Supporting Information

Multicomponent self-sorting of a Pd_7 molecular boat and its use in catalytic Knoevenagel condensation

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Experimental Section

General: All the chemicals were purchased from commercial sources and used without further purification. C*is*-(tmen)Pd(NO_3)$_2$ [tmen = N,N,N',N'-tetramethylethylenediamine][1], 1,3,5-Tris(1-imidazolyl)benzene (timb) and 1,2,4,5-tetrakis(1-imidazolyl)benzene (tim) were synthesized according to the literature procedures. ^{1}H NMR, ^{1}H DOSY and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in the ^{1}H NMR are reported in ppm referenced to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of solvent D_2O at 4.7 ppm, $CDCl_3$ at 7.26 ppm. IR spectra were recorded on Bruker ALPHA FT-IR spectrometer. Electronic absorption spectra were recorded on a Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) experiments were carried out in Bruker Daltonics (Esquire 300 Plus ESI model). HRMS were recorded on a Q-TOF electrospray instrument. Elemental analyses of C, H and N were performed using a Perkin-Elmer 240C elemental analyzer. The TGA analysis was performed using high resolution TGA 2950 instrument with heating rate of 10°C/min in an alumina crucible under N_2 at flow rate of 8 mL/min. Nitrogen

sorption isotherms were analysed at liq. N_2 temperature using micromeritics surface area analyzer model ASAP-2020.

Synthesis of Complex 1: A yellow aqueous solution (2 mL) of *cis*-(tmen)Pd$(NO_3)_2$ (30.0 mg, 0.0866 mmol) was added into the solid mixture of tri- and tetratopic donor, timb (6.9 mg, 0.0248 mmol) and tim (8.5 mg, 0.0248 mmol) and stirred at room temperature. Slowly the yellow color of the solution turned colorless with the consumption of the suspended donors. After 24 h, the reaction mixture was filtered, concentrated under reduced pressure and pure form of the complex **1** was obtained by triturating with acetone. Obtained yield: 96%. Anal. Calcd. for (vacuum dried sample) $C_{108}H_{164}N_{56}O_{42}Pd_7$: C, 35.41; H, 4.51; N, 21.41. Found: C, 35.27; H, 4.73; N, 21.09. IR: υ (cm^{-1}) = 3421, 3120, 1620, 1518, 1469, 1321, 1121, 1077, 1040, 1007, 816, 761. ^{1}H NMR (400 MHz, D_2O): δ = 9.35 (s, 2H, $H_{imidazole}$-tim), 9.09 (s, 2H, $H_{imidazole}$-tim), 8.97 (s, 2H, $H_{imidazole}$-timb), 8.87 (s, 2H, $H_{imidazole}$-tim), 8.80 (s, 2H, $H_{imidazole}$-timb), 8.73 (s, 2H, $H_{imidazole}$-tim), 8.57 (s, 1H, H_{phenyl}-tim), 8.32 (s, 1H, H_{phenyl}-tim), 8.03 (s, 2H, $H_{imidazole}$-timb), 7.98 s, 1H, H_{phenyl}-tim), 7.97 (s, 1H, H_{phenyl}-tim), 7.89 (s, 2H, $H_{imidazole}$-tim), 7.84 (s, 2H, $H_{imidazole}$-timb), 7.78 (s, 2H, $H_{imidazole}$-timb), 7.74 (s, 2H, $H_{imidazole}$-tim), 7.65 (s, 2H, $H_{imidazole}$-timb), 7.62 (s, 2H, $H_{imidazole}$-timb), 7.59 (s, 2H, $H_{imidazole}$-timb), 7.56 (s, 2H, $H_{imidazole}$-timb), 7.51 (s, 2H, $H_{imidazole}$-tim), 7.40 (s, 6H, H_{phenyl}-timb), 7.37 (s, 2H, $H_{imidazole}$-tim), 7.34 (s, 2H, $H_{imidazole}$-tim), 7.00 (s, 2H, $H_{imidazole}$-tim), 6.93 (s, 2H, $H_{imidazole}$-tim), 6.60 (s, 2H, $H_{imidazole}$-tim), 2.98 (m, 28H, H_{CH2}-tmen), 2.58 (m, 84H, H_{CH3}-tmen). ESI-MS (m/z) = 1159.7 [**1**− $3NO_3^-$]$^{3+}$, 852.9 [**1**− $4NO_3^-$]$^{4+}$, 546.5 [**1**− $6NO_3^-$]$^{6+}$, 343.5 [**1**− $9NO_3^-$]$^{9+}$.

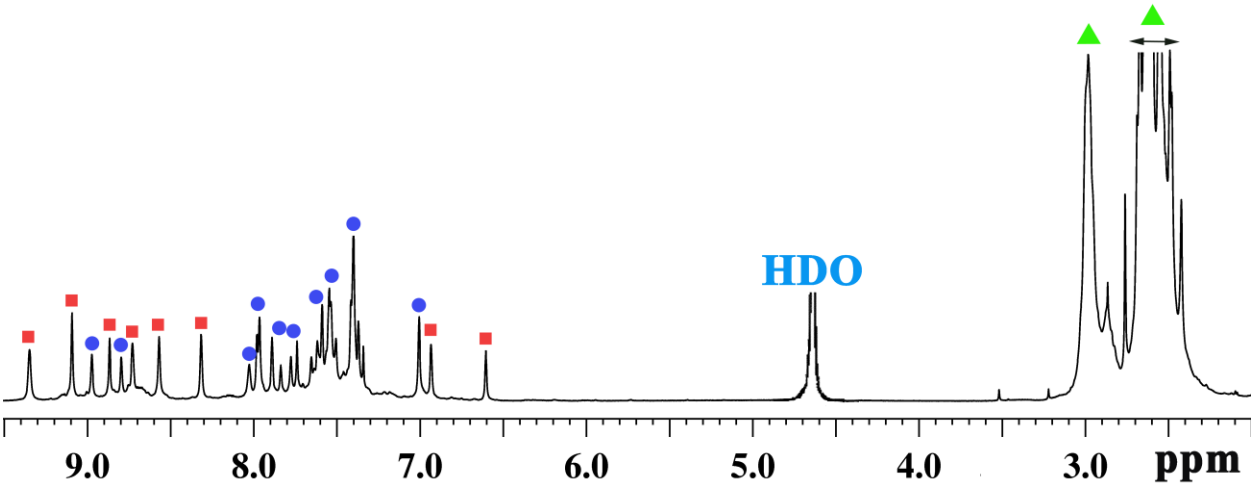


Fig.S1.[1]H NMR spectrum of complex **1** recorded in D_2O (colour codes: blue circles = timb, red squares = tim, green triangles = tmen).

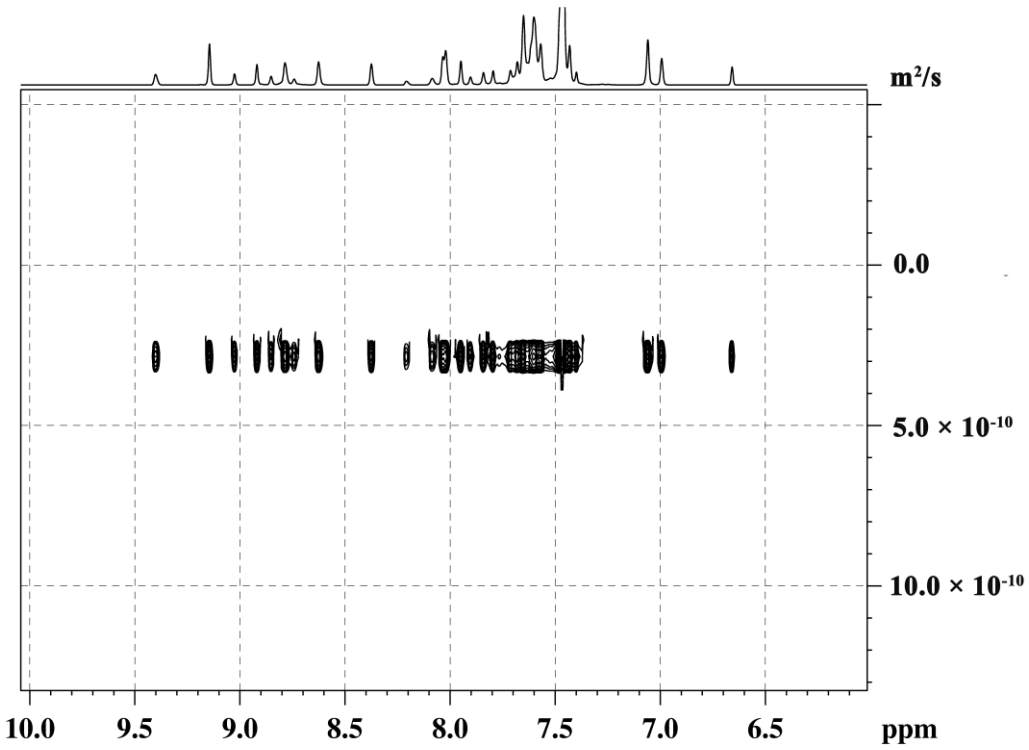


Fig.S2.[1]H DOSY NMR spectrum of the cage **1** in D_2O.

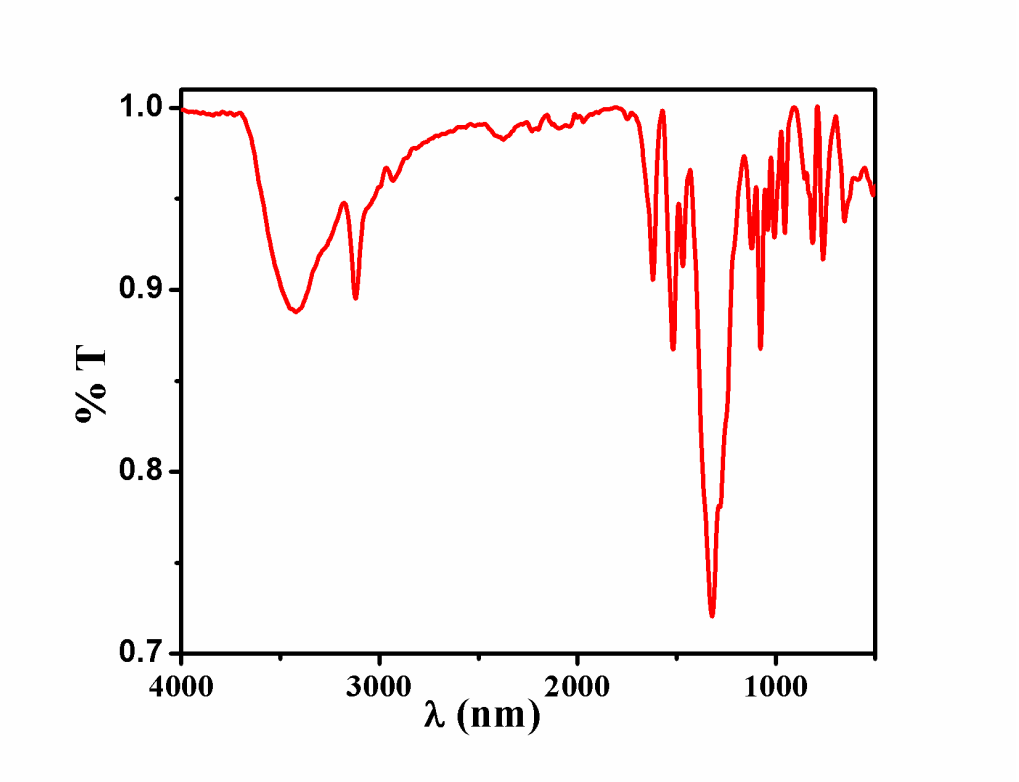


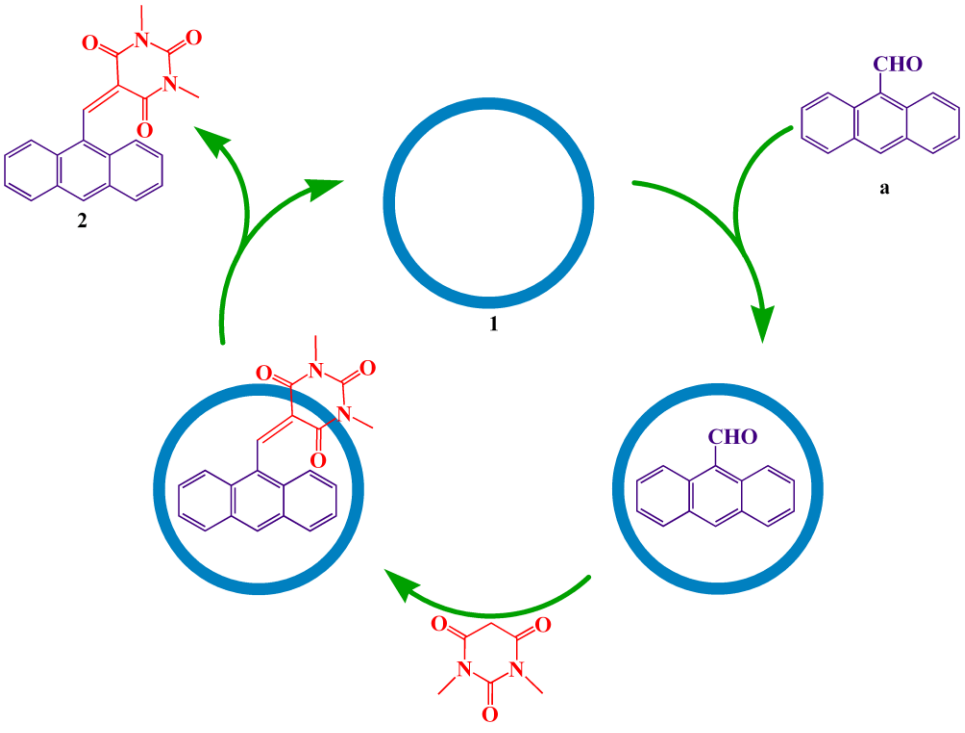
Fig.S3. IR spectrum of the cage **1**.

General procedure for the Knoevenagel condensation of 9-anthracenecarboxaldehyde (a) and 1,3-dimethylbarbituric acid (e) in presence of catalytic amount of complex 1.

9-Anthracenecarboxaldehyde (**a**) (5.4 mg, 0.026 mmol) was added to an aqueous solution (1 mL) of 1,3-dimethylbarbituric acid (**e**) (4.1 mg, 0.026 mmol) in presence of 10 mol % of complex **1** (9.6 mg, 0.0026 mmol) and the reaction was stirred at room temparature. After 72 h, the mixture was extracted with $CDCl_3$. The yield was 35 % yield as determined by NMR analysis.

Table S1. Yields of the Knoevenagel condensation product (**2**) under different conditions.

Serial No.	Additive	Solvent	Yield
1	Complex **1**	H_2O	35 %
2	-	$CDCl_3$	4 %
3	-	CH_2Cl_2	3 %
4	-	Acetone	3 %
5	-	H_2O	5 %



Scheme S1. Proposed mechanism for the cage catalyzed Knoevenagel condensation reaction.

5-(anthracen-10-ylmethylene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (2)

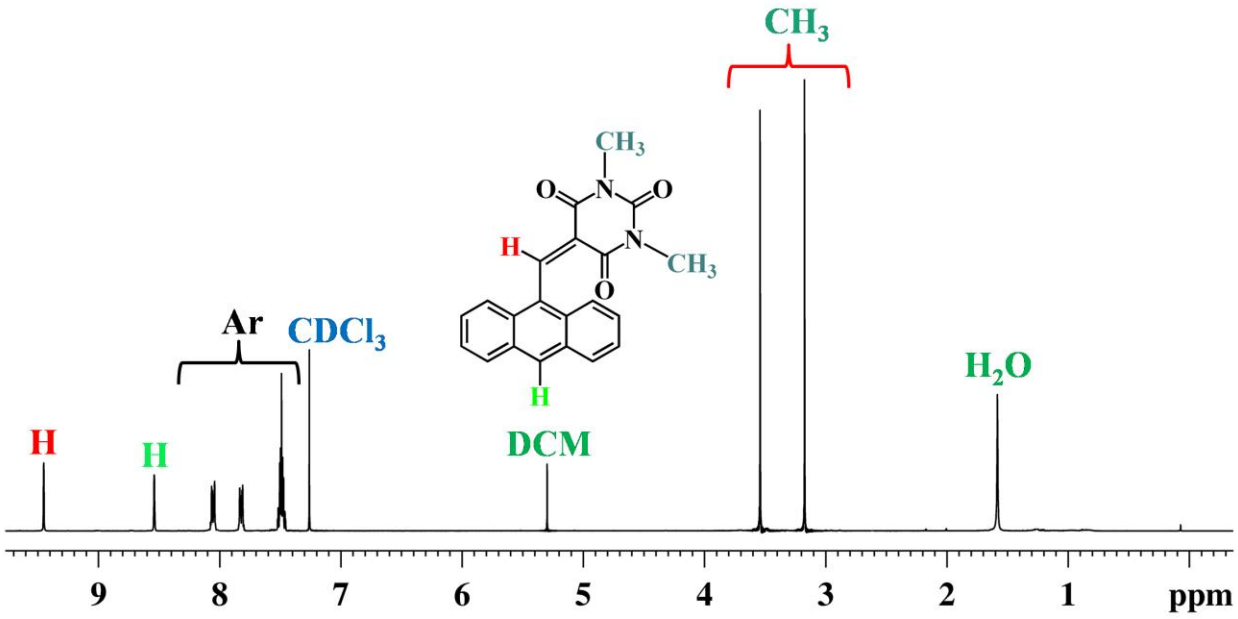


Figure S4. ^{1}H NMR spectra of **2** recorded in $CDCl_3$.

Reaction time: 72 h

Yield: 35% (NMR)

Anal. Calcd. for (vacuum dried sample) $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.41 H, 4.75, N, 8.23. IR: υ (cm^{-1}) = 2952, 1665, 1594, 1518, 1451, 1415, 1371, 1334, 1260, 1161, 1110, 1049, 952, 900. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.45 (s, 1H), 8.54 (s, 1H), 8.05 (dd, 2H), 7.82 (dd, 2H), 7.49(m, 4H), 3.54 (s, 3H), 3.17 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 161.90, 159.36, 157.86, 151.79, 131.40, 129.99 (2C), 129.71 (2C), 128.83, 128.77, 127.19 (2C), 126.01 (2C), 125.41 (2C), 123.67, 29.52, 28.81. HRMS calcd. for $C_{23}H_{16}N_2O_3Na$ $[M + Na]^+$ m/z = 367.1059, found 367.1060.

1,3-dimethyl-5-(pyren-1-ylmethylene)pyrimidine-2,4,6(1H,3H,5H)-trione (3)

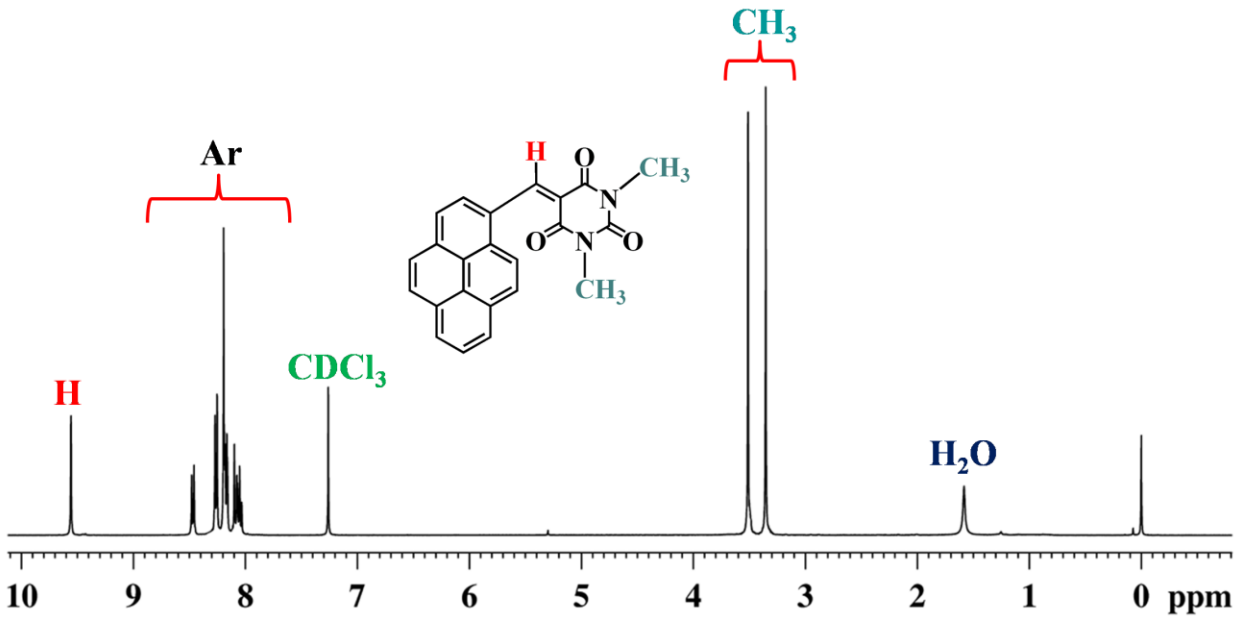


Figure S5. ^{1}H NMR spectra of **3** recorded in $CDCl_3$.

Reaction time: 3 h

Yield: 33% (NMR)

Anal. Calcd. for (vacuum dried sample) $C_{23}H_{16}N_2O_3$:C, 74.99; H, 4.38; N, 7.60. Found: C, 75.78 H, 4.51, N, 7.53. IR: υ (cm^{-1}) = 2918, 1661, 1567, 1453, 1412, 1349, 1237, 1190, 1153, 1054, 951, 838. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (s, 1H), 8.47 (d, 1H), 8.27-8.03 (m, 8H), 3.51 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.94, 160.55, 158.23, 158.19, 151.96, 134.77, 131.53, 131.01, 130.17, 129.84, 129.70, 129.27, 127.88, 127.65, 127.27, 127.18, 126.88, 124.79, 124.23, 123.82, 118.97, 29.56, 28.93. HRMS calcd. for $C_{23}H_{16}N_2O_3Na$ $[M + Na]^+$ m/z = 391.1059, found 391.1057.

Table S2. Yields of the Knoevenagel condensation product (**3**) under same conditions with cage components.

Serial No.	Additive	Yield
1	Complex **1**	33 %
2	*cis*-(tmen)Pd(NO_3)$_2$	2%
3	tim	3 %
4	timb	3 %

1,3-dimethyl-5-(naphthalen-2-ylmethylene)pyrimidine-2,4,6(1H,3H,5H)-trione (4)

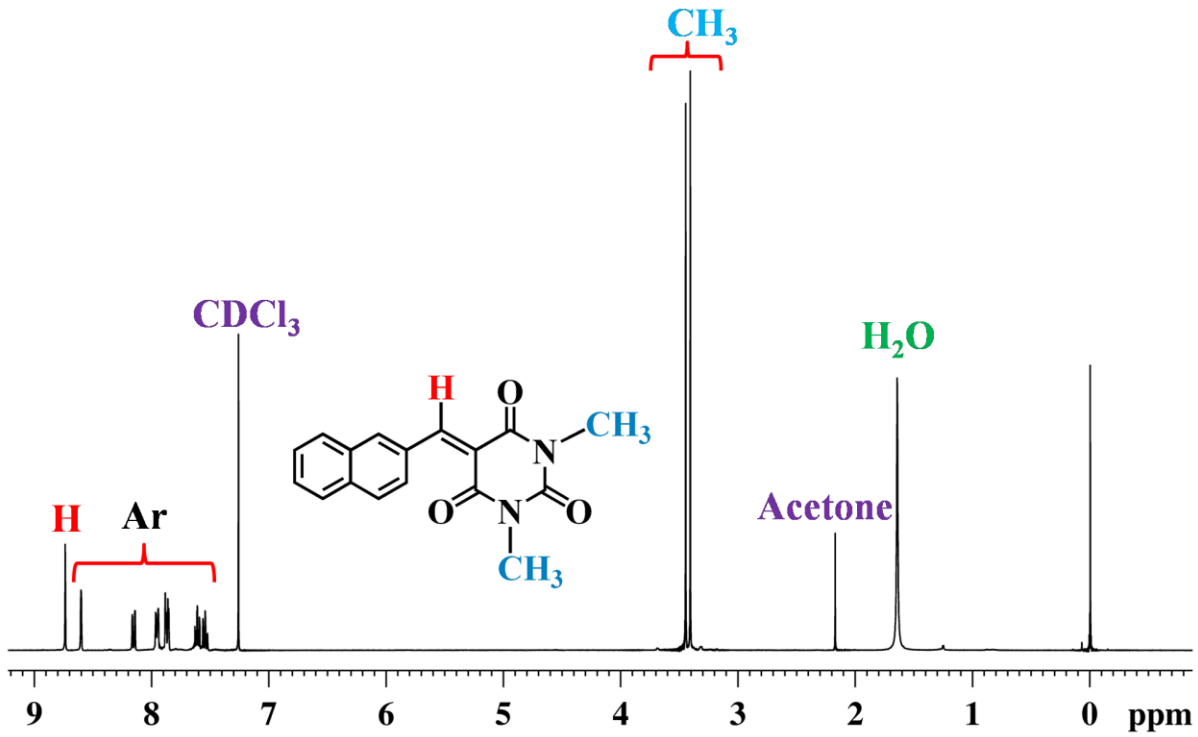


Figure S6. ^{1}H NMR spectra of **4** recorded in $CDCl_3$.

Reaction time: 75 min

Yield: 77% (NMR)

Anal. Calcd. for (vacuum dried sample) $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.01; H, 4.95; N, 9.74. IR: υ (cm^{-1}) = 2951, 1728, 1657, 1566, 1447, 1414, 1369, 1264, 1151, 972, 869, 825, 791. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1H,), 8.51 (s, 1H), 8.14 (d, 1H), 7.94 (d, 1H), 7.87 (dd, 2H), 7.62 (t, 1H), 7.54 (t, 1H), 3.45 (s, 3H), 3.41 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 159.81, 151.84, 136.86, 135.84, 133.02, 130.82, 130.16, 129.59, 129.50, 129.15, 128.20, 128.13, 127.24, 123.28, 117.75, 29.61, 28.97. HRMS calcd. for $C_{17}H_{14}N_2O_3Na$ $[M + Na]^+$ m/z = 317.0902, found 317.0907.

2,2-dimethyl-5-(naphthalen-2-ylmethylene)-1,3-dioxane-4,6-dione (5)

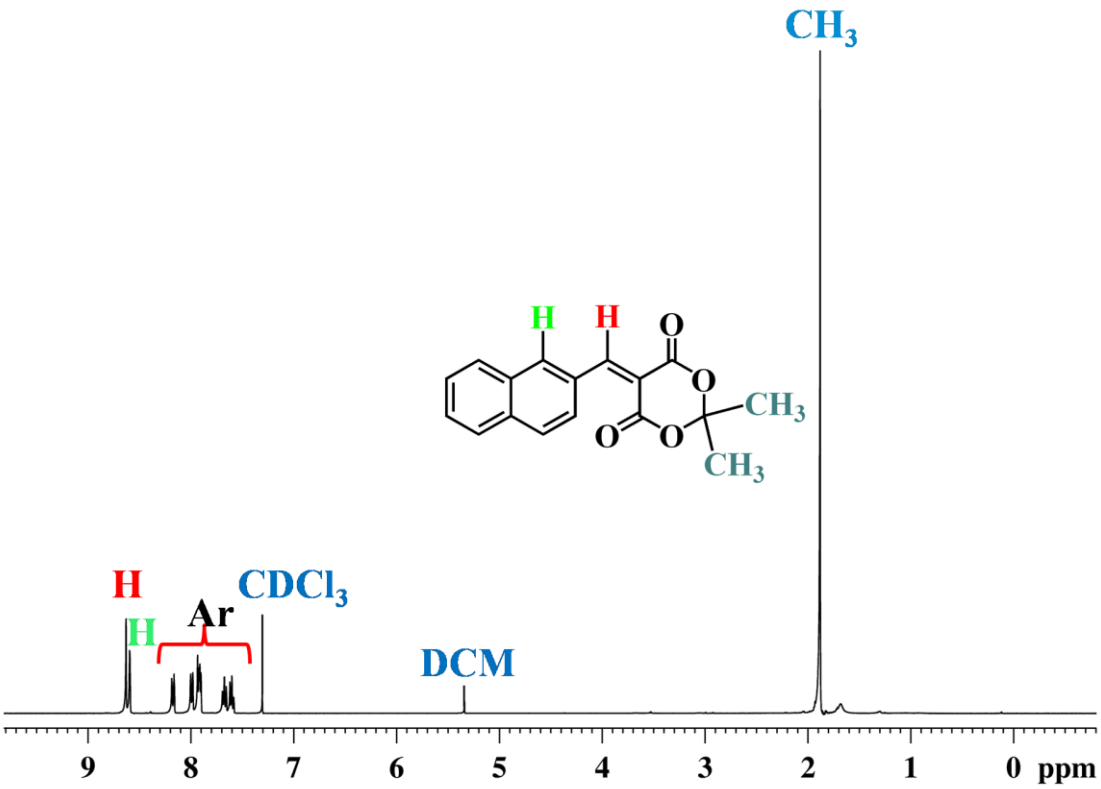


Figure S7. ^{1}H NMR spectra of **6** recorded in $CDCl_3$.

Reaction time: 8 h 30 min

Yield: 51% (NMR)

Anal. Calcd. for (vacuum dried sample) $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.55; H, 5.08. IR: υ (cm^{-1}) = 2992, 1757, 1721, 1592, 1438, 1383, 1286, 1238, 1200, 1162, 1018, 961, 921. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.55 (s, 1H), 8.12 (dd, 1H), 7.94 (d, 1H), 7.88 (d, 1H), 7.86 (d, 1H), 7.63 (td, 1H), 7.56 (td, 1H), 1.84 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.95, 160.49, 158.68, 137.55, 136.12, 133.10, 130.27, 129.93, 129.85, 128.80, 128.53, 128.27, 127.50, 114.83, 105.09, 28.13. HRMS calcd. for $C_{17}H_{14}O_4Na$ $[M + Na]^+$ m/z = 305.0790, found 305.0788.

5-benzylidene-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (6)

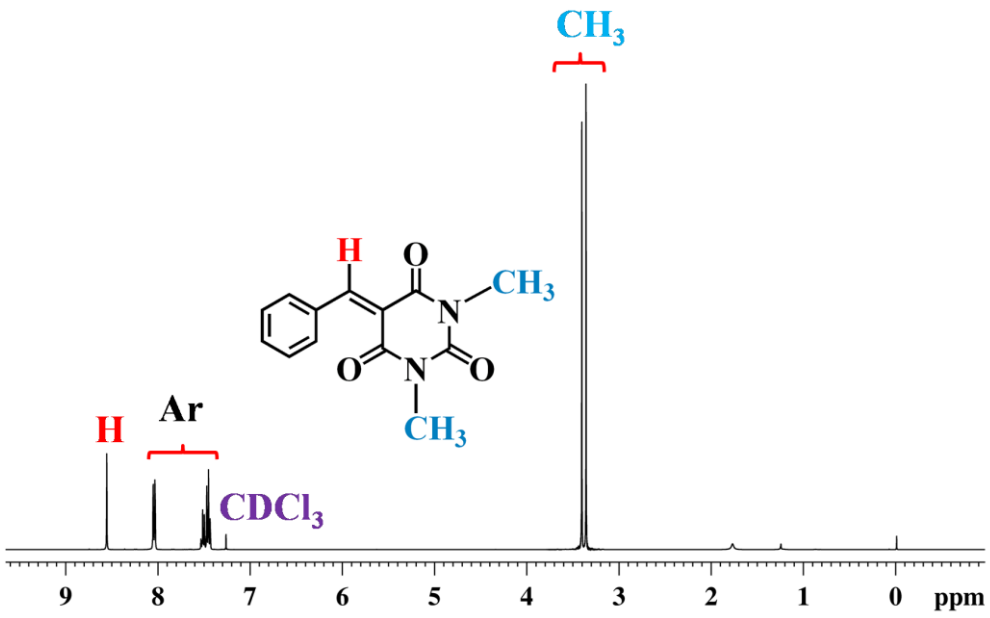


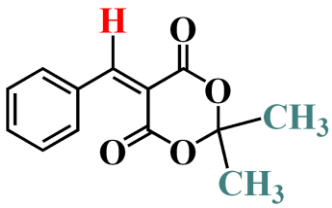
Figure S8. ^1H NMR spectra of **6** recorded in $CDCl_3$.

Reaction time: 4 min

Yield: 69% (NMR)

Anal. Calcd. for (vacuum dried sample) $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 64.07; H, 5.01; N, 11.29. IR: υ (cm^{-1}) = 2954, 1731, 1664, 1572, 1444, 1417, 1366, 1302, 1269, 1210, 1149, 1066, 986, 832. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H,), 8.04 (d, 2H), 7.51 (t, 1H), 7.43 (t, 2H), 3.40 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.92, 160.77, 159.71, 151.68, 133.87, 133.36, 133.08, 128.67, 117.96, 29.52, 28.87. HRMS calcd. for $C_{13}H_{12}N_2O_3Na$ $[M + Na]^+$ m/z = 267.0746, found 267.0745.

5-benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (7)



Reaction time: 6 h

Yield: 58% (NMR)

Anal. Calcd. for (vacuum dried sample) $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.45; H, 5.34. IR: υ (cm^{-1}) = 2859, 1777, 1734, 1386, 1306, 1261, 1233, 1111, 1061, 1015, 969, 903, 864. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 8.05 (d, 2H), 7.57(t, 1H), 7.49 (t, 2H), 1.86 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 161.30, 159.76, 158.15, 133.71, 133.62, 131.71, 128.75, 114.84, 104.60, 27.64. HRMS calcd. for $C_{13}H_{12}O_4Na$ $[M + Na]^+$ m/z = 255.0633, found 255.0638.

X-ray Data Collection and Structure Refinements. The diffraction data of complex **1** was collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.[2] Intensity data were collected using graphite-monochromatic Mo-Kα radiation (0.7107 Å) at 90(2) K on a crystal as obtained after several attempts. The structures were solved by direct methods using the SHELX-97[3]incorporated in WinGX.[4-6] Empirical absorption corrections were applied with SADABS.[7] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, U(H) = 1.2U(C) or 1.5U (C-methyl), and their coordinates were allowed to ride on their respective carbons. The obtained X-ray diffraction data was poor because of the presence of large number of disordered nitrate counter anions and solvent molecules and thus the final R factor turned out to be high. Due to this problem, some of the atoms were refined isotropically.

Table S3. Crystallographic data and refinement parameters of complex **1.**

	1
empirical formula	$C_{108}H_{200}N_{56}O_{60}Pd_7$
fw	3988.02
T (K)	90(2)
crystal system	Triclinic
space group	$P\bar{1}$
a/Å	17.8390 (50)
b/Å	21.1540 (50)
c/Å	23.3440 (50)
α/deg	77.330(5)
β/deg	71.749 (5)
γ/deg	86.769 (5)
V/Å^3	8161.64 (176)
Z	1
ρ_{calcd} (g cm^{-3})	1.618
μ (Mo Kα) (mm^{-1})	0.86
λ/Å	0.71073

F (000)	4036.0
collected reflns	158936
unique reflns	48617
GOF (F^2)	0.987
R_1[a] [I>2σ(I)]	0.1109
wR_2[b][I>2σ(I)]	0.3707

$^{a}R_1 = \Sigma \big| \, |F_o| - |F_c| \, \big| / \Sigma |F_o|$, $^{b}wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

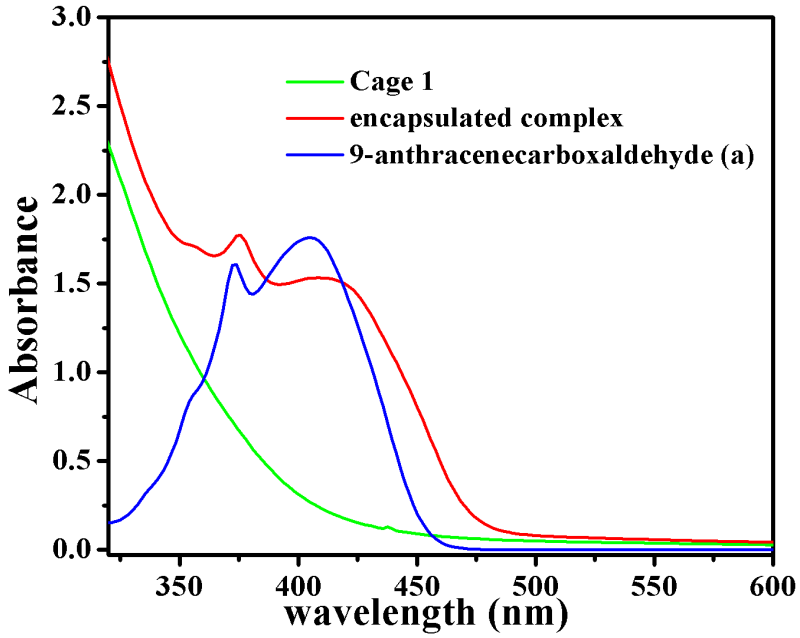


Figure S9. The UV-Visible spectra of cage **1** & encapsulated complex, recorded in H_2O, and 9-anthracenecarboaldehyde (a), recorded in $CHCl_3$.

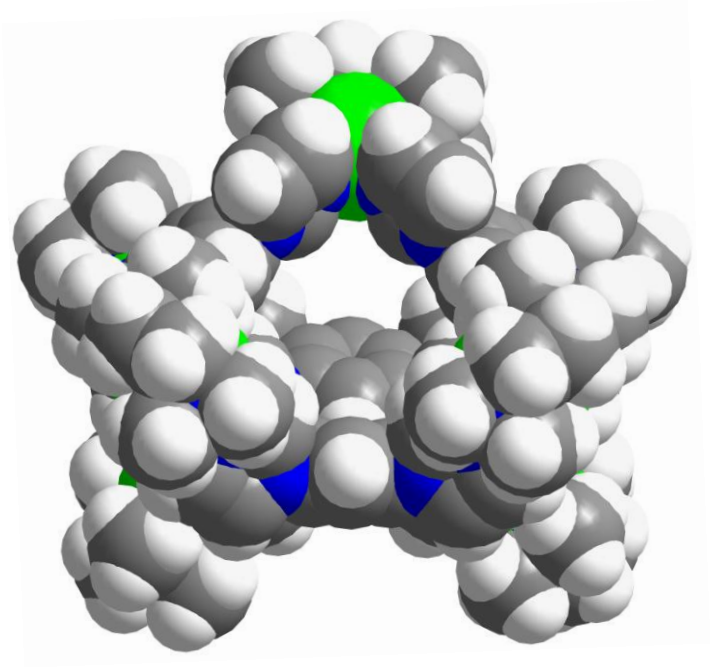


Figure S10. The channel of the cage is shown by the space-filling model. Colour code: green = Pd; blue = N, grey = C, white = H.

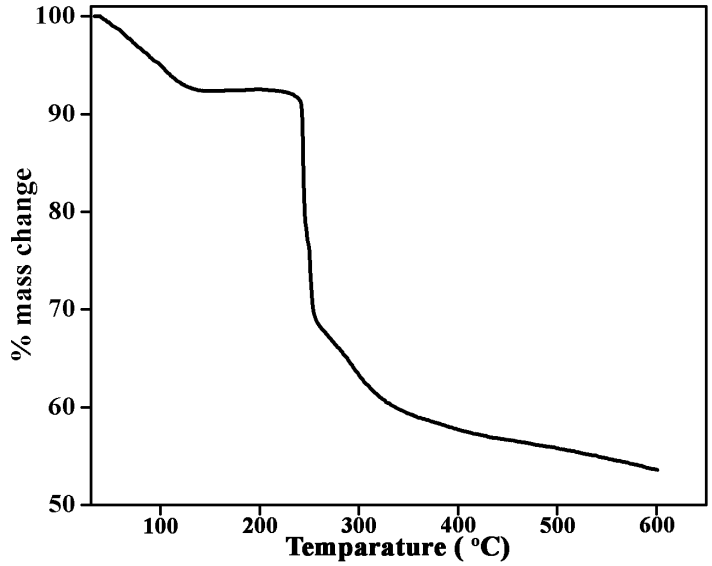


Figure S11. TGA plot of Pd_7 molecular boat (**1**) obtained with a scan rate of 10°C tempertaure change per minute under a stream of N_2 atmosphere.

TGA indicates that the dehydrated cage **1** was stable up to 240°C. The cage is unstable in mineral acids and bases. Even in triethylamine it decomposes and forms $Pd(OH)_2$.

After optimization of the structures using empirical method MMUFF in Argus Lab[8], their energy calculation clearly suggested that, multi-component self-assembly reaction is favorable over two-component self-assembly reaction.

References

1. A. K. Bar, R. Chakrabarty and P. S. Mukherjee, *Inorg. Chem*. 2009, **48**, 10880
2. SMART/SAINT; Bruker AXS, Inc.: Madison, WI, 2004.
3. Sheldrick, G. M. SHELX-97, Program for the Solution and Refinement of Crystal Structures; University of Gottingen: Gottingen, Germany, 1998.
4. Sheldrick, G. M. SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction, version 2.05; University of Gottingen: Gottingen, Germany, 1999.
5. Farrugia, L. J. WinGX: An Integrated System of Windows Programs for the Solution, Refinement and Analysis for Single Crystal X-ray Diffraction Data, version 1.65.04; Department of Chemistry: University of Glasgow, 2003. (Farrugia, L. J. *J. Appl. Crystallogr*. 1999, **32**, 837).
6. Farrugia, L. J. ORTEP-3 for Windows, version 1.08. *J. Appl. Crystallogr*., 1997, **30**, 565.
7. Spek, A. L. *Acta Crystallogr.*, 1990, **A46**, C34.
8. Thompson, M. A. *ArgusLab 4.0.1*; Planaria Software LLC: Seattle, WA, 2009.