Supplementary Material (ESI) for Dalton Transactions
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Supporting Information for

A simple fluorescent probe for Cd^{2+} in aqueous solution with high selectivity and sensitivity

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1. The pH-titration of free PBQ and PBQ/Cd^{2+}

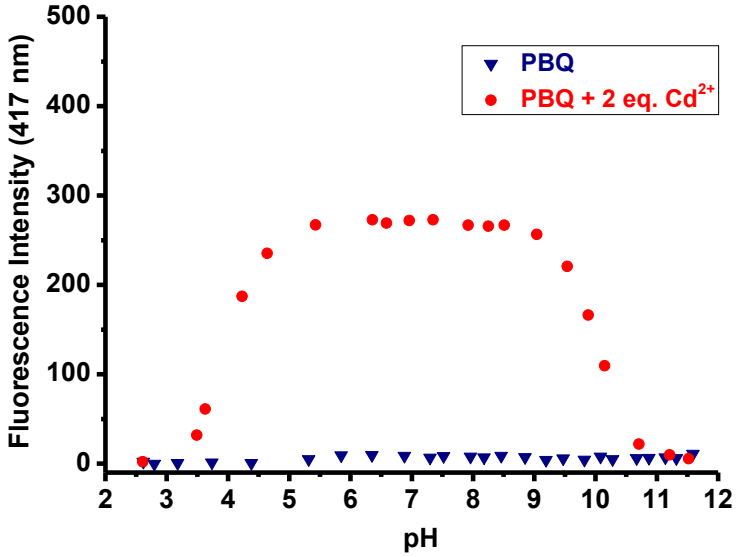
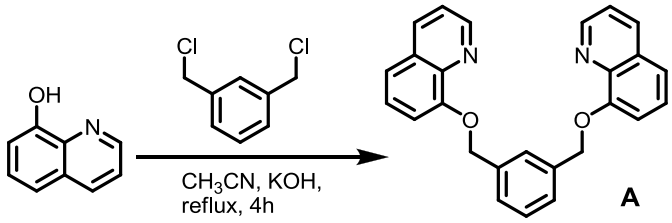


Fig. S1 The influence of pH on the fluorescence of **PBQ** (10 μM) without Cd^{2+} (blue) and with 20 μM Cd^{2+} (red) in water, the pH of the solution was adjusted by adding 10% $HClO_4$ or 2 M NaOH. Excitation was performed at 302 nm.

2. Synthesis of model compounds A-C



Scheme S1 Synthesis of **A**

Compound A: Potassium hydroxide (224 mg, 4 mmol) was added to a solution of 1,3-bis(chloromethyl)benzene (175 mg, 1 mmol) and 8-hydroxyquinoline (290 mg, 2 mmol) in acetonitrile (10 mL), the mixture was held at reflux for 4h. Then the mixture was filtered, and the solvent was removed in vacuum to give a white solid. The crude product was then chromatographed on silica gel using CH_2Cl_2/CH_3OH (30:1, v/v) as eluant to afford 305 mg (78%) **A** as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.43 (s, 4H), 6.98 (d, J = 7.2 Hz, 2H), 7.31-7.37 (m, 5H), 7.40 (q, J = 4.0 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.64 (s, 1H), 8.10 (d, J = 8.4 Hz, 2H), 8.94 (dd, J_1= 2.0 Hz, J_2 = 4.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.59, 109.93, 119.90, 121.63, 125.70, 126.59, 126.62, 129.11, 129.48, 135.93, 137.41, 140.44, 149.39, 154.21. MS (ES+) calcd for $C_{26}H_{20}N_2O_2$: 392.1525, found: 392.1523.

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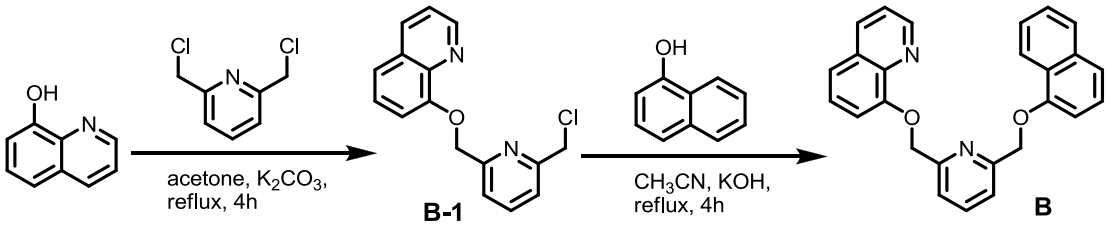

Scheme S2 Synthesis of **B**

Compound B-1: Anhydrous potassium carbonate (300 mg) was added to a solution of 2,6-bis(chloromethyl)pyridine (704 mg, 4 mmol) in acetone (5 mL), and the mixture was held at reflux. An hour later, an acetone solution containing 8-hydroxyquinoline (145 mg, 1 mmol) was added dropwise to the mixture. After the addition, the mixture was held at reflux for another 6h. The mixture was filtered, and the solvent was removed in vacuum to give a white solid. The crude product was then chromatographed on silica gel using ethyl acetate as eluant to afford 182 mg (64%) **B-1** as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.66 (s, 2H), 5.50 (s, 2H), 6.70 (dd, J_1 = 2.4 Hz, J_2 = 6.4 Hz, 1H), 7.32 (s, 1H), 7.34 (d, J = 2.4 Hz, 2H), 7.39 (dd, J_1 = 4.0 Hz, J_2 = 4.2 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.64 (t, J_1 = 7.6 Hz, 1H), 8.08 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 8.94 (dd, J_1 = 1.6 Hz, J_2 = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 46.59, 71.26, 109.82, 120.21, 120.70, 121.69, 126.59, 129.50, 135.92, 137.93, 140.30, 149.42, 153.91, 156.02, 157.08. MS (ES+) calcd for $C_{16}H_{13}ClN_2O$ $([M+H])^+$: 285.2, found: 285.6.

Compound B: Potassium hydroxide (56 mg, 1 mmol) was added to a solution of **B-1** (142 mg, 0.5 mmol) and 1-naphthol (72 mg, 0.5 mmol) in acetonitrile (15 mL), the mixture was held at reflux for 4h. Then the mixture was filtered, and the solvent was removed in vacuum to give a white solid. The crude product was then chromatographed on silica gel using CH_2Cl_2/CH_3OH (30:1, v/v) as eluant to afford 333 mg (85%) **B** as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.44 (s, 2H), 5.58 (s, 2H), 6.90 (d, J = 7.6 Hz, 1H), 7.08 (dd, J_1 = 2.4 Hz, J_2 = 6.8 Hz, 1H), 7.35-7.43 (m, 3H), 7.46 (t, J = 4.0 Hz, 1H), 7.48 (s, 1H), 7.50-7.54 (m, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.73 (t, J = 8.0 Hz, 1H), 7.81-7.85 (m, 1H), 8.16 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 8.41 (q, J = 3.2 Hz, 1H), 9.00 (dd, J_1 = 1.6 Hz, J_2 = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.63, 71.40, 105.39, 109.82, 120.11, 120.21, 120.40, 120.81, 121.78, 122.02, 125.39, 125.63, 125.90, 126.53, 126.67, 127.59, 129.56, 134.58, 136.04, 137.87, 140.33, 149.50, 154.00, 156.67, 156.94. MS (ES+) calcd for $C_{26}H_{20}N_2O_2$: 392.1525, found: 392.1527.

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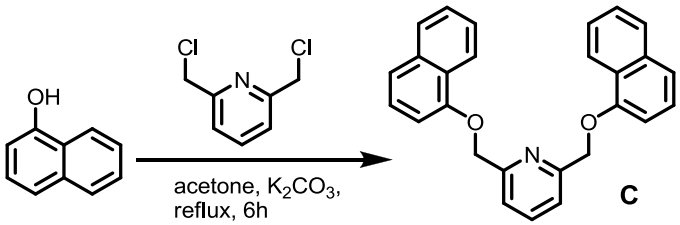

Scheme S3 Synthesis of **C**

Compound C: Anhydrous potassium carbonate (150 mg) was added to a solution of 2,6-bis(chloromethyl)pyridine (176 mg, 1 mmol) and 1-naphthol (288 mg, 2 mmol) in acetone (15 mL), the mixture was held at reflux for 6h. Then the mixture was filtered, and the solvent was removed in vacuum to give a white solid. The crude product was then chromatographed on silica gel using CH_2Cl_2/CH_3OH (40:1, v/v) as eluant to afford 293 mg (75%) **C** as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.45 (s, 4H), 6.91 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.52-7.56 (m, 4H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.83-7.87 (m, 2H), 8.42-8.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.60, 105.39, 120.07, 120.85, 122.05, 125.43, 125.64, 125.93, 126.57, 127.64, 134.60, 137.87, 153.98, 156.94. MS (ES+) calcd for $C_{27}H_{21}N_2O_2$: 391.1572, found: 391.1569.

3. UV-Vis absorption titration spectra of PBQ with Cd^{2+}

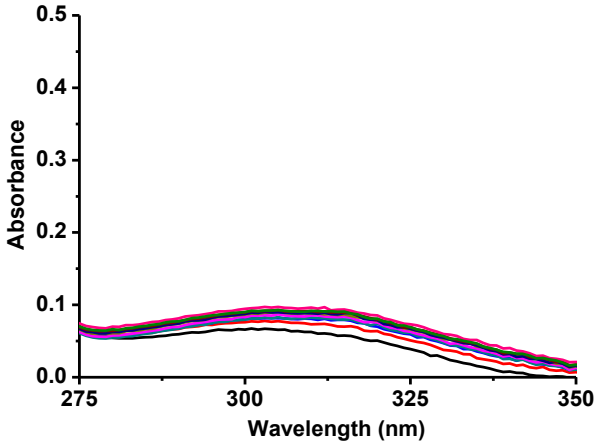

Fig. S2 UV-Vis absorption spectra of **PBQ** (10 μM) upon addition of Cd^{2+} (3 ~ 33 μM) in aqueous solution (20 mM Tris-HCl, pH 7.4).

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4. UV-Vis absorption spectra of PBQ with various metal ions

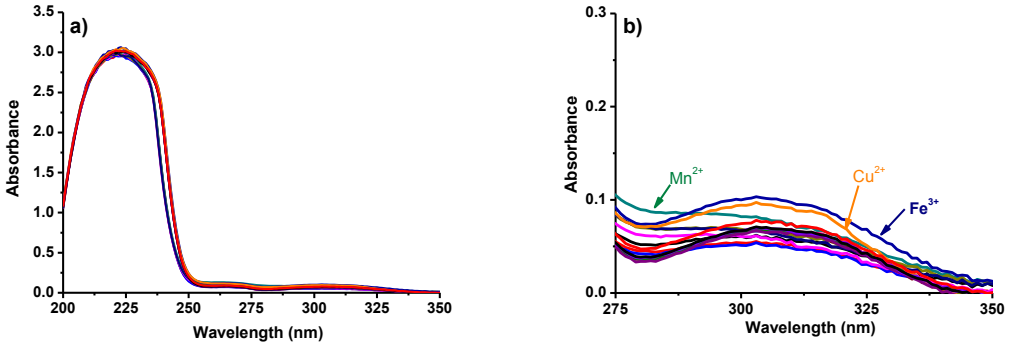

Fig. S3 UV-Vis absorption spectra of **PBQ** (10 μM) in the presence of various metal ions (20 μM) in aqueous solution (20 mM Tris-HCl, pH 7.4).

5. Fluorescence color changes of PBQ with various metal ions

Fig. S4 The photographs shows the fluorescence color changes (irradiated at 254 nm using UV lamp) of **PBQ** (10 μM) with 20 μM of various metal ions, and then added 20 μM of Cd^{2+} in aqueous solution (20 mM Tris-HCl, pH 7.4).

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6. UV-Vis absorption spectra of PBQ in the presence of Na^+ and K^+ in aqueous solution and methanol

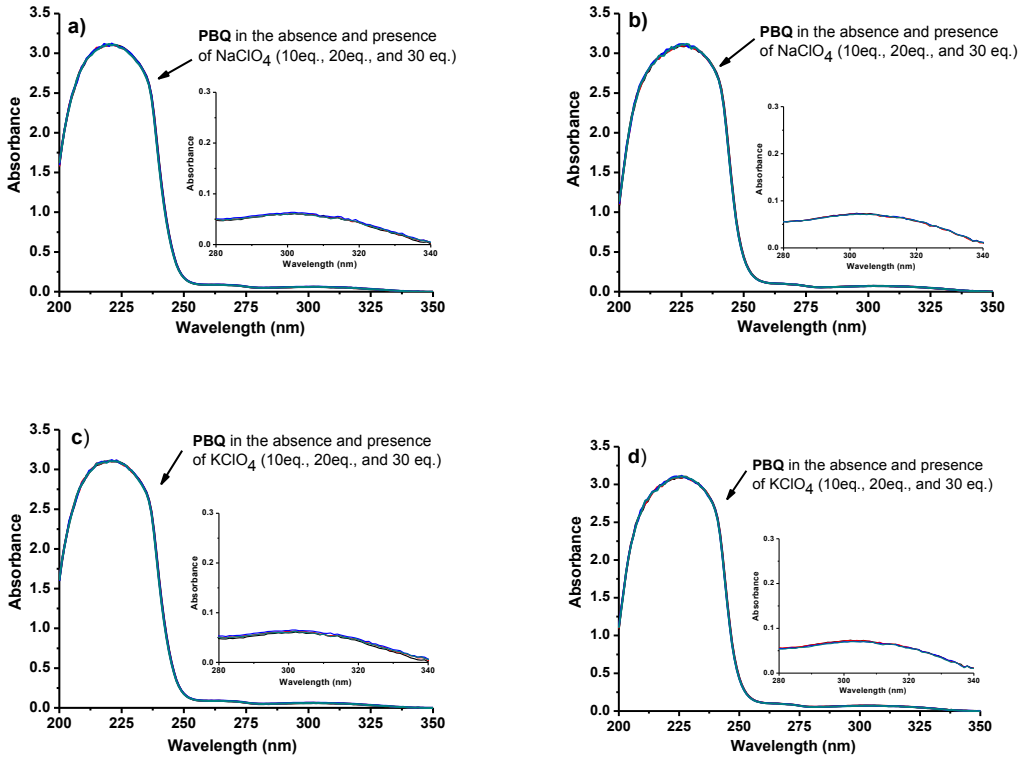

Fig. S5 UV-Vis absorption spectra of **PBQ** (10 μM) in the presence of Na^+ (100 μM, 200 μM, and 300 μM) in aqueous solution (20 mM Tris-HCl, pH 7.4) (a) and CH_3OH (b); UV-Vis absorption spectra of **PBQ** (10 μM) in the presence of K^+ (100 μM, 200 μM, and 300 μM) in aqueous solution (20 mM Tris-HCl, pH 7.4) (c) and CH_3OH (d).

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7. The fluorescent intensity of A , B, and C with various metal ions in aqueous solution

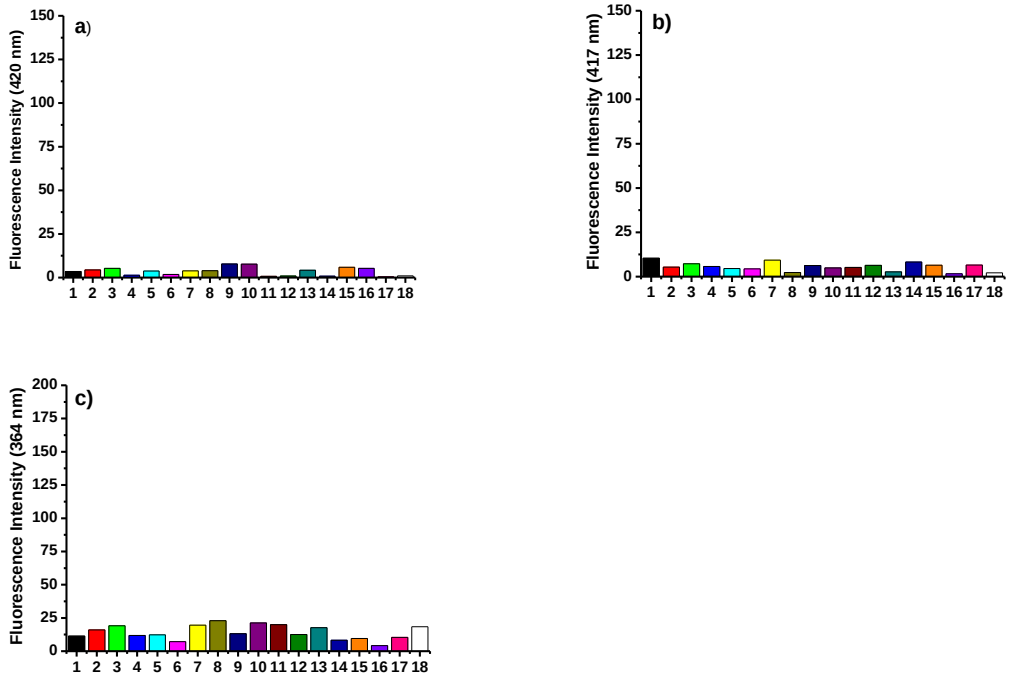

Fig. S6 The fluorescent intensity of **A** (a), **B** (b), and **C** (c) (**A**, **B**, and **C** were 10 μM) with 2 equiv. of various metal ions in aqueous solution (20 mM Tris-HCl, pH 7.4). 1, **A** (a), **B** (b), and **C** (c); 2, Mn^{2+}; 3, Hg^{2+}; 4, Ni^{2+}; 5, Ca^{2+}; 6, Cu^{2+}; 7, Co^{2+}; 8, Pb^{2+}; 9, Mg^{2+}; 10, Fe^{2+}; 11, Fe^{3+}; 12, Cr^{3+}; 13, Ag^{+}; 14, Li^{+}; 15, Zn^{2+}; 16, K^{+}; 17, Na^{+}; 18, Ba^{2+}. λ_{ex} = 302 nm.

8. HRMS of PBQ

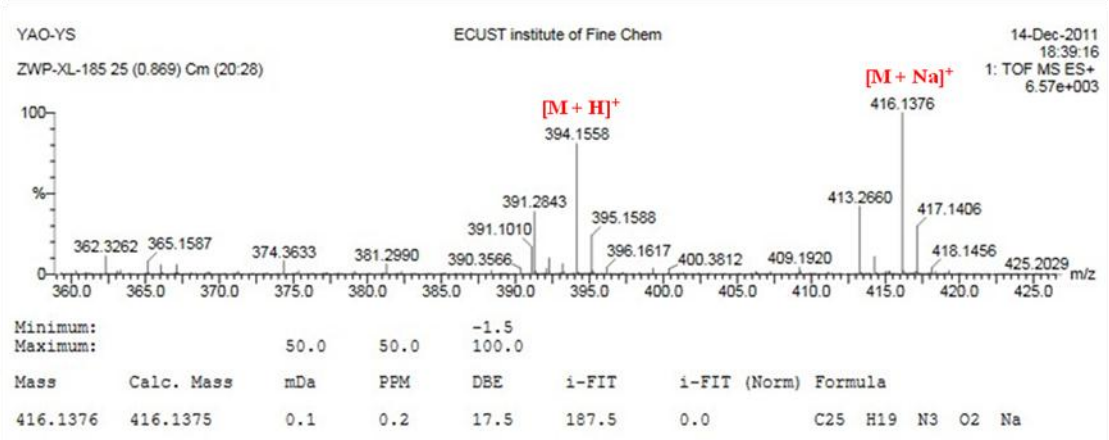

Fig. S7 HRMS of **PBQ**.