Supplementary Information

The crystal packing, morphology and hydrophobicity of polyoxometalate-based amphiphilic materials

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Materials and general measurements

All chemicals were purchased from commercial source except the $H_2[V_6O_{13}\{(OCH_2)_3CNH_2\}_2]$ (Compound **1**), which was prepared by literature method.[1] The dimethylacetamide(DMAc) was dried by refluxing in the presence of CaH_2 and distilled before using. Other chemicals were used as received. IR spectra were obtained using KBr pellets with a Nicolet iS50 FT-IR spectrometer. ^{1}H NMR spectra were recorded on an AV400 NMR spectrometer with DMSO-d6 solvent. Electrospray mass spectra (ESI-MS) were obtained using a Thermo Q Exactive mass spectrometer in acetonitrile solution in negative mode. The SEM images were tested by an instrument of N340 and the surface topography of the materials was tested at an acceleration voltage of 5.0 kV. The TEM images of the materials were measured with a Tecnai G2 F20 U-TWIN electron microscope, after ultrasonic dispersion of all the compounds in a 1:1 mixture of ethanol and water. The contact angle measurements were carried out by a JY-82B Kruss DSA goniometer using drop casting method, the sample surfaces were prepared by compressing 150 mg powder of the sample in the pressure of 3.5 MPa.

Crystallographic information

Single-crystal X-ray diffraction experiments of compound **2** and **3** were performed on a Bruker P4 X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). The raw data was processed by SAINT (version 8.37A) to achieve the reflection data.[2] The XRD data of compound **4** was collected on an Agilent Supernova micro focus single crystal diffractometer using micro-focus sealed Mo Kα radiation (λ=

0.71073 Å). The raw data was handle with CrysAlisPro (version 1.171.39.33c).[3] All the structures were solved by the direct method and refined on F2 by full-matrix least-squares methods using SHELX2014 and OLEX-2 program.[4,5]

Experimental details

Synthesis of $(DIEA)_2[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_4(OC_{12}H_{25})_{-p}\}_2]$ (2):

Compound **2** was synthesized by dissolving a mixture of compound **1** (0.376g, 0.5mmol), 4-dodecanoxy benzoic acid (0.387g, 1.2mmol), PyBOP (0.637g, 1.2mmol) and HOBt (0.164g, 1.2mmol) in 50mL anhydrous DMAc. DIEA was added dropwisely to adjust the pH value to 7-8, and then the solution was heated at 65 ℃ and stirred for 24 hours. After the reaction, the mixture was cooled down to room temperature and the insoluble solids were removed by the filtration. The raw product was obtained as brown powder by removing the solvent with a rotary evaporator and washed with ether for several times. The powder was dissolved in acetonitrile and the insoluble impurities were removed by filtration. Finally, the red acicular crystal of compound **2** was obtained by slow evaporation of the filtration after one week.

IR (KBr-pellets, cm^{-1}): 717 (s), 810 (s), 956 (vs), 1050 (s),1250 (s), 1469 (m), 1500 (s), 1532 (m), 1605 (s), 1663 (m), 2853 (m), 2924 (s).

ESI-MS (m/z): 1327.11 (DIEA)$[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_4(OC_{12}H_{25})\text{-}p\}_2]^{1-}$ (theoretical value 1326.73) and 663.05 $[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_4(OC_{12}H_{25})\text{-}p\}_2]^{2-}$ (theoretical value 663.56). ^1H NMR (400 MHz, d6-DMSO, standardized by solvent peak, ppm): δ = 0.85 (t, 6.2H), 1.26(m, 70.4), 3.15(q, 4.4H), 3.63(m, 4.2H), 3.99(t, 3.9H), 5.27(s, 12.0H), 6.93(d, 3.9H), 7.55(s, 1.6H), 7.79(d, 3.9H).

Synthesis of $(DIEA)_2[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_4(OC_{16}H_{33})\text{-}p\}_2]$•2MeCN (3):

The synthesis and purification of compound **3** were almost the same as compound 2. The red acicular crystals were also obtained by slow evaporation of the acetonitrile solution of the raw products after one week.

IR (KBr-pellets, cm^{-1}): 718 (s), 809 (s), 958 (vs), 1047 (s), 1248 (s), 1468 (m), 1505 (s), 1544 (m), 1607 (s), 1667 (m), 2850 (s), 2919 (vs), 3354 (w). ESI-MS (m/z): 1439.27 (DIEA)$[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_4(OC_{16}H_{33})\text{-}p\}_2]^{1-}$ (theoretical value1438.94) and 719.12 $[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_4(OC_{16}H_{33})\text{-}p\}_2]^{2-}$ (theoretical value 719.47). ^1H NMR (400 MHz, d6-DMSO, standardized by solvent peak, ppm): δ = 0.85(t, 6.4), 1.26(q, 86.4H), 3.15(m, 4.5H), 3.63(m, 4.4H), 4.0(t, 4.4H), 5.26(s, 12H), 6.93(d, 4.1H), 7.58(s, 2.0H), 7.79(d, 4.1H)

Synthesis of $(DIEA)_2[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_3(OC_{12}H_{25})_2\text{-}m_2\}_2]$•2DMac (4):

The synthesis and purification of compound **4** were almost the same as compound **2**. The slow evaporation of the acetonitrile solution of **4** yield tiny plate-shape crystals which was too small to perform a single crystal XRD test. The recrystallization in an acetonitrile/water mixture resulted in orange thin plate-shaped crystals of which the data can be collected on a micro focus single crystal diffractometer.

IR (KBr-pellets, cm^{-1}): 705 (m), 799 (s), 952 (vs), 1059 (s), 1153 (s), 1439 (m), 1463 (m), 1527 (s), 1594 (s), 1641 (m), 2853 (s), 2923 (vs), 3354 (w). ESI-MS (m/z): 1695.49 (DIEA)$[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_3(OC_{12}H_{25})_2\text{-}m_2\}_2]^{1-}$ (theoretical value 1695.37) and 847.24 $[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_3(OC_{12}H_{25})_2\text{-}m_2\}_2]^{2-}$ (theoretical value 847.69). ^1H NMR (400 MHz, d6-DMSO, standardized by solvent peak): δ = 0.85(t, 12.3H), 1.26(m, 110.3H), 3.13(m, 4.3H), 3.62(m, 4.3H), 3.96(t, 8.3H), 5.27(t, 12H), 6.57(s, 1.8H), 6.96(d, 3.6), 7.64(s, 1.6H).

Synthesis of $(DIEA)_2[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_2(OC_{12}H_{25})_3\text{-}m_2,p\}_2]$ (5):

The synthesis and purification of compound **5** were almost the same as compound **2**. The slow evaporation of the acetonitrile solution of **5** only yielded red globular polycrystals. The recrystallization of the polycrystals in an acetonitrile/water mixture resulted in flexible thin crystalline films but its crystal data still cannot be achieved.

IR (KBr-pellets, cm^{-1}): 704 (s), 801 (s), 951 (vs), 1061 (s), 1125 (s), 1337 (s), 1495 (s), 1533 (m), 1582 (s), 1637 (m), 2853 (s), 2923 (vs), 3358 (w). ESI-MS (m/z): 2064.83 (DIEA)$[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_2(OC_{12}H_{25})_3\text{-}m_2,p\}_2]^{1-}$ (theoretical value 2064.01) and 1031.92 $[V_6O_{13}\{(OCH_2)_3CNHCOC_6H_2(OC_{12}H_{25})_3\text{-}m_2,p\}_2]^{2-}$ (theoretical value 1032.05). ^1H NMR (400 MHz, d6-DMSO, standardized by solvent peak): δ = 0.85(t, 18.3H), 1.30(m, 150.3H), 3.12(s, 14.4H), 3.86(t, 4.4H), 3.98(t, 11.8), 5.27(s, 12H), 7.08(s, 3.7), 7.57(s, 1.8H).

[1] Bayaguud A, Chen K, Wei Y G. Facile synthesis of an organically-derivatized hexavanadate containing the remote amino group, $TBA_2[V_6O_{13}\{(OCH_2)_3CNH_2\}_2]$. *CrystEngComm*, **2016**, *18,* 4042-4045.

[2] SAINT+, version v8.37A, Bruker AXS Inc.: Madison, WI, USA, **2015**.

[3] CrysAlisPro, version 1.171. 39.33c, Oxford Diffraction Ltd.: Oxford, UK, **2017**.

[4] Sheldrick, G. M. SHELXT-Integrated space-group and crystal-structure determination. Acta Cryst. **2015**, *C71*, 3-8.

[5] Dolomanov, O.; Bourhis, L.; Gildea, R.; Howard, J.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

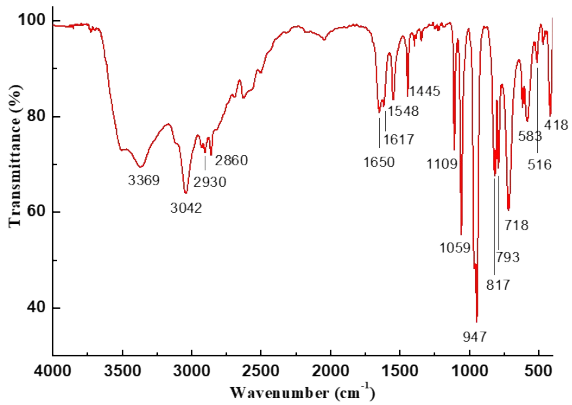

Figure S1. FT-IR spectrum of compound **1**.

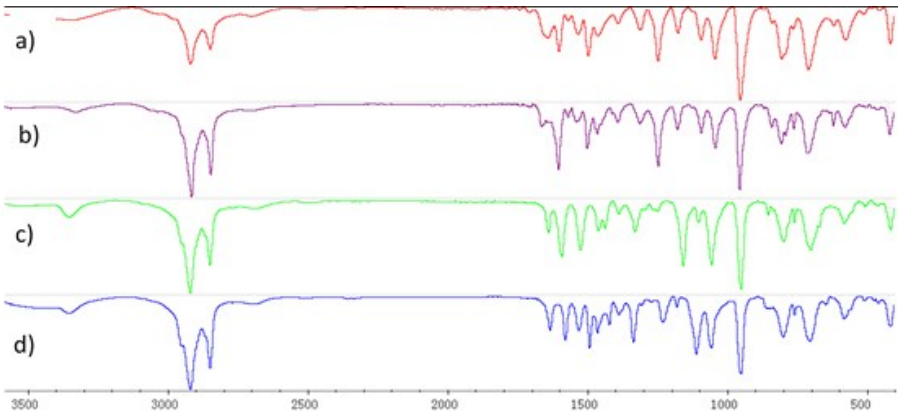

Figure S2. FT-IR spectra of a) compound **2**; b) compound **3**; c) compound **4;** d) compound **5.**

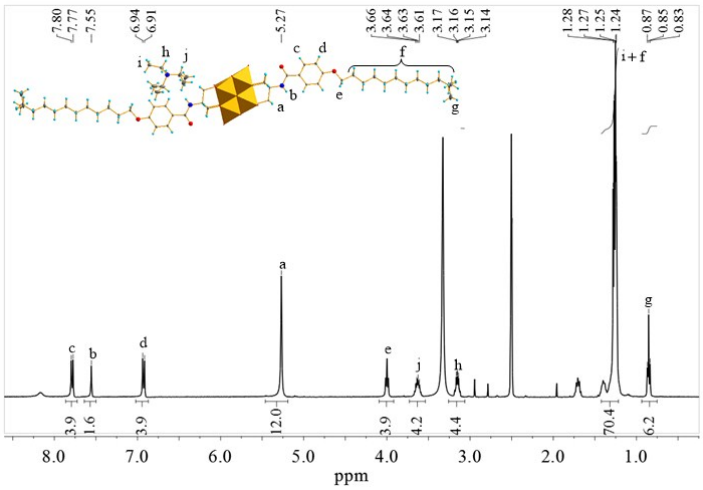

Figure S3. [1] H NMR spectrum of compound **2**.

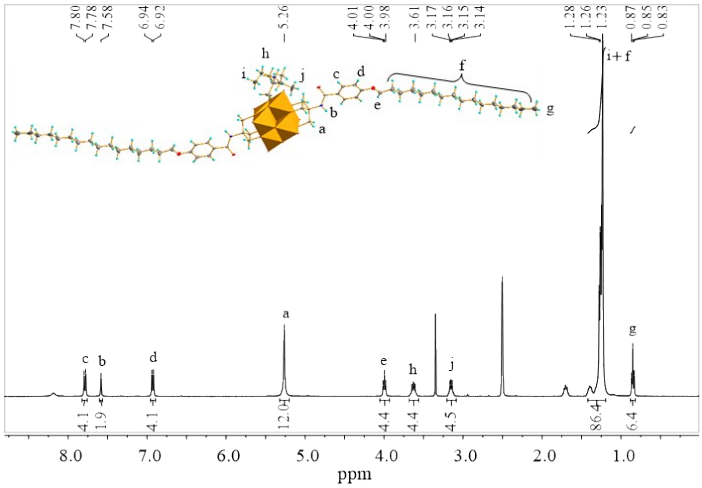

Figure S4. [1] H NMR spectrum of compound **3**.

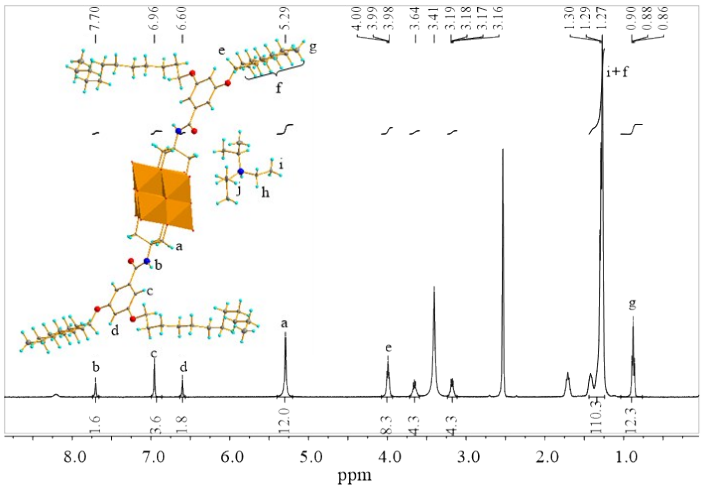

Figure S5. [1] H NMR spectrum of compound **4**.

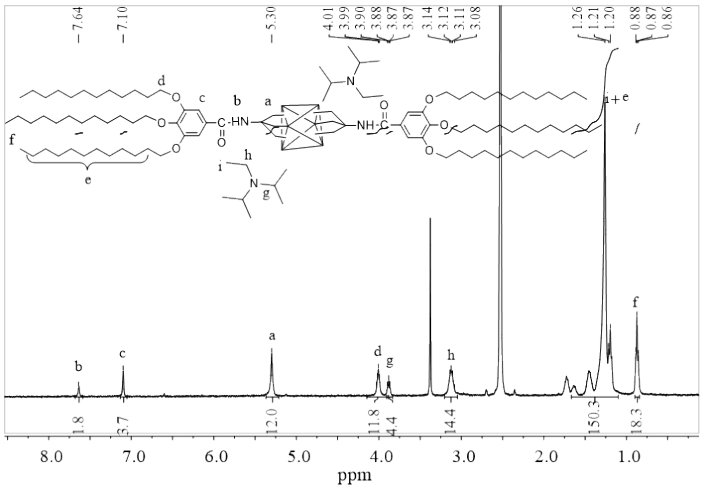

Figure S6. [1] H NMR spectrum of compound **5**.

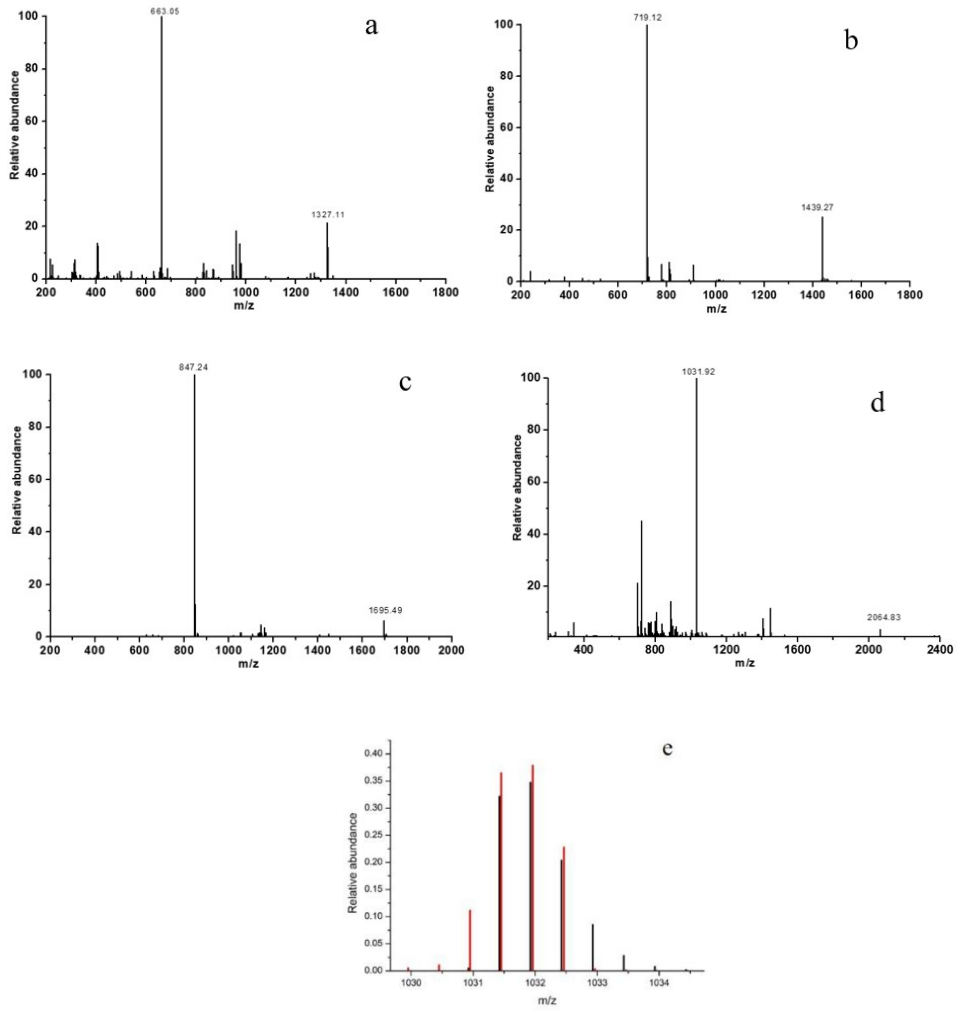

Figure S7. ESI-MS spectra of resulting compounds: a) compound **2**; b) compound **3**; c) compound **4;** d) compound **5;** e) high resolution ESI-MS of compound **5** (m/z=1031.92) Black line: experimental, Red line: calculated.

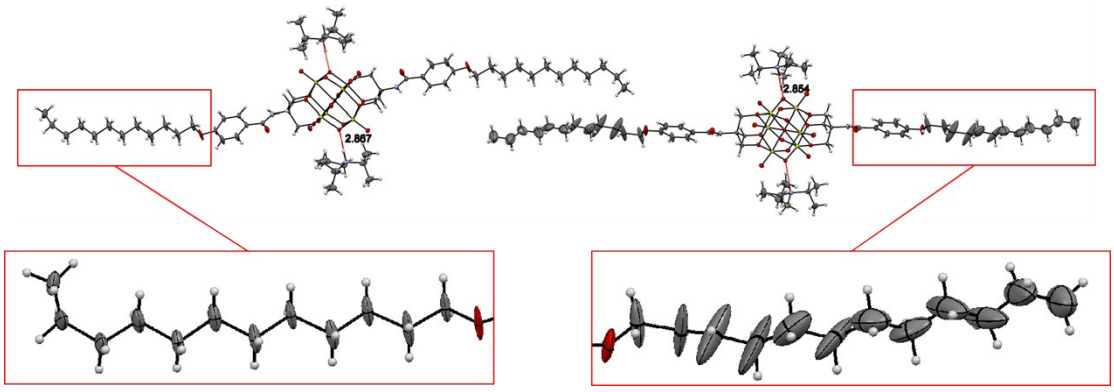

Figure S8. Structural details of compound **2**. Yellow sphere: V; red sphere: O; blue sphere: N; grey sphere: C; light blue sphere: H.

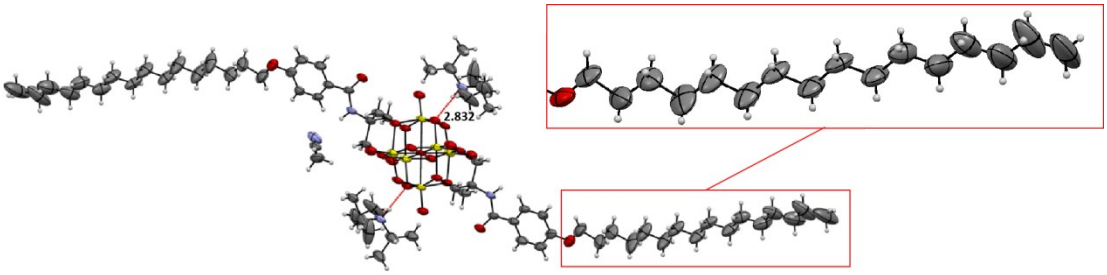

Figure S9. Structural details of compound **3**.Yellow sphere: V; red sphere: O; blue sphere: N; grey sphere: C; light blue sphere: H.

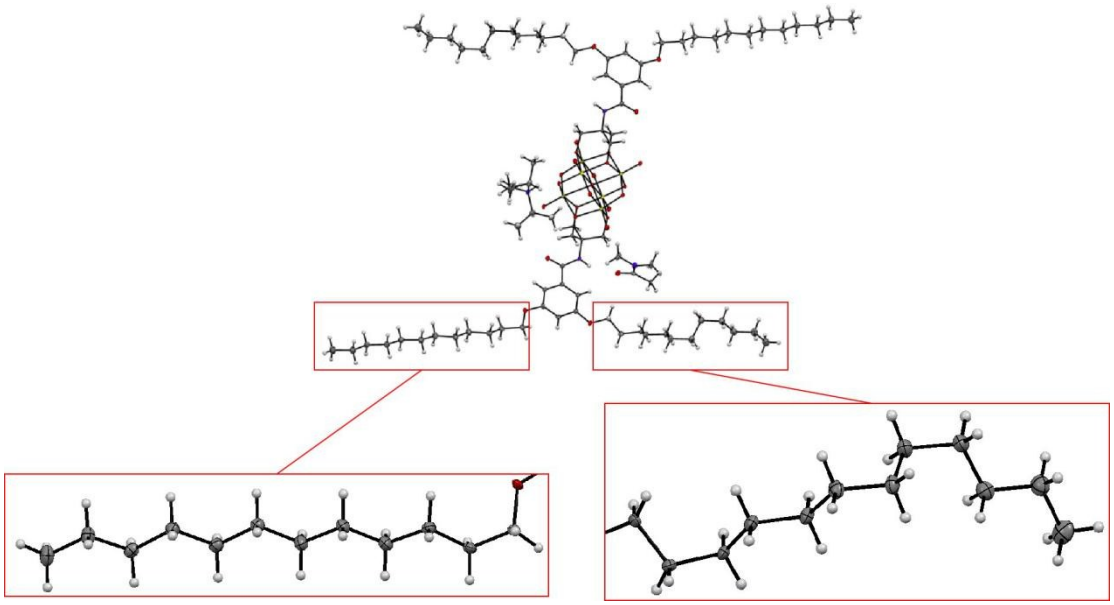

Figure S10. Structural details of compound **4**.Yellow sphere: V; red sphere: O; blue sphere: N; grey sphere: C; light blue sphere: H.

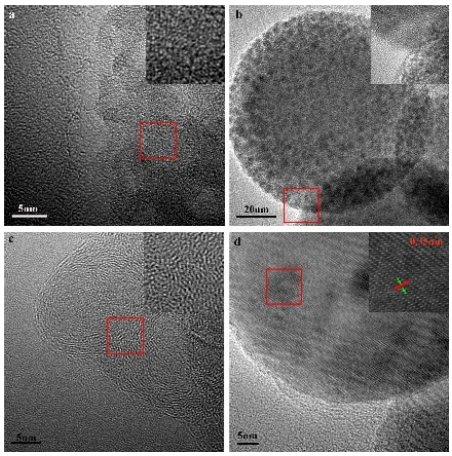

Figure S11 TEM images in water/ethanol mixture of a) compound **2**; b) compound **3**; c) compound **4**; d) compound **5.**

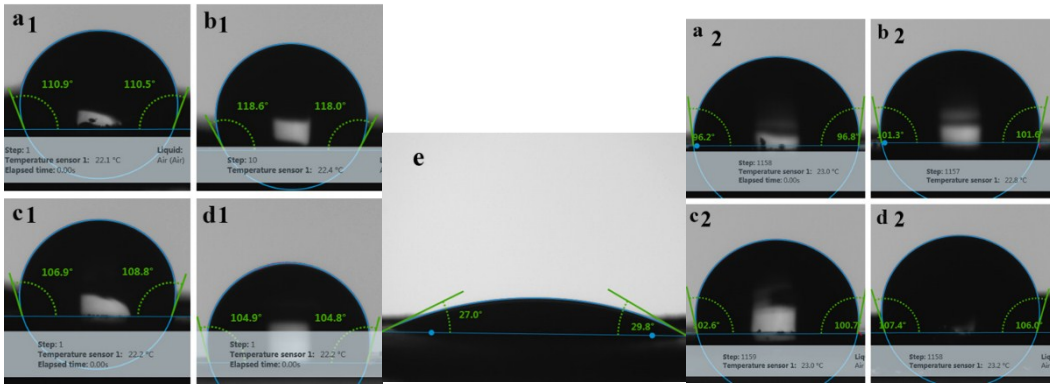

Figure S12. Contact angle measurements for：a1) C12-COOH, b1) C16-COOH, c1) 2C12-COOH, d1) 2C16-COOH; e) compound **1**; a2) compound **2**, b2) compound **3**, c2) compound **4**, d2) compound **5**

Table S1. Contact angle measurement results

Compound	Contact angle						Average
	1	2	3	4	5	6	value
1	27.0	29.8	27.6	29.9	28.9	28.7	28.65
2	96.2	96.8	94.9	94.4	97.2	95.6	95.85
3	101.3	101.6	97.5	97.8	97.9	98.2	99.05
4	102.6	100.7	104.3	103.3	102.6	102.1	102.6
5	107.4	106.0	107.9	106.9	107.5	106.1	106.97

C_{12}-COOH	110.9	110.5	106.9	106	108.5	109.1	108.65
C_{16}-COOH	118.6	118.0	118.5	117.9	118.7	118.3	118.33
$2C_{12}$-COOH	106.9	108.8	106.4	102.5	106.4	102.3	105.55
$3C_{12}$-COOH	104.9	104.8	103.0	103.0	105.0	104.8	104.25

Compound	**2**	**3**	**4**
Empirical formula	$V_6C_{62}H_{110}N_4O_{23}$	$V_6C_{74}H_{132}N_6O_{23}$	$V_6C_{94}H_{178}N_6O_{27}$
Formula weight	1585.17	1779.49	2130.05
T/K	273.15	296(2)	100.00(10)
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	P-1
a/Å	13.709(2)	21.3920(12)	10.1207(4)
b/Å	13.919(2)	10.9779(7)	10.7427(5)
c/Å	19.530(3)	19.1098(11)	27.9069(12)
α/°	97.532(2)	90	99.871(4)
β/°	93.120(3)	105.252(2)	90.774(4)
γ/°	99.117(2)	90	117.159(5)
Volume/Å3	3637.0(9)	4329.7(4)	2645.0(2)
Z	2	2	1
ρ calc g/cm^3	1.447	1.365	1.337
μ/mm^{-1}	0.814	0.693	0.582
F(000)	1664.0	1880.0	1138.0
Crystal size/mm^3	0.28 × 0.11 × 0.11	0.230× 0.20 ×0.14	0.2 × 0.2 × 0.01

Table S2. Crystal data of compounds **2-4**

Radiation	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	2.994 to 56.188	4.202 to 55.04	6.684 to 53.316
Index ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 16$, $-25 \leq l \leq 25$	$-24 \leq h \leq 27$, $-14 \leq k \leq 14$, $-24 \leq l \leq 24$	$-12 \leq h \leq 12$, $-13 \leq k \leq 12$, $-32 \leq l \leq 35$
Reflections collected	32605	33793	24023
Independent reflections	$R_{int} = 0.0528$, $R_{sigma} = 0.0958$]	$R_{int} = 0.0914$, $R_{sigma} = 0.1125$	$R_{int} = 0.0447$, $R_{sigma} = 0.0733$
Data/restraints/parameters	17407/169/880	9951/137/500	11088/0/631
GOF on F^2	1.038	1.113	1.036
Final R indexes [I>=2σ (I)]	$R_1 = 0.0630$, $wR_2 = 0.1605$	$R_1 = 0.1347$, $wR_2 = 0.2015$	$R_1 = 0.0511$, $wR_2 = 0.0900$
Final R indexes [all data]	$R_1 = 0.1011$, $wR_2 = 0.1892$	$R_1 = 0.2423$, $wR_2 = 0.2445$	$R_1 = 0.0768$, $wR_2 = 0.0995$
Largest diff. peak/hole /e $Å^{-3}$	1.38/-1.14	0.96/-0.67	0.46/-0.55