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Supporting Information

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Materials and Methods

The preparation and all manipulations were carried out using break-and-seal^[1] as well as Schlenk and glove-box techniques under an atmosphere of argon. Tetrahydrofuran (THF) was purchased from Sigma Aldrich and dried over Na/benzophenone and distilled prior to use. Potassium was purchased from Sigma Aldrich. YI₃ and LaI₃ were purchased from Alfa Aesar. K₂COT was prepared according to literature^[2] and stored in the glove box. The attenuated total reflection (ATR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. The ¹H NMR spectra of **2** were measured on a Bruker AC-400 spectrometer at 400 MHz; the ¹H NMR spectra of **1** and ¹³C NMR spectra of **2** were measured on a Bruker Ascend-500 spectrometer at 500 MHz. All spectra were referenced to the resonances of the corresponding solvent used.

Characterization

ATR-IR study of 1 and 2

0.5 mg of yellow crystalline product covered in mineral oil was only scanned twice, due to the product moisture and air sensitivity.



Figure S1. ATR-IR spectrum of 1.



Figure S2. ATR-IR spectrum of 2.

¹H NMR study of 1

THF- d_8 (0.6 mL) was added to an NMR probe containing 5 mg of crystalline 1. The probe was sealed under argon and ¹H NMR spectra were collected.



Figure S3. Variable-temperature ¹H NMR spectra of **1** in THF- d_8 .



Figure S4. ¹H NMR spectra of **1** in THF- d_8 at 25 °C and -80 °C, with all peaks labeled and integrated.

¹H NMR study of 2

THF- d_8 (0.7 mL) was added to an NMR probe containing 5 mg of crystalline **2**. The probe was sealed under argon and ¹H NMR spectra were collected.



Figure S5. Variable-temperature ¹H NMR spectra of **2** in THF- d_8 .



Figure S6. ¹H NMR spectra of **2** in THF- d_8 at 25 °C and -80 °C, with all peaks labeled and integrated.



Figure S7. ¹³C NMR spectrum of **2** in THF- d_8 at 25 °C collected over 11 hours, with all peaks labeled.

X-ray powder diffraction study

4 mg of bulk crystalline material of **2** were placed on the holder capped with the dome under Ar in the glove box and quickly scanned. The X-ray powder diffraction spectra were collected. Settings: start: 6.0° , end: 26.0° , step: 0.02° , scan speed: 0.2 s.



Figure S8. X-ray powder diffraction spectra of crystals 2...

Crystal Data and Refinement Details

Data collection was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS shutterless mode detector equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) at T = 100(2) K. Data reduction and integration were performed with the Bruker software package SAINT (version 8.38A).¹ Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).² The structures were solved by SHELXT (version 2018/2)³ and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2018/3)⁴ software package. All non-hydrogen atoms were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with $U_{iso}(H) = 1.2 U_{eq}(C)$. In 1, two COT rings were found to be disordered and were modelled with two orientations having relative occupancies of 0.55:0.45 and 0.53:0.47. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of three COT rings in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.01 Å². They were also restrained to have the same U^{ij} components, with a standard uncertainty of 0.04 Å². In 2, two of three COT rings were found to be disordered and were modelled with two orientations with relative occupancies of 0.60:0.40, and 0.76:0.24 for the two parts respectively. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of three COT rings in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.01 \AA^2 . They were also restrained to have the same U^{ij} components, with a standard uncertainty of 0.04 Å². Further crystal and data collection details are listed in Table S1.

Compound	1	2	
Empirical formula	$C_{32}H_{40}Y_2O_2$	$C_{32}H_{40}La_2O_2$	
Formula weight	634.46	734.46	
Temperature (K)	100(2)	100(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	monoclinic	monoclinic	
Space group	$P2_{1}/c$	$P2_{1}/c$	
<i>a</i> (Å)	15.6822(6)	15.7509(8)	
<i>b</i> (Å)	13.3019(5)	13.4810(7)	
<i>c</i> (Å)	13.5299(5)	13.5200(7)	
α (°)	90.00	90.00	
β (°)	95.5470(10)	96.9710(10)	
γ(°)	90.00	90.00	
$V(Å^3)$	2809.16(18)	2849.6(3)	
Z	4	4	
$\rho_{\text{calcd}} (\text{g} \cdot \text{cm}^{-3})$	1.500	1.712	
$\mu (\mathrm{mm}^{-1})$	4.138	2.984	
F(000)	1304	1448	
Crystal size (mm)	0.06×0.23×0.36	0.06x0.12x0.42	
θ range for data			
collection (°)	3.025-43.200	3.012-36.393	
Reflections collected	388103	146344	
Independent reflections	20905	13847	
	$[R_{\rm int} = 0.0693]$	$[R_{\rm int} = 0.0369]$	
Transmission factors (min/max)			
	0.666/1	0.699/1	
Data/restraints/params.	20905/652/435	13847/818/471	
$R1,^{a} wR2^{b} (I > 2\sigma(I))$	0.0617, 0.1589	0.0240, 0.0454	
$R1$, ^a $wR2^{b}$ (all data)	0.0750, 0.1659	0.0310, 0.0475	
Quality-of-fit ^c	1.139	1.111	

 Table S1. Crystal Data and Structure Refinement Parameters.

 ${}^{a}R1 = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR2 = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]].$ ${}^{c}Quality-of-fit = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / (N_{obs} - N_{params})]^{\frac{1}{2}}, \text{ based on all data.}$



Figure S9. ORTEP drawing of **1**, drawn with thermal ellipsoids at the 40% probability level. All hydrogen atoms are removed for clarity. Color scheme used: C grey, O red and Y pink.



Figure S10. ORTEP drawing of **2**, drawn with thermal ellipsoids at the 40% probability level. All hydrogen atoms are removed for clarity. Color scheme used: C grey, O red and La blue.



Table S2. Major bond length distances in 1 (Å), along with the numbering scheme.

Bond	Distance	Bond	Distance
Y1C1	2.750(5)	Y2C9	2.899(5)
Y1C2	2.669(5)	Y2C16	2.775(5)
Y1-C3	2.686(5)	Y2C17	2.672(4)
Y1-C4	2.719(5)	Y2C18	2.670(4)
Y1-C5	2.682(4)	Y2C19	2.666(4)
Y1-C6	2.656(5)	Y2C20	2.672(4)
Y1-C7	2.675(5)	Y2C21	2.684(4)
Y1-C8	2.771(5)	Y2–C22	2.713(4)
Y1-C9	2.762(5)	Y2C23	2.720(4)
Y1-C10	2.785(5)	Y2C24	2.694(4)
Y1C11	2.772(5)	Y201	2.562(3)
Y1-C12	2.762(5)	Y2–O2	2.553(3)
Y1-C13	2.747(5)	Y1-Ct _{COT-1}	1.991(5)
Y1C14	2.786(5)	Y1-Ct _{COT-2}	2.074(5)
Y1C15	2.790(5)	Y2Ct _{COT-3}	1.962(4)
Y1-C16	2.746(5)		

Bond	Distance	Bond	Distance
La1–C1	2.762(4)	La2-C14	2.897(5)
La1–C2	2.757(4)	La2-C15	2.860(5)
La1–C3	2.721(4)	La2–C17	2.761(2)
La1–C4	2.728(4)	La2–C18	2.760(2)
La1–C5	2.739(4)	La2–C19	2.732(2)
La1–C6	2.762(4)	La2-C20	2.717(2)
La1–C7	2.748(4)	La2-C21	2.703(2)
La1–C8	2.744(4)	La2–C22	2.710(2)
La1–C9	2.860(5)	La2-C23	2.719(2)
La1–C10	2.827(5)	La2–C24	2.747(2)
La1–C11	2.822(5)	La2–O1	2.600(1)
La1–C12	2.852(5)	La2–O2	2.601(1)
La1-C13	2.862(5)	La1-Ct _{COT-1}	2.045(4)
La1–C14	2.880(5)	La1-Ct _{COT-2}	2.154(5)
La1–C15	2.777(5)	La2–Ct _{COT-3}	2.009(2)
La1–C16	2.837(5)		

Table S3. Major bond length distances in 2 (Å).

Table S4. Intermolecular C–H··· π interactions in **1** and **2** (in Å).

	Range of C–H··· π	Avg. C–H···π
1	2.441(5)-2.780(5)	2.604(5)
2	2.453(5)-2.796(5)	2.634(5)

	Individual	Distance from weighted least-squares plane		
	atom	(1) (2)		
COT1	C1	-0.0220(2)	0.0213(78)	
	C2	0.0489(2)	-0.0207(55)	
	C3	0.0070(2)	0.0243(41)	
	C4	-0.0314(1)	0.0127(37)	
	C5	-0.0183(1)	-0.0134(41)	
	C6	0.0289(0)	-0.0222(38)	
	C7	0.0297(0)	0.0177(41)	
	C8	-0.0428(1)	0.0230(57)	
	C1–8	14.841(12)x + 3.500(32)y -	14.768(12)x + 4.345(0.028)y -	
		3.766(37)z - 4.280(31) = 0	3.291(18)z - 4.693(16) = 0 (RMS/A:	
		(RMSD/A: 0.0312)	0.0198)	
	C9	-0.0158(46)	0.0551(26)	
	C10	0.0352(49)	-0.0367(24)	
	C11	0.0158(55)	-0.0478(22)	
	C12	-0.0297(59)	0.0242(21)	
	C13	-0.0228(72)	0.0611(21)	
COT2	C14	0.0293(55)	-0.0332(22)	
	C15	0.0348(48)	-0.0603(23)	
	C16	-0.0469(43)	0.0376(25)	
	C9–16	15.133(7)x + 1.947(4)y -	15.038(4)x + 3.115(11)y -	
		4.1939(4)z - 7.962(2) = 0	4.078(11)z - 8.299(9) = 0	
		(RMSD/A: 0.0304)	(RMS/A: 0.0463)	
	C17	-0.0101(35)	0.0036(14)	
	C18	-0.0009(34)	-0.0011(13)	
	C19	0.0100(33)	-0.0093(13)	
COT3	C20	0.0031(32)	0.0069(13)	
	C21	-0.0151(31)	0.0040(13)	
	C22	0.0035(32)	-0.0021(14)	
	C23	0.0089(35)	-0.0082(14)	
	C24	0.0005(36)	0.0062(14)	
	C17–24	13.307(10)x - 6.1050(14)y -	13.752(4)x - 5.664(6)y - 4.753(6)z	
		4.6566(14)z - 8.050(17) = 0	-8.571(7) = 0 (RMS/A: 0.0059)	
		(RMSD/A: 0.0082)		

 Table S5. Least-squares-plane calculations for the COT rings in 1 and 2.