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An organic-organometallic CO-releasing material comprising 4,4'-bipyridine and molybdenum subcarbonyl building blocks

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Single-crystal X-ray diffraction studies

Experimental section. Single crystals of compounds $[\text{Mo}(\text{CO})_5(4,4'\text{-bpy})]\cdot 4,4'\text{-bpy}$ (**1**·4,4'-bpy) and $[\text{Mo}(\text{CO})_4(4,4'\text{-bpy})_2]\cdot 3\text{C}_7\text{H}_8$ (**2**·3C₇H₈) were manually harvested from the crystallisation vials and immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13, Sigma-Aldrich) to avoid degradation caused by the evaporation of the solvent [1]. Crystals were mounted on either Hampton Research CryoLoops or MiTeGen MicroLoops, typically with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses.

Crystal data for **1**·4,4'-bpy were collected at 150(2) K on a Bruker D8 QUEST equipped with a Mo K α sealed tube ($\lambda = 0.71073 \text{ \AA}$), a multilayer TRIUMPH X-ray mirror, a PHOTON II CMOS detector, and an Oxford Instruments Cryostream 700+ Series low temperature device controlled by the APEX4 software package [2]. Diffraction images were processed using the software package SAINT+ [3], and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS 2016/2 [4].

Crystal data for compound **2**·3C₇H₈ were collected at 150(2) K on a RIGAKU XtaLAB Synergy-i equipped with a Mo K α ($\lambda = 0.71073 \text{ \AA}$) PhotonJet-i microsource, a HyPix3000 detector controlled by the CrysAlisPro [5] software, and equipped with an Oxford Cryosystems Series 800 cryostream. Diffraction images were processed using the CrysAlisPro software and the data were corrected for absorption by the multiscan absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.

Structures were solved using the algorithm implemented in SHELXT-2014/5 [6], which allowed the immediate location of almost all of the heaviest atoms composing their molecular unit. The remaining missing and misplaced non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using the latest SHELXL from the 2018/3 release [7]. All structural refinements were performed using the graphical interface ShelXle [8].

Crystal data collected for compound **1**·4,4'-bpy was found to be that of a twinned crystal. The entire dataset was treated and refined as a twin and using Olex2 by employing the twin law $\{-1\ 0\ 0\ 1\ 0\ 0.353\ 0\ 1\}$, with the two components refining to approximately 83 and 17%, respectively.

Hydrogen atoms bound to carbon were placed at their idealized positions using *HFIX* instructions in SHELXL: *43* for aromatic carbon atoms and *137* for the $-\text{CH}_3$ groups. These hydrogen atoms were included in subsequent refinement cycles with isotropic thermal displacement parameters (U_{iso}) fixed at $1.2 \times U_{\text{eq}}$ (for the aromatic carbons) and $1.5 \times U_{\text{eq}}$ (for the $-\text{CH}_3$ groups) of the parent carbon atoms.

The last difference Fourier map synthesis showed for compound **1**·4,4'-bpy the highest peak (0.796 e\AA^{-3}) and the deepest hole (-0.426 e\AA^{-3}) located at 1.03 and 1.39 \AA from Mo1 and C1, respectively. For compound **2**·3C₇H₈, the highest peak (0.539 e\AA^{-3}) and the deepest hole (-0.318 e\AA^{-3}) were located at 0.68 and 0.63 \AA from C20 and C22, respectively. All structural drawings were created using the software package Crystal Impact Diamond [9].

Crystallographic data (including structure factors) for the two crystal structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. FAX: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

Crystal data for 1·4,4'-bpy: C₂₅H₁₆MoN₄O₅, *M* = 548.36, monoclinic, space group *P*2₁/*c*, *Z* = 4, *a* = 7.1579(8) Å, *b* = 21.788(3) Å, *c* = 15.1954(17) Å, β = 94.752(2)°, *V* = 2361.6(5) Å³, μ(Mo-Kα) = 0.599 mm⁻¹, yellow needle with crystal size of 0.37×0.09×0.08 mm³. Of a total of 9984 reflections collected, 4247 were independent (*R*_{int} = 0.0390). Final *R*1 = 0.0320 [*I* > 2σ(*I*)] and *wR*2 = 0.0823 (all data). Data completeness to theta = 25.24°, 98.2%. CCDC 2330576.

Crystal data for 2·3C₇H₈: C₄₅H₄₀MoN₄O₄, *M* = 796.75, monoclinic, space group *C*2, *Z* = 2, *a* = 15.7557(3) Å, *b* = 10.6519(2) Å, *c* = 11.7860(3) Å, β = 93.202(2)°, *V* = 1974.92(8) Å³, μ(Mo-Kα) = 0.380 mm⁻¹, red plate with crystal size of 0.508×0.179×0.035 mm³. Of a total of 10468 reflections collected, 3484 were independent (*R*_{int} = 0.0245). Final *R*1 = 0.0297 [*I* > 2σ(*I*)] and *wR*2 = 0.0774 (all data). Data completeness to theta = 25.24°, 99.9%. CCDC 2330575.

Crystal description. The compound 1·4,4'-bpy crystallises in the centrosymmetric monoclinic space group *P*2₁/*c*. The asymmetric unit is composed of a molybdenum metal centre, five coordinated carbonyl residues, one coordinated 4,4'-bpy molecule, and one free 4,4'-bpy molecule, as depicted in Fig. S1. The hexacoordinated Mo⁰ atom has a rather regular octahedral coordination environment, {MoC₅N}, with *cis* and *trans* C–Mo–C and C–Mo–N angles found in the ranges of 86.10(13)–93.49(11)° and 174.74(13)–178.06(12)°, respectively. The 4,4'-bpy molecule in the complex coordinates to the Mo⁰ centre by just one of the pyridine rings. The pyridine rings, for both coordinated and free 4,4'-bpy residues, are slightly mutually rotated with dihedral angles of 37.17 and 25.99°, respectively. The crystal packing 1·4,4'-bpy is promoted by weak C–H⋯N [*d*_{C–N} = 3.365(4)–3.392(5) Å] and C–H⋯O [*d*_{C–O} = 3.379(4) Å] supramolecular interactions between adjacent pyridine residues and between one pyridine residue and a carbonyl group. The two organic residues further interact through offset π–π interactions [*d*_{π–π} = 3.778(5) Å].

The compound [Mo(CO)₄(4,4'-bpy)₂]₂·3C₇H₈ (2·3C₇H₈) crystallises in the monoclinic non-centrosymmetric space group *C*2. The asymmetric unit is composed of one half of a molybdenum centre, one 4,4'-bpy molecule, two carbonyl groups and one and a half toluene solvent molecules (Fig. S2). Both the metal centre and one of the toluene molecules are positioned in a centre of inversion. Like 1, the Mo⁰ centre is hexacoordinated with the {MoC₅N} coordination environment resembling an octahedron. The coordination sphere has the *cis* and *trans* C–Mo–C, C–Mo–N and N–Mo–N internal angles in the 87.359(1)–92.778(1)° and 174.343(1)–178.537(1)° ranges, respectively. The two 4,4'-bpy ligands in the molecular unit are coordinated to the metal centre by a single nitrogen atom of one of the pyridine residues. The crystal packing is mediated mainly by weak C–H⋯N [*d*_{C–N} = 3.374(6) Å] and C–H⋯O [*d*_{C–O} = 3.164(7) Å] supramolecular interactions between adjacent pyridine residues and between one pyridine residue and a carbonyl group.

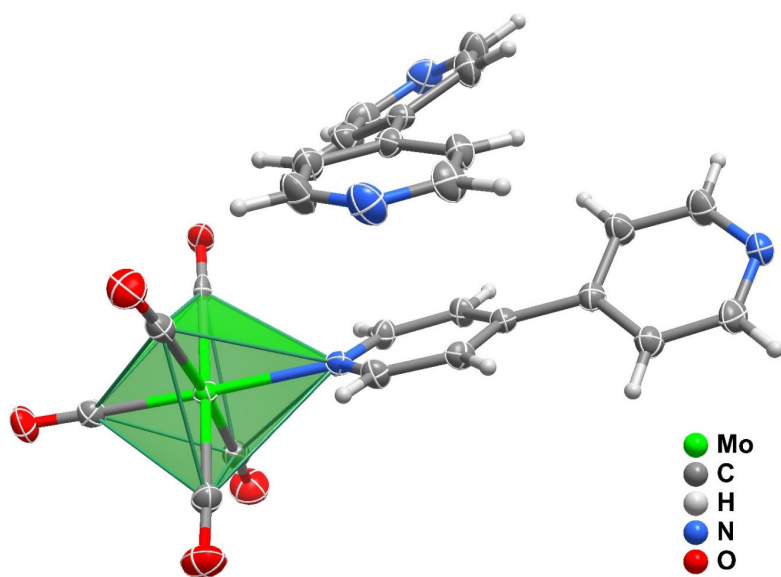


Fig. S1. Representation of the asymmetric unit of compound $[\text{Mo}(\text{CO})_5(4,4'\text{-bpy})]\cdot 4,4'\text{-bpy}$ ($1\cdot 4,4'\text{-bpy}$). Non-hydrogen atoms corresponding to the asymmetric unit are depicted as thermal ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres with arbitrary radii.

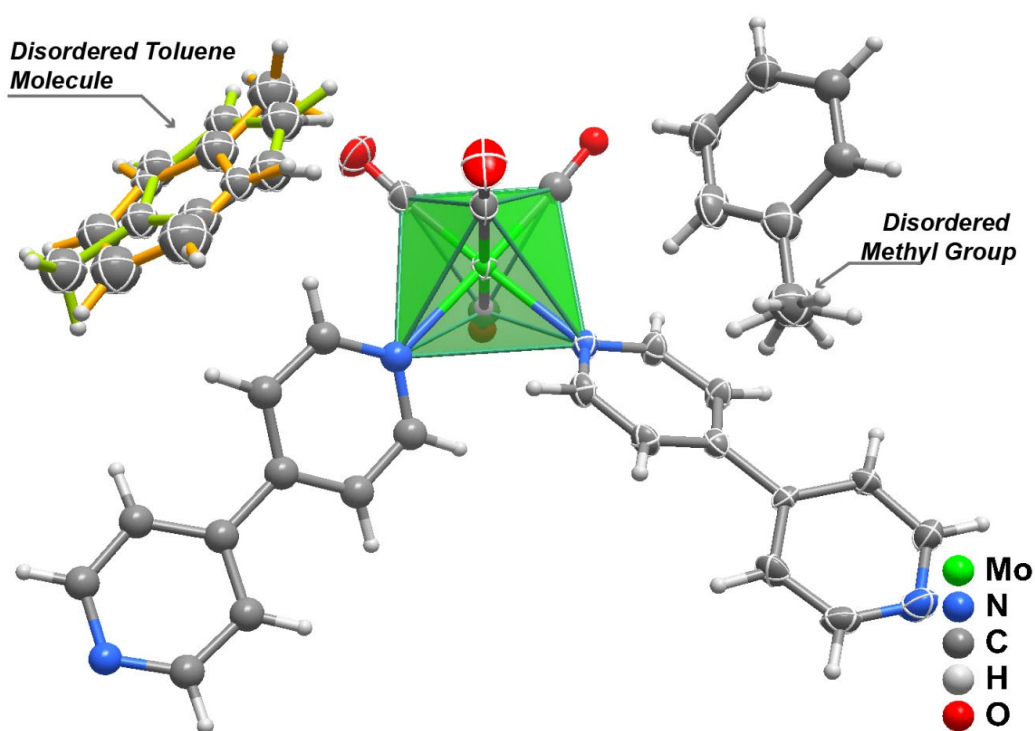


Fig. S2. Schematic representation of the molecular units present in $[\text{Mo}(\text{CO})_4(4,4'\text{-bpy})_2]\cdot 3\text{C}_7\text{H}_8$ ($2\cdot 3\text{C}_7\text{H}_8$). Non-hydrogen atoms corresponding to the asymmetric unit are depicted as ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres with arbitrary radii. The scheme emphasises the presence of a whole disordered toluene molecule, and of a disordered $-\text{CH}_3$ group in the second toluene molecule of crystallisation. The remaining atoms were generated by symmetry.

Taking into consideration these two intermediaries, and comparing with the interpenetrated 3D network structure of **Mobpy** [10], we can infer that there is a gradual incorporation of the 4,4'-bpy residues into the various compounds according to the conditions of the syntheses. Between compounds **1**·4,4'-bpy and **2**·3C₇H₈, and **2**·3C₇H₈ and the reported 3D coordination polymer, a carbonyl group is progressively substituted by a 4,4'-bpy residue (Fig. S3). In the first case, this exchange results in almost no significant conformational change in the obtained structures (Fig. S3a). However, for the formation of the 3D networks in **Mobpy**, the 4,4'-bpy residues are significantly more bent concerning the pyridine rings (Fig. S3b). The addition of a third 4,4'-bpy residue encourages the coordination to an adjacent Mo metal centre, ultimately leading to the formation of the polymeric network.

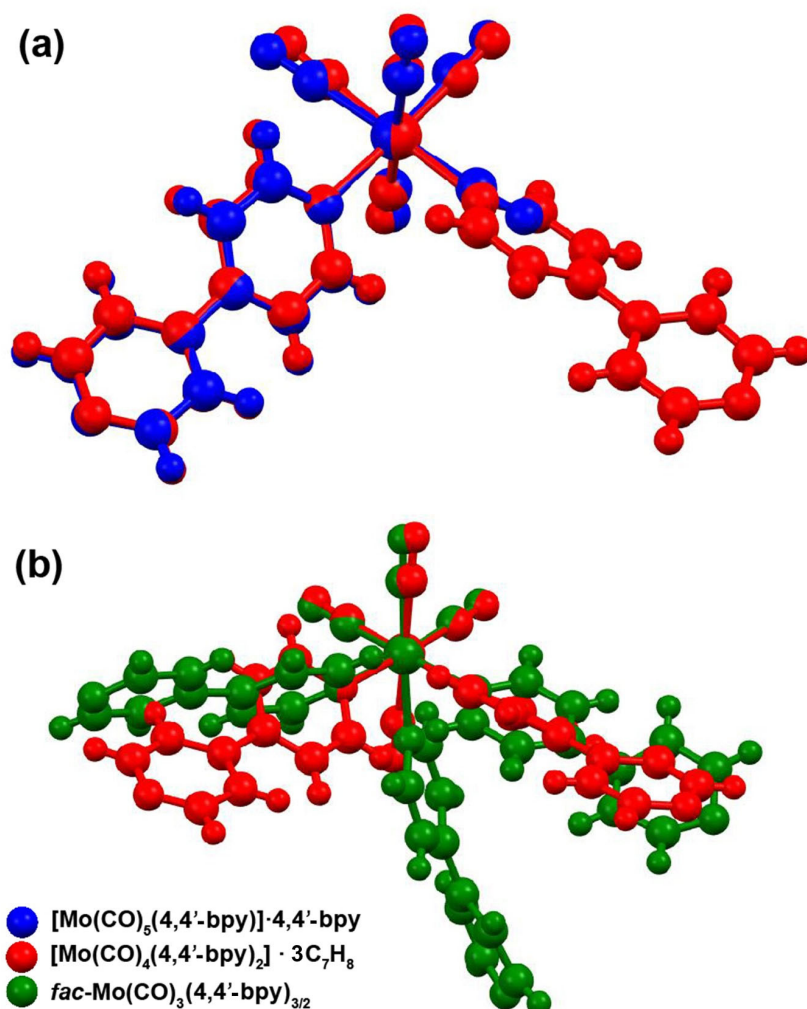


Fig. S3. Overlay representations of the coordination environment and organic ligand backbone of (a) compounds **1**·4,4'-bpy and **2**·3C₇H₈, and (b) compounds **2**·3C₇H₈ and **Mobpy**. Overlay schemes were created using Mercury [11].

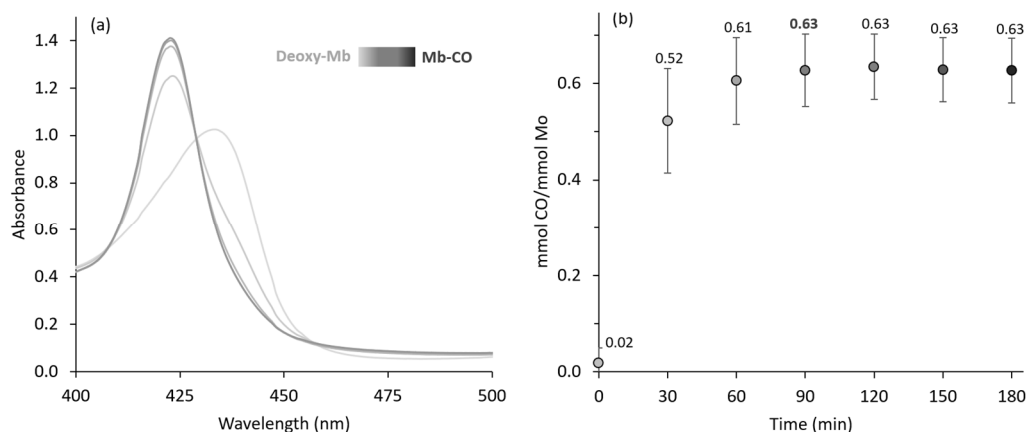


Fig. S4. Mb assay with **Mobby** in 10 mM HEPES, pH 7.4, at 37 °C and in the dark. (a) The conversion of deoxy-Mb to MbCO monitored vs. time using the Soret bands of the heme group. (b) CO-release profile.

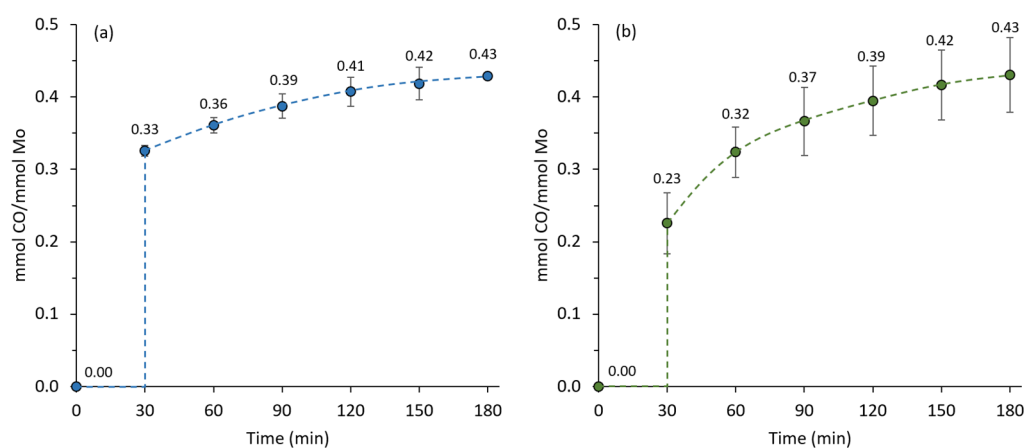


Fig. S5. Mb assays with **Mobby** at 37 °C and in the dark. (a) Time course of CO release where Mb and excess dithionite (4 mg/L) were added 30 min after the addition of **Mobby** to 10 mM PBS (pH = 7.4). (b) Time course of CO release where Mb was added after a 30 min incubation of **Mobby** with 10 mM PBS and dithionite (4 mg/L).

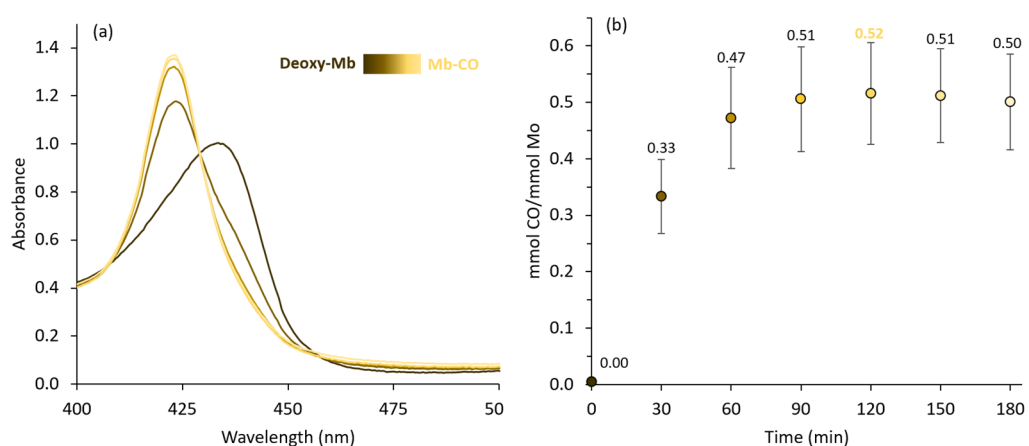


Fig. S6. Mb assay with **Mobby** in 10 mM PBS, pH 7.4, at 37 °C and with irradiation by a low power cold white light LED. (a) The conversion of deoxy-Mb to MbCO monitored vs. time using the Soret bands of the heme group. (b) CO-release profile.

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