Supporting Information

Modulating the Rate of Charge Transport in a Metal–Organic Framework Thin Film Using Host:Guest Chemistry

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Experimental section

Chemicals: All chemicals: benzoic acid (Aldrich, 99.5%), $ZrOCl_2 \times 8H_2O$ (Sigma,), $ZrCl_4$ (Aldrich, 99.5%), N,N-dimethylformamide (DMF) (Macron, 99.8%), hydrochloric acid (Aldrich, 37%), acetone (Macron, 98%), dichloromethane (DCM) (Sigma-Aldrich, 99.6%), ferrocene carboxylic acid (Sigma), β-cyclodextrin (Sigma) and tetrabuthtylammonium hexafluorophosphate ($TBAPF_6$) (Fluka, 98.0%), were used as received without further purification. The chemicals used for the synthesis of the 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H_4 TBzPy) linkers were the same as those reported in our previous work.[1]

Instrumentation:

Scanning electron microscopy (SEM) images were measured on a Hitachi SU8030 SEM.

All cyclic voltammetry (CV) experiments were performed on a Solarton Analytical Modulab Potentiostat. A three-electrode electrochemical setup was used, with a platinum mesh counter electrode, Ag/AgCl/KCl (sat'd) electrode as reference electrode and with the NU-1000 thin-film/FTO working electrode (active area of 1 cm^2). For all measured CVs, the potential scan rate was 50 mV/sec.

Chrono-amperometry measurement were done in the above 3-electrode configuration, by stepping the potential from -0.3V vs Fc/Fc^+ (reducing potential) to 0.6V vs Fc/Fc^+ (oxidizing potential) while recording the current response vs time.

Synthesis of NU-1000:

$ZrOCl_2 \times 8H_2O$ (104 mg, 0.30 mmol) and benzoic acid (2.7 g, 22 mmol) were mixed in 8 mL of DMF inside a 20 mL screw-thread sample vial (Cole-Parmer, 28 mm × 57 mm), equipped with a urea cap and PTFE foam-backed liner, and ultrasonically dissolved. The clear solution was incubated in an oven at 80 ºC for 1 hour. After cooling down to room temperature (40 mg, 0.06 mmol) of H_4TBzPy was added to this solution and the mixture was sonicated for 20 min. The yellow suspension was heated in a gravity convection oven (VWR® symphony™) at 120 ºC for 48 hours. After cooling down to room temperature, yellow polycrystalline material was isolated by filtration (35 mg of as synthesized material, 54% yield) and washed with DMF. Next, Benzoates (modulator) coordinated in the obtained MOF was then removed by the following an HCl activation process: 35 mg of solvated ("wet") material was soaked in 12 mL of DMF and 0.5 mL of 8 M aqueous HCl was added. This mixture was heated in an oven at 100 ºC for 24 hours. After cooling to room temperature, the solution was removed and the material was washed twice with DMF to remove HCl impurities. Subsequently, the solid residue was washed twice with acetone and soaked in acetone for additional 12 hours. NU-1000 was filtered, briefly dried on a filter paper and activated at 120 ºC under vacuum for 12 hours.[1]

Solvent Assisted Ligand Incorporation (SALI) of NU-1000 with Ferrocene carboxylic acid:

Activated NU-1000 (60mg, 0.027 mmol) was loaded in a 2 mL microwave vial (Biotage). Subsequently, ferrocene carboxylic acid (2.4 mL of 0.1M solution in DMF, 0.24 mmol) was added to the reaction vial, which was then sealed and heated at 60 ^{0}C for 18-24 h with occasional swirling. The supernatant of the reaction mixture was decanted and the MOF sample was soaked into fresh hot DMF which was then filtered, washed sequentially with DMF, acetone and ether (60, 40 and 30 mL each), and finally air dried.[2]

Electrophoretic Deposition of MOF Thin Films:

10 mg of MOF powder were suspended in a 20 mL toluene solution and sonicated for 30 sec. Two identical fluorine-doped tin oxide (FTO) glass substrates (15 Ω/sq, Hartford Glass) were dipped in the deposition solution (1 cm separation distance) and a constant DC voltage of 130 V was applied using an Agilent E3 612A DC power supply. The duration of deposition was 3 hours.

Caution: Electrical sparking due to accidental contact of electrodes and/or their leads can result in ignition of toluene. The electrophoretic deposition procedure should be done in a fume hood, clear of flammables.

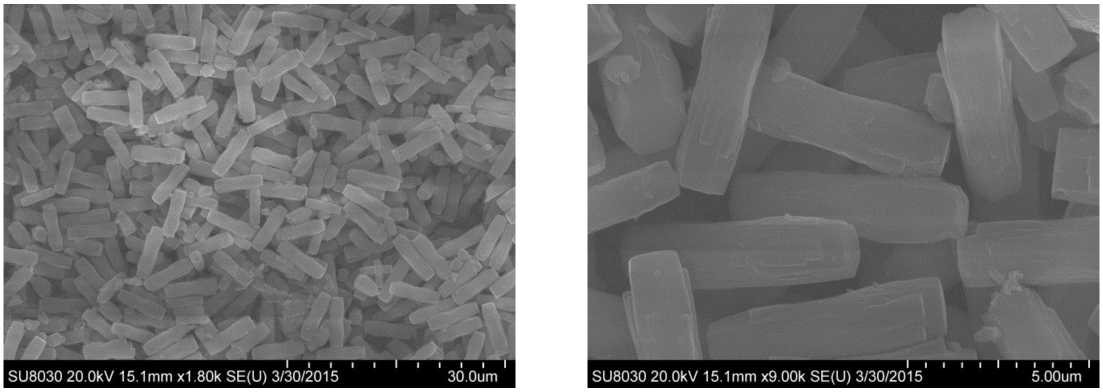
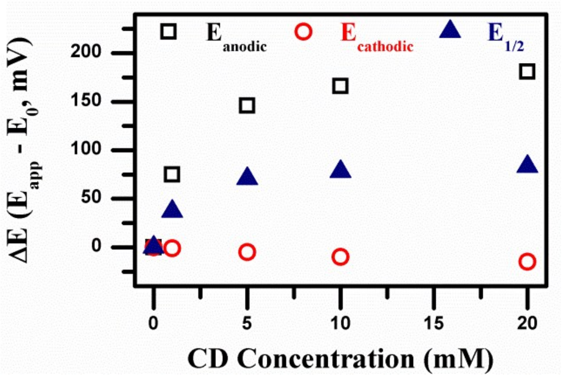


Figure S1. SEM images of Fc-NU-1000 thin films formed by electrophoretic deposition.

A)



B)

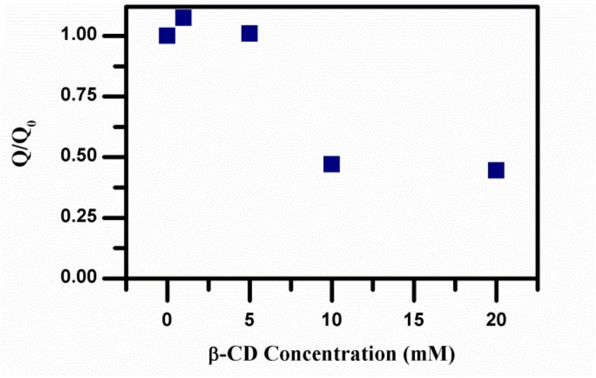


Figure S2. A) Variation of anodic, cathodic and half-wave potentials for Fc-NU-1000, as a function of β-CD concentration in solution, and B) Normalized amount of charge passed through Fc oxidation in Fc-NU-1000, as a function of β-CD concentration.

References

(1) Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. *J Am Chem Soc* **2013**, *135*, 10294.

(2) Hod, I.; Bury, W.; Gardner, D. M.; Deria, P.; Roznyatovskiy, V.; Wasielewski, M. R.; Farha, O. K.; Hupp, J. T. *J Phys Chem Lett* **2015**, *6*, 586.