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Zinc phthalocyanine π-conjugately linked with electron-withdrawing benzothiadiazole towards broad absorption

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ABSTRACT

New zinc phthalocyanine, peripherally functionalized with eight electron-withdrawing benzothiadiazole moieties through alkynic bond linkage, has been designed and synthesized. It was found that DBU acts as a ligand to coordinate with the central zinc ion at the axial direction. By this strategy, not only broad absorption covering the range of 300 ~ 900 nm, but also good solubility in common organic solvents and amorphous stability were achieved, making it an attractive candidate for potential application in solution processed small molecule-based organic photovoltaic devices.

Organic photovoltaic devices (OPVs) have attracted intensively scientific and industrial attention to address the problems of energy crisis and environmental pollution.[1–4] In the past decade, low band-gap (LBG) aromatic small molecules[5,6] and conjugated polymers[7,8] based on intramolecular donor-acceptor (D-A) structure have been developed towards highly efficient OPVs. The D-A structure in the LBG molecular systems may cause partial intramolecular charge transfer (ICT) that enables manipulation of the electronic structure and provides efficient charge separation of the photogenerated excitons.[9,10] Meanwhile, small organic molecules have additional advantages, including well-defined structure, versatile molecular structure and easier band structure control. In view of the absorption property, low band-gap materials often possess broad absorption located in the visible region, which is critical for efficient sunlight-harvesting. Hence, further developments of low band-gap material with ideal optical and electronic properties are still required.[9,11,12]

Phthalocyanines (Pcs), as planar, two-dimensional aromatics, possess strong light-harvesting ability nearby 350 nm and 670 nm of solar spectrum as well as excellent hole-transport ability, and have emerged as promising small molecule materials for OPVs.[13] However, phthalocyanines show a very weak absorbance capacity in 400 ~ 600 nm for solar spectrum. Furthermore, the application of phthalocyanines into organic photovoltaic devices is usually performed in blends via vapour deposition process, and examples based on solution processed OPVs using metallophthalocyanine complexes as donor materials are scarce and the corresponding power conversion efficiencies are still low compared with that of polymer or other small molecule OPVs.[14,15]

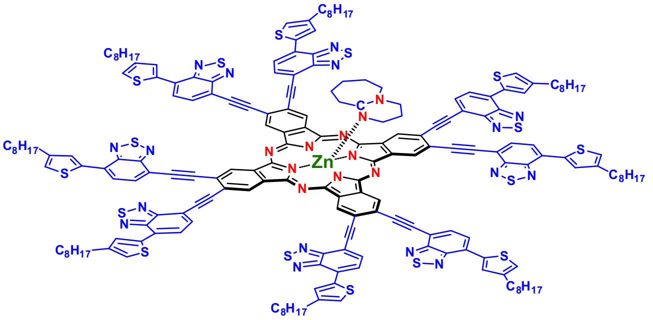

Figure 1. Chemical structure of **ZnPc- π -A** reported herein.

In our previous work, we developed a hybrid (**ZnPc-TDA**) of four low band-gap donor-acceptor moieties, that is, 2,1,3-benzothiadiazole-cored oligoalkylthiophene conjugates, and zinc phthalocyanine via non-conjugated linkage (ether bond).[16] Herein, we would like to report the design, synthesis and properties of a

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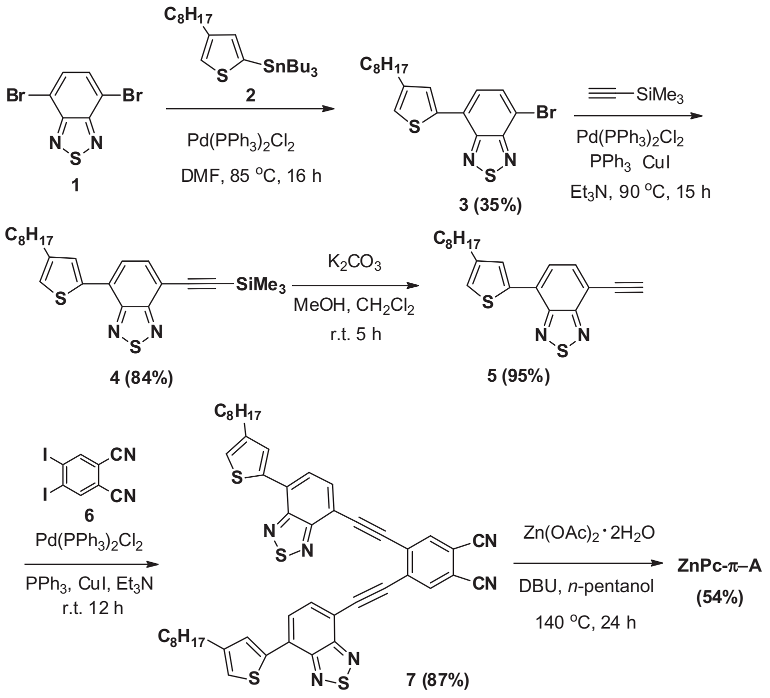

Scheme 1. Synthetic route towards zinc phthalocyanine derivative **ZnPc- π -A**.

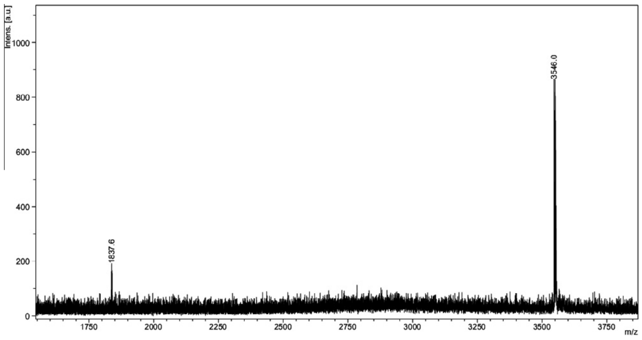

Figure 2. Mass spectrum of **ZnPc- π -A**.

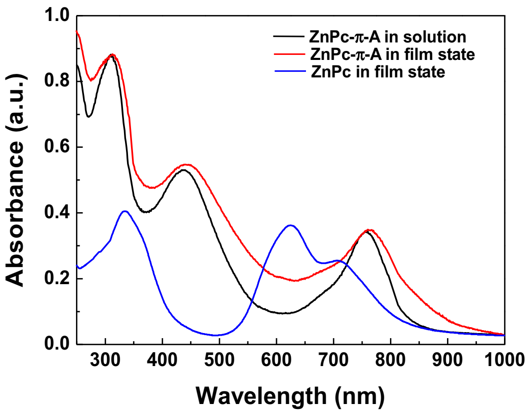

Figure 3. UV–vis absorption spectra of **ZnPc- π -A** in solution (10^{-6} M) and in film state.

structurally regular zinc phthalocyanine functionalized with eight 2,1,3-benzothiadiazole–octylthiophene moieties linked via alkynic bond (denoted as **ZnPc**-π-**A**, see Fig. 1 for structure).

The synthetic route towards **ZnPc-π-A** is depicted in Scheme 1. The phthalonitrile ligand **7** was prepared by a multi-step procedure. Initially, a Stille coupling between 4,7-dibromobenzo[*c*][1,2,5]thiadiazole **1** and excess tributyl(4-octylthiophen-2-yl)stannane **2**, affords monobromo-terminated benzothiadiazole **3** in 35% yield. Then, terminal alkyne **5** was obtained by the Sonogashira reaction of **3** and trimethylacetylsilane, followed by desilytion. A second Sonogashira reaction between **5** and 5,6-diiodophthalocyanine **6** gives compound **7** in high yield. The final zinc phthalocyanine **ZnPc**-π-**A** was successfully prepared by reacting ligand **7** with $Zn(OAc)_2 \cdot 2H_2O$ in refluxing *n*-pentanol using DBU as the base, followed by column chromatographic purification on silica gel. The product was obtained as black powder and characterized by ^1H NMR, FT-IR spectroscopies (see Figs. S1–6, Supplementary data) and TOF-MS (Fig. 2). It should be noted that the molecular ion peak of the compound at 3546, does not match with the molecular weight of the corresponding product (3393). The difference is 152, exactly equal to the molecular weight of DBU. Thus, we think that DBU may act as a ligand to coordinate with the zinc ion of **ZnPc**-π-**A** from the axial direction.[17,18] The driving force for such type of coordination was reasoned by the strong electron-withdrawing character of the eight peripherally conjugately linked benzothiadiazole moieties, which would dramatically decrease the electron density on the central zinc ion.[19] **ZnPc**-π-**A** exhibited good solubility in common organic solvents such as $CHCl_3$ and DMF, due to the introduction of eight flexible *n*-octyl chains on the periphery.

The absorption spectra of **ZnPc**-π-**A** in $CHCl_3$ solution are shown in Figure 3. (The absorption spectrum of **ZnPc** was also included for comparison). The B-band absorption peaks of **ZnPc**-π-**A** located at 337 nm show a slight blue shift (ca. 20 nm). However, the red shift (ca. 130 nm) experienced by the phthalocyanine Q-band in **ZnPc**-π-**A** is very remarkable, indicating that the introduction of electron-withdrawing groups at the β-benzo position of the phthalocyanine skeleton may shift the Q-band to longer wavelength.[20] This clearly indicates that in the ethyne-bridged π -conjugate molecular system, central zinc phthalocyanine functions as electron-donor and outer eight 2,1,3-benzothiadiazole units function as electron-acceptor. At the same time, the shoulder peak of

Q-band of **ZnPc-π-A**, that attributed to ZnPc dimer,[21] disappeared. So, we conjecture that the formation of dimmer of **ZnPc-π-A** is inhibited, partially due to the DBU coordination. The absorption maximum centred at 430 nm was derived from the intramolecular charge-transfer (ICT) transition of donor-acceptor segments attached on the zinc phthalocyanine.[16,22] The **ZnPc-π-A** film showed more intense, broader and slightly red-shifted absorption than that in solution. A large coverage of the solar spectrum from UV to near IR region renders it an ideal light-harvesting material.

We used differential scanning calorimetry (DSC) to investigate the thermal properties of **ZnPc-π-A** (Fig. S7). Under DSC examination, **ZnPc-π-A** revealed no significant melting peak and crystallization peak. The presence of 2,1,3-benzothiadiazole–octylthiophene moieties, along with the axial DBU ligand, renders **ZnPc-π-A** rather bulky and rigid, leading to a significant enhancement in amorphous stability. This suggested it would be a feasible donor material to improve the lifetime of OPVs, and to ameliorate aggregate morphology of **ZnPc-π-A** in the active layer.

In summary, we have successfully synthesized benzothiadiazole-functionalized zinc phthalocyanine with extended π-conjugation. DBU was found to coordinate to the zinc ion at the axial direction. The optical property of **ZnPc-π-A** reveals that the broad absorption covering 300 ~ 900 nm was achieved from single organic molecule. In addition, the compound possesses good solubility in common organic solvents and excellent amorphous stability. All these factors allow **ZnPc-π-A** a potential and attractive candidate in solution processing OPVs.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.08.048.

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