Organic semiconducting materials have been attracted considerable attention as a promising technology for the next generation flexible electronic devices, such as solar cells and field-effect transistors because of their advantages of low-cost, structural versatility and flexibility. Many organic semiconducting materials have been developed in recent years.

In this thesis, four \( \pi \)-conjugated building blocks based on benzodithiophene and quinoxalinedithienothiophene were applied to develop novel photovoltaic materials, including donor-acceptor alternating copolymers as a donor material for polymer solar cells, photosensitizers for dye sensitized solar cells, small molecule hole transporting materials for perovskite solar cells and small molecule acceptors for organic solar cells. A comprehensive review of current development of organic photovoltaic materials was presented in Chapter 1.

In Chapter 2, a series of D-A copolymers (PBB-n) based on 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole and 4,5-bis((2-ethylhexyl)oxy)benzo[2,1-b:3,4-b']dithiophene attached with different solubilizing side-chains were designed, synthesised and characterized. In general, PBB-n polymers showed good absorption in the region of visible light and UV region, indicating such polymers are a promising light harvester.
Also, PBB-n exhibited suitable energy levels, suggesting that they could be applied as the donor materials in polymer solar cells. PBB-n also exhibited various extent of aggregation behaviour.

Chapter 3 described syntheses and the fluorination effect of two series of fluoro-substituted PBB-n copolymers, namely PfBB-n and PfBB-n on optical, electrochemical, and optoelectronic properties. Among them, PfBB-n series was characterized with photovoltaic performance. The champion devices fabricated from PfBB-12 showed a $PCE$ as high as 9.7%, with a $V_{oc}$ of 0.92 V, a $J_{sc}$ of 16.60 mA/cm$^2$ and a $FF$ of 63.49%. Cells fabricated from other PfBB-n copolymers also exhibited good PV performance with $PCE$ ranging from 7.4 – 8.5%. For PfBB-n polymers, temperature-dependent aggregation behaviour was exploited by modulating the coating temperature during device fabrication. PSC devices based on PfBB-n exhibited good PV performance with $PCE$ ranging from 7.4% to 9.9%. Among which, PfBB-n provided the most promising PV performance with $PCE$ of 9.9%, a $V_{oc}$ of 0.92 V, a $J_{sc}$ of 16.8 mA/cm$^2$ and a $FF$ of 64.36%.

Electron deficient conjugated structure was seldom used as the $\pi$-bridge in metal-free photosensitizers. In Chapter 4, four novel organic photosensitizers, namely QC5-m and PC5-n were designed with an electron deficient $\pi$-bridge. Typical sandwich-structured DSSCs based on the newly developed photosensitizers exhibited promising photovoltaic performance with $PCE$ ranging from 5.23 – 7.77 %, with a maximum $J_{sc}$ as high as 15.63 mA cm$^2$. These results suggest that the use of electron deficient $\pi$-bridge provides alternative approach to construct efficient organic photosensitizers.

Chapter 5 and Chapter 6 described the design, synthesis and investigation of novel hole-transporting materials and electron acceptor materials based on benzo[2,1-$b$:3,4-
b\textsuperscript{'}dithiophene-4,5-dione derived building blocks as potential organic photovoltaic materials for solar cell applications.

**Keywords:** organic photovoltaic materials, photosensitizers, polymer solar cell, electron acceptor, hole-transporting materials.
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