Supporting Information for

Two metal-organic frameworks based on a double azolium derivative: post-modification and catalytic activity

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Experimental Section

Materials and Measurements. All of the chemicals were obtained from commercial sources and were used without further purification. 1-(4-methylcarboxyphenyl)-imidazole was prepared according to the literature method.[1] Element analyses were performed on a ThermoFinnigan Flash EA 1112 elementary analyzer. IR spectra (KBr pellets) were taken on an AVATAR-370 Nicolet spectrometer in the 4000-400 cm^{-1} region. Inductively coupled plasma mass spectrometries (ICP-MS) were performed on an XSeries II instrument. Transmission electron microscopy (TEM) experiments were conduced using a JEOL JEM-1230 microscope operated at 80 kV. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a VG ESCALAB MARK II system, and the C_{1s} line at 284.9 eV was used as the binding energy reference. Thermogravimetric analyses (TGA) were carried out on a SDT Q600 compositional analysis instrument from 30 to 800 °C under N_2 atmosphere at a heating rate of 10 °C/min. Powder X-ray diffraction data (PXRD) were recorded on a RIGAKU D/MAX 2550/PC for Cu-Kα (λ = 1.5406 Å). Luminescent spectra for the solid samples were recorded with a Hitachi F4500 fluorescence spectrometer. ^1H NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ or D_2O solution and the chemical shifts were reported relative to internal standard TMS (0 ppm).

X-ray crystal data collections and structure determinations.

The determinations of the unit cells and data collections for the crystals of **1** and **2** were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite–monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[2] The structures were solved by direct methods, and refined by full-matrix least-square methods with the **SHELX-97** program package.[3] All non-hydrogen atoms including solvent molecules were located successfully from Fourier maps and were refined anisotropically. The H atoms on C atoms were generated geometrically.

Synthesis of H_2LCl_2. A mixture of 1-(4-methylcarboxyphenyl)-imidazole (2.02 g, 10 mmol) and CH_2Br_2 (5 mL) in 40 mL toluene was refluxed for 4 days. After the reaction was cooled down to room temperature, the resulting precipitate was filtered, washed with toluene, and dried at 50 °C to give the ester of the ligand. The resultant was subsequently dissolved in 20% HCl aqueous solution (20 mL) and refluxed for 12 h. The solvent was removed under reduced pressure to give white powder, which was recrystallized as colorless crystals in H_2O (Yield: 40%). ^{1}H NMR (500 MHz, D_2O): δ = 2.07 (s, 2H), 6.85 (s, 2H), 7.66 (d, J = 8.5 Hz, 4H), 7.94 (s, 2H), 8.02 (s, 2H), 8.10 (d, J = 8.5 Hz, 4H). ^{13}C NMR (125 MHz, D_2O): δ = 59.9, 122.8, 123.2, 123.4, 131.9, 132.6, 136.6, 137.8, 169.4. IR (KBr pellet, ν/cm^{-1}): 1700(s), 1608(m), 1554(s), 1433(w), 1396(m), 1352(w), 1334(w), 1246(s), 1220(s), 1173(m), 1113(w), 1076(w), 886(w), 854(m), 795(m), 771(m), 749(m), 692(m), 677(m), 626(w), 616(w), 522(w).

Synthesis of 1. H_2LCl_2 (11 mg, 0.02 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (24 mg, 0.1 mmol) were thoroughly dissolved in 10 mL MeOH and 10 mL EtOH, which was subsequently heated 65 °C for 24 h. Blue crystals of **1** were isolated by filtration, washed with EtOH, and dried in air (Yield: 70%). Anal. Cald. for **1** (%): C, 42.83; H, 3.43; N, 13.62. Found: C, 43.12; H, 3.68; N, 13.17. IR (KBr pellet, ν/cm^{-1}): 1610(s), 1551(s), 1384(s), 1331(s), 1215(s), 1073(m), 1042(w), 1017(w), 957(w), 866(w), 847(w), 782(m), 736(w), 700(m), 614(w), 537(w).

Synthesis of 2. The pH value of $H_2\mathbf{L}Cl_2$ (10 mg, 0.02 mmol) in 5 mL water was adjusted to 7 using 1.0 mol/L NaOH aqueous solution, and $CuCl_2 \cdot 2H_2O$ (16 mg, 0.09 mmol) was subsequently added into the mixture. After the mixture was heated at 80 °C for 1 h under stirring, 10 mL EtOH was added in the filtrate. Green crystals of **2** were formed after three days at room temperature, which were isolated by filtration, washed with EtOH, and dried in air (Yield: 53%). Anal. Cald for **2** (%): C, 46.64; H, 3.35; N, 10.36. Found: C, 46.89; H, 3.41; N, 9.88. IR (KBr pellet, ν/cm^{-1}): 1610(s), 1585(s), 1553(s), 1420(m), 1365(s), 1314(m), 1232(m), 1218(m), 1077(m), 1046(w), 1015(m), 955(w), 861(m), 848(m), 785(m), 770(m), 710(m), 617(m), 535(w).

Synthesis of $\boldsymbol{CuL_{0.24}L'_{0.76}Pd_{0.76}(H_2O)_4(NO_3)_2}$ ***(3)***. To a THF solution (20 mL) of $Pd(OAc)_2$ (45 mg, 0.20 mmol), **1** (125 mg, 0.20 mmol) was added, which was stirred at room temperature for 4 h, then refluxed for 12 h in an insert N_2 atomsphere. The resulting light brown powder was filtered, washed with THF, MeOH, and Et_2O, and dried in air. Anal. Cald for **3** (%): C, 34.77; H, 2.85; N, 11.59; Pd, 11.15. Found: C, 34.30; H, 2.82; N, 10.97; Pd, 11.02. IR (KBr pellet, ν/cm^{-1}): 1629(s), 1550(s), 1385(s), 1333(s), 1216(s), 1074(m), 1037(m), 1021(w), 956(w), 862(w), 847(w), 783(m), 733(w), 701(m), 615(w), 542(w).

Synthesis of $\boldsymbol{CuL_{0.76}L'_{0.24}Cl_2Pd_{0.24}(H_2O)_{1.5}}$ ***(4)***. The synthesis procedure of **4** is similar to that of **3**, except **1** was replaced by **2**. Anal. Cald for **4**(%): C, 43.85; H, 3.29; N, 9.74, Pd, 4.44. Found: C, 43.09; H, 3.12; N, 9.27; Pd, 4.40. IR (KBr pellet, ν/cm^{-1}): 1610(s), 1585(s), 1553(s), 1420(m), 1365(s), 1314(w), 1232(s), 1218(s), 1174(w), 1137(w), 1078(m), 1047(w), 1015(m), 956(w), 861(m), 848(m), 785(m), 770(m), 710(m), 694(w), 653(w), 617(m), 583(w), 535(w).

A typical procedure for the Suzuki-Miyaura coupling reaction catalyzed by solid 3. Bromobenzene (0.22 mmol), phenylboronic acid (0.33 mmol), K_2CO_3 (0.44 mmol) and **3** (10 mol% based on Pd) were stirred in 5 mL toluene at 70 °C for 12 h in an air atmosphere. After the reaction was complete, the reaction mixture was cooled down to room temperature, which was filtered, extracted with ethyl acetate/water. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated in vacuum. The residue was subjected to chromatography on silica gel using hexane as eluent to give the isolated yield.

^{1}H NMR spectra data for the Suzuki-Miyaura coupling products.

Biphenyl: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 4H), 7.59 (d, *J* = 7.3 Hz, 4H).

4-Methoxybiphenyl: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.97 (d, *J* = 8.7 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.52-7.56 (m, 4H).

3-Methylbiphenyl: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.45 (s, 3H), 7.17 (t, *J* = 6.8 Hz, 1H), 7.33-7.38 (m, 2H), 7.41-7.47 (m, 4H), 7.61 (d, *J* = 7.2 Hz, 2H).

4-Methylbiphenyl: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.16 (s, 3H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.30-7.36 (m, 1H), 7.41-7.45 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.57-7.60 (m, 2H).

Biphenyl-4-carboxaldehyde: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.2Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 10.06 (s, 1H).

2-Nitro-biphenyl: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.33 (m, 2H), 7.40-7.49 (m, 5H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H).

References

1. a) S. Ahrens, E. Herdtweck, S. Goutal, T. Strassner, *Eur. J. Inorg. Chem.*, 2006, 1268; b) J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, *Synthesis*, 2003, 2661.
2. *CrysAlisPro*, version 1.171.33.56; Oxford Diffraction Ltd.: Oxfordshire, U.K., 2010.
3. G. M. Sheldrick, *Program for Structure Refinement*: University of Göttingen, Germany, 1997.

Figures:

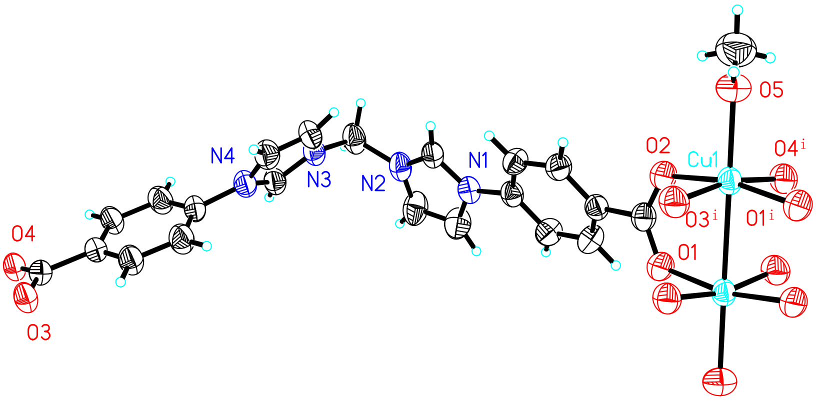


Fig. S1. ORTEP representation of the symmetry expanded local structure for **1**. Displacement ellipsoids are drawn at the 35% probability level.

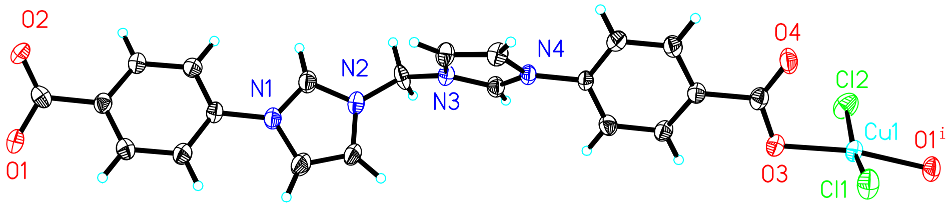


Fig. S2. ORTEP representation of the symmetry expanded local structure for **2**. Displacement ellipsoids are drawn at the 35% probability level.

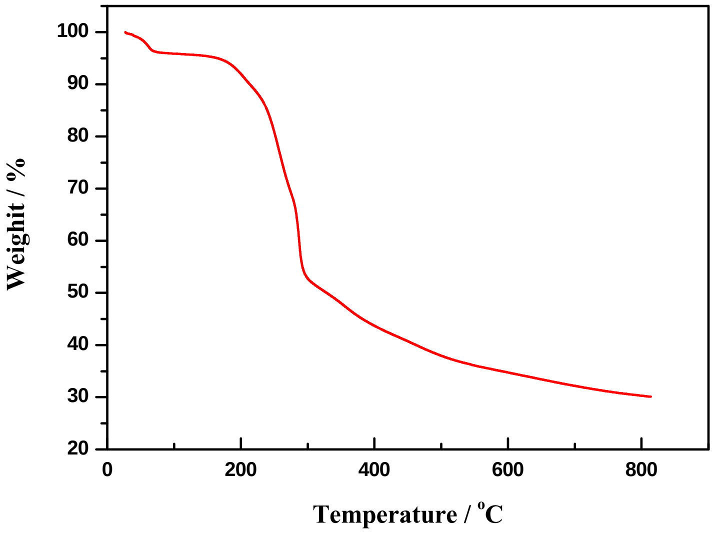


Fig. S3. TG result of **1**.

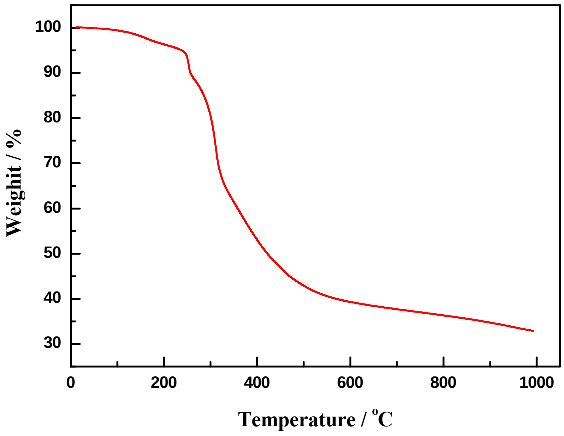


Fig. S4. TG result of **2**.

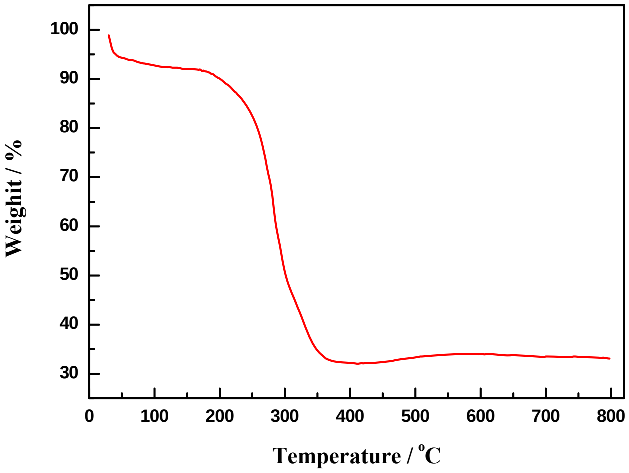


Fig. S5. TG result of **3**.

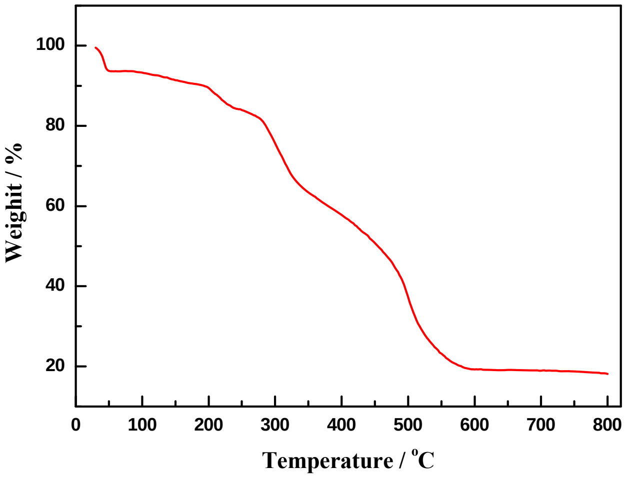


Fig. S6. TG result of **4**.

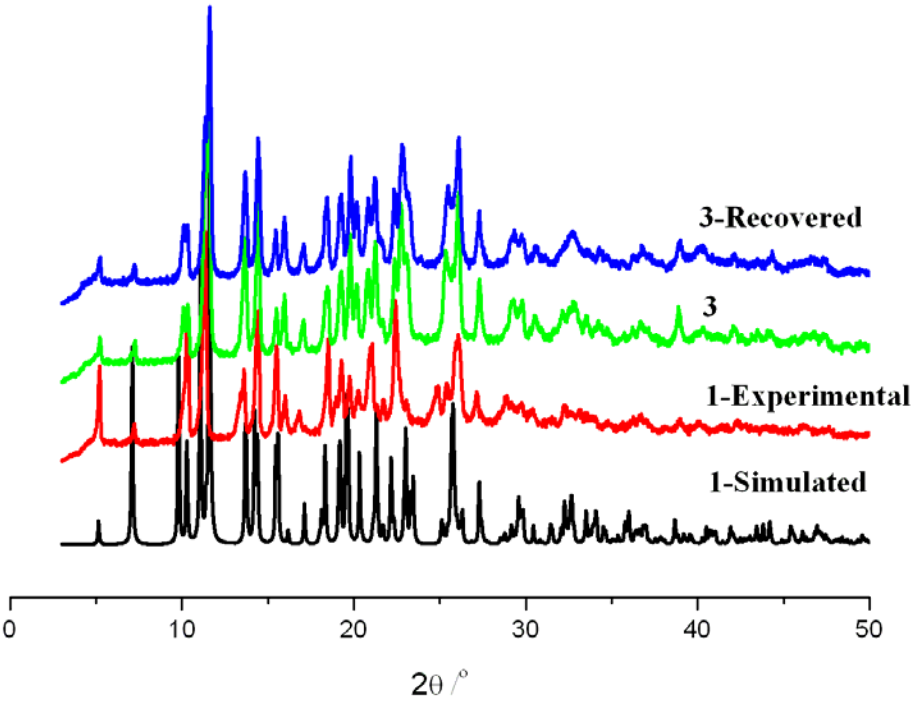


Fig. S7. Powder X-ray diffraction patterns for **1** and **3**.

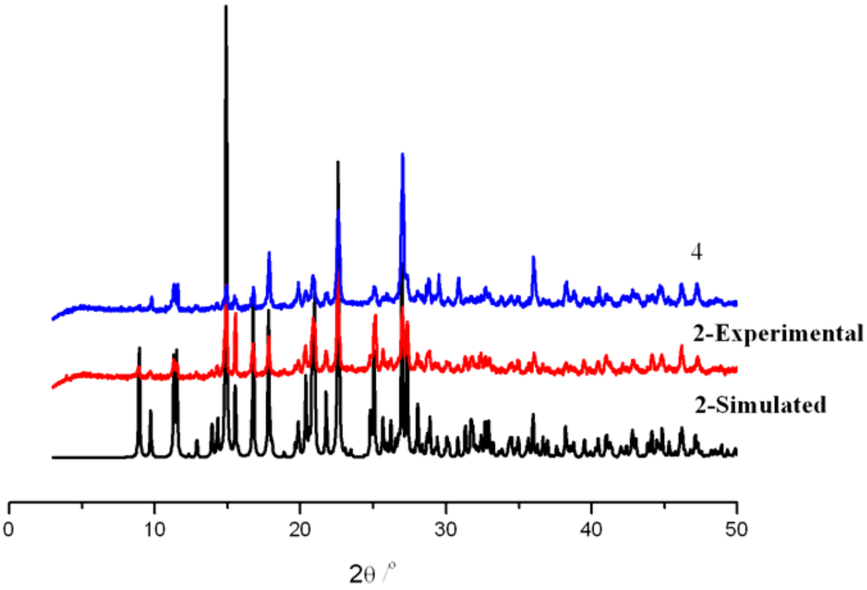


Fig. S8. Powder X-ray diffraction patterns for **2** and **4**.

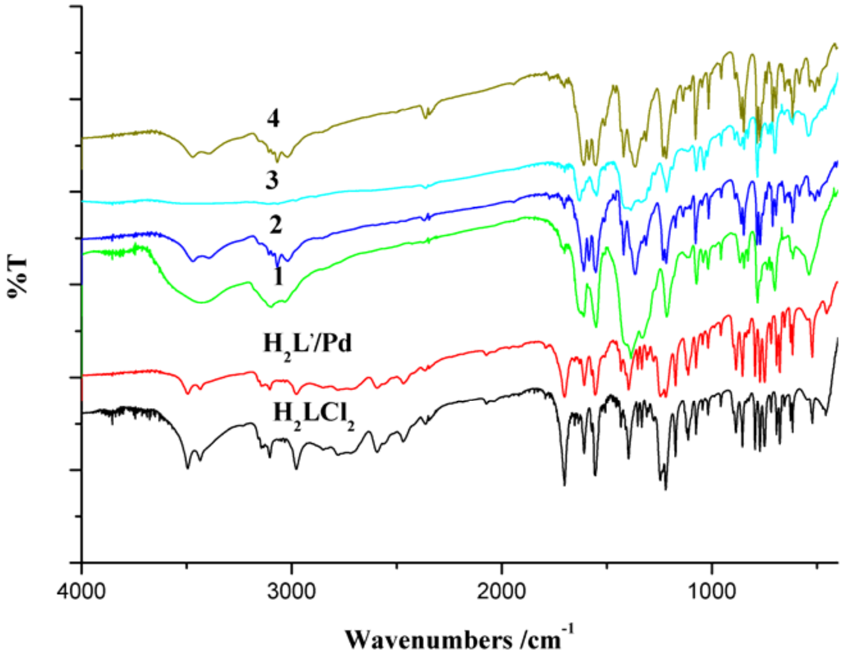


Fig. S9. FT-IR spectra for compounds **1**, **2**, **3**, **4**, $H_2\mathbf{L}Cl_2$ and $H_2\mathbf{L}'$/Pd.

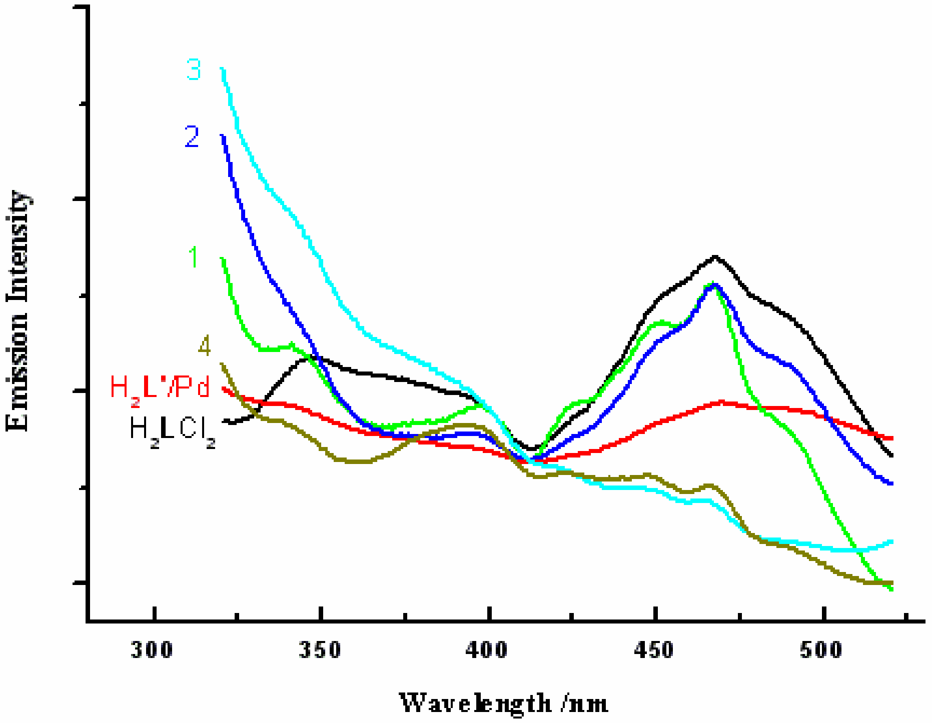
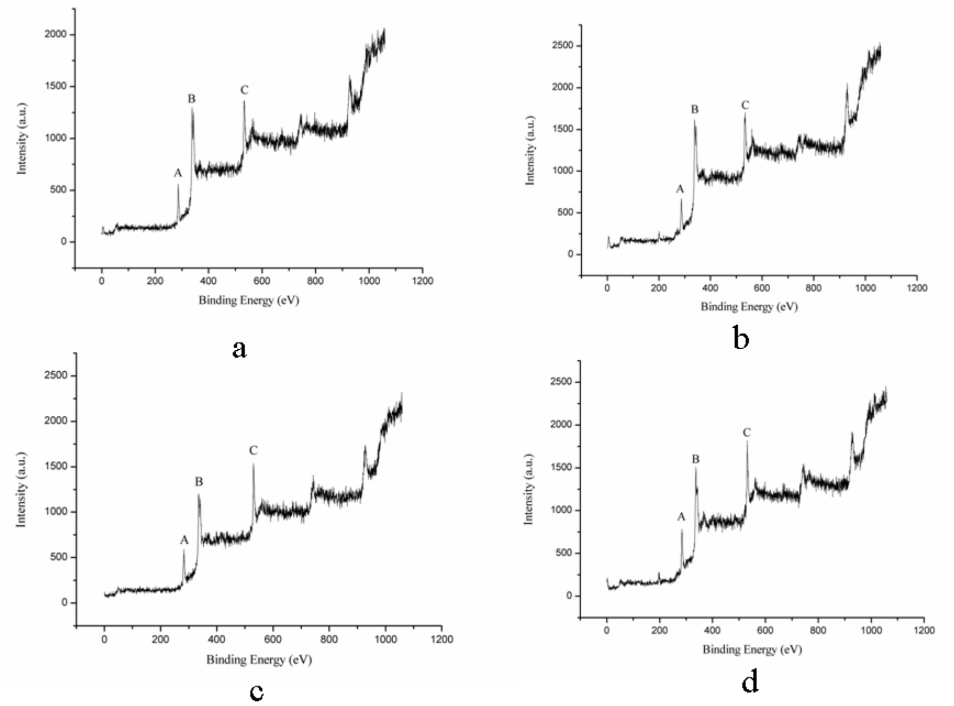
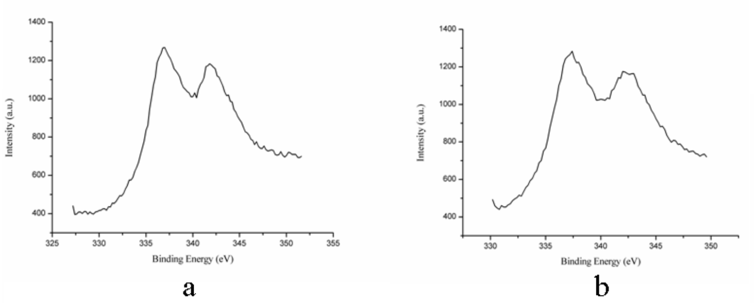


Fig. S10. Solid-state luminescent spectra for **1**, **2**, **3**, **4**, $H_2\mathbf{L}Cl_2$ and $H_2\mathbf{L}'$/Pd (λ_{ex} = 280 nm).



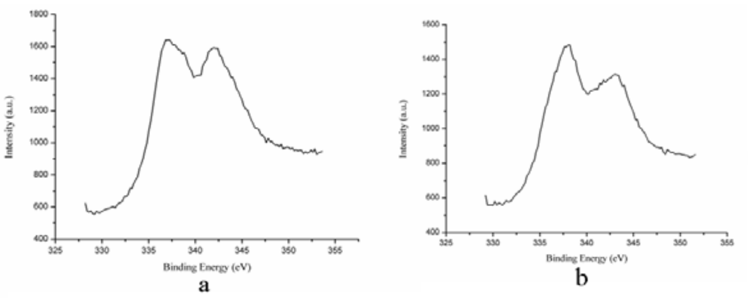
a b c d

Fig. S11. X-Ray photoelectron spectra (XPS): a) for **3**; b) for **4**; c) for the recovered sample of **3** after three catalytic cycles and d) for the recovered sample of **4** after three catalytic cycles (A: C 1s; B: Pd $3d_{5/2}$, $3d_{3/2}$; C: O 1s).



a b

Fig. S12. XPS spectra (Pd 3d level) for **3**: a) freshly prepared sample of **3**; b) recovered sample of **3** after three catalytic cycles.



a b

Fig. S13. XPS spectra (Pd 3d level) for **4**: a) freshly prepared sample of **4**; b) recovered sample of **4** after three catalytic cycles.

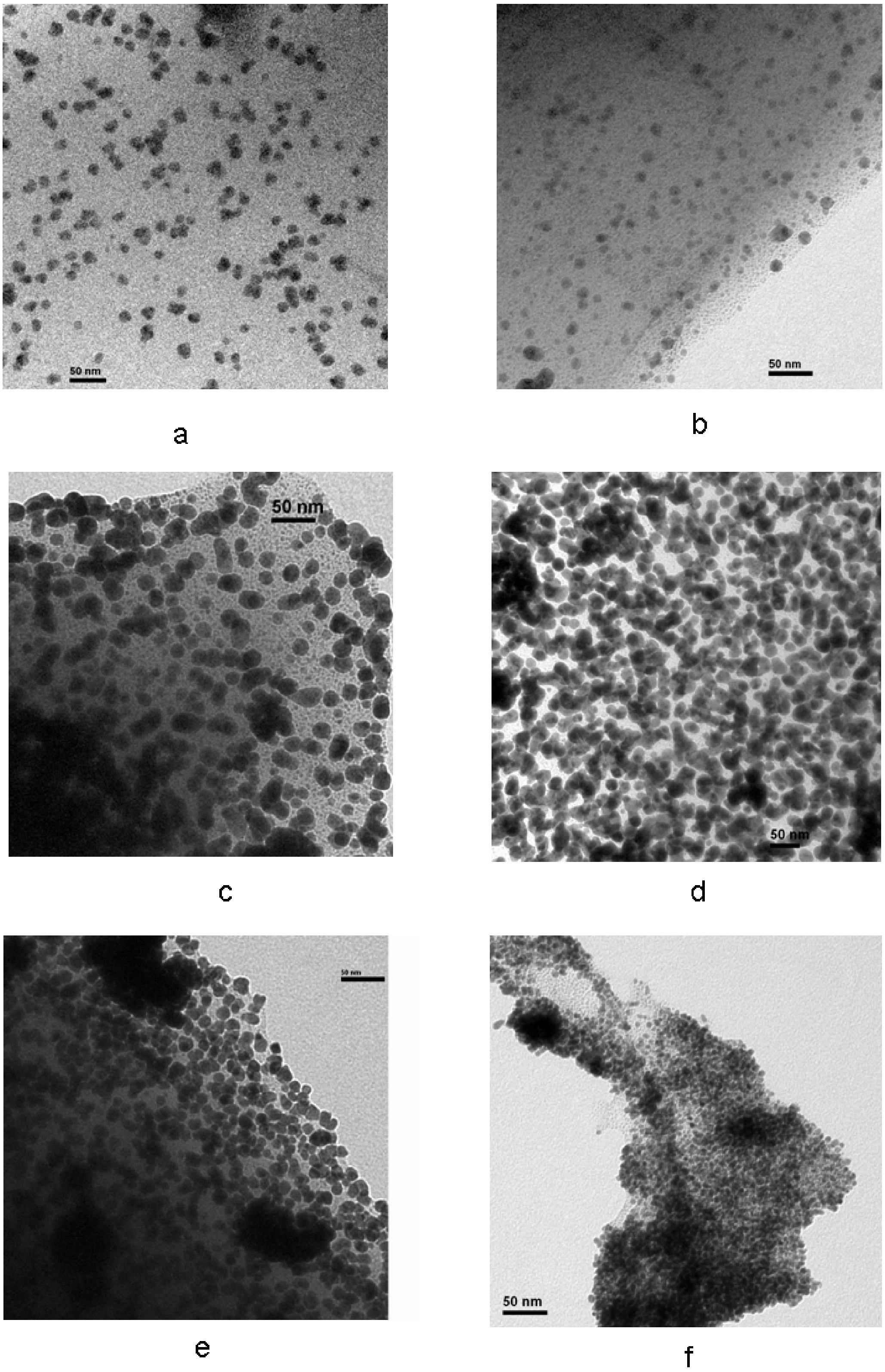


Fig. S14. TEM images for the samples of **1**, **2**, **3** and **4**: a) for **1**; b) for **2**; c) for **3**; d) for **4**; e) for the recovered sample of **3** after three catalytic cycles; f) for the recovered sample of **4** after three catalytic cycles.

Tables:

Table S1. Crystal data and structure refinements for compounds **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{44}H_{42}Cu_2N_{12}O_{23}$	$C_{21}H_{18}Cl_2CuN_4O_5$
Formula weight	1233.98	540.83
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	17.7000(19)	10.7438(7)
b (Å)	18.053(2)	14.3440(7)
c (Å)	8.6682(9)	13.8748(6)
α (°)	90	90
β(°)	103.843(11)	98.959(5)
γ (°)	90	90
V (Å^3)	2689.4(5)	2112.15(19)
Z	2	4
ρ_{calcd} (g.cm^{-3})	1.524	1.701
μ (mm^{-1})	0.883	1.331
F(000)	1264	1100
Data / parameters	5151/370	4309/298
R_{int}	0.0409	0.0497
GOF on F^2	1.167	0.902
R_1, wR_2 [$I > 2\sigma(I)$]	0.0819, 0.1971	0.0438, 0.0495
R_1, wR_2 [all data]	0.1236, 0.2243	0.1084, 0.0532

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{0.5}$.

Table S2. Selected bond parameters of **1** (Å, °)

Cu1-O1^{i}	1.953(4)	Cu1-O3^{ii}	1.952(4)
Cu1-O2	1.965(4)	Cu1-O4^{iii}	1.974(4)
Cu1-Cu1^{i}	2.6506(15)	Cu1-O5	2.146(5)
O1^{i}-Cu1-O4^{iii}	88.46(19)	O4^{iii}-Cu1-O5	94.9(2)
O2-Cu1-O3^{ii}	89.6(2)	O5-Cu1-O2	94.5(2)
O3^{ii}-Cu1-Cu1^{i}	83.78(15)	Cu1^{i}-Cu1-O1^{i}	83.42(15)

Symmetry codes: (i) –x+1, -y + 2, -z + 1; (ii) –x, y – 1/2, -z + 1/2; (iii) x +1, -y +5/2, z + 1/2.

Table S3. Selected bond parameters of **2** (Å, °)

Cu1-O1^{i}	1.960(2)	Cu1-O3	1.931(2)
Cu1-Cl1	2.284(1)	Cu1-Cl2	2.239(1)
O1^{i}-Cu1-Cl1	88.80(8)	Cl1-Cu1-O3	92.06(9)
O3-Cu1-Cl2	89.45(8)	Cl2-Cu1-O1^{i}	91.69(8)

Symmetry codes: (i) x + 1/2, -y + 1/2, z – 3/2; (ii) x – 1/2, -y + 1/2, z +3/2.