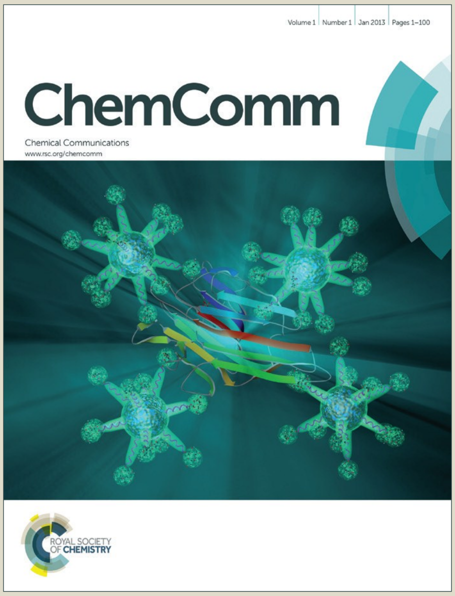
ChemComm

Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications

www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

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 Terms & Conditions and the Ethical guidelines 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.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Nonfullerene Acceptor for Wide Band Gap Polymer Based Organic Solar Cells

1. Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jicheng Zhang[a], Xuejuan Zhang[a], Guangwu Li, Hongmei Xiao, Wenhua Li*, Sufei Xie, Cuihong Li, and Zhishan Bo*

A new 1,8-naphthalimide based planar small molecular acceptor and two benzothiadiazole based wide band gap (WBG) polymer donors P1 and P2 were synthesized for nonfullerene organic photovoltaic cells (OPVs). Devices based on fluorinated polymer P2 achieved a highly improved PCE of 3.71% with an open circuit voltage (V_{oc}) of 1.07 V, which is beyond the current known levels for nonfullerene OPVs with the V_{oc} higher than 1V.

Bulk heterojunction organic photovoltaic cells (BHJ OPVs) with conjugated polymer or small molecule as the donor and (6,6)-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as the acceptor have attracted tremendous attention in the past few years because of their advantages of low cost, light weight and mechanical flexibility.[1, 2] Driven by the synthesis of new donor materials and the optimization of device structure, power conversion efficiency (PCE) over 10% for single junction OPVs has been achieved.[3, 4] Among all donor polymers, wide band gap (WBG) polymers usually exhibit a high molar absorption coefficient in the range from 350 nm to 650 nm. Single junction OPVs based on WBG polymers have reached a PCE of 9%.[5] Moreover, by associating wide and narrow band gap polymers together to fabricate a tandem device, PCEs over 11% have been reported.[6, 7] Although a rapid development has been made for WBG polymers, the highest PCE value of WBG polymer based devices is still inferior to that of narrow band gap polymer based devices. The high lying LUMO level (around -3.4 eV) of WBG polymers hampers the further improvement of their PCE. When blended with $PC_{71}BM$ to fabricate a device, the offset between the LUMO levels of donor materials and $PC_{71}BM$ (-4.04 eV) is too large, which will induce a significant energy loss.[5, 8]

Nonfullerene small molecular acceptors, which exhibit a high molar absorption coefficient in the visible range and possess an easily tuned LUMO level, have the potential to further improve the PCE of WBG polymer based devices.[9, 10] In the last few years, nonfullerene acceptors were extensively pursued and PCEs over 7% have been acquired.[11, 12] The electron mobility of nonfullerene acceptor is usually inferior to that of fullerene. To promote it, one usual strategy is to introduce a strong electron withdrawing group such as perylene diimide (PDI) as the acceptor unit;[13] another one is to conjugate two or more electron withdrawing groups like cyano group.[14] However, both of them will significantly down-shift the LUMO level of acceptor and produce a low-lying LUMO level. Like $PC_{71}BM$, most high efficiency nonfullerene acceptors such as PDI derivatives possess a low lying LUMO level at around -3.9 eV, which are not compatible with WBG donor materials.[15] Rhodamine or 1,8-naphthalimide (**NI**) based small molecular acceptors have a high lying LUMO level, which will reduce the energy loss and produce a high open circuit voltage (V_{oc}).[16, 17] When blending with WBG donor materials, a higher PCE can be expected.

Comparing with common bridge units such as thiophene or selenophene group, alkyne group also exhibits a good electron transporting ability.[18, 19] Besides, using an alkyne group as the bridge could lead to a free internal rotation of two conjugated planes, which might be beneficial for the packing of acceptor units. Although nonfullerene acceptor has been widely studied, it's still a challenge to investigate the relationship between chemical structure and photovoltaic performance. Recent researches have revealed that significantly enhanced PCE could be obtained by using fluorinated polymers as the donor in $PC_{71}BM$ based OPVs,[3] however, whether they will play a positive effect for nonfullerene OPVs is yet to be answered.

In this communication, two WBG polymer donors (**P1**, **P2**) and a novel small molecular acceptor (**NI-AA-NI**) with two **NI** bridged by a diacetylene group were synthesized. For the first time, the influence of fluoro substitution on donor materials for the performance of nonfullerene organic solar cells was investigated. Our investigation has demonstrated that

---

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China
E-mail:liwenhua@bnu.edu.cn, zsbo@bnu.edu.cn

[a] Both authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: Experimental part including ^{1}H NMR spectra of monomers and polymers and TGA, DSC, XRD, UV, CV, SCLC curves. See DOI: 10.1039/x0xx00000x photovoltaic devices using fluorinated polymer **P2** as the donor and **NI-AA-NI** as the acceptor showed a PCE of 3.71% with a V_{oc} up to 1.07 V. To the best of our knowledge, this is the highest PCE for nonfullerene OPVs with a V_{oc} higher than 1 V.

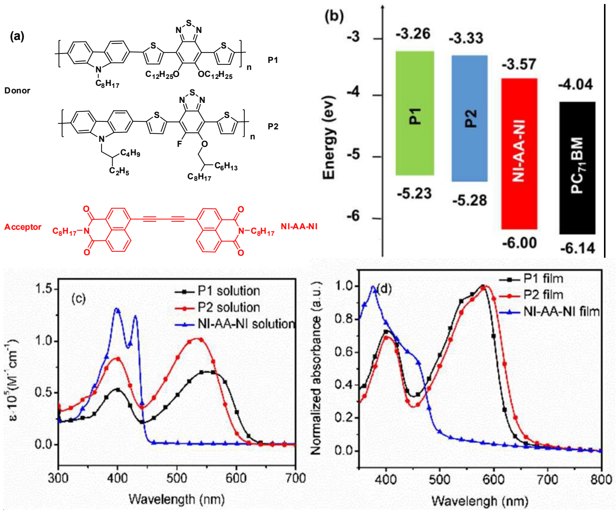


Fig. 1 Chemical structures (a), energy diagram (b), and UV-vis absorption spectra (c), (d) of **P1**, **P2** and **NI-AA-NI**.

The syntheses of **P1**, **P2**, **NI-AA-NI** and intermediates are shown in Scheme S1.1 (refer to ESI†) and detailed characterizations are also provided in the supporting information. **NI-AA-NI** exhibits good solubility in common organic solvents such as chloroform ($CHCl_3$), tetrahydrofuran (THF), and o-dichlorobenzene (DCB) at room temperature. **P1** and **P2** are not soluble in common solvents at room temperature, but can be fully dissolved in DCB at 80 °C. The weight average molecular weights of **P1** and **P2** were determined to be 50.3 kg mol^{-1} and 119.1 kg mol^{-1}, respectively, by gel permeation chromatography (GPC) at 80 °C using chlorobenzene (CB) as an eluent and narrowly distributed polystyrenes as calibration standards. Thermal gravimetric analysis (TGA) revealed that **P1**, **P2** and **NI-AA-NI** own good thermal stability (Fig. S1, ESI†). By differential scanning calorimetry (DSC) test, a good crystallinity with a melting peak at 216.0 °C and a crystallization peak at 201.4 °C were observed for **NI-AA-NI** (Fig. S2, ESI†), but no obvious crystallization peak or transition could be detected for **P1** and **P2**, indicating that both polymers could be amorphous. Besides that, the crystallinity of **NI-AA-NI** could also be confirmed by powdery X-ray diffraction (XRD) measurement (Fig. S3, ESI†).

To shed light on the optimized geometry of **NI-AA-NI**, computational study was carried out by using density functional theory (DFT) method (B3LYP/6-31G(d)). For simplicity, octyl chains were replaced by methyl groups (details refer to Table S1, ESI†). As shown in Fig. 2, **NI-AA-NI** presents a planar molecular structure with an interfacial angle of 0.31° between two NI rings. The planar structure of **NI-AA-NI** is beneficial to its close packing in the solid state.[20]

UV-vis absorption spectra of **P1**, **P2** and **NI-AA-NI** were measured in dilute DCB solutions (1×10^{-5} M) at 100 °C and as films (Fig. 1). In solution, **P1** and **P2** showed two similar absorption peaks with a molar extinction coefficient of 7.1×10^{4} and 1.03×10^{5} M^{-1}cm^{-1}, which could be ascribed to the localized π–π* transition and internal charge transporting from the carbazole donor unit to the benzothiadiazole acceptor unit, respectively. Comparing with polymer donors, **NI-AA-NI** exhibited a narrower absorption spectrum with a molar extinction coefficient of 1.32×10^{5} M^{-1}cm^{-1} in solution. In going from solution to films, the absorption band of **P1** and **P2** obviously red shifted, indicating that both polymers exhibited better packing properties as films; whereas, **NI-AA-NI** as film exhibited a broader absorption with the main absorption peak blue-shifted obviously from 397 nm in solution to 376 nm as film, indicating that **NI-AA-NI** probably formed H-aggregates in the solid state.[17] Determined from the onset absorption of films, the band gap of **P1**, **P2** and **NI-AA-NI** was calculated to be 1.97, 1.95 and 2.43 eV, respectively. Related data are summarized in Table 1.

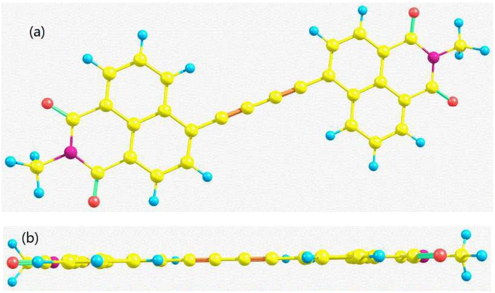


Fig. 2 Top view (a) and side view (b) of optimized geometries of **NI-AA-NI** by DFT calculations (B3LYP/6-31G(d)).

Table 1 Electrochemical and optical properties of **P1, P2** and **NI-AA-NI**.

Materials	λ_{max} (nm) solution	λ_{max} (nm) film	λ_{onset} (nm) film	$E_{g,opt}$ (eV)^{a}	HOMO (eV)	LUMO (eV)
P1	397,539	401,579	630	1.97	-5.23	-3.26^{b}
P2	386,520	401,588	635	1.95	-5.28	-3.33^{b}
NI-AA-NI	397,429	376	510	2.43	-6.00	-3.57^{b}/ -3.56^{c}

[a] Calculated by the equation: $E_{g,opt}=1240/\lambda_{onset}$.
[b] Determined by the equation: $E_{LUMO} = E_{HOMO} + E_{g,opt}$.
[c] Determined by the CV test.

Electrochemical properties of **P1**, **P2** and **NI-AA-NI** were investigated by cyclic voltammetry (CV, details refer to S1.2, ESI†). As shown in Fig. 1 and Fig. S4 (ESI†), HOMO levels of **P1** and **P2** were determined to be -5.23 and -5.28 eV, respectively. The presence of one F atom on the polymer backbone slightly down shifted the HOMO level of **P1**. By the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$, LUMO levels of **P1** and **P2** were calculated to be -3.26 and -3.33 eV, respectively. Similarly, the HOMO and the LUMO level of **NI-AA-NI** were determined to be -6.00 and -3.57 eV, respectively. It is worthy to point out, the LUMO level calculated for $E_{g,opt}$ is close to that determined from the CV curve (-3.56 eV). In comparison with $PC_{71}BM$ (-4.04 eV), **NI-AA-NI** exhibited a high-lying LUMO level (-3.57 eV), which would reduce the energy loss when blended with donor polymers with a high LUMO level. As a result, the low-lying HOMO level of **P1** and **P2** and the high-lying LUMO level of **NI-AA-NI** would lead to a high V_{oc} for nonfullerene OPVs.[21] These data are also summarized in Table 1.

To investigate the photovoltaic performance of **NI-AA-NI** as the acceptor and WBG polymers as the donor, conventional devices with a structure of ITO/PEDOT:PSS/polymer:**NI-AA-NI**/LiF/Al were fabricated (Fig. 3, details refer to S1.2, ESI†). After optimization, both **P1** and **P2** based devices exhibited the best photovoltaic performance with a donor-acceptor ratio of 1:3 and a thickness around 50 nm. **P1** based plain devices showed a PCE of 1.26% with a V_{oc} of 1.06 V. Comparably, devices based on **P2** exhibited a better photovoltaic performance and a PCE of 2.91% with a V_{oc} of 1.08 V was achieved. By attaching one fluorine atom on the backbone, the LUMO level and the HOMO level of **P2** slightly down shifted, which would lead to a smaller energy loss and an increase of V_{oc} (1.06 to 1.08 eV). More importantly, in comparison with the nonfluorinated **P1**, fluorinated **P2** also exhibited a great enhancement of short circuit current (J_{sc}, from 3.40 to 5.27 mA cm^{-2}) and fill factor (*FF*, from 0.35 to 0.51), which was similar as $PC_{71}BM$ based devices expressed.[22] By taking widely used 1-chloronaphthalene (1-CN, 0.5%) as the additive, PCE values were both obviously improved for devices based on **P1** and **P2**. Specifically, all devices with or without 1-CN exhibited a V_{oc} higher than 1.06 V, which is better than most $PC_{71}BM$ based devices, demonstrated that the energy loss caused by the offset between the LUMO levels of donor and acceptor could be significantly reduced by using **NI-AA-NI** as the acceptor. Especially, a PCE of 3.71% with a V_{oc} of 1.07 V was achieved for **P2** based devices, which is the highest PCE with a V_{oc} higher than 1 V for nonfullerene OPVs as we know. The molar extinction coefficients of **P1**, **P2** and **NI-AA-NI** were all very high, which is beneficial to achieve high J_{sc} in devices. But be ascribed to the very thin active layer (50 nm), the J_{sc} of devices was relatively low, which limited the PCE of devices. Furthermore, PCE of devices based on polymer:$PC_{71}BM$, and **polymer:NI-AA-NI** were periodically tested for 7 days to gauge the influence of heat and light on the degradation of devices. All devices were fabricated with a donor/acceptor weight ratio of 1:3 and using 0.5% 1-CN as the processing additive. As shown in Fig. S5 (ESI†), **P1**:$PC_{71}BM$ and **P2**:$PC_{71}BM$ based devices still retained 86% and 82% PCE values after 7 days. For **P1:NI-AA-NI** and **P2:NI-AA-NI** based devices, 89% and 84% PCE values retained after 7 days, demonstrating that devices based on $PC_{71}BM$ or **NI-AA-NI** all exhibited good stability. These results also revealed that devices based on **NI-AA-NI** exhibited better device stability than that based on $PC_{71}BM$.

Table 2 Summary of photovoltaic properties of **polymer**:**NI-AA-NI** based devices.

Active layer	1-CN	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	PCE (%) Best/Ave	Thickness (nm)
P1:NI-AA-NI	No	1.06	3.40	0.35	1.26/1.21	46
	0.5%	1.06	4.10	0.43	1.87/1.73	47
P2:NI-AA-NI	No	1.08	5.27	0.51	2.91/2.82	50
	0.5%	1.07	6.29	0.55	3.71/3.65	52

The external quantum efficiency (EQE) of devices without and with 1-CN was measured to examine the veracity of J_{sc}. As shown in Fig. 2b, all devices exhibited a broad spectrum response from 350 nm to 650 nm with a maximum EQE value at around 400 nm, demonstrating that both polymer donors and **NI-AA-NI** acceptor absorbed photons to generate excitons. J_{sc} values calculated from integrated EQE curves agreed roughly with that obtained from the J-V measurement.

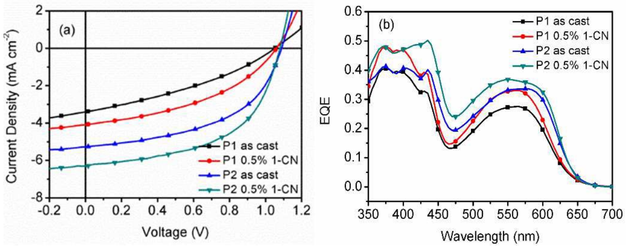


Fig. 3 *J*-V curves (a) and EQE spectra (b) of **P1-2**:**NI-AA-NI** based devices.

Charge transport properties play an important role for achieving high J_{sc} and *FF*. High hole mobility (μ_h) and electron mobility (μ_e) usually lead to high J_{sc}.[12] In addition, more balanced hole and electron mobility is beneficial to obtain high *FF*.[23] To investigate the influence of fluorine substitution on the polymer backbone and 1-CN as the additive on the charge mobility of devices, space-charge limited current (SCLC) method was utilized to evaluate the μ_h and μ_e by fabricating hole-only devices with a configuration of ITO / PEDOT:PSS / **polymer**:**NI-AA-NI** / Au and electron-only devices with a structure of FTO / **polymer**:**NI-AA-NI** / Al. (details refer to S1.3, ESI†). Hole mobilities of **P1**:**NI-AA-NI** and **P2**:**NI-AA-NI** based plain devices were calculated to be 6.94×10^{-7}, and 2.00×10^{-6} cm^2 V^{-1} s^{-1}, respectively. (Fig. S6, ESI†) Similarly, electron mobilities of devices as fabricated based on **P1** and **P2** were ascertained to be 3.34×10^{-8}, and 1.25×10^{-6} cm^2 V^{-1} s^{-1} respectively. Devices based on fluorinated **P2** exhibited higher hole and electron mobilities, demonstrating that fluorinated polymer donor could enhance the charge transporting properties of **NI-AA-NI** based nonfullerene OPVs. After using 0.5% 1-CN as the additive, hole mobilities of **P1** and **P2** based devices were increased to 1.02×10^{-6}, and 3.41×10^{-6} cm^2 V^{-1} s^{-1}, respectively; electron mobilities of **P1** and **P2** based devices were also enhanced to 6.51×10^{-7}, and 2.41×10^{-6} cm^2 V^{-1} s^{-1}, respectively. Compared to amorphous **P1** and **P2**, the packing property of planar and crystalline acceptor **NI-AA-NI** was superior, which induced the electron mobility increasing in a larger extent than that of the hole mobility after optimization with 1-CN. The significant improvement of μ_e led to a more balanced hole and electron mobilities for the active layers, which would improve the J_{sc} and *FF* of **P1-2** based devices.

The morphology of the active layer has a great influence on the photovoltaic performance of OPVs. To investigate the morphology of **polymer:NI-AA-NI** blend films without and with 1-CN, atomic force microscopy (AFM) was used. As shown in Fig. S7 (ESI†), **P1** based plain devices showed a relatively smooth surface, indicating phase separation is mostly on small dimensions.[24] After using 0.5% 1-CN, the root-mean-square (RMS) roughness of **P1:NI-AA-NI** active layer obviously increased from 1.62 nm to 2.75 nm. This could be ascribed to the enhanced aggregation of **P1** and **NI-AA-NI**,[25] which was beneficial for the hole and electron transport in the active layer.[17] With 0.5% 1-CN as the additive, the RMS roughness of fluorinated **P2** based devices further increased from 4.78 nm to 8.94 nm. This indicated the aggregation of **P2** and **NI-AA-NI** was further enhanced, which would lead to higher J_{sc}.

In summary, two WBG polymers (**P1, P2**) were synthesized as the donor, meanwhile, a new planar small molecular acceptor with two **NI** as the terminal groups and a diacetylene group as the bridge was also synthesized as the acceptor. **NI-AA-NI** is crystalline and fully soluble in common solvent. In comparison with $PC_{71}BM$, **NI-AA-NI** exhibits a higher-lying LUMO level which will reduce the offset of LUMO levels between donor and acceptor. By attaching a fluorine atom on the backbone, the LUMO and HOMO levels of **P2** both decreased which could further reduce the energy loss and make V_{oc} increased. Owing to the boosted electron mobility, more balanced hole and electron mobility was achieved in **P2:NI-AA-NI** based OPVs. Consequently, higher J_{sc} and *FF* were achieved. Finally, a PCE of 3.71% with a V_{oc} of 1.07 V was obtained, which is the best for nonfullerene OPVs with a V_{oc} higher than 1 V as we know. These results also illuminated that the use of fluorinated polymers as the donor material is an effective strategy to improve the photovoltaic performance of nonfullerene OPVs. Although the performance of **NI-AA-NI** based nonfullerene OPVs was not very intriguing at the moment, the achievement of a PCE higher than that of WBG polymer:$PC_{71}BM$ based devices could be extremely expected by the optimization of other parameters.

Financial support from the NSF of China (91233205), Program for Changjiang Scholars and Innovative Research Team in University and the Fundamental Research Funds for the Central Universities are gratefully acknowledged.

Notes and references

1 Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245.
2 G. Li, R. Zhu and Y. Yang, *Nat. Photonics*, 2012, **6**, 153.
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 S.-H. Liao, H.-J. Jhuo, P.-N. Yeh, Y.-S. Cheng, Y.-L. Li, Y.-H. Lee, S. Sharma and S.-A. Chen, *Sci. Rep.*, 2014, **4**, 6813.
5 L. Huo, T. Liu, X. Sun, Y. Cai, A. J. Heeger and Y. Sun, *Adv. Mater.*, 2015, **27**, 2938.
6 A. R. b. M. Yusoff, D. Kim, H. P. Kim, F. K. Shneider, W. J. da Silva and J. Jang, *Energ. Environ. Sci.*, 2015, **8**, 303.
7 C.-C. Chen, W.-H. Chang, K. Yoshimura, K. Ohya, J. You, J. Gao, Z. Hong and Y. Yang, *Adv. Mater.*, 2014, **26**, 5670.
8 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.
9 S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant and J. Nelson, *J. Am. Chem. Soc.*, 2015, **137**, 898.
10 H. Li, T. Earmme, G. Ren, A. Saeki, S. Yoshikawa, N. M. Murari, S. Subramaniyan, M. J. Crane, S. Seki and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2014, **136**, 14589.
11 Y.-J. Hwang, B. A. E. Courtright, A. S. Ferreira, S. H. Tolbert and S. A. Jenekhe, *Adv. Mater.*, 2015, **27**, 4578.
12 D. Sun, D. Meng, Y. Cai, B. Fan, Y. Li, W. Jiang, L. Huo, Y. Sun and Z. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 11156.
13 C. H. Wu, C. C. Chueh, Y. Y. Xi, H. L. Zhong, G. P. Gao, Z. H. Wang, L. D. Pozzo, T. C. Wen and A. K. Y. Jen, *Adv. Funct. Mater.*, 2015, **33**, 5326.
14 Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170.
15 S. M. McAfee, J. M. Topple, I. G. Hill and G. C. Welch, *J. Mater. Chem. A*, 2015, **3**, 16393.
16 Y. Kim, C. E. Song, S.-J. Moon and E. Lim, *Chem. Commun.*, 2014, **50**, 8235.
17 X. Zhang, J. Zhang, H. Lu, J. Wu, G. Li, C. Li, S. Li and Z. Bo, *J. Mater. Chem. C*, 2015, **3**, 6979.
18 Z. Mao, W. Senevirathna, J. Y. Liao, J. Gu, S. V. Kesava, C. Guo, E. D. Gomez and G. Sauvé, *Adv. Mater.*, 2014, **26**, 6290.
19 S. Liu, K. Zhang, J. Lu, J. Zhang, H.-L. Yip, F. Huang and Y. Cao, *J. Am. Chem. Soc.*, 2013, **135**, 15326.
20 J. Wang, S. Dai, Y. Yao, P. Cheng, Y. Lin and X. Zhan, *Dyes Pigments*, 2015, **123**, 16.
21 P. Sullivan, G. E. Collis, L. A. Rochford, J. F. Arantes, P. Kemppinen, T. S. Jones and K. N. Winzenberg, *Chem. Commun.*, 2015, **51**, 6222.
22 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649.
23 B. Qi and J. Wang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8972.
24 A. Gadisa, M. Svensson, M. R. Andersson and O. Inganäs, *Appl. Phys. Lett.*, 2004, **84**, 1609.
25 T.-Q. Nguyen, I. B. Martini, J. Liu and B. J. Schwartz, *J. Phys. Chem. B*, 2000, **104**, 237.