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Guanine–copper coordination polymers: crystal analysis and application as thin film precursors†

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Three copper-N9-modified guanine complexes are reported with structures ranging from a discrete trinuclear motif to a mixed-valence coordination polymer. These complexes were used as precursors for the deposition and growth of copper oxide thin films on Si(100), at two different annealing temperatures, by using a CVD technique. Subsequent resistivity measurements suggest the formation of conductive thin films, raising the possibility of using nucleobase-metal complexes as versatile thin film precursors.

Introduction

Fabrication of metallic thin films from versatile metallic precursors is of great technological importance for efficient nextgeneration devices. In recent years, copper has drawn increasing attention due to its multifaceted applications, and hence copper-based thin films are of great significance. Among several methods of deposition, chemical vapor deposition (CVD) is an attractive method due to its capability of forming low-cost, highly pure conformal thin films.¹ The utilization of a variety of copper complexes as precursors is well studied and commercialized in many cases.² However, the development of readily available, stable organometallic precursors with high volatility and low decomposition temperatures is a challenging proposition. In this context, metal-organic frameworks (MOFs)/coordination polymers (CPs) were employed as potential precursors and as self-sacrificial templates for metal/metal oxide nanoparticles synthesis.3

We have been working to develop purine nucleobase coordination polymers.⁴ Among nucleobases, guanine (G) and its derivatives are known to form higher-ordered supramolecular structures namely G-quartets, G-quadruplexes, which not only play key roles in several biological processes but also have emerged as a powerful tool for developing nanoscale materials and devices.⁵ The Cu(π) ion interactions with DNA are mostly studied because of their rich redox chemistry and are closely associated with DNA bases, particularly guanine.⁶ Simple copper salts and their complexes coordinate to N7 of guanine and some redox cofactors are sufficient to induce oxidation reactions.⁷ Hence, the coordination chemistry of copper with nucleic acid constituents is important to unravel the mechanisms of base modification, formation of abasic sites and nucleic acid cleavage.⁸ Interestingly, guanine is also known to aid electrical conductivity through the hopping hole mechanism in oligonucleotides.⁹

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Results and discussion

With this background information, we decided to investigate the possibility of using guanine–copper complexes as potential CVD precursors for growth of thin films. Herein, we report the systematic study of the synthesis of copper oxide thin films on a Si(100) substrate from three structurally characterized guanine– copper complexes (1, 2 and 3), *via* the CVD technique. We reacted N9-allylguanine and N9-propargylguanine with cupric halides, and then determined their crystal structures (Scheme 1,



Scheme 1 Schematic representation of synthesis of 1-3.

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| Identification code | 1 | 2 | 3 |
|-----------------------------------------------|--------------------------------------|---------------------------------------|-------------------------------------|
| Empirical formula | $C_{52}H_{70}Cl_6Cu_3N_{30}O_{10}$ | $C_{16}H_{14}Cl_4Cu_3N_{10}O_2$ | $C_{16}H_{14}Br_4Cu_3N_{10}O_2$ |
| M _r | 1678.70 | 710.79 | 888.63 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_{1}/c$ | $P2_1/c$ |
| a/Å | 10.0805(12) | 7.877(2) | 8.0201(12) |
| b/Å | 10.2327(12) | 19.236(5) | 19.173(3) |
| c/Å | 17.619(2) | 7.151 (2) | 7.3148(11) |
| $\alpha / ^{\circ}$ | 74.604(2) | 90 | 90 |
| $\beta / ^{\circ}$ | 78.168(2) | 93.808(4) | 93.877(3) |
| $\gamma/^{\circ}$ | 87.898(2) | 90 | 90 |
| Volume/Å ³ | 1714.6(4) | 1081.1(5) | 1122.2(3) |
| Ζ | 1 | 2 | 2 |
| $D_{\rm x}/{\rm Mg}~{\rm m}^{-3}$ | 1.626 | 2.183 | 2.630 |
| F(000) | 861 | 702 | 846 |
| μ/mm^{-1} | 1.234 | 3.460 | 9.979 |
| θ range for data collection/° | 2.06 to 26.00 | 2.12 to 28.37 | 2.12 to 26.00 |
| Limiting indices | $-12 \le h \le 6, -12 \le k \le 12,$ | $-10 \le h \le 10, -20 \le k \le 25,$ | $-8 \le h \le 9, -23 \le k \le 20,$ |
| 0 | $-21 \le l \le 21$ | $-9 \le l \le 9$ | $-9 \le l \le 8$ |
| Reflections collected | 9545 | 6879 | 6061 |
| unique reflections | 6571 | 2653 | 2177 |
| R(int) | 0.0252 | 0.0545 | 0.0364 |
| Completeness to θ | 98.3 | 99.6 | 99.3 |
| $T_{\rm max}/T_{\rm min}$ | 0.7904/0.7644 | 0.5445/0.5033 | 0.2402/0.2074 |
| Data/restraints/parameters | 6571/0/456 | 2653/0/160 | 2177/0/160 |
| Goodness-of-fit on F^2 | 1.141 | 1.083 | 1.140 |
| R_1 and $R_2 \left[I > 2\sigma(I) \right]$ | 0.0509, 0.1418 | 0.0550, 0.1692 | 0.0647, 0.1929 |
| R_1 and R_2 (all data) | 0.0593, 0.1594 | 0.0781, 0.2367 | 0.0718, 0.1999 |
| Largest diff. peak and hole/e A^{-3} | 1.281 and -0.906 | 2.003 and -2.096 | 3.406 and -2.938 |
| CCDC no. | 808673 | 808672 | 808671 |

Table 1).¹⁰ N9-allylguanine afforded a novel Cu(π) based discrete M_3L_6 unit, 1 (triclinic- $P\bar{1}$), while N9-propargylguanine afforded two-dimensional coordination polymers (2 and 3, monoclinic- $P2_1/c$) having mixed copper valencies.

Analysis of the crystal lattice of 1 revealed the formation of a novel discrete paddle-shaped trinuclear Cu(II) motif containing M₃L₆ units (Fig. 1a), along with methanol molecules. Each unit was composed of three linearly arranged (Cu-Cu-Cu angle 180°), equidistant Cu(II) ions (4.807 Å). Such linear trinuclear copper complexes are relatively rare in the literature, and they exhibit altered reactivity, magnetic behavior depending upon the bridging angles and supporting ligands.¹¹ Among the three linearly arranged copper ions, the two terminal metal ions exhibited distorted trigonal bipyramidal geometry having three guanine residues (two unequal N7 coordinations in axial positions, one O6 coordination in an equatorial position) and two chlorides in the coordination sphere, whereas the central copper ion shows a square planar geometry having two guanines and two chlorides in its coordination sphere (Fig. 1b, c).

The Cu(π)–N7 bond lengths were in the range of 1.980–1.984 Å and the Cu(π)–O6 bond length was 2.325 Å, which are in close agreement with certain reported values.¹² Careful inspection of the crystal lattice also revealed the presence of guanine–guanine interactions in the range of 2.04–2.05 Å, through the Watson–Crick face, which hold M₃L₆ units together (Fig. 2a).¹³ As depicted in Fig. 2b, c further reinforcement comes from H…Cl interactions ($d_{H...Cl}$ =



Fig. 1 (a) Discrete paddle-shaped Cu(II) based M_3L_6 unit in 1 (allyl side chains are removed for clarity). (b, c) Coordination geometries of two crystallographically distinct cupric ions in 1.

2.31–2.66 Å)¹⁴ and slightly displaced π -stacking interactions (3.787 Å). It is expected that the presence of hydrogen bonding to copper bound chloride ions would stabilize coordination geometries around copper.



Fig. 2 (a) Guanine–guanine interactions between M_3L_6 units. (b) H…Cl interactions between guanine hydrogens and copper bound chloride ions. (c) $\pi - \pi$ stacking interactions in **1**.

The crystal lattice of 2 revealed the formation of mixedvalence copper(1,11) complex, affording box-like architectures supported by chloride ion interactions (Fig. 3a). This in situ reduction of $Cu(\pi)$ is interesting, but not unprecedented. This situation may arise either due to the electronic properties of donor atoms present in the ligand or the coordination geometry of complexes formed.¹⁵ Such mixed-valence metal-nucleobase coordination polymers are scarce in the literature and they possess interesting applications.¹⁶ Both Cu(I) and Cu(II) ions are bound to N9-propargylguanine (Fig. 3b) and show two distinct coordination geometries. The Cu(II) ion exhibits square planar geometry with copper at the centre of inversion having a Cu-N7 distance of 1.952 Å and a Cu-Cl distance of 2.322 Å. The Cu(I) ion exhibits a distorted tetrahedral geometry while being coordinated to N3 of guanine (2.052 Å), two chlorine atoms (2.371, 2.439 Å) and π -bonded to the triple bond of the propargyl pendant arm (Cu(I)-C10 = 2.053 Å; Cu(I)-C11 = 2.077 Å) (Fig. 3c, d). Further, this metal-carbon bonding weakens the triple bond which is evident by the lengthening of the propargylic triple bond (0.03 Å) and lowering of its IR stretching frequency by ~129 cm⁻¹ compared to N9-propargylguanine.^{4*i*,10} Besides, η^2 -coordinated copper–alkyne moieties are known intermediates in several coupling reactions as they play a vital role in layer-by-layer build up of coordination polymer films.¹⁷

The favorable rotation of the propargyl pendant arm towards the guanine moiety plays a vital role in Cu(i) coordination through N3 nitrogen. This strategy has been pioneered by Houlton and coworkers.¹⁸ It is known that minor-groove



Fig. 3 (a) Chloride-supported box-like architecture in 2. (b) Coordination of N9-propargylguanine with Cu(i) and Cu(ii) ions. (c, d) Coordination geometries of cupric and cuprous ions in 2. (Note: Complex 3 also exhibits similar structures.)



Fig. 4 (a) Arrangement of guanines around the infinite Cu(i)–Cl chain. (b) Interconnection of Cu(i)–Cl chains *via* a Cu(ii)–N7 coordination in **2**. (Note: Complex **3** also exhibits similar structures.)

site metal ion interactions may induce double-proton transfer and/or hydrolysis of the glycosidic linkage in DNA, which leads to strand scission.¹⁹ Closer inspection of the lattice reveals the formation of non-planar infinite *zig-zag* Cu(I)–Cl chains propagating along the *c*-axis²⁰ and the guanine residues are arranged in a fern-like alternate pinnate manner (Fig. 4a). Further, these chains are interconnected with Cu(II) ions, and the distance between two consecutive Cu(I) atoms is 3.624 Å Paper



Fig. 5 (a, b) H…Cl interactions between guanine hydrogens and copper bound chloride ions in 2. (Note: Complex 3 also exhibits similar structures.)

and for two nearest $Cu(\pi)$ atoms is 7.151 Å as depicted in Fig. 4a, b. Unlike 1, no guanine–guanine interactions are observed in 2. Guanine hydrogens are involved in H…Cl interactions, which further stabilize the crystal lattice (Fig. 5a, b).

The mixed valence Cu(I,II) complexes, of varying coordination geometry, are formed from cupric salts and N-coordinated ligands *via in situ* solvothermal reduction, in various solvents.²¹ Purines are also known to reduce Cu(II) to Cu(I) and exhibit simultaneous mixed valence coordination, a key principle used in electrochemical anodic stripping of purines and the detection of oligonucleotides.²² Further, such mixed valence complexes are used for *in situ* ligand synthesis and for developing conductive materials.²³

It is known that CuBr₂ based systems show enhanced redox activity compared to CuCl₂.²⁴ Thus, we decided to subject N9propargylguanine with CuBr₂ under conditions similar to the growth of **2**, in order to see if the bromide counteranion will have an effect on the valence state of copper ions in the complex. However, the asymmetric unit in **3** was quite similar to **2** with closely related bond lengths (Cu(II)–N7 = 1.954 Å; Cu(I)– N3 = 2.051 Å; Cu(I)–C10 = 2.066 Å; Cu(I)–C11 = 2.072 Å), but having a slightly higher volume. The distance between two consecutive Cu(I) atoms is raised to 3.719 Å and for two nearest Cu(II) atoms to 7.314 Å.¹⁰

It is known that structural diversity in d¹⁰ metal ion coordinated systems could be achieved by choosing the right alkynyl group containing ligands.²⁵ Alkynes offer effective coordination sites compared to alkenes due to electronic reasons, possibility of 2 or 4e- bonding, and steric considerations. Moreover, additional π -donation in alkynes, when compared to alkenes, usually results in non-linear geometries, when coordinated to transition metal ions. In the case of 1, Cu(II) ions prefer interaction with N7 and O6 to afford distorted trigonal bipyramidal and square planar geometries, without interacting with an N9-allyl substituent. However, Cu(1) interaction in complexes 2 and 3 occurs via a preferential interaction with the N9-propargyl group possibly through σ - and π -interactions,²⁶ while the proximity of the N3 group provides a suitable chelation site to stabilize the overall complex.^{18d} However, the selectivity of Cu(1) for purine N3 nitrogen over



Fig. 6 TGA curves of 1–3 (30–800 °C, heating rate = 10 °C min $^{-1},$ N2 atmosphere).

 $Cu(\pi)$ is curious and it could be ascribed to achievable coordination geometries and the effect of chelation in the two guanine ligands.

These complexes were found to be sufficiently volatile for CVD deposition by looking at their TGA profiles (Fig. 6). All three complexes show similar behavior; initially, they lose solvent molecules/halides and then decompose very rapidly with the increase in temperature. The initial weight losses of 15.9% for 1 (136.9 °C), 10.2% for 2 (90.2 °C) and 7.1% for 3 (188.1 °C) correspond to the loss of four methanol molecules plus four chloride ions, two chloride ions and one bromide ion, respectively. On further heating, these complexes rapidly decompose after 186.7 °C (1), 180.6 °C (2) and 231.2 °C (3), respectively. The results of thin film growth and subsequent studies concerning the formation of only metallic oxide films on Si(100) substrates, without any detectable carbon, nitrogen or halogen contamination, are reported in the next section.

The films obtained through the CVD process were treated at two different temperatures ($T_1 = 450$ °C, 30 min.; $T_2 = 600$ °C, 3 h) and subsequently characterized by Raman spectroscopy and PXRD, and surface morphologies were analyzed by AFM and SEM. Both strong (300 cm^{-1}) and weak (340 cm^{-1}) Raman peaks for the three films, processed at two temperatures, were ascribed to cupric oxide. A broad peak at around 620 cm^{-1} is believed to be contributed by several Cu₂O related sub-peaks such as 570, 618, and 624 cm⁻¹ (Fig. 7, a broad peak at around 500-550 cm⁻¹ corresponds to the silicon surface).²⁷ The PXRD peaks at around 31.3, 33.1, 35.4 and 38.7° corresponded to the monoclinic crystal structure of CuO and the weak peaks at around 30.2, 36.4 and 42.3° corresponded to the cubic crystal structure of Cu₂O (Fig. 8, a peak at 32.9° corresponds to the silicon surface).²⁸ Hence, it can be proposed that all three films were composed of both CuO and Cu_2O phases at T_1 and T_2 temperatures, with CuO being the most dominant phase. A plausible reason for the coexistence of two phases can be attributed to the reduction conditions attained at higher



Fig. 7 Raman spectra of thin films from 1-3 on Si(100).



temperatures under CVD conditions and the presence of both cupric and cuprous ions in 2 and 3. The oxygen present in thin films may come from guanine present in complexes or from air in the CVD reactor.

At temperature T_1 , AFM topographic studies revealed that all the three films were composed of epitaxially grown grains of copper oxide in the sizes varying between 200 and 300 nm, with a Z height amplitude range between 80 and 120 nm (Fig. 9a, c, e).¹⁰ Further, it can be seen in SEM micrographs that all films, processed at T_1 , were polycrystalline and exhibited island-type growth instead of a smooth continuous film (Fig. 10a, d, g).¹⁰ It appears that grains follow Volmer–Weber growth, which happens to be a preferred growth mode for a metal film on a semiconductor substrate.²⁹ The grains evolved from a rectangular shape to an irregular shape, while the presence of copper and oxygen was confirmed by EDX analysis (Fig. 10c, f, i).

On processing the previous sample at temperature T_2 , the grains were grown to ~400 nm (Fig. 9b, d, f). Thus, the



Fig. 9 AFM images of thin films from 1–3 on Si(100) (T_1 = 450 °C; a, c, e), (T_2 = 600 °C; b, d, f).



Fig. 10 SEM images and EDX spectra (c, f, i) of thin films from 1–3 on Si(100) (T_1 = 450 °C; a, d, g), (T_2 = 600 °C; b, e, h). Scale: 200 nm.

coalescence of grains to form bigger non-uniform grains was observed (Fig. 10b, e, h), which could be ascribed to the extra energy gained from heating at higher annealing temperature. This phenomenon could be ascribed to the Ostwald ripening

Table 2 Resistivity measurements of thin films

| Thin film precursor | Thickness (nm) | Sheet resistance $(M\Omega \text{ per square})$ | Resistivity (Ω cm) | Conductivity (S cm ⁻¹) |
|------------------------|-------------------|-------------------------------------------------|-----------------------|---------------------------------------|
| 1 | 480 | 4.461 | 214.122 | 0.005 |
| 2 | 86.7 | 4.675 | 40.537 | 0.025 |
| 3 | 164 | 0.478 | 7.841 | 0.127 |

mechanism.²⁹ It is to be noted here that cupric halide salts (CuX₂, X = Cl, Br) alone failed to develop structured films on Si(100) under the same experimental conditions.¹⁰ Hence, the presence of guanine as a coordinating ligand is critical to developing structured copper oxide thin films.

We further decided to assess the electrical sheet resistance of the films processed at temperature T_2 , with the help of the four-point probe technique. The resistivity values for the three samples 1–3 were found to be 214.122, 40.537 and 7.841 Ω cm, respectively, indicating that a thin film prepared from precursor 3 exhibits the highest conductivity among the three samples studied (Table 2).³⁰ It is proposed that such conducting films, from metal-nucleobase precursors, could be possibly used as a gate or a source/drain of a thin film transistor or as an anode or a cathode in LEDs and solar cells.

Conclusions

Two different N9-substituted guanine derivatives were used to create either a discrete trinuclear copper motif or copperbased coordination polymers, which can act as single molecule CVD precursors for copper oxide (CuO/Cu₂O) thin films on Si(100) substrates, when processed at two temperatures. Subsequent resistivity measurements revealed that the thin film from 3 shows the highest conductivity. It is expected that stable metal–purine nucleobase interactions are not only interesting for preparing aesthetically pleasing coordination complexes, but also serve as important precursors for thin film formation. Device formation and evaluation with these films will be conducted in due course.

Experimental section

General procedures

All solvents were distilled prior to use by using standard procedures. Solvents were evaporated using a rotary evaporator under reduced pressure. ¹H and ¹³C NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer operating at 500 MHz. The spectra were recorded in DMSO- d_6 solution and the chemical shifts were referenced with respect to tetramethylsilane. High resolution (ESI⁺ mode) mass spectra were obtained on a WATERS HAB 213 machine, Department of Chemistry, IIT Kanpur. Infrared spectra were obtained (KBr disk, 400–4000 cm⁻¹) on a Perkin-Elmer Model 1320 spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F_{254}) were used, and compounds were visualized with a UV light at 254 nm. Chromatographic separations were performed on S. D. Fine-chem 100–200 mesh silica gel.

All spin coatings were done by using a Holmarc spin coater (Model HO-TH-05) and CVD treatment was done by using Holmarc spray pyrolysis equipment (Model HO-TH-04). The thermogravimetric analyses were performed by using a Perkin-Elmer Pyris 6 machine with a heating rate of 10 $^{\circ}$ C min⁻¹ under a N2 atmosphere from 30 to 800 °C. PXRD measurements were performed with a PANalytical X-Pert PRO diffractometer with Cu-Ka radiation (1.5405 Å). Raman spectra were acquired with a WITec alpha SNOM Raman instrument and the spectra were registered with the laser at 532 nm. AFM was carried out by using an Agilent Technologies Atomic Force Microscope (Model 5500) operating in a non-contact/ACAFM mode. Microfabricated silicon nitride cantilevers with a spring constant (C) of approximately 50 N m^{-1} and resonant frequency (f) of 178 kHz were used. The average dimension thickness (T), width and length (L) of cantilever were approximately 670, 37 and 228 mm, respectively. The AFM tips (PPP-NCL-10) with a radius of less than 7 nm from NANO-SENSORS were used for the different experiments. Data acquisition and analysis were carried out by using PicoView 1.8.2 and the Pico Image Basic software, respectively. Field emission scanning electron microscopy (FESEM) images were acquired on a FEI QUANTA 200 microscope, equipped with a tungsten filament gun, operating at WD 10.6 mm and 20 kV. Energy dispersive X-ray (EDX) analysis was done on the INCA-7426 Oxford Instruments, operating at WD 9 mm and using 20 kV for the determination of composition of thin films. The sheet resistance measurements were performed at room temperature with an Agilent 34405A $5\frac{1}{2}$ digit multimeter and a Keithley 2602A current SourceMeter. They were determined (four point probe) by measuring the ratio of the voltage drop (V) from the two inner probes to the applied current (I) measured from the two outer probes. The thickness of thin films was determined by using a (AEP Technology) NanoMap-Dual Mode 3D Surface Profilometer in contact mode.

Synthetic procedures

Synthesis of N9-allylguanine (A). N9-allylguanine was synthesized in two steps from 2-amino-6-chloropurine by the following procedure (Scheme 2).

Step 1: N9-allyl-2-amino-6-chloropurine (B). The compound **B** was synthesized based on the literature procedure.³¹ 2-Amino-6-chloropurine (3 g, 17.692 mmol) was suspended in



Scheme 2 Synthesis of N9-allylguanine (A).

DMF (50 ml) followed by the addition of anhydrous K₂CO₃ (2.934 g, 21.228 mmol) and stirred under a N₂ atmosphere for 1 hour. Then, allyl bromide (1.926 g, 15.919 mmol) was added over a period of 30 minutes and the solution was stirred for 48 hours under a N2 atmosphere at ambient temperature. DMF was evaporated under reduced pressure and N9-allyl-2-amino-6-chloropurine (B) was purified by column chromatography eluting with methanol-chloroform to afford a yellowish-white powder (2.662 g, 72% yield). HRMS: $(M + H)^+$ calculated: 210.0546, found: 210.0545; ¹H NMR (500 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm) 4.64 (m, 2H, CH₂), 4.96 (dd, 1H, terminal C-H), 5.13 (dd, 1H, terminal C-H), 5.99 (m, 1H, C-H), 6.88 (s, 2H, NH₂), 8.06 (s, 1H, C8-H); ¹³C NMR (125 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm) δ (ppm) 44.93 (C9), 117.33 (C11), 123.23 (C5), 133.00 (C10), 143.16 (C8), 149.42 (C6), 153.99 (C4), 159.88 (C2).

Step 2: N9-allylguanine (A). The compound **A** was synthesized based on the literature procedure.³² N9-allyl-2-amino-6-chloropurine (**B**) (1 g, 4.784 mmol) was dissolved in a TFA– H₂O mixture (3 : 1, 10 ml) and then stirred for 48 h at ambient temperature. The reaction mixture was evaporated and washed with diethyl ether (2 × 20 ml) to afford N9-allylguanine (**A**) as a white solid (0.872 g, 96% Yield). HRMS: (M + H)⁺ calculated: 192.0885, found: 192.0886; ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ (ppm) 4.62 (m, 2H, CH₂), 5.03 (dd, 1H, terminal C-H), 5.20 (dd, 1H, terminal C-H), 5.98 (m, 1H, C-H), 6.90 (s, 2H, NH₂), 8.41 (s, 1H, C8–H), 11.22 (s, 1H, N1–H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25 °C, TMS): δ (ppm) 45.61 (C9), 111.76 (C11), 118.05 (C5), 132.46 (C10), 137.25 (C8), 150.37 (C2), 154.75 (C4), 155.11 (C6).

Synthesis of N9-propargylguanine. N9-propargylguanine was synthesized and characterized from our previous work.^{4*i*} IR (KBr): 2131.79 cm⁻¹ (C=C).

1: N9-allylguanine (0.010 g, 0.052 mmol) and $CuCl_2 \cdot 2H_2O$ (0.018 g, 0.104 mmol) were suspended in a methanol-water mixture (4:1, 5 ml). The suspension was shaken well until a clear green solution was obtained, filtered and kept for slow evaporation. Dark green crystals of 1 were isolated after three weeks and dried (0.023 g, 92% yield); HRMS: ([$2L + 2Cu^{II} + Cl$]/3)⁺ calculated: 180.9965, 182.9947, found: 180.9837, 182.9829; ([L-allyl] + $Cu^{II} + MeO$)⁺ calculated: 243.9896, 245.9878, found: 244.0065, 246.0057 (where L = N9-allylguanine).

2 and 3: N9-propargylguanine (0.010 g, 0.053 mmol) and $CuCl_2 \cdot 2H_2O$ (0.018 g, 0.105 mmol) [CuBr₂ (0.023 g, 0.105 mmol) for 3] were suspended in a methanol-water mixture (4 : 1, 5 ml). The suspension was shaken well until a clear green solution was obtained, filtered and kept for slow evaporation. Brownish-green crystals of 2 (3) were isolated after three weeks and dried. 2: (0.018 g, 90% yield); IR (KBr): 2002.88 cm⁻¹ (C=C); HRMS: (2L + Cu^{II} + Cl)⁺ calculated: 476.0286, 478.0268, found: 476.0305, 478.0279. 3: (0.023 g, 92% yield); IR (KBr): 2005.70 cm⁻¹ (C=C); HRMS: (L + Cu^I + H₂O)⁺ calculated: 270.0052, 272.0034, found: 270.0004, 271.9972; (L + Cu^I + Br + H₂O + H)⁺ calculated: 349.9314, 351.9293, found: 349.9319, 351.9300 (where L = N9-propargyl-guanine).

Thin film growth

The thin films were grown on Si(100) substrates by spin casting followed by CVD treatment. Silicon (100) wafers were purchased from commercial sources and were cleaned in a solution of 1:1:3 H₂SO₄-H₂O₂-H₂O, heated to 50 °C for 20 min, and then thoroughly rinsed in deionized water, and dried. Isolated crystals of 1–3 were dissolved in (1:1) aqueous methanolic solutions and all solutions were spun cast at room temperature on substrates with a spin coater at 7500, 7600, 7700 rpm for 40 s each. CVD treatment of these samples was done in a horizontal-flow, atmospheric pressure CVD hot wall reactor at 450 °C for 30 minutes (T_1) and at 600 °C for 3 h (T_2) under air.

Crystal structure refinement details for 1-3

Single crystals of 1-3 were coated with a light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with a CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo Ka radiation. The data integration and reduction were processed with the SAINT software.³³ An absorption correction was applied.³⁴ Structures were solved by the direct method using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXL-97 program package.³⁵ Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. It is noted here that the allyl side chain in 1 is disordered and isotropically refined over two positions by using the PART command. Crystal structure refinement parameters are given in Table 1.

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Notes and references

- (a) C. R. Crick and I. P. Parkin, J. Mater. Chem., 2011, 21, 14712; (b) G. Papadimitropoulos, N. Vourdas, V. Em Vamvakas and D. Davazoglou, J. Phys. Conf. Ser., 2005, 10, 182; (c) S. Eisermann, A. Kronenberger, A. Laufer, J. Bieber, G. Haas, S. Lautenschläger, G. Homm, P. J. Klar and B. K. Meyer, Phys. Status Solidi A, 2012, 209, 531.
- Selected examples: (a) R. Becker, A. Devi, J. Weiß,
 U. Weckenmann, M. Winter, C. Kiener, H. Becker and
 R. A. Fischer, *Chem. Vap. Deposition*, 2003, 9, 149;

(b) H. Song, J. A. T. Norman and Y. Shimogaki, *Microelectron. Eng.*, 2010, 87, 249;
(c) G. G. Condorelli, G. Malandrino and I. L. Fragalà, *Chem. Vap. Deposition*, 1999, 5, 237;
(d) P. Piszczek, I. Szymańska, W. Ba1a, K. Bartkiewicz, E. Talik and J. Heiman, *Thin Solid Films*, 2008, 516, 3924;
(e) P. A. Premkumar, N. Bahlawane and K. Kohse-Höinghaus, *Chem. Vap. Deposition*, 2007, 13, 219;
(f) P. A. Premkumar, N. Bahlawane, G. Reiss and K. Kohse-Höinghaus, *Chem. Vap. Deposition*, 2007, 13, 227;
(g) T. Maruyama, *Sol. Energy Mater. Sol. Cells*, 1998, 56, 85.

- 3 (a) W. Cho, S. Park and M. Oh, *Chem. Commun.*, 2011, 47, 4138; (b) W. Cho, Y. H. Lee, H. J. Lee and M. Oh, *Chem. Commun.*, 2009, 4756; (c) H. Thakuria, B. M. Borah and G. Das, *Eur. J. Inorg. Chem.*, 2007, 2007, 524; (d) J. Zhao, M. Li, J. Sun, L. Liu, P. Su, Q. Yang and C. Li, *Chem.-Eur. J.*, 2012, 18, 3163; (e) S. Jung, W. Cho, H. J. Lee and M. Oh, *Angew. Chem., Int. Ed.*, 2009, 48, 1459.
- 4 (a) S. Verma, A. K. Mishra and J. Kumar, Acc. Chem. Res., 2010, 43, 79; (b) J. Kumar and S. Verma, Inorg. Chem., 2009, 48, 6350; (c) M. D. Pandey, A. K. Mishra, V. Chandrasekhar and S. Verma, Inorg. Chem., 2010, 49. 2020: (d) A. K. Mishra, R. K. Prajapati and S. Verma, Dalton Trans., 2010, 39, 10034; (e) C. S. Purohit and S. Verma, J. Am. Chem. Soc., 2006, 128, 400; (f) C. S. Purohit, A. K. Mishra and S. Verma, Inorg. Chem., 2007, 46, 8493; (g) C. S. Purohit and S. Verma, J. Am. Chem. Soc., 2007, 129, 3488; (h) A. K. Mishra, C. S. Purohit and S. Verma, CrystEng-Comm, 2008, 10, 1296; (i) N. Nagapradeep and S. Verma, Chem. Commun., 2011, 47, 1755; (j) N. Nagapradeep, S. Sharma and S. Verma, Cryst. Growth Des., 2013, 13, 455; (k) A. K. Mishra and S. Verma, Inorg. Chem., 2010, 49, 3691.
- 5 (a)G. Biffi, D. Tannahill, J. McCafferty and S. Balasubramanian, Nat. Chem., 2013, 5, 182 and references cited therein; (b) J. Zhu, L. Zhang, T. Li, S. Dong and E. Wang, Adv. Mater., 2013, 25, 2440; (c) I. Gadwal, S. De, M. C. Stuparu, R. J. Amir, S. G. Jang and A. Khan, J. Polym. Sci., Part A: Polym. Chem., 2012, 50, 1844; (d) S. Lena, S. Masiero, S. Pieraccini and G. P. Spada, Chem.-Eur. J., 2009, 15, 7792; (e) C. Arnal-Hérault, A. Pasc, M. Michau, D. Cot, E. Petit and M. Barboiu, Angew. Chem., Int. Ed., 2007, 46, 8409; (f) J. E. Betancourt and J. M. Rivera, Org. Lett., 2008, 10, 2287; (g) L. Ma, M. Melegari, M. Colombini and J. T. Davis, J. Am. Chem. Soc., 2008, 130, 2938.
- 6 (a) T. Theophanides and J. Bariyanga, J. Mol. Struct., 1989, 214, 177; (b) T. Marino, M. Toscano, N. Russo and A. Grand, Int. J. Quantum Chem., 2004, 98, 347.
- 7 (a) R. B. Martin, Acc. Chem. Res., 1985, 18, 32;
 (b) B. H. Geierstanger, T. F. Kagawa, S.-L. Chen,
 G. J. Quigley and P. S. Ho, J. Biol. Chem., 1991, 266, 20185;
 (c) E. Sletten and G. Erevik, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1977, 33, 1633.
- 8 (a) R. Drouin, H. Rodriguez, S. W. Gao, Z. Gebreyes, T. R. O'Connor, G. P. Holmquist and S. A. Akman, *Free Radical Biol. Med.*, 1996, 21, 261; (b) B. Halliwell and O. I. Aruoma, *FEBS Lett.*, 1991, 281, 9.

- 9 (a) S. Delaney and J. K. Barton, *J. Org. Chem.*, 2003, 68, 6475; (b) B. Bixon, B. Giese, S. Wessely, T. Langenbacher, M. E. Michel-Beyerle and J. Jortner, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, 96, 11713.
- 10 See ESI.†
- 11 (a) R. D. Adams, R. Layland and C. Payen, *Chem. Ber.*, 1997, 130, 63; (b) J. Liu, Y. Song, Z. Yu, J. Zhuang, X. Huang and X. You, *Polyhedron*, 1999, 18, 1491; (c) A. K. Sah, M. Kato and T. Tanase, *Chem. Commun.*, 2005, 675; (d) G. A. Van Albada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Eur. J. Inorg. Chem.*, 1998, 1998, 547.
- 12 (a) D. Armentano, T. F. Mastropietro, M. Julve, R. Rossi, P. Rossi and G. De Munno, J. Am. Chem. Soc., 2007, 129, 2740; (b) D. J. Szalda and T. J. Kistenmacher, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1977, 33, 865; (c) D. J. Szalda, L. J. Marzilli and T. J. Kistenmacher, Biochem. Biophys. Res. *Commun.*, 1975, 63, 601: (d) E.-C. Yang, Z.-Y. Liu, Z. Y. Liu, L. N. Zhao and X.-J. Zhao, Dalton Trans., 2010, 39, 8868; (e) T. F. Mastropietro, D. Armentano, E. Grisolia, C. Zanchini, F. Lloret, M. Julve and G. De Munno, Dalton Trans., 2008, 514 and references cited therein.
- 13 (a) M. Roitzsch and B. Lippert, *Chem. Commun.*, 2005, 5991; (b) G. Gottarelli, S. Masiero, E. Mezzina, S. Pieraccini, J. P. Rabe, P. Samorì and G. P. Spada, *Chem.-Eur. J.*, 2000, 6, 3242.
- 14 G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653.
- 15 (a) M. Vetrichelvan, Y.-H. Lai and K. F. Mok, *Dalton Trans.*, 2003, 295; (b) U. Patel, H. B. Singh and G. Wolmershäuser, *Angew. Chem., Int. Ed.*, 2005, 44, 1715; (c) U. Patel, S. Sharma, H. B. Singh, S. Dey, V. K. Jain, G. Wolmershäuser and R. J. Butcher, *Organometallics*, 2010, 29, 4265.
- 16 (a) J. An, C. M. Shade, D. A. Chengelis-Czegan, S. Petoud and N. L. Rosi, J. Am. Chem. Soc., 2011, 133, 1220;
 (b) R. Nishiyabu, N. Hashimoto, T. Cho, K. Watanabe, T. Yasunaga, A. Endo, K. Kaneko, T. Niidome, M. Murata, C. Adachi, Y. Katayama, M. Hashizume and N. Kimizuka, J. Am. Chem. Soc., 2009, 131, 2151; (c) E.-C. Yang, H.-K. Zhao, Y. Feng and X.-J. Zhao, Inorg. Chem., 2009, 48, 3511; (d) F. Zamora, M. P. Amo-Ochoa, P. J. Sanz-Miguel and O. Castillo, Inorg. Chim. Acta, 2009, 362, 691; (e) N. Marino, D. Armentano, T. F. Mastropietro, M. Julve, F. Lloret and G. De Munno, Cryst. Growth Des., 2010, 10, 1757.
- 17 (a) H. Lang, A. Jakob and B. Milde, *Organometallics*, 2012, 31, 7661; (b) D. E. Bergbreiter and K.-S. Liao, *Soft Matter*, 2009, 5, 23.
- 18 (a) C. Price, M. A. Shipman, N. H. Rees, M. R. J. Elsegood, A. J. Edwards, W. Clegg and A. Houlton, *Chem.-Eur. J.*, 2001, 7, 1194; (b) M. M. Cerdà, D. Amantia, B. Costisella, A. Houlton and B. Lippert, *Dalton Trans.*, 2006, 3894; (c) M. A. Shipman, C. Price, A. E. Gibson, M. R. J. Elsegood, W. Clegg and A. Houlton, *Chem.-Eur. J.*, 2000, 6, 4371; (d) M. A. Galindo and A. Houlton, *Inorg. Chim. Acta*, 2009, 362, 625; (e) P. Amo-Ochoa, O. Castillo, R. W. Harrington,

F. Zamora and A. Houlton, *Inorg. Chem.*, 2013, **52**, 2174; (f) M. A. Galindo, D. Amantia, A. Martinez-Martinez, W. Clegg, R. S. Harrington, V. M. Martinez and A. Houlton, *Inorg. Chem.*, 2009, **48**, 11085; (g) G. Rauduschlsieber, H. Schollhorn, U. Thewalt and B. Lippert, *J. Am. Chem. Soc.*, 1985, **107**, 3591; (h) M. A. Shipman, C. Price, M. R. J. Elsegood, W. Clegg and A. Houlton, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 2360.

- 19 (a) M. A. Galindo, D. Amantia, A. M. Martinez, W. Clegg, R. W. Harrington, V. M. Martinez and A. Houlton, *Inorg. Chem.*, 2009, 48, 10295; (b) V. G. Bregadze, E. S. Gelagutashvili, K. J. Tsakadze and S. Z. Melikishvili, *Chem. Biodivers.*, 2008, 5, 1980.
- 20 R. Peng, M. Li and D. Li, Coord. Chem. Rev., 2010, 254, 1.
- 21 Selected examples: (a) J.-C. Chen, A.-J. Zhou, S. Hu, M.-L. Tong and Y.-X. Tong, J. Mol. Struct., 2006, 794, 225;
 (b) D. Li, T. Wu, X.-P. Zhou, R. Zhou and X.-C. Huang, Angew. Chem., Int. Ed., 2005, 44, 4175; (c) L. Hou, D. Li, W.-J. Shi, Y.-G. Yin and S. W. Ng, Inorg. Chem., 2005, 44, 7825; (d) S. M.-F. Lo, S. S.-Y. Chui, L.-Y. Shek, Z. Lin, X. X. Zhang, G.-H. Wen and I. D. Williams, J. Am. Chem. Soc., 2000, 122, 6293; (e) X.-M. Zhang, Y.-F. Zhao, H.-S. Wu, S. R. Batten and S. W. Ng, Dalton Trans., 2006, 3170; (f) M.-L. Tong, L.-J. Li, K. Mochizuki, H.-C. Chang, X.-M. Chen, Y. Li and S. Kitagawa, Chem. Commun., 2003, 428; (g) X.-M. Zhang and X.-M. Chen, Eur. J. Inorg. Chem., 2003, 413.
- 22 (a) H. Shiraishi and R. Takahashi, *Bioelectrochem. Bioenerg.*, 1993, 31, 203; (b) M. Fojta, F. Jelen, L. Havran and E. Palecek, *Curr. Anal. Chem.*, 2008, 4, 250; (c) F. Jelen, B. Yosypchuk, A. Kourilova, L. Novotny and E. Palecek, *Anal. Chem.*, 2002, 74, 4788.
- 23 (a) J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen,
 C. L. Lin, X. Huang and J. Li, *Chem. Commun.*, 2002, 1342;
 (b) X. Zhu, N. Wang, B. Li, H. Zhang, Y. Luo, Y. Pang and

D. Tan, *Inorg. Chim. Acta*, 2012, **383**, 235; (c) P. Amo-Ochoa, L. Welte, R. González-Prieto, P. J. Sanz Miguel, C. J. Gómez-García, E. Mateo-Martí, S. Delgado, J. Gómez-Herrero and F. Zamora, *Chem. Commun.*, 2010, **46**, 3262; (d) X.-M. Chen and M.-L. Tong, *Acc. Chem. Res.*, 2007, **40**, 162.

- 24 R. D. Willett, Inorg. Chem., 2001, 40, 966.
- 25 (a) R. Nast, Coord. Chem. Rev., 1982, 47, 89; (b) H. Lang,
 D. S. A. George and G. Rheinwald, Coord. Chem. Rev., 2000,
 206-207, 101.
- 26 J. E. Hein and V. V. Fokin, Chem. Soc. Rev., 2010, 39, 1302.
- 27 (a) Y. S. Gong, C. Lee and C. K. Yang, *J. Appl. Phys.*, 1995, 77, 5422; (b) B. Balamurugan, B. R. Mehta, D. K. Avasthi, F. Singh, A. K. Arora, M. Rajalakshmi, G. Raghavan, A. K. Tyagi and S. M. Shivaprasad, *J. Appl. Phys.*, 2002, 92, 3304.
- 28 (a) A. Chen, H. Long, X. Li, Y. Li, G. Yang and P. Lu, *Vacuum*, 2009, **83**, 927; (b) L. A. Svetlichnaya, L. P. Mileshko and A. N. Korolev, *Inorg. Mater.*, 2008, **44**, 713; (c) W. Wang, Y. Zhan and G. Wang, *Chem. Commun.*, 2001, 727.
- 29 M. Ohring, *Materials Science of Thin Films*, Mass. Academic Press, Boston, 1992.
- 30 (a) V. F. Drobny and D. L. Pulfrey, *Thin Solid Films*, 1979,
 61, 89; (b) R. Padyath, J. Seth and S. V. Babu, *Thin Solid Films*, 1994, 239, 8.
- 31 W. E. Lindsell, C. Murray, P. N. Preston and T. A. J. Woodman, *Tetrahedron*, 2000, **56**, 1233.
- 32 S. Fletcher, V. M. Shahani and P. T. Gunning, *Tetrahedron Lett.*, 2009, **50**, 4258.
- 33 SAINT+, 6.02 ed, Bruker AXS, Madison, WI, 1999.
- 34 G. M. Sheldrick, *SADABS 2.0*, University of Göttingen, Göttingen, Germany, 2000.
- 35 G. M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.