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Supporting information

An Alternating Conduction-Insulation Molecular "Fence" Model from Fluorinated Metallopolymers

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S1 Materials and Characterizations

1.1 Materials

[1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$, 98%), potassium carbonate (K_2CO_3, analytical reagent), and $RuCl_3 \cdot H_2O$ (99%) were purchased from Energy Chemical. 4'-Bromo-2,2':6',2''-terpyridine (>99%), bis(pinacolato)diboron (>97%), 2,5-dibromobenzene-1,4-diol (>98%), ferric acetate ($Fe(OAc)_2$, >90%), and perfluoro-1-iodohexane ($C_6F_{13}I$, 98%) were purchased from TCI. $C_6F_{13}I$ was used as received and stored in a light-resistant container at 0 ^oC. 6-Bromohex-1-ene (>97%) and bis(pinacolato)diboron were purchased from J&K. Toluene (analytical reagent), acetonitrile (analytical reagent), petroleum ether (analytical reagent), ethyl acetate (EA, analytical reagent), triethylamine (analytical reagent), dichloromethane (CH_2Cl_2, analytical reagent), chloroform ($CHCl_3$, analytical reagent), dimethyl sulfoxide (DMSO, analytical reagent), acetic acid (CH_3COOH, analytical reagent), methanol (CH_3OH, analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd. and were used as received unless otherwise mentioned.

1.2 Characterizations

^1H NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane (TMS) as an internal standard at room temperature. ^{13}C NMR spectrum were recorded on a Bruker 75 MHz NMR instrument using $CDCl_3$ as the solvent at room temperature. The ^{19}F NMR spectrum was measured on a Brucker 600 MHz Advance III instrument using $CDCl_3$ as the solvent at 25 ^oC.

UV-vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer (Shimadzu China, Shanghai, China). MALDI-TOF mass spectroscopy (MS) were acquired on an UltrafleXtreme III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with an Nd:YAG smart beam-II laser with 355-nm wavelength and 200 Hz firing rate. The MALDI sample spots were prepared onto the MTP 384 target plate. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) served as the matrix and was prepared in $CHCl_3$ at a concentration of 20 mg mL^{-1}. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg mL^{-1}. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). The instrument was calibrated prior to each measurement with external PMMA at the molar mass under consideration. All samples were dissolved in $CHCl_3$ at a concentration of 10 mg mL^{-1}. After sample preparation and solvent evaporation, the target plate

was inserted into the MALDI-TOF mass spectrometer. The instrument was operated in the reflector mode and the linear mode.

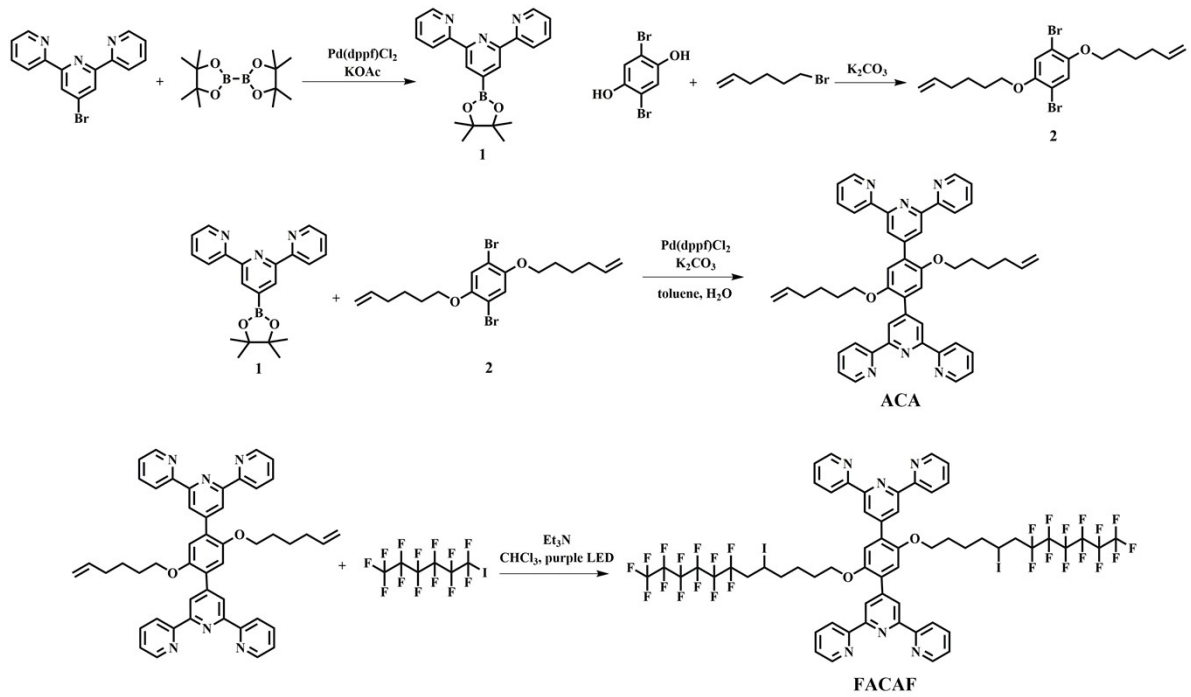
TEM images were taken with a HITACHI HT7700 operated at an accelerating voltage of 120 kV. One of synthesis experiments was performed using a purple LED light source (λ_{max} = 403 nm, W = 29.7 mW cm^{-2}, Suzhou, Linkhou Robot Co. Ltd., China). All STM measurements (Bruker, MultiMode) were conducted at 50 ^{o}C in constant current mode using mechanically cut Pt/Ir tips (80/20, diameter 0.25 mm). The sample was dissolved in n-caprylic acid and was sonicated for several hours before dropping on the highly oriented pyrolytic graphite (HOPG) substrate. The original sample concentration is 0.01 g/L and keep diluting until clear STM images.

The optimization of molecular part <FACAF-Ru> was carried out by $DMol^3$ program. The electronic exchange and correlation effects are described by the generalized gradient approximation with PW91 function.[1] In order to accurately describe the van der Waals forces, dispersion correction (DFT-D) is adopted by OBS approach. The all-electron double numerical atomic orbital including polarized p-function (DNP)[2] is chosen as the basis set with global orbital-cutoff. The convergence threshold values for energies, gradient and displacement are specified as 1×10^{-5} Ha, 2×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively, while the self-consistent-field (SCF) convergence threshold value is 1×10^{-6} Ha. For the structure optimization of <FACAF-Ru(II)-FACAF>, we used the Forcite model in Materials Studio. The convergence tolerance of energy, force and displacement are specified as 2×10^{-5} kcal/mol, 1×10^{-3} kcal/mol/Å and 21×10^{-5} Å, respectively, with the universal force field was used in the energy calculation. Forcite geometry optimization is based on reducing the magnitude of calculated forces and (where appropriate) stresses until they become smaller than defined convergence tolerances. It is also possible to specify an external model to represent the behavior of the system under tension or compression. The forces on an atom are calculated from the potential energy expression and will depend on the forcefield that is selected.

S2 Experimental procedures

2.1 Syntheses of both ACA and FACAF

The synthetic pathways of the ligands ACA and FACAF were shown in Scheme S1, which involved in the syntheses of intermediates compounds **1** and **2**.



Scheme S1. Synthetic pathways of the ligands ACA and FACAF.

2.1.1 Synthesis of compound 1. A mixture of 4'-bromo-2,2':6',2"-terpyridine (0.778 g, 2.5 mmol), bis(pinacolato)diboron (0.762 g, 3 mmol), potassium acetate (0.735 g, 7.5 mmol) and Pd(dppf)Cl_2 (0.073 g, 0.1 mmol) was added to a Schelenk tube with a stir bar. Then, 15 mL of toluene was added to dissolve the mixture. The reaction mixture was degassed by at least four freeze-pump-thaw cycles to totally eliminate the dissolved oxygen, and then the Schlenk tube was sealed in argon with stirring at 95 °C for 12 h. The crude product was subsequently purified by column chromatography (petroleum ether : ethyl acetate = 4:1, v/v) to get compound **1** (yield: 82.5%). δ_H (300 MHz, $CDCl_3$) 8.80 (2 H, s), 8.73 (2 H, dd, *J* 4.8, 0.8), 8.61 (2 H, d, *J* 8.0), 7.86 (2 H, td, *J* 7.7, 1.8), 7.33 (2 H, ddd, *J* 7.3, 4.9, 1.0), 1.38 (12 H, s).

2.1.2 Synthesis of compound 2. A mixture of 2,5-dibromobenzene-1,4-diol (5.32 g, 20 mmol), 6-bromohex-1-ene (8.1 g, 50 mmol) and potassium carbonate (13.82 g, 100 mmol) was added to a 250 mL round-bottom flask. Then, 120 mL of acetonitrile was added to dissolve the mixture. The reaction mixture was magnetically stirred at 90 °C for 6 h. The crude product was subsequently purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1, v/v) to get compound **2** (yield: 86%). δ_H (300 MHz, $CDCl_3$) 7.10 (2 H, s), 5.85 (2 H, ddt, *J* 16.9, 10.2, 6.6), 5.18 – 4.92 (4 H, m), 3.97 (4 H, t, *J* 6.4), 2.25 – 2.08 (4 H, m), 1.92 – 1.74 (4 H, m), 1.69 – 1.53 (4 H, m).

2.1.3 Synthesis of ACA. A mixture of compound 1 (0.431 g, 1.2 mmol), compound 2 (0.215 g, 0.5 mmol) and 40 mL of toluene was added to a 100 mL three-necked round-bottom flask. Then, potassium carbonate (4.14 g, 3 mmol) dissolved in 15 mL of H_2O was added to the mixture. The reaction mixture was purged with

argon and magnetically stirred at 90 °C for 15 min. Finally, $Pd(dppf)Cl_2$ (0.146 g, 0.2 mmol) was added to the mixture for another 24 h. The crude product was subsequently purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1, v/v) to obtain ACA (yield: 55.2%). δ_H (300 MHz, DMSO) 8.86 – 8.58 (12 H, m), 8.04 (4 H, td, *J* 7.8, 1.6), 7.52 (4 H, dd, *J* 6.8, 5.1), 7.37 (2 H, s), 5.55 (2 H, ddt, *J* 16.9, 10.3, 6.6), 4.80 (4 H, dd, *J* 25.0, 6.0), 4.12 (4 H, t, *J* 5.9), 1.91 (4 H, q, *J* 7.0), 1.64 (4 H, dd, *J* 14.6, 5.9), 1.53 – 1.37 (4 H, m). ^{13}C NMR (75MHz, $CDCl_3$, ppm) δ: 156.47 (m, 4C), 155.23 (m, 4C), 150.68 (m, 2C), 149.13 (m, 4C), 148.08 (m, 2C), 138.62 (m, 2C), 136.83 (m, 4C), 129.65 (m, 4C), 123.66 (m, 4C), 121.59 (d, J = 39.9 Hz, 4C), 115.52(m, 2C), 114.38 (m, 2C), 69.59 (m, 2C), 33.45 (m, 2C), 28.83 (m, 2C), 25.42 (m, 2C).

2.1.4 Synthesis of FACAF. A mixture of ACA (73.6 mg, 0.1 mmol), $C_6F_{13}I$ (86.5 μL, 0.4 mmol) and triethylamine (5.6 μL, 0.04 mmol) was added to a 10 mL Schlenk tube with a stir bar. Then, 6.0 mL of mixed solvent of chloroform and acetonitrile with the feed ratio of 5 : 1 (v : v) was added to dissolve the mixture. And then the Schlenk tube was sealed and irradiated under purple LED light (λ_{max} = 403 nm, W = 29.7 mW cm^{-2}) with stirring at room temperature for 12 h. The crude product was subsequently purified by column chromatography (dichloromethane : ethyl acetate = 1 : 3, v/v) to obtain FACAF (yield: 46%).[3] δ_H (300 MHz, $CDCl_3$) 8.89 – 8.59 (12 H, m), 7.88 (4 H, td, *J* 7.8, 1.7), 7.35 (4 H, ddd, *J* 7.4, 4.9, 1.0), 4.08 (6 H, t, *J* 5.8), 2.89 – 2.41 (4 H, m), 1.92 – 1.47 (12 H, m). ^{19}F NMR (600 MHz, $CDCl_3$, ppm) δ: -80.81 (t, J = 11.1 Hz, 6F), -113.20 (d, J = 649.7 Hz, 4F), -121.84 (m, 4F), -122.85 (m, 4F), -123.62 (m, 4F), -126.12 (m, 4F). MALDI-TOF MS for FACAF, Calcd: m/z = 1501.215, Found: 1523.632 of $[M–I]^+$; Calcd: m/z = 1523.197, Found: 1523.632 of $[M–HI+Na]^+$; Calcd: m/z = 1651.110, Found: 1651.581 of $[M+Na]^+$.

2.2 Synthesis of $RuCl_2(DMSO)_4$[4]

A mixture of $RuCl_3 \cdot H_2O$ (0.53 g) and 12 mL of DMSO was added to a 25 mL three-necked round-bottom flask. After refluxing at 150 °C for 15 min, the solvent was removed to one-third by vacuum filtration. Then 60 mL of acetone was added to get a yellow precipitate. The yellow complex which separated was filtered off, washed with acetone and ether, and vacuum dried to get the yellow solid 0.28 g (yield: 28.5%).

2.3 Synthesis of metallopolymers <ACA-Fe(II)-ACA> and <FACAF-Fe(II)-FACAF>[5]

An equimolar amount of $Fe(OAc)_2$ (5.4 mg) and ligand ACA (20.8 mg) or ligand FACAF (50.0 mg) was refluxed in 50 mL of CH_3COOH for 48 h. After cooling to room temperature, the solution was filtrated to remove insoluble residues. Then the solvent was removed slowly to obtain the corresponding metallopolymer <ACA-Fe(II)-ACA> (yield: 87%) or <FACAF-Fe(II)-FACAF> (yield: 92%) in a vacuum oven.

2.4 Synthesis of metallopolymers <ACA-Ru(II)-ACA> and <FACAF-Ru(II)-FACAF>

An equimolar amount of $RuCl_2(DMSO)_4$ (24.2 mg, 0.05 mmol) and ligand ACA (36.8 mg, 0.05 mmol) or ligand FACAF (81.4 mg, 0.05 mmol) was refluxed in the mixture solution (80 mL) of CH_3Cl and CH_3OH (1/1, v/v) at 60 °C for 48 h under magnetic stirring. The solvent was removed to about 5 mL by vacuum filtration. Then the concentrated solution was precipitated in diethyl ether to obtain a dark red powder as <ACA-Ru(II)-ACA> (yield: 90%) and <FACAF-Ru(II)-FACAF> (yield: 95%).

S3 Additional Results

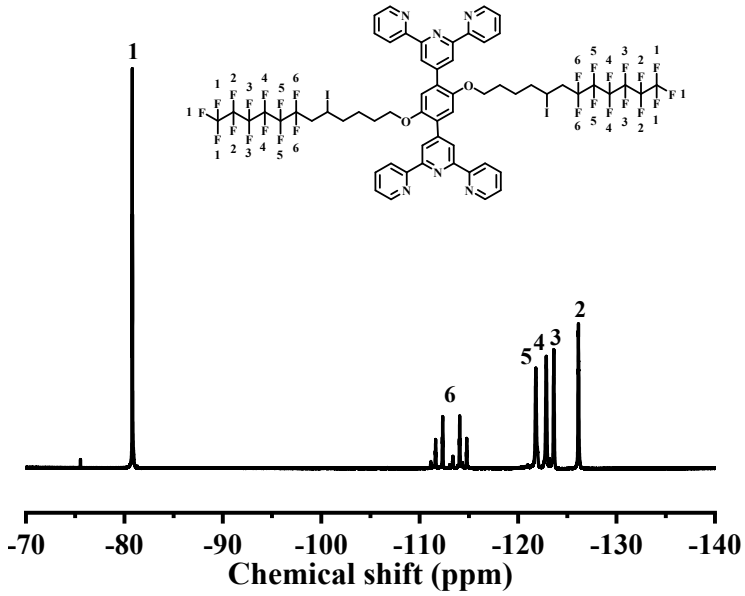


Figure S1. ^{19}F NMR spectrum of the ligand FACAF in $CDCl_3$.

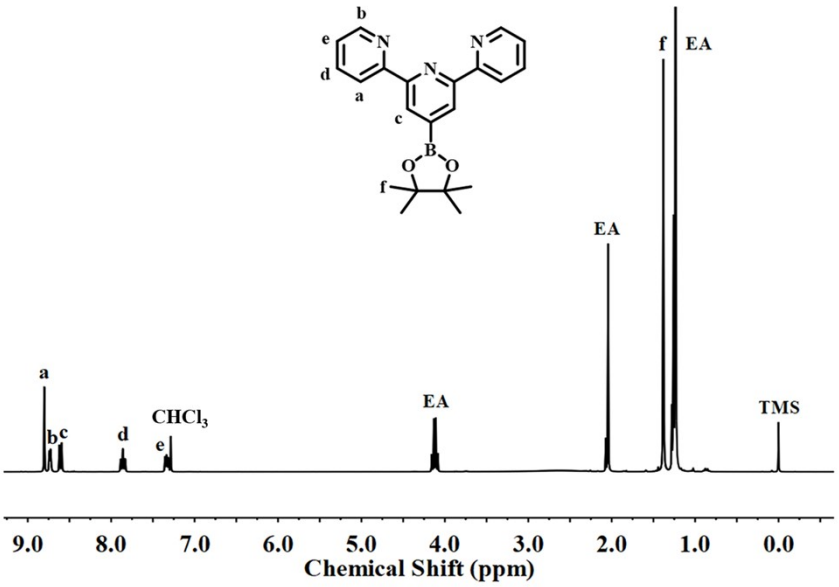


Figure S2. ^{1}H NMR spectrum of compound **1 i**n $CDCl_3$.

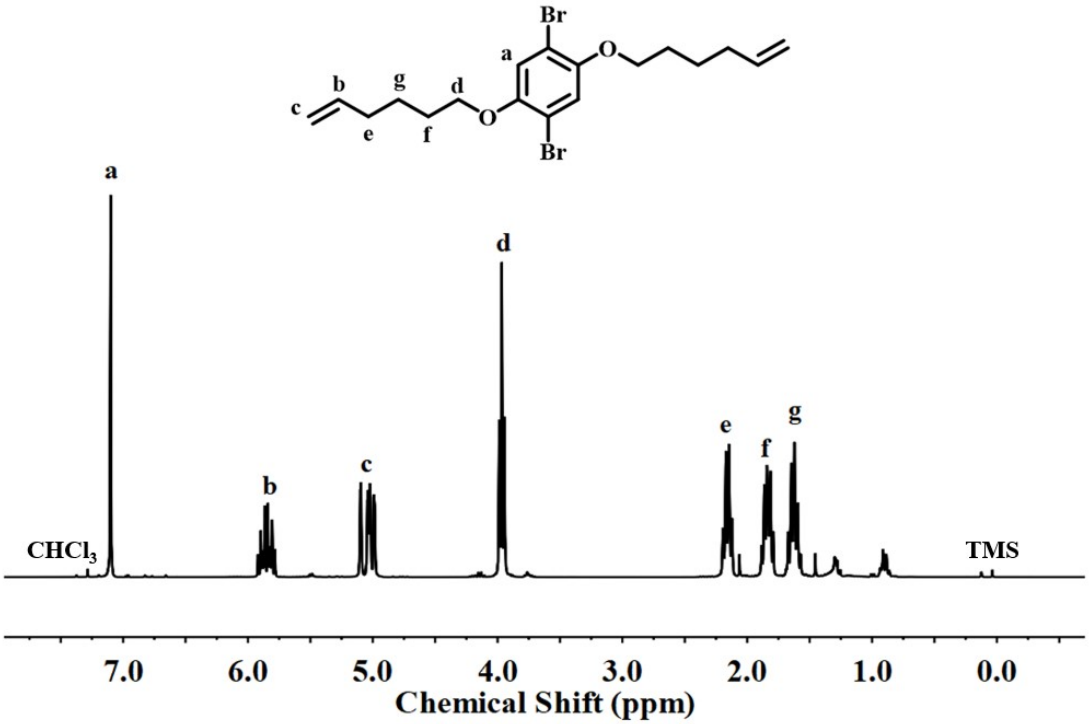


Figure S3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

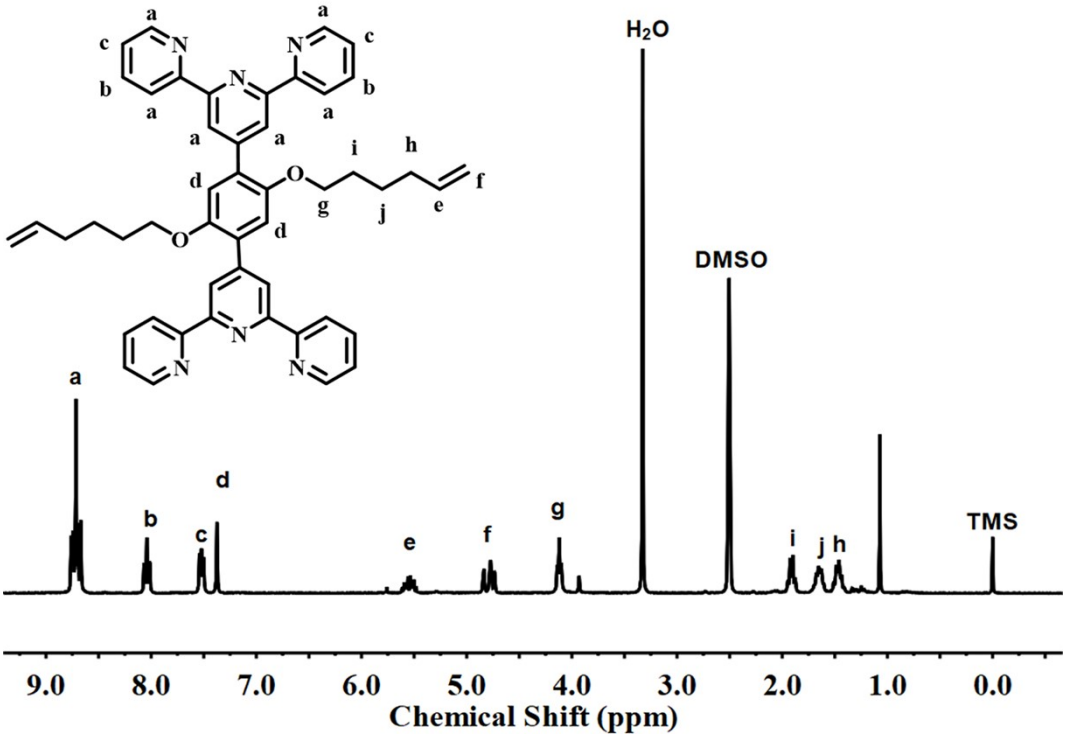


Figure S4. ^{1}H NMR spectrum of the ligand ACA in DMSO-d_6.

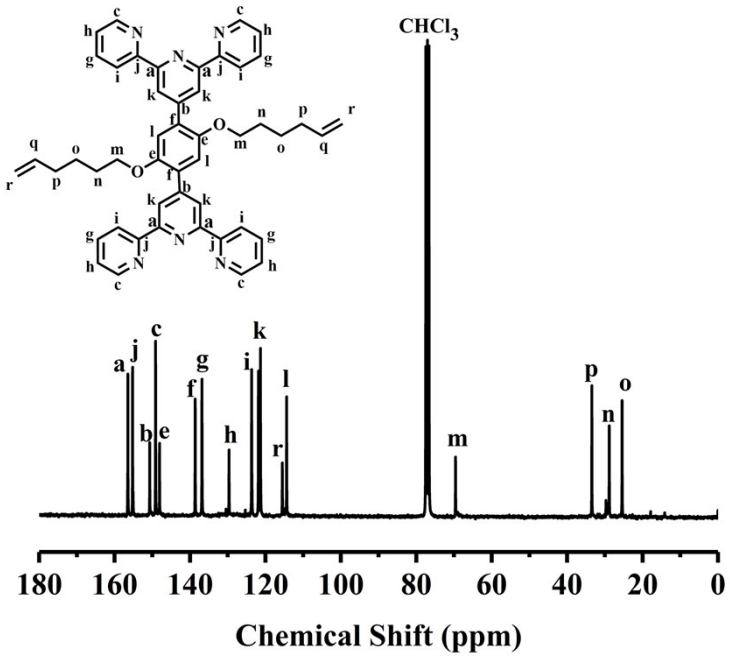


Figure S5. ^{13}C NMR spectrum of the ligand ACA in $CDCl_3$.

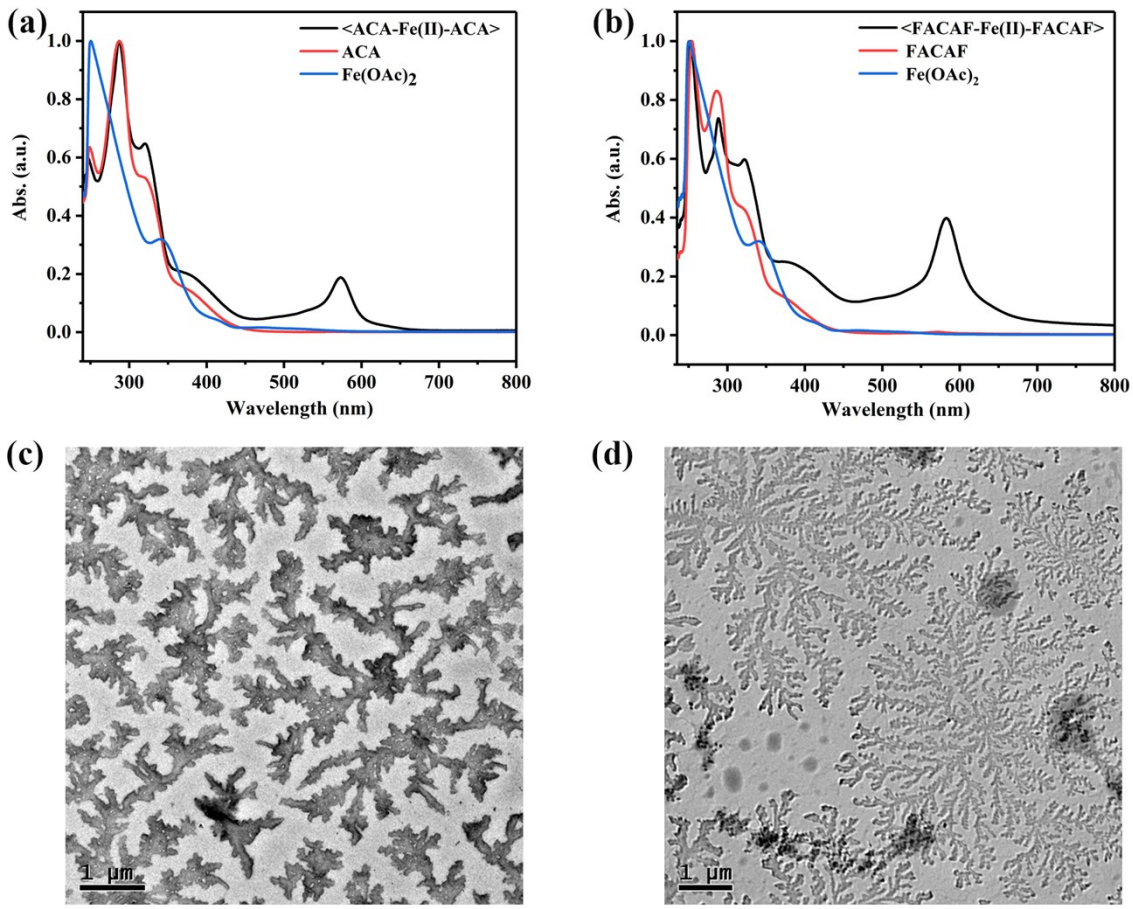


Figure S6. UV-vis absorption spectra of <ACA-Fe(II)-ACA>, ACA and $Fe(OAc)_2$ (a), <FACAF-Fe(II)-FACAF>, FACAF and $Fe(OAc)_2$ (b) in 10^{-4} M CH_3COOH solution. TEM images of <ACA-Fe(II)-ACA>(c) and <FACAF-Fe(II)-FACAF> (d) in 0.05 g L^{-1} of CH_3COOH solution dropped on carbon-coated copper grids followed by solvent evaporated in a vacuum oven.

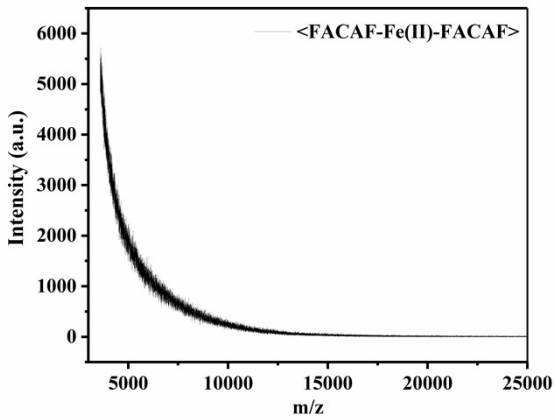


Figure S7. MALDI-TOF MS spectrum of <FACAF-Fe(II)-FACAF> in a linear mode.

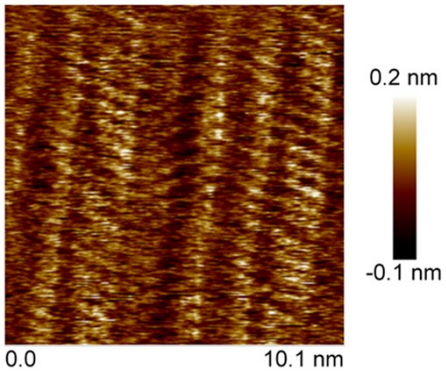


Figure S8. STM image of <ACA-Ru(II)-ACA>.

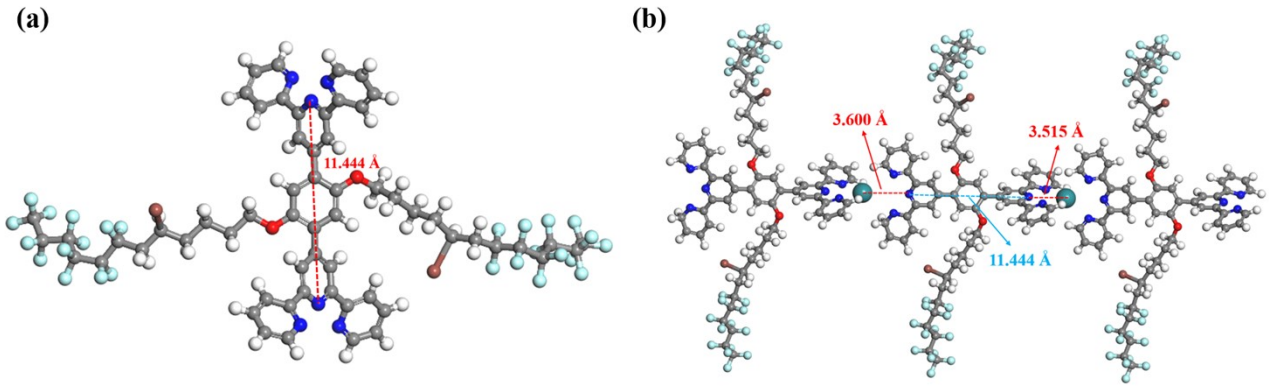
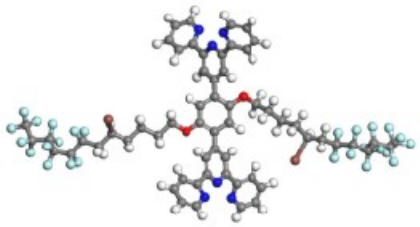


Figure S9. The DFT optimized structure of FACAF (a) and forcite module based on molecular dynamics of the metallopolymer <FACAF-Ru(II)-FACAF (b).

S4 DFT Structure Details



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Direct

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0.827610016	0.415549994	0.417100012
0.280180007	0.449109972	0.464430004
0.264219999	0.450240016	0.505819976
0.268900007	0.361639977	0.459239990
0.257800013	0.356010020	0.501980007
0.217040002	0.353500009	0.467070013
0.215829998	0.407850027	0.497040004
0.237540007	0.420329988	0.430059999
0.225700006	0.469860017	0.460839987
0.189089999	0.389310002	0.424640000
0.174500003	0.420180023	0.462210000
0.199709997	0.477609992	0.405669987
0.178709999	0.502550006	0.441300005
0.158170000	0.457650006	0.413509995

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