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

Journal of
Materials Chemistry C

Materials for optical and electronic devices
www.rsc.org/materialsC

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.

www.rsc.org/materialsC

Journal Name

COMMUNICATION

The Study on Two Kinds of Spiro System for Improving the Performance of Host Materials in Blue Phosphorescent Organic Light-Emitting Diodes

Xiang-Yang Liu, Feng Liang, Lei Ding, Shou-Cheng Dong, Qian Li, Lin-Song Cui, Zuo-Quan Jiang,* Hua Chen, Liang-Sheng Liao*

The introduction of spiro-acridine-fluorene (SAF) can affect the electronic structure of the whole molecule, which made SAF-based material exhibit totally different photophysical properties from conventional spironbifluorene-based material. With these properties, nearly 25% external quantum efficiency in sky-blue phosphorescent organic light-emitting diodes was achieved.

Introduction

Blue host materials of the phosphorescent organic light-emitting diodes (PHOLEDs) have attracted extensive attention in the past decade because a highly efficient blue emission is not only meaningful for itself but also crucial to excite or transfer energy to other emissions with longer wavelengths.[1] Thus, blue hosts are of central importance in highly efficient OLEDs research for future display or solid-lighting applications. It is rather difficult to circumvent a challenge that a good blue host must possess both high triplet energy (E_T) and suitable carrier transport/injection abilities.[2] Despite the difficulty, significant progress has been made in recent years that several materials have exceeded 25% external quantum efficiency (EQE) with sky-blue emitter bis(4,6-(difluorophenyl)pyrudinato-N,C$^{2'}$)picolinateiridium (III) (FIrpic).[3]

It is noticeable that most of the successful blue hosts rely on the incorporation of tricycle organic units, such carbazole,[4] dibenzofuran,[5] dibenzothiophene[6] or fluorene[7] and their derivatives, in molecular design. And this design is a foreseeable result of the two aforementioned attributes: high triplet energy and good carrier transportability. The former needs a confined conjugation size and the latter asks for a good conjugation degree; the two requirements conflict and the tricycle system is the outcome of compromise. The first three units have heteroatoms N, O, S capable of donating their

own lone-pair electrons, leading to higher HOMO (highest occupied molecular orbital) for hole injection or transport; the last unit, fluorene, does not possess this feature but it has another fascinating feature for molecular design. Because of the sp^3 hybridization of C9 in fluorene, a spiro structure is able to be constructed from this position and this structure could be advantageous to the thermal stability of materials.[8] For example, by joining two fluorene units together with spiro linkage, 9,9'-spirobifluorene (SF) results. Though SF is better in thermal/morphological properties, the shortage in carrier transport restricts its performance in PHOLEDs.[9] There are two solutions for this problem: either appending a hole-transport group to SF or substantially changing it to another spiro block, named as spiro-acridine-fluorene (SAF) with one fluorene part replaced by acridine.[10]
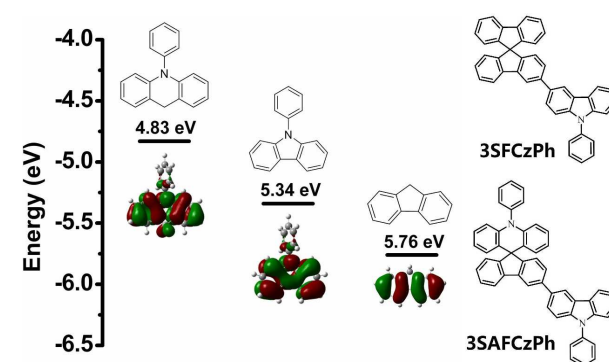

Fig. 1 Energy levels of the HOMOs of the units constructing 3SFCzPh and 3SAFCzPh.

On the other hand, how to suppress triplet-involved quenching effects has been one of the significant challenges for traditional hosts.[11] Because these triplet quenching mechanisms mainly concentrate in the emitting layer with excited and/or charged host matrices molecules.[12] The development of hosts can be therefore considered to use rational structure with different functional moieties to support the independent optical and electrical

Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM) & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University Suzhou 215123, P.R. China
*E-mail: zqjiang@suda.edu.cn; lsliao@suda.edu.cn.*
† X. Y. Liu, F. Liang, Dr. L. Ding, Dr. S. C. Dong, Q. Li, L. S. Cui, Dr. Z. Q. Jiang, Dr. H. Chen, Prof. L. S. Liao.
Electronic Supplementary Information (ESI) available: Experimental detail, physical measurements and other electronic format. See DOI: 10.1039/x0xx00000x

processes, indicating the charge transport process and the triplet states localized on different parts, which could restrain the triplet excitons decomposition under the charge induced.[13] In light of these viewpoints, the SAF unit will provide more possibilities in modifying multiple characteristics of hosts. And in this communication, we synthesized two new host materials, 3SFCzPh and 3SAFCzPh, corresponding to these two ways. Both materials have same 9-phenyl-9H-carbazole as side group through meta-linkage and differ in the spiro-core. The reason why we choose 9-phenyl-9H-carbazole and the linking way is that the HOMO of 9-diphenyl-9H-carbazole is situated between the HOMOs of acridine and fluorene (Fig. 1): the two units consisting of SAF. Thus, it can be anticipated that the HOMO level drop from acridine, through 9-phenyl-9H-carbazole, to fluorene, which could determine the HOMO distributions of entire molecules.[14] Additionally, we will elaborate their differences rather than simply thinking of SAF as "hole-transport" SF. Consequently, phosphorescent emitter FIrpic is used to evaluate their effects on the performance of PHOLEDs. The SAF-based material was turned out to be the better material due to the superior EQE abover 24% in PHOLEDs.

Results and discussion
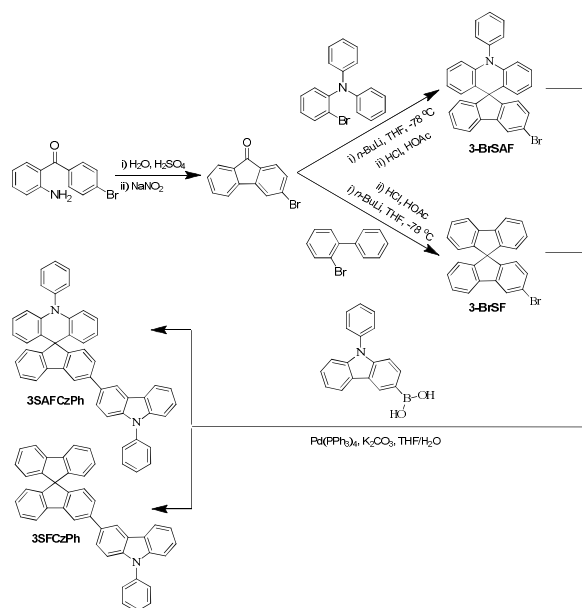
Scheme 1. Synthetic routes of 3SFCzPh and 3SAFCzPh.

Synthetic routes of 3SFCzPh and 3SAFCzPh are outlined in Scheme 1. The key intermediate of 3-bromofluorenone was readily afforded through intermolecular Pschorr reaction with good yield. Then the THF solution of 3-bromofluorenone was added to the lithium reagent solution at -78 ^{o}C to afford corresponding tertiary alcohol. The corresponding lithium reagent of (2-(diphenylamino)phenyl)lithium and biphenyl-2-yllithium were synthesis via 2-bromo-N,N-diphenylaniline and 2-bromobiphenyl reaction with n-BuLi at -78 ^{o}C. And followed by an intramolecular

ring closure through a Friedel–Crafts reaction to afford the spirotriphenylamine and spirofluorene monomers. At last, the final products can be obtained through Pd-catalyzed Suzuki–Miyaura C–C coupling reaction between 9-phenyl-9H-carbazol-3-ylboronic acid and corresponding monomers of 3-BrSF and 3-BrSAF in good yields.

Generally speaking, OLEDs were composed by layered noncrystallized amorphous organic films sandwiched between electrodes. The carrier injection, transport, and recombination properties are markedly dependent on the film qualities. Therefore, uniformity and homogeneity of the film are required for highly efficient devices. The organic and metal layers have usually been constructed by vacuum evaporation, and therefore amorphous organic materials used in the devices should have glass transition temperatures (T_g) at least higher than room temperature and high thermal stability is also essential. The detailed syntheses and thermal analyses (differential scanning calorimetry/thermo-gravimetric analysis, DSC/TGA) results are summarized in supporting information. Both materials exhibited high thermal decomposition temperatures (T_d, corresponding to 5% weight loss) and high glass transition temperature (T_g) with 433/386 ^{o}C and 140/151 ^{o}C for 3SFCzPh/3SAFCzPh, respectively, indicating thermal/morphological stabilities which are essential to filming process in device fabrication.[11a]
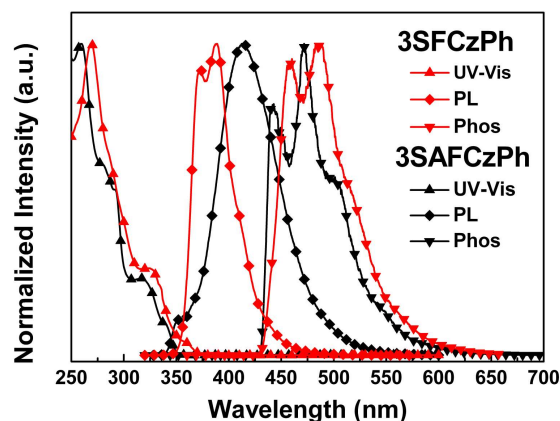

Fig. 2 UV-Vis, PL and Phos spectra of of 3SFCzPh and 3SAFCzPh.

The UV-vis absorption and photoluminescence (PL) spectra of 3SFCzPh and 3SAFCzPh at room temperature in CH_2Cl_2 solution and phosphorescence spectra in 2-methyltetrahydrofuran solution at 77 K are shown in Fig. 2. Both compounds show similar absorption bands except that the maximum absorption wavelengths and the absorption onset of 3SFCzPh are red-shifted by 10 nm and 25 nm, respectively, than those of 3SAFCzPh. Then the optical band gap (E_g) of 3SFCzPh (3.31 eV) is smaller than 3SAFCzPh (3.54 eV). In contrast, they have quite different PL features as the well-defined PL spectrum of 3SFCzPh and the structureless PL spectrum of 3SAFCzPh indicate their different excited states. The phosphorescence spectra showed that the highest vibronic band of 3SFCzPh and 3SAFCzPh are at 459 nm and 442 nm, respectively, corresponding to triplet energy (E_T) of 2.70 and 2.81 eV for 3SFCzPh

Please do not adjust margins

Journal Name COMMUNICATION

and 3SAFCzPh, respectively. It is notable that the E_T presented similar trend to E_g between these two materials. To elaborate these issues, Density Functional Theory (DFT) calculations (B3LYP/6-31g(d)) were carried out to investigate the structure-property relationship. Fig. 3 shows that both the HOMO and LUMO of 3SFCzPh are mainly localized along the longest conjugated moiety of the molecule with little disparity, and then the disparity in ground state would be further reduced in more planar excited state. Therefore, it gives out fluorescence from typical local excited (LE) state with well-defined structure in PL spectrum. On the contrary, the 3SAFCzPh has separated HOMO and LUMO distributions because of the existence of acridine unit, and emission from charge transfer (CT) state results. The CT emission leads to not only the red-shift at maximum peak by also a broader spectrum in 3SAFCzPh, which has better overlap with the metal to ligand charge transfer (MLCT) absorption of FIrpic (Fig. S7).

This kind of separation between HOMO and LUMO is however in a rigid perpendicular conformation, indicative of a spin-forbidden transition process in UV spectrum. Alternatively, the transition from HOMO-1 to LUMO in 3SAFCzPh is permitted, which very resembles the transition from HOMO to LUMO in 3SFCzPh; as a result, similar absorption spectra were observed. A noteworthy feature about spiro structure is the spiroconjugation effect. The overlap of orbital integrals between two units participating in the spiro formation can further affect the photophysical properties of the resulted spiro molecule. But due to the symmetrical requirements, SAF has little likelihood of forming effective spiroconjugation while SF is able to engage in spiroconjugation, which are reflected by the HOMO-1 distributions in Fig. 3.[15] The involvement of spiro-conjugation effect can also account for lower E_g and E_T of 3SFCzPh as compared to those of SAF analogue.
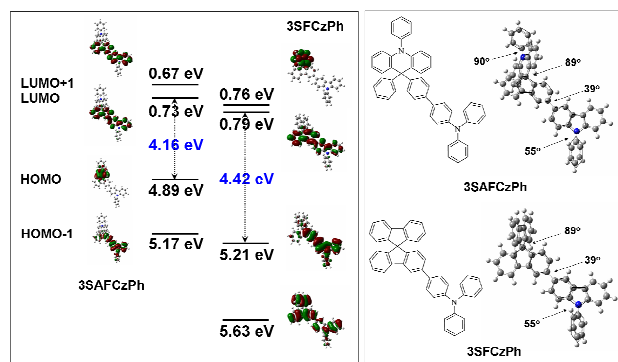
with the trends in CV and DFT calculation, but its LUMO level cannot be directly estimated because the transition from HOMO to LUMO is not observed in the aforementioned discussion. Fortunately, the LUMO of 3SAFCzPh resembles the LUMO of 3SFCzPh in molecular simulation, so the LUMO of 3SAFCzPh could be postulated as -2.42 eV because there is a difference of 0.06 eV between these two values in Fig. 3.

To investigate the electroluminescent (EL) properties of 3SAFCzPh and 3SFCzPh as host materials, blue PHOLEDs based on FIrpic were fabricated using this device structure: ITO/HAT-CN (10 nm)/TAPC (40 nm)/Host: 15% FIrpic (20 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al (150 nm), with which B1 and B2 stood for SF- and SAF-based devices, respectively. The detailed electroluminescence performance data is summarized in Table 1.

Table 1. Summary of electroluminescence data for OLEDs.

Device[a]	V[b]	⊡η$_{CE}$[c]	⊡η$_{PE}$[c]	⊡η$_{ext}$[c]	CIE[d]
	V	cd A^{-1}	lm W^{-1}	%	x, y
B1	3.9	41.5, 39.9	34.3, 24.2	17.6, 16.8	0.17, 0.39
B2	3.5	51.8, 48.5	47.7, 31.2	24.3, 23.0	0.16, 0.38

a) B1 and B2 indicates SF- and SAF-based devices, respectively. b) Voltages at 100 cd m^{-2}. c) Efficiencies in the order of maximum and at 1000 cd/m^2. d) Measured at 5 mA cm^{-2}.
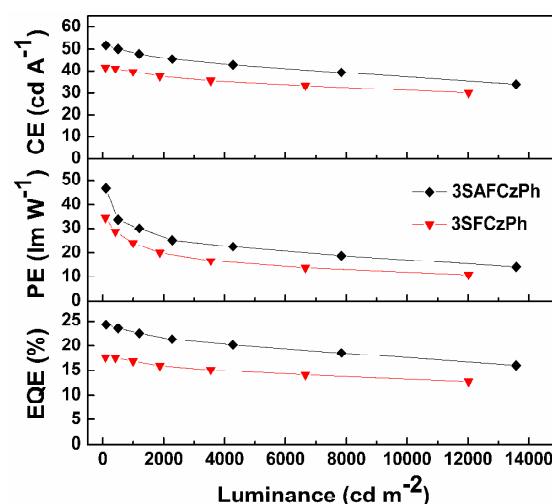

Fig. 3 Calculated frontier molecular orbital distributions and molecular structure/optimized geometry of 3SFCzPh and 3SAFCzPh.

Fig. 4 CE, PE and EQE versus luminance of sky-blue devices.

The HOMO levels of 3SFCzPh/3SAFCzPh are estimated as 5.44 eV and 5.26 eV from cyclic voltammetry (CV) curves (Fig. S8); on the other hand ultraviolet photoemission spectroscopy (UPS) was used to determine the HOMO levels for reliable energy levels (Fig. S9), and the LUMOs can be calculated by $E_{LUMO} = E_g + E_{HOMO}$. As a result, the HOMO/LUMO levels were determined as -5.79/-2.48 eV for 3SFCzPh by UPS and optical energy gap from UV spectrum. As for 3SAFCzPh, its HOMO level is obatined as -5.69 eV, agreeing well

Fig. 4 shows the efficiencies of FIrpic-based sky-blue devices. High efficiencies of these blue phosphorescent devices based on 3SFCzPh and 3SAFCzPh as host materials were achieved and both devices showed relatively flat EQE roll-offs. The maximum efficiencies of current efficiency (CE), power efficiency (PE) and external quantum efficiency (EQE) were reached as 51.8 cd A^{-1}, 46.7 lm W^{-1} and 24.3%, respectively, for the device utilizing 3SAFCzPh as host material, which are notably superior to the results obtained by 3SFCzPh.

COMMUNICATION

Journal Name

Several properties could account for the better performance of 3SAFCzPh. First, 3SAFCzPh has higher E_T than 3SFCzPh, thus, it can be more effectively to prevent reverse energy transfer from dopant back to the host, as well as confine triplet excitons on the dopant.[16] Second, the emission spectrum of 3SAFCzPh in film is largely overlapped with the MLCT absorption of FIrpic (Fig. S7), which facilitates the energy transfer from the excited state of 3SAFCzPh to that of FIrpic.[3a] Finally, the higher HOMO level of SAF unit results in lower driving voltage and followed by higher power efficiency. These properties are more or less related to the separated HOMO/LUMO as stated before, which make the SAF a better spiro unit in constructing host materials.
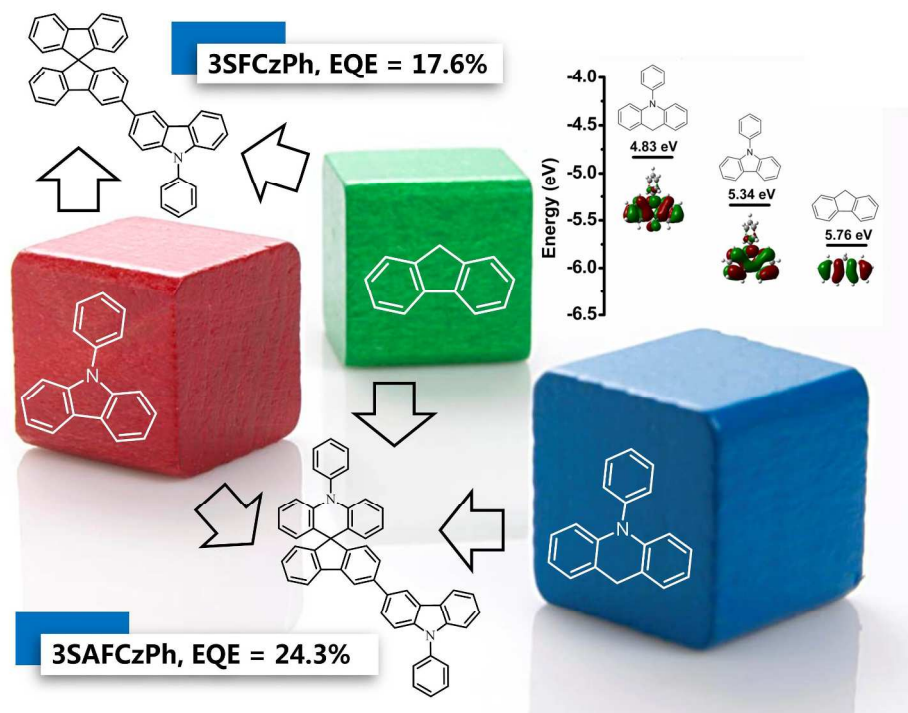
Conclusions

In conclusion, two novel spiro-based host materials 3SFCzPh and 3SAFCzPh were designed and synthesized by appending 9-phenyl-9H-carbazole unit on the fluorene moiety in spiro-structures SF and SAF using meta-linking strategy. In this direct comparison, we found that replacing one fluorene by hole-transport acridine to form SAF is just one reason to use this unit. The introduction of SAF can also affect spiroconjugation, HOMO/LUMO distributions and other relative photophysical properties. As a result, high efficiencies were achieved by using 3SAFCzPh as PHOLEDs host. In FIrpic-doped devices, 51.8 cd A^{-1}, 47.7 lm W^{-1} and 24.3% were achieved for CE, PE and EQE, respectively; as the device based on 3SFCzPh showed obviously inferior performance even it had hole-transport moiety. These results suggest that the SAF-based material has interesting features in modifying the distributions of frontier molecular orbitals of conjugated materials and is promising for further exploration in highly efficient OLED.

Acknowledgements

Notes and references

1 (a) R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **82**, 2422; (b) S. Lai, W. Tong, S. Kui, M. Chan, C. Kwok and C. Che, *Adv. Funct. Mater.*, 2013, **23**, 5168; (c) E. Mondal, W. Hung, H. Dai and K. Wong, *Adv. Funct. Mater.*, 2013, **23**, 3096.

2 A. Chaskar, H. Chen and K. Wong, *Adv. Mater.*, 2011, **23**, 3876.

3 (a) C. Lee and J. Lee, *Adv. Mater.*, 2013, 25, 5450; (b) C. Oh, C. Lee and J. Lee, *Chem. Commum*., 2013, **49**, 3875.

4 (a) L. Cui, Y. Liu, Q. Li, Z. Jiang and L. Liao, *Org. Electron*., 2014, **15**, 1368; (b) J.-K. Bin, N.-S. Cho and J.-I. Hong, *Adv. Mater*., 2012, **24**, 2911; (c) B. Pan, B. Wang, Y. Wang, P. Xu, L. Wang, J. Chen and D. Ma, *J. Mater. Chem. C*, 2014, **2**, 2466.

5 (a) S. Dong, C. Gao, Z. Zhang, Z. Jiang, S. Lee and L. Liao, *Phys. Chem. Chem. Phys*., 2012, **14**, 14224; (b) L. Deng, J. Li, G. Wang and L. Wu, *J. Mater. Chem. C*, 2013, **1**, 8140; (c) C. Han, G. Xie, H. Xu, Z. Zhang, L. Xie, Y. Zhao, S. Liu and W. Huang, *Adv. Mater*., 2011, **23**, 2491.

6 (a) S. Dong, L. Zhang, J. Liang, L. Cui, Q. Li, Z. Jiang and L. Liao, *J. Phys. Chem. C*, 2014, **118**, 2375; (b) W. Lin, W. Huang, M. Huang, C. Fan, H. Lin, L. Chen, Y. Liu, J. Lin, T. Chao and M. Tseng, *J. Mater. Chem. C*, 2013, **1**, 6835.

7 (a) S. Ye, Y. Liu, C. Di, H. Xi, W. Wu, Y. Wen, K. Lu, C. Du, Y. Liu and G. Yu, *Chem. Mater*., 2009, **21**, 1333; (b) Z. Jiang, H. Yao, Z. Zhang, C. Yang, Z. Liu, Y. Tao, J. Qin and D. Ma, *Org. Lett*., 2009, **11**, 2607.

8 (a) J. Yu, W. Huang, A. Heeger, *Adv. Mater*., 2000, **12**, 828; (b) T. Saragi, T. Spehr, A. Siebert, T. Lieker and J. Salbeck, *Chem. Rev*., 2007, **107**, 1011. (c) J. Zhao, G. Xie, C. Yin, L. Xie, C. Han, R. Chen, H. Xu, M. Yi, Z. Deng, S. Chen, Y. Zhao, S. Liu and W. Huang, *Chem. Mater*., 2011, **23**, 5331.

9 (a) M. Romain, S. Thiery, A. Shirinskaya, C. Declairieux, D. Tondelier, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier and C. Poriel, *Angew. Chem. Int. Ed*., 2015, **54**, 1176; (b) S. Thiery, D. Tondelier, C. Declairieux, G. Seo, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Metivier and C. Poriel, *J. Mater. Chem. C*, 2014, **2**, 4156.

10 (a) M. Romain, D. Tondelier, B. Geffroy, A. Shirinskaya, O. Jeannin, J. Rault-Berthelot and C. Poriel, *Chem. Commun*., 2015, **51**, 1313; (b) S. Dong, Y. Liu, Q. Li, L. Cui, H. Chen, Z. Jiang and L. Liao, *J. Mater. Chem. C*, 2013, **1**, 6575; (c) L. Ding, S. Dong, Z. Jiang, H. Chen and L. Liao, *Adv. Funct. Mater*., 2015, **25**, 645.

11 (a) Y. Tao, C. Yang and J. Qin, *Chem. Soc. Rev*. 2011, **40**, 2943; (b) H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang and X. Liu, *Chem. Soc. Rev*. 2014, **43**, 3259; (c) W. Wong and C. Ho, *Coord. Chem. Rev*. 2009, **253**, 1709.

12 (a) S. Reineke, K. Walzer and K. Leo, *Phys. Rev. B* 2007, **75**, 125328; (b) D. Song, S. Zhao, Y. Luo and H. Aziz, *Appl. Phys. Lett*. 2010, **97**, 243304.

13 C. Han, L. Zhu, J. Li, F. Zhao, Z. Zhang, H. Xu, Z. Deng, D. Ma and P. Yan, *Adv. Mater*. 2014, **26**, 7070.

14 Y. Zhang, L. Ding, X. Liu, Z. Jiang, H. Chen, S. Ji and L. Liao, *Org. Electron*., 2015, **20**, 112.

15 (a) H. Simmons and T. Fukunaga, *J. Am. Chem. Soc*. 1967, **89**, 5208; (b) P. Maslak, A. Chopra, C. Moylan, R. Wortmann, S. Lebus, A. Rheingold, and G. Yap, *J. Am. Chem. Soc*. 1996, **118**, 1471.

16 Y. Liu, L. Cui, X. Shi, Q. Li, Z. Jiang and L. Liao, *J. Mater. Chem. C*, 2014, **2**, 8736.

812x609mm (96 x 96 DPI)