Supporting materials

Diversified polyoxovanadate derivatives obtained by copper(I)-catalysed azide–alkyne cycloaddition reaction: Their synthesis and structural characterization

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1. Experimental details

Synthesis of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2N_3\}_2]$, compound 1: Compound **1** was prepared by heating a mixture of $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2SO_3C_7H_4\}_2]\cdot 2.5CH_3CN$ (0.314 g, 0.2 mmol) and NaN_3 (0.104 g, 1.6 mmol) in 10 mL of dry DMF at 80 °C for 2 days. The reaction was monitored by IR spectroscopy and ESI-MS. After the reaction was completed, the mixture solution was cooled down to room temperature, and then, the solvent was completely evaporated out. A minimal amount of CH_3CN was added to the remaining solid to dissolve all the POM materials, and subsequently, the suspension was centrifuged. The precipitates containing excess NaN_3 and the formed NaOTs were discarded. Suitable orange-red block single crystals for X-ray diffraction were grown by slow diffusion of diethyl ether into their acetonitrile solution. Compound 1 was easily crystallized in the mother liquor conveniently by addition of a small amount of acetonitrile and water. The yield was 68% based on V. Calcd: V 23. 25, C 38.38, H 6.75, N 8.52, Found: V 22.97, C 38.33, H 6.72, N 8.48. IR(cm^{-1}): 3361 w, 2921 m, 2851 m, 1659 w, 1633 m, 1470 m, 1363 w, 1176 m, 1130 w, 1065 m, 952 vs, 804 s, 790 s, 717 s. ^1H NMR (400 MHz, DMSO–d_6, standardized by solvent peak): δ = 0.90 (24H, t, J = 7.2 Hz, TBA–H), 1.28 (16H, sextet, TBA–H), 1.53 (16H, quintet, TBA–H), 3.13 (16H, t, J = 8.4 Hz, TBA–H), 3.69 (s, 4H, N_3–CH_2–C), 4.83 (s, 12H, O–CH_2–C). ^{13}C NMR (400MHz, DMSO–d_6, standardized by solvent peak): δ = 83.62, 58.14, 52.43, 49.57, 23.73, 19.76, 14.06. ESI-MS: m/z (%): 1330.00 (10.71%) $\{(Bu_4N)[V_6O_{13}\{(OCH_2)_3CCH_2N_3\}_2]\}^-$, 414.85 (98.89%) $[V_6O_{13}\{(OCH_2)_3CCH_2N_3\}_2]^{2-}$.

2. Additional Structural Figures

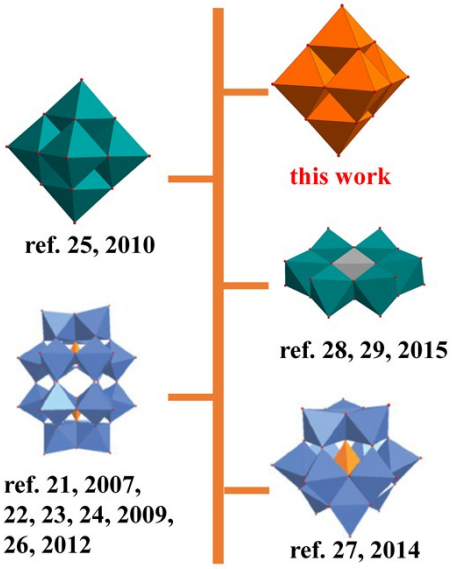

Fig.S1. The POMs archetype of hybrids prepared by click chemistry. Color code: light blue: W, teal: Mo, orange: V.

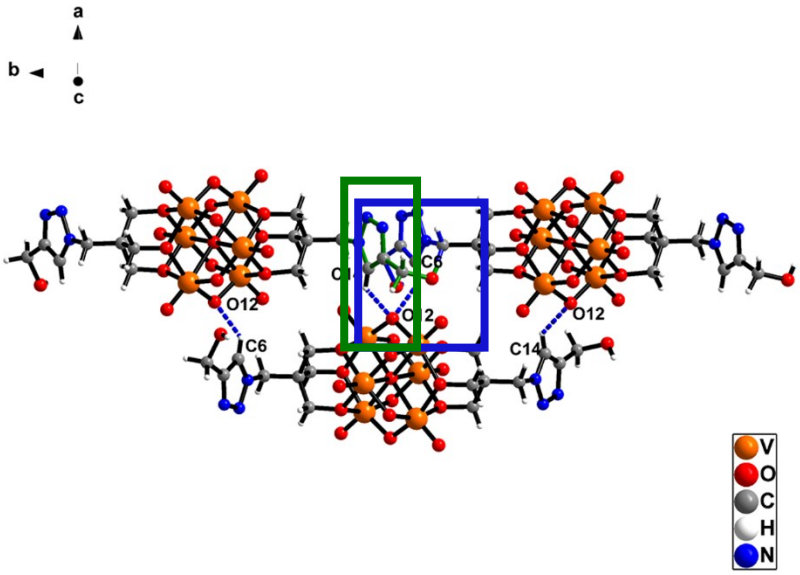

Fig.S2 The hydrogen bonds in compound **2**.

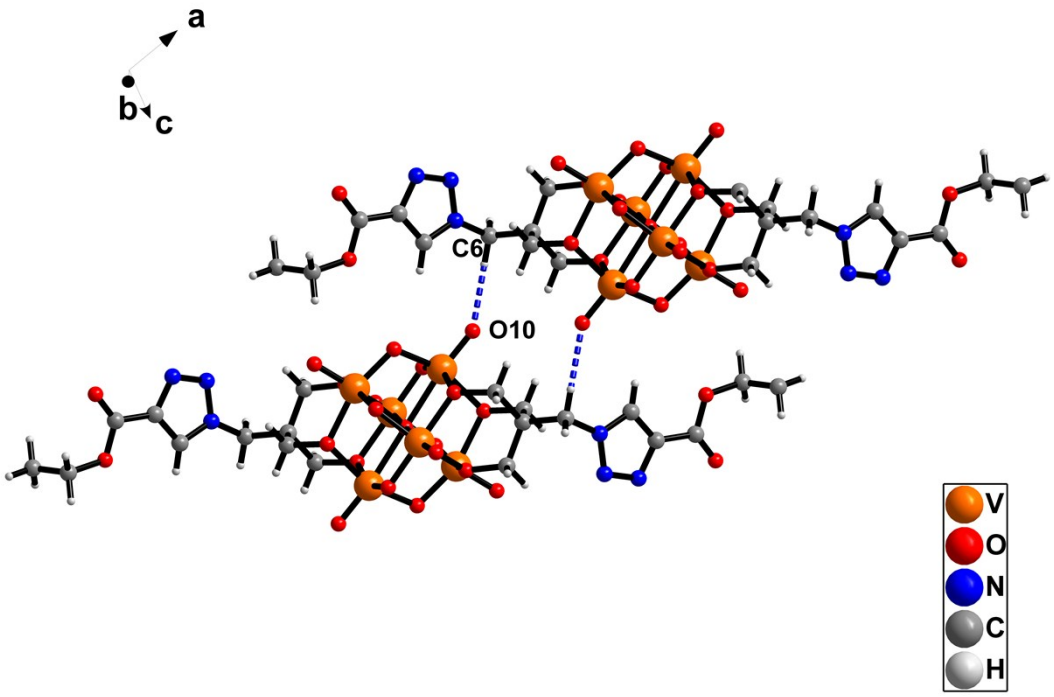

Fig. S3 The hydrogen bonds in compound **3**.

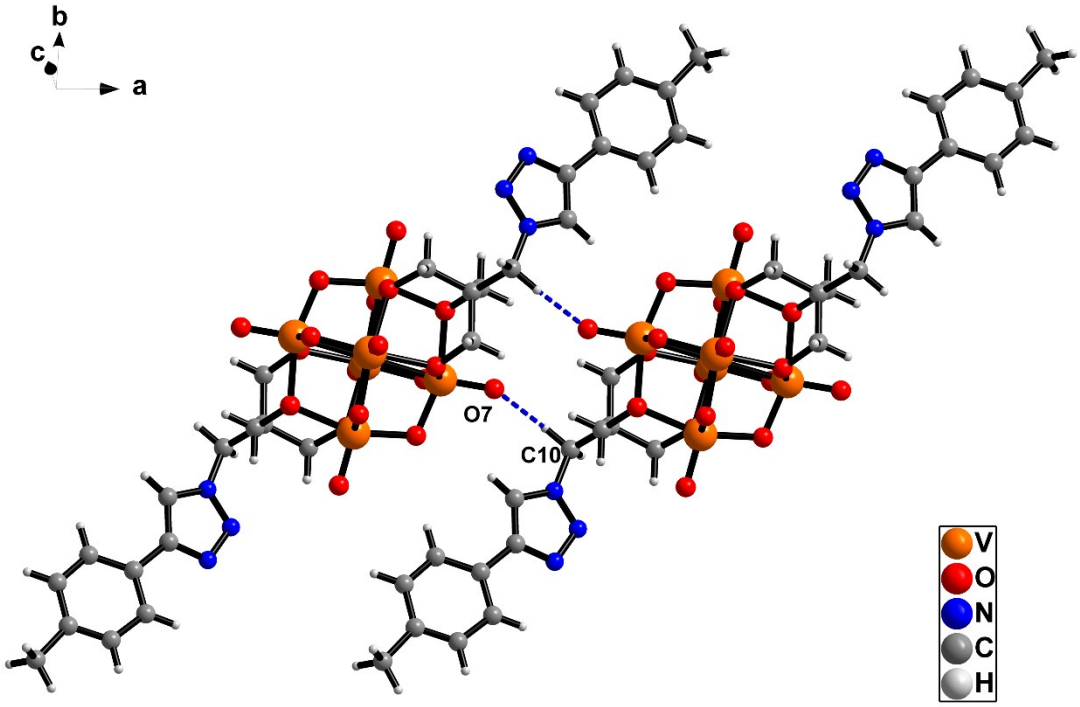

Fig. S4 The hydrogen bonds in compound **4**.

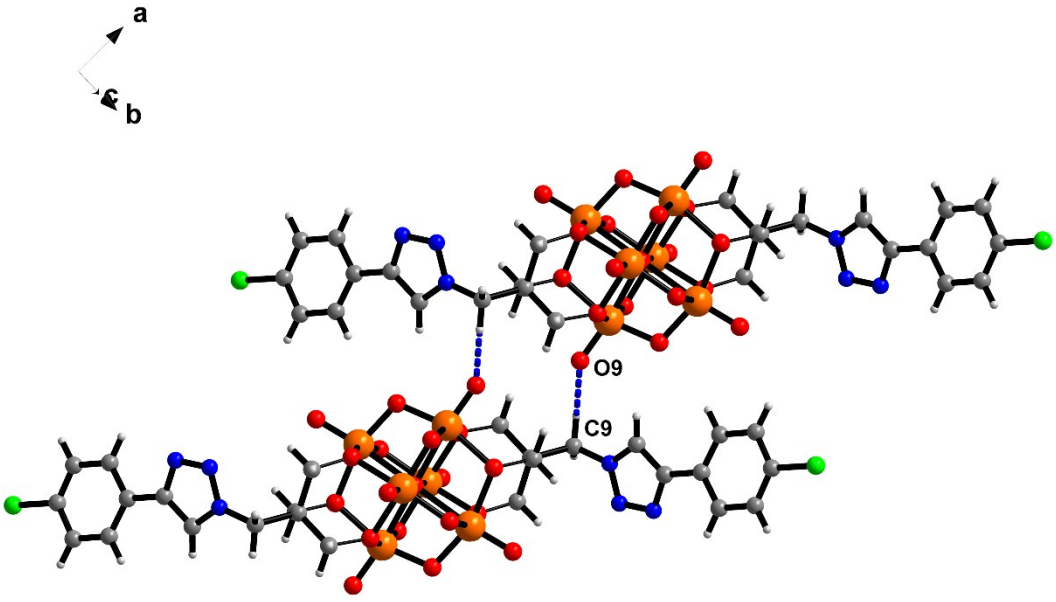

Fig. S5 The hydrogen bonds in compound **5**.

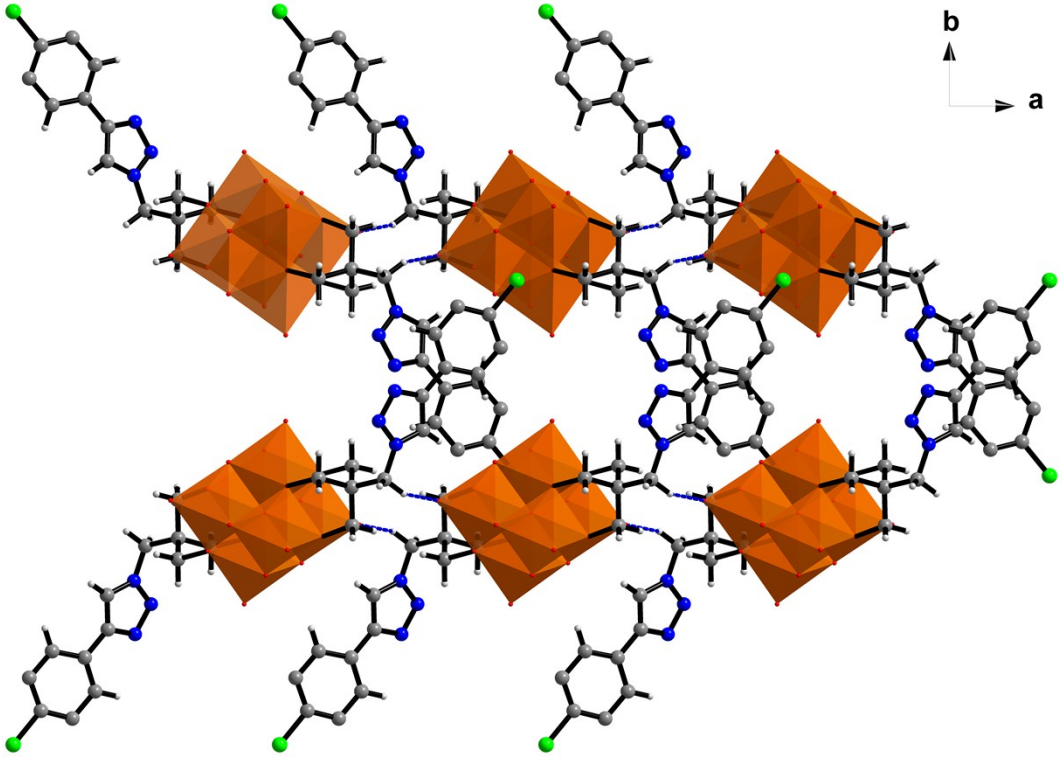

Fig. S6 The 1D chain formed through C–H···O hydrogen bonds in compound **5**.

3. Additional Measurements

3.1 IR spectra

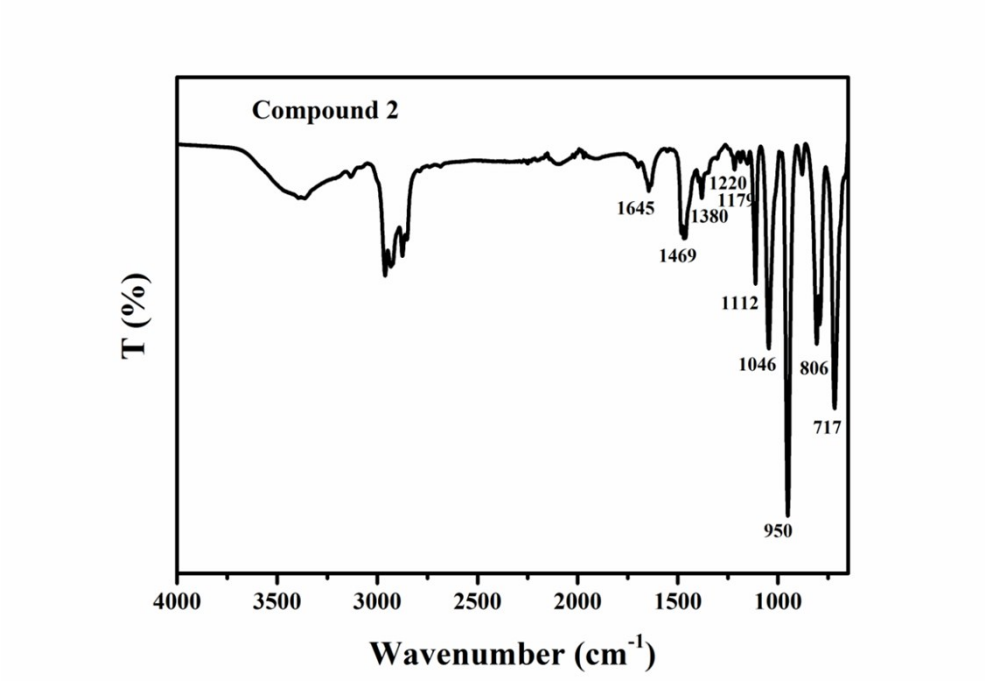

Fig. S7 IR spectrum of compound **2**.

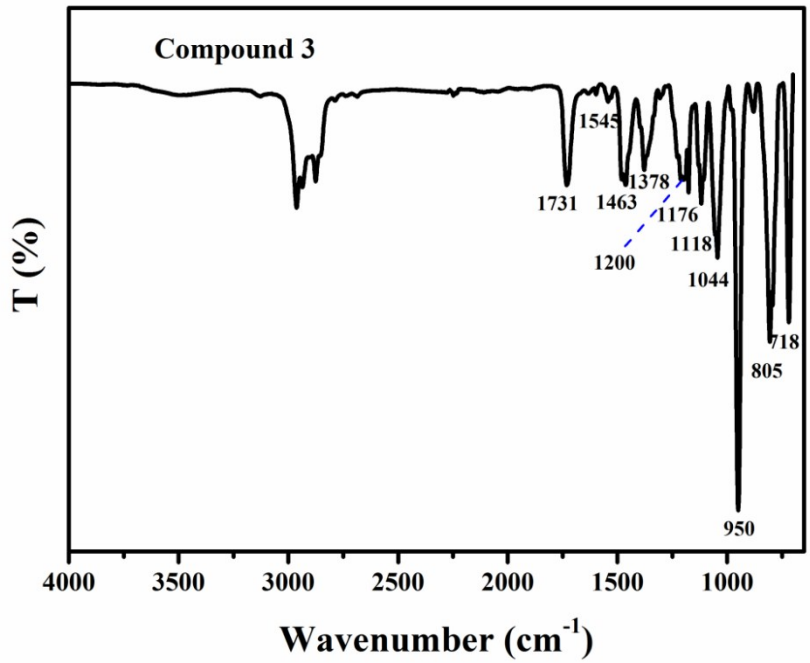

Fig. S8 IR spectrum of compound **3**.

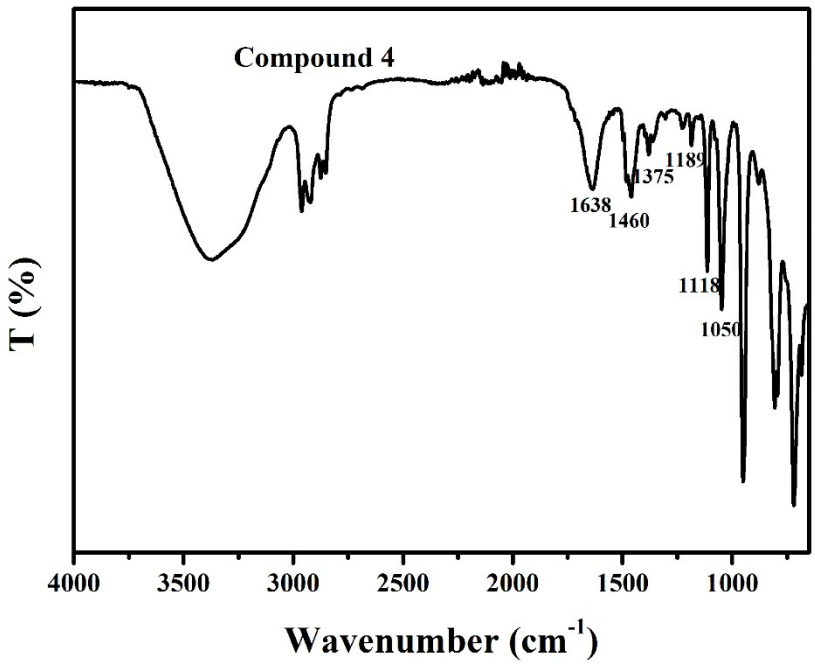

Fig. S9 IR spectrum of compound **4**.

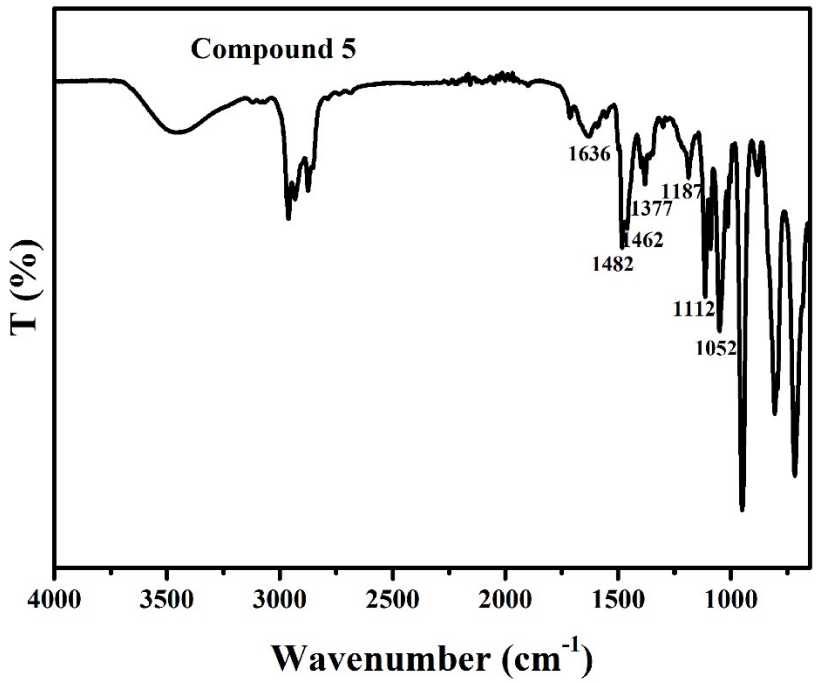

Fig. S10 IR spectrum of compound **5**.

3.2 ESI-MS spectra

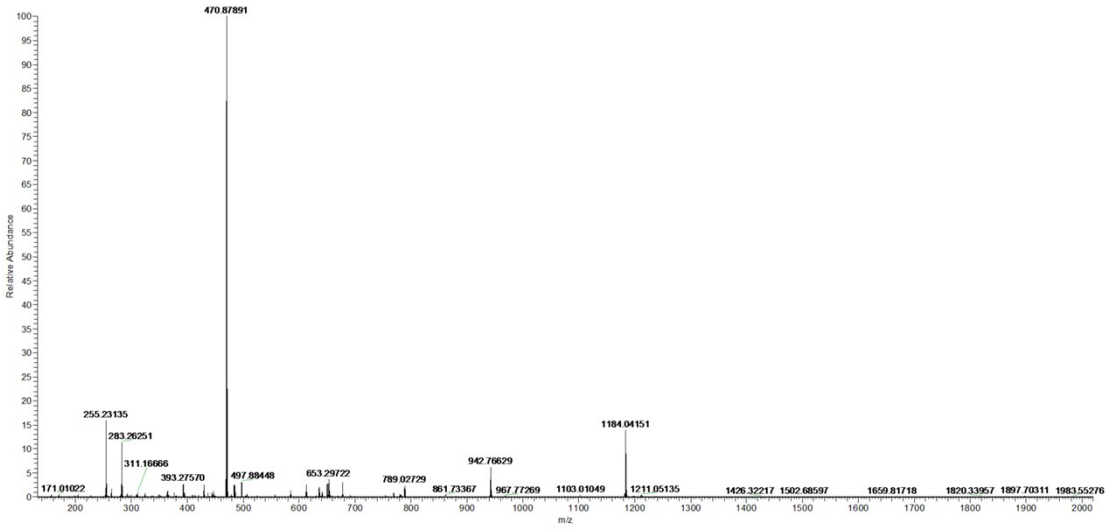

Fig. S11 ESI-MS result of compound **2**.

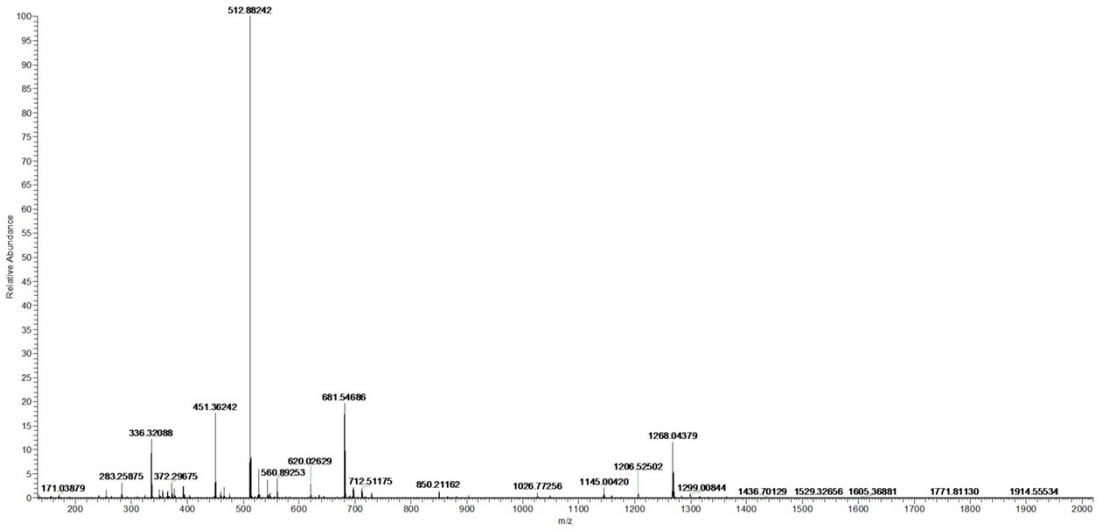

Fig. S12 ESI-MS result of compound **3**.

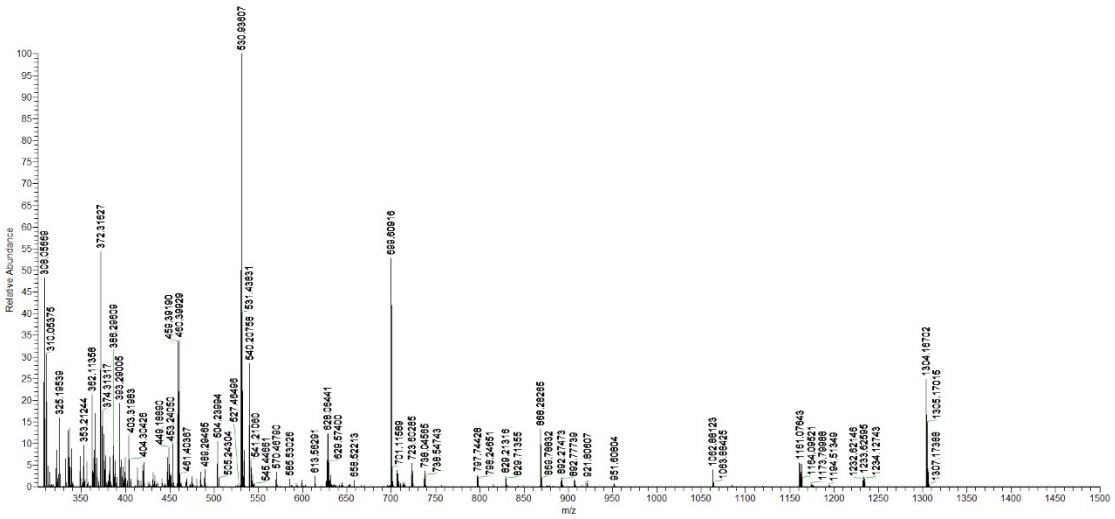

Fig. S13 ESI-MS result of compound **4**.

Fig. S14 ESI-MS result of compound **5**.

3.3. XRD characterization

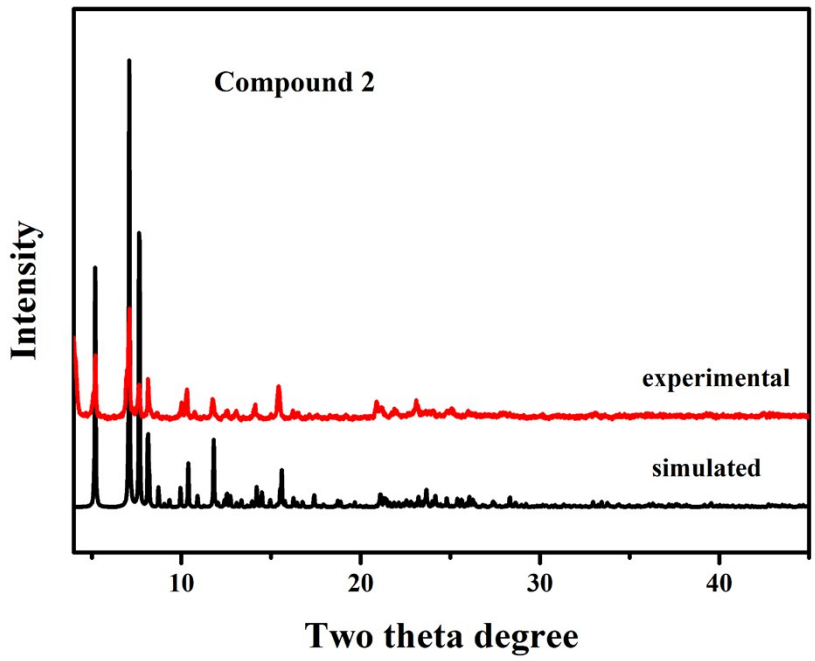

Fig. S15 The simulated (black) and experimental (red) powder XRD patterns for compound **2**.

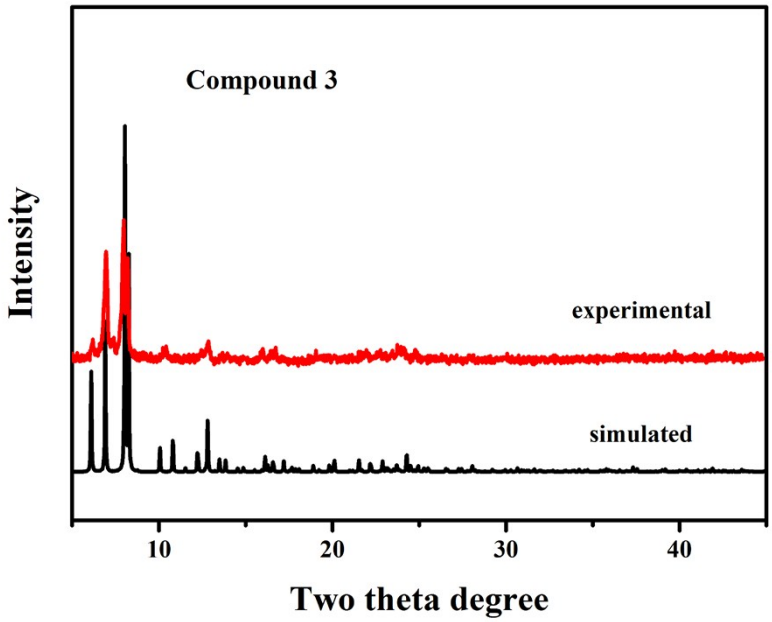

Fig. S16 The simulated (black) and experimental (red) powder XRD patterns for compound **3**.

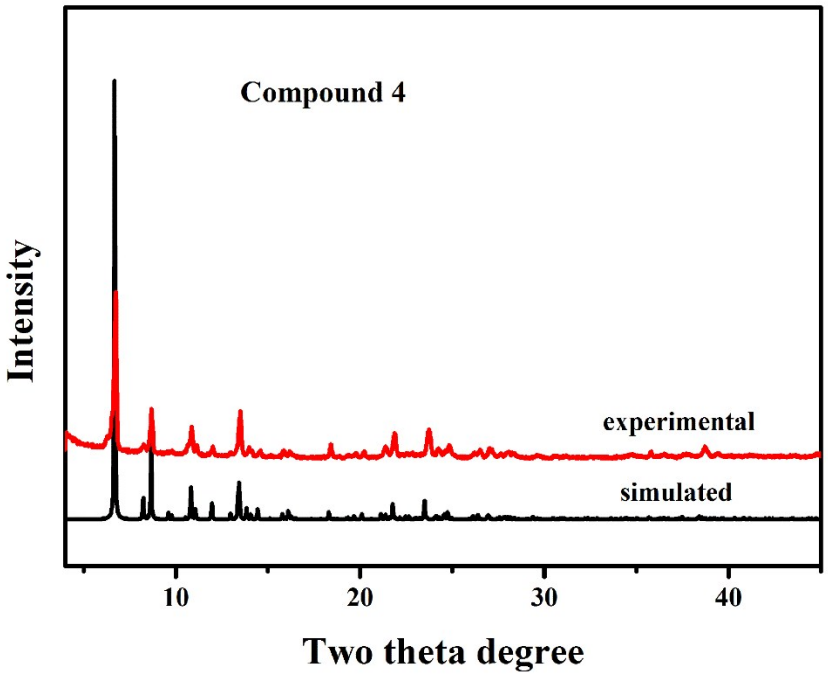

Fig.S17 The simulated (black) and experimental (red) powder XRD patterns for compound **4**.

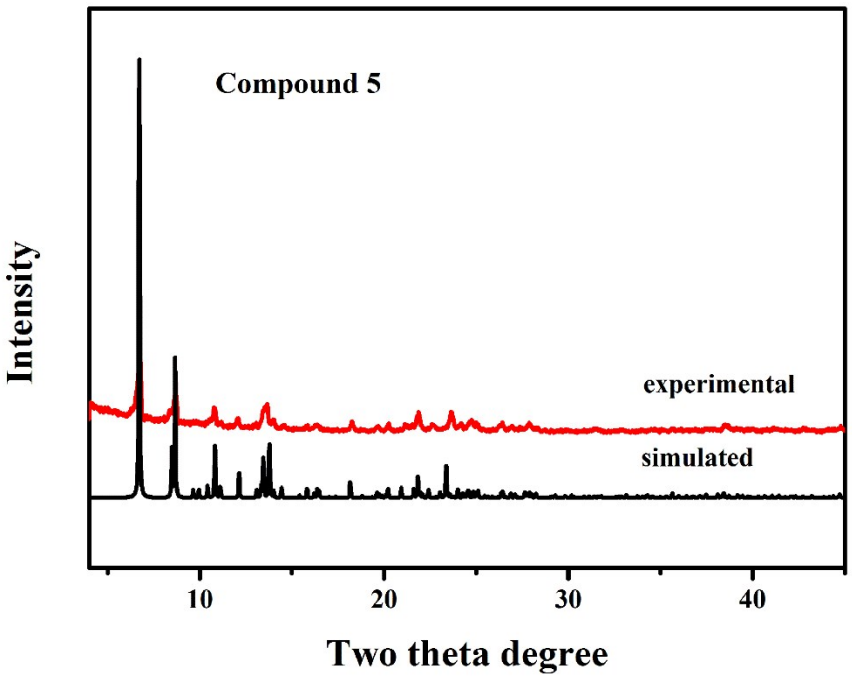

Fig.S18 The simulated (black) and experimental (red) powder XRD patterns for compound **5**.

3.4 NMR Spectra

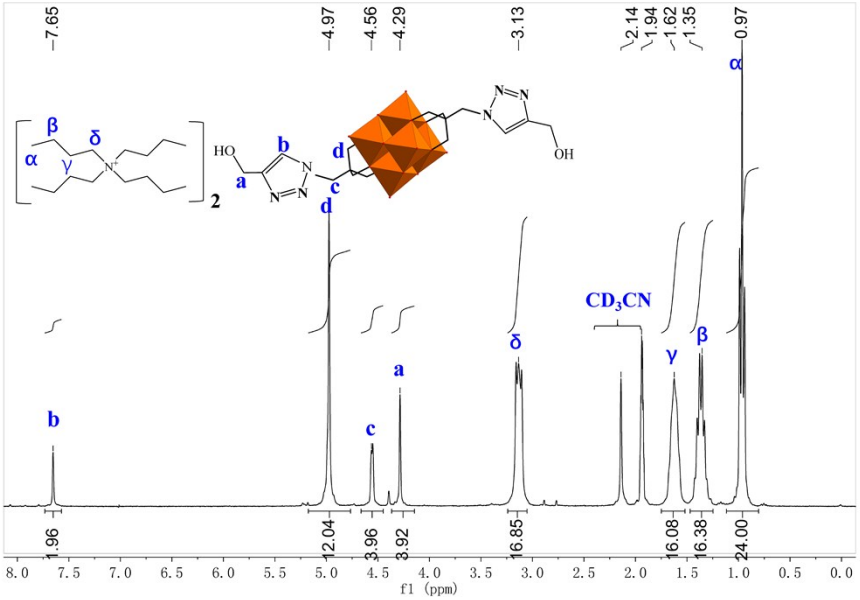

Fig.S19 ^{1}H NMR spectrum of compound **2** in CD_3CN at 400 MH

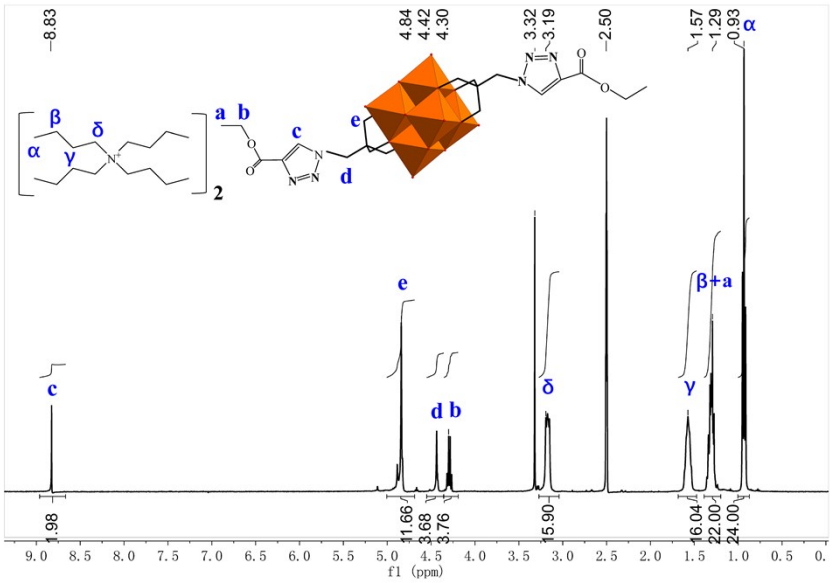

Fig.20 ^{1}H NMR spectrum of compound **3** in DMSO-d_6 at 400 MHz.

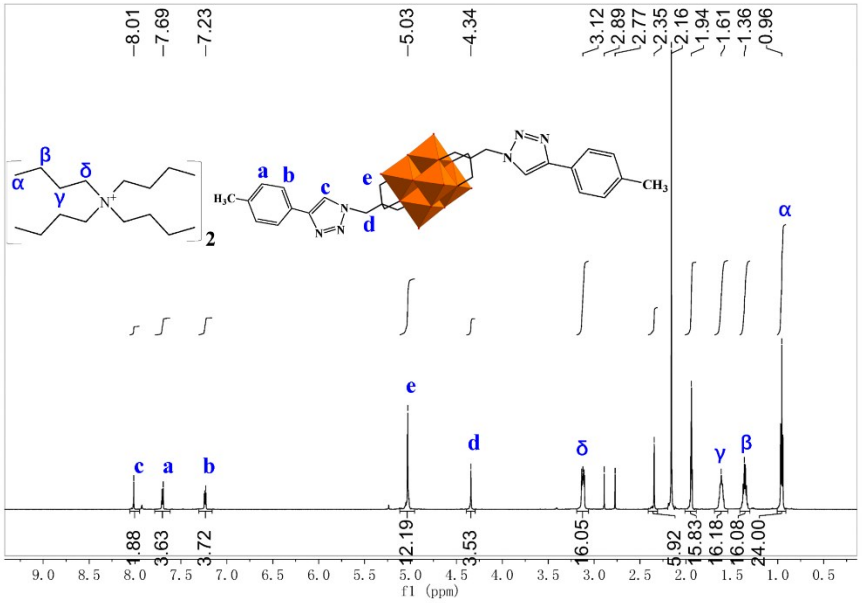

Fig.S21 ^{1}H NMR spectrum of compound **4** in CD_3CN at 400 MHz.

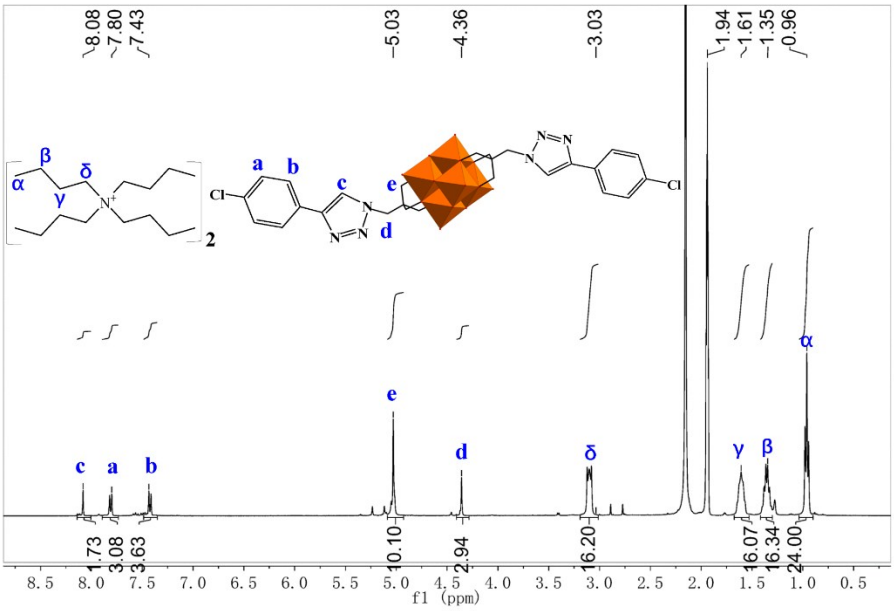

Fig.S22 ^{1}H NMR spectrum of compound **5** in CD_3CN at 400 MHz.

3.5 UV-Vis Spectra

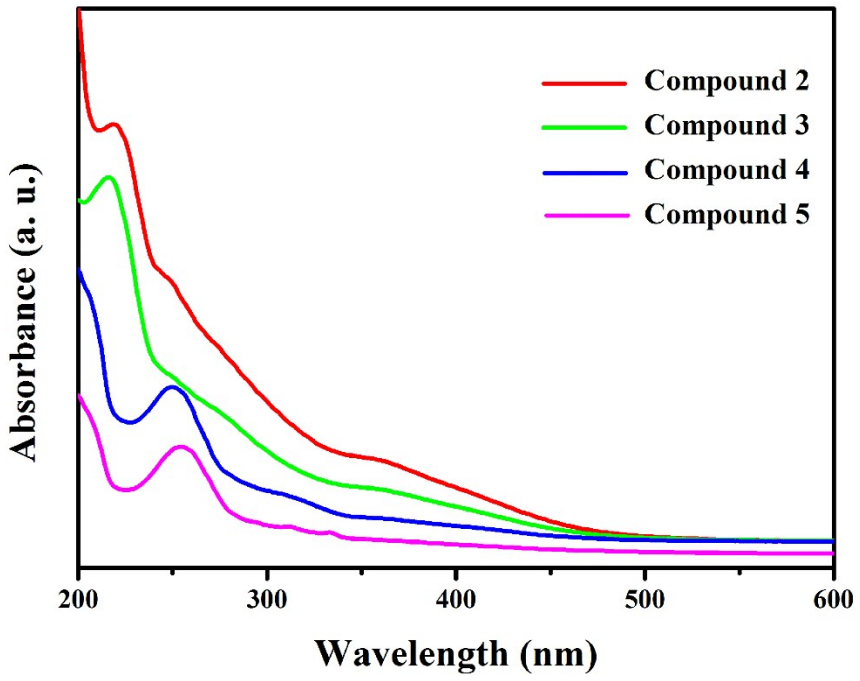

Fig. S23. UV-Vis spectra of compounds **2-5**.

4. Additional Crystallography Data

Table S1 Selected Bond Lengths (Å) and Angles (º) for compound **2.**

Bond	Lengths (Å)	Bond	Lengths (Å)
V(1)-O(1)	1.598(26)	V(5)-O(5)	1.6060 (29)
V(1)-O(11)	1.822(25)	V(5)-O(9)	1.8086 (28)
V(1)-O(10)	1.8414 (27)	V(5)-O(12)	1.8525 (28)
V(1)-O(18)	2.0143 (25)	V(5)-O(17)	2.0095 (26)
V(1)-O(16)	2.0324 (23)	V(5)-O(18)	2.0230 (24)
V(1)-O(19)	2.2321 (22)	V(5)-O(19)	2.2459 (23)
V(2)-O(2)	1.6007 (26)	V(6)-O(6)	1.6039 (29)
V(2)-O(7)	1.8061 (28)	V(6)-O(8)	1.8072 (28)
V(2)-O(8)	1.8061 (28)	V(6)-O(9)	1.8586 (31)
V(2)-O(16)	1.9978 (24)	V(6)-O(15)	2.0014 (30)
V(2)-O(17)	2.0384 (27)	V(6)-O(15)	2.0372 (26)
V(2)-O(19)	2.2456 (21)	V(6)-O(1)	2.2389 (22)
V(3)-O(3)	1.5987 (28)	C(6)-C(7)	1.348 (88)
V(3)-O(10)	1.8043 (28)	C(6)-N(1)	1.372 (92)
V(3)-O(7)	1.8539 (25)	N(1)-N(2)	1.331 (74)
V(3)-O(14)	2.0079 (23)	N(2)-N(3)	1.344(107)
V(3)-O(15)	2.0371 (29)	C(5)-N(1)	1.440(66)
V(3)-O(19)	2.2333 (23)	C(1)-C(4)	1.528(53)
V(4)-O(4)	1.6094 (26)	C(1)-C(3)	1.532(59)
V(4)-O(12)	1.8083 (29)	C(1)-C(2)	1.512(60)
V(4)-O(11)	1.8555 (27)	C(4)-O(15)	1.436(42)
V(4)-O(13)	2.0014 (27)	C(3)-O(14)	1.433(43)
V(4)-O(14)	2.0233 (26)	C(2)-O(13)	1.438(44)
V(4)-O(19)	2.2469 (21)		
Bond	Angles (º)	Bond	Angles (º)
C(5)-N(2)-N(1)	120.67 (41)	C(1)-C(5)-N(1)	115.31 (35)
C(5)-N(1)-C(6)	127.29 (42)		

Table S2 Selected Bond Lengths (Å) and Angles (º) for compound **3**.

Bond	Lengths (Å)	Bond	Lengths (Å)
V(1)-O(12)	1.609 (23)	V(3)-O(11)	2.025 (22)
V(1)-O(11)	2.005(22)	V(3)-O(6)	2.237 (5)
V(1)-O(5)	2.029(23)	C(6)-N(3)	1.437(53)
V(1)-O(6)	2.234(5)	C(5)-N(3)	1.346(56)
V(2)-O(3)	1.606(25)	C(4)-C(5)	1.376(60)
V(2)-O(4)	1.845(24)	C(4)-N(1)	1.371(60)
V(2)-O(5)	2.004(22)	N(1)-N(2)	1.310(64)
V(2)-O(7)	2.037 (22)	N(2)-N(3)	1.349(50)
V(2)-O(6)	2.246 (5)	C(3)-C(4)	1.477(70)

V(3)-O(10)	1.602 (23)	C(3)-O(2)	1.183(60)
V(3)-O(8)	1.801 (24)	C(3)-O(1)	1.327(59)
V(3)-O(9)	1.839 (24)	C(2)-O(1)	1.460(71)
V(3)-O(7)	2.007 (22)	C(1)-C(2)	1.409(90)
Bond	Angles (º)	Bond	Angles (º)
C(3)-C(4)-C(5)	128.86 (41)	N(2)-N(3)-C(6)	121.96 (36)
C(3)-C(4)-N(1)	123.12 (40)	N(2)-N(3)-C(5)	110.70 (37)
C(1)-C(2)-O(1)	111.61 (52)	C(4)-C(5)-N(3)	104.93 (37)
C(5)-N(3)-C(6)	127.29 (34)	C(8)-C(6)-N(3)	116.29 (32)

Table S3 Selected Bond Lengths (Å) and Angles (º) for compound **4**.

Bond	Lengths (Å)	Bond	Lengths (Å)
V(1)-O(5)	1.6008 (40)	C(1)-C(2)	1.5059 (124)
V(1)-O(7)	1.8099 (39)	C(2)-C(3)	1.3411 (146)
V(1)-O(8)	1.8470 (31)	C(2)-C(7)	1.3694 (141)
V(1)-O(4)	2.0140 (28)	C(3)-C(4)	1.4328 (132)
V(1)-O(2)	2.0297 (37)	C(4)-C(5)	1.3836 (111)
V(1)-O(6)	2.2458 (9)	C(5)-C(6)	1.3829 (92)
V(2)-O(10)	1.6012 (30)	C(6)-C(7)	1.3813 (105)
V(2)-O(8)	1.8106 (38)	C(5)-C(8)	1.4692 (92)
V(2)-O(9)	1.8285 (39)	C(8)-C(9)	1.3554 (86)
V(2)-O(1)	2.0071 (35)	C(8)-N(1)	1.3604 (75)
V(2)-O(4)	2.0233 (34)	N(1)-N(2)	1.3115 (87)
V(2)-O(6)	2.2256 (6)	N(2)-N(3)	1.3173 (70)
V(3)-O(3)	1.6095 (39)	N(3)-C(10)	1.4259 (83)
V(3)-O(9)	1.8109 (33)	N(3)-C(9)	1.3646 (72)
V(3)-O(7)	1.8420 (41)	C(10)-C(12)	1.5589 (64)
V(3)-O(2)	2.0109 (38)		
V(3)-O(1)	2.0252 (29)		
V(3)-O(6)	2.2417 (8)		
Bond	Angles (º)	Bond	Angles (º)
C(3)-C(2)-C(7)	118.66 (88)	C(9)-N(3)-N(2)	110.38 (54)
C(3)-C(4)-C(5)	118.86 (86)	N(1)-N(2)-N(3)	107.77 (48)
C(4)-C(5)-C(6)	118.43 (73)	N(2)-N(1)-C(8)	109.08 (54)
C(8)-C(9)-N(3)	105.05 (49)	N(8)-C(9)-N(1)	107.71 (57)
N(3)-C(10)-C(12)	115.00 (50)		

Table S4 Selected Bond Lengths (Å) and Angles (º) for compound **5**.

Bond	Lengths (Å)	Bond	Lengths (Å)
V(1)-O(9)	1.5959 (28)	C(1)-Cl(1)	1.7533 (73)
V(1)-O(10)	1.8060 (35)	C(1)-C(2)	1.3288 (112)
V(1)-O(8)	1.8272 (35)	C(1)-C(6)	1.3596 (114)
V(1)-O(1)	1.9994 (32)	C(2)-C(3)	1.4171 (103)

V(1)-O(3)	2.0180 (31)	C(3)-C(4)	1.3766 (90)
V(1)-O(7)	2.2236 (6)	C(4)-C(5)	1.3681 (75)
V(2)-O(6)	1.5915 (39)	C(5)-C(6)	1.3947 (89)
V(2)-O(8)	1.8111 (30)	C(7)-C(4)	1.4623 (83)
V(2)-O(5)	1.8454 (37)	C(7)-C(8)	1.3672 (80)
V(2)-O(2)	2.0087 (33)	C(7)-N(1)	1.3562 (66)
V(2)-O(1)	2.0271 (26)	N(1)-N(2)	1.3349 (77)
V(2)-O(7)	2.2441 (8)	N(2)-N(3)	1.3259 (62)
V(3)-O(4)	1.5991 (36)	N(3)-C(9)	1.4254 (71)
V(3)-O(5)	1.7980 (37)	N(3)-C(8)	1.3442 (64)
V(3)-O(10)	1.8552 (28)	C(9)-C(10)	1.5561 (63)
V(3)-O(3)	2.0169 (25)		
V(3)-O(2)	2.0328 (33)		
V(3)-O(7)	2.2480 (8)		
Bond	Angles (º)	Bond	Angles (º)
C(3)-C(2)-C(7)	118.66 (88)	C(9)-N(3)-N(2)	110.38 (54)
C(3)-C(4)-C(5)	118.86 (86)	N(1)-N(2)-N(3)	107.77 (48)
C(4)-C(5)-C(6)	118.43 (73)	N(2)-N(1)-C(8)	109.08 (54)
C(8)-C(9)- N(3)	105.05 (49)	N(8)-C(9)- N(1)	107.71 (0.57)
N(3)-C(10)-C(12)	115.00 (50)		

Selected Torsion Angle (°)

Table S5: Selected Torsion Angle (°) for compounds **3**.

Compound 3			
C3 - O1 - C2 - C1	85.92 (69)	N3 - N2 - N1 - C4	-1.26 (52)

Table S6. Hydrogen bond distances and angles of compound **2-5** [**Å** and º].

D-H...A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
Compound 2				
C6-H6…O12	0.93	2.35	3.045	130.44
C14-H14…O12	0.93	2.42	3.078	127.91
Compound 3				
C6-H6B…O10	0.97	2.32	3.199	149.83
Compound 4				
C10-H10B…O7	0.970	2.339	3.145	140.05
Compound 5				
C9-H9A…O9	0.970	2.378	3.165	137.91