Check for updates

View Article Online
View Journal

Journal of
Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Liu, Q. Tian, D. Zhao, Q. Ran, L. Liao and J. Fan, *J. Mater. Chem. C*, 2018, DOI: 10.1039/C8TC02851F.

Volume 4 | Number 1 | 7 January 2016 | Pages 1–224

Journal of
Materials Chemistry C

Materials for optical, magnetic and electronic devices
www.rsc.org/MaterialsC

ISSN 2050-7526

ROYAL SOCIETY OF CHEMISTRY

PAPER
Nguyễn T. K. Thanh, Xiaodi Su et al.
Fine-tuning of gold nanorod dimensions and plasmonic properties using the Hofmeister effects

175 YEARS

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 author guidelines.

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, outlined in our author and reviewer resource centre, 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

rsc.li/materials-c

View Article Online
DOI: 10.1039/C8TC02851F

9-Silafluorene and 9-Germafluorene: Novel Platforms for Highly Efficient Red Phosphorescent Organic Light-Emitting Diodes

Xiang-Yang Liu,† Qi-Sheng Tian,† Danli Zhao, Quan Ran, Liang-Sheng Liao* and Jian Fan*

Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou, Jiangsu 215123, China

**E-mail: lsliao@suda.edu.cn, jianfan@suda.edu.cn*

† The two authors contribute equally to this paper.

Abstract: Two novel heterofluorene motifs consisting of the group 14 elements Si and Ge were developed as robust molecular platforms for the construction of organic light-emitting diode (OLED) materials. These two compounds exhibited similar photophysical properties, thermal stabilities and electrochemical behaviors except the charge transport abilities. The red OLED hosted by 9-silafluorene derivative (**DPS**) with $Ir(MDQ)_2(acac)$ as the emitter exhibited the state-of-the-art current efficiency, power efficiency, and external quantum efficiency (EQE) with maxima of 50.7 cd A^{-1}, 44.7 lm W^{-1}, and 28.3%, respectively. In addition, the maximum EQE of 9-germafluorene derivative (**DPG**)-based red device can reach 20%. These results indicated the great potential of group 14 elements derivatives in the construction of highly efficient OLED materials.

Introduction

Nowadays organic light-emitting diodes (OLEDs) have achieved remarkable progress for the practical application due to the high efficiency, color purity and improved device lifetime.[1-3] The development of high performance host materials is crucial to realize efficient phosphor emission in phosphorescent OLEDs (PHOLEDs). To

View Article Online
DOI: 10.1039/C8TC02851F

develop novel host materials for PHOLEDs, several criteria have to be considered such as high triplet energy, good charge transporting ability, suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level and good thermal and morphological stability.[1] To increase the triplet energy of the host materials, there are several design strategies: i) to introduce high triplet energy units such as dibenzofuran,[4] dibenzothiophene,[5] diphenylamine,[6] and carbazole[7] into the molecular structure; ii) to shorten the conjugation length of the host material. Silicon,[8] sp^3 carbon,[9] and phosphine oxide[10] are often used to break intramolecular π-conjugation. Sterically hindered molecular structure and *ortho* or *meta* linking strategy are also used to reduce the conjugation length. According to these empirical design principles, many highly efficient host materials have been developed with high triplet energy over the last decade.[11]

Recently, fluorene derivatives have been widely used for the applications in OLED materials due to their excellent physical properties, such as high fluorescence quantum yields and good thermal stability.[12] In addition, fluorene moiety demonstrated diverse functionality due to its rich chemistry.[13] However, fluorene readily suffered from oxidative degradation of C9-position to yield fluorenone and intermolecular cross-linking byproducts at high operating temperature and electrical field, leading to a shift of light emission and a decrease in fluorescence quantum yield.[14-18] Obviously, the introduction of substituent group into the *C*9-position of fluorene moiety could effectively suppress the oxidation process.[19] On the other hand, to prevent oxidation in *C*9-position the carbon atom can be replaced with other hetero-atom, such as group 13 elements B[20] and Ga,[21] group 14 elements Si,[22] Ge,[23] and Sn,[24] group 15 elements N,[25] P,[26] and As;[27] and group 16 elements O,[28] S,[29] Se,[30] and Te,[27] etc.[30-33] It should be noted that the lone pair in N atom at the fluorene *C*9-position (also known as carbazole) will affect the electronic structure of overall molecule and make carbazole moiety a fully aromatic species.[25b] So far these tricyclic skeletons have attracted much attention as potential building blocks for novel

View Article Online
DOI: 10.1039/C8TC02851F

optoelectronic materials.

Small molecular organosilicon compounds as good building blocks for OLED materials have been widely studied.[8,34] For instance, Thompson et al. reported a series of tetraaryl silicon compounds as host materials with ultrahigh triplet energies (~3.5 eV).[8a] Yang and coworkers applied organosilicon derivatives as hosts in deep blue and white PHOLEDs.[8d] Furthermore, it has been reported that the utility of Si atom can reduce the conformational disorder and lower the HOMO energy level as compared with C atom.[8] On the other hand, the group 14 element Ge has been extensively used in inorganic semiconductor filed.[35] However, the application of small molecular organogermanium compounds in OLEDs has been rarely reported till now.[36] Herein, two novel Si- and Ge-containing fluorene derivatives, 10,10'-(5,5-diphenyl-5*H*-dibenzo[*b*,*d*]silole-2,8-diyl)bis(10*H*-phenothiazine) (**DPS**) and 10,10'-(5,5-diphenyl-5*H*-dibenzo[*b*,*d*]germole-2,8-diyl)bis(10*H*-phenothiazine) (**DPG**), were designed and synthesized. The further functionalization at 3,6-positions of 9-silafluorene and 9-germafluorene backbones will not only restrict the conjugation degree between phenothiazine and heterofluorenes, but also lead to high triplet energy level of whole molecule.[37] The introduction of heteroatom has minor effect on the photophysical properties of **DPS** and **DPG**. In contrast, **DPS** exhibited excellent electroluminescence performance as compared with **DPG**. The red PHOLED hosted by **DPS** with bis(2-methyldibenzo-[*f*,*h*]-quinoxaline) iridium (III) (acetylacetonate) ($Ir(MDQ)_2(acac)$) as dopant demonstrated the state-of-the-art device performance with external quantum efficiency of 28.3%. This remarkable result indicate the great potentials of silafluorene derivatives for highly efficient OLEDs.

Experimental Section

Materials Synthesis

The synthesis of 2,2'-dibromo-1,1'-biphenyl (**1**)[38] and 2,2'-dibromo-5,5'-diiodo-1,1'-biphenyl (**2**)[39] are prepared by reported methods.

View Article Online
DOI: 10.1039/C8TC02851F

*2,2'-dibromo-1,1'-biphenyl (**1**)*

White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H) ppm.

*2,2'-dibromo-5,5'-diiodo-1,1'-biphenyl (**2**)*

White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 – 7.65 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 2H) ppm.

*10,10'-(6,6'-dibromo-[1,1'-biphenyl]-3,3'-diyl)bis(10H-phenothiazine) (**3**)*

K_2CO_3 (1.93 g, 14 mmol) was added to a solution of **2** (2.0 g, 3.5 mmol), 10*H*-phenothiazine (1.55 g, 7.8 mmol) and Cu (90 mg, 1.4 mmol) in 1,2-dichlorobenzene (*o*-DCB, 30 mL) under N_2. The reaction mixture was heated at 180 °C for 36 hours. After cooling down to the room temperature, the mixture was filtered and washed with dichloromethane, and then the solvent was removed under a reduced pressure. The crude product was purified by column chromatography with petroleum ether/dichloromethane (2/1, v/v) as eluent to yield a white solid (1.5 g, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.40 (s, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 4H), 6.95 – 6.80 (m, 8H), 6.38 (d, *J* = 8.0 Hz, 4H) ppm. MALDI-TOF-MS: m/z: calcd for $C_{36}H_{22}Br_2N_2S_2$: 706.514, found: 705.938. Anal. Calcd for $C_{36}H_{22}Br_2N_2S_2$ (%): C 61.20, H 3.14, N 3.97; found: C 61.23, H 3.22, N 4.02.

*10,10'-(5,5-diphenyl-5H-dibenzo[b,d]silole-2,8-diyl)bis(10H-phenothiazine) (**DPS**)*

To a solution of **3** (2 g, 2.8 mmol) in THF (150 mL) under argon at -78 °C, *n*-butyl lithium (3.88 mL, 6.2 mmol, 1.6 M) was added dropwise via a syringe. After stirring at -78 °C for 1 h, dichlorodiphenylsilane (0.71 g, 2.8 mmol) was added within 1 min. Then, the mixture was gradually warmed up to room temperature and allowed to stir for 16 hours. Then the reaction was eventually quenched by adding water (5 mL). The resulting mixture was placed into 150 mL of water, and the desired product was extracted with dichloromethane (3×50 mL). The organic layer was then separated, dried over sodium sulfate (Na_2SO_4), filtered and evaporated under reduced pressure to give a crude product which was further purified by column chromatography using

View Article Online
DOI: 10.1039/C8TC02851F

petroleum ether/dichloromethane (3/1, v/v) to obtain the final product (1.5 g, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.78 – 7.73 (m, 6H), 7.52 – 7.43 (m, 6H), 7.38 – 7.33 (m, 2H), 7.04 (d, *J* = 7.2, 1.8 Hz, 4H), 6.93 – 6.76 (m, 8H), 6.40 (d, *J* = 8.0 Hz, 4H) ppm. ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.03, 135.96, 135.53, 135.42, 132.02, 130.50, 128.33, 126.90, 117.08 ppm. MALDI-TOF-MS: m/z: calcd for $C_{48}H_{32}N_2S_2Si$: 729.003, found: 728.893. Anal. Calcd for $C_{48}H_{32}N_2S_2Si$ (%): C 79.08, H 4.42, N 3.84; found: C 79.17, H 4.48, N 3.91.

*10,10'-(5,5-diphenyl-5H-dibenzo[b,d]germole-2,8-diyl)bis(10H-phenothiazine) (**DPG**)*

DPG was prepared with similar method as for **DPS** (68%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.85 (s, 2H), 7.70 (d, *J* = 7.3 Hz, 4H), 7.49 – 7.42 (m, 6H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 4H), 6.84 (t, *J* = 7.8 Hz, 4H), 6.79 (t, *J* = 8.1 Hz, 4H), 6.33 (d, *J* = 8.2 Hz, 4H) ppm. ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.52, 143.92, 143.44, 137.87, 135.72, 134.69, 134.38, 130.52, 129.95, 128.72, 126.84, 123.96, 122.67, 120.79, 116.50 ppm. MALDI-TOF-MS: m/z: calcd for $C_{48}H_{32}N_2S_2Ge$: 773.548, found: 774.052. Anal. Calcd for $C_{48}H_{32}N_2S_2Ge$ (%): C 74.53, H 4.17, N 3.62; found: C 74.57, H 4.24, N 3.68.

Results and Discussion

Preparation and Characterization

The synthetic routes of two novel materials, **DPS** and **DPG**, were outline in Scheme 1. 2,2'-dibromo-1,1'-biphenyl (**1**) was obtained in good yield with the reported procedure.[38] 2,2'-dibromo-5,5'-diiodo-1,1'-biphenyl (**2**) was prepared at a relatively lower yield (~40%) by iodination of **1** with the mixture of I_2 and $NaIO_4$ in H_2SO_4.[39] Then the key intermediate of 10,10'-(6,6'-dibromo-[1,1'-biphenyl]-3,3'-diyl)bis(10*H*-phenothiazine) (**3**) was synthesized via the Cu-catalyzed Ullmann coupling reaction between **2** and 10*H*-phenothiazine in moderate yield. At last, the target materials of **DPS** and **DPG**

View Article Online
DOI: 10.1039/C8TC02851F

were readily prepared by cyclization reaction between the double lithiation reagent of **3** and the respective dichloride compounds.[27a] The structure of the precursors and target products were fully characterized by nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR), mass spectrometry (MS) and elemental analysis (EA).

The thermal properties of **DPS** and **DPG** were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. 1, both **DPS** and **DPG** exhibited high thermal stability with decomposition temperature (T_d, 5% weight loss) of 430 and 416 ^{o}C, respectively. Due to the rigidity and robustness of the structures of **DPS** and **DPG**, they showed high glass transition temperature (T_g) over 240 ^{o}C. **DPS** and **DPG** demonstrated similar thermal properties due to their similar molecular configurations. The excellent thermal properties of these two compounds will be beneficial for their OLEDs applications. The Si-aryl and Ge-aryl substituents and phenothiazine groups render the molecular structures rather bulky, providing an effective steric hindrance. As a result, these compounds could form stable and homogeneous amorphous films when co-deposited with dopants,[12h] which were generally featured with smooth and uniform surfaces.[12g]

Photophysical properties

The UV-vis absorption, photoluminescence (PL) spectra in toluene solution at room temperature, and low temperature (77 K) phosphorescence (Phos) spectra in toluene matrix of **DPS** and **DPG** are shown in Fig. 2. The maxima absorption bands of both **DPS** and **DPG** were around 300 nm, which could be assigned to intramolecular π-π* transitions. Si-bridged **DPS** (379 nm) showed a small red-shift of the absorption onset as compared with Ge-bridged **DPG** (372 nm), which could be attributed to their different electronic effects caused by the mutual overlapping between *d*- or *p*-orbitals of heteroatoms and the π-orbitals of the peripheral phenyl rings.[40,41] Therefore, the optical energy gap (E_g) of **DPS** (3.27 eV) is slightly narrower than that of **DPG** (3.33 eV). **DPS** and **DPG** showed similar structureless PL spectra with the maximum emission peaks at 491 nm and 487 nm, respectively. The Phos spectra of **DPS** and

DPG are nearly identical, which means that the introduction of Si and Ge has less affected their triplet-excited states. In addition, the triplet energies (E_Ts) of **DPS** and **DPG** (2.48 eV) could be determined by the short-wavelength emission peak in the Phos spectra. So, we expected that the two compounds could be used as hosts for red PHOLEDs.

Electrochemical properties and theoretical calculation

The electrochemical properties of **DPS** and **DPG** were investigated through cyclic voltammetry (CV) method. As shown in Fig. S1, both **DPS** and **DPG** showed irreversible oxidation profiles during the anodic scan. The HOMO energy levels were estimated based on the onsets of oxidation curves, and the detailed results were listed in Table 1. It is worth noting that both **DPS** and **DPG** exhibited the same HOMO energy levels (-4.99 eV). In addition, the LUMO energy levels calculated from their HOMO energy levels and the corresponding E_gs were -1.72 and -1.66 eV for **DPS** and **DPG**, respectively. These results indicated the heteroatom of Si and Ge in **DPS** and **DPG** showed minor effect on their frontier molecular orbitals (FMOs) energy levels. Moreover, the electronic properties were investigated by density functional theory (DFT) calculations at a B3LYP/6-31G(d) level to further understanding of the structure-property relationship of these two materials. As shown in Fig. 3, the Si-bridged **DPS** and Ge-bridged **DPG** exhibited very similar HOMO/LUMO distributions. The HOMOs were mainly localized on the electron-rich phenothiazine units for both **DPS** and **DPG**. In addition, the LUMOs of the both new materials were dominantly distributed on the heterofluorene cores. Therefore, the HOMO and LUMO energy levels of **DPS** and **DPG** are quite similar, which was consistent well with previously reported results.[42] Furthermore, C-bridged 10,10'-(9,9-diphenyl-9*H*-fluorene-3,6-diyl)bis(10*H*-phenothiazine) (**DPC**) was selected as the reference material to deepen understanding the effect of heteroatoms on the FMOs of whole molecule (Table S1 and Fig. 4). It is worth noting that although the electronegativity of C is larger than those of Si and Ge, the introduction of heteroatom atoms (Si and Ge) led to the low LUMO energy levels as compared with

View Article Online
DOI: 10.1039/C8TC02851F

the C linker (Table S1 and Fig. 4), which might be attributed to the σ^*–π^* hyperconjugation effect[42,43] between the exocyclic σ bonds and the adjacent phenyl π system.

Electroluminescent properties

To explore the potential of **DPS** and **DPG** as host materials in PHOLEDs, the red devices were fabricated with the configuration of ITO/HAT-CN (10 nm)/TAPC (55 nm)/TCTA (10 nm)/Host: 6 wt.% $Ir(MDQ)_2(acac)$ (20 nm)/TmPyPB (35 nm)/Liq (2 nm)/Al (120 nm). The red emitter $Ir(MDQ)_2(acac)$ were doped into the hosts of **DPS** and **DPG** to constitute the emitting layer (EML). Dipyrazino[2,3-*f*:2',3'-*h*]-quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolatolithium (Liq) serve as hole and electron injection layer (HIL and EIL), respectively. In addition, 1,1-bis[4-[*N*',*N*'-di(*p*-tolyl)amino]-phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)phen-3-yl]benzene (TmPyPB) act as hole and electron transport layer (HTL and ETL) as well as electron and hole blocking layer (EBL and HBL), respectively. Furthermore, a thin layer of tris(4-(9*H*-carbazol-9-yl)phenyl)amine (TCTA) was used as another hole transport layer due to its relative low HOMO energy level (-5.90 eV) as compared with that of TAPC (-5.50 eV), which could favor hole transport and improve the recombination efficiency of hole and electron. The detailed electroluminescence (EL) data were listed in Table 2.

As depicted in Fig. 5(a), both devices exhibited relatively lower turn-on voltages of 3.6 V and 3.7 V at 200 cd m^{-2}, and the maximum luminance of **DPS**-based device was over 12300 cd m^{-2}, which could be comparable with the best reported results.[44] The relatively lower driving voltage and very high brightness of **DPS**-based device suggests the efficient charge injection, transport, recombination and the formation of exciton, as well as the radiation transition process of exciton. As shown in Fig. 5(c), **DPS** and **DPG**-based devices displayed the characteristic emission of $Ir(MDQ)_2(acac)$ with the Commission Internationale de l′Eclairage (CIE) coordinates of (0.61, 0.39)

View Article Online
DOI: 10.1039/C8TC02851F

and (0.62, 0.38), respectively. The device hosted by **DPG** exhibited a moderate performance with the maximum current efficiency (CE)/power efficiency (PE)/external quantum efficiency (EQE) of 38.0 cd A^{-1}/33.5 lm W^{-1}/20.0%. Remarkably, the **DPS**-based device demonstrated excellent performance with maximum CE, PE and EQE of 50.7 cd A^{-1}, 44.7 lm W^{-1} and 28.3%, respectively, without any light extraction techniques.[3a,3b] Furthermore, the EQE still can reach 21.8% at the brightness of 5000 cd m^{-2}. The superior device performance might partially be due to the high triplet energy of **DPS**, which could favor the energy transfer process from the host to the Ir-dopant, and control the drift and diffusion of triplet excitons and therefore reduce triplet quenching effect in EML. The hole- and electron-only devices based on **DPS** and **DPG** were fabricated (Fig. 6). The good charge carrier transport ability of **DPS** resulted in its preferable device performance. On the other hand, the photoluminescence quantum yield (PLQY) of $Ir(MDQ)_2(acac)$ (6 wt.%) in **DPS** and **DPG** thin films were measured in an integrating sphere to be 0.78 and 0.68, respectively, which could lead to their superior device performance.[44b,45] Furthermore, in order to understand the efficiency roll-off mechanisms of the devices, we chose triplet-triplet annihilation (TTA) mode (Equation S1)[46] and singlet-polaron annihilation (SPA) mode (Equation S2)[44a] to simulate the EQE-J relationships of the devices (Fig. S2). As shown in Fig. S2, the EQE–J curve of **DPS**-based device exhibited relatively large deviation from TTA mode and fit well with SPA mode, which suggested that the singlet-induced quenching process mainly accounted for its efficiency reduction.[47] In contrast, the fine consistency between the EQE–J curve and the fitting result of TTA mode suggests that TTA mechanism plays an important role in efficiency roll-off of **DPG**-based device.[48]

Conclusion

Novel organosilicon and organogermanium compounds, **DPS** and **DPG**, were designed and synthesized. The influence of Si and Ge in the basic physical and chemical properties of these compounds were fully studied. The results showed that the heteroatom of Si and Ge had a tiny effect on their thermal and photophysical properties and the electrochemical behaviors. However, there is big differences between the hole/electron transport abilities and the EL performance of **DPS** and **DPG**. Excellent device performance was achieved for **DPS**-based device with the maximum CE, PE and EQE of 50.7 cd A^{-1}, 44.7 lm W^{-1} and 28.3%, respectively. On the other hand, the **DPG**-based device also demonstrated nice performance with the maximum EQE of 20%. These results revealed the great potentials of organosilicon and organogermanium derivatives in the exploration of highly efficient OLED materials.

Acknowledgements

We thank to the financial support from the National Key R&D Program of China (2016YFB0400703), the National Natural Science Foundation of China (21472135) and Natural Science Foundation of Jiangsu Province of China (BK20151216). This project is also funded by Collaborative Innovation Center of Suzhou Nano Science and Technology (CIC-Nano), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University and by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

1 (a) L.-X. Xiao, Z.-J. Chen, B. Qu, J.-X. Luo, S. Kong, Q.-H. Gong and J. Kido, *Adv. Mater*., 2011, 23, 926; (b) Y.-T. Tao, C.-L. Yang and J.-G. Qin, *Chem. Soc. Rev*., 2011, 40, 2943; (c) K.-S. Yook and J.-Y. Lee, *Adv. Mater*., 2012, 24, 3169.

2 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, 395, 151.

3 (a) X.-Y. Liu, F. Liang, Y. Yuan, L.-S. Cui, Z.-Q. Jiang and L.-S. Liao, *Chem. Commun*., 2016, 52, 8149; (b) X.-Y. Liu, X. Tang, Y. Zhao, D. Zhao, J. Fan and L.-S. Liao, *ACS Appl. Mater. Interfaces*, 2018, 10, 1925; (c) Y. Tao, Q. Wang, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Funct. Mater*., 2010, 20, 2923; (d) D. Zhang, J. Qiao, D. Zhang and L. Duan, *Adv. Mater*., 2017, 1702847; (e) Y. Shi, W. Wu, H. Dong, G. Li, K. Xi, G. Divitini, C. Ran, F. Yuan, M. Zhang, B. Jiao, X. Hou and Z. Wu, *Adv.*

View Article Online
DOI: 10.1039/C8TC02851F

Mater., 2018, 30, 1800251; (f) J. Dai, J. Xi, L. Li, J. Zhao, Y. Shi, W. Zhang, C. Ran, B. Jiao, X. Hou, X. Duan and Z. Wu, *Angew.Chem. Int. Ed*., 2018, 57, 5754.

4 (a) X.-Y. Liu, F. Liang, L.-S. Cui, X.-D. Yuan, Z.-Q. Jiang and L.-S. Liao, *Chem. Asian J*., 2015, 10, 1402; (b) C. Han, Z. Zhang, H. Xu, J. Li, Y. Zhao, P. Yan and S. Liu, *Chem. Eur. J*., 2013, 19, 1385; (c) M.-M. Xue , C.-C. Huang , Y. Yuan , Y.-X. Zhang , M.-K. Fung and L.-S. Liao, *Chem. Commun*., 2017, 53, 263; (d) J. H. Yun, Y. J. Kang, S. H. Han and J. Y. Lee, *J. Mater. Chem. C*, 2018, 6, 320.

5 (a) J. Li, S.-C. Dong, A. Opitz, L.-S. Liao and N. Koch, *J. Mater. Chem. C*, 2017, 5, 6989; (b) T. Kamata, H. Sasabe, M. Igarashi and J. Kido, *Chem. Eur. J*., 2018, 24, 4590; (c) J.-K. Bin, J. H. Yang and J.-I. Hong, *J. Mater. Chem*., 2012, 22, 21720; (d) S. Y. Byeon, S. H. Han and J. Y. Lee, *Dyes Pigments*., 2018, 155, 114.

6 (a) X.-Y. Liu, Q.-S. Tian, D. Zhao, J. Fan and L.-S. Liao, *Org. Electron*., 2018, 56, 186; (b) X.-K. Liu, C.-J. Zheng, M.-F. Lo, J. Xiao, C.-S. Lee, M.-K. Fung and X.-H. Zhang, *Chem. Commun*., 2014, 50, 2027; (c) Z. Jiang, Y. Chen, C. Yang, Y. Cao, Y. Tao, J. Qin and D. Ma, *Org. Lett*., 2009, 11, 1503.

7 (a) X.-Y. Liu, H.-T. Ge, Y. Zhao, D. Zhao, J. Fan and L.-S. Liao, *J. Mater. Chem. C*, 2018, 6, 4300; (b) M.-H. Tsai, Y.-H. Hong, C.-H. Chang, H.-C. Su, C.-C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J. V. Grazulevicius and C.-P. Hsu, *Adv. Mater*., 2007, 19, 862; (c) C. Bian, Q. Wang, Q. Ran, X.-Y. Liu, J. Fan and L.-S. Liao, *Org. Electron*., 2018, 52, 138.

8 (a) X. Ren, J. Li, R. J. Holmes, P. I. Djurovich, S. R. Forrest and M. E. Thompson, *Chem. Mater*., 2004, 16, 4743; (b) J.-J. Lin, W.-S. Liao, H.-J. Huang, F.-I. Wu and C.-H. Cheng, *Adv. Funct. Mater*., 2008, 18, 485; (c) M.-S. Lin, L.-C. Chi, H.-W. Chang, Y.-H. Huang, K.-C. Tien, C.-C. Chen, C.-H. Chang, C.-C. Wu, A. Chaskar, S.-H. Chou, H.-C. Ting, K.-T. Wong, Y.-H. Liu and Y. Chi, *J. Mater. Chem*., 2012, 22, 870; (d) S. Gong, N. Sun, J. Luo, C. Zhong, D. Ma, J. Qin and C. Yang, *Adv. Funct. Mater*., 2014, 24, 5710.

9 (a) H. Fukagawa, K. Watanabe, T. Tsuzuki and S. Tokito, *Appl. Phys. Lett*., 2008, 93, 133312; (b) H. Fukagawa, N. Yokoyama, S. Irisa and S. Tokito, *Adv. Mater*., 2010, 22, 4775; (c) H. Fukagawa, S. Irisa, H. Hanashima, T. Shimizu and S. Tokito, *Org.*

View Article Online
DOI: 10.1039/C8TC02851F

Electron., 2011, 12, 1638; (d) Y. Gu, L. Zhu, Y. Li, L. Yu, K. Wu, T. Chen, M. Huang, F. Wang, S. Gong, D. Ma, J. Qin and C. Yang, *Chem. Eur. J.*, 2015, 21, 8250.

10 (a) A. B. Padmaperuma, L. S. Sapochak and P. E. Burrows, *Chem. Mater*., 2006, 18, 2389; (b) P. A. Vecchi, A. B. Padmaperuma, H. Qiao, L. S. Sapochak and P. E. Burrows, *Org. Lett*., 2006, 8, 4211; (c) Q. Zhang, B. Wang, J. Tan, G. Mu, W. Yi, X. Lv, S. Zhuang, W. Liu and L. Wang, *J. Mater. Chem. C*, 2017, 5, 8516.

11 (a) W. Li, J. Li, F. Wang, Z. Gao and S. Zhang, *ACS Appl. Mater. Interfaces*, 2015, 7, 26206; (b) W. Li, J. Li, D. Liu and Q. Jin, *ACS Appl. Mater. Interfaces*, 2016, 8, 22382; (c) W. Song, L. Shi, L. Gao, P. Hu, H. Mu, Z. Xia, J. Huang and J. Su, *ACS Appl. Mater. Interfaces*, 2018, 10, 5714; (d) Y. Tao, Q. Wang, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Funct. Mater*., 2010, 20, 2923; (e) J.-K. Bin, N.-S. Cho and J.-I. Hong, *Adv. Mater*., 2012, 24, 2911; (f) C.-W. Lee and J.-Y. Lee, *Adv. Mater*., 2013, 25, 5450; (g) M. Kim and J.-Y. Lee, *Adv. Funct. Mater*., 2014, 24, 4164.

12 (a) A. C. A. Chen, S. W. Culligan, Y. Geng, S. H. Chen, K. P. Klubek, K. M. Vaeth and C. W. Tang, *Adv. Mater*., 2004, 16, 783; (b) C.-F. Shu, R. Dodda, F.-I. Wu, M. S. Liu and A. K.-Y. Jen, *Macromolecules*, 2003, 36, 6698; (c) Y. Li, J. Ding, M. Day, Y. Tao, J. Lu and M. D'iorio, *Chem. Mater*., 2004, 16, 2165; (d) J. Lu, Y. Tao, M. D'iorio, Y. Li, J. Ding and M. Day, *Macromolecules*, 2004, 37, 2442; (e) A. Goel, S. Chaurasia, M. Dixit, V. Kumar, S. Prakash, B. Jena, J. K. Verma, M. Jain, R. S. Anand and S. S. Manoharan, *Org. Lett*., 2009, 11, 1289; (f) N. Matsumoto, T. Miyazaki, M. Nishiyama and C. Adachi, *J. Phys. Chem. C*, 2009, 113, 6261; (g) S. Ye, Y. Liu, J. Chen, K. Lu, W. Wu, C. Du, Y. Liu, T. Wu, Z. Shuai, and G. Yu, *Adv. Mater.*, 2010, 22, 4167; (h) C.-C. Wu, Y.-T. Lin, K.-T. Wong, R.-T. Chen, and Y.-Y. Chien, *Adv. Mater.*, 2004, 16, 61.

13 W.-Y. Wong, *Coord. Chem. Rev*., 2005, 249, 971.

14 (a) M. Gaal, E. J. W. List and U. Scherf, *Macromolecles*, 2003, 36, 4236; (b) E. J. W. List, R. Guentner, F. P. Scanducci de and U. Scherf, *Adv. Mater*., 2002, 14, 374; (c) S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins and A. B. Holmes, *J. Am. Chem. Soc*., 2007, 129, 11910; (d) Q. Zhao, S.-J. Liu and W. Huang, *Macromol. Chem. Phys*., 2009, 210, 1580;

View Article Online
DOI: 10.1039/C8TC02851F

15 (a) U. Scherf and E. J. W. List, *Adv. Mater.*, 2002, 14, 477; (b) V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klärner, R. D. Miller and D. C. Miller, *Macromolecules*, 1999, 32, 361; (c) E. Zojer, A. Pogantsch, E. Hennebicq, D. Beljonne, J.-L. Brédas, P. Scandiucci de Freitas, U. Scherf and E. J. W. List, *J. Chem. Phys.*, 2002, 117, 6794; (d) J. M. Lupton, M. R. Craig and E. W. Meijer, *Appl. Phys. Lett.*, 2002, 80, 4489; (e) M. Sims, D. D. C. Bradley, M. Ariu, M. Koeberg, A. Asimakis, M. Grell and D. G. Lidzey, *Adv. Funct. Mater.*, 2004, 14, 765; (f) K. Becker, J. M. Lupton, J. Feldmann, B. S. Nehls, F. Galbrecht, D. Gao and U. Scherf, *Adv. Funct. Mater.*, 2006, 16, 364; (g) Y.-S. Wu, J. Li, X.-C. Ai, L.-M. Fu, J.-P. Zhang, Y.-Q. Fu, J.-J. Zhou, L. Li and Z.-S. Bo, *J. Phys. Chem. A*, 2007, 111, 11473; (h) S. Kappaun, H. Scheiber, R. Trattnig, E. Zojer, E. J. W. List and C. Slugovc, *Chem. Commun.*, 2008, 5170.

16 (a) B. W. Zhao, T. Cao and J. M. White, *Adv. Funct. Mater.*, 2004, 14, 783; (b) R. Grisorio, G. P. Suranna, P. Mastrorilli and C. F. Nobile, *Adv. Funct. Mater.*, 2007, 17, 538.

17 (a) L. Liu, S. Tang, M. Liu, Z. Xie, W. Zhang, P. Lu, M. Hanif and Y. Ma, *J. Phys. Chem. B*, 2006, 110, 13734; (b) R. Grisorio, G. Allegretta, P. Mastrorilli and G. P. Suranna, *Macromolecules*, 2011, 44, 7977.

18 (a) R. Abbel, M. Wolffs, R. A. A. Bovee, J. L. J. van Dongen, X. Lou, O. Henze, W. J. Feast, E. W. Meijer and A. P. H. J. Schenning, *Adv. Mater.*, 2009, 21, 597; (b) B. Kobin, F. Bianchi, S. Halm, J. Leistner, S. Blumstengel, F. Henneberger and S. Hecht, *Adv. Funct. Mater.*, 2014, 24, 7717.

19 (a) W.-L. Yu, J. Pei, W. Huang and A. J. Heeger, *Adv. Mater.*, 2000, 12, 828; (b) S. Setayesh, A. C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E. J. W. List and G. Leising, *J. Am. Chem. Soc.*, 2001, 123, 946; (c) J.-H. Lee and D.-H. Hwang, *Chem. Commun.*, 2003, 2836; (d) D.-H. Hwang, M.-J. Park and J.-H. Lee, *Mater. Sci. Eng., C*, 2004, 24, 201; (e) D. Vak, C. Chun, C. L. Lee, J.-J. Kim and D.-Y. Kim, *J. Mater. Chem.*, 2004, 14, 1342; (f) Y. Wu, J. Li, Y. Fu and Z. Bo, *Org. Lett.*, 2004, 6, 3485; (g) J. Jacob, S. Sax, M. Gaal, E. J. W. List, A. C. Grimsdale and K. Müllen, *Macromolecules*, 2005, 38, 9933; (h) Y. Wu, J. Zhang, Z. Fei and Z. Bo, *J. Am. Chem. Soc.*, 2008, 130, 7192; (i) B. Kobin, S. Behren, B. Braun-Cula and S.

View Article Online
DOI: 10.1039/C8TC02851F

Hecht, *J. Phys. Chem. A*, 2016, 120, 5474.

20 (a) S. Yamaguchi, T. Shirasaka, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2002, 124, 8816; (b) A. Wakamiya, K. Mishima, K. Ekawa and S. Yamaguchi, *Chem. Commun.*, 2008, 579; (c) A. Iida and S. Yamaguchi, *J. Am. Chem. Soc.*, 2011, 133, 6952; (d) V. D. B. Bonifácio, J. Morgado and U. Scherf, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46, 2878; (e) C. Ribeiro, P. Brogueira, G. Lavareda, C. N. Carvalho, A. Amaral, L. Santos, J. Morgado, U. Scherf and V. D. B. Bonifácio, *Biosens. Bioelectron.*, 2010, 26, 1662; (f) Y. Tokoro, A. Nagai, K. Tanaka and Y. Chujo, *Macromol. Rapid Commun.*, 2012, 33, 550; (g) M. F. Smith, S. J. Cassidy, I. A. Adams, M. Vasiliu, D. L. Gerlach, D. A. Dixon and P. A. Rupar, *Organometallics*, 2016, 35, 3182; (h) J.-F. Brière and M. Côté, *J. Phys. Chem. B*, 2004, 108, 3123.

21 (a) A. Decken, F. P. Gabbaie and A. H. Cowley, *Inorg. Chem.*, 1995, 34, 3853; (b) T. Matsumoto, K. Tanaka and Y. Chujo, *J. Am. Chem. Soc.*, 2013, 135, 4211; (c) T. Matsumoto, K. Tanaka and Y. Chujo, *Macromolecules*, 2015, 48, 1343; (d) T. Matsumoto, H. Takamine, K. Tanaka and Y. Chujo, *Chem. Lett.*, 2015, 44, 1658.

22 (a) K. L. Chan, M. J. McKiernan, C. R. Towns and A. B. Holmes, *J. Am. Chem. Soc.*, 2005, 127, 7662; (b) J. J. McDowell, I. Schick, A. Price, D. Faulkner and G. Ozin, *Macromolecules*, 2013, 46, 6794; (c) J. Ohshita, *Macromol. Chem. Phys.*, 2009, 210, 1360; (d) W. W. H. Wong and A. B. Holmes, Polyfluorenes, Springer, Berlin, 2008, pp. 85–98; (e) X. Zhan, S. Barlow and S. R. Marder, *Chem. Commun.*, 2009, 1948; (f) S. Beaupré, P.-L. T. Boudreault and M. Leclerc, *Adv. Mater.*, 2010, 22, E6; (g) S. A. Ponomarenko and S. Kirchmeyer, Silicon Polymers, Springer, Berlin, 2011, pp. 33–110; (h) S. F. Chen, Y. Tian, J. Peng, H. Zhang, X. J. Feng, H. Zhang, X. Xu, L. Li and J. Gao, *J. Mater. Chem. C*, 2015, 3, 6822.

23 (a) S. M. Parke, M. P. Boone and E. Rivard, *Chem. Commun.*, 2016, 52, 9485; (b) X. He and T. Baumgartner, *RSC Adv.*, 2013, 3, 11334; (c) D. W. Hammerstroem, J. Braddock-Wilking and N. P. Rath, *J. Organomet. Chem.*, 2017, 830, 196.

24 C. Gu, D. Zhu, M. Qiu, L. Han, S. Wen, Y. Li and R. Yang, *New J. Chem.*, 2016, 40, 7787.

25 (a) I. Lévesque, P. Bertrand, N. Blouin, M. Leclerc, S. Zecchin, G. Zotti, C. I.

View Article Online
DOI: 10.1039/C8TC02851F

Ratcliffe, D. D. Klug, X. Gao, F. Gao and J. S. Tse, *Chem. Mater*., 2007, 19, 2128; (b) N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater*., 2007, 19, 2295; (c) T.-Y. Chu, S. Alem, S.-W. Tsang, S.-C. Tse, S. Wakim, J. Lu, G. Dennler, D. Waller, R. Gaudiana and Y. Tao, *Appl. Phys. Lett*., 2011, 98, 253301; (d) N. Dubey and M. Leclerc, *J. Polym. Sci., Part B: Polym. Phys*., 2011, 49, 467; (e) D. Gendron and M. Leclerc, *Energy Environ. Sci*., 2011, 4, 1225.

26 (a) R.-F. Chen, R. Zhu, Q.-L. Fan and W. Huang, *Org. Lett*., 2008, 10, 2913; (b) Y. Makioka, T. Hayashi and M. Tanaka, *Chem. Lett*., 2004, 33, 44; (c) Y. Morisaki, Y. Aiki and Y. Chujo, *Macromolecules*, 2003, 36, 2594; (d) M. Hissler, P. Dyer and R. Réau, *Coord. Chem. Rev*., 2003, 244, 1; (e) J. Crassous and R. Réau, *Dalton Trans*., 2008, 6865.

27 (a) V. H. K. Fell, A. Mikosch, A.-K. Steppert, W. Ogieglo, E. Senol, D. Canneson, M. Bayer, F. Schoenebeck, A. Greilich and A. J. C. Kuehne, *Macromolecules*, 2017, 50, 2338; (b) T. Kato, S. Tanaka and K. Naka, *Chem. Lett*., 2015, 44, 1476; (c) A. A. Diaz, J. D. Young, M. A. Khan and R. J. Wehmschulte, *Inorg. Chem*., 2006, 45, 5568.

28 J. Simonet, J. Rault-Berthelot, M. M. Granger and H. Le Deit, *J. Electroanal. Chem*., 1994, 372, 185.

29 (a) E. Jin, C. Du, M. Wang, W. Li, C. Li, H. Wei and Z. Bo, *Macromolecules*, 2012, 45, 7843; (b) Y.-L. Liu, J.-K. Feng and A.-M. Ren, *J. Phys. Chem. A*, 2008, 112, 3157; (c) N. Nemoto, H. Kameshima, Y. Okano and T. Endo, *J. Polym. Sci., Part A: Polym. Chem*., 2003, 41, 1521.

30 (a) Antimony: D. Hellwinkel and M. Bach, *J. Organomet. Chem*., 1969, 17, 389; (b) Plumbum: D. C. van Beelen, J. Wolters and A. van der Gen, *Recl. Trav. Chim. Pays-Bas*, 1979, 98, 437; (c) Aluminum: J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc*., 1962, 84, 1501; J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc*., 1966, 88, 2976.

31 (a) S. Yamaguchi, Y. Itami and K. Tamao, *Organometallics*, 1998, 17, 4910; (b) L. C. Palilis, a. J. Mäkinen, M. Uchida and Z. H. Kafafi, *Appl. Phys. Lett*., 2003, 82, 2209.

32 G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc*., 2008, 130, 7670.

View Article Online
DOI: 10.1039/C8TC02851F

33 R.-F. Chen, C. Zheng, Q.-L. Fan and W. Huang, *J. Comput. Chem.*, 2007, 28, 2091.

34 (a) H. Chen, Z.-Q. Jiang, C.-H. Gao, M.-F. Xu, S.-C. Dong, L.-S. Cui, S.-J. Ji and L.-S. Liao, *Chem. Eur. J.*, 2013, 19, 11791; (b) S. Choi, M. Godumala, J. H. Lee, G. H. Kim, J. S. Moon, J. Y. Kim, D.-W. Yoon, J. H. Yang, J. Kim, M. J. Cho, J. H. Kwon and D. H. Choi, *J. Mater. Chem. C*, 2017, 5, 6570; (c) H. Li, L. Xu, Y. Tang, Y. Tao, S. Xu, C. Zheng, G. Xing, X. Zhou, W. Huang, R. Chen, *J. Mater. Chem. C*, 2016, 4, 10047; (d) X.-Y. Liu, X. Tang, Y. Zhao, D. Zhao, J. Fan and L.-S. Liao, *J. Mater. Chem. C*, 2018, 6, 1023.

35 (a) Y. Kamata, *Mater. Today*, 2008, 11, 30; (b) E. Simoen, J. Mitard, G. Hellings, G. Eneman, B. De Jaeger, L. Witters, B. Vincent, R. Loo, A. Delabie, S. Sioncke, M. Caymax and C. Claeys, *Mater. Sci. Semicond. Process.*, 2012, 15, 588; (c) D. P. Brunco, B. De Jaeger, G. Eneman, J. Mitard, G. Hellings, A. Satta, V. Terzieva, L. Souriau, F. E. Leys, G. Pourtois, M. Houssa, G. Winderickx, E. Vrancken, S. Sioncke, K. Opsomer, G. Nicholas, M. Caymax, A. Stesmans, J. Van Steenbergen, P. W. Mertens, M. Meuris and M. M. Heyns, *J. Electrochem. Soc.*, 2008, 155, H552.

36 (a) C. Yao, Q. Cui, J. Peng, X. Xu, R. Liu, J. Wang, Y. Tian and L. Li, *J. Mater. Chem. C*, 2015, 3, 5017; (b) C. Yao, Y. Yang, L. Li, M. Bo, C. Peng and J. Wang, *J. Mater. Chem. C*, 2018, 6, 6148.

37 (a) K. Brunner, A. van Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. W. Langeveld, *J. Am. Chem. Soc.*, 2004, 126, 6035; (b) Z. Wu, Y. Xiong, J. Zou, L. Wang, J. Liu, Q. Chen,W. Yang, J. Peng and Y. Cao, *Adv. Mater.*, 2008, 20, 2359; (c) Y. Mo, R. Tian, W. Shi and Y. Cao, *Chem. Commun.*, 2005, 39, 4925.

38 K. Ouyang, Y. Liang and Z. Xi, *Org. Lett.*, 2012, 14, 4572.

39 K. L. Chan, S. E. Watkins, C. S. K. Mak, M. J. McKiernan, C. R. Towns, S. I. Pascua and A. B. Holmes, *Chem. Commun.*, 2005, 46, 5766.

40 V. K. Belsky, I. E. Saratov, V. O. Reikhsfeld and A. A. Simonenko, *J. Organomet. Chem.*, 1983, 258, 283.

41 (a) J. Ohshita, M. Nodono, H. Kai, T. Watanabe, A. Kunai, K. Komaguchi, M.

Shiotani, A. Adachi, K. Okita, Y. Harima, K. Yamashita and M. Ishikawa, *Organometallics*, 1999, 18, 1453; (b) J. Ohshita, H. Kai, A. Takata, T. Iida, A. Kunai, N. Ohta, K. Komaguchi, M. Shiotani, A. Adachi, K. Sakamaki and K. Okita, *Organometallics*, 2001, 20, 4800.

42 (a) F.-B. Zhang, Y. Adachi, Y. Ooyama and J. Ohshita, *Organometallics*, 2016, 35, 2327; (b) H. Cao, I. A. Brettell-Adams, F. Qu and P. A. Rupar, *Organometallics*, 2017, 36, 2565.

43 S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans*., 1998, 22, 3693.

44 (a) Y.-K. Wang, S.-H. Li, S.-F. Wu, C.-C. Huang, S. Kumar, Z.-Q. Jiang, M.-K. Fung and L.-S. Liao, *Adv. Funct. Mater*., 2018, 28, 1706228; (b) K.-H. Kim, S. Lee, C.-K. Moon, S.-Y. Kim, Y.-S. Park, J.-H. Lee, J. W. Lee, J. Huh, Y. You and J.-J. Kim, *Nat. Commun*., 2014, 5, 4769.

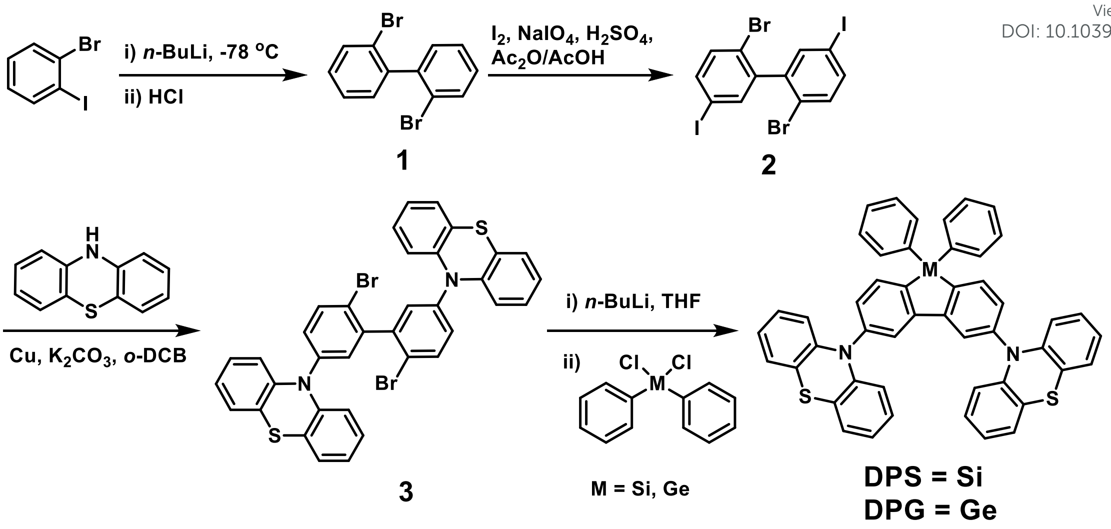
45 Y.-L. Chang, Z. B. Wang, M. G. Helander, J. Qiu, D. P. Puzzo and Z. H. Lu, *Org. Electron*., 2012, 13, 925.

46 (a) M. A. Baldo, C. Adachi and S. R. Forrest, *Phys. Rev. B*, 2000, 62, 10967; (b) S. Reineke, K. Walzer and K. Leo, *Phys. Rev. B*, 2007, 12, 75.

47 (a) K. Masui, H. Nakanotani and C. Adachi, *Org. Electron*., 2013, 14, 2721; (b) H. Yang, Q. Liang, C. Han, J. Zhang and H. Xu, *Adv. Mater*., 2017, 29, 1700553.

48 Q. Zhang, S. Xiang, Z. Huang, S. Sun, S. Ye, X. Lv, W. Liu, R. Guo and L. Wang, *Dyes Pigments*., 2018, 155, 51.

View Article Online
DOI: 10.1039/C8TC02851F



Scheme 1 Synthetic routes of **DPS** and **DPG**.

View Article Online
DOI: 10.1039/C8TC02851F

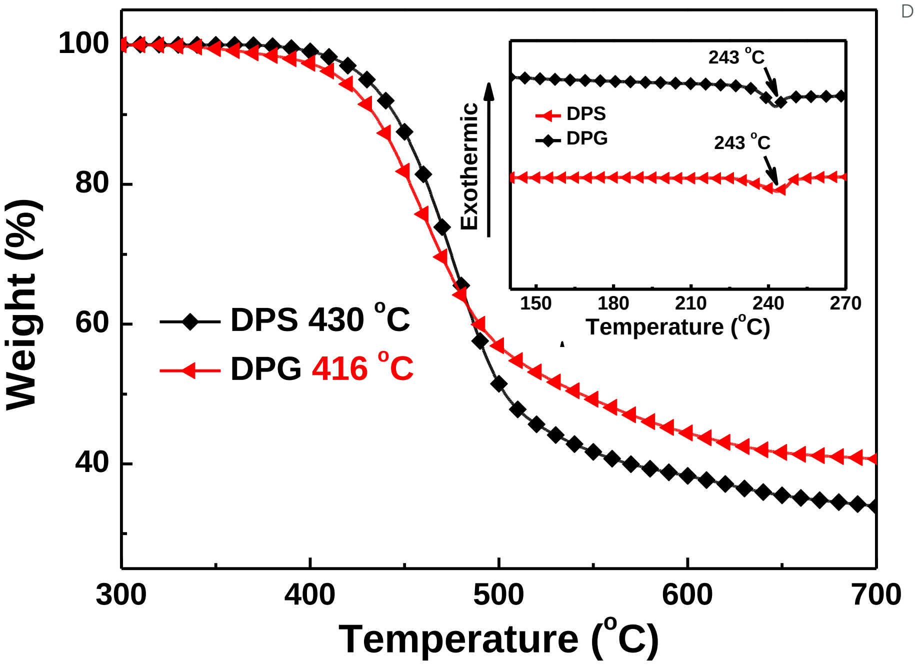


Fig. 1 TGA and DSC (inset) curves of **DPS** and **DPG**.

View Article Online
DOI: 10.1039/C8TC02851F

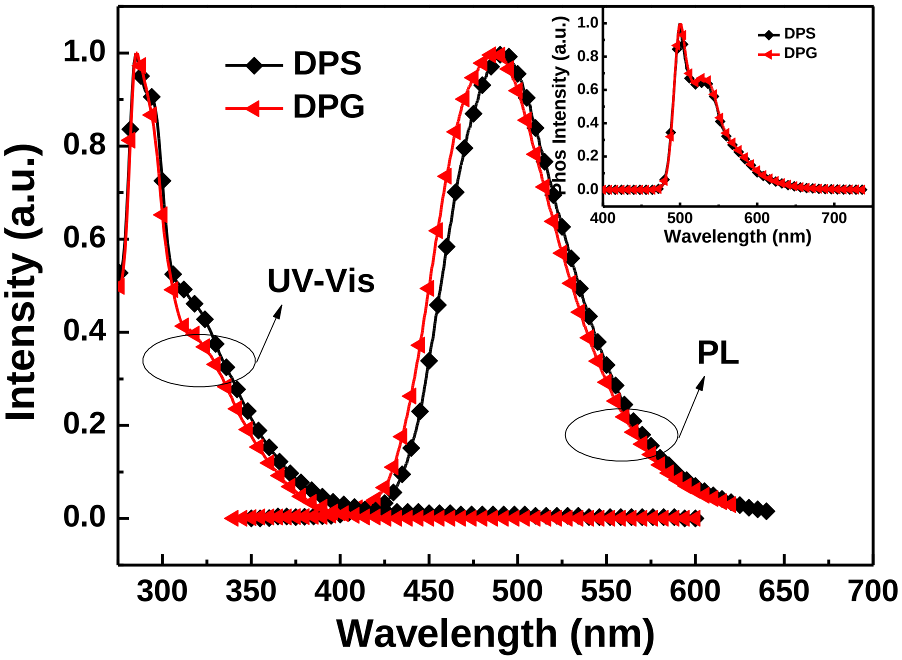


Fig. 2 Room temperature UV-vis absorption, PL spectra, and low temperature Phos spectra (inset) in toluene.

View Article Online
DOI: 10.1039/C8TC02851F

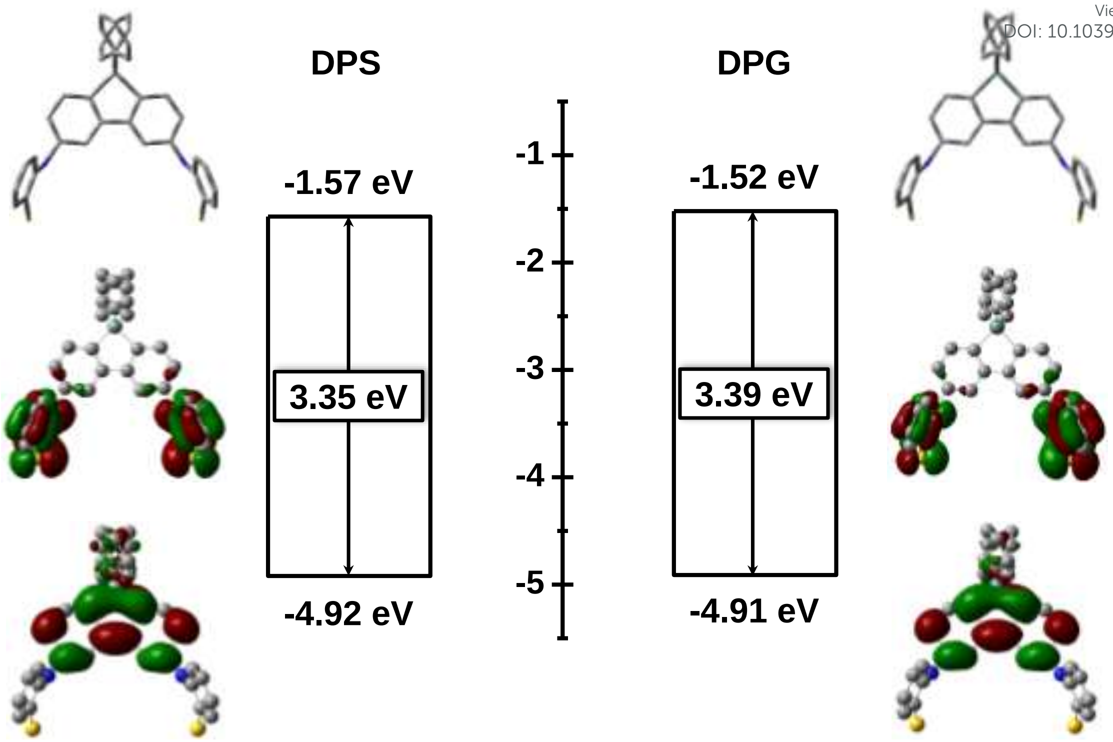


Fig. 3 DFT calculation results of molecule optimized structure, HOMO/LUMO distributions and energy levels, and energy band gaps of **DPS** and **DPG**.

View Article Online
DOI: 10.1039/C8TC02851F

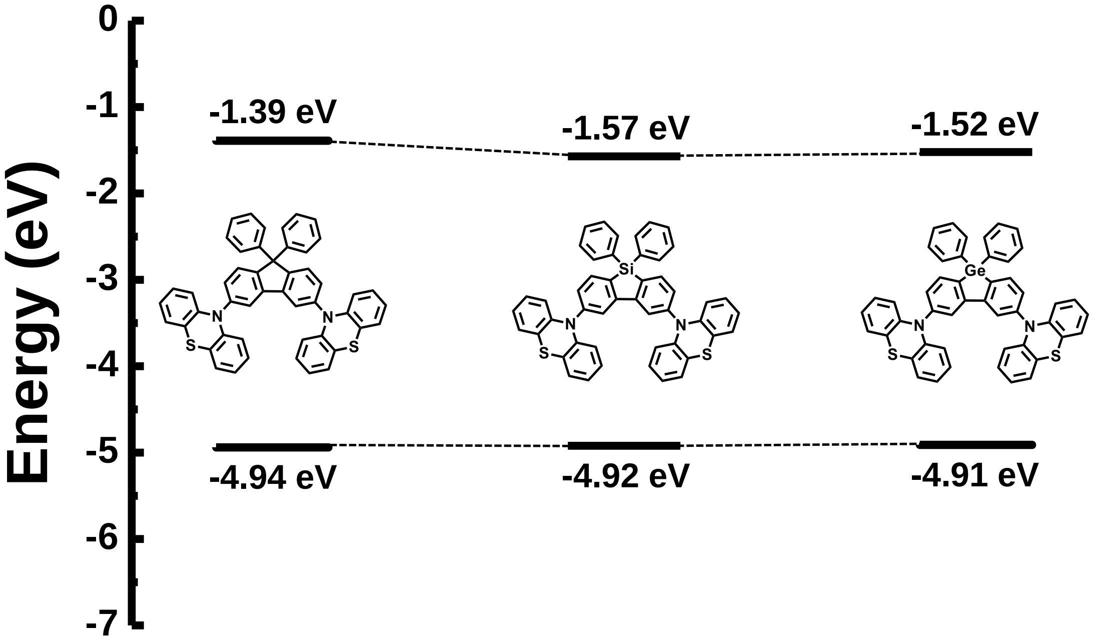


Fig. 4 HOMO and LUMO energy levels for the carbon-, silicon-, and germanium-bridged molecules at the B3LYP 6-31G(d) level.

View Article Online
DOI: 10.1039/C8TC02851F

Table 1. Summary of the physical properties of **DPS** and **DPG**.

Molecule	Abs λ_{max}[a]	PL λ_{max}[a]	T_g[b]/T_d[c]	E_g[d]	E_T[e]	HOMO[f]	LUMO[g]
	[nm]	[nm]	[°C]	[eV]	[eV]	[eV]	[eV]
DPS	285	491	243/430	3.27	2.48	-4.99	-1.72
DPG	285	487	243/416	3.33	2.48	-4.99	-1.66

[a]Measured in toluene solution at room temperature. [b]T_g: Glass transition temperature. [c]T_d: Decomposition temperature. [d]E_g: Optical band gap energies were calculated from the corresponding absorption onset in toluene solution. [e]E_T: Measured in toluene glass matrix at 77 K. [f]HOMO levels were calculated from CV data. [g]LUMO levels were calculated from the HOMOs and E_gs.

View Article Online
DOI: 10.1039/C8TC02851F

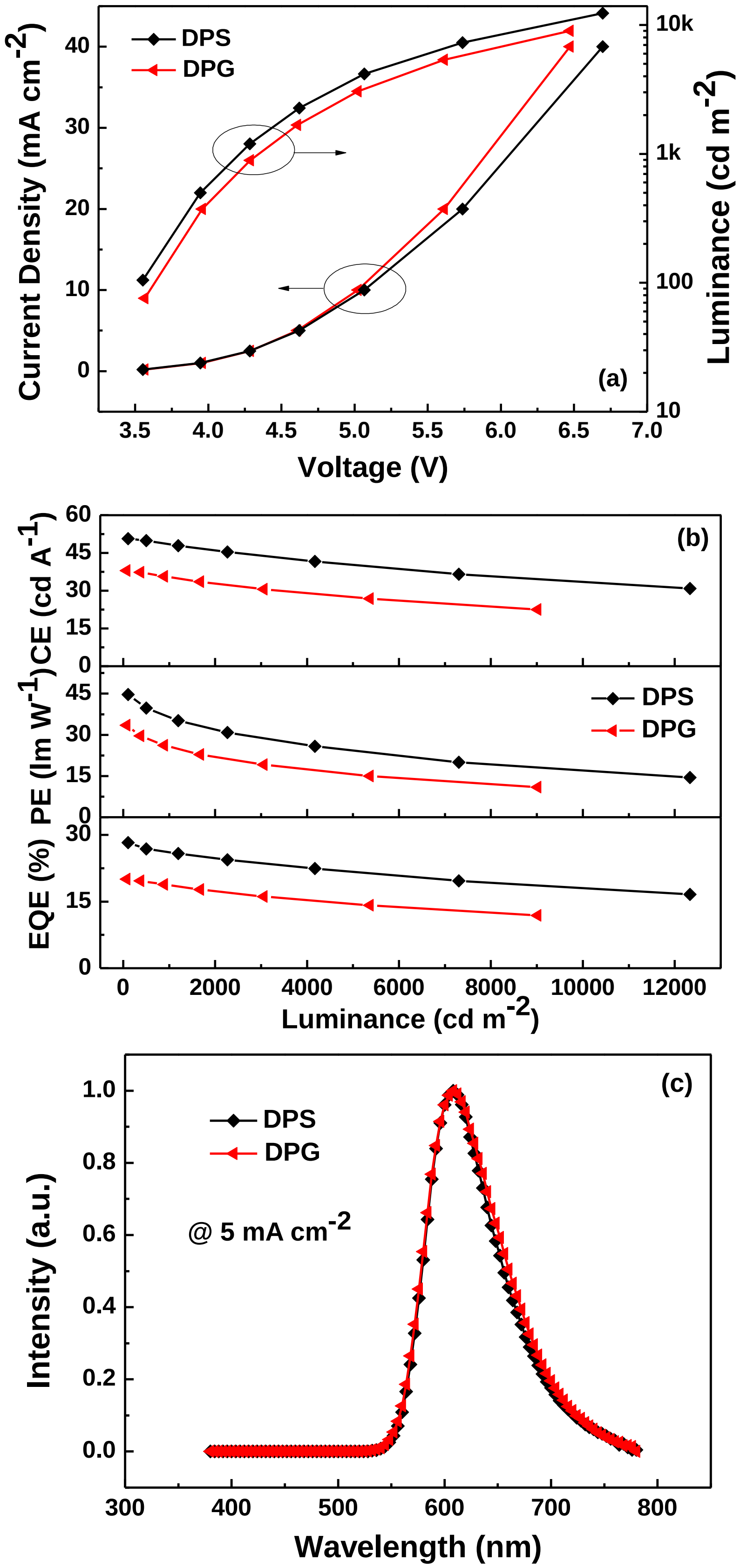


Fig. 5 (a) *J*–V–*L* characteristics, (b) CE–, PE– and EQE–*L* curves, and (c) EL spectra of red devices.

View Article Online
DOI: 10.1039/C8TC02851F

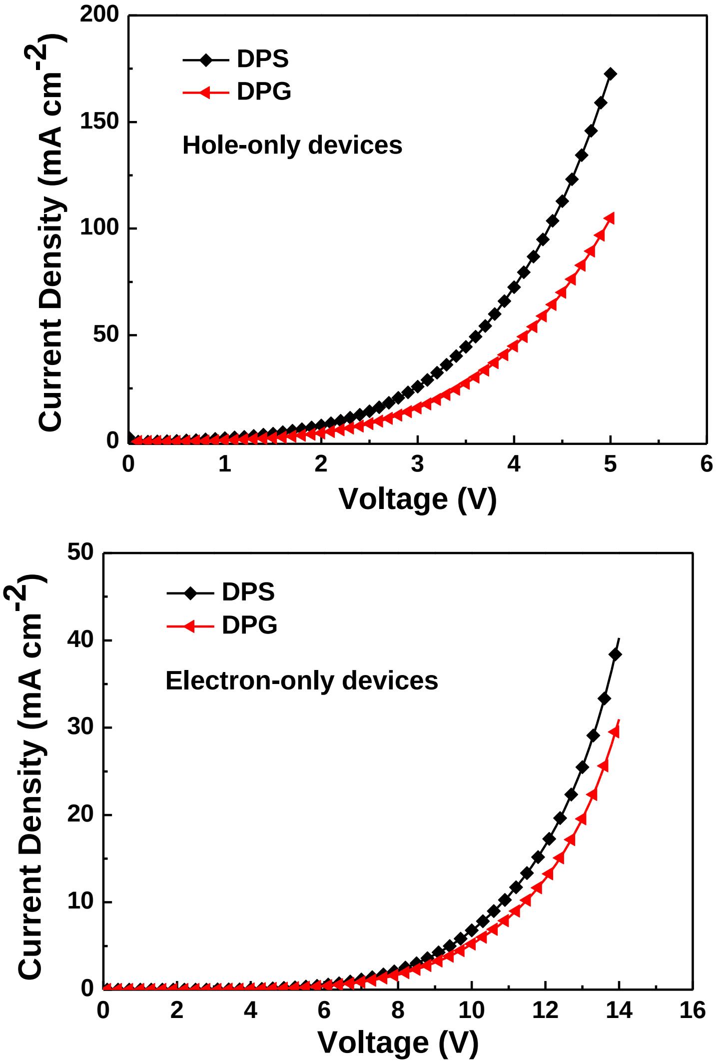


Fig. 6 *J*–V characteristics of hole- and electron-only devices. Device structures: hole-only: ITO/MoO_3 (10 nm)/**DPS** or **DPG** (100 nm)/MoO_3 (10 nm)/Al (100 nm); electron-only: ITO/TmPyPB (20 nm)/**DPS** or **DPG** (100 nm)/TmPyPB (20 nm)/Liq (2 nm)/Al (100 nm).

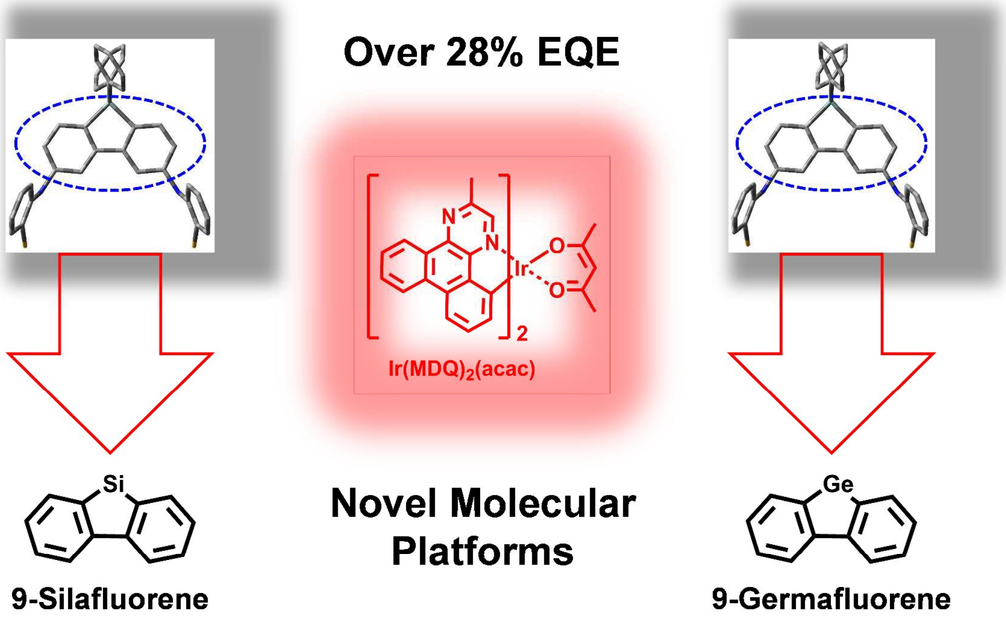
View Article Online
DOI: 10.1039/C8TC02851F

Table 2. Summary of electroluminescence performance for red PHOLEDs.

Host[a]	V[b]	□η_{CE}[c]	η_{PE}[c]	η_{ext}[c]	CIE[d]
	[V]	[cd A^{-1}]	[lm W^{-1}]	[%]	[x, y]
DPS	3.6	50.7, 48.6, 40.4	44.7, 36.4, 24.5	28.3, 26.1, 21.8	0.61, 0.39
DPG	3.7	38.0, 35.4, 27.5	33.5, 25.7, 15.8	20.0, 18.7, 14.6	0.62, 0.38

[a] Device configuration: ITO/HAT-CN (10 nm)/TAPC (55 nm)/TCTA (10 nm)/Host: 6 wt.% Ir(MDQ)$_2$(acac) (20 nm)/TmPyPB (35 nm)/Liq (2 nm)/Al (120 nm). [b] Voltages at 200 cd m^{-2}. [c] Efficiencies in the order of the maxima, at 1000 cd m^{-2} and at 5000 cd m^{-2}. [d] Commission Internationale de l'Eclairage measured at 5 mA cm^{-2}.

View Article Online
DOI: 10.1039/C8TC02851F



De novo molecular platforms have been applied to build host materials for high efficient PHOLEDs. 9-Silafluorene derivative was studied for the first time as hosts and the external quantum efficiency in red PHOLEDs over 28% was achieved successfully.