

Supporting Information

Iodine adsorption in a redox-active metal-organic framework: electrical conductivity induced by host-guest charge-transfer.

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1. Synthesis and Characterisation

1.1 Synthesis of MFM-300(V^{III})

A mixture of biphenyl-3,3',5,5'-tetracarboxylic acid (H₄L, 140 mg, 0.42 mmol), VCl₃ (400 mg, 2.55 mmol), water (10 mL) and hydrochloric acid (0.3 M, 2.0 mL) were placed in a 45mL Teflon autoclave. The solution was degassed under Ar for 0.5h and heated at 483K for 3 days to produce a green microcrystalline powder. The product was separated by filtration, washed with DMF and dried in air (80% yield).

1.2 Synthesis of MFM-300(V^{IV})

MFM-300(V^{III}) was heated under a pure oxygen flow at 150 °C overnight using a tube furnace at a ramping rate of 1 °C min⁻¹. MFM-300(V^{IV}) was obtained as black solid and stored under N₂ in a glovebox.

1.3 Scanning Electron Microscopy

SEM measurements were undertaken on a Quanta 650 at a working voltage of 20kv with a scale bar up to 1 micron.

1.4 Iodine Adsorption and Cycling Test

MFM-300(V^{III}) and MFM-300(V^{IV}) were synthesized following previously reported methods,¹ the as-synthesized MFM-300(V^{III}) and MFM-300(V^{IV}) were exchanged with acetone for a week. Complete activation was achieved by heating the acetone-exchanged samples under vacuum (10⁻⁵ mbar) for 12 h at 150 °C. The activated sample was then inserted into a Schlenk flask which contains a vial with an excess of solid I₂. Pure N₂ (> 99.999%) was slowly dosed into the flask to reach at atmospheric pressure. The flask was then heated at 80 °C for 2 days to allow the full adsorption of I₂ into the desolvated MOFs, a small portion of the samples were taken out for further analysis and the rest of them are still kept in the Schlenk flask and used for further desorbed and cycling experiments.

1.5 Thermogravimetric–Mass Spectrometry (TGA-MS) Analysis

Thermogravimetric analysis (SDTQ600 TA Instruments company) coupled with mass spectrometry (Hiden DSMS analyzer) was used to calculate the uptake of adsorbed I₂ molecules within MFM-300(V^{III}) and MFM-300(V^{IV}). Samples were heated from room temperature to 600 °C at a heating rate of 5 degree min⁻¹ under a flow of air. The uptake of I₂ in MFM-300(V) was determined by the weight loss of adsorbed I₂ confirmed by mass spectrometry and detection of the characteristic peak at 127 (I⁺).

1.6 High Resolution Powder X-ray Diffraction Data

High resolution synchrotron powder X-ray diffraction (PXRD) data were collected at Beamline I11 of Diamond Light Source using multi-analysing crystal-detectors (MACs) and monochromated radiation [$\lambda = 0.824677(10) \text{ \AA}$]. The powder samples were loaded into capillary tubes of 0.7 mm diameter and the data collection was carried out at room temperature.

1.7 Rietveld Refinement and Crystallographic Data of I₂-loaded MFM-300(V^{III}) and MFM-300(V^{IV})

The structural model of MFM-300(V^{III}) was used as a starting point for Rietveld refinements, which were carried out with Topas Academic 5 program (<http://www.topas-academic.net/>). The organic linkers were modelled as semi-rigid bodies where selected bond distances, bond angles and torsion angles could be refined. Crystallographic positions of adsorbed I₂ were found by sequential difference Fourier map calculations and electron density peaks analysis starting from the activated crystal structure. The final Rietveld refinements included crystal cell parameters, background and profile coefficients, all atomic positions and occupancies for iodine atoms, which were constrained to be the same value for the atoms within each I₂ molecule. Crystallographic parameters from the final Rietveld refinement are summarized in Table S1.

1.8 Single Crystal X-ray Structure Determination of I₂@MFM-300(V^{IV}), [V₂(O)₂(L)]·0.4I₂

Data for I₂@MFM-300(V^{IV}) were collected at a temperature of 150 K using a Rigaku FR-X rotating anode diffractometer with Mo radiation ($\lambda=0.71073 \text{ \AA}$), equipped with Hybrid Photon detector HyPix-6000HE and an Oxford Cryosystems nitrogen flow gas system.

1.9 X-ray Photoelectron Spectroscopy

Measurements of the I 3d core level were performed using an Axis Ultra Hybrid spectrometer (Kratos Analytical, United Kingdom), using Al-K α radiation (1486.6 eV, using 10 mA emission at 250 W). Binding energy calibration was performed using the C 1s photoelectron peak from adventitious hydrocarbon (284.8 eV).

1.10 Electrical Conductivity Test

Electrical conductivity measurements were conducted using a Solartron Analytical Modulab XM Materials Test System (Solartron Analytical, Farnborough, UK) over a frequency range from 0.1 Hz to 1 MHz. Ag paste electrodes were coated on both faces of the pellets of MOF. The impedance data were corrected for sample geometry (thickness/area) and analysed using the commercial software package ZView (Version 3.5e, Scribner Associates Inc., USA).

1.11 Electrochemical Measurements

Electrochemical measurements were conducted in a standard three-electrode glass cell connected with a CHI760e electrochemical workstation. The three-electrode electrochemical cell comprised of a glassy carbon (3 mm) working electrode, which was modified with MOF. A carbon rod was chosen as the counter electrode, and a saturated calomel electrode (SCE) or Ag/AgCl electrode was selected as the reference electrode. 10 mg of MOF was dispersed in 1 mL of iso-propanol (970 μL)/Nafion (30 μL) by sonication to form a homogeneous ink and then 6 μL of the ink was loaded onto the working electrode over an area of $\sim 0.0706 \text{ cm}^2$. Electrochemical impedance spectroscopy (EIS) measurements were carried out from 100000 Hz to 0.1 Hz.

1.12 EPR Measurements

The EPR measurements of MFM-300(V^{III}), I_2 @MFM-300($\text{V}^{\text{III/IV}}$), MFM-300(V^{IV}) and I_2 @MFM-300(V^{IV}) were recorded at room temperature (293K) on a Bruker EMX Micro EPR spectrometer, equipped with a X-band (9.8 GHz) microwave bridge, a high-Q resonator and 1.0T electromagnet. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH) with $g = 2.0036$. The spectra were recorded with 5G of modulation amplitude and 2mW of microwave power. Data were analysed with Easyspin package used in MATLAB software version 2013a.²

1.13 Raman Spectroscopy

Raman spectra were obtained using an Xplora PLUS Raman microscope (Horiba Company) with a 785 nm laser and a 1200 lines/mm grating. The acquisition time was 30 s and accumulated for 10 cycles.

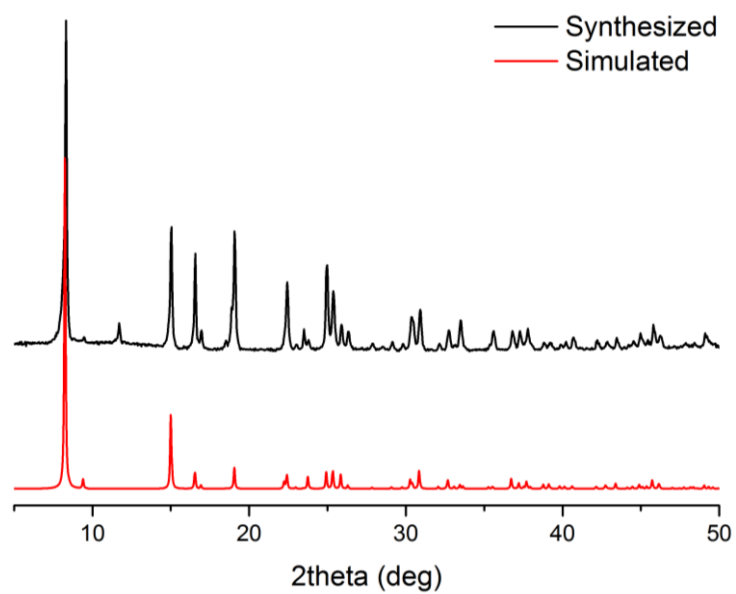


Figure S1. PXRD patterns for as-synthesized MFM-300(V^{III}).

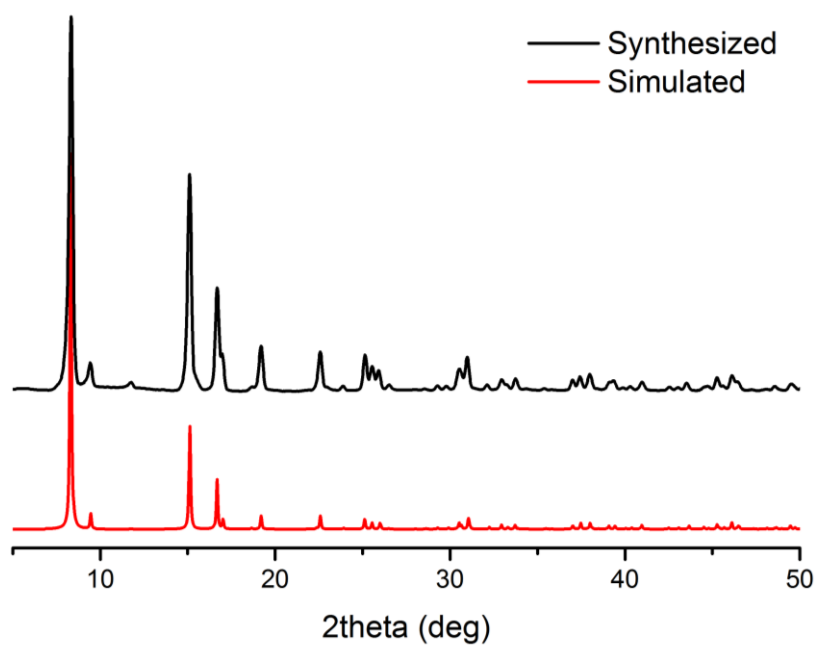


Figure S2. PXRD patterns for as-synthesized MFM-300(V^{IV}).

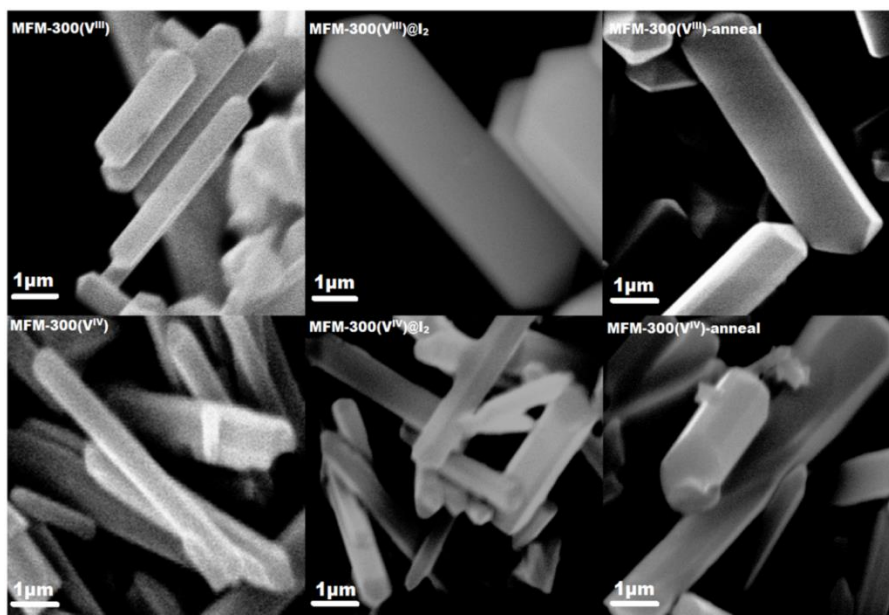


Figure S3. SEM images of MF-300(V^{III}), MF-300(V^{IV}) and I₂-loaded materials.

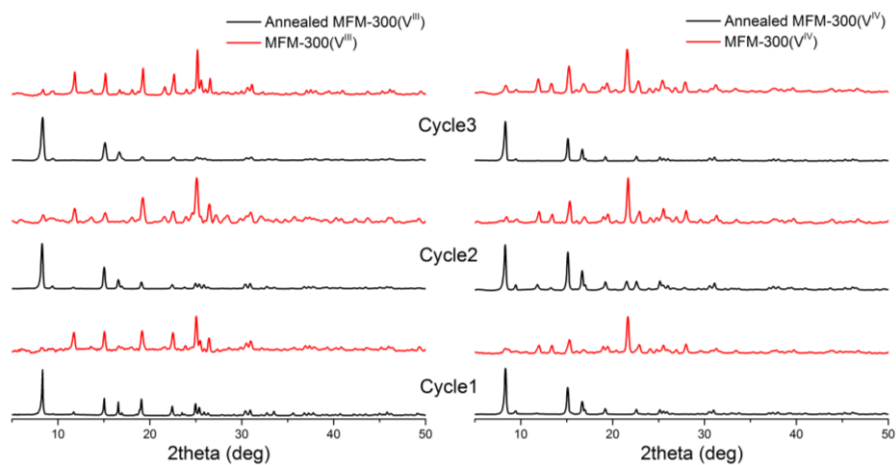


Figure S4. Repeated cycling of I₂ up to 3 cycles for MFM-300(V^{III}) and MFM-300(V^{IV})

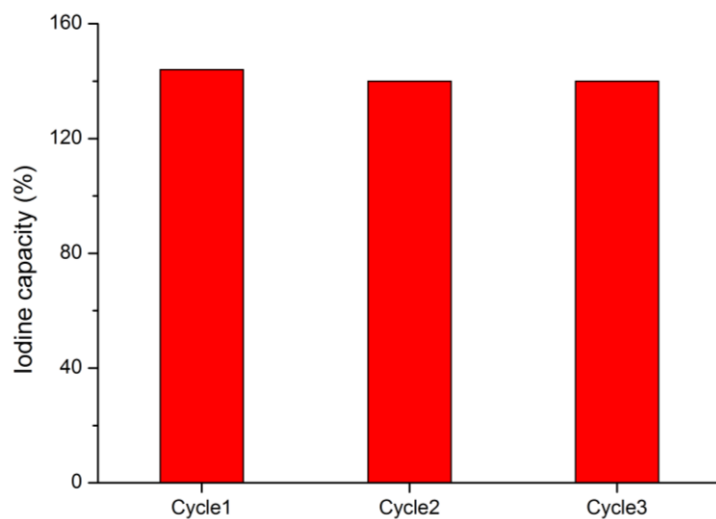


Figure S5: I₂ capacity for three cycles in MFM-300(V^{III}).

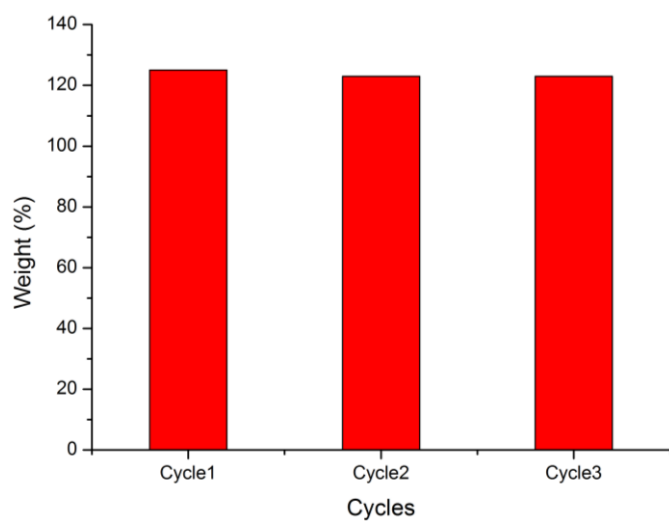


Figure S6: I₂ capacity for three cycles in MFM-300(V^{IV})

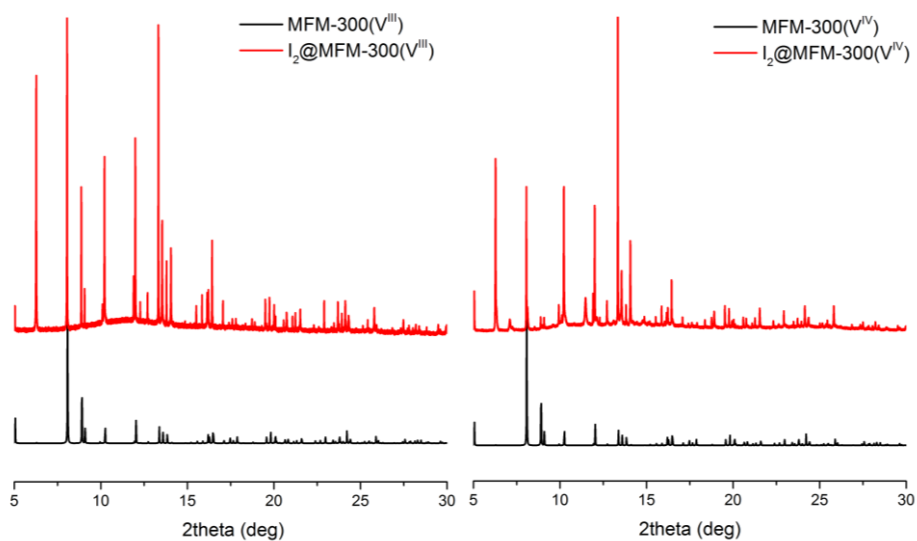


Figure S7. High resolution powder X-ray diffraction data for I₂-loaded MFM-300(V^{III}) and MFM-300(V^{IV}).

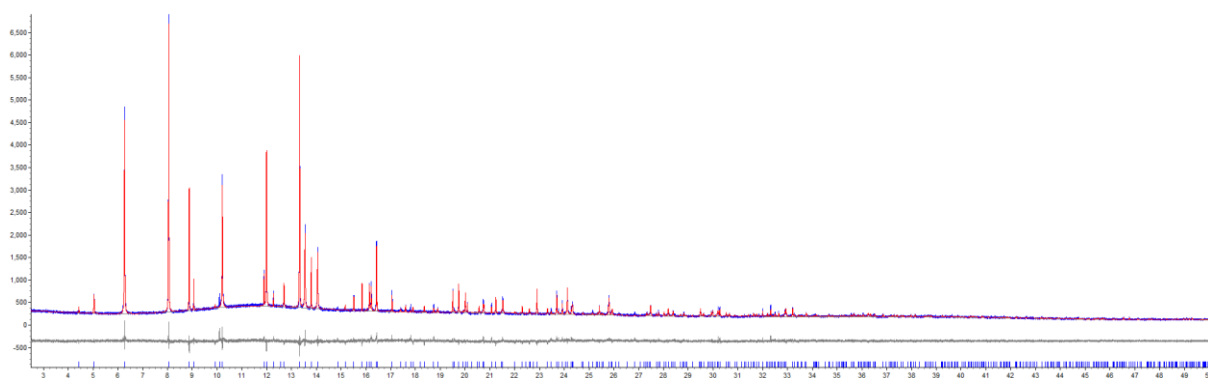


Figure S8. Rietveld structure refinement of $I_2@MFM-300(V^{III/IV})$.

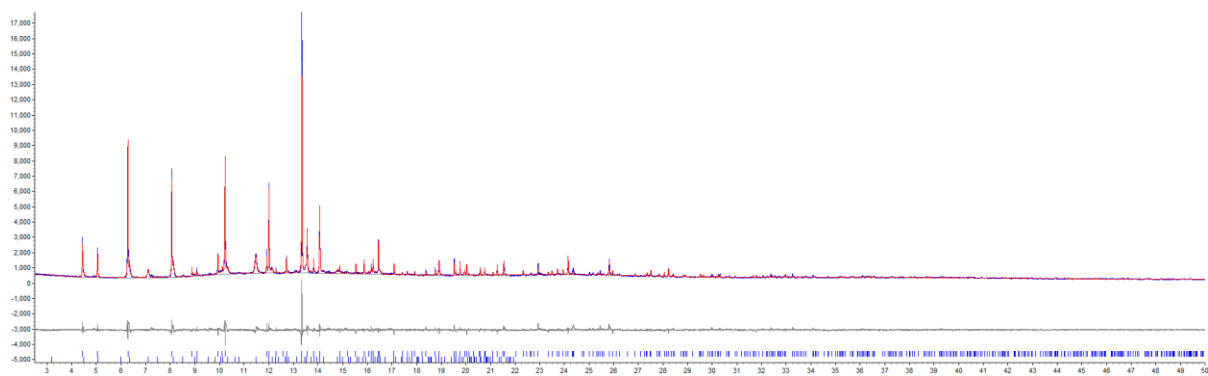


Figure S9. Rietveld structure refinement of $I_2@MFM-300(V^{IV})$.

Table S1. Summary of powder X-ray diffraction refinements for I₂ loaded MFM-300(V^{III}) and MFM-300(V^{IV}) samples.

	I ₂ @MFM-300(V ^{III/IV})	I ₂ @MFM-300(V ^{IV})
Formula	C ₁₆ H ₈ V ₂ O ₁₀ ·1.03(I ₂)·0.6(I ₃)	C ₁₆ H ₆ V ₂ O ₁₀ ·2.204(I ₂)
Formula weight (g/mol)	951.963	1019.49
Temp/K	298	298
Radiation type	Synchrotron	Synchrotron
Diffractometer	Beamline I11 of Diamond Light Source	Beamline I11 of Diamond Light Source
Data collection mode	Transmission	Transmission
Wavelength(Å)	0.824884	0.825258
Crystal system	Tetragonal	Tetragonal
Space group	I4 ₁ 22	I4 ₁ 22
<i>a</i> / Å	15.07864(4)	15.07259(8)
<i>b</i> / Å	15.07864(4)	15.07259(8)
<i>c</i> / Å	11.97001(4)	11.95925(9)
<i>V</i> / Å ³	2721.567(18)	2716.94(3)
D _c /g cm ⁻³	2.32504	2.49210
<i>R</i> _{exp} / %	4.475	3.217
<i>R</i> _{wp} / %	4.979	7.334
<i>R</i> _p / %	3.843	5.088
<i>GoF</i>	1.113	2.280
<i>R</i> _{Bragg}	2.228	2.280

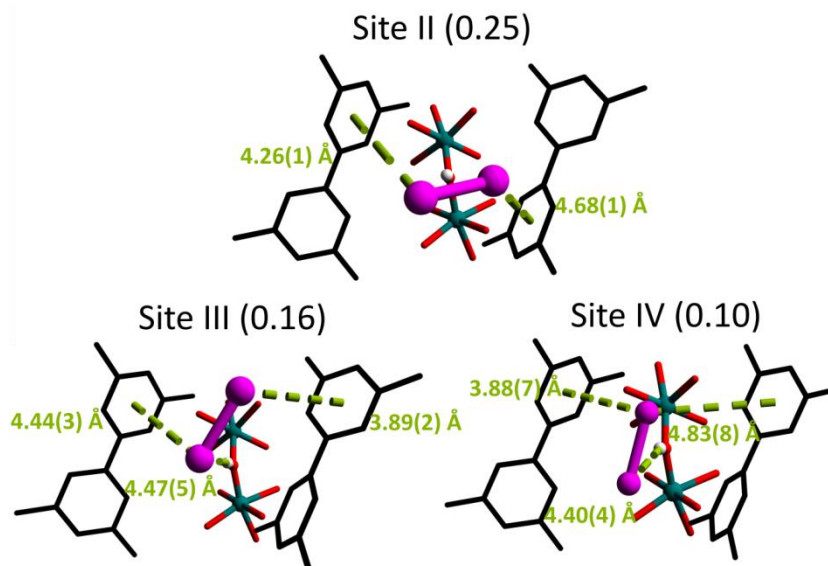


Figure S10. Views of various I₂ binding sites for I₂@MFM-300(V^{III/IV}).

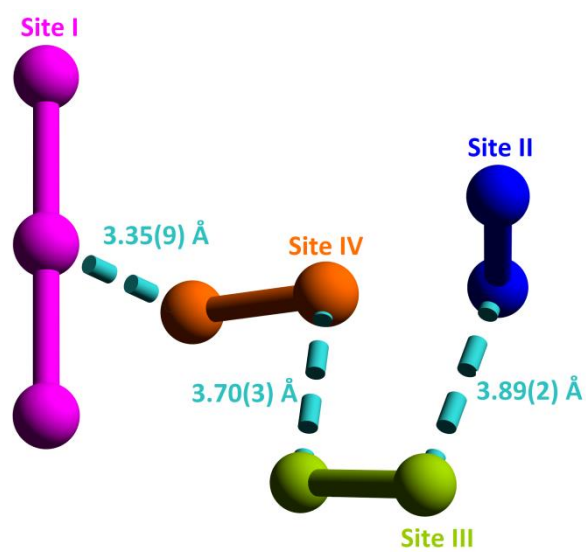


Figure S11. Views of packed I₂ species within the channel of MFM-300(V^{III/IV}).

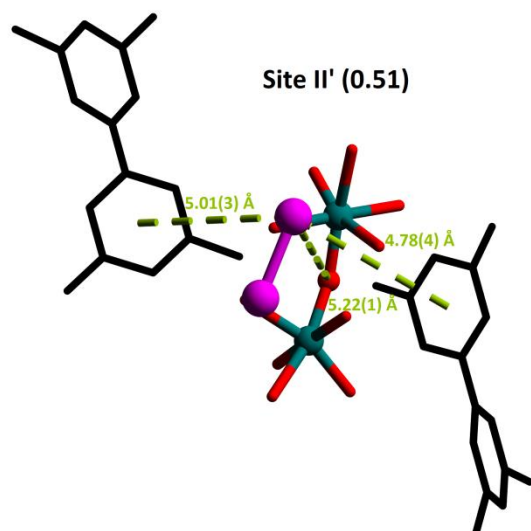


Figure S12. Views of Site II' for I₂@MFM-300(V^{IV}).

Table S2. Summary of single crystal X-ray diffraction refinement for I₂@MFM-300(V^{IV}).

Complex	MFM-300(V ^{IV})·0.4I ₂
Empirical formula	C ₁₆ H ₆ I _{0.8} O ₁₀ V ₂
Formula weight	637.75
Temperature/K	150(2)
Crystal system	tetragonal
Space group	I ₄ 22
a/Å	14.9882(7)
b/Å	14.9882(7)
c/Å	11.9828(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2691.9(3)
Z	4
ρ _{calc} /cm ³	1.574
μ/mm ⁻¹	2.338
F(000)	1209.0
Crystal size/mm ³	0.08 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.844 to 58.25
Index ranges	-15 ≤ h ≤ 12, -20 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	7780
Independent reflections	1615 [R _{int} = 0.0369, R _{sigma} = 0.0324]
Data/restraints/parameters	1615/13/86
Goodness-of-fit on F ²	1.109
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0539, wR ₂ = 0.1525
Final R indexes [all data]	R ₁ = 0.0611, wR ₂ = 0.1562
Largest diff. peak/hole / e Å ⁻³	0.62/-0.40
Flack parameter	0.37(8)

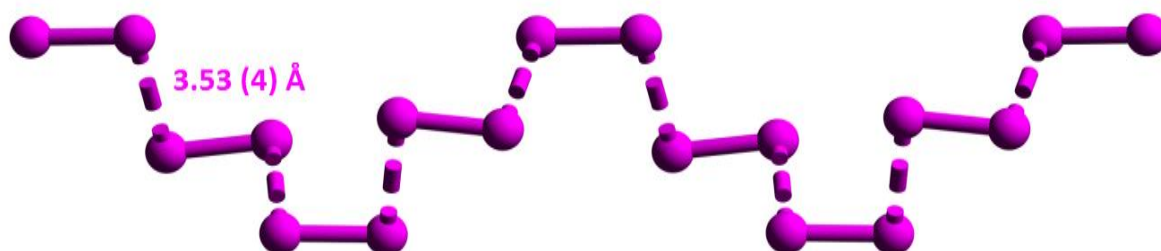


Figure S13. View of single-helical chains of I₂ molecules within MFM-300(V^{IV}) from single crystal diffraction data.

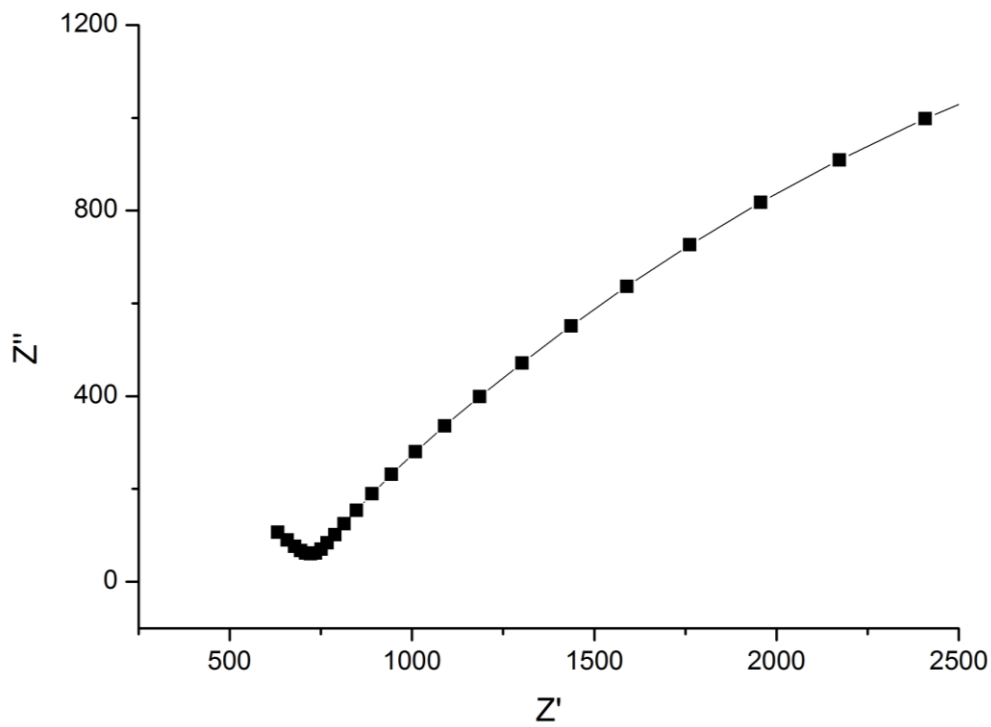


Figure S14: Nyquist plot for $I_2@MFM-300(V^{III/IV})$ under dark condition.

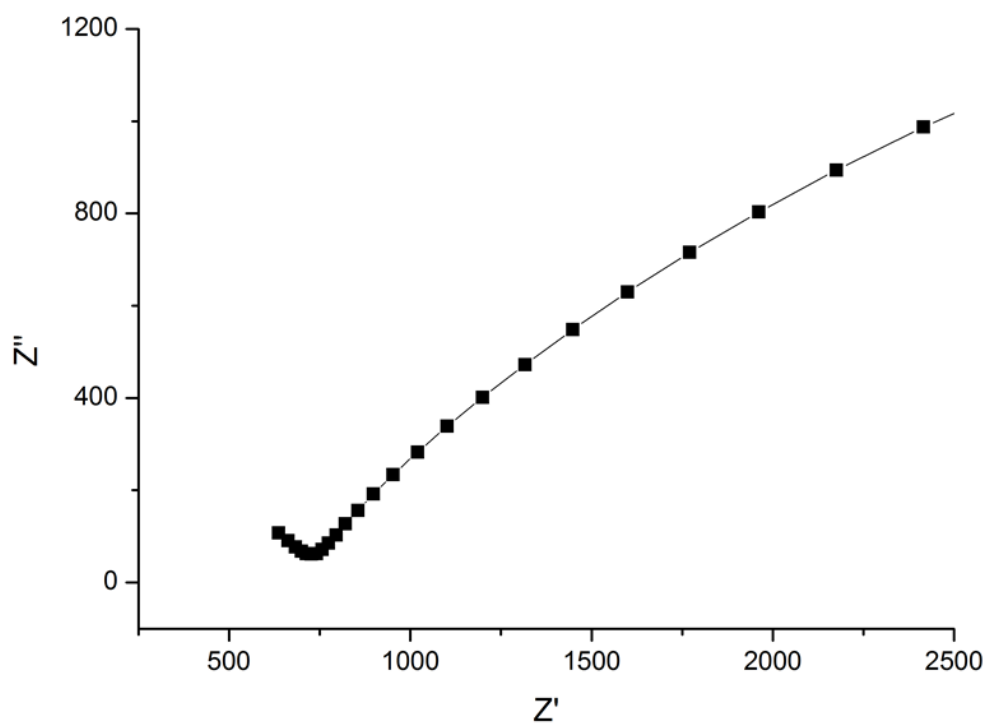


Figure S15: Nyquist plot for $I_2@MFM-300(V^{III/IV})$ under light condition.

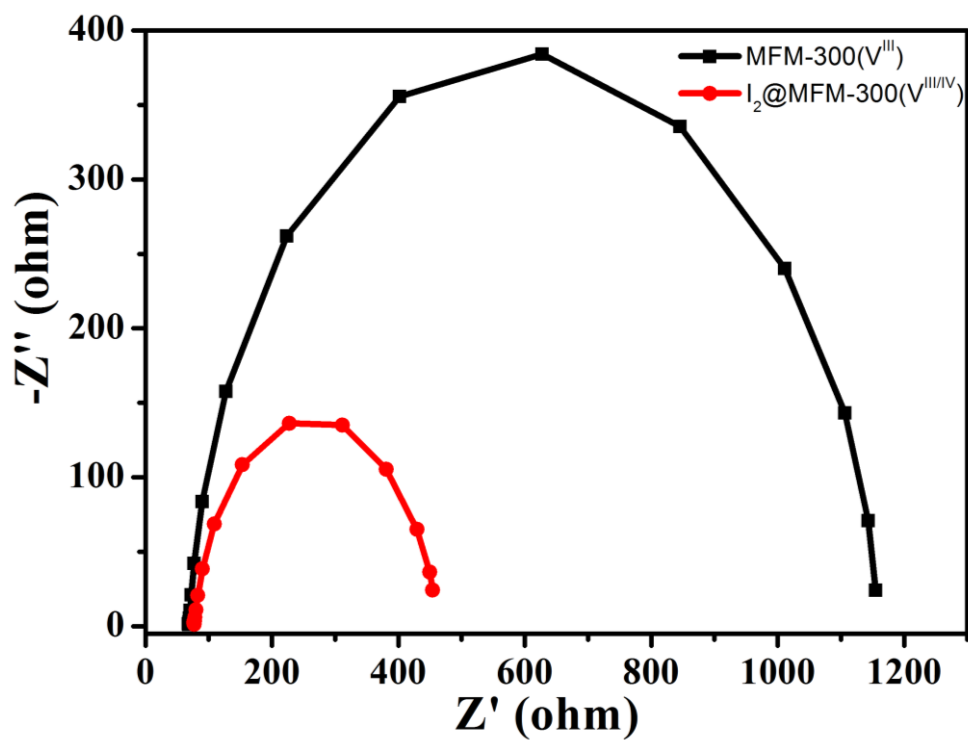


Figure S16: Electrochemical impedance spectrum of MFM-300(V^{III}) and I₂@MFM-300(V^{III/IV})

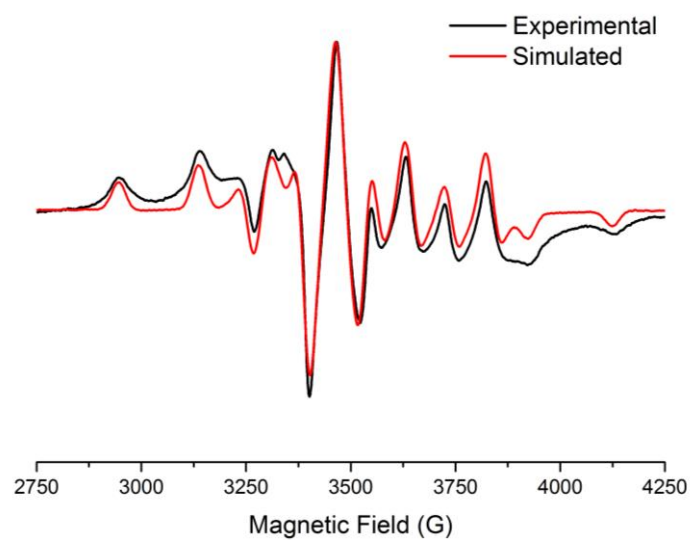


Figure S17. Comparisons between experimental and simulated EPR data of I₂@MFM-300(V^{III/IV}).

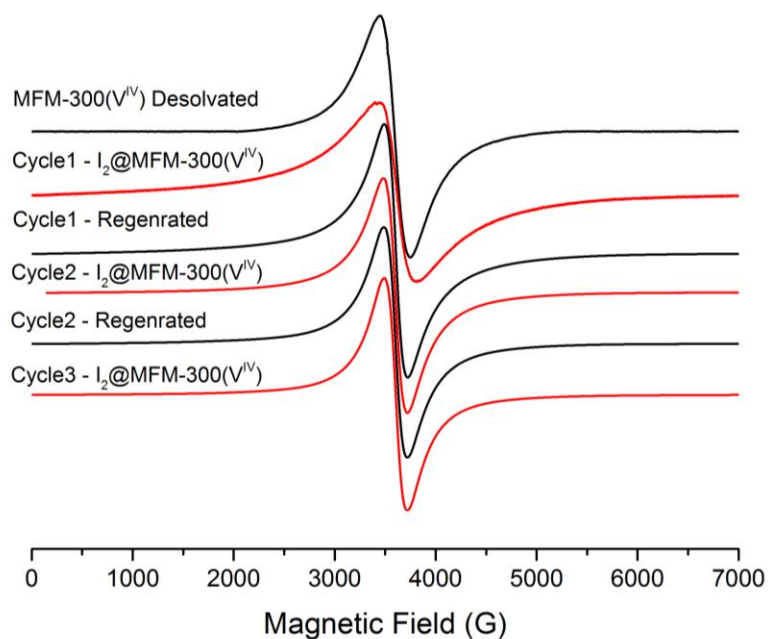


Figure S18. EPR data of MFM-300(V^{IV}) cycling with I₂.

Table S3. EPR parameters for I₂@MFM-300(V^{III/IV}) and MFM-300(V^{IV}) obtained by Easyspin software package simulation.

	$g_{(iso)}$	$g_{//}$	g_{\perp}	$A_{//} (G)$	$A_{\perp} (G)$
I ₂ @MFM-300(V ^{III})	-	1.9370	1.982	190.9	80.2

References

- (1) Lu, Z.; Godfrey, H. G. W.; da Silva, I.; Cheng, Y.; Savage, M.; Tuna, F.; McInnes, E. J. L.; Teat, S. J.; Gagnon, K. J.; Frogley, M. D.; et al. Modulating Supramolecular Binding of Carbon Dioxide in a Redox-Active Porous Metal-Organic Framework. *Nat. Commun.* **2017**, *8*, 14212–14222.
- (2) Stoll, S.; Schweiger, A. EasySpin, a Comprehensive Software Package for Spectral Simulation and Analysis in EPR. *J. Magn. Reson.* **2006**, *178*, 42–55.