Supporting Information

A NEW FUNCTIONAL BIS(*meta*-PHENYLENE)-32-CROWN-10-BASED CRYPTAND HOST FOR PARAQUATS

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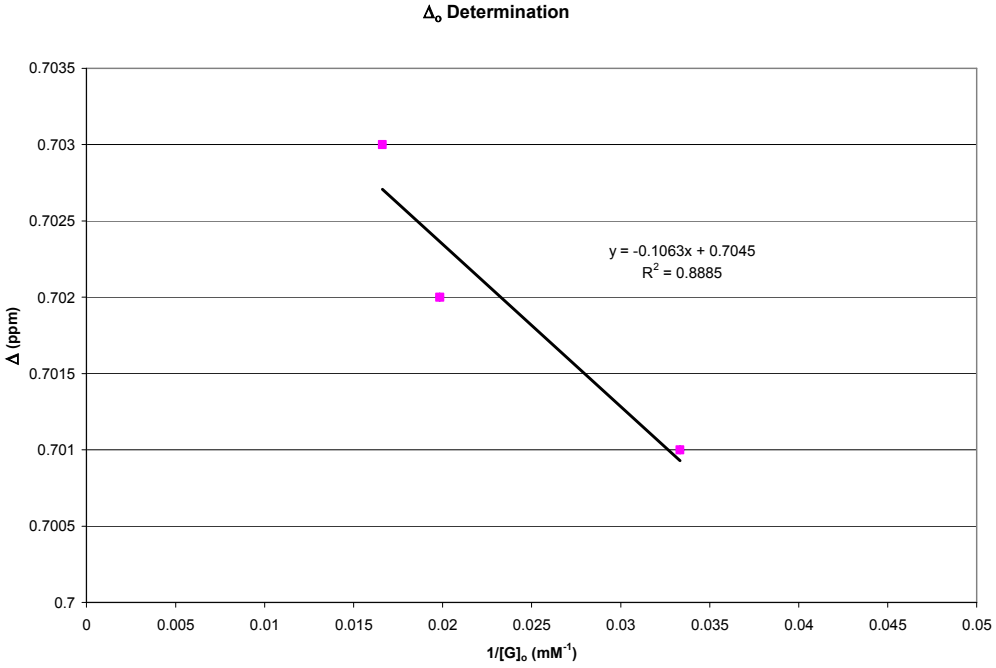
General: All reagents and starting materials were purchased from Sigma-Aldrich or Alfa Aesar. Bis(5-bromomethyl-1,3-phenylene)-32-C-10[1] and N,N'-dimethyl-4,4'-bipyridinium bis(hexafluorophosphate),[2] **$PQ(PF_6)_2$**, were prepared according to literature procedures. Thin layer chromatography (TLC) was performed using PE SIL G/UV from Whatman and aluminum oxide 60 F_{254} from EMD Chemicals, Inc. Column chromatography was performed with 40-63 μm flash silica from Silicycle and aluminum oxide 90 (neutral) from EM Science. Melting points were determined on a Büchi Melting Point B-540 and are uncorrected. NMR analysis was performed in deuterated solvents as received from Cambridge Isotope Laboratories. NMR spectra were obtained on either a Varian Inova 400 MHz or Varian Unity 400 MHz. Chemical shifts are relative to tetramethylenesilane. High resolution fast atom bombardment (HR FAB) mass spectra were obtained on a JEOL HX110 dual focusing mass spectrometer equipped with a FAB probe. Isothermal titration calorimetry was performed on a Microcal instrument.

NMR determination of complexation of 3·PQ(PF_6)$_2$.

Determination of Δ_o was accomplished by measuring the chemical shift of H_1 of **3** at constant host concentration (1.00 mM)while varying the guest concentration from 1.20 mM to 60.0 mM in acetone-d_6 at room temperature (22-23ºC). Δ_o was determined to be 0.70 ppm.

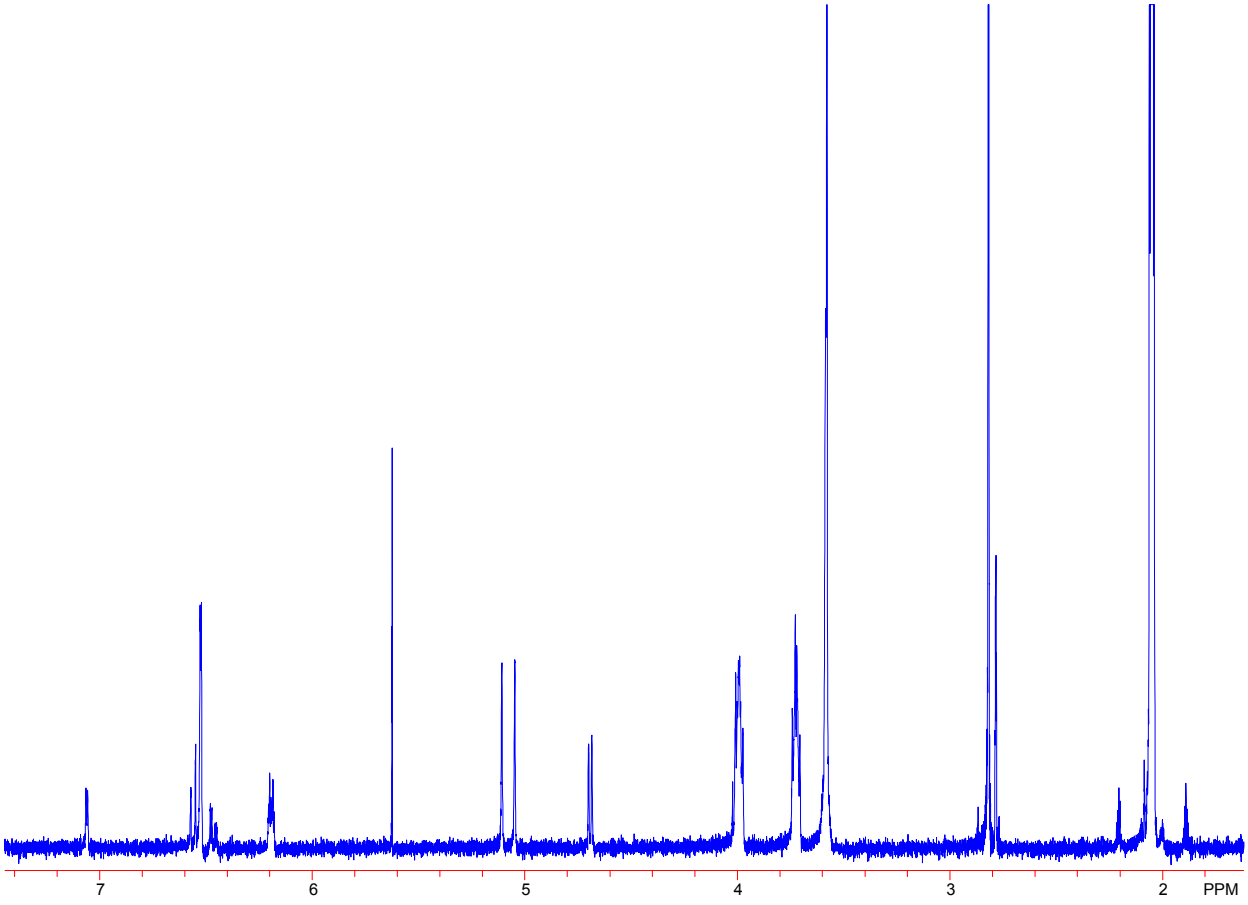
[**PQ(PF_6)$_2$**]$_o$ (mM)	H_1 Chemical Shift (ppm)
0.00	6.160
1.20	5.513
10.3	5.469
30.0	5.467
50.5	5.466
60.2	5.465



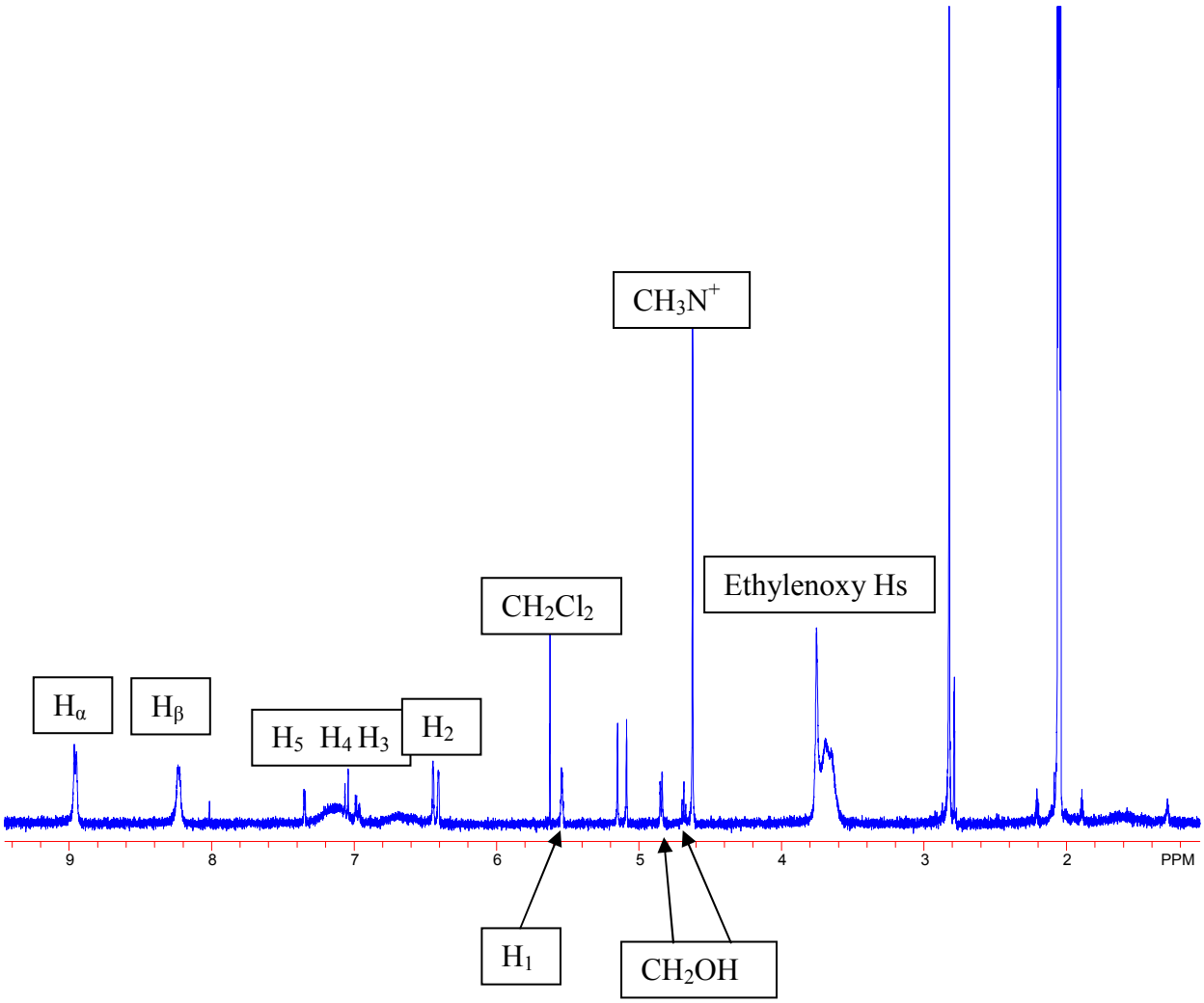
The stoichiometry of **3·PQ(PF_6)$_2$** was determined by the Job plot method[3] (Figure 2). Solutions were made according the following matrix:

[**3**]$_o$ (mM)	[**PQ(PF_6)$_2$**]$_o$ (mM)	H_1 Chemical Shift (ppm)
0.2	0.8	5.499
0.3	0.7	5.510
0.5	0.5	5.473
0.7	0.3	5.845
0.8	0.2	6.006

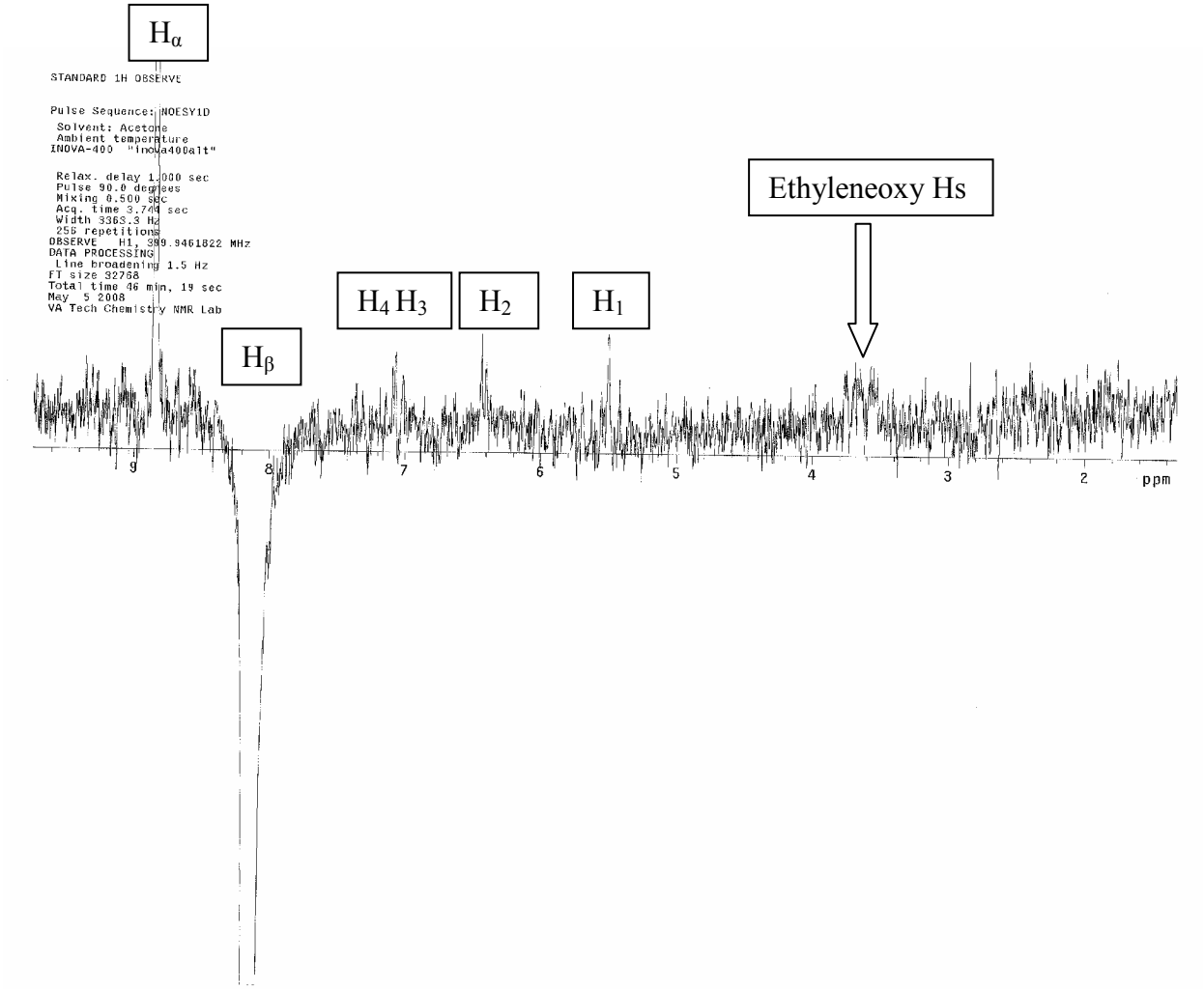
^{1}H NMR Spectrum of 1.0 mM **3** in acetone-d_6 at 23°C



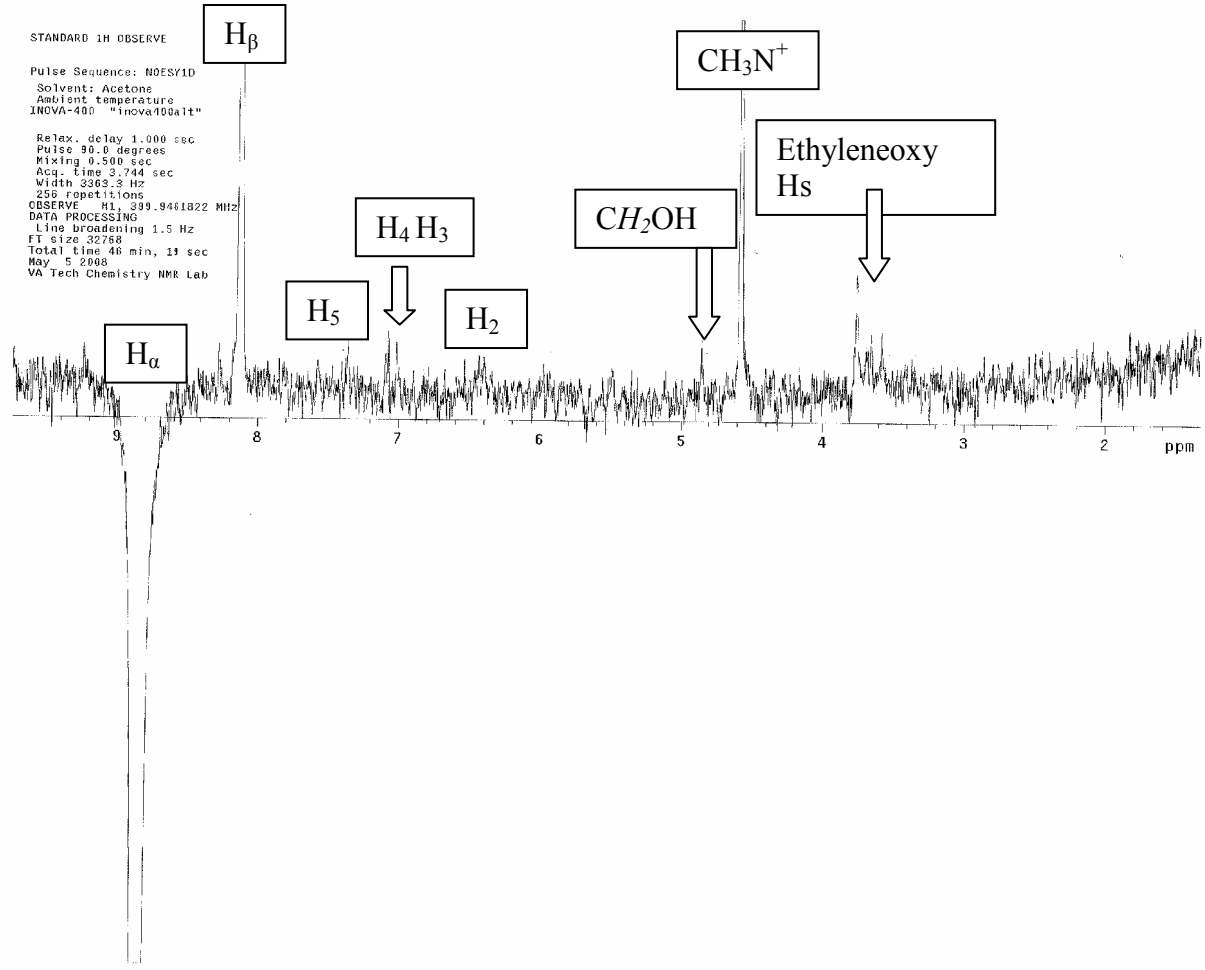
^{1}H NMR Spectrum of 1.0 mM **3** and 1.0 mM **PQ(PF$_6$)$_2$** in acetone-d_6 at 23°C



1D NOESY Spectrum of 10.0 mM **3** and 10.0 mM **PQ(PF$_6$)$_2$** in acetone-d_6 at 23°C. Irradiation occurred at H_β (8.12 ppm) and the relaxation time was 1.0 sec with 256 scans. NOE signals can be seen between H_β and H_1, H_2, H_3, H_4, and the ethyleneoxy hydrogens of **3**.

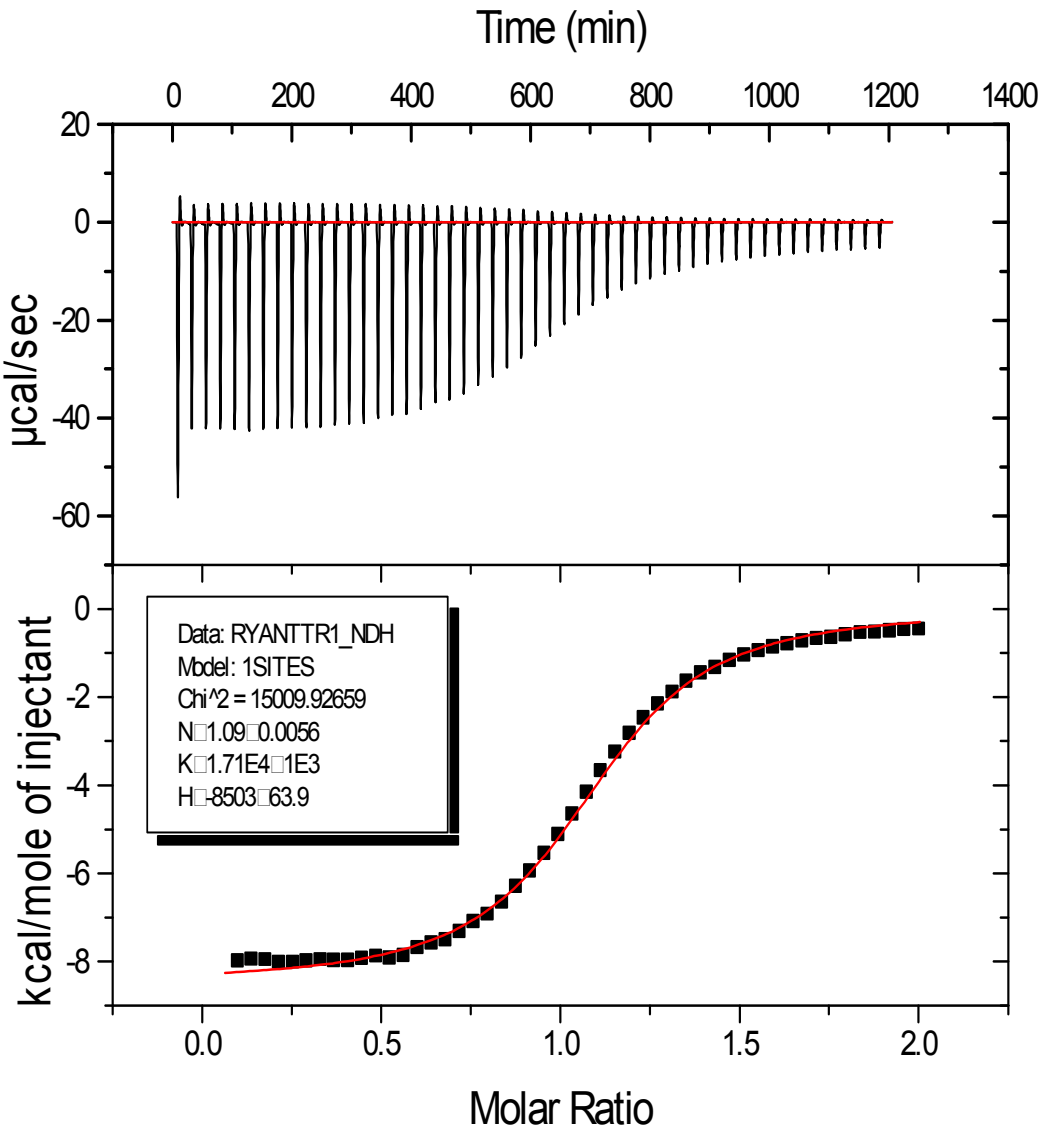


1D NOESY Spectrum of 10.0 mM **3** and 10.0 mM **PQ(PF$_6$)$_2$** in acetone-d_6 at 23°C. Irradiation occurred at H_α (8.84 ppm) and the relaxation time was 1.0 sec with 256 scans. NOE signals can be seen between H_α and H_1, H_2, H_3, H_4, H_5, hydroxymethylene and the ethyleneoxy hydrogens of **3**.



Isothermal titration calorimetry of 3·$PQ(PF_6)_2$.

$PQ(PF_6)_2$ (50.0 mM) was titrated into **3** (1.97 mM) in acetone at 25°C in 30 aliquots of 3.3 µL each.



[1] Gibson, H. W.; Nagvekar, D. S. *Can. J. Chem*. **1997**, 75, 1375-1384.
[2] Shen, Y. X.; Engen, P. T.; Berg, M. A. G.; Merola, J. S.; Gibson, H. W. *Macromolecules* **1992**, 25, 2786-2787.
[3] Job, A. *Liebigs. Ann. Chem.* **1928,** 9, 113.