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Organic solar cells have attracted wide interests due to their potential properties of light-weight, flexibility, low-cost and coatings applicable to large areas.¹ In organic solar cells, polymer solar cells still suffer from some shortcomings, such as batch-to-batch variation, indefinite molecular weight, polydispersity and impurity. In contrast, small-molecule materials intrinsically do not have such drawbacks. Furthermore, small molecule organic materials could exhibit a higher charge carrier mobility, as well as tuning more easily their band structure to absorb sunlight efficiently. Notably, phthalocyanines (Pcs), as a typical small organic material molecule used in organic solar cells, have attracted extensive attention in recent years. Pcs have highly delocalized π -electron systems and show unique electronic and optical properties.²⁻⁴ Consequently, they are very important in the field of photovoltaics and molecular photonics as the p-type photoconductors.⁵⁻⁸ However, Pcs just have the Soret-band $(\sim 340 \text{ nm})$ and Q-band $(\sim 670 \text{ nm})$. The light absorption of Pcs in the range of 400-600 nm, corresponding to the strongest intensity in the sunlight, is very weak. The dissolubility of films of unsubstituted Pcs is relatively lower. Further, the film fabrication processes are complicated and

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Novel porphyrin–phthalocyanine heterodimers and heteropentamers: synthesis, characterization and application in organic solar cells[†]

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Two novel types of covalently ether-linked porphyrin–phthalocyanine (Por–Pc), heterodimer and heteropentamer, connected through the *meso* phenyl group of the porphyrin have been synthesized for the first time. The Por–Pc heterodimer and heteropentamer have more delocalized π -electrons and therefore their conjugated degree is higher. In addition, these compounds possess better solubility and a wider light absorption than typical single porphyrins and phthalocyanines. Solar cell devices based on assynthesized porphyrin–phthalocyanine heterodimers and heteropentamers as donor materials and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as the acceptor material are prepared and show a noticeably better performance. The suitable ZnPor–(O–ZnPc)₄ : PCBM weight ratio for photovoltaic devices is 4 : 1 and the highest photovoltaic properties are achieved based on ZnPor–(O–ZnPc)₄ : PCBM (4 : 1) annealed at 140 °C in a vacuum for 20 min. The highest PCE is 2.08.

require expensive equipments, which result in difficulties for large scale applications. As another kind of typical molecule used in organic solar cell, porphyrins (Pors) have a good absorption in the region of 400-600 nm and better dissolubility in organic solvents. Considering the respective advantages of these two kinds of materials, we have deduced that the conjugates of Pors and Pcs will have potential applications as donor materials in the field of organic photovoltaics. These conjugates should promote absorptions in the visible light region and solubility in organic solvents. Moreover, since the Q-band absorption of Pcs almost overlaps with the fluorescence wavelength of Pors, the excitation and the singlet-state intramolecular energy transfer from Pors to Pcs can be suppressed greatly in Por-Pc dimers. So, these conjugates will become a good candidate in molecular photonics, catalysis and light harvesting architectures.9 However, few studies about the synthesis and application in organic solar cells of Por-Pc compounds have been reported until now.

In this paper, we have designed and synthesized two novel Por-Pc heterodimer and heteropentamer compounds. The obtained novel Por-Pc compounds have more delocalized π -electrons. The properties of the solar cells based on these two novel compounds indicate that these novel compounds have a noticeably better performance than single porphyrin and phthalocyanine.

Two different synthetic approaches have been followed for the synthesis of the dimer (ZnPor–(O–ZnPc)) and pentamer (ZnPor–(O–ZnPc)₄). The synthetic routes for the dimer (ZnPor– (O–ZnPc)) and pentamer (ZnPor–(O–ZnPc)₄) are shown in

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Scheme 1 Syntheses of the Por-Pcs heterodimer and heteropentamer.

Scheme 1. Initially, *meso*-tetra(4-hydroxylphenl) porphyrin (THPP) is prepared as indicated by the literature.¹⁰ The *meso*-tetra [4-(3, 4-dicyanophenoxy) phenyl]-porphyrin (TDPP) is synthesized by a nitro-group displacement reaction (molecular structure of TDPP is shown in the ESI,† Fig. S1a). The yield of the reaction is about 92.8%. Most of the reagent THPP is converted to product and the lost yield is attributed to wastage in the purification procedure. The high yield may benefit from the increased nucleophilic nature of the attacking oxygen on the Por species.

The synthesis of dimer (ZnPor-(O-ZnPc)) is through the direct condensation of TDPP with subphthalocyanine (SubPc) (Scheme 1). The condensation reaction is carried out under the conditions of N₂ protection and zinc chloride as the template. The yield of the reaction is around 33.4%. The mass spectrum reveals a molecular ion peak at 1697.34 m/z [M]⁺. The calculated molecular mass of the dimer (ZnPor-(O-ZnPc)) should be 1697.38 g mol⁻¹. The result indicates that the obtained (ZnPor-(O-ZnPc)) sample has the same molecular mass as the calculated molecular mass. All analysis data of the (ZnPor-(O-ZnPc)) sample such as IR, UV-vis absorption spectrum, ¹HNMR and mass spectrum can be seen in the ESI,† Fig. S2-S5. The results that come from IR, UV-vis absorption, ¹HNMR and the mass spectrum confirm that the (ZnPor-(O-ZnPc)) has the expected molecular structure. The detailed analysis of these results can be seen in the ESI.†

Under N_2 protection, pentamer (ZnPor-(O-ZnPc)₄) is synthesized through the condensation of the excess O-benzenedinitrile and TDPP. O-Dichlorobenzene and N,N-dimethylaminoethanol (DMAE) are the solvents and zinc chloride is the template in this reaction. After a 24 h reflux reaction and purification by column chromatography, the pentamer $(ZnPor-(O-ZnPc)_4)$ is primarily obtained with a 10.8% yield. The low yield is partly due to wastage in the purification procedure. The mass spectrum revealed a molecular ion peak at 3045.86 m/z [M]⁺. The calculated molecular mass of the pentamer (ZnPor-(O-ZnPc)₄) should be 3045.79 g mol⁻¹. The result indicates that the obtained (ZnPor-(O- $ZnPc)_{4}$ sample has the same molecular mass as the calculated molecular mass. All the analysis data of the $(ZnPor-(O-ZnPc)_4)$ sample, such as IR, UV-vis absorption spectrum, HNMR and the mass spectrum can be seen in the ESI,[†] Fig. S6–S9. The results that come from IR, UV-vis absorption, ¹HNMR and the mass spectrum confirm that the ZnPor-(O-ZnPc)₄ has the expected molecular structure. These two novel compounds are the covalently ether-linked Por-Pc heterodimer and heteropentamer (see Fig. S1b and S1c, ESI[†]). We have confirmed that the two novel compounds are synthesized and that they have the structures as we designed them.

The ball-and-stick models of ZnPor–(O–ZnPc) and ZnPor– (O–ZnPc)₄ can be seen in Fig. 1a and 1b. Two macrocycles of the heterodimers are linked through an ether bond. The ends of the ether bond are the *meso*-phenyl groups of the Por and phenyl groups of the Pc, respectively. The heteropentamer is composed of four ZnPc molecules and one ZnPor molecule. The ZnPor molecule is linked with four ZnPc molecules by four ether bonds and located in the centre of these four ZnPc molecules. The oxygen atom, which links two macrocycles, plays the role of "active" spacer.

Fig. 1c shows the UV-vis absorption spectrum of dimer (ZnPor-(O-ZnPc)) and pentamer (ZnPor-(O-ZnPc)₄) in DMF compared with those of zinc meso-tetraphenylporphyrin (ZnTPP) and ZnPc. The strong absorptions at 415 nm and 670 nm are assigned to the Soret band of Por and Q band of Pc, respectively.^{10,11} The absorption spectrum of the ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄ show that they have the characteristic absorptions of the individual two macrocyclic components at the same time. Compared with the absorption of ZnTPP and ZnPc, it is known that the absorptions around 340 nm and 430 nm of ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄ come from the Soret band of Por and Pc respectively, and the absorptions about 600 nm and 670 nm come from the Q band of Pc. The absorption at 638 nm for ZnPor-(O-ZnPc) and $ZnPor-(O-ZnPc)_4$ is a new absorption peak compared with that of Por and Pc. The UV-vis absorption spectrum confirms that the formation of a Pc ring according to the appearance of a Pc Q-band (670 nm). But for ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄, the remarkable red shifts of the Soret band absorption from 415 nm to 426 nm of ZnPor-(O-ZnPc) and 415 nm to 428 nm for ZnPor-(O-ZnPc)₄ are detected, respectively. The red shifts of the Soret bands in ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄ suggest that the Pc substituent possesses an electron-



Fig. 1 (a, b) Ball-and-stick models of the Por–Pc ZnPor–(O–ZnPc) and ZnPor–(O–ZnPc)₄, (c) UV-vis absorption spectrum of ZnPor–(O–ZnPc) and ZnPor–(O–ZnPc)₄ in DMF, ZnTPP and ZnPc, (d) UV-vis absorption spectra of PCBM, ZnPor–(O–ZnPc), ZnPor–(O–ZnPc)₄, ZnPor–(O–ZnPc)₄ : PCBM (film 1) and ZnPor–(O–ZnPc) : PCBM (film 2).

donor character and help to enhance the absorption in the visible light region. This results in a reduction of their HOMO-LUMO gap. As a consequence, the electron-donating peripheral substituent on the Por complexes gives rise to the red shifts in the Q absorption.¹² The relative intensity of the Q band absorption relative to that of the Soret band is higher for ZnPc moieties compared with ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄. There is almost no shift in the Q-band position (670 nm) for ZnPc, ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄. This result excludes the possibility of a charge transfer interaction in the ground states of ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄.¹³ The results of the UV-vis spectra indicate that ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄ have a broader spectral coverage in the visible region, as we expected.

The energy levels of the pentamer $(ZnPor-(O-ZnPc)_4)$ and dimer (ZnPor-(O-ZnPc)) were evaluated by cyclic voltammetric studies. The value of EHOMO, ELUMO and Eg are -5.42 eV, -3.71 eV and 1.72 eV, respectively for ZnPor- $(O-ZnPc)_4$, -5.38eV, -3.62 eV, and 1.7 eV, respectively for ZnPor-(O-ZnPc). According to the reference, the HOMO and LUMO of PCBM, a typical electron acceptor of organic solar cells, are -6.0 eV and 4.3 eV, respectively.¹⁴ The LUMOs of ZnPor- $(O-ZnPc)_4$ and ZnPor-(O-ZnPc) are clearly higher than that of PCBM. Consequently, it is energetically favorable for photoexcited ZnPor- $(O-ZnPc)_4$ and ZnPor-(O-ZnPc) to transfer electrons to PCBM molecules. Therefore ZnPor-(O-ZnPc)₄ and ZnPor-(O-ZnPc) can be used as electron donors and PCBM as an electron acceptor to fabricate solar cells. Fig. 1d shows the UV-vis absorption spectra of the films of ZnPor-(O-ZnPc), ZnPor-(O- $ZnPc)_4$, PCBM and the active films of $ZnPor-(O-ZnPc)_4$: PCBM (film 1) and ZnPor-(O-ZnPc) : PCBM (film 2). It is found that the absorption of active films is the liner superposition of the absorption of the donor and acceptor. This demonstrates that there is no interaction between the ground state of the donor molecules and acceptor molecules. Compared with the absorption spectra of ZnPor-(O-ZnPc) and ZnPor-(O-ZnPc)₄ in solution, the UV absorption of the films has a red shift which indicates a strong interaction between molecules in the solid state. Fig. 1d also shows that the absorption range of the ZnPor-(O-ZnPc)₄ : PCBM film is wider than that of ZnPor-(O-ZnPc): PCBM, as well as the intensity being stronger. Consequently more excitons will occur in ZnPor-(O-ZnPc)₄ : PCBM under sunlight illumination, and thus, the photocurrent of the solar cells should be improved. Devices based on ZnPor-(O-ZnPc), ZnPor-(O-ZnPc)₄ and PCBM were prepared by the spin-coating method. The compared devices based on porphyrin (ZnTPP): PCBM and phthalocyanine (ZnTCPc): PCBM were prepared at the same time. The structures of the four devices are:

Device 1: ITO/PEDOT : PSS/ZnPor-(O-ZnPc) : PCBM/Al.



Fig. 2 *I–V* characteristics of devices based on porphyrin and phthalocyanine compounds.

Device 2: ITO/PEDOT : PSS ZnPor-(O-ZnPc)4 : PCBM/Al. Device 3: ITO/PEDOT : PSS/ZnTPP : PCBM/Al. Device 4: ITO/PEDOT : PSS/ZnTCPc/PCBM/Al.

The weight ratio of the donor and acceptor is 1:1. PEDOT: PSS was prepared by the spin-coating method to modify the anode. 80 nm Al was prepared by the thermal evaporation method. The thickness of PEDOT: PSS is 40 nm. The thickness of the active layer in four devices is the same as 80 nm. Other parameters are listed in the ESI.[†]

In order to investigate the effect of the ratio of donor and acceptor, different devices were prepared with different weight ratios of ZnPor–(O–ZnPc) : PCBM, for example 1:3, 1:2, 1:1, 2:1, 3:1 and 4:1, respectively. In addition, the annealing temperature effect was investigated subsequently. LiF was used to modify the cathode in these devices.

According to the above results, we can confirm that ZnPor-(O–ZnPc) and ZnPor-(O–ZnPc)₄ possess relatively good photovoltaic properties, as we expected. Fig. 2 shows the *I–V* characteristics for these devices under an AM 1.5G 100 mW cm⁻² illumination. Photovoltaic parameters of these cells, such as open circuit voltage (V_{OC}), short circuit current (J_{SC}), filling factor (*FF*) and power conversion efficiency (η) were calculated from the analysis of the *J–V* characteristics (seen in Fig. 2), as shown in Table 1.

The properties of device 1 and device 2 are superior to tose of device 3 and device 4. The results indicate that device 1 and device 2, respectively based on ZnPor–(O–ZnPc) and ZnPor–(O– $ZnPc)_4$ as the electron donor, possess similar V_{OC} . The J_{SC} of device 2 is improved compared to device 1, which is attributed to the enhanced sunlight adsorption of device 2 compared with that of device 1, according to the results shown in Fig. 1d. More excitons are formed correspondingly and the current density of device 2 is improved. These results primarily reveal that $ZnPor-(O-ZnPc)_4$ has shown the best photovoltaic property performance among these materials.

Then we fabricated solar cell devices based on ZnPor– $(O-ZnPc)_4$ as the electron donor and PCBM as the electron acceptor with different weight ratios. The device structure is: ITO/PEDOT : PSS/ZnPor– $(O-ZnPc)_4$: PCBM/LiF/Al.

 $110/PEDO1 : PSS/ZIIPOI-(O-ZIIPC)_4 : PCBM/LIF/AI$

The weight ratio of ZnPor-(O–ZnPc)4 : PCBM is 1 : 1, 2 : 1, 3 : 1, 4 : 1, 1 : 2 and 1 : 3 respectively. The photovoltaic properties were detected under the same conditions. The results are shown in Fig. 3a and the parameters are listed in Table 2. It is found that V_{OC} is almost the same for different devices but the J_{SC} is not. In organic photovoltaic devices with the same structure, V_{OC} depends mainly on the energy difference between the HOMO energy level of the donor and the LUMO of the acceptor. So V_{OC} is almost the same for all devices with different weight ratios of ZnPor-(O– ZnPc)₄ : PCBM. When the weight ratio of the donor and acceptor is different, J_{SC} increases with the increasing donor concentration. J_{SC} achieved a maximum value when the weight ratio was 4 : 1. This means that 4 : 1 is the suitable weight ratio to achieve the best photovoltaic performance.

Table 2 shows that the suitable ratio of ZnPor-(O- $ZnPc)_4$: PCBM is 4 : 1. A decrease of the $ZnPor-(O-ZnPc)_4$ ratio will result in weak sunlight absorption. Correspondingly, the number of formed excitons will decrease. The molecule weight of ZnPor-(O-ZnPc)₄ is about 3000, almost 4 times larger than that of PCBM. When the weight ratio of ZnPor-(O- $ZnPc)_4$: PCBM is 4 : 1, the mole ratio is close to 1 : 1, which is helpful to form uniform domains of phase separation for exciton dissociation. When the ratio of PCBM increases or ZnPor-(O-ZnPc)₄ decreases, the excess PCBM aggregates and forms a big phase domain. The result is that the interface of exciton dissociation decreases and the photovoltaic performance of the device lowers correspondingly. Even though to increase the weight ratio of ZnPor-(O-ZnPc)₄ can help to increase the absorption of sunlight, the recombination of formed excitons will increase too. According to the experiment result the suitable weight ratio is 4 : 1.

Annealing can improve the crystallization of the photo active layer. The better crystallization of the photo active layer is beneficial for carrier transfer in addition to the formation of

Device	Solar cell	$V_{\rm OC}$ (V)	$J_{\rm SC}~({ m m~cm^{-2}})$	FF (%)	η (%)
1	ITO/PEDOT : PSS/ZnPor-(O-ZnPc) : PCBM/Al	0.58	2.38	37.5	0.52
2	ITO/PEDOT : PSS/ZnPor-(O-ZnPc) ₄ : PCBM/Al	0.59	2.94	39.2	0.68
3	ITO/PEDOT : PSS/ZnTPP : PCBM/Al	0.55	1.27	32.3	0.23
4	ITO/PEDOT : PSS/ZnTCPc/PCBM/Al	0.54	1.04	28.3	0.16

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Fig. 3 /-V characteristics of devices with different ratios of ZnPor-(O–ZnPc)₄ : PCBM (a) and devices with ZnPor-(O–ZnPc)₄ : PCBM = 4 : 1 annealed at different temperatures (b).

Table 2 Photovoltaic parameters of devices with different ratios of ZnPor–(O– ZnPc)_4 : PCBM

Weight Ratio	$V_{\rm OC}({ m V})$	$J_{\rm SC}~({ m mA~cm}^{-2})$	FF (%)	η (%)
1:1	0.58	3.30	39.6	0.76
1:2	0.59	3.00	38.5	0.68
1:3	0.6	2.72	39.9	0.65
2:1	0.59	3.50	39.2	0.81
3:1	0.59	3.72	39.9	0.86
4:1	0.61	3.99	39.7	0.97

uniform domains. Therefore, the photoactive layer was annealed at different temperatures in vacuum, 100 °C, 120 °C, 140 °C and 160 °C, respectively, for 20 min. Fig. 3b is the curve of the current density *versus* the voltage. It shows that the current density and filled factor increase along with the increasing of the annealing temperature. The best performance is achieved below 140 °C annealing. The current density increases from 3.99 mA cm⁻² to 4.97 mA cm⁻², and the filled factor increases from 39.7% to 57.5% (shown in Table 3). Combined with the results of AFM shown in Fig. 4, it is concluded that best and uniform phase separation is achieved in the photo active layer annealed at 140 °C. The phase separation implies that an interpenetrating network structure is formed in the photo active layer, which is beneficial for exciton dissociation and charge transfer. In

 Table 3 Photovoltaic parameters of devices with different annealing temperatures

$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	η (%)
0.62	3.82	55.2	1.31
0.61	4.19	55.8	1.43
0.63	4.97	57.5	2.08
0.63	4.34	57.8	1.58
	V _{OC} (V) 0.62 0.61 0.63 0.63	$V_{\rm OC}$ (V) $J_{\rm SC}$ (mA cm ⁻²) 0.62 3.82 0.61 4.19 0.63 4.97 0.63 4.34	$V_{\rm OC}$ (V) $J_{\rm SC}$ (mA cm ⁻²) FF (%)0.623.8255.20.614.1955.80.634.9757.50.634.3457.8

our experiment, the photo active layer was prepared by the solution method by using *N*,*N*-dimethylformamide (DMF) as the solvent. DMF is a high boiling point solvent (152.8 °C). Its volatilizing is very slow during the spincoating process. Therefore, it is necessary to anneal the photo active layer to eliminate the residual DMF. 140 °C is close to the boiling point of DMF. Annealing under 140 °C allows DMF to volatilize slowly. The crystallization of the photo active layer will be improved. The lower annealing temperature is not helpful for DMF volatilizing and residual DMF will affect the carrier



Fig. 4 AFM images of the thin films of ZnPor–(O–ZnPc)₄ : PCBM with different annealing treatments, (a) annealing at 100 °C, (b) annealing at 120 °C, (c) annealing at 140 °C and (d) annealing at 160 °C.

transfer and collection. But at higher annealing temperatures DMF volatilizes faster, which will result in a roughness of the photo active layer and affect the ageing of the photo active layer.

Conclusions

We have designed and synthesized two novel compounds (Por-Pc conjugates) in this work. The Por-Pc heterodimer and heteropentamer have more delocalized π -electrons and therefore their conjugation degree is higher. These compounds possess a better solubility and wider light absorption. Por-Pc conjugates that are linked through covalent linkers are a kind of effective light harvesters. They have a broader spectral coverage in the visible region. These two kinds of ZnPor-ZnPc can be used as electron donor materials in solar cells. The properties of the solar cells based on them have been investigated. The results confirmed that the device properties of ZnPor-(O-ZnPc) : PCBM and ZnPor-(O-ZnPc)₄ : PCBM are superior to single Por and Pc for solar cell applications. The suitable weight ratio of $ZnPor-(O-ZnPc)_4$: PCBM is 4 : 1. The highest photovoltaic properties were achieved with ZnPor-(O- $ZnPc)_4$: PCBM (4 : 1) annealed at 140 °C in a vacuum for 20 min. The highest power conversion efficiency (PCE) is 2.08. The Por-Pc conjugates possess the structure and properties as we expected. Our work has remarkably promoted the performance of the active layer materials of organic solar cells. It can provide a new strategy for the improvement of the power conversion efficiency of organic solar cells.

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