Electronic Supplementary Information (ESI) for

**Donor–Acceptor Polymers with Tunable Infrared Photoresponse**

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Computation. All DFT and TD-DFT calculations were carried out with the Gaussian 09 package (version C.01)\(^1\) employing the B3LYP exchange-correlation functional\(^2\) and a polarized 6-31G(d) basis set using default SCF convergence criteria (density matrix converged to at least \(10^{-8}\)), DFT integration grid (75 radial and 302 angular quadrature points) and optimization convergence criteria (RMS force of at least 0.0003 Hartree/Bohr). The HOMO and LUMO figures for the \(P_2\) and \(P_3\) tetramers are shown in Figures S1-S4.

<table>
<thead>
<tr>
<th></th>
<th>HOMO(^a)</th>
<th>LUMO(^a)</th>
<th>(E_g)(^b)</th>
<th>(f)(^c)</th>
<th>(E_g^{\text{vert}}(n\rightarrow\infty))(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1b</td>
<td>-4.62</td>
<td>-3.15</td>
<td>1.47</td>
<td>6.82</td>
<td>1.08</td>
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<tr>
<td>P1</td>
<td>-4.32</td>
<td>-2.98</td>
<td>1.34</td>
<td>7.02</td>
<td>1.04</td>
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<tr>
<td>P2</td>
<td>-4.25</td>
<td>-3.01</td>
<td>1.24</td>
<td>6.56</td>
<td>0.94</td>
</tr>
<tr>
<td>P3</td>
<td>-4.40</td>
<td>-3.28</td>
<td>1.12</td>
<td>5.91</td>
<td>0.88</td>
</tr>
<tr>
<td>P4</td>
<td>-4.16</td>
<td>-3.25</td>
<td>0.91</td>
<td>10.01</td>
<td>0.68</td>
</tr>
<tr>
<td>P5</td>
<td>-4.14</td>
<td>-3.26</td>
<td>0.88</td>
<td>9.74</td>
<td>0.63</td>
</tr>
</tbody>
</table>

\(^a\)Frontier molecular orbital energies as determined at the the B3LYP/6-31G(d) level of theory. \(^b\)HOMO/LUMO orbital energy gap \((E_g)\). \(^c\)Oscillator strength \((f)\). \(^d\)\(S_0\) to \(S_1\) vertical transition energy extrapolated to \(n = \infty\) using the Kuhn equation \((E_g^{\text{vert}}(n\rightarrow\infty))\). All energies are in eV and oscillator strength is a unitless quantity. \(^3\)Data adopted from reference 3.
**Figure S1.** Optimized ground-state ($S_0$) geometric structures for the **P2** tetramer ($n = 4$) and pictorial representation of the HOMO wavefunction as determined at the B3LYP/6-31G(d) level of theory.

**Figure S2.** Pictorial representation of the LUMO wavefunction for the **P2** tetramer ($n = 4$) as determined at the B3LYP/6-31G(d) level of theory.
Figure S3. Optimized ground-state ($S_0$) geometric structures for the P3 tetramer ($n = 4$) and pictorial representation of the HOMO wavefunction as determined at the B3LYP/6-31G(d) level of theory.

Figure S4. Pictorial representation of the LUMO wavefunction for the P3 tetramer ($n = 4$) as determined at the B3LYP/6-31G(d) level of theory.
Figure S5. Repeat unit of P1a, P1b, and P1 and bond length plots of the (central dimer) of the oligomers with $n = 6$ ($C_1$-$C_{12}$ shown for clarity). Bond length values are in Å.

Figure S6. Repeat unit of P1-P3 and bond length plots of the (central dimer) of the oligomers with $n = 6$ ($C_1$-$C_{12}$ shown for clarity). Bond length values are in Å.
Figure S7. Repeat unit of P4 and P5 and bond length plots of the (central dimer) of the oligomers with $n = 6$ ($C_1-C_{20}$ shown for clarity). Bond length values are in Å.

Figure S8. Side view of the optimized geometry of $(P1)_4$. 
Figure S9. Torsional energy as a function of the dihedral angle for the P1 dimer calculated at the B3LYP/6-31G(d) level of theory.

Figure S10. S1 excitation energy as a function of the dihedral angle for the P1 dimer calculated with time-dependent DFT at the B3LYP/6-31G(d) level of theory.
**Figure S11.** Absorption squared plots of P1-P5 as thin films.

**Figure S12.** CV of P1–P5 (third scan).
Figure S13. Absorption spectra of P3 thin films with varying ratios of [70]PCBM.

Figure S14. $^1$H NMR spectra of 1a.
**Figure S15.** $^{13}$C NMR spectra of 1a.

**Figure S16.** $^1$H NMR spectra of 1b.
Figure S17. $^{13}$C NMR spectra of 1b.

Figure S18. $^1$H NMR spectra of 2a.
Figure S19. $^{13}$C NMR spectra of 2a.

Figure S20. $^1$H NMR spectra of 2b.
Figure S21. $^{13}$C NMR spectra of 2b.

Figure S22. $^1$H NMR spectra of 3a.
Figure S23. $^{13}$C NMR spectra of 3a.

Figure S24. $^1$H NMR spectra of 3b.
Figure S25. $^{13}$C NMR spectra of 3b.

Figure S26. $^1$H NMR spectra of P1.
Figure S27. $^1$H NMR spectra of P2.

Figure S28. $^1$H NMR spectra of P3.
Figure S29. $^1$H NMR spectra of P4.

Figure S30. $^1$H NMR spectra of P5.
References
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