

**ELECTRONIC SUPPORTING INFORMATION (ESI) FOR THE  
PAPER:**

**Redox Properties of LDH Microcrystals Coated with a  
Catechol-bearing Phosphonate derived from Dopamine.**

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**Rietveld refinement procedures**

Rietveld refinement of the Au@ZnAl/P2DOPA diffraction pattern was carried out by using the GSAS program.

A Pseudo-Voigt profile function TCHZ (profile function n. 3)<sup>i</sup> has been used and 7 terms (included two terms for the modeling of the asymmetry at low 2θ angles) have been also refined.

The Lorentzian and Gaussian GW and LY parameters for the phase Au were fixed to the value refined for the standard LaB6 whereas the terms LX, “stec” and “ptec” (referred to the size and strain main parameters) have been refined freely in order to obtain the microstructural parameters. The Scale factor for Au was also refined in order to use the Bish and Howard formula to calculate its weight fraction.

At the end of refinement the shift on the refined parameters was lower than the estimated standard deviations.

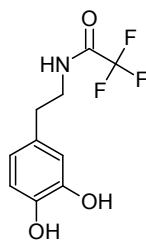
Table 1S reports the experimental and refinement details for the Au@ZnAl/P2DOPA pattern.

Sample	Au@ZnAl/ H <sub>2</sub> P <sub>2</sub> O <sub>6</sub> DOPA
Data range/ $2\theta \cdot \text{deg}^{-1}$	4 - 90
N. of data	2302
Wavelength/Å	1.54056
$wRp$	0.085
$Rp$	0.064
$RF^2$	0.083
GOF	1.98
Wt% (ZnAlLDH/Au/ H <sub>2</sub> P <sub>2</sub> O <sub>6</sub> DOPA)	65.4/16.3/18.3
<i>Au – microstructural parameters</i>	
$D_{\parallel 200}$	16 nm
$D_{\perp 200}$	100 nm
$D_{\parallel 111}$	34 nm
$D_{\perp 111}$	12 nm
$\epsilon_{\perp 200}(\times 10^3)$	1.9

**Table 1S** Rietveld refinement details for sample Au@ZnAl/ H<sub>2</sub>P<sub>2</sub>O<sub>6</sub>DOPA

## Materials and methods

### *N*-[2-(3,4-dihydroxyphenyl)ethyl]-2,2,2-trifluoroacetamide (5)



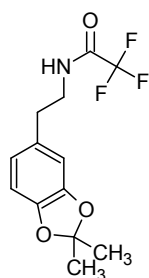
To a 500 mL flask were added dopamine hydrochloride (2.51 g, 13.20 mmol), methanol (29.4 mL), and a magnetic stirring bar. The mixture was degassed with argon for 30 min, followed by addition of methyl trifluoroacetate (2.703 mL, 26.87 mmol) and dried triethylamine (7.53 mL). The mixture was stirred at room temperature overnight. The volatile solvents were removed by rotary evaporation and the residue was treated with 1 N HCl to a pH 1 and extracted by ethyl acetate. The organic layer was washed with water, dried over MgSO<sub>4</sub>, and evaporated to give a grey solid, (2.82 g, 11.30 mmol) (86%).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 6.57 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 2.1 Hz, 1H), 6.37 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.1 Hz, 1H), 3.28 (q, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H).

<sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>) δ (ppm): 144.41, 143.06, 129.69, 119.91, 115.26, 115.00, 41.05, 33.85

<sup>19</sup>F-NMR (282 MHz, CDCl<sub>3</sub>): δ -76.55

### *N*-[2-(2,2-dimethyl-1,3-benzodioxol-5-yl)ethyl]-2,2,2-trifluoroacetamide (4)



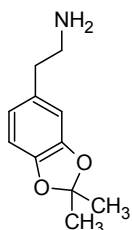
To a two-neck 100 mL flask were added Tfa-dopamine 2.82 g, 11.31 mmol), DMP (5.7 mL, 45.78 mmol), and anhydrous benzene (112.7 mL). One neck of the flask was fitted with a Soxhlet extractor, the thimble of which was filled with granular anhydrous CaCl<sub>2</sub>; the other neck of the flask was sealed with a septum for sampling purpose. After the system was degassed with argon for 5 min and then heated to reflux for another 5 min, *p*-toluenesulfonic acid monohydrate (96.92 mg, 0.51 mmol) was added. The reaction was refluxed during 4 h. After cooled down, the mixture was filtered through a short silica-gel column, which was washed with DCM. The combined filtrate and washings were evaporated to produce a light yellow solid. (2.95 g, 10.20 mmol) (90%).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 6.67 (d, *J* = 8.3 Hz, 1H), 6.58-6.55 (m, 2H), 3.53 (q, *J* = 6.9 Hz, 2H), 2.77 (t, *J* = 6.9 Hz, 2H), 1.66 (s, 6H).

$^{13}\text{C}$ -RMN (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 147.96, 146.50, 130.44, 120.99, 118.06, 108.63, 108.34, 41.15, 34.72, 25.83.

$^{19}\text{F}$ -NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -76.03

### 2-(2,2-dimethyl-1,3-benzodioxol-5-yl)ethanamine (3)



To a 100 mL flask were added Tfa-dopamine(acetonide) (2.95 g, 10.20 mmol) and THF (62 mL), followed by addition of lithium hydroxide (948 mg, 22.59 mmol) in 22 mL water. The mixture was stirred at room temperature for 4 h. After the organic solvents were reduced by rotary evaporation, the mixture was treated carefully with 1N HCl to a pH of 2-3, washed with DCM, adjusted to a pH of 8 with  $\text{NaHCO}_3$ , and extracted with EtOAc. The organic layer was washed with water, dried over  $\text{MgSO}_4$ , and evaporated to give a light yellow oil (1.71 g, 8.87 mmol) (87%).

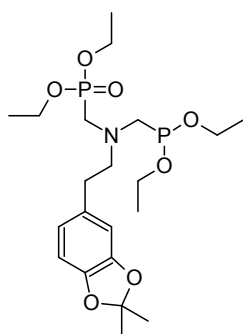
$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.61-6.51 (m, 3H), 4.11 (s, 2H), 2.90 (t,  $J$ = 7.0 Hz, 2H), 2.66 (t,  $J$ = 7.0 Hz, 2H), 1.61 (s, 6H).

$^{13}\text{C}$ -RMN (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 147.55, 145.96, 131.55, 120.95, 117.62, 108.74, 108.00, 42.63, 37.59, 25.70.

### Tetraethyl

### {[2-(2,2-dimethyl-1,3-benzodioxol-5-

### yl)ethyl]imino}di(methylene)]bis(phosphonate) (2)



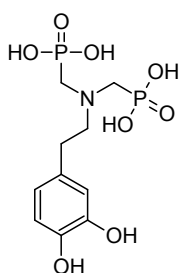
To a 100 mL flask were added Dopamine(acetonide) (189mg, 0.978mmol), diethyl phosphite (290.9 mg, 2.11 mmol) and paraformaldehyde (58.19 mg, 1.94 mmol). The mixture was stirred at 105°C for 2 h. After cooled down diethyl ether (50 mL) and  $\text{K}_2\text{CO}_3$  (194mg, 1.40 mmol) were added and the mixture was stirred at room temperature for 2 h. The aqueous layer was separated and extracted twice with diethyl ether. Combined organic phase was dried over  $\text{MgSO}_4$ , and evaporated to give light yellow oil (265.4 mg, 0.54 mmol) (55%).

**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm):** 6.63-6.56 (m, 3H), 4.17-4.03 (m, 8H), 3.18 (d, *J*= 9.0 Hz, 4H), 3.02 (dd, *J*<sub>1</sub>= 5.9 Hz, *J*<sub>2</sub>= 8.0 Hz, 2H), 2.67 (dd, *J*<sub>1</sub>= 5.9 Hz, *J*<sub>2</sub>= 8.0 Hz, 2H), 1.61 (s, 6H), 1.29 (t, *J*= 7.1 Hz, 12H).

**<sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>) δ (ppm):** 147.34, 145.63, 132.61, 120.88, 117.41, 109.05, 107.84, 61.84 (m), 58.47 (t, *J*= 7.7 Hz), 51.27 (d, *J*= 7.2 Hz), 49.21 (d, *J*= 7.2 Hz), 33.49, 25.74, 16.46 (m).

**<sup>31</sup>P-RMN (121 MHz, CDCl<sub>3</sub>) δ (ppm):** 24.76 (s, 2P).

**[{[2-(3,4-dihydroxyphenyl)ethyl]imino}di(methylene)]bis(phosphonic acid) (1)**

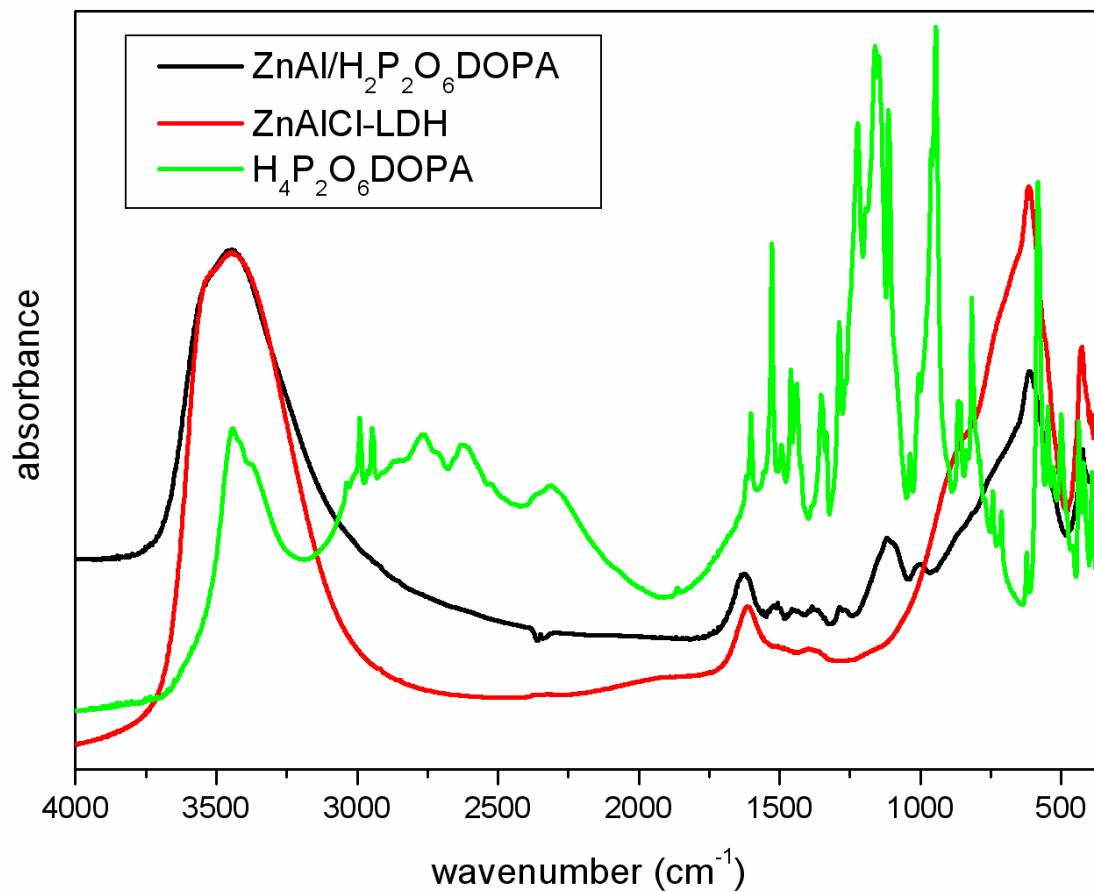


To a 50 mL flask were added Dopamine(acetonide)-bisphosphonate (253.9mg, 0.514mmol) and HCL 37% (6.5mL) The mixture was stirred at 105°C for 12 h. Solvent was removed by rotary evaporation to yield quantitatively final product.

**<sup>1</sup>H-NMR (300 MHz, D<sub>2</sub>O) δ (ppm):** 6.74-6.71 (m, 2H), 6.63 (dd, *J*<sub>1</sub>= 2.0 Hz, *J*<sub>2</sub>= 8.2 Hz, 2H), 3.61 (m, 2H), 3.58 (d, *J*= 12.9 Hz, 4H), 2.93 (m, 2H).

**<sup>13</sup>C-RMN (75.5 MHz, D<sub>2</sub>O) δ (ppm):** 145.13, 144.01, 129.225, 122.20, 117.51, 117.49, 58.52 (m), 53.20 (d, *J*= 4.4 Hz), 51.38 (d, *J*= 4.4 Hz), 29.68.

**<sup>31</sup>P-RMN (121 MHz, D<sub>2</sub>O) δ (ppm):** 8.35 (s, 2P).



**Figure 1S** FT-IR spectra of ZnAl – LDH, pure H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>DOPA molecule and ZnAl/H<sub>2</sub>P<sub>2</sub>O<sub>6</sub>DOPA system