Synthesis and photovoltaic performances in solution-processed BHJs of oligothiophene-substituted organocobalt complexes [(η^4 - C₄(nT)₄Co(η^5 -C₅H₅)]

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I) Synthesis of the CpCoCb(nT)4 complexes

Materials and methods

Palladium coupling reactions and BuLi deprotonations were carried out under argon using dry solvents. All other reactions were performed without precautions. Dry solvents were obtained as follows: Et₃N was distilled over CaH₂, benzene was distilled from NaK2.8, and THF was distilled from sodium benzophenone. Microwave reactions were carried out in a BiotageTM microwave synthesizer (400 W max). Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel. Merck Gerudan SI 60 Å silica gel (35-70 μm) was used for column chromatography. Paper-filtrations were performed on a Whatman Grade No. 40 Quantitative Filter Paper, Ashless from VWR. 1H and 13C NMR spectra were recorded at 20 °C at 400 and 101 MHz respectively on a Bruker AVANCE400 spectrometer or at 300 and 75 MHz respectively, on a Bruker AVANCE300 spectrometer. Chemical shifts (δ) are given in ppm, referenced to the residual proton resonance of the solvents (7.26 ppm for $CDCl_3$) or to the carbon resonance of the solvent (77.16 ppm for $CDCl_3$). Coupling constants (J) are given in Hertz (Hz). The letters m, s, d, t, refer to multiplet, singlet, doublet, and triplet respectively, while the letter b means that the signal is broad. When possible, NMR signals were assigned on the basis of NOE, DEPT and 2D-NMR (COSY, HMBC) experiments. Elemental analysis were performed by the Service de Microanalyse de l'Institut de Chimie des Substances Naturelles (ICSN), Gif-sur-Yvette, France. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. Melting points were measured with a SMP3 Stuart Scientific melting point apparatus and were not corrected.

For the [2+2] cycloadditions, 2 equivalents of diarylacetylene and 1.5 equivalents of $(\eta^{5}-C_{5}H_{5})Co(CO)$ (dimethylfumarate) were dissolved in 4.6 ml of THF and 0.4 ml of EtOH in a 2-5 ml BiotageTM microwave vial. The mixture was heated at 150 °C for 30 min in a BiotageTM initiator 2.0 microwave (P = 60 to 75 W). The crude material was then concentrated under reduced pressure. The remaining solid was washed with 25 ml of EtOH in order to dissolve all organic impurities. The residue was paper-filtered using CH_2Cl_2 . The solution was concentrated under reduced pressure to afford the desired product

The synthesis of CpCoCb(1T)₄ has already been described by Harcourt *et al.* (see ref 17 in the main text) according to another pathway. However we here successfully synthesized CpCoCb(1T)₄ using our novel method based on the use of CpCo(CO)(DMFU) with DMFU=dimethylfumarate. The synthetic route towards CpCoCb(1T)₄ is the following:



1,2-Di(thiophen-2-yl)ethyne.

Ref: M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. Grieco, *Org. Lett.*, 2002, **4**, 3199.



1.68 g (8 mmol) of 2-iodothiophene, 152 mg (0.8 mmol) of copper iodide and 168 mg (0.48 mmol) of bis(triphenylphosphine)palladium(II) dichloride were added in a round bottom flask under argon. 80 mL of dry benzene, 7.18 mL (56 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene, 0.57ml (4 mmol) of trimethylsilylacetylene, and 58 µl (0.32 mmol) of water were successively added. The solution was stirred for 24 h in the dark at rt. The resulting mixture was diluted with 40 mL of aqueous 6M HCl, and then extracted 3 times with 50 mL of CH₂Cl₂. The organic extract was washed with 50 mL of aqueous 1M NaOH, and then dried over Na₂SO₄. The resulting mixture was concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) to give a white powder (310 mg, 41%). ¹H NMR (400 MHz, D₂O): δ 7.28 (d, *J* = 5.2 Hz, 2 H), 7.27 – 7.23 (m, 2 H), 6.99 (t, *J* = 3.4 Hz, 2 H).

 $CpCoCb(1T)_4$



The general procedure for [2+2] cycloadditions was carried out with 48 mg (0.25 mmol) of 1,2-di(thiophen-2-yl)ethyne and 56 mg of $(\eta^5-C_5H_5)Co(CO)$ (dimethylfumarate) (0.19 mmol) to afford

the product as a red powder (41 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ 7.29 (dd, *J* = 5.1 Hz, 1.1 Hz, 4 H), 7.23 (dd, *J* = 3.6 Hz, 1.1 Hz, 4 H), 6.95 (dd, *J* = 5.1 Hz, 3.6 Hz, 1 H), 4.78 (s, 5 H). ¹³C NMR (101 MHz, CDCl₃): δ 137.75, 127.17, 125.42, 125.54, 83.78, 70.01. IR (neat): v_{max} = 693, 817, 1218, 3099, 3746 cm⁻¹. Elemental analysis calcd (%) for C₂₅H₁₇CoS₄: C 59.51, H 3.40; found: C 59.41, H 3.40.

1,2-Di(2,2'-bithiophene)ethyne.

Ref: J. Nakayama, K. Sawada, A. Ishii, M. Hoshino, Heterocycles, 1992, 34, 1487.



0.291 mg (1.5 mmol) of 5-ethynyl-2,2'-bithiophene, 444 mg (1.5 mmol) of 2-iodo(5,2' bithiophène) 3 mg (15 μ mol) of copper iodide and 11 mg (15 μ mol) of bis(triphenylphosphine)palladium(II) dichloride were added in a round bottom flask. The flask was purged three times with argon. 20 ml of Et₃N were added and the reaction was stirred for 24 h at RT. The resulting mixture was diluted with 20 ml of aqueous 6M HCl, and extracted 3 times with 25 ml of CH₂Cl₂. The organic layer was washed with 50 ml of aqueous 1M NaOH, and then dried over Na₂SO₄. The resulting mixture was concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (petroleum ether) to afford the desire product as an orange powder (512 g, 96%). ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, *J* = 5.1Hz, 2 H), 7.20 (d, *J* = 3.6 Hz, 2 H), 7.18 (d, *J* = 3.8 Hz, 2 H), 7.07 (d, *J* = 3.8 Hz, 2 H), 7.20 (dd, *J* = 5.1, 3.6 Hz, 2 H).

 $CpCoCb(2T)_4$



The general procedure for [2+2] cycloadditions was carried out with 51 mg (0.15 mmol) of 1,2-di(2,2'-bithiophene)ethyne and 28 mg of (η^5 -C₅H₅)Co(CO)(dimethylfumarate) (0.11 mmol) to afford the product as a dark red powder (53 mg, 81 %).¹H NMR (400 MHz, CDCl3) δ 7.26 (m, 4 H), 7.10 (d, *J* = 3.7 Hz, 4 H), 7.05 – 7.00 (m, 8 H), 4.85 (s, 5 H). ¹³C NMR (101 MHz, CDCl₃): δ 137.57,

137.33, 136.66, 128.06, 128.00, 124.49, 124.16, 123.75, 83.97, 69.71. m.p.: 230 °C. Elemental analysis calcd (%) for C₄₁H₂₅CoS₈: C 59.11, H 3.02; found: C 59.57, H 3.03.

1,2-Di(5-bromo-thiophen-2-yl)ethyne



In a flame dried 50ml round bottom flask, 330 mg (1.74 mmol) of di(thiophène)ethyne were dissolve in 20 ml of dry THF under argon. Then 1.9 ml of Buli (2,0 M in hexane) was added at -40 °C, the mixture was stirred for 30 min and then 312.5 mg of Br₂ (3.83 mmol) was added. The reaction was allowed to reach room temperature and was stirred for 2 hours. The resulting mixture was wash with a saturated solution of Na₂S₂O₄, dried on MgSO₄ and concentrated under reduce pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ether 99.5/0.5) to afford the product as a white powder (500 mg, 80%).¹H NMR (300 MHz, CDCl₃): δ 7.02 (d, *J* = 3.8 Hz, 2 H), 6.96 (d, *J* = 3.8 Hz, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ 132.75, 130.24, 124.23, 114.05, 86.20.

CpCoCb(2-(5-bromo-thiophene)₄



The general procedure for [2+2] cycloadditions was carried out with 100 mg (0.27 mmol) of di(2-bromo,5-2'-bithiophene)ethyne and 49 mg of (η 5-C5H5)Co(CO)(dimethylfumarate) (0.16 mmol) to afford the product as an orange powder (32 mg, 28 %).¹H NMR (300 MHz, CDCl₃): δ 6.96 (d, *J* = 3.8 Hz, 4 H), 6.93 (d, *J* = 3.8 Hz, 4 H), 4.83 (s, 5 H). ¹³C NMR (75 MHz, CDCl₃): δ 138.49, 130.40, 127.33, 111.87, 83.81, 68.81.

 $CpCoCb(3T)_4$



In a 25 ml round bottom flask 32 mg (37 µmol) of 43, 88 mg (0.3 mmol) of 2-(pinacol ester boronic acid)5-2'bithiophene, 83 mg (0.59 mmol) of K₂CO₃ and 2 mg (3.7μ mol) of PdCl₂dppf were dissolved in 5 ml of water and 10 ml of THF. The mixture was stirred for 3 days at reflux. The crude was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/DCM 8/2) to afford the product as a dark brown powder (187 mg, 99%). ¹H NMR (400 MHz, CDCl3) δ 7.23 (d, *J* = 5.1 Hz, 4 H), 7.19 (d, *J* = 3.6 Hz, 8 H), 7.10 (dd, *J* = 3.7 Hz, 8.9 Hz, 8 H), 7.05 – 7.00 (m, 8 H), 4.86 (s, 5 H). ¹³C NMR (101 MHz, CDCl₃): δ 137.30, 137.04, 136.74, 136.33, 136.26, 128.11, 128.08, 124.64, 124.60, 124.33, 124.11, 123.83, 84.02, 69.68. m.p.: 178 °C. Elemental analysis calcd

II) Physical characterizations of CpCoCb(nT)₄ complexes

Cyclic voltamperometry (CV)

CV measurements were performed in dry and degassed acetonitrile with 0.1 M NBu₄PF₆ as a supporting salt using a Schlumberger Solartron 1286 potentiostat. The working and counterelectrodes were platinum wires while the reference is a silver wire. CV curves (see Figure S1) were recorded with a 1 mmol/mL solution of cobalt complex using ferrocene (Fc^{2+}/Fc^{3+}) as an internal reference.



Figure S1 Cyclic voltamperogram of CpCoCb(3T)₄ in acetonitrile with ferrocene (Fc^{2+}/Fc^{3+}) as the internal reference.

UV-visible absorption

UV-vis spectra were acquired on a Perkin Elmer Lambda 650 spectrometer using an Optech quartz cell with a 1 mm optical path. Measurements were performed with a 1 mmol/mL solution of CpCoCb(nT)₄ complex in CH_2Cl_2 .

Table S1 summarizes the UV-visible absorption and electrochemical parameters for the three complexes as well as the HOMO/LUMO energy levels as deduced from the measured experimental values.

CoCpCb(nT) ₄ complex	λ _{max} (nm)	E ^{ox} _{1/2} (V)	Eg (eV)	E _{HOMO} (eV)	E _{LUMO} (eV)
n=1	295	0.77	3.3	-5.7	-2.4
n=2	354	0.73	2.7	-5.6	-2.9
n=3	399	0.66	2.3	-5.5	-3.2

Table S1: Electronic properties of the CoCpCb(nT)₄ complexes as deduced from optical absorption and cyclic voltamperometry.

Energy diagram of the BHJ based on CpCoCb(3T)₄

The energy diagram of the {ITO/PEDOT:PSS/CpCoCb(3T)₄ /PCBM/AI} BHJ device is built using the optical (Eg=2.3 eV) and electrochemical (E_{HOMO} =-5.5 eV; E_{LUMO} =-3.2 eV) characterizations described above. The energy levels of ITO, PEDOT:PSS, PCBM and Al come from literature. This energy diagram is presented in Figure S2 below:



Figure S2. Energy diagram of a {ITO/PEDOT:PSS/CpCoCb(3T)₄:PCBM/LiF/AI} BHJ device.

Atomic force microscopy (AFM)

AFM images were recorded using a Pico-LE microscope (Molecular Imaging-Agilent Technologies) in taping mode. AFM tips were Si-coated with Pt/Ir alloy with a stiffness in between 0.1 N/m and 0.3 N/m. The contact radius was given at 20 nm.



Figure S3. Top: Typical AFM image of a 80 nm thick layer of PCBM:CpCoCb(3T)₄ blend. Bottom: Height profile along the blue line in the centre of the image.

A typical AFM image of the PCBM/CpCoCb(3T)₄ layers (thickness=80 nm) spin-coated on top of a 20 nm layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is presented in Figures S3. The binary blend forms smooth surfaces (rugosity<2 nm) with flat domains having an average height of 8 nm. Rugosity on top of the terraces of the grains is below 1nm and clearly indicates the propensity of CpCoCb(3T)₄ to crystallize during deposition.

III) BHJ solar cells fabrication

A solution of 1.65 mL of PEDOT:PSS (Sigma-Aldrich; water solution 1.3% in weight) and 1.35 mL of distillated water was sonicated 20 min, degassed with N_2 and introduced in a glovebox for the BHJ fabrication.

In a clean vial, 20 mg of PCBM (Sigma-Aldrich; purity 99.5%) and 10 mg of cobalt complex were sonicated for 20 min in 1 mL of 1-2 dichlorobenzene. The solution was then filtered on VWR 0.4 μ m PTFE filter. The resulting filtrate was then flush with N2 and pumped in a glove box for the BHJ fabrication. The BHJ is prepared from a solution sonicated for 1 hour and passed through a 0.4 μ m PTFE filter. Without this pre-treatment the spin-coated films were inhomogeneous and PCE insignificant.

The ITO-coated glass substrates (Sigma-Aldrich; $2.5 \times 2.5 \text{ cm}^2$; $R=75 \pm 5\Omega \cdot \text{cm}^2$) are patterned, cleaned with decon-glass soap and distillated water, sonicated in ethanol for 20 min, dried with N₂, then sonicated in acetone and dried with N₂. Substrates were exposed to UV ozone for 30 min prior to be pumped in a glovebox for spin-coating.

In a N₂ pressurized glovebox, a 220 μ L droplet of the PEDOT:PSS solution was deposited on an ITO substrate then spin-coated at 1200 rpm for 30 s, 1400 rpm for 30 s and 3000 rpm for 5 s. Film deposition was followed by a thermal annealing at 120°C for 30 minutes. This afforded a 20 nm thick PEDOT:PSS layer onto which the active PCBM:CpCoCb(nT)₄ blend (150 μ L) was coated. The samples were then transferred with patterning masks in a custom-made UHV evaporator linked to the glovebox and purged with N₂. Finally, 8 Å of LiF and 80 nm of Al were thermally evaporated to complete the devices (area=5 mm²). Those were transferred back to the N₂ pressurized glovebox for characterizations.

IV) BHJ solar cells characterizations

In a pressurized N₂ glovebox, small drops of silver paste were painted on the Al electrodes of the devices to ensure good contact. These devices were then placed on a three-points probe platform (Cascade RF-1). Current-voltage characteristics were recorded in the dark and under white light illumination air mass 1.5 global (AM 1.5G) using a Keithley 2602 source meter. The white light source is a xenon lamp (Oriel Instruments, 300 W) coupled with a AM 1.5G filter delivering an incident power of 75 mW·cm⁻². A set of neutral density filters is used for light-intensity measurements. Action spectra were recorded using synchronous detection (Scitech optical chopper

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and a HTDS 7260 DSP lock-in amplifier) coupled with a monochromator (Newport Oriel Cornerstone 130). A low-pass filter was used to avoid optical harmonics (Edmund optic 040072).



Figure S4 Typical I/V curve of a {ITO/PEDOT:PSS/CpCoCb(3T)₄:PCBM/LiF/AI} BHJ device in the dark over the -2.0–2.0 V bias range.



Figure S5 Typical power conversion efficiency (PCE, %) versus incident power Pi (mW/cm²) of a {ITO/PEDOT:PSS/CpCoCb(3T)₄:PCBM/LiF/AI} BHJ device.