Highly selective and sensitive fluorescent PET (photoinduced electron transfer) chemosensor for Zn(II)

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Electronic Supplementary Information

ESI 1. Synthesis and characterisation

Synthesis of 2

N-Ethyl-4-Bromo-1, 8-Naphthalic anhydride (1.5g, 4.93mmol) was heated with stirring at 130^{0}C under argon atmosphere. After 10 minutes 4-Aminobenzylamine (3.01g, 24.65mmol) was added via syringe. The reaction mixture was kept stirring for 30 minutes. After the completion of the reaction (TLC), 20 ml water was added when the yellow solid started precipitation. The yellow solid was dried under vacuum and upon recrystallization (ethanol) **2** was obtained as light fluffy yellow needles (1.53g, 90%). 1H-NMR(400MHz, DMSO-d_6) δ, 1.17 (t, 3H, *J*=7.0Hz), 4.04 (q, 2H, *J*=7.0Hz), 4.54 (d, 2H, *J*=5.2Hz) 4.95(bs, -NH_2), 6.54(d, 2H, *J*=8.0Hz), 6.70(d, 1H, *J*=8.5Hz), 7.07 (d, 2H, *J*=8.0Hz), 7.68(t, 1H, *J*=7.5Hz), 8.18(d, 1H, J=8.5), 8.42(bs, -NH), 8.43(d, 1H, *J*=8.5Hz), 8.74 (d, 1H, *J*=8.5Hz); ^{13}C-NMR (400MHz, DMSO-d_6) δ, 163.53, 162.53, 162.67, 150.54, 147.70, 133.92, 130.54, 129.37, 128.52, 127.93, 124.93, 124.27, 121.95, 120.26, 113.93, 107.81, 104.51, 45.86, 34.23, 13.29; IR (cm^{-1}): 3358.25, 2974.67, 2930.51, 2108.40, 1679.89, 1639.20, 1579.42, 1536.61, 1390.62, 1346.46, 1248.30, 1181.13, 1100.96, 1065.87, 910.04, 876.30, 773.32, 757.12, 694.44, 581.43;MS (ES) Calcd for ($M+H^+$) *m/z* 346.16, Found 346.39, Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.03; H, 5.54; N, 12.17. Found: C, 72.76; H, 5.63; N, 12.06.

Synthesis of 3

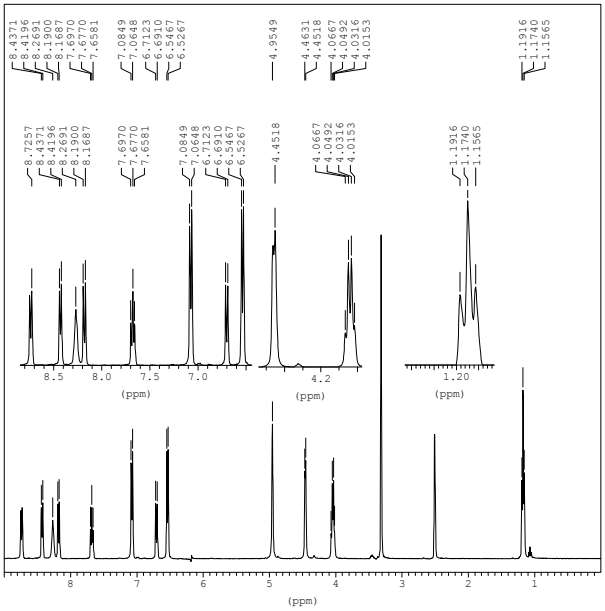
To a solution of 2 (1.5g, 4.3mmol) in dry DMF (50ml) was added K_2CO_3 (1.67g, 9.46mmol) and KI (1.57g, 9.46) under argon atmosphere. The resulting solution was stirred at room temperature, and then Ethyl bromoacetate (1.57g, 9.46mmol) was slowly added *via* a syringe. The resulting mixture was heated at 90^0C overnight. After the completion of the reaction (by TLC) the solvent was evaporated under reduced pressure. The residue was extracted with chloroform and the organic phase was washed with 1M HCl, water and brine, dried over sodium sulfate, and evaporated to dryness. The residue was recrystallized (ethanol) to afford 3 (2.02g, 90%) as light yellow solid. ^{1}H-NMR(400MHz, DMSO-d_6):δ 1.16 (t, 6H), 4.01-4.11 (m, 6H), 4.15 (s, 4H), 6.5 (d, 2H, *J*=8.0Hz), 6.67 (d, 1H, *J*=8.5Hz) 7.21 (d, 2H, *J*=8.0 Hz), 7.69 (t, 1H, *J*=8.0Hz), 8.17 (d, 1H, *J*=8.0Hz), 8.37 (bs, -NH), 8.44 (d, 1H *J*=7.0Hz), 8.73(d, 1H *J*=8.0Hz). ^{13}C-NMR (400MHz, DMSO-d_6) δ, 170.54, 163.55, 162.69, 150.44, 146.84, 133.98, 130.65, 129.32, 128.52, 127.94, 126.53, 124.42, 121.89, 120.89, 111.86, 107.84,104.56, 60.40, 52.66, 45.35, 34.26, 14.08, 13.30. IR (cm^{-1}): 3385.81, 2973.97, 2929.1, 1747.49, 1727.36, 1684.54, 1615.85, 1589.56, 1572.99, 1541.20, 1523.20, 1450.08, 1397.35, 1367.21, 1250.83, 1183.25, 1101.87, 1027.10, 819.22, 801.16, 771.02, 759.54;605.26, 585.30. MS (ES) Calcd for (M) *m/z* 517.22, Found 517.10. Anal. calcd for $C_{29}H_{31}N_3O_6$:C, 67.30; H, 6.04; N, 8.12. Found: C, 67.03; H, 6.02; N, 7.91.

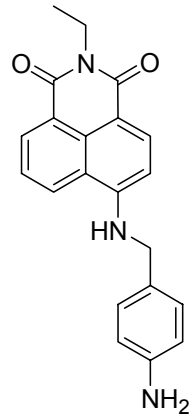
Synthesis of 1

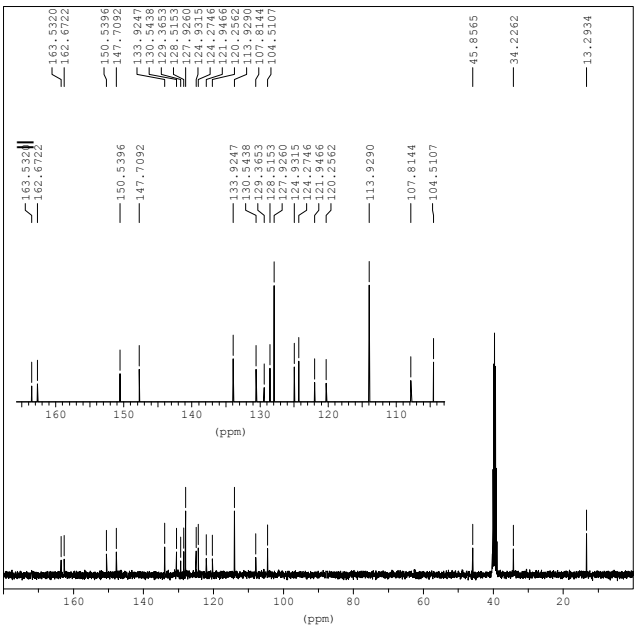
To a solution of **3** (1.43g, 2.76mmol) in dry Ethanol (50ml) was added NaOH (0.300g, 7.5mmol) in 1ml of water. The resulting solution was refluxed for 2hr. Upon cooling, yellow solid precipated afford **1** (.1.33g, 95%) as yellow solid. ^{1}H-NMR(400MHz,D_2O) δ, 1.09 (t, 3H, *J*=7.0Hz), 3.75-3.79 (m, 6H), 4.28 (d, 2H), 6.24(d, 2H, *J*=8.8Hz), 7.11 (t, 1H, *J*=7.6Hz), 7.22 (d, 2H, *J*=8.2Hz), 7.58 (d, 1H, *J*=8.8Hz), 7.69 (d, 1H, *J*=8.2Hz), 7.81 (d, 1H, *J*=7.6Hz), (bs, -NH). ^{13}C-NMR (400MHz, D_2O) δ, 179.06, 164.31, 163.28, 158.55, 149.69, 147.69, 133.50, 129.84, 128.70, 124.20, 122.93, 118.79, 117.80, 111.13, 105.52, 55.21, 45.69, 34.94, 11.99. IR (cm-^{1}): 3525.16, 3381.54, 2874.60, 1684.78, 1633.68, 1547.20, 1519.51, 1434.85, 1393.49, 1368.29, 1349.71, 1313.52, 1248.95, 1178.80, 1130.05, 1106.12, 1062.88, 978.56, 911.46, 876.70821.34 768.94, 756.11,

704.67, 587.15. MS (ES) Calcd for (M) *m/z* 505.12, Found 505.10.Anal. calcd for $C_{25}H_{21}N_3Na_2O_6.2H_2O$:C,55.46, H,4.65 ; N,7.76 . Found: C, 55.29; H, 4.23; N, 7.72

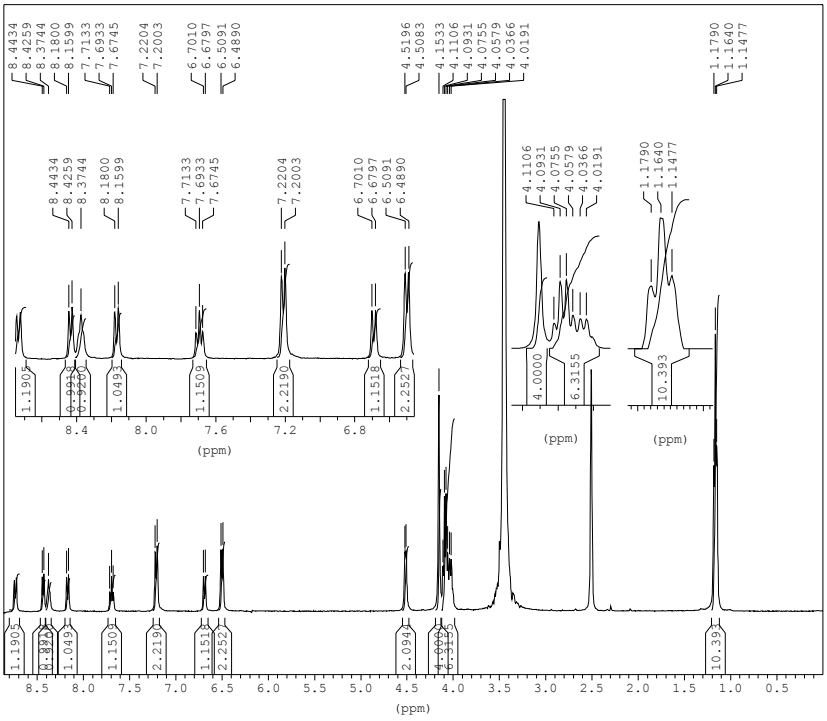
ESI 2. ^{1}H and ^{13}C NMR of 2 in DMSO-d$_6$

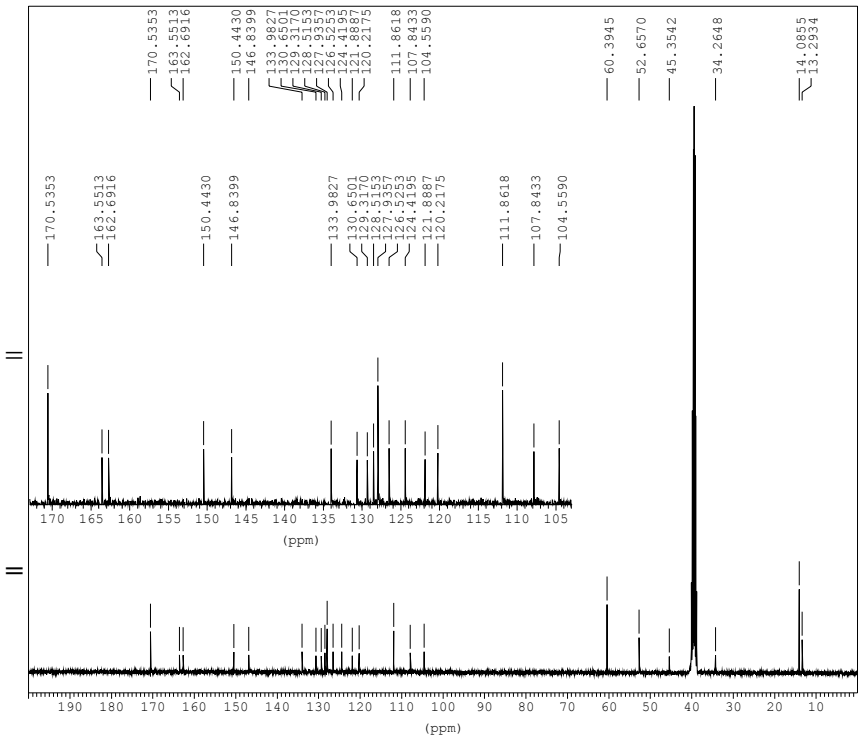


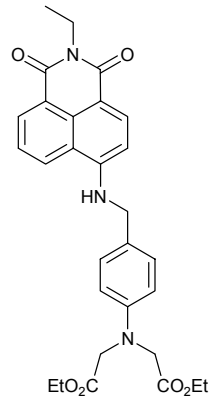




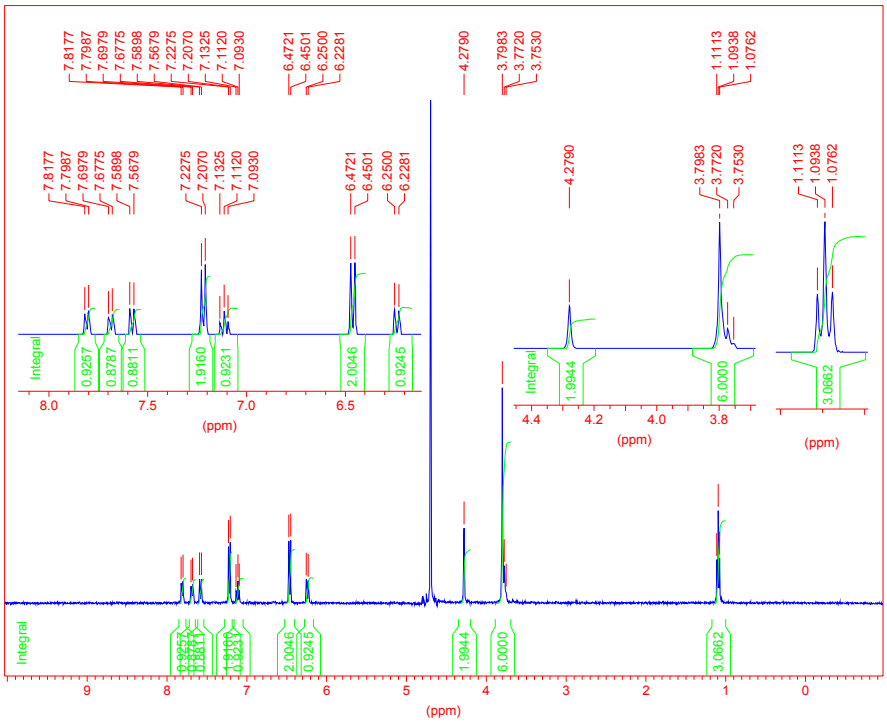
^{1}H and ^{13}C NMR of 3 in DMSO-d_6

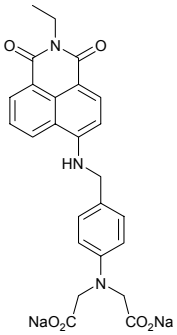


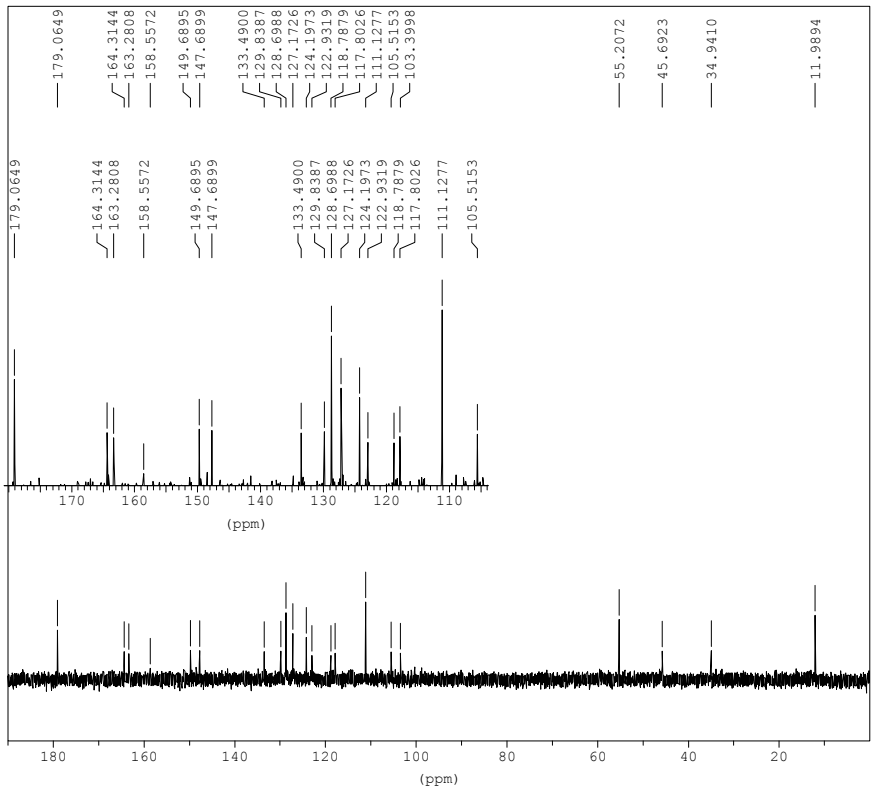




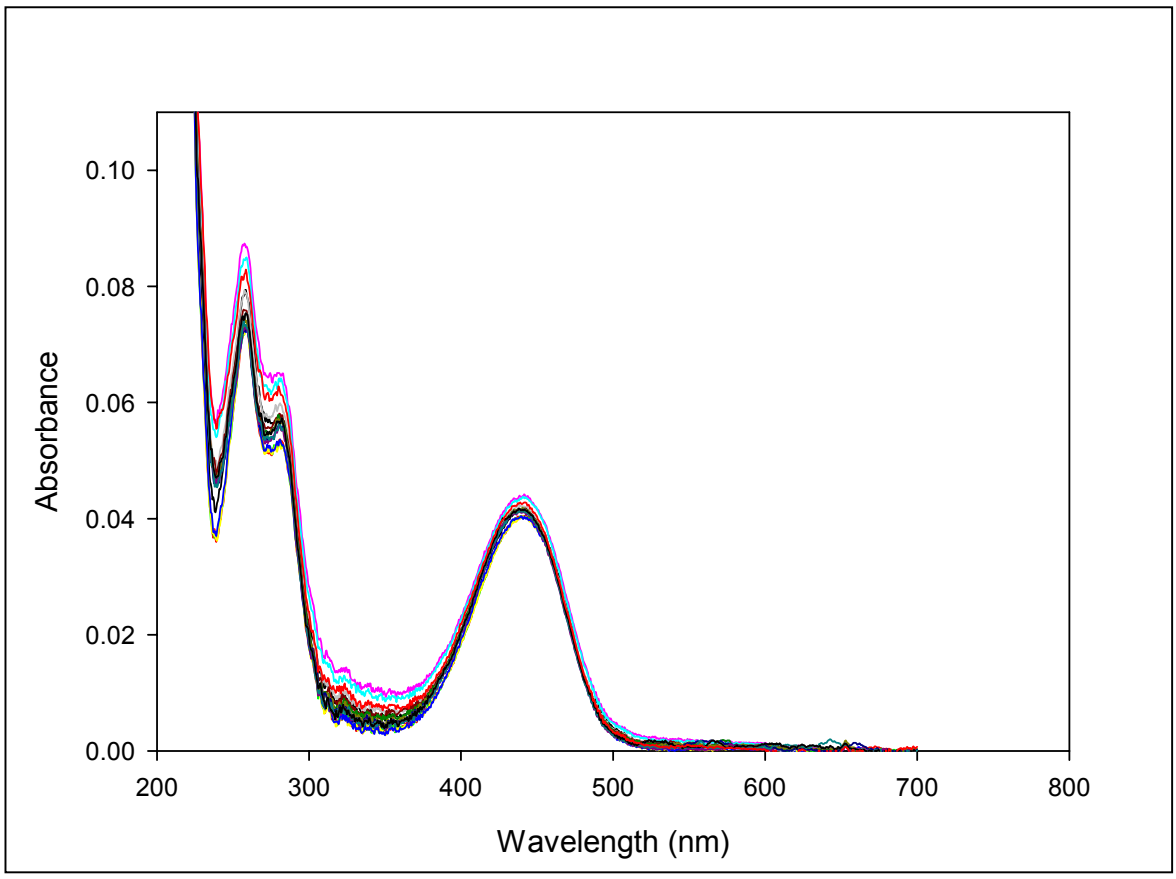
^{1}H and ^{13}C NMR of 1 in D_2O



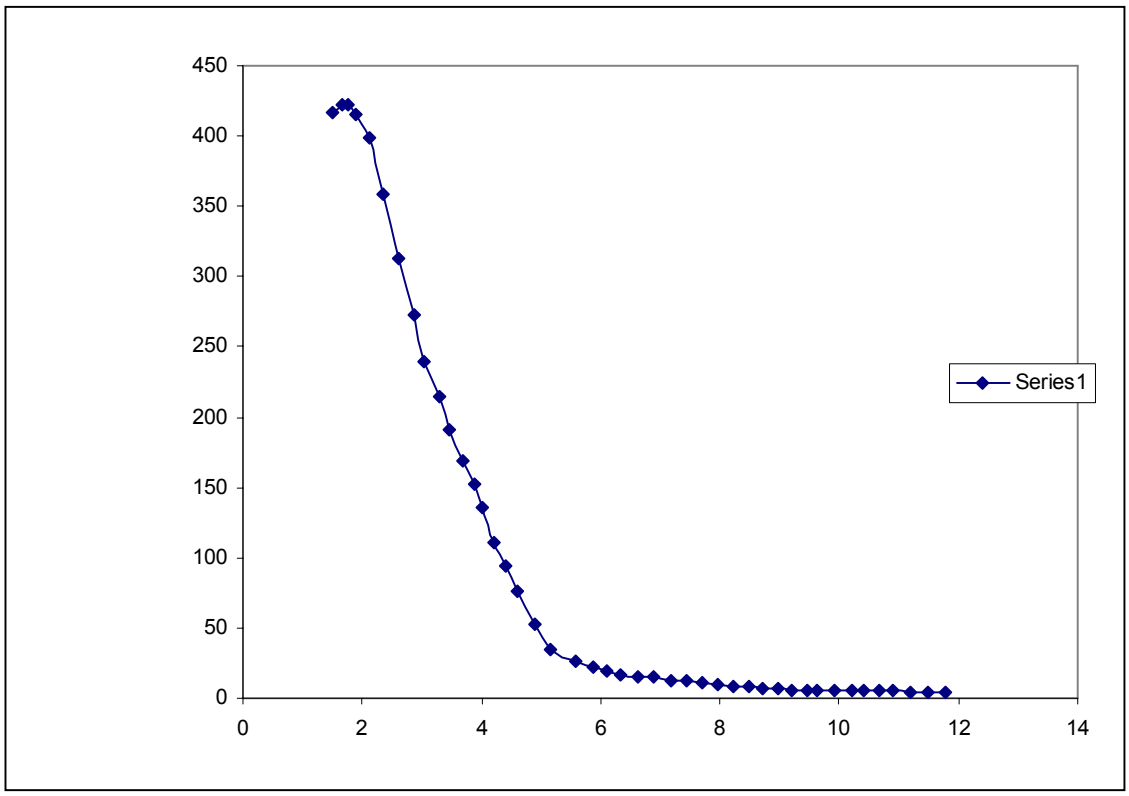




ESI 3. UV-Vis titration of 1 using Zn(II) (Uncorrected for dilution)



ESI 4. Fluorescence pH titration of 1 showing that the emission is only 'switched on' at lot pH.



ESI **5. Titration curves for Cd(II) (left) and Hg(II) (right) (scale is the same as in Figure 3 in paper) and bar chart for 1 with different metal ions (Zn(II), Cd(II), Hg(II), Ca(II), Mg(II)) in the absence of EGTA.**