Electronic Supplementary Information

Triple channel responsive Cu^{2+} probe

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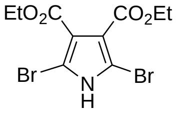
General

All chemicals were purchased from Sigma Aldrich Chemicals or Merck Company and used as received unless otherwise noted. FTIR spectra were recorded on Perkin Elmer Spectrum 100 model FTIR with an attenuated total reflectance (ATR). ^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Bruker DPX-400 or Ultrashield 300 NMR Spectrometers. Combustion analysis were carried out by using a LECO CHNS-932 analyzer. High resolution mass spectra (HRMS) were recorded on Waters SYNAPT MS system. UV-vis and fluorescence measurements were recorded on Varian Cary 50 and Varian Cary Eclipse spectrophotometers, respectively. Melting points were determined on a Schorrp MPM-H2 model apparatus and are uncorrected. Column chromatography was performed on silica gel (60-200 mesh) from Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates. Cyclic voltammetry measurements were carried out with a BioLogic Science Instruments SP 150 model potentiostat-galvanostat. 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) dissolved in acetonitrile (ACN) was used as electrolyte solution. The redox behaviour of **4** was investigated by using a pencil graphite electrode (Tombo, 0.5 mm) as well as a platinum wire as counter electrode and an Ag wire as a pseudo-reference electrode. The synthesis of **3**[11] was carried out according to a published procedure. Metal solutions were freshly prepared in CH_3CN from the corresponding perchlorate salts with the exceptions of Au^{3+} (prepared from $AuCl_3$ in CH_3CN containing 1% water) and Pt^{2+} (prepared from K_2PtCl_4 in CH_3CN containing 1% water).

Synthesis of diethyl 2,5-dibromo-1H-pyrrole-3,4-dicarboxylate (2)

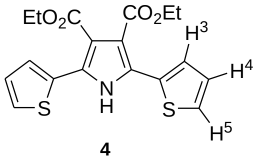


2

Br_2 (0.11 ml, 2.1 mmol) was dropwise added to a magnetically stirred solution/suspension of diethyl-1H-pyrrole-3,4-dicarboxylate (**1**) (211.2 mg, 1 mmol) and $NaHCO_3$ (252 mg, 3 mmol) in CH_2Cl_2 (20 ml) at 0 °C. After the addition was completed, the mixture was stirred at room temperature until **1** was totally consumed (TLC, overnight). The mixture was filtered to remove the solid part, washed with water (100 mL) and dried over $MgSO_4$. The solvent was evoparated and the residue was subjected to column chromatography on silica gel eluting with 5% CH_3OH-

$CHCl_3$ (v/v) to give **2**: R_f = 0.56, 347 mg, 94% yield, white solid, m.p. 102 °C; ^1H NMR (300 MHz, $CDCl_3$) δ/ppm: 9.50 (bs, 1H, -NH), 4.33 (q, J= 7.1 Hz, 4H, $-CH_2$), 1.35 (t, J= 7.1 Hz, 6H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 162.7, 117.5, 104.2, 61.2, 14.1; FTIR (ATR, cm^{-1}): 3106, 3059, 3006, 2973, 2934, 2870, 2639, 1714, 1677, 1492, 1460, 1446, 1375, 1291, 1214, 1191, 1068, 1024, 862, 800, 783, 765, 678; Anal Calcd for $C_{10}H_{11}Br_2NO_4$: C, 32.55; H, 3.00; N, 3.80; Found: C, 32.53; H, 3.05; N, 3.82. HRMS Calcd for $NaC_{10}H_{11}Br_2NO_4$: 389.8952; Found: 389.8951.

Synthesis of diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (4)



4

To an argon degassed solution of compound **2** (185 mg, 0.5 mmol) and **3** (400 mg, 1.1 mmol) in dry toluene (25 ml) was added $Pd(PPh_3)_4$ (20 mg) as catalyst and the solution was heated under reflux until all the starting materials were consumed (TLC, 5 h). The flask was cooled and the solvent was removed under reduced pressure. The residue was filtered through a short pad of silica gel by eluting with CH_2Cl_2 to give **4**: R_f = 0.70, 168 mg, 90% yield; m.p. 129-130 °C; ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.70 (s, 1H, -NH), 7.40 (dd, J=4-2 Hz, 2H, H^3), 7.35 (dd, J=5-2 Hz, 2H, H^5) ve 7.07 (dd, J=5-4 Hz, 2H, H^4), 4.28 (q, J= 8 Hz, 4H, $-CH_2$), 1.30 (t, J= 8

Hz, 6H, $-CH_3$) ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 164.6, 131.3, 128.1, 127.5, 127.4, 126.6, 114.8, 60.9, 14.1; FTIR (ATR, cm^{-1}): 3106, 3100, 2975, 2956, 1689, 1550, 1486, 1437, 1369, 1341, 1298, 1248, 1215, 1112, 1015, 857, 785, 701; UV-Vis (CH_3CN, λ_{max}, nm): 230, 312; Anal Calcd for $C_{18}H_{17}NO_4S_2$: C, 57.58; H, 4.56; N, 3.73; S, 17.08; Found: C, 57.55; H, 4.52; N, 3.75; S, 17.02. HRMS Calcd for $NaC_{18}H_{17}NO_4S_2$: 398.0497; Found: 398.0482.

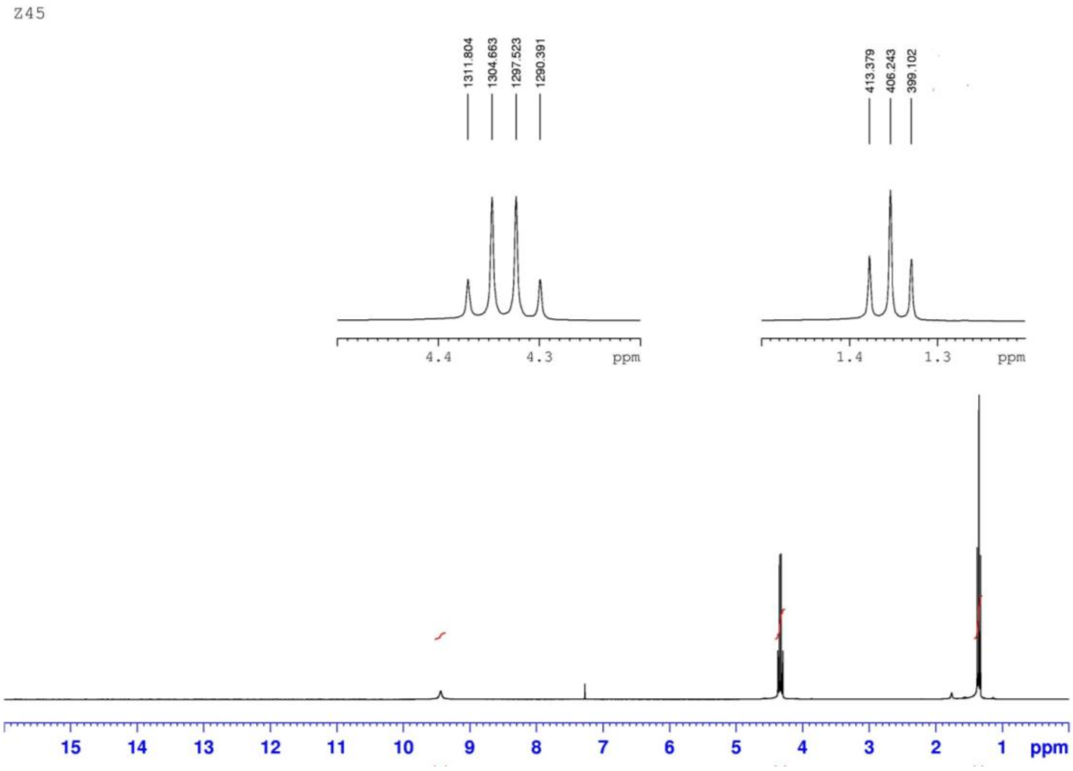


Fig. S1. ^{1}H NMR spectrum of diethyl 2,5-dibromo-1H-pyrrole-3,4-dicarboxylate (**2**) ($CDCl_3$).

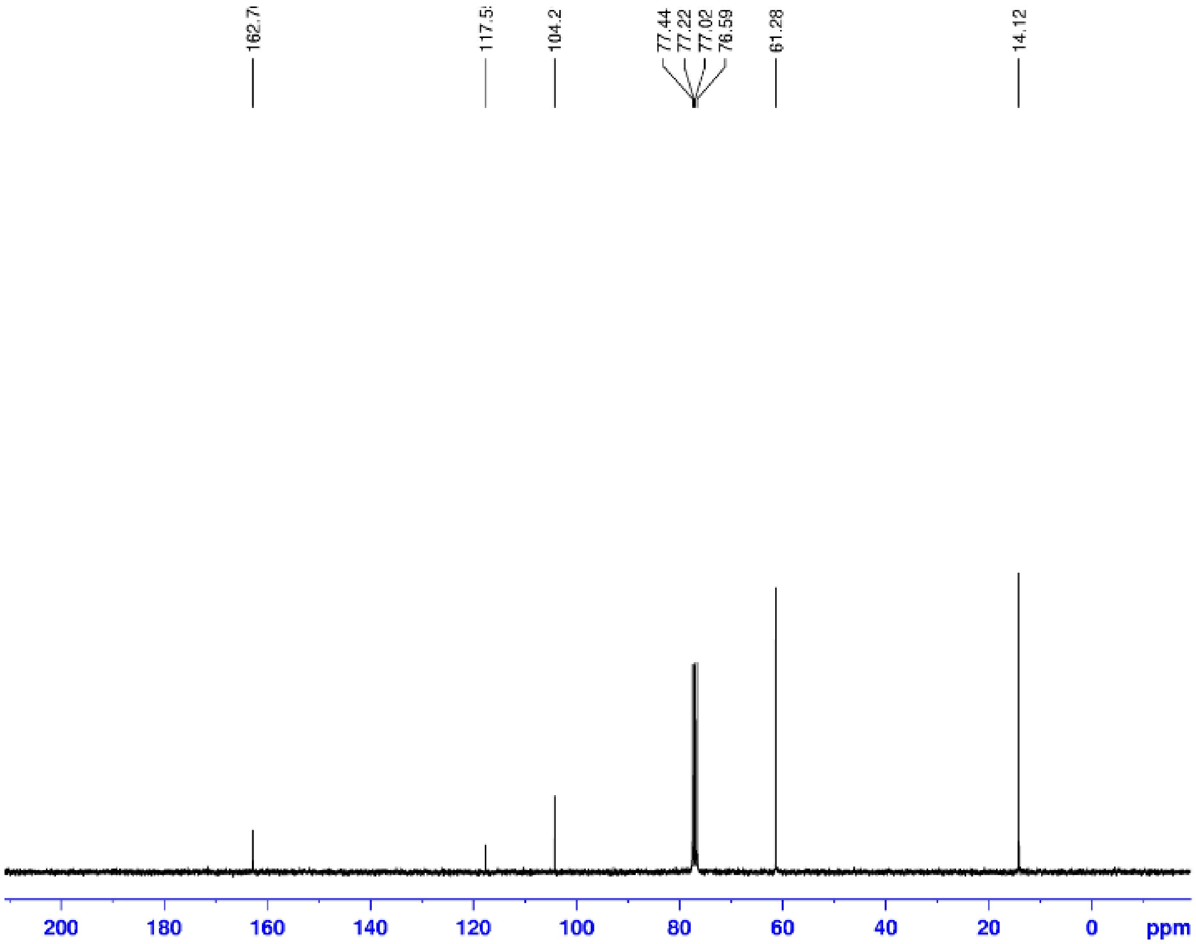
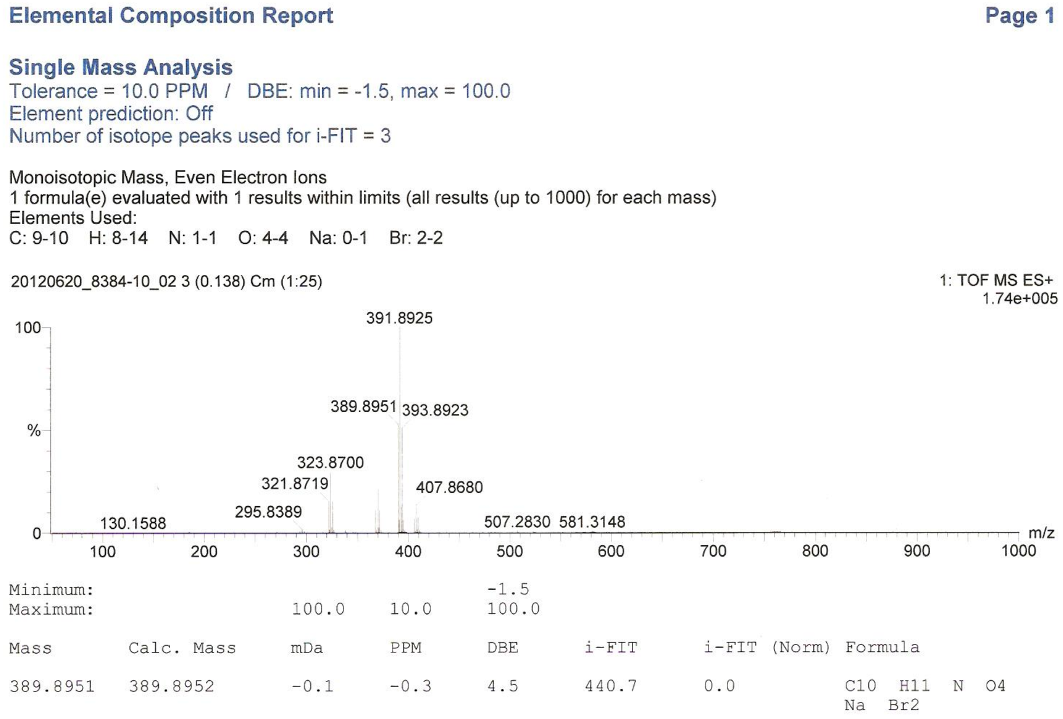


Fig. S2. ^{13}C NMR spectrum of diethyl 2,5-dibromo-1H-pyrrole-3,4-dicarboxylate (**2**) ($CDCl_3$).



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 9-10 H: 8-14 N: 1-1 O: 4-4 Na: 0-1 Br: 2-2

```
Minimum:                                    -1.5
Maximum:                   100.0    10.0    100.0

Mass        Calc. Mass     mDa      PPM     DBE      i-FIT      i-FIT (Norm) Formula

389.8951    389.8952       -0.1     -0.3    4.5      440.7      0.0          C10  H11  N  O4
                                                                             Na   Br2
```

Fig. S3. Mass spectrum of **2**.

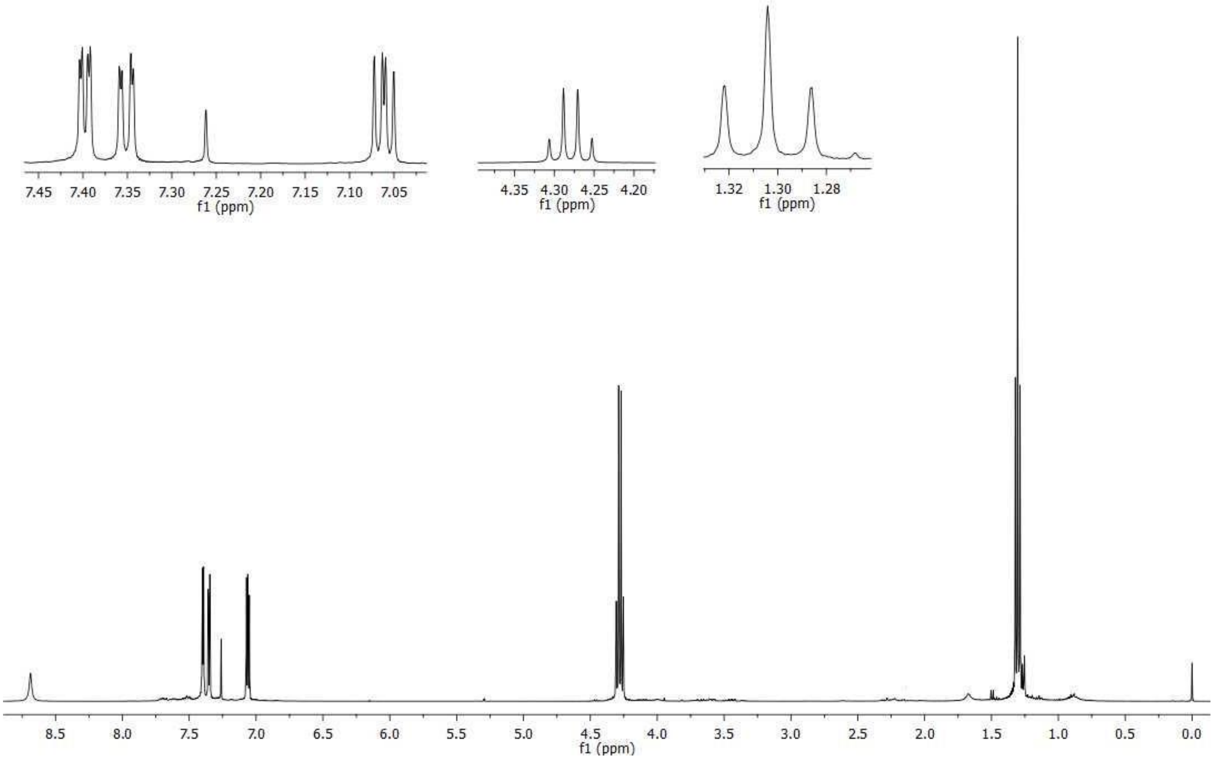


Fig. S4. ^{1}H NMR spectrum of diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (**4**) ($CDCl_3$).

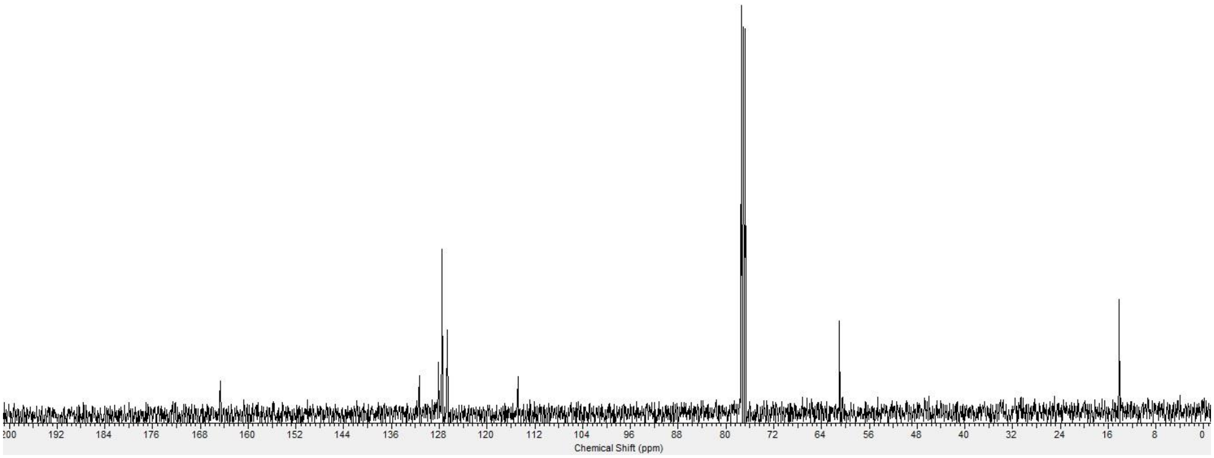
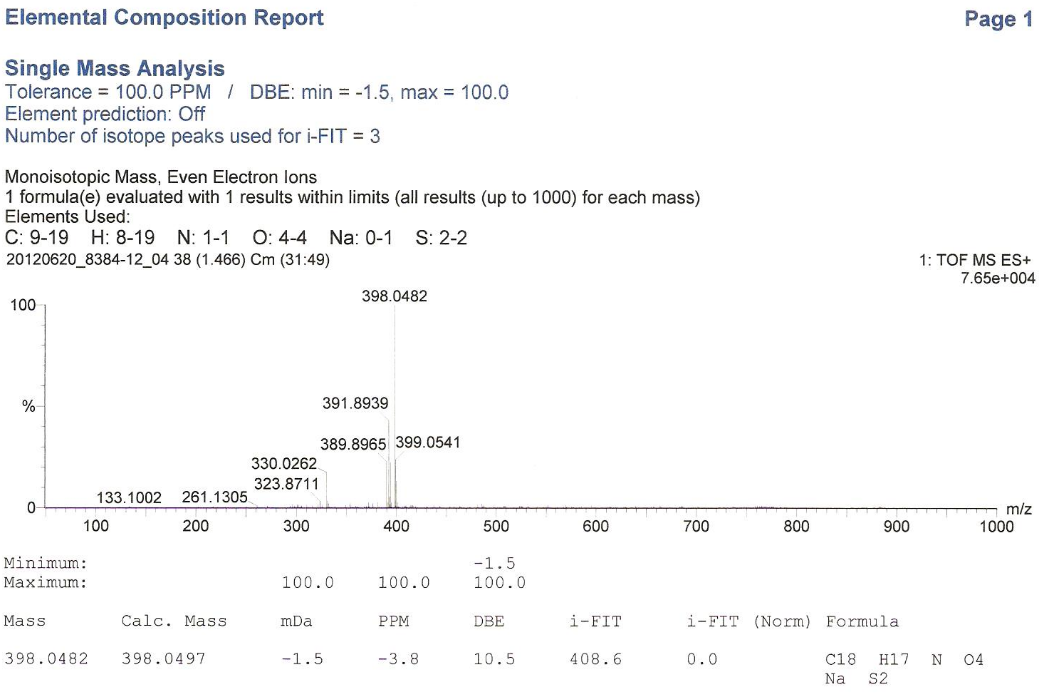


Fig. S5. ^{13}C NMR spectrum of diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (**4**) ($CDCl_3$).



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 9-19 H: 8-19 N: 1-1 O: 4-4 Na: 0-1 S: 2-2
20120620_8384-12_04 38 (1.466) Cm (31:49) 1: TOF MS ES+ 7.65e+004

```
Minimum:                                      -1.5
Maximum:                    100.0     100.0   100.0

Mass        Calc. Mass      mDa       PPM     DBE       i-FIT       i-FIT (Norm) Formula

398.0482    398.0497        -1.5      -3.8    10.5      408.6       0.0          C18  H17  N  O4
                                                                                 Na  S2
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Fig. S6. Mass spectrum of **4**.

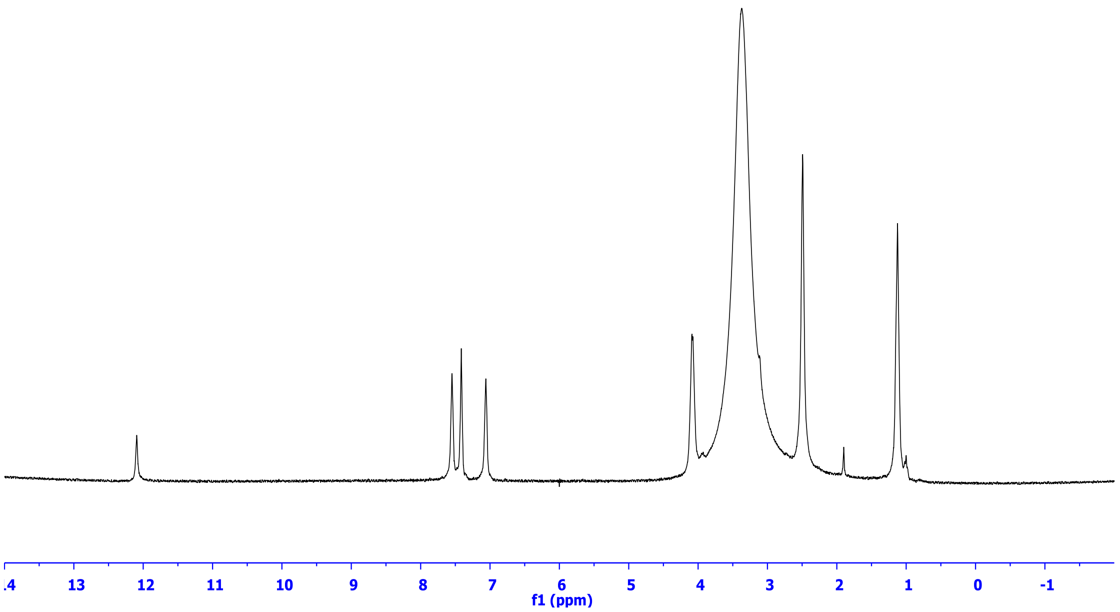

Fig. S7. ^{1}H NMR spectrum of diethyl 2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (**4**) in the presence of Cu^{2+} (2 equiv) in DMSO-d_6.

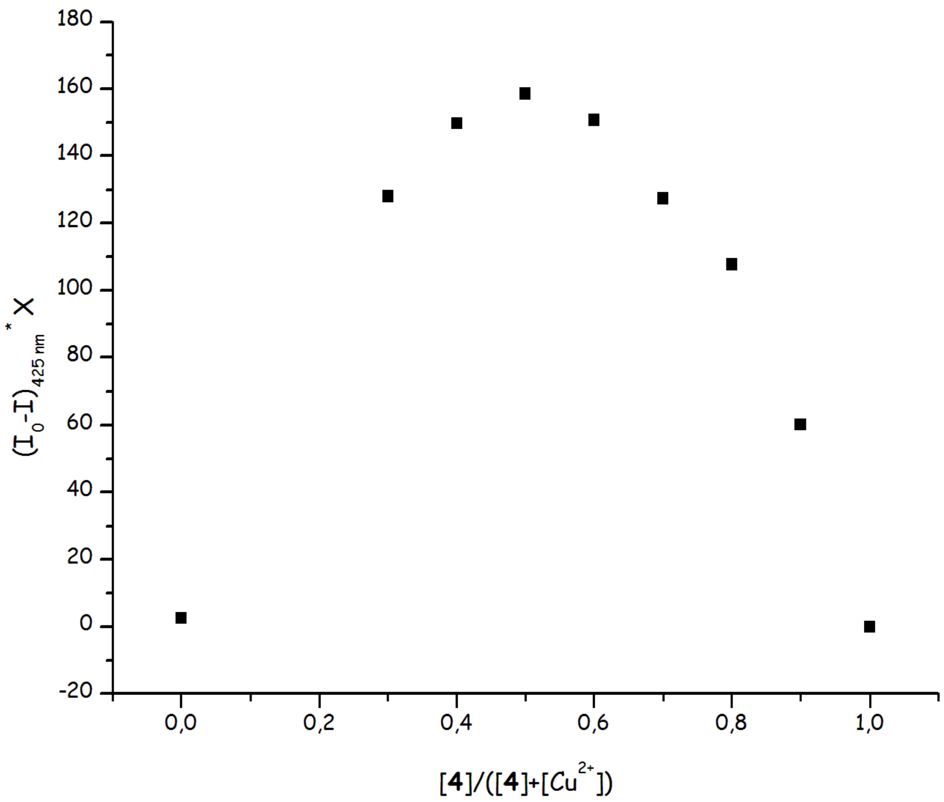

Fig. S8. Job plot diagram of **4** for Cu^{2+} (where X is the mole fraction of **4** and ΔI indicates the change of emission intensity at 425 nm) at a constant total concentration of 3.0 10^{-6} M in acetonitrile solution.

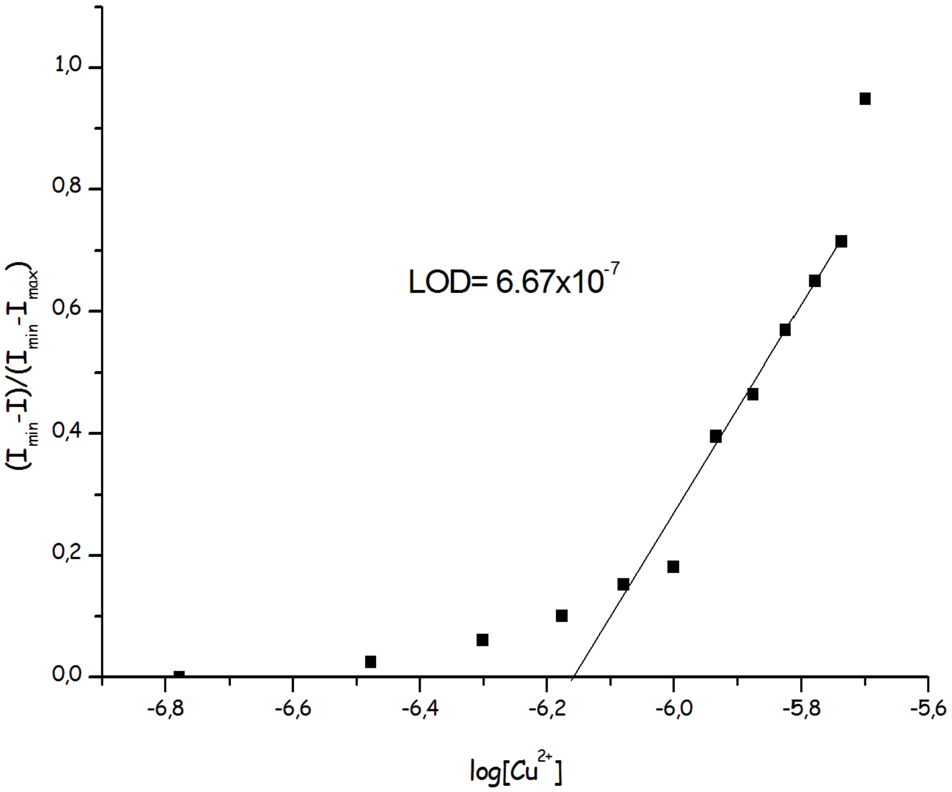

Fig. S9. Plot of normalized fluorescence intensity of **4** as a function of log[Cu^{2+}] in acetonitrile solution (λ_{exc}= 312 nm). (log[Cu^{2+}] = -6.176)

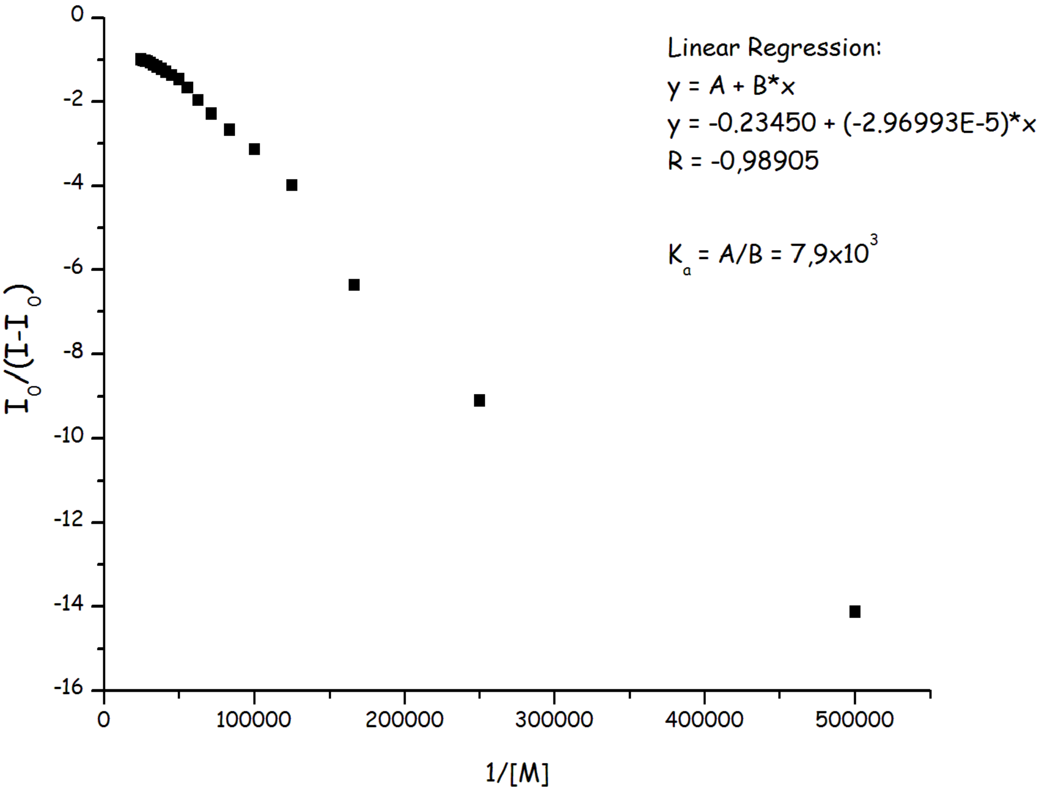

Fig. S10. Linear regression curve for **4**.