Supporting Materials

DMAP-catalyzed esterification of pentaerythritol-derivatized POMs: a new route for the functionalization of polyoxometalates

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Reagents and Measurement. All chemicals purchased were used without purification except acetonitrile, which was dried by refluxing in the presence of CaH_2 and distilled prior to use.

The IR spectra of the products were measure at a Perkin Elmer FT-IR spectrophotometer on KBr pellets in the range of 4000-400 cm^{-1} with the resolution of 4 cm^{-1}. ^1H NMR spectra were obtained on a JOEL JNM-ECA300 spectrometer at 298 K. UV/Vis absorption spectra were recorded on a UN-2100s spectrometer at 298K. Elemental analyses were carried out using an Elemental Vario MICRO CUBE (Germany). The electrospray mass spectra (ESI-MS) were recorded using a Bruker APEX IV FTMS, and all experiments were performed in negative-ion mode using MeCN as solvent. Cyclic voltammetry were performed with a CHI750A electrochemical working station (CHI Instruments) in 1,2-dichloroethane , using glass carbon as working electrode, SCE as reference electrode and Bu_4NPF_6 (0.1mol/L) as supporting electrolyte. Single crystal X-ray diffraction were made on a Rigaku RAXIS-SPIDER IP diffractometer at 50 kV and 20 mA and data collection was performed at 293 K by using graphite-monochromated Mo-Kα radiation (λ = 0.71073Å). The raw frame data were processed using Rigaku RAPID AUTO Ver2.30 to yield the reflection data. Subsequent calculations were carried out using SHELXTL-97 program.[1] Structures were solved by direct methods. Refinement was performed by full-matrix least-squares analysis.

Synthesis of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OH\}_2]$ (1). An amount of 25.9g $NaVO_3 \cdot 2H_2O$ was dissolved into 250mL deionized water. 1M hydrochloric acid was added dropwise until reaching pH=3 and then 8g pentaerythritol was added to the solution. The mixture was stirred at 80℃ for 48h and then filtrated.[2] The dark red filtrate was carefully added to a solution of tetrabutylammonium bromide (50g Bu_4NBr dissolved in 100mL water) and orange solid was collected by filtration. The product was washed by 100mL deionized water for three times and then dried for use.

Synthesis of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_3\}_2]$ (2). A mixture of 1.26g(1mmol) compound **1**, 0.20g(2mmol) acetic anhydride, 0.01g DMAP, 0.20g(2mmol) triethylamine and 20mL MeCN was stirred at room temperature for 48h. Then the solution was poured into 50ml deionized water and the red preicipitate was collected by filtration. The crystals of **2** can be obtained by diffusion of Et_2O into their solution in acetonitrile, but none of them is suitable for XRD characterization. Yield 0.84g (62% based on V). Elemental analysis for: $V_6O_{23}N_2C_{46}H_{94}$; calc: C: 40.94%, N: 2.08%, H: 7.03%; found: C: 40.25%, N: 2.09%, H: 6.96%. ^1H NMR (DMSO, 300Hz) δ=0.94 (m, 24H, J=7.2Hz), 1.32 (m, 16H, J=7.2Hz), 1.57 (m, 16H, J=7.9Hz), 1.99 (s, 6H),

3.16 (m, 16H, J=8.2Hz), 3.91 (s, 4H), 4.90 (s, 12H). ESI-MS(in MeCN, negative): 432.05(100%), 864.75, 1105.90 was assigned to $[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_3\}_2]^{2-}$, $H[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_3\}_2]^-$, $(Bu_4N)[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_3\}_2]^-$, respectively. FT-TR [(KBr) ν/cm^{-1}]: 2959(m), 2873(m), 1744(s), 1630(w), 1481(m), 1383(w), 1236(w), 1129(m), 1069(s), 1040(s), 951(vs), 807(s), 719(s), 583(m). UV/Vis (in MeCN): λ_{max}=352nm, 246nm.

Synthesis of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_2CH_3\}_2]$ (3). The synthesis of **3** is similar to that of **2**, except the use of propionic andydride instead of acetic anhydride. The red block crystals of **3** can be obtained by diffusion of Et_2O into their solution in acetonitrile. Yield 1.05g (76% based on V). Elemental analysis for: $V_6O_{23}N_2C_{48}H_{98}$; calc: C: 41.85%, N: 2.03%, H: 7.18%; found: C: 41.18%, N: 2.42%, H: 7.05%. ^{1}H NMR (DMSO, 300Hz) δ=0.94 (t, 24H, J=7.2Hz), 0.99(t, 6H, J=7.5Hz), 1.32 (m, 16H, J=7.2Hz), 1.57 (m, 16H), 2.30 (m, 4H, J=7.5Hz), 3.17 (m, 16H, J=7.9Hz), 3.93 (s, 4H), 4.94 (s, 12H). ESI-MS(in MeCN, negative): 446.09, 892.71, 1133.83(100%) was assigned to $[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_2CH_3\}_2]^{2-}$, $H[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_2CH_3\}_2]^-$, $(Bu_4N)[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_2CH_3\}_2]^-$, respectively.FT-TR [(KBr) ν/cm^{-1}]: 2960(m), 2873(m), 1735(s), 1636(w), 1481(m), 1382(w), 1238(w), 1126(m), 1064(s), 951(vs), 808(s), 718(s), 583(m). UV/Vis (in MeCN): λ_{max}=352nm, 242nm.

Synthesis of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_4CH_3\}_2]$ (4). The synthesis of **4** is similar to that of **2**, except the use of hexonic andydride instead of acetic anhydride. The red block crystals of **3** can be obtained by diffusion of Et_2O into their solution in acetonitrile. Yield 0.83g (58% based on V). Elemental analysis for: $V_6O_{23}N_2C_{54}H_{110}$; calc: C: 44.37%, N: 1.92%, H: 7.59%; found: C: 43.94%, N: 2.17%, H: 7.54%. ^{1}H NMR ($CDCl_3$, 300Hz) δ=0.86 (t, 6H, J=6.7Hz), 0.99 (t, 24H), 1.25 (m, 12H), 1.53 (m, 16H), 1.74 (m, 16H), 2.26 (t, 4H, J=7.2Hz), 3.47 (m, 16H), 3.99 (s, 4H), 5.22 (s, 12H). ESI-MS(in MeCN, negative): 488.16(100%), 976.77, 1217.91 was assigned to $[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_4CH_3\}_2]^{2-}$, $H[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_4CH_3\}_2]^-$, $(Bu_4N)[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_4CH_3\}_2]^-$, respectively. FT-TR [(KBr) ν/cm^{-1}]: 2958(m), 2872(m), 1731(s), 1636(w), 1469(m), 1384(w), 1242(w), 1134(m), 1062(s), 951(vs), 808(s), 720(s), 584(m). UV/Vis (in MeCN): λ_{max}=352nm, 243nm.

Synthesis of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_{16}CH_3\}_2]$ (5). A mixture of 1.26g(1mmol) compound **1**, 1.10g(2mmol) stearic anhydride, 0.25g(2mmol) DMAP and 20mL MeCN was stirred at 80℃ for 48h. The mixture was cooled down to room temperature and then filtrated. The red, platelet-like crystals of 5 come out from the filtrate within two days. Yield 0.66g (37% based on V). Elemental analysis for: $V_6O_{23}N_2C_{78}H_{158}$; calc: C: 52.09%, N: 1.56%, H: 8.86%; found: C: 52.14%, N: 1.63%, H: 8.80%. ^{1}H NMR ($CDCl_3$, 300Hz) δ=0.88 (t, 6H, J=6.7Hz), 0.99 (m, 24H, J=7.2Hz), 1.25 (m, 52H), 1.53 (m, 16H, J=7.2Hz), 1.75 (m, 16H), 2.26 (t, 4H, J=7.5Hz), 3.47 (m, 16H, J=8.0Hz), 3.98 (s, 4H), 5.21 (s, 12H). ESI-MS(in MeCN, negative): 656.35, 1313.03, 1554.26(100%) was assigned to $[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_{16}CH_3\}_2]^{2-}$, $H[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_{16}CH_3\}_2]^-$, $(Bu_4N)[V_6O_{13}\{(OCH_2)_3CCH_2OOC(CH_2)_{16}CH_3\}_2]^-$,

respectively. FT-TR [(KBr) ν/cm^{-1}]: 2921(m), 2851(m), 1752(s), 1638(w), 1469(m), 1384(w), 1159(m), 1132(m), 1062(s), 961(s), 942(vs), 812(s), 719(s), 581(m). UV/Vis (in MeCN): λ_{max}=350nm, 245nm.

References

1. G. M. Sheldrick, Shelxs-97, Program for X-Ray Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997; G. M. Sheldrick, Shelxs-97, Program for X-Ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
2. A. Müller, J. Meyer, H. Bögge, A. Stammler and A. Botar, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1818.

Table S1. Details of Crystal Data and Structure Refinement for Compound 3

Empirical formula	**C48 H98 N2 O23 V6**
Formula weight	**1376.92**
Temperature	**293(2) K**
Wavelength	**0.71073 A**
Crystal system	**Monoclinic**
Space group	**P2(1)/c**
Unit cell dimensions	**a = 11.135(2) A alpha = 90 deg.**
	b = 14.900(3) A beta = 97.63(3) deg.
	c = 19.855(4) A gamma = 90 deg.
Volume	**3265.1(11) A^3**
Z	**2**
Calculated density	**1.401 Mg/m^3**
Absorption coefficient	**0.894 mm^{-1}**
F(000)	**1444**
Crystal size	**0.5 x 0.3 x 0.2 mm**
Theta range for data collection	**3.25 to 27.48 deg.**
Limiting indices	**-14<=h<=14, -19<=k<=19, -25<=l<=25**
Reflections collected / unique	**31068 / 7439 [R(int) = 0.0647]**
Completeness to theta = 27.48	**99.3 %**
Absorption correction	**Semi-empirical from equivalents**
Max. and min. transmission	**0.836 and 0.732**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**7439 / 23 / 359**
Goodness-of-fit on F^2	**1.135**
Final R indices [I>2sigma(I)]	**R1 = 0.0576, wR2 = 0.1409**
R indices (all data)	**R1 = 0.1157, wR2 = 0.1995**
Extinction coefficient	**0.0079(11)**

Largest diff. peak and hole	**0.580 and -0.738 e.A^{-3}**

Table S2. Details of Crystal Data and Structure Refinement for Compound 4

Empirical formula	**C54 H110 N2 O23 V6**
Formula weight	**1461.08**
Temperature	**293(2) K**
Wavelength	**0.71073 A**
Crystal system	**Monoclinic**
Space group	**P2(1)/c**
Unit cell dimensions	**a = 11.375(2) A alpha = 90 deg.**
	b = 15.453(3) A beta = 97.54(3) deg.
	c = 19.841(4) A gamma = 90 deg.
Volume	**3457.3(12) A^3**
Z	**2**
Calculated density	**1.404 Mg/m^3**
Absorption coefficient	**0.849 mm^{-1}**
F(000)	**1540**
Crystal size	**0.4 x 0.3 x 0.2 mm**
Theta range for data collection	**3.20 to 27.45 deg.**
Limiting indices	**-13<=h<=14, -20<=k<=20, -25<=l<=23**
Reflections collected / unique	**32952 / 7866 [R(int) = 0.0259]**
Completeness to theta = 27.45	**99.5 %**
Absorption correction	**Semi-empirical from equivalents**
Max. and min. transmission	**0.844 and 0.744**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**7866 / 103 / 404**
Goodness-of-fit on F^2	**1.050**
Final R indices [I>2sigma(I)]	**R1 = 0.0413, wR2 = 0.1188**
R indices (all data)	**R1 = 0.0522, wR2 = 0.1281**
Largest diff. peak and hole	**0.398 and -0.460 e.A^{-3}**

Table S3. Details of Crystal Data and Structure Refinement for Compound 5

Empirical formula	**C78 H158 N2 O23 V6**
Formula weight	**1797.70**
Temperature	**293(2) K**
Wavelength	**0.71073 A**
Crystal system	**Triclinic**
Space group	**P-1**
Unit cell dimensions	**a = 11.528(2) A alpha = 94.67(3) deg.**
	b = 12.074(2) A beta = 99.95(3) deg.
	c = 19.371(4) A gamma = 115.39(3) deg.
Volume	**2362.1(8) A^3**
Z	**1**
Calculated density	**1.264 Mg/m^3**
Absorption coefficient	**0.634 mm^{-1}**
F(000)	**962**
Crystal size	**0.3 x 0.3 x 0.1 mm**
Theta range for data collection	**3.08 to 27.48 deg.**
Limiting indices	**-14<=h<=14, -15<=k<=15, -25<=l<=25**
Reflections collected / unique	**23324 / 10660 [R(int) = 0.1004]**
Completeness to theta = 27.48	**98.3 %**
Absorption correction	**Semi-empirical from equivalents**
Max. and min. transmission	**0.939 and 0.827**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**10660 / 32 / 493**
Goodness-of-fit on F^2	**1.002**
Final R indices [I>2sigma(I)]	**R1 = 0.0709, wR2 = 0.0917**
R indices (all data)	**R1 = 0.2273, wR2 = 0.1345**
Largest diff. peak and hole	**0.499 and -0.540 $e.A^{-3}$**

Table S4. Summary of BVS for the vanadium atoms in compound 3, 4 and 5

3		4		5	
V1	5.036	V1	5.003	V1	5.000
V2	5.056	V2	5.025	V2	5.002
V3	5.049	V3	5.034	V3	5.014

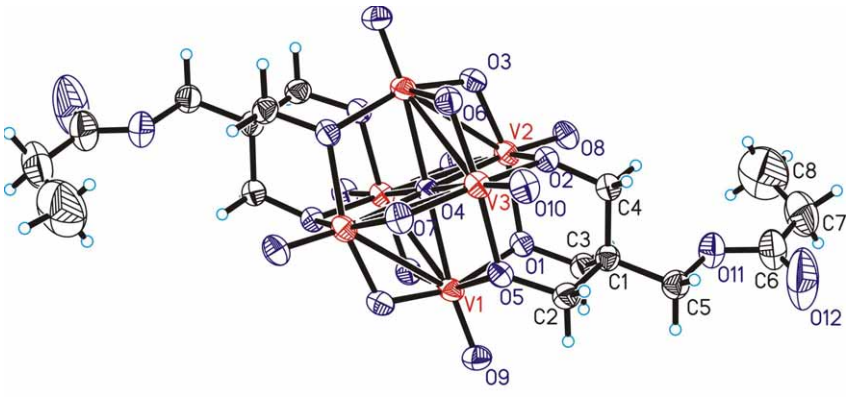

Fig. S1 Anion Structure of Compound **3**

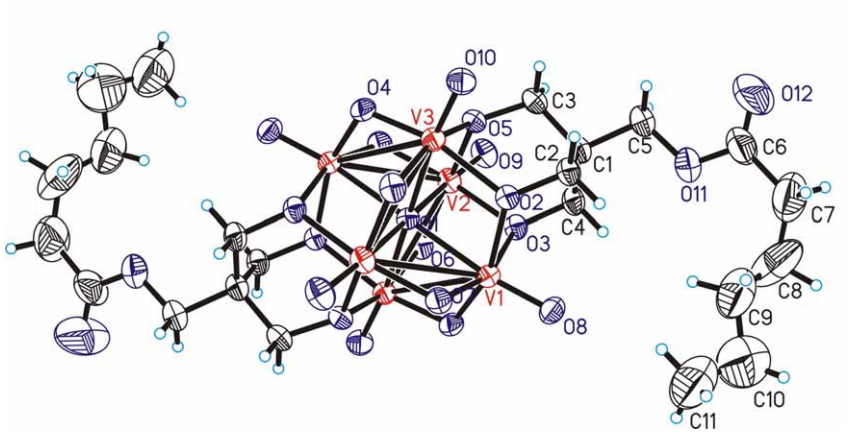

Fig. S2 Anion Structure of Compound **4**

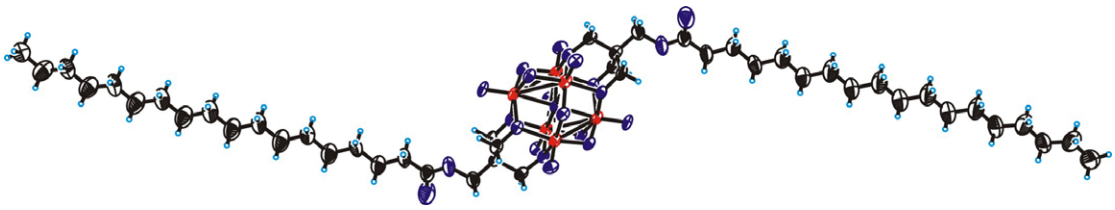

Fig. S3 Anion Structure of Compound **5**

IR Spectra of Compound 2~5

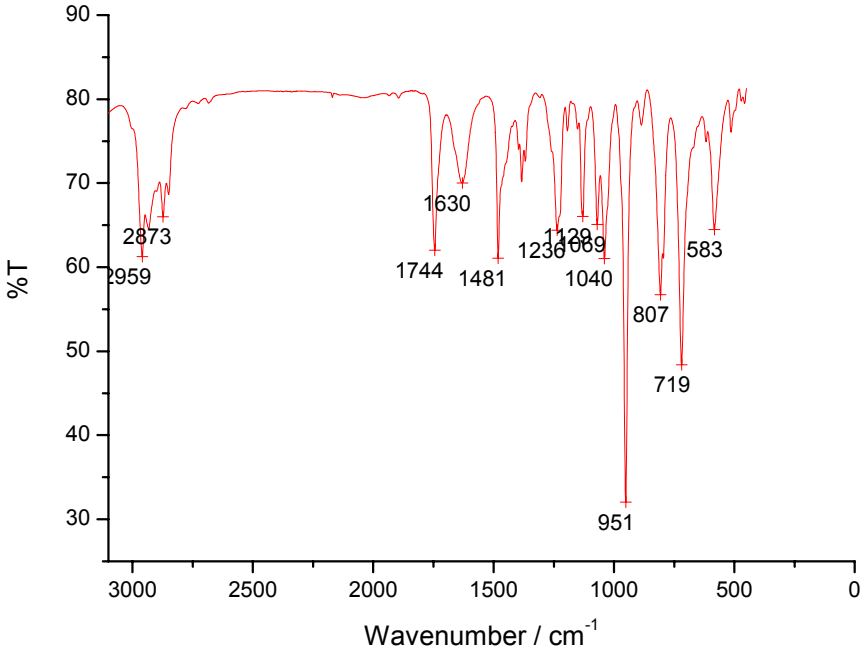

Fig. S4 IR spectrum of compound **2**

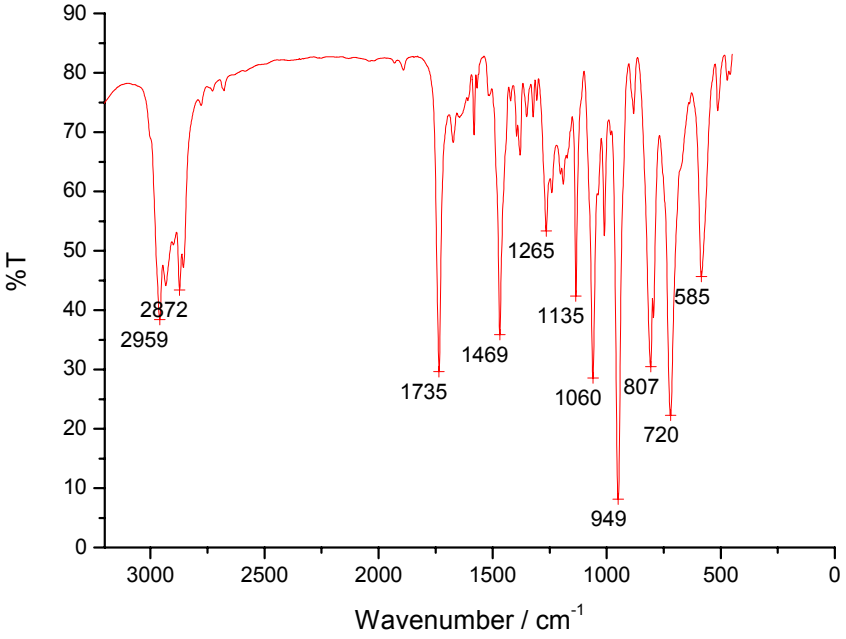

Fig. S5 IR spectrum of compound **3**

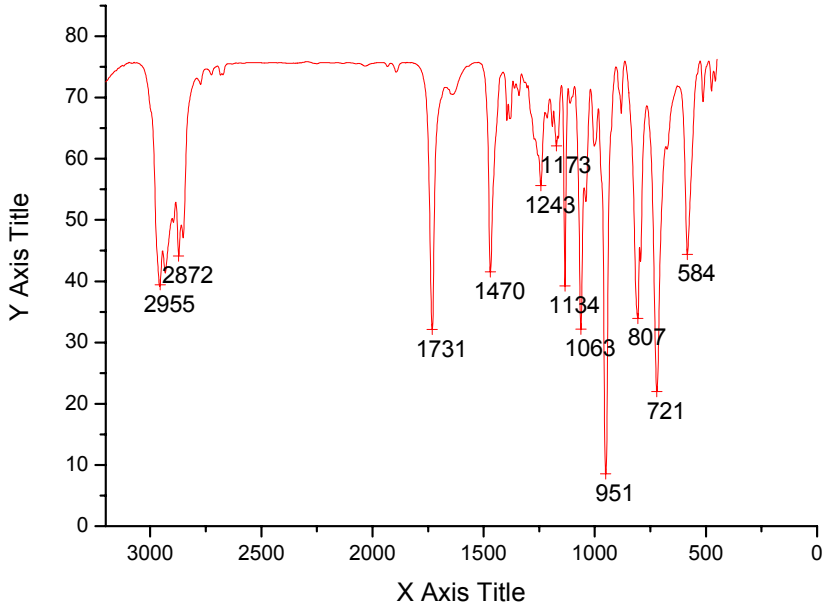

Fig. S6 IR spectrum of compound **4**

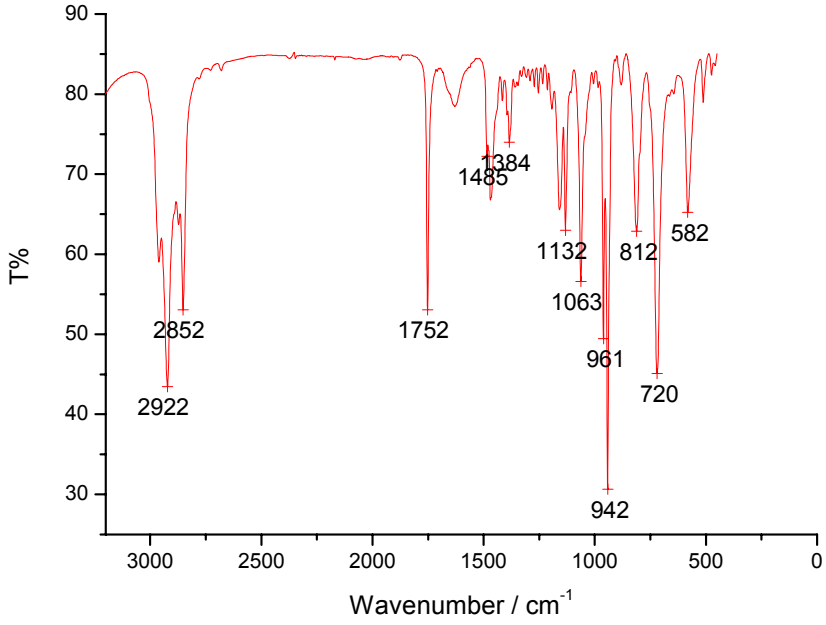

Fig. S7 IR spectrum of compound **5**

^{1}H NMR Spectra of Compound 2~5

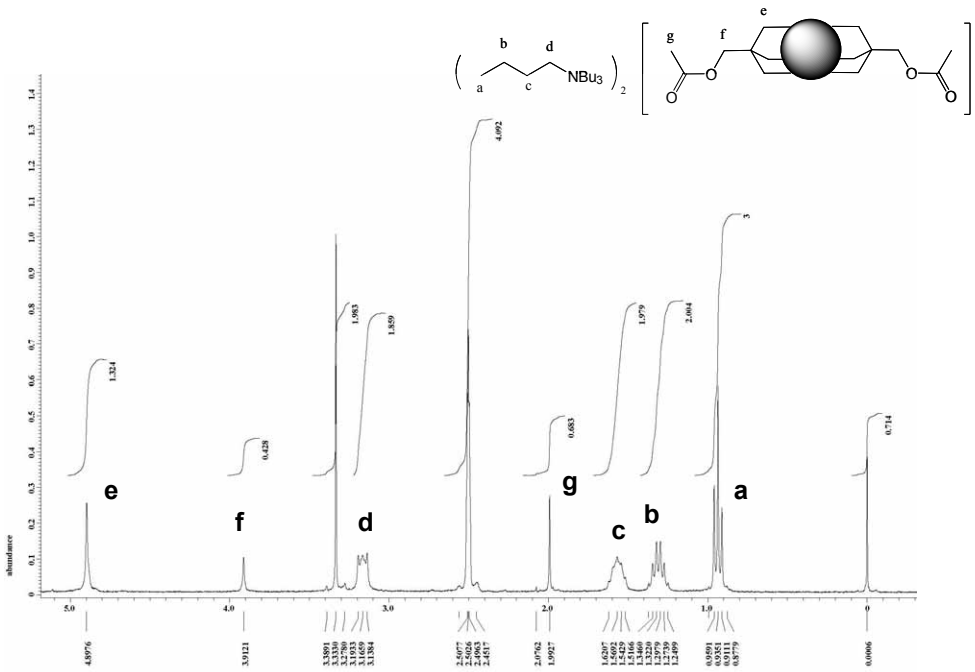

Fig. S8 ^{1}H NMR Spectrum of Compound **2**

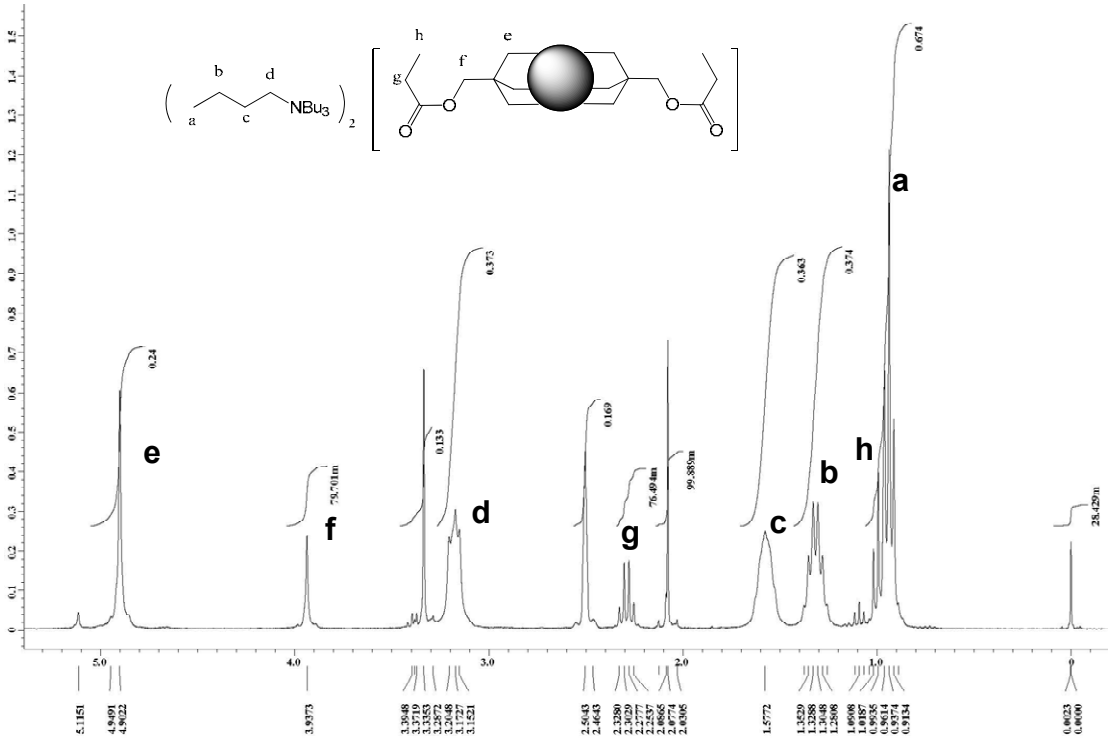

Fig. S9 ^{1}H NMR Spectrum of Compound **3**

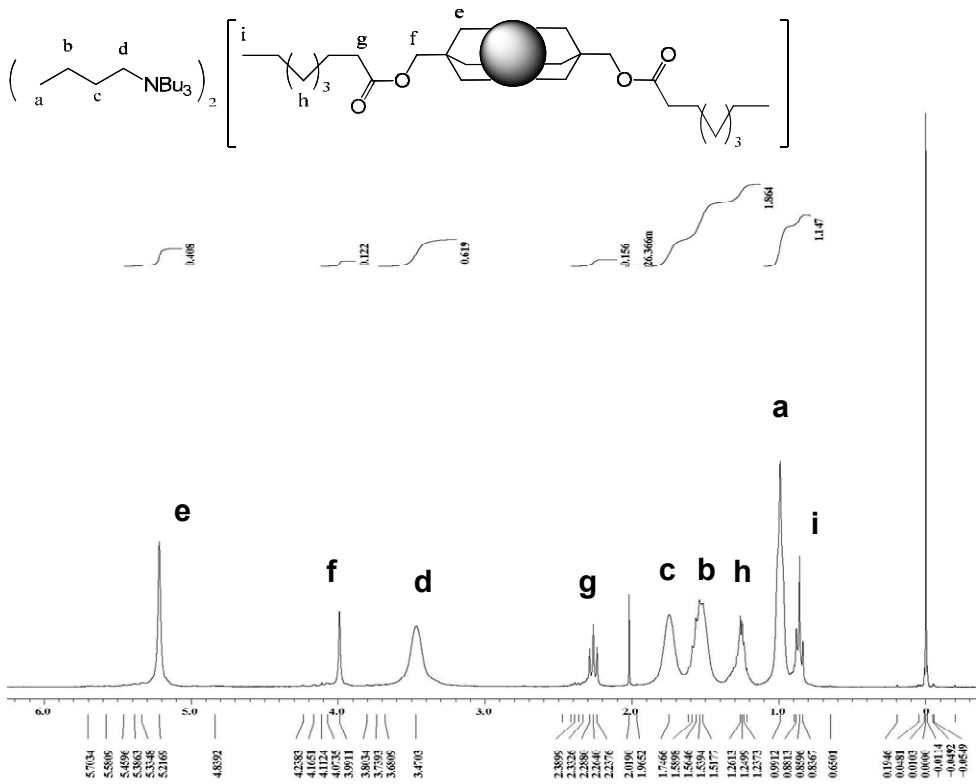

Fig. S10 ^{1}H NMR Spectrum of Compound **4**

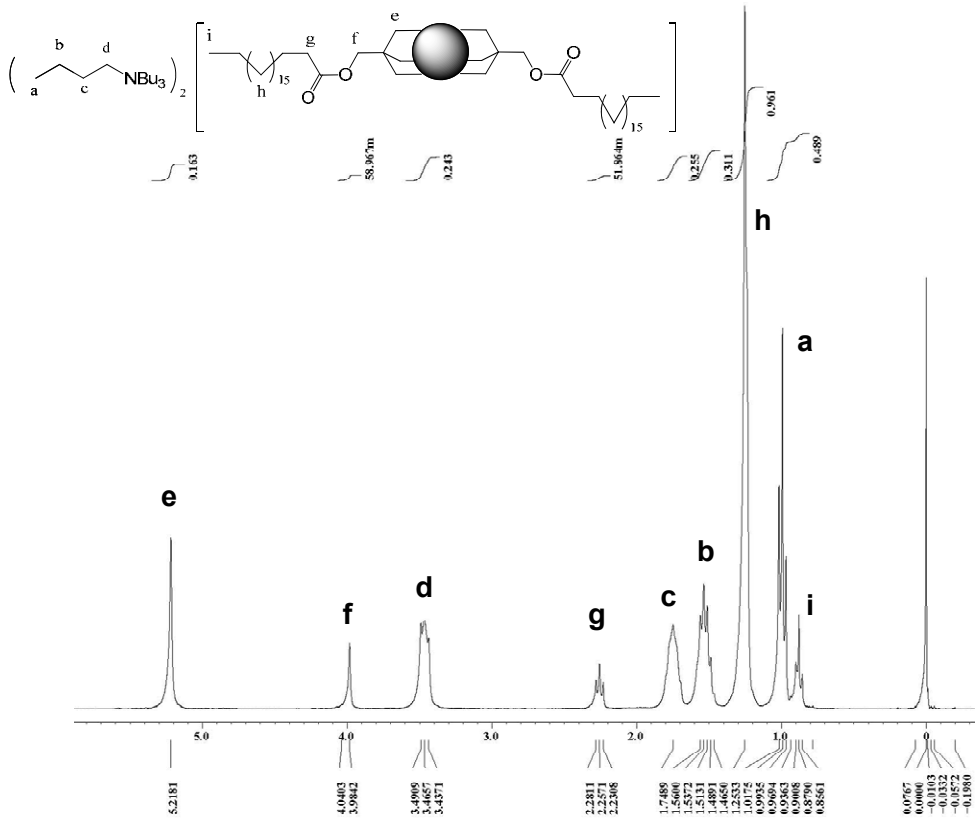

Fig. S11 ^{1}H NMR Spectrum of Compound **5**

Electrospray Mass Spectra of Compound 2~5

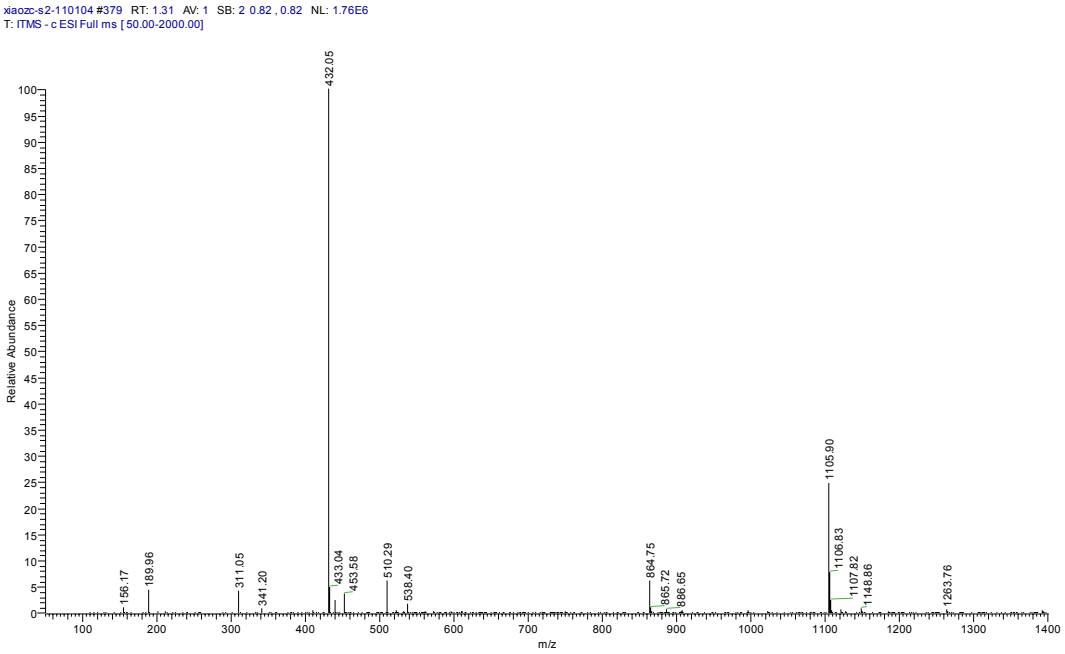

Fig. S12 ESI-MS of compound **2**

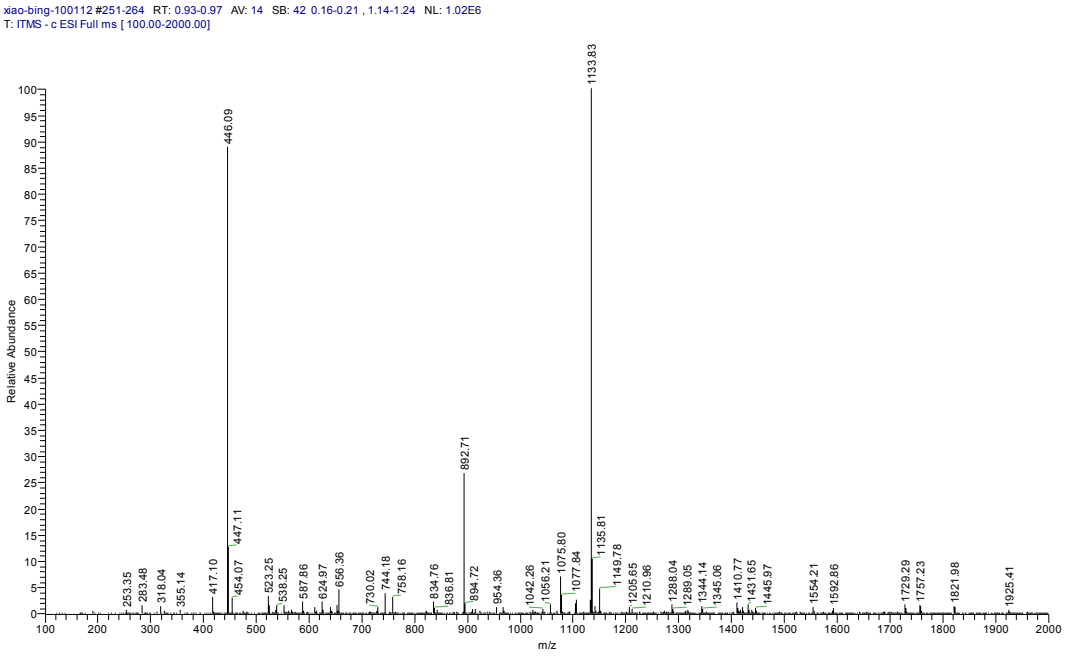

Fig. S13 ESI-MS of compound **3**

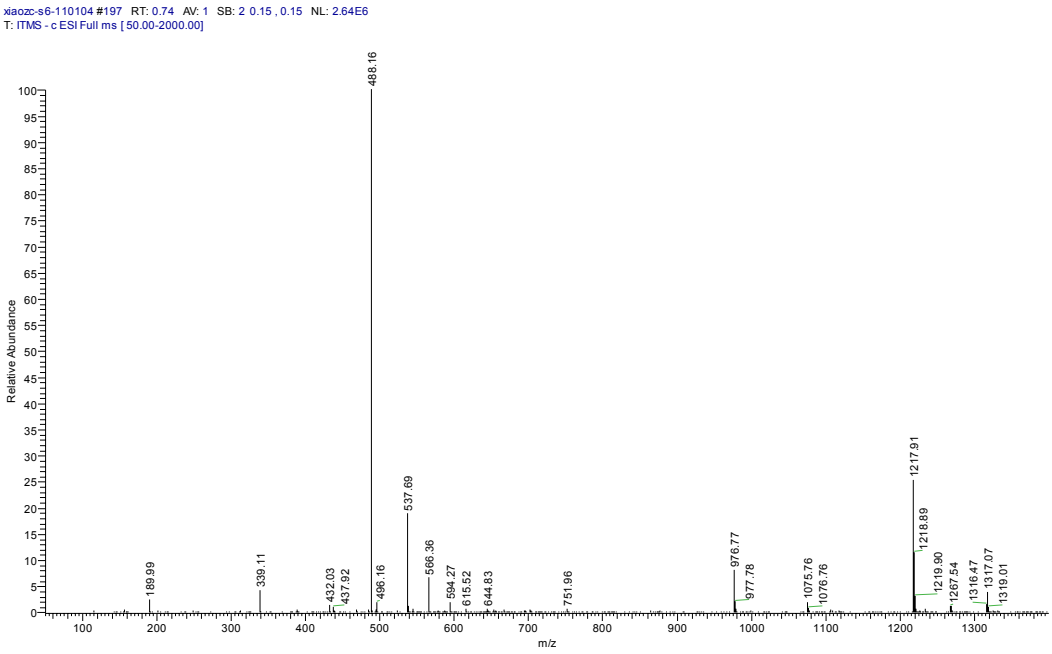

Fig. S14 ESI-MS of compound **4**

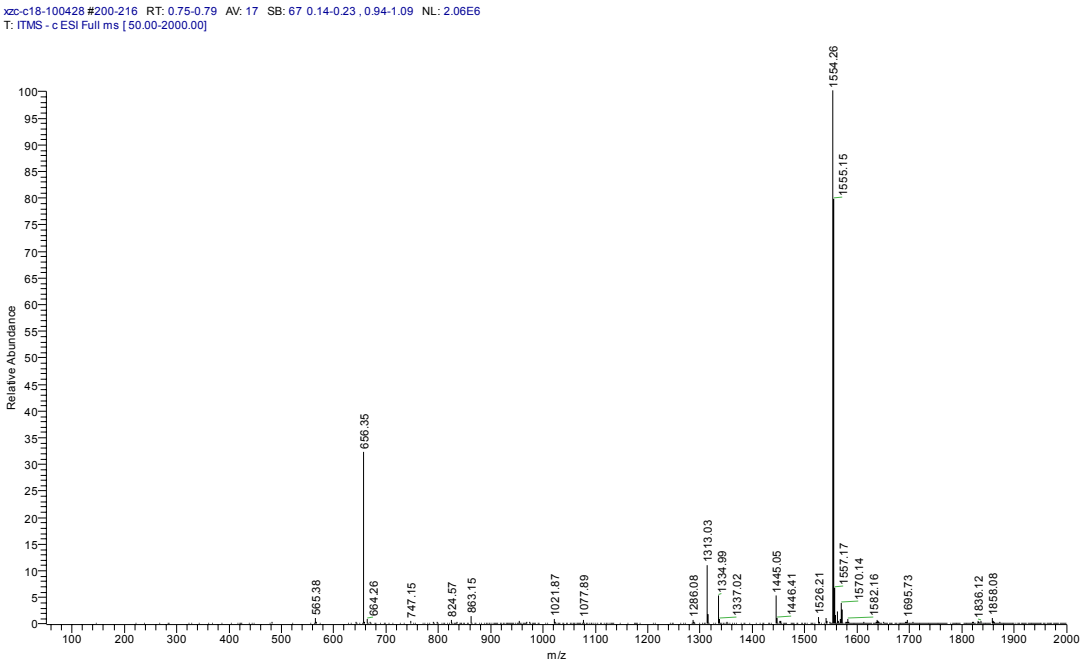

Fig. S15 ESI-MS of compound **5**

Clyclic Voltammetry Studies

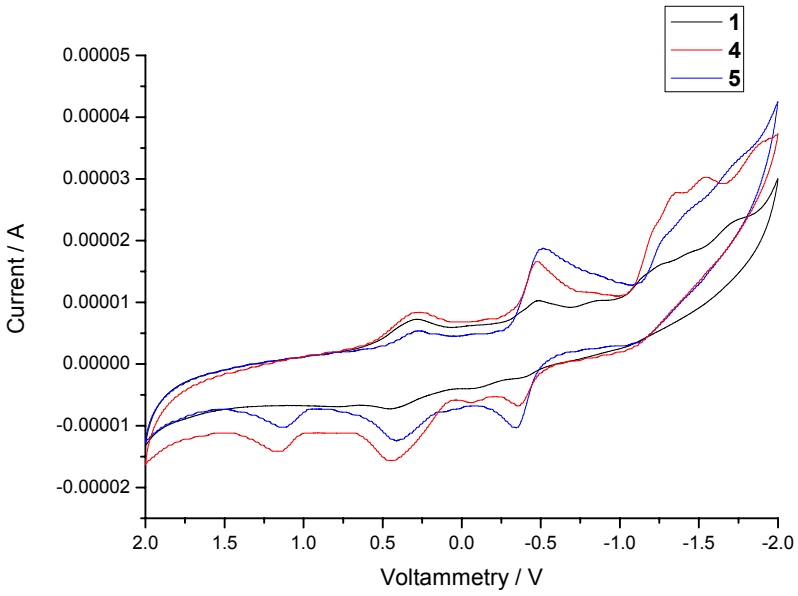

Fig. S16 Cyclic Voltammetry of Compound **1**, **4** and **5**

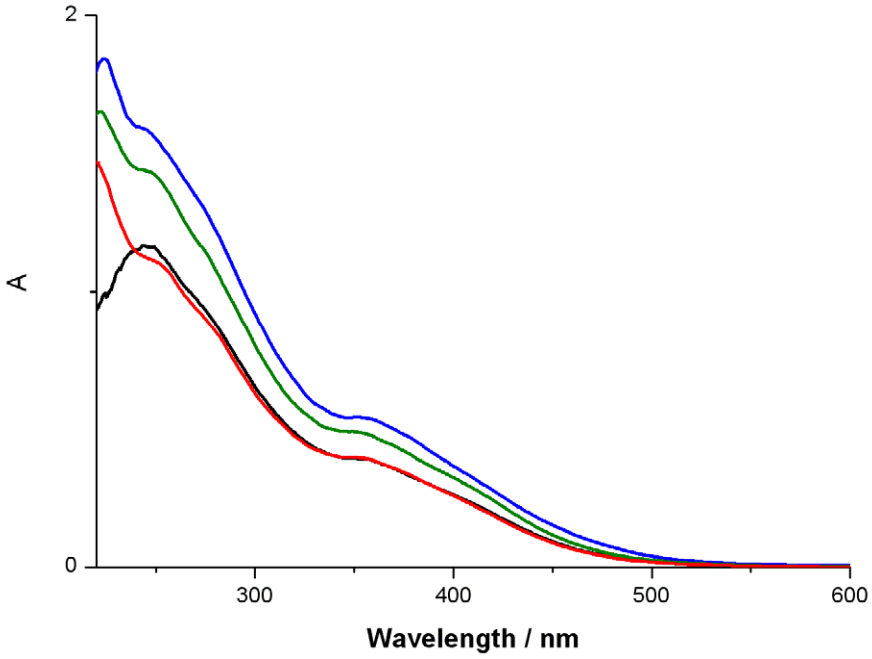

Fig. S17 UV spectra of compound **2** (blue), **3** (red), **4** (green) and **5** (black).