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**Fig. S1** Cathodic cyclic voltammetry scans on WS-2 and WS-9 in CH$_2$Cl$_2$. 
**Fig. S2** Left: Simulated solar light irradiation on dye (WS-9) loaded TiO$_2$ film with an ultraviolet (UV) cut-off filter; Right: A photograph of the sample specimens of WS-2, WS-9 and LS-1 adsorbed on nanocrystalline TiO$_2$ films after 30 min of simulated solar light irradiation.

In case of LS-1, the relatively darker orange-colored edges compared to the central part are due to the light blocking effect of the black holder (as shown in Fig. S2). Hence the edges can be considered as the film color before light irradiation. However, there is no distinct difference between the edges and centres in WS-2 and WS-9 loaded films apparently due to the negligible absorbance variation (Fig. 12) before and after light irradiation for 30 min. Obviously, the photo-stability of benzothiadiazole contained WS-2 and WS-9 is higher than that of dye LS-1.

Electron injection from the excited dye to the semiconductor occurs within 100 fs, suggesting that the dye degradation is not likely to occur during this short lived excited state. When the electron is injected, the dye is oxidized to its cation state until regenerated by a redox mediator (the timescale of this regeneration: 100 ns – 1 ms). For obtaining long-term stability, the sensitizers ideally must remain stable in the cation state for a long time. Generally, in a 10-year operation cycle, sensitizers are regenerated more than $10^7$ times so that the cation state of such sensitizers must remain stable for at least 10 s (R. Katoh, A. Furube, S. Mori, M. Miyashita, K.
Sunahara, N. Koumura and K. Hara, *Energy Environ. Sci.*, 2009, 2, 542–546). The molecular design of stable sensitizers for DSSCs must be tailored to satisfy this criterion for the dyes’ cationic state. We can accelerate the dye aging process upon light irradiation on dye-loaded TiO$_2$ film without redox electrolyte. The dye regeneration process under this condition occurs in the milliseconds time range, thus taking $10^3$ – $10^3$ times longer than that in a complete solar cell (100 ns – 1 μs).

Dyes adsorbed on nanocrystalline TiO$_2$ films were irradiated by simulated solar light without redox mediators. Under these conditions, the lifetime of the dye cation state is limited by the recombination time between an injected electron and a parent cation, which occurs in the millisecond time range. We have monitored the change in absorbance of dye WS-2, WS-9 and LS-1 on TiO$_2$ films before and after 30 min simulated solar light irradiation. The variation of absorption spectra before and after strong light irradiation will give some information on dye photo-stability.
Fig. S3. $^1$H NMR and $^{13}$C NMR spectra of compound 5 recorded in CDCl$_3$. 
Fig. S4. HRMS (ESI) spectrum of compound 5
Fig. S5. $^1$H NMR and $^{13}$C NMR spectra of WS-9 recorded in DMSO-d$_6$
Fig. S6. HRMS (ESI) spectrum of WS-9