Supporting Information

The Switching of Rhenium(I) Complex from Turn-off to Turn-on Sensor System through Protein Binding

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Figure S1. ^{1}HNMR Spectrum of py-3-CO-ala

Figure S2. ^{1}H NMR spectrum of complex **1a**

Figure S3. ^{1}H NMR spectrum of complex **1b**

Figure S4. FT-IR Spectrum of (py-3-CO-ala)

Figure S5. FT-IR Spectra of **1a** (A) and **1b** (B)

Figure S6. Mass spectrum of complex **1a**

Figure S7. Mass spectrum of complex **1b**

Figure S8. Absorption spectra of complex **1a** in the presence of TBACl (A) and TBAClO$_4$ (B). [**1a**] = 20 µM, [Cl$^-$] = 1 → 320 µM.

Figure S9. Absorption (A) and emission (B) spectra of complex **1a** in the presence of TBABr. [**1a**] = 20 µM, [Br$^-$] = 1 → 320 µM. Ex. Maximum: 345 nm.

Figure S10. Emission spectra of complex **1a** in the presence of TBAF (A) and TBACN (B). [**1a**] = 20 µM, [anions] = 1 → 320 µM. Ex. Maximum: 345 nm.

Figure S11. Absorption (A) and emission (B) spectra of complex **1a** in the presence of TBAI. [**1a**] = 20 µM, [I$^-$] = 1 → 320 µM. Ex. Maximum: 345 nm.

Figure S12. Absorption spectra of complex **1b** in the presence of TBACl (A) and TBAClO$_4$ (B). [**1a**] = 20 µM, [anions] = 1 → 320 µM. Ex. Maximum: 365 nm.

Figure 13. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBABr. [**1a**] = 20 µM, [Br$^-$] = 1 → 320 µM.. Ex. Maximum : 365 nm.

Figure S14. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBAF. [**1a**] = 20 µM, [F$^-$] = 1 → 320 µM. Ex. Maximum: 365 nm.

Figure S15. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBACN. [**1a**] = 20 µM, [CN$^-$] = 1 $\rightarrow$ 320 µM. Ex. Maximum:365 nm.

Figure S16. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBAI. [**1b**] = 20 µM, [I$^-$] = 1 $\rightarrow$ 320 µM. Ex. Maximum:365 nm.

NMR spectrum for ligand

One triplet at 1.1ppm which is assigned to –CH₃ (m) and one doublet at 1.3 ppm which is assigned to –CH₃ (j). Two quatrets at 4.0 and 4.5 ppm which are assigned to –CH₂-(l) and –CH-(i) respectively. One singlet at 8.9 ppm may be due to the presence of –NH (h) proton. The peaks which are obtained at aromatic region (7.0 - 8.5) ppm are assigned to protons in the pyridine ring. Similarly, the complexes **1a** and **1b** were also confirmed by H¹ NMR spectra.
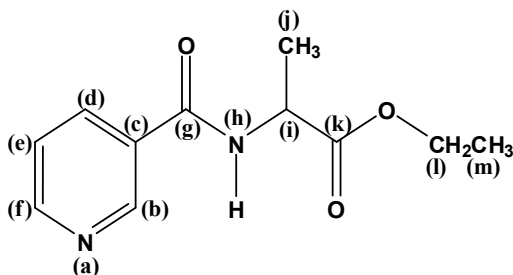
Ethyl-2-(nicotinamido)propanoate (py-3-CO-ala)
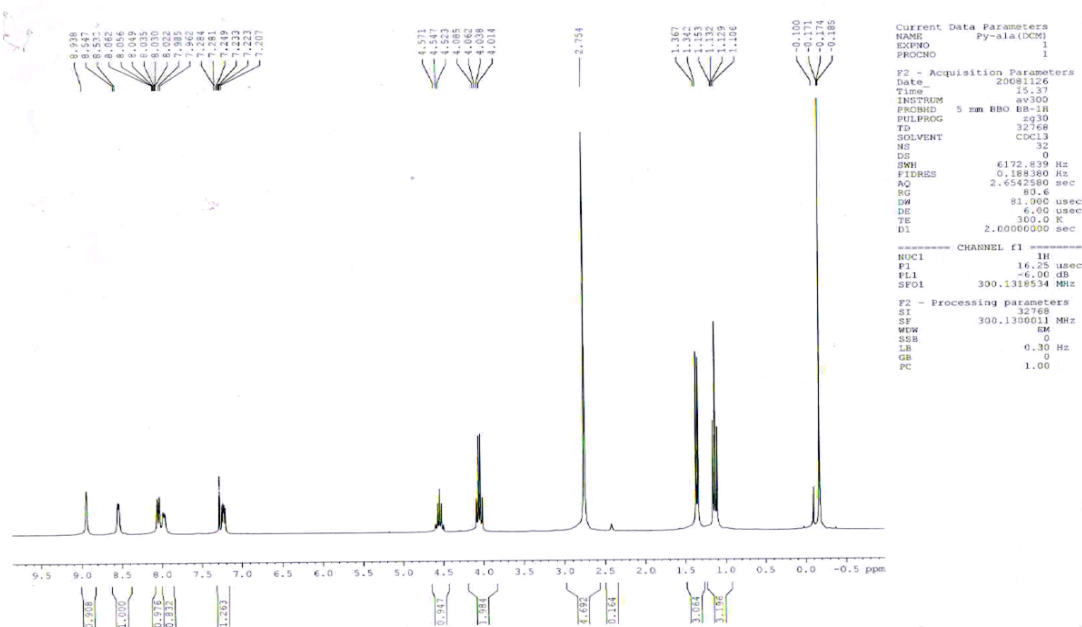
Figure S1. ¹HNMR Spectrum of py-3-CO-ala

Synthesis of Re(I) complexes

The precursor [Re(CO)$_3$(bpy)Br] and [Re(CO)$_3$(phen)Br] was prepared from [Re(CO)$_5$Br] by the general procedure described by Meyer et al [1].

[Re(bpy)(CO)$_3$(py-3-CO-NH-ala)]PF$_6$ (1a): A Sample of 0.107 g (0.211 mmol) [Re(CO)$_3$(bpy)Br] and 0.081 g (0.315 mmol) of AgCF$_3$SO$_3$ were refluxed in 25 ml of CH$_3$CN for three hours under nitrogen atmosphere. After AgBr filtration, 0.043 g (0.197mmol) of py-3-CO-NH-ala was added and refluxed for overnight in nitrogen atmosphere. Then the mixture was evaporated to dryness. The resultant residue was dissolved in small amount of acetone and the saturated solution of NH$_4$PF$_6$ was added. The pure [Re(CO)$_3$(bpy)(py-3-CO-NH-ala)]PF$_6$ was precipitated and dried. Yield = 70%. ^{1}H NMR (300 MHz, CDCl$_3$, RT, TMS): δ 9.31 (s, 1H, Hb of py), 9.09 (s, 1H, NH of py-CO-ala), 9.03 (d, 1H, H3 of bpy), 8.64 (d, 1H, H3' of bpy), 8.56-8.59 (m, 2H, Hd and Hf of py), 8.49 (d, 1H, H4 of bpy), 8.35 (t, 1H, H6 of bpy), 8.22 (t, 1H, H6' of bpy), 7.92 (t, 1H, H5 of bpy), 7.76 (d, 1H, H4' of bpy), 7.67 (m, 1H, He of py), 7.49 (t, 1H, H5' of bpy), 4.50 (q, 1H, Hi of py-3-CO-ala), 4.15 (q, 1H, Hl of py-3-CO-ala), 1.47 (d, 3H, Hj of py-3-CO-ala), 1.28 (t, 3H, Hm of py-3-CO-ala). IR (KBR) ν / cm^{-1}: 3410, 2034, 1911, 1673. ESI-MS *m/z*: 649.11 for [Re(bpy)(CO)$_3$(py-3-CO-ala)]$^+$, 426.97 for [Re(bpy)(CO)$_3$]$^+$. Anal. Calcd. For. C$_{24}$H$_{22}$N$_4$O$_6$RePF$_6$ (M. Wt = 792.55): C = 36.36, H = 2.77, N = 7.06. Found = C = 36.34, H = 2.78, N = 7.05.

[Re(CO)$_3$(phen)((py-3-CO-NH-ala)]PF$_6$ (1b): 1b was synthesized using the same procedure, instead of bpy, here phen was used. Yield = 67 %. ^{1}H NMR (300 MHz,

CDCl$_3$, RT, TMS): δ 9.47-9.58 (m, 2H, H2 and H9 of phen), 8.76 (d, 2H, H4 and H7 of phen), 8.65 (s, 1H, NH of py-CO-ala), 8.35 (d, 1H, Hb of py), 8.08-8.25 (m, 4H, H3, H5, H6, H8 of phen), 7.30-7.35 (m, 2H, Hd and Hf of py), 7.04 (d, 1H, He of py), 4.50 (q, 1H, Hi of py-3CO-ala), 4.16 (q, 2H, Hl of py-3-CO-ala), 1.42 (d, 3H, Hj of py-3-CO-ala), 1.24 (t, 3H, Hm of py-3-CO-ala). IR (KBR) ν / cm^{-1}: 3420, 2034, 1917, 1653. ESI-MS *m / z* : 673.11 for [Re(phen)(CO)$_3$(py-3-CO-ala)]$^+$, 450.97 for [Re(phen)(CO)$_3$]$^+$. Anal. Calcd. For. C$_{26}$H$_{22}$N$_4$O$_6$RePF$_6$ (M. Wt = 817.31): C = 38.20, H = 2.69, N = 6.85. Found = C = 37.12, H = 2.53, N = 6.54.
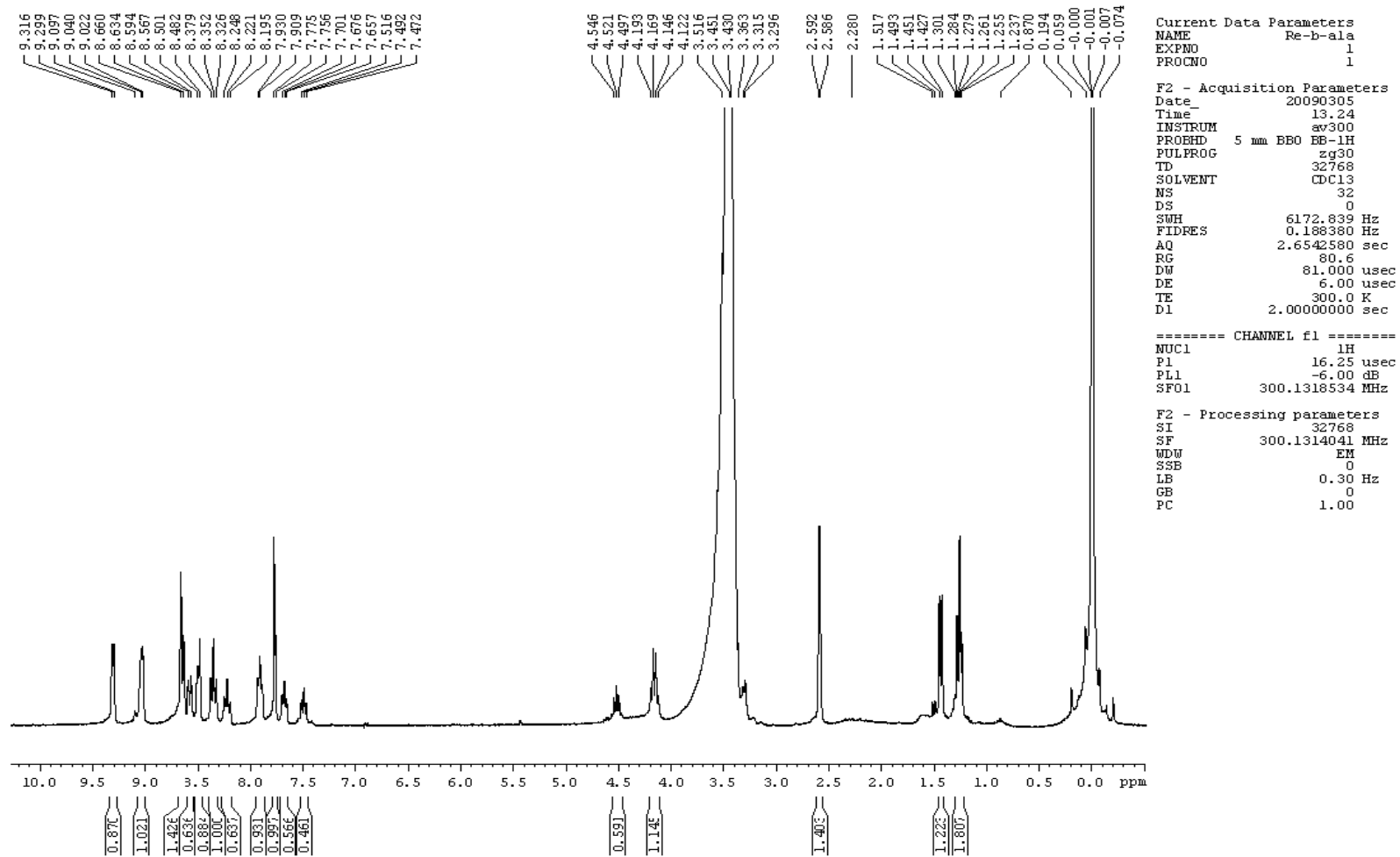
Figure S2. ^{1}H NMR spectrum of complex **1a**
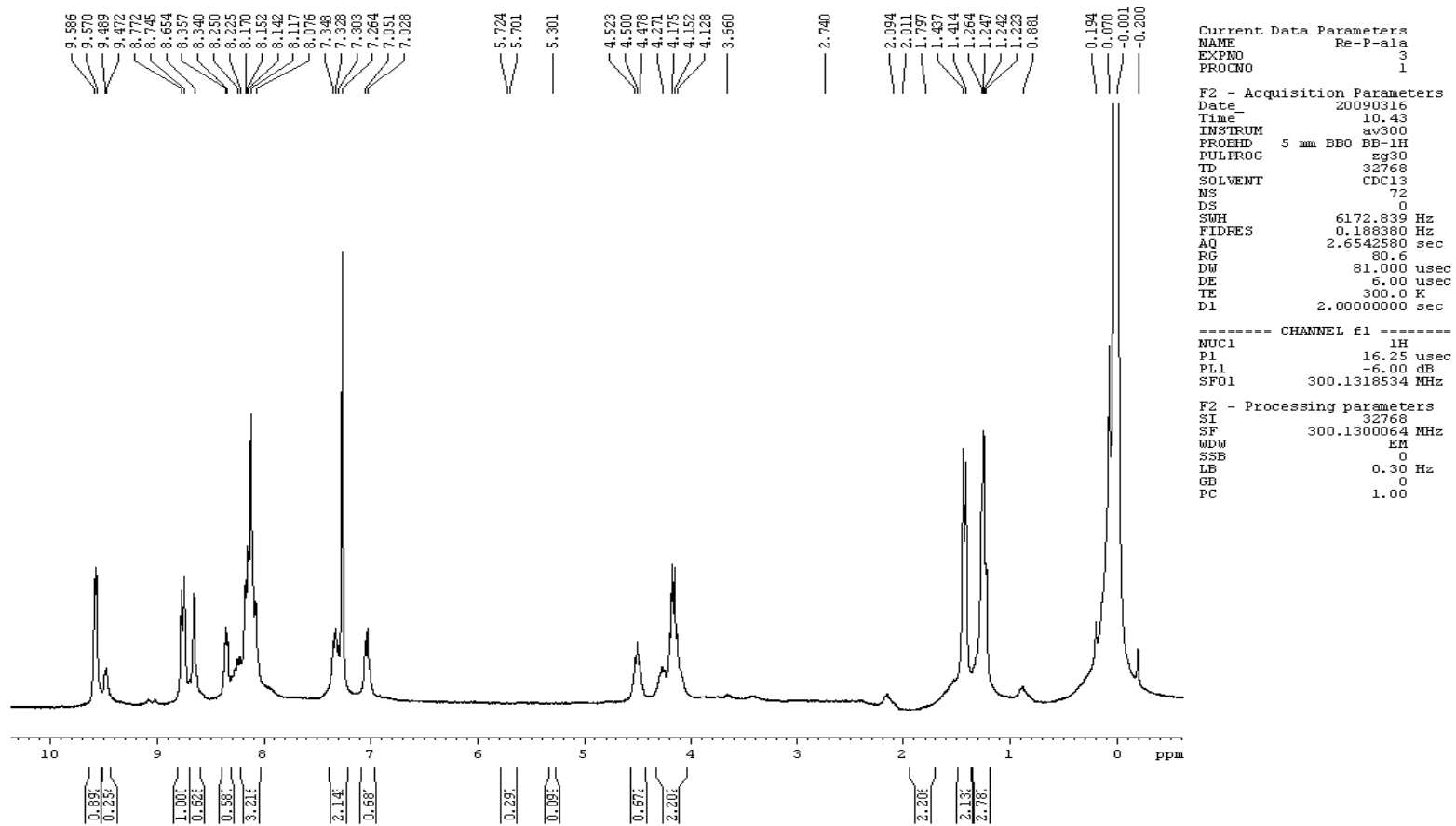
Figure S3. ^{1}H NMR spectrum of complex **1b**

FT-IR spectra
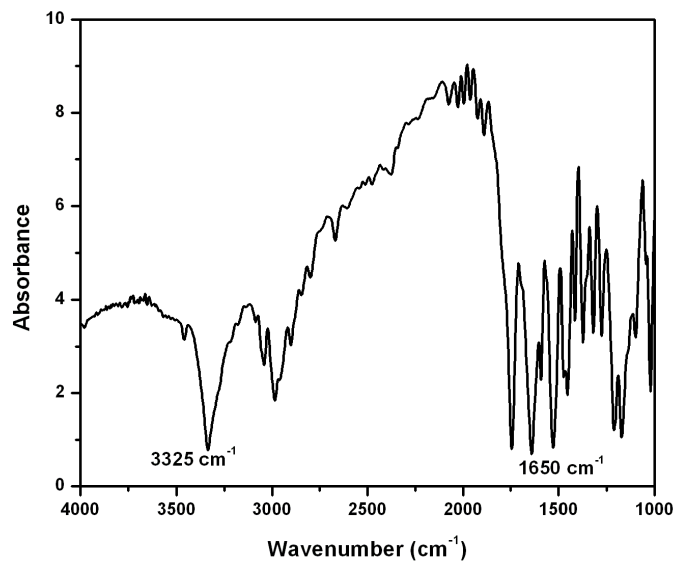
Figure S4. FT-IR Spectrum of (py-3-CO-ala)

A   B

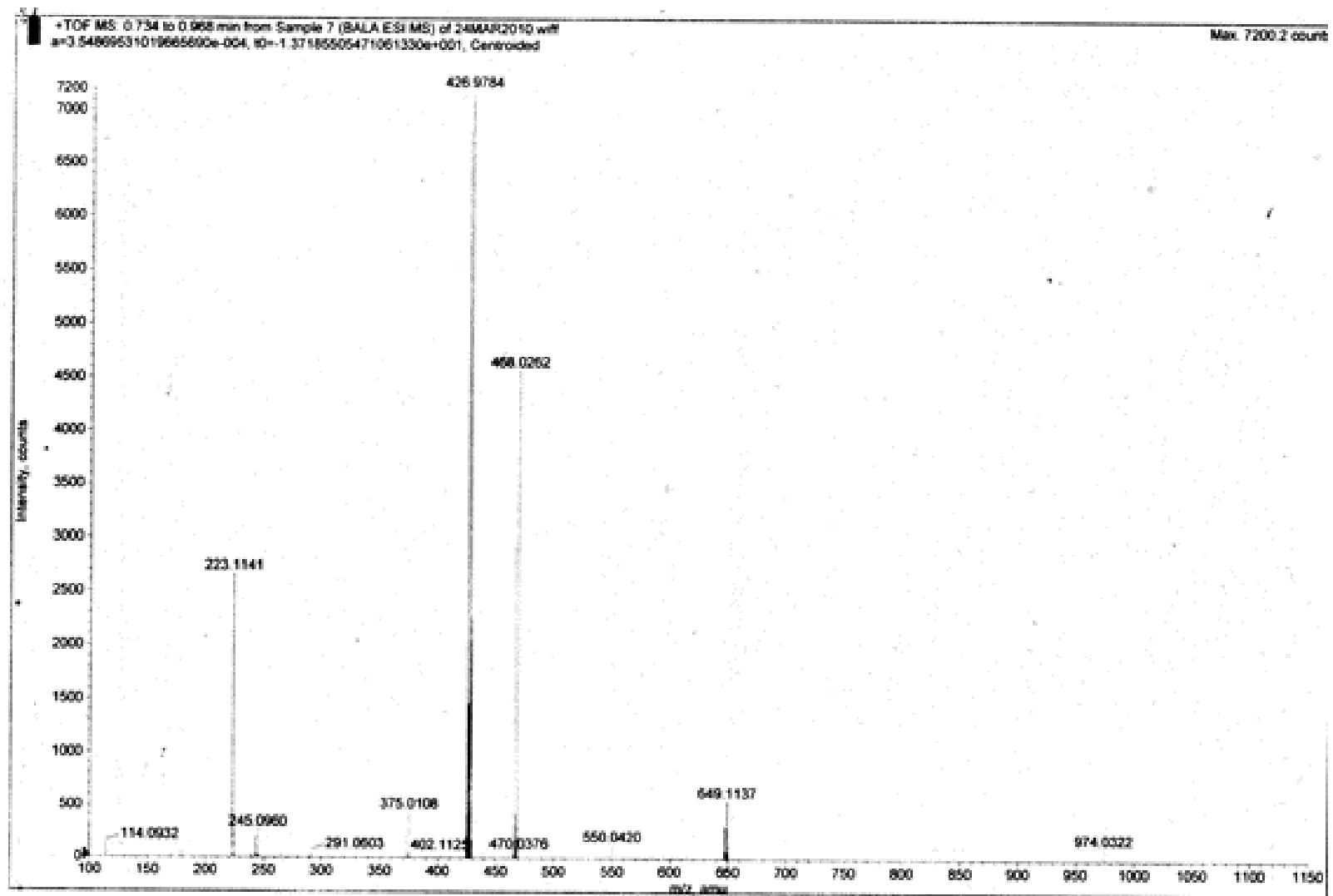Figure S5. FT-IR Spectra of **1a** (A) and **1b** (B)
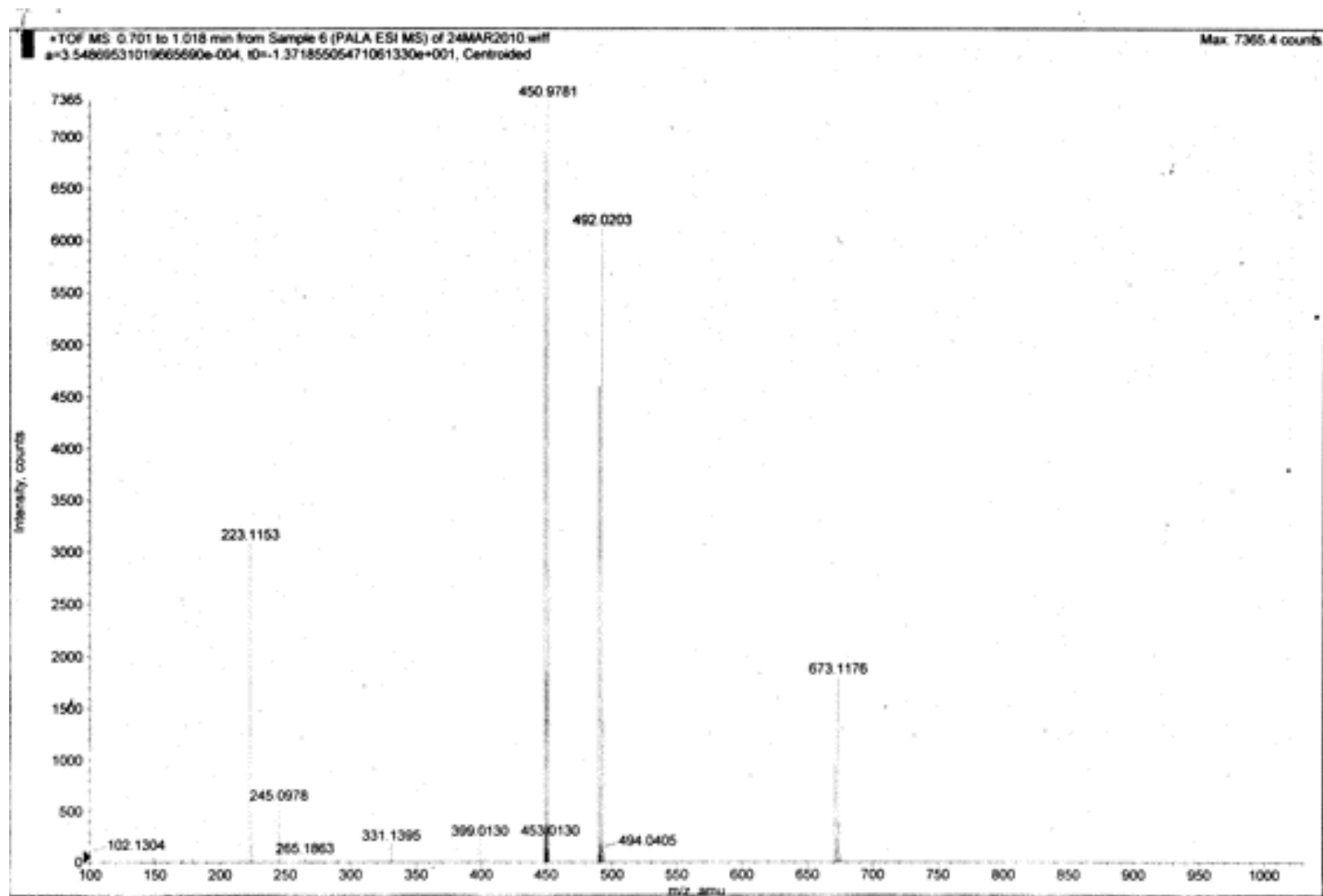
Figure S6. Mass spectrum of complex **1a**
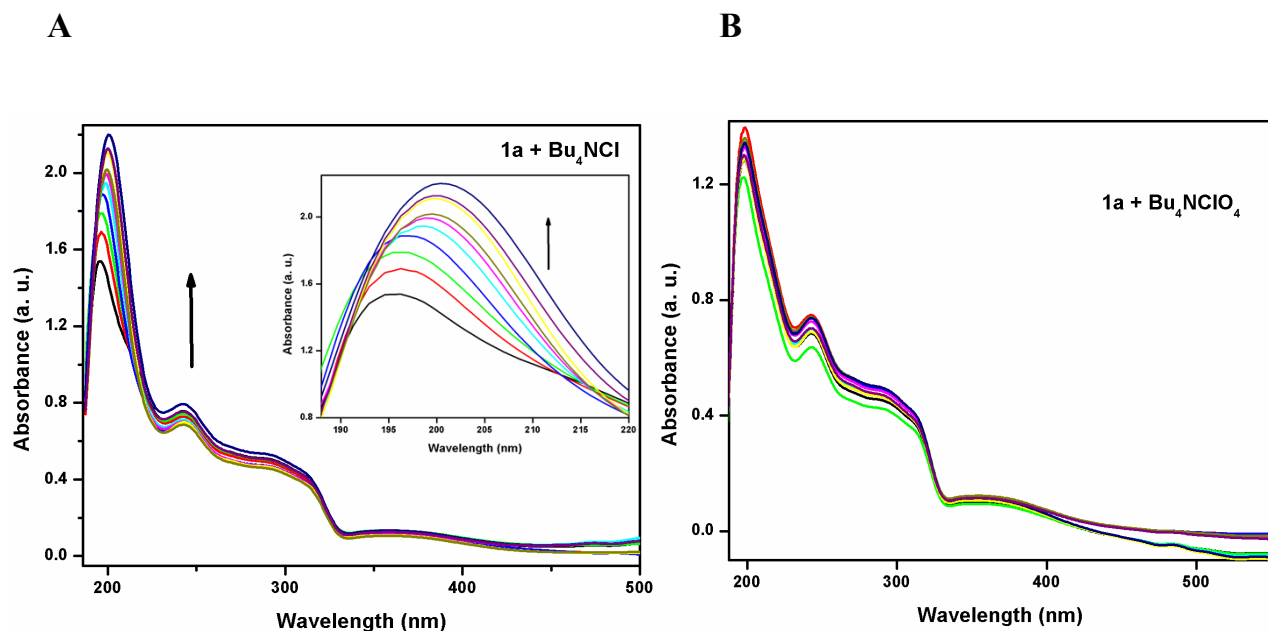
Figure S7. Mass spectrum of complex **1b**

Figure S8. Absorption spectra of complex **1a** in the presence of TBACl (A) and TBAClO$_4$ (B). [**1a**] = 20 μM, [Cl$^-$] = 1 → 320 μM.

Figure S9. Absorption (A) and emission (B) spectra of complex **1a** in the presence of TBABr. [**1a**] = 20 μM, [Br$^-$] = 1 → 320 μM. Ex. Maximum: 345 nm.
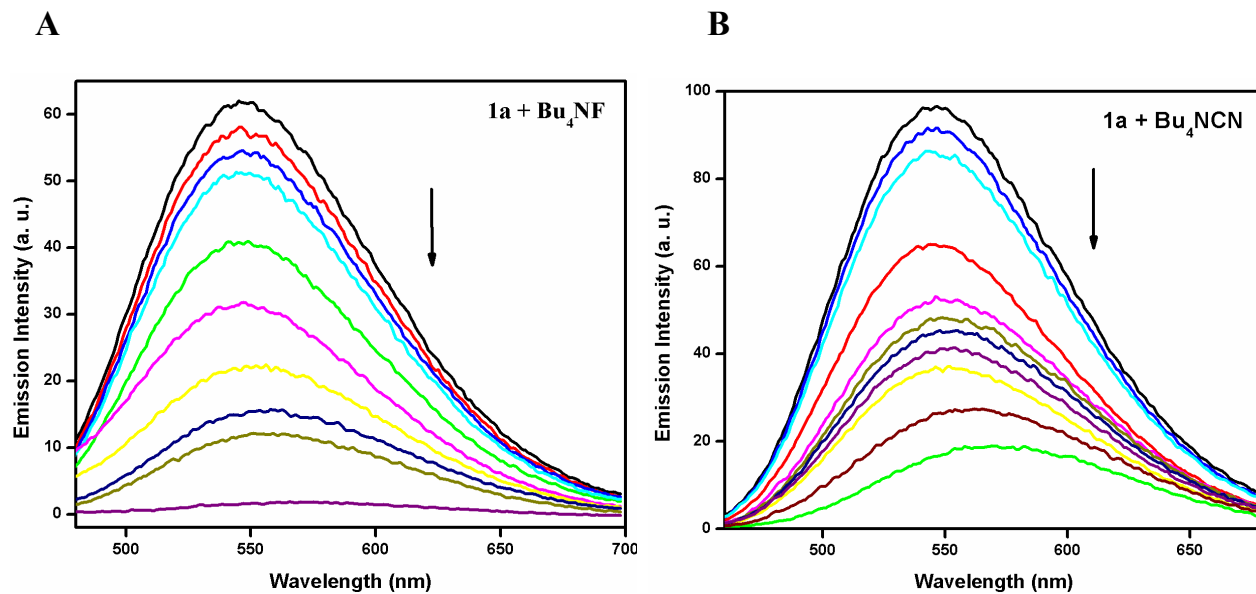
Figure S10. Emission spectra of complex **1a** in the presence of TBAF (A) and TBACN (B). [**1a**] = 20 μM, [anions] = 1 → 320 μM. Ex. Maximum: 345 nm.

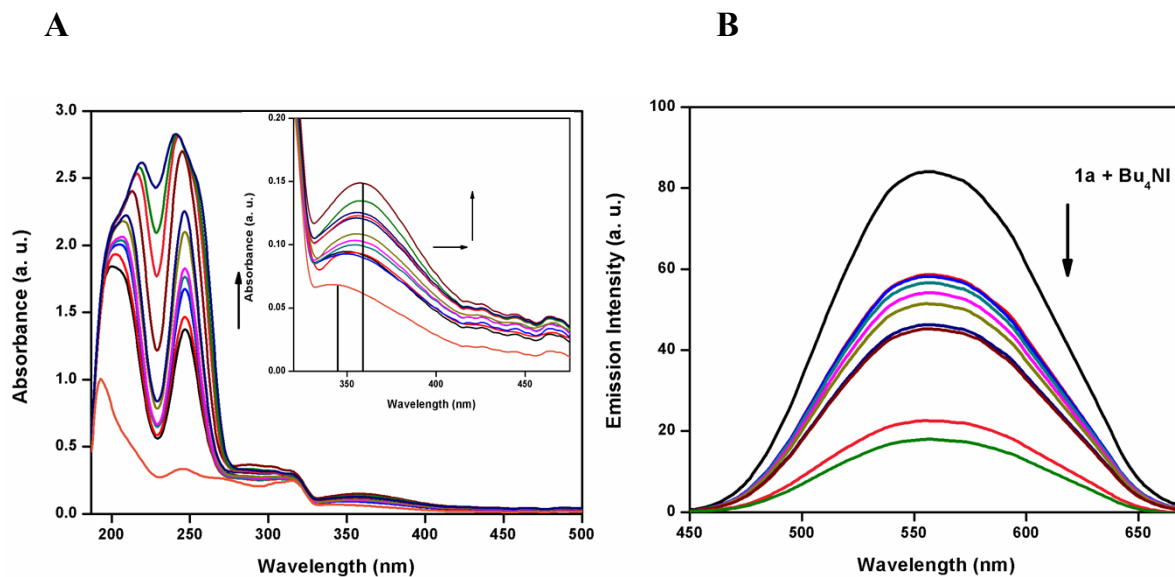Figure S11. Absorption (A) and emission (B) spectra of complex **1a** in the presence of TBAI. [**1a**] = 20 μM, [I⁻] = 1 → 320 μM. Ex. Maximum: 345 nm.

A

B
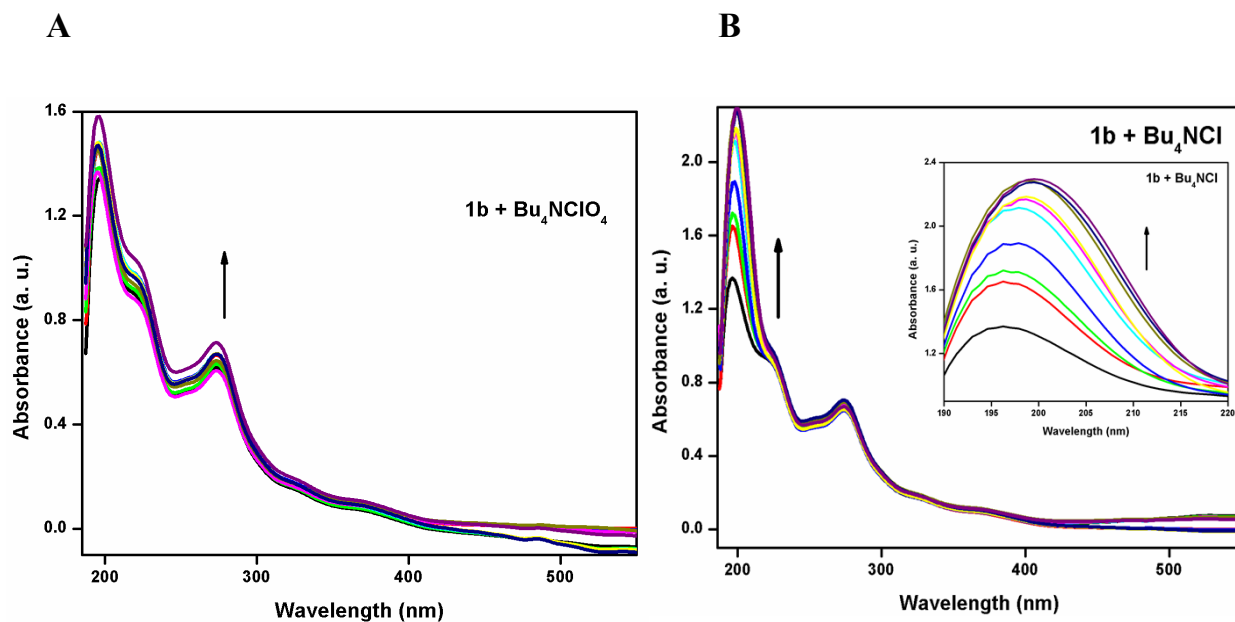

Figure S12. Absorption spectra of complex **1b** in the presence of TBACl O_4 (A) and

TBACl (B). [**1b**] = 20 μM, [anions] = 1 → 320 μM. Ex. Maximum: 365 nm.
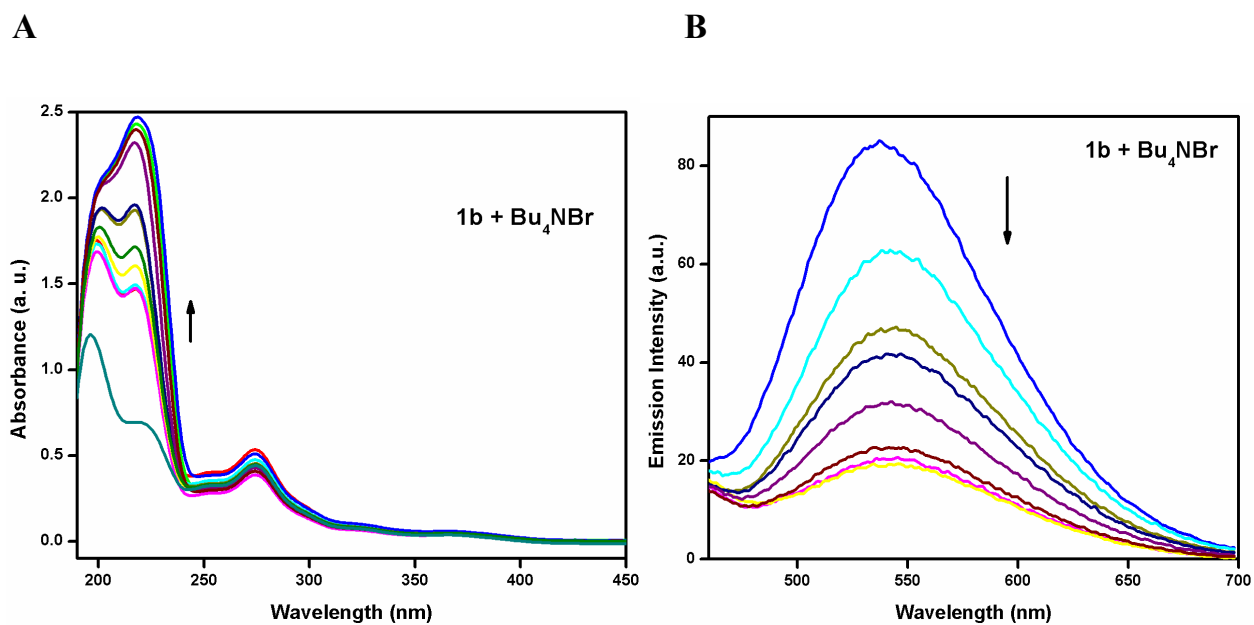
A

B

Figure 13. Absorption (A) and emission (B) spectra of complex **1b** in the presence of

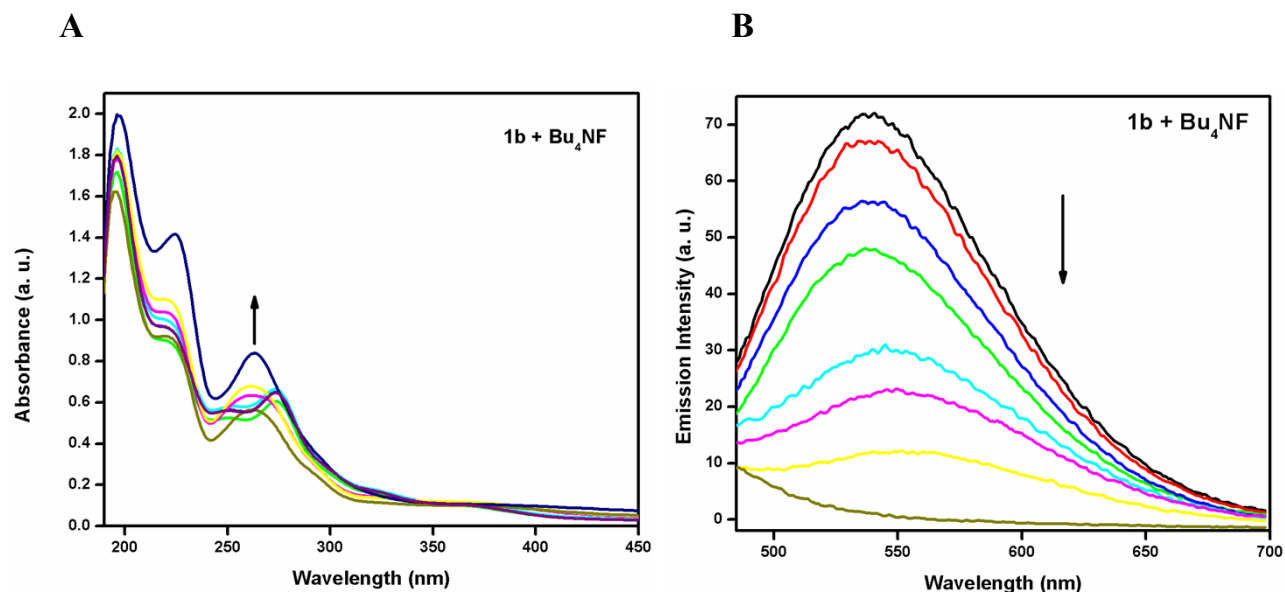TBABr. [**1b**] = 20 μM, [Br⁻] = 1 → 320 μM.. Ex. Maximum : 365 nm.

A

B

Figure S14. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBAF. [**1b**] = 20 μM, [F⁻] = 1 → 320 μM. Ex. Maximum: 365 nm.
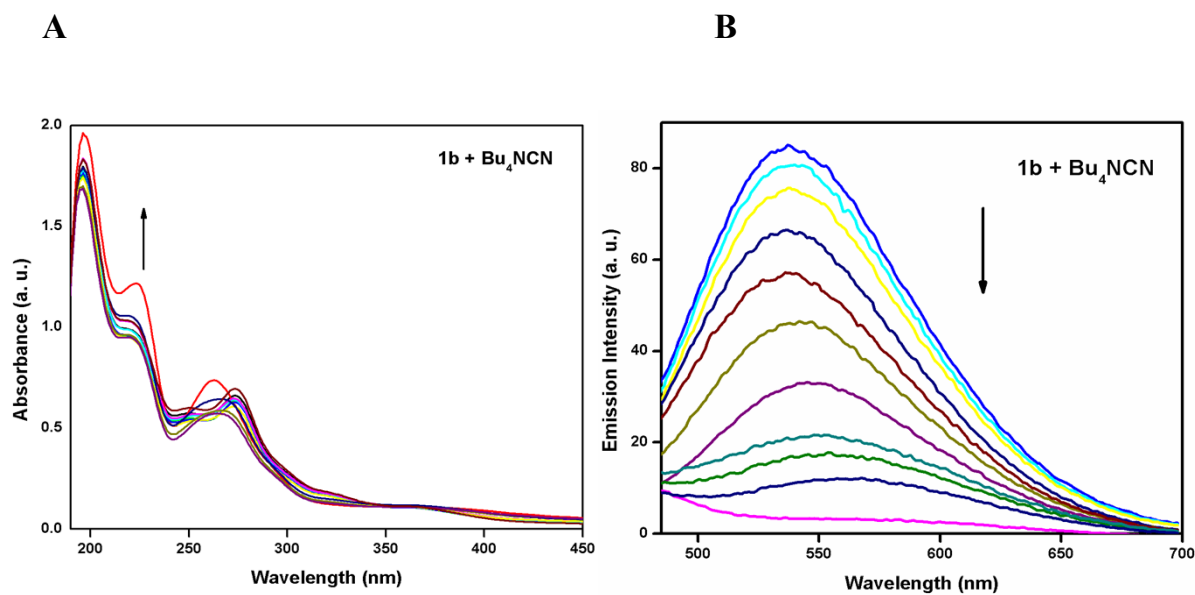
A

B

Figure S15. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBACN. [**1b**] = 20 μM, [CN⁻] = 1 → 320 μM. Ex. Maximum:365 nm.
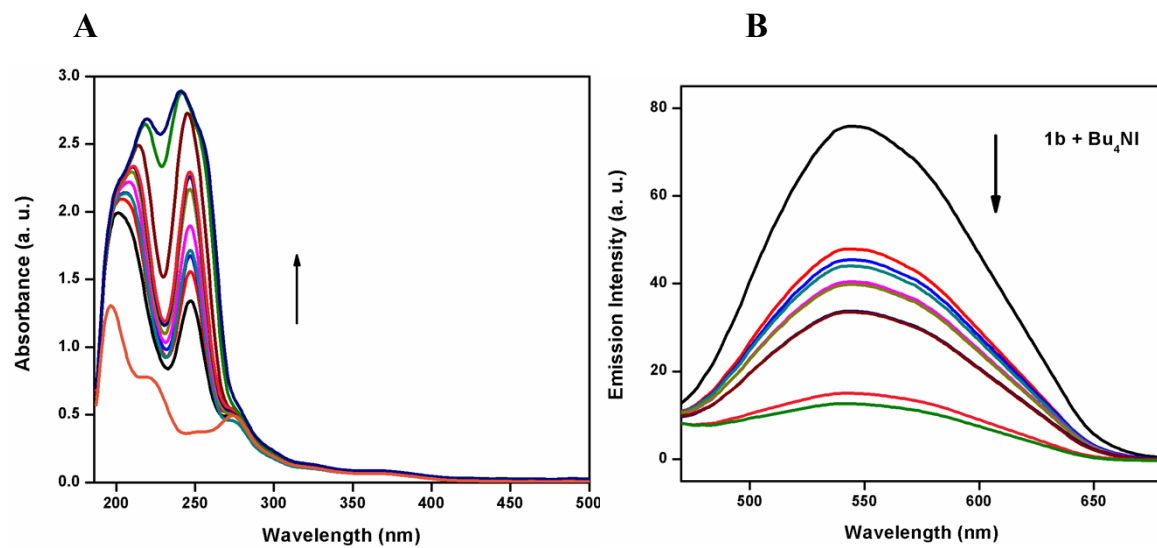
Figure S16. Absorption (A) and emission (B) spectra of complex **1b** in the presence of TBAI. [**1b**] = 20 μM, [I⁻] = 1 → 320 μM. Ex. Maximum: 365 nm.

Reference

[1] J. V. Caspar, T. J. Meyer, *J. Phys. Chem.* **1983**, *87*, 952 – 957.