Supporting Information

N-heterocyclic carbene based MOFs catalyst for Sonogashira cross-coupling reaction

Chizoba I. Ezugwu, a,b Bibimaryam Mousavi a,b, Md. Ali Asraf a,b, Akshay Mehta a,b, Harsh Vardhan a,b, and Francis Verpoort a,b,c,d*

a Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R. China.

b School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, P.R. China.

c National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk Russian Federation.

d Ghent University, Global Campus Songdo, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon, Korea.

Email: frances.verpoort@ghent.ac.kr

e Department of Chemistry, Rajshahi University, Rajshahi-6205, Bangladesh

1. Synthesis and Characterization

All chemicals and regents are commercially available and used as received without further purification. Synthesis of the azolium ligand, 1,3-bis(4-carboxyphenyl)imidazolium chloride (H2L+Cl−) was achieved in two steps following reported literature procedures.1, 2 Compound 1 was synthesized according to a procedure reported in the literature2

1H and 13C-NMR spectra were recorded at 500 MHz and at 100 MHz, respectively, if not otherwise stated using Bruker 500 MHz NMR spectrometer. 1H-NMR spectra were referenced to tetramethylsilane (TMS). Powder X-ray diffraction patterns (XRD) were recorded using an Empyrean instrument from PANalytical by applying a monochromatic Cu Kα radiation at ambient conditions. Fourier transform infrared (FT-IR) spectra were collected on a Perkin-Elmer Spectrum One spectrometer. Scanning electron microscope (SEM) from JEOL (JSM-5610LV, 0.5–35 kV) was used to investigate the texture of the materials. TEM investigation was carried out in a Philips CM20 microscope operated at 200 kV. The solid sample was crushed and dispersed in water-free ethanol. The solution was then ultra-sonicated for 3 min before dropping onto a Cu-grid with lacey carbon film. Imaging and diffraction of the structure was performed at
low electron dose in order to minimize beam damage to the sample. Thermogravimetric analyses (TGA–DSC) were conducted on a Netzsch (STA449c/3/G) instrument at a heating rate of 10 °C/min under inert atmosphere (N₂-flow). The element distribution map measurement was performed on a S4800 field emission scanning electron microscope (FESEM, Hitachi, Japan) equipped with an X-Max 50 energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, Britain) with an accelerating voltage of 10 kV. Dynamic Light Scattering DLS analysis was performed in a ZETASIZER Nano series (ZEN4602) instrument (particle size distribution from 0.6 to 6000 nm and detection limit of 0.1 ppm). The surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA). All the binding energy values are calibrated by using C1s= 284.6 eV as a reference. The content of Pd, are determined by inductively coupled plasma optical emission spectra (ICP, Varian VISTAMPX). The low-pressure gas adsorption isotherms were measured by the volumetric method on a Micromeritics instrument (ASAP2020). In the gas adsorption measurements 60 mg of sample was used. For the N₂ gas adsorption analyses, gas of purity > 99.999% were applied. Prior to the adsorption measurements, the samples were evacuated at 180 °C under vacuum (initial activation) for about 3 h. The micro pore surfaces were calculated by the Brunauer–Emmett–Teller (BET) and Langmuir method.

2. Post-synthetic Modification of 1
To a 250 mL two-necked round bottom flask containing a THF solution (100 mL) of Pd(OAc)₂ (336.75mg) 1 (600.0 mg, 0.1 mmol) was introduced. The reaction mixture was stirred at ambient temperature for 12 h and then refluxed for 24 h under an inert N₂ atmosphere. The light-brown solid formed was collected by filtration followed by washing with THF, MeOH, and Et₂O; and drying in air.

3. Sonogashira Cross-Coupling Reaction
A 100 mL Schlenk flask was charged with 2-bromopyridine (0.92mmol), phenylacetylene (1.1 mmol), Cs₂CO₃ (1.84 mmol), 1-Pd (0.003 mmol based on Pd), DMF (6 mL), and the reaction mixture was stirred at 100°C under atmospheric condition for 12 h. The mixture was cooled to the room temperature; the solid was removed by filtration and washed twice with DMF (3 mL). The filtrate was collected, dried and the residue was extracted with ethyl acetate (3×3 mL) followed by purification with silica gel chromatography (petroleum ether) to give a corresponding product.
References


Figure S1. $^1$H-NMR spectrum of $\text{H}_2\text{L}^+\text{Cl}^-$

Figure S2. $^{13}$C-NMR spectrum of $\text{H}_2\text{L}^+\text{Cl}^-$
Figure S3. $^1$H-NMR spectrum of digested sample of 1

Figure S4. $^{13}$C-NMR spectrum of digested sample of 1
Figure S5. PXRD pattern for 1 and 1-Pd

Figure S6. TGA results of as-synthesized 1 and the modified framework, 1-Pd showing the retention of thermal property of the as-synthesized framework after modification.
Figure S7. FT-IR spectra of $\text{H}_2\text{L}’\text{Cl}^-$, 1 and 1-Pd

Figure S8. EDS Mapping of 1-Pd indicating the presence of Zn, O, C and Pd
Figure S9. $^1$H-NMR spectrum of digested sample of 1-Pd

Figure S10. $^{13}$C-NMR spectrum of digested sample of 1-Pd
Figure S11. XPS measurement of 1-Pd after catalysis

Table S1: BET surface area of 1 and 1-Pd

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET Surface Area (m²/g)</th>
<th>Langmuir Surface Area (m²/g)</th>
<th>Single point total pore volume at P/P⁰=0.993625502: (cm³/g)</th>
<th>DFT Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>102.02</td>
<td>109.87</td>
<td>0.045</td>
<td>0.057</td>
</tr>
<tr>
<td>1-Pd</td>
<td>88.36</td>
<td>96.25</td>
<td>0.032</td>
<td>0.044</td>
</tr>
</tbody>
</table>
Figure S12. Particle size distribution determined by DLS measurements.

4. $^1$H-NMR spectra data for the Sonogashira-cross coupling products

Entry 1

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 8.63 (d, 1H, Py-$H$), 7.69 (t, 1H, Py-$H$), 7.58 (d, 2H, Ar-$H$), 7.53 (d, 1H, Py-$H$), 7.24 (t, 1H, Py-$H$), 6.92 (d, 2H, Ar-$H$), 3.86 (s, 3H, OCH$_3$) ppm.

Entry 2

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 8.64 (d, 1H, Py-$H$), 7.69 (t, 1H, Py-$H$), 7.57 (d, 2H, Ar-$H$), 7.55 (d, 1H, Py-$H$), 7.42 (d, 2H, Ar-$H$), 7.25 (t, 1H, Py-$H$), 1.35 (s, 9H, CH$_3$) ppm.

Entry 3

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 8.64 (d, 1H, Py-$H$), 7.70 (t, 1H, Py-$H$), 7.63 (d, 2H, Ar-$H$), 7.56 (d, 2H, Py-$H$), 7.37-7.43 (m, 3H, Ar-$H$), 7.26 (t, 1H, Py-$H$) ppm.
Entry 4

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 7.56 (d, 2H, Ar-H), 7.47 (d, 2H, Ar-H), 7.37-7.34 (m, 3H, Ar-H), 7.19 (d, 2H, Ar-H), 2.40 (s, 2H, CH$_2$) 0.11 (s, 3H, CH$_3$) ppm.

Entry 5

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 7.50 (d, 2H, Ar-H), 7.44 (d, 2H, Ar-H), 7.18 (d, 2H, Ar-H), 6.91 (d, 2H, Ar-H), 3.85 (s, 3H, OCH$_3$), 2.39 (s, 2H, CH$_2$), 0.11 (s, 3H, CH$_3$) ppm.

Entry 6

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 7.50 (d, 2H, Ar-H), 7.44 (d, 2H, Ar-H), 7.40 (d, 2H, Ar-H), 7.19 (d, 2H, Ar-H), 2.40 (s, 2H, CH$_2$), 1.36 (s, 9H, CH$_3$), 0.11 (s, 3H, CH$_3$) ppm.

Entry 12

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 8.25 (d, 2H, Ar-H), 7.69 (d, 2H, Ar-H), 7.59 (d, 2H, Ar-H), 7.42-7.41 (m, 3H, Ar-H) ppm.

Entry 13

$^1$H-NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 7.97 (d, 2H, Ar-H), 7.64 (d, 2H, Ar-H), 7.58 (d, 2H, Ar-H), 7.40-7.39 (m, 3H, Ar-H), 2.64 (s, 3H, CH$_3$) ppm.