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COMMUNICATION**Synthesis and photovoltaic performances in solution-processed BHJs of oligothiophene-substituted organocobalt complexes $[(\eta^4\text{-C}_4(\text{nT})_4\text{Co}(\eta^5\text{-C}_5\text{H}_5))]^\dagger$** Guillaume H. V. Bertrand,^{a,b} Ludovic Tortech,^{* a,c} Vincent Gandon,^d Corinne Aubert,^{a,b} and Denis Fichou^{* a,b}

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We describe an efficient synthetic route toward novel organocobalt complexes $[(\eta^4\text{-C}_4(\text{nT})_4\text{Co}(\eta^5\text{-C}_5\text{H}_5))]^\dagger$ with **n=1,2,3 thiophene rings. Solution-processed bulk heterojunctions solar cells based on CpCoCb(3T)₄:PCBM blends achieve power conversion efficiencies up to 2.1%.**

Organic solar cells (OSC) based on polymer bulk heterojunctions (BHJ) proved to be a versatile strategy to engineer efficient and low-cost photovoltaic devices.¹ Power conversion efficiencies (PCE) in the range 6-8% have been attained with single BHJ devices using solution-processed polymer/fullerene blends. A tandem cell based on a low band gap polymer has been recently reported to exhibit a certified PCE as high as 10.6%.^{1g}

Meanwhile, BHJs made of small organic molecules emerged as a new approach with the advantages over polymers of a better control of the molecular design, a higher purity, an improved structural organization and an absence of batch-to-batch variations.² A wealth of small organic dyes such as squaraines,³ porphyrins,⁴ diketopyrrolopyrroles,⁵ or oligothiophenes,^{6,7} to name a few, have been experimented in solution-processed BHJs. Note that these small organic molecules are acting as donor (p-type) constituent of the BHJ, often in combination with a fullerene derivative as the acceptor (n-type) although non-fullerene acceptors such as perylenes were also thoroughly investigated.⁸ A PCE of 6.7% has been recorded under AM 1.5 global irradiation (100 mW/cm²) with a BHJ device made from DTS(PTTh₂)₂, a thiadiazole derivative, blended with PC₇₀BM.^{2b} This high efficiency originates essentially from an intense optical absorption over the entire visible spectrum and an appropriate morphology leading to a high hole mobility (0.12 cm²/V.s). Very recently, by using the same thiadiazole dye, the PCE of a BHJ solar cell in an inverted structure reached values as high as 7.88%,⁹ while record PCEs over 8.0% were attained with a benzodithiophene derivative.⁶ These encouraging results pave the way towards small molecule-based OSCs with PCE exceeding 10%.

Among the plethora of small organic molecules currently investigated as active materials for OSCs, organometallic complexes represent an attractive class of materials. In particular organometallic dyes based on noble metals (such as Ru, Rh or Ir) are extensively utilized as photosensitizers solar cells of various types.¹⁰ Besides, organometallic complexes based on 3d-

transition metals (such as Co, Ni, Cu, Zn, etc) are also studied for solar energy conversion, in particular the large family of metallophthalocyanines.¹¹ When attached to organic ligands 3d-transition metals are inducing metal-ligand charge transfer (MLCT) transitions spanning over the visible and near infrared spectrum.^{10b} Finally, note that 3d metals also possess intra-3d transitions absorbing strongly in the visible that have been used to sensitize wide bandgap oxides such as ZnO, TiO₂ or SrTiO₃, in view of solar energy conversion.¹²

We present here the synthesis and photovoltaic behaviour of novel oligothiophene-substituted organocobalt complexes with general formula $[(\eta^4\text{-C}_4\text{R}_4\text{Co}(\eta^5\text{-C}_5\text{H}_5))]^\dagger$. The central Co(I) atom is linked to a cyclopentadienyl ($\eta^5\text{-C}_5\text{H}_5$, noted Cp) and a cyclobutadienyl ($\eta^4\text{-C}_4\text{R}_4$, noted Cb) ligands. Both planar Cp and Cb ligands are located at the apex of each other to form a 3D sandwich molecule. The Cb rings are substituted by four peripheral oligothiophene units nT of various lengths (n=1,2,3). The introduction of π -conjugated oligothiophene substituents on the Cb ring is expected to contribute to the MLCT transitions and to improve charge transport in the BHJ.¹³ Finally, we note that CpCoCb complexes substituted by appropriate groups on both the Cp and Cb rings have been extensively reported as altitudinal molecular rotors,¹⁴ supramolecular cages,¹⁵ or catalysts.¹⁶

The organic solar cells under study here are based on BHJs prepared by mixing the CpCoCb(nT)₄ complexes together with [6,6]-phenyl-C60-butyric acid methyl ester (PCBM) as the acceptor material. The CpCoCb(nT)₄ complexes are soluble in usual organic solvents and could be easily processed by spin-coating. The device architecture was set to be {glass/ITO/PEDOT:PSS/CpCoCb(nT)₄:PCBM/LiF/Al}. PCEs up to 1.87% under 75 mW/cm² and 2.12% under 22 mW/cm² were recorded with CpCoCb(3T)₄.

The three CpCoCb(nT)₄ complexes are conveniently synthesized according to an original strategy (Scheme 1). The synthesis of the shorter analog CpCoCb(1T)₄ has already been described elsewhere,¹⁷ while 2T and 3T are novel compounds. The key step is the use of CpCo(CO)(DMFU)¹⁸ (with DMFU=dimethylfumarate) engaged in a [2+2] cycloaddition under microwave conditions developed in our laboratory.¹⁹ Precursors for CpCoCb(1T)₄ and CpCoCb(2T)₄ were synthesized using Sonogashira type coupling. A first attempt to synthesize CpCoCb(3T)₄ using the same approach was carried out but the

bis(3T)-acetylene precursor proved to be very difficult to isolate due to an ultra-low solubility (<5 mg/L in DCM). Therefore we investigated a second route based on a Suzuki coupling following the [2+2] cycloaddition, leading successfully to the target CpCoCb(3T)₄ product. Surprisingly this complex was highly soluble in organic solvents (~20 mg/mL in CH₂Cl₂ and 35 mg/mL 1,2-dichlorobenzene) in spite of the four 3T units per molecule. The absorption spectra of the three CpCoCb(nT)₄ compounds (Fig. 1) exhibit a broad band with a bathochromic shift of λ_{max} from 1T (254 nm) to 2T (354 nm) and to 3T (399 nm). One can note that molar extinction coefficient of CpCoCb(3T)₄ reached values as high as 10⁴-10⁵ L.mol⁻¹.cm⁻¹ over the 300-600 nm range. Cyclic voltammetry experiments were performed on the three CpCoCb(nT)₄ derivatives in order to complete their electronic structures (Fig. S1, ESI[†]). As expected optical absorption (λ_{max} and ε) and the oxidation potential E^{ox}_{1/2} scale the nT chain length from n=1 to 3. The energetic parameters deduced from optical and electrochemical data allow to determine the HOMO levels using formula (1)²⁰ (Table S1, ESI[†]):

$$E_{HOMO} = -(1.4 \pm 0.1) \times q(E_{ox} - E_{ref}) - (4.6 \pm 0.08) \text{ eV} \quad (1)$$

Energetic data of the CpCoCb(3T)₄ complex were then associated with the HOMO-LUMO levels of PCBM and the Fermi levels of the ITO and Al electrodes used in the devices. The energetic diagram of a BHJ solar cell based on CpCoCb(3T)₄ as the donor or and PCBM as the acceptor (Fig. S2, ESI[†]) shows a typical staircase profile favourable for an efficient PV effect under visible light irradiation.

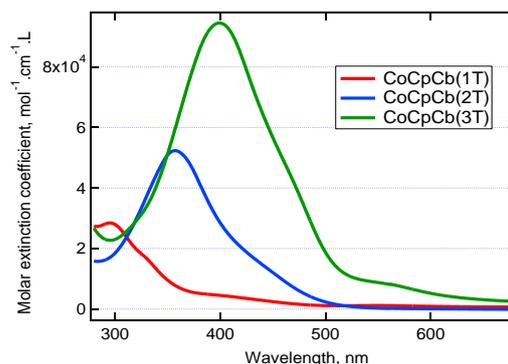
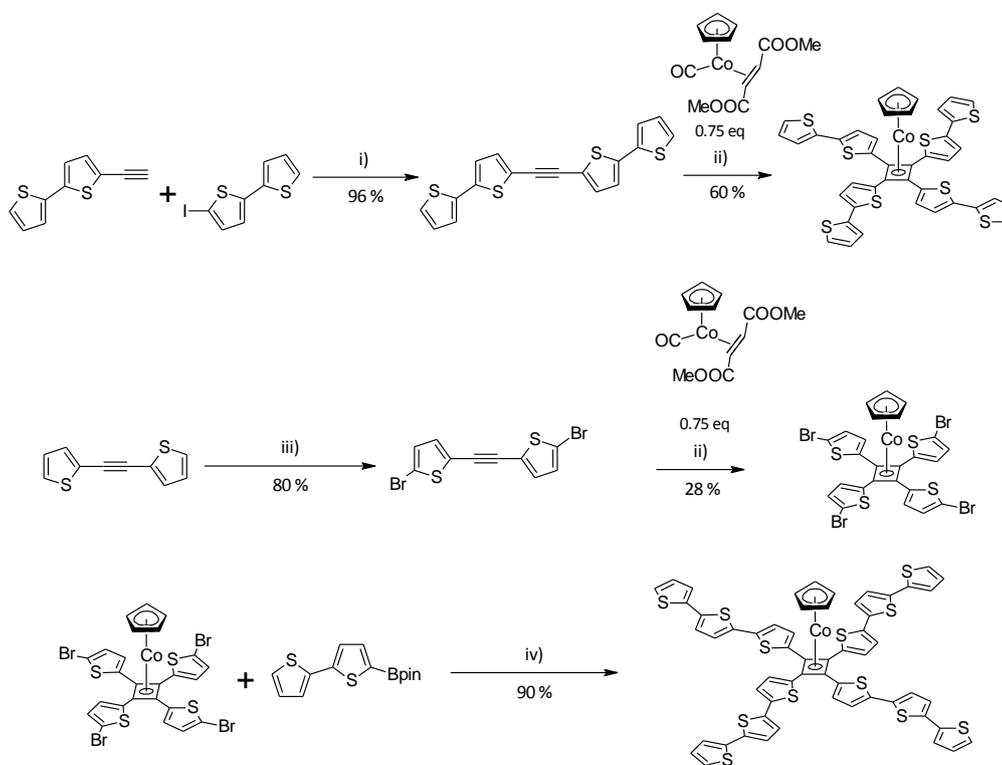


Figure 1: Absorption spectra of the three CpCoCb(nT)₄ complexes (n=1,2,3) in dichloromethane.



Scheme 1. Synthetic pathways to CpCoCb(nT)₄ with n=2,3. i) 10 mol% PdCl₂(PPh₃)₂, 10 mol% CuI NEt₃, RT, 24 h. ii) 14/1 THF/EtOH, microwave 150 °C, 30 min (P=80 W). iii) 2.2 eq BuLi, THF, -40 °C, 30 min, Br₂, RT, 2 h. iv) 20 mol% PdCl₂(dppf), 16 eq K₂CO₃, THF/H₂O, reflux 5 days.

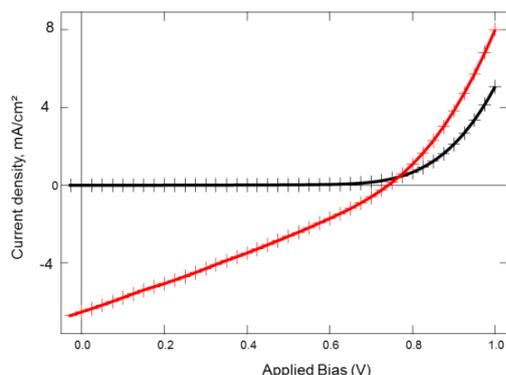
The I/V characteristics of OSCs based on CpCoCb(nT)₄ in the dark and under white light illumination (AM 1.5G, 75 mW/cm²) are presented in Fig. 2a. In the dark the I/V curve reveals an excellent diode behaviour over the -2.0V/+2.0 V range (Fig. S4, ESI[†]). Increasing the length of the four nT units (n=1,2,3) results in a considerable increase in PCE up to 1.9% for CpCoCb(3T)₄ (Table 1). When exposed to lower incident powers, PCE

increases up to 2.1% under 22 mW/cm² (Fig. S5, ESI[†]). Similarly, in open air Voc is higher for the 3T derivative (608 mV) as compared to the shorter 1T (102 mV) and 2T (331 mV) derivatives. The current density are also improved with longer nT units, up to J_{sc}=6.2 mA/cm² for CpCoCb(3T)₄ under N₂. However, for the three complexes the fill factor (FF) remains low with average values in the range 27-32%. Surprisingly, thermal

annealing of the $\text{CpCoCb}(3\text{T})_4$ devices (see experimental details in ESI†) leads to reduced $J_{\text{sc}}=2.2 \text{ mA/cm}^2$. The low PCEs measured in open air indicate that the complexes photooxidize as previously reported for some thiophene derivatives.²¹

The EQE spectrum of OSCs based on $\text{CpCoCb}(3\text{T})_4$ (Fig. 2b) span all over the visible range with two maxima at 390 nm and 430 nm, as well as two shoulders at 490 nm and 600 nm. The peaks at 390 nm and 430 nm probably arise from the absorption of the four conjugated 3T arms. On the other hand the weak intensity shoulder at 600 nm is consistent with a metal-ligand charge transfer (MLCT) transition between the Co atom and the azimuthal organic ligands. Fig. 2b reveals that optical absorption in the 480-700 nm range contributes more efficiently to PV conversion as compared to the 350-480 nm range. This could arise from a longer lifetime of excitons generated by an MLCT transition due to the strong spin-orbit coupling of the Co atom that stabilizes triplet states.

a)



b)

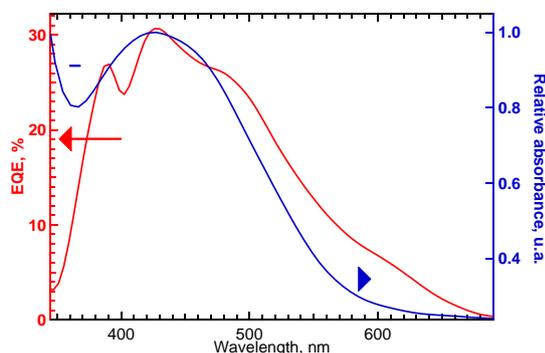


Fig. 2 a) I/V response of an OSC based on a $\text{CpCoCb}(3\text{T})_4$:PCBM BHJ in the dark (black) and under white light irradiation (AM 1.5G, 75 mW/cm^2 , red). b) EQE (red) and absorption (blue) spectra of a BHJ device based on a $\text{CpCoCb}(3\text{T})_4$:PCBM blend.

$\text{CpCoCb}(n\text{T})_4$ complex	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	PCE (%)
n=1 ^[a]	0.015	102	27	0.001
n=2 ^[a]	3.15	331	28	0.05
n=3	1.4 ^[a]	608 ^[a]	30 ^[a]	0.35 ^[a]
	6.4 ^[b]	732 ^[b]	30 ^[b]	1.87 ^[b]
	2.2 ^[c]	664 ^[c]	32 ^[c]	2.12 ^[c]

Table 1 PV characteristics under AM 1.5G (75 mW/cm^2) of the $\text{CpCoCb}(n\text{T})_4$ complexes. [a] in open air, [b] under N_2 , and [c] under N_2 after annealing, under 22 mW/cm^2

In summary, three $\text{CpCoCb}(n\text{T})_4$ complexes bearing four oligothiophene arms of different lengths have been synthesized and investigated as donor materials in solution-processed BHJ solar cells. In particular devices elaborated with $\text{CpCoCb}(3\text{T})_4$ show V_{oc} beyond 0.7 V and reach PCEs of 1.9% and 2.1% under incident power of respectively 75 and 22 mW/cm^2 . Tailoring the four oligothiophene arms (length, substituents, etc) of the $\text{CpCoCb}(n\text{T})_4$ building block should allow to improve considerably these promising PV performances.

Notes and references

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† Electronic supplementary information (ESI) available: experimental details on the synthesis and electronic properties of $\text{CpCoCb}(n\text{T})_4$ complexes, fabrication and testing of the photovoltaic devices. See DOI: 10.1039/b000000x/

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