Synthesis and Structural Characterisation of New Bifunctional *o*-Hydroxyacetophenones – Potential Linker Molecules for Coordinative Framework Construction

Jörg Hübscher[a], Michael Günthel[b], Robert Rosin[a], Wilhelm Seichter[a], Florian Mertens[b], and Edwin Weber[a]

[a] Institut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg/Sachsen, Germany
[b] Institut für Physikalische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg/Sachsen, Germany

Reprint requests to Prof. Edwin Weber. Fax: +49 3731-39-3170.
E-mail: edwin.weber@chemie.tu-freiberg.de

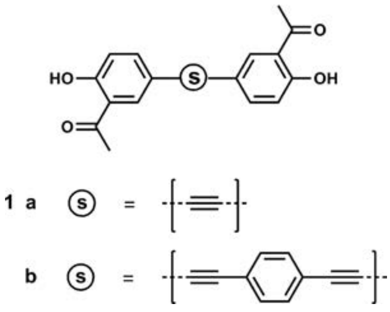
Z. Naturforsch. **2013**, *68b*, 214 – 222 / DOI: 10.5560/ZNB.2013-2332
Received December 19, 2012

Two new linker-type molecules **1a** and **1b** composed of *o*-hydroxyacetophenone coordinative groups attached to linear ethynylene or 1,4-phenylenediethynylene spacer units have been synthesised and structurally characterised. An X-ray crystallographic study for both compounds has shown structures with strong intramolecular hydrogen bonds fitting in the model of 'Intramolecular Resonance Assisted Hydrogen Bond (IRHAB)'. Initial coordination experiments with Cu(II) were performed and the resulting materials characterised by PXRD. The similarity of the copper coordination between these compounds and copper(II) acetylacetonate complexes was demonstrated by XPS measurements. Based on the evidence of these studies, and on elemental analysis, the formation of the corresponding coordination polymers comprising Cu(II) and the linkers has been proposed.

Key words: *o*-Hydroxyacetophenone, Synthesis, Crystal Structure, X-Ray Photoemission, X-Ray Diffraction

Introduction

Coordination polymers have been established as an important class of compounds with promising applications in the fields of catalysis [1 – 3], sensors [4, 5] and gas sorption [6 – 8]. Due to their modular development, relevant properties such as framework topology and pore size are flexibly adjustable by the choice of eligible metal ions and the specific design of the organic linker molecules, which combine several coordination active functions. Outstanding efficiency in the complexation of metal ions show linker molecules comprising chelate functions. Numerous coordination polymers containing organic components with chelate active functions such as carboxylate [9, 10], phosphate [11] and dithiocarbamate [12], but also more complex structures including bisimidazoles [13, 14], bispyrimidines [15] and dioximes [16] have been reported. Nevertheless, there are still open opportunities for usage of chelate units that have not or only marginally been applied as coordinative groups of linker molecules. This is the case for the bidentate ligand *o*-hydroxyacetophenone and its derivatives which are well known for their efficiency in the complexation of transition metal ions, especially of Cu(II) [17 – 19]. Remarkably, there is only one early note in the literature dealing with physicochemical properties of Cr(III), Co(II) and Ni(II) polychelates of a related linker-type molecule featuring a 4,4′-(4,4′-biphenylylenebisazo)di(2-hydroxyacetophenone) structure [20]. But, apart from that, no further investigations about the applicability of *o*-hydroxyacetophenone-containing linker molecules have been reported. In addition, tecton-type molecules having salicylic aldehyde terminal functionalities instead of *o*-hydroxyacetophenone moieties attached to a linear segment, thus bearing structural resemblance to a potential linker molecule, proved to be very useful in the formation of ordered surface nanostructures [21 – 25], but without being applied in the



Scheme 1. Formula structures of the compounds studied.

construction of coordination polymers. These basic principles gave the motivation to focus our attention on related linker molecules with terminal chelating *o*-hydroxyacetophenone groups such as **1a** and **1b** (Scheme 1).

In the present paper, we describe the synthesis of these compounds and discuss their crystal structures. We also show preliminary results obtained from PXRD and XPS investigations including elemental analysis for the corresponding complexes of **1a** and **1b** with Cu(II) which are suggestive of the formation of coordination polymers.

Results and Discussion

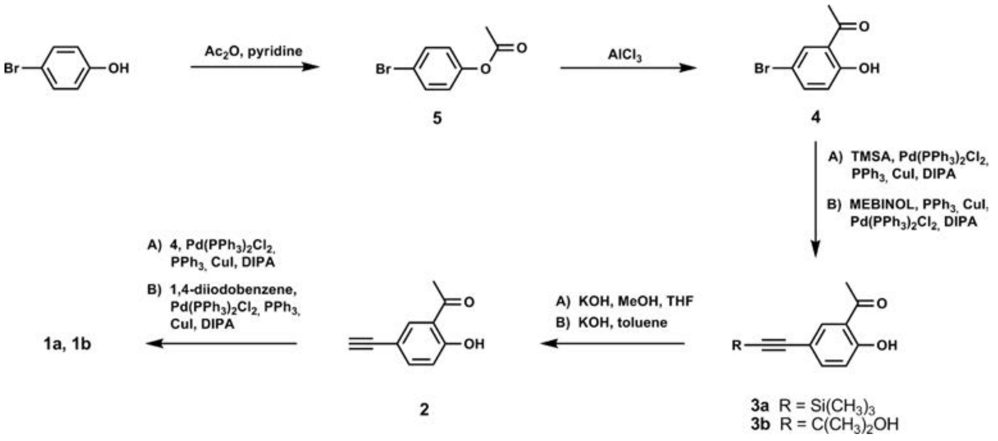
*Synthesis of **1a** and **1b***

The title compounds **1a** and **1b** (Scheme 1) have been synthesised using a multi-step reaction sequence starting from 4-bromophenol and trimethylsilylacetylene (TMSA) or 2-methylbut-3-yn-2-ol (MEBYNOL) as the base materials. As shown in Scheme 2, in the first step 4-bromophenol was acetylated with acetic anhydride to give **5** and then subjected to a Fries reaction [26] yielding 5-bromo-2-hydroxyacetophenone (**4**), which was one of the components for the following cross-coupling reaction. This reaction was carried out with TMSA (method A) or MEBYNOL (method B) using the Sonogashira-Hagihara coupling conditions [27] to produce **3a** and **3b**, respectively, which were subsequently deblocked ending up with 5-ethynyl-2-hydroxyacetophenone (**2**) as the key intermediate. Further cross-coupling of **2** with the bromide **4** or 1,4-diiodobenzene yielded the target linker components **1a** and **1b**, respectively.

*Crystal structures of **1a** and **1b***

Crystal and refinement data for the studied compounds are summarised in Table 1, while geometrical parameters for intermolecular contacts are listed in Table 2. Perspective views of the molecular structures including the numbering of atoms are shown in Fig. 1. Packing diagrams of **1a** and **1b** are presented in Figs. 2 and 3, respectively.

The presence of a strong intramolecular hydrogen bond formed between the phenolic hydrogen atoms and the oxygen atoms of the acetyl group, being a characteristic feature of 2-hydroxyacetophenones [28–30], is also shown in the crystal structures of **1a** and **1b** [O1···O2 2.515(2) and 2.564(1) Å, O1–H1···O2 146 and 145° for **1a** and **1b**, respectively].



Scheme 2. Synthetic pathway for the preparation of the linker molecules.

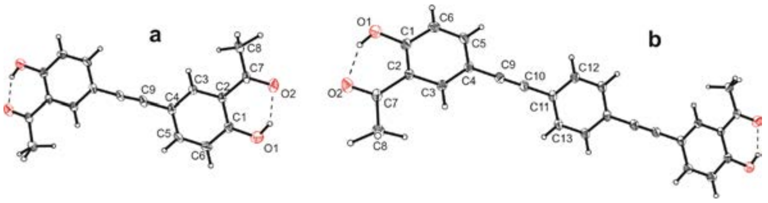


Fig. 1. Perspective views of **1a** (a) and **1b** (b) including the numbering of atoms. Displacement ellipsoids are at the 50% probability level. Hydrogen bonds are presented as dotted lines.

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of the compounds studied.

Compound	**1a**	**1b**
Empirical formula	$C_{18}H_{14}O_4$	$C_{26}H_{18}O_4$
Formula weight, g mol^{-1}	294.29	394.40
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*C*2/*c*
a, Å	7.0835(3)	38.1541(10)
b, Å	12.5830(5)	5.5751(2)
c, Å	16.3032(6)	9.0955(3)
β, deg	90.00	94.9530(10)
V, Å^3	1453.13(10)	1927.51(11)
Z	4	4
$F(000)$, e	616	824
D_{calcd},g cm^{-3}	1.35	1.36
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	0.1	0.1
Data collection		
Temperature, K	100(2)	153(2)
θrange, deg	2.5 – 28.1	1.1 – 28.9
Index ranges h, k, l	−9/9, −16/16, −21/20	−51/51, −7/7, −12/12
Refls. measd / unique / R_{int}	12 030 / 1776 / 0.0344	12 485 / 2539 / 0.0224
Refls. observed [$I > 2\sigma(I)$]	1324	2097
No. of refined parameters	102	138
$R1$ /$wR2$ (all data)[a,b]	0.0653 / 0.1296	0.0506 / 0.1259
Weighting scheme A / B[b]	0.0639 / 0.630	0.0895 / 0.8722
S (Goodness of fit on F^2)[c]	1.038	1.068
Final $\Delta\rho_{\text{max/min}}$, e Å^{-3}	0.30 / −0.24	0.37 / −0.18

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$; [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

The molecular structure element H–O–C=C–C=O of **1a** and **1b** (Fig. 1) correlates with the concept of the so-called 'Intramolecular Resonance Assisted Hydrogen Bond (IRAHB) formation' [31], which suggests a synergistic mutual reinforcement of intramolecular hydrogen bonding due to π-electron delocalisation, but its significance has lately been disputed [32].

Irrespective of this point being at issue, an increase of the bond lengths C(1)–C(2) [1.412(2), 1.410(2) Å] and C(7)–O(2) [1.236(2), 1.234(1) Å] corresponds to a decrease in the C(2)–C(7) bond length [1.477(2) Å] for **1a** and **1b**, respectively, indicating a potential resonance effect since these bond lengths deviate significantly from those found in the crystal structure of acetophenone [33]. Also, the shortening of the bond C(5)–C(6) of the aromatic ring in **1a** and **1b** [1.369(2), 1.375(2) Å] may be ascribed to a similar phenomenon.

The tolane derivative **1a** crystallises in the orthorhombic space group *Pbca* with the asymmetric part of the unit cell containing one half of the molecule, *e. g.* the molecule adopts inversion symmetry (Fig. 1a). The approximately planar geometry of the molecule indicates perfect delocalisation of the π-electron system. Contrary to expectations, the crystal structure lacks arene stacking. Instead, the C=O units of the acetyl groups are sandwiched at a distance of *ca.* 3.2 Å between the aromatic rings of adjacent molecules, which suggests the presence of $\pi(\text{C=O}) \cdots \pi(\text{arene})$ interactions [34]. The molecules are associated by a close network of C–H···O hydrogen bonds [35]

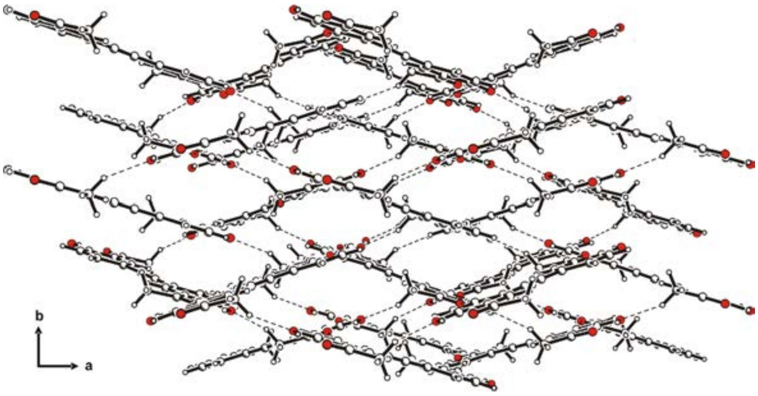


Fig. 2. Packing diagram of **1a** viewed down the crystallographic *c* axis. Hydrogen bonds are marked as broken lines.

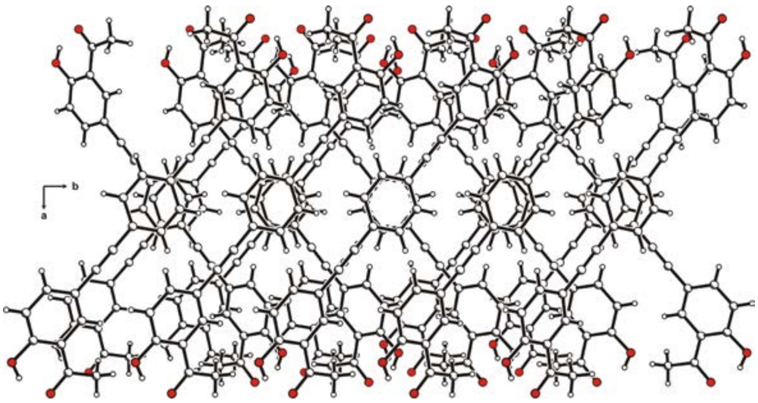


Fig. 3. Packing diagram of **1b** viewed down the crystallographic *c* axis (perspective view).

Table 2. Geometric parameters for intermolecular contacts in compounds **1a** and **1b**.

Interaction	Symmetry code	Distances, Å			Angle, deg
		D–H	D···A	H···A	D–H···A
1a					
O1–H1···O2	x, y, z	0.84	2.515(2)	1.77	146
C5–H5···O2	$x, 1.5-y, -0.5+z$	0.95	3.248(2)	2.30	176
C8–H(8C)···O1	$0.5-x, 0.5+y, z$	0.98	3.393(2)	2.53	148
C7–O2···cg(A)[a]	$-0.5+x, y, 0.5-z$	1.236(2)	3.634(2)	3.826(1)	71.8(1)
C7–O2···cg(A)[a]	$0.5+x, y, 0.5-z$	1.236(2)	3.700(2)	3.336(1)	97.2(1)
1b					
O1–H1···O2	x, y, z	0.84	2.564(1)	1.83	145
C8–H(8A)···O2	$0.5-x, 1.5-y, 1-z$	0.98	3.394(1)	2.61	137
C5–H(5)···C(13)[b]	$-x, 1+y, 1.5-z$	0.95	3.394(1)	2.61	137

[a] Cg means the centre of the aromatic ring. Ring A: C(1)... C(6); [b] to achieve a reasonable hydrogen bond geometry, an individual atom instead of the ring centre was chosen as an acceptor site.

[C(5)–H(5)···O(2) 2.30 Å, 176°, C(8)–H(8C)···O(1) 2.53 Å, 148°] (Fig. 2).

Recrystallisation of **1b** from ethyl acetate yielded colourless plates of the monoclinic space group *C*2/*c* with one half of the molecule in the asymmetric part of the unit cell (Fig. 1b). According to inversion symmetry, the terminal aromatic rings of the molecule are coplanar but twisted by an angle of 14.9(2)° with respect to the central arene ring. The ethynyl parts are slightly bent so that the molecule adopts an S-shaped distortion along its main axis.

A view of the crystal structure down the *b* axis (Fig. 3) reveals stacking-like packing of molecules with a lateral displacement of consecutive molecules, indicating that the crystal structure lacks $\pi \cdots \pi$ arene interactions. Molecular association is restricted to only one weak hydrogen bond [C(8)–H(8A)···O(2) 2.61 Å, 137°] and C–H···π(arene) interactions [36]. The inclination between molecules of adjacent stacks indicates that the crystal structure of **1b** is stabilised by van der Waals forces and close packing of molecules rather than by directed non-covalent bonding.

Preparation and structural characterisation of coordination polymers

Considering the known efficiency of *o*-hydroxyacetophenone to complex the Cu(II) ion [17–19], the linker-type molecules **1a** and **1b** were tested regarding the formation of corresponding coordination polymers. For this to do, Pfeiffer's method [37] was used with $[Cu(NH_3)_4]SO_4$ acting as a precursor. This tetrammine complex was synthesised by treatment of an aqueous solution of $CuSO_4$ with aqueous ammonia. The following polymerisation was realised by a solvothermal synthesis between the copper complex and the linkers **1a** and **1b** at 100 °C to yield **Cu(1a)** and **Cu(1b)**. Elementary analyses of both materials indicate a 1 : 1 ratio between linker molecule and copper(II) ion.

Crystals suitable for X-ray diffraction analysis, giving structural information on the nature of the coordination polymers, could not be obtained. Therefore a number of other characterisation methods were applied to provide some structural information as demonstrated in the following.

PXRD analysis

By using powder X-ray diffraction (PXRD) it is possible to trace the progress of the chemical reaction *via* comparing the diffraction data of **Cu(1a)** or **Cu(1b)** with the one of the reactants. Figures 4 and 5 show the PXRD data of each compound in the reaction batch of the copper precursor with **1a** and **1b**, respectively. In each case, the PXRD data of the reactants are displayed next to the one of the synthesised metal-organic compound.

The differences between the PXRD of the reactants and the coordination polymers **Cu(1a)** and **Cu(1b)** can be traced back to a change in crystal structure, and a loss of reflections marks the completed conversion of the starting materials. In the case of **Cu(1a)**, both broad and sharp reflections are recorded which seem to indicate the presence of two solid phases. In contrast, the reflections for **Cu(1b)** are sharp and furthermore shifted to smaller angles compared to **1b**. As expected, this shift is a sign of an expanded unit cell. After the coordination polymers have been formed, reflections of the reactants are not observed anymore.

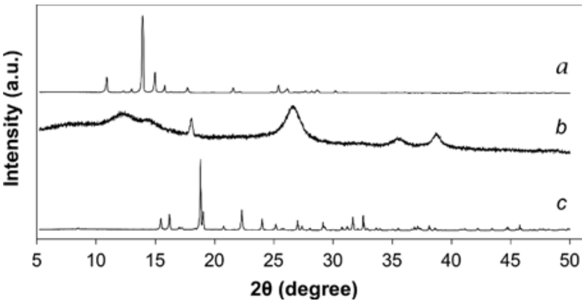


Fig. 4. PXRD data of the plain linker molecule **1a** (*a*), the metal-organic compound **Cu(1a)** (*b*) and the precursor $[Cu(NH_3)_4]SO_4$ (*c*).

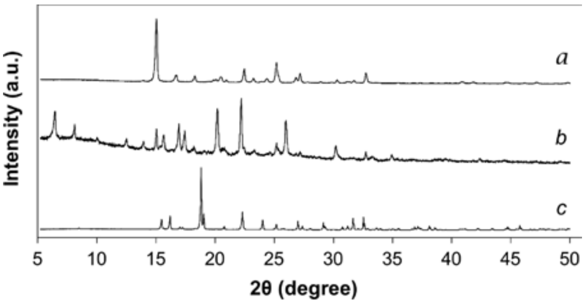


Fig. 5. PXRD data of the plain linker molecule **1b** (*a*), the metal-organic compound **Cu(1b)** (*b*) and the precursor $[Cu(NH_3)_4]SO_4$ (*c*).

X-Ray photoemission

To furnish proof of the presence of copper within the compounds and to analyse the coordination sphere of the metal centres we used XPS (X-ray photoelectron spectroscopy) as the characterisation method of choice. According to the literature, a specific signal for the binding energy of 2p core level electrons of copper (spin 3/2) should appear in the spectrum at 932.7 eV (934.5 eV for CuO) [38–40]. For the compounds **Cu(1a)** and **Cu(1b)** prepared as thin films, the respective values of 934.3 and 934.9 eV were measured (Fig. 6). In copper compounds with acetylacetonate-like ligands, a spin-orbital splitting occurs for the Cu 2*p* core level electrons. This effect can be used to gain

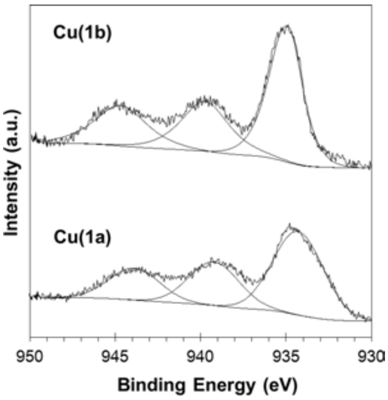


Fig. 6. Photoemission spectra of the compounds **Cu(1a)** and **Cu(1b)** (prepared as thin layers) in the range of the emitted radiation of the $2p_{3/2}$ core level electrons. The fitted Gauss-Lorentzian functions can be used for quantitative analysis.

Table 3. Measured XPS data of **Cu(1a)** and **Cu(1b)** in the Cu $2p$ region. Listed are the binding energies of the $2p_{3/2}$ electrons in eV. In parentheses are the FWHM values. (The signals are listed by increasing binding energies according to Fig. 6).

Signal	**Cu(1a)**	**Cu(1b)**
1	934.3 (3.415)	934.9 (2.018)
2	939.0 (3.045)	939.7 (3.255)
3	943.6 (4.463)	944.7 (3.591)

information on the state of coordination in the compound. Like it is found for the binding energies of copper(II) acetylacetonate, there are three signals shown in Fig. 6. This signal pattern can be explained by using a cluster model which assumes strong hybridisation effects for Cu $3d$ and C $2p$ electrons as well as O $2p_x$ and C $2p_x$ electrons [41]. The split orbital energies are correlated to $2p^5 3d^{10}L_1$-hybridised states, and bonding and anti-bonding states of $2p^5 3d^{10}L_2$ and $2p^5 3d^9$, where L is the corresponding ligand. The corresponding electron binding energies are listed in Table 3. A quantitative comparison between the two satellites and the main signals leads to a ratio of approximately 1 : 1 : 2 for both compounds.

Conclusions

Using a Pd-catalysed coupling process in the key reaction step, the new linker molecules **1a** and **1b** featuring terminating *o*-hydroxyacetophenone groups attached to rigid linear ethynylene and arene building units have been synthesised. Structural characterisation by single-crystal X-ray analysis shows strong intramolecular hydrogen bonding between OH and carbonyl groups of the two compounds typical for the *o*-hydroxyacetophenone moiety. Bond lengths within the H–O–C=C–C=O structural fragment suggest the applicability of the IRAHB concept. The packing of the molecules of both compounds in the crystal involve networks of C–H···O and C–H···π interactions while remarkably lacking $\pi\cdots\pi$ arene stacking contacts. Solvothermal syntheses were carried out with **1a** or **1b** and copper(II) ions leading to the corresponding coordination polymers **Cu(1a)** and **Cu(1b).** Because X-ray single-crystal structural analyses could not be conducted, basic information needed to be derived from elemental analysis, PXRD and XPS measurements. Owing to the nature of the used precursor molecules and the results obtained from the XPS and elemental analysis, a square-planar coordination geometry for the copper(II) centres can be postulated.

Assuming this kind of coordination geometry also found in analogous Cu(II) acetylacetonate complexes [41], the present coordination polymers are bound to possess a completely planar one-dimensional coordination assembly. Since the copper(II) ions therein still have two coordinative vacancies, the formed chains could become interesting building blocks in the design of higher-dimensional coordination polymers, which may be achieved by adding specific oligodentate molecules. Other metal ions may also be used. The molecules **1a** and **1b** may also be suitable tectons for the construction of porous materials (HBNs) [42]. These networks are interesting objects for the stimulation of future research.

Experimental Section

General

Melting points: Kofler melting point microscope (uncorrected). IR: Nicolet FT-IR 510. ^{1}H and ^{13}C NMR (internal standard TMS, δ in ppm): Bruker AVANCE DPX 500. MS (ESI): QUATTRO-LC (positive ion) and ESQUIRE-LC (solvent: chloroform). Elemental analysis: Heraeus CHN rapid analyser. Column chromatography: silica gel 60 (0.040 – 0.063 mm, Merck). TLC-analysis: aluminium sheets precoated with silica gel 60 F_{254} (Merck).

Reagents and materials were obtained from commercial suppliers (Fisher Scientific, ABCR, Aldrich) and were used without further purification. The solvents were purified using standard procedures. Solvents for the Sonogashira-Hagihara coupling reactions were deoxygenated prior to use by ultrasound (20 min) while bubbling argon through the solution.

*Preparation of 4-bromophenyl acetate (**5**) and 5-bromo-2-hydroxyacetophenone (**4**)*

Both compounds were synthesised according to the literature [26]. 4-Bromophenyl acetate (**5**) was isolated as a colourless oil (97 %) and 5-bromo-2-hydroxyacetophenone (**4**) as a pale-yellow solid (75 %, m. p. 58 °C).

*Synthesis of o-hydroxyacetophenones **3a** and **3b** (General procedure)*

The respective aryl bromide and the corresponding terminal alkyne were dissolved in degassed diisopropylamine. To this solution, the catalyst, being composed of triphenylphosphane (2 mol-%), copper(I) iodide (3 mol-%) and *trans*-dichlorobis(triphenylphosphane)palladium(II) (2 mol-%), was added, and the mixture was stirred under reflux until completion of the reaction (TLC analysis). Evaporation of the solvent followed by column chromatography and/or crystallisation yielded the pure compounds. Specifications for each compound are given below.

*5-(Trimethylsilylethynyl)-2-hydroxyacetophenone (**3a**)*

5-Bromo-2-hydroxyacetophenone (**4**) (5.0 g, 23.4 mmol), trimethylsilylacetylene (2.4 g, 24.3 mmol) and the catalyst in diisopropylamine (150 mL) were reacted for 4 h under the coupling conditions. Purification by column chromatography (SiO_2; *n*-hexane-ethyl acetate, 3 : 1) yielded 2.3 g (43 %) of a yellow solid. – M. p. 158 °C. – IR (KBr): $\nu_{max} = 1638, 2113, 2930, 3263\ cm^{-1}$. – ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.26$ (9 H, s, CH_3), 2.66 (3 H, s, CH_3), 6.98 (1 H, d, $^3J = 8.65$ Hz, Ar-H), 7.61 (1 H, d, $^3J = 8.65$ Hz, Ar-H), 7.92 (1 H, s, Ar-H), 12.39 (1 H, s, Ar-H). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.1$, 26.6, 70.5, 87.1, 113.8, 118.9, 119.6, 134.0, 139.1, 162.3, 204.1. – MS (GC-MS): $m/z = 232$ (calcd. 232.09 for $C_{13}H_{16}O_2Si$, $[M]^+$).

*5-(3-Hydroxy-3-methylbut-1-ynyl)-2-hydroxyacetophenone (**3b**)*

5-Bromo-2-hydroxyacetophenone (**4**) (5.0 g, 23.4 mmol), 2-methylbut-2-yn-2-ol (2.0 g, 24.3 mmol) and the catalyst in diisopropylamine (150 mL) were reacted for 4 h under the coupling conditions. Purification by column chromatography (SiO_2; *n*-hexane-ethyl acetate, 8 : 1) yielded 3.9 g (77 %) of an orange solid which was crystallised from cyclohexane. – M. p. 55 °C. – IR (KBr): $\nu_{max} = 1651, 2224, 2984, 3307\ cm^{-1}$. – ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.63$ (6 H, s, CH_3), 2.58 (1 H, s, OH), 2.63 (3 H, s, CH_3), 6.91 (1 H, d, $^3J = 8.60$ Hz, Ar-H), 7.48 (1 H, dd, $^3J = 8.60$ Hz, $^4J = 2.05$ Hz, Ar-H), 7.80 (1 H, d, $^4J = 2.05$ Hz, Ar-H), 12.35 (1 H, s, OH). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 26.6$, 31.4, 65.4, 80.7, 92.8, 113.5, 118.6, 119.3, 134.1, 139.2, 162.0, 204.1. – MS (GC-MS): $m/z = 218$ (calcd. 218.09 for $C_{13}H_{14}O_3$, $[M]^+$). – $C_{13}H_{14}O_3$: calcd. C 71.54, H 6.47; found C 71.40, H 6.67.

*Preparation of 5-Ethynyl-2-hydroxyacetophenone (**2**)*

Method A. To a solution of 5-(trimethylsilylethynyl)-2-hydroxyacetophenone (**3a**) (2.3 g, 9.9 mmol) in THF (20 mL), KOH (0.56 g, 10 mmol) dissolved in methanol (20 mL) was added. After having been stirred for 24 h at room temperature, the solution was diluted with diethyl ether and washed with diluted hydrochloric acid and water. The organic layer was dried and the solvent removed *in vacuo* to yield 1.5 g (95 %) of a yellow solid which was crystallised from *n*-hexane-CH_2Cl_2 (3 : 1). – M. p. 110 °C. – IR (KBr): $\nu_{max} = 1641, 2107, 2931, 3265\ cm^{-1}$. – ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.63$ (3 H, s, CH_3), 3.03 (1 H, s, CH), 6.93 (1 H, d, $^3J = 8.65$ Hz, Ar-H), 7.56 (1 H, dd, $^3J = 8.65$ Hz, $^4J = 2.05$ Hz, Ar-H), 7.88 (1 H, d, $^4J = 2.05$ Hz, Ar-H), 12.38 (1 H, s, OH). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 26.6$, 76.3, 82.4, 112.7, 118.8, 119.4, 134.8, 139.6, 162.6, 204.0. – MS (GC): $m/z = 160$ (calcd. 160.05 for $C_{10}H_8O_2$, $[M]^+$). – $C_{10}H_8O_2$: calcd. C 74.99, H 5.03; found C 74.48, H 5.34.

Method B. 5-(3-Hydroxy-3-methylbutyn-1-yl)-2-hydroxyacetophenone (**3b**) (5.0 g, 22.9 mmol) was dissolved in toluene (50 mL), and KOH (3.85 g, 68.8 mmol) was added. The solution was refluxed for 3 h, acidified with conc. hydrochloric acid (100 mL) and filtered. The filtrate was extracted with methylene chloride (250 mL), the combined organic layers dried over anhydrous Na_2SO_4 and evaporated to dryness. The resulting residue was purified by column chromatography (SiO_2; *n*-hexane-CH_2Cl_2, 6 : 1) to yield 1.7 g (47 %) of a yellow solid corresponding to the data given above.

*Synthesis of **1a** and **1b***

The general procedure for the synthesis of **3a** and **3b** applies.

*5,5′-(Ethyne-1,2-diyl)bis(2-hydroxyacetophenone) (**1a**)*

5-Ethynyl-2-hydroxyacetophenone (**2**) (3.0 g, 18.8 mmol), 5-bromo-2-hydroxyacetophenone (**4**) (3.85 g, 18 mmol) and the catalyst were reacted in diisopropylamine (100 mL) under the coupling conditions. Purification by column chromatography (SiO_2; *n*-hexane-ethyl acetate, 8 : 1) yielded 2.2 g (40 %) of a yellow solid which was crystallised from *n*-hexane. – M. p. 205 °C. – IR (KBr): $\nu_{max} = 1641, 1948, 2920\ cm^{-1}$. – ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.67$ (6 H, s, CH_3), 6.97 (2 H, d, $^3J = 8.65$ Hz, Ar-H), 7.61 (2 H, dd, $^3J = 8.65$ Hz, $^4J = 2.00$ Hz, Ar-H), 7.92 (2 H, d, $^4J = 2.00$ Hz, Ar-H), 12.39 (2 H, s, OH). – ^{13}C NMR

(125 MHz, $CDCl_3$): $\delta = 26.7$, 87.1, 113.8, 118.9, 119.6, 134.0, 139.1, 162.3, 204.0. – MS (GC-MS): $m/z = 295$ (calcd. 294.09 for $C_{18}H_{14}O_4$, $[M]^+$). – $C_{18}H_{14}O_4$: calcd. C 73.46, H 4.80; found C 73.37, H 4.99.

*5,5′-[Benzene-1,4-diyl-di(ethyne-2,1-diyl)]bis(2-hydroxyacetophenone) (**1b**)*

5-Ethynyl-2-hydroxyacetophenone (**2**) (2.0 g, 12 mmol), 1,4-diiodobenzene (1.9 g, 5.8 mmol) and the catalyst were reacted in diisopropylamine (50 mL) under the coupling conditions. The residue was treated with refluxing diluted hydrochloric acid, filtered and crystallised from chloroform to yield 0.8 g (34 %) of a colourless solid which was crystallised from ethyl acetate. – M. p. 253 °C. – IR (KBr): $\nu_{max} = 1644$, 2214, 3031 cm^{-1}. – ^1H NMR (500 MHz, $[D_6]DMSO$): $\delta = 2.67$ (6 H, s, CH_3), 6.97 (2 H, d, $^3J = 8.60$ Hz, Ar-H), 7.54 (4 H, s, Ar-H), 7.64 (2 H, dd, $^3J = 8.60$ Hz, $^4J = 2.10$ Hz, Ar-H), 8.03 (2 H, d, $^4J = 2.10$ Hz, Ar-H), 12.09 (2 H, s, OH). – ^{13}C NMR (125 MHz, $[D_6]DMSO$): $\delta = 27.8$, 87.7, 90.5, 112.8, 118.3, 120.8, 122.4, 131.3, 134.5, 138.4, 160.9, 203.4. – MS ((–)-ESI): $m/z = 393$ (calcd. 394.12 for $C_{26}H_{18}O_4$, $[M–H]^-$). – $C_{26}H_{18}O_4 \cdot {}^2/_3\, H_2O$: calcd. C 76.83, H 4.79; found C 76.53, H 4.58.

General procedure for the synthesis of coordination polymers

To a solution of $CuSO_4 \cdot 5H_2O$ in water, an aqueous solution of ammonia was added until the initially formed light-blue precipitate dissolved giving a dark-blue solution of $[Cu(NH_3)_4]SO_4$. The organic compound dissolved in acetonitrile was then added dropwise, and the solution was stirred for 30 min at 100 °C. The resulting flocculent precipitate was separated by filtration, then washed with water and acetonitrile. Finally the precipitate was desolvated with dichloromethane.

*Preparation of **Cu(1a)***

20.5 mg (0.082 mmol) of $CuSO_4 \cdot 5H_2O$ and 25 mg (0.085 mmol) of **1a** were reacted as given above to yield 22.9 mg of a green solid. – $C_{18}H_{12}CuO_4$: calcd. C 60.76, H 3.40; found C 61.29, H 3.87.

*Preparation of **Cu(1b)***

8.1 mg (0.032 mmol) of $CuSO_4 \cdot 5H_2O$ and 16.5 mg (0.042 mmol) of **1b** were reacted as given above to yield 5.4 mg of a light-green solid. – $C_{26}H_{16}CuO_4$: calcd. C 68.49, H 3.54; found C 68.37, H 3.71.

X-Ray structure determination

Suitable single crystals were obtained by slow cooling of solutions of **1a** and **1b** in *n*-hexane and ethyl acetate, respectively. Information concerning the crystallographic data and the structure refinement is summarised in Table 1. The intensity data were collected on a Bruker APEX II diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) using ω- and ϕ-scans. Intensities were corrected for background, Lorentz and polarisation effects. Preliminary structure models were derived by an application of Direct Methods [43, 44] and were refined by full-matrix least-squares calculations based on F^2 for all reflections [45, 46]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms.

CCDC 859743 and 859744 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction analysis

Compounds **Cu(1a)** and **Cu(1b)** were desolvated with dichloromethane and dried under vacuum. Both powders were pestled to get a homogeneous composition. The intensity data were collected on a PANalytical PW3040/60 X'Pert Pro diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å). The measurements were carried out in reflexion mode, and wide-angle values were recorded from 5 to 70° with a step size of 0.01°.

X-Ray photoelectron spectroscopy

Samples of the compounds **Cu(1a)** and **Cu(1b)** were prepared as thin films on a silicon wafer to obtain planar surfaces. Al K_α radiation was used as photo electron excitation source during the measurement. Electric charging effects were compensated with the help of a flood gun, and any residual charging effect which leads to a shift of the spectra was corrected mathematically. The main value in the C 1*s* region was adjusted to that of aromatic carbon signals with the binding energy value of 284.8 eV. The analysis was carried out with the software CasaXPS from Casa Software Ltd.

Acknowledgement

This work was performed within the Cluster of Excellence 'Structure Design of Novel High-Performance Materials *via* Atomic Design and Defect Engineering (ADDE)', which is financially supported by the European Union (European Regional Development Fund) and by the Ministry of Science and Art of Saxony (SMWK).

[1] M. Fujita, Y. J. Know, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151 – 1152.

[2] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 2607 – 2614.

[3] S. Horike, M. Dinc, K. Tamaki, J. R. Long, *J. Am. Chem. Soc.* **2008**, *130*, 5854 – 5855.

[4] E. Biemmi, A. Darga, N. Stock, T. Bein, *Microporous Mesoporous Mater.* **2008**, *114*, 380 – 386.

[5] Y. Takashima, V. M. Martínz, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa, *Nature Commun.* **2011**, *2*, 168 – 175.

[6] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725 – 1727.

[7] J. L. C. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, *J. Am. Chem. Soc.* **2004**, *126*, 5666 – 5667.

[8] A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998 – 17999.

[9] O. R. Evans, W. Lin, *Cryst. Growth Des.* **2001**, *1*, 9 – 11.

[10] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276 – 279.

[11] O. R. Evans, H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395 – 10396.

[12] P. C. Healy, B. W. Skelton, A. H. White *J. Chem. Soc., Dalton Trans.* **1989**, 971 – 976.

[13] M. A. Martinez Lorente, F. Dahan, Y. Sanakis, V. Petrouleas, A. Bousseksou, J.-P. Tuchagues, *Inorg. Chem.* **1995**, *34*, 5346 – 5357.

[14] Q.-X. Liu, Z.-X. Zhao, X.-J. Zhao, Z.-Q. Yao, S.-J. Li, X.-G. Wang, *Cryst. Growth Des.* **2011**, *11*, 4933 – 4942.

[15] L. Tang, F. Fu, W. Wang, D. Li, Y. Wu, X. Gao, X. Yang, *Chinese J. Chem.* **2009**, *27*, 273 – 280.

[16] A. Schmoldt, H. F. Benthe, G. Haberland, *Biochem. Pharmacol.* **1975**, *24*, 1639 – 1641.

[17] J. H. Weber, *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 243 – 252.

[18] V. F. Duckworth, N. C. Stephenson, *Acta Crystallogr.* **1969**, *B25*, 2245 – 2254.

[19] H. M. Ali, S. N. Abdul Halim, S. W. Ng, *Acta Crystallogr.* **2005**, *E61*, m1429 – m1430.

[20] H. B. Suthar, J. R. Shah, *J. Macromol. Sci. Chem.* **1984**, *A21*, 301 – 307.

[21] S. Weigelt, C. Busse, L. Petersen, E. Rauls, B. Hammer, K. V. Gothelf, F. Besenbacher, T. R. Linderoth, *Nature Materials* **2006**, *5*, 112 – 117.

[22] S. Weigelt, C. Bombis, C. Busse, M. M. Knudsen, K. V. Gothelf, E. Laegsgaard, F. Besenbacher, T. R. Linderoth, *ACS Nano* **2008**, *2*, 651 – 660.

[23] S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, T. Strunskus, C. Wöll, M. Dahlbom, B. Hammer, E. Laegsgaard, F. Besenbacher, T. R. Linderoth, *Angew. Chem. Int. Ed.* **2007**, *46*, 9227 – 9230.

[24] J. A. A. W. Elemans, S. Lei, S. DeFreyter, *Angew. Chem. Int. Ed.* **2009**, *48*, 7298 – 7332.

[25] D. Bonifazi, S. Mohnani, A. Llanes-Pallas, *Chem. Eur. J.* **2009**, *15*, 7004 – 7025.

[26] S. G. Davies, B. E. Mobbs, *J. Chem. Soc., Perkin Trans. 1* **1987**, 2597 – 2604.

[27] K. Sonogashira, N. Hagihara, *Tetrahedron Lett.* **1975**, *50*, 4467 – 4470.

[28] D. E. Hibbs, J. Overgaard, R. O. Piltz, *Org. Biomol. Chem.* **2003**, *1*, 1191 – 1198.

[29] A. Filarowski, A. Kochel, P. E. Hansen, A. Urbanowicz, K. Szymborska, *J. Mol. Struct.* **2007**, *844*, 77 – 82.

[30] V. Barba, I. Betanzos, *J. Organomet. Chem.* **2007**, *692*, 4903 – 4908.

[31] G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023 – 1028.

[32] P. Sanz, O. Mó, M. Yánez, J. Elguero, *Chem. Eur. J.* **2008**, *14*, 4225 – 4232.

[33] Y. Tanimoto, H. Kobayashi, S. Nagakura, S. Saito, *Acta Crystallogr.* **1973**, *B29*, 1822 – 1826.

[34] J. Marten, W. Seichter, E. Weber, U. Böhme, *J. Phys. Org. Chem.* **2007**, *20*, 716 – 731.

[35] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, Oxford, UK, **1999**, chapter 2.

[36] M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, *CrystEngComm* **2009**, *11*, 1757 – 1788.

[37] P. Pfeiffer, S. Golther, O. Angern, *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 305 – 313.

[38] B. V. Crist, *XPS International LLC* **2004**, *1*, 77 – 80.

[39] B. V. Crist, *XPS International LLC* **2004**, *2*, 101 – 109.

[40] G. van der Laan, C. Westra, C. Haas, G. A. Sawatzky, *Phys. Rev. B* **1981**, *23*, 4369 – 4380.

[41] K. Okada, J. Kawai, A. Kotani, *Phys. Rev. B* **1993**, *48*, 10733 – 10738.

[42] L. J. Prins, D. N. Reinhoudt, P. Timmerman, *Angew. Chem. Int. Ed.* **2001**, *40*, 2382 – 2426.

[43] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen: Göttingen (Germany) **1997**.

[44] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

[45] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen: Göttingen (Germany) **1997**.

[46] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.