Ionically Self-Assembled Carboxymethylcellulose-Surfactant Complexes for Antistatic Paper Coatings

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Abstract

We show that ionically self-assembled polyelectrolyte/surfactant complexes allow a facile route to tailor the electrical surface resistance of paper sheets for antistatic dissipative regime. We use anionic polyelectrolyte carboxymethyl cellulose (CMC) where cationic alkyltrimethylammonium chloride surfactants (C_nTAC) with the alkyl chain lengths n = 12, 14 or 16 methyl units are ionically complexed by precipitation from aqueous solutions. Such alkyl chains are sufficiently long to allow self-assembly in solid films after solvent evaporation. Short chain lengths, eg. n = 8, did not lead to precipitation. Small Angle X-Ray Scattering indicates cylindrical self-assembly in bulk samples. Upon exposing bulk samples under humidity of 50 %RH for 18 hours, conductivity of ca. 10^{-5} S/cm at room temperature is achieved based on AC-impedance analysis. Flexographic printing and spray coating were selected to conceptually test the feasibility as paper coatings and surface sheet resistances of ca. 10^9 Ω are reached. The results indicate that self-assembled polyelectrolyte/surfactant complexes can allow sufficient conductivity levels for antistatic paper coatings potentially due to protonic conductivity and suggest to develop processes and materials for realistic applications.

Graphical abstract
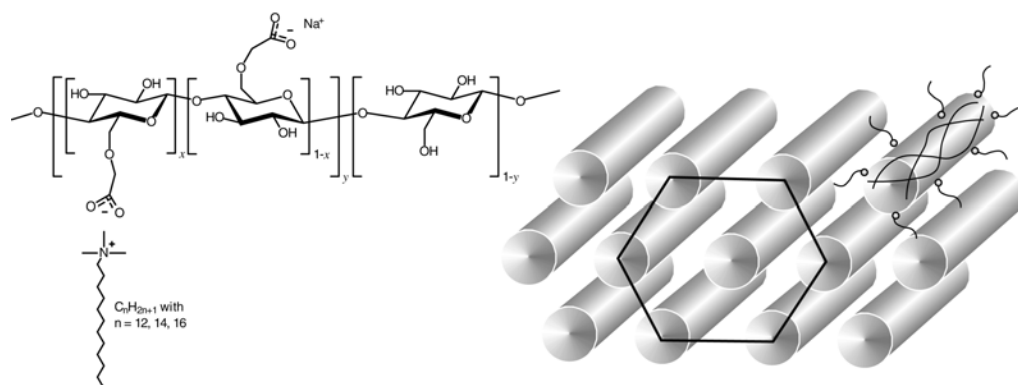
Introduction

There have been considerable recent efforts to combine developments within advanced materials to the longstanding problem to enhance and to tailor the electrical conductivity of paper and cellulosics for various applications, such as using conjugated polymers and carbon nanotubes.[1-17] The electrical properties of paper have long been studied for many fields of science and technology, eg. in xerocopying, laser printing, electrostatically assisted rotagravure printing, and more generally in paper handling.[18-24] Even if it is a routine task to monitor the surface electrical properties of paper sheets[25, 26], it is still untrivial to tailor them in a systematic manner taken that the surfaces have to remain uncolored and therefore there still remain challenges for new material options. The electrical conduction of paper and cellulose is considered to be ionic but it seems not to be fully understood.[23, 27-29] Absorbed water plays an important role, and the resistivity drops several orders of magnitude if the water content is increased from 0 to 20 %. The water molecules can be bound to the carboxylic and hydroxylic moieties. Based on general arguments, electrical conductivity could, therefore, be expected if there exists a sufficient amount

of absorbed water, leading to percolative continuous networks where proton transport could take place by hopping between the dissociated water species[30, 31], and where the ions can be transported. If a more complete understanding of the electrical properties of paper within various printing applications is called for, the dielectric properties as a function of frequency must be measured.[23, 26]

Various types of polymeric coatings could be considered to tune the electrical conductivity of the paper sheets. Conjugated polymers are semiconductors, which can be doped for conductivity, and then allow dc-conductivity, i.e. Ohmic behavior.[32] They find applications in printable electronics, but due to the conjugation they are strongly colored, which limits their use in paper coating applications where bright and uncolored surface finish is called for. On the other hand, conductivity can be achieved upon transporting ions[33-36] and protons[30, 37], which is central for eg. batteries and fuel cell membranes, correspondingly. In contrast to the doped conjugated polymers, ionically and protonically conducting polymers do not allow purely Ohmic behavior and therefore must be characterized using ac-techniques. Polymeric salts have been useful to promote protonic conductivity in fuel cell membranes and smart materials.[38-41] Polyelectrolyte – surfactant complexes have also been reported to allow conductivity[42], in addition of the ionic self-assembly[43-47]. An example is given by polyacrylic acid complexed with dodecyltrimethylammoniumchloride ($C_{12}TAC$), which is prepared by precipitation from water and self-assembles to a lamellar structure after solvent evaporation.[44]

For paper coatings, polyelectrolyte/surfactant complexes could be useful as they contain ionically bonded hydrophobic side chains with reduced solubility in water to

facilitate incorporation into paper processing, still providing hydrophilic salt-like conducting channels within their self-assembled structures. In the paper coatings it would be a natural choice to select ionic polysaccharides as polyelectrolytes due to the compatibility to cellulosics. Cationic starch, being a cationic polyelectrolyte, is known to form self-assembled structures upon ionically complexing with anionic surfactants.[48] In this work we select an anionic polyelectrolyte carboxy methyl cellulose (CMC), which can be complexed with cationic alkyltrimethylammonium surfactants. Cationic starch and CMC are known to adsorb onto cellulose fibers in the process of paper making. This makes them interesting for paper-compatible anti-static coatings. Note that the binding of CMC and cationic surfactants as well as their aqueous micellar aggregates have been investigated.[49-51] Complex conductivity has been reported for solutions but not in bulk.[52]

In the following we first show the complexation by elemental analysis, investigate the structure formation in bulk using Small Angle X-ray scattering, investigate the AC-conductivity by impedance analysis, extract the dc-conductivity by common extrapolation techniques, and finally apply the complexes on base paper to study the surface resistance values.

Materials and Methods

Materials: CMC/C$_n$TAC. CMC (Figure 1) was supplied by Sigma Aldrich (degree of substitution y = 0.9, M_w = 250 000 g/mol). Alkyltrimethylammonium chlorides

with tail lengths n = 8, 12, 14 and 16 were supplied by Fluka and were used as such. Milli-Q® (Millipore) water was used to prepare the complexes in the following way: CMC was dissolved in water (concentration < 4 wt-%) by mixing and heating in water bath at 95 °C for 30 minutes. Alkyltrimethylammonium chloride (C_nTAC, Figure 1) was separately dissolved in water using concentration < 4 wt-%. The solutions were slowly combined using the molar ratio 1 : 1.3 of the CMC monomers and the C_nTAC molecules. Precipitation took place for n = 12, 14, 16, and therefore they were selected for further studies. The precipitated complexes were washed in pure water. The samples were dried in vacuum (10^{-2} mbar) at room temperature for 16 hours. The complexes are partially soluble in methanol: when mixed with methanol, they form an opaque liquid.
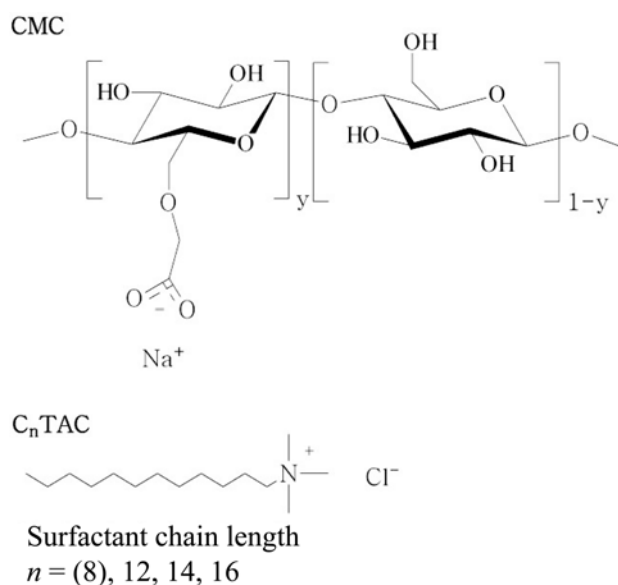

Figure 1. Carboxy methyl cellulose (CMC) with degree of substitution y, and alkyltrimethylammonium chloride (C_nTAC) surfactants.

Elemental analysis. Since the samples were prepared by precipitation, elemental analysis was used to assess the actual compositions in the precipitated and dried samples. The measurements were carried out using a Perkin Elmer CHN2400 device with ca. 2 mg sample size. The fractional amounts of carbon, nitrogen and hydrogen were determined. Two parallel samples were measured and averaged.

Small-angle X-Ray scattering. Small-angle X-Ray (SAXS) measurements were performed using a sealed fine-focus X-ray tube in the point-focus mode.[53] CuK_α radiation (λ = 1.54 Å) was monochromatized with a Ni filter and a totally reflecting mirror (Huber small-angle chamber 701) and the scattered intensity was measured with a Bruker AXS Hi-Star area detector. The distance between the sample and the detector was 20 cm. The scattering vector was calibrated using a silver behenate standard. The intensities were corrected for the absorption and background scattering. Before the measurements, the complexes and alkyltrimethyl ammonium chlorides were redissolved in methanol, followed by the solvent evaporation and vacuum drying to achieve better ordering. For pure CMC, the same was done but with water. After vacuum drying the samples were let to absorb moisture for ca. 24 hours at room temperature under the laboratory atmosphere with humidity of ca. 50 %RH – 60 %RH before measurements.

Conductivity measurements of the bulk complexes. Electrical bulk conductivities of the complexes were measured as a function of temperature with Wayne Kerr precision component analyzer 6440B at frequencies 20 Hz - 3 MHz using a home-made conductivity cell and parallel plate (blocking) geometry. Before the conductivity measurements, the samples have been dried in vacuum and then hydrated

at 25 °C and 50 % RH for 18 hours (the room temperature measurements, Figure 4) or at room temperature and ca. 50% - 60% RH for at least 16 hours (the temperature sweeps, Figure 5).

Flexographic printing. Flexographic printing was done using RK Flexiproof 100 and depth of 8 cm^3/m^2, speed 60m/min and ca. 5 wt-% methanol suspension of CMC/C_{14}TAC. 5, 10 and 20 layers of coating were applied on the base paper. The paper sheets were let to dry from methanol and absorb water from the ambient atmosphere before surface resistance measurements.

Spray coating. Spray coating was done on base paper using a conventional spray coater (type) and 2.5 w-% methanol suspension of CMC/C_{14}TAC. The thickness of the resulting coatings was of the order of a few micrometers, estimated based on the liquid consumption and the surface area of the sheet.

Conductivity measurements of the paper sheets. Surface sheet resistances of the coated base papers were measured with Keithley 8009 Resistivity Test Fixture at room temperature.

Results and Discussion

Since the samples were prepared by precipitation, the actual sample compositions were first investigated using elemental analysis (Table 1). First the ratio of nitrogen

and carbon obtained from elemental analysis is calculated, which allows to determine the molar fraction x in the complex CMC/C$_n$TAC 1:x. One can conclude that $x \approx 0.9$ for all of the samples, i.e. that ca. 90 % of the carboxylate groups have alkyltrimethyl ammonium surfactants as their counterions. Deviation from the nominally full complexation $x = 1.0$ is probably due to reaction kinetics: the complex can start precipitating when already part of the sodium ions have been replaced with C$_n$TAC. While precipitation develops further, parts of the polymer are left inside a solid precipitating aggregates and complete ion exchange can be hindered.

Table 1. The sample compositions based on elemental analysis: the measured nitrogen to carbon weight ratio obtained from the elemental analysis and the calculated molar fraction x in complex CMC/C$_n$TAC 1:x.

	N:C weight ratio from the elemental analysis	Calculated molar fraction x
CMC/C$_{12}$TAC 1:x	0.0472	0.892
CMC/C$_{14}$TAC 1:x	0.0437	0.894
CMC/C$_{16}$TAC 1:x	0.0415	0.951

The structures of the complexes are studied using SAXS, see Figure 2. The scattering intensity maxima of the complexes CMC/C$_n$TAC are different from those of pure CMC or C$_n$TAC, which indicates formation of new structures upon complexation. For CMC/C$_{16}$TAC the scattering intensity maxima are observed for the scattering vector magnitudes 0.159 1/Å, 0.275 1/Å, 0.318 1/Å, and 0.421 1/Å, which are assigned as the reflections q^*, $\sqrt{3}q^*$, $2q^*$, and $\sqrt{7}q^*$, correspondingly. This indicates hexagonal self-assembly and the long period of the structure L is $L=2\pi/q^*=39.5$ Å. Similarly, for

$n = 14$, the observed reflections are at q^*, $\sqrt{3}q^*$, $2q^*$, and $\sqrt{7}q^*$ with q* = 0.172 1/Å, whereas for $n = 12$ only the reflections at q^*, $2q^*$, and $\sqrt{7}q^*$ with q* = 0.193 1/Å are observed, suggesting less developed order. Therefore, all of the structures of Figure 2 are hexagonal, and the long period increases as a function of n.
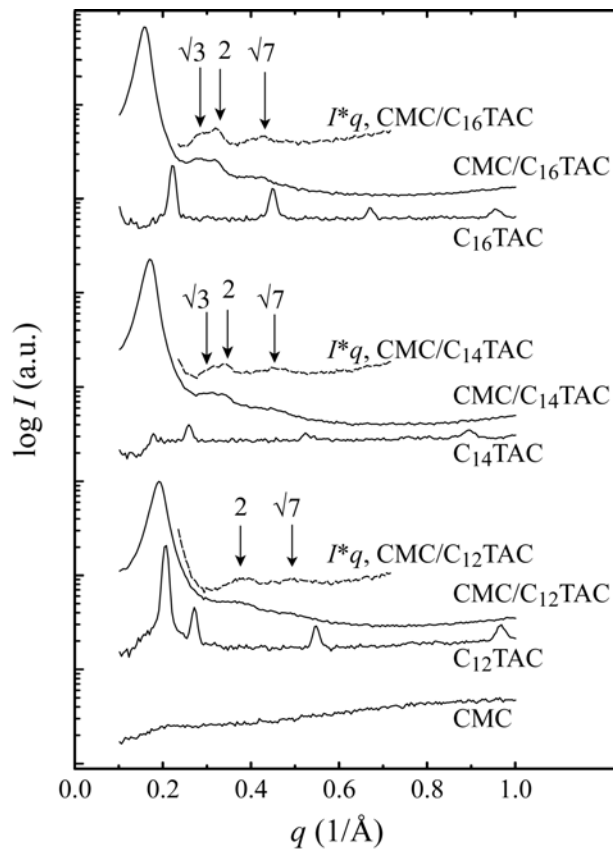

Figure 2: Logarithmic small angle X-ray scattering intensities *vs*. magnitude of scattering vector q for the complexes and the pure compounds at room temperature where $q = (4\pi/\lambda)\sin\theta$, 2θ is the scattering angle and $\lambda = 1.54$ Å. The graphs $q^* I$ have

been added for the complexes to show more clearly the higher order reflections. All complexes show hexagonal order.

According to Table 2, the volume fractions of CMC and C_nTAC are almost equal, and thus it is a priori not self-evident which moieties of the complexes form the cores of the cylinders. However, as the complexes CMC/C_nTAC are plasticized and are able to flow when heated to 150 °C, whereas pure CMC remains unplastized, the cylinders must consist of CMC cores as separated by the matrix of C_nTAC, see Figure 3.

Table 2. Characteristic parameters describing the self-assembly

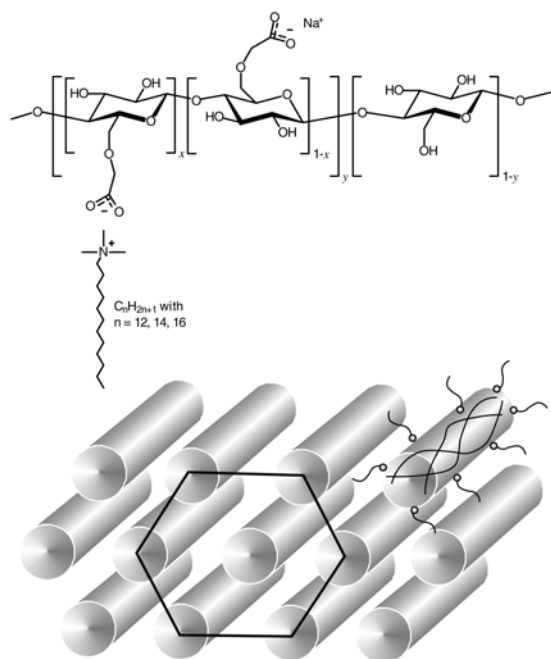|	Calculated molar fraction x from the elemental analysis	Calculated weight fraction of CMC in CMC/C_nTAC 1:x	Long period L of the self-assembled cylindrical structure
CMC/C_{12}TAC 1:x	0.892	53.8 %	32.5 Å
CMC/C_{14}TAC 1:x	0.894	50.8 %	36.5 Å
CMC/C_{16}TAC 1:x	0.951	46.7 %	39.5 Å

Figure 3: Chemical compositions of the complexes and a schematical picture of the hexagonal self-assembly. In the chemical formula, y denotes the degree of carboxylic acid substitution ($y \approx 0.9$), and x the degree of complexation using the surfactants, as realized using the precipitation process (Table 1).

Next, electrical conductivities of the bulk complexes CMC/C_nTAC and the pure surfactants C_nTAC are shown in Figure 4 *vs.* the surfactant chain length n after pretreating at the relative humidity 50 % RH for 18 h at 27 °C. Astonishingly, CMC/C_nTAC and C_nTAC showed very different behavior, where the conductivity of the previous samples increase upon adding n from 12 to 16, whereas the conductivity of the latter ones become reduced, correspondingly. Also the dried samples were measured, but they are not represented here; as a general tendency, the hydrated samples showed much higher conductivities than the corresponding dry samples. This is not surprising as the absorbed water is expected to be the main source of

conductivity. So far the explanation for the observations of Figure 4 remain speculative: For the pure surfactants, increase of the surfactant alkyl chain length leads to reduced hygroscopicity, which, in turn, can lead to lower conductivity values. For the self-assembled complexes CMC/C_nTAC, competing effects may be present: On one hand, the longer surfactant chains cause reduced hygroscopicity. On the other hand, self-assembly leads to well-defined protonically conducting cylindrical channels whose order seems to improve upon increasing n from 12 to 16 based on the more clearly resolved higher order SAXS reflections and slightly reduced half width at half maximum of the main reflections. It would be expected that for much larger n, the conductivity might again be reduced. Finally, the temperature behavior of conductivity of the CMC/C_nTAC complexes is typical for an activated transport (see Figure 5).
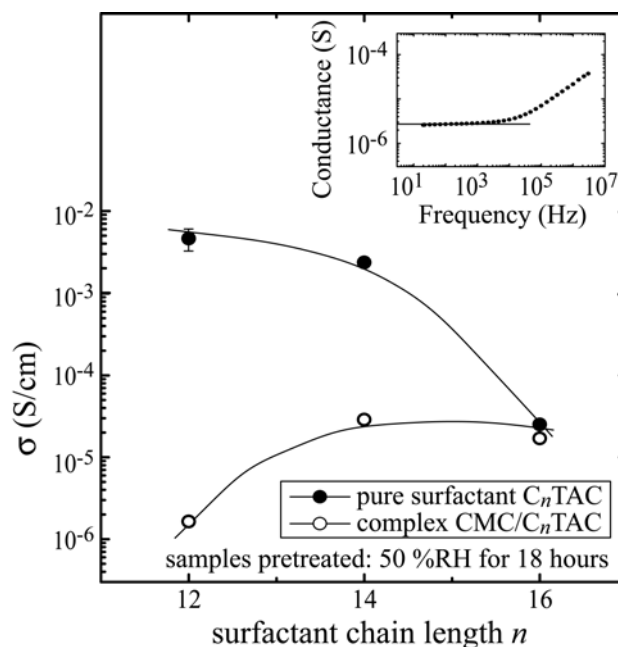

Figure 4. Bulk electrical dc-conductivities of the hydrated complexes CMC/C_nTAC and hydrated surfactants C_nTAC based on ac-impedance studies. The inset shows ac impedance data for $CMC/C_{12}TAC$ as an example to demonstrate how the dc-

conductivity is evaluated based on extrapolation from the plateau conductivity value near 1 kHz. The conductivity of hydrated CMC, ca. $1.0*10^{-6}$ S/cm, is not shown. The samples were pretreated under humidity of 50 %RH for 18 hours to allow moisture absorption.
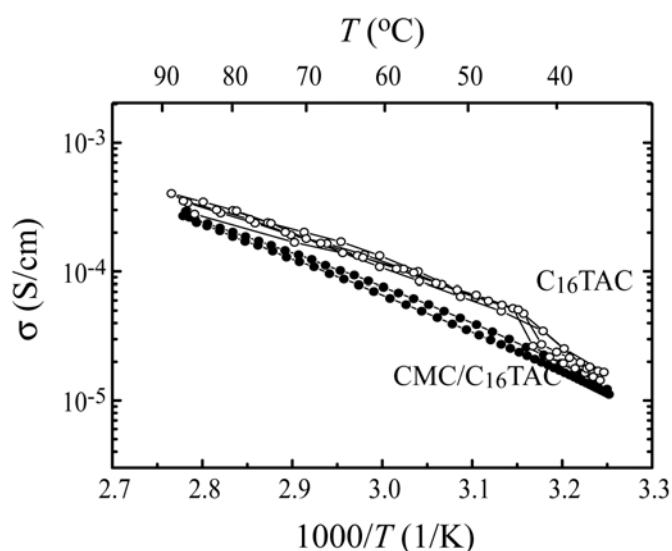

Figure 5. Bulk electrical conductivities of hydrated complex CMC/C_{16}TAC and hydrated pure surfactant C_{16}TAC vs. inverse temperature.

In order to study the conductivity behavior for paper coatings, flexographic printing was first used. The aim was to use a simple model process, which allows systematically controlling the thickness of the coatings based on the number of printed layers and determining whether the dissipative surface sheet resistance values less than 10^{11} Ω [54] can be achieved, i.e. antistatic conductivity. Resistivities of flexographically printed paper sheets are shown in Figure 6 for CMC/C_{14}TAC as a function of number of layers. The surface resistance consistently decreases as a

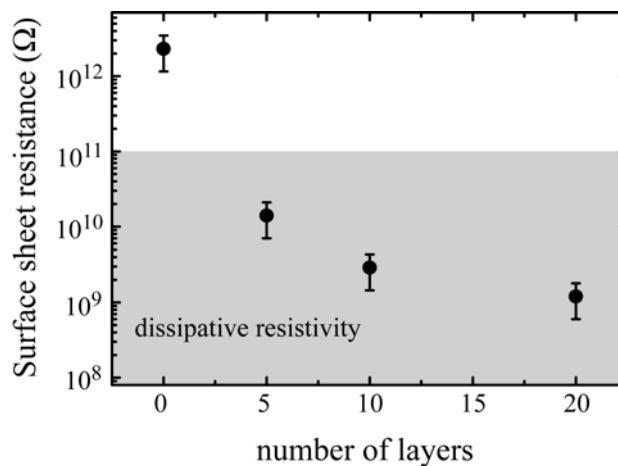function of number of layers, and the dissipative regime is reached upon applying a few layers.

Figure 6. Surface sheet resistances for flexographically printed complex CMC/C$_{14}$TAC (from methanol suspension) on base paper.

Since printing several layers is not a practical coating method, spray coating tests were finally performed also to find out if this more feasible method can lead to antistatic coatings. Surface sheet resistances for spray coated base papers were ca. $9*10^8$ Ω for the CMC/C$_{14}$TAC coated papers. The effect of coating layer thickness on surface sheet resistance could not be studied due to the lack of good control of coating thickness using the present process. Still the results show that spray coating allows antistatic coatings.

One can conclude that antistatic paper coatings can be achieved using self-assembled polyelectrolyte/surfactant complexes. In this context one has to point out that the octylterimethyammonium chloride complexes, i.e. CMC/C$_8$TAC remained water soluble upon complexation and was not regarded feasible for the present application.

Summary

Ionically self-assembled carboxymethyl cellulolose/alkyltrimethylammonium-surfactant complexes are prepared by precipitation from aqueous solvent and are observed to form hexagonal self-assembly for the alkyl chain lengths of 12-16 methyl units of the surfactant tail. These complexes can be applied as paper coatings using various coating methods. Flexographic printing allows to systematically increase the thickness of the coating as a function of the number of the printed layers and dissipative surface sheet resistance values are reached upon printing a few layers. Spray coating allows a more practical coating method where the surface sheet resistances less than 10^9 Ω were achieved. In principle, these conducting complexes could be added to bulk paper in the paper making process, but extensive work on process and materials optimization may be required.

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