Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2017

Helianthus-like Cucurbit[4]uril and Cucurbit[5]uril analogues

Yufan Wu, Lixi Xu, Yenan Shen, Yang Wang, Qiaochun Wang*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science & Technology, Shanghai 200237, P.R. China.

* Corresponding author: qcwang@ecust.edu.cn.

Supporting information

Table of contents:

1. General methods 2

2. Experimental section 2

3. Removal of Ca^{2+} 4

4. Preparation of the single crystal of CyP-TD[n] 4

5. The solubility measurements of the CyP-TD[n] 5

6. Supplementary Figures 6

7. Details of the X-ray Crystal Structure 12

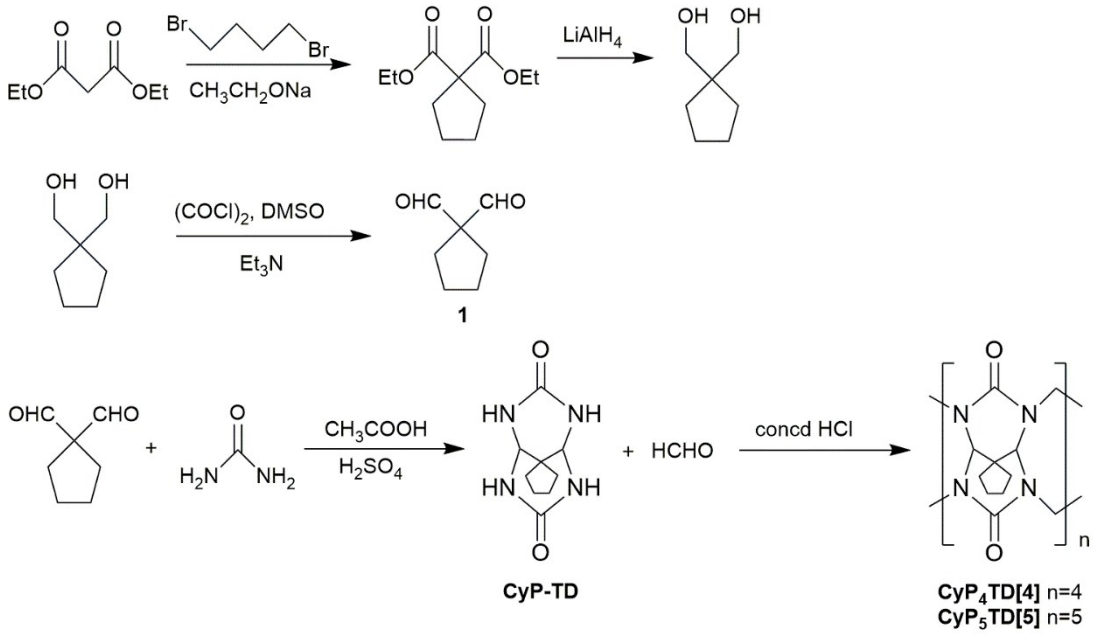
References 15

1. General methods

^{1}H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The molecular mass spectra were recorded on a 4800 Plus M-TOF/TOF Analyzer (AB SCIEX, USA) and a Waters LCT Premier XE mass spectrometer. Thermal stability were measured by thermogravimetric analysis with model SDT Q600 V8.3 Build 101.

Materials: 2,2-Dimethyl-1,3-propanediol was purchased from Aldrich and was used directly; cyclopentane-1,1-dicarbaldehyde (**1**) was prepared from diethyl malonate (Scheme S1) according the literature.[1] Other commercially available chemicals were used without further purification.

2. Experimental section



Scheme S1. The synthetic route of CyP-TD[n]s

1) Synthesis of cyclopentanopropanediurea (**CyP-TD**)

Cyclopentane-1,1-dicarbaldehyde (9ml, 0.07mol) and urea (13g, 0.22mol) were added in the mixture of acetic acid (100ml) and concentrated sulfuric acid (5ml). After stirring the mixture at 95℃ for 12h, the solution was allowed to cool down to room temperature and water (600ml) was added. The precipitate was filtered and washed with acetone. The product was dried under vacuum to give **CyP-TD** as a white powder. （10.5g, 70%）

cyclopentanopropanediurea: ^{1}H NMR (400 MHz, DMSO, 298 K): δ 7.00 (d, J = 4.1Hz, 4H), 3.90 (t, J = 4.1Hz, 2H), 1.63(s, 8H). ^{13}C NMR (100 MHz, DMSO): δ 154.04, 63.39, 41.85, 32.37, 25.04. ESI-MS: m/z 233.1017 $[M+Na]^{+}$ (calcd 233.1014).

2）Synthesis of **CyP_5TD[5]**

Paraformaldehyde (0.72 g, 24.0 mmol) was added into a solution of **CyP-TD** (2.10 g,10.0mmol) in concentrated HCl (5 ml), and the mixture was then heated to 95°C for 24h. The resulting solution was cooled to room temperature. The solid was collected by filtration, and washed with 10ml 2% HCl solution. The resulting solid was dried under vacuum to yield a white powder (184mg, 8%). ^{1}H NMR (400 MHz, D_2O, 298 K): δ 6.44 (d, *J* = 14.8 Hz, 10H) , 4.61(s, 10H) , 3.97 (d, *J* = 14.8 Hz, 10H) , 1.57 (m, 40H). ^{13}C NMR (100 MHz, D_2O): δ 157.2, 79.3, 64.6, 43.9, 34.2, 27.7. ESI-MS m/z 1193.5486 $[M+Na]^{+}$. (calcd 1193.5481)

3）Synthesis of **CyP_4TD[4]**

To a mixture of **CyP-TD** (2.1 g, 10.0 mmol), calcium chloride (0.22g, 2mmol) and paraformaldehyde (0.72 g, 24.0 mmol) was added 37% HCl (5 mL). The mixture was then heated to 90 °C under stirring for 60 h. The resulting solid after cooling was collected by filtration. The crude product was dissolved in methanol (200ml) and then acetic ether (250ml) was added to precipitate a solid. The precipate was filtered and dried under vacuum to give **CyP$_4$TD[4]** as a white powder a white powder (121 mg, 5%). ^{1}H NMR (400 MHz, D_2O, 298 K): δ 6.44 (d, *J* = 15.1Hz, 8H), 4.76(s, 8H), 4.12 (d, *J* = 15.1Hz, 8H), 1.55 (dd, *J1* = 5.3 Hz, *J2* =17.1Hz, 32H). ^{13}C NMR (100 MHz, D_2O): δ 152.35, 77.25, 62.26, 44.27, 31.86, 25.24. MALDI-TOF MS m/z 959.4362 $[M+Na]^+$. (calcd 959.4365)

3. Removal of Ca^{2+}

CyP$_4$TD[4] with Ca^{2+} (119.2mg, 0.1mmol) was dissolved in water (15ml). To this solution was added EDTA (58.4mg, 0.2mmol) and $(CH_3)_4NOH$ (72mg, 0.8mmol). White precipitate was collected by filtration and washed thoroughly with H_2O. Drying the product at 80℃ yielded 45mg, 37.7%.

4. Preparation of the single crystal of CyP-TD[n]

The single crystal of **CyP$_5$TD[5]** was formed from a solution of **CyP$_5$TD[5]** (58.5mg,0.05mmol) and $CaCl_2$ (22 mg, 0.20 mmol) in

distilled water (10mL) which was allowed to slowly evaporate in air at room temperature, yielding colorless crystals within several weeks. The XRD result is shown in Fig. S15.

The single crystals of **CyP$_4$TD[4]** (0.05 mmol in the form of Ca^{2+} complexes obtained from the template-direct synthesis) were prepared from water solutions (10ml) by the slow diffusion of acetone vapor at room temperature. Colorless crystals were obtained after several weeks. The XRD result is shown in Fig. S15.

5. The solubility measurements of the CyP-TD[n]

Excessive amounts of CyP-TD[n] (n = 4 and 5) in a deuterated solvent (0.2 mL) was stirred in a constant temperature water bath (25 °C) for 24 hours. After the removal of undissolved CyP-TD[n] by centrifuge, a 0.1 mL aliquot of the saturated CyP-TD[n] solution was diluted with 0.4 mL of D_2O, and then a standard solution of tetraethylammonium bromide in D_2O (0.20 M, 20 μL) was added. Tetramethylammonium chloride was used instead of tetraethylammonium bromide in those measurements using methanol-d_4 or DMSO-d_6. The amount of dissolved CyP-TD[n] in the solution was estimated by comparing the intensities of its signals with that of the tetraethylammonium ion (or tetramethylammonium ion) in ^{1}H NMR spectrum which was recorded at 25 °C.

6. Supplementary Figures

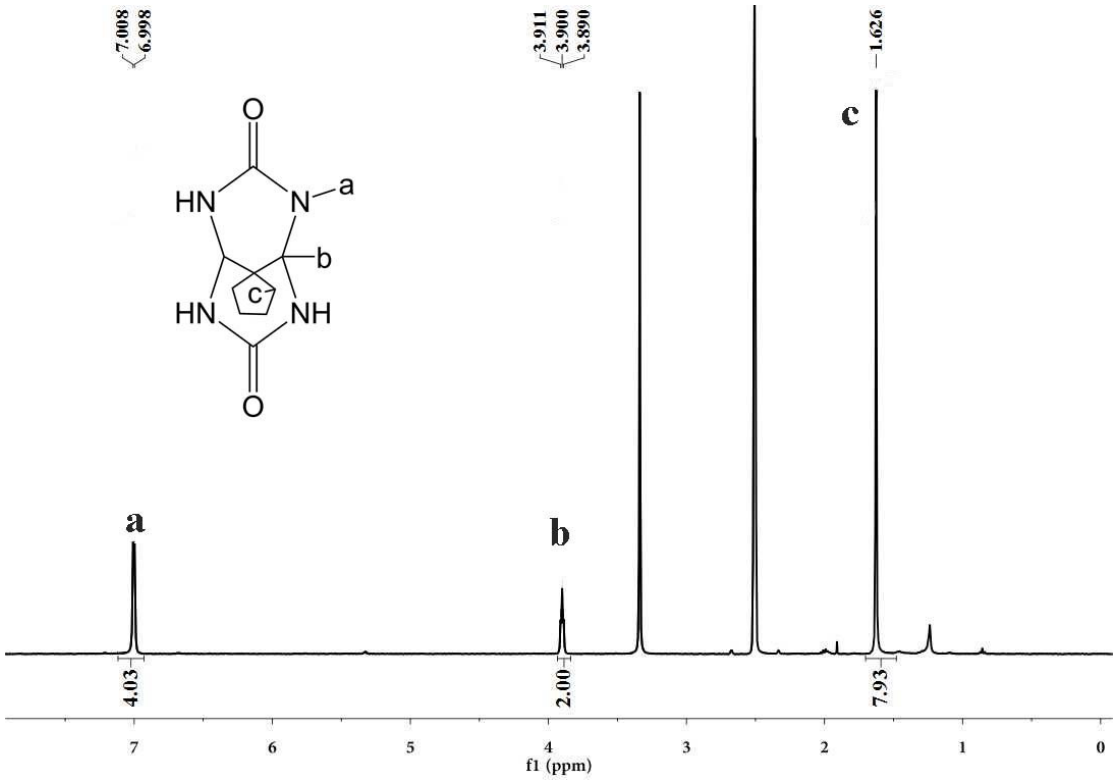


Fig. S1 ^{1}H NMR spectra (400MHz, 99% DMSO-d_6, 298 K) of **CyP-TD**.

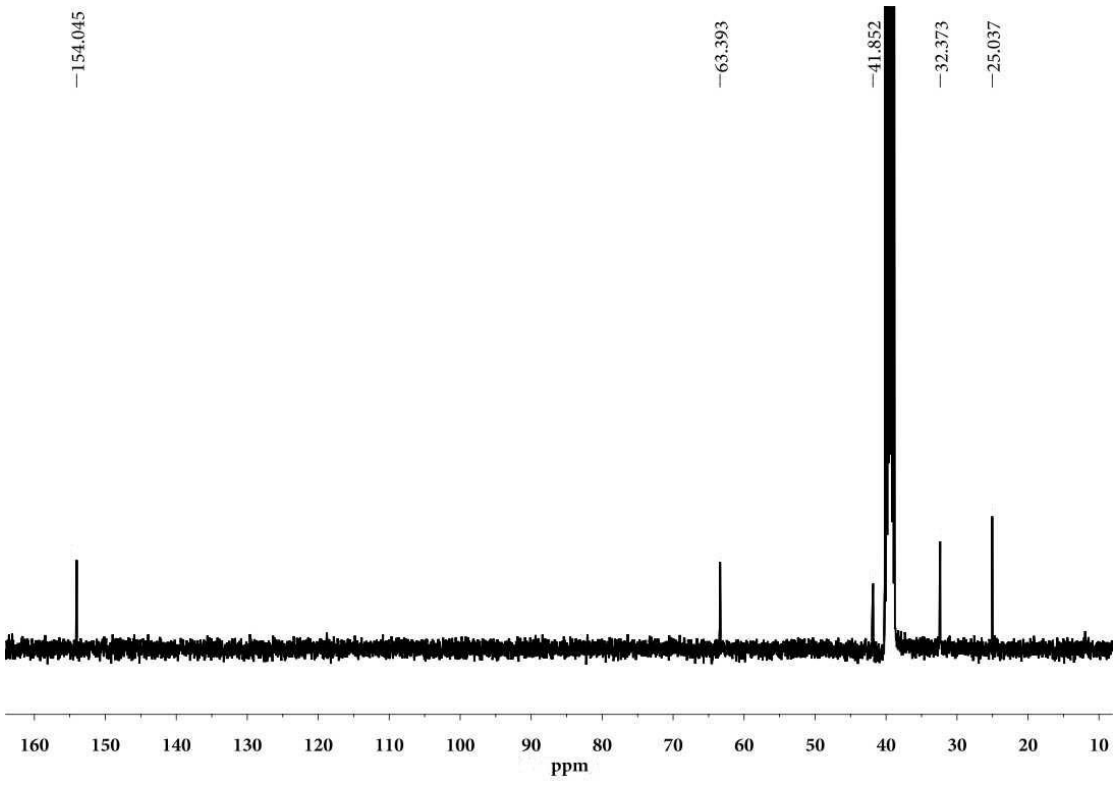


Fig. S2 ^{13}C NMR spectra (100MHz, 99% DMSO-d_6, 298 K) of **CyP-TD**.

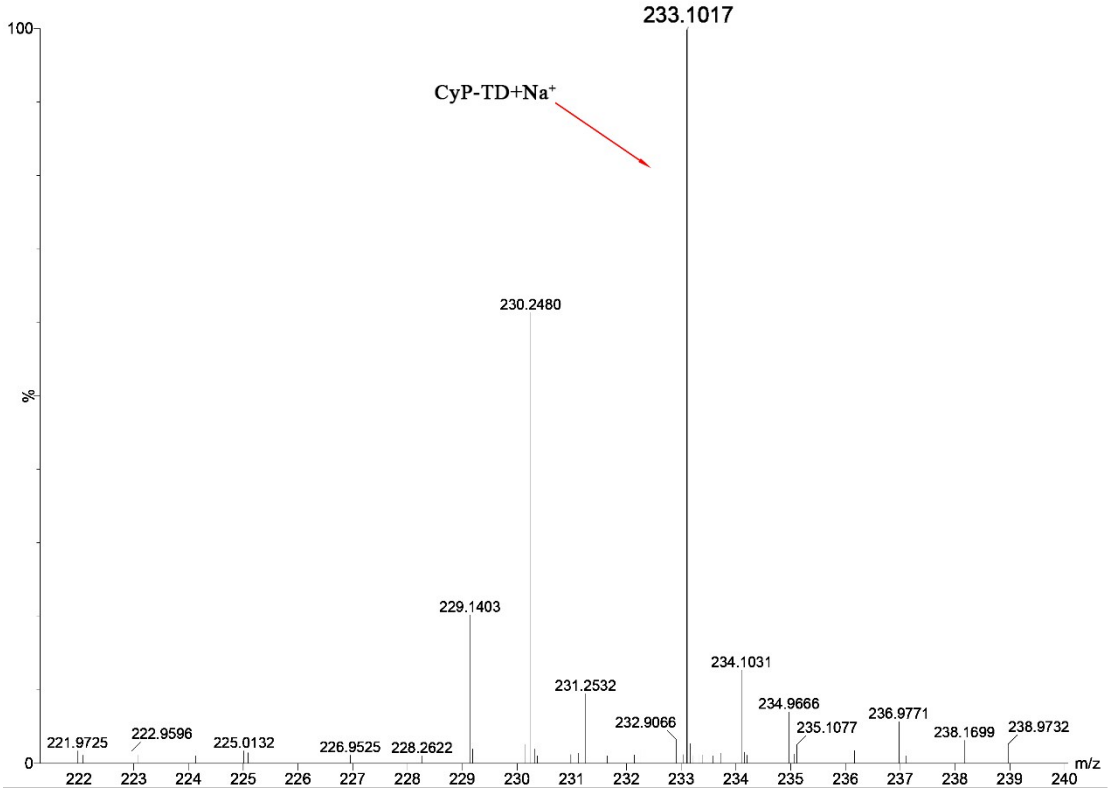


Fig. S3 ESI-MS of **CyP-TD**: m/z 211.1181[M+H] $^{+}$.

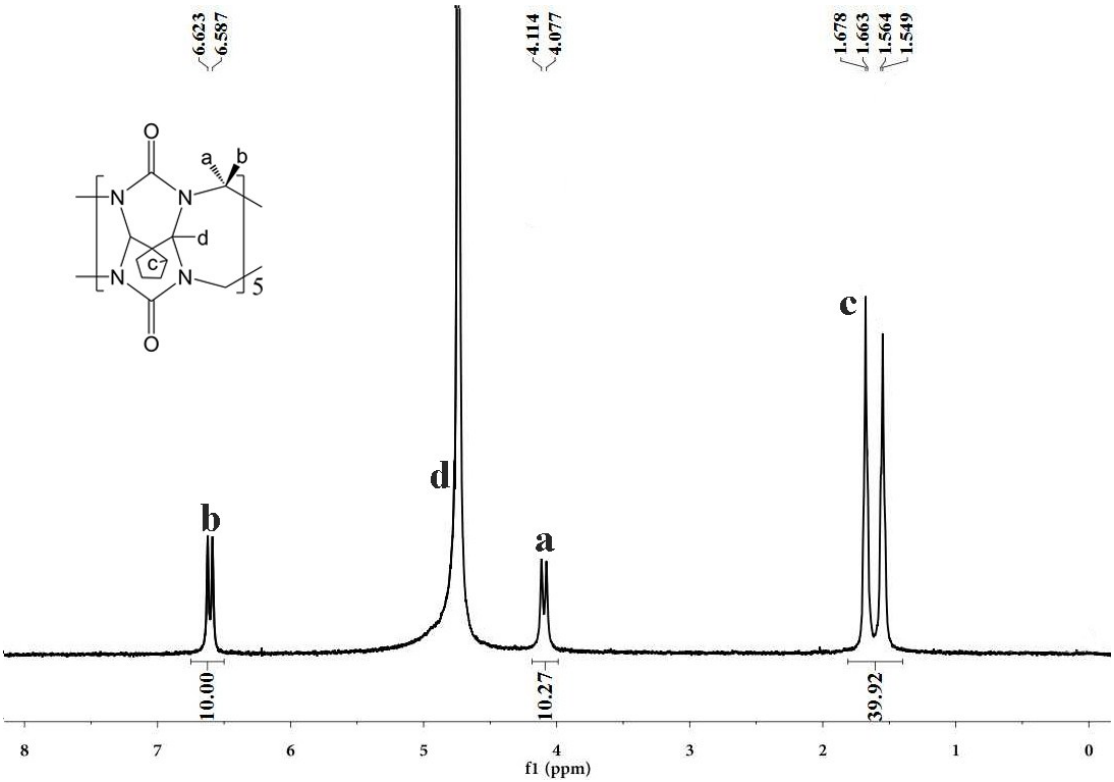


Fig. S4 ^{1}H NMR spectra (400MHz, 99% D_2O, 298 K) of **CyP_5TD[5]**.

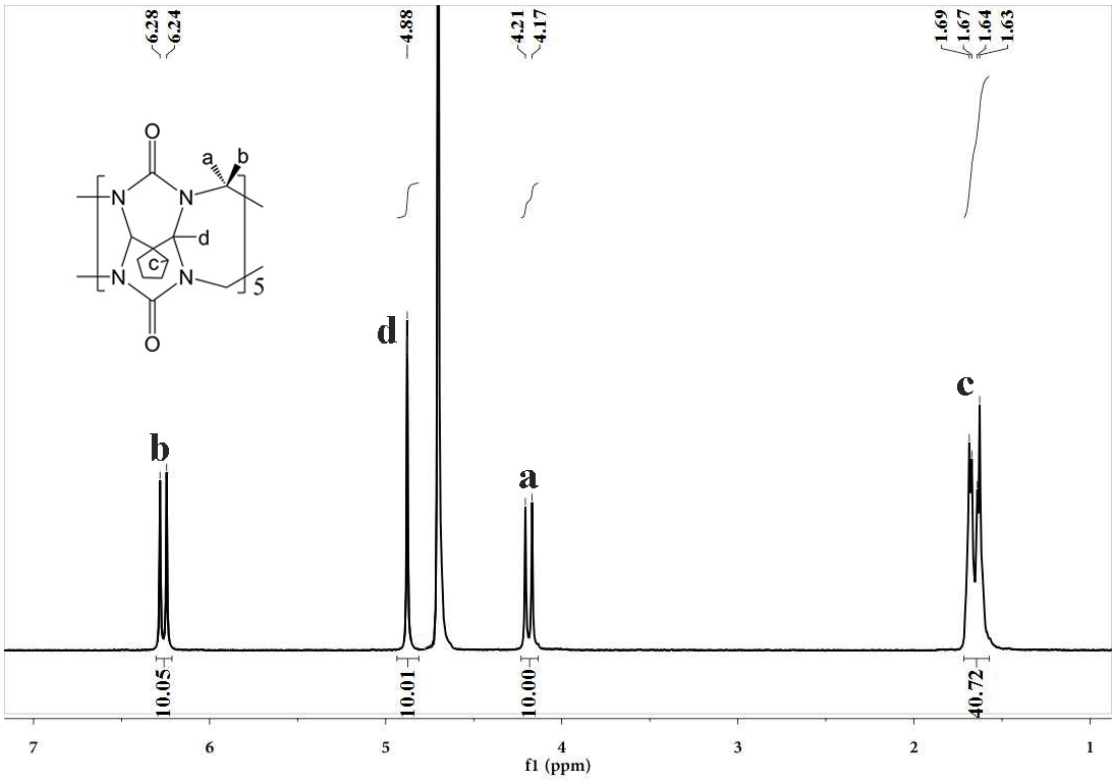


Fig. S5 ^{1}H NMR spectra (400MHz, 99% D_2O, 298 K) of **$CyP_5TD[5]$** in the presence of Ca^{2+}.

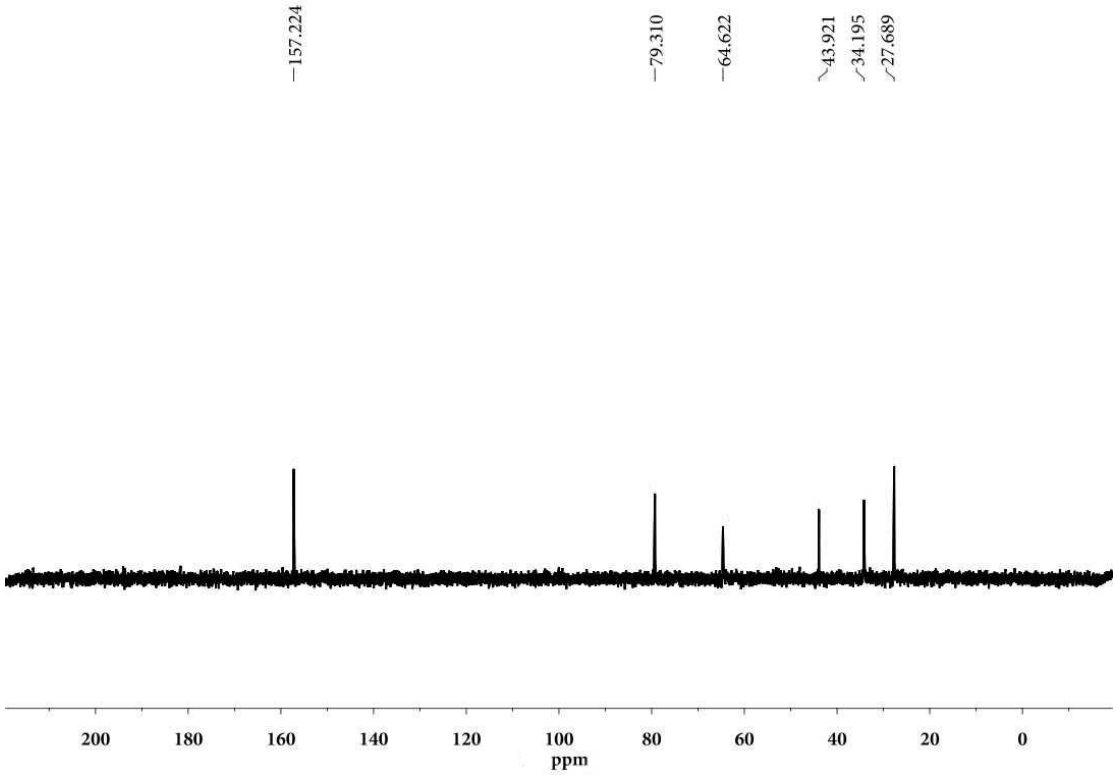


Fig. S6 ^{13}C NMR spectra (100MHz, 99% D_2O, 298 K) of **$CyP_5TD[5]$**.

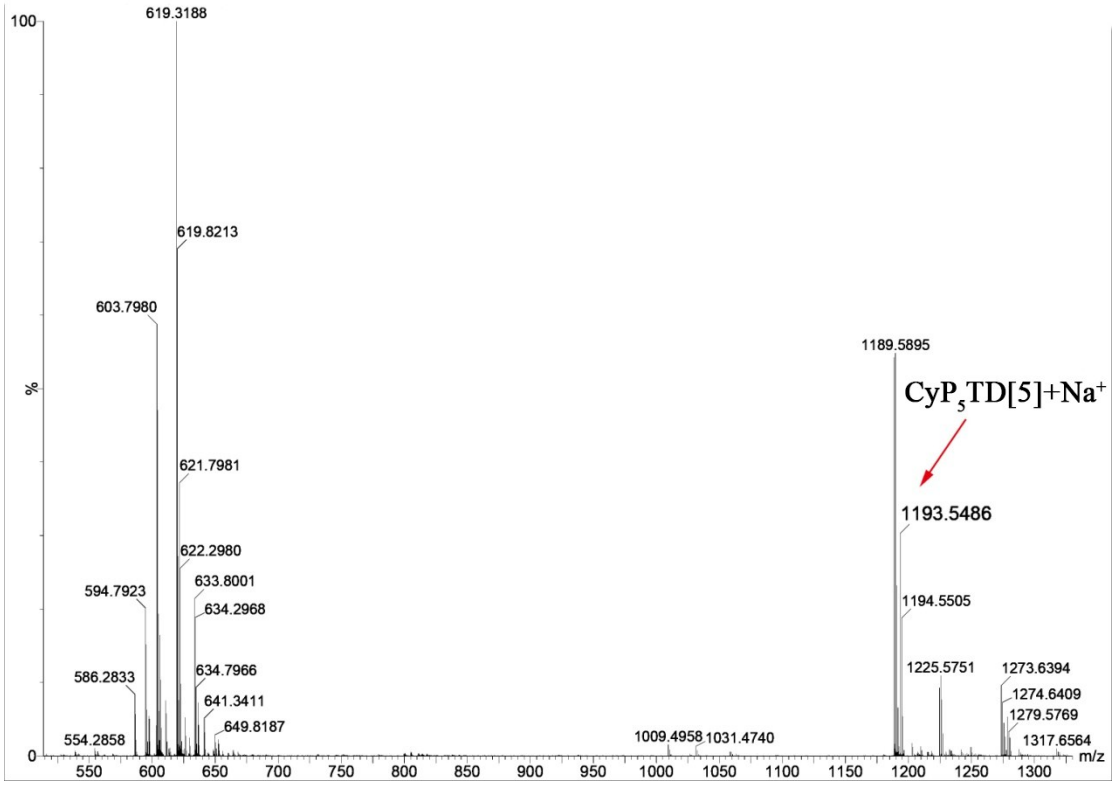


Fig. S7 ESI-MS of **$CyP_5TD[5]$**: 1193.5486 $[M+Na]^+$.

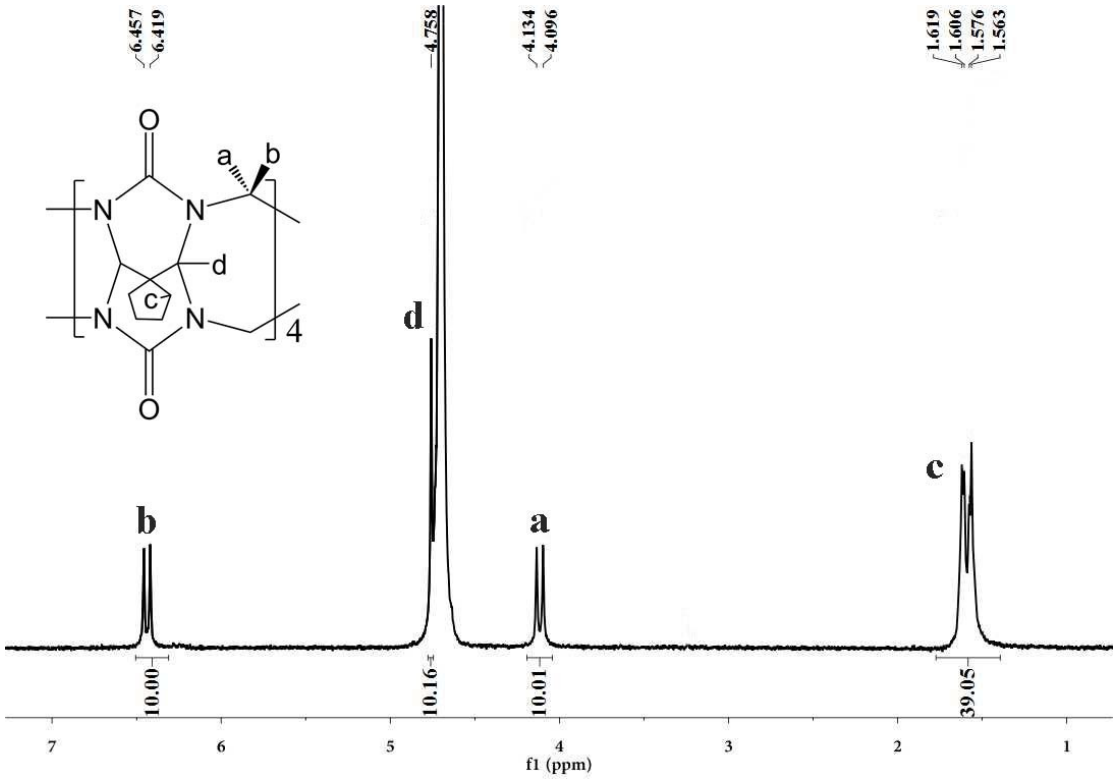


Fig. S8 ^1H NMR spectra (400MHz, 99% D_2O, 298 K) of **$CyP_4TD[4]$**.

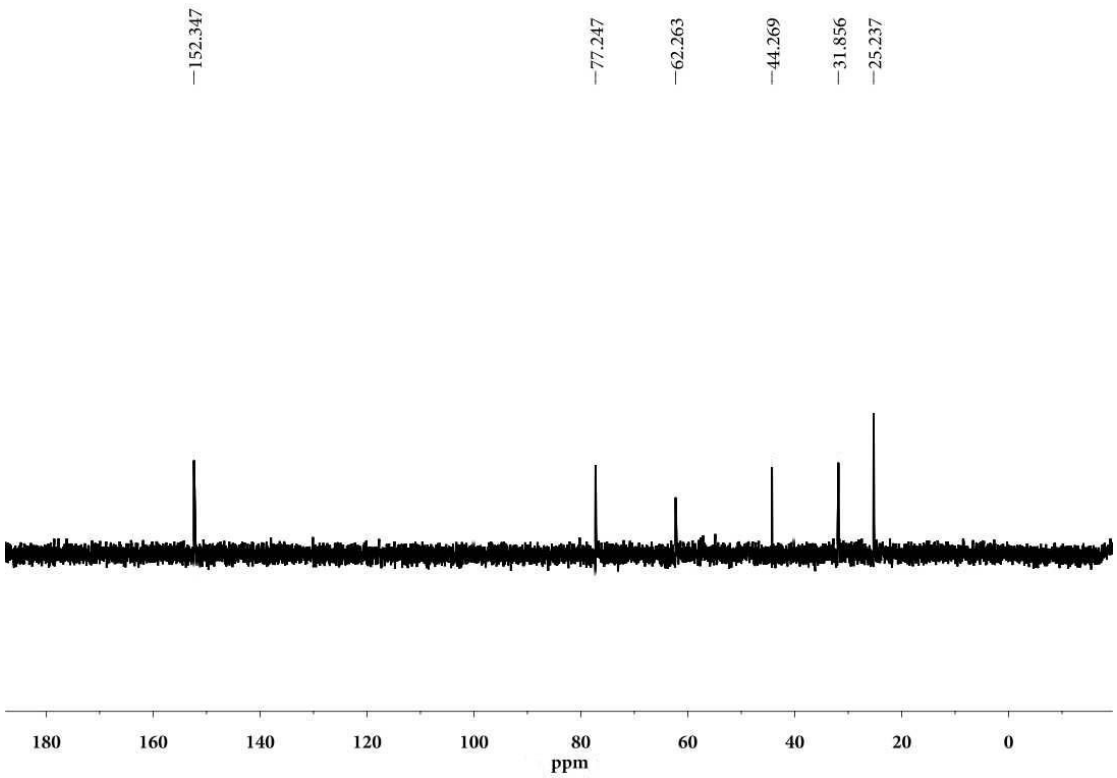


Fig. S9 ^{13}C NMR spectra (100MHz, 99% D_2O, 298 K) of **$CyP_4TD[4]$**.

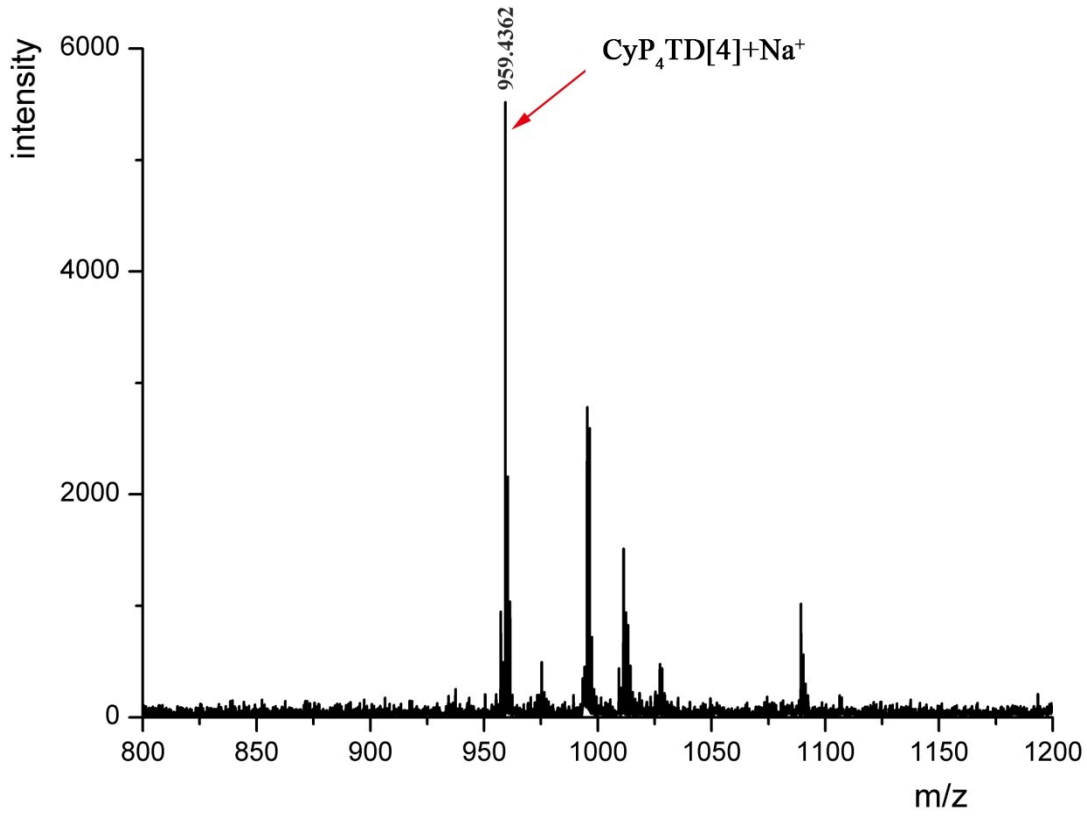


Fig. S10 MALDI-TOF of **$CyP_4TD[4]$**: m/z 959.4362 $[M+Na]^+$.

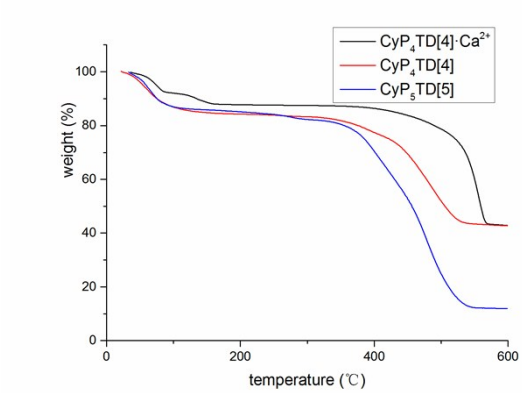


Fig. S11 Thermogravimetric analysis of **$CyP_4TD[4]$** in the presence and absence of Ca^{2+} and **$CyP_5TD[5]$**.

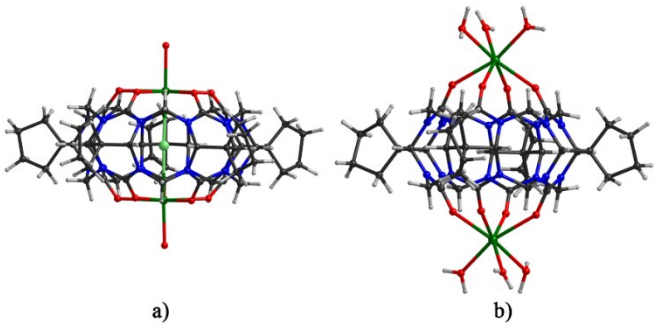


Fig. S12 The single crystal structures of **$CyP_5TD[5]$**-$CaCl_2$ (a) and **$CyP_4TD[4]$**-$CaCl_2$ (b).

华东理工大学分析测试中心

原子光谱室

试 验 数 据

部 门	精细所
试 样 名 称	ok
仪 器 型 号	1、Varian 710ES ☑ 2、Agilent 725ES ☐ 3、ZEEnit 600 ☐ 4、 Mercur ☐
编 号	81486
试 验 日 期	2016.4.28

试样结果：

WQ-XLX-01 Ca: 2.7mg/L

以下空白

ECUST-560-01

Fig. S13 The result of the atomic absorption spectrum test for the calcium content of **CyP$_4$TD[4]** solution (3.3×10^{-5}mol/L). The concentration of Ca^{2+} was 2.7mg/L (6.75×10^{-5}mol/L), indicating an about 1:2 complexation between **CyP$_4$TD[4]** and Ca^{2+} .

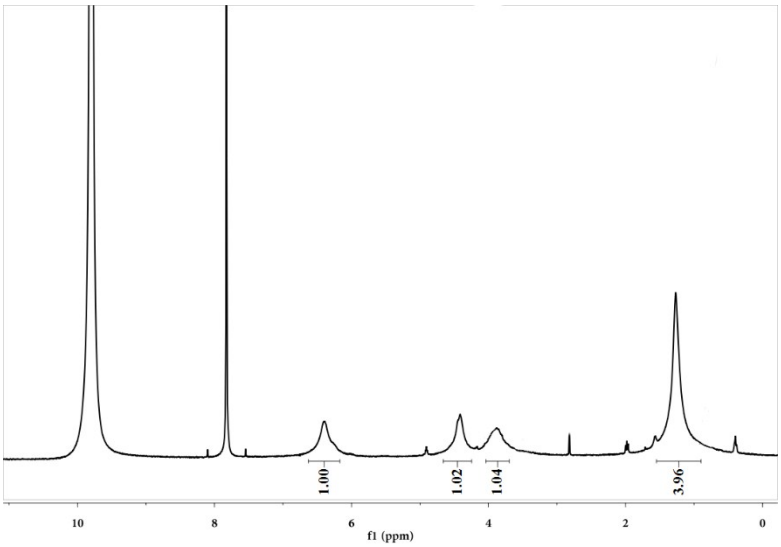


Fig. S14 ^{1}H NMR spectra (400MHz, 99% DCOOD, 298 K) of **CyP$_4$TD[4]**.

华东理工大学分析测试中心

元素分析实验数据

编号:20160410

送 样 单 位	化学院
样 品 名 称	WYF-01，XLX-01
测 试 内 容	N，C，H 元素含量
测 试 仪 器	德国 elementar vario EL III

分析结果：

样品名称	称样量（mg）	N%	C%	H%
WYF-01	1.719	23.63	56.10	5.96
WYF-01	1.586	23.69	56.32	6.18

以下空白

测试日期	2016 年 12 月 14 日

Fig. S15 The Element Analysis of **CyP$_4$TD[4]** (WYF-01). Calcd for $C_{44}H_{56}O_8N_{16}$(**CyP$_4$TD[4]**): C, 56.41; H, 5.98; N, 23.93. Found: C, 56.10; H, 5.96; N, 23.63.

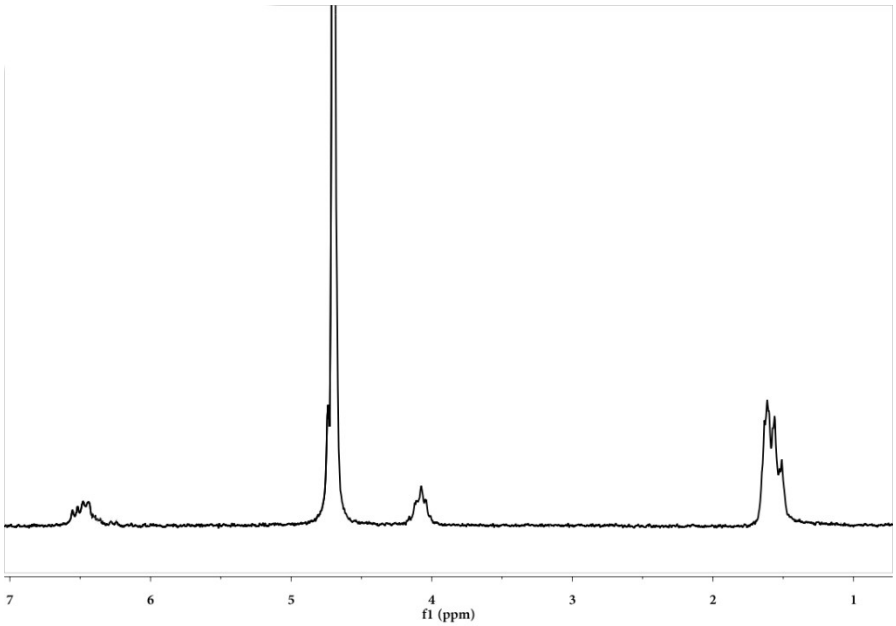


Fig. S16 ^{1}H NMR spectra (400MHz, 99% DCOOD, 298 K) of white precipitate from filtrate in the reaction of **CyP$_4$TD[4]** (bottom).

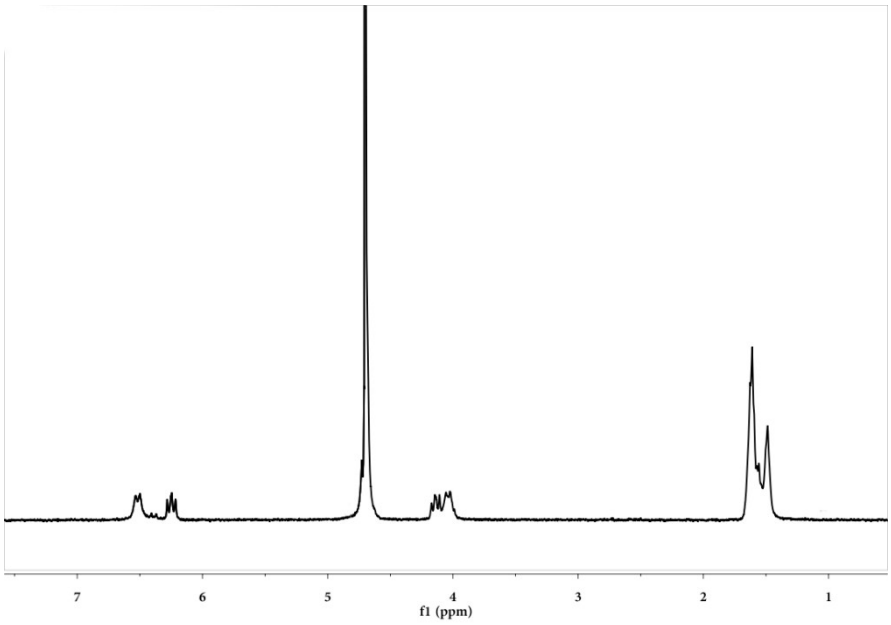


Fig. S17 ^{1}H NMR spectra (400MHz, 99% DCOOD, 298 K) of white precipitate from the filtrate in the reaction of **CyP$_5$TD[5]**.

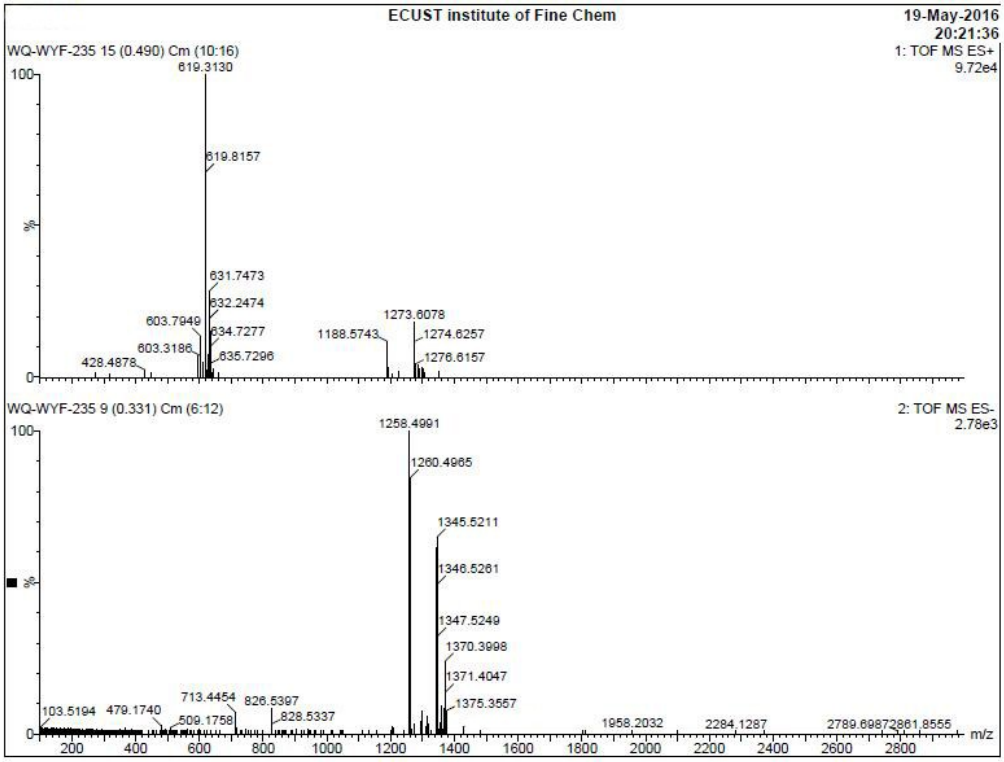


Fig. S18 ESI-MS of the filtrate in the reaction of **$CyP_5TD[5]$**.

7. Details of the X-ray Crystal Structure

	$CyP_5TD[5]$	$CyP_4TD[4]$
Chemical formula	$C_{55}Ca_2Cl_4H_{76}O_{25}N_{20}$	$C_{44}H_{76}Ca_2Cl_4\ N_{16}O_{18}$
Formula weight	1639.31	1339.17
Temperature	173(2) K	203(2) K
Wavelength	0.71073Å	0.71073Å
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 21/c
Unit cell dimensions	a=15.086(4) Å b=17.048(4) Å c=17.876(8) Å α= 103.160(5) ° β=110.463(6)° γ= 107.684(4) °	a=12.6660(10) Å b=20.7418(16) Å c=11.6720(9) Å α=90 ° β=111.6460(10) ° γ=90 °
Volume	3806(2) $Å^3$	2850.2(4) $Å^3$
Z	2	2
Density (calculated)	1.385 Mg/cm^3	1.560 Mg/cm^3
Absorption coefficient	0.371 mm^{-1}	0.473 mm^{-1}
F(000)	1668	1408.0

Crystal size	0.600×0.350×0.270 mm^3	0.250×0.200×0.080 mm^3
Theta range for data collection	1.311 to 25.999°	1.964 to 26.439°
Index ranges	-18<=h<=18, -20<=k<=21, -22<=l<=15	-14<=h<=15, -24<=k<=25, -14<=l<=14
Reflections collected	23780	17930
Independent reflections	14662[R(int) = 0.0387]	5836[R(int) = 0.0202]
Completeness to theta = 25.242°	97.9 %	99.5 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.604	0.745 and 0.689
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	14662 / 2 / 919	5836 / 57 / 454
Goodness-of-fit on F^2	1.483	1.068
Final R indices [I>2sigma(I)]	R1 = 0.1187 wR2 = 0.3621	R1 = 0.0437 wR2 = 0.1323
R indices (all data)	R1 = 0.1471 wR2 = 0.3927	R1 = 0.0533 wR2 = 0.1461
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.797 and -0.985 e.$Å^{-3}$	1.031 and -0.377 e.$Å^{-3}$

References

[1] D. Domin, D. Benito-Garagorri, K. Mereiter, J. Fröhlich, K.Kirchner，*Organometallics*. 2005, **24**, 3957.