Electronic Supplementary Information

Pd(diimine)Cl$_2$ 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 N_2 atmosphere at a scan rate of 10 ºC min^{-1}. Gas sorption experiments were measured with an ASAP-2020 gas adsorption instrument.

Synthesis:

L^{Pd} [Pd(H$_2$bpydc)Cl$_2$]: To a stirred solution of $PdCl_2(CH_3CN)_2$ (1.00 mmol, 0.26 g) in DMF (30 mL) was added 2,2'-bipyridine-5,5'-dicarboxylic acid (1.00 mmol, 0.24 g) and the mixture was stirred at 80 ^{o}C for 2 hours under N_2 atmosphere. The mixture was cooled to room temperature and 30 mL ethyl acetate was added to it. The now orange solid was separated by filtration, washed with DMF and MeOH, and then dried in vacuum. Yield: 94%. Anal. Calcd for $C_{12}H_8N_2O_4Cl_2Pd$: C, 34.19; H, 1.91; O, 15.18. Found: C, 34.28; H, 1.98; O, 15.29. IR (KBr, cm^{-1}): 3448 (s), 1712 (m), 1663 (w), 1609 (m), 1543(m), 1408(s), 1387(s), 1292(w), 1266(w), 1132(w), 783(m).

1 $\{Sm_2[Pd(bpydc)Cl_2]_2[Pd(Hbpydc)Cl_2]_2(H_2O)_4\}_n$: L^{Pd} (0.03 mmol, 0.0127 g), $Sm(NO_3)_3\cdot 6H_2O$ (0.1 mmol, 0.0450 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 ^{o}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 $C_{24}H_{17}Cl_4N_4O_{10}Pd_2Sm$: 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 $\{Eu_2[Pd(bpydc)Cl_2]_2[Pd(Hbpydc)Cl_2]_2(H_2O)_4\}_n$: L^{Pd} (0.03 mmol, 0.0127 g), $Eu(NO_3)_3\cdot 6H_2O$ (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: 90%. Anal. Calcd for $C_{24}H_{17}Cl_4N_4O_{10}Pd_2Eu$: 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 $\{Gd_2[Pd(bpydc)Cl_2]_2[Pd(Hbpydc)Cl_2]_2(H_2O)_4\}_n$: L^{Pd} (0.03 mmol, 0.0127 g), $Gd(NO_3)_3 \cdot 6H_2O$ (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 $C_{24}H_{17}Cl_4N_4O_{10}Pd_2Gd$: 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 $\{Tb_2[Pd(bpydc)Cl_2]_2[Pd(Hbpydc)Cl_2]_2(H_2O)_4\}_n$: L^{Pd} (0.03 mmol, 0.0127 g), $Tb(NO_3)_3 \cdot 6H_2O$ (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 $C_{24}H_{17}Cl_4N_4O_{10}Pd_2Tb$: 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 (λ = 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),[1] 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**.

Compounds	**1** (Pd-Sm)	**2** (Pd-Eu)	**3** (Pd-Gd)	**4** (Pd-Tb)
Formula	$C_{24}H_{17}Cl_4N_4O_{10}Pd_2Sm$	$C_{24}H_{17}Cl_4N_4O_{10}Pd_2Eu$	$C_{24}H_{17}Cl_4N_4O_{10}Pd_2Gd$	$C_{24}H_{17}Cl_4N_4O_{10}Pd_2Tb$
Formula weight	1026.37	1027.98	1033.27	1034.94
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a, Å	9.1629(8)	9.1669(5)	9.1605(8)	9.1570(7)
b, Å	14.7835(12)	14.7619(8)	14.7381(13)	14.7179(11)
c, Å	16.1693(14)	16.2021(8)	16.2023(15)	16.2237(13)
α, °	67.0610(10)	66.9840(10)	66.9550(10)	66.9190(10)
β, °	87.9300(10)	87.9180(10)	87.9010(10)	87.9440(10)
γ, °	77.1940(10)	77.1600(10)	77.0700(10)	77.0270(10)
V, Å^3	1963.8(3)	1964.37(18)	1958.7(3)	1956.8(3)
Z	2	2	2	2
D_c, g cm^{-3}	1.736	1.738	1.752	1.756
μ, mm^{-1}	2.701	2.802	2.902	3.017
θ range/°	1.54 - 28.29	2.45 - 27.01	1.37 - 27.01	1.54 - 27.01
GOF on F^2	1.093	1.117	1.067	1.117
$R1^a$ $[I > 2\sigma(I)]$	0.0395	0.0402	0.0521	0.0558
$wR2^a$ (all data)	0.1434	0.1519	0.1827	0.1896
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	6.106, -1.371	5.409, -1.636	8.452, -1.894	6.538, -1.499

$^a R1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

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

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

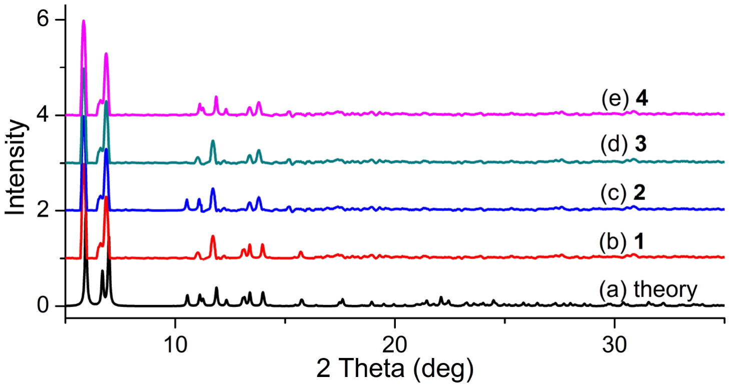


Fig. S1. PXRD patterns for different samples

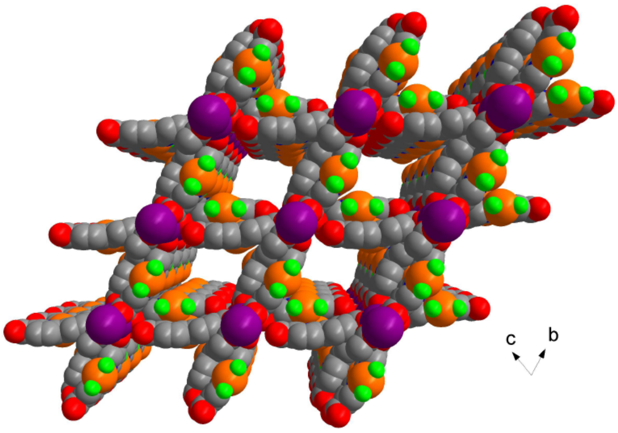


Fig. S2. View the 1D channels of compound **1**

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 (cacld 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, $\{Sm_2[Pd(bpydc)Cl_2]_2[Pd(Hbpydc)Cl_2]_2\}_n$ (**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).

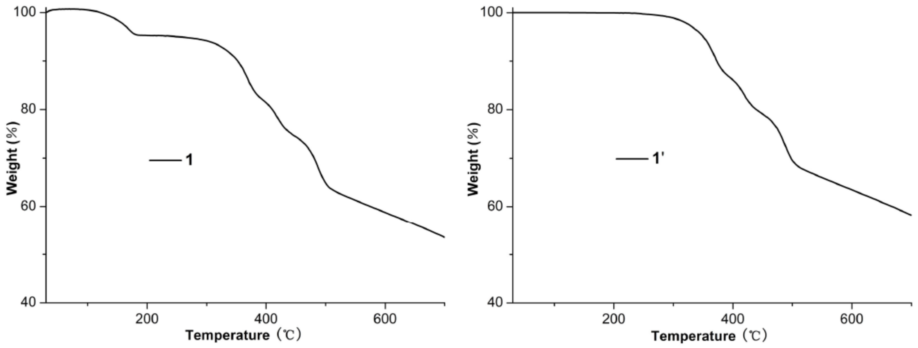


Fig. S3. TGA of compounds **1** and **1'**

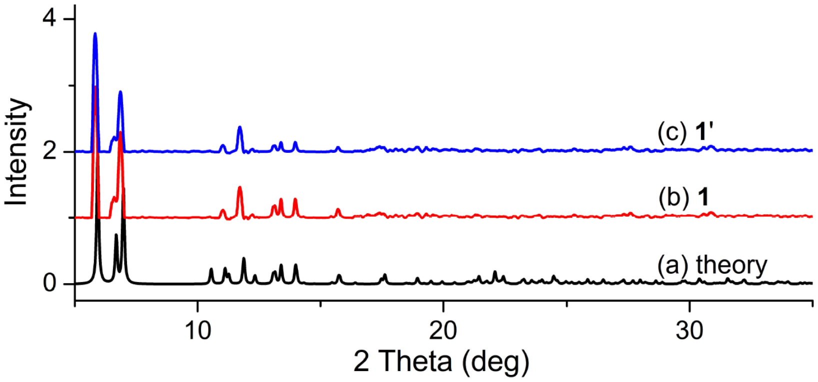


Fig. S4. PXRD patterns for different samples

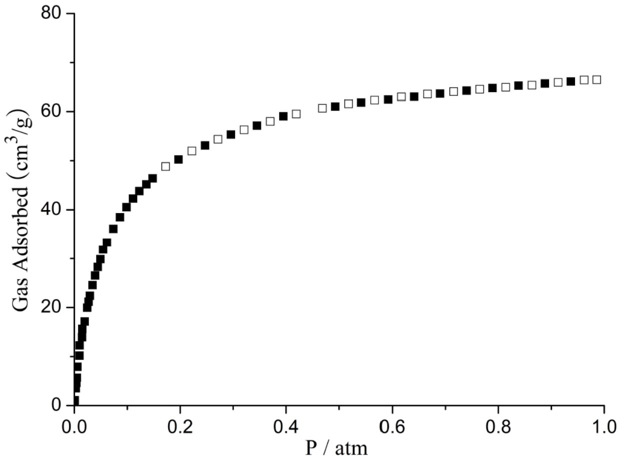
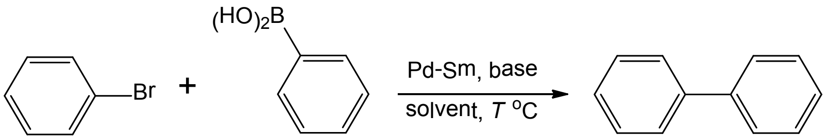


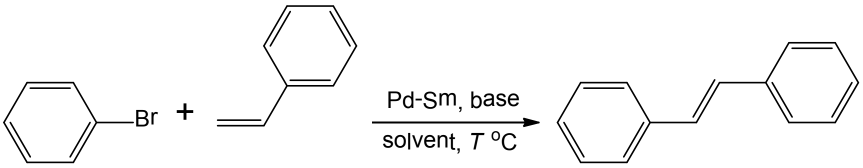
Fig. S5. N_2 sorption curves (77 K) of **1'**

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



Entry	Catalyst (0.5 mol%)	Solvent (5 ml)	Base (1.5 mmol)	T [°C]	Time [h]	Yield [%]
1	**1**	H_2O/EtOH (3ml/2ml)	K_2CO_3	80	4	50
2	**1**	DMF	K_2CO_3	100	4	90
3	**1**	Toluene	K_2CO_3	95	4	94
4	**1**	Toluene	-	95	4	0
5	**1**	Toluene	Na_2CO_3	95	4	88
6	**1**	Toluene	K_2CO_3	80	4	86
7	**1**	Toluene	K_2CO_3	95	2	75

Table S4. Optimization of Heck reactions with bromobenzene and styrene.



Entry	Catalyst (0.5 mol%)	Solvent (3 ml)	Base (1.5 mmol)	*T* [^{o}C]	Time [h]	Yield [%]
1	**1**	H_2O/EtOH (2ml/1ml)	NEt_3	80	4	40
2	**1**	Toluene	NEt_3	95	4	88
3	**1**	DMF	NEt_3	100	4	94
4	**1**	DMF	-	100	4	0
5	**1**	DMF	Na_2CO_3	100	4	83
6	**1**	DMF	NEt_3	80	4	81

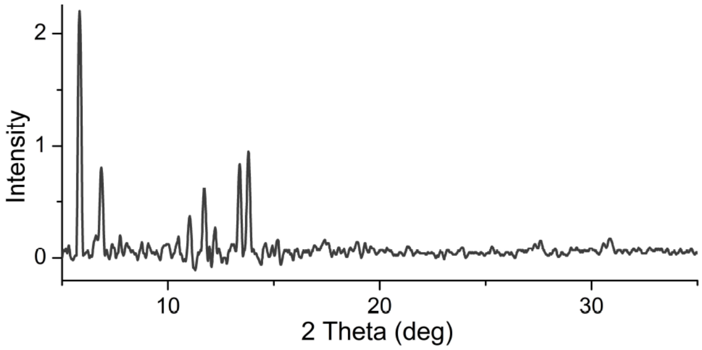


Fig. S6. PXRD pattern for catalyst **1** (Pd-Sm) used in the Suzuki–Miyaura reaction with bromobenzene and phenylboronic acid (solvent: toluene, base: K_2CO_3, temperature: 95 ^{o}C, time: 4h).

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_2CO_3, temperature: 95 ^{o}C, time: 4h].

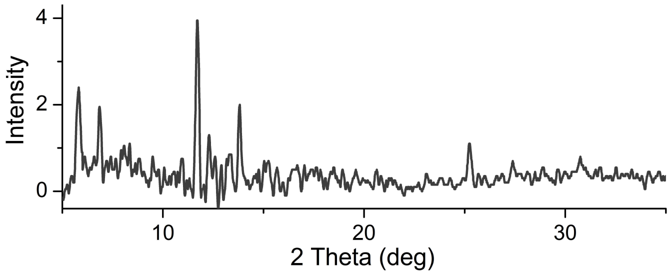


Fig. S7. PXRD pattern for catalyst **1** (Pd-Sm) used in the Heck reaction with bromobenzene and styrene (solvent: DMF, base: NEt_3, temperature: 100 ^{o}C, time: 4h).

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 ^{o}C, time: 4h].

Reference:

(1) G. M. Sheldrick. SHELXL-97, *Program for the Refinement of Crystal Structures*, Universität Gtötingen: Germany, **1997**.

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