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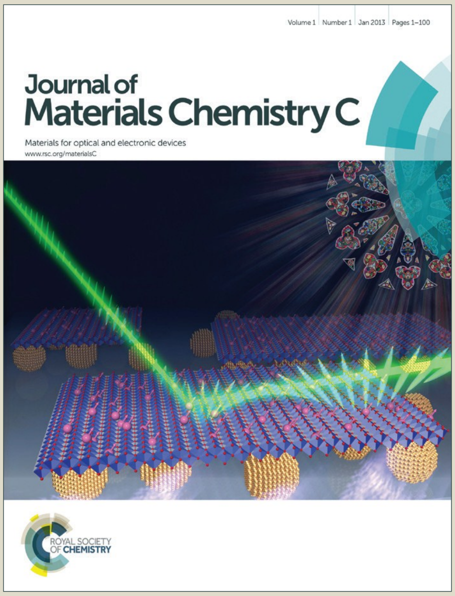

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Highly Selective Palladium-catalyzed Stille Coupling Reaction toward Chlorine-containing NIR Electroluminescence Polymers †

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High selectivity and yield from aryl-aryl coupling reactions between chlorine-containing aromatic bromides and organotin reagents are reported. The variable reaction selectivity between the bromine and chlorine mainly depends on the electronic effects of the aromatic substrates. The reactivity of the chlorine can be completely restrained by employing the optimized Palladium catalysts, which can be used for the preparation of the chlorine-bearing molecules. Then, a series of high molecular weight conjugated copolymers with chlorine on the backbones are straight forward synthesized under Stille condensation reaction. The chlorine-bearing polymers exhibit much lower LUMO, larger Stokes shift and lower self-absorption comparing with the non-chloride analogue, for the electron affinity and large steric hindrance of chlorine atoms. Efficient NIR emission centre at about 758 nm can be obtained based on the single layer system.

Introduction

Aromatic π-conjugated polymers (ACPs) are promising candidates for advanced functional materials and are expected to be applied in such organic devices as organic light-emitting diodes, organic field-effect transistors, organic photovoltaic cells, and chemical biosensors due to their semiconductive and optoelectronic properties.[1-8] The performance and lifetime of these devices are critically dependent on the materials development, device design, deposition processes, and modeling, among which materials play a crucial role. The unique properties of organic semiconductor are largely based on the versatility to synthesize multifunctional APCs by judicious molecular design. Tailoring the energy band gap of the APCs allows variation in emission wavelength, absorptive colors in electrochromic devices, and conductivity in the neutral state. Changes in energy levels also allow optimization of interfacial energy level alignment between the materials and electrode contacts in organic electronics.[9] The chlorine-containing polymers are interesting because of their tendency to achieve tunable optical and electrochemical properties through introduction of chlorine onto the backbones of the polymers.[10-11] But, there are still few reported chlorine-bearing APCs, because of the synthetic difficulties. To acquire chlorine-functionalized organic materials, a post-chlorine-functionalization method has been reported.[12-13] However, controlling the chlorine ratio and chlorine position during the post chlorine processing is extremely difficult and almost impossible. As such, the development of more efficient approaches for the preparation of chlorine-bearing molecules is highly desirable for these kinds of materials. The Stille coupling reaction between aromatic halides and organotin reagents is one of the most powerful methods to prepare organic conjugated molecules.[14-16] For the leaving halogen groups in such a reaction, the reactivity of the coupling partner decreases in the order of I > Br > Cl > F.[17-19] Among the halides, fluoride is much more stable and is not involved in the reaction, which is a significant advantage and has already been used for the construction of fluorine-containing APCs.[20-21] However, it is a challenge to prepare chlorine-containing aryl compounds by the Stille coupling reaction because the aromatic chloride tends to participate in the reaction,[22-23] resulting in poor selectivity with aromatic bromide or iodide, low yield for the target compound and cross-linking reactions for polymerization. In this context, the complete restraint for the reactivity of chlorine is the key process for the synthesis of chlorine-bearing molecules by Stille coupling reaction, especially for the polymers.

Herein, four chlorine-containing aromatic bromides with different electronic effects are chosen as the model substrates to investigate the influence of the different substrates properties on the coupling selectivity between bromine and chlorine. Then, four Pd complexes are used as the catalysts to optimize the coupling reaction conditions so as to completely suppress the coupling reactivity of chlorine. The quinoxaline unit is a well-known electron-deficient system that has found use as the acceptor to construct the donor-acceptor (D-A) conjugated polymers, especially for the light emitting polymers.[24-26] Therefore, finally, the chlorine-bearing D-A alternating quinoxaline-based copolymers are obtained by standard Stille condensation reaction using the optimized coupling reaction conditions. The influence of the chlorine on

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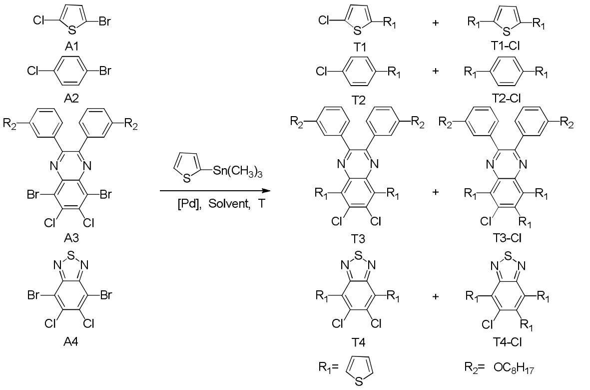


Scheme 1 Optimization for the coupling reactions.

the optical and electrochemical properties of the polymers are investigated and the PLEDs performances of the single layer devices are characterized.

Results and Discussion

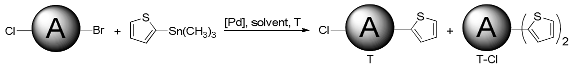
Optimization for the coupling reaction conditions

The optimized processes are shown in Scheme 1. 2-Bromo-5-chlorothiophene (A1), 1-bromo-4-chlorobenzene (A2), 5,8-dibromo-6,7-dichloro-2,3-bis(3-(octyloxy)phen-yl)-quinoxaline (A3), and 4,7-dibromo-5,6-dichlorobenzo[c][1,2,5]thiadiazole (A4) were chosen as the model reagents, which had a strong electron-donating ability, a weak electron-donating ability, a medium electron-withdrawing ability and a strong electron-withdrawing ability, respectively. Four widely used Pd complexes, $Pd(pph_3)_4$ (P-1), $Pd(pph_3)_4$/CuBr (P-2), $Pd_2(dba)_3$/P(o-tol)$_3$ (P-3) and Pd(dppf)Cl_2 (P-4) were investigated to prepare the target compounds T1, T2, T3 and T4. The ratios of the byproducts with one substitution of the chlorine atom, T1-Cl, T2-Cl, T3-Cl and T4-Cl were simultaneously monitored.

For the strong electron-donating compound A1, the Stille coupling reaction occurred chemoselectively at the aryl-bromine without the T1 byproduct, and a perfect yield (greater than 96%) was earned for all four catalysts (Table 1, entries 1-4). When the aromatic unit was a phenyl, which is a relatively weaker electron-donating group than thiophene, A2 provided a similar result to that of A1 when applying $Pd(pph_3)_4$/CuBr and Pd(dppf)Cl_2 as the catalysts (entries 6 and 8). However, the $Pd(pph_3)_4$ and $Pd_2(dba)_3$/P(o-tol)$_3$ catalysts showed different catalyzed couplings performances. The aryl C-Cl bond was involved in the reactions, leading to the existence of 5-6% T2-Cl. Therefore, the yields for the target product T2 were slightly lower than that of T1 (entries 5 and 7). Furthermore, the dibromo-/dichloro-substituents at the ortho/meta position on the above two aromatic substrates did not affect the efficiency of the process(Scheme S2, Table S1, Supporting Information). The Pd catalyzed couplings of aryl C-Cl bonds did not occur for the thiophene substrate. A similar result was found for the $Pd(pph_3)_4$/CuBr and Pd(dppf)Cl_2 catalyzed Stille coupling reaction of the phenyl system, and the couplings of the chlorine were less than 10% when $Pd(pph_3)_4$ and $Pd_2(dba)_3$/P(o-tol)$_3$ were used. In summary, the Stille couplings could undergo smoothly occur for the aromatic bromides on electron-releasing parent structures to afford the chlorine-containing biarlys in high yields.

When the coupling reactions occurred on the electron deficient aromatic quinoxaline, the optimized yields of the target molecule T3 and the byproduct T3-Cl were 33% and 13%, respectively, when $Pd(pph_3)_4$ was utilized as the catalyst, as shown in Table 2. The rest parts were aromatic substrate A3(45%) and the brominated compound T3-T(5%, Scheme S1,

Table 1 Optimization of the Stille coupling reaction conditions[a] for A1 and A2.



Entry	Substrate	Cat.	Solvent[b]	T (°C)	Time (h)	Yield(%)[c,d] T	T-Cl
1	A1	P-1	Toluene	120	24	>96	none
2		P-2	Toluene	120	2	>96	none
3		P-3	THF	80	2	>96	none
4		P-4	THF	80	2	>96	none
5	A2	P-1	Toluene	120	24	91	6
6		P-2	Toluene	120	4	>96	none
7		P-3	THF	80	2	90	5
8		P-4	THF	80	2	>96	none

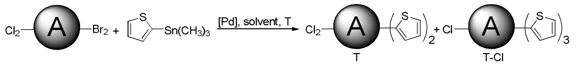
[a] Reaction conditions: unless otherwise noted, all of the reactions were performed with A (100 mg), trimethyltinthiophene (1.5 equiv for A), and the Pd catalyst loading was 8mol%, $Pd(pph_3)_4$/CuBr (1/2), $Pd_2(dba)_3$/P(o-tol)$_3$ (1/4).

[b] Toluene and THF were distilled from Na and benzophenone under nitrogen immediately prior to use.

[c] The Reactions were performed in a sealed tube.

[d] Isolated yield.

Table 2 Optimization of the Stille coupling reaction conditions[a] for A3 and A4.



Entry	Substrate	Cat.	Solvent[b]	T (°C)	Time (h)	Yield(%)[c,d] T	T-Cl
1	A3	P-1	Toluene	120	48	33	13
2		P-2	Toluene	120	4	67	30
3		P-3	THF	80	2	>96	none
4		P-4	THF	80	2	88	10
5	A4	P-1	Toluene	120	48	22	11
6		P-2	Toluene	120	4	35	61
7		P-3	THF	80	4	65	12
8		P-4	THF	80	2	85	12

[a] Reaction conditions: unless otherwise noted, all of the reactions were performed with A (100 mg), trimethyltinthiophene (3.0 equiv for A), and the Pd catalyst loading was 8mol%, $Pd(pph_3)_4$/CuBr (1/2), $Pd_2(dba)_3$/P(o-tol)$_3$ (1/4).

[b] Toluene and THF were distilled from Na and benzophenone under nitrogen immediately prior to use.

[c] The Reactions were performed in a sealed tube.

[d] Isolated yield.

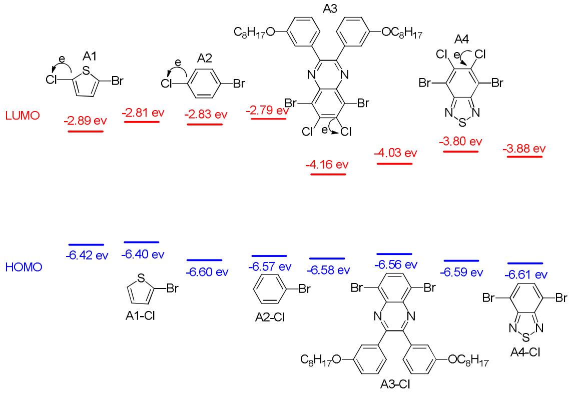


Fig. 1 Electrochemical parameters for the aromatic rings.

Supporting Information). The Pd(pph$_3$)$_4$ catalyst showed poor reactivity for both bromide and chloride, as well as very low selectively between these two halides. The Pd(pph$_3$)$_4$/CuBr catalyst provided increased yields of the product and byproduct (67% and 30%, respectively), indicating a much improved reactivity for both aryl bromine and aryl chlorine compared with the Pd(pph$_3$)$_4$ catalyst. However, the selectivity between bromine and chlorine was still very low. When Pd(dppf)Cl$_2$ was used as the catalyst, the yield of T3 increased to 88% with 10% of the byproduct T3-Cl, meaning that Pd(dppf)Cl$_2$ could maintain the high reactivity of the bromine atom and partly suppress the reactivity of the chlorine atom. Although the Pd(dppf)Cl$_2$ showed much better selectively than the above two catalysts, the resulting yield of the product was still not enough, especially for polymerization because the existence of T3-Cl will lead to cross-linking reactions. The Pd$_2$(dba)$_3$/P(o-tol)$_3$ catalyst exhibited the best performance with a yield of over 96%, and there was no T3-Cl found, which showed that the catalyst could completely restrain the reactivity of the chlorine. The corresponding polymers were synthesized using this catalytic system(Scheme 2).

For the strong electron-poor A4, in which the aromatic group is benzo[c][1,2,5]thiadiazole, the selectivity of the Stille coupling reactions was not as good as A3 and T4-Cl always formed. The yield ratios of T4 and T4-Cl were 22% and 11%, respectively, when Pd(pph$_3$)$_4$ was used as the catalyst (Table 2, entry 5). The rest parts were aromatic substrate A4(59%) and the brominated compound T4-T(4%, Scheme S1, Supporting Information). To optimize the reaction, Pd(pph$_3$)$_4$/CuBr, Pd$_2$(dba)$_3$/P(o-tol)$_3$ and Pd(dppf)Cl$_2$ were also applied as catalysts, and the yield of T4 could be increased stepwise to 85% (entries 6-8). However, the yield of the byproduct was 12%, indicating that the reactive difference between aryl chloride and aryl bromide was smaller than that of A3 with the altered electronic-withdrawing effects.

Density functional theory (DFT) calculations and cyclic voltammetry (CV) measurements of the four starting materials were performed to understand the influence of the electronic effects of the aromatic substrates on the Stille coupling reaction selectivity between aryl-chlorine and aryl-bromine. Four reference compounds without chlorine were also characterized. The electronic densities of the HOMOs and LUMOs were distributed on the entire molecules except for A3 and A3-Cl, in which the LUMOs were distributed on the quinoxaline unit and the HOMOs were distributed on the phenoxyl unit (Figure S1, Supporting Information). According to the CV results (Fig. 1), the E_{LUMO} and E_{HOMO} of A1 were below that of A1-Cl, indicating that the chlorine atom had an electron-withdrawing ability.[27-28] The same results were found for A2 and A3. However, a contrary result was found for A4, in which the chlorine atoms possessed an electron-donating ability,[29-30] leading to a higher E_{LUMO} and E_{HOMO} than that of A4-Cl. In light of these results, from A1 to A4, the coupling reactivity of chloride was improved as the electron-withdrawing ability increased in the aryl rings,[31-32] and the coupling reactivity of bromide was suppressed as the electron-donating ability increased in the chlorine atom.[33] Then, the reaction selectivity between the two halides decreased.

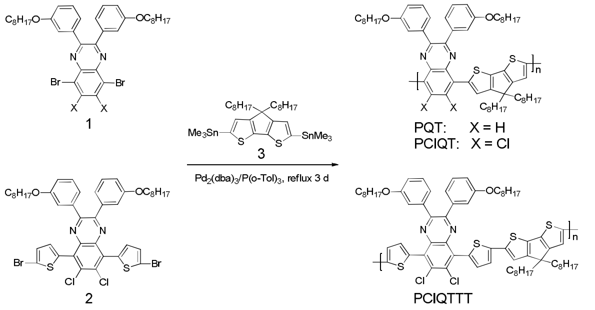
Synthesis and Characterization for the chlorine-containing polymers

Synthesis

As shown in Scheme 2, the polymerization of 5,8-dibromo-6,7-dichloro(or dihydro)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (1) and 5,8-bis(5-bromothiophen-2-yl)-6,7-dichloro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (2) with 3 via Stille condensation reaction with Pd$_2$(dba)$_3$/P(o-Tol)$_3$ as catalyst resulted in the polymers PQT, PClQT and PClQTTT, respectively. All polymers exhibited high molecular weights with Mn = 68500 for PQT, Mn = 35100 for PClQT and Mn = 36600 for PClQTTT. High molecular weights proved to be favorable to achieve better performance of the resulting PLEDs.[34-35]

Calculation

The geometries and electron density distributions of the HOMO and LUMO energy levels of the polymers were obtained by simulation using density functional theory (DFT) when taking one repeat unit with trunked alkyl chains as models, as shown in Fig. 2. The dihedral angle between quinoxaline ring and thiophene of PClQT and PClQTTT were 52.4^o and 50.6^o, respectively, which were much larger than that of control sample PQT, indicating that the planarity along the polymer backbone was reduced because of steric-hindrance effects of the chlorine atoms. Additionally, it's worth to note that the electron density distributions of LUMO levels of the chlorine-bearing polymers were more localized compared with that of PQT.



Scheme 2 Synthesis of the polymers.

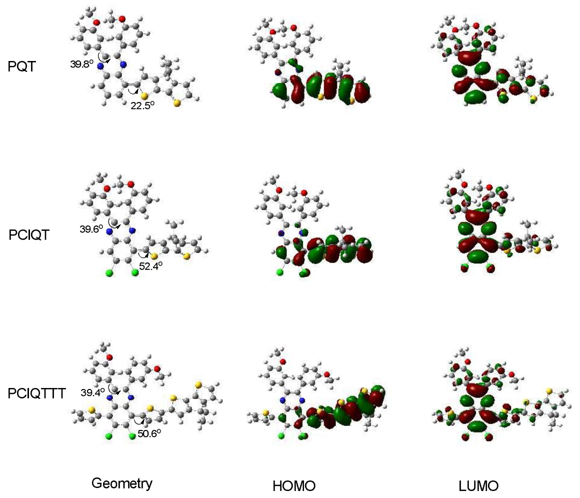


Fig. 2 Geometry and frontier molecular orbitals for model compounds of PQT, PClQT and PClQTTT.

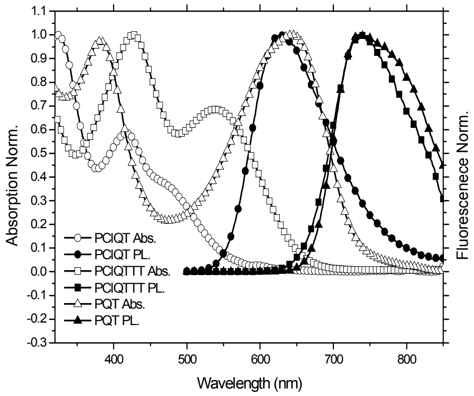


Fig. 3 Normalized absorption and fluorescence spectra of PQT, PClQT and PClQTTT in film.

Table 3 Optical properties and energy levels of the polymers.

	PQT	PClQT	PClQTTT
λ_{abs} (nm)	644	470[a]	533
λ_{emi} (nm)	735	627	738
Stokes shift (nm)	91	157	205
HOMO[b] (eV)	-5.36	-5.50	-5.12
LUMO[b] (eV)	-3.11	-3.44	-3.41
HOMO[c] (eV)	-5.85	-5.91	-5.56
LUMO[c] (eV)	-3.35	-3.66	-3.62
E_g[d] (eV)	2.25	2.06	1.71

[a] Shoulder peak.

[b] From the onset of the first reduction or oxidation waves in CV.

[c] From the DFT calculation.

[d] Band gap from CV(E_{LUMO} - E_{HOMO}).

Absorption and fluorescence

The UV-Vis absorption spectra of the polymers in thin film are plotted in Fig. 3. The peaks within the range of 300 nm-400 nm could be assigned to π-π* transition and the absorption in low energy region was originated from its intramolecular charge transfer.[36] For PClQT, the shoulder peak around 470 nm was assigned to week charge transfer absorption with 174 nm blue shift compared with that of PQT. This dramatic blue shift was induced by the steric hindrance of chlorine atoms which reduced the planarity along the polymer backbone and led to ineffective conjugation, as the results of simulation confirmed. When thiophene units were introduced onto the backbone of PClQT, the charge-transfer absorption peak was red-shifted to 533 nm, meaning that the introduction of the thiophene units could extend the π-conjugation and facilitate intramolecular charge transfer in this twisted conjugated system.[10-11]

Fig. 3 shows fluorescence spectra of the polymers in thin film. Compared with PQT's NIR emission, PClQT exhibited an red spectrum with blue shifts of 108 nm for twisted backbone and weakened intramolecular charge transfer. When thiophene units were adopted in the backbone, the fluorescence peak of the resulting polymer PClQTTT showed large red shifts about 111 nm compared with that of PClQT, which showed more effective intrachain charge-transfer in PClQTTT comparing with the PClQT. Moreover, large Stokes shifts (Table 3) and low self-absorption were realized in PClQT and PClQTTT films. This is caused by steric hindrance of chlorines which hinder the formation of semiquinoid geometry and decrease the order of the thin films.[37] These optical properties indicate that the chlorine-containing polymers are promising light-emitting materials.

Cyclic voltammagram

The redox properties of the polymers were measured in acetonitrile/Bu_4NPF_6 solutions (Table 3). The chlorine-bearing polymers exhibited deeper LUMO level comparing with that of PQT because the chlorine atoms caused more localized LUMO electron density distribution, as shown in Fig. 2. The LUMO level almost remained the same when thiophene units were introduced onto the backbone of the polymer, while the HOMO raised to -5.12 eV which well match the work function of the hole transport layer PEDOT:PSS. The HOMO and LUMO levels of the polymers which obtained from DFT calculation were also listed in Table 3, and the change trend of the energy levels was consistent with that of the energy levels which obtained from CV measurement. This indicates that very narrow bandgap conjugated polymers are available when strong donor moieties are used to copolymerize with the quinoxaline unit as the acceptor moiety.

Electroluminescent properties

The light emitting devices were fabricated with a structure of ITO/PEDOT:PSS/polymer/Ca/Al using a single luminescent layer. Only part of the light from the devices could be calculated for the two materials because of the maximum wavelength of the electroluminescence detector was 780nm. The electroluminescence (EL) peak of PClQTTT showed red shift emission and obviously broadened spectrum than its photoluminescence (PL), which could be attribute to the

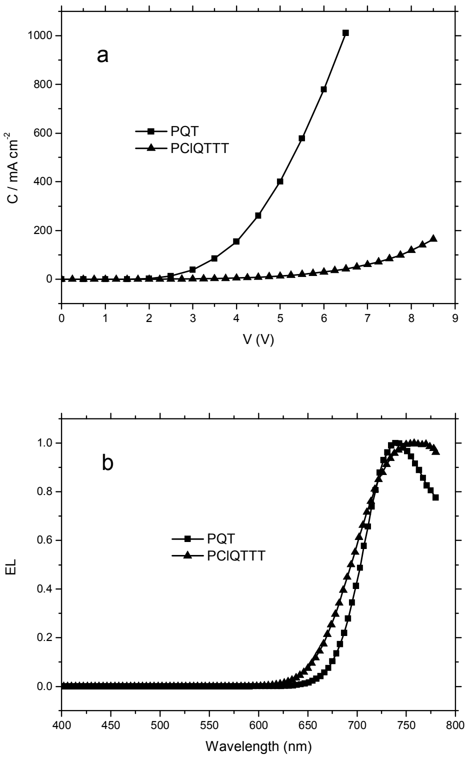


Fig. 4 (a) Current density-voltage (J-V) characteristics of PQT and PClQTTT based single layer PLEDs and (b) the normalized EL spectra of PQT and PClQTTT based single layer PLEDs drove by 0.5 mA current with device structure as ITO/PEDOT:PSS (40 nm)/polymers/Ca (20 nm)/Al (120 nm), measured by Edinburg PLS 920.

Table 4 Electroluminescence properties of the polymers.

	V_{on} (V)[a]	Brightness (cd/m^2)	λ_{max} (nm)[b]	QE (%)[c]
PQT	2.8	78	739	0.34
PClQTTT	3.0	112	758	0.38

[a] Turn-on voltage at the brightness of 1.0 cd/m^2.

[b] At the maximum brightness.

[c] Maximum external quantum efficiency.

intermolecular stacking.[11] Non-doped PLEDs of PQT and PClQTTT exhibited a maximum brightness of 78 and 112 cd m^{-2} with emitting peaks at 739 and 758 nm, respectively. Obviously, the chlorine-bearing polymer PClQTTT exhibited better spectrum for NIR application with brighter emission and higher efficiency when consider that more NIR light was cut off for the PLEDs from PClQTTT. And the real brightness and external quantum efficiency of PClQTTT should be much higher than those listed in Table 4. The above results indicated that the chlorine-containing polymers were competitive candidates for efficient NIR light-emitting materials. Further optimizations are in process to optimize the devices performances.

Conclusions

In conclusion, the reactivities of aryl bromine and aryl chlorine on the same substrates exhibited various tendencies for the Stille coupling reaction when the electron properties of the substrates were changed. For the strong electron-rich aromatic system, the coupling reaction occurred chemoselectively at the aryl bromine. For the weak electron-rich and electron-deficient systems, the aryl chlorine was involved in the coupling reaction to some extent, but which could be completely restrained by utilizing the optimized reaction conditions. Then, the conjugated high molecular weight polymers bearing chlorine atoms on the backbone were obtained using the optimized Stille couplings, indicating that the highly selective Stille coupling reaction could become an efficient method for the synthesis of the chlorine-containing molecules. These chlorine-bearing copolymers exhibited deep LUMO level because chlorine atoms caused more localized electron density distribution on the acceptor unit. And the HOMO level of the materials could be finely tuned by using different donor moieties to realize narrow bandgap and NIR fluorescence. Additionally, the chlorine atoms caused twisted backbone and large Stokes shift about 200 nm. Finally, efficient NIR emissions centre at about 758 nm were obtained based on the simple single layer devices using PClQTTT as emitter, indicating that the chlorine-bearing conjugated polymers were competitive candidates for efficient NIR light-emitting materials.

Acknowledgements

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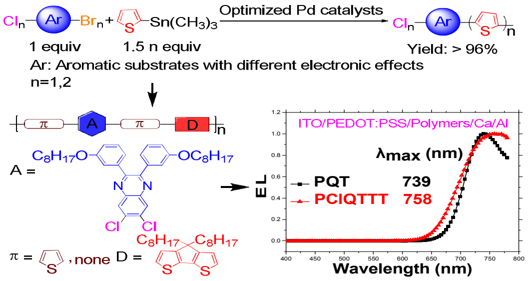

Chlorine-containing conjugated polymers were obtained by optimized Stille couplings, none-doped PLEDs of the polymers exhibited NIR emission.