Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

Ni(II) Complex on Bispyridine-Based Porous Organic Polymer as Heterogeneous Catalyst for Ethylene Oligomerization

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I. General information.

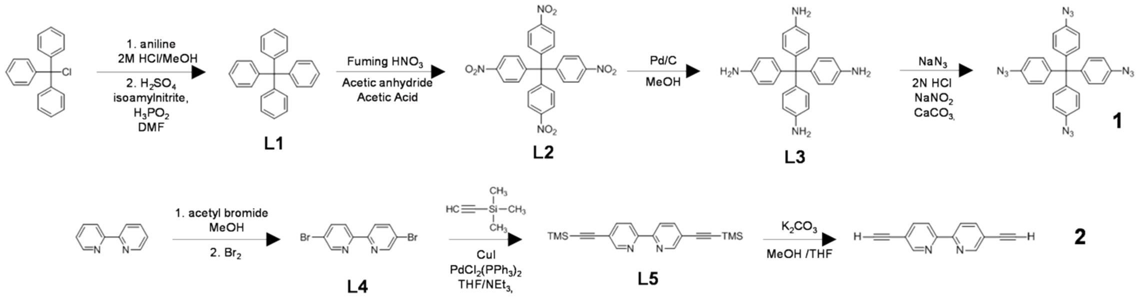
^{1}H-NMR spectra were recorded on a Varian AS400 (399.937 MHz for ^{1}H and 100.573 MHz for ^{13}C) and Bruker 500 MHz Ascend spectrometer. ^{1}H chemical shifts were referenced to the proton resonance resulting from protic residue in deuterated solvent and ^{13}C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Solid-state MAS-NMR experiments were acquired on a Bruker AVANCE II$^+$ 400MHz NMR system (400 MHz for ^{1}H, 100.4 MHz for ^{13}C) in KBSI Seoul Western Center, Korea. The spinning rate was 12 kHz. Spectra were acquired using a ^{1}H-^{13}C CP contact time of 2 ms and a recycle delay of 3 s between scans. ^{13}C NMR chemical shifts were calibrated using tetramethylsilane (TMS) as zero ppm. Fourier-transformed infrared (FTIR) spectroscopy was performed on an ALPHA FT-IR Spectrometer (Bruker Optics) equipped with a single-reflection diamond ATR accessory for all samples. Frequencies are given in reciprocal centimeters (cm^{-1}). Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min under a N_2 flow (50 mL/min) using a Scinco TGA N-1000 instrument. Thermal properties were studied under a nitrogen atmosphere on TA Instruments DSC Q20 and the measurements were performed at a heating (cooling) scan rate of 10 (-10) ^{o}C/min under nitrogen. N_2 adsorption and desorption isotherms were measured on a Micromeritics Tristar II instrument (Micromeritics Instrument Corporation, USA) and BELSORP–mini II (MicrotracBEL Corp., Japan) instrument at 77 K. DFT pore size distributions were obtained from the desorption branch of the resulting isotherms. Before each run, samples were activated at 80 °C for 3 h under high vacuum on a BELSORP Prep II (MicrotracBEL Corp., Japan) or critical point dry on a SAMDRI-PVT-3D (Tousimis, USA). Around 50–80 mg of sample was used in each measurement. All gas chromatography (GC) analyses using an Agilent Technologies 6890N Network GC system (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with an FID detector and HP-5 capillary column (50 m × 320 μm × 0.17 μm film thickness). All samples were prepared by brominating the low-boiling point olefins in pre-cooled solutions (dry ice/acetone bath). Intrinsic activities for butenes (ratio between the amount of butenes formed and the Ni content of the catalyst/h) were estimated based on the ratio of peak area of brominated butene products. GC-MS analyses were performed on a GC 7890B coupled to an MSD 5977A (Agilent) using a DB-624 capillary column (30 m × 250 μm; film thickness, 0.25μm) in Kookmin university, Seoul, Korea. Scanning electron microscopy (SEM) images were collected on a JSM-7001F (JEOL, Japan) microscope. Samples were activated and coated with Pt using a Sputter Coater 108 Auto (Cressington, Watford, UK) before imaging. Nickel contents were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, iCAP 7600, Thermo Scientific), which were compared to the ICP standard solutions. POP-1-supported Ni(Ⅱ) catalysts (ca. 1 mg) were dissolved in 0.75 mL sulfuric acid (ACS reagent, 95−98%, Sigma-Aldrich) and 0.25 mL of 30 wt % H_2O_2 (aqueous, Sigma-Aldrich) mixture, followed by microwave digestion using an Initiator+ (Biotage) at 150 °C for 5 min. Ni(Ⅱ)-POP-1 was characterized by scanning electron microscopy–energy dispersive spectrometry in KBSI Seoul Center. SEM/EDX experiments were carried out using a Hitachi SU-70 SEM equipped with a silicon drift EDX detector (50 mm^2, Horiba, Japan). The accelerating beam voltage was fixed to 15 kV.

II. General materials and synthesis

All reagents and solvents were purchased from commercial sources and were used without further purification, unless otherwise indicated. All of the reactions and manipulations were carried out under air atmosphere unless otherwise noted. Distilled solvents used in inert-atmosphere reactions were dried using standard procedures.[1] All Flash column chromatography was carried out using silica gel 60 (230–400 mesh, Merck, Germany) using wet-packing method and TLC was performed on pre-coated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light. All deuterated solvents were purchased from Cambridge Isotope Laboratories and Aldrich.

Tetraphenylmethane (L1).[2] In a round-bottomed flask, chlorotriphenylmethane (20.0 g) and aniline (17.6 mL) were heated at 190 °C under vigorous stirring for 15 min. After the reaction mixture was allowed to cool down to room temperature, the resulted solid crushed out. Then, a solution of aqueous HCl (2M, 80 mL) and methanol (120 mL) were added and the mixture was heated for another 30 min at 80 °C. After cooling down to room temperature, the resulting solid was filtered off, washed with water (250 mL) and dried *in vacuo* for overnight. The dry solid was also crashed out, suspended in DMF (200 mL) and cooled down to -15 °C. At this temperature, sulfuric acid (96 %, 22 mL) and isoamylnitrite (16 mL) were added slowly and the suspension was stirred for 1 h. Then, hypophosphorous acid (50 %, 60 mL) was added dropwise. Once the addition was completed, the reaction mixture was heated at 70 °C until the evolution of gas ceased. Then, the solid was filtered off and washed subsequently with DMF, water, and ethanol. This washing procedure was repeated twice. Pure tetraphenylmethane was obtained by recrystallization in DMF to give a brownish powder (**L1**, 15.5 g, 67 %). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.20–7.29 (m, 20 H).

Scheme S1



Tetra-(4-nitrophenyl)-methane (L2).[3] **L1** (2 g) was added in portions to 10 mL of fuming nitric acid (96%) at -10 °C with vigorous stirring. To this mixture 3.3 mL of acetic anhydride and 6.6 mL of glacial acetic acid was slowly added and stirred for ~15 min. Finally, the reaction mixture was diluted with 32 mL of glacial acetic acid and the resulting yellow solid was filtered on a glass frit, washed with acetic acid, methanol, chilled THF and dried under dynamic vacuum to obtain **L2** as a yellow crystalline solid (1.6 g, 51.2 %). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 8.23 (d, 8H, J = 8.60 Hz), 7.61 (d, 8H, J = 8.60 Hz), ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) 151.1, 146.1, 131.5, 123.8.

Tetrakis(4-aminophenyl)methane (L3).[4] In a two-necked round-bottomed flask, **L2** (0.5 g) and Pd/C (10 %, 0.01 g) were suspended in degassed methanol (20 mL) under nitrogen. The reaction mixture was degassed and backfilled with hydrogen for five times. The resulting reaction mixture was vigorous stirred under hydrogen atmosphere for 48 h at room temperature. Then, the resulting mixture was filtered on a glass frit, washed with methanol and THF, and evaporated to afford pure **L3** as a light yellow solid (0.94 g, 96 %). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 6.67 (d, 8H, J = 8.60 Hz), 6.38 (d, 8H, J = 8.60 Hz), 4.85 (s,8H), ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) 145.7, 135.9, 131.1, 112.6, 61.1.

5,5′-dibromo-2,2′-bipyridine (L4).[5] To a solution of 2,2′-bipyridine (10 g) in methanol (75 mL) was added acetyl bromide (12 mL) dropwise with vigorous stirring using a disposable plastic syringe at 0 °C. Upon complete addition, the cooling bath was removed and the reaction mixture was stirred for an additional 30 min at room temperature. After removal of volatiles using a rotary evaporator, the residue was dried under high vacuum for 24h. This dried solid (3.2 g) was charged in a mortar and 3.3 mL of bromine was added slowly. Make sure that the tip of the needle is digging into the dried solid. From time to time, the mixture was mixed and ground using the pestle and spoon. After the addition, the reaction mixture was ground until a homogenous orange powder was obtained and the resulting mixture was transferred into a 20 mL vial. This vial was then transferred into a stainless steel bomb and the steel bomb was sealed. The steel bomb was placed in an oven at 185 °C for 72 h. After cooling to room temperature, the bomb was opened and the resulting reaction mixture was placed into a mortar and carefully smashed. After removal of pieces of glass with the tweezers, the reaction mixture was ground until a fine powder was obtained. The crude product was transferred into a large Erlenmeyer flask and 2 M NaOH solution (120 mL), EDTA tetrasodium salt (6 g), Na_2SO_3 (6 g) and CH_2Cl_2 (60 mL) were added. After stirring the reaction mixture for 2 h at room temperature, the organic phase was separated and extracted from the aqueous phase five times with CH_2Cl_2. The organic was combined and dried over anhydrous Na_2SO_4. After recrystallization from CH_2Cl_2, **L4** was obtained as a white solid (1.3 g, 39 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.70 (d, 2H, J = 2.0 Hz), 8.28(d, 2H, J = 8.6 Hz), 7.94 (dd, 2H, J = 8.6 Hz, J = 2.3 Hz).

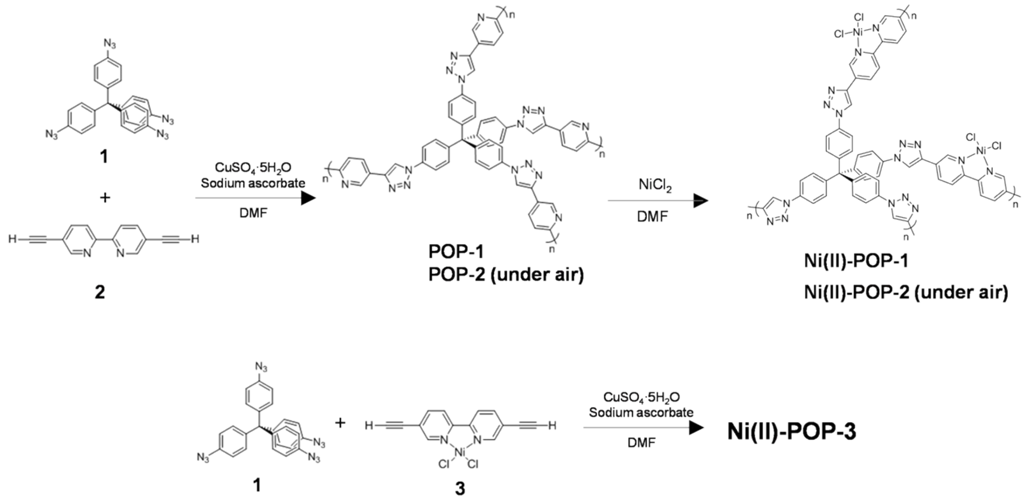
5,5′-Trimethylsilylacetylene-2,2′-bipyridine (L5).[6] In a two-necked round-bottomed flask, **L4** (0.5 g), $PdCl_2(PPh_3)_2$ (0.11 g) and CuI (0.05 g) were suspended in THF (33.5 mL) and NEt_3 (12.5 mL). Then, N_2 was bubbled through the solution for 5 min. Trimethylsilylacetylene (0.65mL) was added to the resulting mixture, and then allowed to stir at 60 °C overnight under nitrogen. After cooling down, the reaction mixture was filtered and concentrated under reduced pressure, and the residue dissolved in CH_2Cl_2 and extracted with an aqueous saturated solution of NH_4Cl, then brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure and purified by column chromatography (CH_2Cl_2 : Hex, 1:2 v/v) to afford **L5** as a pale yellow solid (0.55 g, 95.6 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.72 (s, 2H), 8.36 (d, J = 8.2 Hz, 2H), 7.86 (dd, J = 8.2, 2.1 Hz, 2H), 0.28 (s,18H), ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.1, 152.0, 139.8, 120.5, 120.3, 101.7, 99.4, -0.2.

Tetra(4-azidophenyl)methane (1).[7] **L3** (0.4 g) was dissolved in 2N aqueous HCl (21 mL) in a 500-mL round-bottom flask and cooled down to 0 °C. A solution of $NaNO_2$ (0.45 g) in H_2O (2 mL) was then added drop-wise into the cooled reaction flask with vigorous stirring. The reaction mixture was kept at 0 °C for 30 min before being neutralized with $CaCO_3$ (0.65 g). To this mixture was then added a solution of NaN_3 (0.5 g) in H_2O (2 mL) at 0 °C. The resulting mixture was allowed to stir at 0 °C for an additional 20 min and then filtered. The collected solid was washed with excess H_2O and dried under dynamic vacuum to afford **1** as a white solid (0.5 g, 95 %). ^{1}H NMR

(400 MHz, $CDCl_3$): δ (ppm) 7.13 (d, 8H, J = 8.60 Hz), 6.93(d, 8H, J = 8.60 Hz), ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.8, 138.1, 132.0, 118.4, 63.2.

5,5′-Diethynyl-2,2′-bipyridine (2).[6] **L5** (0.10 g) was dissolved in a mixture of methanol and THF (1:1, 5 mL) and powdered K_2CO_3 (0.04 g) was added. The mixture was stirred for 3 h at room temperature and the solution was filtered and concentrated under reduced pressure. The residue dissolved in CH_2Cl_2 and extracted with brine. The organic fraction was treated with activated charcoal, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. After column chromatography (CH_2Cl_2:Hex ,1:2 v/v) pure **2** was obtained as a beige solid (0.05 g, 89 %). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.76 (d, J = 1.8 Hz, 2H), 8.38 (d, J = 8.2 Hz, 2H), 7.89 (dd, J = 8.2, 2.1 Hz, 2H), 3.31 (s, 2H), ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.4, 152.2, 140.0, 120.5, 119.4, 81.6, 80.5.

Scheme S2



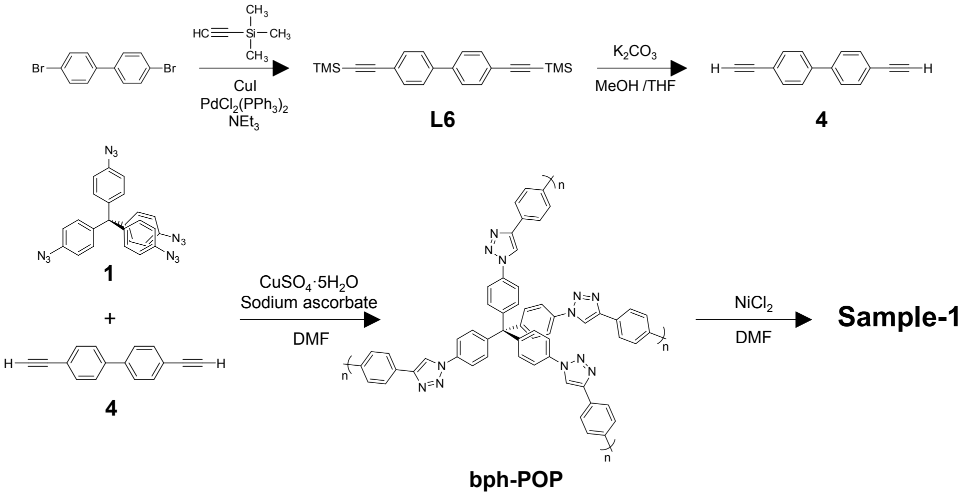
Preparation of POP-1.[7] **1** (200 mg), **2** (168.6 mg) and DMF (82.4 mL, to make a 0.02 M solution of azide functional group, at 1:1 alkyne to azide functional group ratio) were added into a 250-mL flask equipped with a magnetic stir bar and a reflux condenser. Then, resulting mixture heated up to 60 °C to make clear solution. After then, $CuSO_4 \cdot 5H_2O$ (41.2 mg, 0.1 equiv. per acetylene functional group) and sodium ascorbate (32.7 mg, 0.1 equiv. per acetylene functional group) were added subsequently. The reaction mixture was heated at 100 °C for 24 h. After cooling, the reaction mixture was filtered over a fine fritted funnel and successively washed with water (2 × 50 mL), methanol (2 × 50 mL), and THF (2 × 50 mL). The resulting brown solid was shaken in water (10 mL) for 5 h at room temperature before being filtered through a fine fritted funnel. After drying under vacuum, the **POP-1** was obtained as yellow to brown solid (357 mg, 91 % yield).

General procedure for POP metalation.[8] $NiCl_2 \cdot 6H_2O$ (400 mg) was dissolved in distilled DMF (26 mL) and powdered **POP** (0.35 g) was added. The mixture was placed in an 80 °C oven for 24 h. After cooling down to room temperature, the mixture was centrifuged. The liquid was decanted and the remaining solid washed with fresh DMF for three times. The solid was soaked in acetone overnight and washed with acetone twice thereafter. After drying, Ni(II) containing **POP** was obtained as a yellow to brown solid. (~60 %).

Preparation of Ni(Ⅱ)-POP-3. **1** (200 mg), (5,5′-diethynyl-2,2′-bipyridyl)nickel(II) chloride (**3**, 272 mg) and DMF (82.4 mL, to make a 0.02 M solution of azide functional group, at 1:1 alkyne to azide functional group ratio) were added into a 250-mL flask equipped with a magnetic stir bar and a reflux condenser. Then, resulting mixture heated up to 100 °C to make clear solution. After then, $CuSO_4 \cdot 5H_2O$ (41.12 mg, 0.2 equiv per acetylene functional group) and sodium ascorbate (32.64 mg, 0.2 equiv per acetylene functional group) were added subsequently. The reaction mixture was then heated to 130 °C for 24 h before being stopped. After cooling down to room temperature, the reaction mixture was filtered over a fine fritted funnel and successively washed with water (2 × 50 mL), methanol (2 × 50 mL), and THF (2 × 50 mL). The resulting brown solid was shaken in water (10 mL) for 5 h at room temperature before being filtered through a fine fritted funnel. After drying under vacuum, the **Ni(Ⅱ)-POP-3** was obtained as a brown solid (60 mg, 12%).

Preparation of Ni(bpy)Cl$_2$.[9] $NiCl_2 \bullet 6H_2O$ (1 g) and 2,2’-dipyridyl (0.5 g) were dissolved separately with 34 mL of hot absolute ethanol under nitrogen. The two solutions were combined and refluxed for 4.5 h. After cooling, the resulting precipitates were filtered, washed with cold ethanol and dried under vacuum. Pure Ni(bpy)Cl_2 was collected as a light green powder (0.11 g, 12 %). Anal. Calcd for Ni(bpy)Cl_2 + H_2O ($NiC_{10}H_{10}N_2Cl_2O$): C, 39.54; H, 3.32; N, 9.22. Found: C, 40.06; H, 3.28; N, 9.20.

Scheme S3



4,4'-di[(trimethylsilyl)ethynyl]-1,1'-biphenyl (L6).[10] In a two-necked round-bottomed flask, 4,4'-dibromo-1,1'-biphenyl (0.5 g), $PdCl_2(PPh_3)_2$ (0.11 g) and CuI (0.06 g) were suspended in dry Et_3N (11 mL). Then, N_2 was bubbled through the solution for 5 min. Trimethylsilylacetylene (0.54 mL) was added to the resulting mixture. The reaction mixture was stirred at 70 °C for 4 h under N_2. After the solvent was removed under reduced pressure and purified by column chromatography (CH_2Cl_2:Hex, 1:12 v/v) to afford **L6** as a white solid (0.49 g, 88 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.53 (s, 2H), 0.26 (s, 18H).

4,4'-diethynyl-1,1'-biphenyl (4).[10] **L6** (0.49 g) was dissolved in a mixture of methanol (3.2 mL) and THF (7 mL) and powdered K_2CO_3 (1.56 g) was added. The mixture was stirred for 2 h at room temperature and the reaction mixture was neutralized with a 1 M HCl solution and was extracted in CH_2Cl_2 and washed with water three times. The organic fraction was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. After column chromatography (CH_2Cl_2:Hex ,1:12 v/v) to afford **4** as a white solid (0.28 g, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 − 7.53 (m, 8H), 3.14 (s, 2H).

Preparation of bph-POP and Sample-1. The synthesis was carried out in the same procedure as in the preparation of **POP-**1 and **Cu(II)-POP-1**.

III. Catalysis

General procedure for ethylene dimerization reactions in the liquid phase under batch conditions.[11] Inside an Ar-filled glovebox, **Ni(II)-POP-1** (8.5 mg, 7.2 μmol of Ni) was combined with anhydrous heptane (15 mL) and Et_2AlCl (0.5 mL of a 1 M solution in hexane, CAUTION: pyrophoric liquid) in a 45-mL pressure vessel (Parr Instruments Series 4714) fitted with a pressure gauge and charged with a magnetic stir bar. The pressure vessel was closed and taken out of the glovebox. The reaction mixture was allowed to stir for 10 min followed by sonication for 10 min. Next, the pressure reactor was connected to a T-joint assembly together with an ethylene gas tank and a Schlenk line. The reaction mixture was then allowed to stir for 1 h at 20 ^oC under a constant pressure of ethylene. After completion, the reactor was closed from the ethylene source and quickly cooled in a dry ice/acetone bath (-78 °C) and the pressurized ethylene was released. The reactor was opened while still inside the cold bath and an aliquot (1.0 mL) of the reaction mixture was transferred to a 4-mL vial that is also situated inside a dry ice/acetone bath. Excess bromine (0.5 mL, 10 mmol) was added to the sample and vial was capped, shaken, and allowed to warm up to room temperature. The resulting brownish solution was washed with concentrated aqueous solution of $Na_2S_2O_3$ until clear, dried over Na_2SO_4, and analyzed by GC-FID.

IV. Additional data

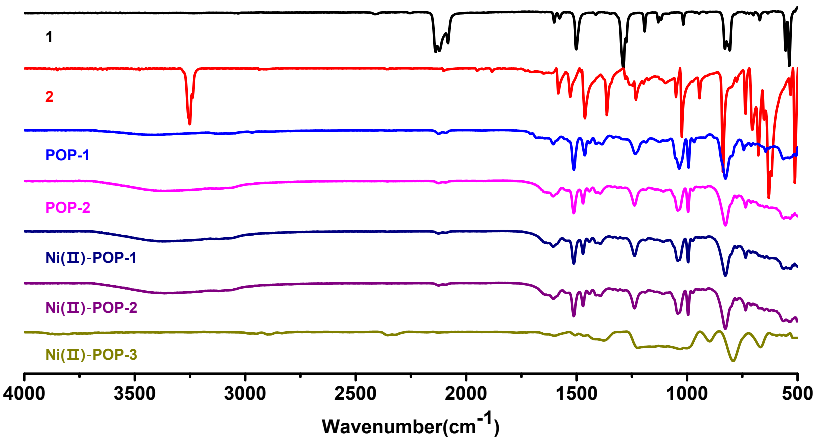


Figure S1. FT-IR spectra of **1**, **2**, **POP-1**, **POP-2**, **Ni(II)-POP-1**, **Ni(II)-POP-2** and **Ni(II)-POP-3**.

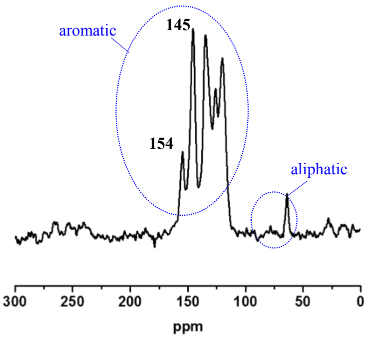
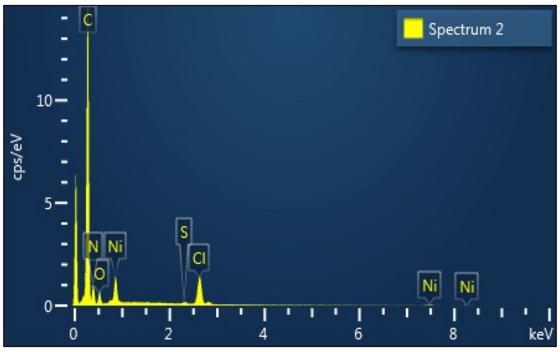


Figure S2. ^{13}C CPMAS NMR spectra of the **POP-1**. The overlapped peaks between 110–160 ppm are assigned to aromatic carbons. The peaks around 145 and 154 ppm are assigned to the carbons in triazole.



Element	Weight (%)
C	69.5
N	16.46
Cl	3.55
Ni	5.65
O	4.63
S	0.18

Figure S3. EDX analysis of **Ni(Ⅱ)-POP-1.**

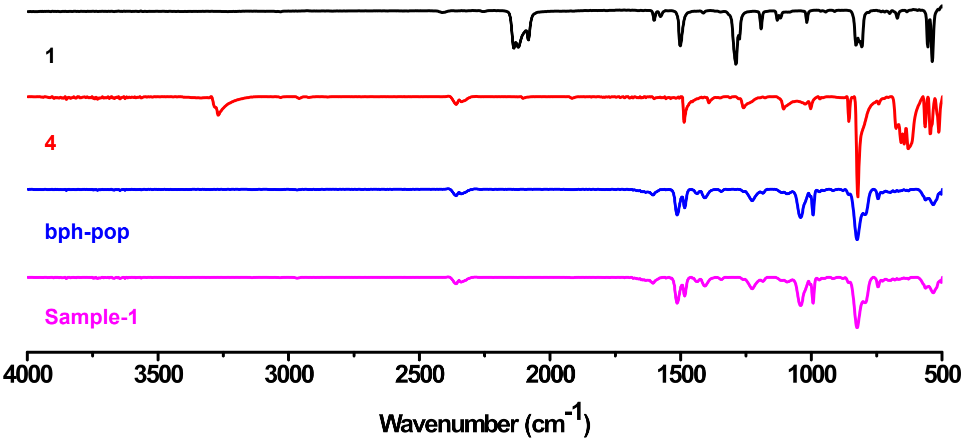


Figure S4. FT-IR spectra of **1**, **4**, **bph-POP**, and **Sample-1**.

Table S1. Ni loading, surface areas and pore sizes of **POP-1**, **POP-2**, **Ni(Ⅱ)-POP-1**, **Ni(Ⅱ)-POP-2** and **Ni(Ⅱ)-POP-3**.

Compound	Ni loading (%)	SA_{BET}^{a,b} [m^2g^{-1}]	Pore size [nm]
POP-1	-	595	11.6
POP-2	-	320	5.9
Ni(Ⅱ)-POP-1	5.0	375	16.9
Ni(Ⅱ)-POP-2	3.4	220	4.5
Ni(Ⅱ)-POP-3	2.5	85	7.4

[a] SA_{BET} = Brunauer–Emmet–Teller (BET) surface area.
[b] Determined from at least three times measurements.

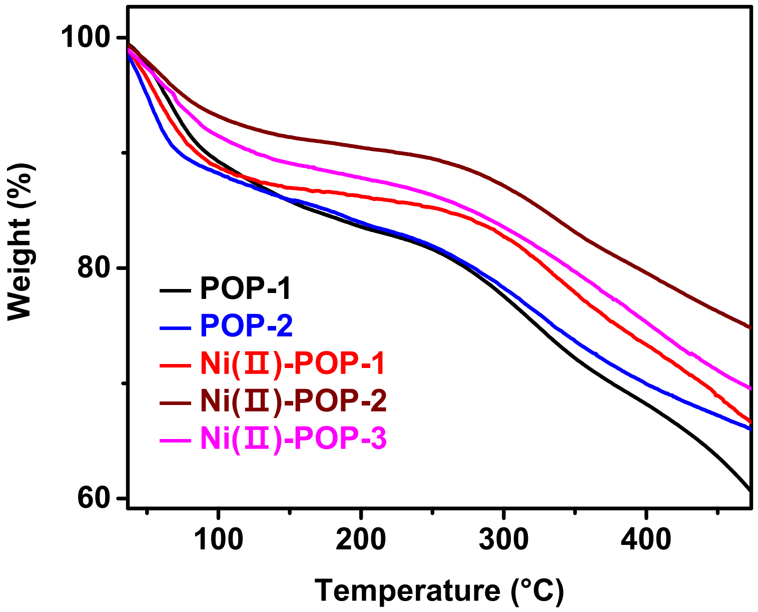


Figure S5. Thermal characteristics of **POP-1**, **POP-2**, **Ni(II)-POP-1, Ni(II)-POP-2** and **Ni(II)-POP-3** analyzed by TGA.

Table S2. Reported catalytic activity of representative Ni-complex supported materials for the ethylene oligomerization.

Compound (Supporter)	T (°C)	P_{C2} (bars)	Al/Ni	C_4 Selectivity (%)	activity	reference
Ni-POP-1 (POP)	20	20	70	54 (*vs* oligom)	800 (IA)	this study
Ni@(Fe)MIL-101 (MOF)	25	30	70	95 (*vs* C6)	10,455 (IA)	12
Ni(bipy)@UiO-66 (MOF)	55	59	100	48 (*vs* oligom)	36,000 (TOF)	13
NU-1000-bpy-$NiCl_2$ (MOF)	21	15	70	93 (*vs* C6 and C8)	1,950 (IA)	14
MixMOFs-Ni-b (MOF)	40	20	100	92.7 (*vs* oligom)	16,400 (TOF)	15

[Ni(N,O)]@IL (Ionic Liquid)	25	0.5	400	15.3 (*vs* oligom)	45,200 (TOF)	16

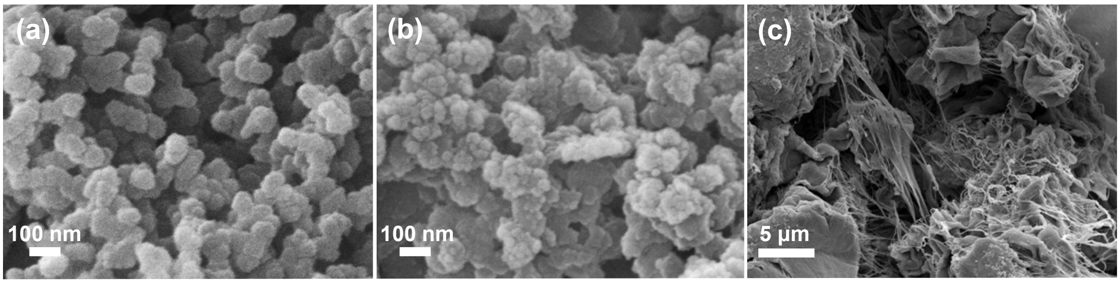


Figure S6. SEM images of (a) **POP-1**, (b) **Ni(II)-POP-1**, and (c) **Ni(II)-POP-1** recovered after the catalytic reaction at 20 ^{o}C under 20 bar of ethylene showing the particles were covered by polyethylene (PE).

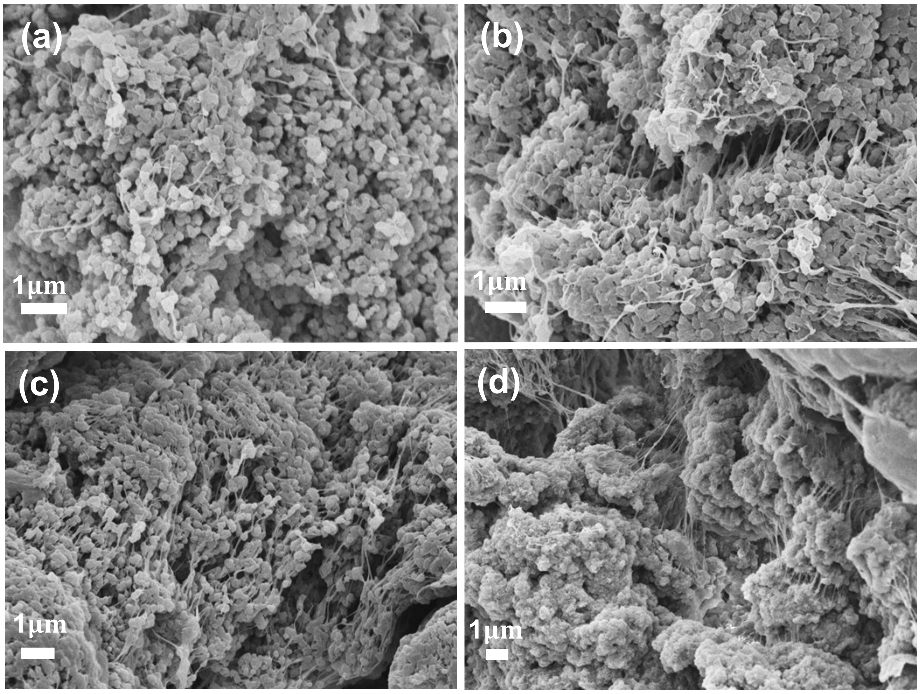


Figure S7. SEM images of **Ni(II)-POP-1** recovered after the 1st (a), 2nd (b), 3rd (c), and 4th catalytic cycles at 0 °C under 5 bar of ethylene, showing the coverage of polyethylene (PE) on particles is dramatically increased after each run.

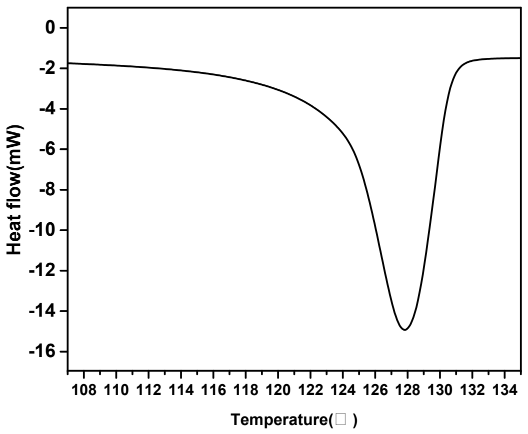


Figure S8. DSC pattern of the solid materials collected after 1st polymerization runs indicating that most of it is polyethylene (PE). The broad melting range (115–131 ˚C) indicates PE with a high polydispersity index.[9]

V. Reference

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