Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

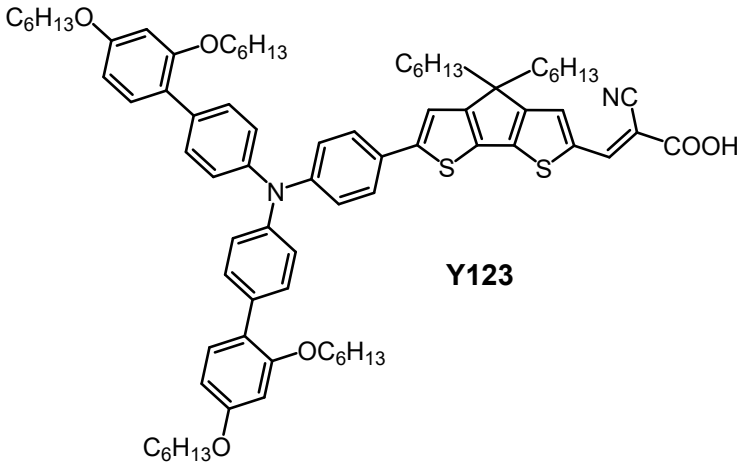
Supporting Information

Investigation on the Coordination between Methylpyridine Additives with $[Cu(dmp)_2]^{2+/+}$ Redox Couple and Its Improvement to the Stability of the Dye-Sensitized Solar Cell

Vinh Son Nguyen[a], Kala Kannankutty[a], Yu-Hsuan Chen,[b] Ding-Chen Wang,[b] Chen-Yu Yeh[b], Tzu-Chien Wei[a]**

[a]Department of Chemical Engineering, National Tsing-Hua University, Hsin-Chu, Taiwan.

[b]Department of Chemistry and Research Center for Sustainable Energy & Nanotechnology, National Chung-Hsing University, Taichung 402, Taiwan



Y123

Scheme S1 The structure of dye Y123

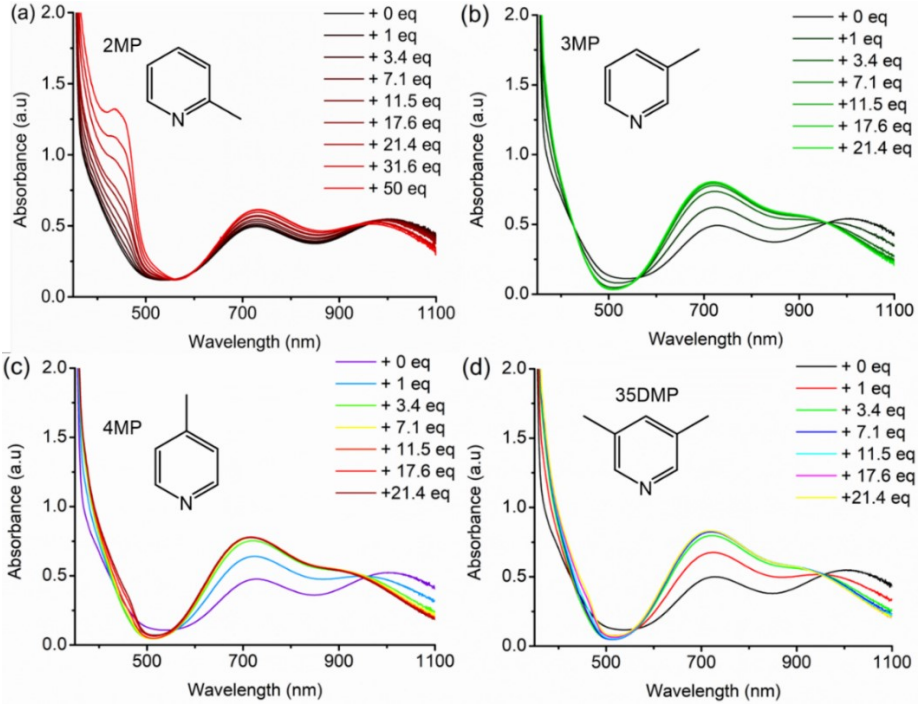


Figure S1. UV-Vis titration of $[Cu(dmp)_2]^{2+}$ with the addition of (a) 2MP, (b) 3MP, (c) 4MP and (d) 35DMP in MeCN

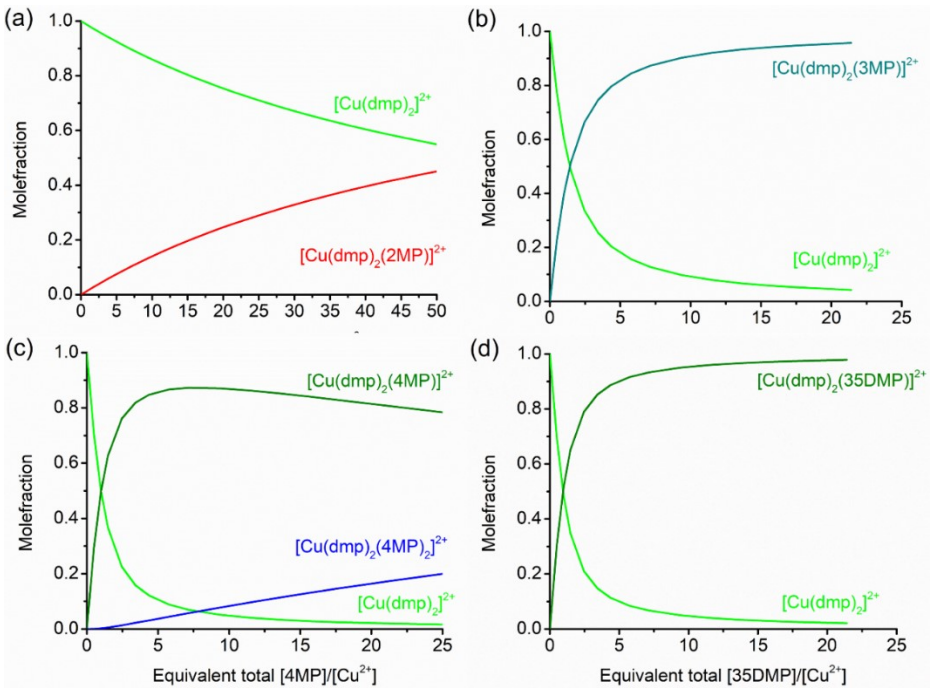


Figure S2. Component change of (a)$[Cu(dmp)_2]^{2+}$ titrated with (a) 2MP, (b) 3MP, (c) 4MP and (d) 35DMP in MeCN.

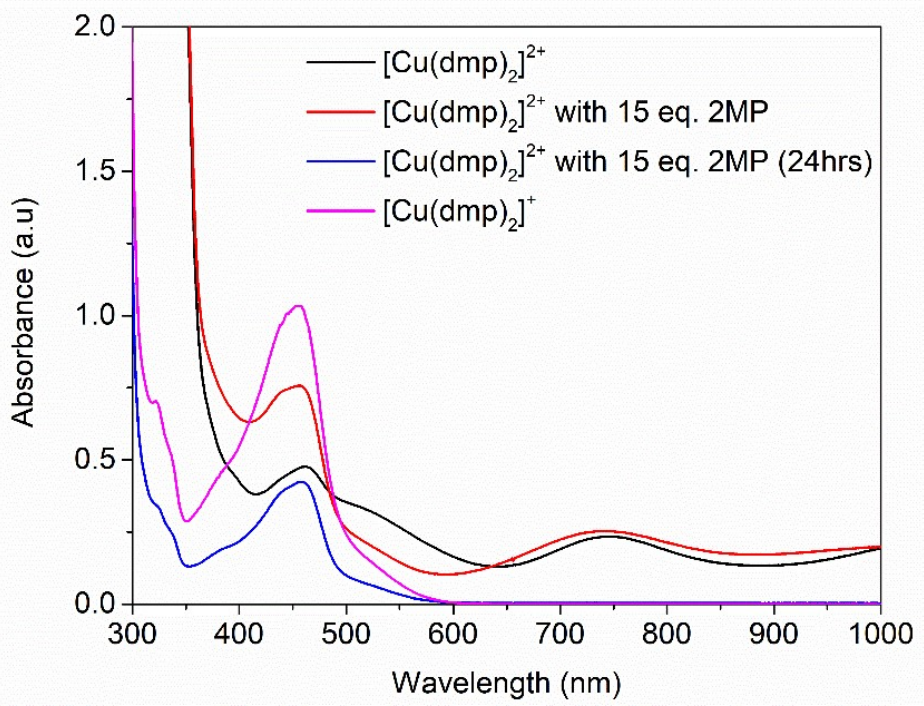


Figure S3. (Top) Photographs of $Cu(dmp)_2]^{2+}$ without and with the addition of TBP, 2MP; and (Bottom) their UV-vis spectra in DCM. The $[Cu(dmp)_2]^{+}$ 0.14mM in DCM also included for comparison (pink solid curve).

Note 1: As shown in the photograph in **Figure S3**, $[Cu(dmp)_2]^{2+}$ in non-coordinating solvent DCM has light brown color. The addition of TBP, (or 3MP, 35DMP, and 4MP) changed the solution to light green

color. In the case of 2MP, the color of the solution is dark yellow, indicating that the reduction of $[Cu(dmp)_2]^{2+}$ occurred. At this stage, the concentration of copper(I) complex is small, therefore, the d-d* band still can observe in fresh 2MP-added $[Cu(dmp)_2]^{2+}$ spectrum. However, we can clearly see that the MLCT band intensity in 2MP-added $[Cu(dmp)_2]^{2+}$ spectrum increased and slightly shifted by 6 nm to 456 nm, which is the MLCT of $[Cu(dmp)_2]^{+}$ .After 24hrs, the color of solution became red (which is also color of $[Cu(dmp)_2]^{+}$, photo was included), and there is not d-d* band observed in $[Cu(dmp)_2]^{2+}$ spectrum, implying $[Cu(dmp)_2]^{2+}$ was reduced to $[Cu(dmp)_2]^{+}$. Please note that the extinction coefficient of $[Cu(dmp)_2]^{+}$ (7300 $M^{-1}cm^{-1}$) is about ten times higher than $[Cu(dmp)_2]^{2+}$ (850 $M^{-1}cm^{-1}$), the 24hr-2MP-added $[Cu(dmp)_2]^{2+}$ spectrum was measured after multiple dilution.

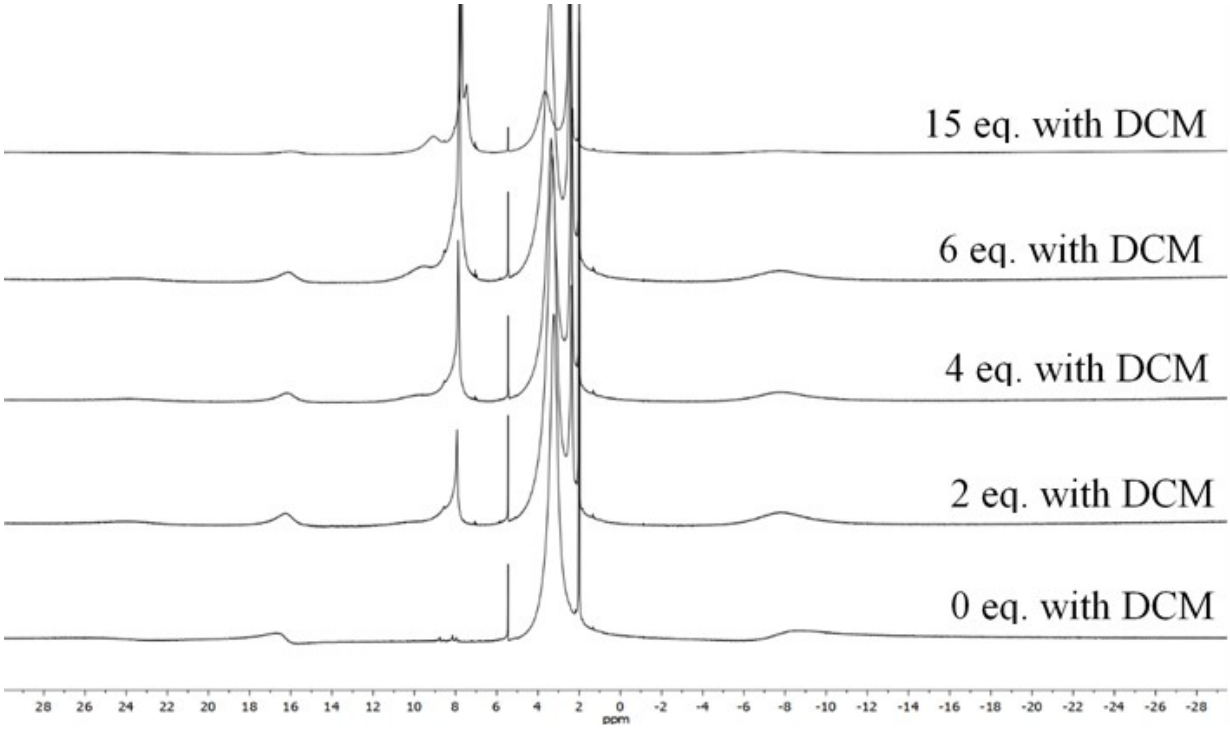


Figure S4. ^{1}H NMR titration of $[Cu(dmp)_2]^{2+}$ with 2MP in d3-MeCN solution using DCM as internal standard.

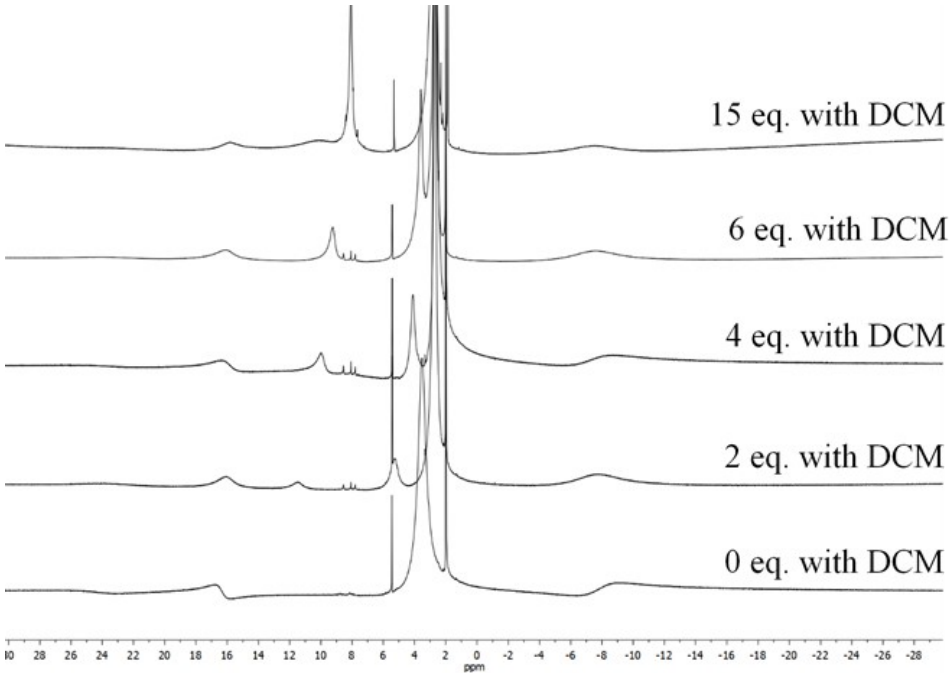


Figure S5. ^{1}H NMR titration of $[Cu(dmp)_2]^{2+}$ with 3MP in d3-MeCN solution using DCM as internal standard.

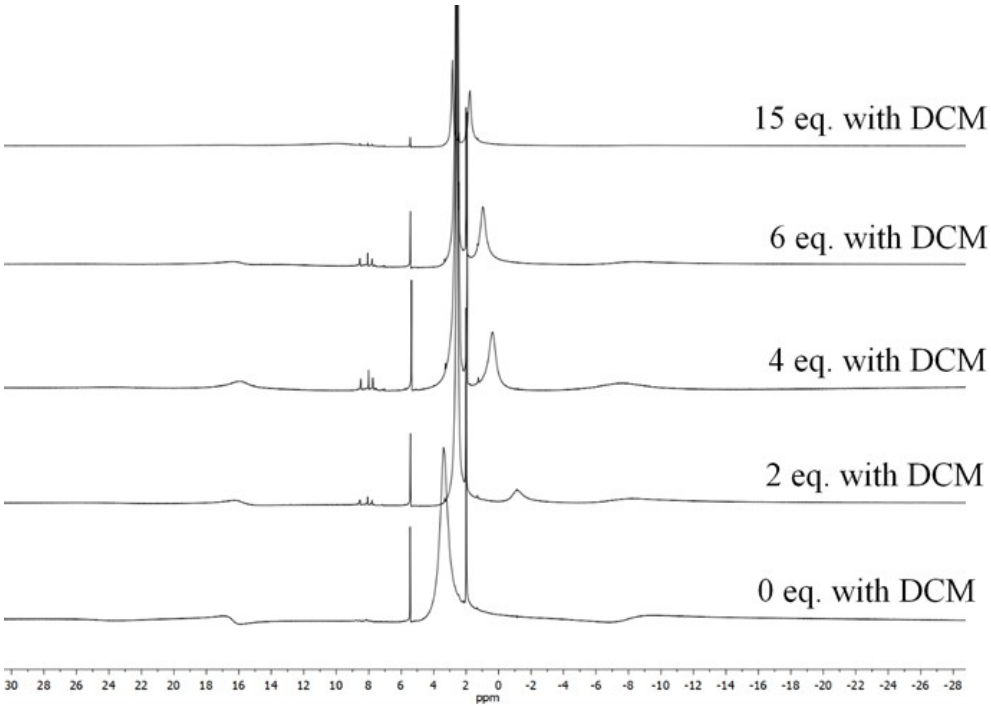


Figure S6. ^{1}H NMR titration of $[Cu(dmp)_2]^{2+}$ with 4MP in d3-MeCN solution using DCM as internal standard.

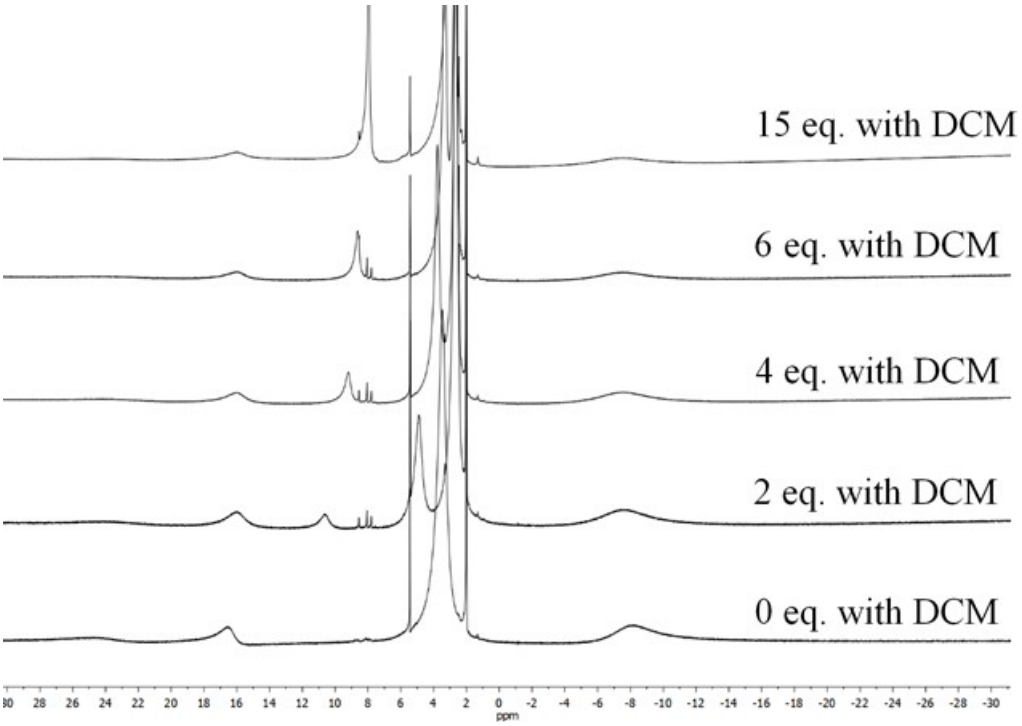


Figure S7. ^{1}H NMR titration of $[Cu(dmp)_2]^{2+}$ with 35DMP in d3-MeCN solution using DCM as internal standard.

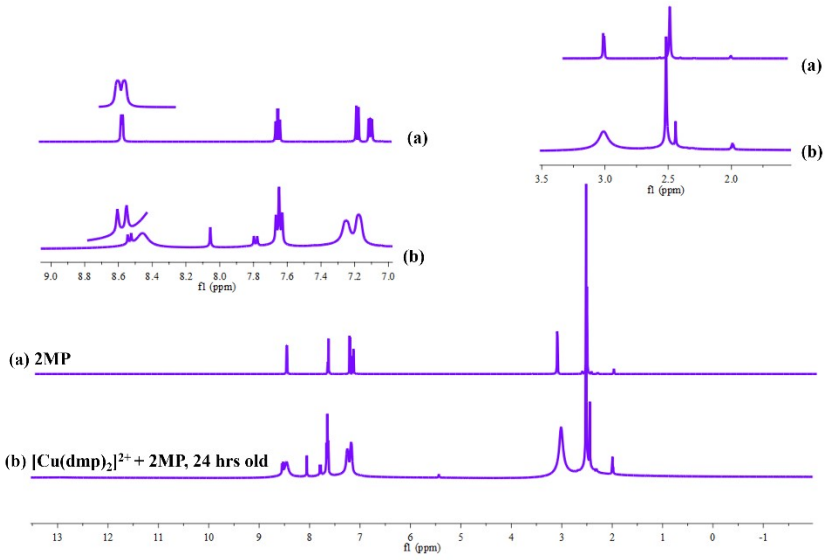


Figure S8 :^{1}H NMR spectrum of $[Cu(dmp)_2]^{2+}$ + 15 eq. 2MP after 24 hrs and 2MP in d3-MeCN.

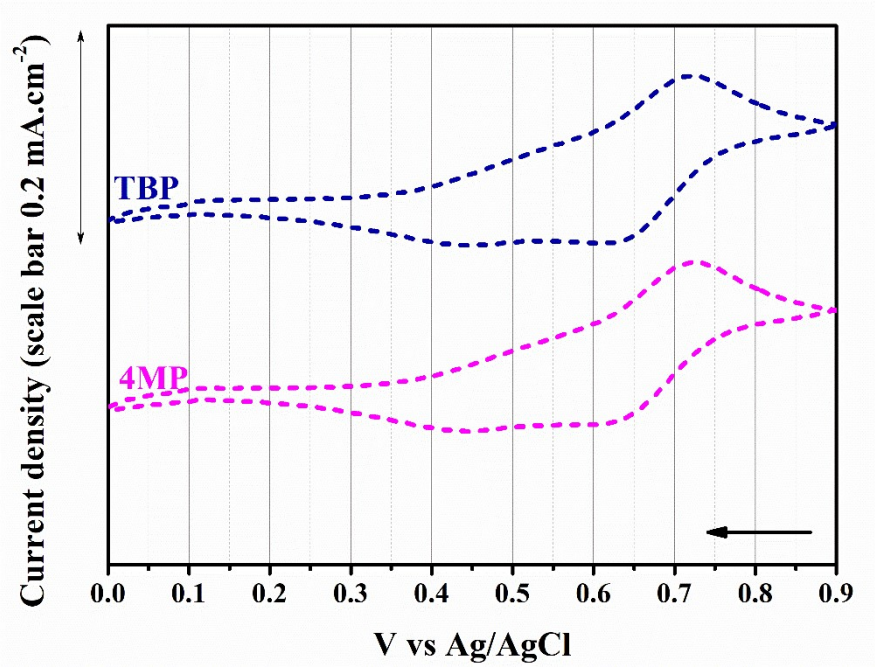


Figure S9. CV waves of fresh 3 mM solutions of $[Cu(dmp)_2]^{2+}$ in acetonitrile with (solid red line) the addition of 15 equivalents of 4MP and TBP. A 0.1 M LiTFSI was added as supporting electrolyte. A standard ferrocene couple was 0.47 V vs Ag/AgCl (saturated LiCl in ethanol).

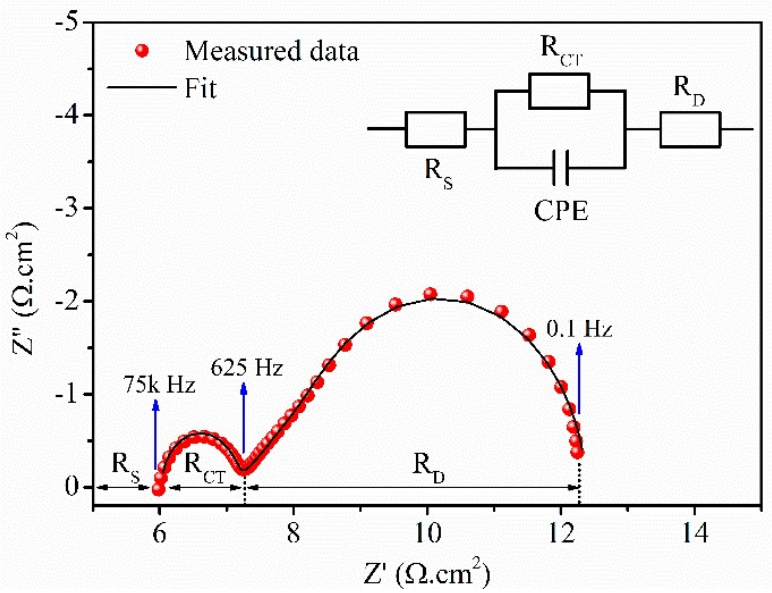


Figure S10. The Nyquist plot of $[Cu(dmp)_2]^{2+/+}$ electrolyte in the addition of 3MP and the equivalent circuit used to fit data.

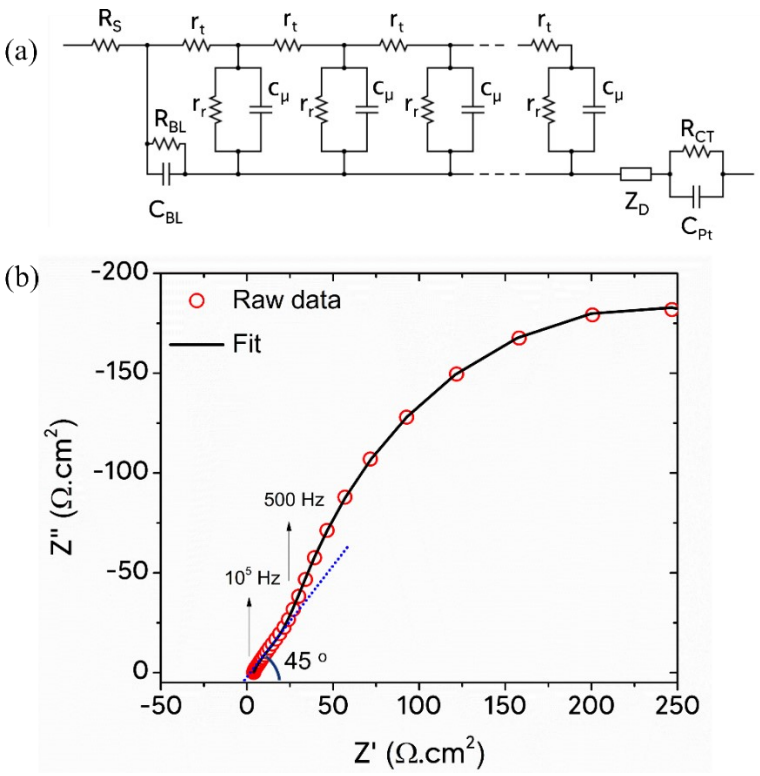


Figure S11 (a) Transmission line model and (b) Nyquist plot of 3MP-based DSSC obtained from EIS measurement applied 0.75 V bias in the dark.

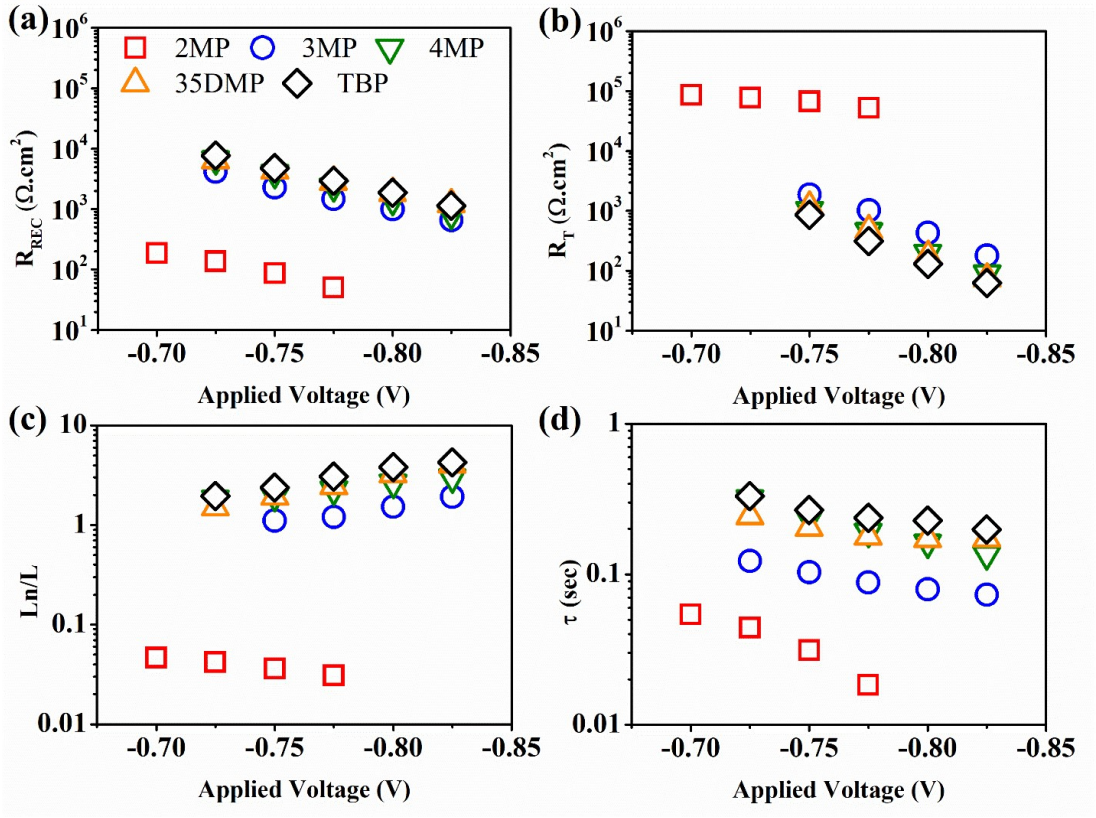


Figure S12. (a) Recombination resistance, (b) Charge transport resistance and (c) effectiveness diffusion length and (d) electron lifetime of $[Cu(dmp)_2]^{2+/+}$-mediated DSSC with addition of different Lewis bases obtained by EIS measurements at dark conditions under applied biases.

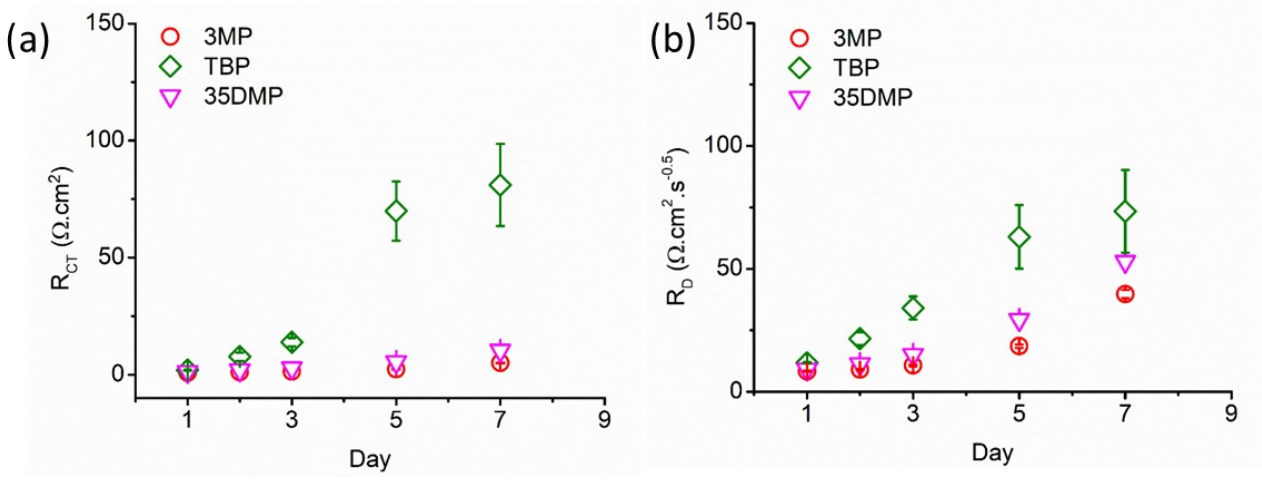


Figure S13. 7-day evolution of (a) R_{CT} and (b) R_D of the symmetric cell using 3MP, 35DMP, and TBP as an additive.