

Supporting Information

Fine-Tunable Absorption of Uniformly Aligned Polyurea Thin Films for Optical Filter using Sequentially Self-Limited Molecular Layer Deposition

*Yi-Seul Park, Sung-Eun Choi, Hyein Kim, Jin Seok Lee**

Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea

*E-mail: jinslee@sookmyung.ac.kr

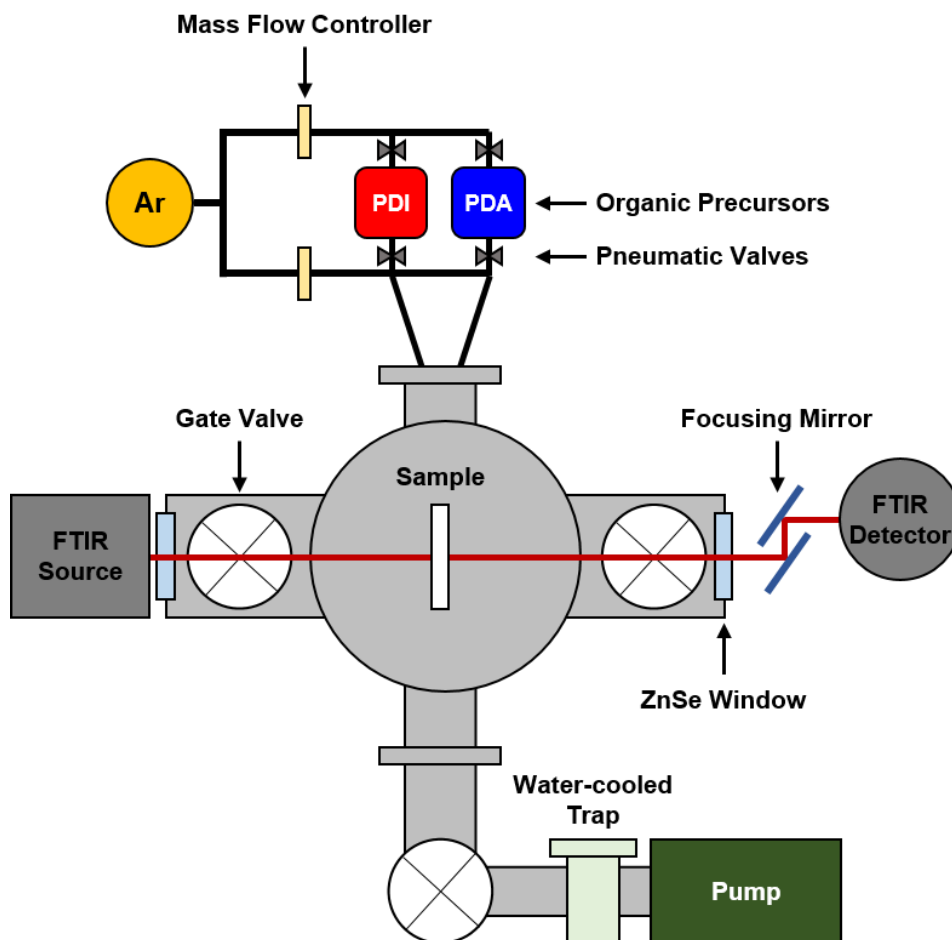


Figure S1. Reactor design. Schematic of the MLD setup, equipped with *in situ* FTIR spectroscopy during alternative exposure for the polyurea MLD film.

| Number of Cycles | 1 Cycle | | | | 2 Cycle | |
|------------------------|-------------|------------------|----------------|--------------------|------------|-----|
| Step | Step 1 | Step 2 | Step 3 | Step 4 | Step 1 | ... |
| (PDI/PDA) _N | PDI 60 s | Exposure 30 s | Purge 120 s | Evacuation 30 s | PDI 60s | ... |
| | Step 5 | Step 6 | Step 7 | Step 8 | Step 5 | ... |
| | PDA 30 s | Exposure 30 s | Purge 120 s | Evacuation 30 s | PDA 30s | ... |

Table S1. MLD sequence. The sequence of the polyurea MLD reaction processes.

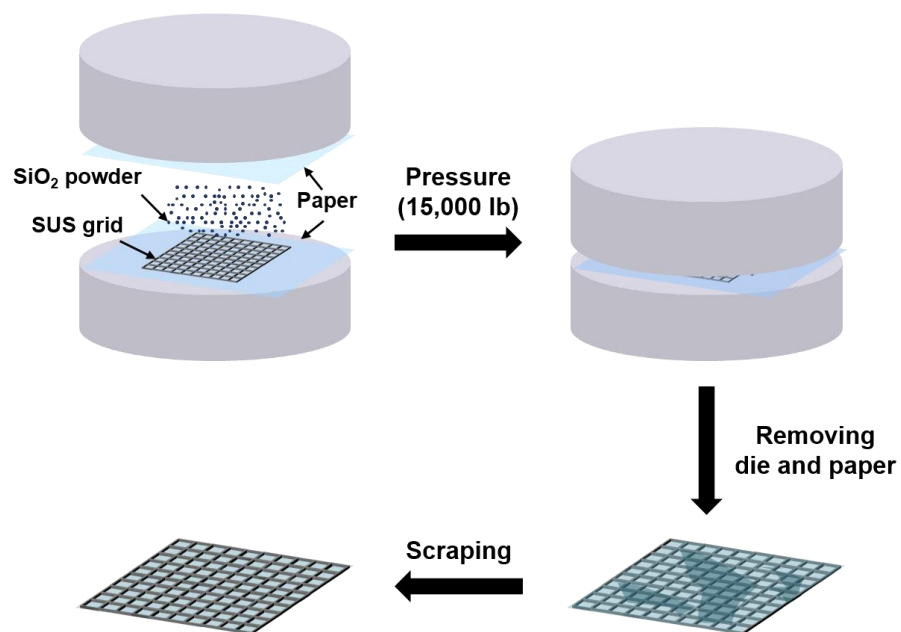


Figure S2. Substrate preparation for *in situ* FTIR spectroscopy. Schematic illustration of the preparation of the SiO₂ particle substrate for *in situ* FTIR measurements using SiO₂ powder on a SUS grid.

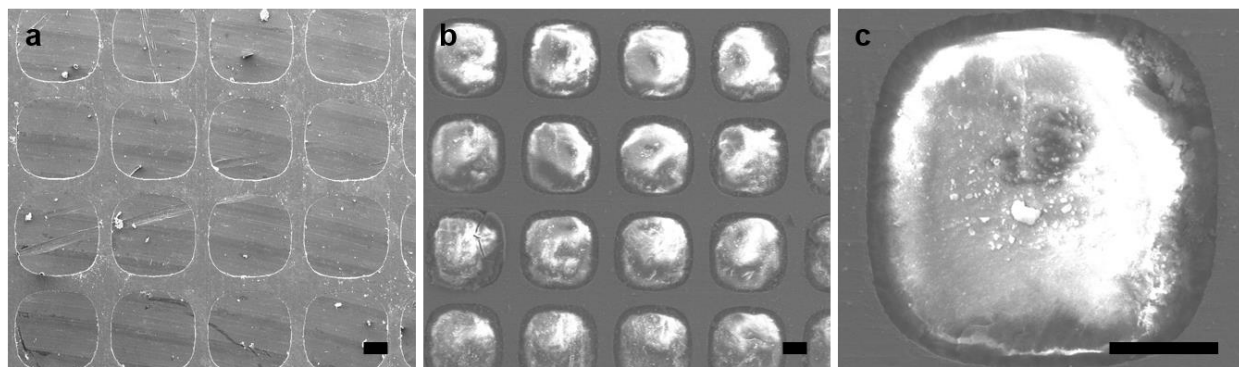


Figure S3. SUS grid for *in situ* FTIR spectroscopy. The SEM images of (a) the blank SUS grid, (b) the grid after SiO₂ powder was pressed into the grid holes, and (c) the pressed SiO₂ powder surface in a single grid hole. The scale bars are 100 μm .

| Wavenumber (cm ⁻¹) | Mode |
|--------------------------------|------------------------------------|
| 3400 - 3100 | N-H stretch |
| 3043 | aromatic C-H stretch |
| 2949 | CH ₂ asymmetric stretch |
| 2851 | CH ₂ symmetric stretch |
| 2270 | N=C=O stretch |
| 1651 | amide I (C=O stretch) |
| 1510 | amide II (CNH) |
| 1404 | N-H deformation in amide |

Table S2. All peak assignments for polyurea film. Mode assignment for the *in situ* FTIR spectra of the polyurea MLD film.

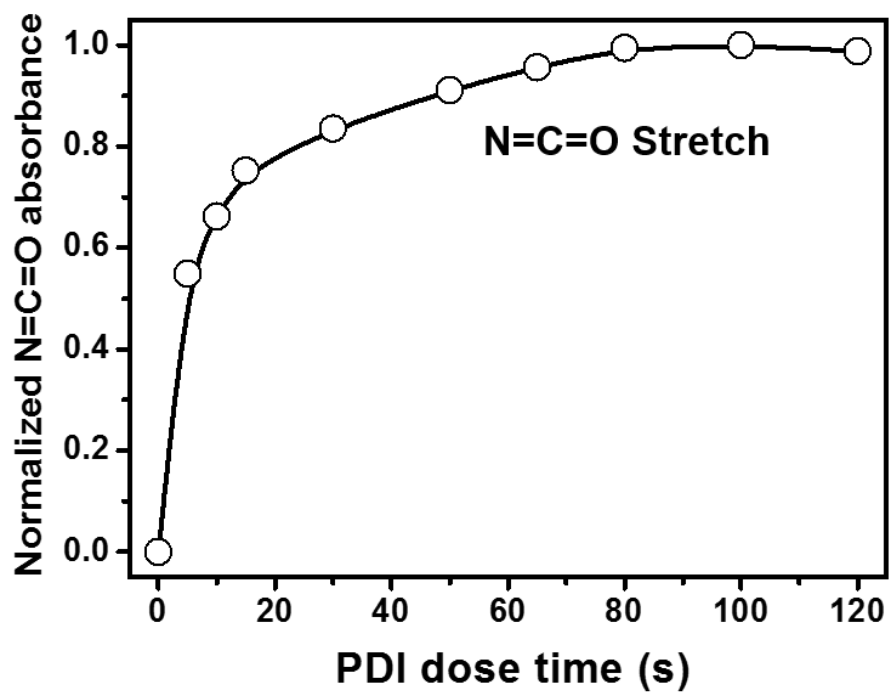


Figure S4. Self-limiting reactions. Normalized absorbance of the N=C=O stretching vibration with respect to the PDI exposure time. The PDI was dosed on an amine-terminated surface, which can be obtained by sufficient PDA dose. When the PDI is exposed for about 60 s, the absorbance of the N=C=O stretching vibration begins to saturate.

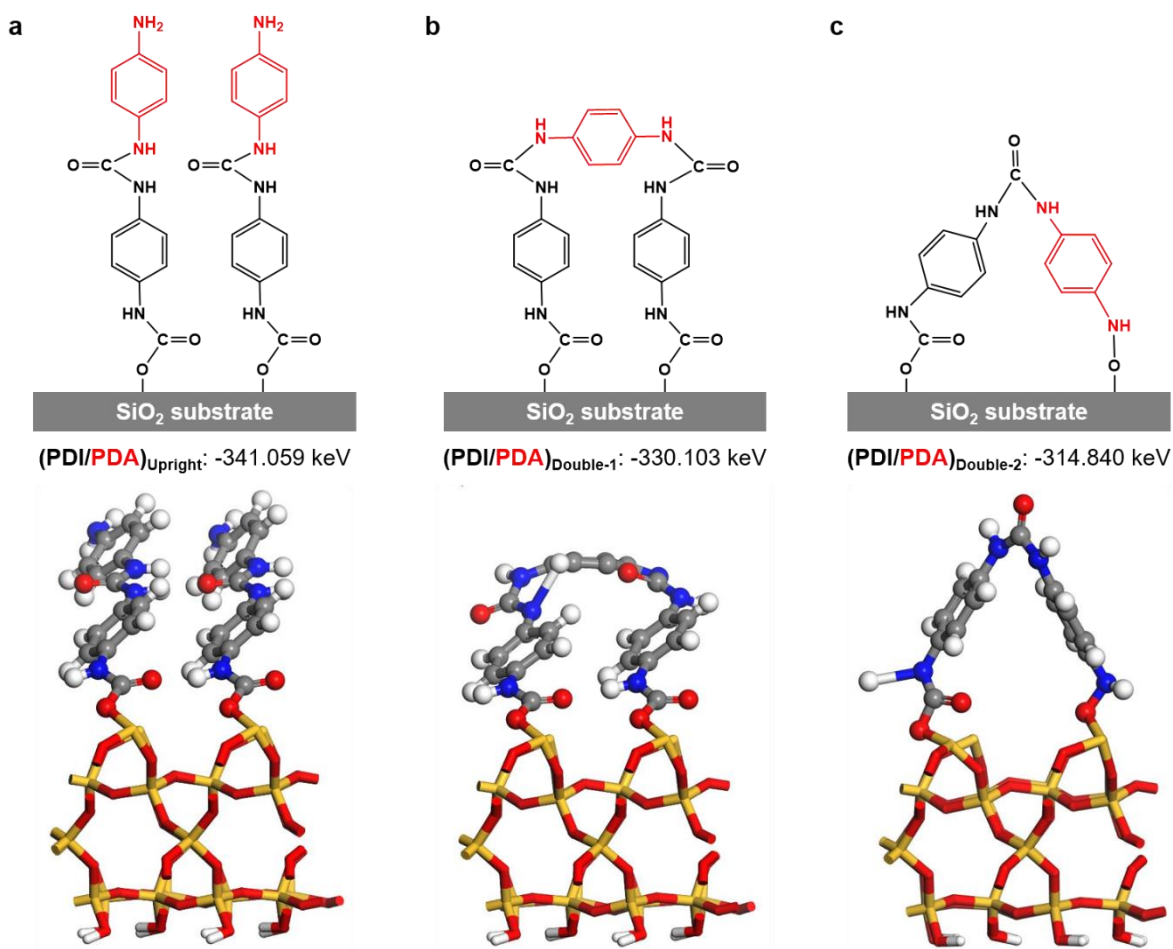


Figure S5. The DFT calculation of potential energy for various molecular geometries of $(\text{PDI}/\text{PDA})_1$ polyurea MLD films. (a) Upright and (b, c) two different double reactions of PDA molecule on PDI molecules tethered to SiO_2 substrate. The potential energies for geometrical optimization are (a) -341.059, (b) -330.103, and (c) -314.840 keV, respectively, resulted from energy minimization of DFT calculation.

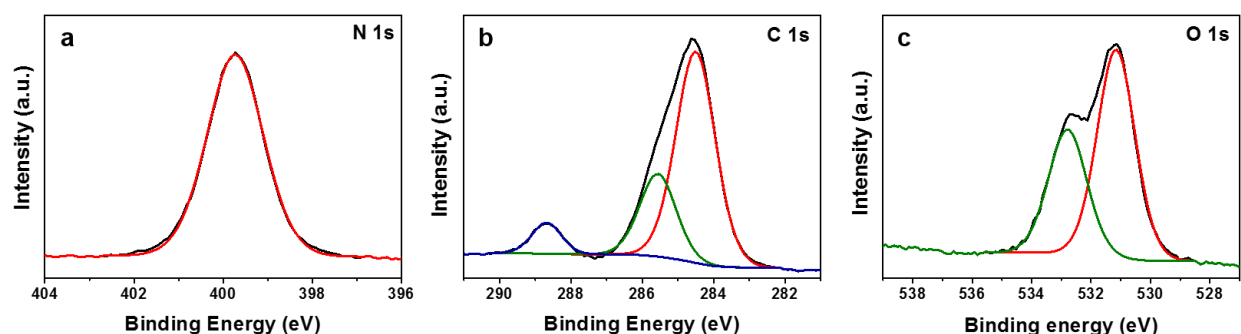


Figure S6. The X-ray photoelectron spectroscopy (XPS) of the polyurea MLD film. High-resolution XPS of (a) N 1s, (b) C 1s, and (c) O 1s in wide XPS of (PDI/PDA)₁₀₀ polyurea MLD film indicate the atomic environment and depend on the bonding in the film. The N 1s high-resolution spectrum reveals that there is a single peak at 399.7 eV, indicating that there is single type of nitrogen in the (PDI/PDA)₁₀₀ film, as expected (Figure S6a). As shown in Figure S6b, three separate peaks at 284.5 (red), 285.7 (green), and 288.8 eV (blue) can be fitted in the C 1s envelope, indicating that there are multiple types of carbon in the (PDI/PDA)₁₀₀ film. The more electronegative substituent would withdraw the electron density from the carbon atom, resulting in a high binding energy of C 1s. Thus we expect that the peak at 284.5 eV results from the electron-rich aromatic C-C hydrocarbons in the film. The middle peak at 285.7 eV is attributed to carbon near nitrogen (C-N), and the highest binding energy peak at 288.8 eV is due to carbonyl carbon in the urea linkage. The ideal composition of each carbon is 7:2:1 for C-C:C-N:C=O, and the measured composition is 7.25:2:0.6, which is nearly matched to the ideal structure. The O 1s high-resolution spectrum contains two separate peaks at 531.0 (red) and 532.8 eV (green). The major peak at 531.0 eV is attributed to the carbonyl group of urea bond in the (PDI/PDA)₁₀₀ film, and the minor peak at 532.8 eV results from the underlying SiO₂ substrate (Figure S6c).

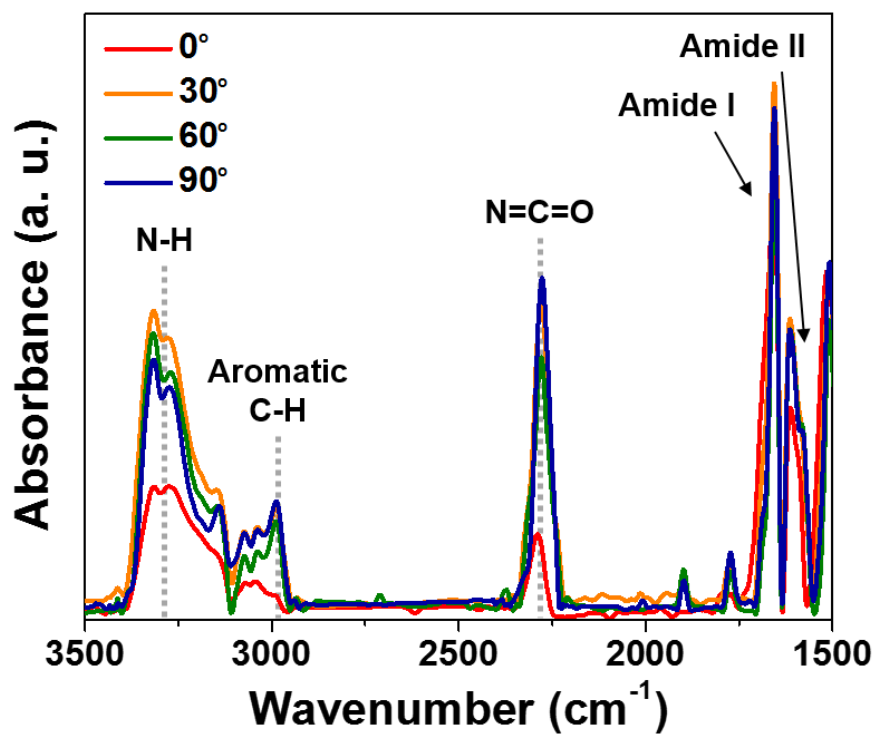


Figure S7. Molecular orientation of randomly oriented (PDI/PDA) polyurea film. The plane-polarized grazing angle FTIR spectra of randomly deposited polyurea film by spin coating. There are no peak shifts, and the intensity tends to change with different dihedral angles between the plane of polarization and the substrate.

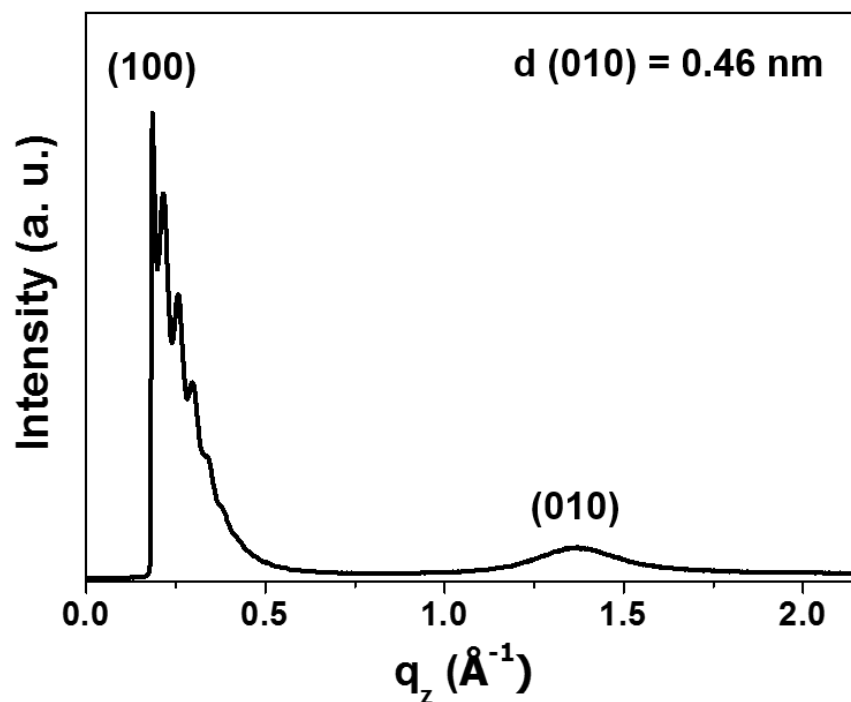


Figure S8. The grazing-incidence wide-angle X-ray scattering (GIWAXS) of the (PDI/PDA)₁₅₀ MLD film. Vertical linecut of out-of-plane with scattering vector (q_z), which are the perpendicular wave vector transfer with respect to (PDI/PDA)₁₅₀ MLD film. The polyurea MLD film showed interlamellar scattering (100) with a lamellar spacing of in between 0.21 and 0.24 \AA^{-1} in the out-of-plane direction and a (010) peak in the out-of-plane direction with face-on π - π stacking ($q_z = 1.37 \text{ \AA}^{-1}$, $d = 0.46$ nm,).

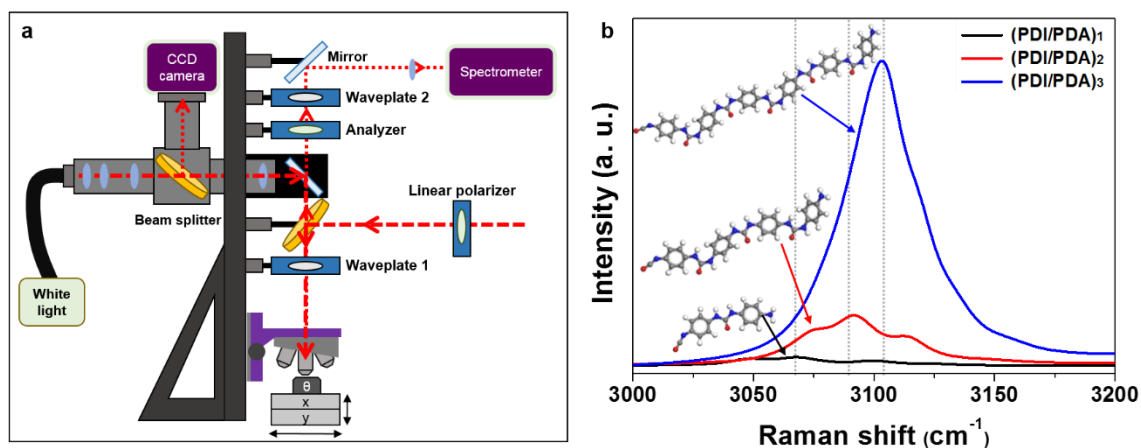


Figure S9. Measurement of Raman spectroscopy. (a) Schematic of the Raman spectroscopy setup. (b) Calculated Raman spectra of the (PDI/PDA) urea linkage regarding the number of cycles by DFT calculations. Blue shift occurred as the number of urea linkages increased, which implies that the peak of the (PDI/PDA)_N polyurea MLD film is shifted at higher energies.

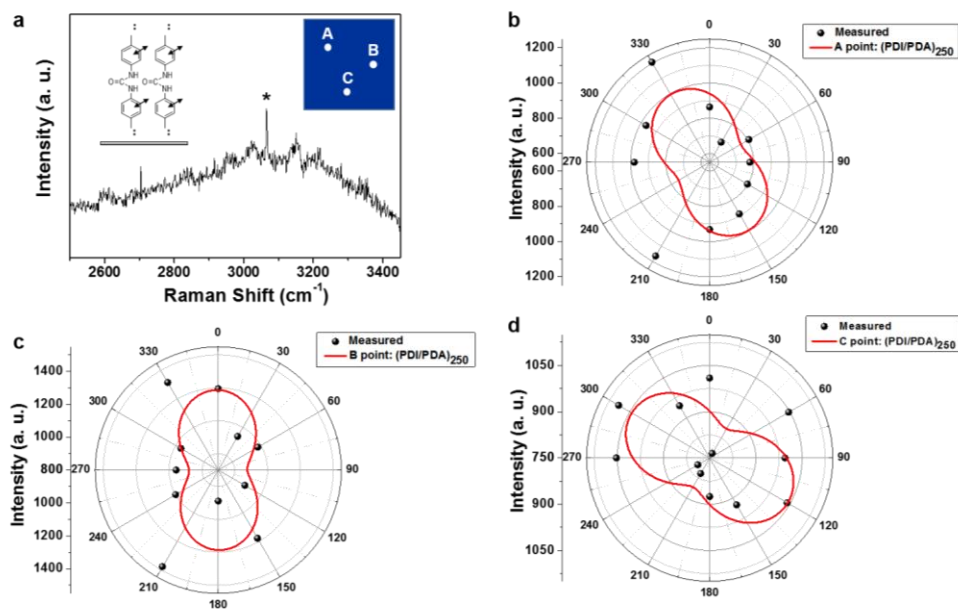


Figure S10. Raman spectrum of the polyurea MLD film at different locations. (a) Raman spectrum of the molecular vibration in (PDI/PDA)₂₅₀ polyurea MLD film using a 514.5 nm Ar ion laser as the excitation source. Polar plot of the peak with an asterisk in (a), showing the polarization dependence of the Raman scattering intensities of (PDI/PDA)₂₅₀ polyurea MLD film at the three different locations, such as (b) A, (c) B, and (d) C point, which were indicated in inset of (a), using the incident laser beam with polarization from 0° to 360°. The red curve indicates fitting for the Waveform sine square function.

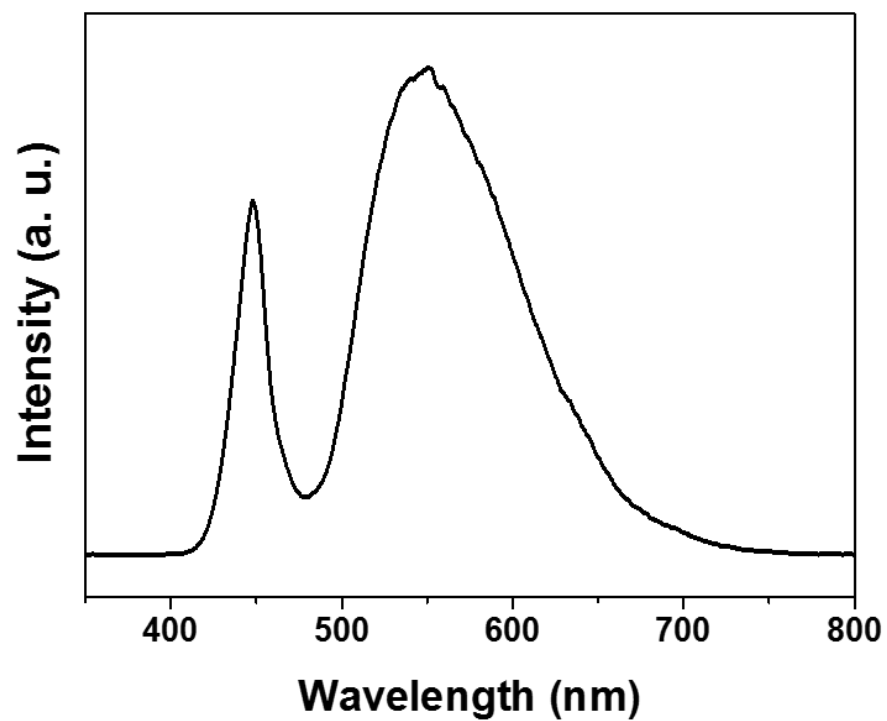


Figure S11. Measurement of Reflection spectroscopy. Spectral output of the white LED used in the reflection measurements.