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## Furan-decorated neutral Re(I)-based 2D rectangle and 3D trigonal prism†‡ §

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**Neutral, stable and luminescent metallacycles decorated with furan units, a 2D rectangle with four furans and a 3D trigonal prism with six furans, were synthesized from readily accessible starting materials through a *fac*-Re(CO)<sub>3</sub>-directed approach.**

The design and synthesis of regularly shaped functional metallacycles has been one of the driving forces to promote the major advances in supramolecular chemistry.<sup>1–2</sup> Among the several coordination driven synthetic methods, the *fac*-Re(CO)<sub>3</sub>-core directed approach is one of the well-established routes to neutral, 2D and 3D metallacycles.<sup>3</sup> Examples of various shapes and sizes of Re(I)-based supramolecular architectures are mononuclear- ML,<sup>4</sup> dinuclear- M<sub>2</sub>LL', M<sub>2</sub>L<sub>2</sub>,<sup>5</sup> trinuclear- M<sub>3</sub>L<sub>3</sub>,<sup>5</sup> tetranuclear- squares M<sub>4</sub>L<sub>4</sub>,<sup>6</sup> rectangles M<sub>4</sub>L<sub>2</sub>L'<sub>4</sub>,<sup>7</sup> M<sub>4</sub>L<sub>2</sub>L'<sub>2</sub>,<sup>8–9</sup> gondolas M<sub>4</sub>L<sub>2</sub>L'<sub>2</sub>,<sup>10</sup> hexanuclear prisms-M<sub>6</sub>L<sub>2</sub>L'<sub>6</sub>,<sup>11</sup> M<sub>6</sub>L<sub>2</sub>L'<sub>3</sub>,<sup>12</sup> and octanuclear cycles M<sub>8</sub>L<sub>2</sub>L'<sub>8</sub>.<sup>13</sup> Due to their interesting functions and potential applications in various fields of chemistry, including host–guest chemistry, catalysis, probes for photoluminescence quenching, anticancer agents, and photo- and electro-chemical sensing, efforts are still being expanded on synthesis of new functional metallacycles.<sup>6–13</sup> Up to now, much attention has been focused either upon expansion of the inner cavities of cyclic frameworks or on decorating the metallacycle with hydrophobic arene or alkyl chains. However, no attention has been paid to developing the

exteriors with biologically and materially useful organic motifs, which not only impart these properties to the metallacycle, but are also capable of interacting selectively with their environments and delivering their contents. The introduction of functional groups, in particular bioactive molecules,<sup>14</sup> onto discrete supramolecular systems in a controlled manner *i.e.* the precise location, orientation, and the number of functional units, is a challenge. Previous works describing furan-containing metallacycles and cages have already been known but furan units in those systems were part of a conjugated bridge, which prevents an efficient interaction with the environment of the complex.<sup>15</sup> Herein we report on the first example of metallacycles decorated with biologically active five membered heterocyclic units. The self-assembly of a furan rich neutral 2D-rectangle with four furans and a 3D-trigonal prism with six furans was achieved from a *fac*-Re(CO)<sub>3</sub>-directed approach using Re<sub>2</sub>(CO)<sub>10</sub>, rigid N-donors, and 2-furanmethanethiol in a one-step process.

As a test case, furan was chosen as a decorating unit onto the metallacyclic frameworks. Furans occur frequently as subunits in a variety of biologically active molecules and have also been used as communicating moieties in molecular materials.<sup>14–17</sup> The number and position of the furans play a key role in the compound activity.

Compounds **1** and **2** were synthesized by reacting Re<sub>2</sub>(CO)<sub>10</sub>, nitrogen donor (*trans*-1,2-bis(4'-pyridyl)ethylene (bpe) for **1** and 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (tpt) for **2**) and 2-furanmethanethiol (H-fmt) in a one-pot procedure (Scheme 1).<sup>11</sup> The resulting crystalline products are air- and moisture-stable and soluble in polar organic solvents. The FT-IR spectrum of **1** exhibits strong bands at 2021, 2007, 1918 and 1907 cm<sup>-1</sup>, characteristic of *fac*-Re(CO)<sub>3</sub> in an asymmetric environment. The <sup>1</sup>H NMR spectrum of **1** showed well-separated signals for the ligands. The

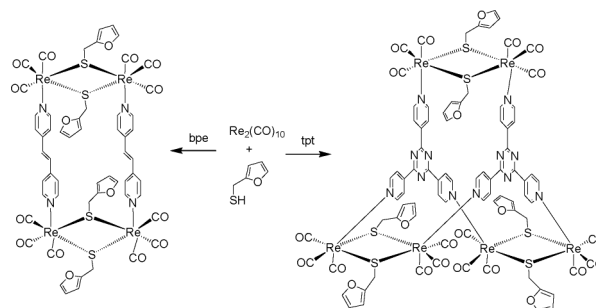
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‡ Crystal data for **1**: C<sub>56</sub>H<sub>40</sub>N<sub>4</sub>O<sub>16</sub>Re<sub>2</sub>S<sub>2</sub>, *M* = 1897.96, monoclinic, *a* = 12.990(5), *b* = 26.243(5), *c* = 18.903(5) Å, β = 109.501(5), *V* = 6074(3) Å<sup>3</sup>, *T* = 183(2) K, space group *P* 1 21/c 1, *Z* = 4, μ(Mo-Kα) = 8.152 mm<sup>-1</sup>, 113830 reflections measured, 11109 unique (*R*<sub>int</sub> = 0.0712) which were used in all calculations. Final *R* indices: *R*<sub>1</sub> = 0.0266 and *wR*<sub>2</sub> = 0.0408 for 11109 reflections [*I* > 2σ(*I*)]; *R*<sub>1</sub> = 0.0505 and *wR*<sub>2</sub> = 0.0434 for all data. GOF = 0.867. CCDC 778832.

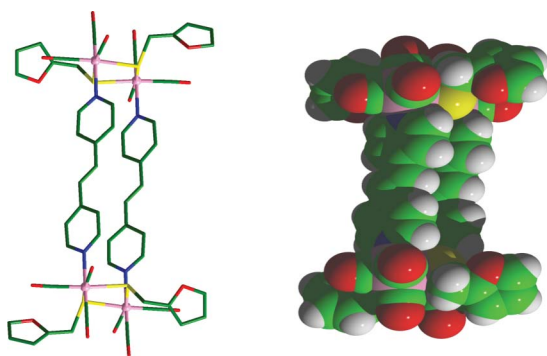
§ Crystal data for **2**: C<sub>84</sub>H<sub>54</sub>N<sub>12</sub>O<sub>24</sub>S<sub>6</sub>Re<sub>6</sub>, *M* = 2924.95, hexagonal, *a* = 23.2217(3), *b* = 23.2217(3), *c* = 29.1908(6) Å, γ = 120°, *V* = 13632.2(4) Å<sup>3</sup>, *T* = 183(2) K, space group *P* 31 2 1, *Z* = 6, μ(Mo-Kα) = 8.178 mm<sup>-1</sup>, 151845 reflections measured, 15483 unique (*R*<sub>int</sub> = 0.1201) which were used in all calculations. Final *R* indices: *R*<sub>1</sub> = 0.0438 and *wR*<sub>2</sub> = 0.0395 for 15483 reflections [*I* > 2σ(*I*)]; *R*<sub>1</sub> = 0.0985 and *wR*<sub>2</sub> = 0.0451 for all data. GOF = 0.814. CCDC 778833. The resolution obtained for the structure of the compounds was limited by the poor quality of the available crystals and by the considerable disorder (Table S3, ESI†).



Scheme 1 Synthesis of **1** and **2**.

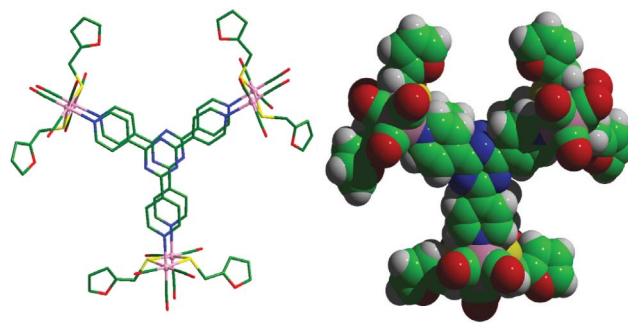
$H^c$  proton signal in bpe was shifted downfield, while  $H^b$  and vinylic protons were shifted upfield relative to those of the free bpe. Similarly, significant downfield shift was observed for the aliphatic protons of the fnt unit (Fig. S1, ESI†). These observations suggest that both ligands are coordinated to the rhenium ions. The upfield shifts observed for the bpe protons indicates that the two bpe units may maintain a face-to-face arrangement, thus shifting the proton signals upfield due to the ring current effect. Elemental analysis, FT-IR,  $^1H$  NMR and HRESI-MS are consistent with the hexanuclear trigonal prism **2**. In the HRESI-MS of **2**, a peak at  $m/z$  2946.89 corresponding to  $[M + Na]^+$  was observed (Fig. S2, ESI†). The experimental isotopic patterns are in excellent agreement with its theoretical distributions thus unambiguously establishing its cyclic structure. The  $^1H$  NMR spectrum of **2** exhibits one set of resonances for tpt and fnt moieties with the 2 : 6 integration ratio, ascribed to the existence of the hexanuclear  $M_6L_2L'_6$  metallacyclic species in solution (Fig. S3, ESI†).

The definitive proof of the structures of **1** and **2** was obtained from a single-crystal X-ray diffraction study. Compound **1** adopts a tetranuclear  $M_4L_2L'_4$ -type structure decorated with four furan units (Fig. 1). The two rigid modules of bpe, four  $\mu_2$ -sulfide, and four rhenium make up the metallacyclic rectangular framework. Examples of rhenium complexes with a  $\mu_2$ -sulfide bridge were also observed previously.<sup>18–19</sup> The size of the rectangle **1** as measured from the rhenium center is  $13.81 \text{ \AA} \times 3.78 \text{ \AA}$ . The coordination geometry around the four rhenium centers is distorted octahedral with a  $C_3NS_2$ -donor environment. The distance of the two face-to-face parallel bpe units ranges from  $3.75 \text{ \AA}$  to  $3.84 \text{ \AA}$ , suggesting  $\pi \cdots \pi$  stacking interactions. Two distinct rectangles are present in a 1 : 1 ratio in the crystal lattice and are readily distinguished by the in and out arrangements of furan units. The *syn*-arrangement of S and O provides a S,O-chelating-type pendant on the exterior of the rectangular metallacyclic framework (Fig. S4, ESI†).



**Fig. 1** Crystal structure of **1**, showing one rectangle (**1a**) with four furan units. Hydrogen atoms in stick model are omitted for clarity. Green = C, gray = H, blue = N, red = O, yellow = S, rose = Re.

Compound **2** adopts a  $M_6L_2L'_6$  trigonal prismatic structure comprised of six *fac*- $Re(CO)_3$ , two tpt, and six anionic fnt moieties (Fig. 2). The six rhenium atoms define a triangular metalloprism with  $13.34$ – $13.58 \text{ \AA}$  trigonal edges and  $3.8 \text{ \AA}$  cage height. In the crystal lattice, two types of prisms are present in a 1 : 1 ratio which differs in the orientation of the furan units. The two tpt units in **2** are arranged in an almost face-to-face arrangement. The distance between both triazine centers is  $3.59 \text{ \AA}$  which is the normal distance usually found for aromatic stacking ( $3.5 \text{ \AA}$ ) (Fig. S5,



**Fig. 2** Molecular structure of **2**, showing one trigonal prism (**2a**), with six furan units. Hydrogen atoms in stick model are omitted for clarity. Green = C, gray = H, blue = N, red = O, yellow = S, rose = Re.

ESI†). The available space between the furan units and part of the two tpt moieties is occupied by a portion of the neighboring prism unit which is stabilized by  $\pi \cdots \pi$  stacking interactions between the pyridine and furan unit.

Metallacycles **1** and **2** display intense absorption bands at *ca.*  $220$ – $320 \text{ nm}$  in THF, which are assigned to spin-allowed ligand centered  $\pi$ – $\pi^*$  transitions (Fig. S6–S8 and Table S1–S2, ESI†). The absorption peaks at  $350 \text{ nm}$  for **1** and  $360 \text{ nm}$  for **2** are assigned to MLCT transition ( $Re \rightarrow N$ -donor). In addition, the charge transfer transition between bpe  $\rightarrow$  bpe in **1** also occurs at  $317 \text{ nm}$  and  $475 \text{ nm}$ , which are assigned based on TDDFT calculations. When excited at  $380 \text{ nm}$  at room temperature, the fluorescence lifetimes for compounds **1** and **2** are  $0.31$  and  $0.88 \text{ ns}$  respectively. The observed data indicates that the emission originated from the ligand centered singlet  $\pi$ – $\pi^*$  excited state.

In conclusion, a 2D rectangle decorated with four furan units and a 3D trigonal prism decorated with six furans were assembled in a one-step *fac*- $Re(CO)_3$ -directed synthetic approach. To our knowledge, this is the first example of 2D and 3D metallacycles exocyclically functionalized with furan moieties. This synthetic method not only facilitates the incorporation of potentially biologically and materially desirable moieties onto a discrete supramolecule at the exterior but also provides control over the number and location of functional units in the molecule.

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