# ***Supplemental Materials***

*Geometrical Effect of Stilbene on the Performance of Organic Dyes-Sensitized Solar Cells*

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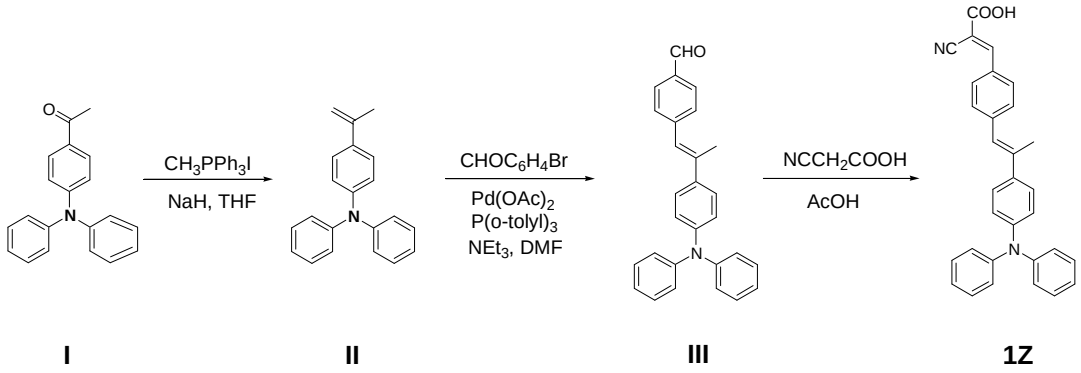
**Synthesis of compound 1Z**




**I** **II** **III** **1Z**

**(4-Isopropenyl-phenyl)diphenylamine** (**II**). Methyltriphenylphosphonium iodide (6.47 g, 16.0 mmol) was dissolved in THF (53 mL). To it was added NaH (1.92 g, 48.0 mmol) slowly in an ice-water bath, and then the mixture was stirring for another 2 h at ambient temperature. Compound **I** (2.3 g, 8.0 mmol) in THF (23 mL) was added dropwise to this reaction mixture by using a pressure-equalizing addition funnel. After the completion of reaction, methanol was added to quench excess NaH in an ice-water bath and then THF was removed by rotary evaporation. The reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. Column chromatograph eluted with ethyl acetate/hexane (1/25) afforded the desired product as a white solid (1.43 g, 63% yield). Mp 65−66 °C Spectral data of **II**: $\delta_H$ (400 MHz, $CDCl_3$) 7.38 (d, $J$ =8.1 Hz, 1H), 7.29−7.25 (m,4H), 7.13−7.02 (m, 8H), 5.35 (s, 1H), 5.04 (s, 1H), 2.16 (s, 1H) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 147.72, 147.16, 142.48, 135.24, 129.22, 126.24, 124.32, 123.40, 122.83, 111.05, 29.70 ppm. *m/z* (FAB) 285.1519 (($M^+$). $C_{21}H_{19}N$ requires 285.1517).

**4-[2-(4-Diphenylaminophenyl)propenyl]benzaldehyde** (**III**). Compound **III** was synthesized via a typical Heck reaction procedure as described above. Column chromatography eluted with ethyl acetate/hexane (1/10) afforded the yellow solid of **III** (0.46 g, 50% yield). Mp 154−155°C. Spectral data of **III**: $\delta_H$ (400 MHz, $CDCl_3$) 10.11 (s, 1H), 7.89 (d, $J$ = 7.9 Hz, 2H), 7.52 (d, $J$ = 7.9 Hz, 2H), 7.43 (d, $J$ = 7.3 Hz, 2H), 7.30−7.26 (m, 4H), 7.17−7.03 (m, 8H), 6.86 (s, 1H), 2.31 (s, 3H) ppm; $\delta_C$ (100 MHz,

$CDCl_3$) 191.67, 147.52, 144.95, 139.70, 136.86, 134.25, 132.39, 130.92, 129.64, 129.62, 126.76, 125.29, 124.52, 123.10, 113.81, 17.54. *m/z* (FAB) 389.1785 ($M^+$. $C_{28}H_{23}NO$ requires 389.1780).

**2-Cyano-3-{4-[2-(4-diphenylaminophenyl)propenyl]phenyl}acrylic acid** (**1Z**). Compound **1Z** was synthesized according to the standard Knoevenagel as described above. Orange solid of **1Z** was afforded in 65%. Mp 242−243°C. Spectral data of **1Z**: $\delta_H$ (400 MHz, $CDCl_3$) 8.27 (s, 1H), 8.01 (d, $J$ = 8.5 Hz, 2H), 7.47 (d, $J$ = 6.8 Hz, 2H), 7.40 (d, $J$ = 7.6 Hz, 2H), 7.28−7.24 (m, 4H), 7.12−7.02 (m, 8H), 6.81 (s, 1H), 2.31 (s, 3H) ppm; $\delta_C$ (100 MHz, $CDCl_3$) 167.01, 155.87, 147.73, 147.52, 144.63, 140.56, 136.78, 131.55, 129.97, 129.32, 129.03, 126.84, 125.18, 124.62, 123.18, 123.03, 115.61, 17.73. *m/z* (FAB) 456.1840 ($M^+$. $C_{31}H_{24}N_2O_2$ requires 456.1838).

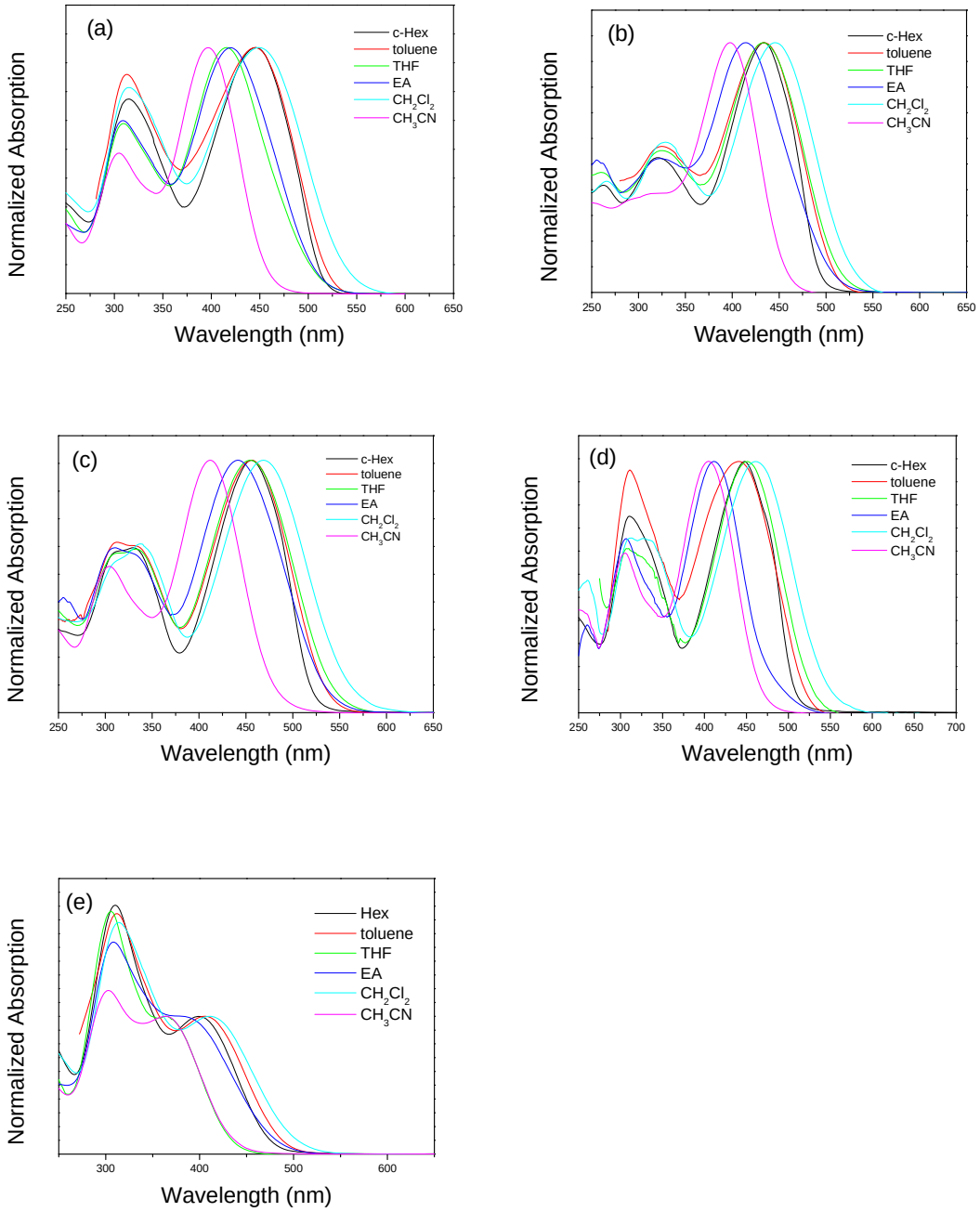



**Fig. S1** Absorption spectra of (a) **1P**, (b) **1N**, (c) **1M**, (d) **1T**, and (e) **1Z** in different solvents

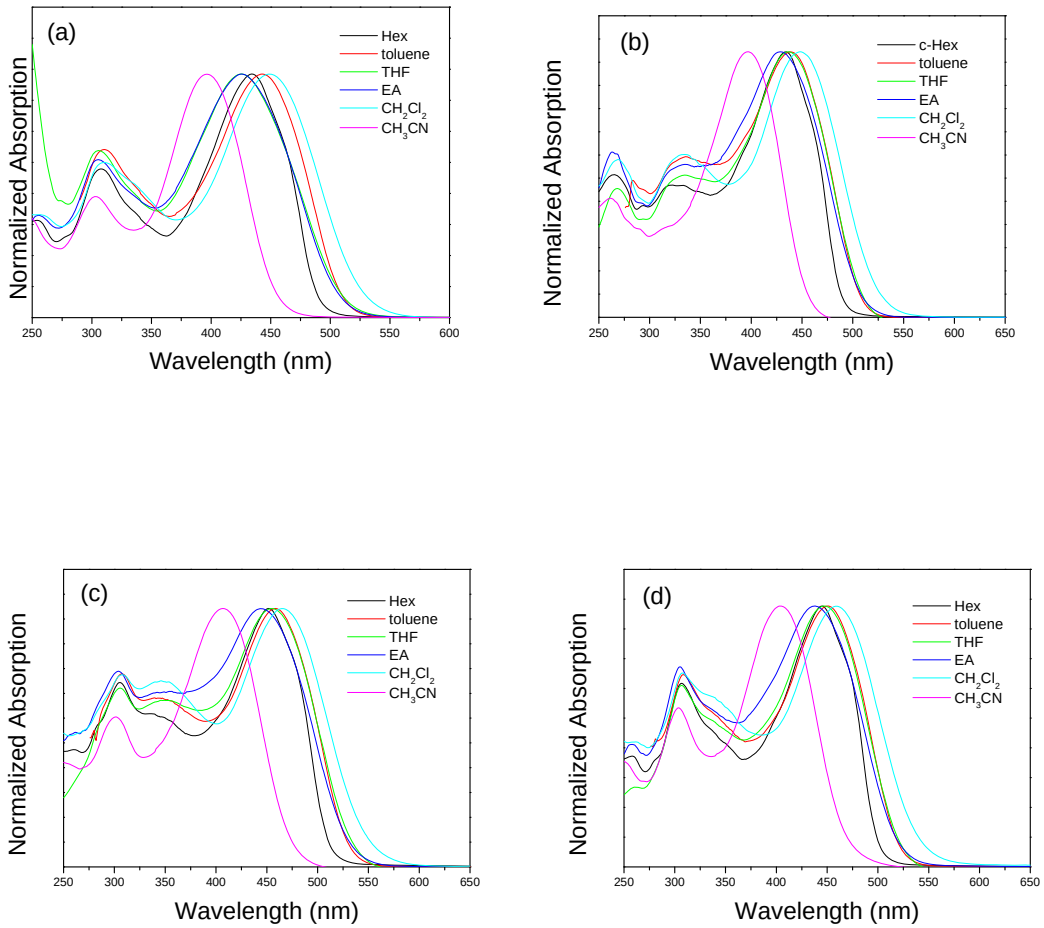



**Fig. S2** Absorption spectra of (a) **2P** (b) **2N** (c) **2M**, and (d) **2T** in different solvents

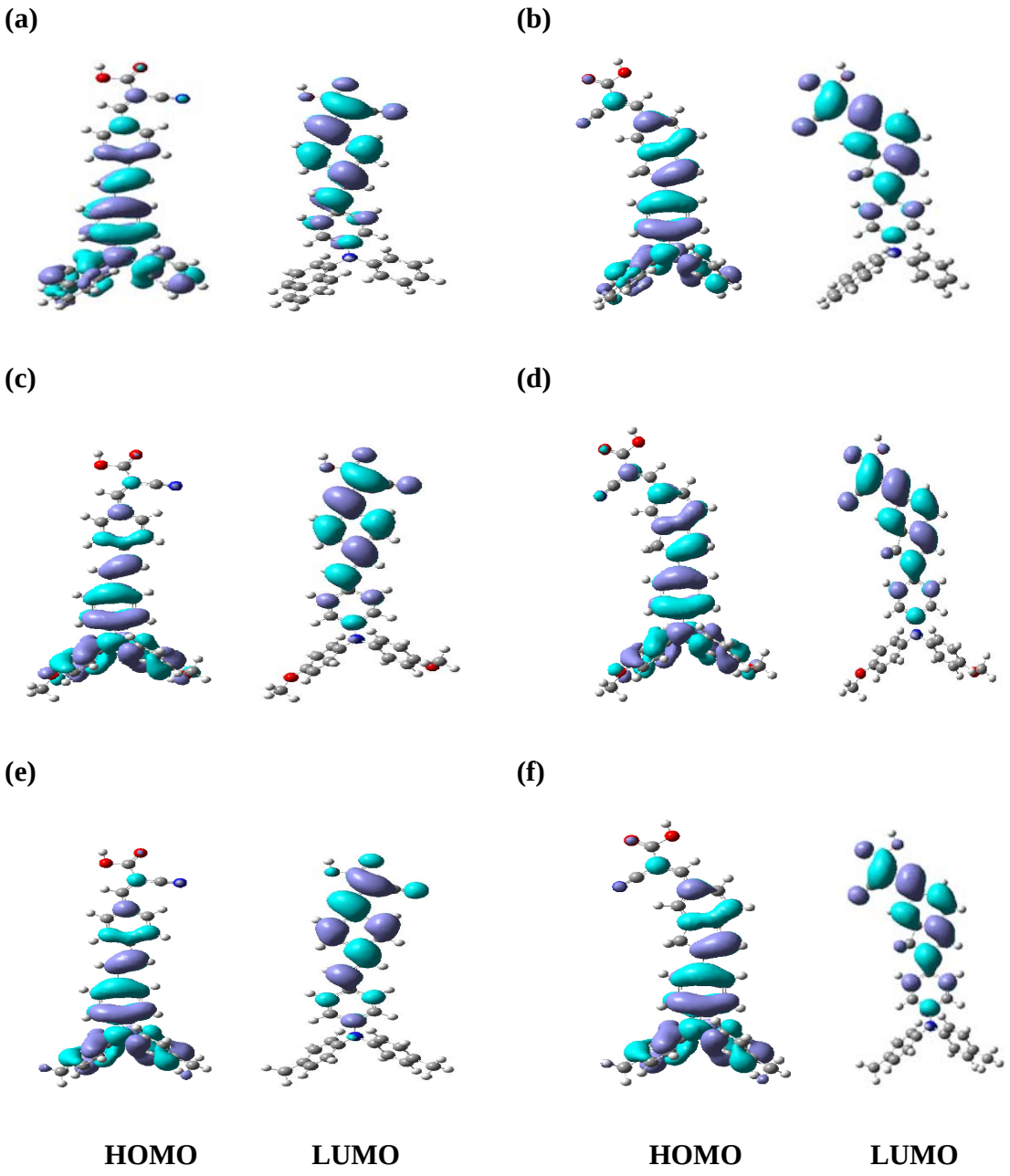



**Fig. S3** Frontier orbitals of (a) **1N**, (b) **2N**, (c) **1M**, (d) **2M**, (e) **1T**, and (f) **2T**, optimized with DFT at the B3LYP/6-31G(d,p) level

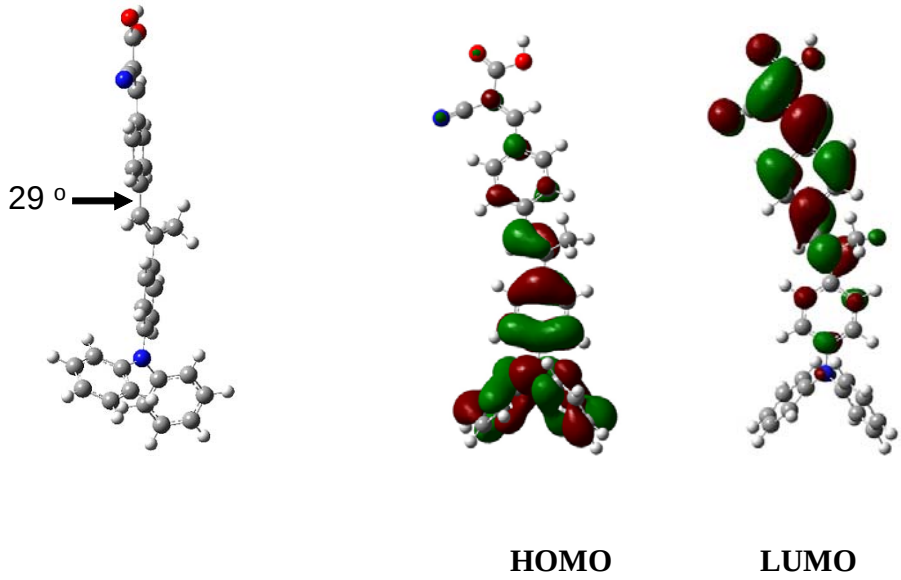



**Fig. S4** Optimized geometry of **1Z** and its electronic maps of Frontier orbitals

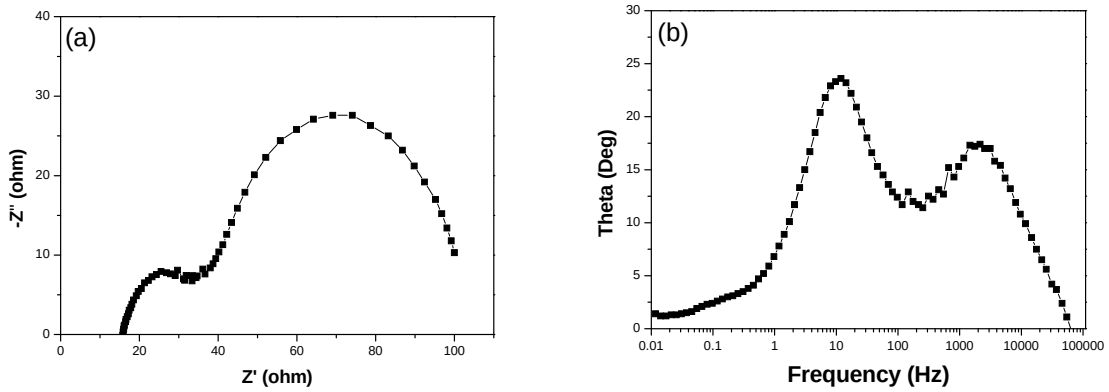



**Fig. S5** The electrochemical impedance spectra of (a) Nyquist plots, and (b) Bode phase plots for the DSSCs made with dye **1Z**.

**Table S1.** Calculated TDDFT excitation energies (*E*), oscillator strengths (*f*), MO compositions and characters, are compared with experimental absorptions for all of dyes.

| dye | n[a] | *E* (ev, nm) | *f* | composition | Character | exptl (ev, nm) |
|---|---|---|---|---|---|---|
| **1P** | 1 | 2.32 (534) | 0.95 | 98% HOMO→LUMO | CT | 2.86 (433) |
| | 2 | 3.31 (375) | 0.98 | 82% HOMO-1→LUMO | π-π* (1) | 4.00 (310) |
| | 5 | 4.01 (309) | 0.13 | 88% HOMO→LUMO+3 | π-π* (2) | |
| **2P** | 1 | 2.43 (510) | 0.88 | 98% HOMO→LUMO | CT | 2.82 (439) |
| | 2 | 3.33 (372) | 0.69 | 79% HOMO-1→LUMO | π-π* (1) | 4.06 (305) |
| | 6 | 4.00 (310) | 0.14 | 93% HOMO→LUMO+3 | π-π* (2) | |
| **1N** | 1 | 2.34 (530) | 1.00 | 99% HOMO→LUMO | CT | 2.86 (433) |
| | 2 | 3.18 (390) | 0.29 | 80% HOMO→LUMO+1 | π-π* (1) | 3.83 (324) |
| | 6 | 3.29 (377) | 0.33 | 77% HOMO-1→LUMO | π-π* (2) | |
| **2N** | 1 | 2.51 (494) | 1.06 | 96% HOMO→LUMO | CT | 2.84 (437) |
| | 2 | 3.22 (385) | 0.17 | 83% HOMO→LUMO+1 | π-π* (1) | 3.30 (335) |
| | 5 | 3.43 (361) | 0.59 | 71% HOMO-1→LUMO | π-π* (2) | |
| **1M** | 1 | 2.14 (579) | 0.87 | 99% HOMO→LUMO | CT | 2.73 (455) |
| | 2 | 3.16 (392) | 1.05 | 87% HOMO-1→LUMO | π-π* (1) | 3.99 (311) |
| **2M** | 1 | 2.30 (539) | 0.82 | 99% HOMO→LUMO | CT | 2.73 (455) |
| | 2 | 3.22 (385) | 0.76 | 86% HOMO-1→LUMO | π-π* (1) | 4.07 (305) |
| | 4 | 3.55 (349) | 0.13 | 80% HOMO→LUMO+1 | π-π* (2) | |
| **1T** | 1 | 2.25 (551) | 0.93 | 99% HOMO→LUMO | CT | 2.84 (437) |
| | 2 | 3.26 (380) | 1.03 | 75% HOMO-1→LUMO | π-π* (1) | 4.04 (307) |
| **2T** | 1 | 2.34 (530) | 0.82 | 99% HOMO→LUMO | CT | 2.77 (447) |
| | 2 | 3.27 (379) | 0.78 | 81% HOMO-1→LUMO | π-π* (1) | 4.04 (307) |
| **1Z** | 1 | 2.29 (542) | 0.53 | 99% HOMO→LUMO | CT | 3.40 (365) |
| | 2 | 3.33 (373) | 1.01 | 88% HOMO-1→LUMO | π-π* (1) | 4.07 (305) |
| | 3 | 3.67 (338) | 0.18 | 85% HOMO→LUMO+1 | π-π* (2) | |
| | 6 | 4.04 (307) | 0.15 | 78% HOMO→LUMO+3 | π-π* (3) | |
| | 10 | 4.24 (292) | 0.11 | 75% HOMO-4→LUMO | π-π* (4) | |

[a] Sequence of calculated transitions in order of energy.