

View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Zhang, C. Liu, T. Lai, H. Huang, X. Peng, F. Huang and Y. CAO, *J. Mater. Chem. A*, 2016, DOI: 10.1039/C6TA05726H.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsA

A water/alcohol soluble conjugated porphyrin small molecule as a cathode interfacial layer for efficient organic photovoltaics

Lin Zhang, Chang Liu, Tianqi Lai, Huadong Huang, Xiaobin Peng*, Fei Huang, Yong Cao

State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer

Optoelectronic Materials and Devices, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China. *Email: chxbpeng@scut.edu.cn

Abstract: A water/alcohol soluble conjugated porphyrin small moleculeFNEZnP-OE, in which two amino-functionalized fluorene 9,9-bis(30-(N,N-dimethylamino)propyl)-2,7fluorenes are linked to a porphyrin core substituted with two polar 3.4-bis-[2-(2-methoxyethoxy)-ethoxy]-phenylsby ethynylene linkages, is designed and synthesized as a cathode interfacial material (CIM) for bulk heterojuction organic solar cells. The PTB7/PC₇₁BM– and PTB7-Th/PC₇₁BM–based devices with FNEZnP-OE as the electron transport layers (ETLs) exhibit power conversion efficiencies (PCEs) of 8.52% and 9.16%, respectively, which are increased by 47% and 41% compared to the devices with no ETL (5.78% and 6.50%), respectively. Most significantly, these PCEs are increased by 13.6% and 8%, respectively, than with widely polymer ETLs PFN (poly[(9,9-bis(30-(N,Nthose used dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-ioctylfluorene)]). The outstanding performance of FNEZnP-OE CIM is contributed by not only the polar groups of 9,9-bis(30-(N,N-dimethylamino)propyl)-2,7-fluorenes and 3,4-bis-[2-(2-methoxy-ethoxy)-ethoxy]phenyls but also the porphyrin-relating π -conjugated backbone of FNEZnP-OE induced by the ethynylene linkages, demonstrating that functionalized porphyrins are very promising interfacial materials.

Keywords: water/alcohol soluble; porphyrin; small molecule; electron transport layer

Journal of Materials Chemistry A Accepted Manuscript

1. Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) have attracted ever increasing interest due to light-weight, mechanical flexibility, and the potential of developing large-area devices through low-cost solution processing.^{1,2} Also, the power conversion efficiencies (PCEs) more than 10% have been achieved in the past few years.^{3,4} Among several factors that contributed to this advance, cathode interfacial materials (CIMs)ranging from inorganic metal compounds to organic polymeric/small molecules have been proven effective in improving OSC performance⁵⁻¹⁶ because an effective electron transport layer (ETL) between a metal cathode and an active layer can decrease the high work function (W_F) of a bare metal cathode to improve the ohmic contact of the metal with the electron acceptor material and thus to enhance the open-circuit voltage ($V_{\rm OC}$) of OSCs.¹⁶⁻¹⁸

Among the numerous CIMs, water/alcohol-soluble conjugated polymers are very promissing in optoelectronic devices since they are processed from environmentally friendly solvents of alcohol, which is important for future industrial applications and can prevent solvent erosion during the multilayer device fabrication since active layers are usually not soluble in alcohol. Especially, the water/alcohol-soluble conjugated CIM poly[(9,9-bis(30-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-ioctylfluorene)] (PFN) has been widely used in organic photovoltoics (OPVs),^{4,19-21} and the amino-functionalized fluorene moiety plays very important roles for the excellent performance.

Compared to polymers, organic small molecule (SM) -based CIMs are attracting attentions recently due to their intrinsic advantages such as well-defined chemical structure. simple synthesis and purification and good batch-to-batch reproducibility. However, the reports on SM CIMs are very limited.^{11,15, 22-27} Therefore, it is very important to develop new and better CIMs. As the analogues of chlorophylls, porphyrins and their derivatives have been intensively investigated as electronic materials due to the big π -conjugated planes, high molar

2

absorption coefficients and easy chemical modifications of the peripheries to improve the intramolecular charge transport and intramolecular electron transfer. We employed ethynylene linkages to connect electron acceptor moieties such BT and DPP with porphyrin core to synthesize conjugated porphyrin donor materials for OSCs. Contributed by the ethynylene linkages, these molecules are planar and the backbones are fully conjugated, significantly enhancing their charge mobilities and OPV performance compared to the corresponding materials without ethynylene linkages.²⁸⁻³⁰ Very recently, *meso*-tetra-pyridinium- and *meso*-tetra-phenyl–derived porphyrins were reported as CIMs with improved OPV performance. However, it is noted that these compounds are not conjugated due to the perpendicular conformation between the pyridiniums or phenyl groups and the porphyrin core, ³¹⁻³³ which can limit the charge mobilities/transportation between the cathode and the active layers even though the self-assembled porphyrin can enhance the electron transportation to some extent.³¹

In this study, using ethynylene linkages, we connect a very typical CIM block 9.9bis(30-(N,N-dimethylamino)propyl)-2,7-fluorene (FN) to a porphyrin core substituented with two polar 3,4-bis-[2-(2-methoxy)-ethoxy]-phenyls to synthesize a conjugated porphyrin small molecule FNEZnP-OE (Figure 1a). Contributed by the polar groups of two FN moieties and two 3,4-bis-[2-(2-methoxy-ethoxy)-ethoxy]-phenyls, FNEZnP-OE shows good solubility in alcohol and is also soluble in pure water. The BHJ OSCs using FNEZnP-OE as the ETL between Al cathode and the active layers of PTB7/ PC₇₁BM and PTB7-Th/PC₇₁BM (Figure1, **PTB7**: poly[[4,8-bis](2-ethylhexyl)oxy]benzo[1,2-b:4,5-b'] dithiophene-2. 6-divl] [3-fluoro-2-[(2-ethylhexy)carbonyl]thieno[3,4-b]thiophenediyl]], **PTB7-Th**: poly[[2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b] dithiophene] [3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] and PC₇₁BM: [6, 6]-phenyl C₇₁ butyric acid methyl ester) exhibit PCEs of 8.52 and 9.16%, which are increased by 47% and 41% compared to the corresponding devices without any interlayer (5.78% and 6.50%),

Journal of Materials Chemistry A Accepted Manuscript

respectively. Most significantly, these PCEs are even higher than those with the widely used polymer PFN ETLs with 13.6% and 8% improvement, respectively.



Figure 1. Molecular structures of a) FNEZnP-OE and c) PTB7 and PTB7-Th, and b) device

architecture.

2. Experimental section

OPV Fabrication: ITO coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 4 min, 40 nm thick PEDOT:PSS (Bayer Baytron 4083) layer was spincoated on the ITO-coated glass substrates at 2500 rpm for 30 s, the substrates were subsequently dried at 150 °C for 10 min in air and then transferred to a N₂-glovebox. Then, an active layer was prepared on the top of PEDOT: PSS layer by spin coating at 1400 rpm for 40 s from a chlorobenzene solution of PTB7 (or PTB7-Th): PC₇₁BM (1:1.5 w/w, total concentration of 25 mg/ml) with 3 vol% 1, 8-diiodoctane. 0.4 mg/ml FNEZnP-OE methanol solution was then spin coated onto the active layer with a speed of 2000 rpm for 30 s (10 nm

thick). For PFN interlayers, methanol solution with concentrations of 0.2 mg/ml was spin coated onto the active layer with a speed of 2000 rpm for 30 s. Finally, Al (~90 nm) was evaporated in a high-vacuum chamber with base pressure $<3\times10^{-6}$ mbar as the top electrode. Masks made from laser beam cutting technology with a well-defined area of 0.16 cm² were attached to define the effective area for accurate measurement.

Thickness measurment: The thicknesses of films more than 100 nm were measured by a profile. But for the very thin films, their thicknesses were calculated according to the absorption and thickness values of thick films and the absorption values of very thin films.

3. Results and discussion

3.1.Synthesis, and Optical and Electrochemical Properties

As shown in **Scheme** S1, **FNEZnP-OE** was obtained from the coupling of 5,15diethynyl-10,20-bis(3,4-bis-[2-(2-methoxy-ethoxy)-ethoxy]phenyl)porphyrin zinc with 2bromo-9,9'-bis(3"-(N,N-dimethylamino)propyl)-fluorene, which were both synthesized and purified according to reported procedures.^{28,34} Contributed by the two FN moieties and two 3,4-bis-[2-(2-methoxy-ethoxy)-ethoxy]-phenyl groups, **FNEZnP-OE** shows excellent solubility in polar solvents such as H₂O, alcohol, DMF, and dimethyl sulfoxide (DMSO) without using any acid. Furthermore, FNEZnP-OE also shows good thermal stability with decomposition temperature higher than 300 °C (Figure S5).

As seen in **Figure 2**a, FNEZnP-OE exhibits a typical porphyrin Soret band at 454 nm and a Q band at 665 nm in CH₃OH. Since none conjugated zinc porphyrins usually exhibit Soret and Q bands at about 420 and 550 nm, respectively,^{31, 35} the significant redshifts of the Soret and Q bands are attributed to the enhanced intramolecular charge transfer (ICT) between the fluorene units and the porphyrin core due to the π -conjugation of the backbone induced by the ethynylene linkages. Furthermore, though the Q band intensity of FNEZnP-OE is much weaker than the Soret band, it is still much stronger than the very weak Q bands of non-conjugated zinc porphyrins, giving a more evidence of the conjugation between FN units and the porphyrin core.

The quantum chemical calculations further confirm the π -conjugation of FNEZnP-OE backbone. Density functional theory (DFT) calculations at the B3LYP/(6-31G(D)+LANL2DZ) level show the optimum geometry is planar(Figure S2), enabling the whole molecule conjugated. And the π -electrons at the highest occupied molecular orbital (HOMO) are delocalized at both the porphyrin core and the two fluorene moieties while those at the lowest unoccupied molecular orbital (LUMO) are mainly localized at the porphyrin core, which is beneficial for the ICT as revealed by its absorption spectrum.

In film, these bands red-shift to 470 and 683 nm, respectively, with the enhanced intensity of the Q band, and the absorption edge is seen at 713 nm, from which the optical band gap (E_g^{opt}) was calculated to be 1.74 eV. The HOMO energy level (E_{HOMO}) of **FNEZnP-OE** was measured by cyclic voltammetry (CV). Since the oxidation onset potential (E_{ox}) of Fc/Fc⁺ was measured to be 0.36 V with respect to the Ag/AgCl reference electrode under the same experimental conditions, the E_{HOMO} of FNEZnP-OE was estimated to be -4.99 eV from its onset oxidation potential (**Figure S3**) and according to the formula of $E_{HOMO} = -(E_{ox} + 4.80 - 0.36)$ (eV).³⁶ From the E_g^{opt} and E_{HOMO} , itsLUMO energy level (E_{LUMO}) was calculated to be -3.25 eV, which is higher than those of PTB7 and PTB7-Th as illastrated in the energy level diagram of **Figure 2b**.^{27, 37,38}

Published on 05 September 2016. Downloaded by New York University on 06/09/2016 11:52:04



Figure 2. (a) Absorption spectra of FNEZnP-OE in CH₃OH solution and in thin film, and (b) energy level diagram of the relating OPV materials.

3.2.Photovoltaic Properties

To evaluate the interfacial performance of **FNEZnP-OE**, itwas spin coated on top of the active layers from methanol solution as an ETL with the conventional BHJ OSC architecture of ITO/ PEDOT:PSS/active layer/**FNEZnP-OE**/Al (ITO: indium tin oxide, PEDOT:PSS: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) (**Figure 1**b) with **PTB7:PC**₇₁**BM** or **PTB7-Th:PC**₇₁**BM** as the active layers. For comparison, devices with no and PFN ETLs were also fabricated at the same condition. And the typical current density–voltage (J-V) characteristics and the corresponding EQE curves of the solar cells are shown in **Figure 3** with the OPV characteristics of the short circuit current (J_{sc}), open circuit voltage (V_{OC}), fill

Journal of Materials Chemistry A Accepted Manuscript

factor (FF) and power conversion efficiency (PCE) summarized in **Table 1**. As seen in Figure 3 and Table1, without any ETL, the OSCs with $PTB7:PC_{71}BM$ as the active layers show a mediate PCE of 5.78% with a J_{SC} of 15.96 mA cm⁻², a V_{OC} of 0.62 V and a FF of 59.48%. When the very typical polymer CIM of PFN was employed, the V_{OC} , J_{SC} , and FF values are increased simultaneously to 16.37 mA cm⁻², 0.72 V and 63.61%, respectively, leading to a much improved PCE of 7.50%. When PFN ETL is replaced by FNEZnP-OE, the PCE can be further enhanced to 8.52% with a significantly enhanced FF to 70.31%, a slightly improved $V_{\rm OC}$ of 0.74 V and the almost same $J_{\rm SC}$ of 16.38 mA cm⁻². The PCE of 8.52% is increased by 13.6% and 47.4% compared to those devices with PFN and no ETL, respectively. For the devices based on PTB7-Th:PC71BM as the active layers, the solar cells with **FNEZnP-OE** ETLs show a J_{SC} of 16.47 mA cm⁻², a V_{OC} of 0.81 V and a FF of 68.69%, leading to a PCE of 9.16%, which is increased by 8% and 41% compared to those devices with PFN and no ETL, respectively. We noted that some groups have already reported high PCE around 9% and the PCEs optimized here are only mediate for devices based on PTB7- or PTB7-Th:PC71BM active layers and PFN ETLs,²⁷ which may be ascribed to the material batch differences.

The J_{SC} values calculated from the external quantum efficiency (EQE) spectra (Figure S4), of the devices without and with ETLs are listed in Table 1, which agree well with the measured ones. It is noted that FNEZnP-OE ETLs can enhance the J_{SC} , V_{OC} and FF simultaneously though only slightly for $J_{\rm SC}$ but significantly for both the $V_{\rm OC}$ and FF compared to those with no ETL for both PTB7-Th:PC71BM- and PTB7:PC71BM-based devices. Even compared to the devices with the widely used PFN ETLs, the OSCs with **FNEZnP-OE** ETLs show slightly improved J_{SC} and V_{OC} , and enhanced FF in different extent, indicating that **FNEZnP-OE** performs excellent as a CIM.



Figure3. J-V curves of OSCs with/without ETLs using a) PTB7:PC₇₁BM and b) PTB7-Th:PC₇₁BM as the active layers.

Active layer	ETL	$J_{\rm SC}({\rm J_{SC}}^{\rm cal})$ (mA cm ⁻²)	V _{OC} (V)	FF (%)	PCE (%) max(ave)	Rs $(\Omega \cdot \mathrm{cm}^2)$
PTB7:PC ₇₁ BM	no	15.96 (15.19)	0.62	59.48	5.78 (5.53±0.25)	7.73
	PFN	16.37 (15.27)	0.72	63.61	7.50 (7.45±0.05)	6.83
	FNEZnP-OE	16.38 (15.82)	0.74	70.31	8.52 (8.39±0.13)	4.76
PTB7- Th:PC ₇₁ BM	no	16.07 (14.97)	0.71	57.00	6.50 (6.40± 0.10)	9.90
	PFN	16.35 (15.29)	0.79	65.70	8.48 (8.42±0.06)	7.09
	FNEZnP-OE	16.47 (16.05)	0.81	68.69	9.16 (9.13±0.03)	5.38

Table 1. Device characteristics of the OSCs.

3.3. Work Functions of the Modified Cathodes

Since it has been reported that the V_{OC} enhancement by an ETL could be attributed to the W_F decreaseof a cathode,²⁵ we employed Kelvin-probe system under N₂ atmosphere to measure the effective W_F values of the Al electrodes bared and modified with the two CIMs of PFN and **FNEZnP-OE** to clarify the effect of the FNEZnP-OE ETL. As listed in **Table S2**, the W_F values of bared, FNEZnP-OE and PFN modified Al electrodes were measured to be

3.9, 3.4 and 3.5 eV, respectively.³⁹ The W_F of **FNEZnP-OE** modified Al electrode is even slightly smaller than PFN modified on, indicating the good electron injection ability of **FNEZnP-OE**.

The electron transport from the active layer to the Al cathode was not very efficient in devices with bare Al cathode because of the Schottky-barrier effect caused by the high contact resistance between the high work-function Al cathode and the LUMO of $PC_{71}BM$.⁴⁰ However, amino-functionalized materials modified metal cathodes (such as Al) could increase built-in potential of the OSCs through the surface dipole interaction between the pendant amino groups and the cathodes, leading to increased V_{OC} values.^{41,42} Since it also has been proved that polar side groups can induce a CIM withexcellent interfacial modification capability to enhance the charge collection from an active layer to a electrode,⁴³ the excellent electron transport and extraction abilities of **FNEZnP-OE** can be ascribed to not only the amino-functionalized side groups but also the polar 3,4-bis-[2-(2-methoxy-ethoxy)-ethoxy]-phenyl groups, which plays very important roles for the reduction of the W_F of the Al electrode due to the large interfacial dipoles.⁴⁴⁻⁴⁶

3.4 Dark J-V Characteristics of the Devices

Published on 05 September 2016. Downloaded by New York University on 06/09/2016 11:52:04

Compared to devices with PFN ETLs, the performance enhancement of FNEZnP-OE– based ones is mainly contributed by the improvement of *FF* especially for PTB7:PC₇₁BM active layer devices. The dark *J*–*V* characteristics of the devices shown in Figure 4 can provide useful information for the *FF* improvement. In dark, the reverse currents of the OSCs in the region from –2 to 0 V are the largest suppressed by FNEZnP-OE ETL among the three devices, suggesting the best charge transport and extraction abilities to reduce the hole and electron recombination near the FNEZnP-OE modified Al cathode.²⁵ These results are also consistent with the decreased series resistances (R_s) by FNEZnP-OE ETLs as summarized in Table 1 since reduced R_s values have been reported to be important for achieving higher *FF*

values in OSCs.⁴⁷ In addition, the reduced leakage currents and R_s in devices are also beneficial for obtaining a higher V_{OC} due to the reduced potential drop across the devices.⁴⁸



Figure 4. Dark *J*–*V* characteristics of the devices with a) PTB7:PC₇₁BM and b) PTB7-

Th:PC₇₁BM as the active layers.

3.5 Electron mobilities

Electron mobilities by the space charge limited current (SCLC) method for the electrononly devices based on the architectures of ITO/ ZnO/PTB7:PC₇₁BM/interlayer/Al provide us more information for the enhanced *FF* by **FNEZnP-OE** ETL.⁴⁹ As calculated from **Figure 5**, the electron mobilities for the devices with no, PFN and **FNEZnP-OE** ETLs are 1.92×10^{-5} , 2.30×10^{-4} and 3.05×10^{-4} cm² V⁻¹ s⁻¹, respectively. While the electron mobilities of the both devices with PFN and **FNEZnP-OE** ETLs show more than 10-folds enhancement compared to that with the bare Al, the mobility of **FNEZnP-OE** modified devices is even larger than that of PFN modified ones, demonstrating the better electron transporting of **FNEZnP-OE**.



Figure 5. J-V curves of the electron-only devices with the device structure of ITO/ZnO/PTB7:PC₇₁BM/interlayer/Al.

4. Conclusions

Published on 05 September 2016. Downloaded by New York University on 06/09/2016 11:52:04

In summary, a new conjugated water/alcohol-soluble small molecule **FNEZnP-OE**, consisting of two amino-functionalized fluorence units and a porphyrin core with the polar 3,4-bis-[2-(2-methoxy)-ethoxy]-phenyls connected by ethylene linkages, is developed as a cathode interface material for OSCs. The BHJ solar cells with FNEZnP-OE–modified Al cathodes, and PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM as the active layers show power conversion efficiencies of 8.52% and 9.16%, which are increased by 47% and 41% compared to the devices with no ETLs (5.78% and 6.50%), respectively.More importantly, FNEZnP-OE performs even better than a widely used polymer CIM PFN with 13.6% and 8% PCE enhancement, respectively. One the one hand, the two amino-functionalized fluorence units and the two polar 3,4-bis-[2-(2-methoxy-ethoxy)-ethoxy]-phenyls at porphyrin core play very important roles for the more favorable W_F of FNEZnP-OE modified cathode to increase the

built-in potential. On the other hand, the extended π -conjugation backbone of FNEZnP-OE by the ethylene linkages is also beneficial for the enhanced electron transport. These preliminary results demonstrate that suitably functionalized porphyrins and their analogues are very promising cathode interfacial materials.

Acknowledgements

This work was financially supported by the grants from International Science and Technology Cooperation Program of China (2013DFG52740, 2010DFA52150), and the National Natural Science Foundation of China (51473053, 51073060).

References

- 1. M. Granström, K. Petritsch, A. Arias, A. Lux, M. Andersson and R. Friend, *Nature*, 1998, **395**, 257-260.
- 2. Y. Huang, E. J. Kramer, A. J. Heeger and G. C. Bazan, Chem. Rev., 2014, 114, 7006-7043.
- 3. Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. Commun.*, 2014, **5**, 5293.
- 4. Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, *Nat. Photonics*, 2015, **9**, 174-179.
- C. J. Brabec, S. E. Shaheen, C. Winder, N. S. Sariciftci and P. Denk, *Appl. Phys. Lett.*, 2002, 80, 1288-1290.
- G. Li, C. Chu, V. Shrotriya, J. Huang and Y. Yang, *Appl. Phys. Lett.*, 2006, 88, 253503-253503.
- W. J. Beek, M. M. Wienk, M. Kemerink, X. Yang and R. A. Janssen, J. Phys. Chem. B, 2005, 109, 9505-9516.
- 8. K. Lee, J. Y. Kim, S. H. Park, S. H. Kim, S. Cho and A. J. Heeger, *Adv. Mater.*, 2007, **19**, 2445-2449.
- 9. P. Peumans, A. Yakimov and S. R. Forrest, J. Appl. Phys., 2003, 93, 3693-3723.
- 10. A. W. Hains, Z. Liang, M. A. Woodhouse and B. A. Gregg, *Chem. Rev.*, 2010, **110**, 6689-6735.
- 11. T. V. Pho, H. Kim, J. H. Seo, A. J. Heeger and F. Wudl, *Adv. Funct. Mater.*, 2011, **21**, 4338-4341.
- 12. K. Sun, B. Zhao, V. Murugesan, A. Kumar, K. Zeng, J. Subbiah, W. W. H. Wong, D. J. Jones and J. Ouyang, *J. Mater. Chem.*, 2012, **22**, 24155-24165.
- 13. K. M. O'Malley, C. Z. Li, H. L. Yip and A. K. Y. Jen, Adv. Energy Mater., 2012, 2, 82-86.
- Y. Zhou, C. Fuentes-Hernandez, J. Shim, J. Meyer, A. J. Giordano, H. Li, P. Winget, T. Papadopoulos, H. Cheun and J. Kim, *Science*, 2012, 336, 327-332.
- W. Y. Tan, R. Wang, M. Li, G. Liu, P. Chen, X. C. Li, S. M. Lu, H. L. Zhu, Q. M. Peng and X. H. Zhu, *Adv. Funct. Mater.*, 2014, 24, 6540-6547.
- 16. Q. Zhang, D. Zhang, X. Li, X. Liu, W. Zhang, L. Han and J. Fang, *Chem. Commun.*, 2015, **51**, 10182-10185.
- 17. Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, Nat. Photonics, 2012, 6, 593–597.

- 18. Z.-G. Zhang, B. Qi, Z. Jin, D. Chi, Z. Qi, Y. Li and J. Wang, *Energy Environ. Sci.*, 2014, 7, 1966-1973.
- 19. J. D. Chen, C. Cui, Y. Q. Li, L. Zhou, Q. D. Ou, C. Li, Y. Li and J. X. Tang, *Adv. Mater.*, 2015, **27**, 1035-1041.
- 20. L. Zuo, C.-Y. Chang, C.-C. Chueh, S. Zhang, H. Li, A. K.-Y. Jen and H. Chen, *Energy Environ. Sci.*, 2015, **8**, 1712-1718.
- Z. Zheng, S. Zhang, M. Zhang, K. Zhao, L. Ye, Y. Chen, B. Yang and J. Hou, *Adv. Mater.*, 2015, 27, 1189-1194.
- 22. C. Duan, C. Zhong, C. Liu, F. Huang and Y. Cao, *Chem. Mater.*, 2012, 24, 1682-1689.
- X. Cheng, S. Sun, Y. Chen, Y. Gao, L. Ai, T. Jia, F. Li and Y. Wang, *J. Mater. Chem. A*, 2014, 2, 12484-12491.
- 24. L. Nian, W. Zhang, N. Zhu, L. Liu, Z. Xie, H. Wu, F. Wurthner and Y. Ma, J. Am. Chem. Soc., 2015, **137**, 6995-6998.
- 25. S. Liu, G. Zhang, J. Lu, J. Jia, W. Li, F. Huang and Y. Cao, *J. Mater. Chem. C*, 2015, **3**, 4372-4379.
- 26. K. Zhao, L. Ye, W. Zhao, S. Zhang, H. Yao, B. Xu, M. Sun and J. Hou, *J. Mater. Chem. C*, 2015, **3**, 9565-9571.
- 27. Z. Wang, Z. Li, X. Xu, Y. Li, K. Li and Q. Peng, *Adv. Funct. Mater.*, 2016, DOI: 10.1002/adfm.201504734.
- 28. Y. Huang, L. Li, X. Peng, J. Peng and Y. Cao, J. Mater. Chem., 2012, 22, 21841-21844.
- 29. H. Qin, L. Li, F. Guo, S. Su, J. Peng, Y. Cao and X. Peng, *Energy Environ. Sci.*, 2014, 7, 1397-1401.
- K. Gao, L. Li, T. Lai, L. Xiao, Y. Huang, F. Huang, J. Peng, Y. Cao, F. Liu, T. P. Russell, R. A. Janssen and X. Peng, *J. Am. Chem. Soc.*, 2015, 137, 7282-7285.
- M. Vasilopoulou, D. G. Georgiadou, A. M. Douvas, A. Soultati, V. Constantoudis, D. Davazoglou, S. Gardelis, L. C. Palilis, M. Fakis, S. Kennou, T. Lazarides, A. G. Coutsolelos and P. Argitis, *J. Mater. Chem. A*, 2014, 2, 182-192.
- 32. T. Jia, W. Zhou, F. Li, Y. Gao, L. Wang, J. Han, J. Zhang and Y. Wang, *Sci. China Chem.*, 2015, **58**, 323-330.
- 33. J. Kesters, P. Verstappen, M. Kelchtermans, L. Lutsen, D. Vanderzande and W. Maes, *Adv. Energy Mater.*, 2015, **5**, 1500218.
- 34. W. Zhang, Y. Wu, Q. Bao, F. Gao and J. Fang, Advanced Energy Materials, 2014, 4, 1400359.
- 35. J. Lu, W. Cai, G. Zhang, S. Liu, L. Ying and F. Huang, *Acta Chim. Sinica* 2015, **73**, 1153-1160.
- 36. J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, 7, 551-554.
- 37. Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135-E138.
- C. Liu, C. Yi, K. Wang, Y. Yang, R. S. Bhatta, M. Tsige, S. Xiao and X. Gong, ACS Appl. Mater. Interfaces, 2015, 7, 4928-4935.
- 39. S. Braun, W. R. Salaneck and M. Fahlman, *Adv. Mater.*, 2009, **21**, 1450-1472.
- 40. H. L. Yip, S. K. Hau, N. S. Baek, H. Ma and A. K. Y. Jen, Adv. Mater., 2008, 20, 2376-2382.
- 41. F. Huang, H. Wu and Y. Cao, Chem. Soc. Rev., 2010, 39, 2500-2521.

- 42. C. Zhong, S. Liu, F. Huang, H. Wu and Y. Cao, Chem. Mater., 2011, 23, 4870-4876.
- 43. K. Zhang, C. Zhong, S. Liu, C. Mu, Z. Li, H. Yan, F. Huang and Y. Cao, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10429-10435.
- 44. S.-H. Oh, S.-I. Na, J. Jo, B. Lim, D. Vak and D.-Y. Kim, *Adv. Funct. Mater.*, 2010, **20**, 1977-1983.
- 45. C. Z. Li, C. C. Chueh, F. Ding, H. L. Yip, P. W. Liang, X. Li and A. K. Y. Jen, *Adv. Mater.*, 2013, **25**, 4425-4430.
- C. Duan, W. Cai, B. B. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan and A. J. Heeger, *Energy Environ. Sci.*, 2013, 6, 3022-3034.
- 47. W. Yu, L. Huang, D. Yang, P. Fu, L. Zhou, J. Zhang and C. Li, *J. Mater. Chem. A*, 2015, **3**, 10660-10665.
- 48. N. Li, B. E. Lassiter, R. R. Lunt, G. Wei and S. R. Forrest, Appl. Phys. Lett., 2009, 94, 023307.
- 49. V. Shrotriya, Y. Yao, G. Li and Y. Yang, Appl. Phys. Lett., 2006, 89, 063505.

Journal of Materials Chemistry A

15

Journal of Materials Chemistry A Accepted Manuscript

Graphical Abstract:

A water/alcohol soluble conjugated porphyrin small molecule exhibits very good ability as a cathode interfacial material in organic solar cells.



Journal of Materials Chemistry A Accepted Manuscript