Electronic supplementary Information

Depropargylation-triggered fluorescence "turn on" probe for the detection of Pd^{2+} based on a bispropargylamine-rhodamine conjugate

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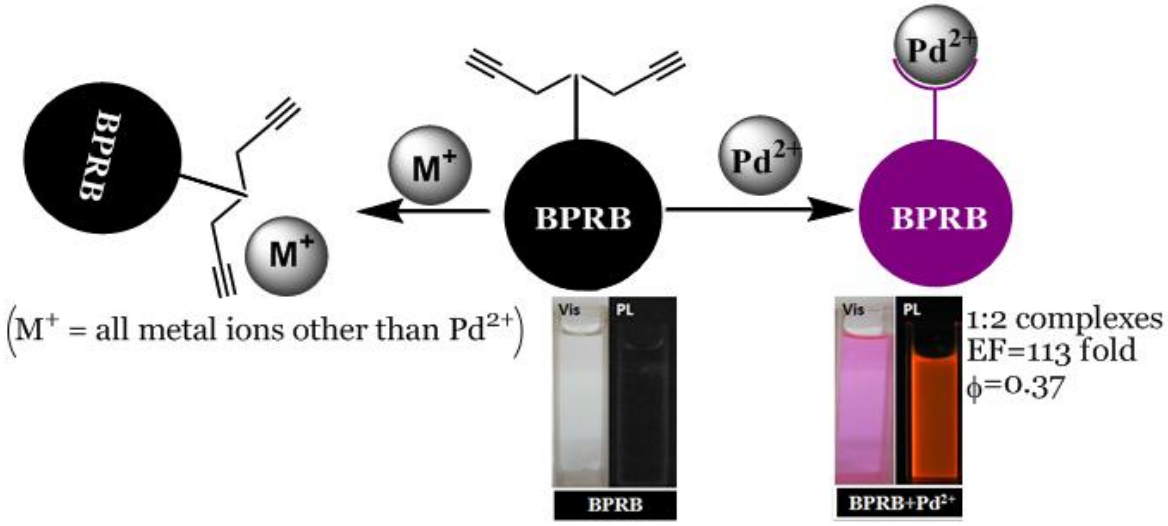
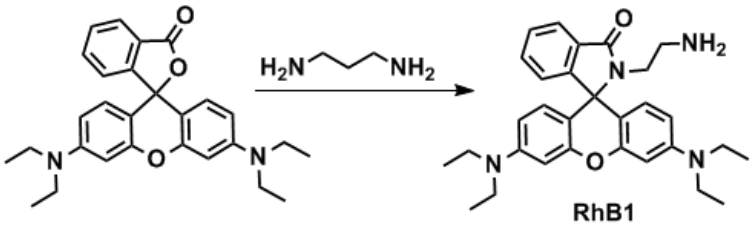


Graphical picture for BPRB and response with Pd^{2+}

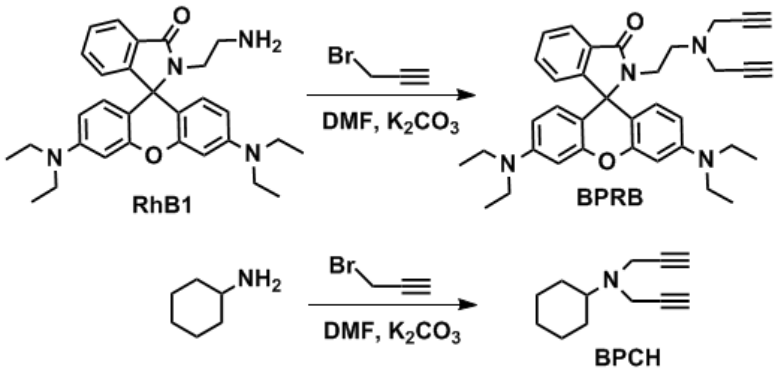
(1) Synthesis of RhB1



The intermediate **RhB1** was synthesised by refluxing rhodamine B (4.8g, 10 mmole) with excess ethylenediamine (5mL) in ethanol until the solution lost its red colour; the solvent was then evaporated[30a, b].The resulting solid was extracted with dichloromethane and washed with water. The organic layer was separated anddried over $MgSO_4$, and then, the solvent was evaporated. Theresulting solid was washed with hot hexane (10 mL) by decantation and dried. Then,the crude solid was purified by column chromatography (EtOAc:hexane, 1:3, R_f= 0.45),yielding **RhB1**as a pale-pink solid (yield, 74%).

FTIR (KBr): 2972 (-NH stretching), 1693(amide carbonyl).^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.89-7.90 (d, 1H, ArH), 7.45-7.43 (m, 2H, ArH), 7.09-7.07 (d, 1H, ArH), 6.41-6.18(m, 6H, ArH), 3.35-3.30 (m, 8H, $NC\underline{H_2}CH_3$), 3.20-3.09 (t, 2H, $NC\underline{H_2}$-CH_2), 2.42-2.38 (t, 2H,NH_2), 1.55-0.85 (m, 12H, $NCH_2C\underline{H_3}$). ^{13}C NMR ($CDCl_3$, δ): 168.62 (C=O), 153.42- 153.23 (ArC linked with -N,-O), 148.72(ArC-C-), 132.36(ArC-carbonyl), 131.15-105.58 (aromatic Cs), 64.92(spiro C), 44.28(heteroN-C), 43.70(C-N), 40.74(C-NH_2), 12.53(C-C-N). These spectral data are in accordance with the literature.

*(2) Synthesis of **BPRB** and model compound (**BPCH**)*



A typical synthetic procedure for the synthesis of compound **BPRB** is as follows[31].The compound **RhB1** (0.01 mol) was added to 300 mL of DMF with K_2CO_3 (0.03 mol). After 5 min, propargyl bromide (0.022 mol) was slowly added to the stirred suspension, and the mixture was heated at 90°C for 3 h. Then, the reaction mixture was poured in to water and extracted with diethyl ether. The organic layer was washed with water and then dried over anhydrous $MgSO_4$. Then,the solvent was evaporated, and the obtained product was purified by column chromatography, (EtOAc:hexane, 4:1, R_f=0.6) yielding **RhB2** (46%).

FTIR (KBr): 3286(≡CH in **BPRB**) and 2111 (C≡C in **BPRB**), 1685(amide carbonyl in **BPRB**).^{1}H-NMR (400 MHz, $CDCl_3$, δ) = 7.91-7.89 (d, 1H, ArH), 7.45-7.27 (m, 2H, ArH), 7.07(d, 1H, ArH), 6.79 -6.31 (m, 6H, ArH), 3.46-3.19 (m, 12H, $C\underline{H_2}C\equiv$, N-$C\underline{H_2}$), 2.30-2.0 (s, 2H, ≡C$\underline{H}$), 1.60-0.88 (m,12H, $NCH_2C\underline{H_3}$).^{13}C NMR ($CDCl_3$, δ): 167.98 (C=O), 153.50-105.59 (all aromatic Cs), 72.52(C of C-C≡), 64.79(spiro C), 50.81- 37.97(all Cs attached to N-), 12.55 (methyl Cs in CH_3CH_2-N).Elemental analysis found C, 77.19; H, 7.07; N, 9.84. A similar procedure was followed for the synthesis of the bispropargyl derivative of cyclohexylamine (**BPCH**); cyclohexylamine was used instead of the rhodamine-amine derivative and yielded a brownish-yellow liquid (66%).

FTIR (KBr): 3290(≡CH in **BPCH**) and 2126 (C≡C in **BPCH**). ^{1}H-NMR (400 MHz, $CDCl_3$, δ) = 3.56 (s, 4H, $CH_2C\equiv$), 2.21 (s, 2H, ≡CH), 1.00-2.00 (m,10H, CH_2 in cyclohexane).^{13}C NMR ($CDCl_3$, δ): 73.45(C of ≡CH), 78.21 ($CH_2\equiv$ of C), 42.87(C at N-CH_2), 25-30 (C of CH_2 in cyclohexane).

References

30. (a) R. Balamurugan, C. C. Chien, B. C. Chen and J. H. Liu, Tetrahedron, 2012, In press.
(b) D. Wu, W. Huang, C. Y. Duan, Z. H. Lin, and Q. J. Meng, *J. Inorg. Chem.*, 2007, **46**, 1538.
(c) X. Zhang, Y. Shiraishi and T. Hirai, Org. Lett., 2007, **9**, 5039.
31. D. C. Choi, S. H. Kim, J. H. Lee, H. N. Cho, and S. K. Choi, *Macromolecules*, 1997**, 30**, 176.

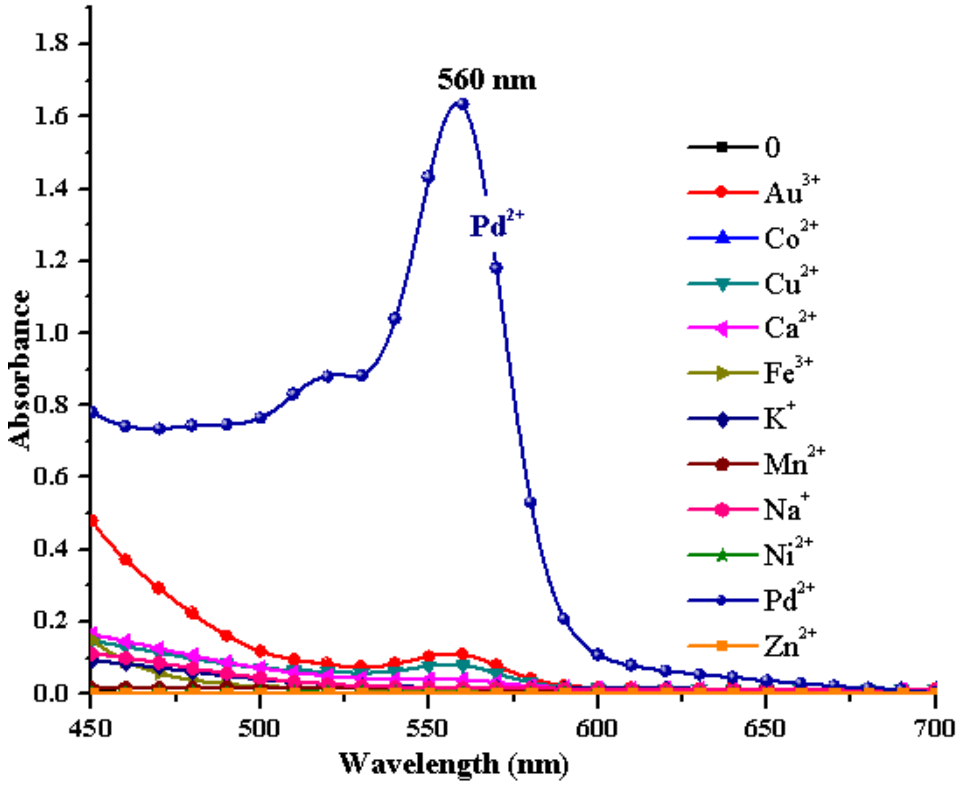


Fig. S1 UV-vis spectral changes of **BPRB**(150μM) upon addition of 10 equivalents of metal ions (Au^{3+}, Co^{2+}, Cu^{2+}, Ca^{2+}, Fe^{3+}, K^{+}, Mn^{2+}, Mg^{2+}, Na^{+}, Ni^{2+}, Pd^{2+}, Zn^{2+}).

Recognizing of metal ion as a function of time

Before recording the spectra of complexes, the samples were incubated for 20 min after each addition of metal solution, and then, the spectra were recorded. Since, the time study revealed that **BPRB** (λ_{max}) recognition of metal is completed within 20 min of the addition of the metal ion as shown below (Time taken for measuring each spectrum was not accounted).

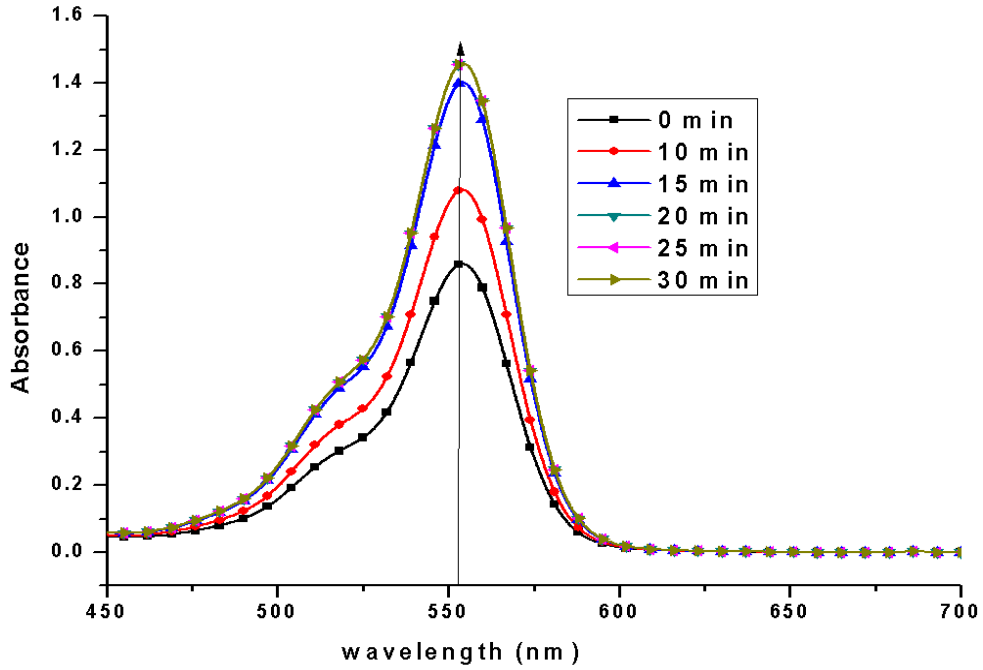


Fig. S2 UV-vis spectral changes of BPRB+Pd^{2+} with respect to time

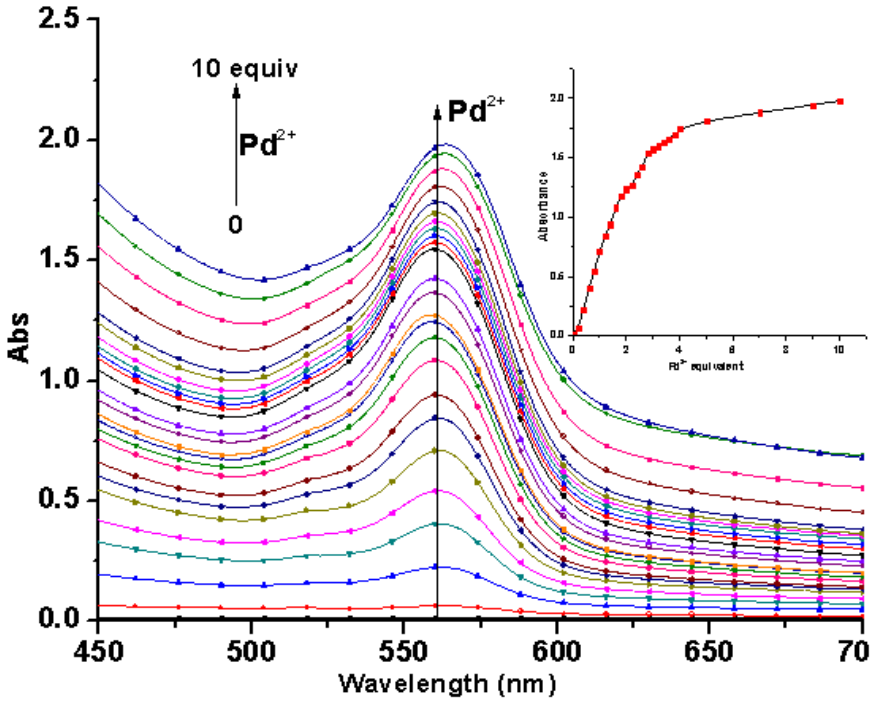


Fig. S3 Changes in the UV-vis spectra of **BPRB** (150μM) titration with Pd^{2+} in CH_3CN:H2O (1:1, v/v).

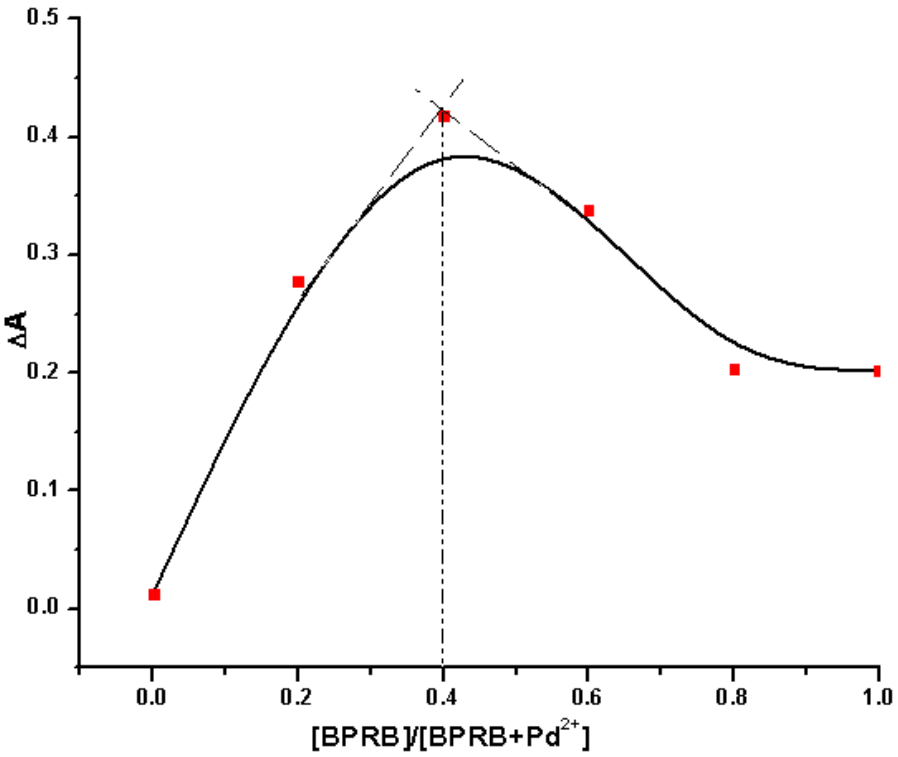


Fig. S4 Job's plot for **BPRB-Pd^{2+}** showed 1:2 complexes

Effect of pH

Fig. S5 shows the effect of pH on the fluorescence intensity of BPRB (5μM) in $CH_3CN:H_2O$ (1:1). The pH of the solution was adjusted by HCl (1M) or NaOH (1M) (λ_{ex}=510nm). The results indicated that BPRB can work well near neutral pH range (6-8) for Pd^{2+} detection.

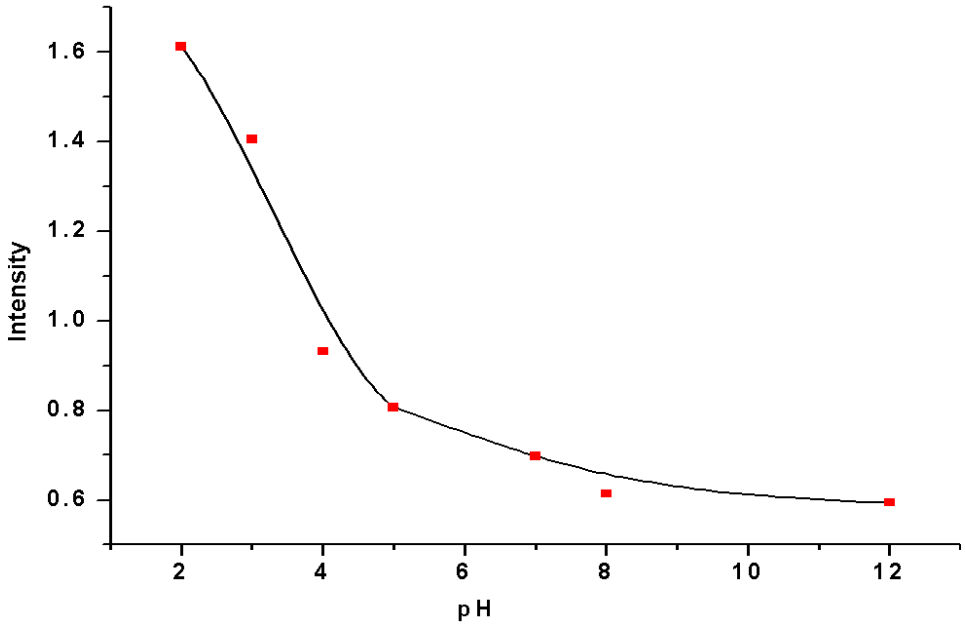


Fig. S5 Acid-base titrations of BPRB

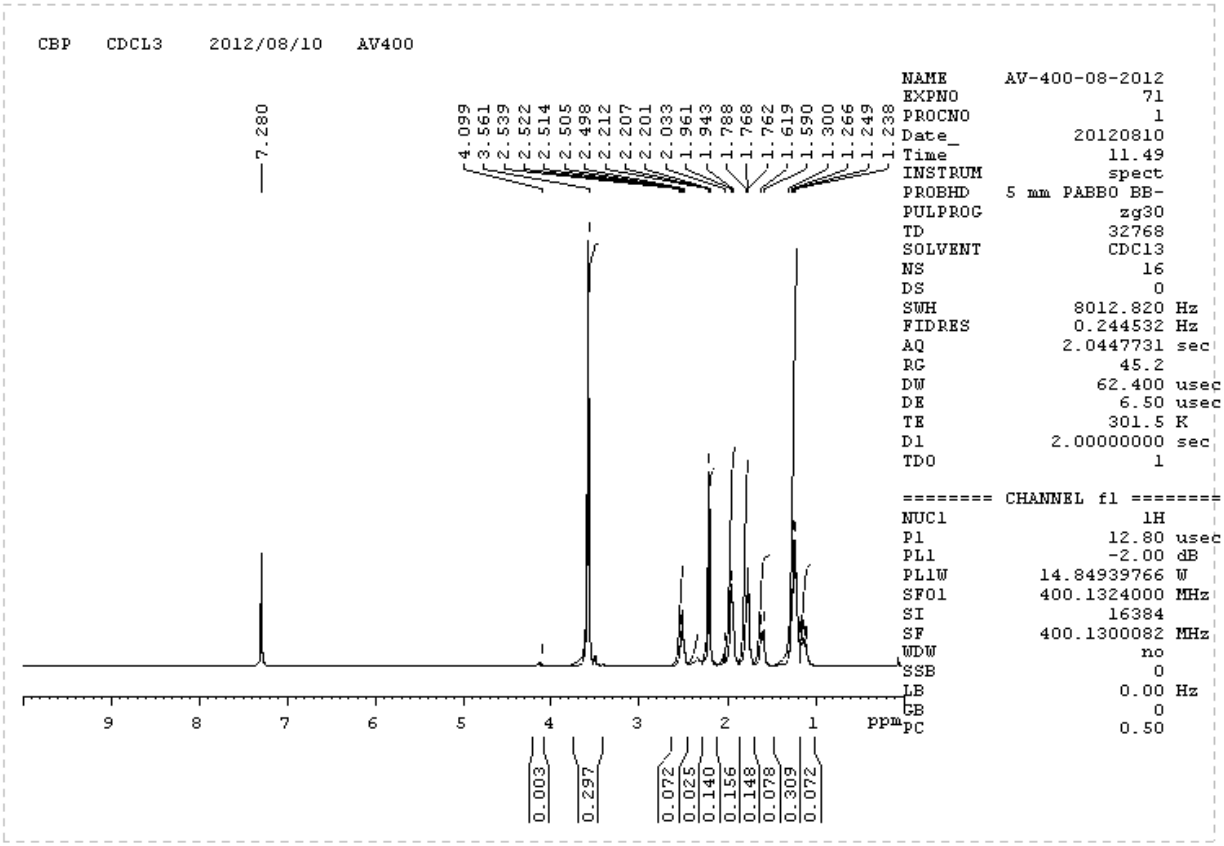


Fig. S6 ^{1}H-NMR spectrum of **BPCH** in $CDCl_3$

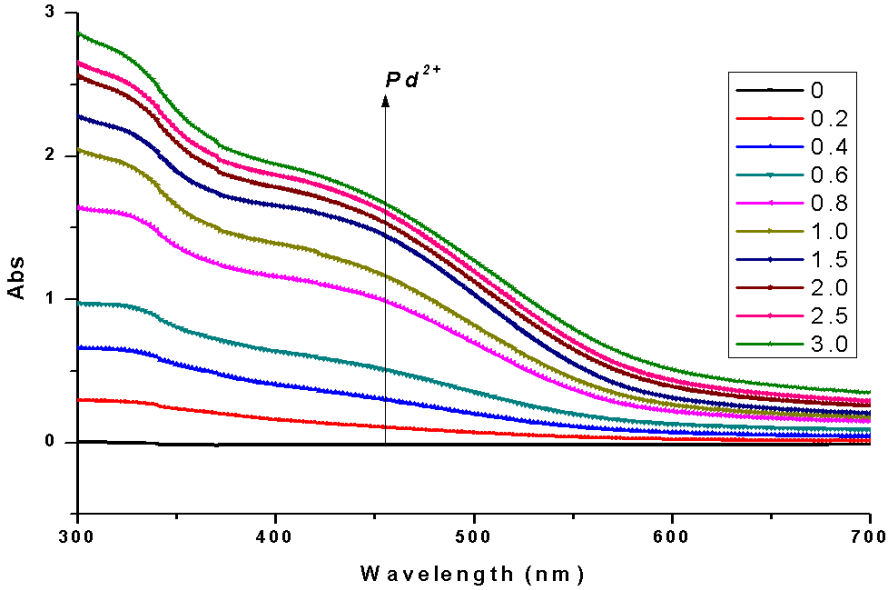


Fig. S7 Changes in the UV-vis spectra of **BPCH** (250μM) with Pd^{2+} in CH_3CN:H2O (1:1, v/v)

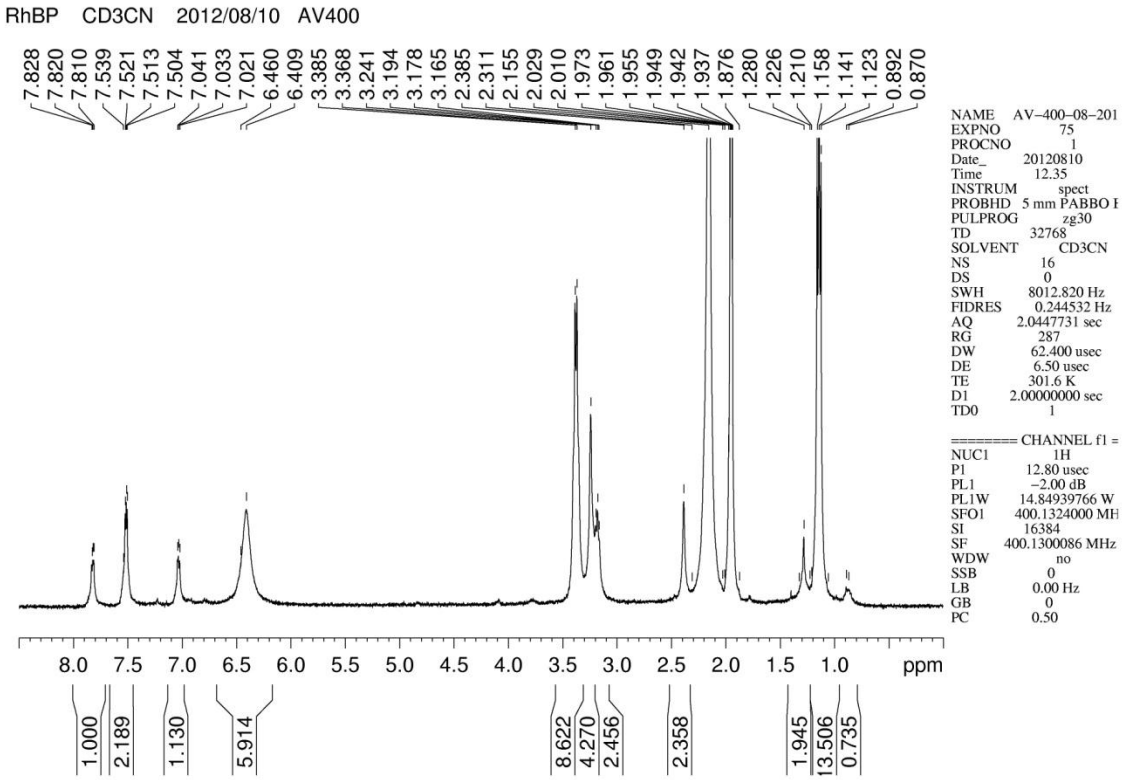


Fig. S8 ^{1}H-NMR spectrum of **BPRB** in CD_3CN

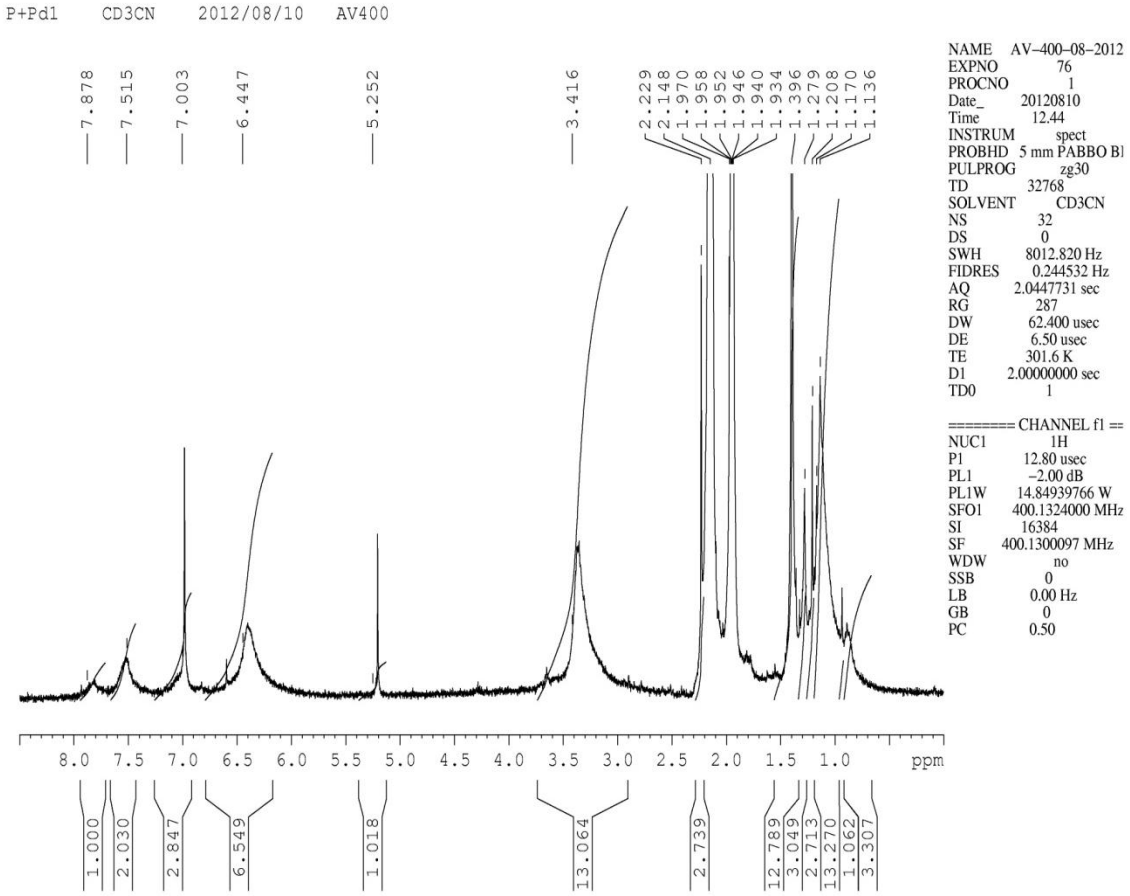


Fig. S9 ^{1}H-NMR spectrum of **BPRB+Pd^{2+}** (1:1 equiv) in CD_3CN

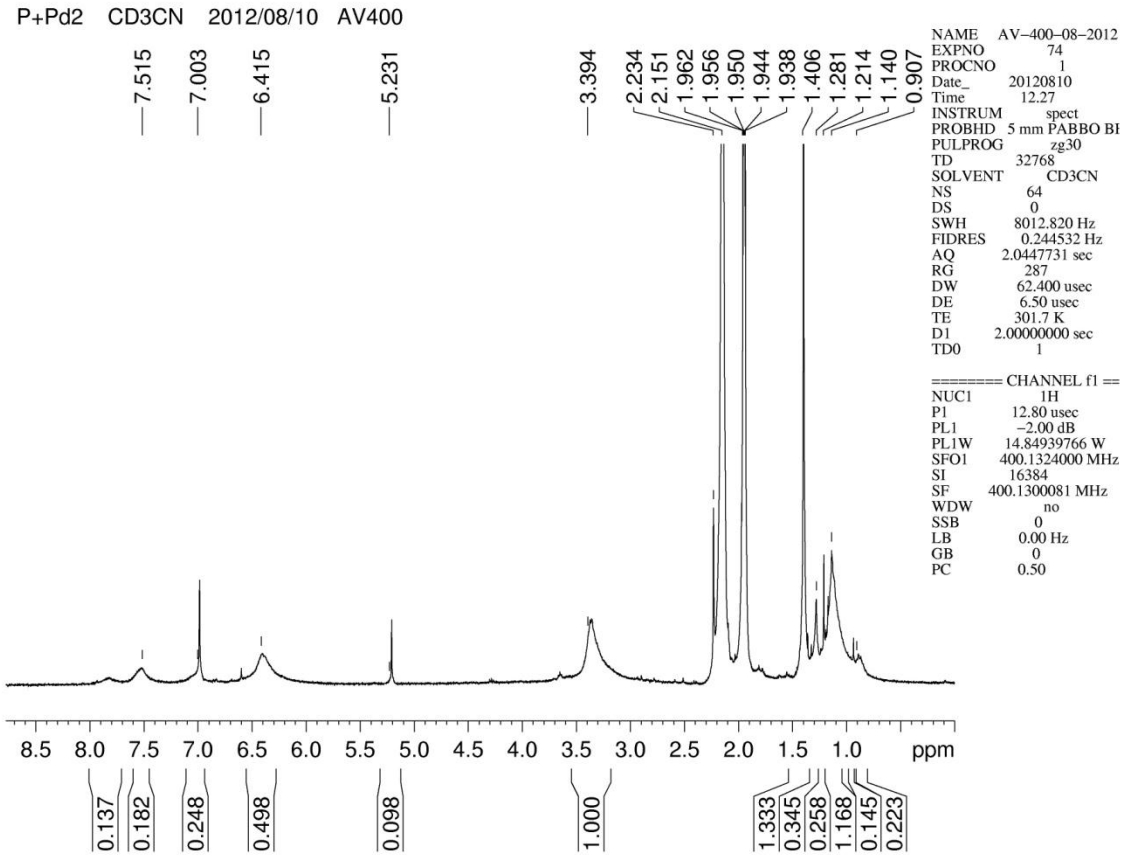


Fig. S10 ^{1}H-NMR spectrum of **BPRB+Pd^{2+}** (1:2 equiv) in CD_3CN