Supporting Information

RSC Advances

Water-Soluble Amino(ethanesulfonate) and [(*bis*(ethanesulfonate)] Anthracenes as Fluorescent Photoinduced Electron Transfer (PET) pH Indicators and Fe^{3+} Chemosensors

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Experimental

The syntheses of the intermediate compounds were carried out according to literature procedures.

9-(Bromomethyl)anthracene[S1]

In a 500 ml round-bottomed flask fitted with a reflux condenser and a 1 inch long magnetic stir bar, 9-anthracenemethanol (1.65 g, 7.92 mmol) and 250 mL of diethyl ether were added. The mixture was stirred and warmed for 1 hour at 45 °C. Hydrobromic acid (4 mL, 80 mmol) was added dropwise to the reaction mixture followed by 0.8 mL of concentrated sulphuric acid and 1.0 g of sodium bromide. The reaction mixture was refluxed for 48 hours. After cooling, saturated potassium carbonate was added to neutralize the solution, as tested with litmus paper. The product was extracted three times with 25 ml of dichloromethane. The organic layer was washed three times with 25 mL of deionised water, dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to give fluffy yellow crystals in 96% yield. R_f = 0.46 (9:1 hexane:ethyl acetate); m.p. 132-133 ^oC (Lit. 137.5-142.5 ^oC);[S1] ^1H NMR (250 MHz, $CDCl_3$, ppm): δ 5.55 (s, 2H, CH_2Br), 7.45-7.55 (m, 2H, Ar-*H*), 7.58-7.71 (m, 2H, Ar-*H*), 8.04 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 8.31 (d, *J* = 9.8 Hz, 2H, Ar-*H*), 8.50 (s, 1H, Ar-*H*); ^{13}C NMR (63 MHz, $CDCl_3$): δ 27.0, 123.5, 125.4, 126.8, 127.9, 129.2, 129.3, 129.7, 131.6; IR (thin film, cm^{-1}): 727, 787, 839, 883, 1155, 1164, 1198, 1258, 1449, 1526, 1622, 2851, 2920, 3053, 3080.

9-(Azidomethyl)anthracene[S1]

9-(bromomethyl)anthracene (1.08 g, 4.00 mmol) was dissolved in 15 ml of *N,N*-dimethylformamide in a 100 ml round-bottomed flask, and the solution was stirred for 5 minutes. Sodium azide (1.05 g, 16.2 mmol) was added and the suspension was stirred at 50 °C for 2 hours. Upon cooling 25 ml of distilled water was added to the mixture. The contents were extracted twice with 25 mL portions of diethyl ether. The ether layers were combined, washed with distilled water (3 × 25 ml), dried over anhydrous sodium sulfate and filtered. The solvent was evaporated under reduced pressure on a rotary evaporator to give yellow crystals in 92% yield. R_f = 0.53 (9:1 hexane:ethyl acetate); m.p. 72 -76 ^oC (Lit. 84-86 ^oC);[S1] ^1H NMR (250 MHz, $CDCl_3$): δ 5.33 (s, 2H, CH_2N_3), 7.45-7.65 (m, 4H, Ar-*H*), 8.05 (d, *J* = 7.9 Hz, 2 H, Ar-*H*), 8.30 (d, *J* = 9.8 Hz, 2H, Ar-*H*), 8.51 (s, 1H, Ar-*H*); ^{13}C NMR (63

MHz, $CDCl_3$): δ 46.2, 123.5, 125.2, 125.8, 126.8, 129.0, 129.3, 130.7, 131.4; IR (thin film, cm^{-1}): 737, 795, 858, 871, 987, 959, 1045, 1157, 1229, 1335, 1445, 1622, 2058, 2093, 2920, 2947, 2999, 3057, 3078.

9-(Aminomethyl)anthracene[S2]

A two-necked 100 ml round bottomed flask was fitted with a dropping funnel and a magnetic stirrer was placed in an ice bath at 0 °C under a nitrogen atmosphere. 9-(Azidomethyl)anthracene (0.72 g, 3.10 mmol) was dissolved in 4 mL THF and added dropwise to the triphenylphosphine (1.32 g, 5.03 mmol). The round-bottomed flask was then removed from the ice-bath and left to stir at room temperature for 2 hours. Water (0.5 mL) was added dropwise and the reaction stirred for an additional hour. The contents were transferred to a beaker and 25 mL of diethyl ether added. The solution was cooled to 0 °C and acidified dropwise with 10 mL of 5 M HCl. A yellow solid precipitated out, which was collected by suction filtration and washed with a small amount of ice-cold 50:50 acetone:water.

To regenerate the amine, the solid was suspended in 30 ml of ethyl acetate in an ice-bath and made basic by the dropwise addition of aqueous ammonia. The resulting solution was transferred to a 250 ml separatory funnel, washed with 50 mL of water and the aqueous layer extracted twice with 25 mL of ethyl acetate. The combined organic layers were washed twice with 50 ml distilled water, dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure to give yellow crystals in 88% yield. R_f = 0.52 (7:3 $CHCl_3$:MeOH); m.p. 104-106 °C (Lit. 102 °C);[S2] ^{1}H NMR (250 MHz, $CDCl_3$, ppm): 4.83 (s, 2H, CH_2NH$_2$), 7.42-7.60 (m, 4 H, Ar-*H*), 8.03 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 8.34 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 8.40 (s, 1H, Ar-*H*); ^{13}C NMR (63 MHz, $CDCl_3$, ppm): δ 38.3, 123.7, 125.0, 126.1, 126.9, 129.3, 129.4, 131.8, 134.7; IR (KBr disc, cm^{-1}): 731, 841, 881, 901, 914, 1061, 1120, 1157, 1177, 1190, 1279, 1331, 1439, 1493, 1589, 1620, 2901, 2963, 3045, 3167, 3238, 3347.

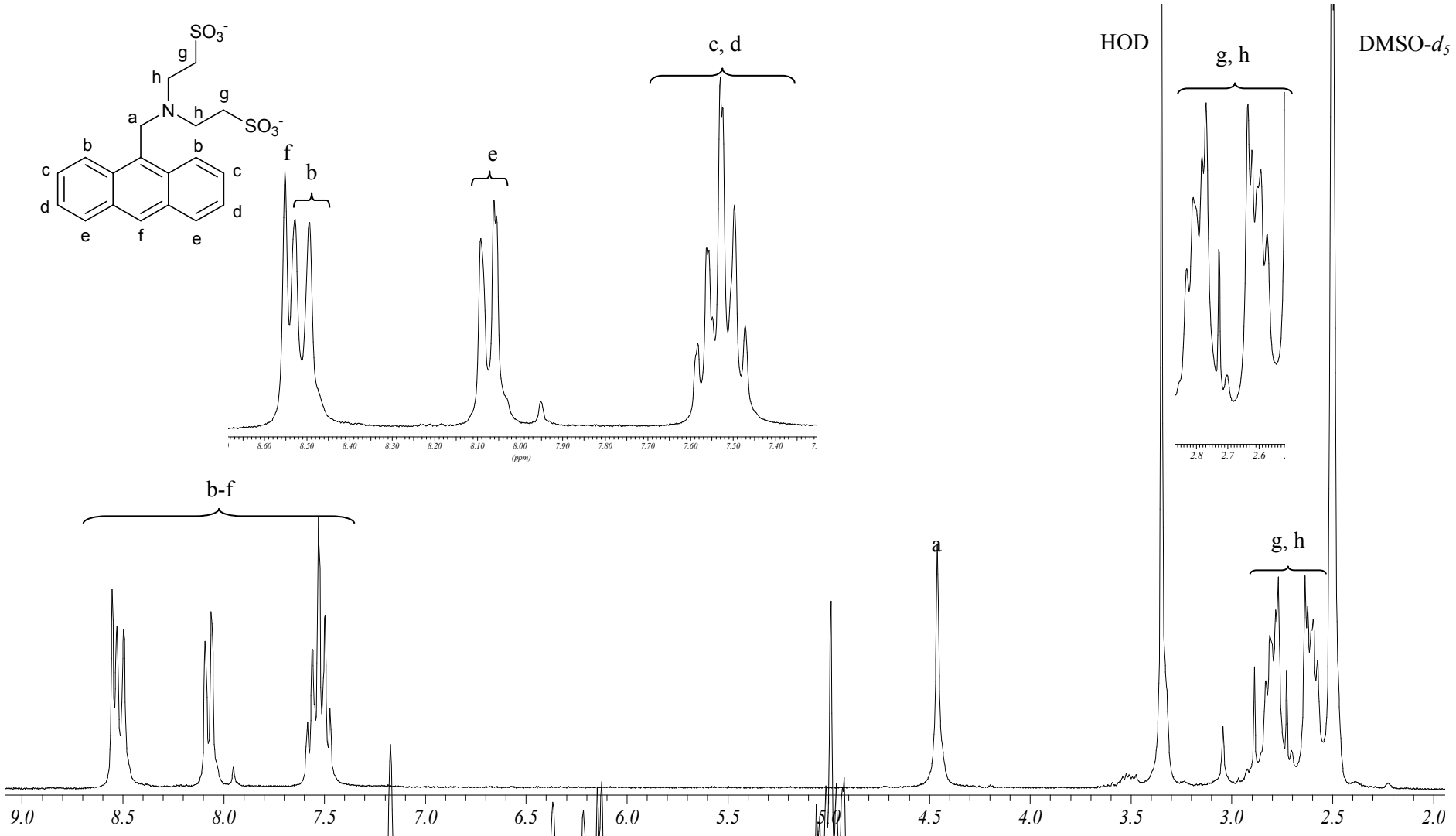

Figure S1: ^{1}H NMR spectrum of **1** in DMSO-d_6 at 250 MHz.

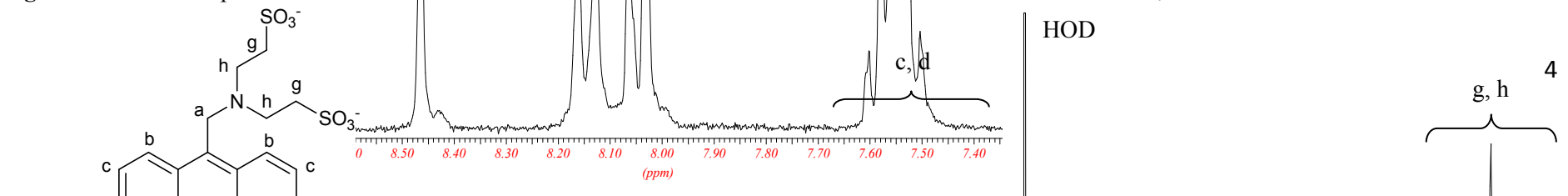

Figure S2: ^{1}H NMR spectrum of **1** in D_2O at 250 MHz.

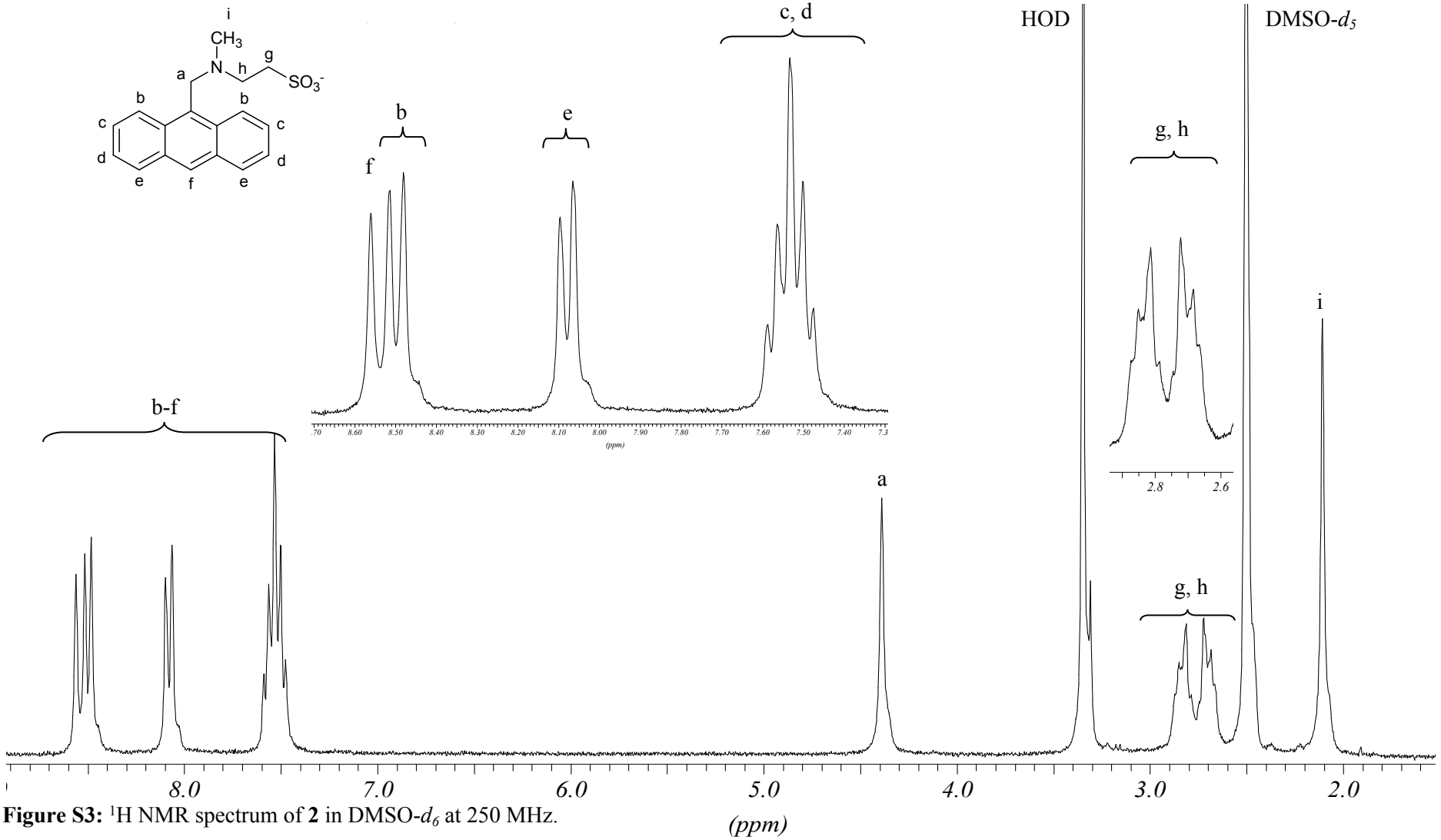

Figure S3: ^{1}H NMR spectrum of **2** in DMSO-d_6 at 250 MHz.

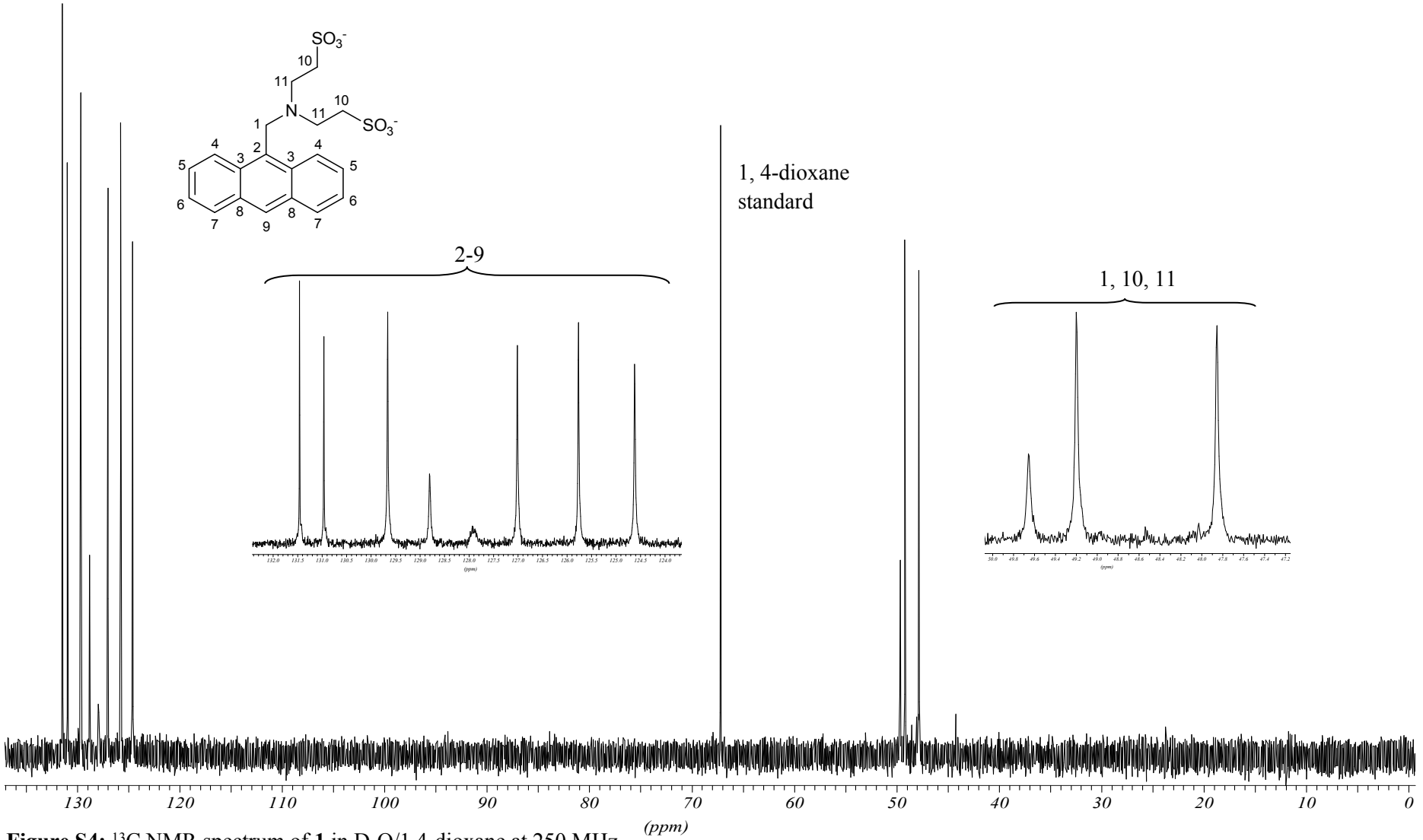

Figure S4: ^{13}C NMR spectrum of **1** in D_2O/1,4-dioxane at 250 MHz.

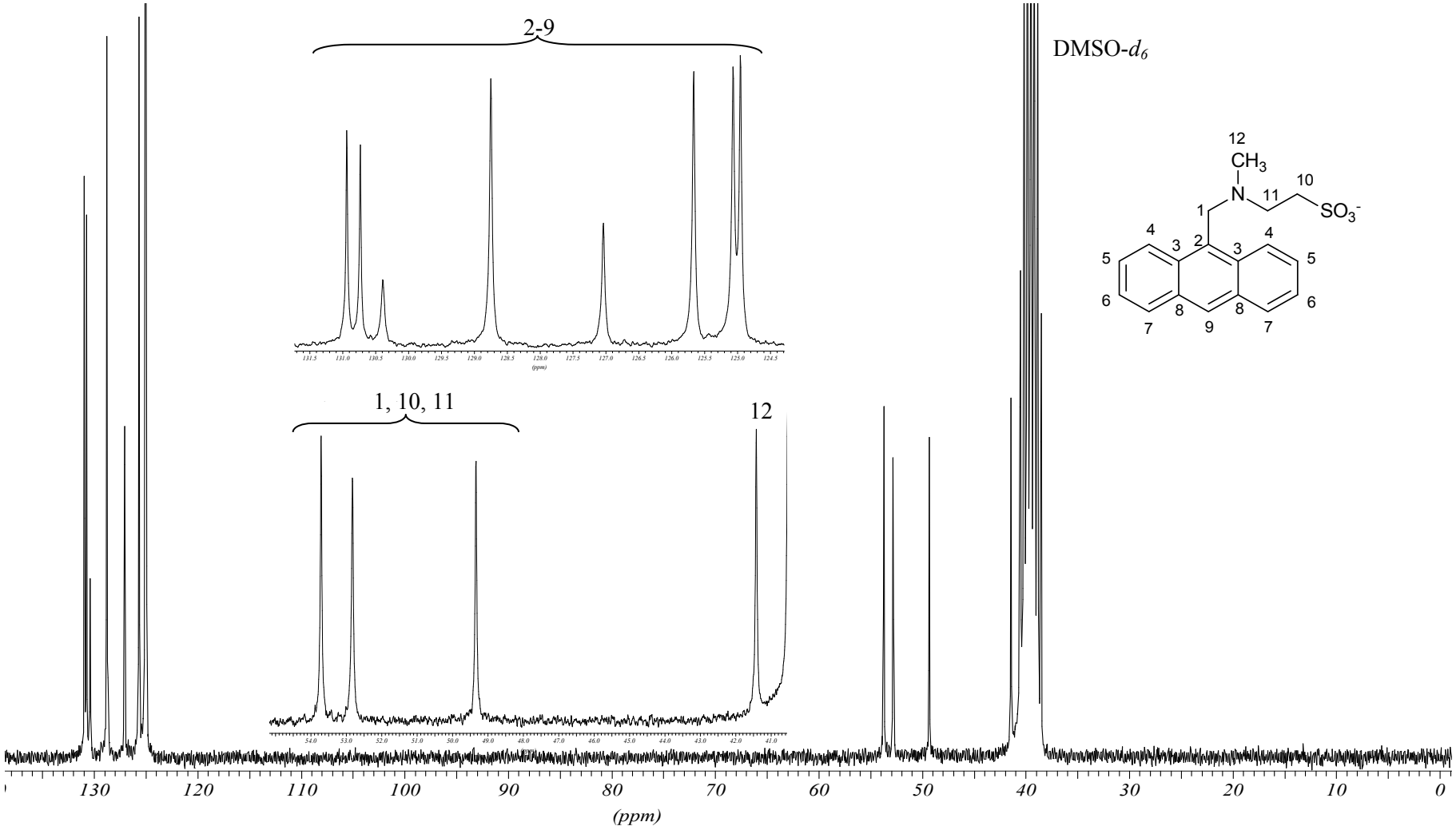

Figure S5: ^{13}C NMR spectrum of **2** in DMSO-d_6 at 250 MHz.

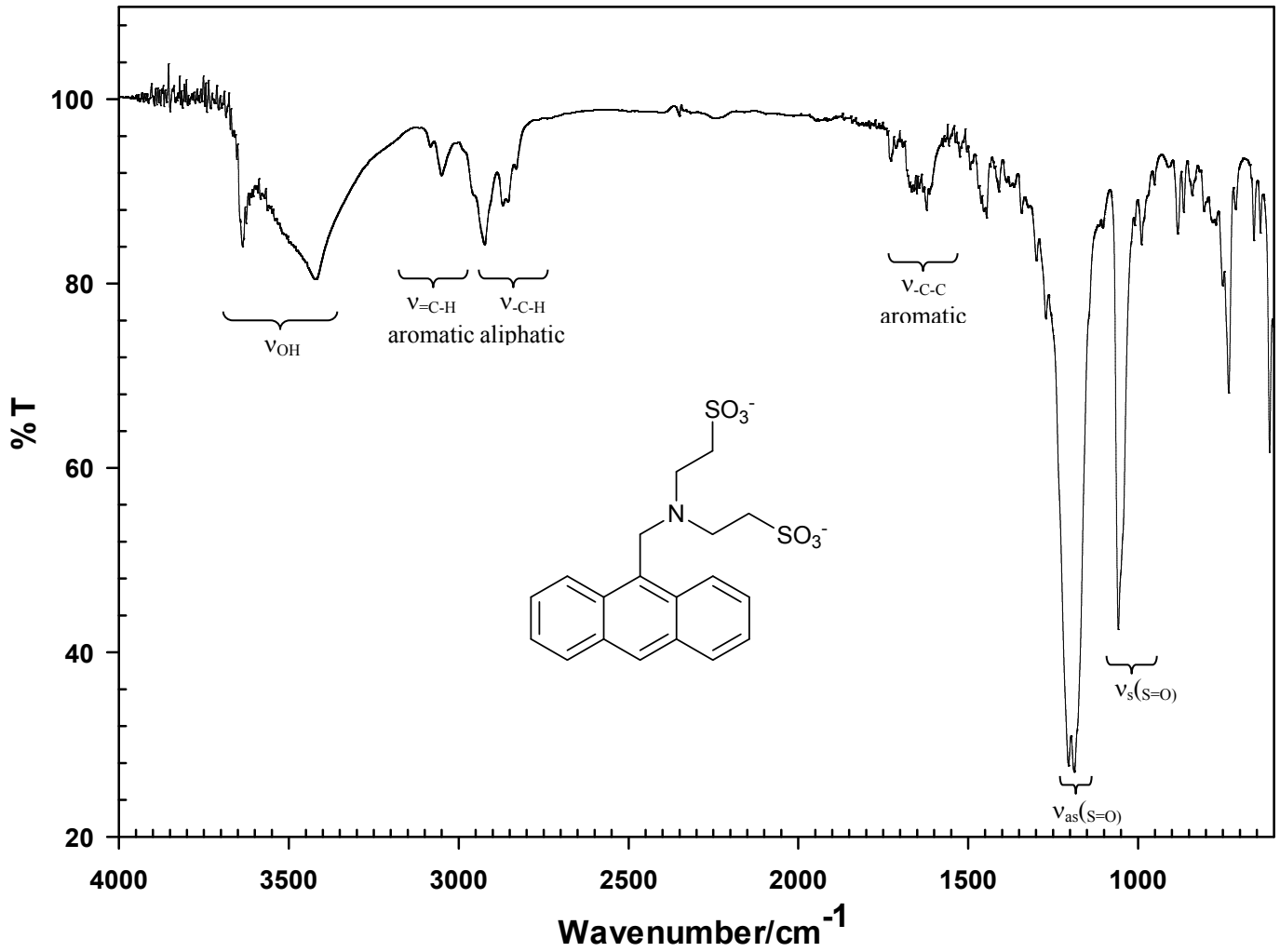

Figure S6: IR spectrum of **1** (KBr disc).

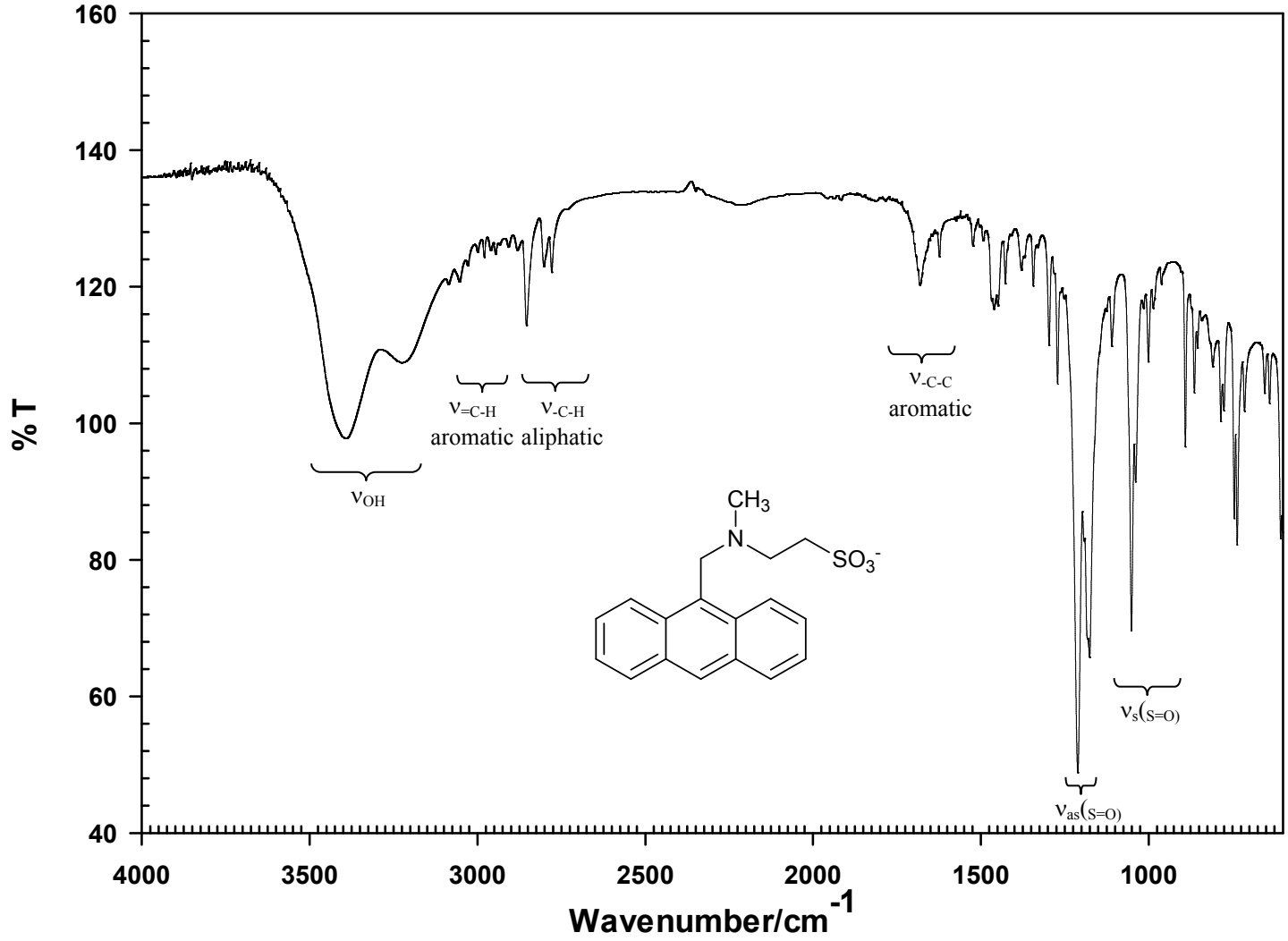

Figure S7: IR spectrum of **2** (KBr disc).

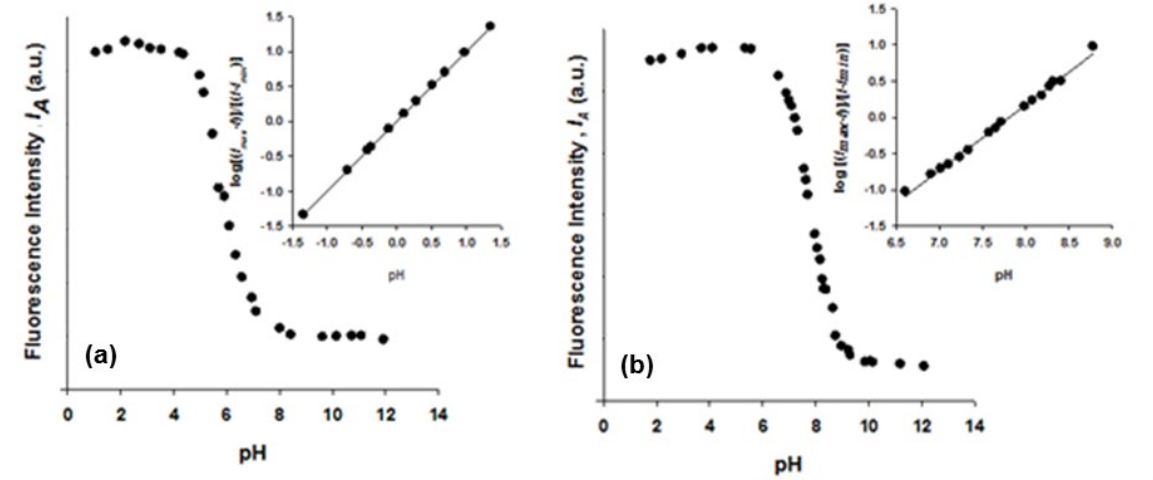

Figure S8: Fluorescence titration curves of 20 μM solutions of **1** (a) and **2** (b) containing 0.2 mM EDTA upon titration with 0.1 M HCl. **Inset**: A plot of log $[(I_{max} - I)]/[(I - I_{min})]$ against pH to determine the pK_a*.

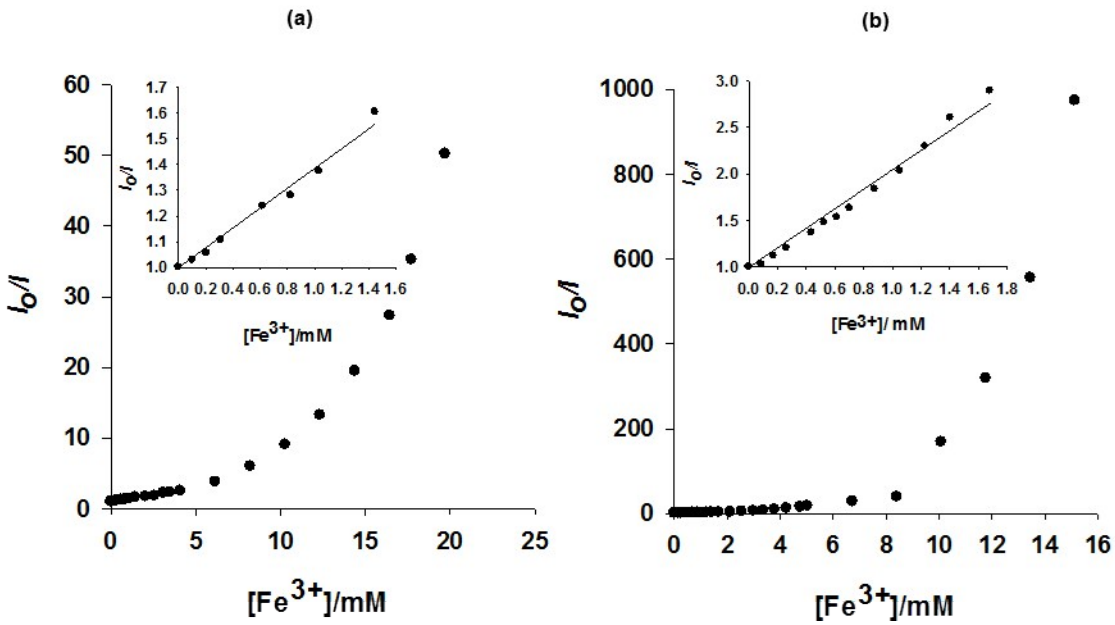

Figure S9: Stern-Volmer plot for **1** (a) and **2** (b) in the presence of increasing concentrations of Fe^{3+} at pH 3. **Inset**: The Stern-Volmer plot at low concentrations of Fe^{3+}. λ_{ex} = 352 nm.

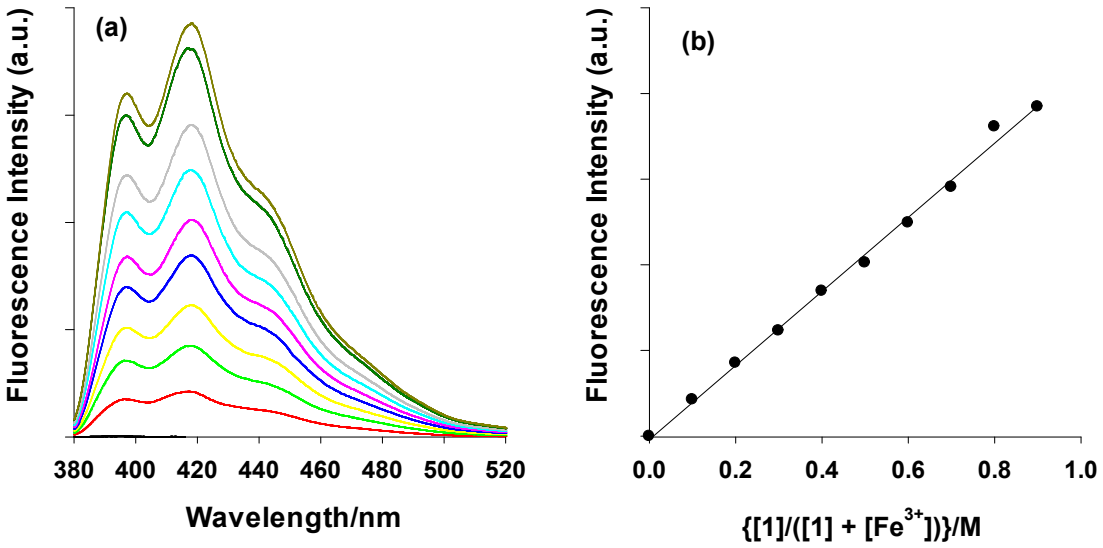

Figure S10: (a) Fluorescence spectra obtained on increasing the mole fraction of **1**. (b) Job's plot showing the fluorescence intensity at 418 nm against the mole fraction of **1** excited at 370 nm.

Crystallographic Data for Anthracene 2

Table S1 Crystal data and structure refinement for anthracene 2.

Empirical formula	$C_{18}H_{22}KNO_5S$
Formula weight/g mol^{-1}	403.52
Temperature/K	120
Crystal system	Monoclinic
Space group	$P2_1/c$
***a*/Å**	23.671(5)
***b*/Å**	8.6038(19)
***c*/Å**	9.530(2)
***α*/°**	90
***β*/°**	99.236(2)
***γ*/°**	90
Volume/Å^3	1915.8(7)
Z	4
ρ_{calc}g/cm^3	1.399
μ/mm^{-1}	0.383
F(000)	848.0
Crystal size/mm^3	0.05 × 0.05 × 0.001
Radiation	Synchrotron (λ = 0.6889)
2Θ range for data collection/°	3.38 to 55.072
Index ranges	$-31 \le h \le 31$, $-9 \le k \le 11$, $-12 \le l \le 12$
Reflections collected	16779
Independent reflections	4615 [R_{int} = 0.0416, R_{sigma} = 0.0431]
Data/restraints/parameters	4615/0/323
Goodness-of-fit on F^2	1.018
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1091
Final *R* indexes [all data]	R_1 = 0.0655, wR_2 = 0.1194
Largest diff. peak/hole / e Å^{-3}	0.74/-0.38

Table S2 Bond lengths for anthracene 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
K1	K1^1	4.4399(9)	N15	C16	1.474(3)
K1	K1^2	4.4399(10)	N15	C17	1.483(3)
K1	K1^3	4.3023(12)	N15	C14	1.487(3)
K1	S19	3.5180(8)	C18	C17	1.523(3)
K1	S19^4	3.4373(8)	C1	C14	1.526(3)
K1	O22	2.7528(16)	C1	C13	1.414(4)
K1	O100	2.7214(18)	C1	C2	1.420(4)
K1	O20^4	3.0978(18)	C8	C9	1.396(5)
K1	O20^5	2.6702(17)	C8	C7	1.385(4)
K1	O21^4	2.7777(16)	C13	C4	1.424(4)
K1	O21	3.3739(17)	C13	C9	1.453(3)
K1	O21^1	2.7370(17)	C2	C3	1.433(4)
S19	K1^6	3.4374(8)	C2	C7	1.455(3)
S19	O22	1.4677(16)	C12	C4	1.369(4)
S19	O20	1.4537(16)	C12	C11	1.435(5)
S19	O21	1.4645(16)	C3	C15	1.365(4)

S19	C18	1.790(2)	C10	C9	1.424(4)
O20	K1[6]	3.0978(18)	C10	C11	1.350(5)
O20	K1[5]	2.6701(17)	C5	C6	1.340(5)
O21	K1[2]	2.7370(17)	C5	C15	1.425(4)
O21	K1[6]	2.7778(16)	C7	C6	1.437(4)

[1]-X,1/2+Y,1/2-Z; [2]-X,-1/2+Y,1/2-Z; [3]-X,2-Y,1-Z; [4]+X,3/2-Y,1/2+Z; [5]-X,2-Y,-Z; [6]+X,3/2-Y,-1/2+Z

Table S3 Bond angles for anthracene 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
K1[1]	K1	K1[2]	151.35(2)	O21[4]	K1	O20[4]	48.33(4)
K1[3]	K1	K1[1]	120.15(2)	O21[2]	K1	O20[4]	125.78(5)
K1[3]	K1	K1[2]	77.674(16)	O21[2]	K1	O21[4]	77.46(5)
S19	K1	K1[1]	60.228(14)	O21[4]	K1	O21	107.79(4)
S19[4]	K1	K1[1]	61.046(16)	O21[2]	K1	O21	162.88(4)
S19[4]	K1	K1[2]	121.08(2)	K1[6]	S19	K1	104.06(2)
S19	K1	K1[2]	91.164(19)	O22	S19	K1[6]	151.18(6)
S19	K1	K1[3]	134.14(2)	O22	S19	K1	47.68(6)
S19[4]	K1	K1[3]	62.302(18)	O22	S19	C18	105.91(10)
S19[4]	K1	S19	88.14(2)	O20	S19	K1	107.69(7)
O22	K1	K1[1]	74.81(4)	O20	S19	K1[6]	64.31(7)
O22	K1	K1[2]	77.65(4)	O20	S19	O22	113.75(10)
O22	K1	K1[3]	111.98(4)	O20	S19	O21	112.26(9)
O22	K1	S19[4]	79.50(4)	O20	S19	C18	105.69(10)
O22	K1	S19	23.22(3)	O21	S19	K1[6]	51.67(6)
O22	K1	O20[4]	72.84(5)	O21	S19	K1	72.27(7)
O22	K1	O21	45.35(4)	O21	S19	O22	111.95(9)
O22	K1	O21[4]	96.04(5)	O21	S19	C18	106.59(10)
O100	K1	K1[2]	138.14(4)	C18	S19	K1	144.10(8)
O100	K1	K1[1]	63.37(4)	C18	S19	K1[6]	101.98(8)
O100	K1	K1[3]	104.35(4)	S19	O22	K1	109.10(8)
O100	K1	S19[4]	94.61(5)	K1[5]	O20	K1[6]	100.40(5)
O100	K1	S19	112.76(4)	S19	O20	K1[6]	90.68(8)
O100	K1	O22	134.45(5)	S19	O20	K1[5]	165.30(10)
O100	K1	O20[4]	83.04(5)	K1[1]	O21	K1	92.60(4)
O100	K1	O21[4]	95.76(6)	K1[6]	O21	K1	125.81(5)
O100	K1	O21[2]	106.71(5)	K1[1]	O21	K1[6]	102.54(5)
O100	K1	O21	89.21(5)	S19	O21	K1[1]	149.98(9)
O20[5]	K1	K1[1]	126.37(4)	S19	O21	K1	83.31(7)
O20[5]	K1	K1[3]	113.47(4)	S19	O21	K1[6]	103.90(8)
O20[5]	K1	K1[2]	43.33(4)	C16	N15	C17	107.82(17)
O20[4]	K1	K1[1]	36.26(3)	C16	N15	C14	109.97(18)
O20[4]	K1	K1[3]	86.72(3)	C17	N15	C14	110.32(18)
O20[4]	K1	K1[2]	138.30(4)	C17	C18	S19	112.01(14)
O20[4]	K1	S19[4]	25.02(3)	N15	C17	C18	113.14(17)
O20[4]	K1	S19	72.51(3)	C13	C1	C14	118.5(2)
O20[5]	K1	S19	83.48(4)	C13	C1	C2	120.6(2)
O20[5]	K1	S19[4]	161.78(4)	C2	C1	C14	120.9(2)

O20[5]	K1	O22	86.59(5)	N15	C14	C1	113.46(19)
O20[5]	K1	O100	103.55(6)	C7	C8	C9	122.2(2)
O20[5]	K1	O20[4]	155.72(3)	C1	C13	C4	123.2(2)
O20[4]	K1	O21	61.20(4)	C1	C13	C9	119.1(3)
O20[5]	K1	O21	95.20(5)	C4	C13	C9	117.6(2)
O20[5]	K1	O21[4]	150.13(5)	C1	C2	C3	124.1(2)
O20[5]	K1	O21[2]	75.29(5)	C1	C2	C7	119.2(2)
O21	K1	K1[1]	38.01(3)	C3	C2	C7	116.7(2)
O21[4]	K1	K1[1]	82.65(4)	C4	C12	C11	119.9(3)
O21[4]	K1	K1[2]	108.11(4)	C15	C3	C2	121.9(2)
O21[2]	K1	K1[2]	49.39(4)	C12	C4	C13	121.6(3)
O21[4]	K1	K1[3]	38.39(3)	C11	C10	C9	121.3(3)
O21[2]	K1	K1[3]	39.07(3)	C8	C9	C13	119.4(3)
O21[2]	K1	K1[1]	156.82(4)	C8	C9	C10	121.6(3)
O21	K1	K1[2]	114.15(3)	C10	C9	C13	119.0(3)
O21	K1	K1[3]	143.63(3)	C6	C5	C15	119.6(3)
O21[2]	K1	S19	138.52(4)	C8	C7	C2	119.4(3)
O21[4]	K1	S19	109.90(4)	C8	C7	C6	121.9(2)
O21[2]	K1	S19[4]	101.15(4)	C6	C7	C2	118.7(3)
O21	K1	S19[4]	83.38(3)	C10	C11	C12	120.5(3)
O21	K1	S19	24.42(3)	C5	C6	C7	122.2(3)
O21[4]	K1	S19[4]	24.43(3)	C3	C15	C5	120.9(3)
O21[2]	K1	O22	118.78(5)				

[1]-X,-1/2+Y,1/2-Z; [2]-X,1/2+Y,1/2-Z; [3]-X,2-Y,1-Z; [4]+X,3/2-Y,1/2+Z; [5]-X,2-Y,-Z; [6]+X,3/2-Y,-1/2+Z

Table S4 Hydrogen bonds for anthracene 2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O100	H10A	O101[1]	0.83(3)	1.92(3)	2.742(3)	173(3)
O101	H10C	N15[2]	0.91(4)	2.01(4)	2.893(3)	163(3)
O101	H10D	O100[3]	0.85(3)	1.98(4)	2.825(3)	174(3)
O100	H10B	O22[4]	0.83(4)	1.95(4)	2.772(3)	172(4)

[1]-X,1/2+Y,1/2-Z; [2]+X,1/2-Y,1/2+Z; [3]-X,1-Y,1-Z; [4]-X,-1/2+Y,1/2-Z

Table S5 Torsion angles for anthracene 2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
K1[1]	S19	O22	K1	13.30(18)	C1	C13	C9	C8	2.7(4)
K1	S19	O20	K1[2]	41.7(4)	C1	C13	C9	C10	-175.4(2)
K1[1]	S19	O20	K1[2]	139.2(4)	C1	C2	C3	C15	-178.5(3)
K1	S19	O20	K1[1]	-97.44(4)	C1	C2	C7	C8	0.9(4)
K1[1]	S19	O21	K1[3]	151.1(2)	C1	C2	C7	C6	179.7(2)
K1	S19	O21	K1[3]	-83.58(18)	C14	N15	C17	C18	64.4(3)
K1	S19	O21	K1[1]	125.30(6)	C14	C1	C13	C4	-2.6(3)
K1[1]	S19	O21	K1	-125.30(6)	C14	C1	C13	C9	176.0(2)
K1[1]	S19	C18	C17	-119.87(16)	C14	C1	C2	C3	1.4(4)
K1	S19	C18	C17	15.9(3)	C14	C1	C2	C7	-177.7(2)
S19	C18	C17	N15	168.67(15)	C8	C7	C6	C5	176.6(3)
O22	S19	O20	K1[1]	-148.26(7)	C13	C1	C14	N15	76.6(3)

O22	S19	O20	K1[2]	-9.1(4)	C13	C1	C2	C3	177.8(2)
O22	S19	O21	K1[3]	-56.6(2)	C13	C1	C2	C7	-1.3(3)
O22	S19	O21	K1[1]	152.32(8)	C2	C1	C14	N15	-106.9(3)
O22	S19	O21	K1	27.01(8)	C2	C1	C13	C4	-179.1(2)
O22	S19	C18	C17	52.75(19)	C2	C1	C13	C9	-0.5(3)
O20	S19	O22	K1	92.77(10)	C2	C3	C15	C5	-0.2(4)
O20	S19	O21	K1[3]	174.07(17)	C2	C7	C6	C5	-2.2(4)
O20	S19	O21	K1[1]	22.95(10)	C3	C2	C7	C8	-178.3(2)
O20	S19	O21	K1	-102.35(8)	C3	C2	C7	C6	0.5(3)
O20	S19	C18	C17	173.76(16)	C4	C13	C9	C8	-178.6(2)
O21	S19	O22	K1	-35.81(11)	C4	C13	C9	C10	3.3(3)
O21	S19	O20	K1[2]	119.3(4)	C4	C12	C11	C10	1.4(4)
O21	S19	O20	K1[1]	-19.84(9)	C9	C8	C7	C2	1.4(4)
O21	S19	C18	C17	-66.62(19)	C9	C8	C7	C6	-177.4(2)
C16	N15	C17	C18	-175.46(19)	C9	C13	C4	C12	-3.5(4)
C16	N15	C14	C1	67.2(3)	C9	C10	C11	C12	-1.5(4)
C18	S19	O22	K1	-151.59(9)	C7	C8	C9	C13	-3.2(4)
C18	S19	O20	K1[2]	-124.9(4)	C7	C8	C9	C10	174.8(3)
C18	S19	O20	K1[1]	95.97(9)	C7	C2	C3	C15	0.6(4)
C18	S19	O21	K1[3]	58.8(2)	C11	C12	C4	C13	1.2(4)
C18	S19	O21	K1	142.38(8)	C11	C10	C9	C8	-178.9(3)
C18	S19	O21	K1[1]	-92.32(9)	C11	C10	C9	C13	-0.9(4)
C17	N15	C14	C1	-174.0(2)	C6	C5	C15	C3	-1.4(5)
C1	C13	C4	C12	175.1(2)	C15	C5	C6	C7	2.6(4)

[1]+X,3/2-Y,-1/2+Z; [2]-X,2-Y,-Z; [3]-X,-1/2+Y,1/2-Z

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S2. K. Ohara, M. Smietana, A. Restouin, S. Mollard, J.-P. Borg, Y. Collette, J.-J. Vasseur, *J. Med. Chem.*, 2007, **50**, 6465.