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Novel Multinuclear Phthalocyanine-fused Molecular Nanoarrays. Synthesis, Spectroscopy, and Semiconducting Property

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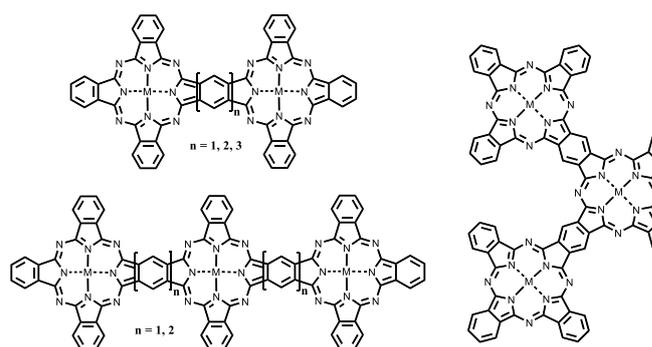
Abstract: The post-cyclization strategy rather than conventional ante-cyclotetramerization method was employed for the synthesis of novel multinuclear phthalocyanine-fused molecular nanoarrays. Reaction of 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-23,24-diaminophthalocyaninato zinc(II) with 2,7-di-tert-butylpyrene-4,5-dione, 2,7-di-tert-butylpyrene-4,5,9,10-tetraone, and hexaketocyclohexane in refluxing acetic acid afforded corresponding mono/bi/trinuclear phthalocyanine-fused zinc complexes (Pz-pyrene){Zn[Pc(OC₆H₉)₆]} (1), (Pz₂-pyrene){Zn[Pc(OC₆H₉)₆]}₂ (2), {(HAT){Zn[Pc(OC₆H₉)₆]}₃ (3) in 46, 13, and 25% yield, respectively, extending the scope of multinuclear phthalocyanine-fused nanoarrays with different molecular skeletons. In particular, the self-assembly behavior of the trinuclear phthalocyanine 3 in THF-CH₃CN was investigated in a systematic manner by electronic absorption spectroscopy and scanning electron microscopy (SEM) with the nanorods fabricated showing interesting semiconducting properties, suggesting the good application potential of these multinuclear phthalocyanine-fused molecular nanoarrays.

Introduction

Conjugated two-dimensional (2D) carbon monolayer nanosheet materials have attracted significant attention because of their unique physical and chemical properties associated with their two-dimensional conjugated electronic structure and great application potentials in electronics, photonics, and spintronics.^[1-3] However, all the research in this field seems to be limited to graphenes/graphynes.^[4,5] Further efforts have been paid in this direction, resulting in the development of conjugated two-dimensional covalent organic frameworks (COFs) that allow the integration of organic units with atomic precision into the 2D structure.^[6] However, thus far the conjugated 2D COFs have also been limited to those constructed from few certain monomers such as benzene-1,2,4,5-tetraamine and hexaketocyclohexane.^[7,8] Developing new conjugated 2D carbon materials with well defined composition and structure therefore becomes highly desired in this field. Due to their intrinsic photonic, electronic, chemical, and physical properties, both porphyrins and phthalocyanines with planar conjugated skeleton

appear to be good building block for the construction of new conjugated 2D materials.^[9]

Despite the still extremely limited reports of truly conjugated tetrapyrrole-fused 2D material at this stage,^[10] the effort paid towards this direction has resulted in a series of multinuclear porphyrin/phthalocyanine-fused molecular arrays with further extended conjugated system.^[11-23] Due to the easy functionalization and relatively high reactivity of porphyrin chromophore, multinuclear porphyrin-fused arrays have usually been prepared by utilizing the so-called post-cyclization strategy with various kinds of porphyrin moieties as starting material. This however, is definitely not the case for the multinuclear phthalocyanine-fused analogues. Replacement of the meso-CH bridges in the tetrapyrrole skeleton of porphyrin chromophore by N atoms in phthalocyanine ring together with the fusion of four peripheral benzene moieties leads to significantly increased difficulty in functionalizing the latter tetrapyrrole species, rendering the thus far-reported multinuclear phthalocyanine-fused systems unexceptionally synthesized by using the so-called ante-cyclization method with tetracyanobenzene and phthalonitrile as starting materials.^[24,25] Nevertheless, because of the limited choice of tetracyanobenzene precursors, the so-far reported phthalocyanine-fused molecular arrays have also been limited to the scope of benzene/naphthalene/anthracene-bridged bi/trinuclear systems with either linear or triangular shape, Scheme 1. As a result, developing new pathway towards preparing novel multinuclear phthalocyanine-fused derivatives with novel molecular skeletons still remains a challenge in this field. Fortunately, quite lately an unprecedented binuclear phthalocyanine dimers sharing one common pyrazine moiety was synthesized by using a post-cyclization strategy.^[26]



Scheme 1. Schematic molecular structures of the existing linear and rectangular bi/trinuclear phthalocyanine compounds.

In the present paper, as part of our continuous efforts towards the phthalocyanine-based conjugated 2D materials, we describe the synthesis, spectroscopic, and electrochemical characterization of novel multinuclear phthalocyanine-fused arrays, namely 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-

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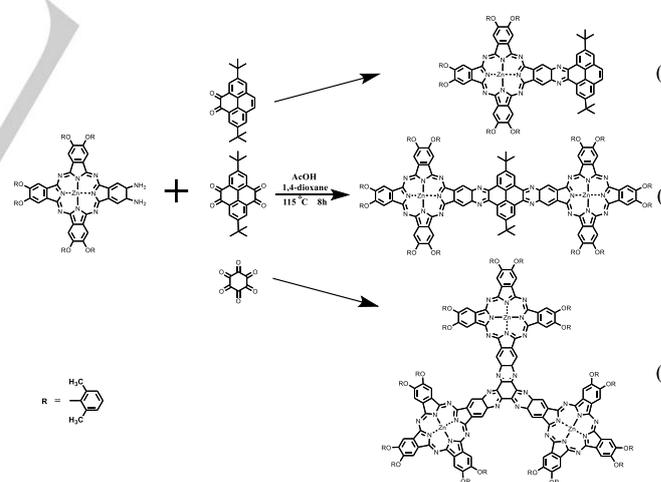
23,24-diaza(2,7-di-tert-butylpyrene)[4,5]phthalocyaninato zinc complex (Pz-pyrene){Zn[Pc(OC₈H₉)₆]} (1), bis(2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)phthalocyaninato zinc)[23,24]-diaza(2,7-di-tert-butylpyrene) (Pz₂-pyrene){Zn[Pc(OC₈H₉)₆]}₂ (2), tris(2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)phthalocyaninato zinc)[23,24-b,n,h]-1,4,5,8,9,12-hexaazatriphenylene {(HAT){Zn[Pc(OC₈H₉)₆]}₃} (3) [Pz-pyrene = 2,7-di-tert-butylpyrene-[4,5]-pyrazine, Pz₂-pyrene = 2,7-di-tert-butylpyrene -[4,5,9,10]-dipyrazine, HAT = 1,4,5,8,9,12-hexaazatriphenylene, Zn[Pc(OC₈H₉)₆] = 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)phthalocyaninato zinc], Scheme 2. It is worth noting that unlike the previously reported dimeric/trimeric phthalocyanine compounds that are bridged by benzene/naphthalene/anthracene moiety, in the present case these new multinuclear phthalocyanine-fused molecular nanoarrays were prepared through a post-cyclization strategy with unsymmetrical diamino substituted phthalocyanine and 2,7-di-tert-butylpyrene-4,5-dione/2,7-di-tert-butylpyrene-4,5,9,10-tetraone/ hexaketocyclohexane as starting materials, providing a new pathway towards the synthesis of truly tetrapyrrole-fused 2D materials with well defined composition and structure, nitrogen-containing conjugated nature, tuneable central metal ions, and therefore extensive application potentials. Nevertheless, the self-assembly behavior of the trinuclear phthalocyanine 3 in THF-CH₃CN was investigated in a systematic manner by electronic absorption spectroscopy and scanning electron microscopy (SEM) with the nanorods fabricated showing interesting semiconducting properties, suggesting the good application potential of these multinuclear phthalocyanine-fused molecular nanoarrays. At the end of this section, it is however noteworthy that during the finalization of the present result, another star-shaped conjugated triphthalocyaninehexaazatriphenylene, similar to our compound 3, was reported by Sastre-Santos,^[27] demonstrating again the efficiency of the present synthesis strategy.

Results and Discussion

Synthesis and spectroscopic characterization.

As mentioned above phthalocyanines are relatively hard to be functionalized, resulting in the difficulty in choosing suitable functionalized phthalocyanine derivatives as starting material for trying the post-cyclization reaction towards the construction of novel multinuclear phthalocyanine-fused systems. Fortunately, inspired by the successful Schiff-base chemistry with efficient C=N bond formation reaction between C=O and NH₂ even in the tetrapyrrole field,^[19,26,32] the unsymmetrical diamino substituted phthalocyanine compound seems to be a good starting material for further post-cyclization reaction. In the present case, 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-23,24-diaminophthalocyaninato zinc(II) Zn[Pc(OC₈H₉)₆(NH₂)₂] was prepared following the published procedure.^[28] For the convenience of future researchers, this newly prepared diamino substituted phthalocyanine compound was characterized by a series of spectroscopic techniques as detailed in Supporting

Information. Further reaction of which with 2,7-di-tert-butylpyrene-4,5-dione in refluxing acetic acid afforded 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-23,24-diaza(2,7-di-tert-butylpyrene)[4,5]phthalocyaninato zinc complex (Pz-pyrene){Zn[Pc(OC₈H₉)₆]} (1) in good yield, 46%, demonstrating the good reactivity of the diamino groups of Zn[Pc(OC₈H₉)₆(NH₂)₂] with diketone groups towards the formation of pyrazine moiety. As a consequence, 2,7-di-tert-butylpyrene-4,5,9,10-tetraone was selected to react with Zn[Pc(OC₈H₉)₆(NH₂)₂], leading to the formation of bis(2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)phthalocyaninato zinc)[23,24]-diaza(2,7-di-tert-butylpyrene) (Pz₂-pyrene){Zn[Pc(OC₈H₉)₆]}₂ (2) according to the mass spectroscopic result, Figure S1 (Supporting Information). This dinuclear phthalocyanine-fused skeleton, however, was quite hard to get dissolved in common organic solvents after purification in the yield of 13%. Again fortunately, reaction between hexaketocyclohexane and unsymmetrical 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-23,24-diaminophthalocyaninato zinc(II) Zn[Pc(OC₈H₉)₆(NH₂)₂] afforded the tris(2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)phthalocyaninato zinc)[23,24-b,n,h]-1,4,5,8,9,12-hexaazatriphenylene {(HAT){Zn[Pc(OC₈H₉)₆]}₃} (3) with novel cloverleaf-shaped planar conjugated molecular structure and good stability in the yield of 25%, not only extending the scope of multinuclear phthalocyanine-fused arrays but more importantly clearly revealing the efficiency of this new post-cyclization pathway (by means of the Schiff-base chemistry) towards the synthesis of multinuclear phthalocyanine-fused materials.



Scheme 2. Synthesis of mono/bi/trinuclear phthalocyanine-fused molecular arrays (Pz-pyrene){Zn[Pc(OC₈H₉)₆]} (1), (Pz₂-pyrene){Zn[Pc(OC₈H₉)₆]}₂ (2), and (HAT){Zn[Pc(OC₈H₉)₆]}₃ (3).

These newly prepared phthalocyanine-fused derivatives gave satisfactory elemental analysis result. As shown in Figures S1-S3 (Supporting Information), their MALDI-TOF mass spectra clearly show intense signal for the corresponding protonated

molecular ions $[M]^+$. These compounds were further characterized with a range of spectroscopic methods including ^1H NMR, electronic absorption, magnetic circular dichroism and IR spectroscopy.

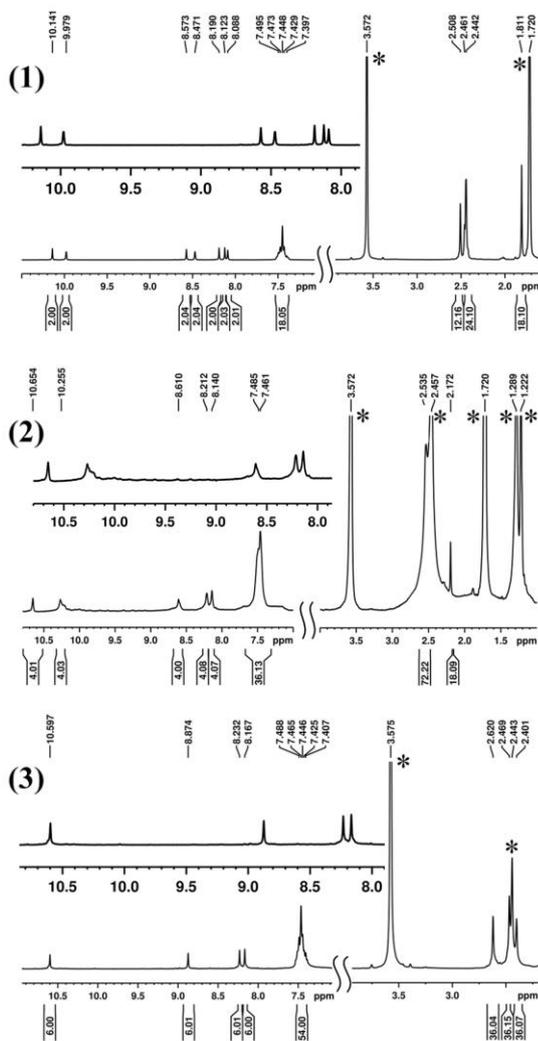


Figure 1. ^1H NMR spectra of **1**, **2**, and **3** in $\text{THF-}d_8$ at 298K; * indicates the signals for residual solvent.

^1H NMR spectra of **1**, **2**, and **3** were recorded in $\text{THF-}d_8$. As shown in Figure 1, all the signals could be unambiguously assigned even without the help of two-dimensional NMR spectroscopy. In the ^1H NMR spectrum of **1**, due to the unsymmetrically substituted pyrene group, the Pc α protons give four singlets at $\delta = 10.14$, 8.57, 8.19, and 8.12 ppm, respectively, owing to the C_{2h} molecular symmetry of this compound. The signals observed at $\delta = 9.98$, 8.47, and 8.09 ppm are attributed to the three types of protons of the pyrene moiety. Signals for the aromatic protons of 2,6-dimethylphenoxy substituents exhibit multiplets at $\delta = 7.50$ –7.40 ppm. The methyl protons and tert-butyl protons give singlets at $\delta = 2.51$, 2.46, 2.44, and 1.81

ppm with the integral ratio of 2:2:2:3. This is also true for **2**, Figure 1. Owing to the C_{2v} molecular symmetry of this compound, the signals at $\delta = 10.65$, 10.26, 8.21, 8.14, and 8.61 ppm can be assigned to the nonperipheral phthalocyanine protons and the pyrene moiety, respectively. In addition, the benzene protons of twelve 2,6-dimethylphenoxy groups resonate at $\delta = 7.49$ –7.46 and methyl ones at 2.54 ppm. The tert-butyl protons give singlets at $\delta = 2.17$ ppm. In a similar manner, the four singlets at $\delta = 10.60$, 8.87, 8.23, and 8.17 ppm in the ^1H NMR spectrum of **3** are assigned to the four Pc α protons, Figure 1. The three singlets at $\delta = 2.62$, 2.47, and 2.40 ppm with the integral ratio of 1:1:1 due to the three methyl protons clearly reveals the C_{3v} molecular symmetry of this trinuclear phthalocyanine-fused skeleton. Also similar to **1** and **2**, a multiplet signal observed at $\delta = 7.49$ –7.41 ppm was attributed to the aromatic protons of the 2,6-dimethylphenoxy substituents.

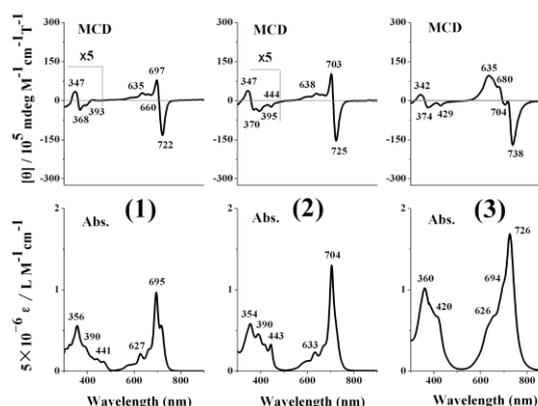


Figure 2. MCD and electronic absorption spectra of **1**, **2**, and **3** in THF.

The electronic absorption spectra and magnetic circular dichroism (MCD) spectra of **1-3** and $\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$ {2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyaninato zinc(II)} were recorded in THF. Figures 2 and S4 (Supporting Information) compare their electronic absorption spectra in the range of 300–900 nm. As can be seen, their spectra show a typical phthalocyanine Soret band at 354–360 nm with medium intensity and a very strong Q band at 695–726 nm accompanied by a weak vibronic shoulder at 626–633 nm. Interestingly, in comparison with the monomeric phthalocyanine compound $\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$, the Q band for the pyrene-fused phthalocyanine derivatives **1-3** take an obvious red shift by 471, 654, and 1084 cm^{-1} due to the extended conjugated system. In addition, the electronic absorption spectra of a series of solutions of **3** in THF with the concentration ranging from 2.0×10^{-7} to $5.0 \times 10^{-6} \text{ mol L}^{-1}$ were recorded to disclose the aggregation behaviour of the trimer **3**.^[29] As shown in Figure 3, no additional absorption band associated with aggregation was revealed. Nevertheless, the Beer-Lambert law was strictly obeyed for **3** in this whole concentration range, excluding the

molecular aggregation of **3** in this concentration range and indicating the intrinsic molecular electronic absorption nature of the spectra shown in both Figures 2 and 3 for this trimeric compound.

Analysis of MCD spectra is based on the three Faraday terms, A, B, and C. In the MCD spectrum of the monomeric phthalocyanine compound $\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$, significant dispersion-type signals with strong negative to positive peaks observed at 681/672 nm in the Q-band region and weak negative to positive peaks at 361/335 nm in the Soret-band range can be attributed to the Faraday A term. In the MCD spectrum of **1**, significant dispersion-type signals with strong negative to positive peaks observed at 722/697 nm in the Q-band region and weak negative to positive peaks at 368/347 nm in the Soret-band range can be attributed to the Faraday A term. These Faraday A term bands with observable intensity represent characteristic electron transitions to the degenerated excited states for tetrapyrrole π -conjugated macrocycle compounds, revealing the degenerated Soret and in particular Q-band absorption for compound **1** despite its diminished molecular symmetry. This in turn indicates the very small effect of the peripheral pyrene substituent on the electronic structure of the central phthalocyanine chromophore. The MCD spectrum of **2** exhibits nearly the same feature as for **1** over the entire region, with negative to positive peaks at the regions of 725/703 and 370/347 nm. In a different manner, in the MCD spectrum of the trimeric compound **3**, relatively weak negative to positive peaks at 704/680 and 374/342 nm centered at 694 and 360 nm, respectively, in the electronic absorption spectrum can be attributed to the pseudo-Faraday A term due to the relatively diminished molecular symmetry.^[30] Actually, due to the lack of three-fold or higher axes of symmetry, the MCD spectrum of **3** is dominated by the negatively and positively-signed Faraday B terms being located at 738 nm and 635 nm, corresponding to the Q bands observed at 726 and 626 nm in the electronic absorption spectrum.

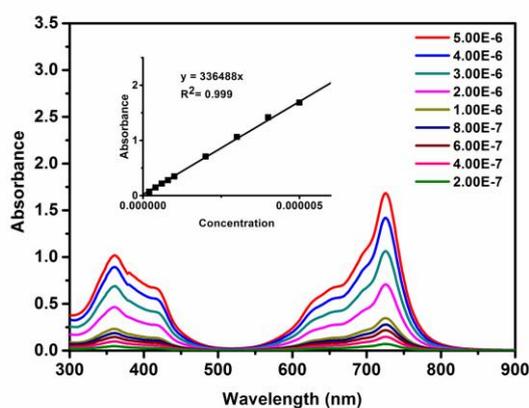


Figure 3. Electronic absorption spectra of **3** in THF at the concentration ranging from 2.0×10^{-7} to 5.0×10^{-6} mol L^{-1} with the inset showing the plot of absorbance versus concentration.

Figure S5 (Supporting Information) shows the IR spectra of **1**, **2**, and **3**. As can be seen, in addition to the absorption bands contributed from the aromatic Pc macrocycle (including the wagging and torsion vibrations of C-H groups, isoindole ring stretching vibrations, and the C=N aza group stretching vibrations), the absorptions observed at 1273-1274 and 1086-1093 cm^{-1} are contributed by the asymmetric and symmetric C-O-C stretching vibrations, while the intense bands observed at 2920-2921 and 2850-2851 cm^{-1} are due to the C-H stretching vibrations of the $-\text{CH}_3$ groups of the 2,6-dimethylphenoxy side chains.^[31]

Table 1. Half-wave redox potentials of the compounds **1**, **2**, **3**, and $\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$ (V vs SCE) in $\text{CH}_2\text{Cl}_2/\text{pyridine}$ (V/V = 100:1) containing 0.1 M $[\text{NBu}_4][\text{ClO}_4]$.

Compound	Oxd ₂	Oxd ₁	Red ₁	Red ₂	$\Delta E_{1/2}^{\circ}$ ^[a]
1		+0.76	-0.85	-1.18	1.61
2	+1.30	+0.76	-0.80	-1.05	1.56
3	+1.25	+0.75	-0.74	-1.01	1.49
$\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$ ^[b]		+0.61	-1.02	-1.38	1.63

^[a] $\Delta E_{1/2}^{\circ}$ is the potential difference between the first oxidation and the first reduction processes, i.e. the HOMO-LUMO gap of the complexes: $\Delta E_{1/2}^{\circ} = \text{Oxd}_1 - \text{Red}_1$. ^[b] Cited from Ref. 30.

Electrochemical Properties.

The electrochemical behavior of **1**, **2**, and **3** was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in $\text{CH}_2\text{Cl}_2/\text{pyridine}$ (V/V = 100:1), Figures S6 and S7 (Supporting Information). The results are summarized in Table 1. As can be seen, **1** shows one quasi-reversible one-electron oxidation at +0.76 V and two quasi-reversible one-electron reductions at -0.85 and -1.18 V. For the compound **2**, there are two quasi-reversible one-electron oxidations at +1.30 and +0.76 V and two quasi-reversible one-electron reductions at -0.80 and -1.05 V, respectively. In a similar manner, the compound **3** exhibits two quasi-reversible one-electron oxidations at +1.25 and +0.75 V together with two quasi-reversible one-electron reductions at -0.74 and -1.01 V. Since the zinc metal ion cannot be reduced and oxidized in this redox range, all the processes are attributed to the addition of, or removal of, one electron to/from the ligand-based orbitals. It is worth noting that all the redox potentials observed for compounds **1-3** show obvious shift to the positive direction relative to those of $\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$, indicating the electron-withdrawing nature of the pyrazine moiety. The HOMO-LUMO gaps of **1**, **2**, and **3** calculated by the potential difference between the first oxidation and first reduction ($\Delta E_{1/2}^{\circ}$) are 1.61, 1.56 and 1.49 V, respectively. Comparison of the values with that for the monomeric compound $\text{Zn}[\text{Pc}(\text{OC}_8\text{H}_9)_8]$, ca. 1.63 V,^[32] reveals the enlargement in the conjugated electronic structure of **1-3**. It is worth noting that both the HOMO and LOMO energies of **1-3** calculated at -5.20, -5.20, -5.19 eV and -3.59, -3.64, -3.70 eV just locate in the energy range that are for good semiconductors,^[33] respectively, revealing the potential of these novel multinuclear

phthalocyanine-fused molecular nanoarrays in electronic devices.

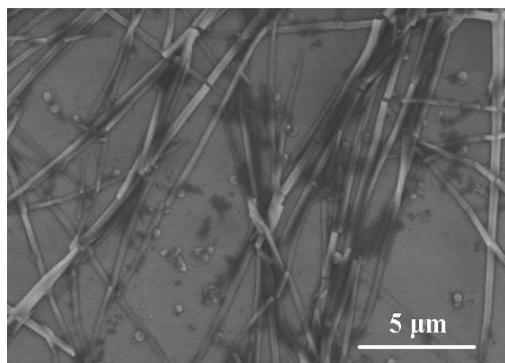


Figure 4. SEM images of nanostructures of the trinuclear phthalocyanine **3** prepared by drop-casting 5 μL 1×10^{-5} mol L^{-1} THF solution followed by 5 μL acetonitrile onto the surface of the SiO_2 substrate at 30°C .

Self-assembly nanostructures and semiconducting property of **3**.

The self-assembling behaviors of the trimeric compound **3** in different solvent systems were studied in a systematic manner by scanning electron microscopy (SEM) and electronic absorption spectroscopy. Samples were prepared by casting a drop of 5 μL of the trinuclear phthalocyanine **3** solution (in THF, concentration 1×10^{-5} mol L^{-1}) onto the surface of SiO_2 substrate, then injected 5 μL of poor solvents including methanol, ethanol, *n*-butanol, *n*-hexanol, *n*-octanol, or acetonitrile, at 30°C , respectively. As shown in Figure S11 (Supporting Information), trimeric compound **3** self-assembled into aggregates with different morphology including nanospheres, nanorods, and furcated nanorods, respectively, at different solvent systems depending on the intermolecular π - π interaction in cooperation with the van der Waals interaction and the solvent effect. By employing acetonitrile as the poor solvent, **3** assembled into nanostructures with rod-like morphology with uniform size with the length over 10 μm and average width of 400 nm, Figure 4. Figure 5 compares the electronic absorption spectra of the film cast from a THF/ CH_3CN (V/V, 1/1) trinuclear phthalocyanine **3** solution, **3** in THF solution, and **3** in THF/ CH_3CN (V/V, 1/1) solution. In comparison with the electronic absorption spectra of **3** in THF and the film cast from a THF/ CH_3CN (V/V, 1/1), the phthalocyanine Q-band of the aggregates of **3** shows a significant blue-shift from 726 to 708 nm, indicating the formation of *H*-type (face-to-face) nanostructures in THF/ CH_3CN and effective π - π interaction between neighboring trimeric molecules.^[34,35] Further support for this point comes from the change in the electronic absorption spectra of **3** in different volume ratios of THF/ CH_3CN mixed solvent, Figure S12 (Supporting Information).

For the purpose of exploring the application potential of the novel multinuclear phthalocyanine-fused molecular nanoarrays in electronic devices, single nanorod obtained from the trinuclear

phthalocyanine **3** in THF/ CH_3CN was fabricated onto the silicon slice with Au electrodes to measure the current-voltage characteristics, Figure 6. According to the equation reported in the literature:^[33] $\sigma = dI/(l^2 \times V)$, where d is the length of the measured single nanorod between the electrodes, I the current, l the width of the nanorods, and V the voltage, the electric conductivity of the nanorod of **3** fabricated at the substrate temperature of 30°C was calculated to be 1.25×10^{-4} S/cm, indicating its semiconducting nature.

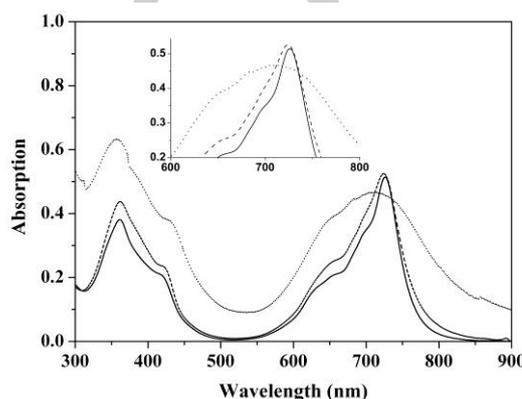


Figure 5. UV-vis spectra of the trinuclear phthalocyanine **3** in THF (solid line), THF/ CH_3CN (V/V, 1/1) (dashed line), and film cast from the THF/ CH_3CN (V/V, 1/1) **3** solution (dotted line). The concentration of the solution is 10^{-6} mol L^{-1} .

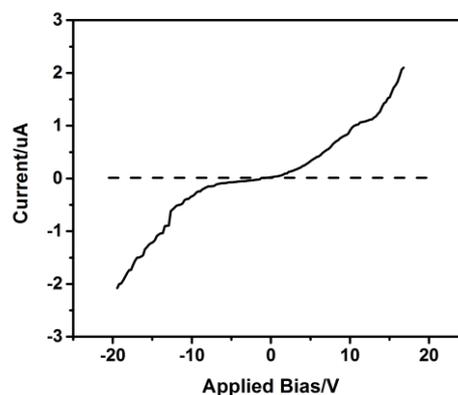


Figure 6. I-V curves measured on the individual single nanorod of trinuclear phthalocyanine **3** fabricated from THF/ CH_3CN at the substrate temperature of 30°C .

Conclusions

In summary, by means of the Schiff-base chemistry a new post-cyclization pathway was developed for the synthesis of novel conjugated multinuclear phthalocyanine-fused arrays. The self-assembled nanorod of trinuclear phthalocyanine displays interesting semiconducting properties. The present result not only extends the multinuclear phthalocyanine-fused arrays

and more importantly makes one step further forward towards the tetrapyrrole-based conjugated two-dimensional materials with well defined composition and structure, nitrogen-containing conjugated nature, tuneable central metal ions, and therefore extensive application potentials.

Experimental Section

General Remarks: THF were distilled from sodium. All other reagents and solvents were used as received. The compounds of 4,5-di(2,6-dimethylphenoxy)phthalonitrile,^[32] 5,6-dicyano-2,1,3-benzothiadiazole,^[36] 2,7-di-tert-butylpyrene-4,5-dione, pyrene-4,5,9,10-tetraone, and hexaketocyclohexane^[36] were prepared according to the published procedure.

¹H NMR spectra were recorded on a Bruker DPX 400 spectrometer. Spectra were referenced internally using the residual solvent resonances relative to SiMe₄. Electronic absorption spectra were recorded on a Lambda 750 spectrophotometer. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm⁻¹ resolution. 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 EI III elemental analyzer. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy-carbon-disk working electrode with a diameter of 2.0 mm in diameter and a silver-ware counter electrode. The reference electrode was Ag⁺/Ag (a solution of 0.01 M AgNO₃ and 0.1 M TBAP in acetonitrile), which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fc⁺/Fc) couple [E_{1/2}(Fc⁺/Fc) = 0.501 V vs. SCE]. Typically, a 0.1 M solution of [NBu₄][ClO₄] in CH₂Cl₂/pyridine (V/V, 100/1) containing 1 mM of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rates were 100 and 20 mV/s for the CV and DPV measurement, respectively.

Synthesis of 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-23,24-thiadiazolo[4,5-b]-phthalocyaninato zinc(II) [ZnPc(II)]: Mg (36.2 mg, 1.5 mmol) in dry *n*-pentanol (2.0 mL) was heated to 150°C for 3 h under nitrogen atmosphere. After being cooled to room temperature, 4,5-bis-(2,6-dimethylphenoxy)phthalonitrile (552 mg, 1.5 mmol) and 5,6-dicyano-2,1,3-benzothiadiazole (93 mg, 0.5 mmol) were added. The mixture was heated at 150°C for 6 h. After being cooled to room temperature, the volatiles were evaporated in vacuo and trifluoroacetic acid (20 mL) was added. This reaction system was further refluxed for 15 min. After filtration, the precipitate together with Zn(OAc)₂·2H₂O (315 mg, 1.5 mmol) was added into DMF (3 mL) and the mixture was refluxed for another 4 h. After being cooled to room temperature, CH₃OH (60 mL) was poured into the resulting green solution. The precipitate was collected by filtration and chromatographed on a silica gel column using CHCl₃ as eluent. After the elution of the first green band containing Zn[Pc(OC₆H₄)₂], the second green band containing the target thiadiazolo ZnPc(I) was collected. Repeated chromatography followed by recrystallization from CHCl₃ and CH₃OH afforded ZnPc(I) as a dark blue powder, 121.3 mg (17.7%). ¹H NMR (THF-*d*₆, 400 MHz): 8.44 (s, 2 H), 8.16 (s, 2 H), 8.10 (s, 2 H), 7.87 (s, 2 H), 7.47–7.12 (m, 18H), 2.42–2.38 (t, 36 H). UV/vis (THF): λ_{max} [nm] (ϵ) = 359 (120 100), 616 (103 600), 682 (268 600) 723 (344 800 M⁻¹cm⁻¹). IR (KBr): ν = 2918, 2850, 1579, 1450, 1425, 1400, 1341, 1271, 1221, 1185, 1138, 1095, 1036, 1018, 922, 893, 875, 766, 744, 719, 649, 511 cm⁻¹.

MALDI-TOF MS: an isotopic cluster peaking at *m/z* 1357.23, Calcd. for ZnC₈₀H₆₂N₁₀O₆S, [M]⁺ 1356.88. Anal. Calcd. For ZnC₈₀H₆₂N₁₀O₆S: C, 70.82; H, 4.61; N, 10.32. Found: C, 70.16; H, 4.90; N, 10.22.

Synthesis of 2,3,9,10,16,17-hexakis-(2,6-dimethylphenoxy)-23,24-diaminophthalocyaninato zinc(II) [ZnPc(II)]: ZnPc(I) (67.8 mg, 0.05 mmol), nickel acetate tetrahydrate (50.5 mg, 0.2 mmol), and sodium borohydride (12 mg, 0.3 mmol) were dissolved in a mixture of dried THF-EtOH 1:2 (3 mL) at 0°C under nitrogen atmosphere. Two hours later the reaction mixture was filtered over celite and the organic layer was washed with NH₄Cl (2 M) and H₂O for two times. The organic layer was dried with NaSO₄ and concentrated under vacuum. The crude product was purified by column chromatography using CHCl₃/THF (V/V, 9/1) as eluent, yielding 50.0 mg of diamino substituted ZnPc(II) (73.7%) as a dark blue powder after repeated chromatography followed by recrystallization from THF and CH₃OH. ¹H NMR (THF-*d*₆, 400 MHz): 8.32 (s, 2 H), 8.31 (s, 2 H), 8.15 (s, 2 H), 8.09 (s, 2 H), 7.46–7.26 (m, 18H), 2.42 (s, 36 H). UV/vis (THF): λ_{max} [nm] (ϵ) = 349 (132 100), 611 (51 000), 675 (245 800), 689 (226 800 M⁻¹cm⁻¹). IR (KBr): ν = 2951, 2919, 1610, 1585, 1454, 1397, 1341, 1272, 1221, 1187, 1139, 1089, 1026, 890, 856, 813, 765, 746, 723, 508 cm⁻¹. MALDI-TOF MS: an isotopic cluster peaking at *m/z* 1331.05, Calcd. for ZnC₈₀H₆₈N₁₀O₆, [M]⁺ 1330.87. Anal. Calcd. For ZnC₈₀H₆₈N₁₀O₆: C, 72.20; H, 5.15; N, 10.52. Found: C, 72.88; H, 5.05; N, 10.48.

Synthesis of complex 1: A mixture of 2,7-di-tert-butylpyrene-4,5-dione (6.88 mg, 0.02 mmol) and diamino substituted ZnPc(II) (26.6 mg, 0.02 mmol) in 1,4-dioxane (1 mL) and acetic acid (4 mL) was heated to reflux under nitrogen atmosphere for 6 h. After being cooled to room temperature, the volatiles were removed under reduced pressure and the residue was purified by a silica gel column using CHCl₃ as eluent. The first green band containing the target complex **1** was collected. Repeated chromatography followed by recrystallization from CHCl₃ and CH₃OH gave a purified product **1** (15.0 mg, 46.0%) as green powder. ¹H NMR (THF-*d*₆, 400 MHz): 10.14 (s, 2 H), 9.98 (s, 2 H), 8.57 (s, 2 H), 8.47 (s, 2 H), 8.19 (s, 2 H), 8.12 (s, 2 H), 8.08 (s, 2 H), 7.50–7.40 (m, 18H), 2.51–2.44 (m, 36 H), 1.81 (s, 18 H). UV/vis (THF): λ_{max} [nm] (ϵ) = 355 (110 180), 627 (42 640), 696 (192 680), 717 (112 140 M⁻¹cm⁻¹). IR (KBr): ν = 2920, 2850, 1650, 1575, 1455, 1421, 1405, 1363, 1342, 1313, 1274, 1257, 1229, 1187, 1135, 1118, 1086, 1024, 987, 889, 860, 766, 747, 721 652, 620, 576 cm⁻¹. MALDI-TOF MS: an isotopic cluster peaking at *m/z* 1638.46, Calcd. for ZnC₁₀₄H₈₈N₁₀O₆, [M]⁺ 1639.29. Anal. Calcd. For ZnC₁₀₄H₈₈N₁₀O₆: C, 76.20; H, 5.41; N, 8.54. Found: C, 75.99; H, 5.46; N, 8.50.

Synthesis of complex 2: A mixture of 2,7-di-tert-butylpyrene-4,5,9,10-tetraone (3.74 mg, 0.01 mmol) and diamino substituted ZnPc(II) (26.6 mg 0.02 mmol) in 1,4-dioxane (1 mL) and acetic acid (4 mL) was heated to reflux under nitrogen atmosphere for 8 h. After being cooled to room temperature, the volatiles were removed under reduced pressure and the residue was purified by a silica gel column using CHCl₃/THF (V/V, 10/1) as eluent. The first green band containing the target complex **2** was collected. Repeated chromatography followed by recrystallization from THF and CH₃OH gave a purified product **2** (3.0 mg, 13.0%) as green powder. ¹H NMR (THF-*d*₆, 400 MHz): 10.65 (s, 4 H), 10.26 (s, 4 H), 8.61 (s, 4 H), 8.21 (s, 4 H), 8.14 (s, 4 H), 7.49–7.46 (m, 36H), 2.54 (m, 72 H), 2.17 (s, 18 H). UV/vis (THF): λ_{max} [nm] (ϵ) = 354 (114 900), 390 (90 900), 416 (65 400), 443 (66 140), 633 (45 920), 704 (261 300 M⁻¹cm⁻¹). IR (KBr): ν = 2920, 2851, 1616, 1587, 1473, 1455, 1399, 1343, 1322, 1273, 1223, 1186, 1140, 1089, 1025, 893, 767, 747, 725 cm⁻¹. MALDI-TOF MS: an isotopic cluster peaking at *m/z* 2958.22, Calcd. for Zn₂C₁₈₄H₁₅₀N₂₀O₁₂, [M]⁺ 2959.02. Anal. Calcd. For Zn₂C₁₈₄H₁₅₀N₂₀O₁₂: C, 74.56; H, 5.10; N, 9.45. Found: C, 74.49; H, 5.12; N, 9.41.

Synthesis of complex 3: A mixture of hexaketocyclohexane octahydrate (2.5 mg, 0.015 mmol) and diamino substituted ZnPc(II) (80.0 mg, 0.06 mmol) in 1,4-dioxane (1 mL) and acetic acid (4 mL) was heated to reflux under nitrogen atmosphere for 8 h. After being cooled to room temperature, the volatiles were removed under reduced pressure and the residue was purified by biobead column chromatography eluting with THF. The first green band containing the target complex **3** was collected. Repeated chromatography followed by recrystallization from THF and CH₃OH gave a purified product **3** (20.0 mg, 25.0%) as green powder. ¹H NMR (THF-*d*₆, 400 MHz): 10.60 (s, 6 H), 8.87 (s, 6 H), 8.23 (s, 6 H), 8.16 (s, 6 H), 7.49–7.41 (m, 54 H), 2.62–2.40 (m, 108 H). UV/vis (THF): λ_{max}[nm] (ε) = 360 (222 100), 419 (133 600), 725 (354 800 M⁻¹cm⁻¹). IR (KBr): ν = 2921, 2850, 1638, 1566, 1407, 1385, 1344, 1274, 1189, 1093, 1024, 981, 891, 855, 808, 767, 725, 648, 542 cm⁻¹. MALDI-TOF MS: an isotopic cluster peaking at *m/z* 4049.42, Calcd. for Zn₃C₂₄₆H₁₉₂N₃₀O₁₈, [M]⁺ 4049.57. Anal. Calcd. For Zn₃C₂₄₆H₁₉₂N₃₀O₁₈: C, 72.91; H, 4.78; N, 10.37. Found: C, 72.99; H, 4.80; N, 10.28.

Preparation of self-assembled nanostructures: Keeping the temperature of the silicon slice at 30°C, samples were prepared by casting a drop of 5 μL of **3** solution (in THF, concentration 1×10⁻⁵ mol L⁻¹) onto the surface of the silicon slice, then injected 5 μL of poor solvents including methanol, ethanol, *n*-butanol, *n*-hexanol, *n*-octanol, or acetonitrile. The mixed solvents evaporated freely in the above-mentioned conditions. Then corresponding nanostructures on the surface of silicon slice were obtained.

Acknowledgements

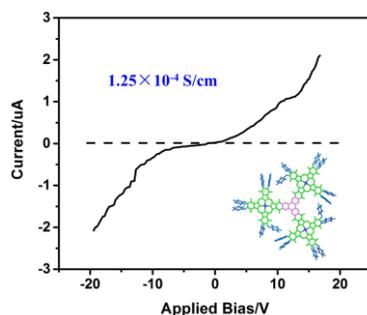
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FULL PAPER

New conjugated multinuclear phthalocyanine molecular arrays with good semiconducting property have been synthesized and characterized.



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