

# Tris(2-(1*H*-pyrazol-1-yl)pyridine)cobalt(III) as p-Type Dopant for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells

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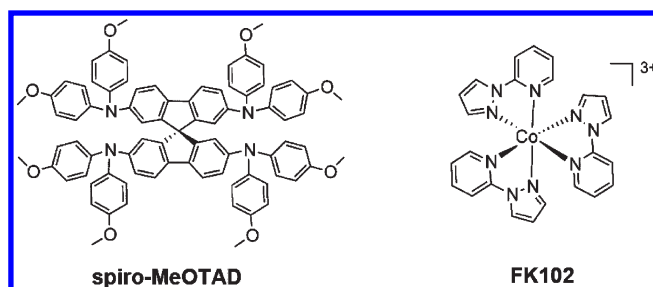
Supporting Information

**ABSTRACT:** Chemical doping is an important strategy to alter the charge-transport properties of both molecular and polymeric organic semiconductors that find widespread application in organic electronic devices. We report on the use of a new class of Co(III) complexes as p-type dopants for triarylamine-based hole conductors such as spiro-MeOTAD and their application in solid-state dye-sensitized solar cells (ssDSCs). We show that the proposed compounds fulfill the requirements for this application and that the discussed strategy is promising for tuning the conductivity of spiro-MeOTAD in ssDSCs, without having to rely on the commonly employed photo-doping. By using a recently developed high molar extinction coefficient organic D- $\pi$ -A sensitizer and p-doped spiro-MeOTAD as hole conductor, we achieved a record power conversion efficiency of 7.2%, measured under standard solar conditions (AM1.5G, 100 mW cm<sup>-2</sup>). We expect these promising new dopants to find widespread applications in organic electronics in general and photovoltaics in particular.

The dye-sensitized solar cell (DSC) has emerged as one of the most promising alternatives to cost-intensive silicon-based photovoltaic devices.<sup>1</sup> The conventional DSC, in its original form, is composed of two conductive substrates, a sensitized, porous structured metal oxide semiconductor and a liquid electrolyte. Although power conversion efficiencies (PCEs) of close to 13% could be achieved with this device architecture, the quest for all solid-state devices has fostered the development of dye solar cells in which the liquid electrolyte has been replaced by a solid hole-transporting material (HTM).<sup>2</sup>

So far, solid-state dye-sensitized solar cells (ssDSCs) have mainly focused on 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD, Figure 1) as HTM, which was introduced in 1998 by Bach et al.<sup>3</sup> Although research interest in identifying competitive alternatives is growing, spiro-MeOTAD remains the material of choice when high efficiencies are demanded.<sup>4,5</sup>

Several desirable properties—glass transition temperature, solubility, ionization potential, absorption spectrum, and solid-state morphology—make spiro-MeOTAD a suitable candidate for DSC applications. However, like other organic hole conductors,



**Figure 1.** Molecular structures of spiro-MeOTAD and FK102. In this study the PF<sub>6</sub><sup>-</sup> salt of FK102 is employed.

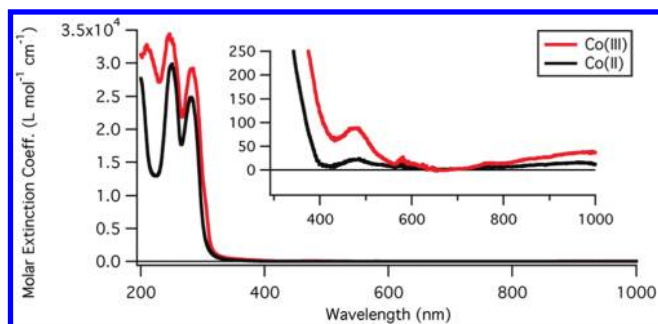
spiro-MeOTAD suffers from low conductivity in its pristine form. To overcome this problem additional charge carriers are generated by doping, a common technique to tune the electrical properties of both organic and inorganic semiconductors.<sup>6</sup>

While Bach et al. employed (*p*-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>NSbCl<sub>6</sub> as a chemical p-dopant,<sup>3</sup> so far no detailed study on p-type doping in ssDSCs has been reported. In fact, most recent publications on spiro-MeOTAD-based ssDSCs do not follow this strategy.<sup>4,5</sup> High PCEs could nevertheless be achieved because the devices were fabricated under aerobic conditions, enabling facile one-electron oxidation of spiro-MeOTAD with molecular oxygen under illumination, a process referred to as photo-doping. Although chemical p-doping is not necessarily the key to high performance, it is expected to be crucial to achieve reproducible results, the fabrication of stable ssDSCs using photo-doping being clearly difficult to control.

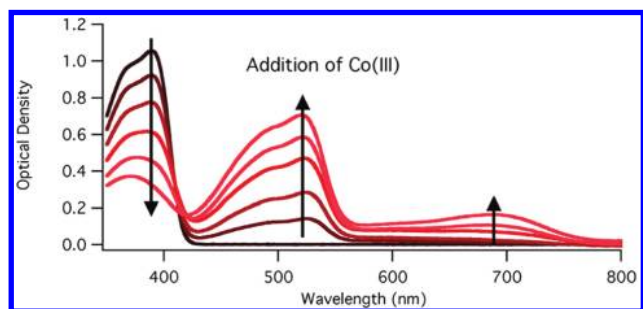
Chemical p-doping is a well-known strategy to increase the conductivity of organic semiconductors and commonly employed, for instance, in organic light-emitting devices.<sup>7</sup> Various materials have been reported for their use as p-dopants, from strongly electron-accepting organic molecules such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ)<sup>8</sup> to transition metal oxides such as WO<sub>3</sub>,<sup>9</sup> metal-organic complexes such as molybdenum tris[1,2-bis(trifluoromethyl)ethane-1,2-dithiolene],<sup>10</sup> and redox-active salts such as NOBF<sub>4</sub><sup>11</sup> or the above-mentioned (*p*-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>NSbCl<sub>6</sub>. Many of these materials are usually applied by vacuum deposition techniques and exhibit low solubility in organic solvents, while others face stability issues or are too reactive and prone to side reactions. For DSC applications,

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**Figure 2.** UV/vis absorption spectra of the FK102 Co(III) complex and its corresponding Co(II) derivative, measured in solution.



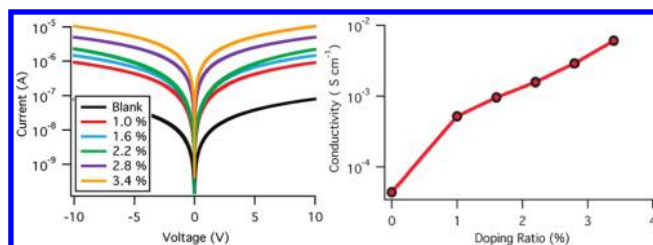
**Figure 3.** Change of the absorption spectrum of a spiro-MeOTAD solution in chlorobenzene upon the gradual addition of FK102. Addition of FK102 decreases the absorption peak at 388 nm and gives rise to two new absorption bands at 520 and 687 nm.

deposition from solution together with the organic HTM would be favorable, although chemical inertness toward HTM, sensitizer, and metal oxide semiconductor is required.

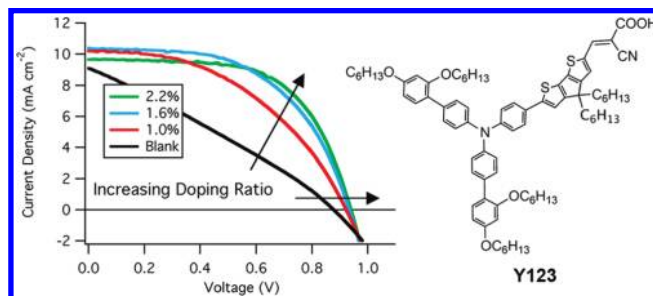
Herein we report the use of a novel cobalt(III) complex as p-type dopant for organic semiconductors and its application in ssDSCs. To the best of our knowledge, this is the first time Co(III) complexes are used for this kind of application; so far, metal–organic complexes have mostly been employed as electron donors, i.e., n-type dopants.<sup>12–14</sup> Moreover, we discuss the influence of doping level on photovoltaic performance, give preliminary data on the long-term stability of chemically doped devices, and achieve a new record efficiency with spiro-MeOTAD-based ssDSCs using this kind of dopant.

The first oxidation potential of spiro-MeOTAD in solution has been found to be 0.72 V versus normal hydrogen electrode (NHE) (Figure S1); thus, the Co(III) complex must have a redox potential above this value. For this reason we selected tris(2-(1*H*-pyrazol-1-yl)pyridine)cobalt(III) (FK102, Figure 1) as a suitable candidate for p-type doping of spiro-MeOTAD. A similar Co(II) compound was synthesized together with its Ni(II) and Cu(II) analogues by Saha et al. in 1977, though the properties of the complexes have not been investigated further.<sup>15</sup>

FK102 has a redox potential of 1.06 V vs NHE as determined by electrochemical measurements (Figure S1), which leaves a sufficient driving force of roughly 350 mV for the spiro-MeOTAD one-electron oxidation reaction. FK102 and its Co(II) analogue have almost no absorption in the visible region and therefore do not compete with the sensitizer for light harvesting (Figure 2). Figure 3 shows the change of the UV/vis absorption spectrum of a spiro-MeOTAD solution upon gradual addition of



**Figure 4.** (Left) *I*–*V* characteristics of spiro-MeOTAD films spin-cast from CHCl<sub>3</sub> solution containing different amounts of FK102 dopant. (Right) Derived electrical conductivity as a function of doping level.



**Figure 5.** *J*–*V* characteristics measured under simulated AM1.5G solar irradiance (100 mW cm<sup>-2</sup>) for devices containing different amounts of FK102 dopant (1.0%, 1.6%, and 2.2%) and an undoped reference (blank). The molecular structure of the employed organic D- $\pi$ -A sensitizer coded Y123 is shown on the right side.

FK102. Increasing the amount of dopant decreases the absorption peak of spiro-MeOTAD at 388 nm and gives rise to two new absorption bands at 520 and 687 nm, which can be attributed to the mono-cation radical of spiro-MeOTAD. Even though it is energetically possible, we do not expect the formation of the two-electron oxidized form, unless >1 equiv of oxidizing agent is added. However, it is difficult to distinguish these two by simple optical absorption measurements.<sup>16</sup>

The basic mechanism of p-type doping is the creation of additional charge carriers (holes), leading to an increased charge carrier density in—and therefore higher conductivity of—the semiconductor film. This corresponds to results obtained from two-probe conductivity measurements showing an increase in conductivity from  $4.4 \times 10^{-5}$  to  $5.3 \times 10^{-4}$  S cm<sup>-1</sup> upon addition of 1.0% FK102. Snaith et al. previously reported conductivity of  $2.0 \times 10^{-5}$  S cm<sup>-1</sup> for undoped spiro-MeOTAD, in agreement with our findings, considering that a slightly different concentration of lithium bis(trifluoromethylsulfonyl)imide was used.<sup>17</sup> For higher doping concentrations, the conductivity increases exponentially with the doping ratio as shown in Figure 4. Note that the given doping ratios correspond to the molar percentage of FK102 added to the spiro-MeOTAD solution prior to spin-coating, but not necessarily to the resulting doping concentration within the amorphous film. Nevertheless, our results clearly show that the proposed Co(III) complex can indeed be used to efficiently p-dope spiro-MeOTAD.

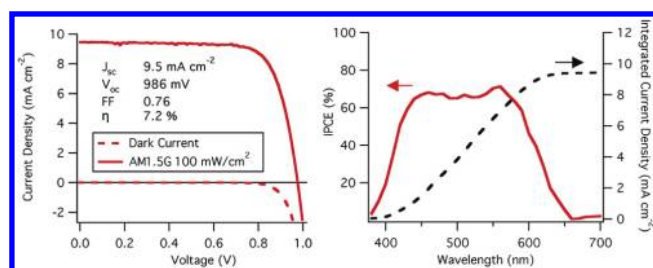
To prove that the increase in conductivity upon p-type doping of spiro-MeOTAD is beneficial for practical application, we fabricated ssDSCs using spiro-MeOTAD as hole conductor containing different concentrations of FK102 dopant, the latter being added to the spiro-MeOTAD solution prior to spin-coating. To avoid excessive photo-doping of the HTM and reveal the

**Table 1. Photovoltaic Parameters Derived from  $J$ – $V$  Measurements at  $100 \text{ mW cm}^{-2}$  AM1.5G for Devices Employing Y123 Dye and Containing Different FK102 Doping Ratios as Well as an Undoped Reference (Blank)**

	blank	1.0%	1.6%	2.2%
Initial Data				
$V_{oc}$ (mV)	878	923	934	940
$J_{sc}$ ( $\text{mA cm}^{-2}$ )	9.1	10.2	10.4	9.6
FF	0.29	0.46	0.55	0.62
$\eta$ (%)	2.3	4.3	5.3	5.6
After 5 Days				
$V_{oc}$ (mV)	887	925	943	947
$J_{sc}$ ( $\text{mA cm}^{-2}$ )	9.9	10.3	10.2	9.8
FF	0.30	0.54	0.63	0.65
$\eta$ (%)	2.6	5.2	6.1	6.1

effect of chemical doping, these photovoltaic devices were fabricated under red light conditions ( $\lambda > 600 \text{ nm}$ ). Doping ratios of 1.0%, 1.6%, and 2.2% were investigated and compared to an undoped reference (blank). For the presented studies we employed a high molar extinction coefficient organic D- $\pi$ -A sensitizer coded Y123 (Figure 5). Using the Y123 dye, our laboratory recently achieved unprecedented PCEs of up to 9.6% with a liquid redox electrolyte based on Co(III)/Co(II)–bipyridyl complexes as redox couple.<sup>18</sup> Herein we show for the first time that the Y123 sensitizer also performs well in spiro-MeOTAD-based ssDSCs.

$J$ – $V$  characteristics measured under simulated AM1.5G solar irradiance ( $100 \text{ mW cm}^{-2}$ ) are represented in Figure 5, and the extracted photovoltaic parameters are summarized in Table 1. For the undoped reference we find an open-circuit potential ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), and fill factor (FF) of 878 mV,  $9.1 \text{ mA cm}^{-2}$ , and 0.29, respectively, yielding an overall PCE ( $\eta$ ) of 2.3%. This device suffers from a low FF that can be attributed to the low conductivity and therefore high charge-transport resistance of the undoped spiro-MeOTAD film contributing to a high series resistance. Upon the addition of 1.0%, 1.6%, and 2.2% FK102, the FF improves to 0.46, 0.55, and 0.62, respectively, resulting in  $\eta = 4.3\%$ ,  $5.3\%$ , and  $5.6\%$ . The addition of FK102 initially increases the  $J_{sc}$  to  $10.2 \text{ mA cm}^{-2}$  (1.0% FK102) and  $10.4 \text{ mA cm}^{-2}$  (1.6% FK102), followed by a decrease to  $9.6 \text{ mA cm}^{-2}$  (2.2% FK102) at higher doping levels. The exact reason for this decrease in  $J_{sc}$  at high doping levels remains to be explored but is likely to arise from filtering of the incoming light by the spiro-MeOTAD cation radical which strongly absorbs at  $520 \text{ nm}$  ( $\epsilon = 4.01 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )<sup>16</sup> and therefore competes with the sensitizer for light harvesting. The  $V_{oc}$  increases to 923 mV upon addition of 1.0% FK102 and surprisingly further increases to 934 and 940 mV when the doping ratio is raised to 1.6% and 2.2%, respectively. This trend is contradictory to our expectations, as a higher hole density in the spiro-MeOTAD film should lead to increased recombination between holes and conduction band electrons and consequently a decrease in  $V_{oc}$ , especially at high doping levels. However, this effect might be compensated by a lowering of the Fermi level in the spiro-MeOTAD film when the dopant is added, expanding the gap to the quasi-Fermi level of the  $\text{TiO}_2$ , enabling higher  $V_{oc}$  values to be realized. Moreover, the higher conductivity facilitates charge extraction and consequently obviates the accumulation of holes near the sensitized junction. Further in-depth studies are required



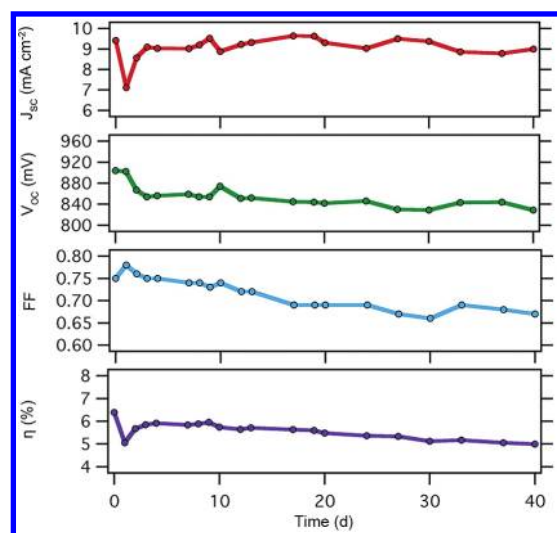
**Figure 6.** (Left)  $J$ – $V$  characteristics of a champion cell containing 1.6% FK102. (Right) Corresponding incident photon-to-electron conversion efficiency spectrum as a function of monochromatic wavelength. The right axis of the graph indicates the current density expected to be generated under standard solar conditions.

to elucidate the detailed effect of p-doping on the electron–hole recombination kinetics and the cause for the observed trend in  $V_{oc}$ . A maximum  $\eta = 5.6\%$  is achieved for the device containing 2.2% FK102, measured directly after cell fabrication.

In general we observe that the PCE of solar cells based on the aforementioned system significantly increases over time when the devices are stored in the dark. Comparison of  $J$ – $V$  data measured several days after cell fabrication and the photovoltaic parameters initially obtained reveals that this performance boost mainly results from an increase in FF (Table 1). We attribute this phenomenon to improved contact behavior at the spiro-MeOTAD/silver interface. However, so far it is unclear whether this process involves any reaction with oxygen or moisture or if it is of pure morphological nature. An influence of oxygen on the charge collection efficiency at the metallic back contact has been previously suspected, although a detailed mechanism has not yet been proven.<sup>19,20</sup> Devices based on the system presented herein generally reach PCEs between 6 and 7% measured 1–2 weeks after their fabrication. For a champion device containing 1.6% FK102 dopant, we achieved an unprecedented and very promising  $\eta = 7.2\%$  measured under simulated AM1.5G solar irradiance ( $100 \text{ mW cm}^{-2}$ ). To the best of our knowledge, this is the first time that such a high PCE has been obtained for an all-ssDSC. For this device, we derive photovoltaic parameters  $V_{oc}$ ,  $J_{sc}$ , and FF of 986 mV,  $9.5 \text{ mA cm}^{-2}$ , and 0.76, respectively. The corresponding  $J$ – $V$  characteristics are illustrated in Figure 6. Compared to previously reported high-efficient ssDSCs, our system particularly benefits from the high  $V_{oc}$  of close to 1 V, a property that is proper for the Y123 sensitizer.

Besides high performance, good long-term stability of photovoltaic devices is highly desirable, but very few studies have been performed on spiro-MeOTAD-based ssDSCs. The influence of p-doping by FK102 on device stability was therefore investigated. Cells employing the recently reported<sup>5</sup> organic D- $\pi$ -A sensitizer coded C220 (Figure S2) were subjected to standard light-soaking conditions ( $60^\circ\text{C}$ ,  $100 \text{ mW cm}^{-2}$ , AM1.5G). To avoid undesired photo-doping, the devices were hermetically sealed and equipped with a  $\lambda < 420 \text{ nm}$  filter. Under these conditions, photovoltaic cells maintained over 80% of their initial performance during a period of 40 days (Figure 7). The  $J_{sc}$  stayed constant during this period, as did the  $V_{oc}$  after an initial drop of 50 mV. Therefore, the gradual decrease of FF is mainly responsible for the loss in PCE. The low doping level of 0.7% employed during these initial runs could have caused this aging effect. However, these preliminary results are nevertheless promising as they clearly indicate that the proposed p-type dopant is not harmful for device stability.





**Figure 7.** Evolution of photovoltaic parameters of a device based on the C220 sensitizer and 0.7% FK102 under thermal stress and constant illumination (60 °C, 100 mW cm<sup>-2</sup>, AM1.5G).

Furthermore, these findings are even more remarkable as—to the best our knowledge—this is the first time that a PCE of 5% could be maintained for a ssDSC under such prolonged test conditions.

In conclusion, we have shown that chemical p-type doping is an effective tool to tune the charge-transport properties of spiro-MeOTAD in ssDSCs, capable of replacing commonly employed photo-doping. Preliminary studies demonstrate that the reported FK102 Co(III) complex fulfills the requirements for this kind of application and promising results could be achieved. Using a recently developed organic D- $\pi$ -A sensitizer, we finally reached a record PCE of 7.2% under standard test conditions.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Structure of the C220 sensitizer, experimental details on device fabrication and characterization, and synthesis and characterization of the FK102 complex and its Co(II) analogue. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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