**Supporting Information**

# Push-pull triarylamine additives that enhance dye sensitized solar cell performance

**Akshay Kokil, J. Matthew Chudomel, Jamie Hominck, Paul M. Lahti,* and Jayant Kumar***

## Experimental Details

*Materials*: **Z907** was provided by Konarka Technologies Inc. and used as received. Commercially available P25 titania nanoparticles having an average size of 25 nm (Evonik Degussa Corporation) were used to fabricate DSSC test cells: these particles typically contain 70-80% of the anatase phase of titania. **9DAAA**, **910BAA, DAAFO**, **BDAAFO**, and **DAAFOPV** were synthesized by literature procedures.[1,2] The purity and identity of all synthesized compounds was confirmed by high performance liquid chromatography (HPLC), proton NMR spectroscopy, and mass spectrometry.

*Device Fabrication*: The devices were fabricated on fluorine-doped tin oxide (FTO) covered glass substrates (sheet resistance 15Ω/□) with an active area of 0.125 $cm^2$. Nanoporous $TiO_2$ films were prepared by spin-coating $TiO_2$ paste on the substrates. The substrates were sintered at 400°C for two hours. After dye adsorption the substrates were washed with ethanol and acetonitrile and dried in air. FTO covered glass substrates coated with platinum (50 nm) were used as the counter electrode.

*Evaluation of DSSC voltage/current/PCE characteristics*: The DSSCs were tested on a conventional setup as previously described in literature.[3] All experiments were performed using AM 1.5 direct irradiation at 100 mW/$cm^2$ light intensity. For best comparison of the effects of each triarylamine additive on DSSC performance, the device characteristics for a standard control cell were first measured, then aliquots of the additive in acetonitrile were added to the electrolyte and the measurements repeated.

## References

[1] J. M. Chudomel, B. Yang, M. D. Barnes, M. Achermann, J. T. Mague, P. M. Lahti, *J. Phys. Chem. A*, 2011, **115,** 8361.

[2] P. J. Homnick, P. M. Lahti, *Phys. Chem. Chem. Phys*., 2012, **14**, 11961.

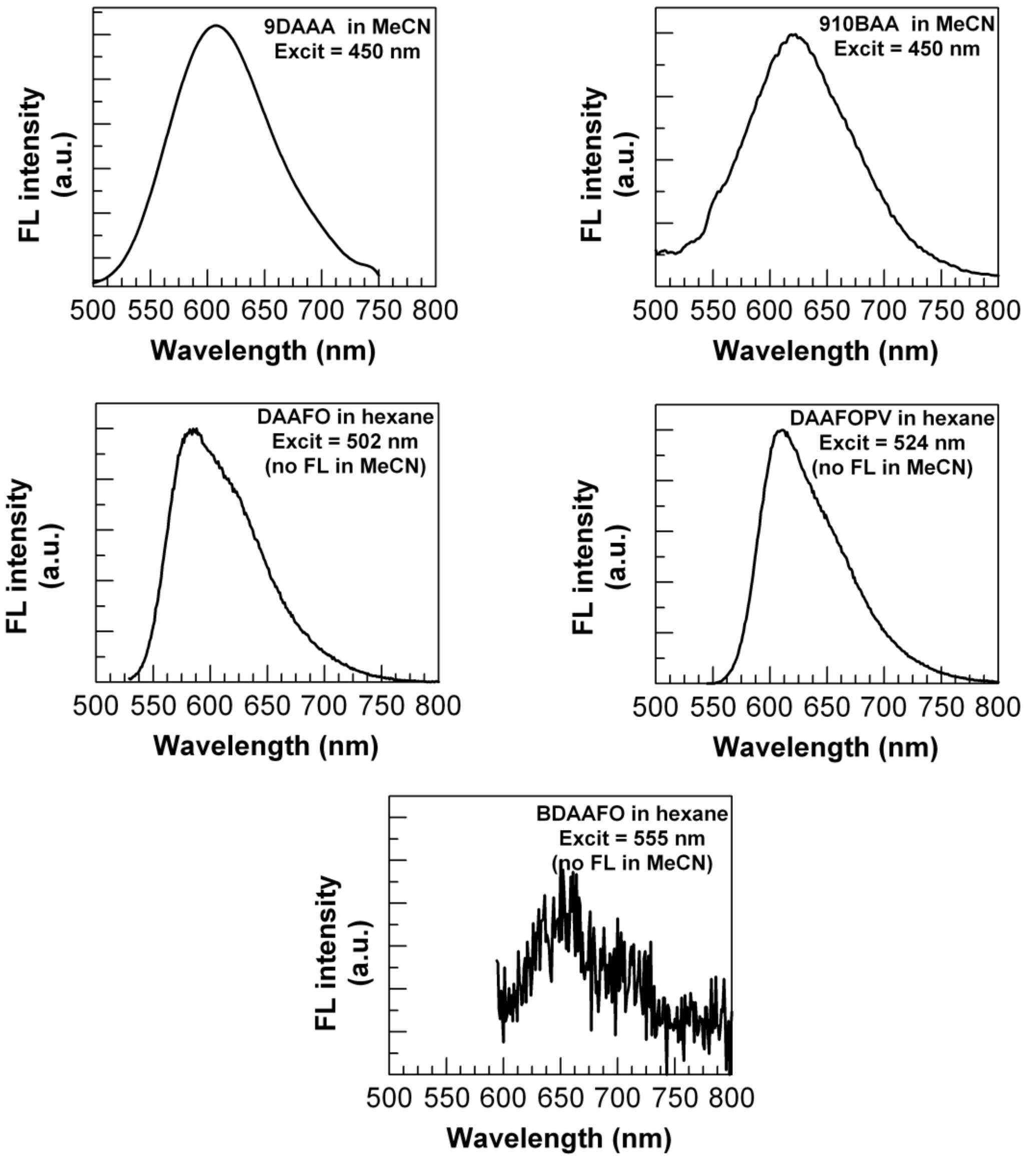
[3] Y. G. Kim, J. Walker, L. A. Samuelson, J. Kumar, *Nano Lett*., 2003, **3**, 523.

**Table 1. Optical and oxidation characteristics of push-pull additives compared to Z907.**

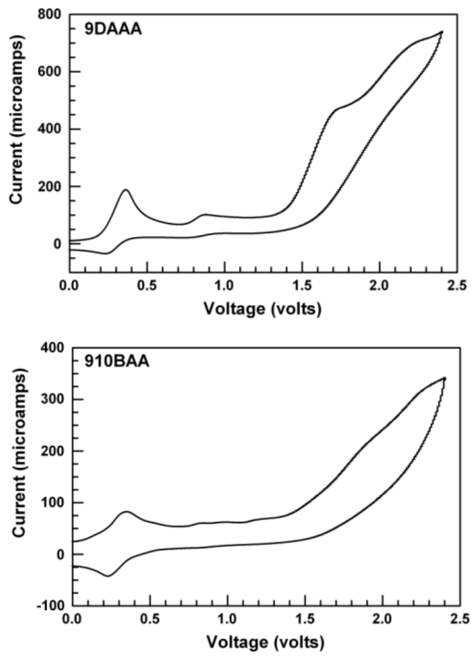
| Compound | Absorption ($\lambda_{max}$, nm[e,cm$^{-1}$M$^{-1}$])[a] | Absorption onset[a] (eV) | $E^{ox}_{1/2}$ (V)[a,b] | $E_{HOMO}$ (eV)[c] | $E_g$ (eV)[d] | $E_{LUMO}$ (eV)[e] |
|---|---|---|---|---|---|---|
| **Z907** | 546 [11600][f] | 1.65 | 0.65[f] | –5.4 | 1.6 | –3.8 |
| **9DAAA** | 442 [3700] | 2.36 | 0.306 | –5.11 | 2.80 | –2.31 |
| **910BAA** | 468 [4000] | 2.14 | 0.288 | –5.09 | 2.65 | –2.44 |
| **DAAFO** | 520 [1260] | 2.01 | 0.323 | –5.12 | 2.39 | –2.73 |
| **BDAAFO** | 586 [1650] | 1.75 | 0.220 | –5.02 | 2.12 | –2.90 |
| **DAAFOPV** | 543 [3280] | 1.93 | 0.326 | –5.13 | 2.29 | –2.84 |

[a] Acetonitrile solution. [b] Lowest voltage oxidation referenced to ferrocene oxidation potential $Fc/Fc^{+}$. [c] $E_{HOMO}$ = –(4.8+[oxdn potential in volts]) eV, using oxidation potential referenced to $Fc/Fc^{+}$. [d] From absorption peak maximum. [e] For all except Z907, $E_{LUMO} = E_{HOMO} + E_g$; for Z907, $E_{LUMO}$ comes from electrochemical measurement. [f] Ref 4.

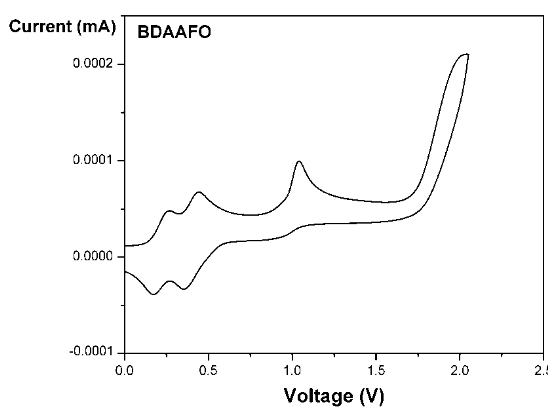
[4] Md. K. Nazeeruddin, S. M. Zakeeruddin, J. J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Grätzel *Coord. Chem. Rev*., 2004, **248**, 1317.



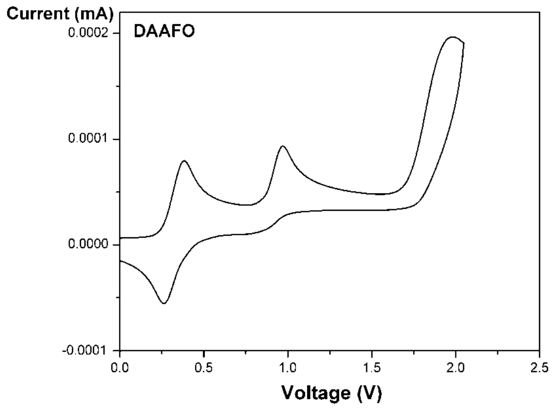

**Supplementary Figure 1.** Photoluminescence spectra for **9DAAA** and **910BAA** in acetonitrile and **DAAFO**, **DAAFOPV** and **BDAAFO** in hexanes. Photoluminescence for **DAAFO**, **DAAFOPV** and **BDAAFO** is not observed in acetonitrile.



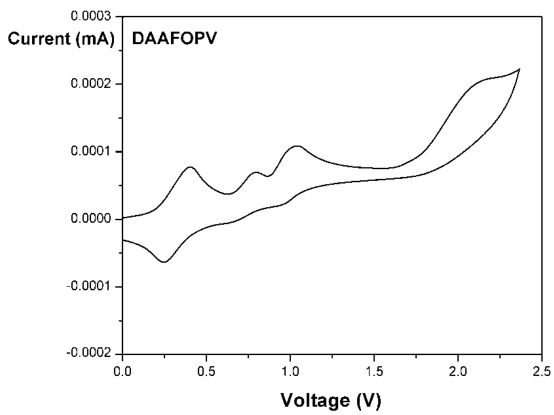

**Supplementary Figure 2.** Cyclic voltammograms for **9DAAA** and **910BAA** in acetonitrile referenced to ferrocene/ferrocenium ($Fc/Fc^+$) in acetonitrile.



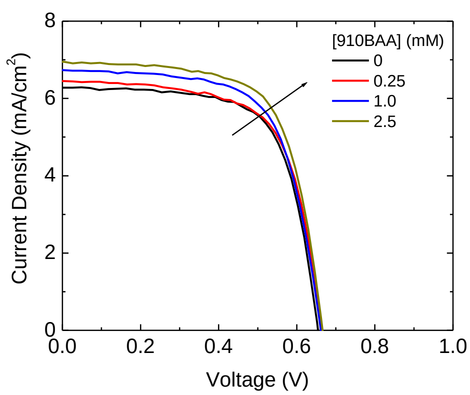

**Supplementary Figure 3.** Cyclic voltammogram for **BDAAFO** in acetonitrile referenced to $Fc/Fc^+$.



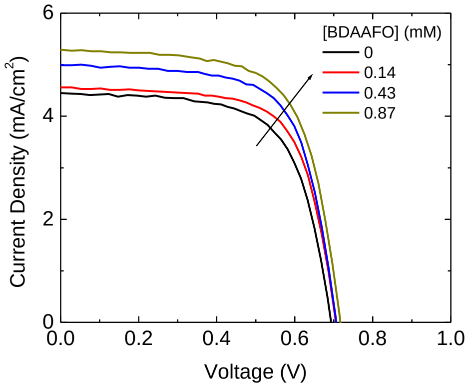

**Supplementary Figure 4.** Cyclic voltammogram for **DAAFO** in acetonitrile referenced to $Fc/Fc^+$.



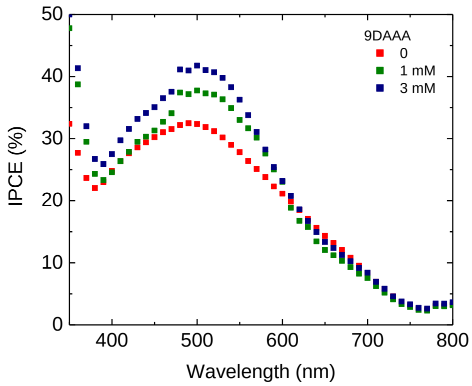

**Supplementary Figure 5.** Cyclic voltammogram for **DAAFOPV** in acetonitrile referenced to $Fc/Fc^+$.




**Supplementary Figure 6.** Current density versus voltage (J-V) curves for DSSCs with varying **910BAA** concentrations. The arrow in the plot shows the trend with increasing **910BAA** concentration.




**Supplementary Figure 7.** Current density versus voltage (J-V) curves for DSSCs with varying **BDAAFO** concentrations. The arrow in the plot shows the trend with increasing **BDAAFO** concentration.




**Supplementary Figure 8.** IPCE spectra for DSSCs with varying **9DAAA** concentrations.

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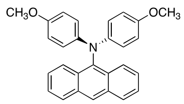
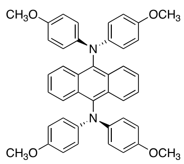
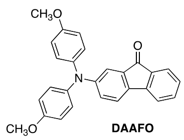
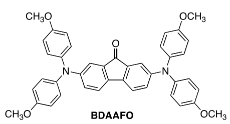
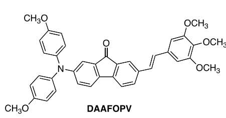
Table 2. **DSSC performance characteristics with various additives.**

| Additive | Additive concentration | $V_{oc}$ (volts) | $J_{sc}$ (mA/cm$^2$) | Fill Factor | PCE | Control PCE | PCE increase | Effect of increasing additive |
|---|---|---|---|---|---|---|---|---|
| None (control) | (0 mM) [a] | 0.68 | 3.98 | 0.59 | 1.63% | 2.58% | -36.8% [a] | $V_{oc}$ steady<br>$J_{sc}$ decreases<br>FF decreases |
|  9DAAA | 3.33 mM [b] | 0.80 | 6.54 | 0.69 | 3.63% | 2.99% | 21.4% | $V_{oc}$ rises<br>$J_{sc}$ steady |
|  910BAA | 2.50 mM [b] | 0.66 | 6.96 | 0.67 | 3.11% | 2.79% | 11.5% | $V_{oc}$ steady<br>$J_{sc}$ rises |
|  DAAFO | 2.22 mM [b] | 0.68 | 6.33 | 0.67 | 2.93% | 2.20% | 33.2% | $V_{oc}$ steady<br>$J_{sc}$ rises |
|  BDAAFO | 0.87 mM [b] | 0.71 | 5.34 | 0.66 | 2.52% | 2.03% | 24.1% | $V_{oc}$ steady<br>$J_{sc}$ rises |
|  DAAFOPV | 1.24 mM [b] | 0.68 | 5.66 | 0.67 | 2.59% | 1.99% | 30.2% | $V_{oc}$ steady<br>$J_{sc}$ rises |

[a] Acetonitrile added in equal volume to additive additions, but without additive molecule. [b] Concentration past which further increase in power conversion efficiency (PCE) was not observed.