Electronic Supplementary Information for
Unlocking the Action Mechanisms of Molecular Nonlinear Optical Absorption
for Optical Conjugated Polymers under Aggregation States

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1. **Materials**

tetrakis(triphenylphosphine)palladium(0) (99.5%), 3,6-dibromo-9H-carbazole (99%), 1-bromohexane (99%), anhydrous potassium carbonate (98%), tetrabutylammonium bromide (98%), bromobenzene (98%) were purchased from Adamas. 2,5-dibromo-3,4-dinitrothiophene (98%) (M2) was used as received from Puyang Huicheng Electronic Material Co. Ltd. 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (M1) (99%) was purchased from Derthon Optoelectronic Materials Science Technology Co LTD (Shenzhen, China). All the reactions were carried out under nitrogen atmosphere. All organic solvents were purchased from commercial sources and were carefully dried and distilled prior to use.

2. **Syntheses and Characterization of Compounds**

2.1 **Synthesis of 3,6-dibromo-9-hexyl-9H-carbazole**

Under argon atmosphere, 3,6-dibromo-9H-carbazole (13.00 g, 0.04 mol), powdered anhydrous potassium carbonate (11.06 g, 0.08 mol), anhydrous acetonitrile (160 mL) and 1,10-dibromodecane (6.60 g, 0.04 mol) were placed in a reaction flask fitted with a condenser. The reaction was refluxed at 95 °C for 36 h and the argon atmosphere was maintained throughout the reaction. After cooling to room temperature, the precipitation was filtered, and the solvent was removed under reduced pressure to get crude product. The crude product was recrystallized from petroleum ether to give white crystals (8.67 g, Yield 53%). ^1H NMR (500 MHz, CDCl₃, δ): 8.09 (s, 2 H, Ar–H), 7.51 (d, J = 8.9 Hz, 2 H, Ar–H), 7.24 (d, J = 8.9 Hz, 2 H, Ar–H), 4.18 (t, J = 7.6 Hz, 2 H, –NCH₂), 1.79 (m, 2 H), 1.28 (m, 6 H), 0.83 (t, J
=9.0 Hz, 3 H, –CH\textsubscript{3}). \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}, δ): 139.1, 129.1, 123.4, 123.2, 112.1, 110.6, 43.4, 31.3, 28.9, 26.7, 22.5, 13.9. Anal. Calcd. For C\textsubscript{22}H\textsubscript{26}Br\textsubscript{3}N: C, 52.84; H, 4.68; N, 3.42. Found: C, 52.67; H, 4.82; N, 3.49.

2.2 Calculation of the actual composition in the main chain of polymers

The actual proportion of donor unit (the copolymer unit from M1 and M3) and acceptor unit (the copolymer unit from M1 and M2) in D1–D2–D1–A-type OCPs could be measured by \textsuperscript{1}H NMR. The characteristic peak \textit{a} at about 4.40 ppm belongs to -NCH\textsubscript{2}, the characteristic peak \textit{b} at about 1.60–0.80 ppm is attributed to –CH\textsubscript{2} for D-A-type OCPs (see Figure S6–S10). Therefore, the proportion of donor unit and acceptor unit could be calculated by the integration area ratio of \textit{a} and \textit{b} peak. The \(x\) and \(y\) values were calculated according to the given equation:

\[
X+Y=1, \quad \frac{I_b}{I_a} = \frac{(4X+2X+4Y)}{2X}
\]

The calculation results were listed in the following table S1.

“\(x\)” refer to the proportion of donor unit in the main chain of polymers, “\(y\)” refer to the proportion of acceptor unit in the main chain of D1–D2–D1–A-type OCPs. “\(I_b/I_a\)” is the integration area ratio of \textit{b} and \textit{a} peak in the \textsuperscript{1}H NMR spectra of \(P_{0.05}, P_{0.1}, P_{0.2}, P_{0.3}, P_{0.4}\).
<table>
<thead>
<tr>
<th>Polymer</th>
<th>The integration area ratio of a and b peak ($I_b/I_a$)</th>
<th>x and y value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{0.05}</td>
<td>3.17</td>
<td>x = 0.92, y = 0.08</td>
</tr>
<tr>
<td>P_{0.1}</td>
<td>3.44</td>
<td>x = 0.82, y = 0.18</td>
</tr>
<tr>
<td>P_{0.2}</td>
<td>3.67</td>
<td>x = 0.75, y = 0.25</td>
</tr>
<tr>
<td>P_{0.3}</td>
<td>4.28</td>
<td>x = 0.61, y = 0.39</td>
</tr>
<tr>
<td>P_{0.4}</td>
<td>5.17</td>
<td>x = 0.48, y = 0.52</td>
</tr>
</tbody>
</table>

Figure S1. Synthesis of D1–D2-type, D1–A-type and D1–D2–D1–A-type OCPs
**Figure S2.** The $^1$H NMR spectra of 3,6-dibromo-9-hexyl-9$H$-carbazole. (500 MHz, CDCl$_3$)

**Figure S3.** The $^{13}$C NMR spectra of 3,6-dibromo-9-hexyl-9$H$-carbazole. (500 MHz, CDCl$_3$)
Figure S4. The $^1$H NMR spectra of $P_0$ (D1-D2 type OCPs). (500 MHz, CDCl$_3$)

Figure S5. The $^1$H NMR spectra of $P_{0.05}$ (D1–D2–D1–A-type OCPs). (500 MHz, CDCl$_3$)
**Figure S6.** The $^1$H NMR spectra of P$_{0.1}$ (D1–D2–D1–A-type OCPs). (500 MHz, CDCl$_3$)

**Figure S7.** The $^1$H NMR spectra of P$_{0.2}$ (D1–D2–D1–A-type OCPs). (500 MHz, CDCl$_3$)
Figure S8. The $^1$H NMR spectra of $P_{0.3}$ (D1–D2–D1–A-type OCPs). (500 MHz, CDCl$_3$)

Figure S9. The $^1$H NMR spectra of $P_{0.4}$ (D1–D2–D1–A-type OCPs). (500 MHz, CDCl$_3$)
Figure S10. The $^1$H NMR spectra of P$_1$ (D1-A type OCPs). (500 MHz, CDCl$_3$)

3. Supplementary Figures of Compounds.

Figure S11. TGA thermograms of the OCPs at a ramp rate of 10 °C/min in nitrogen flow.
Figure S12. DSC curves of $P_0$, $P_{0.1}$, $P_{0.4}$, $P_1$ at a ramp rate of 10 °C/min in nitrogen flow.

For the intermolecular BLA parameter is defined as $\delta_1$ where $d_m$ (m=b-f) denotes the length of each CC bond in the ring. Similarly, BLA parameter in thiophene unit is defined as $\delta_2$. The BLA parameters reflect the degrees of conjugation of the conjugated ring, because they provide a direct measurement of differences in length between single and double CC bonds that involved.

![Diagram](image)

\[
d_i = 0.25(d_b + d_c + d_d + d_e)
\]

\[
\delta_1 = \frac{d_e - d_i}{(d_e + d_i)/2}
\]

\[
d_2 = 0.5(d_f + d_h)
\]

\[
\delta_2 = \frac{d_f - d_2}{(d_f + d_2)/2}
\]
Figure S14. Illustrations of (a) simulation model of $P_{0.1}$ in THF solutions with the definition of the end to end distance $L$ and the numeric labels (1-8) of the eight inter-unit C-C linkage for evaluation of torsion angles ($\theta$) and BLA ($\delta$) and (b) selected snapshots (A-I) with some typical conformations along (c) molecular dynamics trajectories with different concentrations (10 mg/ml and 20 mg/ml) and different initial settings with (double) and without (single) consideration of inter-chain interactions in the simulation box with periodic boundary conditions.
Figure S15. The PL spectra of P_{0.1} under different concentrations (0.3 mg/mL, 10 mg/mL, 20 mg/mL)

Figure S16. Time-resolved fluorescence decay curves of P_{0.1} dilute solution (0.3 mg/mL) at 420 nm and 450 nm
Figure S17. Open-aperture Z-scan curves of $P_{0.1}$ in 0.3 mg/mL THF solution

$a$ $b$

Figure S18. (a) Open-aperture Z-scan curves of pure $P_0$, $P_{0.1}$ and $P_1$ film at 532 nm with 4-ns pulses; (b) Normalized UV-vis spectra of pure $P_0$, $P_{0.1}$ and $P_1$ films. The solid films were obtained by spin-coating 10 mg/mL polymer solution in THF onto quartz glass slide with a spinning rate of 500 rpm.
Figure S19. Normalized PL spectrum of pure P$_{0.1}$ film.

Figure S20. Open-aperture Z-scan curves of OCPs/PMMA composite films doped with a) 0%, b) 0.03% and c) 0.08% mass fraction

Figure S21. Open-aperture Z-scan curves of OCPs/PS composite films doped with a) 0%, b) 0.01%, c) 0.03%, d) 0.05%, e) 0.08%, f) 0.1%, g) 0.3% mass fraction
Figure S22. The normalized ABS spectra of PMMA pure solid film

Figure S23. The normalized PL spectra of OCPs/PS composite films doped with 0.01%, 0.05%, 0.1% and 0.3% mass fraction

Table S2. The Nonlinear Absorption Coefficient of the OCPs in 20 mg/mL THF Solution

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Nonlinear Absorption Coefficient (10^{-10} m/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S3. Details of various simulation models used in NVT MD simulations with PCFF at 298 K.

Table S4. The fluorescence lifetime and QY of different concentrations and their ratio.
The fluorescence lifetime for the emission wavelength at 450 nm, average lifetime $\tau$ calculated by the equation $\tau_a = A_1\tau_1 + A_2\tau_2$, $A_1$ and $A_2$ is the percentage of fluorescence lifetime $\tau_1$ and $\tau_2$ respectively. $\Phi_F = $ fluorescence quantum yield determined using a calibrated integrating sphere.

**Table S5.** The QY of the polymeric solid films

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Phi_F$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>2.17</td>
</tr>
<tr>
<td>P0.05</td>
<td>1.93</td>
</tr>
<tr>
<td>P0.1</td>
<td>1.65</td>
</tr>
<tr>
<td>P0.2</td>
<td>1.21</td>
</tr>
<tr>
<td>P0.3</td>
<td>/</td>
</tr>
<tr>
<td>P0.4</td>
<td>/</td>
</tr>
<tr>
<td>P1</td>
<td>/</td>
</tr>
</tbody>
</table>

$\Phi_F = $ fluorescence quantum yield determined using a calibrated integrating sphere (Edinburgh Instruments FLS980).
Table S6. The fluorescence lifetime and QY of P$_{0.1}$/PMMA composite films

<table>
<thead>
<tr>
<th>Doped mass fraction (%)</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$ (%)</th>
<th>$\tau_a$ (ns)</th>
<th>$\Phi_F$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>1.24</td>
<td>4.56</td>
<td>60.50</td>
<td>39.50</td>
<td>2.55</td>
<td>4.92</td>
</tr>
<tr>
<td>0.03</td>
<td>1.21</td>
<td>4.09</td>
<td>60.32</td>
<td>39.68</td>
<td>2.35</td>
<td>5.88</td>
</tr>
<tr>
<td>0.05</td>
<td>1.02</td>
<td>3.67</td>
<td>66.86</td>
<td>33.14</td>
<td>1.90</td>
<td>7.12</td>
</tr>
<tr>
<td>0.08</td>
<td>0.96</td>
<td>3.58</td>
<td>73.60</td>
<td>26.40</td>
<td>1.65</td>
<td>8.36</td>
</tr>
<tr>
<td>0.3</td>
<td>0.97</td>
<td>3.44</td>
<td>67.71</td>
<td>32.29</td>
<td>1.77</td>
<td>5.07</td>
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