Acridinone-based anion receptors and sensors

Sergio E. García-Garrido, Claudia Caltagirone, Mark E. Light and Philip A. Gale*
School of Chemistry, University of Southampton, Southampton, UK SO17 1BJ.
Fax: +44 23 8059 6805; Tel: +44 23 8059 3332;
E-mail: Philip.gale@soton.ac.uk

Supplementary information

Experimental procedures:

All reactions were performed in oven-dried glassware under a slight positive pressure of nitrogen. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were determined on a Bruker AV300. Chemical shifts for ^{1}H NMR are reported in parts per million, calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet and br = broad. Chemical shifts for ^{13}C NMR are reported in ppm, relative to the central line of a septet at 39.52 ppm for deuterio-dimethylsulfoxide. Deuterated solvents were purchased from Apollo Ltd. ES MS were measured on Micromass Mattro II instrument. Infrared (IR) spectra were recorded on a Mattson Satellite (ATR) FTIR and are reported in wavenumbers (cm^{-1}). Uv-vis absorbance spectra were recorded on a Hitachi U-2001 spectrophotometer with fluorescence emission spectra recorded on a Hitachi F-2000 spectrofluorimeter with a 150W Xenon lamp. The photomultiplier voltage was set to 400V with excitation and emission slits set to 2.5 mm. Melting points were measured on a Gallenkamp melting point apparatus. Elemental analyses were performed by Medac Ltd.

4,5-dibenzamido-9(10H)-acridinone (2):

4,5-Diamino-9(10H)-acridinone (**1**, 0.2 g, 0.888 mmol) was placed in a dry round bottomed flask under N_2 atmosphere and 100 mL of pyridine was added. The mixture was heated at 100 °C for 5 min. and then a second solution of benzoyl chloride (0.31 mL, 2.64 mmol) in 50 mL of DMF was added dropwise over the course of 3 hours. The dark yellow solution was heated

at reflux for 1 hour and then filtered. The solution was concentrated *in vacuo* and 20 mL of boiling water was added to the resulting residue. The obtained precipitate was filtered, washed with water (3 x 10 mL) and dried to obtain a yellow-brown solid which was washed with 100 mL of a 1.0 M NaOH solution in water and filtered. This solid was washed with MeOH (3 x 20 mL) and filtered again to obtain a dark yellow powder which was dried under vacuum overnight (0.188 g, 49% yield); mp>300°C; ^{1}H NMR: (300 MHz, DMSO, δ): 10.56 (s, 2H, NH), 9.79 (s, 1H, acridinone NH), 8.24 (d, *J* = 9.0 Hz, 2H, Ar. H), 7.85 (m, 6H, Ar. H), 7.59 (t, *J* = 7.2 Hz, 2H, Ar. H), 7.37 (m, 6H, Ar. H); ^{13}C NMR: (75 MHz, DMSO, δ): 175.3 (C), 164.5 (C), 141.1 (C), 135.2 (C), 131.9 (C), 131.3 (CH), 128.7 (CH), 126.9 (CH), 121.7 (C), 120.6 (CH), 117.8 (CH), 116.8 (CH); LRMS (ES^-): 432.3 (M-H), 865.4 (2M-H); IR (film, cm^{-1}): 3363, 3324, 3050, 1684, 1674, 1623, 1599, 1583, 1543, 1506, 1486, 1433, 1339, 1276, 1258, 1222, 746, 703, 684, 608; Elemental analysis calcd (%) for $C_{27}H_{19}N_3O_3$: C: 74.81; H: 4.42; N: 9.69. Found C: 74.92; H: 4.40; N: 9.61.

4,5-bis(N-phenylureido)-9(10H)-acridinone (3):

4,5-Diamino-9(10H)-acridinone (**1**, 0.2 g, 0.888 mmol) was placed in a dry round bottomed flask under N_2 atmosphere and 50 mL of DMF was added. To this was then added a second solution of phenylisocyanate (1.99 mL, 17.76 mmol) in 10 mL of DMF and the mixture was stirred for 1 hour. The yellow solution was then evaporated *in vacuo* and the resulting residue was treated with a mixture of diethyl ether/hexane (1:1) (100 mL), filtered and washed with diethyl ether (3 x 20 mL) and MeOH (3 x 20 mL) to obtain a yellow solid which was dried under vacuum overnight (0.362 g, 88% yield); mp>300°C; ^{1}H NMR (300MHz, DMSO, *δ*): 10.65 (s, 1H, acridinone NH), 8.89 (s, 2H, NH), 8.73 (s, 2H, NH), 8.12 (d, *J* = 7.9 Hz, 2H, Ar. H), 7.68 (d, *J* = 7.2 Hz, 2H, Ar. H), 7.42 (d, *J* = 7.9 Hz, 4H, Ar. H), 7.30 (t, *J* = 7.6 Hz, 2H, Ar. H), 7.14 (t, *J* = 7.6 Hz, 4H, Ar. H), 6.94 (t, *J* = 7.2 Hz, 2H, Ar. H); ^{13}C NMR (75MHz, DMSO, *δ*): 176.9 (C), 153.9 (C), 139.4 (C), 135.6 (C), 129.2 (CH), 128.6 (CH), 127.1 (C), 122.7 (CH), 122.0 (CH), 121.5 (C), 121.1 (CH), 118.6 (CH); LRMS (ES^-): 462.3 (M-H),

926.3 (2M-H); IR (film, cm^{-1}): 3393, 3281, 3053, 1636, 1622, 1596, 1553, 1516, 1497, 1441, 1330, 1314, 1215, 754, 692; Elemental analysis calcd (%) for $C_{27}H_{21}N_5O_3$: C: 69.97; H: 4.57; N: 15.10. Found C: 69.82; H: 4.48; N: 15.12.

4,5-bis(N-phenylthioureido)-9(10H)-acridinone (4):

4,5-Diamino-9(10H)-acridinone (**1**, 0.2 g, 0.888 mmol) was placed in a dry round bottomed flask under N_2 atmosphere and 50 mL of DMF was added. To this was then added a second solution of phenylisothiocyanate (2.17 mL, 17.76 mmol) in 10 mL of DMF and the mixture left stirring for 3 hours. The yellow solution was then evaporated *in vacuo* and the resulting residue was treated with a mixture of diethyl ether/hexane (1:1) (100 mL), filtered and washed with diethyl ether (3 x 20 mL) and MeOH (3 x 20 mL) to obtain a yellow solid which was dried under vacuum overnight (0.370 g, 84% yield); mp>300°C; ^{1}H NMR: (300 MHz, DMSO, δ): 10.07 (s, 2H, NH), 9.75 (s, 2H, NH), 9.19 (s, 1H, acridinone NH), 8.19 (d, J = 8.0 Hz, 2H, Ar. H), 7.66 (d, J = 7.7 Hz, 2H, Ar. H), 7.51 (d, J = 8.0 Hz, 4H, Ar. H), 7.28 (m, 6H, Ar. H), 7.13 (t, J = 7.3 Hz, 2H, Ar. H); ^{13}C NMR (75MHz, DMSO, δ): 181.4 (C), 176.9 (C), 139.0 (C), 136.7 (C), 133.0 (CH), 128.4 (CH), 127.6 (C), 124.9 (CH), 124.6 (CH), 124.5 (CH), 121.3 (C), 121.1 (CH); LRMS (ES^-): 494.2 (M-H), 989.3 (2M-H); IR (film, cm^{-1}): 3291, 3204, 3025, 1619, 1581, 1542, 1522, 1496, 1439, 1344, 1320, 1278, 1217, 746, 722, 690, 647; Elemental analysis calcd (%) for $C_{27}H_{21}N_5S_2O$: C: 65.43; H: 4.27; N: 14.13. Found C: 65.31; H: 4.46; N: 14.07.

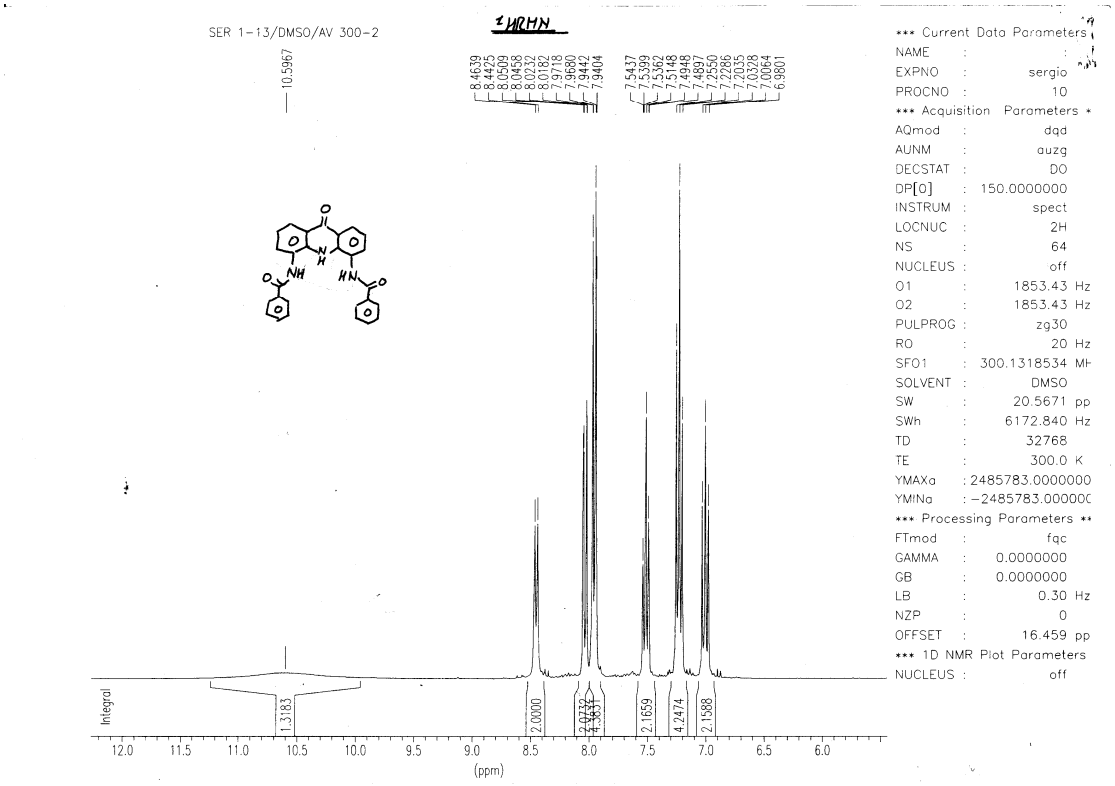


Figure S1 ^{1}H NMR spectrum of compound **2** in DMSO-d_6

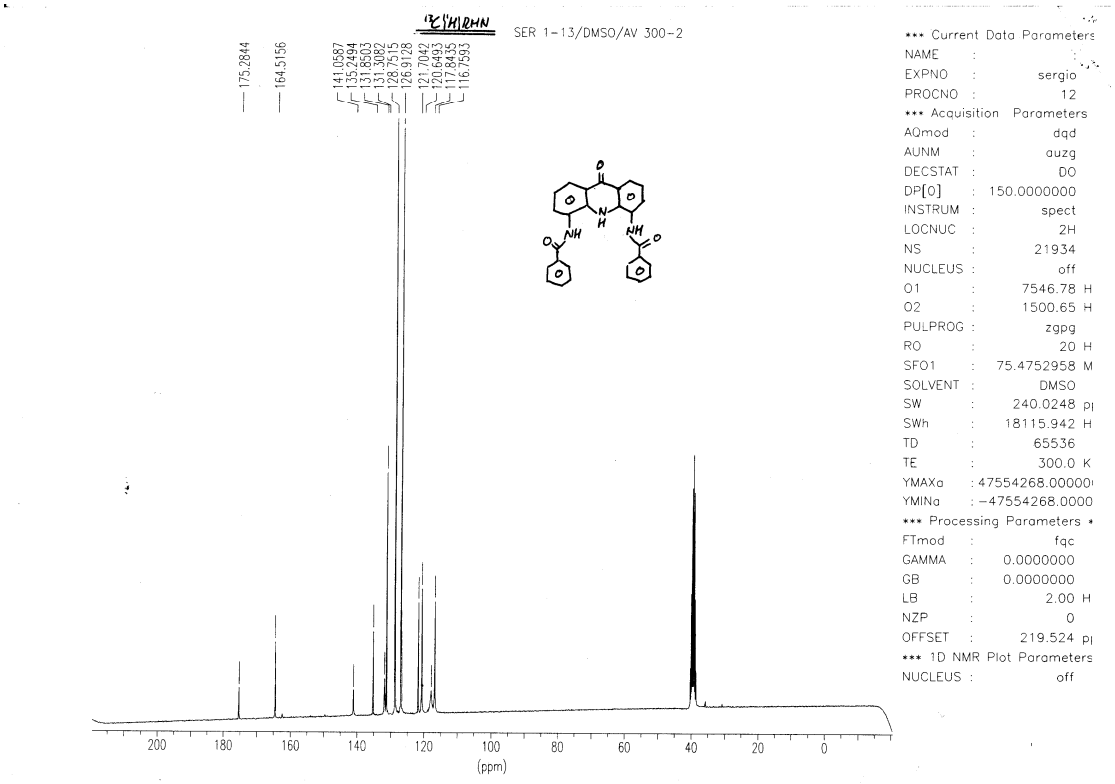


Figure S2 ^{13}C{^{1}H} NMR spectrum of compound **2** in DMSO-d_6

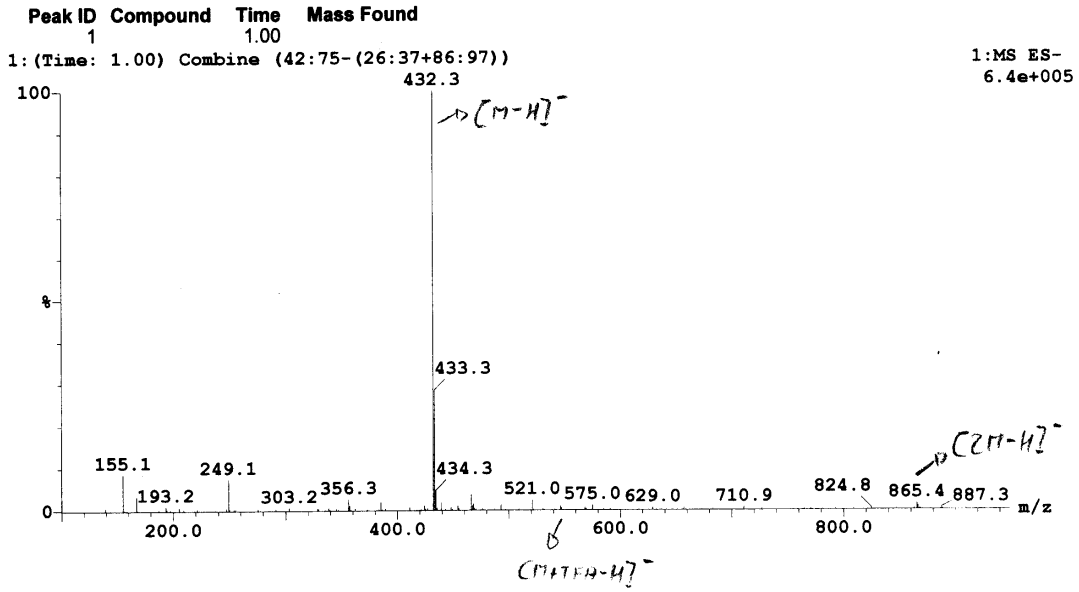
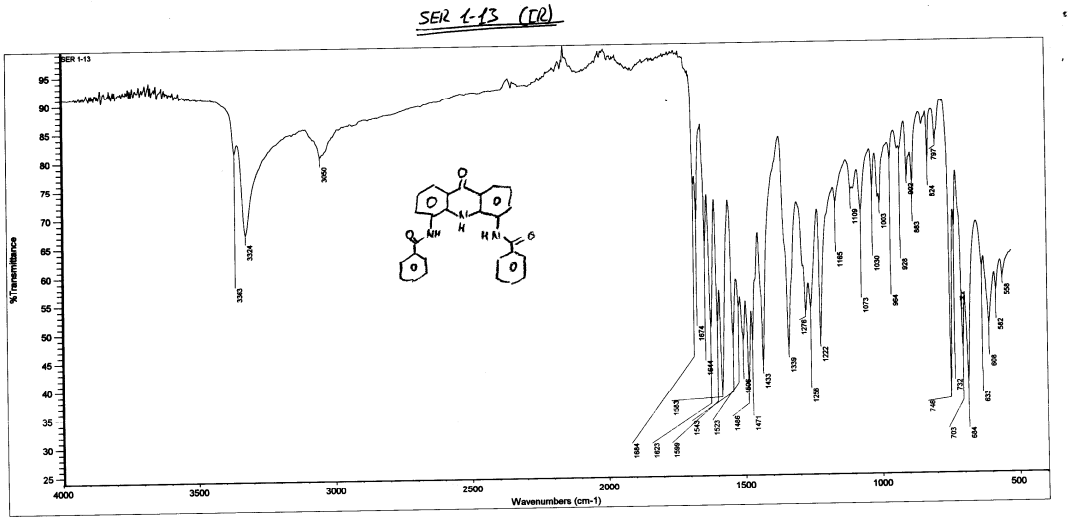


Figure S3 ESMS (-ve) of compound **2**



Thu Nov 16 11:07:10 2006 (GMT+00:00)
FIND PEAKS:
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Region: 4000 400
Absolute threshold: 82.756
Sensitivity: 57
Peak list:

Position:	558	Intensity:	58.367
Position:	582	Intensity:	55.984
Position:	608	Intensity:	49.927
Position:	633	Intensity:	60.117
Position:	684	Intensity:	39.630
Position:	703	Intensity:	45.894
Position:	732	Intensity:	66.879
Position:	746	Intensity:	37.830
Position:	797	Intensity:	82.038
Position:	824	Intensity:	78.377
Position:	883	Intensity:	74.823
Position:	902	Intensity:	75.512
Position:	928	Intensity:	80.539
Position:	964	Intensity:	78.837
Position:	1003	Intensity:	70.828

Figure S4 IR spectrum of compound **2**

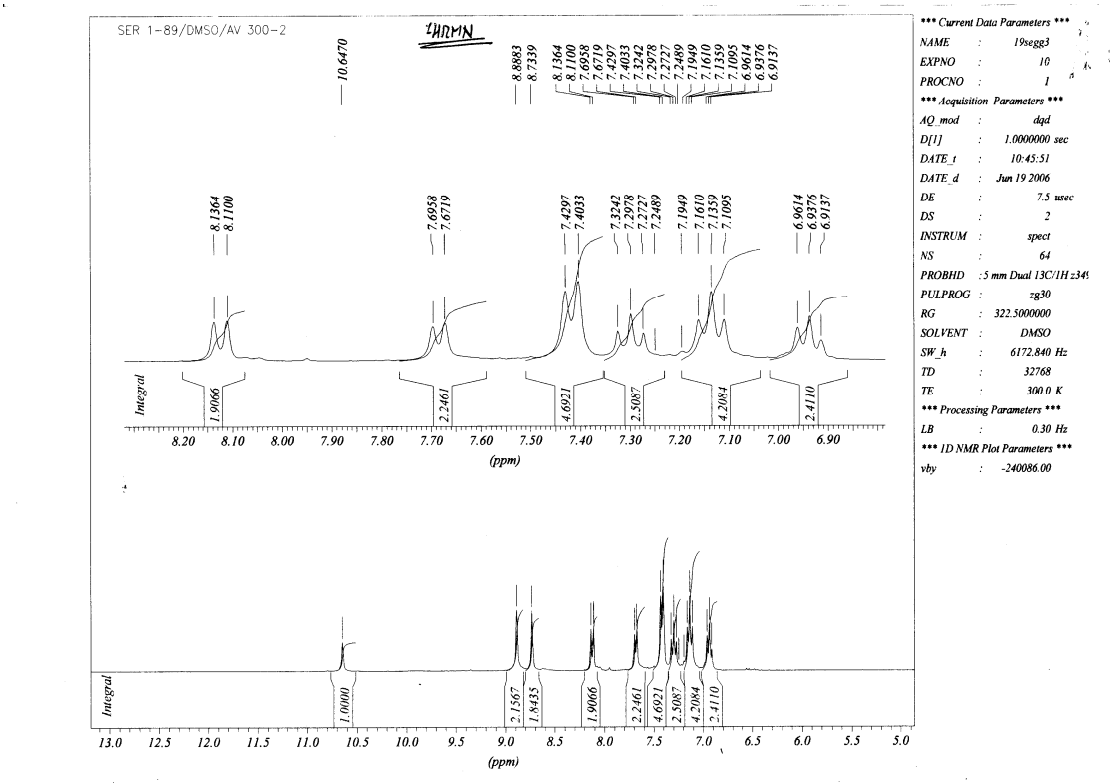


Figure S5 ^{1}H NMR spectrum of compound **3** in DMSO-d$_6$

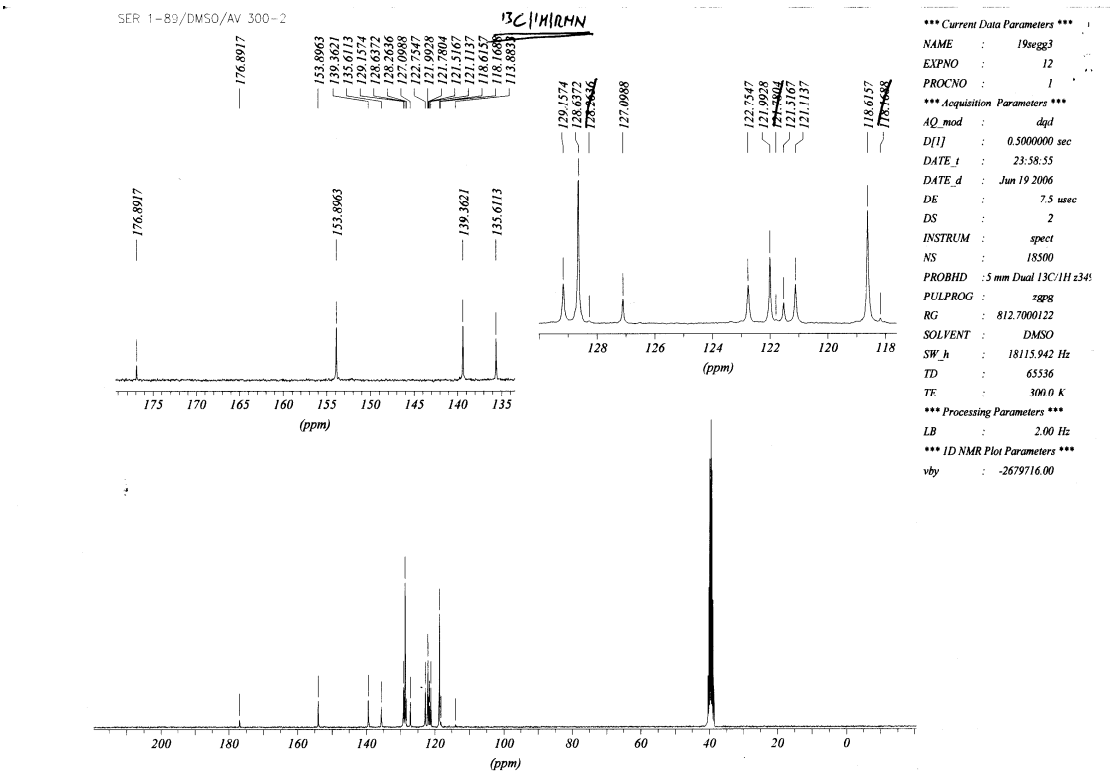


Figure S6 ^{13}C{^{1}H} NMR spectrum of compound **3** in DMSO-d$_6$

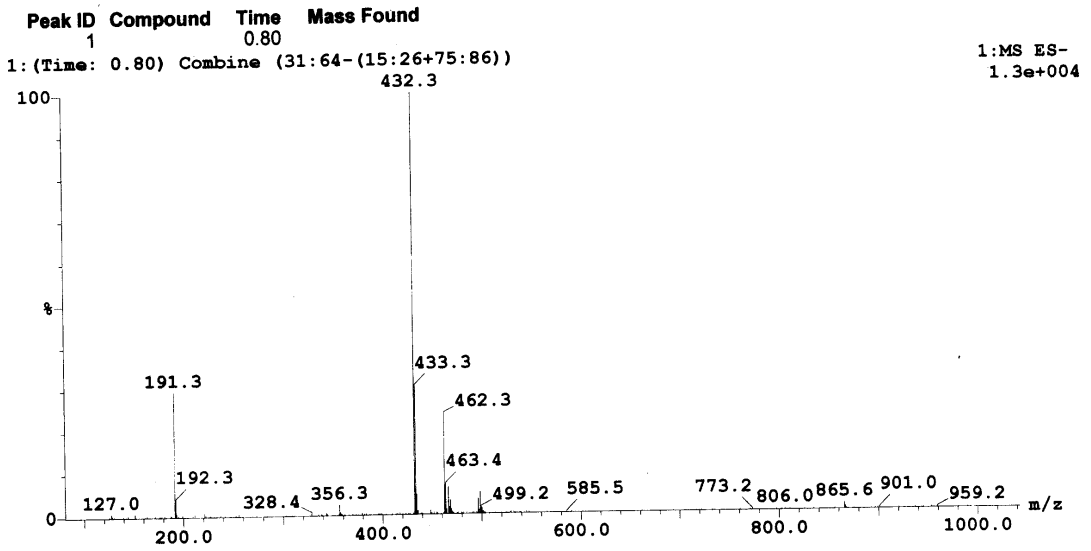
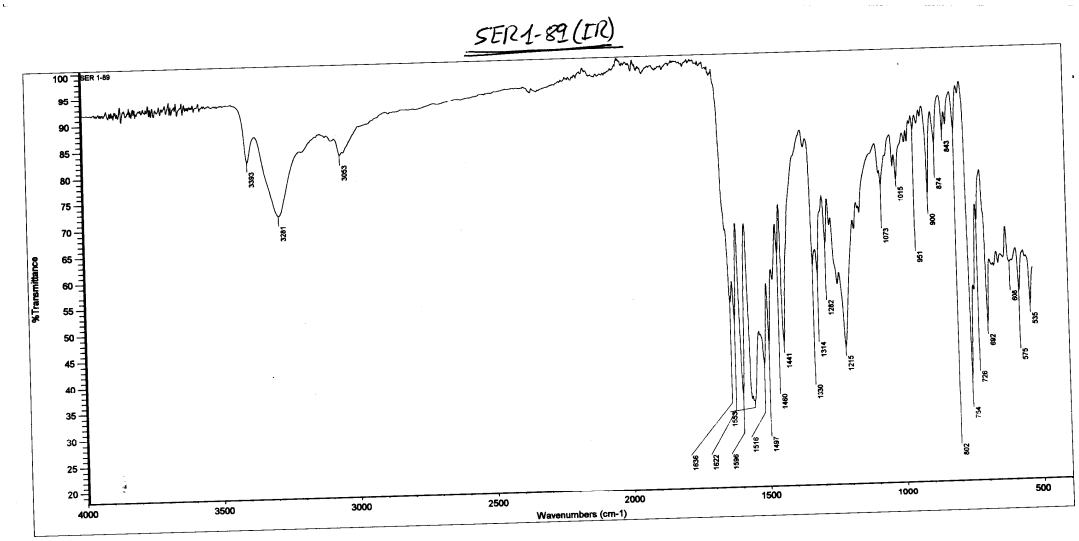


Figure S7 ESMS (-ve) of compound **3**



Thu Nov 16 12:43:01 2006 (GMT+00:00)
FIND PEAKS:
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Region: 4000 400
Absolute threshold: 86.584
Sensitivity: 50
Peak list:

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Position:	575	Intensity:	53.804
Position:	608	Intensity:	59.537
Position:	692	Intensity:	47.318
Position:	726	Intensity:	67.433
Position:	754	Intensity:	36.842
Position:	802	Intensity:	84.960
Position:	843	Intensity:	84.522
Position:	874	Intensity:	82.538
Position:	900	Intensity:	72.561
Position:	951	Intensity:	84.977
Position:	1015	Intensity:	75.924
Position:	1073	Intensity:	74.853
Position:	1215	Intensity:	44.137
Position:	1282	Intensity:	63.979

Figure S8 IR spectrum of compound **3**

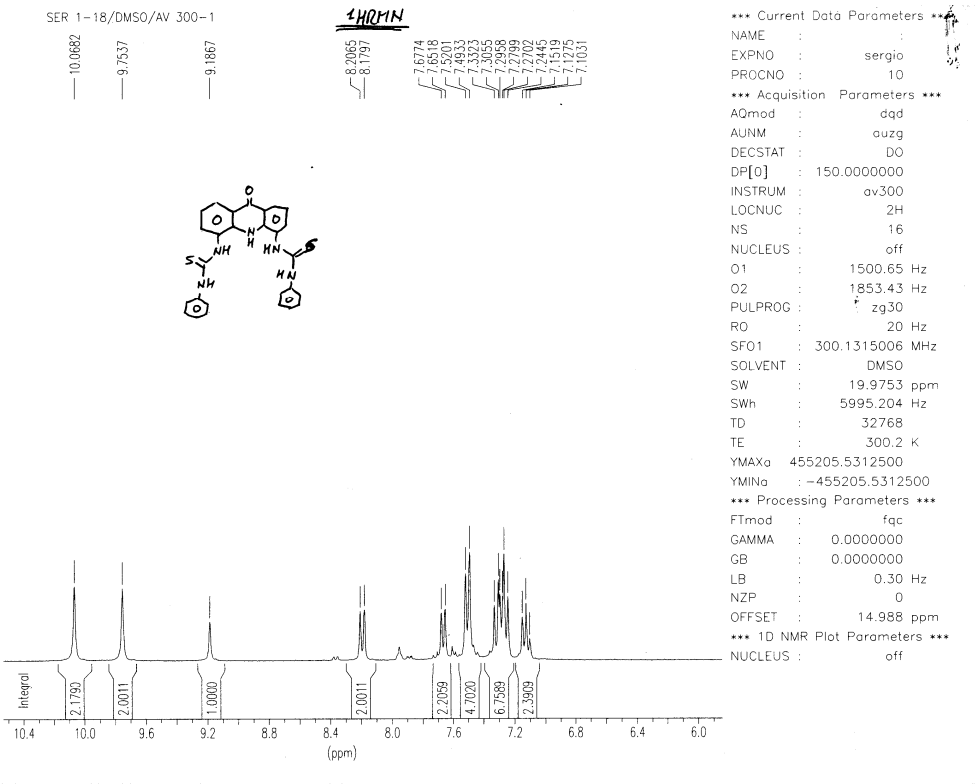


Figure S9 ^{1}H NMR spectrum of compound **4** in DMSO-d$_6$

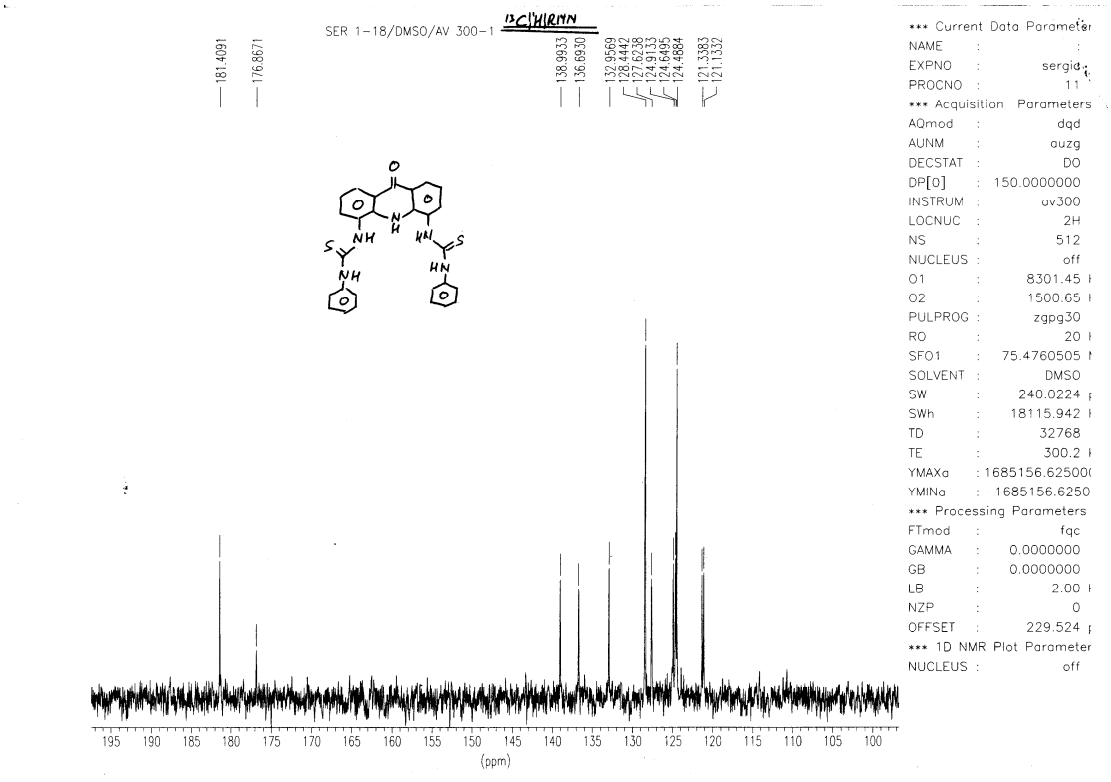


Figure S10 ^{13}C{^{1}H} NMR spectrum of compound **4** in DMSO-d$_6$

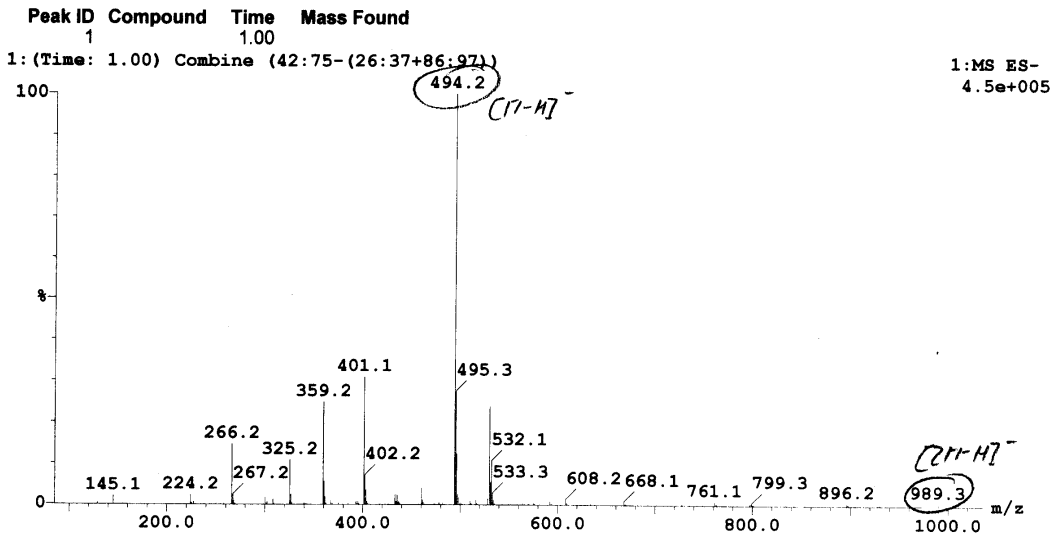
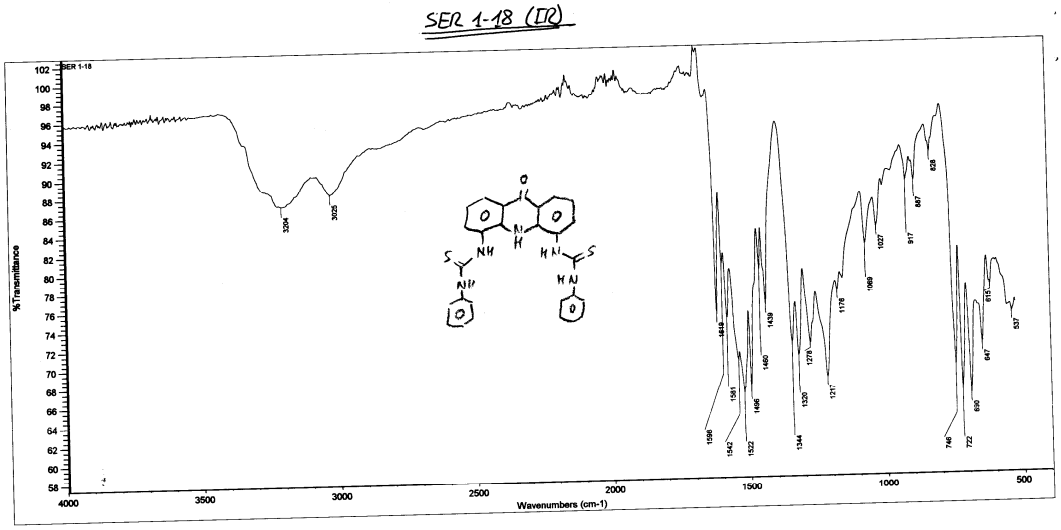


Figure S11 ESMS (-ve) of compound **4**



Thu Nov 16 11:14:36 2006 (GMT+00:00)
FIND PEAKS:
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Region: 4000 400
Absolute threshold: 91.892
Sensitivity: 60
Peak list:

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Position:	615	Intensity:	77.183
Position:	647	Intensity:	71.002
Position:	690	Intensity:	65.652
Position:	722	Intensity:	66.213
Position:	746	Intensity:	68.763
Position:	828	Intensity:	91.130
Position:	887	Intensity:	88.274
Position:	917	Intensity:	88.286
Position:	1027	Intensity:	83.459
Position:	1069	Intensity:	81.579
Position:	1176	Intensity:	76.826
Position:	1217	Intensity:	67.751
Position:	1278	Intensity:	71.320
Position:	1320	Intensity:	70.074

Figure S12 IR spectrum of compound **4**

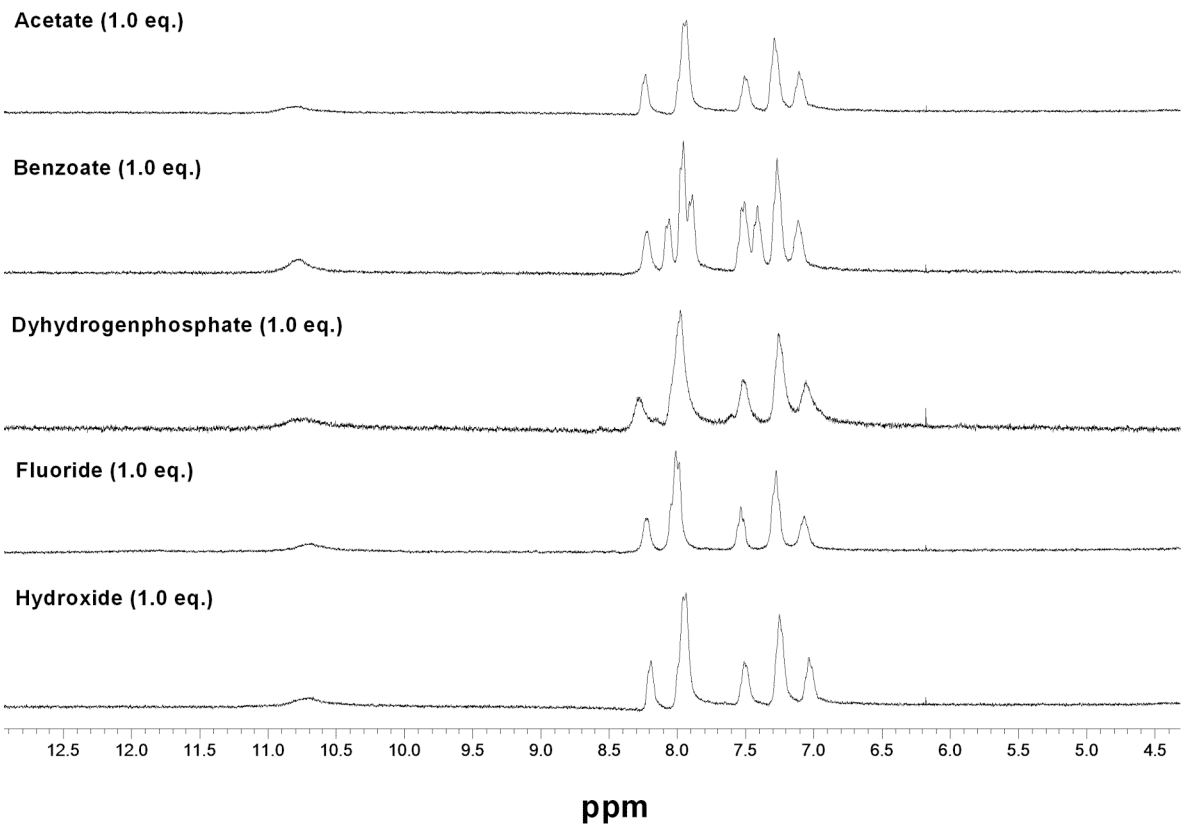

Figure S13 ^{1}H NMR spectra (selected region) of 0.01 mol. dm^{-3} solution of **2** with one equivalent of tetrabutylammonium acetate, benzoate, dihydrogenphosphate, fluoride and hydroxide in DMSO-d_6–0.5% water as solvent.

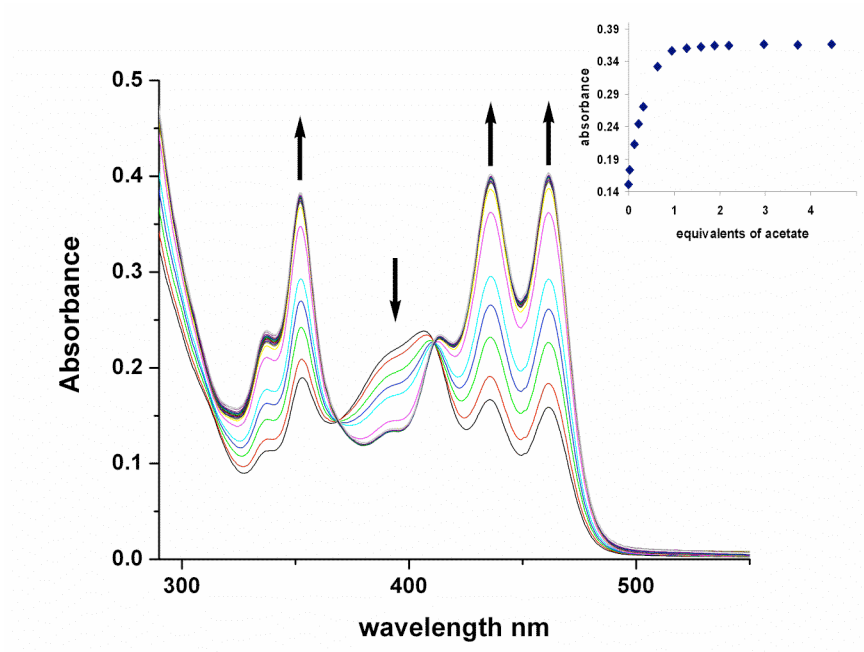

Figure S14 UV-vis absorption spectrophotometric titration of compound **2** with tetrabutylammonium acetate in DMSO at 25 °C. Inset: variation of absorbance at 440 nm *vs.* equivalents of acetate.

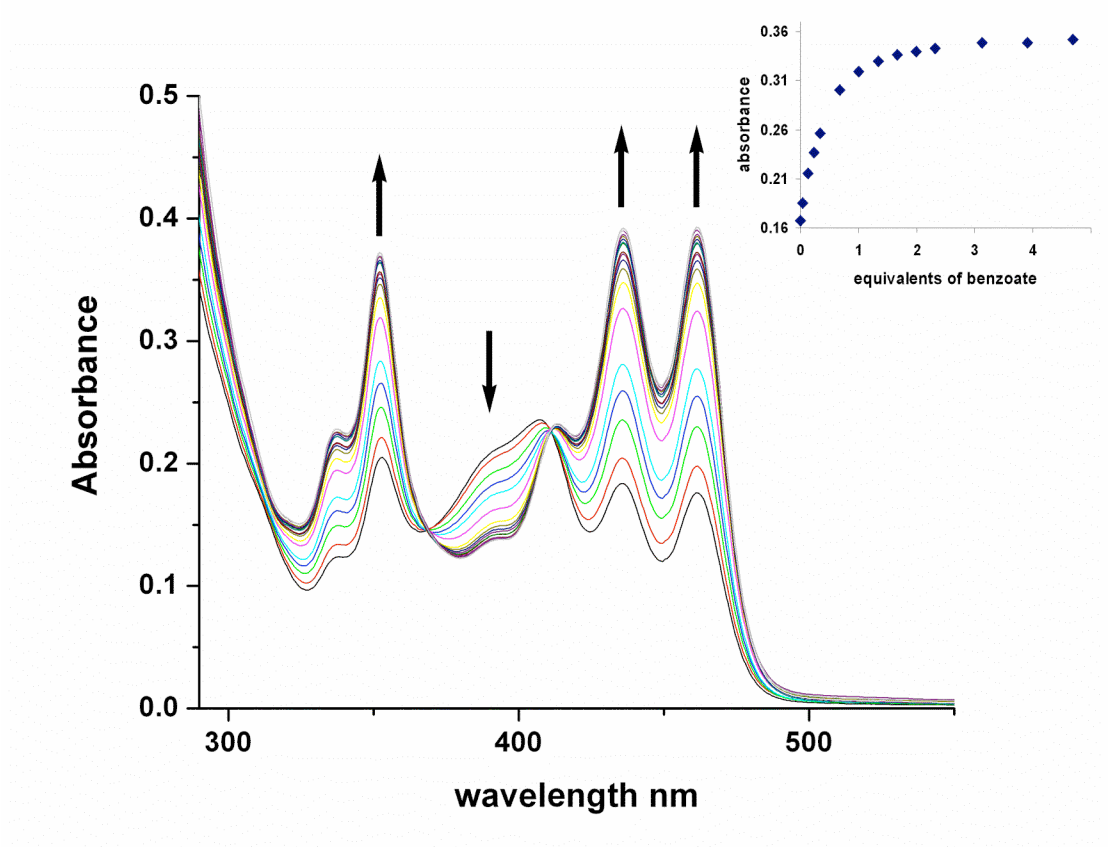

Figure S15 UV-vis spectrophotometric titrations of **2** with tetrabutylammonium benzoate.

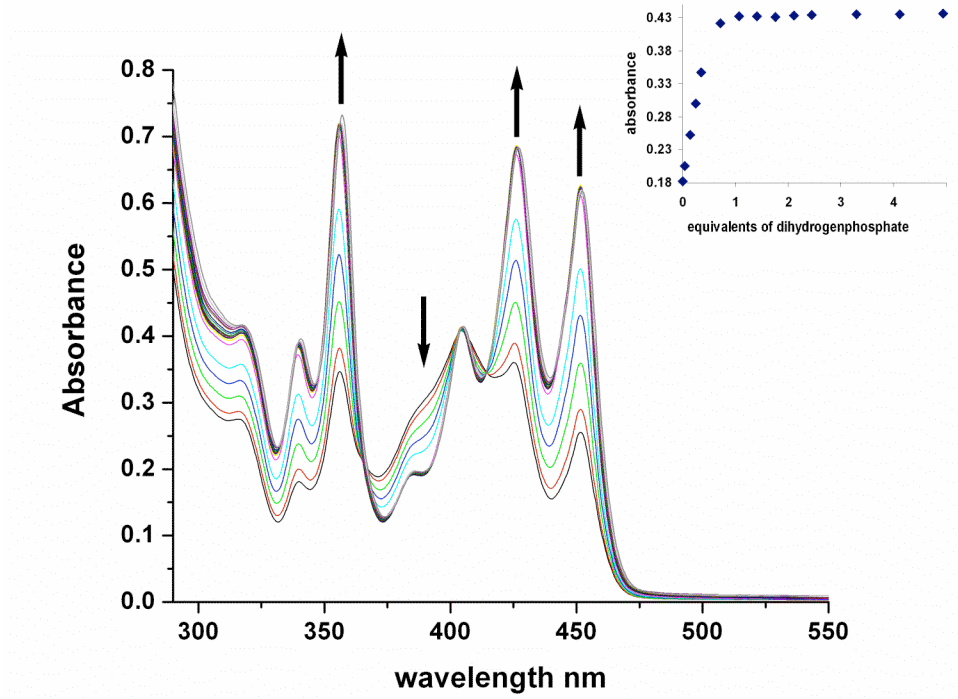

Figure S16 UV-vis spectrophotometric titrations of **2** with tetrabutylammonium dihydrogenphosphate.

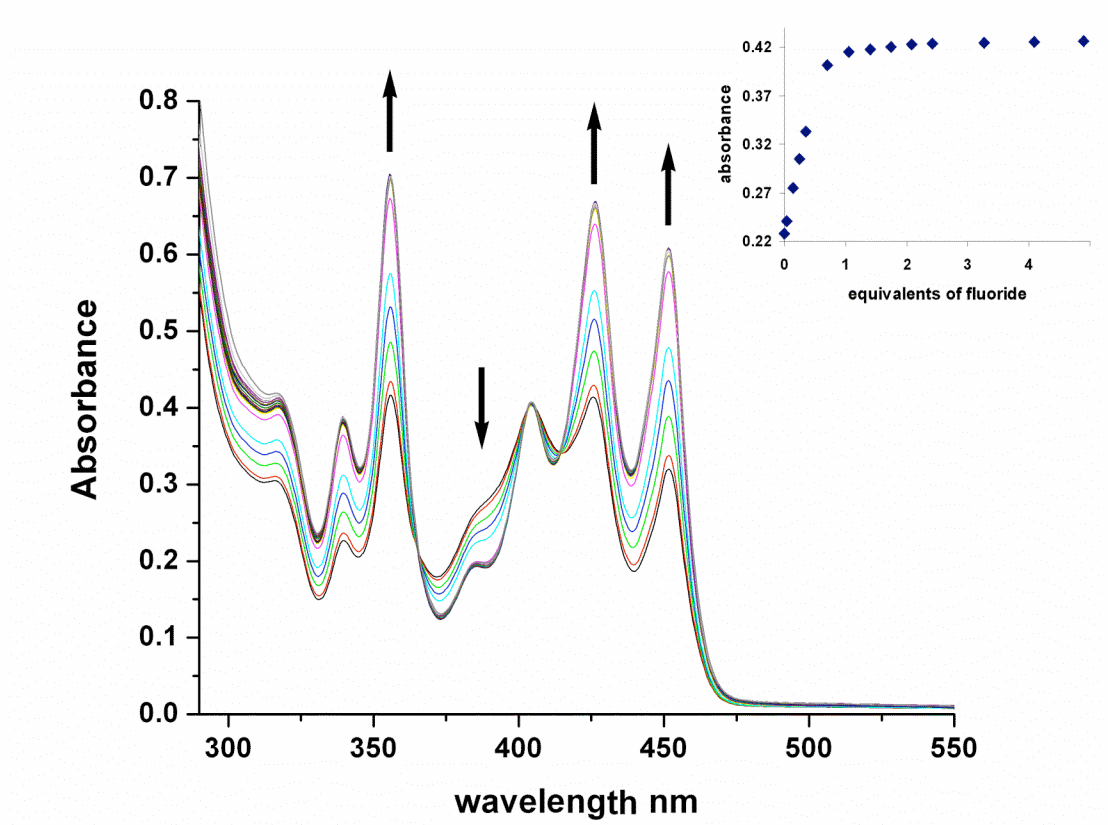

Figure S17 UV-vis spectrophotometric titrations of **2** with tetrabutylammonium fluoride.

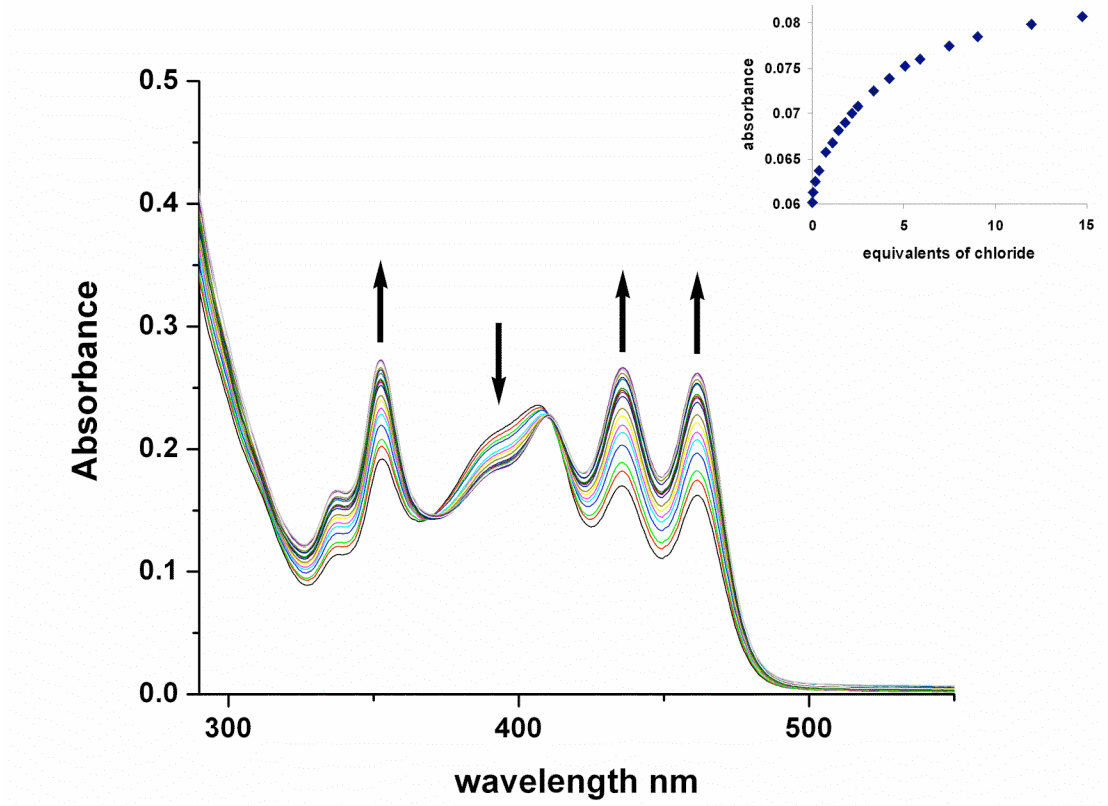

Figure S18 UV-vis spectrophotometric titrations of **2** with tetrabutylammonium chloride.

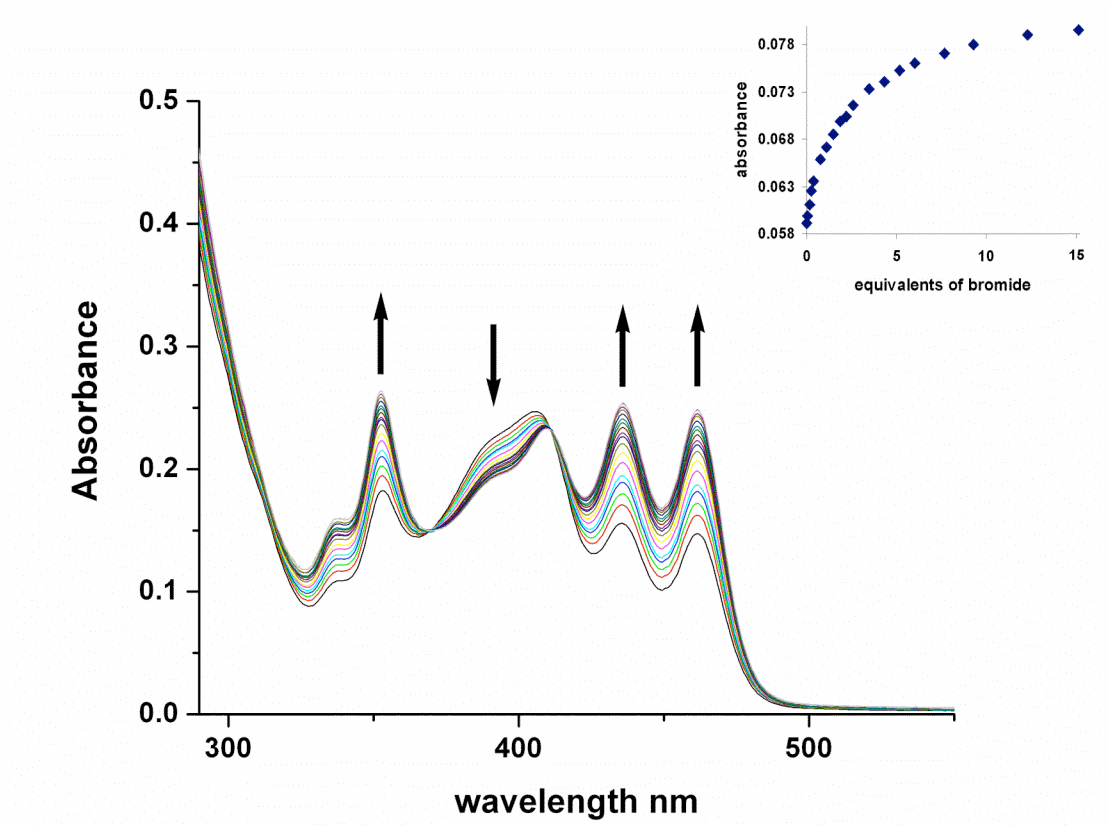

Figure S19 UV-vis spectrophotometric titrations of **2** with tetrabutylammonium bromide.

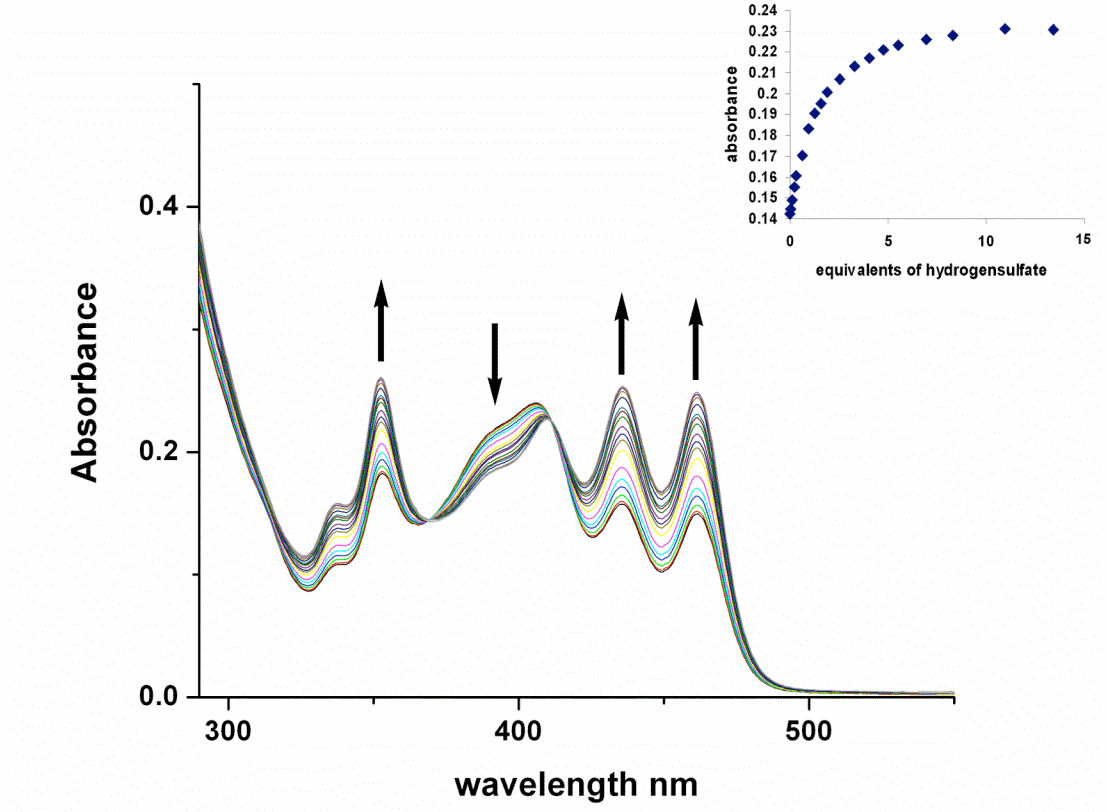

Figure S20 UV-vis spectrophotometric titrations of **2** with tetrabutylammonium hydrogensulfate.

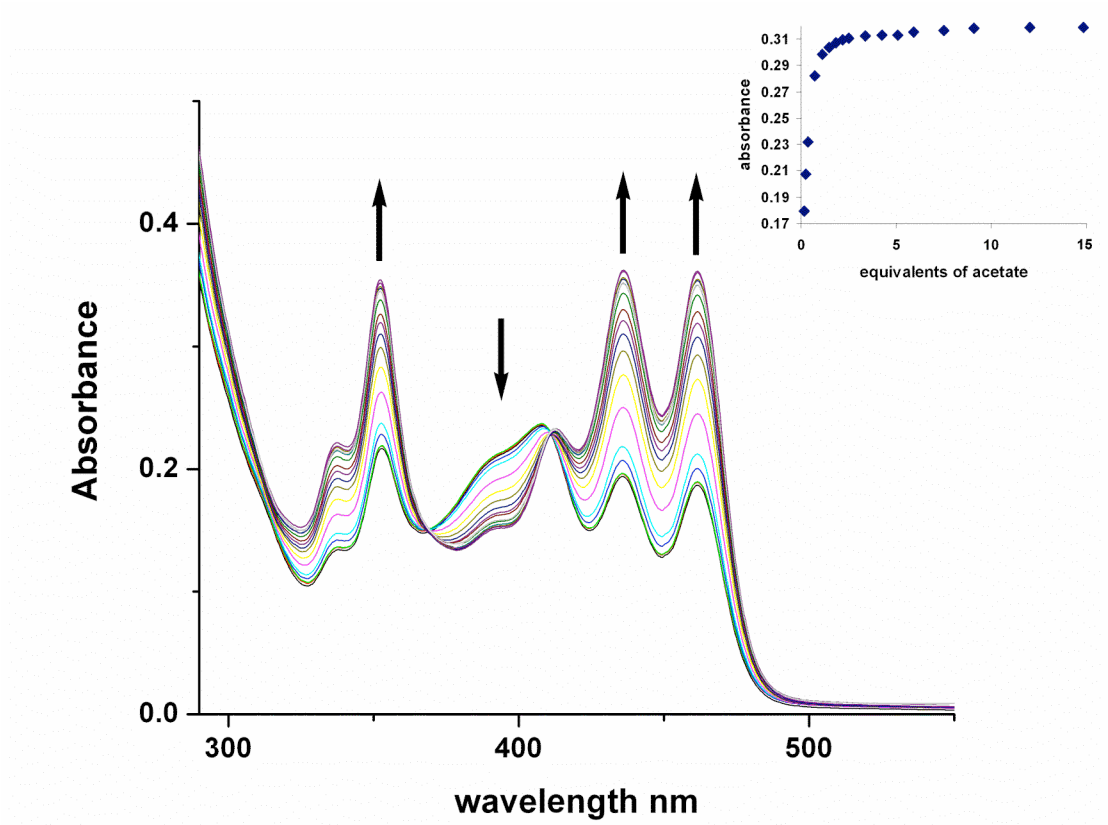

Figure S21 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium acetate.

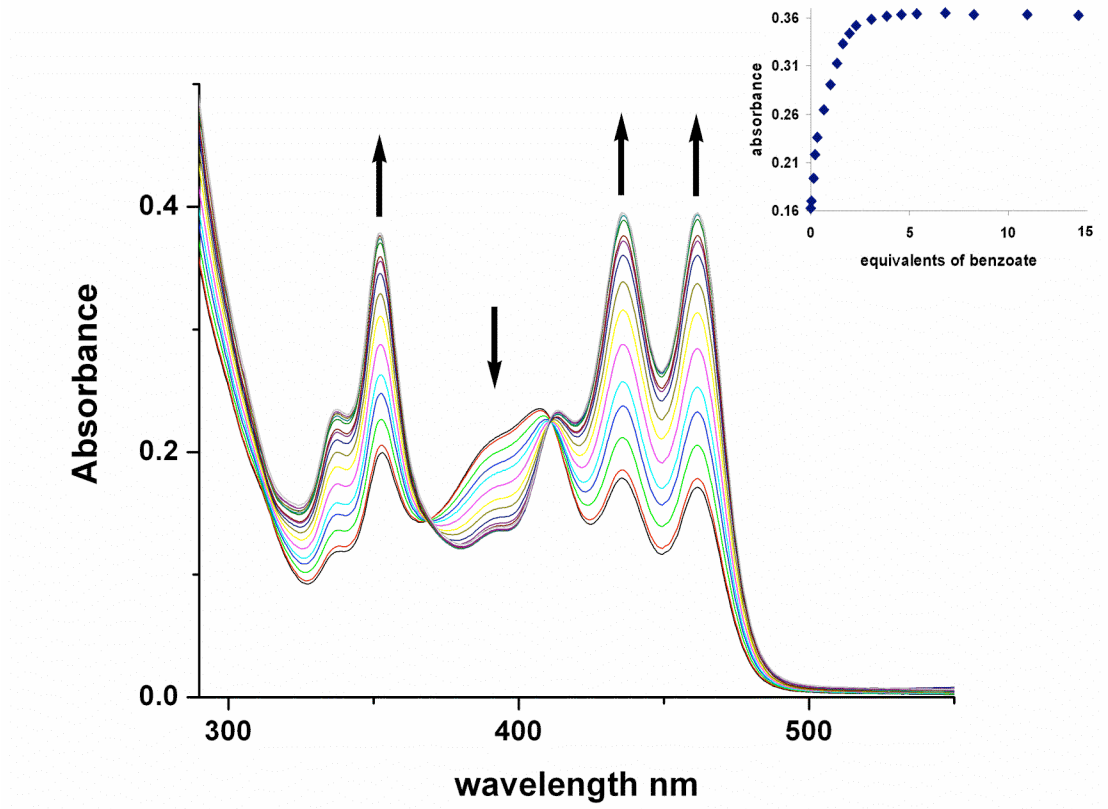

Figure S22 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium benzoate.

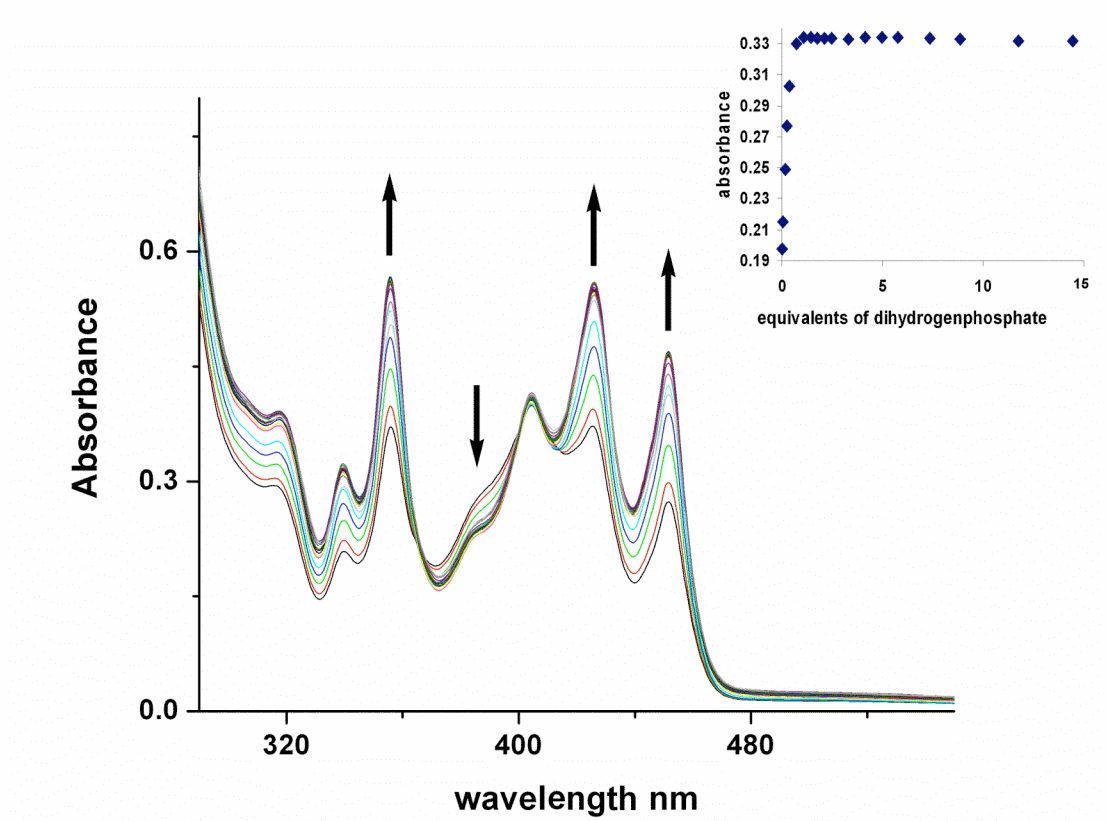

Figure S23 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium dihydrogenphosphate.

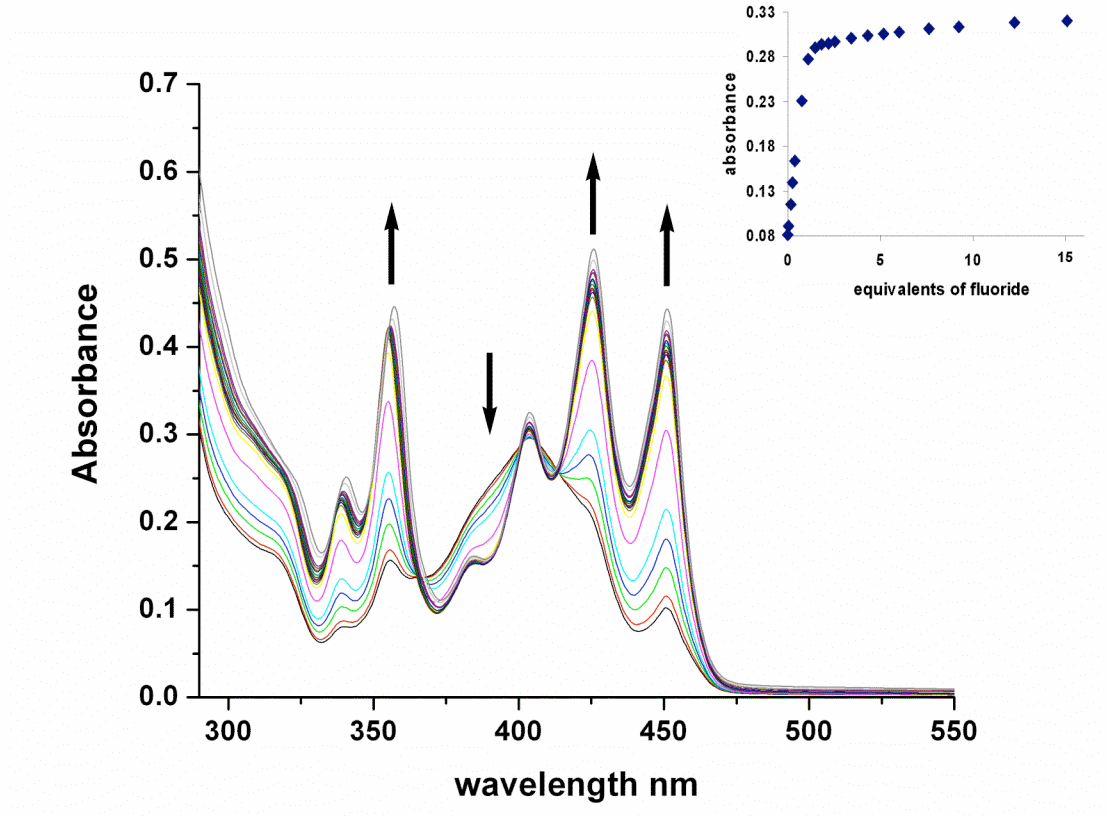

Figure S24 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium fluoride.

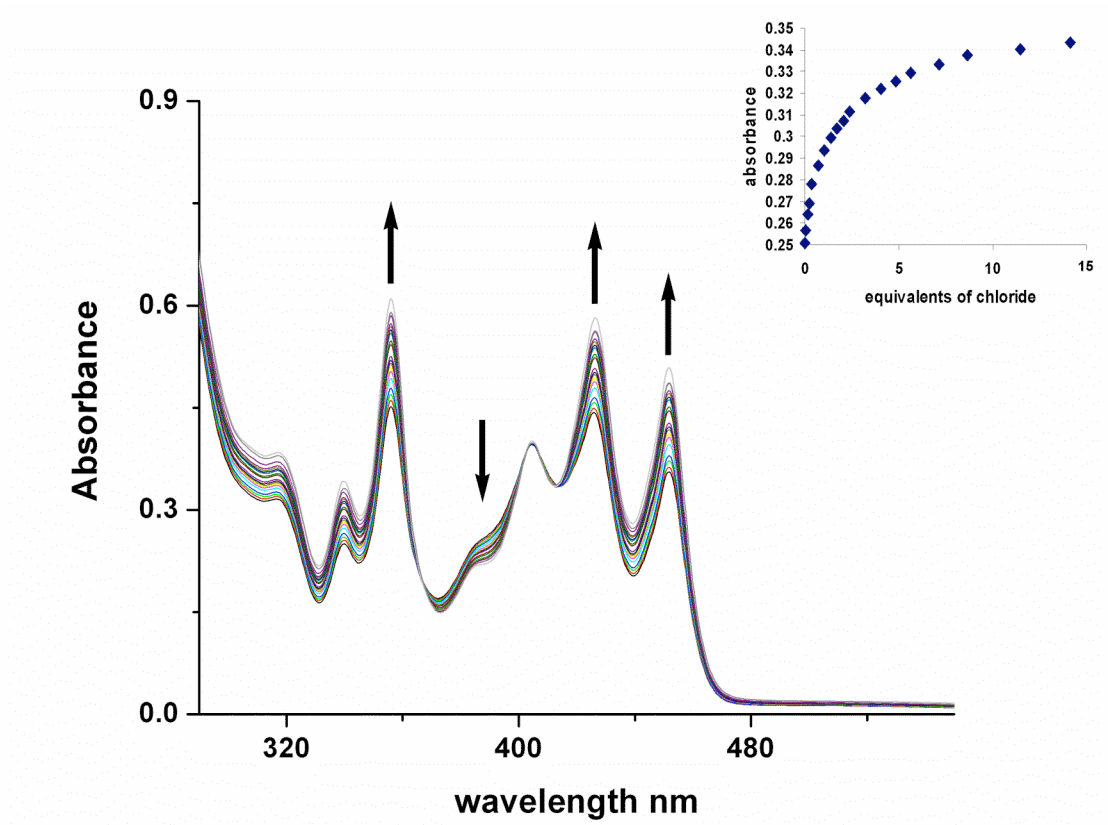

Figure S25 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium chloride.

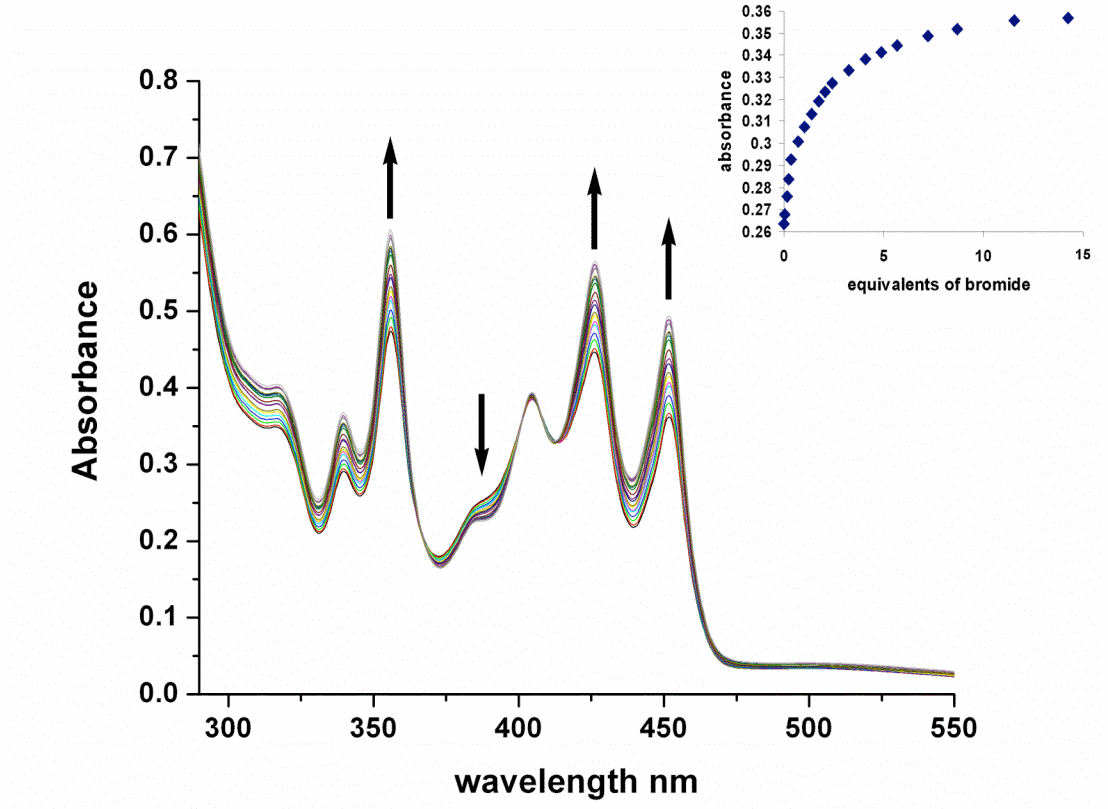

Figure S26 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium bromide.

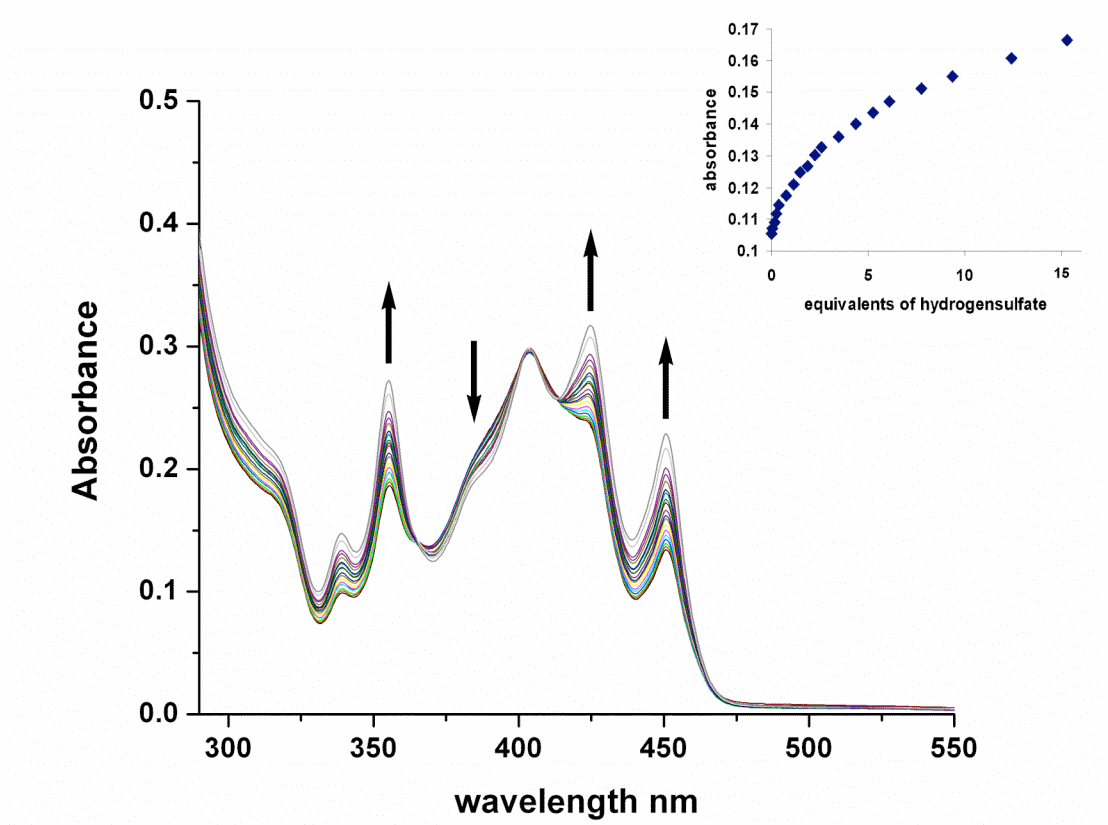

Figure S27 UV-vis spectrophotometric titrations of **3** with tetrabutylammonium hydrogensulfate.

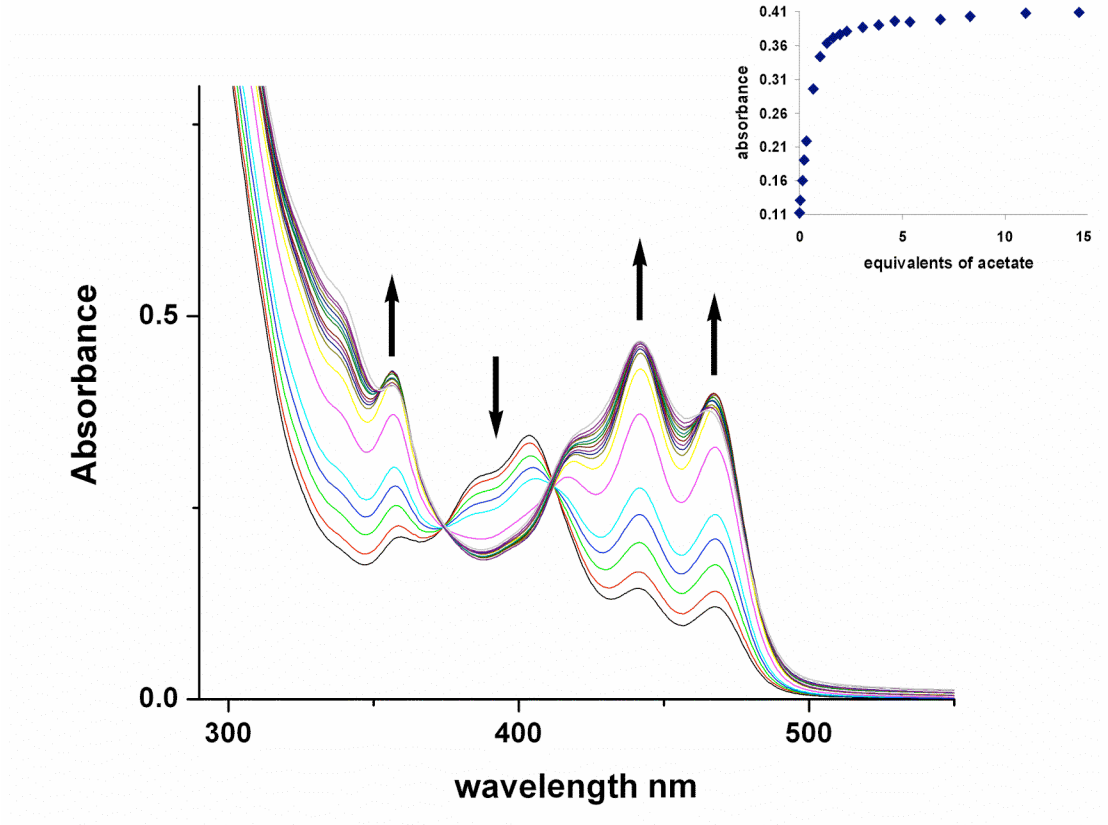

Figure S28 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium acetate.

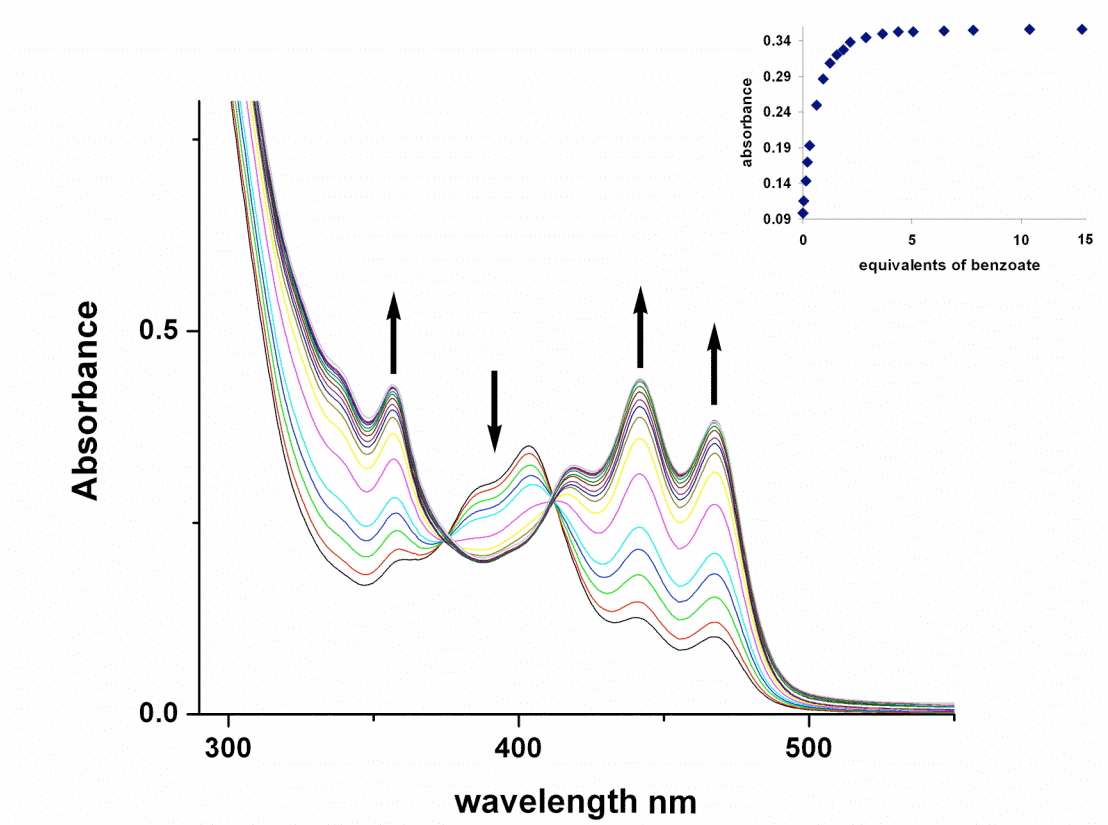

Figure S29 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium benzoate.

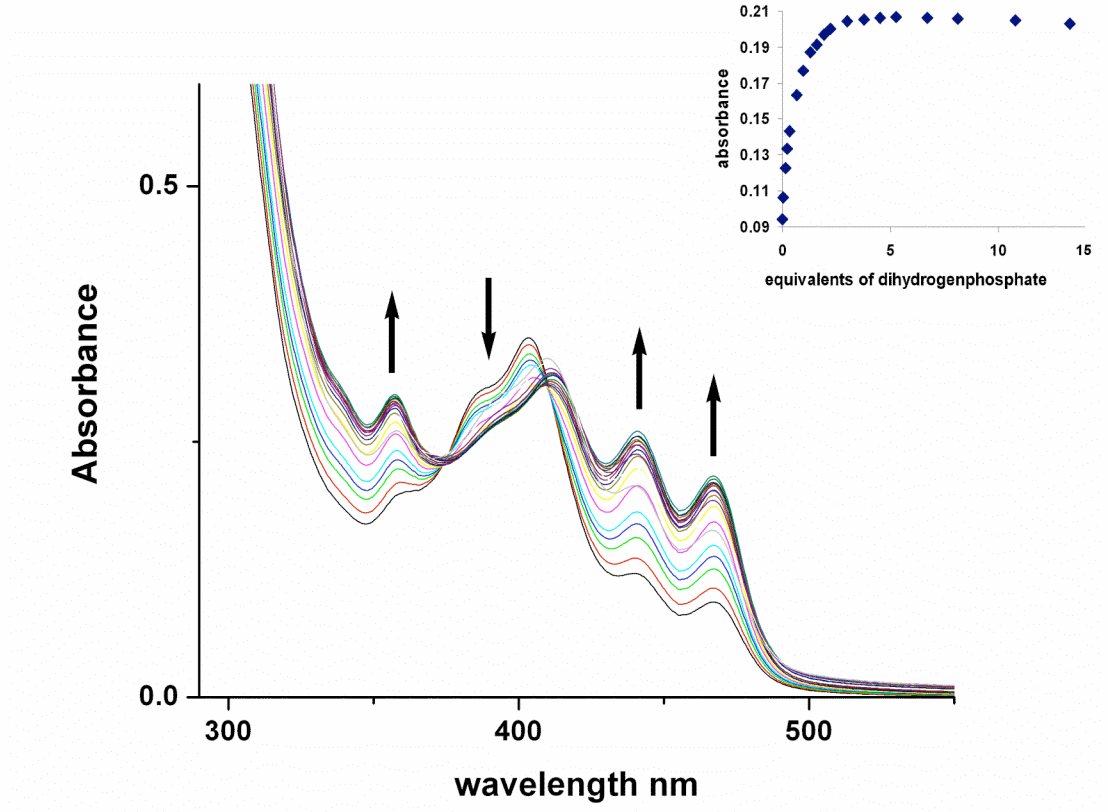

Figure S30 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium dihydrogenphosphate.

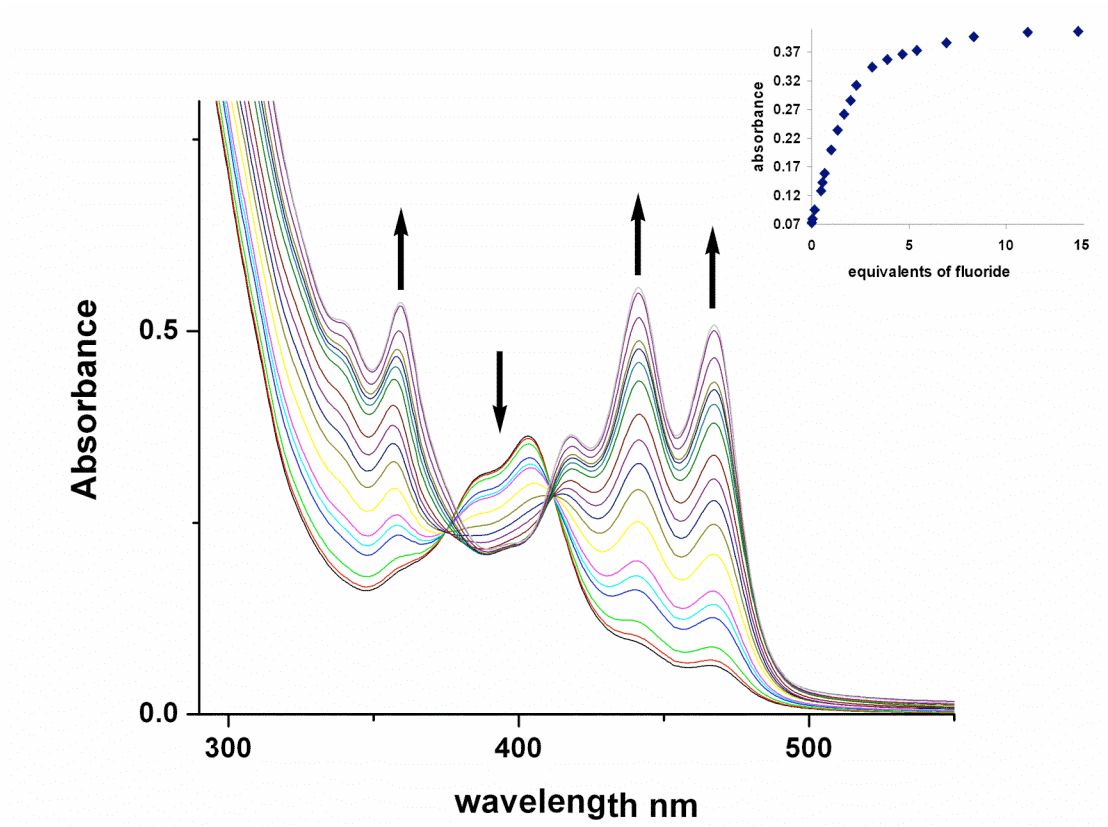

Figure S31 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium fluoride.

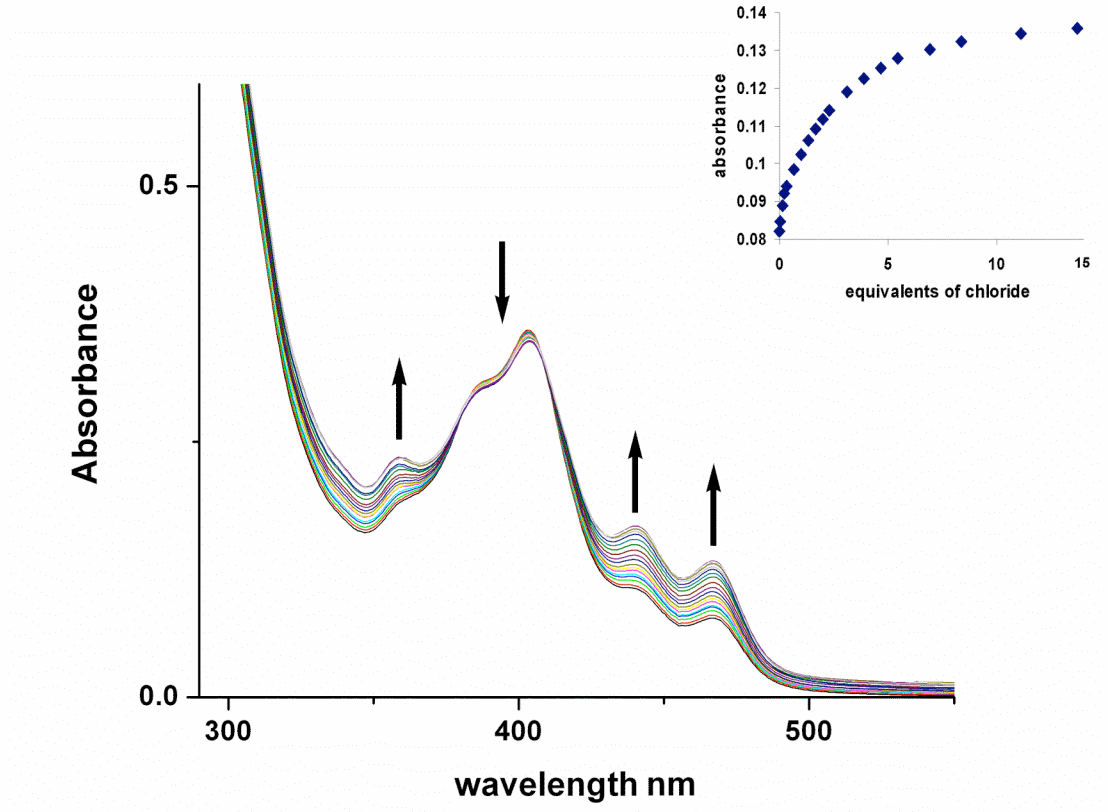

Figure S32 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium chloride.

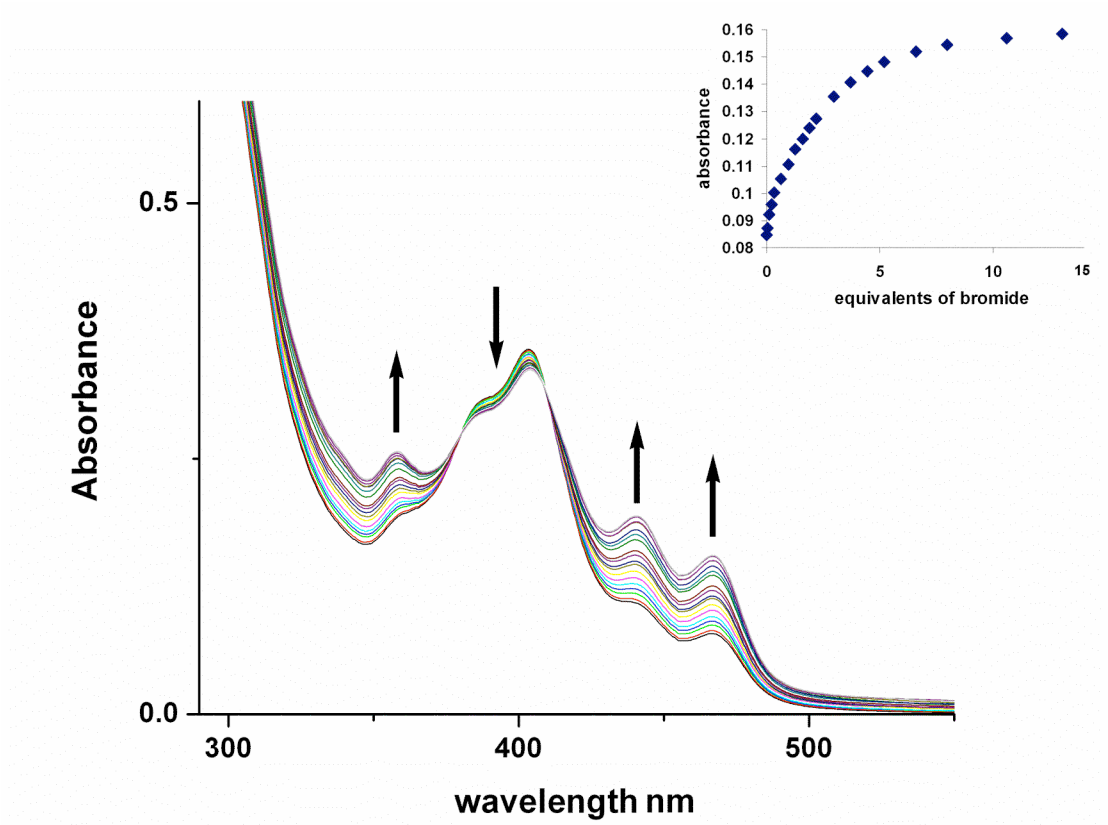

Figure S33 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium bromide.

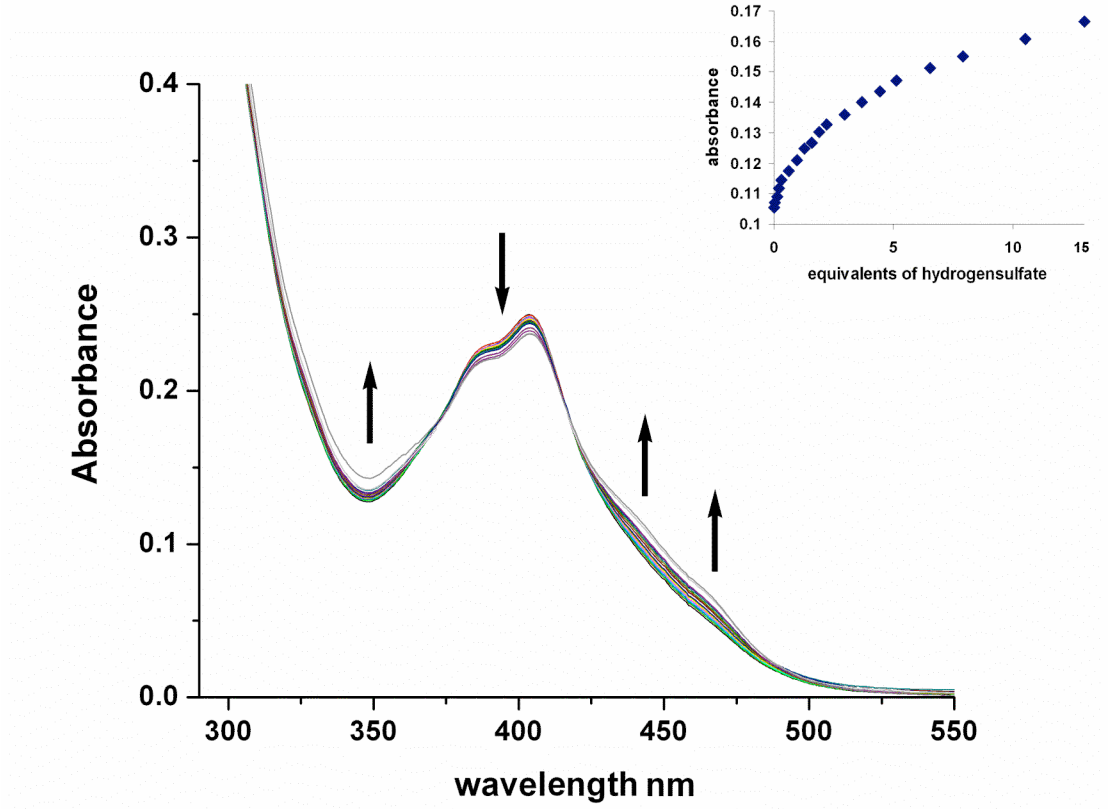

Figure S34 UV-vis spectrophotometric titrations of **4** with tetrabutylammonium hydrogensulfate.

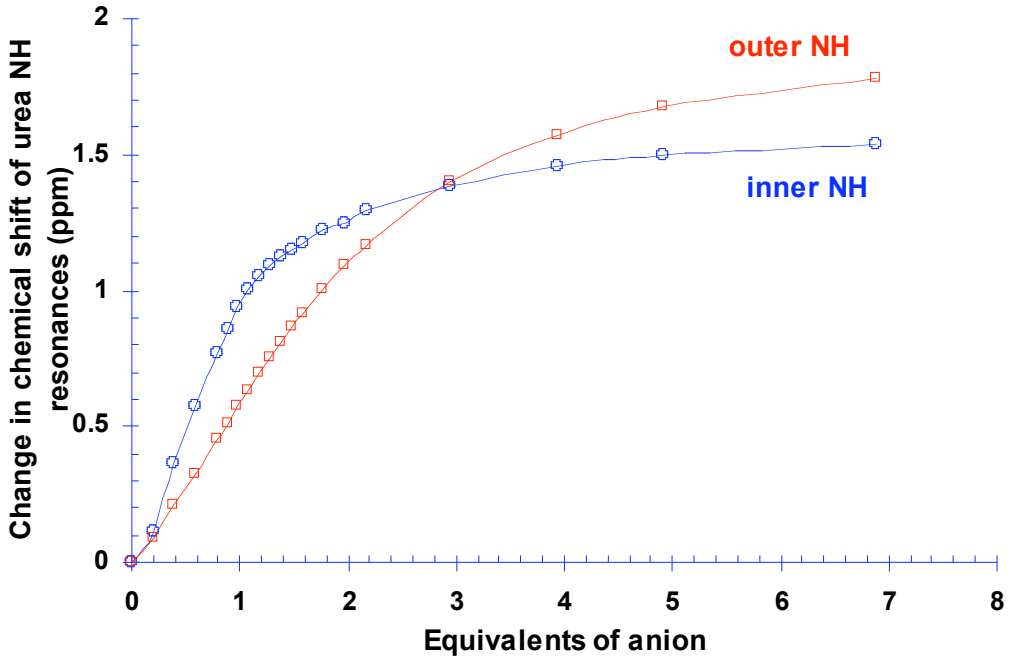

Figure S35 Shifts of the NH groups of compound **3** upon the addition of tetrabutylammonium benzoate in DMSO-d_6–0.5% water.

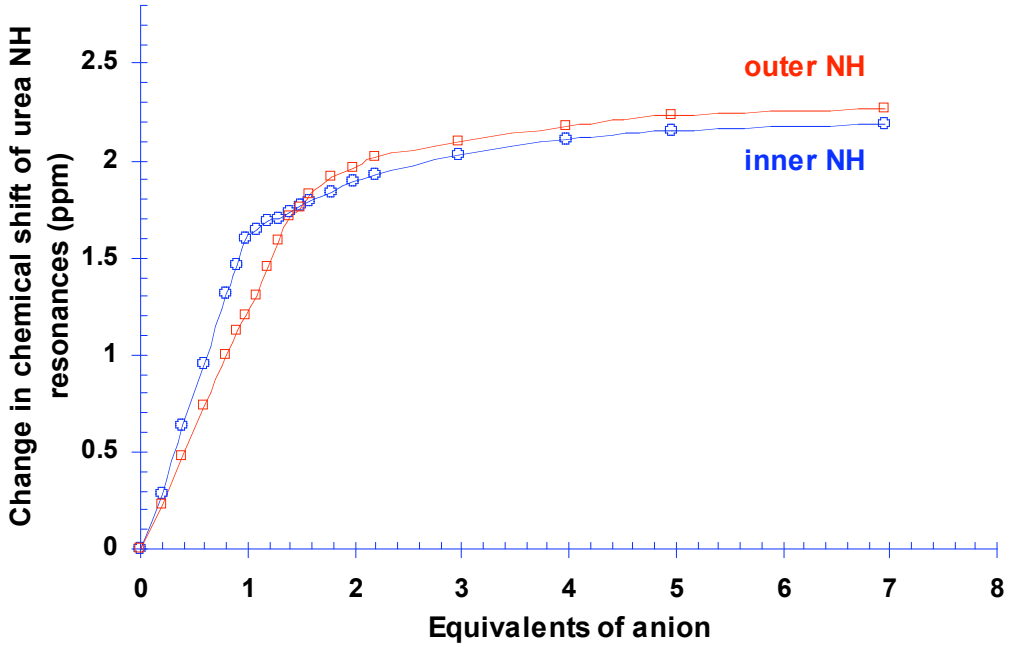

Figure S36 Shifts of the NH groups of compound **3** upon the addition of tetrabutylammonium dihydrogenphosphate in DMSO-d_6–0.5% water.

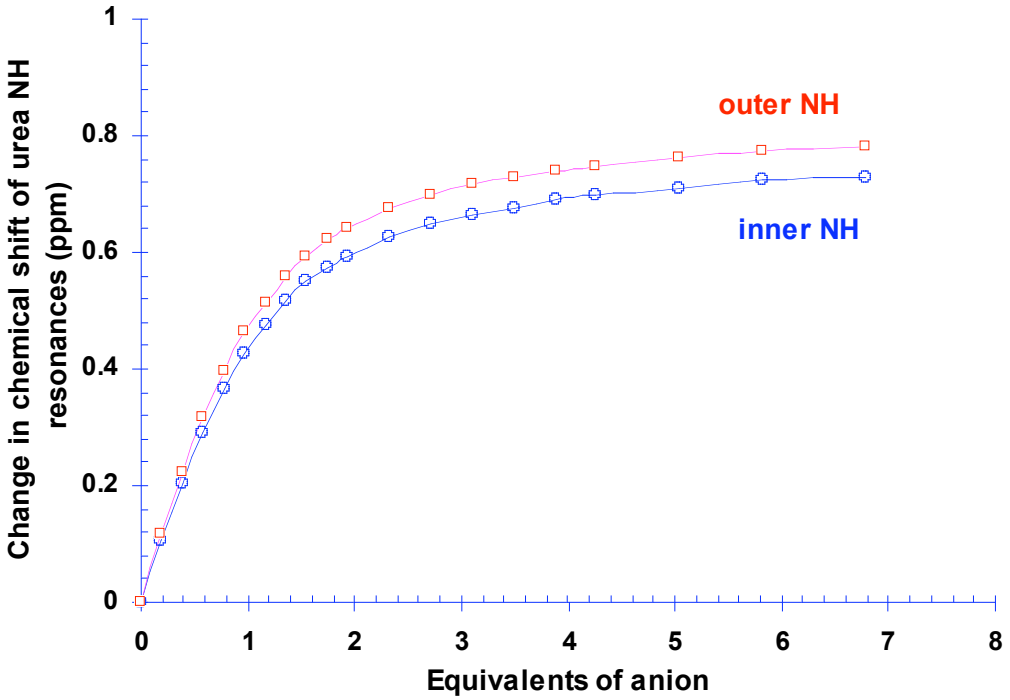

Figure S37 Shifts of the NH groups of compound **3** upon the addition of tetrabutylammonium chloride in DMSO-d_6–0.5% water.

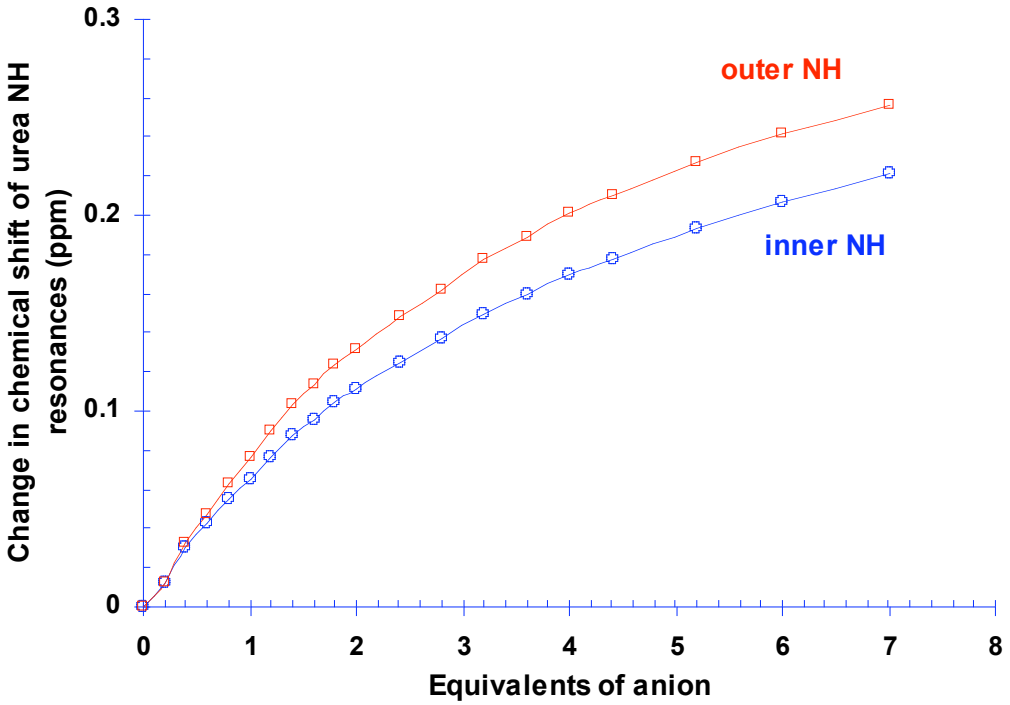

Figure S38 Shifts of the NH groups of compound **3** upon the addition of tetrabutylammonium bromide in DMSO-d_6–0.5% water.

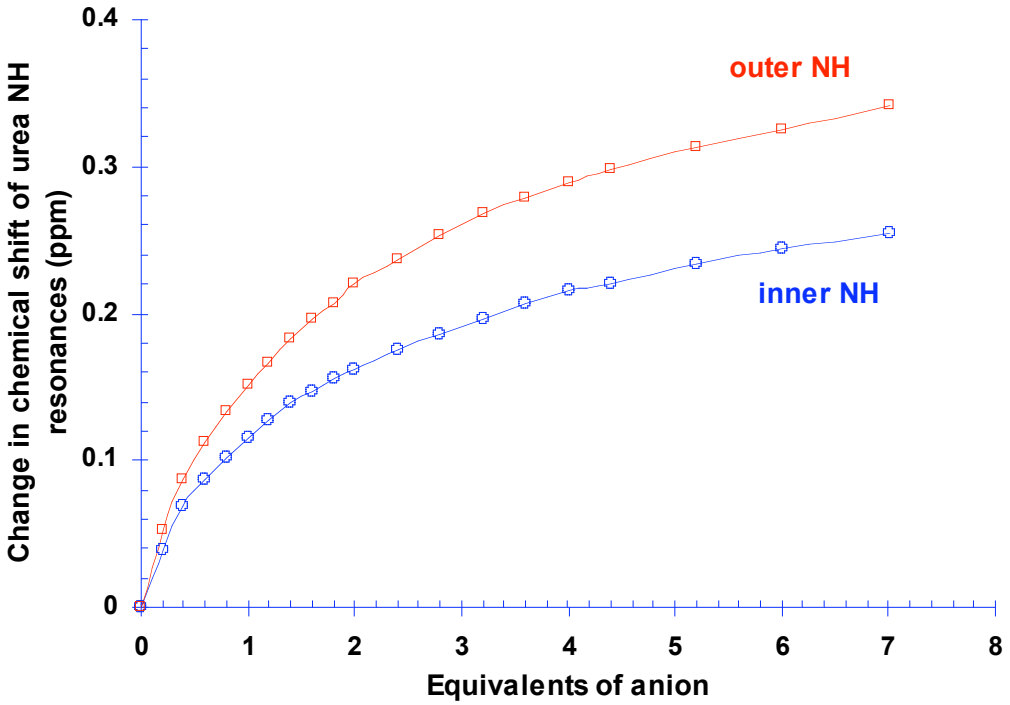

Figure S39 Shifts of the NH groups of compound **3** upon the addition of tetrabutylammonium bromide in DMSO-d_6–0.5% water.

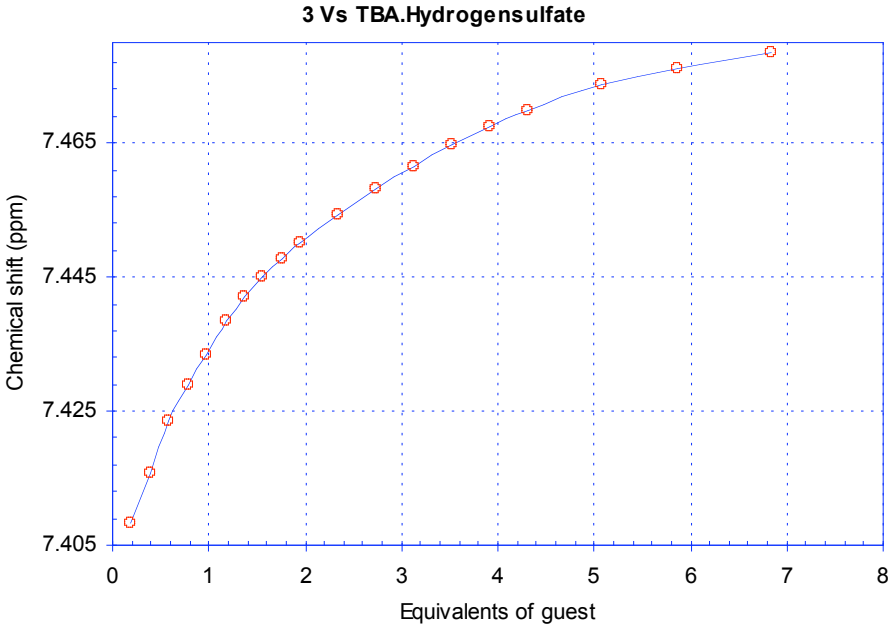

Figure S40 ^{1}H NMR titration curve of **3** with tetrabutylammonium hydrogensulfate.

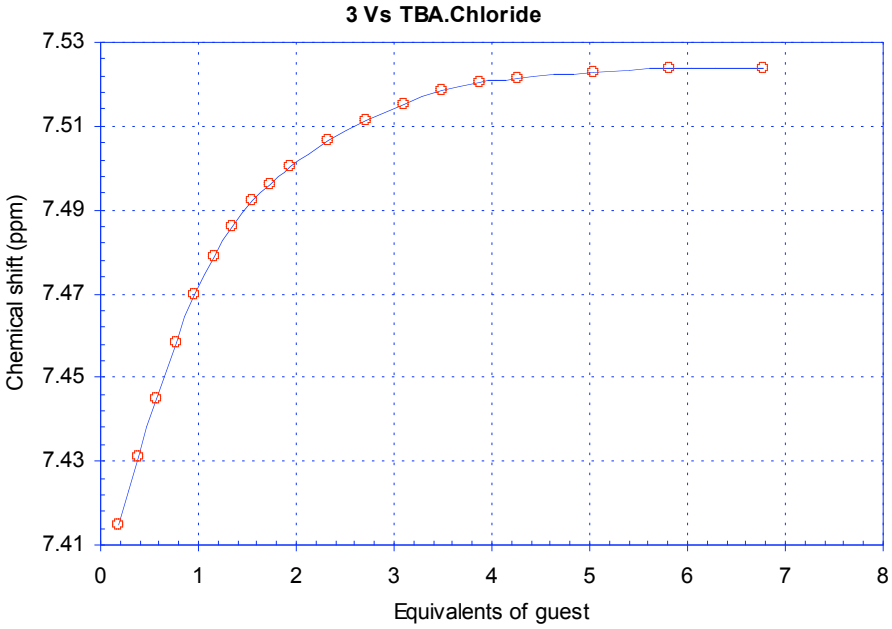

Figure S41 ^{1}H NMR titration curve of **3** with tetrabutylammonium chloride.

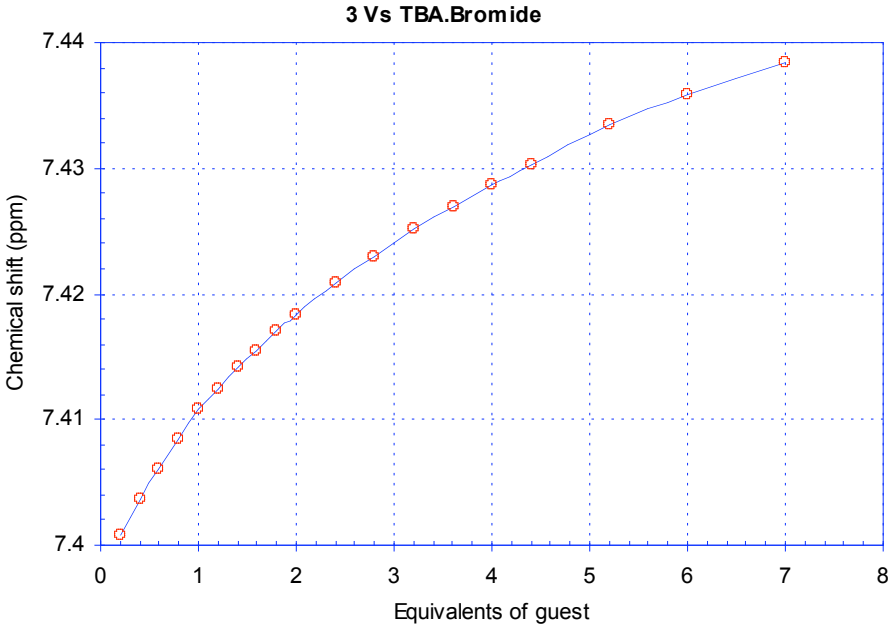

Figure S42 ^{1}H NMR titration curve of **3** with tetrabutylammonium bromide.

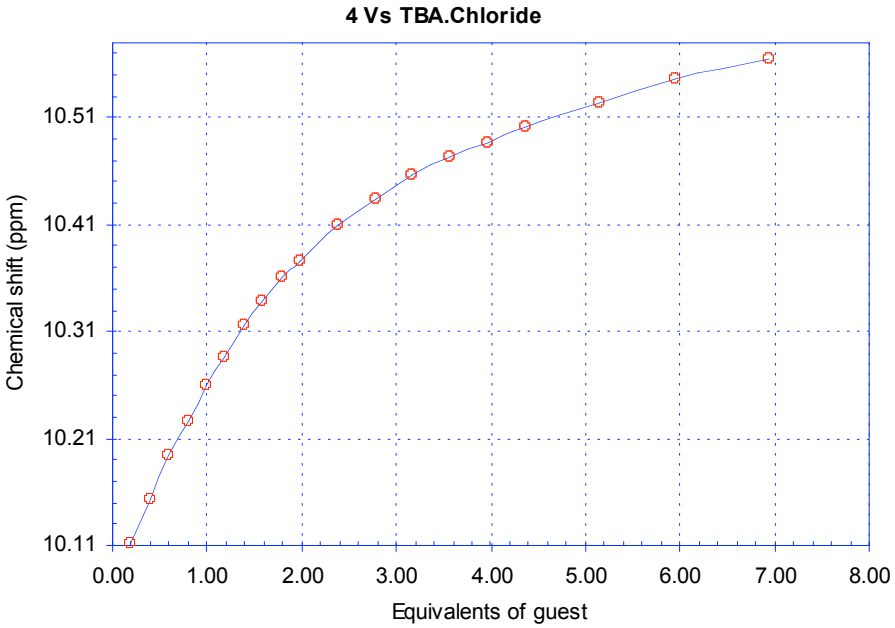

Figure S43 ^{1}H NMR titration curve of **4** with tetrabutylammonium chloride.

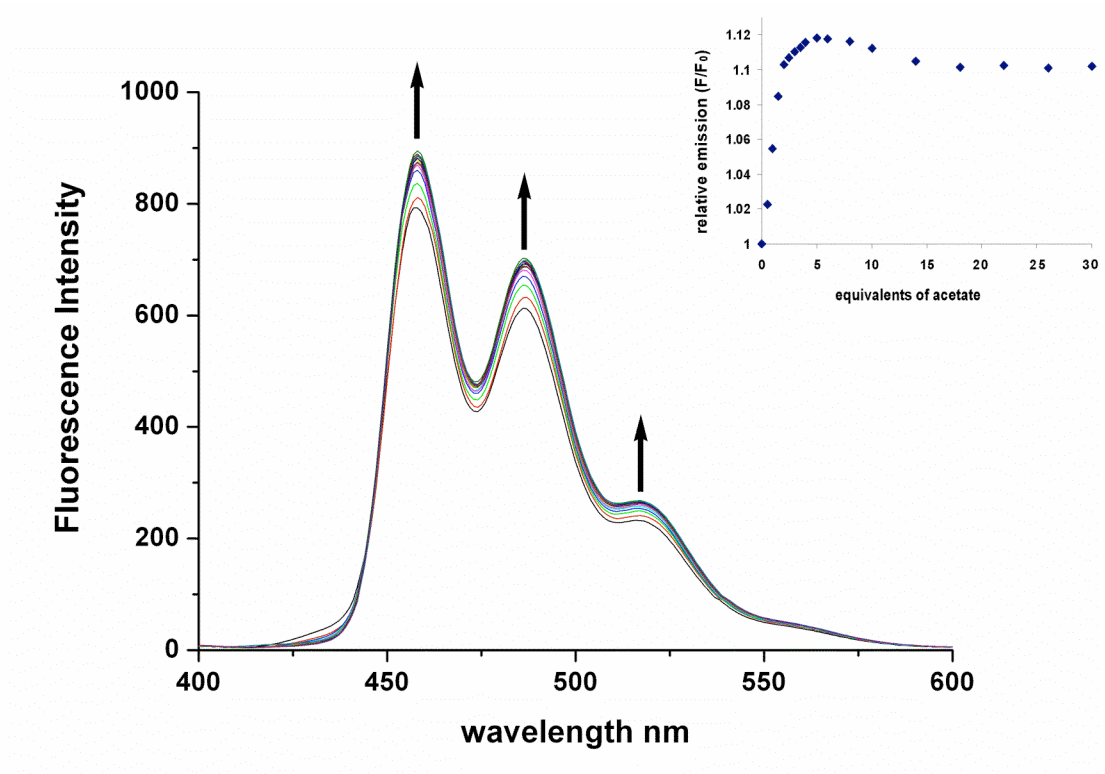

Figure S44 Fluorescence of **3** in MeCN/DMSO (96/4 v/v) upon the addition of tetrabutylammonium acetate.

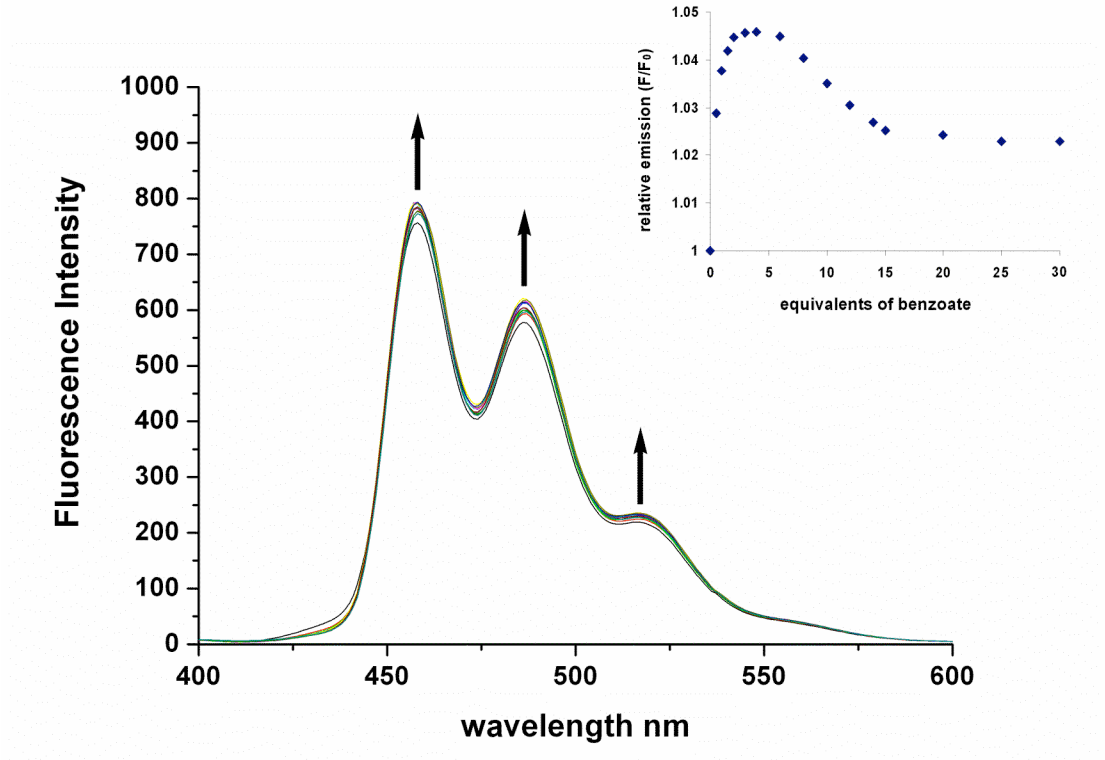

Figure S45 Fluorescence of **3** in MeCN/DMSO (96/4 v/v) upon the addition of tetrabutylammonium benzoate.

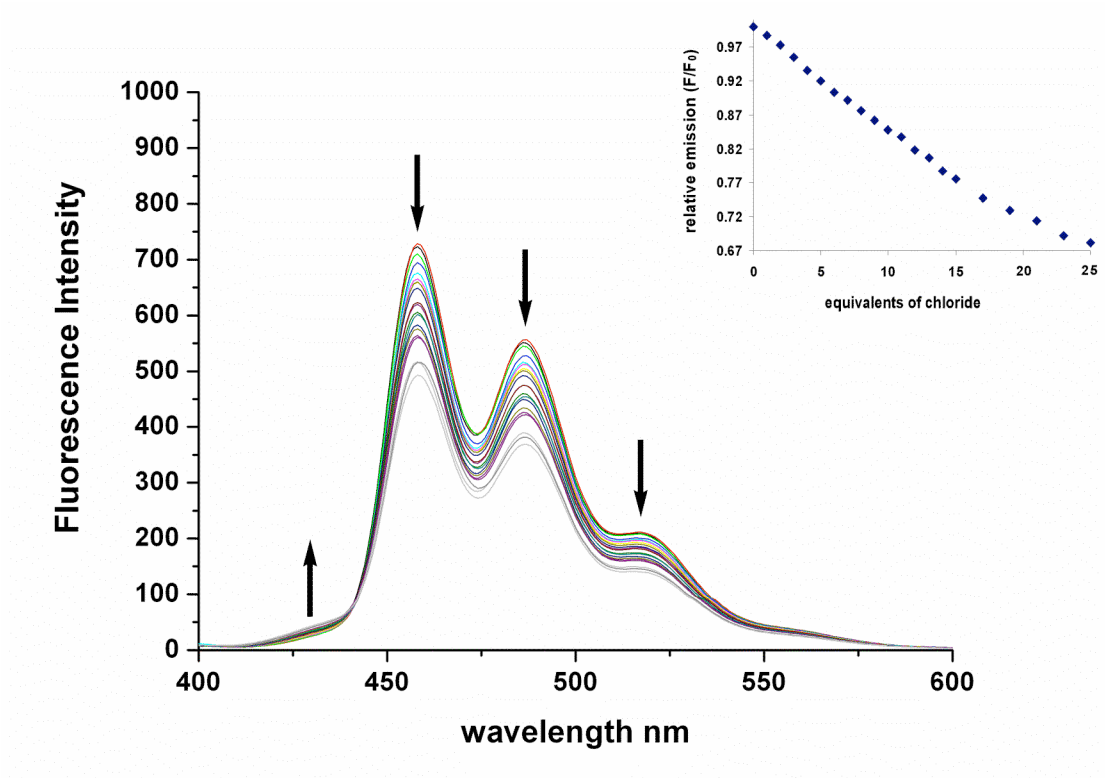

Figure S46 Fluorescence of **3** in MeCN/DMSO (96/4 v/v) upon the addition of tetrabutylammonium chloride.

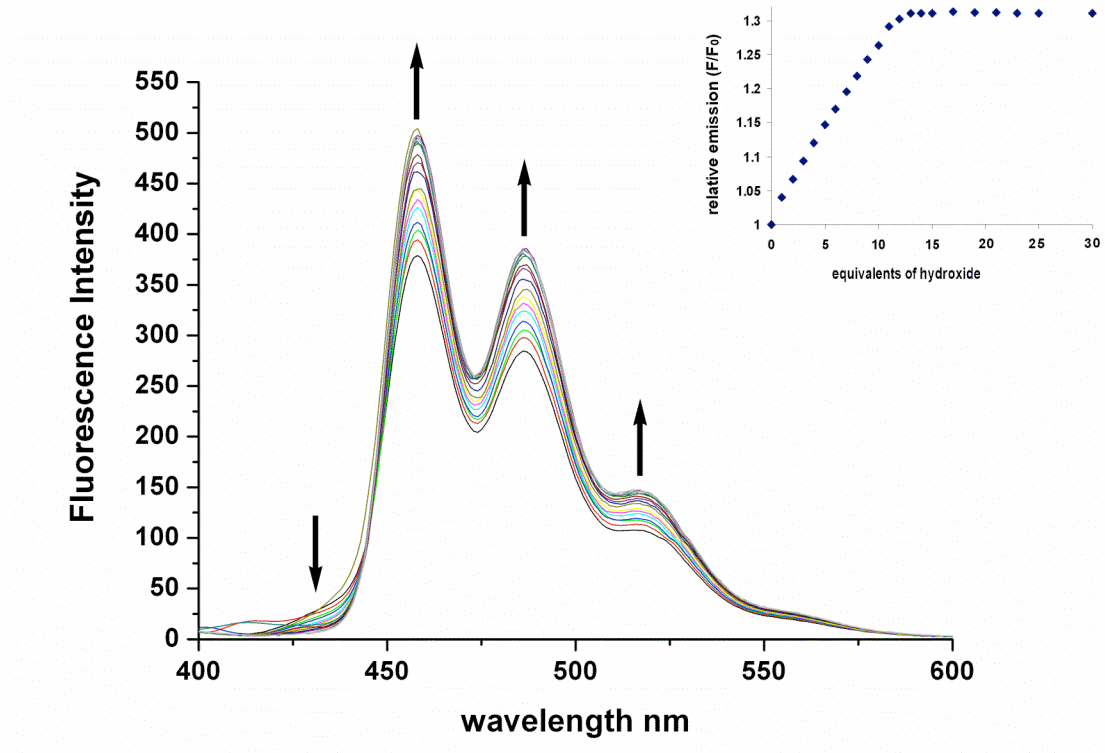

Figure S47 Fluorescence of **3** in MeCN/DMSO (96/4 v/v) upon the addition of tetrabutylammonium hydroxide.