Effect of n-alkyl substitution on Cu(II)-selective chemosensing of Rhodamine-B derivatives

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Electronic Supplementary Information

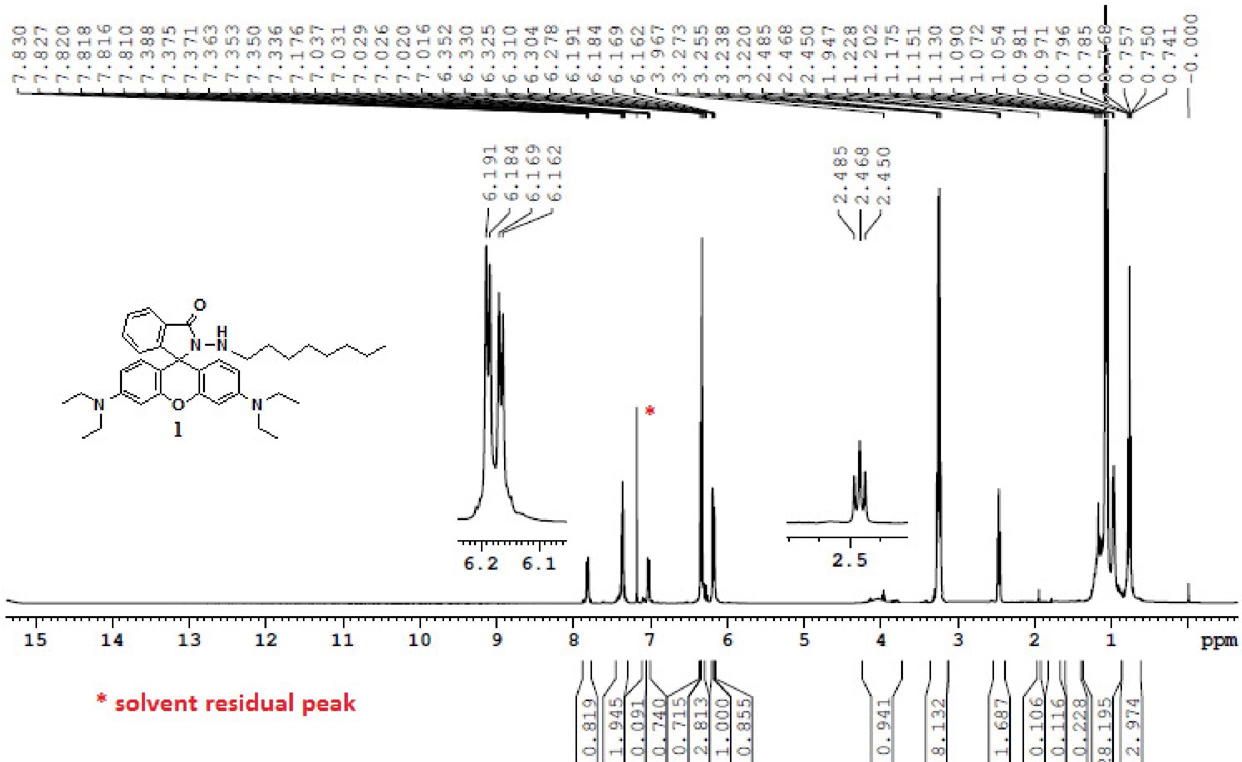


Fig. S1: [1]H-NMR spectrum of compound **1** (in $CDCl_3$)

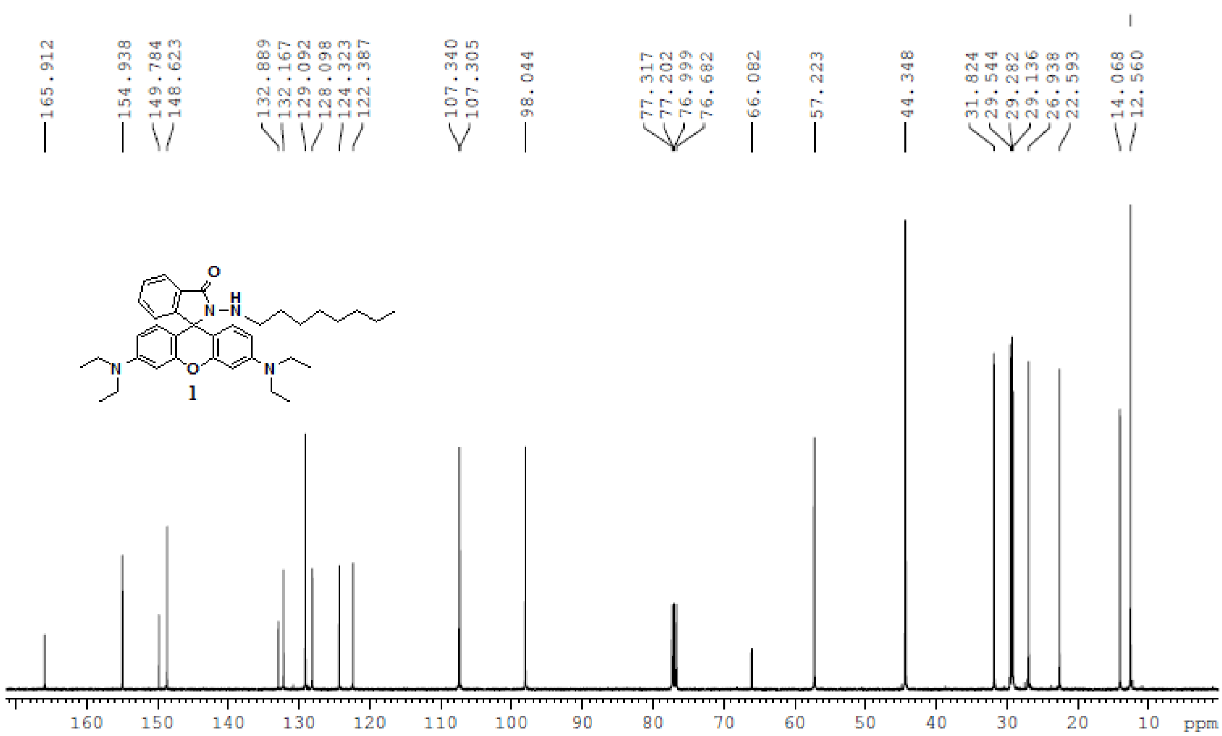


Fig. S2: [13]C-NMR spectrum of compound **1** (in $CDCl_3$).

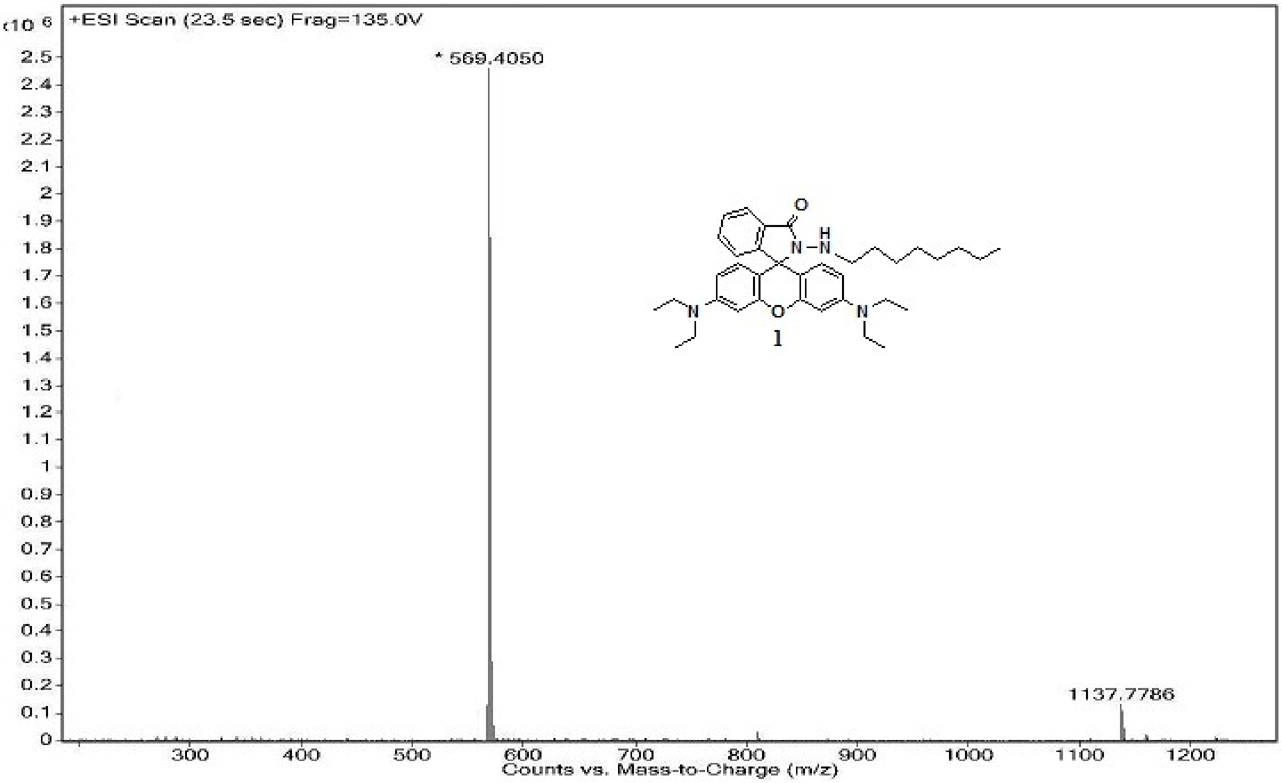


Fig. S3: MS (ESI) spectrum of compound **1**.

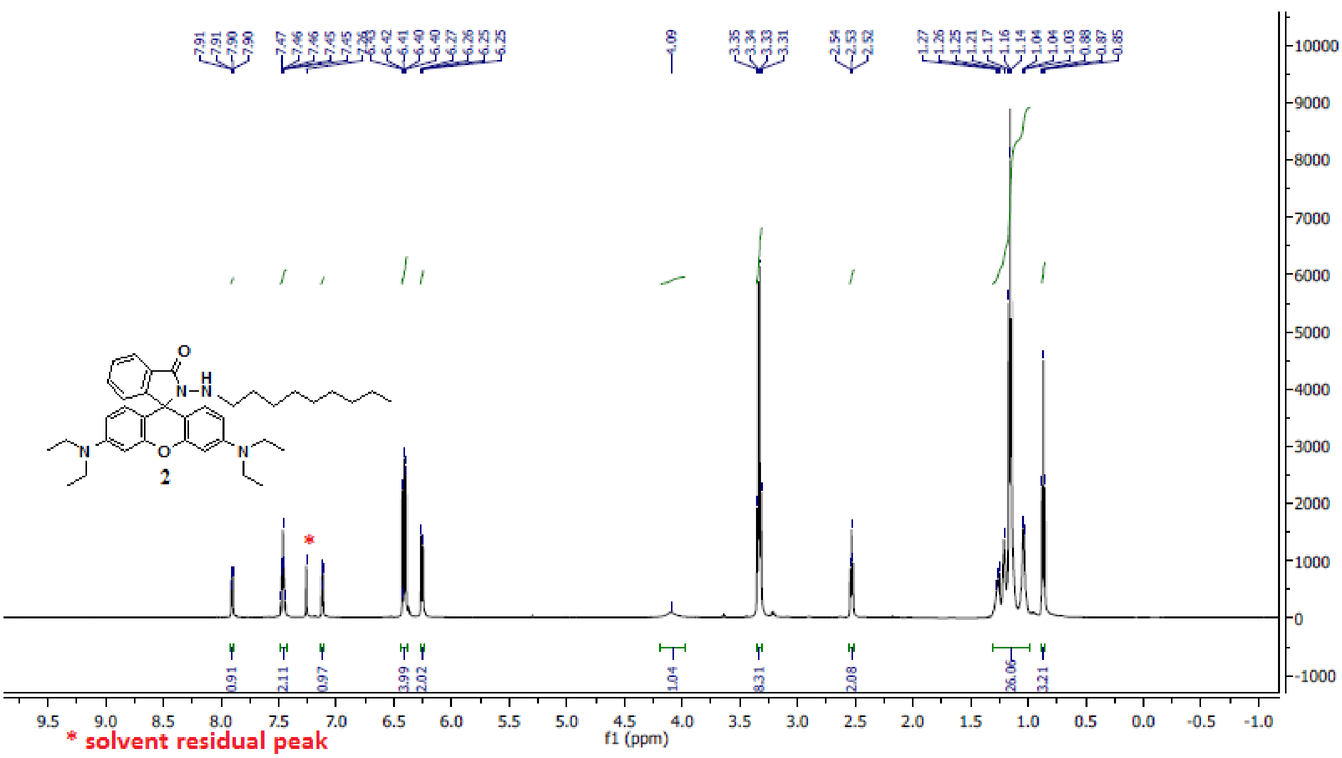


Fig. S4: ^{1}H-NMR spectrum of compound **2** (in $CDCl_3$)

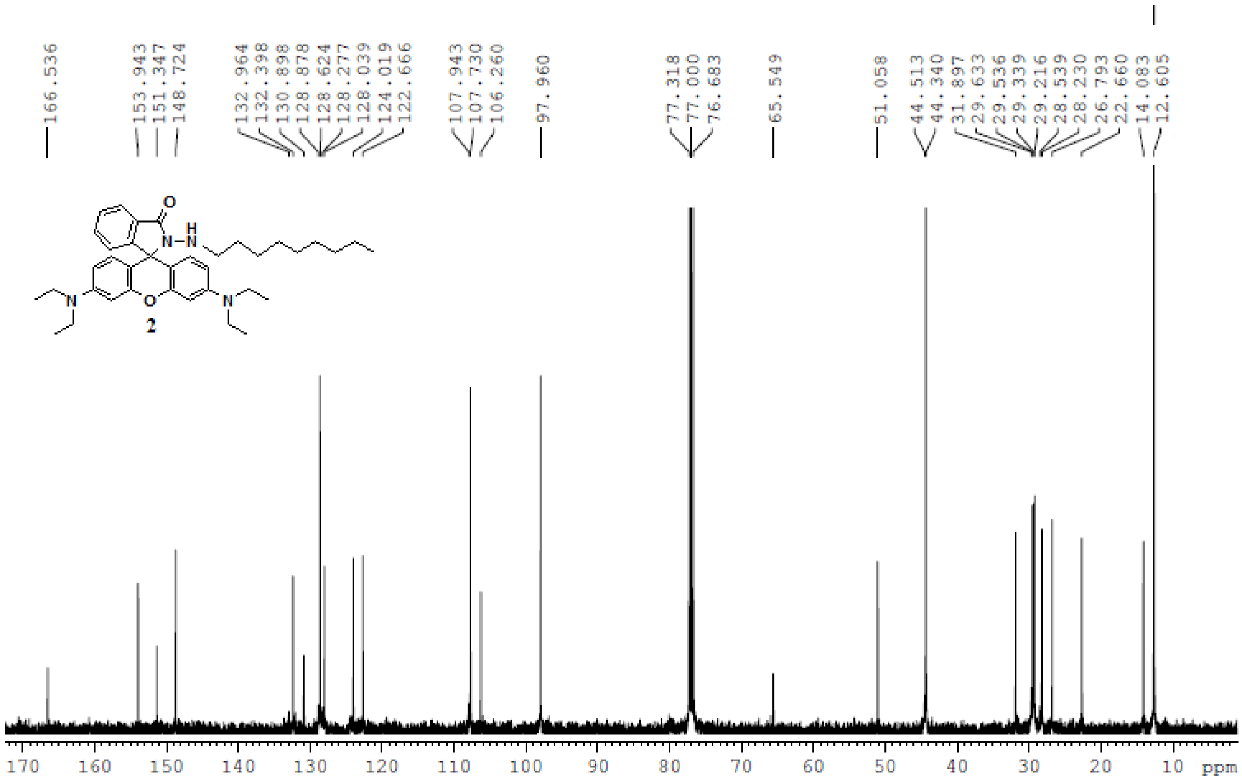


Fig. S5: ^{13}C-NMR spectrum of compound **2** (in $CDCl_3$).

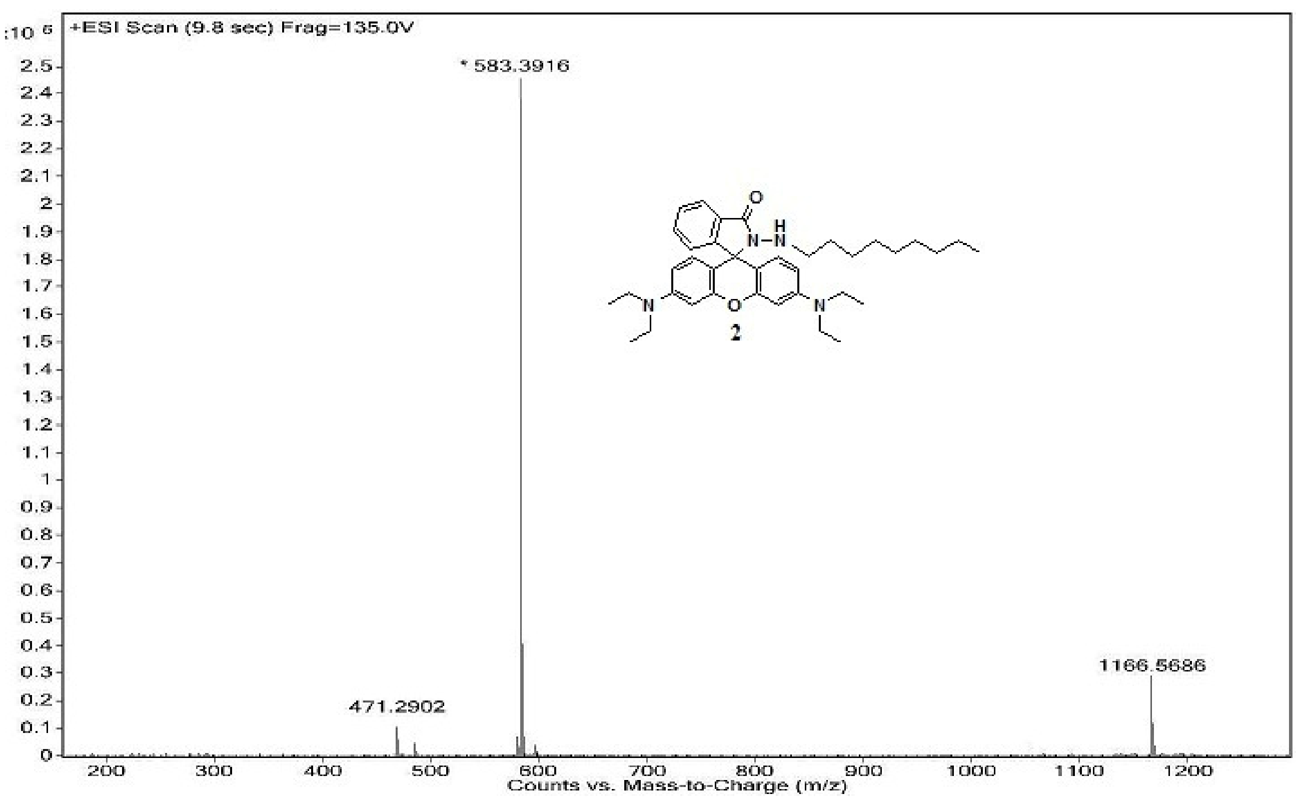


Fig. S6: MS (ESI) spectrum of compound **2**.

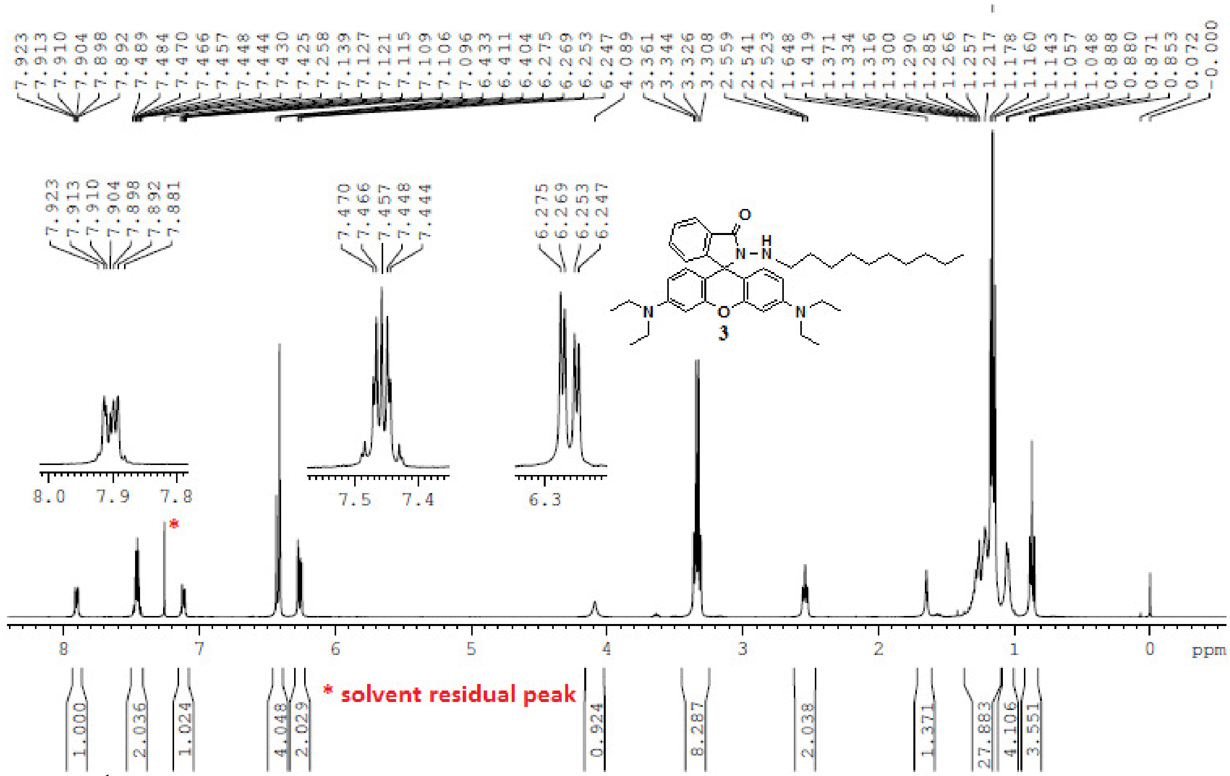


Fig. S7: ^{1}H-NMR spectrum of compound **3** (in $CDCl_3$).

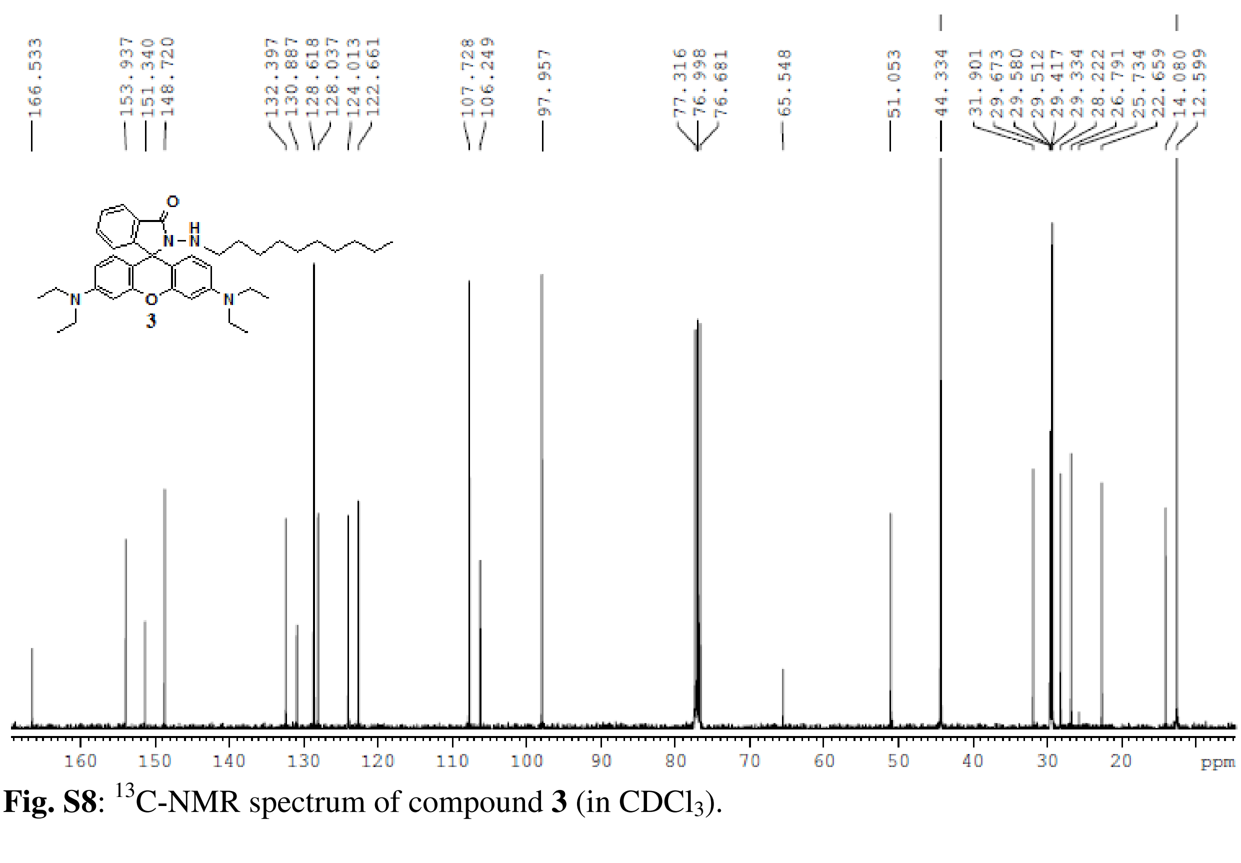


Fig. S8: ^{13}C-NMR spectrum of compound **3** (in $CDCl_3$).

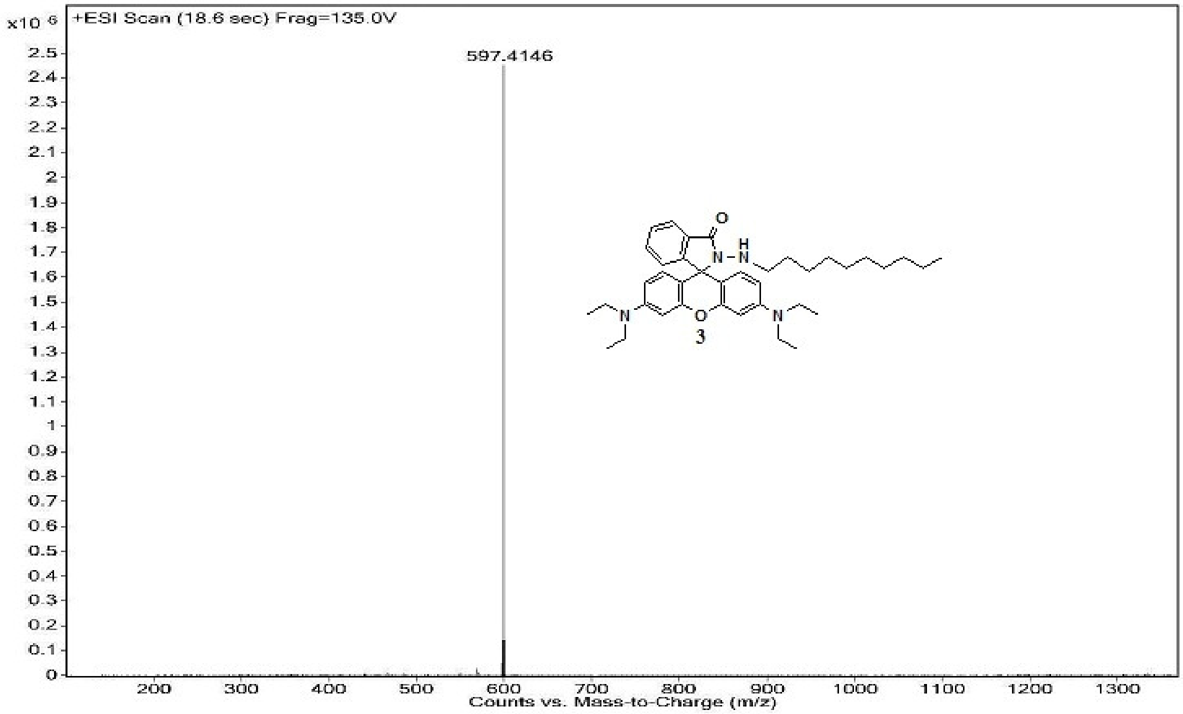


Fig. S9: MS (ESI) spectrum of compound **3**.

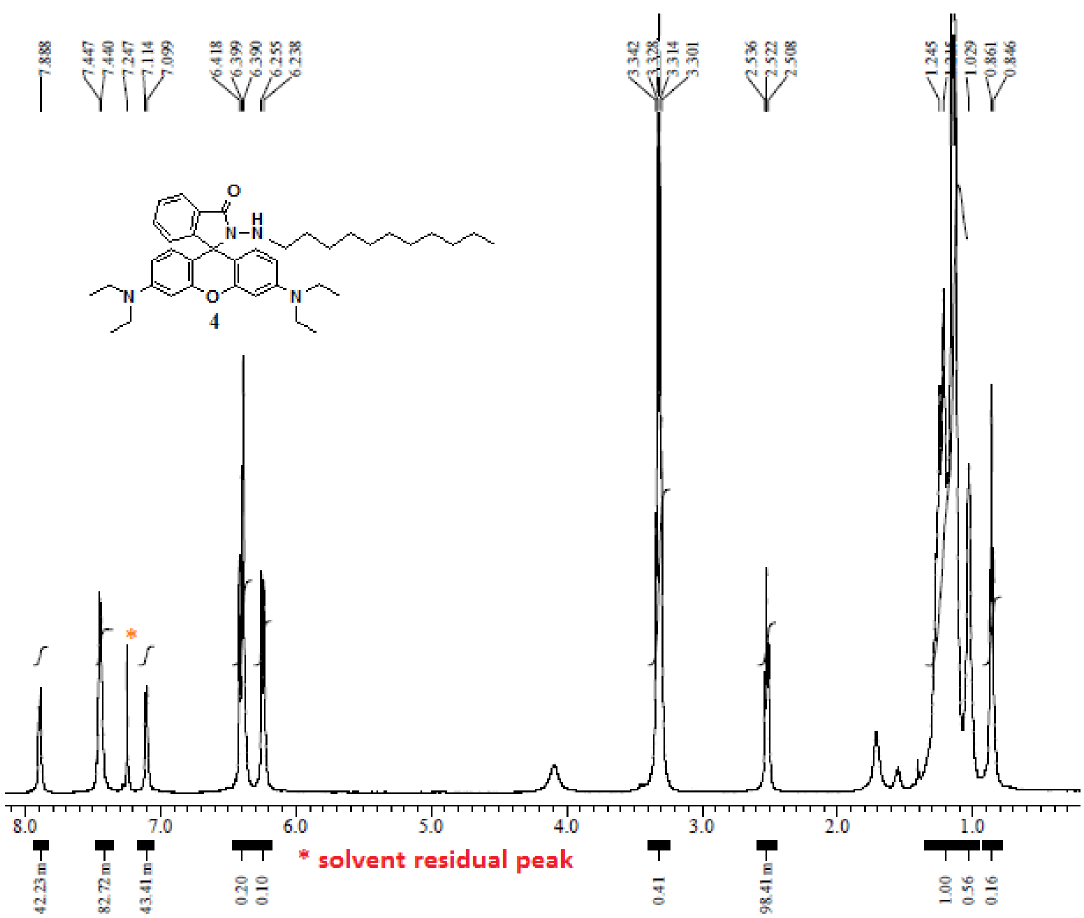


Fig. S10: ^{1}H-NMR spectrum of compound **4** (in $CDCl_3$).

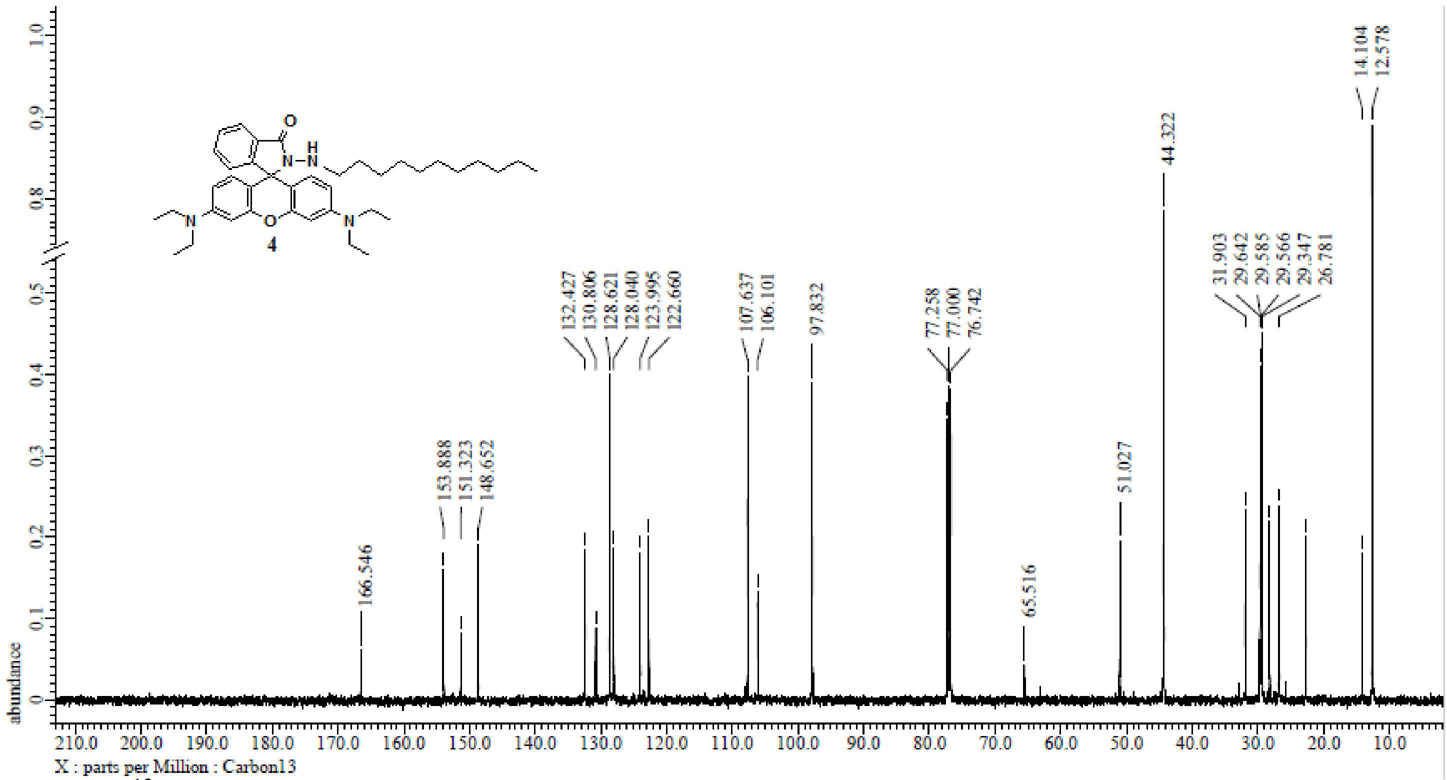


Fig. S11: ^{13}C-NMR spectrum of compound **4** (in $CDCl_3$).

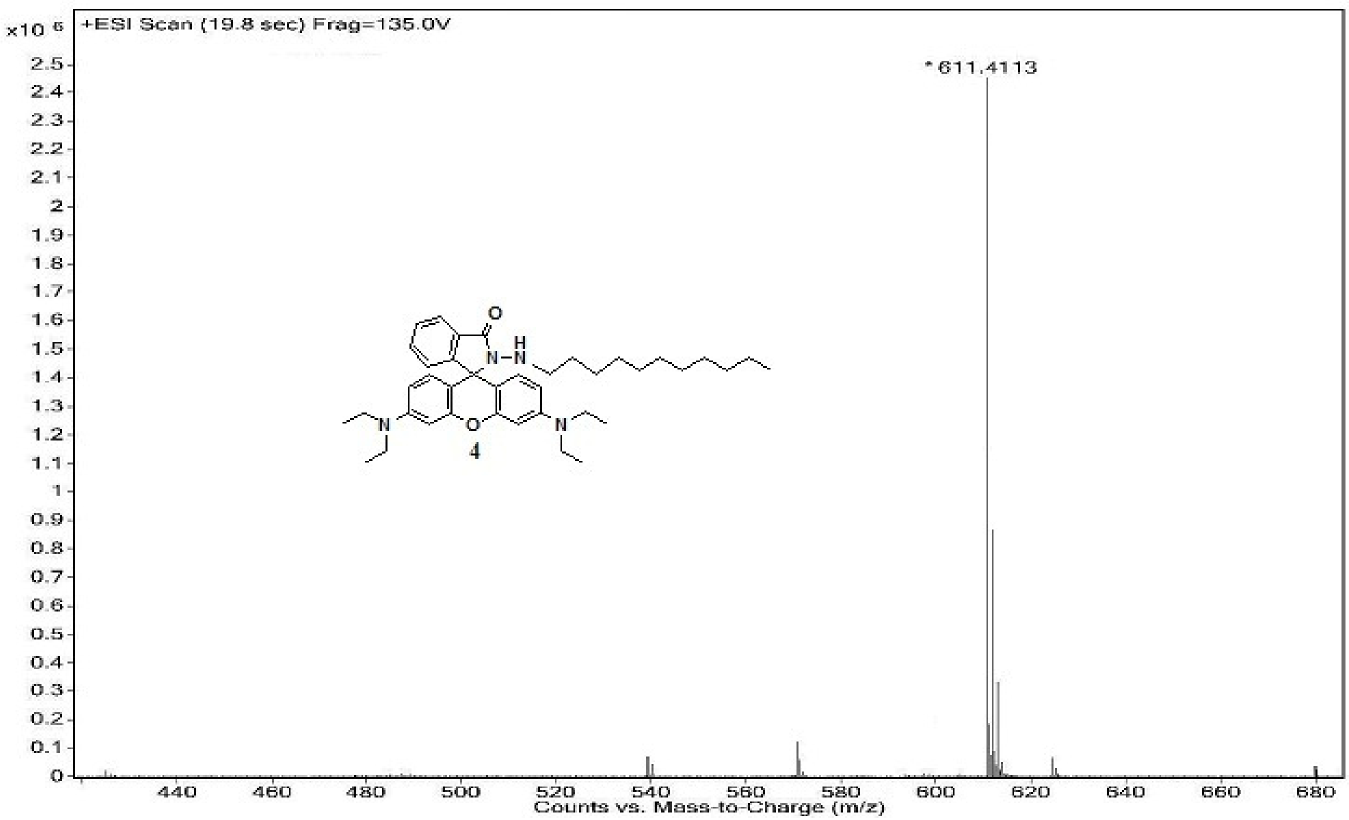


Fig. S12: MS (ESI) spectrum of compound **4**.

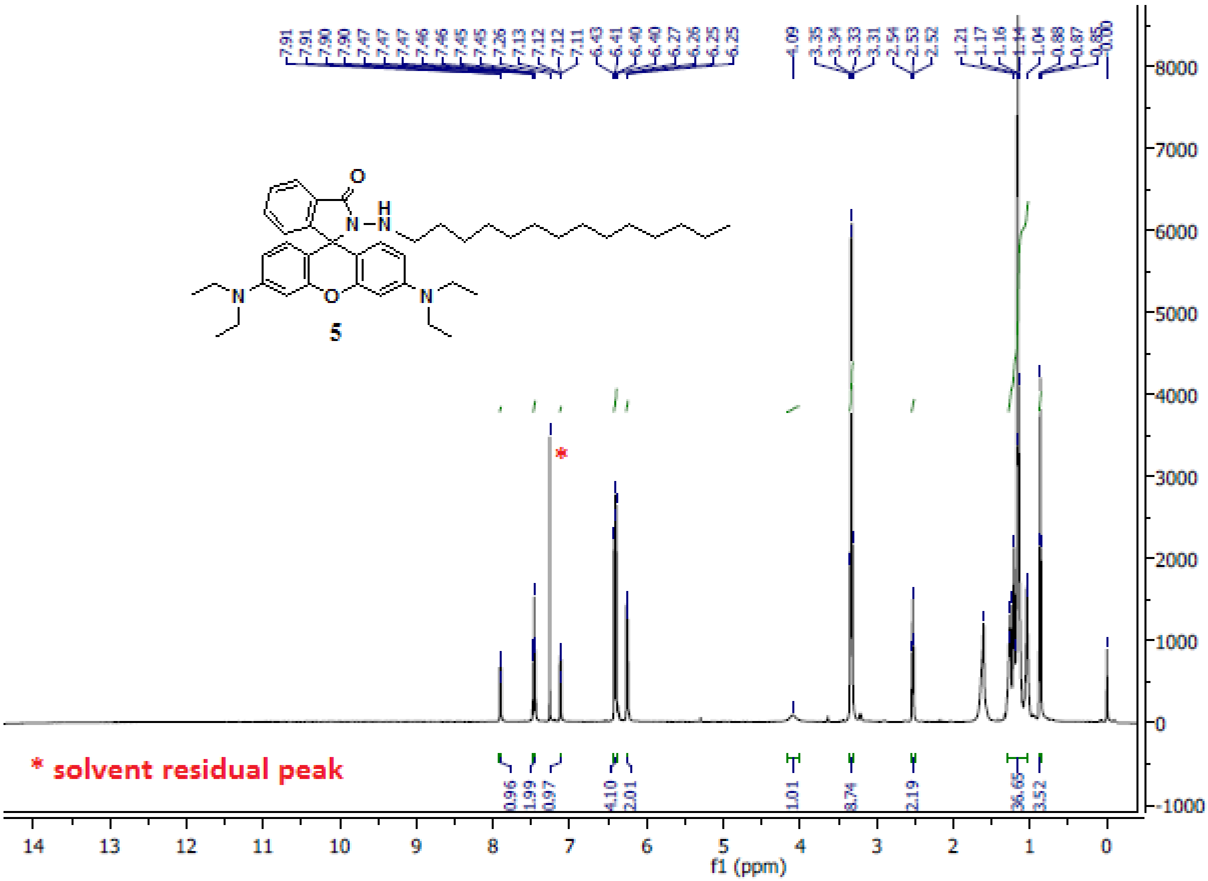


Fig. S13: ^{1}H-NMR spectrum of compound **5** (in $CDCl_3$).

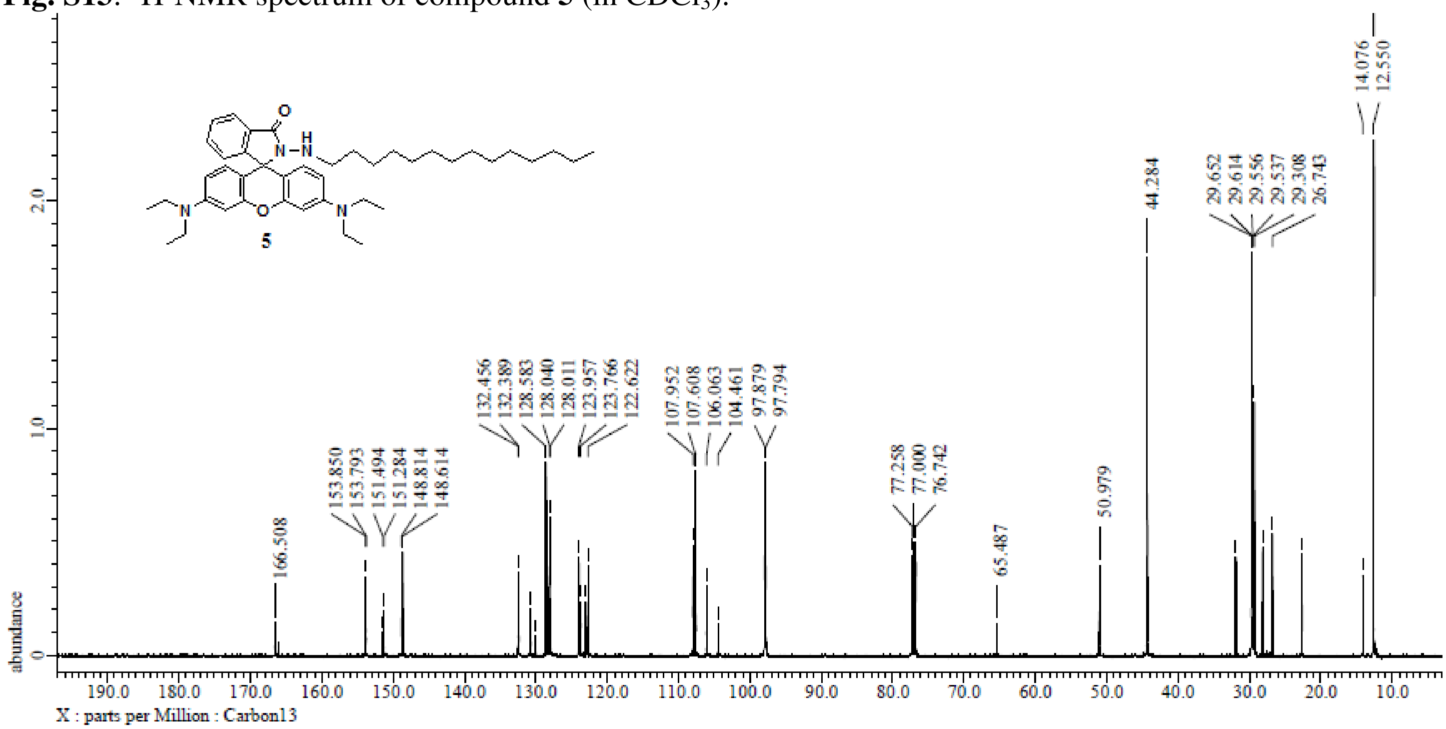


Fig. S14: ^{13}C-NMR spectrum of compound **5** (in $CDCl_3$).

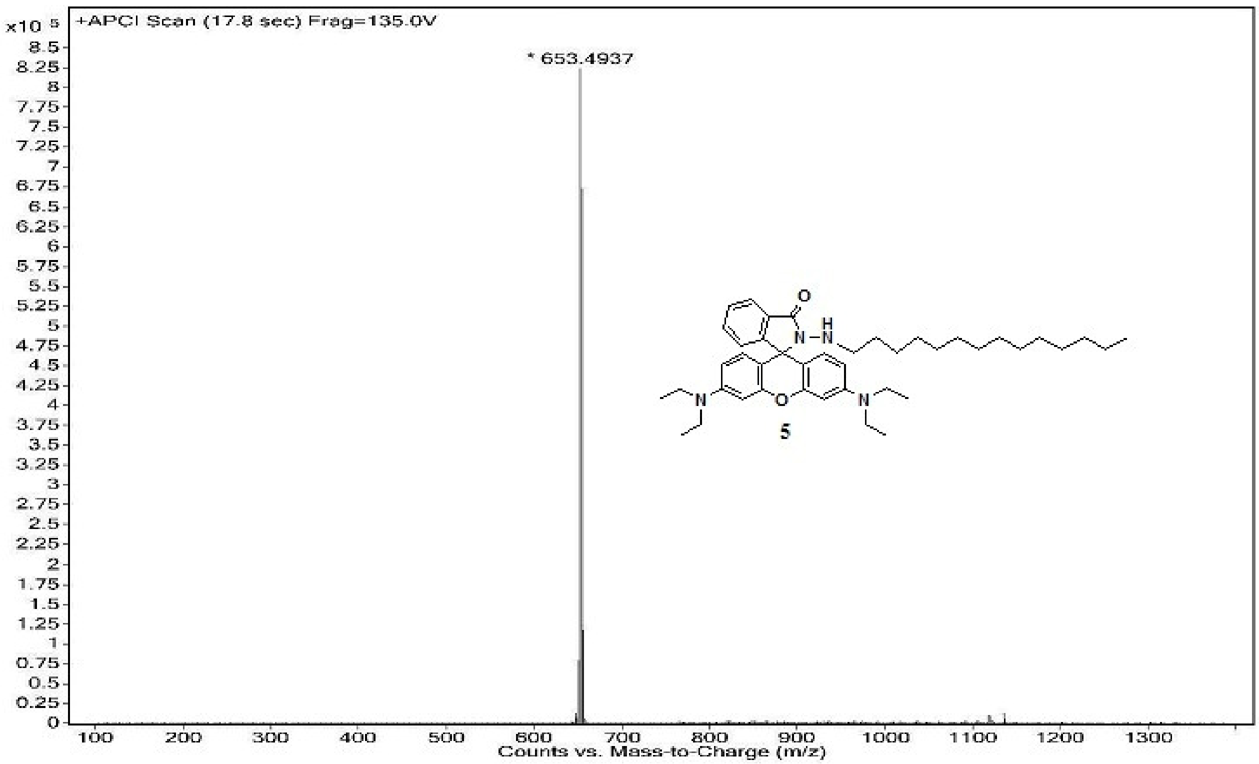


Fig. S15: MS (ESI) spectrum of compound **5**.

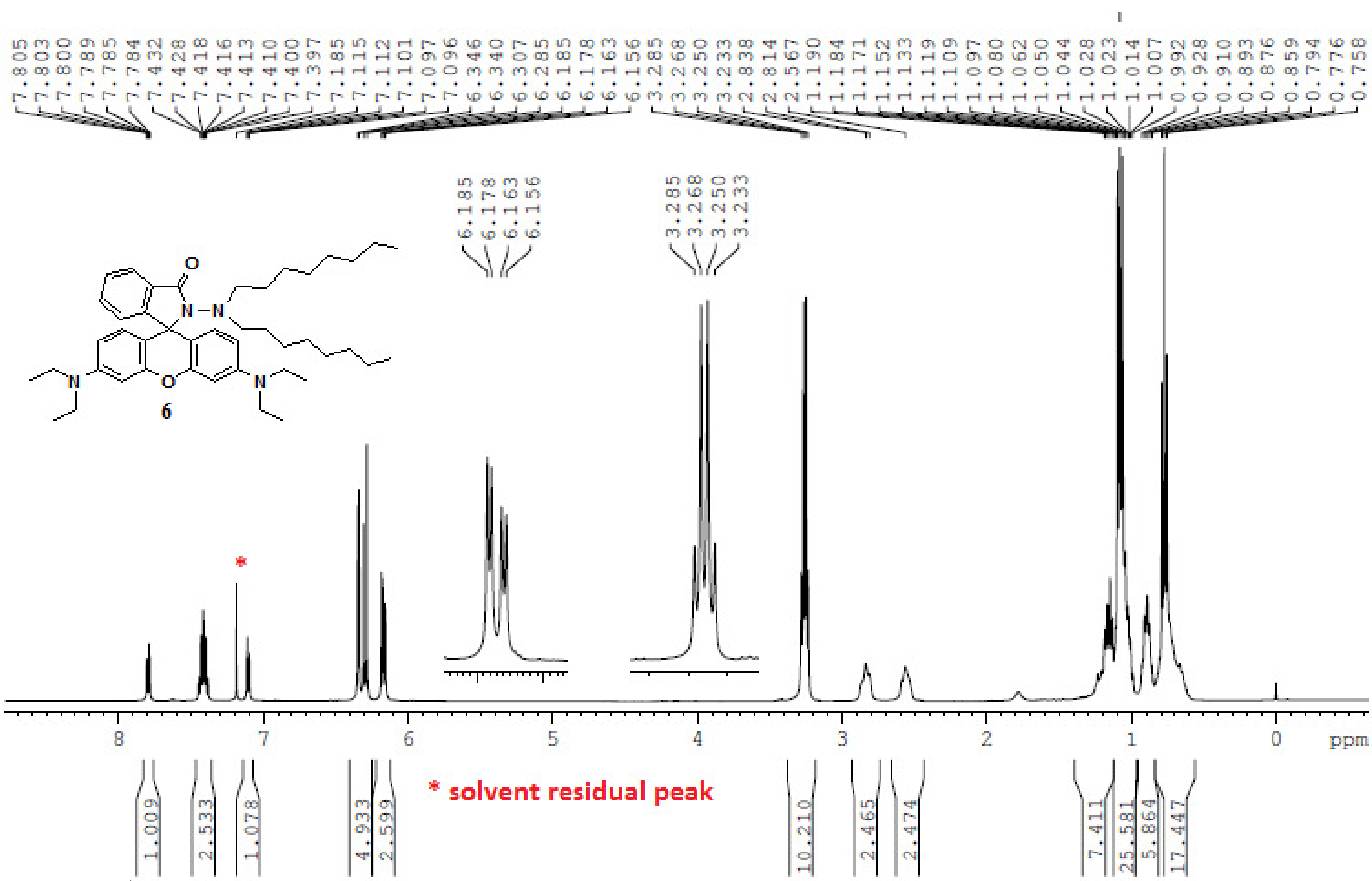


Fig. S16: [1]H-NMR spectrum of compound **6** (in $CDCl_3$).

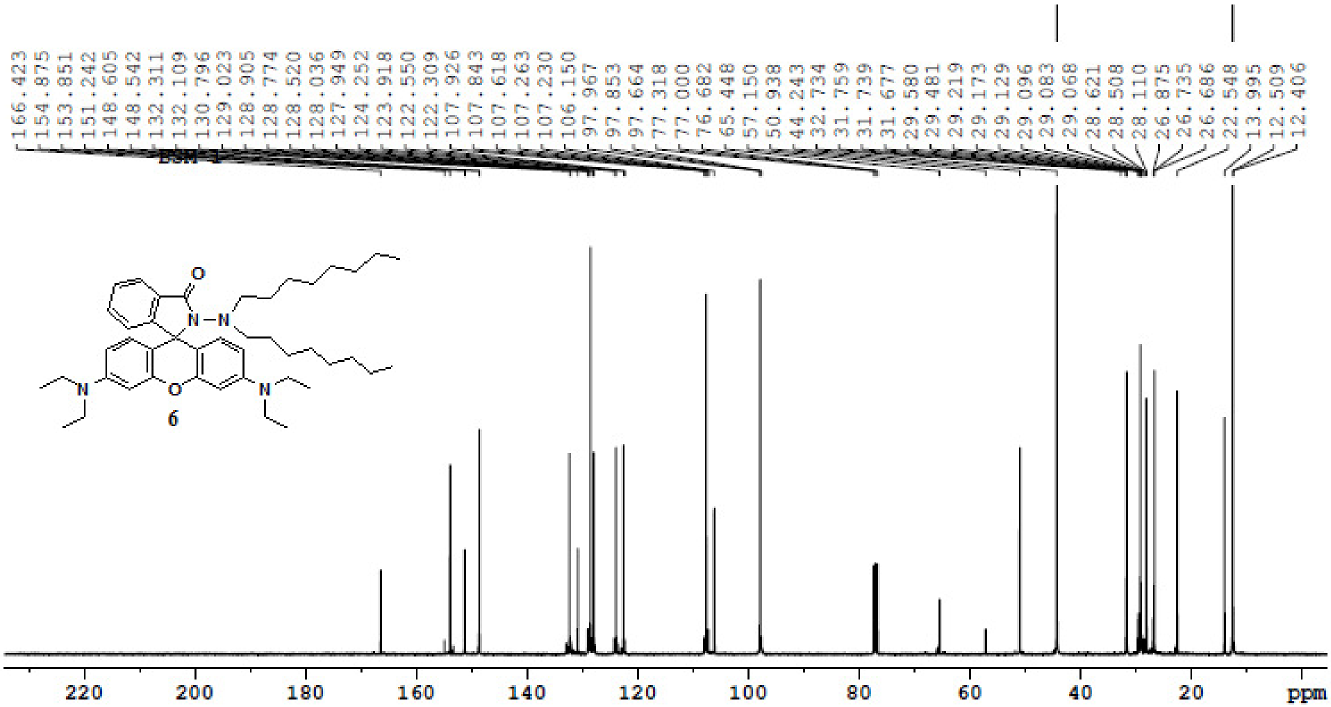


Fig. S17: ^{13}C-NMR spectrum of compound **6** (in $CDCl_3$).

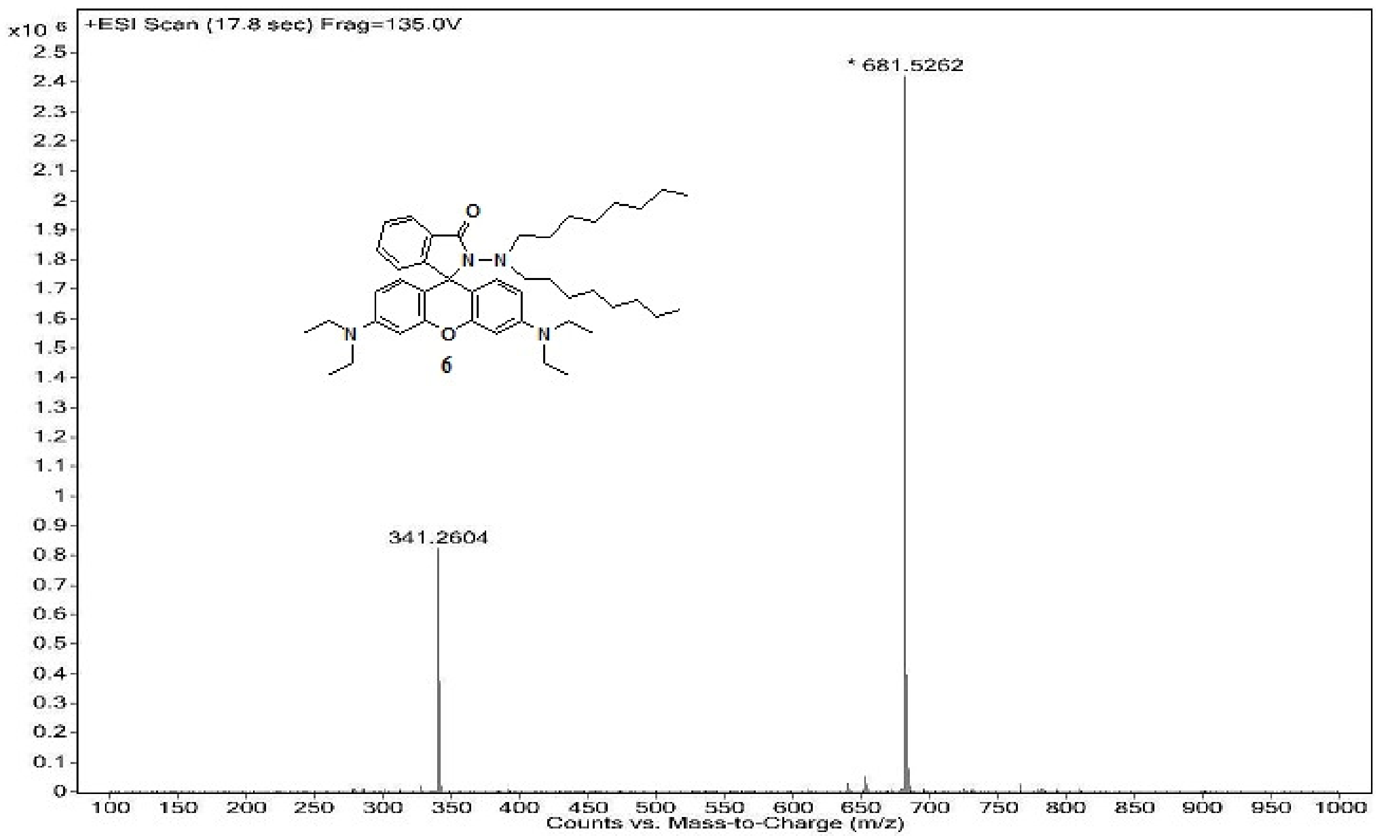


Fig. S18: MS (ESI) spectrum of compound **6**.

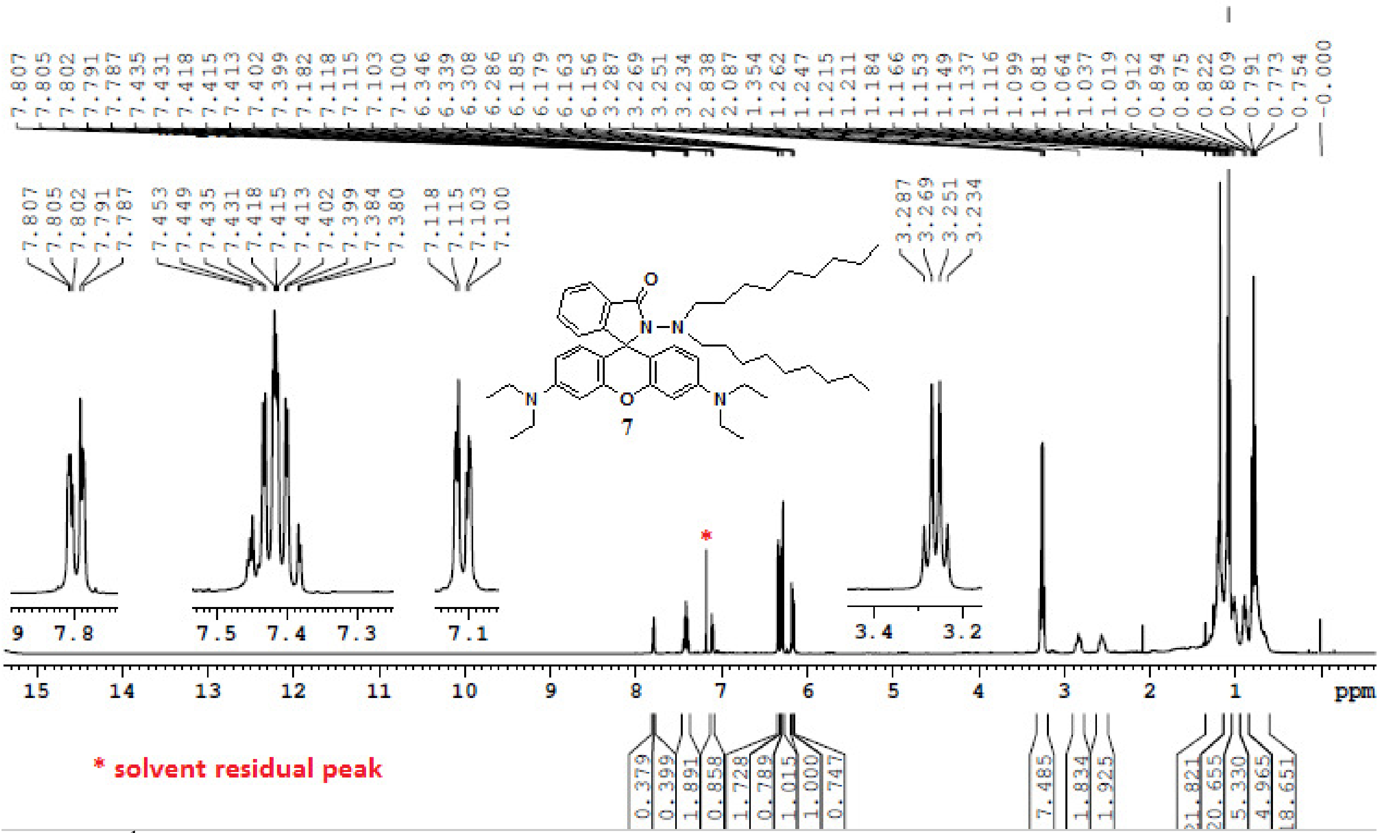


Fig. S19: ^{1}H-NMR spectrum of compound **7** (in $CDCl_3$).

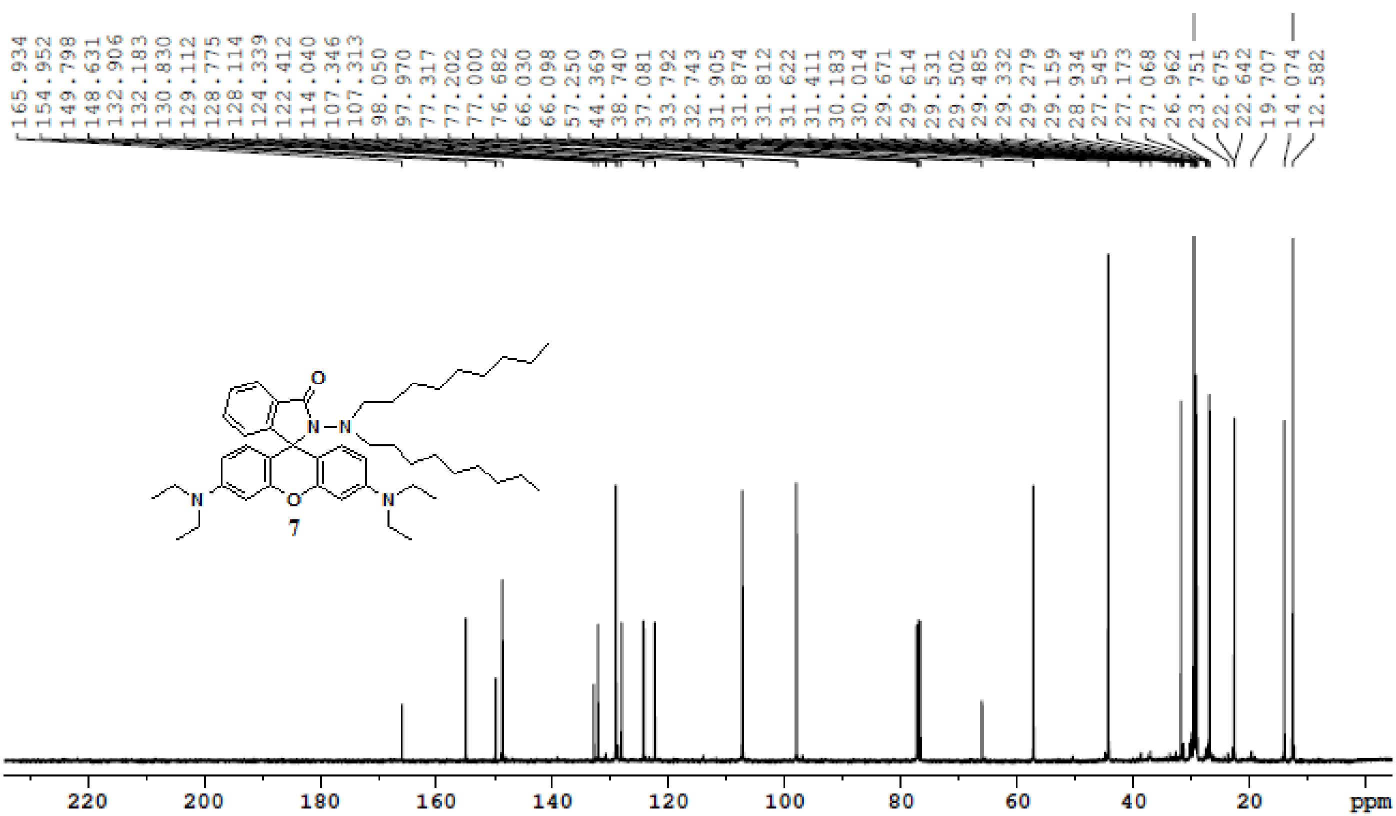


Fig. S20: ^{13}C-NMR spectrum of compound **7** (in $CDCl_3$).

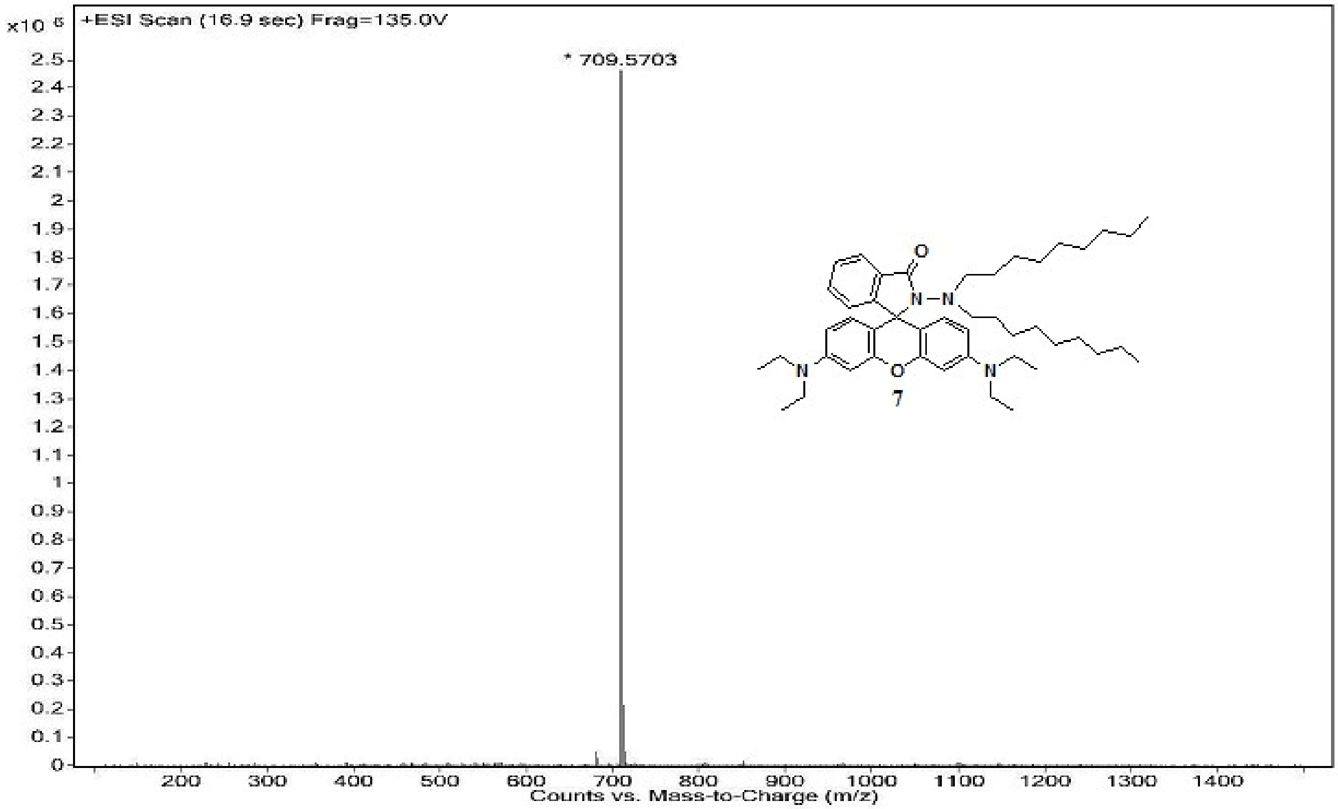


Fig. S21: MS (ESI) spectrum of compound **7**.

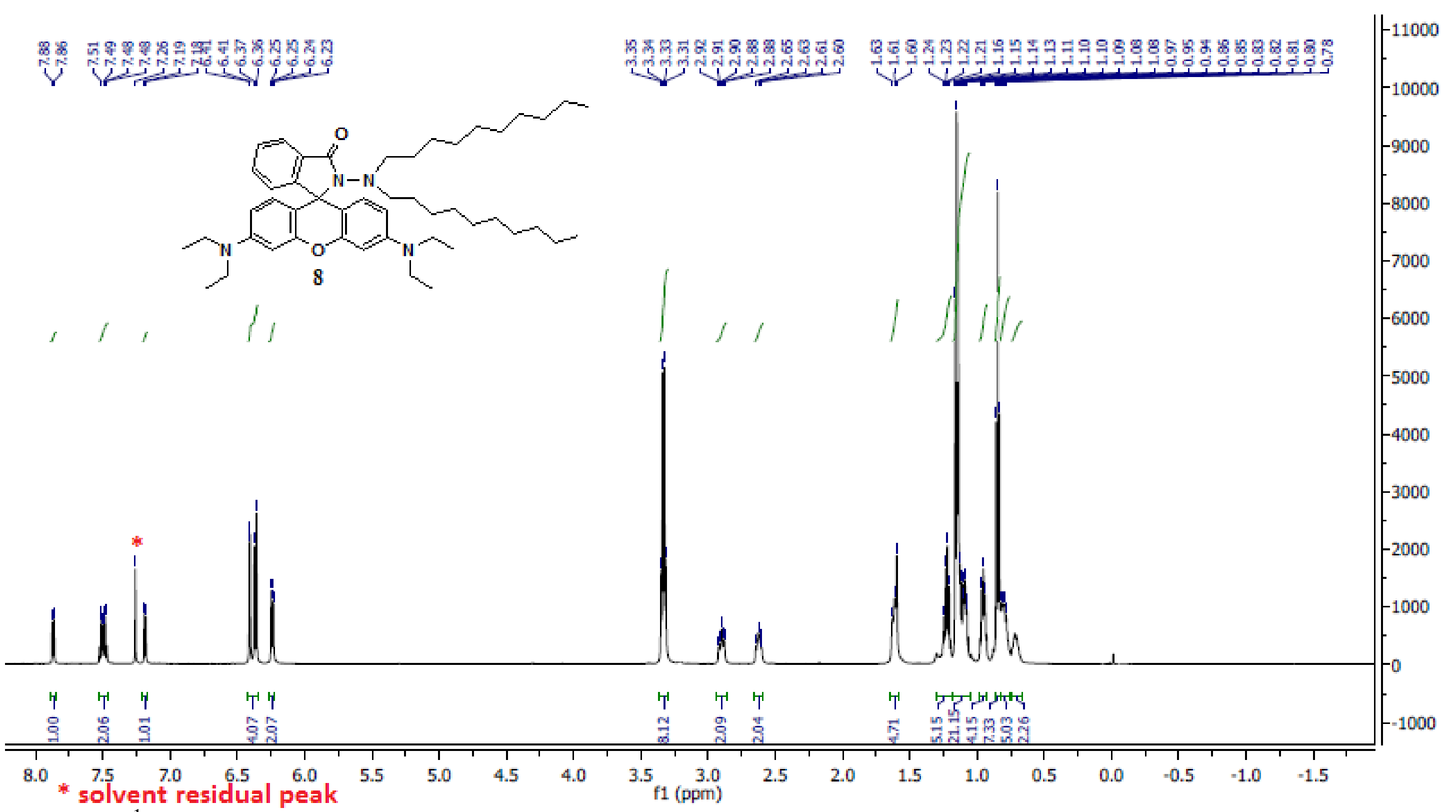


Fig. S22: ^{1}H-NMR spectrum of compound **8** (in $CDCl_3$).

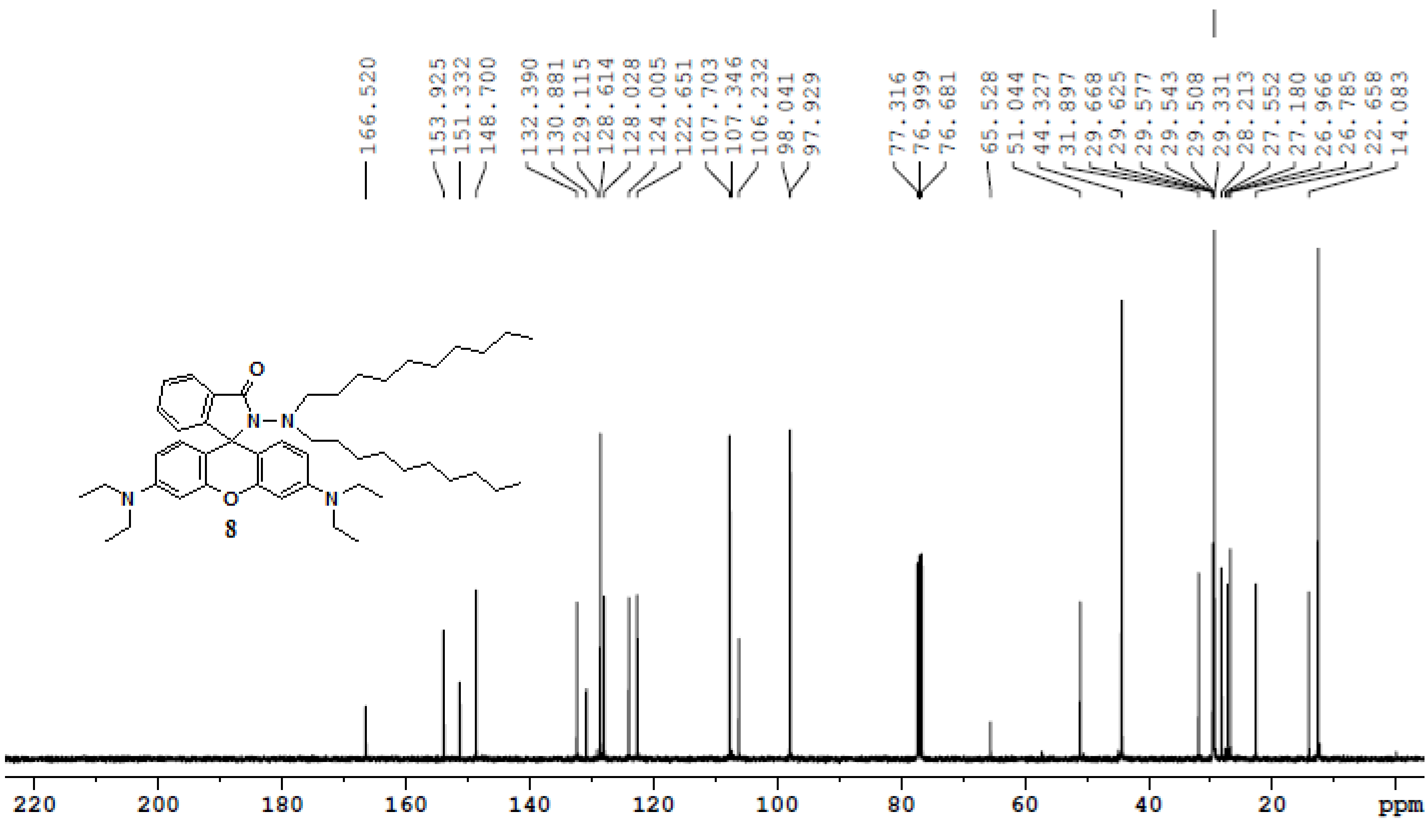


Fig. S23: ^{13}C-NMR spectrum of compound **8** (in $CDCl_3$).

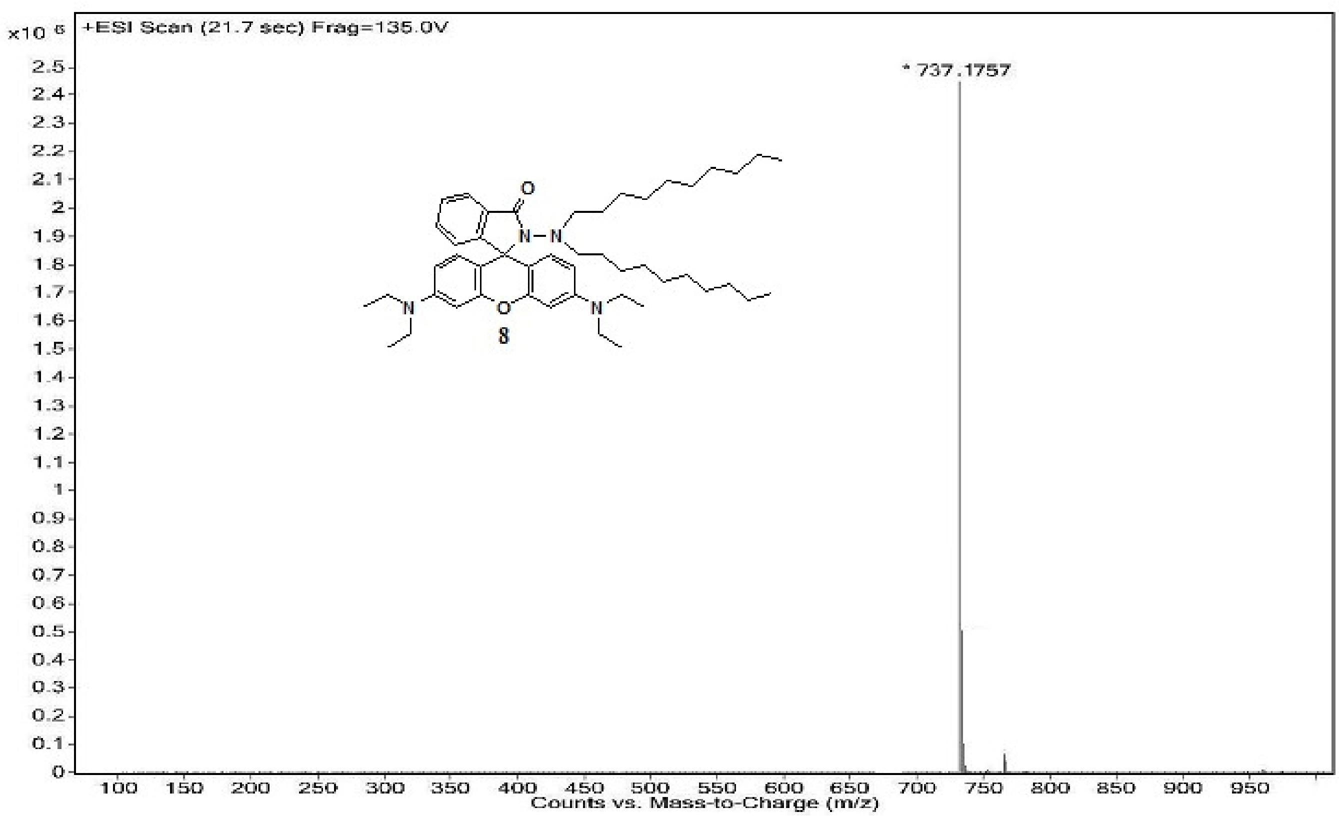


Fig. S24: MS (ESI) spectrum of compound **8**.

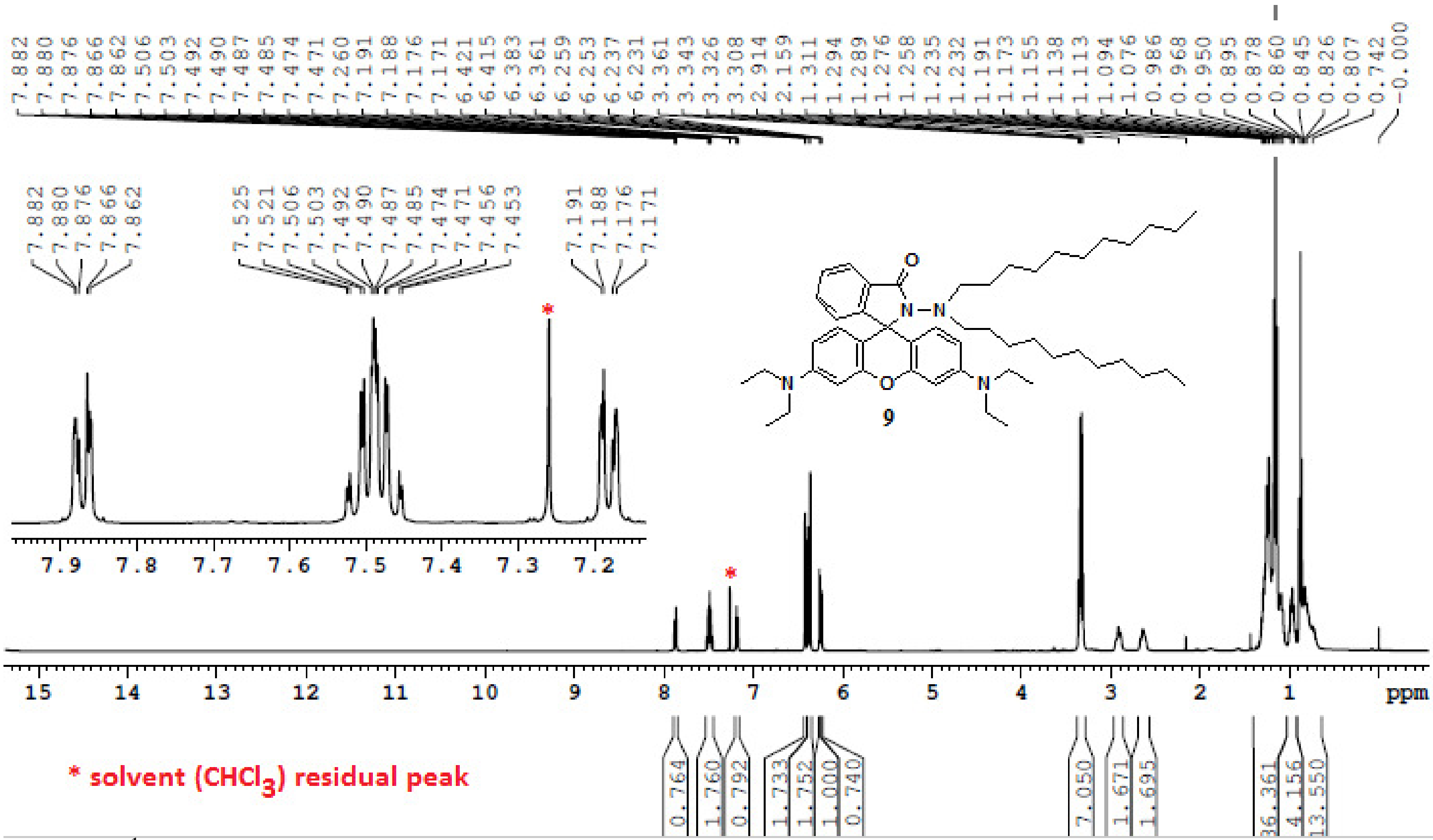


Fig. S25: [1]H-NMR spectrum of compound **9** (in $CDCl_3$).

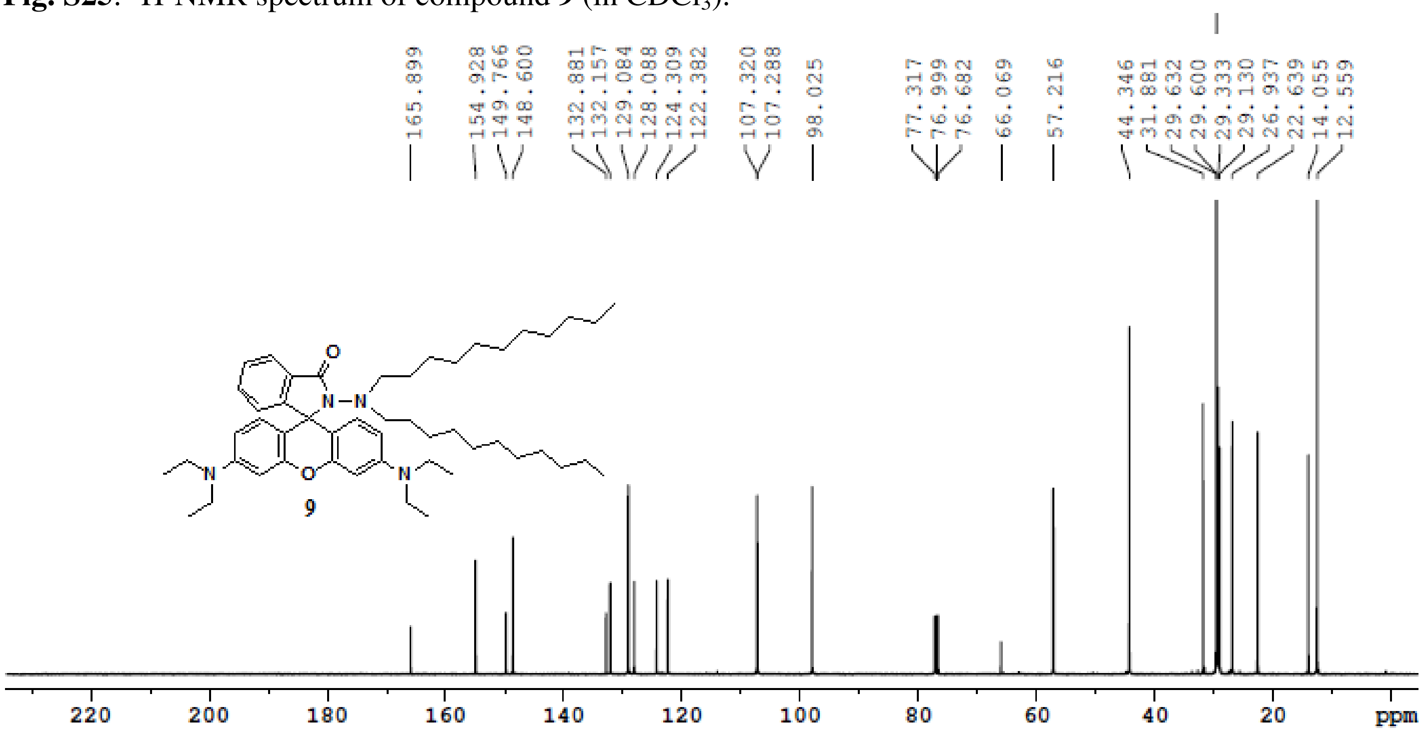


Fig. S26: [13]C-NMR spectrum of compound **9** (in $CDCl_3$).

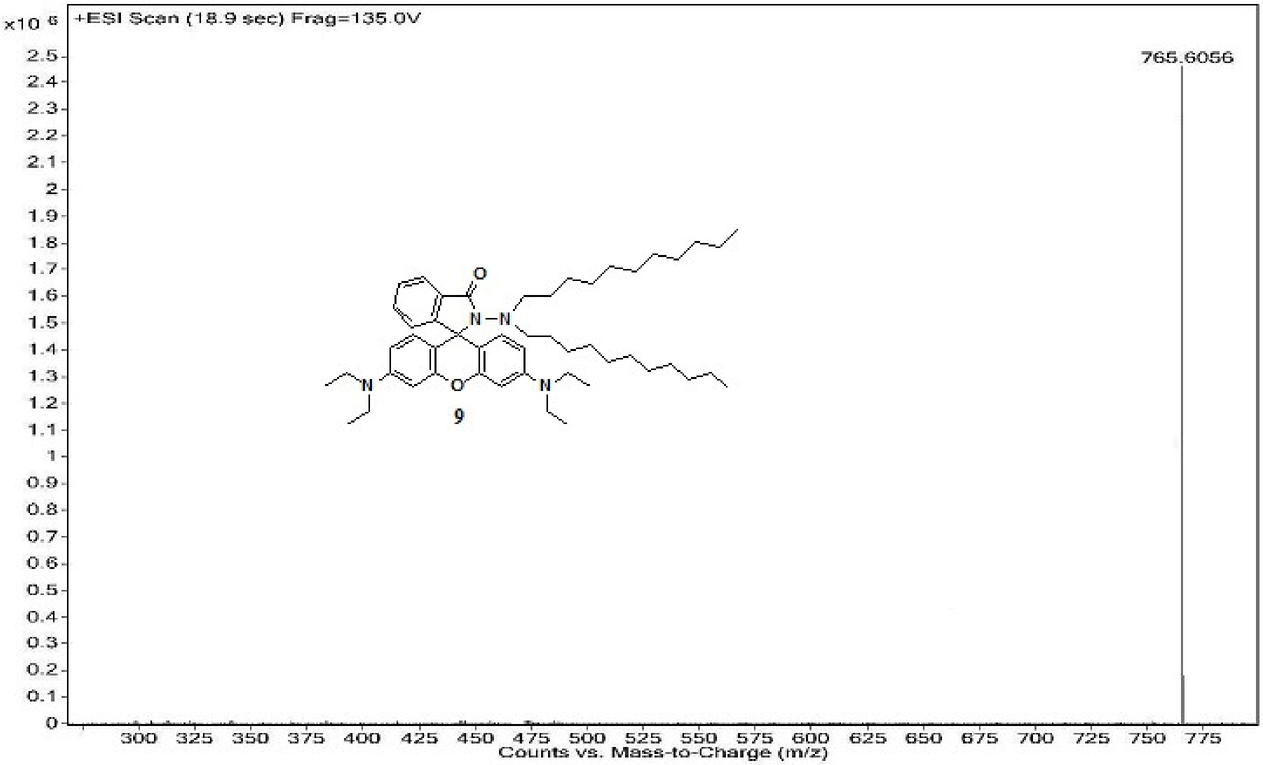


Fig. S27: MS (ESI) spectrum of compound **9**.

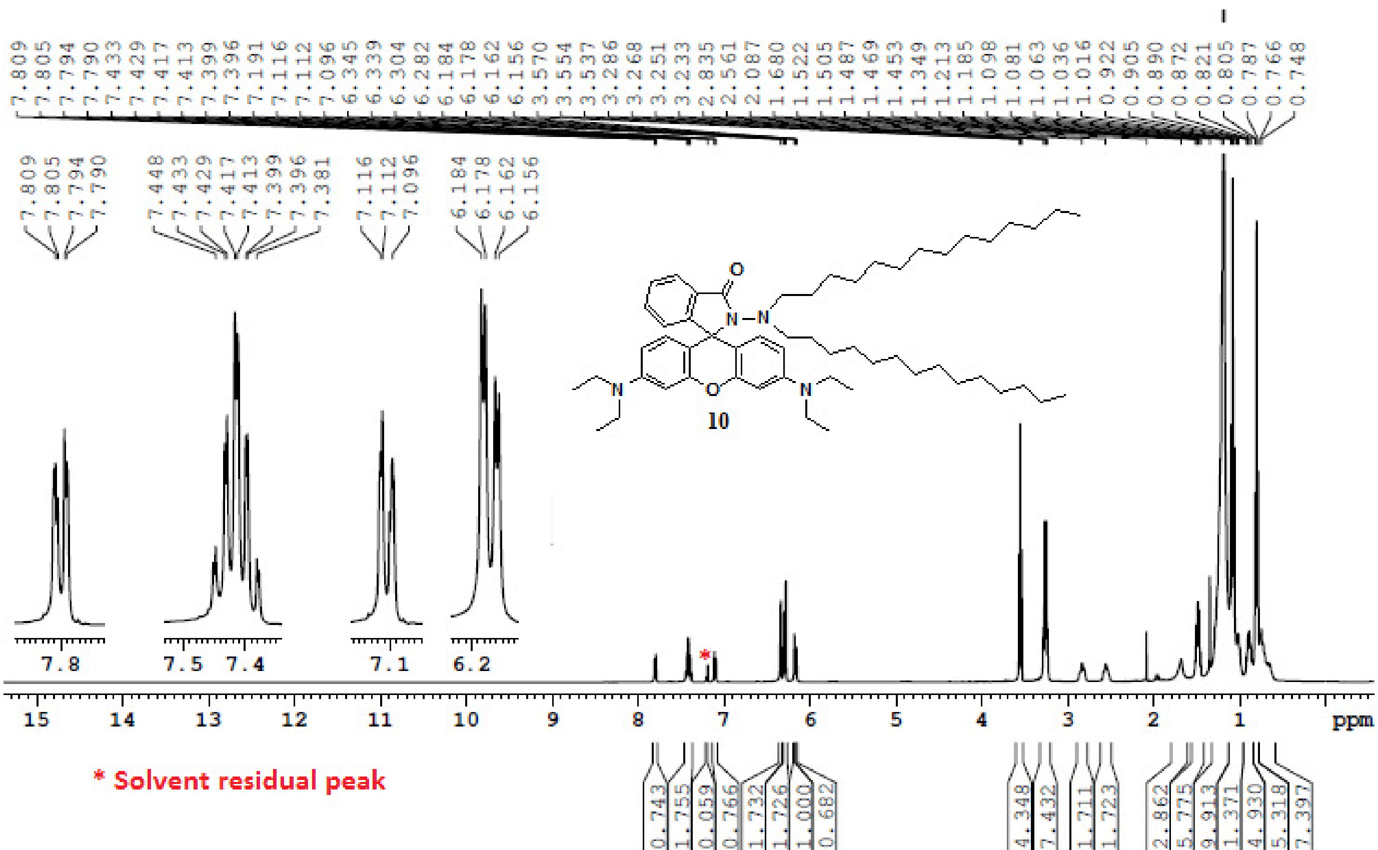


Fig. S28: [1]H-NMR spectrum of compound **10** (in $CDCl_3$).

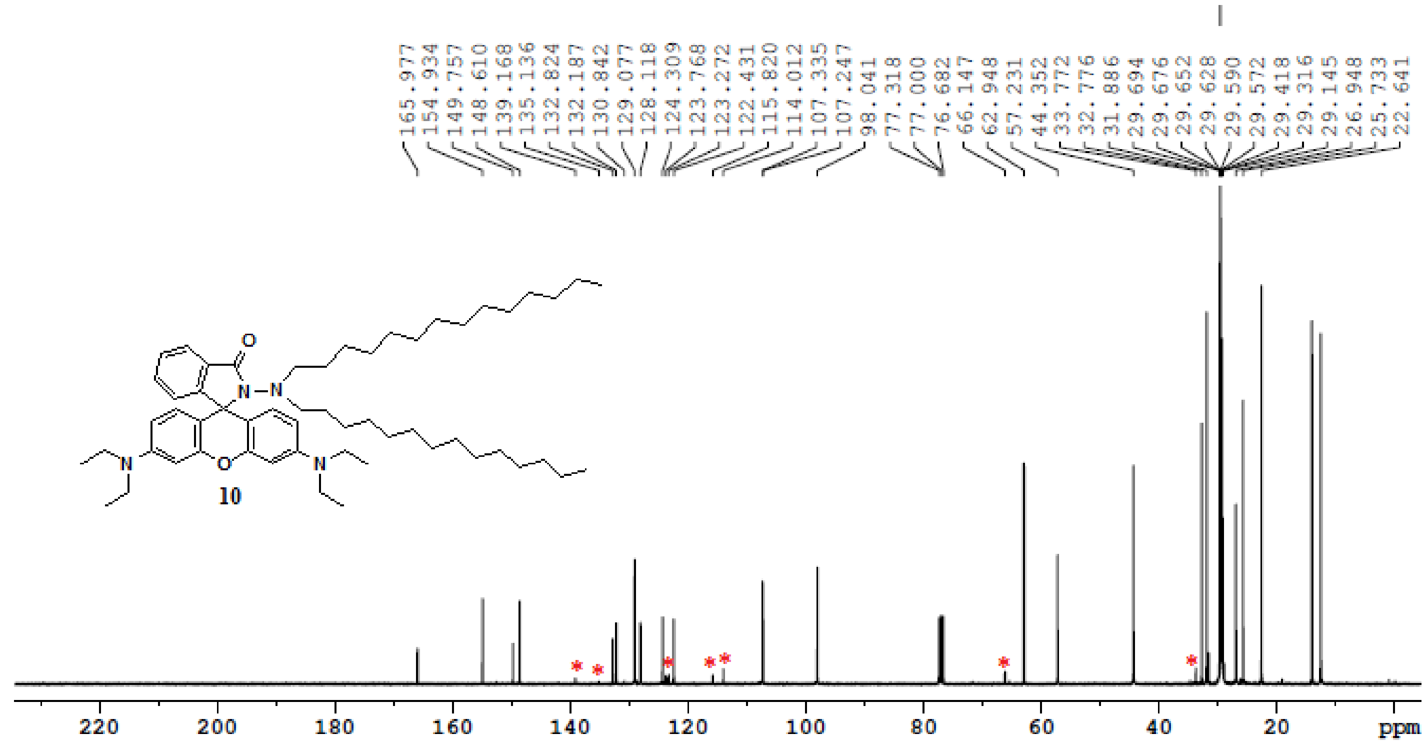


Fig. S29: [13]C-NMR spectrum of compound **10** (in $CDCl_3$).

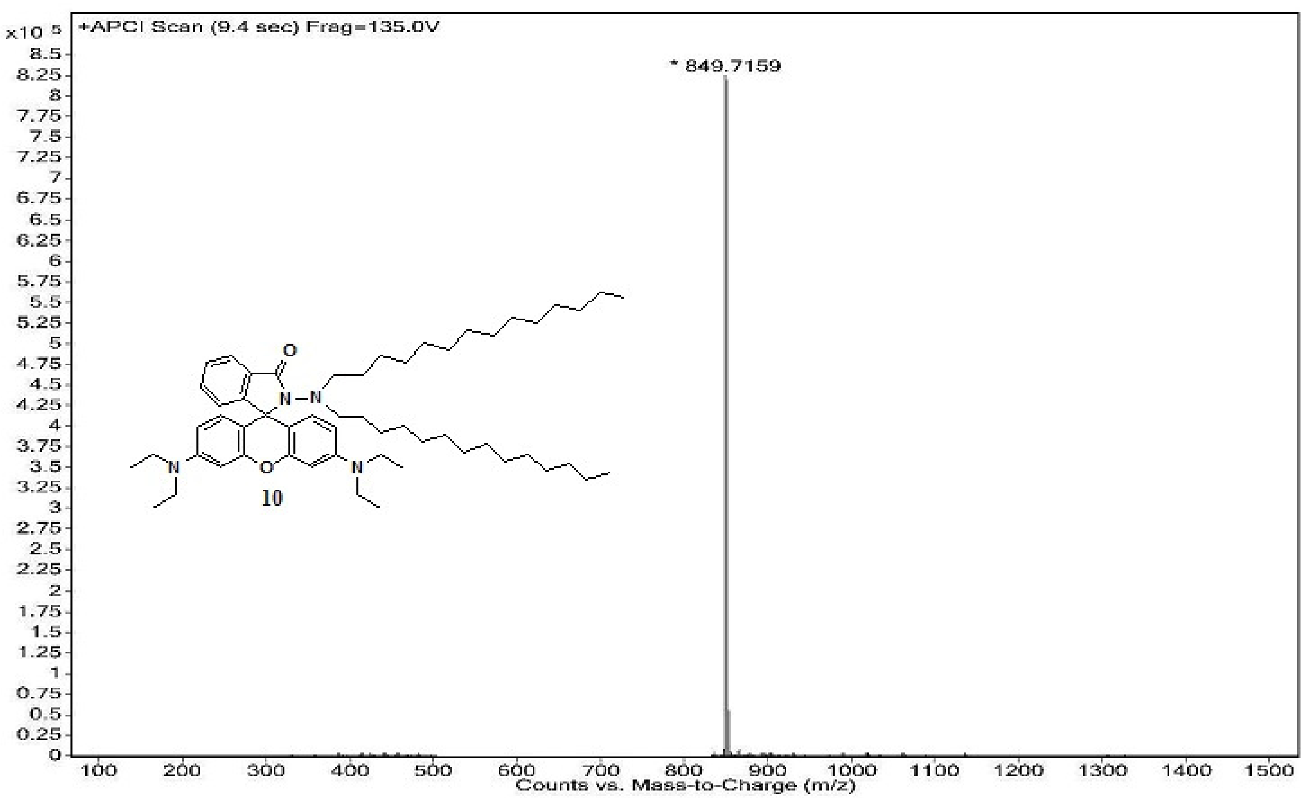


Fig. S30: MS (ESI) spectrum of compound **10**.

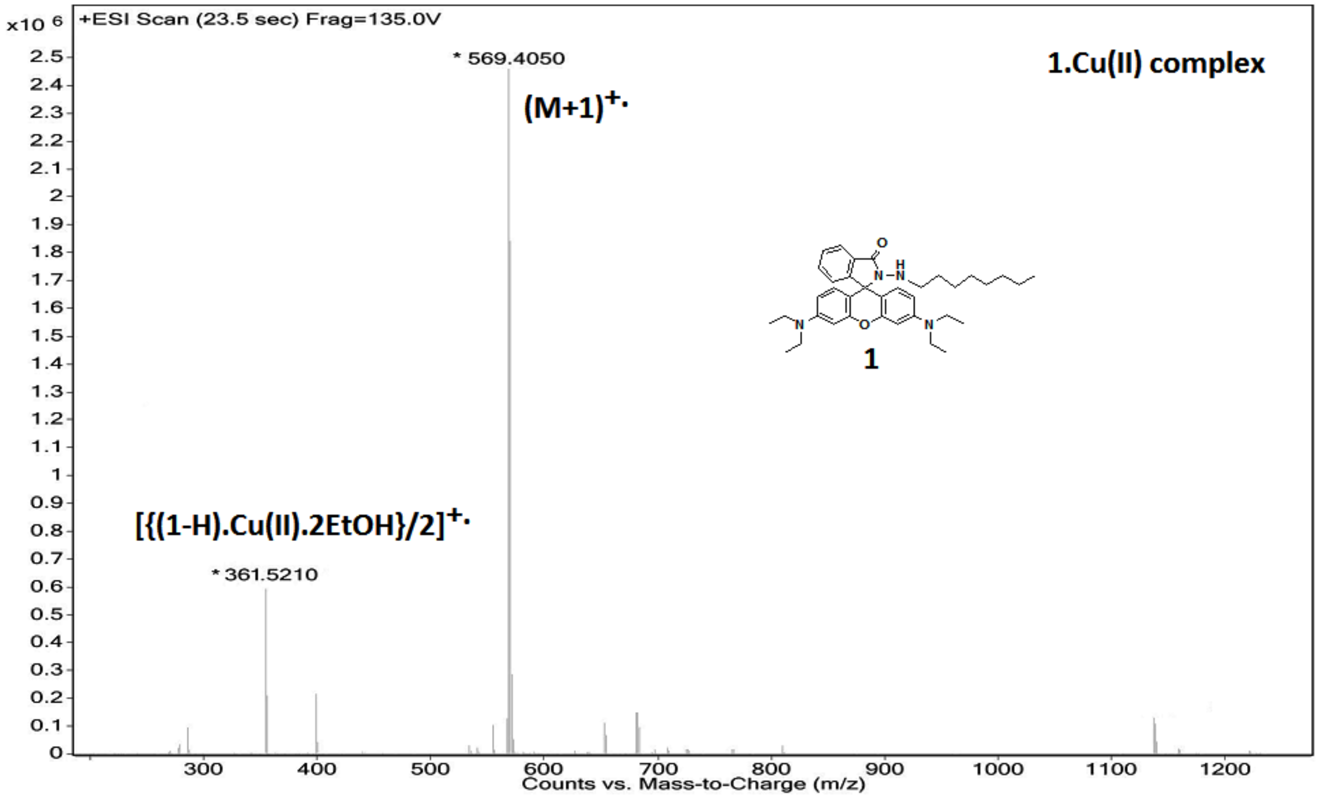


Fig. S31: MS (ESI) spectrum of **1**⊂Cu(II) complex.

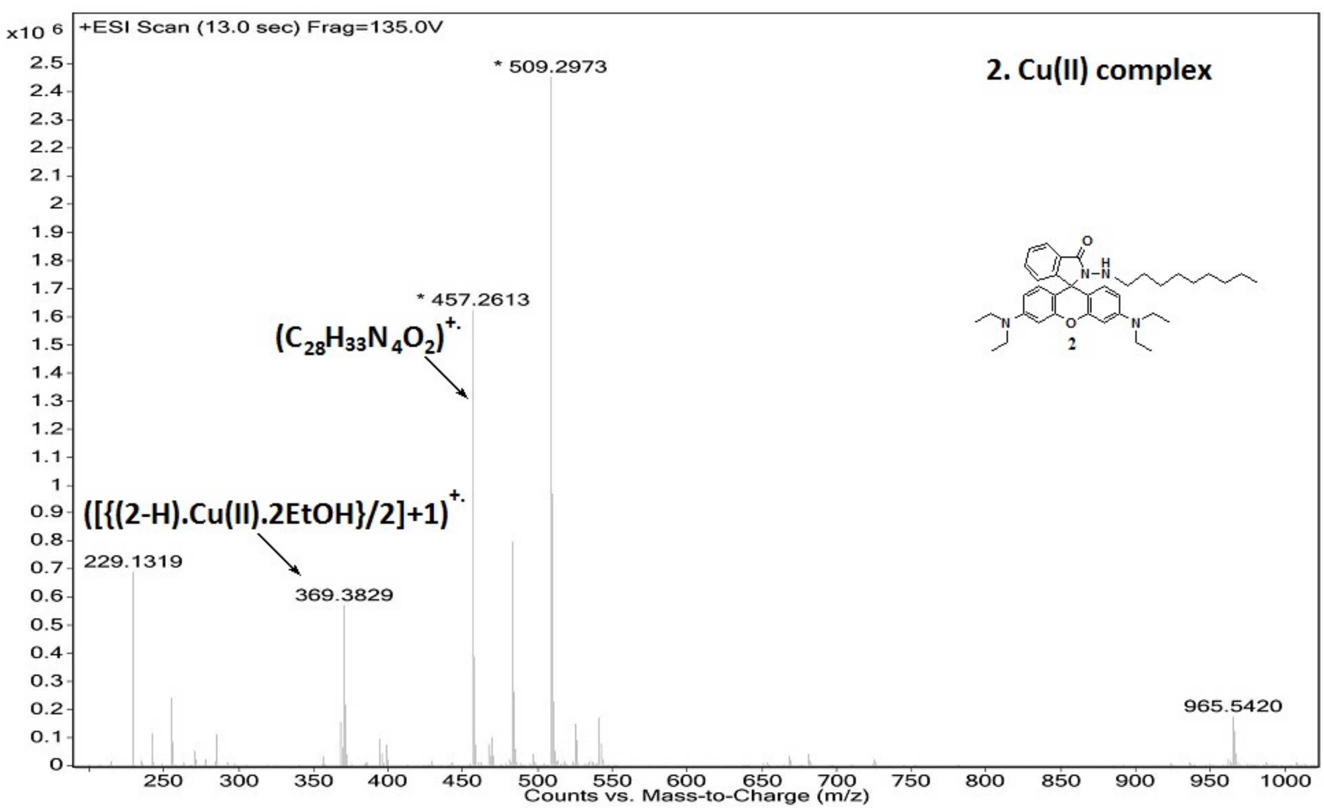


Fig. S32: MS (ESI) spectrum of **2**⊂Cu(II) complex.

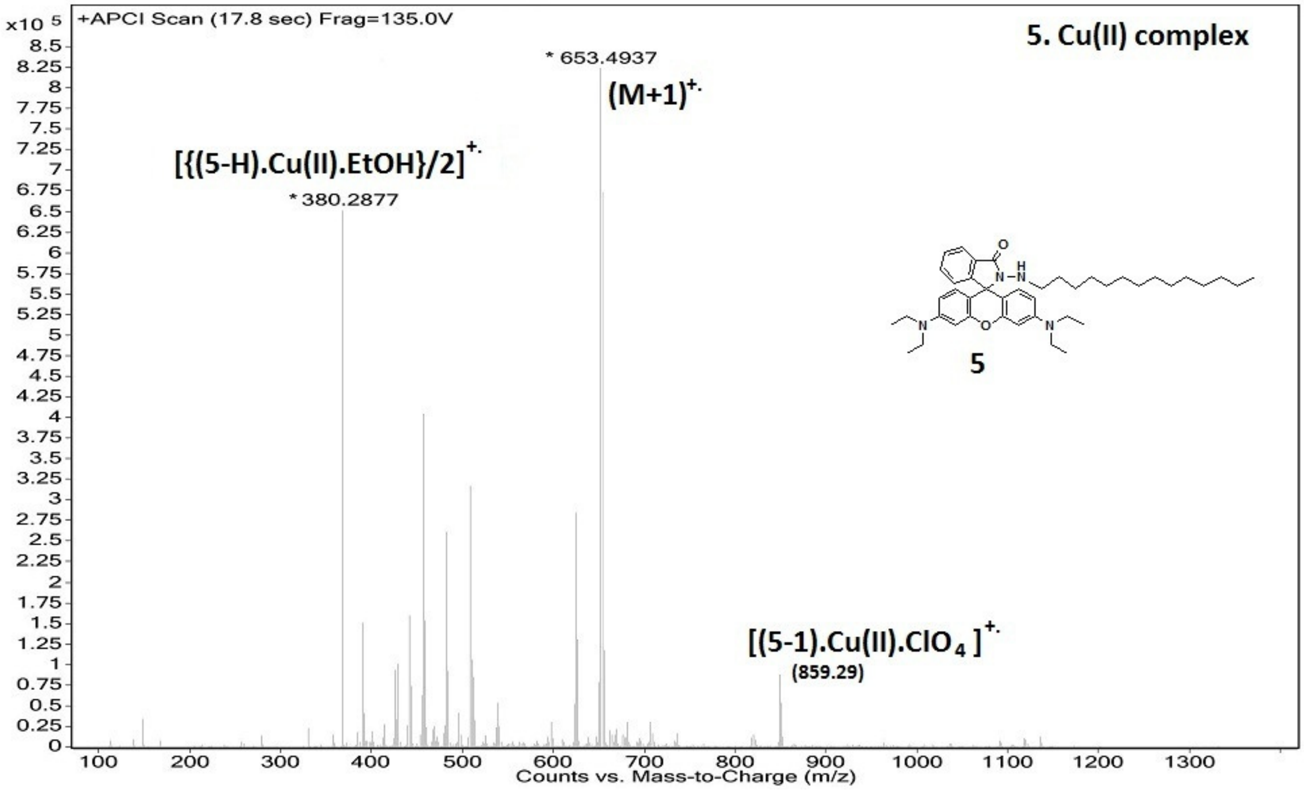


Fig. S33: MS (ESI) spectrum of **5**⊂Cu(II) complex.

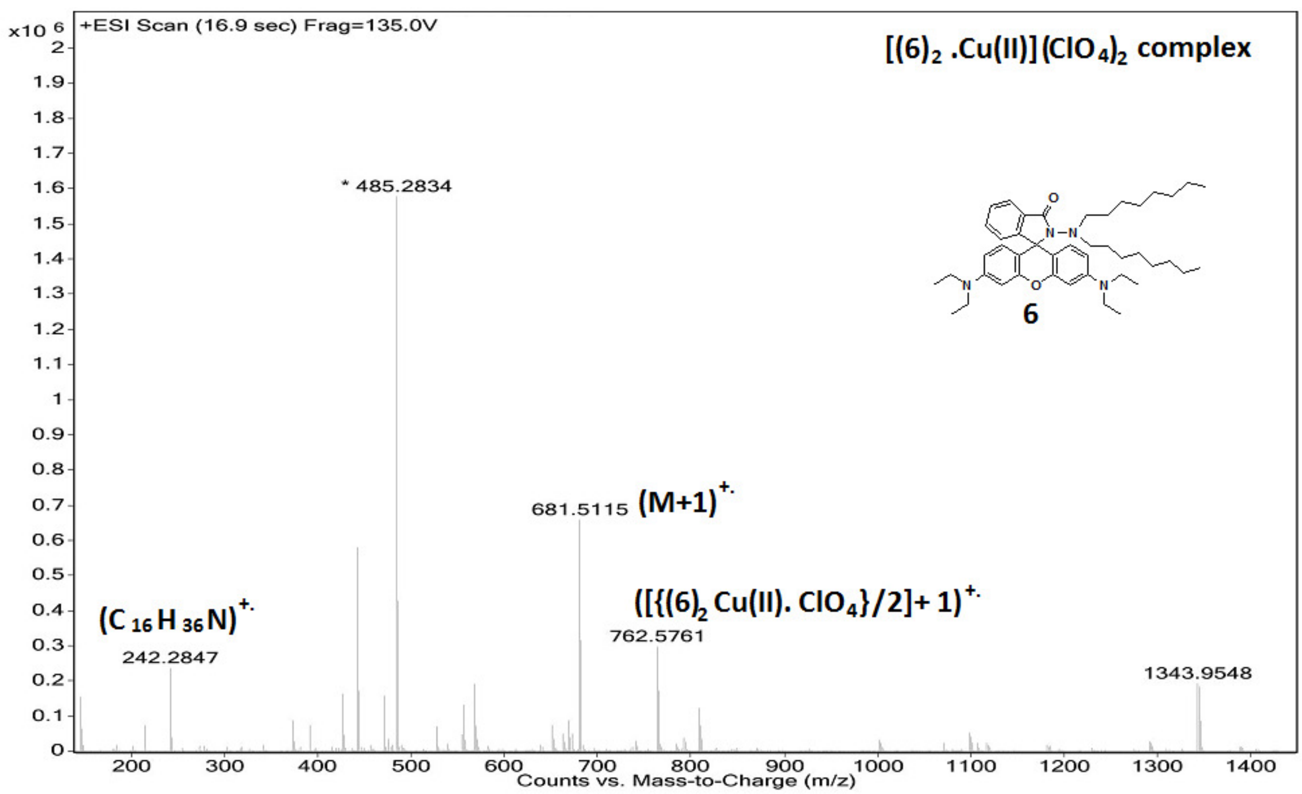


Fig. S34: MS (ESI) spectrum of **6**⊂Cu(II) complex.

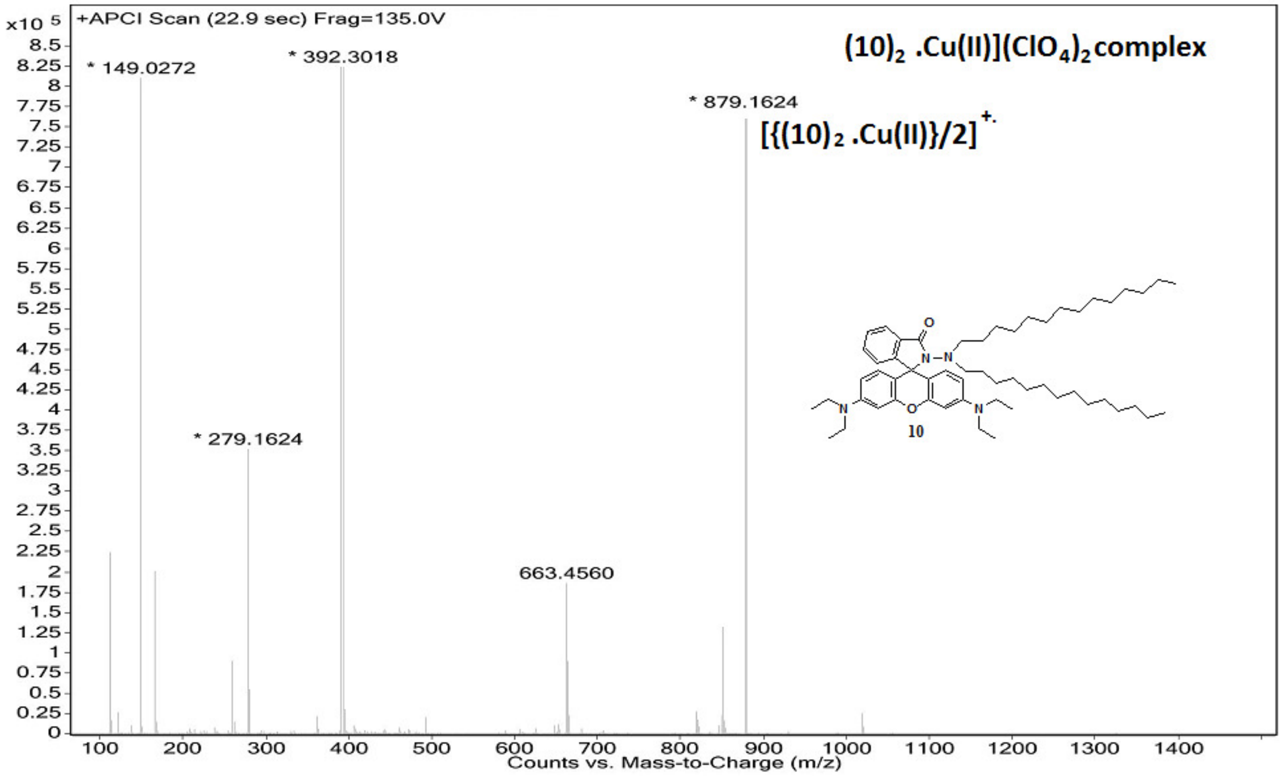


Fig. S35: MS (ESI) spectrum of **10**⊂Cu(II) complex.

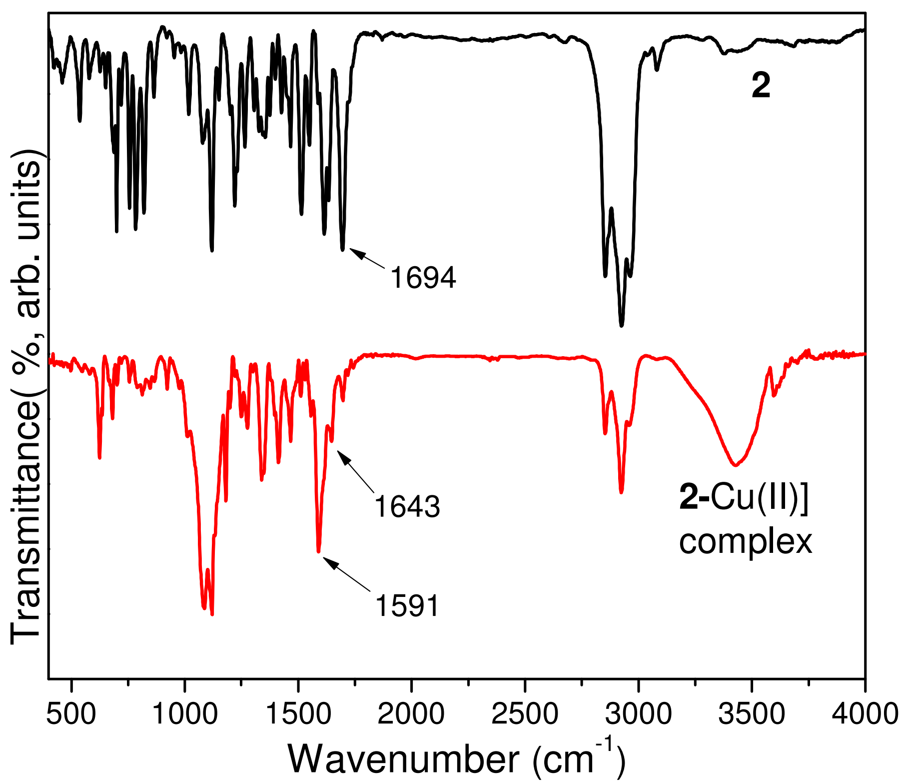


Fig. S36: Comparison between IR-spectra of **2** and its Cu(II)-complex.

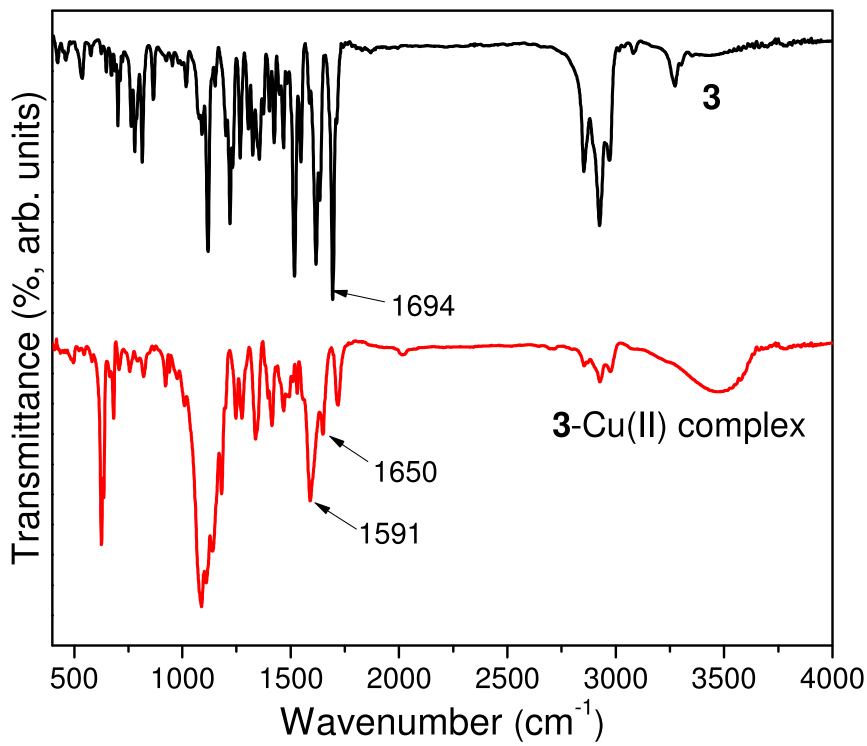


Fig. S37: Comparison between IR-spectra of **3** and its Cu(II)-complex.

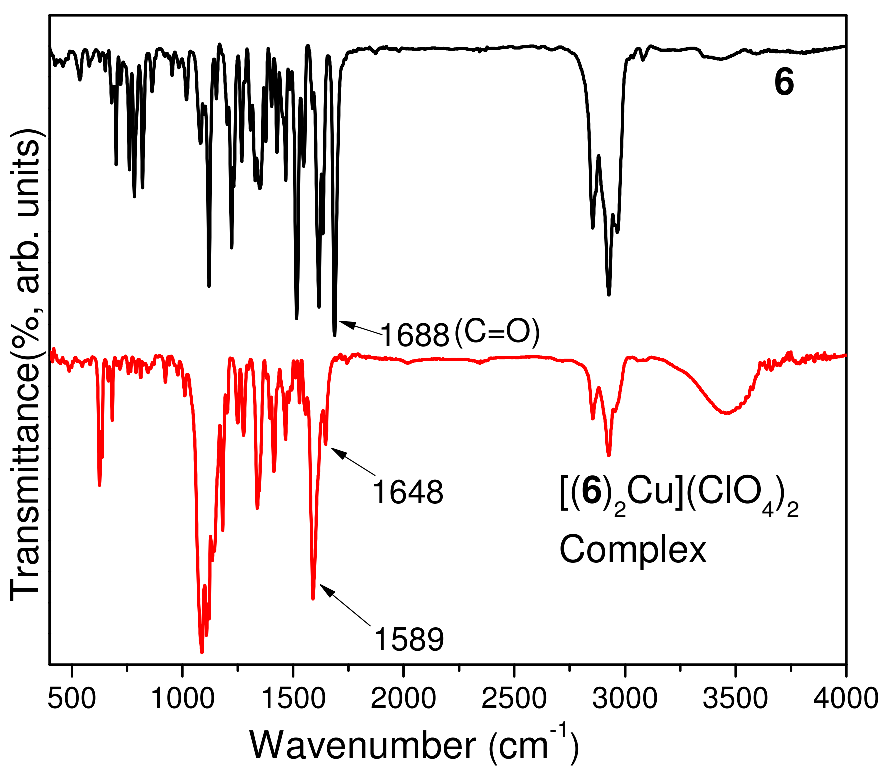


Fig. S38: Comparison between IR-spectra of **6** and its Cu(II)-complex.

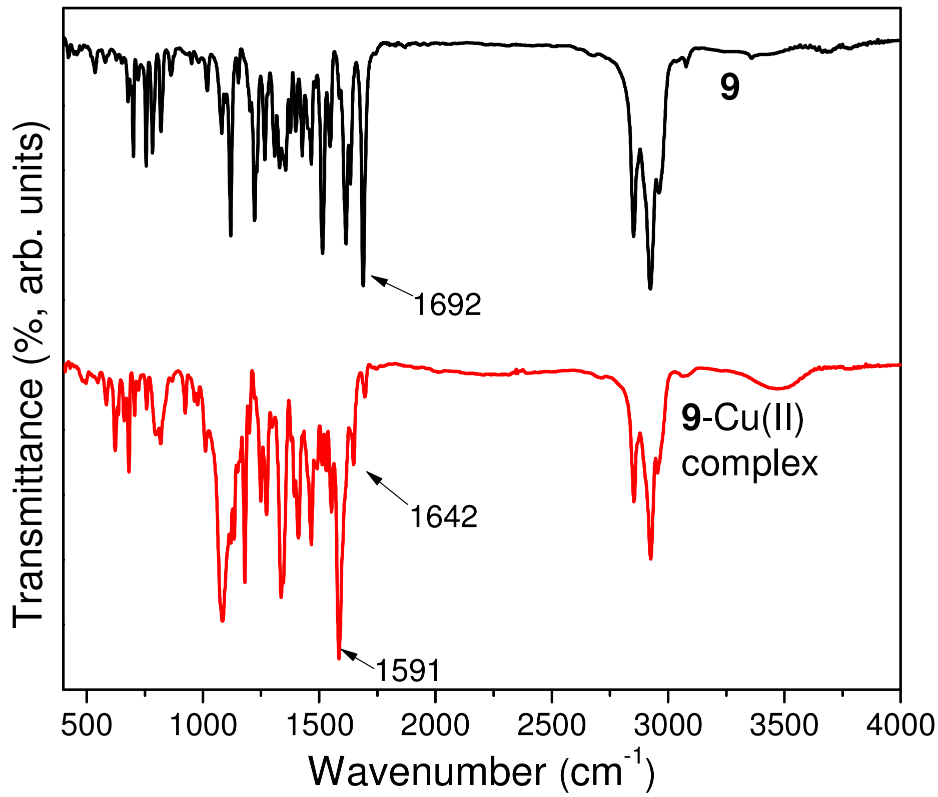


Fig. S39: Comparison between IR-spectra of **9** and its Cu(II)-complex.

Absorption and Fluorescence spectral investigation of the probes in presence of various metal ions

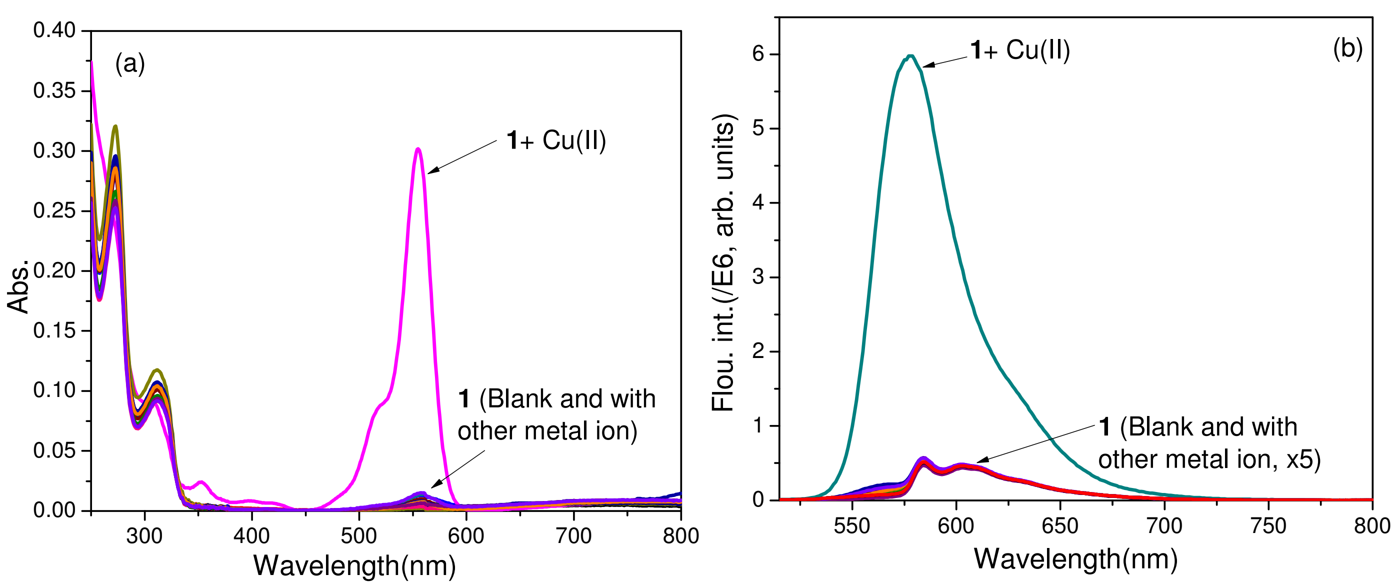


Fig. S40: (a) Absorption and (b) steady-state fluorescence spectra of **1** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**1**] = 1×10^{-5}M, [M(I/II/III)] =1×10^{-4}M in all the cases. Fluorescence (Fluo.): [**1**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 1×10^{-5}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

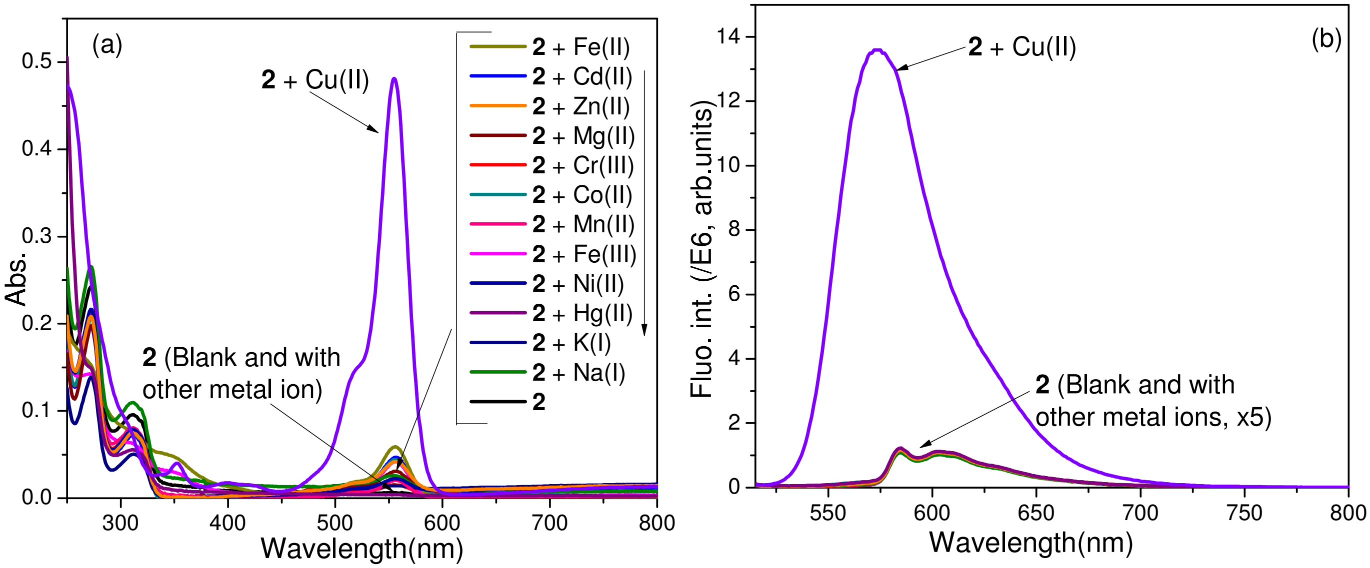


Fig. S41: (a) Absorption and (b) steady-state fluorescence spectra of **2** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**2**] = 1×10^{-5}M, [M(I/II/III)] =1×10^{-4}M in all the cases. Fluorescence (Fluo.): [**2**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 1×10^{-5}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

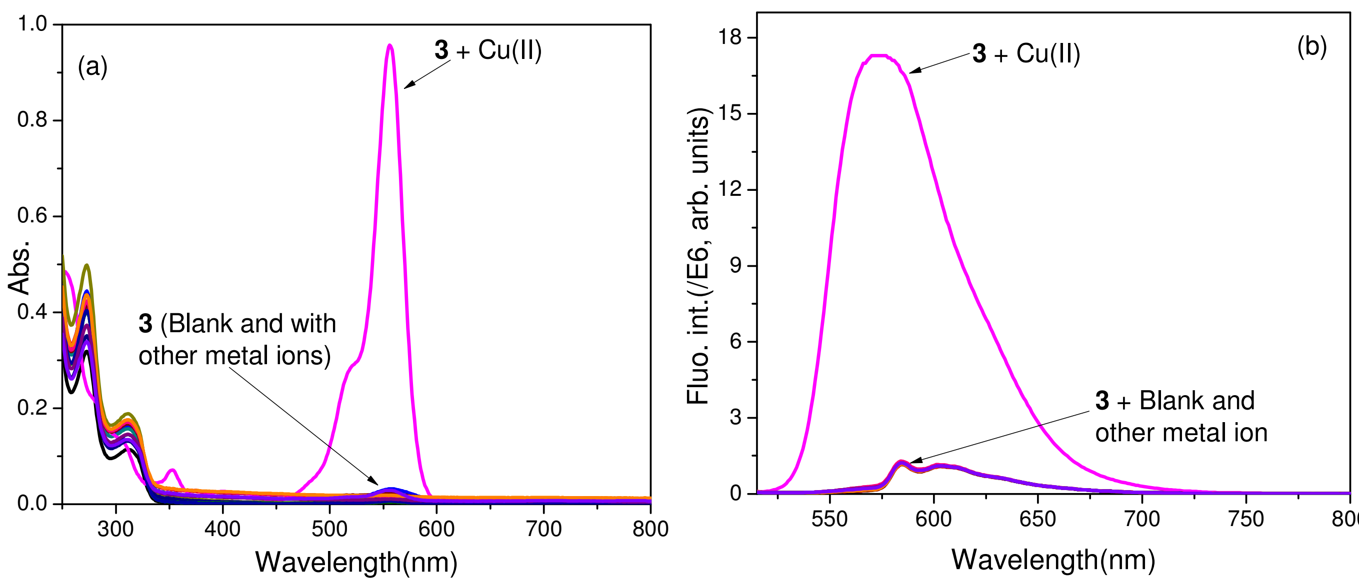


Fig. S42: (a) Absorption and (b) steady-state fluorescence spectra of **3** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**3**] = 1×10^{-5}M, [M(I/II/III)] =1×10^{-4}M in all the cases. Fluorescence (Fluo.): [**3**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 1×10^{-5}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

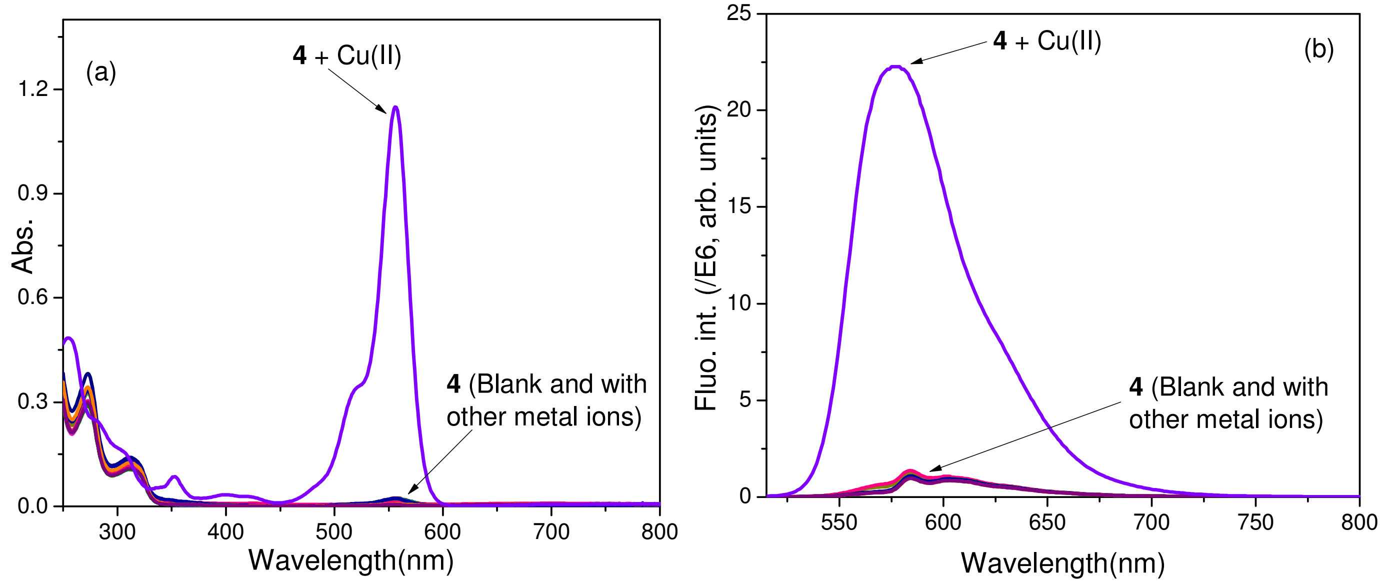


Fig. S43: (a) Absorption and (b) steady-state fluorescence spectra of **4** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**4**] = 1×10^{-5}M, [M(I/II/III)] =1×10^{-4}M in all the cases. Fluorescence (Fluo.): [**4**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 1×10^{-5}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

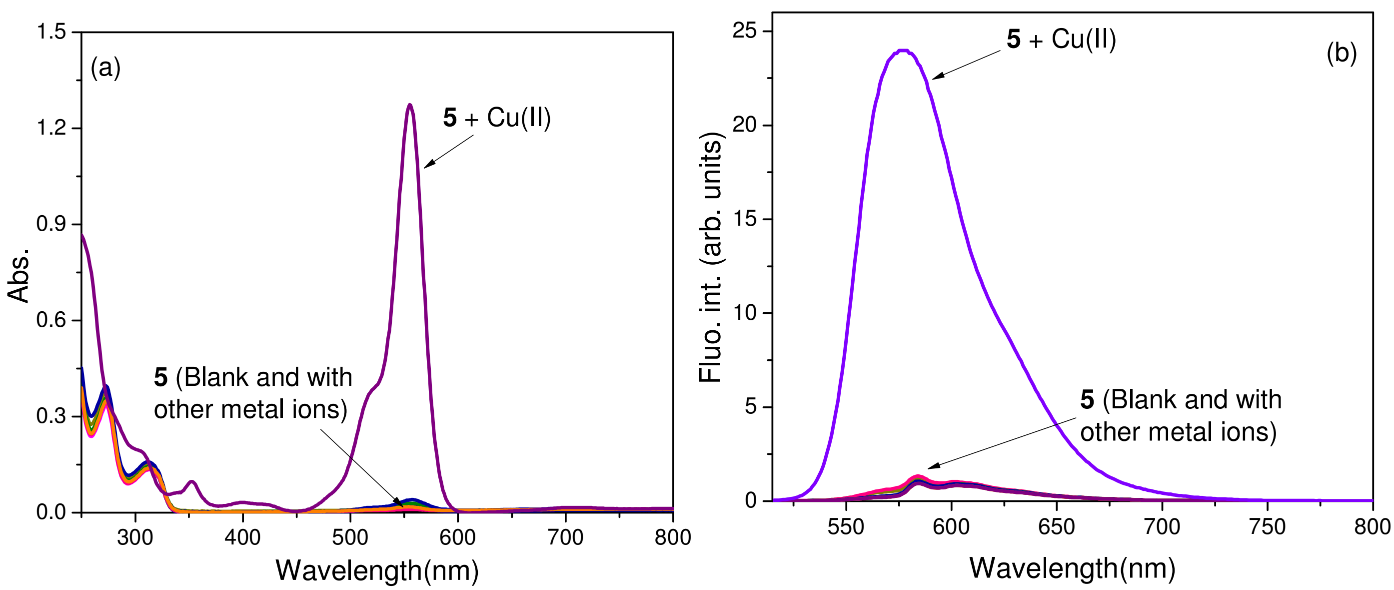


Fig. S44: (a) Absorption and (b) steady-state fluorescence spectra of **5** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**5**] = 1×10^{-5}M, [M(I/II/III)] =1×10^{-4}M in all the cases. Fluorescence (Fluo.): [**5**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 1×10^{-5}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

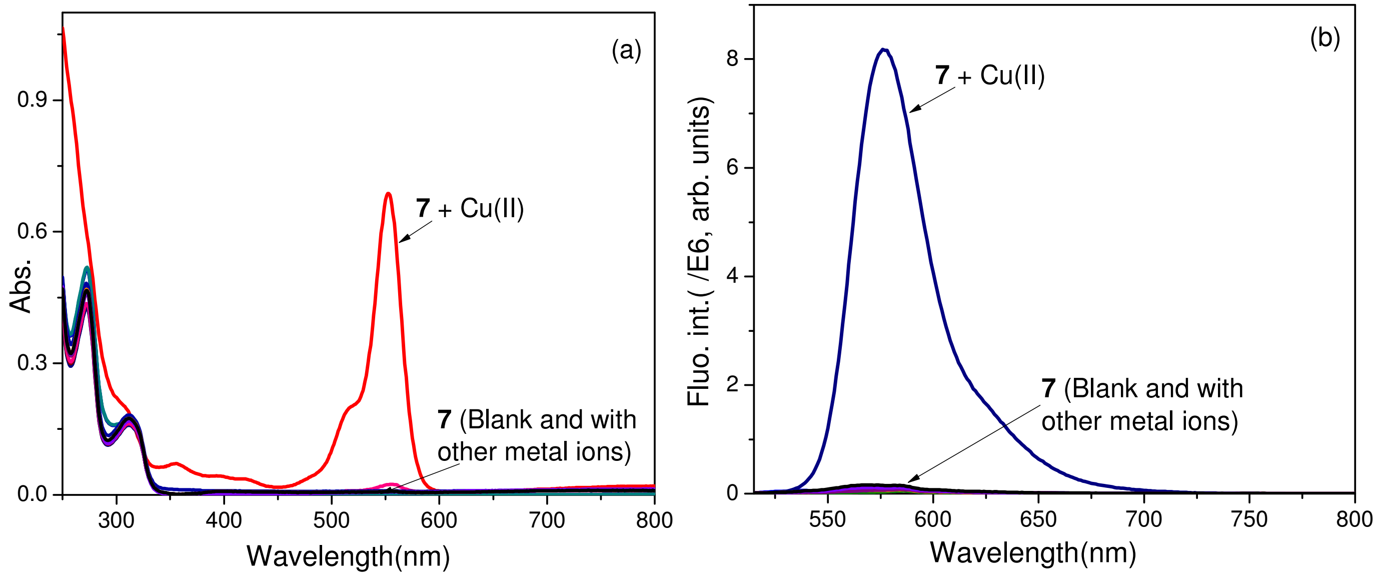


Fig. S45: (a) Absorption and (b) steady-state fluorescence spectra of **7** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**7**] = 1×10^{-5}M, [M(I/II/III)] =5×10^{-5}M in all the cases. Fluorescence (Fluo.): [**7**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 5×10^{-6}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

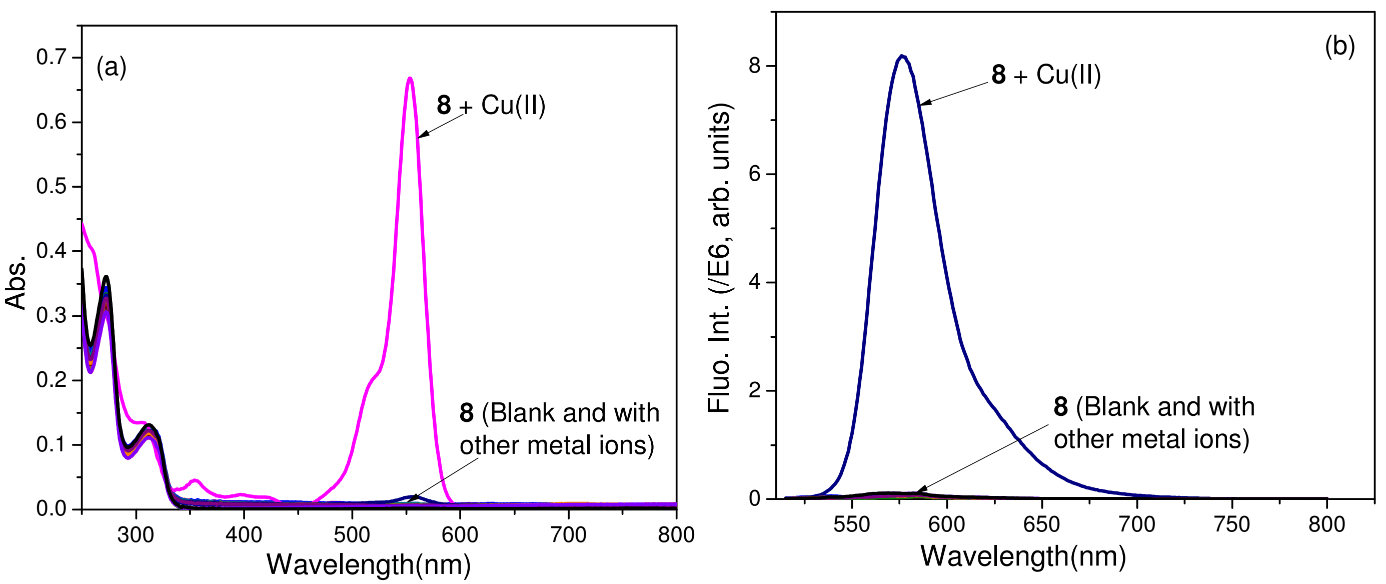


Fig. S46: (a) Absorption and (b) steady-state fluorescence spectra of **8** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**8**] = 1×10^{-5}M, [M(I/II/III)] =5×10^{-5}M in all the cases. Fluorescence (Fluo.): [**8**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 5×10^{-6}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm.

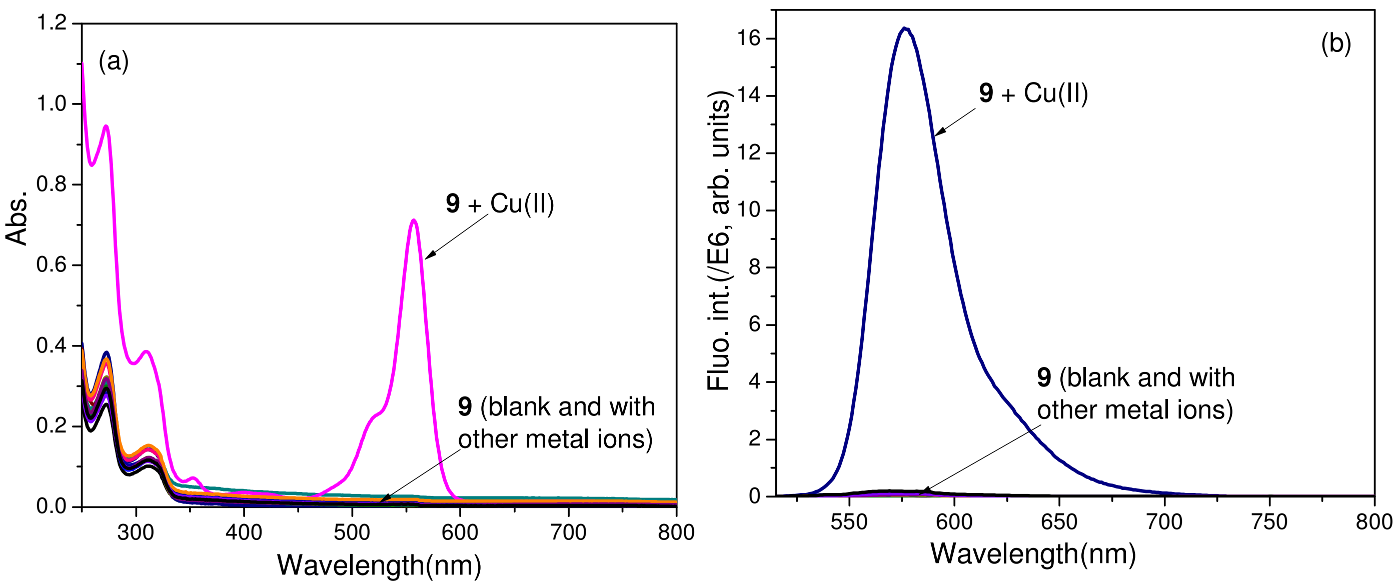


Fig. S47: (a) Absorption and (b) steady-state fluorescence spectra of **9** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**9**] = 1×10^{-5}M, [M(I/II/III)] =5×10^{-5}M in all the cases. Fluorescence (Fluo.): [**9**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 5×10^{-6}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm

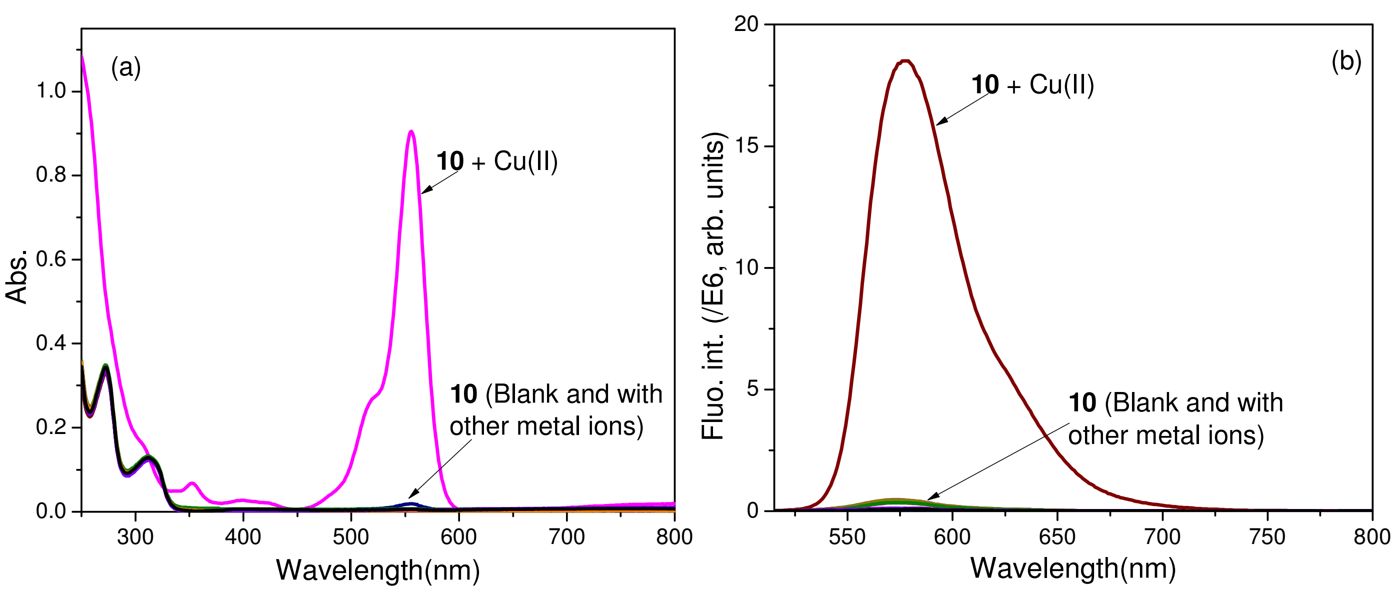


Fig. S48: (a) Absorption and (b) steady-state fluorescence spectra of **10** alone and in presence of various metal ions in EtOH-H_2O(0.1 M PBS, 9:1 v/v) medium. Conditions: Absorption (Abs.): [**10**] = 1×10^{-5}M, [M(I/II/III)] =5×10^{-5}M in all the cases. Fluorescence (Fluo.): [**10**] = 1 $\times10^{-6}$M, [M(I/II/III)] = 5×10^{-6}M, λ_{ex}=500nm, RT, ex. and em. b. p. = 5 nm

Metal ions added: (a) Blank, (b) Cd(II), (c) Co(II), (d) Mn(II), (e) Cu(II), (f) Na(I), (g) K(I), (h) Cr(III) (i) Hg(II), (j) Ni(II), (k) Mg(II), (l) Fe(II), (m) Fe(III), (n) Pb(II) and (o) Zn(II)
Solvent: Buffered Ethanol (EtOH, 0.1M PBS, 9:1 v/v)

Fig. S49: Photograph depicting colorimetric sensing of 1 in presence of various metal ions. [1] = 10μM.

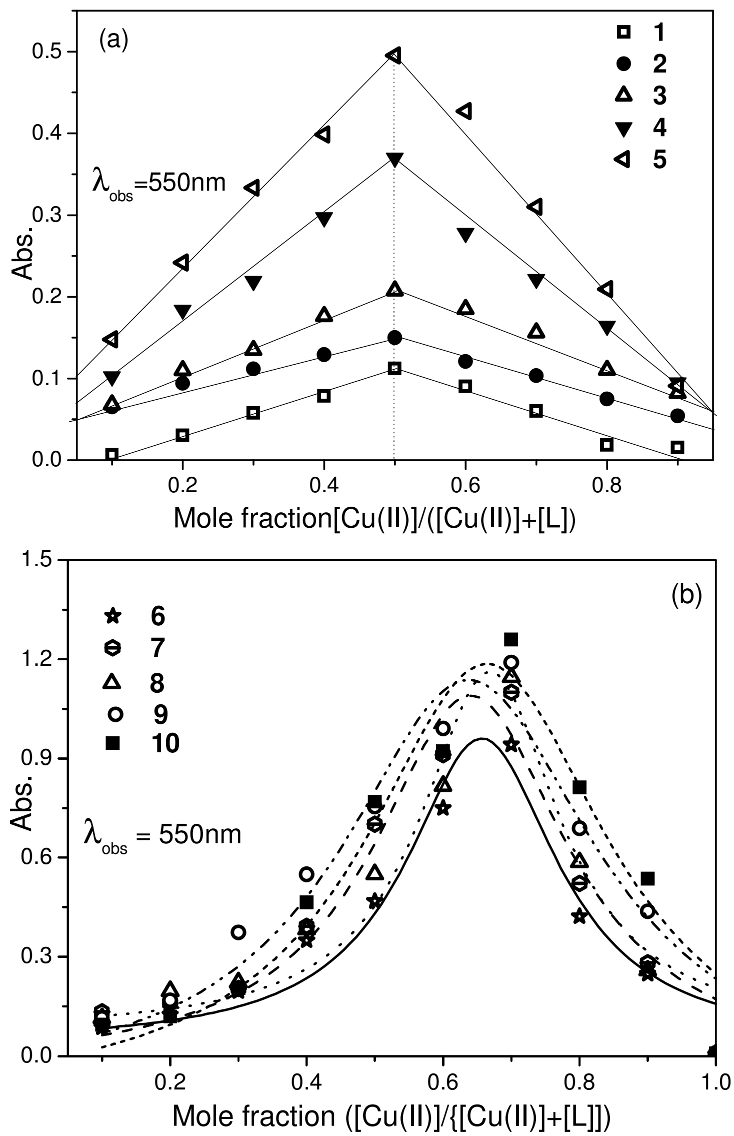


Fig. S50: The plot of absorption of these probes(**L**) with Cu(II) in buffered EtOH (EtOH: 0.1M PBS, 9:1 v/v) medium showing 1:1(for **1-5**) and 2:1(for **6-10**) L-Cu(II) complexation stoichiometry. The absorbances were monitored at 550nm wavelength. [**L**] = 1×10^{-5}M.

Absorption and Fluorescence titration of the probes with Cu(II) ion and association constants(Ka)

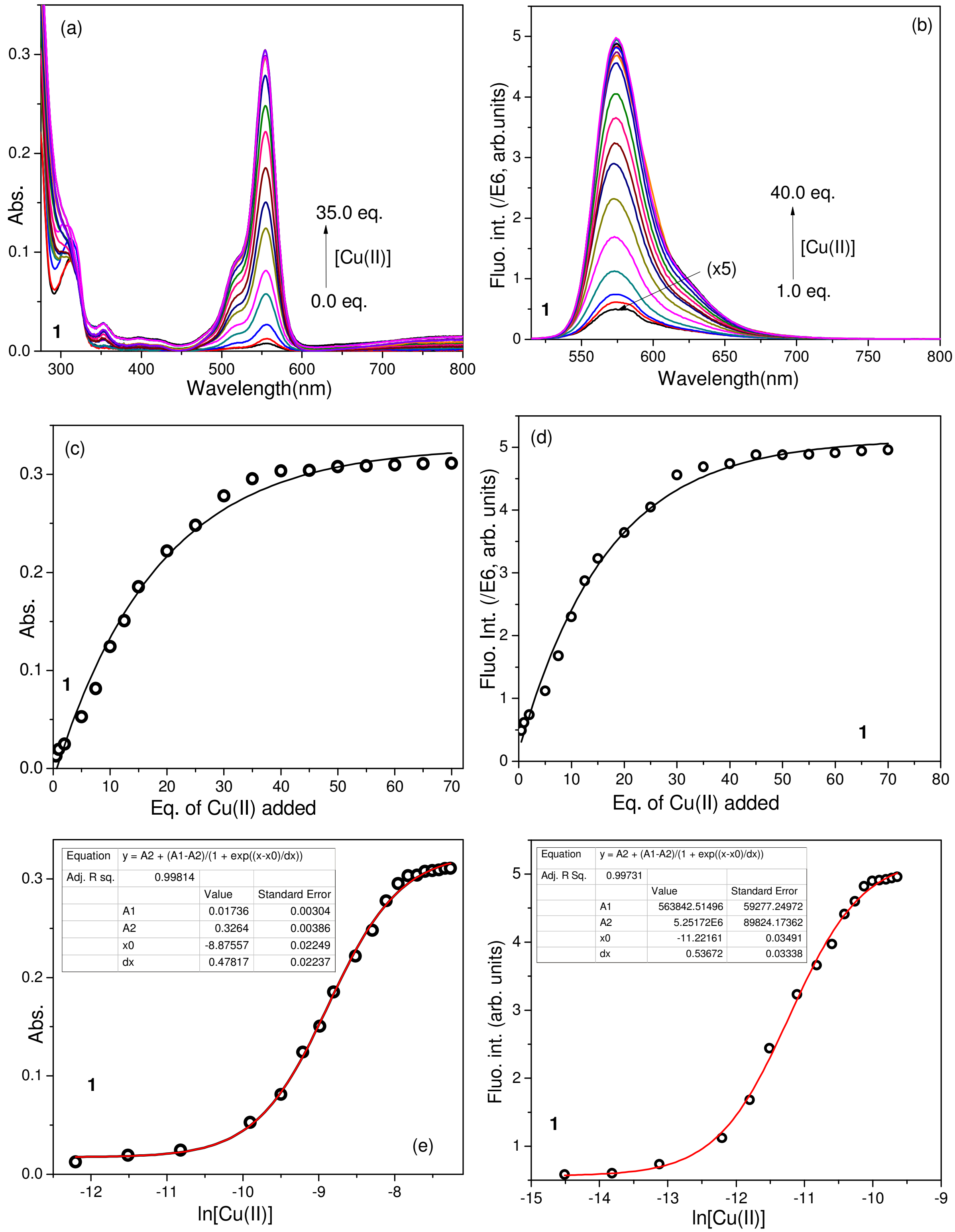


Fig. S51: Absorption (a) and fluorescence(b) titrations of **1** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, their corresponding titration profiles (c and d)and intensity versus concentration(ln[Cu(II)] plots(e and f) for determination of association constants. [**1**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm.

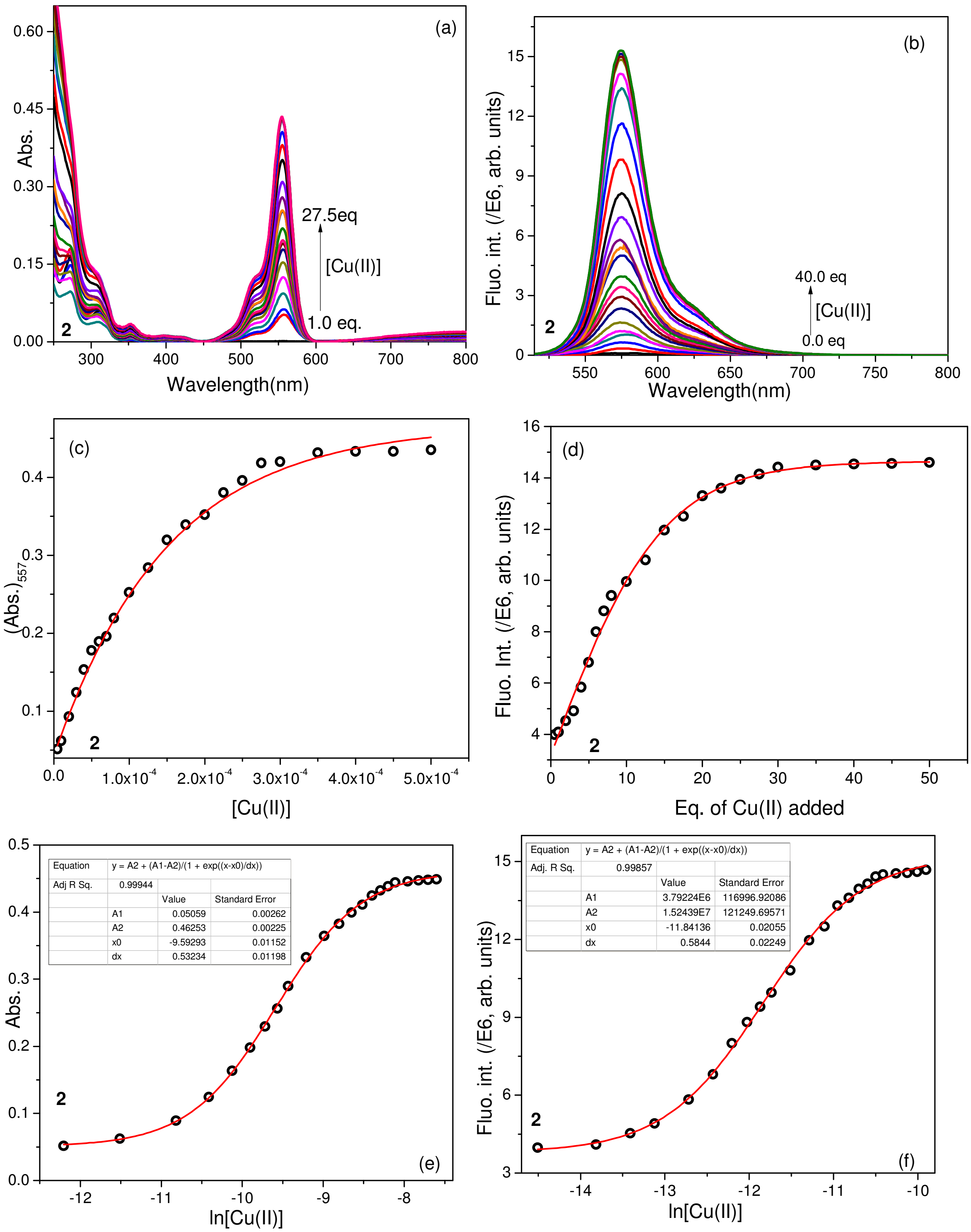


Fig. S52: Absorption (a) and fluorescence(b) titrations of **2** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, their corresponding titration profiles (c and d)and intensity versus concentration(ln[Cu(II)] plots(e and f) for determination of association constants. [**2**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm.

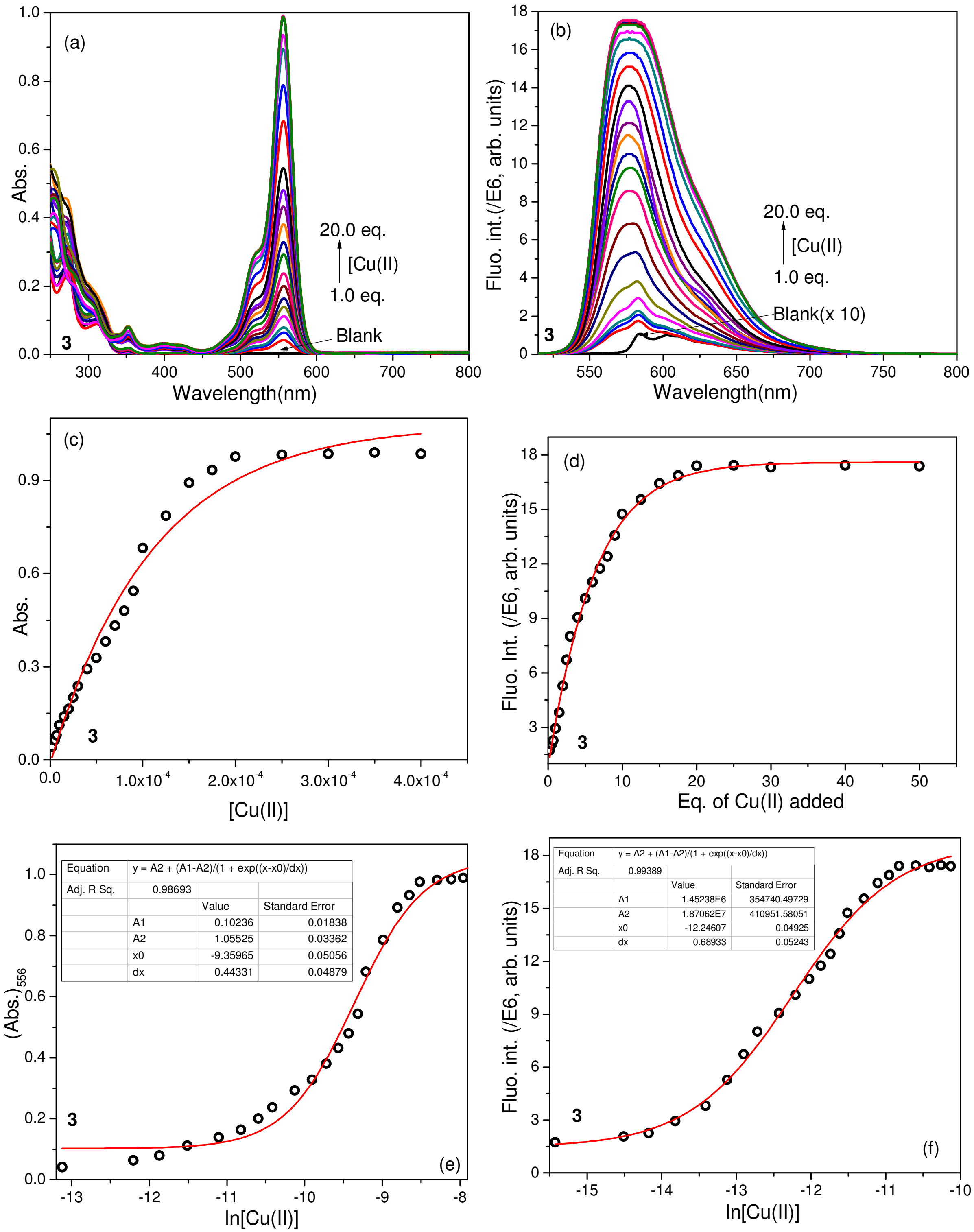


Fig. S53: Absorption (a) and fluorescence(b) titrations of **3** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, their corresponding titration profiles (c and d)and intensity versus concentration(ln[Cu(II)] plots(e and f) for determination of association constants. [**3**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm.

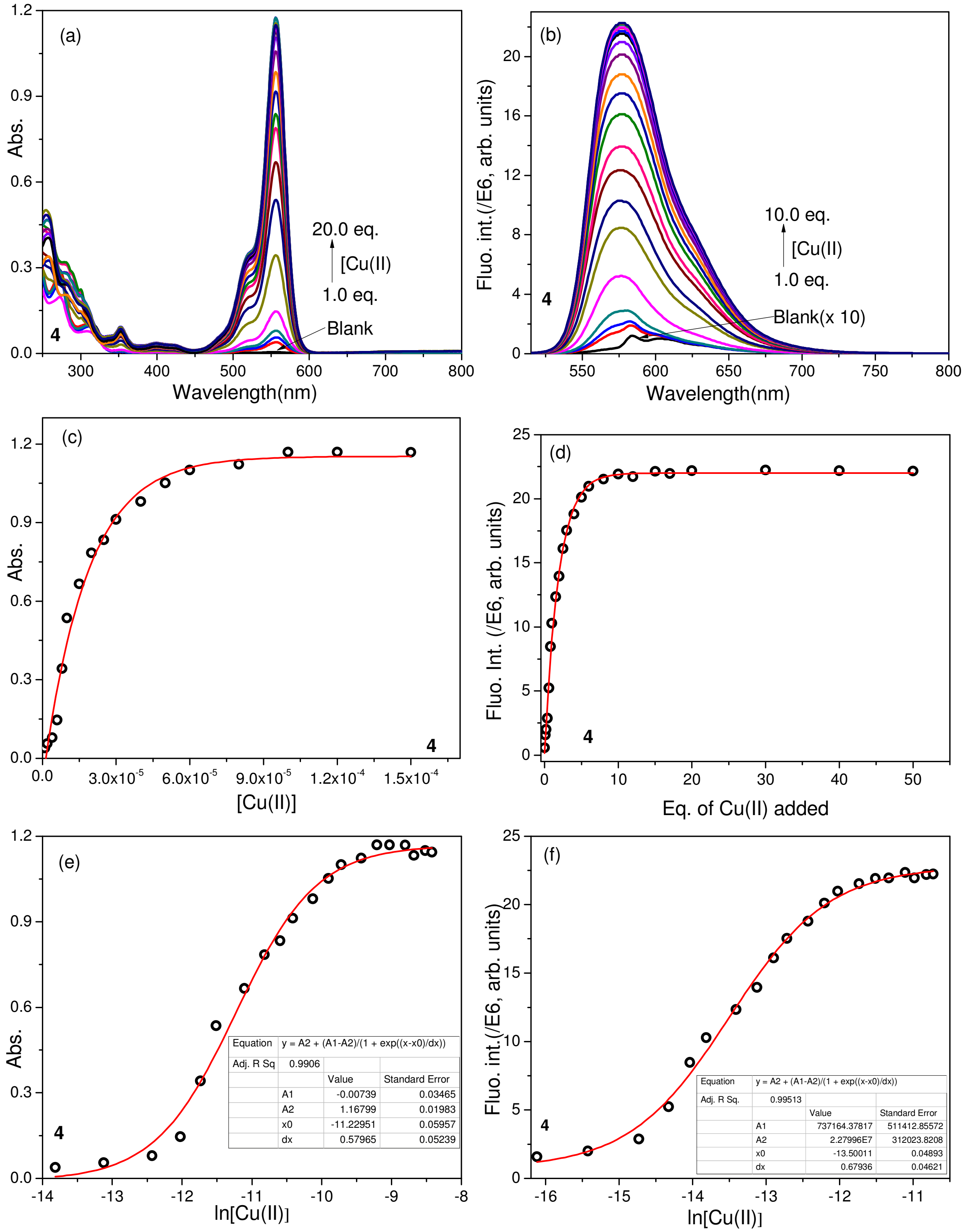


Fig. S54: Absorption (a) and fluorescence(b) titrations of **4** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, their corresponding titration profiles (c and d)and intensity versus concentration(ln[Cu(II)] plots(e and f) for determination of association constants. [**4**] = 0.1µM(abs.), 1µM(fluo.); λex = 500nm, em and ex band pass = 5nm.

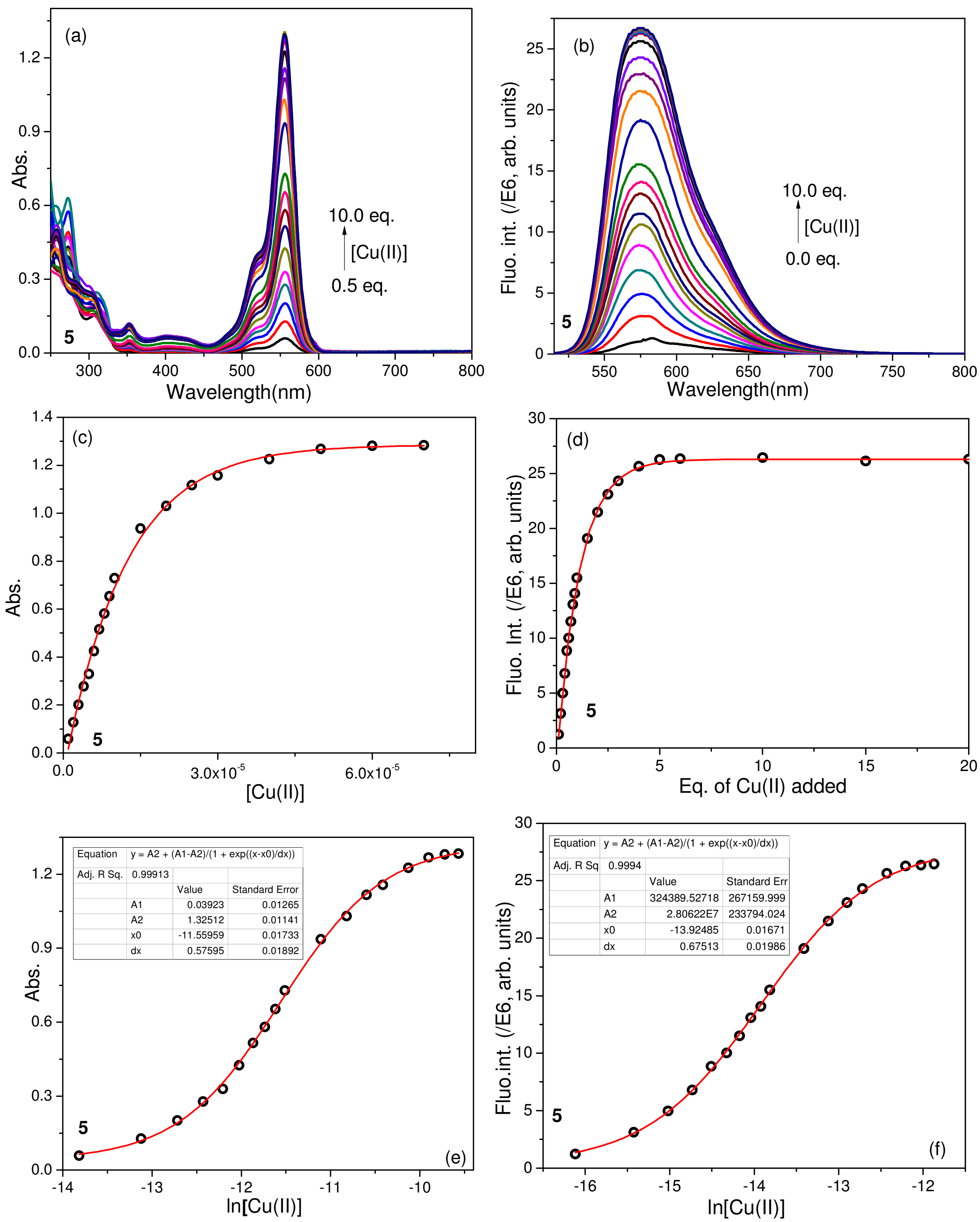


Fig. S55: Absorption (a) and fluorescence(b) titrations of **5** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, their corresponding titration profiles (c and d)and intensity versus concentration(ln[Cu(II)] plots(e and f) for determination of association constant (Ka). [**5**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm.

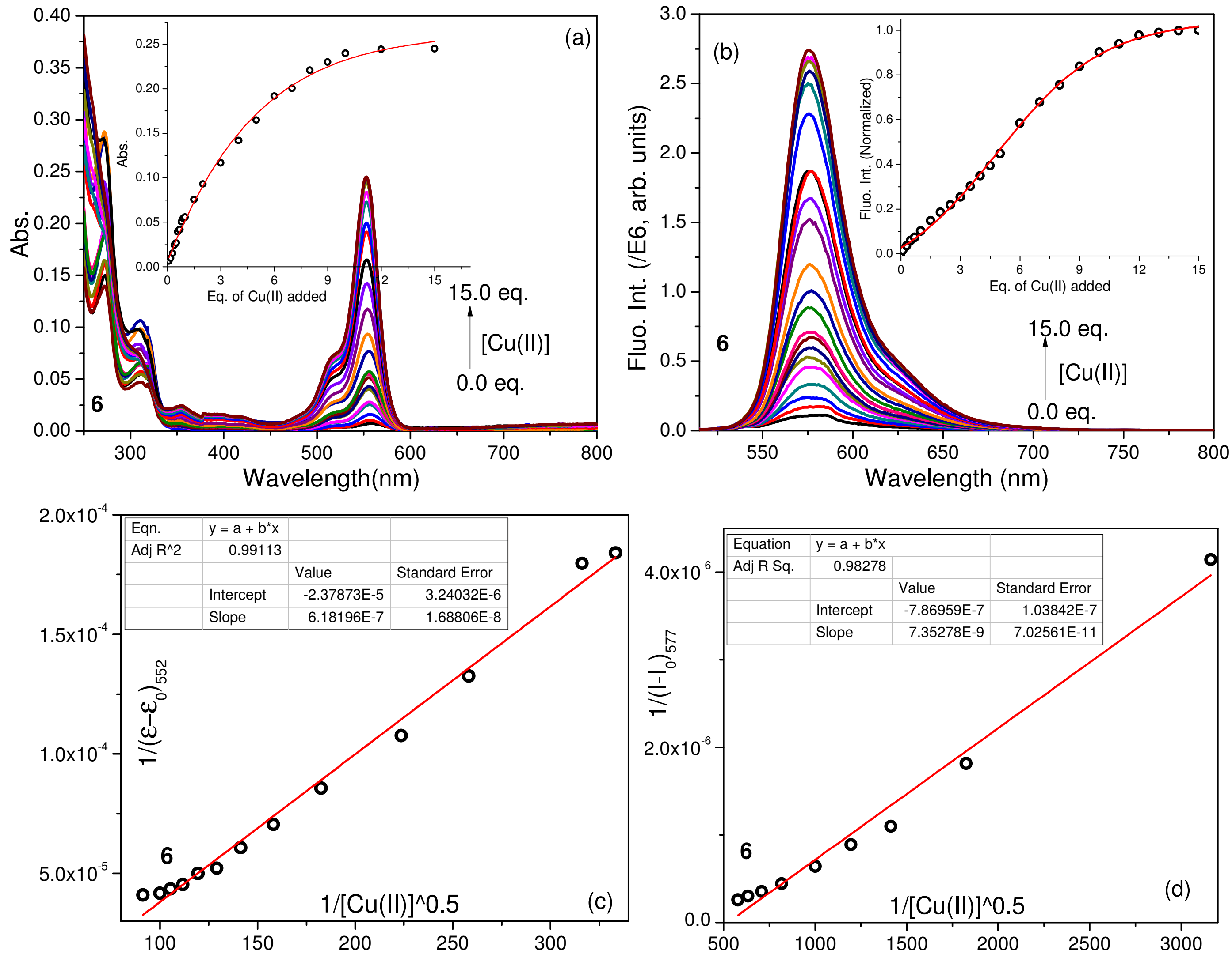


Fig. S56: Absorption (a) and fluorescence(b) titrations of **6** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, (Insets) their corresponding titration profiles. Linear regression to the double reciprocal plot of absorption(c) and fluorescence(d) intensities($1/(X-X_0)$) as a function of concentration ($1/[Cu(II)]^{0.5}$) of metal ion added, which determined Ka. [**6**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm, RT.

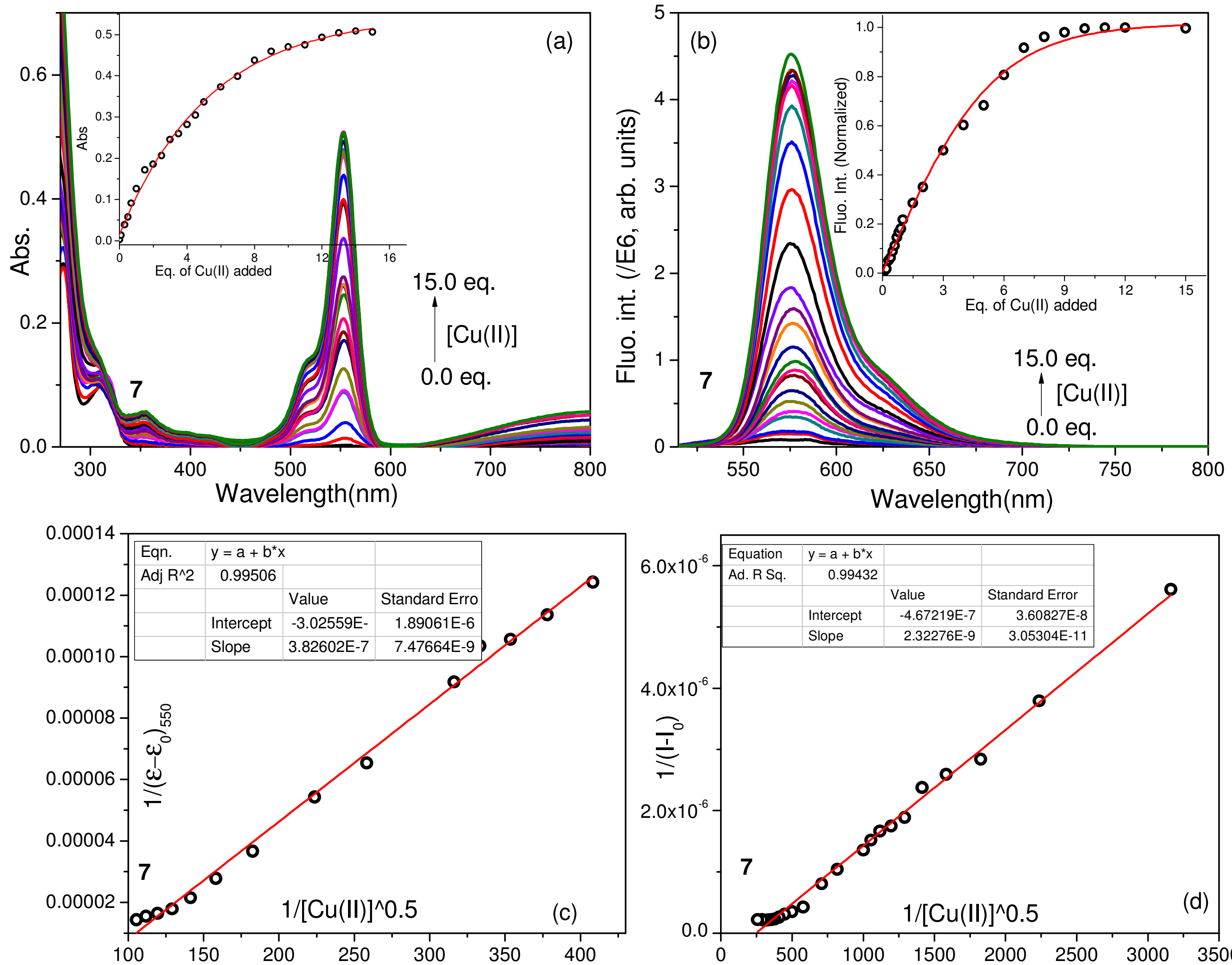


Fig. S57: Absorption (a) and fluorescence (b) titrations of **7** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, (Insets) their corresponding titration profiles. Linear regression to the double reciprocal plot of absorption(c) and fluorescence (d) intensities ($1/(X-X_0)$) as a function of concentration ($1/[Cu(II)]^{0.5}$) of metal ion added, which determined Ka. [**7**] = 0.1μM(abs.), 1.0μM(fluo.); λex = 500nm, em and ex band pass = 5nm, RT.

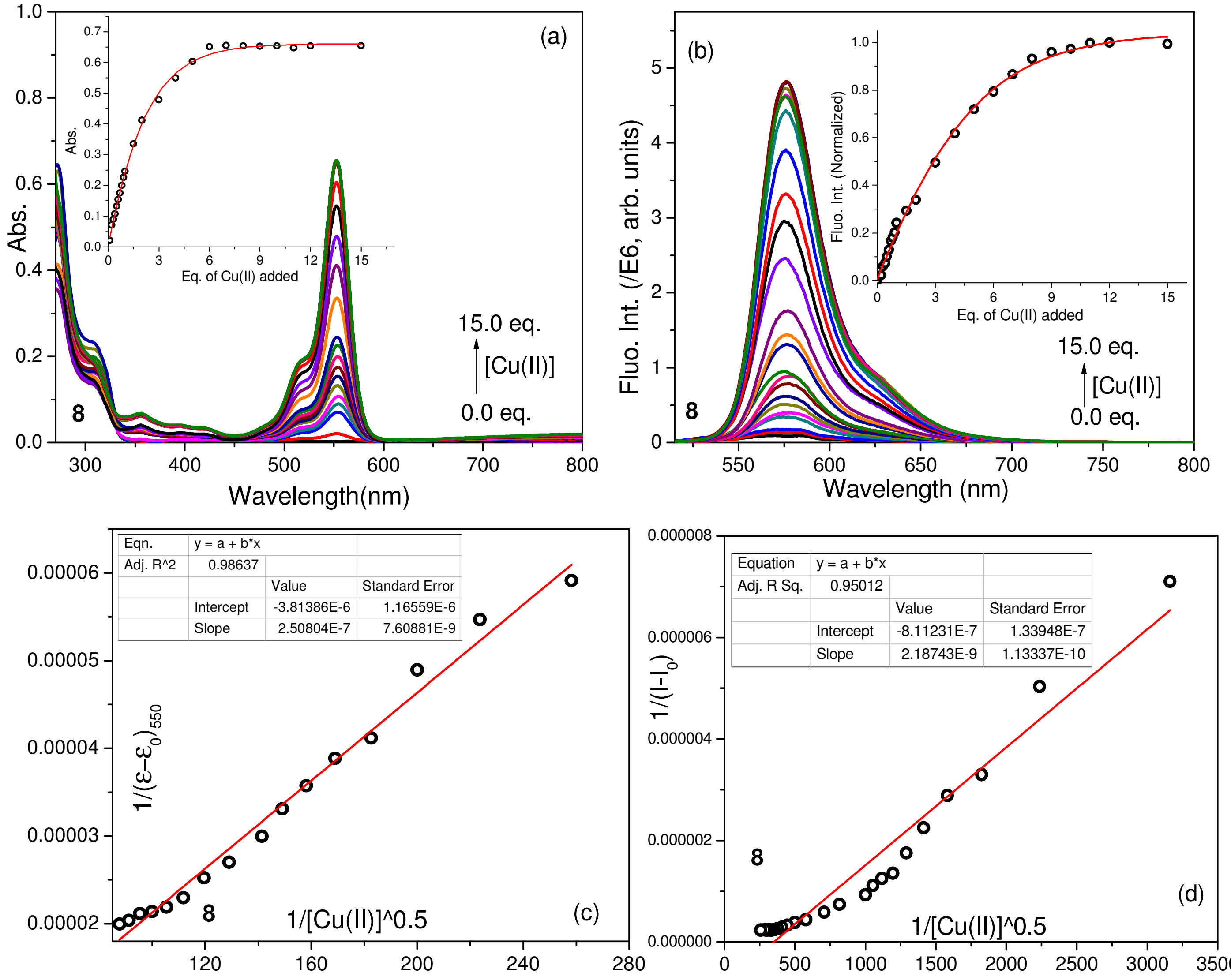


Fig. S58: Absorption (a) and fluorescence (b) titrations of **8** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, (Insets) their corresponding titration profiles. Linear regression to the double reciprocal plot of absorption(c) and fluorescence (d) intensities ($1/(X\text{-}X_0)$) as a function of concentration ($1/[Cu(II)]^{0.5}$) of metal ion added, which determined Ka. [**8**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm, RT.

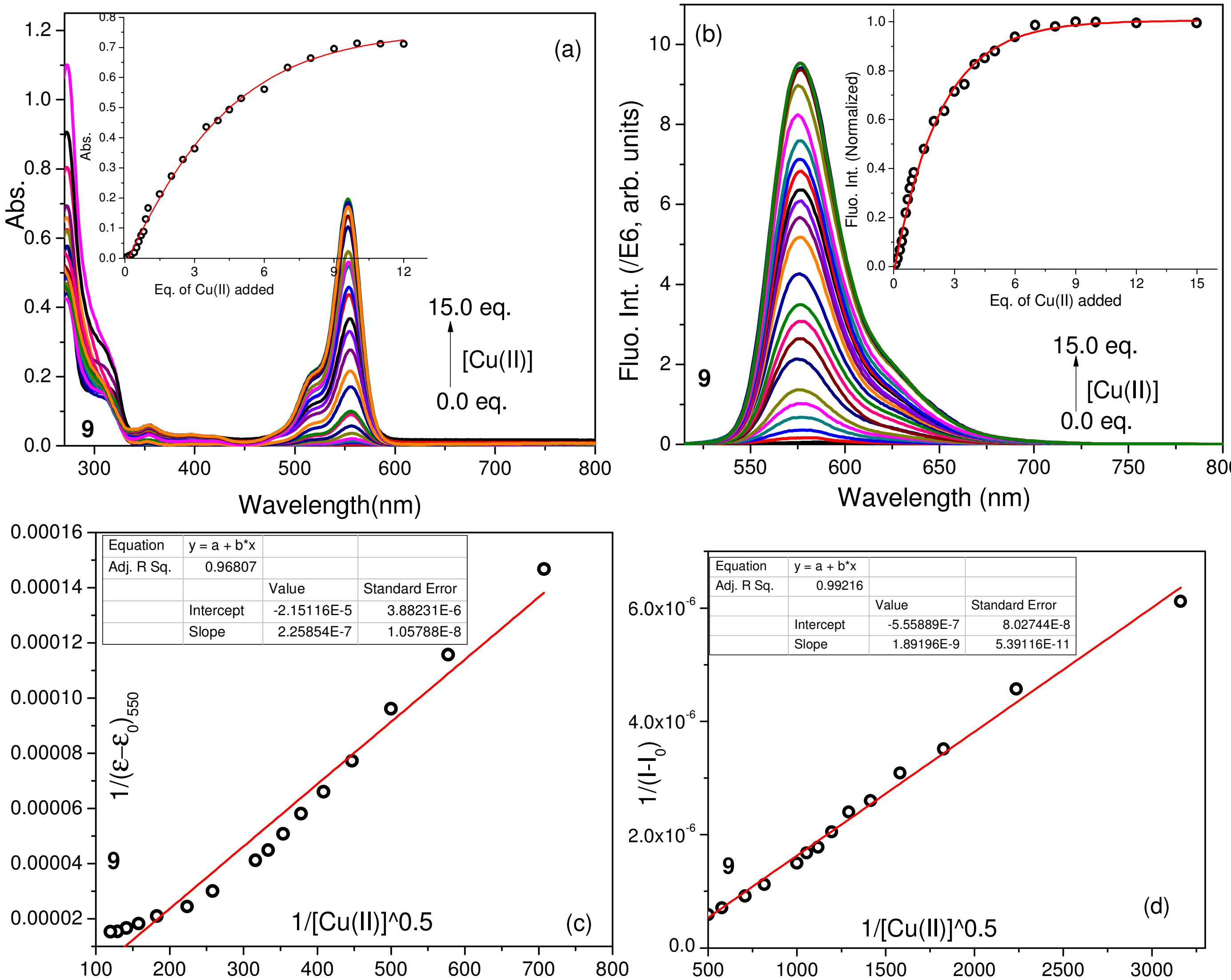
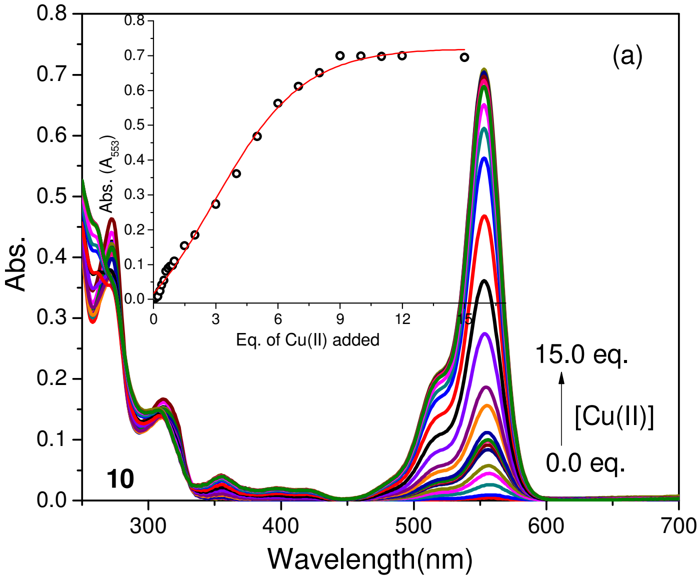
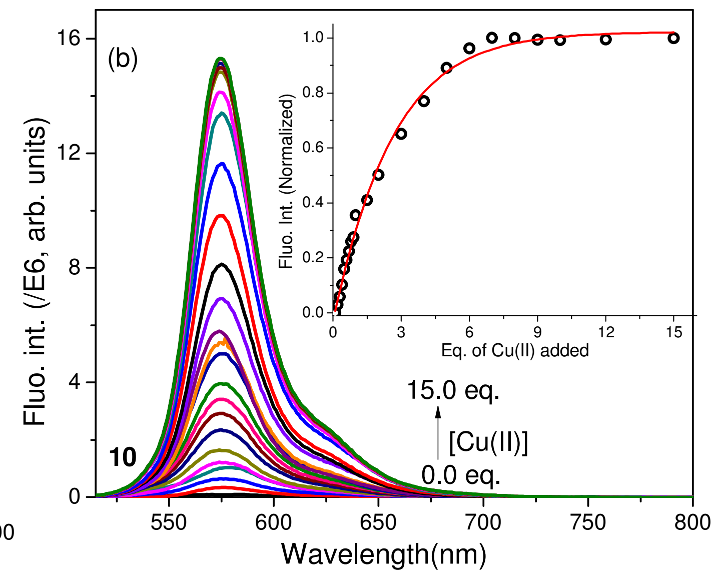
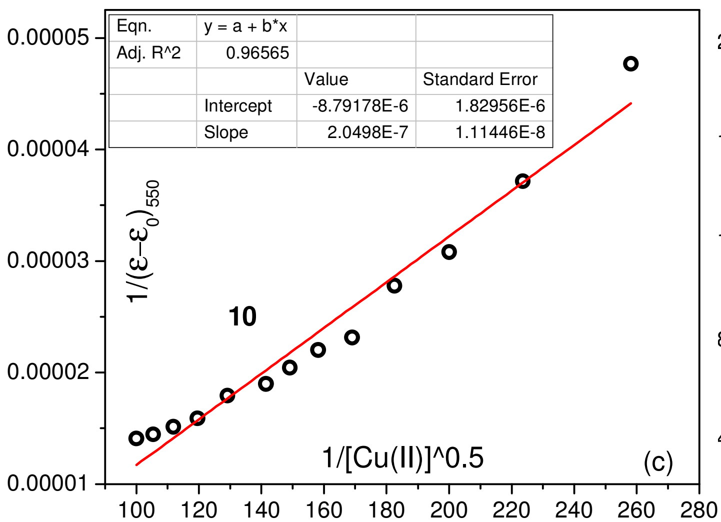


Fig. S59: Absorption (a) and fluorescence (b) titrations of **9** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, (Insets) their corresponding titration profiles. Linear regression to the double reciprocal plot of absorption(c) and fluorescence (d) intensities ($1/(X-X_0)$) as a function of concentration ($1/[Cu(II)]^{0.5}$) of metal ion added, which determined Ka. [**9**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm, RT.







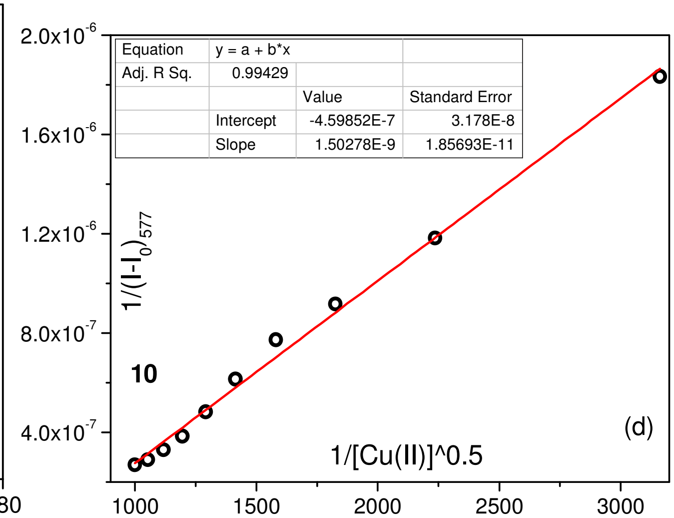


Fig. S60: Absorption (a) and fluorescence (b) titrations of **10** with Cu(II) ions in EtOH-H_2O(0.1M PBS, 9:1 v/v) medium, (Insets) their corresponding titration profiles. Linear regression to the double reciprocal plot of absorption(c) and fluorescence (d) intensities ($1/(X-X_0)$) as a function of concentration ($1/[Cu(II)]^{0.5}$) of metal ion added, which determined Ka. [**10**] = 0.1μM(abs.), 1μM(fluo.); λex = 500nm, em and ex band pass = 5nm, RT.

(a)

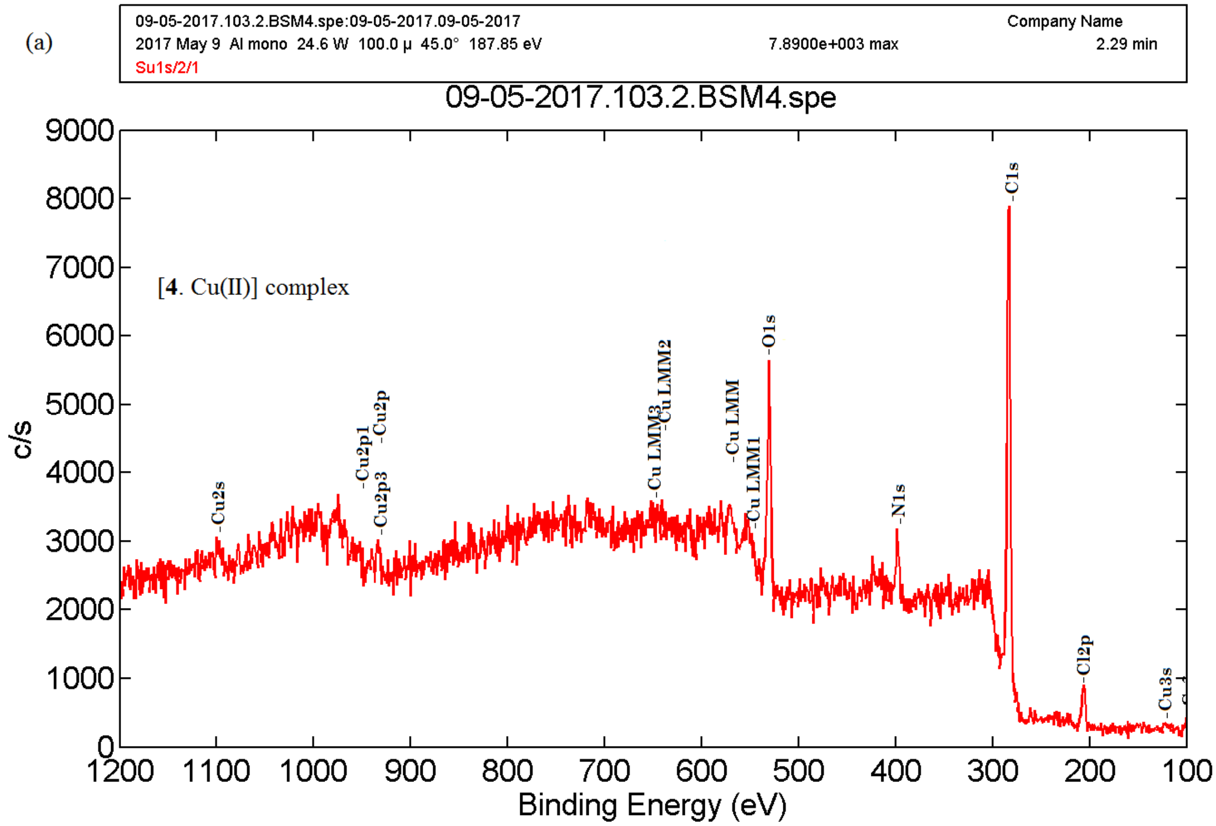


Fig. S61: XPS spectra (wide scan) of Cu(II) complex of **4**.

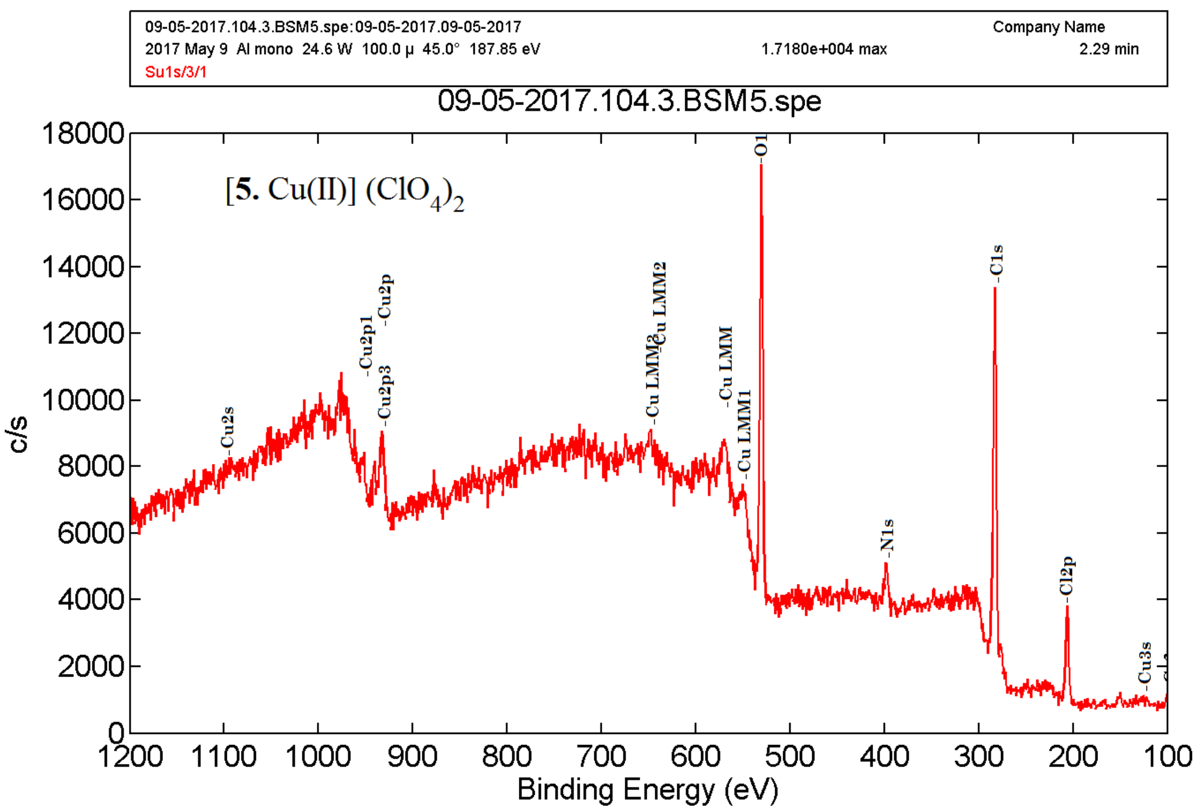


Fig. S62: XPS spectra (wide scan) of Cu(II) complex of **5**.

(b)

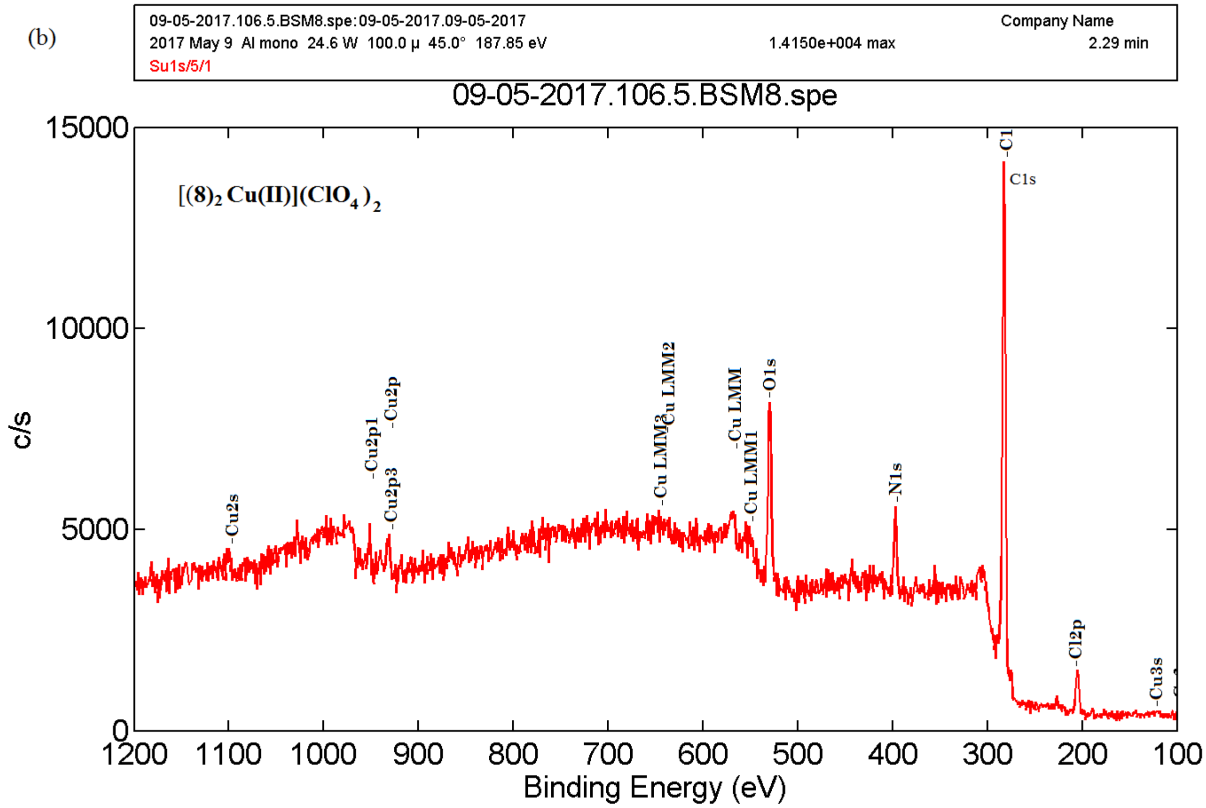


Fig. S63: XPS spectra (wide scan) of Cu(II) complex of **8**.

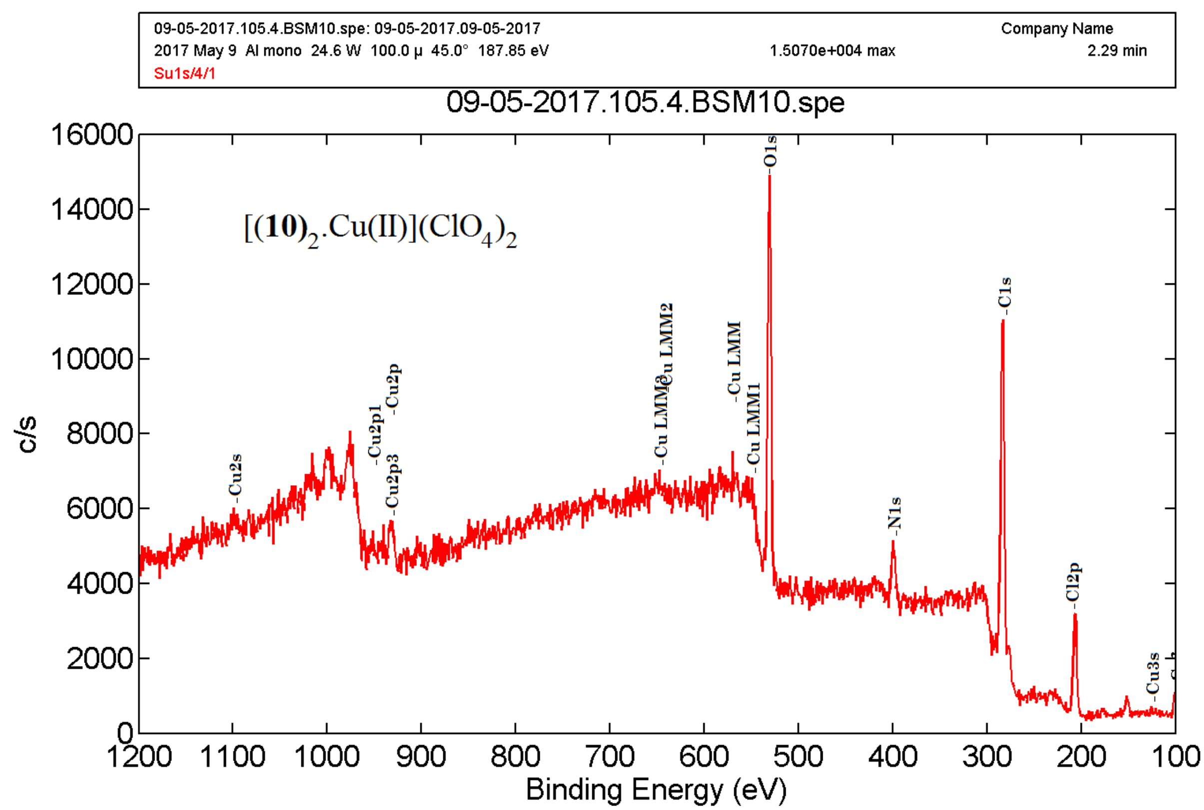


Fig. S64: XPS spectra (wide scan) of Cu(II) complex of **10**.

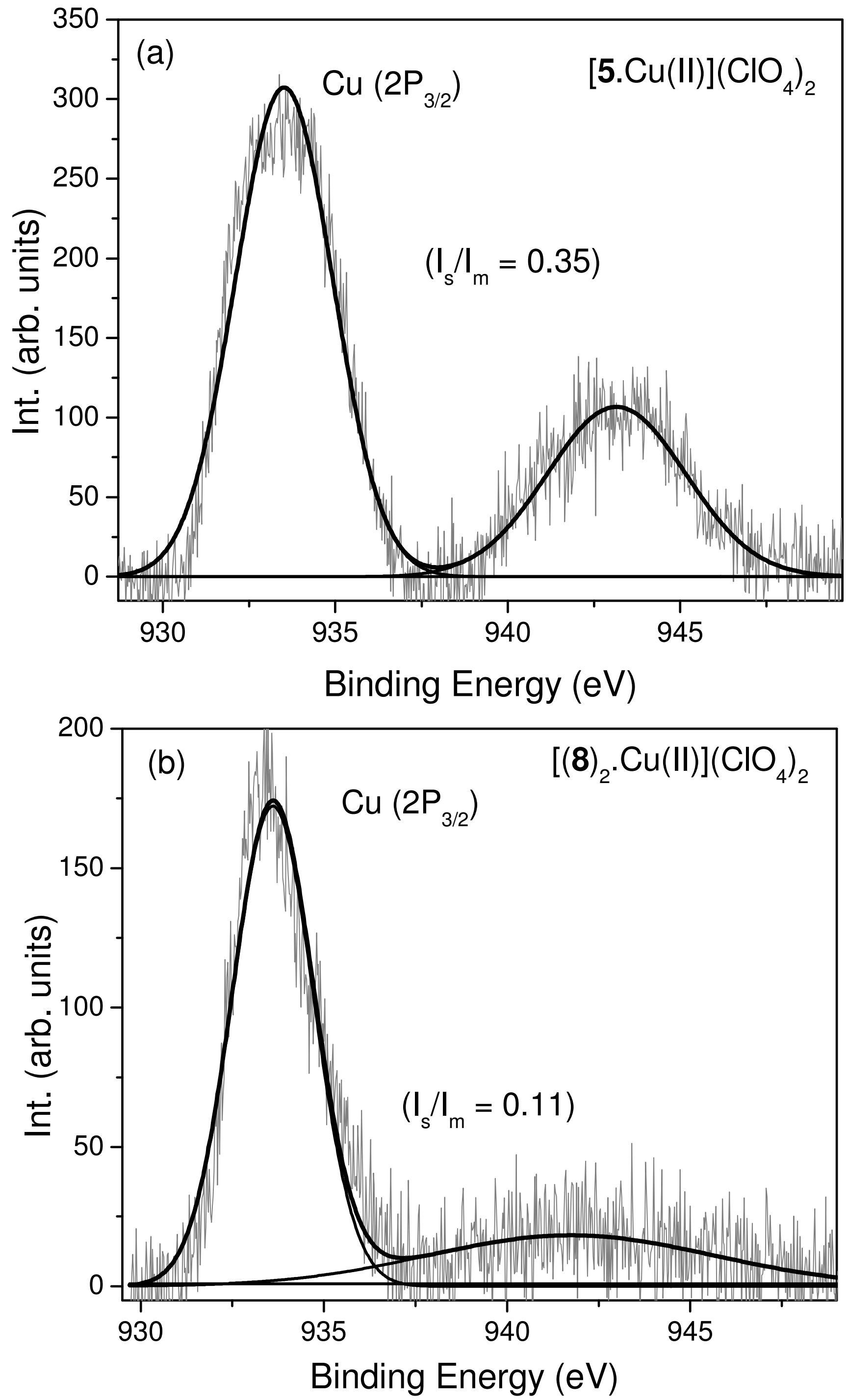


Fig. S65: XPS spectral profile and corresponding component fitting of Cu($2P_{3/2}$) region in Cu(II)-complexes of (a) **5** and (b) **8**.

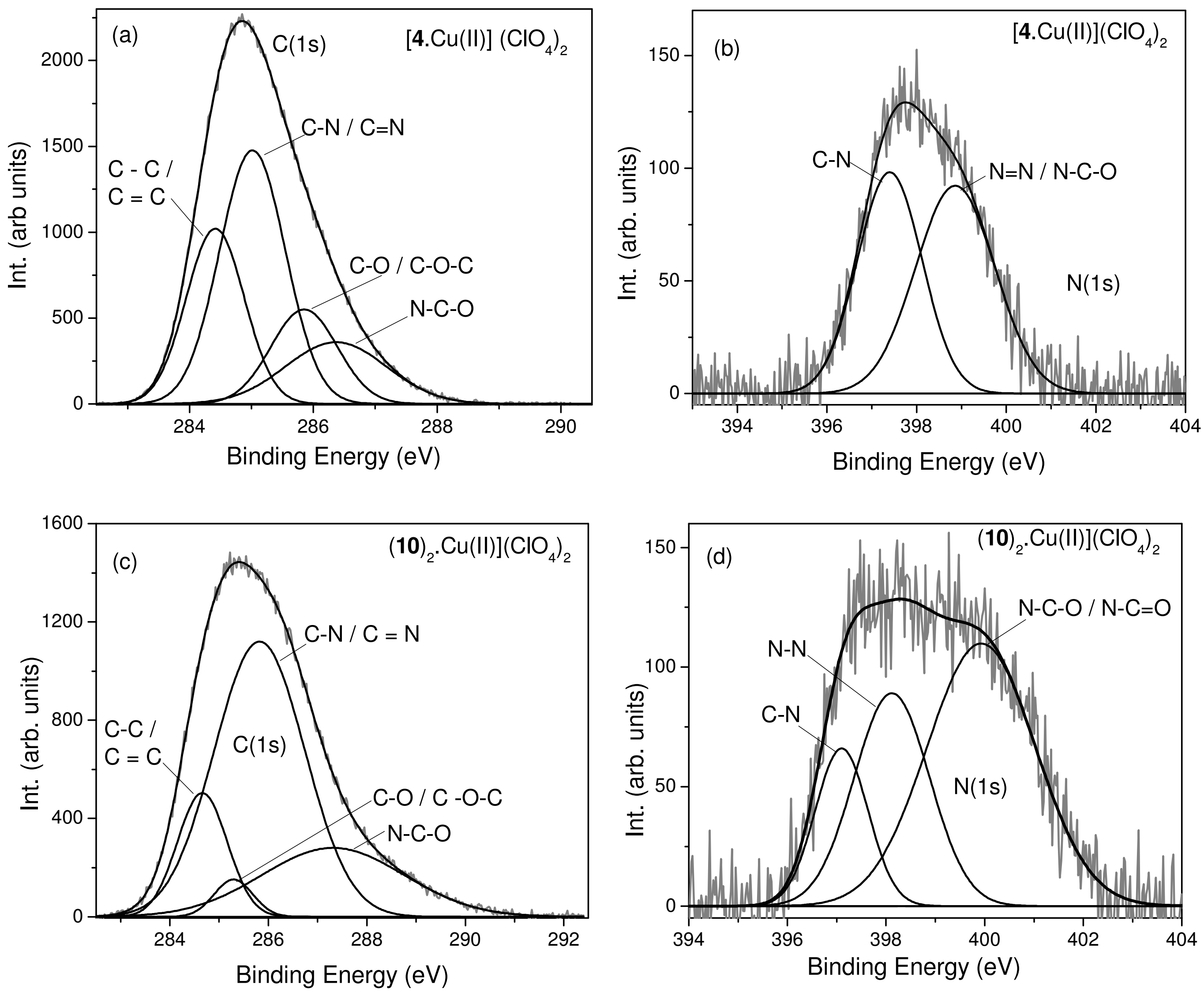


Fig. S66: XPS spectral profile and corresponding component fitting of (a) C(1s) and (b) N(1s) region in [**4**.Cu(II)] $(ClO_4)_2$-complexes, similar that of (c) C(1s) and (d) N(1s) region in [(**10**)$_2$.Cu(II)] $(ClO_4)_2$