Inclusion of viologen cations leads to switchable metal-organic frameworks

Laura K. Cadman, Mary F. Mahon and Andrew D. Burrows

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

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1. General experimental details

Methyl viologen diiodide,^{S1} ethyl viologen dibromide^{S2} and viologen diacetic acid dichloride^{S3} were prepared using reported methods. All other starting materials and solvents were purchased from commercial sources and were used without further purification.

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker AXS D8 Advance diffractometer with copper K α radiation of wavelength 1.5406 Å at 298 K. Samples were placed on a flat plate, and measured with a 2 θ range of 5-60°. The step size was 0.024° with time per step of 0.3 s. Samples for PXRD analysis were air dried at room temperature for 1-2 minutes prior to analysis.

¹H NMR spectroscopy was carried out on a 300 MHz Bruker Avance spectrometer. Samples were dried at 100 °C for 20 minutes and digested in a solution of d_6 -DMSO and DCl. The digestion solution was prepared by combining 3 ml d_6 -DMSO with 0.1 ml DCl (35% wt in D₂O). Each sample was dissolved in 0.4 ml of d_6 -DMSO and 0.2 ml of the digestion solution.

EPR spectra were recorded by Dr Floriana Tuna at the National EPR Facility, University of Manchester. TGA experiments were carried out on a Perkin Elmer TGA 4000 thermogravimetric analyser. The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C/min, under a flow of nitrogen (20 mL/min). UV irradiation experiments were conducted using a Photochemical Reactor Ltd small quartz RQ125 Immersion Well reactor with a 125 W mercury, medium pressure lamp.

2. Synthesis and characterisation

2.1 Synthesis of [MV][Zn₃(mbdc)₄] (1-lt and 1-ht)

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.502 mmol, 0.149 g), H_2mbdc (0.493 mmol, 0.082 g) and $[MV]I_2$ (0.502 mmol, 0.22 g) were combined in a vial with 7 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 85 °C for 2 days. Orange and blue crystals (1-lt) were produced in a yield of 0.174 g (34% based on H_2mbdc). The reaction was repeated using the same procedure but heating at to 120 °C. Blue crystalline product (1-ht) was produced with a yield of 0.211 g (41% based on H_2mbdc). PXRD patterns for 1-lt and 1-ht are shown in Figure S1, ¹H NMR spectra of digested 1-lt and 1-ht are shown in Figure S2 and the TGA of 1-ht is shown in Figure S3.



Figure S1. Powder X-ray diffraction patterns for **1-lt** and **1-ht** in comparison to that simulated from the crystal structure of [MV][Zn₃(mbdc)₄].^{S4}



Figure S2. ¹H NMR spectra of digested samples of 1-lt (blue) and 1-ht (red). The resonances at δ 6.80 and 6.59 ppm originate from water.



Figure S3. Thermogravimetric analysis of 1-ht confirming the absence of included solvent.

2.2 Synthesis of [MV]_{0.44}[MVH₂]_{0.36}[NMe₂H₂]_{0.4}[Zn₃(bdc)₄]·0.6DMF (2-lt and 2-ht)

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.0.498 mmol, 0.148 g), H_2bdc (0.498 mmol, 0.083 g) and $[MV]I_2$ (0.502 mmol, 0.22 g) were combined in a vial with 7 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 85 °C for 2 days. Orange and blue crystals (2-lt) were produced in a combined yield of 0.236 g (40% based on H_2bdc). The reaction was repeated using the same procedure but with a temperature of 120 °C. Blue crystalline product (2-ht) was produced with a yield of 0.284 g (48% based on H_2bdc).

PXRD patterns for **2-lt** and **2-ht** are shown in Figures S4 and S5. ¹H NMR spectra of digested **2-ht** are shown in Figure S6 and S7, with the COSY and NOESY spectra shown in Figures S8 and S9 respectively. The TGA of **2-ht** is shown in Figure S10.



Figure S4. Powder X-ray diffraction patterns for **2-lt** and **2-ht** in comparison to that simulated from the crystal structure of $(NMe_2H_2)_2[Zn_3(bdc)_4] \cdot DMF \cdot H_2O.^{S5}$



Figure S5. Powder X-ray diffraction patterns for 2-ht in comparison to that simulated from the crystal structure.



Figure S6. ¹H NMR spectrum of 2-ht digested in DCl/D₂O/DMSO-*d*₆.



Figure S7. ¹H NMR spectrum of **2-ht** digested in DCl/D₂O, and filtered to remove the majority of the D₂bdc. The resonances marked H_E , H_F and H_G are from a species with the same symmetry as $[MV]^{2+}$.



Figure S8. ¹H-¹H COSY spectrum of **2-ht**, following digestion in DCl/D₂O/DMSO- d_6 . The resonances due to D₂bdc (H_A), methyl viologen (H_B, H_C and H_D) and the other species (H_E, H_F, and H_G) are labelled.



Figure S9. NOESY spectrum of **2-ht**, following digestion in DCl/D₂O/DMSO- d_6 . The resonances due to D₂bdc (H_A), methyl viologen (H_B, H_C and H_D) and the other species (H_E, H_F, and H_G) are labelled.



Figure S10. Thermogravimetric analysis of 2-ht.

2.3 Synthesis of [MV]_{0.8}[NMe₂H₂]_{0.4}[Zn₃(bdc)₄] (3-ht)

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.502 mmol, 0.149 g), H_2bdc (0.481 mmol, 0.080 g) and viologen diacetic acid dichloride (0.631 mmol, 0.217 g) were combined in a vial with 7 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 120 °C for 2 days. Blue crystals (**3-ht**) were produced in a yield of 0.244 g (47% based on H_2bdc). PXRD patterns for **3-lt** and **3-ht** are shown in Figure S11, and the ¹H NMR spectrum of digested **3-lt** is shown in Figure S12.



Figure S11. Powder X-ray diffraction patterns for 3-lt and 3-ht in comparison to that for 2ht. The Bragg peaks marked with an asterisk are from an identified phase.



Figure S12. ¹H NMR spectrum of **3-lt** following digestion in DCl/D₂O/DMSO- d_6 . The peak labelled H_A is due to D₂bdc.

2.4 Synthesis of [MV]_{0.5}[Zn(btc)]·DMF (4-lt and 4-ht)

 $Zn(NO_3)_2 \cdot 6H_2O(0.502 \text{ mmol}, 0.149 \text{ g})$, $H_3btc(0.501 \text{ mmol}, 0.106 \text{ g})$ and $[MV]I_2(0.547 \text{ mmol}, 0.24 \text{ g})$ were combined in a vial with 7 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 85 °C for 2 days. Orange and blue crystals (4-lt) were produced in a yield of 0.075 g (32% based on H_3btc). The reaction was repeated using a similar procedure heating to 120 °C. Blue crystalline product (4-ht) was produced with a yield of 0.080 g (38 % based on H_3btc).

PXRD patterns for 4-lt and 4-ht are shown in Figures S13 and S14. The EPR spectrum for 4ht is shown in Figure S15 and the ¹H NMR spectrum of digested 4-ht is shown in Figure S16. The TGA of 4-ht is shown in Figure S17.



Figure S13. Powder X-ray diffraction patterns for 4-lt and 4-ht in comparison to that simulated for the structure of (NMe₂H₂)[Zn(btc)].^{S6}



Figure S14. Powder X-ray diffraction pattern for 4-ht in comparison to that simulated from the crystal structure.



Figure S15. EPR spectrum for 4-ht.



Figure S16. ¹H NMR spectrum of 4-ht following digestion in DCl/D₂O/DMSO-d₆.



Figure S17. Thermogravimetric analysis of 4-ht.

2.5 Synthesis of [MV][Zn₄(bpdc)₅]·8DMF·10H₂O (5-lt and 5-ht)

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.253 mmol, 0.075 g), H_2 bpdc (0.512 mmol, 0.124 g) and $[MV]I_2$ (0.251 mmol, 0.11 g) were combined in a vial with 7.5 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 85 °C for 2 days. Blue crystals (**5-lt**) were produced in a yield of 0.280 g (23% based on $Zn(NO_3)_2 \cdot 6H_2O$). The reaction was repeated using the same procedure but heating to 120 °C. Blue crystalline product (**5-ht**) was produced with a yield of 0.311 g (26% based on $Zn(NO_3)_2 \cdot 6H_2O$).

PXRD patterns for **5-lt** and **5-ht** are shown in Figures S18 and S19. The ¹H NMR spectrum of digested **5-ht** is shown in Figure S20.



Figure S18. Powder X-ray diffraction patterns for **5-lt** and **5-ht** in comparison to that simulated for the structure of (NMe₂H₂)₂[Zn₃(bpdc)₄]·5DMF.^{S7}



Figure S19. Powder X-ray diffraction pattern for 5-ht in comparison to that simulated from the crystal structure.



Figure S20. ¹H NMR spectrum of 5-ht following digestion in DCl/D₂O/DMSO-*d*₆.

2.6 Synthesis of [EV][Zn₃(mbdc)₄] 6

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.502 mmol, 0.149 g), H_2mbdc (0.498 mmol, 0.083 g) and $[EV]Br_2$ (0.615 mmol, 0.23 g) were combined in a vial with 7 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 120 °C for 2 days. Blue crystals of **6** were produced in a yield of 0.170 g (37% based on H_2mbdc).

The PXRD pattern for **6** is shown in Figure S21. The ¹H NMR spectrum of digested **6** is shown in Figure S22 and the TGA for **6** is shown in Figure S23.



Figure S21. Powder X-ray diffraction pattern for 6 in comparison to that for 1-ht.



Figure S22. ¹H NMR spectrum of 6 following digestion in DCl/D₂O/DMSO-*d*₆.



Figure S23. Thermogravimetric analysis of 6.

2.7 Synthesis of [EV]_{0.53}[EVH₂]_{0.26}[NMe₂H₂]_{0.42}[Zn₃(bdc)₄] 7

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.502 mmol, 0.149 g), H_2bdc (0.501 mmol, 0.082 g) and [EV]Br₂ (0.513 mmol, 0.192 g) were combined in a vial with 7 ml anhydrous DMF and sealed. The reactants were sonicated for 15 minutes until dissolved and heated to 120 °C for 2 days. Blue crystals of 7 were produced in a yield of 0.158 g (30%). The PXRD pattern for 7 is shown in Figure S24. The ¹H NMR spectrum of digested 7 is shown in Figure S25 and the TGA for 7 is shown in Figure S26.



Figure S24. Powder X-ray diffraction patterns for 7 in comparison to that for 2-ht.



Figure S25. ¹H NMR spectrum of 7 following digestion in DCl/D₂O/DMSO-*d*₆.



Figure S26. Thermogravimetric analysis of 7.

3. Crystallographic details

3.1 Crystal structure of 2-ht

A suitable crystal of **2-ht** was selected and mounted on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. Using Olex2,^{S8} the structure was solved with the olex2.solve^{S9} structure solution program using Charge Flipping and refined with the ShelXL^{S10} refinement package using Least Squares minimisation. Details of the crystal data and structure refinement for **2-ht** are given in Table S1.

Empirical formula	C_{44} 2H35 32N2 6O16 6Zn3
Formula weight	1064 58
Temperature/K	150,00(10)
Crystal system	monoclinic
Space group	$C^{2/c}$
a/Å	32 7998(10)
h/Å	9 7204(4)
	18 3042(6)
	00
a.∕ β/°	96 453(3)
p/ 2// ^o	90
Y/ Volumo/Å ³	5708 0(2)
Z	A
$\sum_{\alpha, \beta, \alpha} \frac{1}{\alpha \beta \beta$	1 210
	1.219
	1.936
$\frac{F(000)}{2}$	2166.0
Crystal size/mm ³	0.104 × 0.073 × 0.030
Radiation	$CuK\alpha (\lambda = 1.54184 \text{ Å})$
2θ range for data collection/°	5.42 to 145.7
Index ranges	$-40 \le h \le 39, -7 \le k \le 11, -18 \le l \le 22$
Reflections collected	13781
Independent reflections	5632 [$R_{\text{int}} = 0.0366, R_{\text{sigma}} = 0.0656$]
Data/restraints/parameters	5632/77/292
Goodness-of-fit on F ²	1.055
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0655, wR_2 = 0.1912$
Final <i>R</i> indexes [all data]	$R_1 = 0.0800, wR_2 = 0.2023$
Largest diff. peak/hole / e Å ⁻³	1.31/-0.69

 Table S1. Crystal data and structure refinement for 2-ht.

The asymmetric unit in this structure comprises one full zinc centre, one zinc at half occupancy, one complete bdc ligand, half of an ordered bdc ligand, 2 independent bdc halves, a region of electron density that corresponds to an overlay between 0.22 of half of an MV moiety and 0.18 of an H₂MV fragment, plus an area of diffuse solvent. ¹H NMR digestion studies showed that the total MV and H₂MV content equated to 0.8 molecules per 3 zinc centres, and that the MV:H₂MV ratio is 44:36. The electron density is somewhat smeared in this region, precluding any possibility of resolving these two moieties, with the exception of a tentative effort pertaining to the methyl group attached to N1 (which has been refined over 2 positions). ADP and planarity restraints were also employed for these guest species. The diffuse solvent and dimethylammonium counter ion could not be reliably located, and residual electron density arising from same has been treated via the solvent mask algorithm in Olex-2. The formula as presented is [MV]_{0.44}[H₂MV]_{0.36}[NMe₂H₂]_{0.4}[Zn₃(bdc)₄]·0.6DMF. The overall DMF solvent content was determined via TGA measurements. The acetone exchanged with the DMF via the washing was not detectable via TGA - and may well have left the framework because of its low vapour pressure. As such, no allowance has been made in the formula as presented herein for guest acetone.

3.2 Crystal structure of 4-ht

A suitable crystal of **4-ht** was selected and mounted on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. Using Olex2,^{S8} the structure was solved with the olex2.solve^{S9} structure solution program using Charge Flipping and refined with the ShelXL^{S10} refinement package using Least Squares minimisation. Details of the crystal data and structure refinement for **4-ht** are given in Table S2.

J	
Empirical formula	$C_{36}H_{34}N_4O_{14}Zn_2$
Formula weight	877.41
Temperature/K	150.01(10)
Crystal system	monoclinic
Space group	$P2_{1}/n$
a/Å	9.6981(2)
b/Å	16.1078(5)
c/Å	11.5458(4)
α/°	90
β/°	90.923(3)
$\gamma/^{\circ}$	90
Volume/Å ³	1803.41(9)
Ζ	2
$\rho_{\text{calc}} g/\text{cm}^3$	1.616
μ/mm^{-1}	2.305
<i>F</i> (000)	900.0
Crystal size/mm ³	0.08 imes 0.03 imes 0.025
Radiation	$CuK\alpha (\lambda = 1.54184 \text{ Å})$
2θ range for data collection/°	9.426 to 146.132
Index ranges	$-6 \le h \le 11, -19 \le k \le 19, -14 \le l \le 14$
Reflections collected	7613
Independent reflections	3527 [$R_{\text{int}} = 0.0382, R_{\text{sigma}} = 0.0515$]
Data/restraints/parameters	3527/10/285
Goodness-of-fit on F^2	1.045
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0430, wR_2 = 0.1085$
Final <i>R</i> indexes [all data]	$R_1 = 0.0559, wR_2 = 0.1157$
Largest diff. peak/hole / e Å ⁻³	0.74/-0.55

Table S2. Crystal data and structure refinement for 4-ht.

The asymmetric unit comprises one zinc centre, one btc ligand, one DMF molecule (disordered over 2 sites in a 75:25 ratio) and half of one viologen moiety. Some similarity distance and ADP restraints were applied in the disordered solvent area to assist convergence of the minor

component. The latter was also refined subject to being flat. A search for hydrogen atoms attached to O2 and/or O5 did not afford a convincing case for either based on these data. Adding hydrogens with plausible calculated positions and 'free' U_{iso} values to these two oxygens resulted in the isotropic displacement for both 'blowing up' to a value of 2.0 post least-squares.

3.3 Crystal structure of 5-ht

A suitable crystal of **5-ht** was selected and mounted on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. Using Olex2,^{S8} the structure was solved with the olex2.solve^{S9} structure solution program using Charge Flipping and refined with the ShelXL^{S10} refinement package using Least Squares minimisation. Details of the crystal data and structure refinement for **5-ht** are given in Table S3.

Empirical formula	$C_{212}H_{260}N_{20}O_{76}Zn_8$
Formula weight	4827.34
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	36.4926(13)
b/Å	14.6058(4)
c/Å	45.4204(13)
α/°	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	24209.2(13)
Ζ	4
$\rho_{calc}g/cm^3$	1.324
μ/mm^{-1}	1.588
<i>F</i> (000)	10080.0
Crystal size/mm ³	$0.129 \times 0.067 \times 0.016$
Radiation	$CuK\alpha (\lambda = 1.54184)$
2θ range for data collection/°	6.052 to 136.502
Index ranges	$-43 \le h \le 17, -17 \le k \le 16, -53 \le l \le 54$
Reflections collected	52150
Independent reflections	$32875 [R_{int} = 0.0508, R_{sigma} = 0.0940]$
Data/restraints/parameters	32875/625/2701
Goodness-of-fit on F ²	1.047
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0788, wR_2 = 0.2031$
Final R indexes [all data]	$R_1 = 0.0980, wR_2 = 0.2252$
Largest diff. peak/hole / e Å ⁻³	1.29/-0.98
Flack parameter	0.51(4)

Table S3.	Crystal data	and structure	refinement	for 5-ht .
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The 16 guest DMF moieties in the asymmetric unit have been located. Possible disorder is evident in some cases in terms of the ADPs (which was not modelled). Distance and ADP restraints have been included for the molecules based on N5, N6, N7, N8, N10, N12, N13, N17 and N18. Additional ADP restraints have been invoked, on merit, in the model in order to assist convergence. The water content, which was not resolved, has been treated using the PLATON SQUEEZE algorithm. A value of 20 water molecules has been included on the basis of an estimate from the TGA data, as well as the output from the SQUEEZE analysis.

3.4 Crystal structure of 7'

A suitable crystal of **7'** was selected and mounted on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. Using Olex2,^{S8} the structure was solved with the olex2.solve^{S9} structure solution program using Charge Flipping and refined with the ShelXL^{S10} refinement package using Least Squares minimisation. Details of the crystal data and structure refinement for **7'** are given in Table S4.

Empirical formula	C48.2H46.52N3.4O18.7Zn3
Formula weight	1168.72
Temperature/K	150.01(10)
Crystal system	monoclinic
Space group	<i>C</i> 2/ <i>c</i>
a/Å	32.6406(6)
b/Å	9.63384(16)
c/Å	18.4404(4)
a/°	90
β/°	102.534(2)
$\gamma/^{\circ}$	90
Volume/Å ³	5660.48(19)
Ζ	4
$\rho_{calc}g/cm^3$	1.371
µ/mm ⁻¹	2.085
F(000)	2396.0
Crystal size/mm ³	$0.091 \times 0.068 \times 0.034$
Radiation	$CuK\alpha (\lambda = 1.54184 \text{ Å})$
2θ range for data collection/°	9.592 to 145.74
Index ranges	$-40 \le h \le 39, -11 \le k \le 11, -22 \le l \le 22$
Reflections collected	26374
Independent reflections	26374 [$R_{\text{int}} = 0.0437, R_{\text{sigma}} = 0.0523$]
Data/restraints/parameters	26374/153/463
Goodness-of-fit on F ²	1.031
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0568, wR_2 = 0.1495$
Final R indexes [all data]	$R_1 = 0.0698, wR_2 = 0.1597$
Largest diff. peak/hole / e Å ⁻³	0.71/-0.70

 Table S4. Crystal data and structure refinement for 7'.

The asymmetric unit comprises 1.5 zinc centres, 1 full bdc, 2 crystallographically independent bdc halves, an ethyl viologen moiety with 40% occupancy, 2 DMF fragments each with 35% occupancy, a tentative partial occupancy water (also present at 35%) and some diffuse electron

density. The partial occupancy DMF fragments were refined subject to distance, planarity and ADP restraints, in order to achieve a chemically sensible convergence. Some ADP restraints were also included for atoms in one of the viologen rings.

¹H NMR digestion studies on the bulk sample suggested that the ethyl viologen moiety (EV) fragment co-exists as a guest with the dihydrogenated analogue (HEVH) in a 27:13 ratio within the asymmetric unit. However, these mutually disordered components could not be credibly resolved from the electron density, although some indicative puckering of the rings therein is evident as well as a degree of pyramidalisation at N1. To balance the charge the overall formula must contain an additional amount of cation. This is presumed to be some dimethyl ammonium, originating from DMF hydrolysis. Pore cations and additional diffuse guest solvent were treated with PLATON SQUEEZE.

This stoichiometry aligns with the ¹H NMR digestion studies for the framework composition, though the guest DMF is higher than that expected from the TGA of the bulk material. However, it is not unreasonable to suggest that some DMF was lost from the crystals prior to TGA being recorded.

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