Tandem post-synthetic modification for functionalized metal-organic frameworks *via* epoxidation and subsequent epoxide ring-opening

Konrad Hindelang, Sergei I. Vagin, Christian Anger and Bernhard Rieger

Wacker Lehrstuhl für Makromolekulare Chemie, Technische Universität München, 85747 Garching b. München, Lichtenbergstraße 4, Germany.

Supplementary information

General experimantal

All reactions of air- and/or moisture-sensitive compounds and product manipulations were performed under dry argon using standard Schlenk techniques. All chemicals were purchased from Aldrich, Acros or ABCR. Solvents were obtained from a MBraun MB-SPS solvent purification system. Diisopropylamine was stirred over calcium hydride for 7 days, distilled and stored over molecular sieve (4 Å). 3,3'-dimethyl-4,4'-bipyridine and dimethyldioxirane solution were prepared according to literature methods.[1, 2] Microwave assisted reactions were performed using a CEM Discover synthesis microwave. NMR spectra were recorded on a Bruker Avance 500 UltraShield (500 MHz) and a Bruker Avance 300 (300 MHz). They were recorded in ppm and the solvent was used as an internal standard ($CDCl_3$ at 7.26 ppm for ^1H and at 77.16 ppm for $^{13}C\{1H\}$). Infrared spectra were recorded on a Bruker VERTEX 70 using a Bruker Platinum ATR unit. SEM imaging was carried using a Hitachi TM-1000 tabletop microscope. X-Ray Powder Diffraction was measured on a STOE STADI P system with an IP-PSD detector. TGA was carried out on a Texas Instruments TGA-Q5000 with a heating rate of 10 °C min^{-1}. Brunauer-Emmett-Teller (BET) adsorption isotherms were obtained using a Quantachrome Nova 4000e sorption apparatus. Elemental analyses were measured at the Laboratory for Microanalytics at the Institute of Inorganic Chemistry at the Technische Universität München. ESI MS analytical measurements were performed with acetonitrile solutions on a Varian 500-MS spectrometer, using 70 eV in the positive ionization mode. High resolution mass spectra were recorded on a Thermo Scientific DFS (electron impact, EI, 70 eV).

Isolation of the bipyridine linkers for NMR spectroscopy

20 mg of dried **1**, **2** and **3** were decomposed with 1 mL of 1 M aqueous NaOH, extracted with 4 mL of chloroform and dried under vacuum. This procedure yielded approximately 4 mg of the corresponding bipyridine linker which was dissolved in $CDCl_3$ for solution NMR spectroscopy.

---

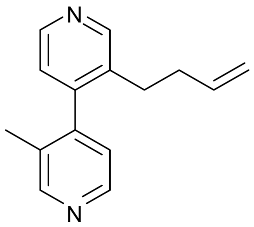
[1] B. H. Klanderman and J. W. H. Faber, *patent*, FR 1520625, 1968.

[2] R. W. Murray and M. Singh, *Org. Synth.*, 1997, **74**, 91-96.

Kinetic investigation

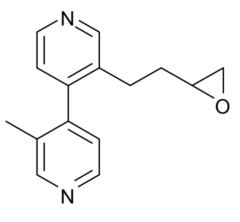
For kinetic studies of the post-synthetic epoxidation 20 mg of **1** had to stay under 3 mL of a 0.05 M solution of DMDO in acetone (8 eq.) at 4 °C. To stop the reaction the solution was first removed *via* syringe then the crystals were immediately dried under vacuum. NMR spectra were obtained as described before. For the homogeneous reaction 40 mg (0.178 mmol) of $\mathbf{L^1}$ were dissolved in 35 mL of a 0.05 M DMDO solution (10 eq.) at 4 °C. To the corresponding points in time samples of 3 mL were immediately dried in vacuo and dissolved in $CDCl_3$ for NMR spectroscopy.

Synthesis and characterization of 3-(but-3-enyl)-3’-4,4’-bipyridine $\mathbf{L^1}$



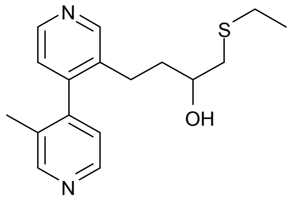
To a solution of diisopropylamine (2.40 mL, 17.1 mmol) in THF (40 mL) was slowly added 2.5 M *n*-butyllithium in hexane (6.80 mL, 17.0 mmol) at -40 °C. The solution was stirred at 0 °C for 1 h. Then a solution of 3,3’-dimethyl-4-4’bipyridine (3.00 g, 16.3mmol) in THF (50 mL) was added drop wise at -78 °C. The reaction was stirred at -78 °C for 30 min and 1 h at 0 °C. Chlorotrimethylsilane (3.10 mL, 24.3 mmol) was added at -78 °C and the solution was stirred at -78 °C for 1 h and 16 h at ambient temperature. After drying in vacuo, the residue was dissolved in water and extracted three times with chloroform (100 mL). The organic phases were dried over Na_2SO_4 and concentrated by rotary evaporation. 3-(but-3-enyl)-3’-4,4’-bipyridine ($\mathbf{L^1}$) (R_f ~ 0.16 (CH_2Cl_2:MeOH 95:5) was purified by flash chromatography on silica gel, eluting with 2% methanol in dichloromethane. Yield 3.36 g (92%). Found: C, 70.85; H, 7.19; N, 12,45. $C_{15}H_{16}N_2$ requires C, 80.32; H, 7.19; N, 12.49. δH (300 MHz; $CDCl_3$) 2.05 (3H, s), 2.14 (2H, q, *J* = 7,6 Hz), 2.39 (1H, m) 2.57 (1H, m), 4.87 (2H, m), 5.62 (1H, m), 7.01 (2H, m), 8.54 (4H, m); δC (75.5 MHz, $CDCl_3$) 16.86, 29.92, 34.55, 116.03, 123.33, 123.38, 130.74, 134.23, 136.82, 146.41, 147.26, 147.46, 151.01, 151.27. *m/z* (ESI) 225.1 ($[M + H]^+$. $[C_{15}H_{16}N_2 + H]^+$ requires 225.1).

Characterization of isolated 3-methyl-3'-(2-(oxiran-2-yl)ethyl)-4,4'-bipyridine $\mathbf{L^2}$



δH (500 MHz; $CDCl_3$) 1.62 (2H, m), 2.06 (3H, s), 2.31 (1H, m) 2.47 (1H, m), 2.66 (2H, m), 2.76 (1H, m), 7.01 (1H, d, *J* = 4.9 Hz), 7.03 (1H, d, *J* = 4.9 Hz), 8.54 (4H, m); δC (125.8 MHz, $CDCl_3$) 16.83, 29.94, 33.30, 33.53, 47.08, 47.12, 51.40, 51.42, 122.97, 123.15, 123.40, 123.43, 130.60, 133.68, 133.72, 146.08, 146.25, 147.52, 147.93, 150.94, .151.00, 151.38, 151.50, 151.52. *m/z* (ESI) 241.1 ($[M + H]^+$. $[C_{15}H_{16}N_2O + H]^+$ requires 241.1). *m/z* (EI) 240.1249 ($[M]^+$. $[C_{15}H_{16}N_2O]^+$ requires 240.1257).

Characterization of isolated 1-(ethylthio)-4-(3'-methyl-4,4'-bipyridin-3-yl)butan-2-ol L[3]



δH (500 MHz; $CDCl_3$) 1.62 (3H, t, J = 7.4 Hz), 1.59 (2H, m), 2.07 (3H, s), 2.35 – 2.75 (2H, m), 2.35 (1H, dd, J = 8.8 Hz, 13.6 Hz), 2.47 (2H, q, J = 7.4 Hz), 2.59 (1H, dd, J = 3.6 Hz, 13.6 Hz), 3.47 (1H, m), 7.04 (2H, m), 8.56 (4H, m); δC (125.8 MHz, $CDCl_3$) 14.99, 16.85, 26.27, 26.73, 26.77, 36.84, 36.96, 39.72, 68.11, 68.18, 123.03, 123.20, 123.29, 123.43, 130.69, 133.79, 134.55, 150.85, 150.91, 151.21, 151.24, 151.40. *m/z* (ESI) 303.1 ($[M + H]^+$. $[C_{17}H_{22}N_2OS + H]^+$ requires 303.2).

Structure of $[Zn_2(TDC)_2(4,4'\text{-bipyridine})]$

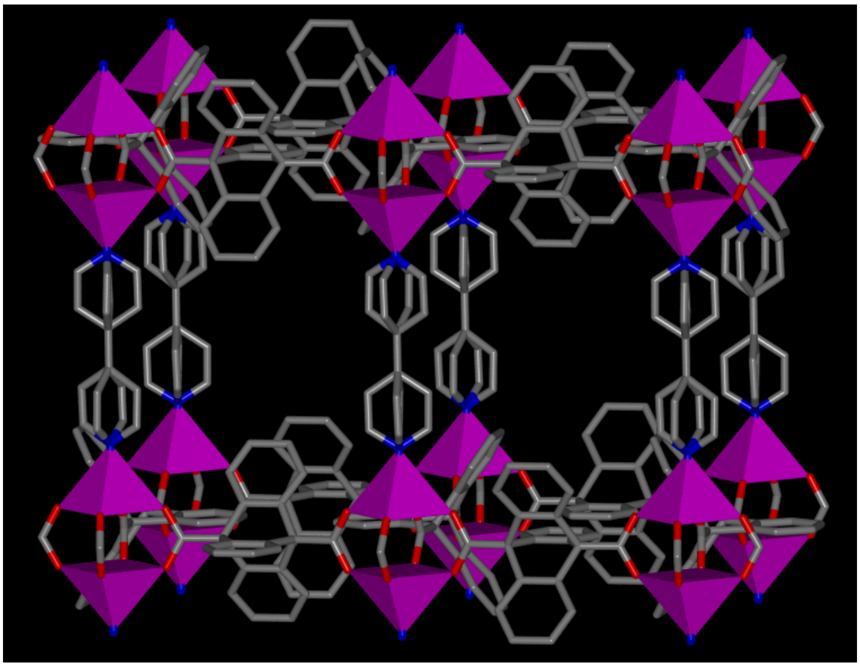


Figure S1. Structure of zinc - tripycenedicarboxylic acid – bipyridine paddle-wheel MOF obtained from single crystal data.[3]

---

[3] S. I. Vagin, A. K. Ott, S. D. Hoffmann, D. Lanzinger and B. Rieger, *Chemistry – A European Journal*, 2009, **15**, 5845-5853.

Elemental analysis of MOF compounds 1, 2 and 3

[$Zn_2(TDC)_2$**L**^{1}] **1**:
Found: C, 66.88; H, 4.28; N, 3.12. $C_{59}H_{40}N_2O_8Zn_2\cdot H_2O\cdot 0.4DMF$ requires C, 66.76; H, 4.17; N, 3.10.

[$Zn_2(TDC)_2$**L**^{2}] **2**:
Found: C, 65.65; H, 4.05; N, 2.94. $C_{59}H_{40}N_2O_9Zn_2\cdot H_2O\cdot 0.3DMF$ requires C, 65.90; H, 4.07; N, 2.95.

[$Zn_2(TDC)_2$**L**$^2_{0.5}$**L**$^3_{0.5}$] **3**:
Found: C, 65.12; H, 4.17; N, 2.58; S, 1.40. $C_{60}H_{43}N_2O_9S_{0.5}Zn_2\cdot H_2O$ requires C, 66.00; H, 4.06; N, 2.57; S, 1.47.

SEM analysis of 1, 2 and 3

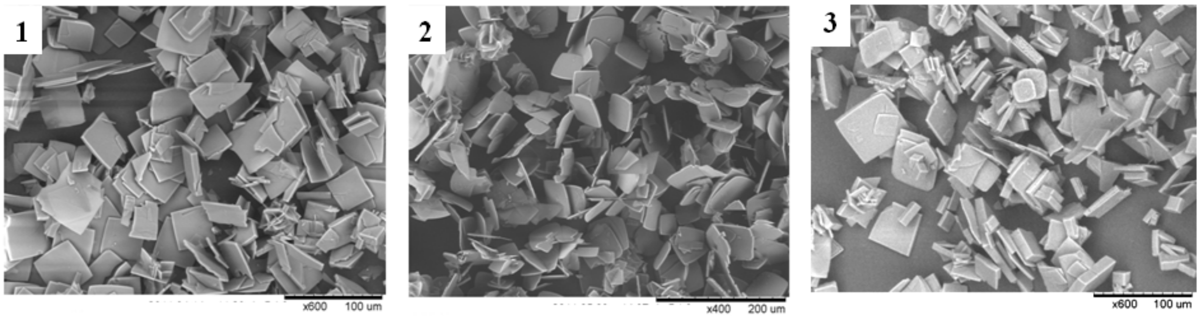


Figure S2. SEM images of [$Zn_2(TDC)_2$**L**^{1}] **1**, [$Zn_2(TDC)_2$**L**^{2}] **2** and [$Zn_2(TDC)_2$**L**$^2_{0.5}$**L**$^3_{0.5}$] **3**.

Calculated and measured powder diffraction

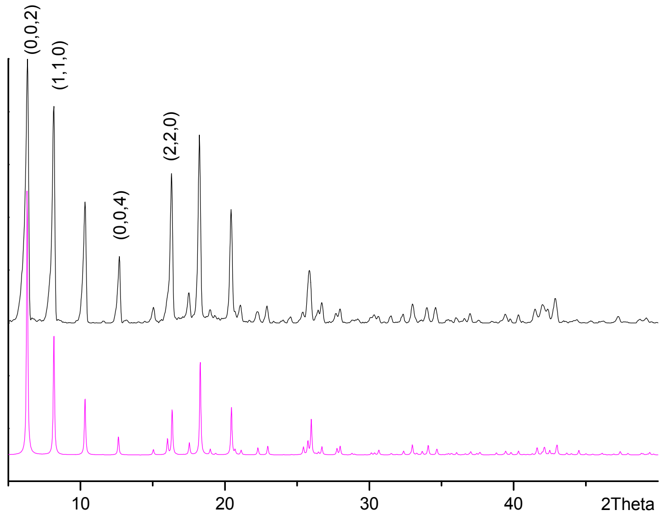


Figure S3. Comparison of calculated XRPD obtained from single crystal data (magenta) and experimental XRPD data (black) of zinc - tripycenedicarboxylic acid - bipyridine paddle-wheel MOF.[3]

IR analysis of isolated L^1, L^2, and L^3

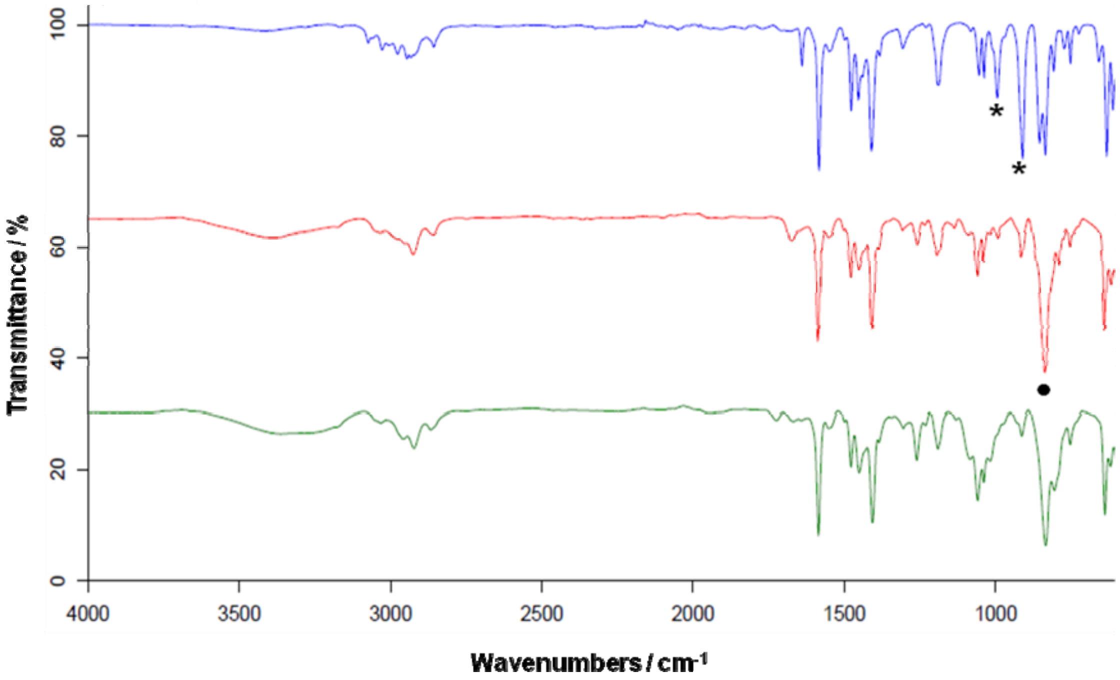


Figure S4. IR spectra of bipyridine linkers **L**^{1} (blue), **L**^{2} (red) and the mixture of **L**^{2} and **L**^{3} isolated from MOF **3** (green). Deformations bands of vinylic side group at 994 cm^{-1} and 911 cm^{-1} (∗) and epoxy ring vibration at 833 cm^{-1} (•).

Thermogravimetric analysis of MOF compounds 1, 2 and 3

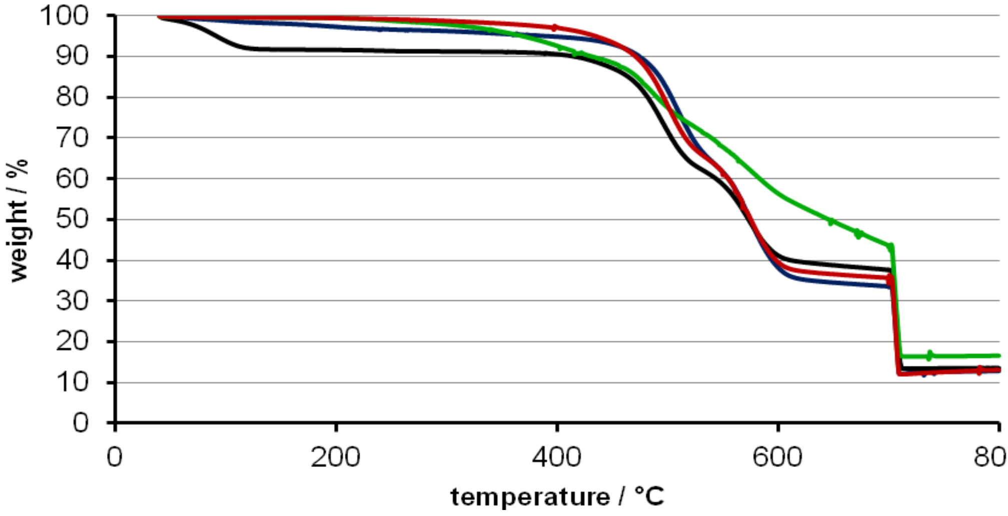


Figure S5. Thermogravimetric analysis (TGA) of compounds **1** (blue), **2** (red) and **3** (green) after activation in vacuo at 100 °C. TGA of **2** after drying in vacuo without heating (black). Heating rate: 10 °C min^{-1}; Flow gas: nitrogen between 40 °C and 700 °C; synthetic air between 700 °C and 800 °C.

Gas sorption analysis of compound 1, 2 and 3

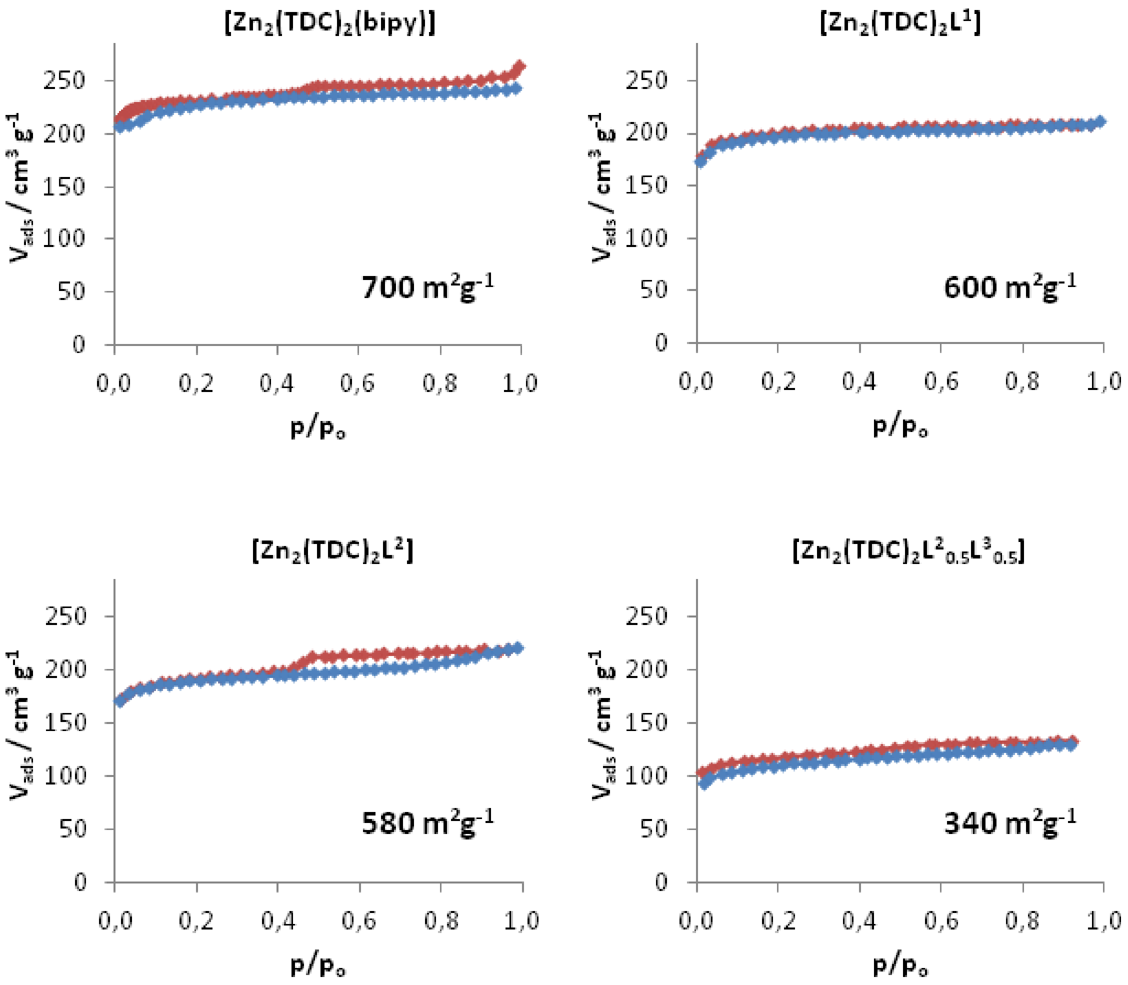


Figure S6. N_2 isotherms and calculated BET surface area of $[Zn_2(TDC)_2(bipy)]$, **1**, **2** and **3** at 77 K. For gas sorption analysis the samples were pre-activated for 24 h by evacuation at 180 °C and 4 h at 200 °C immediately before measurement. The surface area was determined by multi-point BET method using the adsorption data in the relative pressure (p/p_o) range of 0.05 to 0.3.