Supplementary Information

Enhancing strategies for the assembly of metal-organic systems with inherent cavity-containing calix[4]arenes

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Content

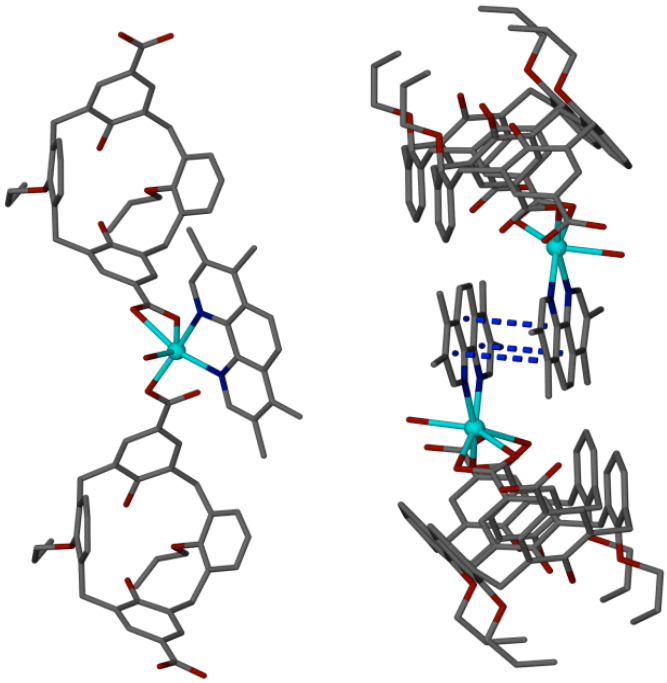

Figure S1. Coordination sphere of **5** and π-stacking interaction between symmetry equivalent TMePhens.

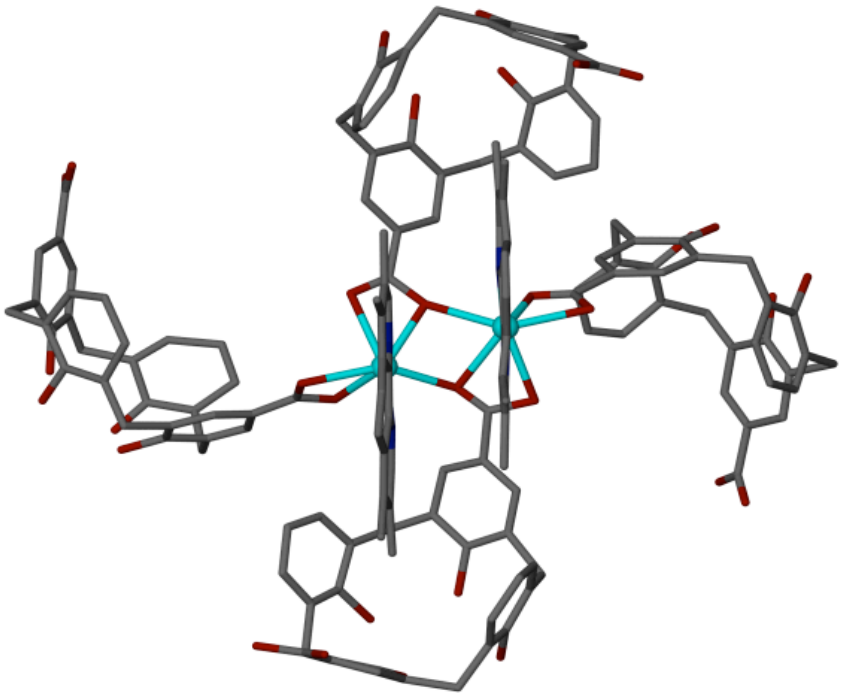

Figure S2. Cd(II) binuclear panel comprising four *p*CO_2[4]s and two TMePhens (**6**)

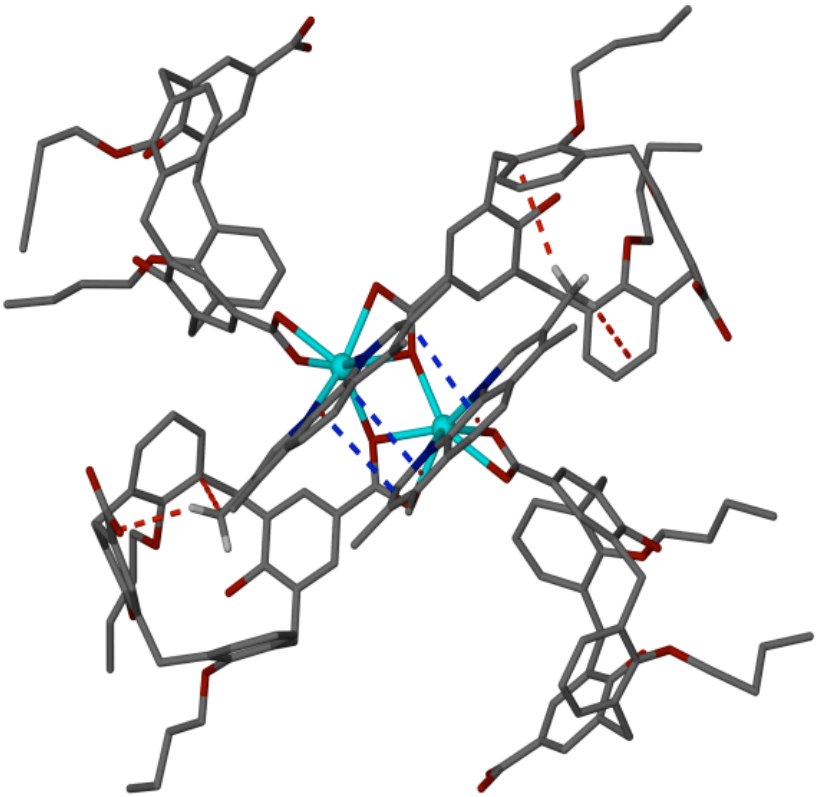

Figure S3. π-stacking interactions (blue lines) and CH···π interactions (red lines) in **6**.

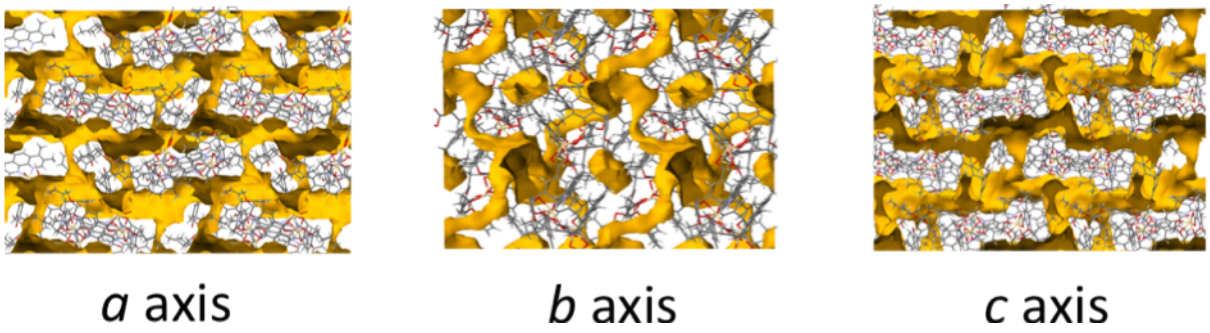

Figure S4. Solvent channels along all axes running the crystal of **6**.

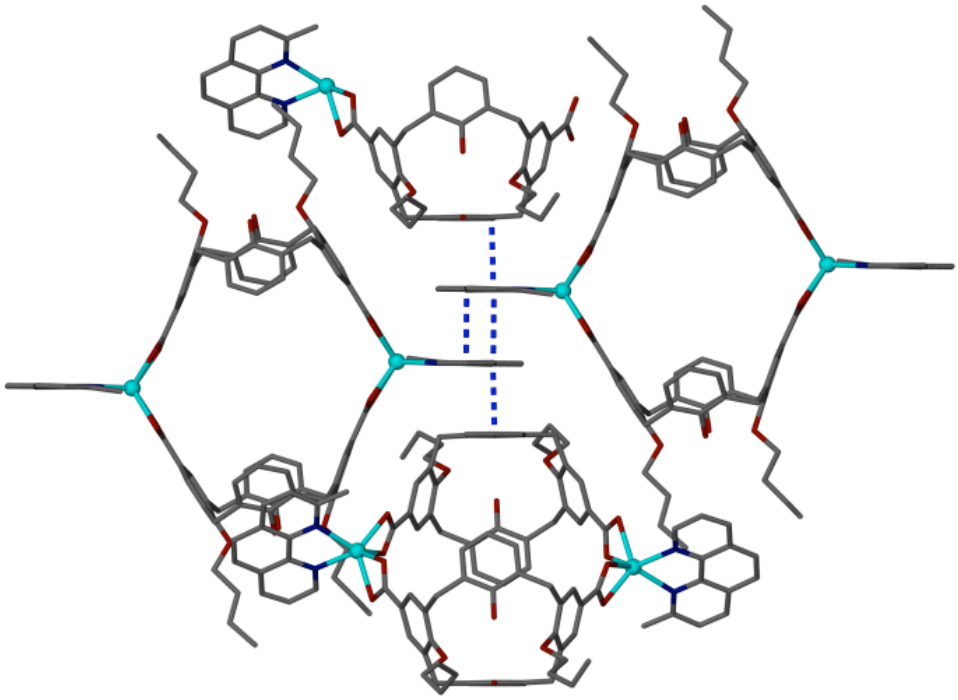

Figure S5. π-stacking interactions (blue lines) between 2-Me-Phen and arenes of the *p*CO_2[4]s observed in **7**.

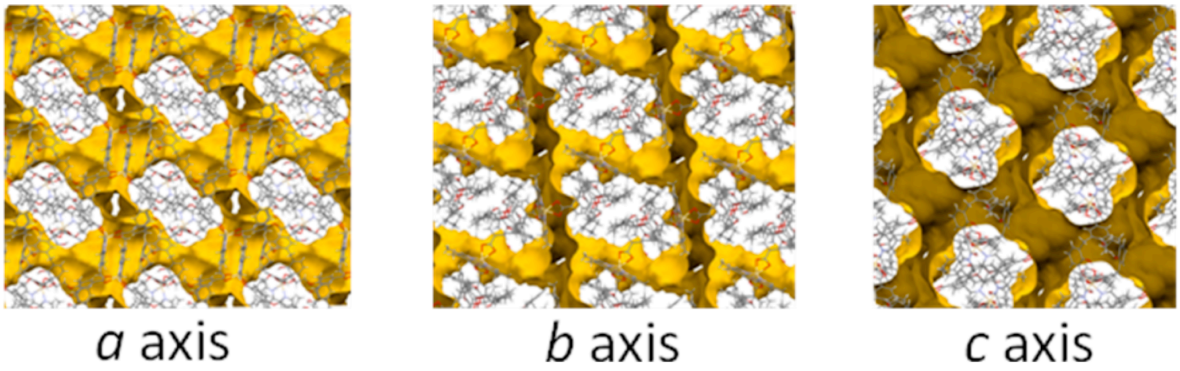

Figure S6. Solvent channels along all axes running the crystal of **7**.

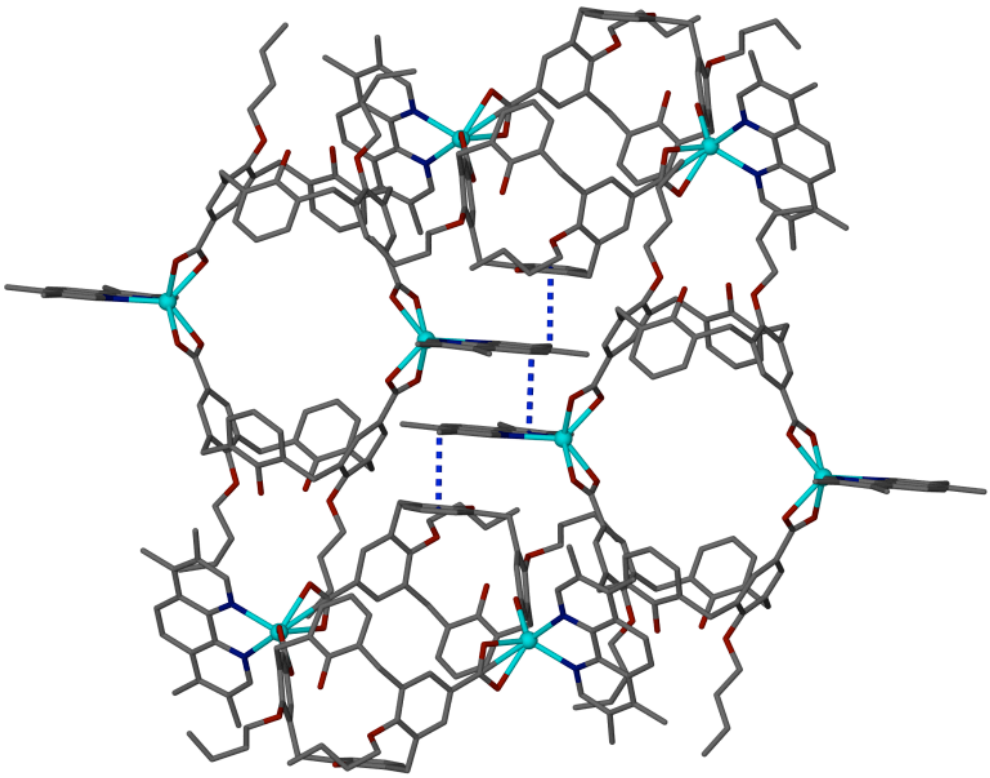

Figure S7. π-stacking interactions (blue lines) between TMePhens and arenes of the *p*CO_2[4]s observed in **8**.

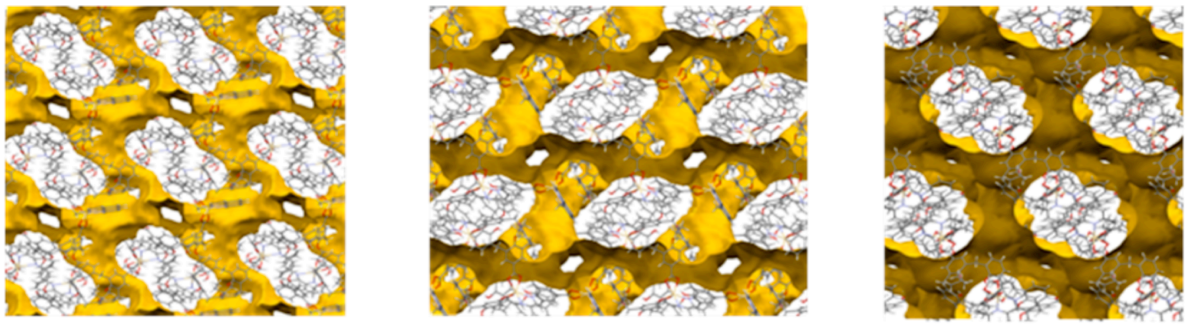

Figure S8. Solvent channels along all axes running the crystal of **8**.

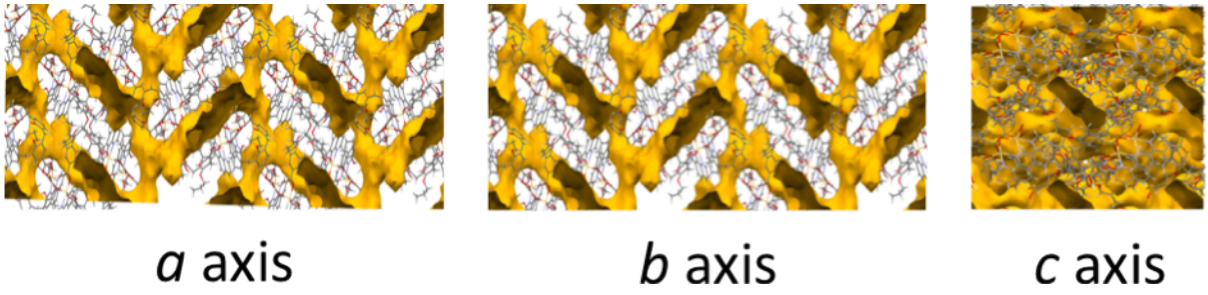

Figure S9. Solvent channels along all axes running through the crystal of **9**.

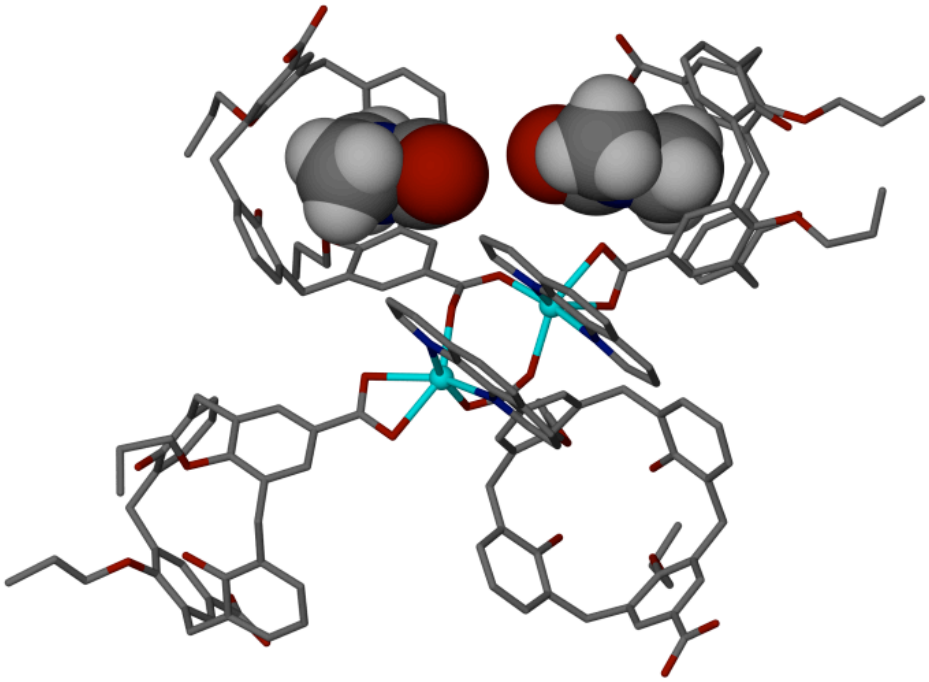

Figure S10. Unbound dmf of crystallization occupying Type II cavities in **9**.

Experimental Details

All starting materials were purchased from Aldrich and used as supplied. Calixarenes **1** and **2**,[S1] **3** and **4**,[S2] and both 2- and 3-methyl-1,10-phenanthrolines were synthesised according to literature procedures.[S3]

Synthesis of 5: A mixture of **1** (50.0 mg, 0.084 mmol) and $Cd(NO_3)_2.4H_2O$ (64.6 mg, 0.209 mmol) was dissolved in 3 mL of DMF, followed by layering of 1 ml of a MeOH solution of TMePhen (19.8 mg, 0.084 mmol). Slow evaporation over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies. The precipitate was filtered and washed with DMF to afford 34 mg (33 %) of **5**. Elemental analysis for $[Cd(\mathbf{1}\text{-}2H)(TMePhen)(H_2O)\subset(dmf)]\cdot(dmf)(H_2O)_2$, $Cd_1C_{58}H_{70}N_4O_{13}$, calc. C 60.92; H 6.17; N 4.90%, found C 61.43; H 6.45, N 4.61%.

Synthesis of 6: An analogous procedure to **5** was carried out but using **2** (54.0 mg, 0.084 mmol) instead of **1**. Slow evaporation over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies. The precipitate was filtered and washed with DMF to afford 45 mg (51 %) of **6**. Elemental analysis for $[Cd_4(\mathbf{2}\text{-}2H)_4(TMePhen)_4]\cdot(dmf)_5$, $Cd_4C_{231}H_{251}N_{13}O_{37}$, calc. C 65.27; H 5.95; N 4.28%, found C 65.69; H 6.32, N 4.37%.

Synthesis of 7: An analogous procedure to **5** was carried out but using **4** (54.0 mg, 0.084 mmol) instead of **1** and 2-MePhen (16.3 mg, 0.084 mmol) instead of TMePhen. Slow evaporation over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies. The precipitate was filtered and washed with DMF to afford 38 mg (39.8%) of **7**. Elemental analysis for $[Cd_2(\mathbf{4}\text{-}2H)_2(2\text{-}MePhen)_2\subset(dmf)_2]\cdot(dmf)_2(H_2O)_6$, $Cd_4C_{114}H_{136}N_8O_{26}$, calc. C 60.61; H 6.07; N 4.96%, found C 60.92; H 6.38, N 5.21%.

Synthesis of 8: An analogous procedure to **5** was carried out but using **4** (54.0 mg, 0.084 mmol) instead of **1**. Slow evaporation over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies. The precipitate was filtered and washed with DMF to afford 58 mg (52 %) of **8**. Elemental analysis for $[Cd_2(\mathbf{4}\text{-}2H)_2(TMePhen)_2\subset(dmf)_2]\cdot(dmf)_5(H_2O)_9$, $Cd_2C_{129}H_{175}N_{11}O_{32}$, calc. C 59.21; H 6.74; N 5.89%, found C 59.68; H 7.09, N 6.36%.

Synthesis of 9: An analogous procedure to **5** was carried out but using **3** (50.0 mg, 0.084 mmol) instead of **1** and 1,10-Phen (15.3 mg, 0.084 mmol). Slow evaporation over several weeks resulted in the formation of colourless blocks suitable for X-ray diffraction studies. The precipitate was filtered and washed with DMF to afford 46 mg (49 %) of **9**. Elemental analysis for $[Cd(\mathbf{3}\text{-}2H)(Phen)\subset(dmf)]\cdot(dmf)_2(H_2O)$, $Cd_1C_{57}H_{65}N_5O_{11}$, calc. C 60.88; H 5.83; N 6.23%, found C 61.11; H 6.09.29, N 6.50%.

General Crystallographic Details: Data for **5**, **6** and **8** were collected on a Bruker X8 ApexII diffractometer operating with Mo-Kα radiation (0.71073 Å) at 100(2)K. Data for **7** and **9** were collected on a Bruker ApexII diffractometer operating with synchrotron radiation (0.77490 Å) at 100(2)K.

Crystal data for 5 (CCDC 959943): $C_{58}H_{70}CdN_4O_{13}$, M = 1143.58, Colourless Block, 0.45 · 0.40 · 0.30 mm^3, triclinic, space group P-1 (No. 2), a = 11.3697(6), b = 15.0647(7), c = 17.6480(9) Å, α = 103.253(2), β = 101.955(2), γ = 105.345(2)°, V = 2719.4(2) $Å^3$, Z = 2,

$2\theta_{max}$ = 52.7º, 40944 reflections collected, 11071 unique (R_{int} = 0.0348). Final *GooF* = 1.057, *R1* = 0.0439, *wR2* = 0.1027, *R* indices based on 9347 reflections with I >2sigma(I) (refinement on F^2).

Crystal data for 6 (CCDC 959944): $C_{231}H_{251}Cd_4N_{13}O_{37}$, *M* = 4251.05, Colourless Block, 0.30 · 0.30 · 0.25 mm^3, monoclinic, space group $P2_1$ (No. 4), *a* = 19.5995(9), *b* = 28.7424(12), *c* = 20.4414(9) Å, β = 91.627(3)°, *V* = 11510.7(9) $Å^3$, *Z* = 2, $2\theta_{max}$ = 42.0º, 100144 reflections collected, 24417 unique (R_{int} = 0.0833). Final *GooF* = 1.820, *R1* = 0.1130, *wR2* = 0.2668, *R* indices based on 19001 reflections with I >2sigma(I) (refinement on F^2).

Crystal data for 7 (CCDC 959945): $C_{234}H_{286}Cd_4N_{16}O_{54}$, *M* = 4636.39, Colourless Block, 0.05 · 0.03 · 0.02 mm^3, triclinic, space group *P*-1 (No. 2), *a* = 17.4037(6), *b* = 18.8062(7), *c* = 21.2318(7) Å, α = 89.389(2), β = 73.509(2), γ = 65.333(2)°, *V* = 6008.7(4) $Å^3$, *Z* = 1, $2\theta_{max}$ = 67.4º, 93166 reflections collected, 36511 unique (R_{int} = 0.0438). Final *GooF* = 1.013, *R1* = 0.0629, *wR2* = 0.1913, *R* indices based on 25589 reflections with I >2sigma(I) (refinement on F^2).

Crystal data for 8 (CCDC 959946): $C_{258}H_{350}Cd_4N_{22}O_{64}$, *M* = 5233.20, Colourless Block, 0.30 · 0.25 · 0.25 mm^3, triclinic, space group *P*-1 (No. 2), *a* = 17.7359(10), *b* = 19.8660(15), *c* = 21.1162(12) Å, α = 79.620(5), β = 74.012(3), γ = 63.599(3)°, *V* = 6392.0(7) $Å^3$, *Z* = 1, $2\theta_{max}$ = 56.6º, 96526 reflections collected, 31621 unique (R_{int} = 0.0551). Final *GooF* = 1.068, *R1* = 0.0873, *wR2* = 0.2529, *R* indices based on 22901 reflections with I >2sigma(I) (refinement on F^2).

Crystal data for 9 (CCDC 959947): $C_{57}H_{65}CdN_5O_{12}$, *M* = 1124.54, Colourless Square base pyramid, 0.10 · 0.10 · 0.10 mm^3, tetragonal, space group $P4_32_12$ (No. 96), *a* = *b* = 15.8642(4), *c* = 42.9758(15) Å, *V* = 10815.8(5) $Å^3$, *Z* = 8, $2\theta_{max}$ = 56.6º, 76809 reflections collected, 10325 unique (R_{int} = 0.0965). Final *GooF* = 1.048, *R1* = 0.0643, *wR2* = 0.1764, *R* indices based on 9279 reflections with I >2sigma(I) (refinement on F^2).

References

S1. Arduini, A.; Fabbi, M.; Mantovani, M.; Mirone, L.; Pochini, A.; Secchi A.; Ungaro, R.; *J. Org. Chem.*, 1995, **60**, 1454-1457.

S2. Kennedy S.; Cholewa P. P.; McIntosh R. D.; Dalgarno S. J.; *CrystEngComm,* **2013**, *15*, 1520.

S3. Belser, P.; Bernhard, S.; Guerig, U.; *Tetrahedron*, **1996**, *52*, 2937.