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**Supporting Information** 

## Intrinsic Low Dielectric Constant Polyimides: Relationship between Molecular Structures and

## **Dielectric Properties**

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Scheme S1. Reaction mechanism discussion of synthesizing mBPPy and mTPPy.



8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 fl (ppm)



 $\begin{array}{c} 8.2 \ 8.1 \ 8.0 \ 7.9 \ 7.8 \ 7.7 \ 7.6 \ 7.5 \ 7.4 \ 7.3 \ 7.2 \ 7.1 \ 7.0 \ 6.9 \ 6.8 \ 6.7 \ 6.6 \ 6.5 \ 6.4 \ 6.3 \ 6.2 \ 6.1 \ 6.0 \ 5.9 \ 5.8 \ 5.7 \ 5.6 \ 5.5 \ 5.4 \ 5.3 \\ fl \ (ppm) \end{array}$ 



Figure S1. <sup>1</sup>H-NMR spectra of the diamines PPy (a), mBPPy (b) and mTPPy (c).



158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 fl  $(\rm ppm)$ 

Figure S2. <sup>13</sup>C-NMR spectra of diamines PPy (a), mBPPy (b) and mTPPy (c).



Figure S3. FT-IR spectra of diamines PPy, mBPPy and mTPPy.



8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 fl (ppm)



8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 fl (npm)

Figure S4. <sup>1</sup>H-NMR spectra of polyimides PPy6F (a), mBPPy6F (b) and mTPPy6F (c).



Figure S5. Thermal properties of polyimides PPy6F, mBPPy6F and mTPPy6F: (a)DMA; (b)TMA; (c)TGA.

Polyimides	$A (\times 10^{-4} \mathrm{m^2})$	$k_0 (\times 10^{-12} \mathrm{F} \cdot \mathrm{m}^{-1})$	<i>l</i> (×10 <sup>-6</sup> m)	<i>C</i> (×10 <sup>-11</sup> F)	k
PPy6F	1.0404	8.854	113	2.29	2.81
mBPPy6F	1.0404	8.854	105	2.29	2.61
mTPPy6F	1.0404	8.854	100	2.25	2.44

Table S1. The details in dielectric measurements of polyimides at 10<sup>4</sup> Hz

The error of the film thickness is  $1 \times 10^{-6}$  m, the relative error is 0.9%-1%, the error of the capacitance is  $1 \times 10^{-13}$  F, the relative error is about 0.5%. According to the Eqn.1, the relative error of *k* is 1.5%.

Polyimides	Structure				
FPTTPI	$F_{3,C} \xrightarrow{0} F_{3,C} \xrightarrow{F_{3,C}} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} \xrightarrow{F_{3,C}} \xrightarrow{F_{3,C}} \xrightarrow{0} \xrightarrow{F_{3,C}} F_{3,C$				
PFCBBPPI	$\left( \left( \begin{array}{c} \\ \end{array}\right) - \left( \begin{array}{c} \\ \end{array}\right) - \left( \begin{array}{c} \\ \\ \end{array}\right) - \left( \begin{array}{c} \end{array}\right) - \left( \begin{array}{c} \\ \end{array}\right) - \left( \begin{array}{c} \end{array}\right) - \left( \end{array}) - \left( \end{array}) - \left( \begin{array}{c} \\ \end{array}\right) - \left( \begin{array}{c} \end{array}\right) - \left( \end{array}) - \left( \end{array}) - \left( \end{array}) - \left( \begin{array}{c} \end{array}\right) - \left( \end{array}) -$				
PI-8	$\left( \left( \begin{array}{c} \\ \\ \\ \end{array} \right)^{CF_3} \left( \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$				
7d"	$\left( \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ $				
7d'	$\left( \begin{array}{c} \\ \end{array} \right) - 0 - \left( \begin{array}{c} \end{array} \right) - 0 - \left( \begin{array}{c} \\ \end{array} \right) - 0 - \left( \begin{array}{c} \end{array} \right) - 0 - $				
PI-1	$\left( \left( \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$				
5d	$\left( \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$				

Table S2. Intrinsic low-k polyimides and their structure. <sup>20, 21, 50-57</sup>



Figure S6. Schematic diagram of the devices fabricated with PIs.