

## Supporting Information

### **Direct Access to Metal or Metal Oxide Nanocrystals Integrated with One-Dimensional Nanoporous Carbons for Electrochemical Energy Storage**

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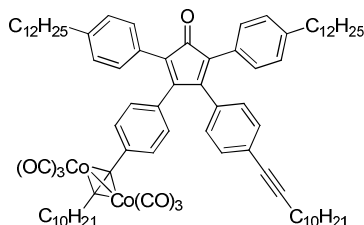
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## Synthesis

### Co-Cp

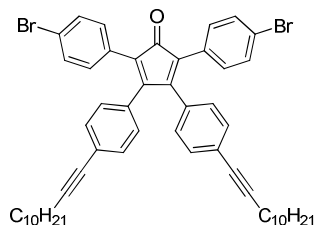


100 mg (0.95 mmol) of 3,4-bis(4-dodecynylphenyl)-2,5-bis(4-dodecylphenyl)-cyclopentadienone (Cp)<sup>1</sup> and 33 mg (0.95 mmol) dicobalt octacarbonyl were dissolved in dichloromethane (5 mL) and stirred at room temperature for 12 h under an inert atmosphere. Co-Cp was obtained after removal of the solvent as a purple oily solid and was used for the following step without further purification. The MALDI-TOF mass spectrum of the reaction mixture (Figure S1a) indicates the presence of the starting compound Cp, product Co-Cp as well as a small amount of the double functionalized compound. The yield of Co-Cp is nearly 41% as derived from peak intensities.

MS (FS, 8kV):  $m/z$  (%) = 1335.0 (calculated for  $\text{C}_{83}\text{H}_{108}\text{Co}_2\text{O}_7$  = 1335.61 g/mol)



**2,5-bis(4-bromophenyl)-3,4-bis(4-(dodec-1-yn-1-yl)phenyl)-cyclopenta-2,4-dienone (1)**



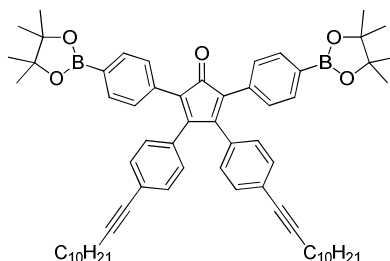
0.50 g (0.93 mmol) 1,2-bis(4-(dodec-1-yn-1-yl)phenyl)ethane-1,2-dione<sup>1</sup> and 0.41 g (1.11 mmol) 1,3-bis(4-bromophenyl)propan-2-one<sup>2</sup> were dissolved in 3.2 mL of *t*-butanol and heated to 80 °C under an inert atmosphere. Then, 0.56 mL of tetrabutylammonium hydroxide (40 wt% in methanol) was added and the reaction mixture was stirred for 30 min at 80 °C. The reaction was quenched by addition of water. The aqueous phase was extracted several times with dichloromethane and the crude product was purified by column chromatography (hexane/ dichloromethane = 2/1) to yield 0.55 g (0.63 mmol) of **1** as a purple oil in 68 % which solidified after several hours.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.39 (d, *J* = 8.7, 4H), 7.21 (d, *J* = 8.5, 4H), 7.09 (d, *J* = 8.7, 4H), 6.83 (d, *J* = 8.5, 4H), 2.39 (t, *J* = 7.0, 4H), 1.66 – 1.18 (m, 32H), 0.88 (t, *J* = 6.7, 6H).

<sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 199.35, 154.69, 132.06, 131.98, 131.69, 131.64, 129.96, 129.58, 125.27, 125.02, 122.34, 92.98, 80.40, 32.30, 29.98, 29.92, 29.71, 29.54, 29.31, 29.08, 23.08, 19.73, 14.28.

MS (FD, 8kV): *m/z* (%) = 869.7 (100.0 %, M<sup>+</sup>), (calc. for C<sub>53</sub>H<sub>58</sub>Br<sub>2</sub>O = 870.84 g mol<sup>-1</sup>).

**3,4-bis(4-(dodec-1-yn-1-yl)phenyl)-2,5-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopenta-2,4-dienone (2)**



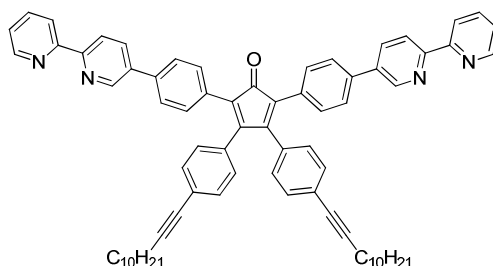
0.50 g (0.57 mmol) of **1**, 0.56 (2.21 mmol) bis(pinacolato)diboron, 0.55 g (5.60 mmol) of anhydrous potassium acetate were dissolved in 100 mL of anhydrous dioxane. Then, 75 mg (0.092 mmol) of Pd(dppf)Cl<sub>2</sub> were added. The reaction mixture was heated to 100 °C and stirred under an inert atmosphere for 12 h. After cooling, the crude product was extracted with dichloromethane and then purified by column chromatography (dichloromethane) to yield 0.40 g (0.42 mmol) of **2** in 73 % as a purple solid.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.63 (d, *J* = 8.3, 4H), 7.19 (dd, *J* = 1.6, 8.3, 8H), 6.83 (d, *J* = 8.5, 4H), 2.38 (t, *J* = 7.0, 4H), 1.57 – 1.16 (m, 56H), 0.87 (t, *J* = 7.1, 6H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 201.14, 154.72, 134.57, 133.83, 132.33, 131.45, 129.72, 129.66, 126.17, 125.09, 124.98, 92.71, 84.18, 80.43, 32.28, 30.97, 29.90, 29.68, 29.52, 29.08, 25.22, 25.01, 23.05, 19.70, 14.25.

MS (FD, 8kV): *m/z* (%) = 963.6 (100.0 %, M<sup>+</sup>), (calc. for C<sub>65</sub>H<sub>82</sub>B<sub>2</sub>O<sub>5</sub> = 964.97 g mol<sup>-1</sup>).

**2,5-bis(4-([2,2'-bipyridin]-5-yl)phenyl)-3,4-bis(4-(dodec-1-yn-1-yl)phenyl)cyclopenta-2,4-dienone (BpCp)**



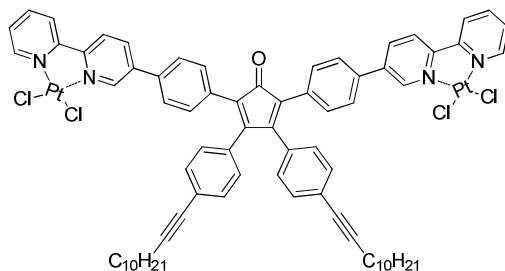
0.20 g (0.21 mmol) of **2**, 0.15 g (0.63 mmol) 5-bromo-2,2'-bipyridine<sup>3</sup> and a few drops of phase transfer catalyst Aliquat 336 were added to 4 mL of dioxane and 2 mL of aqueous potassium carbonate solution (2 M). The mixture was degassed by argon bubbling and then 40 mg (0.034 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> was added. The reaction mixture was heated to 100°C and stirred under an inert atmosphere for 12 h. After cooling, the crude product was extracted with dichloromethane and then purified by column chromatography (dichloromethane /methanol = 9/1) to yield 124 mg (0.12 mmol) of **BpCp** in 58 % as a purple solid.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.92 (d, *J* = 1.9, 2H), 8.68 (d, *J* = 4.0, 2H), 8.48 (t, *J* = 8.9, 4H), 8.04 (dd, *J* = 2.3, 8.3, 2H), 7.84 (td, *J* = 1.8, 7.8, 2H), 7.62 (d, *J* = 8.5, 4H), 7.39 (d, *J* = 8.5, 4H), 7.37 – 7.29 (m, 2H), 7.26 (d, *J* = 8.4, 4H), 6.94 (d, *J* = 8.5, 4H), 2.40 (t, *J* = 7.0, 4H), 1.53 – 1.18 (m, 32H), 0.87 (t, *J* = 6.6, 6H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 200.03, 156.12, 155.35, 154.66, 149.57, 147.77, 137.19, 137.04, 136.08, 135.25, 132.37, 131.61, 131.17, 131.00, 129.68, 126.98, 125.45, 125.05, 124.07, 121.16, 121.10, 92.84, 80.41, 32.26, 29.94, 29.89, 29.67, 29.51, 29.29, 29.06, 23.04, 19.70, 14.25.

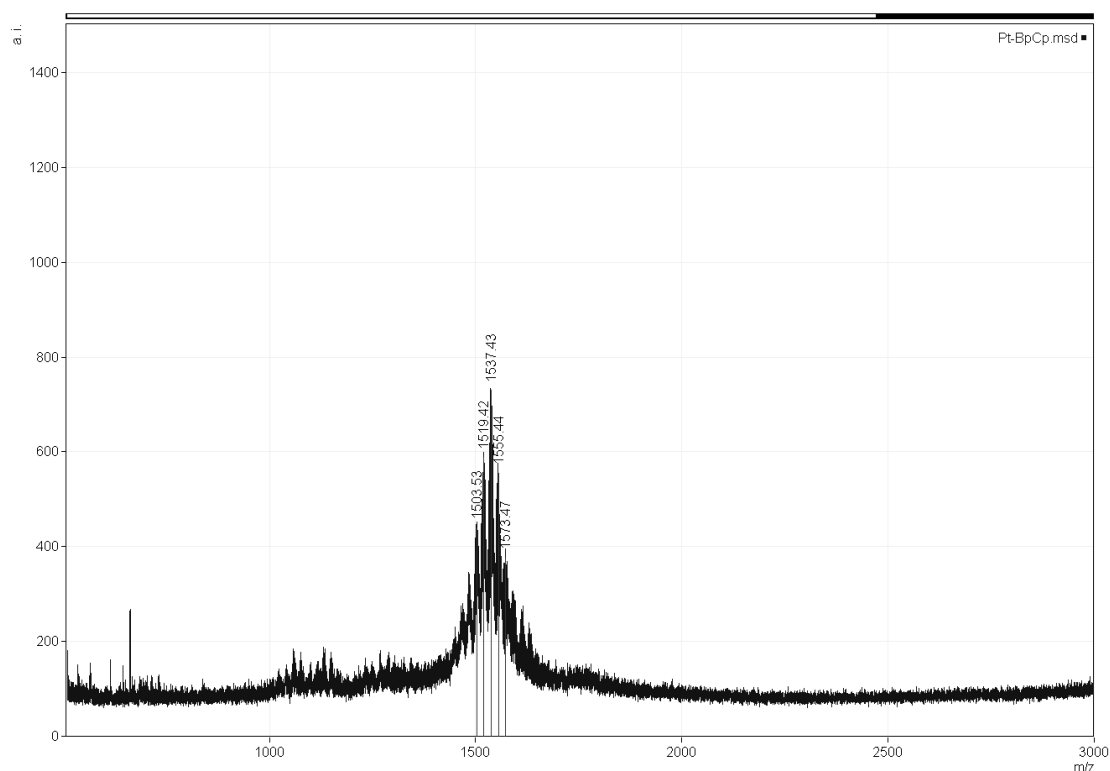
MS (FD, 8kV): *m/z* (%) = 1020.7 (100.0 %, M<sup>+</sup>), (calc. for C<sub>73</sub>H<sub>72</sub>N<sub>4</sub>O = 1021.38 g mol<sup>-1</sup>).

## Pt-BpCp



20 mg (0.020 mmol) **BpCp** and 41 mg (0.01 mmol) K<sub>2</sub>PtCl<sub>4</sub> were dissolved in 30 mL of acetone and 10 mL of water. The reaction mixture was heated to reflux for 12 h. Then, 100 mL dichloromethane was added and the aqueous phase was extracted several times with dichloromethane. **Pt-BpCp** was obtained after removal of the solvent as a brownish oily solid and was used for the following step without further purification.

**MS** (MALDI-TOF):  $m/z$  (%) = 1503.53 (60.3 %), 1519.42 (80.5 %), 1537.43 (100.0 %), 1555.44 (76.1 %), 1573.47 (51.6 %), (calc. for  $C_{73}H_{72}Cl_4N_4OPT_2 = 1553.36 \text{ g mol}^{-1}$ ).



**Figure S2.** MALDI-TOF spectrum of as-prepared **Pt-BpCp**.

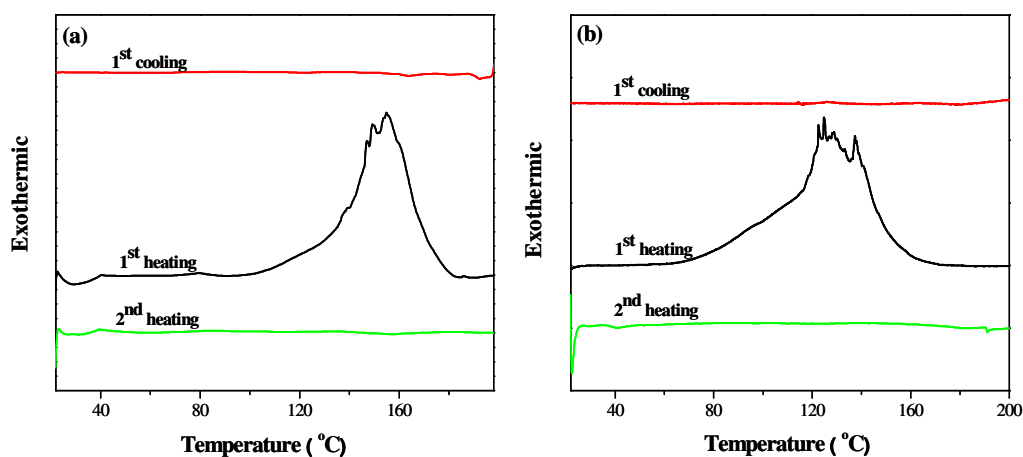
### Synthesis of CNTs/Co<sub>3</sub>O<sub>4</sub>

Purified (>90%) CNTs (MWCNTs, BASF) were used as supporting material for the preparation of CNTs/Co<sub>3</sub>O<sub>4</sub>. Prior to impregnation, the CNTs were treated with HNO<sub>3</sub> (30 wt%) at 100 °C for 12 h, washed with water, and dried at 120 °C for 6 h. In a typical experimental procedure, 5 mg CNTs were dispersed in 100 mL distilled water in the presence of 2 mg block copolymer surfactant F127 (Aldrich,  $M_w = 126000$ ) by ultrasonication for 1 h. Then, 5 mg Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added to the solution and stirred at room temperature for 1 h. Subsequently, 0.2 M aqueous NaOH solution was slowly added until pH = 10. The resulting precipitate was washed several times with ethanol and water, respectively, and dried at 80 °C overnight under

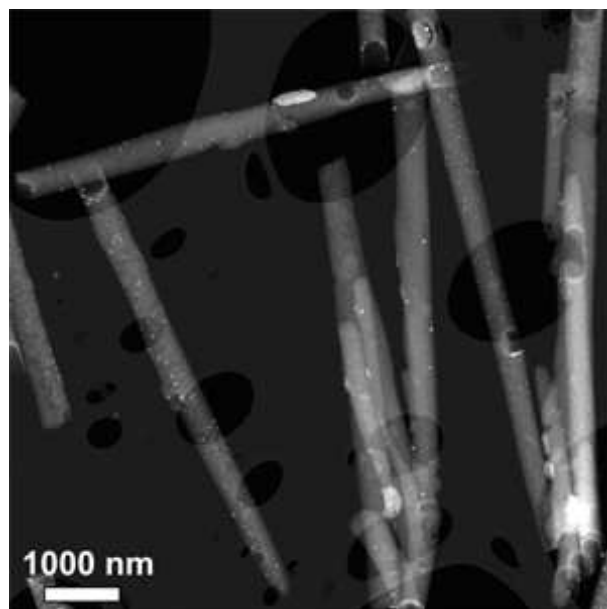


vacuum. The CNTs/Co<sub>3</sub>O<sub>4</sub> composite was obtained from a thermal treatment of the dried precipitate under argon atmosphere at 450 °C for 1 h.

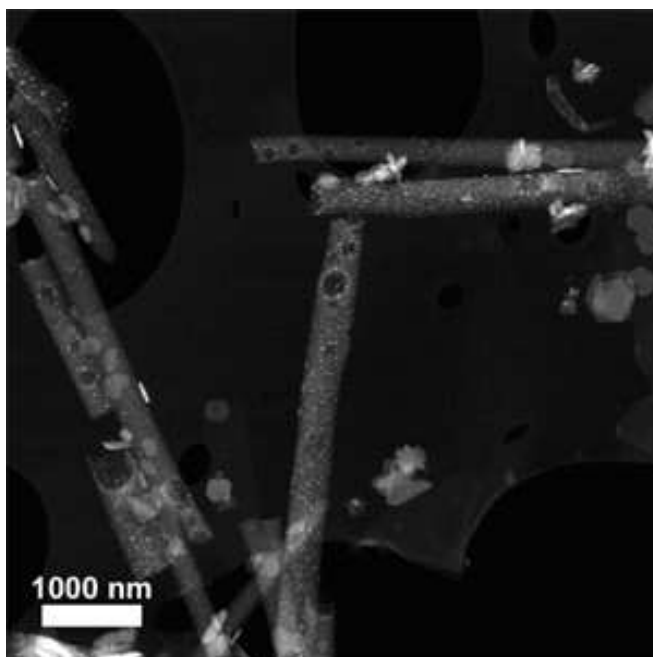
## Results and discussion



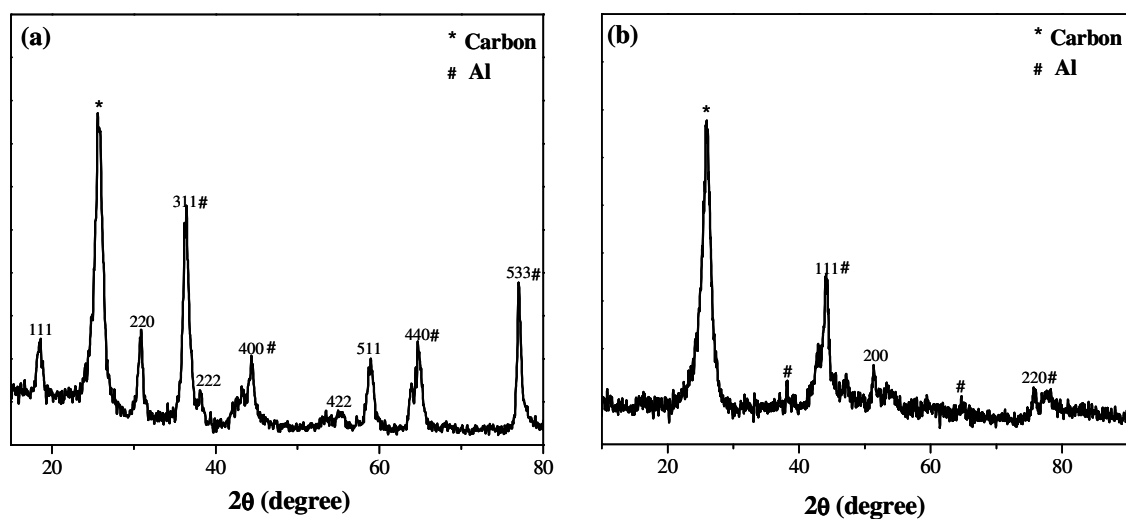
**Figure S3.** DSC curves (a) the precursors of Cp and Co-Cp with the temperature range of 25~200 °C; (b) the precursors of BpCp and Pt-BpCp with the temperature range of 25~200 °C, respectively.



**Figure S4.** STEM (dark field) image of the synthetic NPCs/Co<sub>3</sub>O<sub>4</sub> hybrid overview shows the typical tubular feature.



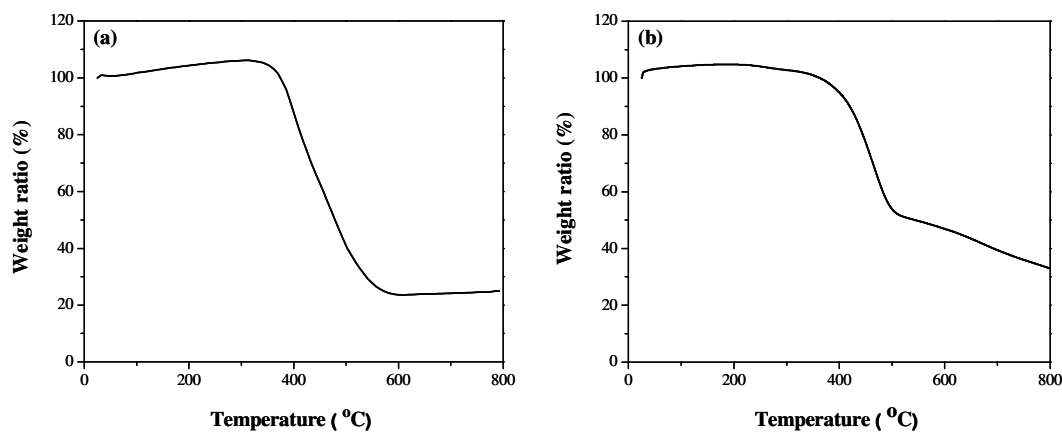
**Figure S5.** STEM (dark field) image of the synthetic NPCs/Co<sub>3</sub>O<sub>4</sub> hybrid after oxidation shows the typical tubular feature.



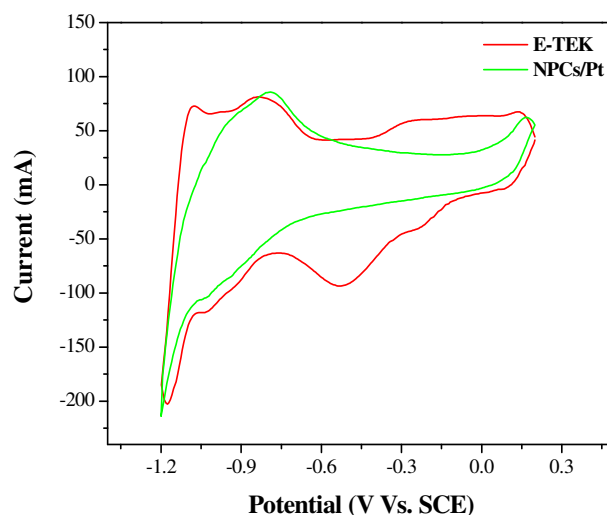
**Figure S6.** XRD patterns of (a) the precursors of Cp and Co-Cp (the molecular ratio of 1:1) after heating at 700 °C; (b) NPCs/Co<sub>3</sub>O<sub>4</sub> oxidized in air for 10min.

Figure S6 shows the XRD patterns of the precursors of Cp and Co-Cp after heating at 700 °C and NPCs/Co<sub>3</sub>O<sub>4</sub> oxidized in air for 10min, respectively. The XRD pattern in

Figure S6a matches well that of cubic Co (PDF#15-0806), indicating the surface oxidation of metallic cobalt into cobalt oxide after the long-time impregnation in concentrated NaOH solution. In Figure S6b, except the diffraction peaks from carbon and Al substrate, the main diffraction peaks of  $\text{Co}_3\text{O}_4$  nanoparticles are well consistent with the standard cubic  $\text{Co}_3\text{O}_4$  (PDF#65-2869).



**Figure S7.** Thermogravimetric analysis (TGA) (a) NPCs/ $\text{Co}_3\text{O}_4$  under oxygen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . It indicates that about 21 wt% Co is loaded on the composites; (b) NPCs/Pt under oxygen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . It indicates that about 32 wt% Pt is loaded on the composites.



**Figure S8.** Cyclic voltammograms of NPCs/Pt and commercial available E-TEK catalyst (with 30% Pt weight loading) in a  $N_2$ -saturated 5M KOH solution with the scan rate of  $50\text{mVs}^{-1}$ .

The electroactive surface area was obtained by measuring the charge from hydrogen adsorption peaks after subtracting the charge from the double-layer region. In our experiments of testing the catalytic activity for methanol oxidation, the charge for hydrogen adsorption on electrode of NPCs/Pt was measured to be  $7.14\text{ mC mg}^{-1}$ , and commercial E-TEK catalyst electrode was to be  $10.08\text{ mCmg}^{-1}$ . By dividing the electric charge density for hydrogen adsorption of  $210\text{ }\mu\text{C cm}^{-2}$ , the electroactive surface area of NPCs/Pt and E-TEK catalysts were  $34\text{ and }47\text{ cm}^2\text{ mg}^{-1}$ , respectively.

#### References:

- (1) Zhi, L.; Wu, J.; Li, J.; Stepputat, M.; Kolb, U. Müllen, K. *Adv. Mater.* **2005**, *17*, 1492-1496.
- (2) Ito, S.; Wehmeier, M.; Brand, J. D.; Kübel, C.; Epsch, R.; Rabe, J. P.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 4327 – 4342.
- (3) Pefkianakis, E. K.; Tzanetos, N. P.; Kallitsis, J. K. *Chem. Mater.* **2008**, *20*, 6254–6262.