

University of Groningen

Photophysics of Self-Assembled Monolayers of a pi-Conjugated Quinquethiophene Derivative

Gholamrezaie, Fatemeh; Kirkus, Mindaugas; Mathijssen, Simon G. J.; de Leeuw, Dago M.; Meskers, Stefan C. J.

Published in:
The Journal of Physical Chemistry A

DOI:
[10.1021/jp3045127](https://doi.org/10.1021/jp3045127)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2012

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gholamrezaie, F., Kirkus, M., Mathijssen, S. G. J., de Leeuw, D. M., & Meskers, S. C. J. (2012). Photophysics of Self-Assembled Monolayers of a pi-Conjugated Quinquethiophene Derivative. *The Journal of Physical Chemistry A*, 116(29), 7645-7650. DOI: 10.1021/jp3045127

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Photophysics of Self-Assembled Monolayers of a π -Conjugated Quinque-Thiophene Derivative

Fatemeh Gholamrezaie,^{1,2} Mindaugas Kirkus,³ Simon G. J. Mathijssen², Dago M. de Leeuw^{1,2} and Stefan C. J. Meskers^{3*}*

¹ Molecular Electronics, Zernike Institute for Advanced Materials, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

² Philips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

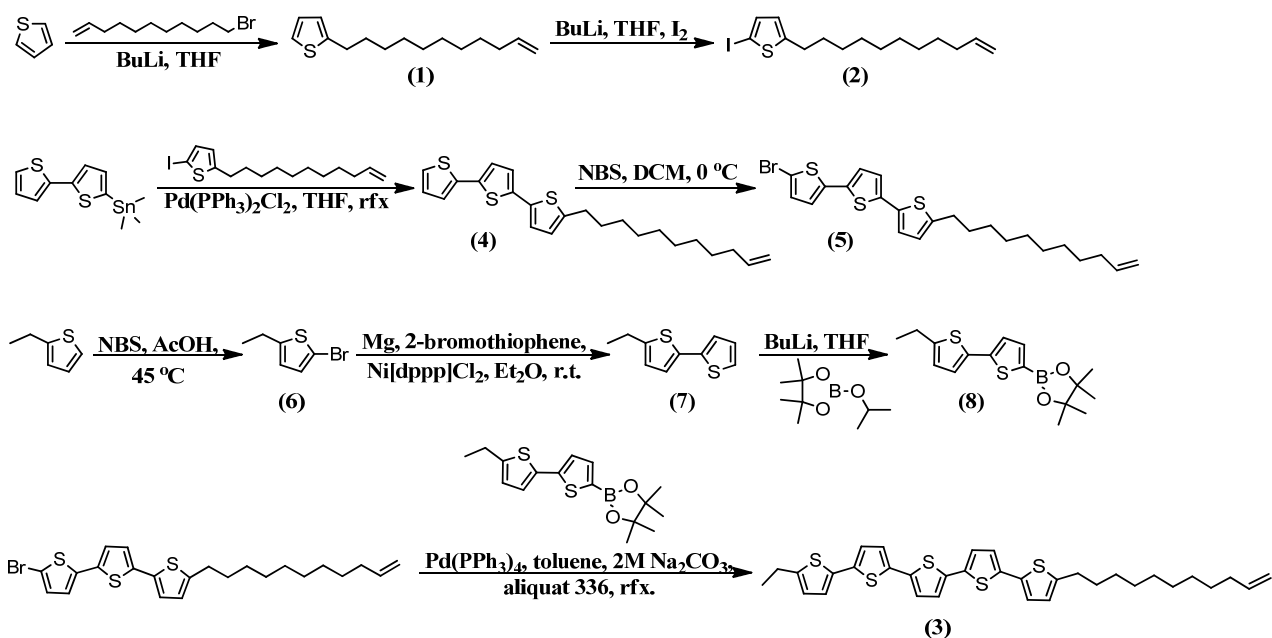
³ Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

SUPPORTING INFORMATION

-Synthesis of 5-Ethyl-5''''-(undec-10-enyl)-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (**3**)

- Fluorescence decay measurements

- Complete references Fluorescence decay measurements



Thiophene, 2-bromothiophene, n-BuLi (2.5M solution in hexane), iodine, trimethyltin chloride, sodium carbonate were purchased from Acros Organics, 11-bromoundec-1-ene, 2-ethylthiophene, bis(triphenylphosphine)palladium(II) dichloride, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride, N-bromosuccinimide, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Aliquat 336 were purchased from Aldrich, magnesium turnings were purchased from Merck, and tetrakis(triphenylphosphine)palladium(0) was purchased from Strem Chemicals. 5-Trimethylstannyl-2,2'-bithiophene¹ was synthesized according to literature procedure. All reactions were carried out under inert argon atmosphere using dry organic solvents.

2-(Undec-10-enyl)thiophene (1) n-BuLi (23.8 mL of 2.5M solution in hexane, 59.42 mmol) was added dropwise to a solution of thiophene (5 g, 59.42 mmol) in THF (40 mL) at -78 °C under argon. The solution was stirred at -78 °C for 2h, then warmed to room temperature, and kept for 30 minutes. The solution was cooled to -78 °C again and 11-bromoundec-1-ene (13.86 g, 59.42 mmol) was added in one portion. The solution was allowed to warm to room temperature and then stirred for 22 h before being poured into water. The product was extracted twice with diethyl ether. The combined organic solutions were subsequently washed with brine and dried over magnesium sulfate, filtered and the solvent was removed by rotary evaporation to give 12 g of raw product, which was purified by distillation in high vacuum (0.2 mBar, 80 °C) to give 8.1 g (57.9 % yield) of pure product as a colorless oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.10 (d, J=5.1 Hz, 1H), 6.91 (t, J=4.1 Hz, 1H), 6.77 (d, J=3.0 Hz, 1H), 5.76-5.86 (m, 1H), 4.99 (d, J=17.1 Hz, 1H), 4.93 (d,

J=10.1 Hz, 1H), 2.82 (t, J=7.5 Hz, 2H), 2.03 (q, J=6.9 Hz, 2H), 1.63-1.70 (m, 2H), 1.28-1.37 (m, 12H).

2-Iodo-5-(undec-10-enyl)thiophene (2) n-BuLi (17.8 mL of 2.5M solution in hexane, 44.41 mmol) was added dropwise to a solution of **(1)** (7 g, 29.60 mmol) in THF (80 mL) at -78 °C under argon. The solution was stirred at -78 °C for 2h, then warmed to room temperature, and kept for 30 minutes. The solution was cooled to -78 °C again and iodine (13.52 g, 53.29 mmol) in 40 mL of THF was added in one portion. The solution was allowed to warm to room temperature and then stirred overnight before being quenched with saturated Na₂S₂O₃ solution. The product was extracted twice with diethyl ether. The combined organic solutions were subsequently washed with brine and dried over magnesium sulfate, filtered and the solvent was removed by rotary evaporation to give 11 g of raw product, which was purified by flash chromatography (silica gel, n-hexane) to give 9.8 g (91.4 % yield) of pure product as a yellowish oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.03 (d, J=3.4 Hz, 1H), 6.46 (d, J=3.0 Hz, 1H), 5.76-5.86 (m, 1H), 4.99 (d, J=17.1 Hz, 1H), 4.93 (d, J=10.1 Hz, 1H), 2.79 (t, J=7.5 Hz, 2H), 2.02 (q, J=6.9 Hz, 2H), 1.59-1.66 (m, 2H), 1.27-1.38 (m, 12H).

5-(Undec-10-enyl)-2,2':5',2''-terthiophene (4) A mixture of 5-trimethylstannyl-2,2'-bithiophene (3.54 g, 10.76 mmol) and iodo derivative **(2)** (3 g, 8.28 mmol) in anhydrous THF (20 mL) was degassed with argon for 10 min before addition of bis(triphenylphosphine)palladium(II) dichloride (290 mg, 0.41 mmol). The reaction mixture was refluxed for 18 h under argon atmosphere, cooled to room temperature, filtered through a plug of Celite, and the filtrate was concentrated to dryness in vacuo. The product was then recrystallized twice from n-hexane. Yellow crystals 1.1 g (33.2 % yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.15-7.23 (m, 2H), 6.97-7.08 (m, 4H), 6.66-6.70 (m, 1H), 5.76-5.86 (m, 1H) 4.99 (d, J=17.1 Hz, 1H), 4.93 (d, J=10.1 Hz, 1H), 2.79 (t, J=7.5 Hz, 2H), 2.06 (q, J=6.9 Hz, 2H), 1.64-1.71 (m, 2H), 1.29-1.37 (m, 12H).

5-Bromo-5'-(undec-10-enyl)-2,2':5',2''-terthiophene (5) A 100 mL flask was charged with (1 g, 2.49 mmol) of 5-(Undec-10-enyl)-2,2':5',2''-terthiophene **(4)** and 40 mL of CHCl₃ and cooled in an ice-water bath. Then, NBS (0.46 g, 2.62 mmol) was added in several portions and the mixture was stirred for 2h in the dark. The solution was poured into ice and extracted subsequently with

CHCl₃. The organic phase was washed with brine, dried over magnesium sulfate, and the solvent was removed under pressure. The product was then recrystallized from n-hexane to offer 1.1 g of the product as a yellow solid (91.9 % yield): ¹H NMR (400 MHz, CDCl₃, ppm): δ 6.95-6.98 (m, 4H), 6.88 (d, J=2.9 Hz, 1H), 6.69 (d, J=3.6 Hz, 1H), 5.76-5.86 (m, 1H), 4.99 (d, J=17.1 Hz, 1H), 4.93 (d, J=9.9 Hz, 1H), 2.77 (t, J=5.3 Hz, 2H), 2.05 (q, J=6.9 Hz, 2H), 1.64-1.71 (m, 2H), 1.24-1.40 (m, 12H).

2-Bromo-5-ethylthiophene (6) NBS (17.45 g, 98.04 mmol) was added in one portion to a stirred solution of 2-ethylthiophene (10 g, 89.13 mmol) in glacial AcOH (35 mL). The mixture was stirred for 2h at 45 °C and then cooled to room temperature. The reaction was quenched with cold water (200 mL), and the mixture was extracted with CH₂Cl₂, the organic phase was washed with brine (2×100 mL), dried over magnesium sulfate, filtered and the solvent was removed in vacuo to afford 16 g of raw product, which was purified by flash chromatography (silica gel, n-hexane) to give 15.2 g (89.2 % yield) of title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 6.84 (d, J=3.64 Hz, 1H), 6.54 (d, J=3.57 Hz, 1H), 2.78 (q, J=7.50 Hz, 2H), 1.28 (t, J=7.5 Hz, 3H); ¹³C NMR (CDCl₃): δ= 149.2, 129.5, 123.8, 108.7, 23.8, 15.9.

5-Ethyl-2,2'-bithiophene (7) To a suspension of magnesium turnings (iodine etched) (3.81 g, 157 mmol) in anhydrous diethyl ether (100 mL) a solution of 2-bromothiophene (12.79 g, 78.49 mmol) in 30 mL of anhydrous diethyl ether was added drop wise at such a rate that the solvent boiled gently. On the complete addition the solution was refluxed for 1h, then cooled to room temperature and the resultant Grignard reagent was added drop wise to a mixture of 2-bromo-5-ethylthiophene (**6**) (10 g, 52.33 mmol), [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (283 mg, 0.52 mmol) and dry diethyl ether (100 mL) maintained at 0 °C. The reaction mixture was stirred for 12h at room temperature, cooled to -15 °C, quenched with 1M aqueous solution of HCl and extracted with diethyl ether (2×100 mL). The combined organic layers were washed with brine (2×200 mL), dried over magnesium sulfate, filtered and the solvent was removed in vacuo to afford 12 g of raw product, which was purified by column chromatography (silica gel, n-hexane) to give 7.8 g (76.7 % yield) of title compound as a colorless oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.16 (d, J=5.1 Hz, 1H), 7.10 (d, J=3.5 Hz, 1H), 6.98-7.00 (m, two overlapping signals, 2H), 6.70 (d, J=3.5 Hz, 1H), 2.84 (q, J=7.5 Hz, 2H), 1.32 (t, J=7.5 Hz, 3H).

2-(5'-Ethyl-2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8) To a solution of (7) (5 g, 25.73 mmol) in THF (100 mL) in a flame-dried 250 mL flask at -78 °C was added dropwise n-BuLi (15.4 mL of 2.5M solution in hexane, 38.59 mmol). The mixture was stirred at -78 °C for 2h, then warmed to room temperature, and kept for 30 min. The solution was cooled to -78 °C again and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.4 mL, 46.31 mmol) was added in one portion. The solution was allowed to warm to room temperature and then stirred overnight before being poured into water. The product was extracted twice with diethyl ether. The combined organic solutions were subsequently washed with brine and dried over magnesium sulfate, filtered and the solvent was removed by rotary evaporation to give 6.5 g (86.2 % yield) of product as white crystals. The product was used in the next step without purification. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.50 (d, J=3.7 Hz, 1H), 7.16 (d, J=3.7 Hz, 1H), 7.05 (d, J=3.7 Hz, 1H), 6.70 (d, J=3.7 Hz, 1H), 2.80 (q, J=7.5 Hz, 2H), 1.30-1.35 (m, overlapping peaks with maximum at 1.35 ppm, 15H).

5-Ethyl-5'-(undec-10-enyl)-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (3) A mixture of 2-(5'-ethyl-2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8) (1 g, 3.12 mmol), 5-bromo-5'-(undec-10-enyl)-2,2':5',2''-terthiophene (5) (1 g, 2.08 mmol), two drops of Aliquat 336 and toluene (8 mL) were degassed with argon before tetrakis(triphenylphosphine)palladium(0) (120 mg, 0.1 mmol) and 2M aqueous Na₂CO₃ solution (5 mL), which had been deaerated for 2h, were added under argon. The mixture was stirred vigorously and heated at reflux for 18h before cooling down to room temperature. The reaction mixture was added dropwise to methanol/water (20:1, 600 mL) to precipitate crude product which was filtered, washed with water, methanol and cold acetone. The product was purified by column chromatography (silica, CHCl₃/n-hexane, 1:4) and remaining orange solid was recrystallized twice from toluene to give 0.55 g (44.5% yield) of the title compound as orange crystals. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.03-7.07 (m, 4H), 6.96-7.01 (m, 4H), 6.99 (d, J=7.7 Hz, 2H), 5.75-5.86 (m, 1H), 4.99 (d, J=17.0 Hz, 1H), 4.93 (d, J=9.5 Hz, 1H), 2.73-2.87 (m, 4H), 2.04 (q, J=6.7 Hz, 2H), 1.63-1.72 (m, 2H), 1.25-1.42 (m, 15H).

(1) Parab K.; Venkatasubbaiah K.; Jakle F.; *J. Am. Chem. Soc.* **2006**, *128*, 12879-12885.

Fluorescence decay measurements

Fluorescence lifetime from the monolayer on quartz Substrates were measured at room temperature using the single photon counting method. Figure S1, left shows the fluorescence decay for a substrate exposed for 10 min. to the 5T solution when monitored at a photon energy of 2.53 eV following a 50 ps wide excitation pulse at $t=0$ with 3.1 eV photons. The decay is approximately exponential with a lifetime close to 1 ns. This lifetime is comparable to the lifetime observed for solutions of the 5T molecule. Figure S1, right shows the fluorescence decay for the complete monolayer obtained by exposing for 24hr to the solution containing the 5T molecule, monitoring the fluorescence at 2.07 eV using the 3.1 eV excitation pulse. The initial decay of the complete monolayer occurs with a higher decay rate than for the substrate exposed for 10 min. The initial fast decay is followed a slower decay process with decay constant 0.5 ns^{-1} ; this multiexponential nature indicates heterogeneity in the population of excited state species emitting the fluorescence.

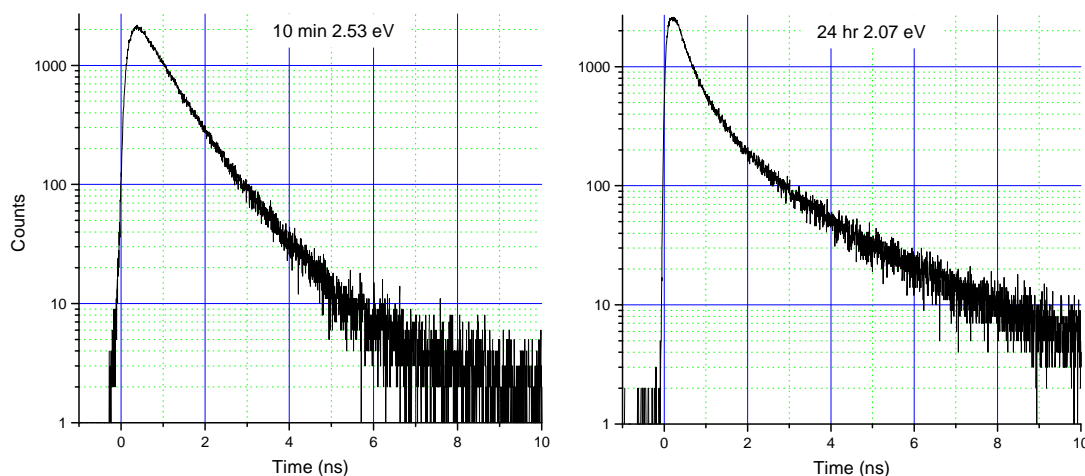


Figure S1 Decay of the fluorescence from (left) quartz substrate exposed for 10 min monitored at 2.53 eV, (right) substrate exposed for 24 hr monitored at 2.07 eV.

Complete References Main manuscript:

(8) Defaux, M.; Gholamrezaie, F.; Wang, J.; Kreyes, A.; Ziener, U. D.; Anokhin, V.; Ivanov, D. A.; Moser, A.; Neuhold, A.; Salzmann, I.; Resel, R.; de Leeuw, D. M.; Meskers, S. C. J., Moeller, M.; Mourran, A. *Adv. Mater.* **2012**, *24*, 973-978.

(22) Gholamrezaie, F.; Mathijssen, S. G. J.; Smits, E. C. P.; Geuns, T. C. T.; van Hal, P. A.; Ponomarenko, S. A.; Flesch, H. G.; Resel, R.; Cantatore, E.; Blom, P. W. M.; de Leeuw, D. M. *Nano Lett.* **2010**, *10*, 1998-2002.

(23) Smits, E. C. P.; Mathijssen, S. G. J.; van Hal, P. A.; Setayesh, S.; Geuns, T. C. T.; Cantatore, E.; Wondergem, H. J.; Werzer, O.; Resel, R.; Kemerink, M.; Kirchmeyer, S.; Muzafarov, A. M.; Aziz, M.; Ponomarenko, S. A.; de Boer, B.; Blom, P. W. M.; de Leeuw, D. M. *Nature*, **2008**, *455*, 956-959.

(24) Mathijssen, S. G. J.; Smits, E. C. P.; van Hal, P. A.; Wondergem, H. J.; Ponomarenko, S. A. Moser, A.; Resel, R.; Bobbert, P. A.; Kemerink, M.; Janssen, R. A. J.; et al. *Nature Nano. Tech.* **2009**, *4*, 674-680.

(25) Flesch, H-G. Mathijssen, S. G. J.; Gholamrezaie, F.; Moser, A.; Neuhold, A.; Novak, J.; Ponomarenko, S. A.; Shen, Q.; Teichert, C.; Hlawacek, G.; Puschnig, P.; Ambrosch-Draxl, C.; Resel, R.; de Leeuw, D. M. *J. Phys. Chem. C* **2011**, *115*, 22925-22930.