

Supporting Information

Block-Copolymer-Like Supramolecules Confined in Nanolamellas

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Experimental section

The detail syntheses of **MD-POSS**, **MD-POSS** and **U-PBLG** were showed in scheme S1.

Materials : Propargyl alcohol, succinic anhydride, 4-aminophenol, 1,10-dibromodecane, hydrazine were obtained from Aldrich Chemical. Triethylamine was obtained from TEDIA. Thionyl chloride was obtained from TCI-UK. Sodium azide, potassium carbonate, diaminopyridine, acetic anhydride, copper bromide, n,n,n',n',n-Pentamethyldiethylenetriamine and γ -benzyl-L-glutamate were obtained from Acros Organics. N-phenylaminopropyl POSS cage mixture and octa(isobutyl) POSS were purchased from Hybrid Plastics. HPLC-grade solvents were used as received.

Measurements

Using appropriate d solvent, ^1H NMR spectra were recorded on a Varian Unity Inova 300 FT NMR spectrometer operated at 500 MHz; chemical shifts are reported in parts per million (ppm). Molecular weight and molecular weight distribution were determined through gel permeation chromatography (GPC) using a Waters 510 HPLC equipped with a 410 differential refractometer, a refractive index (RI) detector, and three Ultrastaygel columns (100, 500, and 10^3) connected in series for increasing pore size (eluent: DMF- d_7 , flow rate: 0.6 mL \cdot min $^{-1}$). A Biflex III (Bruker Daltonics) time-of-flight mass spectrometer equipped with a 337-nm nitrogen laser was used to record MALDI-TOF mass spectra of the samples. FTIR spectrum of the KBr disk was measured using a Nicolet Avatar 320 FTIR Spectrometer, 32 scans were collected at a resolution of 1 cm^{-1} . The sample chamber was purged with nitrogen to maintain film dryness. Thermal analysis was carried out using a DSC instrument (TA Instruments Q-20). The sample (ca. 4–6 mg) was weighed and sealed in an aluminum pan. The glass transition temperature (T_g) was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated glass and liquid lines with a scan rate of 20 $^{\circ}\text{C} \cdot \text{min}^{-1}$ and a temperature range of -50–150 $^{\circ}\text{C}$.

TA Instruments thermogravimetric analyzer, operated at a scan rate of 20 $^{\circ}\text{C}$ over temperatures ranging from 30 to 800 $^{\circ}\text{C}$ under a nitrogen purge of 40 mL/min, was used to record TGA thermograms of samples on a platinum holder. TEM images were recorded using an FEI T12 transmission electron microscope with a low-energy electron beam (120 keV). Ultrathin sections of the samples were prepared using a Leica Ultracut S microtome equipped with a diamond knife. The ultrathin sections were picked onto the copper grids coated with carbon supporting films followed by staining by exposure to the vapor of 4% RuO_4 aqueous solution for 30 min. Wide-angle X-ray scattering (WAXS) measurements were performed using a BL17A1 wiggler beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The 3-D molecule size was simulated with Gaussian program (ChemOffice 2008). Each sample was solved in THF (0.1 g in 1 ml) for CD-spectrum (JASCO, J-815 CD spectrometer), scanning range from 350 nm to 180 nm, scanning speed is 50 nm/min, accumulation is 5.

Synthesis of MD-POSS

4-Oxo-4-(prop-2-ynyloxy)butanoic acid (1).

Propargyl alcohol (40.0 g, 0.741 mol), DMAP (17.43 g, 0.143 mol) and succinic anhydride (85.7g, 0.856 mol) were dissolved in DCM (100 ml) to react overnight. 75 ml of water added to the solution followed by extraction with NaHSO₄ (10 %) for three times. The organic phase was then dried with MgSO₄, filtered and concentrated. Transparent colorless liquid was corrected. Yield: 82% (107.6 g). ¹H-NMR (CDCl₃, 300 MHz), δ 2.48 (t, 1H, -CH), 2.62 - 2.70 (m, 4H, -CH₂C=O-), 4.67 (d, 2H, -OCH₂CCH); ¹³C-NMR (CDCl₃, 300MHz) δ 28.46, 28.67, 52.23, 75.05, 77.27, 171.32, 178.19. EI⁺-MS: 157 (calculated: 156.14). m.p.: 62.47°C.

(Prop-2-ynyl 4-oxo-4-(phenyl(propyl)amino)butanoate) POSS cage mixture (3)

Compound (1) (30.0g, 0.192mol) was added to a reaction flask with a reflux condenser, vacuum-change-Argon for three times. Increase the temperature to 60 °C to be melt and add thionyl chloride (45.71g, 0.384mol) slowly, stirred for 2 hrs at 60 °C. After 2 hrs, take the reaction flask to rotary evaporator to remove all the additional thionyl chloride, the product (2), light yellow liquid stored in Argon system. Yield: 95%.

POSS mixture (2.83g, 0.0019mol) was added to the three-neck-flask and made a vacuum-change-argon for three times then solved into 200ml of dry THF, added dry TEA (0.28g, 0.00285mol) into the bottom of the flask. Compound (2) was also solved into 50ml of dry THF in the feed-pipe then slowly dropped into the three-neck-flask in the ice bath. After adding, the reaction was stirred at room temperature for overnight and removed THF by rotary evaporator. Extracted by EA and NaHCO₃ saturated water solution for three times, collected the organic layer then dried from anhydride MgSO₄, concentrated in the rotary evaporator. Use an elution ratio of EA:CH₂Cl₂ = 1:3 (R_f=0.64), the red viscous liquid product (3) was collected. Yield: 89%. ¹H-NMR (CDCl₃, 300 MHz), δ 7.33 (m, 4H, C₆H₆, 4H), 7.13 (d, 1H, C₆H₆, 1H), 4.60 (d, 2H, OCCCH₂CCH), 3.51 (t, 2H, -CH₂CH₂N-), 2.57 (m, 2H, -O=CCH₂CH₂-), 2.42 (s, 1H, OCCCH₂CCH), 2.27 (m, 2H, -CH₂CH₂C=O-), 1.36 (m, 2H, -CH₂CH₂CH₂-), 0.56-0.09 (m, 2H, -SiCH₂CH₂-).

11-Azidoundecanoic acid (4).

11-bromoundecanoic acid (10g, 0.0377mole) was solved into DMSO then added sodium azide (4.91g, 0.0754mole) stirred at room temperature for overnight. Dried by vacuum distillation then extracted by EA and NaHCO₃ saturated water solution, dried from anhydride MgSO₄ then concentrated in the rotary evaporator. The white solid was collected. Yield: 99%. m.p.: 34.44°C. ¹H-NMR (CDCl₃, 300 MHz), δ 11.28 (s, 1H, OH), 3.21 (t, 2H, HOOCCH₂CH₂-), 2.31 (t, 2H, -CH₂CH₂CH₂-), 1.67-1.46 (m, 12H, -CH₂C₆H₁₂CH₂-), 1.29 (m, 4H, -C₂H₄N₃) ¹³C-NMR (CDCl₃, 300MHz). δ 180.69, 51.63, 34.29, 29.69, 29.41, 29.12, 29.01, 26.88, 24.83

N-(6-aminopyridin-2-yl)acetamide (6).

Compound (4) (7g, 0.0308mole) was added to a reaction flask with a reflux condenser, vacuum-change-Argon for three times then increased to 60 °C to be melt. Added thionyl chloride (7.32g, 0.0616mole) stirred for 2 hrs at 60 °C. After 2 hrs, take the reaction to rotary evaporator to remove all the additional thionyl chloride, the product was light yellow liquid, compound (5) stored in Argon system. Yield: 95%. Diaminopyridine was firstly recrystallized in CH₂Cl₂, solved in dry 400ml of THF after treated vacuum-change-argon for three times and added dry TEA (0.925g, 0.265738mole) into the bottom of the two-neck-flask. Succinic anhydride was solved in dry THF into feed-pipe, slowly dropped into the flask, stirred at room temperature overnight. After concentrated by rotary evaporator, the column chromatography purification was used by pure EA as an elution (R_f=0.8). The white solid product (6) was collected after concentrated. Yield: 52%. m.p.: 166.72°C. ¹H-NMR (CDCl₃, 300 MHz), δ 7.31 (t, 1H, HC=CH-CH), 7.18 (d, 1H, -HC=CH-C-), 6.15 (dd, 1H, -HC=CH-CH=), 3.45 (s, 2H, -NH₂), 2.01 (s, 3H, O=CCH₃). ¹³C-NMR (CDCl₃, 300MHz) δ 174.29, 163.81, 155.85, 144.26, 108.71, 106.28, 29.34

***N*-(6-acetamidopyridin-2-yl)-11-azidoundecanamide (7).**

Compound (6) (4.2g, 0.02779mol) was added to the three-neck-flask and made a vacuum-change-argon for three times then solved into 200ml of dry THF. Dry TEA(4.2471g, 0.04205mol) was added into the bottom of the flask. Compound (5) was also solved into 50ml of dry THF in the feed-pipe then slowly dropped into the three-neck-flask in the ice bath. After finishing adding, the reaction was stir at room temperature for overnight then removed THF by rotary evaporator. Extracted by EA and NaHCO₃ saturated water solution, dried from anhydride MgSO₄ then concentrated in the rotary evaporator. Purified by column chromatography, used the elution ratio of EA:CH₂Cl₂=3:1(R_f=0.85). Light yellow powders (7) were collected. Yield: 76%. m.p.: 92.25°C. ¹H-NMR (CDCl₃, 300 MHz), δ9.99 (d, 1H, O=CNH-), 7.67 (m, 3H, C₆H₆), , 2.47 (s, 3H, -O=CCH₃), 2.35 (t, 2H, -O=CCH₂CH₂-), 2.06 (s, 2H, -CH₂CH₂C₆H₁₂-), 1.49 (dd, 4H, -C₂H₄N₃), 1.22 (m, 12H, -CH₂C₆H₁₂CH₂-). ¹³C-NMR (CDCl₃, 300MHz) δ172.21 , 150.37 , 139.84 , 108.95 , 108.82 , 50.63 , 40.34 , 40.07 , 38.95 , 36.12 , 28.59 , 28.26 , 26.17 , 25.00 , 24.02

Muti Diaminopyridine functional POSS cage mixture (MD-POSS)

MD-POSS was synthesized by click 1,3-cycloaddition reaction. Compound (7) (5g, 0.01387mole), compound (3) (3g, 0.00114mole) and CuBr(0.15g) were solved in 50 ml of DMF then made trap-vacuum-change-argon for three times. PMDETA (0.25ml) was added into the flask reflux at 80°C for several hour traced by the shift to lower elution time without any original peak in GPC. Finally, DMF was distilled by vacuum evaporator and washed several times by ethyl ether. The light brown powder MD-POSS was collected in the vacuum drying. Yield: 83%. ¹H-NMR (CDCl₃, 300 MHz), δ1.93-1.57 (m, 12H, -CH₂C₆H₁₂CH₂-), 1.47-1.09 (m, 2H, -CH₂CH₂CH₂C=O-), 2.45-2.20 (m, 2H, triazoleCH₂CH₂C₆H₁₂-), 2.18-2.06 (m, 2H, -CH₂CH₂(C=O)NH-), 2.61-2.48 (m, 4H, -O=CC₂H₄C=O-), 3.58-3.30 (m, 2H, (O=C)PhN-CH₂-), 5.24-5.02 (m, 2H, (O=)OC-CH₂-pyrrole), 7.15 (m, 2H, octa-C₆H₆), 7.40 (m, 1H, para-C₆H₆, triazole-H), 7.72 (m, 2H, meta-C₆H₆), 7.91 (m, 2H, meta-C₆H₆), 8.31-8.08 (m, 3H, pyrrole-H)

Synthesis of U-PBLG

1-(10-(4-aminophenoxy)decyl)pyrimidine-2,4(1H,3H)-dione (9)

4-Aminophenol (14.16g, 0.102mol) and potassium carbonate (14.07g, 0.102mol) were solved into 300ml of acetone in the flask. 1,10-dibromodecane (45.68ml, 0.203mol) was added in the flask, reflux for 12 hrs. The precursor was collected by firstly filtrated then removed all solvent by rotary evaporator. Precursor was added to a flask which uracil (10g, 0.089mol) and potassium carbonate (14.07g, 0.102mol) were solved in DMF in stirred for 48 hrs then filtrated to remove all salt. DMF was removed by vacuum distillation, reflux by large amount of CH₂Cl₂ to remove additional uracil for one day. The precursor compound (8) was collected by recrystallization in CH₂Cl₂ until filtrated and concentrated by rotary evaporator. Yield: 78%. Compound (8) (14.62g, 0.0375mol) and 100ml of hydrazine with little amount of Pt/C catalyst were added to a flask and reflux with ethanol at 70°C for 3 hrs. The dark-brown solid (9) was collected after filtrated and recrystallization in ethanol. Yield: 71%. ¹H NMR (300 MHz, CDCl₃) δ: 11.21 (s, 1H, NH), 7.64 (d, 1H, CHCHN), 6.27-6.55 (dd, 4H, C₆H₄NH₂), 5.53 (d, 1H, CHCHN), 4.59 (s, 2H, NH₂), 3.79 (t, 2H, NCH₂CH₂), 3.61 (t, 2H, OCH₂CH₂), 1.67-1.50 (m, 12H, (CH₂)₈) ¹³C NMR (500 Hz, CDCl₃) δ: 176.8, 164.6, 151.1, 146.6, 143.1, 132.2, 118.6, 116.1, 115.8, 101.6, 84.0, 68.7, 48.3, 29.77, 29.71, 26.4, 18.03

Synthesis of U-PBLG (Uracil functionalized poly γ-benzyl-L-glutamate)

UPBLG was synthesized by NCA ring-opening polymerization. γ-benzyl-L-glutamate NCA was referred to the reference.³⁷ γ-benzyl-L-glutamate NCA (0.8g) and suitable amounts of compound (9) were added to a flask and made vacuum-change-argon for three times then added dry 60 ml of dry DMF at -4°C stirred for 3 days. The off-white solid U-PBLG was collected by the participation in ethyl ether and dried in the vacuum at 0 °C.

MD-POSS/U-PBLG Blend Preparation

Blends of MD-POSS/U-PBLG were prepared through solution casting. Separate THF solutions of MD-POSS and U-PBLG were stirred together in various weight ratios (shown in Table 1). The resulting mixtures were stirred for 2 days and left to evaporate slowly at 100 °C for 1 day. The blends were then dried for 3 days under vacuum at 100 °C.

Characteristics of MD-POSS

MD-POSS were characteristic by SEC, ^1H NMR, MALDI-TOF and FT-IR spectrometry. In SEC spectra of M(*sec*)A-POSS, MA-POSS and MD-POSS (**S1.**), the major signal of Elution time 21 minutes for M(*sec*)A-POSS was shift to 19.5 minutes without any crude original elution peak, indicated that M(*sec*)A-POSS totally proceed SN_2 on secondary amine functional group to produce MA-POSS. Similarly, signal of elution time 19.5 minutes shifted to 18 minutes without any crude original elution peak, pointed out MA-POSS proceed successfully click reaction to produce multi-diaminopyridine functional group tethered to apex of POSS, MD-POSS. The small shoulders of signal position higher than major peaks in SEC were aggregation of POSS since small size of POSS cage easily aggregated by it-self. ^1H NMR spectra (**S2**) of M(*sec*)A-POSS, MA-POSS and MD-POSS obtained through the suitable d-solvent. The broaden peaks at 3.48 ppm for secondary amine proton of M(*sec*)A-POSS in S2(c) disappeared and peaks at 4.61, 4.09 ppm for propargyl functional group appeared in S1(b), supporting the completely SN_2 substitution reaction on M(*sec*)A-POSS. In addition, peaks replaced (ca.4.61, 4.09 ppm) with (ca. 5.16, 7.57 ppm) in **S 2.(a)**, suggested that click reaction was successfully and completely carried out. The integral value of α -proton position of secondary amine marked a (ca. 3.51 ppm) to proton on ester position marked i (ca. 5.18 ppm) in **S2.(a)** was near 1 which supported successfully click reaction on each propargyl and azide functional group rather than fractionally reaction between these two functional groups. MALDI-TOF mass spectrum (**S3**) of MD-POSS obtained by using 2,5-dihydroxybenzoic acid as matrix, observed that three distribution of the molecular ions for $[\text{MD-POSS} + \text{Na}]^+$ at 5500g/mol, 6876g/mol and 8243g/mol, illustrated that molecular weight of POSS cage mixture of $n=8, 10$ and 12 . In other word, the most POSS cage mixture of n value is 10. FT-IR spectra of M(*sec*)A-POSS, MA-POSS and MD-POSS (**S4**) obtained through solution casting onto KBr disks, observed Si-O-Si stretching vibration peak of POSS at 1100 cm^{-1} . N-H stretching vibration at 3422 cm^{-1} in **S4.(a)** disappeared with appeared alkyne C-H and $\text{C}\equiv\text{C}$ stretching peak at $3290, 2122\text{ cm}^{-1}$ and amide, ester C=O stretching peak at $1741, 1655\text{ cm}^{-1}$, supporting that SN_2 reaction was successfully proceed. In addition, free and bound N-H peaks of diaminopyridine were observed at $3422, 3290\text{ cm}^{-1}$ and the peak of alkyne C-H peak was totally disappeared after click reaction in **S4.(c)**, illustrated that all of propargyl functional groups completely react. Thus SEC, ^1H NMR, MALDI-TOF and FT-IR spectrometry confirmed that MD-POSS products were successful synthesized, pure but comprised three kinds of cage mixture.

Characteristics of U-PBLG

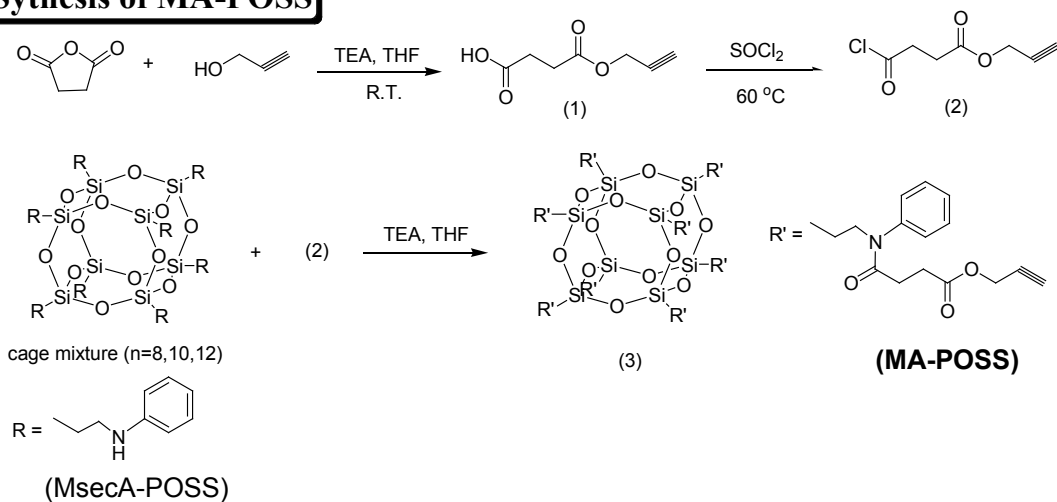
U-PBLG were characteristic by ^1H NMR, solid state ^{13}C NMR and FT-IR spectrometry. **S5** displayed ^1H NMR spectra of U-PBLG, amine-U and NCA monomer. Since the interaction between N-H proton of uracil functional group occurred in d-CDCl_3 which cannot be observed in **S5.(a)** but protons of initiator amine-U were shown in **S5.(a)**, indicated that the initiator was successfully synthesized onto poly γ -benzyl-L-glutamate. The repeat unit calculated from the ratio of benzylic proton (ca. 5.08 ppm) to long alkyl chain (ca. 1.30 ppm) was ca. 30 (the molecular weight is 6837g/mol) which is familiar with SEC data ($M_n=7213\text{g/mol}$, $\text{PDI}=1.21$). **S6** shows the spectra of (a) Solid state ^{13}C NMR and (b) FT-IR of U-PBLG. The secondary structures of PBLG can be identified on the basis of the distinctly different resonances observed in solid state ^{13}C NMR spectra ($\delta = 57.5\text{ ppm}$ for the α -helix; $\delta = 52.7\text{ ppm}$ for the β -sheet)⁽¹⁾. U-PBLG (degree of polymerization (DP) is 29) exhibited (**S6 (a)**) only the resonance at 57.35 ppm, implying that only the α -helix conformation existed in the bulk state. FT-IR (**S6(b)**) can also be used to verify the types of secondary structures based on the amide N-H vibration peak. For the α -helix and β -sheet

conformation, these two signals appear at 1655 cm^{-1} and 1630 cm^{-1} . Our U-PBLG exhibited its amide band at 1652 cm^{-1} , with no signal present at 1630 cm^{-1} , again suggesting that only the α -helical conformation exists in the bulk state.

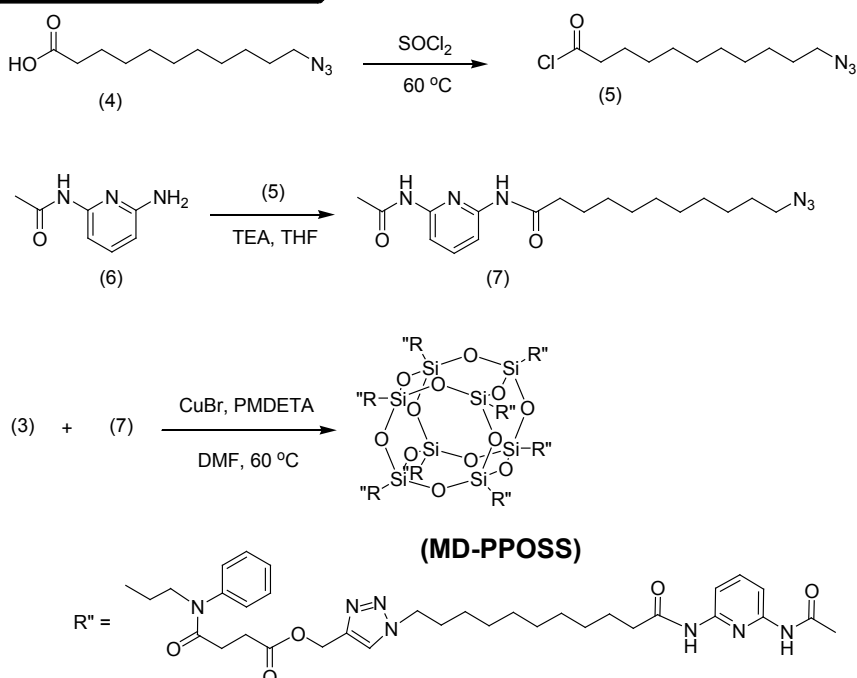
Thermal analyses of MD-POSS/U-PBLG blends

Thermal analyses of MD-POSS/U-PBLG were characteristic by DSC and TGA. **S7** displays TGA thermograms of MD-POSS, U-PBLG and MD-POSS/U-PBLG blends. In the curve of MD-POSS, the decomposition temperature at 255.37°C of $T_{d5\%}$ was the decomposition of long organic alkyl chain segment. Its char yield of 19.63% was higher than the calculated 7.6% siloxane content might due to some aromatic units tend to form aromatic char structures, rather than small molecular vapors. In the curve of U-PBLG, the decomposition temperature at 315.63°C of $T_{d5\%}$ is from the main chain peptide, the char yield of 8.73% might because of the interaction between the uracil group results into the char substance. The increase of $T_{d5\%}$, $T_{d10\%}$ and char yield with increasing MD-POSS segment in MD-POSS/U-PBLG blends is because of POSS inorganic siloxane part become more and more, trends to higher char yield. Table.1 displays the thermo properties of MD-POSS, U-PBLG and MD-POSS/U-PBLG blends.

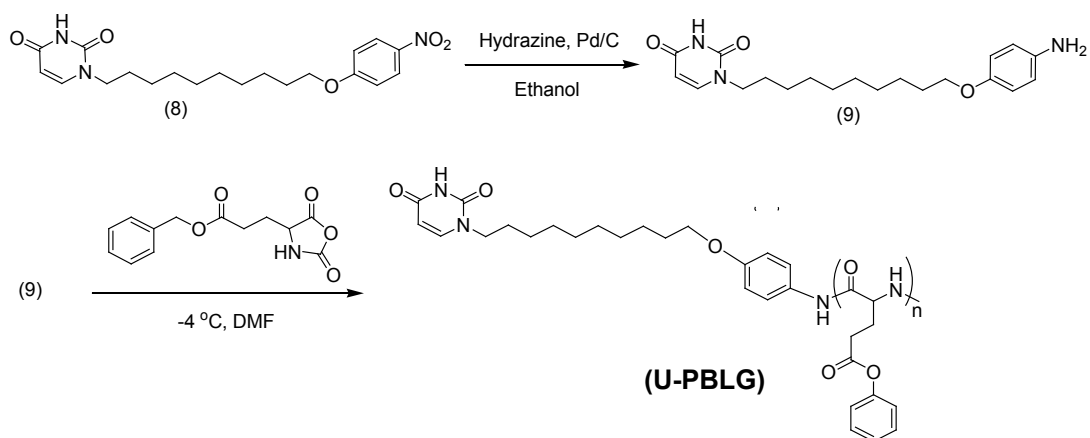
Synthesis of MA-POSS



Synthesis of MD-POSS



Synthesis of U-PBLG



Scheme S1. Synthesis of MD-POSS and U-PBLG

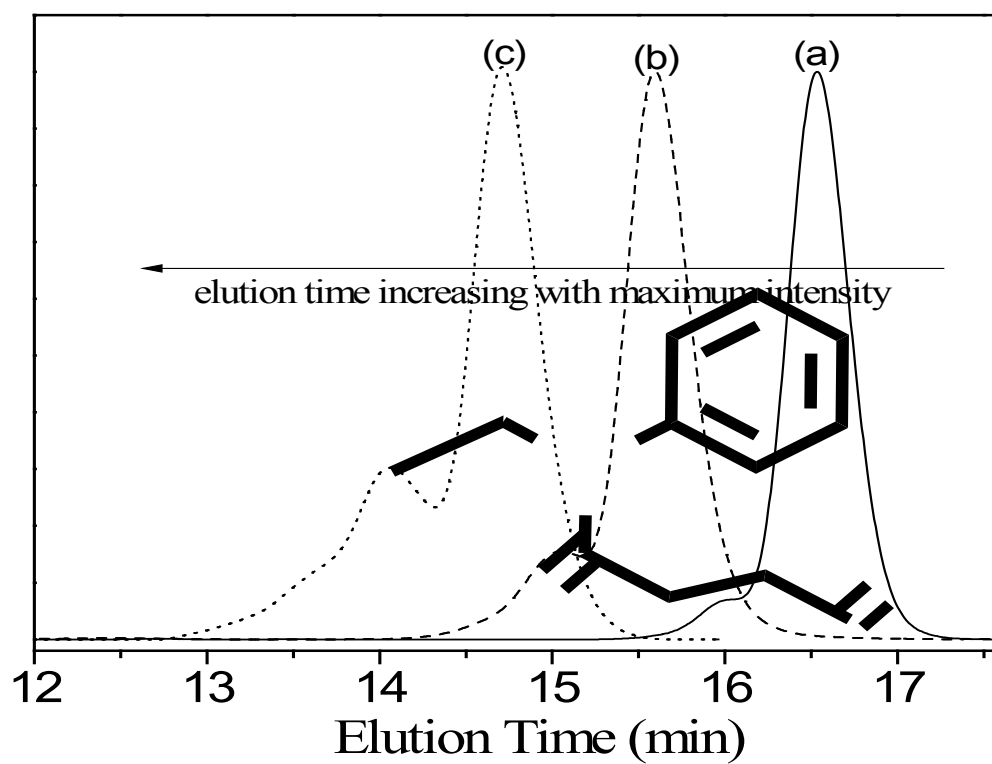


Figure S1. SEC of (a) M(secA)-POSS for solid line (b) MA-POSS for dash line (c) MD-POSS for dot line

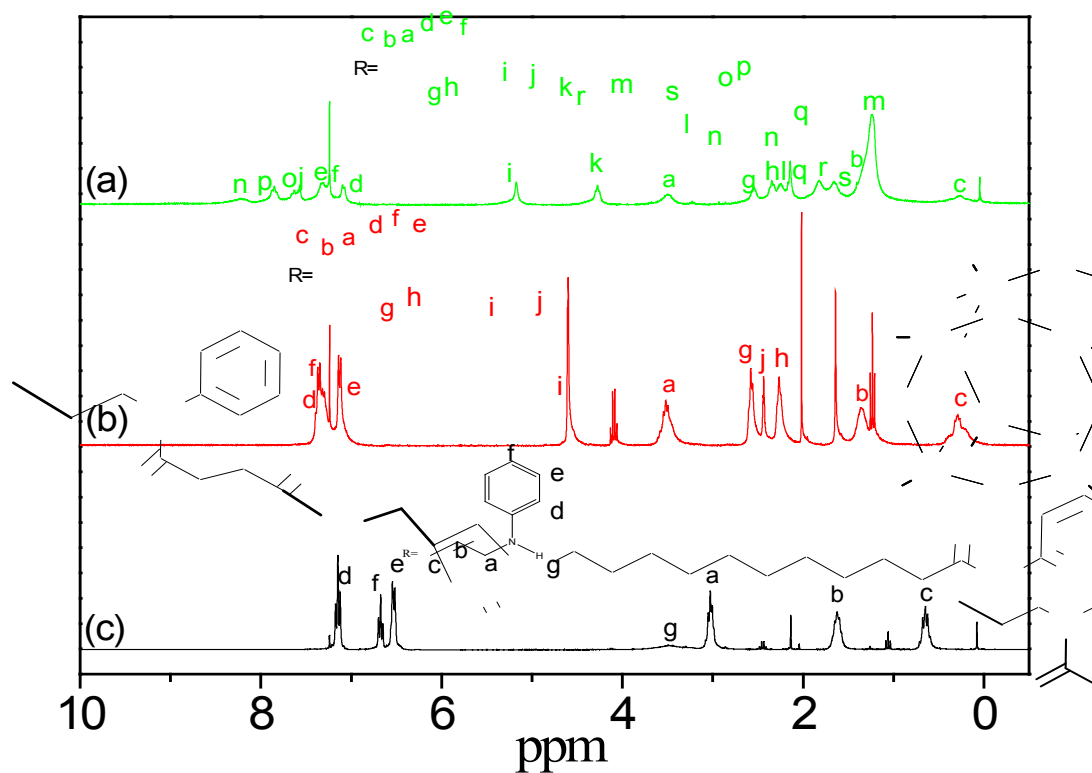


Figure S2. ^1H NMR of (a) MD-POSS (b) MA-POSS (c) M(secA)-POSS in CDCl_3

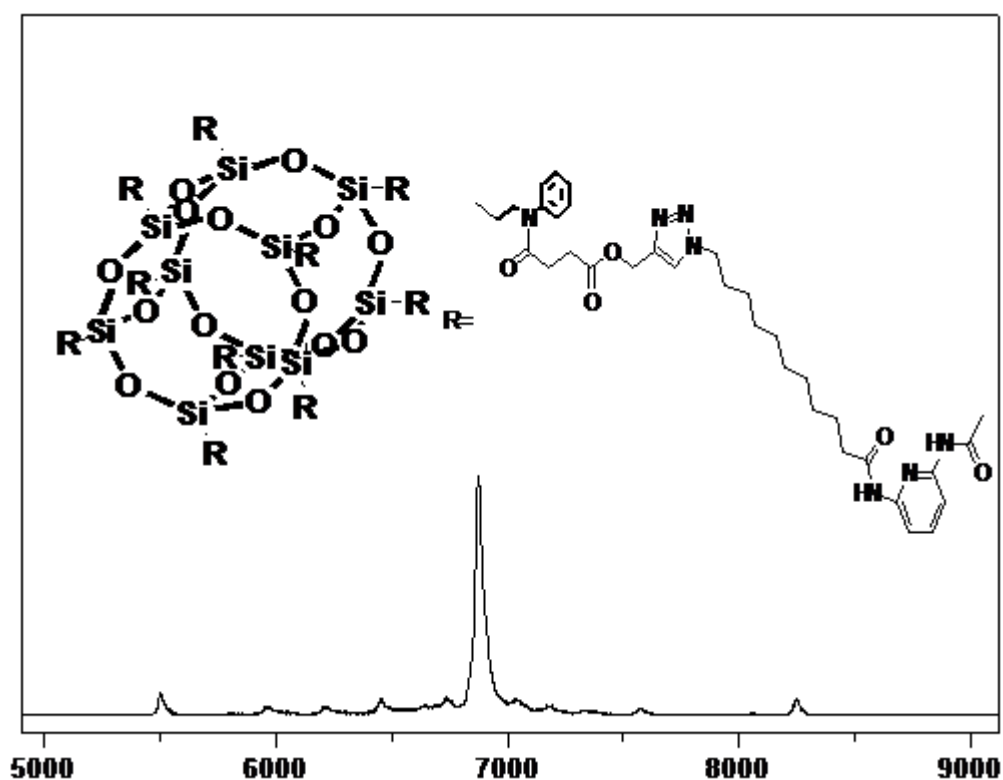


Figure S3. MALDI-TOF mass spectra of MD-POSS

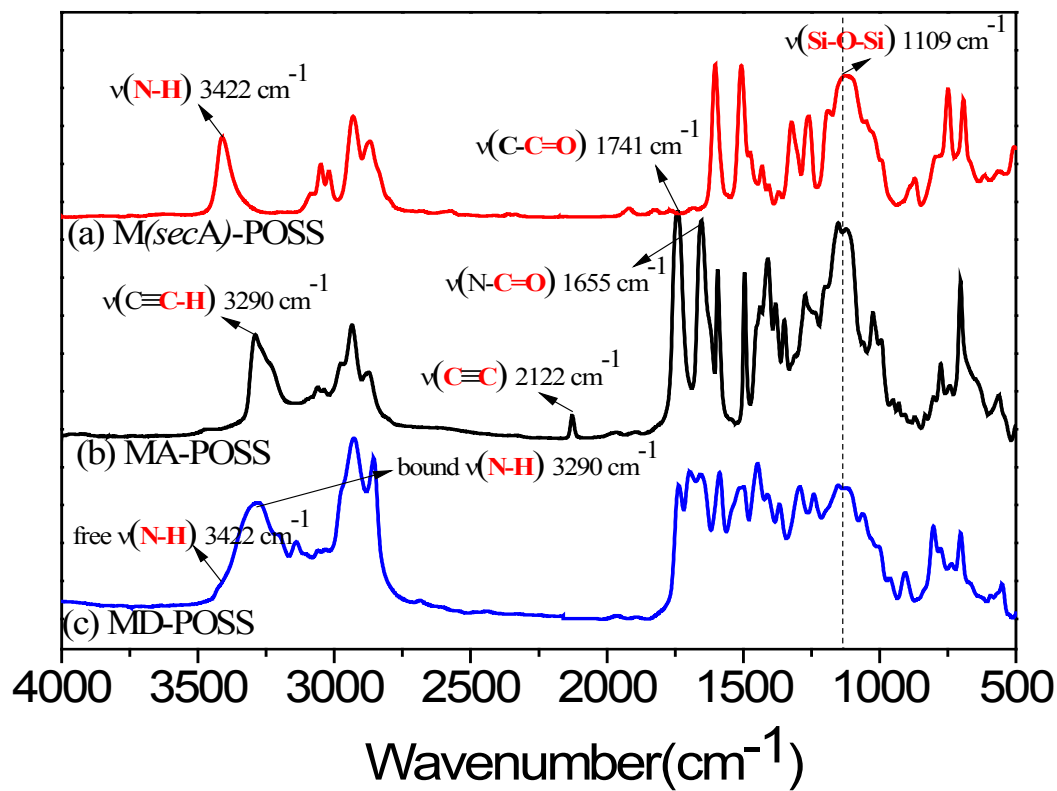
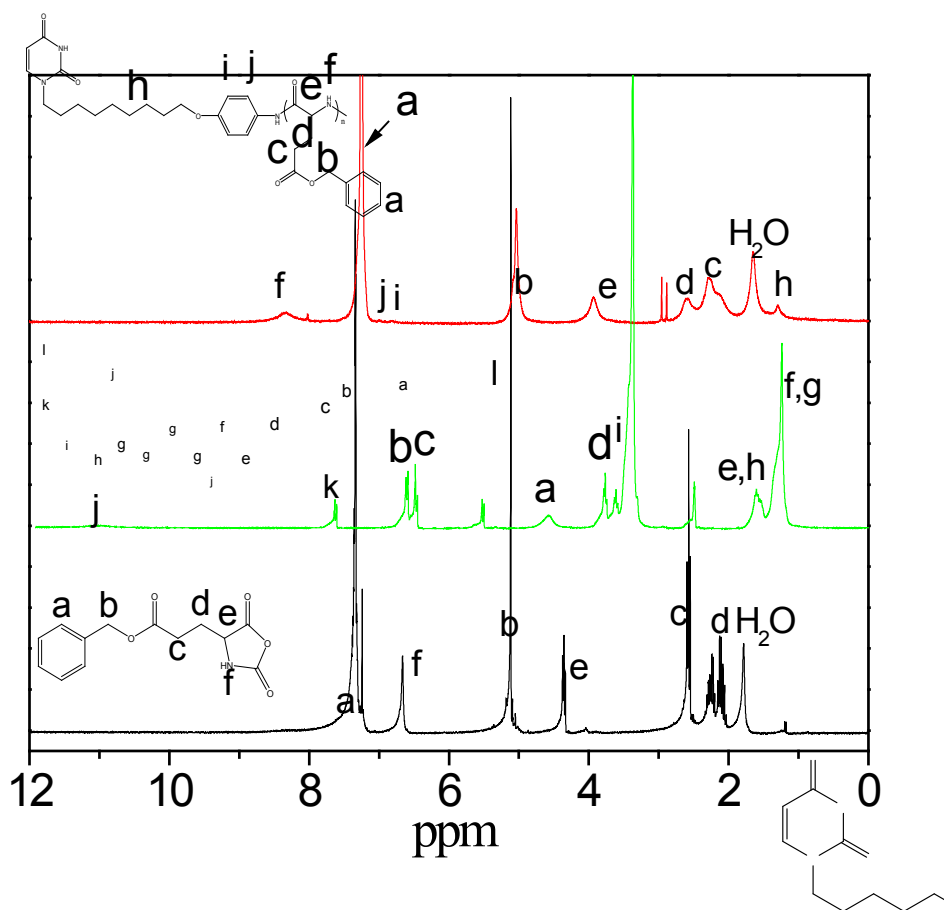


Figure S4. FT-IR spectra of (a) M(*secA*)-POSS (b) MA-POSS (c) MD-POSS



S5. ^1H NMR of (a) U-PBLG in CDCl_3 (b) amine-U in $d\text{-DMSO}$ (c) NCA monomer in CDCl_3

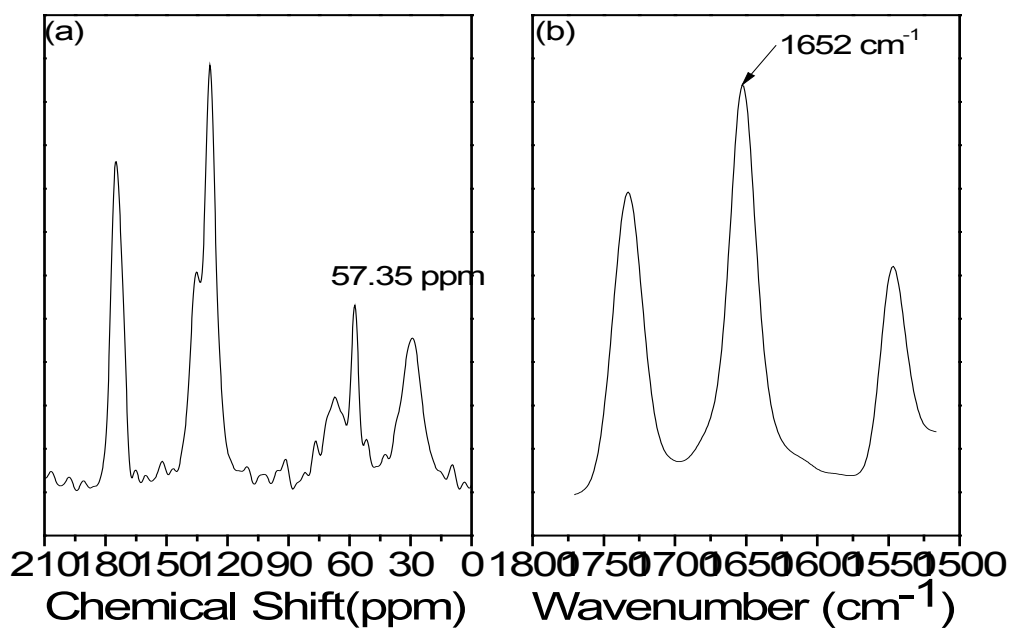


Figure S6. spectra of (a) Solid state ^{13}C NMR and (b) FT-IR of U-PBLG

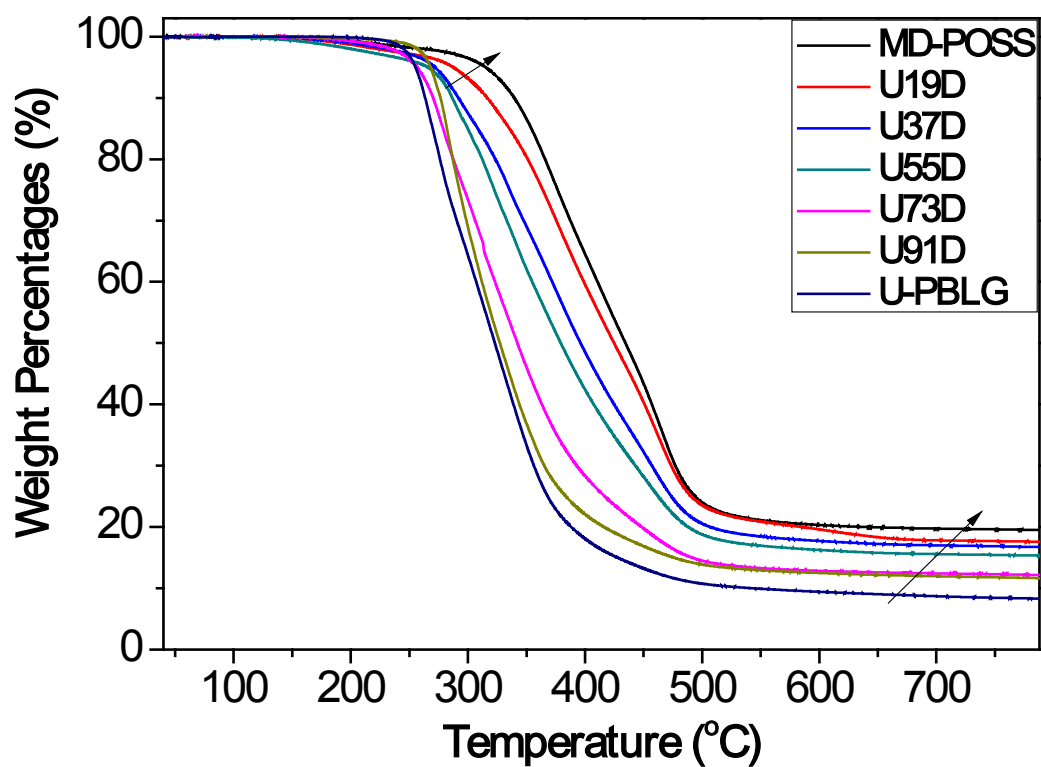


Figure S7. TGA of (a) MD-POSS (b) U19D (c) U37D (d) U55D (e) U73D (f) U91D (g) U-PBLG

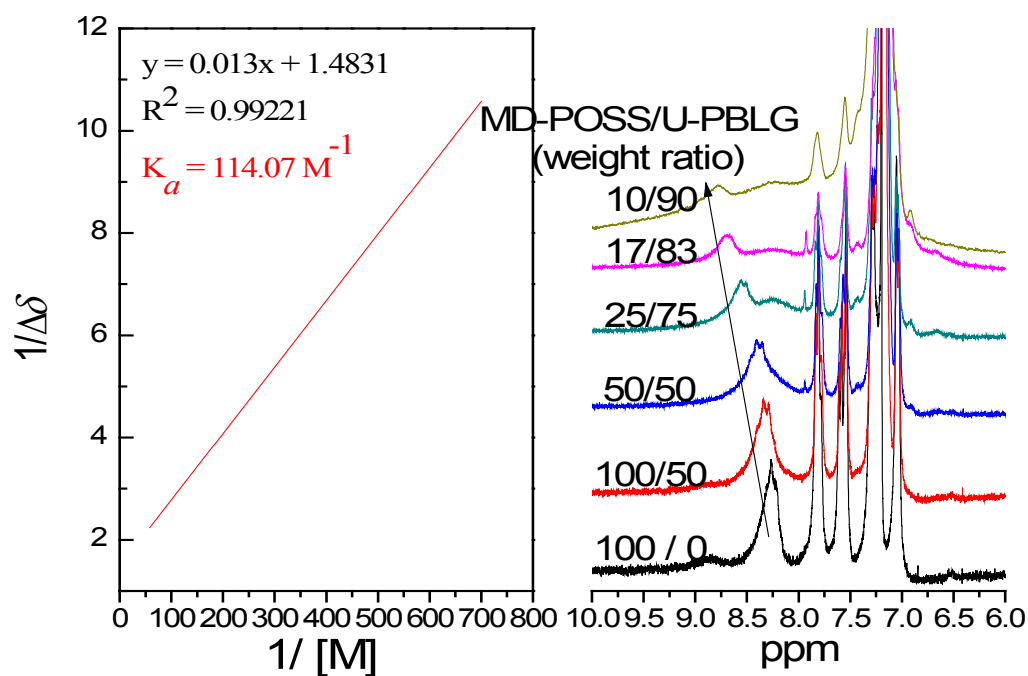


Figure S8. ^1H NMR titration of U-PBLG blending with MD-POSS

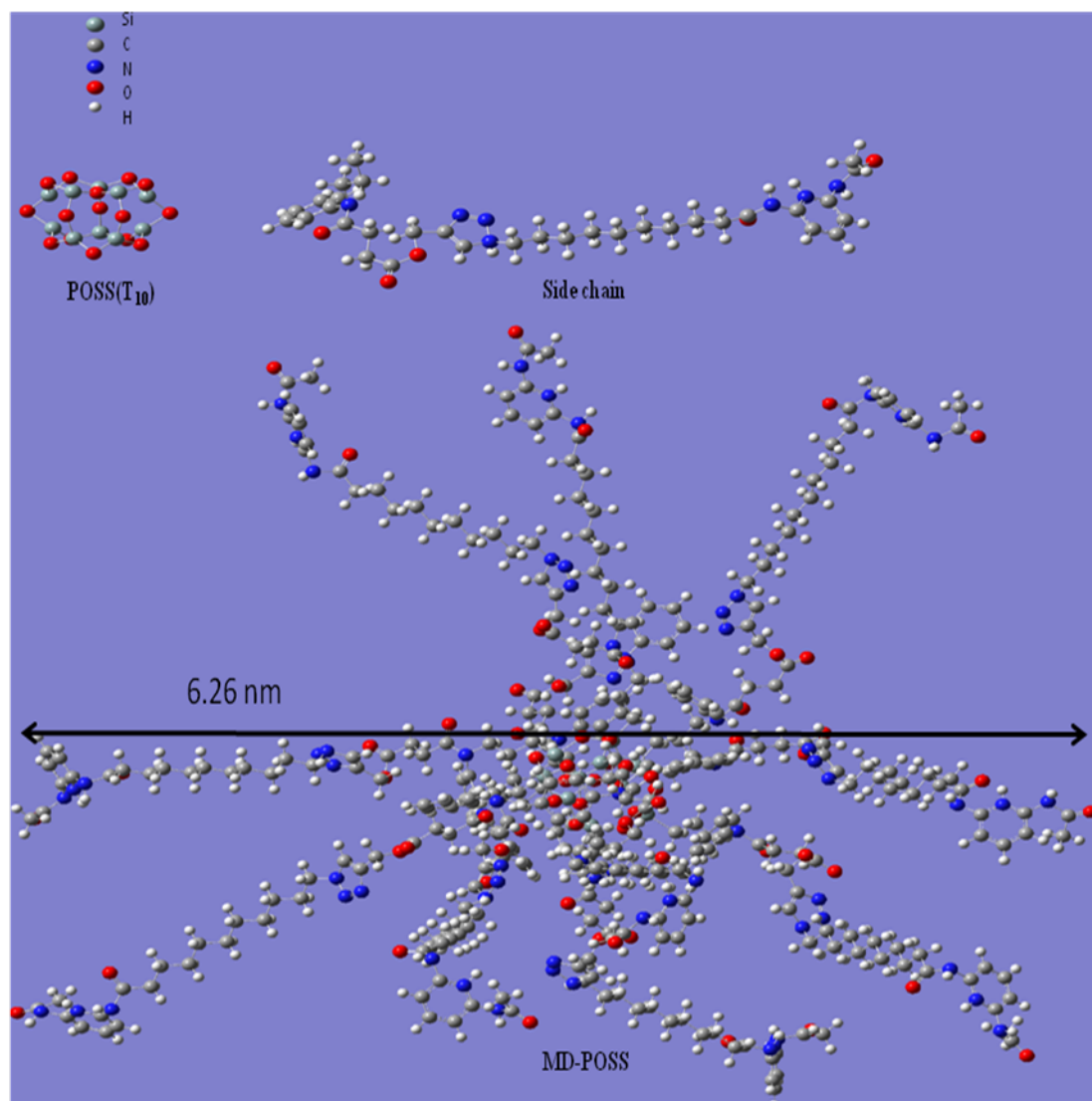


Figure S9. Gaussion calculations and 3-D structures of POSS(T₁₀) and side chain MD-POSS

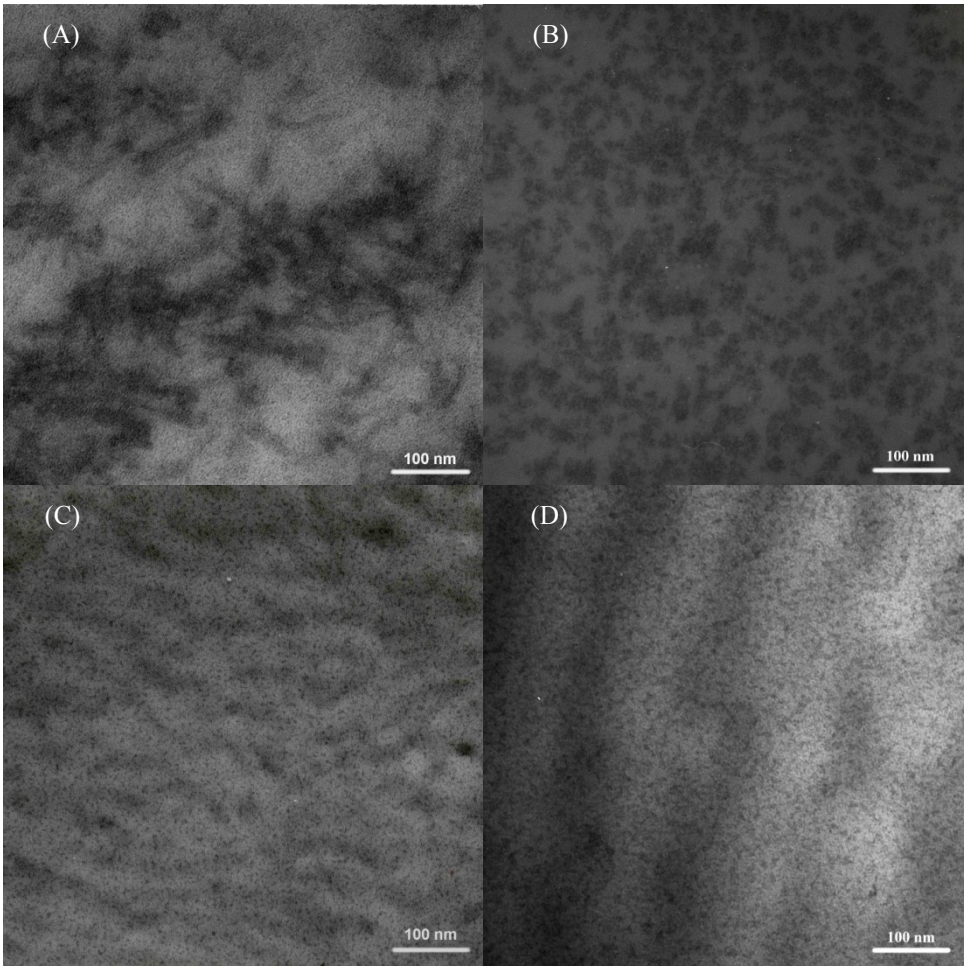


Figure S10. TEM images of (A) U-PBLG (B) MD-POSS (c) U19D (d) U37D

Table. S1. Thermo properties of U-PBLG, MD-POSS and blending materials				
entry	T _g (°C)	T _{d5%} (°C)	T _{d10%} (°C)	Char yield (%)
MD-POSS	60.30	315.63	340.48	19.63
U19D	62.68	287.42	316.67	17.85
U37D	49.94	272.74	292.91	17.01
U55D	26.13, 69.06	266.46	286.86	15.66
U73D	26.01, 73.34	257.32	270.66	12.53
U91D	24.95, 65.87	268.29	276.37	11.98
U-PBLG	23.87	255.37	263.21	8.73