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Supporting Information

Structure and Charge Control in Metal-Organic Frameworks Based on the Tetrahedral Ligand Tetrakis(4-tetrazolylphenyl)methane

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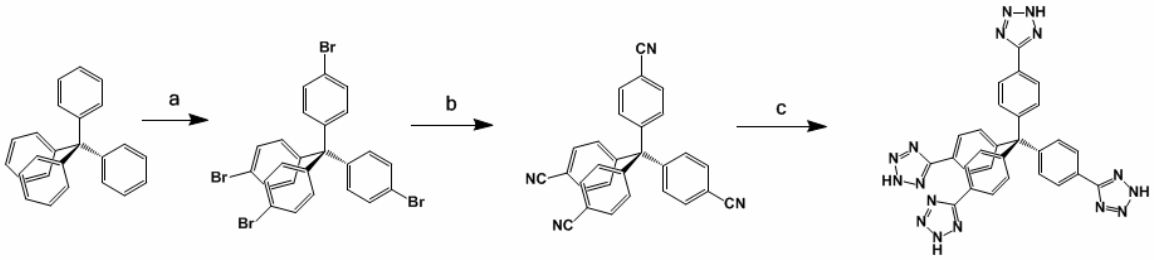
Table S1. Crystallographic data[a] for compounds **1**, **2**, and **2d**.

	1	**2**	**2d**
formula	$C_{816}H_{712}Mn_{48}N_{424}O_{64}$	$C_{131}H_{121}Cl_4Cu_{10}N_{69}O_{16}$	$C_{116}H_{64}Cl_{2.8}Cu_{9.4}N_{64}$
FW	20119.2	3695.2	3050.85
T, K	171(2)	165(2)	154(2)
cryst. syst., space group	Cubic, *Ia*-3*d*	Tetragonal, *I*4*/mmm*	Tetragonal, *I*4*/mmm*
Z	24	1	1
a, Å	35.451(1)	15.501(1)	16.091(1)
c, Å		29.401(4)	28.187(3)
V, Å^3	44555(5)	7064(1)	7299(1)
d_{calc}, g/cm^3	0.750	0.869	0.694
μ, mm^{-1}	0.37	0.82	0.73
F(000)	10288	1876	1528.2
crystal size, mm^3	0.52 × 0.37 × 0.30	0.43 × 0.25 × 0.15	0.30 × 0.10 × 0.10
theta range	4.596 to 35.242	4.636 to 51.587	4.601 to 39.691
index ranges	$-29 \le h \le 30$ $-30 \le k \le 30$ $-27 \le l \le 30$	$-14 \le h \le 19$ $-19 \le k \le 17$ $-30 \le l \le 36$	$-14 \le h \le 16$ $-16 \le k \le 16$ $-25 \le l \le 29$
refl. collected	51888	20293	14360
data / restr. / param.	1293 / 0 / 159	2092 / 0 / 128	1311 / 0 / 71
GOF on F^2	2.251	1.194	0.935
Larg. peak / hole, e/Å^3	0.463 and -0.354	0.90 and -0.91	0.65 and -0.31
R_1 (wR_2), %, [I>2sigma(I)][b]	14.74 (43.36)	7.66 (23.17)	4.00 (10.84)

[a] Obtained with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation.

[b] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma |F_o|$, $wR_2 = \{ \Sigma [w(F_o^2-F_c^2)^2]/ \Sigma [w(F_o^2)^2]\}^{1/2}$.



Scheme S1. Synthetic approach for the formation of H_4TTPM. Conditions and reactants: a = Br_2 (neat, 30 min); b = CuCN/DMF (reflux, 2 days); c = NaN_3 (toluene:MeOH solvent mixture, 7:3 ratio, reflux, 3 days)

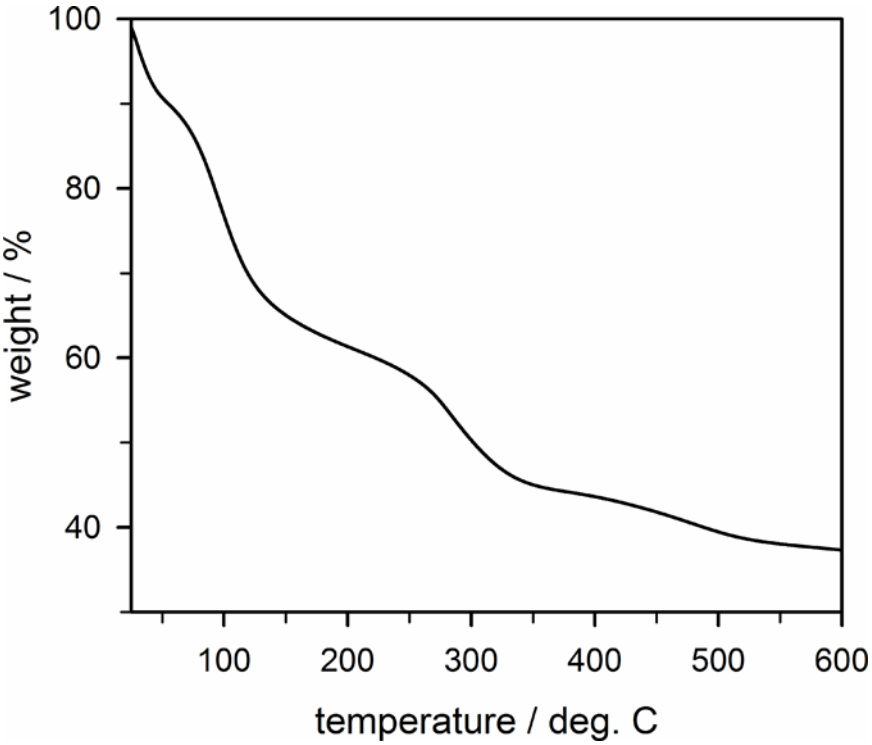


Figure S1. Thermogravimetric analysis plot for compound **1**.

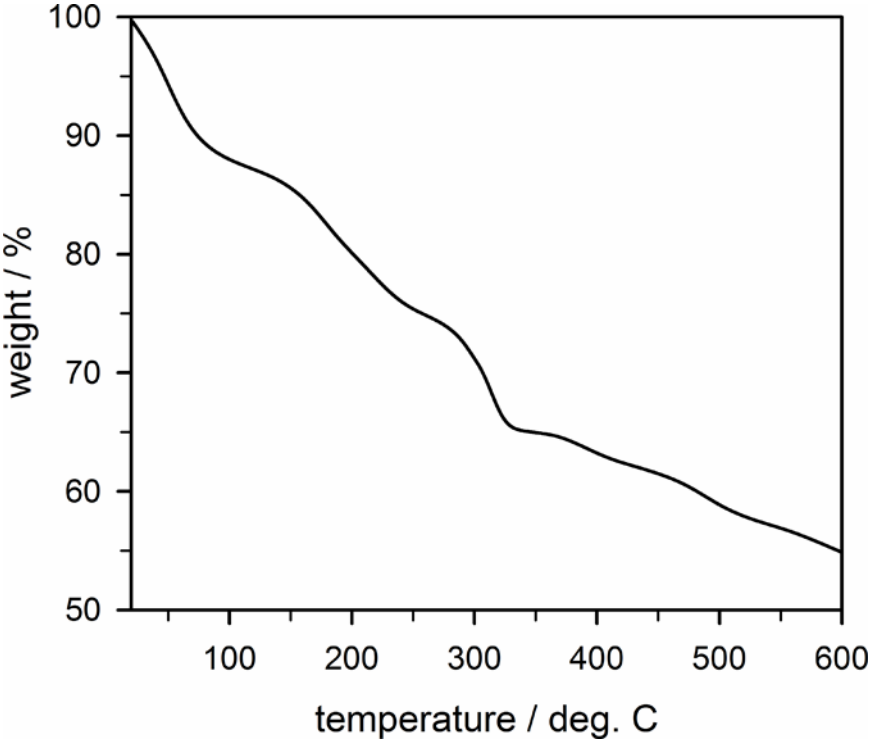


Figure S2. Thermogravimetric analysis plot for compound **2**.

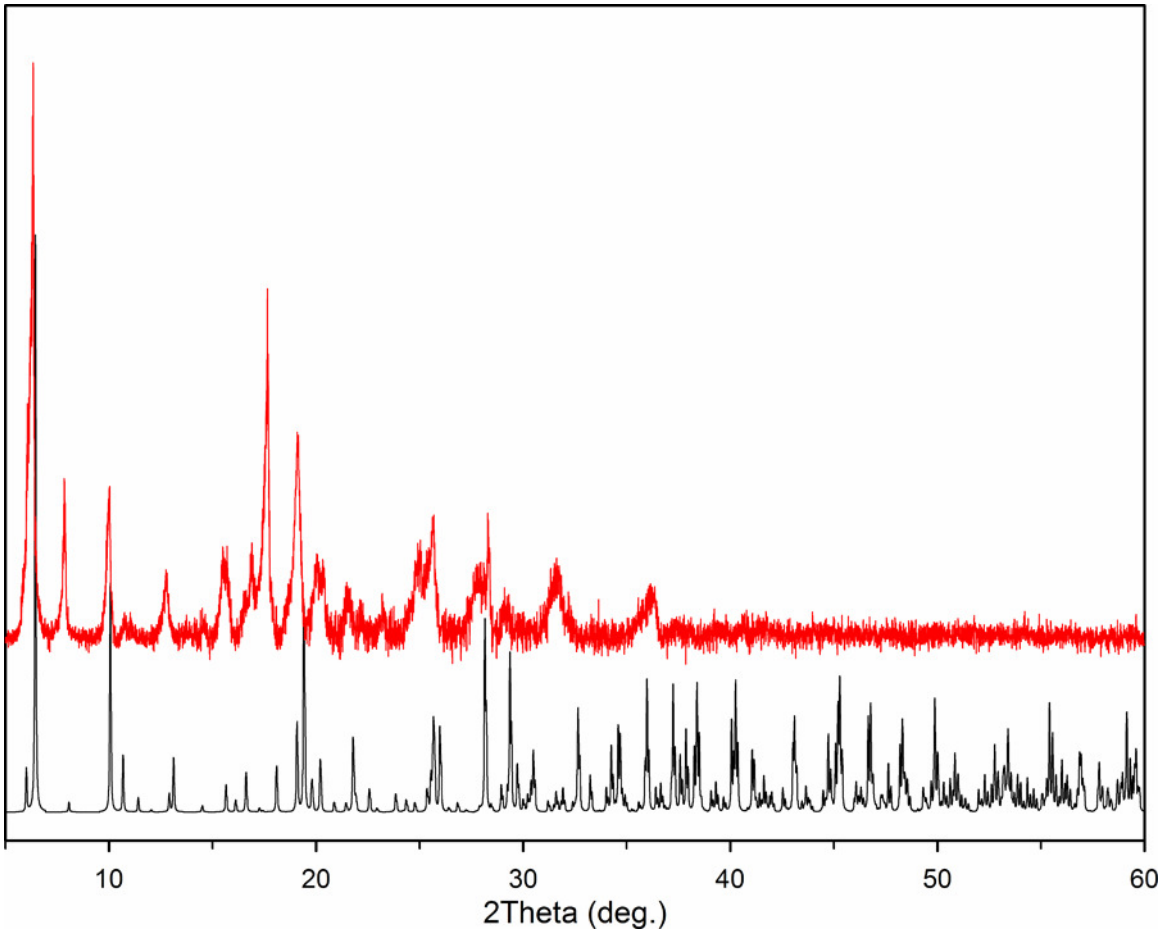


Figure S3. Powder X-ray diffraction patterns for as-synthesized **2** (red) and simulated from the X-ray crystal structure of **2** (black). Note that the widening of the diffraction peaks and the weak intensity of high-angle diffraction data denotes a small particle size and possible loss of long-range ordering.