Supporting Information

On the Divergent Electrically Conductive Pathways in Yttrium-Based 2- and 3-Dimensional Metal–Organic Frameworks

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Contents:

	YHOTP	Y_6HOTP_2
Chemical Formula	$Y_{1.17}(C_{18}H_6O_6)(H_2O)_{1.17}$	$Y_6(CO_3)(C_{18}H_6O_6)_2(H_2O)_6Cl_6$
Node SBU	$YO_6(H_2O) = [Y]^{3+}$	$Y_6O_{12}(CO_3)(H_2O)_6(Cl)_6 = [Y_6]^{10+}$
Linker SBU	$C_{18}H_6O_6 = [HOTP]^{3-}$	$C_{18}H_6O_6 = [HOTP]^{5-}$
Chemical Composition	$Y_{1.17}C_{18}H_{8.34}O_{7.17}$	$Y_6C_{37}H_{12}O_{21}Cl_6$
Crystal System	Hexagonal	Cubic
Space Group	P6cc (no. 184)	Fd-3m (no. 227)
a (Å)	21.901	34.548
b (Å)	21.901	34.548
c (Å)	6.1825	34.548
α (°)	90	90
β (°)	90	90
γ (°)	120	90
Density (mL g^{-1})	1.15	0.99
Network Connectivity	3D	3D
Pore Connectivity	1D	3D

Table S1. Structural models for YHOTP and Y_6HOTP_2. Coordinated water molecules (identified as one-sided O atoms in single-crystal studies) are included. Charge balance is indicated based on EPR results.

	Y_6HOTP_2
Empirical Formula	$Y_6C_{37}H_{12}O_{21}Cl_6$
Formula Weight	1538.64
Temperature (K)	100
Crystal System	Cubic
Space Group	Fd-3m
a (Å)	34.548(6)
b (Å)	34.548(6)
c (Å)	34.548(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	41235(2)
Z	16
Density (g mL^{-1})	0.9914
F(000)	126888
μ (mm^{-1})	7.475
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range (°)	4.43–158.724
Reflections collected	151190

Table S2. Single-crystal XRD structure refinement of Y_6HOTP_2.

	Y	C	N	O	Cl
Y_6HOTP_2	5.1	57.2	6.9	19.1	11.7
YHOTP	7.1	69.5	2.9	20.5	0.0

Table S3. Chemical composition of YHOTP and Y_6HOTP_2 (in at%, excluding H) determined by XPS analysis.

	Y	C	N	O	Cl
Y_6HOTP_2	7.5	32.1	4.5	50.9	5.0
YHOTP	3.1	44.8	1.1	50.3	0.7

Table S4. Chemical composition of YHOTP and Y_6HOTP_2 (in at%, excluding H) determined by combustion analysis (C, N), inductively-coupled plasma (ICP) analysis (Y, Cl), and the difference (O).

	Y	C	N	O	Cl
Y_6HOTP_2	8.6	52.9	0.0	30.0	8.6
YHOTP	4.4	68.3	0.0	27.2	0.0

Table S5. Model chemical composition of YHOTP and Y_6HOTP_2 (in at%, excluding H) based on the combined experimental analyses: XPS, CHN, ICP-OES, and XRD.

	Y	C	N	O	Cl
$YCl_3 \cdot 6H_2O$	8.1	39.1	0.0	32.0	20.8

Table S6. Chemical composition of $YCl_3 \cdot 6H_2O$ (in at%) determined by energy dispersive X-ray spectroscopy (EDX) using a 10 kV accelerating voltage.

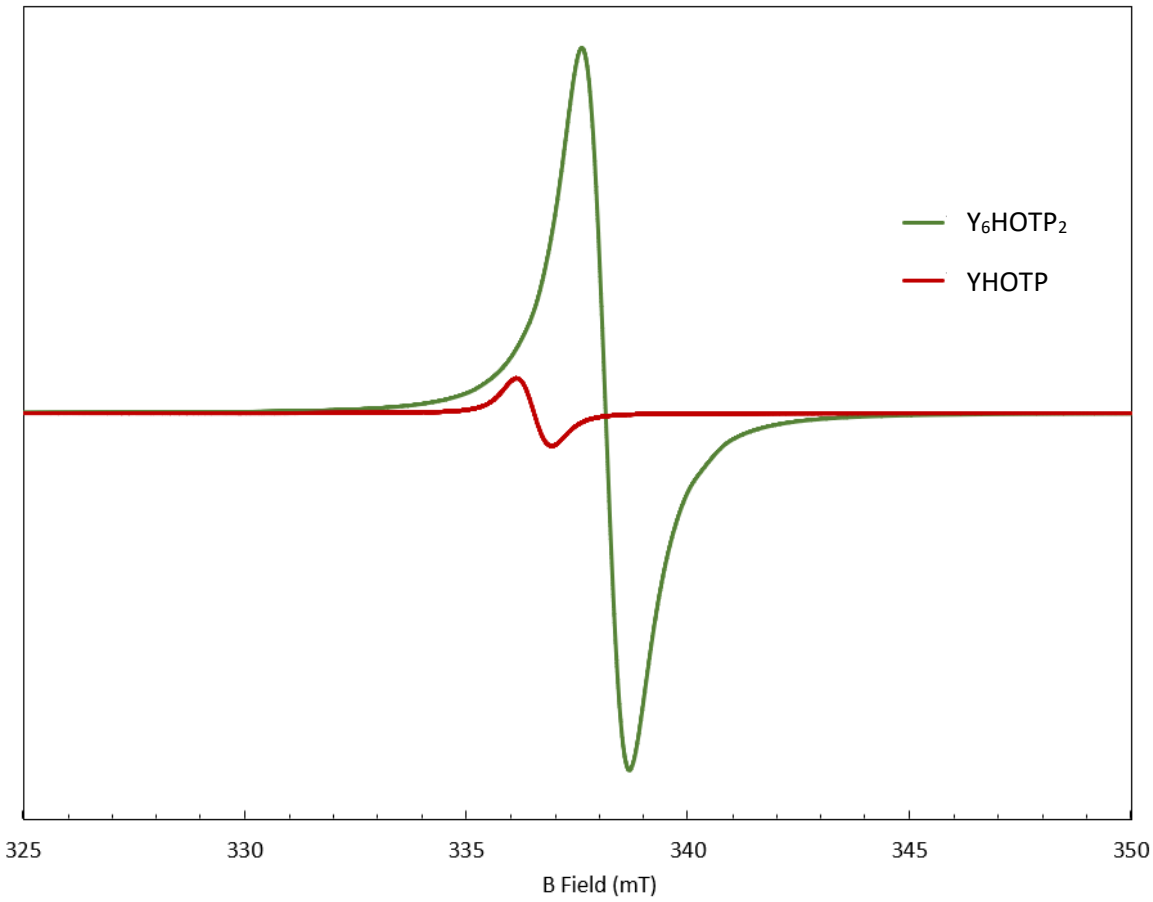

Figure S1. EPR spectra of YHOTP and Y_6HOTP_2 between 325-350 mT, normalized by mass.

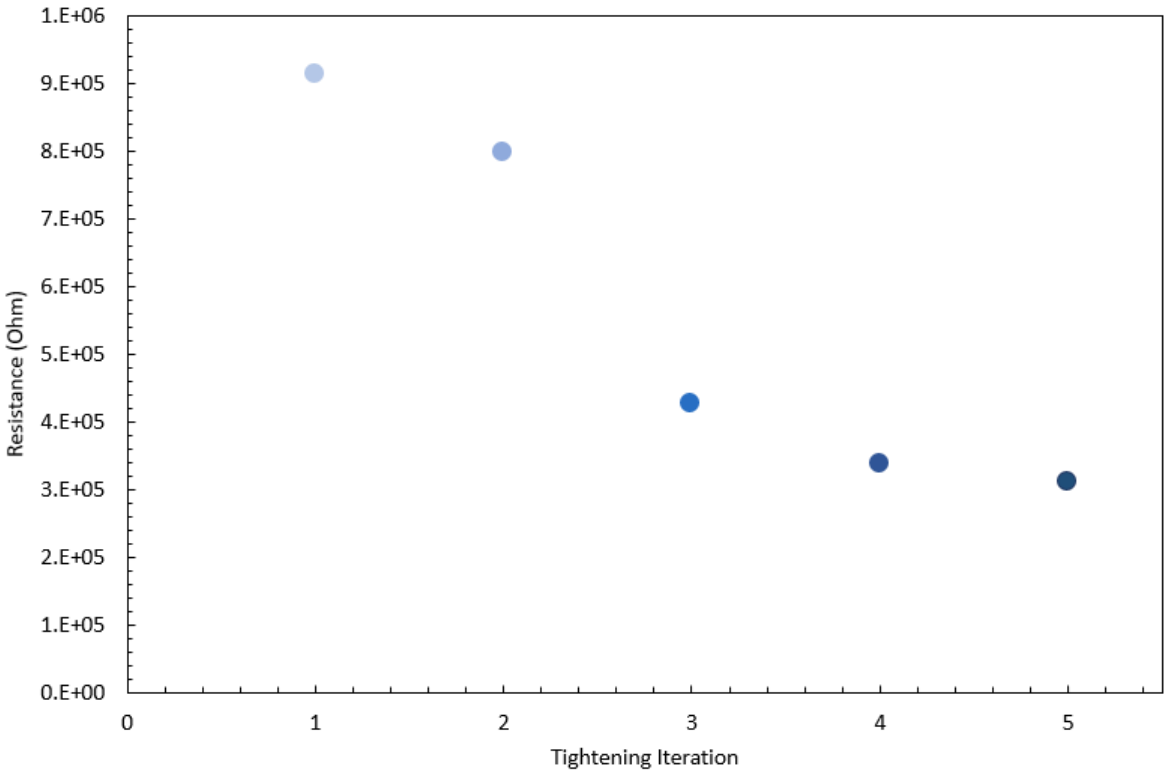

Figure S2. Iterative two-point probe measurements of packed pellet resistance of YHOTP (I-V curve swept from -1.0 to 1.0 V), upon hand tightening between measurements.

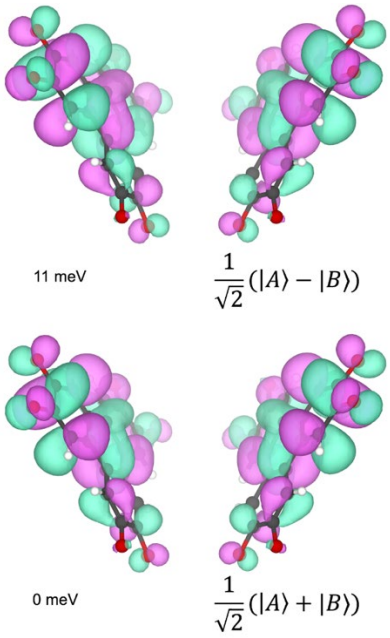

Figure S3. Molecular orbitals of HOTP placed at positions consistent with Y_6HOTP_2, consisting of symmetric (bottom) and antisymmetric (top) combinations of the individual linker molecular orbitals. The antisymmetric state is higher in energy, suggesting J-like aggregation behavior.

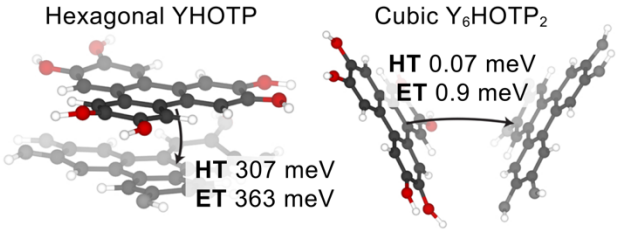

Figure S4. Charge transfer interactions between HOTP ligands in the hexagonal MOF (left) and the cubic MOF (right) calculated using the ZINDO method. The electron and hole couplings were calculated using the open-source code py-MOO. The HT values are comparable to those calculated using ab initio methods (Figure 3), but the ET value for the cubic MOF is much lower. Despite this, the ET values are consistently larger than the HT values using both methods.