

# Supporting Information

## **Cathode Interface Materials Based on Perylene-Dimide Derivatives for Thickness Insensitivity and High Fill Factor Heterojunction Organic Solar Cells**

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## 1. Materials

The 3-dimethylamino-1-propylamine, *N, N'*-dimethyl formamide, and bromoethane were purchased from Energy Chemical, chloroform and methanol were purchased from Xilong Chemical. PM6 and Y6 were purchased from Shuolun Organic Photoelectric respectively. PEDOT: PSS (4083) was purchased from Xi'an Baolite. Indium tin oxide (ITO) was purchased from Delta Technologies Limited.

## 2 Devices fabrication

The OSCs were fabricated using the conventional structure of ITO/PEDOT: PSS/active layer/cathode interlayer/Ag. The conductive ITO glass was sequentially cleaned by ultrasonic treatment in detergent water, deionized water, acetone, and isopropanol. After drying the ITO substrates, they were treated in an ultraviolet ozone cleaner for 20 min. The aqueous solution of PEDOT:PSS was filtered through a 0.45mm filter and then spin-coated on pre-cleaned ITO substrates at 4000 rpm for 45 s. Subsequently, the film was annealed at 150 °C for 15 min in air and transferred to the glove box. The PM6:Y6 (1:1.2) blends were dissolved in chloroform at a total weight concentration of 16 mg/mL. 1-chloronaphthalene (0.5%, v/v) was added as a solvent additive. The active layer solution was spin-coated on top of the PEDOT: PSS layer at 4000 r/min, followed by thermal annealing at 100 °C for 10 min. Different CIMs methanol solutions prepared in advance were spin-coated onto the active layer surface at 3000 r/min. Finally, silver was vaporized onto the cathode interface layers by vacuum vaporization. The effective area of the prepared cell device is 0.04 cm<sup>2</sup>. All device fabrication processes are carried out in a N<sub>2</sub>- filled glove box.

### 3. *J-V* characteristics, light intensity dependence and IPCE measurements

The *J-V* characteristics of the OSCs were measured by a Keithley 2450 Source Measure unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450W xenon lamp and an AM 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm<sup>-2</sup> by a Newport Oriel 91,150 V reference cell. The voltage step and delay time were 10 mV and 1 ms, respectively. The scan started from -0.2 V to 1.5 V. The IPCE was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The relationship of *J<sub>sc</sub>* and *V<sub>oc</sub>* to the light intensity was measured by steady state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD).

### 4. Characterizations

Nuclear magnetic resonance (NMR) was measured with a NMR spectrometer. High resolution mass spectra (HRMS) experiments were recorded on a Shimadzu Biotech Axima Assurance 03030714 MALDI-TOF. UV-vis absorption spectra were recorded on a PerkinElmer Lambda 750 Spectrophotometer. Cyclic voltammetry (CV) was performed with an electrochemical analyzer with a three-electrode system. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire; electrolyte: tetrabutylammonium hexafluoro-phosphate (Bu<sub>4</sub>NPF<sub>6</sub>); internal standard: ferrocene (Fc). LUMO energy level were calculated using the approximation:  $E_{\text{LUMO}} = -e(\phi_{\text{red}} - \phi_{\text{Fc}} + 4.8)$  (eV). HOMO energy values were obtained from LUMO values and optical bandgap  $E_{\text{g}}^{\text{opt}}$  values ( $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}^{\text{opt}}$ ). Optical band gaps ( $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ ) were estimated from the absorption onset of the as-cast compound films. Thermogravimetric analysis (TGA) measurements were recorded on a Perkin-Elmer

TGA-7 thermogravimetric analyzer under air atmosphere at a heating rate of 10 °C/min. The Electron Paramagnetic Resonance (EPR) spectra of target compound with the same amount were recorded at room temperature by Bruker A300 EPR Spectrometer.

## 5. UPS measurement

The 2NBr-PDI in methanol were spin-coated on glass substrates with a film thickness of ~20 nm. And parallel silver electrodes (thickness of 90 nm) were deposited by thermal evaporation under a vacuum chamber.

Ultraviolet Photoelectron Spectroscopy (UPS) spectra were performed on Thermo ESCALAB 250XI PHI5000 VersaProbe III multifunction X-ray photoelectron spectrometer. In UPS, the secondary electron cut-off ( $E_{cutoff}$ ) in the high binding energy region of the spectrum reflects the influence of contacting materials on metal work function (WF), then the WF values calculated by the equation  $\phi = 21.2 - E_{cutoff}$ .

## 6. Conductivity measurement

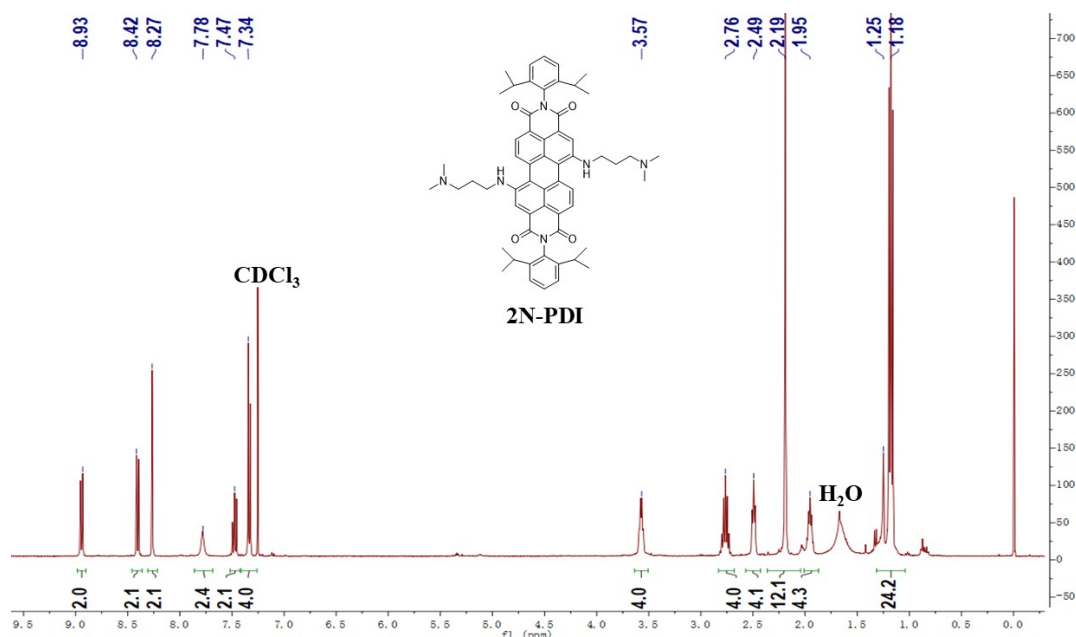
The 2NBr-PDI and PDINO in methanol were spin-coated on glass substrates with a film thickness (T) of ~20 nm. And parallel silver electrodes (thickness of 90 nm) were deposited by thermal evaporation under a vacuum chamber. The length of the electrode (W) was 5000  $\mu\text{m}$  and the distance (L) between the two electrodes was 50  $\mu\text{m}$ . Electrical characterization was conducted using a Keithley 4200 SCS equipped with probe station under a nitrogen atmosphere. The conductivity was extracted from the equation of  $\sigma = I \times L / (V \times W \times T)$ . The sample preparations were prepared following the fabrication method of the organic solar cells, without HTL and active layers.

## 7. AFM characterizations and contact angle measurements

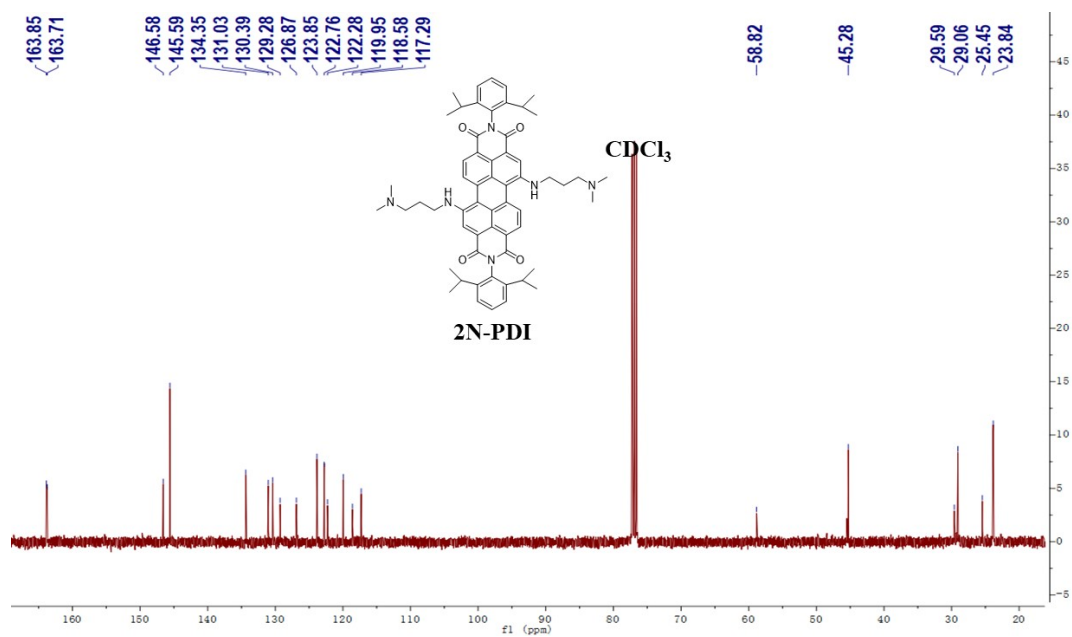
The film morphology was measured by atomic force microscopy (AFM) with the tapping mode from Asylum Research. The contact angle was measured by using a Kruss DSA100s Drop Shape Analyzer, the test liquid was water. The film samples were prepared following the fabrication method of the organic solar cells, without metal electrodes on the cathode interlayer.

## 8. $^1\text{H}$ , $^{13}\text{C}$ NMR, and HRMS spectra

### $^1\text{H}$ NMR of 2N-PDI in $\text{CDCl}_3$ (400 MHz)



### $^{13}\text{C}$ NMR of 2N-PDI in $\text{CDCl}_3$ (101 MHz)



## HMRS of 2N-PDI

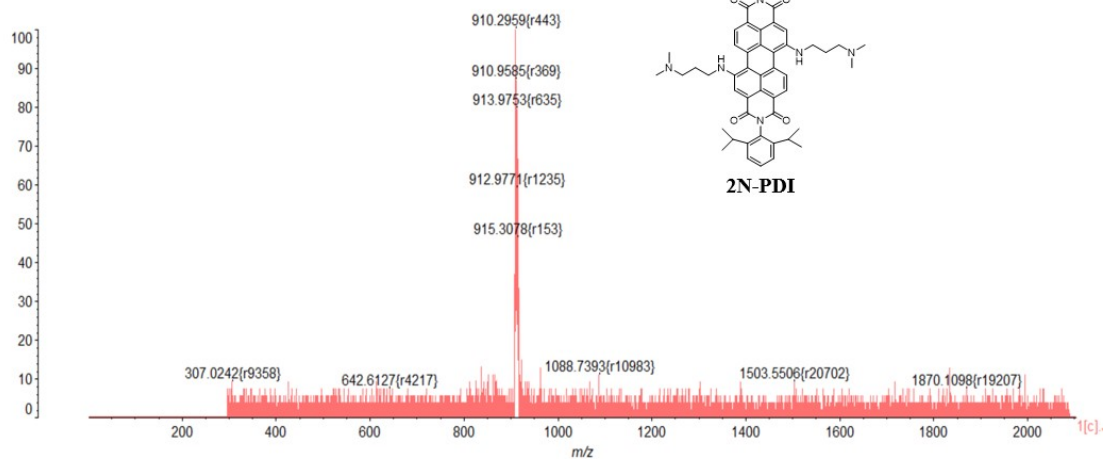
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Assurance

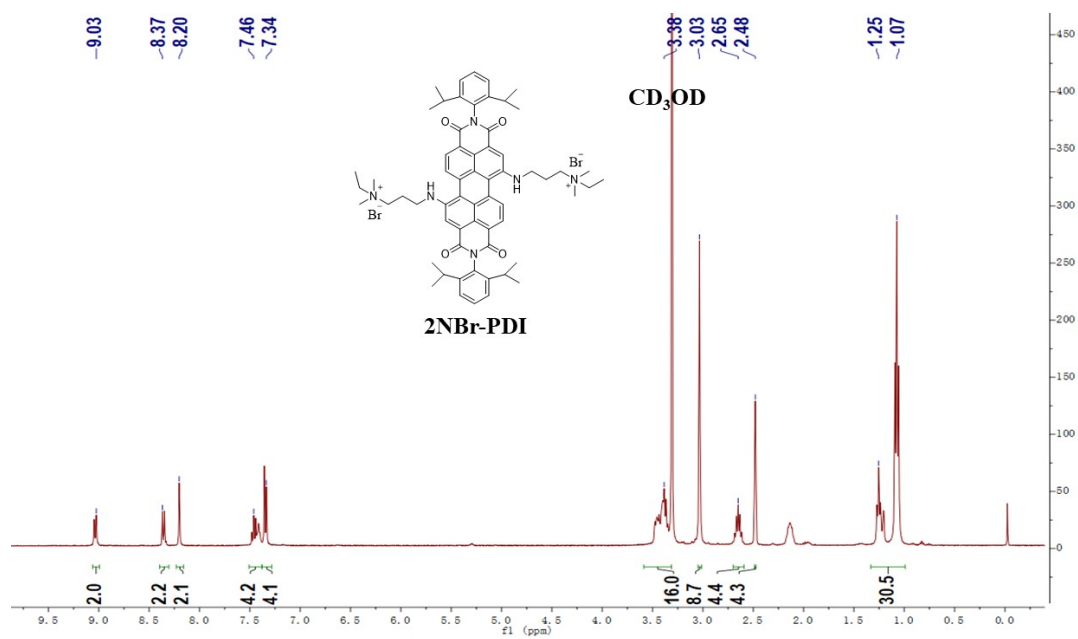
Data: 2.6-N0001.J7[c] 13 Mar 2023 18:35 Cal: tof 16 Oct 2017 12:36

Shimadzu Biotech Axima Assurance 2.9.4.1: Mode Linear, Power: 80, Blanked, P.Ext. @ 940 (bin 57)

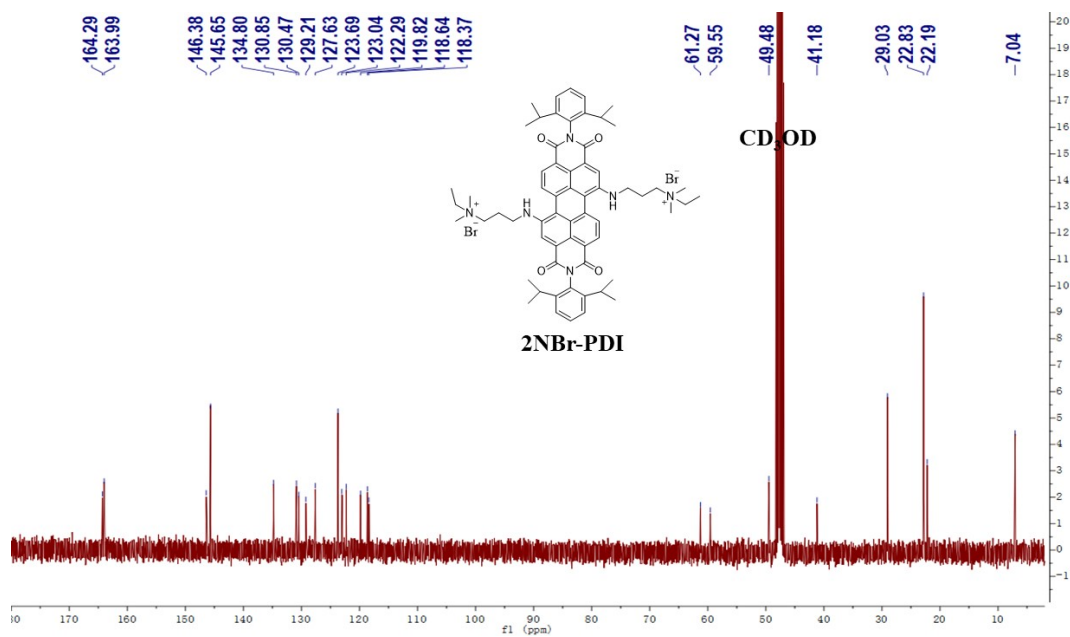
%Int. 7.1 mV[sum= 42 mV] Profiles 1-6 Unsmoothed



## $^1\text{H}$ NMR of 2NBr-PDI in $\text{CD}_3\text{OD}$ (400 MHz)



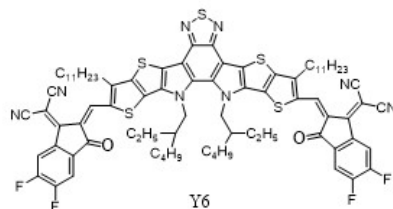
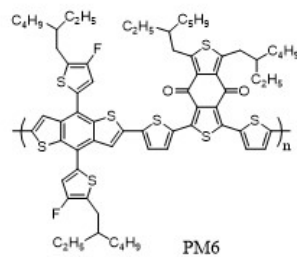
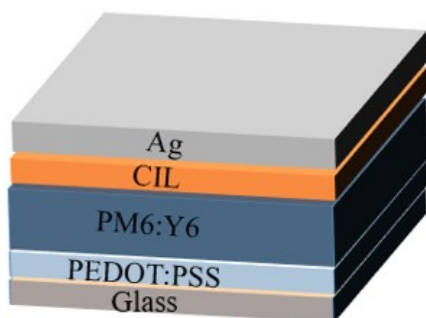
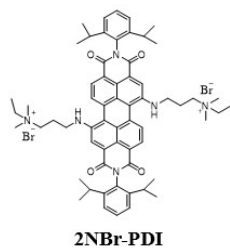
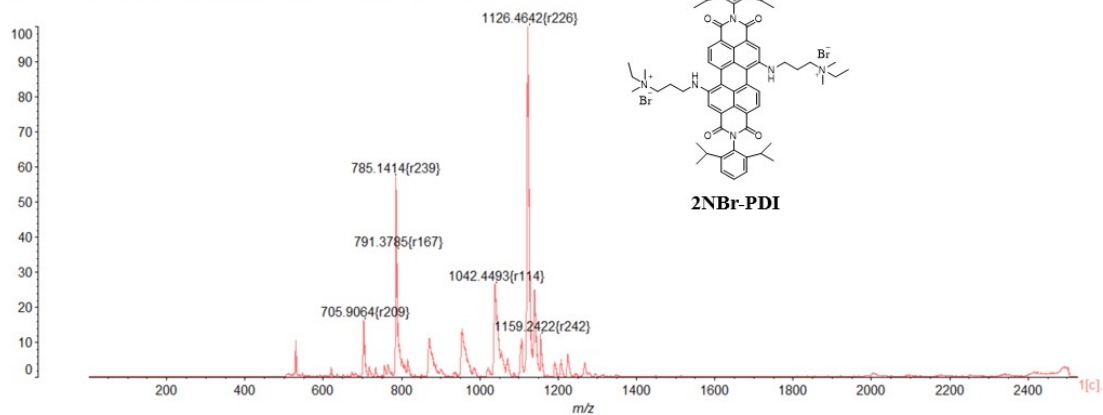
### <sup>13</sup>C NMR of 2NBr-PDI in CD<sub>3</sub>OD (101 MHz)



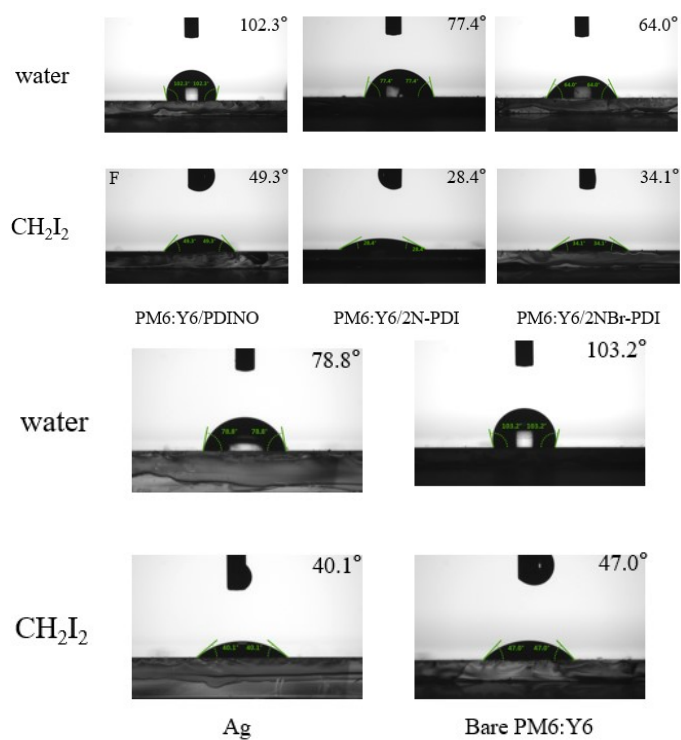
### HMRS of 2NBr-PDI



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 Assurance  
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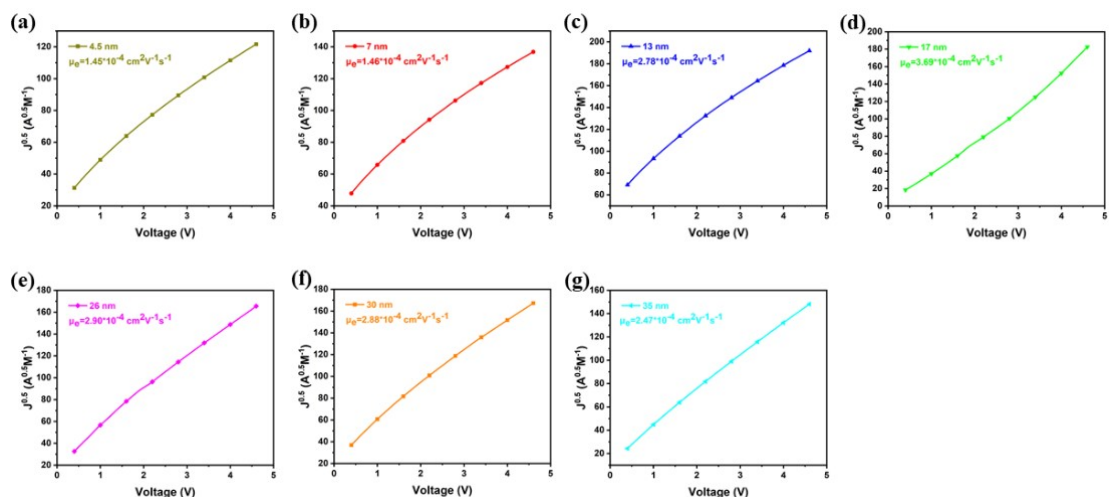
**Figure S1.** Structures of PM6, Y6, and OSCs



**Figure S2.** Water and  $\text{CH}_2\text{I}_2$  contact angles

**Table S1.** Surface energies for various surface

Surface	Water Contact angle (°)	$\text{CH}_2\text{I}_2$ Contact angle (°)	Surface energy (mN m <sup>-1</sup> )
Ag	78.8	40.1	46.48
PM6:Y6	103.2	47	47.02
PDINO	102.3	49.3	35.98
2N-PDI	77.4	28.4	53.23
2NBr-PDI	64	34.1	60.38



**Figure S3.** Electron mobility curves for different 2NBr-PDI film thicknesses

**Table S2.** Electron mobility for different film thicknesses

Thickness (nm)	Electron mobility ( $\mu_e$ )( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
4.5	$1.45 \times 10^{-4}$
7	$1.46 \times 10^{-4}$
13	$2.78 \times 10^{-4}$
17	$3.69 \times 10^{-4}$
25	$2.90 \times 10^{-4}$
30	$2.88 \times 10^{-4}$
35	$2.47 \times 10^{-4}$