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Co(III) Complexes as p-Dopants in Solid-State Dye-sensitized Solar Cells

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ABSTRACT: Following our recent work on the use of Co(III) complexes as p-type dopants for triarylamine-based organic holeconductors, we herein report on two new Co(III) complexes for doping applications. With the aim of ameliorating the dopant's suitability for its use in solid-state dye-sensitized solar cells, we show how the properties of the dopant can be easily adjusted by a slight modification of the molecular structure. We prove the eligibility of the two new dopants by characterizing their optical and electrochemical properties and give evidence that both of them can be used to oxidize the molecular hole-transporter spiro-MeOTAD. Finally, we fabricate high-performance solid-state dye-sensitized solar cells using a state-of-the-art metal-free organic sensitizer in order to elucidate the influence of the type of dopant on device performance.

Keywords: p-type doping, organic semiconductor, cobalt(III) complex, spiro-MeOTAD, dye-sensitized solar cell

1. Introduction

Electronic doping is a powerful tool to carefully control the type and density of charge carriers in both organic and inorganic semiconducting materials.⁽¹⁾ Doping of organic semiconductors is usually based on a charge-transfer reaction between the organic host and the dopant, the latter being either a donor (n-type doping) or acceptor (p-type doping) species that leaves part of the host molecules in a reduced or oxidized state. The key parameter for efficient doping is therefore the position of the ionization potential or electron affinity of the dopant with respect to the host's energy levels. However, depending on the application, other features such as ease of processing might become equally important, finally rendering a dopant suitable for only a specific type of device architecture and/or fabrication process. Thus, materials such as MoO₃ or WO₃ both extensively studied p-type dopants,⁽²⁾ are remarkably performing when thermally evaporated onto or together with the organic semiconductor but suffer from lack of solubility when solution processing is required.

Recently we reported on a new class of p-type dopants based on cobalt(III) complexes that have been designed to be processed from solution and are particularly promising due to their ambient stability, ease of preparation and the possibility to tune their chemical and physical properties.⁽³⁾ We employed tris(hexafluorotris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) phosphate) (FK102, Figure 1c), as p-type dopant and showed that it can be efficiently used to dope triarylamine-based holeconductors such as 2,2',7,7'-tetrakis(N,N-di-pmethoxyphenyl-amine)-9.9'-spirobifluorene (spiro-MeOTAD, Figure S1a). Spiro-MeOTAD is a molecular hole-transporter that is commonly used in solid-state dye-sensitized solar cells (ssDSCs)⁽⁴⁾, presently one of the most promising thirdgeneration photovoltaic (PV) technologies, but has also been

used in conjunction with n-type silicon nanowires⁽⁵⁾ and more recently with organic-inorganic hybrid perovskite sensitizers ^(6,7). A typical ssDSC is composed of a sensitized, mesostructured wide bandgap metal-oxide semiconductor that is infiltrated with a molecular or polymeric organic holetransporter, usually by solution processing (e.g. spin-coating). In this device photo-excitation of the sensitizer and subsequent ultrafast electron injection into the conduction band of the metal-oxide semiconductor is followed by hole-transfer from the oxidized sensitizer to the organic hole-transporter. Charge transport of both the electron and the hole through the two bicontinuous phases and charge migration through the external circuit complete the photovoltaic operation of the cell. Even though molecular p-type doping of spiro-MeOTAD in such a device configuration has been previously introduced,⁽⁸⁾ it is usually not essential due to device fabrication under ambient conditions and the facile one-electron oxidation of spiro-MeOTAD by oxygen under illumination. Nevertheless, controlled doping via the introduction of molecular p-dopants is expected to be favorable in terms of controllability and reproducibility of photovoltaic results and is expected to be indispensable if the devices are fabricated in an inert atmosphere.⁽⁹⁾ In our recent work we showed that the strategy of using molecular p-dopants is indeed beneficial for controlling the charge transport properties of spiro-MeOTAD in ssDSCs and were able to directly relate the conductivity of the doped holetransporter to device performance. In this report we investigate two new Co(III) complexes, namely tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III)

tris(bis(trifluoromethylsulfonyl)imide)) and bis(2,6- di(1Hpyrazol-1-yl)pyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)), herein denoted as FK209 and FK269 (Figure 1c), respectively, and compare them to FK102. These new complexes were designed to develop further the previously proposed concept of using Co(III) complexes as dopants. We demonstrate that the properties of the dopant can be easily adjusted by modifying the organic ligands and/or the counterion. The complexes were characterized by optical as well as electrochemical techniques in order to scrutinize their suitability for doping applications. The degree of one-electron oxidation of spiro-MeOTAD was determined by UV/Vis absorption spectroscopy. Finally, high-performance ssDSCs employing a state-of-the-art organic sensitizer were fabricated in order to probe the effect of the type of dopant on photovoltaic device performance.

2. Experimental Section

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Materials. All chemicals were purchased from Sigma-Aldrich (Switzerland) or Acros Organics (Belgium) and used as received unless stated otherwise. 2,2',7,7'-tetrakis(N,N-dip-methoxyphenyl-amine)-9,9'spirobifluorene (spiro-MeOTAD) was obtained from Merck KGaA (Germany) and used as received. The synthesis of Y123 sensitizer (Figure S1b) followed our published method.⁽¹⁰⁾ 4-tert-butylpyridine was purified by distillation before use. Tris(1-(pyridin-2-yl)-1H-pyrazol)cobalt(III) tris(hexafluorophos-phate) (FK102) and the corresponding Co(II) analog tris(1-(pyridin-2-yl)-1Hpyrazol)cobalt(II) bis(hexafluorophosphate) were synthesized as previously reported.⁽³⁾ The ligand 2-(1H-pyrazol-1-yl)-4tert-butylpyridine was synthesized according to a published procedure.⁽¹¹⁾ 2,6-di(1H-pyrazol-1-yl)pyridine was synthesized in a similar manner reacting 2,6-dichloropyridine with two equivalents of pyrazole.

Synthesis of Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyritris(bis(trifluoromethylsulfonyl)imide)) dine)cobalt(III) (FK209). 3.45 g (17.1 mmol, 3 eq) of 2-(1H-pyrazol-1-yl)-4tert-butylpyridine was suspended in a 2:1 mixture of water (120 mL) and methanol (60 mL) and heated to 70 °C. Then 1.36 g (5.7 mmol, 1 eq) of CoCl₂·6H₂O was added and the mixture was stirred at the same temperature for 10 minutes. 10 mL of H₂O₂ (30%) and 10 mL of HCL (25 %) were added to oxidize the cobalt and the mixture was further heated to 70 °C for 2 h. Then a concentrated solution of 8.18 g (28.5 mmol, 5 eq) lithium bis(trifluoromethylsulfonyl)imide in water was added slowly at 50 °C to precipitate the product. The mixture was allowed to cool to room temperature and the orange solid was collected on a sintered glass-frit and washed with water. The solid was dried in air and then *in vacuo* to obtain the pure product as an orange solid. Yield: 7.76 g (5.16 mmol, 91%). ¹H NMR (400 MHz, Acetone-D6): δ 9.87–9.64 (m, 3H, ArH), 8.79-8.65 (m, 3H, ArH), 8.00-7.79 (m, 6H, ArH), 7.78-7.62 (m, 3H, ArH), 7.37–7.17 (m, 3H, ArH), 1.72–1.15 (m, 27H, ^tBu).

Synthesis of Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(II) bis(bis(trifluoromethylsulfonyl)imide)). The Co(II) analog of FK209 was synthesized using the same procedure as described above, but omitting the oxidation step. No peaks are visible in the ¹H NMR (400 MHz, Acetone-D6).

Synthesis of Bis(2,6-di(1H-pyrazol-1-yl)pyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)) (FK269). 0.26 g (1.23 mmol, 2 eq) of 2,6-di(1H-pyrazol-1yl)pyridine was suspended in 30 mL of acetonitrile. Then 0.21 g (0.86 mmol, 1.4 eq) of CoCl₂*6H₂O was added and the mixture was stirred at room temperature for 10 minutes. Upon adding a solution of 0.47g (0.86 mmol, 1.4 eq) of ammonium cerium nitrate in acetonitrile the color of the solution changed and a pale orange precipitate formed. Then a concentrated solution of 0.62 g (2.15 mmol, 3.5 eq) of LiTFSI in water was added and the mixture was stirred at room temperature for 3 hours. The solid cobalt complex was collected on a sintered glass-frit, washed with water and then dried in vacuum to obtain the pure product as a pale orange solid. Yield: 0.75 g (0.60 m)mmol, 70%). ¹H NMR (400 MHz, DMSO-D6): δ 9.65–9.53 (m, 4H, ArH), 9.34-9.24 (m, 2H, ArH), 8.86-8.71 (m, 4H, ArH), 7.90-7.85 (m, 4H, ArH), 6.97-6.87 (m, 4H, ArH).

SynthesisofBis(2,6-di(1H-pyrazol-1-yl)pyri-dine)cobalt(II)bis(bis(trifluoromethylsulfonyl)imide)). TheCo(II)analog of FK269 was synthesized using the same pro-cedure as described above, but omitting the oxidation step. ¹HNMR (200 MHz, Acetone-D6) δ 76.36 (s, 4H, ArH), 75.39 (s,4H, ArH), 60.38 (s, 4H, ArH), 56.62 (s, 4H, ArH), 14.73 (s,2H, ArH).

UV/Vis Absorption Spectroscopy. UV/Vis absorption spectra were recorded on a Varian Cary 5 spectrophotometer using a 10 mm path length quartz cuvette. Spiro-MeOTAD was dissolved in chlorobenzene. The dopants were pre-dissolved in acetonitrile and then added to the spiro-MeOTAD/chlorobezene solution.

Electrochemical Measurements. The electrochemical characterization was performed on an Autolab Potentiostat (PGSTAT30, Metrohm) in a classical three-electrode configuration. Platinum wires were used as counter and reference electrode. A platinum wire or gold disc was used as working electrode. The solvent was dichloromethane containing 0.1M tetramethylammonium hexafluorophosphate. The measured potential was internally referenced versus the Ferrocenium/Ferrocene standard. DPV and CV measurements were performed at a scan rate of 0.1 V s⁻¹. Redox potentials were estimated from the DPV polarograms calculating the average of values obtained from the forward and backward scan.

Device Fabrication and Characterization. Photovoltaic devices were fabricated and characterized following recently published procedures.⁽³⁾ The dopants were predissolved in acetonitrile at a concentration of 20 mg mL⁻¹ and added to the spiro-MeOTAD solution prior to spin-coating. JV-curves presented herein have been measured directly after device fabrication without any additional light-soaking or ageing.

3. Results and Discussion

Although the earlier reported compound FK102 can be used as an efficient p-dopant, we found its solubility to be one of the major limiting factors, e.g. impeding the investigation of high 1

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Figure 1. A) Differential pulse voltammetry (DPV) and B) Cyclic Voltammetry (CV) measurements of the three different complexes in CH_2Cl_2 solution containing the dopant, 0.1 M TBAPF₆ and the Fc⁺/Fc standard as an internal reference. C) Molecular structures of FK102, FK209 and FK269.

doping ratios. In order to achieve p-type doping of the bulk HTM, a deposition of the dopant together with the holeconductor is required. Therefore the dopant should be soluble in the spin-coating formulation of the HTM, which comprises spiro-MeOTAD, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (TBP) in chlorobenzene. We find that the solubility of the Co(III) complexes depends strongly on the presence and concentration of the two latter additives. The main reason for the relatively low solubility of FK102 in organic solvent is its PF₆ counter-ion, whereas salts of bis(trifluoromethyl-sulfonyl)imide (TFSI) are usually much more soluble. In addition to changing the counter-ion, we also introduced a solubilizing tert-butyl group on the pyridinepyrazole (py-pz) ligand. The 2-(1H-pyrazol-1-yl)-4-tertbutylpyridine ligand has recently been successfully used for improved solubility of cationic Ir(III) complexes.⁽¹¹⁾ The TFSI salt of the Co(III) complex bearing this ligand is denoted as FK209 (Figure 1c). Apart from the solubility, we increased the oxidation potential of the dopant in order to maximize the driving force for the doping reaction as well as making it suitable for a larger number of host materials. This was done by changing the aromatic ligand. Compared to pyridine (py), pyrazol (pz) is a weaker σ -donor as well as a stronger π acceptor.⁽¹²⁾ Therefore we replaced the three bidentate py-pz ligands by two tridentate pz-py-pz ligands which is expected to stabilize the metal-centered HOMO level of the complex. The TFSI salt of the corresponding Co(III) complex is denoted as FK269 (Figure 1c). The Co(II) analog of FK269 has previously been reported and characterized by Holland et al. and Ayers et al.^(13, 14)

All three Co(III) complexes compared herein are diamagnetic low-spin complexes. The diamagnetism is confirmed by ¹H-NMR spectroscopy and the appearance of the peaks from the aromatic ligands in the region <10ppm. Upon the reduction to Co(II), all three complexes become paramagnetic in agreement with a strong downfield shift (FK269) or complete disappearance (FK102 and FK209) of the ¹H-NMR signals. Holland et al. found that the Co(II) analog of FK269 takes up a high spin quartet configuration, which results from the weak splitting of the metal d orbitals induced by the pyrazole-based ligands. A high spin configuration was also confirmed by Saha et al. for a Co(II) complex bearing a methyl-substituted py-pz ligand.⁽¹⁵⁾ All three complexes appear as orange/red solids and give slightly orange colored solutions in organic solvent. UV/Vis absorption spectra taken from CH₃CN solutions are shown in Figure S2. All complexes show strong absorption bands in the UV region below 350 nm arising from ligand centered π - π * transitions. The orange color, however, results from the very weak d-d transition that lies in the region between 400-600 nm, having a molar extinction coefficient of less than 30 and 600 L mol⁻¹ cm⁻¹ in case of the Co(II) and Co(III) species, respectively. Both new complexes are therefore very suitable for doping applications due to their visible transparency that avoids filtering of incoming light by the dopant in the photovoltaic device.

The complexes were characterized by differential pulse voltammetry (DPV) as well as cyclic voltammetry (CV) in order to evaluate their redox potentials. Results are given in Figure 1a/b. All three complexes show oxidation/reduction waves in dichloromethane that correspond to the Co(III)/Co(II) redox couple situated in the region of 0.2-0.8 V vs. the ferrocenium/ferrocene (Fc^+/Fc) standard. The redox processes are irreversible in the case of FK102 and FK269 and guasi-reversible in the case of FK209. From the DPV measurements, we estimate the redox potentials of FK102, FK209 and FK269 to be around 0.38, 0.32 and 0.58 V vs. Fc⁺/Fc, respectively. The lower redox potential of FK209 compared to FK102 can be rationalized by the inductive electron-donating effect of the tert-butyl groups on the py-pz ligand that destabilizes the HOMO of the complex. In agreement with our predictions, the change from a total number of 3 py/3 pz rings (FK102, FK209) to 2 py/4 pz rings (FK269) coordinated to the Co(III) metal center increases the redox potential, even though the large shift of roughly 200 mV was unexpected. Considering the first redox potential of spiro-MeOTAD at 0.02 V vs. Fc+/Fc,⁽³⁾ all three dopants should exhibit a driving force of more than 300 mV sufficient for the complete one electron oxidation.

The oxidation of spiro-MeOTAD by the three Co(III) complexes was confirmed by UV/Vis absorption spectroscopy in chlorobenzene solution. The gradual addition of any of the three complexes to a spiro-MeOTAD solution causes a decrease of the absorption band of spiro-MeOTAD at 389 nm together with a rise of two new absorption bands at 523 and



Figure 2. A-C) Change of the UV/Vis absorption spectrum of a spiro-MeOTAD solution in chlorobenzene upon the gradual addition of either of the three dopants A) FK102, B) FK209 or C) FK269. The change in coloration from black to red corresponds to increasing Co(III) levels, with black being pure spiro-MeOTAD in chlorobenzene. Percentages given in the legend are the amount of Co(III) added to the solution in mol% relative to spiro-MeOTAD. D-F) Plots of the amount of oxidized spiro-MeOTAD (mol%) calculated from the absorbance at 523 nm using a molar extinction coefficient of $3.4 \times 10^4 1 \text{ mol}^{-1} \text{ cm}^{-1}$ versus the amount of Co(III) added to the solution (mol%). Solid lines are linear fits, dashed lines indicate a theoretically expected conversion of 100%.

689 nm corresponding to the spiro-MeOTAD radical cation (Figure 2). We note that the addition of the Co(II) analog of any of the complexes to a spiro-MeOTAD solution, does not lead to the formation of the spiro-MeOTAD radical cation as confirmed by UV/Vis absorption measurements. This proves that the oxidation of spiro-MeOTAD is linked to the reduction of Co(III) to Co(II) as expected. Monitoring the appearance of the absorption peak at 523 nm or the disappearance of the peak at 389 nm allows the calculation of a Co(III)-to-spiro-MeOTAD⁺ conversion yield. For the neutral spiro-MeOTAD molecule we find an average molar extinction coefficient of $7.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, which is in good agreement with previously reported values.⁽⁸⁾ From the disappearance of the peak at 389 nm we calculate conversion yields of 59%, 62% and 71% for the three different oxidants FK102, FK209 and FK269, respectively. However, this calculation might underestimate the conversion yield as it does not take into account any possible contribution from absorption by the reaction products, i.e. the spiro-MeOTAD radical cation and the generated Co(II) complex at this wavelength. Therefore monitoring the appearance of the absorption band at 523 nm is preferred even though values for the extinction coefficient of spiro-MeOTAD⁺ reported in the literature range from 2.7 to $4.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. ^{1,(9, 16, 8)} Using an average value of 3.4 x $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, we estimate the conversion yield to be 65%, 68% and 78% for FK102, FK209 and FK269, respectively. The results indicate similar conversion yields for FK102 and FK209 and a significantly higher yield for FK269, a trend that can be rationalized by the difference in driving force for the one-electron oxidation of spiro-MeOTAD, which is similar for FK102 and FK209, but much higher for FK269. Overall, our findings suggest that the oxidation of spiro-MeOTAD using the proposed Co(III) complexes is an equilibrium reaction in solution, although the equilibrium constant is likely to be shifted for the doping of the solid-state hole-conductor. From the offset in redox potential we calculate equilibrium constants of 3.3×10^6 , 2.7 x 10⁵, 1.4 x 10¹⁰ for FK102, FK209 and FK269, respective-

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59 60 ly. From these values one would expect a nearly quantitative reaction contrary to our experimental findings. We attribute the discrepancy to uncertainties in the estimation of the redox potentials from the poorly reversible DPV polarograms as well as the extinction coefficient of the spiro-MeOTAD cation radical.

In order to confirm that all three materials are effective as pdopants for organic hole-conductors, solid-state dye-sensitized solar cells using the organic D- π -A sensitizer Y123 (Figure S1b) and spiro-MeOTAD were fabricated. Current (J) Voltage (V)-characteristics measured at 100 mW cm⁻² AM1.5G simulated solar irradiance for devices containing the three different dopants are shown in Figure 3a. In all three cases 2.0% of dopant with respect to the molar concentration of spiro-MeOTAD was added to the spin-coating formulation. Photovoltaic parameters derived from the JV-characteristics are summarized in Table 1.

For an undoped device that has been fabricated under identical conditions, we find values of 878 mV, 9.1 mA cm⁻² and 0.29 for open-circuit potential (Voc), short-circuit photocurrent density (J_{SC}) and fill factor (FF), respectively, corresponding to a power conversion efficiency (PCE) of 2.3%.⁽³⁾ In the presence of the Co(III) complexes the FF increases to 0.62, 0.69 and 0.69, the V_{OC} to 896 mV, 925 mV and 918 mV and the J_{SC} to 9.9 mA cm⁻², 9.4 mA cm⁻² and 9.6 mA cm⁻² for FK102, FK209 and FK269, respectively, boosting the PCE to 5.5%, 6.0% and 6.0% (Table 1). In general we would not expect the type of dopant to have an influence on device performance when the same doping level is maintained. In this regard, the difference in PCE and mainly FF for devices doped with FK102 compared to FK209/FK269 is somewhat unexpected but is likely to arise from the difference in the nature of the counter-ion. On one hand, a strong influence on ssDSC performance has for example been reported for LiTFSI and EMIM TFSI (EMIM = 1-ethyl-3-methylimidazolium).^(17, 18) A more recent publication however attributes this effect to the role of LiTFSI acting as a p-dopant in the presence of oxygen, 1

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its effect on charge-transport being negligible in the absence of oxygen.⁽¹⁹⁾ On the other hand, the greatly enhanced solubility of FK209/FK269 compared to FK102 leads to a better dispersion of the remaining Co(II) complex in the spiro-MeOTAD matrix, enhancing charge transport within the HTM and avoiding the crystallization of the Co(II) salt during the solution processing.



Figure 3. JV-Curves for photovoltaic devices based on the Y123 sensitizer and p-doped spiro-MeOTAD, measured under 100 mW cm⁻² simulated AM1.5G solar irradiance (solid line) and in the dark (dashed line). A) JV-Curves of devices containing different p-dopants FK102, FK209 and FK269 at a doping ratio of 2.0%. B) JV-Curve of a device doped at 10% using FK209.

To further support this hypothesis we also tested devices with much higher doping levels. Doping with 10% FK209, resulted in values of 941 mV, 9.1 mA cm⁻² and 0.73 for V_{OC} , J_{SC} and FF, yielding a PCE of 6.2%. The corresponding JVcurve is displayed in Figure 3b. The increase of the doping level improves the FF and the PCE. We note, that this efficiency is measured directly after device fabrication without the need of any additional ageing or light-soaking treatments. This data clearly shows the benefit and potential of these new dopants that we expect to find widespread application in organic electronic devices based on triarylamine-based semiconductors. Future studies will focus more on the optimization of the doping level as well as a device fabrication under inert atmosphere as the dopants have the potential to obviate the necessity of any oxygen-induced doping for an efficient device functioning.

Table 1. Photovoltai	c parameters	of ssDSCs	using dif-
ferent p-type dopants	s (AM 1.5 G, 1	00 mW cm	²). ^a

	Blank	FK102	FK209	FK269	FK209
Doping Level	-	2.0%	2.0%	2.0%	10%
V _{OC} (mV)	878 ^b	896 ± 9	925 ± 3	918 ± 5	941 ± 7
J _{SC} (mA cm ⁻²)	9.1 ^b	9.9 ± 0.1	9.4 ± 0.2	9.6 ± 0.1	9.1 ± 0.2
FF	0.29 ^b	0.62 ± 0.02	0.69 ± 0.01	0.69 ± 0.01	0.73 ± 0.01
PCE (%)	2.3 ^b	5.5 ± 0.2	6.0 ± 0.1	6.0 ± 0.1	6.2 ± 0.1

^a The average of three devices is given for each condition.

^b Data taken from reference (3).

4. Conclusion

In conclusion we proposed two new Co(III) complexes as pdopants for organic semiconductors to complement the previously reported FK102. Their redox potential and solubility was adjusted by modifying the ligands and the counter-ion, respectively. The high solubility of the TFSI salts enabled doping levels of more than 10% for the new complexes,x underlining their potential as a potent p-dopants for triarylamine-based hole-conductors in solid-state dye-sensitized solar cells.

ASSOCIATED CONTENT

Supporting Information. Molecular Structures of Y123 and spiro-MeOTAD as well as additional UV/Vis absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org

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FK102

300 400 FK269

3 TFSI

0.8

0.2 0.4 0.6 Voltage (V)

3 TFSI

OD @ 523 nm 10 20 30 Co(III) Dopant added (10⁻⁶ mol L⁻¹)

FK209

00

0.6 -0.5 -0.4 -0.3 -

0.

800

3 PF6

500 600 700 Wavelength (nm)

