## Benzotriazole-Bridged Sensitizers Containing a Furan Moiety for Dye-Sensitized Solar Cells with High Open-Circuit Voltage Performance

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Abstract: Two new benzotriazolebridged sensitizers are designed and synthesized (BTA-I and BTA-II) containing a furan moiety for dye-sensitized solar cells (DSSCs). Two corresponding dyes (BTA-III and BTA-IV) with a thiophene spacer were also synthesized for comparison. All of these dyes performed as sensitizers for DSSCs, and the photovoltaic performance data of these benzotriazolebridged dyes showed a high open-circuit voltage ( $V_{oc}$ : 804–834 mV). Among the four dyes, DSSCs based on **BTA-II**, with a furan moiety and branched alkyl chain, showed the highest  $V_{oc}$ (834 mV), a photocurrent density ( $J_{sc}$ )

**Keywords:** dyes/pigments • electrochemistry • electron transfer • heterocycles • solar cells

Introduction

Dye-sensitized solar cells (DSSCs) based on organometallic and metal-free organic sensitizers have attracted considerable attentions since the seminal report by Grätzel and coworkers.<sup>[1]</sup> On the one hand, DSSCs based on ruthenium(II) polypyridyl organometallic complex photosensitizers, such as N3, N719, and the black dye, have achieved record lightto-power conversion efficiencies exceeding 12% under AM 1.5 simulated sunlight within the past 20 years.<sup>[2]</sup> On the other hand, in view of the high cost associated with the production and purification of the ruthenium dyes, metal-free organic dyes are considered to be an alternative due to their high molar absorption coefficient, simple synthesis, low cost, and easy molecular tailoring. A large number of studies have been devoted to the molecular engineering of organic chromophores to direct their interaction with the wideband-gap semiconductors and to improve the light-harvesting of the DSSCs.<sup>[3-5]</sup>

For most of the pure organic sensitizers, the donor-( $\pi$  conjugation)-acceptor (D- $\pi$ -A) system is the basic feature, because it facilitates effective photoinduced intramolecular charge transfer. Compared with the ruthenium(II) polypyridyl organometallic complexes, organic sensitizers have some drawbacks for DSSCs. Firstly, organic sensitizers have poor light response in the NIR (near-infrared) region.

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of 12.64 mA cm<sup>-2</sup>, and a fill factor (FF) of 0.64, corresponding to an overall conversion efficiency ( $\eta$ ) of 6.72%. Most importantly, long-term stability of the **BTA-I–IV**-based DSSCs with ionicliquid electrolytes under 1000 h lightsoaking was demonstrated, and **BTA-II** exhibited better photovoltaic performance of up to 5.06% power conversion efficiency.

Research activities have been focused on creating dyes with broad light absorption, but no satisfying results have been achieved to date.<sup>[6]</sup> Second, the open-circuit voltage ( $V_{oc}$ ) for DSSCs based on organic dyes is still lower than that for ruthenium dves.<sup>[7]</sup> Benzotriazole, as a very cheap and commercially available chemical material, has been used in electroplating the surface of purified silver, copper, and zinc. In recent years, benzotriazole-based  $\pi$ -conjugated polymers have been widely used in photovoltaic cells because of their chemical and environmental stability as well as their electronic tenability.<sup>[8]</sup> Recently, a fluorine-substituted benzotriazole conjugated polymer with a medium band gap yielded 7% efficiency in polymer-fullerene solar cells, which were designed to possess a high hole mobility.<sup>[9]</sup> Also, Wang and co-workers incorporated a benzotriazole moiety attached to a thiophene into an organic sensitizer for DSSCs and yielded a power conversion efficiency of 8.02% with an open-circuit voltage of 780 mV.<sup>[10]</sup> Particularly, benzotriazole is a close analogue of benzothiadiazole; the lone pair on the nitrogen atom is more basic than the lone pairs on sulfur and is more easily donated into the triazole ring.<sup>[9]</sup> This difference causes dyes employing benzotriazole as the  $\pi$ -conjugation unit to be more electron-rich, which leads to a higher LUMO energy level.<sup>[8]</sup> Moreover, pyrimidine, and benzimidazole have been tested as additives in the electrolyte for the sake of increasing  $V_{\rm oc}$ , so the alkyl-containing benzotriazole group can be expected to improve  $V_{oc}$ .<sup>[10]</sup> Therefore, benzotriazole-based  $\pi$ -conjugated organic sensitizers have stronger electron injection ability than their benzothiadiazole-based counterparts, and a high open circuit voltage may be obtained with them.

Most of the metal-free organic sensitizers with high efficiency and good stability reported to date rely on thiophene or thiophene-based heterocycles as the  $\pi$  spacer. This trend

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could be explained by the fact that holes in such dyes were located on the thiophene moieties. And furan, as oxygen analogue of thiophene, which has a higher oxidation potential, would be more efficient for the hole location and reinforce the stability of the dye sensitizers.<sup>[11]</sup> However, furan has received much less attention than the thiophene unit. Recently, furan units have also been incorporated into some conjugated polymers and oligomers as an alternative to thiophenes for photovoltaics and have revealed that the optical and charge-carrier mobility can be comparable to that of thiophenes.<sup>[12]</sup> There have been reports showing that the incorporation of a furan moiety can somewhat improve polymer solubility and gain high molecular weight.<sup>[13]</sup> Moreover, furan can provide more effective conjugation and lower the energy of the charge-transfer transition because of its smaller resonance energy (furan 16 kcalmol<sup>-1</sup>, thiophene 29 kcal mol<sup>-1</sup>) in the spacer.<sup>[14]</sup> Organic sensitizers containing a furan unit applied in DSSCs have also been reported and showed relatively high efficiency.<sup>[15]</sup>

To decrease dye aggregation and enhance tolerance towards water in the electrolyte, a hydrophobic alkyl chain (octyl or 2-ethylhexyl) was introduced to modify the N-H bond of the benzotriazole group; the 2ethylhexyl group has more steric hindrance than octyl and might lead to a better open-circuit voltage. On the basis of the above consideration, herein we have designed and synthesized two new benzotriazole-bridged sensitizers (BTA-I and BTA-II) containing a furan moiety for DSSCs. Two corresponding dyes (BTA-III and BTA-IV) with

thiophene spacers were also synthesized for the purpose of comparison. Consequently, we expect to introduce benzo-triazole and furan as  $\pi$  spacer to organic dyes for improving their photovoltaic performance and long-term stability. Molecular structures of **BTA-I–IV** are presented in Scheme 1.

## **Results and Discussion**

### Synthesis

The synthetic route to the four dyes **BTA-I–IV** containing the benzotriazole moiety is depicted in Scheme 2. The octyl or 2-ethylhexyl chain attached to the benzotriazole group can improve the solubility, form a tightly packed insulating monolayer blocking the  $I_3^-$  or cations approaching the TiO<sub>2</sub>, and enhance the open-circuit voltage. The syntheses of **BTA-I–IV** started from compound 1 (in the synthesis of **BTA-I,III**) or 2 (**BTA-II,IV**). Asymmetrical Suzuki coupling reaction of compound 1 (or 2) with 4-(diphenylamino)phe-



Scheme 1. Molecular structures of the dyes BTA-I-IV.





nylboronic acid gave a strong yellowish green compound **3** (or **4**). Then Suzuki coupling of **3** (or **4**) with 5-formylthiophen-2-boronic acid (in the synthesis of **BTA-III**, **IV**) or 5formylfuran-2-boronic acid (**BTA-I**, **II**), respectively, afforded monoaldehyde-substituted precursors **5–8**. Finally, compounds **5–8** were treated with cyanoacetic acid under typical Knoevenagel condensation conditions to obtain the target dyes **BTA-I–IV**. All the intermediates and target dyes were characterized by standard spectroscopic methods. Clearly, the synthetic process is easy, because all the intermediates and target compounds are stable and the synthesis method is very common.

#### **Optical and Electrochemical Properties**

UV/Vis absorption spectra of the four dyes in a diluted solution of  $CH_2Cl_2$  are shown in Figure 1 a and their absorption data are listed in Table 1. In the UV/Vis spectra, the dyes exhibit two major absorption bands, appearing at 300 and

450–460 nm. All of the dyes have a relatively broad and strong absorption, with the maximum absorption at 450, 449, 458, and 454 nm, respectively. The absorption band around 300 nm was ascribed to the localized aromatic  $\pi$ – $\pi$ \* transition of triphenylamine, and the maximum absorption at around 450–460 nm can be attributed to the intramolecular charge transfer (ICT) between the triphenylamine donor and the cyanoacetic acid acceptor.<sup>[16]</sup> As this series of sensitizers contains the same electron donor and acceptor and similar conjugated bridges, the absorption peaks for **BTA-I**–



Figure 1. a) UV/Vis absorption spectra of **BTA-I–IV** in  $CH_2Cl_2$  and b) UV/Vis absorption spectra of **BTA-I–IV** adsorbed on 4  $\mu$ m TiO<sub>2</sub> transparent films.

Table 1. Optical and electrochemical properties of the dyes BTA-I-IV.

Dye	$\begin{array}{l} \lambda_{max}^{[a]}  [nm] \\ (\epsilon \times 10^4 \ M^{-1} \ cm^{-1}) \end{array}$	$\lambda_{\max}^{[b]}$ [nm]	HOMO <sup>[c]</sup> [V] (vs. NHE)	$E_{0-0}^{[d]}$ [eV]	LUMO <sup>[e]</sup> [V] (vs. NHE)
BTA-I BTA-II BTA-III BTZ-IV	458 (2.14) 450 (3.33) 454 (3.31) 449(3.96)	432 435 426 425	1.03 0.94 0.91 0.92	2.16 2.11 2.13 2.15	-1.13 -1.17 -1.22 -1.23

[a] Absorption maximum in CH<sub>2</sub>Cl<sub>2</sub>  $(1.5 \times 10^{-5} \text{ M})$ . [b] Absorption maximum on 4 µm TiO<sub>2</sub> transparent films. [c] HOMO energy levels were measured in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as electrolyte (working electrode: Pt; reference electrode: SCE; calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an external reference. Counter electrode: Pt. [d]  $E_{0-0}$  was estimated from the onset of UV/Vis absorption of the dyes. [e] LUMO energy levels were estimated by subtracting  $E_{0-0}$  from the HOMO energy level. NHE = normal hydrogen electrode.

IV are almost the same. It is well known that sunlight at the wavelength of 475 nm has a maximum radiation energy, so **BTA-I–IV** should possess excellent light-harvesting ability in DSSCs. The corresponding maximum molar extinction coefficients of the four dyes are  $2.14 \times 10^4$ ,  $3.33 \times 10^4$ ,  $3.31 \times 10^4$ , and  $3.96 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ , respectively. Notably, **BTA-IV** has a higher molar extinction coefficient than the other three dyes, which may be due to the introduction of the thiophene moiety and the branched alkyl chain can effectively improve its light-harvesting ability.<sup>[17]</sup>

The absorption spectra of **BTA-I–IV** on thin transparent TiO<sub>2</sub> films (4  $\mu$ m thick) after 12 h adsorption in CH<sub>2</sub>Cl<sub>2</sub> solution are shown in Figure 1b. The maximum absorption peaks for **BTA-I–IV** on the TiO<sub>2</sub> film are located at 432, 435, 426, and 425 nm, respectively. The absorption peaks are blue-shifted by 18, 14, 32, and 29 nm, respectively, from the solution spectra. The blue shift of the absorption spectra of **BTA-I–IV** on TiO<sub>2</sub> could be ascribed to deprotonation and formation of H-aggregates (extended head-to-tail stacking).<sup>[18]</sup> It is worth noting that the absorption maximum of **BTA-II** is blue-shifted less than that of **BTA-I**, suggesting that **BTA-II** with branched alkyl may have a lower tendency to form H-aggregates than **BTA-II** and **BTA-IV**.

In addition to the resemble absorption spectra, the four dyes display very similar electrochemical oxidation characteristics as well. Cyclic voltammetry (CV) was employed to measure the electrochemical properties and evaluate the possibility of electron transfer from the excited dye to the conduction band of TiO<sub>2</sub>. The examined highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO) levels are collected in Table 1. Cyclic voltammetry was performed in acetonitrile/ tetrahydrofuran solution, using 0.1M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, Pt as working electrode and counter electrode, saturated, calomel electrode (SCE) as reference electrode. The HOMO levels of BTA-I-IV are 1.03, 0.94, 0.91, and 0.92 V (vs. NHE), respectively. Their HOMO levels show only minor differences as all four dyes have the same electron donor. The band-gap energies  $(E_{0-0})$  of the four dyes are 2.16, 2.11, 2.13, and 2.15 eV for BTA-I-IV, respectively, which were estimated from the absorption onset of the UV/Vis absorption spectra of the dyes. The estimated excited-state potentials for BTA-I-IV calculated from  $E_{\text{HOMO}} - E_{0-0}$ , are -1.13, -1.17, -1.22, and -1.23 V, respectively. These dyes can be reversibly oxidized at proper oxidation potentials, which are more positive than ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) and  $I^{-}/I_{3}^{-}$  redox couples, suggesting sufficient driving force for dye regeneration. The LUMO levels of these dyes are sufficiently more negative than the conduction band edge energy level  $(E_{CB})$ of the TiO<sub>2</sub> semiconductor (-0.5 V vs. NHE),<sup>[5c]</sup> indicating that the electron injection process from the excited dye molecule to the TiO<sub>2</sub> conduction band is more efficient.

### **Molecular Orbital Calculations**

To gain an insight into the molecular structure and electron distribution, density functional theory (DFT) calculations were performed at the B3LYP/6-31G\* level of theory with Gaussian03. <sup>[19]</sup> The electron distributions of the HOMOs and LUMOs of the dyes are shown in Figure 2. In the ground state for all the dyes, electrons are homogeneously



Figure 2. Calculated HOMOs and LUMOs of BTA-I-IV.

distributed in the donor (triphenylamine), and upon illumination with light, electrons move from the HOMO to the LUMO by intramolecular charge transfer and are finally located in anchoring group (cyanoacetic acid) through the  $\pi$  bridge. The results indicated that the high electron density from the donor unit moved to the cyanoacrylic acid moiety in the HOMO–LUMO excitation induced by light, thus allowing an efficient photoinduced electron transfer from the dye to the TiO<sub>2</sub> electrode.

# Effect of Different Dye Baths on the Performance of DSSCs

In different solvents, dyes exhibit diversified interactions with the solvents,<sup>[20]</sup> which could cause changes of the physical and chemical properties between the dyes and semiconductor surface. Therefore, the suitable solvent for semiconductor sensitization is important to obtain good overall conversion efficiency ( $\eta$ ). To optimize the dye baths of these dyes for TiO<sub>2</sub> sensitization, **BTA-I–IV** in different solvents (toluene, CH<sub>2</sub>Cl<sub>2</sub>, THF and DMF) with coadsorbent (chenodeoxycholic acid, CDCA) were employed to sensitize TiO<sub>2</sub>; the photovoltaic performance of **BTA-I–IV**-based DSSCs were measured and are shown in Table 2 and Figure 3 a. The data reveal large differences in the performance of **BTA-I– IV**-based DSSCs fabricated in various dye-bath solutions. When CH<sub>2</sub>Cl<sub>2</sub> solutions of **BTA-I–IV** were introduced to sensitize the semiconductor electrode, the DSSCs obtained optimized  $\eta$  values of 6.85, 6.72, 7.02, and 7.05%, respectively. This variation is mainly due to differences in solubility and in the incident photon-to-current conversion efficiency (IPCE) spectra. For example, the IPCE of **BTA-II**-based DSSCs (Figure 3b) is higher in CH<sub>2</sub>Cl<sub>2</sub> than in the other three solutions.

Table 2. Current–voltage characteristics obtained from **BTA-I–IV**-sensitized solar cells in various solvents with CDCA.

Dye	Solvent	$J_{\rm sc}[{ m mAcm^{-2}}]$	$V_{\rm oc}[{ m mV}]$	FF	η [%]
BTA-I	DMF	8.96	714	0.67	4.29
	THF	10.20	773	0.65	5.12
	$CH_2Cl_2$	12.58	824	0.66	6.85
	toluene	10.93	784	0.69	5.90
BTA-II	DMF	10.11	722	0.62	4.50
	THF	11.04	793	0.62	5.44
	$CH_2Cl_2$	12.64	834	0.64	6.72
	toluene	12.33	808	0.62	6.15
BTA-III	DMF	9.38	708	0.67	4.43
	THF	11.27	754	0.64	5.47
	$CH_2Cl_2$	13.26	804	0.66	7.02
	toluene	11.47	741	0.67	5.65
BTA-IV	DMF	7.84	685	0.70	3.73
	THF	11.75	732	0.62	5.36
	$CH_2Cl_2$	13.36	806	0.66	7.05
	toluene	12.24	778	0.67	6.39



Figure 3. a) Overall conversion efficiency spectra for DSSCs based on **BTA-I-IV** in different solvents and b) IPCE spectra of DSSCs based on **BTA-II** sensitized in different solvents with CDCA.

#### Photovoltaic Performance of DSSCs

To reduce aggregation, nonchromophoric adsorbates, such as deoxycholic acid (DCA) or chenodeoxycholic acid (CDCA), have been co-deposited onto semiconductor surfaces. In this work, CDCA was used as the co-adsorbent for **BTA-I–IV** to effectively improve the photoelectric conversion efficiency. Figure 4 shows the photovoltaic performance



Figure 4. a) IPCE action spectra for DSSCs based on dyes **BTA-I-IV** coadsorbed with CDCA and b) current-voltage characteristics of DSSCs based on **BTA-I-IV** co-adsorbed with CDCA.

of DSSCs based on BTA-I-IV co-adsorbed with CDCA 0.1 м 1,2-dimethyl-3-propylimidazolium using iodide (DMPII), 0.1 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M 4-tertbutylpyridine (TBP) as redox electrolyte. Figure 4a shows the action spectra of incident photon-to-current conversion efficiency (IPCE) as a function of incident wavelength for DSSCs. In good agreement with absorption spectra, the IPCE action spectra for DSSCs based on BTA-I-IV keep a high plateau in the visible region up to 600 nm. Taking the absorption and reflection of the conductive glass and dye aggregation into account, all the four dyes have a maximum of IPCE of about 80%. The strong absorption band of the four dyes is located at 350-600 nm, where incident photon-to-current conversion exhibits great efficiency. These features explain why the dyes can achieve high photoelectric conversion efficiency. We have also measured the photovoltaic performance of BTA-I-IV-based DSSCs without co-adsorbents for comparison, and the dyes exhibited inferior conversion efficiency of 5.77, 6.17, 6.26, and 6.35%, respectively. Therefore co-adsorbents are still needed to improve the photovoltaic performance, although long or branched alkyl chains have been introduced to these sensitizers.

Figure 4b shows the current-voltage characteristics of DSSCs fabricated with these benzotriazole dyes BTA-I-IV as sensitizers under standard global AM 1.5 solar light. The detailed parameters of short-circuit current density  $(J_{sc})$ , open-circuit voltage  $(V_{oc})$ , fill factor (FF), and photovoltaic conversion efficiency  $(\eta)$  are summarized in Table 2. In general, the short-circuit current  $J_{sc}$  is related to the molar extinction coefficient of the dye, in which a higher molar extinction coefficient correlates with good light-harvesting ability and a higher short-circuit current density. Among the four dyes, BTA-III- and BTA-IV-based DSSCs (with the thiophene group) show higher short-circuit currents than BTA-I- and BTA-II-based ones (with furan) due to the better molar extinction coefficient and IPCE value. On the other hand, BTA-II- and BTA-IV-sensitized devices with branched alkyl chains exhibit larger open-circuit voltages than those sensitized with the corresponding dyes with linear alkyl chains, BTA-I and BTA-III. The addition of different alkyl chains to the π-conjugated linkers suppressed electron recombination in DSSCs by blocking the approach of  $I_3^-$  to the TiO<sub>2</sub> surface, and the branched alkyl chain could suppress dye aggregation and retard charge recombination in DSSCs more effectively than the linear alkyl chain.[21]

Significantly, the **BTA-I**, **II**-sensitized devices incorporating a furan moiety exhibit a higher open-circuit voltage than **BTA-III**, **IV**-sensitized devices with a thiophene unit, and the significant improvement of  $V_{oc}$  from 804 mV (**BTA-III**) to 834 mV (**BTA-II**) should be attributed to the reduction of charge recombination. To understand the role of furanbridged dyes in improving  $V_{oc}$ , their effect on dark current was studied (Figure 4b). It is obvious that the dark current onset potential of the furan-bridged dyes shifted to a larger value from that of the thiophene-bridged dyes. This darkcurrent change indicates that the introduction of furan chains into bridged rings can inhibit charge recombination between injected electrons and I<sup>3-</sup> ions in the electrolyte.

## **Electrochemical Impedance Spectroscopy**

Charge recombination and electron injection efficiency are correlated with the open circuit voltage  $(V_{oc})$ .<sup>[22]</sup> To further demonstrate that the introduction of conjugated furan can effectively improve the open-circuit voltage, electrochemical impedance spectroscopy (EIS) was employed to study the electron recombination in DSSCs based on these **BTA-I–IV** dyes under -0.70 V bias applied voltage in the dark. The Nyquist plot, Bode plot, and equivalent circuit are shown in Figure 5. Some important parameters can be obtained by fitting the EIS spectra with an electrochemical model.<sup>[23]</sup>  $R_{s}$ ,  $R_{rec}$ , and  $R_{CE}$  represent series resistance and charge-transfer resistances at the dye/TiO<sub>3</sub>/electrolyte interface and counter



Figure 5. a) Nyquist plot, b) Bode plot, and c) equivalent circuit of DSSCs based on **BTA-I-IV** dyes. The lines of (a) and (b) show theoretical fits using the equivalent circuits (c).

electrode (CE), respectively. The series resistance  $(R_s)$  and electrolyte reduction resistance  $(R_{CE})$  corresponding to the first semicircle show almost the same value in the four dyesbased DSSCs, because the devices use the same electrode material and same electrolyte, and  $R_{\rm rec}$  corresponds to the middle semicircle (Figure 5a). From the EIS measurements, the electron lifetime  $(\tau_e)$  expressing the electron recombination between the electrolyte and TiO<sub>2</sub> may be extracted from the angular frequency ( $\omega_{rec}$ ) at the mid-frequency peak in the Bode phase plots using the relation  $\tau_e = 1/\omega_{rec}$  (Figure 5b). The reaction resistance of the DSSCs consisting of TiO<sub>2</sub>/dye/electrolyte and Pt/electrolyte interface based on BTA-I-IV were analyzed by software (ZSimpWin) using an equivalent circuit.<sup>[24]</sup> As shown in Table 3, the  $R_{\rm rec}$  of the BTA-I–IV dyes are 850.7, 971.3, 384.9, and 635.7  $\,\Omega\,cm^{-1}$  , respectively. Estimated from  $\tau_{\rm e} = 1/\omega_{\rm rec}$ , the electron lifetime of the BTA-I-IV dyes are 87, 93, 59, and 63 ms, respectively. BTA-II has the longest electron lifetime among the four dyes, indicating that the electron recombination rate between the TiO<sub>2</sub> film and the electrolyte is indeed suppressed by introduction of a furan group and branched alkyl chain

Table 3. Parameters obtained by fitting the impedance spectra of the DSSCs with sensitizers **BTA-I–IV**, using the equivalent circuit (Figure 4c).

Dye	$R_{\rm S} \left[\Omega{ m cm}^{-2} ight]$	$R_{ m rec} \left[\Omega   m cm^{-2} ight]$	$R_{ m CE} \left[\Omega{ m cm}^{-2} ight]$	$\tau_e [{ m ms}]$
BTA-I	39.3	850.7	29.7	87
BTA-II	35.5	971.3	13.8	93
BTA-III	40.6	384.9	13.1	59
BTA-IV	31.7	635.7	19.2	63

[a] The reaction resistance of the DSSCs consisting of  $TiO_2/dye/electro$ lyte and Pt/electrolyte interface based on**BTA-I–IV**were analyzed bysoftware (ZSimpWin) using an equivalent circuit.

on the benzotriazole unit. This result is in agreement with the observed shift in the  $V_{oc}$  value under standard global AM 1.5 illumination.

## Photovoltaic Performance of Solvent-Free Ionic Liquid Electrolyte DSSCs

Long-term stability is also a vital parameter for sustained cell operation for future applications. However, the use of organic solvents is undesirable as they are likely to be volatile, so we substituted the liquid electrolyte with a solventfree ionic liquid electrolyte.<sup>[25]</sup> BTA-I-IV were evaluated as sensitizers for the ionic liquid electrolyte DSSCs using 1butyl-3-methylimidazolium, 1-methyl-3-trimethylsilylimidazolium, iodine, benzimidazole, and guanidine thiocyanate  $(BMII:MSII:I_2:BI:GNCS = 20:20:1.67:0.67:3.33)$  as redox electrolyte.<sup>[26]</sup> Figure 6a shows the IPCE spectra of DSSCs based on BTA-I-IV with a solvent-free ionic liquid electrolyte. We can see that the four dyes can efficiently convert visible light to photocurrent in the region from 350 to 650 nm, in which the maximum IPCE is 71.7% for BTA-I at 520 nm, 75.0% for BTA-II at 520 nm, 69.2% for BTA-III at 480 nm, and 69.8% for BTA-IV at 540 nm. In the spectral range 450-550 nm, the conversion efficiency of BTA-I, II is higher than that of BTA-III, IV, but the IPCE value of BTA-III, IV is higher than that for BTA-I, II in the range of 550-650 nm. As a result, the IPCE performance of the ionic liquid electrolyte DSSCs based on BTA-I-IV is similar. Photovoltaic performances of BTA-I-IV-sensitized TiO<sub>2</sub> film electrodes with a solvent-free ionic liquid electrolyte under standard global AM 1.5 solar condition are listed in Table 4, and the corresponding photocurrent-voltage curves are shown in Figure 6b. Obviously, BTA-I, II show higher opencircuit voltages than BTA-III, IV, which can be tentatively attributed to the prevention of dye aggregation on the semiconductor when a furan moiety is incorporated into the organic sensitizer. Also, the conversion efficiency of the solvent-free ionic liquid DSSC based on BTA-II is the highest, while the opposite result is found for liquid electrolyte. This difference could be explained by the highest IPCE value and open-circuit voltage of BTA-II. Long-term stability measurements of devices with solvent-free ionic liquid electrolyte were tested, and Figure 7 shows the photovoltaic performance recorded over a period of 1000 h. The overall efficiency for BTA-I-IV-based DSSCs remained at 95% of the



Figure 6. a) The IPCE spectra of DSSCs based on **BTA-I–IV** with a solvent-free ionic liquid electrolyte and b) current–voltage characteristics of DSSCs based on **BTA-I–IV** with solvent-free ionic liquid electrolyte.

Table 4. Photovoltaic performance of DSSCs based on **BTA-I-IV** with solvent-free ionic liquid electrolyte.

Dye	$J_{\rm sc}[{ m mAcm^{-2}}]$	$V_{\rm oc}[{ m mV}]$	FF	η [%]
BTA-I	10.24	708	0.64	4.66
BTA-II	11.23	709	0.64	5.06
BTA-III	11.88	672	0.62	4.97
BTA-IV	11.73	673	0.62	4.92

initial value after 1000 h of visible-light illumination. On continuous 1000 h of light soaking, the  $J_{sc}$  and  $V_{oc}$  for **BTA-I–IV**-sensitized solar cells showed fluctuation during the initial 600 h and then remained almost constant for 1000 h. This result demonstrates that **BTA-I–IV** sensitizers are efficient in solvent-free ionic liquid electrolyte DSSCs, and they have comparable long-term stability. The results demonstrate that benzotriazole-bridged sensitizers containing a furan moiety are promising candidates for improving the performance and long-term stability of DSSCs.

## Conclusions

In summary, two new benzotriazole-bridged sensitizers (**BTA-I** and **BTA-II**) containing a furan moiety for DSSCs have been designed and synthesized; the corresponding dyes (**BTA-III** and **BTA-IV**) with thiophene spacer were also



Figure 7. Variations of photovoltaic parameters  $(J_{sc}, V_{oc}, FF, and \eta)$  with aging time for the DSSC devices based on **BTA-I–IV** and ionic liquid electrolyte under visible-light soaking.

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synthesized for comparison. Significantly, the  $V_{oc}$  values of **BTA-I**, **II** with a furan moiety are higher than those of **BTA-III**, **IV** with a thiophene group. **BTA-II**-based DSSCs with a furan moiety and a branched alkyl chain exhibit the highest  $V_{oc}$  of 834 mV. Most importantly, the long-term stability of the **BTA-I–IV**-based DSSCs with ionic liquid electrolytes under 1000 h illumination was demonstrated, and **BTA-II** exhibited better conversion efficiency of 5.06%. As an alternative to thiophene, the furan moiety can be advantageously incorporated into the dye sensitizer as a  $\pi$  spacer and improve the cell efficiency and stability. It should be noted that the benzotriazole unit could become a simple and efficient building block for the future sensitizer molecular design in DSSCs due to favorable optical and electronic properties.

### **Experimental Section**

#### Instruments and Characterization

NMR spectra were obtained on a Brücker AM 400 spectrometer. The absorption spectra of the dyes in solution and adsorbed on  $TiO_2$  films were measured with a Varian Cary 500 spectrophotometer. Mass spectra were recorded on an ESI mass spectrometer. The cyclic voltammograms of dyes were obtained with a Versastat II electrochemical workstation (Princeton applied research) using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution.

The photocurrent action spectra were measured with a Model SR830 DSP Lock-In Amplifier, a Model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp with power supply, and a 7ISW301 Spectrometer. The irradiation source for the photocurrent density–voltage (J–V) measurement is an AM 1.5 solar simulator (91160, Newport Co., USA). The photocurrent action spectra were measured with an IPCE test system consisting of a model SR830 DSP Lock-In Amplifier and a model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp and power supply, and a 7ISW301 spectrometer. The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany). The frequency range is 0.1 Hz–100 kHz. The applied voltage bias is -0.70 V. The magnitude of the alternative signal is 10 mV.

#### Fabrication of Dye-Sensitized Solar Cells

A screen-printed TiO<sub>2</sub> particle was used as photoelectrode. The thickness of TiO<sub>2</sub> film (4  $\mu$ m paste, T/SP) was controlled by the mesh size (0.5 cm× 0.5 cm) of screen printing and then dried for 6 min at 125 °C. This procedure was repeated twice (to give a thickness of ca. 8 µm), and the resulting surface was finally coated by a layer (ca. 5 µm) of TiO<sub>2</sub> paste (Tinanoxide 300) as the scattering layer. The three-layer TiO2 electrodes were gradually heated under an air flow at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min. Before immersion in the dye solution, these films were soaked in 0.05 M aqueous  $TiCl_{4}$  overnight in a closed chamber and washed with water and ethanol, which can significantly increase the short-circuit photocurrent. Then sintering was carried out at 450 °C for 30 min. After the film was cooled to room temperature, it was immersed in a  $3 \times 10^{-4}$  M dye bath in CH<sub>2</sub>Cl<sub>2</sub> (or other solvent) and maintained in the dark for 24 h at room temperature. If chenodeoxycholic acid (CDCA) was used as a co-adsorbent, the  $\mathrm{TiO}_{2}$ film was soaked in a 20 mm CDCA bath in ethanol for 8 h and then in a  $3 \times 10^{-4}$  M dye bath in CH<sub>2</sub>Cl<sub>2</sub> (or other solvent) for 16 h at room temperature. The electrode was then rinsed with CH2Cl2 and dried. To prepare the counter electrode, the Pt catalyst was deposited on the cleaned fluorine-doped tin oxide (FTO) glass by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution (0.02 M in 2-propanol solution) with heat treatment at 400°C for 20 min. A hole (0.8 mm diameter) was drilled on the counter electrode by a drill press. The perforated sheet was cleaned by ultrasound in an ethanol bath for 15 min. The dye-covered TiO<sub>2</sub> electrode and Pt counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt gasket of 25 µm thickness made of the ionomer Surlyn 1702 (Dupont). The electrolyte consisting of 0.1 M 1,2-dimethyl-3-propylimida-zolium iodide (DMPII), 0.1 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M 4-tertbutylpyridine (TBP) in a mixture of acetonitrile and methoxypropionitrile (volume ratio 7:3) was introduced into the cell via vacuum backfilling from the hole in the back of the counter electrode. Finally, the hole was sealed by a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar. The cell active area was tested with a mask, the size of which was about 1.5 mm lager than the side length of the TiO<sub>2</sub> electrode.

#### Materials and Reagents

Optically transparent FTO conducting glass (fluorine doped SnO<sub>2</sub>, transmission >90% in the visible, sheet resistance 15  $\Omega$  per square) was obtained from the Geao Science and Educational Co. Ltd. of China and cleaned by a standard procedure. Methoxypropionitrile (MPN) was purchased from Aldrich. Tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>), 4-tert-butylpyridine (4-TBP), and lithium iodide were bought from Fluka and iodine (99.999% purity) was purchased from Alfa Aesar. Triphenylamine-4-boronic acid was bought from Sun Chemical Technology (Shanghai) Co, Ltd. Tetrahydrofuran (THF) was pre-dried over 4 Å molecular sieves and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. Dichloromethane was distilled under normal pressure and dried over calcium hydroxide. All other chemicals were purchased from Aldrich and used as received without further purification. The starting materials 4,7-dibromo-2-octyl-2Hbenzo[d]-[1,2,3]-triazole (1) and 4,7-dibromo-2-(2-ethylhexyl)-2Hbenzo[d][1,2,3]-triazole (2) were prepared according to published procedures.[8

#### Synthesis

4-(7-bromo-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)-N,N-diphenylaniline (3): Compound 1 (390 mg, 1.00 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (100 mg, 0.087 mmol), and  $K_2 CO_3 \ (1.00 \ g, \ 7.25 \ mmol)$  in THF (30 mL) and  $H_2 O \ (5 \ mL)$  were heated to 55 °C under a nitrogen atmosphere for 30 min. A solution of 4-(diphenylamino)phenylboronic acid (288 mg, 1.00 mmol) in THF (10 mL) was added slowly, and the mixture was heated at reflux for further 12 h. After cooling to room temperature, the mixture was extracted with  $CH_2Cl_2$  (3×50 mL). The organic portion was combined and dried over MgSO<sub>4</sub>, and volatile components were removed by rotary evaporation. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether=1:3, v/v) to give a green solid (230 mg). Yield: 41.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): D = 7.91 (d, J = 8.8 Hz, 1H), 7.60 (d, J=2.0 Hz, 1 H), 7.29 (d, J=7.7 Hz, 4 H), 7.21–7.15 (m, 8 H), 7.06 (dd, J= 4.4, 2.8 Hz, 2H), 4.77 (dd, J=10.3, 4.5 Hz, 2H), 2.19–2.08 (m, 2H), 1.27 (d, J=11.9 Hz, 10H), 0.87 ppm (t, J=6.9 Hz, 3H). HRMS (ESI, m/z): [M]<sup>+</sup> calcd for C<sub>32</sub>H<sub>33</sub>BrN<sub>4</sub> 552.1889; found 552.1876.

4-(7-bromo-2-(2-ethylhexyl)-2*H*-benzo[d][1,2,3]triazol-4-yl)-*N*,*N*-diphenylaniline (**4**): The synthesis method resembles that of compound **3**, but using **2** as starting material, and the product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether=1:3, v/v) to give a green solid (450 mg). Yield: 48.5 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): D = 7.94 (d, J=8.7 Hz, 1H), 7.87–7.82 (m, 1H), 7.55–7.51 (m, 1H), 7.32 (d, J=7.7 Hz, 1H), 7.22–7.17 (m, 5H), 7.11 (dd, J=5.1, 3.9 Hz, 6H), 7.02– 6.96 (m, 2H), 4.61 (d, J=7.2 Hz, 2H), 2.27–2.17 (m, 1H), 1.30–1.21 (m, 8H), 0.88–0.79 ppm (m, 6H). HRMS (ESI, m/z): [*M*]<sup>+</sup> calcd for C<sub>32</sub>H<sub>33</sub>BrN<sub>4</sub> 552.1889; found 552.1828.

5-(7-(4-(diphenylamino)phenyl)-2-octyl-2*H*-benzo[d][1,2,3]triazol-4-yl)furan-2-carbaldehyde (**5**): Compound **3** (120 mg, 0.22 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (100 mg, 0.087 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.00 g, 7.25 mmol) in THF (30 mL) and H<sub>2</sub>O (5 mL) were heated to 55 °C under a nitrogen atmosphere for 30 min. A solution of 2-formylfuran-5-boronic acid (31 mg, 0.22 mmol) in THF (5 mL) was added slowly, and the mixture was heated at reflux for further 12 h. After cooling to room temperature, the mixture was extract-

ed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The organic portion was combined and dried over MgSO<sub>4</sub>, and volatile components were removed by rotary evaporation. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether=2:1, v/v) to give a yellow solid (100 mg). Yield: 80.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): D=9.71 (s, 1H), 8.10 (d, J=7.7 Hz, 1H), 8.03–8.00 (m, 2H), 7.67 (d, J=3.7 Hz, 1H), 7.63 (d, J=7.7 Hz, 1H), 7.42 (d, J=3.7 Hz, 1H), 7.32–7.27 (m, 4H), 7.22–7.16 (m, 7H), 7.07 (t, J=7.3 Hz, 2H), 4.80 (t, J=7.3 Hz, 2H), 2.22–2.13 (m, 2H), 1.35–1.19 (m, 10H), 0.88–0.85 ppm (m, 3H). HRMS (ESI, m/z):  $[M]^+$  calcd for C<sub>37</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub> 568.2838; found 568.2842.

5-(7-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2H-benzo[d]-

[1,2,3]triazol-4-yl)furan-2-carbaldehyde (6): The synthesis method resembles that of compound **5**, but starts from **4**, and the product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether=2:1, v/v) to give a yellow solid (74 mg). Yield: 69.2 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): D = 9.71 (s, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.04–7.99 (m, 2H), 7.65 (dd, J = 10.7, 5.7 Hz, 2H), 7.43 (d, J = 3.7 Hz, 1H), 7.33–7.27 (m, 4H), 7.21–7.16 (m, 6H), 7.07 (t, J = 7.3 Hz, 2H), 4.73 (d, J = 6.9 Hz, 2H), 2.31–2.22 (m, 1H), 1.41–1.30 (m, 8H), 0.97 (t, J = 7.4 Hz, 3H), 0.88 ppm (t, J = 6.2 Hz, 3H). HRMS (ESI, m/z):  $[M]^+$  calcd for C<sub>37</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub> 568.2838; found 568.2852.

5-(7-(4-(diphenylamino)phenyl)-2-octyl-2*H*-benzo[d][1,2,3]triazol-4-yl)thioph-ene-2-carbaldehyde (**7**): The synthesis method resembles that of compound **5**, but uses 2-formylthiophene-5-boronic acid as reagent, and the product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether=2:1, v/v) to give a yellow solid (100 mg). Yield: 41.1 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): D=9.88 (s, 1 H), 8.10 (d, J=4.0 Hz, 1 H), 7.93 (d, J=8.7 Hz, 2 H), 7.78–7.73 (m, 2 H), 7.51 (d, J=7.6 Hz, 1 H), 7.23 (t, J=7.8 Hz, 4 H), 7.12 (dd, J=8.1, 4.1 Hz, 6 H), 7.00 (t, J=7.3 Hz, 2 H), 4.73 (t, J=7.3 Hz, 2 H), 2.10 (dd, J=14.5, 7.3 Hz, 2 H), 1.21 (dd, J=20.4, 11.1 Hz, 10 H), 0.87 ppm (t, J=6.9 Hz, 3 H). HRMS (ESI, m/z):  $[M+H]^+$  calcd for C<sub>37</sub>H<sub>36</sub>N<sub>4</sub>OS 585.2692; found, 585.2690.

5-(7-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2H-benzo[d]-

[1,2,3]triazol-4-yl) thiophene-2-carbaldehyde (8): The synthesis method resembles that of compound 5, but starts from 4 and uses 2-formylthiophene-5-boronic acid as reagent; the compound was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 2:1, v/v) to give a yellow solid (83 mg). Yield: 61.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>: 400 MHz): D = 9.95 (s, 1H), 8.18 (d, J = 4.0 Hz, 1H), 8.01 (d, J = 8.8 Hz, 2H), 7.85–7.80 (m, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.33–7.27 (m, 4H), 7.21–7.16 (m, 6H), 7.07 (t, J = 7.3 Hz, 2H), 4.73 (d, J = 6.9 Hz, 2H), 2.34–2.23 (m, 1H), 1.36 (ddd, J = 22.6, 8.9, 4.0 Hz, 8H), 0.97 (t, J = 7.4 Hz, 3H), 0.88 ppm (t, J = 7.1 Hz, 3H). HRMS (ESI, m/z): [M+H]<sup>+</sup> calcd for C<sub>37</sub>H<sub>36</sub>N<sub>4</sub>OS 585.2692; found 585.2688.

2-Cyano-3-(5-(7-(4-(diphenylamino)phenyl)-2-octyl-2H-benzo[d]-

[1,2,3]triazol-4-yl) furan-2-yl)acrylic acid (BTA-I): A mixture of aldehyde 5 (120 mg, 0.21 mmol) with cyanoacetic acid (178 mg, 2.10 mmol) in acetic acid (15 mL) was heated at reflux in the presence of ammonium acetate (300 mg) for 12 h under argon. After cooling the solution, water was added to quench the reaction. The precipitate was filtered and washed with water. The residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/ethanol=10:1, v/v) to give a red solid (80 mg). Yield: 60.1 %. <sup>1</sup>H NMR (DMSO; 400 MHz): D = 8.11 (d, J = 8.8 Hz, 2H), 7.99 (d, J=7.7 Hz, 1 H), 7.81 (d, J=7.7 Hz, 1 H), 7.79 (s, 1 H), 7.56 (d, J= 3.6 Hz, 1H), 7.39-7.34 (m, 4H), 7.30 (d, J=3.6 Hz, 1H), 7.14-7.06 (m, 8H), 4.85 (t, J=7.0 Hz, 2H), 2.08 (d, J=6.7 Hz, 2H), 1.28-1.16 (m, 10H), 0.79 ppm (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (DMSO; 100 MHz): D =171.46, 152.48, 148.88, 147.44, 146.75, 142.10, 140.44, 139.57, 133.73, 129.75, 129.65, 129.60, 129.31, 124.56, 123.61, 123.28, 122.08, 119.34, 116.92, 113.44, 56.24, 31.0, 30.39, 29.30, 28.45, 25.84, 21.98, 13.86 ppm. HRMS (ESI, m/z):  $[M+H]^+$  calcd for  $C_{40}H_{38}N_5O_3$  636.2975; found 636.2980.

2-Cyano-3-(5-(7-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2H-

*z*):  $[M+H]^+$  calcd for C<sub>40</sub>H<sub>38</sub>N<sub>5</sub>O<sub>3</sub> 636.2975; found 636.2979. 2-Cyano-3-(5-(7-(4-(diphenylamino)phenyl)-2-octyl-2*H*-benzo[d]-

[1,2,3]triazol-4-yl)thiophen-2-yl)acrylic acid (**BTA-III**): The synthesis method resembles that of compound **BTA-I** but starts from **7**, and the product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/ ethanol=10:1, v/v) to give a red solid (80 mg). Yield: 75.5%. <sup>1</sup>H NMR (DMSO; 400 MHz): D = 8.16 (d, J = 4.0 Hz, 1H), 8.15 (s, 1H), 8.06 (d, J =8.7 Hz, 2H), 7.87 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 4.1 Hz, 1H), 7.71 (d, J =7.7 Hz, 1H), 7.36 (t, J = 7.9 Hz, 4H), 7.10 (m, 8H), 4.83 (t, J = 6.8 Hz, 2H), 2.08 (s, 2H), 1.26–1.15 (m, 10H), 0.78 ppm (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (DMSO; 100 MHz): D = 170.93, 153.47, 149.11, 148.27, 146.80, 142.27, 141.52, 141.10, 137.05, 129.73, 129.67, 129.47, 127.32, 124.53, 123.65, 122.32, 121.25, 117.81, 115.13, 114.09, 59.58, 31.08, 29.33, 28.47, 28.23, 26.10, 21.99, 14.22 ppm. HRMS (ESI, *m/z*): [*M*+H]<sup>+</sup> calcd for C<sub>40</sub>H<sub>38</sub>N<sub>5</sub>O<sub>2</sub>S 652.2746; found 652.2745.

2-Cyano-3-(5-(7-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2*H*benzo[d][1,2,3] triazol-4-yl)thiophen-2-yl)acrylic acid (**BTA-IV**): The synthesis method resembles that of compound **BTA-I** but starts from **8**, and the product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/ethanol=10:1, v/v) to give a red solid (80 mg). Yield: 72.7%. <sup>1</sup>H NMR (DMSO; 400 MHz): D=8.15 (d, J=4.0 Hz, 1H), 8.15 (s, 1H), 8.06 (d, J=8.6 Hz, 2H), 7.86 (d, J=7.6 Hz, 1H), 7.81 (d, J=4.0 Hz, 1H), 7.71 (d, J=7.7 Hz, 1H), 7.36 (t, J=7.8 Hz, 4H), 7.15–7.04 (m, 8H), 4.77 (d, J=6.5 Hz, 2H), 2.24–2.10 (m, 1H), 1.26 (m, 8H), 0.91 (t, J=7.4 Hz, 3H), 0.80 ppm (t, J=7.2 Hz, 3H). <sup>13</sup>C NMR (DMSO; 100 MHz): D=

163.08, 156.86, 147.76, 146.76, 142.48, 141.76, 135.76, 129.66, 129.63, 129.59, 129.27, 127.21, 124.55 (s), 123.92, 123.61, 122.19, 121.38, 119.07, 116.65, 113.53, 59.61, 30.25, 28.09, 27.81, 23.68, 22.33, 13.81, 10.43 ppm. HRMS (ESI, m/z):  $[M+H]^+$  calcd for  $C_{40}H_{38}N_5O_2S$  652.2746; found 652.2745.

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benzo[d]-[1,2,3] triazol-4-yl)furan-2-yl)acrylic acid (**BTA-II**): The synthesis method resembles that of compound **BTA-I** but starts from 6, and the product was purified by column chromatography on silica gel ( $CH_2Cl_2/$  ethanol=10:1, v/v) to give a red solid (85 mg). Yield: 74.6%. <sup>1</sup>H NMR

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