

Supporting Information

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Covalent Attachment of a Fluorescent ‘Pourbaix Sensor’ onto a Polymer Bead for Sensing in Water

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1 Experimental

1.1 Instrumentation

Syntheses were performed with an IKA C-MAG HS 7 hot plate assisted by an IKA ETS-D5 temperature probe to help maintain a constant temperature during reflux. Thin-layer chromatography (TLC) was performed on pre-coated silica plates (Sigma-Aldrich) using glass capillary tubes. The spots were observed under long wavelength (365 nm) and short wavelength (254 nm) UV light from a UVGL-58 handheld lamp. Melting points were measured with a Stuart SMP11 melting point apparatus.

NMR spectra were acquired with a Bruker Avance III HD NMR spectrometer fitted with an Ascend 500 11.75 Tesla superconducting magnet and a multinuclear 5mm PABBO probe. The frequency is 500.13 MHz for ^1H NMR and 125.76 MHz for ^{13}C NMR. Data was analysed and processed by means of the software Topspin ver.3.2. Chemical shifts were reported in ppm downfield with respect to TMS at 0.00 ppm at 298 K. Infra-red spectra were recorded using a Shimadzu IR-Affinity-1 spectrophotometer between 4000-400 cm^{-1} . The instrument was calibrated against 1601 cm^{-1} polystyrene absorption peak. IR analyses were performed as KBr disks or as a thin film between NaCl plates. The high resolution mass spectrometry (HRMS) was performed by ESI-ToF outsourced to Medac Ltd (UK). <http://medacltd.com/>

UV-visible absorption spectra were acquired on a Jasco V-650 spectrophotometer. Quartz cells with a pathlength of 1.0 cm were used for the measurements. Parameters of the instrument were set at 0.5 nm bandwidth and 400 nm/min scan speed. Blank spectrum was performed on the neat solvent as a reference prior the measurements of the spectra. Fluorescent measurements were acquired with a Jasco FP-8300 spectrophotometer. Quartz cells with a pathlength of 1.0 cm were used for the measurements. The parameters were excitation and emission bandwidths of 2.5 nm, 50 msec response time, and a scanning speed of 200 nm min^{-1} . The absorbance of the solutions for fluorescence was set to less than 0.1 to prevent quenching of the emission.

Photos of beads were taken with a fluorescent microscope Axiovert 40 CLF, manufactured by Carl Zeiss MicroImaging. The microscope had an ocular magnification of $\times 10$, and the magnification that was used was $\times 40$. As a source UV light, a low pressure mercury lamp was used. A UV filter with an excitation band between 450-490 nm was used. The emission of light started from 515 nm and the beam splitter was adjusted to 510 nm.

Synthesis

Synthesis of *N*-Ferrocenyl-4-((4-(2-methyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)piperazin-1-yl)methyl)benzoic acid **3**

N-Ferrocenylmethyl-4-piperazine-1,8-naphthalimide **2** (76 mg, 0.16 mmol), 4-(bromomethyl)benzoic acid (114 mg, 0.53 mmol) and triethylamine (88 μ L, 0.63 mmol) were dissolved in 4 mL of 1,2-dichloroethane and refluxed at 90 $^{\circ}$ C for 3 hours. The solution was extracted with 1,2-dichloromethane and washed with 10% aqueous NaOH. The product was recrystallised from acetone to give an orange powder in 19% yield (22 mg). m.p. > 250 $^{\circ}$ C; R_f = 0.44 (9:1 (v/v) CH_2Cl_2 /methanol); FTIR (KBr, salt, cm^{-1}): 3051, 2950, 2850, 1695 (C=O), 1653, 1585, 1382, 1183, 1110; MS (ES-TOF, 1.56 mV) m/z (%): 177 (59), 178 (10), 410 (100), 411 (28), 412 (5); HRMS for $\text{C}_{32}\text{H}_{43}\text{N}_4\text{O}_5\text{FeNa}$ [M+Na] calculated 642.2481, found 642.2484.

Attachment of **3** onto Tentagel

To a 50 mL round-bottom flask, 16 mg (0.025 mmol) of **3**, 26 mg (0.13 mol) of DCC and 100 μ L of HOBT were dissolved in 1 mL of DMF. The reaction was stirred at 40 $^{\circ}$ C for 4 hours. The beads were washed sequentially with 10 mL of DMF, 1:1 (v/v) DMF/MeOH and MeOH.

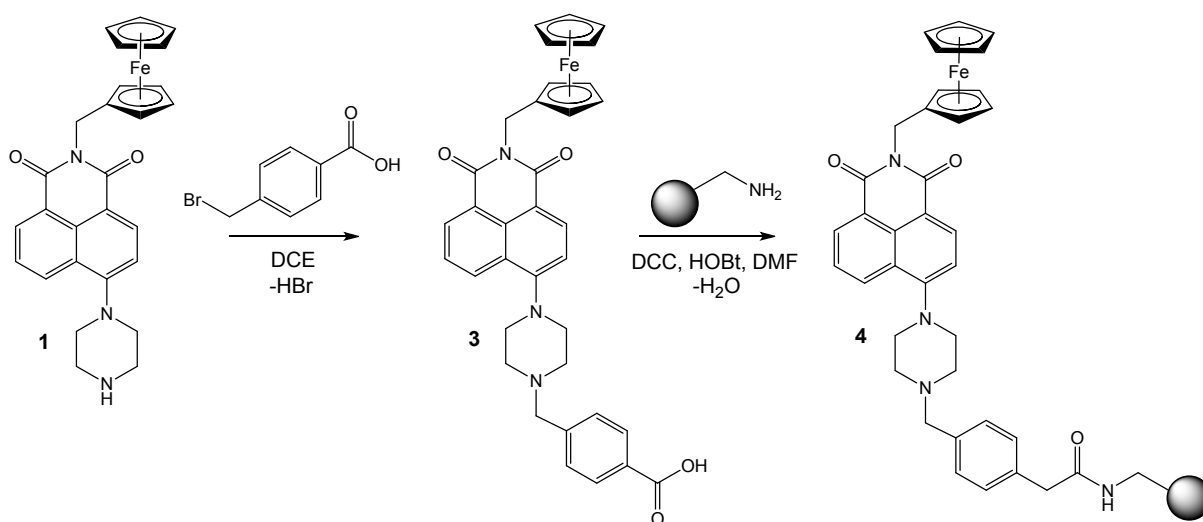


Figure S1. Reaction scheme for the synthesis of **3** and covalent attachment on the polymer bead to yield **4**.

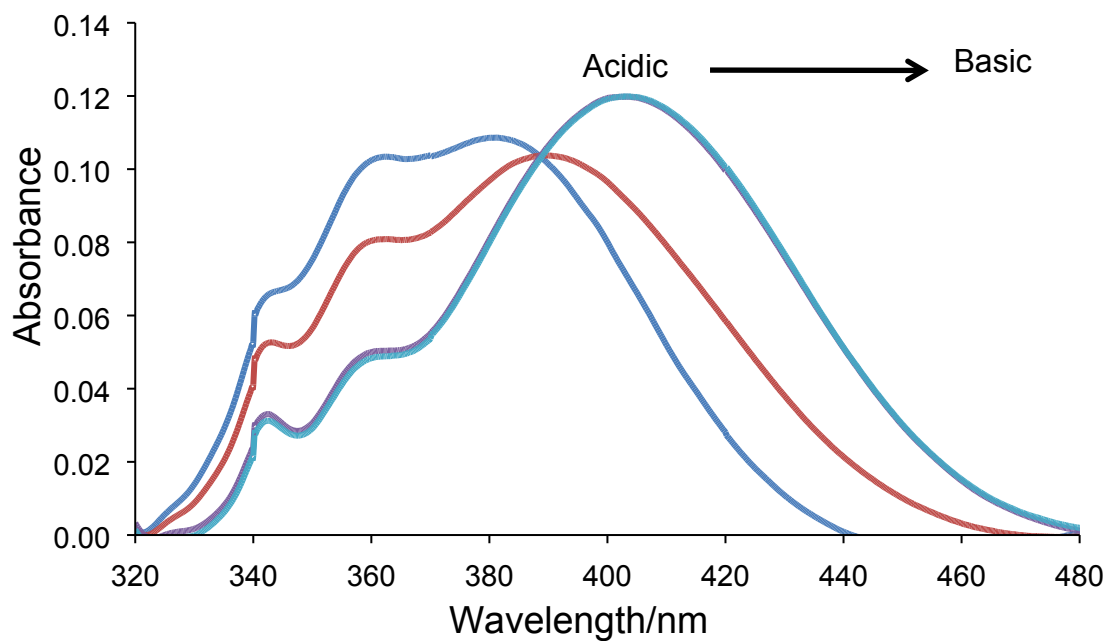


Figure S2. UV-visible absorption spectra of 10 μM **3** in 1:1 (v/v) methanol/water at pH 3.0, 7.0 and 10.5.

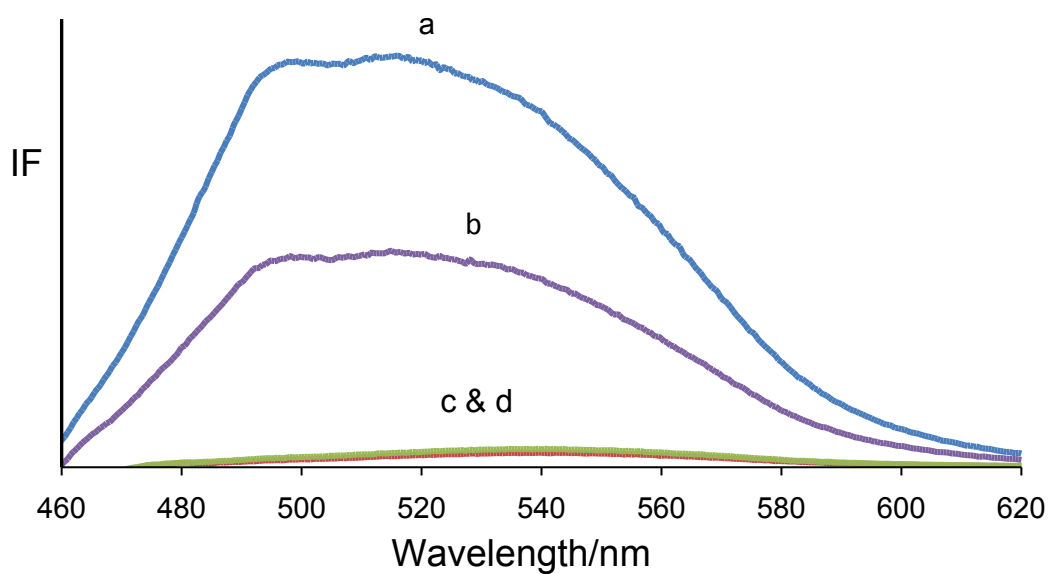


Figure S3. Fluorescent spectra of 10 μM **3** in 1:1 (v/v) methanol/water excited at 385 nm. The input conditions are: (a) high H^+ and high Fe^{3+} , (b) high H^+ , (c) high Fe^{3+} , and (d) neat sensor. The H^+ and Fe^{3+} concentrations are 200 μM and 20 μM , respectively.

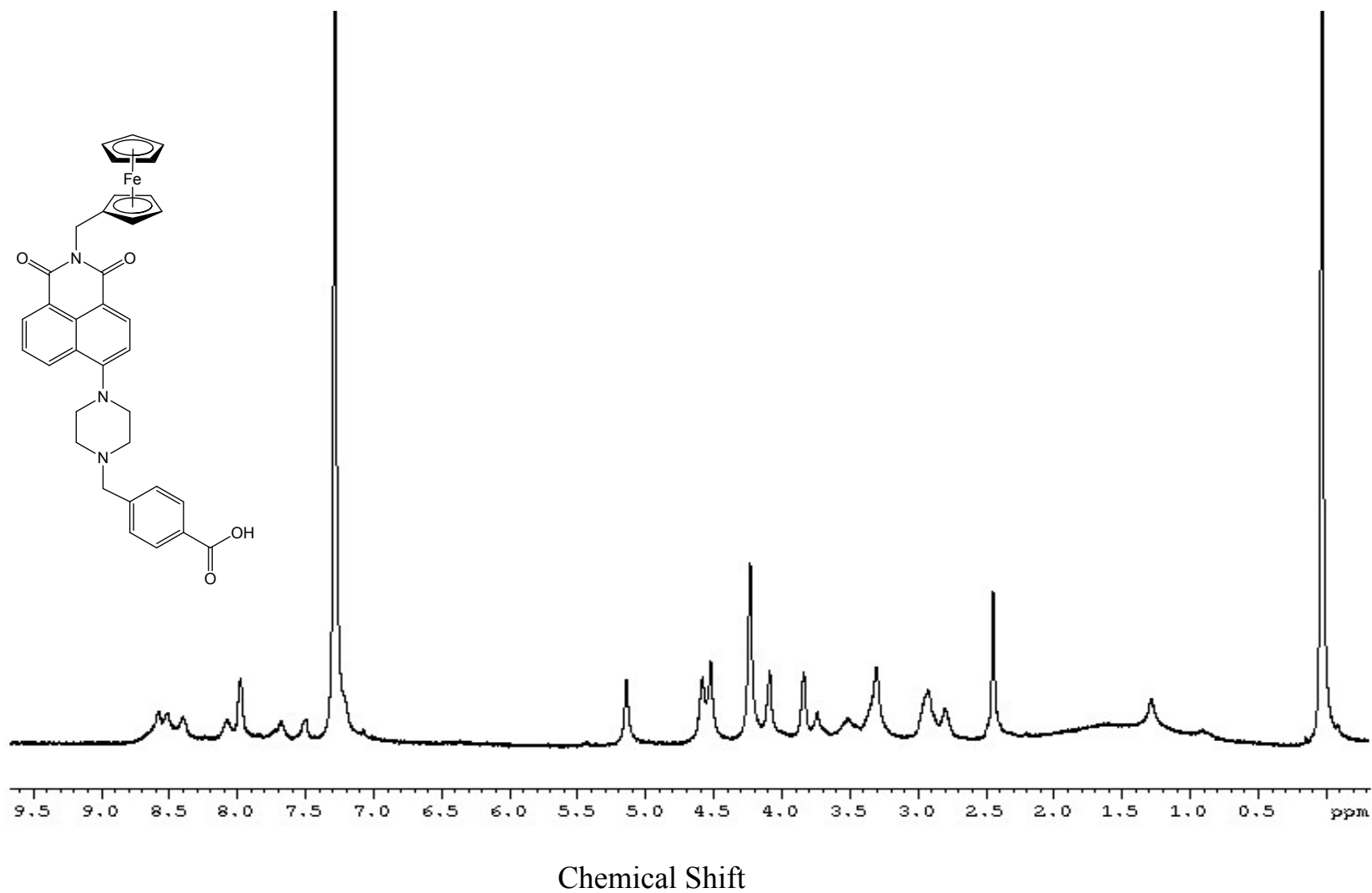


Figure S4. ^1H NMR spectrum of **3** in CDCl_3 .

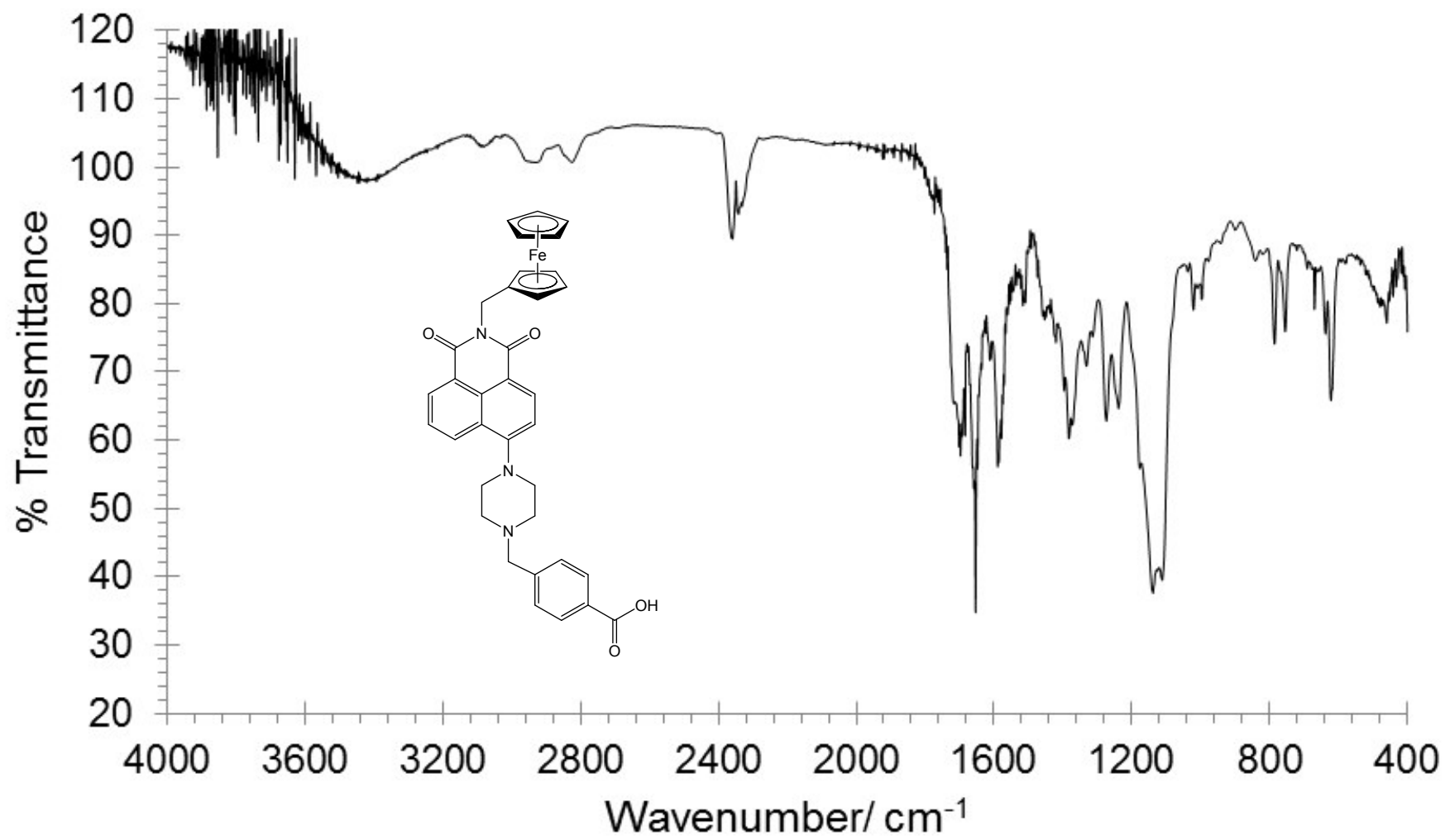


Figure S5. FTIR spectrum of 3.

MEDAC_MVUMS2
MEDAC_MVUMS2 7 (0.227)

ES-ToF

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1: TOF MS ES-
1.50e3

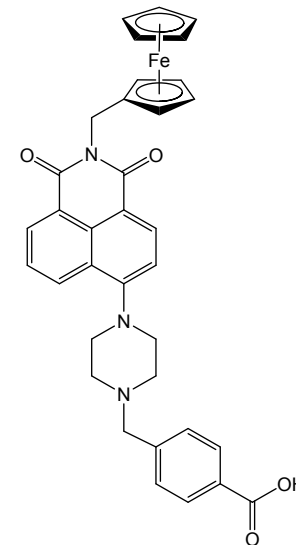
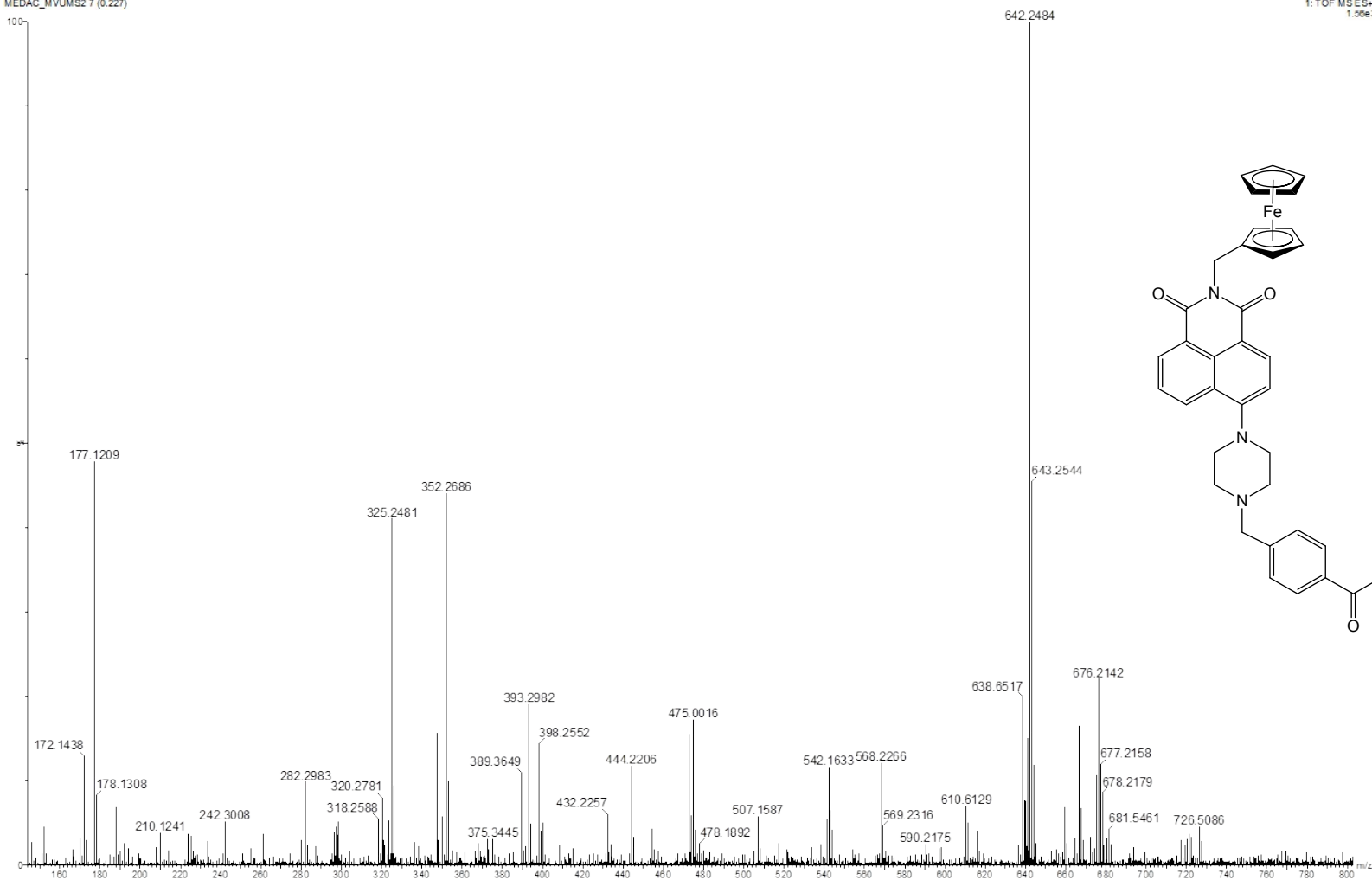


Figure S6. HRMS of compound 3.