Supplementary Material (ESI) for New Journal of Chemistry

SUPPORTING INFORMATION

Switching the ligand-exchange reactivities of chloro-bridged cyclopalladated azobenzenes for chromogenic sensing of thiocyanate

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Contents

1. Reagents

Potassium tetrachloropalladate(II) was purchased from Sigma-Aldrich Co., Ltd. Methyl orange was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and used without further purification.

4,4'-bis(hydroxy)-azobenzene: 4,4'-Dihydroxyazobenzene was prepared based on the method of Willstätter and Benz [1]. A mixture of KOH (25 g, 380 mmol), *p*-nitrophenol (5 g, 36 mmol), and water (6 mL) was heated to 120 °C and left to stand for 1 h. When the temperature slowly rose to 195-200 °C, the reaction vigorously started to give a brown viscous liquid with a large number of bubbles developing. After the reaction was completed, products were dissolved in water. A dark-red solution was acidified to pH 3 with concentrated HCl and extracted with ether. Combined ether extracts were dried over Na_2SO_4 overnight. Ether was removed to dryness under vacuum. Residue was recrystallized from 50% (v/v) ethanol aqueous solution to give yellow crystals of 4,4'-Dihydroxyazobenzene (2.3 g). TOF-MS: *m/z* 215 (M + H). Selected ^{1}H NMR (400 MHz, DMSO-d_6, ppm) data of the product: δ = 6.90 (d, 2 H, Ph-H, J(HH) = 8 Hz), 7.71 (d, 2 H, Ph-H, J(HH) = 9 Hz), 10.13 (s, 1 H, Ph-OH).

MoP: MoP was prepared as we have reported elsewhere.[2,3] 5 mL aqueous solution of potassium tetrachloropalladate(II) (66 mg, 0.2 mmol) was slowly added into a solution of methyl orange (100 mg, 0.3 mmol) in 30 mL dioxan/water (1:1) mixture. The reaction mixture was stirred at room temperature for a week to give a claret solution. The solvent was evaporated to ca. 1.5 mL under vacuum. The precipitate was collected and washed with ethanol and diethyl ether. The obtained solid was dried under vacuum to give 53 mg of **MoP**-2K (52% yield). Potassium tetrachloropalladate(II) was used as needle crystals in this preparation. Selected ^{1}H NMR (400 MHz, DMSO-d_6, ppm) data of the product: δ = 3.17 (s, 6H, N-CH_3), 6.77 (d, 2 H, Ph-H, J(HH) = 9 Hz), 6.85 (d, 1 H, Ph-H, J(HH) = 9 Hz), 7.72 (s, 1 H, Ph-H), 7.80 (d, 2 H, Ph-H, J(HH) = 9 Hz), 7.88 (d, 2 H, Ph-H, J(HH) = 9 Hz), 2.50 (DMSO).

AbP: In a typical preparation, 4,4'-bis(hydroxy)-azobenzene (44 mg, 0.2 mmol) and potassium tetrachloropalladate(II) (66 mg, 0.2 mmol) were dissolved in 30 mL dioxane-water (1:1) mixture. The mixture was stirred at room temperature for a week to give a brown solution. The solvent was evaporated to ca. 1.5 mL under vacuum. The precipitate was collected and washed with ethanol and diethyl ether, respectively. The obtained solid was dried under vacuum to give 62 mg of **AbP**$\cdot 3H_2O$ (76% yield). Elemental analysis (%) calcd for $C_{24}H_{24}N_4O_7Cl_2Pd_2$: N 7.33, C 37.72, H 3.17; found: N 7.00, C 37.77, H 3.06. XPS: Pd (4d, 3p, MNV, $3d_{5/2}$ = 337.9 eV, $3d_{3/2}$ = 343.1 eV); Cl (2p, $2d_{3/2}$ = 198.6 eV, $2d_{1/2}$ = 200.1 eV); C (1s); N (1s); O(1s). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 6.59 (d, 1 H, Pd-Ph-*H*), 6.82 (d, 2 H, Ph-*H*), 7.10 (s, 1 H, Pd-Ph-*H*), 7.60 (d, 2 H, Ph-*H*), 7.66 (d, 1 H, Pd-Ph-*H*), 10.09 (s, 1 H, O*H*), 10.52 (s, 1 H, O*H*), 2.50 (DMSO), 3.35 (H_2O). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 114.80, 115.11, 115.42, 125.68, 125.83, 131.14, 143.96, 156.95, 159.42, 159.75. MOLDI-TOF-MS: m/z 709 (M - H), 727 (M + OH).

2. NMR spectra of AbP (Fig. S1)

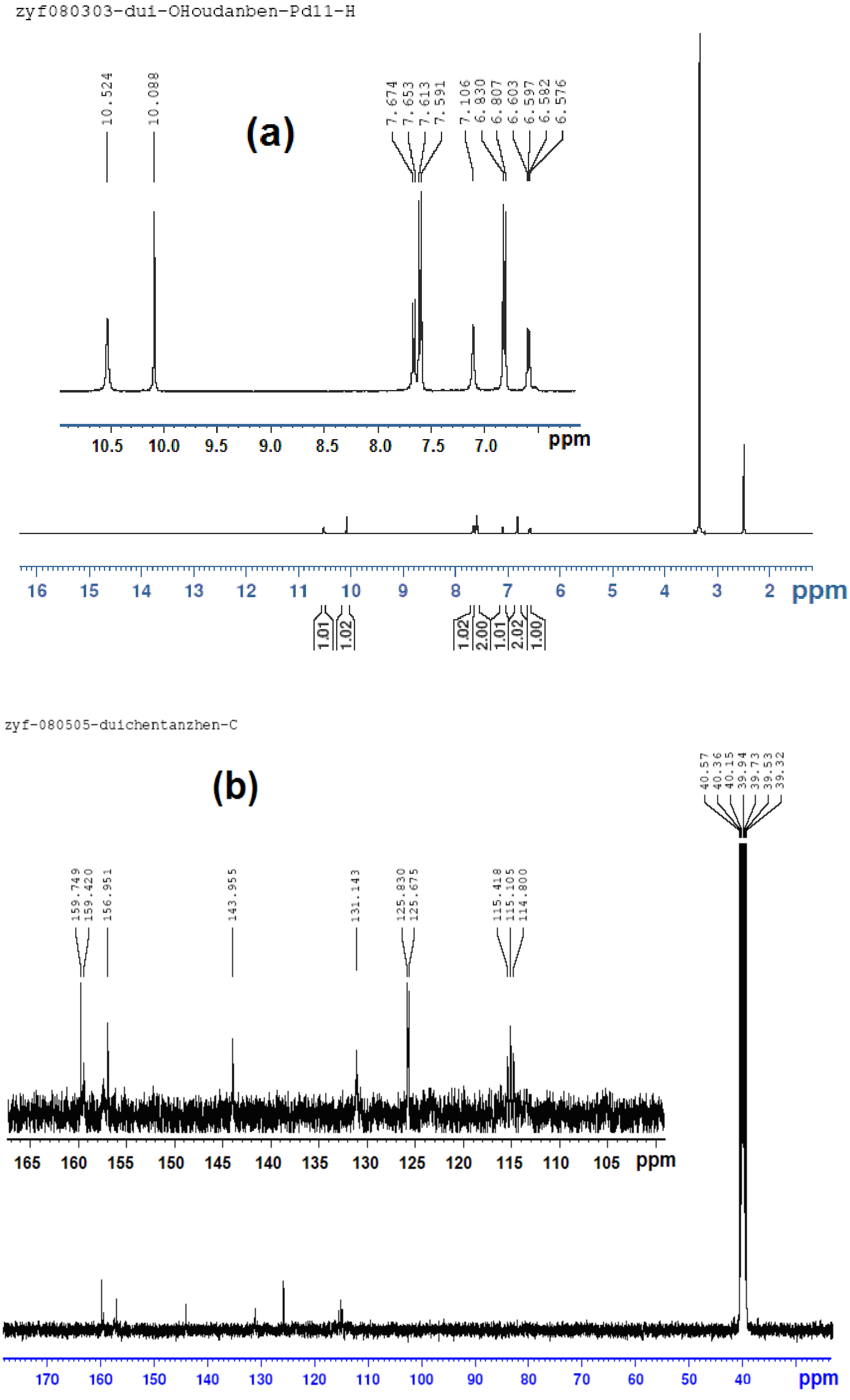
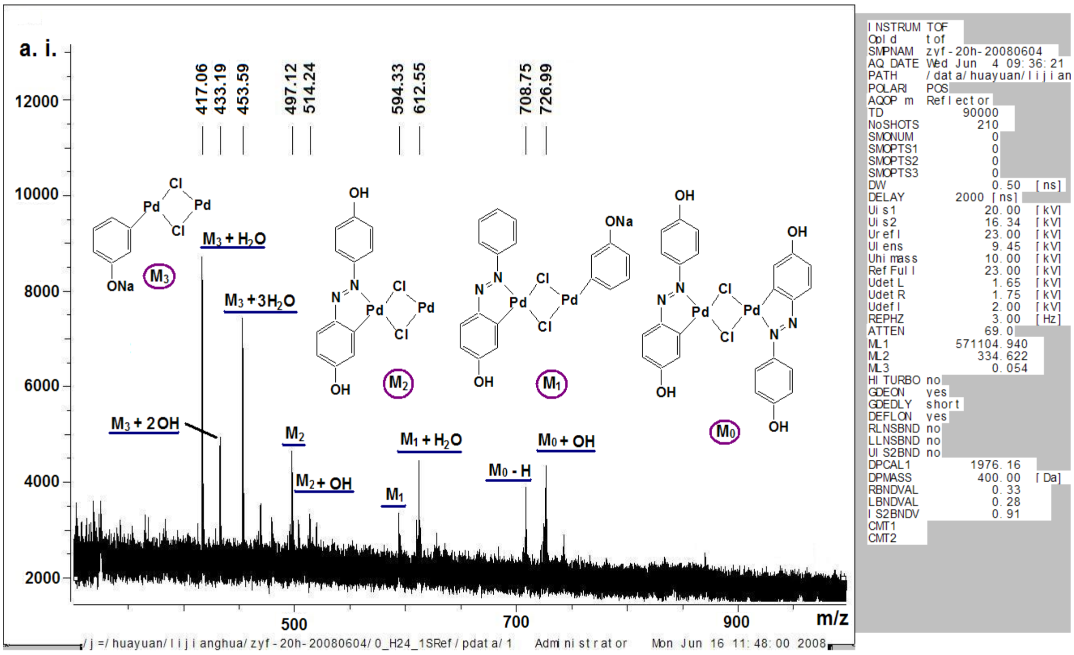


Fig. S1. ^{1}H (a) and ^{13}C (b) NMR spectra of **AbP**.

3. TOF-MS spectrum of AbP (Fig. S2)



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SMOPTS3            0
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Uis2              16.34   [kV]
Urefl             23.00   [kV]
Ulens              9.45   [kV]
Uhimass           10.00   [kV]
Ref Full          23.00   [kV]
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UIS2BND  no
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Fig. S2. MALDI-TOF-MS spectrum of **AbP**.

4. XPS spectra of AbP (Fig. S3)

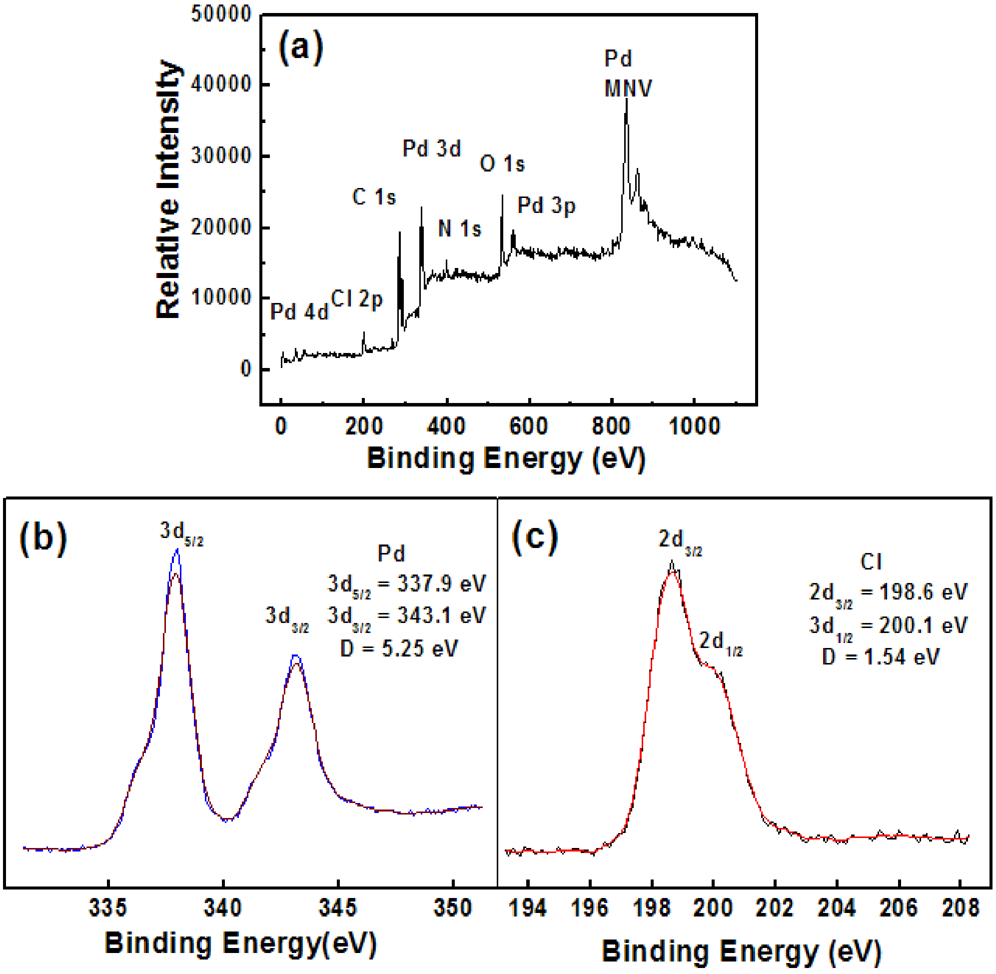

Fig. S3. Total (A), Pd 3d (B) and Cl 2d (C) XPS spectra of **AbP** solid.

5. FT-IR spectra of the relative compounds of AbP and MoP (Fig. S4)

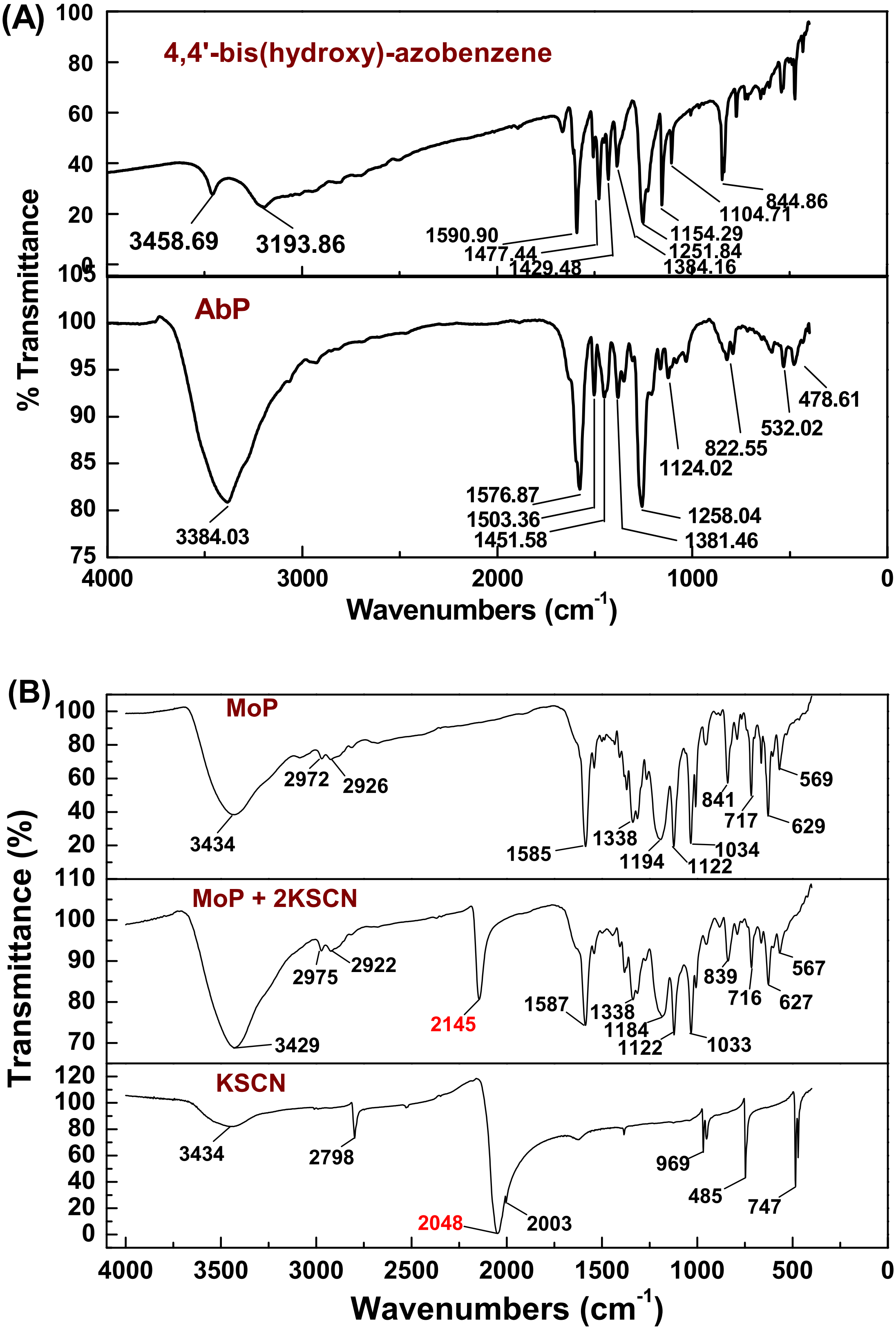

Fig. S4. IR absorption spectra of the relative compounds of **AbP** (A) and **MoP** (B) in KBr.

6. Effect of pH on the thiocyanate-sensing responses of MoP (Fig. S5)

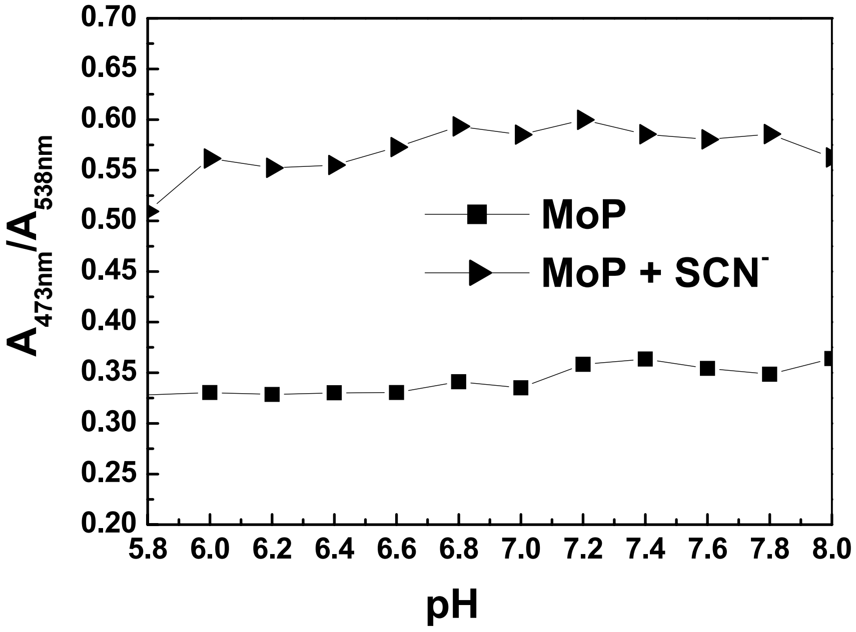

Fig. S5. Effect of pH on absorption changes of **MoP** solution upon addition of thiocyanate. [**MoP**]: 1.0×10^{-5} mol L^{-1}; [SCN^-]: 5.0×10^{-6} mol L^{-1}; pH buffer: 0.02 mol L^{-1} phosphates. Absornbance were measured after reacting for 0.5 h at room temperature.

7. Spectral traces of AbP upon addition of thiocyanate (Fig. S6)

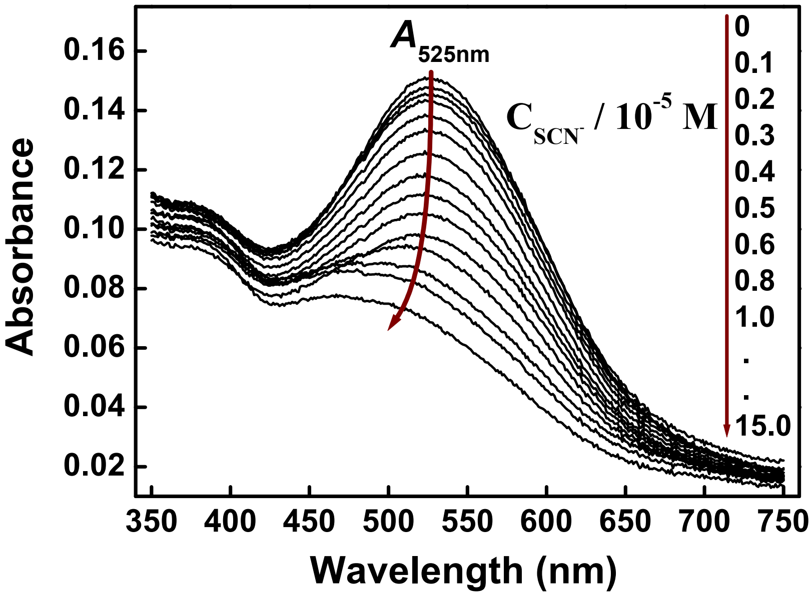

Fig. S6. Absorption evolution of **AbP** solution upon titration with sodium thiocyanate at pH 7.4. The sensing solutions of **AbP** were prepared as aqueous mixtures of **AbP** (1.0×10^{-5} mol L^{-1}), NaCl (0.1 mol L^{-1}), Na_2SO_4 (0.02 mol L^{-1}), $NaHCO_3$ (0.03 mol L^{-1}), $NaNO_2$ (2.0×10^{-4} mol L^{-1}), KNO_3 (1.0×10^{-3} mol L^{-1}) and buffer phosphates. Absorption spectra were recorded after reacting for 0.5 h at room temperature.

8. Plots for measuring the binding stoichiometry between MoP and thiocyanate (Fig. S7)

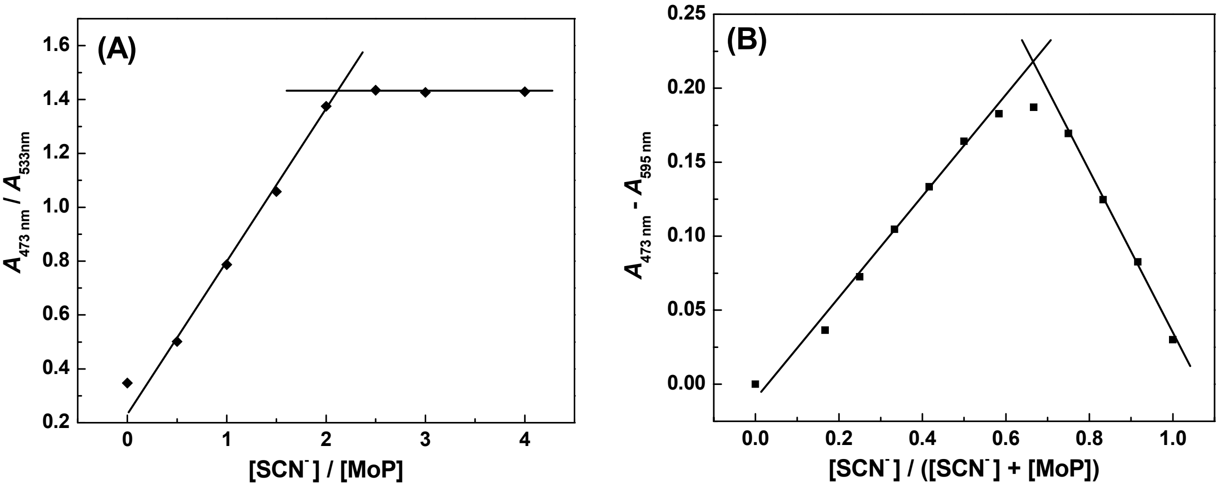

Fig. S7. Molar ratio variation plot (A) and Jot plot (B) suggesting the 1:2 binding stoichiometry between **MoP** and thiocyanate. (A): [**MoP**] = 2.0 × 10^{-5} mol L^{-1}; (B): [**MoP**] + [SCN^-] = 6.0 × 10^{-5} mol L^{-1}; buffer: pH 7.4, 0.02 mol L^{-1} phosphates. Molar absorption coefficient of **MoP** at 473 nm was equal to that at 495 nm in aqueous solution at pH 7.4.

8. References in *Supporting Imformation*

[1] R. Willstätter and M. Benz, *Chem. Ber.*, 1906, **339**, 3492-3503.

[2] S.-H. Li, C.-W. Yu, J.-G. Xu, *Chem. Commun.*, 2005, 250-252.

[3] C.-W. Yu, S.-H. Li, J.-G. Xu, *Chinese J. Chem.*, 2007, **25**, 797-801.