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Phthalocyanine-based dumbbell-shaped molecule: Synthesis, structure and charge transport studies

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ABSTRACT

We describe the synthesis of a fully conjugated donor-acceptor-donor triad (ZnPc-BTD-ZnPc) made of zinc phthalocyanine donor fragments (ZnPc) at both ends of a benzothiadiazole-based central dye (BTD). The molecule exhibits a broad absorption in the whole visible range. The introduction of sterically demanding alkoxy chains to the ZnPc fragments is found to limit the molecular organization to a short-range columnar order and the charge-carrier mobility to moderate values, but provides outstanding solubilities in organic solvents.

1. Introduction

Synthesis of multi-chromophoric systems, such as dyads or supra-molecular arrays, has attracted a considerable amount of scientific interest due to their unique photophysical and photochemical properties. Molecular systems made of the association of electron-donating (D) and electron-accepting (A) chromophores have drawn tremendous attention for their applications, in particular in artificial photosynthetic systems or in organic photovoltaics (OPV) [1–4].

In photovoltaics, considerable development was observed in the design of novel multi-component molecular and polymer systems, for their particular use in solution-processable bulk heterojunction (BHJ) solar cells [3,5–7]. In particular, the combination of D and A units give rises to internal charge transfer that enhances light-absorption efficiency and open-circuit voltage (V_{OC}) of solar cells [8]. Peripheral chains are the third necessary component of the molecular systems, primarily to confer the crucial solubility for solution processing [9,10], but also because the design of the aliphatic substitution drives the molecular organization [11]. The quality of the molecular packing is indeed a prerequisite for performing OPV devices, since the charge transport between close packed conjugated units limits the short-circuit current (J_{SC}) and fill factor (FF) parameters [12]. Among possible molecular designs, different systems with triad architecture have been reported in the literature [5,6,13–18] since the seminal work of Lee

et al. [19], who highlighted the prominent role of the π -stacking platforms at both extremities of a diketopyrrolopyrrole (DPP) unit, to promote molecular packing. In particular, N. Leclerc et al. designed several series of so-called “dumbbell-shaped” molecules, where electron-rich triazatruxene (TAT) platform was inserted at opposite sides of electron-deficient dyes of different nature, following the TAT-dye-TAT molecular architecture [10,20–23]. According to the alkyl chain functionalization at the TAT unit, the authors could decouple to some extent, the molecular organization from the optoelectronic properties of the molecules. More precisely, TAT platforms were found to govern the solid state packing as well as the HOMO level of the molecule, while the central dye could determine the LUMO level and optical absorption of the molecules. In light of these results, the use of BODIPY- and diketopyrrolopyrrole-based dyes, associated to a proper side-chain functionalization at the TAT, led to over 6% power conversion efficiencies [23].

Willing to deepen the understanding of these dumbbell-shaped molecular systems, we considered the replacement of the TAT molecular unit by a larger π -conjugated platform. Among many possible large π -conjugated electron-rich systems, phthalocyanines and related compounds have emerged as quite promising candidates [24]. These systems have a high light-collecting property in the UV and in the visible/infrared regions and show unique self-assembling properties from their strong π -stacking interactions that are favorable to charge

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transport. Phthalocyanines have also been proven to be good building blocks for constructing supramolecular systems because their physical and physicochemical properties could easily be modulated by multiple chemical modifications at the metal center, the peripheral groups/chains or else at the axial position to metal [25–28].

Examples of fully conjugated dumbbell-shaped molecules including zinc phthalocyanine units (ZnPc-dye-ZnPc) have already been reported [16–18, 29–32]. In particular, Jiménez et al. [16] inserted a dye based on perylene-3,4,9,10-tetracarboxylic diimide (PDI), and Molina et al. [17,18] used a diketopyrrolopyrrole (DPP) derivative. A broad absorption in the visible region and a clear photovoltaic effect were measured for the ZnPc-DPP-ZnPc triad, thus demonstrating the potential of these phthalocyanine-based materials for BHJ solar cells [17,18]. However, both materials showed moderate solubility with presence of aggregates, since the ZnPc fragments were only substituted with *t*-butyl groups. Moreover, the absence of information on the solid state organization prevented a comprehensive assessment of the relative modest performances.

In this line, the present contribution analyzes the effect of substituting the TAT by ZnPc platforms in one representative of the dumbbell-shaped triad series [21]. Specifically, the electron-deficient unit consists of a benzothiadiazole (BTD) moiety and the platforms are functionalized with ramified alkyl chains, namely, three 2-ethylhexyl chains connected to the aza bridges of the TAT fragments, and six 2-butyloctyl chains connected to the equatorial positions of the ZnPc fragments through ether bridges. These bulky chains hindered face-to-face stacking of TAT fragments in the original material, which was hence amorphous, but unexpectedly led to significant OPV performances, with maximum PCE as high as 2.9% [21]. This study first aims at constructing the triad molecule from ZnPc and BTD precursors.

2. Results and discussion

The synthetic pathway of the targeted ZnPc-BTD-ZnPc triad is

Scheme 1. Synthetic route for the preparation of the dumbbell-shaped ZnPc-BTD-ZnPc compound: i) $\text{Zn}(\text{CN})_2$, $\text{Pd}_2(\text{PPh}_3)_4$, DMF, 90 °C; ii) ZnCl_2 , DMAE, 150 °C; iii) $\text{Pd}_2(\text{dba})_3$, P(*o*-tol) $_3$, toluene, reflux.

depicted in Scheme 1. To ensure a high solubility of the triad, the phthalocyanine fragments are carrying six sterically-demanding 2-butyloctyloxy chains. In the literature, the construction of phthalocyanine-based multichromophoric systems is usually performed by using Suzuki, Heck or Sonogashira cross-coupling reactions, for their high yield and ease of implementation [4,28,33]. When a direct C-C connection to phthalocyanine is targeted, Suzuki reaction remains the synthetic procedure of choice. It most generally involves the coupling between a halogenated phthalocyanine and a borylated counterpart [28]. In our case, the phthalocyanine mono iodide could be satisfactorily prepared (*vide infra*), but the attempts to isolate the bis-boronate ester BTD derivative have failed because of its poor stability. This led us to waive the use of Suzuki reaction for the Stille cross-coupling reaction, which can also be very efficient, although it has rarely been applied to phthalocyanines, so far [34,35].

The iodo-substituted phthalocyanine was prepared by a classical cross condensation between phthalonitrile precursors [36]. The bis-dialkoxyphthalonitrile **2** was prepared by adapting the well-known catechol pathway (3 steps, 65% overall yield) [37]. The synthesis starts with the preparation of the 1,2-dibromo-4,5-bis[(2-butyloctyl)oxy]benzene **1** by etherification of the 1,2-dibromocatechol [37]. Then, compound **1** was cyanated to produce the 4,5-bis[(2-butyloctyl)oxy]phthalonitrile **2**, by using a palladium-catalyzed reaction in the presence of $\text{Zn}(\text{CN})_2$ in DMF at 90 °C. This reaction demonstrated to be a better alternative of the classical high temperature CuCN-promoted (Rosenmund-Von Braun) reaction [38], since it was higher yielding (82%) and avoided the parasite phthalocyanine formation [39,40]. The iodo-substituted zinc phthalocyanine **3** was then prepared by a statistical cross-condensation between the dialkoxyphthalonitrile **2** and the commercially available 4-iodophthalonitrile in presence of ZnCl_2 in refluxing 2-dimethylaminoethanol (DMAE) for 12 h. It should be noted that the use of ZnCl_2 led to better yield than with $\text{Zn}(\text{OAc})_2$. However, the reaction time should be limited to 12 h in order to avoid a

subsequent deiodination reaction, probably caused by the Lewis acid character of ZnCl_2 . With these conditions, pure phthalocyanine **3** (26% yield) was obtained after chromatographic separation.

The final triad ZnPc-BTD-ZnPc was prepared by Stille cross-coupling reaction between the iodo phthalocyanine fragment **3** and the bis-trimethylstannyl derivative **4** [41], in the presence of $\text{Pd}(\text{dba})_3$ catalyst and $\text{P}(\text{o-tolyl})_3$ ligand in refluxing toluene [42]. As already reported in the literature, this Stille cross-coupling reaction was found to compete with organotin homocoupling side-reactions [43–45], leading to by-products that were identified by MALDI-ToF analysis as D-A-A, D-A-A-A, D-A-A-D and D-A-A-A-D, where D and A stand for ZnPc and BTD units, respectively (Figs. S1 and S2 in supporting information). The targeted triad could however be efficiently isolated after chromatographic separations on silica and size exclusion (Bio-Beads SX1) gels with toluene as eluent, offering pure ZnPc-BTD-ZnPc as a dark green sticky compound in a fair yield of 26% (Fig. S1 in Supporting Information).

It is worth reporting that the triad and its ZnPc precursor **3** were found to show a relatively poor photostability in solution, as evidenced by photobleaching after long-time exposition to light. This photo-oxidation phenomenon is most likely favored by the high density of electro-donating alkoxy chains attached to the phthalocyanine rings [46,47]. This phenomenon could however be satisfactorily circumvented by avoiding the use of (acid- and radical-containing) chloroform solvent and by manipulating the materials as much as possible under inert atmosphere and away from the light.

The triad shows a noteworthy solubility in a large variety of organic solvents, and readily solubilizes in toluene, hexane, and even diethyl ether. As seen from Fig. 1, the UV–vis spectra in THF or toluene fully superpose and give a fine structure with well-defined bands. The absence of aggregation is confirmed by the linearity of the Lambert-Beer law for the whole concentration measurement range (up to 5 mg/mL in toluene). The presence of aggregates in solution is only found in the case of poor diethyl ether or hexane solvents, as deduced from the broad absorption spectra with poorly discernible band structure. The spectra of the nanosegregated diethyl ether and hexane solutions however, do not spread as much as in the solid state, which nearly extend to 900 nm. The remarkable solubility of the triad is explained by the high space-requirement of the bulky ramified chains onto the phthalocyanine fragments which significantly reduces the cohesion of the self-assembling driven by the π -stacking of ZnPc units. The determinant role of the alkyl chains is confirmed by the similar high

Fig. 1. Comparison of UV–vis absorption spectra of the triad ZnPc-BTD-ZnPc recorded in different solvents (THF, toluene, hexane and diethyl ether), and in solid state. In insert: plot of Q band absorption intensities of ZnPc-BTD-ZnPc (708 nm) vs concentration in toluene.

Fig. 2. UV–vis absorption spectra in THF solution of the ZnPc-BTD-ZnPc compounds and its constitutive fragments. BTD stands for 4,7-di(2-thienyl)-2,1,3-benzothiadiazole.

solubility found for the reference TAT-based triad [21], while other TAT-based triads with linear chains were found to be less soluble [10,22].

Fig. 2 compares the UV–vis spectrum of ZnPc-BTD-ZnPc with the ones of its phthalocyanine **3** and BTD **4** precursors. Compound **3** shows a typical UV–vis spectrum of phthalocyanines with the *B* (soret) band centered at 367 and 684 nm, respectively. A slight *Q* band splitting (10 nm) is observed, which is attributed to the molecular symmetry breaking [48,49]. The BTD unit **4** exhibits a broad absorption in the visible region, centered at 471 nm. By inserting the BTD unit between two ZnPc fragments, the intense *Q*-band of the phthalocyanine is significantly redshifted to 708 nm ($\epsilon = 425,000 \text{ Mol}^{-1} \text{ cm}^{-1}$) and a stronger *Q*-band splitting is observed (28 nm). This phenomenon is attributed to the enlargement of the π -conjugation system and brings evidence of a strong electronic conjugation between the electron donating ZnPc units and the electro-deficient BTD dye [16,18,29–32]. Moreover, the BTD-ZnPc conjugation, allows a panchromatic absorption in the whole UV to near infrared region, especially by filling the 400–600 nm region lacking in neat phthalocyanines.

For structural aspects, the triad ZnPc-BTD-ZnPc is only found to exhibit an amorphous solid state with short-range organization. This triad turns out to be a dark glassy solid, softening gradually to a non-birefringent thick past above 180 °C. The amorphous state is further deduced from the absence of phase transition in DSC traces up to degradation at $T_{\text{deg}} \approx 250 \text{ °C}$ (Fig. S3 in supporting information). GIWAXS experiments on a thin film further confirm the absence of any long-range order, as it has led to a pattern without sharp reflection (Fig. S4). In the GIWAXS profile shown in Fig. 3a, several broad signals from nanosegregated self-assembling are nevertheless present, namely the broad scattering maximum h_{ch} around 4.5 Å from lateral distances between molten chains, a scattering maximum h_{π} at 3.5 Å from π -stacked phthalocyanine (ZnPc) rings, and a local-range periodicity D of 24 Å from the arrangement of the ZnPc ring piles. This pattern composition complies with a columnar mesophase-like structure, in which the ZnPc columns, separated by an undifferentiated periphery of aliphatic tails and BTD bridges, arrange in a short-range correlated two-dimensional lattice (Fig. 3b–d). Such persisting columnar short-range order in amorphous states was already reported for molecular architectures with incompatible terminal chain segments [50]. The preservation of mesogen piles was in this former case induced by the nanosegregation interfaces in the periphery, while it is here a consequence of the bridging of ZnPc columns with the BTD cores. The possible influence of bridging on the geometry of the structure is best appreciated from the molecular slice thickness h_{mol} (i.e. the columnar segment height

Fig. 3. a) GIWAXS intensity profile of triad ZnPc-BTD-ZnPc, obtained from pattern shown in Fig. S4; b) Model molecular structure of the triad; c,d) Molecular organization models of the triads illustrating the short-range molecular packing of the triads.

corresponding to one molecule, which is obtained from the ratio of the (half-)molecular volume ($V_{\text{mol}} \approx 5500 \text{ \AA}^3$) and of the columnar section assuming hexagonal geometry ($S \approx 2/\sqrt{3} D^2 = 650 \text{ \AA}^2$) [51]). This h_{mol} value is found to exceed the average spacing of ZnPc rings h_{π} (4.2 Å vs. 3.5 Å), as for columnar mesophases of numerous Pc derivatives [52] and for crystalline polymorphs of neat CuPc (CSD- 2103883 [53]), which stack with lateral shifts into tilted columns. The self-assembling geometry is thus little affected by the bridging, contrasting with its deleterious effect on the long-range order.

To gain an insight into the geometric and electronic properties of the ZnPc-BTD-ZnPc triad, density functional theory (DFT) calculations was performed using SPARTAN at the B3LYP/6-31G* level of theory in vacuum. The long peripheral alkoxy chains were replaced by methoxy groups to keep a reasonable calculation time. From a conformational point of view, the triad shows a quite planar structure with the highest rotation angle (found between a thiophene of the central dye and the adjacent ZnPc platform: green planes in Fig. S5) as low as 21° . Such a planar structure suggests a good electronic conjugation between the ZnPc and BTD fragments all throughout the molecule. The calculated frontier molecular orbitals given in Fig. 4 clearly show the strong localizations of the highest and lowest occupied molecular orbitals (HOMO and LUMO). The HOMO is essentially located on the ZnPc fragments, while the LUMO is mainly located on the benzothiadiazole unit of the BTD moieties, clearly demonstrating that ZnPc and BTD units have an electro-donating and electro-deficient character, respectively. The calculated HOMO and LUMO energy values for the ZnPc-BTD-ZnPc triad were found to be -4.71 and -2.80 eV, respectively.

Energy levels were also determined experimentally. The HOMO level was measured from photoelectron spectroscopy (PESA) analysis on thin film in air (Fig. S6), while the LUMO value was deduced from the optical energy bandgap ($E_g = 1.41$ eV) determined from the thin film absorption onset. It is worth noting that PESA is a very convenient method to determine HOMO values, and it was found to give very similar results as by cyclic voltammetry on films [54,55]. As seen from Table 1, the measured HOMO value (-4.97 eV) is very close to the

calculated ones (-4.71 eV), while the LUMO value determined experimentally (-3.56 eV) differs markedly from the calculated value (-2.80 eV). Three complementary reasons may explain this discrepancy between experimental and calculated LUMO values. First, the experimental LUMO level is determined from the thin-film absorption onset and therefore, the exciton binding-energy (often in the 0.3 eV range) is neglected in the experimental value [56]. Second, the experimental values are measured in the solid-state, while the calculations are based on isolated molecules in vacuum and are more comparable to experimental values in solution. Third, DFT calculations for LUMO energies are known to be less reliable than for HOMO energies as the virtual orbitals are generally more difficult to describe theoretically than the occupied ones [57]. Interestingly, the HOMO value of the triad is very similar to the value found for the model ZnPc(OR)₈ fragment (-4.97 vs -5.04 eV), indicating that the electro-donating platform seems to govern the HOMO energy of the whole triad, as already observed in TAT-based dumbbell-shaped systems [21]. The same holds for the calculated HOMO levels as shown in Table 1. The sensitivity of our phthalocyanine derivatives against oxidation is explained by their relatively high HOMO values (≈ -5.0 eV), as Wörle et al. could make a correlation between high HOMO values and low photobleaching rate constants k of phthalocyanine compounds [58]. Finally, as regards a possible use in photovoltaics, the high HOMO value of the triad is also found to limit the open-circuit voltage (Voc) value, which is one the parameter determining the solar cell performances, as $q \cdot \text{Voc}$ (q being the elementary charge) roughly corresponds to the difference of energy ($\text{HOMO}_{\text{donor}} - \text{LUMO}_{\text{acceptor}}$) necessary for charge dissociations minus 0.3 eV [59]. Therefore, by considering the classical PC₇₁BM acceptor with a LUMO energy level ≈ -4.2 eV, the expected Voc value is as low as 0.5 V.

Charge transport properties were determined in organic field-effect transistors (OFET) devices with a bottom contact-bottom gate configuration. Only hole-transport was observed and the mobility values (Table 2) were estimated from the transfer characteristics in the linear regime. Details of the OFET devices fabrication can be found in the

Fig. 4. Localization of the HOMO (top) and LUMO (bottom) frontier orbitals in ZnPc-BTD-ZnPc calculated by DFT.

experimental section. The hole-mobility was found to be highly dependent of thermal annealing as the values increase exponentially from $\mu_h = 3 \times 10^{-8} \text{ cm}^2/\text{V}$ (as cast) to fair values of about $6 \times 10^{-6} \text{ cm}^2/\text{V}$ after 10 min annealing at 200 °C. This result presumably comes from an improved molecular organization of the columnar stacks after softening of the materials at elevated temperature. As the material only exhibited short-range molecular stacks, the hole-mobility remained limited to moderate values, yet.

From all the results reported above, it appears that the properties of the ZnPc-TBD-ZnPc triad resemble to those of the reference TAT-BTD-TAT triad [21]. The replacement of TAT by ZnPc units consistently maintained the high solubility in organic solvents conferred by the longer branched alkyl chains. The solid state is also in both cases amorphous, with however a different local-range structure explainable by the type of connection of the chains to the donor platform. The connection to amine groups in bay position prevents the face-to-face stacking of the TAT platforms, so that SAXS patterns only present the signals from the alternation of juxtaposed conjugated and aliphatic domains, and from irregular lateral distances inside these domains.

Pattern features on the contrary confirm that the chains in the peripheral positions of ZnPc allow π -stacking of the rings into piles and arrangement of these piles in a local-range columnar lattice. These different local-range organizations manifest themselves in thermal behavior: unlike TAT-BTD-TAT that flows to liquid by passing through a low-temperature glass transition [21], ZnPc-BTD-ZnPc remains solid at high temperature and only gradually softens on further heating. Counterintuitively, this more developed local-range organization of the ZnPc-based triad led to one order of magnitude lower hole-mobility, which is a limiting factor for photovoltaic performances.

A further limitation is brought by the large number of ether bridges between alkyl chains and ZnPc fragments, which is responsible in a large part, for the high HOMO level. Such high HOMO limits the V_{OC} values potentially reachable for blends with PCBM in BHJ devices, and is likely the cause for its drastically reduced stability against photo-oxidation. The associated technical issues considerably complicated the synthesis of the triad, and made its manipulation delicate, so that we renounced the OPV devices fabrication. As a clear outcome of the study, HOMO level needs to be lowered to reduce stability issues and improve

Table 1
Energy levels determined experimentally and by DFT calculation.

Compound	DFT calculations			Measurements		
	HOMO (eV)	LUMO (eV)	Eg (eV)	HOMO ^a (eV)	LUMO ^b (eV)	Eg ^c (eV)
ZnPc(OR) ₈ ^d	−4.66	−2.49	2.17	−5.04		
TBD ^e	−5.35	−2.61	2.74	−5.79		
ZnPc-BTD-ZnPc	−4.71	−2.80	1.91	−4.97	−3.56	1.41

^a Determined from photoelectron spectroscopy (PESA) in air.

^b Determined from equation $\text{LUMO} = \text{HOMO} + E_g$.

^c Measured from the absorption edge in the solid state.

^d ZnPc molecule octasubstituted with alkoxychains.

^e 4,7-bis(thiophene-2-yl)-2,1,3-benzothiadiazole.

Table 2

Hole-mobility values determined from OFET.

Hole-mobility (cm ² /Vs)	As-cast	Annealing conditions		
		100 °C for 10 min.	150 °C for 10 min.	200 °C for 10 min.
$\mu_h \pm \Delta\mu$	$(3.3 \pm 1.1) \times 10^{-8}$	$(4.3 \pm 0.1) \times 10^{-7}$	$(1.2 \pm 1.1) \times 10^{-6}$	$(5.9 \pm 0.1) \times 10^{-6}$

the OPV potential, which could be reached by a reduction of the number of alkoxy chains, or else by using other type of chains (e.g. electro-accepting SO₂R chains) [60]. Reducing the number of peripheral chains could also promote a long-range molecular organization, and would *a priori* be more favorable to charge transport. Such variations of the molecular structure are currently under progress, in order to produce phthalocyanine-based dumbbell-shaped materials with performing photovoltaic characteristics.

3. Conclusion

This study reports on a donor-acceptor dumbbell-shaped molecule made of ZnPc platforms at both ends of a benzothiadiazole core derivative (ZnPc-BTD-ZnPc). In an original way, the triad was synthesized by using the Stille cross-coupling, a reaction that has rarely been applied to phthalocyanines, so far. The triad is found to exhibit a continuous and broad absorption in the whole visible range, provided by the high electronic conjugation of the constitutive units. As each ZnPc fragment is carrying six 2-butyloctyloxy chains, the molecule showed a remarkable solubility in a broad range of solvents, including diethyl ether. The high number of sterically-demanding chains however, is found to be detrimental to self-organization, as the thin film structure investigated by X-Rays, only shows the presence of columnar stacks at short-range order. Alternatively, the hole-charge carrier mobility measured in OFET devices are limited to moderate values.

In the whole, this study brings valuable insight in the design of phthalocyanine-based donor-acceptor systems for optoelectronic properties. In particular, it helps to rationalize the role of peripheral alkyl chains that govern the antagonistic aspects of solubility and self-assembling properties of phthalocyanine-based complex structures. It remains that ZnPc-TBD-ZnPc triad constitutes one of the rare examples of fully conjugated phthalocyanine-based dumbbell-shaped molecules and as such, paves the way towards the realization self-assembling phthalocyanine-based systems for optoelectronics.

4. Experimental section

4.1. Materials and techniques

All reactions were conducted under argon atmosphere using standard Schlenk techniques. The reaction solvents (DMF, toluene, DMAE) were purchased of anhydrous grade and used as received. Chloroform solvent used for the manipulation of the phthalocyanine derivatives was systematically passed through a pad of alumina prior use (to remove possible traces of radical and acidic impurities). Unless specified, all reagents were used as commercially supplied. The permeation gel Bio-Beads SX1 from Bio-Rad was purchased from Merck. ¹H and ¹³C NMR spectra were recorded at room temperature using deuterated solvents as internal standards on a 300 MHz Bruker Advance spectrometer. Absorption spectra in solution and in thin films were recorded on a Cary 100 spectrophotometer. In solid state, the absorption spectra were measured on thin films spin-coated on quartz substrates from a 0.5 mg/mL chloroform solution. DSC measurements were performed with TA Instruments Q1000 instrument, operated at scan rate of 5 °C/min on heating and on cooling. GIWAXS measurements were conducted at PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory (PAL) in Korea. The X-rays coming from the vacuum undulator (IVU) were

monochromated using Si(111) double crystals and focused on the detector using K-B type mirrors. Patterns were recorded with a 2D CCD detector (Rayonix SX165). The sample-to-detector distance was about 225 mm for energy of 11.08 keV (1.119 Å). The sample consisted in a triad layer spin-coated on silicon wafer from 10 mg/mL solution in chloroform. Photoelectron spectroscopy analysis (PESA) was carried out on a Riken Keiki AC-2 instrument by using spin-coated sample (20 mg/mL in chloroform solution) on ITO glass plates. Organic field-effect transistors were elaborated in the bottom contact bottom gate configuration using commercially available substrates. Lithographically defined Au (30 nm)/ITO (10 nm) bilayers were used as source and drain electrodes and 230 nm thick SiO₂ layer as a gate dielectric. Channel length and width were $L = 25 \mu\text{m}$ and $W = 10 \text{ mm}$, respectively. Substrates were cleaned consecutively in ultrasonic baths at 45 °C for 15 min each step using soapsuds, acetone, and isopropanol and followed by 15 min UV-ozone treatment. Then, substrates were transferred into a nitrogen filled glove box where hexamethyldisilazane (HMDS) was spin-coated on top of the SiO₂ followed by annealing at 135 °C for 10 min. Finally, a solution (7 mg/mL in *o*-dichlorobenzene) of the triad was spin-coated on substrates to complete the FET devices. Prior to characterization, completed devices were dried under high vacuum ($\approx 10^{-5}$ – 10^{-6} mbar). Transistor output and transfer characteristics were measured using a Keithley 4200 semiconductor characterization system. Hole-mobilities were extracted in the linear regime using a standard device model. The OFET were further isochronally (10 min) thermally annealed with the temperatures ranging from 100 to 200 °C.

4.2. Materials synthesis

4.2.1. 1,2-dibromo-4,5-bis[(2-butyloctyl)oxy]benzene (1)

This compound was prepared using a modified procedure [61]. 4,5-dibromocatechol [36] (8.0 g, 29.8 mmol, 1.0 eq.) and 2-butyloctyl 4-methylbenzenesulfonate [62] (29.0 g, 89.5 mmol, 3.0 eq.) were dissolved in 30 mL of DMF. Potassium carbonate (41.3 g, 300 mmol, 10 eq.) was then added followed by stirring at 100 °C for 24 h. The reaction mixture was cooled down, quenched with distilled water (300 mL), and extracted by Et₂O (2 × 150 mL). The organic extract was washed respectively by HCl aq. (1 M), water, NaHCO₃ aq., and water, followed by drying using MgSO₄. The crude was purified by column chromatography using (cyclohexane/CH₂Cl₂: 6/1). The product was collected as a colorless oil (15.8 g, 88%). ¹H NMR (300 MHz, CDCl₃) δ 7.05 (s, 2H), 3.80 (d, 4H), 1.77 (m, 2H), 1.28 (m, 32H), 0.89 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 155.9, 120.8, 118.5, 108.0, 77.2, 37.5, 31.7, 28.8, 26.4, 22.8, 13.4.

4.2.2. 4,5-bis[(2-butyloctyl)oxy]phthalonitrile (2)

This compound was synthesized by using a modified procedure [19]. A mixture of 1,2-dibromo-4,5-bis[(2-butyloctyl)oxy]benzene **1** (5.00 g, 8.3 mmol) and Zn(CN)₂ (1.36 g, 11 mmol) was added to anhydrous DMF (10 mL) under argon. After stirring for 30 min, Pd(PPh₃)₄ (1.91 g, 1 mmol) was added into the solution in one portion followed by refluxing for 24 h under argon. Then, the reaction mixture was cooled to room temperature, quenched with distilled water, and extracted with diethyl ether. The combined organic extracts were dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (cyclohexane/ethyl acetate: 8/1) as eluent to obtain the desired phthalonitrile compound **2** as a colorless oil

(3.25 g, 78%). ^1H NMR (300 MHz, CDCl_3) δ 7.10 (s, 2H), 3.90 (d, 4H), 1.87 (m, 2H), 1.29 (m, 32H), 0.89 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 155.0, 116.6, 111.3, 108.2, 77.0, 72.1, 37.5, 31.7, 29.6, 26.7, 22.4, 14.0. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{N}_2\text{O}_2$: C 77.37, H 10.53, N 5.64. Found: C 77.37, H 10.55, N 5.64.

4.2.3. Iodo-substituted phthalocyanine (3)

A mixture of 4,5-bis[(2-butyloctyl)oxy]phthalonitrile **2** (1.00 g, 2.00 mmol), 4-iodophthalonitrile (102 mg, 0.40 mmol), and ZnCl_2 (91 mg, 0.66 mmol) was refluxed in DMAE (2 mL) under argon for 12 h. After cooling, the solvent was concentrated under reduced pressure to offer a green solid residue composed of a statistical mixture of the octa (alkyloxy)-substituted phthalocyanine (A4) and the iodo-containing phthalocyanines (A3B, A2B2 and AB3). Silica gel chromatography (toluene/ethyl acetate: 98/2) has been found to be effective in the separation of the targeted mono-iodinated phthalocyanine A3B (R_f = 0.65) from A4 (R_f = 0.70) and the multi-iodinated phthalocyanines (R_f < 0.6). The monoiodo-substituted phthalocyanine A3B (compound **3**) was obtained in good purity as a dark green solid paste in 26% yield. FT-IR (KBr): ν (cm^{-1}) = 2955, 2922, 2853, 1715, 1597, 1493, 1453, 1378, 1275, 1205, 1110, 1097 (C-I), 1052, 887, 856, 742, 726. MALDI-ToF (m/z) $[\text{M}-\text{H}]^+$ calculated for $\text{C}_{104}\text{H}_{159}\text{IN}_8\text{O}_6\text{Zn}$: 1809.75, found: 1807.83.

4.2.4. 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)-2,1,3-benzothiadiazole (4)

This compound was synthesized by stannylation of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole using a method described in the literature [21]. The final purification was performed by recrystallization from acetonitrile to offer pure **4** as a brown solid in 71% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.20 (d, 3J = 3.45 Hz, 1H), 7.90 (s, 1H), 7.30 (d, 3J = 3.45 Hz, 1H), 0.45 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 152.7, 145.1, 140.2, 136.1, 128.4, 125.8, –8.1.

4.2.5. ZnPc-BTD-ZnPc triad

The iodo-substituted phthalocyanine **3** (250 mg, 0.130 mmol), the benzothiadiazole derivative **4** (35.0 mg, 0.055 mmol), and $\text{P}(o\text{-tol})_3$ (2.70 mg, 0.008 mmol) were dissolved in dry toluene (5 mL) in a Schlenk tube. Argon was bubbled through the mixture for 30 min Pd_2dba_3 (2.02 mg, 0.002 mmol) was added and the mixture was stirred at 110 °C under argon for 24 h. The solution was cooled down to room temperature and filtered through a celite pad. The volatiles were evaporated *in vacuo* and the crude was first roughly purified by silica gel chromatography (toluene/ethyl acetate: 98/2) to separate a fraction (R_f > 0.3) containing the triad ZnPc-BTD-ZnPc (D-A-D: blackish-green color, 3664 Da), along with a number of homocoupling by-products such as D-A-A-D (blackish-blue, 3962 Da), D-A-A-A (green, 2579 Da) and D-A-A (green, 2280 Da). A subsequent purification by size exclusion chromatography (Biobeads SX1, toluene eluent) led to obtain the pure triad ZnPc-BTD-ZnPc as a black powder in 25% yield. FT-IR (KBr): ν (cm^{-1}) = 2954, 2922, 2853, 1602, 1493, 1454, 1378, 1363, 1275, 1203, 1091, 1047, 884, 857, 828 ($\nu\text{N-S}$), 796 ($\nu\text{C-H}$ thiophene), 744, 726, 509. MALDI-ToF (m/z): $[\text{M}]^+$ calculated for $\text{C}_{222}\text{H}_{324}\text{N}_{18}\text{O}_{12}\text{S}_3\text{Zn}_2$: 3664.09, found: 3662.90.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2018.03.017>.

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Supporting information

Phthalocyanine-based dumbbell-shaped molecule: synthesis, structure and charge transport studies

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Figure S1. Maldi-ToF mass spectrum of the isolated ZnPc-BTD-ZnPc

Figure S2. Maldi-ToF mass spectrum of the crude Stille cross-coupling reaction mixture revealing the formation of multiple parasite homocoupling reactions leading to the formation of DAAAD, DAAD, DAAA and DAA side products (D and A stand for the ZnPc and BTD units, respectively).

Figure S3. Thermal Gravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC) traces recorded for the triad ZnPc-BTD-ZnPc.

Figure S4. Grazing incidence wide angle X-Rays scattering (GIWAXS) pattern recorded from thin film of ZnPc-BTD-ZnPc triad.

Figure S5. Conformation of the ZnPc-BTD-ZnPc triad obtained from density functional theory (DFT) calculations using SPARTAN at the B3LYP/6-31G* level of theory in vacuum. The green planes stand for the highest measured rotation angle (21°) in this triad.

Figure S6. HOMO energy levels of the molecules, as determined by photoelectron spectroscopy analysis (PESA) on thin film in air.

Figure S7. a) Transfer OFET characteristic after thermal annealing at 200°C and b) evolution of the hole mobility as a function of the annealing temperature.