Supporting information

para-Azaquinodimethane based quinoidal polymers for opto- electronic applications: Impact of donor units on opto-electronic properties

Bharath Dyaga,^a Sasikumar Mayarambakam,^{a,b} Olzhas A. Ibraikulov,^c Nicolas Zimmermann,^c Sadiara Fall,^c Olivier Boyron,^d Thomas Heiser,^c Nicolas Leclerc,^e Nicolas Berton,^a Bruno Schmaltz^{*a}

- ^a Laboratoire de Physico-Chimie des Matériaux et des Electrolytes pour l'Energie (PCM2E), EA6299, Université de Tours, 37200 Tours, France
- ^b Department of Chemistry, Indian Institute of Science Education and Research (IISER)-Tirupati-517507, India.
- ^c Laboratoire ICube, Université de Strasbourg, CNRS UMR 7357, 67037 Strasbourg, France.
- ^d Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5128, Laboratoire CP2M, Equipe PCM, 69100 Villeurbanne, France.
- ^e Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), Université de Strasbourg, CNRS UMR 7515, 67087 Strasbourg, France

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1. Experimental section

a) Materials

All the chemicals are purchased from various suppliers and used without any further purification unless otherwise stated. 5-Bromo-2-thiophenecarboxaldehyde, 1,4-Diacetyl-2,5-piperazinedione, 2,2'-Bithiophene, thiophene, 2,5-Bis(trimethylstannyl)-thieno[3,2-b]thiophene, n-butyl lithium (2.5M in hexane), tri methyl tin chloride (1M in THF), titanium tetrachloride, Tetrakis(triphenylphosphine)palladium(0), 2-(Tributylstannyl)thiophene, bromobenzene, Triethylamine, anhydrous THF, anhydrous Toluene, anhydrous DMF,

Acetone, CHCl₃, and chlorobenzene were purchased from TCI Europe, Sigma-Aldrich, and Across organics and used as received.

b) Characterization

NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm). UV-Vis spectra were recorded with a Jasco V-670 spectrometer. Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-400 (heating/cooling rate 10 °C min⁻¹). Thermogravimetric analysis (TGA) was fulfilled using a Perkin Elmer STA 6000 at a heating rate of 10 °C.min⁻¹ under N₂. High temperature size exclusion chromatography (HT-SEC) analyses were performed using a Viscotek system, from Malvern Instruments. 1,2,4-trichlorobenzene (TCB) was used as the sample solvent and the eluent phase at 150 °C. The separation was performed on a combination of three columns (PLgel Olexis from Agilent Technologies, $300 \text{ mm} \times 7.5 \text{ mm}$, $13 \mu \text{m}$). Cyclic voltammetry (CV) was performed on a Biologic Applied Research MPG2 multi-channel potentiostat, and CV experiments were performed at room temperature with a conventional three-electrode setup consisting of a platinum disk working electrode, silver wire and platinum wire respectively as reference and counter electrodes. The potential of the reference electrode was calibrated using Fc/Fc⁺ couple as an internal standard. All the measurements were conducted in anhydrous acetonitrile media under a nitrogen atmosphere using Bu4NClO4 (0.1 M) as a supporting electrolyte at a scan rate of 50 mV/s. The HOMO energy levels of polymers, were calculated from the equation $E_{HOMO} = -[5.1 + E_{ox}]eV$.¹

c) Organic Field-Effect Transistors fabrication

Bottom contact bottom gate OFET structures were fabricated using commercially available silicon substrates. Lithographically defined Au (30 nm)/ITO (10 nm) bilayers were used as source and drain electrodes and 230 nm thick SiO₂ layer as a gate dielectric. Channel length and width were L=20 μ m and W=10 mm, respectively. Substrates were cleaned consecutively in ultrasonic baths at 45 °C for 15 min each step using soap, acetone, and isopropanol and followed by 15 min UV-ozone treatment. Then substrates were transferred into a nitrogen filled glove box where they were treated by ODTS. Finally, solutions of PAQM3T, PAQM4T, PAQM2T-TT and PAQM2T-TVT were spin-coated to complete the FET devices. For each molecule, a concentration of 10 mg/mL in *o*-DCB was used. Prior to characterization, completed devices were dried under high vacuum ($\approx 10^{-6}-10^{-7}$ mbar). Transistor output and transfer characteristics were measured using a Keithley 4200 semiconductor characterization system. Hole mobilities were extracted in the saturated regime using a standard device model.

d) Organic Photovoltaic devices fabrication and measurements

ITO coated glass substrates were cleaned in ultrasonic bath of deionized water, acetone and 2propanol at 45 °C for 15 minutes for each step. Then, they were dried by nitrogen and were treated in a UV/Ozone oven to remove residual organic contaminants. ZnO layer (\approx 20 nm) was spin-coated onto pre-cleaned ITO and thermally annealed at 110 °C for 15 min and used as an electron extracting contact. The photoactive layer was prepared from different solutions containing polymer:PC₇₁BM blends. The solution were spin-coated onto the ZnO/ITO substrates. The 7 nm thick MoO₃ and 120 nm thick Ag layers were thermally evaporated (Pressure \approx 1x10⁻⁶ mbar). The effective area of each cell was 12 mm².

The (J-V) curves of the OPV devices were measured under AM 1.5G-100 mW/cm² simulated sunlight irradiation. (J-V) characteristic measurements of photovoltaic devices were conducted using LabView-controlled Keithley 2400 SMU. The performance of solar cells under the dark and illumination were measured using a BET Technologies Sun 3000 solar simulator with an AM1.5G filter. All the photovoltaic parameters of solar devices (*Voc*, *Jsc*, *FF* and *PCE*) were extracted using the LabView software.

2. Synthesis



Scheme S1. Synthesis of (E)-1,2-bis(5-bromothiophen-2-yl)ethene (4) and distannyl monomers

Synthesis of 2-dodecyl 1-bromohexadecane (1):

2-dodecyl 1-bromohexadecane was synthesized according to a modified procedure from the literature.² In a round bottom flask, 2-decyl hexadecane 1-ol (20 gr, 48.6 mmol, 1eq) and

triphenylphosphine (25.54 gr, 97.3 mmol, 2 eq) were dissolved in dichloromethane. The mixture was cooled to 0 °C. At this temperature, NBS (12.99 gr, 73 mmol, 1.5 eq) was added slowly by portion to the reaction mixture over the period of 30 min. The reaction mixture was let warm to room temperature and stirred for 12 h. The reaction was quenched with water and extracted with dichloromethane. The organic phase was dried over MgSO4, filtered and the crude product was purified by column chromatography to give a colourless liquid (22 gr, 90%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.44-3.45 (d, *J* = 4.7 Hz, 2H), 1.56-1.62 (m, 1H), 1.40-1.21 (m, 48H), 0.84-0.91 (m, 6H); ¹³C NMR: δ 39.68, 39.50, 32.56, 31.93, 29.79, 29.69, 29.67, 29.64, 29.59, 29.37, 26.56, 22.70, 14.11.

Synthesis of 3,6-bis((5-bromothiophen-2-yl)methylene)piperazine-2,5-dione (2): Into a mixture of 2,5-Piperazinedione (2 g, 10 mmol, 1 eq.) and 5-bromothiophene 2-carboxaldehyde (4.82 g, 25 mmol, 2.5 eq.) in DMF (46 mL), triethylamine was added dropwise via syringe (5.62 g, 40 mmol, 4 eq.) at 120 °C under N₂. Upon addition, the original colourless solution was turned into red and a yellow precipitate was formed during the overnight reaction. After cooling to room temperature, the precipitate was collected by filtration and rinsed with acetone. The product was used for the next step without further purification (Yield 2.8 g, 60%). ¹H NMR (300 MHz, CDCl₃, ppm): 10.16 (s, 2H), 7.37 (d, J = 3.9 Hz, 2H), 7.29 (d, J = 3.9 Hz, 2H), 6.88 (s, 2H).

Synthesis of (2Z,5Z)-2,5-bis((5-bromothiophen-2-yl)methylene)-3,6-bis(2dodecylhexadecyloxy)-2,5-dihydropyrazine (3):

A mixture of the diarylene-diketopiperazine 1 (1.5 g, 3.2 mmol, 1 eq.), K_2CO_3 (2.25 g, 16 mmol, 5 eq.) and alkyl bromide (6.17 g, 13 mmol, 4 eq.) in DMF (15 mL) was stirred at 100 °C for 2 hours under N₂. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was distilled under reduced pressure. The solid was purified by column chromatography to give an orange solid (2.63 g, 65%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 6.97-7.05 (m, 6H), 4.34-4.41 (d, 4H), 1.86-2.00 (m, 2H), 1.16-1.49 (m, 96H), 0.82-0.93 (m, 12H); ¹³C NMR: δ 157.90, 140.64, 129.89, 129.16, 128.56, 118.67, 116.46, 71.24, 37.18, 31.93, 31.63, 30.11, 29.71, 29.67, 29.37, 26.80, 22.69, 14.12.

(E)-1,2-bis(5-bromothiophen-2-yl)ethene (4):

TiCl₄ (1.37 mL, 0.0125 mol) was added dropwise to anhydrous THF (50 mL) under Ar atmosphere at -10 °C and the suspension was stirred at -10 °C for 15 min, then Zn powder (1.50 g, 0.023 mol) was added portion wise. The resulted mixture was heated under reflux for 1 h. Afterward, the reaction mixture was cooled to room temperature and 5-Bromo-2-thiophenecarboxaldehyde (2 g, 0.0104 mol) was added slowly. The reaction was then refluxed

for 12 additional hours. The mixture was cooled to room temperature poured into ice-cold water bath, extracted with DCM and the organic layer were dried over MgSO₄. The product was purified by recrystallization in cyclohexane to give pure (E)-1,2-bis(5-bromothiophen-2-yl)ethene as a yellow solid (1.46 g, 80%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 6.94 (d, *J* = 3.8 Hz, 2H), 6.80 (s, 2H), 6.77 (d, *J* = 3.8 Hz, 2H); ¹³C NMR: 143.53, 130.60, 126.56, 121.09, 111.44.

General procedure for synthesis of distannyl monomer: example for 2,5bis(trimethylstannyl)thiophene (5)

2,5-dibromo thiophene (1 g, 4.1 mmol, 1 eq) was dissolved in anhydrous THF (1 g in 30 mL THF) under argon atmosphere. The solution was cooled to -78 °C and n-BuLi (4.1 mL, 2.5M in hexane, 2.5 eq) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h, then a 1.0 M solution of trimethyltin chloride in THF (11.7 mL, 2.6 eq) was added. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with water and extracted with diethyl ether. The combined organic phase was dried over MgSO₄, filtered and concentrated. The crude product was recrystallized from methanol to give 5 as a white solid (0.67 g, 38%).

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.36 (s, 2H), 0.349 (t, 18H); ¹³C NMR: 143.02, 135.80, -8.20.

5,5'-bis(trimethylstannyl)-2,2'-bithiophene (6): white solid yield: 80%

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.27 (d, *J* = 3.4 Hz, 2H),7.08 (d, *J* = 3.4 Hz, 2H), 0.39 (s, 18H); ¹³C NMR: δ 143.00, 137.04, 135.84, 124.83, -8.24.

(E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (7): Tan needles. yield: 80%
¹H NMR (300 MHz, CDCl₃, ppm): δ 7.12 (d, J = 3.3 Hz, 2H), 7.09 (s, 2H), 7.07 (d, J = 3.3 Hz, 2H), 0.37 (s, 18H); ¹³C NMR: δ 148.20, 137.49, 135.74, 127.02, 121.19, -8.28.

General procedure for Stille polymerization: example for PAQM3T

A mixture of **3** (300 mg, 240 μ mol, 1 eq.), **5** (98.6 mg, 240 μ mol, 1 eq.) and Pd(PPh₃)₄ (8.3 mg, 0.03 eq.) in dry toluene (15 mL) was sealed in an argon flushed Schlenk tube and heated to 110 °C while stirring for 48 h. 2-(tributylstannyl)thiophene (0.1 mL) and bromobenzene (0.1 mL) were injected successively as end-capping reagents. The reaction mixture was stirred for 2 h after each injection. After cooling down to room temperature, the mixture was precipitated into methanol. The precipitate was purified by Soxhlet extraction with methanol (24h), acetone (24h), cyclohexane (24h), successively. The cyclohexane fraction was concentrated and precipitated in methanol. The polymer (0.24 g, 85%) was collected by filtration.

PAQM4T: Soxhlet extraction with methanol (24h), acetone (24h), cyclohexane (24h), CHCl₃ (24h), and chlorobenzene (24h) successively. The chlorobenzene fraction was concentrated and precipitated into methanol. The polymer (0.28 g, 93%) was collected by filtration.

PAQM2T-TT: Soxhlet extraction with methanol (24h), acetone (24h), cyclohexane (24h), CHCl₃ (24h), and chlorobenzene (24h) successively. The chlorobenzene fraction was concentrated and precipitated into methanol. The polymer (0.27 g, 91%) was collected by filtration.

PAQM2T-TVT: Soxhlet extraction with methanol (24h), acetone (24h), cyclohexane (24h), CHCl₃ (24h), and chlorobenzene (24h) successively. The chlorobenzene fraction was concentrated and precipitated into methanol. The polymer (0.26 g, 84%) was collected by filtration.

3. Supplementary details

3.1) Size exclusion chromatography



Figure S1: Molecular weight distribution of samples obtained by high temperature size exclusion chromatography in 1,2,4-trichlorobenezene at $150 \,^{\circ}\text{C}$

3.2) Photoelectron spectroscopy in air



Figure S2: Photoelectron spectroscopy of all polymers in air

3.3) Thermal analysis of all *p*-AQM polymers



Figure S3: (a) TGA plots of *p*-AQM polymers, thermal decomposition temperature (T_d) corresponding to 5% weight loss (b) Differential scanning colorimetry (DSC) of *p*-AQM polymers (2^{nd} heating and cooling)

3.4) EQE of PAQM2T-TT/PC71BM



Figure S4: EQE of optimized device of PAQM2T-TT/PC₇₁BM (1/1.5) and EQE of optimized device of PAQM2T-TT/PC₇₁BM (1/1.5) with DPE is an additive.

3.5) OPV data of PAQM2T-TT with EH-IDTBR as non-fullerene acceptor

Device configuration: ITO/ZnO/Active layer/MoO₃/Ag

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| Polymer | D-A Ratio | Voc | J_{sc} | FF | PCE |
|-----------|------------------|------|----------|-------|------|
| PAQM2T-TT | 1:2 | 0.25 | 2.14 | 30.22 | 0.16 |

3.6) NMR



Figure S6: ¹³C NMR spectrum of 2-dodecyl hexadecyl bromide (1)



Figure S8: ¹H NMR spectrum of Dibromo p-AQM (3)



Figure S9: 13 C NMR spectrum of Dibromo *p*-AQM (3)



Figure S10: ¹H NMR spectrum of (E)-1,2-bis(5-bromothiophen-2-yl)ethene (4)



Figure S11: ¹³C NMR spectrum of (E)-1,2-bis(5-bromothiophen-2-yl)ethene (4)



Figure S12: ¹H NMR spectrum of 2,5-Bis(trimethylstannyl)thiophene (5)



Figure S13: ¹³C NMR spectrum of 2,5-Bis(trimethylstannyl)thiophene (5)



Figure S14: ¹H NMR spectrum of 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (6)



Figure S15: ¹³C NMR spectrum of 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (6)



Figure S16: ¹H NMR spectrum of (E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (7)



Figure S17: ¹³C NMR spectrum of (E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (7)

3.7) References:

- 1. N. Berton, C. Ottone, V. Labet, R. de Bettignies, S. Bailly, A. Grand, C. Morell, S. Sadki, F. Chandezon, *Macromolecular Chemistry and Physics* **2011**, *212*, 2127.
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