Organic/inorganic hybrids formed by polyoxometalate-based surfactants with cationic polyelectrolytes and block copolymers

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Materials and Instruments. Poly(4-vinylpyridine) (PVP) with a molecular weight of 60,000 was obtained from Aldrich. PMV and POV were synthesized by the quantization of PVP with iodomethane and 1-iodooctadecane as described in previous literatures.[s1] Infrared (IR) showed that the bands at 1597 and 1414 cm^{-1} associated with the pyridine rings disappeared completely, while the new bands appeared at 1644 and 1466 cm^{-1}, corresponding to the valence oscillations in the quarternized pyridine rings. S_{480}-*b*-V_{57} and poly(ethylene glycol-*b*-4-vinylpyridine) were purchased from Polymer Source Inc. and used without further purification. The numbers in subscript denote the degree of polymerization. EG_{193}-*b*-V_{57} was synthesized by the quantization of poly(ethylene glycol-*b*-4-vinylpyridine) with iodomethane, which was similarly confirmed by the IR spectra. The POM-based surfactant of An-16 was prepared according to the literature's procedures[2] and further confirmed by the ^1H NMR and infrared spectra. IR spectra (KBr) were measured with a Nicolet NEXUS 670 spectrometer. ^1H NMR spectra were measured in dimethyl sulfoxide DMSO-d_6 solutions with a Varian 600 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer with a He-Ne laser (532 nm). TEM images were obtained with a JEOL JEM-1230 operating at 120 kV. SEM images were obtained with a Hitachi S-4800. To prevent electric charging, a 4-nm thick gold layer was deposited on the specimen by using a Hitachi E-1045 ion sputter. Powder X-ray diffraction (XRD) measurements were performed with an Bruker D8 ADVANCE X'Pert Pro X-ray diffractometer using Cu–Ka radiation (λ =1.5418 Å). Elemental analyses were performed with an Elementar VarioELcube. Thermogravimetric analysis

(TGA) was measured on a Perkin-Elmer 7 Series Thermal Analysis System. All spectroscopic measurements were carried out at room temperature.

Preparation and Characterization of the Hybrids of Polyelectrolytes and An_{16}. PMV-An_{16} was prepared as follows: An_{16} (0.2 g, 7.6 $\times 10^{-5}$ mol) was dissolved into 20 mL of the mixed solvents of acetonitrile/water containing 50 v% acetonitrile. The dropwise addition of the aqueous solution of PMV (0.0563 g, 2.3 $\times 10^{-4}$ mol) into the solution of An_{16} yielded an orange suspension. The resultant suspension was further stirred for three hours to allow complete electrostatic interaction between An_{16} and PMV. The orange solid product was collected by filtration, washed with water, and dried in vacuo. IR (KBr): 3461, 3274, 3122, 3054, 2960, 2924, 2854, 1670, 1642, 1568, 1547, 1515, 1467, 1375, 1307, 1228, 1186, 1108, 1028, 942, 921, 850, 666, 562, 463 cm^{-1}. Elemental analysis calcd. for $(C_8H_{10}N)_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_2)_{14}CH_3\}_2]\cdot(H_2O)_7$ (2118.23): C 36.29, H 5.71, N, 3.31. Found: C 36.29, H 5.35, N 3.41. PMV-An_{16} was prepared according to the similar procedure except that POV was dissolved into tetrahydrofuran. IR (KBr): 3471, 3279, 3053, 3122, 2961, 2924, 2853, 1670, 1642, 1568, 1547, 1515, 1465, 1375, 1312, 1261, 1225, 1171, 1098, 1027, 942, 921, 850, 805, 667, 562, 463 cm^{-1}. Elemental analysis calcd. for $(C_{25}H_{42}N)_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_2)_{14}CH_3\}_2]\cdot(H_2O)_6$ (2809.64): C 49.16, H 7.68, N 2.49. Found: C 49.17, H 7.39, N 2.43.

References:

S1. (*a*) J. P. Gouin, F. Bosse, D. Nguyen, C. E. Williams and A. Eisenberg, *Macromolecules*, 1993, **26**, 7250; (*b*) J. P. Gouin, C. E. Williams and A. Eisenberg, *Macromolecules*, 1989, **22**, 4573.

S2. Y.-F. Song, N. McMillan, D.-L. Long, J. Thiel, Y. Ding, H. Chen, N. Gadegaard and L. Cronin, *Chem. Eur. J.*, 2008, **14**, 2349.

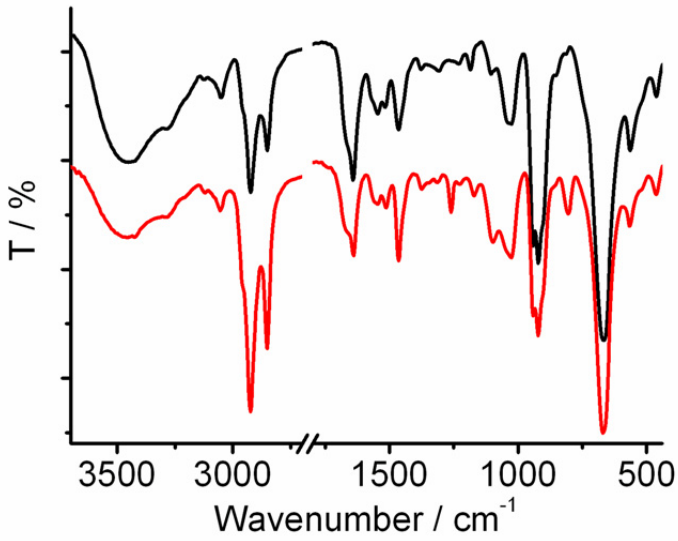

Fig. S1 IR spectra of the POM-based PSCs, PMV-An_{16} (black line) and POV-An_{16} (red line).

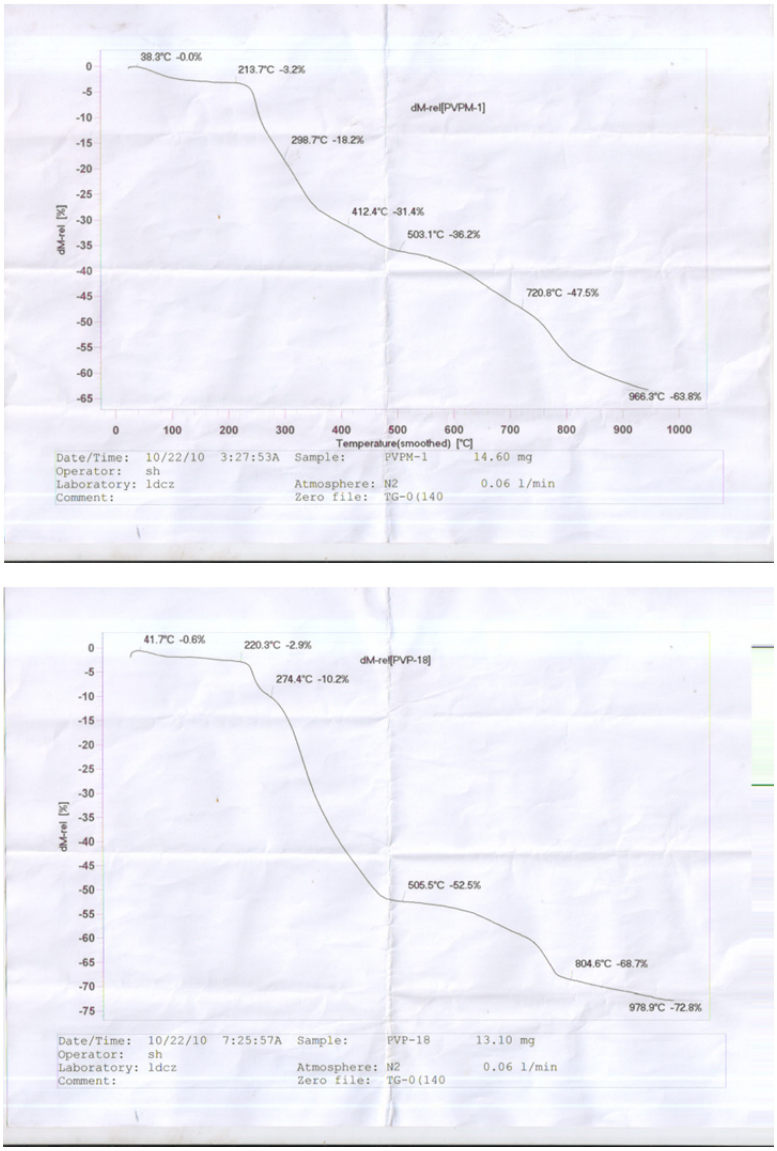

Fig. S2 TGA curves of PMV-An$_{16}$ (top) and POV-An$_{16}$ (bottom).

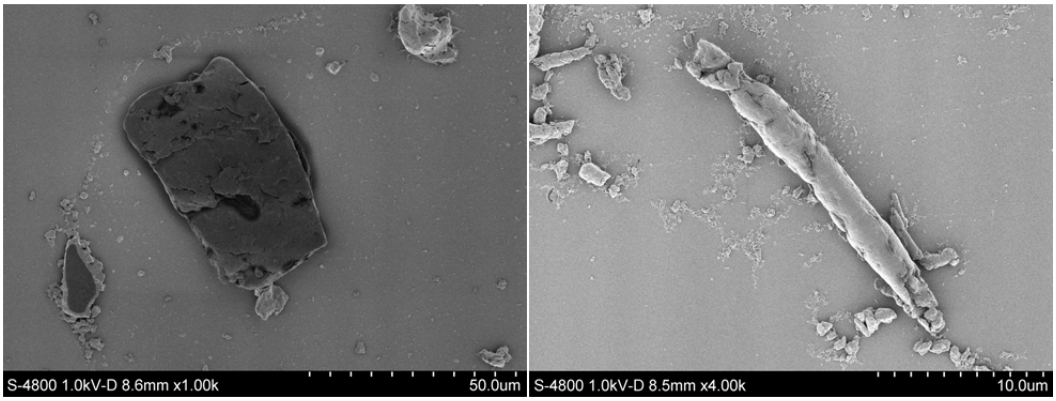

Fig. S3 SEM images of PMV-An$_{16}$ (left) and POV-An$_{16}$ (right).

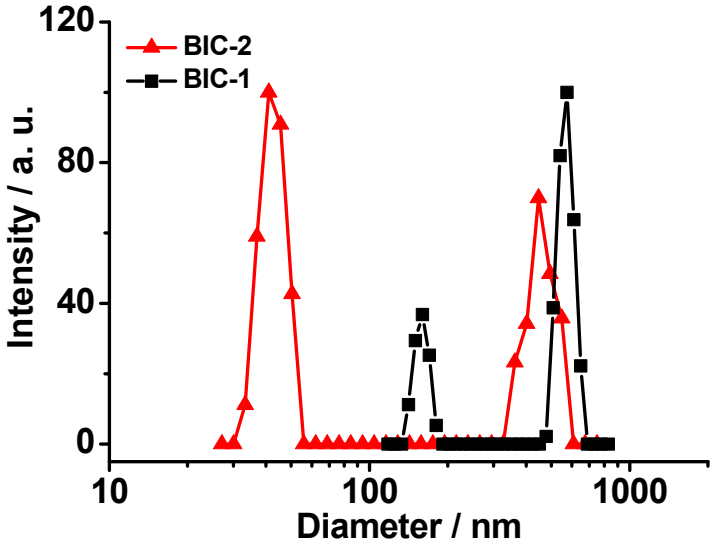

Fig. S4 DLS plots of BIC-1 in water and BIC-2 in toluene.

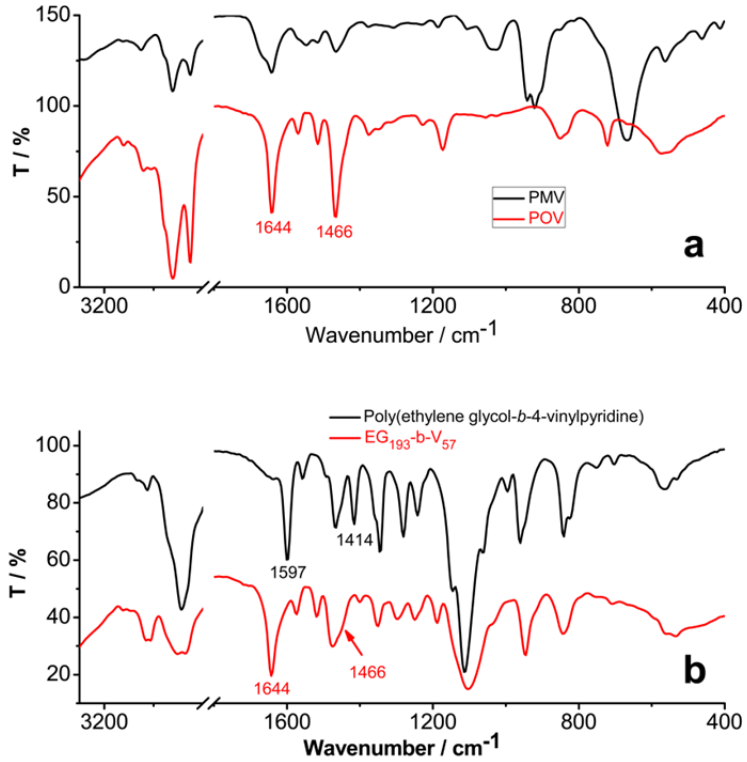

Fig. S5 IR spectra of the PMA, POV, and EG_{193}-*b*-V_{57}.