

Band Bending Effect of LiI/NaI treated TiO₂ Photoanode on Performance of Dye-sensitized Solar Cells

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Supplementary Information

Fig. S1 FTIR spectra of (a) TiO₂ (b) L1, L2, L3 and (c) N1, N2, N3, respectively.

Fig. S2 Tauc plot of (a) T, L1, L2, L3 and (b) T, N1, N2, N3 samples with the corresponding bandgap values, respectively.

Fig. S3 absorption spectra of (a) glass/T/N719, glass/L1/N719, glass/L2/N719, glass/L3/N719, and (a) glass/T/N719, glass/N1/N719, glass/N2/N719, and glass/N3/N719, respectively.

Fig. S4 High resolution XPS spectrum of (a) Li 1s, (b) Na 1s, (c) Ti 2p, (d, e) I 3d, (f) O 1s of T, L2, and N3, respectively.

Fig. S5 Nyquist plot of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 samples (a, c) under dark and (b, d) under illumination conditions, using N719 dye respectively.

Fig. S6 Ac equivalent circuit of DSSC using N719 dye.

Fig. S7 Bode plots under (a) dark and (b) illumination conditions. (c, d) $J-V$ plots of DSSCs fabricated with T, L1, L2, L3, N1, N2, and N3 under dark using N719 dye.

Fig. S8 Bode plots under (a) dark and (b) illumination conditions. (c, d) Dark $J-V$ plots of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 using N719 dye respectively.

Fig. S9 Comparison of (a) V_{OC} , (b) J_{SC} and (c) %PCE of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 using N719 dye respectively.

Fig. S10 $(QE \cdot E)^2$ as a function of photon energy E data for DSSCs fabricated with T, L1, L2, L3 (a) T, N1, N2, N3 (b) using N719 dye respectively. Inset is the obtained bandgap values from the intercept on the energy axis.³

Fig. S11 The EQE plot, bandgap as determined from the EQE inflection point of DSSCs fabricated with T, L1, L2, L3 (a, b, c, d) using N719 dye respectively.

Fig. S12 The EQE plot, bandgap as determined from the EQE inflection point of DSSCs fabricated with T, N1, N2, N3 (a, b, c, d) using N719 dye respectively.

Fig. S13 $J-V$ characteristics (a, b) and % EQE (c, d) of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 using N3 dye respectively.

Table S1 Crystallite size and stain values of T, L1, L2, L3, N1, N2, N3 samples respectively.

Table S2 Flat band potential, donor density and V_{OC} of T, L1, L2, L3, N1, N2, N3 samples, respectively.

Table S3 EIS parameters of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 photoanode measured under dark conditions using N719 dye.

Table S4 EIS parameters of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 photoanode measured under illumination conditions using N719 dye.

Table S5 Photovoltaic parameters of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 photoanode using N3 dye respectively.

Experimental

Materials

TiO₂ (P25-Degussa), Chloroplatinic acid hexahydrate (H₂[Pt(Cl)₆].6H₂O), N719 dye (di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II), N3 dye (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)), Polyethylene glycol (PEG; MW = 10000), Sodium iodide (NaI), Lithium iodide (LiI), Acetylacetone (CH₃COCH₂COCH₃), Iodine (I₂) and Fluorine doped Tin oxide (FTO) glass plates (8 Ω), Ethanol, and Propan-2-ol (Isopropyl alcohol-IPA) Titanium(IV) chloride (1M in toluene) were purchased from Sigma Aldrich and used as received.

Photoanode (TiO₂ and LiI/NaI treated TiO₂) preparation

2 × 2 cm sized fluorine-doped tin oxide (FTO) glass plates were cleaned in an ultrasonic bath subsequently in an alkaline solution, deionized water, acetone and isopropyl alcohol for 10 min each. The blocking layer of TiO₂ was coated on the cleaned FTO glass plates to avoid the recombination reaction between liquid electrolyte and FTO by immersing it (facing conductive side upwards) in a 40 mM aqueous solution of TiCl₄ for 30 min at 70°C. FTO/TiO₂ (blocking layer) coated glass plates were rinsed with distilled water and ethanol and dried at 100°C for 10 min. Then, a mesoporous layer of TiO₂ was coated by adopting the

doctor-blade technique onto the FTO/TiO₂ substrates using an invisible tape (thickness 55 μm) as a spacer to maintain a uniform thickness of the film and the coated films were dried to evaporate the solvents. At this stage, the films were treated with LiI/NaI solution (0.1, 0.25, 0.5mmol% of the salts were taken and dissolved in ethanol) and finally these FTO/TiO₂ plates were sintered at 450°C for 30 min. The TiO₂ paste used to coat the mesoporous layer was prepared by mixing 0.16 mg of PEG (MW 10000) in 1M HNO₃ followed by the addition of 0.21 mL acetylacetone, 0.04 mL Triton-X and TiO₂ (P25 Degussa) nanopowder. The solution mixture was sonicated for 1 h and magnetically stirred for 24 h to get homogeneous TiO₂ paste.^{1,2}

Pt Counter electrode (CEs) preparation

4 mM solution of H₂[Pt(Cl)₆].6H₂O in IPA were drop-casted onto a pre-cleaned FTO glass plate and sintered at 450 °C for 30 min.

Fabrication of DSSC

The dye-sensitization was performed by immersing the prepared photoanodes into 5 mM of N719 dye dissolved in tert-butanol/acetonitrile (v/v = 1:1) solution for 24 h under dark conditions. Now, these dye coated FTO plates were rinsed with ethanol and the active area (0.25 cm²) was selected by removing the excess portion of the dye-coated TiO₂ film layer by scrapping. DSSCs were fabricated with bare TiO₂ and LiI/NaI treated TiO₂ photoanodes by clipping the photoanode and counter electrode together using two binder clips. To avoid the short circuit between two conductive surfaces of the electrodes, a thin layer of parafilm was used to separate the electrodes from contacting each other. The electrolyte solution consisted of 0.05 M I₂/0.5 M LiI/0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile.

Characterization and measurements

All the sample preparation for the analytical study was followed by the same as TiO₂ film preparation mentioned in the experimental section but onto the pre-cleaned 1 x 1 glass plates instead of FTO glass plates unless otherwise mentioned. X-ray diffraction (XRD) analysis was performed by X'Pert Pro-PAnalytic Diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of $0.01^\circ \text{ min}^{-1}$. Thermo Scientific X-ray photoelectron spectroscopy (XPS) was used to study the surface analysis. Renishaw InVia Raman microscope was employed to measure the Raman spectrum. Thermo Scientific Nicolet iS5 FT-IR Spectrometer was employed to record Fourier Transform-Infrared (FT-IR) measurements using the KBr pellet method. Metrohm AUTOLAB12/FRA2 PGSTAT302N was employed for the electrochemical analysis assembled with NOVA software 1.10 version. Mott-Schottky measurements were carried out using 3 electrode systems with the samples coated in FTO glass plates as a working electrode, Ag/AgCl as reference electrode and Pt wire as a counter electrode with the supporting electrolyte consist of 0.05 M LiI, 0.01 M I₂, and 0.5 M LiClO₄ in acetonitrile at the scan rate of 10 mV. AC signal with the frequency of 100 Hz was applied and the DC voltage bias was swept from -1 to +1 V. The samples were prepared as mentioned in the experimental section onto the pre-cleaned FTO glass plates ($4 \times 1 \text{ cm}$) in such a way that the area of the sample was $1 \times 1 \text{ cm}^2$. The J - V measurements of the DSSCs were characterized by Metrohm AUTOLAB12/FRA2 PGSTAT302N associated with a solar simulator with Xe arc lamp (85 mW cm^{-2} , AM 1.5 G) for a cell area of 0.25 cm^2 . The EQE% of the DSSCs were recorded using Oriel 300 W Xe Arc lamp in combination with an Oriel Cornerstone monochromator. The monocrystalline silicon diode was calibrated and used as a reference. ZSimpWin software (version 3.21) was employed to fit EIS data. The point of zero charges (pH_{ZPC}) of the TiO₂ and NaI doped TiO₂ samples were measured by pH drift method. First, 0.01 M NaCl, HCl, and NaOH solutions were prepared in de-ionized water. The pH values were set in the range of 2-12 and the pH of the solution was adjusted by adding either

HCl or NaOH solution. 15 ml of the solution in the pH range of 2 to 12 were taken. Pure and LiI/NaI treated TiO₂ films were dipped into this solution facing coated side downward; sonicated for 30 min and left aside for 24 h. The initial and final pH of the solutions were measured for each pH value using EUTECH instruments pH Tutor and plotted against each other. The point of zero charge of the samples was measured at the point of the curve which crosses the line $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$.

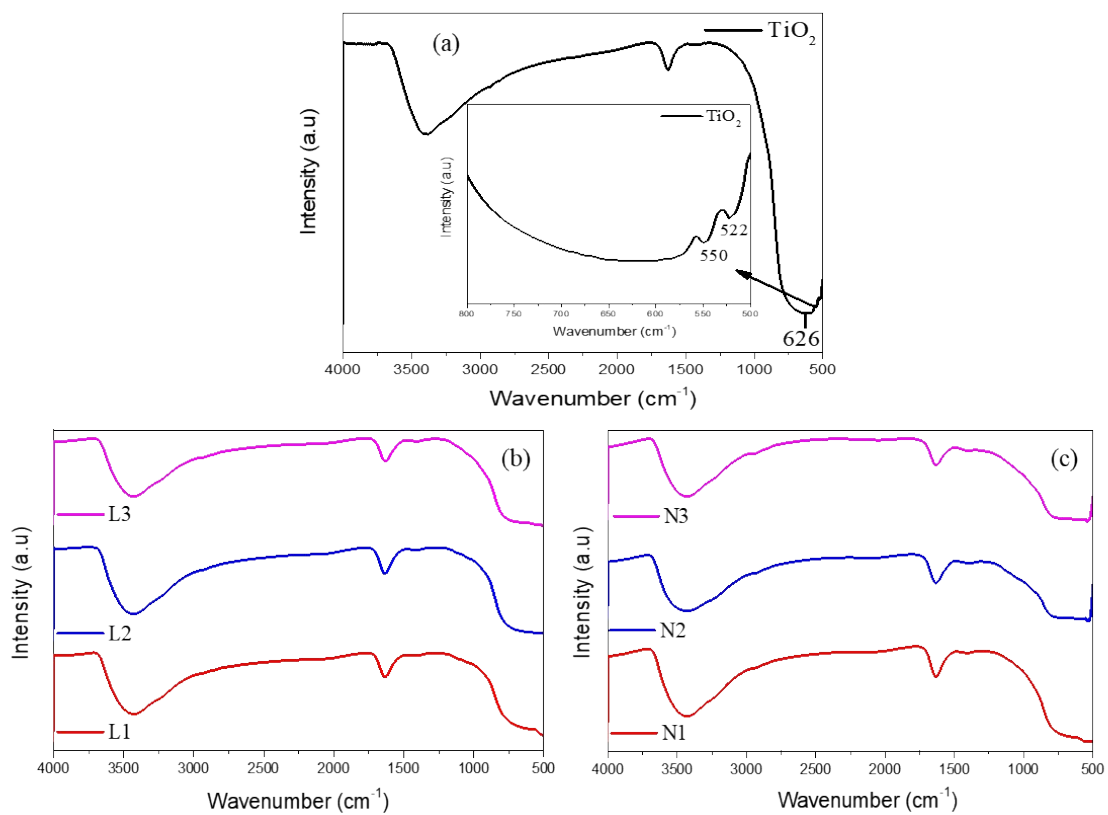


Fig. S1 FTIR spectra of (a) TiO₂ (b) L1, L2, L3 and (c) N1, N2, N3, respectively.

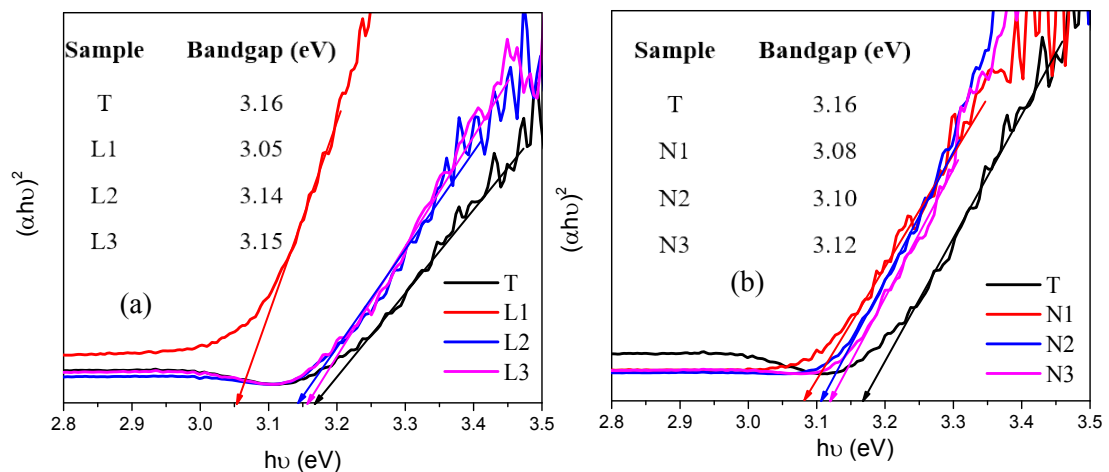


Fig. S2 Tauc plot of (a) T, L1, L2, L3 and (b) T, N1, N2, N3 samples with the corresponding bandgap values, respectively.

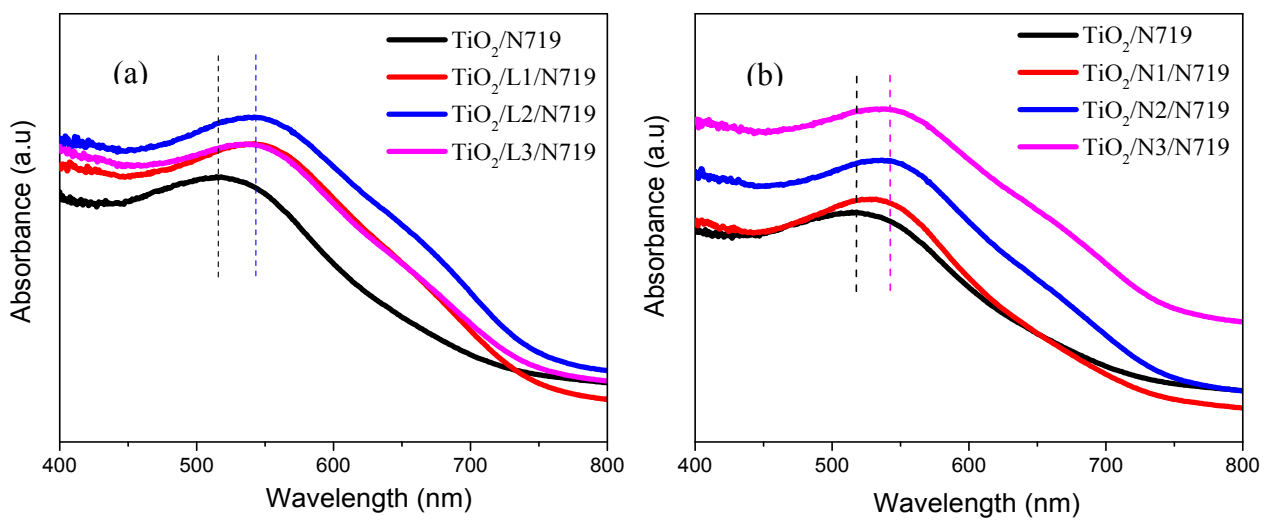


Fig. S3 absorption spectra of (a) glass/T/N719, glass/L1/N719, glass/L2/N719, glass/L3/N719, and (a) glass/T/N719, glass/N1/N719, glass/N2/N719, and glass/N3/N719, respectively.

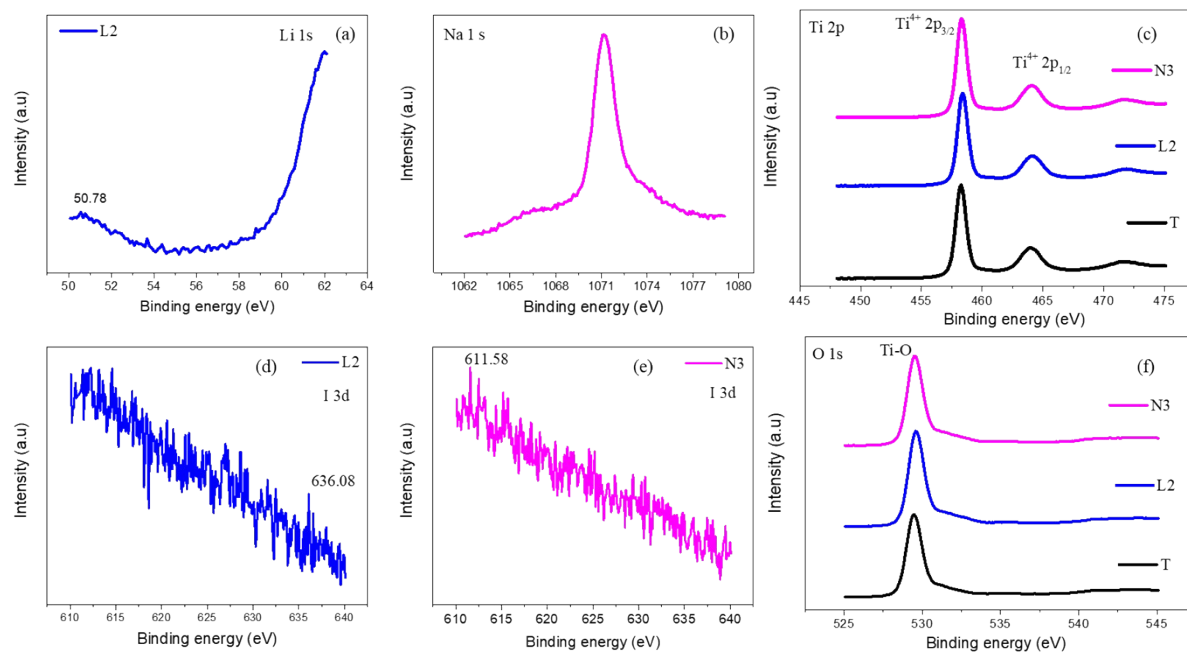


Fig. S4 High resolution XPS spectrum of (a) Li 1s, (b) Na 1s, (c) Ti 2p, (d, e) I 3d, (f) O 1s of T, L2, and N3, respectively.

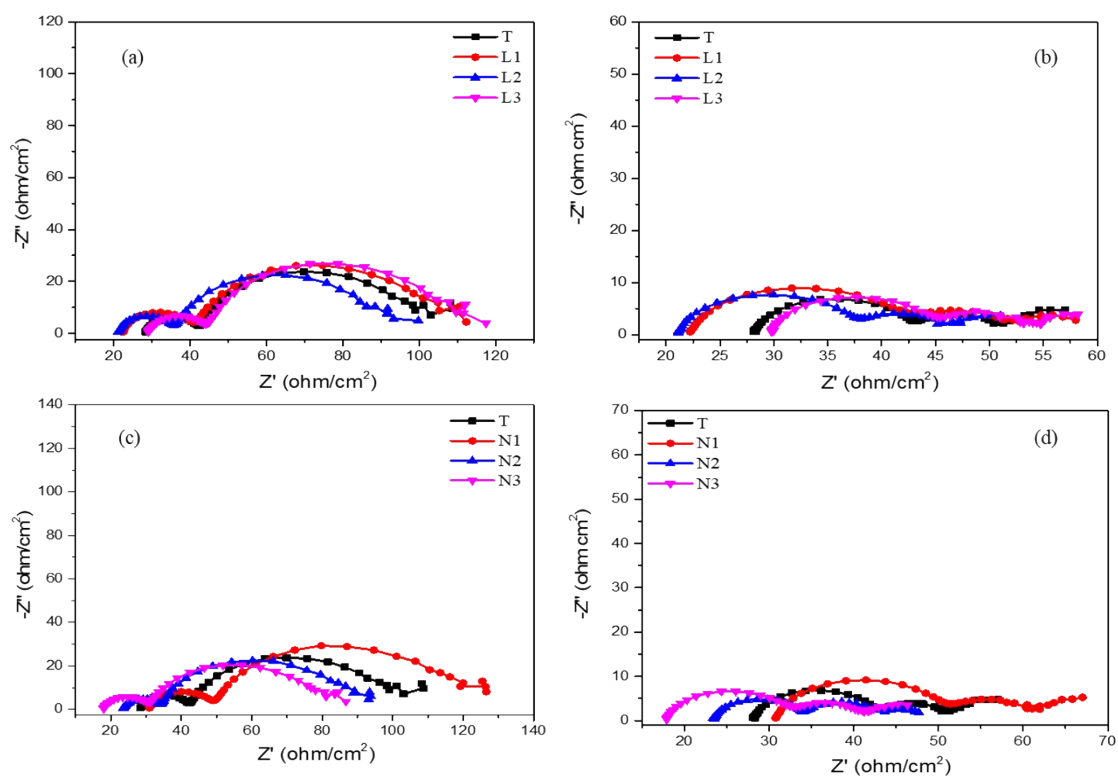


Fig. S5 Nyquist plot of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 samples (a, c) under dark and (b, d) under illumination conditions, using N719 dye respectively.

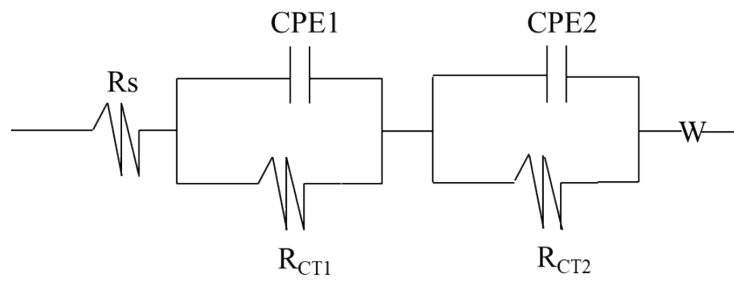


Fig. S6 Ac equivalent circuit of DSSC using N719 dye.

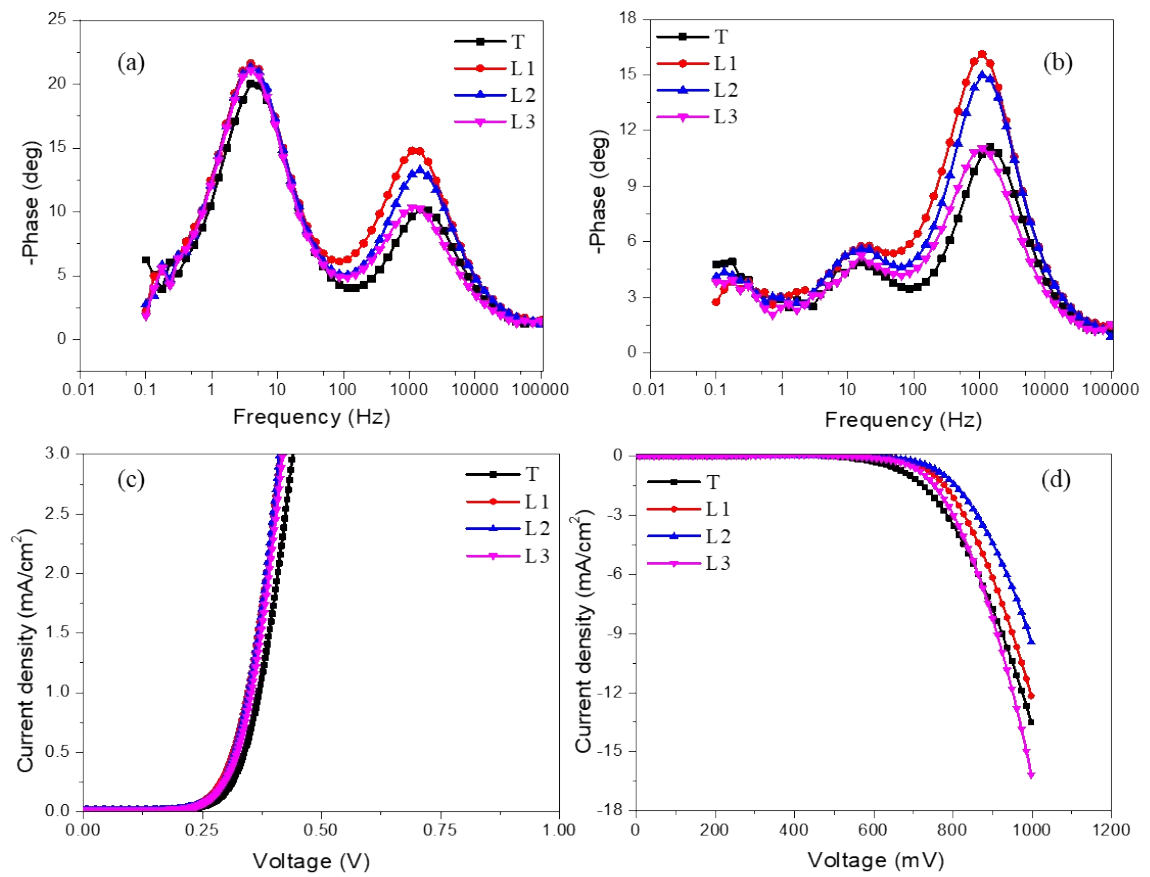


Fig. S7 Bode plots under (a) dark and (b) illumination conditions. (c, d) J - V plots of DSSCs fabricated with T, L1, L2, L3, N1, N2, and N3 under dark using N719 dye.

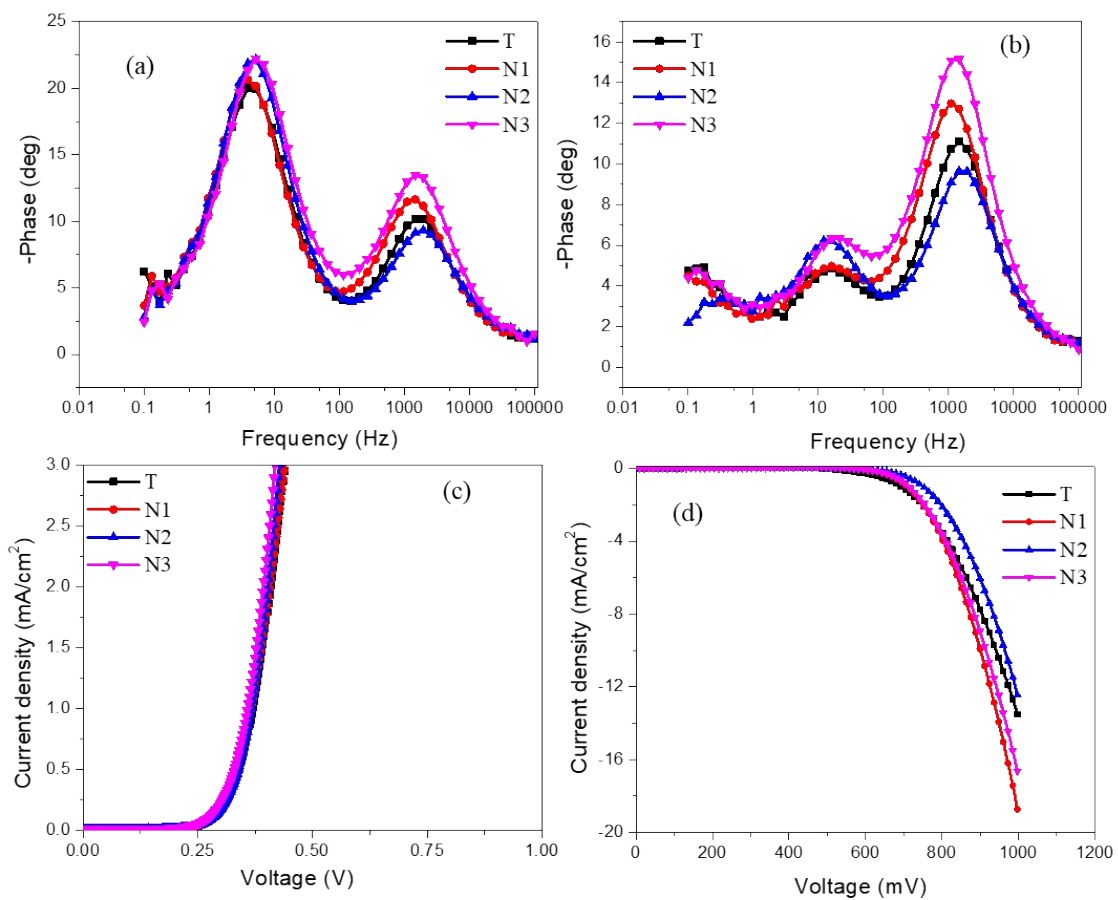


Fig. S8 Bode plots under (a) dark and (b) illumination conditions. (c, d) Dark J - V plots of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 using N719 dye respectively.

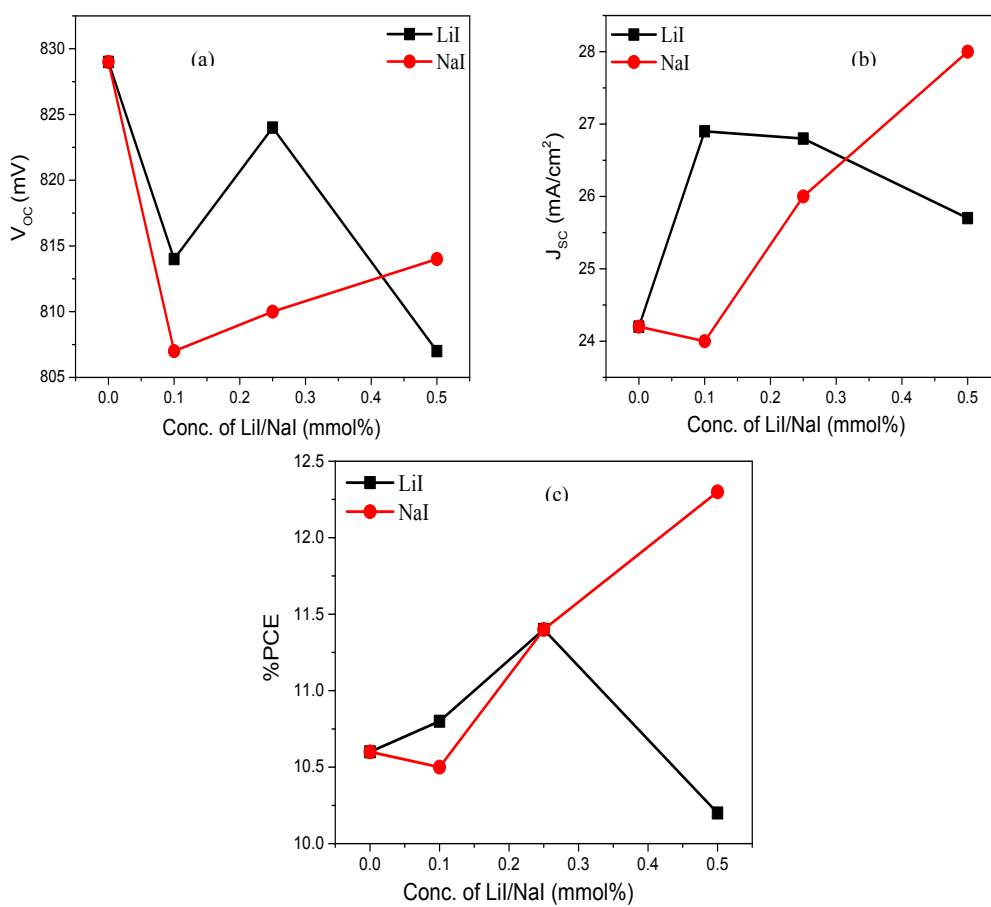


Fig. S9 Comparison of (a) V_{OC} , (b) J_{SC} and (c) %PCE of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 using N719 dye respectively.

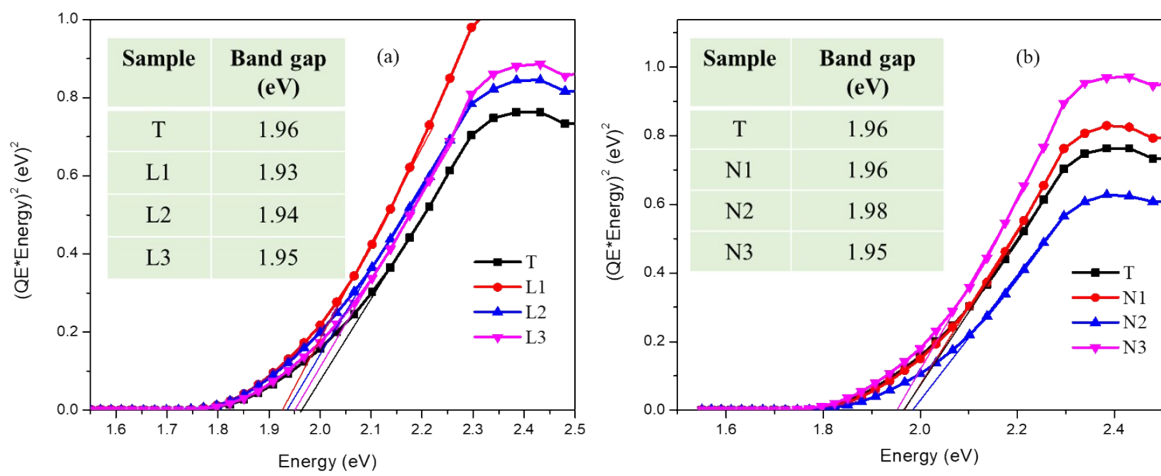


Fig. S10 $(QE \cdot E)^2$ as a function of photon energy E data for DSSCs fabricated with T, L1, L2, L3 (a) T, N1, N2, N3 (b) using N719 dye respectively. Inset is the obtained bandgap values from the intercept on the energy axis.³

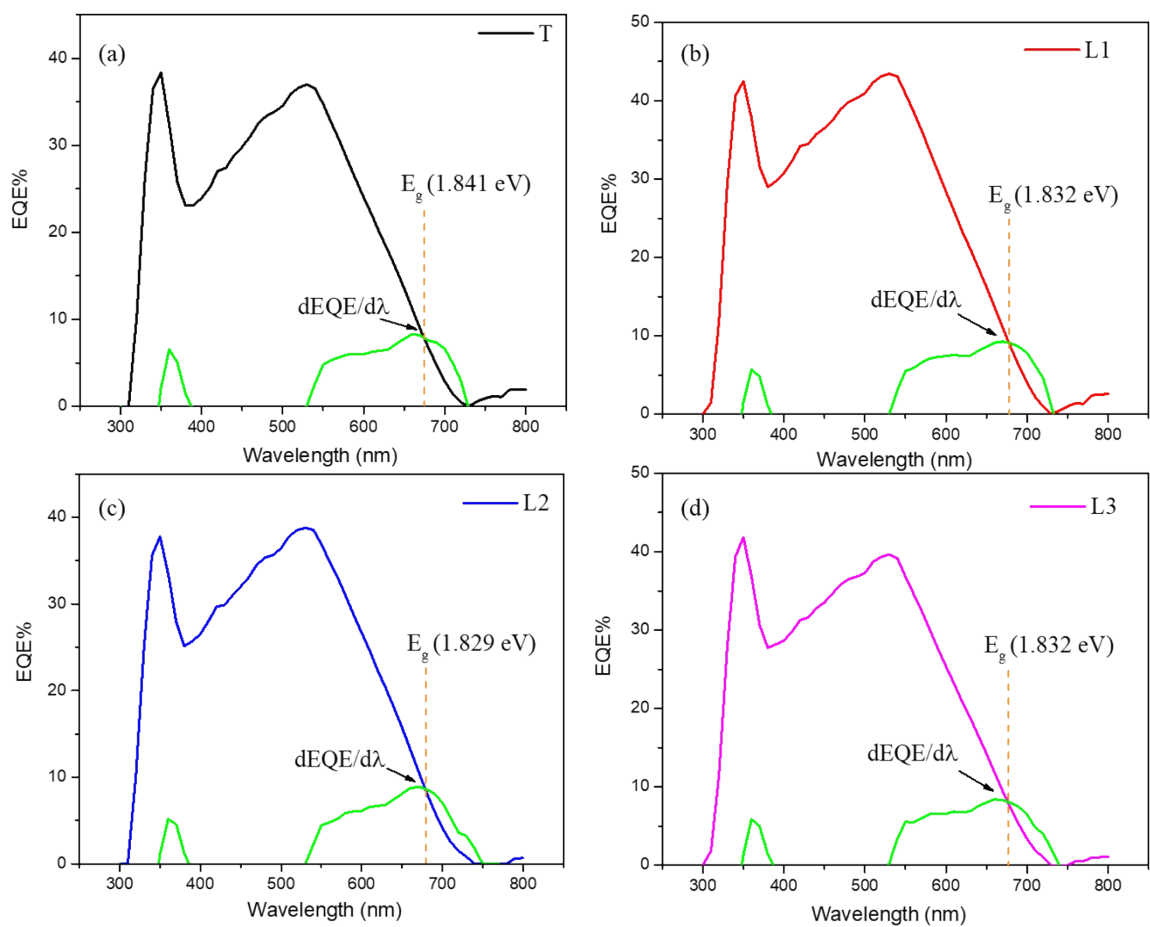


Fig. S11 The EQE plot, bandgap as determined from the EQE inflection point of DSSCs fabricated with T, L1, L2, L3 (a, b, c, d) using N719 dye respectively.⁴

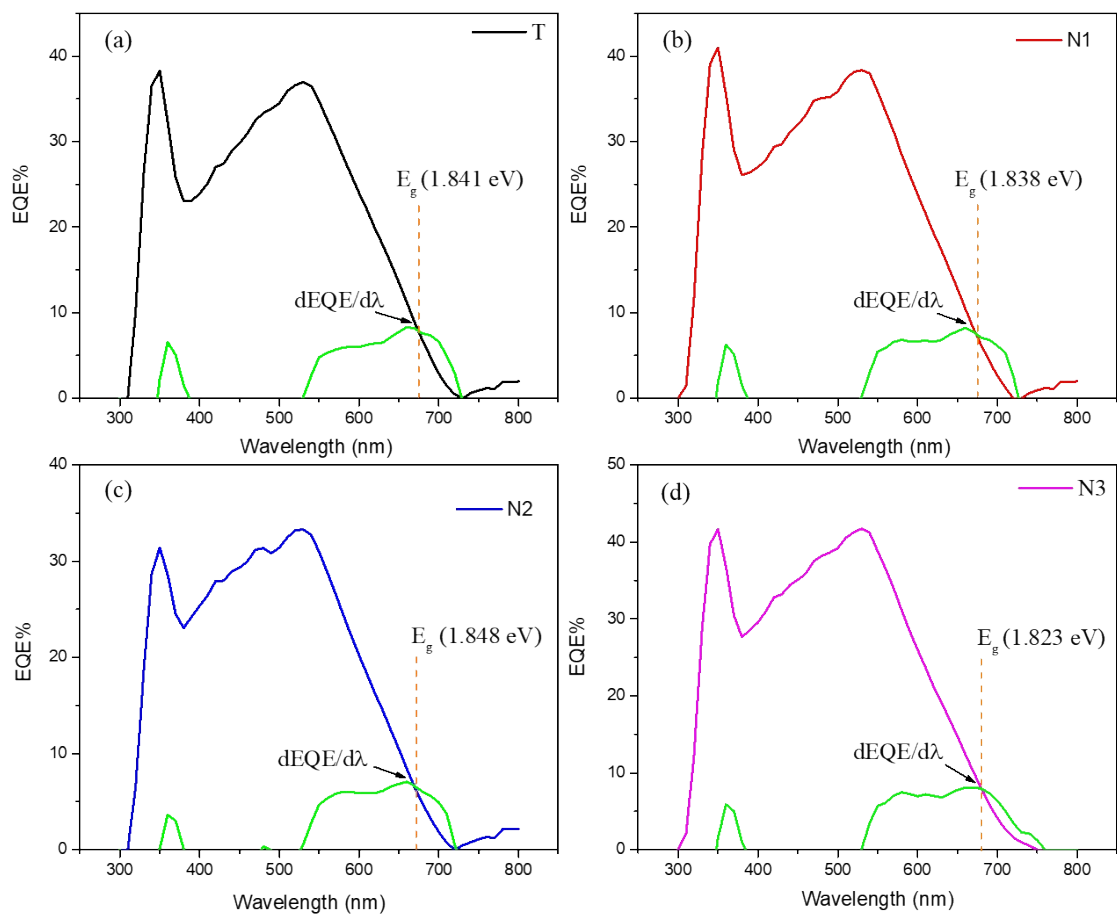


Fig. S12 The EQE plot, bandgap as determined from the EQE inflection point of DSSCs fabricated with T, N1, N2, N3 (a, b, c, d) using N719 dye respectively.⁴

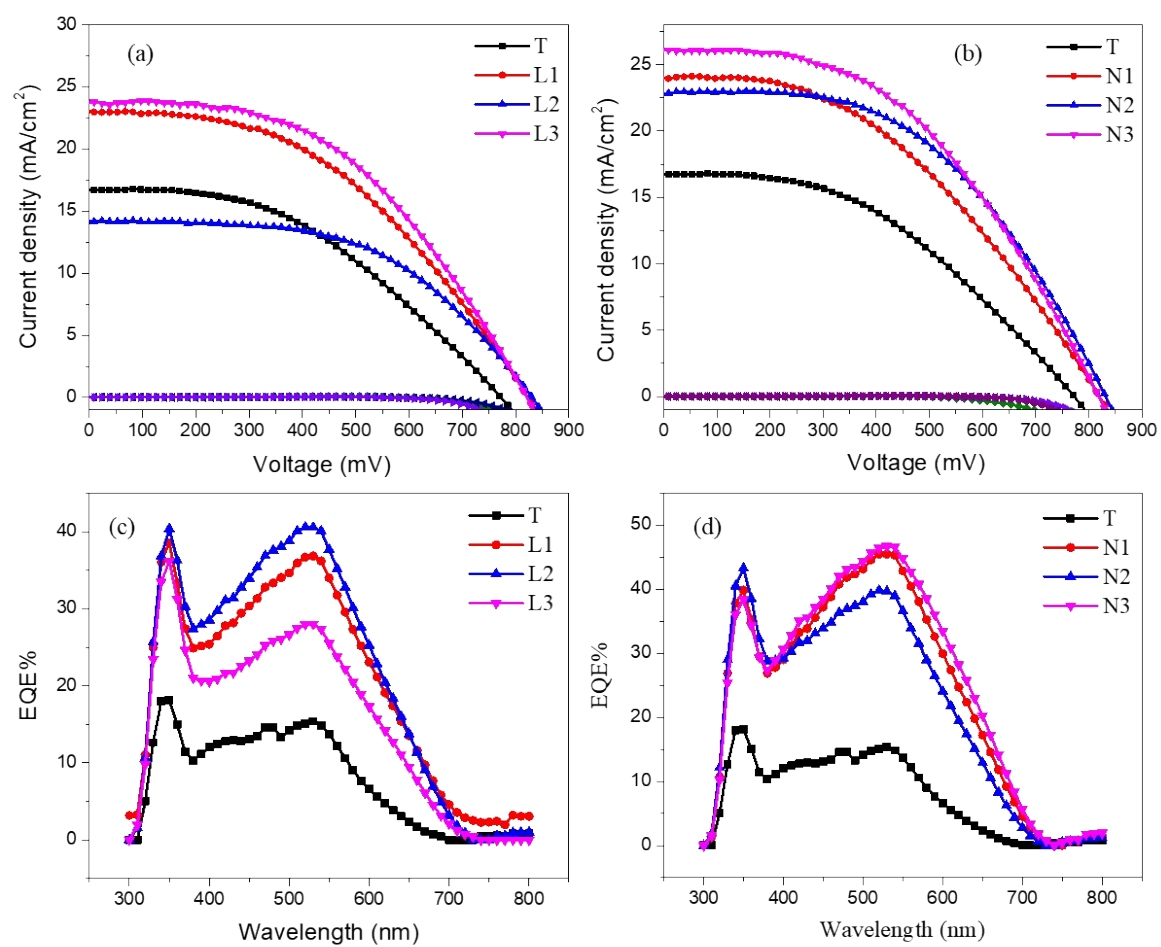


Fig. S13 J - V characteristics (a, b) and % EQE (c, d) of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 using N3 dye respectively.

Table S1 Crystallite size and stain values of T, L1, L2, L3, N1, N2, N3 samples respectively.

Sample	Crystallite size (nm)	Strain
T	17.5	36
L1	14.1	88
L2	12.9	110
L3	9.6	167
N1	13.5	67
N2	12.9	100
N3	12.9	88

Table S2 Flat band potential, donor density and V_{OC} of T, L1, L2, L3, N1, N2, N3 samples, respectively.

Sample	V_{FB} (V)	$N_D (\times 10^{19} \text{ cm}^{-3})$	V_{OC} (mV)
T	0.49	5.2	829
L1	0.43	11	814
L2	0.46	8.8	824
L3	0.43	12	807
N1	0.37	9.3	807
N2	0.36	12	810
N3	0.29	9.2	814

Table S3 EIS parameters of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 photoanode measured under dark conditions using N719 dye.

Dark	R_S ($\Omega \text{ cm}^2$)	R_{CT1} ($\Omega \text{ cm}^2$)	R_{CT2} ($\Omega \text{ cm}^2$)
T	7.18	3.45	12.22
L1	5.69	4.54	13.44
L2	5.37	3.62	11.45
L3	7.38	3.74	13.74
N1	7.84	14.85	4.48
N2	5.96	2.61	11.69
N3	4.57	3.17	10.48

Table S4 EIS parameters of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 photoanode measured under illumination conditions using N719 dye.

Light	R_S ($\Omega \text{ cm}^2$)	R_{CT1} ($\Omega \text{ cm}^2$)	R_{CT2} ($\Omega \text{ cm}^2$)
T	7.09	1.74	3.53
L1	5.64	4.72	2.29
L2	5.33	1.89	3.97
L3	7.49	3.64	1.92
N1	7.77	2.22	4.80
N2	5.91	2.55	2.09
N3	4.53	3.47	1.94

Table S5 Photovoltaic parameters of DSSCs fabricated with T, L1, L2, L3, N1, N2, N3 photoanode using N3 dye respectively.

Device details	V_{oc} (mV)	J_{sc} (mA/cm²)	FF	PCE%	τ (ms) (dark)	EQE%
T	771	16.7	44	6.7	32.0	18.1
L1	822	23.0	45	10	40.8	38.5
L2	829	14.2	54	7.5	31.2	40.5
L3	819	23.8	48	11	54.9	36.2
N1	819	24.0	43	9.9	40.8	45.4
N2	832	23.0	50	11.3	31.2	43.2
N3	817	26.1	47	11.8	40.8	46.7

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