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Supporting Information

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

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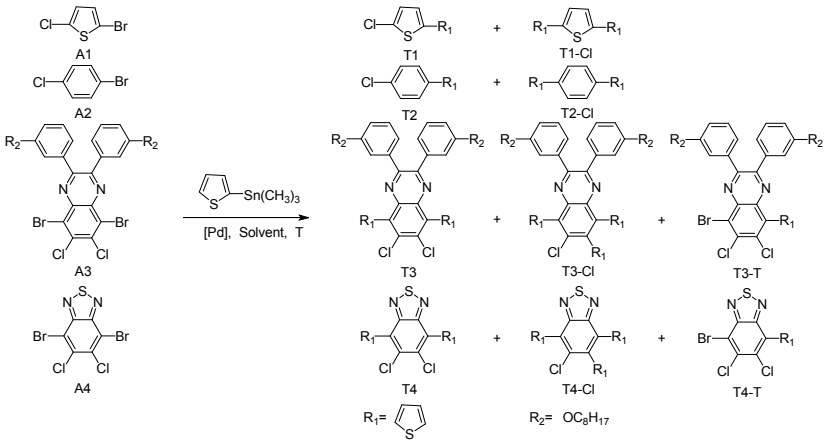
1. Synthetic Procedures and Characterizations

1.1 General Methods

Chemicals were used as received unless otherwise indicated. All reactions were performed under nitrogen atmosphere. Reaction solvents were distilled from Na and benzophenone under nitrogen immediately prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 MHz spectrometer using $CDCl_3$ as the solvent and chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane standard. Fourier transform mass spectra (FTMS) were recorded on a Bruker Apex Fourier transformation mass spectrometer. All GC analyses were performed on a GC9160 Gas-Chromatograph. The capillary column used was SE-54 (Length: 30 m, Column ID: 0.25 mm, Film Thickness: 0.25 um).

1.2 General Procedures

1.2.1 Optimization for the Stille coupling reaction conditions



Scheme S1 Optimization for the coupling reactions.

The aryl halides were dissolved in toluene and palladium catalyst was added then trimethyl-2-thienyl-stannane was added. The reaction mixture was stirred at 120°C and monitored by GC and TLC analysis. Then the solution was dropped by water and

the organic layer was washed successively by water and dried over anhydrous $MgSO_4$. Then the solvent was evaporated. Coupling products were isolated by column chromatography on silica gel.

5-chloro-2,2'-bithiophene (T1)

The crude product was purified by column chromatography using petroleum ether to obtain T1 as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (dd, 1H), 7.13 (dd, 1H), 7.03 (dd, 1H), 6.96 (d, 1H), 6.85 (d, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.6, 136.2, 128.7, 127.9, 126.9, 124.8, 124.0, 122.9. FTMS (APCI): found m/z =199.95331; Calc. for $C_8H_5ClS_2$: 199.95.

2-(4-chlorophenyl)-thiophene (T2)

The crude product was purified by column chromatography using petroleum ether to obtain T2 as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, 2H), 7.37 (d, 2H), 7.32 (dd, 2H), 7.10 (t, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.1, 133.2, 133.0, 129.1, 128.1, 126.9, 125.0, 123.5. FTMS (APCI): found m/z =194.00473; Calc. for $C_{10}H_7ClS$: 194.00.

2,2'-(1,4-phenylene)bis-thiophene (T2-Cl)

The crude product was purified by column chromatography using petroleum ether to obtain T2-Cl as a white solide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (s, 4H), 7.37 (d, 2H), 7.32 (t, 2H), 7.12 (dd, 2H). ^{13}C NMR (150 MHz, $CDCl_3$):δ 144.0, 133.5, 128.1, 126.3, 124.9, 123.1. FTMS (APCI): found m/z =242.02171; Calc. for $C_{14}H_{10}S_2$: 242.02.

6,7-dichloro-2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophene-2-yl)quinoxaline (T3)

The crude product was purified by column chromatography using petroleum ether/dichloromethane (10/1, V/V) to obtain T3 as a yellow solide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, 2H), 7.50 (t, 2H), 7.25 (dd, 2H), 7.23 (s, 2H), 7.15 (t, 2H), 7.07 (d, 2H), 6.89 (dd, 2H), 3.83 (t, 4H), 1.71 (m, 4H), 1.42 (m, 4H), 1.31 (m, 16H), 0.90 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0, 156.4, 151.2, 140.0, 138.5, 137.6, 136.5, 131.8, 130.7, 129.6, 128.3, 122.9, 116.6, 115.3, 68.1, 32.0, 30.2, 29.8, 29.4, 25.6, 22.8, 14.3. FTMS (APCI): found m/z =770.25276; Calc. for $C_{44}H_{48}Cl_2N_2O_2S_2$: 770.25.

6-chloro-2,3-bis(3-(octyloxy)phenyl)-5,7,8-tri(thiophene-2-yl)quinoxaline (T3-Cl)

The crude product was purified by column chromatography using petroleum ether/dichloromethane (8/1, V/V) to obtain T3-Cl as an orange solide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, 1H), 7.50 (d, 1H), 7.43 (t, 2H), 7.25 (t, 3H), 7.16 (t, 2H), 7.10 (t, 4H), 7.06 (d, 1H), 6.98 (t, 1H), 6.89 (t, 2H), 3.84 (t, 4H), 1.72 (m, 4H), 1.32 (m, 20H), 0.90 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0, 156.8, 156.4, 152.2, 151.7, 140.3, 139.7, 139.3, 138.9, 137.6, 136.4, 131.8, 130.7, 129.8, 129.1, 122.5, 116.8, 115.3, 68.1, 32.0, 30.3, 29.7, 29.4, 26.0, 22.7, 14.2. FTMS (APCI): found m/z =818.27769; Calc. for $C_{48}H_{51}ClN_2O_2S_3$: 818.28.

5-bromo-6,7-dichloro-2,3-bis(3-(octyloxy)phenyl)-8-(thiophene-2-yl)quinoxaline (T3-T)

The crude product was purified by column chromatography using petroleum ether/dichloromethane (10/1, V/V) to obtain T3-T as a yellow solide. ^{1}H NMR (600

MHz, $CDCl_3$): δ 7.65 (d, 1H), 7.48 (t, 1H), 7.31 (dd, 2H), 7.28 (d, 1H), 7.19 (t, 2H), 7.11 (d, 2H), 6.93 (dd, 2H), 3.85 (t, 4H), 1.73 (m, 4H), 1.40 (m, 4H), 1.29 (m, 16H), 0.91 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 156.9, 151.0, 149.5, 142.6, 141.5, 140.0, 138.6, 135.6, 131.3, 129.9, 129.2, 128.5, 122.9, 119.2, 116.3, 115.6, 68.7, 32.1, 30.1, 29.6, 29.1, 25.5, 22.7, 14.1. FTMS (APCI): found m/z =768.16851; Calc. for $C_{40}H_{45}BrCl_2N_2O_2S$: 768.17.

5,6-dichloro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (T4)

The crude product was purified by column chromatography using petroleum ether/dichloromethane (5/1, V/V) to obtain T4 as a yellow solide. ^1H NMR (600 MHz, $CDCl_3$): δ 7.69 (t, 2H), 7.66 (d, 2H), 7.30 (d, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.7, 146.3, 137.0, 131.3, 128.3, 126.9, 122.1. FTMS (APCI): found m/z =367.91108; Calc. for $C_{14}H_6Cl_2N_2S_3$: 367.91.

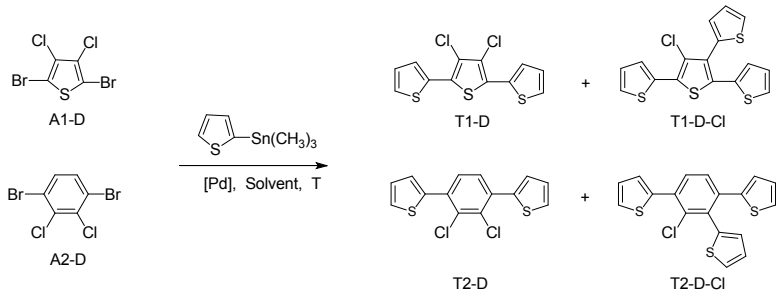
5-chloro-4,6,7-tri(thiophen-2-yl)benzo[c][1,2,5]thiadiazole(T4-Cl)

The crude product was purified by column chromatography using petroleum ether/dichloromethane (3/1, V/V) to obtain T4-Cl as an orange solid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.66 (dd, 1H), 7.63 (d, 1H), 7.48 (m, 2H), 7.43 (t, 1H), 7.28 (d, 1H), 7.12 (m, 1H), 7.10 (t, 1H), 7.07 (dd, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.3, 154.2, 146.3, 137.8, 131.1, 130.7, 130.3, 128.0, 126.9, 122.4. FTMS (APCI): found m/z =415.93120; Calc. for $C_{18}H_9ClN_2S_4$: 415.93.

4-bromo-5,6-dichloro-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (T4-T)

The crude product was purified by column chromatography using petroleum ether/dichloromethane (5/1, V/V) to obtain T4-T as a yellow solide. ^1H NMR (600

MHz, $CDCl_3$): δ 7.71 (t, 1H), 7.68 (d, 1H), 7.32 (d, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.5, 152.9, 144.5, 143.7, 138.2, 131.3, 128.6, 128.1, 127.6, 121.9. FTMS (APCI): found m/z =365.83047; Calc. for $C_{10}H_3BrCl_2N_2S_2$: 365.83.



Scheme S2 Optimization for the coupling reactions of A1-D and A2-D.

3',4'-dichloro-2,2':5',2''-terthiophene(T1-D)

The crude product was purified by column chromatography using petroleum ether to obtain T1-D as a yellow solid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.19 (dd, 2H), 7.15 (dd, 2H), 6.99 (t, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.1, 135.2, 127.9, 124.5, 124.3, 123.7. FTMS (APCI): found m/z =315.90112; Calc. for $C_{12}H_6Cl_2S_3$: 315.90.

2,2'-(2,3-dichloro-1,4-phenylene)dithiophene(T2-D)

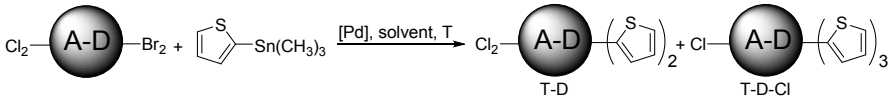
The crude product was purified by column chromatography using petroleum ether to obtain T2-D as a white solide. ^1H NMR (600 MHz, $CDCl_3$): δ 7.60 (dd, 2H), 7.29 (d, 2H), 7.22 (t, 2H), 7.08 (dd, 2H). ^{13}C NMR (150 MHz, $CDCl_3$):δ 140.2, 139.5, 130.2, 128.4, 128.1, 127.2, 125.9. FTMS (APCI): found m/z =309.94072; Calc. for $C_{14}H_8Cl_2S_2$: 309.94.

2,2',2''-(3-chlorobenzene-1,2,4-triyl)trithiophene(T2-D-Cl)

The crude product was purified by column chromatography using petroleum ether to obtain T2-D-Cl as a light blue solide. ^1H NMR (600 MHz, $CDCl_3$): δ 7.80-7.71 (m,

5H), 7.26 (dd, 3H), 7.13 (t, 3H). ^{13}C NMR (150 MHz, $CDCl_3$):δ 140.6, 138.1, 137.2, 136.6, 135.7, 131.5, 129.4, 128.4, 128.1, 127.3, 126.1. FTMS (APCI): found m/z =357.97322; Calc. for $C_{18}H_{11}ClS_3$: 357.97.

Table S1 Optimization of the Stille coupling reaction conditions [a] for A1-D and A2-D.



Entry	Substrate	Cat.	Solvent [b]	T (°C)	Time (h)	Yield (%)[c, d]	
						T-D	T-D-Cl
1	A1-D	P-1	Toluene	120	16	>96	none
2		P-2	Toluene	120	12	>96	none
3		P-3	THF	80	2	>96	none
4		P-4	THF	80	2	>96	none
5	A2-D	P-1	Toluene	120	24	90	8
6		P-2	Toluene	120	16	>96	none
7		P-3	THF	80	2	90	7
8		P-4	THF	80	2	>96	none

[a] Reaction conditions: unless otherwise noted, all reactions were performed with A-D (100mg), 2-(9,9-dioctyl-9-*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 equiv for A-D), the [Pd] catalyst loading was 8mol%, $Pd(pph_3)_4$/CuBr(1/2), $Pd_2(dba)_3$/$P(o\text{-}tol)_3$(1/4). [b] Toluene was distilled from Na and benzophenone under nitrogen immediately prior to use. [c] Reactions were carried out in a sealed tube. [d] Isolated yield.

1.2.2 Synthesis of the chlorine-containing polymers

In a 50 mL dry flask, 0.5 mmol 5,8-dibromo-6,7-dichloro-2,3-bis(3-(octyloxy)-

phenyl)quinoxaline or 5,8-bis(5-bromothiophen-2-yl)-6,7-dichloro-2,3-bis(3-(octyloxy)phenyl)quinoxaline, 0.55 mmol (4,4-dioctyl-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(trimethylstannane), $Pd_2(dba)_3$ (15mg) and $P(o\text{-}Tol)_3$ (25mg) were dissolved in degassed toluene (5 mL). The mixture was vigorously stirred at 100 °C for 3 d under nitrogen. After cooling down, the solution was diluted by 100 mL toluene and then was mixed with a solution of sodium diethyldithiocarbamate trihydrate (5 g) in distilled water (100 mL). The mixture was stirred at 80 °C overnight under nitrogen. The organic phase was separated and washed three times with water. Then it was poured into 400 mL of methanol. The precipitate was collected by thimble and Soxhlet-extracted with methanol, acetone, hexane, ethyl acetate, dichloromethane, and chloroform in order. The final fraction was precipitated in methanol. Finally, the polymer was collected by filtration and dried under vacuum at 40 °C overnight.

PQT：The yield is 80.1%. Mn = 68.5 k，PDI = 3.59。^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (b, 2H), 7.30-7.12 (b, 8H), 6.81 (b, 2H), 3.70 (b, 4H), 1.56 (b, 8H), 1.17 (b, 44H), 0.83 (b, 12H).

PClQT：The yield is 91.5%。Mn = 35.1 k，PDI = 1.65。^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (b, 2H), 7.31 (b, 2H), 7.19-7.08 (m, 4H), 6.79 (d, 2H), 3.62 (b, 4H), 1.56 (b 8H), 1.20 (b, 44H), 0.80 (t, 12H)。

PClQTTT：The yield is 52.2%. Mn = 36.6 k，PDI = 1.88。^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (b, 2H), 7.45 (b, 2H), 7.35 (b, 2H), 7.25 (b, 2H), 7.19 (b, 2H), 7.06 (b, 2H), 6.80 (b, 2H), 3.60 (b, 4H), 2.2-1.0 (b, 52H), 0.88 (b, 12H).

2. DFT Calculations

The Density Functional Theory (DFT) using B_3LYP hybrid functional with a basis set limited to 6-31g (d, p). Molecular orbital shapes and energies were obtained at optimized geometries.

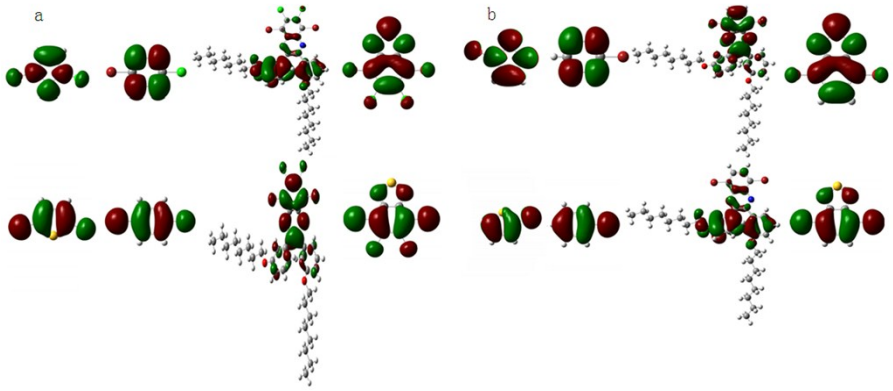


Figure S1. (a) DFT calculated LUMO (top) and HOMO (bottom) of A1-4 (from left to right). (b) DFT calculated LUMO (top) and HOMO (bottom) of A1-4 (Cl) (from left to right).

3. Electrochemical Characterizations

Cyclic voltammetry was performed using BASI Epsilon workstation and the measurements were carried out in dichloromethane containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum sheet as a counter electrode. All potentials were recorded versus Ag/AgCl as a reference electrode, and ferrocene/ferrocenium as an external reference. CH_2Cl_2 was freshly distilled over CaH_2 prior to use. The redox potential of Fc/Fc^+ is assumed to be -4.8eV below the vacuum level. The LUMO and HOMO levels were estimated from the onset potentials of the first reduction and oxidation waves in CV, respectively. The onset potential of oxidation peak of Fc^+/Fc was measured to be 0.06 V against Ag/AgCl.

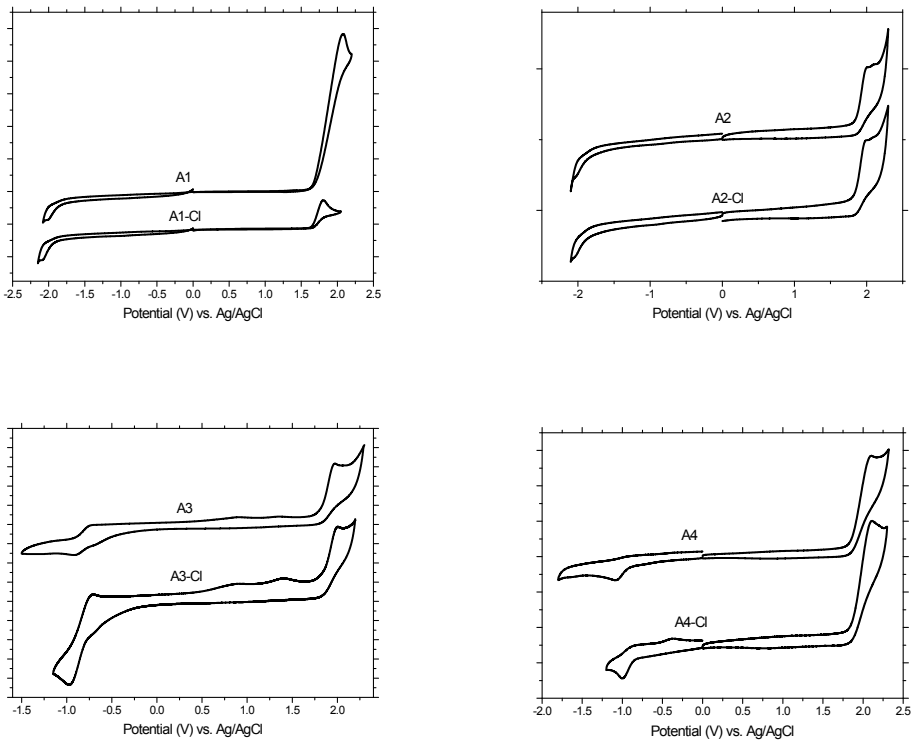


Figure S2 CV figures of the aromatic substrates, A1-4 and A1-4(Cl).

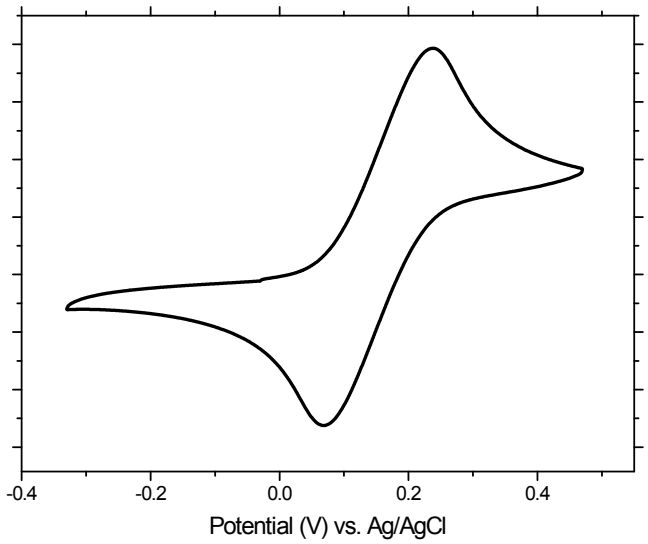


Figure S3 CV figure of the ferrocene.

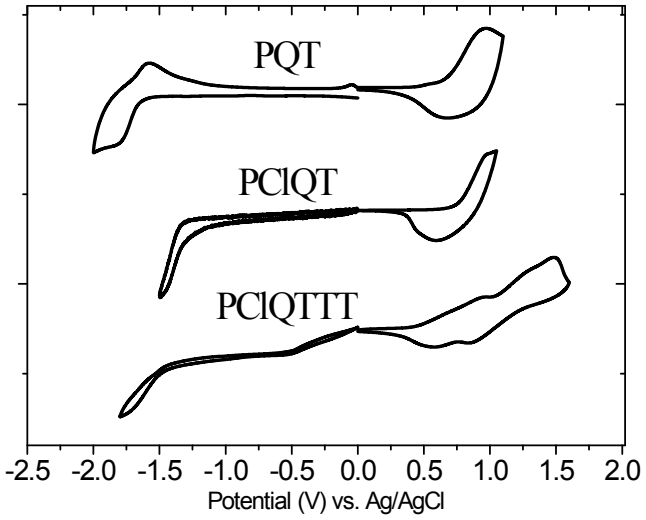


Figure S4 CV figures of the polymers.

Table S2 Electrochemical parameters of the polymers.

	PQT	PClQT	PClQTTT
Eonset ox (V)	0.62	0.76	0.38
Eonset red (V)	-1.63	-1.30	-1.33