Electronic Supplementary Information

Quinoidal Dicyanomethylene-endcapped Cyclopentadithiophenes as

Vacuum-Processable n-Type Semiconductor

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1. Materials and Methods

UV-vis spectroscopy in CH₂Cl₂ were measured at room temperature on a Jasco V770 spectrophotometer in 10 mm cuvettes (SUPRASIL[®], Hellma[®] Analytics). For the thin-film spectra on quartz substrates (SUPRASIL[®], Hellma[®] Analytics) as well as of the active layer of the OSC, the same spectrometer with an integration sphere was used. Thin films of investigated compounds were fabricated by thermal sublimation of 30 nm thick layer on quartz substrates analogue to the OTFTs fabrication, while the substrate was not heated.

Fluorescence spectroscopy in CH₂Cl₂ solution (10^{-7} M, $A_{max} < 0.05$, spectroscopic grade, Uvasol[®], Merck) were measured at room temperature on an Edinburgh Instruments FLS980-D2D2-ST spectrometer and were corrected against the photomultiplier sensitivity and the lamp intensity. Fluorescence lifetimes were determined with an EPL picosecond pulsed diode laser ($\lambda_{ex} = 505.8$ nm) for time correlated single photon counting (TCSPC) with the same spectrometer. Fluorescence quantum yields were measured in CH₂Cl₂ on a Hamamatsu Absolute PL Quantum Yield Measurement System CC9920-02.

Cyclic voltammetry was performed with an electrochemical analyser (EC epsilon; BAS Instruments) with a three-electrode single component cell. CV data was measured in CH_2Cl_2 (2.5×10⁻⁴ M) with addition of Bu₄NPF₆ versus Fc/Fc⁺ standard. The working and the auxiliary electrodes consist of Pt and the reference electrode of Ag/AgCI.

NMR spectroscopy was performed on a Bruker *Avance III HD* 400 MHz NMR spectrometer relative to residue undeuterated solvent signals. The chemical shifts (δ)

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are listed in parts per million (ppm). Multiplicities for proton signals are abbreviated as s, d, t and m for singlet, doublet, triplet and multiplet, respectively.

Mass spectrometry was performed in the negative mode via MALDI-TOF on a Bruker Daltonics Autoflex *II* with 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile) (DCBT) as matrix.

Thermogravimetric analysis was performed using a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer under nitrogen atmosphere at a heating rate of 5 °C min⁻¹ up to a maximum temperature of 500 °C.

Differential scanning calorimetry thermograms were recorded using a DSC 8000 (Perkin Elmer) equipped with an Intracooler 2 refrigerated cooling system at a scan rate of 10 °C min⁻¹.

DFT calculations for HOMO and LUMO energies as well as for the ground state dipole moments were performed with GAUSSIAN 09.^{S1} Start structures were energy minimized by using B3LYP^{S2,S3,S4} functional and 6-31G^{**S5-S7} basis set.

ADF (Amsterdam Density Functional) calculation^{S8-S10} for the transfer integral was performed employing the TZP^{S11} basis set and the PW91^{S12} functional.

Single crystal X-ray diffraction for compounds CPTQ-Oc, CPTQ-EH, CPTQ-Pr and CTPQ-Ph was measured at 100 ± 1 K on a Bruker D8 Quest Kappa diffractometer with a Photon II CMOS detector and multi-layered mirror monochromated $Cu_{K\alpha}$ radiation. The solved structure was obtained with Fourier techniques and the Shelx software package.^{S13} Crystallographic data are deposited with the Cambride Crystallographic Data Centre as supplementary publication no. CCDC 2011168 (CPTQ-Oc), CCDC 2011165 (CPTQ-EH), CCDC 2011167 (CPTQ-Pr) and CCDC 2011166 (CPTQ-Ph).

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Thin-film X-ray diffraction data were collected on a Bruker D8 Discover diffractometer with a LynxEye-1D-Detecter and $Cu_{K_{\alpha}}$ radiation.

Organic thin-film transistors were fabricated on Si/SiO₂ (100 nm)/AIO_x (8 nm)/ntetradecvlphosphonic acid (TPA, 1.7 nm) substrates with a capacitance C_i = 32.4 nF cm⁻². The pre-cleaned wafers were placed in the vacuum chamber. For OTFTs fabricated at room temperature, the wafer was placed into the thermal evaporation system Auto306 (BocEdwards) followed by depositing 30 nm of the respective compound (r = 0.02 - 0.05 Å s⁻¹) at a pressure of about 10⁻⁶ mbar from a guartz crucible enclosed by a ceramic boat. On top of the organic material 30 nm gold as electrode material was deposited through a shadow mask (r = 0.2 Å s⁻¹) to obtain the device geometry ($L = 100 \,\mu\text{m}$, $W = 200 \,\mu\text{m}$). Each resulting film growth was monitored by a quartz crystal microbalance. OTFTs, which were fabricated with higher substrate temperature were processed in the OPVIvap-XL (Creaphys GmbH). The semiconductor layer was deposited (15 nm, r = 0.04 Å s⁻¹) from a quartz crucible enclosed by a ceramic boat at a pressure below 10⁻⁶ mbar followed by the evaporation of gold electrodes (30 nm, r = 0.2 Å s⁻¹). The resulting transfer and output characteristics were measured under inert conditions (M. Braun Inertgas Systeme GmbH; $c(O_2) < 0.1$ ppm, $c(H_2O) < 0.1$ ppm) with an Agilent 4055C parameter analyzer and a Cascade EPS150 probe station.

AFM morphologies of thin films were investigated with NT-MDT Next Solver System in semi-contact mode by using a SCOUT 350 RAI (Nu Nano Ltd) silicon cantilever (spring constant = 42 N m^{-1} ; resonance frequency = 350 kHz).

Organic Photovoltaics were processed on ITO-glass substrates (Soluxx GmbH), which were cleaned by sonication with acetone, detergent solution (mucasol[®]), deionized water and isopropanol followed by an ozone/UV treatment for 30 min. The

substrates are placed into the evaporation system OPTIvap-XL and MoO₃ (*d* = 6 nm, r = 0.1 Å s⁻¹, *Rotation* = 10 rpm, $p < 10^{-6}$ mbar) were sublimated on top of the ITO as hole-transporting layer followed by a thickness variation of merocyanine dye **MD376** (r = 0.1 Å s⁻¹, *Rotation* = 10 rpm, $p < 10^{-6}$ mbar) and the acceptor molecules **CPTQ-R/C**₆₀ (r = 0.1 Å s⁻¹, *Rotation* = 10 rpm, $p < 10^{-6}$ mbar). Bathocuproine (BCP, d = 10 nm, r = 0.1 Å s⁻¹, *Rotation* = 10 rpm, $p < 10^{-6}$ mbar) and aluminium (d = 100 nm, r = 1.2 Å s⁻¹, *Rotation* = 10 rpm, $p < 10^{-6}$ mbar) and aluminium (d = 100 nm, r = 1.2 Å s⁻¹, $p < 10^{-6}$ mbar) was used as electron transport layer and top electrode. *J*-*V*-characteristics were measured after calibration with a standard silicon solar cell with a KG filter (ISE Freiburg) under an AM1.5G Oriel Sol3ATM Class AAA solar simulator (Newport[®]) by a parameter analyzer (Botest Systems GmbH). *EQE* measurements were carried out with a Quantum Efficiency/IPCE Measurement Kit (Newport[®]) by using a 300 W Xe lamp and a Cornerstone monochromator with a Merlin Lock-In Amplifier for detection.

2. Synthesis

Synthesis of precursor compounds CPDT-R



The precursors were synthesized analogue to literature-known procedure. **CPDT-Oc** and **CPDT-Pr** were reported by Zottl *et al.*,^{S14} **CPDT-EH** by Zhu *et al.*,^{S15} and **CPDT-Ph** by Hanamura *et al.*^{S16} The structure of the synthesized precursors were confirmed by ¹H NMR spectroscopy.

Synthesis of target compounds CPTQ-R



Synthesis of **CPTQ-Oc** (as general procedure): Compound **CPDT-Oc** (200 mg, 0.49 mmol) was dissolved in anhydrous DMF (3 mL), and tetracyanoethylene (TCNE, 145 mg ,1.99 mmol) was added to the reaction solution. The color of the reaction solution changed into dark red immediately after addition of TCNE. The reaction mixture was heated at 100 °C for 30 min. TLC analysis showed that the complete consumption of starting materials and the formation of monotricyanovinyl product (upper fraction) and quinoidal target compound **CPTQ-Oc** (second fraction) as major product. After cooling down to room temperature, water was added to the mixture. The aqueous phase was extracted with diethyl ether four times. The combined organic

phase was washed with brine to remove residual DMF, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified via column chromatography by using hexane/chloroform (2/1 to 1/4, V/V) as eluent to afford the final product **CPTQ-Oc** as a dark solid with the yield of 31% (83 mg, 0.16 mmol).

2,2'-(4,4-Dioctyl-2H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6(4H)-

diylidene)dimalono-nitrile (CPTQ-Oc)

Yield = 31%

¹H NMR (CDCl₃, 400 MHz): δ 6.88 (s, 2H), 1.82 (m, 4H), 1.3-1.2 (m, 20H), 1.02 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 177.5, 175.6, 145.6, 119.1, 112.6, 112.3, 73.2, 53.0, 38.8, 31.7, 29.6, 29.2, 24.8, 22.6, 14.1.

HRMS (MALDI-TOF, neg. mode, DCTB:CHCl₃ (3:1)): *m*/*z* calculated for C₃₁H₃₆N₄S₂⁻ [M⁻] = 528.24, found: = 528.23.

UV-vis absorption (CH₂Cl₂): λ_{max} = 531 nm; ε_{max} = 88200 M⁻¹ cm⁻¹

MP = 142 °C (DSC)

Sublimation Temperature = 95 °C ($p < 10^{-6}$ mbar)

2,2'-(4,4-Bis(2-ethylhexyl)-2H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6(4H)-

diylidene)dimalononitrile (CPTQ-EH)

Yield: 25%

¹H NMR (CDCl₃, 400 MHz): δ 6.88 (s, 2H), 1.90 (m, 4H), 1.1 (m, 16H), 0.92 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 6H), 0.74 (t, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 176.8, 175.7, 145.9, 119.5, 112.5, 112.1, 73.2, 52.5,
44.1, 35.9, 33.8, 28.2, 27.2, 22.9, 14.0, 10.4.

HRMS (MALDI-TOF, neg. mode, DCTB:CHCl₃ (3:1)): *m*/*z* calculated for C₃₁H₃₆N₄S₂⁻ [M⁻] = 528.24, found: = 528.23.

UV-vis absorption (CH₂Cl₂): λ_{max} = 534 nm; ε_{max} = 81400 M⁻¹ cm⁻¹

MP = 202 °C (DSC)

Sublimation Temperature = 80 °C ($p < 10^{-6}$ mbar)

2,2'-(4,4-Dipropyl-2*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-2,6(*4H*)-diylidene)dimalononitrile (CPTQ-Pr)

Yield = 18%

¹H NMR (CDCl₃, 400 MHz): δ 6.89 (s, 2H), 1.9 (m, 4H), 1.15 - 1.05 (m, 4H), 0.9 (t, J = 7.2 Hz, 6H),

¹³C NMR (CDCl₃, 100 MHz): δ 177.5, 175.6, 145.7, 119.2, 112.6, 73.2, 53.1, 40.8, 18.2, 14.1.

HRMS (MALDI-TOF, neg. mode, DCTB:CHCl₃ (3:1)): *m*/*z* calculated for C₂₁H₁₆N₄S₂⁻ [M⁻] = 388.08, found: = 388.08.

UV-vis absorption (CH₂Cl₂): λ_{max} = 531 nm; ε_{max} = 89100 M⁻¹ cm⁻¹

MP = 271 °C (DSC)

Sublimation Temperature = 90 °C ($p < 10^{-6}$ mbar)

2,2'-(4,4-Diphenyl-2*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-2,6(*4H*)-diylidene)dimalononitrile) (CPTQ-Ph)

Yield = 29%

¹H NMR (400 MHz, CD₂Cl₂): δ 7.4 (m, 6H), 7.15 (m, 4H), 6.94 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 175.7, 173.1, 143.8, 138.6, 128.6, 126.4, 120.6, 111.4, 111.0, 73.1, 59.9.

HRMS (MALDI-TOF, neg. mode, DCTB:CHCl₃ (3:1)): *m*/*z* calculated for C₂₇H₁₂N₄S₂⁻ [M⁻] = 456.05, found: = 456.05.

UV-vis absorption (CH₂Cl₂): λ_{max} = 534 nm; ε_{max} = 83200 M⁻¹ cm⁻¹

MP = 331 °C (DSC)

Sublimation Temperature = 115 °C ($p < 10^{-6}$ mbar)

3. ¹H NMR Spectra



Fig. S1 ¹H NMR spectrum (400 MHz) of CPTQ-Oc measured in CDCl₃ at room temperature. * CHCl₃, # H₂O.



Fig. S2 ¹H NMR spectrum (400 MHz) of CPTQ-EH measured in CDCl₃ at room temperature. * CHCl₃, # H₂O.



Fig. S3 ¹H NMR spectrum (400 MHz) of CPTQ-Pr measured in CDCl₃ at room temperature. * CHCl₃, # H₂O.



Fig. S4 ¹H NMR spectrum (400 MHz) of CPTQ-Ph measured in CDCl₃ at room temperature. * CHCl₃, #H₂O.

4. ¹³C NMR Spectra



Fig. S5 ¹³C NMR spectrum (100 MHz) of CPTQ-Oc measured in CDCl₃ at room temperature. * CHCl₃.



Fig. S6 ¹³C NMR spectrum (100 MHz) of CPTQ-EH measured in CDCl₃ at room temperature. * CHCl₃.



Fig. S7 ¹³C NMR spectrum (100 MHz) of CPTQ-Pr measured in CDCl₃ at room temperature. * CHCl₃.



Fig. S8 ¹³C NMR spectrum (100 MHz) of CPTQ-Ph measured in CDCl₃ at room temperature. * CHCl₃.



5. High-Resolution Mass Spectra

Fig. S9 Mass spectrum of CPTQ-Oc measured by MALDI-TOF in DCTB:CHCl₃ (3:1).



Fig. S10 Mass spectrum of CPTQ-EH measured by MALDI-TOF in DCTB:CHCl₃ (3:1).



Fig. S11 Mass spectrum of CPTQ-Pr measured by MALDI-TOF in DCTB:CHCl₃ (3:1).



Fig. S12 Mass spectrum of CPTQ-Ph measured by MALDI-TOF in DCTB:CHCl₃ (3:1).

6. Fluorescence



Fig. S13 UV-vis (solid line) and fluorescence (dashed line) spectra of CPTQ-Oc measured in CH₂Cl₂.

	λ _{Em} (nm)	Stokes Shift (cm ⁻¹)	<i>∲</i> ⊧। (%)	τ ^a (ns)
CPTQ-Oc	551	680	< 1	< 0.5
CPTQ-EH	549	510	< 1	< 0.5
CPTQ-Pr	549	620	< 1	< 0.5
CPTQ-Ph	549	510	< 1	< 0.5

Table S1 Results from fluorescence measurements for **CPTQ-R** derivatives in CH₂Cl₂ giving rise to emission maxima (λ_{Em}), Stokes shifts, fluorescence quantum yields (ϕ_{FI}) as well as fluorescence lifetimes (τ).

^a The fluorescence lifetimes are below the instrument response time of the TCSPC setup.

7. X-Ray

Table S2 X-ray structure characteristics for CPTQ-R derivatives.

	CPTQ-Oc	CPTQ-EH	CPTQ-Pr	CPTQ-Ph
Empirical formula	$C_{31}H_{36}N_4S_2$	$C_{31}H_{36}N_4S_2$	$C_{21}H_{16}N_4S_2$	$C_{27}H_{12}N_4S_2$
$M_{\rm empirical}$ (g mol ⁻¹)	528.76	528.76	388.50	456.53
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178
Т (К)	100	100	100	100
Description of the crystal				
Color	Red	Red	Red	Red
Habit	Needle	Block	Block	block
Crystal System	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P-1	P 21/c
Unit cell dimension				
a (Å)	36.1243	11.2766	8.0883	15.1209
b (Å)	13.4326	14.5164	9.7191	10.3600
c (Å)	26.6643	19.2705	12.9959	16.1591
α (°)	90	81.129	95.349	90
β (°)	115.541	78.6665	103.060	117.608
γ (°)	90	88.437	96.387	90
Volume (Å ³)	11674.3	3056.0	981.6	2243.1
Z	16	2	2	4
$p_{\text{calc.}}$ (g cm ⁻³)	1.203	1.149	1.314	1.352
<i>F</i> (000)	4512	1128	404	936
Range of θ (°)	2.71 – 71.91	2.36 – 68.45	3.51 – 72.52	3.29 – 72.16
Goodness of Fit	1.051	1.109	1.063	1.062
CCDC	2011168	2011165	2011167	2011166

$2\Theta_{\mathrm{TF}}$	20 _{SC}	h	k	1
(°)	(°)			
4.8	5.4	2	0	0
6.4	7.1	1	1	0
7.0	7.3	0	0	2
14.4	14.7	0	0	4
19.3	-	-	-	-
21.2	22.1	0	0	6
24.2	-	-	-	-
28.4	29.6	0	0	8
29.2	-	-	-	-

Table S3 Indexed thin-film diffraction reflexes for sublimated thin film of **CPTQ-Oc** on TPA-modified Si/SiO₂/AlO_x substrates with a substrate temperature of 40 $^{\circ}$ C.

Table S4 Calculated transfer integrals for holes (t_+) and electrons (t_-) between closest neighbors in **CPTQ-R** singlecrystal structures via ADF. For the indexed neighbors see Figure 3.

CPTQ-R	Neighbor	<i>t</i> ₊ (meV)	<i>t</i> - (meV)	CPTQ-R	Neighbor	<i>t</i> ₊ (meV)	<i>t</i> - (meV)
CPTQ-Oc	(1)	-27	24	CPTQ-Pr	(1)	38	32
	(2)	-26	23		(2)	8	5
	(3)	-106	1		(3)	105	-1
	(4)	-3	1		(4)	27	35
	(5)	-17	-120		(5)	37	-3
	(6)	198	-128		-	-	-
CPTQ-EH	(1)	-22	19	CPTQ-Ph	(1)	5	-6
	(2)	4	1		(2)	-34	1
	(3)	133	1		(3)	-34	1
	(4)	-1	-4		(4)	24	-28
	(5)	5	0		(5)	22	-29

8. DSC & TGA



Fig. S14 Differential scanning calorimetry traces of **CPTQ-Oc** (black), **CPTQ-EH** (red), **CPTQ-Pr** (blue) and **CPTQ-Ph** (pink) in second heating process. The heating and cooling rates were 10 °C min⁻¹. **CPTQ-Ph** shows a decomposition directly after its melting point at 331 °C.



Fig. S15 Representative TGA trace of **CPTQ-Oc**. The measurement was performed with ceramic pans under a flow of N_2 with a heating rate of 5 °C min⁻¹. Due to the sublimation process, which also occurs at 1 atm, the informative value of TGA experiments is limited.

9. OTFT



Fig. S16 Output characteristics for Si/SiO₂/AIO_x/**TPA/CPTQ-R**/Au based OTFTs processed at different substrate temperatures. For OTFTs at elevated substrate temperature, the semiconductor layer thickness was decreased from 30 nm to 15 nm.



Fig. S17 Square-root plot for Si/SiO₂/AlO_x/TPA/**CPTQ-R**/Au based OTFTs processed at different substrate temperatures and layer thicknesses (left: 30 nm, right: 15 nm).

10. AFM



Fig. S18 AFM images of vacuum-processed layers of **CPTQ-R** on TPA-modified Si/SiO₂/AIO_x substrates deposited at different substrate temperatures of 20 °C (top), 40 °C (middle) or 50 °C (bottom, $10 \times 10 \ \mu m^2$). The negative images (40 °C) clearly show the substrate stage as white background for all thin films. However, while the domains of **CPTQ-Oc** increase in size and are in contact with each other to maintain charge percolation pathways, the domains of the other derivatives at elevated substrate temperatures are not connected and accordingly this discontinuous thin films only show minor or no charge transport.

11. OPV



Fig. S19 Thin-film absorption spectra of a 30 nm layer obtained by sublimation of CPTQ-Oc (black line) compared with MD376 (green line).



Fig. S20 a) Schematic representation of the architecture of the vacuum-processed planar heterojunction (PHJ) organic solar cells. b) *J*-*V* curves of vacuum-processed PHJ organic solar cells based on **MD376** as donor and **CPTQ-Oc** (black), **CPTQ-EH** (red), **CPTQ-Pr** (blue) and **CPTQ-Ph** (pink) as acceptor materials, which were measured under AM 1.5G conditions. c) EQE (bottom) and UV-vis (top) spectra of **CPTQ-R** based OSC combined with merocyanine dye **MD376** as donor and its thin-film absorption (green). EQE spectra could not be obtained for **CPTQ-Ph** due to insufficient J_{SC} .

Table S5 Photovoltaic parameters^a for ITO/MoO₃/MD376/CPTQ-R/BCP/AI based OPV measured under inert conditions and under AM 1.5G irradiation.

Acceptor	d Do.	d Ak.	$J_{ m SC}$	Voc	FF	PCE	PCE _{max}
	(nm)	(nm)	(mA cm ⁻²)	(V)	(%)	(%)	(%)
CPTQ-EH ^a	15	15	-0.46	0.88	27	0.11	0.11
	15	15	± 0.01	± 0.01	± 1	± 0.01	0.11
CPTQ-Pr ^a	20	20	-0.40	0.74	17	0.05	0.09
	20	20	± 0.1	± 0.04	± 1	± 0.02	0.06
CPTQ-Ph [⊳]	10	10	-0.02	0.48	28	0.004	0.06
	10	10	± 0.001	± 0.01	± 1	± 0.001	0.00

Average of at least five^a or three^b independent working devices.



Fig. S21 *J-V* curves (a) and *EQE* and UV-vis spectra (b) of vacuum-processed planar-heterojunction organic solar cells based on different layer thicknesses of **MD376** as donor and of C_{60} as acceptor (20 nm, 30 nm, 40 nm), which were measured under AM 1.5G conditions.

Table S6 Photovoltaic parameters^a for ITO/MoO₃/**MD376/C**₆₀/BCP/AI based OPV measured under inert conditionsand under AM 1.5G irradiation.

d _{Do.}	d _{Ak.}	J _{SC}	Voc	FF	PCE	PCE _{max}
(nm)	(nm)	(mA cm⁻²)	(V)	(%)	(%)	(%)
10	10	-2.9	1.02	43	1.25	1 30
10	10	± 0.1	± 0.03	± 2	± 0.08	1.59
15	15	-2.8	1.04	26	0.79	1.05
	15	± 0.1	± 0.01	± 2	± 0.17	1.05
20	20	-3.1	1.04	26	0.82	1 20
	20	± 0.1	± 0.01	± 2	± 0.22	1.20

^a Average of at least five independent working devices.

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