Supporting Information

Surface Segregation of Star-Shaped Polyhedral Oligomeric Silsesquioxane in Polymer Matrix

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Differential scanning calorimetric (DSC) chart

Figure S1 shows a DSC chart of the third scan for the poly(methyl methacrylate) (PMMA) used. A glass transition temperature (T_g) was determined to be 396 K.

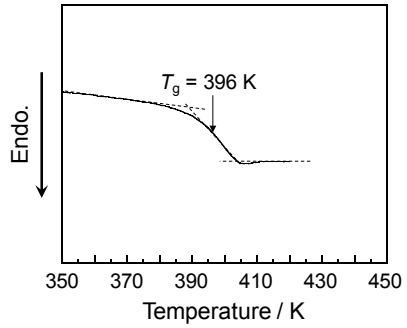

Figure S1. A DSC chart of the third scan for the PMMA used in this study. Dotted lines denote the extrapolated baselines. A heating rate was 10 K•min^{-1}.

Fabrication of the organic field-effect transistor (OFET)

Pentacene was purchased from Sigma-Aldrich Co. LCC (St Louis, MO, USA). Silicon substrates with a size of 30 mm × 30 mm × 0.5 mm were cleaned in piranha solution (H_2SO_4 : H_2O_2 = 80 : 20 v/v) at 353 K for 2 h, then washed by deionized water, isopropanol, and finally ultraviolet-ozone treatment. As a gate electrode, a 50-nm-thick Al layer was vacuum-deposited onto the Si substrate at a deposition rate of 0.1 nm•s^{-1} under a pressure of 10^{-4} Pa. Then, blend of star-shaped polyhedral oligomeric silsesquioxane (s-POSS) and PMMA and homo-PMMA films with a thickness of ca. 200 nm were prepared by a spin-coating method from a toluene solution onto the gate electrodes. The films were annealed at 433 K for 24 h under vacuum. After drying, pentacene and gold were successively vacuum-deposited at a deposition rate of 0.1 nm•s^{-1} under a pressure of 10^{-4} Pa. Separately, we prepared the pentacene-deposited s-POSS/PMMA blend film by the same method as that of transistors without electrodes for the grazing incidence wide-angle X-ray diffraction (GIWAXD) measurement.

Concentration depth profile

Figure S2(a) shows take-off angle of photoelectron (ϕ_e) dependence of intensity ratio of Si_{2p} to C_{1s} (I_{Si2p}/I_{C1s}) for the s-POSS/PMMA films. Symbols are the experimental data collected at ϕ_e from 15 to 90°. Solid curves in Figure S2(a) show the best-fit calculated I_{Si2p}/I_{C1s} – sin ϕ_e relationship using eq. (2) in the main text based on the two-layer model, as shown in Figure S2(b). Although the two-layer model reproduced the experimental I_{Si2p}/I_{C1s} – sin ϕ_e relationship, the $n_{Si/C}$ values for the surface s-POSS enriched layer were larger than the value of the neat s-

POSS (= 0.31). Thus, it is apparent that the two-layer model with the 1.0 nm-thick s-POSS enriched layer was not suitable for the s-POSS/PMMA blend films.

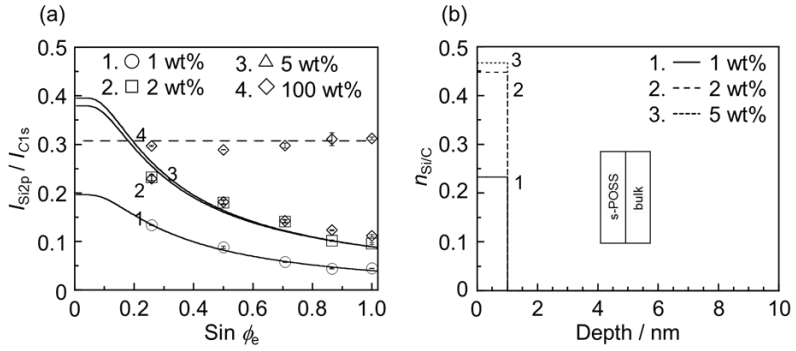

Figure S2. (a) Sin ϕ_e dependence of the integral intensity ratio of Si_{2p} to C_{1s} (I_{Si2p}/I_{C1s}) for s-POSS/PMMA blend films. (b) Model depth profile of molar fraction of Si to C ($n_{Si/C}$) to best-fit experimental data shown in panel (a).

Surface POSS fraction

The surface POSS fraction in weight (w^s_{POSS}) shown in Figure 3(c) was defined as the sum of the surface weight fraction of the outlying and central POSS units ($w^s_{POSS\text{-}o}$ and $w^s_{POSS\text{-}c}$). The number ratio of the outlying to central POSS units is 8:1. Thus, the w^s_{POSS} can be given by,

$$w^s_{POSS} = w^s_{POSS\text{-}o}+w^s_{POSS\text{-}c} = w^s_{POSS\text{-}o}+(1/8)\bullet w^s_{POSS\text{-}o}\bullet(M_{POSS\text{-}c}/M_{POSS\text{-}o}) \quad \text{(S1)}$$

where $M_{POSS\text{-}o}$ and $M_{POSS\text{-}c}$ are the molecular weight of the outlying and central POSS units, respectively. Then, the w^s_{POSS} can be extracted from the $n_{Si/C}$ value averaged over the first and second layers shown in Figure 3(b) using the eq. (S1) and (S2),

$$n_{Si/C} = (8\ w^s_{POSS\text{-}o}/M_{POSS\text{-}o}+16\ w^s_{POSS\text{-}c}/M_{POSS\text{-}c})/$$
$$[5\bullet\{(1-w^s_{POSS\text{-}o}-w^s_{POSS\text{-}c})/M_{PMMA}\}+30\bullet w^s_{POSS\text{-}o}/M_{POSS\text{-}o}+16\bullet w^s_{POSS\text{-}c}/M_{POSS\text{-}c})] \quad \text{(S2)}$$

where M_{PMMA} is the molecular weight of the methyl methacrylate monomer.

Crystalline structure

The grazing incidence X-ray wide-angle diffraction (GIWAXD) measurements for pentacene-deposited s-POSS/PMMA films were carried out at BL03XU at SPring-8, Hyogo, Japan. The wavelength of the incident X-ray was 0.1 nm. The incident angle of X-ray was 0.14 deg. A flat panel (C9827DK-10, Hamamatsu Photonics K. K., Japan) was used as a detector for the GIWAXD measurement. The sample-to-detector distance of the GIWAXD measurement was calibrated to 112 mm.

Figure S3 shows one-dimensional GIWAXD patterns for the pentacene on the s-POSS/PMMA blend films. The weight fractions of s-POSS in the bulk were 1 and 2wt%, respectively. For both samples, two diffraction peaks were observed at the scattering vector, q = 4.1 and 4.4 nm^{-1}, respectively, which were assignable to (001) in the orthorhombic and triclinic phases, the so-called "bulk phase" and "thin-film phase", respectively [1,2].

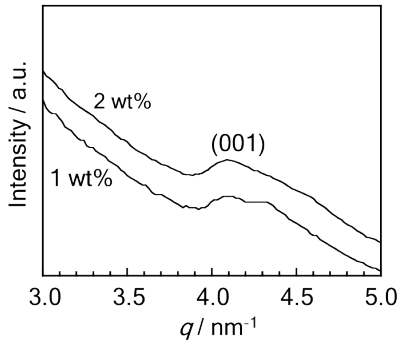

Figure S3. One-dimensional GIWAXD patterns for a pentacene layer on s-POSS/PMMA blend films.

References

1. Yoshida, H.; Inaba, K.; Sato, N., X-Ray Diffraction Reciprocal Space Mapping Study of the Thin Film Phase of Pentacene. *Appl. Phys. Lett.* **2007,** *90*, 181930.
2. Kakudate, T.; Yoshimoto, N.; Saito, Y., Polymorphism in Pentacene Thin Films on SiO_2 Substrate. *Appl. Phys. Lett.* **2007,** *90*, 081903.