

Supplementary Materials

Table S1. Hydrogen bonding geometry (distances in Å and angles in degrees) for Hpto.

$D-H\cdots A^a$	$d(D\cdots A)$	$\angle(DHA)$
C1–H1 \cdots N7	3.278(7)	129
C2–H2 \cdots N8 ⁱ	3.425(7)	150
C9–H9 \cdots N3 ⁱⁱ	3.400(7)	138
C11–H11 \cdots N4 ⁱⁱⁱ	3.502(7)	155
N2–H2A \cdots O1	2.634(5)	117
N2–H2A \cdots O1 ^{iv}	2.784(6)	148
N10–H10N \cdots O2	2.630(5)	117
N10–H10N \cdots O2 ^v	2.731(6)	144

^a Symmetry codes used to generate equivalent atoms: (i) $x, y+1, z$; (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $x+1/2, -y+3/2, z-1/2$; (iv) $-x+3/2, y-1/2, -z+3/2$; (v) $-x+3/2, y-1/2, -z+1/2$.

Table S2. Hydrogen bonding geometry (distances in Å and angles in degrees) for compound [MoO₂Cl₂(Hpto)]·THF (**1**).

$D-H\cdots A^a$	$d(D\cdots A)$	$\angle(DHA)$
N3–H3A \cdots O4	2.619(2)	173
C5–H5 \cdots Cl1 ⁱ	3.528(2)	128
C5–H5 \cdots O2 ⁱ	3.284(2)	137
C6–H6 \cdots Cl1 ⁱ	3.569(2)	124
C10–H10B \cdots Cl1 ⁱⁱ	3.760(3)	142

^a Symmetry codes used to generate equivalent atoms: (i) $-x+1, -y+1, -z$; (ii) $x, -y+3/2, z+1/2$.

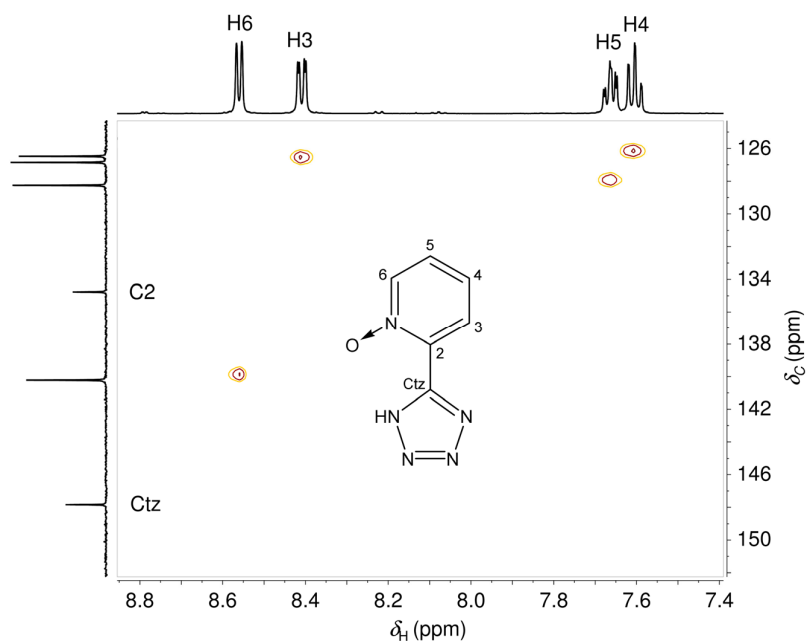


Figure S1. ¹H-¹³C HSQC NMR spectrum of Hpto in DMSO-*d*₆.

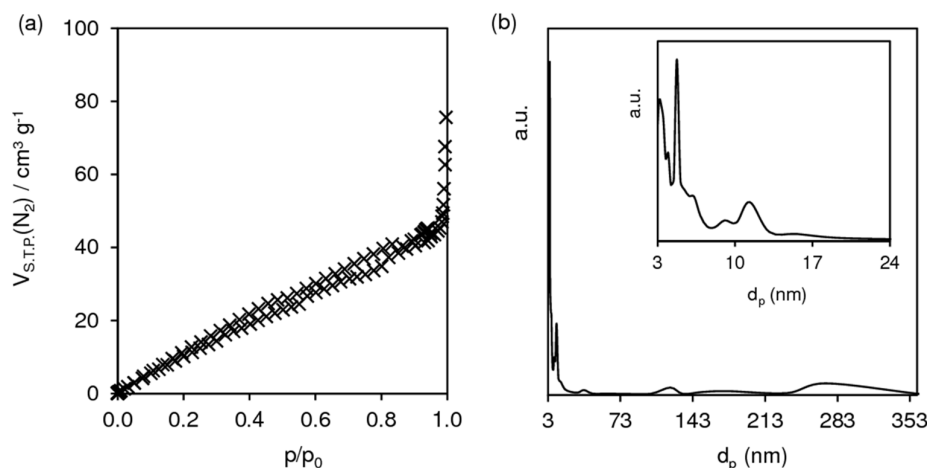


Figure S2. (a) N_2 sorption isotherm and (b) pore size distribution of **2**. The inset is an amplification of the pore size range up to 24 nm.

Single-crystal X-ray diffraction studies

Single crystals of Hpto and **1** were manually collected from the crystallization 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 [71]. 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 Hpto were collected at 150(2) K on a Bruker D8 QUEST equipped with a Mo $K\alpha$ sealed tube ($\lambda = 0.71073 \text{ \AA}$), a multilayer TRIUMPH X-ray mirror, a PHOTON 100 CMOS detector, and an Oxford Cryosystems 700+ Series Cryostream cooler. Data for **1** were collected at 150(2) K on a Bruker X8 Kappa APEX II CCD area-detector diffractometer (Mo $K\alpha$ graphite-monochromated radiation, $\lambda = 0.71073 \text{ \AA}$) controlled by APEX3 software [72] and equipped with an Oxford Cryosystems 700 Series Cryostream cooler monitored remotely using the software interface Cryopad [73]. Diffraction images were processed using SAINT+ [74], and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS 2016/2 [75].

The structures were solved using the algorithm implemented in SHELXT-2014/5 [76], which allowed the immediate location of almost all the heaviest atoms composing their molecular units. 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 [77]. All structural refinements were performed using the graphical interface ShelXle [78].

Hydrogen atoms bound to carbon were placed at their idealized positions using *HFIX* instructions in SHELXL: 43 (for aromatic carbon atoms and $-\text{NH}$ groups) and 23 (for the $-\text{CH}_2-$ groups). These hydrogen atoms were included in subsequent refinement cycles with isotropic thermal displacement parameters (U_{iso}) fixed at $1.2 \times U_{\text{eq}}$ of the parent carbon atoms.

The last difference Fourier map synthesis showed, for Hpto, the highest peak (0.34 e\AA^{-3}) and the deepest hole (-0.34 e\AA^{-3}) located at 0.91 and 1.13 \AA from C6 and N9, respectively, and, for **1**, the highest peak (0.46 e\AA^{-3}) and the deepest hole (-0.55 e\AA^{-3}) located at 0.86 and 0.65 \AA from C7 and Mo1, respectively. Table S3 lists the relevant crystal data and structure refinement parameters. Structural drawings were created using Crystal Impact Diamond [79]. CCDC 2193086 (Hpto) and 2193085 (**1**) contain the supplementary crystallographic data (including structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S3. Crystal data and structure refinement details for the organic ligand Hpto and complex [MoO₂Cl₂(Hpto)]·THF (**1**).

	Hpto	1
Formula	C ₁₂ H ₁₀ N ₁₀ O ₂	C ₁₀ H ₁₃ Cl ₂ MoN ₅ O ₄
Formula weight	326.30	434.09
Temperature / K	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /c
<i>a</i> / Å	19.165(7)	9.4102(16)
<i>b</i> / Å	3.6461(14)	9.3032(15)
<i>c</i> / Å	19.599(7)	18.550(3)
α / °	90	90
β / °	98.968(7)	102.399(2)
γ / °	90	90
Volume / Å ³	1352.8(9)	1586.1(5)
<i>Z</i>	4	4
μ (Mo K α) / mm ⁻¹	0.12	1.19
Crystal type	Yellow plate	Colorless block
Crystal size / mm	0.27×0.09×0.02	0.32×0.30×0.22
θ range (°)	2.77–25.31	2.80–29.16
Index ranges	–23 ≤ <i>h</i> ≤ 23 –4 ≤ <i>k</i> ≤ 4 –23 ≤ <i>l</i> ≤ 23	–12 ≤ <i>h</i> ≤ 12 –10 ≤ <i>k</i> ≤ 12 –22 ≤ <i>l</i> ≤ 25
Collected reflections	14968	11445
Independent reflections	2435 (<i>R</i> _{int} = 0.052)	4262 (<i>R</i> _{int} = 0.020)
Completeness to θ = 25.24°	98.0%	99.6%
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^{a–c}	<i>R</i> 1 = 0.0873 <i>wR</i> 2 = 0.2397	<i>R</i> 1 = 0.0237 <i>wR</i> 2 = 0.0579
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.0973 <i>wR</i> 2 = 0.2353	<i>R</i> 1 = 0.0288 <i>wR</i> 2 = 0.0557
Largest diff. peak and hole / eÅ ⁻³	0.34 and –0.34	0.46 and –0.55

^a
$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

^b
$$wR2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}$$

^c
$$w = 1 / \left[\sigma^2(F_o^2) + (mP)^2 + nP \right] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

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