Electronic Supplementary Information (ESI)

Rigid triarylamine-based efficient DSSC sensitizers with high molar extinction coefficients

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Computational analysis

The charge distribution in the frontier molecular orbitals are depicted in Fig. S1. As shown in the graphs. For all the dyes, the HOMO level are dominated by contribution from the π orbital of the donor unit with a small contribution from the π orbital of the donor unit with a small contribution from the π orbital of the π -conjugated linker part while the LUMO is mostly at the cyanoacrylic acid (A) and the π -conjugated linker part . The distribution of the LUMO for all the dyes implies that after being illuminated by the light the excited electrons could be successively transferred to acceptor part and then injected into the conduction band of TiO₂. The differences between electron density distribution of their HOMO and LUMO orbitals strongly indicate the prominent charge-transfer character.



Figure S1 Computed frontier orbitals of dyes.

Optimization for photovoltaic device

In different solvents, dyes exhibit diversified interactions with the solvents, which could cause changes of the physical and chemical properties between the dyes and semiconductor surface. To optimize the dye baths for TiO_2 sensitization, **DIA3** in different solvents were employed to sensitize TiO_2 and the corresponding photovoltaic performance for DSSCS based on **DIA3** were tested and shown in table 1S. The table reveals that **DIA3**-based DSSCs fabricated with dye baths in CH₃CN

exhibit the best performance with the overall efficiency increased to 6.80%. The difference can be mainly due to the different photoelectric properties between the dyes and semiconductor surface which could be resulted from the different interactions with the solvents.

Table S1 Photovoltaic performance of DSSCs based on DIA3 employing different solvents for TiO_2 sensitization

Dye	Solvents ^{<i>a</i>}	$J_{\rm sc}/{\rm mAcm}^{-2}$	$V_{\rm oc}/{ m V}$	FF(%)	E _{ff} (%)
DIA3	THF	13.7	0.690	69.1	6.53
DIA3	CH ₃ CN	15.4	0.675	65.4	6.80
DIA3	CH_2Cl_2	13.0	0.675	70.4	6.17
DIA3	iPrOH	12.70	0.699	66.3	5.90
^{<i>a</i>} solvents for TiO ₂ sensitization					



Fig. S2. Cyclic voltammetry plots of **DIA1-5** and **TPS** attached to a nanocrystalline TiO_2 film deposited on conducting FTO glass

As shown in **Table 2**, we got the best optimized condition for **DIA2**, **DIA3**, **DIA4** and **TPS** devices. The devices were fabricated with 12 μ m (T/SP) and 5 μ m scattering films with dye baths in mixture solvents CHCl₃/EtOH (v/v 3:7) for 40h. It could be seen that under this optimized condition, the J_{sc} of these dyes based devices all increased correspondingly compared with that before optimized which employed THF as the solvent for dye loading. To investigate on the reasons why the J_{sc} increased, the dye adsorbed amount and absorption spectra of **DIA2**, **DIA3**, **DIA4** and **TPS** on TiO₂ surfaces fabricated with two conditions (before optimized and the best optimized conditions) were all measured. By desorbing the dyes into a basic solution of THF/0.1M NaOH aqueous(v/v 1:1), the dye absorbed amount was estimated by

measuring the absorption spectrum of the resultant solution. As shown in Table S2, the amount of dyes all correspondingly increased under the best optimized condition. Moreover, sensitized on the same TiO₂ films, the absorption spectrum of dyes were all redshifted by 10-20 nm when CHCl₃/EtOH instead of THF as the solvent for dye loading. The two reasons above may both contributed to enhanced J_{sc} . These results were in accordance with that Sun's previous work.^{45(c)}



Fig. S3 Absorption spectra when DIA2, DIA3, DIA4 and TPS were adsorbed on $7\mu m$ (T/SP) TiO₂ films employing THF or CHCl₃/EtOH (v/v 3:7) as dye baths respectively.

Table. S2 Adsorbed amount of **DIA2**, **DIA3**, **DIA4** and **TPS** under the following two conditions: (a) THF was used as the solvent for dye loading; the TiO₂ films are consisted of 7 μ m (T/SP); the dip time is 12h; (b) Mixture solvents CHCl₃/EtOH (v/v 3/7) was used as the solvents for dye baths; the TiO₂ films are consisted of 12 μ m (T/SP); the dip time is 40h.

Dye	Condition	Adsorbed amount (mol cm^{-2})
DIA2	(a)	6.5×10^{-8}
	(b)	9.5×10^{-8}
DIA3	(a)	6.0×10^{-8}
	(b)	1.0×10^{-7}
DIA4	(a)	7.8×10^{-8}
	(b)	1.4×10^{-7}
TPS	(a)	1.4×10^{-7}
	(b)	2.2×10 ⁻⁷

Synthesis:

(E)-methyl 2-(2-allylideneindolin-1-yl)benzoate(2)

A mixture of carbazole (33.3g, 0.199mol), methyl 2-iodobenzoate (57g, 0.218mol), 1,2-dichlorobenzene (150ml), copper powder(4.5g, 70.3mmol), CuI (3.4g, 17.8mmol) and K₂CO₃ (42g, 0.304mol) were heated to reflux under N₂ for 8h. After cooling down to r.t., the resulting mixture was diluted with CH₂Cl₂ (200ml) and filtered. The filtrate was firstly evaporated to remove CH₂Cl₂ and then distilled under reduced pressure to exclude 1, 2-dichlorobenzene. The residue was slurried with EtOH (100ml) under reflux for 2h. After cooling down, the resulting mixture was filtered. The precipitate was rinsed with EtOH. After dry up, the pure product(53.9g, 90%) was obtained. ¹HNMR(CDCl₃,400MHz), δ : 8.12 (t, *J*=8.1Hz, 3H), 7.75 (t, *J*=7.6Hz, 1H), 7.59 (t, *J*=7.7Hz, 2H), 7.37 (t, *J*=7.6Hz, 2H), 7.26 (t, *J*=6.1Hz, 2H), 7.12 (d, *J*=8.2Hz, 2H), 3.18 (s, 3H).

methyl 2-(3-bromo-9H-carbazol-9-yl)benzoate(3)

Compound 2 (55g, 0.183mol) was dissolved in 1LCCl₄. NBS(35.7g, 0.201mol) was added at room temperature. The mixture was refluxed for 4h and then cooling down. The resulting mixture was filtered and the filtercake was rinsed with CCl₄. The filtrate was washed with water for three times. The combined organic layer was dried (MgSO₄), filtered and distillation of the solvents gave brown-blackish crude product. Recrystallization from the pure product EtOH gave (55.5g, 80%). ¹HNMR(CDCl₃,400MHz), δ: 8.50 (d, J=1.9Hz, 1H), 8.30 (d, J=7.7, 1H), 8.09 (dd, J=7.8, 1.5Hz, 2H), 7.90 (d, J=7.6Hz, 1H), 7.73 (dd, J=21.3, 7.8Hz, 2H), 7.51 (dd, J=8.7, 1.8Hz, 1H), 7.41 (d, J=7.9Hz, 1H), 7.29 (t, J=7.5Hz, 1H), 7.04 (dd, J=14.2, 8.5Hz, 2H), 3.24 (s, 3H).

3-(2-(3-bromo-9H-carbazol-9-yl)phenyl)pentan-3-ol (4)

A dry three-necked flask equipped with an argon inlet, a dropping funnel and a thermometer was charged with magnesium turnings (4.3g, 180 mmol). A small amount of Et₂O was added to cover the magnesium and a solution of bromoethane (13.7ml, 190mmol) in Et₂O (150ml) was added dropwise, keeping the mixture reflux lightly. After the addition was completed, the mixture was heated to reflux for 2h and then a solution of **3** (20.0g, 52.6mmol) in 400ml toluene was added dropwise keeping the mixture reflux. After the completion of the addition, the mixture was continued to reflux for 1h and then allowed to cool down. A saturated solution of NH₄Cl in water was added to quench the reaction. The resulting mixture was extracted with CH₂Cl₂ (3×200ml). The organic extracts were dried over anhydrous Na₂SO₄ and concentrated. The crude product was chromatographed by petroleum:EtOAc=20:1 and the pure yellow product (8.6g, 40%) was obtained. ¹HNMR (CDCl₃,400MHz), δ : 8.23 (d, *J*=1.8Hz, 1H), 8.06 (d, *J*=7.7Hz, 1H), 7.78 (dd, *J*=8.1, 1.2Hz, 2H), 7.54 (m, 1H), 7.43 (dd, *J*=8.7, 1.9Hz, 1H), 7.38 (dd, *J*=10.6, 4.5Hz, 2H), 7.28 (m, 1H), 6.94 (d, *J*=7.9Hz, 2H), 6.83 (m, 1H), 5.30 (s, 1H), 1.75 (m, 3H), 1.58 (m, 2H), 0.77 (t, *J*=7.3Hz, 6H).

3-bromo-8,8-diethyl-8H-indolo[3,2,1-de]acridine(5)

Compound 4 (7.0g, 17.2mmol) was dissolved in 50ml CF₃COOH. The mixture was refluxed for 4h and then evaporated to remove the solvent of CF₃COOH. The

residue was chromatographed on silica. Light petroleum eluted gave the crude product. The pure product (3.3g, 50%) was obtained after recrystallization from hexane. ¹HNMR(CDCl₃,400MHz), δ : 8.24 (d, *J*=2.0Hz, 1H), 8.01 (dd, *J*=12.4, 4.9Hz, 2H), 7.83 (dd, *J*=5.4, 3.3Hz, 1H), 7.61 (dd, *J*=8.9,2.1Hz, 1H), 7.50 (dd, *J*=7.9, 1.4Hz, 1H), 7.36 (m, 3H), 7.18 (m, 1H), 2.09 (m, 4H), 0.49 (t, *J*=9.1, 5.6Hz, 6H).



Scheme S1 Synthetic route of intermediate 5.