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PAPER

Synthesis, self-assembly, and semiconducting properties of phenanthroline-fused phthalocyanine derivatives†

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Two novel unsymmetrical phenanthroline-fused phthalocyanine derivatives, namely metal free 2,3,9,10,16,17-hexakis(*n*-butyloxy)-22,25-diaza(1,10-phenanthrolino)[5,6-c_1]phthalocyanine $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) and its zinc complex $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**), were designed, synthesized, and characterized by a series of spectroscopic methods in addition to elemental analysis. Their self-assembly properties in $CHCl_3$–methanol were comparatively investigated by electronic absorption spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques. Effective intermolecular π–π interactions between metal free phenanthroline-fused phthalocyanine molecules in a face-to-face manner led to the formation of nanowires in $CHCl_3$–methanol, whereas the phenanthroline-fused phthalocyaninato zinc complex self-assembles into ribbonlike nanobundles with a head-to-tail arrangement depending mainly on Zn–N coordination bonding with a slipped π-stacking interaction between neighboring phthalocyanine molecules. Nevertheless, the aggregates formed from both compounds, in particular the metal free one, were revealed to show good semiconducting properties with a conductivity as high as 1.0×10^{-4} S cm^{-1}.

Introduction

Phthalocyanines (Pcs) have been an important class of dyes and pigments with extensive applications in the paint, printing, and textile industries ever since their serendipitous discovery at the beginning of the past century.[1] More recently, these macrocyclic molecular materials have found important applications in flexible display and active-matrix electronic paper as well as smart cards in low-cost memory devices.[2] Phthalocyanines have also been revealed to have important potential applications in the fields of medicine,[3] optical storage,[4] photocatalysis,[5] and molecular-based nanoelectronic devices.[6] In particular, very lately these artificial tetrapyrrole derivatives together with their naturally occurring analogues, porphyrins, have stimulated great research interest in organic heterojunction solar cells and dye-sensitized solar cells associated with their excellent semiconducting properties and photophysical characteristics.[7]

To be applicable in electro- and photo-induced energy- and electron-transfer process-based systems such as dye-sensitized solar cells, novel unsymmetrical phthalocyanine compounds simultaneously possessing peripheral electron-donating groups and electron-withdrawing groups—which not only lends correspondingly phthalocyanines good solubility and a lesser degree of aggregation but more importantly the directionality in the excited state[8]—should therefore be developed at the first step. Due to the good photoelectronic properties, conjugated electronic structure, and nice coordination ability,[9] phenanthroline represents one of the most interesting functional groups that should be introduced onto the tetrapyrrole skeleton. Actually, quite a number of the phenanthroline-fused porphyrin derivatives have been reported in the past twenty years.[10] However, the phenanthroline-fused phthalocyanine derivatives reported thus far still remain extremely rare because of their significantly low solubility in common organic solvents, limited to tetra-1′,4′,8′,9′-tetraazatriphenyleno[2,3-c_1]-phthalocyanine,[11] tetra-2,3-(dipyrido[3,2-*f*:2′,3′-*h*]quinoxalino)porphyrazines,[12] 2,3,9,10,16,17-hexakis(3,5-di-*tert*-butylphenoxy)-1′,4′,8′,9′-tetraazatriphenyleno-[2,3-c_1]-phthalocyanine derivatives,[13] and 2(3),9(10),16(17)-tri-*tert*-butyl-22,25-diaza-(1,10-phenanthrolino)[5,6-c_1]phthalocyaninato zinc,[14] to the best of our knowledge. Nevertheless, both tetra-1′,4′,8′,9′-tetraazatriphenyleno[2,3-c_1]-phthalocyanine and tetra-2,3-(dipyrido[3,2-*f*:2′,3′-*h*]quinoxalino)porphyrazines have been prepared and in particular isolated through unusual recrystallization and Soxhlet extraction processes, respectively (it is worth noting that phthalocyanine compounds have usually been purified and isolated by column chromatography), while reports on 2(3),9(10),16(17)-tri-*tert*-butyl-22,25-diaza-(1,10-phenanthrolino)[5,6-c_1]phthalocyaninato zinc seem a bit ambiguous due to the lack of reliable NMR and mass spectroscopic

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characterization. As a consequence, developing a more common process for the synthesis of phenanthroline-fused phthalocyanine derivatives still remains challenge for the phthalocyanine chemists.

As part of our continuous effort to develop new phthalocyanine molecular materials, we have developed an efficient synthetic pathway for preparing phenanthroline-fused phthalocyanine derivatives using 10,12-diimino-11*H*-pyrrolo[3,4-*b*]dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline as one of the starting materials. Mixed cyclic tetramerization of this compound together with 4,5-di(butyloxy)phthalonitrile in the presence of lithium and zinc ions led to the isolation of novel 2,3,9,10,16,17-hexakis(butyloxy)-22,25-diaza-(1,10-phenanthrolino)[5,6-c_1]phthalocyaninato derivatives $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) and $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**), Scheme 1, respectively, in quite good yields. In addition to elemental analysis, both the MALDI-TOF and NMR spectroscopy clearly reveal the nature of these two novel unsymmetrical phenanthroline-fused phthalocyanine in a confirmed manner.

Results and discussion

Molecular design, synthesis, and characterization

In addition to their multifunctionalites, phthalocyanine compounds have also been very famous for their notorious aggregation properties associated with their large and rigid conjugated molecular structure.[15] Fusing an additional planar and rigid conjugated moiety like phenanthroline directly onto the phthalocyanine skeleton further enlarges the conjugated system of resulting compounds, which in turn induces an increase in the intermolecular π–π interaction and further intensifies their intrinsic aggregation behavior, resulting in enhanced difficulty in the isolation and purification of desired product. As a result, unsymmetrical phenanthroline-fused phthalocyanine derivatives with peripheral butyloxy groups were selected as the target compounds in the present work.

Unsymmetrical metal free 2,3,9,10,16,17-hexakis(*n*-butoxy)-22,25-diaza(1,10-phenanthrolino)[5,6-c_1]phthalocyanine $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) was synthesized in good yield by mixed cyclic tetramerization of 4,5-di(butyloxy)phthalonitrile[16] and 10,12-diimino-11*H*-pyrrolo[3,4-*b*]dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline[12*b*,17] with the lithium ion as template. This is also true for the synthesis of 2,3,9,10,16,17-hexakis(*n*-butoxy)-22,25-diaza(1,10-phenanthrolino)[5,6-c_1]phthalocyaninato zinc complex $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**) when the lithium ion was replaced by a zinc ion. Satisfactory elemental analysis results were obtained for these two newly prepared compounds after repeated column chromatography and recrystallization. The MALDI-TOF mass spectra of these two compounds clearly showed intense signals for the molecular ion $[MH]^+$, Fig. S1 (ESI†), clearly demonstrating their phenanthroline-fused phthalocyanine nature. Nevertheless, the unsymmetrical molecular structures for these two novel phthalocyanine compounds were unambiguously revealed by their ^1H NMR spectra as shown in Fig. 1 and S2 (ESI†).

As shown in Fig. 1, the ^1H NMR spectrum for $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) was recorded in $CDCl_3$. The signals at δ 8.96 (2H) and 7.10 (4H) are due to the α ring protons of $Pc(OC_4H_9)_6(dicqn)$, while the phenanthroline group resonates at δ 8.11–8.56 (2H) and 7.26–7.58 (4H). The six butyloxy groups resonate at δ 4.26–3.85 (12H, OCH_2), 2.15–1.88 (12H, OCH_2CH_2), 1.86–1.68 (12H, $OCH_2CH_2CH_2$), and 1.30–1.15 (18H, $OCH_2CH_2CH_2CH_3$). In a similar manner, assignments of the ^1H NMR spectrum for $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**) is reached, Fig. S2 (ESI†). However, it is noteworthy that the ^1H NMR spectrum for **2** was recorded in $CDCl_3$–[D_5]pyridine (10 : 1) due to the indistinguishable signals recorded in pure $CDCl_3$ associated with aggregation.

Electronic absorption spectra

The electronic absorption spectra of the two unsymmetrical phthalocyanines **1** and **2** in $CHCl_3$ were recorded and the data

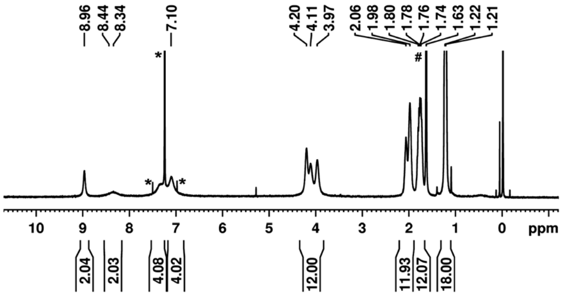
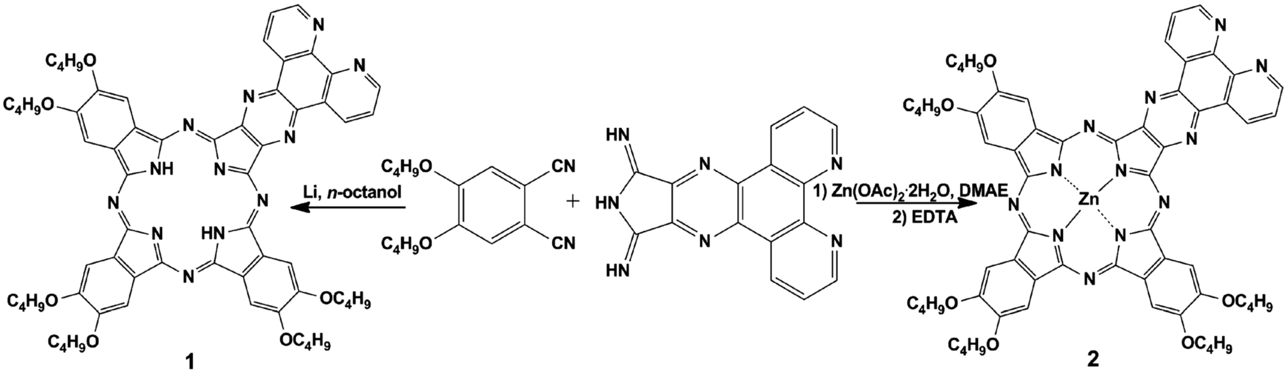


Fig. 1 ^1H NMR spectrum for $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) in $CDCl_3$. The signals due to residues of $CHCl_3$ and H_2O are denoted as * and #, respectively.



Scheme 1 Synthesis of $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) and $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**).

are summarized in Table S1 (ESI†). As shown in Fig. 2A, the metal free phenanthroline-fused phthalocyanine **1** shows an usual Soret band with a medium intensity at 354 nm. However, unlike other metal free phthalocyanine compounds with symmetrical molecular symmetry, the strong Q band at 696 nm with a shoulder at 626 nm of the unsymmetrical metal free phthalocyanine **1** remains unsplit, which also red-shifts in comparison with that for 2,3,9,10,16,17,22,23-octakis(butyloxy) phthalocyanine $H_2Pc(OC_4H_9)_8$ at 682 = (663 + 702)/2 nm in $CHCl_3$[18] associated with the unsymmetrically extended conjugated system. The weak band appearing at 458 nm in the electronic absorption spectrum of **1** is attributed to the $n \rightarrow \pi^*$ transitions due to the lone pair of electron of oxygen atom.[19] This is also true for the phenanthroline-fused phthalocyaninato zinc complex $Zn[Pc(OC_4H_9)_6\text{-}(dicqn)]$ (**2**), which in $CHCl_3$ shows the Soret band at 374 nm with medium intensity and Q absorption at 698 nm with strong intensity, respectively, Fig. 2B.

For the purpose of revealing the self-assembling properties of these two phenanthroline-fused phthalocyanine derivatives, the aggregates of **1** and **2** were prepared by the phase transfer method.[20] As a consequence, the electronic absorption spectra for the aggregates of both compounds dispersed in methanol are comparatively displayed in Fig. 2, which are very much different from those recorded in $CHCl_3$. Due to the significant intermolecular interaction in the self-assembled aggregates, obvious band broadening was observed in the electronic absorption spectra of the aggregate of **1** and **2**. In comparison with the chloroform solution spectrum, the main phthalocyanine Soret and Q bands of aggregates of **1** dispersed in methanol show a significant blue-shift from 354 and 696 nm to 335 and 631 nm, respectively. On the basis of Kasha's exciton theory,[21] significant blue shifts in the main absorption bands of **1** upon aggregation are typically a sign of the effective intermolecular π–π interaction in a face-to-face manner (*H* aggregation mode). Interestingly, introduction of a zinc ion into the central hole of the phenanthroline-fused phthalocyanine induces a large degree of red shift in the main Q absorption band from 698 nm in $CHCl_3$ to 729 nm upon the aggregation in methanol, with the Soret band remaining almost unchanged, Fig. 2B, indicating the different self-assembling properties of $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**) in methanol. Actually, on the basis of Kasha's exciton theory,[21] the large degree of red-shift of the Q absorption band of **2** upon aggregation in methanol implies that the molecules of compound **2** are enforced to adopt the *J*-aggregation mode depending on the strong intermolecular π–π interaction in a head-to-tail manner, revealing the effect of the zinc ion introduced onto the central of phthalocyanine ring on the molecular packing mode and in turn the morphology of nanostructures as detailed below.

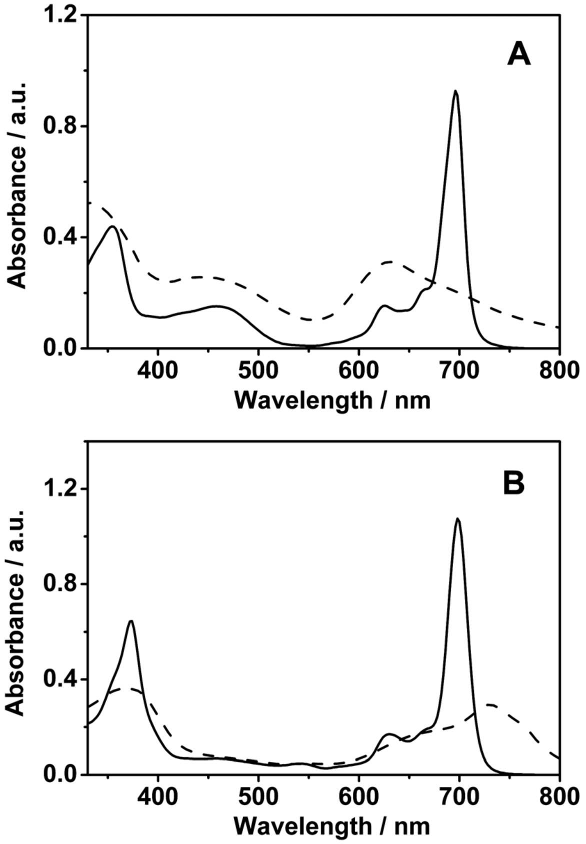


Fig. 2 Electronic absorption spectra of **1** (A) and **2** (B) in dilute $CHCl_3$ (solid line) and their aggregates dispersed in methanol (dashed line), respectively.

X-Ray diffraction patterns

The internal structures of self-assembled aggregates of **1** and **2** were investigated by X-ray diffraction (XRD) analysis, Fig. 3. As shown in Fig. 3A, in the low angle range, the XRD diagram for the aggregates of **1** formed in methanol shows a diffraction peak at $2\theta = 4.3°$, corresponding to 2.06 nm and originating from the (001) plane.[22] As can be seen from Fig. S3A (ESI†), the molecular dimension size of **1** is *ca.* 2.42 nm (length) × 2.22 nm (width) × 0.44 nm (thickness) obtained on the basis of geometry optimization and the energy minimized molecular structure using Gaussian 03 program at B3LYP/6-31G(d) level.[23] According to the XRD result and the simulated molecular structure of **1**, the unit cell consists of six molecules of metal free phthalocyanine **1**, Fig. 3C. The *d*-spacing of 2.06 nm could be attributed to the thickness along the perpendicular direction to the tetrapyrrole cores of neighbouring phthalocyanine molecules, implying a favorable molecular packing with co-facial conformation in this direction. In addition, the XRD pattern displays a well-defined peak at the wide angle region corresponding to the distance of 0.42 nm that relates to the liquid-like order of the alkyl chains.[24] It is worth noting that in the wide angle region, the XRD pattern also presents a sharp diffraction peak at 0.31 nm for the aggregates of **1** formed in methanol, assignable to the stacking distance between tetrapyrrole cores of neighbouring phthalocyanine molecules.[25] This, in combination with the electronic absorption spectroscopic result, therefore indicates the formation of *H*-aggregates for **1** in methanol depending on strong intermolecular π–π interaction, revealing the face-to-face molecular arrangement in the self-assembly aggregates, as displayed in Fig. 3C.

As shown in Fig. 3B, the XRD pattern for the aggregates of **2** formed in methanol shows a sharp diffraction peak at 1.95 nm in the low angle range, originating from the (100) plane,

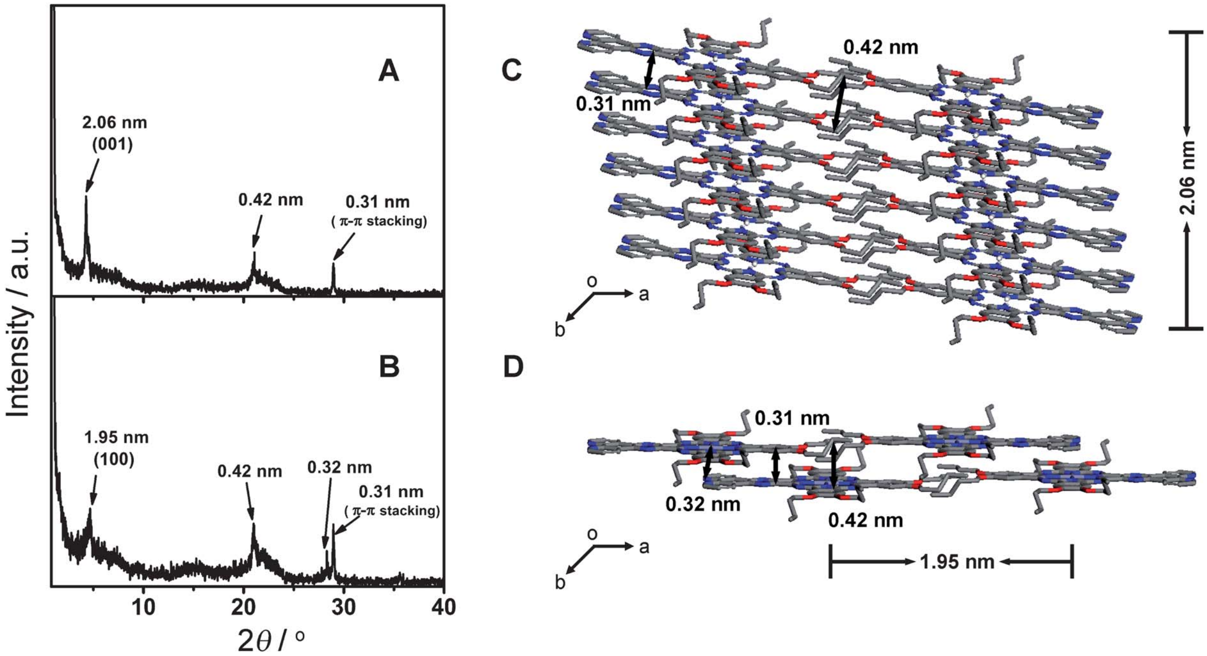


Fig. 3 X-Ray diffraction patterns of the nanostructures of **1** (A) and **2** (B) formed in methanol, respectively, and the schematic representation of the molecular packing mode in the nanostructures for **1** (C) and **2** (D) with all the hydrogen atoms omitted for clarity.

which should be assigned to the average length along the long axis of molecule **2**, Fig. 3D, on the basis of the energy-optimized structure of **2**, Fig. S3B (ESI†). Similarly to the metal free analogue, the well-defined peaks at 0.42 and 0.31 nm in the wide angle region of the XRD pattern for the aggregates of **2** are assigned to the liquid-like order of the alkyl chains and the stacking distance between tetrapyrrole cores of neighbouring phthalocyanine molecules, respectively. However, an additional diffraction peak at 0.32 nm exhibited in the XRD pattern of the aggregates of **2**, which is absent in that of **1**, is associated with the Zn–N metal–ligand coordination bonding interaction between the phenanthroline group of one molecule and the zinc center of a neighboring phthalocyaninato zinc molecule.[22,26] This result is in line with the *J* aggregation mode revealed by UV-vis absorption spectroscopy as detailed above.

At the end of this section, it is worth noting that despite the fact that two peaks at different $2\theta = ca.$ 21 and 29 degrees (corresponding to two *d*-spacings of 0.42 and 0.31 nm) should have independent indices. However, their Miller indices could not be provided *via* the insufficient X-ray diffraction data of self-assembled aggregates of **1** and **2**, which is common for the organic nanostructures with a rigid conjugated core and soft peripheral substituents in the present case.[27]

Morphology of the aggregates

The morphology of the aggregates formed was examined by scanning electron microscopy (SEM). In accordance with the electronic absorption spectroscopic and XRD results, different morphologies were observed for the aggregates fabricated from **1** and **2** in methanol, Fig. 4. Depending mainly on the intermolecular π–π interaction in cooperation with the van der Waals interaction, molecules of metal free phenanthroline-fused phthalocyanine **1** in methanol assemble into long one-dimensional nanowires with uniform size and an average width of *ca.* 310 nm and over 10 μm in length, Fig. 4A. However,

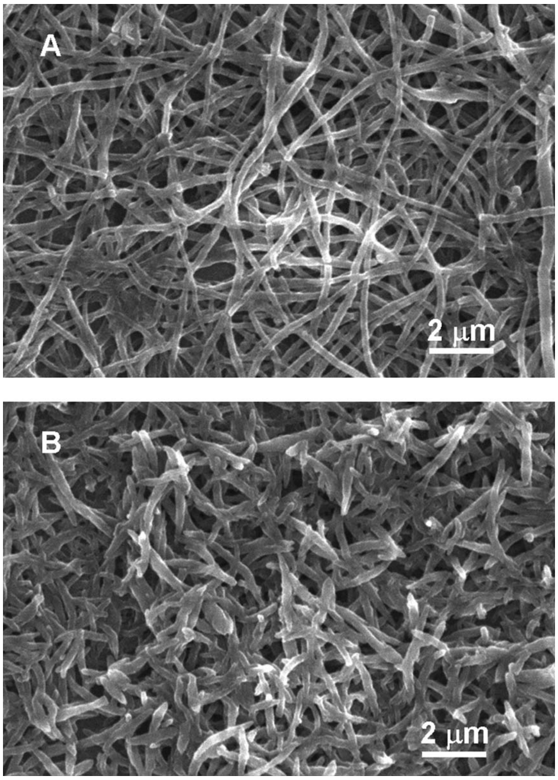


Fig. 4 SEM images of self-assembled nanostructures of **1** and **2**. (A) Nanowires formed from compound **1** and (B) ribbonlike nanobundles formed from compound **2**.

self-assembly of **2** in methanol results in nanostructures with the ribbonlike nanobundles, about 300 nm in width and 2–4 μm in length, Fig. 4B, indicating again the effect of zinc ion introduced onto the central of phthalocyanine ring on the self-assembly properties of these compounds. It is worth noting that the size- and morphology-adjustable nanostructures are highly desired for fabricating nano-scale molecular (opto)-electronic devices which often require a wide variety of channel lengths to achieve the optimum gate or optical modulation.

I–V properties

To demonstrate the potential application of these nanostructures fabricated from novel phenanthroline-fused phthalocyanines **1** and **2** in nano-electronic devices, Au electrodes were thermally evaporated onto these well defined nanostructures to measure their current–voltage characteristics. The conductivity, σ, can be calculated by the following equation:[28] $\sigma = d \times I/[(2n - 1) \times L \times h \times V]$, where d is the interelectrode spacing, I the current, n the number of electrode digits, L the overlapping length of the electrodes, h the calculated thickness of the aggregates, and V the voltage. Fig. 5 shows the current–voltage (*I–V*) characteristics of nanostructures fabricated from **1** and **2**, respectively. According to the SEM images of the aggregates of **1** and **2**, the channel coverage of their devices is estimated to be about 80 and 100%, respectively. The conductive capability of nanowires fabricated from metal free phenanthroline-fused phthalocyanine derivative **1**, 1.0×10^{-4} S cm^{-1}, is quite high, even about 2 orders of magnitude higher than that measured from the self-assembled aggregates of other metal free phthalocyanine systems[22b,29] and about 1 order of magnitude higher than that of undoped silicon[30] most probably due to the long-range one-dimensional π–π stacking which favors the conductivity through face-to-face intermolecular π-delocalization. However, the conductivity of the nanostructures of **2** is a bit lower with a value of about 4.4×10^{-7} S cm^{-1}. The good semiconducting properties of these aggregates, in particular, the one-dimensional nanowires fabricated from metal-free **1** clearly reveal their great potential applications in a wide range of nano-electronic and sensory devices.

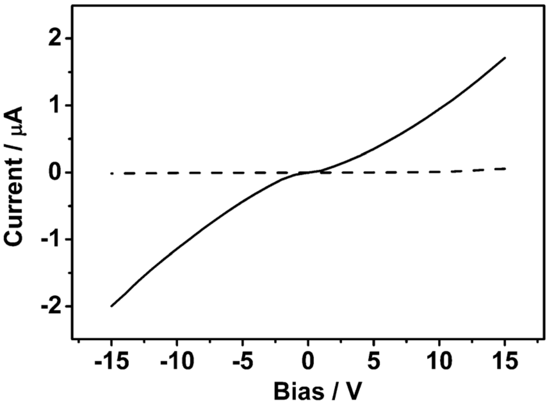


Fig. 5 *I–V* curves measured on the nanowires formed from **1** (solid line) and ribbonlike nanobundles formed from **2** in methanol (dash line) from −15 V to 15 V, respectively.

Conclusions

Briefly summarizing above, two novel unsymmetrical phenanthroline-fused phthalocyanine derivatives have been designed, synthesized, and unambiguously characterized by the mass and NMR spectroscopy. The self-assembled nanostructures fabricated from these two compounds, in particular the metal-free one exhibit good semiconducting properties, revealing their potential applications in nano-electronic and sensory devices. The present result, representing the first example of organic nanostructures self-assembled from unsymmetrical phenanthroline-fused phthalocyanine derivatives, will be helpful for the design, synthesis, and self-assembly properties of phthalocyanine derivatives with extended π-conjugation.

Experimental section

Measurements

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ or in $CDCl_3$–[D_5]Pyridine (10 : 1). Spectra were referenced internally using the residual solvent resonance ($\delta = 7.26$ for ^{1}H NMR) relative to $SiMe_4$. Electronic absorption spectra were recorded with a HITACHI U-2910 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed on an Elementar Vavio El III. X-Ray diffraction experiments were carried out on a Rigaku D/max-γB X-ray diffractometer. SEM images were obtained using a JEOL JSM-6700F field-emission scanning electron microscopy. For SEM imaging, Au (1–2 nm) was sputtered onto the grids to prevent charging effects and to improve the image clarity.

Chemicals

Methanol and *n*-octanol were distilled from sodium. Dimethylaminoethanol (DMAE) was distilled from K_2CO_3. Column chromatography was carried out on silica gel column (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. All other solvents and reagents such as $Zn(OAc)_2 \cdot 2H_2O$ were used as received. The compounds of 4,5-di(butyloxy)phthalonitrile and 10,12-diimino-11*H*-pyrrolo[3,4-*b*]dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline were prepared according to published procedures.[12b,16,17] EDTA was used to chelate the excess zinc ions in the procedure of the synthesis of $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**) following the early report.[10a]

Synthesis of metal free 2,3,9,10,16,17-hexakis(*n*-butoxy)-22,25-diaza-(1,10-phenanthrolino)[5,6-*c*$_1$]phthalocyanine compound $H_2[Pc(OC_4H_9)_6(dicqn)]$ (1)

Li (10 mg, 1.43 mmol) in dry *n*-octanol (2.0 mL) was heated to 140 °C for 1 h under N_2 atmosphere. After being cooled to room temperature, a mixture containing 4,5-di(butyloxy)phthalonitrile (163 mg, 0.60 mmol) and 10,12-diimino-11*H*-pyrrolo[3,4 *b*] dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (90 mg, 0.30 mmol) was added to it. The resulting mixture was heated at 140 °C for another 12 h and then cooled to room temperature. The volatiles were evaporated *in vacuo* and the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. A green band containing symmetrical metal-free 2,3,9,10,16,17,23,24-octakis(butyloxy) phthalocyanine $H_2[Pc(OC_4H_9)_8]$ was eluted first. Then $CHCl_3$–triethylamine (100 : 1) developed a second green band which was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure unsymmetrical metal free phthalocyanine target compound $H_2[Pc(OC_4H_9)_6(dicqn)]$ (**1**) as dark-green powder (15 mg, 6%). UV-vis [λ_{max} (nm) (log(ε), M^{-1} cm^{-1})]: $CHCl_3$, 354 (4.93), 458 (4.47), 626 (4.47), 664 (4.61), 696 (5.25). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (2H, phthalocyanine), 8.11–8.56 (2H, phenanthroline), 7.26–7.58 (4H, phenanthroline), 7.10 (4H, phthalocyanine), 4.26–3.85 (12H, OCH_2), 2.15–1.88 (12H, OCH_2CH_2), 1.86–1.68 (12H, $OCH_2CH_2CH_2$), 1.30–1.15 (18H, $OCH_2CH_2CH_2CH_3$) ppm. MALDI-TOF MS: an isotopic cluster peaking at *m*/*z* 1101.7, calcd for $C_{240}H_{120}Eu_2F_{24}N_{24}O_{24}$, $[MH]^+$ 1101.5. Anal. calcd for $C_{64}H_{68}N_{12}O_6\cdot0.75CHCl_3$: C, 65.31; H, 5.82; N, 14.11; found C, 65.05; H, 6.17; N, 13.94%.

Synthesis of 2,3,9,10,16,17-hexakis(*n*-butoxy)-22,25-diaza-(1,10-phenanthrolino)[5,6-c_1]phthalocyaninato zinc complex $Zn[Pc(OC_4H_9)_6(dicqn)]$ (2)

A mixture of 4,5-di(butyloxy)phthalonitrile (163 mg, 0.60 mmol), 10,12-diimino-11*H*-pyrrolo[3,4-*b*]dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (90 mg, 0.30 mmol), and $Zn(OAc)_2\cdot2H_2O$ (51 mg, 0.23 mmol) in DMAE (5 mL) was heated to 145 °C under an N_2 atmosphere for 12 h and then cooled down to 100 °C. To the resulting solution was added EDTA (112 mg, 0.3 mmol) and the resulting mixture was further heated at this temperature for another 12 h. After being cooled to room temperature, the volatiles were evaporated *in vacuo* and the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. A green band containing the symmetrical 2,3,9,10,16,17,23,24-octakis(butyloxy)phthalocyaninato zinc complex $Zn[Pc(OC_4H_9)_8]$ was eluted first. Then $CHCl_3$–triethylamine (100 : 1) developed a dark-green band which was collected and rotary evaporated. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure unsymmetrical phthalocyaninato zinc complex $Zn[Pc(OC_4H_9)_6(dicqn)]$ (**2**) as dark-green powder (33 mg, 12%). UV-vis [λ_{max} (nm) (log(ε), M^{-1} cm^{-1})]: $CHCl_3$, 374 (5.10), 629 (4.53), 668 (4.58), 698 (5.10). ^{1}H NMR (400 MHz, $CDCl_3$–[D_5]Pyridine (10 : 1)): δ = 10.11–7.40 (12H, Ph-*H* of phenanthroline-fused phthalocyanine), 5.01–3.98 (12H, OCH_2), 2.32–1.98 (12H, OCH_2CH_2), 1.98–1.58 (12H, $OCH_2CH_2CH_2$), 1.30–1.15 (18H, $OCH_2CH_2CH_2CH_3$) ppm. MALDI-TOF MS: an isotopic cluster peaking at *m*/*z* 1163.6, calcd for $C_{240}H_{120}Eu_2F_{24}N_{24}O_{24}$, $[MH]^+$ 1163.5. Anal. calcd for $C_{64}H_{66}N_{12}O_6Zn\cdot0.75CHCl_3$: C, 62.01; H, 5.45; N, 13.87; found C, 62.01; H, 5.45; N, 13.40%.

Preparation of self-assembled aggregates

The self-assembled aggregates of the two compounds **1** and **2** were fabricated by the phase transfer method according to the following procedure. A minimum volume (20–50 μL) of concentrated chloroform of compounds (**1** and **2**) (1 mM) was injected rapidly into a large volume of methanol (2.5 mL) and subsequently mixed with a microinjector. After being kept at room temperature for 24 h, the aggregates were used to observe the aggregate behaviours. The results were reproducible under the experimental conditions described above. Substrates used in the present study were successively cleaned with pure water, acetone, and methanol.

Device fabrication

A volume of 20 μL of concentrated chloroform solution for **1** or **2** (1 mM) was injected rapidly into a large volume of methanol (2.5 mL). After being kept at room temperature for 24 h, the aggregates obtained were cast onto one SiO_2/Si substrate (1.1 cm × 1.3 cm) uniformly. After the solvent was evaporated, the Au electrodes were thermally evaporated onto the structures by using a shadow mask. These electrodes have a interelectrode spacing (*d*) of 0.24 mm, the overlapping length of the electrodes of (*L*) of 2.6 mm, the number of electrode digits (*n*) of 6, and the calculated thickness of the aggregates (*h*) of about 120 nm. The current–voltage characteristics were obtained with a Keithley 4200 semiconductor characterization system at room temperature in air.

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