

## Supplementary Information

### Novel pyrrolo[3,4-*c*]pyrrole-1,3-dione based high crystallinity donor-acceptor polymer semiconductors for organic thin film transistors

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**Figure S1.** 300 MHz <sup>1</sup>H NMR spectrum of diethyl 1*H*-pyrrole-3,4-dicarboxylate (**1**) in CDCl<sub>3</sub>.

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**Figure S4.** 75 MHz <sup>13</sup>C NMR spectrum of 4-((2-octyldodecyl)carbonyl)-1*H*-pyrrole-3-carboxylic acid (**3**) in DMSO-*d*<sub>6</sub>.

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**Figure S6.** 75 MHz <sup>13</sup>C NMR spectrum of 2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**4**) in CDCl<sub>3</sub>.

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**Figure S8.** 75 MHz <sup>13</sup>C NMR spectrum of 2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**5a**) in CDCl<sub>3</sub>.

**Figure S9.** 300 MHz <sup>1</sup>H NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**5b**) in CDCl<sub>3</sub>.

**Figure S10.** 75 MHz <sup>13</sup>C NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**5b**) in CDCl<sub>3</sub>.

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**Figure S12.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-dibromo-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**6a**) in  $\text{CDCl}_3$

**Figure S13.** 300 MHz  $^1\text{H}$  NMR spectrum of 4,6-dibromo-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**6b**) in  $\text{CDCl}_3$

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**Figure S15.** 300 MHz  $^1\text{H}$  NMR spectrum of 2,5-bis(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**7a**) in  $\text{CDCl}_3$

**Figure S16.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 2,5-bis(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**7a**) in  $\text{CDCl}_3$

**Figure S17.** 300 MHz  $^1\text{H}$  NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**7b**) in  $\text{CDCl}_3$

**Figure S18.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**7b**) in  $\text{CDCl}_3$

**Figure S19.** 300 MHz  $^1\text{H}$  NMR spectrum of 4,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**8a**) in  $\text{CDCl}_3$

**Figure S20.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**8a**) in  $\text{CDCl}_3$

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**Figure S22.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-bis(5-bromothiophen-2-yl)-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**8b**) in  $\text{CDCl}_3$

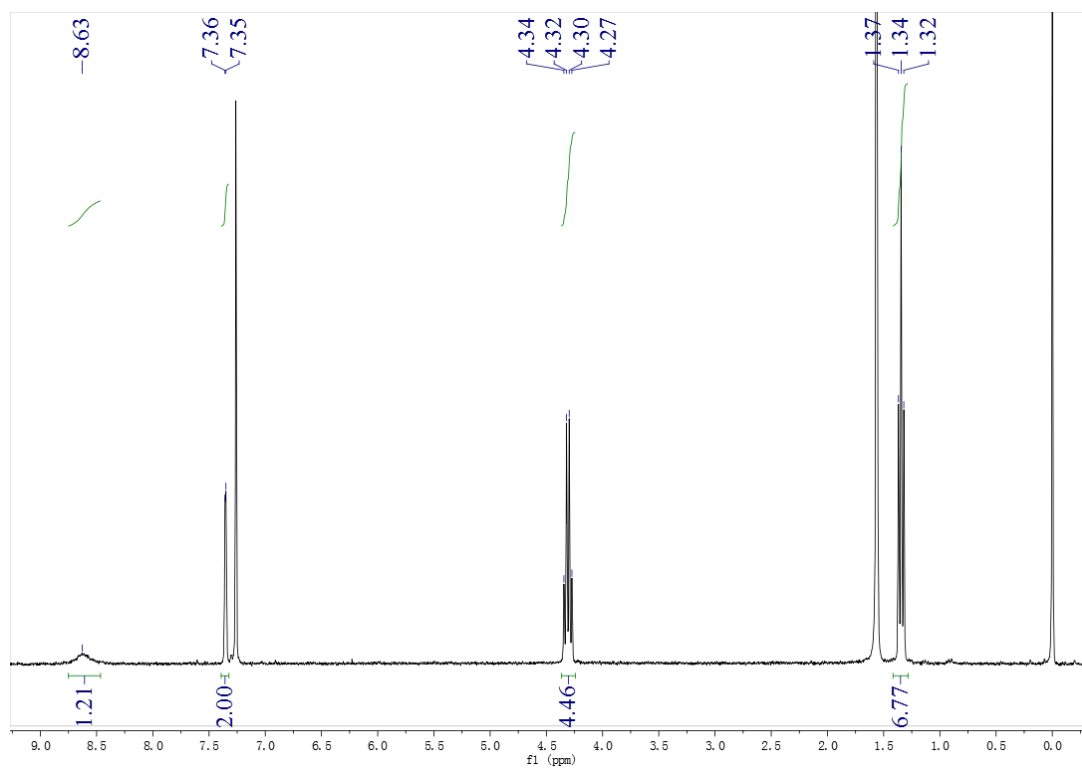
**Figure S23.** 300 MHz  $^1\text{H}$  NMR spectrum of **P1** measured in  $\text{CDCl}_3$ .

**Figure S24.** 300 MHz  $^1\text{H}$  NMR spectrum of **P2** measured in  $\text{CDCl}_3$ .

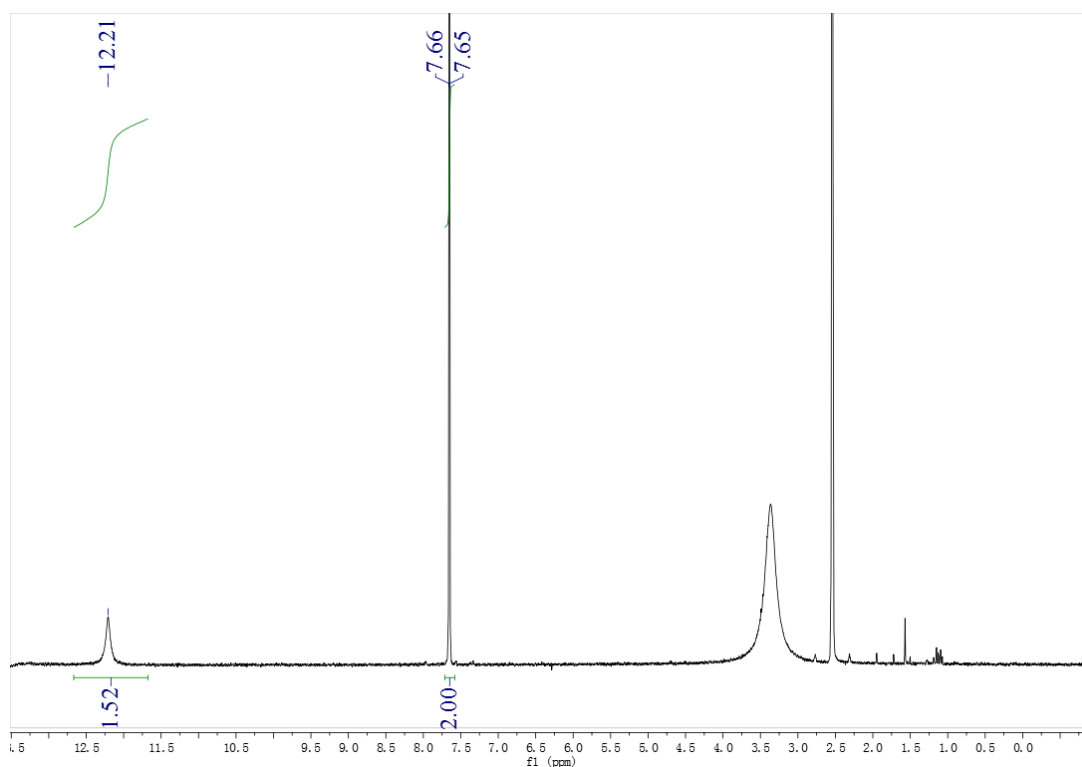
**Figure S25.** TGA curves of **P1**&**P2** with a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  under  $\text{N}_2$ .

# Supplementary Information

## Additional data

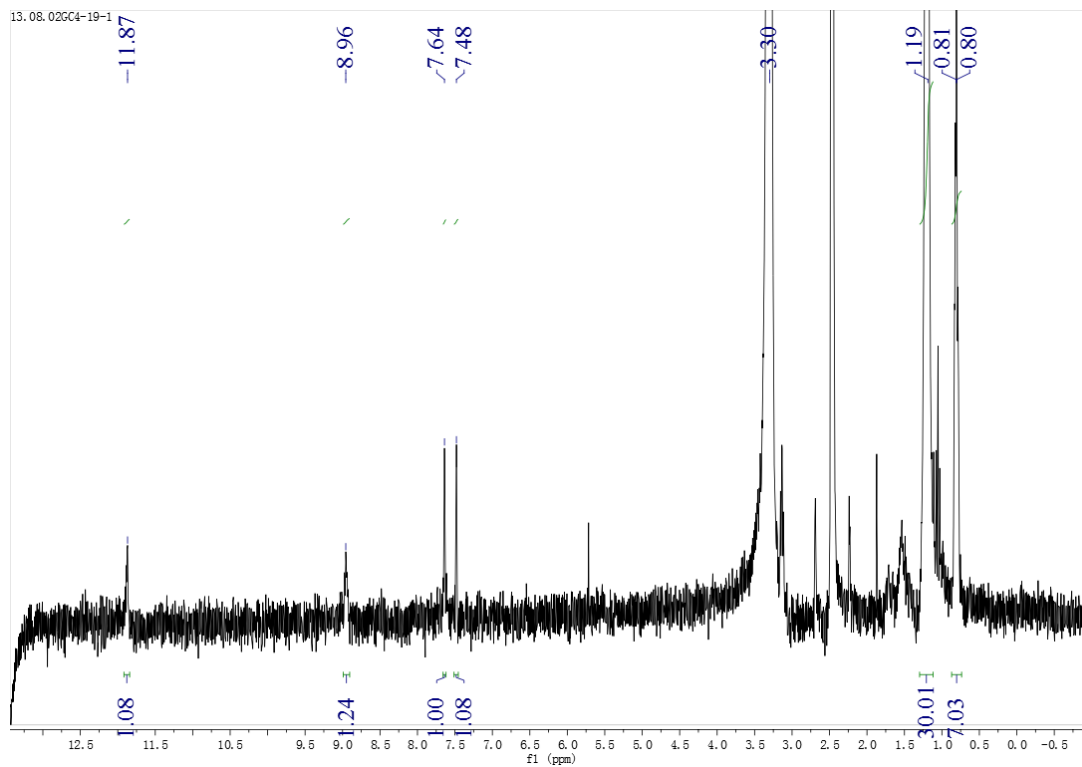


**Figure S1.** 300 MHz  $^1\text{H}$  NMR spectrum of diethyl 1H-pyrrole-3,4-dicarboxylate (**1**) in  $\text{CDCl}_3$ .

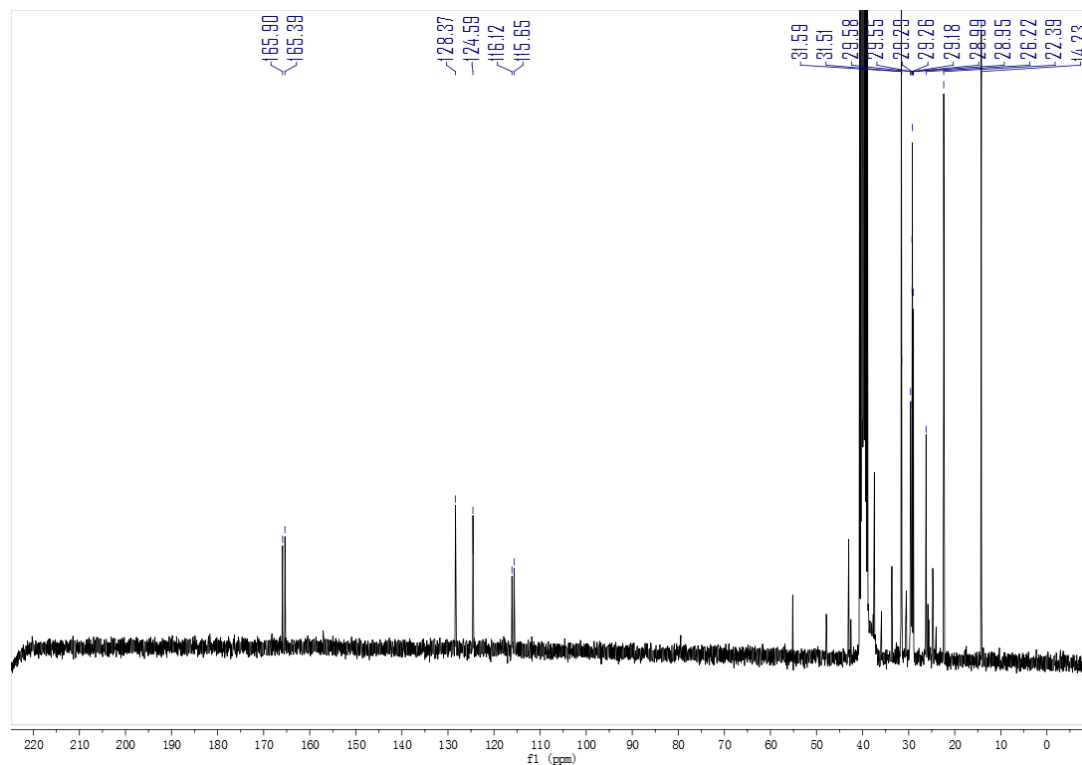


**Figure S2.** 300 MHz  $^1\text{H}$  NMR spectrum of 1H-pyrrole-3,4-dicarboxylic acid (**2**) in  $\text{DMSO-d}_6$ .

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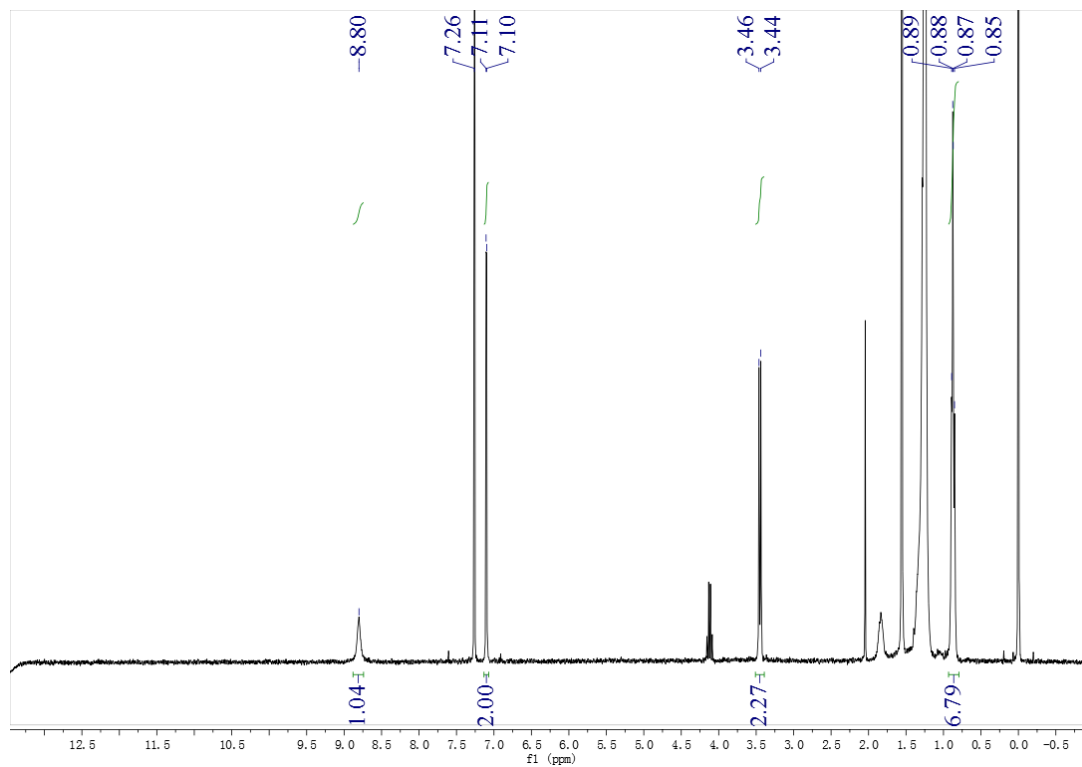


**Figure S3.** 300 MHz  $^1\text{H}$  NMR spectrum of 4-((2-octyldodecyl)carbamoyl)-1H-pyrrole-3-carboxylic acid (3) in DMSO- $d_6$ .

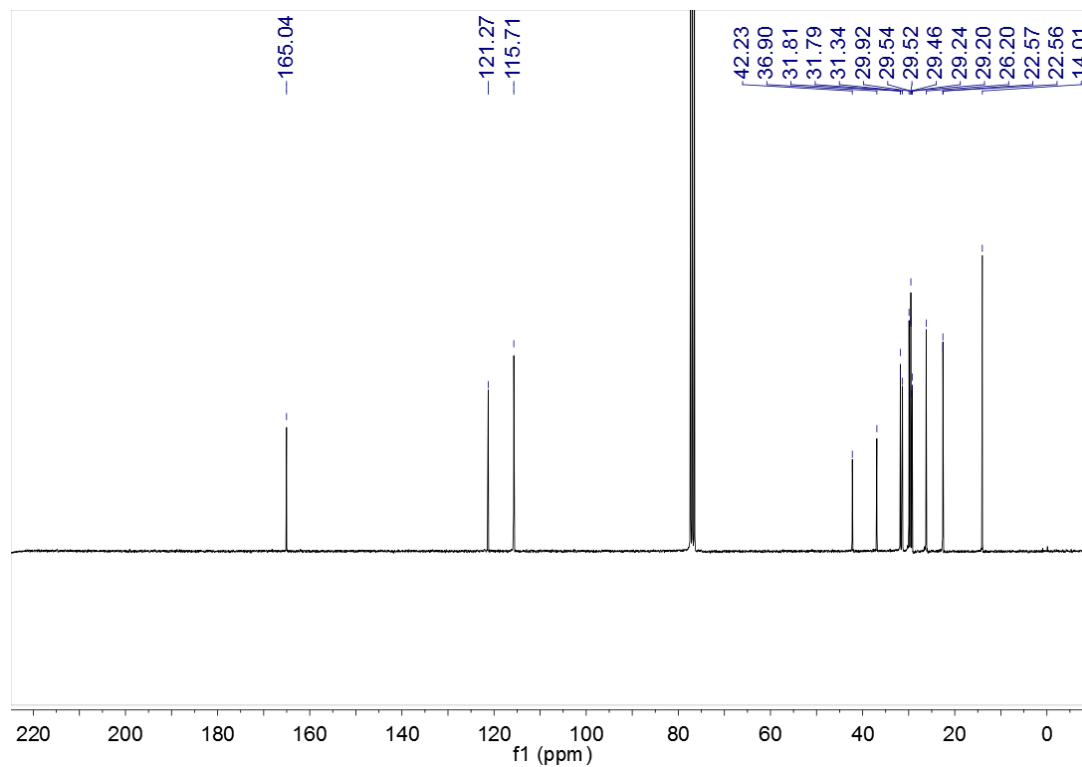


**Figure S4.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4-((2-octyldodecyl)carbamoyl)-1H-pyrrole-3-carboxylic acid (3) in DMSO- $d_6$ .

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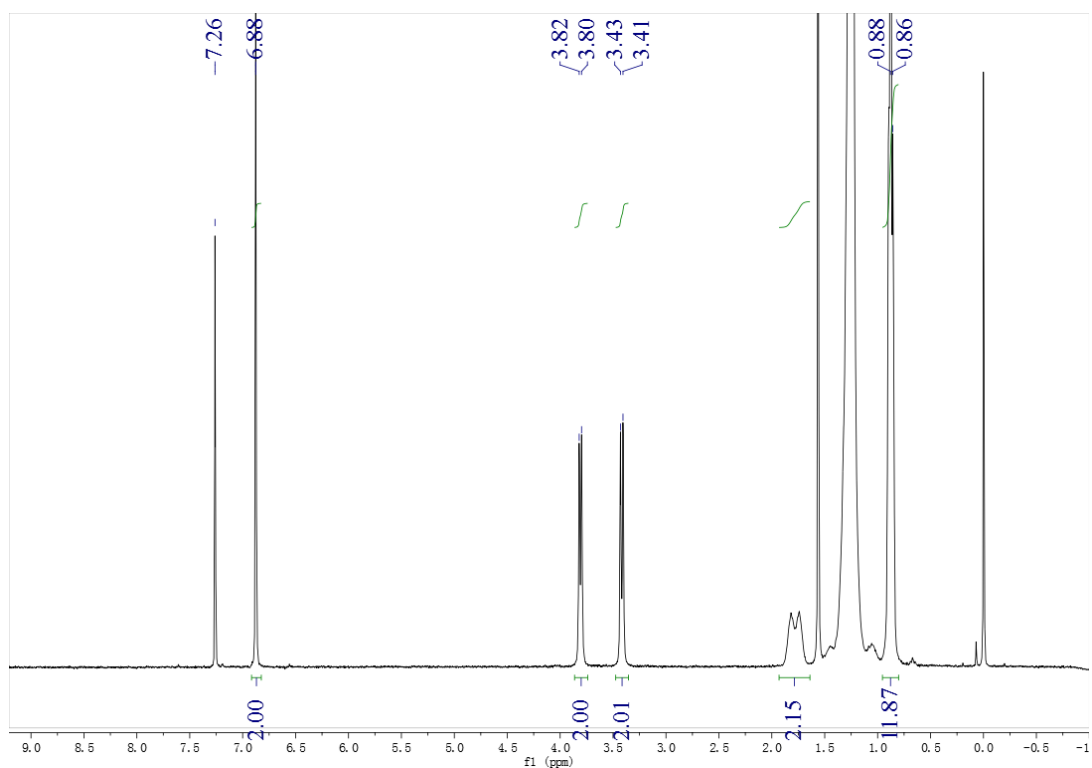


**Figure S5.** 300 MHz  $^1\text{H}$  NMR spectrum of 2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2*H*,5*H*)-dione (**4**) in  $\text{CDCl}_3$ .

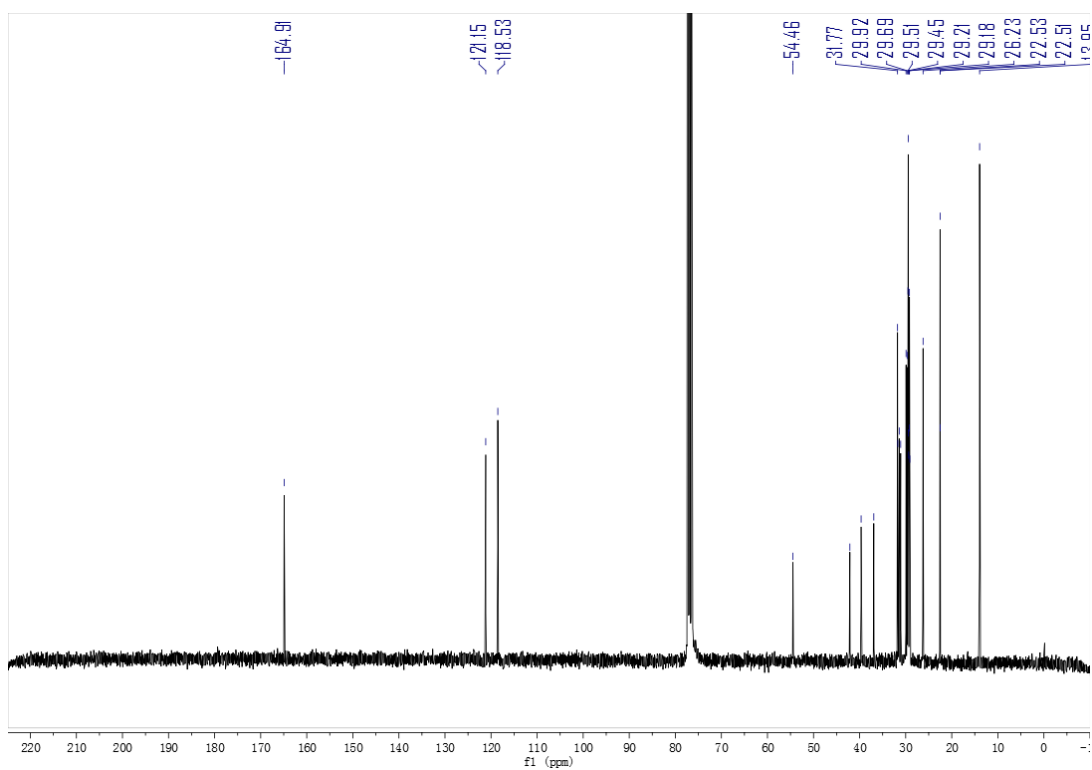


**Figure S6.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2*H*,5*H*)-dione (**4**) in  $\text{CDCl}_3$ .

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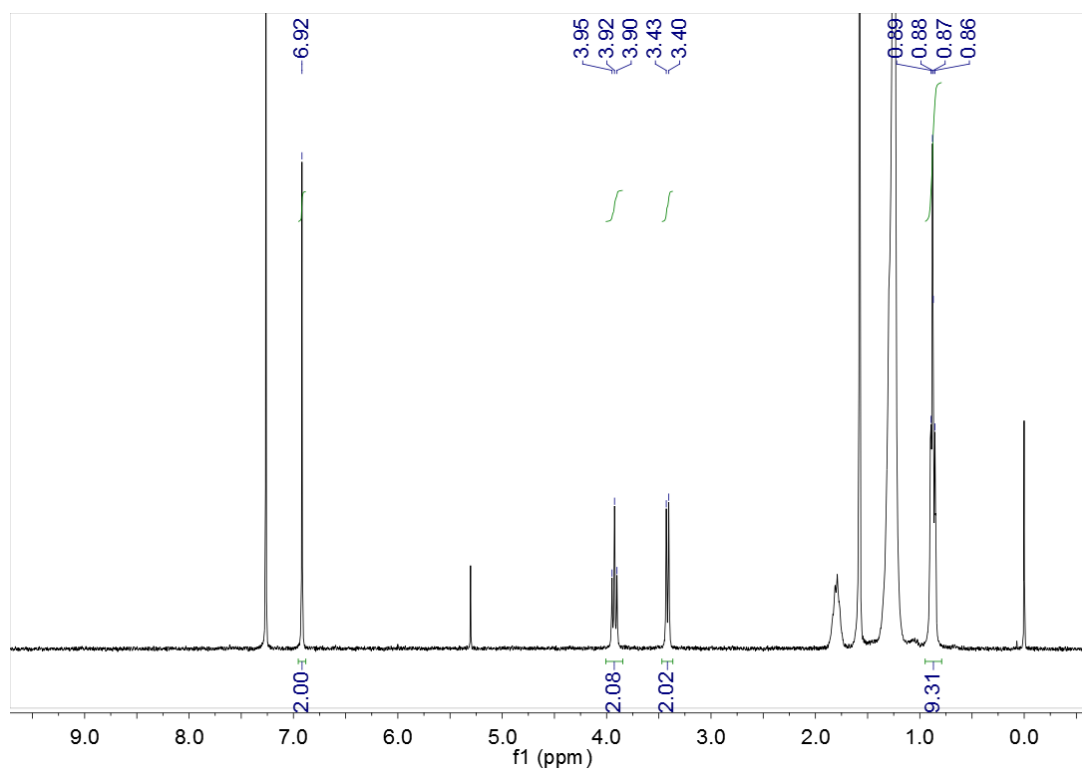


**Figure S7.** 300 MHz <sup>1</sup>H NMR spectrum of 2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2*H*,5*H*)-dione (**5a**) in CDCl<sub>3</sub>.

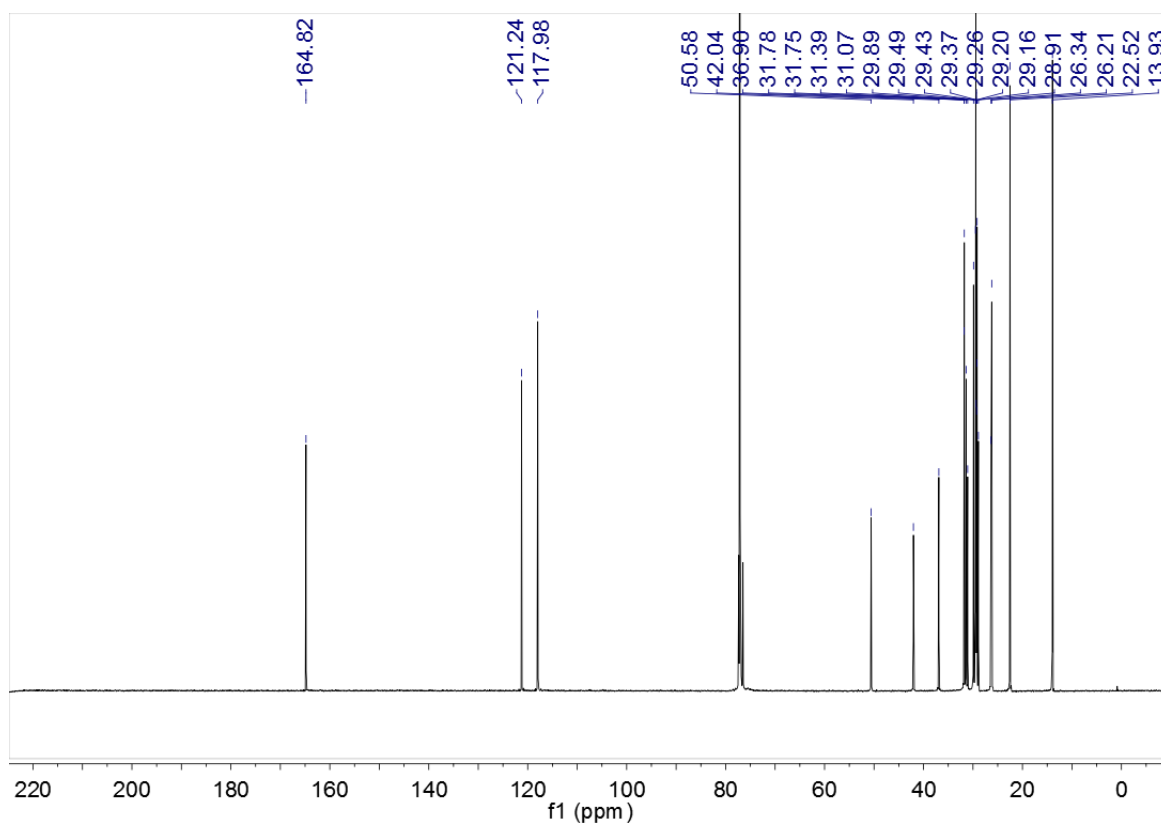


**Figure S8.** 75 MHz <sup>13</sup>C NMR spectrum of 2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2*H*,5*H*)-dione (**5a**) in CDCl<sub>3</sub>.

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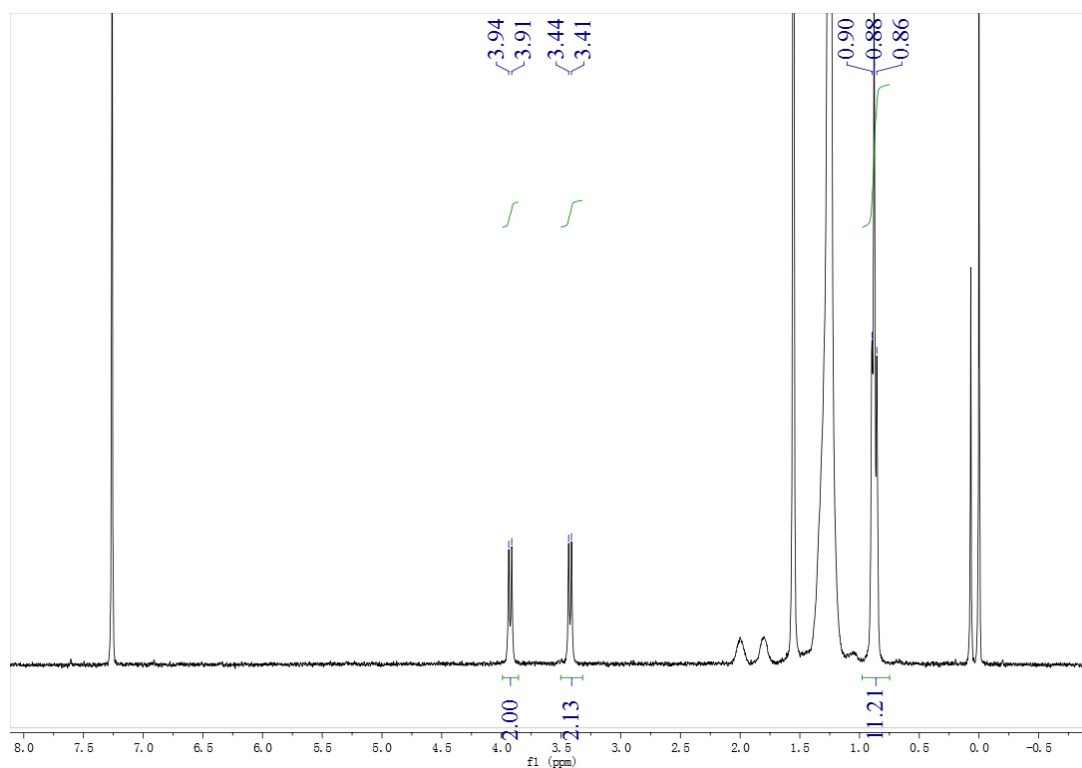


**Figure S9.** 300 MHz  $^1\text{H}$  NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**5b**) in  $\text{CDCl}_3$ .

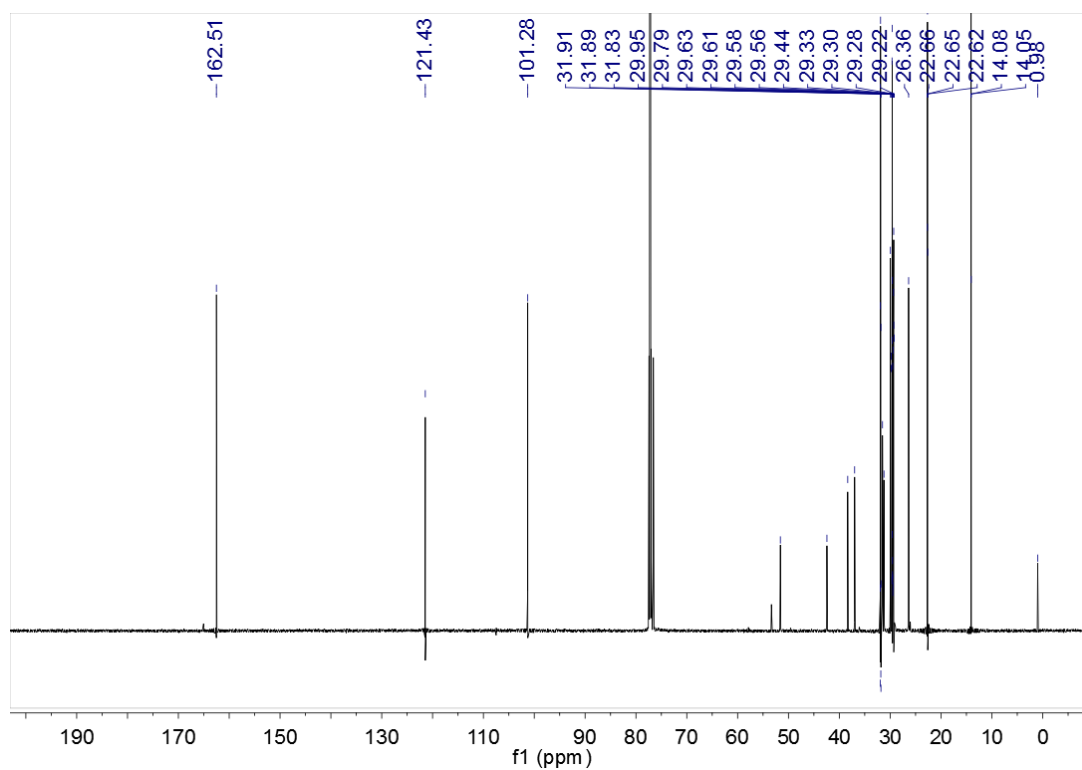


**Figure S10.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**5b**) in  $\text{CDCl}_3$ .

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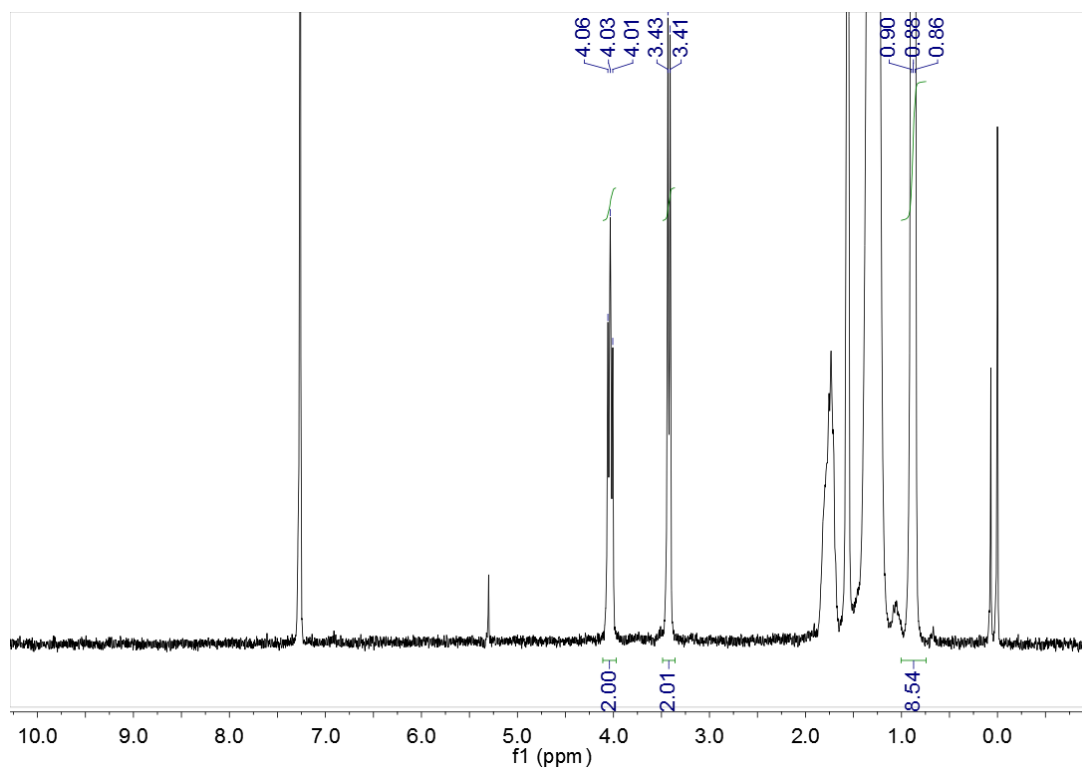
**Figure S11.** 300 MHz  $^1\text{H}$  NMR spectrum of 4,6-dibromo-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**6a**) in  $\text{CDCl}_3$ .



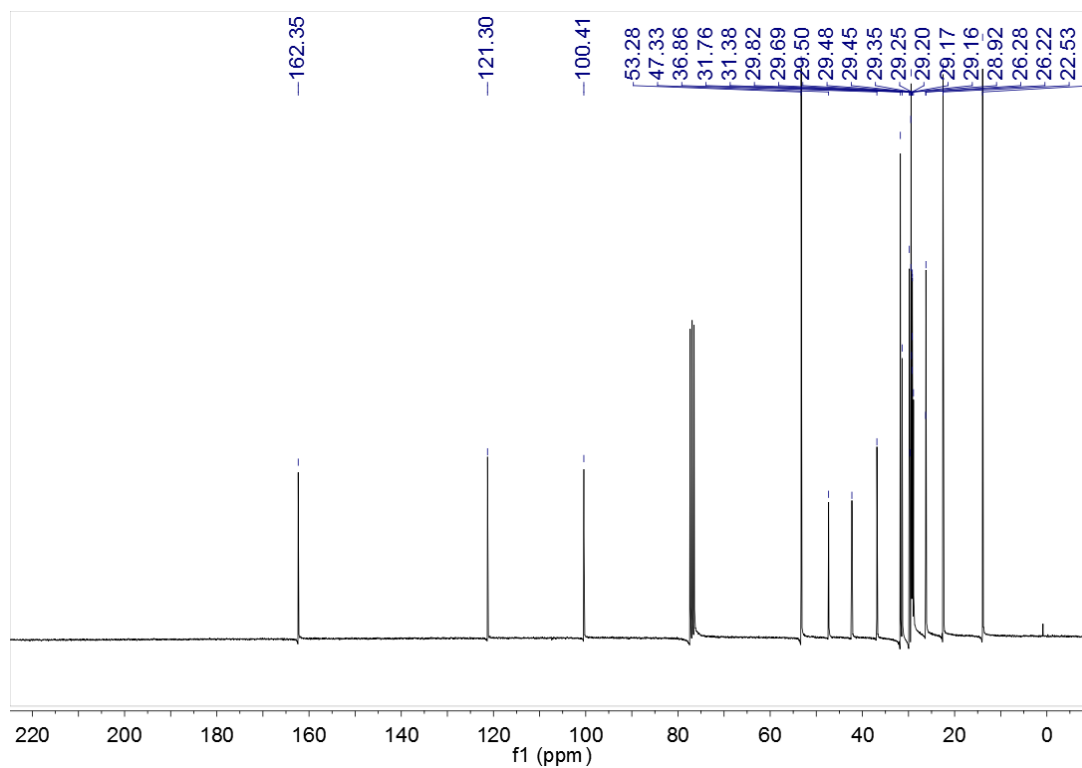
**Figure S12.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-dibromo-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (**6a**) in  $\text{CDCl}_3$ .



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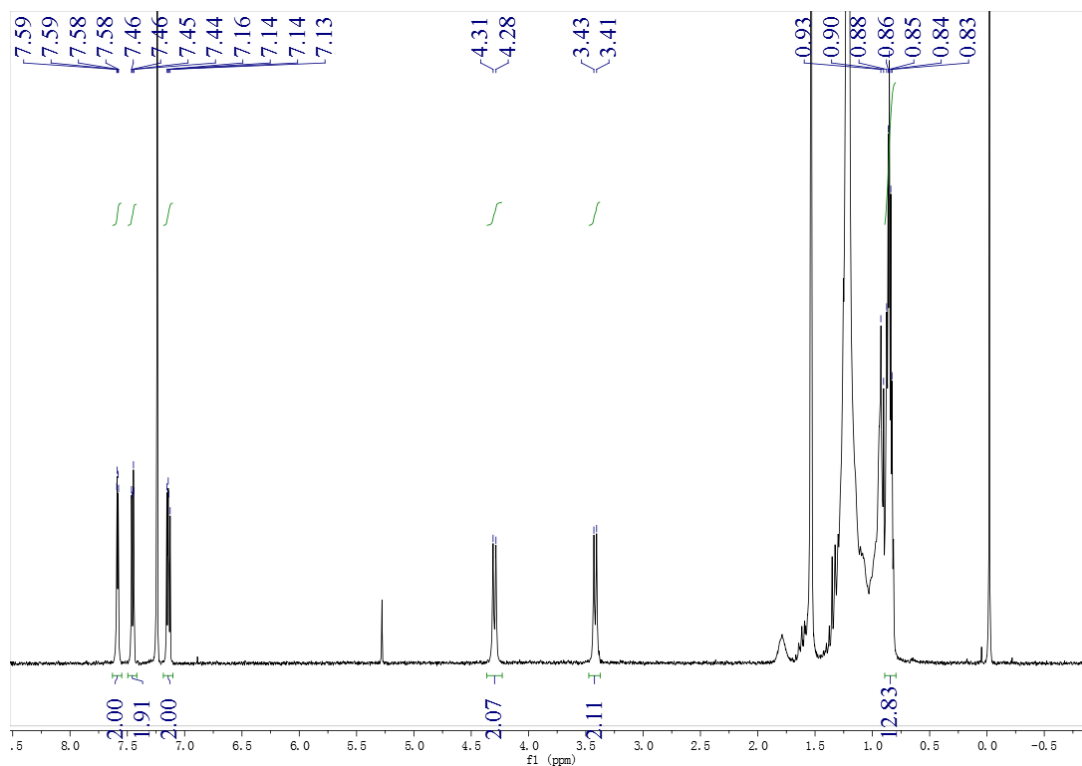


**Figure S13.** 300 MHz  $^1\text{H}$  NMR spectrum of 4,6-dibromo-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**6b**) in  $\text{CDCl}_3$ .

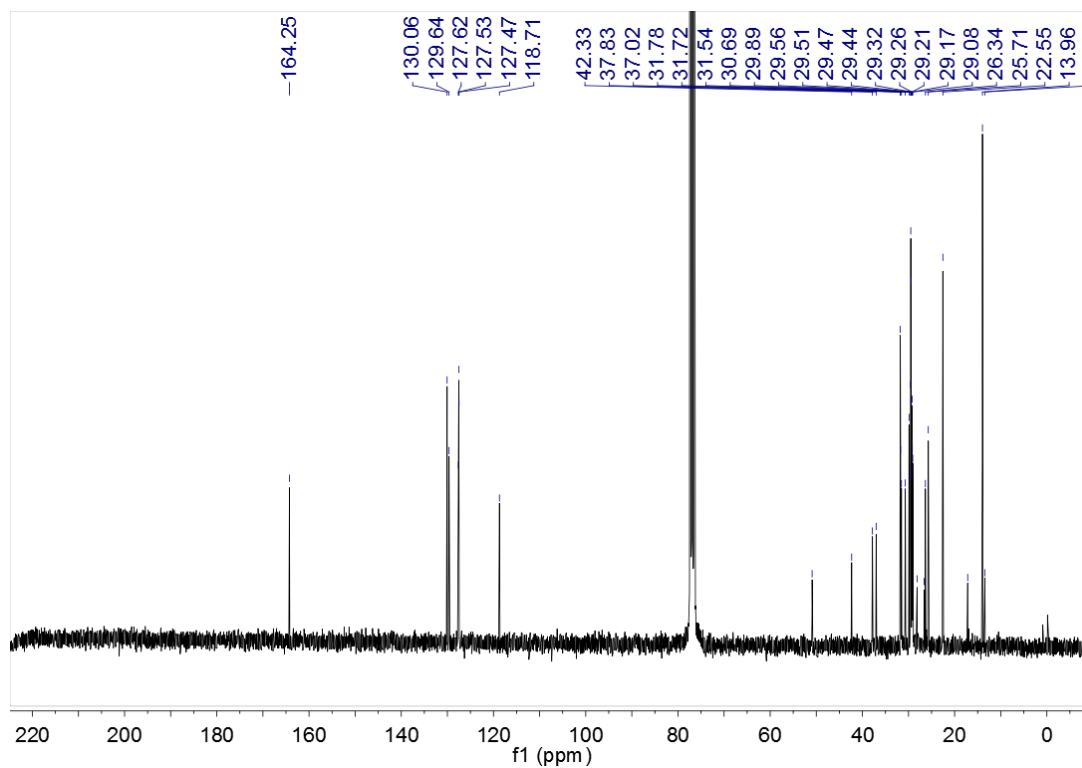


**Figure S14.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-dibromo-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**6b**) in  $\text{CDCl}_3$ .

## Supplementary Information

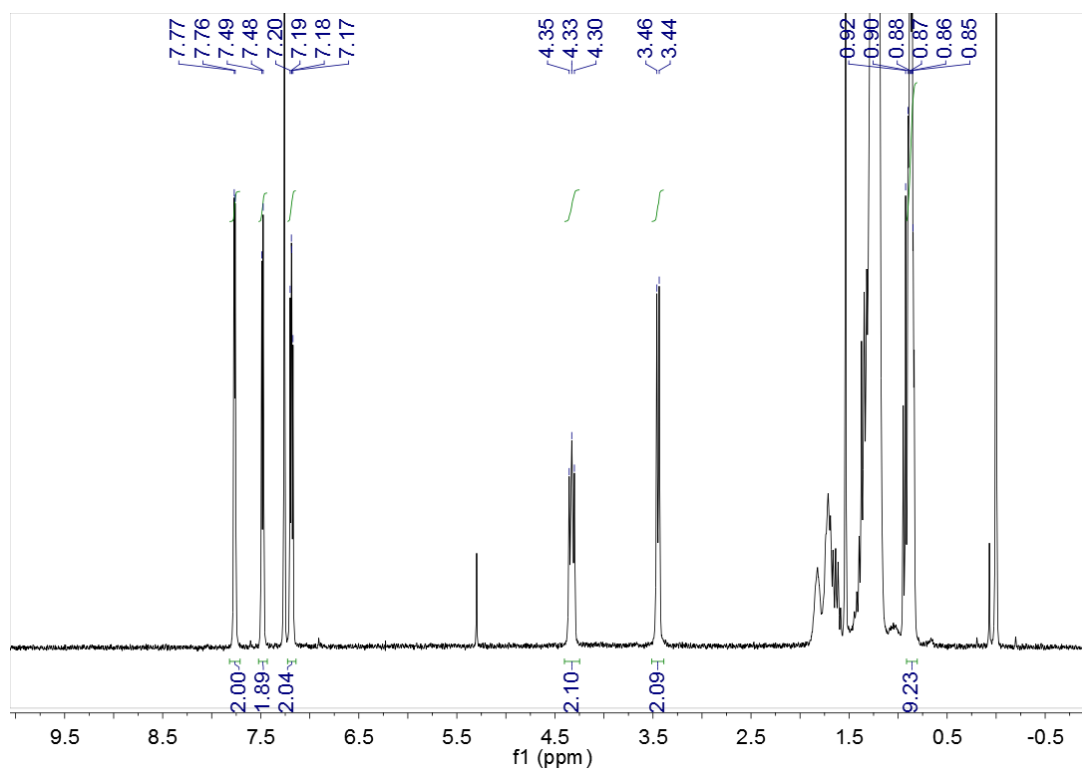


**Figure S15.** 300 MHz  $^1\text{H}$  NMR spectrum of 2,5-bis(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**7a**) in  $\text{CDCl}_3$ .

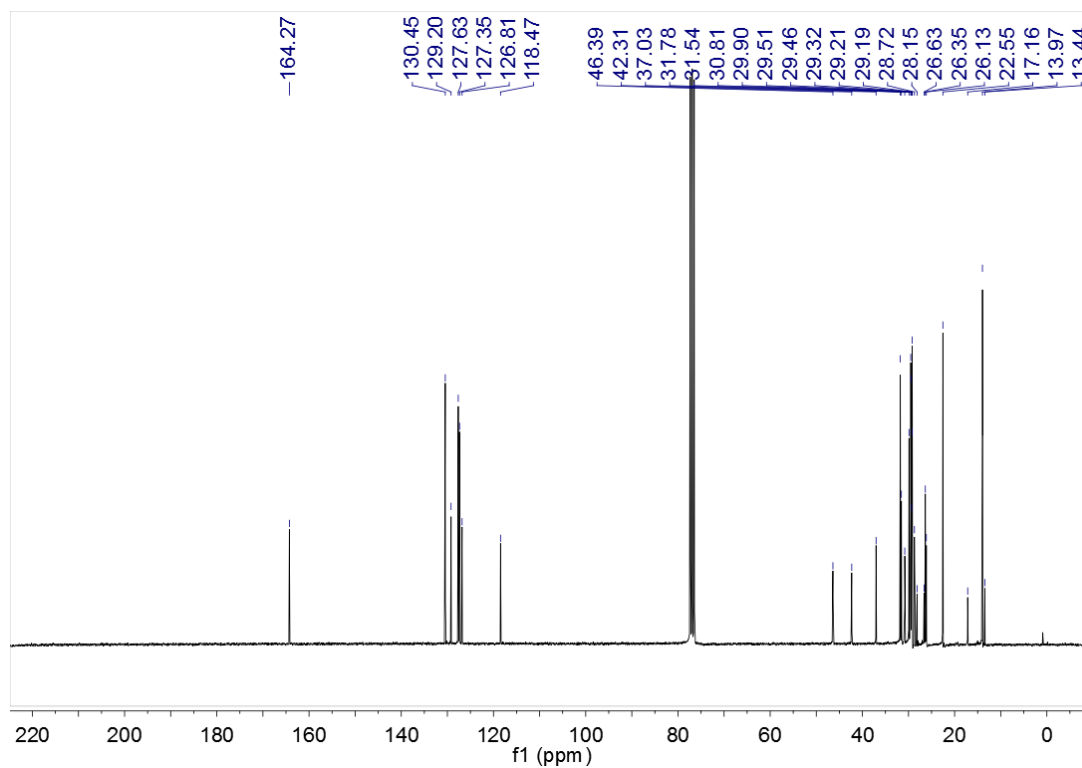


**Figure S16.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 2,5-bis(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**7a**) in  $\text{CDCl}_3$ .

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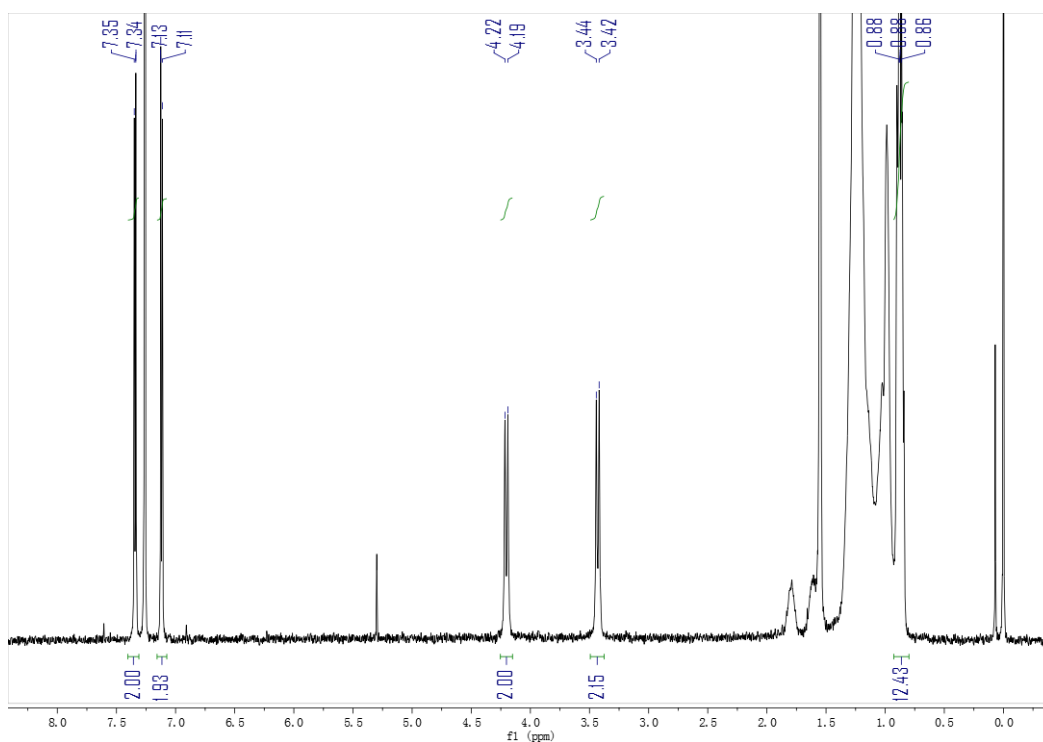


**Figure S17.** 300 MHz  $^1\text{H}$  NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**7b**) in  $\text{CDCl}_3$ .

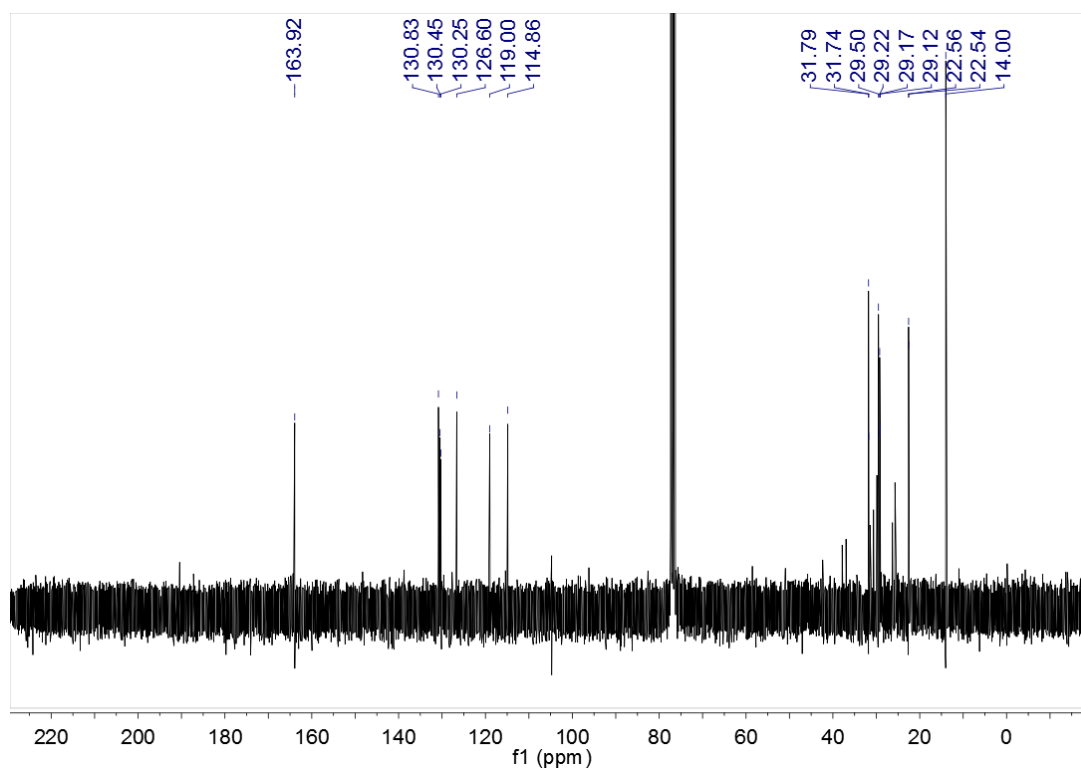


**Figure S18.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 5-dodecyl-2-(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**7b**) in  $\text{CDCl}_3$ .

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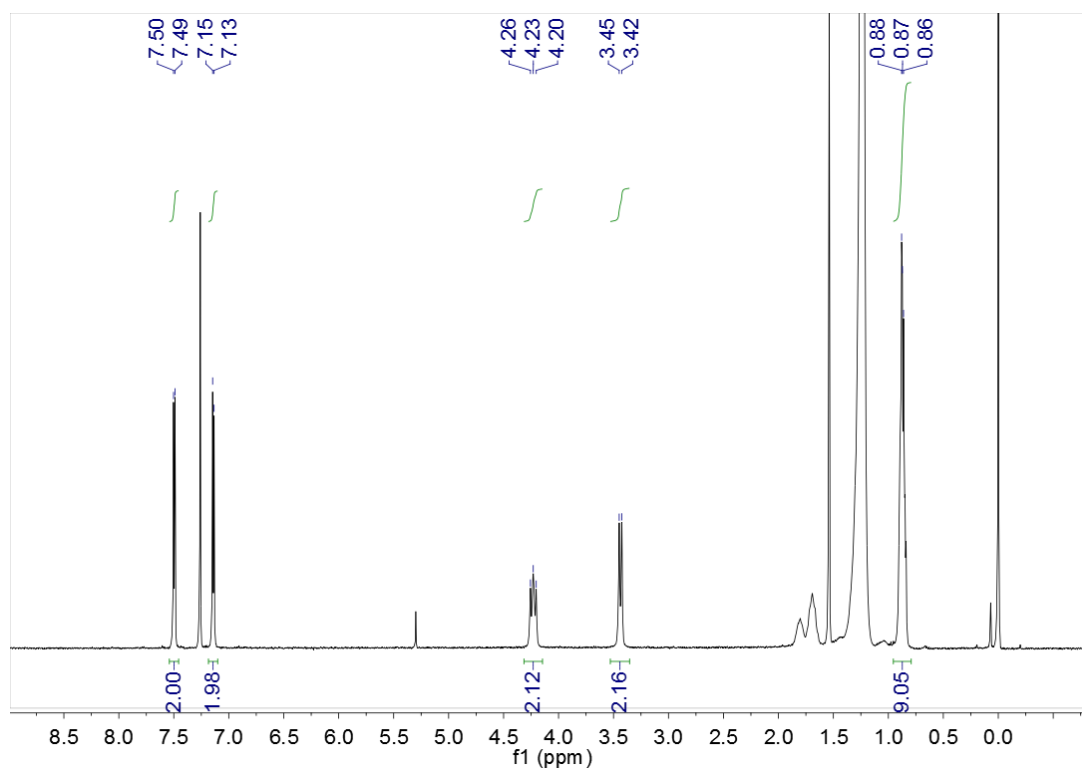


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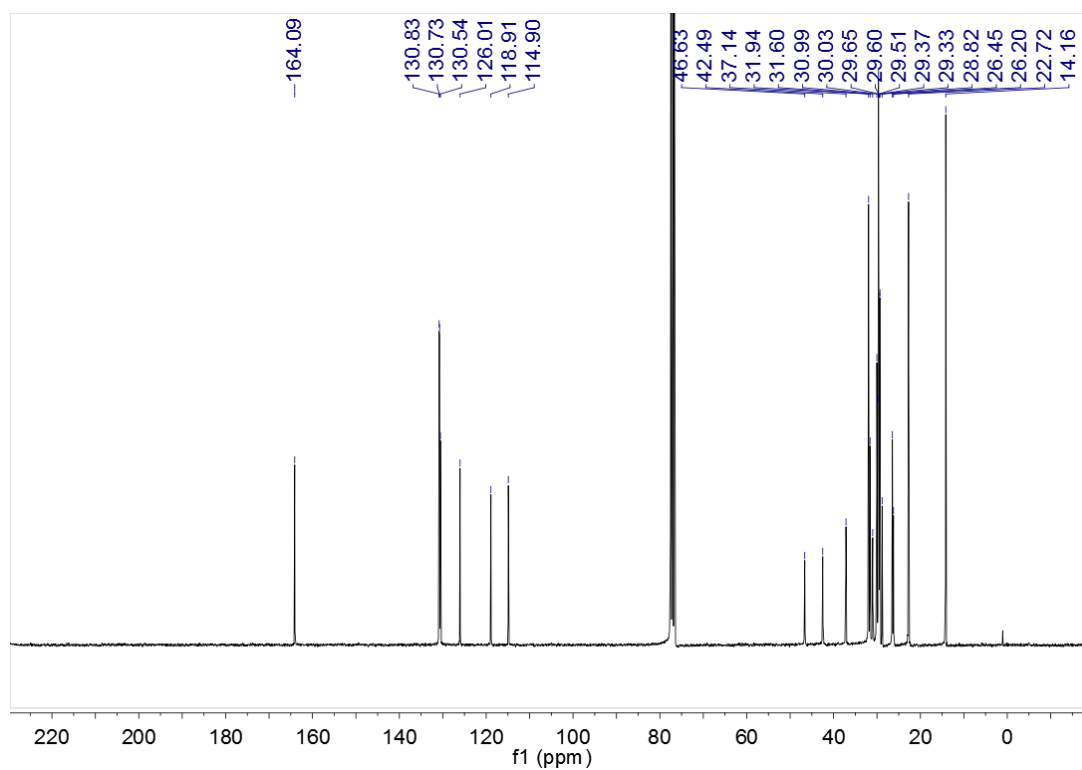


**Figure S20.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**8a**) in  $\text{CDCl}_3$ .

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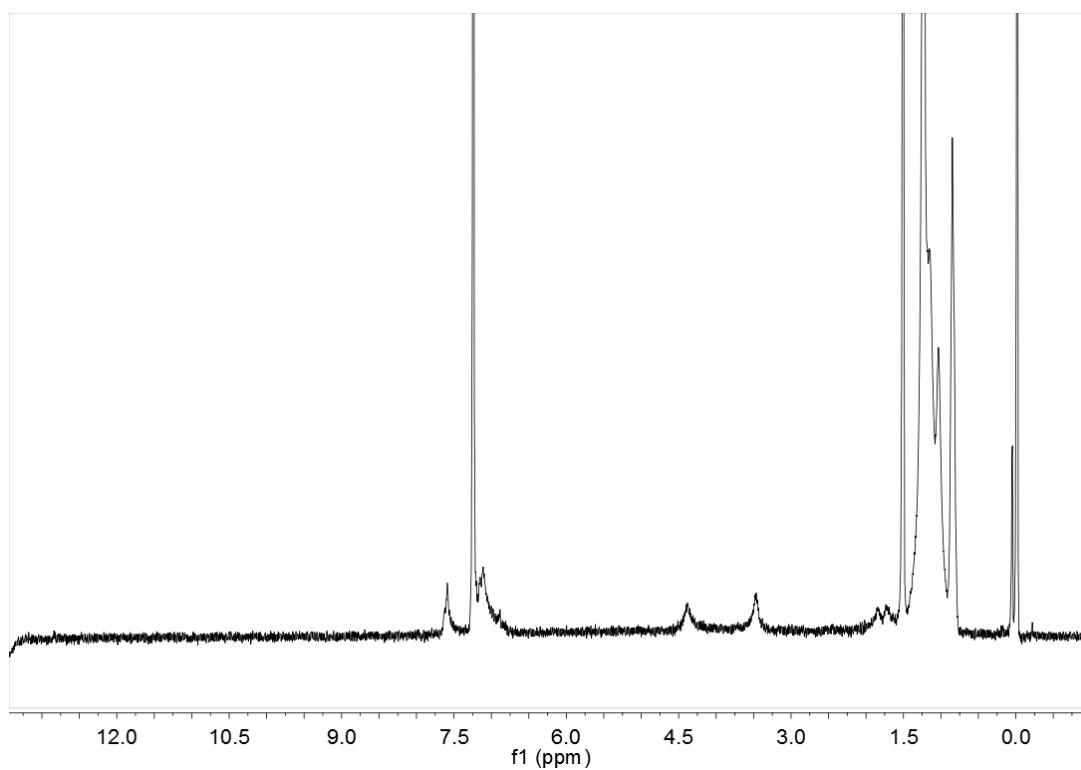


**Figure S21.** 300 MHz  $^1\text{H}$  NMR spectrum of 4,6-bis(5-bromothiophen-2-yl)-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2*H*,5*H*)-dione (**8b**) in  $\text{CDCl}_3$ .

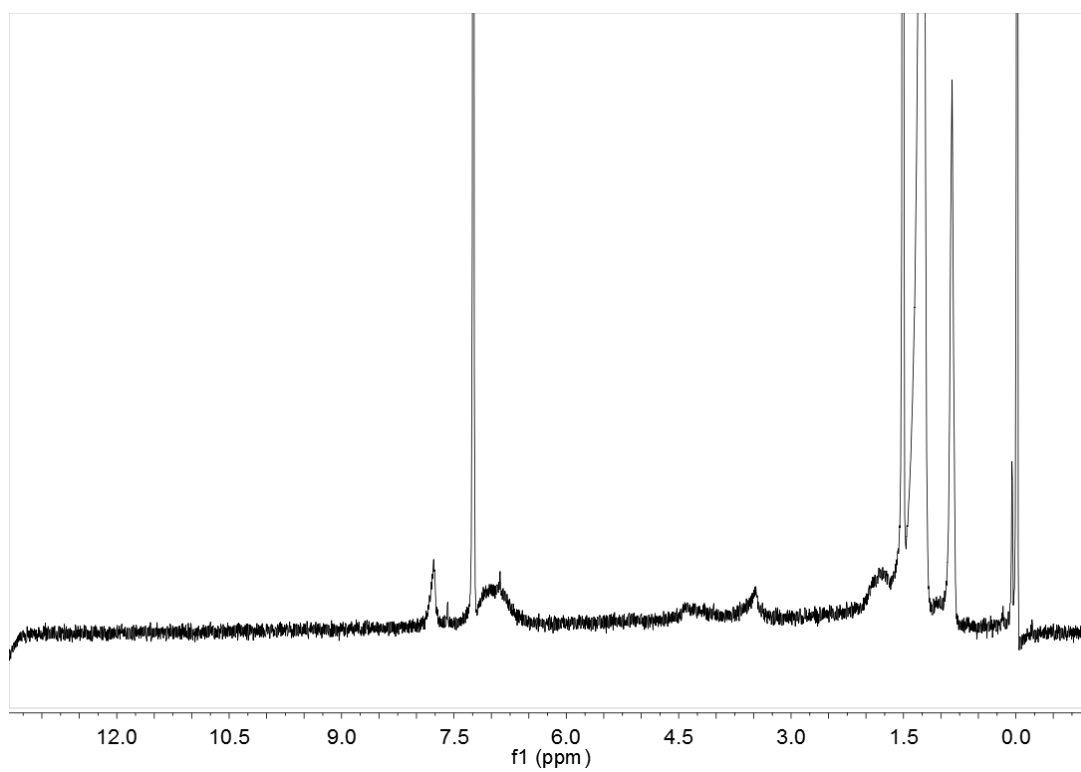


**Figure S22.** 75 MHz  $^{13}\text{C}$  NMR spectrum of 4,6-bis(5-bromothiophen-2-yl)-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,3(2*H*,5*H*)-dione (**8b**) in  $\text{CDCl}_3$ .

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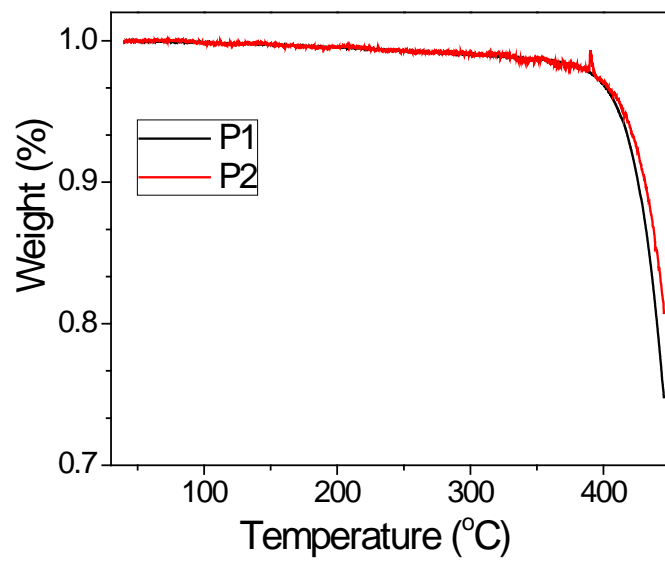


**Figure S23.** 300 MHz  $^1\text{H}$  NMR spectrum of **P1** measured in  $\text{CDCl}_3$ .



**Figure S24.** 300 MHz  $^1\text{H}$  NMR spectrum of **P2** measured in  $\text{CDCl}_3$ .

## Supplementary Information



**Figure S25.** TGA curves of **P1&P2** with a heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  under  $\text{N}_2$ .