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Abstract

Four triarylethylene (TAE) π -spacers have been applied for Y-shaped dyes in dye-sensitized solar cells (DSSCs) and their effects on photovoltaic performance have been fully investigated. All photosensitizers inherit the ability of three-dimensional TAE to weaken the π - π stacking in aggregation state, while their suppression on charge recombination in electrolytes presents a high reliance on the position and proportion of phenyl/thienyl groups embedded in TAE moieties. In iodine electrolytes, benzene-rich triphenylethene-based dye **JY65** achieves the best open-circuit voltage of 739 mV, sharply higher than that of 614 mV for trithienylethene (TTE)-based dye **JY63**. Moreover, dyes **JY64** and **D-1** with hetero-TAE-bridge tend to show better power convention efficiency (PCE) stemming from the higher short-circuit current density and moderate open-circuit voltage. Whereas in cobalt electrolytes, the TTE-bridged **JY63** attains a superior PCE of 5.84%, inversely surpassing the value of 5.28% based on **D-1** under the same condition. Therefore, tuning the TAE skeletons *via* altering the position and proportion of aryl groups in it would bring in a promising design for anti-stacking sensitizers to meet the varied demand in DSSCs.

Keywords: Dye-sensitized solar cells; Triarylethylene; Thiophene; Aggregation-induced emission

1. Introduction

As a new generation of photovoltaic technology, dye-sensitized solar cells (DSSCs) have attracted worldwide attention because of their advantages in low cost, easy fabrication and high efficiency [1-3]. Tremendous efforts have been engaged over the past two decades in exploring highly efficient sensitizers for DSSCs. Compared with Ru-complex and porphyrin-based dyes, metal-free organic sensitizers have recently drawn increasing interest owing to their additionally ecological-friendliness and flexibility in structural manufacture [4-8]. Typical metal-free organic dyes generally adopt donor- π spacer-acceptor (D- π -A) structure where intramolecular charge transfer (ICT) from donor to acceptor can be effectively realized through π -spacer after excitation. Structure of π -spacer has proven to be vital for the photovoltaic performance of dye-sensitized devices [9-13].

Thiophene-like π -spacers, such as oligothiophene, thieno[3,2-b]thiophene and dithieno[3,2-b:2',3'-d]pyrrole, have been widely applied in DSSCs owing to their good electron delocalization, which could broaden the visible absorption and thus increase the photocurrent [14-17]. However, the expanded planarity of thiophene-involved dyes often makes them inevitable to endure both excited-state self-quenching resulted from the aggravated π - π stacking in aggregation, and charge recombination between the injected electrons into semiconductor and electrolytes, which will generally harm the photovoltaic performance [18-20]. In order to overcome such drawbacks, many strategies have been taken into account, such as reducing the planarity of the main chain [21,22], introducing flexible alkyl chains to the lateral position of π -spacer [23], incorporating crown ether to cap the thiophene rings[24] or wrapping the skeleton with special frameworks like rotaxanes and spiros [25-27]. In short, establishing a steric framework would still be one of the promising methods to modify the

thiophene-based π -bridges.

To construct three-dimensional backbones, triphenylethene (TPE) and tetraphenylethene derivatives, well-known as aggregation-induced emission (AIE) molecules, have aroused our concern because of the specially twisted configuration which can diminish the intermolecular π - π stacking by forming intermolecular C-H… π interactions between phenyl rings in adjacent molecules at aggregation state, and thus inhibit the excited-state self-quenching of the luminogens [28, 29]. Actually, TPE units have been adopted as hindrance groups to the peripheral position of indoline donors and resulted in a positive impact on the photovoltaic performance of DSSCs [30-32]. A theoretical support has also been given by Voorhis and coworkers in 2017 [33], where the restriction of the intramolecular motions and twisted configuration of the TPE part at high dye coverage could be coincidentally similar to the aggregation mode of general AIE luminogens. In other words, the special aggregation conformation caused by TPE units would also help to overcome the unfavorable stacking mode of the dyes on semiconductor surface in DSSCs.

However, the investigation of TPE building block as the π -spacer is very limited. According to Han and coworkers' studies, the twisted dye **D-1** shows obviously better photovoltaic performance than its planar counterpart owing to the enhanced suppression on the unfavorable π - π stacking and intermolecular energy transfer in aggregation [34], preliminarily revealing the potential significance of TPE-like units for the design of anti-stacking π -linker in dyes. On the other hand, benzene-involved π -spacers also sensitizers, fluorenes, have been applied for e.g., benzothieno[3,2-b]benzothiophene or di(1-benzothieno)[3,2-b:2',3'-d]pyrrole and achieved much promoted photovoltaic performance [35-38]. Overall, it would be promising to put electron-rich thienyl unit and benzene-rich TPE entity together to

create effective π -spacers, where the propeller-like triarylethylene (TAE) backbone is anticipated to weaken the intermolecular π - π stacking, meanwhile, the proportion of phenyl and thienyl groups embedded within TAE is expected to tune its electronic communication and steric conformation.



Fig.1. Molecular structure of dyes JY63-65 and D-1.

In this paper, TAE structure was selected as π -bridge skeleton to build up Y-shaped dyes where triphenylamine (TPA) was chosen as electron donor while cyanoacrylic acid worked as electron acceptor (Fig.1). Thiophene was adopted to pursue a good electron delocalization and hence better light response. Phenyl ring was further introduced to replace partial (near-acceptor/near-donor replacement) or all the thienyl groups to form a hetero-TAE-bridge or benzene-rich TPE, no additional decoration of the main skeleton was employed so as to clearly understand the relationship between TAE-based π -spacer and device's photovoltaic performance.



Scheme 1. Synthetic routes for dyes JY63-65 and D-1.

2. Results and discussion

2.1. Synthesis

The synthetic routes of four TAE-based dyes are shown in Scheme 1. Briefly, the initial TPA-substituted aryl methanone **5** and **6** were attained through Suzuki reaction of 4-(diphenylamino)phenylboronic acid with corresponding brominated aryl methanone. Afterwards, the precursors **7**, **8**, **9** and **10** prepared from resultant methanone with aryl phosphonate through Wittig-Horner reaction, were reacted with the 5-formylthiophen-2-yl-boronic acid *via* Suzuki reaction to afford the relevant aldehydes **11**, **12**, **13** and **14**, respectively. Finally, the target dyes were obtained through Knoevenagel condensations with cyanoacetic acid. More details of the synthesis are provided in Supporting Information.



Fig. 2. UV-Vis absorption spectra of dyes JY63-65 and D-1 (a) in THF solutions and (b) on TiO₂ films.

2.2. Photophysical properties

The UV-Vis absorption spectra of the dye JY63-65 in THF solution and on TiO₂ films are shown in Fig. 2 and the detailed spectroscopic data are summarized in Table 1. The high energy absorption bands attributed to the π - π * transition lie around 350 nm similarly, while low energy absorption bands belongs to the ICT transition from TPA donor to cyanoacrylic acid acceptor vary a lot from 430 to 490 nm, indicating such modification on TAE-type π -spacer would considerably dominate the ICT process. Specifically, the TTE-based dye **JY63** presents the longest absorption λ_{max} while the TPE-based dye JY65 exhibits the shortest (488 nm for JY63 and 429 nm for JY65). On the other hand, it is notable that dye D-1 where phenyl rings were introduced at the near-donor position displays clearly red-shifted (23 nm) absorption in comparison to dye **JY64** where phenyl ring was incorporated at the near-acceptor position of TAE, demonstrating that the former substitution mode is more beneficial for ICT process (475 nm for D-1 and 452 nm for JY64). As a result, the ICT effect in this class can be easily tuned by altering both the proportion and the position of phenyl/thienyl rings in TAE moiety. After adsorbed onto TiO₂ films, the ICT bands of all these dyes present almost the same order as those in THF solution with about 50 nm bathochromical shifted onsets, which will favor the light harvesting ability of the sensitizers in DSSCs.

Table 1

Dye	$\lambda_{ m max}/ m nm$	$\varepsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\rm TiO2}/\rm nm$	E _{ox} /V (vs. NHE)	E_{0-0}/eV	<mark>E_{red}/V</mark> (vs. NHE)
JY63	488	3.53	461	<mark>1.11</mark>	1.91	<mark>-0.80</mark>
JY64	452	3.55	447	<mark>1.17</mark>	2.08	<mark>-0.91</mark>
D-1	475	3.43	453	<mark>1.12</mark>	2.05	<mark>-0.93</mark>
JY65	429	5.12	405	<mark>1.15</mark>	2.25	<mark>-1.10</mark>

Optical and electrochemical properties of dyes JY63-65 and D-1.^a

 $^{a} \lambda_{\text{max}}$ was attained from the absorption spectra in THF solution; E_{ox} was determined on dye-sensitized TiO₂ films and calibrated with ferrocene (0.63 V vs. NHE) in THF containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte; E_{0-0} was estimated from the onsets of UV-Vis spectra in THF solution; $E_{\text{red}} = E_{\text{ox}} - E_{0-0}$.

Considering the fluorescence of dyes could be well reduced by the strong electron-withdrawing cyanoacrylic acid groups owing to the solvent polarity effect and ICT/TICT effect according to the previous studies [39-41], the aldehyde precursors keeping similar main skeletons as relevant target dyes were selected instead to estimate their intrinsic capabilities of suppressing the intermolecular energy transfer in aggregation state. The fluorescence properties of aldehydes **11**, **12**, **13** and **14** were characterized in the diluted solutions of H₂O/THF with different H₂O fractions (Fig S1 and S2). After the water fraction surpassing 50%, an obvious AIE phenomenon could be observed in all these TAE-based derivatives, confirming that theses TAE-based dyes could still maintain the beneficial anti π - π stacking ability of the well-known twisted TPE building blocks.



Fig. 3. HOMOs, LUMOs and energy gaps of dyes JY63–65 and D-1.

2.3. Electrochemical properties

Electrochemical properties of these four dyes-sensitized TiO₂ films were carried out by cyclic voltammetry (CV) calibrated with ferrocene (0.63 V vs. NHE) in THF solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte (Fig. S3). The schematic energy levels for **JY63-65** are listed in Fig. 3. The first oxidation potentials (E_{OX}) relating to the highest occupied molecular orbital (HOMO) levels of the dyes exhibit values around 1.14 V, rising from the uniform electron donating ability of TPA donors. JY64 and JY65 present a somewhat lower HOMO compared with JY63 and D1, respectively, indicating that replacing the phenyl ring at the end of TAE which is close to acceptor by thiophene might be advantageous for electron conjugation hence decrease the E_{OX} . With the band gaps E_{0-} ₀ calculated from the onsets of UV-Vis spectra, the lowest unoccupied molecular orbital (LUMO) levels were evaluated using $E_{\rm red} = E_{0-0} - E_{\rm ox}$ and present strong correlation to the π -spacers. The TTE-involved **JY63** gives the lowest LUMO while benzene-rich JY65 exhibits the largest upshift. Dyes JY64 and D-1 featuring hetero-TAE-bridge show medium LUMO levels and are very close to each other (-0.91 and -0.93 V for JY64 and D-1, respectively). Notably, both HOMOs and LUMOs of the four dyes can guarantee an efficient regeneration of oxidized dye by iodine redox couples (0.4 V vs. NHE) and sufficient photo-excited electron injection into TiO₂ conduction band (-0.5 V vs. NHE).

2.4. Theoretical calculations

To gain insight into the molecular structure and electron distribution, the geometries of dyes **JY63-65** were optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level (Table 2 and Fig. 4). For the near-donor aryl ring π_1 and near-acceptor aryl ring π_3 which locate at the different sides of olefin center in TAE bridge, the dihedral angle α (between π_1 and the olefin plane) increases in the order of **JY63**<**JY64**<**D-1**<**JY65** while the dihedral angle γ (between the olefin plane and π_3) rises in the sequence of **JY63**<**D-1**<**JY64**<**JY65**, indicating that replacing the thiophene with phenyl ring can induce a slightly enlarged distortion. For the near-donor ring π_2 , all the dihedral angles β (between π_2 and the olefin plane) exhibit a considerable large distortion beyond 50°, which would play a crucial role in building up the three-dimensional configuration. With respect to charge distribution, the HOMOs in these four dyes mainly delocalize at the TPA donor parts and partial TAE-based π -bridges, while the LUMOs diffuse on the cyanoacrylic acid acceptors and also a portion of TAE moieties. Specifically, dye JY63 displays more overlap between the HOMOs and LUMOs, aroused from the higher co-planarity of TTE π -spacer. By contrast, the larger distortion of TPE π -linker provides dye **JY65** a remarkable charge separation. When coming to dyes JY64 and D-1 with hetero-TAE-bridge, a medium scale between the charge overlap and separation can be observed. Clearly, such type of charge distribution of four Y-shape dyes fits the need for charge transfer from the excited sensitizers to the conduction band of TiO₂.

Table 2

Dihedral angles in the geometry optimized dyes JY63-65 and D-1.^a







Fig. 4. The frontier molecular orbitals of JY63-65 and D-1 optimized at the B3LYP/6-31G* level.

2.5.Photovoltaic performance

The photovoltaic performances of DSSCs based on dyes JY63-65 were

measured under standard AM 1.5G illumination (100 mW \cdot cm⁻²). The photocurrent density-voltage (J-V) curves of the dyes in iodine electrolytes are plotted in Fig. 5a, and detailed photovoltaic data are collected in Table 3. Surprisingly, the TTE-based dve JY63 which has the broadest absorption range does not give the highest short-circuit current density (J_{SC}). In detail, the J_{SC} of 8.75 mA cm⁻² for dye **JY63** is only slightly higher than that of 8.13 mA cm⁻² for TPE-based dye **JY65** featuring the narrowest light absorption, but dramatically lower than dyes JY64 and D-1 containing hetero-TAE-bridge, implying that the photocurrent would not be dominated only by the light harvesting region under this condition. Specifically, dye D-1 where the phenyl rings are incorporated at the donor side displays superior J_{SC} of 10.57 mA cm⁻² than that of dye JY64 where the replacement occurs at the near-acceptor position, agreeing with its relatively bathochromic absorption band. With respect to open-circuit voltage (V_{OC}), the TTE-contained dye **JY63** endures the sharply lowest $V_{\rm OC}$ of 614 mV, dooming its power conversion efficiency (PCE) to only 3.67%. By contrast, benzene-rich TPE-based dye JY65 attains the highest V_{OC} of 739 mV, leading the PCE up to 4.01%. With the good balance of V_{OC} and J_{SC} , two hetero-TAE-embedded dyes show superior PCE than TTE-based dye JY63 and TPE-based dye JY65, and dye D-1 gets the best PCE of 5.20%. In total, all the benzene-blended TAE π -bridges work better than the TTE-based π -spacer on the photovoltaic performance of DSSCs using Γ/I_3^- redox shuttle. The order of V_{OC} values stands in accordance with the number of phenyl rings in TAE units, but the J_{SC} shows less reliance on the proportion of thienyl groups in π -spacers.



Fig. 5. The J-V curves (a) and IPCE curves (b) of DSSCs based on **JY63-65** and **D-1** in iodine electrolytes, the J-V curves (c) and the IPCE curves (d) of DSSCs based on **JY63** and **D-1** in iodine and cobalt electrolytes.

The incident photon-to-current conversion efficiency (IPCE) spectra of DSSCs using Γ/I_3^- redox shuttle are presented in Fig. 5b. All these four TAE-based dyes cover the IPCE response region in agreement with the tendency of their UV-Vis absorption spectra. The bathochromic shift in IPCE response region can well explain the promotion of J_{SC} in the sequence of **JY65**<**JY64**<**D-1** where the IPCE values approximately approach to 70%. Different from that, due to the significantly decreased IPCE less than 56%, TTE-based dye **JY63** which has the broadest absorption and most bathochromic IPCE response can only give an inferior J_{SC} .

Table 3

Dye	Electrolytes	$V_{\rm OC}[\rm mV]$	$J_{\rm SC}[{\rm mA~cm}^{-2}]$	FF[%]	PCE[%]
JY63		614±5	8.75±0.20	68.3±0.8	3.67±0.03
JY64	Iodine	685±5	9.32±0.14	68.6±1.2	4.38±0.08
D-1		721±5	10.57±0.18	68.3±1.2	5.20±0.05
JY65		739±5	8.13±0.13	66.8±0.6	4.01±0.02
JY63	Cobalt	736±10	11.41±0.06	69.5±1.2	5.84±0.03
D-1		817±10	9.74±0.21	66.4±0.6	5.28±0.02

Photovoltaic performance of JY63-65 and D-1.^a

^{*a*} An average value was obtained from three devices.



Fig. 6. Electrochemical impedance spectra (a) Nyquist plots and (b) Bode phase plots for the DSSCs based on **JY63-65** and **D-1** in iodine electrolytes measured at -0.60 V bias in the dark, (c) Nyquist plots and (d) Bode phase plots for the DSSCs based on **JY63** and **D-1** in cobalt electrolytes measured at -0.72 V bias in the dark.

2.6. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) analysis in iodine electrolytes was determined in the dark condition under the bias of -0.60 V within a frequency

range of 0.1 Hz-100 kHz. The EIS Nyquist and Bode phase plots are displayed in Fig. 6, and the detailed data are summarized in Table 4. The larger semicircle in Nyquist plots represents the charge-transfer resistance at the TiO₂/dye/electrolyte interface $(R_{\rm CT})$. A smaller $R_{\rm CT}$ means a faster charge recombination and thus induces a lower $V_{\rm OC}$. The fitted $R_{\rm CT}$ witnesses an distinguishable increase in the order of **JY63** \leq **JY64** <**D-1**<**JY65**, which is in accordance with the trend of V_{OC}. Although all these TAE-based dyes can maintain the three-dimensional structures, the capability of preventing the charge recombination between Γ/I_3^- redox couples and the injected electron into the TiO₂ presents high reliance on the position and proportion of the phenyl groups blended in TAE moiety. TTE-based dye **JY63** gives a relative low V_{OC} because of the insufficient hindrance to the electrolyte penetration through the dye layer, which might be caused by the general sulfur-iodine interactions throughout the whole chain. However, replacing only one of the thiophenes in TTE unit with phenyl ring near the acceptor in dye **JY64** can clearly promote the V_{OC} , indicating that a slightly increased distortion induced by the phenyl group with larger size can effectively resist the charge back transfer from the semiconductor surface to the electrolytes. On the other hand, the **D-1** where the phenyl groups incorporated closely to the donor position can further stem the electrolytes caused by the much strengthened shielding effect. Finally, TPE-based dye JY65 can apparently minimize the charge recombination, owing to the largest volume constructed by benzene-rich TPE unit. Totally speaking, all the benzene-blended TAEs present better charge barriers than TTE counterpart in iodine electrolytes. The model of the TAE units blocking the I/I_3 redox shuttle near TiO₂ surface is inferred in Fig. S4. Besides the interfacial $R_{\rm CT}$, electron lifetime relates also to the $V_{\rm OC}$ value, and a longer electron lifetime stands for a lower dark current and thus a higher photovoltage. The electron

lifetime (τ) can be calculated from the peak frequency at lower frequency region in the Bode phase plots by adopting the equation $\tau = 1/2\pi f$. The lifetime also meets an elevation trend of **JY63 JY64 D-1 JY65**, which can further explain the variation of the V_{OC} in DSSCs.

Table 4

Parameters obtained by fitting the impedance spectra of the DSSCs based on JY63-65 and D-1.

Dye	Electrolytes	Bias/V	$R_{\rm CT}/\Omega$	<i>f</i> /Hz	τ/ms
JY63	Iodine	<mark>-0.60</mark>	64.2	22.459	7.1
JY64			325.2	7.931	20.1
D-1			413.1	7.080	22.5
JY65			753.5	5.482	29.0
JY63	Cobalt	-0.72	<mark>88.9</mark>	<mark>71.72</mark>	<mark>2.22</mark>
D-1			<mark>308.1</mark>	<mark>25.76</mark>	<mark>6.18</mark>

As investigated above, the presence of phenyl groups around the ethylene core can effectively hinder the charge recombination, and an appropriate proportion of thienyl groups embedded in TAE π -spacer can improve the photovoltaic performance owing to the expansion of light harvesting region. Nevertheless, the absence of phenyl group in TAE π -bridge leads to the unexpected loss on photocurrent in iodine electrolytes to some extent. To deeply understand the charge barrier built by TAE-spacers, the Co(phen)₃^{2+/3+} redox shuttle (0.61 V vs. NHE) was chosen for further experiments. Dye **JY63** which holds the intriguingly broadest absorption but presents inferior J_{SC} , and **D-1** which covers the second broadest light harvesting but exhibits the highest J_{SC} in iodine electrolytes, were selected as the subjects. The J-Vcurves of the DSSCs are shown in Fig. 5c and photovoltaic performances are summarized in Table 3. In contrast to the results in Γ/I_3^- redox couple, a superior J_{SC} of 11.41 mA cm⁻² has been obtained for TTE-based dye **JY63** against **D-1** of 9.74 mA cm⁻². This variation of the J_{SC} is further explained by the IPCE spectra displayed in Fig. 5d, the maximum value of dye **JY63** witnesses an approximate 10% elevation ranging from 350 to 700 nm in comparison to that in iodine electrolytes, while dye **D-1** meets a slight decrease in whole absorption region. The above results could attribute to the larger volume of Co(phen)₃^{2+/3+} mediator and less sulfur-electrolyte interaction, demonstrating that the charge barrier established by the propeller-like TTE unit is more suitable for blocking the penetration of cobalt complex than iodine mediator [42,43]. Benefitted from the obviously enhanced J_{SC} , TTE-based **JY63** achieves higher PCE of 5.84% than that of 5.28% for **D-1**. The EIS Nyquist and Bode phase plots are presented in Fig. 6, and the detailed data are listed in Table 4. The order of R_{CT} and τ matching with the sequence of corresponding V_{OC} (**JY63**<**D-1**) indicates that the benzene-involved TAE π -spacer could still act as an ideal building blocks to suppress the charge recombination in cobalt electrolytes.

3. Conclusion

In summary, four different TAEs were applied as π -bridge to construct photosensitizer for DSSCs, and the π -bridge effect on the photovoltaic performance has been fully investigated. In addition to the uniformly three-dimensional configuration of TAE, both the proportion and position of phenyl/thienyl groups in TAE moieties have been observed to pose a significant impact on the devices' photovoltaic performance. In iodine electrolytes, the order of V_{OC} agrees well with the increasing proportion of phenyl rings in TAE-bridge. Suffering from the undesirable charge recombination, TTE-based dye **JY63** gives a poor V_{OC} of 614 mV and mediocre J_{SC} of 8.75 mA cm⁻² although it shows the broadest light harvesting. On the contrary, benefitted from the largest volume of benzene-rich TPE-bridge working as

an ideal barrier to minimize the back charge transfer, dye **JY65** achieved the highest V_{OC} of 739 mV. A hetero-TAE-bridge has proven to be more effective to maintain the balance between the suppression on charge recombination and the enhancement on photocurrent, leaving **JY64** and **D-1** with better PCEs. Whereas in cobalt electrolytes, **JY63** with less-twisted TTE also can effectively retard the charge recombination and thus make promoted photocurrent into reality. As a result, **JY63** achieved higher PCE of 5.84% than that of 5.28% for **D-1** with hetero-TAE. In total, the three-dimensional TAE-bridge provides a facile tool to tune the photovoltaic properties of dyes and a balance design should be carefully taken in account to meet the individual requirements in device.

4. Experimental

4.1. Materials and instruments

All the synthesis procedures were carried out under the argon atmosphere. Solvents for reaction and other sections were re-distilled before use. The ¹H NMR and ¹³C NMR spectra were characterized on Bruker 400 MHz spectrometer adopting TMS as the internal standard. HR-MS data were collected on a Varian 7.0T FTMS. UV–Vis spectra were scanned on a Varian Cary 300 Conc UV-Visible spectrophotometer. Cyclic voltammetry, J-V curves and EIS experiments were detected on a Zennium electrochemical workstation (Zahner Corporation).

4.2. Fabrication and characterization of DSSCs

The photoanodes were manufactured by screen printing the TiO_2 paste (Heptachroma Corporation) onto FTO conductive glasses (Nippon Sheet Glass, Japan, 15 Ω /sq) with 20 nm nanoparticles for transparent layer and then 200 nm nanoparticles for scattering layer, respectively. Specially, the transparent layers for photoanode in iodine electrolytes were printed for three times while for photoanode in

cobalt electrolytes were printed for one time. The active area of photoanode is 0.196 cm². After that, the photoanodes were heated by a ramped temperature profile (gradually heated to 450 °C and kept for 15 min, then heated to 500 °C and kept for 30 min). After cooling down to room temperature, the obtained photoanode were immersed in a TiCl₄ aqueous solution (40 mM) at 70 °C for 30 min and sintered again at 500 °C for 40 min. At last, the resulting photoanodes were immersed into 0.3 mM dye solution in THF for 12 h under dark. The Pt electrodes were prepared by spin-coating the 0.02 M H₂PtCl₆ in *iso*-propanol onto the FTO conductive glasses and then heated at 400 °C for 30 min. The iodine electrolytes consisted of 0.6 M 1-propyl-3-methylimidazolium iodide (PMII), 0.1 M LiI, 0.03 M I₂, 0.1 M GuSCN and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile/valeronitrile (v/v = 85/15). The cobalt electrolytes were composed of 0.25 M [Co(II)(phen)₃](PF₆)₂, 0.05 M [Co(III)(phen)₃](PF₆)₃, 0.5 M TBP and 0.1 M LiTFSI in acetonitrile. The DSSCs were illuminated under a solar simulator (CHF-XM-500W, Trusttech Co. Ltd.) under 100 mW cm⁻² irradiation calibrated by a standard silicon solar cell (91150V, Newport Corporation). The IPCE was detected by a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA).

4.3. Theoretical calculation methods

All the theoretical calculations were accomplished by the Gaussian 09 program package. The ground-state geometries were fully optimized at the B3LYP/6-31G* level in vacuum. The electron density distributions on HOMOs and LUMOs were also calculated at the same level.

Notes

The authors declare no competing financial interest.

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Highlights:

1. Effect of TAE-spacer on photovoltaic performance has been systematically explored.

2. All the TAE-based dyes show capability to weaken the π - π stacking in aggregation.

3. In iodine electrolytes, benzene-blended TAE-based dyes exhibit better performance.

4. In cobalt electrolytes, thiophene-rich JY63 inversely achieves superior PCE.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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