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ARTICLE

Synthesis and Photophysical Properties of Novel Phthalocyanine-Perylenediimide-Phthalocyanine Triad and Phthalocyanine-Perylenediimide Dyads

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A series of novel multi-component chromophores, one phthalocyanine-perylenediimide-phthalocyanine triad and two phthalocyanine-perylenediimide dyads were synthesized by covalent linkage between phthalocyanines and perylene-3,4,9,10-bis(dicarboximide) at the bay position of perylene core in one condensation reaction. The photophysical properties of the dyes were presented with wider light absorption from 300 to 800 nm and discussed by interpretation and correlations with previous dyes. Density functional theory at the B3LYP level with 6-31G(d) was performed for geometry and energy optimization. Furthermore, a substitution and elimination reaction at the perylene bay position by using 1,8-Diazabicyclo[5,4,0]undec-7-ene as catalyst was proceeded and discussed with probable mechanism.

Introduction

Synthesis of giant multi-component molecular chromophores has continuously attracted much attention due to their unique photophysical and photochemical properties.¹ The energy, charge and photon-transfer processes in these multi-chromophore molecular systems are promising and worthy of systematic research to develop high efficient photoelectronic devices.² Photoinduced electron transfer in organic molecules containing both electron-donating and electron-accepting chromophores has been studied extensively.³ The efficiency of those processes is governed by the selected building block functionalities, linkers and geometrical arrangements.⁴ There has been intensive research in the synthesis and photophysical study of donor-acceptor chromophores using different coupling partners for applications in artificial photosynthetic systems and photoinduces charge separation.⁵

As promising molecular donors for artificial photosynthetic apparatus, phthalocyanines (Pcs) have excellent optoelectronic properties as well as good chemical and physical stability. They have been widely used in the fields of solar cells, nonlinear optics, and photocatalysts, etc.⁶ The big planar π -conjugated system made Pcs as excellent electron-donating chromophores and high charge carrier mobility organic semiconductors with characteristic electronic absorption from the ultraviolet to visible region. And, they have been proven to be good building blocks for constructing supramolecular systems because their physical and physicochemical properties could be easily tuned by multiple modification possibilities of chemical functionalization, such as metal center, peripheral positions, and axial positions to metal.⁷

On the other hand, perylenediimide (PDI) unit is well-known electron-accepting chromophore. PDI derivatives represent a class *n*-type semiconductors with relatively high electron affinity and excellent transport property.⁸ They have a characteristic absorption in the visible region. PDI based materials have been widely used in

the fields of solar cells, field-effect transistor and optical switches, etc.⁹

Multifunctionality, as a leading strategy in building electron donor and acceptor system, has shown much more interest for photochemistry, photophysics and energy conversion. The systems describe the basics in photoinduced charge separation, and also play a key role in organic photovoltaic property.¹⁰ Wasielewski et al. reported an electron donor-acceptor-donor (D-A-D) molecule based on PDI unit, which synthesized by covalent linking of the electron-donor porphyrins with PDI through its imide position. The D-A-D type molecules exhibit interesting properties originating from the photoinduced electron transfer.¹¹ Recently, Torres et al. have incorporated PDI unit as the oxidizing complement of phthalocyanines, which towards versatile D-A arrays to give rise to energy transfer products and/or long-lived radical ion-pair states.¹²

In the past years, we have paid more attention on synthesis and photophysical properties of large π -extended molecular materials with Pcs or PDI groups as functional blocks. Several Pcs-based functional materials have been synthesized with symmetrically and asymmetrically substituted structures, which have been used as active materials for electronic devices, such as gas sensor, organic field-effect transistor, molecular rectifier and organic light-emitting diodes.¹³ For PDI part, we also got some progresses on synthesis of multinuclear systems. We firstly incorporated oligothiophene moieties to the bay position of PDI core.¹⁴ Later, a tetra-substituted functional PDI unit by aryl groups at the four bay positions and the corresponding derivatives were synthesized with high yields.¹⁵ Our extensive experiences in Pcs and PDI have motivated us to use them as building blocks to design novel electron donor-acceptor functionalized chromophores.

Up to now, a few Pcs-PDI based donor-acceptor multi-chromophores have been reported.^{5,16} However, most of them presented that the two chromophores were connected through the PDI imide position. The modification at the PDI bay position is very

scarce due to the great difficulties in both synthesis and purification.^{5b,17} The key point for introducing groups at PDI bay positions is to make use of an electronic coupling to enhance electron mobility through strong π - π stacking interactions between the planar PDI moieties, and even to exploit an ultrafast photoinduced charge separated state.¹⁸ However, the introduction of substituent at the imide position would not significantly work on electronic structures of perylene unit due to the frontier molecular orbital nodes with the imide nitrogen atoms.^{3d,19}

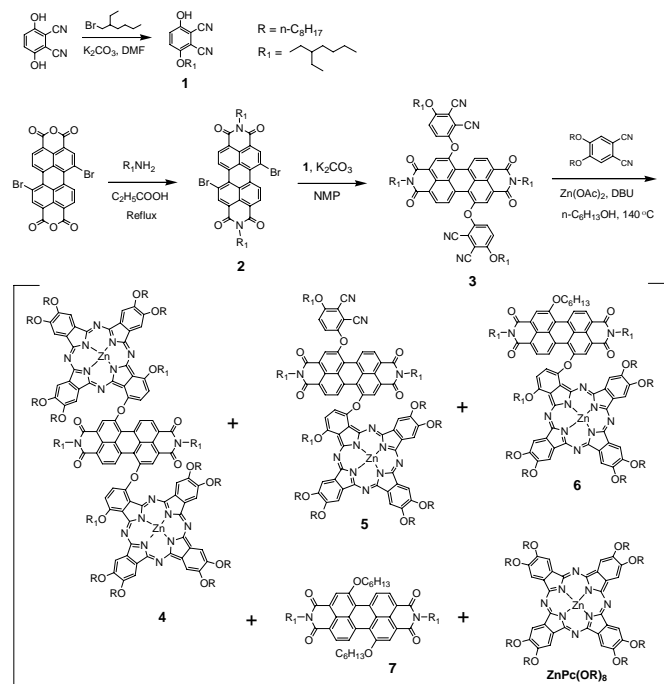
In this study, we expect to incorporate two functional chromophores Pcs and PDI into one molecular system through PDI bay positions. A covalently linked phthalocyanine-perylene-diimide-phthalocyanine triad and two phthalocyanine-perylene-diimide dyads have been synthesized. The metal phthalocyanine units are linked to the bay position of the perylene core. The substitution and elimination reactions at the PDI bay position will be discussed. The steady-state absorption properties and geometry and energy optimization are presented for these multifunctional chromophores.

Results and Discussion

1. Synthesis and characterization

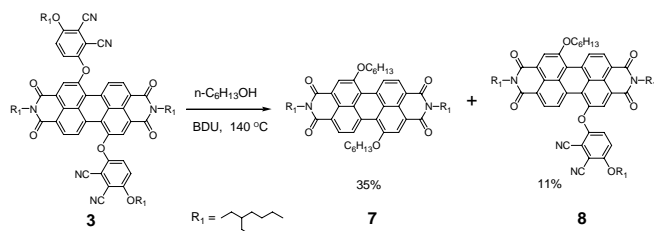
Synthesis. The target molecule, Pc-PDI-Pc triad **4** (Scheme 1), is composed of an electron rich phthalocyanine subunit bearing several electron-donating alkoxy groups linked to a strongly electron-demanding PDI substituted at the 1,7-bay positions. For most of PDI derivatives, multi-component chromophores are directly assembled between suitable Pc chromophore and PDI moiety by covalent coupling reaction through the PDI imide positions. It is hard to construct multi-components at the PDI bay positions due to the reactive activity and large steric hindrance.^{5b,17} Torres et al. firstly reported a conjugated donor-acceptor array composed of two Pc moieties connected to the bay positions of PDI moiety by using palladium-catalyzed coupling reaction.^{5b} Here, we chose another approach to fabricate the system: first, the phthalonitrile function group was connected to the 1,7 bay positions of PDI moiety; then, two phthalonitrile function groups (octyloxyphthalonitrile group and PDI modified phthalonitrile groups) were used to prepare asymmetric Pcs.

The synthetic route and molecular structures of triad and dyads are shown in Scheme 1. The first phthalonitrile function group, 4,5-di-*n*-octyloxyphthalonitrile, was synthesized with three steps according to the previous literature.²⁰ The second phthalonitrile function group (compound **3**) was prepared by combination of two intermediates (compound **1** and **2**). 3-(2-ethylhexyloxy)-6-hydroxyphthalonitrile **1** was synthesized from the controlled alkylation of 2,3-dicyano-1,4-dihydroquinone with 2-ethylhexylbromide in molar ratio of 1:1. After reaction, we can easily remove the di-alkyl substituted product by standard column chromatography, then a pale yellow **1** was achieved with yield 53 % by using methanol as additional partly eluent. And, dibrominated PDI derivative **2** was obtained by bromination of perylene bisanhydride, followed by imidation in propionic acid.¹⁴ Then, compound **2** was reacted with compound **1** to generate the 1,7-disubstituted PDI derivative **3**. The introduction of four alkyl chains is very helpful to improve the solubility of PDI derivative, so compound **3** could be easily purified by silica gel column chromatography. Consequently, a catalytic amount of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was added to a mixture of 4,5-di-*n*-octyloxyphthalonitrile, compound **3**, Zn(OAc)₂ and *n*-hexanol. The resultant mixture was stirred and heated at 140 °C for 8 h to afford the compounds **4**, **5** and zinc phthalocyanine ZnPc(OR)₈ as we supposed.



Scheme 1 Synthetic route and reagents

Separation and Purification. As we thought, the separation and purification of mixture is quite difficult due to their similar molecular structures with high molecular mass. Silica gel column chromatography was firstly carried out to separate the crude mixtures. A first pink fraction with a small amount of sample was shown, in which compound **7** is assigned. The second black-like fraction with large amount samples was collected until the eluted-out solution started to show clear green color, which contain the target D-A products as we supposed. The third green fraction should belong to the symmetrical product ZnPc(OR)₈ as we know. Then, the crude products in the second fraction were further purified by size-exclusion chromatography (Bio-Beads SX-2) with THF as eluent.²¹ By this method, the compounds could be isolated based on the different molecular sizes. A proper amount of the sample solution was eluted in the column, then several new colorful bands were appeared: the first brown-black band, the second purple one and the third green one (ZnPc(OR)₈). In order to obtain high purity compounds, each colorful fraction was performed over 5 times by the size exclusion column. By surprise, a purple solid was separated from the second fraction, which is not agree with compounds **4** and **5**. After characterization, a new compound **6** is confirmed as shown in the Scheme 1. As mass spectra indicated, the first brown-black band was found to be a mixture of compounds **4** and **5**, which could not be separated even by Bio-beads column. Fortunately, compounds **4** and **5** showed totally different solubilities in the mixed solvents (THF/CH₃OH 1:2 v/v). So, the mixture containing **4** and **5** was dissolved in 10 mL of THF, then 20 mL of CH₃OH was added slowly. After the resultant mixtures were kept overnight, a brown precipitate appeared. The brown precipitate was filtered with remaining a neat green filtrate solution. Then, CH₃OH was added to the green filtrate to give a green precipitate. These precipitation procedures were repeated by several times until the filtrate showed colorless. Finally, high purity compounds **4** and **5** were successfully isolated as the brown and green color solids.



Scheme 2 Reference reaction to synthesize compounds **7** and **8**.

Synthesis Mechanism. In the condensation reaction, excess 4,5-di-*n*-octyloxyphthalonitrile and compound **3** should be assembled to afford compounds **4**, **5** and by-product **ZnPc(OR)₈**. However, a new compound **6** and a trace amount of **7** were isolated accidentally in the reaction after the careful multi-step purification. It is easy to understand the generation of products **4** and **5**, but it is hard to explain the formation of compounds **6** and **7**. As known, the substituents at the PDI bay position are possible to be attacked by basic reagents.²² The strong electron-withdrawing -CN groups in compound **3** make the phthalonitrile-like part as a leaving group under basic conditions. In this case, the basic DBU may react with the solvent (*n*-hexanol) to generate C₆H₁₃O⁻ ion, and then C₆H₁₃O⁻ ions attack the PDI bay positions, which lead to a elimination reaction on the phthalonitrile-like substituent. Finally, a -OC₆H₁₃ group would be introduced to the PDI bay position.

In order to confirm this deduction, a reference reaction has been designed and proceeded as shown in Scheme 2. In the modeling chemical reaction, compound **3**, a catalytic amount of DBU and *n*-C₆H₁₃OH were mixed under the same reaction conditions as described previously. With this reaction, compound **7** was formed by double replacement reaction at 1,7-bay positions with relative high yield. Meantime, a small amount of compound **8** was isolated from single replacement reaction. The most likely mechanism for the single replacement reaction can be explained as: the second bay position of 1,7-disubstituted PDI (as compound **8**) was passivated after one bay position of 1,7-disubstituted PDI (as compound **3**) was substituted by the -OC₆H₁₃ group. It is much more difficult to continue replacement reaction due to the electron-donating effect of -OC₆H₁₃ group. Therefore, both compound **7** and **8** could be coexisted. The mechanism can also be used to explain the generation of compound **5** with one phthalonitrile function group remaining. As shown in the IR spectra, the absorption peak of -CN group is detected near 2230 cm⁻¹ for compounds **5** and **8**, which is a direct evidence of the existence of -CN group in the molecules.

Characterization. Three D-A compounds **4-6** have been synthesized by using one condensation reaction. The yield for compounds **4-6** is 3%, 4% and 7% (calculation based on **3**), respectively. Though the yield of each product is low, the total yield (17% = 3% × 2 + 4% + 7%) is a typical for asymmetrical phthalocyanines if we consider all compounds as related asymmetrical phthalocyanines. In order to confirm the molecular structure directly, MALDI-TOF MS is used as an effective technique for the determination of high molecular mass compounds. Compounds **4-6** show clear molecular ionic peaks (M⁺ or M⁺+1) at *m/z* 3593.4, 2372.1, and 2201.6, respectively (see the spectra in ESI). For compound **4**, the M⁺ peak is more difficult to be detected due to its much higher molecular mass. So, a theoretically calculated pattern from the molecular formula C₂₁₆H₂₉₄N₁₈O₂₀Zn₂ was used to compare with the experimental isotopic distribution of the M⁺ peaks. A good agreement was found to further confirm the molecular structure for compound **4** (see the spectrum in ESI). For NMR characterization, poorly informative ¹H NMR spectra of compounds

4-6 were shown as very broad peaks of aromatic protons due to their complicated molecular structures and aggregation trend between large molecules in solution.^{5b} Therefore, elemental analysis is needed to further confirm the purities of the compounds. Other structural evidences can be checked in IR spectra. All the compounds **3-8** show characteristic C=O stretching vibration absorptions between 1710 and 1650 cm⁻¹, which can be assigned to the imide units. It is also worthy to be mentioned that the -CN group absorption is detected near 2230 cm⁻¹ for compounds **3**, **5** and **8**, which is the direct evidence for the existence of -CN group in the molecules. On the contrary, there was no -CN stretching absorption found for compounds **4**, **6**, and **7** in the IR spectra.

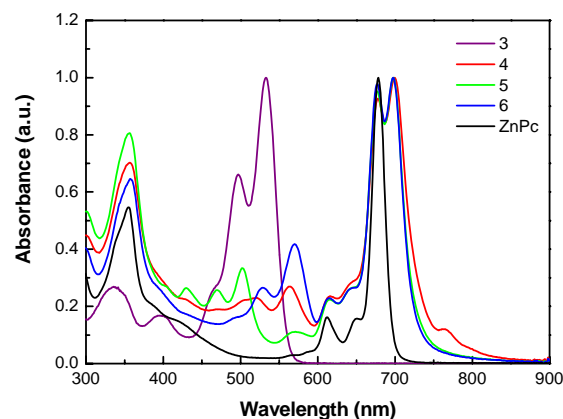


Figure 1 Normalized UV-vis absorption spectra of compounds **3** (purple line), **4** (red line), **5** (green line), **6** (blue line) and **ZnPc(OR)₈** (black line) in CHCl₃ at room temperature.

2. Steady-State Absorption Properties

Figure 1 shows the normalized UV-vis absorption spectra of the triad and dyads **4-6** together with those corresponding to the fragments, PDI derivative **3** and **ZnPc(OR)₈**. The spectrum of reference compound **ZnPc(OR)₈** exhibits characteristic absorption of metal Pcs with the strong Q-band absorption located at 678 nm and the B-band absorption at 356 nm.²³ The shoulder peak at 612 nm comes from the strong π - π aggregation effect between planar phthalocyanine molecules. The spectrum of compound **3** illustrates the characteristic absorption of the bay position substituted PDI derivatives. From 450 nm to 600 nm, the absorption bands of compound **3** are located at 533 and 497 nm, which attributed to the symmetrically substituted perylene imides.^{5c} Compounds **4-6** strongly aggregates due to their big π -structure, as is clearly evidenced by its broad, abnormally low intense Q-band.^{5b} The use of diluted solutions produces photophysical study (10⁻⁶ M). The UV-vis spectra of compounds **4-6** clearly show the characteristic absorptions of the combination of phthalocyanine **ZnPc(OR)₈** and PDI derivative **3** (see Table 1). The Q-band absorptions of **4-6** are located at 677 and 699 nm as well as the shoulder peaks at 645 nm and the B-band absorptions at 357 nm. These characteristic absorptions undoubtedly come from those of the phthalocyanine parts, which compared those to maxima at 356 and 678 nm for the phthalocyanine fragment **ZnPc(OR)₈**. Importantly, the large splitting of the Q-bands (677 and 699 nm), as well as broadening peaks, indicate

a strong coupling of transition dipoles.^{5b} Kasha et al. have developed the simple point-dipole exciton coupling theory to position that the transition dipoles of two identical chromophores.²⁴ The stacked geometry results in exciton coupling of the two transition dipoles causing the lowest-energy electronic transition of the dimer to split into two bands.^{16a} Moreover, the broad band near 645 nm of compounds **4–6** is also characteristic of zinc phthalocyanine H-aggregates, which have been revealed by several groups.²⁵

Table 1 Steady-state UV-vis absorption data for compounds **3–8** and **ZnPc(OR)₈** in anhydrous CHCl₃

| Sample | λ_{abs} (nm) | | | | | | | | |
|-------------|-----------------------------|-----|-----|-----|-----|-----|-----|-----|--|
| 3 | | | 497 | 533 | | | | | |
| 4 | 357 | | 520 | 564 | 612 | 645 | 677 | 699 | |
| 5 | 357 | 430 | 470 | 502 | 612 | 645 | 677 | 698 | |
| 6 | 357 | | 528 | 570 | 612 | 650 | 677 | 699 | |
| 7 | | | 532 | 573 | | | | | |
| 8 | | 503 | 532 | 574 | | | | | |
| ZnPc | 356 | | | | 612 | 650 | 678 | | |

For PDI transitions, more information is shown in the region from 400 to 600 nm, where compounds **4–6** exhibit the obvious absorption character. The location and pattern of the absorption bands in compounds **6** (λ_{max} at 570 nm, 528 nm) and **4** (λ_{max} at 564 nm, 520 nm) are quite similar to those of **7** (λ_{max} = 573 nm, 532 nm, see Fig S-4). But, compared with those of compound **3**, the PDI transitions are red shifted with 40 nm for both peaks. However, for the compound **5**, a totally different phenomenon is achieved that the PDI transitions are blue shifted to 502 nm and 470 nm in the reference to compound **3** and **7**. Part of these changes arise from the bay substituted PDI, which has a strong influence on the planarity of the PDI chromophore.^{5b} And, all compounds **3–8** could be studied as donor-acceptor-donor (D-A-D) structures with PDI or phthalonitrile as acceptors and Pc part or $-\text{OC}_6\text{H}_{13}$ group as donors.

For compounds **4–6**, their Q-band and B-band absorption are also quite similar to each other, but PDI absorptions show very different behaviors as well as the color in solution and solid state. Compound **5** is special because of its bearing an electron-donating Pc unit and an electron-accepting unit (phthalonitrile) at the same time, which could be viewed as donor-acceptor-acceptor (D-A-A) type. A set of absorption bands of **5** at λ_{max} = 502, 470, and 430 nm are blue shifted. This result could be possibly attributed to strong electronic communication from ZnPc (i.e., electron donor) to PDI (i.e., acceptor) units.

3. Molecular Modeling

To gain further insight into the geometric and electronic properties of these dyes, density functional theory (DFT) at the B3LYP level with 6-31G(d) as the basis set is used for geometry and energy optimization. The optimized structures of the respective molecules and the distribution of frontier orbitals were calculated for compound **4** (double bay position substituent, Pc-PDI-Pc) and compound **6** (single bay position substituent, Pc-PDI), which shown in Figure 2. The HOMO-level of compound **4** and **6** is dominated by the molecular orbitals of the phthalocyanine fragments. On transition to the LUMO-level, the molecular orbitals of the perylene moiety are

dominant, as expected. The compounds show that molecular orbital amplitude plots are typical D- π -A system with dominant electron distribution around the donor moiety in the HOMO-level and dominant electron distribution around the acceptor moiety in the LUMO-level.²⁶ No interaction among the subunits could be predicted due to the absence of any orbital overlap.^{5c} The calculated HOMO and LUMO energy values were found to be -4.60 and -2.96 eV for compound **4**, and -4.63 and -3.01 eV for compound **6**, separately. Compound **4** and **6** show similar energy level, and this trend was in agreement with Valiyaveetil's reports on triphenylamine bay substituent PDI dyes.²⁷

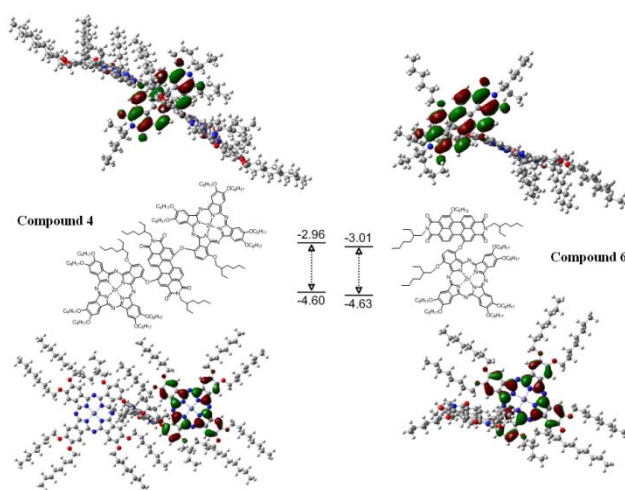


Figure 2 The optimized geometric structure of compounds and their frontier orbital plots were calculated by DFT at the B3LYP/6-31G(d) level.

Conclusions

We have successfully synthesized one phthalocyanine-perylenediimide-phthalocyanine triad and two phthalocyanine-perylenediimide dyads. The combination of the silica gel, size-exclusion column chromatography and fractionating precipitation is testified as a effective to separate and purify the high molecular mass compounds with similar molecular structures. By chemical bonding, these compounds possess a wider light absorption from 300 to 800 nm with apparent combination of the properties of phthalocyanine and perylenediimide fragments. A large splitting of the Q-bands indicates a strong coupling of transition dipoles in this molecular system. Possible investigation of the photoinduced electron- and energy-transfer process of the triad and dyads are worthy of further study.

Experimental Section

Materials: Normal chemicals were purchased from Aldrich and used as received. Solvents and other normal reagents were obtained from the Beijing Chemical Plant. Solvents for reactions and photophysical measurements were all distilled after dehydration according to conventional methods. 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), 2-ethylhexylbromide, 2-ethylhexylamine and 1-methyl-2-pyrrolidinone (NMP) were purchased from Acros. Perylene-

3,4,9,10-tetracarboxylic acid anhydride was purchased from Aldrich. 2,3-dicyano-1,4-dihydroquinone was purchased from TCI. Bio-Beads SX-2 was bought from Bio-Rad Co.

Instrumentation: NMR spectra were measured with Bruker 400 MHz spectrometers. Mass spectra were recorded on AEI-MS50-MS spectrometer for EI MS and Bruker BIFLEXIII spectrometer for matrix assisted laser desorption–ionization with time of-flight mass spectrometry (MALDI-TOF-MS). Elemental analysis was performed on Carlo-Erba-1106 instrument. Infrared spectra were determined with Pekin-Elmer Tensor 27 spectrometer. Electronic absorption spectra were measured on a Hitachi (model U-3010) UV-vis spectrophotometer.

Synthesis and Characterization of Compounds:

4,5-di-n-octyloxyphthalonitrile²⁰ FT-IR (KBr, cm^{-1}) ν 2231 (s, –CN); ¹H NMR (400 MHz, CDCl_3 , 25 °C): δ = 7.11 (s, 2H, Ar–H), 4.04 (t, J = 6.5 Hz, 4H, O–CH₂), 1.85 (m, 4H, CH₂), 1.45 (m, 4H, CH₂), 1.33 (m, 16H, CH₂), 0.89 (m, 6H, CH₃); MS (EI^+): m/z 384 (M^+); Anal. Calcd for ($\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_2$): C, 74.96; H, 9.44; N, 7.28. Found C, 75.14; H, 9.57; N, 7.39.

3-(2-ethylhexyloxy)-6-hydroxyphthalonitrile (1): A mixture of 1.60 g (10 mmol) 2,3-dicyano-1,4-dihydroquinone, 1.93 g (10 mmol) 2-ethylhexylbromide, 1.38 g (10 mmol) K_2CO_3 and 15 mL DMF was stirred vigorously under nitrogen atmosphere at room temperature for 24 h. The resultant mixture was poured into 100 mL H_2O , it was then extracted by the mixed solvent (petroleum ether/ethyl acetate 4:1 v/v, 100 mL \times 3). The organic layers were combined and washed by water. The further purification was carried out by column chromatography (silica gel, 100–200 mesh). By using dichloromethane as eluent, di-alkyl substituted product is separated, then eluting with dichloromethane/methanol 20:1 (v/v) is to give compound **1** as a pale yellow solid after removing the solvent (1.40 g, 53%). **1:** FT-IR (KBr, cm^{-1}) ν 3265 (br, –OH), 2246 (s, –CN); MS (EI^+): m/z 272 (M^+); ¹H NMR (400 MHz, CDCl_3 , 25 °C): δ = 7.30 (d, J = 9.3 Hz, 1H, Ar–H), 7.18 (d, J = 9.4 Hz, 1H, Ar–H), 7.15–6.30 (s, br, 1H, –OH), 3.95 (m, 2H, O–CH₂), 1.76 (m, 1H, CH), 1.52 (m, 4H, CH₂), 1.31 (m, 4H, CH₂), 0.92 (m, 6H, CH₃); Elemental analysis (%), calcd. for ($\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$): C, 70.56; H, 7.40; N, 10.29. Found: C, 70.90; H, 7.47; N, 10.27.

N,N'-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-bisdicarboximide (2): A solution of 1,7-dibromo-erylene tetracarboxylic acid anhydride 2.0 g (3.6 mmol), 2-ethylhexylamine 1.9 g (15 mmol, excess) in propionic acid was refluxed for 16 h. Rotary evaporation to remove the solvent, then the compound was purified by column chromatography (silica gel, dichloromethane / petroleum ether 4:1 v/v) to yield **2** as a red solid (2.1 g, 78%). **2:** UV/Vis (CHCl_3) λ_{max} 524, 489, 272 nm; FT-IR (KBr, cm^{-1}) ν 2958, 2929, 2860, 1702 (s, C=O), 1662 (s, C=O), 1591, 1393, 1333, 1239; MS (MALDI-TOF): m/z 771.1 (M^+); ¹H NMR (400 MHz, CDCl_3 , 25 °C): δ = 9.43 (d, J = 8.2 Hz, 2H, perylene-H), 8.87 (s, 2H, perylene-H), 8.65 (d, J = 8.1 Hz, 2H, perylene-H), 4.09–4.19 (m, 4H, –CH₂–N), 1.92–1.96 (m, 2H, –CH–), 1.32–1.42 (m, 16H, –CH₂–), 0.95 (t, 6H, –CH₃), 0.90 (t, 6H, –CH₃); ¹³C NMR (400 MHz, CDCl_3 , 25 °C): δ = 162.8 (C=O), 162.3 (C=O), 137.8, 132.3, 132.2, 129.6, 128.7, 128.1, 126.5, 122.9, 122.5, 120.7, 44.4, 37.9, 30.7, 28.6, 23.9, 23.0, 14.1, 10.5; Elemental analysis (%), calcd. for ($\text{C}_{40}\text{H}_{40}\text{Br}_2\text{N}_2\text{O}_4$): C 62.19, H 5.22, N 3.69; found: C 62.30, H 5.23, N 3.44.

Synthesis of compound 3: A mixture of compound **2** (770 mg, 1.0 mmol), **1** (816 mg, 3.0 mmol, excess), K_2CO_3 (420 mg, 3.0 mmol) and NMP 8 mL was stirred and heated at 80 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was poured into 200 mL of water and stand for

hours before filtration. The filter residue was washed by water repeatedly to ensure the completed removal of NMP. The compound was purified by column chromatography (silica gel, dichloromethane) two times to yield **3** as red-orange powder (690 mg, 60%). **3:** UV/Vis (CHCl_3) λ_{max} 533, 497 nm; FT-IR (KBr, cm^{-1}) ν 2959, 2930, 2864, 2234 (s, –CN), 1701 (s, C=O), 1661 (s, C=O), 1597, 1480, 1461, 1406, 1335, 1255, 1056; MS (MALDI-TOF): m/z 1154.9 (M^+), 1177.9 [$\text{M} + \text{Na}$]⁺; ¹H NMR (400 MHz, CDCl_3 , 25 °C): δ = 9.40 (d, J = 8.4 Hz, 2H, perylene–H), 8.65 (d, J = 8.3 Hz, 2H, perylene–H), 8.12 (s, 2H, perylene–H), 7.36 (d, J = 9.4 Hz, 2H, Ar–H), 7.28 (d, J = 7.8 Hz, 2H, Ar–H), 4.10 (m, 4H, N–CH₂), 4.04 (m, 4H, O–CH₂), 1.84 (m, 4H, CH), 1.55 (m, 16H, CH₂), 1.36 (m, 16H, CH₂), 0.94 (m, 24H, CH₃); ¹³C NMR (400 MHz, CDCl_3 , 25 °C): δ = 163.1, 162.7, 158.9, 153.6, 149.7, 132.3, 130.8, 129.6, 129.0, 126.1, 125.4, 124.3, 123.7, 122.7, 121.9, 118.9, 112.1, 112.1, 109.6, 106.2, 72.9, 44.5, 39.2, 37.9, 30.7, 30.2, 29.0, 28.7, 24.0, 23.7, 23.0, 22.9, 14.1, 14.0, 11.1, 10.6; Elemental analysis (%), calcd. for ($\text{C}_{72}\text{H}_{78}\text{N}_6\text{O}_8$): C, 74.84; H, 6.80; N, 7.27; Found: C, 74.66; H, 6.82; N, 7.15.

Synthesis of compound 4, 5, and 6: Five droplets of DBU was added to a mixture of **3** (410 mg, 0.35 mmol), 4,5-di-n-octyloxyphthalonitrile (1.090 g, 2.83 mmol, 8 equiv.), anhydrous $\text{Zn}(\text{OAc})_2$ (160 mg, 0.88 mmol, 2.5 equiv.), and n-hexanol (10 mL) under nitrogen atmosphere. The resultant mixture was stirred and heated at 140 °C for 8 h. After cooling to room temperature, the dark green reaction mixture was poured into 200 mL methanol, and it was put to stand for hours and then filtered. The filter residue was washed by methanol completely. Silica gel column chromatography (100–200 mesh, diameter 80 mm, length 20 cm) was carried out to purify the product roughly by the use of chloroform as eluent. The first band is pink and proved to contain small amount of compound **7**. The second black-like band was gathered until the eluted-out solution became clear green, so as to ensure the overlapped bands to be gathered. The third band is the main product and characterized to be **ZnPc(OR)**₈. Then, the crude products in the second band were further purified by size-exclusion chromatography (Bio-Beads SX-2, column size: diameter 50 mm, length 80 cm). A proper amount of the sample solution in THF was put onto the column and eluted with THF, then several new bands appeared, the first band is brown-black, the second purple band, and the third green one. The bands with same colour were collected and combined, put into Bio-beads column again. The size exclusion column separation was performed over 5 times for each sample to obtain high pure compounds. In our isolation process, the second band enriched compound **6**, therefore, **6** could be isolated ideally to give a purple solid. And, the first brown-black band should contain compounds **4** and **5**, which are impossible to be separated by column chromatography methods, but they could be separated by fractionating precipitation procedure. The mixture of **4** and **5** was dissolved in 10 mL of THF, then 20 mL of CH_3OH was added slowly. After the resulting mixtures were kept overnight, a brown precipitate appeared. The brown precipitate was filtered with remaining a neat green filtrate solution. Then, CH_3OH was added to the green filtrate to give a green precipitate. These precipitation procedures were repeated by several times until the filtrate showed colorless. Finally, high purity compounds **4** and **5** were successfully isolated as the brown and green color solids.

Compound **4** (35 mg, 3%, calculation based on **3**): UV/Vis (CHCl_3) λ_{max} 699, 677, 645, 612, 564, 520, 357 nm; FT-IR (KBr, cm^{-1}) ν 2958, 2926, 2856, 1699 (s, C=O), 1661 (s, C=O), 1595, 1494, 1463, 1383, 1335, 1278, 1107, 1038; MS (MALDI-TOF): m/z 3593.4 (M^+); Elemental analysis (%), calcd. for ($\text{C}_{216}\text{H}_{294}\text{N}_{18}\text{O}_{20}\text{Zn}_2\cdot\text{H}_2\text{O}$): C, 71.83; H, 8.26; N, 6.98; Found: C, 71.69; H, 8.02; N, 6.75.

Compound **5** (31 mg, 4%, calculation based on **3**): UV/Vis (CHCl₃) λ_{\max} 698, 677, 645, 612, 502, 470, 430, 357 nm; FT-IR (KBr, cm⁻¹) ν 2956, 2927, 2856, 2230 (s, -CN), 1702 (s, C=O), 1663 (s, C=O), 1597, 1495, 1463, 1382, 1335, 1277, 1106, 1038; MS (MALDI-TOF): m/z 2372.1 (M⁺+1); Elemental analysis (%), calcd. for (C₁₄₄H₁₈₆N₁₂O₁₄Zn-H₂O): C, 72.29; H, 7.92; N, 7.03; Found: C, 72.52; H, 7.77; N, 6.81.

Compound **6** (55 mg, 7%, calculation based on **3**): UV/Vis (CHCl₃) λ_{\max} 699, 677, 650, 612, 570, 528, 357 nm; FT-IR (KBr, cm⁻¹) ν 2956, 2926, 2857, 1695 (s, C=O), 1657 (s, C=O), 1593, 1496, 1463, 1384, 1334, 1278, 1107, 1038; MS (MALDI-TOF): m/z 2201.6 (M⁺); Elemental analysis (%), calcd. for (C₁₃₄H₁₈₀N₁₀O₁₃Zn-H₂O): C, 72.42; H, 8.25; N, 6.30; Found: C, 72.17; H, 7.96; N, 6.30.

Characterization of ZnPc(OR)₈. UV/Vis (CHCl₃) λ_{\max} 678, 650, 612, 356 nm; FT-IR (KBr, cm⁻¹) ν 2924, 1605, 1496, 1461, 1384, 1279, 1202, 1107, 1046; ¹H NMR (CDCl₃, 400 MHz): δ = 8.10 (s, br, 8H, Ar-H), 4.49 (s, br, 16H, O-CH₂), 2.15 (s, br, 16H, CH₂), 1.79 (m, 16H, CH₂), 1.70–1.10 (m, 64H, CH₂), 0.99 (s, br, 24H, CH₃); MS (MALDI-TOF): m/z 1599.7 (M⁺); Elemental analysis (%), calcd. for (C₉₆H₁₄₄N₈O₈Zn): C, 71.90; H, 9.05; N, 6.99; Found C, 71.86; H, 8.95; N, 6.93.

Reference reaction: Synthesis of **7** and **8**

A solution of compound **3** (100 mg), three droplets of DBU and 5 mL of n-hexanol was stirred under nitrogen atmosphere at 140 °C for 8 h. After cooling to room temperature, the mixture was evaporated at reduced pressure to remove all the solvent. The solid residue was purified by silica gel column chromatography by using dichloromethane/hexane 4:1 v/v as eluent. The first pink band was collected as compound **7**. Then, dichloromethane was used to elute out the third band, which is characterized to be compound **8**.

Compound **7** (25 mg, 35%, calculation based on **3**): UV/Vis (CHCl₃) λ_{\max} 573, 532 nm; FT-IR (KBr, cm⁻¹) ν 2958, 2860, 1694 (s, C=O), 1653 (s, C=O), 1598, 1436, 1336, 1270; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 9.37 (d, *J* = 8.4 Hz, 2H, perylene-H), 8.37 (d, *J* = 8.4 Hz, 2H, perylene-H), 8.19 (s, 2H, perylene-H), 4.32 (t, *J* = 6.5 Hz, 4H, O-CH₂), 4.12 (m, 4H, N-CH₂), 2.04 (m, 4H, CH₂), 1.92 (m, 2H, CH), 1.66 (m, 4H, CH₂), 1.39 (m, 24H, CH₂), 0.97 (m, 12H, CH₃), 0.90 (t, *J* = 7.1 Hz, 6H, CH₃); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 163.8, 163.5, 135.8, 133.4, 128.6, 128.6, 128.3, 128.2, 125.5, 123.0, 122.8, 121.0, 70.5, 44.3, 38.0, 31.6, 30.9, 29.4, 28.8, 26.1, 24.2, 23.1, 22.7, 14.1, 14.1, 10.7; MS (MALDI-TOF): m/z 815.6 (M⁺+1); Elemental analysis (%), calcd. for (C₅₂H₆₆N₂O₆): C, 76.62; H, 8.16; N, 3.44; Found: C, 76.89; H, 8.25; N, 3.35.

Compound **8** (9 mg, 11%, calculation based on **3**): UV/Vis (CHCl₃) λ_{\max} 574, 532, 503 nm; FT-IR (KBr, cm⁻¹) ν 2958, 2869, 2231 (s, -CN), 1695 (s, C=O), 1658 (s, C=O), 1593, 1437, 1330, 1270; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 9.53 (d, *J* = 8.1 Hz, 1H, perylene-H), 8.81 (d, *J* = 8.2 Hz, 1H, perylene-H), 8.52 (d, *J* = 8.3 Hz, 1H, perylene-H), 8.43 (d, *J* = 8.3 Hz, 1H, perylene-H), 8.18 (s, 1H, perylene-H), 8.06 (s, 1H, perylene-H), 7.05 (s, 1H, Ar-H), 6.94 (s, 1H, Ar-H), 4.36 (m, 2H, O-CH₂), 4.03 (m, 2H, O-CH₂), 3.88 (m, 2H, N-CH₂), 3.71 (m, 2H, N-CH₂), 2.05 (m, 2H, CH₂), 1.91 (m, 3H, CH), 1.73 (m, 6H, CH₂), 1.67–0.97 (m, 24H, CH₂), 0.95–0.77 (m, 21H, CH₃); MS (MALDI-TOF): m/z 985.4 (M⁺+1); Elemental analysis (%), calcd. for (C₆₂H₇₂N₄O₇): C, 75.58; H, 7.37; N, 5.69; Found: C, 75.39; H, 7.26; N, 5.75.

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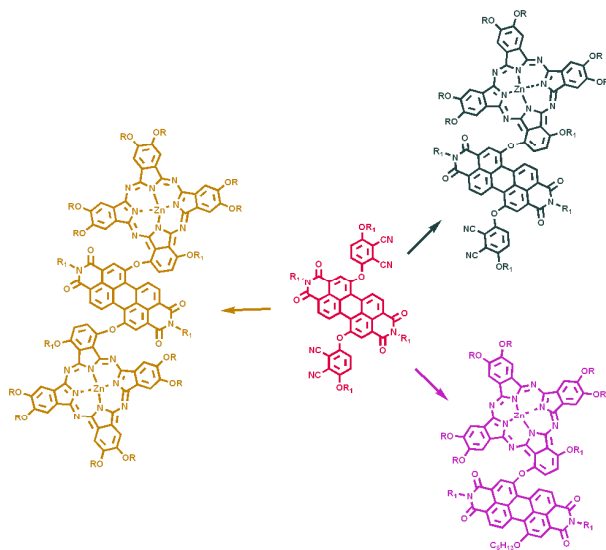
Notes and references

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Graphical Abstract:

Three novel multi-component chromophores based on phthalocyanine and perylenediimide moieties were synthesized by one condensation reaction.