# Supplementary Information

**Dye–sensitized solar cells containing mesoporous $TiO_2$ spheres as photoanode and methyl sulfate anion based bi–ionic liquid electrolytes**

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**S1.** SEM image of CSL particles

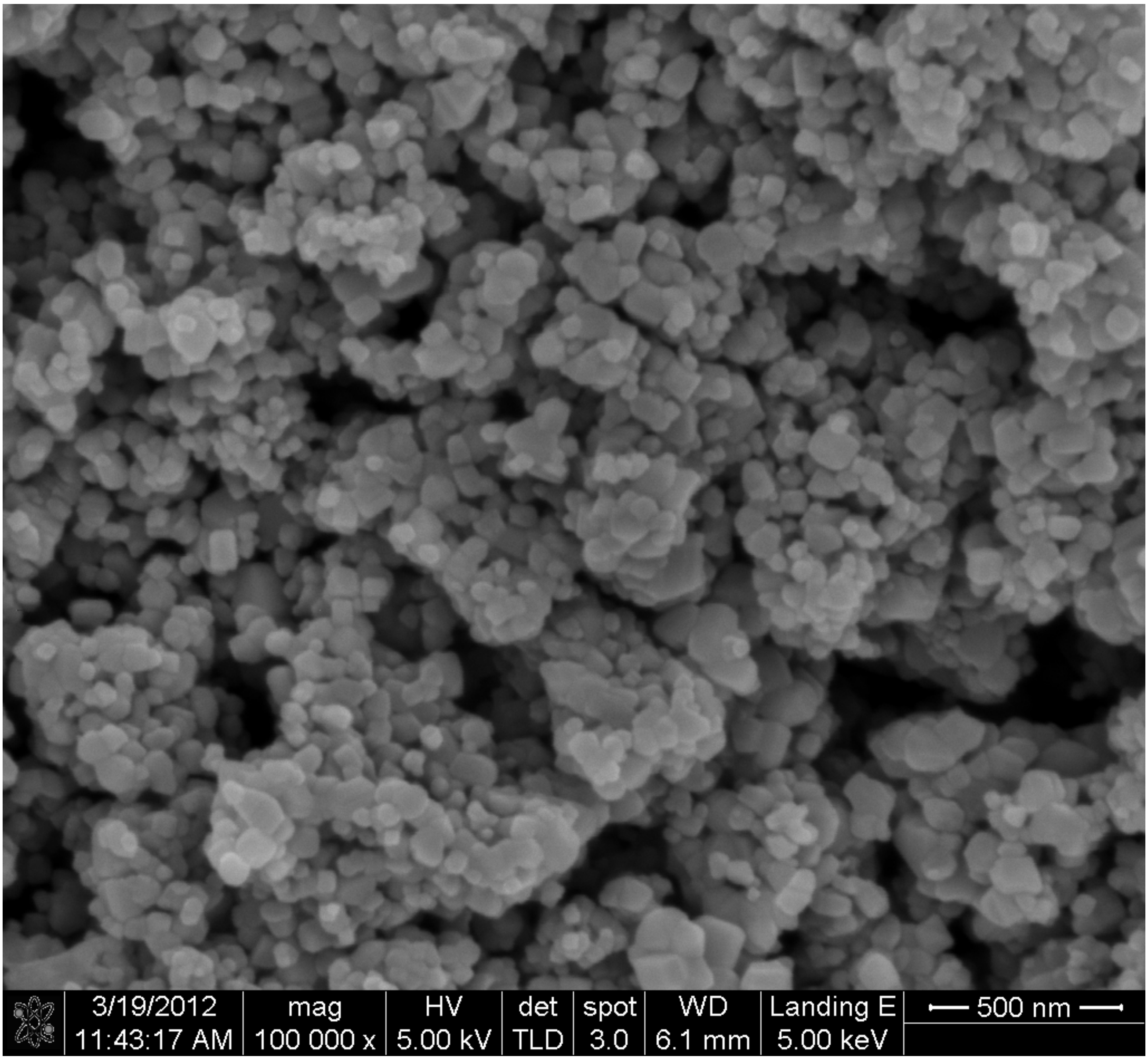


**Figure S1.** SEM image of commercial scattering layer (CSL) particles.

**S2.** Diffuse reflection spectra of the films of CSL and MS

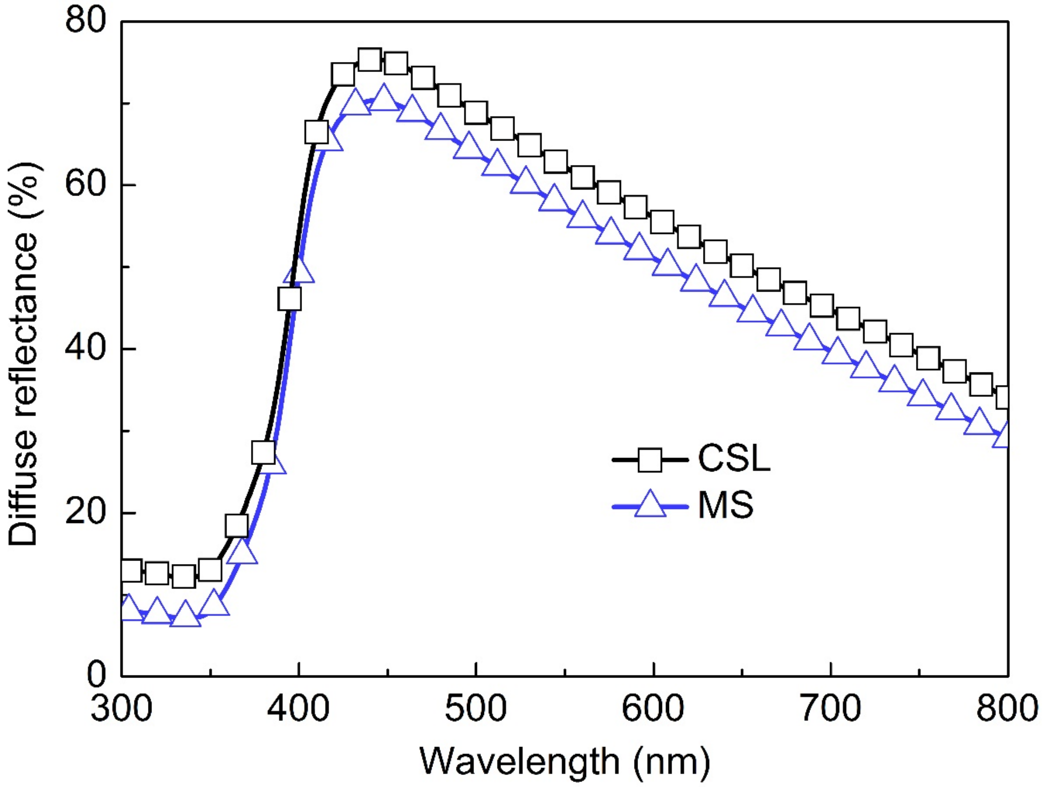


**Figure S2.** Diffuse reflection spectra of the films of commercial scattering layer (CSL) and mesoporous $TiO_2$ spheres (MS) at *ca.* 6 μm thickness.

S3. The photovoltaic properties and electrochemical impedance behavior of DSSCs with different ratios of PMII/TEMAMS or PMII/$EMIBF_4$ based ILs

Figure S3 shows the photocurrent density-voltage curves of DSSCs fabricated with the bi–IL electrolyte consisting of 0.2 M iodine, 0.4 M NMBI, 0.15 M GuSCN with various volume ratios of PMII/TEMAMS under 100 mW/cm$^2$ illumination. The optimal volume ratio of PMII/TEMAMS (65:35 = v/v) effectively enhances the cell efficiency from 3.21 to 6.18%, as listed in Table S1. Furthermore, ionic conductivity of the PMII/TEMAMS bi–IL electrolyte initially increases as the TEMAMS content increases, reaching a maximum conductivity of 15.36×10$^{-3}$ S/cm at the optimal volume ratio of PMII/TEMAMS (65:35 = v/v), and then decreases when the ratio increases. The EIS technique is also used, as shown in Figure S4, to realize the effect of various volume ratios of PMII/TEMAMS on the properties of bi-IL electrolyte. Surprisingly, the EIS spectra show that Rct2 decreases from 42.62 to 21.93 Ω, when the optimal volume ratio of PMII/TEMAMS is incorporated into the bi-IL electrolyte. Moreover, the diffusion coefficient of $I_3^-$ in the electrolyte ($D(I_3^-)$), calculated from the EIS spectra, increases from 0.63×10$^{-6}$ to 1.73×10$^{-6}$ cm$^2$/s in the presence of the optimal volume ratio of PMII/TEMAMS in the bi-IL electrolyte. However, excess of TEMAMS does not provide this beneficial effect as evidenced by the cell performance displays in Figure S3. The photocurrent density-voltage curves of DSSCs and the EIS spectra based on various volume ratios of PMII/$EMIBF_4$ bi–IL electrolyte are also shown in Figure S5 and S6, and the related experimental data are listed in Table S2.

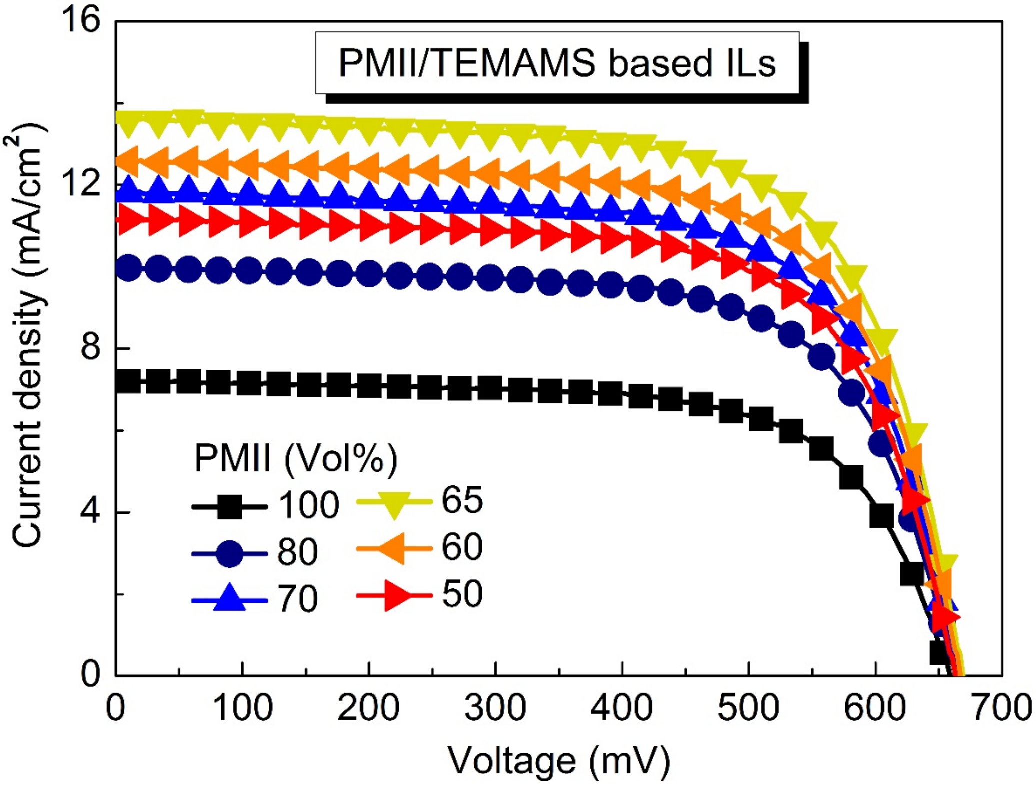


**Figure S3.** Photovoltaic properties of DSSCs with different ratios of PMII/TEMAMS based ILs, measured under 100 mW/cm$^2$. The DSSCs are composed of photoanodes containing commercial transparent layer (CTL) and mesoporous$TiO_2$ spheres (MS) at *ca.* 15 μm thickness.

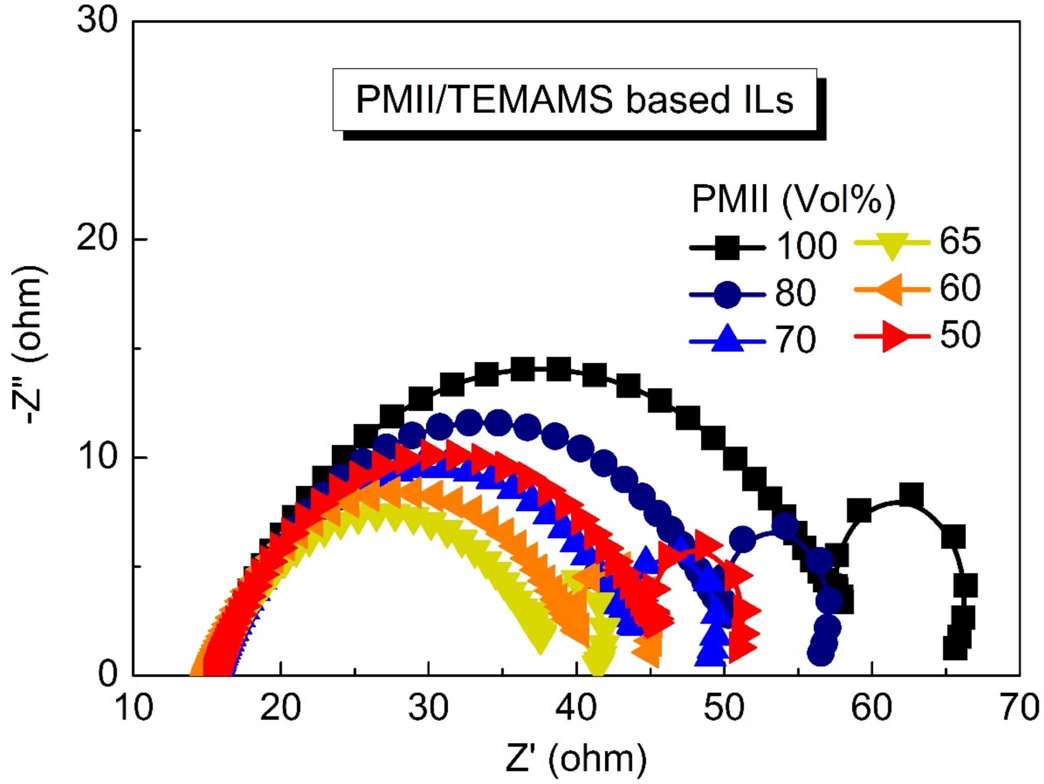


**Figure S4.** Nyquist plots of DSSCs with different ratios of PMII/TEMAMS based ILs (cell gap: 60 μm).

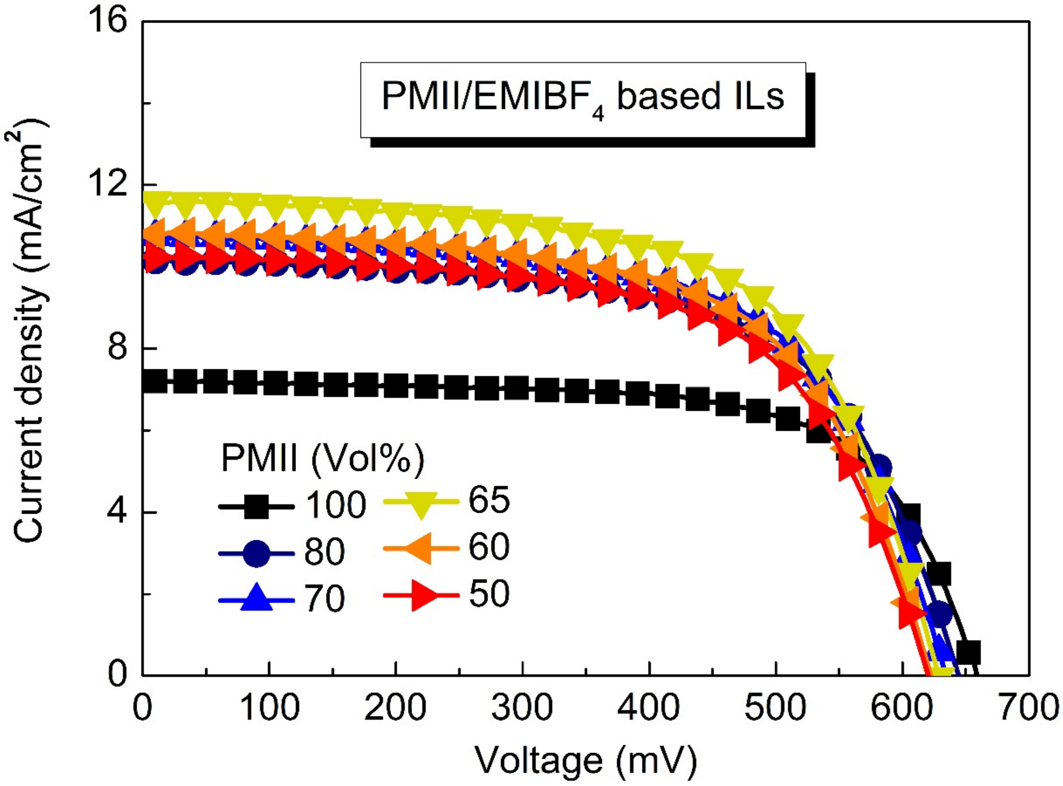


**Figure S5.** Photovoltaic properties of DSSCs with different ratios of $PMII/EMIBF_4$ based ILs, measured under 100 $mW/cm^2$. The DSSCs are composed of photoanodes containing commercial transparent layer (CTL) and mesoporous$TiO_2$ spheres (MS) at *ca.* 15 µm thickness.

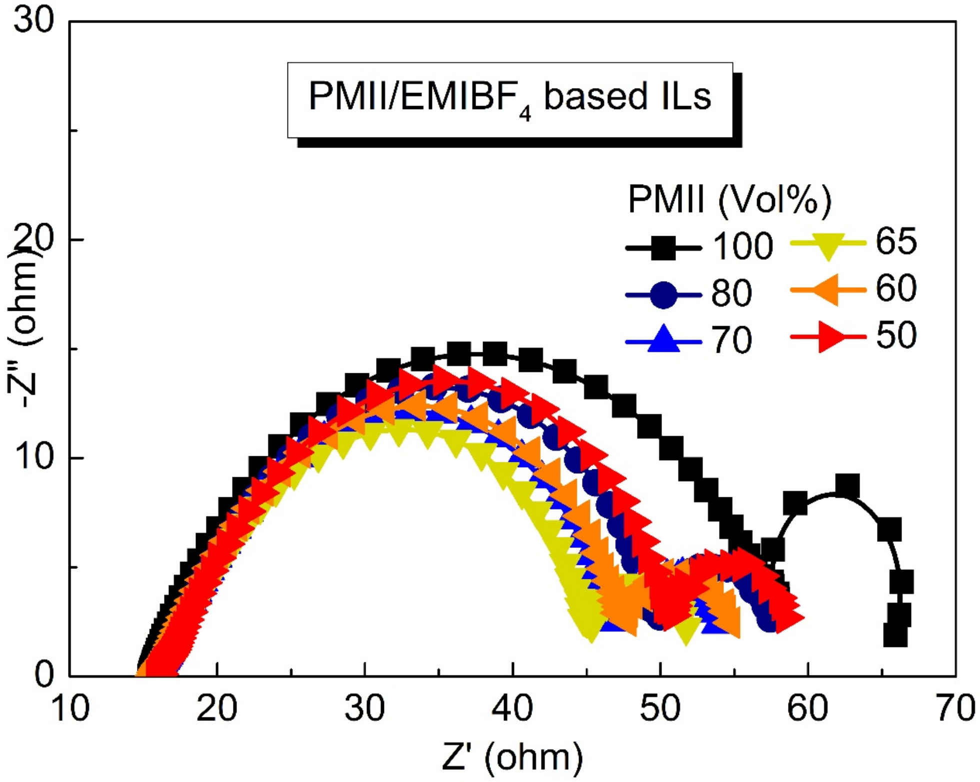


**Figure S6.** Nyquist plots of DSSCs with different ratios of PMII/$EMIBF_4$ based ILs (cell gap: 60 μm).

**Table S1.** Photovoltaic parameters of DSSCs, calculated by the average of 5 cells, with different ratios of PMII/TEMAMS based ILs, measured under 100 mW/cm$^2$. The table also shows the corresponding values of the conductivity and diffusion coefficient of $I_3^-$ in the electrolyte ($D(I_3^-)$). The DSSCs are composed of photoanodes containing commercial transparent layer (CTL) and mesoporousTiO$_2$ spheres (MS) at *ca.* 15 μm thickness.

| PMII (vol%) | Conductivity ($\times10^{-3}$ S/cm) | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (mV) | $FF$ | $\eta$ (%) | $D(I_3^-)$ ($\times10^{-6}$ cm$^2$/s) |
|---|---|---|---|---|---|---|
| 100 | 6.19 ± 0.15 | 7.19 ± 0.14 | 659 ± 5 | 0.68 ± 0.002 | 3.21 ± 0.03 | 0.63 ± 0.1 |
| 80 | 12.28 ± 0.19 | 9.97 ± 0.13 | 663 ± 3 | 0.68 ± 0.003 | 4.48 ± 0.04 | 0.90 ± 0.1 |
| 70 | 13.96 ± 0.17 | 11.77 ± 0.13 | 665 ± 3 | 0.68 ± 0.002 | 5.32 ± 0.03 | 1.36 ± 0.2 |
| 65 | 15.36 ± 0.17 | 13.56 ± 0.18 | 669 ± 5 | 0.68 ± 0.003 | 6.18 ± 0.03 | 1.73 ± 0.2 |
| 60 | 14.12 ± 0.18 | 12.52 ± 0.16 | 667 ± 4 | 0.68 ± 0.003 | 5.69 ± 0.04 | 1.49 ± 0.2 |
| 50 | 13.12 ± 0.16 | 11.16 ± 0.15 | 663 ± 5 | 0.68 ± 0.003 | 5.01 ± 0.03 | 1.12 ± 0.1 |

**Table S2.** Photovoltaic parameters of DSSCs, calculated by the average of 5 cells, with different ratios of PMII/EMIBF$_4$ based ILs, measured under 100 mW/cm$^2$. The table also shows the corresponding values of the conductivity and diffusion coefficient of $I_3^-$ in the electrolyte ($D(I_3^-)$). The DSSCs are composed of photoanodes containing commercial transparent layer (CTL) and mesoporousTiO$_2$ spheres (MS) at *ca.* 15 μm thickness.

| PMII (vol%) | Conductivity ($\times10^{-3}$ S/cm) | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (mV) | $FF$ | $\eta$ (%) | $D(I_3^-)$ ($\times10^{-6}$ cm$^2$/s) |
|---|---|---|---|---|---|---|
| 100 | 6.19 ± 0.15 | 7.19 ± 0.14 | 659 ± 5 | 0.68 ± 0.002 | 3.21 ± 0.03 | 0.63 ± 0.1 |
| 80 | 11.23 ± 0.12 | 9.74 ± 0.13 | 643 ± 4 | 0.65 ± 0.003 | 4.08 ± 0.04 | 0.79 ± 0.1 |
| 70 | 11.92 ± 0.16 | 10.28 ± 0.11 | 633 ± 3 | 0.65 ± 0.004 | 4.23 ± 0.04 | 0.86 ± 0.1 |
| 65 | 12.36 ± 0.16 | 11.61 ± 0.10 | 627 ± 5 | 0.62 ± 0.002 | 4.53 ± 0.03 | 0.93 ± 0.1 |
| 60 | 11.56 ± 0.16 | 10.83 ± 0.12 | 621 ± 4 | 0.62 ± 0.003 | 4.16 ± 0.05 | 0.82 ± 0.1 |
| 50 | 10.65 ± 0.12 | 10.25 ± 0.12 | 619 ± 3 | 0.62 ± 0.003 | 3.93 ± 0.03 | 0.73 ± 0.1 |