# Supporting Information

## Systematically studied the relationship between high-frequency dielectric dissipation factor and water adsorption of polyimide film

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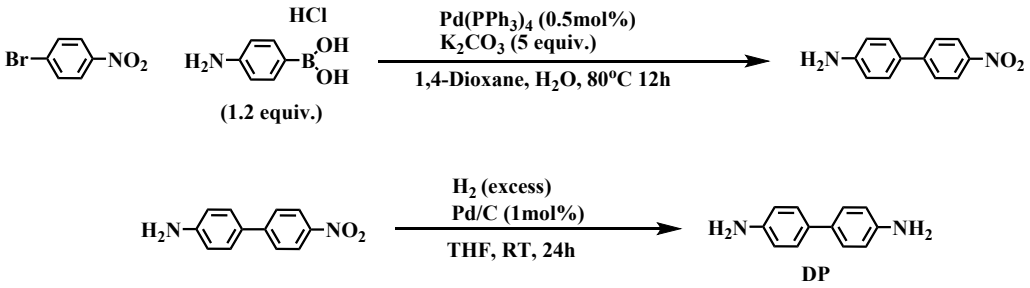
## Synthesis of monomers

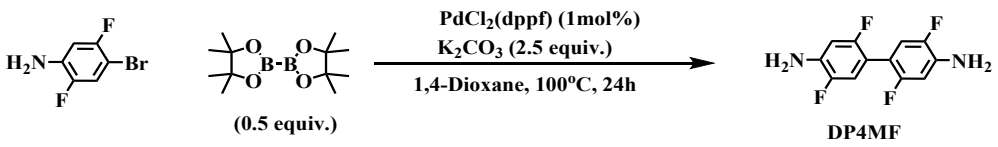
Among the seven diamines, DP and DP4MF (no commercially available) were synthesized by ourself, and the synthetic route was shown as follows.




**Scheme S1.** Synthetic route of diamine DP

1-Bromo-4-nitrobenzene (5.00 g, 24.7 mmol), (4-aminophenyl) boronic acid hydrochloride (5.15 g, 29.7 mmol), 1,4-dioxane (200 mL) and 2 M potassium carbonate aqueous solution (62 mL) and catalytic $Pd[P(C_6H_5)_3]_4$ were added in a 500 mL flask with argon atmosphere. The rection mixture was heated at 80 °C for 12 h and then purified through silica-gel column to obtain 4'-nitro-4-biphenylamine (4.71 g, 88.8%). $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 8.20 (d, $J$ = 8.9 Hz, 2H), 7.82 (d, $J$ = 8.9 Hz, 2H), 7.53 (d, $J$ = 8.6 Hz, 2H), 6.68 (d, $J$ = 8.6 Hz, 2H), 5.59 (s, 2H).

Then the 4'-nitro-4-biphenylamine (4.50 g, 21.0 mmol), Pd/C (0.5 g) and THF (150 mL) were added in a flask to react with hydrogen at room temperature for 24 h. The mixture was purified through silica-gel column to obtain the target monomer DP (3.5 g, 90.5%, white solid). $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 7.19 (d, $J$ = 8.5 Hz, 4H), 6.57 (d, $J$ = 8.5 Hz, 4H), 4.99 (s, 4H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, δ, ppm): 146.85, 128.65, 126.01, 114.33. HRMS m/z: $[m+H]^+$ calcd for $C_{12}H_{13}N_2$, 185.10732, found 185.10681.




**Scheme S2.** Synthetic route of diamine DP4MF

2,5-Difluoro-4-bromonitrobenzene (10.0 g, 48.1 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (6.10 g, 24.0 mmol), potassium carbonate (16.6 g, 120 mmol), 1,4-dioxane (200 mL) and catalytic $PdCl_2$ (dppf) were added to a 500 mL flask and the reaction was carried out in argon atmosphere for about 24 h. Through silica-gel column, the mixture was purified to produce the target monomer DP4MF (3.80 g, 61.7%, white solid). $^1$H NMR (400 MHz, DMSO-$d_6$, δ, ppm): 7.03 - 6.94 (m, 2H), 6.61 - 6.48 (m, 2H), 5.55 (s, 4H). $^{19}$F NMR (377 MHz, DMSO-$d_6$, δ, ppm): -120.45, -140.54. $^{13}$C NMR (101 MHz, DMSO-$d_6$, δ, ppm): 156.88, 154.49, 147.74, 145.85, 137.44, 116.73, 108.55, 101.95. HRMS m/z: $[m+H]^+$ calcd for $C_{12}H_9F_4N_2$, 257.06964, found 257.06946.

## Other Figures and Tables

**Table S1.** Inherent viscosities ($\eta_{inh}$) and molecule weight of seven poly(amic acid)s (PAAs)

| PAAs | $\eta_{inh}$ (dL/g) | $M_n$ ($10^3$ g/mol) | $M_w$ ($10^3$ g/mol) | PDI |
|---|---|---|---|---|
| **APBIA-BPDA** | **1.44** | **25** | **32** | **1.29** |
| **DABA-BPDA** | **2.13** | **79** | **111** | **1.41** |
| **DP-BPDA** | **4.85** | **112** | **170** | **1.51** |
| **MT-BPDA** | **1.44** | **65** | **97** | **1.49** |
| **TFMB-BPDA** | **1.17** | **90** | **140** | **1.55** |
| **APAB-BPDA** | **1.49** | **57** | **75** | **1.31** |
| **DP4MF-BPDA** | **0.71** | **7.8** | **13** | **1.68** |

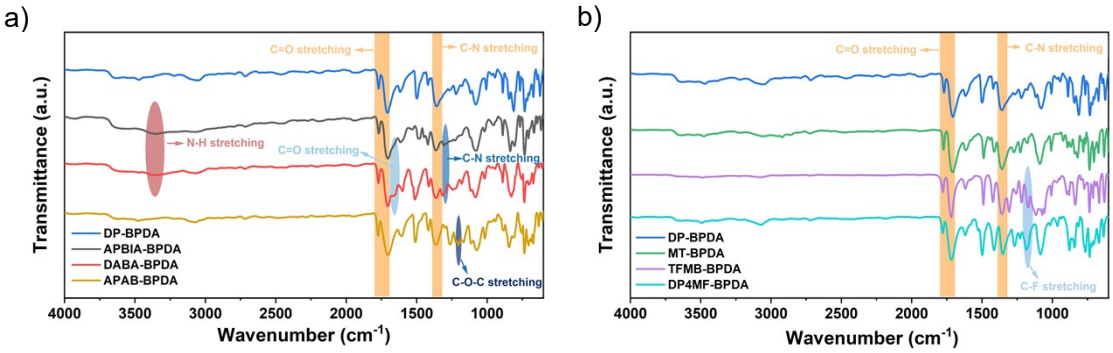



**Figure S1.** Fourier-transform infrared (FT-IR) spectra of seven PI films: a) DP-BPDA, APBIA-BPDA, DABA-BPDA and APAB-BPDA; b) DP-BPDA, MT-BPDA, TFMB-BPDA and DP4MF-BPDA.

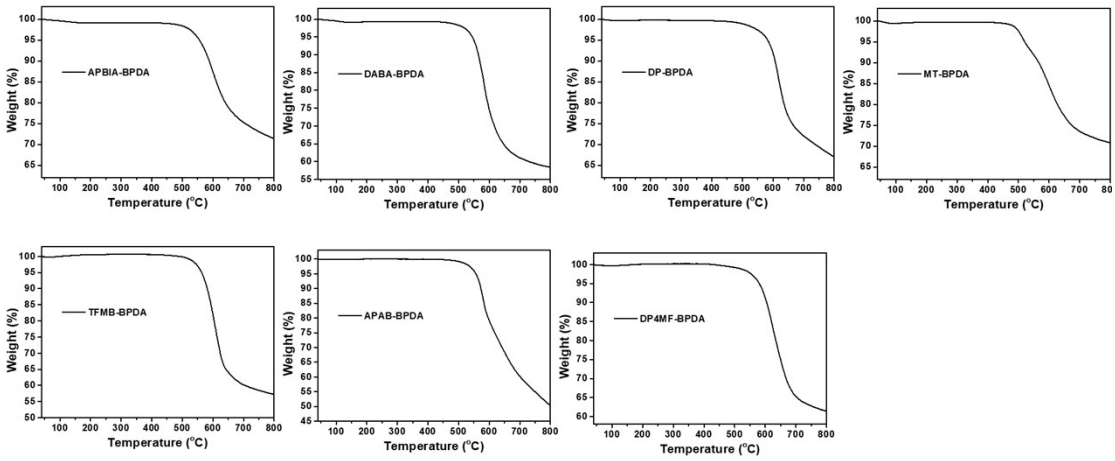



**Figure S2.** TGA curves of PI films.

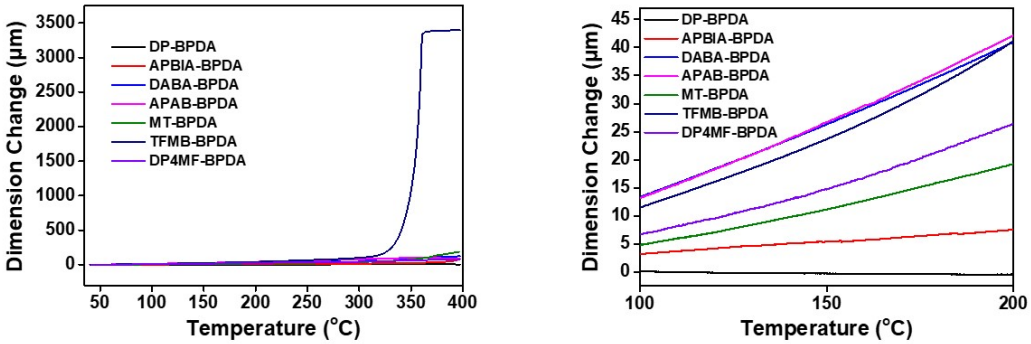



**Figure S3.** TMA curves of PI films.

**Table S2.** Thermal properties of PI films

| Polyimide | $T_s$[a] (°C) | CTE[b] (ppm·K$^{-1}$) | $T_d$[c] (°C) | | Char Yield[d] |
|---|---|---|---|---|---|
| | | | 1 wt% | 5 wt% | (wt%) |
| **APBIA-BPDA** | >400 | 2.8 | 509 | 562 | 71.5 |
| **DABA-BPDA** | >400 | 18.4 | 504 | 549 | 58.5 |
| **DP-BPDA** | >400 | -0.4 | 510 | 584 | 67.0 |
| **MT-BPDA** | >400 | 10.1 | 490 | 525 | 70.8 |
| **TFMB-BPDA** | 351 | 22.3 | 509 | 559 | 57.2 |
| **APAB-BPDA** | >400 | 19.6 | 506 | 556 | 50.5 |
| **DP4MF-BPDA** | >400 | 15.3 | 512 | 580 | 61.4 |

[a] Softening temperature, measured by TMA at a heating rate of 10 °C·min$^{-1}$.

[b] Calculated by TMA second heating curves (100 to 200 °C).

[c] Measured by TGA at a heating rate of 10 °C·min$^{-1}$ in nitrogen.

[d] Residual weight percentage at 800 °C in nitrogen.

## Mechanical properties of polyimide films

**Table S3.** Mechanical properties of PI films

| Polyimide | Tensile Strength (MPa) | Tensile Modules (GPa) | Elongation at Break (%) |
|---|---|---|---|
| **APBIA-BPDA** | 220 | 6.3 | 16.7 |
| **DABA-BPDA** | 307 | 7.3 | 20.9 |
| **DP-BPDA** | 385 | 7.6 | 36.5 |
| **MT-BPDA** | 325 | 7.3 | 19.7 |
| **TFMB-BPDA** | 180 | 5.3 | 12.6 |
| **APAB-BPDA** | 170 | 6.4 | 5.0 |
| **DP4MF-BPDA** | 185 | 8.0 | 2.9 |

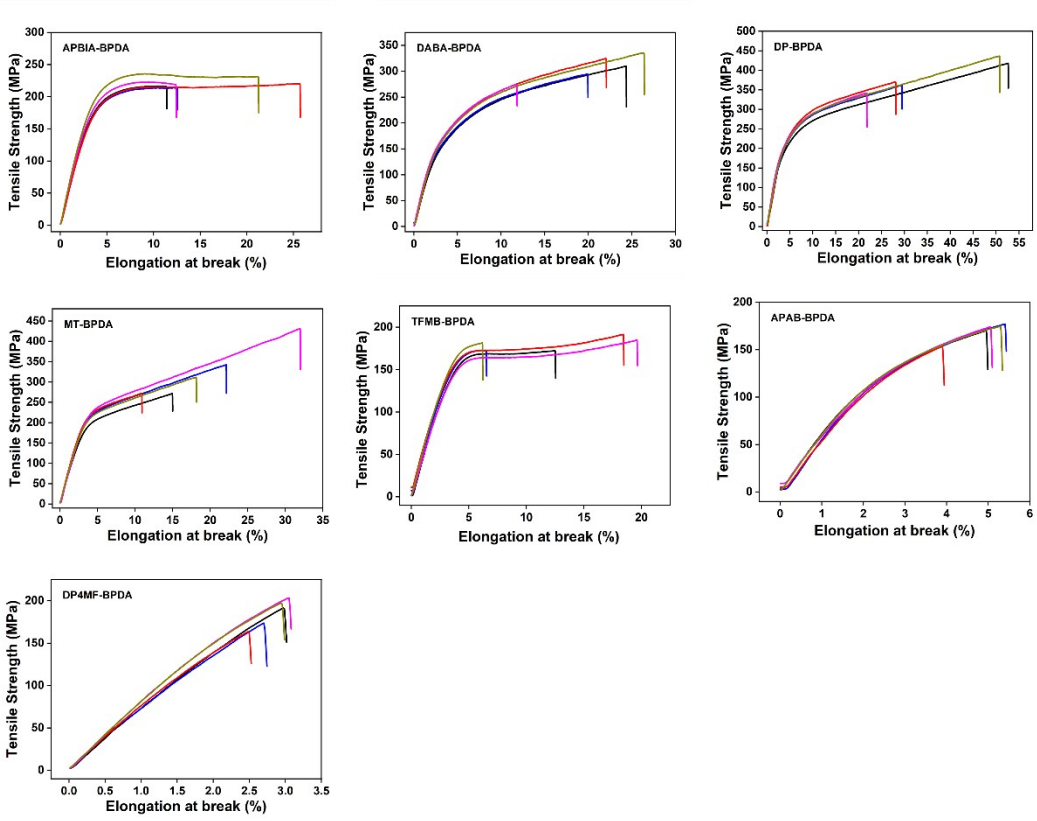
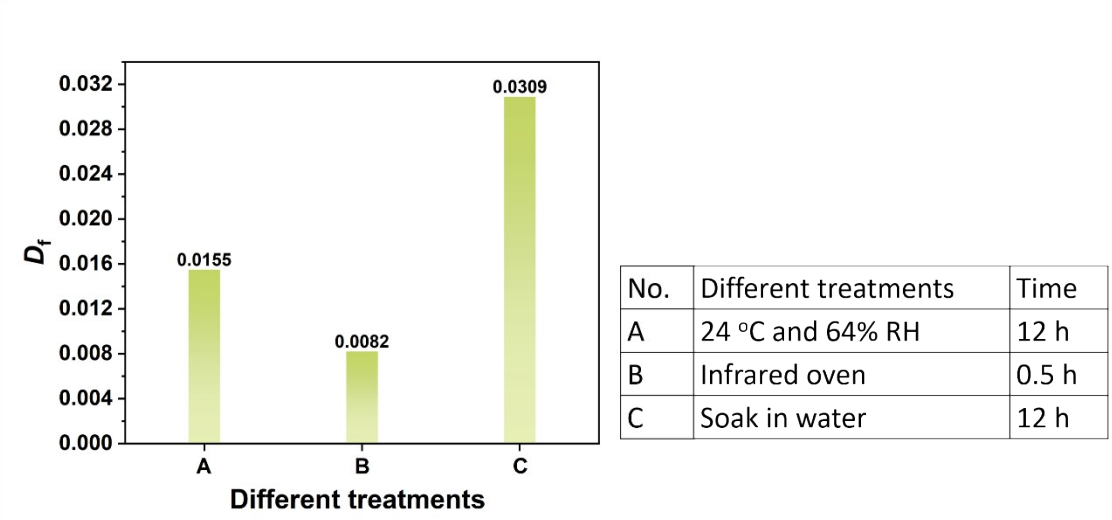



**Figure S4.** Stress-strain curves of PI films

**Table S4.** Imide ring density of PI films

| Polyimide | Imide ring density (%) |
|---|---|
| **APBIA-BPDA** | 29.0 |
| **DABA-BPDA** | 28.8 |
| **DP-BPDA** | 31.6 |
| **MT-BPDA** | 29.8 |
| **TFMB-BPDA** | 24.2 |
| **APAB-BPDA** | 28.8 |
| **DP4MF-BPDA** | 27.2 |




| No. | Different treatments | Time |
|---|---|---|
| A | 24 °C and 64% RH | 12 h |
| B | Infrared oven | 0.5 h |
| C | Soak in water | 12 h |

**Figure S5.** $D_f$ of polyimide film (ODA-PMDA) after different treatments.

**Table S5.** $D_k$ at different relative humidity of the seven PI films

| Polyimide | $D_k$ at different RH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 11% | 25% | 38% | 50% | 60% | 75% | 85% | 99% |
| **APBIA-BPDA** | 3.82 ±0.05 | 4.02 ±0.05 | 4.13 ±0.05 | 3.94 ±0.04 | 4.01 ±0.05 | 4.06 ±0.06 | 4.22 ±0.06 | 4.25 ±0.06 |
| **DABA-BPDA** | 3.80 ±0.05 | 3.85 ±0.05 | 3.91 ±0.06 | 3.89 ±0.05 | 3.97 ±0.04 | 3.96 ±0.04 | 4.01 ±0.05 | 4.09 ±0.05 |
| **DP-BPDA** | 3.61 ±0.06 | 3.71 ±0.07 | 3.68 ±0.06 | 3.67 ±0.06 | 3.78 ±0.06 | 3.71 ±0.06 | 3.85 ±0.06 | 3.88 ±0.06 |
| **MT-BPDA** | 3.28 ±0.04 | 3.38 ±0.05 | 3.40 ±0.04 | 3.41 ±0.04 | 3.45 ±0.06 | 3.48 ±0.05 | 3.44 ±0.05 | 3.52 ±0.06 |
| **TFMB-BPDA** | 3.07 ±0.08 | 3.06 ±0.04 | 3.08 ±0.03 | 3.15 ±0.04 | 3.19 ±0.04 | 3.22 ±0.04 | 3.22 ±0.04 | 3.26 ±0.04 |
| **APAB-BPDA** | 3.57 ±0.05 | 3.58 ±0.05 | 3.60 ±0.05 | 3.61 ±0.04 | 3.64 ±0.05 | 3.65 ±0.05 | 3.66 ±0.05 | 3.69 ±0.05 |
| **DP4MF-BPDA** | 3.40 ±0.05 | 3.44 ±0.06 | 3.46 ±0.06 | 3.48 ±0.07 | 3.47 ±0.05 | 3.52 ±0.06 | 3.52 ±0.07 | 3.54 ±0.06 |

**Table S6.** $D_f$ at different relative humidity of the seven PI films

| Polyimide | $D_f$ at different RH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 11% | 25% | 38% | 50% | 60% | 75% | 85% | 99% |
| **APBIA-BPDA** | 0.0042 ±2*10$^{-5}$ | 0.0062 ±4*10$^{-5}$ | 0.0083 ±4*10$^{-5}$ | 0.0105 ±6*10$^{-5}$ | 0.0125 ±7*10$^{-5}$ | 0.0145 ±7*10$^{-5}$ | 0.0168 ±7*10$^{-5}$ | 0.0194 ±9*10$^{-5}$ |
| **DABA-BPDA** | 0.0089 ±4*10$^{-5}$ | 0.0102 ±5*10$^{-5}$ | 0.0125 ±6*10$^{-5}$ | 0.0132 ±8*10$^{-5}$ | 0.0166 ±8*10$^{-5}$ | 0.0172 ±8*10$^{-5}$ | 0.0194 ±9*10$^{-5}$ | 0.0226 ±1*10$^{-4}$ |
| **DP-BPDA** | 0.0027 ±2*10$^{-5}$ | 0.0035 ±2*10$^{-5}$ | 0.0052 ±4*10$^{-5}$ | 0.0058 ±4*10$^{-5}$ | 0.0072 ±4*10$^{-5}$ | 0.0078 ±5*10$^{-5}$ | 0.0086 ±6*10$^{-5}$ | 0.0103 ±6*10$^{-5}$ |
| **MT-BPDA** | 0.0021 ±1*10$^{-5}$ | 0.0032 ±2*10$^{-5}$ | 0.0046 ±3*10$^{-5}$ | 0.0054 ±4*10$^{-5}$ | 0.0064 ±4*10$^{-5}$ | 0.0074 ±5*10$^{-5}$ | 0.0081 ±5*10$^{-5}$ | 0.0094 ±6*10$^{-5}$ |
| **TFMB-BPDA** | 0.0048 ±3*10$^{-5}$ | 0.0053 ±4*10$^{-5}$ | 0.0062 ±4*10$^{-5}$ | 0.0074 ±5*10$^{-5}$ | 0.0083 ±5*10$^{-5}$ | 0.0092 ±6*10$^{-5}$ | 0.0104 ±6*10$^{-5}$ | 0.0118 ±8*10$^{-5}$ |
| **APAB-BPDA** | 0.0025 ±1*10$^{-5}$ | 0.0030 ±2*10$^{-5}$ | 0.0040 ±2*10$^{-5}$ | 0.0045 ±3*10$^{-5}$ | 0.0055 ±3*10$^{-5}$ | 0.0063 ±3*10$^{-5}$ | 0.0067 ±4*10$^{-5}$ | 0.0081 ±4*10$^{-5}$ |
| **DP4MF-BPDA** | 0.0015 ±2*10$^{-5}$ | 0.0021 ±2*10$^{-5}$ | 0.0036 ±3*10$^{-5}$ | 0.0040 ±4*10$^{-5}$ | 0.0050 ±4*10$^{-5}$ | 0.0059 ±5*10$^{-5}$ | 0.0069 ±5*10$^{-5}$ | 0.0078 ±6*10$^{-5}$ |

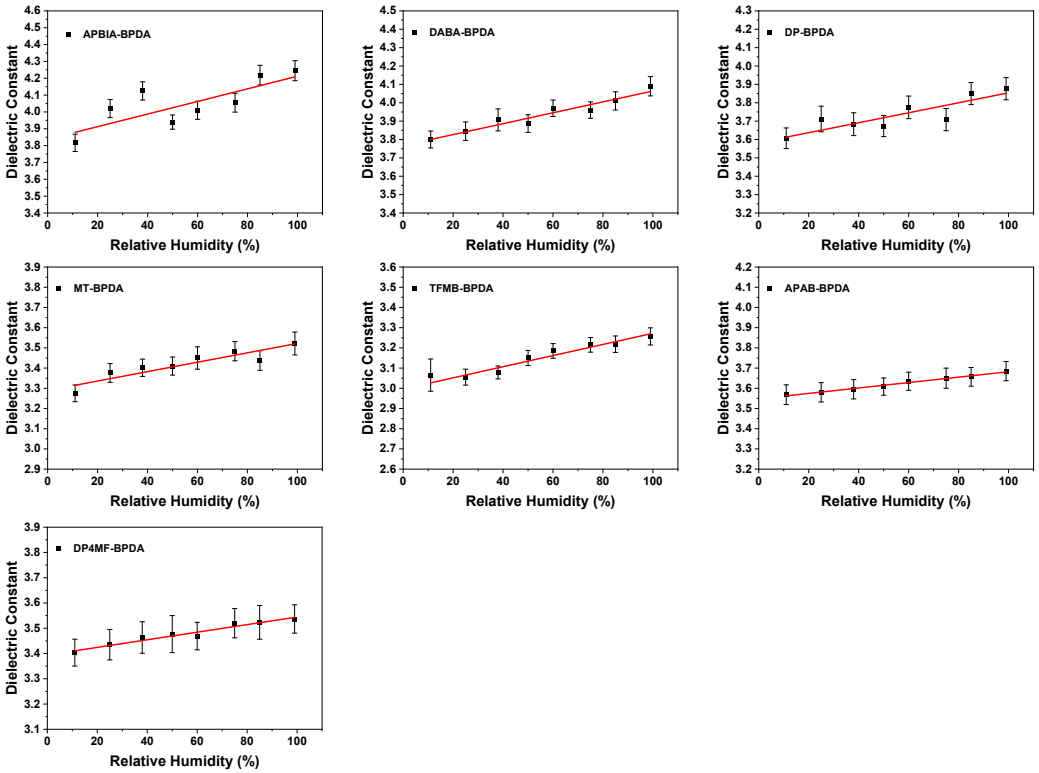



**Figure S6.** Dielectric constant ($D_k$) at 10 GHz of seven polyimide films at 23±2 °C with different relative humidity and its fitting curves.

**Table S7.** Slope, intercept, and R square of fitting curve equation for $D_k$ and relative humidity

| Polyimide | $D_k$ (Y) -RH (X): Y =aX+b | | |
|---|---|---|---|
| | a | b | $R^2$ |
| **APBIA-BPDA** | 0.37 | 3.84 | 0.60 |
| **DABA-BPDA** | 0.30 | 3.77 | 0.93 |
| **DP-BPDA** | 0.27 | 3.58 | 0.77 |
| **MT-BPDA** | 0.23 | 3.29 | 0.84 |
| **TFMB-BPDA** | 0.27 | 2.99 | 0.93 |
| **APAB-BPDA** | 0.13 | 3.55 | 0.98 |
| **DP4MF-BPDA** | 0.15 | 3.39 | 0.95 |

**Table S8.** Slope, intercept, and a/b*100 of fitting curve equation for $D_k$ and relative humidity, $D_f$ and relative humidity

| Polyimide | $D_k$ (Y) -RH (X) $Y(\%) = a_1X(\%) + b_1$ | | | $D_f$ (Y) -RH (X) $Y(\%) = a_2X(\%) + b_2$ | | |
|---|---|---|---|---|---|---|
| | $b_1$ | $a_1$ | $a_1/b_1*100$ | $b_2$ | $a_2$ | $a_2/b_2*100$ |
| **APBIA-BPDA** | 3.84 | 0.37 | 9.6 | 0.0020 | 0.0173 | 865 |
| **DABA-BPDA** | 3.77 | 0.30 | 8.0 | 0.0066 | 0.0154 | 233 |
| **DP-BPDA** | 3.58 | 0.27 | 7.5 | 0.0017 | 0.0084 | 494 |
| **MT-BPDA** | 3.29 | 0.23 | 7.0 | 0.0013 | 0.0082 | 631 |
| **TFMB-BPDA** | 2.99 | 0.27 | 9.0 | 0.0035 | 0.0081 | 231 |
| **APAB-BPDA** | 3.55 | 0.13 | 3.7 | 0.0016 | 0.0063 | 394 |
| **DP4MF-BPDA** | 3.39 | 0.15 | 4.4 | 0.0006 | 0.0073 | 1217 |

**Table S9.** Water adsorption at different relative humidity of the seven PI films

| Polyimide | Water adsorption (%) at different RH | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 11% | 25% | 38% | 50% | 60% | 75% | 85% | 99% |
| **APBIA-BPDA** | 0.53 | 1.15 | 1.38 | 1.68 | 2.22 | 2.53 | 2.76 | 3.09 |
| **DABA-BPDA** | 0.45 | 0.76 | 1.12 | 1.29 | 1.72 | 1.83 | 2.03 | 2.47 |
| **DP-BPDA** | 0.24 | 0.44 | 0.59 | 0.67 | 0.82 | 0.90 | 0.97 | 1.23 |
| **MT-BPDA** | 0.17 | 0.36 | 0.54 | 0.71 | 0.84 | 0.98 | 1.11 | 1.35 |
| **TFMB-BPDA** | 0.25 | 0.43 | 0.43 | 0.58 | 0.70 | 0.82 | 0.85 | 1.11 |
| **APAB-BPDA** | 0.16 | 0.30 | 0.41 | 0.49 | 0.63 | 0.69 | 0.80 | 0.97 |
| **DP4MF-BPDA** | 0.14 | 0.29 | 0.36 | 0.49 | 0.54 | 0.70 | 0.79 | 0.90 |

**Table S10.** MPI, Binding energy, and free volume (FV) of seven PI films

| Polyimide | MPI[a] (eV) | Binding energy[b] (kcal/mol) | FV (%) |
|---|---|---|---|
| **APBIA-BPDA** | 0.57 | -9.96 | 36.2 |
| **DABA-BPDA** | 0.56 | -9.88 | 35.2 |
| **DP-BPDA** | 0.50 | -7.23 | 36.2 |
| **MT-BPDA** | 0.45 | -7.05 | 38.6 |
| **TFMB-BPDA** | 0.53 | -6.06 | 40.6 |
| **APAB-BPDA** | 0.52 | -8.55 | 36.1 |
| **DP4MF-BPDA** | 0.51 | -6.42 | 38.6 |

[a] calculated by Multiwfn.

[b] value was $\Delta E_{p+w}$ /300.

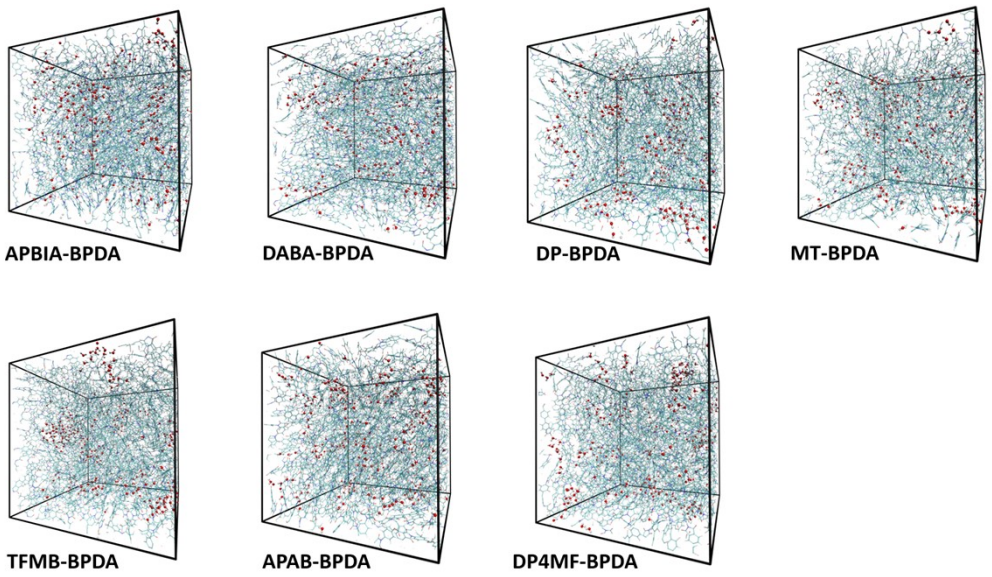



**Figure S7.** Molecular dynamics simulation models of PIs containing $H_2O$.

**Table S11.** Slope, intercept and R square of fitting curve equation between water adsorption (Y) and relative humidity (X) through three methods

| Polyimide | Method 1: Improved weighing method Y(%) =aX(%)+b | | | Method 2: Gravimetric method Y(%) =aX(%)+b | | | Method 3: Volumetric method Y(%) =aX(%)+b | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | $R^2$ | a | b | $R^2$ | a | b | $R^2$ |
| **APBIA-BPDA** | 0.0289 | 0.317 | 0.99 | 0.0345 | -0.090 | 0.99 | 0.0310 | 0.158 | 0.99 |
| **DABA-BPDA** | 0.0222 | 0.227 | 0.99 | 0.0259 | 0.004 | 0.99 | 0.0229 | 0.088 | 0.99 |
| **DP-BPDA** | 0.0103 | 0.162 | 0.98 | 0.0146 | 0.051 | 0.99 | 0.0129 | 0.037 | 0.99 |
| **MT-BPDA** | 0.0130 | 0.040 | 0.99 | 0.0164 | 0.027 | 0.99 | 0.0154 | 0.009 | 0.99 |
| **TFMB-BPDA** | 0.0091 | 0.141 | 0.97 | 0.0160 | 0.032 | 0.99 | 0.0146 | -0.026 | 0.99 |
| **APAB-BPDA** | 0.0088 | 0.068 | 0.99 | - | - | - | 0.0099 | -0.004 | 0.99 |
| **DP4MF-BPDA** | 0.0086 | 0.051 | 0.99 | 0.0109 | -0.031 | 0.99 | 0.0100 | -0.029 | 0.99 |

The dielectric relaxation of water can be described by the classical Debye equation.

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \quad \text{(S1)}$$

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad \text{(S2)}$$

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad \text{(S3)}$$

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{(S4)}$$

$$\omega = 2\pi f \quad \text{(S5)}$$

where $\varepsilon^*(\omega)$ is the complex dielectric permittivity, $\varepsilon'$ is the real part of the complex dielectric permittivity, representing the dielectric constant ($D_k$), $\varepsilon''$ is the imaginary part of the complex dielectric permittivity, representing the dielectric loss, $tan\delta$ is the dissipation factor ($D_f$), $i$ is the imaginary unit, $\varepsilon_s$ is the static dielectric constant, $\varepsilon_\infty$ is the infinite frequency dielectric constant. $\omega$ is the angular frequency of the electric field, $f$ is the frequency of the electric field, and $\tau$ is the relaxation time.

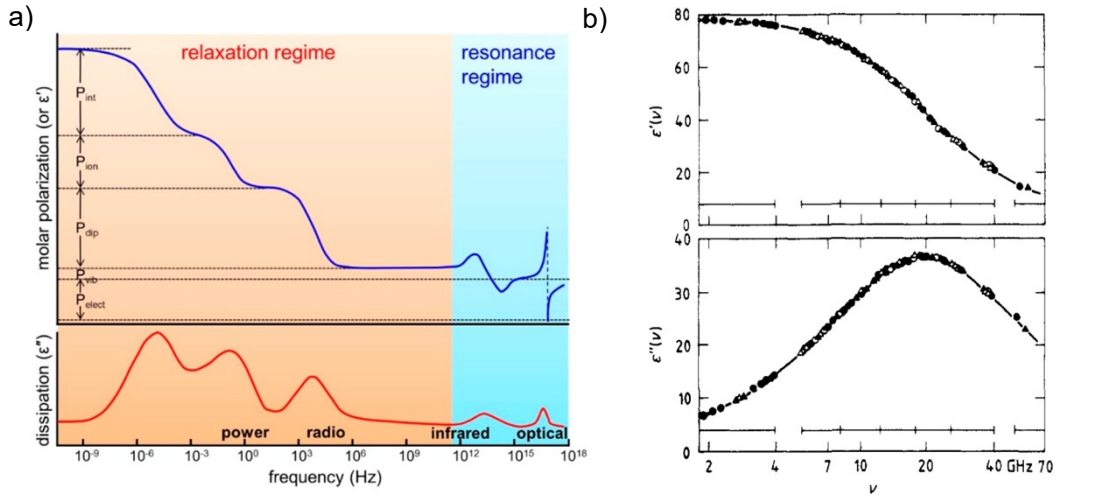



**Figure S8.** a) Schematic diagram of polymer polarization types *(L. Zhu, Journal of Physical Chemistry Letters, 2014, 5, 3677-3687)*; b) Real part and negative imaginary part of the complex permittivity displayed as a function of frequency for water at 25 °C (*U. Kaatze, Journal of Chemical & Engineering Data, 1989, 34, 371-374*).

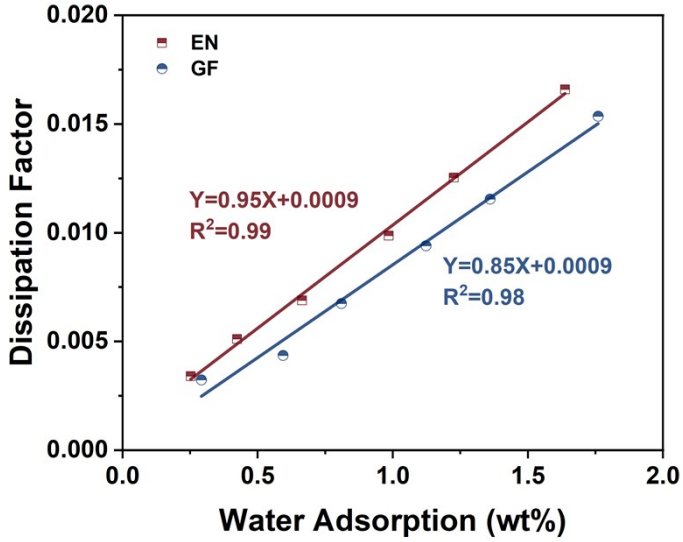



**Figure S9.** Relationship between $D_f$ and water adsorption of commercial PI films EN (Toray Industries, Japan) and GF (SKC hi-tech&markeing, Korea). Since the commercial films may have additives and surface treatment processes added, its slope deviates more from the 0.74 we mentioned.