Six rhenium atoms define a triangular metallaprism with ~16.29−17.93 Å trigonal edges and ~5.68 Å pillar heights. Each rhenium center is in a distorted octahedral geometry with three terminal CO groups, one N atom from pyridyl moiety of ptin and one N and O atom from dibenzyloxamidato bridge. In each arm of the prism, the ester C=O groups are oriented *anti* with respect to each other. The benzyl groups of oxamidato bridge are oriented *syn* in one edge, whereas in remaining two edges they are oriented *anti* with respect to each other.

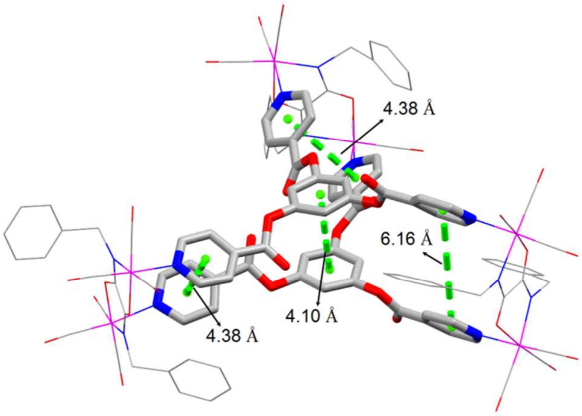


Fig. 2 Parallel π···π stacking distances between two ptin units in **4**.

The centroid···centroid distance between the central benzene rings is 4.10 Å (Fig. 2). The centroid···centroid distances between the pyridyl moieties are slightly longer (4.38–6.16 Å), in comparison with structurally analogous trigonal prisms.[45] Maximum centroid···centroid distance of 6.16 Å is observed in an arm, wherein the benzyl substituents are *syn* oriented. At this arm, the aromatic rings of the benzyl groups are partly projected in between the pyridyl moieties of ptin units that are stabilized by CH···π and π···π interactions. The (benzyl aromatic)CH···π(pyridyl) and (benzyl aromatic)π···π(pyridyl) interaction distances are found to be 3.208 and 4.070 Å. The pillars of the prism constituted by {(CO)$_3$Re(μ-η^4-dibenzyloxamidato)Re(CO)$_3$} moieties are tilted by an angle of 11.21° out of the plane of ptin ligands. Therefore, two ptin ligands occupying the opposite trigonal faces are staggered, generating a double-rosette helicity with *P* configuration. The Bailar twist angles that indicate the degree of deviation from trigonal prismatic geometry are 11.6, 18.4 and 18.4°. Apart from this, the pyridyl rings of two ptin units are slanted by 39.23° out of plane of central phenyl ring, which creates a three-bladed propeller chirality with *Λ* configuration (Fig. 3). Such type of double helical chirality has been reported for few Re, Ru and Rh based metallaprisms.[44d,45,46] The formation of **4** is further confirmed by ESI-Mass analysis that showed a molecular ion peak at m/z 3303.04 for [{(CO)$_3$Re(μ-η^4-dibenzyloxamidato)Re(CO)$_3$}$_3$(μ_3-ptin)$_2$]$^+$.

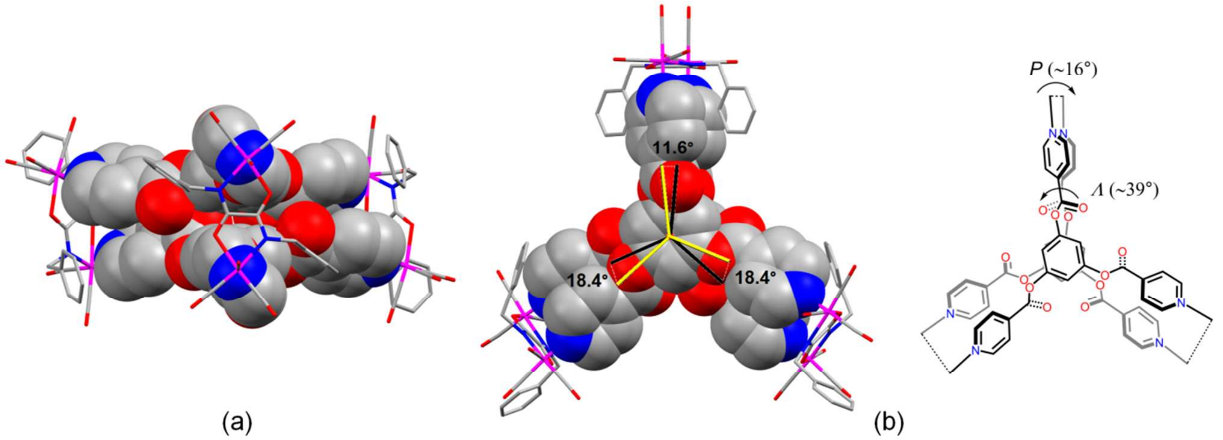


Fig. 3 (a) Van der Waals representation of **4** depicting the twisting of pyridyl moieties (*Λ* isomer). (b) Bailar twist angles and schematic representation of double *P* (double rosette) and *Λ* (propeller) helicity.

Table 1 Selected Bond Lengths (Å) and Angles (deg) for **4**

Re1–N1	2.31(5)	N1–Re1–O4	76.4(13)
Re1–N2	2.219(9)	N1–Re1–N2	82(3)
Re1–O4	2.13(7)	O4–Re1–N2	86.8(13)
Re1–C1	1.900(15)	C1–Re1–N1	175(3)
Re1–C2	1.899(15)	C1–Re1–N2	93.4(5)
Re1–C3	1.843(16)	C1–Re1–O4	101.6(12)

The incorporation of ester functionality in the prismatic architecture facilitated host-guest interaction studies with suitable aromatic guest molecules. Studies related to guest binding ability of **2** with few aromatic alcohols such as catechol, *p*-chloro-*m*-cresol, resorcinol, phloroglucinol and an amino acid, L-tryptophan were carried out using electronic absorption and emission spectral titration experiments (Fig. S2–S6). Compound **2** was selected as host owing to its good solubility in organic solvents. In UV–vis spectral titration studies, the changes in absorption intensities of the aromatic guests (concentrations of guests were kept constant) were monitored while increasing the concentration of host **2**. The initial absorption intensities of the guests were enhanced significantly upon addition of **2** due to host–guest complex formation. A double reciprocal plot of change in concentration of host ([H]) versus change in absorbance (ΔA) of guest species gave a good linear correlation. The binding constants (K_a) calculated from the slope and intercept of linear Benesi-Hildebrand plots were listed in Table 2.[47] In case of fluorescence titration experiments, the emission intensities of aromatic guests were effectively quenched due to incremental addition of host prism **2** that further endorsed the formation of host–guest complexes. The Stern-Volmer constants (K_{SV}) calculated from linear Stern-Volmer plot derived from the emission titration data were also listed in Table 2.[48] The observed enhancement in the UV–vis titration and quenching in emission titration experiments might be due to the formation of donor-acceptor complex between the host and guest molecules.

Table 2 Binding constants (K_a) and Stern-Volmer constants (K_{SV}) for various guest species.

Guest	K_a (M^{-1})	K_{SV} (M^{-1})
Catechol	1.91×10^5	7.03×10^5
Resorcinol	3.10×10^5	5.70×10^5
p-chloro-*m*-cresol	9.61×10^5	3.13×10^5
Phloroglucinol	3.20×10^5	2.50×10^5
L-tryptophan	4.20×10^5	2.60×10^5

The solution-state ^{1}H NMR spectra of a mixture of **2** and (0.5–3 equiv) catechol in $CDCl_3$ at room temperature revealed that the broad signal corresponding to OH protons of alcohols were significantly sharpened and upfield-shifted ($\Delta\delta \approx 0.19$ ppm) in comparison to the free catechol. The aromatic protons of catechol also experienced a shielding effect due to which there was a minor upfield shift in their signals when compared to free catechol. Similar ^{1}H NMR spectral studies carried out for *p*-chloro-*m*-cresol in $CDCl_3$ showed that the broad signal corresponding to OH protons of free *p*-chloro-*m*-cresol has considerably shifted upfield with concurrent sharpening of signal ($\Delta\delta \approx 0.28$ ppm). Furthermore, the H^5 and H^2 aromatic protons and the methyl protons of *p*-

chloro-*m*-cresol experienced slight downfield-shift, whereas, the H^6 aromatic protons showed an upfield-shift. ^1H NMR spectra of a mixture of **2** and resorcinol displayed a similar trend with respect to OH protons ($\Delta\delta \approx 0.11$ ppm). H^2 and H^4 aromatic protons of resorcinol were also shifted upfield, whereas, H^5 protons showed a marginal downfield shift. The consistent and significant upfield-shift as well as sharpening of signals observed for OH protons of the guest species in the presence of host **2** indicates the probable existence of guest molecules in the cleft between the three arms of the prism, which might also disrupt the intermolecular hydrogen bonding between the guests (Fig. S7–S9). In addition, the shifting of peaks pertaining to the protons of **2** in these mixtures implied the formation of host–guest complex between **2** and aromatic alcohols in solution.[47c,49]

Recently, it has been shown that the luminescence properties of Re(I)-rectangles with long alkyl substituents are enhanced in organic-aqueous solvent mixtures due to the formation of self-aggregates.[44b,50] Taking cue from these observations, we have attempted to tune the emission properties of **2** and **3** that are having long alkyl substituents, by recording their absorption and emission spectra in various ratios of CH_3CN/H_2O solvent mixtures (Fig. S10–S13). In the UV–vis spectra, the absorbance of **2** and **3** were found to be enhanced while increasing the water content. The MLCT band at λ_{max}^{ab} 391 nm was red-shifted by 6 nm, whereas no substantial shift was observed for other bands. In the emission spectra, a significant enhancement in the emission intensity corresponding to MLCT absorption (λ_{max}^{ab} 391 nm) was observed beyond 70% water content. As the emission intensity of the prisms increased, a concurrent blue shift was also noticed in the emission maxima (λ_{max}^{em} 607 to 568 nm for **2**; λ_{max}^{em} 609 to 555 nm for **3**) due to rigidochromism.[50c] The quantum yields of **2** and **3** were increased tenfold while increasing the water content (Table S1 and S2). Considerable improvement in the emission properties of prisms **2** and **3** in presence of water is probably due to the formation of self-aggregates facilitated by the hydrophobicity of long alkyl substituents.[50d]

Conclusions

In conclusion, we have successfully shown the multicomponent self-assembly of hexarhenium trigonal prisms using semi-rigid tritopic linkers and oxamidato pillars. The solubility of metallaprisms **2** and **3** in organic solvents has been dramatically increased by the introduction of long alkyl substituents. Assessment of guest binding ability of **2** with few aromatic alcohols and L-tryptophan revealed large binding constant (K_a) values. Also, metallaprisms **2** and **3** showed superior emission properties in organic-aqueous solvent mixtures. Interestingly, the single-crystal X-ray structure of metallaprism **4** manifested the presence of double helical chirality, rendered by a twist of ptin units and a concerted canting of pyridyl moieties. Incorporation of ptin as triangular faces in trigonal prisms has the potential to generate double helical chirality consistently. Current efforts are directed toward developing diverse metallaprismatic architectures using ptin and various organic pillars in order to understand the double helical chirality.

Experimental

Materials and methods

Solvothermal methods were adopted for the syntheses of compounds **1**–**4**. $Re_2(CO)_{10}$ was purchased from Sigma-Aldrich Chemicals. The oxamide ligands (H_2L1–H_2L4) and phenyl-1,3,5-tris(isonicotinate) (ptin) were synthesised by literature methods.[51] The solvents were dried using standard methods and freshly distilled prior to use.[52] IR spectra were recorded on a Thermo Nicolet-6700 FT-IR spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu UV-2450 spectrophotometer. Emission spectra were recorded on a Fluoromax-4 spectrofluorometer. Solvents used for UV–vis and Fluorescence spectroscopic titration experiments were of spectral grade. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer.

Elemental analyses were performed in a Thermo Scientific Flash 2000 CHNS analyser. ESI-Mass spectrum was recorded on a Bruker micrOTOF-Q II mass spectrometer. Compounds **1−4** were dried thoroughly under high vacuum condition for several hours, prior to the submission of samples for spectral characterisation and elemental analyses.

Synthesis of $[\{(CO)_3Re(\mu\text{-}\eta^4\text{-dibutyloxamidato})Re(CO)_3\}_3(\mu_3\text{-ptin})_2]$ (1)

A mixture of $Re_2(CO)_{10}$ (97 mg, 0.15 mmol), N,N′-dibutyloxamide (20 mg, 0.15 mmol) and phenyl-1,3,5-tris(isonicotinate) (44 mg, 0.1 mmol) in mesitylene (5 mL) was taken in a 23 mL PTFE flask and placed inside a steel bomb. The bomb was kept in an oven maintained at 160 °C for 4 h and then cooled to room temperature. Yellow crystalline product was obtained. The crystals were separated, washed with hexane and dried under vacuum (0.089 g, 58 %). Calc. for $C_{96}H_{84}N_{12}O_{36}Re_6$: C, 37.21; H, 2.73; N, 5.42. Found: C, 37.32; H, 2.70; N, 5.38. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2025 (s), 2018 (s), 1914 (s), 1892 (s), ν(ester C=O) 1755 (m), ν(oxamidato C=O) 1602 (s). ^1H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 8.70 (m, 12H, H^2_{py}, ptin), 8.03 (m, 12H, H^3_{py}, ptin), 7.30 (d, 6H, H_{Ph}, ptin), 4.18 (m, 6H, H^1, CH_2-oxamidato), 3.30 (m, 6H, $H^{1'}$, CH_2-oxamidato), 1.76 (m, 12H, H^2, CH_2-oxamidato), 1.46 (m, 6H, H^3, CH_2-oxamidato), 1.37 (m, 6H, $H^{3'}$, CH_2-oxamidato), 1.02 (m, 18H, H^4, CH_3-oxamidato). UV−vis (CH_2Cl_2, λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 227 (63 000), 268 (49 000) (LIG); 321 (41 000), 391 (14 000) (MLCT). Emission (CH_2Cl_2, nm): λ_{max}^{em} 610 ($\Phi_{em} = 3.12 \times 10^{-4}$).

Synthesis of $[\{(CO)_3Re(\mu\text{-}\eta^4\text{-dioctyloxamidato})Re(CO)_3\}_3(\mu_3\text{-ptin})_2]$ (2)

A mixture of $Re_2(CO)_{10}$ (97 mg, 0.15 mmol), N,N′-dioctyloxamide (46 mg, 0.15 mmol) and phenyl-1,3,5-tris(isonicotinate) (44 mg, 0.1 mmol) in mesitylene (5 mL) was taken in a 23 mL PTFE flask and placed inside a steel bomb. The bomb was kept in an oven maintained at 160 °C for 4 h and then cooled to room temperature. Yellow crystals were obtained. The crystals were separated, washed with hexane and dried under vacuum (0.096 g, 56 %). Calc. for $C_{120}H_{132}N_{12}O_{36}Re_6$: C, 41.95; H, 3.87; N, 4.89. Found: C, 42.02; H, 3.92; N, 4.85. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2025 (s), 2018 (s), 1915 (s), 1893 (s), ν(ester C=O) 1756 (s), ν(oxamidato C=O) 1602 (s). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, ppm): δ 8.69 (m, 12H, H^2_{py}, ptin), 8.10 (m, 12H, H^3_{py}, ptin), 7.47 (d, 6H, H_{Ph}, ptin), 4.20 (m, 6H, H^1, CH_2-oxamidato), 3.27 (m, 6H, $H^{1'}$, CH_2-oxamidato), 1.78 (m, 12H, H^2, CH_2-oxamidato), 1.36 (m, 60H, H^{3-7}, CH_2-oxamidato), 0.91 (m, 18H, H^8, CH_3-oxamidato). ^{13}C NMR (100 MHz, $(CD_3)_2CO$, ppm): δ 198.1, 197.9, 196.2 ($Re(CO)_3$), 173.2 (oxamidato CO), 162.1 (ester CO), 154.5 (C^2, py-ptin), 151.1 (C^1, Ph-ptin), 139.1 (C^4, py-ptin), 126.0 (C^3, py-ptin), 113.8 (C^2, Ph-ptin), 50.2 (C^1, CH_2-oxamidato), 29.7–23.4 (C^{2-7}, CH_2-oxamidato), 14.4 (C^8, CH_3-oxamidato). UV−vis (CH_2Cl_2, λ_{max}^{ab} nm (ε, M^{-1} cm^{-1})): 227 (75 000), 268 (54 000) (LIG); 321 (44 000), 389 (14 000) (MLCT). Emission (CH_2Cl_2), nm): λ_{max}^{em} 611 ($\Phi_{em} = 1.60 \times 10^{-3}$). ESI-MS: m/z 3474.59 [**2**+ K]$^+$, calcd for [**2**+ K]$^+$ 3474.58.

Synthesis of [{(CO)$_3$Re(μ-η^4-didodecyloxamidato)Re(CO)$_3$}$_3$(μ$_3$-ptin)$_2$] (3)

A mixture of $Re_2(CO)_{10}$ (97 mg, 0.15 mmol), N,N′-didodecyloxamide (63 mg, 0.15 mmol) and phenyl-1,3,5-tris(isonicotinate) (44 mg, 0.1 mmol) in mesitylene (5 mL) was taken in a 23 mL PTFE flask and placed inside a steel bomb. The bomb was kept in an oven maintained at 160 °C for 4 h and then cooled to room temperature. Yellow crystalline product was obtained. The crystals were separated, washed with hexane and dried under vacuum (0.098 g, 53 %). Calc. for $C_{144}H_{180}N_{12}O_{36}Re_6$: C, 45.85; H, 4.81; N, 4.46. Found: C, 45.92; H, 4.79; N, 4.49. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2026 (s), 2018 (s), 1915 (s), 1893 (s), ν(ester C=O) 1755 (s), ν(oxamidato C=O) 1601 (s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (m, 12H, H^2_{py}, ptin), 7.77 (m, 12H, H^3_{py}, ptin), 7.21 (d, 6H, H_{Ph}, ptin), 4.03 (m, 6H, H^1, CH_2-oxamidato), 3.19 (m, 6H, $H^{1'}$, CH_2-oxamidato), 1.75 (m, 12H, H^{2}, CH$_2$-oxamidato), 1.30 (m, 108H, H$^{3-11}$, CH$_2$-oxamidato), 0.86 (m, 18H, H^{12}, CH$_3$-oxamidato). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 197.3, 197.2, 194.4 (Re(CO)$_3$), 172.2 (oxamidato CO), 161.1 (ester CO), 153.3 (C^{2}, py-ptin), 149.8, (C^{1}, Ph-ptin), 137.4 (C^{4}, py-ptin), 113.8 (C^{2}, Ph-ptin), 124.4 (C^{3}, py-ptin), 50.2, (C^{1}, CH$_2$-oxamidato), 32.1–22.9 (C$^{2-11}$, CH$_2$-oxamidato), 14.3 (C^{12}, CH$_3$-oxamidato). UV−vis (CH$_2$Cl$_2$, $\lambda_{max}{}^{ab}$ nm (ε, M^{-1} cm^{-1})): $\lambda_{max}{}^{ab}$ (dm^{3} mol^{-1} cm^{-1}) 227 (74 000), 268 (52 000) (LIG); 320 (43 000), 390 (15 000) (MLCT). Emission (CH$_2$Cl$_2$), nm): $\lambda_{max}{}^{em}$ 611 (Φ_{em} = 2.61×10^{-3}).

[{(CO)$_3$Re(μ-η^4-dibenzyloxamidato)Re(CO)$_3$}$_3$(μ$_3$-ptin)$_2$] (4)

A mixture of Re$_2$(CO)$_{10}$ (97 mg, 0.15 mmol), N,N′-dibenzyloxamide (41 mg, 0.15 mmol) and phenyl-1,3,5-tris(isonicotinate) (44 mg, 0.1 mmol) in mesitylene (5 mL) was taken in a 23 mL PTFE flask and placed inside a steel bomb. The bomb was kept in an oven maintained at 160 °C for 4 h and then cooled to room temperature. Good quality yellow brown crystals were obtained. The crystals were separated, washed with hexane and dried under vacuum (0.104 g, 64 %). Calc. for C$_{114}$H$_{72}$N$_{12}$O$_{36}$Re$_6$: C, 41.46; H, 2.20; N, 5.09. Found: C, 41.40; H, 2.23; N, 5.05. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2027 (s), 2020 (s), 1918 (s), 1895 (s), ν(ester C=O) 1756 (s), ν(oxamidato C=O) 1597 (s). ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO, ppm): δ 8.61 (m, 12H, H$^{2}_{py}$, ptin), 8.06 (m, 12H, H$^{3}_{py}$, ptin), 7.42 (m, 30H, H^{2}, H^{3} & H^{4}, CH-oxamidato), 7.52 (s, 4H, H$_{Ph}$, ptin), 5.25 (m, H, 6H, CH$_2$-oxamidato), 4.69 (m, H', 6H, CH$_2$-oxamidato). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 197.9, 197.8, 195.1 (Re(CO)$_3$), 173.5 (oxamidato CO), 162.3 (ester CO), 154.7 (C^{2}, py-ptin), 151.1, (C^{1}, Ph-ptin), 139.4 (C^{4}, py-ptin), 113.8 (C^{2}, Ph-ptin), 125.9 (C^{3}, py-ptin), 54.9, (CH$_2$-oxamidato), 139.4 (C^{1}, oxamidato), 130.0 (C^{2}, oxamidato), 129.5 (C^{3}, oxamidato) 128.5 (C^{4}, oxamidato). UV−vis (CH$_2$Cl$_2$, $\lambda_{max}{}^{ab}$ nm (ε, M^{-1} cm^{-1})): 227 (86 000), 268 (57 000) (LIG); 320 (46 000), 390 (17 000) (MLCT). Emission (CH$_2$Cl$_2$), nm): $\lambda_{max}{}^{em}$ 612 (Φ_{em} = 4.51×10^{-4}). ESI-MS: m/z 3303.04 [**4**]$^{+}$, calcd for [**4**]$^{+}$ 3303.09.

X-ray Crystallography

Single crystal X-ray structural studies of **4** was performed on Oxford Diffraction XCALIBUR-EOS CCD equipped diffractometer, with an Oxford Instrument low-temperature attachment. Data were collected at 150 K using graphite-monochromated Mo Kα radiation (λ_α = 0.7107 Å). The strategy for data collection was evaluated using CrysAlisPro CCD software. The crystal data were collected by standard '$\psi-\omega$ scan' techniques and were scaled and reduced using CrysAlisPro RED software. The structure was solved by direct methods using SHELXS and refined by full matrix least squares with SHELXL refining on F^2.[53–55] Positions on all the atoms were obtained by Direct Methods. Atoms N1 and O4 and N3 and O5 of oxamidato bridge are substitutionally disordered with occupancy of 49/51 and hence the benzyl groups substituted at N1 and N3 are also disordered accordingly. Apart from this, the pyridine ring constituted by N6, C53, C54, C55, C56, C57 atoms and the ester moiety constituted by O11, C35 and O12 atoms are positionally disordered with occupancy of 60/40. Examination of the structure with PLATON revealed solvent accessible voids. Therefore, a new data set corresponding to omission of the missing solvent was generated with SQUEEZE algorithm and the structure was refined to convergence.[56] 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 Ueq of their parent atoms.

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Electronic Supplementary Information (ESI) available: The crystallographic data and structure refinement details of **4**, UV−vis spectra of **1−4**, experimental procedure for molecular recognition and molecular aggregation studies, figures and CIF file for **4**.

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One-pot Synthesis of Oxamidato-Bridged Hexarhenium Trigonal Prisms Adorned with Ester Functionality

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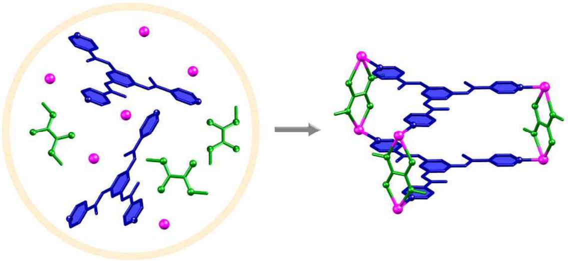

Self-assembly of hexarhenium trigonal prisms using *fac*-Re(CO)$_3$ cores (pink), bischelating oxamide ligands (green) and ester-containing tritopic linkers (blue) has been accomplished via orthogonal bonding approach.