Unusual emission from norbornene derived phosphonate molecule– A Sensor for Fe^{III} in Aqueous Environment

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Experimental Section

Materials: 5-norborene-2-carboxylic acid (mixture of endo and exo isomers), diethyl(hydroxylmethyl)phosphonate were purchased from Alfa Aesar, 5-norbornene-2-ol (mixture of endo and exo isomers), 3-(diethoxyphosphoryl)propanoate**,** ethyl 6-(diethoxyphosphoryl)hexanoate**,** p-toluenesulphonic acid monohydrate (PTSA monohydrate)**,** second generation Grubbs' catalyst, $CDCl_3$ and DMSO-D_6 were purchased from Sigma Aldrich. Dichloromethane (DCM) and Toluene were dried and used for reactions.

Characterization:

Gel Permeation Chromatography (GPC). Molecular weights and PDIs were measured by Waters gel permeation chromatography in THF relative to PMMA standards on systems equipped with Waters Model 515 HPLC pump and Waters Model 2414 Refractive Index Detector at 35 0C with a flow rate of 1 mL/min. HRMS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments by +ve mode electrospray ionization.

Fluorometry. Fluorescence emission spectra were recorded on a Fluorescence spectrometer (Horiba Jobin Yvon, Fluromax-3, Xe-150 W, 250-900 nm).

Nuclear Magnetic Resonance (NMR). The ^{1}H NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using CDCl3 as a solvent. ^{1}H NMR spectra of solutions in CDCl3 were calibrated to tetramethylsilane as internal standard (δH 0.00).

Fourier Transform Infra Red (FT-IR). FT-IR spectra were obtained on FT-IR Perkin-Elmer spectrometer at a nominal resolution of 2 cm^{-1}.

Ultra Violet (UV) Spectroscopy. UV-visible absorption measurements were carried out on U-4100 spectrophotometer HITACHI UV-vis spectrometer, with a scan rate of 500 nm/min.

Dynamic Light Scattering (DLS). Particle size of QDs were measured by dynamic light scattering (DLS), using a Malvern Zetasizer Nano equipped with a 4.0 mW He-Ne laser operating at λ = 633 nm. All samples were measured in aqueous as well as methanol at room temperature and a scattering angle of 173°.

Transmission Electron Microscopy (TEM). Low resolution transmission electron microscopy (TEM) was performed on a JEOL 200 CX microscope. TEM grids were purchased from Ted Pella, Inc. and consisted of 3-4 nm amorphous carbon film supported on a 400-mesh copper grid.

Isolation of 5-norbornene-2-exo-carboxylic acid: Exo-5-norbornene-2-carboxylic acid was separated from the commercially available mixture of endo and exo 5-norbornene-2-carboxylic acid by the iodolactonization method of Ver Nooy and Rondestvedt.[S1] ^{1}H NMR (DMSO-D_6, 500 MHZ) (): δ 1.13-1.17 (m, 2H), 1.28-1.29 (d, J = 8.5 Hz, 1H), 1.66-1.71 (m, 1H), 1.97-2.05 (dt, J = 12.7Hz, 1H), 2.76 (s, 1H), 2.9 (s, 1H), 6.03-6.05 (m, 2H), 12.00 (br, 1H). ^{13}C NMR ($CDCl_3$, 500 MHZ)(Figure S1): 182.7, 138.1, 135.7, 46.7, 46.4, 43.2, 41.7, 30.3. IR (KBr, cm^{-1}))(Figure S8): 2919, 2852, 1700, 1421, 1218, 909, 766. MS (ESI) calculated for $C_8H_{10}O_2Na$ $[M + H]^+$, 138.07; observed 138.09.

Synthesis of (diethoxyphosphoryl) methyl bicycle[2.2.1]hept-5-ene-2-carboxylate: 100 mg (0.72 mmol, 1equiv) of norbornene exo carboxylic acid was dissolved in 5 ml Toluene in a properly dried single neck flask, followed by 9.1 mg (10 mol%) of PTSA monohydrate and 129.3 mg (0.769 mmol, 1.0625 equiv) of diethyl(hydroxylmethyl) phosphonate, fitted with Dean-stark apparatus and heated upto 90^0 C for 15 hrs. After cooling the reaction mixture concentrated the solution by evaporating toluene and worked up with 10 ml ethyl acetate and washed with saturated sodium bicarbonate solution (2x 10 ml). The organic layer was dried over Na_2SO_4 and concentrated under vacuum to yield compound **NDP1** as a white solid as crude product which was purified by column chromatography on nutral alumina.

^{1}H NMR (CDCl3, 500 MHZ): δ 1.28-1.30 (t, 6H, J = 6.88 Hz, CH3), 1.81-1.84 (m, 2H), 2.24-2.25 (m, 1H), 2.934 (s, 1H), 3.067 (s, 1H), 3.80-3.90 (dd, 2H), 4.155-4.177 (q, 4H),6.106-6.176 (m, 2H). ^{13}C NMR (CDCl3, 500 MHz) (Figure S2): 175.15, 138.35, 135.42, 62.73,61.9, 48, 42.6, 46.3, 43, 29, 16.34. IR (KBr, cm^{-1}) (Figure S9) : 3272, 2922, 2850, 1745, 1237, 1178, 1021, 965, 750. MS (ESI) calculated for $C_{13}H_{21}O_5P$ $[M + NH_4]^+$; 288.11, found 288.21.

Ester hydrolysis of ethyl 3-(diethoxyphosphoryl)propanoate: Ethyl 3-(diethoxyphosphoryl)propanoate (500 mL, 2.1 mmol) was added dropwise to 1 M NaOH (5 ml). After stirring for 3 h at RT, EtOH was partially evaporated and the reaction mixture was treated with 2 N HCl (until pH 1). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to yield 3-(diethoxyphosphoryl)propanoic acid (0.36 g, 79%) as a greenish oil. ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta = 12.04$ (s, 1 H, OH); 4.27-4.12 (m, 4 H, OCH2); 2.33 (t, 2 H,); 2.04(t, 2H) 1.34 (t, 6 H, CH3). The acid was used for the subsequent reaction without further purification.

Synthesis of bicyclo[2.2.1]hept-5-en-2-yl 3-(diethoxyphosphoryl)propanoate :100 mg (0.90 mmol) of norbornene-2-ol (exo,endo mixture) was dissolved in 5ml toluene in single neck flask, followed by 6.2 mg (10 mol%) of PTSA monohydrate and 152 mg(0.723 mmol) of 3-(diethoxyphosphoryl)propanoic acid, fitted with Dean-stark apparatus and heated upto 90^0 C for 15 hrs. After cool the reaction mixture concentrated the solution by evaporating toluene and worked up with 10 ml ethyl acetate washed with saturated sodium bicarbonate solution (2 x 10 ml). The organic layer was dried over Na_2SO_4 and concentrated under vacuum to yield compound **NDP2** as a brownish liquid as crude product which was purified by column chromatography on nutral alumina.

^{1}H NMR ($CDCl_3$, 500 MHZ) : δ 0.776-0.739 (dd, 2H, CH_2), 1.30 (t, 3H), 2.15-1.30 (m, 5H), 3.12-2.54 (m, 5H), 4.104-4.05 (m, 2H), 5.2 (s, 2H), 6.45-5.95 (m, 2H). ^{13}C NMR (CDCl3, 500 MHz) (Figure S3): 175.15, 140.35, 138.35, 133.32, 132.42, 62.73, 61.9, 48, 42.6, 46.3, 43, 29, 16.34. IR (KBr, cm^{-1}) (Figure S11) : 2991, 1737, 1250, 1173, 1017, 964. MS (ESI) calculated for $C_{14}H_{23}O_5P$ $[M + Na]^+$; 302.13, found 325.07.

Ester hydrolysis of ethyl 6-(diethoxyphosphoryl)hexanoate : Ethyl 6-(diethoxyphosphoryl)hexanoate (500 mL, 1.78 mmol) was added dropwise to 1 M NaOH (4 mL). After stirring for 3 h at RT, EtOH was partially evaporated and the reaction mixture was treated with 2 N HCl (until pH 1). The aqueous layer was extracted with

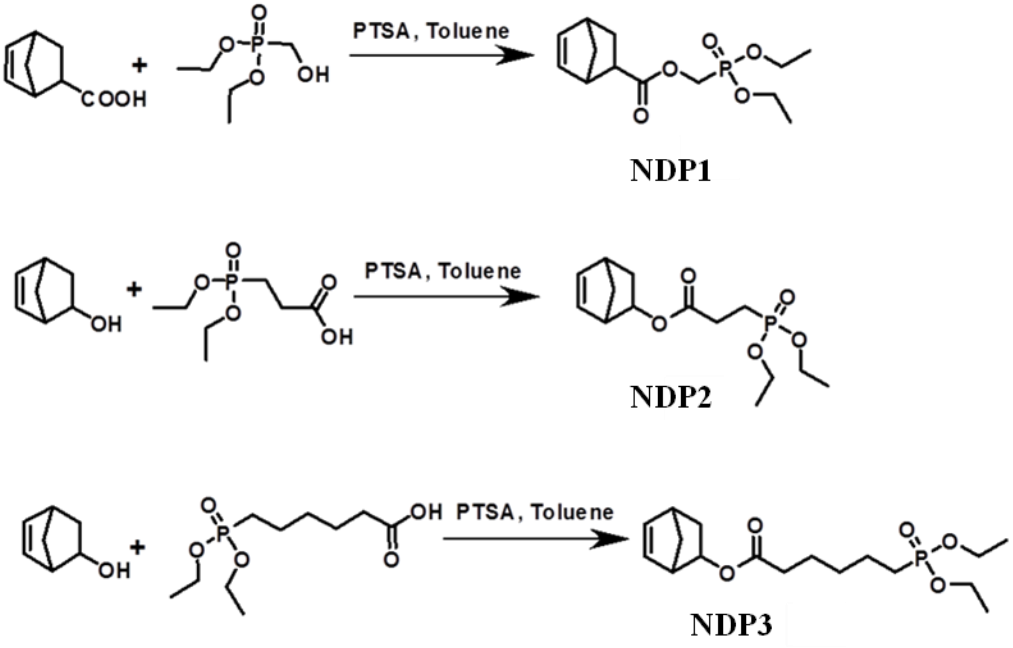
CH_2Cl_2. The combined organic layers were washed with brine dried overanhydrous Na_2SO_4. The solvent was removed *in vacuo* to yield 6-(diethoxyphosphoryl)hexanoic acid (0.35 g, 77%) as a greenish oil. ^{1}H-NMR (CDCl3, 500 MHz): δ = 12.19 (s, 1 H, OH); 4.27-4.12 (m, 4 H, OCH2); 2.33 (t, 2H,); 1.77(t, 2H); 1.54-1.52 (m, 4H); 1.36-1.35 (m, 2H); 1.34 (t, 6 H, CH3). The acid was used for the subsequent reaction without further purification.

Synthesis of bicyclo[2.2.1]hept-5-en-2-yl 6-(diethoxyphosphoryl)hexanoate: 100 mg (0.90 mmol,) of norbornen-2-ol (exo,endo mixture) was dissolved in 5ml Toluene in single neck flask, followed by 5.5 mg (l0 mol%) of PTSA monohydrate and 200 mg (0.79 mmol) of yield 6-(diethoxyphosphoryl)hexanoic acid ,fitted with DEAN-STARK apparatus and heated upto 90^0 C for 15 hrs. After cool the reaction mixture concentrated the solution by evaporating toluene and worked up with 10 ml ethyl acetate washed with saturated sodium bicarbonate solution (20 ml). The organic layer was dried over Na_2SO_4 and concentrated under vacuum to yield compound **NDP3** as a faint brownish liquid as crude product which was purified by column chromatography on nutral alumina.
^{1}H NMR ($CDCl_3$, 500 MHZ) (Figure S3): δ 1.248 (dd, 2H), 1.32 (t,6H), 1.74-1.40 (m, 7H), 3.12-2.12 (m, 7H), 4.12-4.05 (m, 4H), 5.33 (d, 1H), 6.322-5.947 (m, 2H). ^{13}C NMR ($CDCl_3$, 500 MHz) (Figure S4): 175.15, 141.04, 138.49, 132.57, 131.50, 75.62, 61.45, 42.17, 45.73, 46.20, 47.26, 34.60, 30.04, 29.90, 26.08, 16.48. IR (KBr, cm^{-1}) (Figure S12) 2929, 2867, 1730, 1265, 1017, 964, . MS (ESI) calculated for $C_{17}H_{29}O_5P$ $[M + Na]^+$; 367.11, found 367.09.

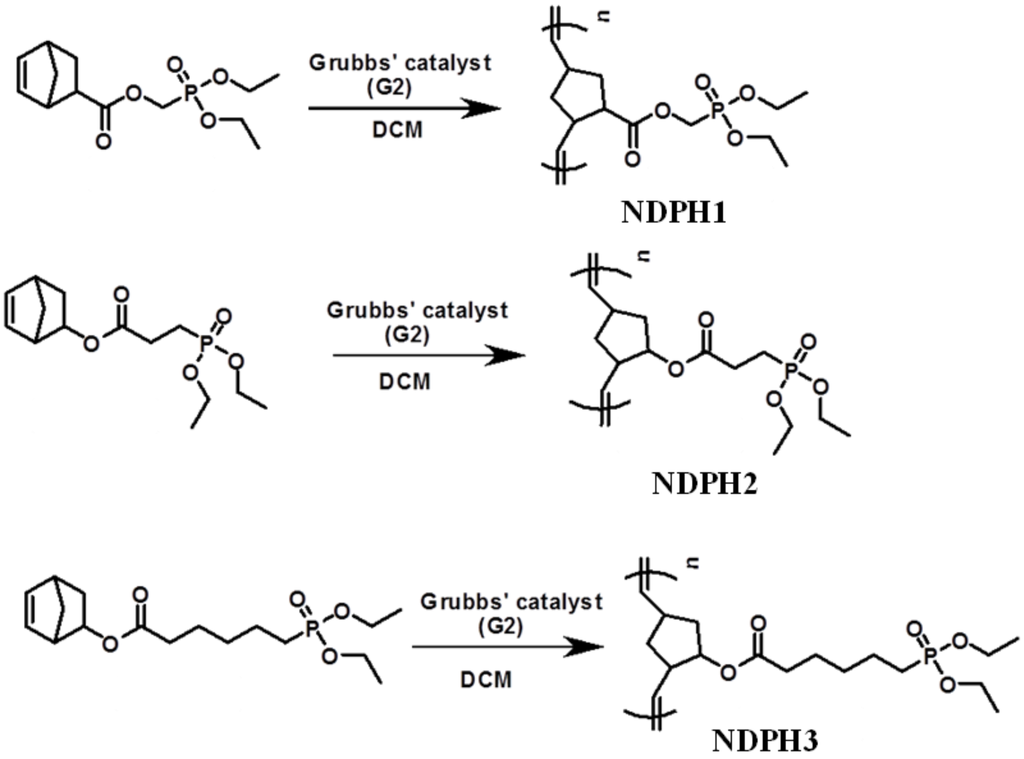
Homopolymerization of phosphonate derived norbornene (NDPH1): 10 mg (0.0347 mmol) of Monomer **1** was weighed into a separate Schlenk flask, placed under an atmosphere of nitrogen, and dissolved in 1 ml of dry DCM. Into another Schlenk flask, a desired amount of second generation Grubbs' catalyst 1.4 mg (G2, 20 mol %) was added, flushed with nitrogen, dissolved in minimum (0.5 ml) anhydrous dichloromethane. All two flasks were degassed three times by freeze-pump-thaw cycles. The Monomer **1** was transferred to the flask containing the catalyst via a cannula. The reaction was allowed to stir at room temperature until the polymerization was complete (50 minutes) before it was quenched with vinyl ethyl ether (0.5 ml). An aliquot was taken for GPC analysis, and the remaining product was precipitated with diethyl ether, dissolved it again THF, passed it through neutral alumina to remove the catalyst and precipitated again with diethyl ether to get pure polymer (8 mg, 80% yield). Gel permeation chromatography (GPC) was done in tetrahydrofuran (flow rate = 1ml/1min). The molecular weight of homopolymer **1**, was measured using polystyrene standards. Mn = 18,000 and PDI = 1.2 suggested the homopolymerization of **1**. ^{1}H NMR ($CDCl_3$, 500 MHz,) : δ 1.2-1.306 (m, protons of y), 1.67-1.96, (m, c, e), 2.44-2.68 (m, protons of d), 2.93-3.11 (m, protons of bb$'$), 3.89-4.29 (m, protons of x), 4.28-4.39 (m, protons of z), 5.0-5.4 (m, protons of a, new olefinic protons).

Homopolymerization of phosphonate derived norbornene (NDPH2): 10 mg (0.0331 mmol) of Monomer **2** was weighed into a separate Schlenk flask, placed under an atmosphere of nitrogen, and dissolved in 1 ml of dry DCM. Into another Schlenk flask, a desired amount of second generation Grubbs' catalyst 1.4 mg (G2, 20 mol %) was added, flushed with nitrogen, dissolved in minimum (0.5 ml) anhydrous dichloromethane. All two flasks were degassed three times by freeze-pump-thaw cycles. The Monomer **1** was transferred to the flask containing the catalyst via a cannula. The reaction was allowed to stir at room temperature until the polymerization was complete (50 minutes) before it was quenched with vinyl ethyl ether (0.5 ml). An aliquot was taken for GPC analysis, and the remaining product was precipitated with diethyl ether, dissolved it again THF, passed it through neutral alumina to remove the catalyst and precipitated again with diethyl ether to get pure polymer (6 mg, 74% yield). Gel permeation chromatography (GPC) was done in tetrahydrofuran (flow rate = 1ml/1min). The molecular weight of homopolymer **1**, was measured using polystyrene standards. Mn = 6000 and PDI = 1.06 suggested the homopolymerization of ^{1}H NMR ($CDCl_3$, 500 MHz,): δ 1.27-1.31 (t, 6H), 2.15-1.30 (m, 5H), 3.12-2.54 (m,5H); 4.10-4.05 (m, 2H); 5.0-5.4 (m, protons of a, new olefinic protons).

Homopolymerization of phosphonate derived norbornene (NDPH3): 10 mg (0.0290 mmol) of Monomer **3** was weighed into a separate Schlenk flask, placed under an atmosphere of nitrogen, and dissolved in 1 ml of dry DCM. Into another Schlenk flask, a desired amount of second generation Grubbs' catalyst 1.4 mg (G2, 20 mol %) was added, flushed with nitrogen, dissolved in minimum (0.5 ml) anhydrous dichloromethane. All two flasks were degassed three times by freeze-pump-thaw cycles. The Monomer **1** was transferred to the flask containing the catalyst via a cannula. The reaction was allowed to stir at room temperature until the polymerization was complete (50 minutes) before it was quenched with vinyl ethyl ether (0.5 ml). An aliquot was taken for GPC analysis, and the remaining product was precipitated with diethyl ether, dissolved it again THF, passed it through neutral alumina to remove the catalyst and precipitated again with diethyl ether to get pure polymer (5 mg, 73% yield). Gel permeation chromatography (GPC) was done in tetrahydrofuran (flow rate = 1ml/1min). The molecular weight of homopolymer **1**, was measured using polystyrene standards. Mn = 5800 and PDI = 1.04 suggested the homopolymerization. ^{1}H NMR (CDCl$_3$, 500 MHz,): δ 1.32 (t, 6H), 1.74-1.40 (m, 7H), 3.12-2.12 (m,7H); 4.10-4.05 (m, 2H); 5.0-5.4 (m, protons of a, new olefinic protons).



Scheme 1. Schematic representation of synthesis of norbornene derived NDP1, NDP2 and phosphonate NDP3 respectively.



Scheme 2: Schematic representation of synthesis of polymer via ROMP of NDPH1, NDPH2, and NDPH3 using Grubbs' 2nd generation catalyst.

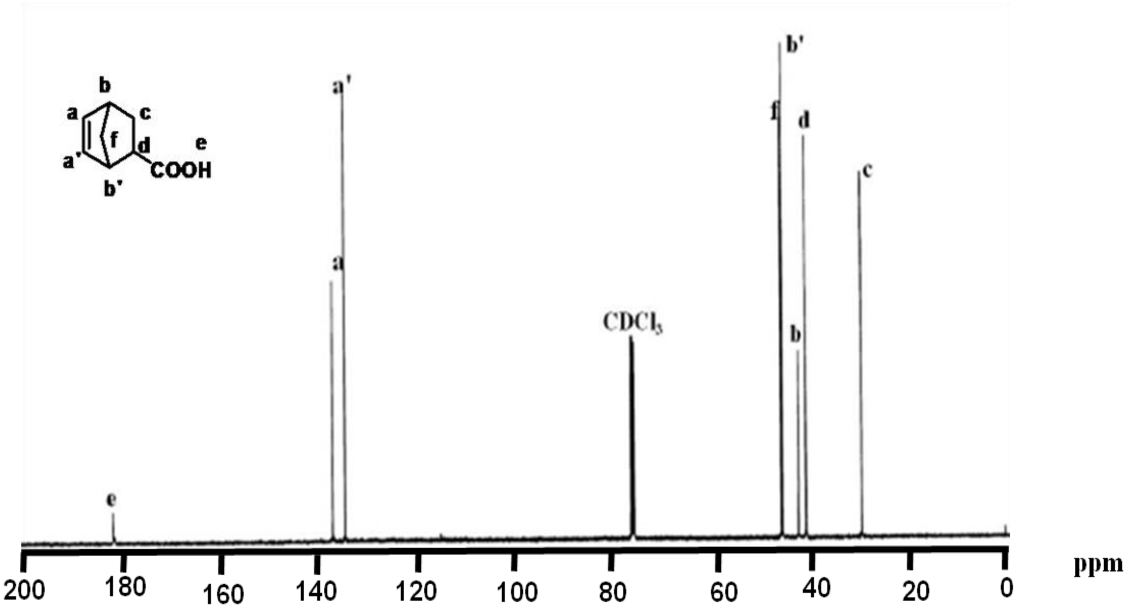


Figure S1. ^{13}C NMR spectra of exo-5-norbornene-2-carboxylic acid.

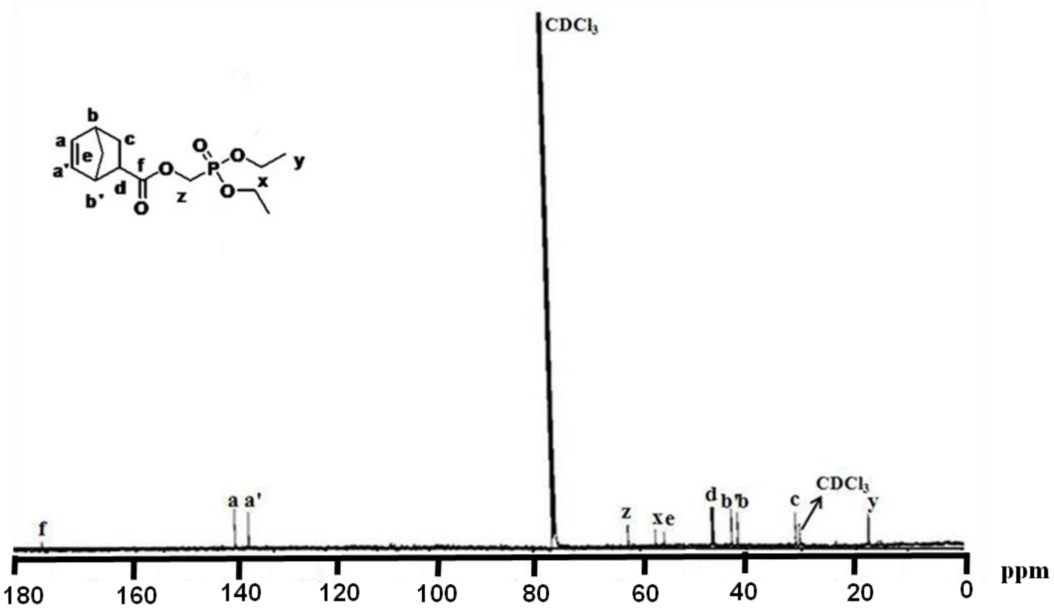


Figure S2. ^{13}C NMR spectra of norbornene derived phosphonate NDP1.

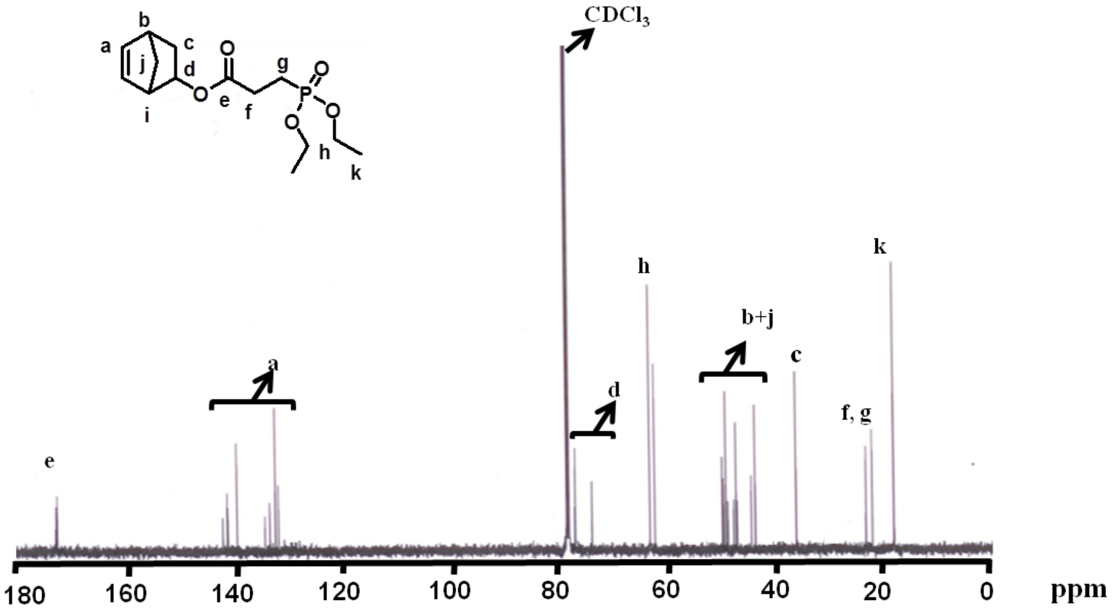


Figure S3. ^{13}C NMR spectra of norbornene derived phosphonate NDP2.

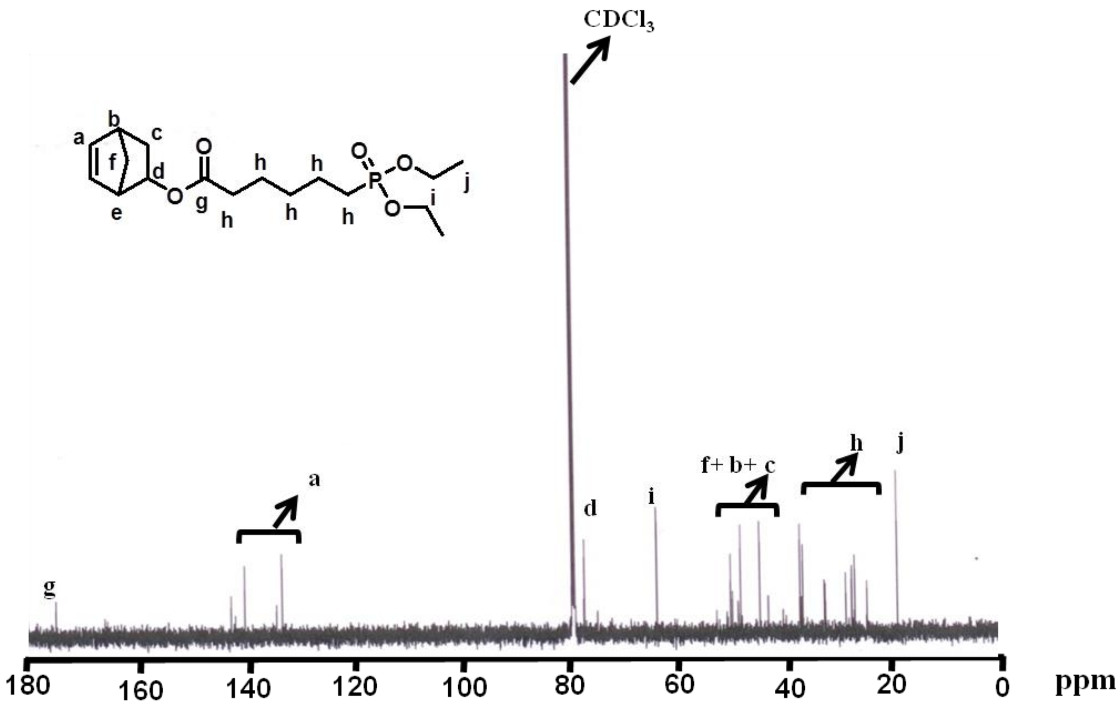


Figure S4. ^{13}C NMR spectra of norbornene derived phosphonate NDP3.

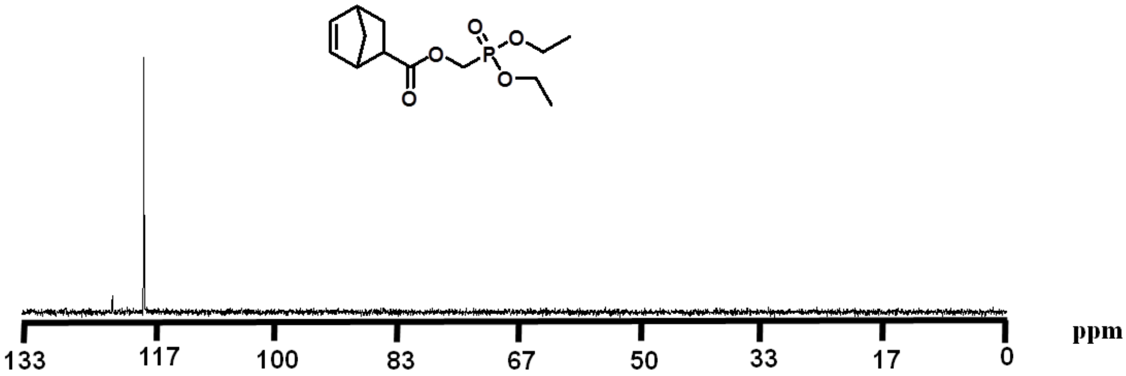


Figure S5. ^{31}P NMR spectra of norbornene derived phosphonate NDP1.

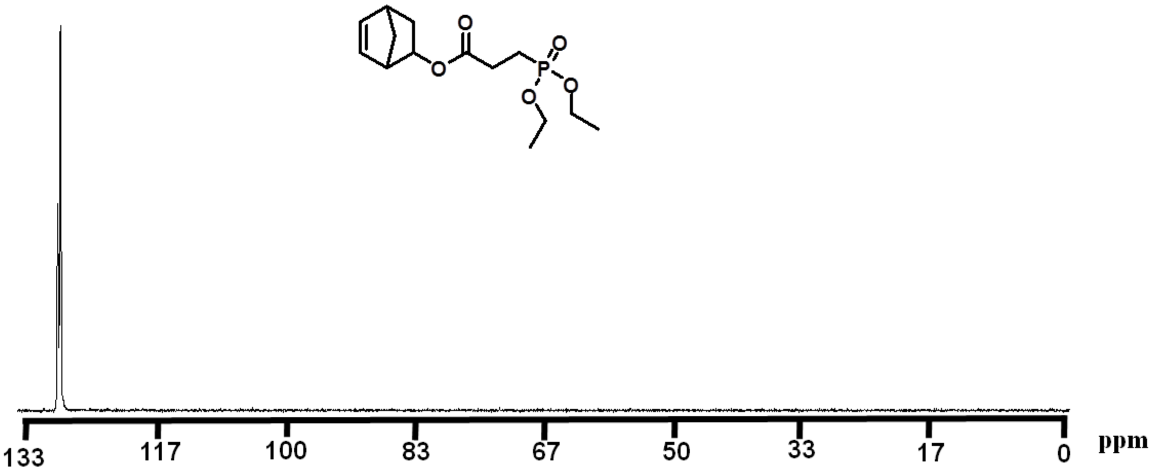


Figure S6. ^{31}**P NMR spectra of norbornene derived phosphonate NDP2.**

Figure S7. ^{31}**P NMR spectra of norbornene derived phosphonate NDP3.**

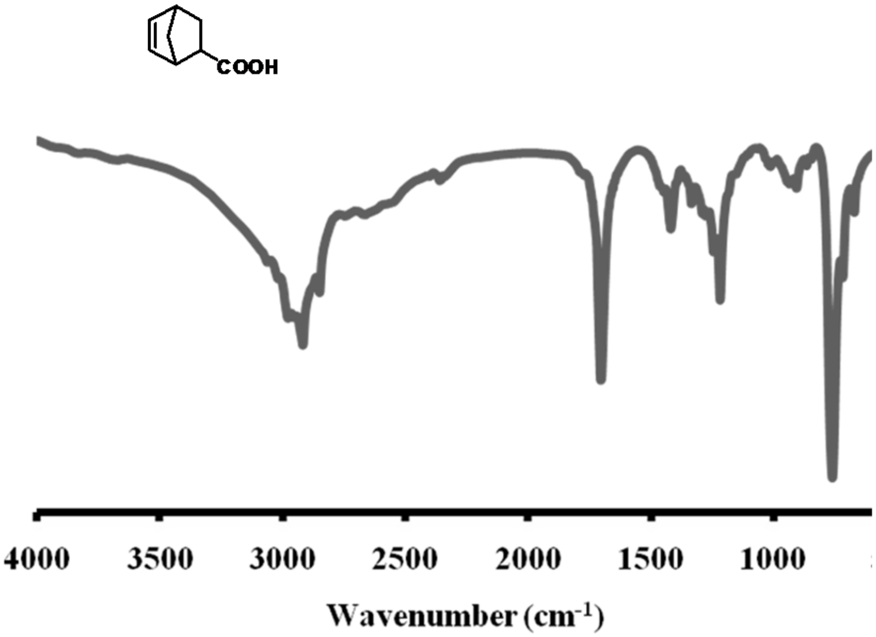


Figure S8. **IR spectra of exo-5-norbornene-2-carboxylic acid.**

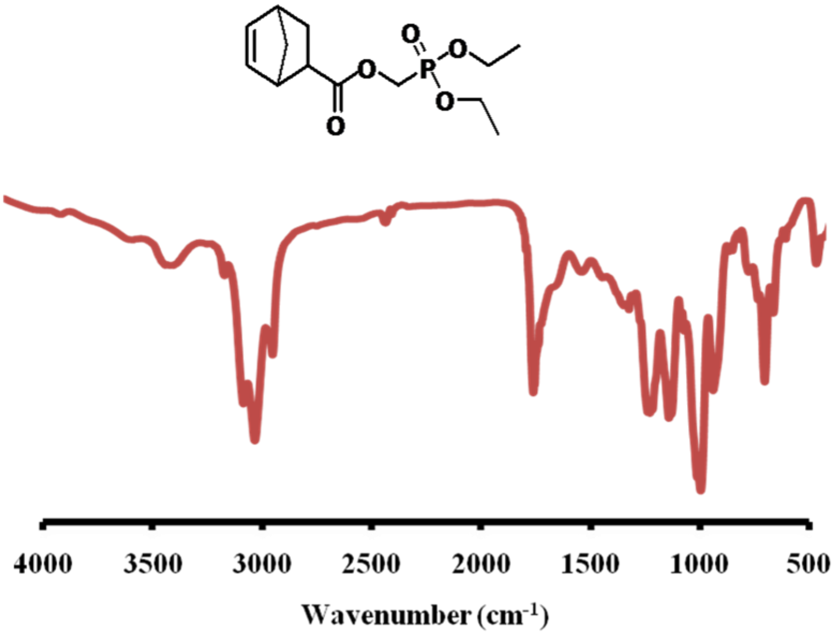


Figure S9. **IR spectra of norbornene derived phosphonate NDP1.**

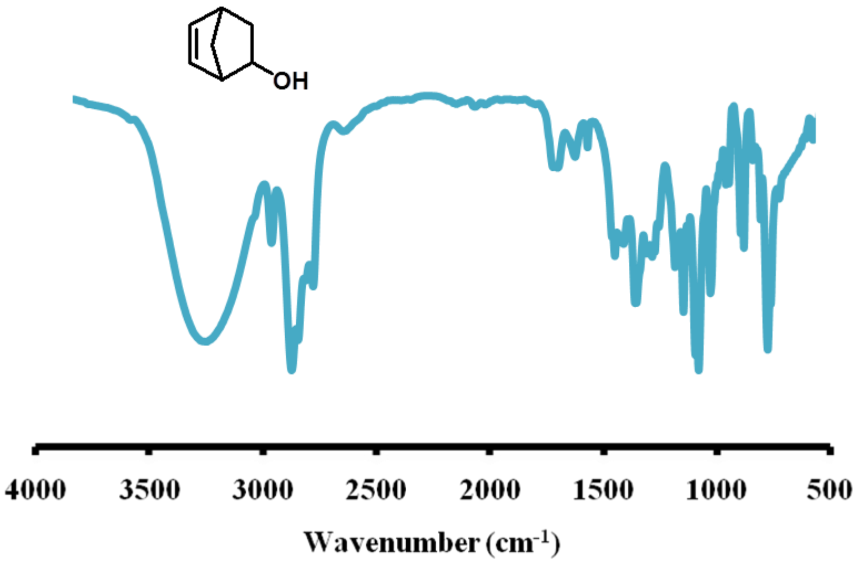


Figure S10. IR spectra of norbornene alcohol (exo-endo mixture).

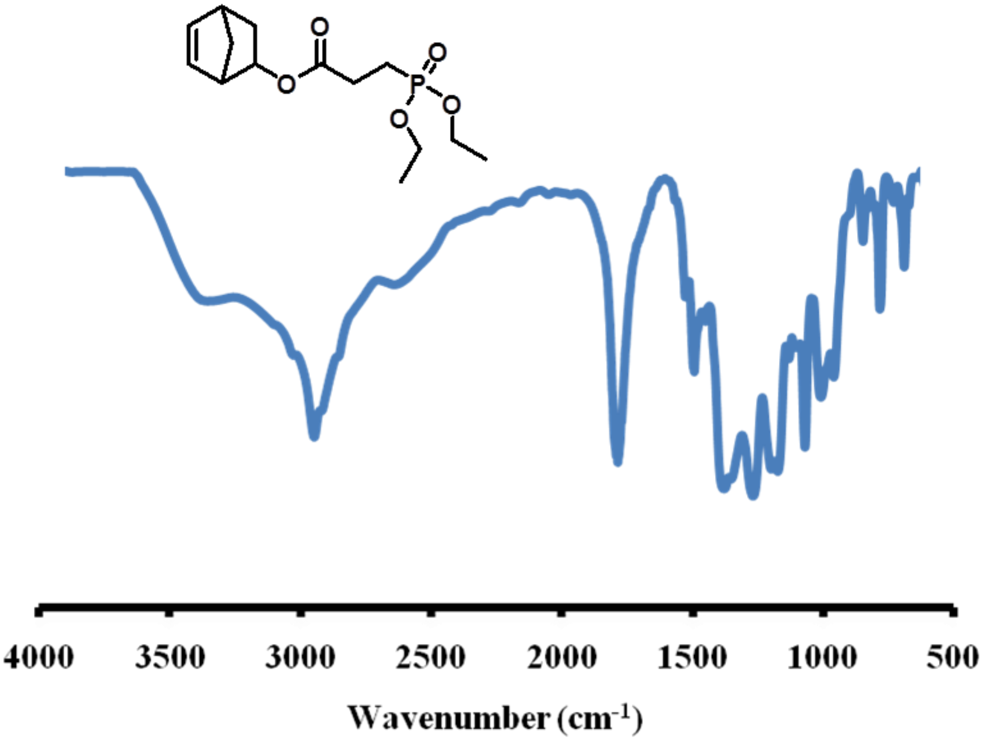


Figure S11. IR spectra of of norbornene derived phosphonate NDP2.

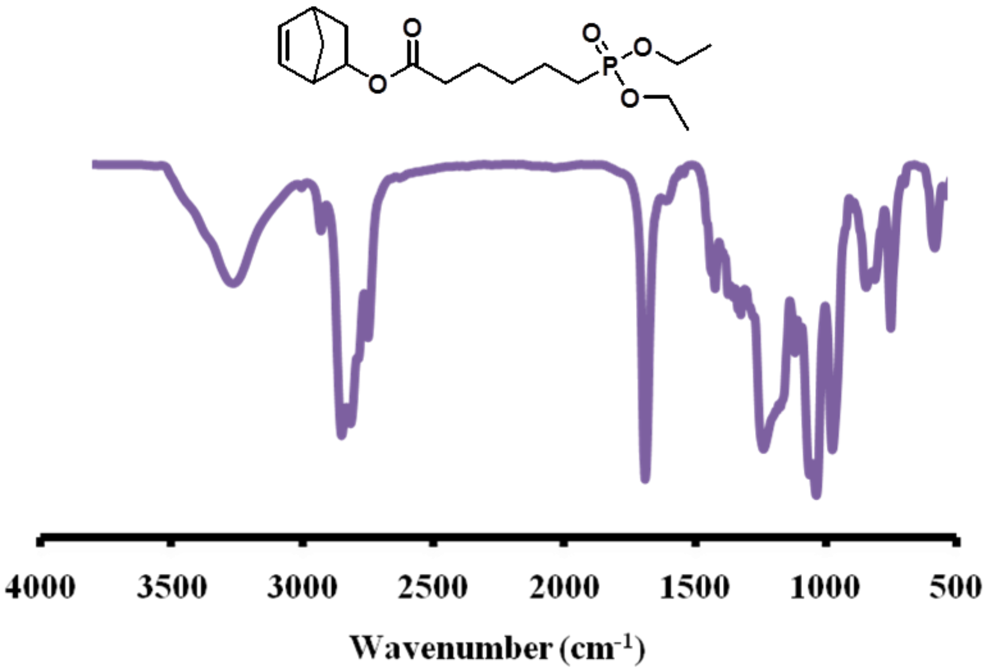


Figure S12. **IR spectra of of norbornene derived phosphonate NDP3.**

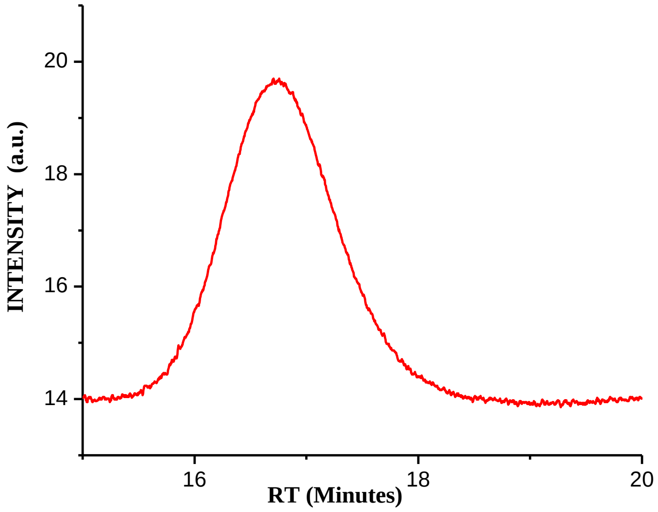


Figure S13. **Gel permeation chromatogram (GPC) of polymer NDPH1. The observed Mn = 18,000 g/mol and PDI = 1.2 suggested the controlled polymerization of NDP1**.

polymer	M/I ratio	M.W.	PDI
NDPH1	20	18000	1.20
NDPH2	20	6000	1.06
NDPH3	20	5800	1.04

Figure S14. Gel permeation chromatogram (GPC) data of homopolymers derived from NDP1, NDP2 & NDP3.

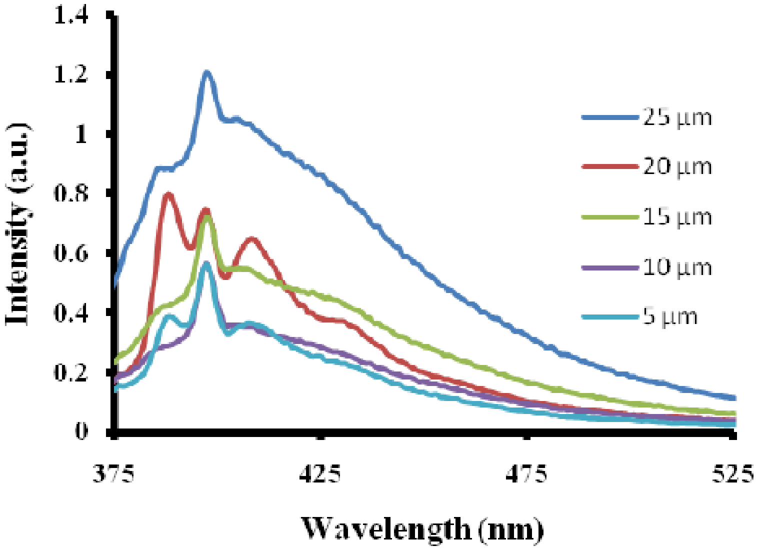


Figure S15. Control experiment to understand the unusual emission. The emission spectra weremeasured with increasing concentration of NDP1 in THF starting from 5 µM to 25 µM. . λex = 350 nm.

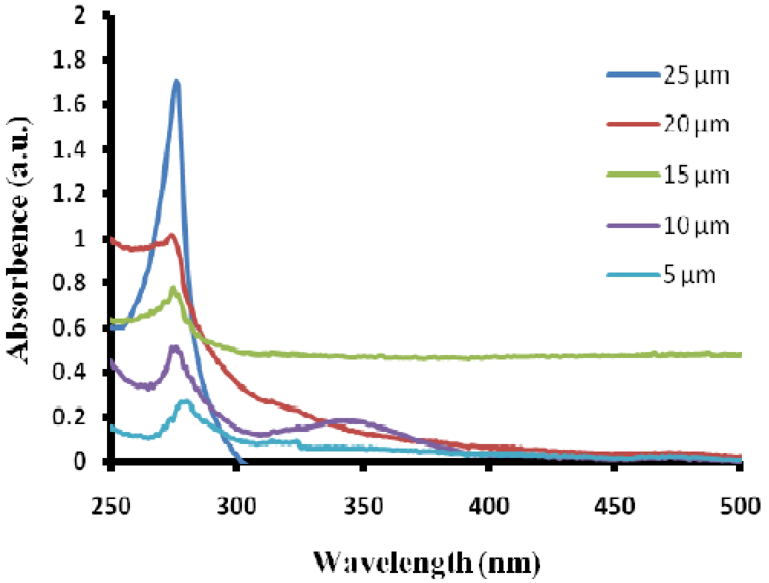


Figure S16. The absorption spectra were measured with increasing concentration of NDP1 in THF starting from 5 µM to 25 µM.

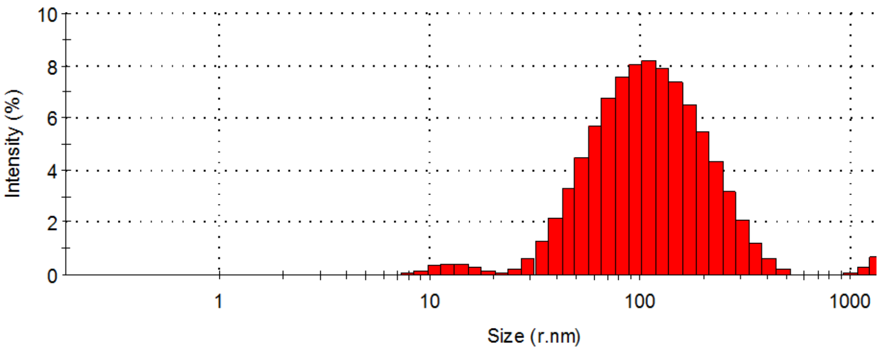


Figure S17. The DLS data of NDP1 in methanol (25 µM).

References:

S1. C. C.Ver Nooy, and C. S. Rondestvedt, *J. Am. Chem. Soc*. **1955**, *77*, 3583-3584.