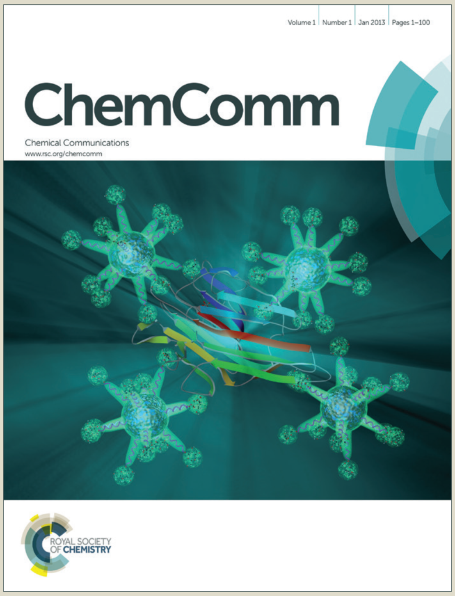

Volume 1 | Number 1 | Jan 2013 | Pages 1–100
ChemComm
Chemical Communications
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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Zn(II) and Cu(II) Complexes of Thiophene-Based Salphen-Type New Ligand: Solution-Processable High-Performance Field-Effect Transistor Materials

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Thiophene-based salphen-type new ligand 1 and its Cu(II) and Zn(II) complexes, 1·Cu and 1·Zn·MeOH, respectively, were designed and synthesized. These metal organic complexes (MOCs) having ultra-close π-stacking interactions were explored as novel class active materials for organic field effect transistors (OFETs). The top-contact bottom gated OFETs fabricated from solution-processed thin films of 1·Cu and 1·Zn·MeOH exhibited excellent p-type mobility (upto 0.7 and 1.5 cm^2 V^{-1} s^{-1}, respectively).

Development of semiconducting materials for OFET has become an area of current research.[1] Major challenges in this field include the development of cheaper, solution-processable and high conducting materials with low temperature device fabrications for light-weight flexible devices. The well-ordering of molecules possessing π-π interactions is a quite important criteria for facile charge transport in OFET materials.[2]

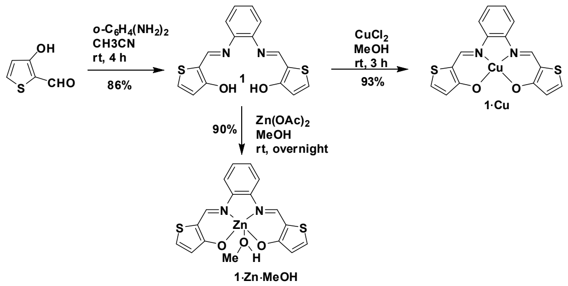
Salen/salphen are the Schiff-base ligands prepared from two equivalents of salicylaldehyde with one equivalent of 1,2-diaminobenzene/ethylenediamine, affording a potential N2O2 tetradentate chelating system to form square planar, square pyramidal and octahedral complexes. In square planar and square pyramidal complexes, the ligand framework adopts nearly planar geometry due to coordination with metal and thus affords strong intermolecular π-π interaction. Driven by the ease of synthesis of salen/salphen based metal complexes and their versatile potential applications in catalysis, biological studies, sensory materials, molecular magnetism and material science,[3] there has been a tremendous growth in the research on these class of materials in last few decades.[4] Thiophene-capped salen/salphen complexes were explored to obtain metalloorganic conducting polymers for the application in solution-processable electronics.[5]

It is fundamentally important to understand the role of metal-atoms in the frame work of electrically functional conjugated systems. Important examples of such materials include metal-dithiolene complexes and metal-phthalocyanines.[6] The vacuum deposited thin film of phthalocyanine based vanadium and titanium complexes have shown appreciable results.[7] However, the devices of these complexes were constructed using vacuum deposition technique which is not compatible with low cost flexible electronic applications.

In this communication, we demonstrate FETs based on solution processable Cu(II) and Zn(II) complexes of thiophene-based salphen-type ligands with p-type mobility as high as ~ 0.7 and 1.5 cm^2 V^{-1} s^{-1}. Additionally, these μ_{FET} values are obtained from the active films, which do not require any high temperature annealing process. Such high performing solution-processable metal organic complexes (MOCs) open up a new family of materials for the applications in large surface area based electroactive applications, which include flexible electronics, bio-electronics and optoelectronics. The ease of synthesis of these MOCs and use of abundant and cheaper metals like copper and zinc will be ideal for low-cost production of large surface area flexible electronic devices.

Basic idea behind replacing salicylaldehyde by 2-formyl-3-hydroxythiophene to construct the new salphen-type ligands is to avail the ultra-close intermolecular π-π interactions in addition to S...S interactions in the solid state for the resulting complexes. This can facilitate effective charge transport in the FET devices. Additionally, the incorporation of thiophene rings directly in the coordination-sphere of MOCs affords potential precursors for metalloorganic conjugated polymers.[8]

New Schiff base ligand **1** was synthesized in high yield by the coupling of 2-formyl-3-hydroxythiophene and 1,2-diaminobenzene in 2:1 molar ratio in dry acetonitrile at room temperature (Scheme 1). Reactions of ligand **1** with $CuCl_2$ and $Zn(OAc)_2$ in 1:1 molar ratio in dry methanol at room temperature afforded the neutral complexes **1·Cu** and **1·Zn·MeOH**, respectively, with excellent yields.

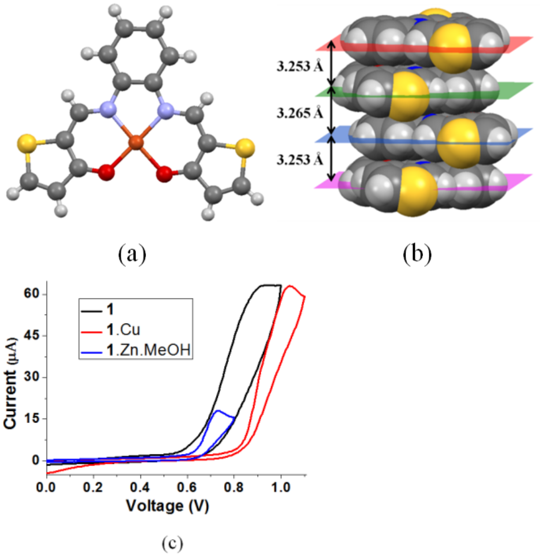


Scheme 1 Synthesis of ligand **1** and complexes **1·Cu** and **1·Zn·MeOH**.

Elemental analysis and ESI-MS of Cu(II) and Zn(II) complexes indicated the formation of 1:1 ligand-metal complexes

1·Cu and **1·Zn·MeOH**. ^{1}H and ^{13}C NMR spectra of complex **1·Zn·MeOH** in DMSO-d_6 revealed the presence of metal-coordinated MeOH molecule suggesting the square pyramidal geometry around metal center.[9] It also indicated that the MeOH remained coordinated with Zn even in the presence of DMSO. All attempts to grow the single crystals of the complex **1·Zn·MeOH** suitable for single crystal X-ray diffraction (SCXRD) were unsuccessful. The complex **1·Cu** crystallizes in acentric monoclinic space group *C*2/*c*. The complex has square planar geometry around the metal center with the dihedral angle between Cu-N(1)-O(2) and Cu-N(2)-O(1) planes of 10.144(78)° (Fig. 1a). Molecules possess nearly planar extended π-conjugated system with excellent π-π stacking between adjacent molecules with the least-square mean plane distances of 3.265 Å and 3.253 Å (Fig. 1b). Overall, the crystal structure shows close packing of the molecules with various van der Waals interactions in addition to ultra-close π stacking interactions and S…S contacts of 3.374 Å.

Cyclic voltammetry (CV) experiments were performed on 0.01 M solution of **1**, **1·Cu** and **1·Zn·MeOH** in dry DMF. In anodic scan, **1**, **1·Cu** and **1·Zn·MeOH** showed an onset oxidation potentials (E^{ox}_{onset}) of 0.65, 0.83 and 0.63 V (Fig. 1c) which correspond to HOMO energy level of −5.05, −5.23 and −5.03 eV for **1**, **1·Cu** and **1·Zn·MeOH**, respectively.[10] The low-lying HOMOs indicate a good environmental stability of the ligand and complexes. The higher HOMO level of **1·Zn·MeOH** compared to that of **1·Cu** may be attributed to the presence of electron donating methanol molecule as axial ligand.[11] So, the HOMO energy level of **1·Zn·MeOH** is closer to that of the work function potential of gold (−5.0 eV) than that of **1·Cu** by 0.2 eV. This, in turn, may facilitate the injection of holes from the gold electrodes to the active layer in transistors[12] containing **1·Zn·MeOH** due to the decrease in hole-injection barrier,[13] compared to the device containing **1·Cu**. All attempts to polymerize **1**, **1·Cu** and **1·Zn·MeOH** electrochemically at their oxidation potentials in dry DMF were unsuccessful.



(a) (b)

(c)

Fig. 1 (a) Molecular structure of complex **1·Cu**. (b) Spacefill view of **1·Cu** showing π-π stacking. (c) Cyclic voltammograms of **1**, **1·Cu** and **1·Zn·MeOH** in TBAPC/DMF solvent/electrolyte system at a scan rate of 50 mV s^{-1}.

Detailed study of transport measurements were performed on the ligand and MOCs using top-contact bottom gated field effect transistor (FET) architecture. Measurements indicated excellent p-type transport with distinctive linear and saturation behavior (Fig. 2). **1·Zn·MeOH** and **1·Cu** show μ_{FET} as high as 1.5 and 0.7 cm^2 V^{-1} s^{-1}, respectively, with ON/OFF ratios > 10^3. Though no annealing was performed on these spin coated films, the mobility values are three orders of magnitude greater than other solution processable metal-organic based molecules reported so far.[14] Moreover, the mobility achieved is comparable to the best values of μ_{FET} obtained with similar MOCs from vacuum deposited devices.7 However, FETs fabricated with **1** showed relatively lower μ_{FET} of 10^{-3} – 10^{-4} cm^2 V^{-1} s^{-1}. The insertion of metal atoms in ligand framework enhanced the hole mobility by 3-4 order of magnitude. This trend of increase in μ_{FET} with MOCs compared to the corresponding ligand can be related to the inherent crystallinity and efficient packing with ultra-close π stacking interactions. In both, square planar and square pyramidal complexes, metal ions force the ligand framework to adopt the planar geometry and, in turn, show intermolecular ultra-close π-stacking interactions. The higher mobility of the devices containing **1·Zn·MeOH** compare to that of **1·Cu** is also in agreement with the observations that the polar square pyramidal complexes show better mobility than square planar complexes.7 The high mobility of the square pyramidal complex is expected due to the capability of strong π-π interactions between concave and convex pairs in such complexes.7[a] Monomeric Zn(II) square pyramidal complexes based on salphen derivatives have shown strong π-π stacking.[15] Conductivity (σ) values obtained from the linear regime of the FET characteristics is given as 0.07 - 0.13 S cm^{-1} for **1·Cu** which increases to 0.16 – 0.2 S cm^{-1} for **1·Zn·MeOH**.

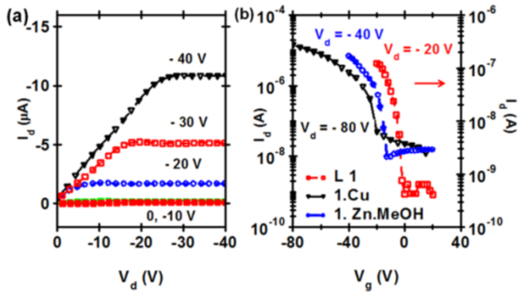


Fig. 2 Typical (a) output curve for **1·Zn·MeOH** and (b) transconductance curve for **1·Zn·MeOH**, **1·Cu** and Ligand **1** (L1) in a FET geometry with W = 1 mm and L = 60 - 80 μm.

Thin films of **1**, **1·Cu** and **1·Zn·MeOH** for X-ray diffraction (XRD) study were prepared using the identical procedure used for the device fabrications. XRD measurements obtained from the thin film of ligand **1** show predominantly amorphous features whereas the complexes show crystalline peaks in thin film XRD with inter-planar distance of around 3.1 Å for **1·Cu** complex (2θ = 25.88) and around 2.9 Å for **1·Zn·MeOH** (2θ = 27.96) using Cu-Kβ filter (Fig. 3). The inter-planar distance calculated from thin film XRD for **1·Cu** complex is comparable with that from SCXRD. This magnitude of inter-planar distance is comparatively smaller than other organic molecules hence enhanced overlap of the π-electrons is expected in these MOCs which can support disorder free 2D transport (Fig. 1b).

Furthermore, the thin film and powder XRD patterns for **1.Zn.MeOH** were found to be similar (Fig. S5) indicating the identical coordination around the metal center. SEM image of thin film of **1·Cu** complex also revealed its highly crystalline nature with micro-crystals of around 20 µm, while that of **1·Zn·MeOH** showed crystallites of particle size of around 5 µm (Fig. S7).

Metal atom attached to the conjugated moiety can modify the transport behavior if the metal-organic combination is redox-active.6[a,b] It was observed that $\mu_{\mathrm{FET}}^{\mathrm{MOC}} > \mu_{\mathrm{FET}}^{\mathrm{ligand}}$. A clearer picture of the role of metal atom is evolved upon comparing the MOCs based on Cu and Zn. Mobility of **1·Cu** was observed to be smaller than **1·Zn·MeOH**. Probably, the lower electronegativity of zinc compare to the copper and the presence of electron donating group in complex **1·Zn·MeOH** can facilitate the hole formation/stabilization and thus responsible for the observed trends in mobility from these molecules. CV measurements also demonstrate this ease of oxidizing **1·Zn·MeOH** compared to **1·Cu** validating the role of metal atom and additional donor (methanol) in modifying the electronic structure in these complexes. We define a parameter D $= d\sigma/dV_g$ which is a measure of "ease of doping" with an external bias. The magnitude of D estimated from the output characteristics turns out to be 4.5 × 10^{-3} S cm^{-1} V^{-1} for **1·Zn·MeOH** which is three time greater than the **1·Cu** clearly demonstrating the role of metal atom in modifying the donor property.

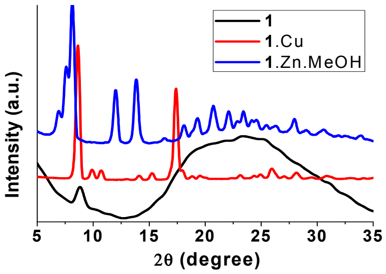


Fig. 3 Thin film XRD of 1, 1·Cu and 1·Zn·MeOH

In summary, new thiophene-based salphen-type ligand **1** and its Cu(II) and Zn(II) complexes were synthesized in high yields. The planar delocalized π-electron system in the MOCs resulted in the ultra-close π-stacking interactions, in turn, MOCs exhibited excellent p-type mobility using solution processed thin films (as high as 0.7 and 1.5 cm^2 V^{-1} s^{-1} for **1·Cu** and **1·Zn·MeOH**, respectively). The incorporation of metal ion in conjugated ligand framework and the geometries of the resulting MOCs plays an important role in tuning the performance of the OFET devices.

Notes and References

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† Electronic Supplementary Information (ESI) available: Details experimental procedures, characterization data and device fabrication methods. CCDC Nos. 920697, 920799. See DOI: 10.1039/b000000x/

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Zn(II) and Cu(II) Complexes of Thiophene-Based Salphen-Type New Ligand: Solution-Processable High-Performance Field-Effect Transistor Materials

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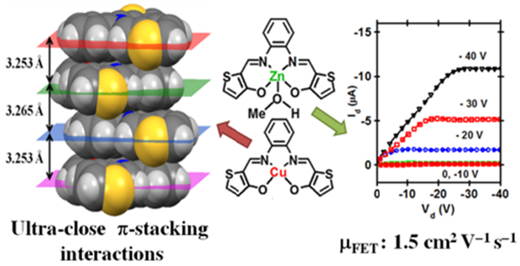

Organic field-effect transistor (OFET) devices based on solution-processed Cu(II) and Zn(II) complexes of new thiophene-based salphen-type ligand exhibited high p-type mobility (up to 1.5 cm^2 V^{-1} s^{-1}).