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Supporting Information

Polyoxometalate-based Organic-Inorganic Hybrids for Stabilization and Optical Switching of Liquid Crystal Blue Phase

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1 Synthesis and Characterization of POM Hybrids

Chemical materials: All chemicals were purchased from Alpha Aesar and used as received. Acetonitrile and chloroform were distilled from CaH_2 prior to use. $[(C_4H_9)_4N]_4[(SiW_{11}O_{39})O\{Si(CH_2)_3NH_2{\bullet}HCl\}_2]$ (**SiW_{11}-NH_2**), 4-octyloxyazobenzoic acid, and 4-octyl-oxyazophenol were prepared according to the published procedure and fully characterized.[1,2]

Measurements: ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR spectra were obtained on a Bruker AV400 NMR spectrometer at resonance frequency of 400 MHz. Fourier transform infrared (FT-IR) spectra were carried out on a Bruker Vector 22 infrared spectrometer using KBr pellet method. Electrospray ionisation mass spectra (ESI-MS) were recorded on a Xevo G2 QT ESI-MS calibrated using a 5 mM sodium formate solution in 90:10 2-propanol:water, and all experiments were performed in negative mode using acetonitrile as solvent. Elemental Analyses were completed by using varioEL cube from Elementar Analysensysteme GmbH.

Synthesis of POM Hybrid 1

$[(C_4H_9)_4N]_4[(SiW_{11}O_{39})O\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]$ (POM Hybrid 1): POM Hybrid 1 was prepared according to our previous work.[3] Yield: 76.90%. ^{1}H-NMR (CD_3CN-d_3, ppm): δ = 0.80 (t, 4H), 0.92 (t, 6H), 1.00 (t, 48H), 1.39 (m, 48H), 1.52 (m, 4H), 1.66 (m, 32H), 1.84 (m, 4H), 1.93 (m, 4H), 3.16 (t, 32H), 3.52 (m, 4H), 4.14 (m, 4H), 7.43 (t, 2H), 7.84 (m, 8H), 7.95 (m, 8H). ^{13}C-NMR (CD_3CN-d_3, ppm): δ = 8.10, 9.61, 12.59, 13.08, 19.06, 22.06, 23.08, 25.32, 28.66, 31.24, 41.65, 46.96, 58.02, 64.95, 69.17, 112.85, 122.05, 124.89, 127.97, 156.82, 158.01, 165.90.

^{29}Si-NMR (CD_3CN-d_3, ppm): δ = -52.00, -84.69. FT-IR (KBr, cm^{-1}): ν = 3413, 2970, 2932, 2873, 1645, 1586, 1532, 1485, 1380, 1249, 1186, 1046, 967, 949, 903, 856, 802, 755, 532. Elemental analysis (%) calcd for $C_{112}H_{208}N_{10}O_{44}Si_3W_{11}$ (4505.39): C 29.83, H 4.62, N 3.11; found: C 29.19, H 4.39, N 3.09.

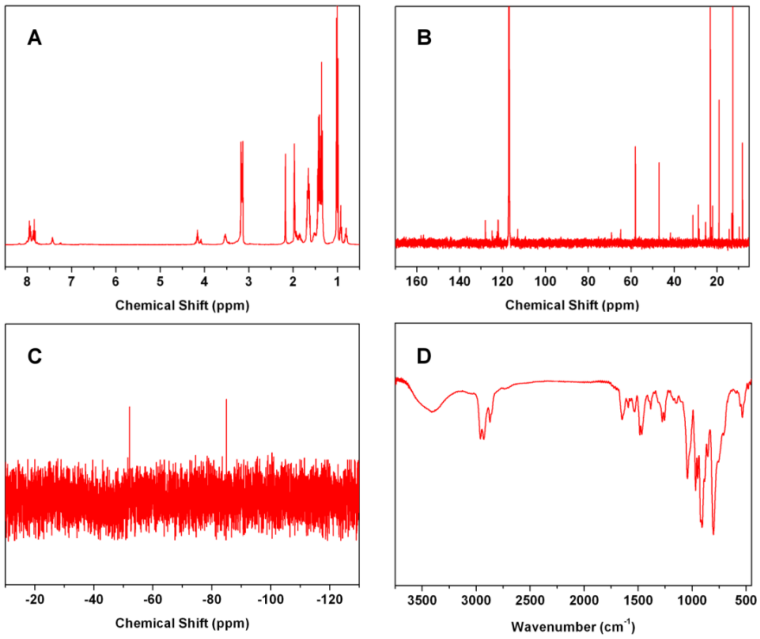


Figure S1. ^{1}H-NMR (A), ^{13}C-NMR (B), ^{29}Si-NMR (C), and FT-IR (D) spectra of POM Hybrid 1

Synthesis of POM Hybrid 2

4-(12-bromododecyloxy)-4’-octyloxyazobenzene (3): 4-octyloxyazophenol (3.26 g, 10 mmol) was added to a solution of 1,12-dibromododecane (6.56 g, 20 mmol) and K_2CO_3 (4.14 g, 30 mmol) in 150 mL acetone. The reaction mixture was refluxed for 24 hours. After removing the solvent under vacuum, the residue was dissolved in chloroform. Organic phase was washed with water, dried over anhydrous Na_2SO_4, and then evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/acetic ether (2:1, v/v) as eluent. Yield: 51.6%. ^{1}H-NMR

($CDCl_3$, ppm): δ = 0.89 (t, 3H), 1.29 (m, 20H), 1.48 (m, 6H), 1.82 (m, 6H), 3.41 (t, 2H), 4.03 (t, 4H), 7.00 (d, 4H), 7.86 (d, 4H). ^{13}C-NMR ($CDCl_3$, ppm): δ = 161.16, 146.95, 124.29, 114.67, 68.35, 34.06, 32.85, 31.82, 29.53, 29.37, 29.23, 28.77, 28.18, 26.04, 22.67, 14.11.

Methyl-3,5-bis((12-(4-((4-(octyloxy)phenyl)diazenyl)phenoxy)dodecyl)oxy) benzoate (4): 3 (1.27 g, 2.2 mmol) was added to a solution of methyl 3,5-dihydroxybenzoate (168 mg, 1 mmol), K_2CO_3 (470 mg, 3.3 mmol), and a catalytic amount of KI in butan-2-one 25 mL. The mixture was stirred at reflux for 36 hours and then butan-2-one was evaporated. The residue was washed with petroleum ether and methanol successively for several times. The product was obtained after recrystallization in acetone. Yield: 72%. ^{1}H-NMR ($CDCl_3$, ppm): δ = 0.89 (t, 6H), 1.30 (m, 40H), 1.47 (m, 12H), 1.79 (m, 12H), 3.89 (s, 3H), 3.96 (t, 4H), 4.03 (t, 8H), 6.63 (s, 1H), 6.98 (d, 8H), 7.15 (s, 2H), 7.86 (d, 8H). ^{13}C-NMR ($CDCl_3$, ppm): δ = 167.01, 161.18, 160.16, 146.93, 131.83, 124.30, 114.67, 107.63, 106.60, 68.33, 52.19, 31.82, 29.56, 29.37, 29.23, 29.19, 26.03, 22.67, 14.11.

3,5-bis((12-(4-((4-(octyloxy)phenyl)diazenyl)phenoxy)dodecyl)oxy)benzoic acid (5): 4 (1.15 g, 1 mmol) and KOH (700 mg, 12.5 mmol) were dissolved in THF/EtOH (1:1, v/v) 100 mL, and heated at 78 °C for 4 hours. After evaporating the solvent under reduce pressure, the residue was suspended in 100 mL H_2O and adjusted pH value to 1. The solid compound was collected by filtration and dried in the air. Yield: 98%. ^{1}H-NMR ($CDCl_3$, ppm): δ = 0.92 (t, 6H), 1.33 (m, 40H), 1.49 (m, 12H), 1.84 (m, 12H), 4.00 (t, 4H), 4.04 (t, 8H), 6.71 (s, 1H), 7.00 (d, 8H), 7.24 (s, 2H), 7.88 (d, 8H).

^{13}C-NMR ($CDCl_3$, ppm): δ = 170.01, 161.17, 160.22, 146.94, 130.81, 124.30, 114.67, 108.14, 107.34, 68.34, 31.82, 29.56, 29.37, 29.23, 29.16, 26.04, 22.67, 14.11.

$[(C_4H_9)_4N]_4[(SiW_{11}O_{39})O\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_6H_4N_2C_6H_4OC_8H_{17})_2\}_2]$ (POM Hybrid 2): Yield: 80%.[3] ^{1}H-NMR ($CDCl_3$, ppm): δ = 0.91 (t, 16H), 1.00 (t, 48H), 1.31 (m, 80H), 1.50 (m, 56H), 1.69 (m, 32H), 1.82 (m, 24H), 2.03 (m, 4H), 3.32 (t, 32H), 3.71 (m, 4H), 4.03 (m, 24H), 6.50 (s, 2H), 7.00 (d, 16H), 7.87 (d, 16H). ^{13}C-NMR ($CDCl_3$, ppm): δ = 166.68, 161.22, 160.17, 146.90, 124.29, 114.66, 105.10, 68.38, 58.61, 31.82, 29.70, 29.65, 29.62, 29.45, 29.37, 29.24, 26.04, 24.02, 22.66, 19.72, 15.28, 14.11, 13.86. ^{29}Si-NMR ($CDCl_3$, ppm): δ = -51.42, -84.97. FT-IR (KBr, cm^{-1}): ν = 3404, 2926, 2858, 1648, 1593, 1535, 1468, 1385, 1321, 1249, 1156, 1113, 1040, 956, 908, 848, 803, 756, 545. Elemental analysis (%) calcd for $C_{212}H_{360}N_{14}O_{54}Si_3W_{11}$ (6075.68): C 41.87, H 5.92, N 3.22; found: C 41.36, H 5.59, N 3.02.

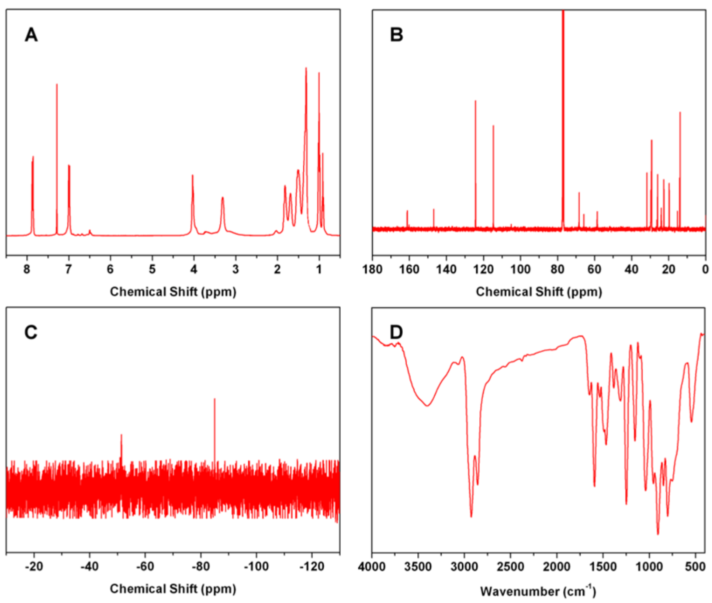


Figure S2. ^{1}H-NMR (A), ^{13}C-NMR (B), ^{29}Si-NMR (C), and FT-IR (D) spectra of POM Hybrid 2

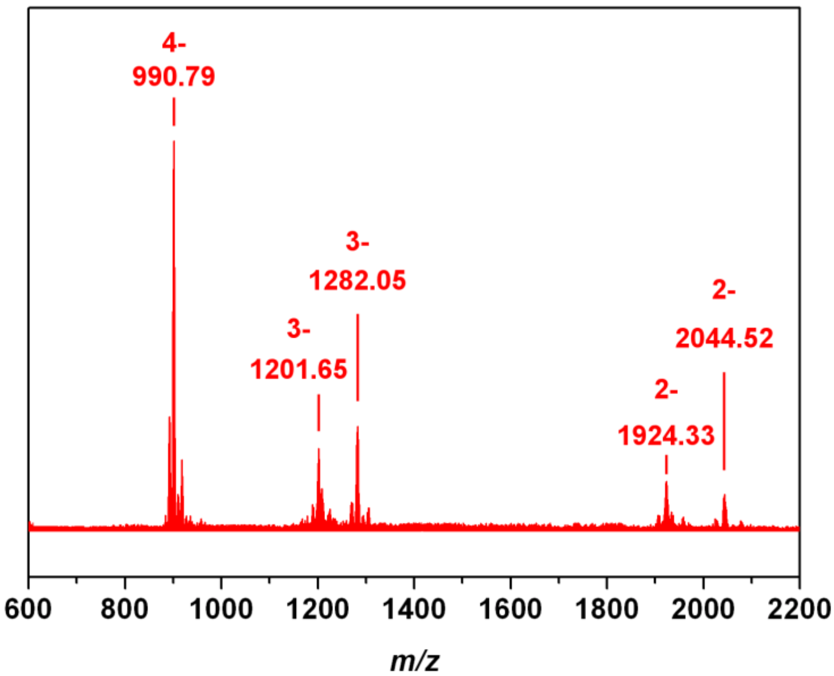


Figure S3. ESI-MS spectrum of POM Hybrid 1

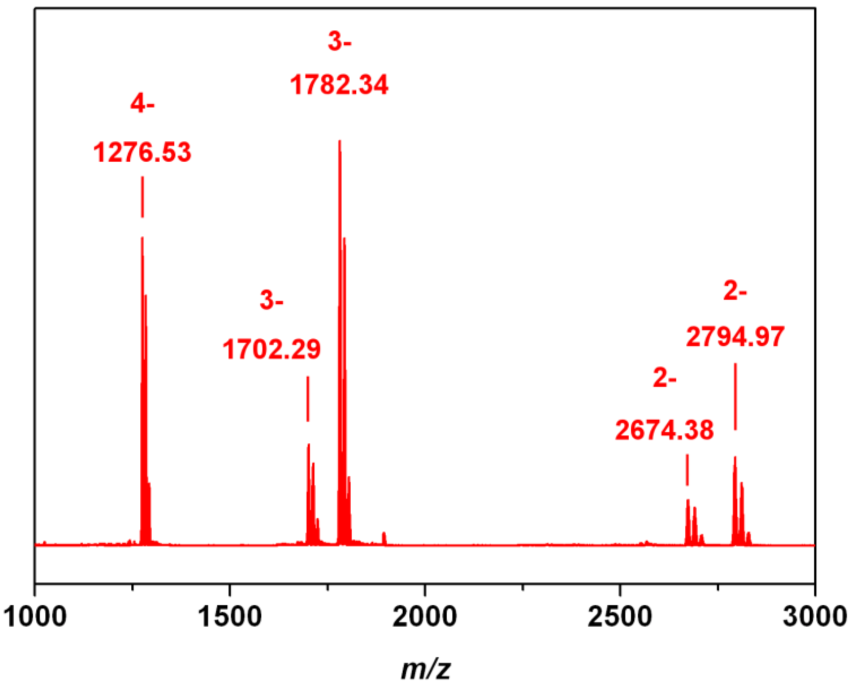


Figure S4. ESI-MS spectrum of POM Hybrid 2

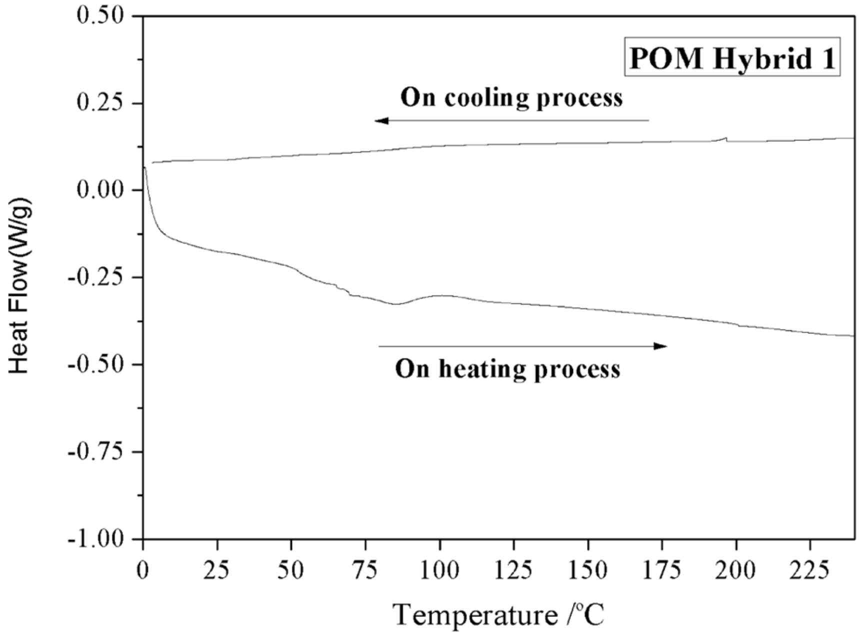
Table S1. Detailed assignment of ESI-MS spectra for POM Hybrid 1.

No.	Ion	m/z Calculated	m/z Observed
1	$2H_2O + [(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]^{4-}$	892.88	892.81
2	$HCOONa + [(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]^{4-}$	900.90	900.79
3	$2H_2O + HCOONa + [(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]^{4-}$	909.89	909.53
4	$4H_2O + HCOONa + [(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]^{4-}$	918.89	918.52
5	$2H_2O + \{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1190.35	1190.34
6	$HCOONa + \{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1201.69	1201.65
7	$2H_2O + HCOONa + \{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1213.52	1213.31
8	$4H_2O + HCOONa + \{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1225.52	1225.30
9	$2H_2O + \{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1271.34	1271.40
10	$HCOONa + \{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1282.00	1282.05
11	$2H_2O + HCOONa + \{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1294.00	1294.04
12	$4H_2O + HCOONa + \{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{3-}$	1306.00	1306.02
13	$2H_2O + \{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	1907.51	1907.48
14	$HCOONa + \{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	1923.52	1923.44
15	$2H_2O + HCOONa + \{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	1941.51	1941.42
16	$4H_2O + HCOONa + \{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	1959.51	1959.40
17	$2H_2O + \{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	2028.23	2028.54
18	$HCOONa + \{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	2044.24	2044.52
19	$2H_2O + HCOONa + \{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	2062.24	2062.52
20	$4H_2O + HCOONa + \{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_4N_2C_6H_4OC_8H_{17}\}_2]\}^{2-}$	2080.23	2080.48

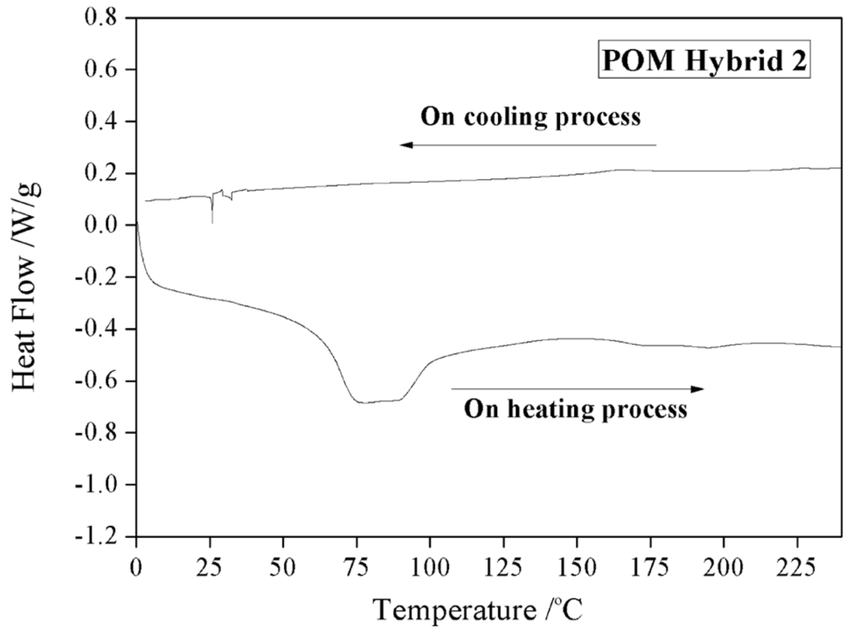
Table S2. Detailed assignment of ESI-MS spectra for POM Hybrid 2.

No.	Ion	m/z Calculated	m/z Observed
1	$[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]^{4-}$	1276.46	1276.53
2	$2H_2O + [(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]^{4-}$	1285.46	1285.52
3	$4H_2O + [(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]^{4-}$	1294.46	1294.50
4	$\{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{3-}$	1702.28	1702.29
5	$2H_2O + \{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{3-}$	1714.28	1714.27
6	$4H_2O + \{H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{3-}$	1726.28	1726.26
7	$\{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{3-}$	1782.77	1782.34
8	$2H_2O + \{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{3-}$	1794.77	1794.33
9	$4H_2O + \{(TBA)[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{3-}$	1806.77	1806.32
10	$\{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{2-}$	2674.65	2674.38
11	$2H_2O + \{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{2-}$	2692.65	2692.35
12	$4H_2O + \{(TBA)H[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{2-}$	2710.65	2710.32
13	$\{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{2-}$	2795.38	2794.97
14	$2H_2O + \{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{2-}$	2813.38	2812.95
15	$4H_2O + \{(TBA)_2[(SiW_{11}O_{40})\{Si(CH_2)_3NHCOC_6H_3(O(CH_2)_{12}OC_{12}H_8N_2OC_8H_{17})_2\}_2]\}^{2-}$	2831.38	2830.91

2 The DSC of POM Hybrids



(a)



(b)

Figure S5 DSC measurement of POM Hybrid 1 (a) and POM Hybrid 2 (b) on heating and cooling recycle. Note: the peaks observed at ca. 75 ℃ during the heating processes could be attributed to the loss of crystalliferous water molecules.

3 Measurement of elastic constants

Table S3. Temperature dependency of elastic constants in samples 1 and 2; K_{11} and K_{33}, elastic constant ratio; K_{33}/K_{11}, dielectric constant anisotropy; Δε, threshold voltage; V_{th}

BYLC-X								
T-Tc(^{o}C)	Δε	$C_{//}$	C_{-eff}	V_{th}(V)	r_1	K_{11}(PN)	K_{33}(PN)	K_{33}/K_{11}
-1.0	25.7	5410	4410	31.9	10.59	13.7	13.9	1.01
-2.0	27.5	4890	3780	71.2	11.54	12.5	17.0	1.36
-3.0	34.83	4750	3350	70.8	18.33	15.7	25.2	1.61
-4.0	37.7	4560	3160	72.4	21.09	16.0	26.6	1.66
-5.0	35.8	4420	2850	73.1	19.49	15.5	35.0	2.26
BYLC-X +3% POM Hybrid 1								
T-Tc(^{o}C)	Δε	$C_{//}$	C_{-eff}	V_{th}(V)	r_1	K_{11}(PN)	K_{33}(PN)	K_{33}/K_{11}
-1.0	49.8	9680	7630	87.4	10.36	30.0	64.0	2.13
-2.0	57.5	8800	6470	86.9	15.57	36.0	61.6	1.71
-3.0	58.9	8080	5720	87.1	17.69	40.0	64.5	1.61
-4.0	59.9	7490	5070	86.4	17.76	38.0	75.0	1.97
-5.0	58.5	6830	4480	85.3	20.37	39.5	66.0	1.67
BYLC-X +3% POM Hybrid 2								
T-Tc(^{o}C)	Δε	$C_{//}$	C_{-eff}	V_{th}(V)	r_1	K_{11}(PN)	K_{33}(PN)	K_{33}/K_{11}
-1.0	37.0	8530	6770	99.3	6.676	35.3	196.0	5.55
-2.0	45.8	7990	5990	86.5	10.94	26.0	240.0	9.23
-3.0	45.1	7380	5440	95.2	11.43	34.1	260.0	7.62
-4.0	46.0	6880	4800	78.3	12.69	25.6	251.0	9.80
-5.0	45.1	6270	4320	85.0	13.05	32.3	230.0	7.12

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