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A Cu(II) MOF with a flexible bifunctionalised terpyridine as an efficient catalyst for the single-pot hydrocarboxylation of cyclohexane to carboxylic acid in water/ionic liquid medium

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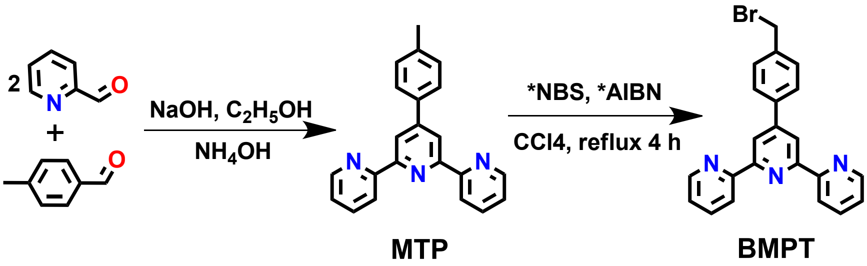
Synthesis and characterization

4’-(4-methylphenyl)-2,2’:6’,2’’-terpyridine (MTP)

2-acetylpyridine (4.84g; 40mmol) and 4-methylbenzaldehyde (2.40g; 20mmol) were added to 100 mL of ethanol while stirring. KOH pellets (3.08g; 85%; 40 mmol) were dissolved in an aqueous ammonia solution (60 mL; 30%) and this mixture was added to the previous one. The final mixture was then left under vigorous stirring for 24 h at 34 °C. The solution was cooled at room temperature, filtered and the solid was then washed with cold EtOH. The light yellow solid was recrystallized from EtOH to afford a white crystalline solid (4.76g; 74 %). ^{1}H-NMR (*δ*, ppm, 300 MHz; $CDCl_3$): 2.6 (s, 3H), 7.35 (m, 4H), 7.90 (m, 4H), 8.70 (d, 2H), 8.77 (m, 4H).

4’-[4-(bromomethyl)phenyl]-2,2’:6’,2’’-terpyridine (BMPT)

A mixture of MTP (4.76g; 14.7mmol), NBS (3.3g; 18.5mmol) and AIBN (0.2g; 1.2mmol) in dry CCl_4 was refluxed for 3h. The warm solution was filtered and the solvent was removed by distillation to dryness. The yellow solid thus obtained was then dissolved in CH_2Cl_2 and washed several times with water until neutral. The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated to afford a light yellow solid (yield: 4.73g; 80%). ^{1}H-NMR (*δ*, ppm, 300 MHz; $CDCl_3$): 4.57 (s, 2H), 7.35 (dd, 2H), 7.55 (d), 7.88 (m, 4H), 8.68 (d), 8.74 (m, 4H).



*N-Bromosuccinimide (NBS)
*Azobisisobutyronitrile (AIBN)

Scheme S1

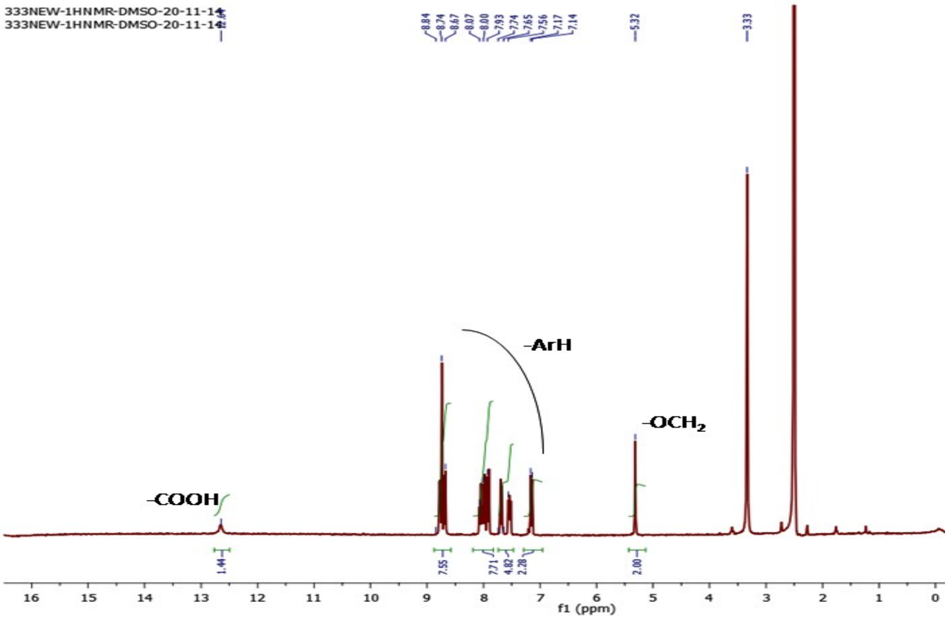


Fig. S1. ^{1}H NMR of **HL** recorded in DMSO-d_6.

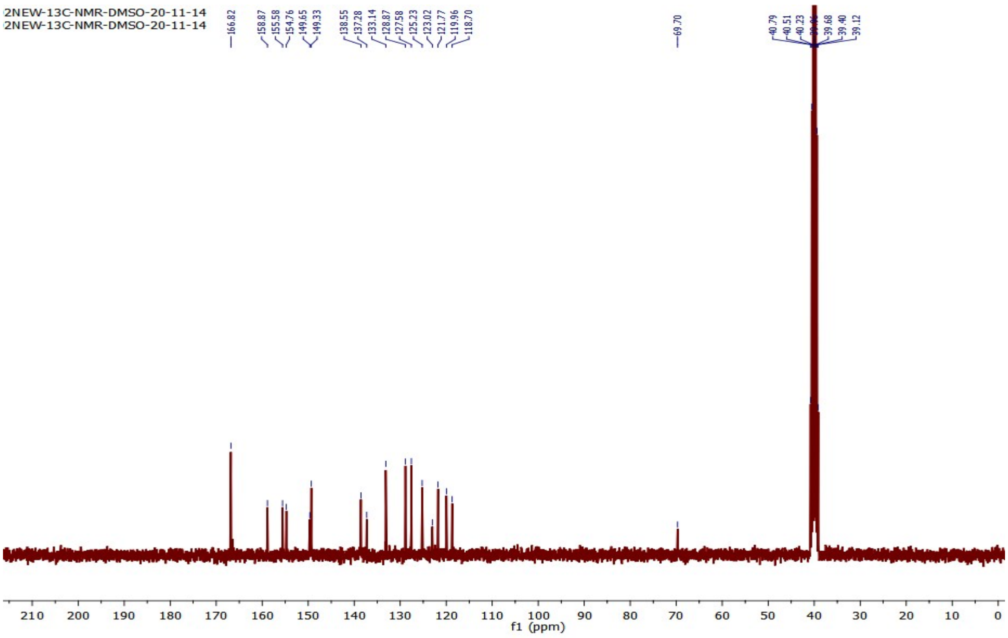


Fig. S2. ^{13}C NMR of **HL** recorded in DMSO-d_6.

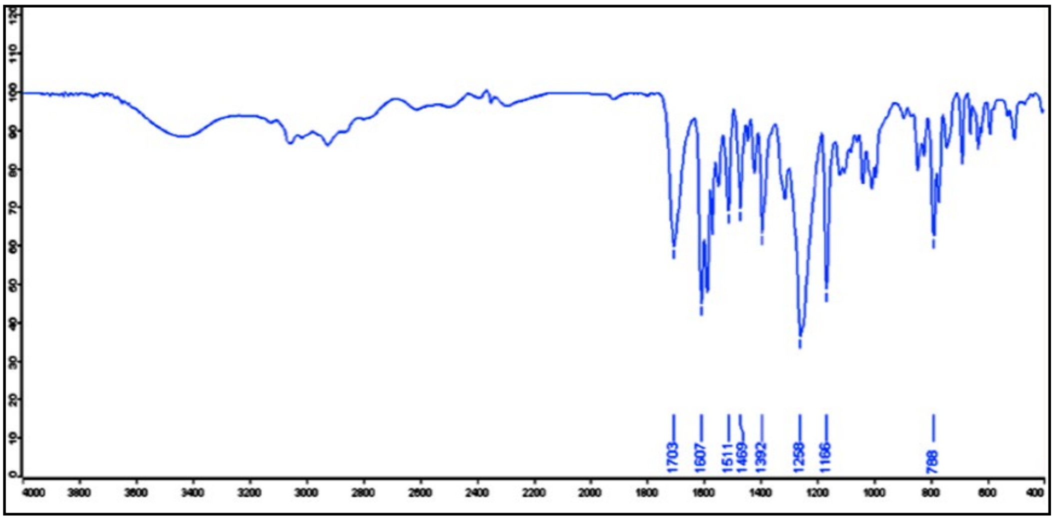


Fig. S3. FT-IR spectrum of **HL**.

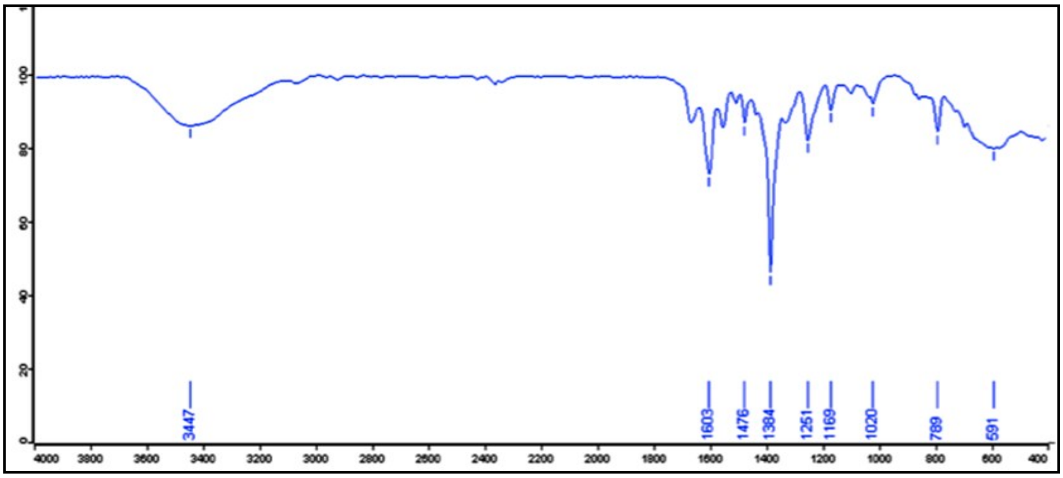


Fig. S4. FT-IR spectrum of **1**.

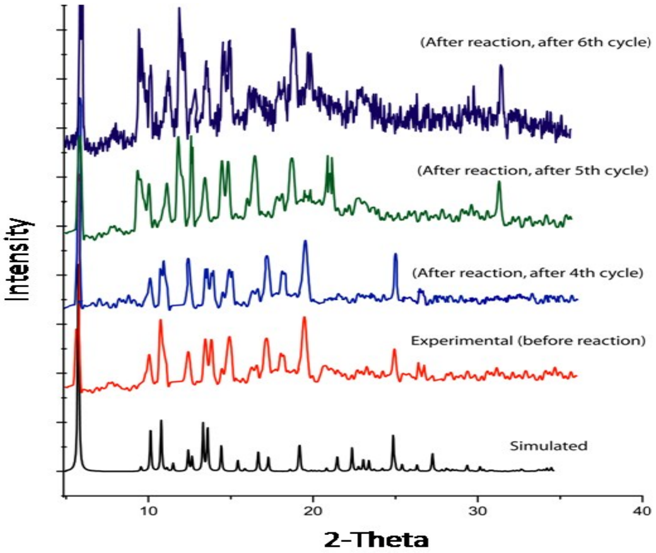


Fig. S5. Powder-XRD of **1.**

Table S1: Selected bond distances (Å) and angles (°) for **1.**

Bond distances		Bond angles	
Cu1-N1	1.922(5)	<N1-Cu1-O2	165.1(2)
Cu1-O2	1.918(4)	<N1-Cu1-N3	80.0(2)
Cu1-N3	2.031(6)	<O2-Cu1-N3	98.7(2)
Cu1-N2	2.037(6)	<N1-Cu1-N2	80.0(2)
Cu1-O4	2.282(6)	<O2-Cu1-N2	100.1(2)
Cu1-O3	1.967(3)	<N3-Cu1-N2	159.9(2)
		<N1-Cu1-O4	100.8(2)
		<O2-Cu1-O4	94.1(2)
		<N3-Cu1-O4	90.6(2)
		<N2-Cu1-O4	95.2(2)

Table S2: Hydrogen bond geometry (Å, °) in compound **1.**

1					
D-H---A	D-H (Å)	H···A (Å)	D···A (Å)	<D−H···A(°)	Symmetry
C29-H29····O6	0.93	2.61	3.310(13)	132.8	x, -y+1, z+1/2
C6-H6····O5	0.93	2.40	3.211(11)	145.7	-x+1/2, y-1/2, -z+1/2
C16-H16····O3	0.93	2.64	3.487(8)	151.1	-x+1/2, -y+3/2, -z+1
C22-H22····O3	0.93	2.42	3.307(8)	159.6	-x+1/2, -y+3/2, -z+1