Supporting Information

Exploring the Host-Guest Interactions of Small Molecules in UoC–9(Ca)

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Table S1. Details of X-ray Single Crystal Structure Analyses of Hacac@UoC-9, THF@UoC-9 and PhMe@UoC-9.

	Hacac@UoC-9	THF@UoC-9	PhMe@UoC-9
Formula	$(Ca_5C_{83}H_{39}O_{23}F_9)(C_5O_2H_8)_2$ [+solvent]	$(Ca_5C_{83}H_{39}O_{22}F_9)(C_4OH_8)_3$ [+solvent]	$(Ca_5C_{83}H_{39}O_{21}F_9)(C_3NOH_7)_{3.97}(C_7H_8)_{1.24}$ [+solvent]
Formula weight [g/mol]	1975.77 (without solvent)	1975.85 (without solvent)	2148.46 (without solvent)
Crystal description	prism, colorless	prism, colorless	prism, colorless
Crystal size [mm]	0.26 · 0.24 · 0.10	0.17 · 0.12 · 0.08	0.56 · 0.25 · 0.17
Space group; *Z*	*Ima*2 (no. 46); 4	$Pna2_1$ (no. 33); 4	$Pna2_1$ (no. 33); 4
a [Å]	31.5957(19)	31.6409(19)	31.7465(13)
b [Å]	16.8364(9)	16.5291(9)	16.6974(7)
c [Å]	28.2441(16)	28.7463(15)	28.4978(11)
V [Å^3]	15024.7(15)	15034.2(14)	15106.2(11)
Absorption correction	SADABS-2016/2 (Bruker, 2016/2)	SADABS-2016/2 (Bruker, 2016/2)	SADABS-2016/2 (Bruker, 2016/2)
Diffractometer, radiation	Bruker D8 Venture Dual Beam, Cu Kα	Bruker D8 Venture Dual Beam, Mo Kα	Bruker D8 Venture Dual Beam, Mo Kα
Temperature [K]	100(2)	100(2)	100(2)
$2\theta_{max}$ [°]	145.382	51.362	50.70
Index ranges	$-39 \le h \le 31$ $-20 \le k \le 20$ $-34 \le l \le 34$	$-38 \le h \le 38$ $-20 \le k \le 20$ $-30 \le l \le 35$	$-38 \le h \le 37$ $-20 \le k \le 20$ $-34 \le l \le 33$
Reflections collected / independent	190537 / 15105	158745 / 27394	161459 / 27268
Significant reflections	13825 with $I > 2\sigma(I)$	22297 with $I > 2\sigma(I)$	23583 with $I > 2\sigma(I)$
R_{int}	0.1253	0.0566	0.0484
Data / parameters / restraints	15105 / 820 / 319	27394 / 1532 / 1430	27268 / 1746 / 1499
GooF = S_{all}	1.040	1.039	1.024
R [$F^2 > 2\sigma(F^2)$]	0.0608	0.0739	0.0726
wR(F^2), all data	0.1658	0.2144	0.2096
Solvent accessible volume, electrons found in s.a.v. (SQUEEZE)	7189 Å^3, 2568	7482 Å^3, 1777	5434 Å^3, 1206
$\Delta\rho_{min}$ / $\Delta\rho_{max}$ [e·10^{-6} pm^{-3}]	-0.381 / 0.312	-0.454 / 0.795	-0.681 / 0.655
Flack(x)	0.121(11) (refined as inversion twin)	0.23(4) (refined as inversion twin)	0.15(4) (refined as inversion twin)
CCDC deposition number	CCDC-2383895	CCDC-2383896	CCDC-2383897

Table S2. Details of X-ray Single Crystal Structure Analyses of PC@UoC-9, PhCN@UoC-9 and NMP@UoC-9.

	PC@UoC-9	PhCN@UoC-9	NMP@UoC-9
Formula	$(Ca_5C_{83}H_{39}O_{21}F_9)(C_4O_3H_6)_5$ [+solvent]	$(Ca_5C_{83}H_{39}O_{21}F_9)$ $(C_3NOH_7)_4(C_7NH_5)_{3.25}$ [+solvent]	$(Ca_5C_{83}H_{39}O_{20}F_9)$ $(C_5H_9NO)_{5.77}$ [+solvent]
Formula weight [g/mol]	2253.98 (without solvent)	2371.26 (without solvent)	2298.26 (without solvent)
Crystal description	prism, colorless	prism, colorless	prism, colorless
Crystal size [mm]	0.30 · 0.18 · 0.06	0.25 · 0.25 · 0.10	0.18 · 0.14 · 0.10
Space group; *Z*	*Pna*2$_1$ (no. 33); 4	*Ima*2 (no. 46); 4	*Pna*2$_1$ (no. 33); 12
a [Å]	31.6786(8)	31.8875(14)	32.033(6)
b [Å]	16.5991(5)	16.6009(7)	49.659(10)
c [Å]	28.8107(8)	28.7479(11)	28.956(6)
V [Å^3]	15149.7(7)	15218.0(11)	46062(16)
Absorption correction	SADABS-2016/2 (Bruker, 2016/2)	SADABS-2016/2 (Bruker, 2016/2)	CrysAlisPro 1.171.41.112a (Rigaku Oxford Diffraction, 2021)
Diffractometer, radiation	Bruker D8 Venture Dual Beam, Mo Kα	Bruker D8 Venture Dual Beam, Mo Kα	Beamline P24 @ DESY, 0.500000 Å
Temperature [K]	100(2)	100(2)	100(2)
$2\theta_{max}$ [°]	52.748	52.798	36.898
Index ranges	-39 ≤ *h* ≤ 39 -20 ≤ *k* ≤ 20 -35 ≤ *l* ≤ 35	-39 ≤ *h* ≤ 39 -20 ≤ *k* ≤ 20 -35 ≤ *l* ≤ 35	-40 ≤ *h* ≤ 33 -62 ≤ *k* ≤ 62 -26 ≤ *l* ≤ 36
Reflections collected / independent	305303 / 29404	472470 / 15817	165206 / 71589
Significant reflections	25369 with I > 2σ(I)	15349 with I > 2σ(I)	32322 with I > 2σ(I)
R_{int}	0.0673	0.0392	0.0715
Data / parameters / restraints	29404 / 1550 / 516	15817 / 907 / 571	71589 / 4678 / 1507
GooF = S_{all}	1.065	1.068	0.956
R [$F^2 > 2\sigma(F^2)$]	0.0623	0.0478	0.0970
wR(F^2), all data	0.1913	0.1408	0.3181
Solvent accessible volume, electrons found in s.a.v. (SQUEEZE)	6051 Å^3, 1619	4386 Å^3, 1423	16266 Å^3, 4633
$\Delta\rho_{min}$ / $\Delta\rho_{max}$ [e·10^{-6} pm^{-3}]	-0.363 / 1.792	-0.328 / 0.727	-0.633 / 1.462
Flack(x)	0.030(9) (refined as inversion twin)	0.07(3) (refined as inversion twin)	0.20(8) (refined as inversion twin)
CCDC deposition number	CCDC-2383898	CCDC-2383899	CCDC-2383900

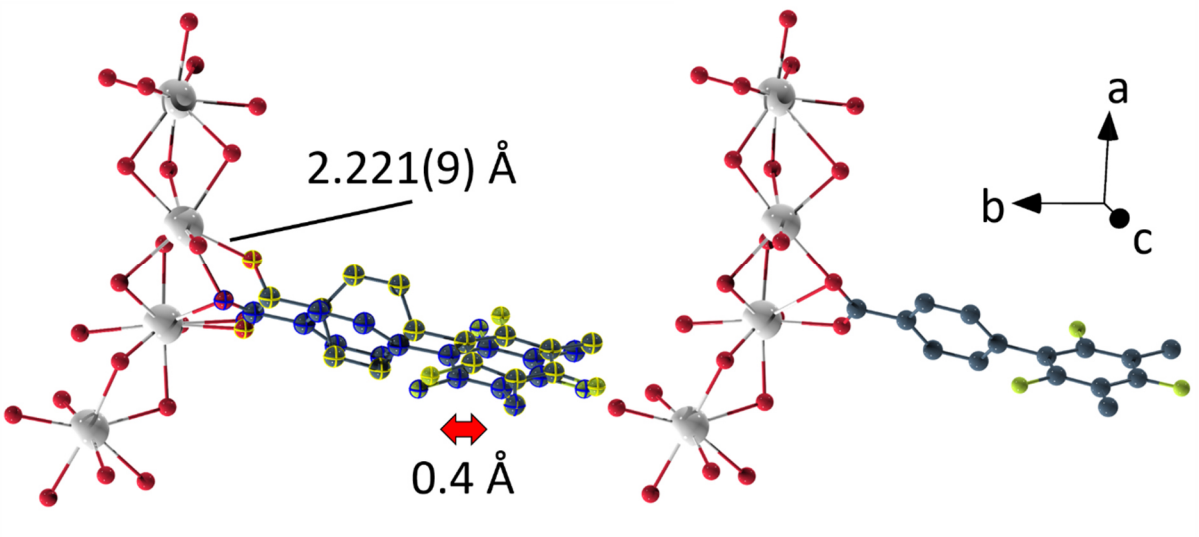

Figure S1. Excerpt of the crystal structure of Hacac@UoC-9 (left) showing a fragment of the disordered linker coordinating to the SBU; the two individual disordered linker fragments are highlighted in blue and yellow, respectively. For comparison, an excerpt of the crystal structure of DMF@UoC-9 with an ordered linker fragment is shown (right).

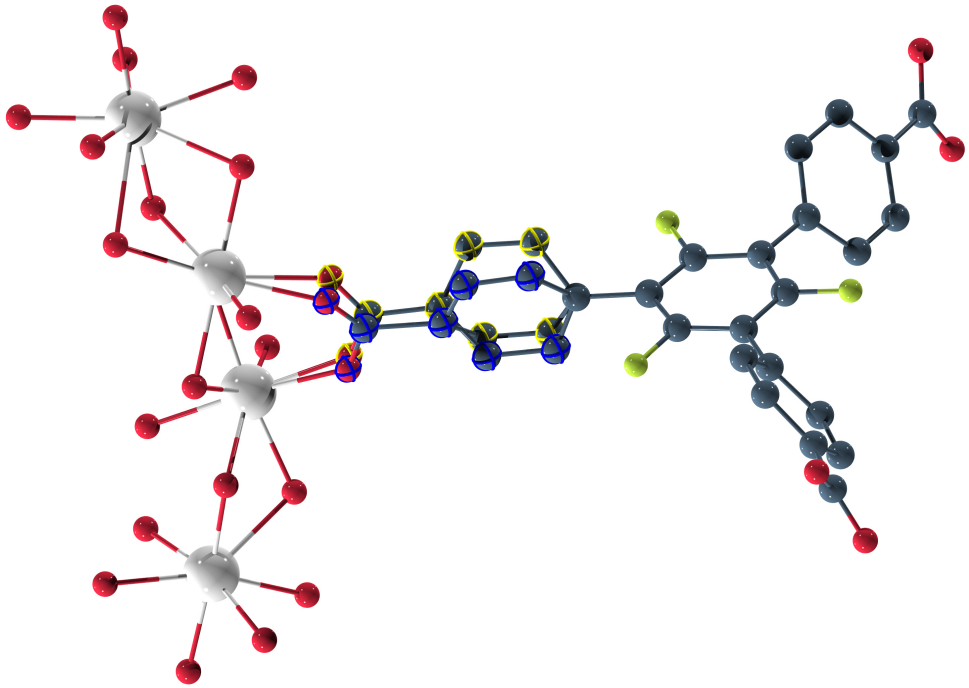

Figure S2. Excerpt of the crystal structure of PC@UoC-9 showing a disordered linker coordinating to the SBU. The two individual disordered fragments are highlighted in blue and yellow, respectively.

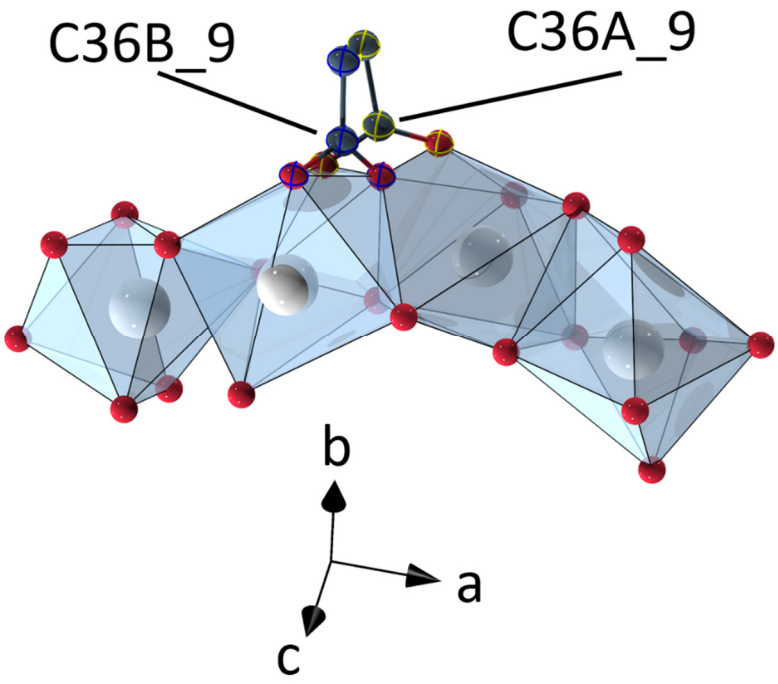

Figure S3. Excerpt of the crystal structure of NMP@UoC-9 showing a fragment of the SBU with two coordinating disordered carboxylate groups. The two individual disordered fragments are highlighted in blue and yellow, respectively.

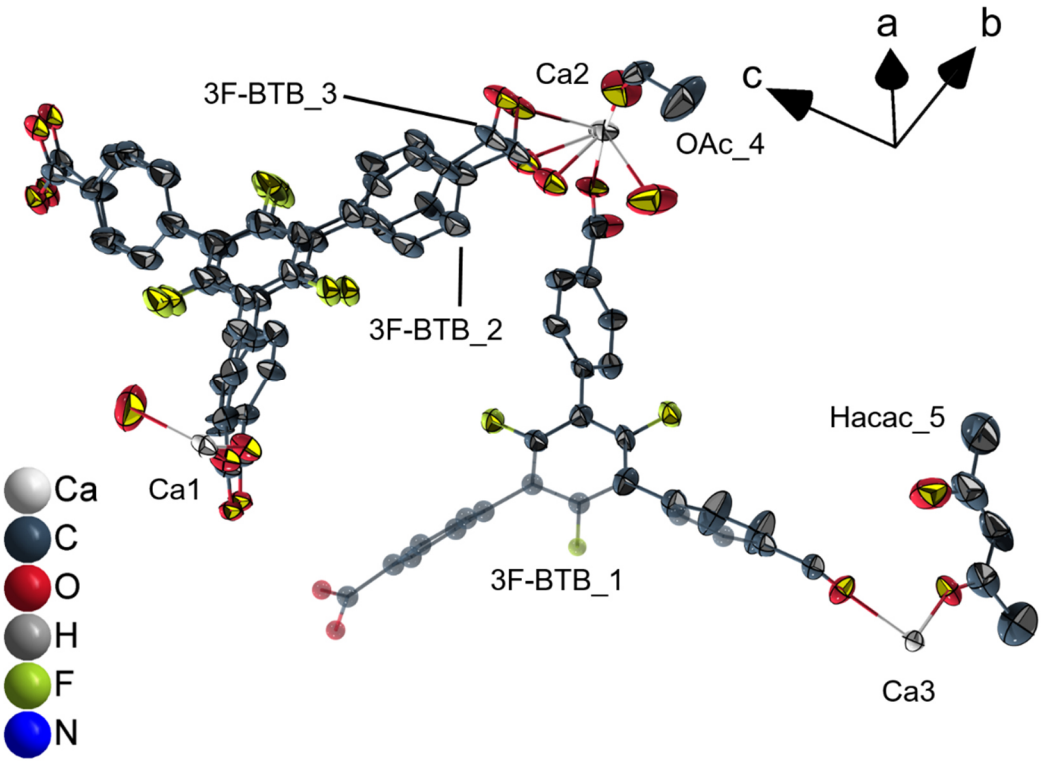

Figure S4. Asymmetric unit of Hacac@UoC-9 refined from X-ray single-crystal diffraction data recorded at 100 K and displayed as thermal ellipsoids (50% probability). Molecular entities are labelled according to the refinement. Non-coordinating DMF molecules and hydrogen atoms are omitted for clarity.

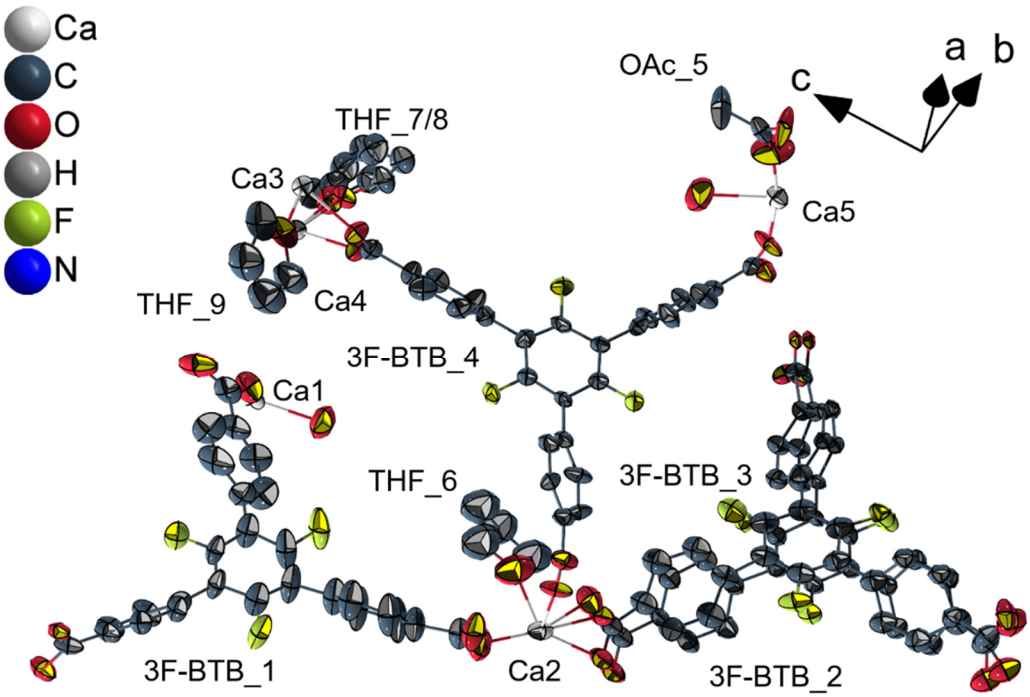

Figure S5. Asymmetric unit of THF@UoC-9 refined from X-ray single-crystal diffraction data recorded at 100 K and displayed as thermal ellipsoids (50% probability). Molecular entities are labelled according to the refinement. All moieties being part of the framework are shown in a transparent mode without labels. Hydrogen atoms are omitted for clarity.

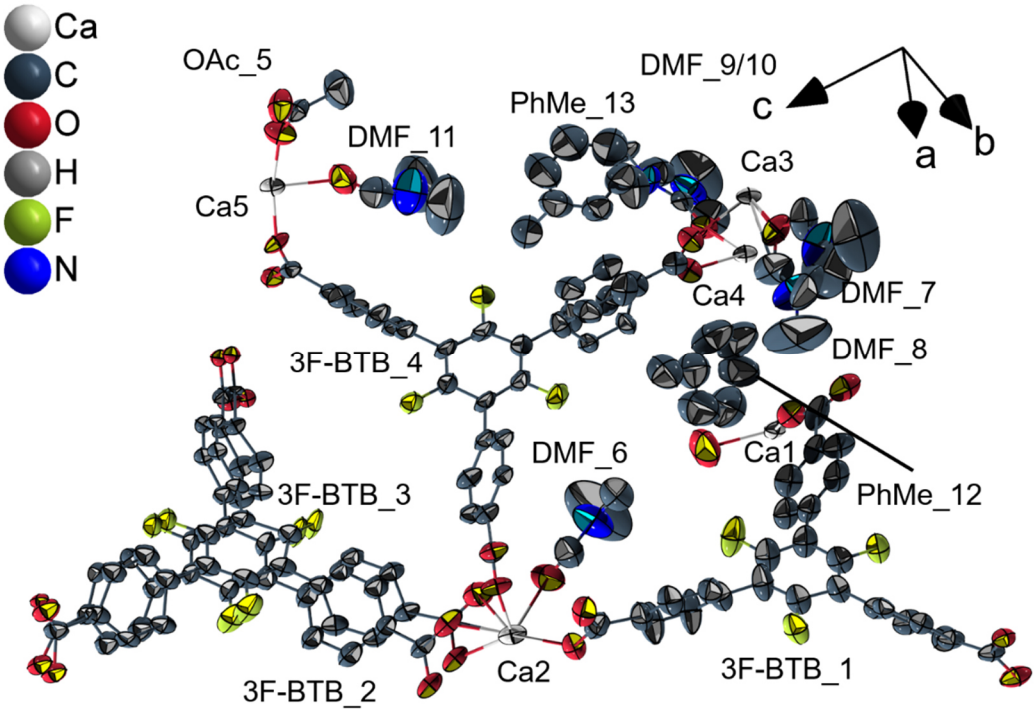

Figure S6. Asymmetric unit of PhMe@UoC-9 refined from X-ray single-crystal diffraction data recorded at 100 K and displayed as thermal ellipsoids (50% probability). Molecular entities are labelled according to the refinement. Hydrogen atoms are omitted for clarity.

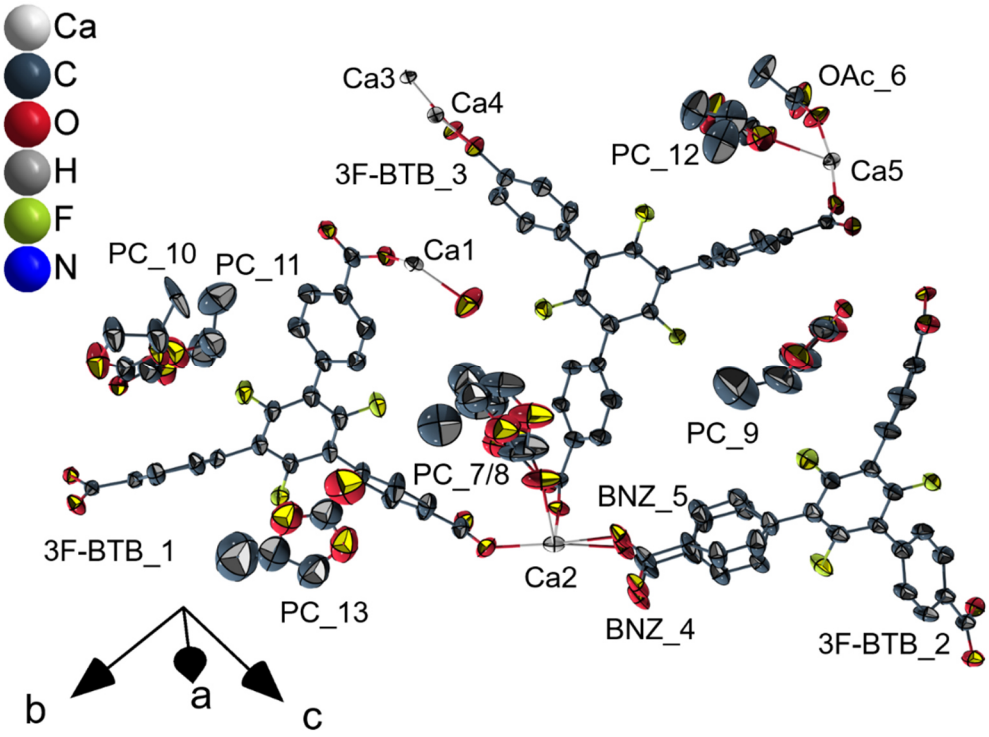

Figure S7. Asymmetric unit of PC@UoC-9 refined from X-ray single-crystal diffraction data recorded at 100 K and displayed as thermal ellipsoids (50% probability). Molecular entities are labelled according to the refinement. All moieties being part of the framework are shown in a transparent mode without labels. Hydrogen atoms are omitted for clarity.

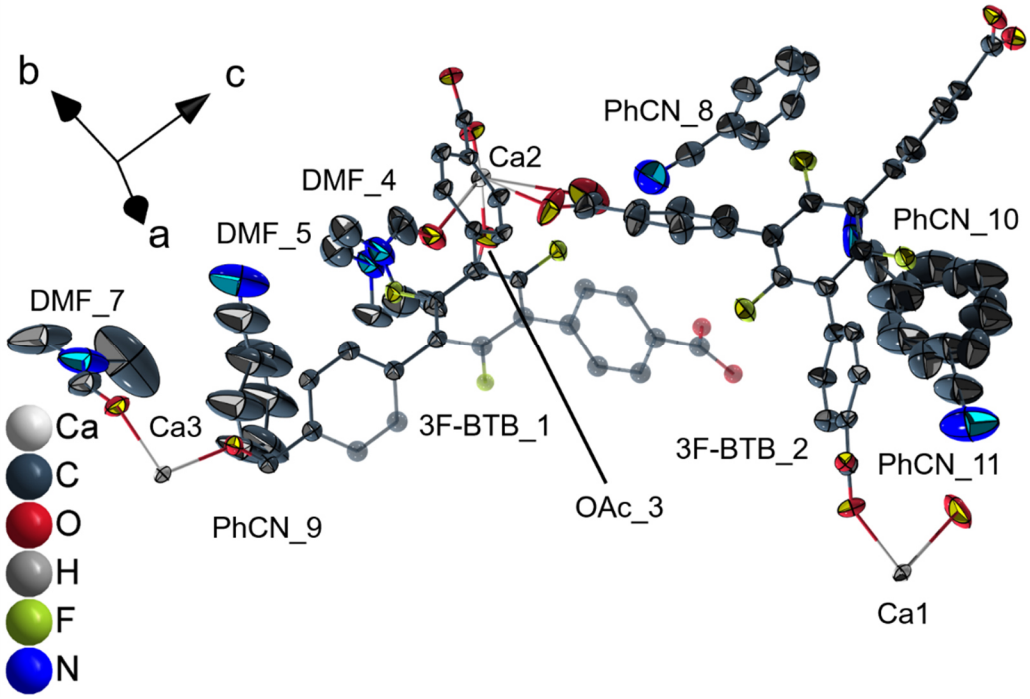

Figure S8. Asymmetric unit of PhCN@UoC-9 refined from X-ray single-crystal diffraction data recorded at 100 K and displayed as thermal ellipsoids (50% probability). Molecular entities are labelled according to the refinement. Hydrogen atoms are omitted for clarity.

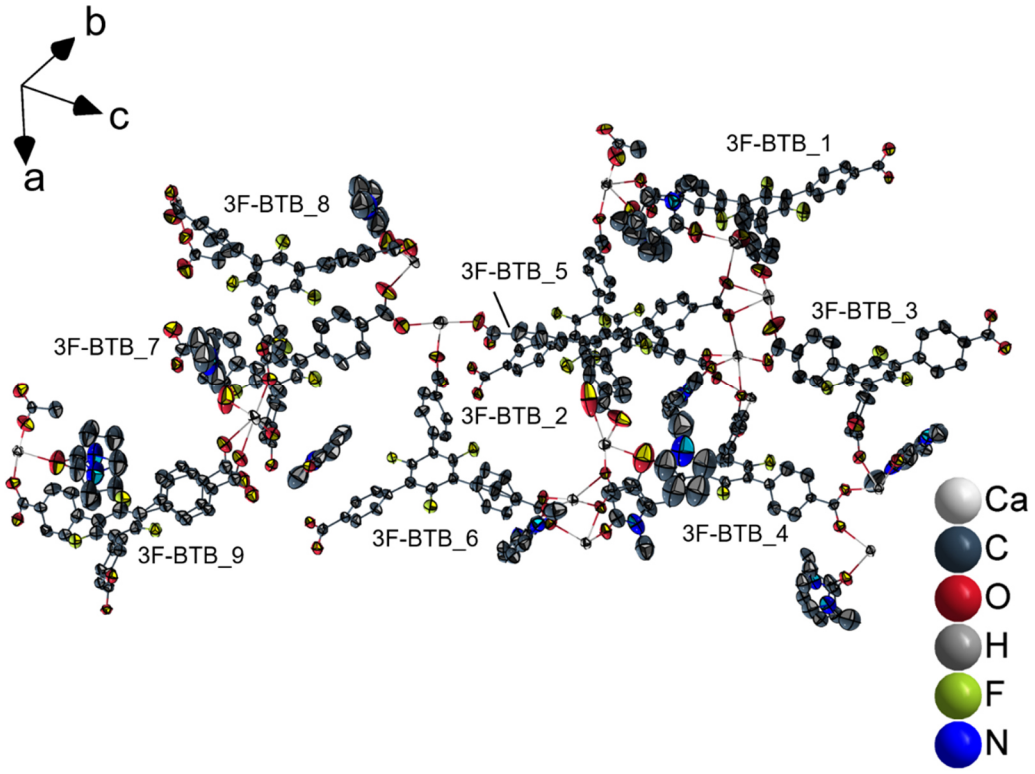

Figure S9. Asymmetric unit of NMP@UoC-9 refined from synchrotron single-crystal diffraction data recorded at 100 K and displayed as thermal ellipsoids (50% probability). Molecular entities are labelled according to the refinement. Hydrogen atoms are omitted for clarity.

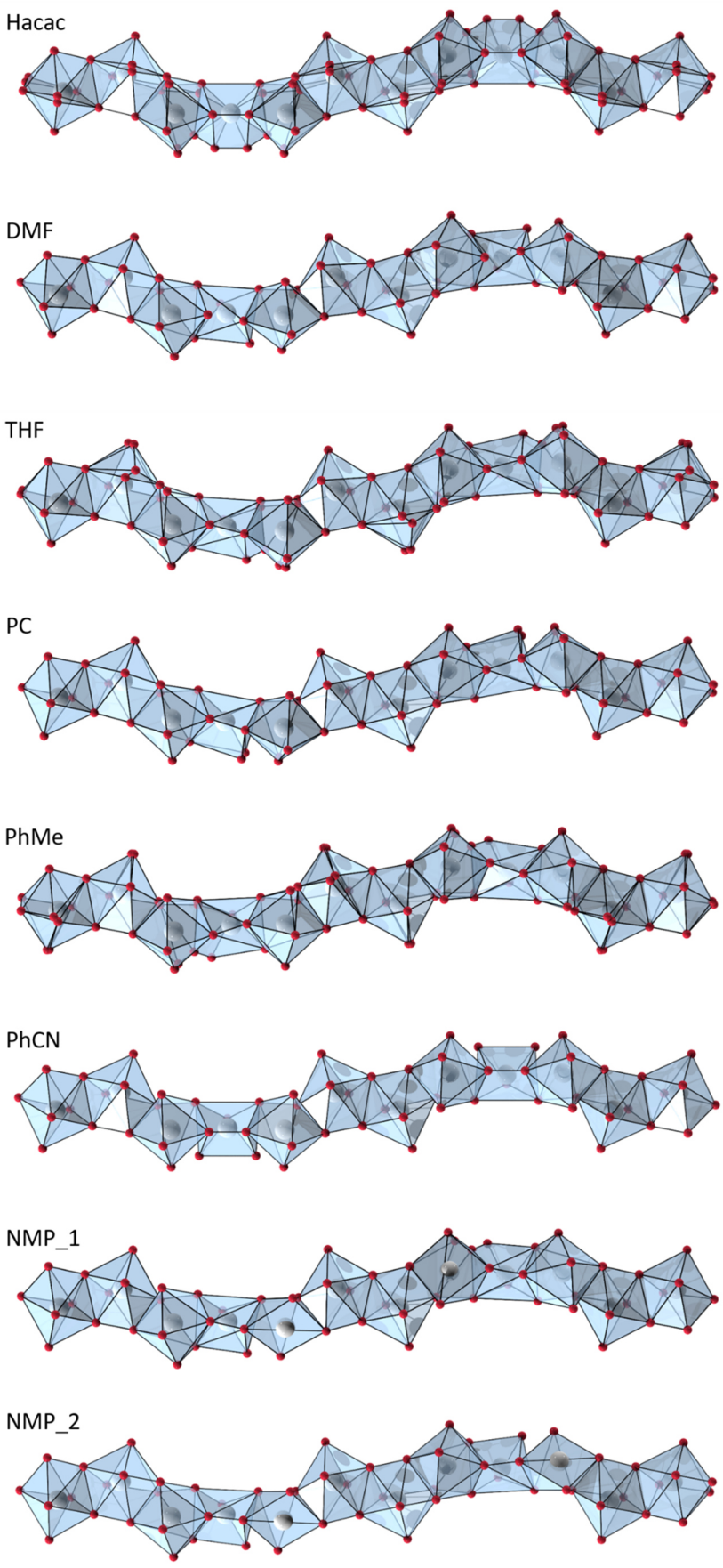

Figure S10. Excerpts of the SBUs of all Guest@UoC-9 systems shown along the crystallographic *c*-axis from the shortest (top) to the longest *a*-axis (bottom).

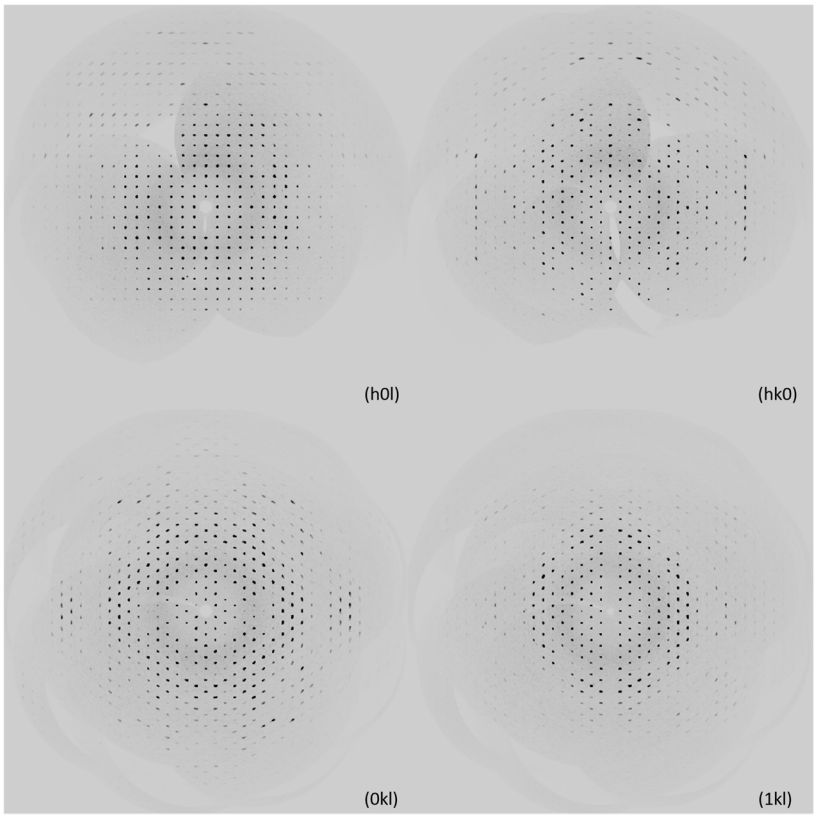

Figure S11. Digitally generated precession images of the from left to right, top to bottom (h0l), (hk0), (0kl) and (1kl) layers, from the dataset of the Hacac@UoC-9 system.

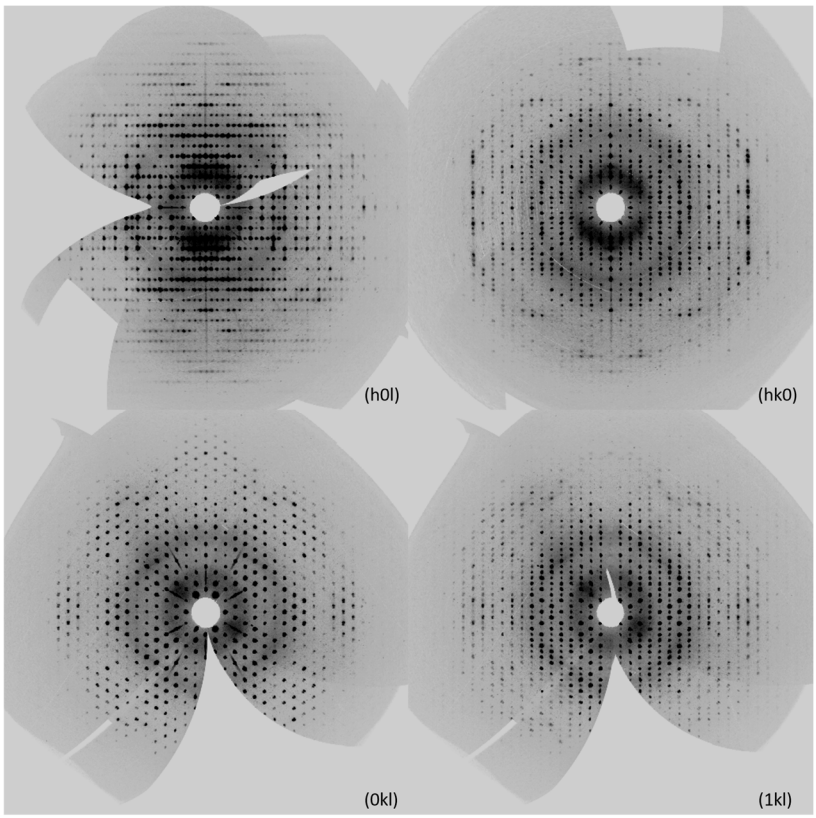

Figure S12. Digitally generated precession images of the from left to right, top to bottom (h0l), (hk0), (0kl) and (1kl) layers, from the dataset of the THF@UoC-9 system.

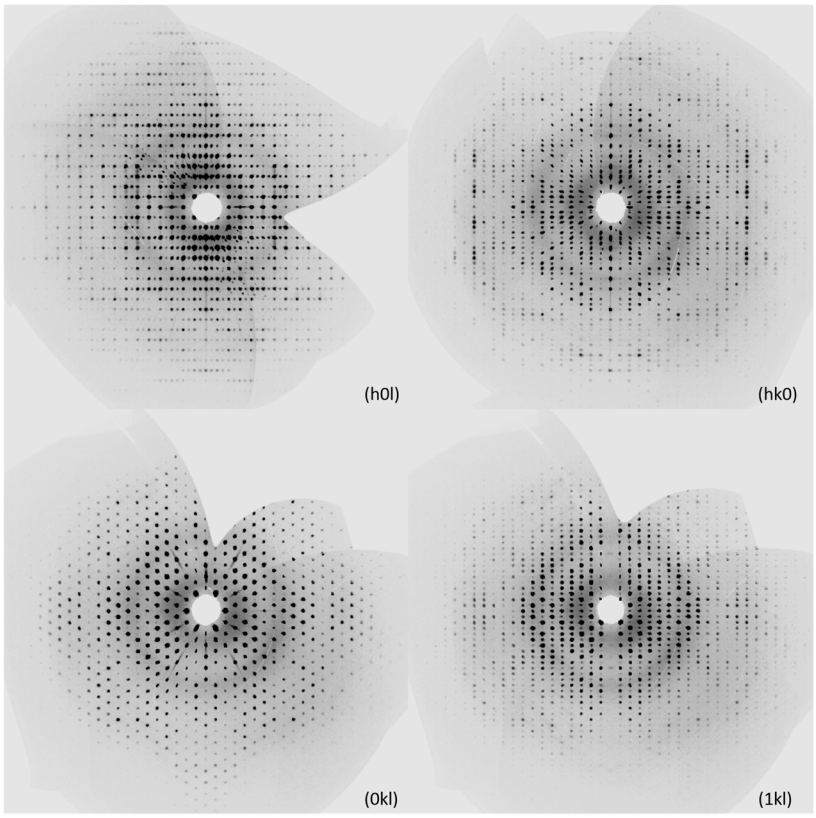

Figure S13. Digitally generated precession images of the from left to right, top to bottom (h0l), (hk0), (0kl) and (1kl) layers, from the dataset of the PhMe@UoC-9 system.

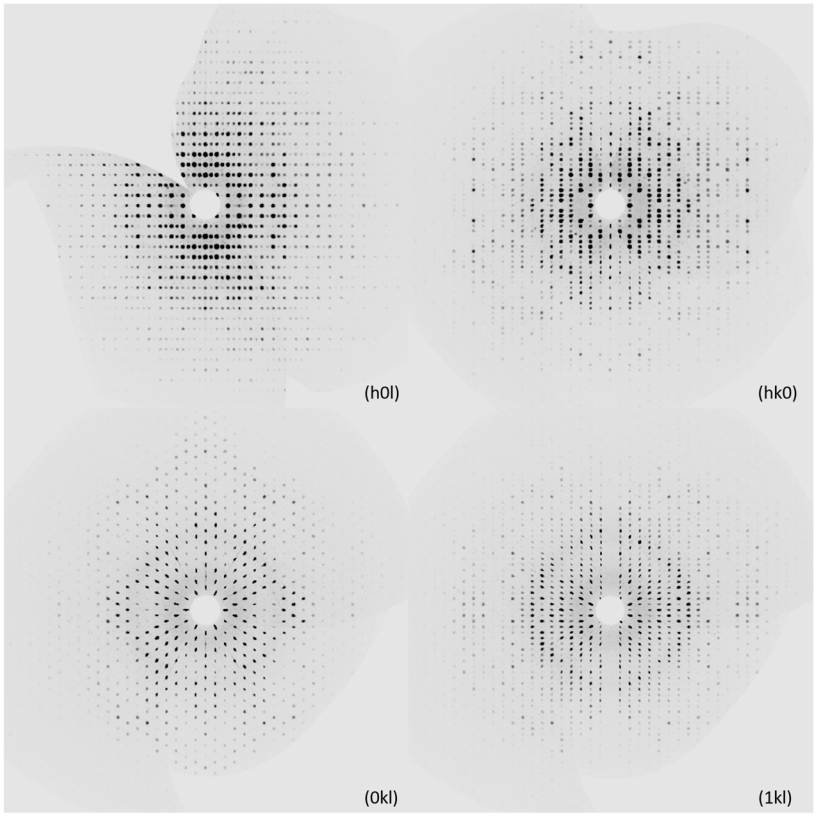

Figure S14. Digitally generated precession images of the from left to right, top to bottom (h0l), (hk0), (0kl) and (1kl) layers, from the dataset of the PC@UoC-9 system.

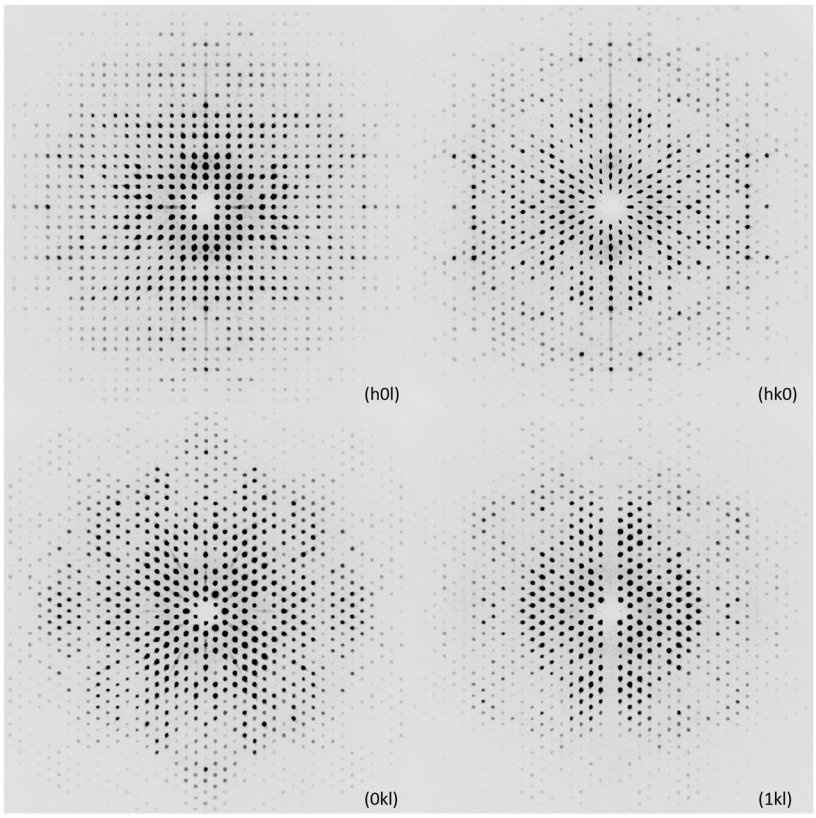

Figure S15. Digitally generated precession images of the from left to right, top to bottom (h0l), (hk0), (0kl) and (1kl) layers, from the dataset of the PhCN@UoC-9 system.

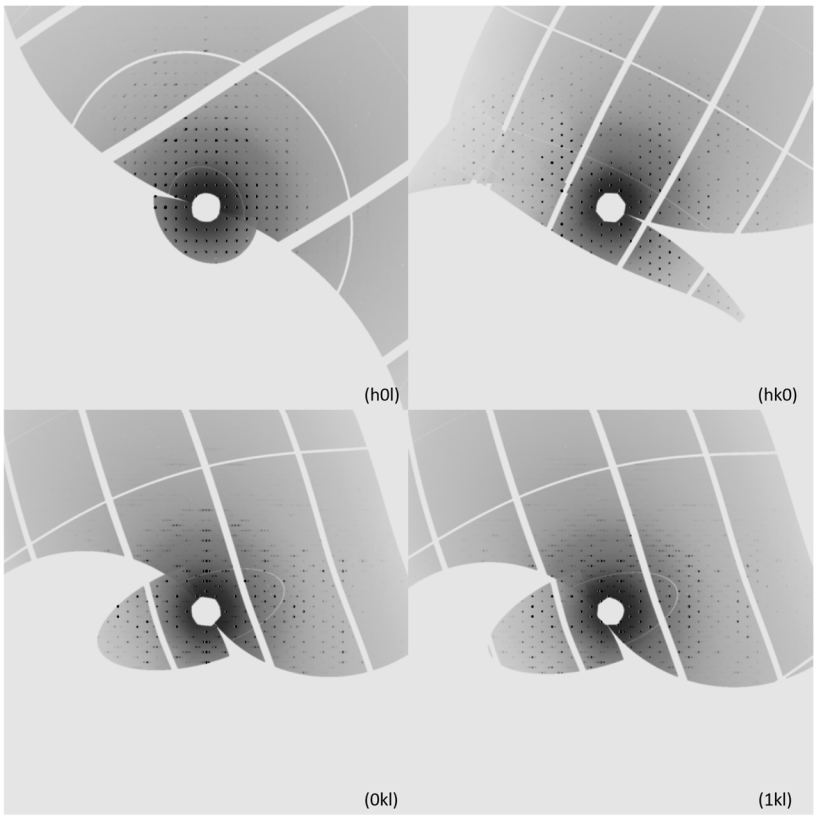

Figure S16. Digitally generated precession images of the from left to right, top to bottom (h0l), (hk0), (0kl) and (1kl) layers, from the dataset of the NMP@UoC-9 system.

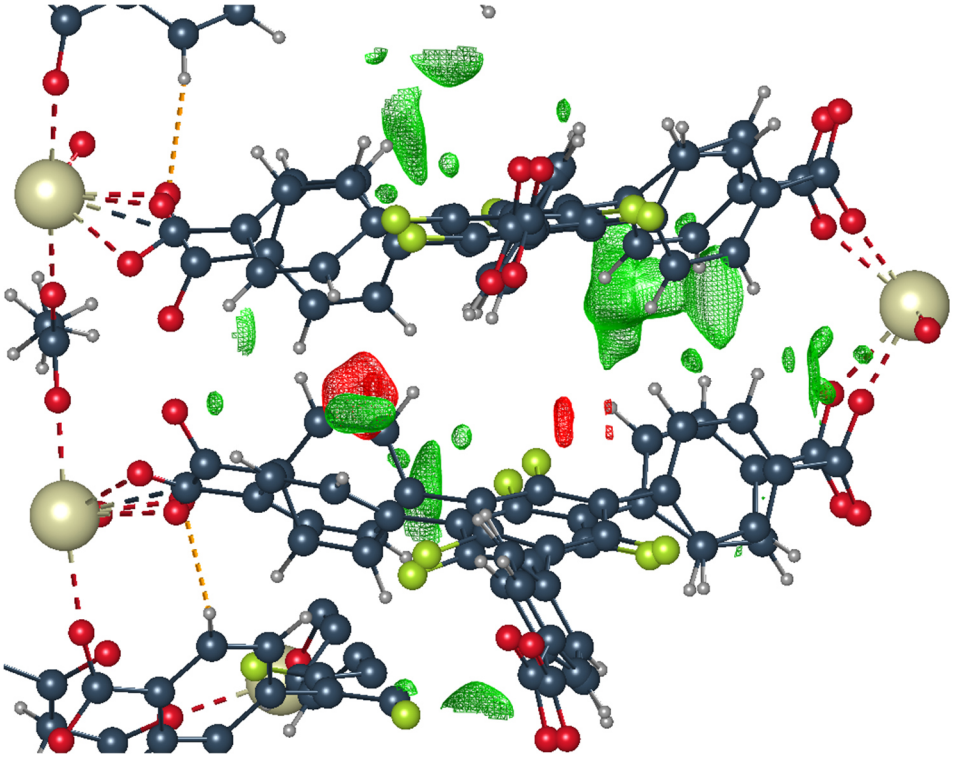

Figure S17. Excerpt of the crystal structure of Hacac@UoC-9(Ca) showing the difference *Fourier* map in a 7 Å radius around the one carbon of the central ring in the centre of the figure. Green and red colours correspond to positive and negative electron densities, respectively. The maps are drawn with a threshold of 0.51 e/Å³.

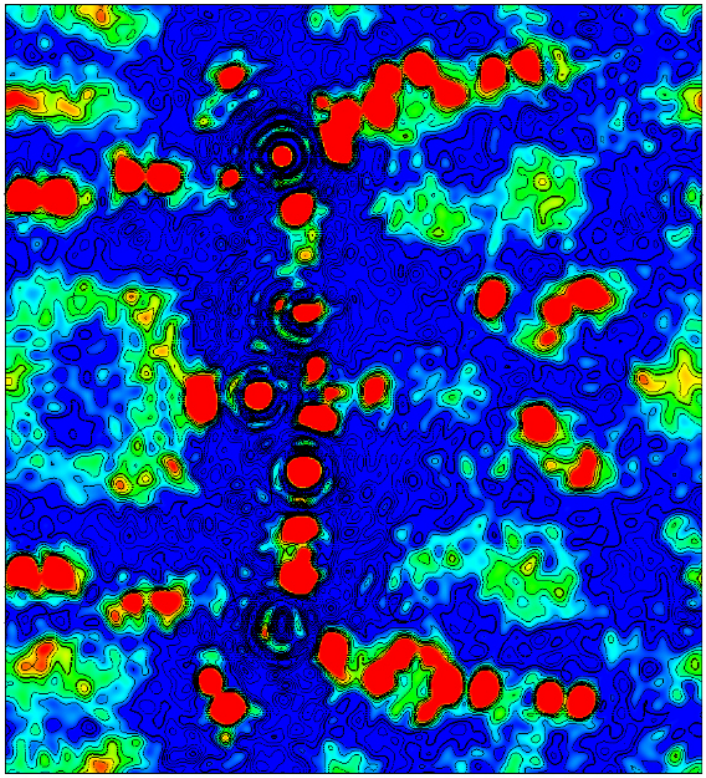

Figure S18. 2D slice of the F_o-map through one unit cell of THF@UoC-9 shown along the crystallographic *b*-axis, offset from the origin: 2.1 Å. The gradient from red to blue corresponds to high and low electron density, respectively.