Electronic Supplementary Information

Pd(diiimine)Cl2 Embedded Heterometallic Compounds with Porous Structures as Efficient Heterogeneous Catalysts

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Experimental Section

Materials and physical measurements:
All reagents and solvents employed were commercially available and used as supplied without further purification. Powder XRD patterns were recorded with CuKα radiation by using a PANalytical X’Pert PRO diffractometer. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer. GC-MS data were obtained on a GC/MS-QP2010 system. TGA analyses of the complexes were performed on a NETZSCH STA 409 PC Simultaneous Thermal Analyzer under an N2 atmosphere at a scan rate of 10 ºC min⁻¹. Gas sorption experiments were measured with an ASAP-2020 gas adsorption instrument.

Synthesis:

1. \{Sm₂[\text{Pd(bpydc)Cl}_2]\text{H}_2\text{O}_4\}_n \text{ L}^{\text{Pd}} (0.03 \text{ mmol, 0.0127 g}), \text{Sm(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} (0.1 \text{ mmol, 0.0450 g}), \text{HCl} (0.1 \text{ mmol}), \text{and distilled water 1 mL were mixed in a Teflon-lined vessel. The solution was pre-treated by stirring for 10 min at ambient temperature in air. The vessel was closed in an autoclave and heated rapidly to 180 ºC, at which temperature it was held for 24 h. The product was collected by filtration, washed with water, and dried in air under ambient temperature. Yield: 91%. Anal. Caled for C_{24}H_{17}Cl_{14}N_{24}O_{10}Pd_{2}Sm: C, 28.08; H, 1.67; O, 15.59. Found: C, 28.01; H, 1.75; O, 15.69. IR (KBr, cm⁻¹): 3450 (s), 1709 (m), 1658 (w), 1612 (m), 1586 (m), 1555(m), 1411(s), 1396(s), 1288(w), 1262(w), 1129(w), 780(m).}

2. \{\text{Eu}_2[\text{Pd(bpydc)Cl}_2]\text{H}_2\text{O}_4\}_n \text{ L}^{\text{Pd}} (0.03 \text{ mmol, 0.0127 g}), \text{Eu(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} (0.1 \text{ mmol, 0.0440 g}), \text{HCl} (0.1 \text{ mmol}), \text{and distilled water 1 mL were mixed in a Teflon-lined vessel. The solution was pre-treated by stirring for 10 min at ambient temperature in air. The vessel was closed in an autoclave and heated
rapidly to 180 °C, at which temperature it was held for 24 h. The product was
collected by filtration, washed with water, and dried in air at ambient temperature.
Yield: 90%. Anal. Calcd for C_{24}H_{17}Cl_{4}N_{4}O_{10}Pd_{2}Eu: C, 28.04; H, 1.67; O, 15.56.
Found: C, 28.01; H, 1.73; O, 15.61. IR (KBr, cm^{-1}): 3455 (s), 1709 (m), 1617 (m),
1586 (m), 1555 (m), 1421 (s), 1386(m), 1287(w), 1252(w), 1124(w), 780(m).

3 \{Gd_{2}[Pd(bpydc)Cl_{2}]_{2}[Pd(Hbpydc)Cl_{2}]_{2}(H_{2}O)_{4}\}_{n}: L^{Pd}
(0.03 mmol, 0.0127 g), Gd(NO_{3})_{3}·6H_{2}O (0.1 mmol, 0.0440 g), HCl (0.1 mmol), and distilled water 1 mL
were mixed in a Teflon-lined vessel. The solution was pre-treated by stirring for 10
min at ambient temperature in air. The vessel was closed in an autoclave and heated
rapidly to 180 °C, at which temperature it was held for 24 h. The product was
collected by filtration, washed with water, and dried in air at ambient temperature.
Yield: 91%. Anal. Calcd for C_{24}H_{17}Cl_{4}N_{4}O_{10}Pd_{2}Gd: C, 27.90; H, 1.66; O, 15.48.
Found: C, 27.82; H, 172; O, 15.55. IR (KBr, cm^{-1}): 3419 (s), 1714 (m), 1663 (m),
1617(m), 1591 (m), 1555(m), 1416(s), 1386(s), 1293 (m), 1257 (m), 1129 (w), 769
(w).

4 \{Tb_{2}[Pd(bpydc)Cl_{2}]_{2}[Pd(Hbpydc)Cl_{2}]_{2}(H_{2}O)_{4}\}_{n}: L^{Pd}
(0.03 mmol, 0.0127 g), Tb(NO_{3})_{3}·6H_{2}O (0.1 mmol, 0.044 g), HCl (0.1 mmol), and distilled water 1 mL
were mixed in a Teflon-lined vessel. The solution was pre-treated by stirring for 10 min
at ambient temperature in air. The vessel was closed in an autoclave and heated
rapidly to 180 °C, at which temperature it was held for 24 h. The product was collected by
filtration, washed with water, and dried in air at ambient temperature. Yield: 90%.
Anal. Calcd for C_{24}H_{17}Cl_{4}N_{4}O_{10}Pd_{2}Tb: C, 27.85; H, 1.66; O, 15.46. Found: C,
27.79; H, 1.73; O, 15.53. IR (KBr, cm^{-1}): 3445 (s), 1704 (m), 1668 (m), 1611 (s),
1581 (m), 1560 (m), 1421(s), 1391(s), 1288(w), 1252(w), 1134(w), 780 (w).

Crystallographic Studies:
Diffraction data of 1 - 4 were collected on a Bruker Smart APEX CCD diffractometer
with graphite-monochromated Mo Ka radiation (\lambda = 0.71073 Å). The data was
collected at 173 K temperature and the structures were solved by direct methods and
subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL),
SADABS^{2} absorption corrections were applied to the data. All the non-hydrogen
atoms were refined anisotropically, and hydrogen atoms were located at calculated
positions.
Table S1. Crystallographic data and structure refinement results for compounds 1 - 4.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>1 (Pd-Sm)</th>
<th>2 (Pd-Eu)</th>
<th>3 (Pd-Gd)</th>
<th>4 (Pd-Tb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₂₄H₁₇Cl₄N₄</td>
<td>C₂₄H₁₇Cl₄N₄</td>
<td>C₂₄H₁₇Cl₄N₄</td>
<td>C₂₄H₁₇Cl₄N₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1026.37</td>
<td>1027.98</td>
<td>1033.27</td>
<td>1034.94</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>9.1629(8)</td>
<td>9.1669(5)</td>
<td>9.1605(8)</td>
<td>9.1570(7)</td>
</tr>
<tr>
<td>α, °</td>
<td>67.0610(10)</td>
<td>66.9840(10)</td>
<td>66.9550(10)</td>
<td>66.9190(10)</td>
</tr>
<tr>
<td>β, °</td>
<td>87.9300(10)</td>
<td>87.9180(10)</td>
<td>87.9010(10)</td>
<td>87.9440(10)</td>
</tr>
<tr>
<td>γ, °</td>
<td>77.1940(10)</td>
<td>77.1600(10)</td>
<td>77.0700(10)</td>
<td>77.0270(10)</td>
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<tr>
<td>V, Å³</td>
<td>1963.8(3)</td>
<td>1964.37(18)</td>
<td>1958.7(3)</td>
<td>1956.8(3)</td>
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<tr>
<td>Dc, g cm⁻³</td>
<td>1.736</td>
<td>1.738</td>
<td>1.752</td>
<td>1.756</td>
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<tr>
<td>μ, mm⁻¹</td>
<td>2.701</td>
<td>2.802</td>
<td>2.902</td>
<td>3.017</td>
</tr>
<tr>
<td>θ range, °</td>
<td>1.54 - 28.29</td>
<td>2.45 - 27.01</td>
<td>1.37 - 27.01</td>
<td>1.54 - 27.01</td>
</tr>
<tr>
<td>GOF on F²</td>
<td>1.093</td>
<td>1.117</td>
<td>1.067</td>
<td>1.117</td>
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<tr>
<td>R1 [I &gt; 2σ(I)]</td>
<td>0.0395</td>
<td>0.0402</td>
<td>0.0521</td>
<td>0.0558</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.1434</td>
<td>0.1519</td>
<td>0.1827</td>
<td>0.1896</td>
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<tr>
<td>∆ρ max, ∆ρ min, e Å⁻³</td>
<td>6.106, -1.371</td>
<td>5.409, -1.636</td>
<td>8.452, -1.894</td>
<td>6.538, -1.499</td>
</tr>
</tbody>
</table>

*R1 = | Σ||F||F| - | Σ||F||I||F| | Σ||F||I||F|.

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Table S2. Selected bond lengths (Å) of compounds 1 - 4.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>1 (Pd-Sm)</th>
<th>2 (Pd-Eu)</th>
<th>3 (Pd-Gd)</th>
<th>4 (Pd-Tb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-N (Å)</td>
<td>2.024(4)</td>
<td>2.024(5)</td>
<td>2.012(6)</td>
<td>2.016(7)</td>
</tr>
<tr>
<td>Pd-N (Å)</td>
<td>2.025(4)</td>
<td>2.028(5)</td>
<td>2.028(6)</td>
<td>2.031(7)</td>
</tr>
<tr>
<td>Pd-N (Å)</td>
<td>2.027(4)</td>
<td>2.033(5)</td>
<td>2.010(6)</td>
<td>2.015(8)</td>
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<tr>
<td>Pd-N (Å)</td>
<td>2.034(4)</td>
<td>2.035(5)</td>
<td>2.026(6)</td>
<td>2.037(7)</td>
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<tr>
<td>Pd-Cl (Å)</td>
<td>2.2950(12)</td>
<td>2.2936(14)</td>
<td>2.2927(18)</td>
<td>2.289(2)</td>
</tr>
<tr>
<td>Pd-Cl (Å)</td>
<td>2.2955(11)</td>
<td>2.2955(15)</td>
<td>2.2930(19)</td>
<td>2.293(2)</td>
</tr>
<tr>
<td>Pd-Cl (Å)</td>
<td>2.2898(11)</td>
<td>2.2909(15)</td>
<td>2.2881(19)</td>
<td>2.288(2)</td>
</tr>
<tr>
<td>Pd-Cl (Å)</td>
<td>2.2968(12)</td>
<td>2.2957(15)</td>
<td>2.292(2)</td>
<td>2.292(2)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.349(3)</td>
<td>2.326(4)</td>
<td>2.319(5)</td>
<td>2.298(6)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.351(3)</td>
<td>2.333(4)</td>
<td>2.342(5)</td>
<td>2.305(6)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.389(3)</td>
<td>2.379(4)</td>
<td>2.375(5)</td>
<td>2.356(6)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.398(3)</td>
<td>2.387(4)</td>
<td>2.382(5)</td>
<td>2.366(6)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.410(3)</td>
<td>2.394(4)</td>
<td>2.382(5)</td>
<td>2.370(6)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.415(3)</td>
<td>2.399(4)</td>
<td>2.387(5)</td>
<td>2.387(6)</td>
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<tr>
<td>Ln-O (Å)</td>
<td>2.519(3)</td>
<td>2.503(4)</td>
<td>2.490(6)</td>
<td>2.486(7)</td>
</tr>
<tr>
<td>Ln-O (Å)</td>
<td>2.563(3)</td>
<td>2.550(4)</td>
<td>2.522(5)</td>
<td>2.506(6)</td>
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</table>

Fig. S1. PXRD patterns for different samples

Fig. S2. View the 1D channels of compound 1
Gas sorption of compound 1

Compound 1 is insoluble in water and in common organic solvents. Thermogravimetric analysis of 1 shows weight loss of 4.0% at about 180 °C (Fig. S2), which correspond to the loss of two coordinated water (cald 3.5%) molecules. The solid is thermally stable up to 350 °C. The powder X-ray diffraction (PXRD) pattern of 1 accords with the simulated pattern, which indicates that the bulk sample is the same as single crystal. Heating 1 at 120 °C under vacuum for 6 h, {Sm₂[Pd(bpyde)Cl₂]₂[Pd(Hbpyde)Cl₂]₂}ₙ (1') formed, compared with 1, guest solvent molecules have been removed as evidenced by TG analysis (Fig. S2). Powder X-ray diffraction analysis shows that following removal of the guest molecules, not only crystalline states but also the structural integrity of frameworks was kept (Fig. S3).

![TGA of compounds 1 and 1'](image1)

**Fig. S3.** TGA of compounds 1 and 1'

![PXRD patterns for different samples](image2)

**Fig. S4.** PXRD patterns for different samples
Fig. S5. N\textsubscript{2} sorption curves (77 K) of I'

Table S3. Optimization of Suzuki–Miyaura reactions with bromobenzene and phenylboronic acid.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (0.5 mol%)</th>
<th>Solvent (5 ml)</th>
<th>Base (1.5 mmol)</th>
<th>T [°C]</th>
<th>Time [h]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>H\textsubscript{2}O/EtOH (3ml/2ml)</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>80</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>DMF</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>100</td>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>Toluene</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>95</td>
<td>4</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>Toluene</td>
<td>-</td>
<td>95</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>Toluene</td>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>95</td>
<td>4</td>
<td>88</td>
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<tr>
<td>6</td>
<td>1</td>
<td>Toluene</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>80</td>
<td>4</td>
<td>86</td>
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<tr>
<td>7</td>
<td>1</td>
<td>Toluene</td>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>95</td>
<td>2</td>
<td>75</td>
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Table S4. Optimization of Heck reactions with bromobenzene and styrene.
<table>
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<tr>
<th>Entry</th>
<th>Catalyst (0.5 mol%)</th>
<th>Solvent (3 ml)</th>
<th>Base (1.5 mmol)</th>
<th>(T) [°C]</th>
<th>Time [h]</th>
<th>Yield [%]</th>
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<tr>
<td>1</td>
<td>1</td>
<td>H(_2)O/EtOH (2ml/1ml)</td>
<td>NEt(_3)</td>
<td>80</td>
<td>4</td>
<td>40</td>
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<tr>
<td>2</td>
<td>1</td>
<td>Toluene</td>
<td>NEt(_3)</td>
<td>95</td>
<td>4</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>DMF</td>
<td>NEt(_3)</td>
<td>100</td>
<td>4</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>DMF</td>
<td>-</td>
<td>100</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>DMF</td>
<td>Na(_2)CO(_3)</td>
<td>100</td>
<td>4</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>DMF</td>
<td>NEt(_3)</td>
<td>80</td>
<td>4</td>
<td>81</td>
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</table>

**Fig. S6.** PXRD pattern for catalyst 1 (Pd-Sm) used in the Suzuki–Miyaura reaction with bromobenzene and phenylboronic acid (solvent: toluene, base: K\(_2\)CO\(_3\), temperature: 95 °C, time: 4h).

After the Suzuki–Miyaura reaction, the used catalyst 1 (Pd-Sm) was thoroughly washed with dichloromethane, then dilute hydrochloric acid, and last water before reuse. Powder X-ray diffraction analysis shows that after the catalytic reaction, not only crystalline state but also the structural integrity of catalyst 1 was kept (Fig. S6). The reusability of catalyst 1 (Pd-Sm) was investigated in the Suzuki–Miyaura reaction with high yield (Second-use 91% yield; Third-use: 90% yield) [substrate: bromobenzene and phenylboronic acid, solvent: toluene, base: K\(_2\)CO\(_3\), temperature: 95 °C, time: 4h].

**Fig. S7.** PXRD pattern for catalyst 1 (Pd-Sm) used in the Heck reaction with bromobenzene and styrene (solvent: DMF, base: NEt\(_3\), temperature: 100 °C, time: 4h).
After the Heck reaction, the used catalyst 1 (Pd-Sm) was thoroughly washed with dichloromethane before reuse. Powder X-ray diffraction analysis shows that after the catalytic reaction, not only crystalline state but also the structural integrity of catalyst 1 was kept (Fig. S7). The reusability of catalyst 1 (Pd-Sm) was investigated in the Heck reaction with high yield (Second-use 89% yield; Third-use: 87% yield) [substrate: bromobenzene and styrene, solvent: DMF, base: NEt$_3$, temperature: 100 ºC, time: 4h].

Reference:


(2) G. M. Sheldrick. SADABS (2.01), *Bruker/Siemens Area Detector Absorption Correction Program*; Bruker AXS: Madison, WI, 1998.