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Conducting films based on single-component molecular metals†

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We demonstrate that single component molecular metals can be used as conductive inks for printed electronics. The resistance is $0.3 \text{ k}\Omega \text{ sq}^{-1}$, in a Ni complex, which is one order of magnitude better than that of commercial carbon based conductive inks.

Conductive inks are particularly attractive for electronic devices using printing or other solution processing technology such as flexible displays, photovoltaics or sensors integrated in textiles or paper.¹ Materials like metallic nanoparticles, polymers and carbon derivatives, like graphite, carbon nanotubes or graphene and different processing techniques have been tested.² Their use represents the simplification of the technological fabrication process at lower cost. However, several disadvantages arise from the use of such compounds. These include the need for high annealing or sintering temperature, surface tension due to grain size or a hydrophilic surface, or ineffective charge transport due to the presence of water.³ Moreover, functionalisation of these materials is difficult, hindering a more selective interface.⁴ Even in conducting polymers, the best strategy to modify their properties is mixing compounds, making it difficult to control the reproducibility and anticipate the final effect.⁵

Small organic molecules have proven to be easier to control by strategic chemical modification, both the electronic properties and chemical sensitivity.⁶ This is the case, for instance, of the perylenediimides, used as organic semiconductors in field-effect transistors. The introduction of electronegative groups, such as halogens, on bay positions of the core aromatic scaffold can modify the energy levels with direct consequences on the transport and electrochemical properties, whereas additional side groups in the imide positions lead to changes in solubility

and fluorescence.⁷ To reach metallic conduction, an appropriate combination of molecular order and chemical interactions is necessary for producing charge carrier drift with minimal scattering. Defects and steric constraints seriously affect the transport mechanism and, as a result, only a few materials have been developed.⁸ Single component molecular metals (SCMM) are a recent class of molecular conductors composed of a single neutral molecule, with a transition metal bisdithiolene core, offering the simplicity of only one molecule to be engineered and processed. Conductivity as high as 400 S cm^{-1} and even superconductivity have been reported, both measured in single-crystals.⁹ In compressed polycrystalline powder samples the values decrease substantially due to a grain-boundary effect, yet, some tetrathiafulvalenedithiolate compounds were able to achieve 200 S cm^{-1} .¹⁰ Even if these materials present low solubility, a trimethylenetetrathiafulvalenedithiolate derivative was successfully used as a conductive film,¹¹ whereas a thiophenedithiolene derivative was used as a flexible metallic film for piezo-resistive sensors. However, these were achieved either as highly viscose mixtures that become rapidly rigid, or as bilayer composite films prepared *in situ* by a modified reticulated doping technique,¹² which is incompatible with printing processes. Moreover, similar approaches for compounds with a more extended chemical structure and higher conductivity were restricted by their lower solubility.

In this communication, we report the fabrication of highly conductive and durable SCMM films using a solution process compatible with printing technology. To the best of our knowledge, this is the first evidence of using a single component molecular metal ink by drop cast which achieved a highly conductive film in air, at room temperature, and exhibits stable electronic performance. The inks were based on thiophenedithiolene derivatives. Conductive performance of films was highly dependent on the solvent, even if these presented similar solubility compatibility, which affected mostly the film morphology. The chosen materials were $[\text{Ni}(\text{dtdt})_2]$ (dtdt = dihydrothiophenetetrathiafulvalenedithiolene)¹⁰ and $[\text{Au}(\alpha\text{-tpdt})_2]$ ($\alpha\text{-tpdt}$ = 2,3-thiophenedithiolene) (Fig. 1a).¹³

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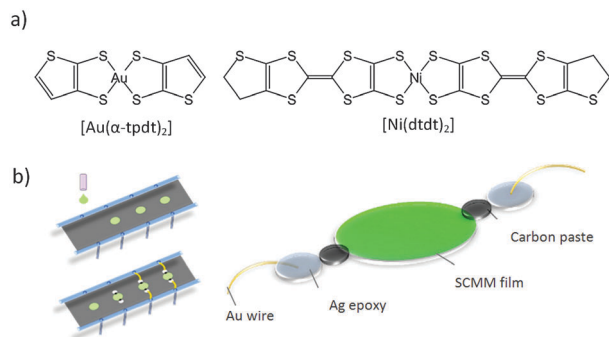


Fig. 1 (a) Molecular structures of $[\text{Au}(\alpha\text{-tpdt})_2]$ and $[\text{Ni}(\text{dtdt})_2]$. (b) Schematic illustration of the SCMM drop casting and measurement layout.

The two compounds were readily synthesised using procedures already developed in our previous work and available in the literature.^{10,13} A 2 wt% solution was prepared in different high purity solvents. Sonication of the SCMM in the above 2 wt% solution for two hours resulted in a stable dispersion. The dispersion was drop cast onto a silicon substrate with a 200 nm SiO_2 layer, in air, yielding continuous and homogeneous films of average length $L \approx 1.55$ mm, width $W \approx 1.14$ mm, and thickness ≈ 6.3 μm . Electrodes were also deposited by solution. All samples were bonded with silver epoxy and Au wires, and in some samples an additional layer of carbon paste was used between the conductive SCMM and the epoxy contact.

The electrical transport properties of the SCMM films were investigated by a two-point probe configuration. Fig. 2 presents the current–voltage characteristics (I – V) of drop-cast SCMM films under ambient conditions. All curves present a linear behaviour, yet the film resistance varies several orders of magnitude depending on the dispersion solvent (Fig. 2a and Fig. S1, ESI†). The resistance per square was lower on films of dichlorobenzene, and was three orders of magnitude higher than on films of toluene, chlorobenzene and dichloromethane. An additional layer of SCMM, also added by drop cast, improved the film conductivity. However, apart from solvent, the most significant improvement was achieved with the use of carbon contacts in direct contact with the film, instead of the silver epoxy (Fig. 2b). Such an effect can be related to the presence of solvents in the silver epoxy, which destroy the contacting interface and lead to higher contact resistance. Baking the films at 100 $^\circ\text{C}$, after deposition, systematically lead to higher resistance (Fig. S1, ESI†). Under the best deposition conditions, two drops of SCMM in dichlorobenzene and using carbon paste contacts, the sheet resistance is 1.3 $\text{k}\Omega \text{ sq}^{-1}$ and 0.3 $\text{k}\Omega \text{ sq}^{-1}$ for $[\text{Au}(\alpha\text{-tpdt})_2]$ and $[\text{Ni}(\text{dtdt})_2]$ respectively. This difference between the resistance of nickel and gold compounds is in accordance with what is observed in compressed powder pellets.¹⁰ $[\text{Au}(\alpha\text{-tpdt})_2]$ film resistance is consistent with the resistance found for a film obtained as a bilayer composite film processed by a reticulated doping technique.¹² When compared with other carbon-based conductive inks such as PEDOT-PSS ($\sim 1.5 \text{ k}\Omega \text{ sq}^{-1}$) or graphite paint ($1.2 \text{ k}\Omega \text{ sq}^{-1}$) the gold ink presents a similar sheet resistance whereas the nickel ink is approximately one order of magnitude lower. Films are stable in air over long periods of time. This is illustrated in

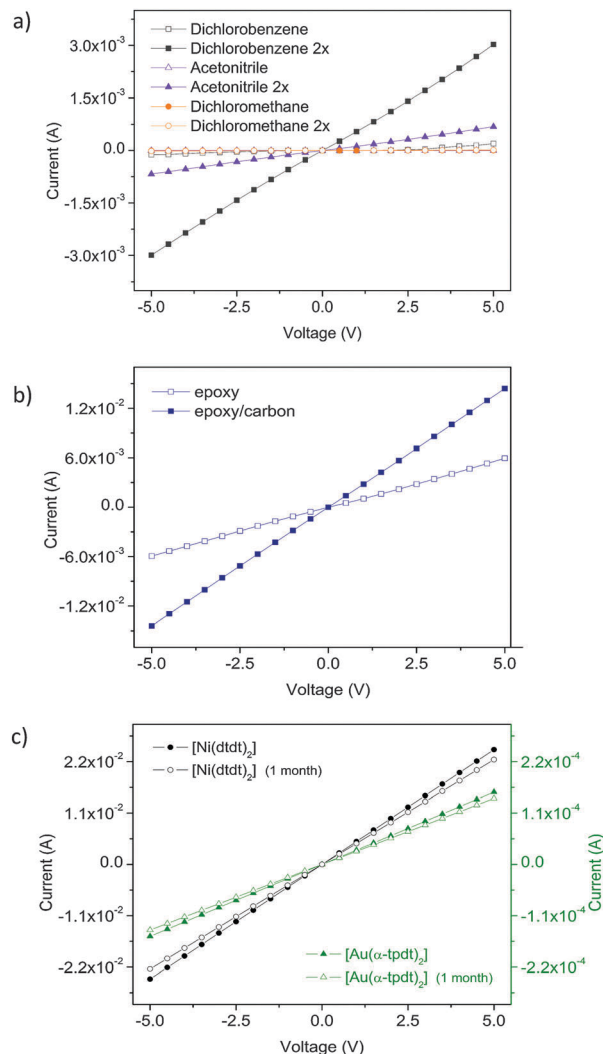


Fig. 2 I – V characteristics of (a) the $[\text{Au}(\alpha\text{-tpdt})_2]$ film under different conditions, (b) carbon paste contact effect on the $[\text{Ni}(\text{dtdt})_2]$ film, (c) SCMM films with time, showing no signs of degradation after one month storage under ambient conditions.

Fig. 2c, and the conductivity does not change significantly over a one month period.

SEM imaging on different films was used to investigate the impact of surface morphology on electrical performance.† These confirm that SCMM in dichlorobenzene are well dispersed, forming uniform films (Fig. 3a and b). Films prepared with acetonitrile are less homogeneous and have different grain sizes (Fig. 3c), indicating aggregation, which is in agreement with the lower currents measured for the corresponding films. The use of dichloromethane as dispersion solvent leads to uneven coverage domains, which interrupts conduction and explains the low conductivity observed (Fig. 3d). Addition of a second SCMM layer leads to different morphology effects (Fig. S2, ESI†). In dichlorobenzene, film uniformity is improved, with a wider coverage. Yet, in acetonitrile, film roughness and uneven size particles are more evident when another layer is added. The same trend is observed for other solvents, where an additional SCMM layer leads to a surface with more defects and roughness therefore

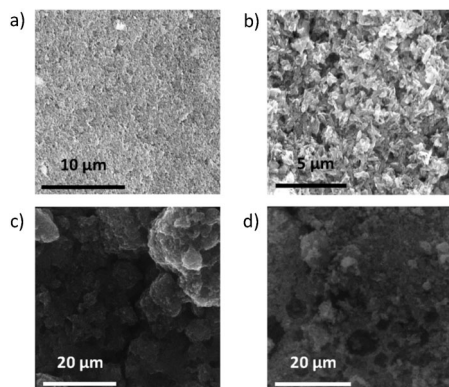


Fig. 3 SEM images of SCMM films prepared from suspensions in different solvents: (a) $[\text{Au}(\alpha\text{-tpdt})_2]$ in dichlorobenzene, (b) $[\text{Ni}(\text{dtdt})_2]$ in dichlorobenzene, (c) $[\text{Au}(\alpha\text{-tpdt})_2]$ in acetonitrile, and (d) $[\text{Au}(\alpha\text{-tpdt})_2]$ in dichloromethane.

more prone to charge traps. The use of baking can originate larger crystalline domains and enable removal of possible solvent trapped within the conductive layers. This effect leads to better electrical performance on organic semiconductors. However, baking the SCMM results in a lower conductance. SEM surface images provide an explanation (Fig. S3, ESI[†]). Baking has a different effect, depending on the solvent used. In acetonitrile, aggregation is induced, leading to an uneven and rough surface. In toluene, film cracks appear and in dichloromethane the effect of uneven coverage is more pronounced. In all cases, baking induces more defects in surface morphology causing an uneven film surface, which explains the decrease in conductivity. These results reveal that dispersion solvent and annealing can have a dramatic impact on SCMM film resistance.

In conclusion, we have demonstrated the use of SCMM as conductive inks, processed by the drop casting technique, starting from fine suspensions. A suspension solvent environment and film post deposition treatments have a striking impact on surface morphology, which leads to differences in electrical performance of several orders of magnitude. In dichlorobenzene suspensions, $[\text{Au}(\alpha\text{-tpdt})_2]$ and $[\text{Ni}(\text{dtdt})_2]$ exhibit the best performance, with sheet resistances of $1.3 \text{ k}\Omega \text{ sq}^{-1}$ and $0.3 \text{ k}\Omega \text{ sq}^{-1}$ respectively. These values are comparable or one order of magnitude better than those of the available commercial carbon-based conductive inks. This opens way for such compounds into printed electronics applications and the possibility of manipulating the working function by chemical modification.

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Notes and references

† SEM images were collected in a Hitachi S-2500 operating at 30 kV. Electric conductivity was measured by a two-probe method using a Keithley 237 measure unit.

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