**One-step rapid synthesis of π-conjugated large oligomers via C–H activation coupling**

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Fig. S1 The molecular structures of Herr Pd, Pd\(_2(dba)_3\), PCy\(_3\) and P(o-MeOPh)\(_3\).

Scheme S1 The Pd-catalyzed DA reaction, the reduction of Pd\(^{II}\) pre-catalyst to Pd\(^0\) catalytic species, the catalytic cycle of the DA coupling, and the palladation of C-H bond.
Fig. S2 The reaction between DPP and \( p \)-dibromobenzene with and without ligand \( \text{P(o-MeOPh)}_3 \) using toluene as reaction medium (entries 10 and 11 in Table 1). Digital photos of (a) The reaction mixtures after reacting for 12 h and cooling to room temperature. (b) The TLC analysis of both reaction mixtures, using \( \text{CH}_2\text{Cl}_2 : \text{hexane (2:1, v/v)} \) as eluent, and the spots marked with green and red frame are the reactant DPP and target product \( \text{p-B(DPP)}_2 \), respectively.

Fig. S3 The TLC analysis of the reactions between DPP and \( p \)-dibromobenzene (left) or \( p \)-diiodobenzene (right). (see Entries 12 and 13 in Table 1). The spots marked with green and red frame are the reactant DPP and target product \( \text{p-B(DPP)}_2 \), respectively.
Fig. S4 Digital photos of TLC analysis of the synthetic reactions for the eight oligomers. From left to right are respectively \( p\)-B-(DPP)\(_2\), \( m\)-B-(DPP)\(_2\), \( o\)-B-(DPP)\(_2\), DPP-DPP-DPP, TB-(DPP)\(_3\), Py-(DPP)\(_4\), TBE-(DPP)\(_4\) and SF-(DPP)\(_4\). For all the TLC plates, the spots on the left are the starting DPP, and the spots marked with red dotted frames are the target oligomers.
**Fig. S5** The shortest pathways of π-electron delocalization (marked with blue color) of the phenyl-cored DPP-based oligomers *o*-B-(DPP)$_2$, *m*-B-(DPP)$_2$, *p*-B-(DPP)$_2$ and TB-(DPP)$_3$, and the corresponding normalized UV-vis spectra (below).
Fig. S6 DFT optimized geometries of phenyl-cored DPP-based oligomers, $o$-$B$-(DPP)$_2$, $m$-$B$-(DPP)$_2$, $p$-$B$-(DPP)$_2$ and $TB$-(DPP)$_3$ (the alkyl chains replaced by methyl groups).
Fig. S7 The shortest pathways of π-electron delocalization (marked with blue color) of the Py-, TBE- and SF-(DPP)$_4$ oligomers, and the corresponding normalized UV-vis spectra (below).
Fig. S8 The Uv-vis spectra of the starting DPP, oligomers o-B-(DPP)$_2$, m-B-(DPP)$_2$, p-B-(DPP)$_2$, Py-(DPP)$_4$, TBE-(DPP)$_4$ and SF-(DPP)$_4$ in CHCl$_3$ at concentrations of 4.54, 2.54, 2.03, 1.55, 2.16, 1.89, 1.07, 1.69 and 1.27 × 10$^{-5}$ mol/L.

<table>
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<th>DPP</th>
<th>o-B-(DPP)$_2$</th>
<th>m-B-(DPP)$_2$</th>
<th>p-B-(DPP)$_2$</th>
<th>TB-(DPP)$_3$</th>
<th>DPP-DPP-DPP-DPP</th>
<th>Py-(DPP)$_4$</th>
<th>TBE-(DPP)$_4$</th>
<th>SF-(DPP)$_4$</th>
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Table S1 The extinction coefficients of the DPP materials at $\lambda_{\text{max}}$ (×10$^4$ M$^{-1}$ cm$^{-1}$).
Fig. S8 The $^1$H and $^{13}$C NMR spectra of $\mu$-B-(DPP)$_2$ in CDCl$_3$. 
Fig. S9 The $^1$H and $^{13}$C NMR spectra of $m$-B-(DPP)$_2$ in CD$_2$Cl$_2$. 
Fig. S10 The $^1$H and $^{13}$C NMR spectra of $\text{o-B-(DPP)}_2$ in CD$_2$Cl$_2$. 
Fig. S11 The $^1$H and $^{13}$C NMR spectra of DPP-DPP-DPP in CDCl$_3$. 
Fig. S12 The $^1$H and $^{13}$C NMR spectra of TB-(DPP)$_3$ in CDCl$_3$. 

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Fig. S13 The $^1$H and $^{13}$C NMR spectra of Py-(DPP)$_4$ in CD$_2$Cl$_2$. 
Fig. S14 The $^1$H and $^{13}$C NMR spectra of TBE-(DPP)$_4$ in CD$_2$Cl$_2$ and in CDCl$_3$, respectively.
Fig. S15 The $^1$H and $^{13}$C NMR spectra of SF-(DPP)$_4$ in CD$_2$Cl$_2$. 
**Fig. S16** The MALDI-TOF MS spectrum of $p$-B-(DPP)$_2$, calcd. 1572.51, found 1572.43.
**Fig. S17** The MALDI-TOF MS spectrum of \textit{m-B-(DPP)}_2, calcd. 1572.51, found 1572.31.

**Fig. S18** The MALDI-TOF MS spectrum of \textit{o-B-(DPP)}_2, calcd. 1572.51, found 1572.64.
Fig. S19 The MALDI-TOF MS spectrum of **DPP-DPP-DPP**, calcd. 2007.13, found 2007.82.
Fig. S20 The MALDI-TOF MS spectrum of TB-(DPP)$_3$, calcd. 2319.71, found 2319.77.
**Fig. S21** The MALDI-TOF MS spectrum of $\text{Py-(DPP)}_4$, calcd. 3191.05, found 3191.63.
Fig. S22 The MALDI-TOF MS spectrum of TBE-(DPP)$_4$, calcd. 3321.34, found 3321.30.
Fig. S23 The MALDI-TOF MS spectrum of SF-(DPP)$_4$, calcd. 3305.20, found 3305.50.