## Supporting Information

# The Origin of Thermally-Stable White-Light Emission Property of POSS–Conjugated Polymer Hybrid films

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#### **Experimental section**

#### Materials.

Propylamine, potassium *tert*-butoxide (*tert*-BuOK),  $Pd_2(dba)_3$ , 4-(N,N-9diphenylamino)-benzaldehyde, 2,2'-bithiophene-5-carboxaldehyde, anthracenecarboxaldehyde, 2-bromo-9,9-dibromofluorene, triphenylamine, anthracene, 2,2'-bithiophene, 9,10-diphenylanthracene, 9,9-diphenylfluorene, 2,1,3-benzothiadiazole were purchased from Tokyo Chemical Industry Co, Ltd. and used without purification. Methanol (MeOH), ethanol (EtOH), acetone, n-hexane, chloroform (CHCl<sub>3</sub>), toluene, *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), pyridine, Cs<sub>2</sub>CO<sub>3</sub>, phenylboronic acid were purchased from FUJIFILM Wako Pure Chemical Corporation without 4,7-Dibromo-2,1,3-benzothiadiazole, 4and used purification. formylphenylboronic acid, A Phos Pd G3, 9,9-dihexyl-2,7-dibromofluorene, 9,9dihexylfluorene-2,7-diboronic acid were purchased from sigma Aldrich Co. LLC. and 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl without purification. used (XPhos) was purchased from Strem Chemicals, Inc. and used without purification. n-Butyllithium in n-hexane was purchased from Kanto Chemical Co. Inc. and used without purification. 2,1,3-Benzothiazole-4-carboxaldehyde was purchased from Apollo Scientific Ltd. and used without purification. Tetrahydrofuran (THF) (FUJIFILM Wako Pure Chemical Corporation) and triethylamine (Et<sub>3</sub>N) (Kanto Chemical Co., Inc.) were purified by passage through solvent purification columns under N2 pressure. Octakis(3aminopropyl) POSS hydrochloride (Amino-POSS),<sup>1</sup> 4-(1,2,2-triphenylethenyl)benzaldehyde,<sup>2</sup> 1,1,2,2-tetraphenylethene  $(TPE)^{3}$ 1,4-bis(chloromethyl)-2-(2'- ethylhexyloxy)-5-methoxybenzene,<sup>4</sup> 9-(4-formylphenyl)-10-phenylanthracene,<sup>5</sup> poly(3-hexylthiophene-2,5-diyl) (P3HT),<sup>6</sup> 4-bromo-7-(5-thienykthiophene-2ly)-2,1,3-benzothiadiazole,<sup>7</sup> 5,5'-bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene,<sup>8</sup> **TPE-POSS**,<sup>9</sup> , **Propyl TPE**<sup>9</sup>, and **MEH-PPV**<sup>9</sup> were synthesized according to literatures.

#### Methods.

<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded on JEOL AL400 instruments at 400, 100 and 80 MHz respectively. Samples were analyzed in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, and C<sub>5</sub>D<sub>5</sub>N. The chemical shift values were expressed relative to Me<sub>4</sub>Si as an internal standard in CDCl<sub>3</sub>. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel<sup>®</sup> C-300 silica gel. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Scientific EXACTIVE spectrometer for Fisher Matrix Assisted Laser Desorption/Ionization (MALDI) and a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI). UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed at room temperature. Fluorescence emission spectra were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer and an Oxford Optistat DN for temperature control. Absolute photoluminescence quantum efficiency ( $\Phi_{PL}$ ) was recorded on a Hamamatsu Photonics Quantaurus-QY Plus C13534-01. Elemental

analyses were performed at the Microanalytical Center of Kyoto University. Differential scanning calorimetry (DSC) was recorded on a Hitachi High-Tech Science Corporation. TA DSC7020. The sample on the aluminum pan was heated at the rate of 10 °C/min under nitrogen flowing (50 mL/min). Scanning electron microscopy (SEM) was recorded on a JEOL JSM-6610A. Transmission Electron Microscope (TEM) was recorded on a JEOL JEM-2200FS. Contact angle was recorded on Kyowa Kaimenkagaku Co., Ltd. CA-D.

#### **Synthetic Procedures and Characterization**

#### Synthesis of anth-POSS



**Amino-POSS** (100 mg, 0.085 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (10 mL) and Et<sub>3</sub>N (118  $\mu$ L, 0.852 mmol) were added to the flask. 9-Anthracenecarboxaldehyde (0.426 M in THF, 2.0 mL, 0.852 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the yellow precipitate was washed with MeOH. The residue was purified by reprecipitation with THF (good solvent) and -78 °C MeOH (poor solvent) to afford **anth-POSS** (178 mg, 0.075 mmol, 88% yield) as a yellow solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 9.13$  (8H, s), 8.35 (16H, d, J = 8.04 Hz), 8.26 (8H, s), 7.83 (16H, d, J = 8.32 Hz), 7.38-7.26 (32H, m), 3.85 (16H, t, J = 6.56 Hz), 2.10 (16H, tq, J = 8.28, 8.28 Hz), 0.98 (16H, t, J = 8.52 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 160.1$ , 131.1, 129.8, 129.0, 128.7, 128.1, 126.4, 125.0, 124.7, 65.4, 24.6, 10.0 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 80 MHz):  $\delta = -66.3$  (s) ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 2385.7879; found, m/z 2385.7802. Elemental analysis calcd. for C<sub>144</sub>H<sub>128</sub>N<sub>8</sub>O<sub>12</sub>Si<sub>8</sub>, C 72.45 H 5.40 N 4.69, found, C 72.23 H 5.36 N 4.64.



Chart S1. <sup>1</sup>H NMR spectrum of anth-POSS in CDCl<sub>3</sub>.



Chart S2. <sup>13</sup>C NMR spectrum of anth-POSS in CDCl<sub>3</sub>.



Chart S3. <sup>29</sup>Si NMR spectrum of anth-POSS in CDCl<sub>3</sub>.

#### Synthesis of Propyl anth



9-Anthracenecarboxaldehyde (100 mg, 0.485 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (30.0 mL) was added to the flask and the solution was heated to 70 °C. Propylamine (39.8  $\mu$ L, 0.485 mmol) was added to this stirred yellow solution. After the mixture was stirred at a reflux temperature for 24 h, the solvent was removed with a rotary evaporator to afford **Propyl anth** (111 mg, 448 mmol, 92% yield) as a yellow solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 9.43$  (1H, t, J = 1.48 Hz), 8.51-8.49 (3H, m), 8.02 (2H, dd, J = 8.04, 1.44 Hz), 7.55-7.46 (4H, m), 3.92 (2H, td, J = 7.08, 1.20 Hz), 1.96 (2H, qt, J = 7.32, 7.32 Hz), 1.03 (3H, t, J = 7.32 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 159.9$ , 131.3, 129.9, 129.1, 128.8, 128.5, 126.6, 125.2, 124.8, 65.1, 24.3, 12.1 ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 248.1434; found, m/z 248.1434. Elemental analysis calcd. for C<sub>18</sub>H<sub>17</sub>N, C 87.41 H 6.93 N 5.66, found, C 87.34 H 6.84 N 5.49.



Chart S4. <sup>1</sup>H NMR spectrum of Propyl anth in CDCl<sub>3</sub>.



Chart S5. <sup>13</sup>C NMR spectrum of Propyl anth in CDCl<sub>3</sub>.

#### Synthesis of BT-POSS



**Amino-POSS** (100 mg, 0.085 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (10 mL) and Et3N (118  $\mu$ L, 0.853 mmol) were added to the flask. 2,2'-Bithiophene-5-carboxaldehyde (0.426 M in THF, 2.0 mL, 0.853 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the brown precipitate was washed with MeOH. The residue was purified by reprecipitation with THF (good solvent) and MeOH (poor solvent). Centrifugal separation (3000 rpm, 30 min) gave **BT-POSS** (103 mg, 0.045 mmol, 53% yield) as a brown sticky solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.25$  (8H, s), 7.21 (8H, dd, J = 5.12, 1.00 Hz), 7.18 (8H, dd, J = 3.40, 0.96 Hz), 7.10 (8H, d, J = 3.92 Hz), 7.03 (8H, d, J = 3.68 Hz), 6.98 (8H, dd, J = 5.12, 3.68 Hz), 3.55 (16H, t, J = 3.84 Hz), 1.81 (16H, tt, J = 7.08, 7.08 Hz), 0.68 (16H, t, J = 8.28 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 154.1$ , 141.1, 140.2, 137.2, 130.9, 1218.0, 125.1, 124.5, 123.6, 63.6, 24.3, 9.7 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 80 MHz):  $\delta = -66.8$  (s) ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 2289.0906; found, m/z 2289.0836. Elemental analysis calcd. for C<sub>96</sub>H<sub>96</sub>N<sub>8</sub>O<sub>12</sub>S<sub>16</sub>Si<sub>8</sub>, C 50.32 H 4.22 N 4.89, found, C 47.15 H 4.28 N 4.59.



Chart S6. <sup>1</sup>H NMR spectrum of BT-POSS in CDCl<sub>3</sub>.



Chart S7. <sup>13</sup>C NMR spectrum of BT-POSS in CDCl<sub>3</sub>.



Chart S8. <sup>29</sup>Si NMR spectrum of BT-POSS in CDCl<sub>3</sub>.

#### **Synthesis of Propyl BT**



2,2'-Bithiophene-5-carboxaldehyde (100 mg, 0.515 mmol) was placed in a roundbottom flask equipped with a magnetic stirring bar. MeOH (30.0 mL) was added to the flask and the solution was heated to 70 °C. Propylamine (42.3  $\mu$ L, 0.515 mmol) was added to this stirred yellow solution. After the mixture was stirred at a reflux temperature for 24 h, the solvent was removed with a rotary evaporator. The viscous oil was dissolved in benzene, freeze drying was carried out to afford **Propyl BT** (106 mg, 0.451 mmol, 88%) as a brown oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.29$  (1H, t, J = 1.20 Hz), 7.26-7.23 (2H, m), 7.17 (1H, d, J = 3.68 Hz), 7.12 (1H, d, J = 3.64 Hz), 7.03 (1H, dd, J = 5.12, 3.64 Hz), 3.54 (2H, td, J = 6.84, 1.20 Hz), 1.72 (2H, qt, J = 7.08, 7.08 Hz), 0.95 (3H, t, J = 7.32 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 153.9$ , 141.2, 140.3, 137.2, 130.7, 128.0, 125.2, 124.6, 123.6, 63.2, 24.1, 11.8 ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 236.0562; found, m/z 236.0563. Elemental analysis calcd. for C<sub>12</sub>H<sub>13</sub>NS<sub>2</sub>, C 61.24 H 5.57 N 5.95, found, C 61.00 H 5.44 N 5.92.



Chart S9. <sup>1</sup>H NMR spectrum of Propyl BT in CDCl<sub>3</sub>.



Chart S10. <sup>13</sup>C NMR spectrum of Propyl BT in CDCl<sub>3</sub>.

#### synthesis of Btz-POSS



**Amino-POSS** (300 mg, 0.256 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (30 mL) and Et<sub>3</sub>N (355  $\mu$ L, 2.56 mmol) were added to the flask. 2,1,3-Benzothiadazole-4-carboxaldehyde (0.511 M in THF, 5.0 mL, 2.56 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the orange precipitate was washed with MeOH. The residue was purified by reprecipitation with THF (good solvent) and -78 °C MeOH (poor solvent) to afford **Btz-POSS** (400 mg, 0.195 mmol, 76% yield) as a light pink solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 9.01$  (8H, s), 8.05 (8H, d, J = 7.08 Hz), 7.97 (8H, d, J = 8.76 Hz), 7.55-7.50 (8H, m), 3.74 (16H, t, J = 6.56 Hz), 1.91 (16H, tt, J = 7.44, 7.44 Hz), 0.77 (16H, t, J = 8.08 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 156.8$ , 155.1, 153.5, 129.2, 128.5, 127.1, 123.0, 64.6, 24.4, 3.8 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 80 MHz):  $\delta = -66.7$  (s) ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 2071.2200; found, m/z 2071.2182. Elemental analysis calcd. for C<sub>80</sub>H<sub>80</sub>N<sub>24</sub>O<sub>12</sub>S<sub>8</sub>Si<sub>8</sub>, C 46.85 H 3.93 N 16.39, found, C 46.60 H 3.88 N 16.19.



Chart S11. <sup>1</sup>H NMR spectrum of Btz-POSS in CDCl<sub>3</sub>.



Chart S12. <sup>13</sup>C NMR spectrum of Btz-POSS in CDCl<sub>3</sub>.



Chart S13. <sup>29</sup>Si NMR spectrum of Btz-POSS in CDCl<sub>3</sub>.

#### Synthesis of Propyl Btz



2,1,3-Benzothiadiazole-4-carboxaldehyde (200 mg, 1.22 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (70 mL) was added to the flask and the solution was heated to 70 °C. Propylamine (100  $\mu$ L, 1.22 mmol) was added to this stirred brown solution. After the mixture was stirred at a reflux temperature for 24 h, the solvent was removed with a rotary evaporator to afford **Propyl Btz** (241 mg, 1.17 mmol, 96% yield) as an orange oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 9.11$  (1H, s), 8.19 (1H, d, J = 7.08 Hz), 8.08 (1H, dd, J = 8.76, 0.96 Hz), 7.68 (1H, dd, J = 8.52, 6.84 Hz), 3.75 (2H, td, J = 7.08, 1.44 Hz), 1.81 (2H, qt, J = 7.04, 7.04 Hz), 1.00 (3H, t, J = 7.56 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 156.6$ , 155.3, 153.7, 129.4, 128.7, 127.1, 123.1, 64.1, 24.1, 11.9 ppm. HRMS(ESI): Calcd for [M+Na]<sup>+</sup>, 228.0566; found, m/z 228.0565. Elemental analysis calcd. for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>S, C 58.51 H 5.40 N 20.47, found, C 58.11 H 5.26 N 20.45.



Chart S14. <sup>1</sup>H NMR spectrum of Propyl Btz in CDCl<sub>3</sub>.



Chart S15. <sup>13</sup>C NMR spectrum of Propyl Btz in CDCl<sub>3</sub>.

#### Synthesis of DPA-POSS



**Amino-POSS** (100 mg, 0.085 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (10 mL) and Et<sub>3</sub>N (237  $\mu$ L, 1.71 mmol) were added to the flask. 9-(4-formylphenyl)-10-phenylanthracene (0.426 M in THF, 2.0 mL, 0.852 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the white precipitate was washed with MeOH. The residue was purified by reprecipitation with THF (good solvent) and -78 °C acetone (poor solvent) to afford **DPA-POSS** (152 mg, 0.042 mmol, 49% yield) as a white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.52$  (8H, s), 7.99 (16H, d, J = 8.04 Hz), 7.62-7.51 (56H, m), 7.47 (16H, d, J = 8.04 Hz), 7.38 (16H, dd, J = 7.80, 1.92 Hz), 7.21-7.14 (32H, m), 3.80 (16H, t, J = 6.84 Hz), 2.05 (16H, t, J = 8.28 Hz), 0.92 (16H, t, J = 8.04 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 160.9$ , 141.6, 139.0, 137.3, 136.3, 135.7, 131.7, 131.3, 129.8, 129.6, 128.4, 128.2, 127.4, 126.9, 126.6, 125.1, 125.0, 64.3, 24.6, 10.0 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 80 MHz):  $\delta = -66.3$  (s) ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 3602.2887; found, m/z 3602.2848. Elemental analysis calcd. for C<sub>240</sub>H<sub>192</sub>N<sub>8</sub>O<sub>12</sub>Si<sub>8</sub>, C 79.96 H 5.37 N 3.11, found, C 79.73 H 5.53 N 3.14.



Chart S16. <sup>1</sup>H NMR spectrum of DPA-POSS in CDCl<sub>3</sub>.



Chart S17. <sup>13</sup>C NMR spectrum of DPA-POSS in CDCl<sub>3</sub>.



Chart S18. <sup>29</sup>Si NMR spectrum of DPA-POSS in CDCl<sub>3</sub>.

#### Synthesis of Propyl DPA



9-(4-Formylphenyl)-10-phenylanthracene (100 mg, 0.279 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (30 mL) and THF (6 mL) were added to the flask and the solution was heated to 70 °C. Propylamine (22.9  $\mu$ L, 0.279 mmol) was added to this stirred colorless solution. After the mixture was stirred at a reflux temperature for 24 h, the solvent was removed with a rotary evaporator to afford **Propyl DPA** (102 mg, 0.256 mmol, 91% yield) as a white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.47$  (1H, s), 7.98 (2H, d, J = 8.28 Hz), 7.69 (4H, m), 7.63-7.54 (5H, m), 7.49 (2H, dd, J = 8.28, 1.68 Hz), 7.33 (4H, m), 3.68 (2H, td, J = 6.84, 1.24 Hz), 1.81 (2H, qt, J = 7.08, 7.08 Hz), 1.03 (3H, t, J = 7.32 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 160.6$ , 141.6, 139.0, 137.4, 136.4, 135.7, 131.7, 131.3, 129.9, 129.7, 128.4, 128.1, 127.5, 127.1, 126.8, 125.2, 125.1, 63.7, 24.2, 11.9 ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 400.2060; found, m/z 400.2065. Elemental analysis calcd. for C<sub>30</sub>H<sub>25</sub>N, C 90.19 H 6.31 N 3.51, found, C 90.31 H 6.30 N 3.33.



Chart S19. <sup>1</sup>H NMR spectrum of Propyl DPA in CDCl<sub>3</sub>.



Chart S20. <sup>13</sup>C NMR spectrum of Propyl DPA in CDCl<sub>3</sub>.

#### Synthesis of DPFL-carboxaldehyde



A solution of 2-bromo-9,9-diphenylfluorene (500 mg, 1.26 mmol) in THF (3.2 mL) was cooled at -78 °C under N<sub>2</sub> atmosphere. To this stirred colorless solution was added dropwise *n*-butyllithium (1.59 M in *n*-hexane, 8.9 mL, 1.4 mmol) by a syringe over 30 min. After the mixture was stirred for 60 min., to this stirred yellow suspension was added *N*,*N*-dimethylformamide (DMF) (291  $\mu$ L, 3.8 mmol) by a syringe over 5 min. The mixture was stirred for 2 h, after the solution was allowed to warm to room temperature. Then the reaction was quenched by addition of 2 M HCl aqueous solution. The mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with brine (100 mL), and then dried over MgSO4. After filtration, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO<sub>2</sub> with *n*-hexane and ethyl acetate (*n*-hexane/ethyl acetate = 9/1 v/v) as an eluent and recrystallization from *n*-hexane and THF to afforded **DPFL-carboxaldehyde** (318 mg, 0.919 mmol, 73%) as a white crystalline.

 $R_{\rm f} = 0.34$  (*n*-hexane/ethyl acetate = 9/1 v/v). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 9.98$ (1H, s), 7.98-7.89 (4H, m), 7.49-7.38 (3H, m), 7.30-7.20 (10H, m) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta = 191.9$ , 152.9, 152.4, 146.7, 145.4, 139.0, 136.5, 130.5, 129.7, 128.8, 128.4, 128.3, 127.4, 127.3, 126.8, 121.9, 121.0, 65.9 ppm. HRMS(APCI): Calcd for [M+H]<sup>+</sup>, 347.1430; found, m/z 347.1435. Elemental analysis calcd. for C<sub>26</sub>H<sub>18</sub>O, C 90.14 H 5.24, found, C 89.93 H 5.24.



Chart S21. <sup>1</sup>H NMR spectrum of DPFL-carboxaldehyde in CD<sub>2</sub>Cl<sub>2</sub>.



Chart S22 <sup>13</sup>C NMR spectrum of DPFL-carboxaldehyde in CD<sub>2</sub>Cl<sub>2</sub>.

### Synthesis of DPFL-POSS



**Amino-POSS** (100 mg, 0.085 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (10 mL) and Et<sub>3</sub>N (118  $\mu$ L, 0.852 mmol) were added to the flask. **DPFL-carboxaldehyde** (0.426 M in THF, 2.0 mL, 0.852 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the white precipitate was washed with MeOH. The residue was purified by reprecipitation with THF (good solvent) and -78 °C MeOH (poor solvent) to afford **DPFL-POSS** (221 mg, 0.063 mmol, 72% yield) as a white solid.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 8.13$  (1H, s), 7.72 (8H, d, J = 7.56 Hz), 7.67 (24H, s), 7.39-7.28 (24H, m), 7.15-7.11 (80H, m), 3.45 (16H, t, J = 7.08 Hz), 1.72 (16H, tt, J = 8.52, 8.52 Hz), 0.63 (16H, t, J = 8.52 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 161.0$ , 152.0, 151.6, 145.5, 142.5, 139.5, 136.0, 128.3, 128.2, 128.2, 127.6, 127.6, 126.7, 126.3, 126.2, 120.6, 120.3, 65.5, 64.1, 24.4, 9.8 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 80 MHz):  $\delta = -66.8$  (s) ppm. HRMS(APCI): Calcd for [M+H]<sup>+</sup>, 3506.2887; found, m/z 3506.2736. Elemental analysis calcd. for C<sub>232</sub>H<sub>192</sub>N<sub>8</sub>O<sub>12</sub>Si<sub>8</sub>, C 79.42 H 5.52 N 3.19, found, C 78.43 H 5.63 N 3.23.



Chart S23. <sup>1</sup>H NMR spectrum of DPFL-POSS in CD<sub>2</sub>Cl<sub>2</sub>.



Chart S24. <sup>13</sup>C NMR spectrum of DPFL-POSS in CDCl<sub>3</sub>.



Chart S25. <sup>29</sup>Si NMR spectrum of DPFL-POSS in CDCl<sub>3</sub>.

Synthesis of Propyl DPFL



**DPFL-carboxaldehyde** (200 mg, 0.577 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (50 mL) was added to the flask and the solution was heated to 70 °C. Propylamine (47.4  $\mu$ L, 0.577 mmol) was added to this stirred colorless solution. After the mixture was stirred at a reflux temperature for 24 h, the solvent was removed with a rotary evaporator. The viscous oil was dissolved in benzene, freeze drying was carried out to afford **Propyl DPFL** (205 mg, 0.529 mmol, 92% yield) as a white solid.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 8.25$  (1H, s), 7.83 (1H, d, J = 2.92 Hz), 7.81 (1H, t, J = 1.96 Hz), 7.77-7.72 (2H, m), 7.42-7.38 (2H, m), 7.31 (1H, td, J = 6.84, 1.24 Hz), 7.25-7.19 (10H, m), 3.52 (2H, td, J = 7.32, 1.48 Hz), 1.67 (2H, qt, J = 7.32, 7.32 Hz), 0.93 (3H, t, J = 7.32 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 160.9$ , 152.0, 151.6, 145.6, 142.6, 139.5, 136.0, 128.3, 128.3, 128.2, 127.6, 127.6, 126.7, 126.6, 126.1, 120.6, 120.3, 65.5, 63.6, 24.1, 11.9 ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 388.2060, found, m/z 388.2068. Elemental analysis calcd. for C<sub>29</sub>H<sub>25</sub>N, C 89.99 H 6.50 N 3.61, found, C 89.95 H 6.61 N 3.41.



Chart S26. <sup>1</sup>H NMR spectrum of Propyl DPFL in CD<sub>2</sub>Cl<sub>2</sub>.



Chart S27. <sup>13</sup>C NMR spectrum of Propyl DPFL in CDCl<sub>3</sub>.

#### Synthesis of TPA-POSS

![](_page_31_Figure_1.jpeg)

**Amino-POSS** (100 mg, 0.085 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (10 mL) and Et<sub>3</sub>N (118  $\mu$ L, 0.852 mmol) were added to the flask. 4-(*N*,*N*-Diphenylamino)-benzaldehyde (0.426 M in THF, 2.0 mL, 0.852 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the light yellow precipitate was washed with MeOH. The residue was purified by reprecipitation with THF (good solvent) and MeOH (poor solvent). Centrifugal separation (3000 rpm, 30 min) gave **TPA-POSS** (178 mg, 0.061 mmol, 71% yield) as a yellow solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.14$  (8H, s), 7.53 (16H, d, J = 8.52 Hz), 7.24-7.19 (32H, m), 7.09 (64H, m), 3.54 (16H, t, J = 6.84 Hz), 1.79 (16H, tt, J = 8.08 Hz), 0.65 (16H, t, J = 8.28 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 160.3$ , 149.9, 147.2, 130.0, 129.3, 129.1, 125.0, 123.5, 122.3, 64.0, 24.4, 9.7 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 80 MHz):  $\delta = -66.7$  (s) ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 2922.1255; found, m/z 2922.1266. Elemental analysis calcd. for C<sub>176</sub>H<sub>168</sub>N<sub>16</sub>O<sub>12</sub>Si<sub>8</sub>, C 72.29 H 5.79 N 7.66, found, C 71.28 H 5.70 N 7.56.

![](_page_32_Figure_0.jpeg)

Chart S28. <sup>1</sup>H NMR spectrum of TPA-POSS in CDCl<sub>3</sub>.

![](_page_32_Figure_2.jpeg)

Chart S29. <sup>13</sup>C NMR spectrum of TPA-POSS in CDCl<sub>3</sub>.

![](_page_33_Figure_0.jpeg)

Chart S30. <sup>29</sup>Si NMR spectrum of TPA-POSS in CDCl<sub>3</sub>.

#### Synthesis of Propyl TPA

![](_page_34_Figure_1.jpeg)

4-(*N*,*N*-Diphenylamino)-benzaldehyde (300 mg, 1.10 mmol) was placed in a roundbottom flask equipped with a magnetic stirring bar. MeOH (70 mL) was added to the flask and the solution was heated to 70 °C. Propylamine (90.1  $\mu$ L, 1.098 mmol) was added to this stirred colorless solution. After the mixture was stirred at a reflux temperature for 24 h, the solvent was removed with a rotary evaporator. The viscous oil was dissolved in benzene, freeze drying was carried out to afford **Propyl TPA** (345 mg, 1.10 mmol, quantitative) as a yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.18$  (1H, s), 7.57 (2H, dt, J = 8.76, 1.96 Hz), 7.29-7.25 (4H, m), 7.12-7.03 (8H, m), 3.54 (2H, td, J = 6.84, 1.20 Hz), 1.71 (2H, qt, J = 7.32, 7.32 Hz), 0.94 (3H, t, J = 7.56 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 160.2$ , 149.9, 147.2, 130.0, 129.4, 129.0, 125.0, 123.6, 122.2, 77.3, 77.0, 76.7, 63.5, 24.2, 11.8 ppm. HRMS(ESI): Calcd for [M+H]<sup>+</sup>, 315.1856; found, m/z 315.1860. Elemental analysis calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>, C 84.04 H 7.05 N 8.91, found, C 84.04 H 7.05 N 8.91.

![](_page_35_Picture_0.jpeg)

![](_page_35_Figure_1.jpeg)

Chart S31. <sup>1</sup>H NMR spectrum of Propyl TPA in CDCl<sub>3</sub>.

![](_page_35_Figure_3.jpeg)

Chart S32. <sup>13</sup>C NMR spectrum of Propyl TPA in CDCl<sub>3</sub>.

#### Synthesis of BT-Btz-Ph-carboxaldehyde

![](_page_36_Figure_1.jpeg)

The solution of 4-bromo-7-(5-thienykthiophene-2ly)-2,1,3-benzothiadiazole (430 mg, 1.13 mmol), 4-formylphenylboronic acid (204 mg, 1.36 mmol), A Phos Pd G3(36.0 mg, 0.057 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (3693 mg, 11.34 mmol) in toluene (27 mL), water (4.7 mL), and ethanol (4.7 mL) were heated to 80 °C under N<sub>2</sub> atmosphere for 14 h. After cooling to room temperature, the reaction was quenched by addition of saturated NaHCO<sub>3</sub> aqueous solution. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL), and then dried over MgSO<sub>4</sub>. After filtration, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on SiO<sub>2</sub> with *n*-hexane and ethyl acetate (*n*-hexane/ethyl acetate = 3/1 v/v) as an eluent and recrystallization from *n*-hexane and THF to afford **BT-Btz-Ph-carboxaldehyde** (356 mg, 0.879 mmol, 76%) as a red crystalline.

 $R_{\rm f} = 0.50 \ (n\text{-hexane/ethyl acetate} = 3/1 \text{ v/v}). {}^{1}\text{H} \text{NMR} \ (\text{CD}_{2}\text{Cl}_{2}, 400 \text{ MHz}): \delta = 10.10 \ (1\text{H}, \text{s}), 8.20 \ (2\text{H}, \text{dd}, J = 8.28, 1.48 \text{ Hz}), 8.13 \ (1\text{H}, \text{dd}, J = 3.88, 0.96 \text{ Hz}), 8.05\text{-}8.00 \ (3\text{H}, \text{m}), 7.86 \ (1\text{H}, \text{dd}, J = 7.48, 1.32 \text{ Hz}), 7.35\text{-}7.31 \ (3\text{H}, \text{m}), 7.10 \ (1\text{H}, \text{dd}, J = 5.08, 3.56 \text{ Hz}) \ \text{ppm}. {}^{13}\text{C} \text{NMR} \ (\text{CD}_{2}\text{Cl}_{2}, 100 \text{ MHz}): \delta = 192.1, 154.1, 153.0, 143.5, 139.7, 138.2, 137.5, 136.3, 131.5, 130.2, 130.1, 129.3, 129.2, 128.5, 127.5, 125.5, 125.4, 125.0, 124.6 \ \text{ppm}. \ \text{HRMS} \ (\text{ESI}) \ \text{Calcd. for} \ [\text{M}+\text{H}]^{+}, 405.0185, \ \text{found}, \ \text{m/z} \ 405.0192. \ \text{Elemental analysis}$ 

![](_page_37_Figure_0.jpeg)

calcd. for  $C_{21}H_{12}N_2OS_3$ , C 62.35 H 2.99 N 6.93, found, C 62.42 H 2.93 N 6.91.

Chart S33. <sup>1</sup>H NMR spectrum of BT-Btz-Ph-carboxaldehyde in CD<sub>2</sub>Cl<sub>2</sub>.

![](_page_37_Figure_3.jpeg)

Chart S34. <sup>13</sup>C NMR spectrum of BT-Btz-Ph-carboxaldehyde in CD<sub>2</sub>Cl<sub>2</sub>.

#### Synthesis of DA-POSS

![](_page_38_Figure_1.jpeg)

**Amino-POSS** (50 mg, 0.043 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (60 mL) and Et<sub>3</sub>N (118  $\mu$ L, 0.852 mmol) were added to the flask. **BT-Btz-Ph-carboxaldehyde** (0.053 M in THF, 8.0 mL, 0.426 mmol) was added dropwise to this stirred colorless solution. After the mixture was stirred at room temperature for 2 h, the white precipitate was washed with MeOH. The residue was purified by recrystallization with pyridine to afford **DA-POSS** (154 mg, 0.039 mmol, 91% yield) as an orange solid.

<sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N, 110 °C, 600 MHz):  $\delta$  = 8.52 (8H, t, *J* = 4.92 Hz), 8.10 (16H, d, *J* = 8.28 Hz), 8.06 (8H, d, *J* = 3.84 Hz), 8.03 (16H, d, *J* = 8.22 Hz), 7.78 (8H, d, *J* = 7.38 Hz), 7.62 (8H, d, *J* = 7.14 Hz), 7.37-7.36 (16H, m), 7.32 (8H, d, *J* = 3.54 Hz), 7.08 (8H, d, *J* = 4.92, 3.54 Hz), 3.92 (16H, tt, *J* = 7.14, 7.14 Hz), 2.30 (16H, qq, *J* = 7.44, 7.44 Hz), 1.26 (16H, tt, *J* = 8.22, 8.22 Hz) ppm. <sup>13</sup>C NMR (C<sub>5</sub>D<sub>5</sub>N, 110 °C, 600 MHz):  $\delta$  = 160.7, 154.4, 153.2, 139.8, 139.5, 138.8, 138.0, 137.5, 132.3, 130.0, 128.9, 128.7, 128.6, 127.0, 125.7, 125.7, 125.3, 125.0, 124.0, 64.1, 25.4, 10.6 ppm. <sup>29</sup>Si NMR (C<sub>5</sub>D<sub>5</sub>N, 110 °C, 600 MHz):  $\delta$  = -64.9 (s) ppm. HRMS (MALDI) Calcd. for [M+H]<sup>+</sup>, 3969.292, found, m/z 3969.291. Elemental analysis calcd. for C<sub>192</sub>H<sub>144</sub>N<sub>24</sub>O<sub>12</sub>S<sub>8</sub>Si<sub>8</sub>, C 58.04 H 3.65 N 8.46, found, C 57.50 H 3.46 N 8.33.

**DA-POSS** has poor solubility to common solvents. NMR measurement can be done only with  $C_5D_5N$  at 110 °C. Under such a hard condition, the imine structure was decomposed. The decomposition was observed by time tracking NMR measurement.

![](_page_39_Figure_1.jpeg)

Chart S35. <sup>1</sup>H NMR spectrum of DA-POSS in C<sub>5</sub>D<sub>5</sub>N.

![](_page_40_Figure_0.jpeg)

-64.95

**Chart S36.** <sup>13</sup>C NMR spectrum of **DA-POSS** in C<sub>5</sub>D<sub>5</sub>N.

![](_page_40_Figure_2.jpeg)

Chart S37. <sup>29</sup>Si NMR spectrum of DA-POSS in C<sub>5</sub>D<sub>5</sub>N.

#### Synthesis of Propyl DA

![](_page_41_Figure_1.jpeg)

**BT-Btz-Ph-carboxaldehyde** (50.0 mg, 0.124 mmol) was placed in a round-bottom flask equipped with a magnetic stirring bar. MeOH (15 mL) and THF (3.0 mL) were added to the flask and the solution was heated to 70 °C. Propylamine (10.1  $\mu$ L, 0.124 mmol) was added to this stirred red solution. After the mixture was stirred at a reflux temperature for 12 h, the solvent was removed with a rotary evaporator to afford **Propyl DA** (54.5 mg, 0.122 mmol, 98% yield) as a red solid.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 8.36$  (1H, s), 8.11 (1H, d, J = 3.88 Hz), 8.06 (2H, d, J = 8.32 Hz), 7.99 (1H, d, J = 7.56 Hz), 7.89 (2H, d, J = 7.80 Hz), 7.82 (1H, d, J = 7.56 Hz), 7.34 (1H, dd, J = 7.32, 1.12 Hz), 7.32-7.30 (2H, m), 7.09 (1H, dd, J = 5.12, 3.68 Hz), 3.61 (2H, dd, J = 7.12, 6.08 Hz), 1.74 (2H, qt, J = 7.32, 7.32 Hz), 0.98 (3H, t, J = 7.32 Hz) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta = 160.3$ , 154.3, 153.0, 139.5, 139.3, 138.4, 137.5, 136.9, 132.4, 131.8, 129.8, 128.8, 128.6, 128.5, 126.6, 125.6, 125.4, 124.9, 124.5, 63.9, 24.5, 12.0 ppm. HRMS (APCI) Calcd. for [M+H]<sup>+</sup>, 446.0814, found, m/z 446.0813. Elemental analysis calcd. for C<sub>24</sub>H<sub>19</sub>N<sub>3</sub>S<sub>3</sub>, C 64.69 H 4.30 N 9.43, found, C 64.49 H 4.45 N 9.33.

![](_page_42_Figure_0.jpeg)

Chart S38. <sup>1</sup>H NMR spectrum of Propyl DA in CD<sub>2</sub>Cl<sub>2</sub>.

![](_page_42_Figure_2.jpeg)

Chart S39. <sup>13</sup>C NMR spectrum of Propyl DA in CD<sub>2</sub>Cl<sub>2</sub>.

Synthesis of PDA

![](_page_43_Figure_1.jpeg)

The solution of 4,7-dibromo-2,1,3-benzothiadiazole (44 mg, 0.150 mmol), 5,5'bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene (124 mg, 0.150 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (6.87 mg, 0.0075 mmol) and XPhos (7.15 mg, 0.015 mmol) in toluene (3.0 mL) was heated to 80 °C under N<sub>2</sub> atmosphere for 24 h. After cooling to room temperature, the reaction solution was filtered through SiO<sub>2</sub> with chloroform as an eluent. After filtration, the solvent was removed with a rotary evaporator. The residue was purified by reprecipitation with chloroform (good solvent) and EtOH (poor solvent) to afford **PDA** (90.4 mg, 95% yield) as a purple solid. The molecular weights were determined by GPC with polystyrene standards with chloroform as an eluent. That was  $M_n = 10,600$  and  $M_w/M_n = 2.2$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 8.11 (2H, br), 7.88 (2H, br), 2.71 (4H, br), 1.71 (4H, br), 1.37–1.21 (36H, br), 0.85 (6H, t, *J* = 6.84 Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 152.7, 143.7, 139.1, 130.4, 129.5, 125.7, 125.4, 31.9, 30.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 22.7, 14.1 ppm.

![](_page_44_Figure_0.jpeg)

Chart S40. <sup>1</sup>H NMR spectrum of PDA in CDCl<sub>3</sub>.

![](_page_44_Figure_2.jpeg)

Chart S41. <sup>13</sup>C NMR spectrum of PDA in CDCl<sub>3</sub>.

#### Synthesis of PF

![](_page_45_Figure_1.jpeg)

The solution of 9,9-dihexyl-2,7-dibromofluorene (3.00 g, 6.09 mmol), 9,9dihexylfluorene-2,7-diboronic acid (2.57 g, 6.09 mmol), A Pho Pd G3(387 mg, 0.609 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (19.85 g, 60.94 mmol) in toluene (200.0 mL) and water (100.0 mL) was heated to 80 °C under N<sub>2</sub> atmosphere for 24 h. After cooling to room temperature, the reaction was quenched by addition of saturated NaHCO<sub>3</sub> aqueous solution. The mixture was extracted with DCM (3 × 100 mL), and then filtered through SiO<sub>2</sub>. After filtration, the solvent was removed with a rotary evaporator. The residue was purified by reprecipitation with THF (good solvent) and MeOH (poor solvent) to afford **PF** (3.59 g, 89% yield) as a bluish gray solid. The molecular weights were determined by GPC with polystyrene standards with chloroform as an eluent. That was  $M_n = 19,500$  and  $M_w/M_n =$ 3.5.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.84 (2H, br), 7.69 (4H, br), 2.13 (4H, br), 1.14 (12 H, br), 0.81–0.78 (10H, br) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 151.8, 140.6, 140.0, 126.2, 121.6, 120.0, 55.4, 40.4, 31.5, 29.7, 23.9, 22.6, 14.0 ppm.

![](_page_46_Figure_0.jpeg)

Chart S42. <sup>1</sup>H NMR spectrum of PF in CDCl<sub>3</sub>.

![](_page_46_Figure_2.jpeg)

Chart S43. <sup>13</sup>C NMR spectrum of PF in CDCl<sub>3</sub>.

#### **Interaction parameter**

The affinity with polymer and fullerene each other described by the thermodynamic Flory-Huggins interaction parameter ( $\chi_{ij}$ ). The parameters are usually obtained by thermodynamic methods like osmotic pressure or direct fitting to the observed phase diagram.<sup>10</sup> In this study, the parameters were calculated using the Hildebrand solubility parameters ( $\delta$ ) of the components that were derived from the surface energies ( $\gamma$ ) like previous studies.<sup>11–13</sup> The surface energy was evaluated by contact angle measurements which were in turn conducted using a sessile drop of water and formamide on the spin-coated neat films.

The measured contact angles were converted to surface energies using the relation by Li and Neumann.<sup>14,15</sup> The resulting contact angles and surface energies are shown in Table S5 with water as test liquid and shown in Table S6 with formamide. For apolar materials, with surface energies via calculation, the solubility parameters can be estimated through the relationship.

$$\delta = K \sqrt{\gamma}$$

in which the proportionally factor (K) is obtained from Moons et al.'s reported data<sup>13,16</sup> for poly(9,9'-dioctylfluorenyl-2,7-diyl) (**F8**) with  $\delta$ = 9.2 (cal/cm<sup>3</sup>)<sup>1/2</sup> and  $\gamma$ = 25.3 mJ/m<sup>2</sup>. In this study the same K was used for all components. The results are summarized in Tables S5 and S6. Using the same K means that possible effects from variations in segment volume of the POSSs and repeating unit of polymers are ignored. However, because the square of the solubility parameter is proportional to cubic root of volume, the effect is not decisive. As is emphasized below, it is the relative ordering between hybrid

components that is important here.

The interaction parameters are defined by the Hildebrand-Scott equation

$$\chi = (V_m/RT) (\delta_1 - \delta_j)^2 + 0.34$$

where  $V_m$  is the molar volume of the solvent, which defines the unit lattice size. The term 0.34 is an entropic correction to the original FH interaction parameter defined by enthalpy per thermal energy, which comes from the presence of free volume.<sup>17–19</sup> The calculated interaction parameters between **MEH-PPV** and several POSSs are shown in Table S7.

Note that the conversion from contact angles to interaction parameters is of course an approximation. However, what is important in this context is the relative ordering between the POSSs rather than precise numerical values. This is especially so considering that the use of solubility parameters to describe thermodynamic properties is in itself an approximation. The main purpose here is understanding the trends when varying POSSs. In fact, the same tendency was observed from different solvents, water and formamide. Therefore, the tendency of  $\chi_{MEH-PPV, POSS}$  is of significance.

![](_page_49_Figure_0.jpeg)

Figure S1. Chemical structures of model compounds.

![](_page_49_Figure_2.jpeg)

Figure S2. Chemical structures of polymers.

![](_page_50_Figure_0.jpeg)

**Figure S3.** SEM (a~c) and TEM (d~f) images of **MEH-PPV** neat film (a, d), hybrid films which consist of 10 wt% of **MEH-PPV** and 90 wt% of fillers (**TPE-POSS** (b, e) or **Propyl TPE** (c, f).

	TPE-	TPA-	DPA-	DT DOSS	anth-	DPFL-	Dta DOSS	DA DOSS
	POSS	POSS	POSS	b1-P055	POSS	POSS	D12-1 055	DA-1'055
<b>)</b> (mm) <sup>a</sup>	220	252	270, 361,	245	262, 375,	202 227	225	221 462
$\lambda_{abs}$ (nm) <sup>a</sup>	552	333	381, 401	343	394	303, 327	323	551, 405
$\lambda_{\rm em}  ({\rm nm})^a$	487	457	437	463	554	425	412, 535	643
${I\!\!\!/} {I\!\!\!/}_{ m film}(\%)^b$	35.1	17.9	8.0	1.7	0.3	0.3	0.2	1.9

Table S1. Optical properties of POSS in neat film

 ${}^{a}\lambda_{abs}$  and  $\lambda_{em}$  mean the peak top wavelength of absorption and emission spectra, respectively.  ${}^{b}\Phi_{film}$  means the photoluminescent quantum yield with excited at  $\lambda_{abs}$  and determined as an absolute value with the integration sphere method.

	MEH-PPV	PDA	РЗНТ	PF
$\lambda_{\rm abs}({\rm nm})^a$	508	541	540	385
$\lambda_{\rm em}  ({\rm nm})^a$	585, 618	747	745	425, 448
${I\!\!\!\!/} \Phi_{ m film}(\%)^b$	10.5	8.7	1.5	13.4

Table. S2. Optical properties of polymers in neat film

 ${}^{a}\lambda_{abs}$  and  $\lambda_{em}$  mean the peak top wavelength of absorption and emission spectra, respectively.  ${}^{b}\Phi_{film}$  means the photoluminescent quantum yield with excited at  $\lambda_{abs}$  and determined as an absolute value with the integration sphere method.

Table S3. The optical properties of the model compounds

	Propyl	Propyl	Propyl	Propyl	Propyl	Propyl	Propyl	Propyl
	TPE	ТРА	DPA	ВТ	anth	DPFL	Btz	DA
$\lambda_{abs} (nm)^a$	342	299, 367	360, 380, 401	331	384	303, 327	314	322, 441
$\lambda_{\rm em}  ({\rm nm})^a$	498	541	441	467	563	427	405, 526	651
${I\!\!\!/}_{ m film}(\%)^b$	22.6	7.3	11.8	4.8	3.2	0.4	1.3	1.6

 ${}^{a}\lambda_{abs}$  and  $\lambda_{em}$  mean the peak top wavelength of absorption and emission spectra, respectively.  ${}^{b}\Phi_{film}$  means the photoluminescent quantum yield with excited at  $\lambda_{abs}$  and determined as an absolute value with the integration sphere method.

![](_page_52_Figure_0.jpeg)

**Figure S4.** UV–vis absorption spectra of the hybrid films containing POSSs. The wt% means POSS content.

![](_page_53_Figure_0.jpeg)

**Figure S5.** PL spectra of the hybrid films containing POSSs excited at  $\lambda_{abs}$  of POSSs (Table S1). The wt% means content of the POSS. Photographs of hybrid films irradiated by UV lamp (365 nm). Asterisks mean the optical overtone of the excitation wavelength.

![](_page_54_Figure_0.jpeg)

Figure S6. UV-vis absorption spectra of the hybrid films containing model compounds.

The wt% means content of model compounds.

![](_page_55_Figure_0.jpeg)

**Figure S7.** PL spectra of the hybrid films containing model compounds excited at  $\lambda_{abs}$  of model compounds (Table S3). The wt% means content of the model compound. Photographs of hybrid films irradiated by UV lamp (365 nm). Asterisks mean the optical overtone of the excitation wavelength.

	Propyl						
	TPE	TPA	DPA	BT	anth	DPFL	Btz
MEH-PPV	•	•	•	•	•	•	•
PDA	0	0	_b	•	_b	_b	-
РЗНТ	0	0	_b	0	_b	_b	_b

**Table S4.** Luminescent behaviors of the combinations of model compounds and polymers<sup>a</sup>

<sup>*a*</sup>The combination indicated by a circle showed dual emission from both model compound and polymer. The combination indicated by black squares showed the single emission from polymers. Various content rates of model compounds (0, 50, 90, and 100 wt%) were loaded for testing each combination. <sup>*b*</sup>The test was not conducted.

![](_page_56_Figure_3.jpeg)

**Figure S8.** The plots of emission efficiencies of hybrid films containing model compounds. The horizontal and vertical axis represent  $\Phi_{\text{film, polymer}}$  and  $\Phi_{\text{film, model}}$ , respectively. The samples inside the area II showed dual emission from both model compound and polymer. The samples inside the areas I and III showed the single emission from model compound and polymer, respectively.

![](_page_57_Figure_0.jpeg)

**Figure S9.** (a) Variable-temperature emission spectra with the excitation light at 330 nm and (b) intensity ratios at 479 nm for **TPE-POSS** and 597 nm for **MEH-PPV** with the hybrid film containing 10 wt% of **MEH-PPV** and 90 wt% of **TPE-POSS**.<sup>9</sup>

![](_page_57_Figure_2.jpeg)

**Figure S10.** (a) Variable-temperature emission spectra with the excitation light at 330 nm and (b) intensity ratios at 696 nm for **PDA** neat film.

![](_page_58_Figure_0.jpeg)

**Figure S11.** (a) Variable-temperature emission spectra with the excitation light at 330 nm and (b) intensity ratios at 483 nm for **Propyl TPE** and 696 nm for **PDA** with the hybrid film containing 10 wt% of **PDA** and 90 wt% of **Propyl TPE**.

![](_page_58_Figure_2.jpeg)

**Figure S12.** (a) Variable-temperature emission spectra with the excitation light at 340 nm and (b) intensity ratios at 450 nm for **BT-POSS** and 580 nm for **MEH-PPV** with the hybrid film containing 10 wt% of **MEH-PPV** and 90 wt% of **BT-POSS**.

![](_page_59_Figure_0.jpeg)

**Figure S13.** (a) Variable-temperature emission spectra with the excitation light at 330 nm and (b) intensity ratio at 597 nm with the **MEH-PPV** neat film.<sup>9</sup>

![](_page_59_Figure_2.jpeg)

**Figure S14.** (a) Variable-temperature emission spectra with the excitation light at 310 nm and (b) intensity ratios at 580 nm for **MEH-PPV** with the hybrid film containing 10 wt% of **MEH-PPV** and 90 wt% of **DPFL-POSS**.

![](_page_60_Figure_0.jpeg)

**Figure S15.** The first heating process of DSC curves with (a) **MEH-PPV** neat film and hybrid films containing 10 wt% of **MEH-PPV** and 90 wt% of (b) **TPA-POSS**, (c) **BT-POSS**, (d) **TPE-POSS**, and (e) **DPFL-POSS**. The drop-casted film was put on the aluminum pan and was heated at the rate of 10 °C/min under nitrogen flowing (50 mL/min).

	$\theta(\text{deg})$	∕sv (mJ/m <sup>2</sup> )	$\delta$ [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ]
MEH-PPV	97.6	23.8	8.9
TPE-POSS	84.2	32.2	10.4
TPA-POSS	80.7	34.4	10.7
DPFL-POSS	83.6	32.6	10.4
<b>BT-POSS</b>	80.2	34.8	10.8
anth-POSS	75.9	37.5	11.1
Btz-POSS	77.7	36.4	11.0
DPA-POSS	91.5	27.6	9.6

**Table S5.** Contact angles (water), surface energies, Hildebrand solubility parameters for the indicated POSSs and **MEH-PPV**<sup>*a*</sup>

<sup>*a*</sup> $\theta$  is contact angle.  $\chi_{V}$  is surface energy.  $\delta$  is Hildebrand solubility parameter. The film was prepared by a spin-coating method from chloroform solution on quartz substrate.

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	$\theta(\text{deg})$	≯sv (mJ/m²)	$\delta$ [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ]	
MEH-PPV	78.7	26.3	9.4	
<b>TPE-POSS</b>	72.1	29.9	10.0	
TPA-POSS	67.4	32.5	10.4	
DPFL-POSS	68.6	31.8	10.3	
<b>BT-POSS</b>	62.7	35.1	10.8	
anth-POSS	62.7	35.1	10.8	
Btz-POSS	60.8	36.0	11.0	
DPA-POSS	71.1	30.5	10.1	

**Table S6.** Contact angles (formamide), surface energies, Hildebrand solubility

 parameters for the indicated POSSs and MEH-PPV<sup>a</sup>

<sup>*a*</sup> $\theta$  is contact angle.  $\gamma_{SV}$  is surface energy.  $\delta$  is Hildebrand solubility parameter. The film was prepared by a spin-coating method from chloroform solution on quartz substrate.

	Xмен-рр∨, poss (water)	Xмен-ррv, poss (formamide)
TPE-POSS	0.63	0.39
<b>TPA-POSS</b>	0.78	0.49
DPFL-POSS	0.65	0.46
<b>BT-POSS</b>	0.81	0.62
anth-POSS	1.04	0.62
<b>Btz-POSS</b>	0.94	0.68
DPA-POSS	0.40	0.41

**Table S7.** Flory-Huggins interaction parameters for **MEH-PPV** and several POSSscalculated from contact angles (water and formamide) $^{a}$ 

<sup>a</sup>Calculated at 300 K.

![](_page_64_Figure_0.jpeg)

**Figure S16.** Flory-Huggins interaction parameters calculated from contact angle measurements using (a) water and (b) formamide. *X*<sub>MEH-PPV, POSS</sub> at 300 K was calculated.

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