A Comprehensive Study of Substituent Effects on Poly(dibenzofulvene)s

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Figure S1. ¹H NMR spectrum of 2-N,N-dimethylaminodibenzofulvene in CDCl₃.
Figure S2. $^{13}$C NMR spectrum of 2-$N,N$-dimethylaminodibenzofulvene in CDCl$_3$.

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Figure S8. $^1$H NMR spectrum of poly(NMe2DBF) in CDCl$_3$.

Figure S9. GPC traces of some substituted poly(DBF)s.
Figure S10. Comparison of IR spectra between poly(CNDBF) (both soluble and insoluble fractions) and 2-cyanofluorene with peak assignments. The spectra suggest that both fractions contain same chemical composition.

Figure S11. Comparison of IR spectra between poly(NO2HexODBF) and 2-hexoxy-7-nitrofluorene with peak assignments.
Figure S12. Normalized absorption spectra of some substituted poly(DBF)s in THF. Arrows indicate the lowest-energy absorption peak wavelengths.

Figure S13. Normalized emission spectra of some substituted poly(DBF)s in THF. Arrows indicate the defect emissions.
Figure S14. Normalized absorption spectra of poly(BrHexODBF) and 2-bromo-7-hexoxyfluorene in THF.

Figure S15. Normalized emission spectra of poly(BrHexODBF) and 2-bromo-7-hexoxyfluorene in THF. Arrow indicates the emission of defect in the polymer which matches the emission maximum of 2-bromo-7-hexoxyfluorene.
Figure S16. Normalized emission spectra of poly(CNDBF) and 2-cyanofluorene in THF. The arrow indicates the emission of the stereochemical defect in the polymer which matches the emission maximum of 2-cyanofluorene. Note the excimer emission strongly outweighs that of the defects despite the low molecular weight of the polymer.
Figure S17. Cyclic voltammograms of some substituted poly(DBF)s in THF with 0.1 M $n$-Bu$_4$NPF$_6$ as the supporting electrolyte. Arrows indicate oxidation potentials.

Figure S18. Cyclic voltammograms of poly(NMe2DBF)s in THF with 0.1 M $n$-Bu$_4$NPF$_6$ as the supporting electrolyte.
Figure S19. GPC traces of poly(DBF) after annealing (top, in blue) and before annealing (bottom, in red).

Table S1. Electrochemical data of the substituted poly(DBF)s.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>ΔE (eV)</th>
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<tr>
<td>Poly(DBF)</td>
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<td>3.87</td>
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<td>-1.96</td>
<td>3.70</td>
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<tr>
<td>Poly(NMe2DBF)</td>
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<td>-1.90</td>
<td>3.11</td>
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<td>Poly(FDBF)</td>
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<td>Poly(IDBF)</td>
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<tr>
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<tr>
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<td>Poly(BrMeODBF)</td>
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<tr>
<td>Poly(Br2DBF)</td>
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</tr>
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</table>

*Perform in degassed THF under N₂ with 0.1 M nBu₄NPF₆ as the supporting electrolyte. HOMO energies are obtained with reference to ferrocene internal standard by relation: HOMO = − (E_{Fc}^{1/2} + 4.8) eV. LUMO energies are estimated from HOMO and bandgap (ΔE) by relation: ΔE = |HOMO| - |LUMO|. Bandgap is estimated from the absorption onset wavelength.