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Deprotonation of N3 Adsorbed on TiO_2 for High-Performance Dye-Sensitized Solar Cells (DSSCs)

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Fig. S1 Fourier transform infrared spectra of (a) 0.3 mM N3 prior to and after chemical modification with 0.6 mM MPA in ethanol for 6 h (N3-MPA), (b) **E(N3)**, **E(N3-MPA, 0.1)**, and MPA, and (c) TiO_2 treated with 0.6 mM MPA in ethanol for 6 h.

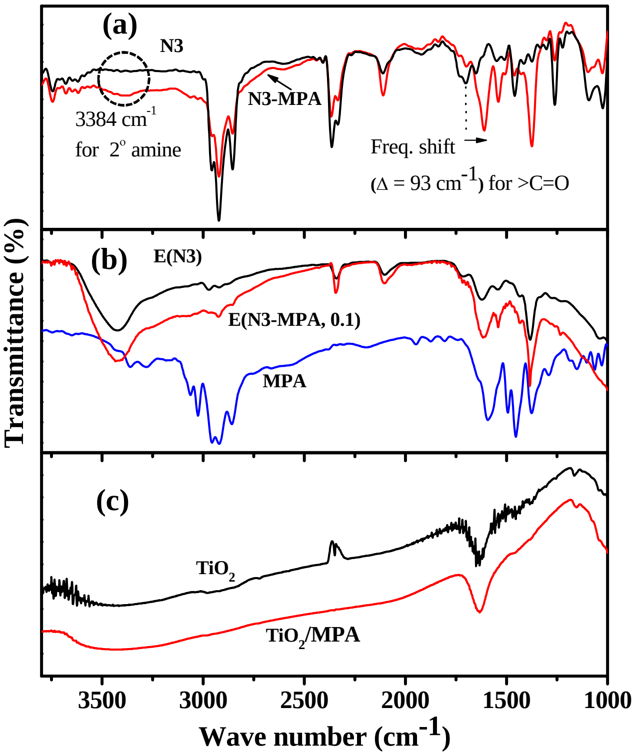

Fig. S2 ^{1}H NMR spectra of N3 and N3-MPA, using deuterated chloroform and tetramethylsilane as the solvent and internal reference, respectively.

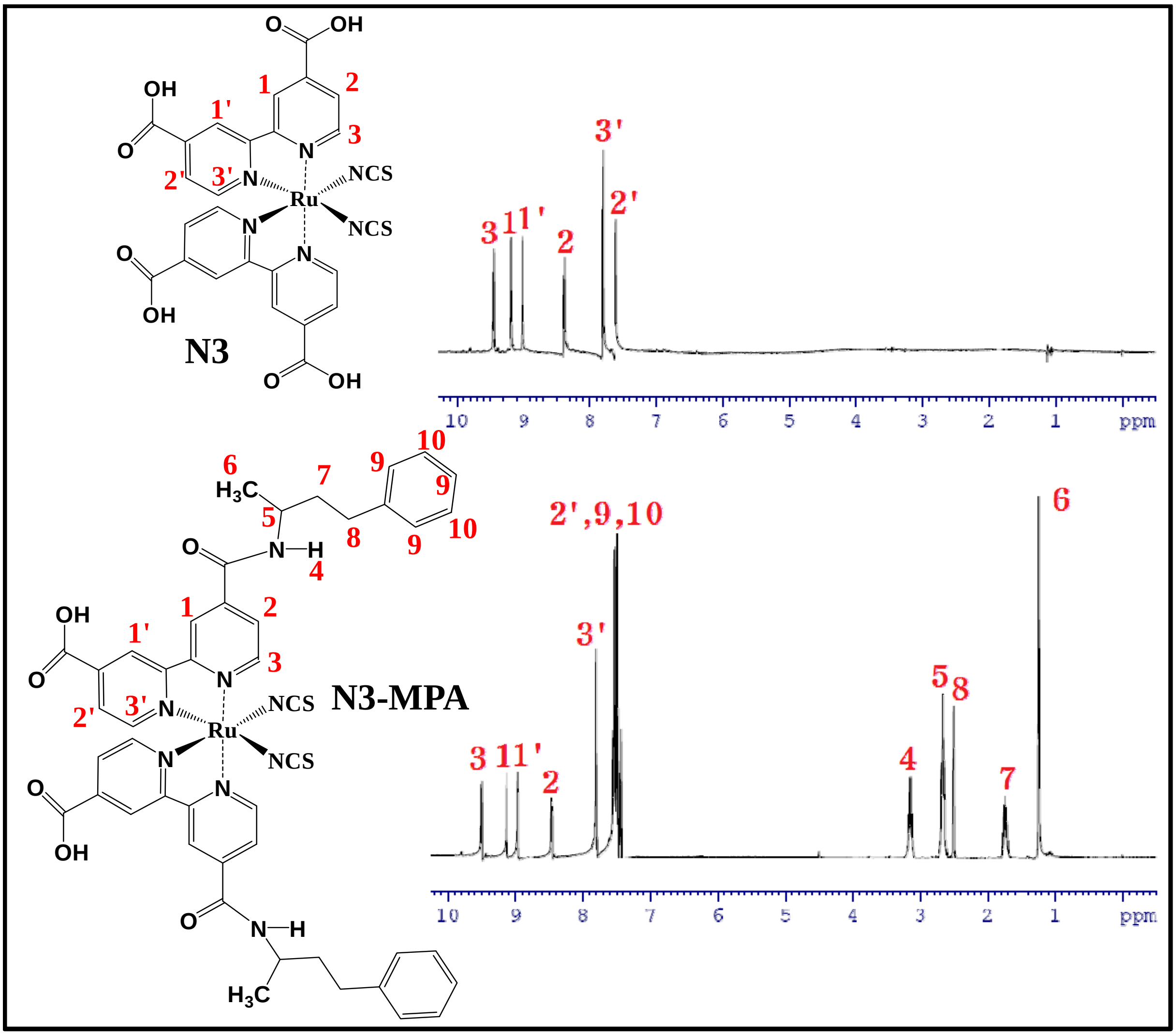

Fig. S3 (a) Gold Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of (a) N3 and (b) N3-MPA dissolved in anhydrous ethanol at positive mode. The calculated m/z of N3 ($C_{26}H_{16}O_8N_6S_2Ru$) is about 705.00, which was found at 686.18 for (N3-NCS+K). The m/z response of N3-MPA adduct was found at 1209.11 for ([N3-MPA]-NCS+K), where the calculated m/z of N3-MPA ($C_{66}H_{68}O_4N_{10}S_2Ru$) is about 1229.00. The spectrum also showed the response for N3 due to the presence of trace amount of unmodified N3 molecules.

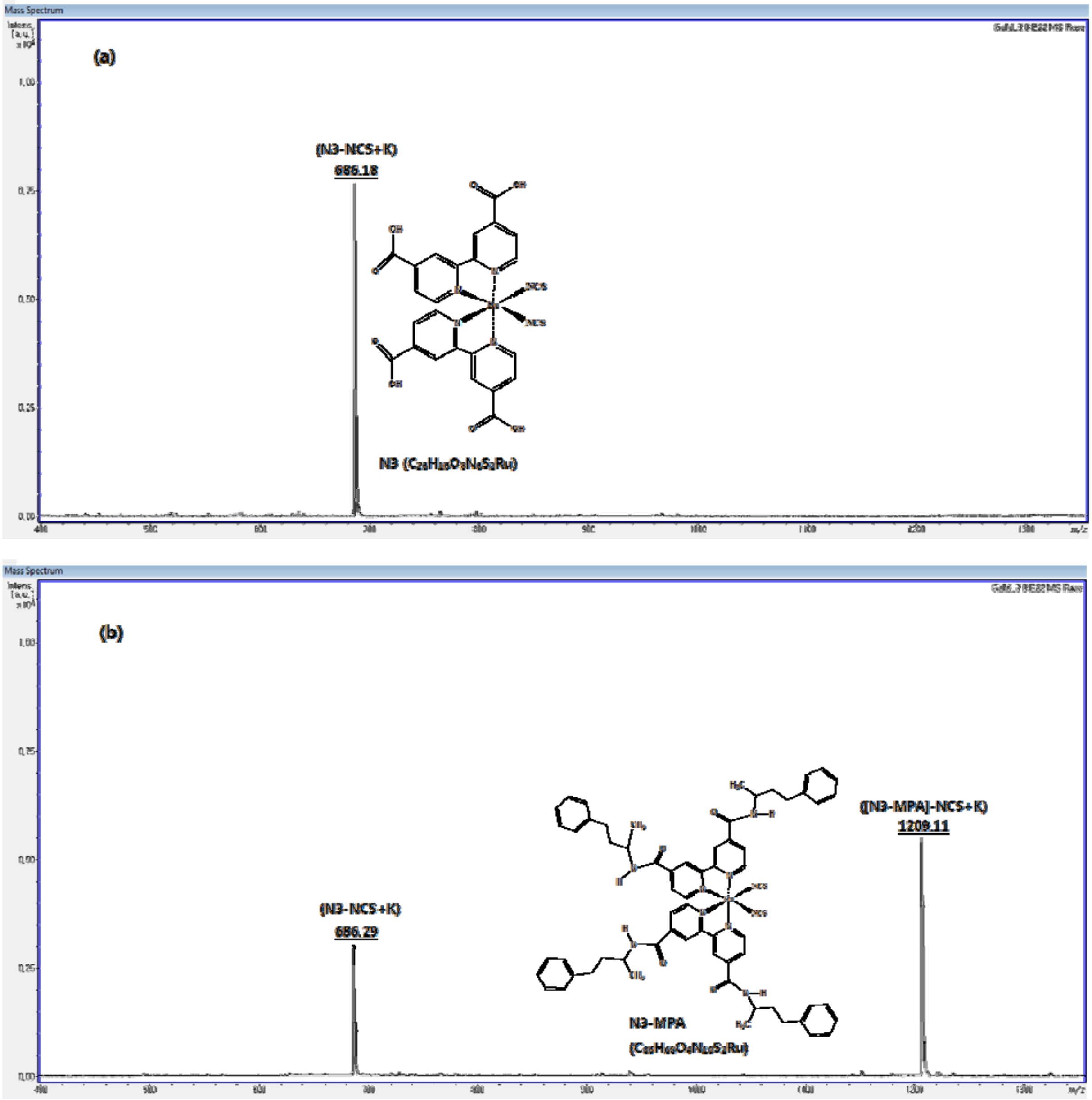

Fig. S4 Cyclic voltammograms (CVs) of 0.3 mM N3 and N3-MPA in dimethylformamide containing 0.1 M tetrabutylammonium perchlorate, using a Pt disk as a working electrode at scan rate of 50 mV/s. The electrochemical redox behaviour of N3 is consistent with the previous report.[S1] The inset shows the UV-vis absorption spectra of 0.3 mM of N3 and N3-MPA in ethanol.

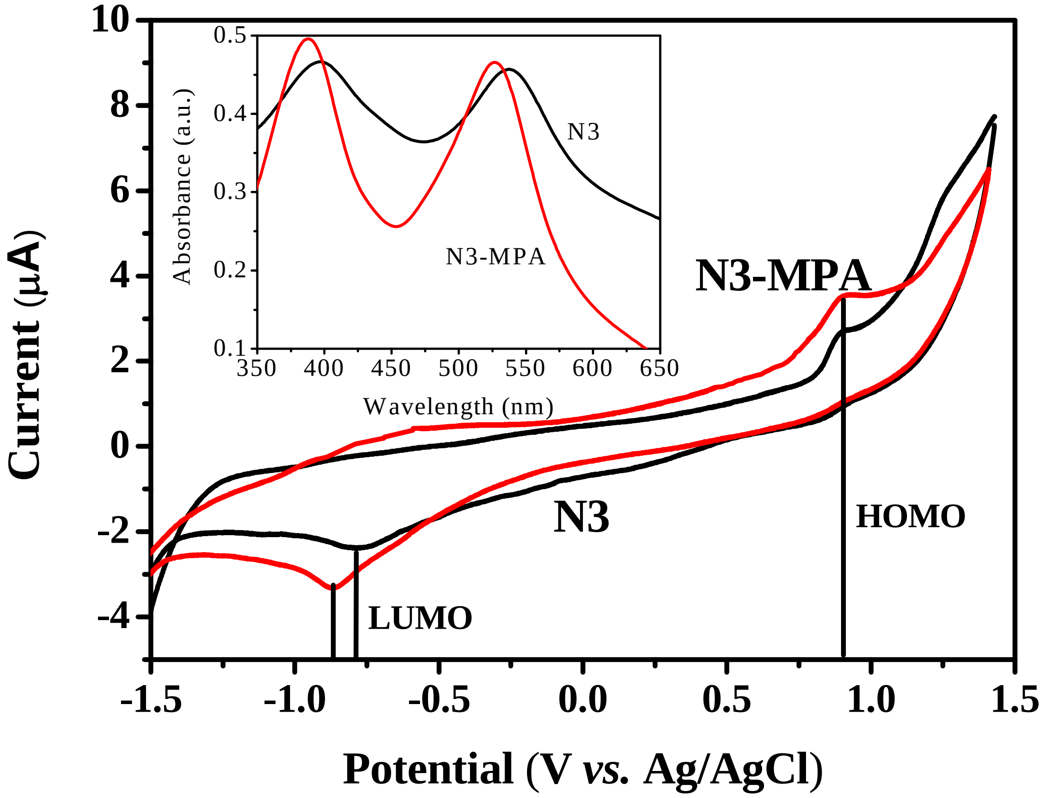

Fig. S5 Photovoltaic parameters of DSSCs with photoelectrodes **E(N3)** and **E(N3-MPA, 0.1)** measured over 500 h.

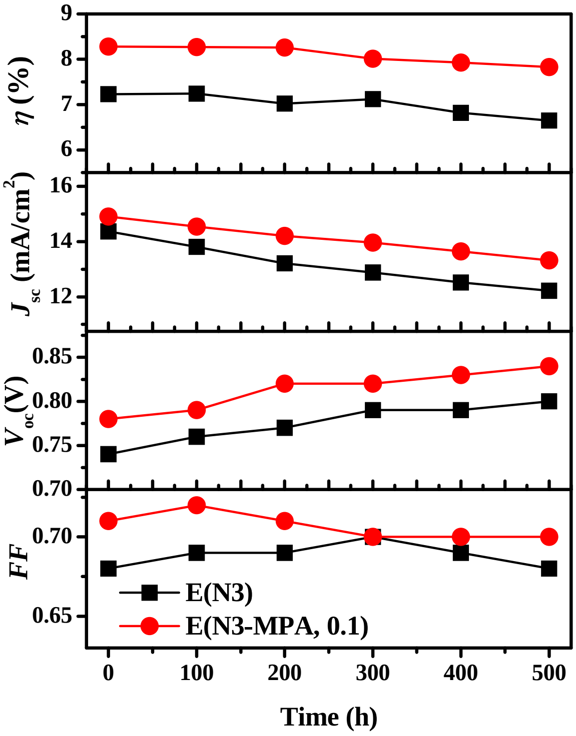

Fig. S6 Photographic image of TiO_2 films sensitized with N3, (TiO_2-N3) and after chemically modification with MPA, (TiO_2-N3-MPA).

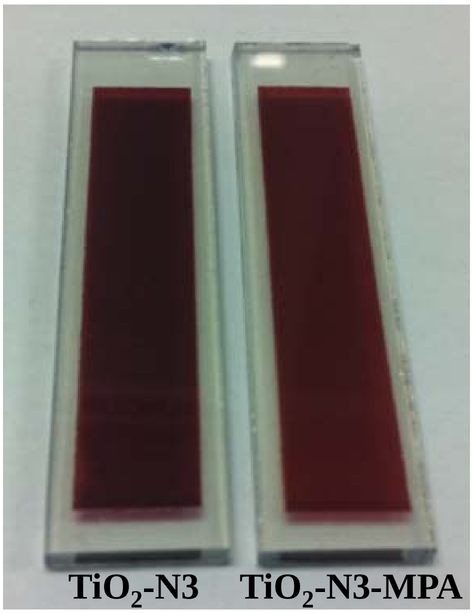

Table S1 pH values without/with modification of N3 with MPA in ethanol.

Solution	0.3 mM N3	0.3 mM N3 + 0.05 mM MPA	0.3 mM N3 + 0.1 mM MPA	0.3 mM N3 + 0.3 mM MPA
pH	6.42	7.32	7.72	9.10

Table S2 *J-V* performances of DSSCs sensitized chemically prepared N3-MPA. The *J-V* performances of the cells were very poor, which attributed to worse anchoring of N3-MPA on TiO_2 surface because of the deprotonation of all anchoring groups (-COOH) of N3 molecule with MPA.

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF* (%)	η (%)	Dye-loading $\times 10^{4}$ (mole/cm^2)
N3-MPA	0.47	4.55	65.67	1.4	0.091

References

S1. R. Gao, L. Wang, B. Ma, C. Zhan, and Y. Qiu *Langmuir*, 2010, **26 (4)**, 2460.