Supporting Information

Reduced fluorenoazomethine based photoluminescence turn-on sensors for transition metal ions

Pradip Kr. Dutta, Snigdha Panda*, Debangshu Chaudhuri*, Sanjio S. Zade*

Department of Chemical Sciences,

Indian Institute of Science Education and Research Kolkata

PO: BCKV campus main office, Mohanpur 741252, Nadia, West Bengal, India

Email: sanjiozade@iiserkol.ac.in, dchaudhuri@iiserkol.ac.in, snigdha@iiserkol.ac.in

Fax: +91-33-25873020

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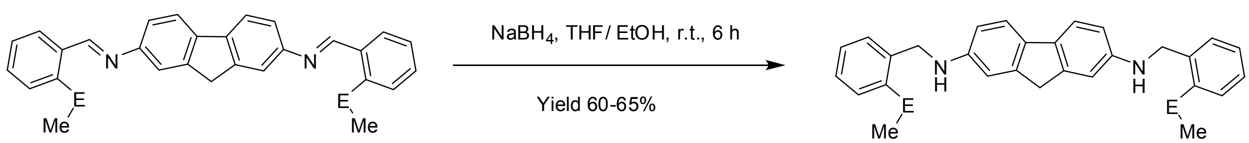
Synthesis and characterization details

General. All the reagents were purchased from Aldrich / Merck and used without further purification. AR grade THF was passed through alumina to remove hydrogen peroxide and partial drying and kept over the molecular sieves. AR grade acetonitrile was distilled from P_2O_5 and kept over molecular sieves. All optical measurements were carried out at room temperature. UV-vis spectra were recorded on a Hitachi U4100 spectrophotometer, with a quartz cuvette (path length, 1 cm). The fluorescence spectra were recorded with a Fluoromax-3 spectrofluorimeter. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-FT NMR-AL 400 MHz spectrophotometer using $CDCl_3$/DMSO-d_6 as solvent and tetramethylsilane $SiMe_4$ as internal standards. UV-vis studies were performed in THF AR grade. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s=singlet, d=doublet, br=broad singlet, m= multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60-120 mesh) was used for column chromatography. Solutions of compounds **3**, and **4** and perchlorate salts were prepared in THF.



E = S **1**
E = Se **2**

E = S **3**
E = Se **4**

Syntheses

Compound 3: Sodium borohydride (0.875 g, 23.12 mmol) was added portion-wise to compound **1**[1] (0.5 g, 1.08 mmol) in C_2H_5OH:THF mixture (1:1) at room temperature under inert atmosphere. After 6 hour stirring at room temperature, the solvent was evaporated and the residue washed with saturated brine solution and was extracted with DCM to get light yellowish crystalline solid. Yield: 313 mg (62%); Mp: 137.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.70 (s, 1H), 4.06 (br, 1H, NH),.4.42 (s, 2H), 6.60 (dd, 1H), 6.78 (s, 1H), 7.13 (m, 1H), 7.26 (m, 2H), 7.38 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.74, 36.99, 46.75, 109.74, 111.90, 119.10, 125.05, 125.63, 127.81, 128.15, 132.94, 137.02, 137.16, 144.01, 146.21; HRMS(ESI): $[M]^+$: 468.1694 (calculated) 468.1633 (found).

Compound **4** was analogously prepared starting from **2**1.

Compound 4: Light yellowish crystalline solid. Yield: 65%; Mp: 142.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.72 (s, 1H), 3.99 (br, 1H, NH),.4.42 (s, 2H), 6.61 (dd, 1H), 6.79 (s, 1H), 7.20 (m, 2H), 7.40 (m, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.95, 37.00, 48.78, 109.75, 111.90, 119.12, 126.12, 128.02, 128.41, 129.63, 132.48, 133.01, 139.11, 144.01, 146.07; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 207.25; HRMS(ESI): $[M]^+$: 564.0583 (calculated) 564.0563 (found).

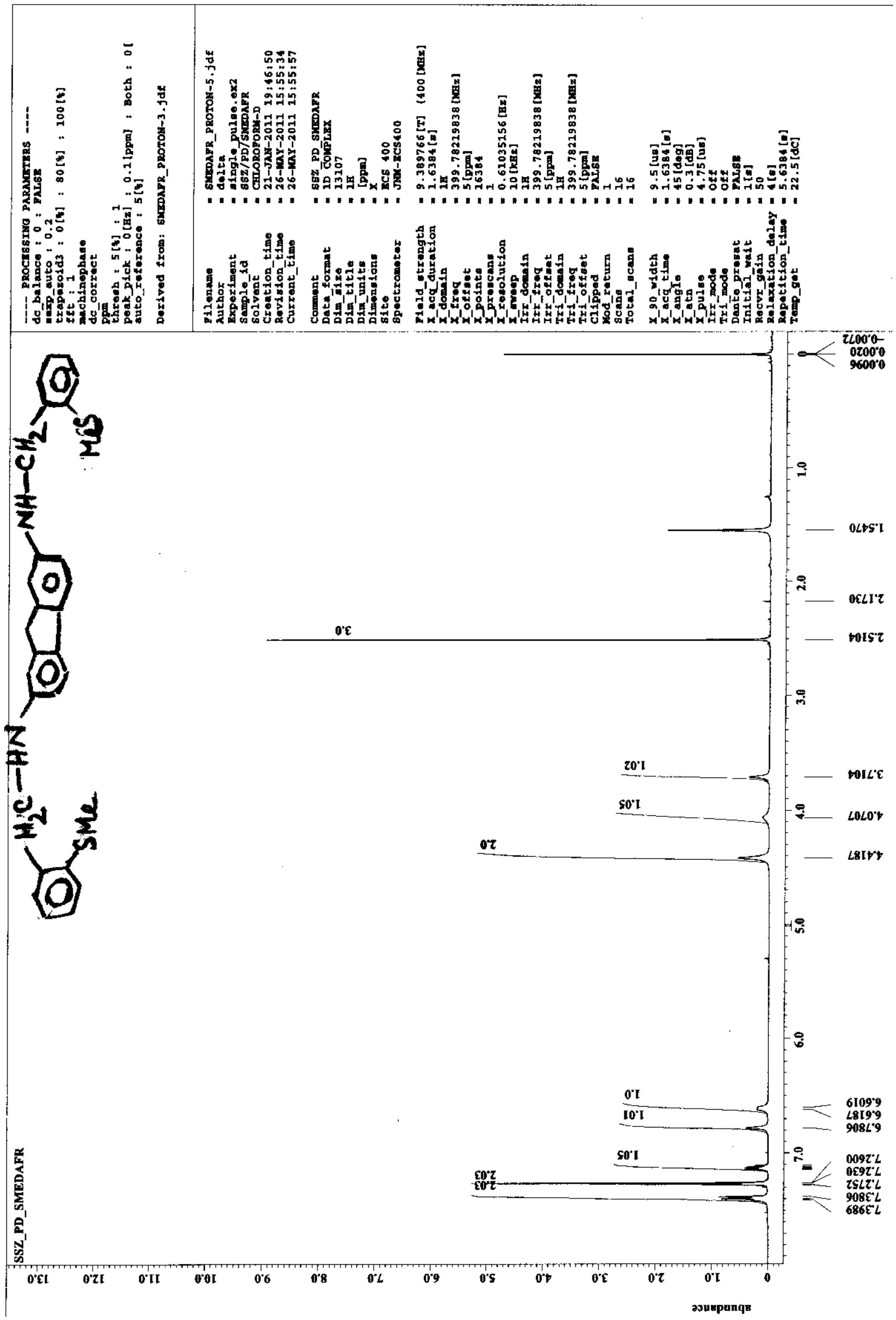


Fig. S1 ^{1}H NMR spectrum of reduced podand **3**.

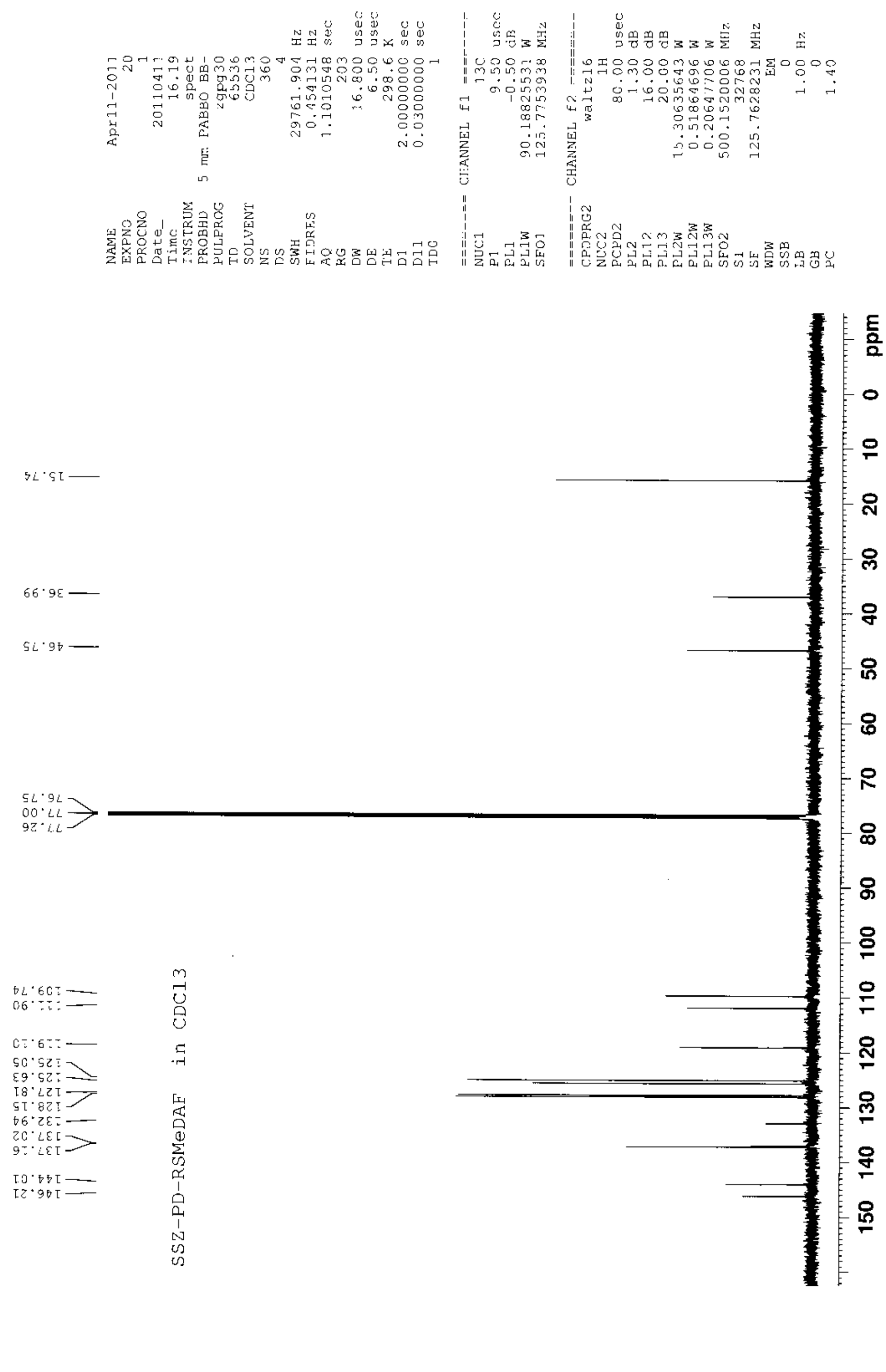


Fig. S2 ^{13}C NMR spectrum of reduced podand **3**.

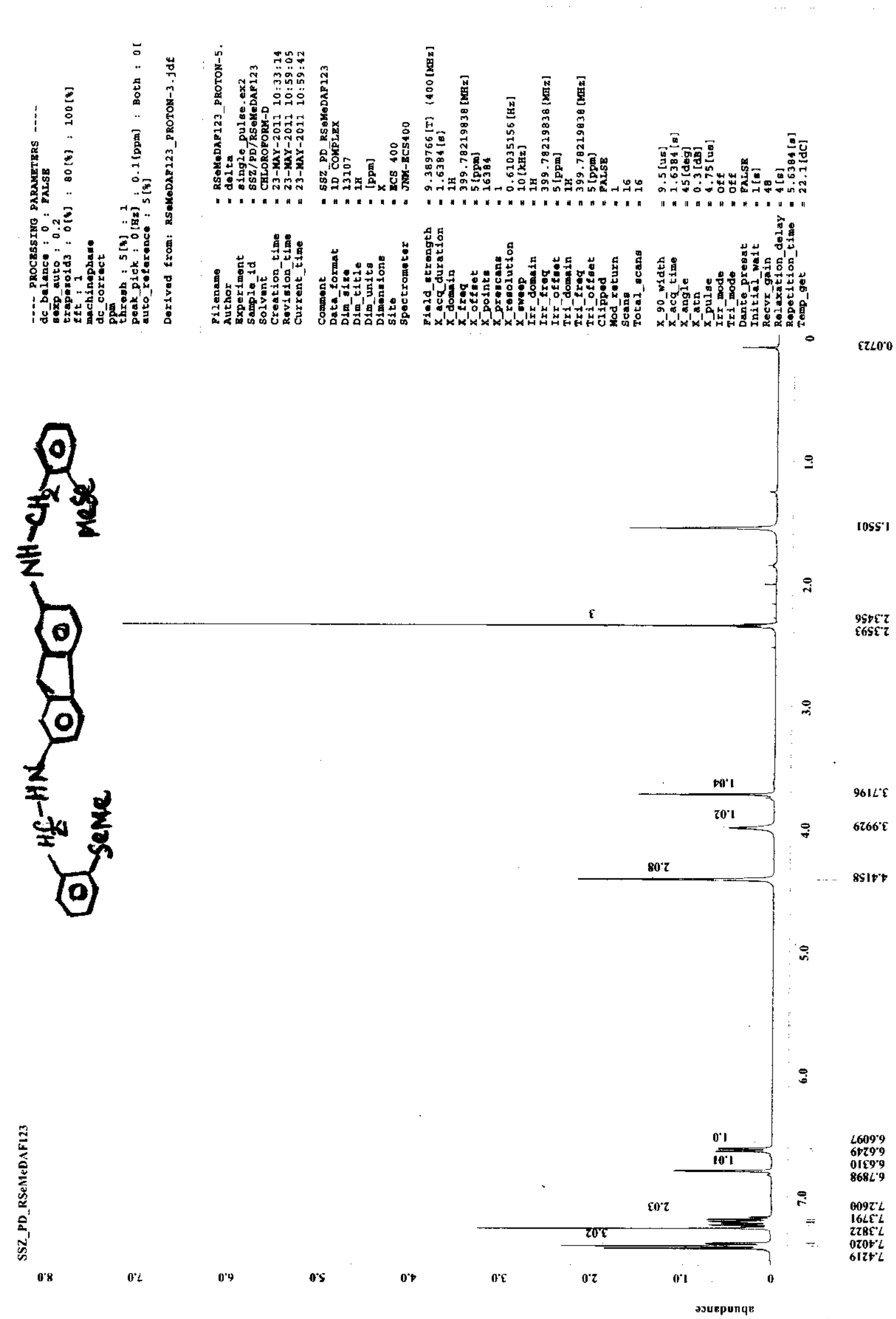


Fig. S3 [1]H NMR spectrum of reduced podand **4**.

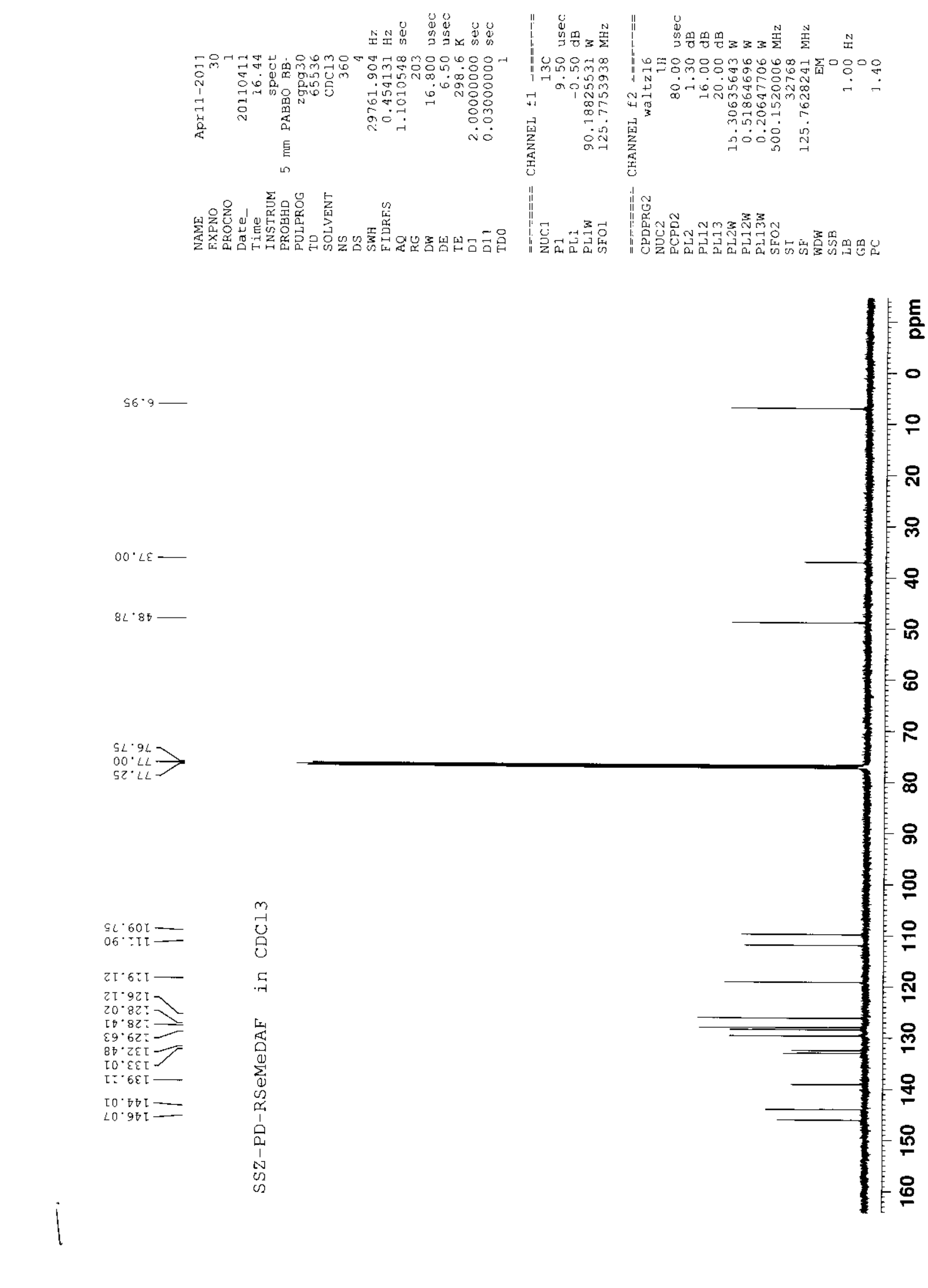


Fig. S4 ^{13}C NMR spectrum of reduced podand **4**.

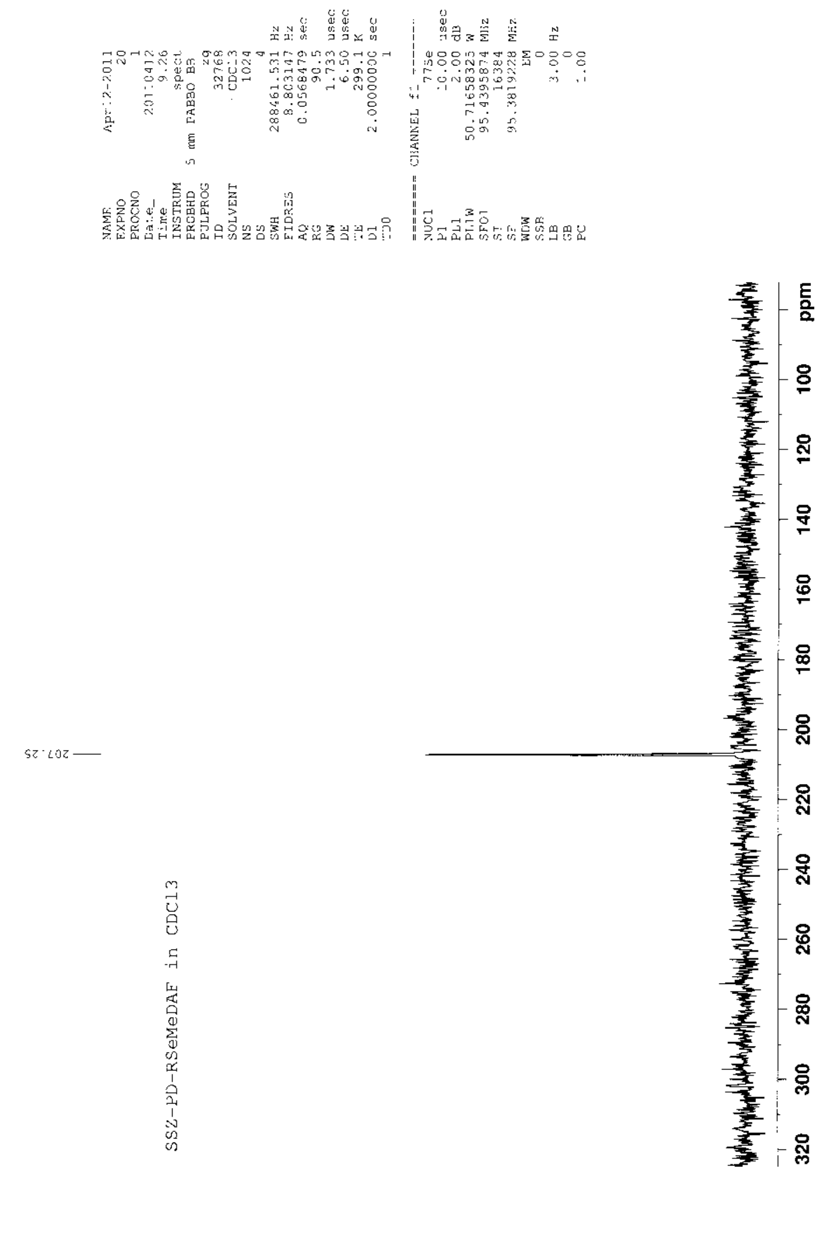


Fig. S5 ^{77}Se NMR spectrum of reduced podand **4**.

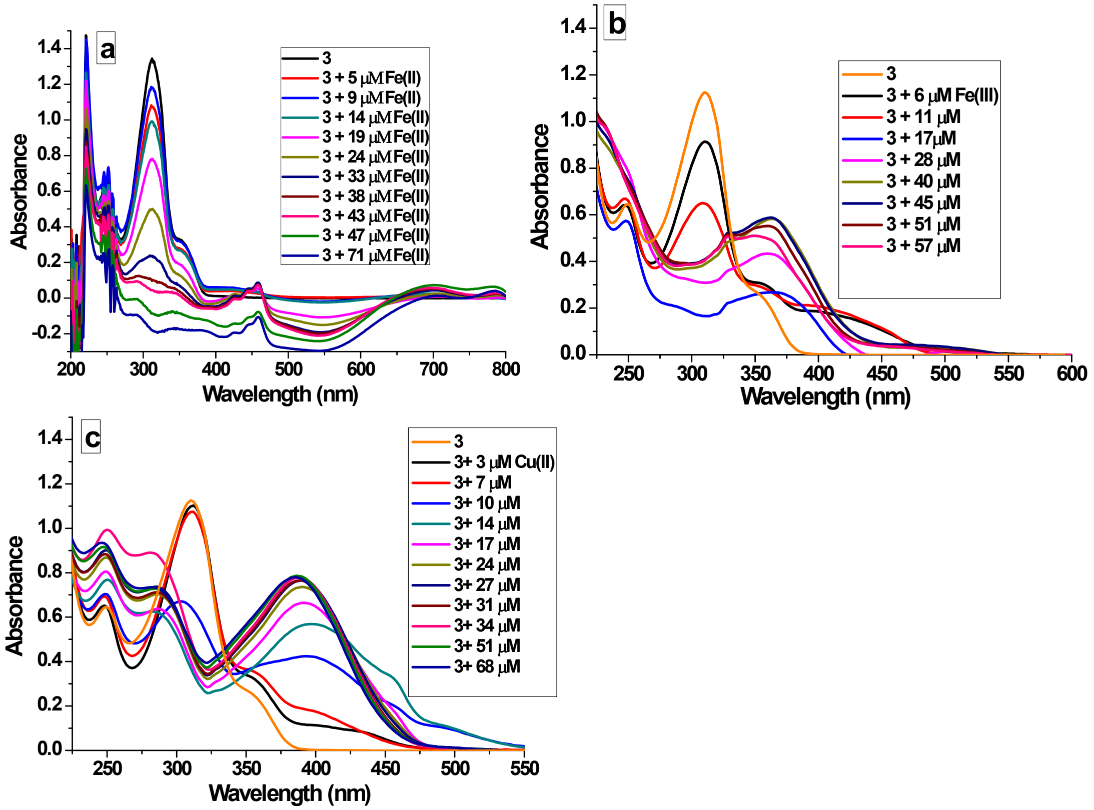
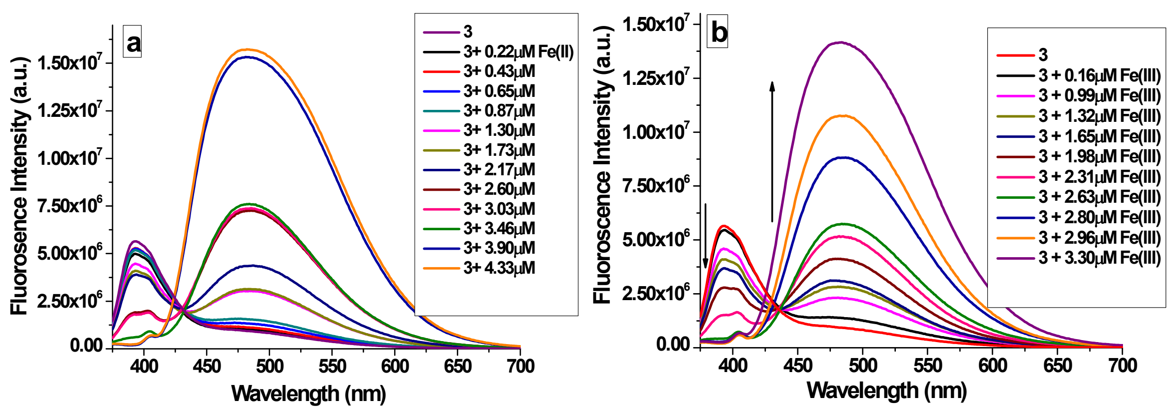


Fig. S6 Change in absorption spectra upon addition of (a) Fe(II), (b) Fe(III) and (c) Cu(II) solution in THF to the solution of reduced podand **3** (33 μM).



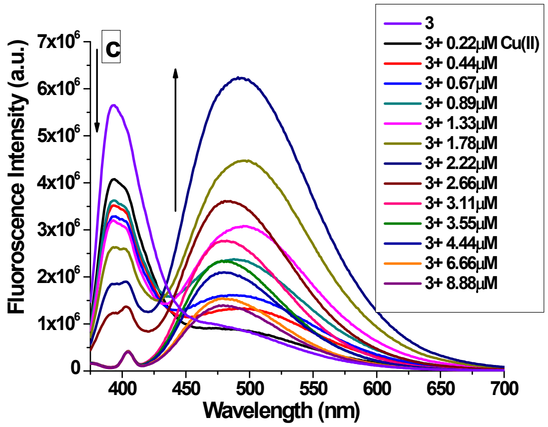


Fig. S7 Fluorescence response following excitation at 360 nm from reduced podand **3** solution upon addition of (a) Fe(II), (b) Fe(III) and (c) Cu(II) ion in THF.

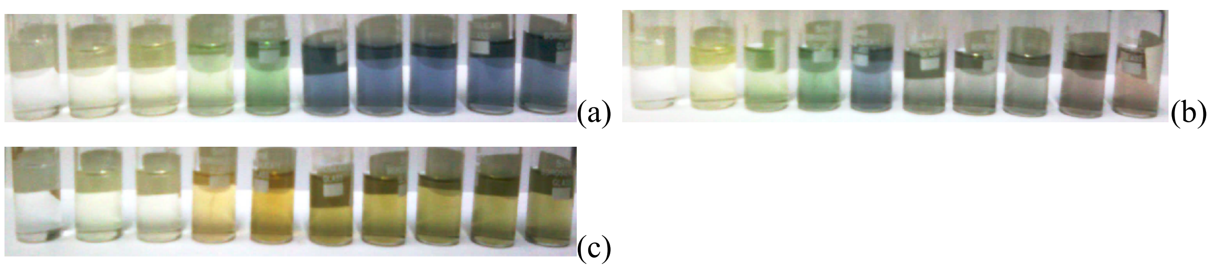


Fig. S8 Visual Changes in color after addition of aliquots of (a) Fe(II), (b) Fe(III) and (c) Cu(II) ion to the reduced podand **3**.

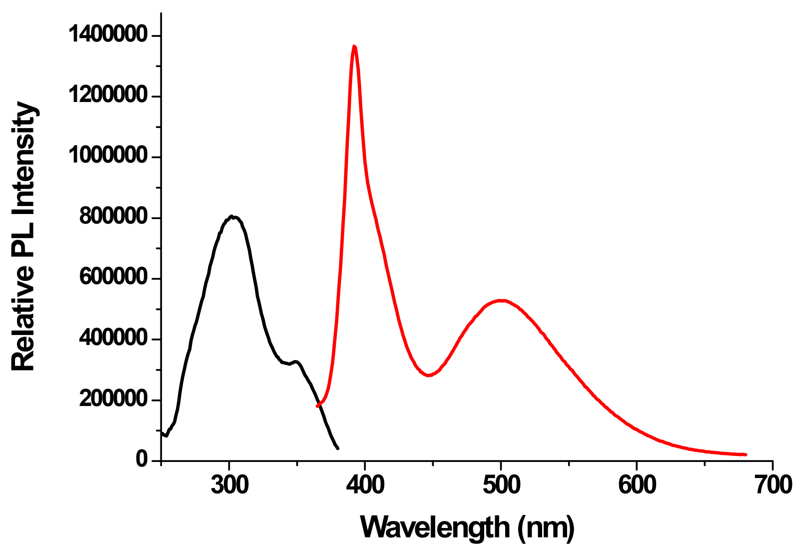


Fig. S9 Excitation and emission spectra of podand **4**.

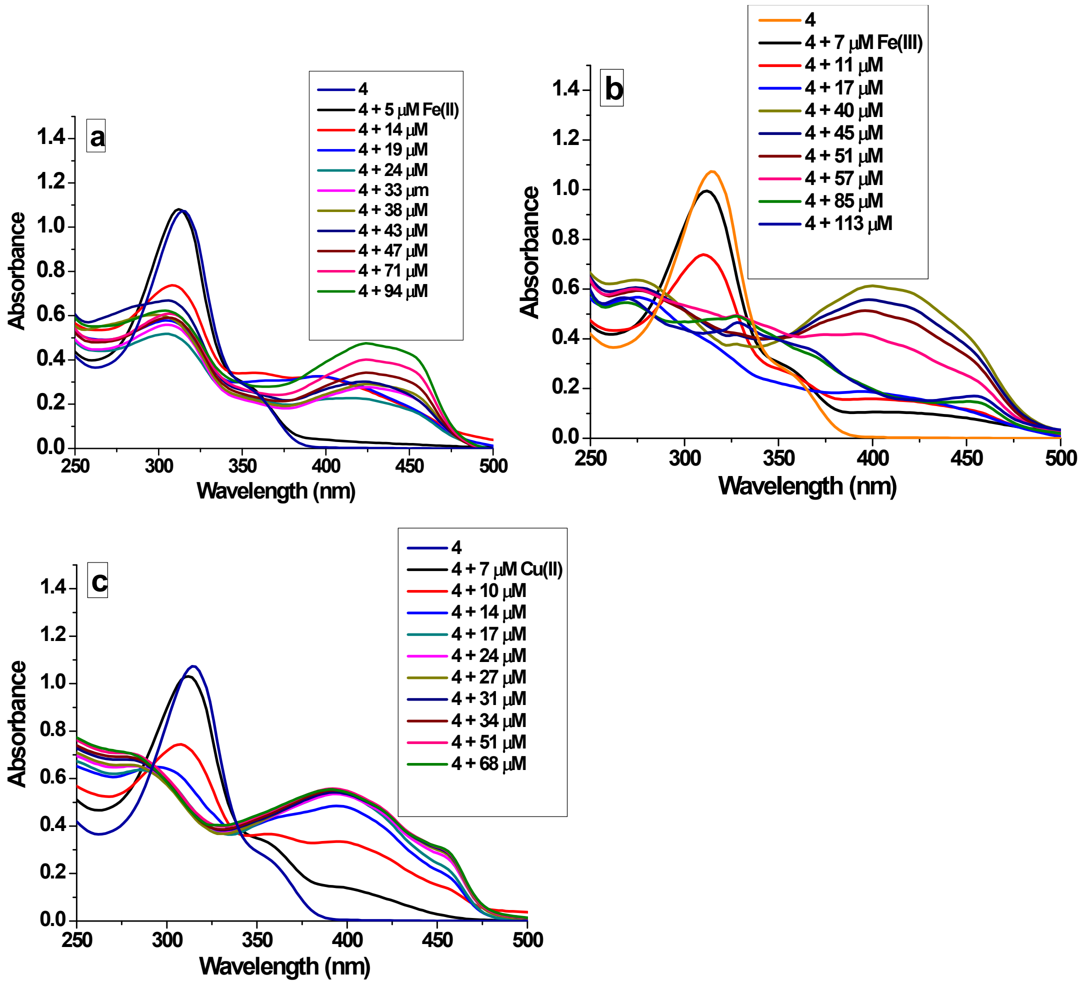
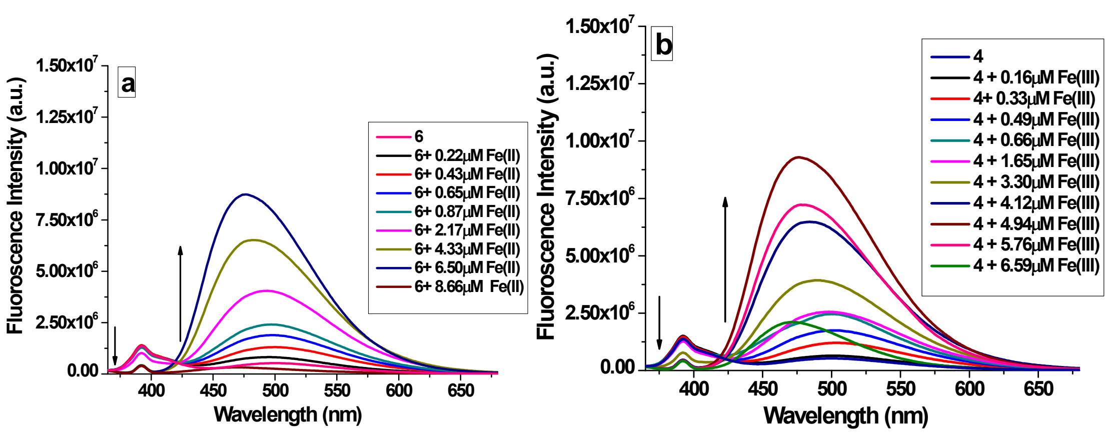


Fig. S9 Change in absorption spectra upon addition of (a) Fe(II), (b) Fe(III) and (c) Cu(II) solution in THF to the solution of reduced podand **4** (35 μM).



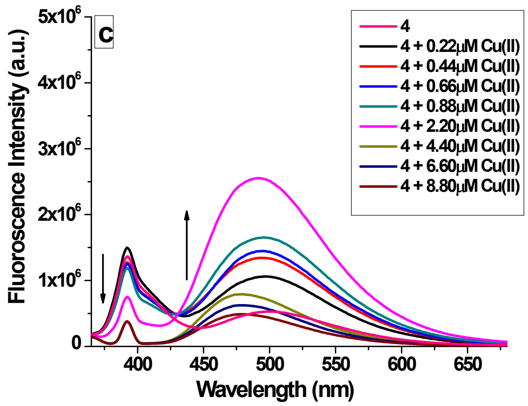
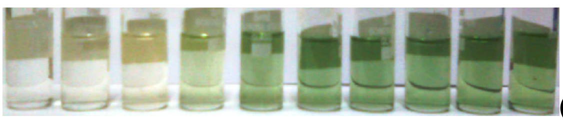
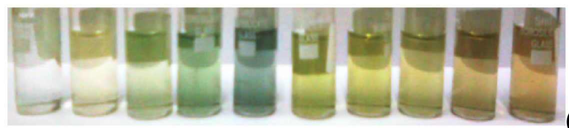


Fig. S10 Fluorescence response following excitation at 350 nm from reduced podand **4** solution upon addition of (a) Co(II), (b) Fe(II), (c) Fe(III) and (d) Cu(II) ion in THF.


(a)


(b)

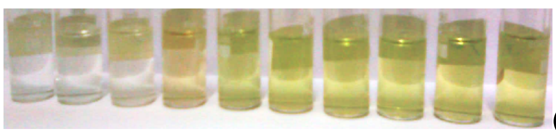

(c)

Fig. S11 Visual Changes in color after addition of aliquots of (a) Co(II), (a) Fe(II), (b) Fe(III) and (c) Cu(II) ion to the reduced podand **4**.

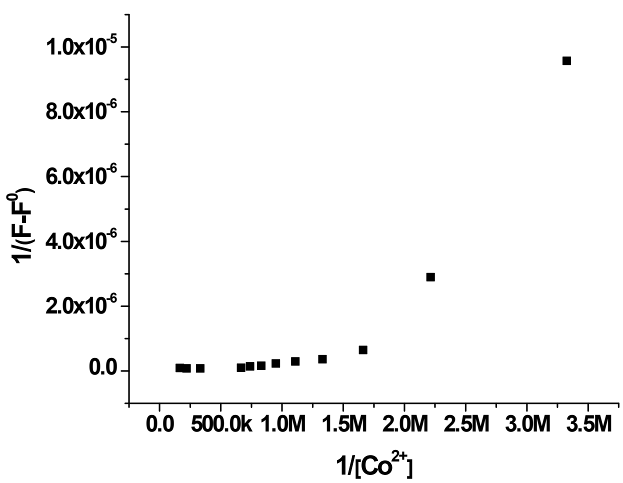


Fig. S12 Double reciprocal plot for the complexation of podand **3** and Co(II).

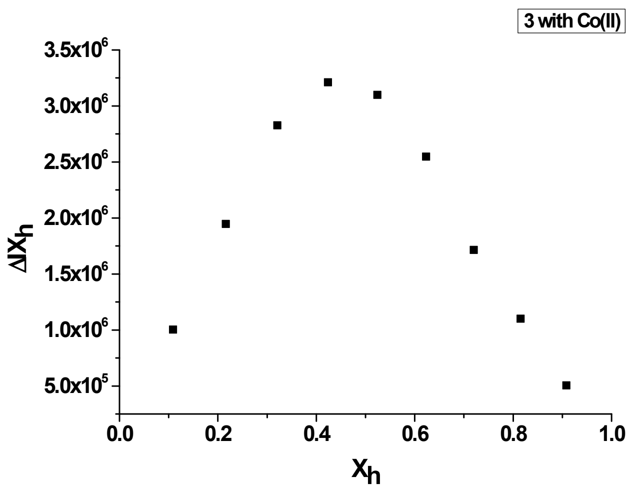


Fig. S13 Jobs plot of titration of **3** with Co(II) (where X_h is the mole fraction of Co(II) and ΔI indicates the change of the Fluorescence).

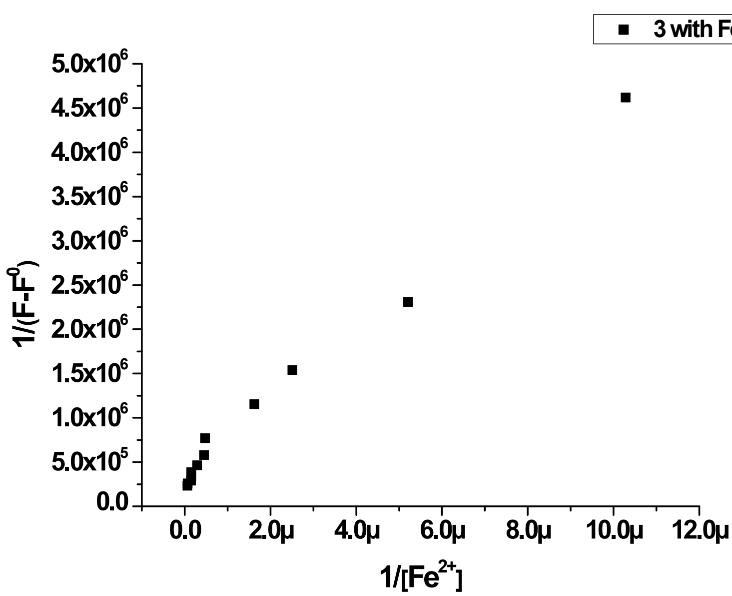


Fig. S14 Double reciprocal plot for the complexation of podand **3** and Fe(II).

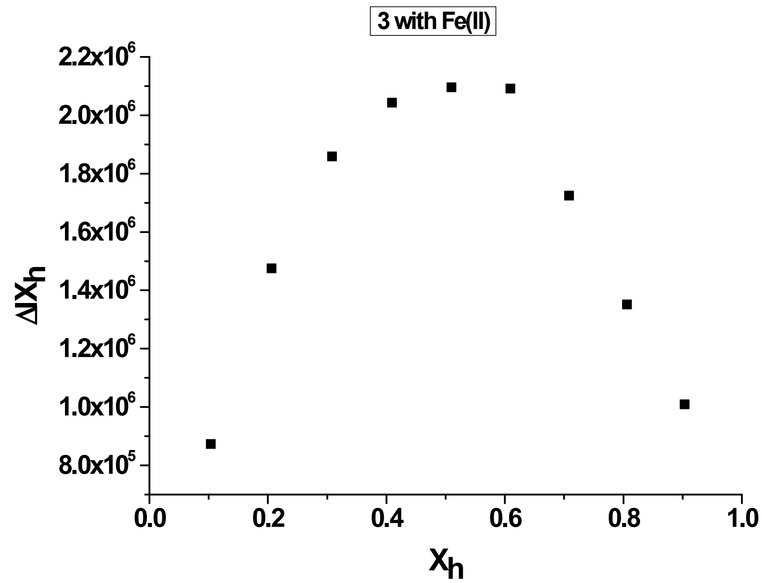


Fig. S15 Jobs plot of titration of **3** with Fe(II) (where X_h is the mole fraction of Fe(II) and ΔI indicates the change of the Fluorescence).

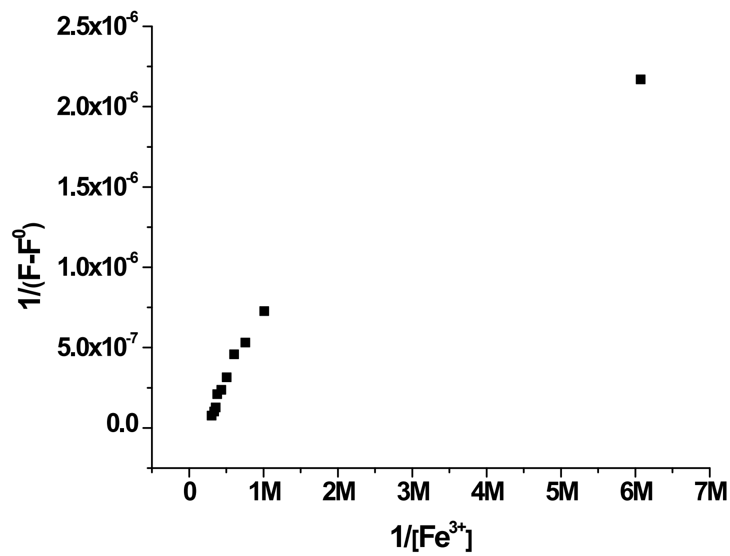


Fig. S16 Double reciprocal plot for the complexation of podand **3** and Fe(III).

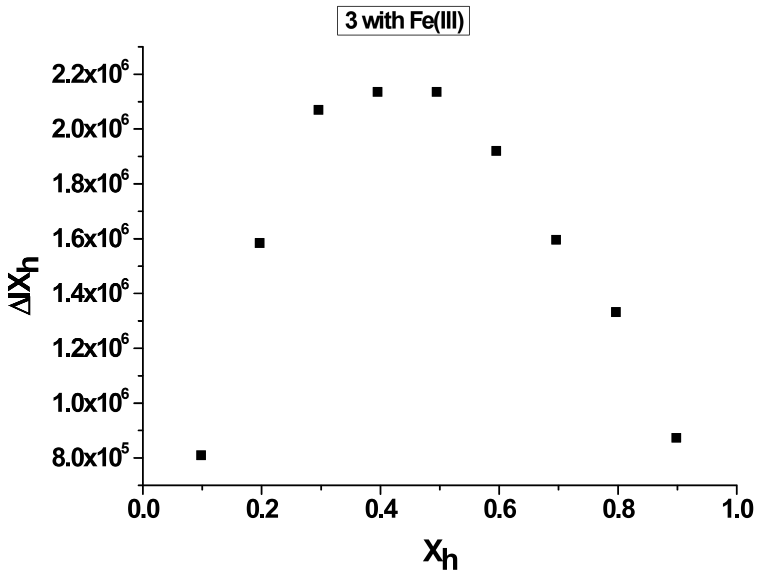


Fig. S17 Jobs plot of titration of **3** with Fe(III) (where X_h is the mole fraction of Fe(III) and ΔI indicates the change of the Fluorescence).

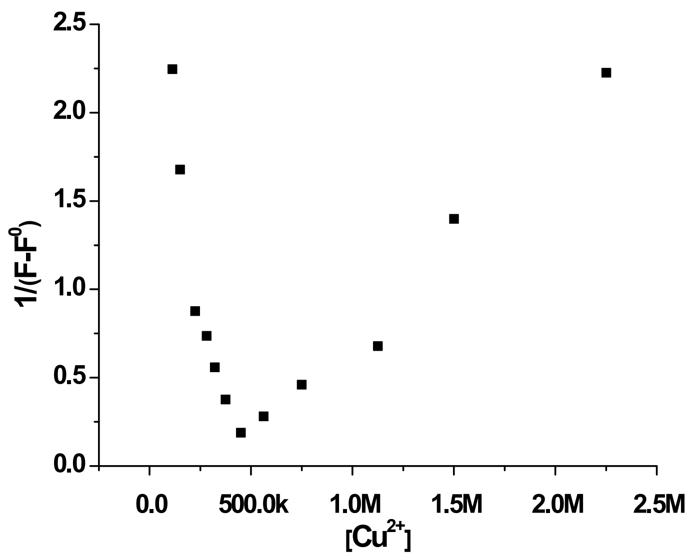


Fig. S18 Double reciprocal plot for the complexation of podand **3** and Cu(II).

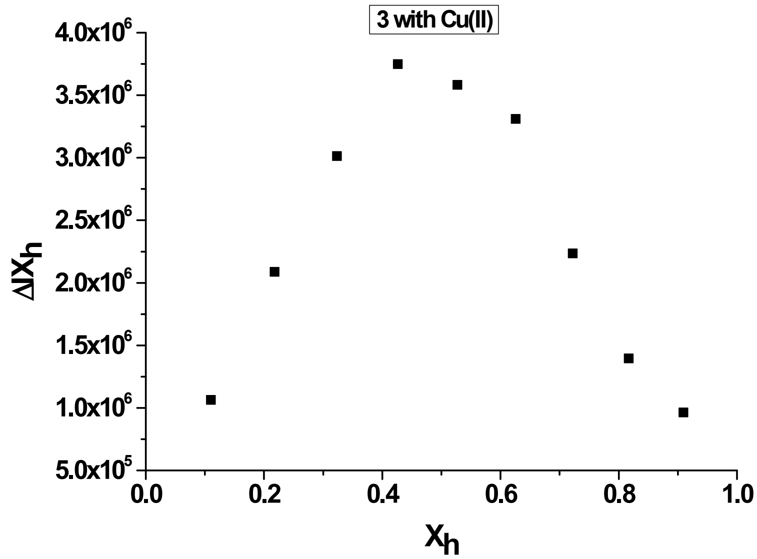


Fig. S19 Jobs plot of titration of **3** with Cu(II) (where X_h is the mole fraction of Cu(II) and ΔI indicates the change of the Fluorescence).

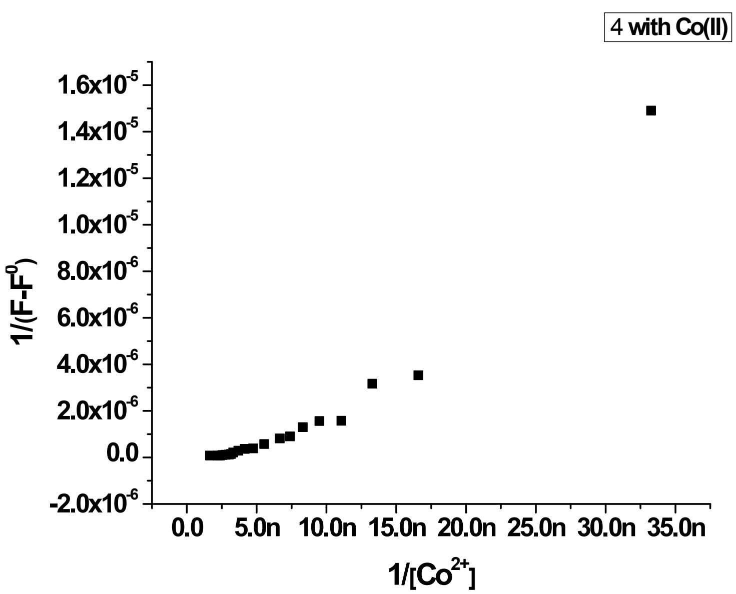


Fig. S20 Double reciprocal plot for the complexation of podand **4** and Co(II).

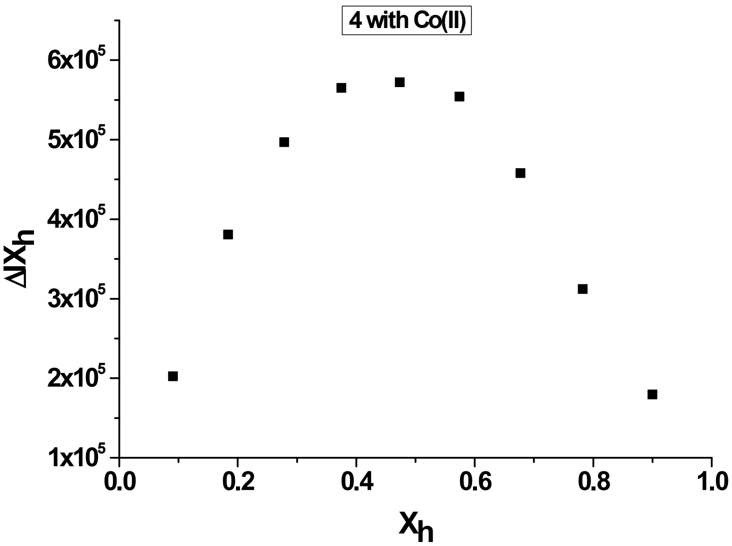


Fig. S21 Jobs plot of titration of **4** with Co(II) (where X_h is the mole fraction of Co(II) and ΔI indicates the change of the Fluorescence).

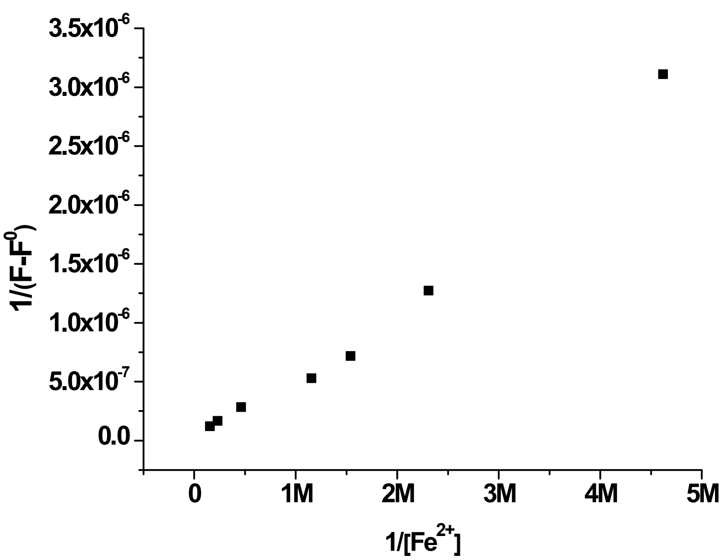


Fig. S22 Double reciprocal plot for the complexation of podand **4** and Fe(II).

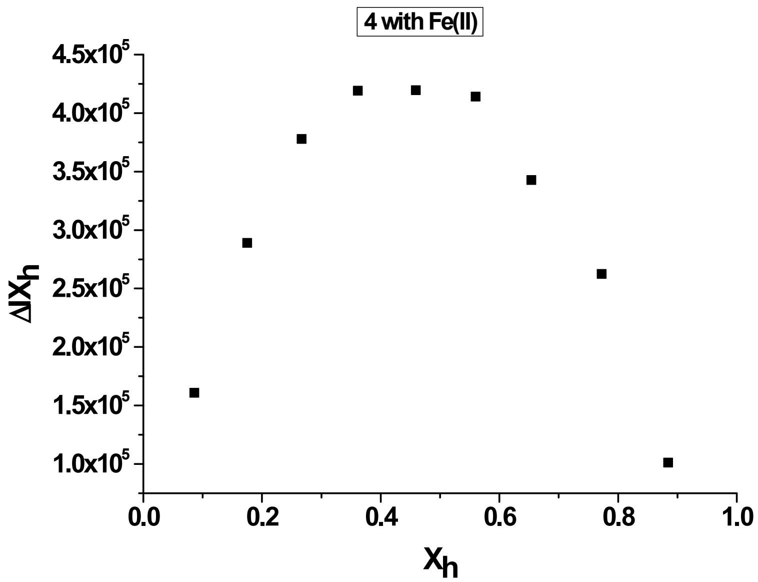


Fig. S23 Jobs plot of titration of **4** with Fe(II) (where X_h is the mole fraction of Fe(II) and ΔI indicates the change of the Fluorescence).

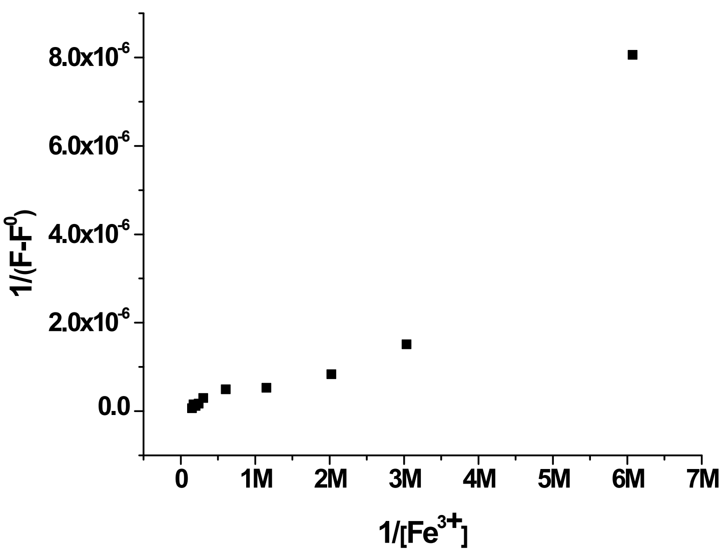


Fig. S24 Double reciprocal plot for the complexation of podand **4** and Fe(III).

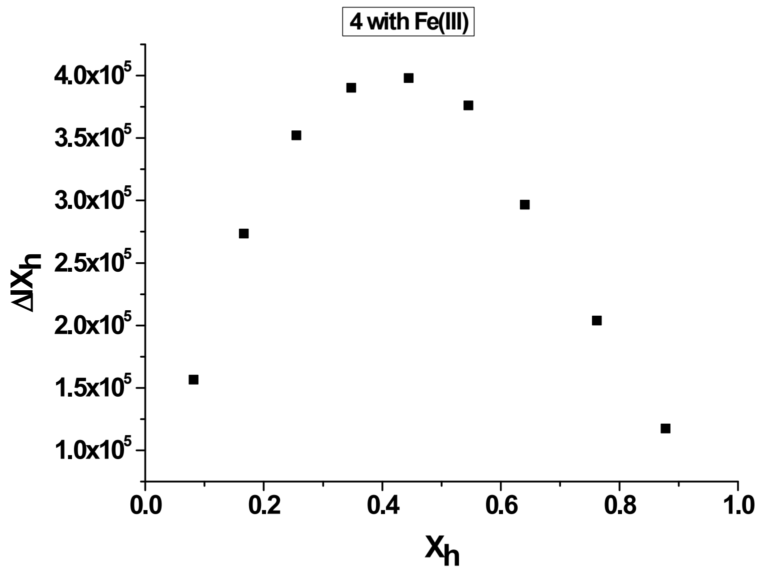


Fig. S25 Jobs plot of titration of **4** with Fe(III) (where X_h is the mole fraction of Fe(III) and ΔI indicates the change of the Fluorescence).

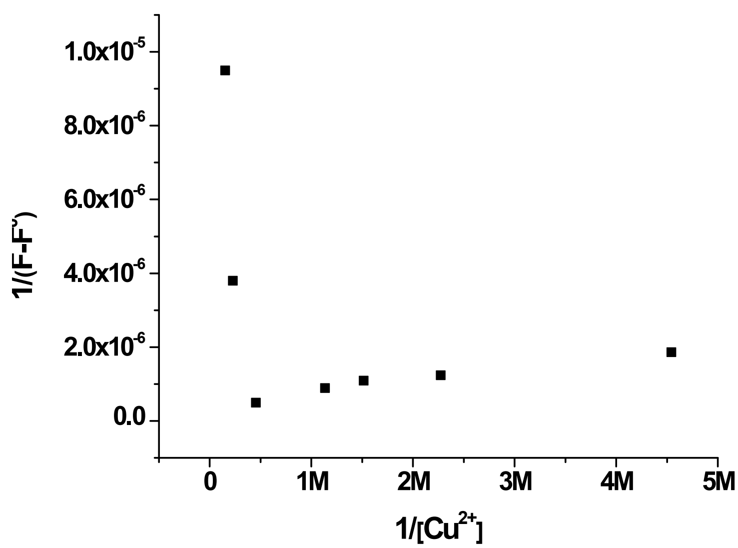


Fig. S26 Double reciprocal plot for the complexation of podand **4** and Cu(II).

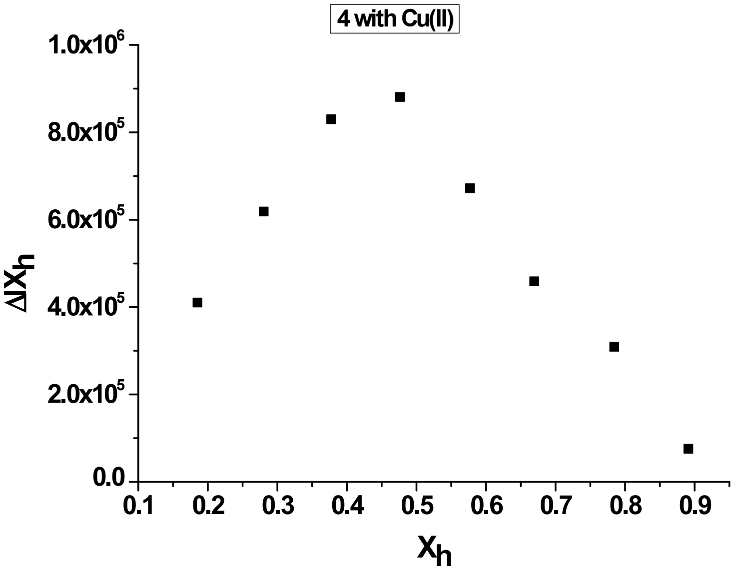


Fig. S27 Jobs plot of titration of **4** with Cu(II) (where X_h is the mole fraction of Cu(II) and ΔI indicates the change of the Fluorescence).

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1 S. Panda, P. B. Pati and S. S. Zade, *Chem. Commun.*, 2011, **47**, 4174.