Electronic Supplementary Information for:

Novel syntheses of carbazole-3,6-dicarboxylate ligands and their utilization for porous coordination cages

Casey A. Rowland,[a] P. A. Yap[a] and Eric D. Bloch*[,a]

[a]Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States

Dalton Trans.

List of Contents

General Considerations: Benzyl bromide and 9-H carbazole were purchased from Combi-Blocks. Aluminum chloride, bromine, NaOH, KOH, and all solvents were purchased from Sigma-Aldrich at purity of 98% or higher.

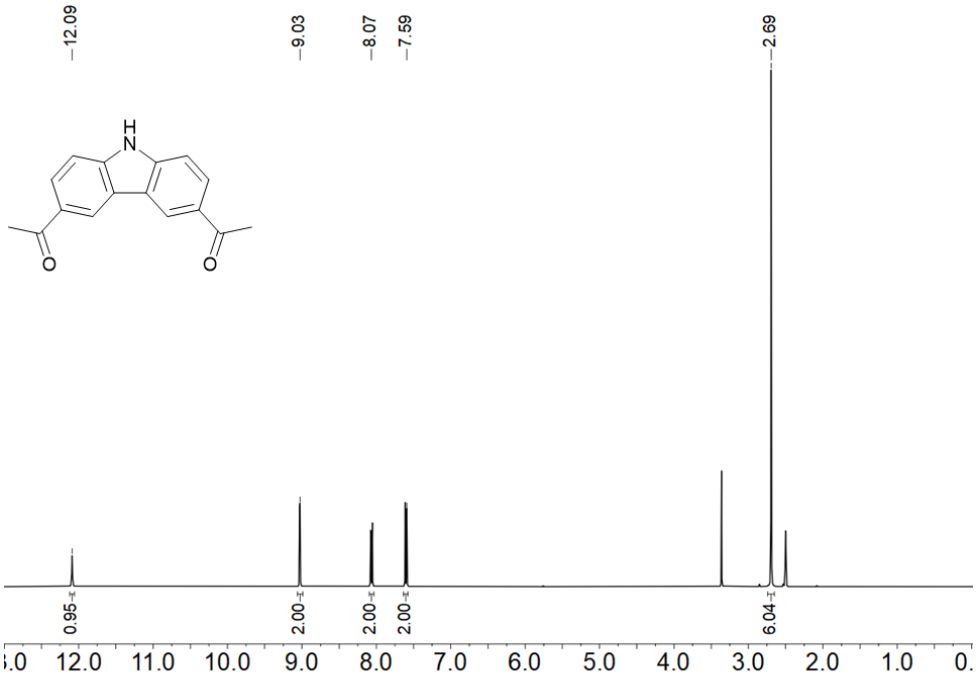

Figure S1. NMR spectra of 3,6-diacetyl-9H-carbazole.

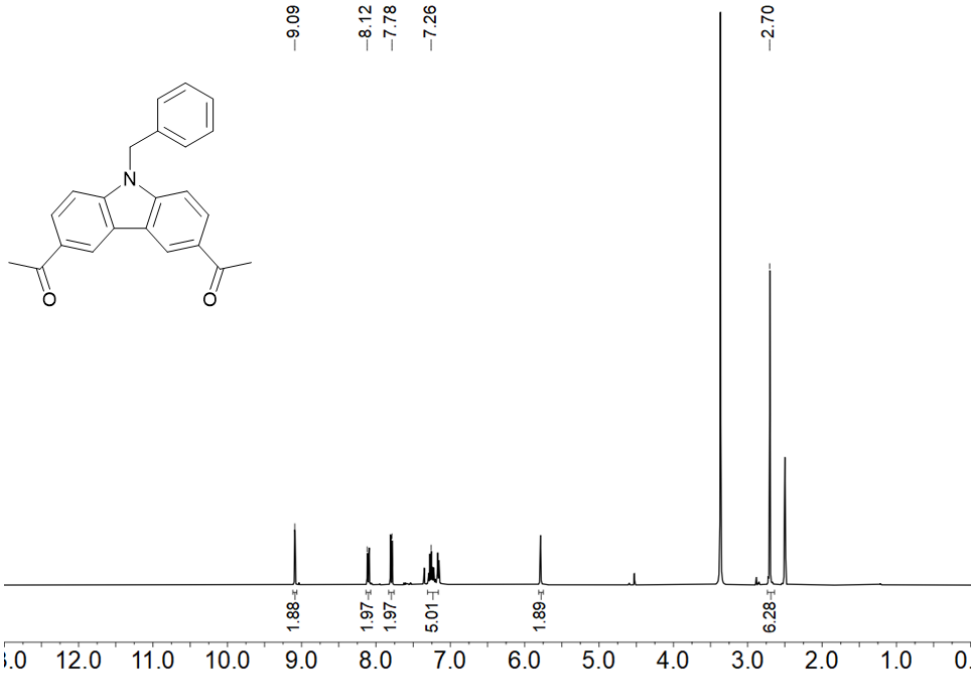

Figure S2. NMR spectra of 3,6-dicetyl-9-benzyl-carbazole.

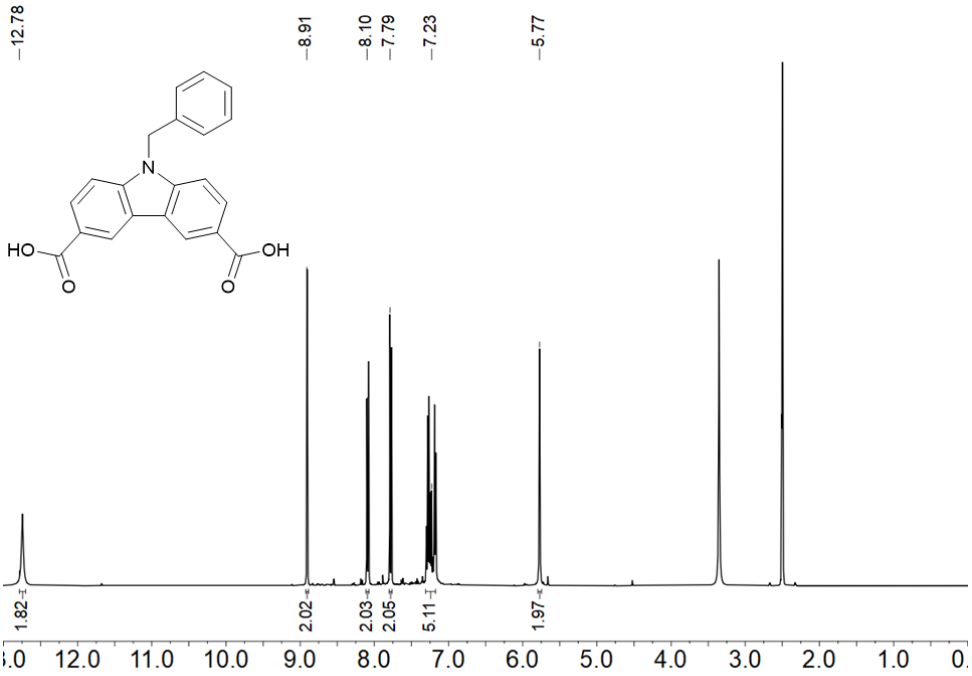

Figure S3. NMR spectra of 9-benzyl-carbazole-3,6-dicarboxylic acid.

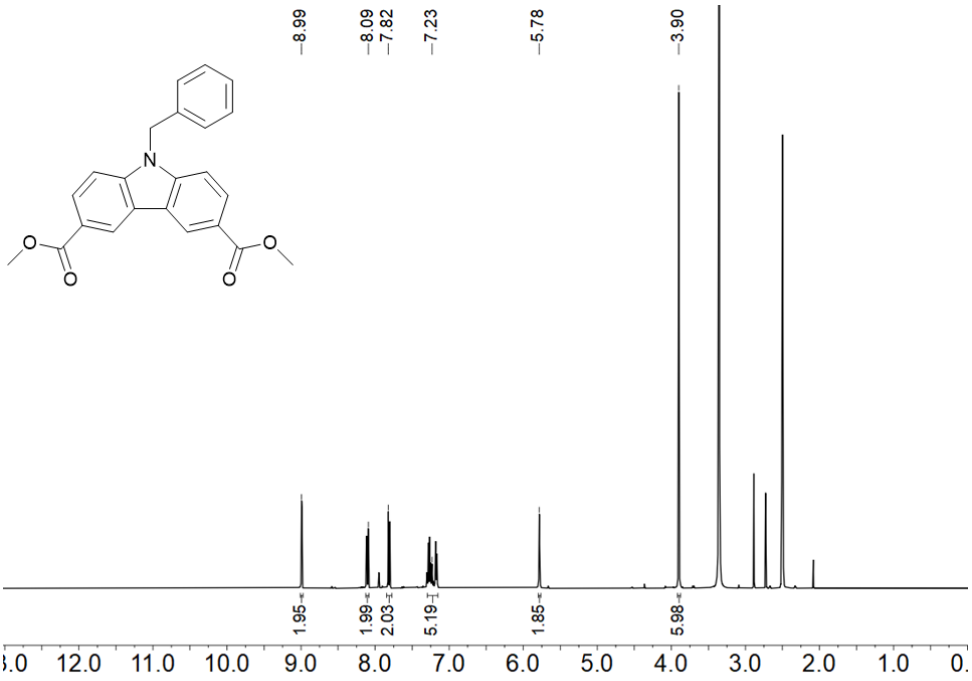

Figure S4. NMR spectra of Dimethyl 9-benzyl-carbazole-3,6-dicarboxylate.

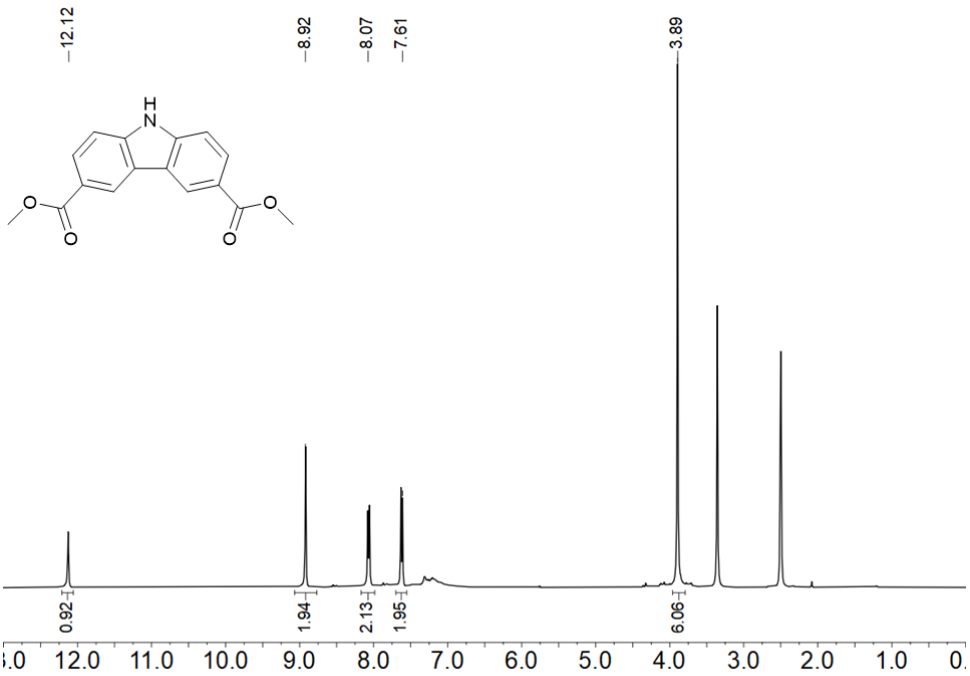

Figure S5. NMR spectra of Dimethyl 9H-carbazole-3,6-dicarboxylate.

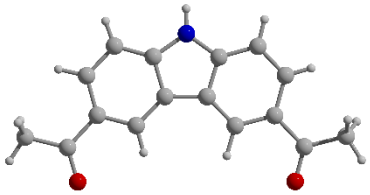

Figure S6. Crystal structure of 3,6-diacetyl-9H-carbazole.

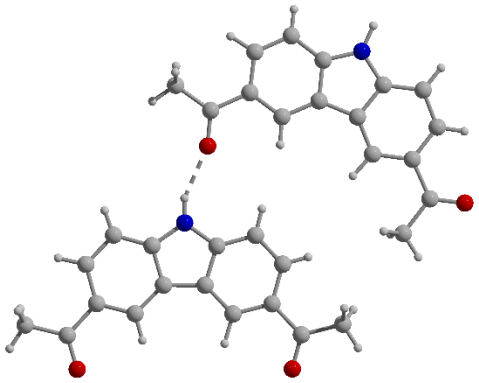

Figure S7. Packing diagram of 3,6-diacetyl-9H-carbazole displaying the H-bonding interaction between molecules.

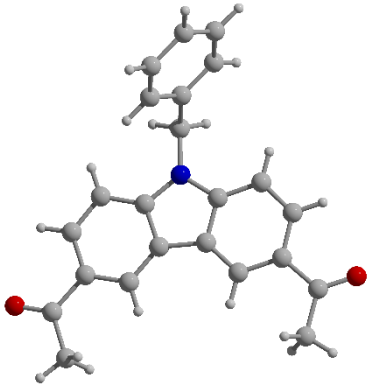

Figure S8. Crystal structure of 3,6-diacetyl-9-benzyl-carbazole.

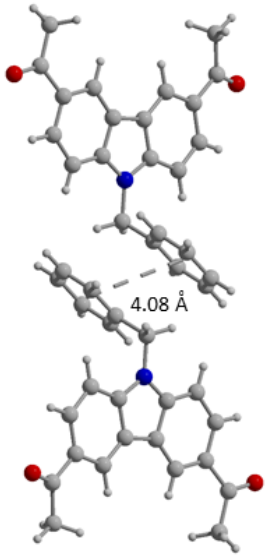

Figure S9. Packing diagram of 3,6-diacetyl-9H-carbazole displaying the benzyl-to-benzyl π- π interactions between molecules.

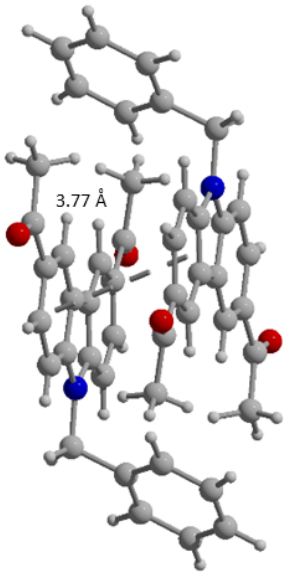

Figure S10. Packing diagram of 3,6-diacetyl-9H-carbazole displaying the carbazole-to-carbazole π- π interactions between molecules.

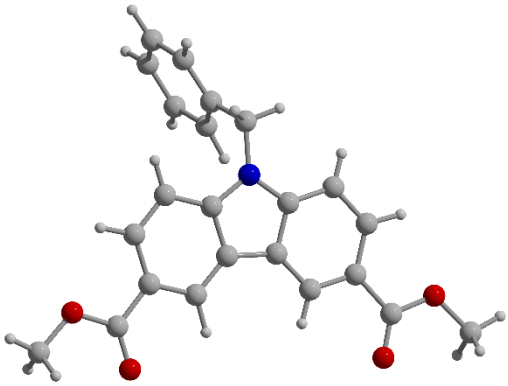

Figure S11. Crystal structure of Dimethyl 9-benzyl-carbazole-3,6-dicarboxylate.

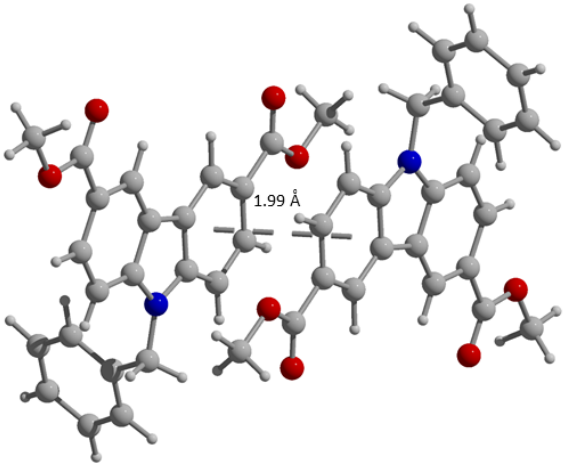

Figure S12. Packing diagram of Dimethyl 9-benzyl-carbazole-3,6-dicarboxylate displaying the π- π interactions between molecules.

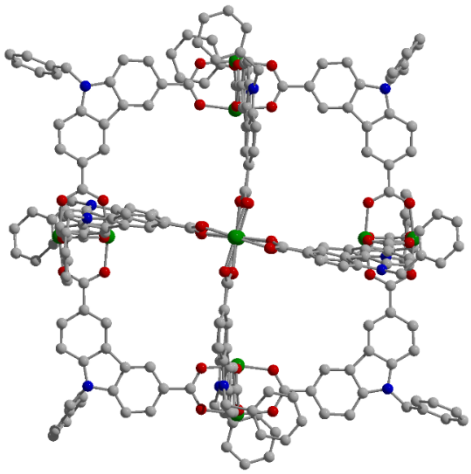

Figure S13. Crystal structure of Cu_{12}(9-benzyl-cdc)$_{12}$ displaying the pinwheel-like orientation of the ligands. H-atoms have been omitted for clarity.

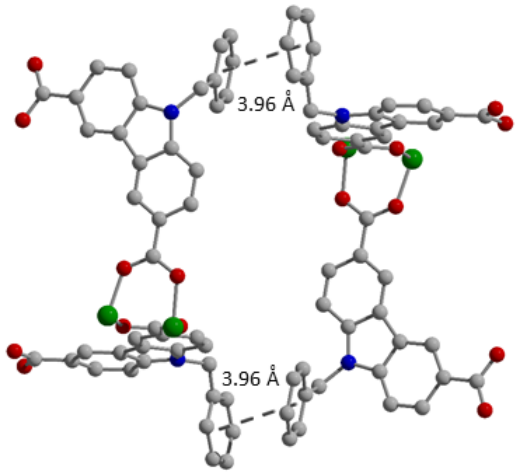

Figure S14. Packing diagram of Cu_{12}(9-benzyl-cdc)$_{12}$ displaying the benzyl-to-benzyl π- π interaction between cages. H-atoms have been omitted for clarity.

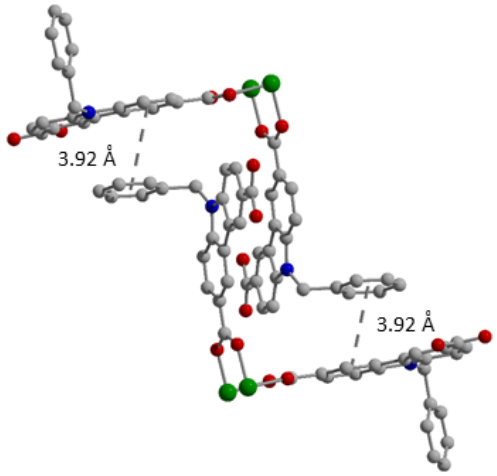

Figure S15. Packing diagram of Cu_{12}(9-benzyl-cdc)$_{12}$ displaying the benzyl-to-carbazole π- π interactions between cages. H-atoms have been omitted for clarity.

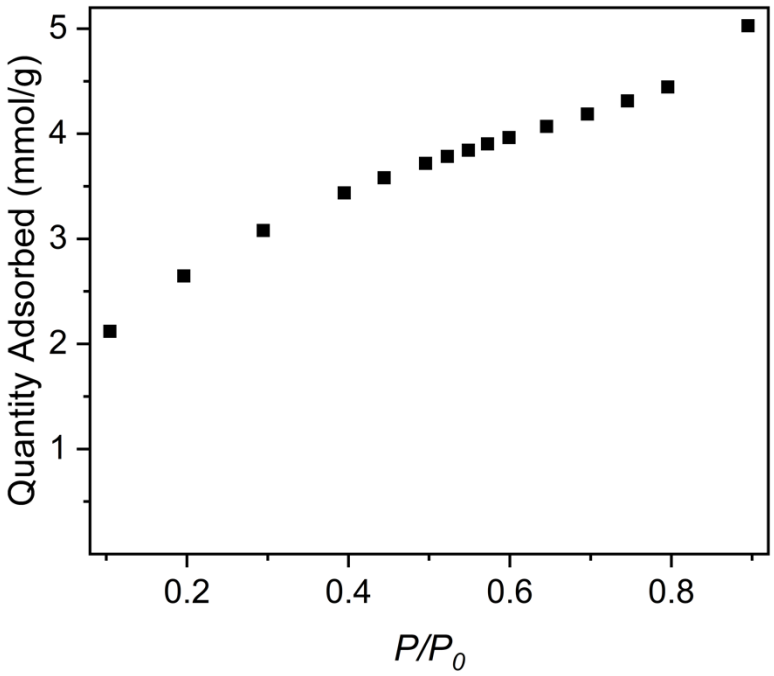

Figure S16. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 25 °C under flowing N_2.

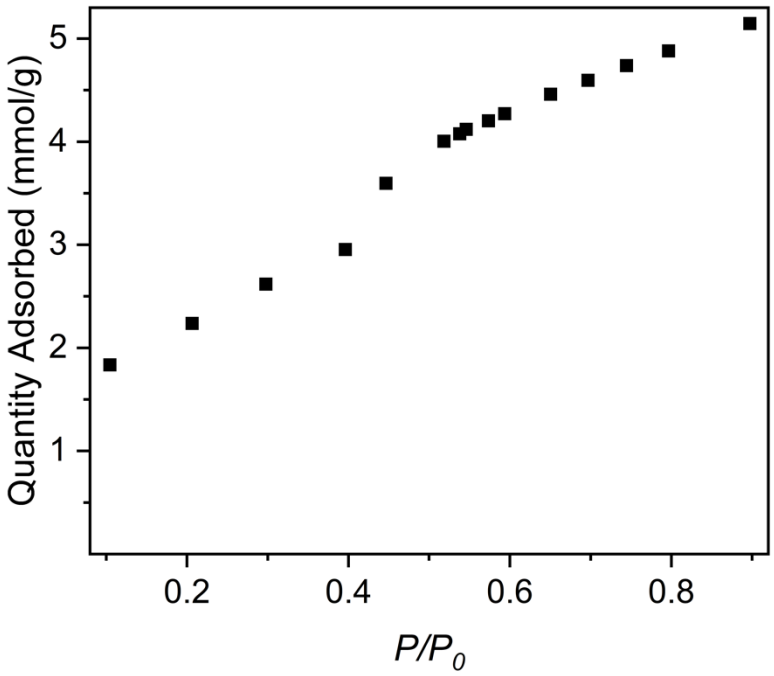

Figure S17. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 50 °C under flowing N_2.

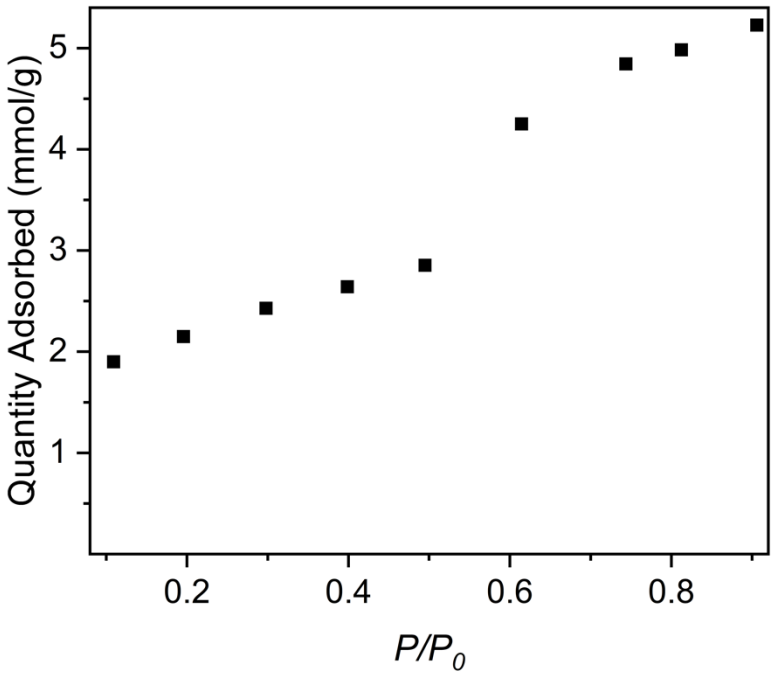

Figure S18. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 75 °C under flowing N_2.

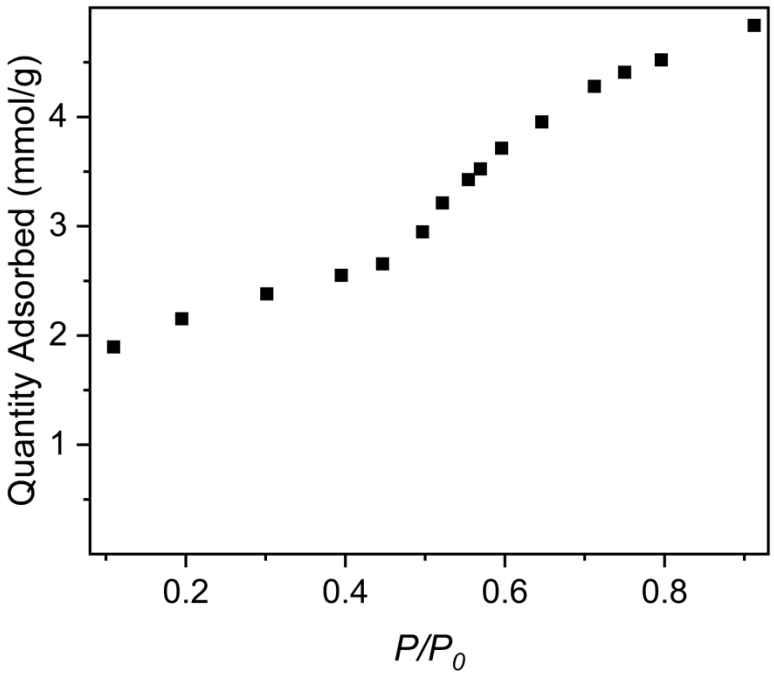

Figure S19. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 100 °C under flowing N_2.

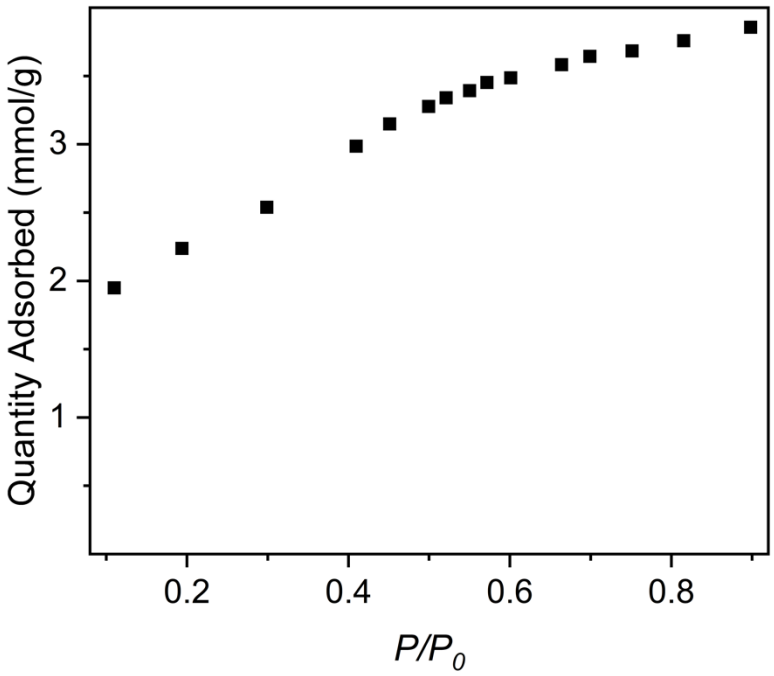

Figure S20. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 125 °C under flowing N_2.

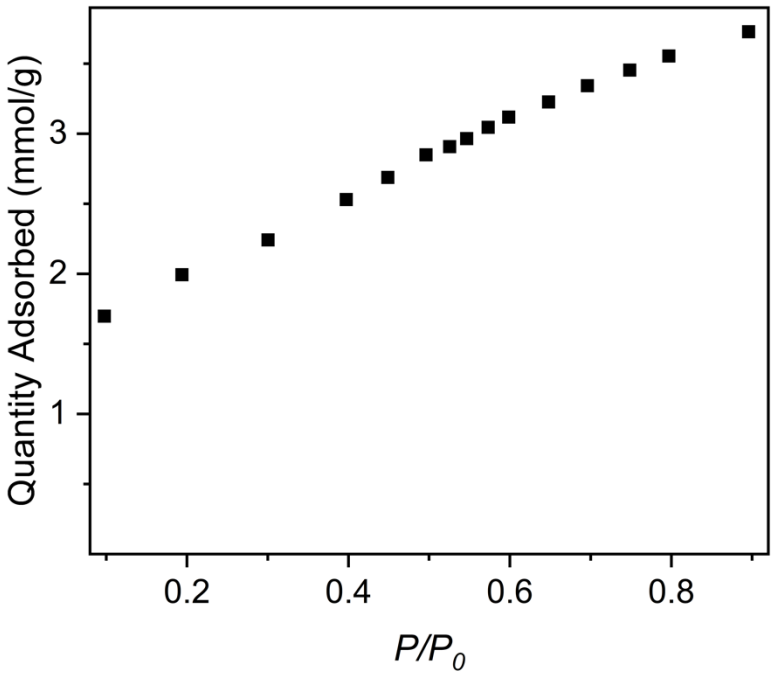

Figure S21. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 150 °C under flowing N_2.

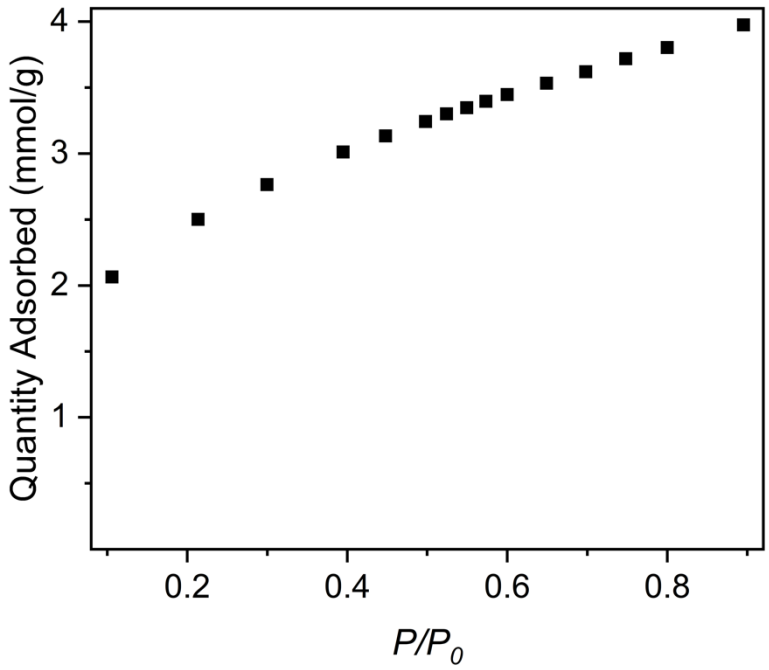

Figure S22. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 175 °C under flowing N_2.

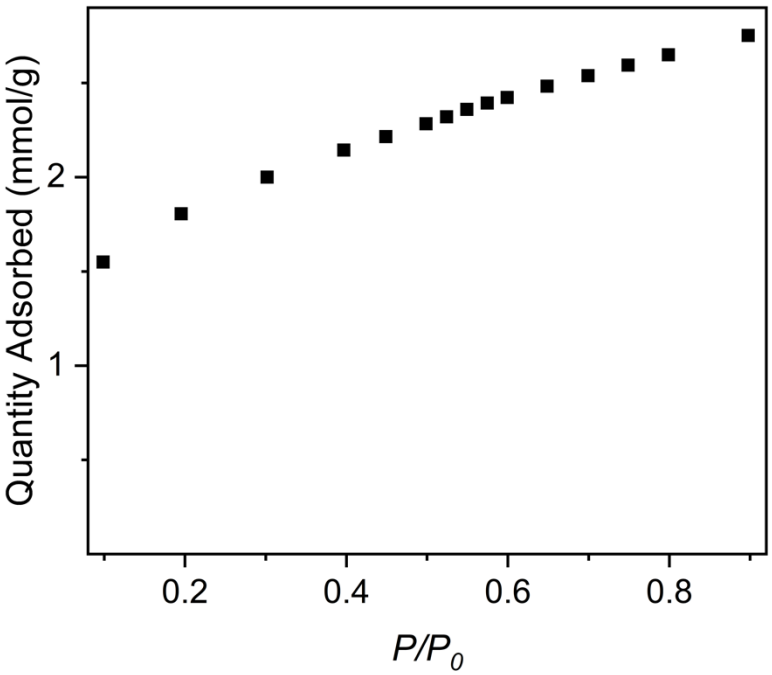

Figure S23. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 200 °C under flowing N_2.

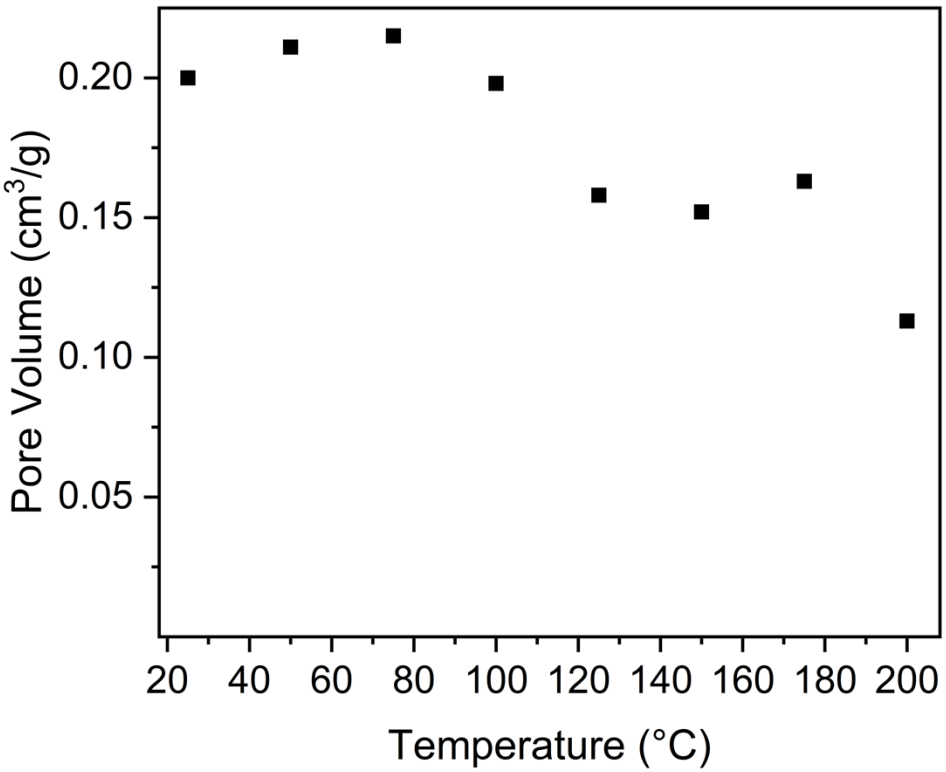

Figure S24. Pore volume as a function of activation temperature as determined from CO_2 uptake at P/P_o of 0.90 at 195 K.

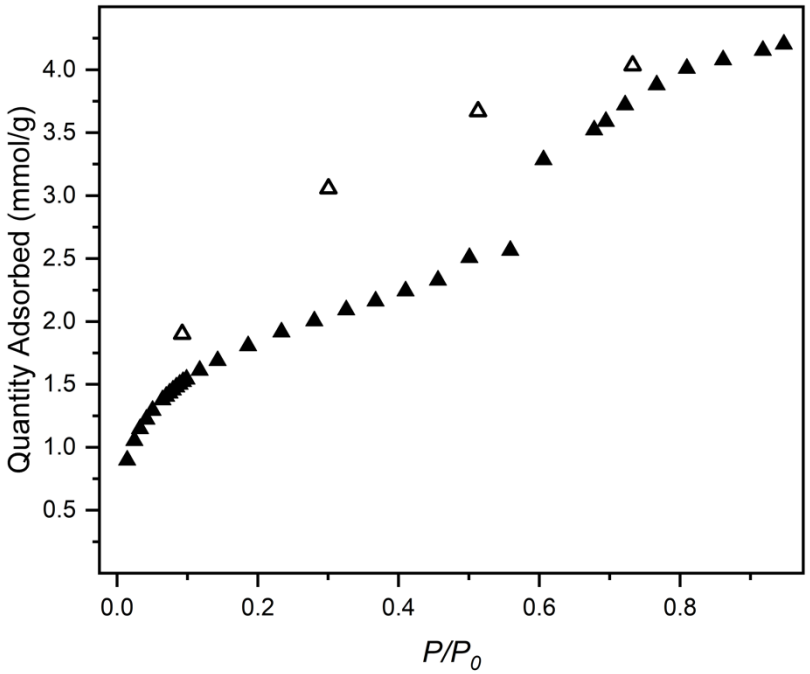

Figure S25. CO_2 adsorption in Cu_{12}(9-benzyl-cdc)$_{12}$ at 195 K. The sample was degassed at 75 °C under flowing N_2. Filled and open symbols represent adsorption and desorption, respectively.

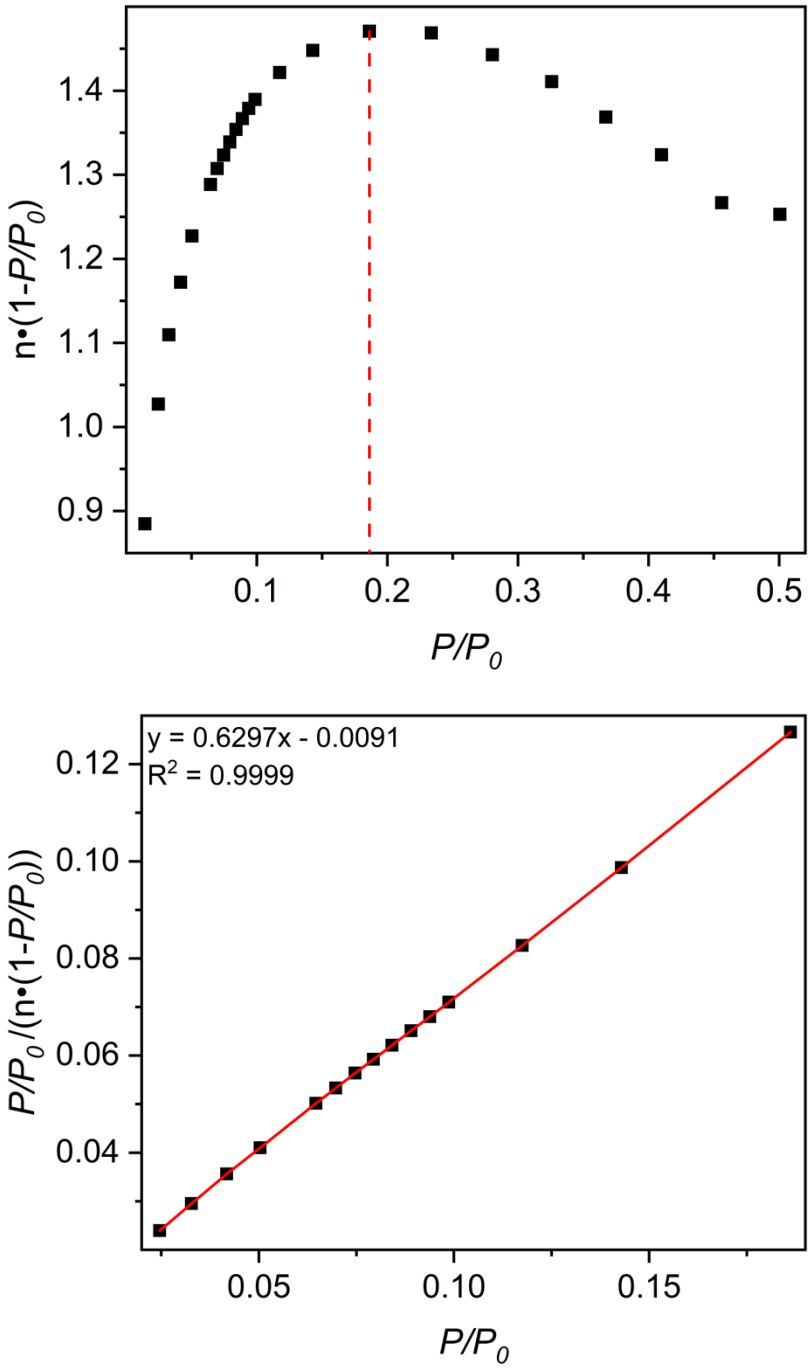

Figure S26. BET consistency criteria plots.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) eric410

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 9-benzyl-3,6-diacetyl carbazole

```
Bond precision:  C-C = 0.0021 A          Wavelength=1.54178

Cell:          a=11.9548(5)      b=11.9760(5)     c=14.6392(7)
               alpha=85.735(2)   beta=70.006(2)   gamma=60.546(1)
Temperature:   100 K
```

	Calculated	Reported
Volume	1703.72(13)	1703.72(13)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C23 H19 N O2	C23 H19 N O2
Sum formula	C23 H19 N O2	C23 H19 N O2
Mr	341.39	341.39
Dx,g cm-3	1.331	1.331
Z	4	4
Mu (mm-1)	0.672	0.672
F000	720.0	720.0
F000’	722.08	
h,k,lmax	14,14,17	14,14,17
Nref	5828	5641
Tmin,Tmax	0.761,0.842	0.625,0.753
Tmin’	0.661	

```
Correction method= # Reported T Limits: Tmin=0.625 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.968          Theta(max)= 65.186

R(reflections)= 0.0384( 5297)     wR2(reflections)= 0.1030( 5641)

S = 1.029                 Npar= 577
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Click on the hyperlinks for more details of the test.

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Structure factors have been supplied for datablock(s) eric406

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 9H-3,6-diacetyl carbazole

```
Bond precision:  C-C = 0.0037 A          Wavelength=1.54178

Cell:            a=8.0842(4)    b=11.3339(5)       c=26.9495(13)
                 alpha=90       beta=91.201(4)     gamma=90
Temperature:     110 K
```

	Calculated	Reported
Volume	2468.7(2)	2468.7(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H13 N O2	C16 H13 N O2
Sum formula	C16 H13 N O2	C16 H13 N O2
Mr	251.27	251.27
Dx,g cm-3	1.352	1.352
Z	8	8
Mu (mm-1)	0.722	0.722
F000	1056.0	1056.0
F000’	1059.19	
h,k,lmax	10,14,33	10,14,33
Nref	5059	5049
Tmin,Tmax	0.918,0.939	0.559,0.754
Tmin’	0.918	

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Correction method= # Reported T Limits: Tmin=0.559 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 74.684

R(reflections)= 0.0625( 3613)     wR2(reflections)= 0.1817( 5049)

S = 1.128                 Npar= 402
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Structure factors have been supplied for datablock(s) eric412

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: dimethyl-9-benzyl-3,6-dicarboxylate

```
Bond precision:  C-C = 0.0009 A          Wavelength=0.71073

Cell:            a=8.5221(7)    b=18.6073(14)      c=11.5804(8)
                 alpha=90       beta=90.784(2)     gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	1836.2(2)	1836.2(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C23 H19 N O4	C23 H19 N O4
Sum formula	C23 H19 N O4	C23 H19 N O4
Mr	373.39	373.39
Dx,g cm-3	1.351	1.351
Z	4	4
Mu (mm-1)	0.093	0.093
F000	784.0	784.0
F000’	784.39	
h,k,lmax	14,31,19	14,31,19
Nref	8985	8985
Tmin,Tmax	0.943,0.971	0.707,0.747
Tmin’	0.938	

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Correction method= # Reported T Limits: Tmin=0.707 Tmax=0.747
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 36.451

R(reflections)= 0.0490( 7542)     wR2(reflections)= 0.1479( 8960)

S = 1.035                 Npar= 307
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Structure factors have been supplied for datablock(s) eric399_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Cu12(benzyl-cdc)12

```
Bond precision:  C-C = 0.0168 A          Wavelength=1.54178

Cell:          a=20.3600(11)     b=21.1957(11)    c=23.9825(13)
               alpha=81.376(3)   beta=71.855(3)   gamma=68.009(3)
Temperature:   109 K
```

	Calculated	Reported
Volume	9112.8(9)	9112.7(9)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C287.74 H236.41 Cu12 N20.93 O60, 4(C4 H9 N O) [+ solvent]	?
Sum formula	C303.74 H272.41 Cu12 N24.93 O64 [+ solvent]	C303.74 H272.41 Cu12 N24.93 O64
Mr	6058.39	6058.24
Dx,g cm-3	1.104	1.104
Z	1	1
Mu (mm-1)	1.283	1.283
F000	3129.4	3129.0
F000’	3114.63	
h,k,lmax	18,19,21	18,19,21
Nref	14353	14136
Tmin,Tmax	0.843,0.939	0.615,0.749
Tmin’	0.781	

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Correction method= # Reported T Limits: Tmin=0.615 Tmax=0.749
AbsCorr = MULTI-SCAN

Data completeness= 0.985          Theta(max)= 44.516

R(reflections)= 0.0849( 9917)     wR2(reflections)= 0.2718( 14136)

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