Synthesis, Optical and Electrochemical Properties of High-quality Cross-conjugated Aromatic Polyketones

In this chapter, we report the synthesis and characterization of three new aromatic polyketones with repeating units based on 2,2’-(2,5-dihexyl-1,4-phenylene) dithiophene (PTK), 2,2’-(9,9-dihexyl-9H-fluorene-2,7-diyl)dithiophene (PFTK), and 4,7-bis(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (PBTK). These polymers were obtained with a one-pot Suzuki-Miyaura cross-coupling promoted homopolymerization, which offered good chemical integrity. Experimental as well as theoretical calculation studies were applied to investigate the optical and electrical properties of these polymers. These new aromatic polyketones possess excellent thermal stability. Especially, they exhibited tunable opto-electronic properties when exposed to acidic conditions.

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2. Synthesis, Optical and Electrochemical Properties of High-quality Cross-conjugated Aromatic Polyketones

2.1. Introduction

Aromatic polyketones, where the backbones are composed of arylene and ketonic carbonyl unit, are well-known as high-performance polymers with excellent chemical-physical properties and remarkable thermal stability.[1] These materials have exhibited potential applications as super-engineering plastics.[1–3] Besides that, aromatic polyketones have shown promise as electro-active materials as n-type optoelectronic semiconductor.[4, 5] Furthermore, our previous contributions demonstrated that cross-conjugated aromatic polyketones could be used as the precursor to developing new linear conjugated polymers by the addition of nucleophiles. These polymers are highly charged, pristine semiconductors, that bear charges in the backbone but do not spin. These conjugated polyions showed high potential in green-solvent-processing organic opto-electronic devices[6, 7].

Band-gap and molecular energy levels are significant parameters for organic semiconductors[8]. Aromatic polyketones and conjugated polyions, as new semiconducting materials, need to be studied in depth, because the band-gaps and molecular energy levels have not been thoroughly explored. This is largely due to polymerization challenges of aromatic polyketones, pointing to the significance of new synthetic protocols towards these exotic polymers[9].

To the best of our knowledge, there are only a few reports about novel polymerization methods for cross-conjugated aromatic polyketones by Curtis and co-workers,[10–12] Hudson and co-workers[13], Gibson and co-workers[2, 3] and Ito and co-workers[9]. Curtis and co-workers developed the synthesis of cross-conjugated aromatic poly(3-alkylthiophene)ketones by a Pd-catalyzed copolymerization of bis(chloromercury)-thiophenes (highly toxic) with carbon oxides (high pressure) in hot pyridine. Hudson and co-workers reported the synthesis of aromatic polyketone through an aldol condensation of cyclic ketones with aromatic dialdehydes. However, these aromatic polyketone materials suffered from low solubility because they were partially cross-linked. Gibson and co-workers reported the synthesis of aromatic polyketones via the nucleophilic aromatic substitution between arylene dihalides and dicarbanions derived from bis(α-amino nitrile)s, followed by hydrolysis. However, the synthesis of bis(α-amino nitrile)s involved NaCN, and the post-polymerization was hard to achieve high yields and would produce side products. Ito and co-workers reported a palladium-catalyzed alternating copolymerization of formal arylene with carbon monoxide. Subsequent acid promoted dehydration yielded the new aromatic polyketones. This method produced aromatic polyketones together with the corresponding polyketal isomers.

The most common strategy for the synthesis of aromatic polyketones is electrophilic Friedel-Crafts polymerization between bifunctional aromatic acyl chlorides and electron-rich aromatic compounds to generate the ketone linkages.[14–17] However, this method has a narrow scope of substrates. The Friedel-Crafts acylation reactivity is sensitive to the extent of electron-deficiency of the acyl-acceptant arenes. The substrate needs to contain at least one electron-donating group. Therefore, this approach is particularly suitable to the synthesis of aromatic polyketones with electron-rich conjugation moieties. Hence, it is highly valuable to develop a new pathways towards aromatic polyketones that allows a broader substrate
scope.

Transition metal (palladium or nickel) catalyzed polymerization promoted by cross-couplings such as Stille, Suzuki-Miyaura have been widely used to construct conjugated polymers. However, only a few papers reported that a transition metal catalyzed polymerization method was used to synthesize the aromatic polyketones[4, 18–20]. In 2005, Chiechi et al. tried to use Suzuki cross-coupled polymerization to prepare aromatic polyketones from dibromo monomer and diboronic acid monomer, but it yielded low molecular weight product.[4] And Suzuki cross-coupled copolymerization has the problem of a monomer scope limited to mildly electron-rich building blocks such as carbazoles and fluorenes. In our earlier contributions, we demonstrate that one-pot borylation/cross-coupling polymerization exhibited a general superiority over the Stille copolymerization in control end group in symmetrical molecular model systems.[21, 22] Here we further develop the scope of this polymerization method to synthesize of aromatic polyketones.

In this chapter, we report the synthesis and characterization of three new aromatic polyketones with electron-neutralizing (PTK) electron-withdrawing (PBTK), and electron-donating groups (PFTK) in the backbone. These polymers were synthesized with a one-pot Suzuki-Miyaura cross-coupling promoted homopolymerization, which offered good chemical integrity. We systematically investigate band-gap and molecular energy level of these aromatic polyketones by absorption spectroscopy, cyclic voltammetry and theoretical calculation. As with conventional conjugated polymers, the aromatic polyketones exhibited tunable opto-electroic properties.

2.2. Results and Discussion

2.2.1. Synthesis and Characterization

![Synthesis of aromatic polyketones via one-pot Suzuki-Miyaura cross-coupling promoted homo-polymerization.](image)

The synthetic route of the three aromatic polyketones are shown in Figure 2.1. The synthesis of carbonyl containing monomers is shown in the experimental section. The polymers (PTK, PBTK, and PFTK) were synthesized via one-pot Suzuki homo-coupling polymerization from the symmetric, bisbromo, ketone containing monomers. We employed the same polymerization condition for the synthesis of aromatic polyketones as our previous contribution[21, 22]. We chose DMF and
toluene as polymerization co-solvents because DMF can accelerate standard Suzuki polymerization and toluene is a good solvent for the resulting polymer. Polymers were obtained by refluxing the polymerization mixture overnight. Impurities and low-molecular-weight fractions were removed by methanol and hexane in a Soxhlet extractor. Finally, the polymers were extracted with chloroform, precipitated in methanol, and further dried under vacuum. Some insoluble solid remained after extracting, likely due to the low solubility of the very high molecular weight fractions. This phenomenon has also been observed in previous work.[22] The molecular weights of these aromatic polyketones were determined by gel permeation chromatography (GPC) using polystyrene as standards. The resulting data are shown in Table 2.1. The $M_n$ values of PTK, PBTK and PFTK are 57.7, 12.7, and 7.6 kDa, respectively, and the dispersity index ($D$) values of PTK, PBTK, and PFTK are 7.88, 2.03 and 1.83, respectively. The chemical structures of aromatic polyketone were characterized by $^1$HNMR (see the experimental section) and Fourier transform infrared (FT-IR) spectroscopy. The inclusion of carbonyl group into the polymer was confirmed by the appearance of the C=O stretching mode around 1600 cm$^{-1}$ in the (FT-IR) spectroscopy which is shown in Figures 2.13.

The clear peaks in $^1$HNMR, especially in the aliphatic region, can be viewed as an indicator of the high quality and regioregularity of these aromatic polyketones, which are shown in Figures 2.13. The high uniformity and clean end-group of these aromatic polyketones were analysed by MALDI-TOF-MS spectrometry. The MALDI-TOF-MS spectra of PTK, PBTK, and PFTK are shown in Figure 2.2a. As seen in the figure, all spectra show cleanly repeating peaks, with a repetition interval of 630 Da for PTK, 688 Da for PBTK and 718 Da for PFTK, respectively, which is consistent with the mass of the monomer unit. In addition, there are no residual Br and boronic ester end groups in all the aromatic polyketones. Some side peaks with higher m/z values around the major peaks are observed as shown in Figure 2.2b. In PFTK, one of extra peak at tetramer $+17$ m/z, might corresponding to the addition of hydroxyl group to a polymer chain that transferred from the 2,5-Dihydroxybenzoic acid matrix. The origin of the other extra peaks are not clear yet.

| Polymer | $M_n$ (kg mol$^{-1}$) | $M_W$ (kg mol$^{-1}$) | $D$  | $T_g$ ($^\circ$C) | $T_d$ ($^\circ$C) | $T_m$ ($^\circ$C) |
|---------|----------------------|----------------------|------|------------------|------------------|------------------|
| PTK     | 7.3                  | 57.7                 | 7.88 | 76               | 380              | 230              |
| PBTK    | 6.3                  | 12.7                 | 2.03 | 100              | 330              | 250              |
| PFTK    | 4.2                  | 7.6                  | 1.83 | 124              | 400              | 225              |

2.2.2. Thermal Properties

The thermal properties of PTK, PBTK, and PFTK were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA and DSC results are shown in Figure 2.3, and the corresponding data are summarized in Table 2.1. All PTK, PBTK, and PFTK showed excellent thermal stability and exhibited double thermal decomposition process. The decomposition temperature ($T_d$),
defined where 5% weight loss is reached, is at 380 °C, 330 °C and 400 °C for PTK, PBTK, and PFTK, respectively. The loss weight of first decomposition step is around 37 wt%, 23 wt%, and 41 wt% for PTK, PBTK and PFTK, respectively, which likely correspond to the loss of hexyl pendant group. The molecular weight ratio of hexyl pendant group is 39%, 20%, and 46% for PTK, PBTK, and PFTK, respectively. Given that the high Th temperatures of these aromatic polyketones, it is rational to anticipate that they can be thermally processed without degradation, which may facilitate their eventual use in organic opto-electronic devices.

The DSC results reveal that these aromatic polyketones are semicrystalline materials. The glass transition temperature (Tg) of PTK, PBTK and PFTK is at 76 °C, 100 °C, 124 °C. The increasing Tg from PTK to PBTK to PFTK is consistent with increasing the degree of backbone rigidity of these aromatic polyketones. Broad melting endotherm peak was observed at 230 °C for PTK and 250 °C for PBTK respectively, while the small melting transition was observed for 225 °C PFTK from the full DSC curves. The decreasing melting endotherm trend of aromatic polyketones from PTK to PBTK to PFTK indicates the decrease of crystallinity.

2.2.3. Photophysical Properties
Figure 2.4A shows the UV-Vis absorption spectra for these aromatic polyketones in CHCl₃ solution and thin films state. Their photophysical properties and the estimated optical band gap are summarized in Table 2.2. The maximum absorption
peak of PTK, PBTK, and PFTK is at 408 nm, 428 nm, and 445 nm in CHCl₃, respectively, which is attributable to the characteristic absorption of the $\pi - \pi^*$ transition of the polymer backbone. The maximum thin film absorption peak of PTK, PBTK, and PFTK is at 420 nm, 445 nm, and 450 nm respectively. Compared with solution absorption, all aromatic polyketone thin film absorptions show a red-shift, indicating the enhanced interchain $\pi - \pi$ stacking in the solid state. According to the thin films absorption onset, the estimated optical band gap of PTK, PBTK, and PFTK is 2.51 eV, 2.36 eV, and 2.30 eV, respectively, which indicates that inserting an electron donor or acceptor group can effectively reduce the band gap in this cross-conjugated system. This tunable opto-electronic properties of aromatic polyketones are the same as conventional linear conjugated polymer.

The steady-state fluorescence spectra of PTK, PBTK, and PFTK in CHCl₃ are shown in Figure 2.5A with steady-state emission peaks at 490 nm, 541 nm, and 520 nm respectively. Time-resolved fluorescence spectra are shown in Figure 2.5B. PBTK and PFTK clearly showed mono-exponential photoluminescence decay; with PBTK exhibiting the longest fluorescence lifetime of 745 ps while PBTK had a shorter lifetime of 500 ps. On the other hand, PTK showed bimodal-exponential photoluminescence decay with lifetimes of 35 ps and 267 ps.

More interestingly, PTK shows a Stokes shift of 82 nm, while PFTK has smallest Stokes shift of 75 nm and PBTK have the highest Stokes shift of 113 nm. These Stokes shifts are not consistent with the changes in absorption spectra, which indicates that the different central group may introduce significant conformational flexibility which was also confirmed by DSC measurements.

We also acquired the absorption spectrum of protonated aromatic polyketones by H₂SO₄, as shown in Figure 2.4B. The protonation process in aromatic polyketones was shown in Figure 2.6. Protonation of the carbonyl units breaks the cross-conjugation, generating as carbocations inside the conjugated backbone, and converting the cross-conjugation to linear conjugation. Therefore, the conjugation is extended along with the backbone, leading to a decrease in the band gap from 2.51 eV to 1.76 eV for PTK, 2.36 eV to 1.85 eV for PBTK, and 2.30 eV to 1.41 eV.
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Figure 2.4: A) Normalized UV-Vis absorption spectra for PTK, PBTK and PFTK in CHCl₃ solution and thin films, B) Normalized absorption of aromatic polyketone as synthesized(red line) and when protonated with H₂SO₄ (black line).

Figure 2.5: A) Normalized Steady-State fluorescence spectra for PTK, PBTK and PFTK in CHCl₃ solution. B) Time-resolved fluorescence spectra of aromatic polyketone. PFTK and PBTK showed mono-exponential photoluminescence decay; with PBTK exhibiting lifetime of 745 ps, PBTK lifetime of 500 ps. PTK showed bimodal-exponential photoluminescence decay with lifetimes of 35 ps and 267 ps.

for PFTK. The electron-donating nature of fluorene group can increase stabilization of the carbocation and lead to the highest shift. The smallest change of PBTK may indicate that the electron-deficient group (benzothiadiazole) is not favored for forming positive charge.

2.2.4. Electrochemical Properties

In order to gain an insightful understanding of the electrochemical properties of PTK, PBTK, and PFTK, the cyclic voltammetry (CV) characterization was carried out, and the results are shown in Figure 2.7. Half-wave reduction potentials and the estimated LUMO levels of aromatic polyketones are listed in Table 2.3. Ferrocene/ferrocenium (Fe/Fc⁺) was used as a standard reference, which was assigned absolute energy of −4.8 eV vs vacuum level. As expected, all the aromatic polyke-
Figure 2.6: The protonation process in aromatic polyketones

Table 2.2: Photophysical properties data of PTK, PBTK and PFTK.

| Polymer | PTK | PBTK | PFTK |
|---------|-----|------|------|
| $\lambda_{sor.\ max}$ (nm) | 408 | 428 | 445 |
| $\lambda_{film\ max}$ (nm) | 420 | 445 | 450 |
| $\lambda_{pro.abs.\ max}$ (nm) | 580 | 565 | 665 |
| $\lambda_{film\ onset}$ (nm) | 494 | 526 | 539 |
| $E_g$ (eV) | 2.51 | 2.36 | 2.30 |
| $E_{opt.}$ (eV) | 1.76 | 1.85 | 1.41 |
| Absorption shift (nm) | 172 | 127 | 220 |
| $\lambda_{ems.\ max}$ (nm) | 490 | 541 | 520 |
| Stokes shift (nm) | 82 | 113 | 75 |

tones exhibited two fully reversible reduction waves. The first half-wave reduction peak of PTK, PBTK, and PFTK is $-1.81\text{V}$, $-1.76\text{V}$, and $-1.86\text{V}$, respectively, relative to the redox potential of Fc/Fc$^+$. The LUMO energy levels of aromatic polyketones are calculated from the first half-wave reduction potentials using the equation $E_{LUMO} = -(4.80 + E_{\text{red}}^{1/2})\text{eV}$. The estimated LUMO energy levels of PTK, PBTK, and PFTK are $-2.99\text{eV}$, $-3.04\text{eV}$, and $-2.94\text{eV}$, respectively. The HOMO energy level was calculated based on the optical band gap and LUMO energy level. The estimated HOMO energy levels of PTK, PBTK, and PFTK are $-5.50\text{eV}$, $-5.34\text{eV}$, and $-5.30\text{eV}$, respectively. The LUMO energy level of PBTK is 0.1eV lower than that of PTK, and HOMO energy level is 0.16eV higher than that of PTK. The LUMO energy level of PFTK is 0.05eV higher than that of PTK, and HOMO energy level show 0.2eV higher than that of PTK. Aromatic polyketones PBTK exhibited lowest LUMO energy level, and PFTK showed highest HOMO energy level, which indicates that the electron-deficient group (benzothiadiazole) can reduce the LUMO energy level and electron-rich group (fluorene) increase the HOMO energy level in this cross-conjugated system.
2.2. Results and Discussion

2.2.5. Density Functional Theory Calculation

To investigate the electronic structures, density functional theory (DFT) calculations were carried out at the B3LYP/6-311G* level using the Gaussian 09 program. All polymers having two repeat units with methyl substituent were used to reduce the calculation time. The calculated molecular FMOs are shown in the Figure 2.8 and Table 2.3. All polymers exhibit twisted geometries, which might originate from the conformational flexibility link of ketone unit. The twisted backbone geometries typically are unfavorable for charge delocalization and transfer. In PTK and PBTK, the HOMO distribute across the entire backbones of polymers. While in PFTK, the HOMO are mainly localized on the fluorene moiety, slight extended to the thiophene unit. The LUMO of PTK and PFTK are mainly dispersed over the thiophene and ketone group. The LUMO of the PBTK is mainly localized on the benzothiadiazole unit and slightly extended to the thiophene and ketone units owing to the electron-deficient nature of benzothiadiazole and the ketone. Therefore, aromatic polyketones with the electron-deficient group (benzothiadiazole) show the lowest LUMO energy level, and electron-rich group (fluorene) show the highest HOMO energy level in this cross-conjugated system.
Table 2.3: Electrochemical properties data and molecular energy levels of PTK, PBTK and PFTK.

| Polymer | $E_{\text{red}}^{1/2}$ (V) | LUMO(eV)$^a$ | HOMO(eV)$^b$ | LUMO(eV)$^c$ | HOMO(eV)$^c$ |
|---------|----------------------------|--------------|--------------|--------------|--------------|
| PTK     | -1.81                      | -2.99        | -5.50        | -3.07        | -6.076       |
| PBTK    | -1.76                      | -3.04        | -5.34        | -3.32        | -5.95        |
| PFTK    | -1.86                      | -2.94        | -5.30        | -3.09        | 5.78         |

$^a$ Calculated from CV: $E_{\text{LUMO}} = -(4.80 + E_{\text{red}}^{1/2})$ eV.

$^b$ Calculated from $E_{\text{LUMO}}$ and $E_{\text{opt}}$: $E_{\text{HOMO}} = E_{\text{LUMO}} + E_{\text{opt}}$.

$^c$ The DFT calculation data.

2.2.6. Film morphology

The film morphology of aromatic polyketones semiconductors was investigated by atomic force microscopy (AFM). The AFM height images of aromatic polyketones semiconductors are depicted in Figure 2.9. Both PTK and PFTK exhibit smooth morphology, while PBTK show worse morphology than PTK and PFTK. Distinctive pin holes were observed in PBTK film. The root-mean-square (RMS) surface roughness of PTK and PFTK is 0.72 and 1.81 nm, respectively, PBTK show higher value of 2.93 nm.

Figure 2.8: The calculated LUMO and HOMO for aromatic polyketones.

Figure 2.9: AFM height images (5×5 μm) of PFK, PFTK and PBTK films after annealing at the 100 °C.
2.3. Conclusion

In summary, we reported a new synthetic approach for the preparation of aromatic polyketones. Unlike Friedel-Crafts polymerization methods, this strategy shows higher substrate scope. Aromatic polyketones with electron rich, neutral and deficient units were developed and the band-gap and molecular energy level of these aromatic polyketones were investigated by absorption spectroscopy and cyclic voltammetry. This intensive focus on the structure-property relationship of aromatic polyketones can lead us to a better understanding of how their photo-physics and opto-electronic properties can be effected.

2.4. Experimental

**Measurement and characterization** $^1$H and $^{13}$C NMR spectra were measured using a Varian AMX400 (400 MHz) instrument at room temperature. NMR shifts are reported in ppm, relative to the residual protonated solvent signals of CDCl$_3$ ($\delta = 7.26$ ppm) or at the carbon absorption in CDCl$_3$ ($\delta = 77.23$ ppm). Multiplicities are denoted as: singlet (s), doublet (d), triplet (t) and multiplet (m). High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5m mixed-C) (Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in THF at a concentration of 1 mg mL$^{-1}$ and filtered through a Gelman GHP Acrodisc 0.45 µm membrane filter before injection. Thermal properties of the polymers were determined on a TA Instruments DSC Q20 and a TGA Q50 DSC measurements were executed with two heating-cooling cycles with a scan rate of 10 °C min$^{-1}$, and from each scan, the second heating cycle was selected. TGA measurements were done from 20 to 700 °C with a heating rate of 20 °C min$^{-1}$. UV/vis measurements were carried out on a Shimadzu UV 3600 spectrometer. Photoluminescence measurements were carried out on solutions contained in quartz cuvettes. The samples were excited by the second harmonic (approximately 400 nm) of a mode-locked Mira 900 Ti:Sapphire laser delivering 150 ps pulses at a repetition rate of 76 MHz. The laser power was adjusted using neutral density filters; and the excitation beam was spatially limited by an iris. The beam was focused with a 150 mm focal length in reflection geometry. Steady state spectra were collected by a spectrometer with a 50 lines/mm grating and recorded with a Hamamatsu em-CCD array. For time resolved measurements, the same pulsed excitation source was used. Spectra were in this case collected on a Hamamatsu streak camera working in Synchroscan mode (time resolution 2 ps) with a cathode sensitive in the visible. All plotted spectra were corrected for the spectral response of the setup using a calibrated lamp. Cyclic voltammetry (CV) was carried out with an Autolab PGSTAT100 potentiostat in a three-electrode configuration where the working electrode was platinum electrode, the counter electrode was a platinum wire, and the pseudo-reference was an Ag wire that was calibrated against ferrocene.
Synthesis, Optical and Electrochemical Properties of High-quality Cross-conjugated Aromatic Polyketones (Fc/Fc\textsuperscript{+}). Cyclic voltammograms of aromatic polyketones (0.001 mol L\textsuperscript{-1}) in ODCB-CHCN\textsubscript{3} (9 : 1) solution containing Bu\textsubscript{4}NPF\textsubscript{6} (0.1 mol L\textsuperscript{-1}) electrolyte at a scanning rate of 100 mV s\textsuperscript{-1}.

**Materials** All reagents and solvents were commercial and were used as received unless otherwise indicated. The solvents were further purified by normal procedures and distilled before used. All air and water sensitive synthetic manipulations were performed under dry argon or nitrogen atmosphere.

**Figure 2.10:** Synthetic route for TK.

2-(2,5-dihexyl-4-(thiophen-2-yl)phenyl)thiophene

To a dried flask containing magnesium turnings (320 mg, 13.2 mmol) and anhydrous tetrahydrofuran (THF; 12 mL) was added 2-bromothiophene (1956 mg, 12 mmol) drop-wise. After complete addition, the mixture was refluxed for 3 hours. In another dried flask, 1,4-dihexyl-2,5-diiodobenzene (2000 mg, 4 mmol) was dissolved in dry THF (20 mL), then the catalyst Ni(dppf)\textsubscript{2}Cl\textsubscript{2} (80 mg) was added, and the solution was degassed by purging with bubbling nitrogen for 30 min. The clear gray/brown Grignard reagent was then transferred to a dropping funnel and slowly added to the degassed solution. After complete addition, the reaction mixture was refluxed for overnight. After cooling to the room temperature, the mixture was quenched by pouring it over 1 N HCl/ice and extracted with CH\textsubscript{2}Cl\textsubscript{2}; the combined organic layers were washed with water and brine, and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvents were removed by rotary evaporation. The crude product was purified by silica gel column chromatography with hexane as the eluent afforded target compound as light yellow solid (85% yield). \textsuperscript{1}HNMR (400 MHz, CDCl\textsubscript{3}) \textdelta: 7.35 (d, J=4.4 Hz, 2H), 7.28 (s, 2H), 7.10 (m, 2H), 7.06 (m, 2H), 2.69 (m, 4H), 1.55 (s, 4H), 1.24 (m, 12H), 0.85 (t, J=8 Hz, 6H). \textsuperscript{13}CNMR (100 MHz, CDCl\textsubscript{3}) \textdelta: 142.70, 138.57, 133.47, 132.22, 127.02, 126.37, 125.19, 33.10, 31.61, 31.53, 29.29, 22.59, 14.11.

((2,5-dihexyl-1,4-phenylene)bis(thiophene-5,2-diyl))bis((5-bromothiophen-2-yl)methanone) Monomer TK

To a nitrogen-purged 3-neck flask fitted with a distillation apparatus was added 2-bromo-5-thiophenoic acid (450 mg, 2.2 mmol), SOCl\textsubscript{2} (10 mL) and 1 drop Dimethylformamide (DMF). The reaction was stirred at 80 °C for 4 hours, and the excess SOCl\textsubscript{2} was removed by rotary evaporation to yield pure 5-bromothiophene-2-carbonyl chloride as a yellow solid (assumed quantitative yield). AlCl\textsubscript{3} (400 mg, 2.98 mmol) was suspended in anhydrou dichloromethane (DCM, 100 mL) in a dried
flask and 5-bromothiophene-2-carbonyl chloride was added. The slurry was cooled to 0 °C and 2-(2,5-dihexyl-4-(thiophen-2-yl)phenyl)thiophene (300 mg, 0.735 mmol) was added slowly. The reaction mixture was kept stirring for overnight at room temperature. The mixture was quenched by pouring it over 1 N HCl/ice and extracted with CH₂Cl₂, the combined organic layers were washed with water and brine, and dried over Na₂SO₄. The solvents were removed by rotary evaporation. The crude product was purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) as the eluent afforded target compound Monomer TK as light yellow solid (64 % yield). 

HNMR (400 MHz, CDCl₃) δ: 7.86 (d, J=3.9 Hz, 2H), 7.70 (d, J=4.0 Hz, 2H), 7.34 (s, 2H), 7.18 (d, J = 4.0 Hz, 2H), 7.15 (d, J = 3.9 Hz, 2H), 2.74 (m, 4H), 1.55 (s, 4H), 1.25 (m, 12H), 0.85 (t, J= 8 Hz, 6H).

CNMR (100 MHz, CDCl₃) δ: 179.89, 154.04, 147.00, 144.32, 141.53, 135.95, 135.92, 135.77, 134.87, 133.75, 130.29, 124.99, 35.68, 34.18, 34.09, 31.83, 25.18, 16.69. HRMS(ESI) calcd. for C₃₆H₃₇Br₂O₂S₄ [M+H⁺]: 787.00376, found: 787.00427.

Figure 2.11: Synthetic route for BTK.

Synthesis of (5-bromo-4-hexylthiophen-2-yl)(thiophen-2-yl)methanone
AlCl₃ (2500 mg, 18.66 mmol) was suspended in 100 mL anhydrous dichloromethane in a dried flask and 2-Thiophenecarbonyl chloride (1.82 mL, 17 mmol) was added. The slurry was cooled to 0 °C. Then, 2-bromothiophene (3800 mg, 15.45 mmol) was added under a N₂ atmosphere and the resulting mixture was stirred overnight at room temperature. The reaction mixture was poured into a mixture of ice and 1M HCl, then extracted with CH₂Cl₂. The organic phase was washed with brine, dried over anhydrous Na₂SO₄ and removed solvent by rotary evaporator. The crude product was purified by silica gel column chromatography with hexane/CH₂Cl₂ (4:1) as the eluent afforded 3000 mg (54 % yield) target compound as a viscous brown oil. 

HNMR (400 MHz,CDCl₃) δ: 7.84 (d, J = 3.6 Hz, 1H), 7.69 (d, J = 4.2 Hz, 1H), 7.58 (s, 1H), 7.18 (m, 1H), 2.59 (t, J = 8 Hz, 2H), 1.60 (m, 2H), 1.40–1.22 (m, 6H), 0.89 (t, J = 6.2 Hz, 3H).

CNMR (100 MHz, CDCl₃) δ: 177.58, 143.61, 142.26, 141.92, 133.80, 133.62, 132.96, 128.07, 119.52, 31.57, 29.62, 29.60, 28.86, 22.61, 14.13.

Synthesis of (benzo[c][1,2,5]thiadiazole-4,7-diylbis(4-hexylthiophene-5,2-diyl))bis(thiophen-2-ylmethanone)
To a degassed solution of 5-bromo-4-hexylthiophen-2-yl)(thiophen-2-yl)methanone
(920 mg, 2.58 mmol) and 2,1,3-Benzothiadiazole-4,7-bis(pinacolato)diboronic ester (400 mg, 1.03 mmol) in toluene (20 mL) was added a degassed solution of K$_2$CO$_3$ (1.38 g, 10 mmol) in water (2 mL). Then, the catalyst Pd(PPh$_3$)$_4$ (20 mg) was added under N$_2$ atmosphere. The solution was then sparged with nitrogen for 10 min. The resulting mixture was refluxed overnight. Upon the mixture cooled to room temperature, the reaction mixture was poured into a water, then extracted with CH$_2$Cl$_2$. The organic phase was washed with brine, dried over anhydrous sodium sulfate and removed solvent by rotary evaporator. The crude product was purified by silica gel column chromatography with hexane/CH$_2$Cl$_2$ (4:1) as the eluent afforded 320 mg (45% yield) target compound as a yellow solid. $^1$HNMR (400 MHz, CDCl$_3$) δ: 7.98 (dd, J = 3.8 Hz, J = 1.0 Hz, 2H), 7.90 (s, 2H), 7.77 (s, 2H), 7.73 (dd, J = 4.9 Hz, J = 1.0 Hz, 2H), 7.22 (dd, J = 4.9 Hz, J = 3.9 Hz, 2H), 2.70 (t, J = 7.8 Hz, 4H), 1.65 (m, 4H), 1.28-1.14 (m, 12H), 0.82 (t, J = 6.8 Hz, 6H). $^{13}$CNMR (100 MHz, CDCl$_3$) δ: 178.60, 153.60, 142.96, 142.93, 142.22, 140.33, 135.02, 133.51, 133.15, 130.12, 128.01, 127.39, 31.48, 30.48, 29.52, 29.14, 22.49, 14.00.

(benzo[c][1,2,5]thiadiazole-4,7-diylbis(4-hexylthiophene-5,2-diyl))bis((5-bromothiophen-2-yl)methanone) Monomer BTK

To a solution of (benzo[c][1,2,5]thiadiazole-4,7-diylbis(4-hexylthiophene-5,2-diyl))bis(thiophene-2-ylmethanone) (320 mg, 0.465 mmol) in CHCl$_3$ (10 mL), Br$_2$ (0.1 mL) was added. The mixture was stirred overnight at room temperature. An aliquot was taken out and subject to thin-layer chromatography (TLC) analysis. If a relative abundance of the starting materials was detected, two equimolar amount of Br$_2$ was added and the reaction was allowed to continued for an additional 2 hours. Upon the consuming the starting material, the reaction mixture was poured into solution water, then extracted with CH$_2$Cl$_2$. The organic phase was washed with brine, dried over Na$_2$SO$_4$ and removed the solvent by rotary evaporator. The crude product was purified by silica gel column chromatography with hexane/toluene (1:1) as the eluent afforded 130 mg (33% yield) target compound Monomer BTK as a yellow solid. $^1$HNMR (400 MHz, CDCl$_3$) δ: 7.86 (s, 1H), 7.76 (s, 1H), 7.73 (d, J=4.0 Hz, 2H), 7.19 (d, J=4.0 Hz, 2H), 2.69(t, J=8.0 Hz, 4H), 1.70-1.57 (m, 4H), 1.30-1.15 (m, 12H), 0.82 (t, J=6.7 Hz, 6H). $^{13}$CNMR (100 MHz, CDCl$_3$) δ: 177.39, 153.67, 144.48, 143.23, 141.53, 140.72, 135.06, 133.42, 131.28, 130.23, 127.44, 122.58, 77.44, 77.12, 76.80, 31.60, 30.60, 29.63, 29.13, 22.61, 14.13. HRMS(ESI) calcd. for C$_{36}$H$_{35}$Br$_2$O$_2$S$_5$ [M+H]$^+$: 844.96633, found: 844.96744.

Figure 2.12: Synthetic route for FTK. 

((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis((5-bromo...
thiophen-2-yl)methanone) Monomer FTK

To a nitrogen-purged 3-neck flask fitted with a distillation apparatus was added 2-bromo-5-thiophenoic acid (1.97 g, 9.6 mmol), SOCl₂ (10 mL) and 1 drop Dimethyl-formamide (DMF). The reaction was stirred at 80 °C for 4 hours, and the excess SOCl₂ was removed by rotary evaporation to yield pure 5-bromothiophene-2-carbonyl chloride as a yellow solid (assumed quantitative yield). AlCl₃ (1.88 g, 14.03 mmol) was suspended in 100 mL anhydrous dichloromethane in a dried flask and 5-bromothiophene-2-carbonyl chloride was added. The slurry was cooled to 0 °C and 2,2’-(9,9-dihexyl-9H-fluorene-2,7-diyl)dithiophene (1.4 g, 2.81 mmol) was added slowly. The reaction mixture was kept stirring for overnight at room temperature. The mixture was quenched by pouring it over 1 N HCl/ice and extracted with CH₂Cl₂, the combined organic layers were washed with water and brine, and dried over Na₂SO₄. The solvents were removed by rotary evaporation. The crude product was purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) as the eluent afforded target compound Monomer FTK as yellow solid (80% yield).

¹HNMR (400 MHz, CDCl₃) δ: 7.88 (d, J=4.0 Hz, 2H), 7.76 (d, J=8.0 Hz, 2H), 7.74-7.67 (m, 4H), 7.64 (s, 2H), 7.46 (d, J=4.0 Hz, 2H), 7.19 (d, J=4.0 Hz, 2H), 2.11-2.00 (m, 4H), 1.55 (m, 4H), 1.06 (m, 12H), 0.75 (t, J= 8 Hz, 6H).

¹³CNMR (100 MHz, CDCl₃) δ: 179.73, 156.18, 154.86, 146.98, 144.12, 143.19, 136.91, 135.60, 135.07, 133.74, 128.21, 126.54, 124.80, 123.34, 123.26, 58.20, 42.94, 34.07, 32.23, 26.42, 25.18, 16.62. HRMS(ESI) calcd. for C₄₃H₄₁Br₂O₂S₄ [M+H]⁺: 875.03507, found: 875.03592.

General aromatic polyketones synthesis procedures

All reactions were performed under anhydrous conditions under a nitrogen atmosphere. To a flame-dried flask containing a mixture of DMF:Toluene were added equal molar quantities of monomer and bis(pinacolato) diboron (BiPi). The solution was then purged with bubbling nitrogen for 10 min before the addition of 5 mol% to 10 mol% 1,10-bis(diphenylphosphino)-ferrocenepalladium(II)dichloromethane complex Pd(dppf)₂Cl₂ and 5 eq. of crushed K₃PO₄ and the solution was used a freeze-pump-thaw cycle technique to remove O₂ for three times. The reaction mixture was carried out to 110 °C and stirred for overnight (about 15 hours), cooled to room temperature, and the solvent removed by rotary evaporation. The remaining residue was dissolved in a minimal amount of CHCl₃ and precipitated by pouring slowly into large excess of CH₃OH. The resulting slurry was stirred for an hour and the precipitate collected by filtration and then further purified by Soxhlet extraction with hexane, methanol, and chloroform, successively. The chloroform fraction polymer was collected. The purified polymer dissolved before being re-precipitated into cold CH₃OH and dried in vacuo.

Poly[(2,5-dihexyl-1,4-phenylene)bis(thiophene-5,2-diyl)]bis(thiophen-2-ylnethanone)] PTK

K₃PO₄ (495 mg, 2.33 mmol), Monomer 1 (367 mg, 0.467 mmol), BiPi (119 mg, 0.467 mmol), Pd(dppf)₂Cl₂ (35 mg, 0.047 mmol) were reacted in 20 mL dry mixture solvents of DMF and toluene (1:1) according to the general aromatic polyketones polymerization procedure. Pure PTK (30 mg, 11%) was obtained as a yellow powder.

¹HNMR (400 MHz, CDCl₃) δ: 8.11-7.11 (m, 8H), 3.05-2.52 (m, 4H), 1.75-1.41 (m,
2. Synthesis, Optical and Electrochemical Properties of High-quality Cross-conjugated Aromatic Polyketones

Poly[((9,9-dihexyl-9H-fluorene-2,7-diyi) bis(thiophene-5,2-diyi))bis(thiophen-2-ylmethanone)] PFTK

K₃PO₄ (265 mg, 1.25 mmol), Monomer 2 (219 mg, 0.25 mmol), BiPi (64 mg, 0.25 mmol), Pd(dppf)₂Cl₂ (10 mg, 0.014 mmol) were reacted in 10 mL dry mixture solvents of DMF and toluene (1:1) according to the general aromatic polyketones polymerization procedure. Pure PFTK (40 mg, 23%) was obtained as a red powder. ¹HNMR (400 MHz, CDCl₃) δ: 8.16-7.18 (m, 14H), 2.22-1.88 (m, 4H), 1.77-1.33 (m, 12H), 0.82-0.68 (m, 6H). IR (cm⁻¹): 22924, 2853, 1606, 1507, 1427, 1299, 1265, 1118, 1056, 892, 839, 811, 787, 722.

Poly[(benzo[c][1,2,5]thiadiazole-4,7-diyi)bis(4-hexylthiophene-5,2-diyi)] bis(thiophen-2-ylmethanone)] PBTK

K₃PO₄ (156 mg, 0.74 mmol), Monomer 3 (125 mg, 0.15 mmol), BiPi (38 mg, 0.15 mmol), Pd(dppf)₂Cl₂ (5 mg, 0.007 mmol) were reacted in 10 mL of dry mixture solvents of DMF and toluene (1:1) according to the general aromatic polyketones polymerization procedure. Pure PBTK (24 mg, 24%) was obtained as a red powder. ¹HNMR (400 MHz, CDCl₃) δ: 8.14-7.13 (m, 8H), 2.98-2.49 (m, 4H), 1.85-1.51 (m, 4H), 1.42-0.98 (m, 12H), 0.93-0.68 (m, 6H). IR (cm⁻¹): 2922, 2853, 1600, 1529, 1507, 1424, 1298, 1270, 1194, 1090, 1049, 875, 836, 777, 722.

¹HNMR and IR data

Figure 2.13: ¹HNMR and IR spectra of aromatic polyketones.
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