Supplementary Material (ESI) for Dalton Transactions
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Supporting Information for

A highly selective and sensitive fluorescence "turn-on" probe for Ag^+ in aqueous solution and live cells

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1. The pH-titration of free NPQ and NPQ-Ag^+

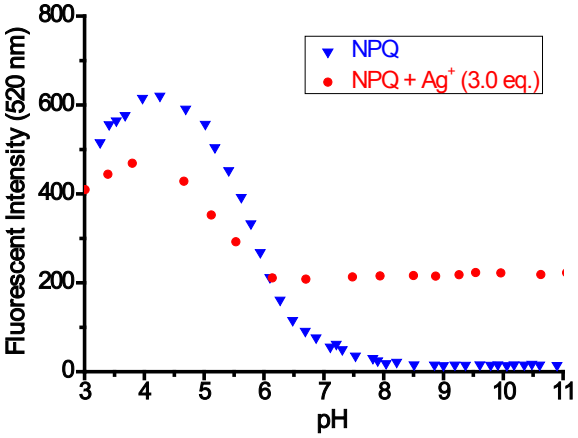

Fig. S1 The influence of pH on the fluorescence of **NPQ** (10 μM) without Ag^+ (blue) in DMF/water solution (2:1, v/v) and with 30 μM Ag^+ in CH_3CH_2OH/water solution (4:6, v/v), the pH of the solution was adjusted by adding 10% $HClO_4$ or 2 M NaOH. Excitation was performed at 300 nm.

2. Synthesis of various control compounds

Scheme S1 Synthesis of **A**

Compound A: 4-bromo-N-*n*-butyl-1,8-naphthalimide (332 mg, 1 mmol) and N-methyl piperazine (450 mg, 4.5 mmol) were dissolved in 2-methoxyethanol (10 mL), and the reaction mixture was refluxed for 6h under N_2 atmosphere. After removal of 2-methoxyethanol under reduced pressure, the product was then chromatographed on silica gel using dichloromethane/methanol 40: 1 (v/v) as eluant to afford 302 mg (86%) **A** as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.99 (t, J = 7.2 Hz, 3H), 1.41-1.53 (m, 2H), 1.67-1.76 (m, 2H), 2.46 (s, 3H), 2.76 (s, 4H), 3.31 (d, J = 3.6 Hz, 4H), 4.18 (t, J = 7.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.85, 20.40, 30.26, 40.07, 46.11, 52.96, 55.16, 114.98, 116.85, 123.35, 125.61, 126.18, 129.86, 130.15, 131.02, 132.49, 155.84, 164.00, 164.48. MS (ES+) calcd for $C_{21}H_{25}N_3O_2$ ($[M+H]$)$^+$: 352.2025, found: 352.2022

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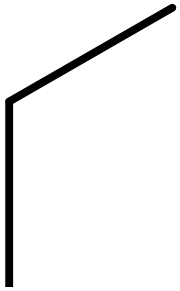

Scheme S2 Synthesis of **B**

Compound 3: Anhydrous potassium carbonate (276 mg, 2 mmol), compounds **2** (337 mg, 1 mmol) and 2,6-bis(chloromethyl)pyridine (880 mg, 5 mmol) were dissolved in acetonitrile (10 mL), and the reaction mixture was refluxed for 12h under N_2 atmosphere. The mixture was filtered, and the solvent was removed in vacuum to give a yellow solid. The crude product was then chromatographed on silica gel using dichloromethane/methanol 30: 1 (v/v) as eluant to afford 324 mg (68%) **3** as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.98 (t, J = 7.2 Hz, 3H), 1.41-1.52 (m, 2H), 1.68-1.78 (m, 2H), 2.89 (s, 4H), 3.35 (s, 4H), 3.86 (s, 2H), 4.18 (t, J = 7.6 Hz, 2H), 4.72 (s, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.59 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.88, 20.41, 30.27, 40.09, 46.81, 52.98, 53.36, 64.24, 114.93, 116.88, 121.38, 122.56, 123.32, 125.66, 126.16, 129.86, 130.21, 131.06, 132.49, 137.59, 156.24, 164.03, 164.49. MS (ES+) calcd for $C_{27}H_{29}ClN_4O_2$ $([M+H])^+$: 477.2057, found: 477.2057

Compound B: Anhydrous potassium carbonate (100 mg, 0.72 mmol), compounds **3** (215 mg, 0.45 mmol) and 1-naphthol (78 mg, 0.54 mmol) were dissolved in acetone (10 mL), and the reaction mixture was refluxed for 8h. The mixture was filtered, and the solvent was removed in vacuum to give a yellow solid. The crude product was then chromatographed on silica gel using dichloromethane/methanol 20: 1 (v/v) as eluant to afford 189 mg (72%) **B** as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.00 (t, J = 7.2 Hz, 3H), 1.47 (q, J = 7.2 Hz, 2H), 1.70-1.77 (m, 2H), 2.89 (s, 4H), 3.33 (s, 4H), 3.88 (s, 2H), 4.18 (t, J = 7.2 Hz, 2H), 5.44 (s, 2H), 6.90 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 5.6 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.52 (dd, J_1 = 4.0 Hz, J_2 = 5.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.81-7.83 (m, 1H), 8.41 (t, J = 7.6 Hz, 2H), 8.50 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.95, 20.45, 30.29, 40.09, 53.03, 53.42, 64.46, 70.79, 105.35, 114.87, 116.74, 119.62, 120.75, 122.01, 122.19, 123.28, 125.35, 125.63, 125.88, 126.11, 126.51, 127.59, 129.83, 130.24, 131.02, 132.50, 134.57, 137.39, 154.01, 155.90, 157.06, 157.75, 164.00, 164.46. MS (ES+) calcd for $C_{37}H_{36}N_4O_3$ $([M+H])^+$: 585.2866, found: 585.2861.

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Scheme S3 Synthesis of **C**

Compound 4: Anhydrous potassium carbonate (300 mg) was added to a solution of 1,3-Bis(chloromethyl)benzene (875 mg, 5 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 dichloromethane as eluant to afford 201 mg (71%) **4** as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.55 (t, J = 5.6 Hz, 2H), 5.39 (t, J = 5.6 Hz, 2H), 7.01 (t, J = 5.1 Hz, 1H), 7.31-7.42 (m, 5H), 7.47 (d, J = 5.2 Hz, 1H), 7.54 (s, 1H), 8.09 (t, J = 8.4 Hz, 1H), 8.97 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 46.10, 70.46, 109.90, 120.07, 121.68, 126.61, 127.24, 127.32, 128.13, 129.11, 129.52, 136.01, 137.55, 137.88, 140.38, 149.41, 154.21. MS (ES+) calcd for $C_{17}H_{14}ClNO$ ($[M+H]$)$^{+}$: 284.0842, found: 284.0841.

Compound C: Anhydrous potassium carbonate (150 mg), compounds **4** (180 mg, 0.63 mmol) and **2** (214 mg, 0.63 mmol) were dissolved in acetonitrile (10 mL), and the reaction mixture was refluxed for 12h under N_2 atmosphere. The mixture was filtered, and the solvent was removed in vacuum to give a yellow solid. The crude product was then chromatographed on silica gel using dichloromethane/methanol 40: 1 (v/v) as eluant to afford 302 mg (82%) **C** as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95 (t, J = 7.2 Hz, 3H), 1.37-1.47 (m, 2H), 1.65-1.72 (m, 2H), 2.69 (s, 4H), 3.19 (s, 4H), 3.62 (s, 2H), 4.14 (t, J = 7.6 Hz, 2H), 5.43 (s, 2H), 7.02 (dd, J_1 = 3.2 Hz, J_2 = 5.6 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.29-7.40 (m, 5H), 7.43 (d, J = 7.2 Hz, 1H), 7.54 (s, 1H), 7.61 (t, J = 8.0 Hz, 1H), 8.06 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 7.2 Hz, 1H), 8.94 (dd, J_1 = 1.6 Hz, J_2 = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.91, 20.41, 30.26, 40.03, 52.97, 53.02, 62.76, 70.73, 109.92, 114.79, 116.55, 119.88, 121.62, 123.19, 125.50, 126.02, 126.23, 126.53, 127.95, 128.68, 129.47, 129.76, 130.23, 130.94, 132.44, 135.88, 137.04, 138.19, 140.48, 149.37, 154.32, 155.92, 163.94, 164.40. MS (ES+) calcd for $C_{37}H_{36}N_4O_3$ ($[M+H]$)$^{+}$: 585.2866, found: 585.2864.

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3. UV-Vis absorption spectra of NPQ with various metal ions

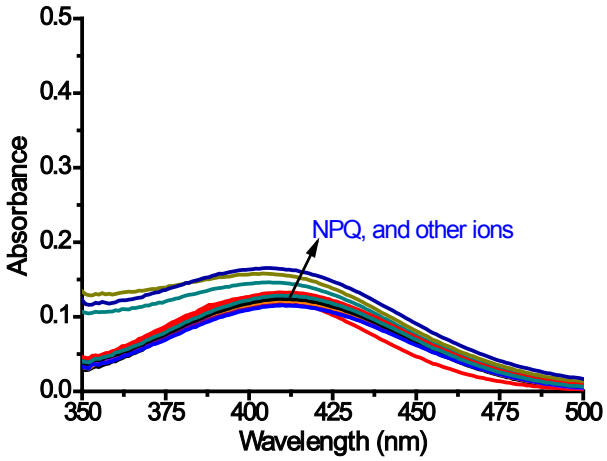

Fig. S2 The absorption spectras of **NPQ** (10 μM) in the presence of 30 μM of Ag^{+} and 60 μM of various metal ions such as Fe^{2+}, Zn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Pb^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, K^{+}, Na^{+}, Li^{+}, Hg^{2+} and Cd^{2+} in CH_3CH_2OH/H_2O (4:6, v/v, 10 mM Tris-$HClO_4$, pH 7.5).

4. UV-Vis absorption titration spectra of NPQ with Ag^{+}

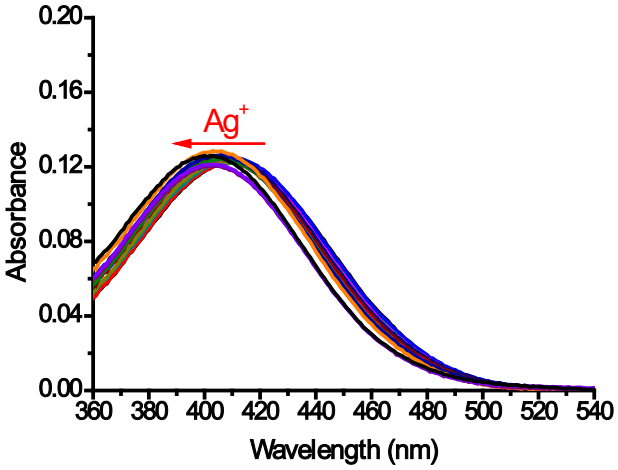

Fig. S3 UV-Vis absorption spectra of **NPQ** (10 μM) upon addition of Ag^{+} (2 ~ 50 μM) in CH_3CH_2OH/H_2O (4:6, v/v, 10 mM Tris-$HClO_4$, pH 7.5).

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5. The selectivity of NPQ-Ag^+ for I^-

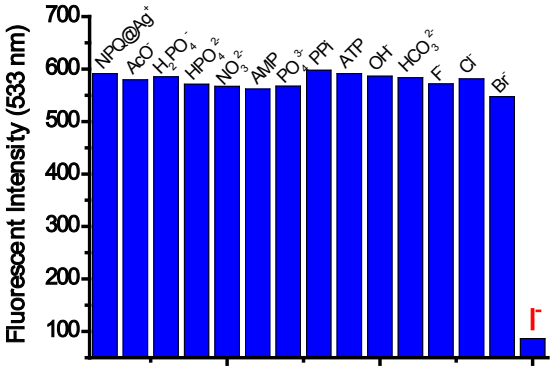

Fig. S4 The fluorescence intensity at 533 nm of **NPQ-Ag^+** (10 μM **NPQ** and 30 μM Ag^+) in the presence of 30 μM of various anions as F^-, Cl^-, Br^-, I^-, ATP, AMP, PPi, $H_2PO_4^-$, PO_4^{3-}, OH^-, AcO^-, SO_4^{2-}, HCO_3^-, NO_3^-, HPO_4^{2-} in CH_3CH_2OH-H_2O (4:6, v/v, 10 mM Tris-$HClO_4$, pH 7.5).