Supporting Information for the paper entitled

The first crystallographic observation of up to third hydration layer of Cu(II) ion in an unusual ‘water-cation layer’ templated by an Anderson polyoxometallate

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Experimental Section

0.004 M (0.92 g) of H_2TeO_4. $2H_2O$, 0.0042 M (1.016 g) of $Na_2MoO_4.2H_2O$, 4 M (8 ml) HCl, 0.0093 M (0.692 g) KCl, 3 mmol (0.595 g) 1,10-phenanthroline and 1 mmol (0.242 g) $CuNO_3.3H_2O$ were added in 40 ml H_2O and stirred for 2.5 h. Then the mixture was transferred to a Teflon bomb and kept in oven at 160^0C for 6 days. The green solution obtained on cooling to room temperature in steps of 5^0C was filtered and allowed to undergo slow evaporation at ambient temperature. Green hexagonal crystals suitable for X-ray diffraction were obtained in 15 days.

Crystal data: Compound 1: $2(C_{36}H_{24}CuN_6)$, $Mo_6O_{24}Te$, $CuH_{12}O_6$, $27(H_2O)$, Mr =2953.64 , Trigonal, P-31c(No.163), a = 17.2848(6), b = 17.2848(6) c = 19.2560(11) Å; $\alpha = \beta = 90$, $\gamma = 120^0$; V= 4982.3(4) $Å^3$, Z = 2, D(calc)[g/cm^3] 1.960, Crystal Size[mm] = 0.20 x 0.30 x 0.30; Mu(MoK_α) [mm^{-1}] 1.754 F(000) = 2954. A total of 37123 reflections were collected and 2951 Unique R = 0.056, wR_2 = 0.1353, S = 1.15 Observed data [$I > 2.0\sigma(I)$] = 2580. diffractometer Kuma KM-4 equipped with a CCD detector using monochromated (monochromator Enhance, Oxford Diffraction) MoKα (λ= 0.71073) at 120(2) K. diffractometer Kuma KM-4 equipped with a CCD detector using monochromated (monochromator Enhance, Oxford Diffraction) MoKα (λ= 0.71073) at 120(2) K. Additional Crystallographic data are available (**CCDC 706251**) from the Cambridge Crystallographic Data Centre. 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1 – Details of hydrogen bonding parameter of the complex

D-H...A	d(D-H)**(Å)**	d(H...A)**(Å)**	d(D...A)**(Å)**	<(DHA)**(^{0})**
O(1)-H(1W)...O(8)#1	0.918(13)	1.771(12)	2.683(5)	172(4)
O(1)-H(1V)...O(4)#1	0.950(13)	1.647(16)	2.524(6)	152(3)
O(2)-H(2V)...O(10)	0.93(3)	1.83(3)	2.754(7)	174(2)
O(2)-H(2W)...O(5)#2	0.95(6)	1.86(6)	2.813(8)	178(11)
O(3)-H(3W)...O(5)	0.93(3)	1.83(3)	2.753(8)	170(7)
O(3)-H(3V)...O(3)#3	0.92(2)	1.70(2)	2.614(10)	176(7)
O(3)-H(3X)...O(3)#4	0.921(15)	1.973(15)	2.889(12)	173(2)
O(4)-H(4W)...O(2)	0.916(15)	1.504(15)	2.386(8)	160(3)
O(5)-H(5W)...O(6)	0.915(15)	1.81(3)	2.710(7)	167(5)
O(5)-H(5V)...O(9)#5	0.935(15)	2.03(3)	2.956(6)	171(5)
O(6)-H(6W)...O(4)	0.913(14)	1.722(15)	2.629(7)	172(4)
O(6)-H(6V)...O(1)#1	0.969(13)	1.870(14)	2.836(7)	174(7)

Symmetry transformations used to generate equivalent atoms:
#1 -y,x-y,z #2 -x+y,y,-z+1/2 #3 -y+1,-x+1,-z+1/2
#4 x,x-y,-z+1/2 #5 y,x,z-1/2

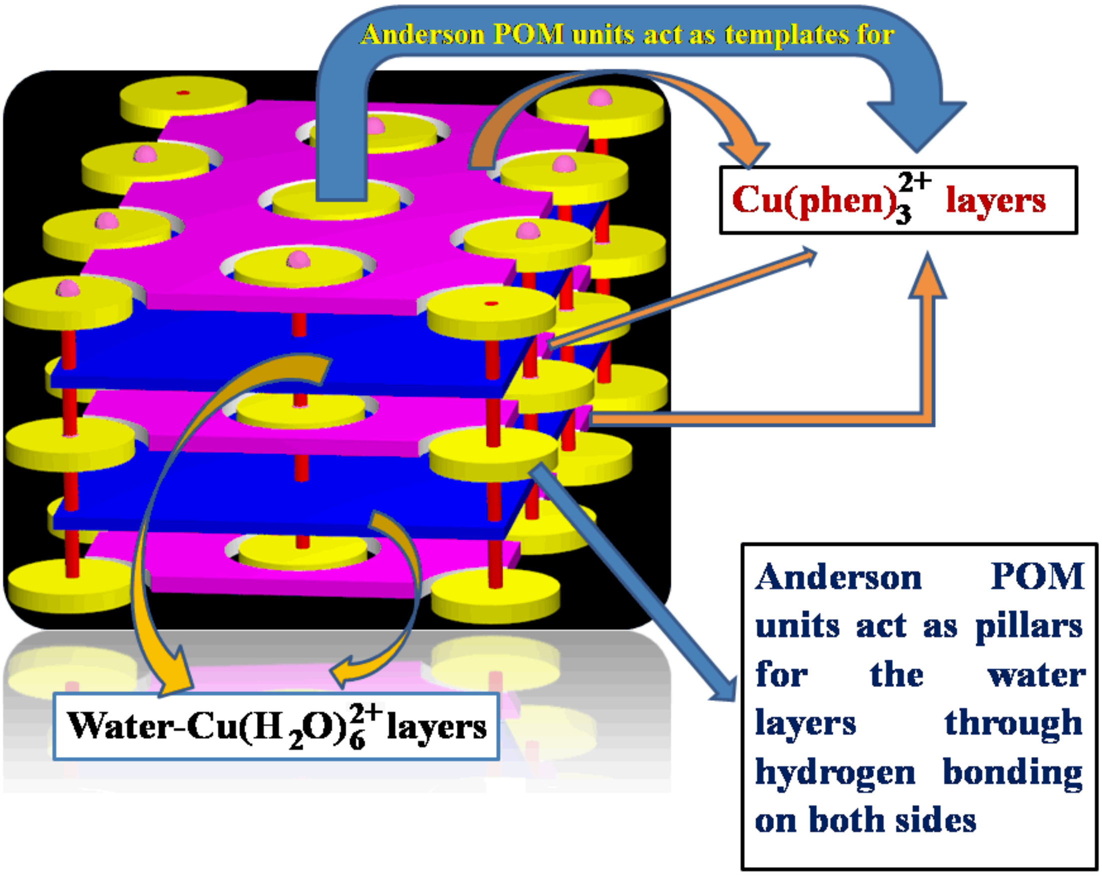

Figure S1: The overall supramolecular assembly in complex **1** depicting the interpenetration of 3D pillar-layered hydrogen bonded [Cu(H$_2$O)$_6$]$^{2+}$-water-POM network and π- π layer of [Cu(phen)$_3$]$^{2+}$ units

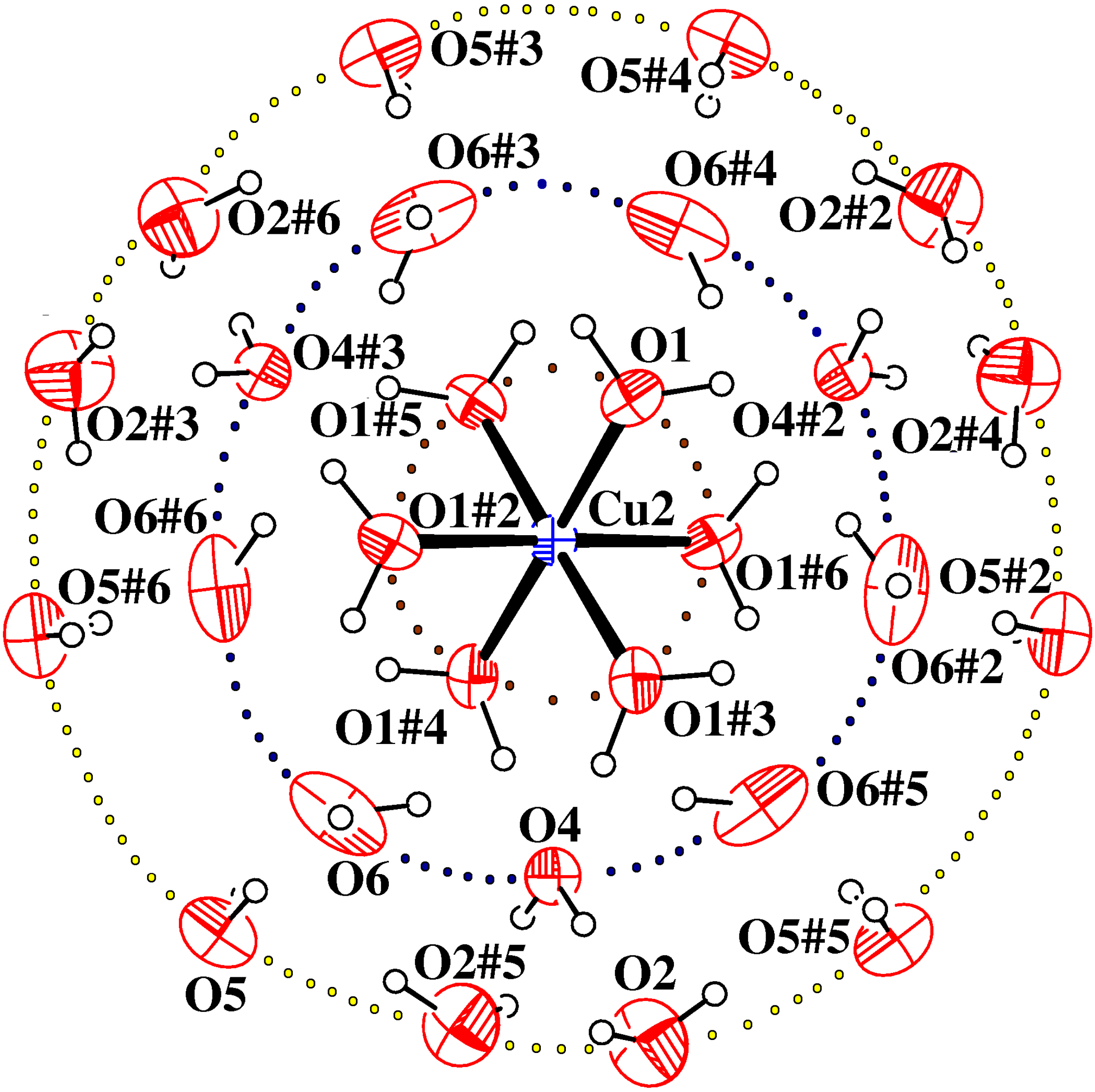

Figure S2: The ORTEP diagram(30% ellipsoidal probability) of the hydration layers around $[Cu(H_2O)_6]^{2+}$ unit. {#1 = -y,x-y,z; #2=-x+y,-x,z ;#3=-x,-y,1-z ;#4= y,-x+y,1-z ;#5= x-y,x,1-z }

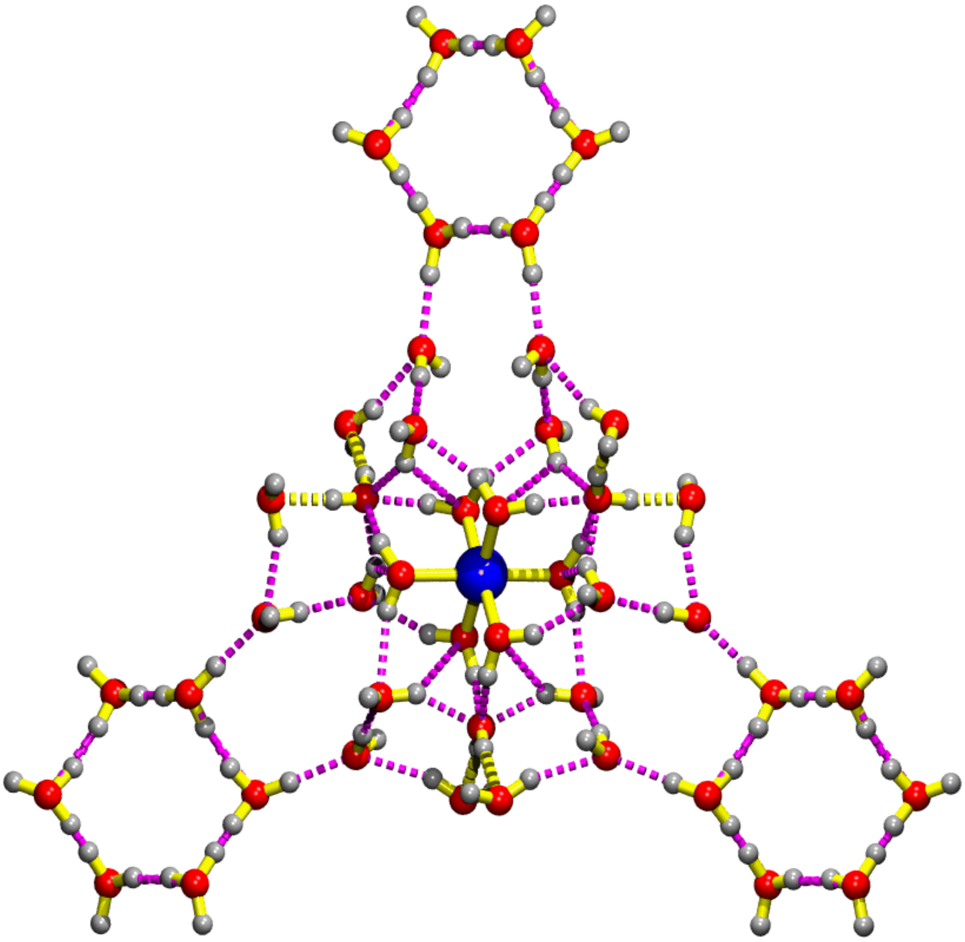

Figure S3: View showing the hydrogen bonded network of three water hexamer with the central hydrated Cu(II) cation.

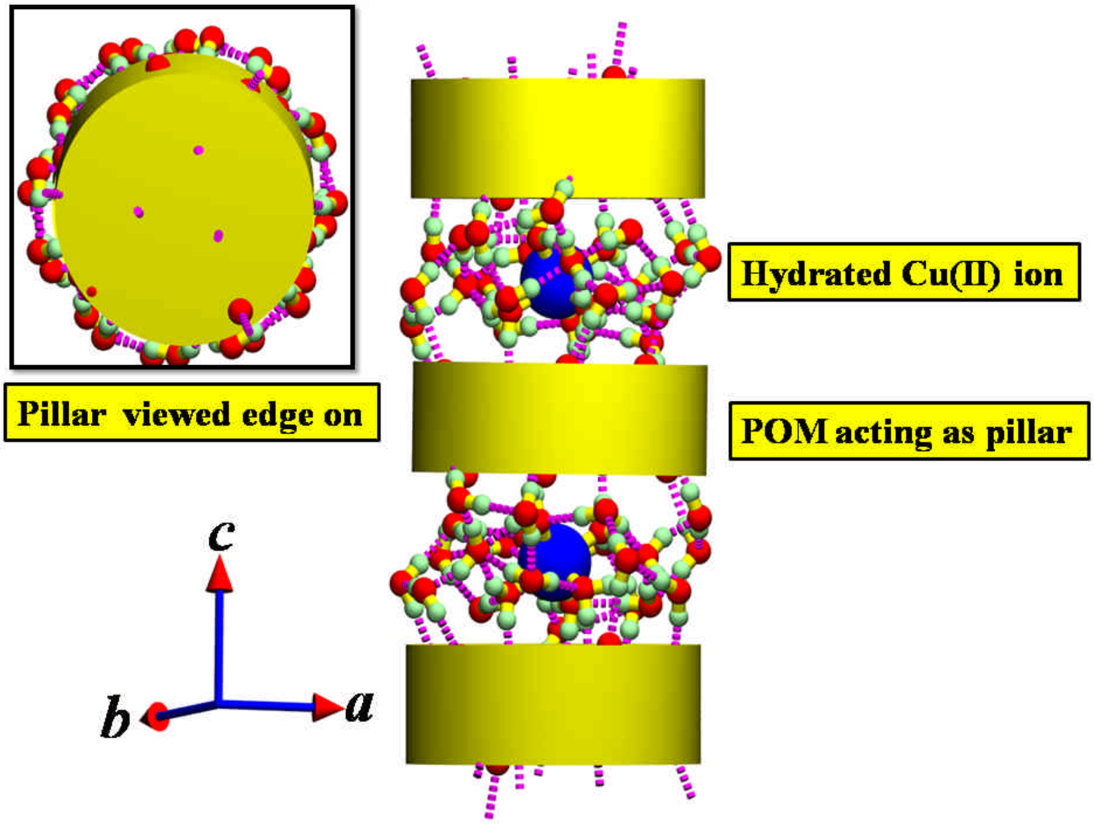

Figure S4: The view showing the pillar formed through the hydrogen bonding water molecules with the POM units (shown in yellow).