

Supporting Information

Ultrafine Pt Nanoclusters Confined in a Calixarene-based {Ni₂₄}

Coordination Cage for High-efficient Hydrogen Evolution Reaction

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Table of Contents

I.	Experimental Section	S2
II.	Crystallographic Analysis	S3
III.	Structural figures for CIAC-121 and - 122.....	S7
IV.	TGA-DSC Analysis	S10
V.	FT-IR Spectra	S11
VI.	MALDI mass spectra of CIAC-121.....	S12
VII.	MALDI mass spectra of Pt NC@CIAC-121	S13
VIII.	Far-Infrared spectra of the Pt NC@CIAC-121, CIAC-121, H₄TC4A-SO₂ and H₂TDC	S14
IX.	UV-Vis absorption spectra of CIAC-121 and Pt@CIAC-121.....	S14
X.	Polarization curves of Pt NC@CIAC-121 and the commercial Pt/C.....	S15
XI.	TEM images of the H₂PtCl₆ /CIAC-122 or H₄TC4A-SO₂-H₂TDC mixture or H₄TC4A-SO₂ systems.....	S15
XII.	Comparison of the polarization curves for the Pt NPs from different systems.....	S16
XIII.	XPS spectrum of the as-synthesized Pt NC@CIAC-121.....	S16
XIV.	The S deconvoluted XPS spectra of the Pt NC@CIAC-121 and CIAC-121	S17
XV.	References	S17

Experimental Section

Chemicals and Materials:

p-tert-butylsulfonylcalix[4]arene (H₄TC4A-SO₂) was synthesized by literature method.^[S1] Chloroplatinic (IV) acid (H₂PtCl₆·6H₂O, Beijing Chemical Works), dichloromethane (DCM, A.R., Beijing Chemical Works), ethanol (A.R., Beijing Chemical Works), perfluorosulf acid-PtFE copolymer (Nafion, 5%w/w Solution, Alfa Aesar), sulfuric acid (H₂SO₄, 98%, Beijing Chemical Works), E-TEK Pt/C (nominally 20% by wt of 2-5 nm Pt nanoparticles on Vulcan XC-72R carbon support, Alfa Aesar).

Synthesis of CIAC-121 ($\{Ni_{24}(TC4A-SO_2)_6(TDC)_{12}(H_2O)_6\}$):

Green block crystals of **CIAC-121** were obtained from the reaction of the mixture of *p*-tert-butylsulfonylcalix[4]arene (H₄TC4A-SO₂) (0.085 g, 0.1 mmol), NiCl₂·6H₂O (0.10 g, 0.42 mmol), H₂TDC (0.026 g, 0.15 mmol), tetramethylammonium hydroxide solution (25%, 0.3mL), CH₃OH (2 mL) and CHCl₃ (2 mL), in a 20 mL Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The crystals were isolated by filtration and then washed with 1:1 methanol-chloroform and dry in air. Yield (0.103 g): ca. 72% with respect to H₄TC4A-SO₂. Elemental analysis: calculated (%) for C₃₁₂H₃₀₀Ni₂₄O₁₂₆S₃₆, C 43.43, H 3.50; found (after dried in vacuum): C 43.45, H 3.49. FT-IR (cm⁻¹): 3423(m), 2964(m), 2908(w), 2871 (w), 1608(m), 1587(w), 1493(s), 1453(m), 1391(s), 1365(m), 1264(s), 1130(m), 1079(m), 1024(w), 907(w), 841(w), 800(s), 744(m), 626(w), 569(s), 528(w), 438(w).

Synthesis of CIAC-122 ($\{[Co_{12}(TC4A-SO_2)_3(TDC)_6Cl_3]\}^3-$):

Purple block crystals of **CIAC-122** were obtained under the similar reaction conditions like **CIAC-121** from the reaction of the mixture of H₄TC4A-SO₂ (0.08 g, 0.1 mmol), CoCl₂·6H₂O (0.10 g, 0.42 mmol), H₂TDC (0.026 g, 0.15 mmol), tetramethylammonium hydroxide solution (25%, 0.3 ml), CH₃OH (3.5 mL) and CHCl₃ (3.5 mL), in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The crystals were isolated by filtration and then washed with 1:1 methanol-chloroform and dry in air. Yield (0.118 g): ca. 81% with respect to H₄TC4A-SO₂. Elemental analysis: calculated (%) for C₁₅₆H₁₄₄Cl₃Co₁₂O₆₀S₁₈, C 42.88, H 3.32; found (after dried in vacuum): C 42.91, H 3.33. FT-IR (cm⁻¹): 3430(m), 2963(s), 2909(w), 2871 (w), 1589(m), 1530(m), 1484(s), 1395(s), 1321(m), 1262(m), 1136(m), 1082(m), 1023(w), 907(w), 837(s), 799(s), 772(m), 743(w), 627(m), 571(s), 509(m), 433(w).

Synthesis of the Pt @CIAC-121 hybrid nanomaterials. Facilely, the ethanol solution of H₂PtCl₆ (200 μL, 4 mM) and 0.5 ml ethanol were added into the 3 mL DCM solution with 5 mg **CIAC-121** under the ambient atmosphere. Then, the reaction was kept for 24 h with the constant stirring. After that, rotary evaporator was used to remove solvent. The remaining solid was collected and washed with ethanol and water. Finally, the product was dispersed in ethanol for further use.

Synthesis of the control samples. To study the effect of cage structure on the formation of Pt nanoclusters, compound CIAC-122, the precursors for the cage such as the sole calixarene and the

mixture of calixarene and 2, 5-thiophenedicarboxylic acid were chosen as the template for the preparation of Pt nanoclusters. The syntheses of three control samples were performed by using the similar procedures of the Pt@CIAC-121. Briefly, 5 mg of CIAC-122 or H₄TC₄A-SO₂, or the mixture of H₄TC₄A-SO₂ and H₂TDC was dissolved in the 3 mL DCM and then 200 μ L, 4 mM H₂PtCl₆ was introduced under the constant stirring. After 24 h, the product was collected by centrifugation and washed with ethanol and water.

Material characterization.

High-resolution transmission electron microscopy (HRTEM) measurements were conducted on a JEM-2010 (HR) microscope operated at 200 kV. MALDI-TOF mass data were collected on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Thermo ESCALAB 250 spectrometer (VG Scientific) operated at 120 W. The composition of the products was obtained by using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, X Series 2, Thermo Scientific USA). Elemental analysis for C, H, N was recorded on a VarioEL instrument. TGA measurement is performed on a NETZSCH STA 449F3. FT-IR spectra (KBr pellets) were taken on a Bruker Vertex 70 spectrometer.

Electrochemical Measurements.

The whole electrochemical experiment was completed by using a CHI 750D electrochemical workstation with a standard three-electrode cell under the ambient atmosphere. The catalyst inks were prepared by dispersing a certain amount of solid catalysts (such as Pt NCs@CIAC-121, the coordination cage CIAC-121, Pt NCs@CIAC-122, Pt NCs-(H₄TC₄A-SO₂ + H₂TDC)) into the mixture of ethanol and water (v/v=2:1, 1ml), which contained 5 μ l of Nafion. The rotary disk electrode (geometric area = 0.196 cm²) coated with appropriate amount of catalyst inks was used as working electrode. A Pt coil and an Ag/AgCl with saturated KCl solution were used as counter electrode and reference electrode, respectively. Note that all the electrochemical data were given without any iR drop correction during the measurements. In this work, 0.5 M H₂SO₄ aqueous solution was used as electrolyte.

The electrocatalytic activity of the Pt NC@CIAC-121 was evaluated by using linear sweep voltammetry with a rotation speed of 1600 rpm and a scan rate of 5 mV/s in 0.5 M H₂SO₄. The accelerated durability tests (ADTs) were performed by using cyclic voltammetry between 0 to -0.6 V in 0.5 M H₂SO₄, aiming to acquire the stability of the products.

X-Ray crystallography

The intensity data were recorded on a Bruker D8 QUEST system with Cu-K α radiation (λ = 1.54178 Å) for CIAC-121 and a Bruker APEX-II CCD system with Mo-K α radiation (λ = 0.71073 Å) for CIAC-122. The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).^[S2] The high R_1 and wR_2 factor of compounds CIAC-121 and -122 might be due to the weak high-angle diffractions and the disorder of *p-tert*-butyl atoms. It was not possible to model the disordered solvent molecules appropriately even with the low temperature data obtained at about 120 K and 190 K for CIAC-121 and CIAC-122, respectively. The diffraction data were treated by the “SQUEEZE” method as implemented in PLATON^[S3] to remove the contributions of the highly disordered

solvent molecules. The SQUEEZE results for both structures are listed below. The selected crystallographic parameters are given in Table S1. The crystallographic information files (CIFs, CCDC 1511483-1511484) and the IUCr CheckCIF reports (PDF formats) can be found in the supplemental materials.

SQUEEZE RESULTS for CIAC-121

```
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
  1 -0.022 -0.015 -0.006      21430      5600 ''
```

SQUEEZE gives 5600 electrons per unit cell in **CIAC-121**, which can be assigned to the contributions of the disordered species in the voids. For there is one formula unit per cell, each formula would contain 5600 e⁻ for the disordered organic salts and solvent molecules. From the results of MALDI-TOF MS, one can find that there are 2 (CH₃)₄N⁺Cl⁻ (2×60 e⁻) in the void. The rest 5480 e⁻ correspond to about 304 CH₃OH (18 e⁻) molecules or 94 CHCl₃ (58 e⁻) molecules. When all the results of SQUEEZE, MALDI-TOF MS and TG are considered, the appropriate chemical formula can be proposed as {[Ni₂₄(TC4A-SO₂)₆(TDC)₁₂(H₂O)₆}·[(CH₃)₄N⁺Cl⁻]₂·76CH₃OH or {[Ni₂₄(TC4A-SO₂)₆(TDC)₁₂(H₂O)₆}·[(CH₃)₄N⁺Cl⁻]₂·22CHCl₃.

SQUEEZE RESULTS for CIAC-122

```
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
  1 0.250 0.750 0.000      1270      520 ''
  2 0.250 0.250 0.000      297      141 ''
  3 0.750 0.250 0.000      1270      520 ''
  4 0.750 0.750 0.000      297      141 ''
  5 0.000 0.907 0.250      219      32 '*
  6 0.500 0.407 0.250      219      32 '*
  7 0.006 0.251 0.153       7       0 ''
  8 0.506 0.751 0.153       7       0 ''
  9 0.003 0.368 0.173      14       1 ''
```

10	0.503	0.868	0.173	14	1''
11	0.000	0.422	0.255	13	1''
12	0.500	0.922	0.255	13	1''
13	0.250	0.250	0.500	1270	519''
14	0.750	0.750	0.500	1270	519''
15	0.250	0.750	0.500	297	140''
16	0.497	0.864	0.332	13	1''
17	0.750	0.250	0.500	297	140''
18	0.997	0.364	0.332	13	1''
19	0.494	0.751	0.347	6	0''
20	0.994	0.251	0.347	6	0''
21	0.000	0.093	0.750	219	33''*
22	0.500	0.593	0.750	219	33''*
23	0.006	0.749	0.653	7	0''
24	0.506	0.249	0.653	7	0''
25	0.003	0.632	0.673	14	1''
26	0.503	0.132	0.673	14	1''
27	0.000	0.578	0.755	12	1''
28	0.500	0.078	0.755	12	1''
29	0.497	0.135	0.832	13	1''
30	0.997	0.635	0.832	13	1''
31	0.494	0.249	0.847	6	0''
32	0.994	0.749	0.847	6	0''

(* indicates that the void can be occupied by CH₃OH.)

The structure refinement revealed a formula of C₁₅₆H₁₄₄Cl₃Co₁₂N₈O₆₀S₁₈, which is equivalent to Co²⁺₁₂(TC4A-SO₂⁴⁻)₃(TDC²⁻)₆Cl₃ carrying three negative charges. There are four formula units per unit cell. So 12 (CH₃)₄N⁺ (C₄H₁₂N, 43 e⁻) cations are required to balance the charge, which would occupy the voids (Nr. 2, 4, 15 and 17). Void-Nr. 5, 6, 21 or 22 can be occupied by only one CH₃OH (18 e⁻). Voids-Nr. 1, 3, 13 or 14 might be occupied by 28 CH₃OH (18 e⁻) or 9 CHCl₃ (58 e⁻) molecules. When the results of SQUEEZE and TG are considered, the appropriate chemical formula can be proposed as {[Co₁₂(TC4A-SO₂)₃(TDC)₆Cl₃]}³⁻·[(CH₃)₄N⁺]₃·17CH₃OH or {[Co₁₂(TC4A-SO₂)₃(TDC)₆Cl₃]}³⁻·[(CH₃)₄N⁺]₃·CH₃OH·5CHCl₃.

Table S1. Crystal data and structure refinement for **CIAC-121** and **-122**

	CIAC-121	CIAC-122
Common name	{Ni ₂₄ (TC4A-SO ₂) ₆ (TDC) ₁₂ (H ₂ O) ₆ }	{[Co ₁₂ (TC4A-SO ₂) ₃ (TDC) ₆ Cl ₃] ₃ } ³⁻
Formula*	C ₃₁₂ H ₃₀₀ Ni ₂₄ O ₁₂₆ S ₃₆	C ₁₅₆ H ₁₄₄ Cl ₃ Co ₁₂ O ₆₀ S ₁₈
formula wt.	8628.72	4369.30
T/K	120	190
Wavelength/ Å	1.54178 (Cu-Kα)	0.71073 (Mo-Kα)
Crystal system	hexagonal	monoclinic
space group	<i>P</i> -6 <i>m</i> 2	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	32.5352(11)	38.513(8)
<i>b</i> (Å)	32.5352(11)	22.180(4)
<i>c</i> (Å)	30.2469(10)	27.380(6)
α (°)	90.00	90.00
β (°)	90.00	102.49(3)
γ (°)	120.00	90.00
<i>V</i> (Å ³)	27728(2)	22835(8)
<i>Z</i>	1	4
<i>D_c</i> /g cm ⁻³	0.517	1.271
μ /mm ⁻¹	1.297	1.113
<i>F</i> (000)	4428	8892
Total Data	3935	11925
Unique Data	3865	7562
<i>R</i> _{int}	0.1453	0.1217
<i>GOF</i>	1.080	0.986
<i>R</i> 1 ^a [<i>I</i> >2σ(<i>I</i>)]	0.0743	0.0651
<i>wR</i> 2 ^b (all data)	0.1905	0.1826

$$^aR1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|; ^bWR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$$

* The formula is based on the contents without the unidentified disordered solvent molecules and (CH₃)₄N⁺ ions.

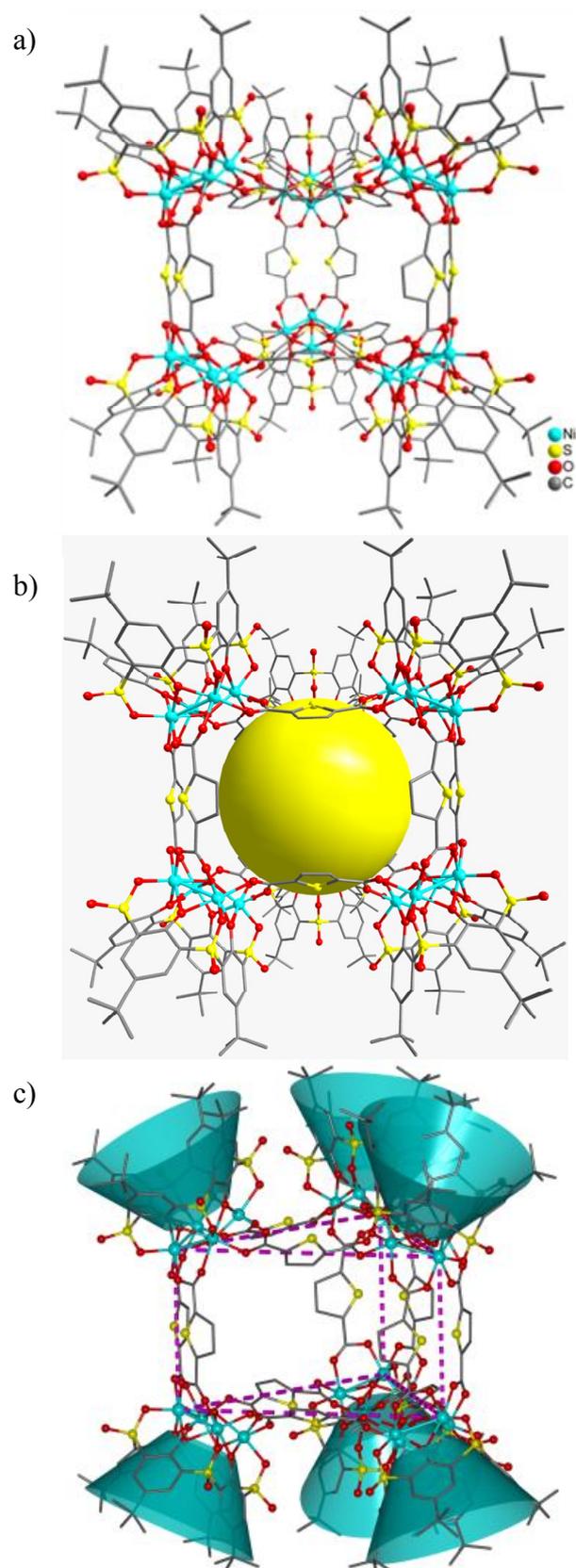


Figure S1. Molecular structure of **CIAC-121**. Cyan cones represent the calixarene molecules and big yellow sphere represents the cage cavity.

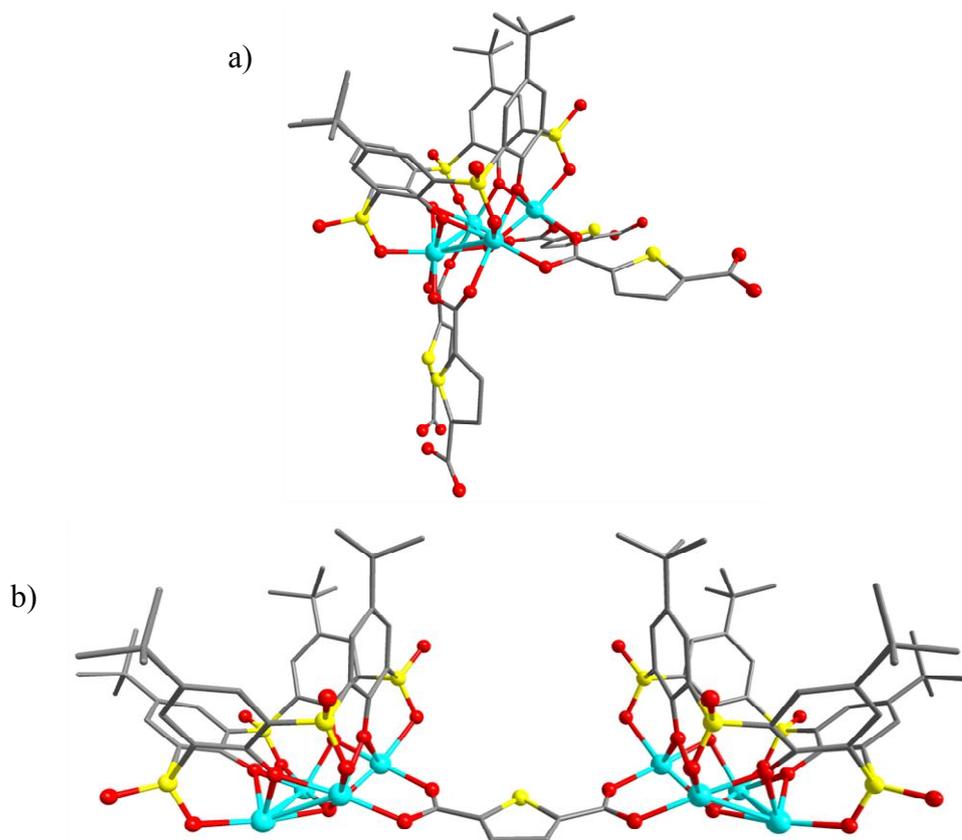


Figure S2. Coordination of a Ni₄-(TC4A-SO₂) SBU (a) and TDC ligand (b) in CIAC-121.

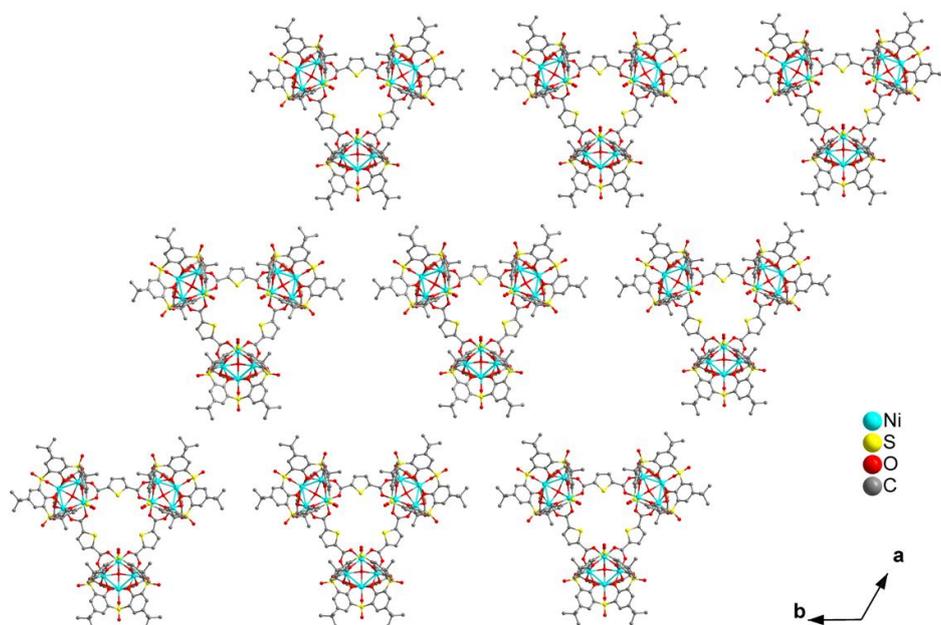


Figure S3. Packing diagram of the trigonal prisms in CIAC-121.

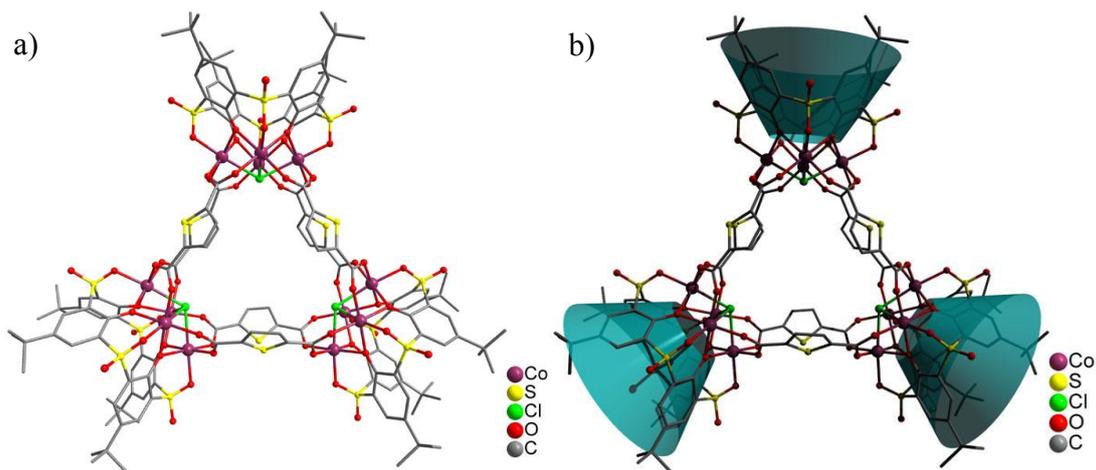


Figure S4. Molecular structure of CIAC-122. Cyan cones represent the calixarene molecules.

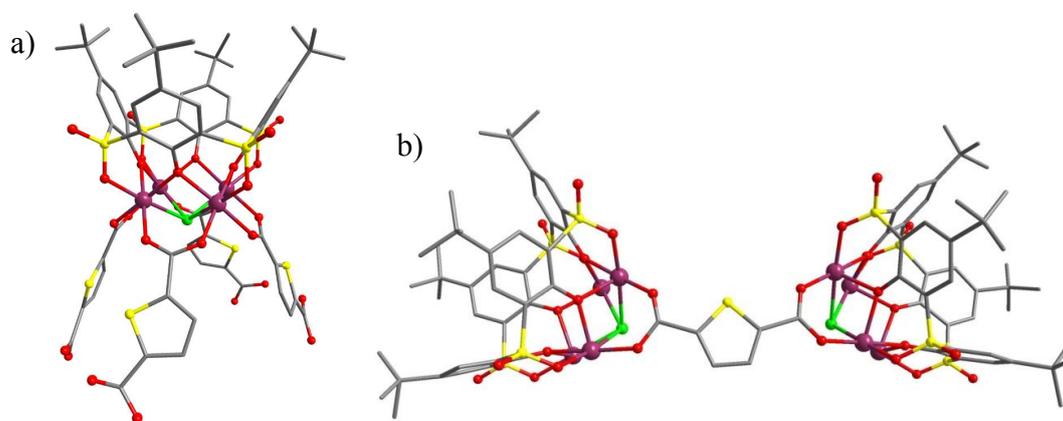


Figure S5. Coordination of a Ni_4 -(TC4A-SO₂) SBU (a) and TDC ligand (b) in CIAC-122.

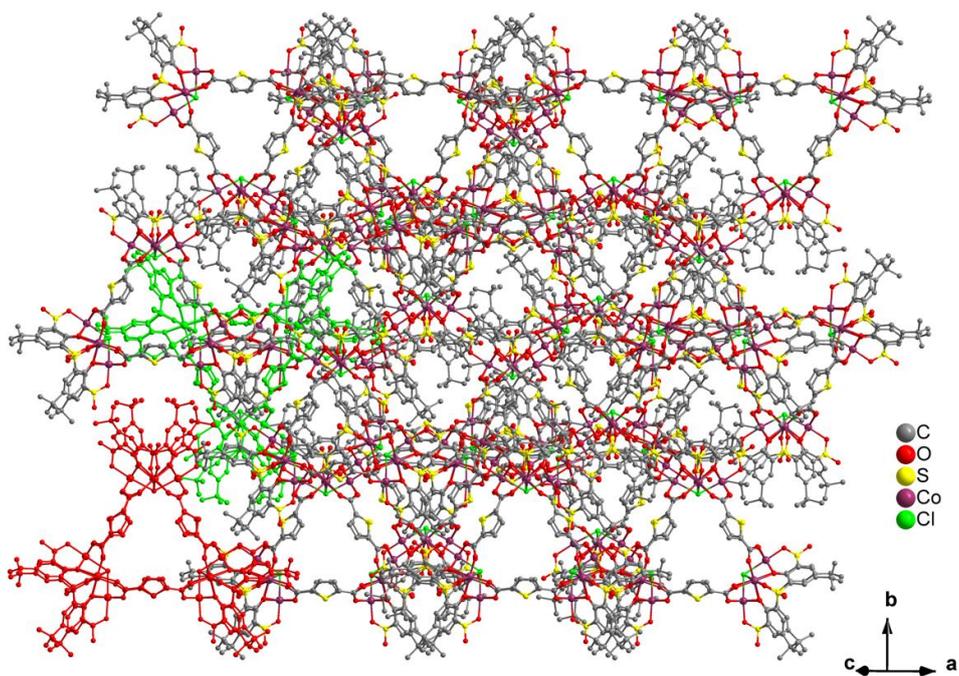


Figure S6. Packing diagram of the coordination triangles in CIAC-122.

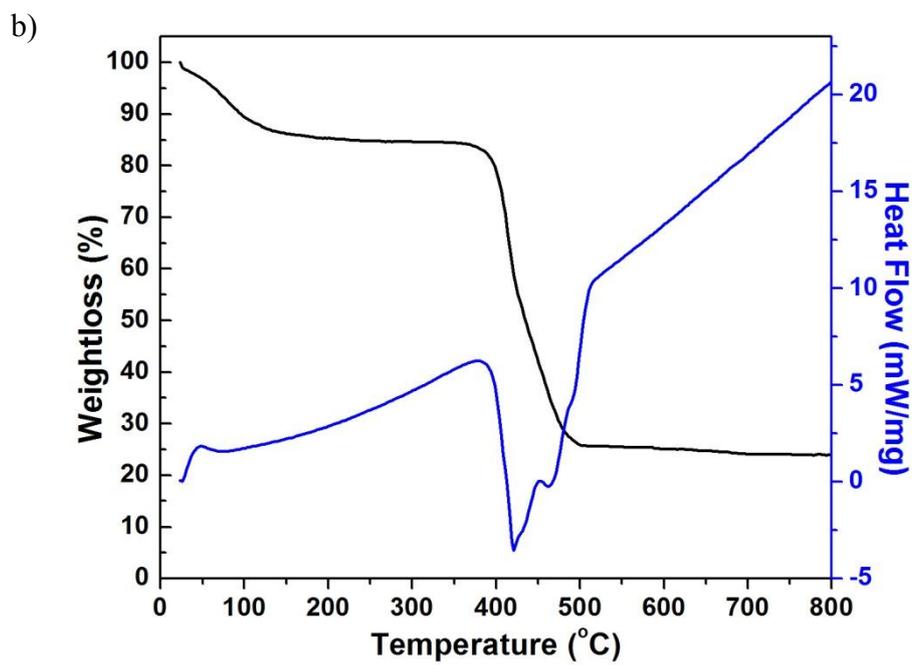
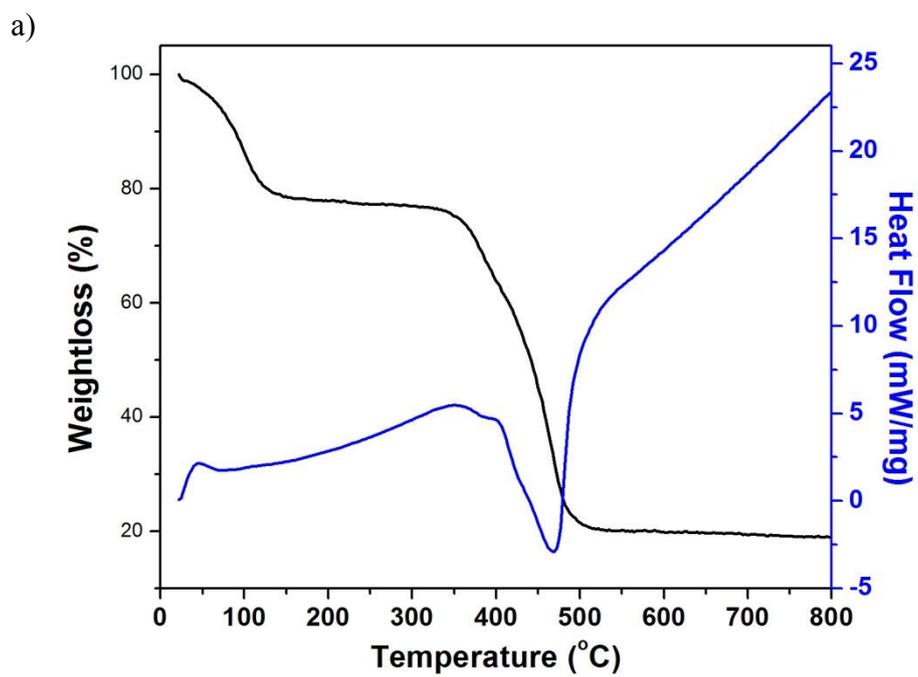


Figure S7. TG/DSC curves of CIAC-121 (a) and CIAC-122 (b) (in air).

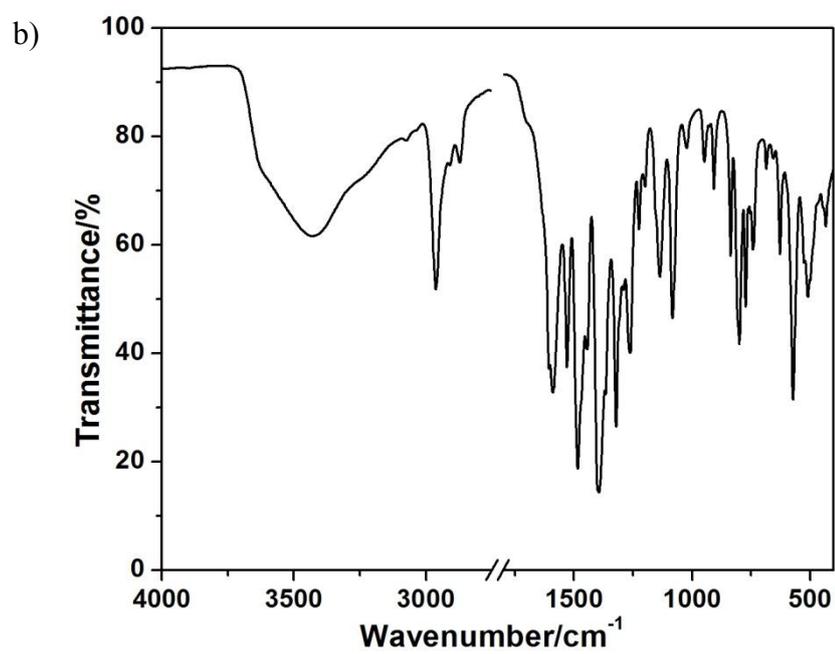
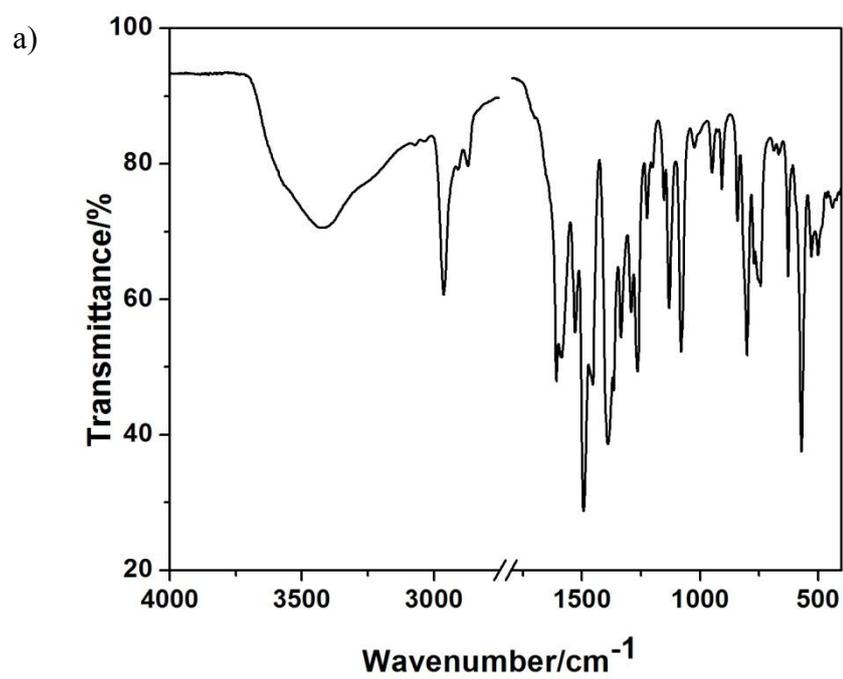
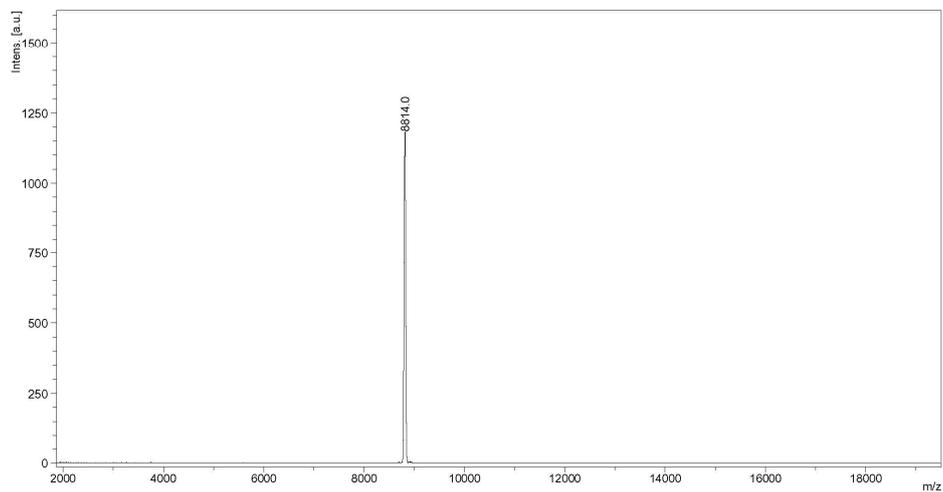


Figure S8. FT-IR spectra of Compounds **CIAC-121** (a) and **CIAC-122** (b).

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Comment 1

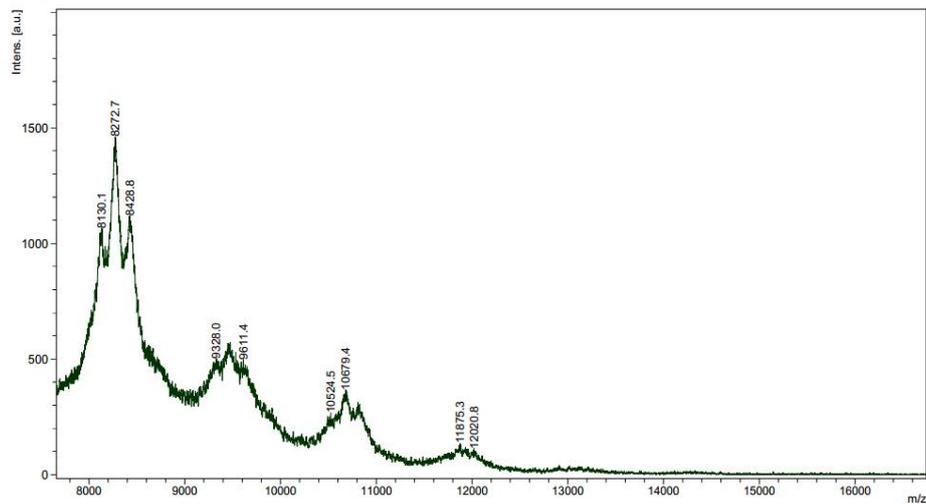
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Figure S9. MALDI mass spectrum of CIAC-121 presenting a sharp peak assigned to the $[\text{Ni}_{24}(\text{TC4A-SO}_2)_6(\text{TDC})_{12}(\text{H}_2\text{O})_6] \cdot [(\text{CH}_3)_4\text{N}^+\text{Cl}^-] \cdot [(\text{CH}_3)_4\text{N}^+]$ assembly.

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Figure S10. MALDI mass spectra of Pt NC@CIAC-121.

Compared to the sole sharp peak for CIAC-121 before Pt loading, MALDI mass spectra of Pt NC@CIAC-121 gives four groups of triplets with the mass higher than 8000. The first group with the mass in the range of 8000-9000 would be assigned to the coordination cages without Pt NCs, whose lower mass indicates that the coordination cage might be not so much stable at the presence of Pt NCs and some pieces might be produced under the beam and removed from the cage structure. The peaks around 9461.9, 10679.4 and 11875.3 would be assigned to the composites encapsulating Pt₆, Pt₁₂ and Pt₁₈, respectively. There are no obvious peaks observed in the range higher than 13000.

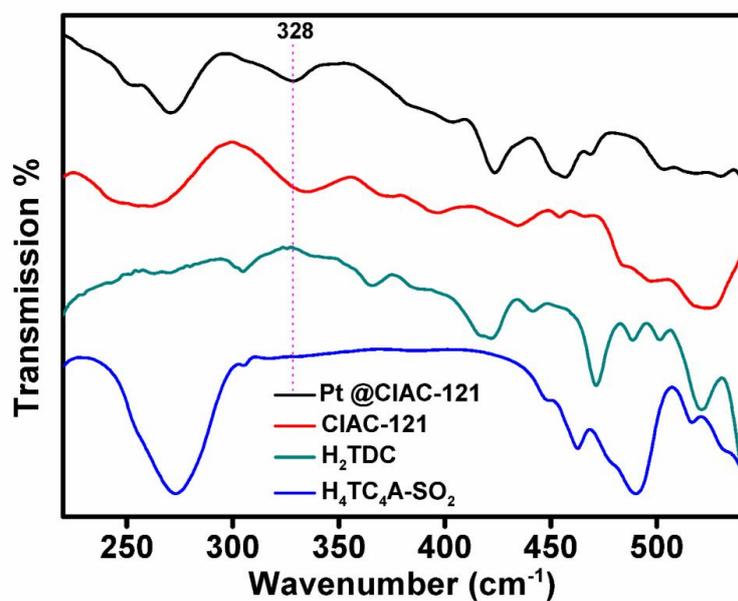


Figure S11. Far-Infrared spectra of the Pt NC@CIAC-121, CIAC-121, H₄TC₄A-SO₂ and H₂TDC.

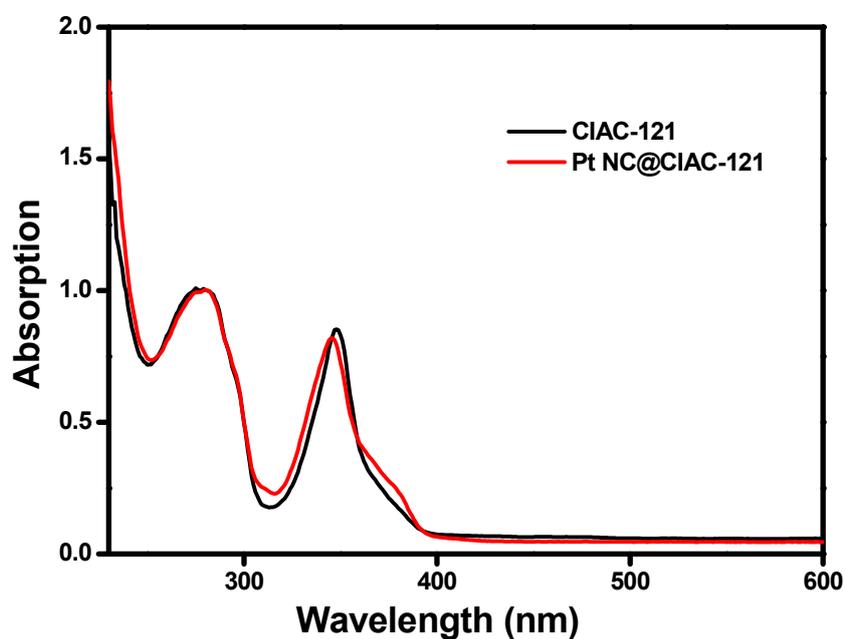


Figure S12. UV-Vis absorption spectra of CIAC-121 and Pt@CIAC-121 in ethanol. $C_{\text{sample}} = 10 \mu\text{g/ml}$.

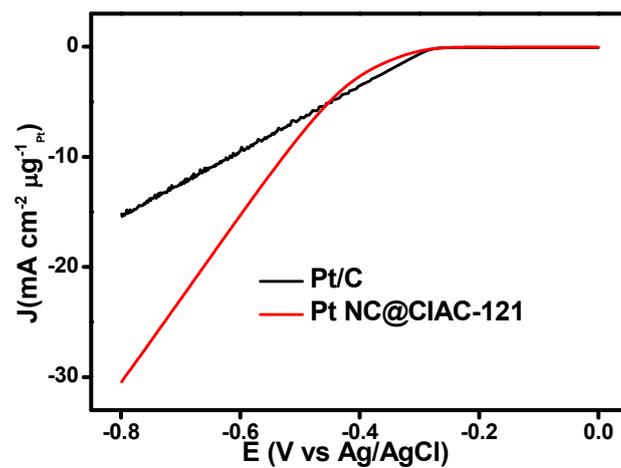


Figure S13. Polarization curves of the Pt NC@CIAC-121 and the commercial Pt/C after 5000 cycle tests in 0.5 M H₂SO₄.

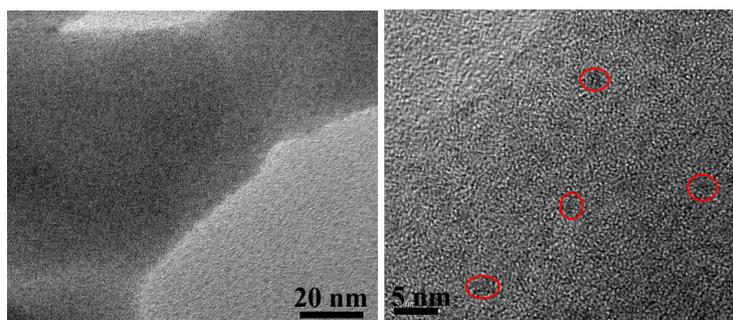


Figure S14. TEM images of the Pt@CIAC-122.

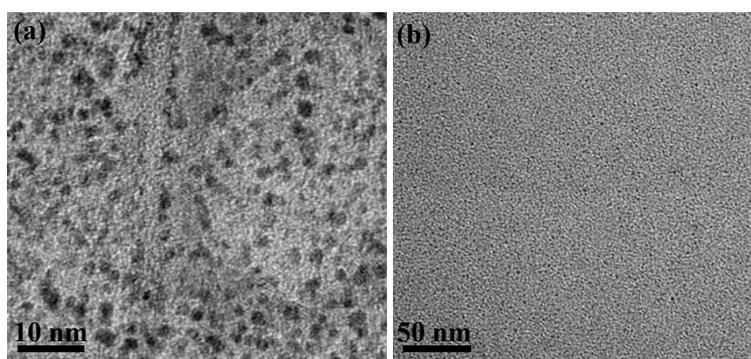


Figure S15. TEM images of the Pt NP/(H₄TC₄ASO₂-H₂TDC mixture) (a) and the H₂PtCl₆/H₄TC₄A-SO₂ system (b). In fact, (b) shows only the image of carbon film.

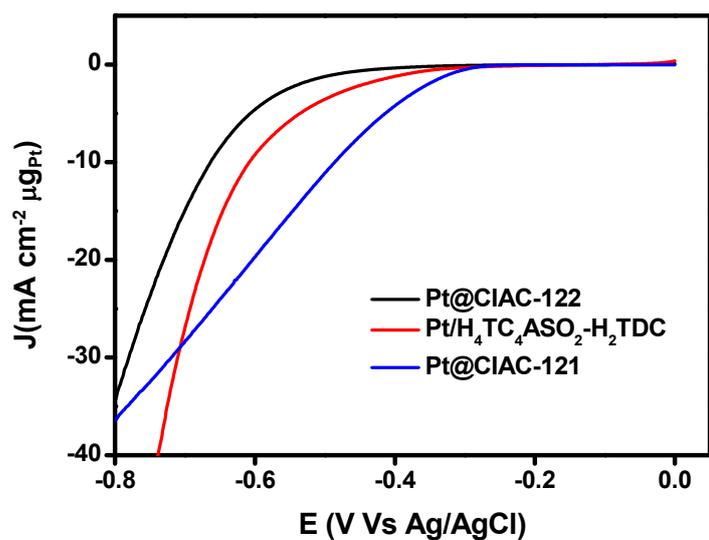


Figure S16. The comparison of the polarization curves for the Pt@CIAC-122 (black line), Pt/ $\text{H}_4\text{TC}_4\text{ASO}_2\text{-H}_2\text{TDC}$ (red line) and Pt@CIAC-121 (blue line).

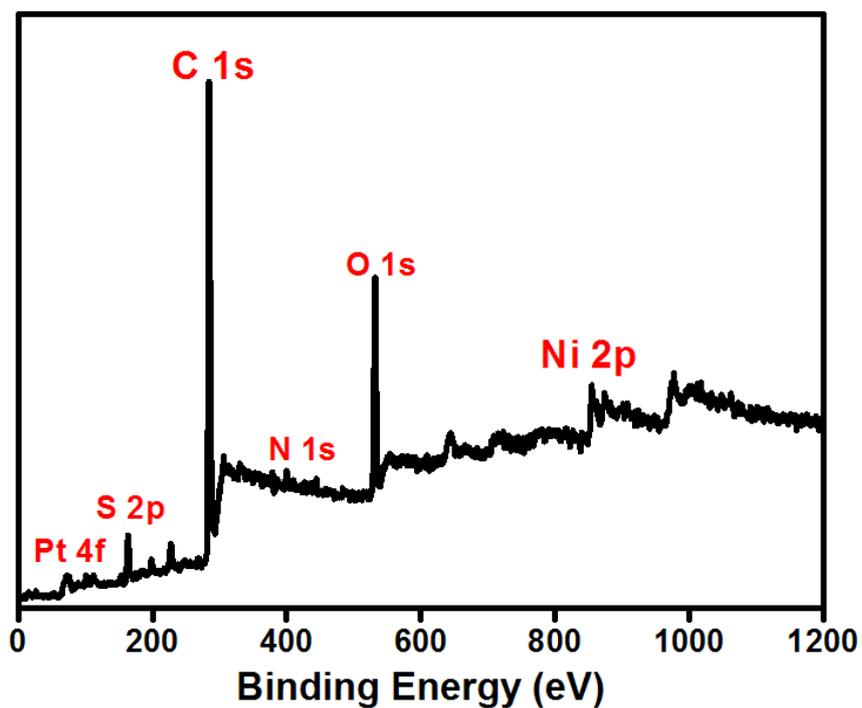


Figure S17. The X-ray photoelectron energy spectrum of the as-synthesized Pt NC@CIAC-121.

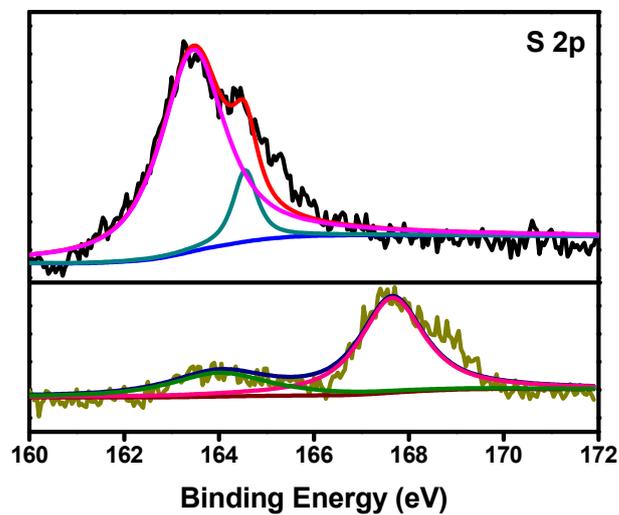


Figure S18. The S deconvoluted X-ray photoelectron energy spectrum of the **Pt NC@CIAC-121** (upper) and **CIAC-121** (bottom).

References:

- [S1] (a) Iki, N.; Kumagai, H.; Morohashi, N.; Ejima, K.; Hasegawa, M.; Miyanari, S.; Miyano, S. *Tetrahedron Lett.* **1998**, *39*, 7559. (b) Morohashi, N.; Iki, N.; Sugawara, A.; Miyano, S. *Tetrahedron*, **2001**, *57*, 5557.
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- [S3] van der Sluis, P.; Spek, A. L. *Acta Cryst. Sect. A*, **1990**, *46*, 194.