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

Angela Punzi, Davide Blasi, Alessandra Operamolla, Roberto Comparelli, Gerardo Palazzo and Gianluca M. Farinola*

*Department of Chemistry, Università degli Studi di Bari “Aldo Moro”, Via Orabona 4, I-70125 Bari, Italy.
† Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via G. Moruzzi 13, I-56124 Pisa, Italy.
‡ CNR-IPCF, Istituto per i Processi Chimico-Fisici, S.S. Bari, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy.
‡‡ CSGI (Center for Colloid and Surface Science), via Orabona 4, 70125, Bari, Italy.
†† Authors equally contributing.

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$_2$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$_3$)$_4$ as the palladium source, aqueous sodium carbonate as the base and n-Bu$_4$NCl as the phase-transfer catalyst. The subsequent displacement of bromine atoms by treatment with potassium thioacetate provided the DPP4T-CH$_2$SAc in 66% yield. A similar approach based on the coupling between 4 and 1 yielded DPP4T-CH$_3$ in one step in 53% yield (Scheme S1b).

Scheme S1: Synthetic route to a) DPP4T-CH$_2$SAc, and b) DPP4T-CH$_3$. 

Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2021
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 1H-NMR, 13C-NMR and LC-MS analysis. 1H-NMR and 13C-NMR spectra were on a Varian Inova at 400 and at 100.6 MHz, respectively, by using the residual proton peak of CDCl3 at $\delta = 7.26$ ppm as internal standard for 1H spectra and the signals of CDCl3 at $\delta = 77.16$ ppm as internal standard for 13C 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. Melt points were determined on a Stuart Scientific Melting point apparatus SMP3.

3,6-bis(5′-[6-bromomethyl]-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 (0.249 g, 0.365 mmol), Pd(PPh3)4 (17 mg, 0.015 mmol), n-Bu4NCI (22 mg, 0.08 mmol), a solution of 2-[5-(6-bromomethyl)thiophen-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.300 g, 0.804 mmol) in anhydrous toluene (9 mL) and, finally, a nitrogen degassed aqueous solution of 2M K2CO3 (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 an aqueous solution of NaCl (3x30 mL) and extracted with hexane, dichloromethane and diethyl ether in volumetric ratio 5:5:0.5. After washing with hexane and subsequently with methanol, compound 3 was isolated as a greenish solid (0.144g, 39% yield). Mp: 144-147°C (dichloromethane/methanol). IR (KBr): $\mu$: 3032, 2971, 2922, 2870, 1718, 1652, 1542, 1512, 1458, 1423, 1228, 1099, 959, 803 cm$^{-1}$. NMR and LC-MS analysis.

$\delta$= 4.08-3.94 (m, 4H), 3.39 (t, $J$= 7.2 Hz, 4H), 2.80 (t, $J$= 7.6 Hz, 4H), 2.14-1.82 (m, 6H), 1.70 (quintet like, $J$= 4.0 Hz, 2H), 1.52-1.20 (m, 2H), 0.89 (t, $J$= 7.6 Hz, 6H), 0.85 (t, $J$= 7.2 Hz, 6H); 13C NMR (100.6 MHz, CDCl3): $\delta$ 136.7, 133.7, 127.5, 125.4, 125.0, 124.1, 108.2, 46.0, 39.2, 33.6, 31.3, 30.3, 30.1, 28.5, 28.1, 27.8, 23.7, 23.1, 14.1, 10.6; LC-MS-IT-TOF calculated for C51H50BrN2O5S4 (M+Na)$^+$: 1035.2266, found: m/z 1035.2269.

5,5′-[((5′,5′′-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyli)bisl(hexane-6,1-diyli)]diethanethioate (DPP4T-CH3S4Ac). 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, 0.235 mmol) in anhydrous toluene (9 mL) and, finally, a nitrogen degassed 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 Na2SO4 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. After washing with hexane and subsequently with methanol, DPP4T-CH3S4Ac was isolated as a dark purple solid (0.113g, 53% yield). Mp: 144-147°C (dichloromethane/methanol). IR (KBr): $\mu$: 3031, 2970, 2920, 2870, 1717, 1651, 1543, 1425, 1323, 1250, 1249, 1240, 108, 45, 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; LC-MS-IT-TOF calculated for C51H50BrN2O5S4 (M+Na)$^+$: 1035.2266, found: m/z 1035.2269.

5,5′-(5′,5′′-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyli)bisl([2′,2′-bithiophene]-5′,5′-diyl)]bis(hexane-6,1-diyli)]diethanethioate (DPP4T-CH3S4Ac). 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, 0.235 mmol) in anhydrous toluene (9 mL) and, finally, a nitrogen degassed 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 Na2SO4 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. After washing with hexane and subsequently with methanol, DPP4T-CH3S4Ac was isolated as a dark purple solid (0.113 g, 53% yield). IR (KBr): $\mu$: 3031, 2970, 2920, 2870, 1717, 1651, 1543, 1425, 1323, 1250, 1249, 1240, 108, 45, 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; LC-MS-IT-TOF calculated for C51H50BrN2O5S4 (M+Na)$^+$: 1035.2266, found: m/z 1035.2269.
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⁻¹). The solutions were prepared as follows: a 0.1 M solution of nBu₄NPF₆ in anhydrous dichloromethane as supporting electrolyte was prepared in a glove box; the required amount of compound (DPP4T-CH₃ or DPP4T-CH₂SAc) was dissolved in the desired volume of nBu₄NPF₆ solution and put inside the three electrodes cell. All measurements were calibrated using the Fc⁺/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⁺/Fc reference and 5.1eV is the position of the formal potential of the Fc⁺/Fc redox couple in the Fermi scale.⁴ The energy levels of DPP4T-CH₃ or DPP4T-CH₂SAc were measured by cyclic voltammetry in CH₂Cl₂ solution. Cyclic voltammograms are displayed in the Figure S1, while the corresponding electrochemical data are reported in the Table S2.

![Cyclic voltammograms](image)

Figure S1: Cyclic voltammograms on a Pt working electrode in 0.1M n-Bu₄NPF₆/anhydrous dichloromethane at room temperature for DPP4T-CH₃ (A) and DPP4T-CH₂SAc (B).

Table S1: Electrochemical data of DPP4T-CH₂SAc and DPP4T-CH₃ in dichloromethane solution

| Compound        | $E_{\text{ox}}$ (V)⁴ | $E_{\text{red}}$ (V)⁴ | HOMO (eV)⁴ | LUMO (eV)⁴ | $E_{\text{g}}$ (eV)⁴ |
|-----------------|----------------------|-----------------------|-------------|-------------|---------------------|
| DPP4T-CH₃       | 0.280                | -1.608                | -5.38       | -3.49       | 1.89                |
| DPP4T-CH₂SAc    | 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 CH₂Cl₂ solution (10⁻⁴ M) vs Fc⁺/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 $E_{\text{g}} = -e(E_{\text{ox}} - E_{\text{red}})$.⁴
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.

![Normalized UV-vis absorption and emission spectra](image)

**Figure S2.** Top: Normalized UV-vis absorption spectra of DPP4T-CH$_3$ (A) and DPP4T-CH$_2$SAC (B) in CHCl$_3$, THF or toluene solution (10$^{-5}$ M). Bottom: Normalized emission spectra of DPP4T-CH$_3$ (C) and DPP4T-CH$_2$SAC (D) in CHCl$_3$, THF or toluene solution (10$^{-5}$ M).

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

| Compound      | Solvent    | $\lambda_{\text{max,abs}}$ (nm) | $\epsilon_{\text{max}}$ (M$^{-1}$cm$^{-1}$) | $\lambda_{\text{onset}}$ (nm) | $E_g$ (eV)$^\text{[b]}$ | $\lambda_{\text{max,PL}}$ (nm)$^\text{[c]}$ |
|---------------|------------|---------------------------------|---------------------------------------------|------------------------------|-------------------------|-----------------------------------------------|
| DPP4TH        | CHCl$_3$   | 586, 621                        | 5.81x10$^4$                                 | 664                          | 1.87                    | 655                                           |
| DPP4TSAc      | CHCl$_3$   | 584, 621                        | 5.78x10$^4$                                 | 664                          | 1.87                    | 655                                           |
| DPP4TSAc      | Toluene    | 584, 624                        | 6.49x10$^4$                                 | 663                          | 1.87                    | 655                                           |
| DPP4TSAc      | THF        | 581, 621                        | 6.51x10$^4$                                 | 660                          | 1.88                    | 652                                           |
| DPP4TSAc      | Toluene    | 583, 624                        | 6.45x10$^4$                                 | 663                          | 1.87                    | 653                                           |
| DPP4TSAc      | THF        | 580, 620                        | 6.60x10$^4$                                 | 660                          | 1.88                    | 650                                           |

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

4. Film Preparation and Characterization

Films of DPP4T-CH$_3$ and DPP4T-CH$_2$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$_2$SAC and 4 mg/mL for DPP4T-CH$_3$. DPP4T-CH$_3$ exhibited poor filming properties, leading to extremely irregular deposition, while uniform films were obtained with DPP4T-CH$_2$SAC. In particular, DPP4T-CH$_2$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 µm length, about 330 kHz resonance frequency, 42 N m$^{-1}$ 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 STAR e 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 µL 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 DPPT-CH₃ measured immediately after the preparation, after 8 day and after 20 days.](image)

![Figure S4. Correlogram (left) and corresponding intensity size distribution (right) for colloidal suspension of DPPT-CH₃SAc measured immediately after the preparation, after 8 day and after 20 days.](image)
Figure S5. (left) absorption spectra of DPP4T-CH$_3$ ONPs in water at 20°C and 70°C. (middle) Absorption spectra of DPP4T-CH$_2$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$_2$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 µl 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 µl of phosphotungstic acid on the grid for 2 min before draining off. The samples were stable under the electron beam and did not degrade within the typical observation time.
8. NMR spectra

Figure S6. $^1$H NMR spectrum of compound 8 (400 MHz, CDCl$_3$).

Figure S7. $^{13}$C NMR spectrum of compound 8 (100.6 MHz, CDCl$_3$).
Figure S8. $^1$H NMR spectrum of DPP4TSAc (400 MHz, CDCl$_3$).

Figure S9. $^{13}$C NMR spectrum of DPP4TSAc (100.6 MHz, CDCl$_3$).
**Figure S10.** $^1$H NMR spectrum of DPP4T (400 MHz, CDCl$_3$).

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

1. A. Punzi, E. Maiorano, F. Nicoletta, D. Blasi, A. Ardizzone, N. Ventosa, I. Ratera, J. Veciana, G. M. Farinola, *Eur. J. Org. Chem.* **2016**, *2617-262*.

2. A. Punzi, A. Operamolla, O. Hassan Omar, F. Brunetti, A. D. Scaccabarozzi, G. M. Farinola, N. Stingelin, *Chem. Mater.* **2018**, *30*, 2213-2217.

3. V. S. Gevaerts, E. M. Herzig, M. Kirkus, K. H. Hendriks, M. M. Wienk, J. Perlich, P. Müller-Buschbaum, R. A. J. Janssen, *Chem. Mater.* **2014**, *26*, 2, 916-926.

4. C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.* **2011**, *23*, 2367-2371.