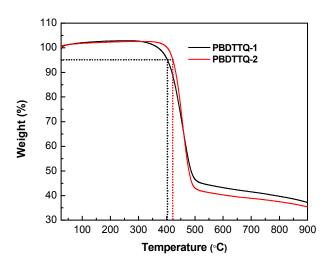
## Benzodithiophene-Thiadiazoloquinoxaline as an Acceptor for Ambipolar Copolymers with Deep LUMO Level and Distinct Linkage Pattern

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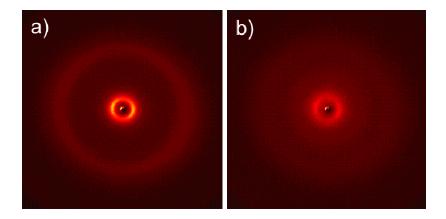
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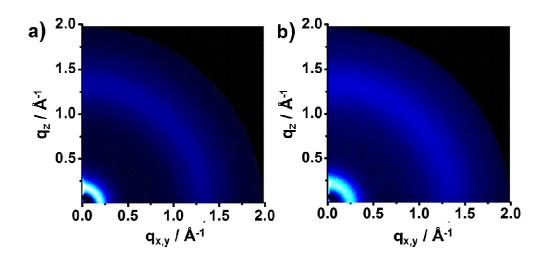
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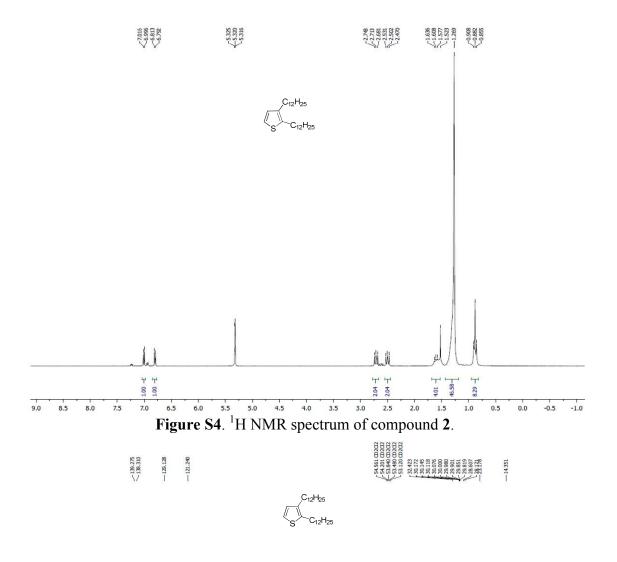
**Figure S1**. TGA curves for **PBDTTQ-1** and **PBDTTQ-2** measured under a nitrogen atmosphere at a heating rate of 10 °C/min.



**Figure S2**. 2DWAXS of a) PBDTTQ-1 and b) PBDTTQ-2. The fiber sample was mounted vertical towards the 2D detector.



**Figure S3**. GIWAXS of a) PBDTTQ-1 and b) PBDTTQ-2.



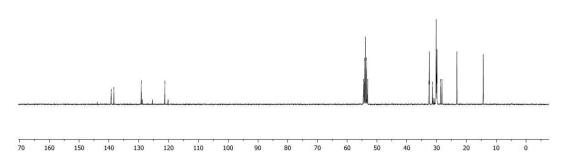


Figure S5. 13 C NMR spectrum of compound 2.

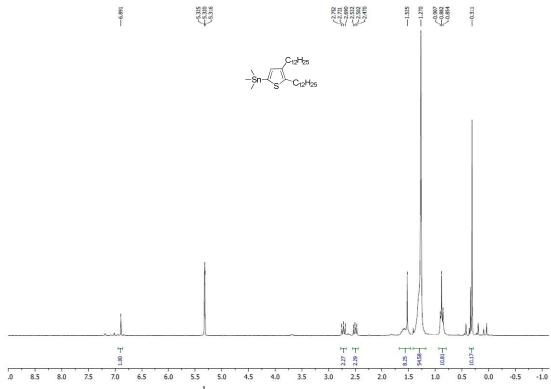
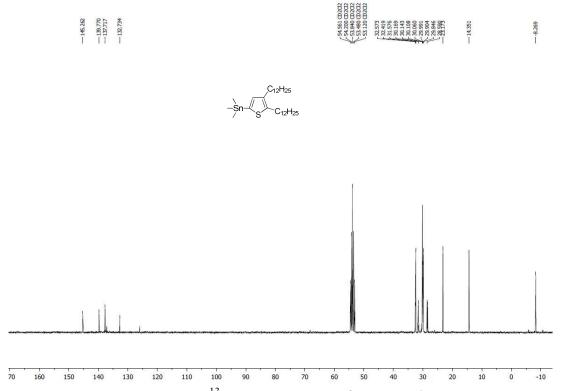
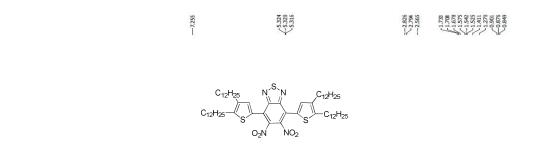
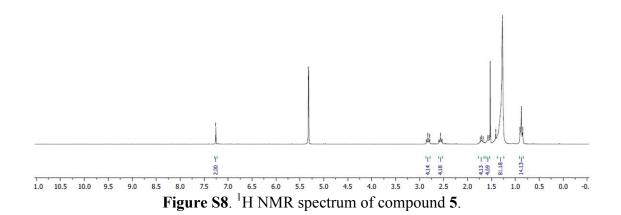


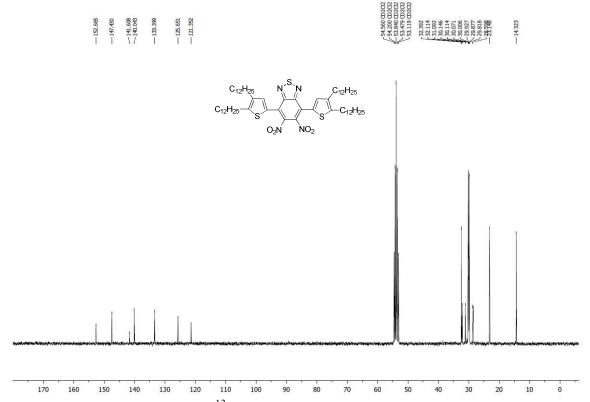
Figure S6. <sup>1</sup>H NMR spectrum of compound 3.



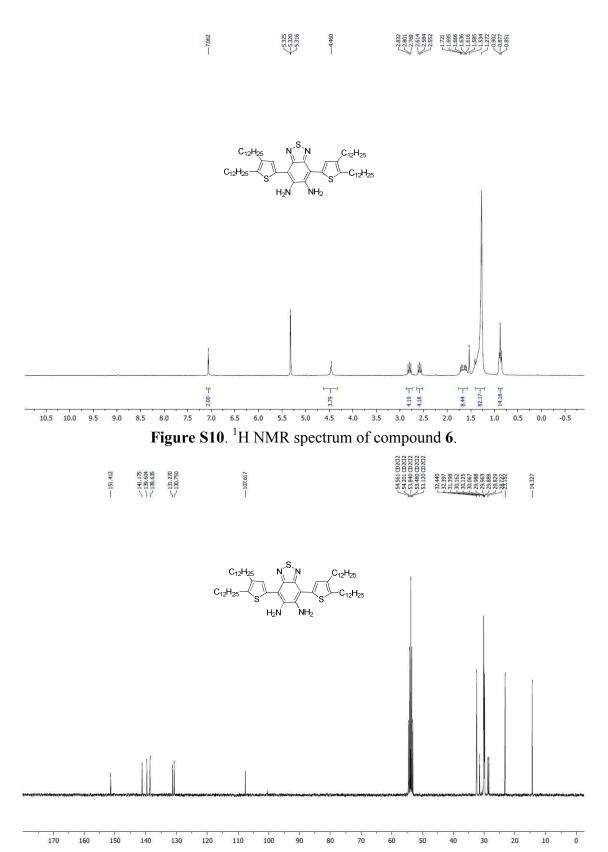
**Figure S7**. <sup>13</sup>C NMR spectrum of compound **3**.



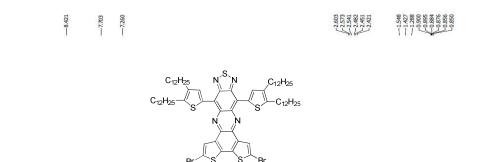




**Figure S9**. <sup>13</sup>C NMR spectrum of compound **5**.



**Figure S11**. <sup>13</sup>C NMR spectrum of compound **6**.



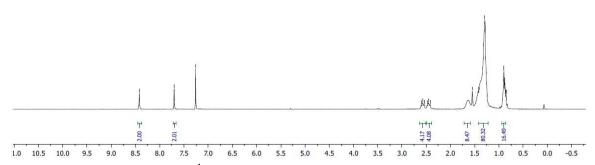


Figure S12. <sup>1</sup>H NMR spectrum of compound BDTTQ-1.

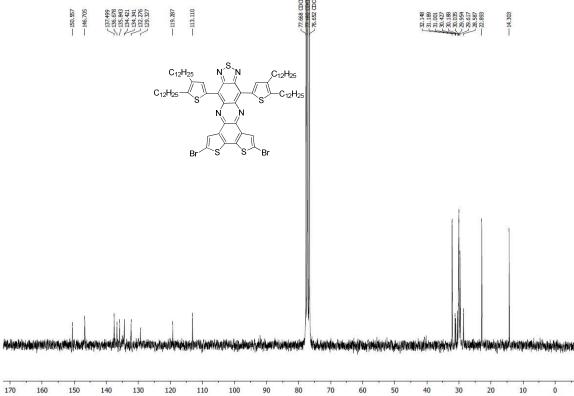
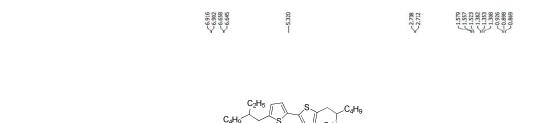
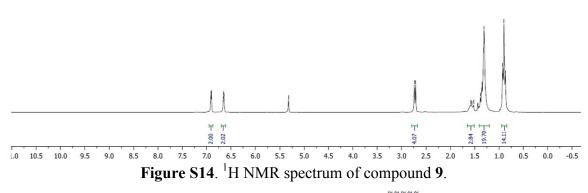


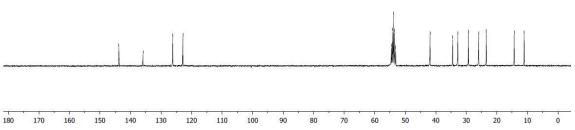
Figure S13. <sup>13</sup>C NMR spectrum of compound BDTTQ-1.





-143.785
-135.886
-135.170
-122.836
-122.836
-122.836
-122.836
-122.836
-133.19 0.02dd
-13.19 0.02dd
-14.332
-14.332
-14.332

$$C_2H_5$$
  $S$   $C_4H_9$   $C_4H_5$ 



**Figure S15**. <sup>13</sup>C NMR spectrum of compound **9**.

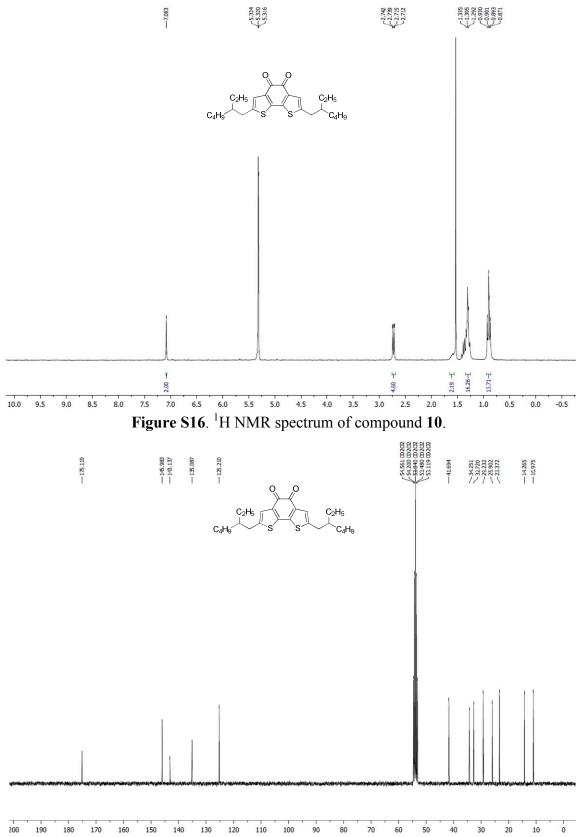


Figure S17.<sup>13</sup>C NMR spectrum of compound 10.

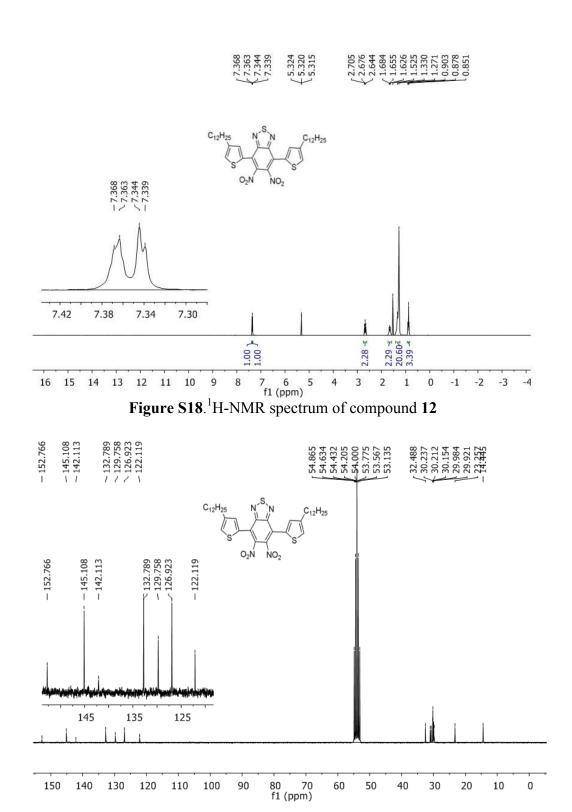
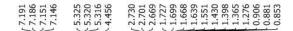


Figure S19.<sup>13</sup>C NMR spectrum of compound 12



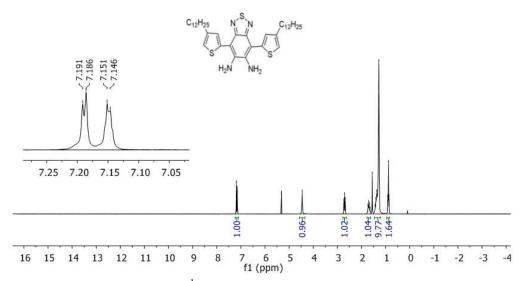


Figure S20. <sup>1</sup>H NMR spectrum of compound 13

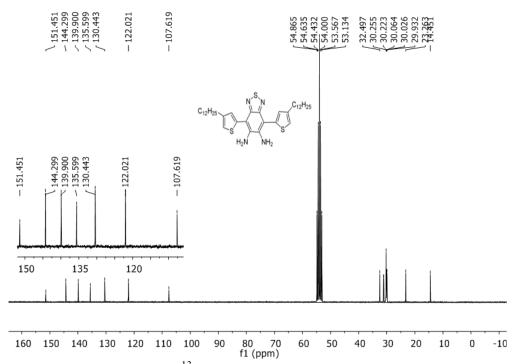


Figure S21. 13C NMR spectrum of compound 13

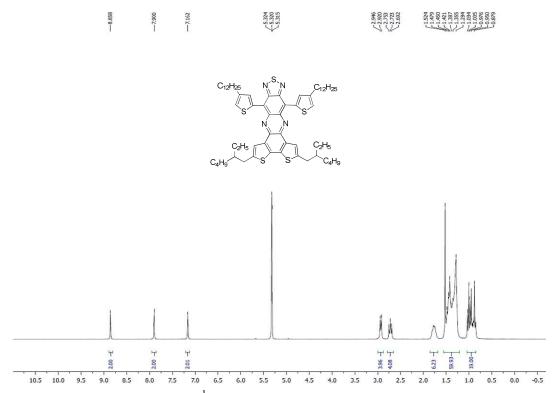


Figure S22. <sup>1</sup>H NMR spectrum of compound 14.

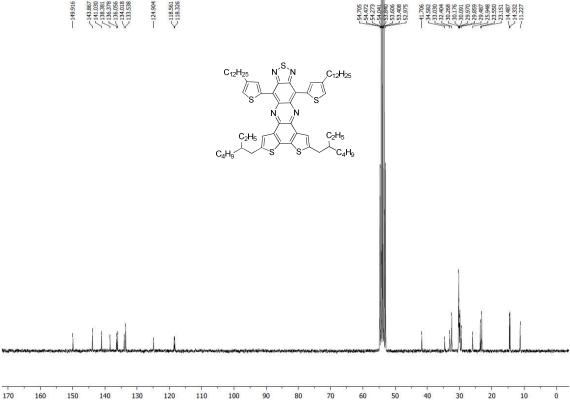


Figure S23.<sup>13</sup>C NMR spectrum of compound 14

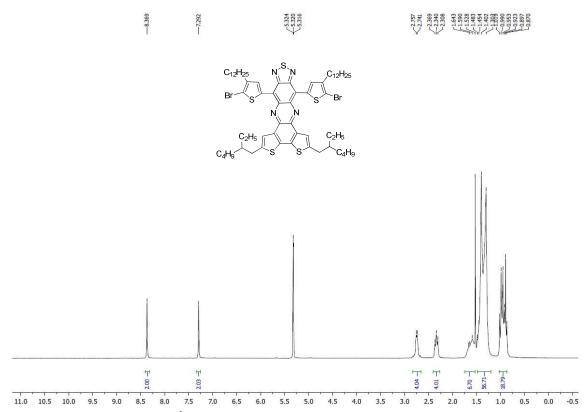


Figure S24. H NMR spectrum of compound BDTTQ-2.

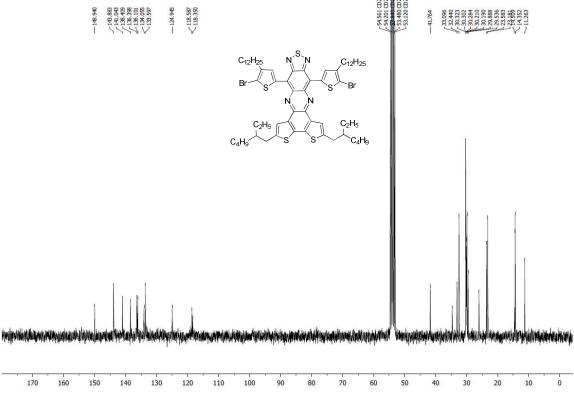
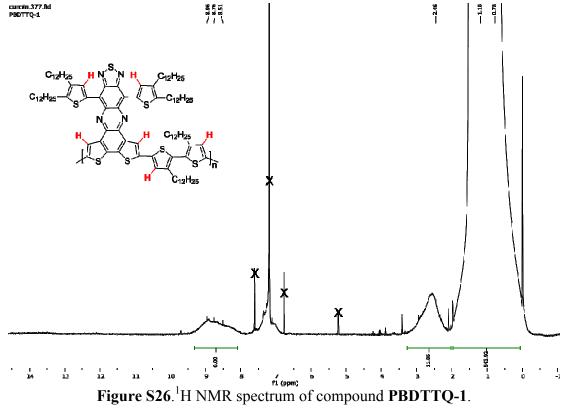


Figure S25.<sup>13</sup>C NMR spectrum of compound BDTTQ-2.



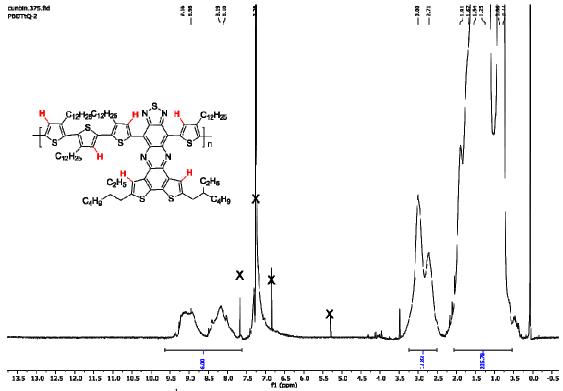
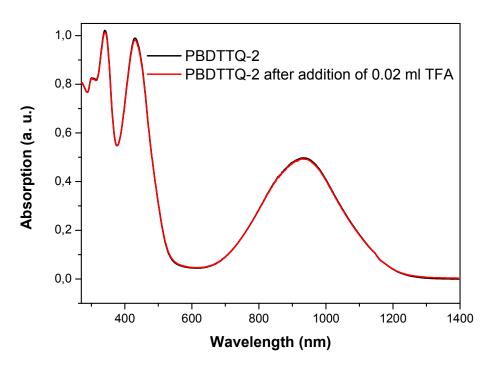


Figure S27. H NMR spectrum of compound PBDTTQ-2.



 $\begin{tabular}{ll} Figure S28. UV-Visible absorption spectra of PBDTTQ-2 in chloroform solution (c=2\times10^{-5} \, M) \\ with and without TFA. \end{tabular}$