## Supporting Information

## For

# A chiral Pt<sub>12</sub> tetrahedral cage and its use in catalytic Michael addition reaction

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Table of contents		Page No.	
Experiment section			
Table S1: Crystallographic information and structure solution parameters of T.		6-7	
Fig. S1	<sup>1</sup> H NMR spectrum of <b>L</b> in CDCl <sub>3</sub> .	8	
Fig. S2	<sup>1</sup> H NMR spectrum of cage <b>T</b> in $D_2O$ : $CD_3OD$ .	8	
Fig. S3	DOSY NMR spectrum of cage <b>T</b> in $D_2O: CD_3OD$ .	9	
Fig. S4	Full ESI-MS spectra of cage <b>T</b> in $H_2O$ : methanol.	9	
Fig. S5	ESI-MS isotopic distribution patterns of the fragment $[T-4NO_3^-]^{4+}$ ,		
	[ <b>T</b> -5NO₃ <sup>−</sup> ] <sup>4+</sup> , [ <b>T</b> -6NO₃ <sup>−</sup> ] <sup>6+</sup>	10	
Fig. S6	<sup>1</sup> H NMR spectrum of $T \supset 1a$ complex in D <sub>2</sub> O: CD <sub>3</sub> OD.	11	
Fig. S7	DOSY NMR spectrum of $\mathbf{T} \supset \mathbf{1a}$ complex in $D_2O: CD_3OD$	11	
Fig. S8	Comparison <sup>1</sup> H NMR spectrum of <b>T</b> and <b>T⊃1a</b> complex.	12	
Fig. S9	<sup>1</sup> H NMR spectrum of $\mathbf{T} \supset \mathbf{1f}$ complex in $D_2O: CD_3OD$ .	12	
Fig. S10	DOSY NMR spectrum of $\mathbf{T} \supset \mathbf{1f}$ complex in D <sub>2</sub> O: CD <sub>3</sub> OD.	13	
Fig. S11	comparison <sup>1</sup> H NMR spectrum of <b>T</b> and $T \supset 1f$ complex	13	
Fig. S12	<sup>1</sup> H NOESY NMR spectrum of $\mathbf{T} \supset \mathbf{1f}$ complex in D <sub>2</sub> O: CD <sub>3</sub> OD.	14	
Fig. S13	UV-Visible spectra of <b>1a</b> , <b>1f</b> , <b>T⊃1a</b> and <b>T⊃1f</b> in H <sub>2</sub> O.	14	
Figs. S14-S15 <sup>1</sup> H spectra of crude product followed by non-catalyzed			

	and catalyzed method in H2O: $CH_3OH$ (9:1) medium.	15
Figs. S16-S17	NMR and ESI-MS characterization of product 2a.	16
Figs. S18-S19	NMR and ESI-MS characterization of product <b>2b</b> .	17
Figs. S20-S21	NMR and ESI-MS characterization of product 2c.	18
Figs. S22-S23	NMR and ESI-MS characterization of product 2d.	19
Figs. S24-S25	NMR and ESI-MS characterization of product 2e.	20
Figs. S26-S27	NMR and ESI-MS characterization of product <b>2f</b> .	21
Figs. S28-S29	NMR and ESI-MS characterization of product 2g.	22

#### **Experimental Section:**

Materials and Methods. All the chemicals used in this study were purchased from reputed commercial sources. Ligand (L) was synthesized by reported procedure<sup>1</sup>. NMR spectra were recorded using a Bruker 400 MHz instrument and the chemical shifts ( $\delta$ ) are accounted in ppm relative to Me<sub>4</sub>Si as an internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of (D<sub>2</sub>O at 4.79 ppm and CDCl<sub>3</sub> at 7.26 ppm. UV-Vis spectra and CD spectra were recorded using Perkin Elmer Lambda-750 and JASCO-410 spectrophotometers, respectively. ESI-MS experiments were done in Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer. . Single crystal X-Ray data of **T** was collected in synchrotron radiation source and the structure was solved by direct methods using SHELX-2014<sup>2</sup> software package incorporated in WinGX<sup>3</sup>.

**Synthesis of L**. A mixture of *tris*(4-bromophenyl)amine (500.0 mg, 1.04 mmol), pyrimidine-5boronic acid (578.0 mg, 4.66 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.38 gm, 10.0 mmol) were taken in 50 mL of THF : water (5:1) solvent. The mixture was degassed and Pd(PPh<sub>3</sub>)<sub>4</sub> (59.5 mg, 5.0 mol%) was added under N<sub>2</sub> flow and the reaction was refluxed for 48 h at 75 °C. The reaction mixture was extracted with chloroform and the product was purified by column chromatography. Isolated yield: 60 %. Anal. Calcd for (activated sample) C<sub>30</sub>H<sub>21</sub>N<sub>7</sub>: C, 75.14; H, 4.41; N, 20.45. Found: C, 74.78; H, 4.79; N, 20.42. IR: υ (cm<sup>-1</sup>) = 3028, 1596, 1547, 1270, 830, 723, 556. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.20 (s, 3H), 8.96 (s, 6H), 7.55 (d, 6H), 7.31 (d, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 157.38, 154.64, 147.82, 133.71, 129.39, 128.25, 125.17. HRMS calcd for C<sub>30</sub>H<sub>21</sub>N<sub>7</sub>H [M + H]<sup>+</sup> m/z = 480.1937, found 480.1911.

Synthesis of T. Ligand (L) (0.0110 g, 0.023 mmol) and chiral cis-[(1S, 2S)-N,N'-eda]Pt(NO<sub>3</sub>)<sub>2</sub> (**M**) (0.030 g, 0.069 mmol) were taken in 8 mL vial; and 3 mL of water : methanol (9:1) was added to it. The suspension was kept at constant stirring at 45 °C for 36 h. The resulting yellow colored solution was centrifuged and the clear supernatant solution was diffused with acetone to get the off-yellow precipitate of (**T**) in pure form. Isolated yield: 0.035 g, 85%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta = 9.27$  (s, 12H), 9.52 (s, 12H), 9.39 (s, 12H), 7.46 (d, 24H, J = 8 Hz), 7.21 (d, 24H, J = 8 Hz), 2.77 (b, 24H), 2.14 (b, 48H), 1.65 (b, 24H), 1.44 (b, 24H) and 1.24 (b, 24H). ESI-MS (m/z) = 1719.3245 [**T** - 4NO<sub>3</sub><sup>-</sup>]<sup>+4</sup>, 1363.1253 [**T** - 5NO<sub>3</sub><sup>-</sup>]<sup>+5</sup> and 1125.2143 [**T** - 6NO<sub>3</sub><sup>-</sup>]<sup>+6</sup>.

**Encapsulation of 1a and 1f guests.** 5 mg of **T** was taken in 4ml vial and 1 ml of  $D_2O$ : CD<sub>3</sub>OD (9:1) was added. To this 1mg of **1a** guest was added as solid powder and the suspension was stirred for 36 hours at room temperature. After centrifugation the clear solution obtained was taken and NMR was recorded. Same procedure was adopted for guest **1f**.

**UV-Visible experiment procedure:** The 50  $\mu$ L of stock solution of **T** (1×10<sup>-3</sup> M) in H<sub>2</sub>O: MeOH (9:1) was taken in 8 mL vial and to this 1 mg of guest **1a** was added. The suspension obtained was diluted to 3ml final volume with distilled water and stirred for 12 h at room temperature. The suspension was then centrifuged and the clear solution obtained was taken for UV measurement. Same procedure was adopted for guest **1f**.

**General procedure for the Michael addition promoted by supramolecular catalysis:** To a solid nitro-alkene **1** (0.08 mmol), 2 mL solution (9:1, water: methanol) of the cage T (10 mol %) was added followed by an addition of indole (0.096 mmol). The mixture was stirred at room temperature for the time periods as mentioned in Table 1. Then the reaction mixture was extracted with chloroform and further column chromatography using silicagel, eluting with EtOAc: Hexanes afforded the pure product **2** which was characterized by <sup>1</sup>H and <sup>13</sup>C NMR and mass spectroscopy (HRMS).

Synthesis of 2a: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.10$  (bs, 1H), 7.34 - 7.04 (m, 10H), 5.20 (t, 1H, J = 8Hz), 5.10-4.93 (m, 2H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 139.73$ , 136.98, 129.42, 128.27, 128.07, 126.60, 123.17, 122.15, 120.44, 119.41, 114.82, 111.94, 80.04, 42.05. HRMS calcd for 2a [M + H]<sup>+</sup> m/z = 267.1133, found 267.1735.

**Synthesis of 2b:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.15$  (d, 1H, J = 8Hz), 8.00 (bs, 1H), 7.41-6.85 (m, 11H), 5.96 (t, 1H, J = 8 Hz), 4.99 - 4.96 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 137.08$ , 135.15, 134.65, 129.64, 128.81, 127.33, 126.33, 126.42, 125.83, 125.13, 123.17, 123.13, 120.46, 119.28, 114.76, 111.92, 79.01, 37.48. HRMS calcd for **2b** [M + Na]<sup>+</sup> (m/z) = 339.1109, found 339.1401.

Synthesis of 2c: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.15$  (bs, 1H), 7.44-7.07 (m, 9H), 5.75 (t, 1H, J = 8 Hz), 5.01-4.98 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 136.96$ , 134.34, 130.63, 129.45, 129.31, 127.75, 126.67, 123.27, 122.44, 120.52, 119.41, 113.76, 111.86, 78.20, 38.46. HRMS calcd for 2c [M + H]<sup>+</sup> (m/z) = 301.0743, found 301.0902.

Synthesis of 2d: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.12$  (bs, 1H), 7.44-6.99 (m, 9H), 5.18-4.88 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 138.27$ , 137.00, 133.89, 129.64, 129.59, 126.39, 123.34, 122.06, 120.58, 119.28, 114.36, 112.01, 79.78, 41.45. HRMS calcd for 2d [M + Na]<sup>+</sup> (m/z) = 323.0563, found 323.0828.

Synthesis of 2e : <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.20 (bs, 1H), 7.35-7.08 (m, 8H), 5.69 (t, 1H J = 8 Hz), 5.02-4.91 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 135.68, 135.00, 134.50, 130.41, 130.37, 128.10, 126.47, 123.43, 122.38, 120.66, 119.25, 113.33, 111.94, 77.93, 38.10. HRMS calcd for **2e** [M + H]<sup>+</sup> (m/z) = 335.0354, found 335.0109.

Synthesis of 2f : <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.10$  (bs, 1H), 7.45-6.87 (m, 8H), 5.17- 4.90 (m, 3H), 3.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.39$ , 137.01, 131.70, 129.28, 126.59, 123.14, 121.93, 120.40, 119.47, 114.77, 111.83, 80.24, 55.72, 41.35. HRMS calcd for 2f [M + Na]<sup>+</sup> (m/z) = 319.1058, found 319.0499.

Synthesis of 2g : <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.05 (bs, 1H), 7.46-6.99 (m, 9H), 5.16-4.90 (m, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.67, 137.00, 136.67, 130.07, 128.10, 126.63, 123.12, 122.04, 120.40, 119.43, 115.13, 111.84, 80.13, 41.70, 21.49. HRMS calcd for 2g [M + Na]<sup>+</sup> (m/z) = 303.1109, found 303.0656.

#### X-Ray data collection and structure refinements.

The single crystal diffraction data for complex (**T**) were collected at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron of Trieste (Italy), with a Pilatus 2M image plate detector and a monochromatic wavelength of 0.700 Å. Complete dataset was collected at 100 K with nitrogen stream and the structure was solved by direct methods using SHELX-2007<sup>2</sup> software package incorporated in WinGX.<sup>3</sup>. The structure was solved by direct methods and Fourier analyses and refined by the full-matrix least-squares method based on F<sup>2</sup> with all observed reflections using the SHELX-2013 program incorporated in WinGX. Non-hydrogen atoms were refined with anisotropic displacement coefficients.

Table S1: Crystallographic information and structure solution parameters of T.

Identification code	Т
Empirical formula	C <sub>384</sub> H <sub>396</sub> N <sub>108</sub> O <sub>12</sub> Pt <sub>24</sub>
Colour and shape	yellow, block shaped
F <sub>w</sub>	11398.22
<i>T</i> (K)	100(2)
$\gamma(\text{\AA})$	0.7000
Crystal system	Orthorhombic
Space group	P222
<i>a</i> /Å	33.966 (7)
b /Å	19.359 (4)
<i>c</i> /Å	26.794 (5)
lpha /°	90
$\beta$ /°	90
$\gamma/^{\circ}$	90
V/Å <sup>3</sup>	17618(6)
Ζ	1
$\rho_{\text{calcd}}$ (g/cm <sup>-3</sup> )	1.074
$\mu$ (Mo K $\alpha$ )/ mm <sup>-1</sup>	4.572
h, k, l	42,24,33
<i>F</i> (000)	5424.0

Reflections collected	98600
Unique reflections	28385
Data / restraints / parameters	28385/1162/1130
Largest diff. peak and hole	1.794 and -1.982
(e.Å <sup>3</sup> )	
$\operatorname{GOF}(F^2)$	0.976
Final <i>R</i> indexes $[I \ge 2s(I)]$	$R_1^{\ a} = 0.0735$
	$wR_2^{\ b} = 0.2036$
Final <i>R</i> indexes [all data]	$R_1^{\ a} = 0.1046$
	$wR_2^{\ b} = 0.2177$



Fig. S1 <sup>1</sup>H NMR spectrum of L in CDCl<sub>3</sub>.



**Fig. S2** <sup>1</sup>H NMR spectrum of cage **T** in  $D_2O$ :  $CD_3OD$  (1:1).



Fig. S3 DOSY NMR spectrum of cage T in D<sub>2</sub>O: CD<sub>3</sub>OD (1:1).



Fig. S4 Full ESI-MS spectrum of cage T in H<sub>2</sub>O: CH<sub>3</sub>OH (1:1).



**Fig. S5** Experimental isotopic distribution pattern of (a)  $[T-4NO_3^-]^{+4}$ , (b)  $[T-5NO_3^-]^{+5}$  and (c)  $[T-6NO_3^-]^{+6}$  charged fragments in H<sub>2</sub>O: CH<sub>3</sub>OH (1:1).



**Fig. S6** <sup>1</sup>H NMR spectrum of  $T \supset 1a$  in D<sub>2</sub>O: CD<sub>3</sub>OD (9:1).



**Fig. S7** DOSY NMR spectrum of  $T \supset 1a$  in D<sub>2</sub>O: CD<sub>3</sub>OD (9:1).



**Fig. S8** Comparison of <sup>1</sup>H NMR spectra of (a) **T**, (b) **T** $\supset$ **1a** complex. The NMR spectra were recorded in D2O: CD<sub>3</sub>OD (9:1).



**Fig. S9** <sup>1</sup>H NMR spectrum of  $\mathbf{T} \supset \mathbf{1f}$  in D<sub>2</sub>O: CD<sub>3</sub>OD (9:1).



**Fig. S10** DOSY NMR spectrum of  $T \supset 1f$  in D<sub>2</sub>O: CD<sub>3</sub>OD (9:1).



**Fig. S11** Comparison of <sup>1</sup>H NMR spectra of (a) **T**, (b) **T** $\supset$ **1f** complex. The NMR spectra were recorded in D2O: CD<sub>3</sub>OD (9:1).



**Fig. S12** <sup>1</sup>H NOESY NMR spectrum of  $T \supset 1f$  complex in D<sub>2</sub>O: CD<sub>3</sub>OD (9:1).



Fig. S13 UV-Visible spectra of guests 1a, 1f in methanol and host-guest complexes  $T \supset 1a$ ,  $T \supset 1f$  in water.



**Fig. S14** <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> for the products obtained by heating **1a** at rt for 5h in H<sub>2</sub>O:CH<sub>3</sub>OH (9: 1) in presence of 10 mol% of **T**.



**Fig. S15** <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> for the products obtained by heating **1a** at rt for 5h in H<sub>2</sub>O: CH<sub>3</sub>OH (9: 1).



Fig. S16 <sup>1</sup>H NMR spectrum of product 2a recorded in CDCl<sub>3</sub>.



Fig. S17 <sup>13</sup>C NMR spectrum of product 2a recorded in CDCl<sub>3</sub>.



Fig. S18 <sup>1</sup>H NMR spectrum of product 2b recorded in CDCl<sub>3</sub>.



Fig. S19 <sup>13</sup>C NMR spectrum of product 2b recorded in CDCl<sub>3</sub>.



Fig. S20 <sup>1</sup>H NMR spectrum of product 2c recorded in CDCl<sub>3</sub>.



Fig. S21 <sup>13</sup>C NMR spectrum of product 2c recorded in CDCl<sub>3</sub>.



Fig. S22 <sup>1</sup>H NMR spectrum of product 2d recorded in CDCl<sub>3</sub>.



Fig. S23 <sup>13</sup>C NMR spectrum of product 2d recorded in CDCl<sub>3</sub>.



Fig. S24 <sup>1</sup>H NMR spectrum of product 2e recorded in CDCl<sub>3</sub>.



Fig. S25 <sup>13</sup>C NMR spectrum of product 2e recorded in CDCl<sub>3</sub>.



Fig. S26 <sup>1</sup>H NMR spectrum of product 2f recorded in CDCl<sub>3</sub>.



Fig. S27 <sup>13</sup>C NMR spectrum of product 2f recorded in CDCl<sub>3</sub>.



Fig. S28 <sup>1</sup>H NMR spectrum of product 2g recorded in CDCl<sub>3</sub>.



Fig. S29 <sup>13</sup>C NMR spectrum of product 2g recorded in CDCl<sub>3</sub>.

### **Supporting References**

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