Supporting Information

Synthesis and characterization on novel fluorescent sensors for Pd^{2+}/Pd^0 with high selectivity

You Zi, Hua Meng, Xue-Qiang Chu, Xiao-Ping Xu* and Shun-Jun Ji* Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China

Fax : (+86)-512-65880307; *phone*: (+86)- 512-65880307; *E-mail*: xuxp@suda.edu.cn; shunjun@suda.edu.cn

Table of Contents

General Information
Materials and general methods
Synthetic procedures for the preparation of L1-L3
Synthetic procedure
The plausible mechanismS3
Determination of fluorescence quantum yieldS4
Comparison of some chemosensors for the detection of Pd species
The absorption spectra of L1-L3S6
Spectral data for productsS8
¹ H NMR and ¹³ C NMR spectra

General Information:

All reactions were carried out in air and using undistilled solvent, without any precautions to exclude air and moisture unless otherwise noted. Flash column chromatography was performed using silica gel. Melting points were measured on an Electrothermal digital melting point apparatus and uncorrected. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or D₆-DMSO on 400 MHz spectometers. Tetramethylsilane (TMS) served as internal standard for ¹H NMR and ¹³C NMR. IR spectra were recorded on a FT-IR spectrometer. Mass spectra were carried out using Quadrupole LC/MS system with ESI resource. HRMS was recorded on a commercial apparatus (ESI Source). UV-VIS experiment was performed on a TU-1901 spectrophotometer and fluorescence experiment was done using FLS920 Edinburgh instruments with a fluorescence cell of 10 mm path. X-ray diffraction data were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo Ka; radiation.

Materials and general methods:

Analyte solutions were prepared from KCl, NaCl, CaCl₂, BaCl₂, FeCl₃, NiCl₂, CoCl₂, HgCl₂, CuCl₂, ZnCl₂, LiCl, SnCl₂, PdCl₂, RuCl₃, PtCl₂, Pb(NO₃)₂, MgSO₄, CdSO₄ by separately dissolved in water, 0.5 mM. 0.5 mM solutions of L1, L2, L3 was prepared in DMF. Measurements were done after addition of different metal ions to sensor solutions, diluted by CH₃CN, 2-3 hours later.

Synthetic procedures for the preparation of L1-L3:

Under an air atmosphere, different benzaldehydes (4 mmol), 2-cyanopyrimidine (2 mmol), ammonium acetate (6 mmol) and DMF (2 ml) were added into a flask and vigorously stirred at 100 °C. The reaction was stopped until the reactants were completely consumed as monitored by TLC analysis. After the completion of reaction, water (10 mL) was added to the mixture. Then the mixture was extracted with EtOAc (3×15 mL) and the organic layer was dried (Na₂SO₄) and evaporated. Then the crude product was purified by column chromatography on silica gel.

Synthetic procedure:



The plausible mechanism of this reaction:



Based on our previous work, a plausible mechanism for the reaction was proposed. Firstly, 2- pyrimidyl formamide (A), which is generated via the hydrolization of 2-cyanopyrimidine, reacted with aldehyde to give the intermediate **B**.

With the nucleophilic addition reaction of one N atom from pyrimidine to another aldehyde, intermediate C was thus formed. Subsequently, D can be generated through a hydrogen transfer procedure. Then, the intramolecular nucleophilic addition reaction led to the generation of intermediate E which was followed by the formation of intermediate F. The following nucleophilic attack by NH_3 made the pyrimidine cycle opening and afforded intermediate H. The aromatization promoted the electron transformation and the C-N bond break, resulting in the generation of I. The intermediates I can be isomerized to I' which could react with the imine to afford the intermediate J through a intermolecular cyclization process. Finally, the desired product could be achieved via the dehydration and aromatization of J.

Determination of fluorescence quantum yield (Φ) of the sensor L1 itself and after complexation with Pd²⁺:

The quantum yield of L1, L1-Pd²⁺ were determined according to the method bellow.

$$\varphi_u = \frac{(\varphi_s)(FA)(A_s)}{(FA_s)(A_u)}$$

Where φ is fluorescence quantum yield; FA is integrated area under the corrected emission spectra; A is the absorbance at the excitation wavelength; the subscripts u and s refer to the unknown and the standard, respectively. We chose tryptophan as standard, which has the fluorescence quantum yield of 0.14 in water.¹

Following the above equation, the quantum yield value obtained for the sensor L1 is 0.23 and after complexation with Pd²⁺ the quantum yield value for L1-Pd²⁺ is 0.05. Therefore, fluorescence quantum yield decreases as a result of metal complexation.

Comparison of some chemosensors for the detection of Pd species.

NO	Chemosensors	Detection mechanism	Detection type	Oxidation state of Pd	Concentration of sensor (µM)	Interference	Reference
1	Fuorescein-based propargyl ether derivative	Chemical reaction	Turn on	0, +2, +6	10	Au ³⁺	2
2	Perylene-3,4:9,10-tetracarboxylic bisimide (PBI) derivative	Chemical reaction	Turn off	+2	5	^a	3
3	Polybenzanthrone (PBA) derivative	Complexation	Turn off	+2	1	Fe ³⁺	4
4	Hemicyanine based dye	Chemical reaction	Turn on	0, +2,	10	a	5

5	Modular-based fluorescent polymer	Complexation	Turn off	+2	5	Ag^+	6
6	Rhodamine based dye	Chemical reaction	Turn on	+2	20	Ru ³⁺ , Pt ²⁺	7
7	Rhodamine B derivative	Chemical reaction	Turn on	0, +2,	10	a	8
8	Rhodamine based dye	Chemical reaction	Turn on	0, +2,	10	Pt^{2+}	9
9	Rhodamine based dye	Chemical reaction	Turn on	0, +2,	10	a	10
10	Conjugated polymer	Complexation	Turn off	+2	4	Pt ⁴⁺	11
11	Quinoline-2-carboxalde- hyde 2-pyridylhydrazone	Complexation	Turn off	+2	10	^a	12
12	Anthracenophane-type fluoroionophore	Complexation	Turn on	+2	5	a	13
13	Triaryl 1H-imidazo[4,5-b] pyrazine	Complexation	Turn off	0, +2,	10	a	This work

a Not mentioned.

References:

- 1 E. P. Kirby and R. F. Steiner J. Phys. Chem., 1970, 74, 4480.
- 2 I. Shin, K. H. Ahn, M. Santra and S. K. Ko, Chem. Commun., 2010, 3964.
- 3 L. Zhang, Y. Wang, J. Yu, G. Zhang, X. Cai, Y. Wu and L. Wang Tetrahedron Lett., 2013, 54, 4019.
- 4 G. Zhang, Y. Wen, C. Guo, J. Xu, B. Lu, X. Duan, H. He and J. Yang, Anal. Chim. Acta, 2013, 805, 87.
- 5 X. Chen, H. Li, L. Jin and B. Yin, *Tetrahedron Lett.*, 2014, 55, 2537.
- 6 H. Huang, K. Wang, W. Tan, D. An, X. Yang, S. Huang, Q. Zhai, L. Zhou and Y. Jin, Angew. Chem., Int. Ed., 2004, 43, 5635.
- 7 S. Goswami, D. Sen, N. K. Das, H. K. Fun and C. K. Quah, Chem. Commun., 2011, 47, 9101.
- 8 K. H. Ahn and M. E. Jun, Org. Lett., 2010, 12, 2790.
- 9 F. Song, A. L. Garner and K. Koide, J. Am. Chem. Soc., 2007, 129, 12354.
- 10 H. Li, J. Fan, J. Du, K. Guo, S. Sun, X. Liu and X. Peng, Chem. Commun., 2010, 46, 1079.
- 11 B. Liu, Y. Bao, F. Du, H. Wang, J. Tian and R. Bai, Chem. Commun., 2011, 47, 1731.
- 12 S. Mukherjee, S. Chowdhury, A. K. Paul and R. Banerjee, J. Lumin., 2011, 131, 2342.
- 13 T. Schwarze, C, Dosche, R, Flehr, T. Klamroth, H. G. Lohmannsroben, P. Saalfrank, E. Cleve, H. J. Buschmanne and H. J. Holdt, *Chem. Commun.*, **2010**, *46*, 2034.

The absorption spectra of L1-L3 in the presence of various metal ions:



Figure S1 The fluorescence spectra of L1 (10^{-5} M) in the presence of various metal ions (5 equiv) in CH₃CN. Excitation wavelength was 360 nm.



Figure S2 The fluorescence spectra of L2 (10^{-5} M) in the presence of various metal ions (5 equiv) in CH₃CN.



Figure S3 The fluorescence spectra of L3 (10^{-5} M) in the presence of various metal ions (5 equiv) in CH₃CN.

Spectral data for products

2, 5, 6-triphenyl-1H-imidazo[4,5-b]pyrazine (L1)

White solid (m.p. 307-308 °C), 51% Yield; ¹H NMR (400 MHz, DMSO-d6) δ 8.35-8.31 (m, 2H), 7.65-7.62 (m, 3H), 7.41-7.38 (m, 4H), 7.36-7.30 (m, 7H); ¹³C NMR (101 MHz, DMSO-d6) δ 156.88, 140.12, 132.03, 130.38, 129.68, 129.46, 128.46, 128.32, 127.64; HRMS (ESI): Calcd. For C₂₃H₁₇N₄: [M+H] ⁺ 349.1453, found: 349.1457.

2,5,6-tri-p-tolyl-1H-imidazo[4,5-b]pyrazine (L2)

Light yellow solid (m.p. 244-245 °C), 30% Yield; ¹H NMR (400 MHz, DMSO-d6) δ 13.91 (s, 1H), 8.20 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 4H), 7.13 (d, J = 7.9 Hz, 4H), 2.42 (s, 3H), 2.31 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 157.03, 149.11, 146.50, 141.44, 140.51, 138.18, 137.77, 136.74, 136.36, 130.18, 129.94, 129.56, 128.98, 128.76, 126.90, 125.87, 21.55, 21.29, 21.08; HRMS (ESI): Calcd. For C₂₆H₂₃N₄: [M+H] ⁺ 391.1923, found: 391.1942.

2,5,6-tris(4-methoxyphenyl)-1H-imidazo[4,5-b]pyrazine (L3)

Yellow solid (m.p. 167-168 °C), 27% Yield; ¹H NMR (400 MHz, CDCl₃) δ 12.79 (s, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 6.6 Hz, 2H), 7.32 (d, J = 6.4 Hz, 2H), 6.81 (d, J = 6.5 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 6.5 Hz, 2H), 3.80 (s, 6H), 3.65 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.86, 159.63, 159.61, 159.44, 159.39, 157.00, 131.54, 131.50, 131.40, 131.37, 131.34, 131.32, 128.72, 121.12, 114.24, 113.73, 113.52, 55.31, 55.23, 55.00; HRMS (ESI): Calcd. For C₂₆H₂₃N₄O₃: [M+H] + 439.1770, found: 439.1758.

¹H NMR and ¹³C NMR spectra



2, 5, 6-triphenyl-1H-imidazo[4,5-b]pyrazine (L1)





2, 5, 6-tri-p-tolyl-1H-imidazo[4,5-b]pyrazine (L2)



2, 5, 6-tris(4-methoxyphenyl)-1H-imidazo[4,5-b]pyrazine (L3)