Unusual face-to-face π–π stacking interactions within an indigo-pillared M_3(tpt)-based triangular metalloprism†

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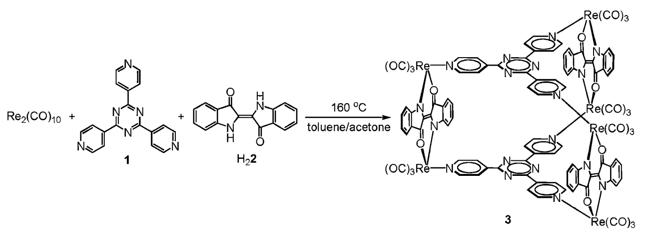
A triangular metalloprism, [{$(CO)_3Re(\mu$-2)$Re(CO)_3$}$_3(\mu_3$-1)$_2$], self-assembled from $Re_2(CO)_{10}$, 2,4,6-tri-4-pyridyl-1,3,5-triazine (tpt, 1), and indigo ($H_2$2), represents a fairly novel example of strong face-to-face π–π interactions between the central triazine rings of the tpt ligands that bow significantly inward distorting the prismatic structure.

The elegance of supramolecular architectures stems from the simultaneous operation of several weak interactions between building blocks, such as hydrogen bonding, π–π stacking interactions, van der Waals forces, and metal–ligand interactions.[1] Among these, aromatic–aromatic π-stacking interactions, approximately 2 kJ mol^{-1},[2] are of critical importance for biological recognition,[3,4] controlling the stacking of aromatic molecules in the crystalline state, conformational preferences, and development of supramolecular assemblies.[5] Recently, Fujita and co-workers constructed a multi-stack aromatic host–guest π-stacking system, in which d^8-metal-hinged and organic-pillared M_3(tpt)-based box-shaped hosts (prismatic cages) have cavities large enough to accommodate large π-conjugated molecules (tpt = 2,4,6-tri-4-pyridyl-1,3,5-triazine, **1**).[6] A smaller number of Re(I)-, Ru(II)-, Ir(I)-, and Rh(I)-based metalloprisms, in addition to the d^8-metal-containing ones, with the tridentate ligating unit, tpt, and simple N,N′- or O,O′-donor spacers have also been reported.[7–9] In these organic-pillared M_3(tpt)-based triangular metalloprisms, π–π interaction of the core ligand, tpt, is enhanced; in particular, its geometry is altered.[6–9] We report herein a novel indigo-containing Re_3(tpt)-based triangular metalloprism [{$(CO)_3Re(\mu$-**2**)$Re(CO)_3$}$_3(\mu_3$-**1**)$_2$] (**3**, H_2**2** = indigo), which is obtained in a one-pot synthesis using a solvothermal method.[7c] The prismatic compound exhibits strong aromatic–aromatic π–π stacking interactions, but has no internal intercalated aromatic guests. Interestingly, this face-to-face π–π stacking interaction is so strong that the inner core of the prism bows inwards with a distance only one-half that of the outer rims, and seriously distorts the prismatic structure of **3** from a high apparent symmetry of D_{3h} to the low symmetry of C_1.

We recently developed the *orthogonal-bonding approach* as an effective strategy for simple assembly of Re(I)-based functional materials. This method simultaneously introduces one bis(chelating) dianion that coordinates to two equatorial sites of two *fac*-$(CO)_3$Re cores and one N-containing *exo*-multidentate ligand that coordinates to the remaining orthogonal axial site.[10] In the present study, the neutral luminescent metalloprism **3** was prepared in a moderate yield (55%) by treating $Re_2(CO)_{10}$ with tpt **1** and indigo H_2**2** in a toluene–acetone solvent system at 160 °C (Scheme 1).‡ Metalloprism **3**, which is stable in air, was characterized by spectroscopic methods. The FAB mass spectrum showed a molecular ion peak for [{$(CO)_3Re(\mu$-**2**)$Re(CO)_3$}$_3(\mu_3$-**1**)$_2$]$^+$ at *m/z* 3026. The ^{1}H NMR spectrum of **3** showed nonequivalent neutral tpt proton signals. Three sets of signals at δ 8.25–8.36 and δ 7.85–7.96 ppm originating from the H_α and H_β protons of the three pyridyl groups in the tpt ligand, are indicative of the low symmetry of the prismatic structure of **3**. This result was also supported by one set of anionic indigo proton signals in complex multiple patterns observed in the range of δ 6.97–7.77 ppm. To our knowledge, the utilization of a structural motif with N,O-donor spacers such as indigo in the construction of metallocycles remains unexplored. The molecular structure of **3** was also determined by single-crystal X-ray diffraction analysis.§ X-Ray crystallography reveals that **3** adopts a $M_6L_3L'_2$ cage structure comprised of six *fac*-$Re(CO)_3$ metallo-corners, two tpt ligands, and three anionic indigo ligands (Fig. 1). Within the structure, the anionic indigo ligand is in a keto form rather than a leuco form, as the C–O distances



Scheme 1 Synthesis of **3**.

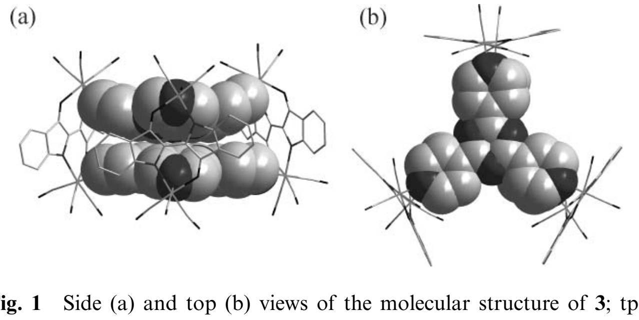


Fig. 1 Side (a) and top (b) views of the molecular structure of **3**; tpt ligands are drawn as space-filling models.

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range from 1.176(19) to 1.23(2) Å.[11] The six rhenium atoms define a triangular metalloprism with 11.56–13.56 Å trigonal edges and 6.38–6.48 Å cage heights (Fig. 2a). Interestingly, the two central face-to-face triazine rings from the two distinct tpt ligands are separated by a distance of 3.52 Å. This distance is approximately only one-half that of the outer rims (Re···Re distances, 6.38–6.48 Å, Fig. 2b). Hupp and co-workers reported a bis(benzimidazolate) (BiBzIm)-pillared Re(I)-prism $[\{(CO)_3Re(\mu\text{-}BiBzIm)Re(CO)_3\}_3(\mu_3\text{-tpt})_2]$ which is structurally closely analogous to **3** in which the triazine cores of tpt ligands bowed slightly inward.[7a] Interestingly, the serious distortion in the triangular prismatic structure of **3** exhibits a low C_1 symmetry, which is significantly different from the high symmetry of D_{3h} or apparent D_{3h} in other tpt-based triangular metalloprisms.[6–9] This result was corroborated by the observation of nonequivalent aromatic proton signals for neutral tpt and anionic indigo ligands in the ^{1}H NMR spectrum.

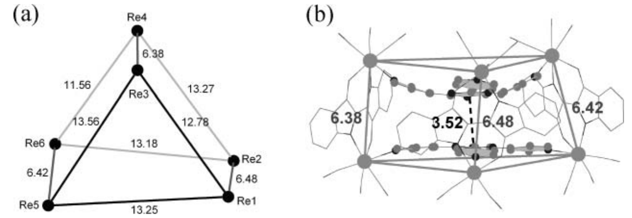
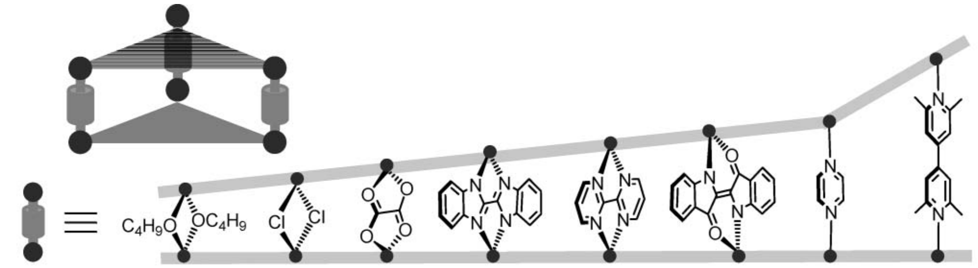


Fig. 2 Schematic representation of geometric parameters (distance in Å) for Re-based triangular metalloprism **3** (a), and the face-to-face π–π interactions between the central triazine rings of bowed tpt ligands (b).

Fig. 3 illustrates a survey of M_3(tpt)-based triangular metalloprisms. The structural features of these metalloprisms and their host–guest behaviors resulting from π–π interactions were dependent on the utilization of organic-pillared ligands that offer different cage heights and support different box-shaped cavities. When the interplanar surface-to-surface distance between the two tpt-planes forming the "floor" and the "roof" of the prism is inadequate, aromatic guests cannot be included.[7–9] The tpt ligands may bow slightly inward to minimize the centroid···centroid distance (approximate 3.5 Å) between the two triazine moieties, and to maximize face-to-face π–π stacking interactions.[7a,8,12] Alternatively, if the spaces within the box-shaped hosts are large enough, planar aromatic guests can be accommodated by π stacking interactions with short interplanar distances.[6,13,14] As a result, the four aromatic rings (one triazine and three pyridine rings) of tpt are almost co-planar and sustain the high symmetry of the prismatic host.[6] The indigo-containing compound **3** is of particular interest. First, among these organic pillars, indigo lies at the upper limit for tpt-based triangular prisms which cannot accommodate aromatics. Second, face-to-face π–π interactions are so strong that the triazine rings of the two tpt ligands cause the triangular prism bow significantly inward with a distance (3.52 Å) only one-half that of the outer rims.

Metalloprism **3** in THF displays intense bands in the near UV region (200–300 nm), which can be assigned to π–π* transitions of both tpt and indigo ligands. The shoulder at 325 nm probably results from an intra-ligand transition localized on the indigo ligand.[11] The absorption bands at 335 and 410 nm might be attributed to Re → indigo and Re → tpt metal-to-ligand charge transfer (MLCT) transitions, respectively. In air-equilibrated THF solution, luminescence from **3** was observed at 25 °C. The maximum observed at approximately 392 nm was assigned to a ligand localized π–π* excited state of the indigo moiety. Upon excitation of **3** at 350 nm, a broad luminescence peak was observed at 77 K, originating from the lowest lying ^{3}MLCT state of the Re → tpt transition. This emission, for which the quantum yield was 0.01 with respect to $Ru(bpy)_3^{2+}$, decays with a lifetime (τ) of 5.5 ns. The static fluorescence quenching of **3** was also studied using nitroaromatics, which effectively quenched the emission of **3** in THF. The quenching constants ranged from 8.0×10^{10} to 3.2×10^{11} M^{-1} s^{-1}.[15] The binding constant expression in this plot was valid when the quencher concentration was significantly greater than the concentration of **3** and the binding molecularity and stoichiometry were both 1 : 1.[16] Significant differences in K_a values (2.0×10^2 to 4.2×10^3 M^{-1}) were observed for nitrobenzene derivatives. Electron-releasing substitutes produced a high K_a value, whereas electron-withdrawing groups reduced K_a. Furthermore, the emission maximum was red-shifted from 392 nm to 397 nm upon the addition of nitroaromatic quenchers.

In summary, we successfully synthesized a light-emitting neutral Re(I)-based molecular cage in a one-pot self-assembly reaction. An



d(M···M),[a] Å	3.39	3.69	5.49	5.71	5.86[c]	6.43	6.77	11.06
d(tpt···tpt),[b] Å	3.54	3.42	3.42	3.43	4.2[d]	3.52	6.58[e]	10.01[f]
no. of aromatic guests	0	0	0	0	0	0	1	2
ref	7c	8b	8c,9	7a	7b,14	this work	6d	6c

Note: [a]average distance. [b]shortest distance. [c]from compound $[\{(CO)_3Re(\mu\text{-bpym})Re(CO)_3\}_2(\mu\text{-bpy})_2](CF_3SO_3)_4$, see ref. 14. [d]by MM2 molecular modeling. [e]involving one aromatic guest with inter-plane distances of 3.29 and 3.29 Å. [f]involving two aromatic guests with inter-plane distances of 3.29, 3.43, and 3.29 Å in sequence.

Fig. 3 A survey of M_3(tpt)-based triangular metalloprisms $[M_6(tpt)_2L_3]$ with relative prism parameters..

unprecedented structural feature of **3** is that the face-to-face π–π stacking interactions are so strong that the inner-core of the prism bows inwards with a distance one-half that of the outer rims.

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Notes and references

‡ A suspension consisting of a mixture of $Re_2(CO)_{10}$ (0.19 mmol), tpt (0.22 mmol), and indigo (0.18 mmol) in a toluene–acetone solvent system (7 mL, v/v = 6 : 1) in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 160 °C for 72 h and then cooled to room temperature. Good quality, black-colored, single crystals of **3**·C_7H_8 were obtained in a yield of 55%. IR (THF): ν(CO) = 2015, 2003, 1923, 1894 cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 8.36$ (d, $J = 6.2$ Hz, 4H), 8.29 (d, $J = 6.2$ Hz, 4H), 8.25 (d, $J = 6.4$ Hz, 4H), 7.96 (d, $J = 6.7$ Hz, 4H), 7.91 (d, $J = 6.7$ Hz, 4H), 7.85 (d, $J = 6.4$ Hz, 4H), 7.81–7.76 (m, 6H), 7.71–7.64 (m, 6H), 7.61–7.52 (m, 6H), 6.99–6.95 (m, 6H) ppm. FAB-MS: $m/z = 3026$ (M^+). Elemental analysis calcd (%) for **3**·C_7H_8: C, 41.97; H, 1.81; N, 8.08. Found: C, 41.25; H, 1.85; N, 8.06.

§ Crystal data for **3**·$1.5C_7H_8\cdot 2C_3H_6O$: $C_{118.50}H_{72}N_{18}O_{26}Re_6$, $M_r = 3281.14$, triclinic, $a = 17.2626(6)$ Å, $b = 20.1493(7)$ Å, $c = 20.6851(7)$ Å, $\alpha = 116.094(1)°$, $\beta = 109.629(1)°$, $\gamma = 97.093(1)°$, $U = 5764.7(3)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 2$, 60 933 reflections measured, 20 322 unique ($R_{int} = 0.0541$) which were used in all calculations. Final R indices: $R_1 = 0.0849$ and w$R_2 = 0.1863$ for 13 989 reflections [$I > 2\sigma(I)$]; $R_1 = 0.1204$ and w$R_2 = 0.2040$ for all data. GOF = 1.074. CCDC 678030. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b809489f

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