

## Peripheral thioester functionalization induces *J*-aggregation in bithiophene-DPP films and nanoparticles

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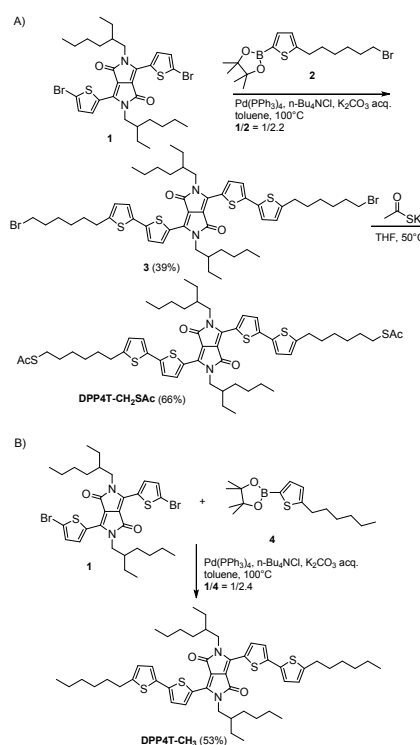
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### SUPPLEMENTARY INFORMATION

#### 1. Synthesis and Characterization

**General remarks:** reagents and solvents were purchased at the highest commercial quality and used without further purification. 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **1** and 2-[5-(6-bromohexyl)thiophen-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2** were prepared according to a literature procedures. 2-(5-Hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4** was purchased from Sigma-Aldrich. **DPP4T-CH<sub>2</sub>SAc** was synthesized via Suzuki-Miyaura coupling reaction between **2** and **1** (Scheme S1a). The cross-coupling reaction, leading to intermediate **3**, was performed in toluene at 100°C in the presence of 4% amount of Pd(PPh<sub>3</sub>)<sub>4</sub> as the palladium source, aqueous sodium carbonate as the base and *n*-Bu<sub>4</sub>NCl as the phase-transfer catalyst. The subsequent displacement of bromine atoms by treatment with potassium thioacetate provided the **DPP4T-CH<sub>2</sub>SAc** in 66% yield. A similar approach based on the coupling between **4** and **1** yielded **DPP4T-CH<sub>3</sub>**<sup>3</sup> in one step in 53% yield (Scheme S1b).



Scheme S1: Synthetic route to a) **DPP4T-CH<sub>2</sub>SAc**, and b) **DPP4T-CH<sub>3</sub>**.

Preparative column chromatography was carried out using Macherey-Nagel silica gel (60, particle size 0.063-0.2 mm). Macherey-Nagel aluminum sheets with silica gel 60 F254 were used for TLC analyses. All new compounds were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and LC-MS analysis. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were on a Varian Inova at 400 and at 100.6 MHz, respectively, by using the residual proton peak of CDCl<sub>3</sub> at δ = 7.26 ppm as internal standard for <sup>1</sup>H spectra and the signals of CDCl<sub>3</sub> at δ = 77.16 ppm as internal standard for <sup>13</sup>C spectra. High-resolution mass spectra were acquired with a Shimadzu high-performance liquid chromatography ion trap time of flight (LC-IT-TOF) mass spectrometer *via* direct infusion of the samples. IR spectra were recorded with a Perkin-Elmer FTIR Spectrometer. Melting points were determined on a Stuart Scientific Melting point apparatus SMP3.

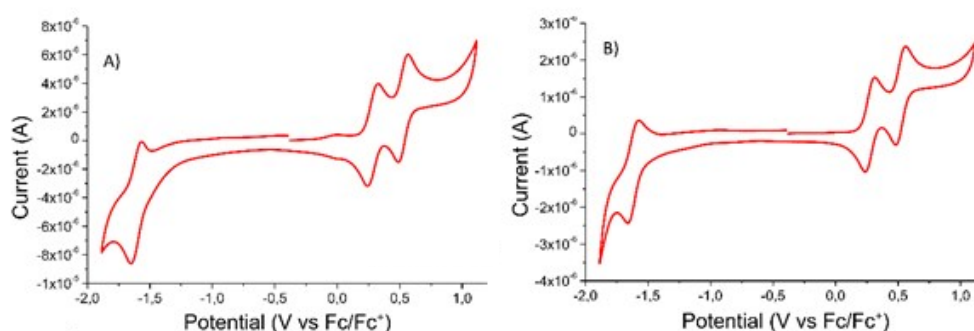
**3,6-bis(5'-(6-bromohexyl)-[2,2'-bithiophen]-5-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3).** An oven-dried Schlenk tube equipped with a magnetic stirrer and a condenser was evacuated and backfilled with nitrogen (3 times). Then it was charged, under nitrogen, with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione<sup>1</sup> (0.249 g, 0.365 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (17 mg, 0.015 mmol), *n*-Bu<sub>4</sub>NCl (22 mg, 0.08 mmol), a solution of 2-[5-(6-bromohexyl)thiophen-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>2</sup> (0.300 g, 0.804 mmol) in anhydrous toluene (9 mL) and, finally, a nitrogen degassed aqueous solution of 2M K<sub>2</sub>CO<sub>3</sub> (2.8 mL, 1.40 mmol). The mixture was heated at 100 °C for 24 h and monitored *via* TLC for reaction completion. The reaction mixture was cooled to room temperature, then quenched with a saturated aqueous solution of NH<sub>4</sub>Cl (30 mL) and extracted with dichloromethane (3x60 mL). The organic extracts were washed with an aqueous solution of NaCl (3x30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude product was purified by column chromatography on silica gel eluting with a mixture of hexane, dichloromethane and diethyl ether in volumetric ratio 5:5:0.2. After washing with methanol, compound 3 was isolated as a greenish solid (0.144g, 39% yield). *R*<sub>f</sub> = 0.60 (hexane:dichloromethane:diethyl ether 5:5:0.2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.90 (d, *J* = 4.0 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 2H), 7.11 (d, *J* = 3.6 Hz, 2H), 6.72 (d, *J* = 4.0 Hz, 2H), 4.07-3.94 (m, 4H), 3.39 (t, *J* = 6.8 Hz, 4H), 2.81 (t, *J* = 7.6 Hz, 4H), 1.94-1.82 (m, 6H), 1.70 (quintet like, *J* ≈ 7 Hz, 4H), 1.52-1.20 (m, 24H), 0.89 (t, *J* = 7.6 Hz, 6H), 0.85 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 161.6, 147.2, 143.2, 139.4, 136.7, 133.8, 127.5, 125.5, 124.9, 124.0, 108.1, 45.9, 39.2, 33.8, 32.6, 31.3, 30.3, 30.1, 28.5, 28.1, 27.8, 23.7, 23.1, 14.1, 10.6; LCMS-IT-TOF calculated for C<sub>50</sub>H<sub>66</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (M+Na)<sup>+</sup>: 1035.2266, found: *m/z* 1035.2269.

***S,S'*-((5',5''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5',5'-diyl))bis(hexane-6,1-diyl)) diethanethioate (DPP4T-CH<sub>2</sub>Sac).** A nitrogen-purged three-necked round bottom flask equipped with a magnetic stirrer and a condenser was charged, under nitrogen, with a solution of compound 3 (0.239 g, 0.235mmol) in anhydrous tetrahydrofuran (20 mL) and potassium thioacetate (0.057 g, 0.50 mmol). The mixture was heated at 50 °C and, after completion (5h, TLC analysis), was cooled to room temperature, then quenched with an aqueous solution of NaCl (30 mL) and extracted with dichloromethane (3x50 mL). The organic extracts were washed with an aqueous solution of NaCl (3x30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude product was purified by column chromatography on silica gel eluting with a mixture of hexane, dichloromethane and diethyl ether in volumetric ratio 5:5:0.5. *R*<sub>f</sub> = 0.64 (hexane:dichloromethane:diethyl ether 5:5:0.5). After washing with hexane and subsequently with methanol, DPP4T-CH<sub>2</sub>Sac was isolated as a dark purple solid (0.156g, 66% yield). Mp: 120-123°C (dichloromethane/methanol). IR (KBr): *v*<sub>max</sub> 2955, 2927, 2852, 1688, 1652, 1545, 1425, 1225, 1100, 1072, 1020, 809, 628 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.90 (d, *J* = 4.0 Hz, 2H), 7.21 (d, *J* = 4.0 Hz, 2H), 7.11 (d, *J* = 3.6 Hz, 2H), 6.72 (d, *J* = 3.6 Hz, 2H), 4.08-3.96 (m, 4H), 2.85 (t, *J* = 7.2 Hz, 4H), 2.80 (t, *J* = 7.4 Hz, 4H), 2.31 (s, 3H), 1.95-1.86 (m, 2H), 1.73-1.65 (m, 4H), 1.62-1.52 (m, 4H), 1.43-1.22 (m, 24H), 0.89 (t, *J* = 7.8 Hz, 6H), 0.85 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 196.0, 161.7, 147.4, 143.3, 139.4, 136.7, 133.7, 127.5, 125.4, 125.0, 124.1, 108.2, 46.0, 39.2, 31.3, 30.6, 30.4, 30.2, 29.4, 29.0, 28.5, 28.5, 28.4, 23.7, 23.1, 14.1, 10.6; LCMS-IT-TOF calculated for C<sub>54</sub>H<sub>72</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub> (M+Na)<sup>+</sup>: 1027.3709, found: *m/z* 1027.3738.

**2,5-Bis(2-ethylhexyl)-3,6-bis(5'-hexyl-[2,2'-bithiophen]-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP4T-CH<sub>3</sub>).**<sup>3</sup> An oven-dried Schlenk tube equipped with a magnetic stirrer and a condenser was evacuated and backfilled with nitrogen (3 times). Then it was charged, under nitrogen, with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione<sup>1</sup> (0.169 g, 0.25 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (12 mg, 0.01 mmol), *n*-Bu<sub>4</sub>NCl (15 mg, 0.05 mmol), a solution of 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.170 g, 0.58 mmol) in anhydrous toluene (8 mL) and, finally, a nitrogen degassed aqueous solution of 2M K<sub>2</sub>CO<sub>3</sub> (1.3 mL, 2.60 mmol). The mixture was heated at 100 °C for 24 h and monitored *via* TLC for reaction completion. The reaction mixture was cooled to room temperature, then quenched with a saturated aqueous solution of NH<sub>4</sub>Cl (30 mL) and extracted with dichloromethane (3x60 mL). The organic extracts were washed with an aqueous solution of NaCl (3x30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude product was purified by column chromatography on silica gel eluting with a mixture of hexane and dichloromethane in volumetric ratio 1:1. *R*<sub>f</sub> = 0.38 (hexane:dichloromethane 1:1). After washing with hexane, DPP4T-CH<sub>3</sub> was isolated as a dark purple solid (0.113g, 53% yield). Mp: 144-147°C (dichloromethane/methanol). IR (KBr): *v*<sub>max</sub> 2952, 2922, 2852, 1652, 1542, 1506, 1458, 1423, 1228, 1099, 1075, 1019, 803 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.90 (d, *J* = 4.0 Hz, 2H), 7.21 (d, *J* = 4.0 Hz, 2H), 7.12 (d, *J* = 3.2 Hz, 2H), 6.72 (d, *J* = 3.2 Hz, 2H), 4.09-3.95 (m, 4H), 2.80 (t, *J* = 7.6 Hz, 4H), 1.97-1.86 (m, 2H), 1.68 (quintet like, *J* ≈ 7 Hz, 4H), 1.42-1.20 (m, 28H), 0.94-0.82 (m, 18H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 161.6, 147.7, 143.3, 139.4, 136.7, 133.6, 127.5, 125.3, 124.9, 124.0, 108.1, 45.9, 39.2, 31.5, 31.5, 30.4, 30.3, 28.7, 28.5, 23.7, 23.1, 22.5, 14.1, 10.6 (two coincident peaks not observed); LCMS-IT-TOF calculated for C<sub>50</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (M+H)<sup>+</sup>: 857.4236, found: *m/z* 857.4268.

## 2. Electrochemical Characterization in Solution

Cyclic voltammetry measurements were carried out with a Metrohm Autolab potentiostat (model PGSTAT128N) using a conventional three electrodes cell consisting of a platinum working electrode, a platinum counter electrode and an Ag wire coated with AgCl pseudo reference electrode. All CV measurements were recorded at room temperature under nitrogen atmosphere in anhydrous dichloromethane solution (scan rate 0.05/0.1 Vs<sup>-1</sup>). The solutions were prepared as follows: a 0.1 M solution of *n*Bu<sub>4</sub>NPF<sub>6</sub> in anhydrous dichloromethane as supporting electrolyte was prepared in a glove box; the required amount of compound (**DPP4T-CH<sub>3</sub>** or **DPP4T-CH<sub>2</sub>Sac**) was dissolved in the desired volume of *n*Bu<sub>4</sub>NPF<sub>6</sub> solution and put inside the three electrodes cell. All measurements were calibrated using the Fc<sup>+</sup>/Fc redox couple as external standard. The HOMO and LUMO energy levels were estimated using the following empirical equations:  $E_{\text{HOMO}} = e(E_{\text{ox}} + 5.1\text{V})$  and  $E_{\text{LUMO}} = e(E_{\text{red}} + 5.1\text{V})$ , where  $E$  is the average value between the peak potential and the related reverse one measured for the compounds in solution versus Fc<sup>+</sup>/Fc reference and 5.1eV is the position of the formal potential of the Fc<sup>+</sup>/Fc redox couple in the Fermi scale.<sup>4</sup> The energy levels of **DPP4T-CH<sub>3</sub>** or **DPP4T-CH<sub>2</sub>Sac** were measured by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> solution. Cyclic voltammograms are displayed in the **Figure S1**, while the corresponding electrochemical data are reported in the **Table S2**.



**Figure S1:** Cyclic voltammograms on a Pt working electrode in 0.1M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/anhydrous dichloromethane at room temperature for **DPP4T-CH<sub>3</sub>** (A) and **DPP4T-CH<sub>2</sub>Sac** (B).

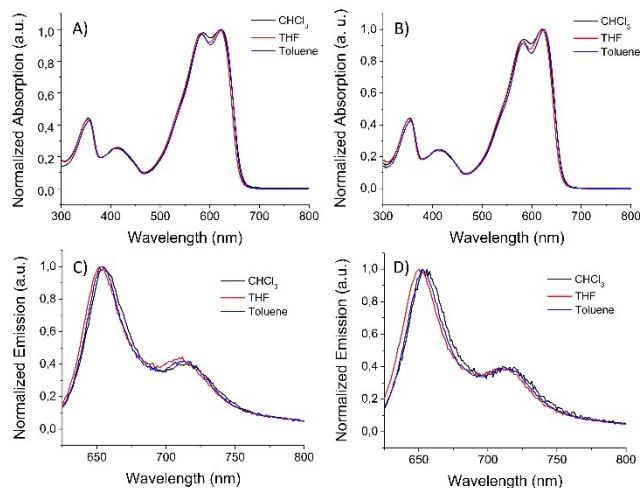
**Table S1:** Electrochemical data of **DPP4T-CH<sub>2</sub>Sac** and **DPP4T-CH<sub>3</sub>** in dichloromethane solution

Compound	$E_{\text{ox}}$ (V) <sup>[a]</sup>	$E_{\text{red}}$ (V) <sup>[a]</sup>	HOMO (eV) <sup>[b]</sup>	LUMO (eV) <sup>[b]</sup>	$E_g^{\text{ec}}$ (eV) <sup>[c]</sup>
<b>DPP4T-CH<sub>3</sub></b>	0.280	-1.608	-5.38	-3.49	1.89
<b>DPP4T-CH<sub>2</sub>Sac</b>	0.274	-1.619	-5.37	-3.48	1.89

[a]  $E$  is the average value between the peak potential and the related reverse one measured for the compounds in CH<sub>2</sub>Cl<sub>2</sub> solution (10<sup>-4</sup> M) vs Fc<sup>+</sup>/Fc reference. [b] HOMO and LUMO energy levels were estimated by empirical equations: HOMO =  $-e(E_{\text{ox}} + 5.1\text{V})$  and LUMO =  $-e(E_{\text{red}} + 5.1\text{V})$ . [c] Electrochemical band gap calculated from  $E_g = -e(E_{\text{ox}} - E_{\text{red}})$ .<sup>4</sup>

### 3. UV-VIS and Fluorescence Characterization

UV Vis measurements were performed on a Shimadzu UV 2401PC spectrophotometer; PL spectra were recorded on a VARIAN Cary Eclipse fluorescence spectrophotometer. Spectrophotometric grade solvents were used for the preparation of samples.



**Figure S2.** Top: Normalized UV-vis absorption spectra of **DPP4T-CH<sub>3</sub>** (A) and **DPP4T-CH<sub>2</sub>SAc** (B) in CHCl<sub>3</sub>, THF or toluene solution (10<sup>-5</sup> M). Bottom: Normalized emission spectra of **DPP4T-CH<sub>3</sub>** (C) and **DPP4T-CH<sub>2</sub>SAc** (D) in CHCl<sub>3</sub>, THF or toluene solution (10<sup>-5</sup> M).

**Table S2.** Optical data of **DPP4TH** and **DPP4TSAc** in solution

Compound	Solvent	$\lambda_{\max,abs}$ (nm)	$\epsilon_{\max}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\text{onset}}$ (nm)	$E_g$ (eV) <sup>[b]</sup>	$\lambda_{\max,PL}$ (nm) <sup>[c]</sup>
<b>DPP4TH</b>	CHCl <sub>3</sub>	586, 621	5.81x10 <sup>4</sup>	664	1.87	655
<b>DPP4TH</b>	Toluene	584, 624	6.49x10 <sup>4</sup>	663	1.87	655
<b>DPP4TH</b>	THF	581, 621	6.51x10 <sup>4</sup>	660	1.88	652
<b>DPP4TSAc</b>	CHCl <sub>3</sub>	584, 621	5.78x10 <sup>4</sup>	664	1.87	655
<b>DPP4TSAc</b>	Toluene	583, 624	6.45x10 <sup>4</sup>	663	1.87	653
<b>DPP4TSAc</b>	THF	580, 620	6.60x10 <sup>4</sup>	660	1.88	650

<sup>[a]</sup> 10<sup>-5</sup> M solution. <sup>[b]</sup>  $E_g = 1240/\lambda_{\text{onset}}$ . <sup>[c]</sup> Excitation wavelength 599 nm.

### 4. Film Preparation and Characterization

Films of **DPP4T-CH<sub>3</sub>** and **DPP4T-CH<sub>2</sub>SAc** were deposited on square quartz substrates (1 cm x 1 cm) by spin-coating (1000 rpm for 60 s). Solutions were prepared in different solvents (typically chloroform, chlorobenzene, *o*-xylene or 1:1 mixture of chloroform and chlorobenzene) at the concentration of 8 mg/mL for **DPP4T-CH<sub>2</sub>SAc** and 4 mg/mL for **DPP4T-CH<sub>3</sub>**. **DPP4T-CH<sub>3</sub>** exhibited poor filming properties, leading to extremely irregular deposition, while uniform films were obtained with **DPP4T-CH<sub>2</sub>SAc**. In particular, **DPP4T-CH<sub>2</sub>SAc** film processed from a chloroform solution was characterized by atomic force microscopy (AFM). AFM micrographs were taken using a Park XE-100 SPM system microscope. Images were acquired in non-contact mode using tips (Type PPP-NCHR) on a cantilever of 125  $\mu\text{m}$  length, about 330 kHz resonance frequency, 42 N m<sup>-1</sup> nominal force constant and <10 nm guaranteed tip curvature radius. Surface areas were sampled with a scan rate of 0.5 Hz. Topographies were analyzed using the software XEI (Park System Corporation, version 1.8.0). Films spin-coated from chloroform were also used for the spectroscopic characterization.

## 5. DSC Characterization

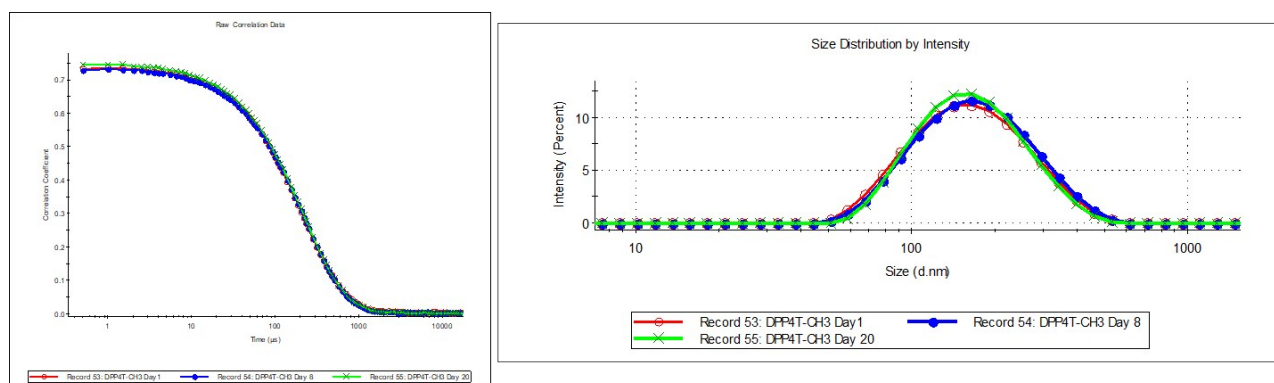
DSC measurements were conducted under nitrogen atmosphere with a Mettler Toledo STARe system DSC. The scan rate was 10 °C/min. Material was placed in standard Mettler aluminum crucibles; sample weights were ~ 2-3 mg for neat compounds. To avoid influence of thermal decomposition on the thermal data, the first heating and cooling scan loop is displayed.

## 6. Organic Nanoparticles (ONPs) Preparation and Characterization

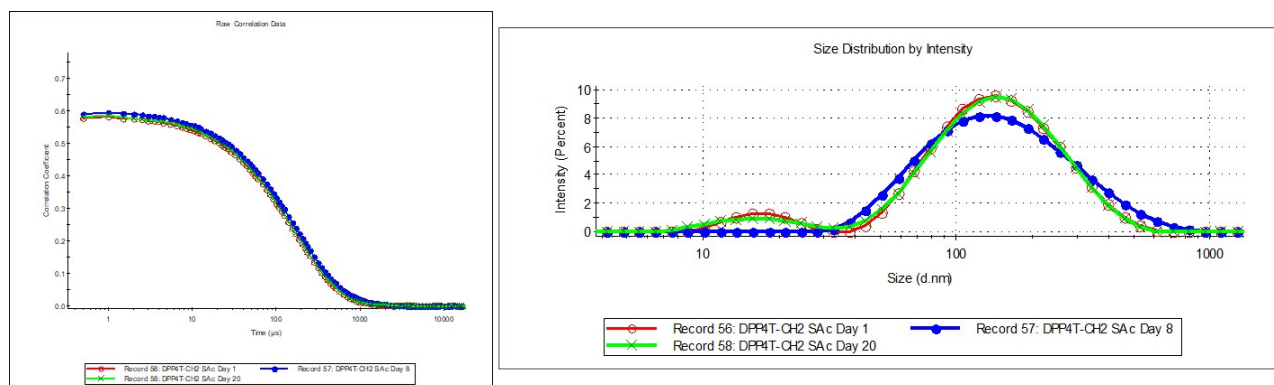
ONPs of both molecules were prepared with the standard re-precipitation procedure: a 2mM solution of dye in THF was prepared and filtered using PTFE filters of 220 nm. 100  $\mu$ L of this solution were slowly dropped in 9.9 mL of pure water (LC-MS-CHROMASOLV, Fluka) at room temperature under vigorous stirring (1000 rpm). A first determination of the colloidal stability was performed measuring the absorption spectra of the two suspensions during four weeks. Meanwhile, the size distribution of the nanoparticles was probed by Dynamic Light Scattering (DLS). DLS measurements were performed using a Zetasizer-Nano S from Malvern operating with a 4 mW He-Ne laser (633 nm wavelength) and a fixed detector angle of 173° (non-invasive backscattering geometry NIBS™) and with the cell holder maintained at 25 °C by means of a Peltier element. Data were collected leaving the instrument free to optimize the instrumental parameters (attenuator, optics position and number of runs). Usually the time autocorrelation function (ACF) of scattered light intensity was the average of 12-16 consecutive runs of 10 s each.

The ACF of scattered light intensity was converted into the ACF of scattered electric field. This last quantity is the Laplace transform of the intensity weighted size distribution function that has been retrieved using a standard regularised non-negative least squares analysis, operated by means of the software implemented by the manufacturer. The obtained intensity weighted size distribution function represents the fraction of the light intensity scattered by particles of different size.

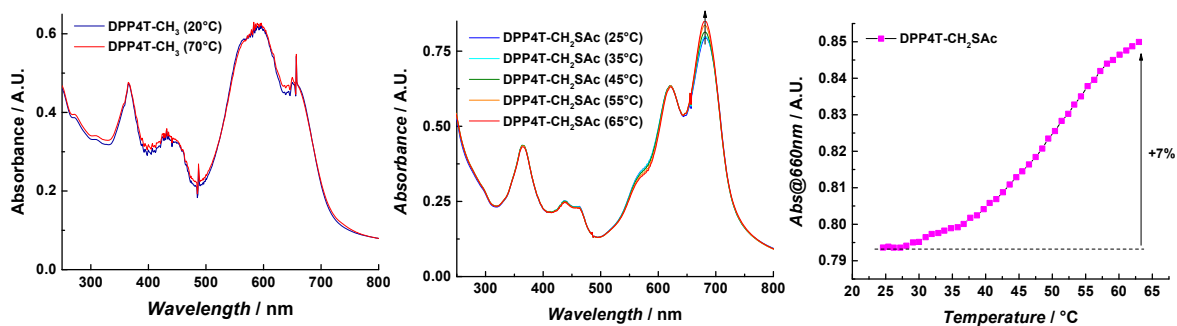
As anticipated in the main text there are not significant changes in the intensity size distribution for the suspension of both the molecules. Below are reported the size distributions measured immediately after the colloid's preparation, after 8 day and after 20 days together with the corresponding ACF.



**Figure S3.** Correlogram (left) and corresponding intensity size distribution (right) for colloidal suspension of DPP4T-CH<sub>3</sub> measured immediately after the preparation, after 8 day and after 20 days.



**Figure S4.** Correlogram (left) and corresponding intensity size distribution (right) for colloidal suspension of DPP4T-CH<sub>2</sub>SAc measured immediately after the preparation, after 8 day and after 20 days.



**Figure S5.** (left) absorption spectra of DPP4T-CH<sub>3</sub> ONPs in water at 20°C and 70°C. (middle) Absorption spectra of DPP4T-CH<sub>2</sub>SAC ONPs in water at different temperatures. The maximum of absorption at 660 nm increases its intensity increasing the temperature of about 7%. (Right) Detail of the temperature dependence of the DPP4T-CH<sub>2</sub>SAC ONP maximum of absorption in the temperature range 25 - 65 °C.

## 7. Transmission Electron Microscopy

Transmission electron microscopy (TEM) micrographs were recorded using a Jeol JEM-1011 microscope operated at an accelerating voltage of 100 kV. The samples were prepared by dropping 10  $\mu$ l of their water dispersion on a carbon-coated Cu grid (400 mesh), and letting to settle for 5 min. Then the samples were stained with a 2% (w/v) phosphotungstic acid solution by placing 10  $\mu$ l of phosphotungstic acid on the grid for 2 min before draining off. The samples were stable under the electron beam and did not degraded within the typical observation time.

## 8. NMR spectra

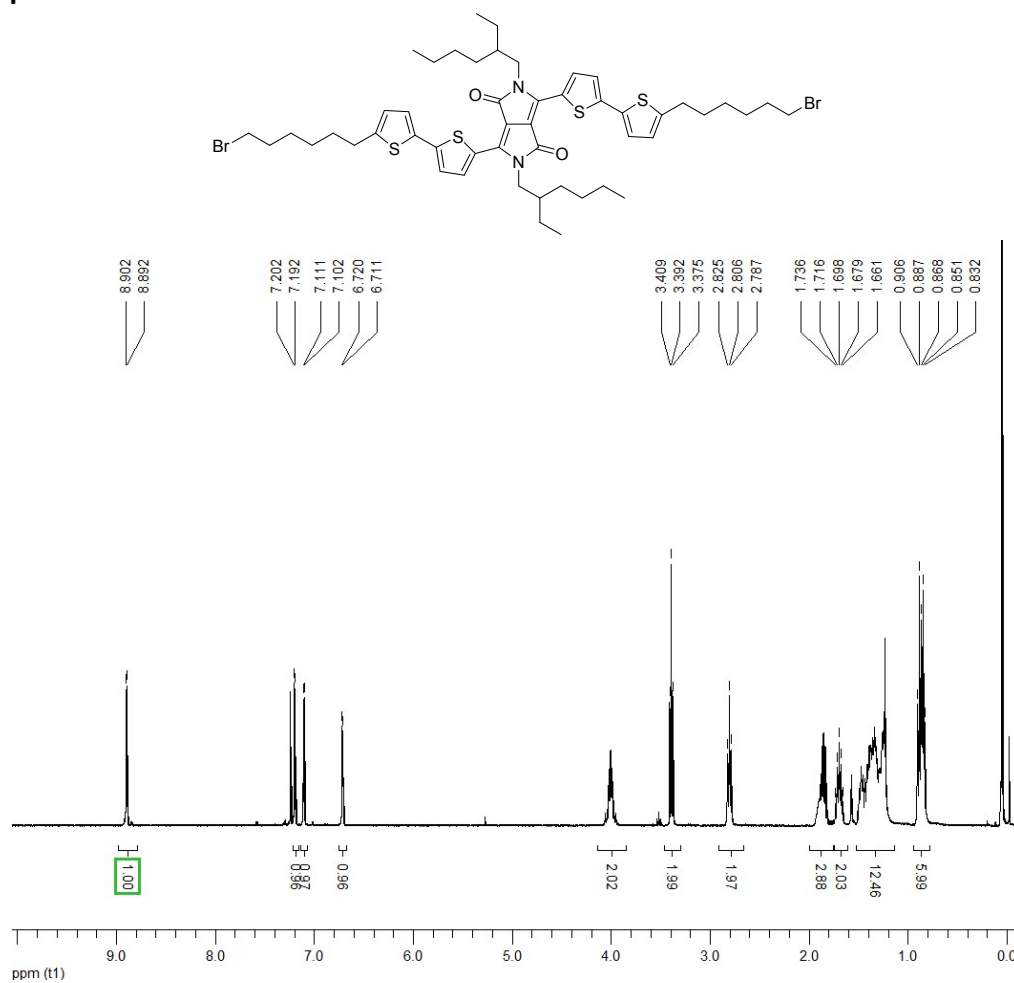


Figure S6.  $^1\text{H}$  NMR spectrum of compound **8** (400 MHz,  $\text{CDCl}_3$ ).

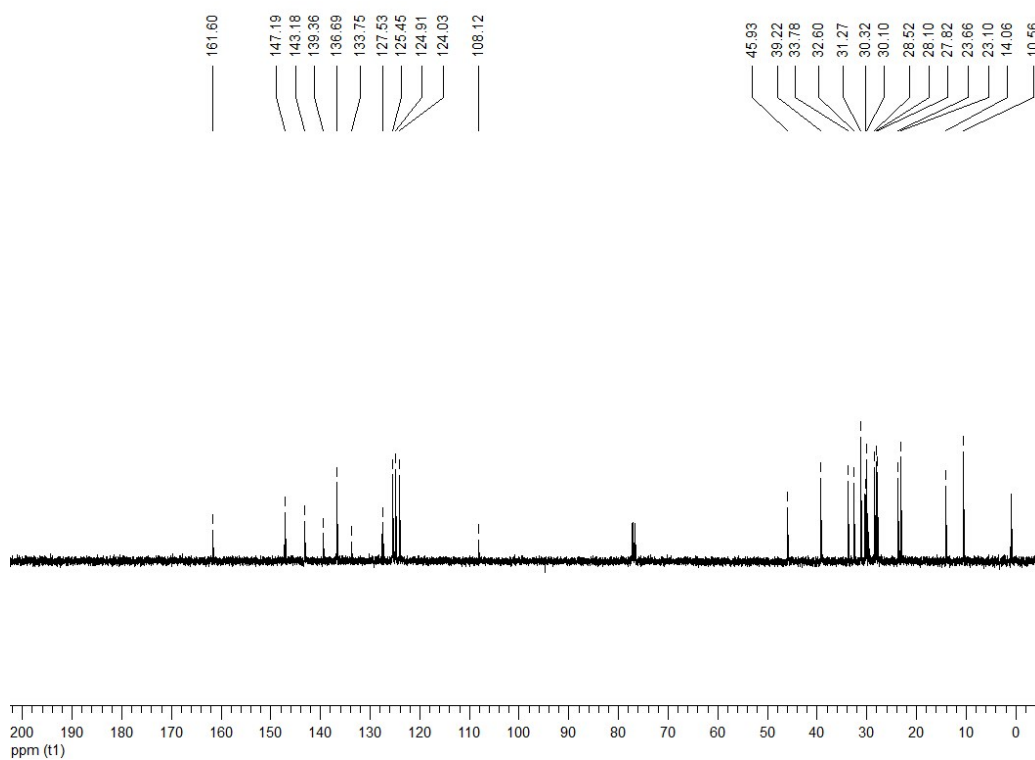


Figure S7.  $^{13}\text{C}$  NMR spectrum of compound **8** (100.6 MHz,  $\text{CDCl}_3$ ).

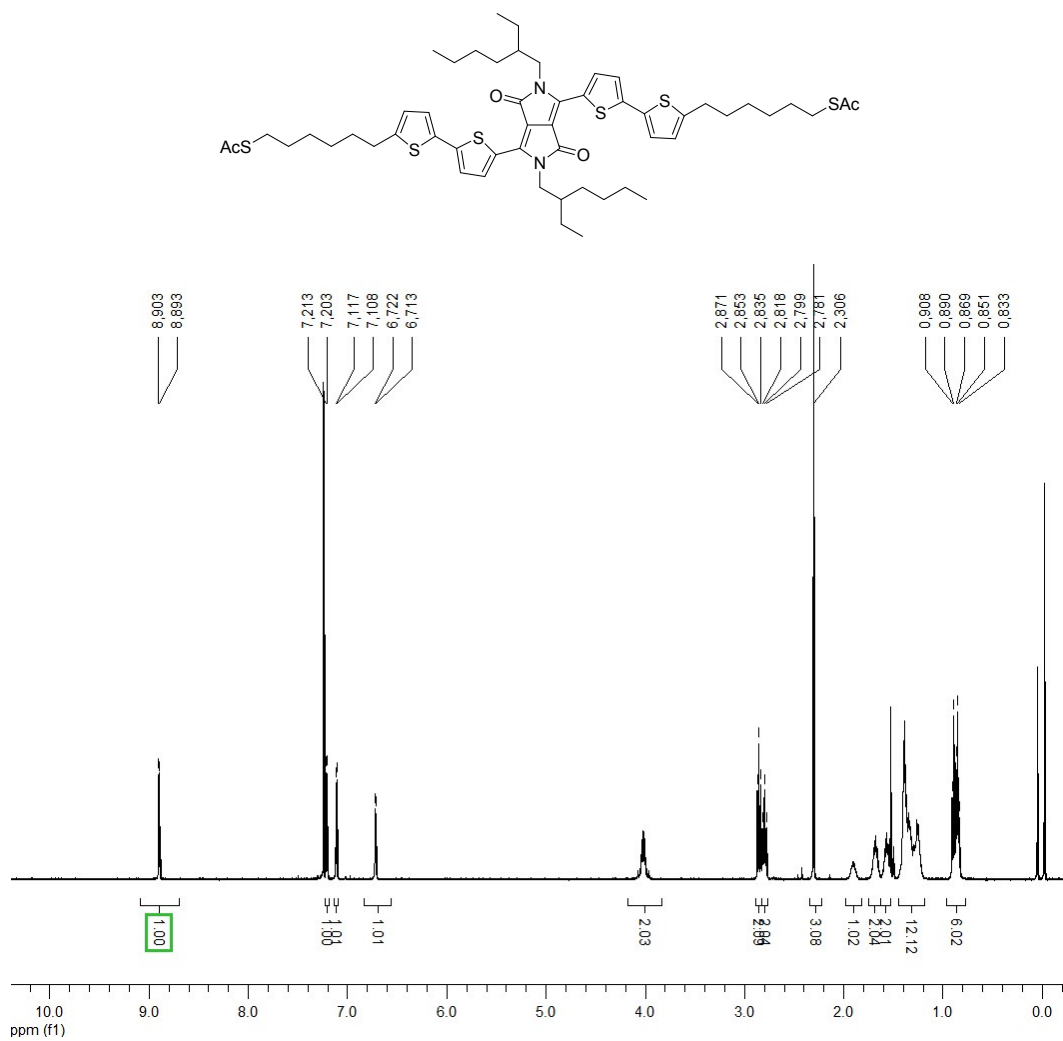


Figure S8.  $^1\text{H}$  NMR spectrum of DPP4TSac (400 MHz,  $\text{CDCl}_3$ ).

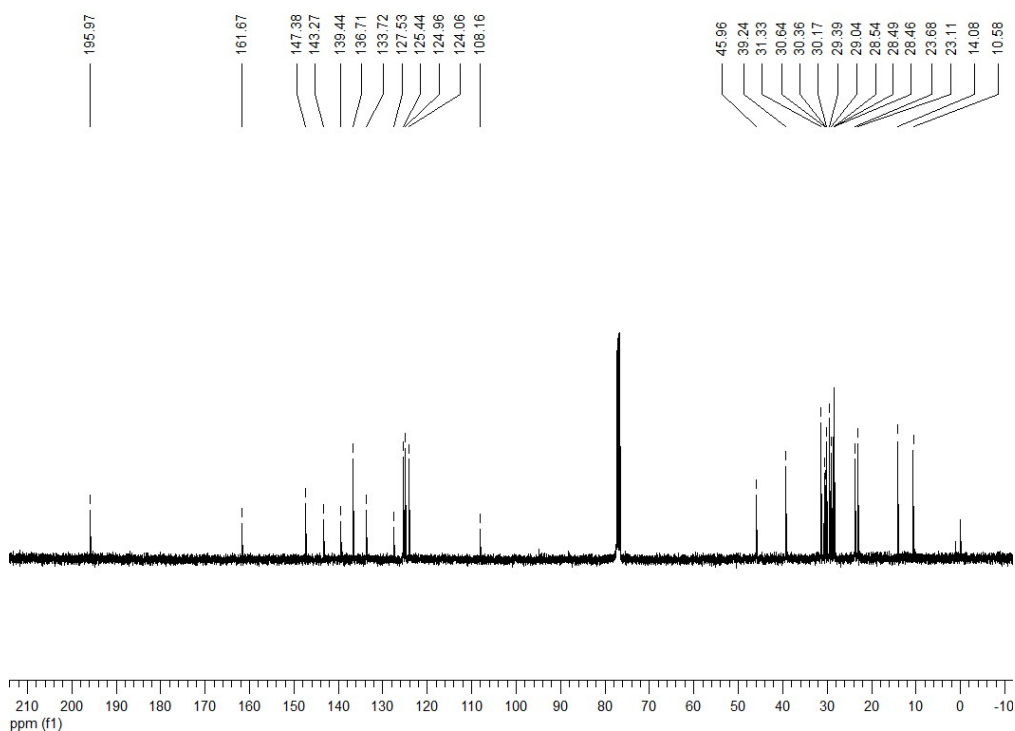


Figure S9.  $^{13}\text{C}$  NMR spectrum of DPP4TSac (100.6 MHz,  $\text{CDCl}_3$ ).



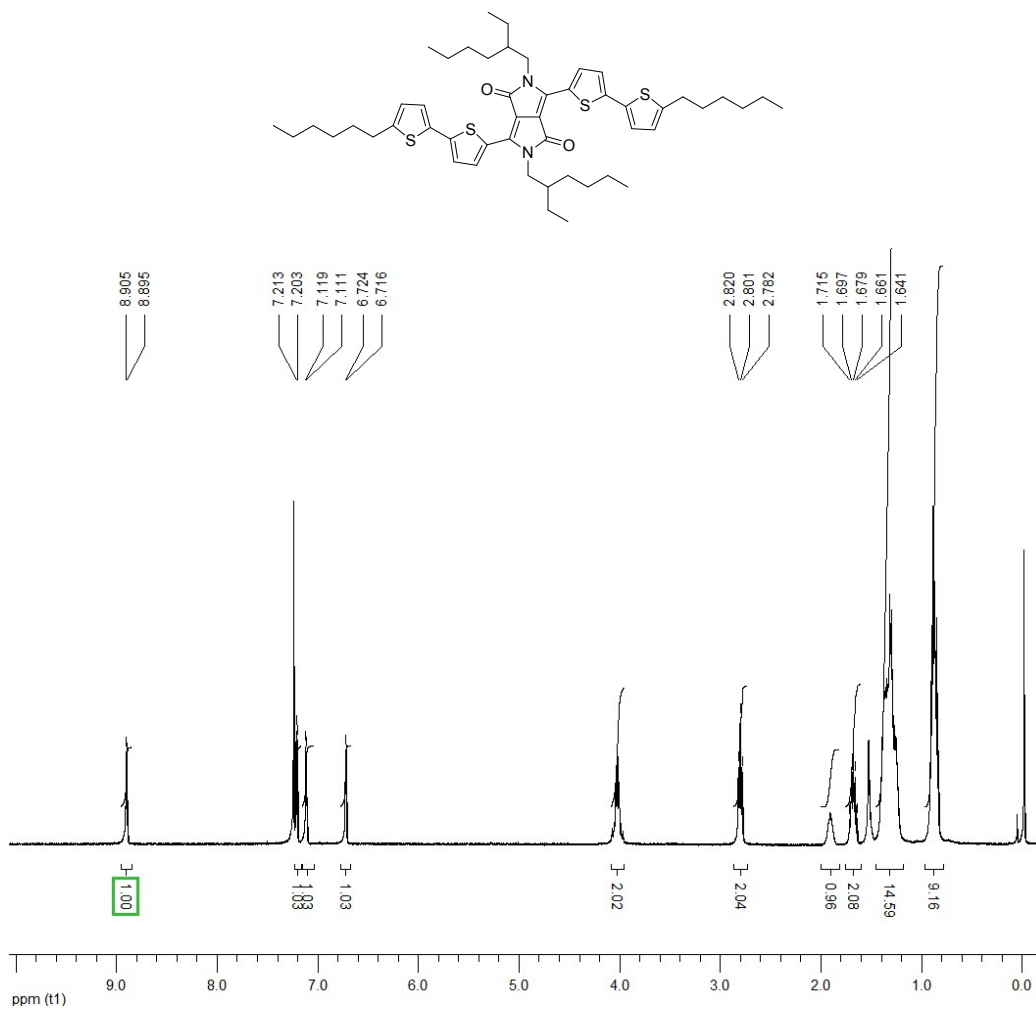


Figure S10.  $^1\text{H}$  NMR spectrum of DPP4T (400 MHz,  $\text{CDCl}_3$ ).

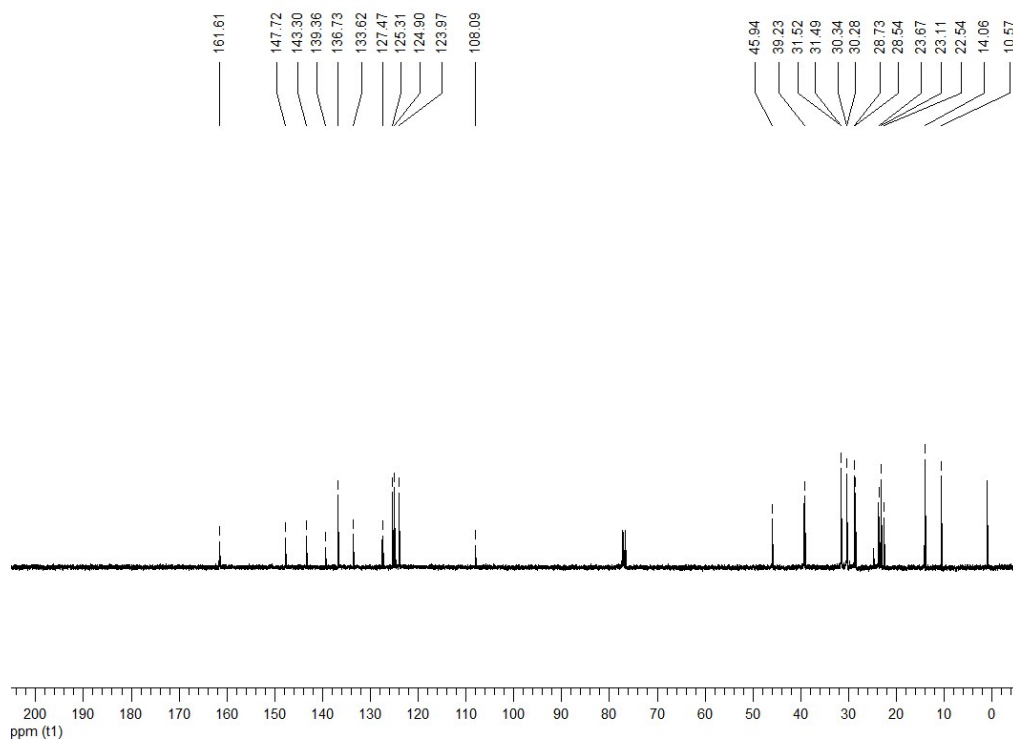


Figure S11.  $^{13}\text{C}$  NMR spectrum of DPP4T (100.6 MHz,  $\text{CDCl}_3$ ).

## 9. References

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