

## Electronic Supplementary Information for

# Arene-perfluoroarene Interactions for Crystal Engineering of Metal Complexes: Controlled Self-assembly of Paddle-wheel Dimers

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## Experimental section

### *General Methods*

All solvents and reagents are of the highest quality available and used as received except for diethyl amine and triethylamine. Diethyl amine and triethylamine were dried by reflux over KOH, distilled under argon, and degassed with a freeze-and-pump thaw.  $\text{Rh}(\text{O}_2\text{CCF}_3)_4(\text{acetone})_2$  were prepared by the literature methods. All syntheses were performed under an atmosphere of dry nitrogen or dry argon unless otherwise indicated.

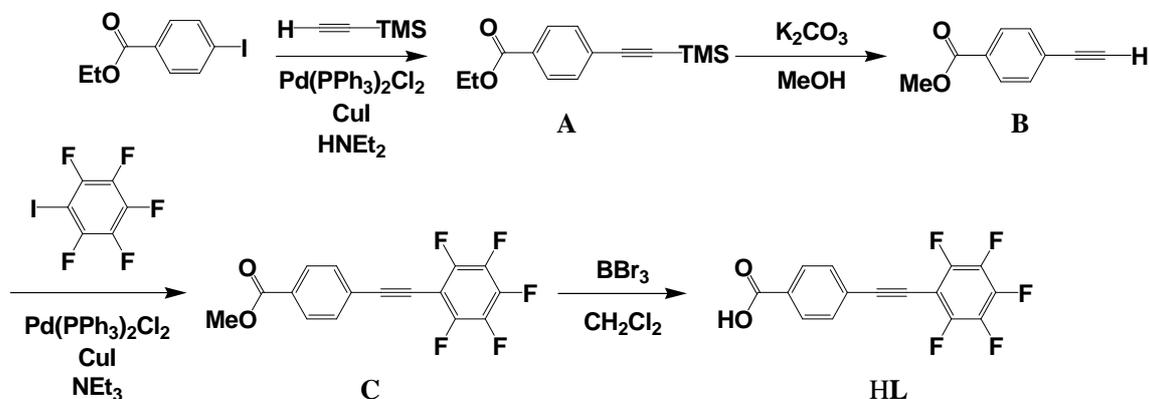
### *Measurement Apparatus*

Elemental analyses were carried out on a J-SCIENCE LAB MICRO CORDER JM10 elemental analyser.  $^1\text{H}$  NMR spectra were acquired on a JEOL JNM-LA500 spectrometer, where chemical shifts in  $(\text{CD}_3)_2\text{CO}$  were referenced to internal tetramethylsilane.  $^{19}\text{F}$  NMR spectra were acquired on a JEOL JNM-LA500 spectrometer, where chemical shifts in  $(\text{CD}_3)_2\text{CO}$  were referenced to external trifluorotoluene.

### *X-ray crystallography*

A crystal of **1** was mounted in a loop. Diffraction data at 123 K were measured on a Rigaku AFC8 diffractometer using a Rigaku Saturn CCD system. Graphite-monochromated Mo-K $\alpha$  radiation (0.71075 Å) was used. Cell parameters were retrieved using the Crystal Clear-SM 1.4.0 software and refined using Crystal Clear-SM 1.4.0 on all observed reflections. Data reduction and empirical absorption correction using equivalent reflections and Lorentzian polarization were performed with the program Crystal Clear-SM 1.4.0. The structure was solved by direct methods using *SIR-97* and refined on  $F^2$  by the full-matrix least squares techniques with *SHELXL-97*. All nonhydrogen atoms were refined anisotropically. A crystal of **2** was mounted in a loop. Diffraction data at 123 K were measured on a RAXIS-RAPID Imaging Plate diffractometer equipped with confocal monochromated Mo-K $\alpha$  radiation and data was processed using RAPID-AUTO (Rigaku). Structures were solved by direct methods and refined by full-matrix least squares techniques on  $F^2$  (*SHELXL-97*). All non-hydrogen atoms were anisotropically refined, while all hydrogen atoms were placed geometrically and refined with a riding model with  $U_{\text{iso}}$  constrained to be 1.2 times  $U_{\text{eq}}$  of the carrier atom. For **2**, the diffused electron densities resulting from residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.

### Syntheses



**Scheme S1** Syntheses of HL

Ethyl 4-(2-trimethylsilylethynyl)benzoate (**A**)<sup>S1</sup>, ethyl 4-ethynylbenzoate (**B**)<sup>S1</sup>, methyl 4-[(perfluorophenyl)ethynyl]benzoate (**C**)<sup>S2</sup> which are the precursors of HL were prepared by the literature methods.

#### Synthesis of 4-[(perfluorophenyl)ethynyl]benzoic acid (HL) :

Methyl 4-[(perfluorophenyl)ethynyl]benzoate (**C**) (2.15 g, 6.59 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and cooled to -60°C. BBr<sub>3</sub> (2 eq.) was added and the solution was stirred for 30 min under argon in the cold. Then, the cooling bath was removed and the stirring continued for another 90 min, while the solution was allowed to reach r.t. The solution was then washed twice with brine, dried over MgSO<sub>4</sub> and evaporated in vacuo to afford the yellow solid. The solid was washed with CH<sub>2</sub>Cl<sub>2</sub> to obtain HL as a white solid. Yield 24%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm: 7.78 (d, *J* = 10.0 Hz, 2H), 8.14 (d, *J* = 10.0, 2H); <sup>19</sup>F NMR (470.4 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) δ ppm: -164.0 (dt, *J* = 4.7, 18.8 Hz, 2F), -154.3 (t, *J* = 18.8 Hz, 1F), -138.3 (dd, *J* = 4.7, 18.8 Hz, 2F); *Anal.* Calcd. for C<sub>6</sub>F<sub>5</sub>C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H: C, 57.71; H, 1.61; N, 0.00%. Found: C, 57.31; H, 1.77; N, 0.00%.

#### Synthesis of Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub>(3-pentanone)<sub>2</sub> (**1**)

Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>(acetone)<sub>2</sub> (195 mg, 0.25 mmol) and HL (312 mg, 1.0 mmol) in 5 ml of diethyleneglycol dimethylether were stirred for 2 h at 100 °C. After evaporation of the solvent, the residue was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/AcOMe 1:1). Recrystallization from Et<sub>2</sub>O/3-pentanone gave green platelet crystals of **1**. The yield of [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub>] was 40 mg (13.3% based on [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>(acetone)<sub>2</sub>]). *Anal.* Calcd. for Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>C<sub>2</sub>C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O: C, 41.33; H, 2.48; N, 0.00%. Found: C, 41.39; H, 2.27; N, 0.14%.

### Synthesis of $\text{Cu}_2(\text{L})_4(\text{THF})_2$ (**2**)

HL (37.5 mg, 0.12 mmol) was dissolved in acetone (3.5 ml) and layered on top of a solution of Copper(II) acetate monohydrate (5.0 mg, 0.025 mmol) in THF (2.5 ml). After the solution was fully diffused, it was left to evaporate and blue platelet crystals were obtained. *Anal.* Calcd. for  $\text{Cu}_2(\text{O}_2\text{CC}_6\text{H}_4\text{C}_2\text{C}_6\text{F}_5)_4(\text{H}_2\text{O})_2$ : C, 51.19; H, 1.43; N, 0.00%. Found: C, 51.15; H, 1.72; N, 0.00%.

### References

- S1. A. Schaate, P. Roy, T. Preuße, S. J. Lohmeier, A. Godt, P. Behrens, *Chem. Eur. J.*, 2011, **17**, 9320-9325.
- S2. Z. Yadong, W. Jianxun, *Journal of Fluorine Chemistry*, 1990, **47**, 533-535.