Supporting Information

Development of a borondipyrromethene-based Zn^{2+} fluorescent probe: solvent effects on modulation sensing ability

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Table of contents

Experimental Section

General. All chemicals were purchased from commercial suppliers unless otherwise specified. Et_3N, chloroform and 1,2-dichloroethane were used as received without further purification. Anhydrous *N,N*-dimethylformamide (DMF) and toluene were dried and distillated immediately prior to use. 2-chloro-5-benzoyl-pyrrole[1], 2,4-dimethyl-3-ethylpyrrole[2] were prepared according to literature procedures.

^1H NMR and ^{13}C NMR spectra were recorded on spectrometer operating at 400 MHz and 100 MHz, respectively. Deuterated chloroform was used as the solvent, TMS as internal standard. Mass spectra were measured on a HP 1100 LC-MS spectrometer. UV-vis spectra were measured using a shimadzu UV-2550 spectrophotometer. Fluorescence spectroscopic measurements were conducted on a Varian Cary eclipse fluorescence spectrophotometer.

For absorption or fluorescence measurements, compounds were dissolved in DMSO to obtain stock solutions (2-5 mM). These stock solutions were diluted with CH_3CN or aqueous solutions to the desired concentration.

1. Petruso, S.; Caronna, S. *J. Hetero. Chem.* **1992**, *29*, 355-357.
2. Mula, S.; Ray, A. K.; Banerjee, M.; Chaudhuri, T.; Dasgupta, K.; Chattopadhyay, S. *J. Org. Chem.* **2008**, *73*, 2146-2154.

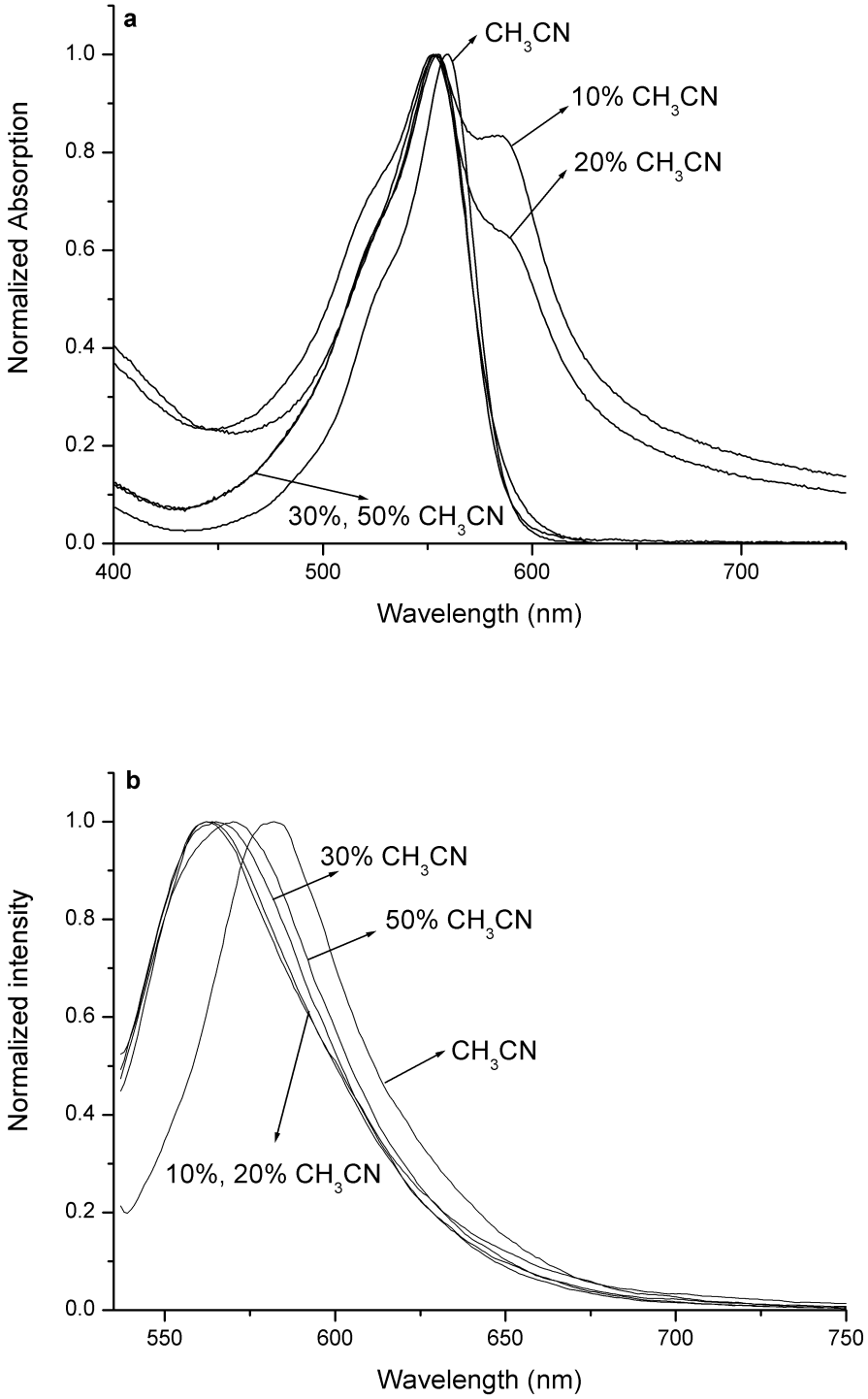


Figure S1. a) Absorption and b) emission spectra of **BODPAQ** in aqueous solutions.

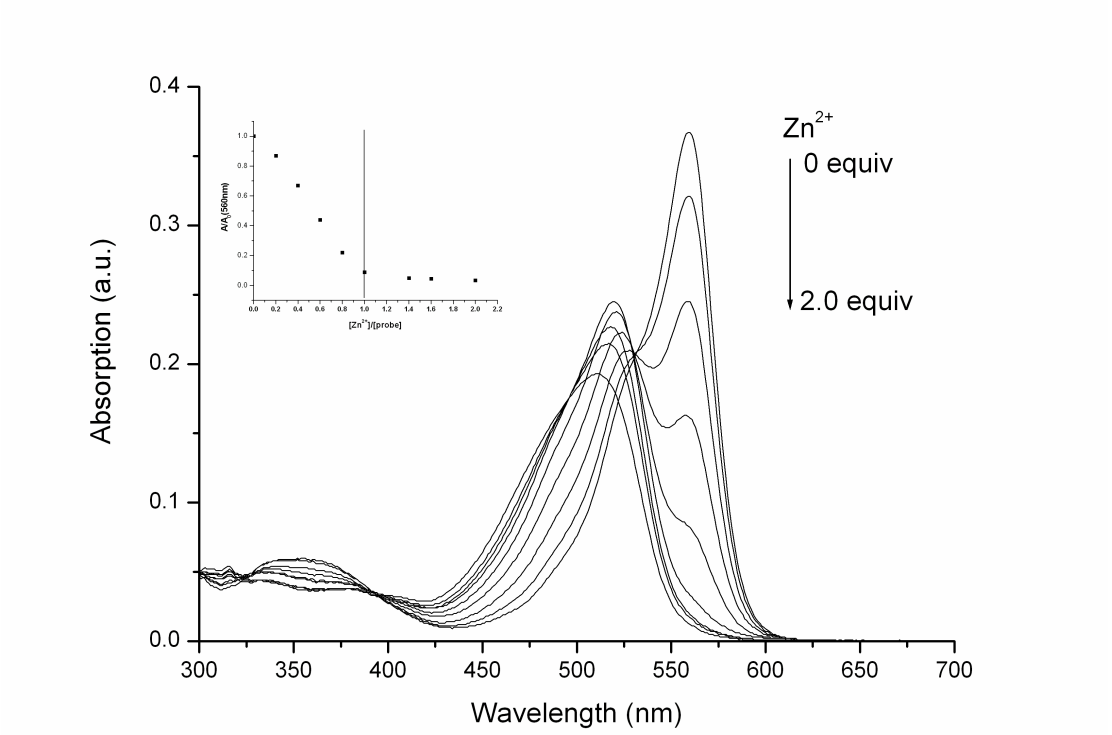


Figure S2. Absorption spectra of **BODPAQ** (5 μm) upon addition of Zn^{2+}(0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.6, 2.0 with respect to **BODPAQ**) in CH_3CN. Inset is the titration profile according to the absorbance at 560 nm.

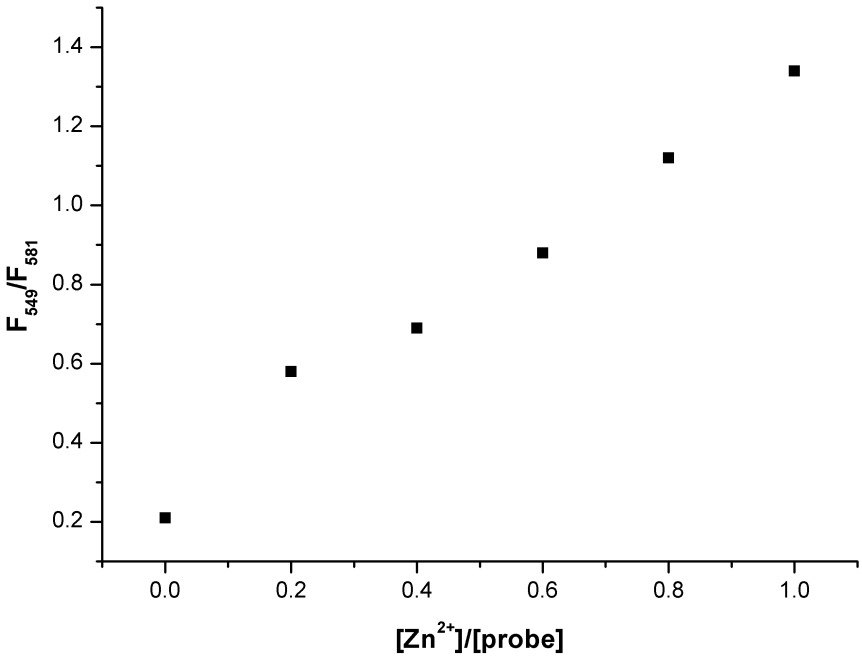


Figure S3. Ratiometric calibration curve F_{549nm}/F_{581nm} as a function of Zn^{2+} concentration (**BODPAQ** 5 μm).

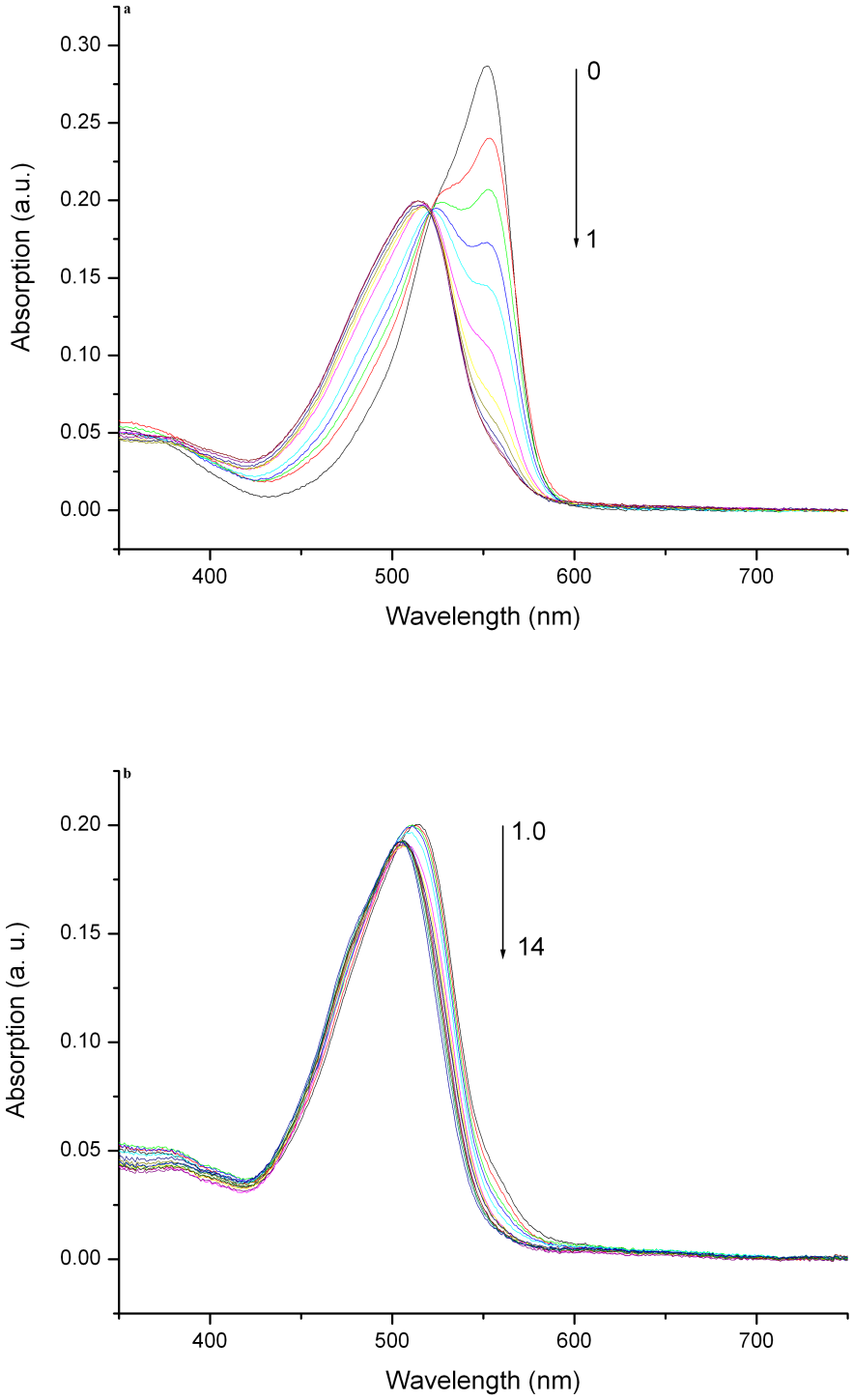


Figure S4. Absorption spectra of **BODPAQ** (5 μm) upon addition of Zn^{2+} (a) 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 equiv with respect to **BODPAQ** in methanol; (b) 1.0, 1.2, 1.4, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 8.0, 14 equiv with respect to **BODPAQ** in methanol.

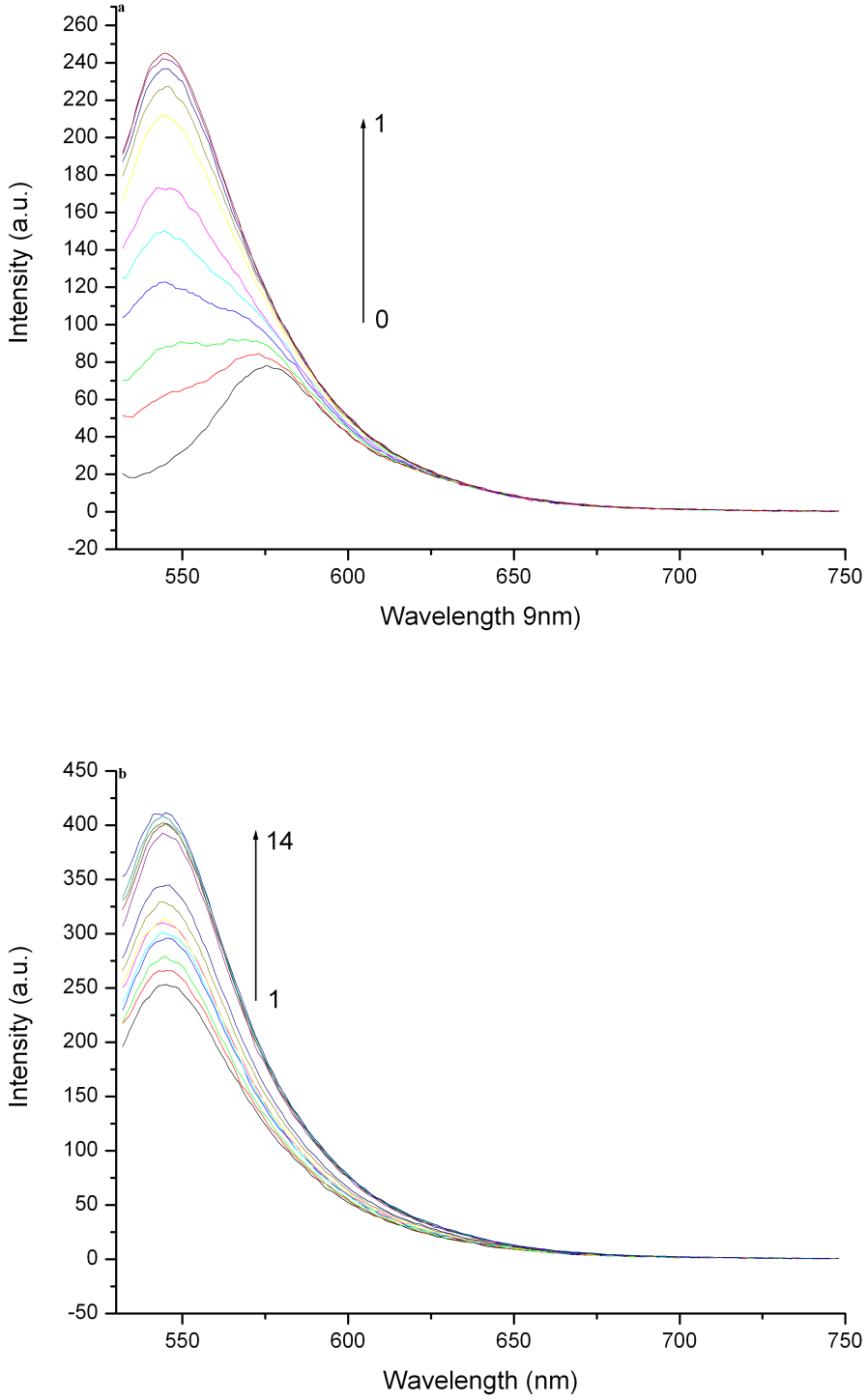


Figure S5. Emission spectra of **BODPAQ** (5 μm) upon addition of Zn^{2+} (a) 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 equiv with respect to **BODPAQ** in methanol; (b) 1.0, 1.2, 1.4, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 8.0, 14 equiv with respect to **BODPAQ** in methanol.

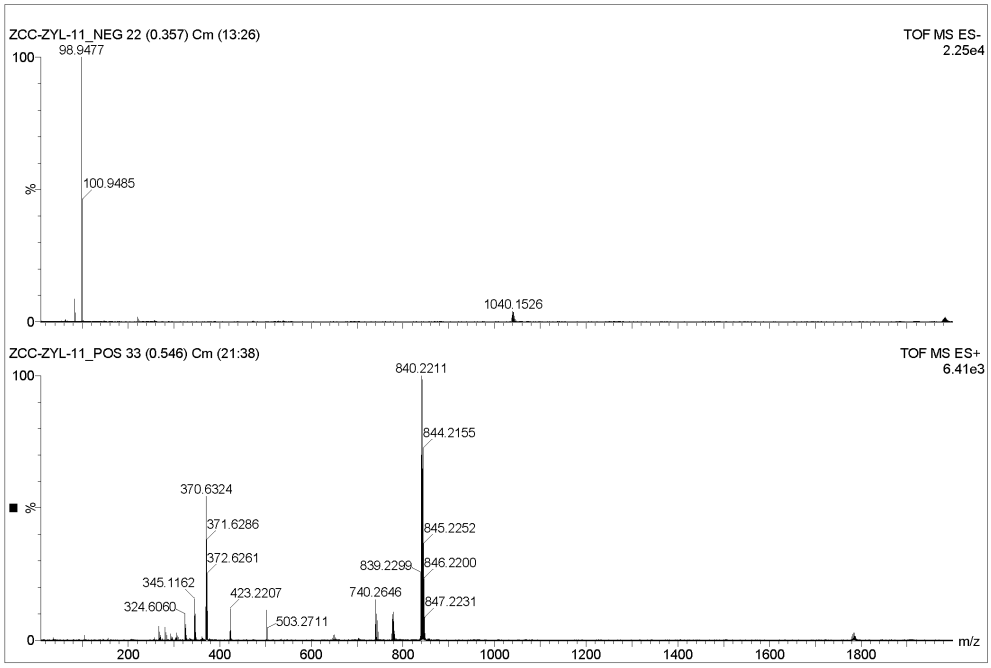


Figure S6. The HRMS spectrum of **BODPAQ**+ Zn^{2+} complex.

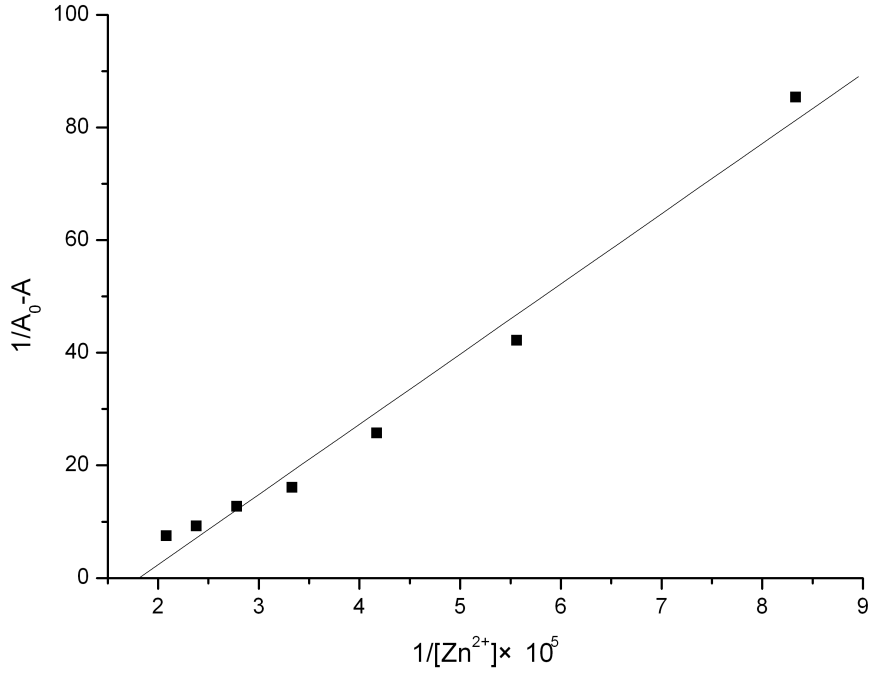


Figure S7. Benesi-Hildebrand plot for **BODPAQ**-Zn^{2+} system in CH_3CN.

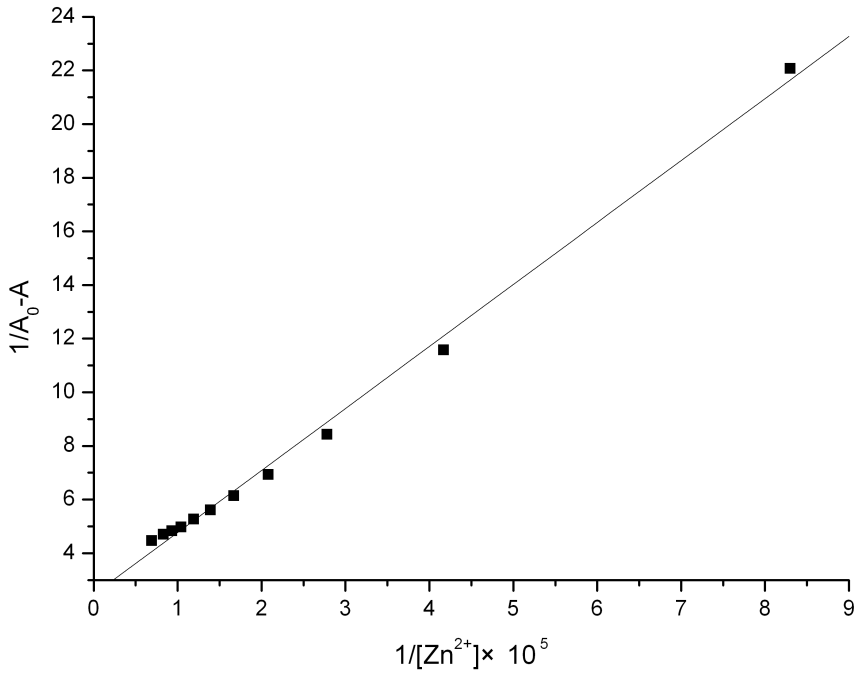


Figure S8. Benesi-Hildebrand plot for **BODPAQ**-Zn^{2+} system in MOPS buffer.

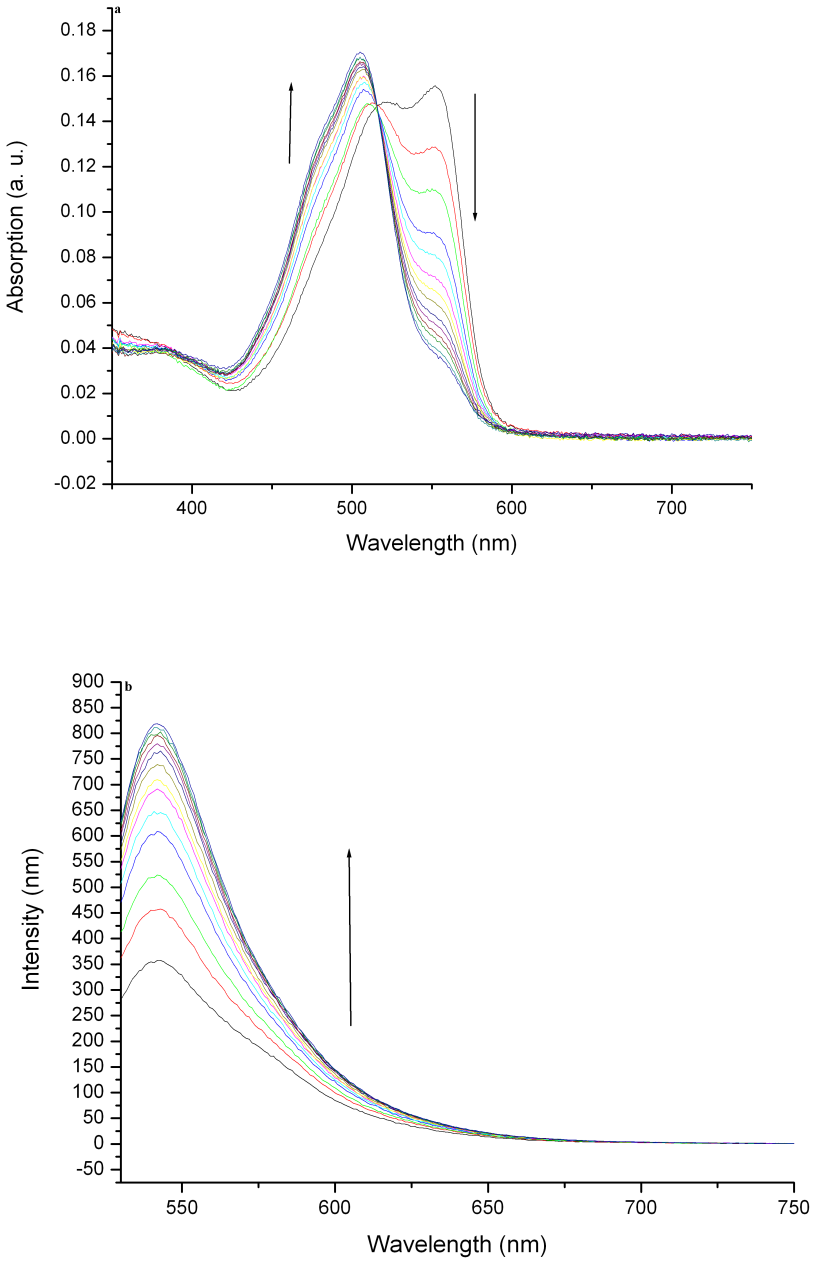
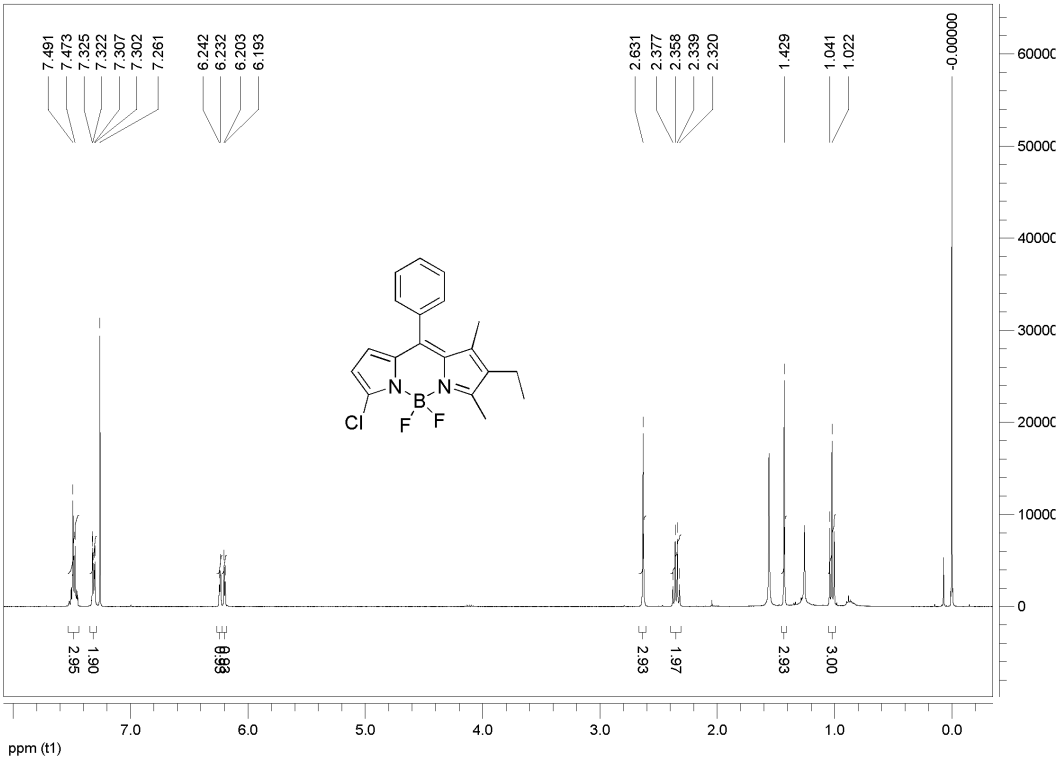
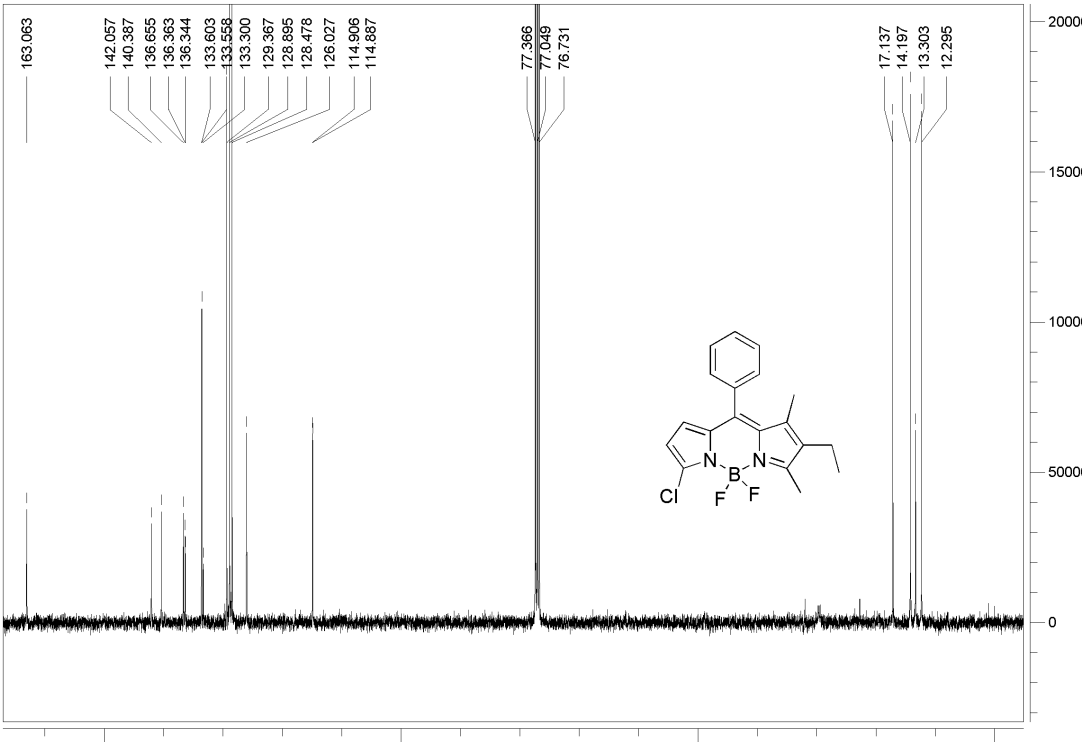
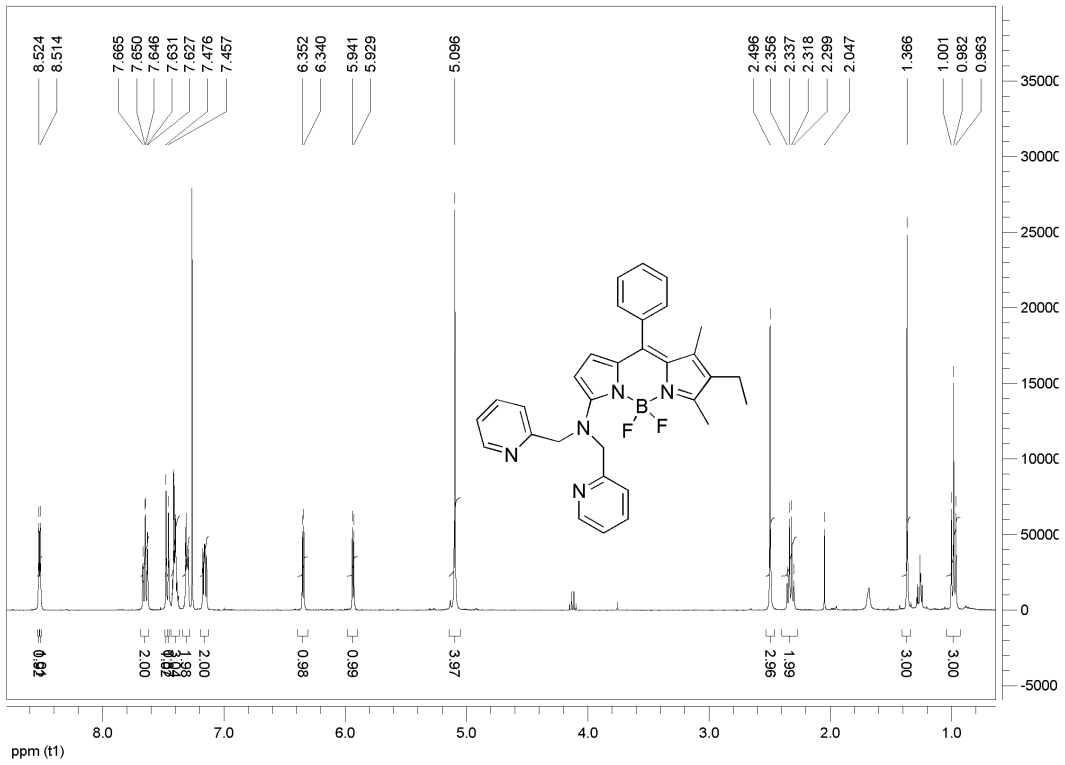


Figure S9. (a) Absorption spectra of **BODPAQ** (5 μM) upon addition of Zn^{2+} (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0 equiv with respect to **BODPAQ** in Methanol/MOPS buffer(50:50); (b) Emission spectra of **BODPAQ** (5 μm) upon addition of Zn^{2+} (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0 equiv with respect to **BODPAQ** in Methanol/MOPS buffer(50:50).

^{1}H MNR and ^{13}C NMR



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5.929
5.096
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2.337
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2.299
2.047
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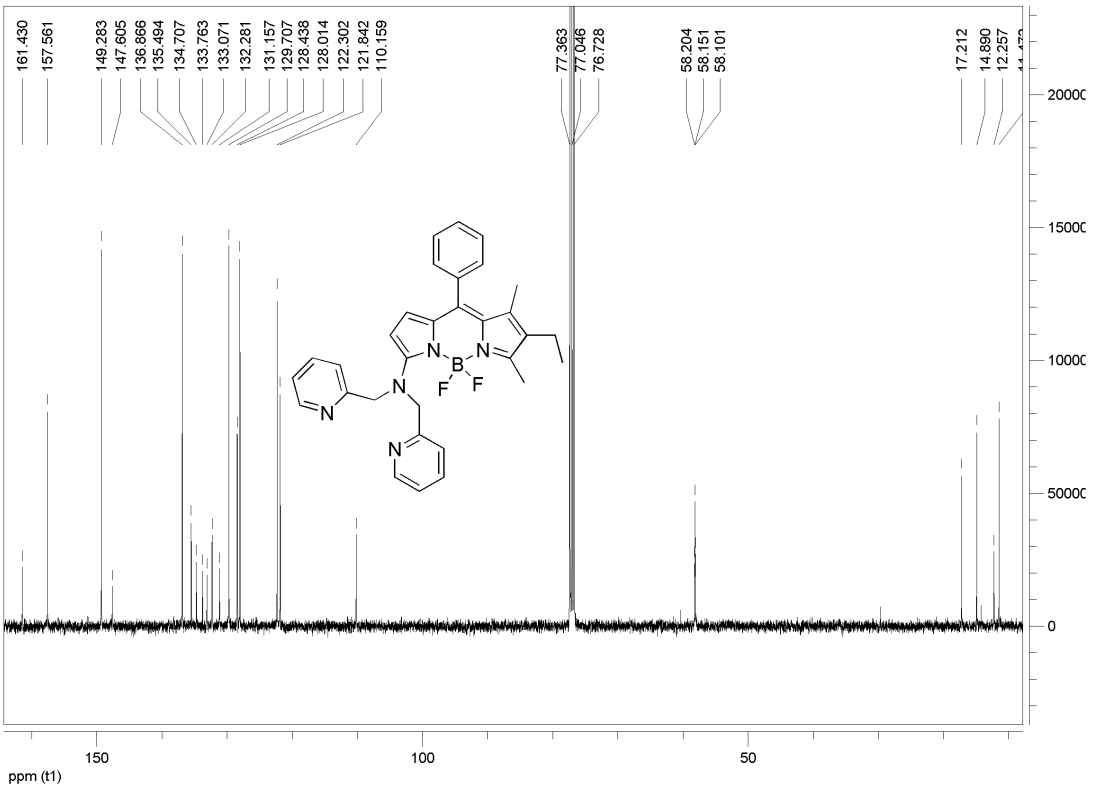
1.001
0.982
0.963
ppm (t1)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128.014
122.302
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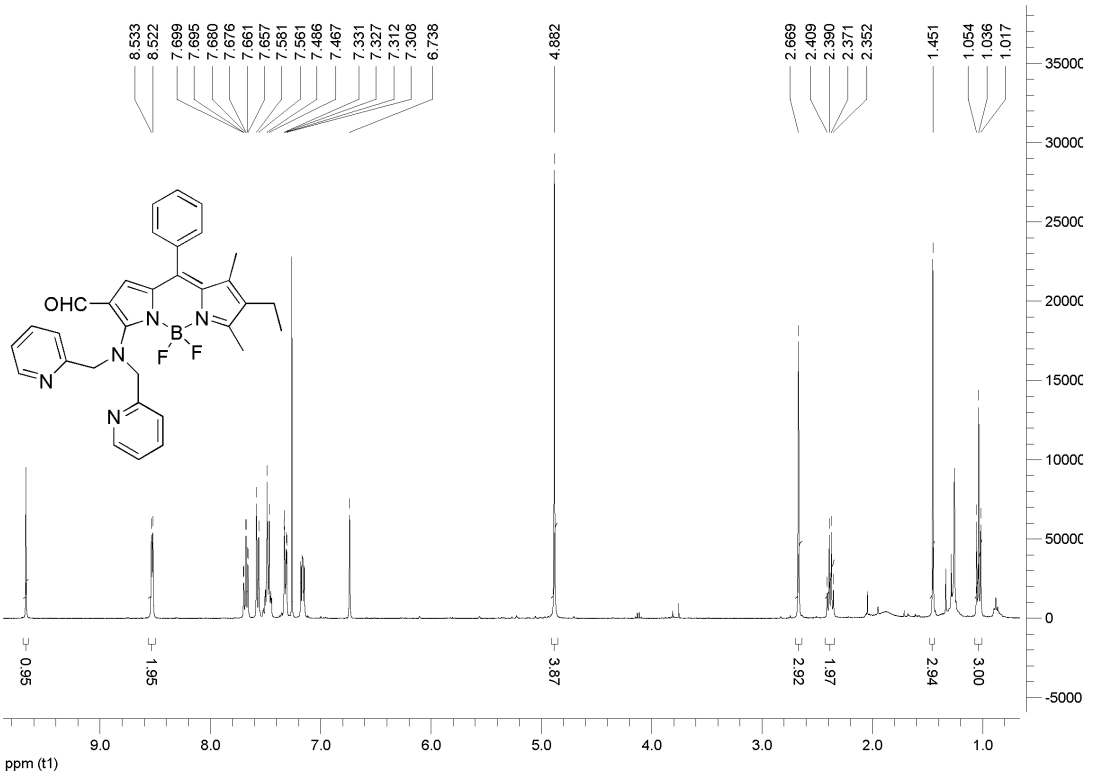
ppm (t1)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7.312
7.308
6.738
4.882
2.669
2.409
2.390
2.371
2.352
1.451
1.054
1.036
1.017
OHC
N
B
F
F
N
N
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1.95
3.87
2.92
1.97
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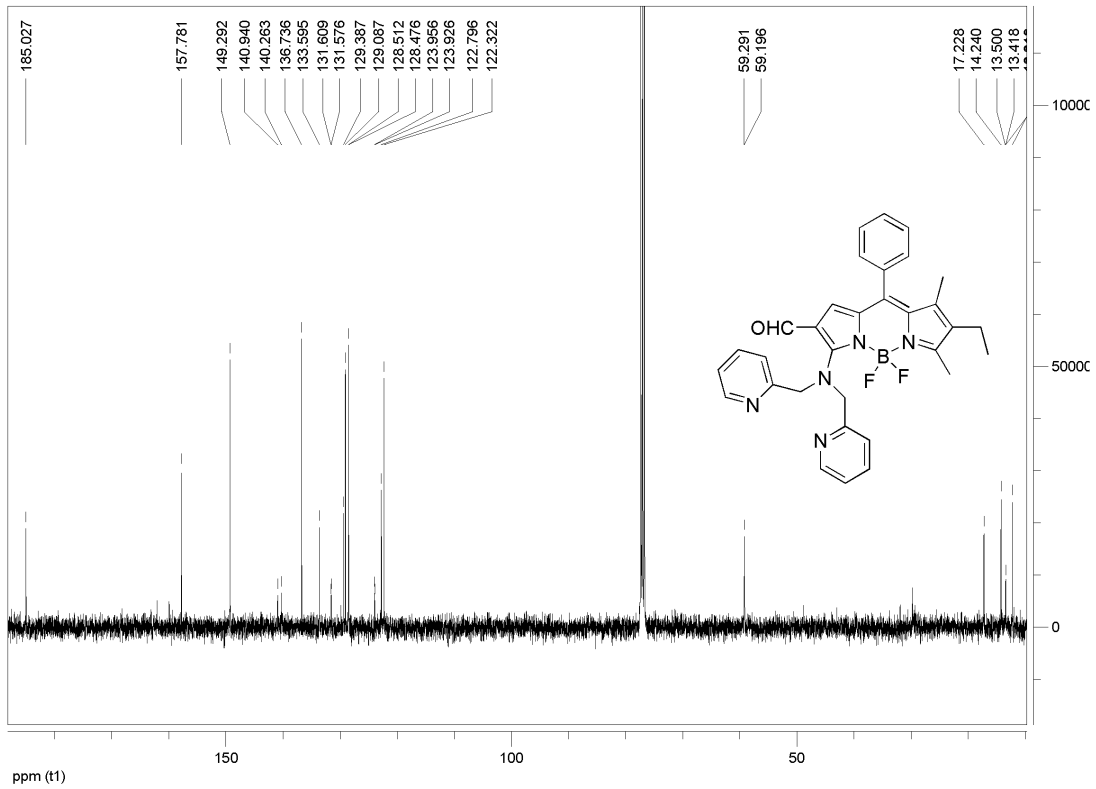
1.0
ppm (t1)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123.926
122.796
122.322
59.291
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N
B
F
F
N
N
150
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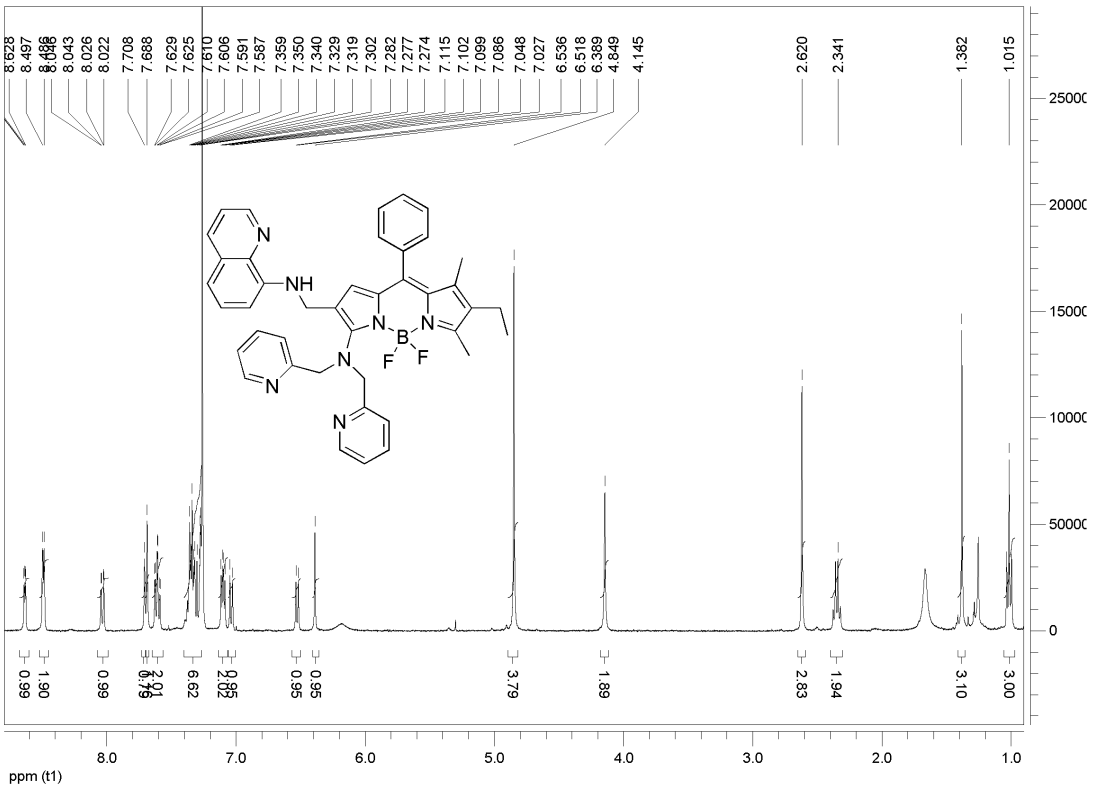
50
ppm (t1)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7.048
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0.95
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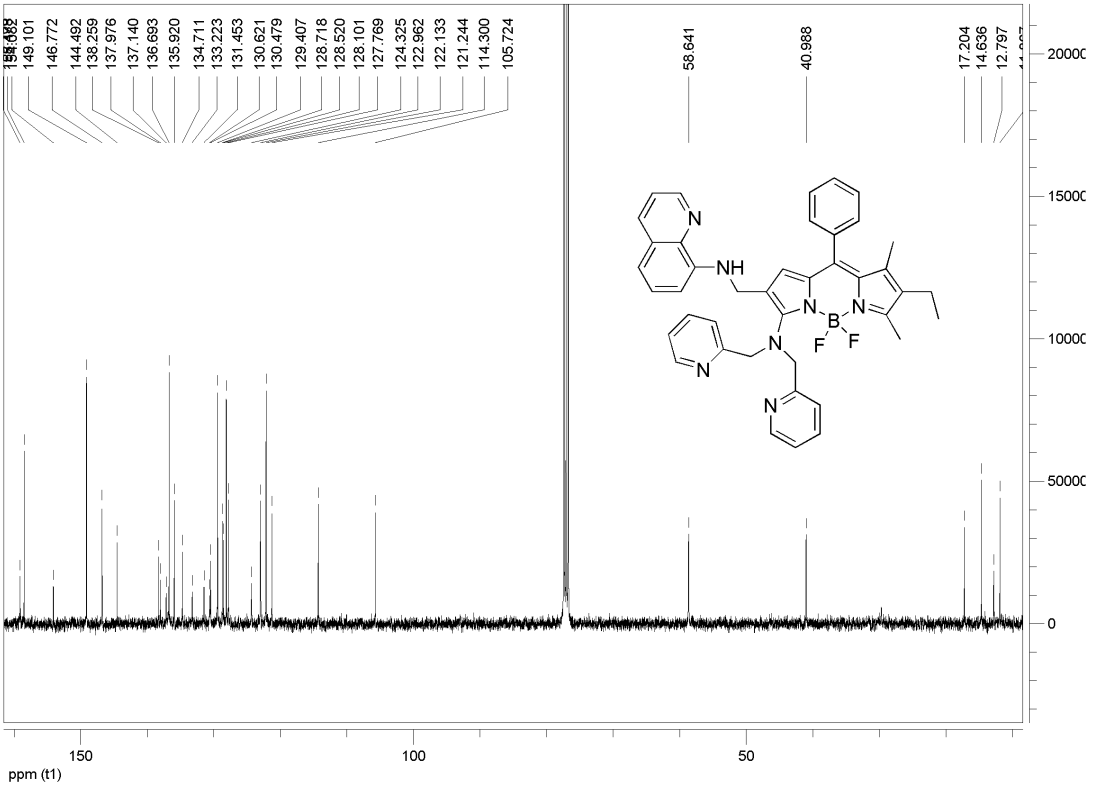
ppm (t1)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129.407
128.718
128.520
128.101
127.769
124.325
122.962
122.133
121.244
114.300
105.724
58.641
40.988
17.204
14.636
12.797
150
100
50
ppm (t1)