Single-crystal to single-crystal guest exchange and phase transformations in a porous metallocycle

Marike du Plessis, Vincent J. Smith and Leonard J. Barbour*

Electronic Supplementary Information (ESI)

Contents

Thermogravimetric analysis

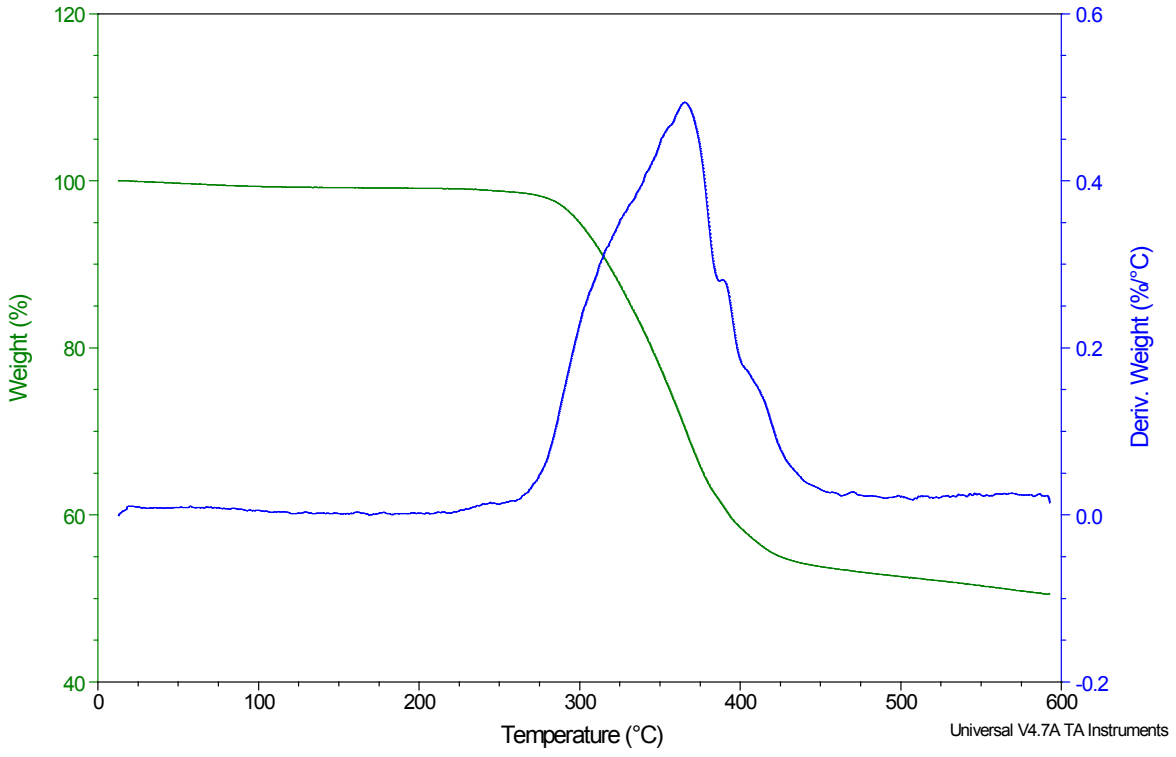

Figure 1. TGA plot for $\mathbf{1}_{apohost}$. The second derivative curve (blue line) indicates no significant mass change up to decomposition of the compound at ~270°C, indicating that no guest is present in the channels formed by the host metallocycles.

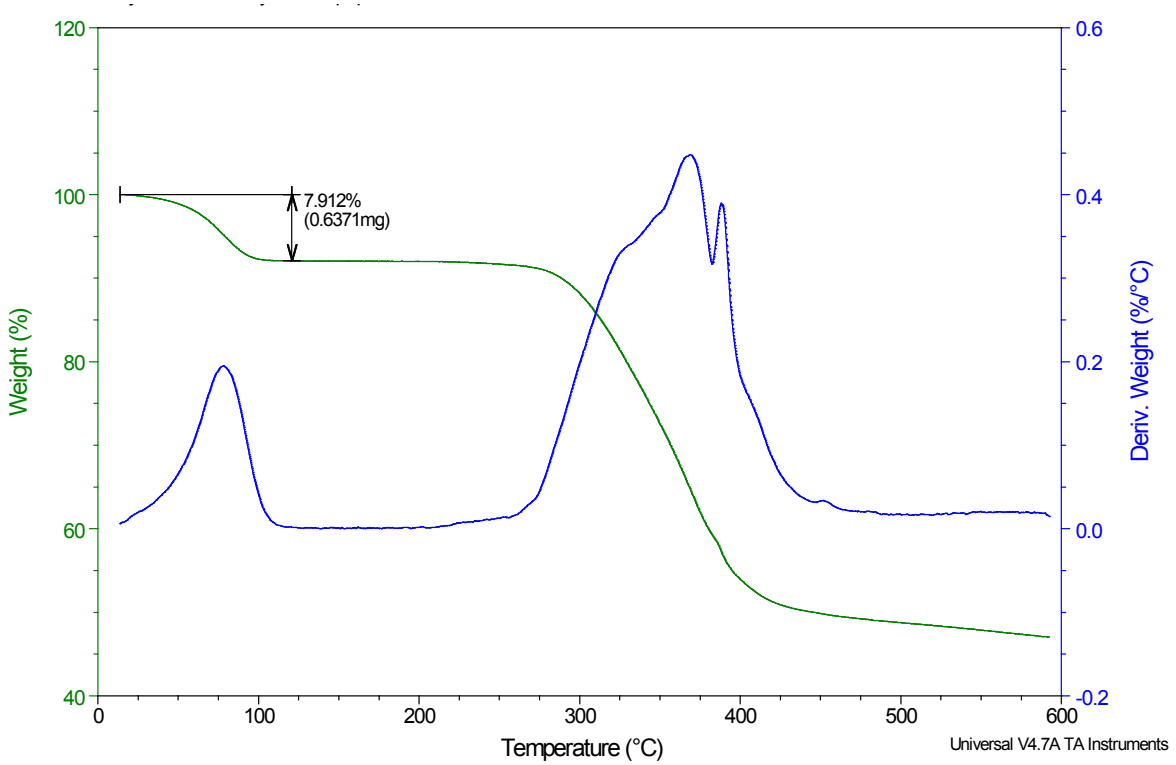

Figure 2. TGA plot for Solvate **1**. The observed mass loss of 7.9% correlates with the predicted value of 8.9% for two acetonitrile molecules per metallocycle host, taken into account that some solvent loss occurs at room temperature during sample preparation.

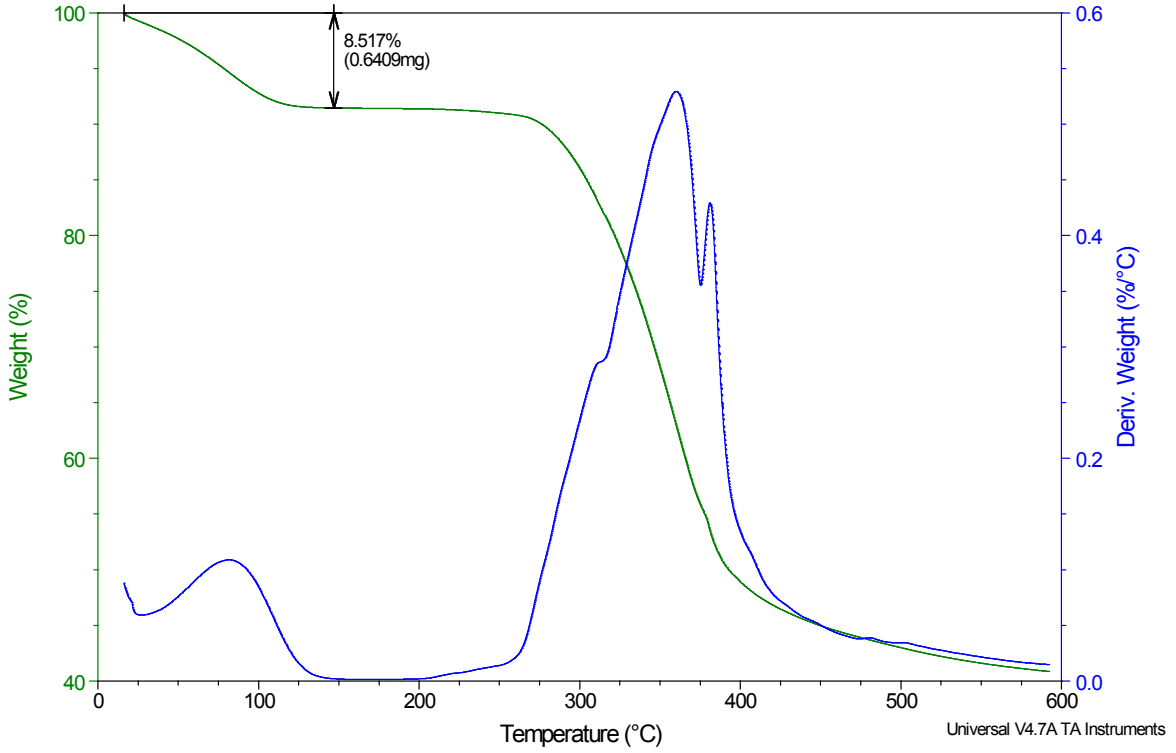

Figure 3. TGA plot for Solvate **2**. The observed mass loss of 8.5% correlates with the predicted value of 11.2% for two acetone molecules per metallocycle host, taken into account that some solvent loss occurs at room temperature during sample preparation.

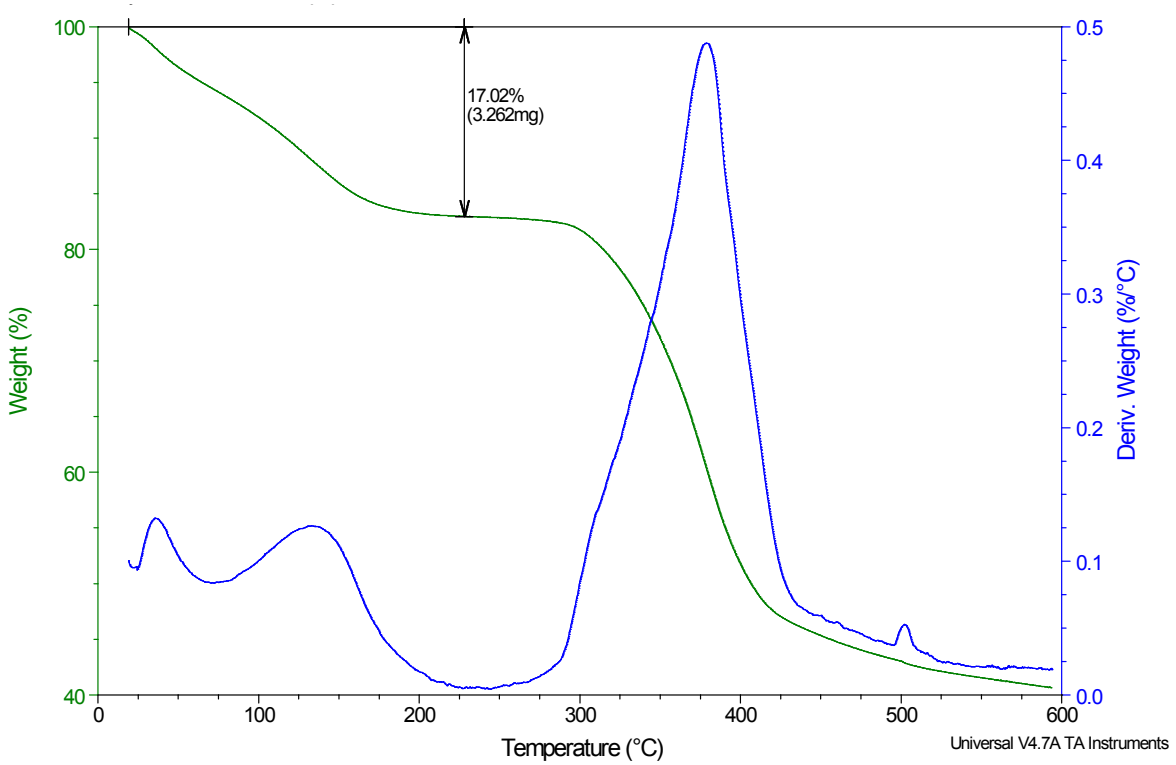

Figure 4. TGA plot for Solvate **3**. The observed mass loss of 17.0% correlates with the predicted value of 20.6% for two chloroform molecules per metallocycle host, taken into account that some solvent loss occurs at room temperature during sample preparation.

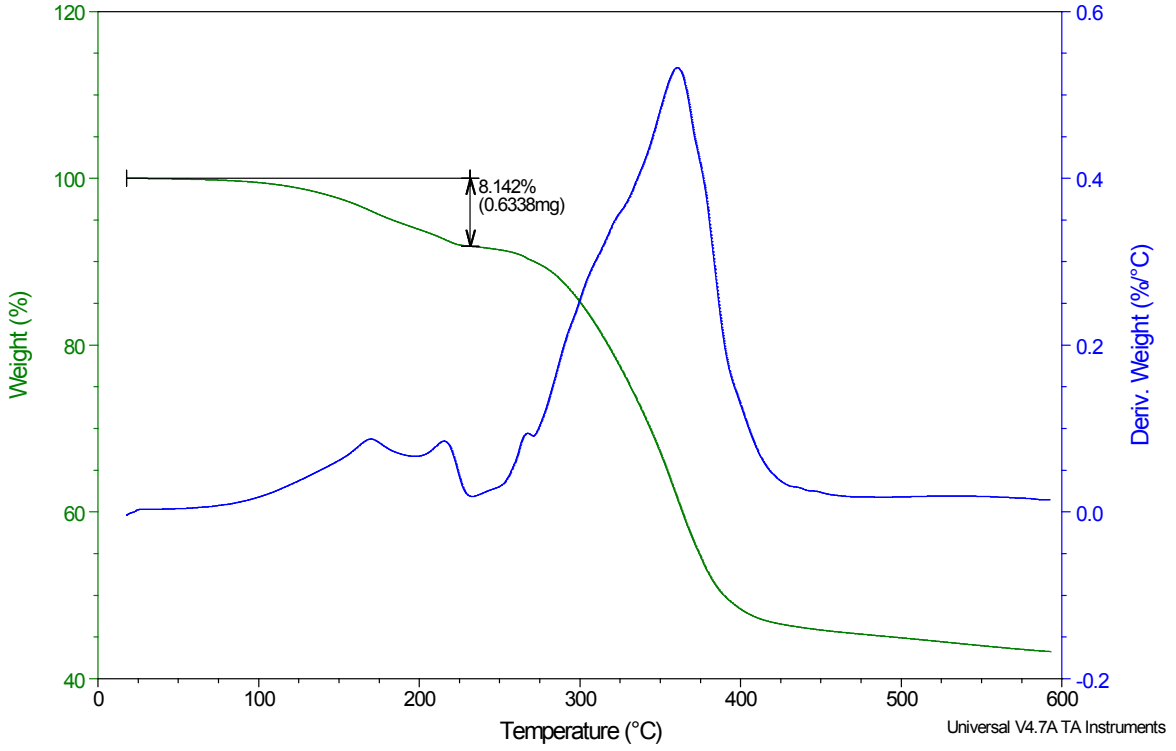

Figure 5. TGA plot for Solvate **4**. The observed mass loss of 8.1% correlates with the predicted value of 7.8% for one benzene molecule taken into account that some solvent is lost from the surface of the crystals.

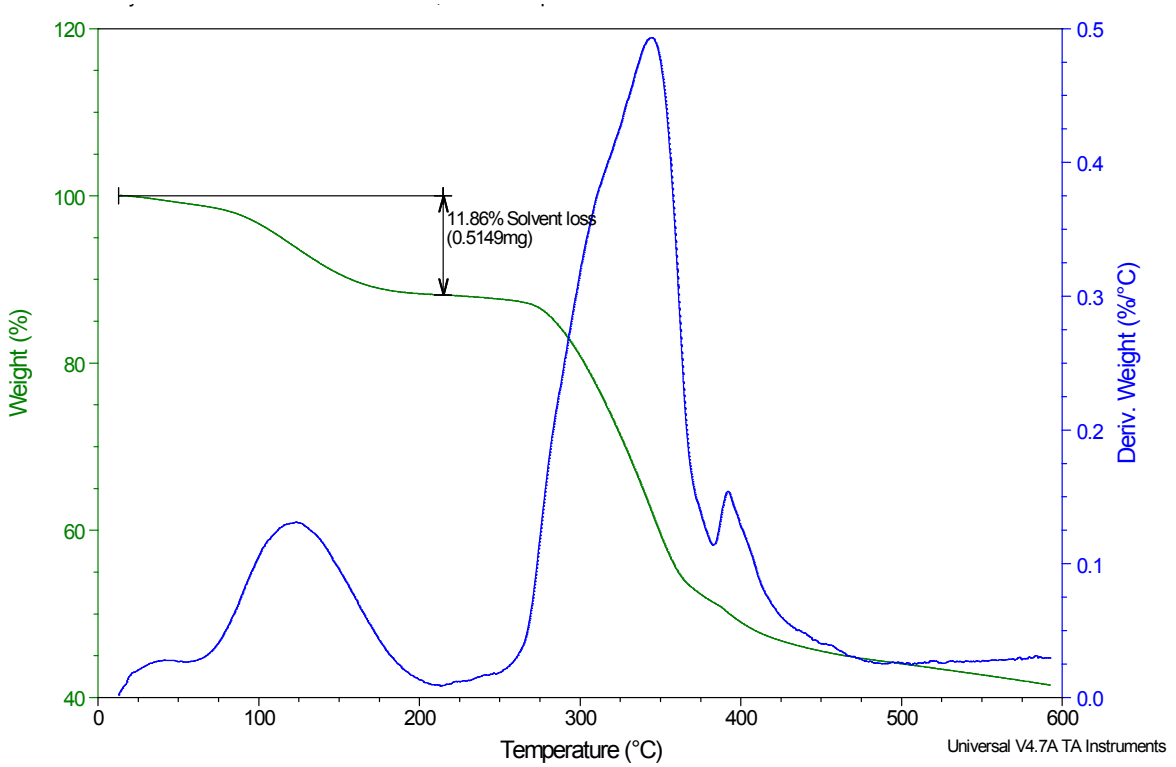

Figure 6. TGA plot for Solvate **5**. The observed mass loss of 11.9% correlates with the predicted value of 11.9% for one difluorobenzene molecule per metallocycle host.

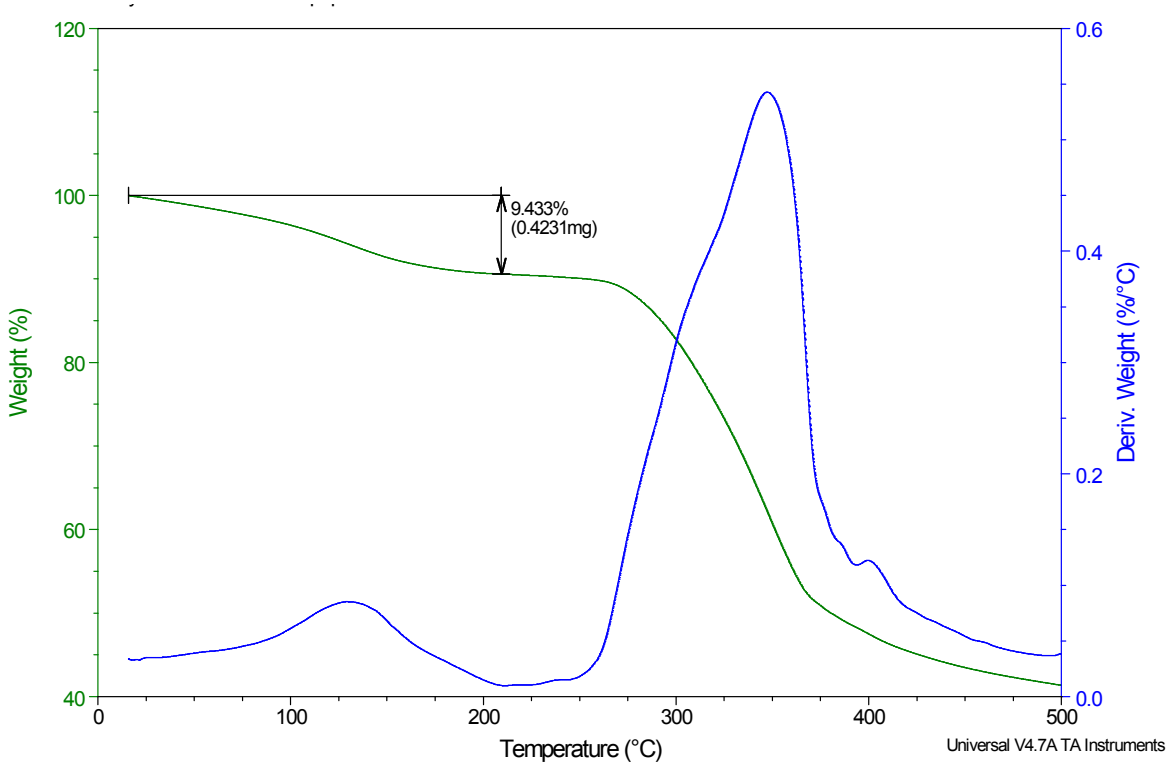

Figure 7. TGA plot for Solvate **6**. The observed mass loss of 9.4% correlates with the predicted value of 9.1% for one toluene molecule per metallocycle host.

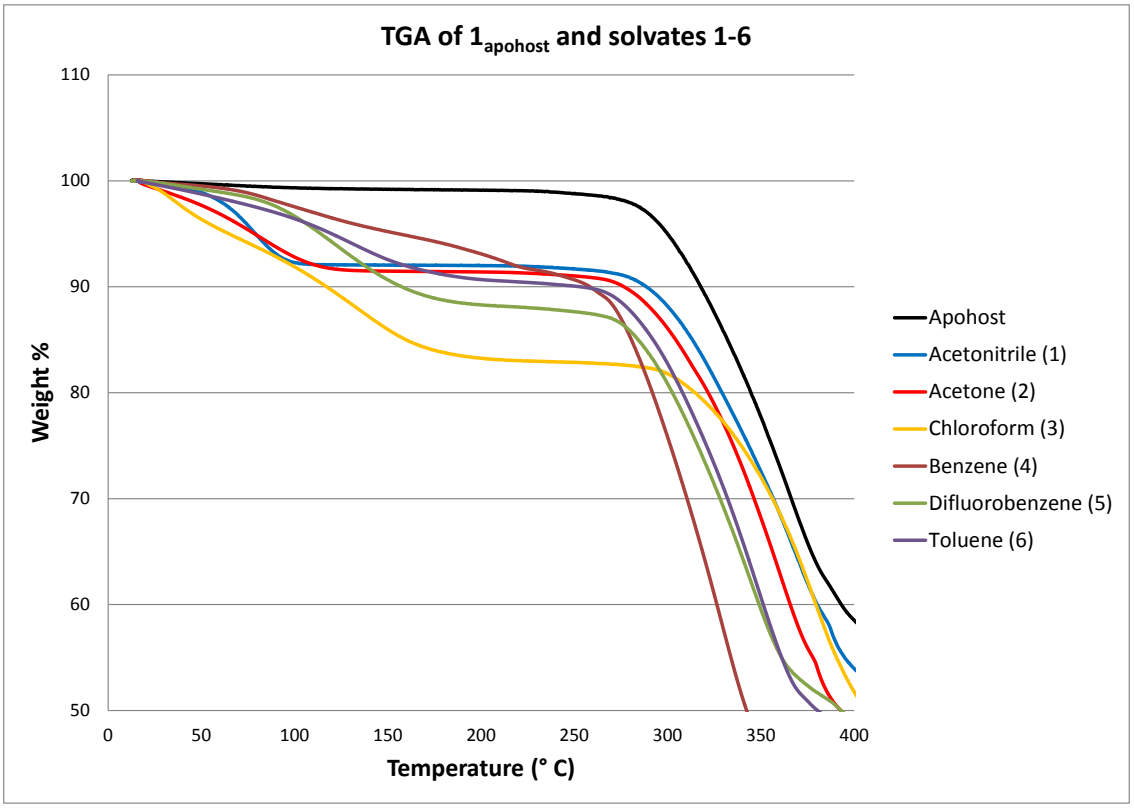

Figure 8. Combined TGA plots for $\mathbf{1}_{apohost}$ and solvates **1**-**6**.

Table 1. Summary of observed and predicted TGA results. The host:guest ratio from TGA results support the ratio observed from the single-crystal X-ray diffraction (SCD) data.

Structure	Guest	% Mass loss (TGA observed)	% Mass loss (TGA predicted)	Host:Guest (TGA)	Host:Guest (SCD)
$\mathbf{1}_{apohost}$	-	0	0	-	-
1	Acetonitrile	7.9	8.9	1:2	1:2
2	Acetone	8.5	11.2	1:2	1:2
3	Chloroform	17.0	20.6	1:2	1:2
4	Benzene	8.1	7.8	1:1	1:1
5	Difluorobenzene	11.9	11.9	1:1	1:1
6	Toluene	9.4	9.1	1:1	1:1

Structure parameters

Table 2. Additional structure parameters for $\mathbf{1}_{apohost}$ and solvates **1**-**6** that was not included in the main text. [a]The angle formed by the N-Ag-N atoms of the host metallocycle. [b]The N-C-C angle that is formed by the corners of the metallocycle. [c]The distance between phenylene moieties of adjacent metallocycles in the crystal packing arrangement as shown in Figure 12 of the main text. [d]The distance between imidazolyl moieties of adjacent metallocycles in the crystal packing arrangement as shown in Figure 12 of the main text.

Structure	Guest	N-Ag-N[a]	N-C-C[b]	$Ar_{bz}\cdots Ar_{bz}$[c]	$Ar_{im}\cdots Ar_{im}$[d]
$\mathbf{1}_{apohost}$	-	175.51(8)	111.26(1)	3.749	3.608
1	Acetonitrile	178.59(8)	110.43(1)	3.666	3.688
2	Acetone	176.93(8)	110.1(2)/111.5(2)	3.634(4)	3.770(4)/3.681(3)
3	Chloroform	177.35(2)	111.5(4)	3.704(8)	3.590(8)
4	Benzene	179.03(9)	110.2(2)/110.7(2)	3.667(4)	3.608(3)/3.781(3)
5	Difluorobenzene	176.66(1)	109.9(3)/111.6(2)	3.689(4)	3.793(4)/3.656(4)
6	Toluene	175.94(11)	109.9(3)/111.7(3)	3.781(5)	3.626(5)/3.544(5)

Crystal data tables

Table 3. Crystal data and structure refinement for **2**.

Empirical formula	$C_{38}H_{48}Ag_2B_2F_8N_8O_2$	
Formula weight	1038.20	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions (Å, °)	a = 7.1272(12)	α = 71.973(2)
	b = 12.249(2)	β = 89.308(2)
	c = 12.943(2)	γ = 89.483(2)
Volume (Å^3)	1074.4(3)	
Z	1	
Calculated density (g cm^{-3})	1.605	
Absorption coefficient (mm^{-1})	0.990	
F_{000}	524	
Crystal size (mm^3)	0.17 × 0.11 × 0.10	
θ range for data collection (°)	1.65 to 27.53	
Miller index ranges	$-9 \le h \le 9$, $-15 \le k \le 15$, $-16 \le l \le 16$	
Reflections collected	13534	
Independent reflections	4907 [R_{int} = 0.0276]	
Completeness to θ_{max} (%)	98.9	
Max. and min. transmission	0.9092 and 0.8521	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4907 / 0 / 275	
Goodness-of-fit on F^2	1.174	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0310, $wR2$ = 0.0753	
R indices (all data)	$R1$ = 0.0322, $wR2$ = 0.0759	
Largest diff. peak and hole (e Å^{-3})	1.490 and -0.856	

Table 4. Crystal data and structure refinement for **3**.

Empirical formula	$C_{34}H_{38}Ag_2B_2Cl_6F_8N_8$	
Formula weight	1160.78	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	a = 7.0910(19)	α = 90.00
	b = 20.479(6)	β = 91.038(4)
	c = 14.855(5)	γ = 90.00
Volume (Å^3)	2156.9(11)	
Z	2	
Calculated density (g cm^{-3})	1.787	
Absorption coefficient (mm^{-1})	1.352	
F_{000}	1152	
Crystal size (mm^3)	0.21 × 0.21 × 0.19	
θ range for data collection (°)	1.69 to 28.33	
Miller index ranges	$-9 \le h \le 9$, $-26 \le k \le 27$, $-8 \le l \le 19$	
Reflections collected	13383	
Independent reflections	5366 [R_{int} = 0.0483]	
Completeness to θ_{max} (%)	99.7	
Max. and min. transmission	0.7841 and 0.7634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5366 / 0 / 273	
Goodness-of-fit on F^2	1.061	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0573, $wR2$ = 0.1403	
R indices (all data)	$R1$ = 0.0807, $wR2$ = 0.1515	
Largest diff. peak and hole (e Å^{-3})	0.902 and -1.778	

Table 5. Crystal data and structure refinement for **4**.

Empirical formula	$C_{38}H_{42}Ag_2B_2F_8N_8$	
Formula weight	1000.16	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	*P*□	
Unit cell dimensions (Å, °)	*a* = 7.1020(18)	α = 72.237(4)
	b = 12.388(3)	β = 89.284(4)
	c = 12.794(3)	γ = 89.239(4)
Volume (Å^3)	1071.8(5)	
Z	1	
Calculated density (g cm^{-3})	1.550	
Absorption coefficient (mm^{-1})	0.986	
F_{000}	502	
Crystal size (mm^3)	0.20 × 0.19 × 0.18	
θ range for data collection (°)	1.73 to 30.86	
Miller index ranges	$-9 \le h \le 10$, $-17 \le k \le 17$, $-18 \le l \le 18$	
Reflections collected	15794	
Independent reflections	6181 [R_{int} = 0.0438]	
Completeness to θ_{max} (%)	91.4	
Max. and min. transmission	0.8449 and 0.8257	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6181 / 249 / 288	
Goodness-of-fit on F^2	1.005	
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0372, $wR2$ = 0.0868	
R indices (all data)	$R1$ = 0.0510, $wR2$ = 0.0937	
Largest diff. peak and hole (e Å^{-3})	0.887 and -0.545	

Table 6. Crystal data and structure refinement for **5**.

Empirical formula	$C_{38}H_{40}Ag_2B_2F_{10}N_8$	
Formula weight	1036.14	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	*P*□	
Unit cell dimensions (Å, °)	*a* = 7.0814(11)	α = 71.505(2)
	b = 12.445(2)	β = 89.185(2)
	c = 12.837(2)	γ = 89.430(2)
Volume (Å^3)	1072.7(3)	
Z	1	
Calculated density (g cm^{-3})	1.604	
Absorption coefficient (mm^{-1})	0.994	
F_{000}	518	
Crystal size (mm^3)	0.13 × 0.13 × 0.10	
θ range for data collection (°)	1.67 to 30.74	
Miller index ranges	$-10 \le h \le 9$, $-17 \le k \le 17$, $-18 \le l \le 18$	
Reflections collected	15820	
Independent reflections	6139 [R_{int} = 0.0331]	
Completeness to θ_{max} (%)	91.7	
Max. and min. transmission	0.9080 and 0.8799	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6139 / 14 / 310	
Goodness-of-fit on F^2	1.146	
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0463, $wR2$ = 0.1134	
R indices (all data)	$R1$ = 0.0514, $wR2$ = 0.1159	
Largest diff. peak and hole (e Å^{-3})	1.753 and -0.969	

Table 7. Crystal data and structure refinement for **6**.

Empirical formula	$C_{39}H_{43}Ag_2B_2F_8N_8$	
Formula weight	1013.17	
Temperature (K)	100(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	*P*□	
Unit cell dimensions (Å, °)	*a* = 6.9746(10)	α = 72.422(2)
	b = 12.0647(17)	β = 87.762(2)
	c = 13.1454(18)	γ = 86.363(2)
Volume (Å^3)	1052.1(3)	
Z	1	
Calculated density (g cm^{-3})	1.599	
Absorption coefficient (mm^{-1})	1.005	
F_{000}	509	
Crystal size (mm^3)	0.17 × 0.13 × 0.11	
θ range for data collection (°)	1.63 to 28.15	
Miller index ranges	$-9 \le h \le 9$, $-14 \le k \le 16$, $0 \le l \le 17$	
Reflections collected	4849	
Independent reflections	4849 [R_{int} = 0.0354]	
Completeness to θ_{max} (%)	94.2	
Max. and min. transmission	0.8975 and 0.8493	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4849 / 0 / 274	
Goodness-of-fit on F^2	1.026	
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0412, $wR2$ = 0.0911	
R indices (all data)	$R1$ = 0.0552, $wR2$ = 0.0962	
Largest diff. peak and hole (e Å^{-3})	0.803 and -0.913	